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Supporting Information

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Remote Enantioselective Friedel–Crafts Alkylations of Furans through HOMO Activation**

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Supporting Information

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1. General methods

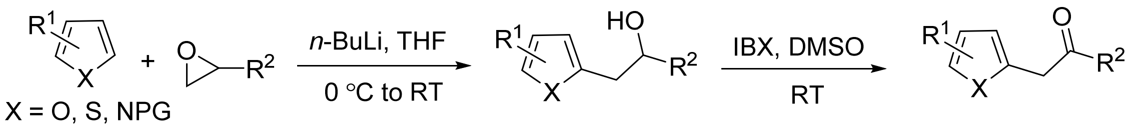
NMR data were obtained for ^{1}H at 400 MHz, and for ^{13}C at 100 or 150 MHz. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ solution. ESI HRMS was recorded on a Waters SYNAPT G2. In each case, enantiomeric ratio was determined by HPLC analysis on a chiral column in comparison with authentic racemate, using a Daicel Chiralcel OD-H Column (250 x 4.6 mm), Chiralpak AD-H Column (250 x 4.6 mm) or Chiralpak IC Column (250 x 4.6 mm). UV detection was monitored at 220 nm or 254 nm. Optical rotation was examined in $CHCl_3$ solution at 20 °C. Column chromatography was performed on silica gel (200-300 mesh) eluting with ethyl acetate and petroleum ether. TLC was performed on glass-backed silica plates. UV light and I_2 were used to visualize products. All chemicals including 2-furylacetone **1a** were used without purification as commercially available unless otherwise noted. Alkylidenemalononitriles were prepared according to the literature procedures.[1] The primary amines were also synthesized according to the literature procedures.[2]

[1] K. M. Guo, J. Thompson, B. Chen, *J. Org. Chem.* **2009**, *74*, 6999.
[2] a) H. Brunner, J. Bügler, B. Nuber, *Tetrahedron: Asymmetry* **1995**, *6*, 1699; b) T. He, J.-Y. Qian, H.-L. Song, X.-Y. Wu, *Synlett* **2009**, 3195; c) K. Mei, S. Zhang, S. He, P. Li, M. Jin, F. Xue, G. Luo, H. Zhang, L. Song, W. Duan, W. Wang, *Tetrahedron Lett.* **2008**, *49*, 2681.

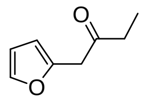
2. Procedure for the preparation of ketone substrates

The ketone substrates **1** were synthesized according to the literature procedures.[3]

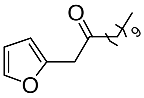
[3] A. S. K. Hashmi, M. Wölfle, *Tetrahedron* **2009**, *65*, 9021.



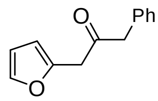
To the solution of furan in THF was added *n*-BuLi (2.4 M solution in hexane) at 0 °C under Ar atmosphere. Then the solution was warmed to room temperature and stirred for 3 h. The solution was cooled to 0 °C again and the corresponding epoxide was added slowly. After completion, the solution was quenched with NH_4Cl solution and extracted with DCM. The combined organic layers were washed with brine and dried with $MgSO_4$, filtered and concentrated. The obtained alcohol was dissolved in DMSO and IBX was added at 0 °C. The reaction was allowed to warm to room temperature and stirred for about 2 h. After completion, the reaction was quenched with water and extracted with ethyl acetate. The combined organic layers were washed with brine and dried with $MgSO_4$, filtered and concentrated. The desired ketone **1** was obtained as a colorless oil after purification by flash chromatography.



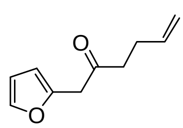
1-(Furan-2-yl)butan-2-one (1b): [1]H NMR (400 MHz, $CDCl_3$): δ = 7.36 (s, 1H), 6.34 (d, *J* = 1.6 Hz, 1H), 6.19 (d, *J* = 2.4 Hz, 1H), 3.71 (s, 2H), 2.47 (q, *J* = 7.2 Hz, 2H), 1.04 (t, *J* = 7.2 Hz, 3H) ppm.



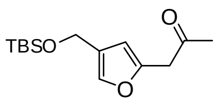
1-(Furan-2-yl)dodecan-2-one (1c): [1]H NMR (400 MHz, $CDCl_3$): δ = 6.35 (d, *J* = 1.2 Hz, 1H), 6.34-6.33 (m, 1H), 6.18 (d, *J* = 2.4 Hz, 1H), 3.69 (s, 2H), 2.43 (d, *J* = 7.6 Hz, 2H), 1.57-1.54 (m, 2H), 1.28-1.25 (m, 14H), 0.88 (t, *J* = 7.2 Hz, 3H) ppm.



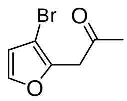
1-(Furan-2-yl)-3-phenylpropan-2-one (1d): [1]H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.25 (m, 4H), 7.18-7.16 (m, 2H), 6.35 (d, *J* = 1.6 Hz, 1H), 6.17 (d, *J* = 2.4 Hz, 1H), 3.74 (s, 2H), 3.73 (s, 2H) ppm.



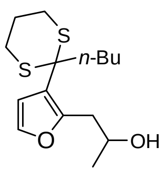
1-(Furan-2-yl)hex-5-en-2-one (1e): [1]H NMR (400 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 0.8, 1H), 6.35-6.34 (m, 1H), 6.19 (d, *J* = 3.2 Hz, 1H), 5.81-5.72 (m, 1H), 5.02-4.95 (m, 2H), 3.70 (s, 2H), 2.55 (t, *J* = 7.2, 2H), 2.34-2.28 (m, 2H) ppm.



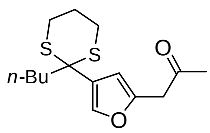
1-(4-(((tert-Butyldimethylsilyl)oxy)methyl)furan-2-yl)propan-2-one (1g): [1]H NMR (400 MHz, $CDCl_3$): δ = 7.28 (s, 1H), 6.18 (s, 1H), 4.56 (s, 2H), 3.67 (s, 2H), 2.17 (s, 3H), 0.91 (s, 9H), 0.08 (s, 6H) ppm.



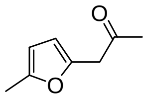
1-(3-Bromofuran-2-yl)propan-2-one (1h): [1]H NMR (400 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 1.6 Hz, 1H), 6.42 (d, *J* = 1.6 Hz, 1H), 3.72 (s, 2H), 2.16 (s, 3H) ppm.



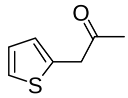
1-(3-(2-Butyl-1,3-dithian-2-yl)furan-2-yl)propan-2-ol (alcohol of **1i)**: [1]H NMR (400 MHz, $CDCl_3$): δ = 7.28 (d, *J* = 1.6 Hz, 1H), 6.56 (d, *J* = 1.6 Hz, 1H), 4.19-4.16 (m, 1H), 3.21-3.09 (m, 2H), 2.86-2.73 (m, 4H), 2.06-1.91 (m, 4H), 1.40-1.26 (m, 7H), 0.87 (t, *J* = 7.2 Hz, 3H) ppm. *The alcohol of **1i** was oxidized by IBX and the corresponding ketone **1i**, which was not stable enough, was directly used in the aminocatalytic reaction.*



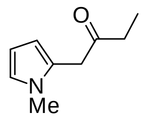
1-(4-(2-butyl-1,3-dithian-2-yl)furan-2-yl)propan-2-one (1k): [1]H NMR (400 MHz, $CDCl_3$): δ = 7.44 (s, 1H), 6.28 (s, 1H), 3.68 (s, 2H), 2.89-2.82 (m, 2H), 2.70-2.65 (m, 2H), 2.19 (s, 3H), 2.04-1.87 (m, 4H), 1.38-1.21 (m, 4H), 0.86 (t, *J* = 7.2 Hz, 3H) ppm. *This substrate is inert in the current catalytic system due to steric hindrance.*



1-(5-Methylfuran-2-yl)propan-2-one (1l): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.03 (d, *J* = 2.4 Hz, 1H), 5.88 (d, *J* = 2.0 Hz, 1H), 3.61 (s, 2H), 2.23 (s, 3H), 2.13 (s, 3H) ppm. *No reaction was observed for the combination of* ***1l*** *and acceptor* ***2a*** *under current catalytic conditions.*



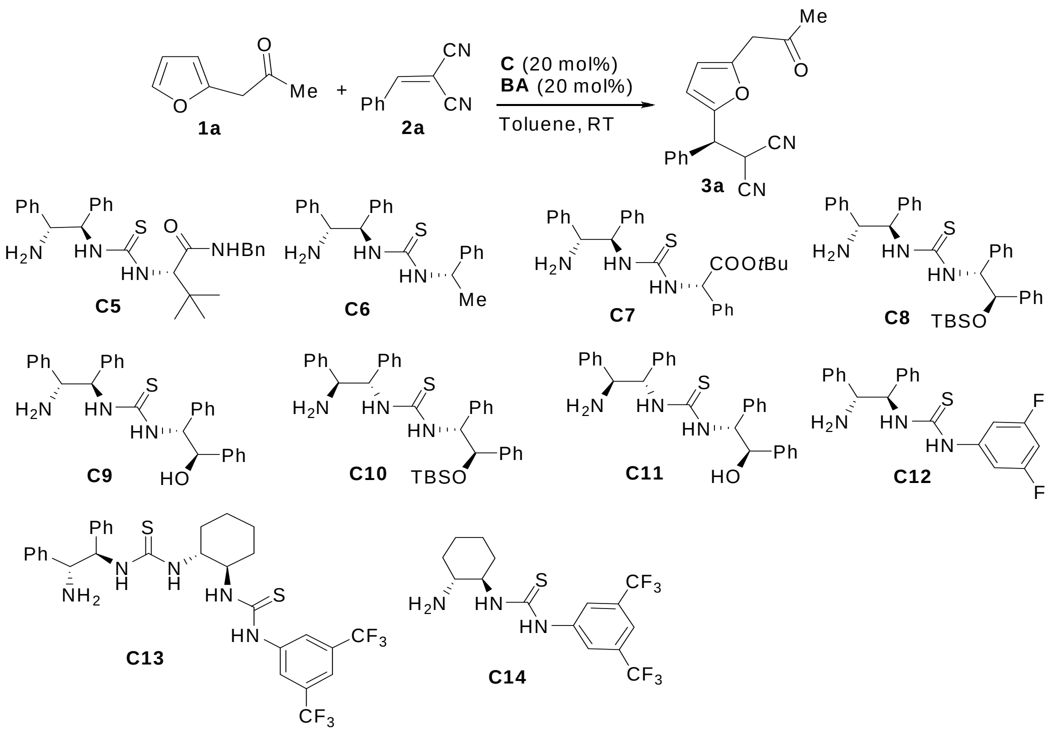
1-(Thiophen-2-yl)propan-2-one (12): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22-7.21 (m, 1H), 6.98-6.96 (m, 1H), 6.89-6.88 (m, 1H), 3.89 (s, 2H), 2.19 (s, 3H) ppm.



1-(1-Methyl-1H-pyrrol-2-yl)butan-2-one: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.59 (s, 1H), 6.08 (br s, 1H), 6.01 (s, 1H), 3.65 (s, 2H), 3.51 (s, 3H), 2.46 (q, *J* = 7.2 Hz, 2H), 1.03 (t, *J* = 7.2 Hz, 3H) ppm.

3. More screening conditions for enantioselective Friedel–Crafts alkylation

Table 1. More bifunctional catalyst screenings[a]

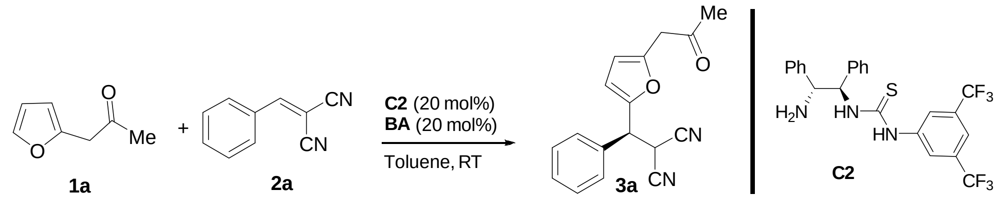


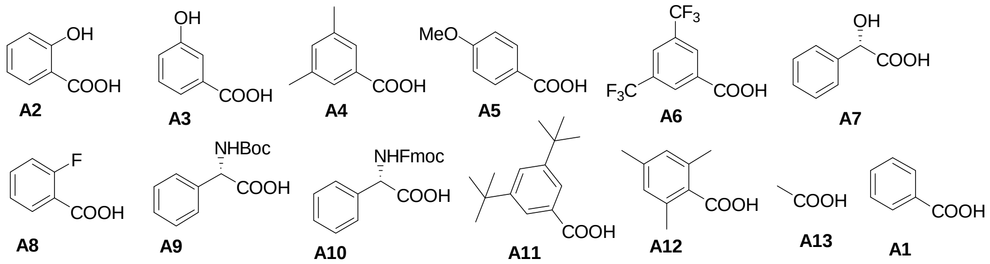
Entry	Catalyst	Yield (%)[b]	*ee* (%)[c]
1	**C5**	81	27
2	**C6**	85	83
3	**C7**	78	54
4	**C8**	70	60
5	**C9**	59	48
6	**C10**	70	–9
7	**C11**	56	–37
8	**C12**	81	78

9	**C13**	74	58
10	**C14**	<10	ND[d]

[a] Reactions were conducted with **1a** (0.3 mmol), **2a** (0.1 mmol), catalyst **C** (0.02 mmol), benzoic acid (0.02 mmol) in toluene at rt for 12 h. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] Not determined.

Table 2. More acid additive screenings[a]





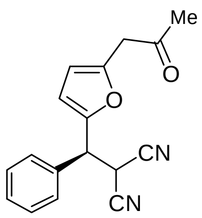
Entry	Acid	Yield (%)[b]	*ee* (%)[c]
1	**A2**	74	63
2	**A3**	70	73
3	**A4**	85	88
4	**A5**	78	75
5	**A6**	59	81
6	**A7**	63	77
7	**A8**	71	82
8	**A9**	56	67
	A10	52	65
9	**A11**	81	76
10	**A12**	76	78
11	**A13**	63	80
12	**A1**	**85**	**88**
13	/	44	23

[a] Reactions were conducted with **1a** (0.3 mmol), **2a** (0.1 mmol), catalyst **C2** (0.02 mmol), acid **A** (0.02 mmol) in toluene at rt for 12 h. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

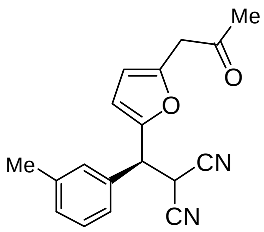
4. General procedure for catalytic asymmetric Friedel–Crafts alkylation

The reaction was carried out with α,α-dicyanoolefin **2** (0.1 mmol) and 2-furfuryl ketone **1** (0.3 mmol) in toluene (1.0 mL) in the presence of primary amine catalyst **C2** (9.7 mg, 0.02 mmol), benzoic acid (2.8 mg, 0.02 mmol) at 0 °C or −10 °C for 24 h or 48 h. After completion, the solution was concentrated and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1 to 6:1) to afford the chiral product **3**.

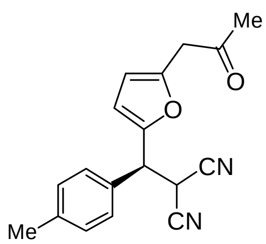
The racemic products were generally obtained by the catalysis of racemic ethyl phenylglycinate. Benzylamine also could promote the FC reaction but more complex reactions were observed.



***(S)*-2-((5-(2-Oxopropyl)furan-2-yl)(phenyl)methyl)malononitrile (3a)** was obtained in 85% yield and the enantiomeric excess was determined to be 92% by HPLC analysis on Chiralpak IC column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 220 nm, t_{minor} = 9.43 min, t_{major} = 10.73 min. $[\alpha]_D^{20}$ = 20.8 (*c* = 0.75 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.43 (br s, 5H), 6.30 (d, *J* = 3.2 Hz, 1H), 6.22 (d, *J* = 3.2 Hz, 1H), 4.61 (d, *J* = 7.2 Hz, 1H), 4.44 (d, *J* = 7.2 Hz, 1H), 3.73 (s, 2H), 2.18 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.4, 149.3, 149.0, 134.6, 129.3, 128.2, 111.4, 110.7, 109.6, 46.0, 43.1, 29.2, 28.7 ppm; ESI HRMS: calcd. for $C_{17}H_{14}N_2O_2$+Na^+ 301.0947, found 301.0951.

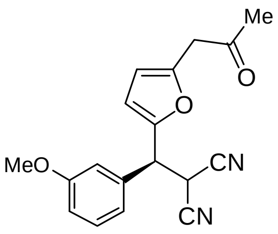


***(S)*-2-((5-(2-Oxopropyl)furan-2-yl)(*m*-tolyl)methyl)malononitrile (3b)** was obtained in 88% yield and the enantiomeric excess was determined to be 90% by HPLC analysis on Chiralcel OD column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 220 nm, t_{major} = 17.75 min, t_{minor} = 19.67 min. $[\alpha]_D^{20}$ = 21.5 (*c* = 0.72 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33-7.21 (m, 4H), 6.29 (d, *J* = 3.2 Hz, 1H), 6.21 (d, *J* = 3.2 Hz, 1H), 4.57 (d, *J* = 7.2 Hz, 1H), 4.43 (d, *J* = 7.2 Hz, 1H), 3.73 (s, 2H), 2.37 (s, 3H), 2.18 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.5, 149.3, 149.1, 139.1, 134.5, 130.1, 129.2, 128.8, 125.1, 111.4, 110.7, 109.6, 46.0, 43.1, 29.2, 28.7, 21.4 ppm; ESI HRMS: calcd. for $C_{18}H_{16}N_2O_2$+Na^+ 315.1104, found 315.1109.

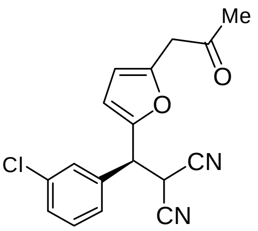


***(S)*-2-((5-(2-Oxopropyl)furan-2-yl)(*p*-tolyl)methyl)malononitrile (3c)** was obtained in 89% yield and the enantiomeric excess was determined to be 90% by HPLC analysis on Chiralpak AD column (10% 2-propanol/*n*-hexane, 1 mL/min), UV 220 nm, t_{major} = 16.99 min, t_{minor} = 19.36 min. $[\alpha]_D^{20}$ = 19.5 (*c* = 0.65 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.31 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* =8.0 Hz, 2H), 6.28 (d, *J* = 3.2 Hz, 1H), 6.22 (d, *J* = 3.2 Hz, 1H), 4.57 (d, *J* = 7.6 Hz, 1H), 4.41 (d, *J* = 7.6 Hz, 1H), 3.72 (s, 2H), 2.36 (s, 3H), 2.18 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.5, 149.3, 139.3, 131.5, 130.0, 128.1, 111.4, 110.6, 109.6, 45.8, 43.1, 29.2, 28.8, 21.1 ppm; ESI HRMS: calcd. for $C_{18}H_{16}N_2O_2$+Na^+ 315.1104, found 315.1109.

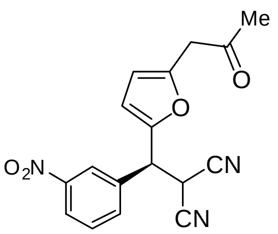
***(S)*-2-((3-Methoxyphenyl)(5-(2-oxopropyl)furan-2-yl)methyl)malononitrile (3d)** was obtained in 82% yield and the enantiomeric excess was determined to be 86% by HPLC analysis on Chiralpak IC column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 220 nm, t_{minor} = 14.08 min, t_{major} = 16.25



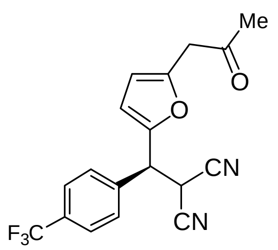
min. $[\alpha]_D^{20}$ = 11.6 (*c* = 0.75 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.34 (t, *J* = 8.0 Hz, 1H),7.01-6.92 (m, 3H), 6.31 (d, *J* = 3.2 Hz, 1H), 6.22 (d, *J* = 3.2 Hz, 1H), 4.57 (d, *J* = 7.6 Hz, 1H), 4.42 (d, *J* = 7.6 Hz, 1H), 3.82 (s, 3H), 3.73 (s, 2H), 2.18 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.4, 160.1, 149.4, 148.9, 136.0, 130.4, 120.3, 114.5, 114.0, 111.4, 111.3, 110.7, 109.6, 55.3, 46.0, 43.1, 29.2, 28.6 ppm; ESI HRMS: calcd. for $C_{18}H_{16}N_2O_3$+Na^+ 331.1053, found 331.1059.



***(S)*-2-((3-Chlorophenyl)(5-(2-oxopropyl)furan-2-yl)methyl)malononitrile (3e)** was obtained in 89% yield and the enantiomeric excess was determined to be 92% by HPLC analysis on Chiralpak IC column (20% 2-propanol/*n*-hexane, 1 mL/min), UV 220 nm, t_{minor} = 11.37 min, t_{major} = 12.92 min. $[\alpha]_D^{20}$ = 14.0 (*c* = 0.65 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.41-7.33 (m, 4H), 6.33 (d, *J* = 3.2 Hz, 1H), 6.23 (d, *J* = 3.2 Hz, 1H), 4.59 (d, *J* = 7.2 Hz, 1H), 4.46 (d, *J* = 7.2 Hz, 1H), 3.74 (s, 2H), 2.19 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.2, 149.7, 148.2, 136.5, 135.1, 130.6, 129.6, 128.4, 126.4, 111.1, 111.0, 109.7, 45.6, 43.0, 29.2, 28.5 ppm; ESI HRMS: calcd. for $C_{17}H_{13}ClN_2O_2$+Na^+ 335.0558, found 335.0563.

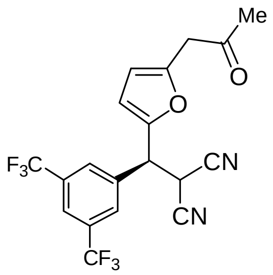


***(S)*-2-((3-Nitrophenyl)(5-(2-oxopropyl)furan-2-yl)methyl)malononitrile (3f)** was obtained in 92% yield and the enantiomeric excess was determined to be 86% by HPLC analysis on Chiralcel OD column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 220 nm, t_{minor} = 29.23 min, t_{major} = 33.93 min. $[\alpha]_D^{20}$ = 6.6 (*c* = 0.65 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.32-8.29 (m, 2H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.66 (t, *J* =8.0 Hz, 1H), 6.38 (d, *J* = 3.2 Hz, 1H), 6.27 (d, *J* = 3.2 Hz, 1H), 4.77 (d, *J* = 7.2 Hz, 1H), 4.54 (d, *J* = 7.2 Hz, 1H), 3.77 (s, 2H), 2.21 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.0, 150.1, 147.3, 136.6, 134.4, 130.6, 124.4, 123.4, 111.4, 110.8, 109.8, 45.5, 42.9, 29.4, 28.4 ppm; ESI HRMS: calcd. for $C_{17}H_{13}N_3O_4$+Na^+ 346.0798, found 346.0791.

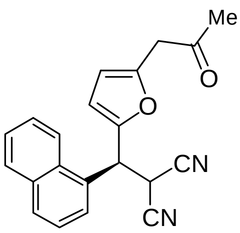


***(S)*-2-((5-(2-Oxopropyl)furan-2-yl)(4-(trifluoromethyl)phenyl)methyl)malononitrile (3g)** was obtained in 90% yield and the enantiomeric excess was determined to be 88% by HPLC analysis on Chiralpak AD column (10% 2-propanol/*n*-hexane, 1 mL/min), UV 220 nm, t_{minor} = 17.48 min, t_{major} = 20.04 min. $[\alpha]_D^{20}$ = 7.7 (*c* = 0.35 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 6.33 (d, *J* = 3.2 Hz, 1H), 6.24 (d, *J* = 3.2 Hz, 1H), 4.68 (d, *J* = 7.2 Hz, 1H), 4.47 (d, *J* = 7.2 Hz, 1H), 3.75 (s, 2H), 2.20 (s, 3H) ppm; ^{13}C NMR

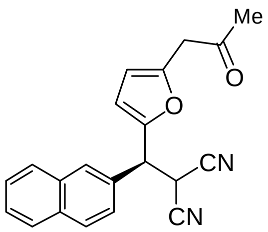
(150 MHz, $CDCl_3$): δ = 203.2, 149.8, 147.9, 138.4, 131.5 (q, $J_{C\text{-}F}$ = 33.0 Hz), 128.8, 126.3 (q, $J_{C\text{-}F}$= 3.0 Hz), 123.6 (q, $J_{C\text{-}F}$ = 271.5 Hz), 111.1, 111.0, 110.9, 109.7, 45.6, 42.9, 29.3, 28.4 ppm; ESI HRMS: calcd. for $C_{18}H_{13}F_3N_2O_2+Na^+$ 369.0821, found 369.0829.



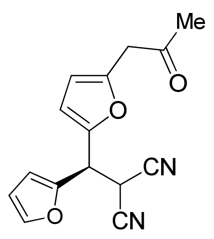
***(S)*-2-((3,5-Bis(trifluoromethyl)phenyl)(5-(2-oxopropyl)furan-2-yl)methyl)malononitrile (3h)** was obtained in 92% yield and the enantiomeric excess was determined to be 84% by HPLC analysis on Chiralcel OD column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 220 nm, t_{minor} = 10.49 min, t_{major} = 11.65 min. $[\alpha]_D^{20}$ = 9.8 (*c* = 0.70 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.95 (s, 1H), 7.91 (br s, 2H), 6.39 (d, *J* = 3.2 Hz, 1H), 6.27 (d, *J* = 3.2 Hz, 1H), 4.78 (d, *J* = 7.2 Hz, 1H), 4.53 (d, *J* = 7.2 Hz, 1H), 3.76 (s, 2H), 2.19 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 203.0, 150.3, 146.9, 137.2, 132.7 (q, $J_{C\text{-}F}$ = 34.5 Hz), 128.7, 128.6, 123.4 (q, $J_{C\text{-}F}$ = 3.0 Hz), 122.7 (q, $J_{C\text{-}F}$ = 271.5 Hz), 111.6, 110.7, 110.6, 109.9, 45.4, 42.9, 29.2, 28.4 ppm; ESI HRMS: calcd. for $C_{19}H_{12}F_6N_2O_2+Na^+$ 437.0695, found 437.0702.



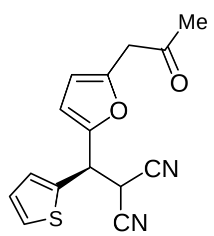
***(S)*-2-(Naphthalen-1-yl(5-(2-oxopropyl)furan-2-yl)methyl)malononitrile (3i)** was obtained in 75% yield and the enantiomeric excess was determined to be 90% by HPLC analysis on Chiralpak AD column (20% 2-propanol/*n*-hexane, 1 mL/min), UV 220 nm, t_{minor} = 14.62 min, t_{major} = 19.76 min. $[\alpha]_D^{20}$ = 12.1 (*c* = 0.65 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.00-7.89 (m, 3H), 7.63-7.50 (m, 4H), 6.38 (d, *J* = 3.2 Hz, 1H), 6.23 (d, *J* = 3.2 Hz, 1H), 5.57 (d, *J* = 6.8 Hz, 1H), 4.60 (d, *J* = 6.8 Hz, 1H), 3.73 (s, 2H), 2.17 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.4, 149.4, 149.0, 134.0, 130.5, 130.4, 129.9, 129.5, 127.4, 126.3, 125.8, 125.4, 121.4, 111.6, 111.4, 111.1, 109.7, 43.1, 40.9, 29.2, 27.8 ppm; ESI HRMS: calcd. for $C_{21}H_{16}N_2O_2+Na^+$ 351.1104, found 351.1109.



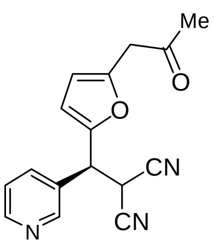
***(S)*-2-(Naphthalen-2-yl(5-(2-oxopropyl)furan-2-yl)methyl)malononitrile (3j)** was obtained in 84% yield and the enantiomeric excess was determined to be 91% by HPLC analysis on Chiralpak IC column (20% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{minor} = 20.95 min, t_{major} = 22.37 min. $[\alpha]_D^{20}$ = 13.0 (*c* = 0.98 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.91-7.85 (m, 4H), 7.55-7.49 (m, 3H), 6.33 (d, *J* = 3.2 Hz, 1H), 6.23 (d, *J* = 3.2 Hz, 1H), 4.78 (d, *J* = 7.2 Hz, 1H), 4.53 (d, *J* = 7.2 Hz, 1H), 3.74 (s, 2H), 2.18 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.4, 149.5, 149.0, 133.4, 133.2, 131.9, 129.4, 128.2, 128.0, 127.7, 127.0, 126.7, 125.0, 111.4, 110.9, 109.7, 46.3, 43.1, 29.3, 28.7 ppm; ESI HRMS: calcd. for $C_{21}H_{16}N_2O_2+Na^+$ 351.1104, found 351.1115.



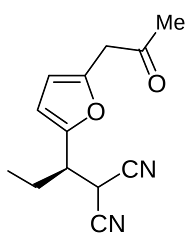
(S)-2-(Furan-2-yl(5-(2-oxopropyl)furan-2-yl)methyl)malononitrile (3k) was obtained in 77% yield and the enantiomeric excess was determined to be 75% by HPLC analysis on Chiralpak AD column (40% 2-propanol/*n*-hexane, 1 mL/min), UV 254nm, t_{major} = 5.41min, t_{minor} = 6.61min. $[\alpha]_D^{20}$ = 6.4 (*c* = 0.50 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38-7.47 (m, 1H), 6.46 (d, *J* = 3.2 Hz, 1H), 6.46-6.42 (m, 2H), 6.25-6.24 (d, *J* = 3.2 Hz, 1H), 4.81 (d, *J* = 6.8 Hz, 1H), 4.46 (d, *J* = 6.8 Hz, 1H), 3.74 (s, 2H), 2.20 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.4, 149.6, 146.9, 146.6, 143.6, 111.0, 110.9, 110.8, 110.2, 109.7, 43.1, 40.3, 29.3, 27.7 ppm; ESI HRMS: calcd. for $C_{15}H_{12}N_2O_3$+Na^+ 291.0740, found 291.0746.



***(R)*-2-((5-(2-Oxopropyl)furan-2-yl)(thiophen-2-yl)methyl)malononitrile (3l)** was obtained in 81% yield and the enantiomeric excess was determined to be 80% by HPLC analysis on Chiralpak IC column (20% 2-propanol/*n*-hexane, 1 mL/min), UV 220 nm, t_{minor} = 17.53 min, t_{major} = 23.07 min. $[\alpha]_D^{20}$ = 5.7 (*c* = 0.60 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.36 (m, 1H), 7.25-7.24 (m, 1H), 7.07-7.05 (m, 1H), 6.40 (d, *J* = 3.2 Hz, 1H), 6.23 (d, *J* = 3.2 Hz, 1H), 4.95 (d, *J* = 6.8 Hz, 1H), 4.42 (d, *J* = 6.8 Hz, 1H), 3.74 (s, 2H), 2.20 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.3, 149.6, 148.3, 135.9, 128.0, 127.5, 126.9, 111.2, 111.1, 111.0, 109.7, 43.1, 41.7, 30.1, 29.3 ppm; ESI HRMS: calcd. for $C_{15}H_{12}N_2O_2S$+Na^+ 307.0512, found 307.0519.

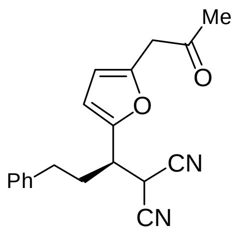


***(S)*-2-((5-(2-Oxopropyl)furan-2-yl)(pyridin-3-yl)methyl)malononitrile (3m)** was obtained in 83% yield and the enantiomeric excess was determined to be 82% by HPLC analysis on Chiralcel OD column (40% 2-propanol/*n*-hexane, 1 mL/min), UV 220 nm, t_{minor} = 18.40 min, t_{major} = 21.86 min. $[\alpha]_D^{20}$ = -14.1 (*c* = 0.85 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.69-8.66 (m, 2H), 7.84-7.82 (m, 1H), 7.40-7.37 (m, 1H), 6.32 (d, *J* = 3.2 Hz, 1H), 6.23 (d, *J* = 3.2 Hz, 1H), 4.67 (d, *J* = 7.6 Hz, 1H), 4.54 (d, *J* = 7.6 Hz, 1H), 3.74 (s, 2H), 2.18 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.1, 150.6, 149.8, 149.5, 147.7, 135.8, 130.6, 124.0, 111.2, 111.0, 110.9, 109.7, 43.6, 42.9, 29.3, 28.5 ppm; ESI HRMS: calcd. for $C_{16}H_{13}N_3O_2$+H^+ 280.1081, found 280.1086.

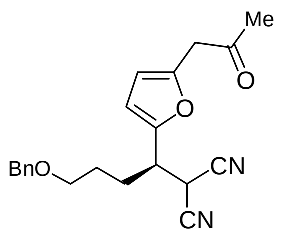


***(R)*-2-(1-(5-(2-Oxopropyl)furan-2-yl)propyl)malononitrile (3n)** was obtained in 86% yield and the enantiomeric excess was determined to be 89% by HPLC analysis on Chiralpak IC column (20% 2-propanol/*n*-hexane, 1 mL/min), UV 220 nm, t_{minor} = 23.94 min, t_{major} = 26.34 min. $[\alpha]_D^{20}$ = 23.7 (*c* = 0.35 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.33 (d, *J* = 3.2 Hz, 1H), 6.20 (d, *J* = 3.2 Hz, 1H), 4.00 (d, *J* = 6.0 Hz, 1H), 3.70 (s, 2H), 3.29-3.23 (m, 1H), 2.17 (s, 3H), 2.01-1.93 (m, 2H), 0.99 (t, *J*

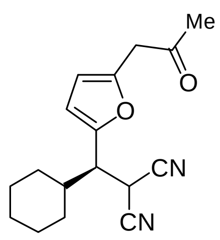
= 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.6, 149.3, 149.1, 111.5, 111.4, 110.4, 109.4, 43.1, 42.1, 29.2, 28.1, 24.2, 11.5 ppm; ESI HRMS: calcd. for $C_{13}H_{14}N_2O_2+K^+$ 269.0687, found 269.0692.



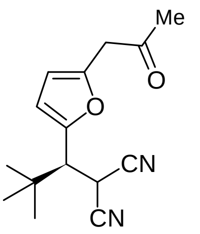
(*R*)-2-(1-(5-(2-Oxopropyl)furan-2-yl)-3-phenylpropyl)malononitrile (3o) was obtained in 87% yield and the enantiomeric excess was determined to be 90% by HPLC analysis on Chiralpak IC column (20% 2-propanol/*n*-hexane, 1 mL/min), UV 220 nm, t_{minor} = 15.77 min, t_{major} = 19.30 min. $[\alpha]_D^{20}$ = 30.8 (*c* = 0.70 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33-7.22 (m, 3H), 7.14-7.12 (m, 2H), 6.38 (d, *J* = 3.2 Hz, 1H), 6.24 (d, *J* = 3.2 Hz, 1H), 3.94 (d, *J* = 6.4 Hz, 1H), 3.74 (s, 2H), 3.35-3.29 (m, 1H), 2.76-2.70 (m, 1H), 2.59-2.51 (m, 1H), 2.33-2.23 (m, 2H), 2.21 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.4, 149.3, 148.9, 139.5, 128.7, 128.3, 126.6, 111.3, 110.9, 109.5, 43.1, 39.6, 32.7, 32.2, 29.3, 28.5 ppm; ESI HRMS: calcd. for $C_{19}H_{18}N_2O_2+Na^+$ 329.1260, found 329.1267.



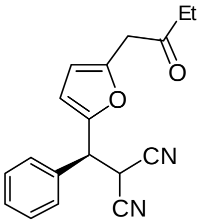
(*R*)-2-(4-(Benzyloxy)-1-(5-(2-oxopropyl)furan-2-yl)butyl)malononitrile (3p) was obtained in 82% yield and the enantiomeric excess was determined to be 81% by HPLC analysis on Chiralpak IC column (20% 2-propanol/*n*-hexane, 1 mL/min), UV 220 nm, t_{minor} = 16.99 min, t_{major} = 18.20 min. $[\alpha]_D^{20}$ = 8.5 (*c* = 0.55 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38-7.31 (m, 5H), 6.31 (d, *J* = 1.6 Hz, 1H), 6.18 (d, *J* = 1.6 Hz, 1H), 4.48-4.45 (m, 2H), 4.03 (d, *J* = 6.4 Hz, 1H), 3.68 (s, 2H), 3.49-3.47 (m, 2H), 3.41-3.36 (m, 1H), 2.16 (s, 3H), 2.07-2.01 (m, 2H), 1.70-1.59 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.5, 149.4, 149.1, 138.0, 128.4, 127.7, 127.6, 111.5, 111.4, 110.5, 109.4, 73.1, 69.0, 43.1, 40.2, 29.2, 28.2, 28.0, 26.9 ppm; ESI HRMS: calcd. for $C_{21}H_{22}N_2O_3+Na^+$ 373.1523, found 373.1529.



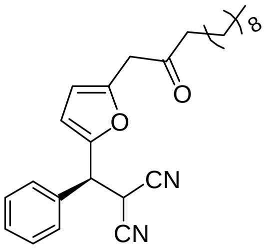
(*R*)-2-(Cyclohexyl(5-(2-oxopropyl)furan-2-yl)methyl)malononitrile (3q) was obtained in 90% yield and the enantiomeric excess was determined to be 92% by HPLC analysis on Chiralpak IC column (20% 2-propanol/*n*-hexane, 1 mL/min), UV 220 nm, t_{minor} = 15.35 min, t_{major} = 25.96 min. $[\alpha]_D^{20}$ = 12.0 (*c* = 0.55 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.32 (d, *J* = 2.8 Hz, 1H), 6.21 (d, *J* = 2.8 Hz, 1H), 4.17 (d, *J* = 6.8 Hz, 1H), 3.71 (s, 2H), 3.12 (t, *J* = 7.2 Hz, 1H), 2.18 (s, 3H), 2.00-1.92 (m, 1H), 1.81-1.58 (m, 5H), 1.36-1.20 (m, 2H), 1.13-0.86 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.7, 149.2, 148.9, 111.9, 111.6, 110.8, 109.3, 46.1, 43.2, 38.8, 31.0, 29.7, 29.1, 25.7, 25.6, 25.5 ppm; ESI HRMS: calcd. for $C_{17}H_{20}N_2O_2+Na^+$ 307.1422, found 307.1421.



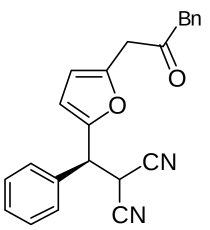
(S)-2-(2,2-Dimethyl-1-(5-(2-oxopropyl)furan-2-yl)propyl)malononitrile (3r) was obtained in 80% yield and the enantiomeric excess was determined to be 86% by HPLC analysis on Chiralpak IC column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 220 nm, t_{minor} = 9.50 min, t_{major} = 11.47 min. $[\alpha]_D^{20}$ = -15.1 (*c* = 0.41 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 6.41 (d, *J* = 3.2 Hz, 1H), 6.23 (d, *J* = 3.2 Hz, 1H), 4.16 (d, *J* = 5.2 Hz, 1H), 3.72 (s, 2H), 3.16 (d, *J* = 5.2 Hz, 1H), 2.19 (s, 3H), 1.10 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.7, 149.3, 148.8, 112.8, 112.4, 111.3, 109.2, 50.8, 43.2, 35.0, 29.1, 28.1, 23.9 ppm; ESI HRMS: calcd. for $C_{15}H_{18}N_2O_2+Na^+$ 281.1260, found 281.1266.



(S)-2-((5-(2-Oxobutyl)furan-2-yl)(phenyl)methyl)malononitrile (3s) was obtained in 79% yield and the enantiomeric excess was determined to be 94% by HPLC analysis on Chiralpak IC column (20% 2-propanol/*n*-hexane, 1 mL/min), UV 220 nm, t_{minor} = 15.80 min, t_{major} = 18.82 min. $[\alpha]_D^{20}$ = 11.6 (*c* = 1.15 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.42 (br s, 5H), 6.29 (d, *J* = 3.2 Hz, 1H), 6.20 (d, *J* = 3.2 Hz, 1H), 4.60 (d, *J* = 7.2 Hz, 1H), 4.43 (d, *J* = 7.2 Hz, 1H), 3.72 (s, 2H), 2.48 (q, *J* = 7.6 Hz, 2H), 1.05 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.0, 149.5, 148.9, 134.6, 129.3, 128.2, 111.4, 110.8, 109.5, 46.1, 42.0, 35.3, 28.7, 7.6 ppm; ESI HRMS: calcd. for $C_{18}H_{16}N_2O_2+Na^+$ 315.1104, found 315.1110.

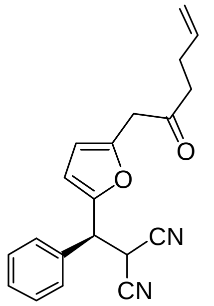


(S)-2-((5-(2-Oxododecyl)furan-2-yl)(phenyl)methyl)malononitrile (3t) was obtained in 84% yield and the enantiomeric excess was determined to be 93% by HPLC analysis on Chiralpak IC column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 220 nm, t_{minor} = 6.86 min, t_{major} = 7.51 min. $[\alpha]_D^{20}$ = -10.4 (*c* = 0.50 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.42 (br s, 5H), 6.30 (d, *J* = 3.2 Hz, 1H), 6.20 (d, *J* = 3.2 Hz, 1H), 4.60 (d, *J* = 7.6 Hz, 1H), 4.42 (d, *J* = 7.6 Hz, 1H), 3.71 (s, 2H), 2.44 (t, *J* = 7.2 Hz, 2H), 1.57-1.55 (m, 2H), 1.30-1.24 (m, 14H), 0.88 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.7, 149.6, 148.9, 134.6, 129.3, 128.2, 111.3, 110.8, 109.5, 46.2, 42.3, 42.1, 31.9, 29.5, 29.4, 29.3, 29.2, 29.1, 28.8, 23.6, 22.7, 14.1 ppm; ESI HRMS: calcd. for $C_{26}H_{32}N_2O_2+Na^+$ 427.2356, found 427.2361.

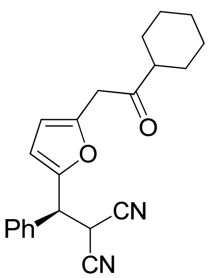


(S)-2-((5-(2-Oxo-3-phenylpropyl)furan-2-yl)(phenyl)methyl)malononitrile (3u) was obtained in 79% yield and the enantiomeric excess was determined to be 90% by HPLC analysis on Chiralpak IC column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 220 nm, t_{minor} = 9.29 min, t_{major} = 10.72 min. $[\alpha]_D^{20}$ = 17.6 (*c* = 0.55 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.41 (br s, 5H), 7.34-7.26 (m, 3H), 7.16-7.14 (m, 2H), 6.28 (d, *J* = 3.2 Hz, 1H), 6.18 (d, *J* = 3.2 Hz, 1H), 4.56 (d, *J* = 7.2 Hz, 1H), 4.37

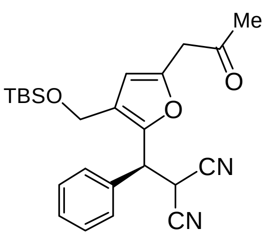
(d, J = 7.2 Hz, 1H), 3.75 (d, J = 6.4 Hz, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.8, 149.0, 148.9, 134.6, 133.4, 129.4, 129.3, 129.2, 128.8, 128.2, 127.2, 111.4, 111.3, 110.7, 109.8, 49.1, 46.1, 41.4, 28.7 ppm; ESI HRMS: calcd. for $C_{23}H_{18}N_2O_2$+Na^+ 377.1260, found 377.1267.



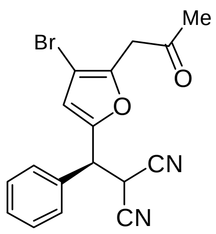
***(S)*-2-((5-(2-Oxohex-5-en-1-yl)furan-2-yl)(phenyl)methyl)malononitrile (3v)** was obtained in 81% yield and the enantiomeric excess was determined to be 92% by HPLC analysis on Chiralpak IC column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 220 nm, t_{minor} = 7.55 min, t_{major} = 8.65 min. $[\alpha]_D^{20}$ = 4.1 (c = 0.75 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (br s, 5H), 6.30 (d, J = 2.8 Hz, 1H), 6.21 (d, J = 2.8 Hz, 1H), 5.77-5.73 (m, 1H), 5.03-4.96 (m, 2H), 4.60 (d, J = 7.6 Hz, 1H), 4.43 (d, J = 7.6 Hz, 1H), 3.72 (s, 2H), 2.58-2.54 (m, 2H), 2.34-2.29 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.6, 149.3, 149.0, 136.6, 134.6, 133.6, 130.1, 129.3, 128.4, 128.2, 115.5, 111.3, 110.8, 109.6, 46.1, 42.4, 41.0, 28.7, 27.4 ppm; ESI HRMS: calcd. for $C_{20}H_{18}N_2O_2$+Na^+ 341.1260, found 341.1275.



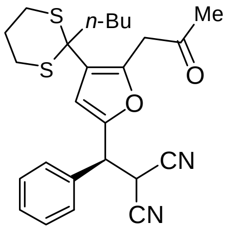
(S)-2-((5-(2-Cyclohexyl-2-oxoethyl)furan-2-yl)(phenyl)methyl)malononitrile (3w) was obtained in 78% yield and the enantiomeric excess was determined to be 93% by HPLC analysis on Chiralpak IC column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{minor} = 8.12 min, t_{major} = 9.42 min. $[\alpha]_D^{20}$ = 15.1 (c = 1.1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (s, 5H), 6.29 (d, J = 2.8 Hz, 1H), 6.20 (s, J = 2.8 Hz, 1H), 4.60 (d, J = 7.2 Hz, 1H), 4.46 (d, J = 7.2 Hz, 1H), 3.76 (s, 2H), 2.46-2.40 (m, 1H) 1.83-1.75 (m, 4H), 1.67-1.65 (m, 1H), 1.42-1.46 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.3, 149.6, 148.7, 134.6, 129.3, 128.2, 111.4, 110.7, 110.2, 109.4, 49.9, 46.1, 40.3, 28.7, 28.3, 25.7, 25.4 ppm; ESI HRMS: calcd. for $C_{22}H_{22}N_2O_2$+Na^+ 369.1573, found 369.1577.



***(S)*-2-((3-(((tert-Butyldimethylsilyl)oxy)methyl)-5-(2-oxopropyl)furan-2-yl)(phenyl)methyl)malononitrile (3x)** was obtained in 83% yield and the enantiomeric excess was determined to be 93% by HPLC analysis on Chiralcel OD column (20% 2-propanol/*n*-hexane, 1 mL/min), UV 220 nm, t_{minor} = 9.45 min, t_{major} = 10.64 min. $[\alpha]_D^{20}$ = 13.1 (c = 0.12 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40-7.35 (m, 5H), 6.15 (s, 1H), 4.96 (d, J = 7.2 Hz, 1H), 4.53 (d, J = 2.8 Hz, 2H), 4.46 (d, J = 7.2 Hz, 1H), 3.71 (s, 2H), 2.18 (s, 3H), 0.90 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.4, 148.5, 144.5, 135.2, 129.5, 129.2, 128.9, 128.1, 124.3, 111.6, 111.5, 109.9, 57.5, 44.6, 43.2, 29.2, 28.4, 25.9, 25.8, 18.3, -5.57 ppm; ESI HRMS: calcd. for $C_{24}H_{30}N_2O_3Si$+Na^+ 445.1918, found 445.1923.

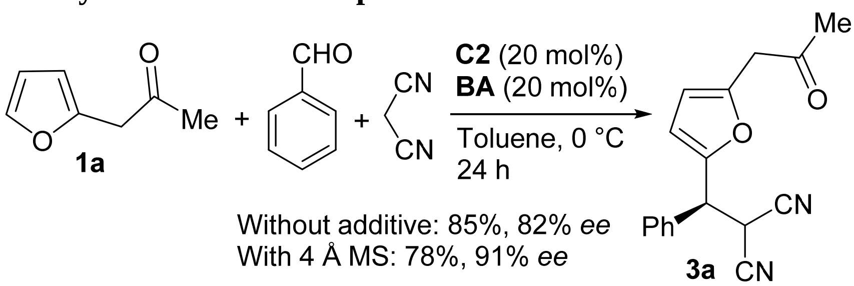


***(S)*-2-((4-Bromo-5-(2-oxopropyl)furan-2-yl)(phenyl)methyl)malononitrile (3y)** was obtained in 81% yield and the enantiomeric excess was determined to be 90% by HPLC analysis on Chiralpak IC column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 220 nm, t_{minor} = 7.47 min, t_{major} = 8.68 min. $[\alpha]_D^{20}$ = 10.0 (*c* = 0.65 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.43-7.40 (m, 5H), 6.38 (s, 1H), 4.59 (d, *J* = 7.2 Hz, 1H), 4.44 (d, *J* = 7.2 Hz, 1H), 3.75 (s, 2H), 2.18 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.1, 149.6, 147.2, 133.8, 129.6, 129.5, 128.2, 113.8, 111.1, 100.1, 46.0, 41.3, 29.3, 28.4 ppm; ESI HRMS: calcd. for $C_{17}H_{13}BrN_2O_2+Na^+$ 379.0058 (^{79}Br), 381.0038 (^{81}Br), found 379.0060, 381.0040.



***(S)*-2-((4-(2-Butyl-1,3-dithian-2-yl)-5-(2-oxopropyl)furan-2-yl)(phenyl)methyl)malononitrile (3z)** was obtained in 75% yield and the enantiomeric excess was determined to be 95% by HPLC analysis on Chiralpak IC column (20% 2-propanol/*n*-hexane, 1 mL/min), UV 220 nm, t_{minor} = 9.22 min, t_{major} = 11.02 min. $[\alpha]_D^{20}$ = 13.9 (*c* = 0.80 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45 (br s, 5H), 6.58 (s, 1H), 4.58 (d, *J* = 7.2 Hz, 1H), 4.41 (d, *J* = 7.2 Hz, 1H), 4.16 (s, 2H), 2.82-2.75 (m, 2H), 2.68-2.64 (m, 2H), 2.20 (s, 3H), 1.99-1.86 (m, 4H), 1.37-1.23 (m, 4H), 0.86 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.5, 147.2, 147.0, 134.4, 129.4, 129.1, 128.3, 126.5, 125.8, 114.1, 111.3, 51.8, 46.1, 43.5, 43.1, 29.7, 28.9, 28.0, 26.3, 25.1, 22.7, 13.8 ppm; ESI HRMS: calcd. for $C_{25}H_{28}N_2O_2S_2+Na^+$ 475.1484, found 475.1490.

Procedure for the asymmetric three-component reaction

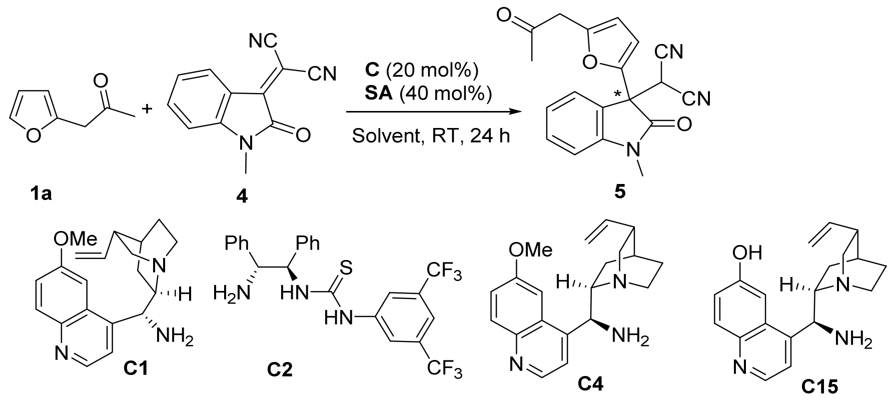


The reaction was carried out with benzaldehyde (0.1 mmol), malononitrile (0.1 mmol) and 2-furylacetone **1a** (0.3 mmol) in toluene (1.0 mL) in the presence of amine catalyst **C2** (0.02 mmol), benzoic acid (0.02 mmol) at 0 °C for 24 h. Then the solution was concentrated and the residue was purified by flash chromatography on silica gel to afford the chiral product **3a** in 85% yield and with 82% *ee*. In another reaction, 4 Å MS (15 mg) was simultaneously added. Product **3a** was obtained in 78% yield and with 91% *ee* after 24 h.

5. More explorations of activated alkenes and heterocyclic ketones

For further study, a diversity of activated alkenes and heterocyclic ketones were explored in the potential Friedel–Crafts alkylations via HOMO activation.

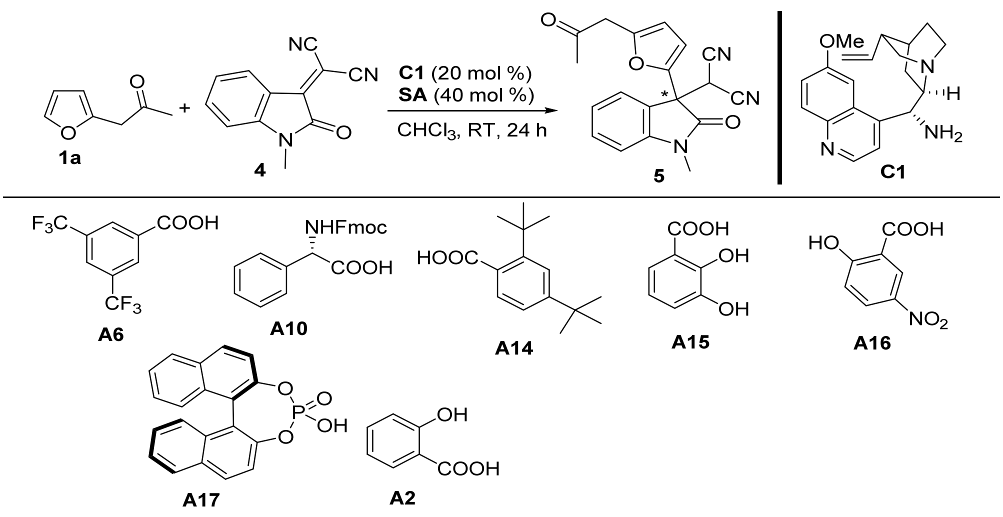
Table 3. Catalyst screenings of remote Friedel–Crafts alkylation of 2-furylacetone **1a** with 2-oxoindolin-3-ylidenemalononitrile **4**[a]



Entry	Cat.	Solvent	*t* (h)	Yield (%)[b]	*ee* (%)[c]
1	**C4**	DCM	24	75	–24
2	**C4**	Toluene	24	74	–30
3	**C4**	$CHCl_3$	24	87	–36
4	**C4**	CH_3CN	24	53	–16
5	**C4**	THF	24	53	–16
6	**C4**	1,4-Dioxane	24	66	–20
7	**C1**	**$CHCl_3$**	**24**	**84**	**41**
8[d]	**C2**	$CHCl_3$	24	66	–24
9	**C15**	$CHCl_3$	24	77	–2
10[e]	**C1**	$CHCl_3$	24	86	32

[a] Unless noted otherwise, reactions were performed with 2-furylacetone **1a** (0.3 mmol), 2-oxoindolin-3-ylidenemalononitrile **4** (0.1 mmol), amine **C** (20 mol%) and salicylic acid (**SA**) (40 mol%) in solvent (1.0 mL) at ambient temperature for 24 h. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] Benzoic acid (20 mol%) was used. [e] At 0 °C.

Table 4. More acid additive screenings[a]

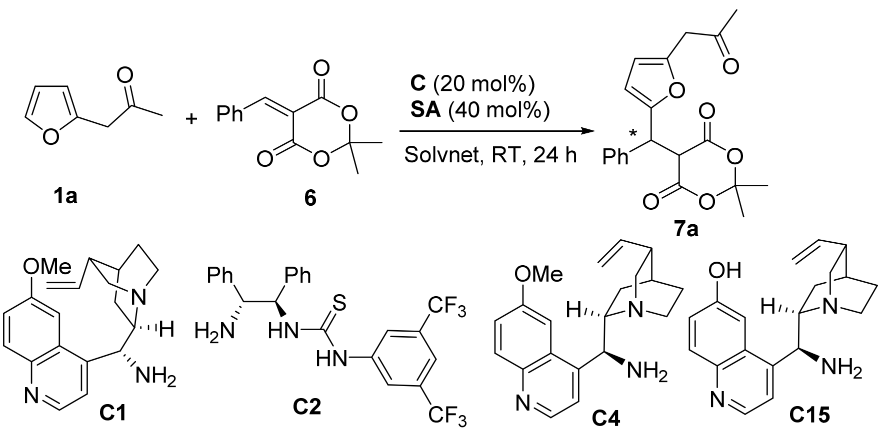


Entry	Acid	Yield (%)[b]	*ee* (%)[c]
1	**A6**	56	20
2	**A10**	30	12
3	**A14**	31	13
4	**A15**	72	38
5	**A16**	89	25
6	**A17**	<10	ND[d]
7	**A2**	**84**	**41**

[a] Reactions were conducted with **1a** (0.3 mmol), **4** (0.1 mmol), catalyst **C1** (0.02 mmol), acid (0.04 mmol) in $CHCl_3$ (1.0 mL) at ambient temperature for 24 h. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] Not determined.

2-Oxoindolin-3-ylidenemalononitrile **4** showed good reactivity with ketone **1a**, affording the desired remote Friedel–Crafts product **5** with a quaternary chiral center. After extensive explorations with a number of amine catalysts and reaction conditions, as outlined in Tables 3 and 4, only a fair *ee* value could be attained.

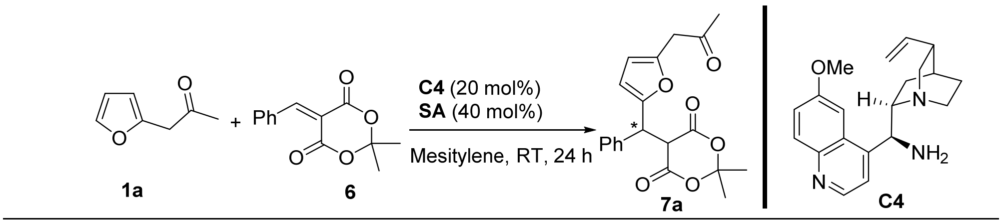
Table 5. Catalyst screenings of remote FC alkylation of 2-furylacetone **1a** with activated alkene **6**[a]

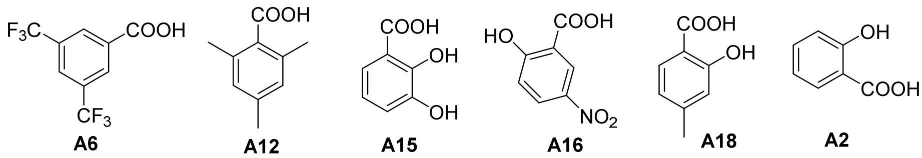


Entry	Cat.	Solvent	*t* (h)	Yield (%)[b]	*ee* (%)[c]
1	**C4**	Toluene	24	79	49
2	**C4**	*o*-Xylene	24	92	60
3	**C4**	*m*-Xylene	24	86	48
4	**C4**	**Mesitylene**	**24**	**87**	**62**
5	**C1**	Mesitylene	24	83	–34
6[d]	**C2**	Mesitylene	24	80	–1
7	**C15**	Mesitylene	24	78	4
8[e]	**C4**	Mesitylene	48	36	2

[a] Unless noted otherwise, reactions were performed with 2-furylacetone **1a** (0.3 mmol), activated alkene **6** (0.1 mmol), amine **C** (20 mol%) and salicylic acid (SA) (40 mol%) in solvent (1.0 mL) at ambient temperature for 24h. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] Benzoic acid (20 mol%) was used. [e] At 0 °C.

Table 6. More acid additive screenings[a]



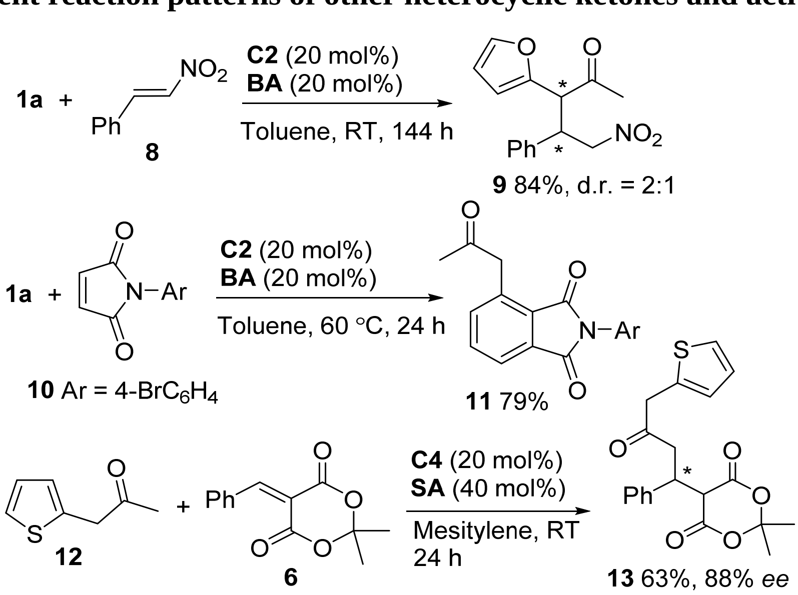


Entry	Acid	Yield (%)[b]	*ee* (%)[c]
1	**A6**	92	43
2	**A12**	<10	ND[d]
3	**A15**	<10	ND[d]
4	**A16**	<10	ND[d]
5	**A18**	<10	ND[d]
6	**A2**	**87**	**62**

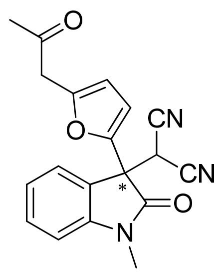
[a] Reactions were conducted with **1a** (0.3 mmol), **6** (0.1 mmol), catalyst **C4** (0.02 mmol), acid (0.04 mmol) in mesitylene (1.0 mL) at ambient temperature for 24 h. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] Not determined.

Activated alkene **6** derived from Meldrum's acid also smoothly gave the desired remote FC product **7a** in the reactions with ketone **1a** catalyzed by chiral amine, as outlined in Tables 5 and 6, while the enantioselectivity was still unsatisfactory after extensive screenings.

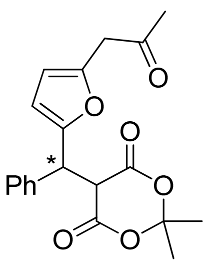
Completely different reaction patterns of other heterocyclic ketones and activated alkenes



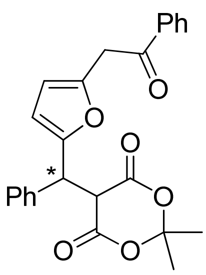
In contrast, completely different reaction patterns were observed for other electrophiles. α-Regioselective Michael addition of ketone **1a** to less electrophilic β-nitrostyrene **8** was noticed, as illustrated above scheme, in the presence of amine **C2** and benzoic acid, and adduct **9** was isolated as a inseparable diastereomeric mixture. A Diels–Alder cycloaddition reaction of ketone **1a** was noticed in reaction with maleimide **10** catalyzed by chiral amine **C2** and **SA** in toluene at 60 °C, delivering aromatic product **11** in a good yield. Moreover, we also successfully synthesized 2-thienylacetone **12**, and α′-regioselective Michael addition product **13** was obtained in reaction with the activated alkene **6**. However, 2-pyrrolylacetone was unstable under the catalytic conditions.



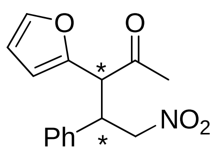
2-(1-Methyl-2-oxo-3-(5-(2-oxopropyl)furan-2-yl)indolin-3-yl)malononitrile (5) was obtained in 84% yield and the enantiomeric excess was determined to be 41% by HPLC analysis on Chiralpak IC column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{minor} = 12.15 min, t_{major} = 13.81 min. $[\alpha]_D^{20}$ = -17 (*c* = 0.50 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.21-6.19 (m, 2H), 4.92 (s, 1H), 3.74 (s, 2H), 3.29 (s, 3H), 2.04 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.0, 170.2, 151.2, 144.8, 143.8, 131.4, 125.2, 124.0, 123.1, 112.2, 110.4, 109.7, 109.5, 109.4, 52.6, 43.1, 29.8, 29.2, 27.0 ppm; ESI HRMS: calcd. for $C_{19}H_{15}N_3O_3+Na^+$ 356.1006, found 356.1010.



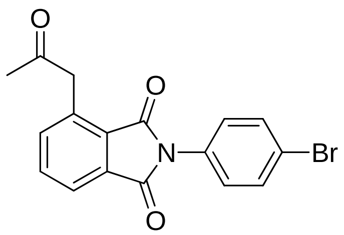
2,2-Dimethyl-5-((5-(2-oxopropyl)furan-2-yl)(phenyl)methyl)-1,3-dioxane-4,6-dione (7a) was obtained in 87% yield and the enantiomeric excess was determined to be 62% after methylation with CH_3I (acetone, Na_2CO_3, rt) by HPLC analysis on Chiralpak IC column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 8.89 min, t_{minor} = 11.34 min. $[\alpha]_D^{20}$ = -10 (*c* = 0.75 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.49-7.46 (m, 2H), 7.37-7.31 (m, 3H), 6.15 (d, *J* = 3.2 Hz, 1H), 6.00-5.99 (m, 1H), 5.26 (s, 1H), 4.23 (d, *J* = 3.2 Hz, 1H), 3.65 (s, 2H), 2.04 (s, 3H), 1.73 (s, 3H), 1.51 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.4, 164.2, 152.8, 147.2, 137.1, 129.8, 128.6, 128.1, 109.5, 109.1, 105.2, 50.4, 44.0, 43.4, 28.8, 28.1, 27.7 ppm; ESI HRMS: calcd. for $C_{20}H_{20}O_6+Na^+$ 379.1152, found 379.1153.



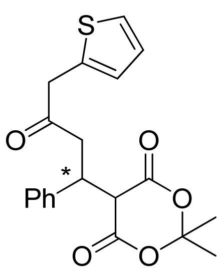
2,2-Dimethyl-5-((5-(2-oxo-2-phenylethyl)furan-2-yl)(phenyl)methyl)-1,3-dioxane-4,6-dione (7b) was obtained in 80% yield and the enantiomeric excess was determined to be 37% after methylation with CH_3I (acetone, Na_2CO_3, rt) by HPLC analysis on Chiralpak AD column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 9.66 min, t_{minor} = 11.81 min. $[\alpha]_D^{20}$ = -14 (*c* = 0.35 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.49-7.42 (m, 4H), 7.34-7.27 (m, 3H), 6.18 (d, J = 3.2 Hz, 1H), 6.01 (d, J = 3.2 Hz, 1H), 5.25 (m, 1H), 4.27 (s, 2H), 4.24 (m, 1H), 1.71 (s, 3H), 1.48 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.8, 164.2, 164.0, 152.5, 147.2, 137.1, 136.1, 133.3, 129.7, 128.7, 128.6, 128.5, 128.0, 109.4, 109.3, 105.1, 50.3, 44.0, 38.6, 28.1, 27.7 ppm; ESI HRMS: calcd. for $C_{25}H_{22}O_6$+Na^+ 441.1309, found 441.1300.



3-(furan-2-yl)-5-nitro-4-phenylpentan-2-one (9) was obtained in 84% yield after flash chromatography. dr = 2:1 ; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47-7.46 (m, 0.67H), 7.33-7.19 (m, 4.66H), 7.10-7.08 (m, 0.67H), 6.42-6.41 (m, 0.67H), 6.32 (d, J = 3.2 Hz, 0.67H), 6.20-6.19 (m, 0.33H), 6.03 (d, J = 3.2 Hz, 0.33H), 4.90-4.76 (m, 0.67H), 4.55-4.51 (m, 1.33H), 4.38-4.30 (m, 1H), 4.25-4.21 (m, 1H), 2.15 (s, 1H), 1.98 (s, 2H) ppm; ESI HRMS: calcd. for $C_{15}H_{15}NO_4$+Na^+ 296.0893, found 296.0900. *In addition, attempts to determine the ee values of the diastereomers were unsuccessful.*

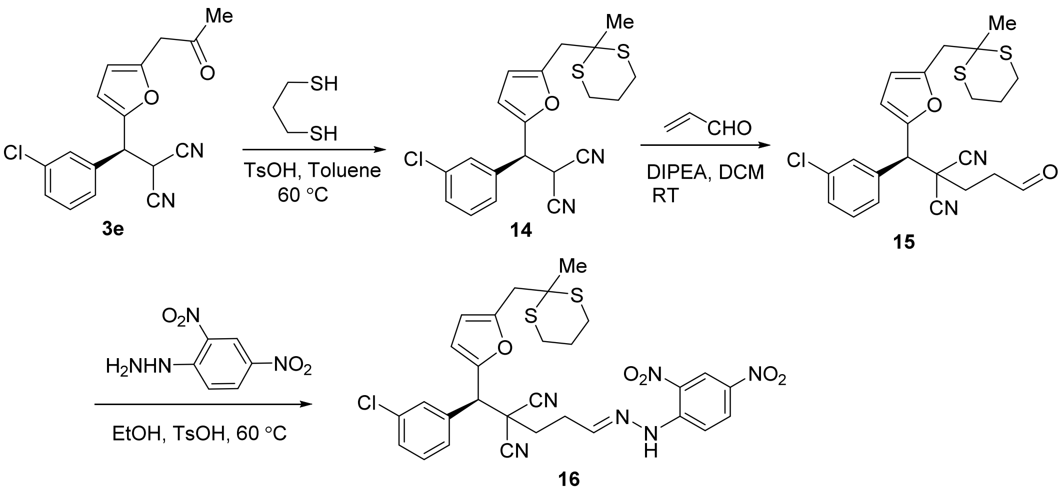


2-(4-Bromophenyl)-4-(2-oxopropyl)isoindoline-1,3-dione (11) was obtained in 79% yield after flash chromatography; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, J = 7.6 Hz, 1H), 7.73 (t, J = 7.6 Hz, 1H), 7.62 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 7.6 Hz , 1H), 7.32 (d, J = 8.8 Hz, 2H), 4.27 (s, 2H), 2.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.1, 137.2, 134.4, 134.1, 132.2, 132.0, 128.9, 128.0, 122.8, 121.8, 45.7, 30.3 ppm; ESI HRMS: calcd. for $C_{17}H_{12}BrNO_3$+Na^+ 379.9898 (^{79}Br), 381.9878 (^{81}Br), found 379.9893, 381.9872.



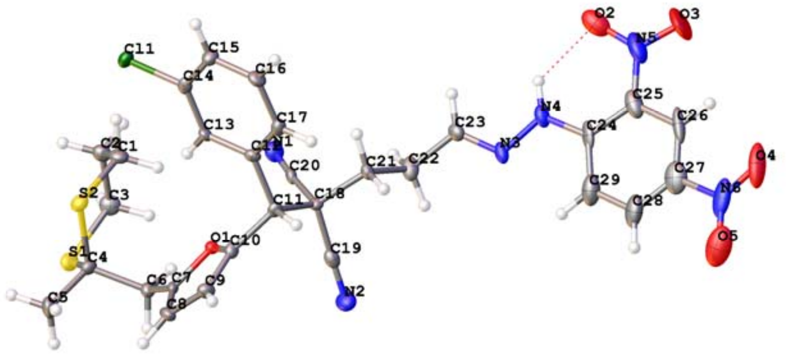
2,2-Dimethyl-5-(3-oxo-1-phenyl-4-(thiophen-2-yl)butyl)-1,3-dioxane-4,6-dione (13) was obtained in 63% yield and the enantiomeric excess was determined to be 88% after methylation with CH_3I (acetone, Na_2CO_3, rt) by HPLC analysis on Chiralpak IC column (40% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{minor} = 9.04 min, t_{major} = 20.17 min. $[\alpha]_D^{20}$ = -20.9 (c = 0.75 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30-7.22 (m, 6H), 6.98-6.96 (m, 1H), 6.90-6.89 (m, 1H), 4.30-4.25 (m, 1H), 4.20 (d, J = 3.6 Hz, 1H), 3.96 (s, 2H), 3.82-3.74 (m, 1H), 3.16-3.10 (m, 1H), 1.65 (s, 3H), 1.31 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.1, 165.3, 165.0, 139.3, 136.6, 134.4, 130.7, 128.8, 128.7, 127.8, 127.1, 125.3, 119.4, 117.6, 105.3, 48.8, 43.8, 43.7, 28.0, 27.8, 27.6 ppm; ESI HRMS: calcd. for $C_{20}H_{19}O_5S$+Na^+ 395.0924, found 395.0920.

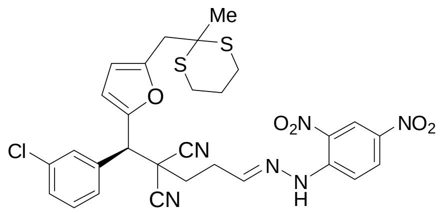
6. Synthetic transformations of the chiral product



To an anhydrous toluene solution of product **3e** (32 mg, 0.1 mmol) was added 1,3-propanedithiol (11 mg, 0.1 mmol) and a catalytic amount of TsOH (2 mg, 0.01 mmol) at ambient temperature. Then the solution was stirred overnight at 60 °C. After completion, the solution was evaporated and purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford product **14** which was directly dissolved by dichloromethane and reacted with acrolein (8.4 mg, 0.15 mmol) and DIPEA (19 mg, 0.15 mmol) at room temperature. After 10 min, diluted hydrochloric acid was added. Then the mixture was extracted by DCM. The organic solvent was evaporated and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1) to afford product **15**. To the solution of EtOH of product **15** was added 2,4-dinitrophenylhydrazine (29 mg, 0.15 mmol) and a catalytic amount of TsOH (3 mg, 0.02 mmol) at ambient temperature. The mixture was stirred overnight at 60 °C. When the reaction was completed, the solution was evaporated and purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1) to afford product **16** in 79% yield for three steps and the enantiomeric excess was determined to be 92%, determined by HPLC analysis on Chiralpak IC column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 220nm, t_{minor} = 47.88 min, t_{major} = 53.89 min. $[\alpha]_D^{20}$ = 23.3 (*c* = 0.15 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.08 (s, 1H), 9.10 (d, *J* = 1.6 Hz, 1H), 8.33 (dd, *J* = 9.6 Hz, *J* = 1.6 Hz, 1H), 7.81 (d, *J* = 9.6 Hz, 1H), 7.65 (s, 1H), 7.56-7.50 (m, 2H), 7.41-7.35 (m, 2H), 6.39 (d, *J* = 2.8 Hz, 1H), 6.21 (d, *J* = 2.8 Hz, 1H), 4.41 (s, 1H), 3.35 (d, *J* = 3.6 Hz, 2H), 3.07-3.00 (m, 2H), 2.89-2.78 (m, 4H), 2.36-2.29 (m, 2H), 2.08-2.04 (m, 1H), 1.92-1.89 (m, 1H), 1.60 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.0, 147.0, 146.9, 144.8, 138.3, 136.1, 135.0, 130.3, 130.1, 129.5, 129.3, 127.5, 123.4, 116.4, 114.2, 114.1, 111.7, 110.0, 51.0, 48.0, 42.3, 39.8, 33.2, 28.8, 27.9, 26.8, 26.7, 24.8 ppm; ESI HRMS: calcd. for $C_{29}H_{27}ClN_6O_5S_2+Na^+$ 661.1065, found 661.1066.

7. Crystal data and structure refinement for enantiopure 16



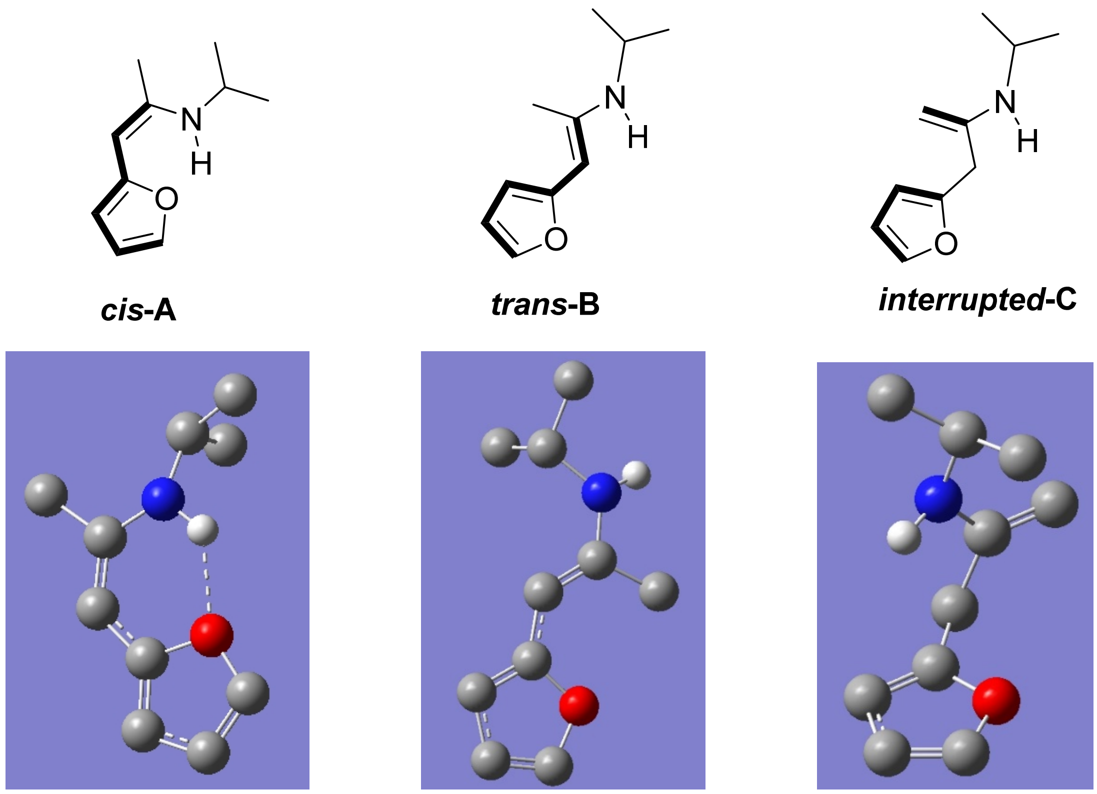


16

Identification code	**16**
Empirical formula	$C_{29}H_{27}ClN_6O_5S_2$
Formula weight	639.14
Temperature	98.4 K
Crystal system	monoclinic
Space group	C2
a / Å, b / Å, c / Å	37.1283(19), 7.9035(4), 10.3537(7)
α/°, β/°, γ/°	90.00, 93.769(5), 90.00
Volume / Å3	3031.7(3)
Z	4
ρ_{calc} / mg mm^{-3}	1.400
μ / mm^{-1}	0.313
F(000)	1328
Crystal size	0.20 x 0.08 x 0.03 mm
Theta range for data collection	6.12 to 52 deg.
Index ranges	-45<=h<=45, -9<=k<=9, -12<=l<=12
Reflections collected	14244
Independent reflections	5871[R(int) = 0.0679 (inf-0.9Å)]
Data / restraints / parameters	5871 / 1 / 389
Goodness-of-fit on F^2	0.942
Final R indices [I>2sigma(I)]	R_1 = 0.0484, wR_2 = 0.0897
R indices (all data)	R_1 = 0.0719, wR_2 = 0.0947
Absolute structure parameter	0.05(6)
Largest diff. peak/hole / e Å-3	0.720/-0.299

8. Proposed catalytic mechanism for the remote Friedel–Crafts reaction

In order to gain some insight into the catalytic mechanism for the Friedel–Crafts reaction of 2-furylacetone **1a** and electron-deficient alkene, we first investigated the possible enamine intermediate between ketone **1a** and a simplified primary amine catalyst 2-propylamine by computational calculations. To find out the global minimum conformation of enamines ***cis*-A**, ***trans*-B**, and ***interrupted*-C**, a conformational search was performed using Discovery Studio software[4] with a systematic searches method. The total 74 corresponding minimum geometries were fully optimized using DFT at the B3LYP/6-31G(d) level, as implemented in the Gaussian 03 program package.[5] All of them displayed no imaginary frequencies. It shows that the energy of enamine ***cis*-A** is lower than that of enamine ***trans*-B** by 2.63 kcal/mol, which can be ascribed to the intramolecular hydrogen bonding between N-H and O-atom of furan ring. In contrast, as outlined in the following scheme, enamine ***interrupted*-C** has much higher energy than enamine ***cis*-A** by 8.37 kcal/mol, indicating that the conjugated enamine ***cis*-A** would be favored.



(0 kcal/mol) O…H 2.03Å (2.63 kcal/mol) (8.37 kcal/mol)

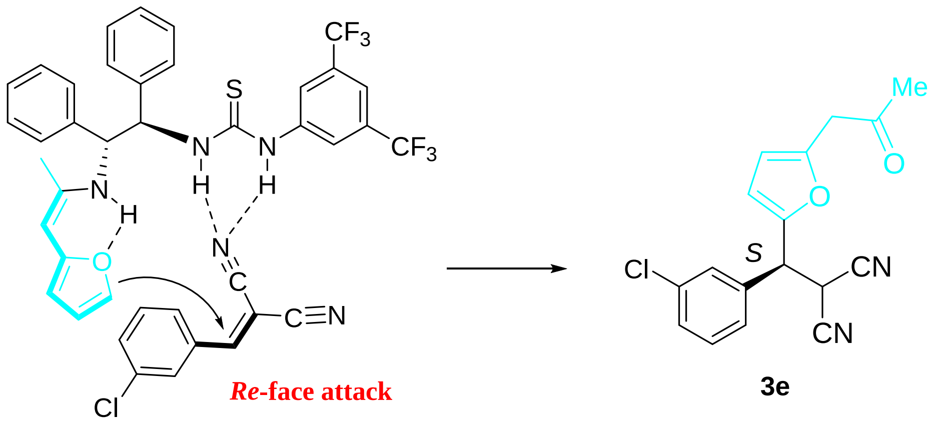
Proposed simplified enamine species and DFT computational calculations

[4] Discovery Studio, version 3.1; Accelrys Inc.: San Diego, CA, 2011.

[5] Gaussian 03, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E.

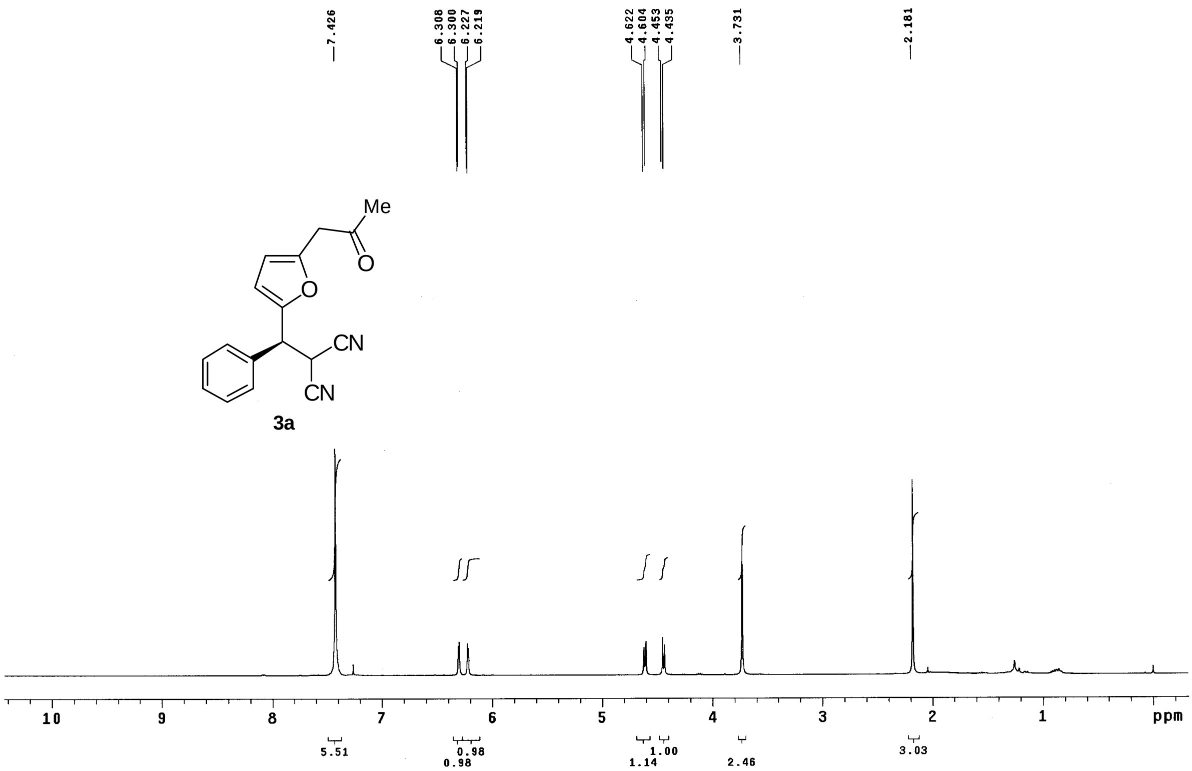
Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2003.

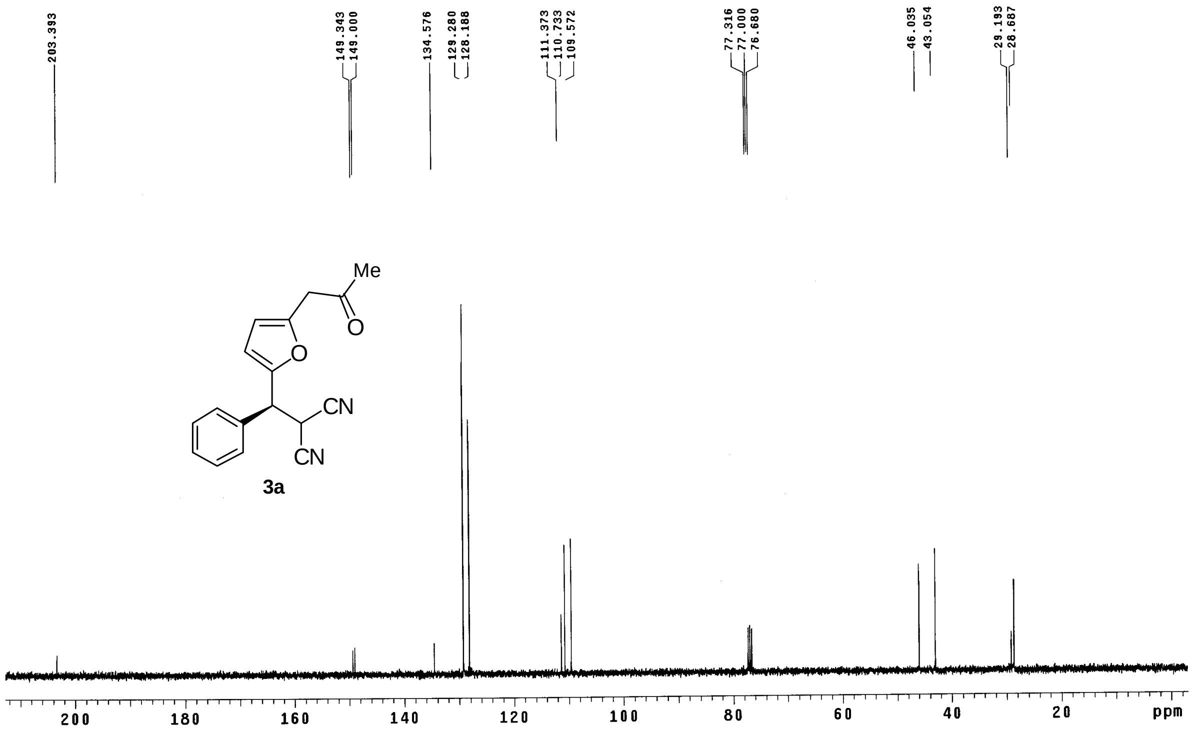
Based on the preliminary computational studies on enamine intermediates and the absolute configuration of product **3e**, a plausible catalytic mechanism was proposed. As outlined in the following scheme, a conjugated *cis*-enamine is formed between primary amine group and 2-furylacetone **1a**. Owing to the interesting intramolecular hydrogen-bonding interaction between NH group and furan ring, the remote 5-site would be closer to alkylidenemalononitrile which is concertedly activated by bifunctional thiourea group of catalyst **C2**. Subsequently, *Re*-face attack by HOMO-raised furan ring would give the observed enantioenriched product (*S*)-**3e**.

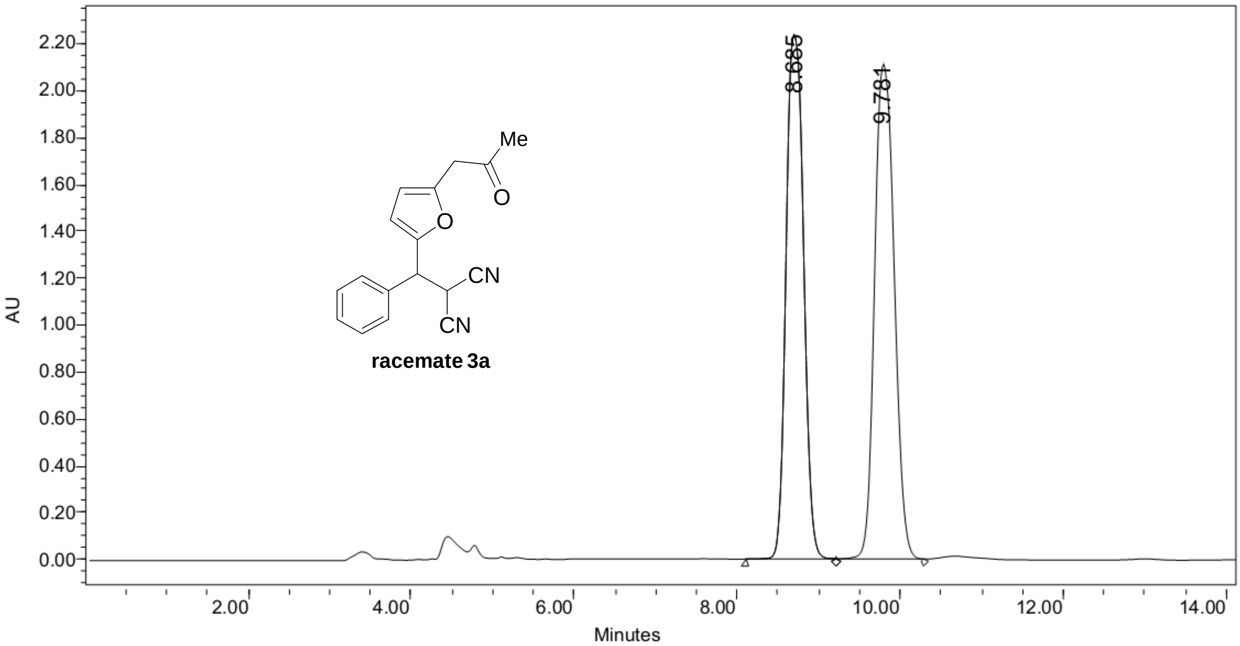


Proposed catalytic transition state

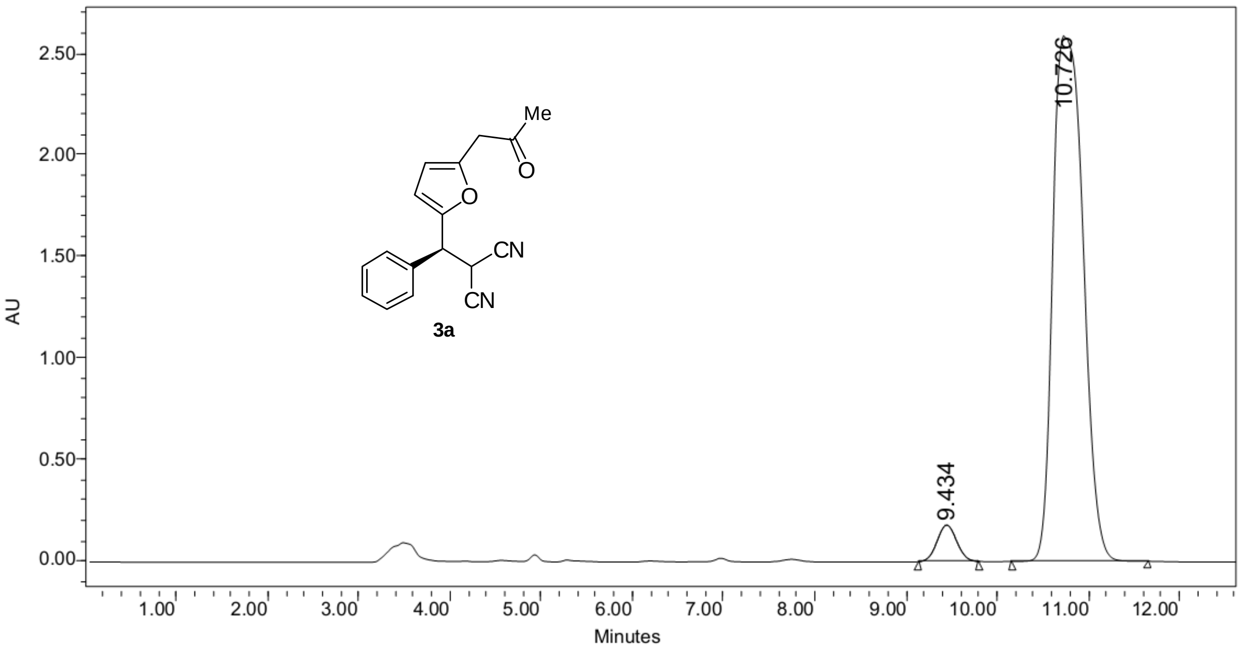
9. NMR spectra and HPLC chromatograms



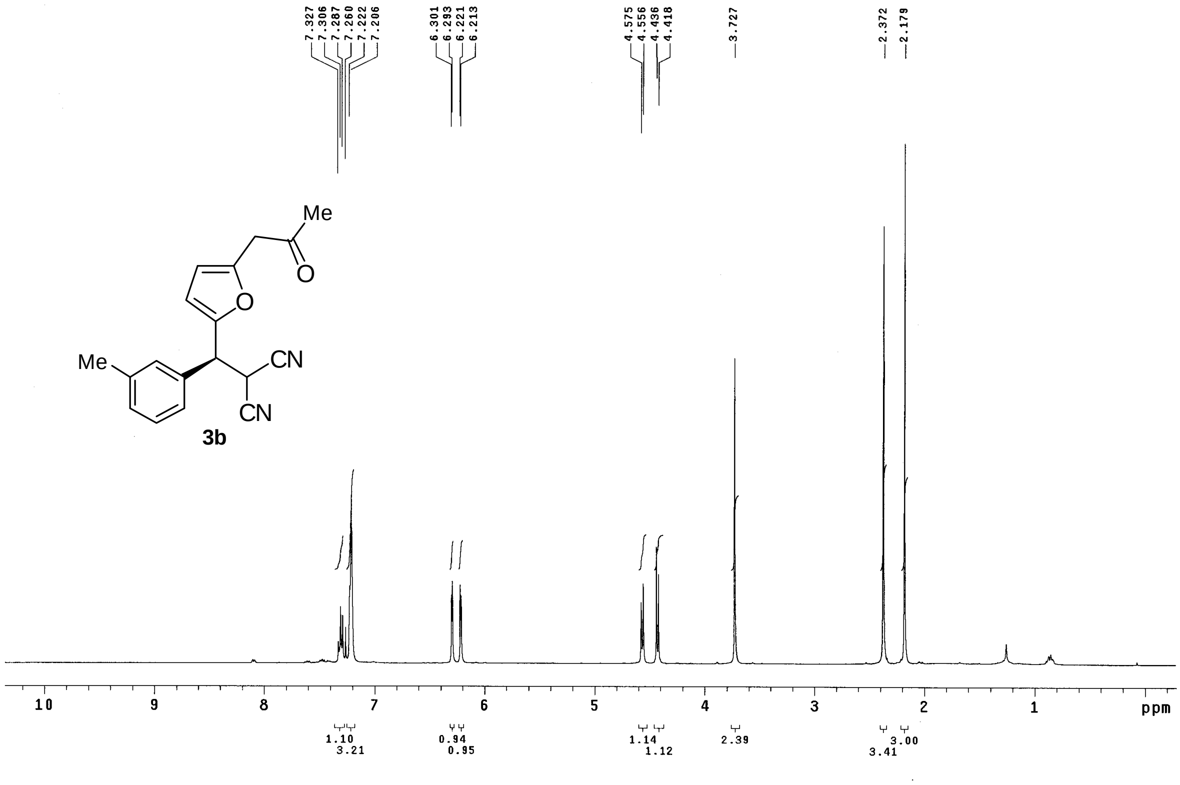


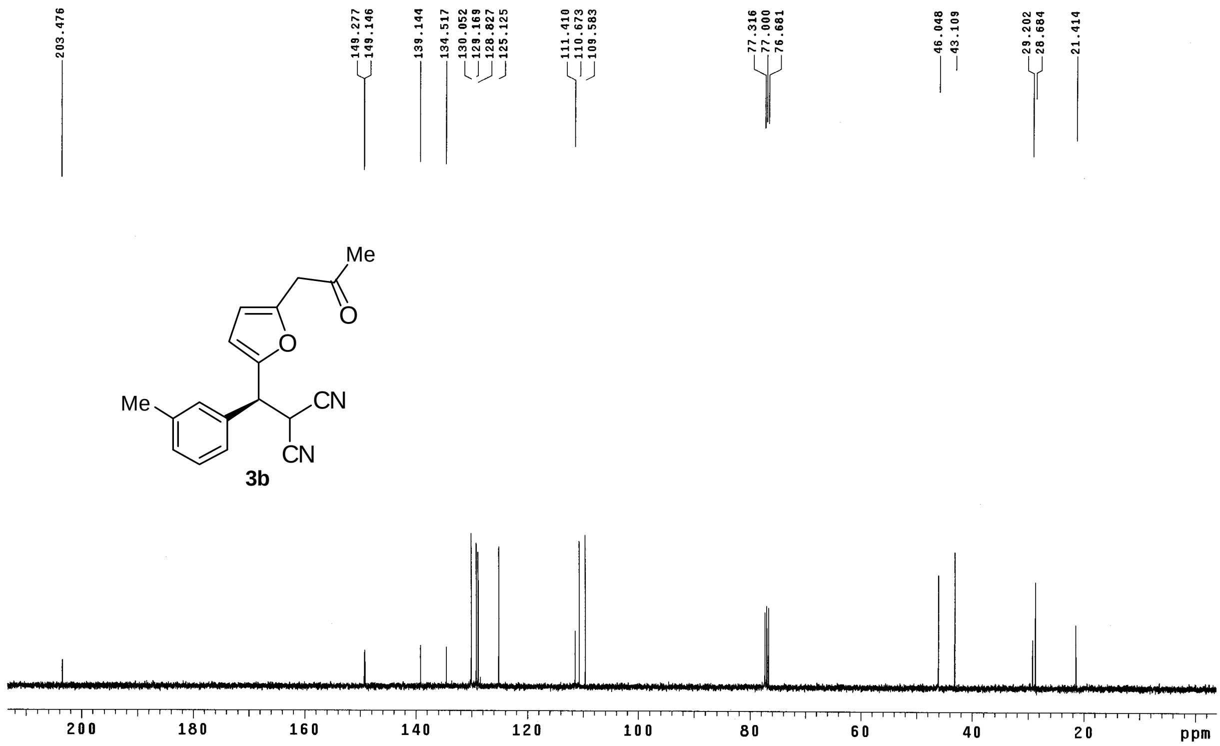


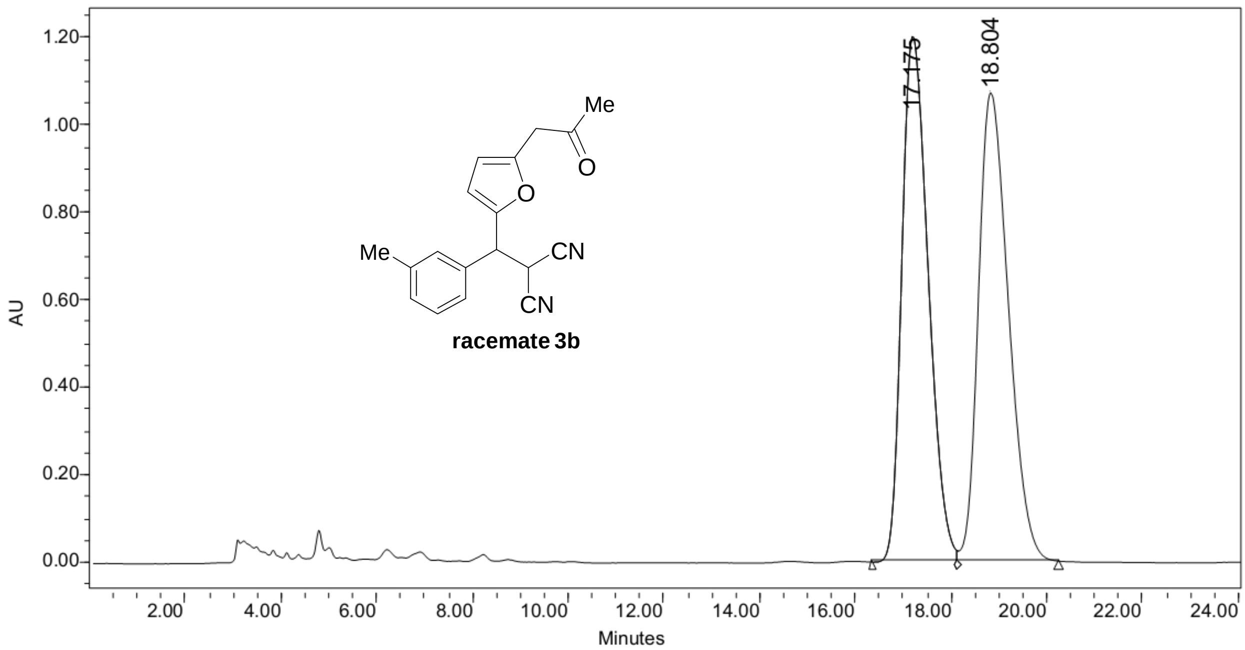
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	8.685	33366040	48.56	2238942	51.46
2	9.781	35349009	51.44	2112074	48.54



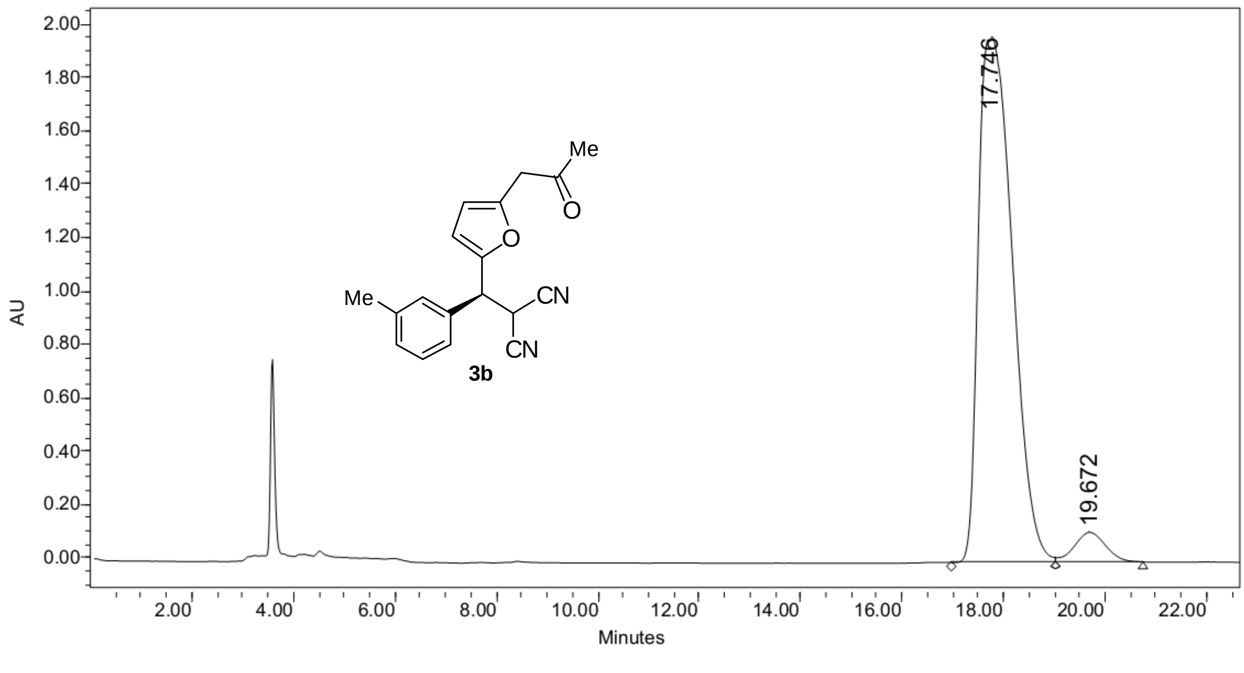
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	9.434	2583597	4.15	176472	6.38
2	10.726	59655940	95.85	2591379	93.62


7.327 7.306 7.287 7.260 7.222 7.206
6.301 6.293 6.221 6.213
4.575 4.556 4.436 4.418
3.727
2.372 2.179
Me
O
Me
CN
CN
3b
10 9 8 7 6 5 4 3 2 1 ppm
1.10 3.21 0.94 0.95 1.14 1.12 2.39 3.41 3.00


203.476
149.277 149.146
139.144
134.517
130.052 129.169 128.827 125.125
111.410 110.673 109.583
77.316 77.000 76.681
46.048 43.109
29.202 28.684
21.414
Me
O
Me
CN
CN
3b
200 180 160 140 120 100 80 60 40 20 ppm



	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	17.175	46080192	49.68	1201182	52.85
2	18.804	46673832	50.32	1071548	47.15



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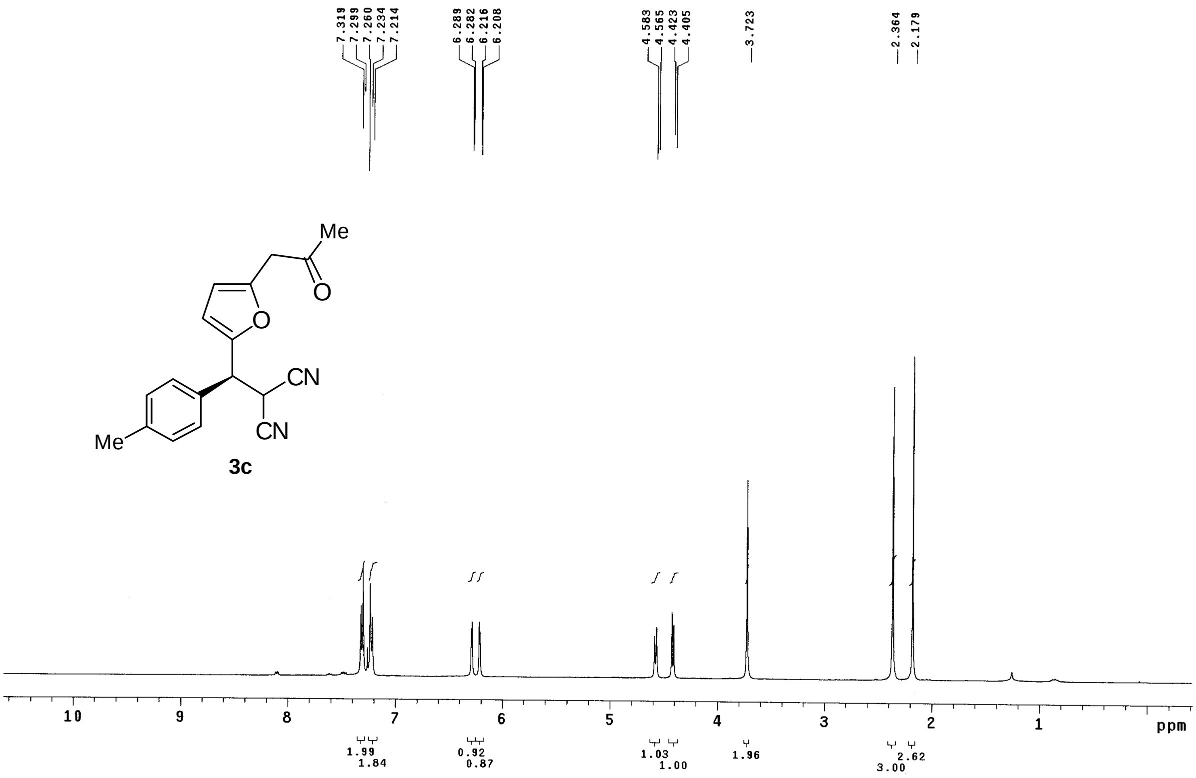
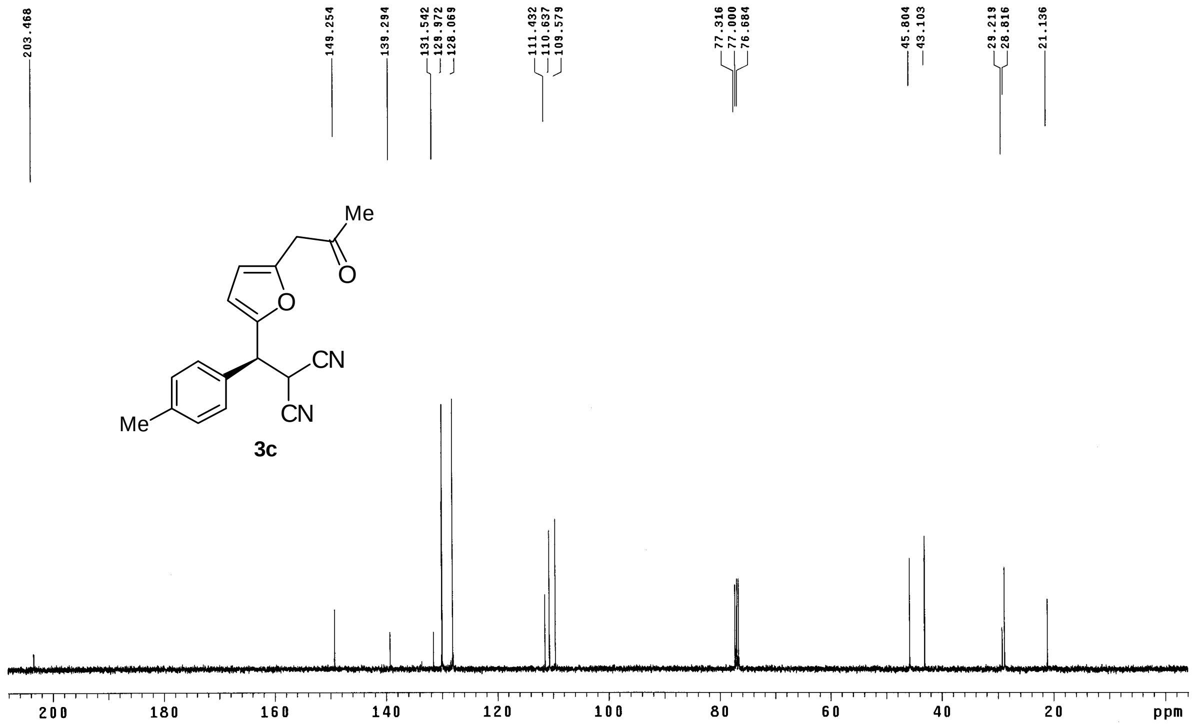
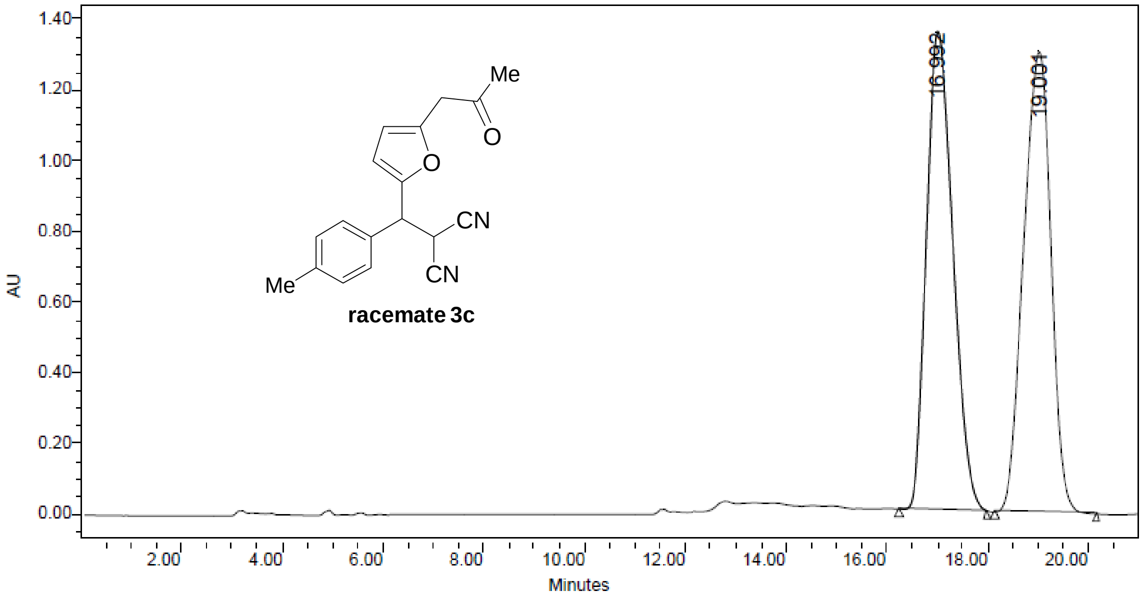
1	17.746	91914534	95.02	1972122	94.62
2	19.672	4816481	4.98	112053	5.38


7.319
7.299
7.260
7.234
7.214
6.289
6.282
6.216
6.208
4.583
4.565
4.423
4.405
3.723
2.364
2.179
Me
O
CN
CN
Me
3c
10
9
8
7
6
5
4
3
2
1
ppm
1.99
1.84
0.92
0.87
1.03
1.00
1.96
3.00
2.62


203.468
149.254
139.294
131.542
129.972
128.069
111.432
110.637
109.579
77.316
77.000
76.684
45.804
43.103
29.219
28.816
21.136
Me
O
CN
CN
Me
3c
200
180
160
140
120
100
80
60
40
20
ppm



	RT (min)	Area (*sec)	% Area	Height ( )	% Height
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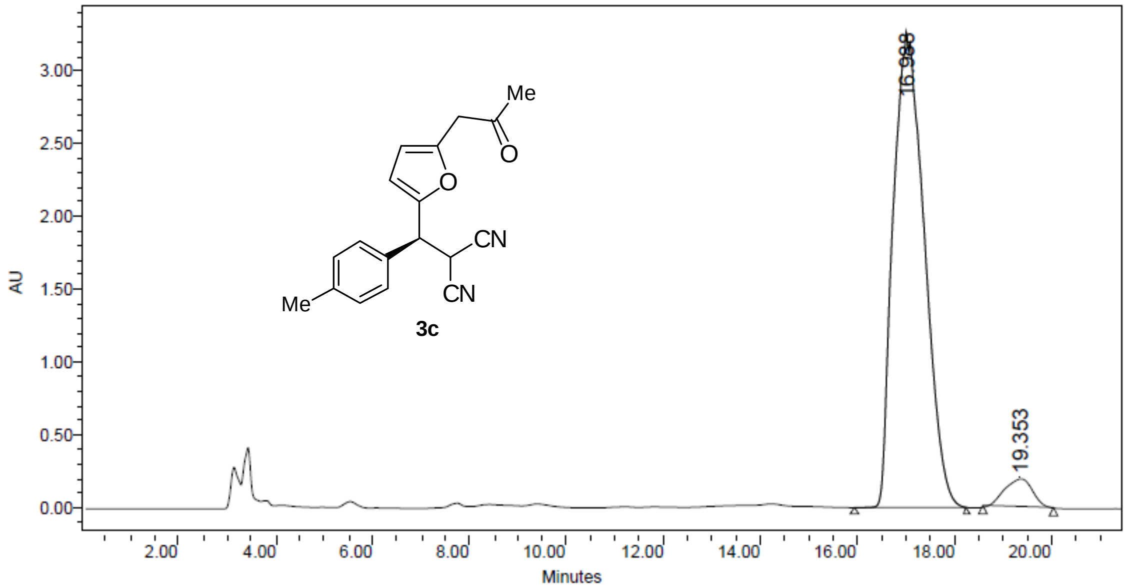
2	19.001	49292663	50.02	1304616	49.07



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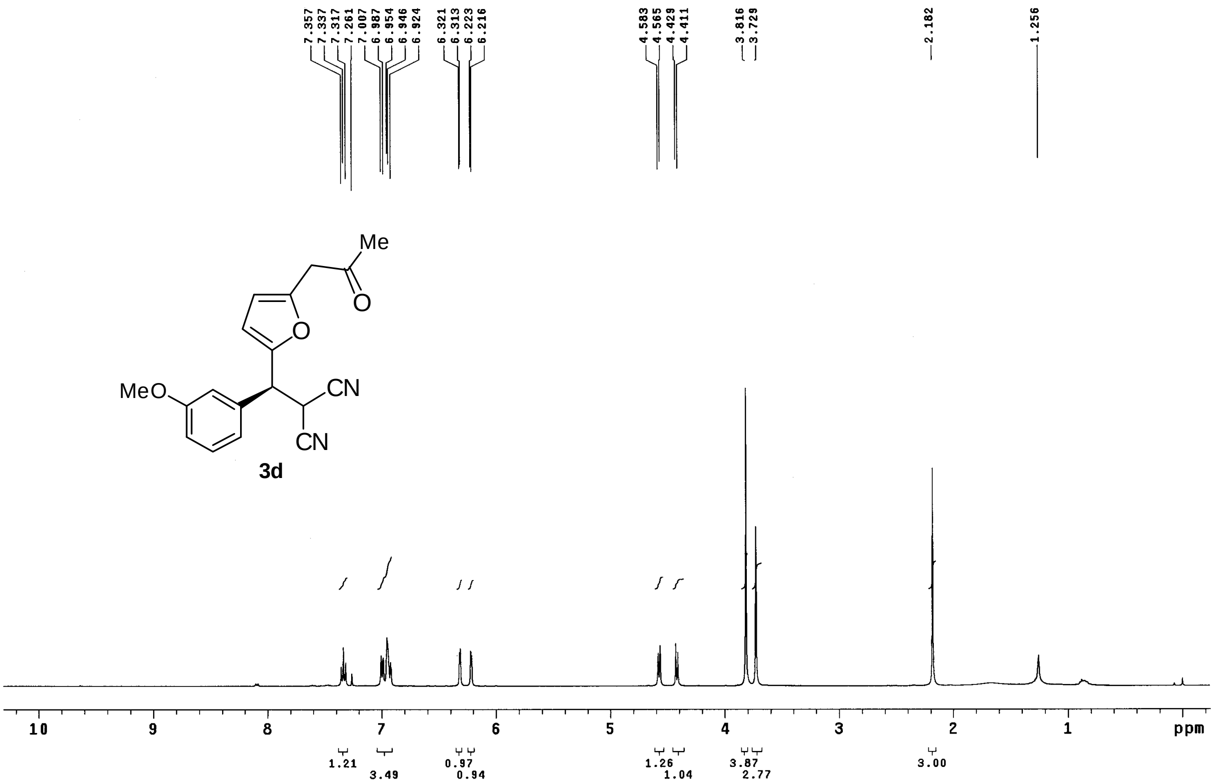
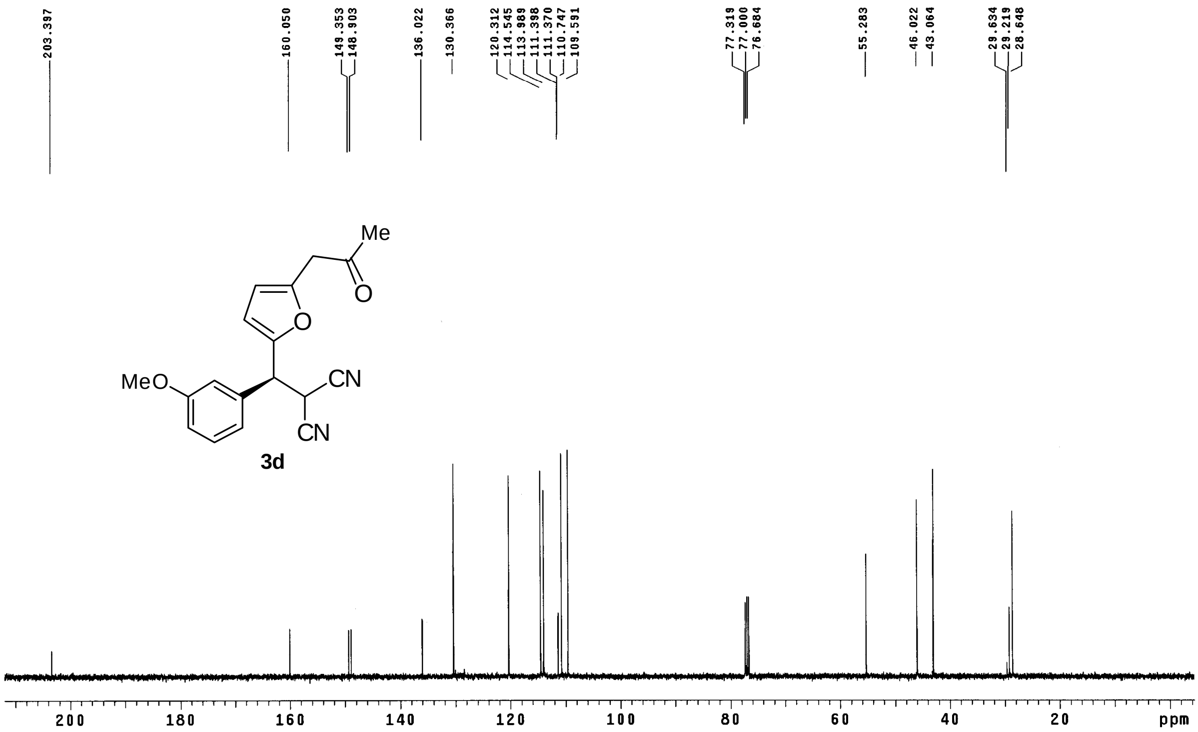
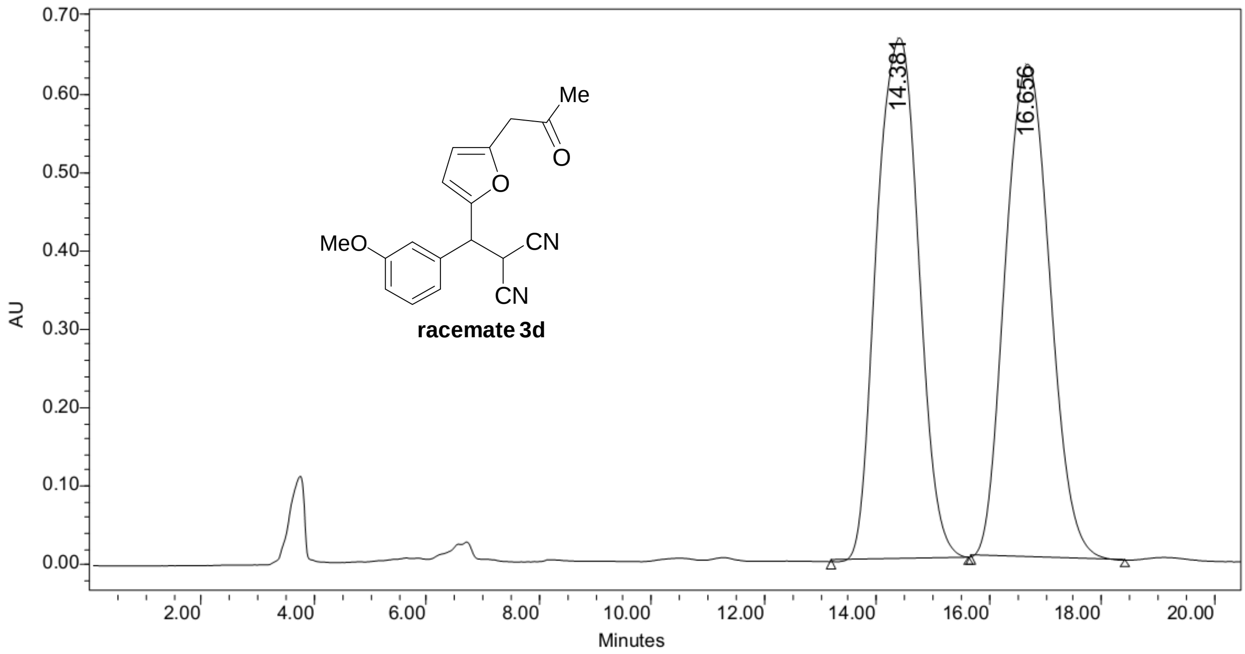


7.357
7.337
7.317
7.261
7.007
6.987
6.954
6.946
6.924
6.321
6.313
6.223
6.216
4.583
4.565
4.429
4.411
3.816
3.729
2.182
1.256
Me
O
O
MeO
CN
CN
3d
10
9
8
7
6
5
4
3
2
1
ppm
1.21
3.49
0.97
0.94
1.26
1.04
3.87
2.77
3.00



203.397
160.050
149.353
148.903
136.022
130.366
120.312
114.545
113.989
111.398
111.370
110.747
109.591
77.319
77.000
76.684
55.283
46.022
43.064
29.634
29.219
28.648
Me
O
O
MeO
CN
CN
3d
200
180
160
140
120
100
80
60
40
20
ppm



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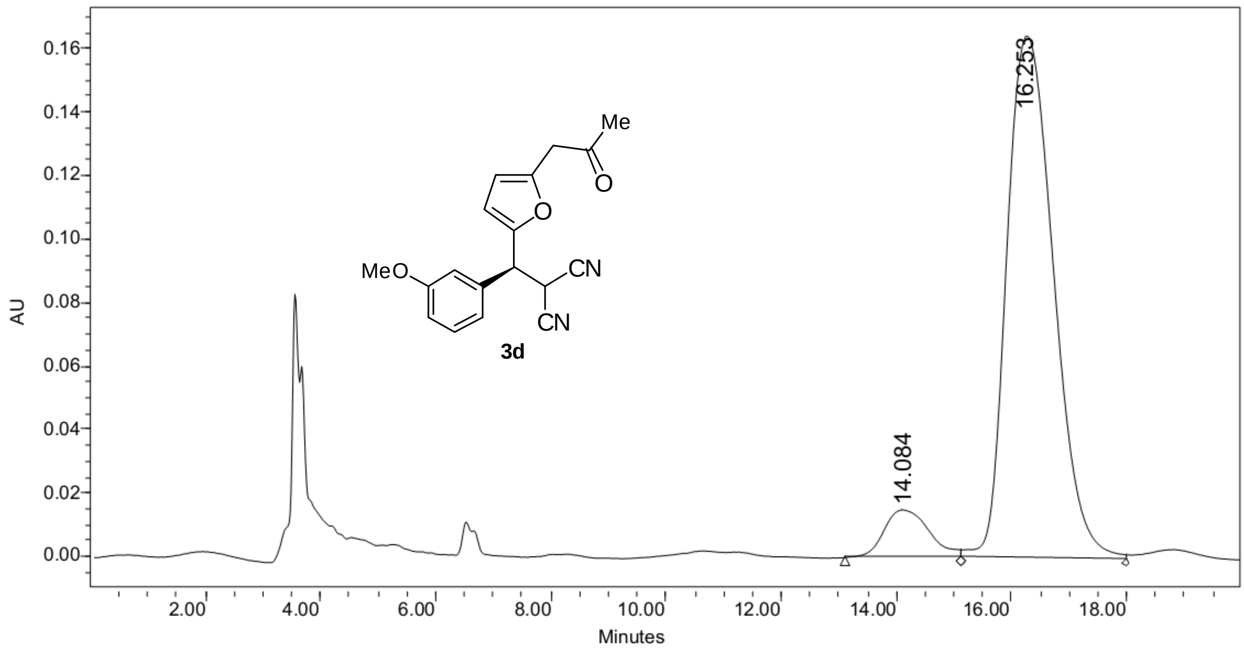
1	14.381	34535619	49.86	664387	51.37
2	16.656	34733431	50.14	628831	48.63



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1	14.084	663932	6.91	13699	7.79
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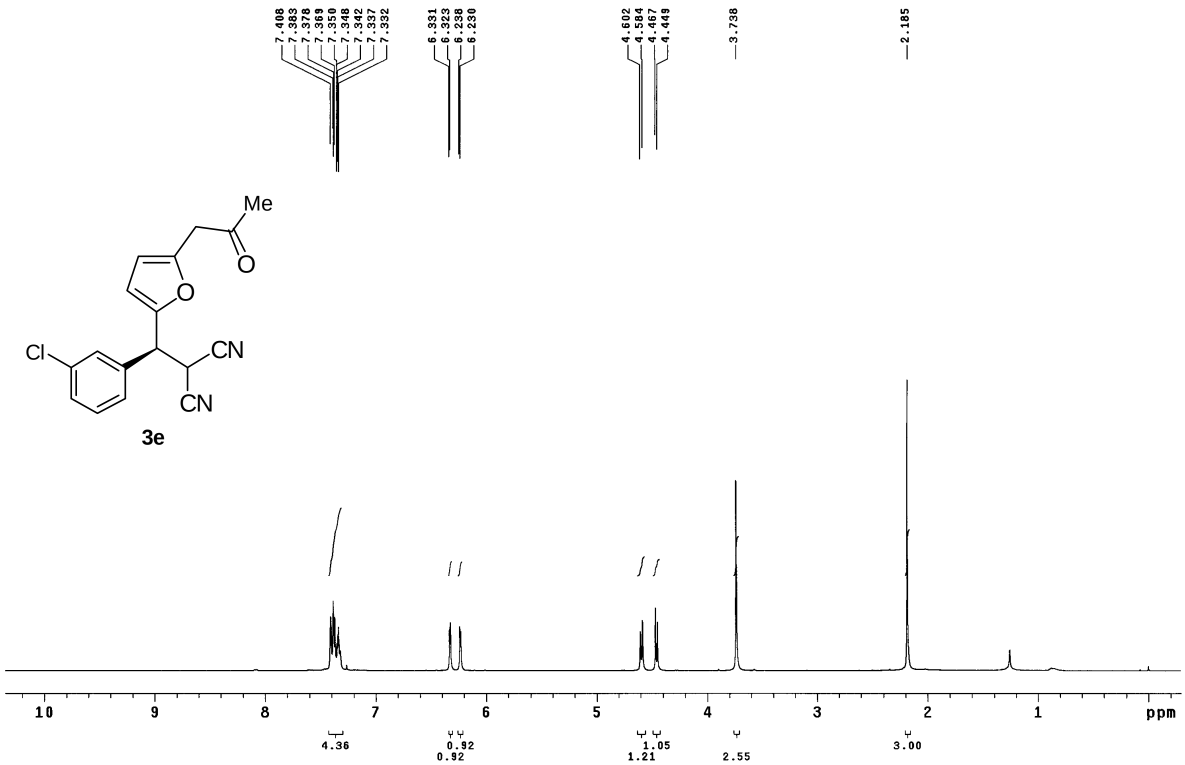
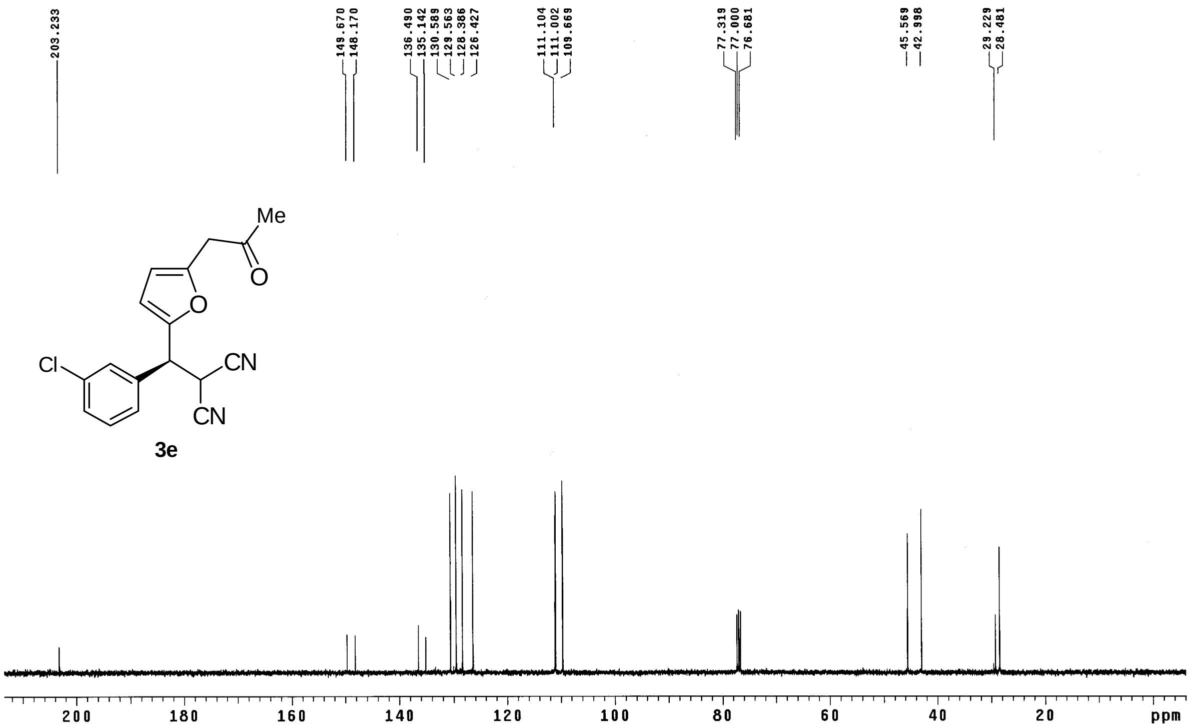
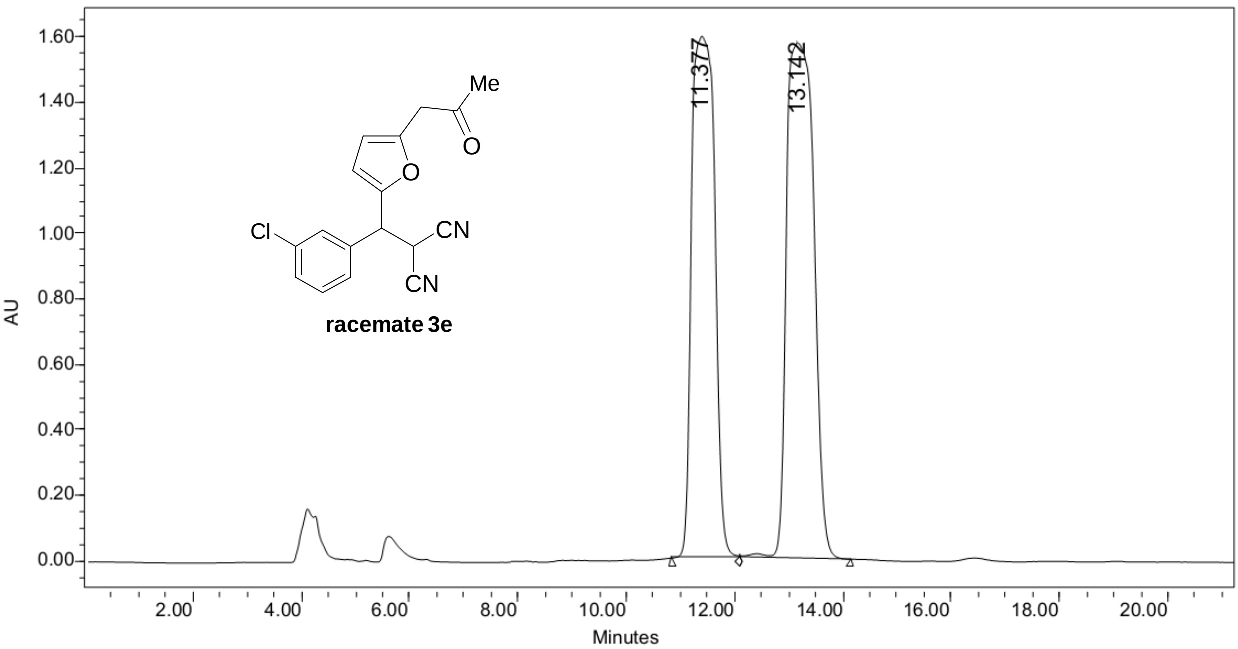

7.408
7.383
7.378
7.369
7.350
7.348
7.342
7.337
7.332
6.331
6.323
6.238
6.230
4.602
4.584
4.467
4.449
3.738
2.185
Me
O
O
Cl
CN
CN
3e
10 9 8 7 6 5 4 3 2 1 0 ppm
4.36
0.92
0.92
1.21
1.05
2.55
3.00


203.233
149.670
148.170
136.490
135.142
130.589
129.563
128.386
126.427
111.104
111.002
109.669
77.319
77.000
76.681
45.569
42.998
29.229
28.481
Me
O
O
Cl
CN
CN
3e
200 180 160 140 120 100 80 60 40 20 ppm



	RT (min)	Area (*sec)	% Area	Height ( )	% Height
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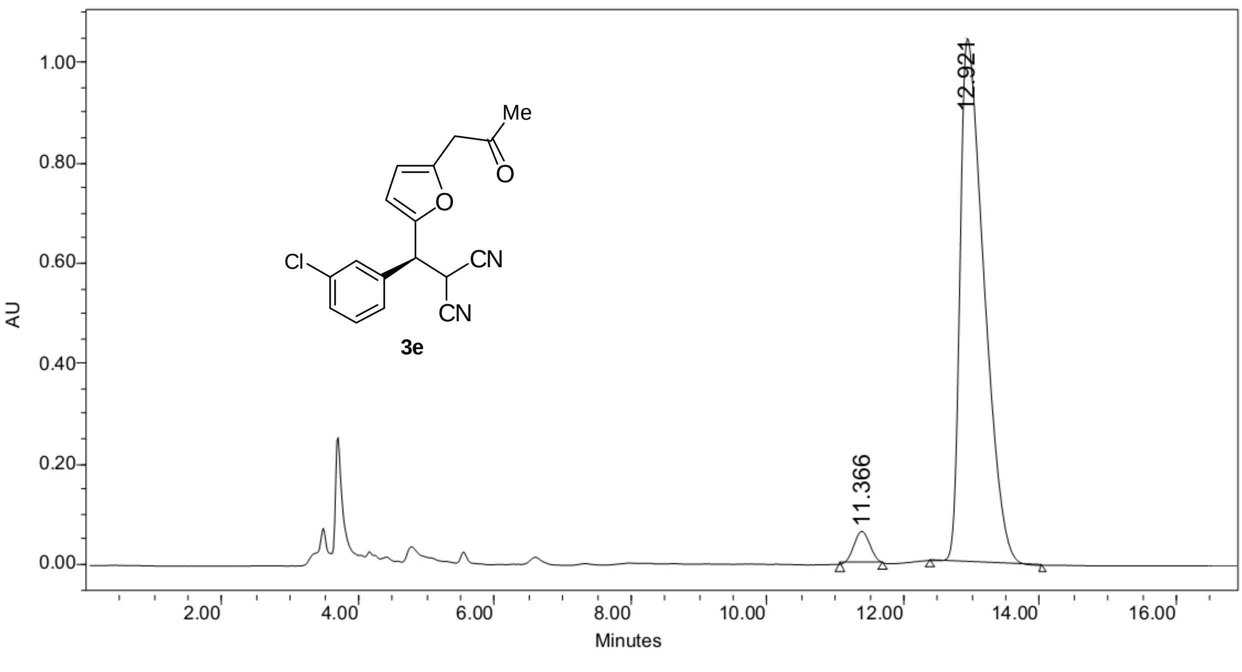
2	13.142	53713916	49.70	1560043	49.56



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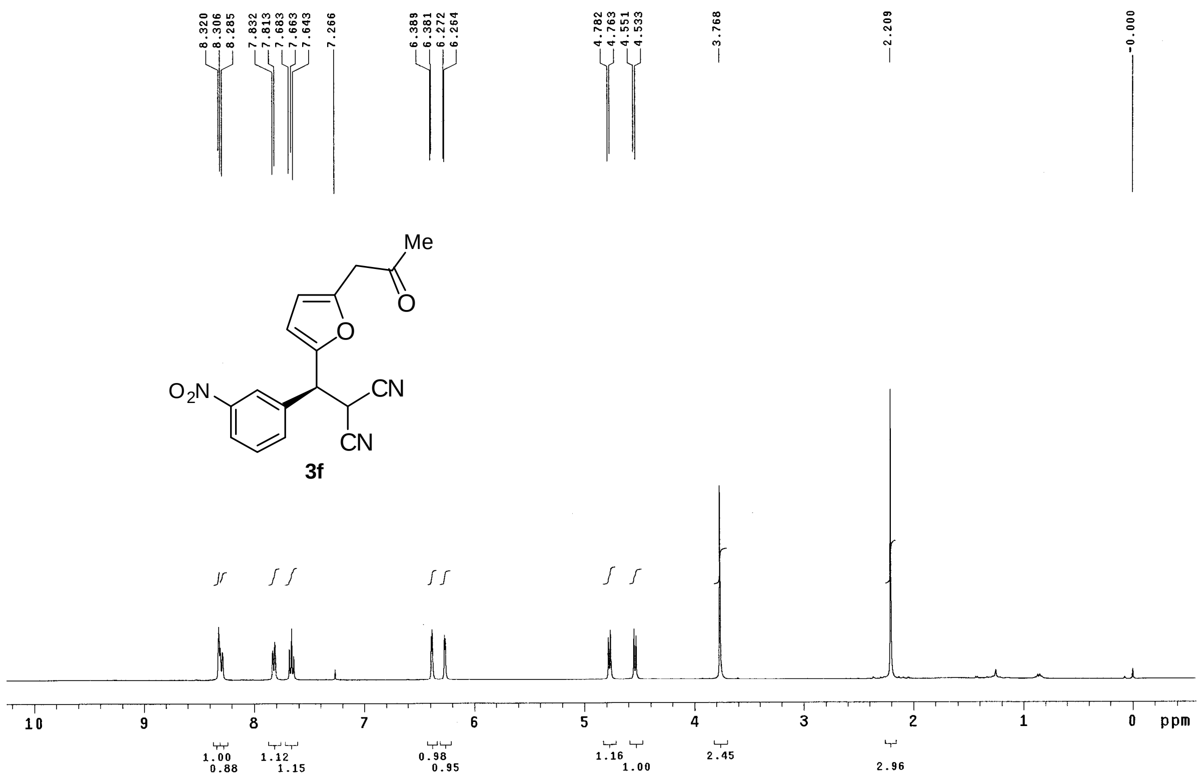
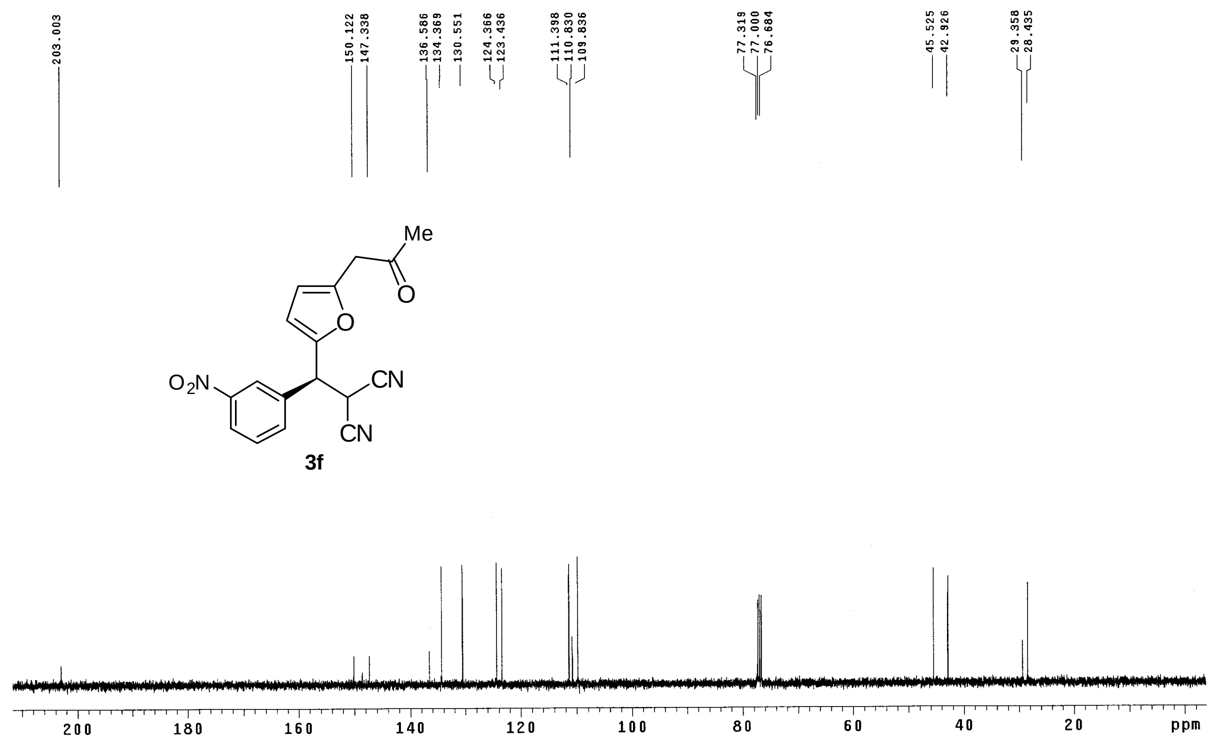
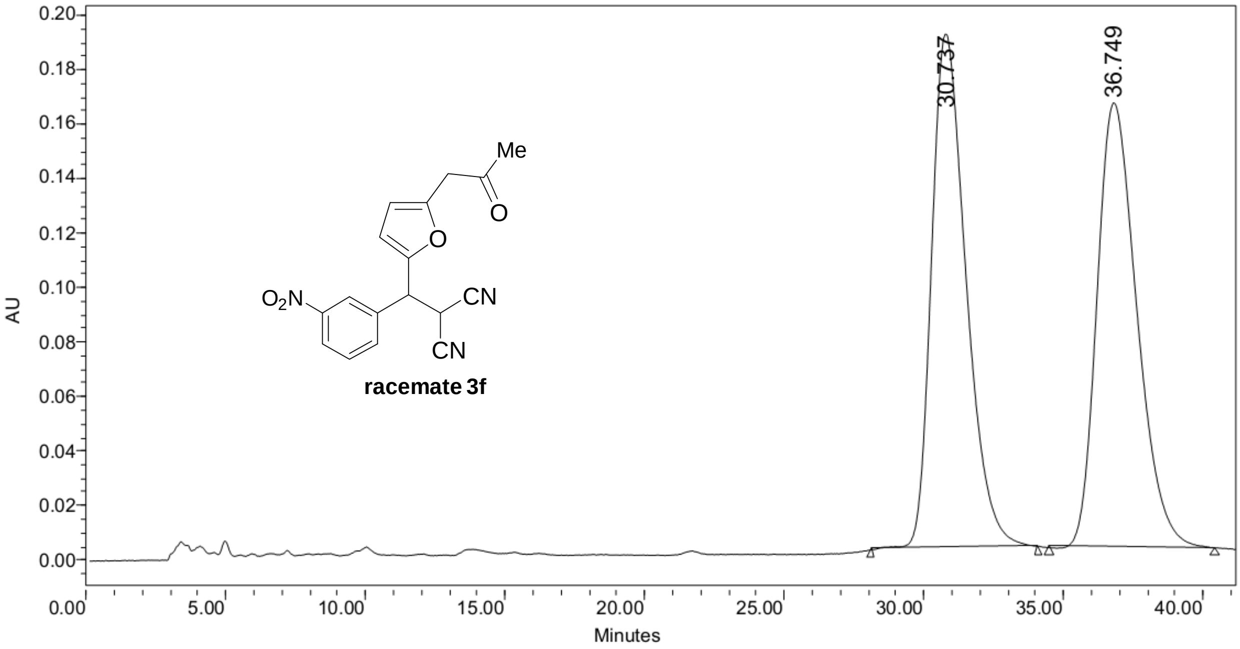
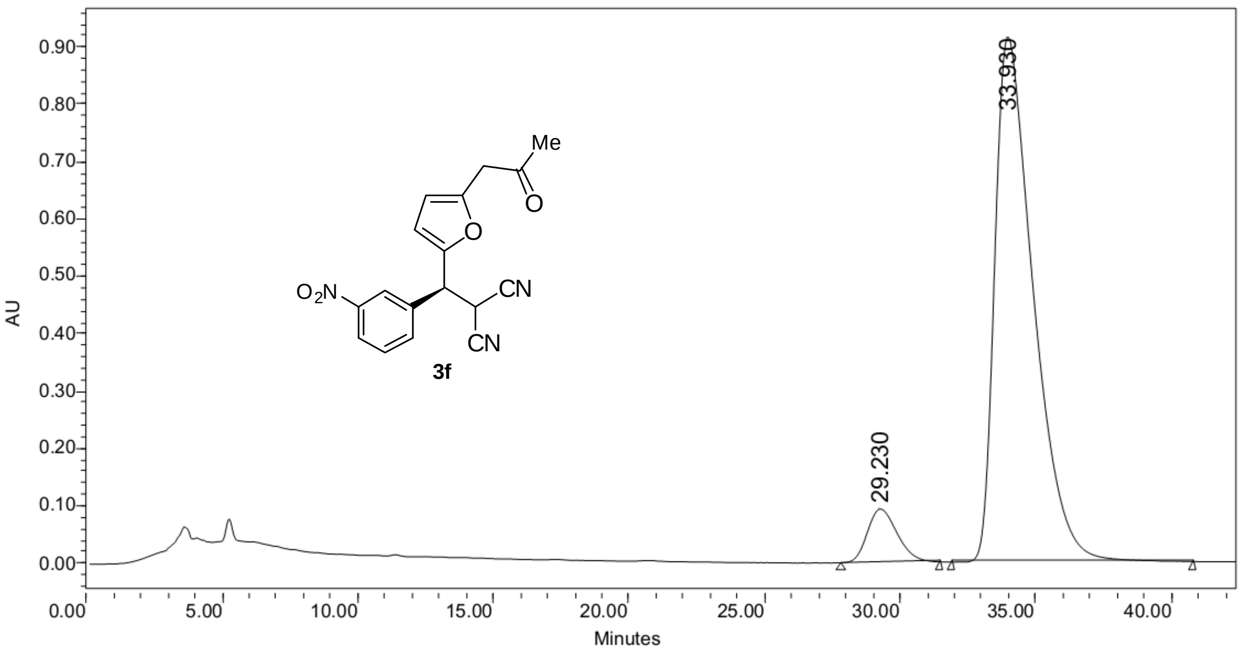

8.320
8.306
8.285
7.832
7.813
7.683
7.663
7.643
7.266
6.389
6.381
6.272
6.264
4.782
4.763
4.551
4.533
3.768
2.209
-0.000
Me
O
O
O$_2$N
CN
CN
3f
1.00
0.88
1.12
1.15
0.98
0.95
1.16
1.00
2.45
2.96
ppm

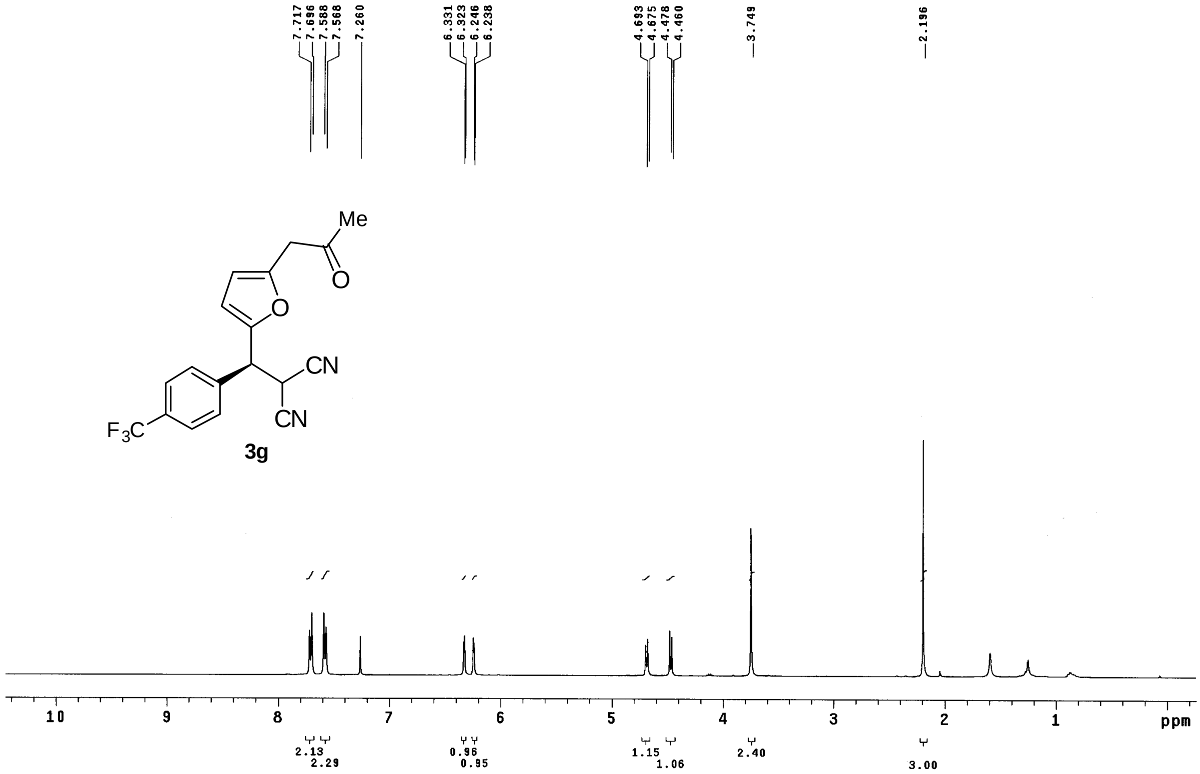

203.003
150.122
147.338
136.586
134.369
130.551
124.366
123.436
111.398
110.830
109.836
77.319
77.000
76.684
45.525
42.926
29.358
28.435
Me
O
O
O$_2$N
CN
CN
3f
ppm

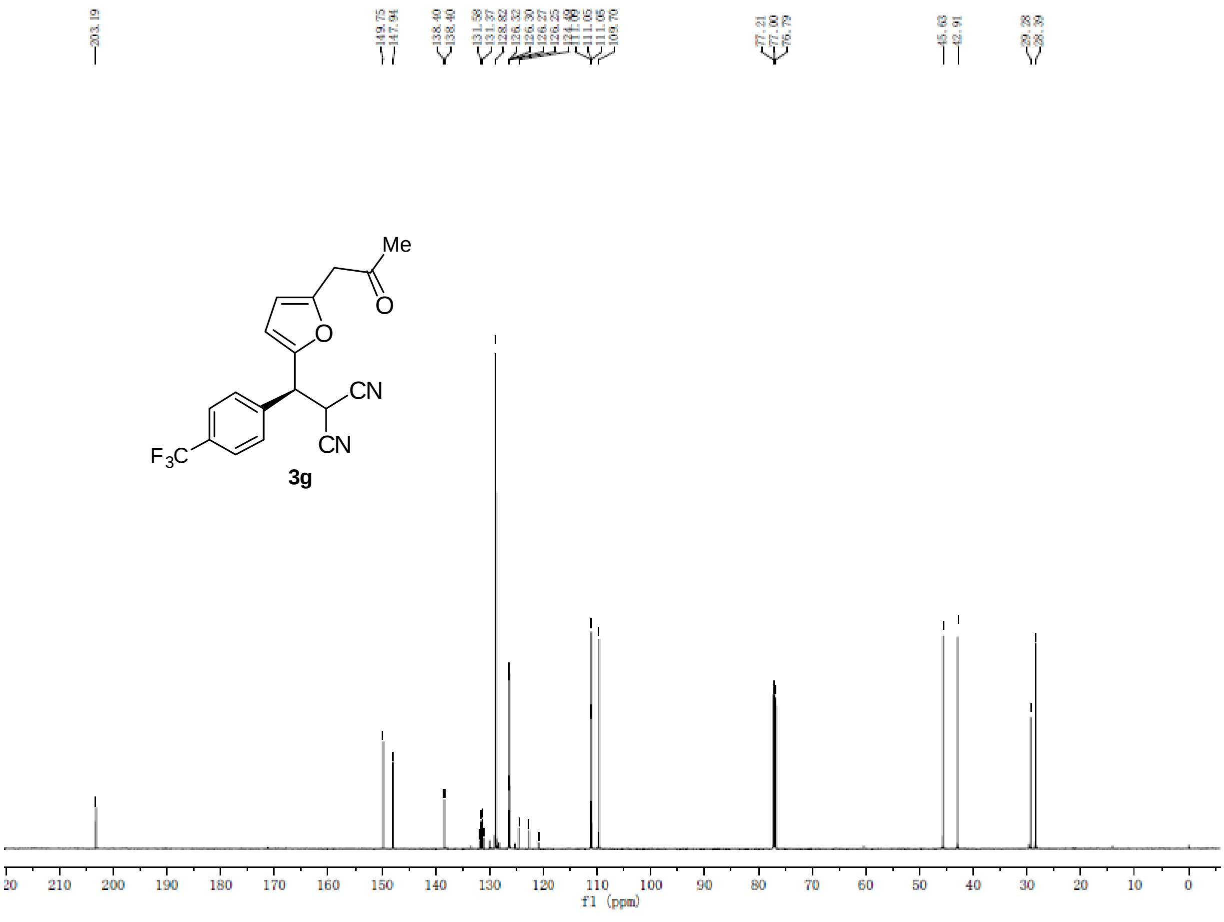


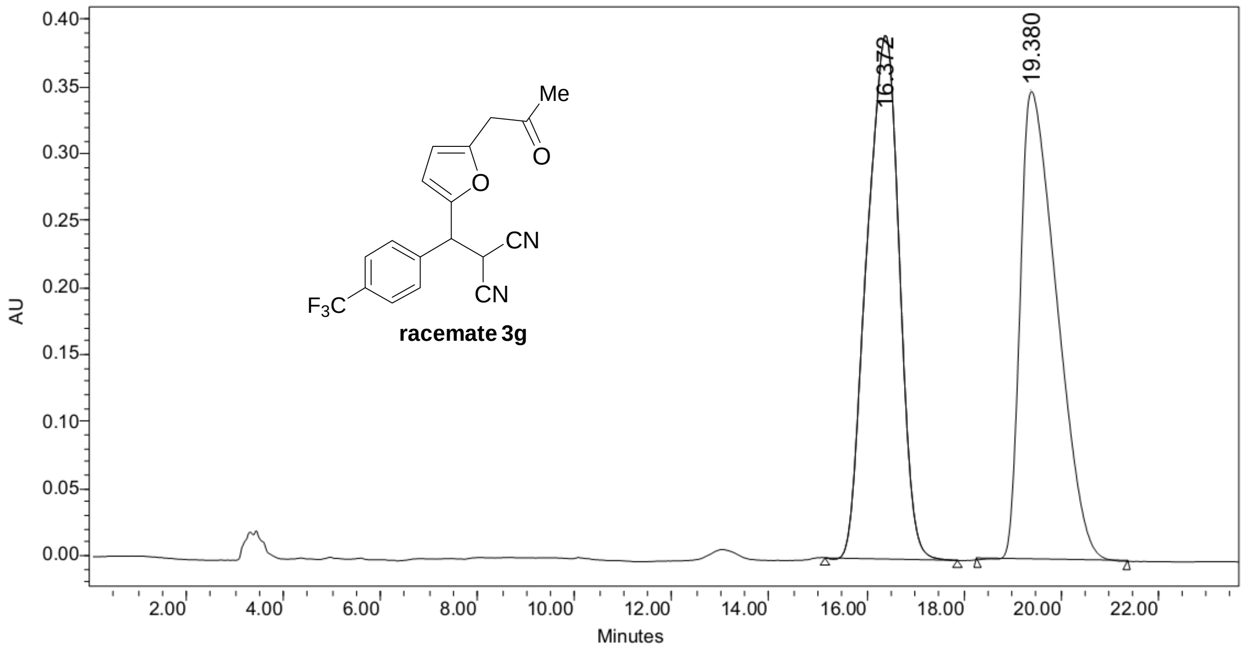
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	30.737	16259347	50.06	188712	53.60
2	36.749	16219491	49.94	163342	46.40



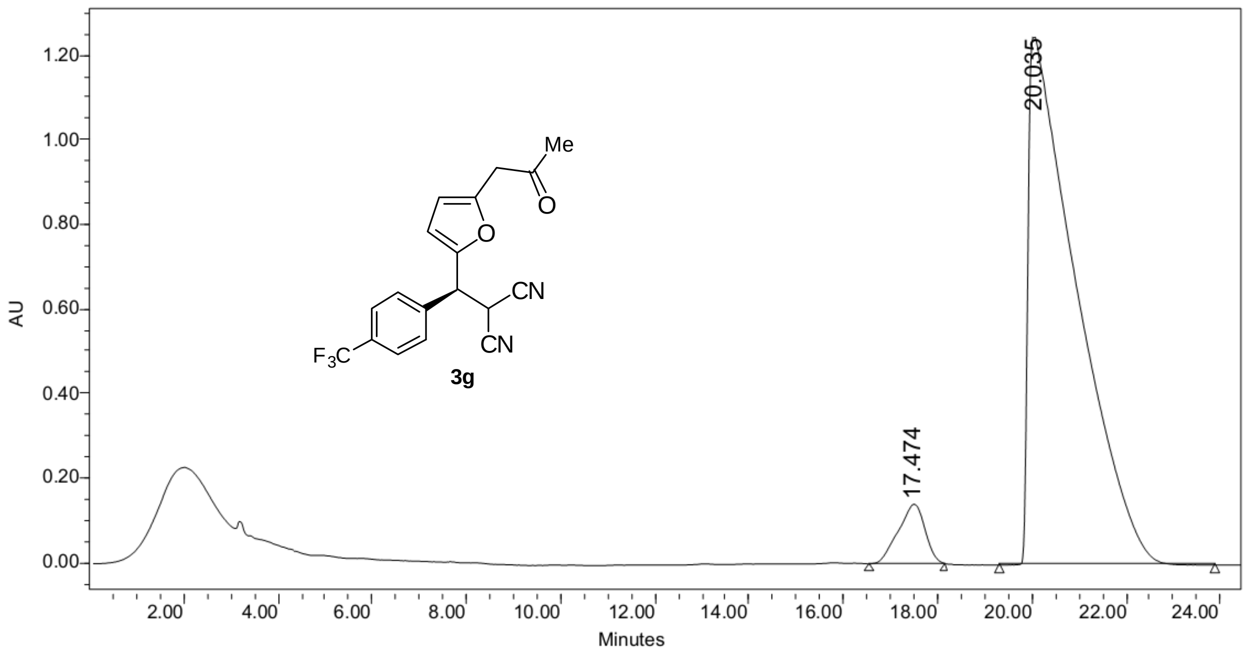
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	29.230	6905322	7.11	91924	9.13
2	33.930	90284086	92.89	915220	90.87



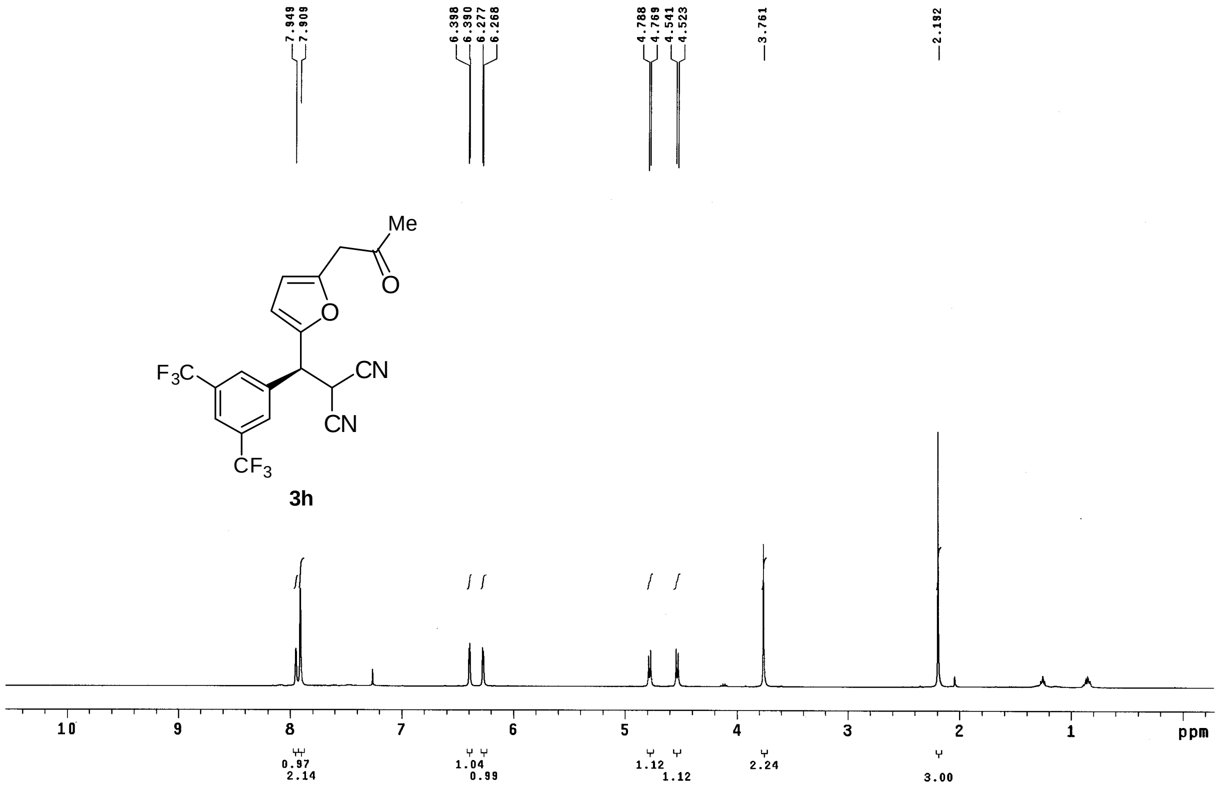




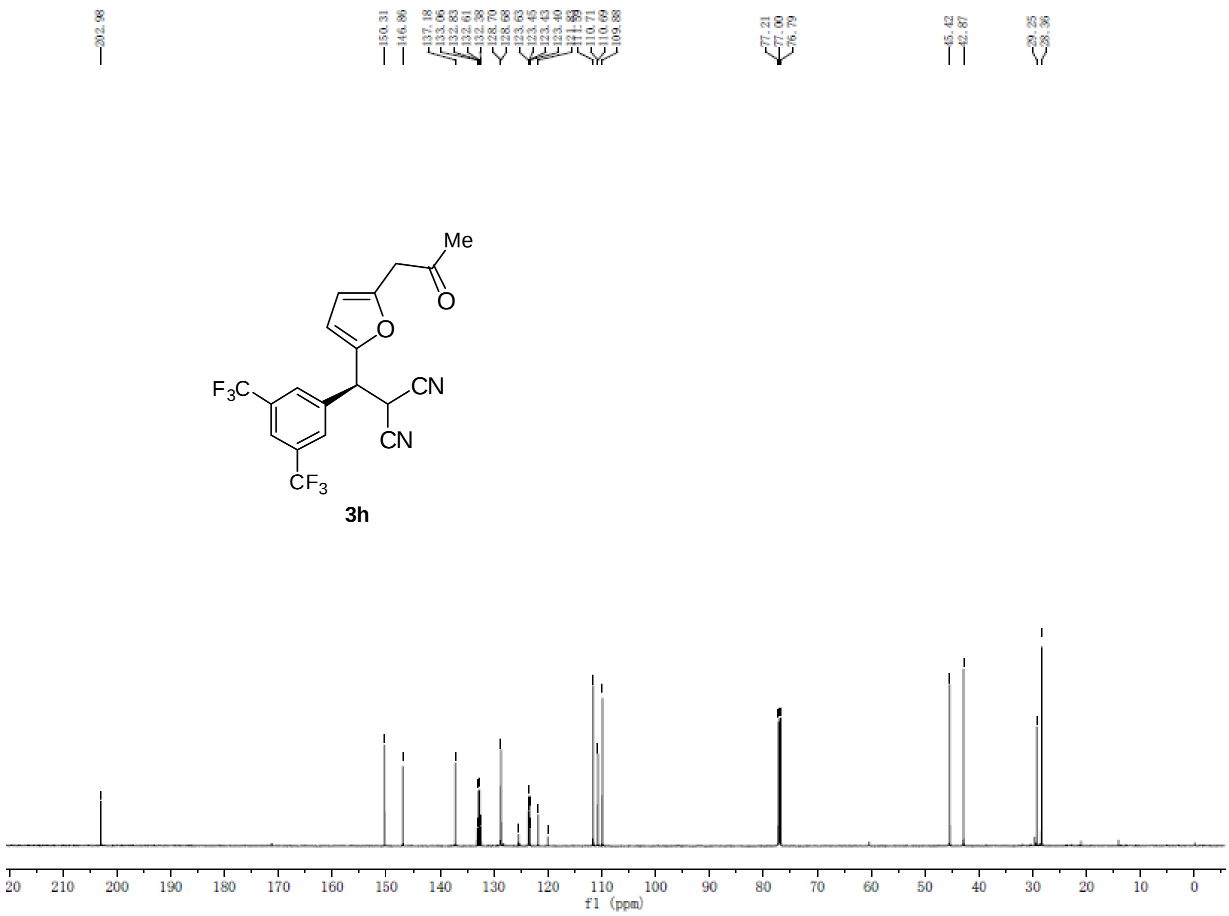
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	16.372	18173660	49.89	391017	52.76
2	19.380	18253428	50.11	350166	47.24



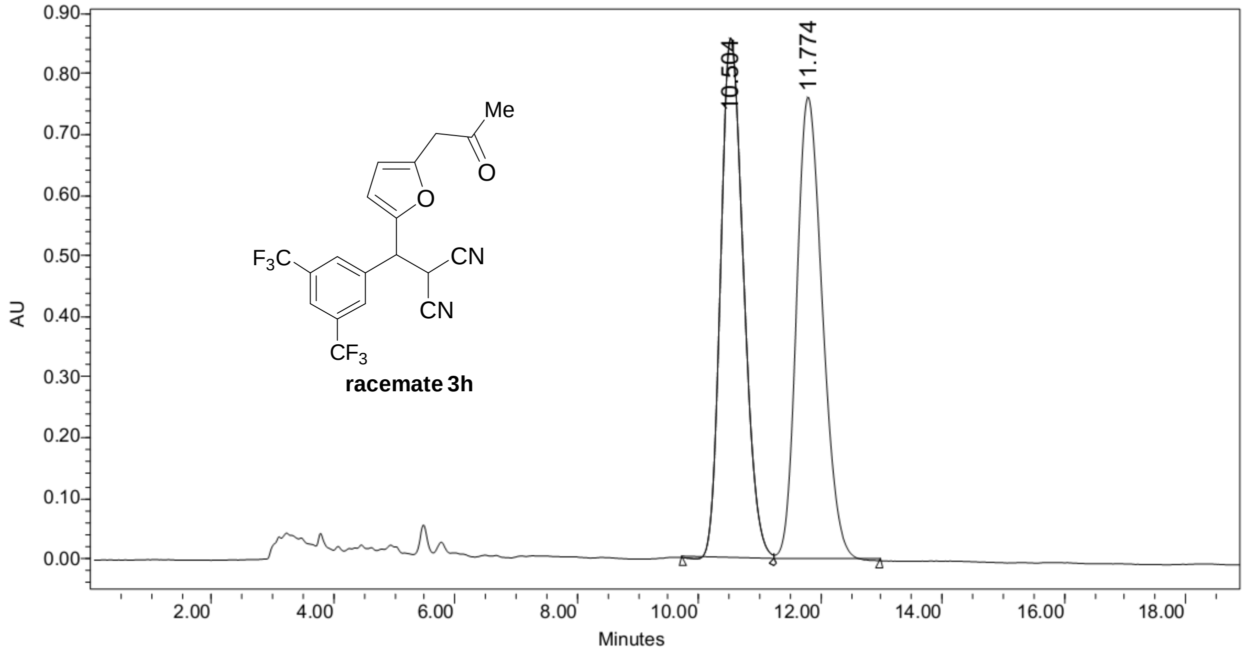
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	17.474	5565690	5.89	140794	10.13
2	20.035	88965251	94.11	1249069	89.87



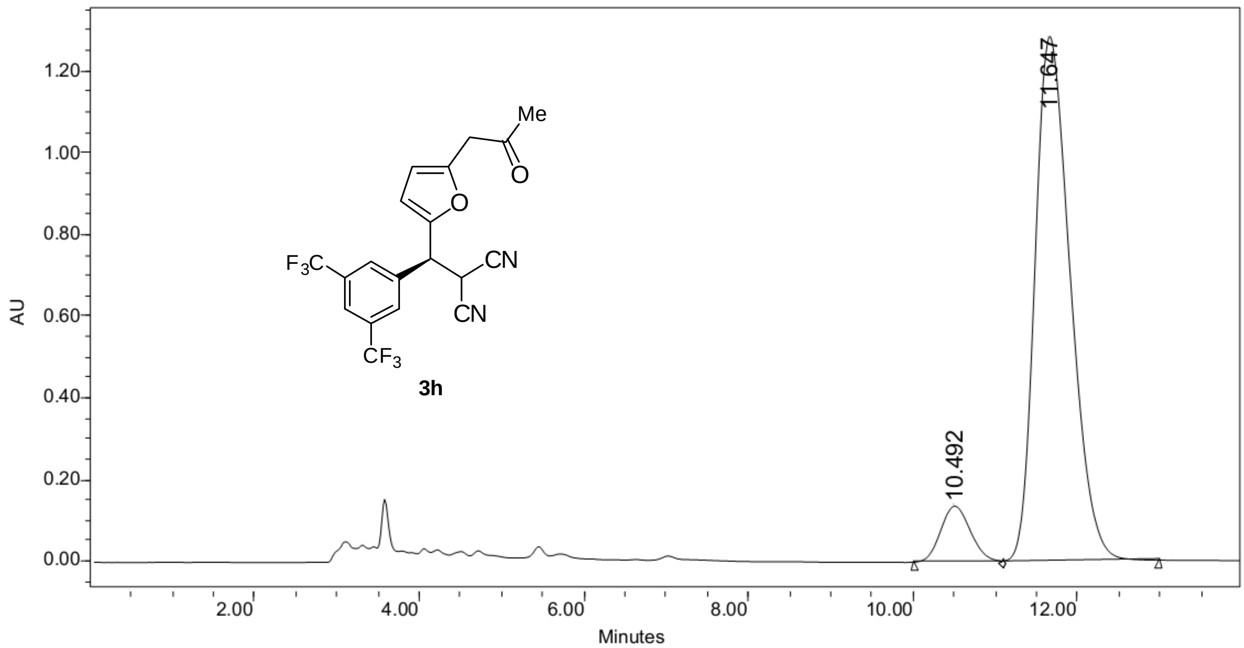
Me
O
F3C
CN
CN
CF3
3h
ppm



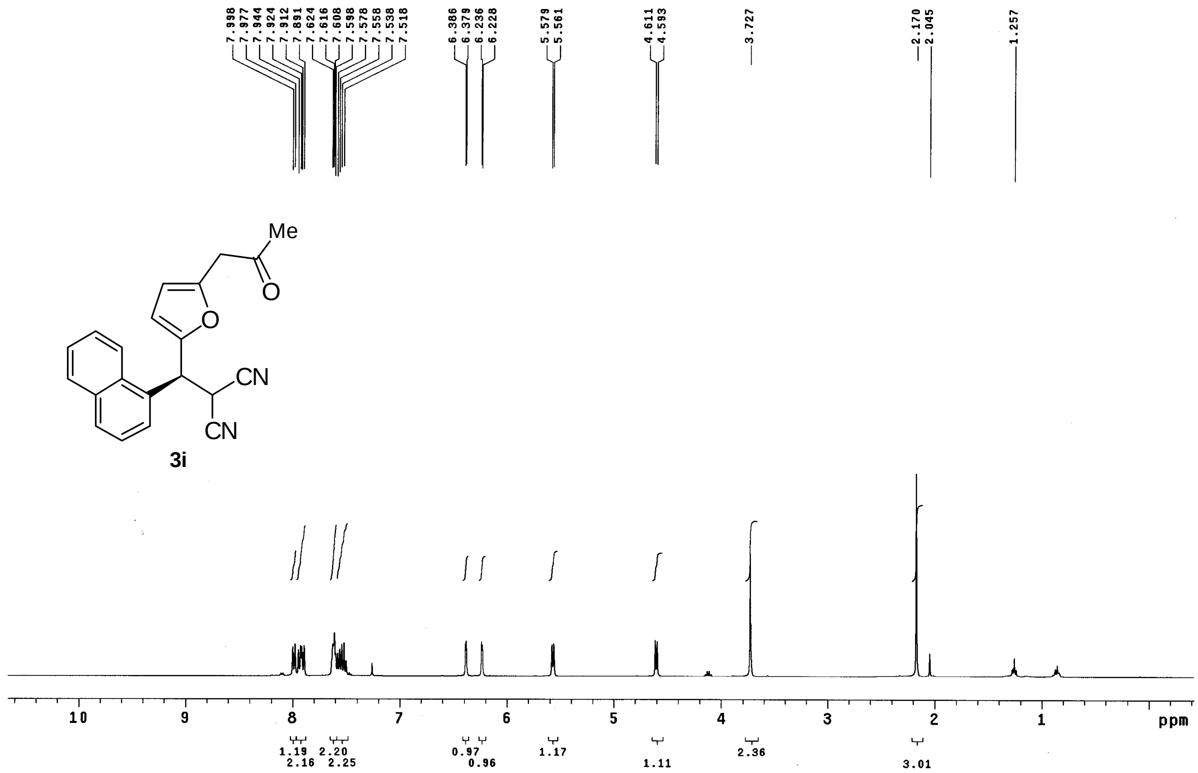
Me
O
F3C
CN
CN
CF3
3h
f1 (ppm)

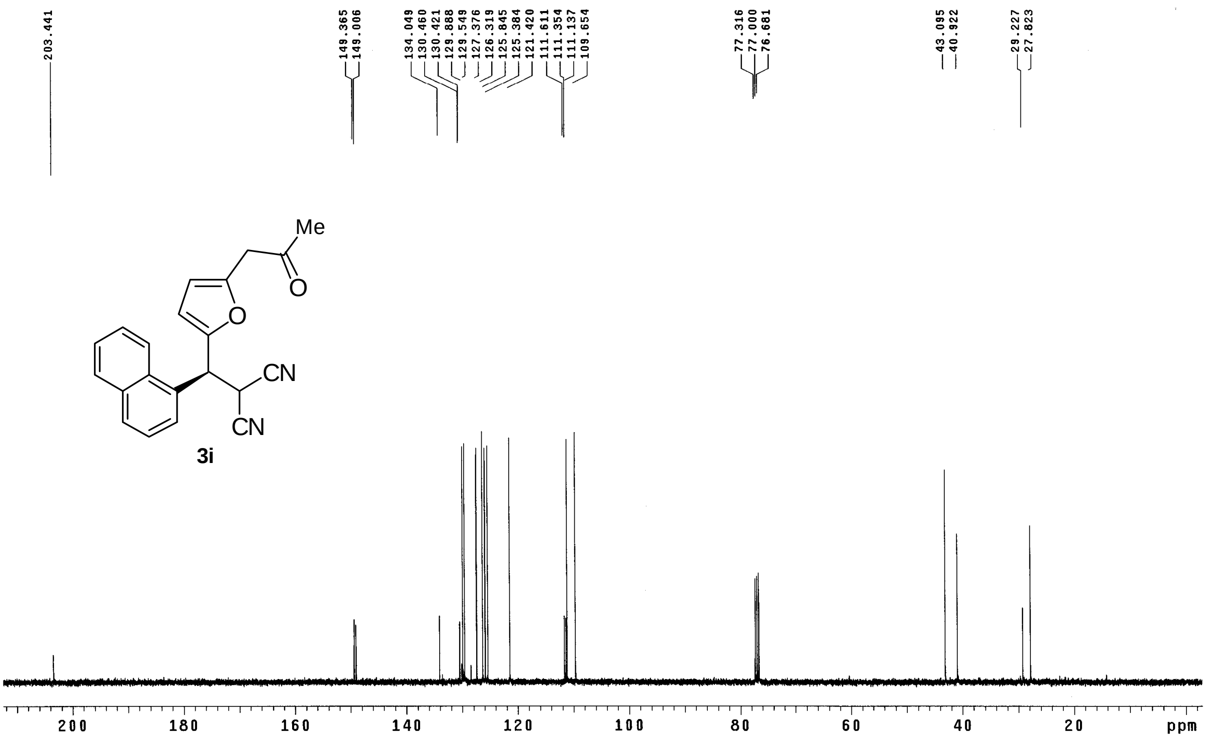


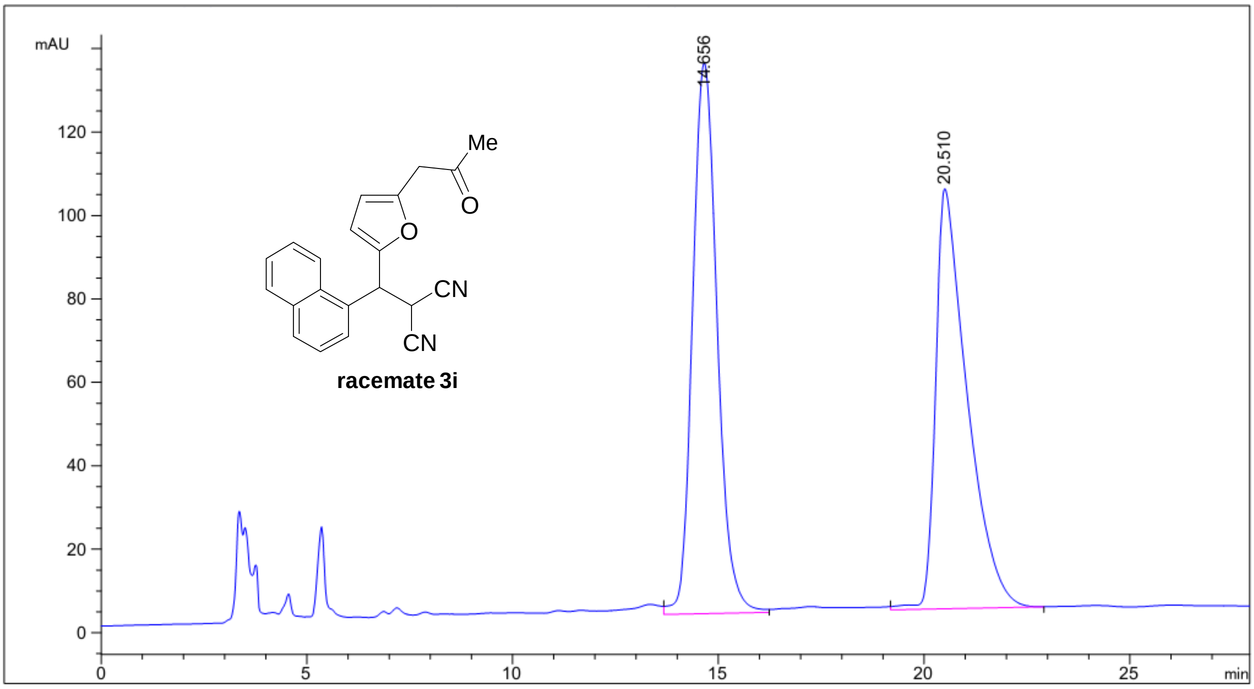
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	10.504	22524638	49.95	859394	52.95
2	11.774	22567422	50.05	763654	47.05



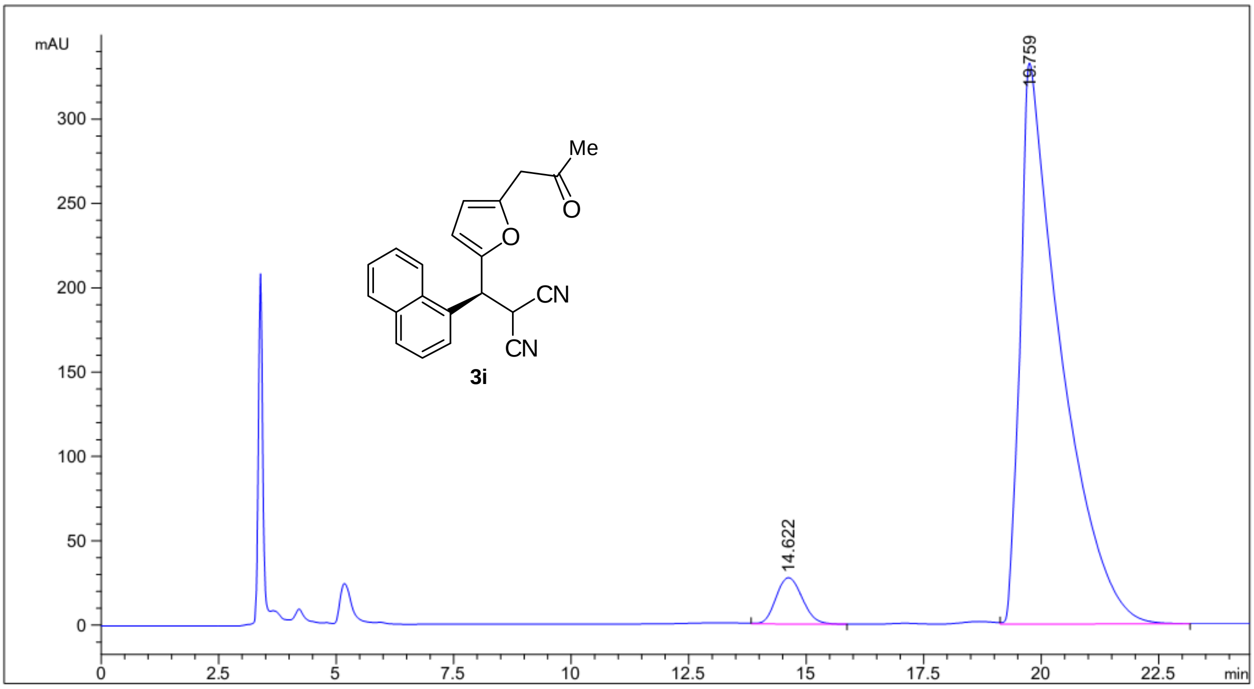
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	10.492	3408326	8.19	136302	9.60
2	11.647	38187860	91.81	1283886	90.40



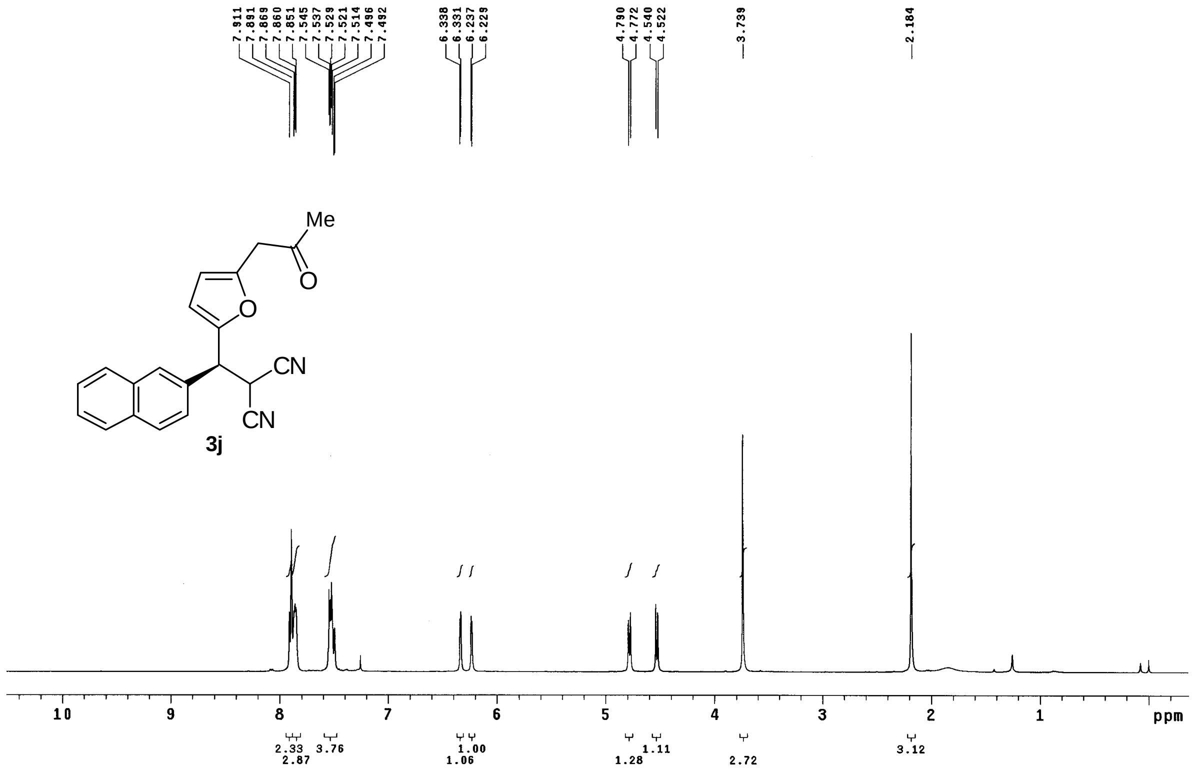


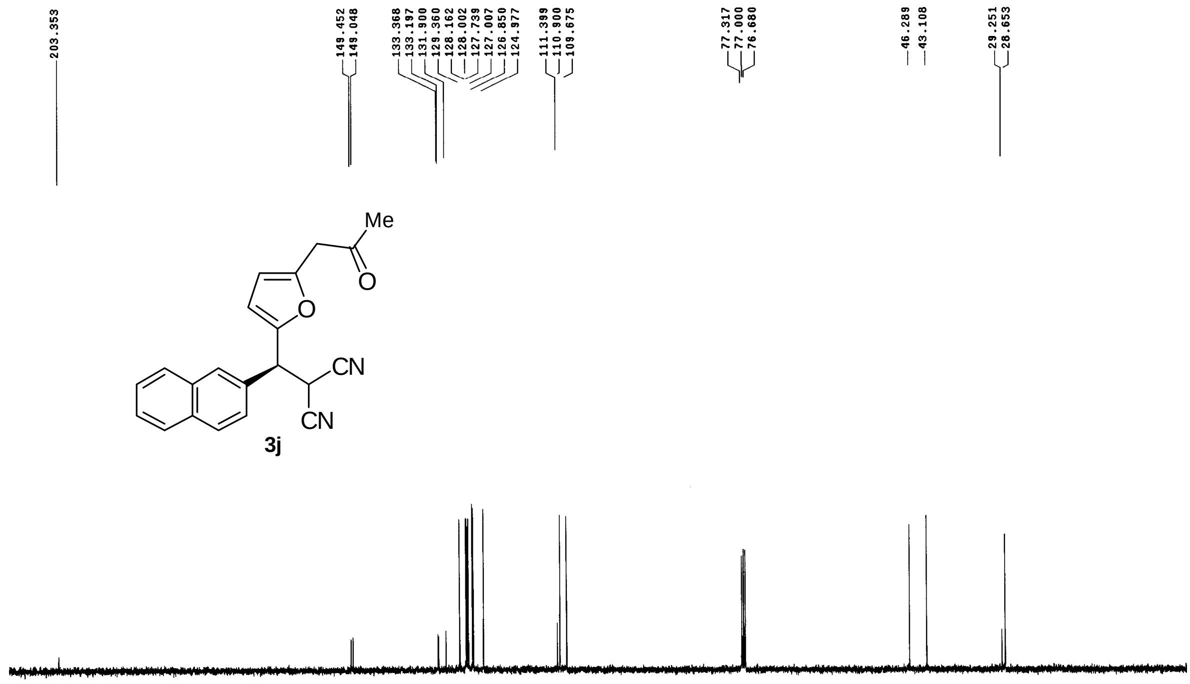


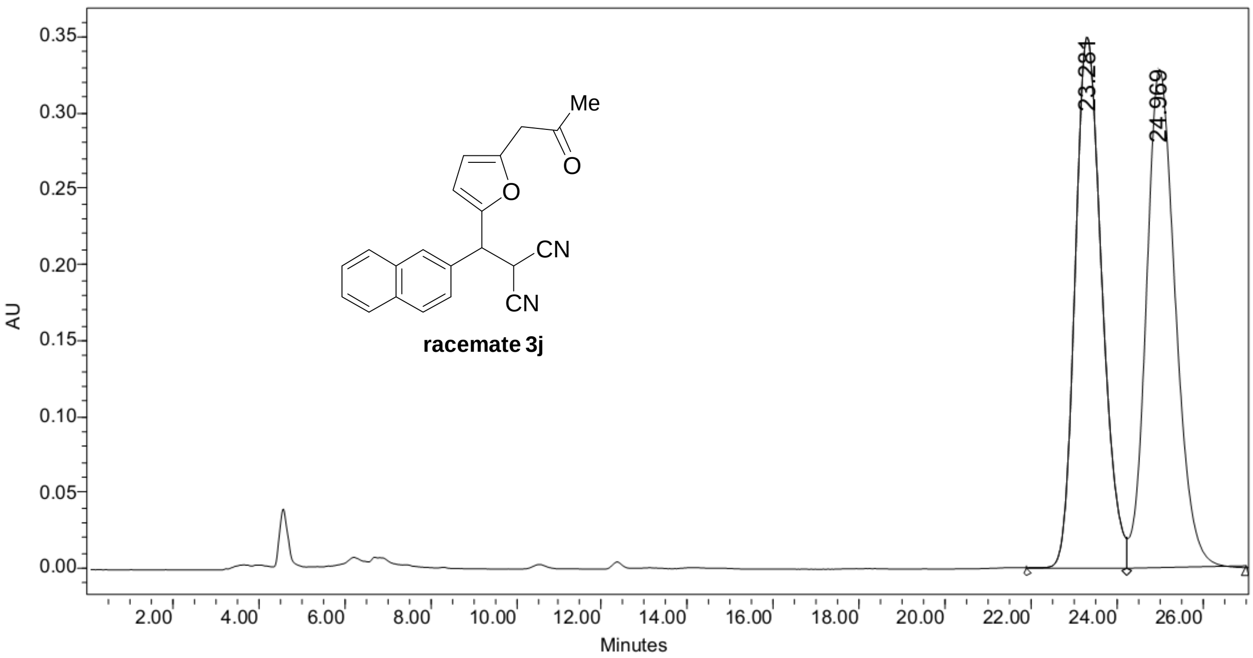
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.656	VB	0.6544	5491.00342	131.96187	50.6149
2	20.510	BB	0.7609	5357.59814	100.63396	49.3851



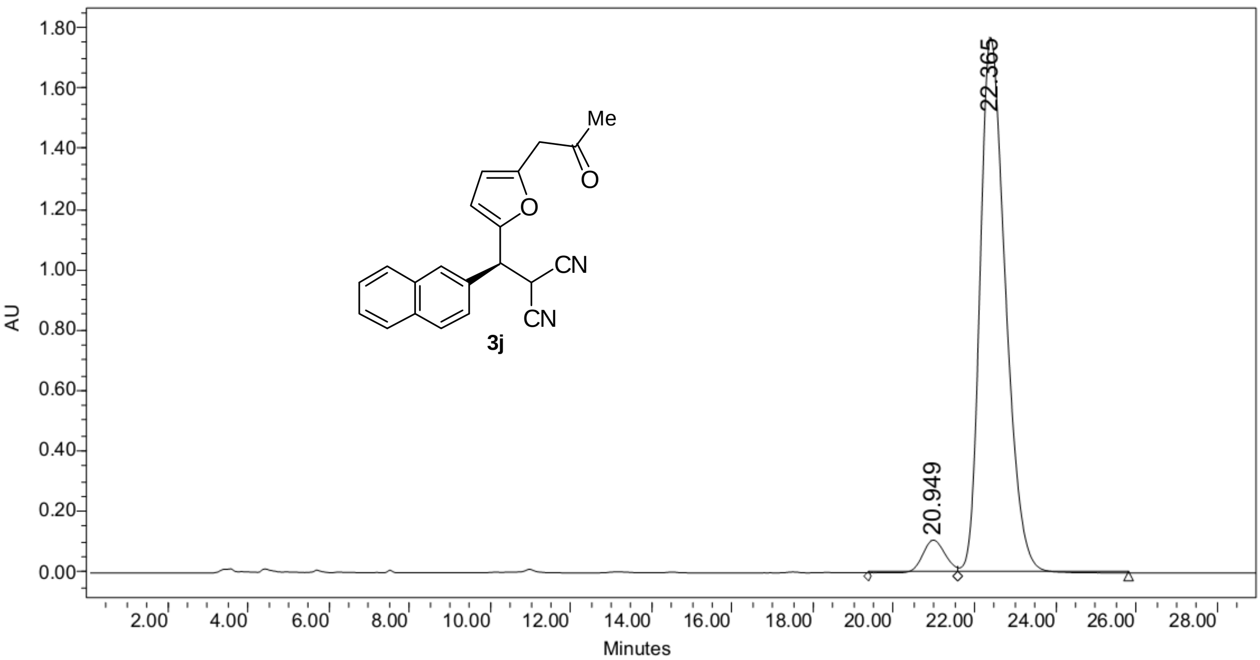
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.622	BB	0.6165	1065.87439	27.42767	5.0675
2	19.759	VB	0.8049	1.99677e4	332.75562	94.9325


7.911
7.891
7.869
7.860
7.851
7.545
7.537
7.529
7.521
7.514
7.496
7.492
6.338
6.331
6.237
6.229
4.790
4.772
4.540
4.522
3.739
2.184
Me
O
O
CN
CN
3j
10
9
8
7
6
5
4
3
2
1
ppm
2.33
2.87
3.76
1.00
1.06
1.28
1.11
2.72
3.12

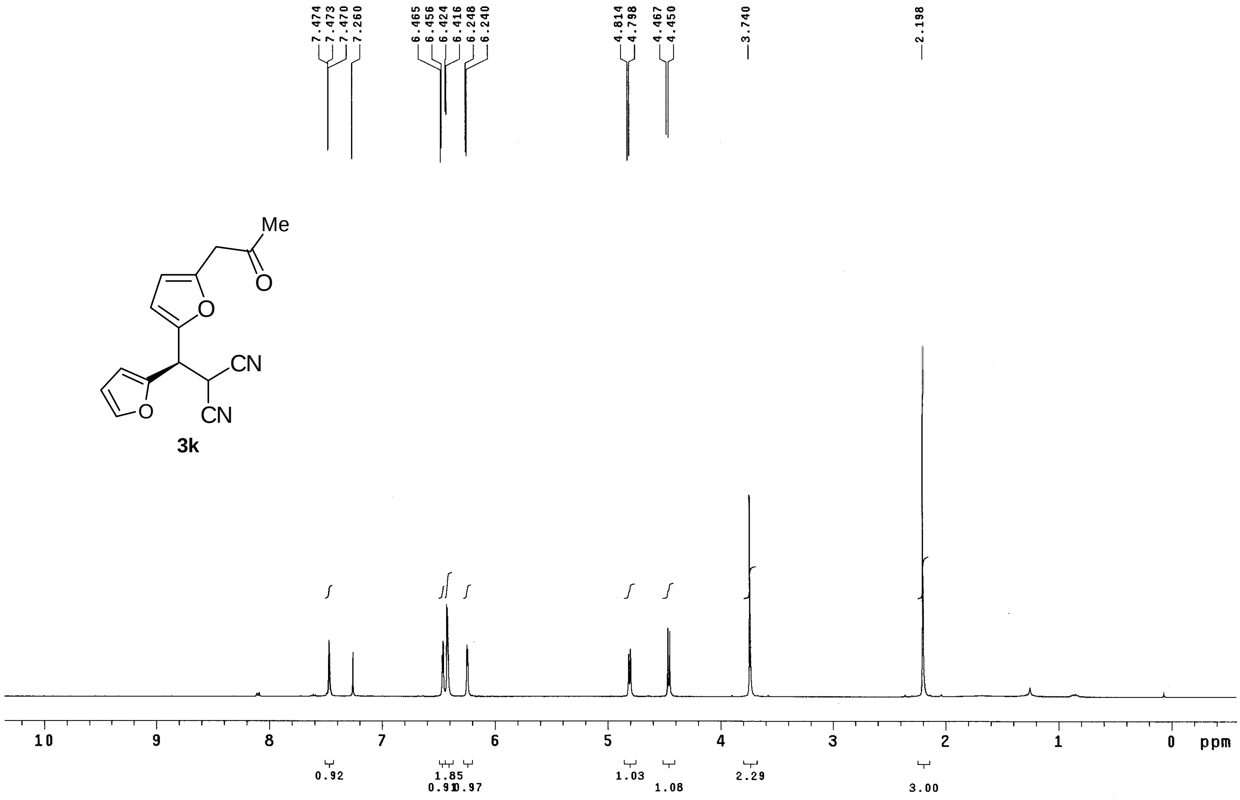

203.353
149.452
149.048
133.368
133.197
131.900
129.360
128.162
128.002
127.739
127.007
126.850
124.977
111.399
110.900
109.675
77.317
77.000
76.680
46.289
43.108
29.251
28.653
Me
O
O
CN
CN
3j
200
180
160
140
120
100
80
60
40
20
ppm

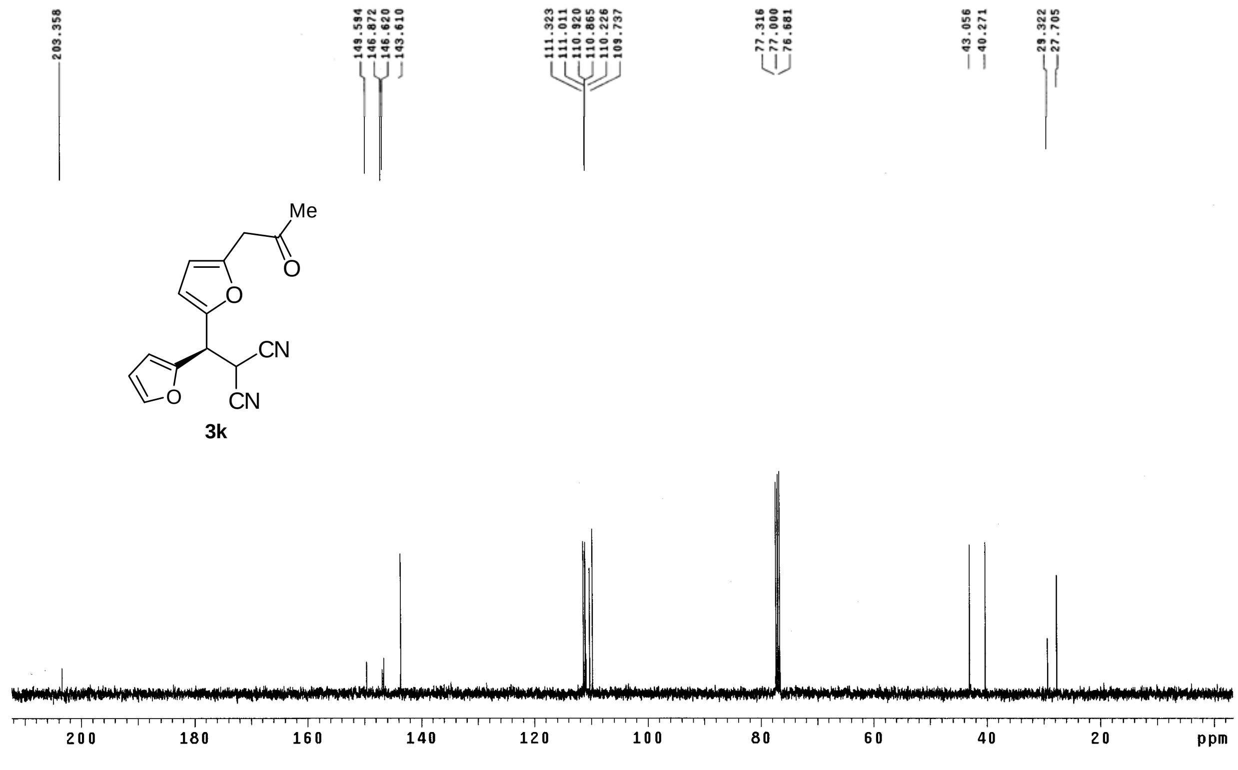


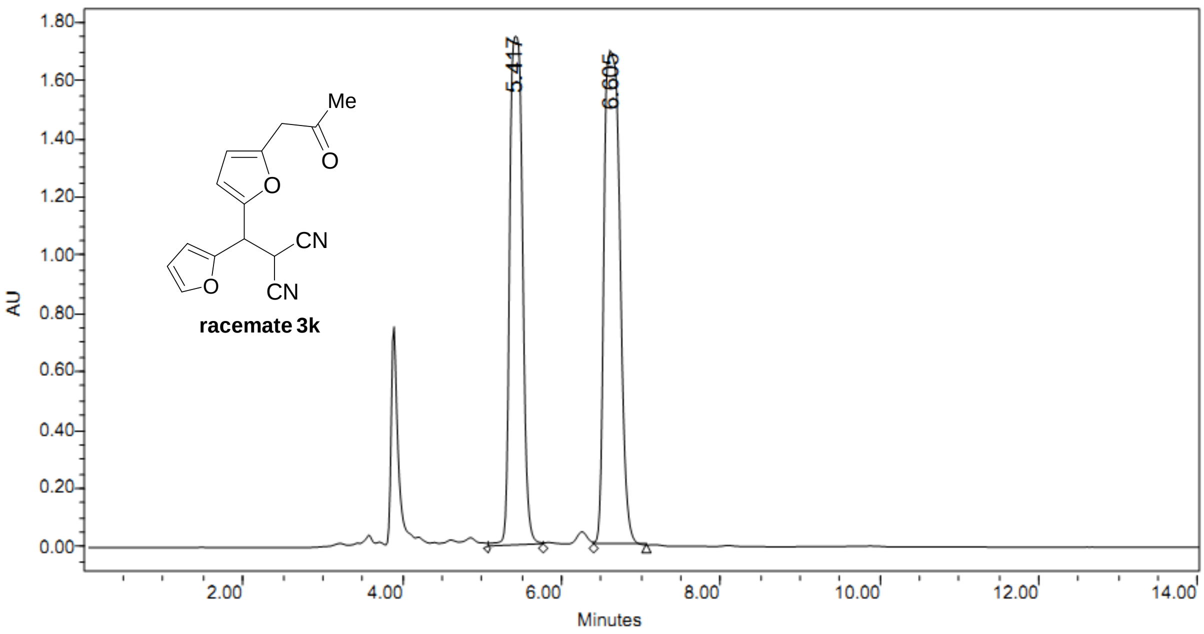
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	23.281	15219408	49.53	349852	51.58
2	24.969	15511303	50.47	328426	48.42



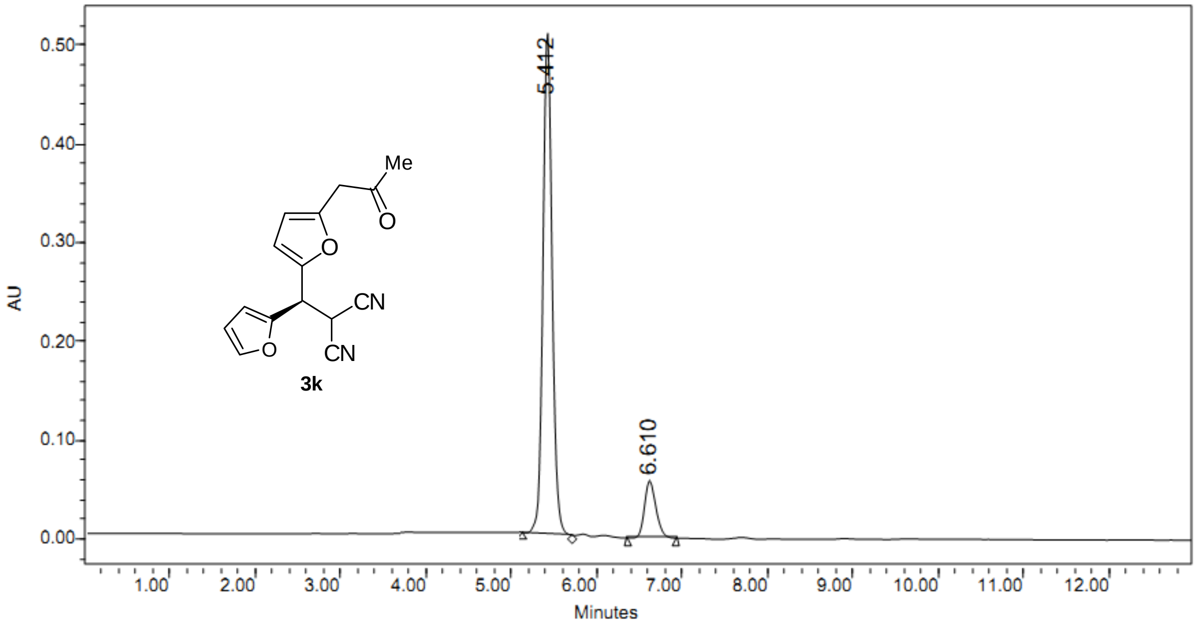
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	20.949	3478106	4.31	98406	5.26
2	22.365	77183448	95.69	1771133	94.74


7.474
7.473
7.470
7.260
6.465
6.456
6.424
6.416
6.248
6.240
4.814
4.798
4.467
4.450
3.740
2.198
Me
O
O
CN
CN
O
3k
10
9
8
7
6
5
4
3
2
1
0
ppm
0.92
1.85
0.91
0.97
1.03
1.08
2.29
3.00

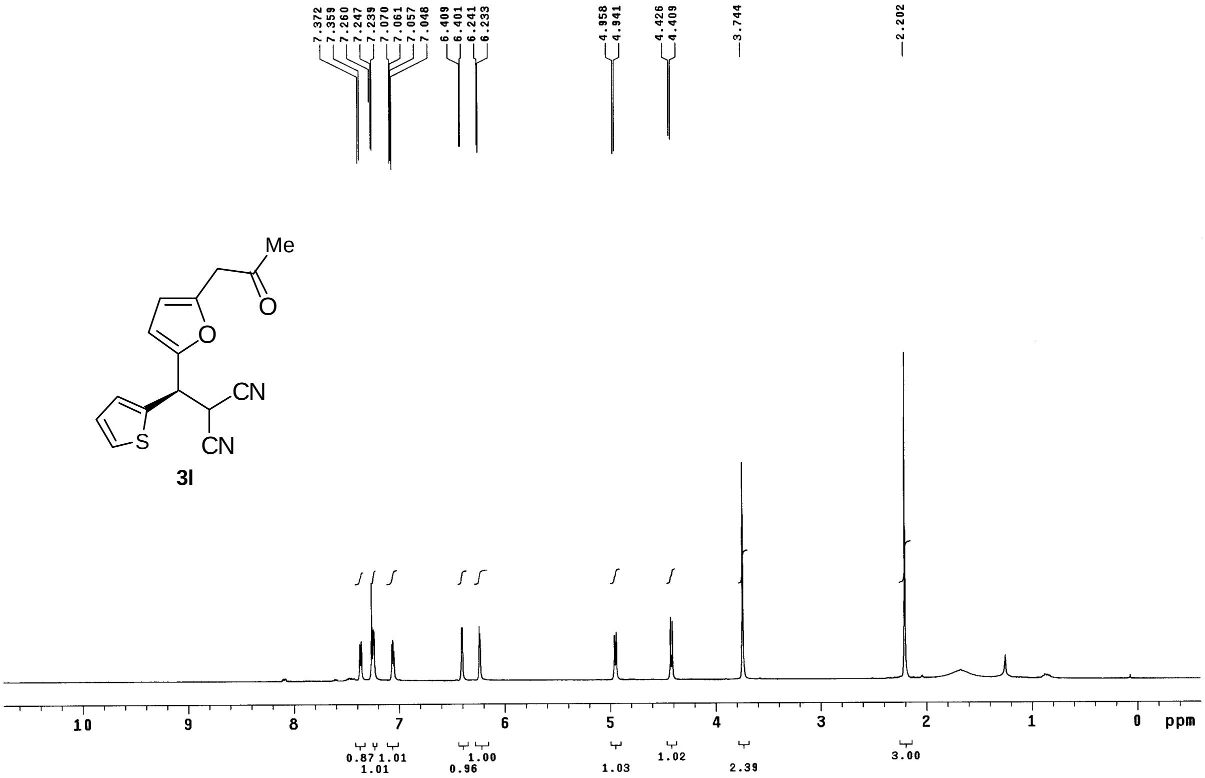

203.358
149.594
146.872
146.620
143.610
111.323
111.011
110.920
110.865
110.226
109.737
77.316
77.000
76.681
43.056
40.271
29.322
27.705
Me
O
O
CN
CN
O
3k
200
180
160
140
120
100
80
60
40
20
ppm

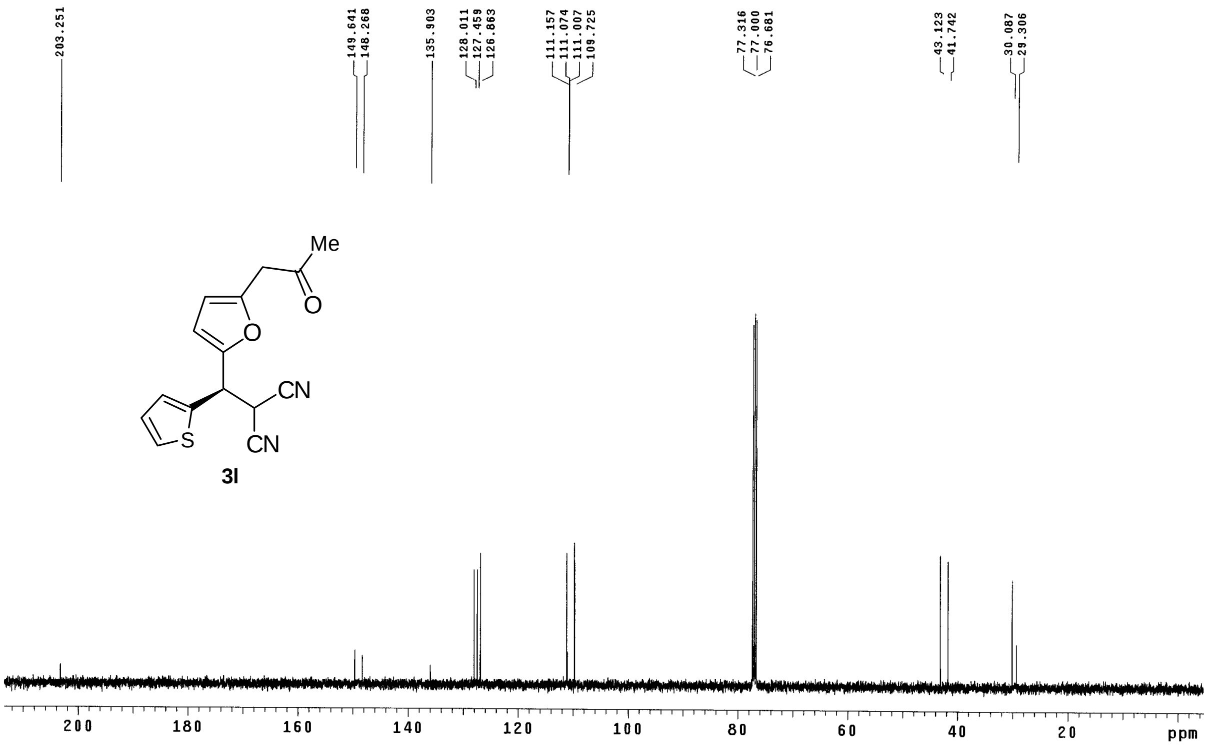


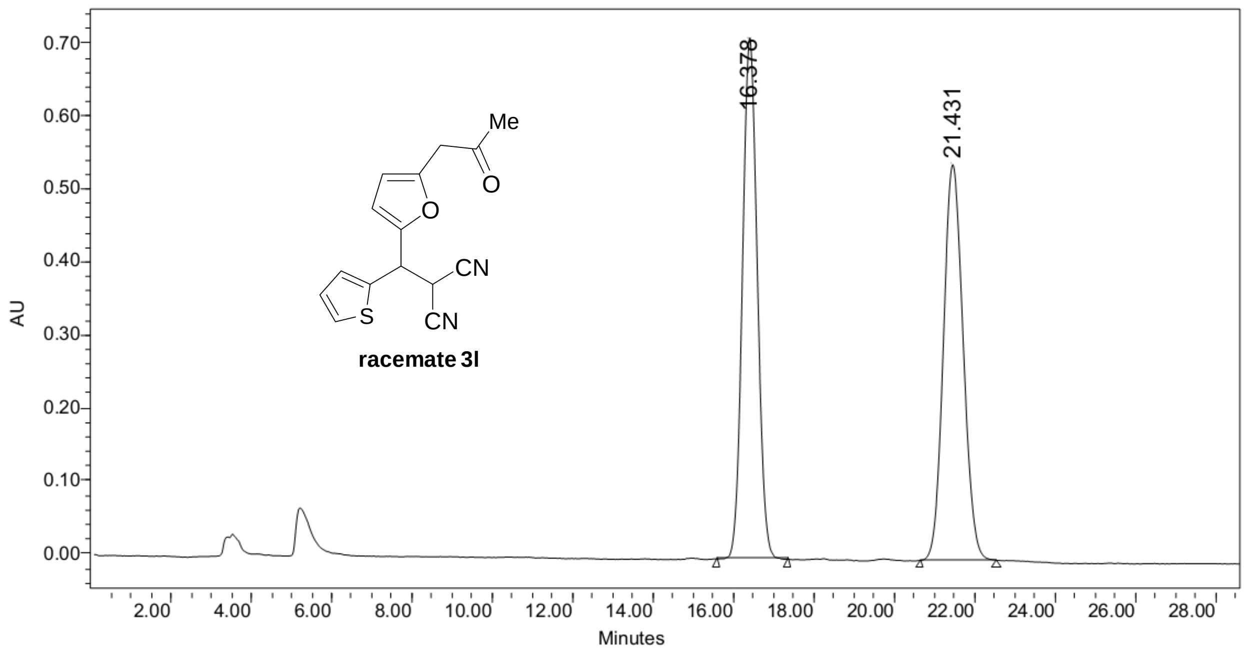
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	5.417	19609038	45.54	1752525	50.80
2	6.605	23449654	54.46	1697283	49.20



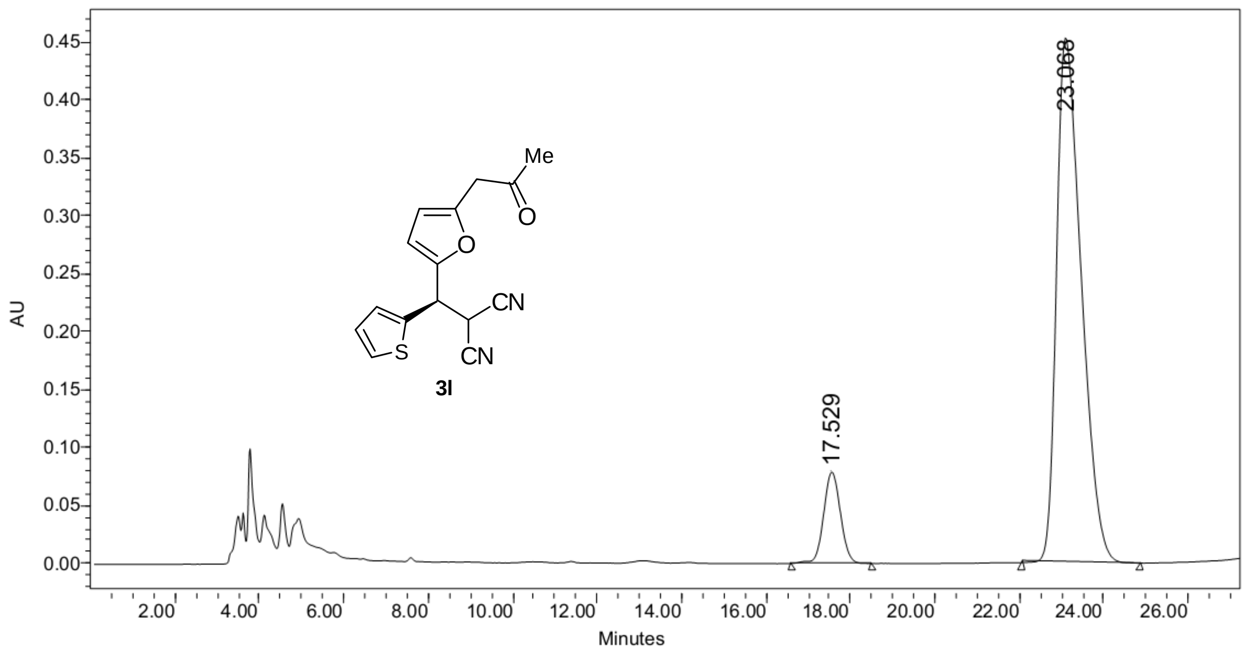
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	5.412	3800591	87.53	507705	89.81
2	6.610	541466	12.47	57585	10.19


7.372
7.359
7.260
7.247
7.239
7.070
7.061
7.057
7.048
6.409
6.401
6.241
6.233
4.958
4.941
4.426
4.409
3.744
2.202
Me
O
O
CN
S
CN
3l
0.87
1.01
1.01
0.96
1.00
1.03
1.02
2.39
3.00
ppm

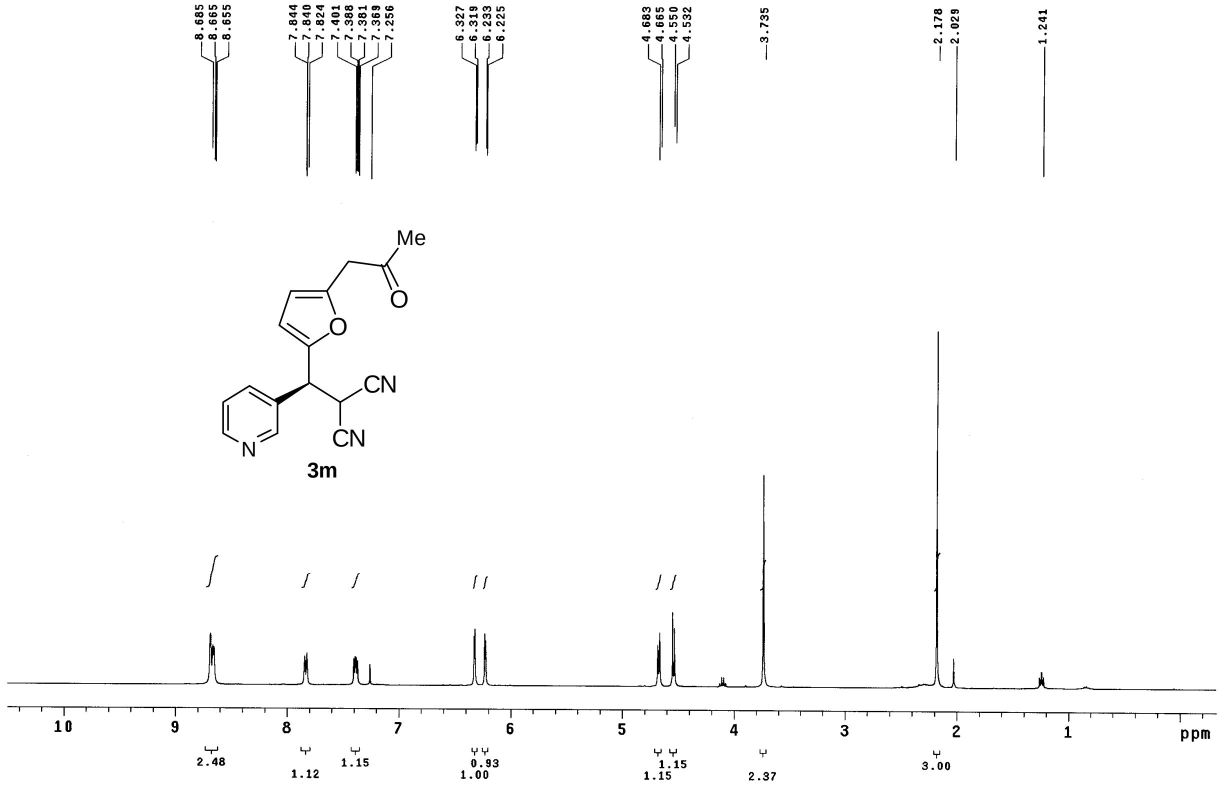

203.251
149.641
148.268
135.903
128.011
127.459
126.803
111.157
111.074
111.007
109.725
77.316
77.000
76.681
43.123
41.742
30.087
29.306
Me
O
O
CN
S
CN
3l
ppm

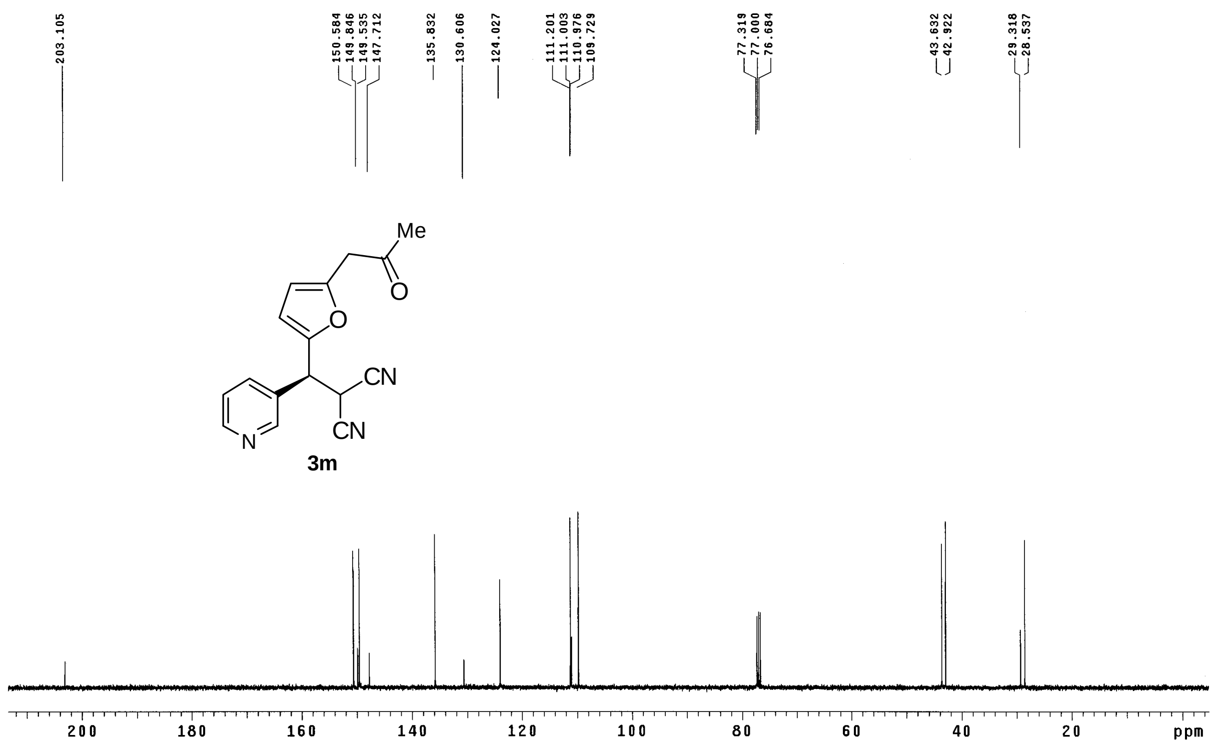


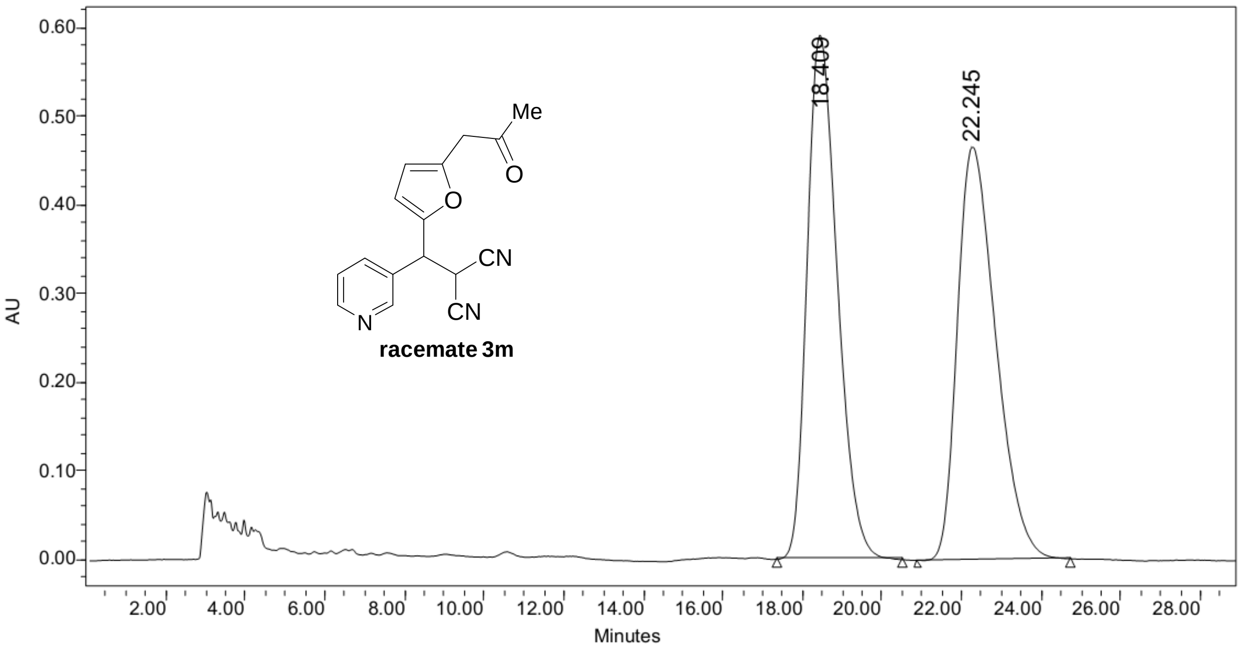
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	16.378	18274933	49.63	715196	56.84
2	21.431	18547359	50.37	542956	43.16



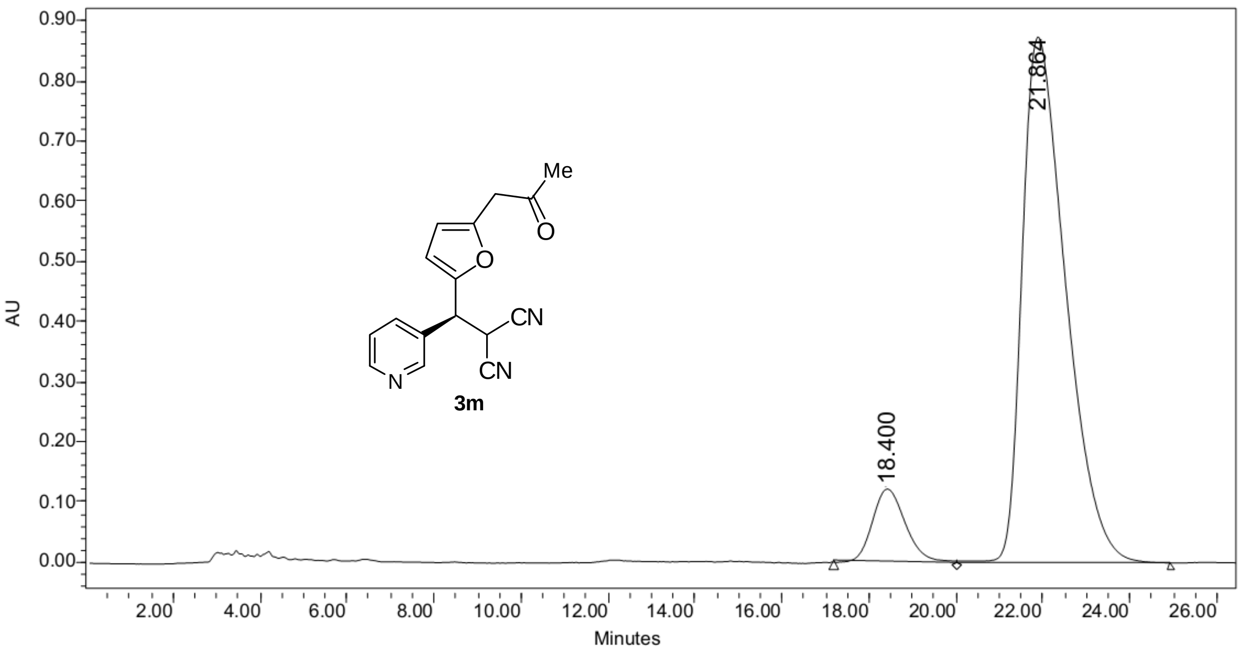
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	17.529	2057675	10.02	77380	14.59
2	23.068	18470750	89.98	452823	85.41


Me
O
CN
N
CN
3m
ppm

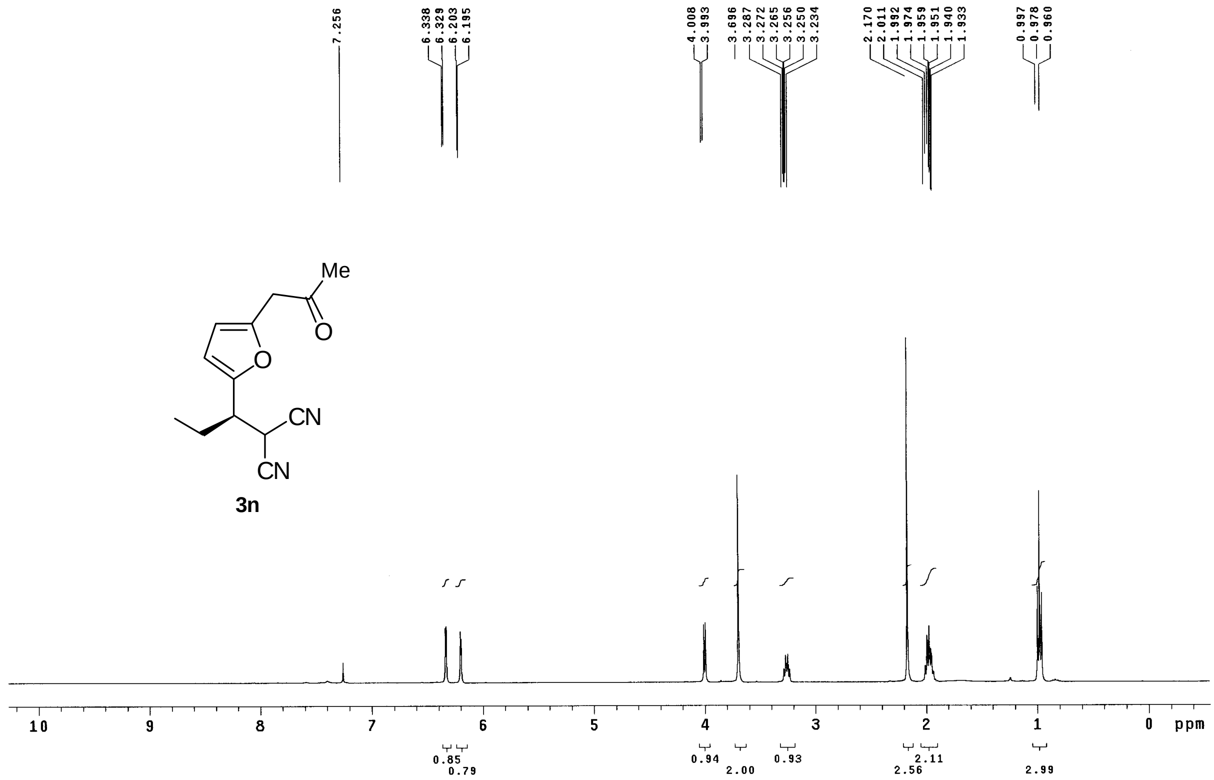

Me
O
CN
N
CN
3m
ppm

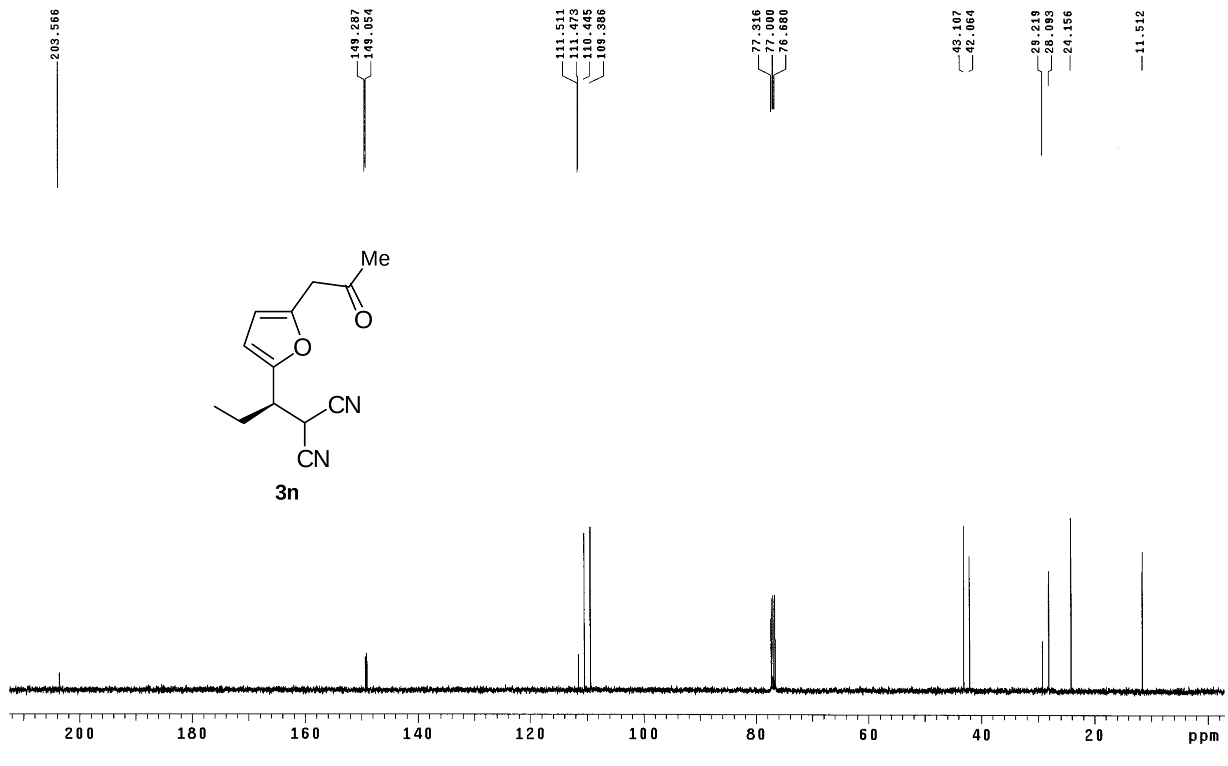


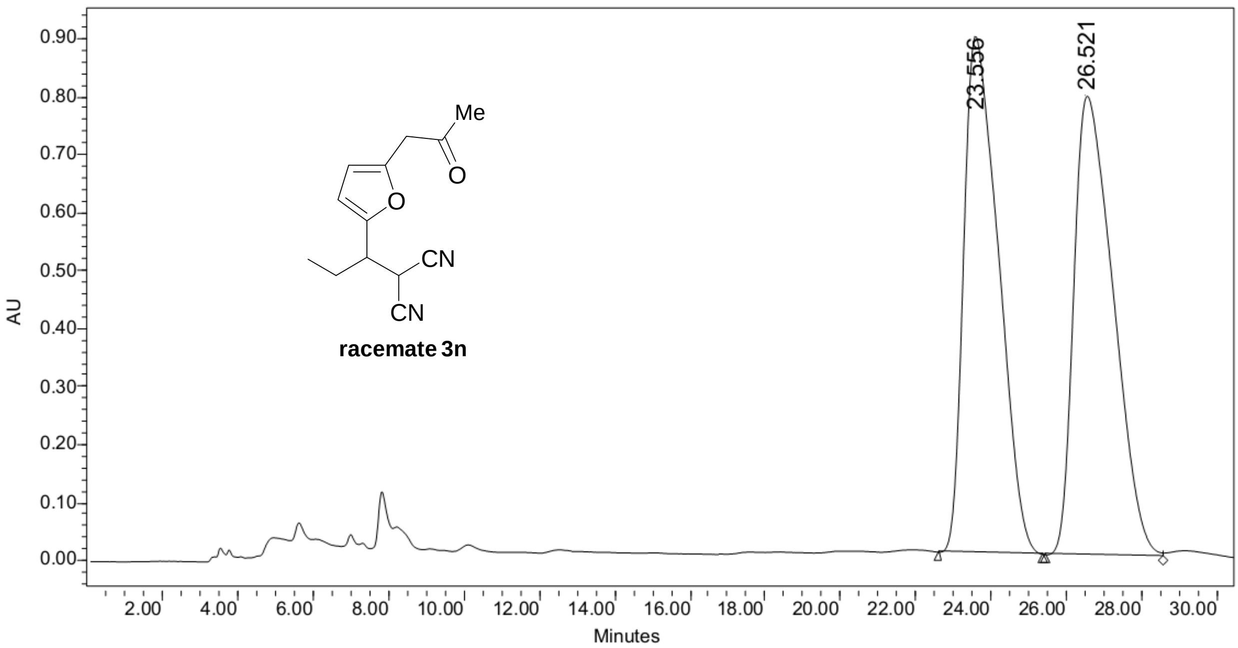
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	18.409	31295162	50.02	591043	55.96
2	22.245	31267881	49.98	465186	44.04



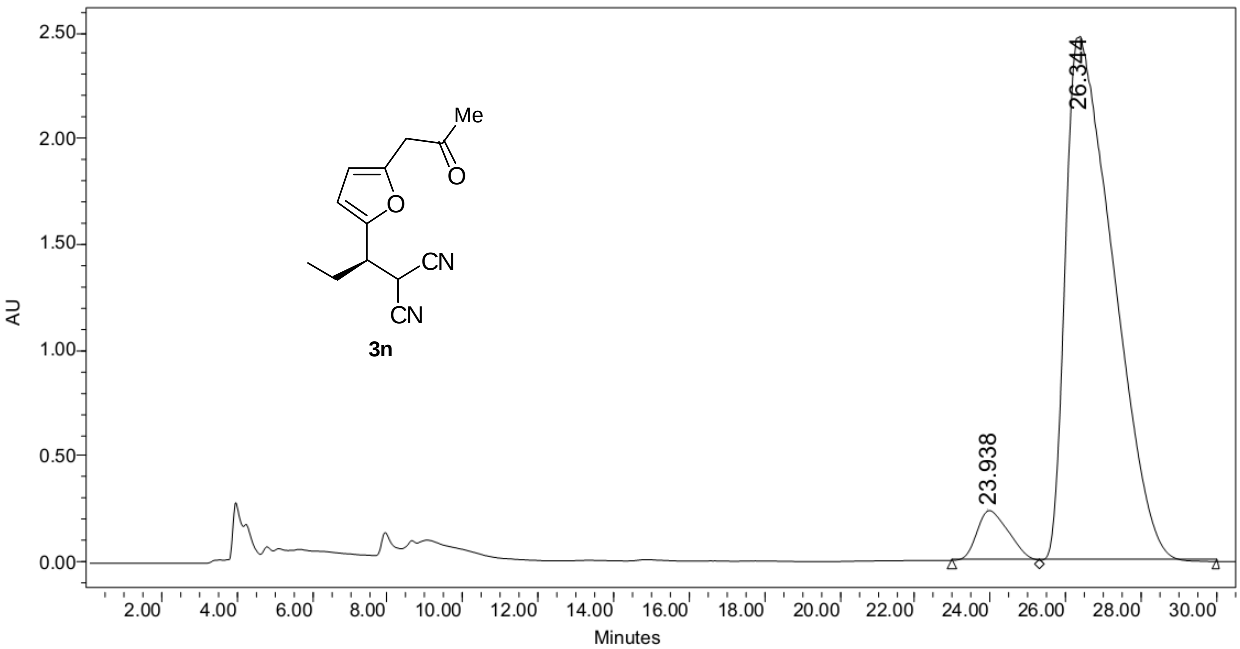
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	18.400	5964908	9.01	118914	12.00
2	21.864	60272239	90.99	871874	88.00


7.256
6.338 6.329 6.203 6.195
4.008 3.993
3.696
3.287 3.272 3.265 3.256 3.250 3.234
2.170 2.011 1.992 1.974 1.959 1.951 1.940 1.933
0.997 0.978 0.960
Me
O
O
CN
CN
3n
10 9 8 7 6 5 4 3 2 1 0 ppm
0.85 0.79 0.94 2.00 0.93 2.56 2.11 2.99

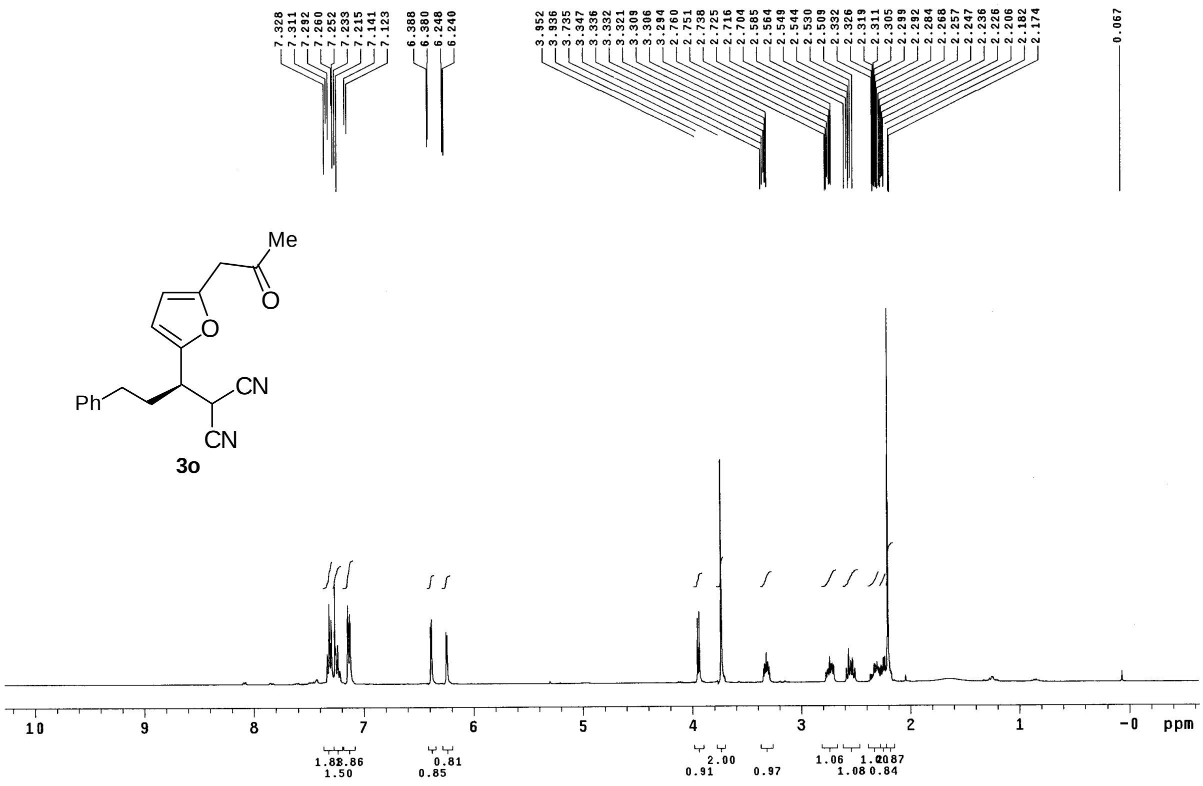

203.566
149.287 149.054
111.511 111.473 110.445 109.386
77.316 77.000 76.680
43.107 42.064
29.219 28.093 24.156
11.512
Me
O
O
CN
CN
3n
200 180 160 140 120 100 80 60 40 20 ppm

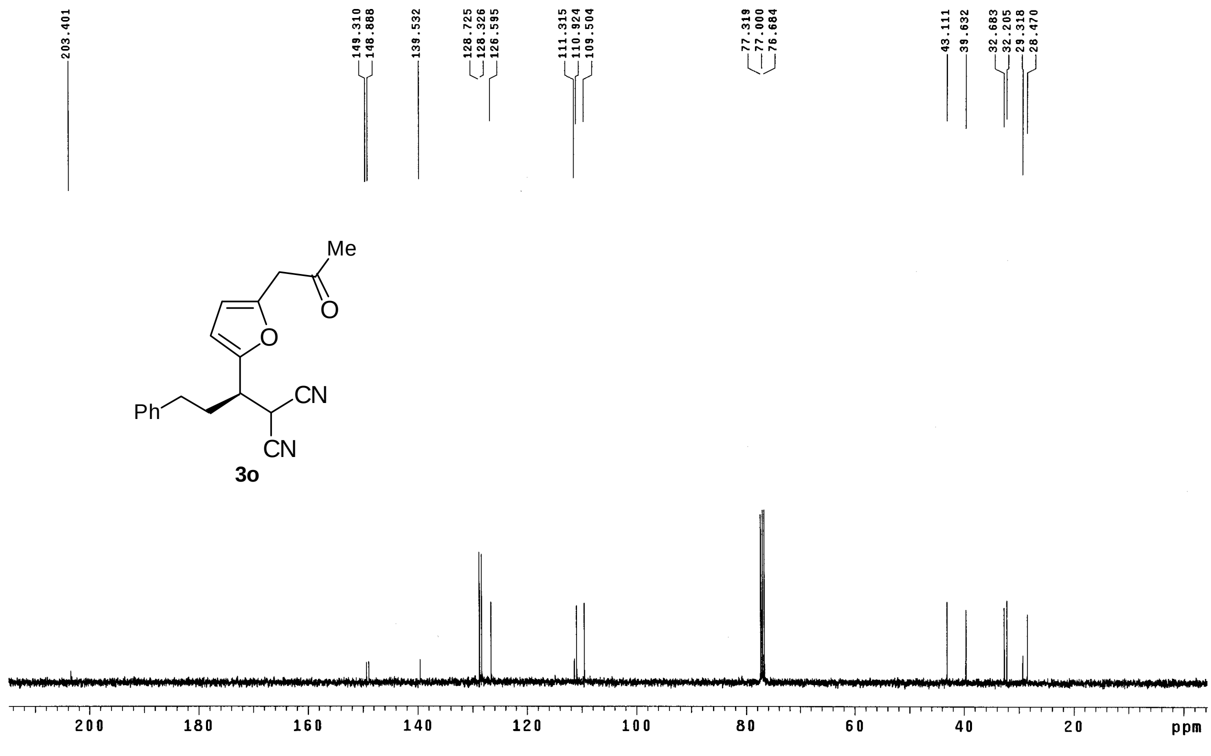


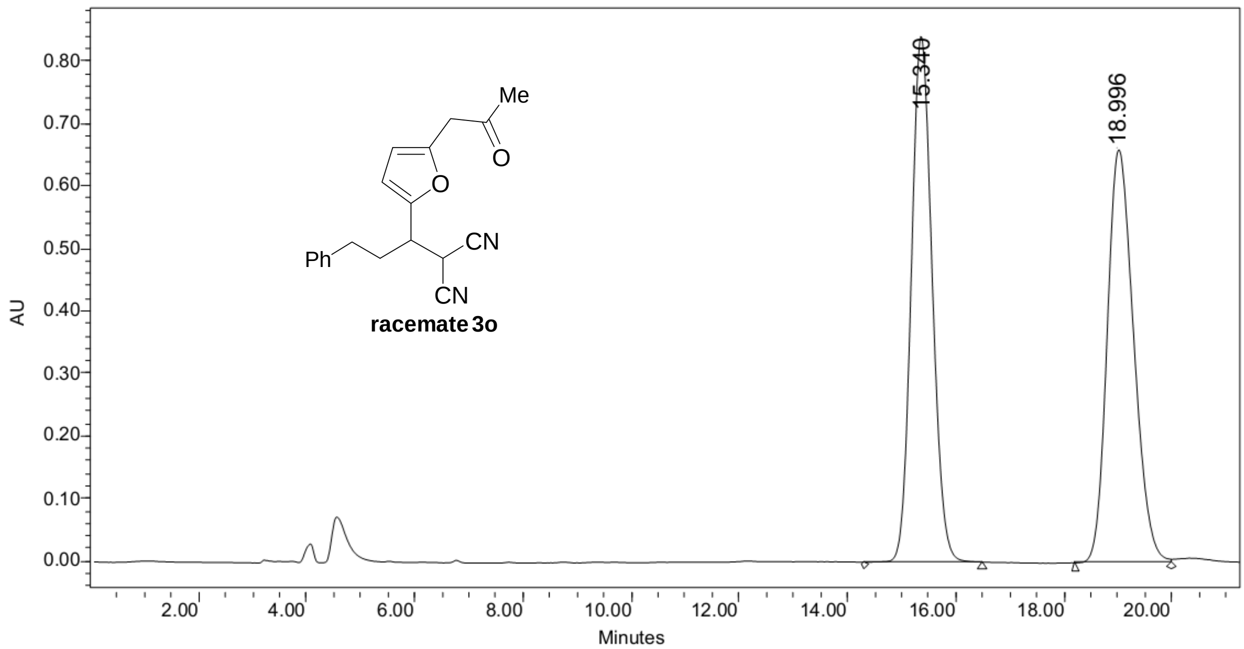
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	23.556	56961716	49.74	891382	52.93
2	26.521	57567335	50.26	792543	47.07



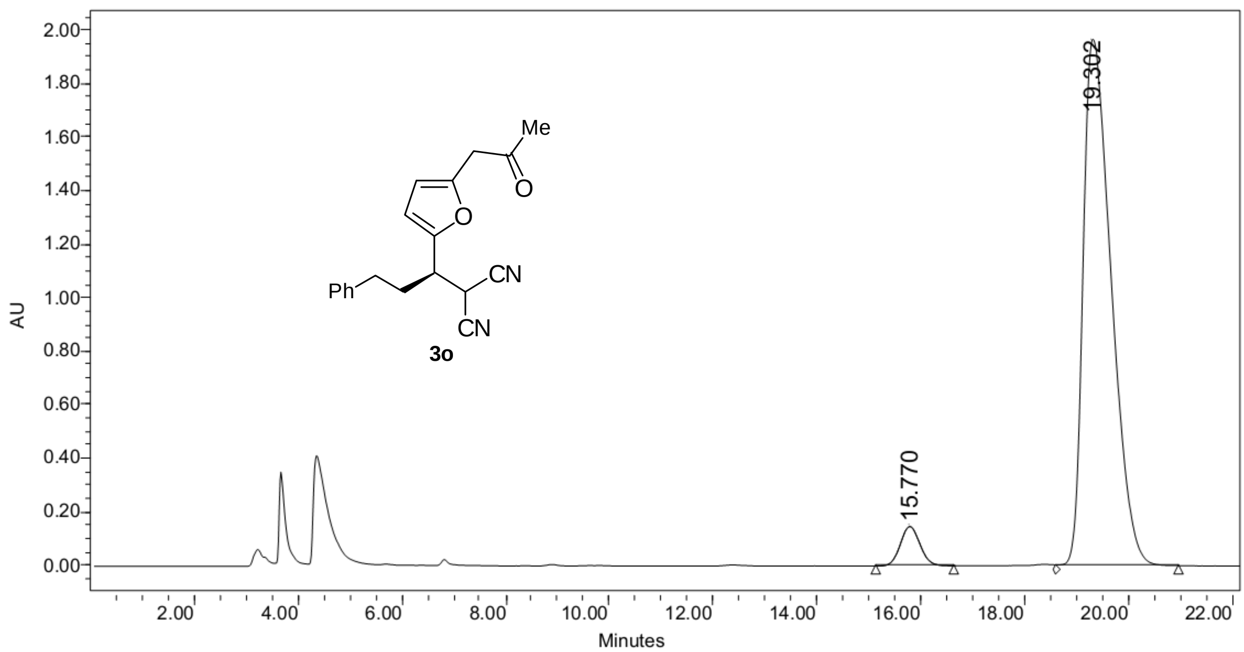
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	23.938	12512593	5.43	226324	8.38
2	26.344	217846948	94.57	2475873	91.62



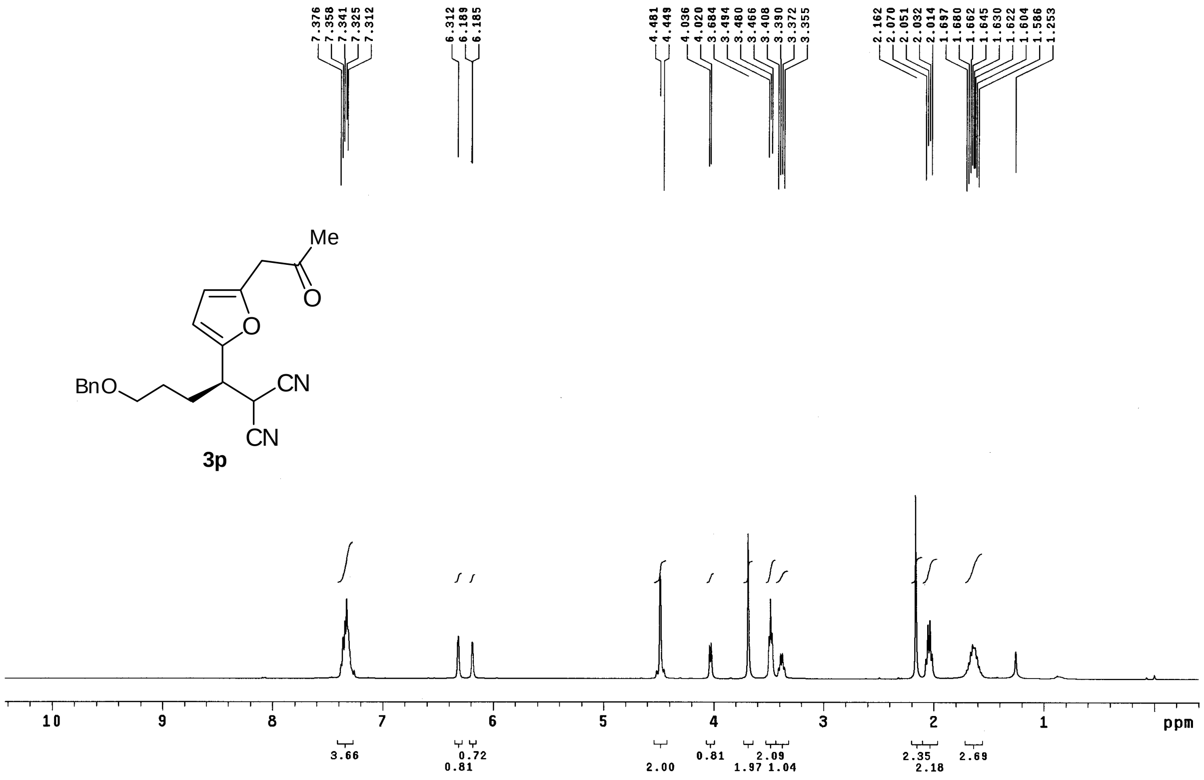


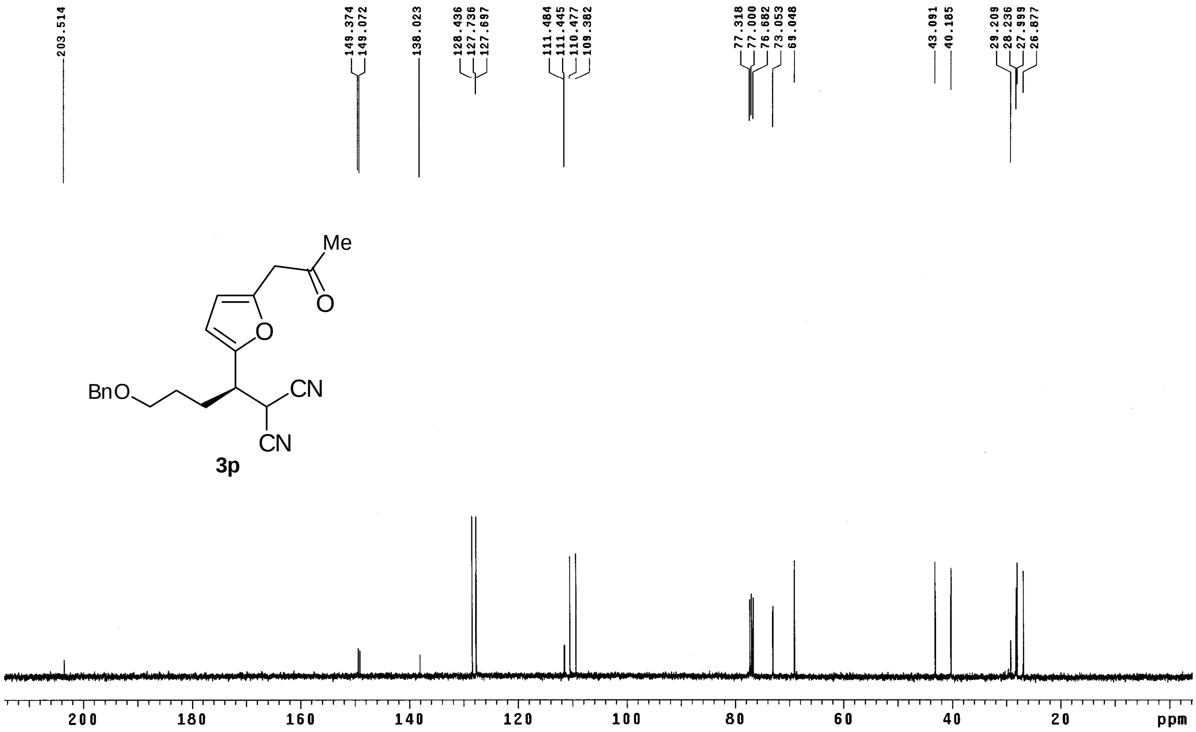


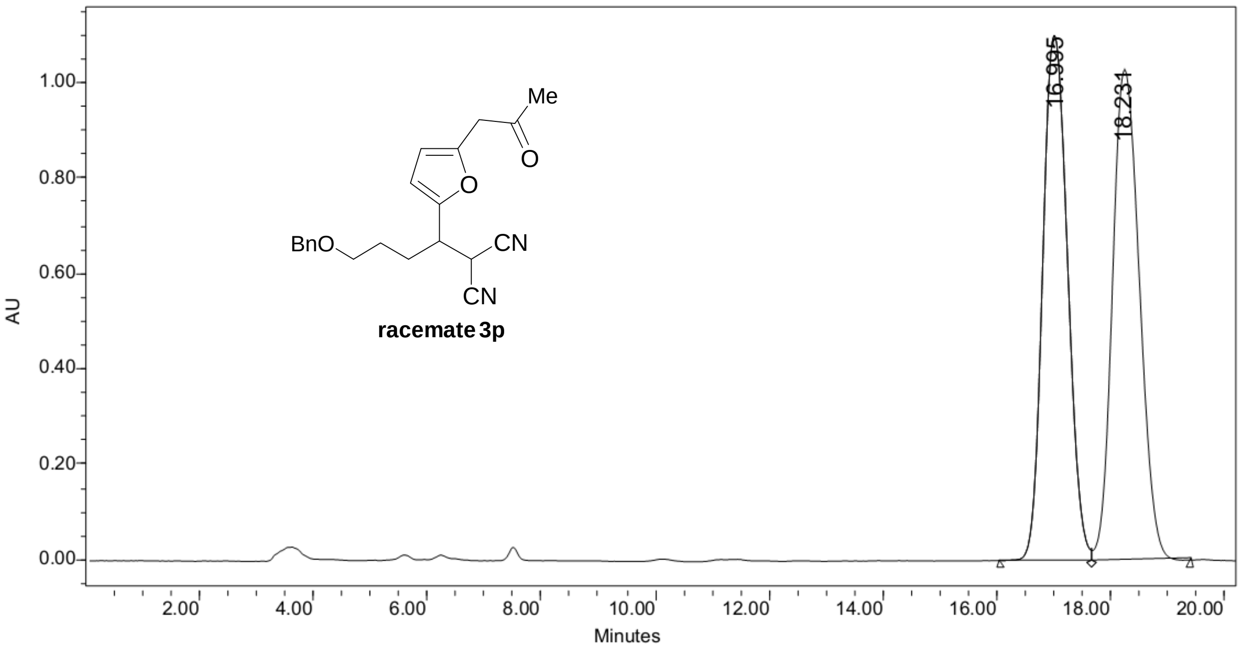
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	15.340	22501333	50.03	841462	56.01
2	18.996	22470040	49.97	660849	43.99



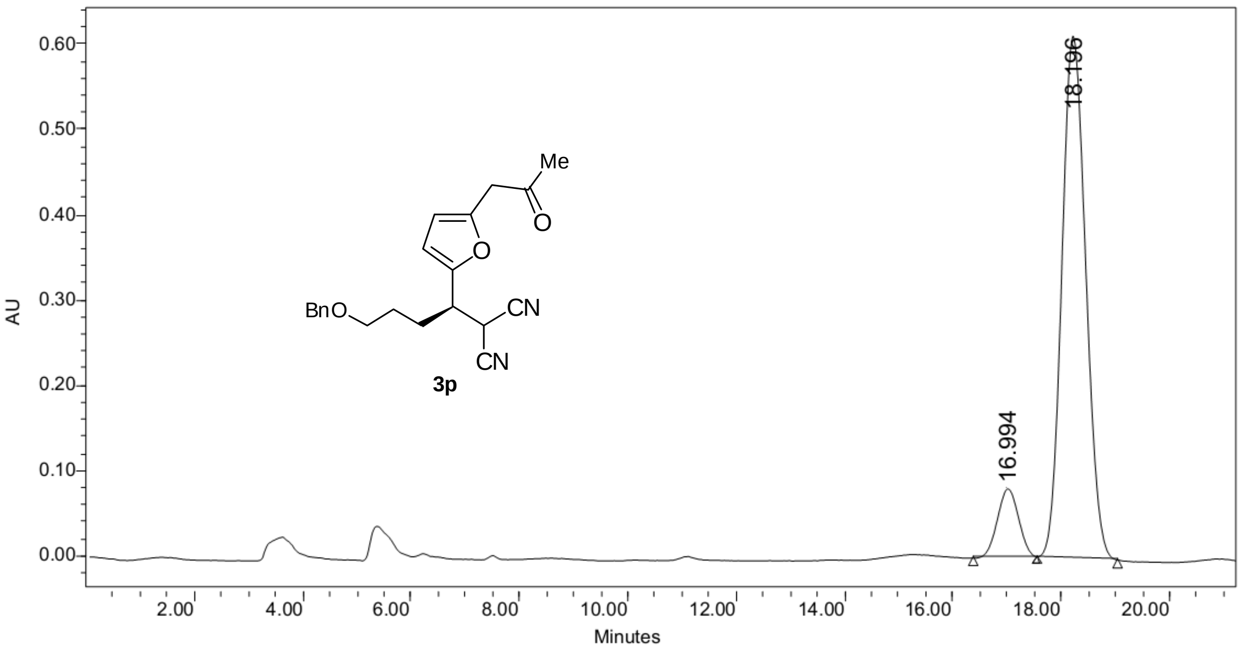
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	15.770	3875190	4.99	147093	6.96
2	19.302	73745014	95.01	1967498	93.04


7.376 7.358 7.341 7.325 7.312
6.312 6.189 6.185
4.481 4.449 4.036 4.020 3.684 3.494 3.480 3.466 3.408 3.390 3.372 3.355
2.162 2.070 2.051 2.032 2.014 1.697 1.680 1.662 1.645 1.630 1.622 1.604 1.586 1.253
Me
O
BnO
CN
CN
3p
10 9 8 7 6 5 4 3 2 1 ppm
3.66 0.81 0.72 2.00 0.81 1.97 2.09 1.04 2.35 2.18 2.69

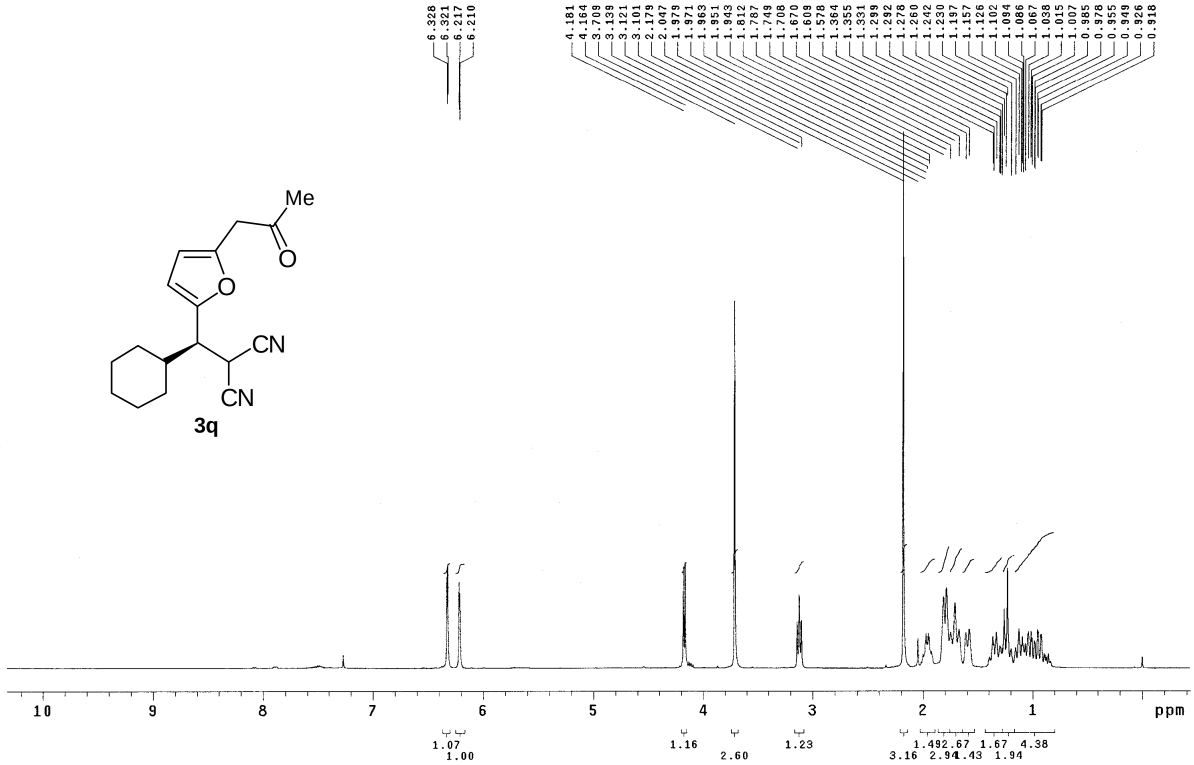

203.514
149.374 149.072 138.023
128.436 127.736 127.697
111.484 111.445 110.477 109.382
77.318 77.000 76.682 73.053 69.048
43.091 40.185
29.209 28.236 27.999 26.877
Me
O
BnO
CN
CN
3p
200 180 160 140 120 100 80 60 40 20 ppm



	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	16.995	33307228	49.60	1099824	51.70
2	18.231	33850268	50.40	1027661	48.30



	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	16.994	1970959	9.52	76597	11.12
2	18.196	18725605	90.48	612084	88.88


6.328
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6.210
4.181
4.164
3.709
3.139
3.121
3.101
2.179
2.047
1.979
1.971
1.963
1.951
1.943
1.812
1.787
1.749
1.708
1.670
1.609
1.578
1.364
1.355
1.331
1.299
1.292
1.278
1.260
1.242
1.230
1.197
1.157
1.126
1.102
1.094
1.086
1.067
1.038
1.015
1.007
0.985
0.978
0.955
0.949
0.926
0.918
Me
O
O
CN
CN
3q
ppm
1.07
1.00
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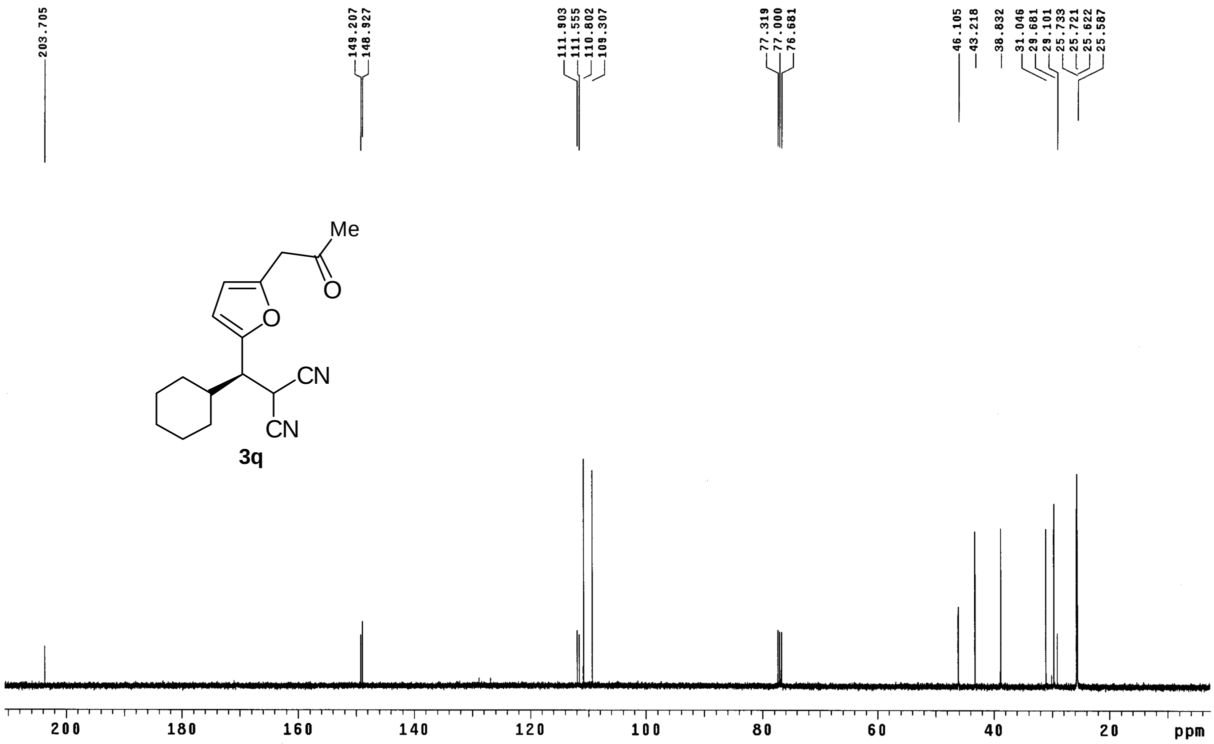
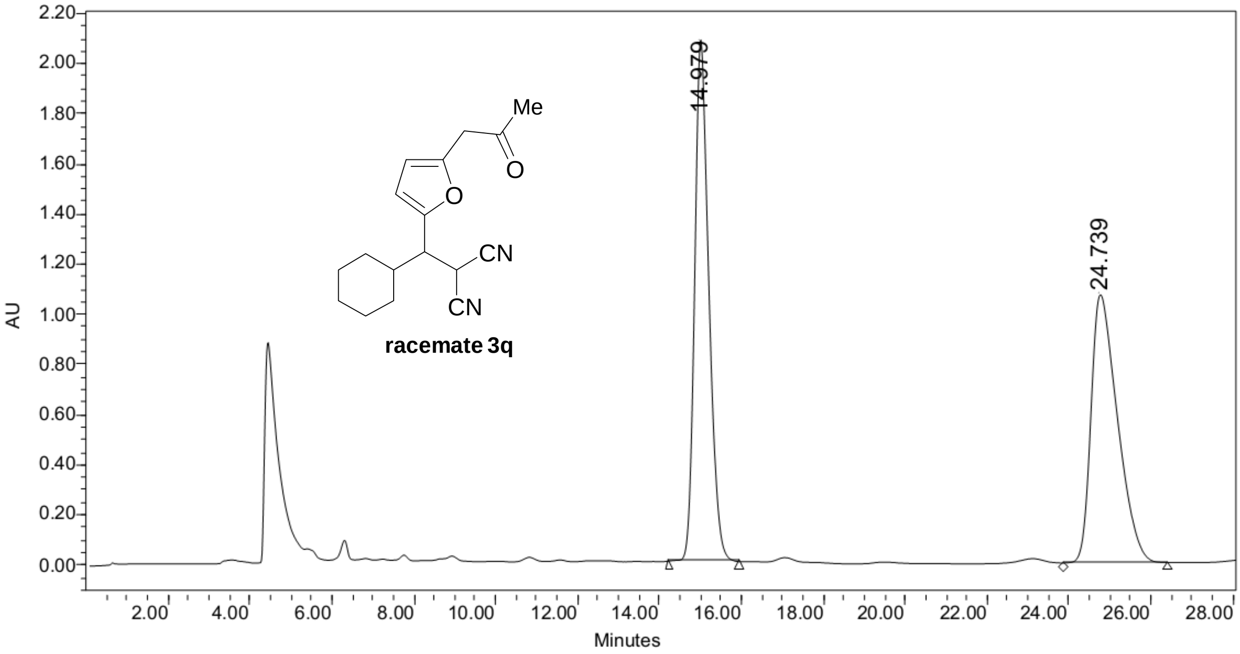
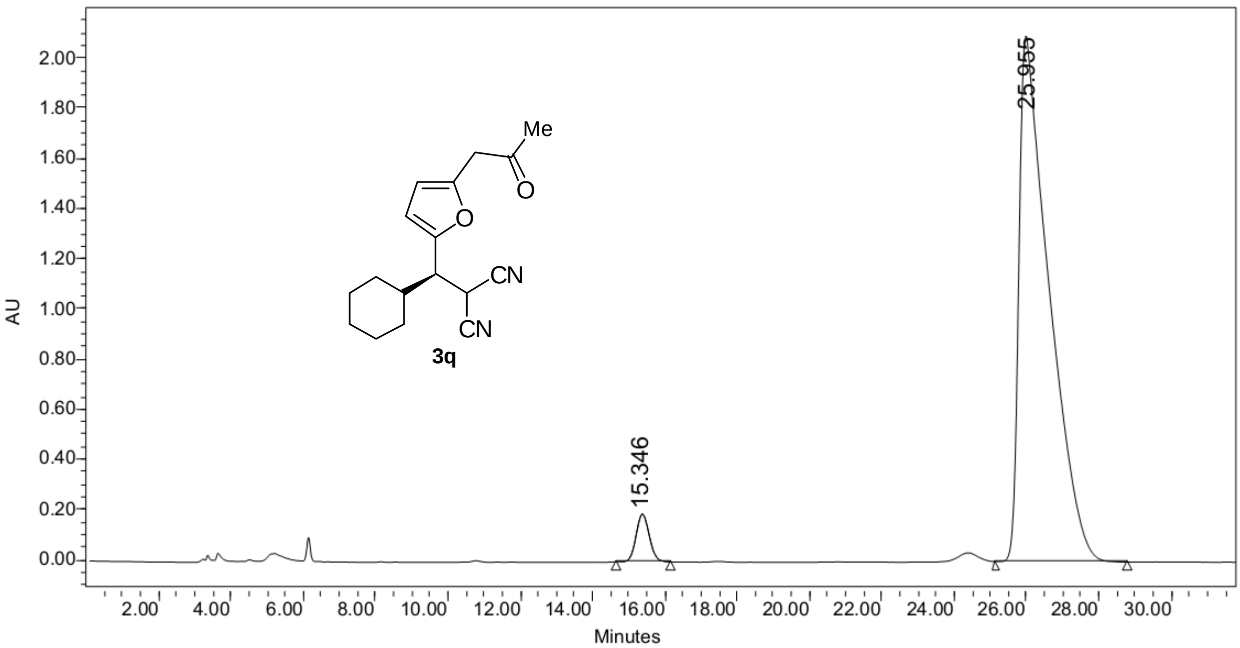
2.94
1.43
1.67
1.94
4.38

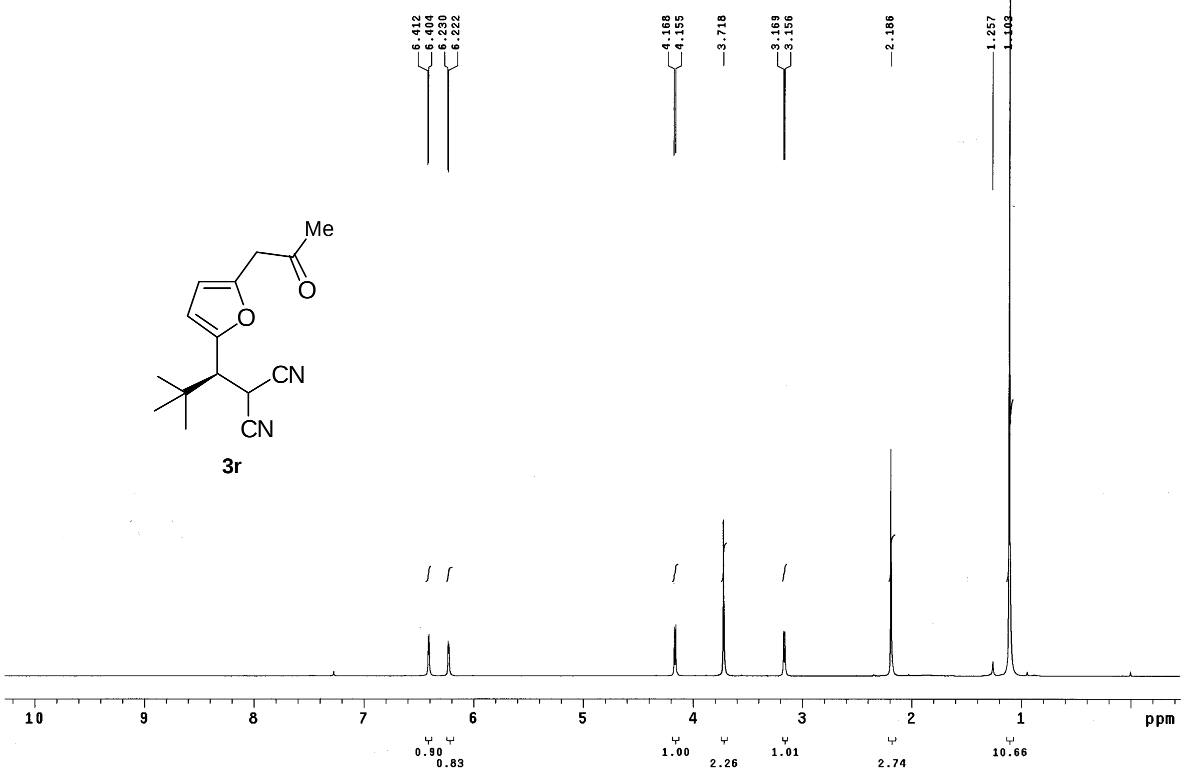

203.705
149.207
148.927
111.903
111.555
110.802
109.307
77.319
77.000
76.681
46.105
43.218
38.832
31.046
29.681
29.101
25.733
25.721
25.622
25.587
Me
O
O
CN
CN
3q
ppm



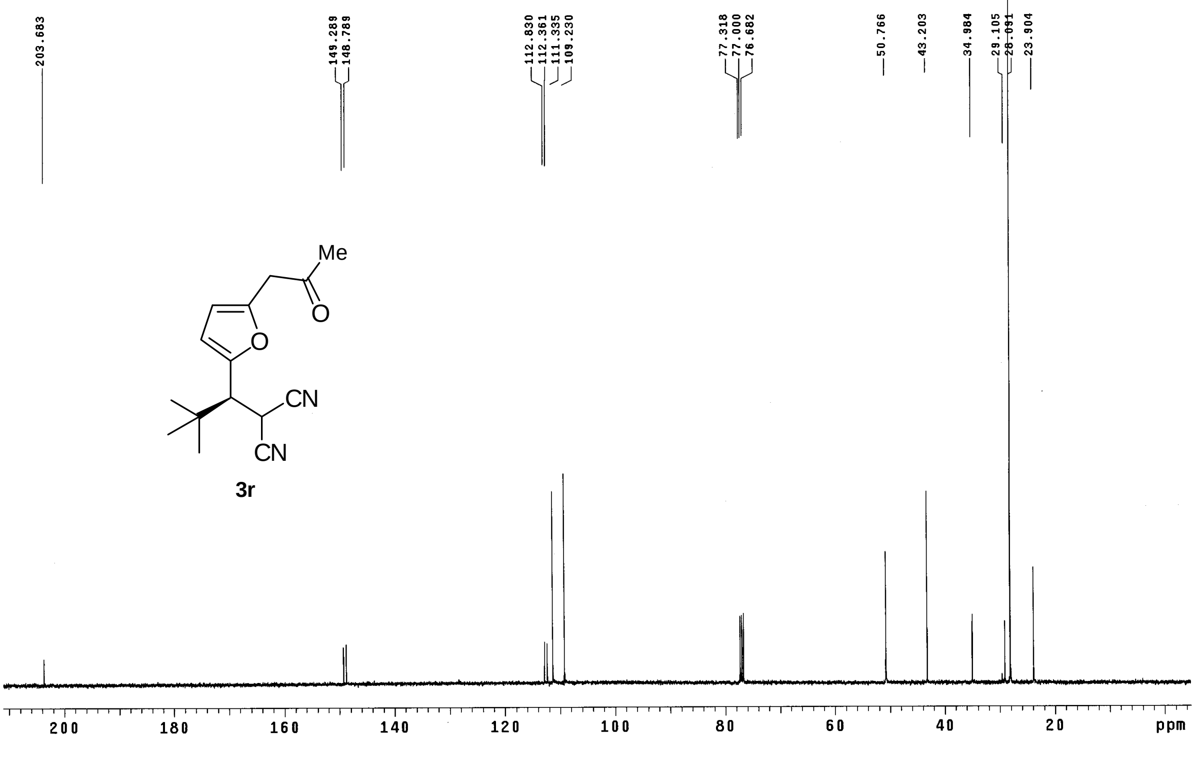
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	14.979	49833412	50.88	2080015	66.03
2	24.739	48103362	49.12	1070284	33.97



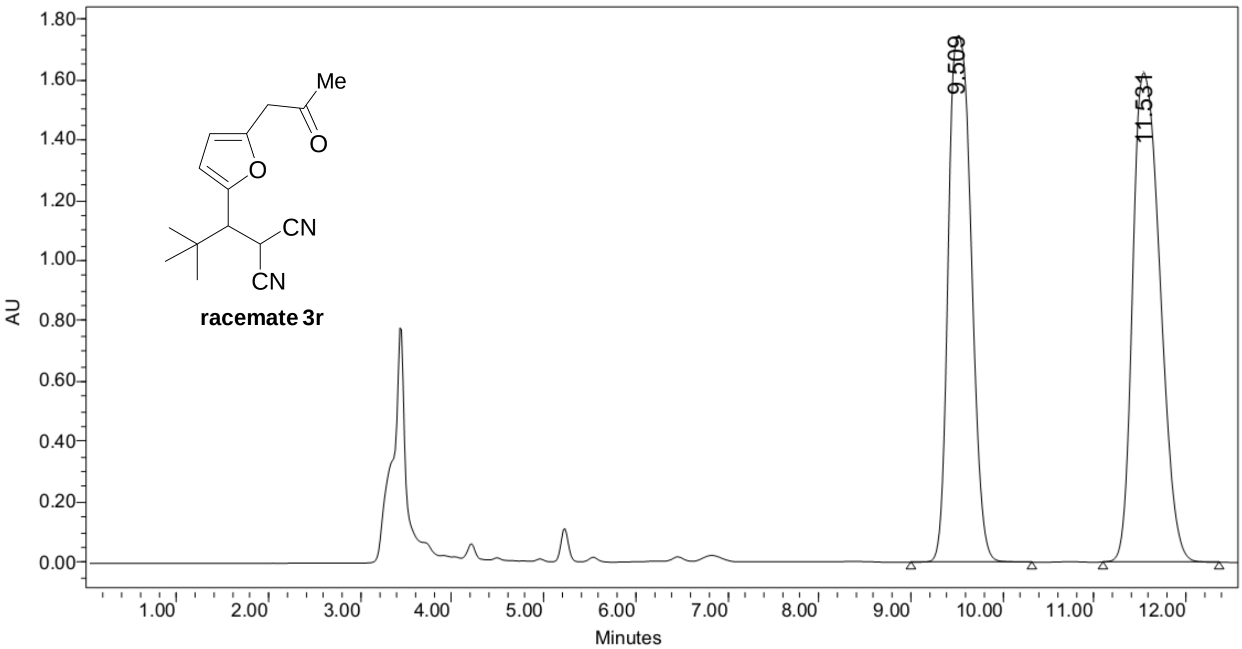
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	15.346	4792005	3.82	189509	8.29
2	25.955	120688766	96.18	2095141	91.71



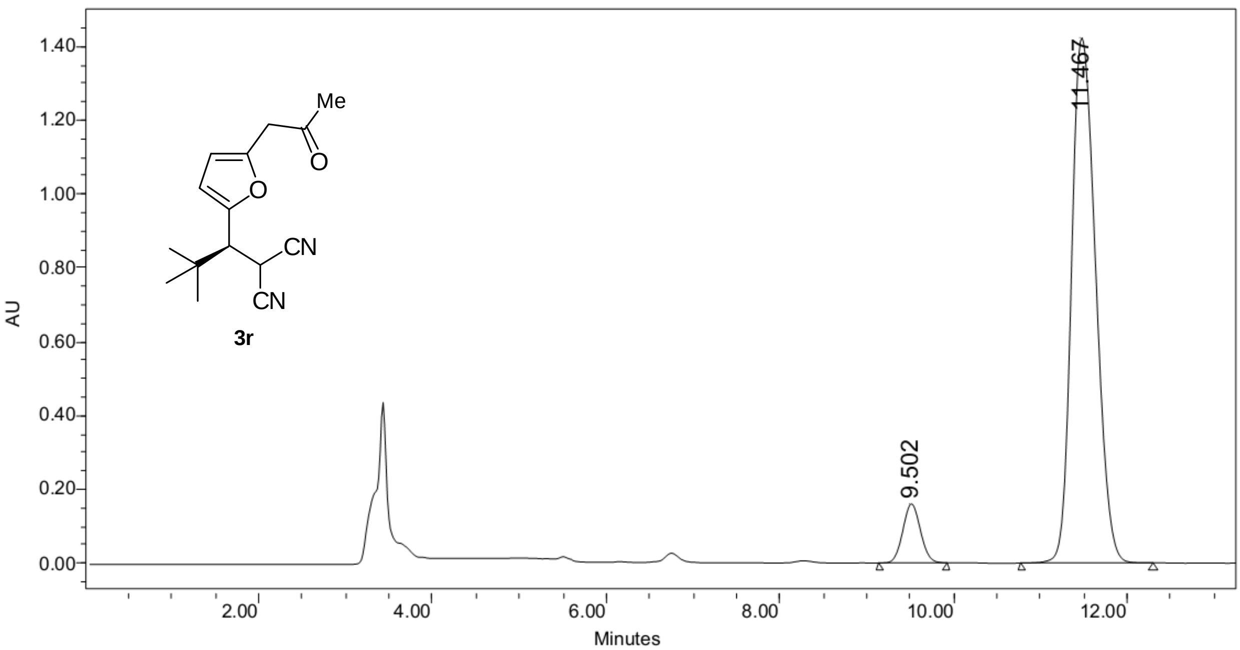
6.412
6.404
6.230
6.222
4.168
4.155
3.718
3.169
3.156
2.186
1.257
1.103
Me
O
O
CN
CN
3r
10
9
8
7
6
5
4
3
2
1
ppm
0.90
0.83
1.00
2.26
1.01
2.74
10.66



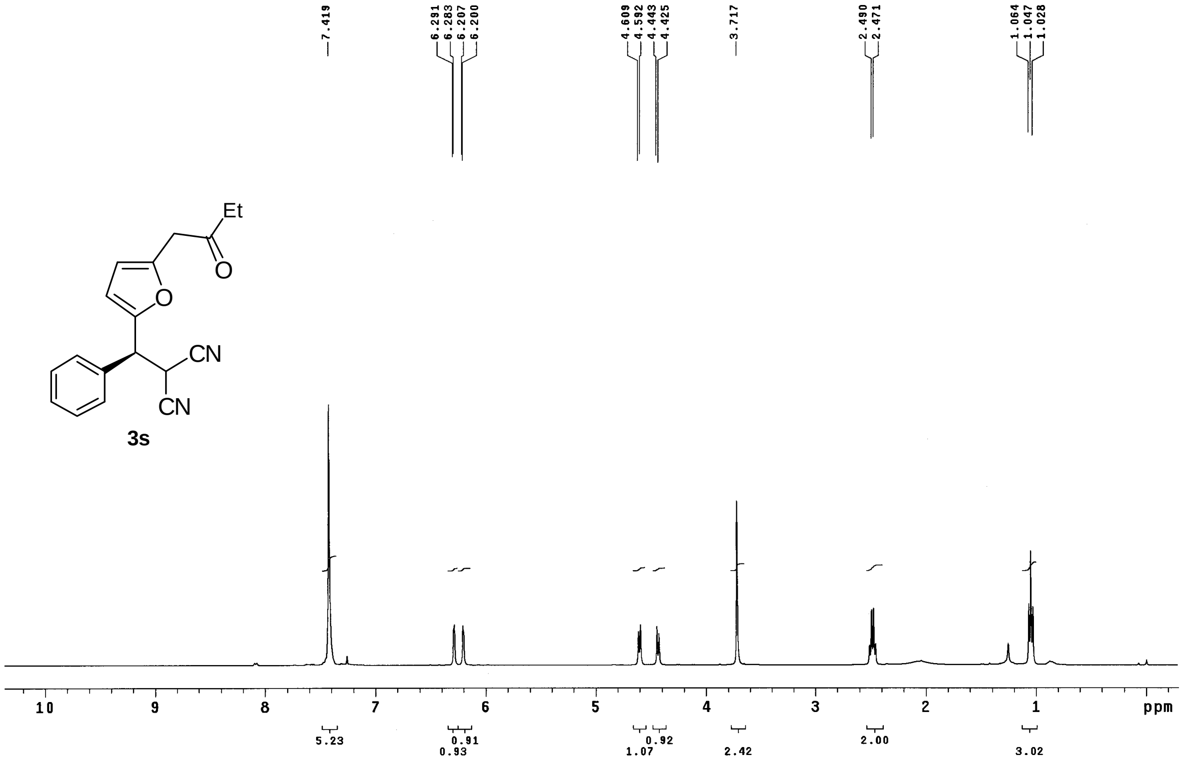
203.683
149.289
148.789
112.830
112.361
111.335
109.230
77.318
77.000
76.682
50.766
43.203
34.984
29.105
28.091
23.904
Me
O
O
CN
CN
3r
200
180
160
140
120
100
80
60
40
20
ppm



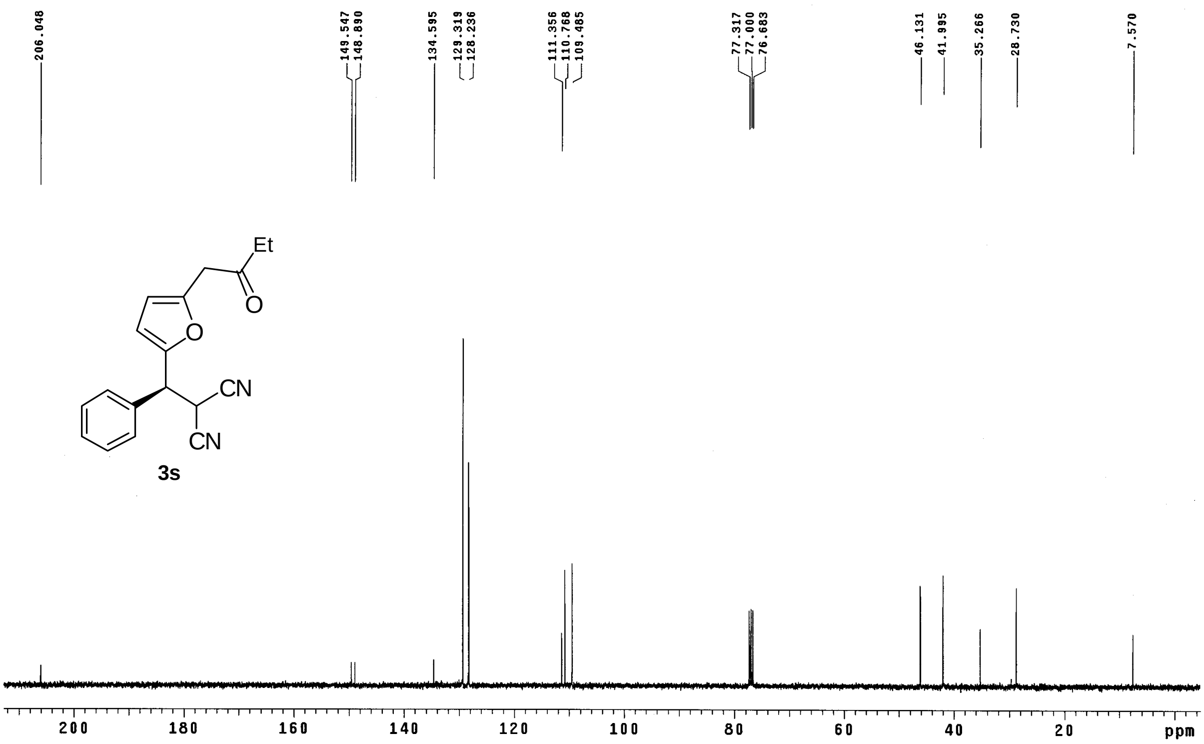
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	9.509	30391024	49.69	1747245	52.90
2	11.531	30765667	50.31	1555655	47.10



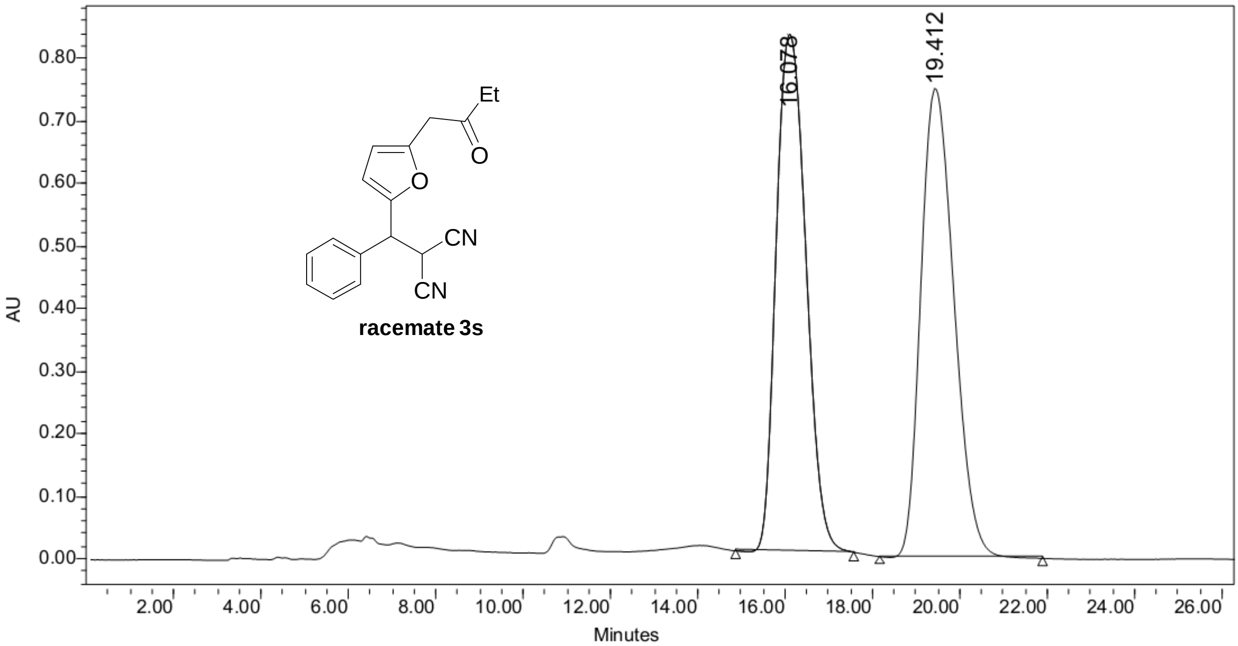
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	9.502	2108016	7.13	156230	9.89
2	11.467	27449696	92.87	1423261	90.11



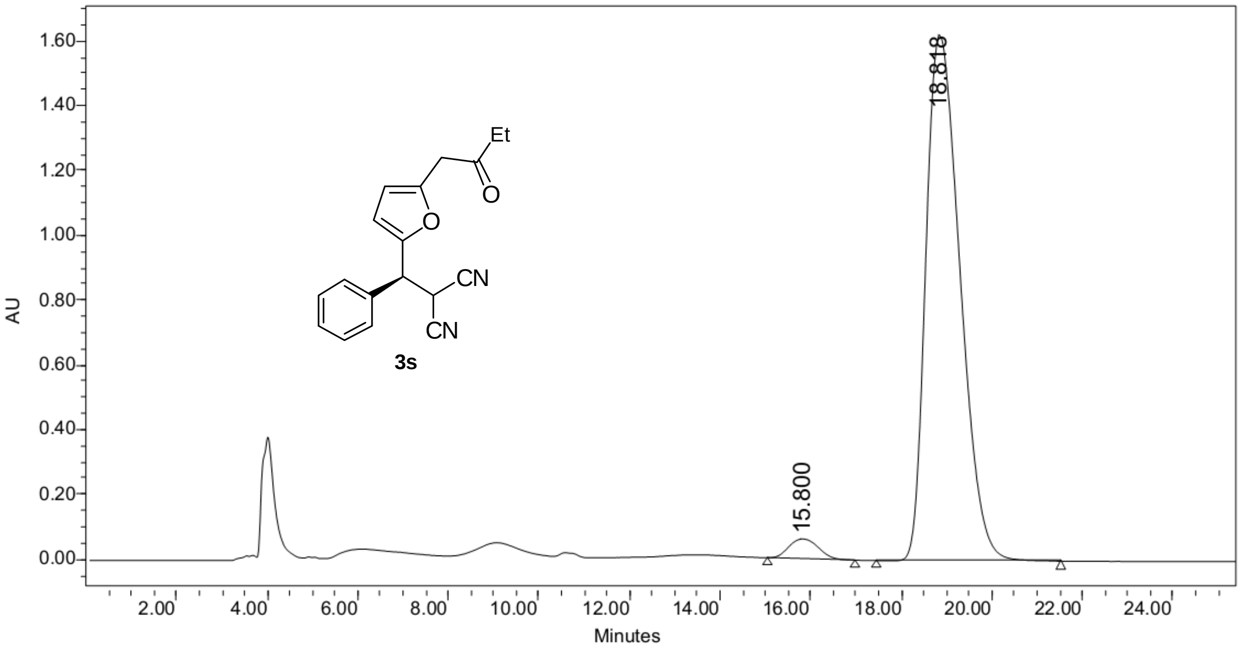
7.419
6.291
6.283
6.207
6.200
4.609
4.592
4.443
4.425
3.717
2.490
2.471
1.064
1.047
1.028
Et
O
CN
CN
3s
5.23
0.91
0.93
1.07
0.92
2.42
2.00
3.02
ppm



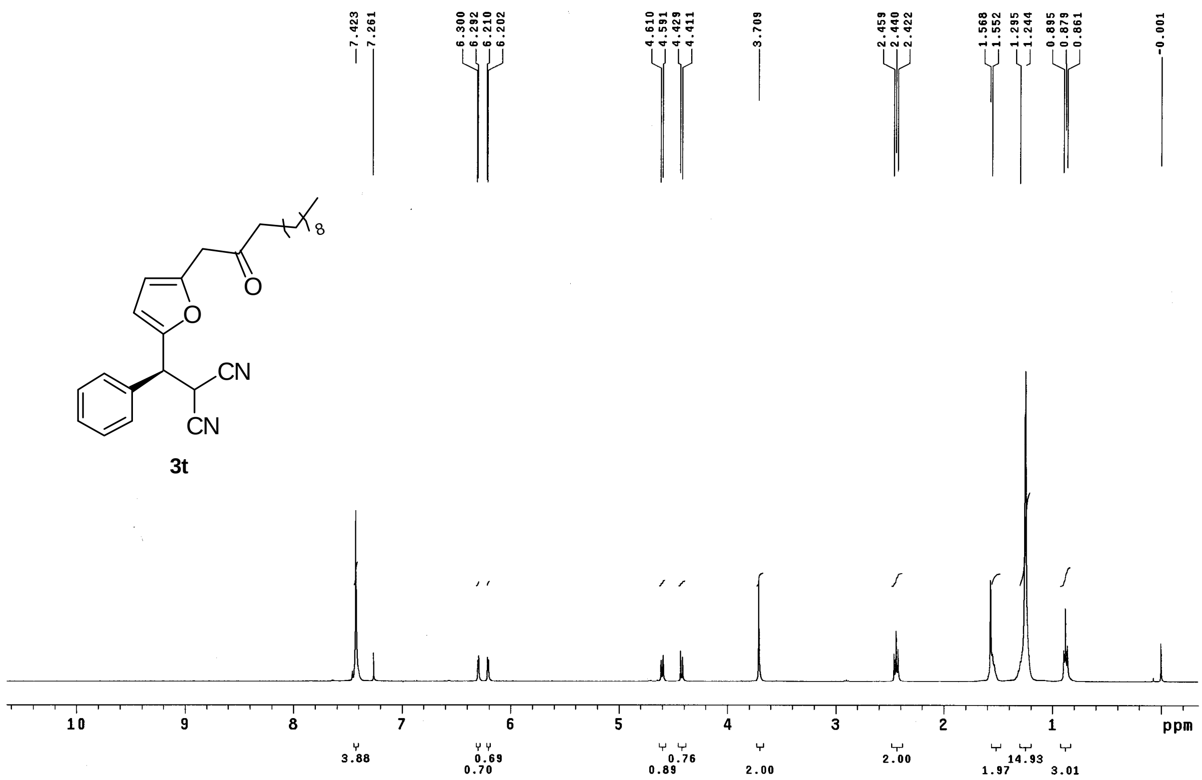
206.048
149.547
148.890
134.595
129.319
128.236
111.356
110.768
109.485
77.317
77.000
76.683
46.131
41.995
35.266
28.730
7.570
Et
O
CN
CN
3s
ppm

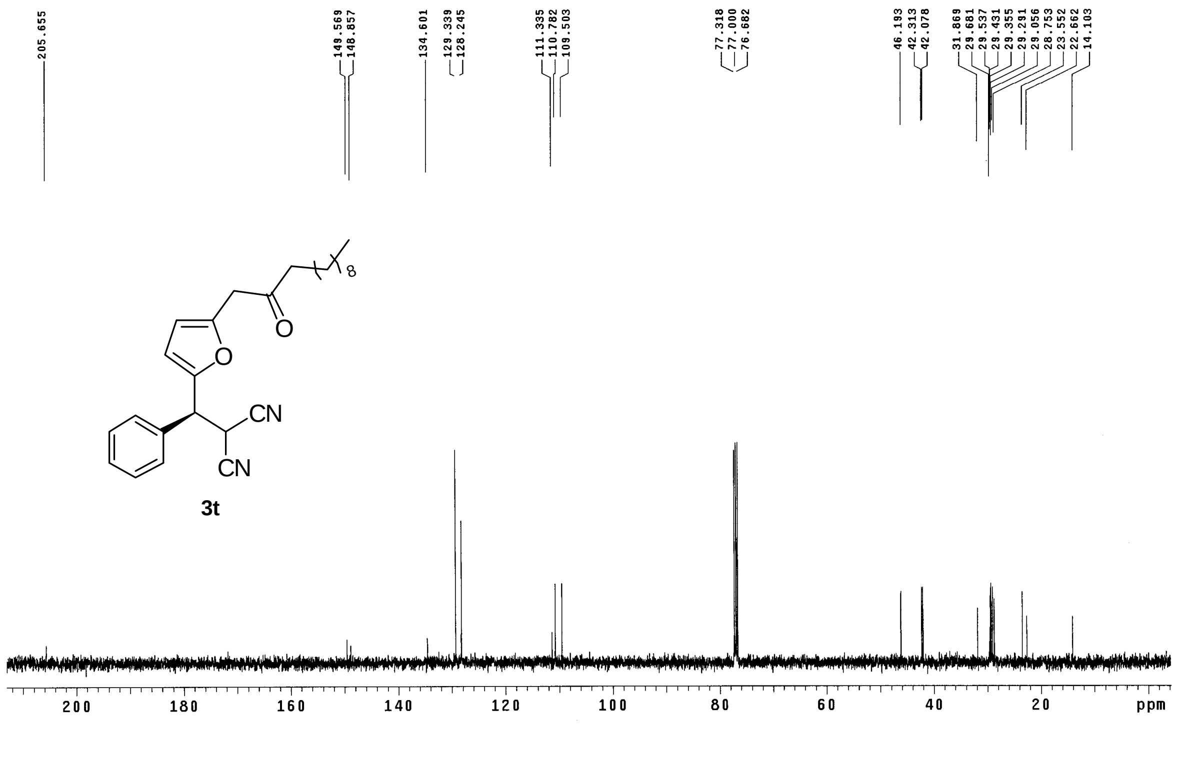


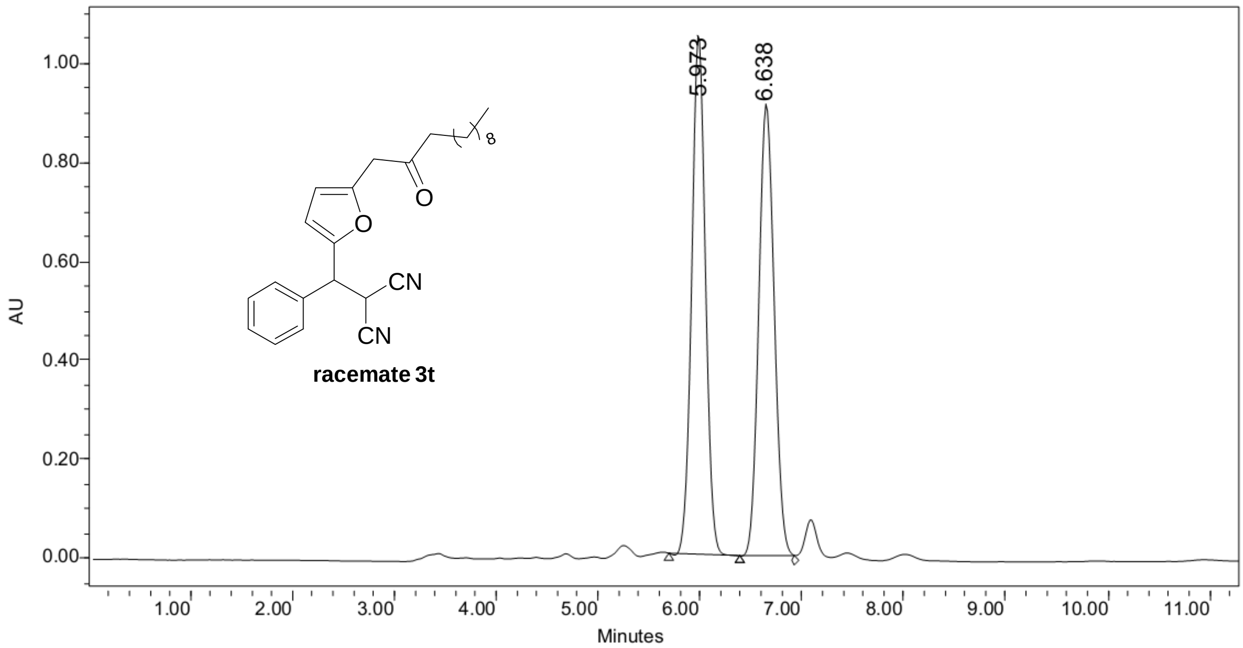
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	16.078	39230660	49.76	826874	52.46
2	19.412	39609225	50.24	749187	47.54



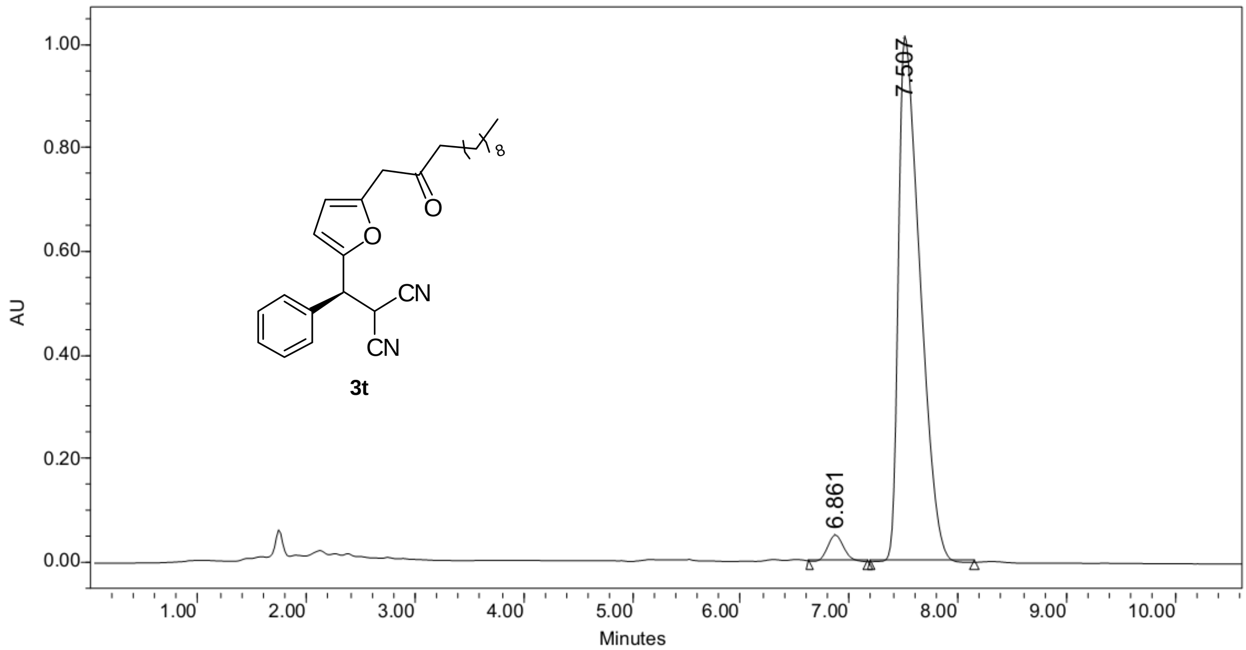
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	15.800	2750312	3.14	60872	3.61
2	18.818	84835774	96.86	1623642	96.39


7.423
7.261
6.300
6.292
6.210
6.202
4.610
4.591
4.429
4.411
3.709
2.459
2.440
2.422
1.568
1.552
1.295
1.244
0.895
0.879
0.861
-0.001
CN
CN
O
O
8
3t
10 9 8 7 6 5 4 3 2 1 ppm
3.88
0.69
0.70
0.76
0.89
2.00
2.00
1.97
14.93
3.01

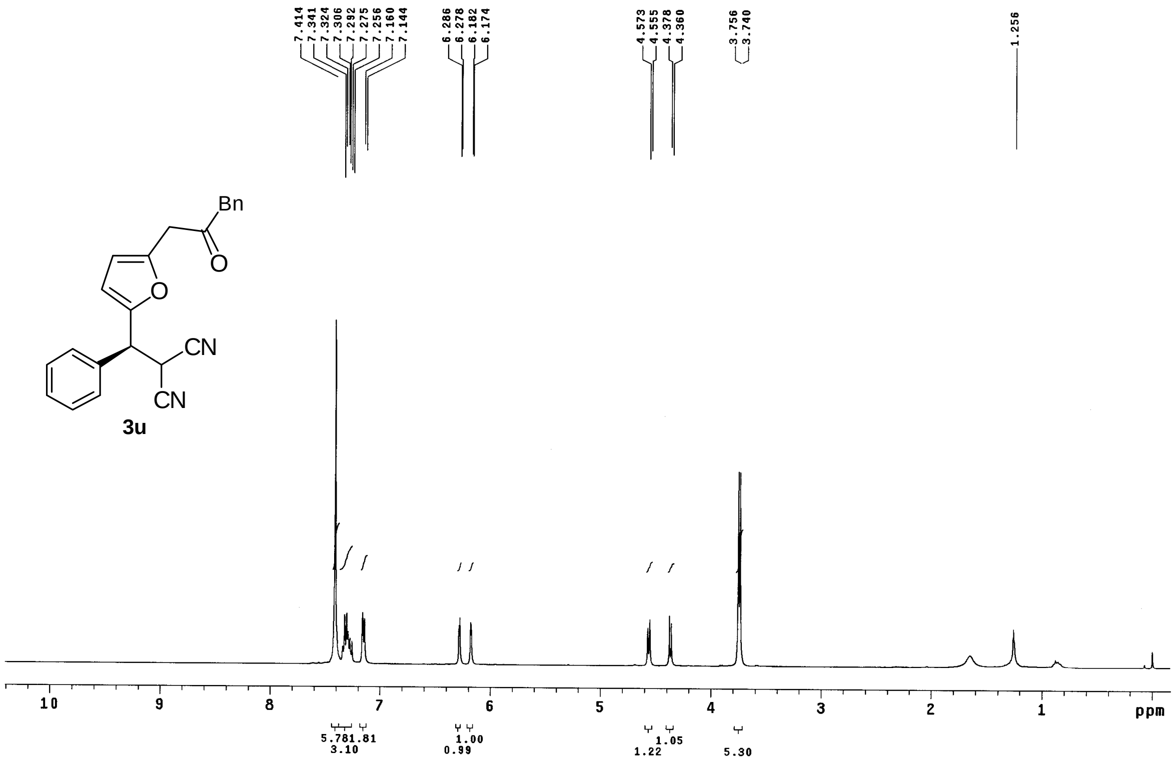

205.655
149.569
148.857
134.601
129.339
128.245
111.335
110.782
109.503
77.318
77.000
76.682
46.193
42.313
42.078
31.869
29.681
29.537
29.431
29.355
29.291
29.056
28.753
23.552
22.662
14.103
CN
CN
O
O
8
3t
200 180 160 140 120 100 80 60 40 20 ppm

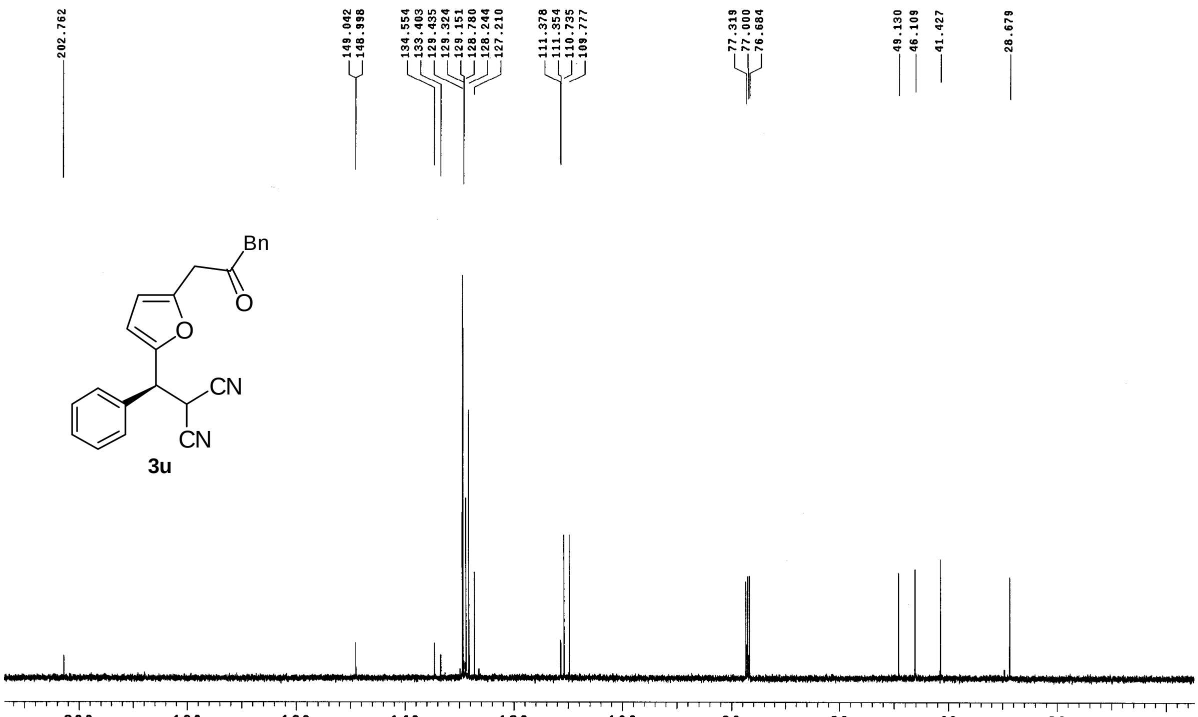


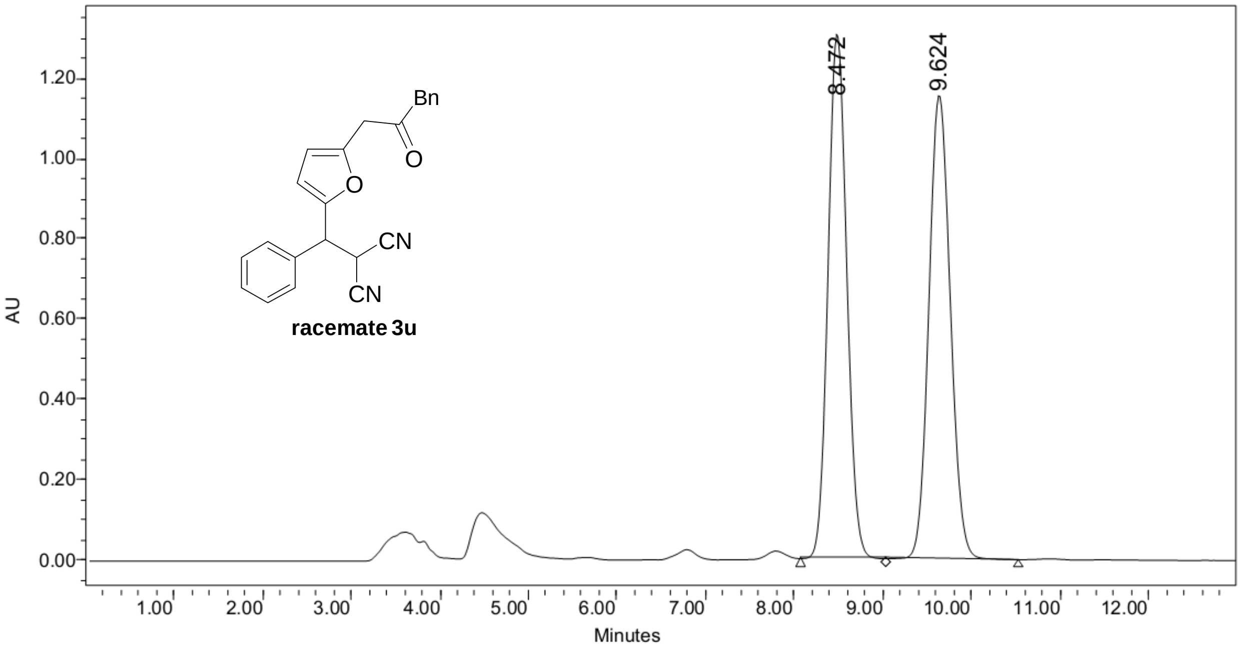
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	5.973	9926955	50.45	1053126	53.52
2	6.638	9751779	49.55	914765	46.48



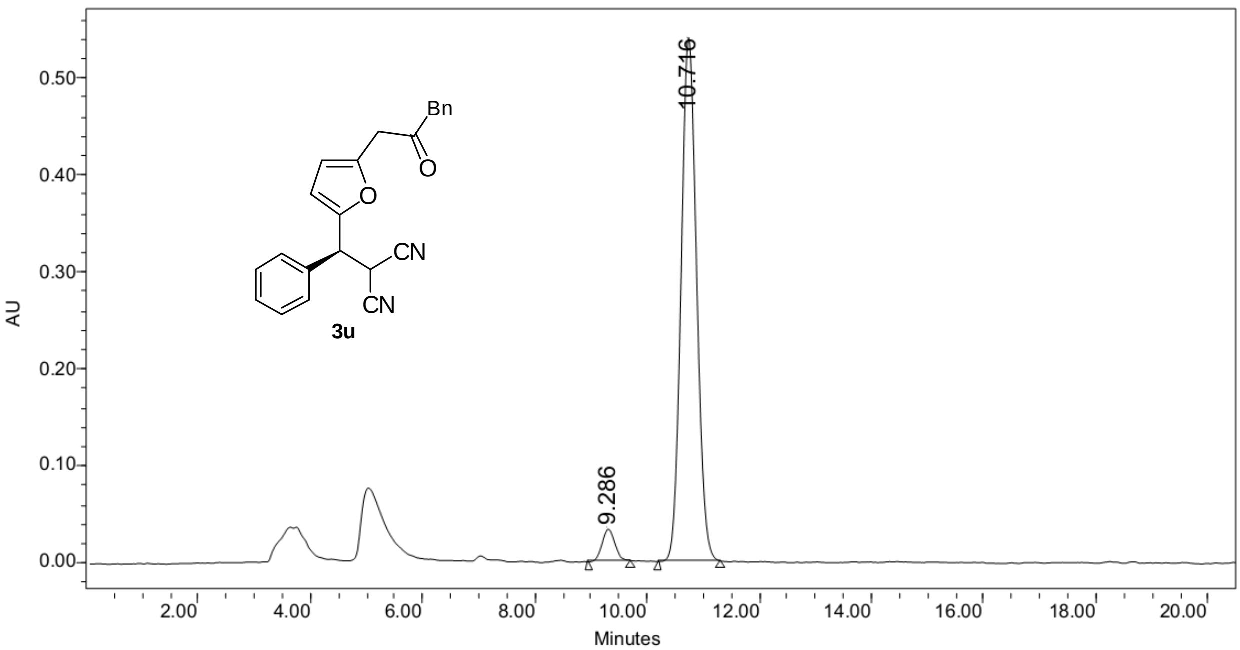
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	6.861	524749	3.60	50813	4.74
2	7.507	14036547	96.40	1021056	95.26


7.414
7.341
7.324
7.306
7.292
7.275
7.256
7.160
7.144
6.286
6.278
6.182
6.174
4.573
4.555
4.378
4.360
3.756
3.740
1.256
Bn
O
O
CN
CN
3u
10 9 8 7 6 5 4 3 2 1 ppm
5.78 1.81
3.10
1.00
0.99
1.22
1.05
5.30

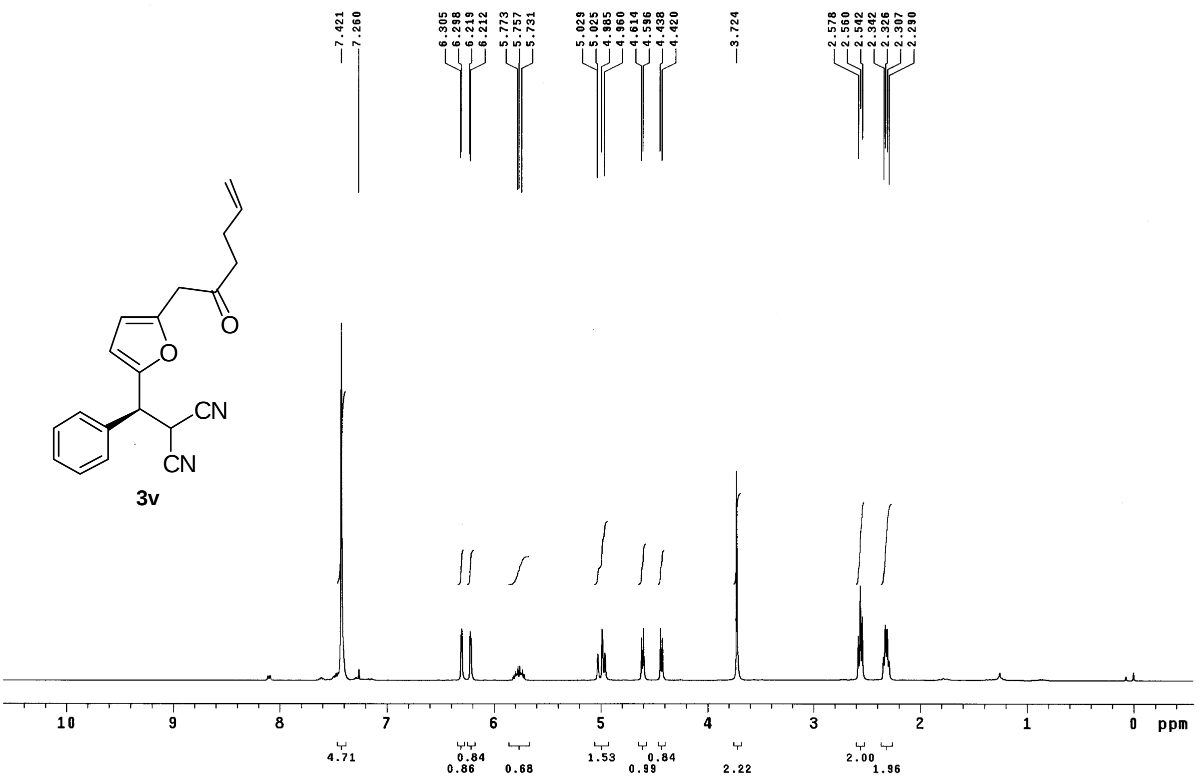

202.762
149.042
148.998
134.554
133.403
129.435
129.324
129.151
128.780
128.244
127.210
111.378
111.354
110.735
109.777
77.319
77.000
76.684
49.130
46.109
41.427
28.679
Bn
O
O
CN
CN
3u
200 180 160 140 120 100 80 60 40 20 ppm



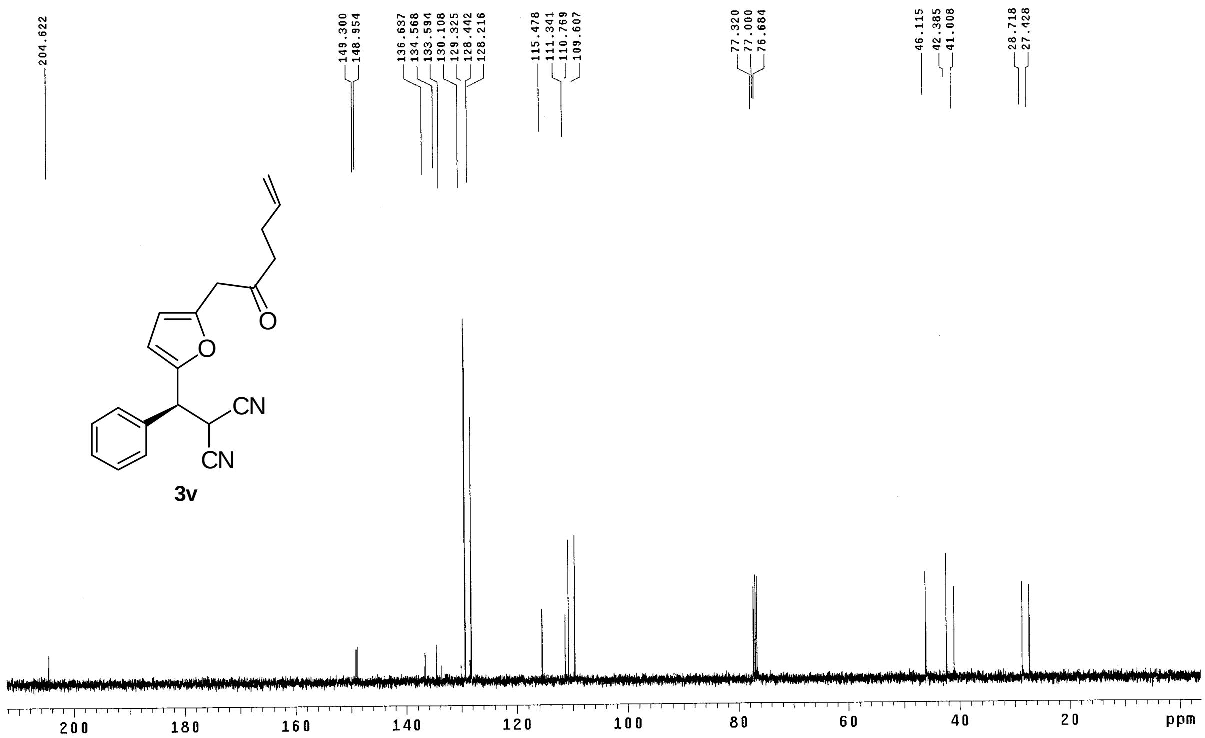
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	8.472	19244113	49.65	1308505	53.07
2	9.624	19514263	50.35	1157287	46.93



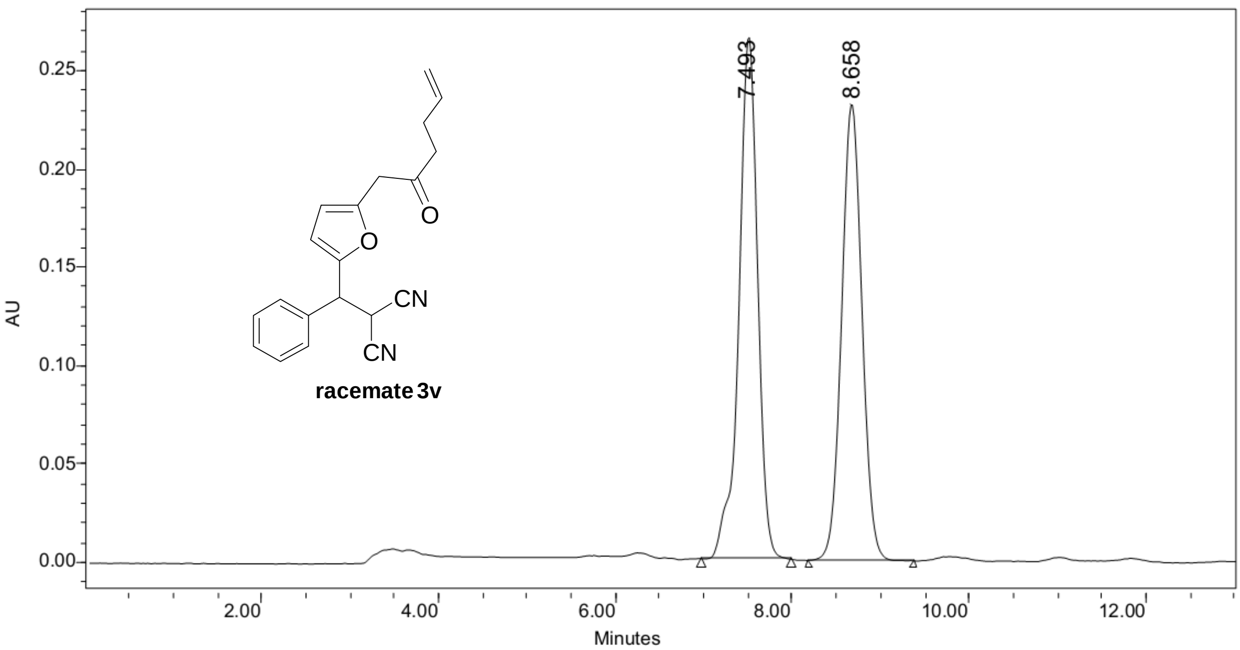
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	9.286	531105	4.88	33073	5.77
2	10.716	10345537	95.12	540106	94.23



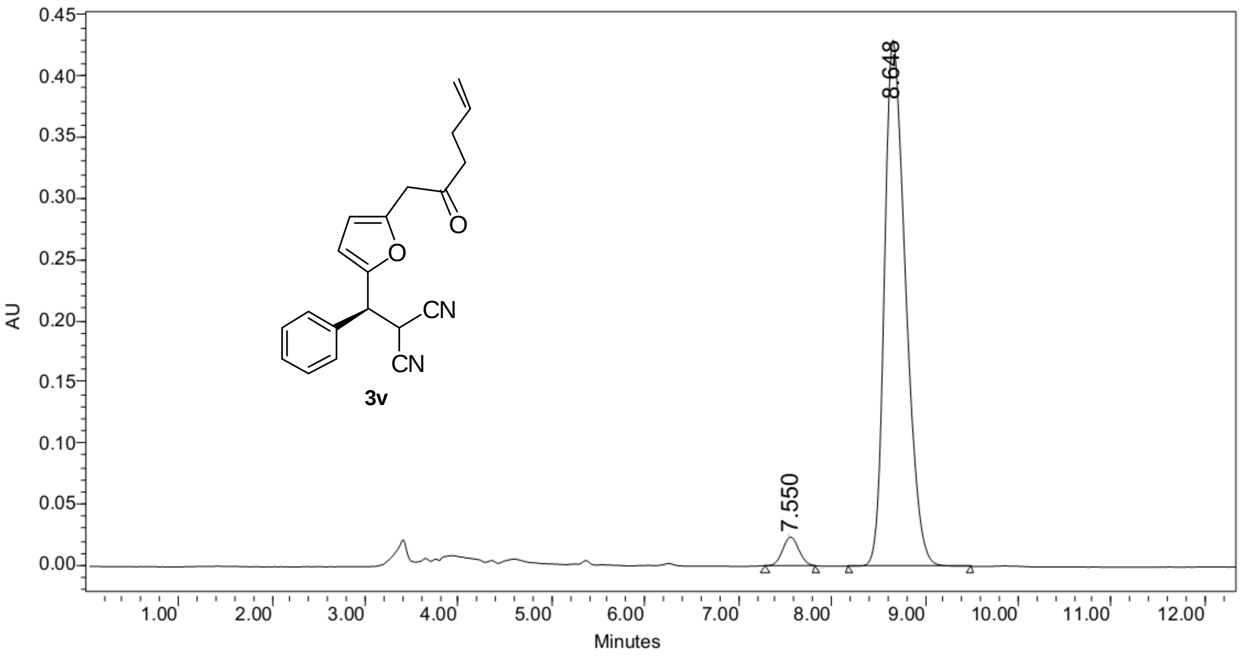
7.421
7.260
6.305
6.298
6.219
6.212
5.773
5.757
5.731
5.029
5.025
4.985
4.960
4.614
4.596
4.438
4.420
3.724
2.578
2.560
2.542
2.342
2.326
2.307
2.290
CN
CN
O
O
3v
ppm
4.71
0.84
0.86
0.68
1.53
0.84
0.99
2.22
2.00
1.96



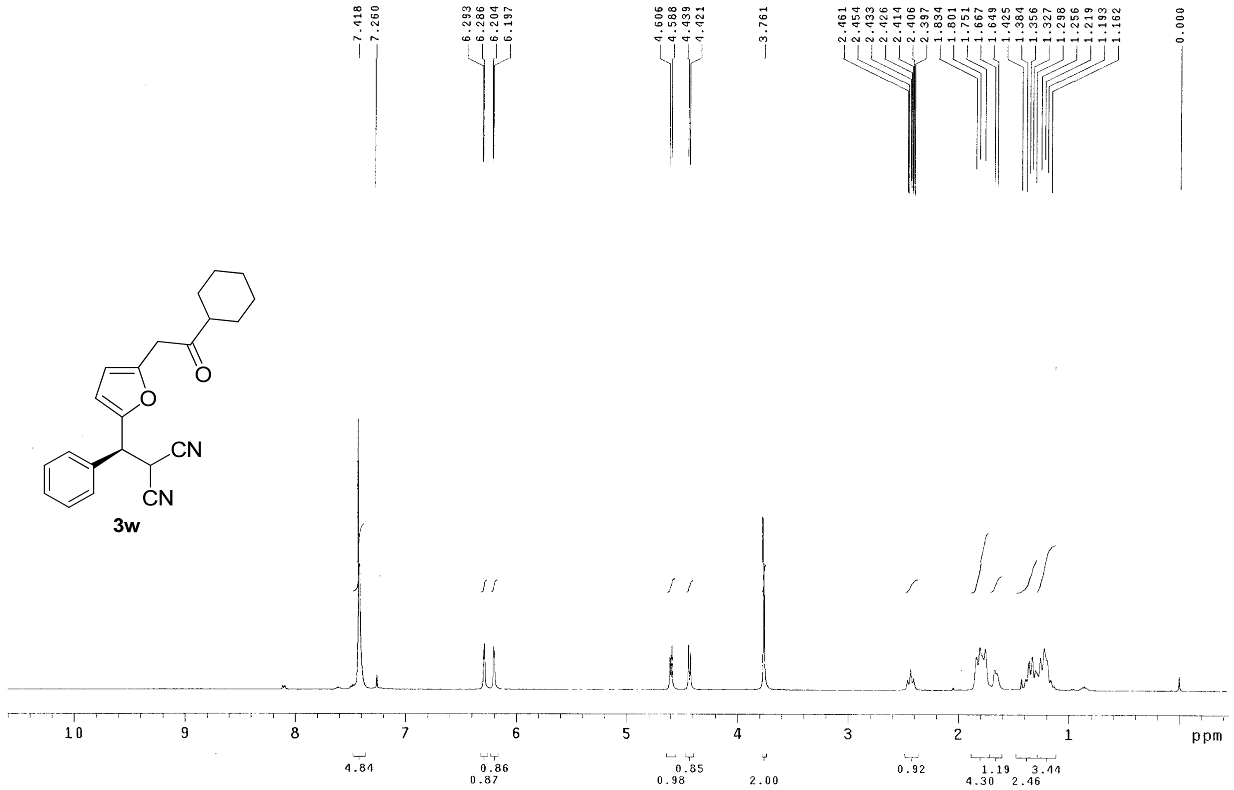
204.622
149.300
148.954
136.637
134.568
133.594
130.108
129.325
128.442
128.216
115.478
111.341
110.769
109.607
77.320
77.000
76.684
46.115
42.385
41.008
28.718
27.428
CN
CN
O
O
3v
ppm



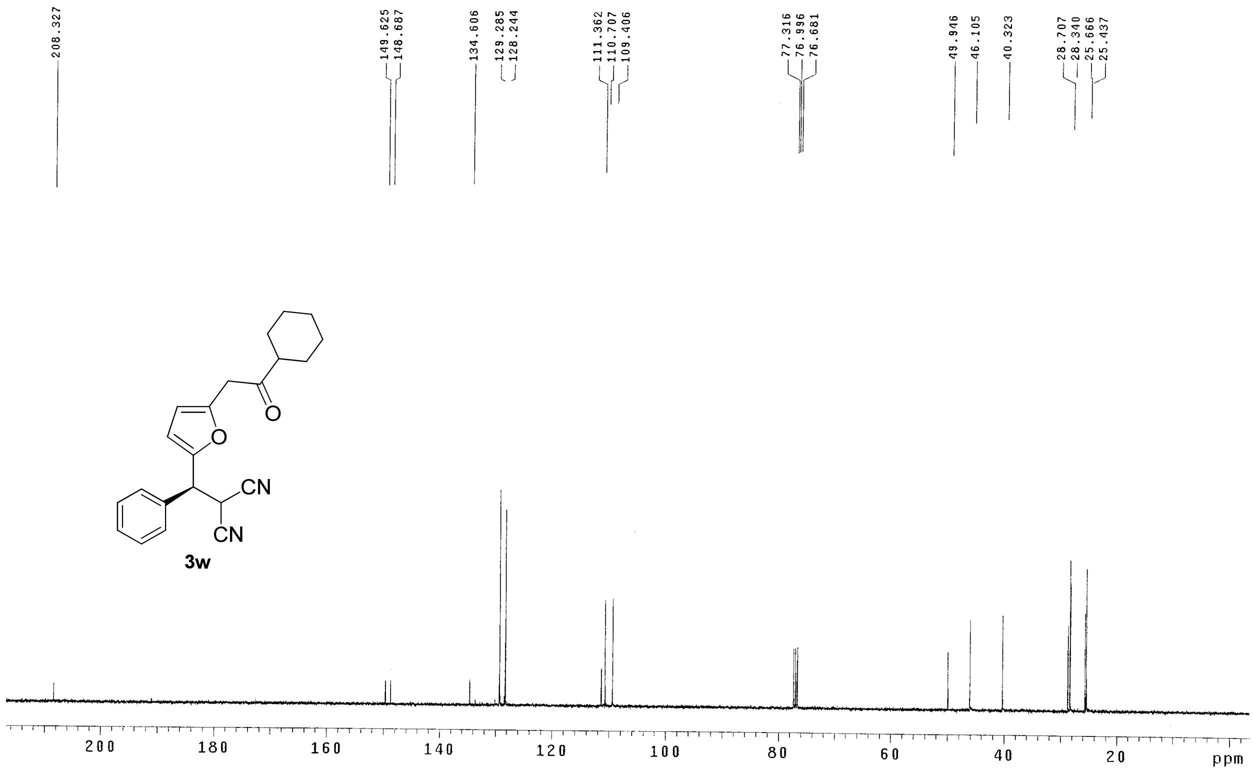
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	7.493	3932633	51.41	265695	53.35
2	8.658	3717658	48.59	232370	46.65



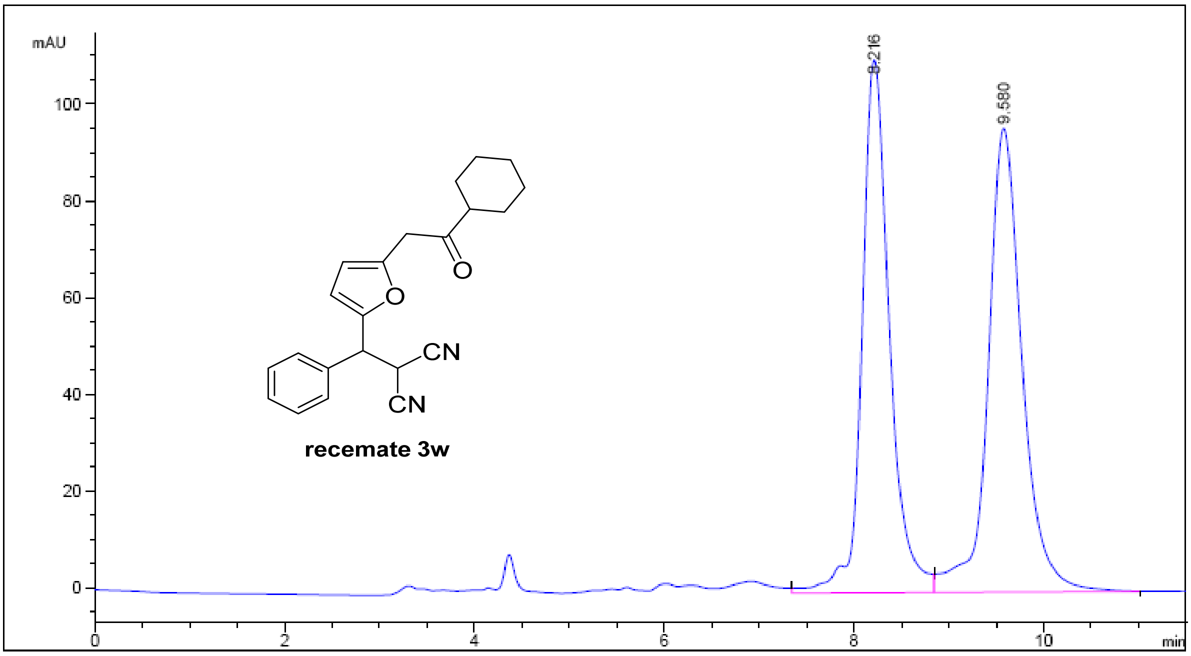
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	7.550	284314	4.03	23496	5.18
2	8.648	6772867	95.97	429890	94.82



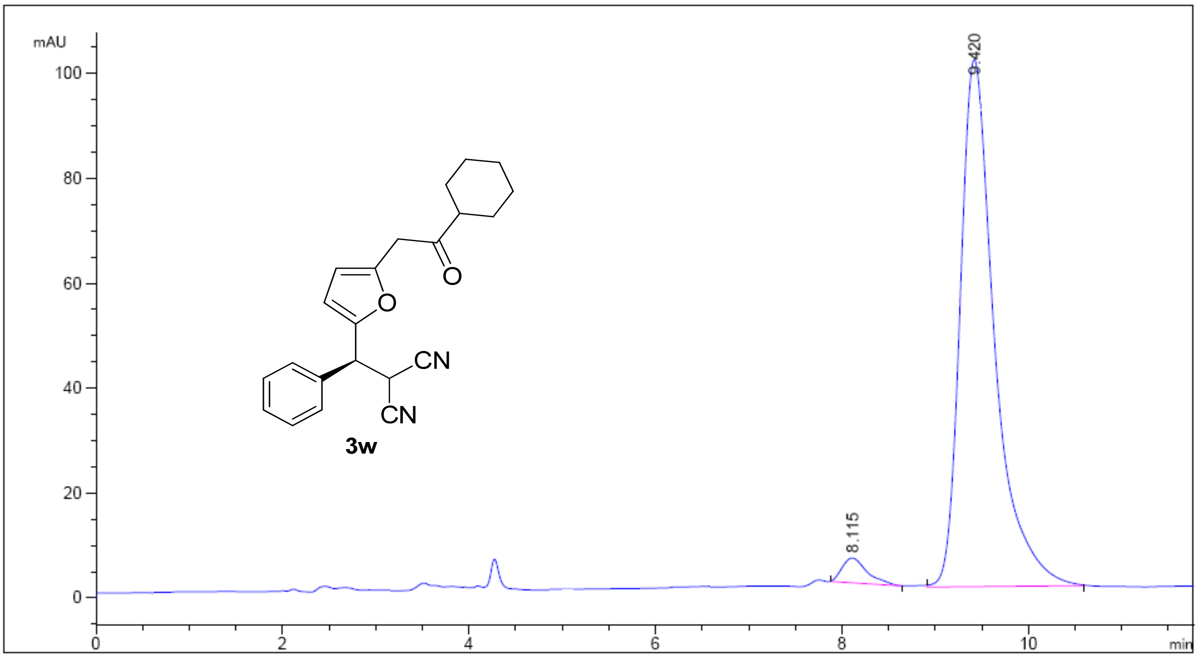
7.418
7.260
6.293
6.286
6.204
6.197
4.606
4.588
4.439
4.421
3.761
2.461
2.454
2.433
2.426
2.414
2.406
2.397
1.834
1.801
1.751
1.667
1.649
1.425
1.384
1.356
1.327
1.298
1.256
1.219
1.193
1.162
0.000
O
O
CN
CN
3w
ppm
4.84
0.86
0.87
0.85
0.98
2.00
0.92
1.19
4.30
3.44
2.46



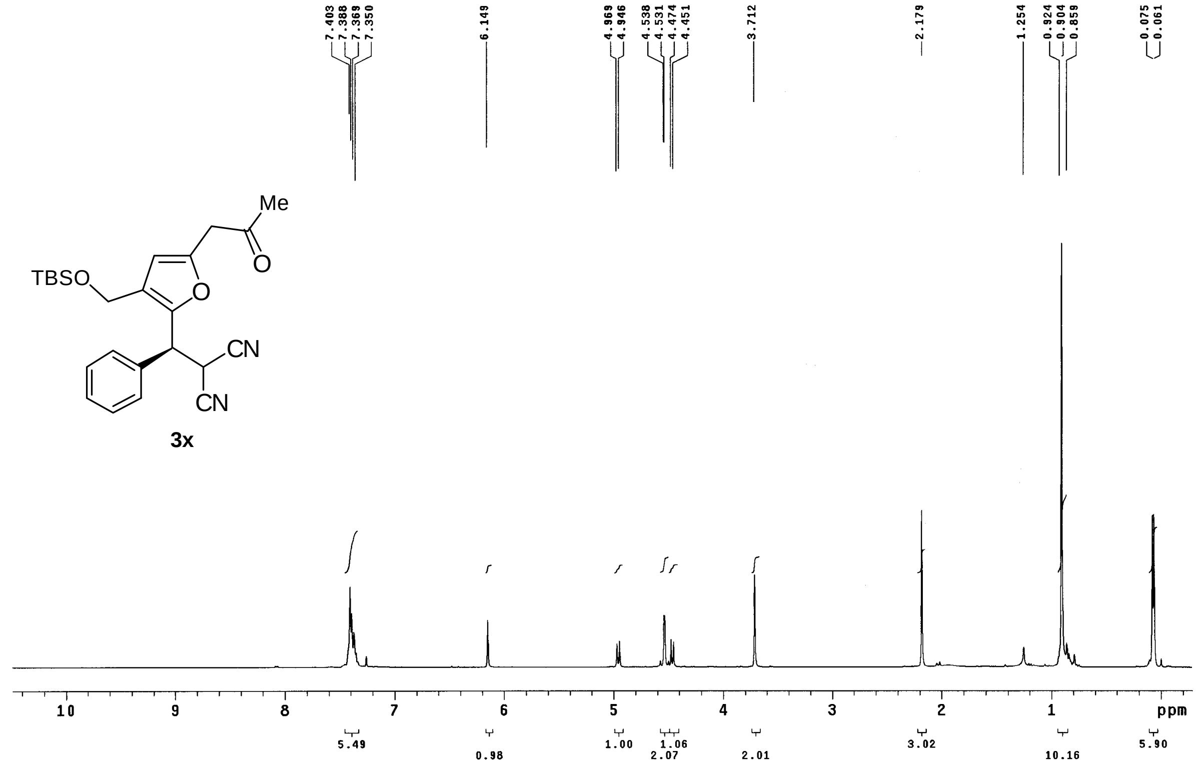
208.327
149.625
148.687
134.606
129.285
128.244
111.362
110.707
109.406
77.316
76.996
76.681
49.946
46.105
40.323
28.707
28.340
25.666
25.437
O
O
CN
CN
3w
ppm



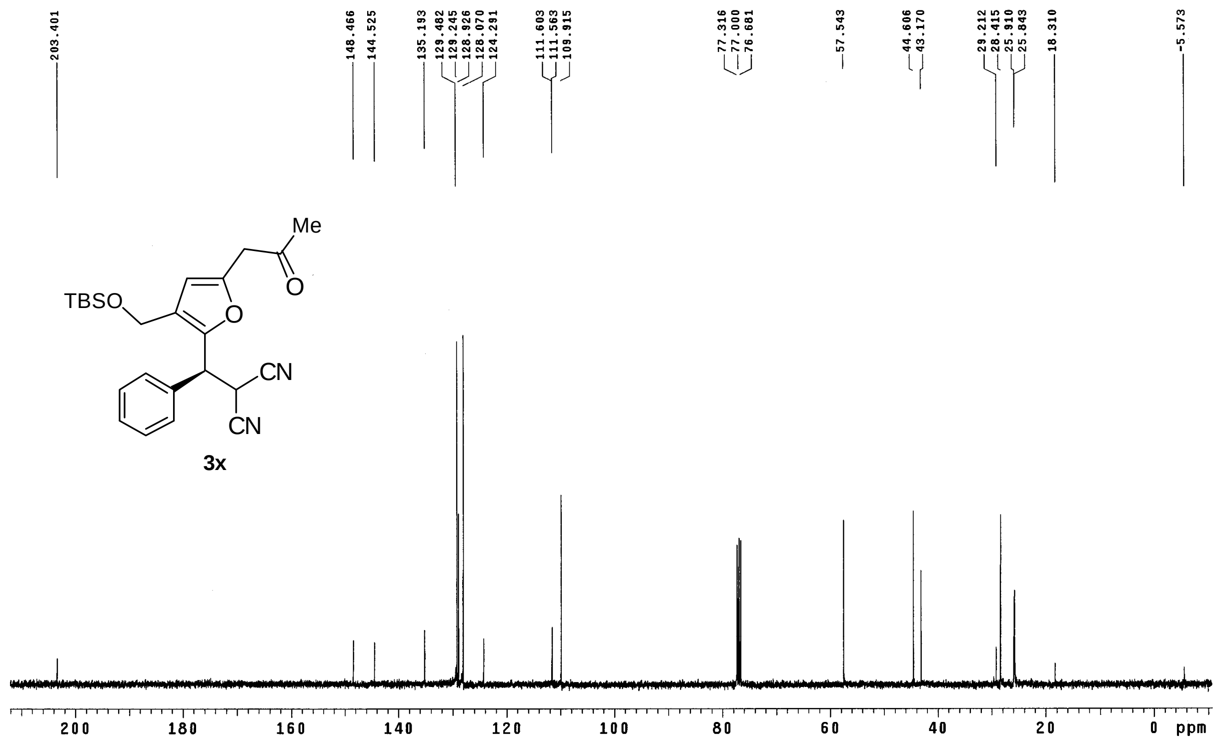
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.216	VV	0.3058	2224.13037	109.97224	48.0011
2	9.580	VB	0.3809	2409.37012	95.77406	51.9989



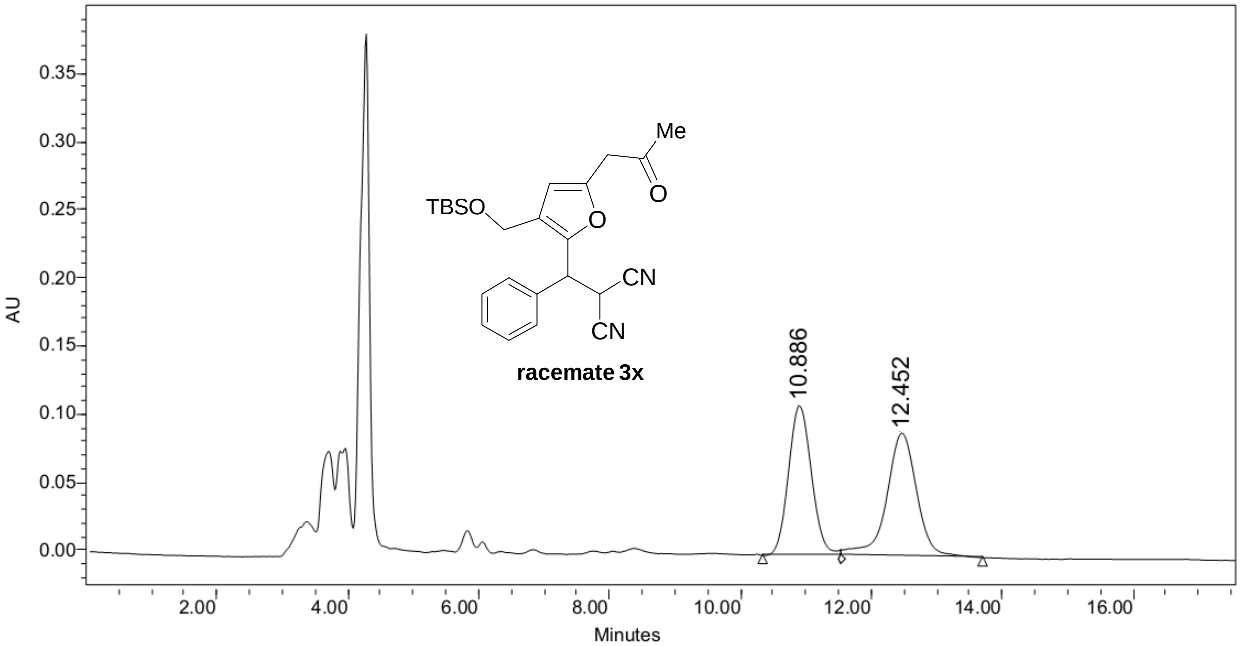
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.115	MM	0.3121	88.36767	4.71838	3.3262
2	9.420	MM	0.4257	2568.34497	100.56468	96.6738


TBSO
Me
O
O
CN
CN
7.403
7.388
7.369
7.350
6.149
4.969
4.946
4.538
4.531
4.474
4.451
3.712
2.179
1.254
0.924
0.904
0.859
0.075
0.061
ppm
5.49
0.98
1.00
2.07
1.06
2.01
3.02
10.16
5.90

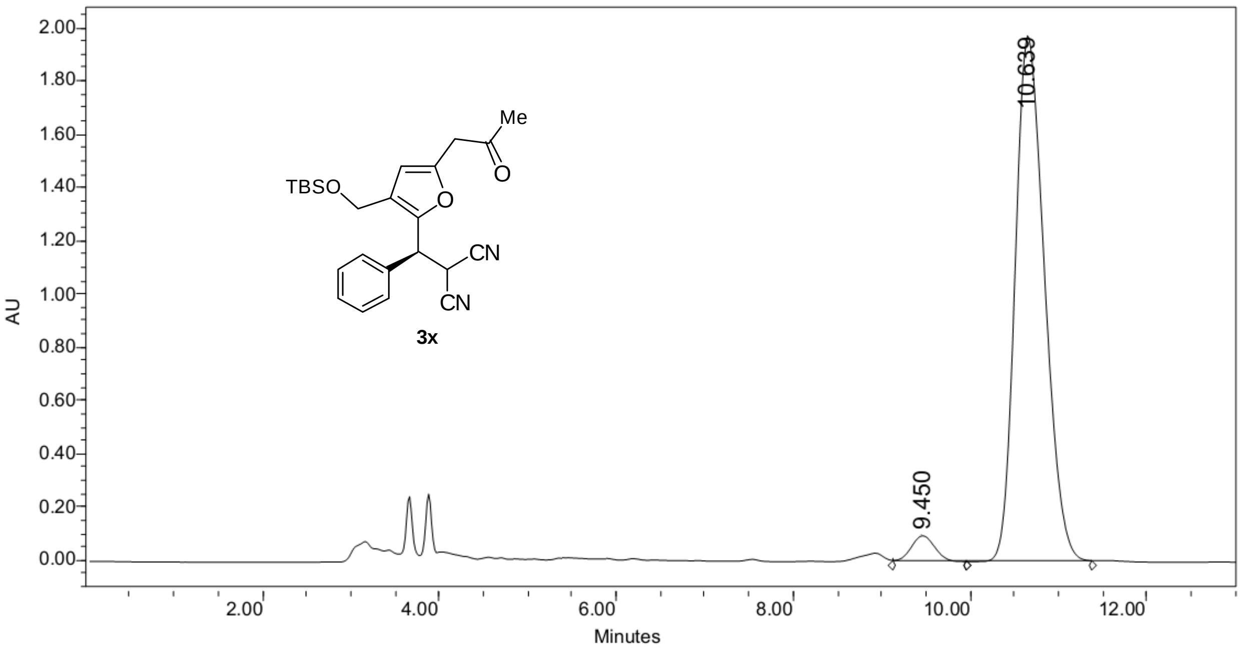
3x


TBSO
Me
O
O
CN
CN
203.401
148.466
144.525
135.193
129.482
129.245
128.926
128.070
124.291
111.603
111.563
109.915
77.316
77.000
76.681
57.543
44.606
43.170
29.212
28.415
25.910
25.843
18.310
-5.573
ppm

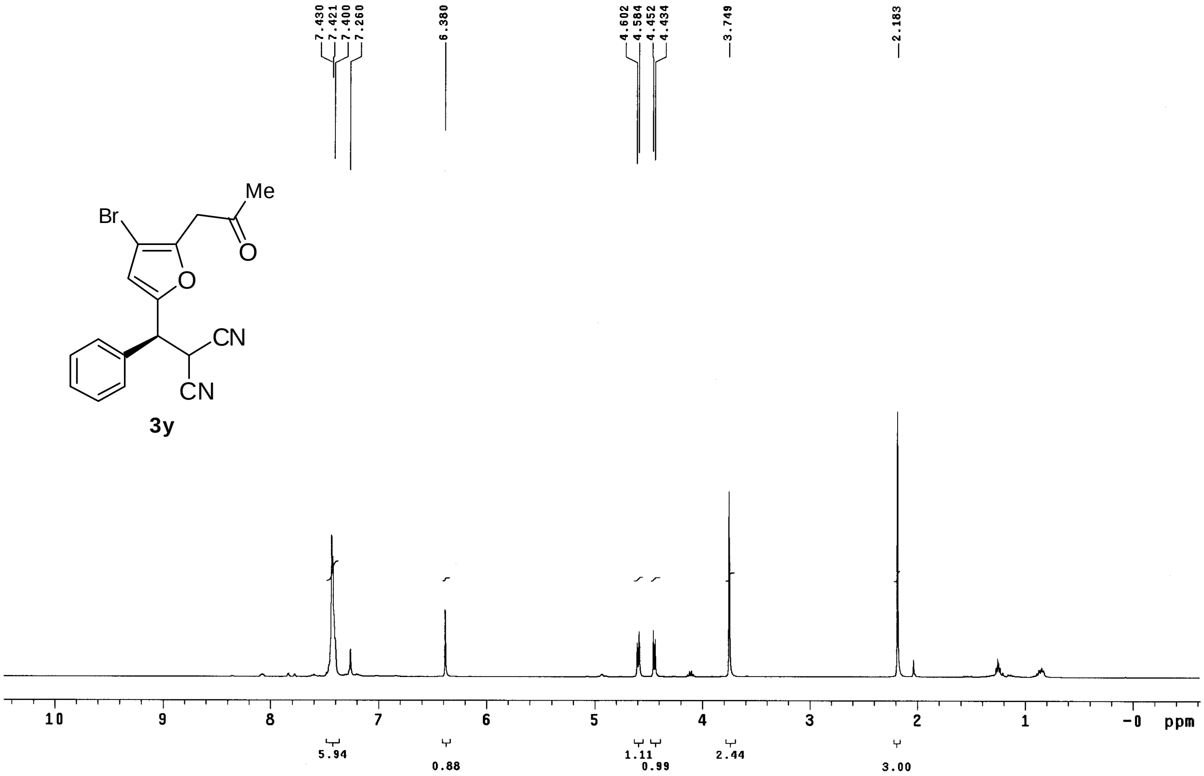
3x

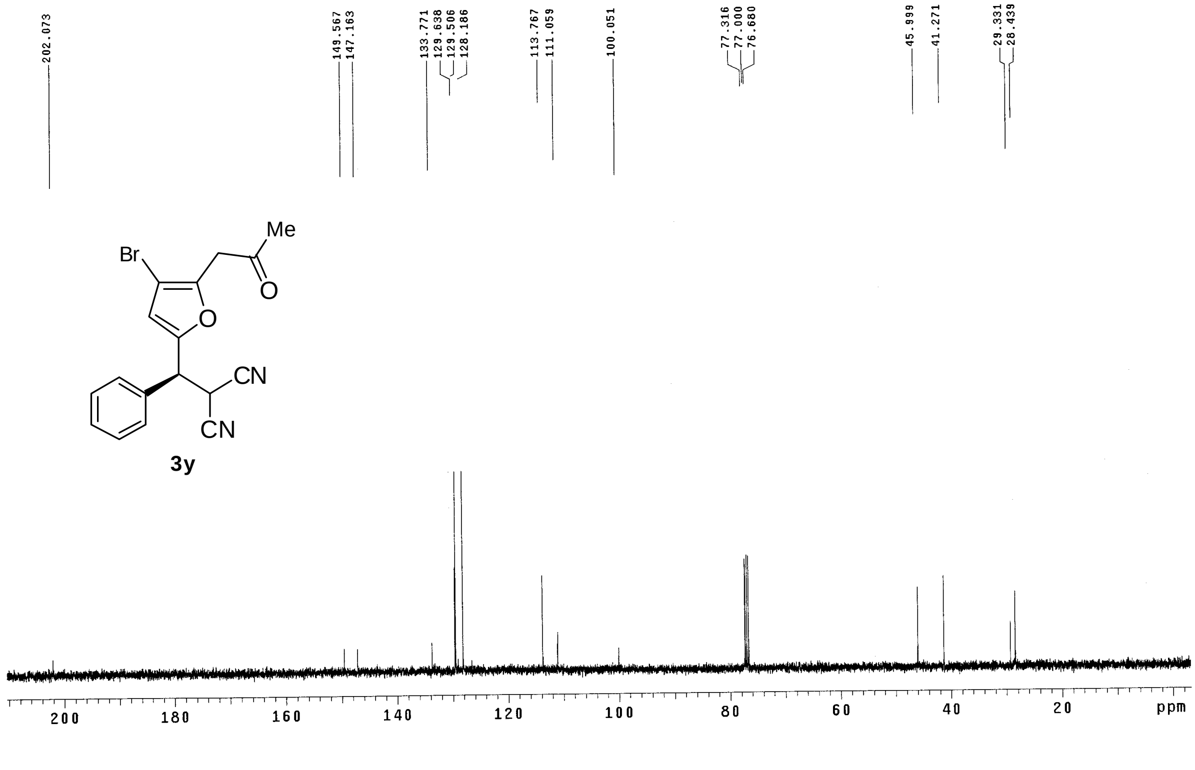


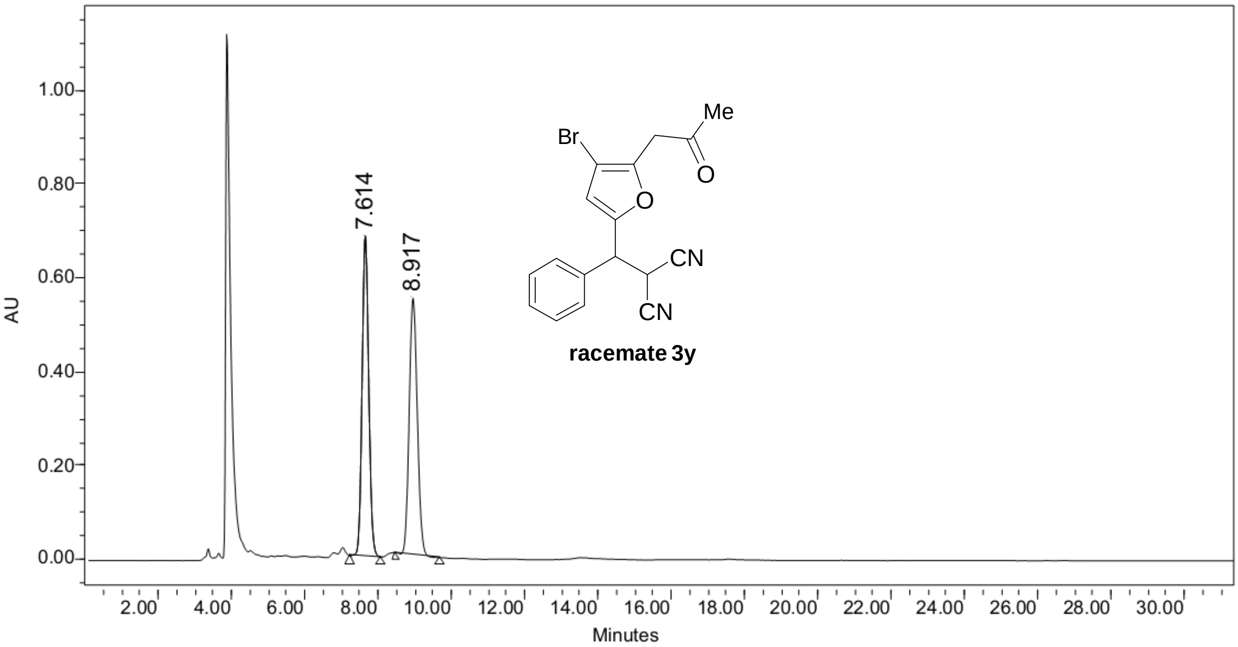
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	10.886	2721161	48.03	109909	54.78
2	12.452	2943878	51.97	90745	45.22



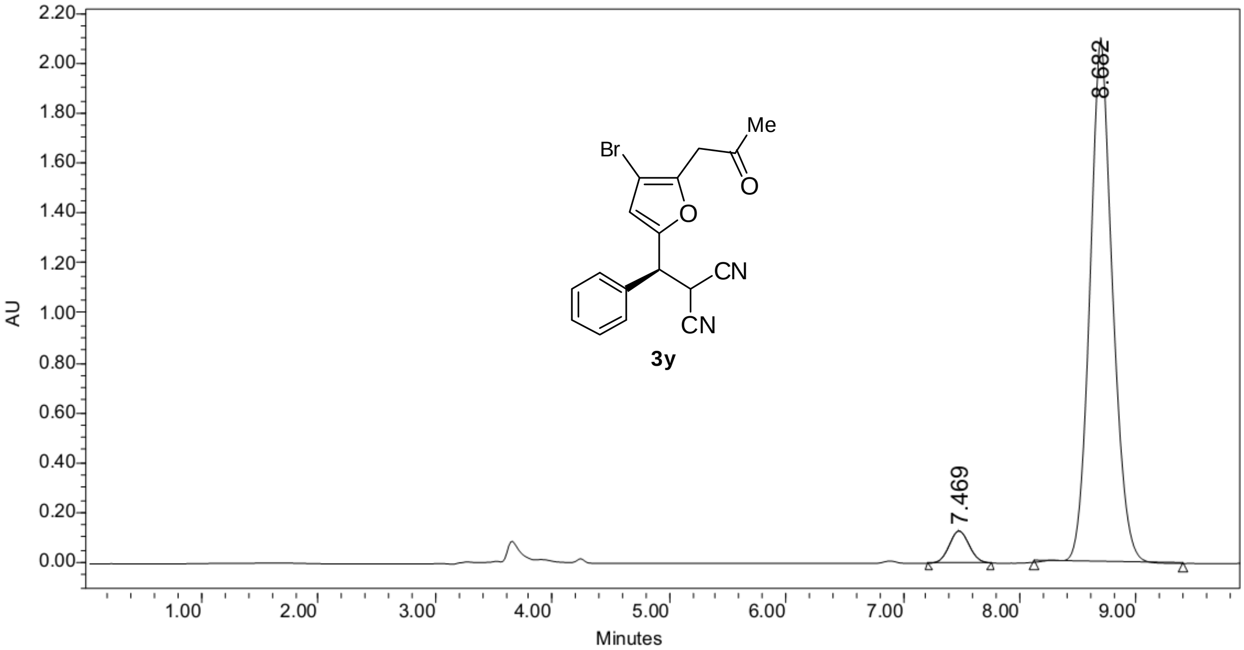
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	9.450	1659566	3.53	93571	4.53
2	10.639	45381130	96.47	1974183	95.47


7.430
7.421
7.400
7.260
6.380
4.602
4.584
4.452
4.434
3.749
2.183
Br
Me
O
O
CN
CN
3y
10
9
8
7
6
5
4
3
2
1
-0
ppm
5.94
0.88
1.11
0.99
2.44
3.00

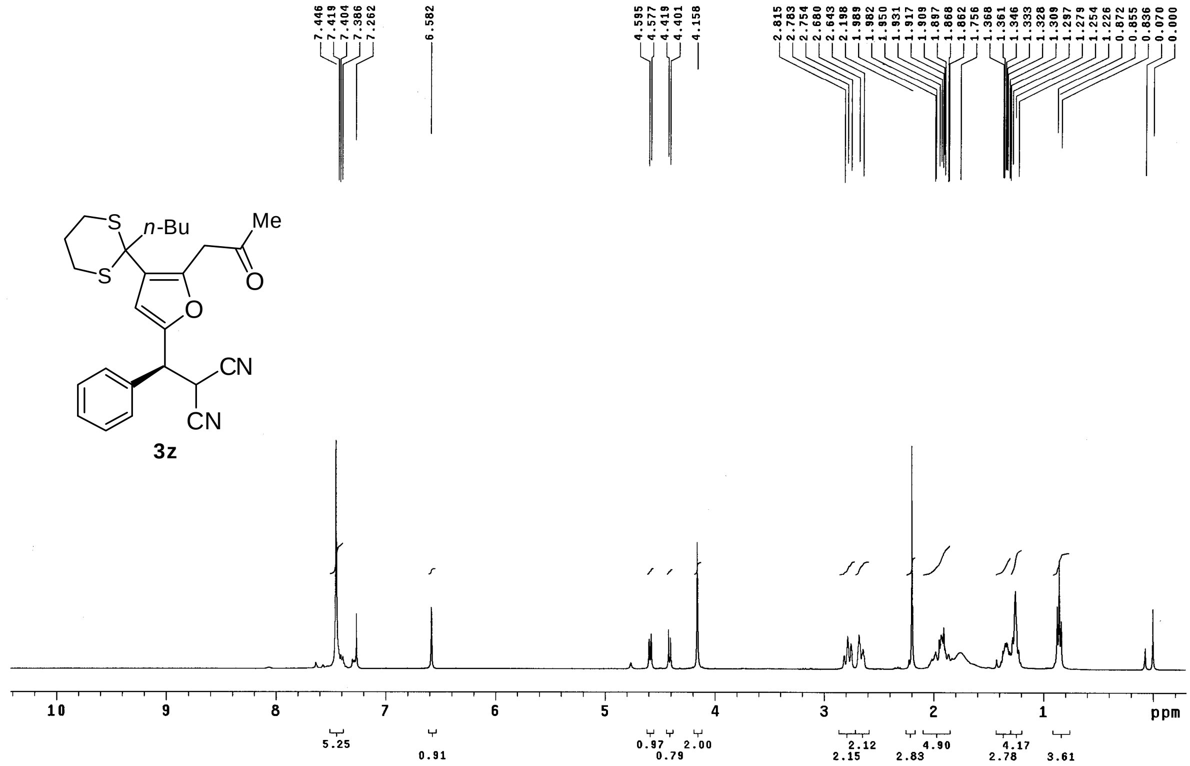

202.073
149.567
147.163
133.771
129.638
129.506
128.186
113.767
111.059
100.051
77.316
77.000
76.680
45.999
41.271
29.331
28.439
Br
Me
O
O
CN
CN
3y
200
180
160
140
120
100
80
60
40
20
ppm

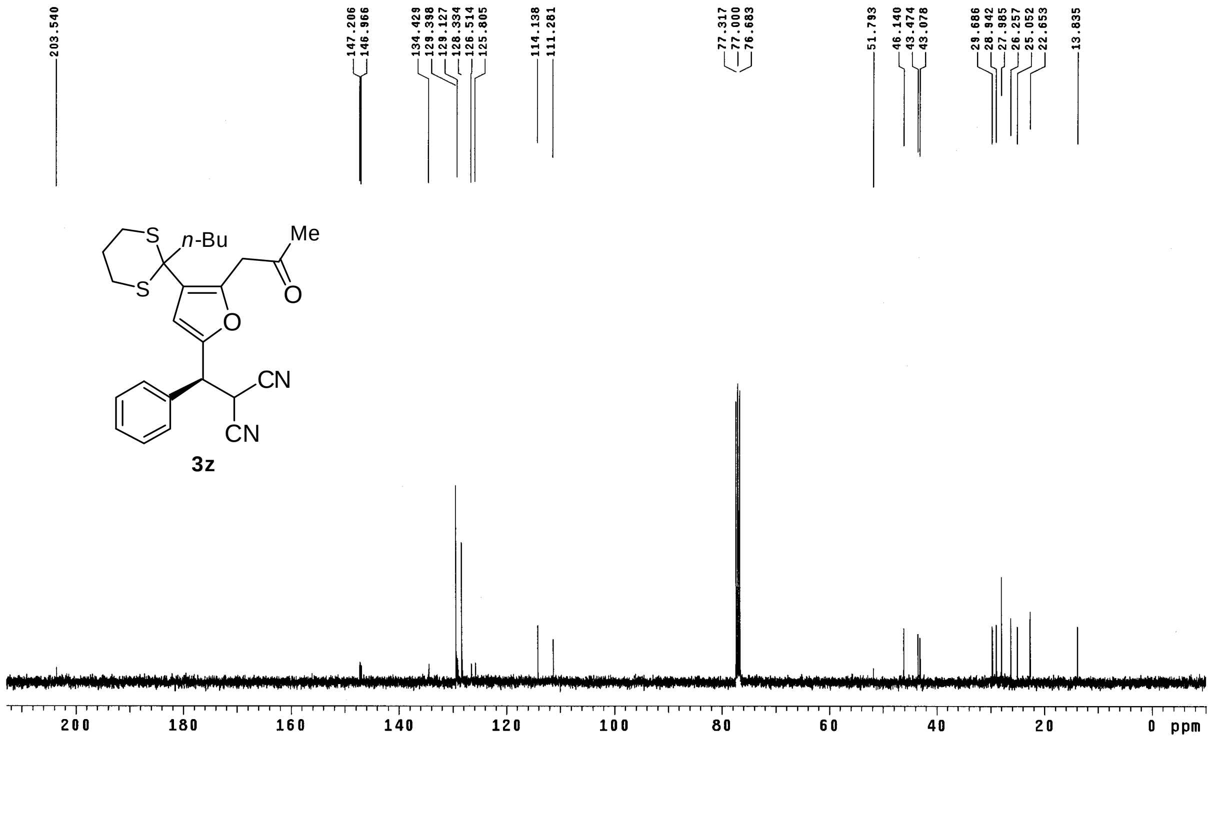


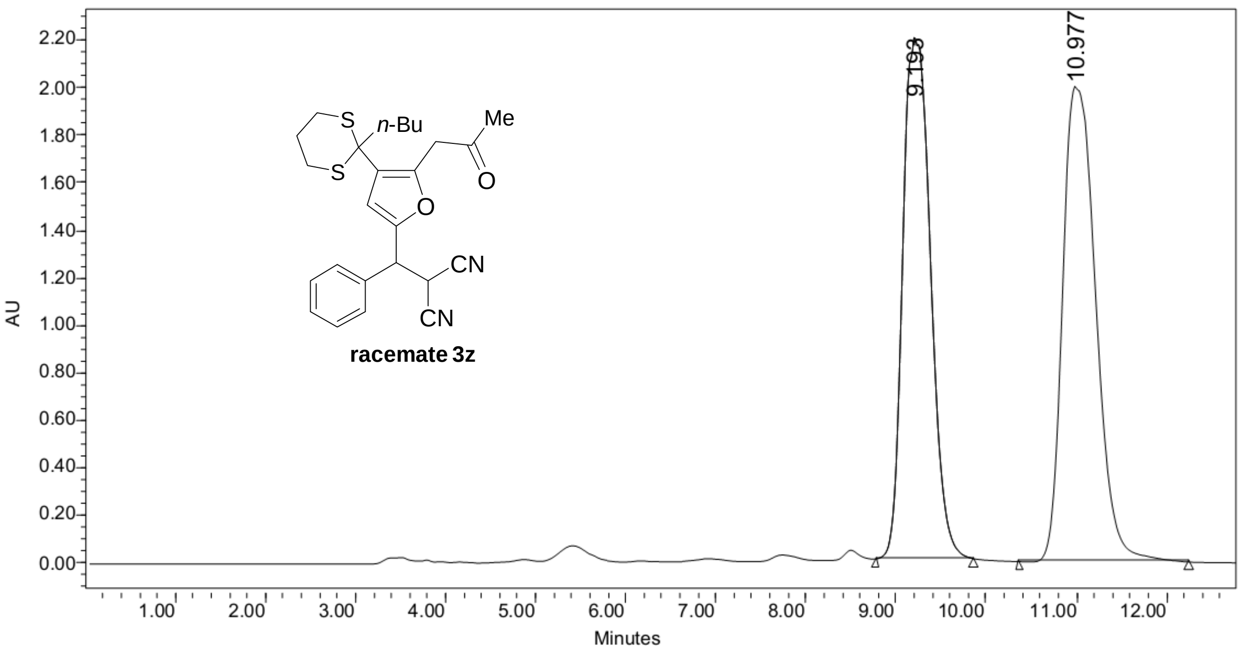
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	7.614	8585861	50.53	682739	55.56
2	8.917	8405217	49.47	546166	44.44



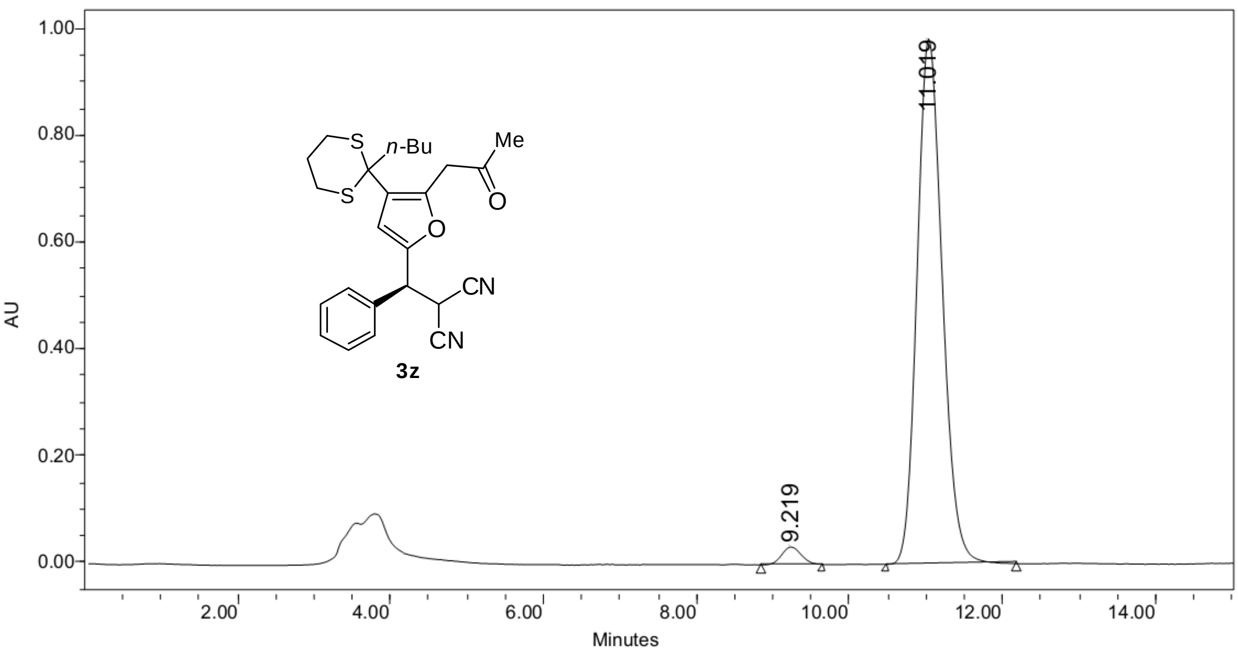
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	7.469	1523792	5.11	128615	5.78
2	8.682	28279611	94.89	2095019	94.22


7.446
7.419
7.404
7.386
7.262
6.582
4.595
4.577
4.419
4.401
4.158
2.815
2.783
2.754
2.680
2.643
2.198
1.989
1.982
1.950
1.931
1.917
1.909
1.897
1.868
1.862
1.756
1.368
1.361
1.346
1.333
1.328
1.309
1.297
1.279
1.254
1.226
0.872
0.855
0.836
0.070
0.000
n-Bu
Me
S
S
O
O
CN
CN
3z
10 9 8 7 6 5 4 3 2 1 ppm
5.25
0.91
0.97
0.79
2.00
2.12
2.15
2.83
4.90
4.17
2.78
3.61

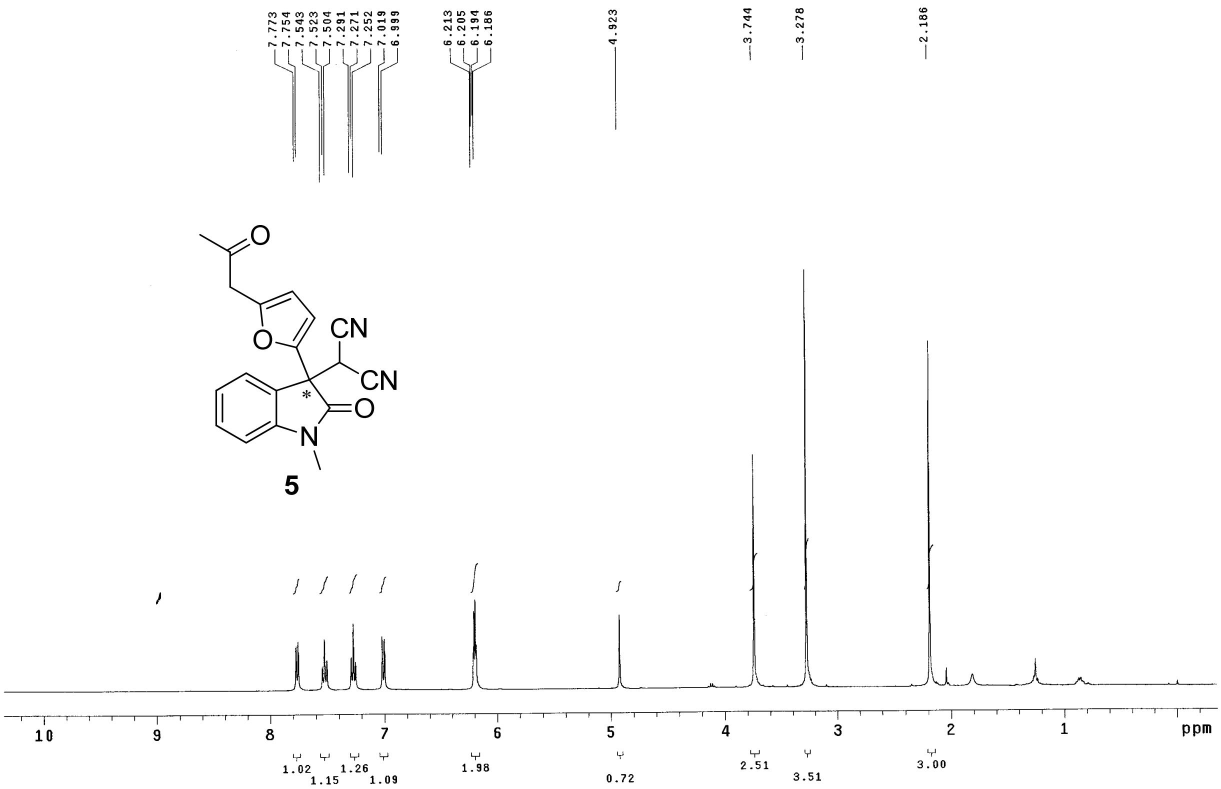

203.540
147.206
146.966
134.429
129.398
129.127
128.334
126.514
125.805
114.138
111.281
77.317
77.000
76.683
51.793
46.140
43.474
43.078
29.686
28.942
27.985
26.257
25.052
22.653
13.835
n-Bu
Me
S
S
O
O
CN
CN
3z
200 180 160 140 120 100 80 60 40 20 0 ppm

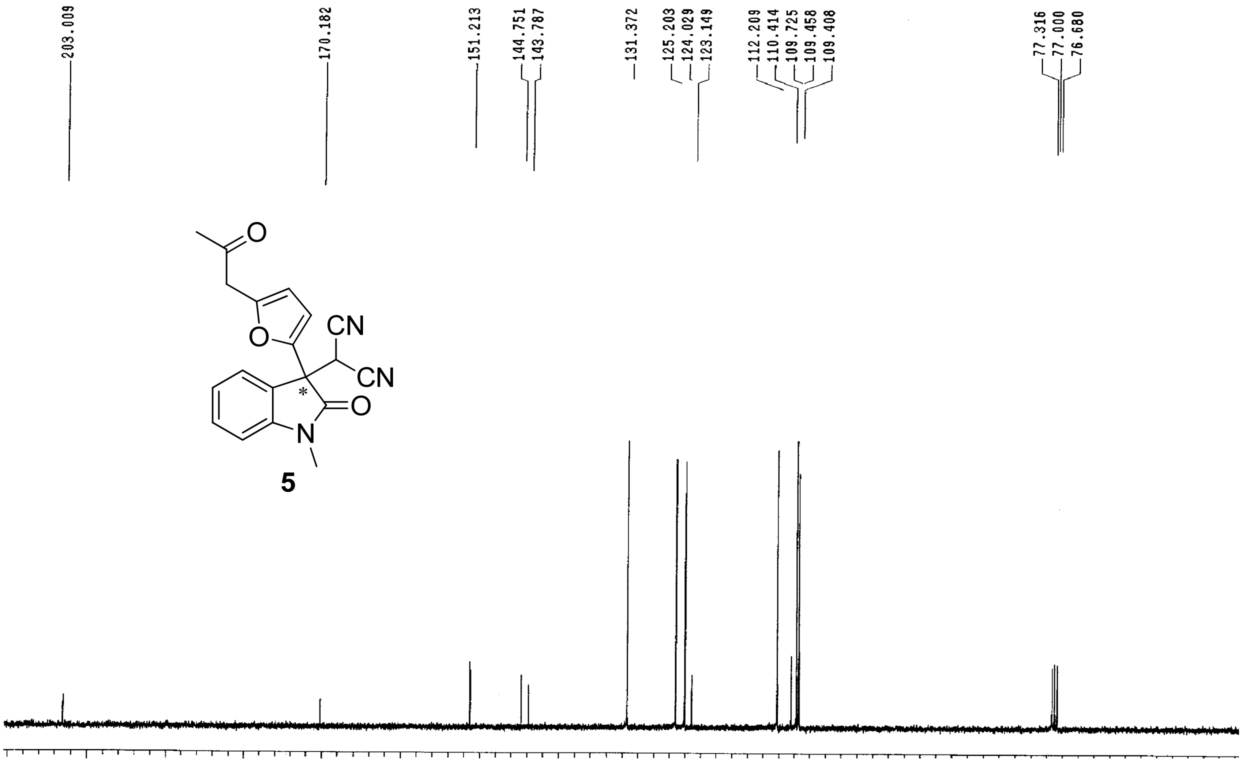


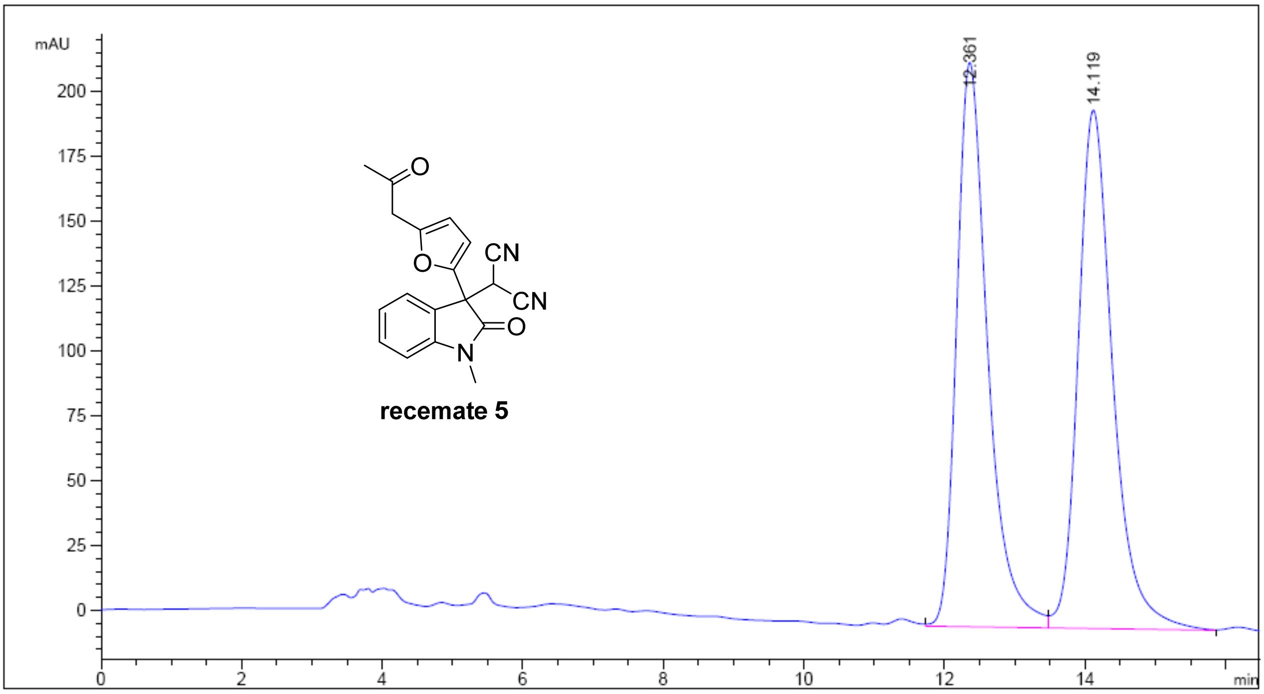
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	9.193	46918182	49.07	2186488	52.57
2	10.977	48704569	50.93	1972882	47.43



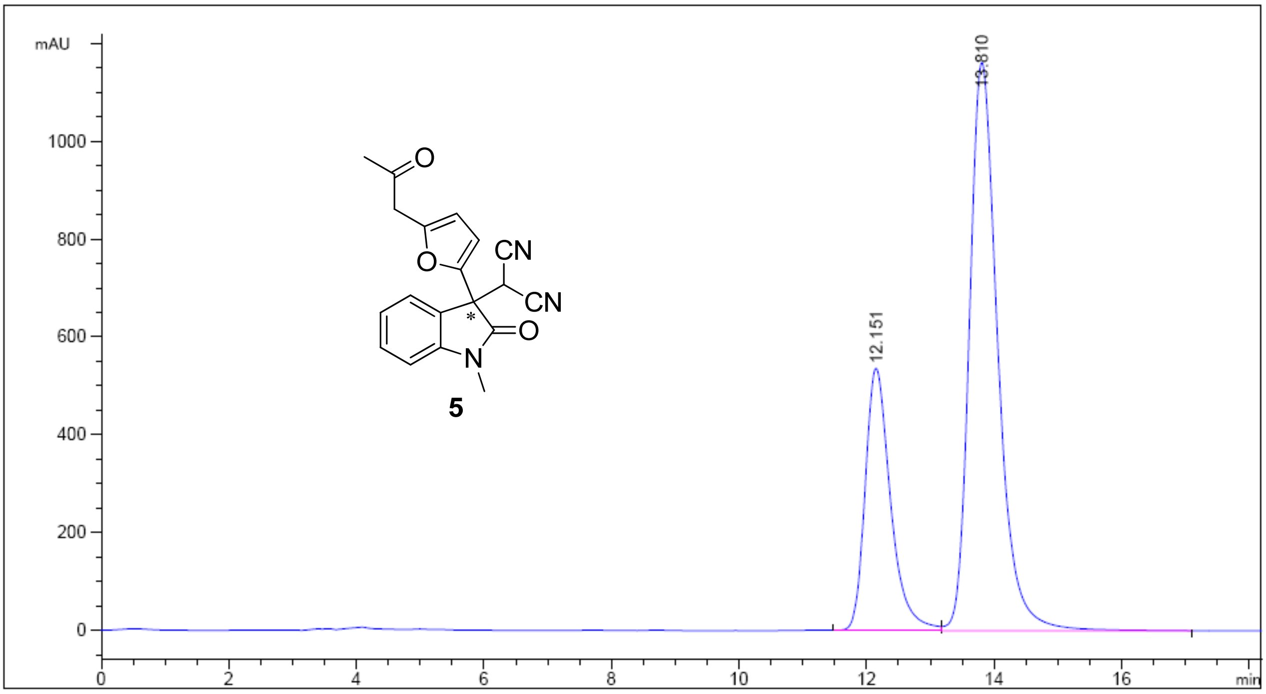
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	9.219	588993	2.55	33115	3.26
2	11.019	22501620	97.45	983364	96.74


7.773
7.754
7.543
7.523
7.504
7.291
7.271
7.252
7.019
6.999
6.213
6.205
6.194
6.186
4.923
3.744
3.278
2.186
O
CN
CN
O
N
O
*
5
10
9
8
7
6
5
4
3
2
1
ppm
1.02
1.15
1.26
1.09
1.98
0.72
2.51
3.51
3.00

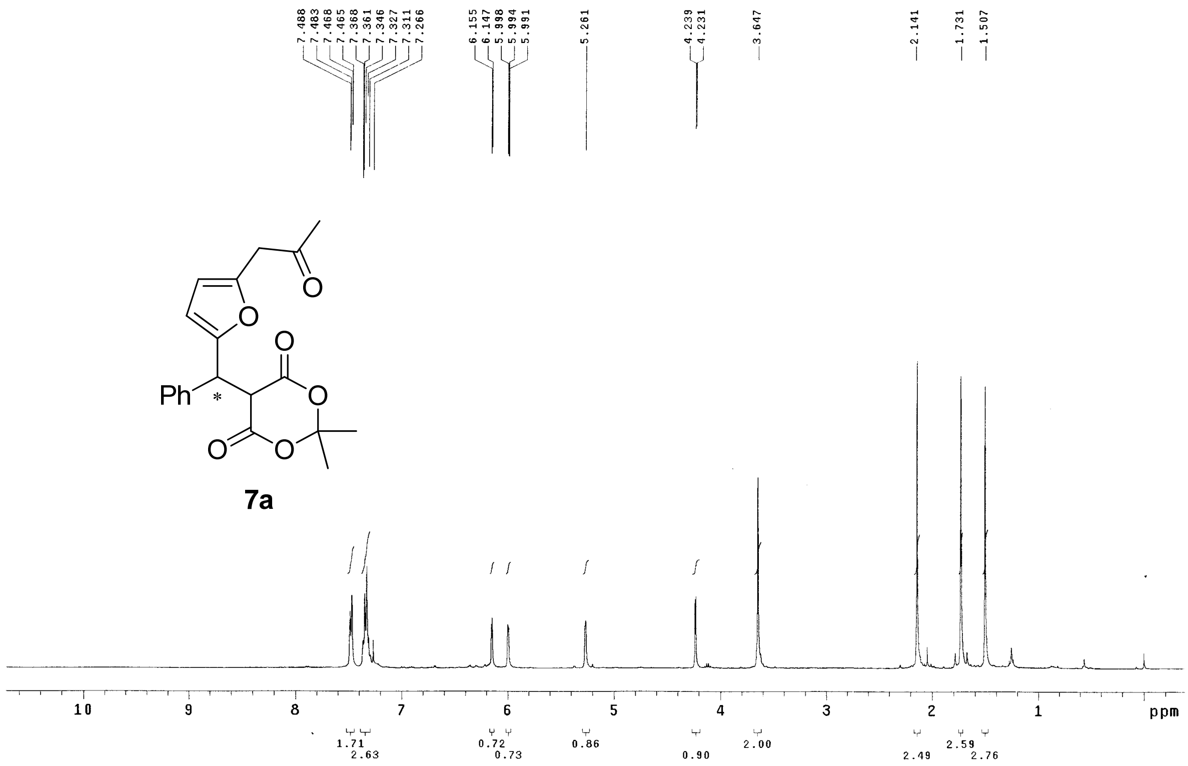

203.009
170.182
151.213
144.751
143.787
131.372
125.203
124.029
123.149
112.209
110.414
109.725
109.458
109.408
77.316
77.000
76.680
O
CN
CN
O
N
O
*
5



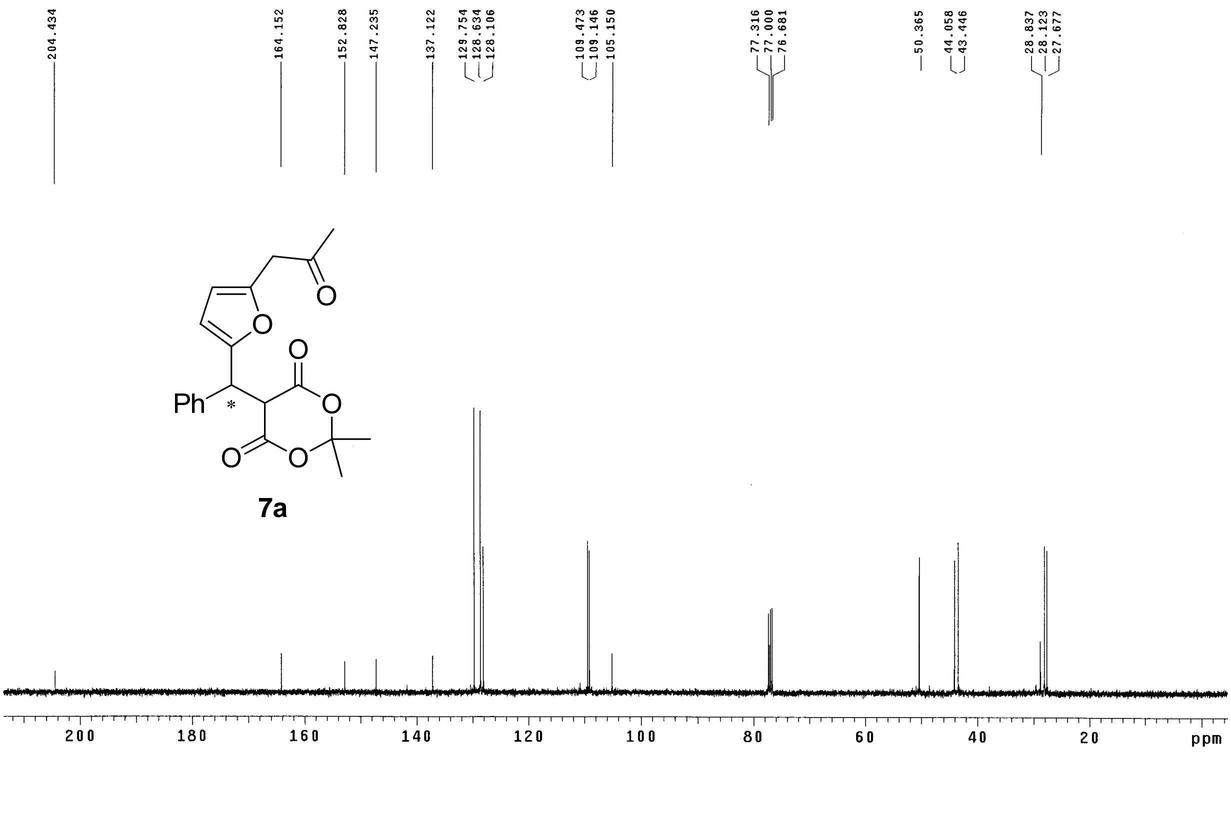
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.361	VV	0.4651	6717.33838	217.52261	49.4799
2	14.119	VV	0.5227	6858.55176	199.83501	50.5201



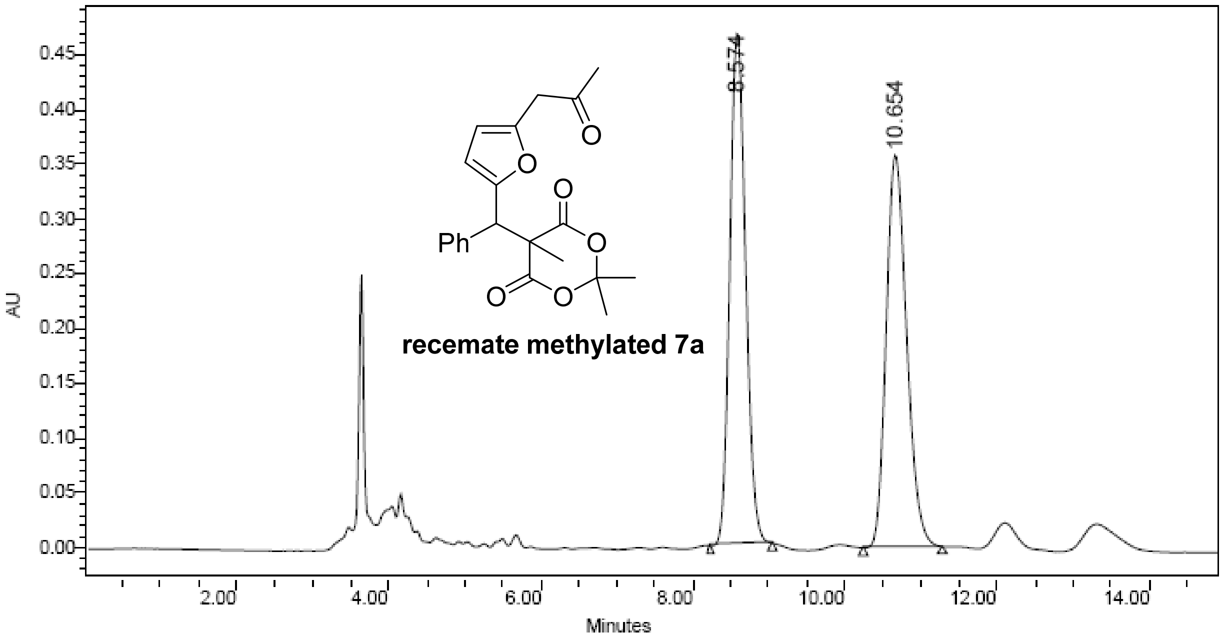
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.151	VV	0.4279	1.48350e4	535.75250	29.2120
2	13.810	VB	0.4718	3.59489e4	1161.21765	70.7880


7.488
7.483
7.468
7.465
7.368
7.361
7.346
7.327
7.311
7.266
6.155
6.147
5.998
5.994
5.991
5.261
4.239
4.231
3.647
2.141
1.731
1.507
Ph
O
*
1.71
2.63
0.72
0.73
0.86
0.90
2.00
2.49
2.59
2.76
10
9
8
7
6
5
4
3
2
1
ppm

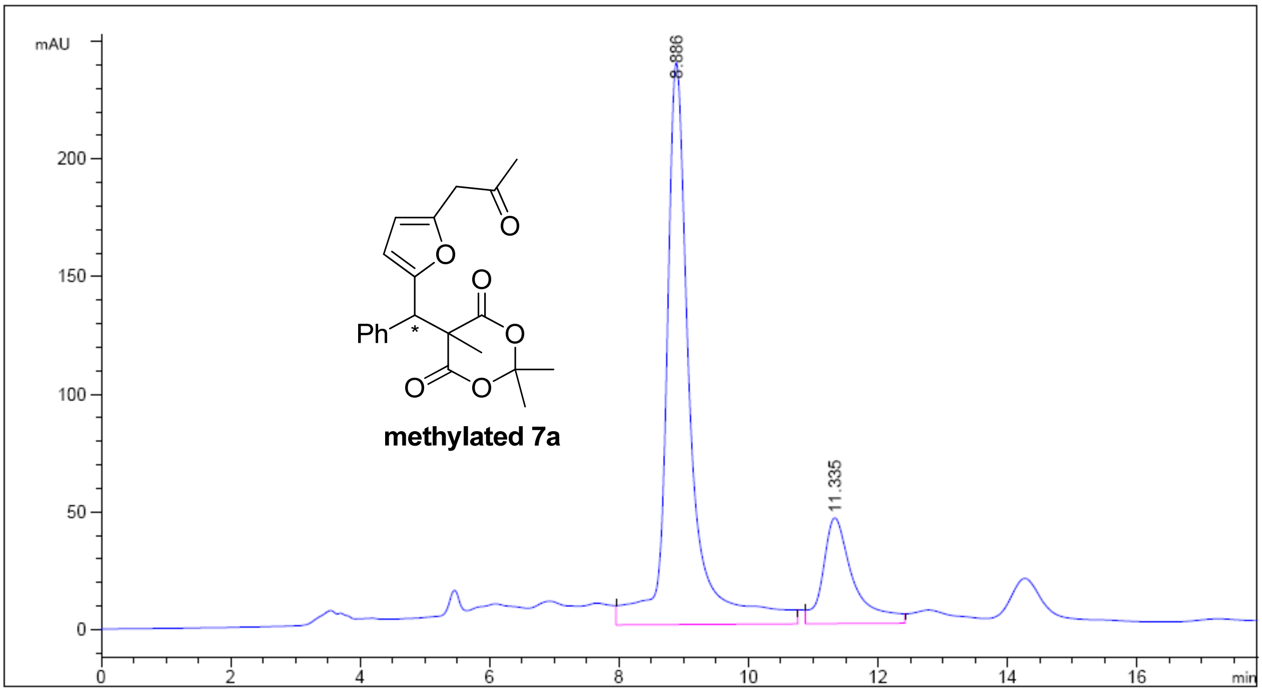
7a


204.434
164.152
152.828
147.235
137.122
129.754
128.634
128.106
109.473
109.146
105.150
77.316
77.000
76.681
50.365
44.058
43.446
28.837
28.123
27.677
Ph
O
*
200
180
160
140
120
100
80
60
40
20
ppm

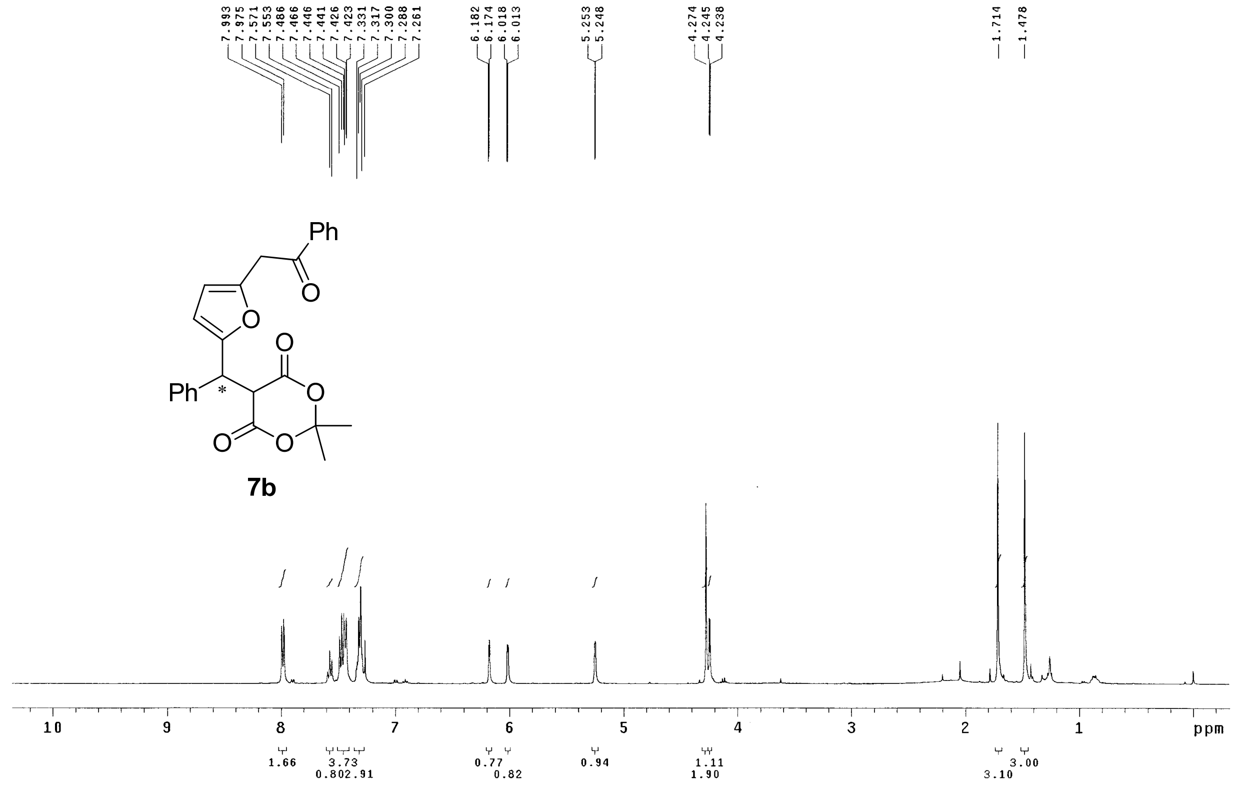
7a



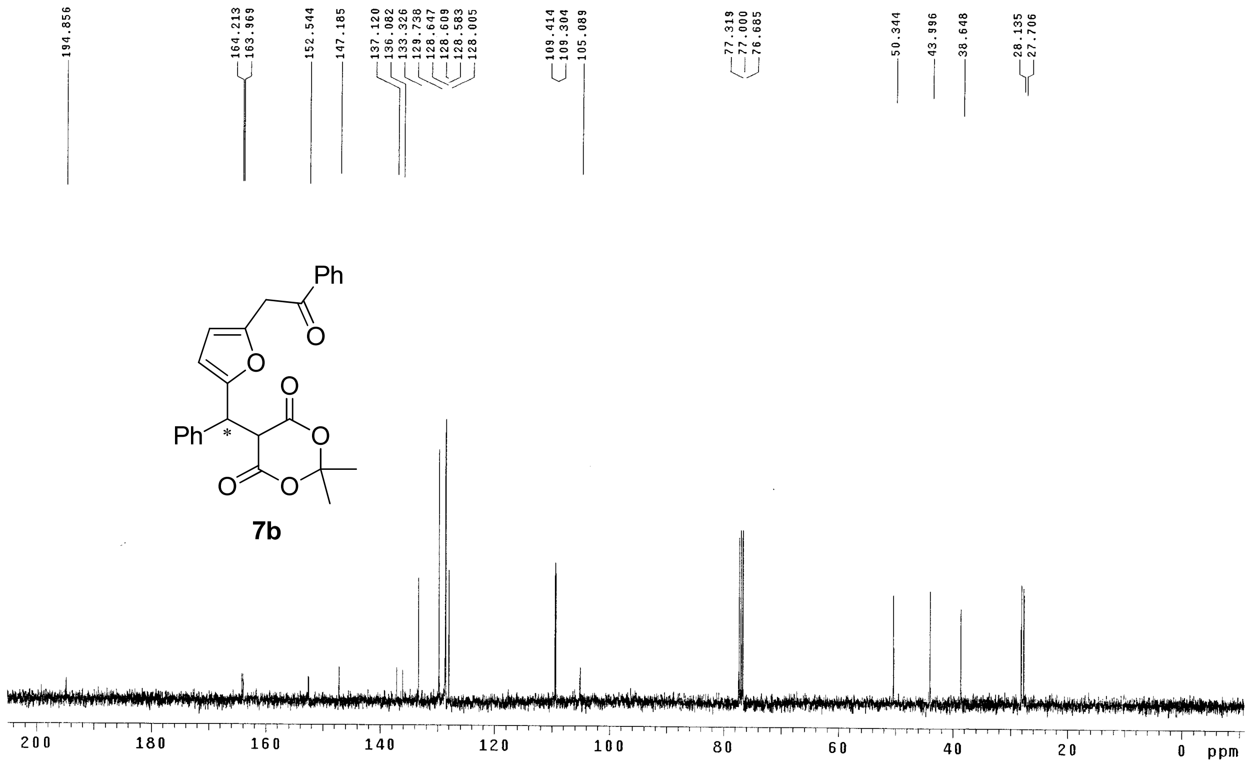
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	8.574	6747053	49.94	467646	56.63
2	10.654	6763364	50.06	358090	43.37



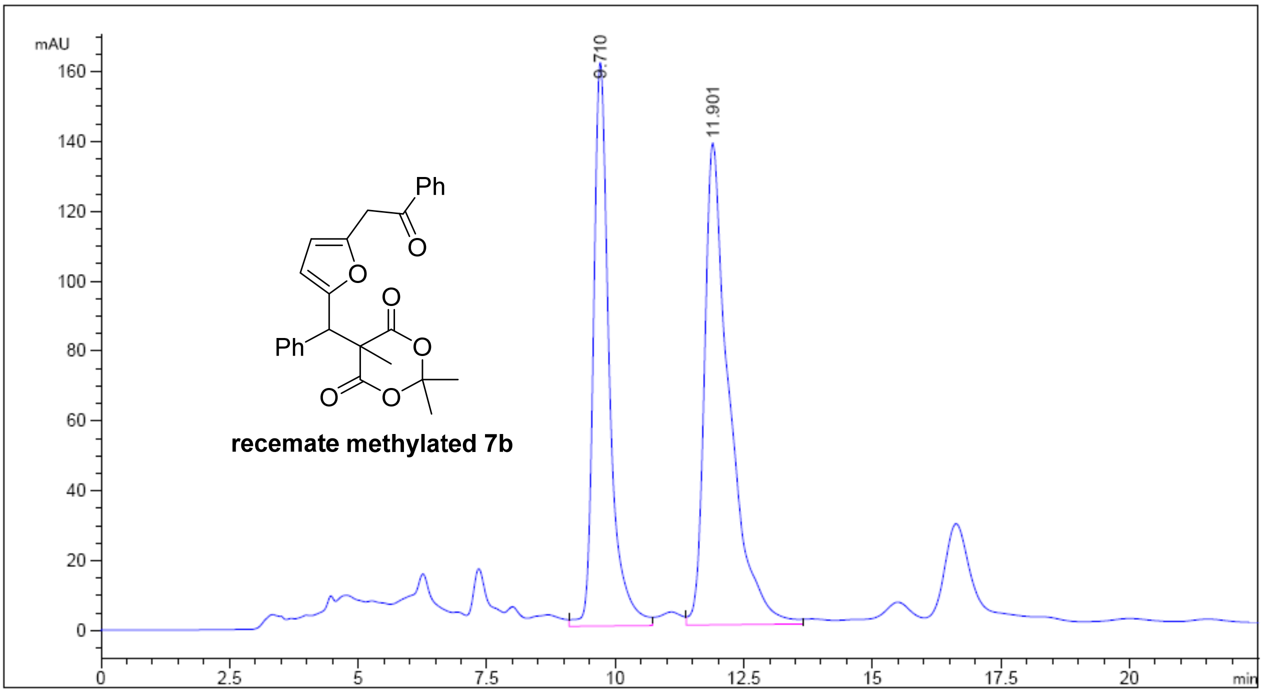
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.886	VB	0.3775	6174.40723	238.70786	80.7507
2	11.335	BV	0.4752	1471.85095	44.94854	19.2493



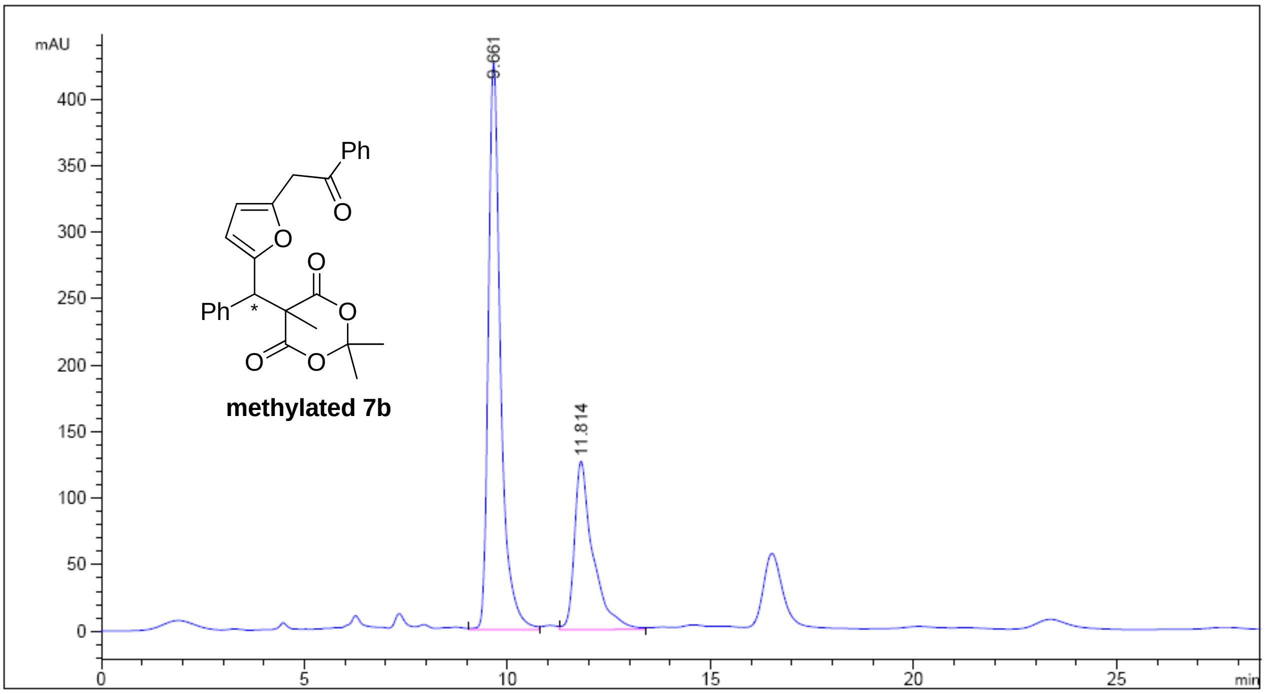
7.993
7.975
7.571
7.553
7.486
7.466
7.446
7.441
7.426
7.423
7.331
7.317
7.300
7.288
7.261
6.182
6.174
6.018
6.013
5.253
5.248
4.274
4.245
4.238
1.714
1.478
Ph
O
O
O
Ph
*
O
O
O
7b
ppm
1.66
3.73
0.80
2.91
0.77
0.82
0.94
1.11
1.90
3.10
3.00



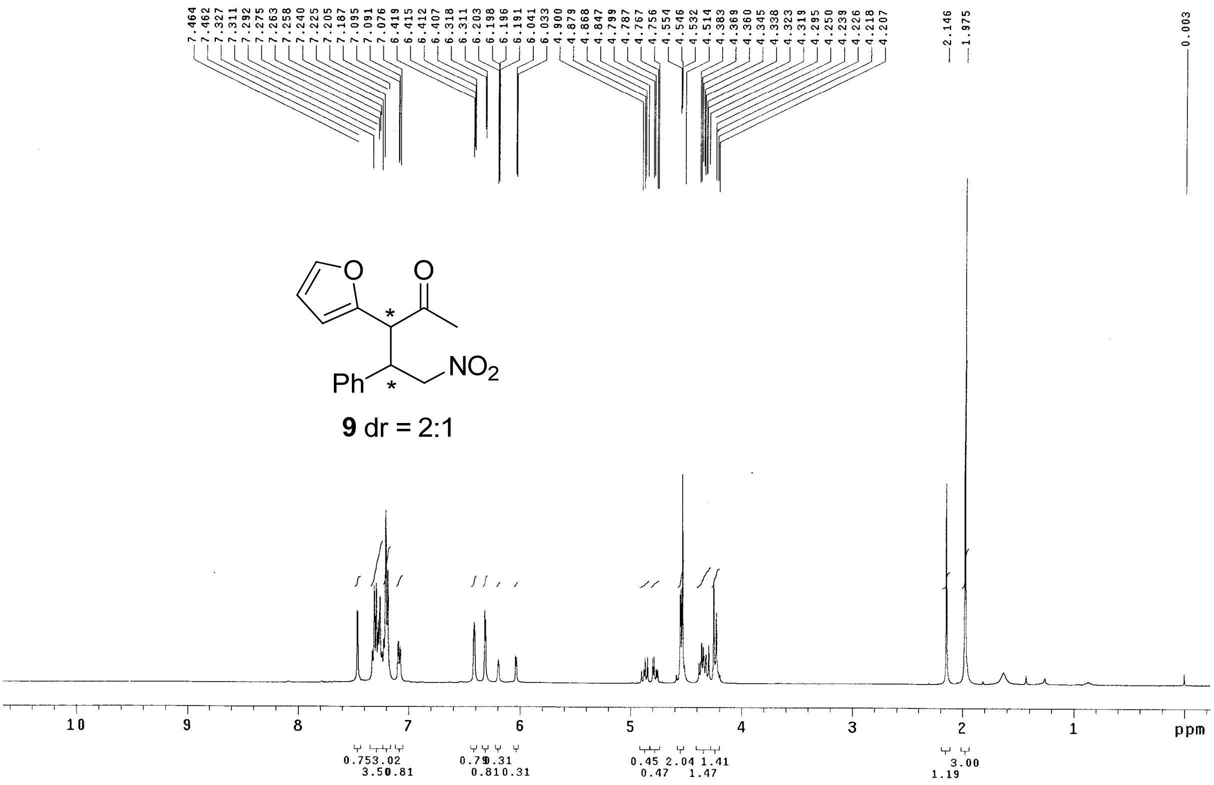
194.856
164.213
163.969
152.544
147.185
137.120
136.082
133.326
129.738
128.647
128.609
128.583
128.005
109.414
109.304
105.089
77.319
77.000
76.685
50.344
43.996
38.648
28.135
27.706
Ph
O
O
O
Ph
*
O
O
O
7b
ppm



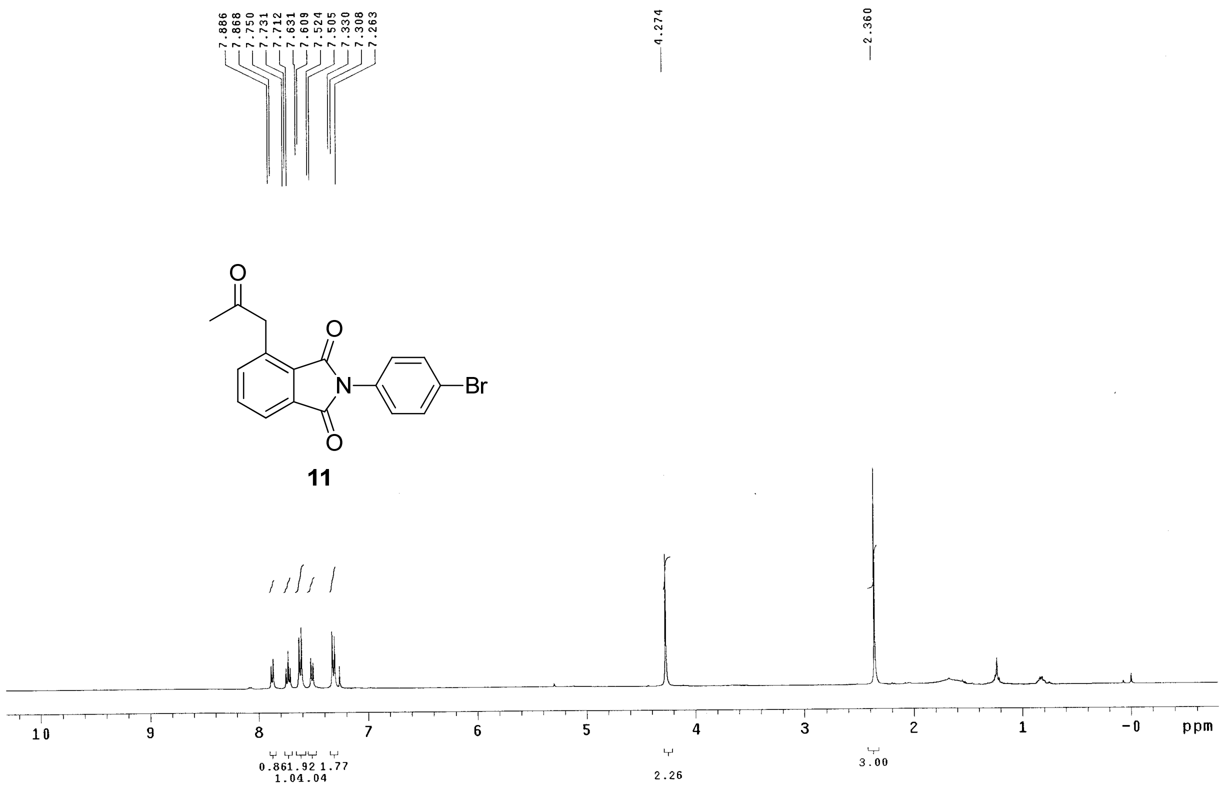
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.710	VV	0.3222	3483.82153	161.11940	42.8559
2	11.901	VB	0.4747	4645.32764	137.84871	57.1441

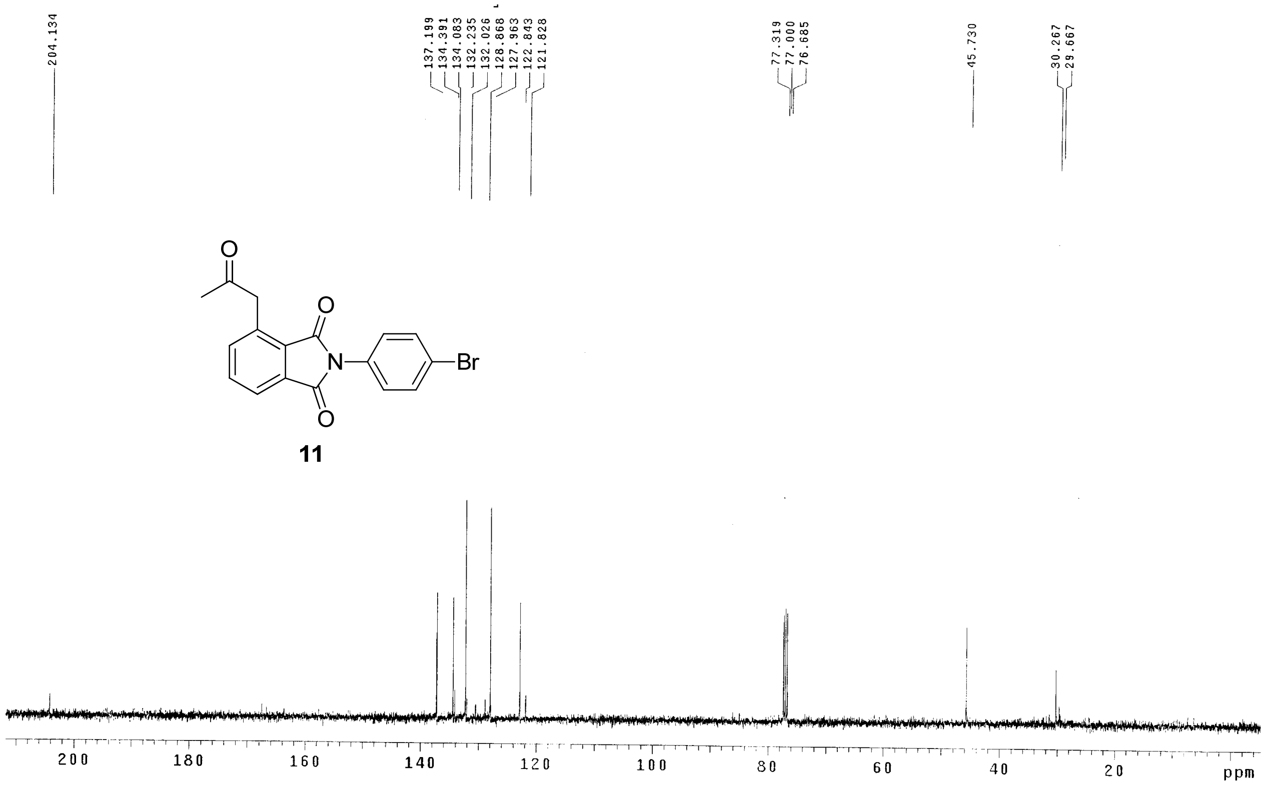


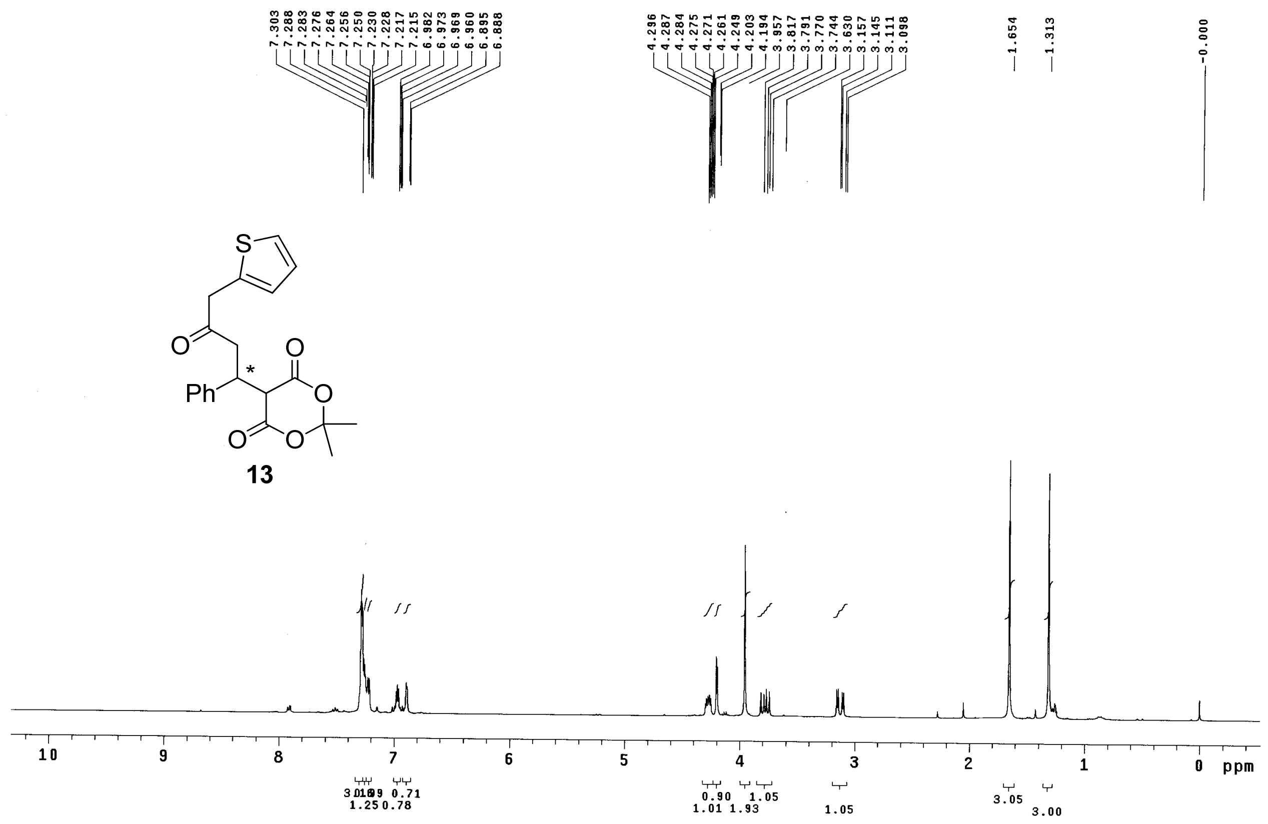
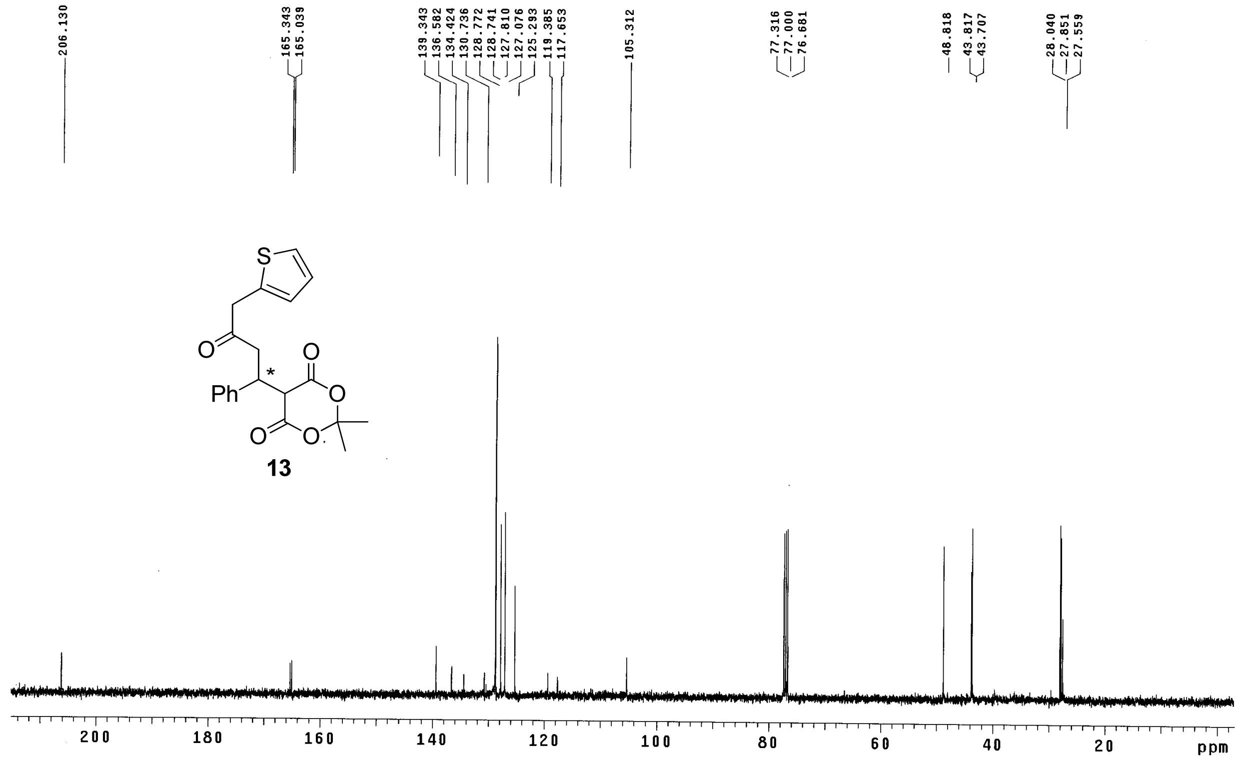
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.661	VV	0.3213	8965.58984	425.93033	69.0352
2	11.814	VV	0.4527	4021.38770	126.40136	30.9648

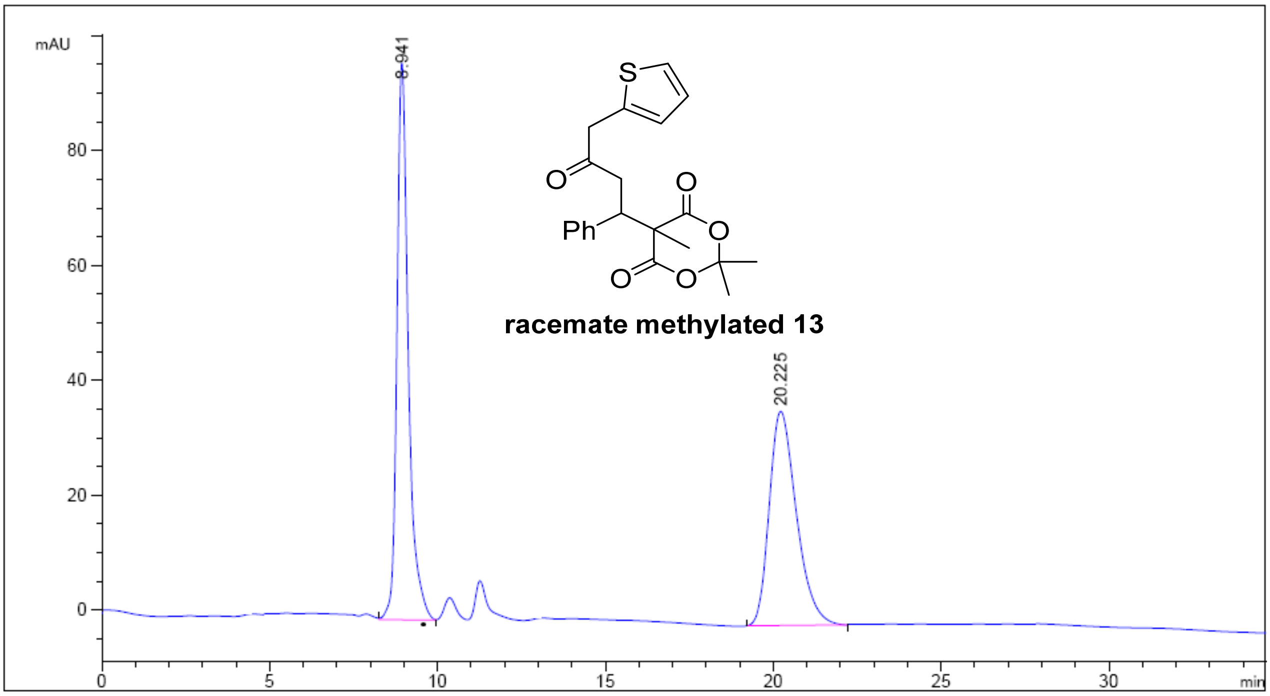


O
O
*
*
Ph
NO2
9 dr = 2:1
ppm

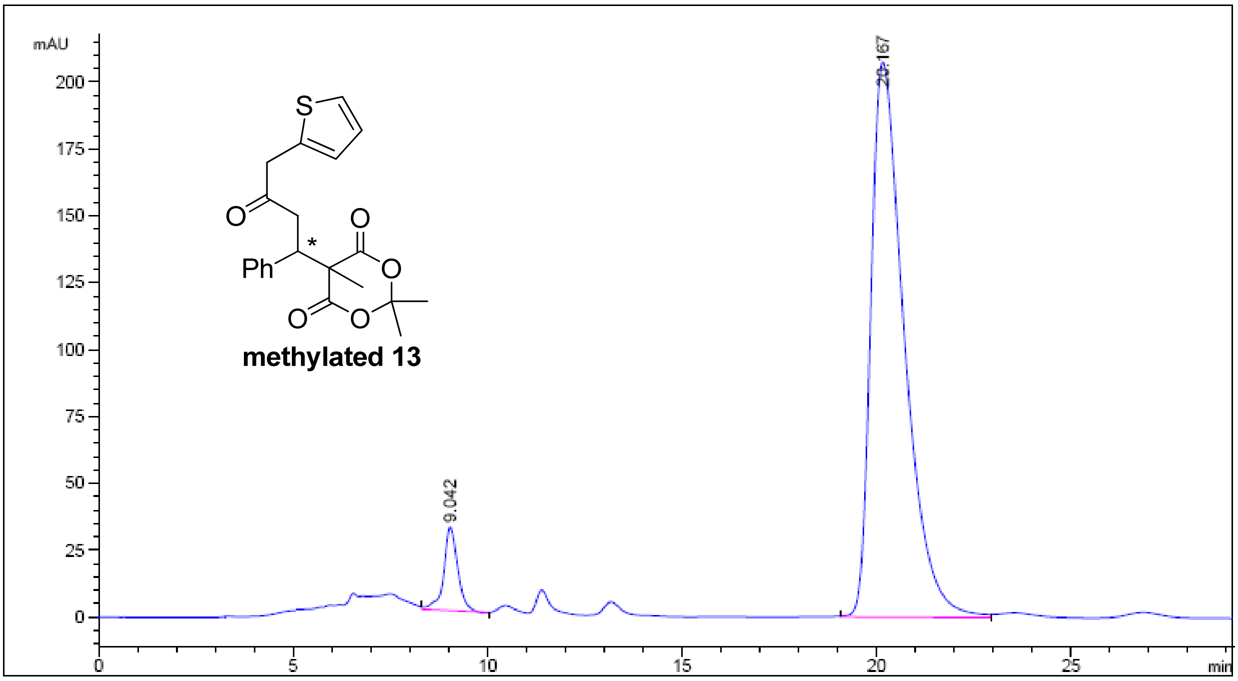

7.886
7.868
7.750
7.731
7.712
7.631
7.609
7.524
7.505
7.330
7.308
7.263
4.274
2.360
O
N
O
O
Br
11
10
9
8
7
6
5
4
3
2
1
-0
ppm
0.86
1.92
1.77
1.04
1.04
2.26
3.00


204.134
137.199
134.391
134.083
132.235
132.026
128.868
127.963
122.843
121.828
77.319
77.000
76.685
45.730
30.267
29.667
O
N
O
O
Br
11
200
180
160
140
120
100
80
60
40
20
ppm

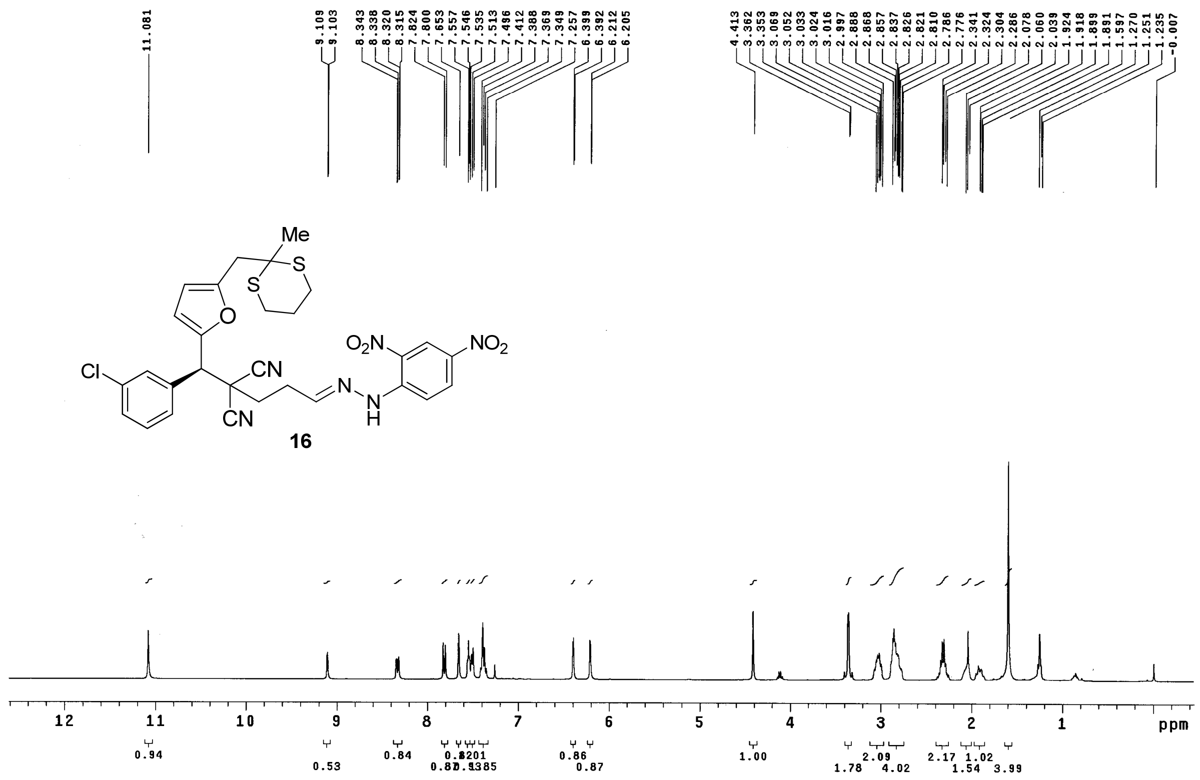

7.303 7.288 7.283 7.276 7.264 7.256 7.250 7.230 7.228 7.217 7.215 6.982 6.973 6.969 6.960 6.895 6.888
4.296 4.287 4.284 4.275 4.271 4.261 4.249 4.203 4.194 3.957 3.817 3.791 3.770 3.744 3.630 3.157 3.145 3.111 3.098
1.654
1.313
0.000
S
O
O
O
Ph
*
O
O
13
10 9 8 7 6 5 4 3 2 1 0 ppm
1.25 0.78 0.71
0.90 1.05
1.01 1.93
1.05
3.05
3.00

206.130
165.343 165.039
139.343 136.582 134.424 130.736 128.772 128.741 127.810 127.076 125.293 119.385 117.653
105.312
77.316 77.000 76.681
48.818 43.817 43.707
28.040 27.851 27.559
S
O
O
O
Ph
*
O
O
13
200 180 160 140 120 100 80 60 40 20 ppm

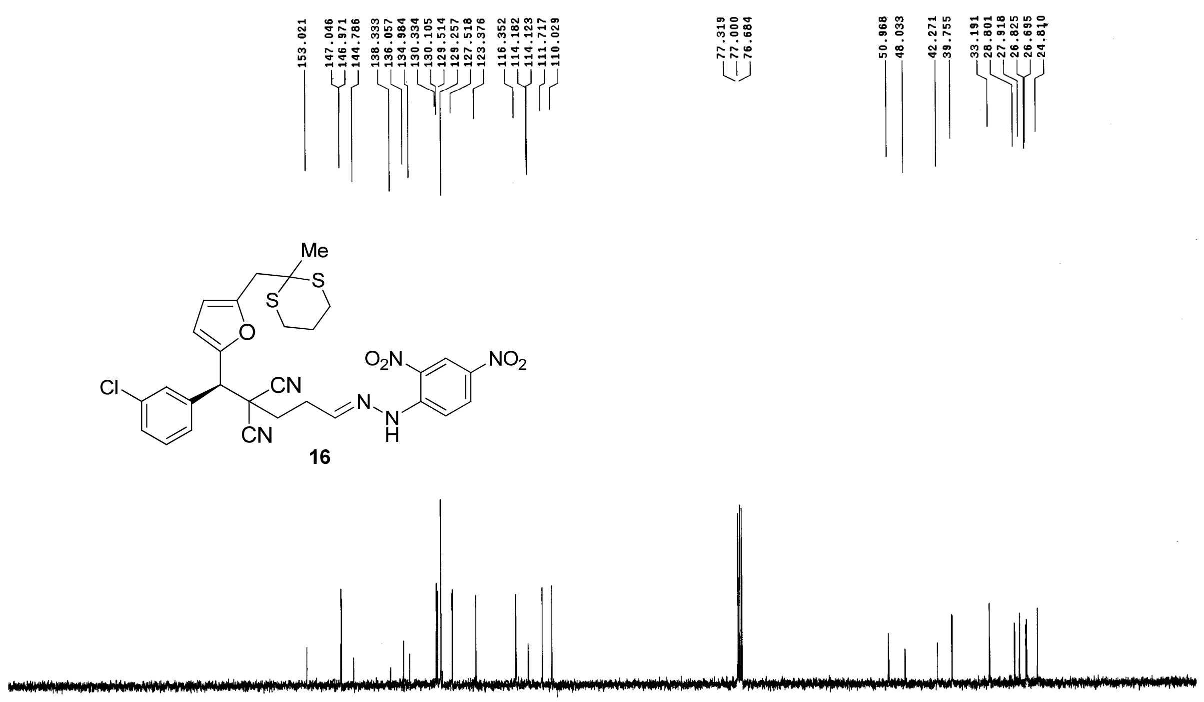


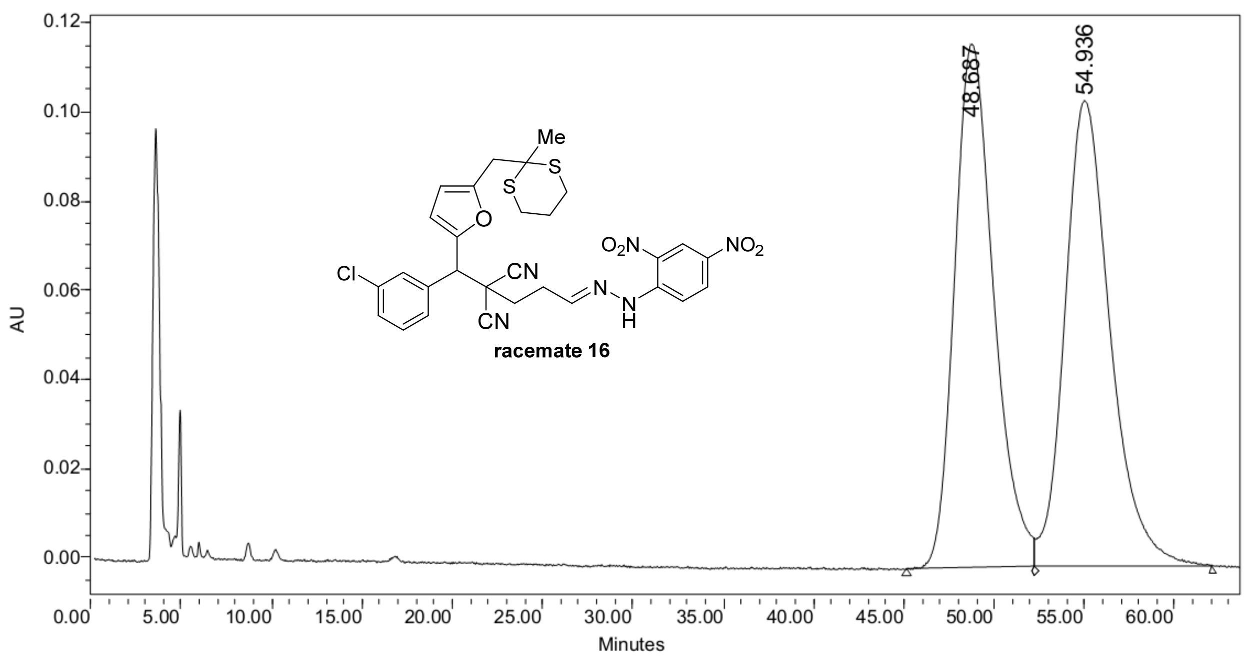
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.941	VV	0.3508	2285.90161	96.93803	52.1607
2	20.225	BB	0.8653	2096.52100	37.30585	47.8393



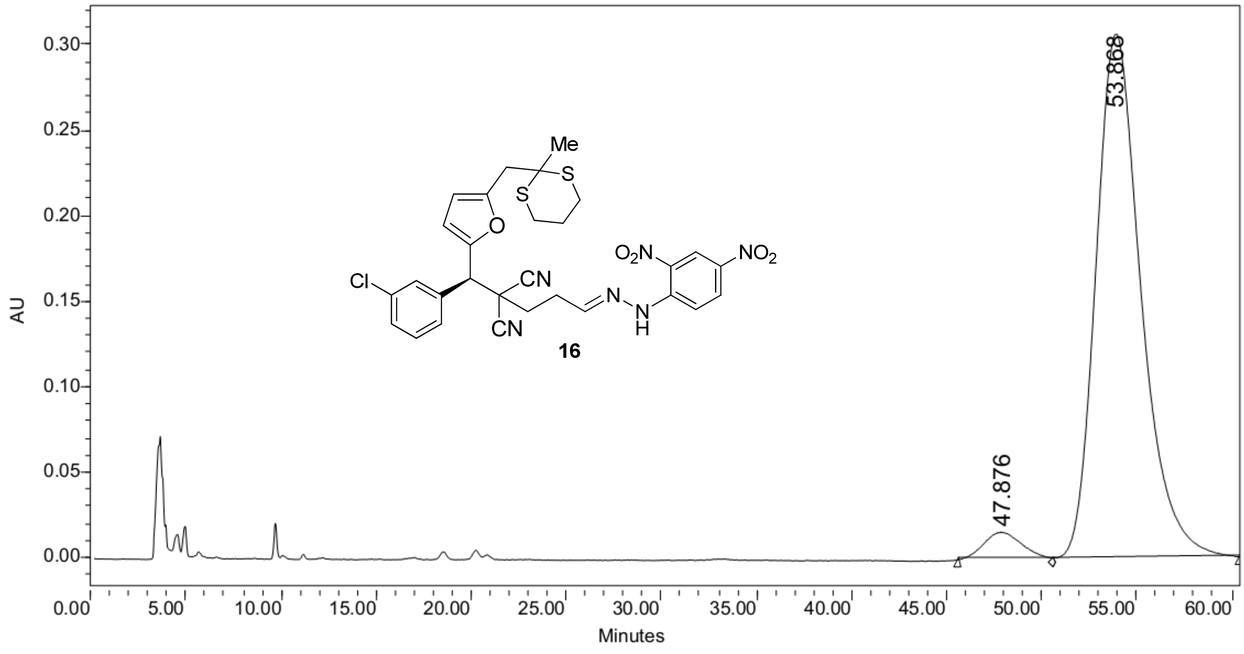
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.042	MM	0.4167	780.15155	31.20147	5.9270
2	20.167	BV	0.9062	1.23825e4	207.40407	94.0730


Me
S
S
O
O2N
NO2
Cl
CN
CN
N
N
H
16
12 11 10 9 8 7 6 5 4 3 2 1 ppm


Me
S
S
O
O2N
NO2
Cl
CN
CN
N
N
H
16
200 180 160 140 120 100 80 60 40 20 ppm



	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	48.687	17807561	49.27	117602	52.91
2	54.936	18332324	50.73	104672	47.09



	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	47.876	2201959	4.17	15703	4.87
2	53.868	50571860	95.83	306459	95.13