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Supporting Information

Unexpected Synthesis of N-Acyl Indolines via A Consecutive Cyclization of iminophosphorane

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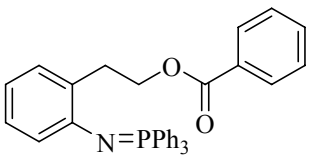
General Methods:

Reactions were generally carried out in an appropriate round bottom flask with magnetic stirring. Thin layer chromatography (TLC) was performed on a silica gel. All melting points were taken on a Digital Melting Point without correction. ^{1}H, and ^{13}C spectra were recorded on a 400 MHz or 600 MHz spectrometer. Chemical shifts for ^{1}H NMR spectra are reported in ppm downfield from TMS, chemical shifts for ^{13}C NMR spectra are reported in ppm relative to internal chloroform (δ 77.0 ppm for ^{13}C), and chemical shifts. The terms m, s, d, t, q refer to multiplet, singlet, doublet, triplet, quartlet; br refers to a broad signal.

General Procedure for the Synthesis of Iminophosphorane 2:

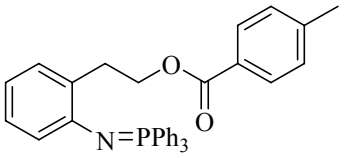
To a stirred solution of 2-(2-azidophenyl)ethanol (0.33 g, 2.0 mmol) and Et_3N (0.60 g, 6.0 mmol) in CH_2Cl_2 (15 mL) was added a solution of acyl chloride (2.0 mmol) in CH_2Cl_2 (10 mL) at r.t. The reaction mixture was stirred for 30 min. It was then pour into water to remove the Et_3NHCl, and extracted with CH_2Cl_2 three times. The organic phase was combined and dried with anhydrous Na_2SO_4. The crude product was purified by flash chromatography (15:1, PE–Et_2O) to yield azide **1**. To a stirred solution of azide **1** (2 mmol) in CH_2Cl_2 (15 mL) was added a solution of Ph_3P (0.52 g, 2 mmol) in dry CH_2Cl_2 (10 mL). After the reaction mixture was stirred for 1 h, the solvent was removed under reduced pressure, and the residue was recrystallized from Et_2O and CH_2Cl_2 (2:1; v/v) to give the iminophosphorane **2**.

2-(Triphenylphosphoranylideneamino)phenethyl benzoate (2a):



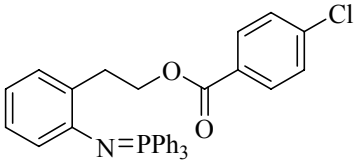
yield 93%, white solid, mp: 140-141 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.07 (d, 2H, *J* = 7.8 Hz, Ar-H), 7.78-6.46 (m, 22H, Ar-H), 4.68 (t, 2H, *J* = 6.6 Hz, OCH_2), 3.39 (t, 2H, *J* = 6.6 Hz, CH_2). MS: *m/z* (%) = 501 (8) [M^+], 396 (38), 380 (29), 262 (42), 183 (100), 108 (36), 105 (45), 77 (48). Anal. Calcd for $C_{33}H_{28}NO_2P$: C, 79.02; H, 5.63; N, 2.79. Found: C, 79.24; H, 5.74; N, 2.61.

2-(Triphenylphosphoranylideneamino)phenethyl 4-methylbenzoate (2b):



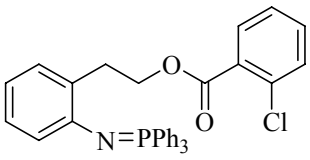
yield 81%, white solid, mp: 118-119 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.96-6.47 (m, 23H, Ar-H), 4.66 (m, 2H, OCH_2), 3.38 (m, 2H, CH_2), 2.41 (s, 3H, CH_3). MS: *m/z* (%) = 515 (8) [M^+], 396 (44), 380 (37), 262 (59), 183 (100), 119 (50), 108 (40), 91 (60). Anal. Calcd for $C_{34}H_{30}NO_2P$: C, 79.20; H, 5.86; N, 2.72. Found: C, 79.02; H, 5.68; N, 2.78.

2-(Triphenylphosphoranylideneamino)phenethyl 4-chlorobenzoate (2c):



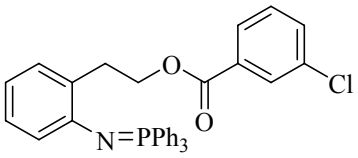
yield 85%, yellow solid, mp: 127-128 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.98 (d, 2H, *J* = 7.8 Hz, Ar-H), 7.77-6.46 (m, 21H, Ar-H), 4.67 (t, 2H, *J* = 6.6 Hz, OCH_2), 3.37 (t, 2H, *J* = 6.6 Hz, CH_2). MS: *m/z* (%) = 535 (5) [M^+], 396 (36), 380 (32), 262 (44), 184 (17), 183 (100). Anal. Calcd for $C_{33}H_{27}ClNO_2P$: C, 73.95; H, 5.08; N, 2.61. Found: C, 73.84; H, 5.29; N, 2.35.

2-(Triphenylphosphoranylideneamino)phenethyl 2-chlorobenzoate (2d):



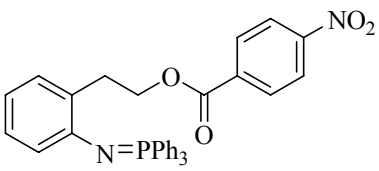
yield 83%, white solid, mp: 121-122 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.81-6.46 (m, 23H, Ar-H), 4.70 (t, 2H, *J* = 6.6 Hz, OCH_2), 3.39 (t, 2H, *J* = 6.6 Hz, CH_2). MS: *m/z* (%) = 535 (4) [M^+], 396 (38), 380 (28), 262 (36), 184 (16), 183 (100). Anal. Calcd for $C_{33}H_{27}ClNO_2P$: C, 73.95; H, 5.08; N, 2.61. Found: C, 73.67; H, 5.26; N, 2.52.

2-(Triphenylphosphoranylideneamino)phenethyl 3-chlorobenzoate (2e):



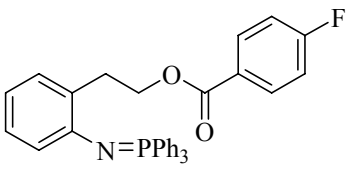
yield 87%, white solid, mp: 125-126 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.04 (s, 1H, Ar-H), 7.93 (d, 1H, *J* = 7.8 Hz, Ar-H), 7.77-6.47 (m, 21H, Ar-H), 4.68 (t, 2H, *J* = 7.2 Hz, OCH_2), 3.38 (t, 2H, *J* = 7.2 Hz, CH_2). MS: *m/z* (%) = 535 (8) [M^+], 396 (27), 380 (27), 277 (30), 262 (42), 184 (19), 183 (100). Anal. Calcd for $C_{33}H_{27}ClNO_2P$: C, 73.95; H, 5.08; N, 2.61. Found: C, 74.17; H, 5.22; N, 2.35.

2-(Triphenylphosphoranylideneamino)phenethyl 4-nitrobenzoate (2f):



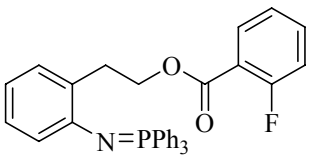
yield 85%, orange solid, mp: 146-147 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.23 (d, 2H, *J* = 9.0 Hz, Ar-H), 8.18 (d, 2H, *J* = 9.0 Hz, Ar-H), 7.76-6.47 (m, 19H, *J* = 7.8 Hz, Ar-H), 4.74 (t, 2H, *J* = 6.6 Hz, OCH_2), 3.40 (t, 2H, *J* = 6.6 Hz, CH_2). MS: *m/z* (%) = 546 (13) [M^+], 277 (26), 183 (25), 119 (58), 118 (100), 117 (30). Anal. Calcd for $C_{33}H_{27}N_2O_4P$: C, 72.52; H, 4.98; N, 5.13. Found: C, 72.23; H, 4.74; N, 5.38.

2-(Triphenylphosphoranylideneamino)phenethyl 4-fluorobenzoate (2g):



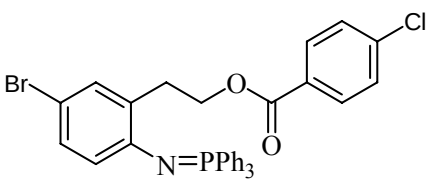
yield 91%, white solid, mp: 150-151 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.07 (t, 2H, *J* = 7.2 Hz, Ar-H), 7.77-6.46 (m, 21H, Ar-H), 4.67 (t, 2H, *J* = 6.6 Hz, OCH_2), 3.37 (t, 2H, *J* = 6.6 Hz, CH_2). MS: *m/z* (%) = 519 (8) [M^+], 396 (36), 380 (34), 262 (48), 184 (18), 183 (100). Anal. Calcd for $C_{33}H_{27}FNO_2P$: C, 76.29; H, 5.24; N, 2.70. Found: C, 76.46; H, 5.05; N, 2.85.

2-(Triphenylphosphoranylideneamino)phenethyl 2-fluorobenzoate (2h):



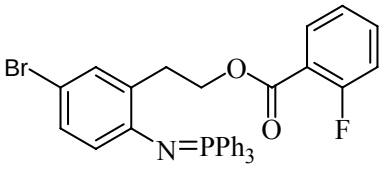
yield 90%, white solid, mp: 131-132 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.95 (t, 1H, *J* = 7.2 Hz, Ar-H), 7.78-6.46 (m, 22H, Ar-H), 4.69 (t, 2H, *J* = 6.6 Hz, OCH_2), 3.39 (t, 2H, *J* = 6.6 Hz, CH_2). MS: *m/z* (%) = 519 (7) [M^+], 396 (35), 380 (33), 262 (41), 184 (18), 183 (100). Anal. Calcd for $C_{33}H_{27}FNO_2P$: C, 76.29; H, 5.24; N, 2.70. Found: C, 76.55; H, 5.52; N, 2.56.

5-Bromo-2-(triphenylphosphoranylideneamino)phenethyl 4-chlorobenzoate (2i):



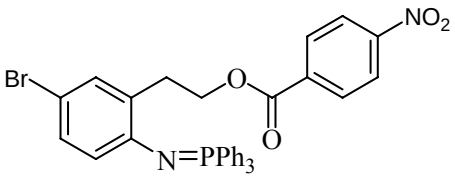
yield 84%, white solid, mp: 158-159 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, 2H, *J* = 8.4 Hz, Ar-H), 7.74-6.28 (m, 20H, Ar-H), 4.63 (t, 2H, *J* = 6.8 Hz, OCH_2), 3.31 (t, 2H, *J* = 6.8 Hz, CH_2). MS: *m/z* (%) = 613 (10) [M^+], 476 (21), 277 (21), 262 (51), 189 (18), 183 (100). Anal. Calcd for $C_{33}H_{26}BrClNO_2P$: C, 64.46; H, 4.26; N, 2.28. Found: C, 64.19; H, 4.47; N, 2.15.

5-Bromo-2-(triphenylphosphoranylideneamino)phenethyl 2-fluorobenzoate (2j):



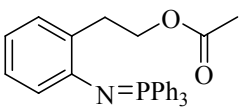
yield 81%, white solid, mp: 166-167 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.94-7.13 (m, 20H, Ar-H), 6.86 (d, 1H, *J* = 8.0 Hz, Ar-H), 6.28 (d, 1H, *J* = 8.4 Hz, Ar-H), 4.65 (t, 2H, *J* = 7.2 Hz, OCH_2), 3.32 (t, 2H, *J* = 7.2 Hz, CH_2). MS: *m/z* (%) = 597 (10) [M^+], 476 (22), 458 (15), 262 (49), 183 (100), 123 (51). Anal. Calcd for $C_{33}H_{26}BrFNO_2P$: C, 66.23; H, 4.38; N, 2.34. Found: C, 66.12; H, 4.58; N, 2.12.

5-Bromo-2-(triphenylphosphoranylideneamino)phenethyl 4-nitrobenzoate (2k):



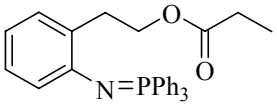
yield 87%, red solid, mp: 174-175 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25-7.27 (m, 20H, Ar-H), 6.86 (d, 1H, *J* = 8.0 Hz, Ar-H), 6.29 (d, 1H, *J* = 8.4 Hz, Ar-H), 4.70 (t, 2H, *J* = 6.8 Hz, OCH_2), 3.34 (t, 2H, *J* = 6.8 Hz, CH_2). MS: *m/z* (%) = 624 (9) [M^+], 474 (18), 277 (43), 262 (57), 199 (20), 183 (100). Anal. Calcd for $C_{33}H_{26}BrN_2O_4P$: C, 63.37; H, 4.19; N, 4.48. Found: C, 63.15; H, 4.31; N, 4.64.

2-(triphenylphosphoranylideneamino)phenethyl acetate (2l):



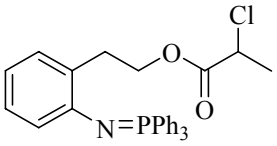
yield 86%, yellow solid, mp: 76-78 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.76-6.44 (m, 19H, Ar-H), 4.42 (t, 2H, *J* = 6.6 Hz, OCH_2), 3.24 (t, 2H, *J* = 6.6 Hz, CH_2), 2.04 (s, 3H, CH_3). MS: *m/z* (%) = 439 (10) [M^+], 396 (25), 380 (39), 262 (34), 183 (100), 152 (15), 108 (34). Anal. Calcd for $C_{28}H_{26}NO_2P$: C, 76.52; H, 5.96; N, 3.19. Found: C, 76.27; H, 5.74; N, 3.38.

2-(triphenylphosphoranylideneamino)phenethyl propionate (2m):



yield 87%, white solid, mp: 101-102 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.77-6.44 (m, 19H, Ar-H), 4.43 (t, 2H, *J* = 6.6 Hz, OCH_2), 3.24 (t, 2H, *J* = 7.2 Hz, CH_2), 2.33 (q, 2H, *J* = 7.2 Hz, CH_2), 1.14 (t, 3H, *J* = 7.2 Hz, CH_3). MS: *m/z* (%) = 453 (8) [M^+], 396 (31), 380 (40), 262 (34), 184 (17), 183 (100), 152 (13). Anal. Calcd for $C_{29}H_{28}NO_2P$: C, 76.80; H, 6.22; N, 3.09. Found: C, 76.94; H, 6.01; N, 3.23.

2-(triphenylphosphoranylideneamino)phenethyl 2-chloropropanoate (2n):

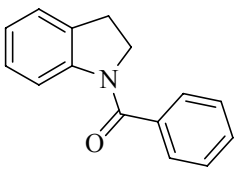


yield 88%, yellow solid, mp: 121-124 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.76-6.45 (m, 19H, Ar-H), 4.54 (t, 2H, *J* = 7.2 Hz, OCH_2), 4.40 (q, 1H, *J* = 4.8 Hz, CHCl), 3.30-3.24 (m, 2H, CH_2), 1.67 (d, 3H, *J* = 7.2 Hz, CH_3). MS: *m/z* (%) = 487 (6) [M^+], 397 (7), 380 (42), 277 (35), 183.1 (100). Anal. Calcd for $C_{29}H_{27}ClNO_2P$: C, 71.38; H, 5.58; N, 2.87. Found: C, 71.15; H, 5.65; N, 2.99.

General Procedure for the Synthesis of N-Acyl indolines 4 and 5:

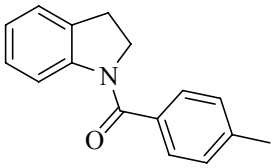
The solution of iminophosphorane **2** (2 mmol) in xylene or 1,2-dichlorobenzene was heated to reflux for 1-24 h. The crude product was purified by flash chromatography to yield N-acyl indolines **4** and **5**.

1-Benzoylindoline (4a):



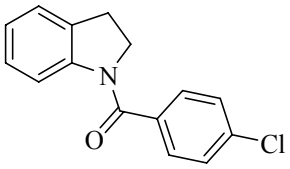
white solid, mp: 121-123 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.31-7.03 (m, 9H), 4.06 (br, 2H), 3.12 (t, *J* = 8.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 168.8, 142.4, 136.8, 132.1, 130.1, 128.4, 126.9, 124.7, 123.9, 123.8, 117.3, 50.7, 28.1. MS: *m/z* (%) = 223 (66) [M^+], 105 (100), 77 (33). Anal. Calcd for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.53; H, 5.85; N, 6.42.

1-(4-Methylbenzoyl)indoline (4b):



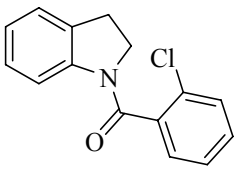
white solid, mp: 102-104 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.45-6.99 (m, 8H), 4.06 (br, 2H), 3.08 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.0, 142.6, 140.4, 133.9, 132.4, 132.2, 129.0, 127.1, 124.7, 123.6, 117.4, 50.7, 28.1, 21.5. MS: *m/z* (%) = 237 (14) [M^+], 119.1 (100), 91.1 (38), 65.1(16). Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 80.81; H, 6.48; N, 5.72.

1-(4-Chlorobenzoyl)indoline (4c):



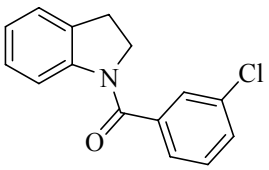
white solid, mp: 116-117 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.30-7.03 (m, 8H), 4.04 (br, 2H), 3.11(t, *J* = 8.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 167.0, 141.9, 135.6, 134.8, 131.7, 129.3, 128.1, 127.1, 126.6, 124.4, 123.6, 117.0, 50.3, 27.7. MS: *m/z* (%) = 257 (18) [M^+], 141 (33), 139 (100), 111 (33), 75 (11). Anal. Calcd for $C_{15}H_{12}ClNO$: C, 69.91; H, 4.69; N, 5.43. Found: C, 69.64; H, 4.85; N, 5.31.

1-(2-Chlorobenzoyl)indoline (4d):



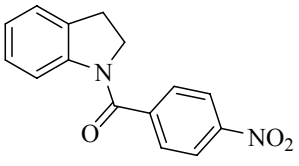
white solid, mp: 93-94 °C. ^{1}H NMR (600 MHz, $CDCl_3$): major rotamer (75:25) δ = 8.35 (d, *J* = 14.4 Hz, 0.75H), 7.43-6.81 (m, 7.54H), 5.71 (d, *J* = 8.4 Hz, 0.25H), 4.37-4.27 (m, 0.52H), 3.84-3.75 (m, 1.47H), 3.18-3.10 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.1, 142.7, 137.1, 132.5, 130.4, 128.7, 127.2, 125.0, 124.1, 117.5, 50.9, 28.3. MS: *m/z* (%) = 257 (19) [M^+], 141 (34), 139 (100), 111 (29), 75 (12). Anal. Calcd for $C_{15}H_{12}ClNO$: C, 69.91; H, 4.69; N, 5.43. Found: C, 69.72; H, 4.58; N, 5.67.

1-(3-Chlorobenzoyl)indoline (4e):



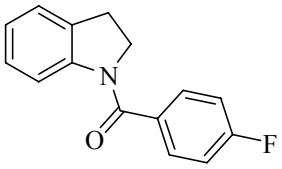
white solid, mp: 158-159 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.24-7.06 (m, 8H), 4.03 (br, 2H), 3.13 (t, *J* = 8.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 167.1, 142.3, 138.5, 134.4, 132.0, 130.2, 129.8, 127.0, 125.0, 117.8, 51.2, 28.2. MS: *m/z* (%) = 257 (20) [M^+], 141 (33), 139 (100), 111 (37), 75 (11). Anal. Calcd for $C_{15}H_{12}ClNO$: C, 69.91; H, 4.69; N, 5.43. Found: C, 70.15; H, 4.84; N, 5.27.

1-(4-Nitrobenzoyl)indoline (4f):



yellow solid, mp: 203-204 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.32-5.86 (m, 8H), 4.27-3.97 (m, 2H), 3.16(t, J = 7.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 166.4, 148.4, 142.2, 131.8, 127.9, 127.5, 124.8, 123.8, 122.9, 117.7, 50.8, 28.4. MS: *m/z* (%) = 268 (35) [M^+], 150 (100), 139 (18), 120 (58), 104 (34), 91 (27), 76 (21), 65 (22). Anal. Calcd for $C_{15}H_{12}N_2O_3$: C, 67.16; H, 4.51; N, 10.44. Found: C, 67.37; H, 4.75; N, 10.27.

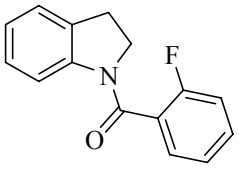
1-(4-Fluorobenzoyl)indoline (4g):



white solid, mp: 104-105 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.24-7.03 (m, 8H), 4.08 (br, 2H), 3.13 (t, *J* = 8.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 167.3, 164.0, 162.4, 142.1, 132.6, 132.0, 129.1, 126.7, 124.5, 123.6, 117.0, 116.2, 115.1, 114.1, 50.4, 28.0. MS: *m/z* (%) = 241 (17) [M^+], 123 (100), 95 (35). Anal. Calcd for $C_{15}H_{12}FNO$: C, 74.67; H, 5.01; N, 5.81. Found: C, 74.58;

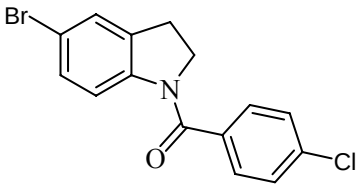
H, 5.24; N, 5.61.

1-(2-Fluorobenzoyl)indoline (4h):



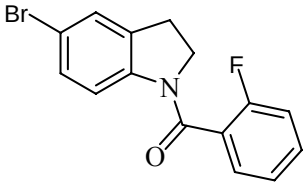
white solid, mp: 96-97 °C. ^{1}H NMR (600 MHz, $CDCl_3$): major rotamer (79:21) δ = 8.31 (d, *J* = 7.8 Hz, 0.79H), 7.48-6.83 (m, 7.34H), 5.92 (d, *J* = 6.6 Hz, 0.21H), 4.38-4.28 (m, 0.42H), 3.92 (t, *J* = 7.8 Hz, 1.57H), 3.12 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.7, 162.7, 158.8, 158.3, 157.2, 156.6, 141.8, 140.6, 132.9, 131.7, 131.0, 128.5, 128.1, 126.8, 126.4, 125.0, 124.3, 123.9, 116.8, 115.5, 112.6, 48.7, 47.9, 27.4, 26.2. MS: *m/z* (%) = 241 (17) [M^+], 123 (100), 95 (35). Anal. Calcd for $C_{15}H_{12}FNO$: C, 74.67; H, 5.01; N, 5.81. Found: C, 74.42; H, 4.87; N, 5.97.

5-Bromo-1-(4-chlorobenzoyl)indoline (4i):



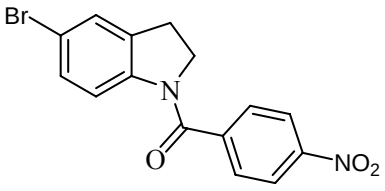
white solid, mp: 142-143 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51-7.26 (m, 7H, Ar-H), 4.07 (br, 2H, OCH_2), 3.12 (t, *J* = 8.0 Hz, 2H, CH_2). MS: *m/z* (%) = 335 (11) [M^+], 139 (100), 111 (27). Anal. Calcd for $C_{15}H_{11}BrClNO$: C, 53.52; H, 3.29; N, 4.16. Found: C, 53.74; H, 3.43; N, 4.04.

5-Bromo-1-(2-fluorobenzoyl)indoline (4j):



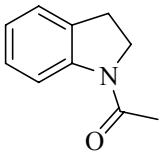
white solid, mp: 149-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$): major rotamer (75:25) δ = 8.19 (d, *J* = 8.4 Hz, 0.72H, Ar-H), 7.49-6.95 (m, 6.42H, Ar-H), 5.77 (br, 0.25H, Ar-H), 4.39-4.22 (m, 0.47H, OCH_2), 3.95 (t, *J* = 8.4 Hz, 1.49H, OCH_2), 3.12 (t, *J* = 8.0 Hz, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.4, 159.2, 156.8, 141.5, 134.3, 131.8, 131.7, 130.3, 128.7, 127.7, 124.8, 118.8, 116.9, 116.1, 115.9, 49.2, 27.8. MS: *m/z* (%) = 319 (12) [M^+], 123 (100), 95 (20). Anal. Calcd for $C_{15}H_{11}BrFNO$: C, 56.27; H, 3.46; N, 4.37. Found: C, 56.13; H, 3.58; N, 4.51.

5-Bromo-1-(4-nitrobenzoyl)indoline (4k):



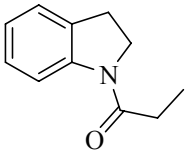
yellow solid, mp: 215-216 °C. ^{1}H NMR (400 MHz, $CDCl_3$): = 8.35-7.29 (m, 7H, Ar-H), 4.00 (br, 2H, OCH_2), 3.16 (t, *J* = 8.0 Hz, 2H, CH_2). MS: *m/z* (%) = 346 (17) [M^+], 150 (100), 117 (24), 104 (32). Anal. Calcd for $C_{15}H_{11}BrN_2O_3$: C, 51.90; H, 3.19; N, 8.07. Found: C, 51.67; H, 3.11; N, 8.26.

1-Acetylindoline (4l):



white solid, mp: 98-100 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.20 (d, *J* = 7.8 Hz, 1H), 7.17 (q, *J* = 7.8 Hz, 2H), 7.00 (t, *J* = 7.8 Hz, 1H), 4.12 (t, *J* = 7.8 Hz, 0.29H), 4.01 (t, *J* = 8.4 Hz, 1.71H), 3.17 (t, *J* = 7.8 Hz, 1.72H), 3.05 (t, *J* = 7.8 Hz, 0.29H), 2.43 (s, 0.43H), 2.20 (s, 2.67H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 168.2, 142.4, 130.8, 126.8, 125.3, 124.1, 122.9, 122.5, 116.1, 113.5, 48.1, 47.4, 27.3, 26.2, 24.1, 23.6. MS: *m/z* (%) = 161 (32) [M^+], 119 (67), 118 (100), 91 (17). Anal. Calcd for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.58; H, 6.63; N, 8.94.

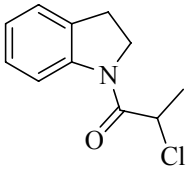
1-Propionylindoline (4m):



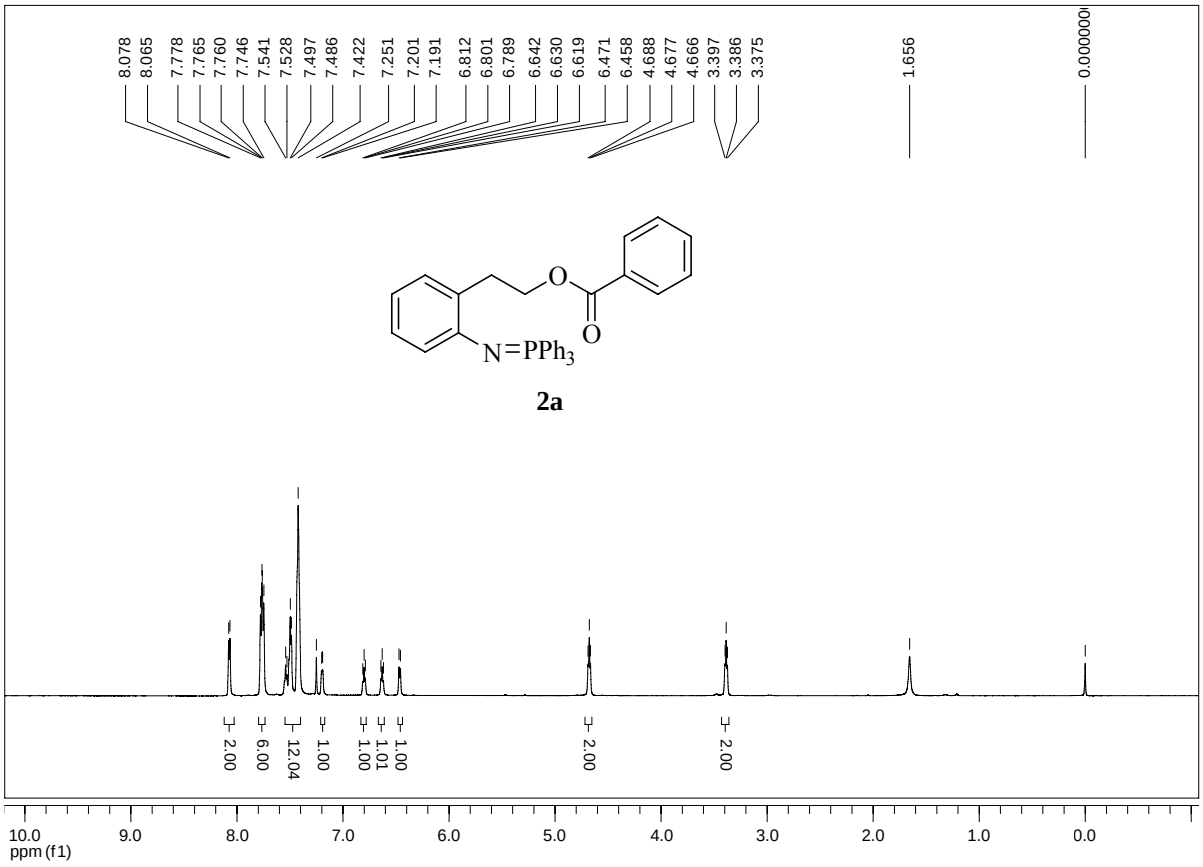
white solid, mp: 101-102 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 7.8 Hz, 1H), 7.18 (q, *J* = 7.8 Hz, 2H), 6.99 (t, *J* = 7.8 Hz, 1H), 4.14 (s, 0.29H), 4.01 (t, *J* = 8.4 Hz, 1.71H), 3.18 (t, *J* = 8.4 Hz, 1.71H), 3.05 (s, 0.29H), 2.68 (s, 0.29H), 2.43 (q, *J* = 7.8 Hz,

1.71H), 1.22 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 171.4, 142.6, 130.7, 126.8, 124.0, 122.8, 116.1, 47.1, 29.1 28.4, 27.4, 26.2, 9.2, 8.1. MS: *m/z* (%) = 175 (29) [M^+], 119 (100), 91 (18), 65 (9). Anal. Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.67; H, 7.45; N, 7.78.

1-(2-Chloropropanoyl)indoline (4n):



yellow solid; m.p.: 110-112 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 8.4 Hz, 1H), 7.21 (q, *J* = 7.8 Hz, 2H), 7.06 (t, *J* = 7.8 Hz, 1H), 4.58 (q, *J* = 6.6 Hz, 1H), 4.39 (q, *J* = 9.6 Hz, 1H), 4.09 (q, *J* = 10. 2 Hz, 1H), 3.27-3.20 (m, 2H), 1.75 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 166.5, 142.5, 131.4, 127.4, 124.5, 124.2, 117.2, 51.9, 47.5 27.9, 20.4; MS: *m/z* (%) = 209 (31) [M^+], 146 (32), 128 (18), 119 (100), 91 (33), 65 (15); Anal. Calcd for $C_{11}H_{12}ClNO$: C, 63.01; H, 5.77; N, 6.68. Found: C, 63.25; H, 5.58; N, 6.60.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7.765
7.760
7.746
7.541
7.528
7.497
7.486
7.422
7.251
7.201
7.191
6.812
6.801
6.789
6.642
6.630
6.619
6.471
6.458
4.688
4.677
4.666
3.397
3.386
3.375
1.656
0.000000
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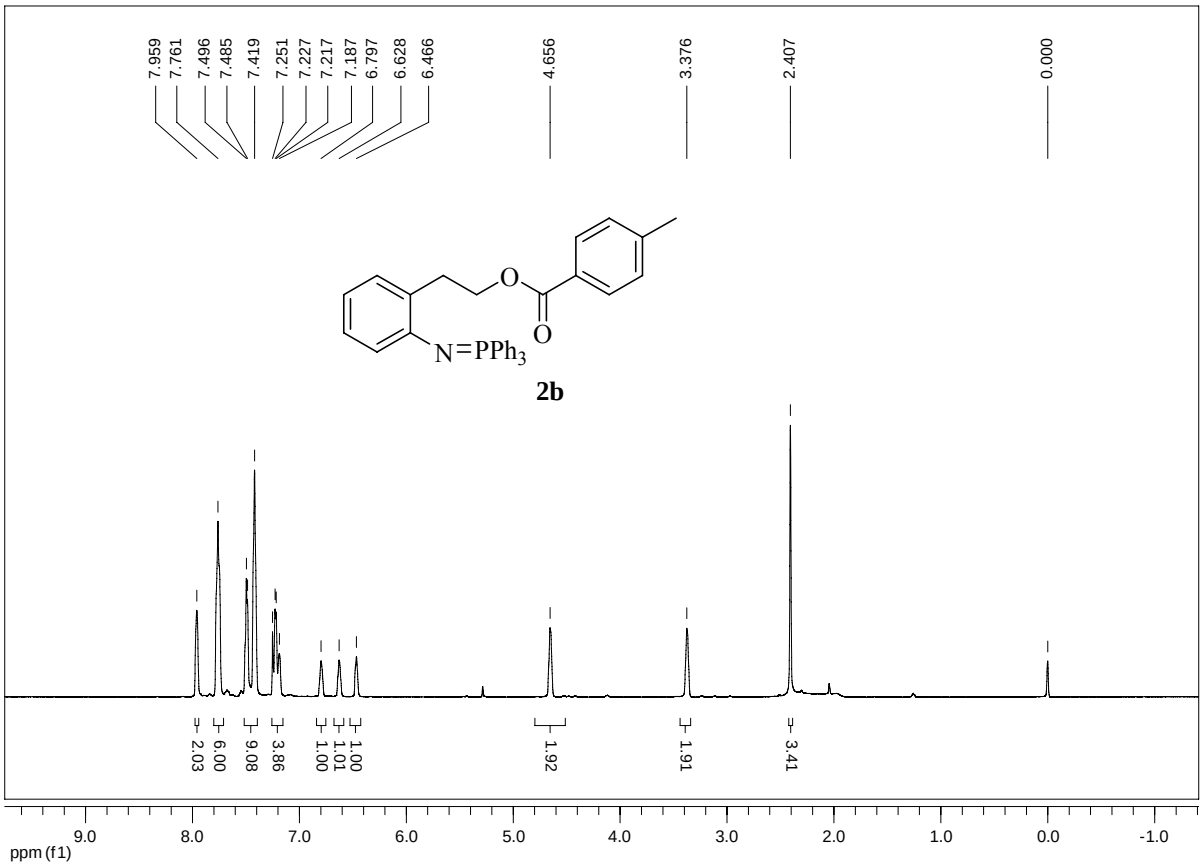
O
N=PPh3
2.00
6.00
12.04
1.00
1.00
1.01
1.00
2.00
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

2a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7.485
7.419
7.251
7.227
7.217
7.187
6.797
6.628
6.466
4.656
3.376
2.407
0.000
O
O
N=PPh3
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6.00
9.08
3.86
1.00
1.01
1.00
1.92
1.91
3.41
9.0
8.0
7.0
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5.0
4.0
3.0
2.0
1.0
0.0
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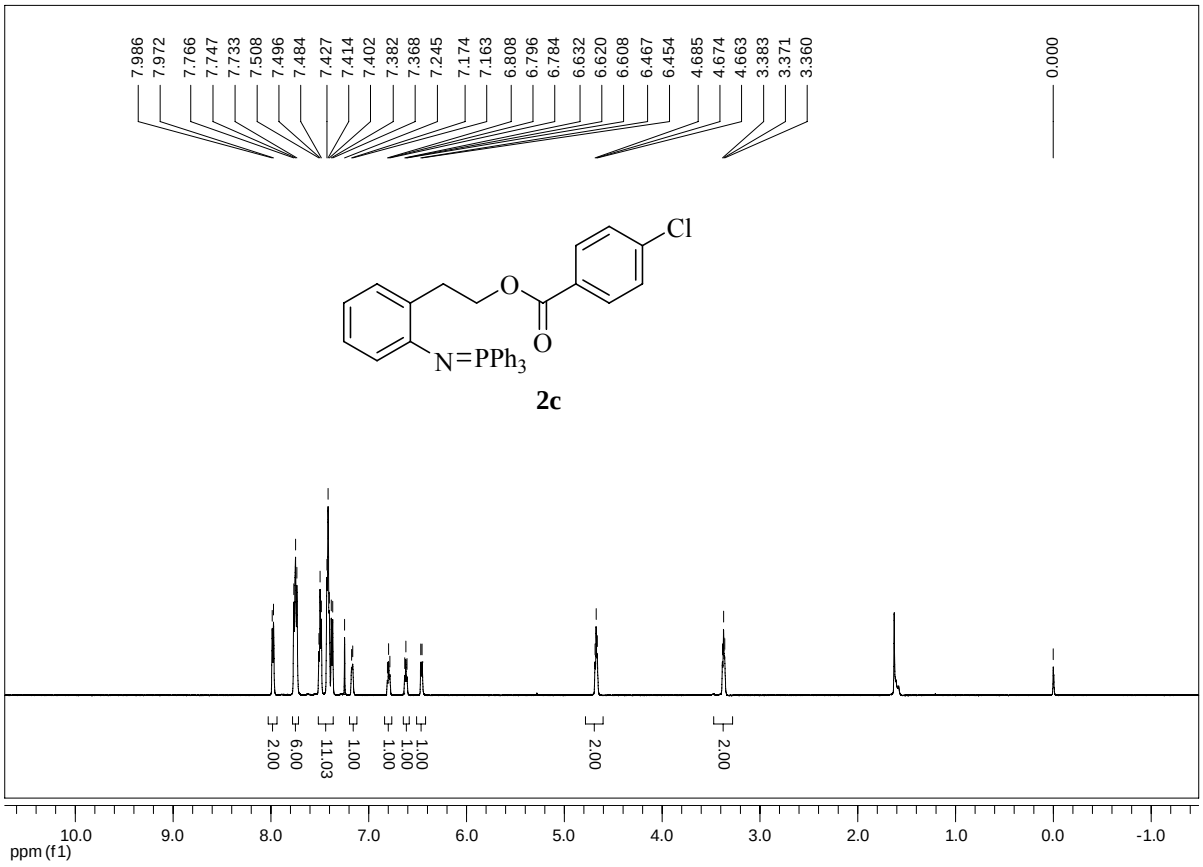
ppm (f1)

2b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7.733
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7.496
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7.402
7.382
7.368
7.245
7.174
7.163
6.808
6.796
6.784
6.632
6.620
6.608
6.467
6.454
4.685
4.674
4.663
3.383
3.371
3.360
0.000
Cl
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O
N=PPh3
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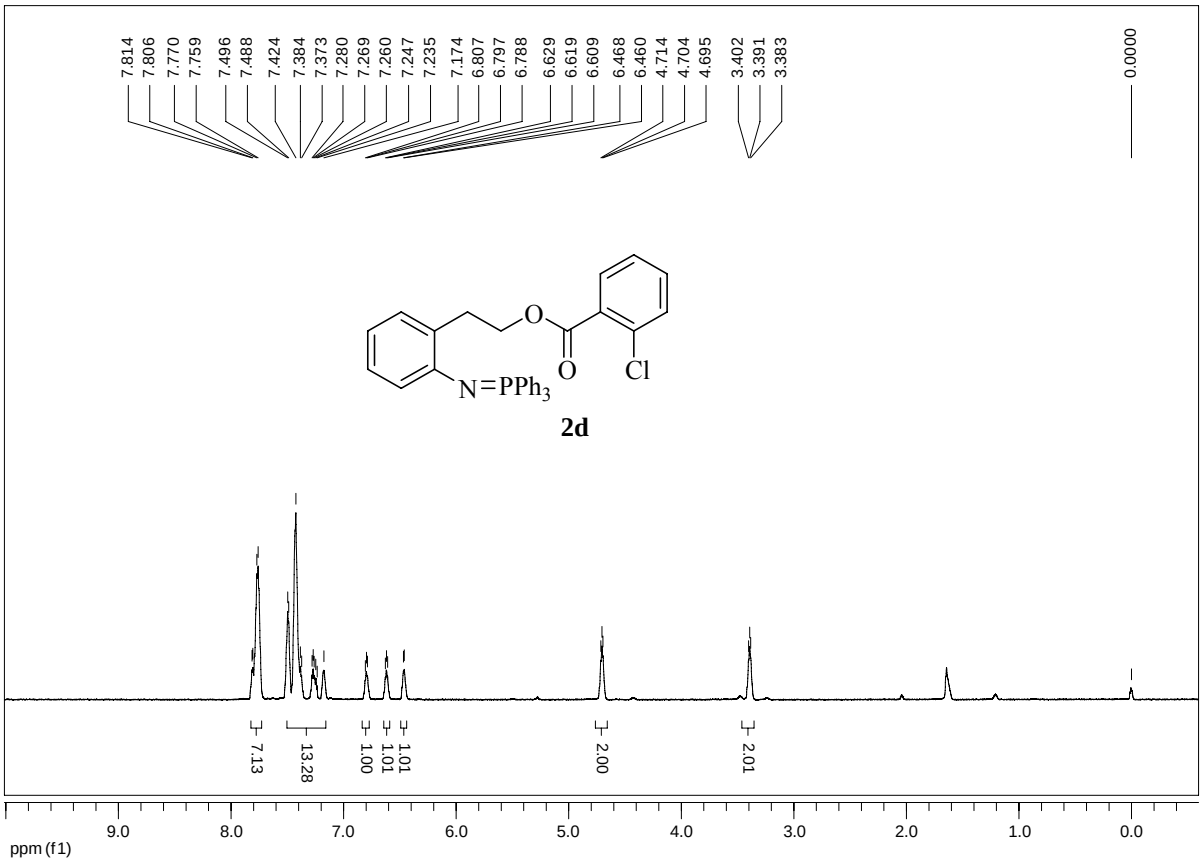
6.00
11.03
1.00
1.00
1.00
1.00
2.00
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
ppm (f1)

2c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7.424
7.384
7.373
7.280
7.269
7.260
7.247
7.235
7.174
6.807
6.797
6.788
6.629
6.619
6.609
6.468
6.460
4.714
4.704
4.695
3.402
3.391
3.383
0.0000
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O
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13.28
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1.01
2.00
2.01
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8.0
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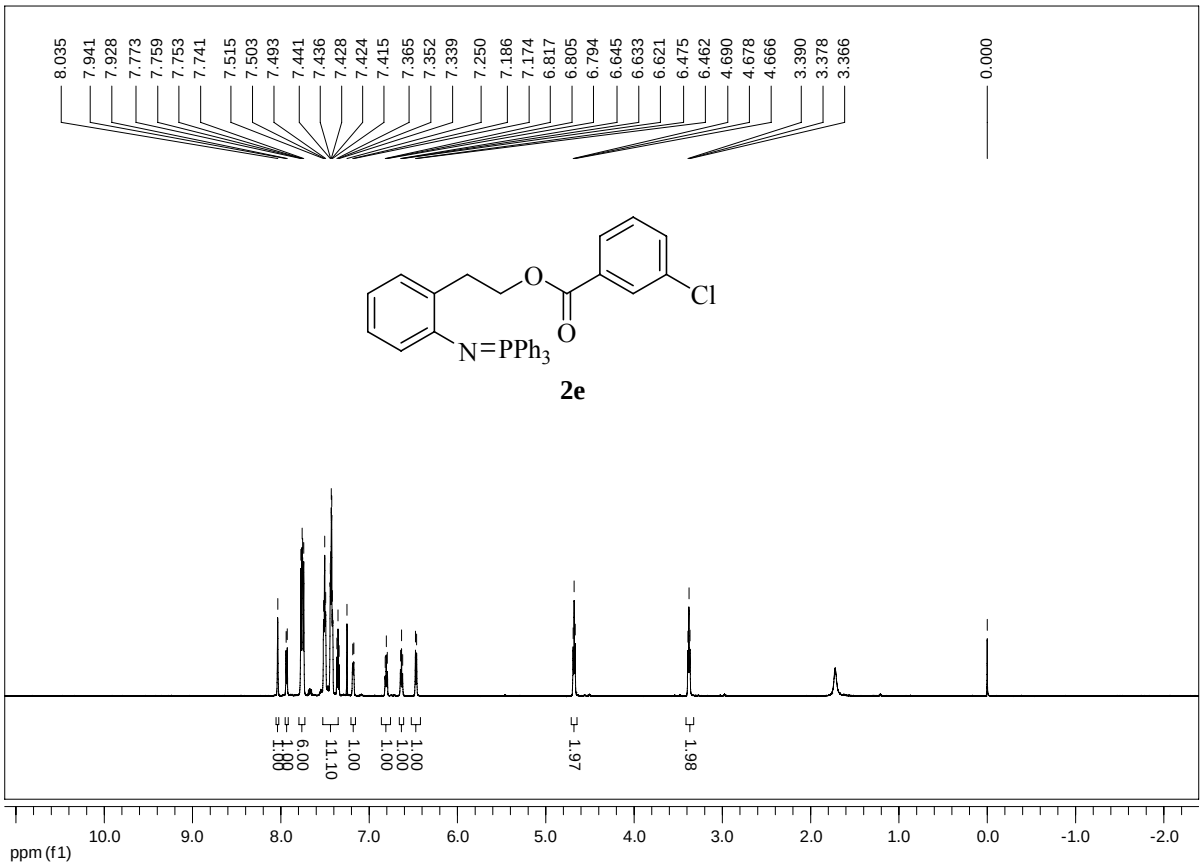
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

2d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7.759
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7.503
7.493
7.441
7.436
7.428
7.424
7.415
7.365
7.352
7.339
7.250
7.186
7.174
6.817
6.805
6.794
6.645
6.633
6.621
6.475
6.462
4.690
4.678
4.666
3.390
3.378
3.366
0.000
O
Cl
O
N=PPh3
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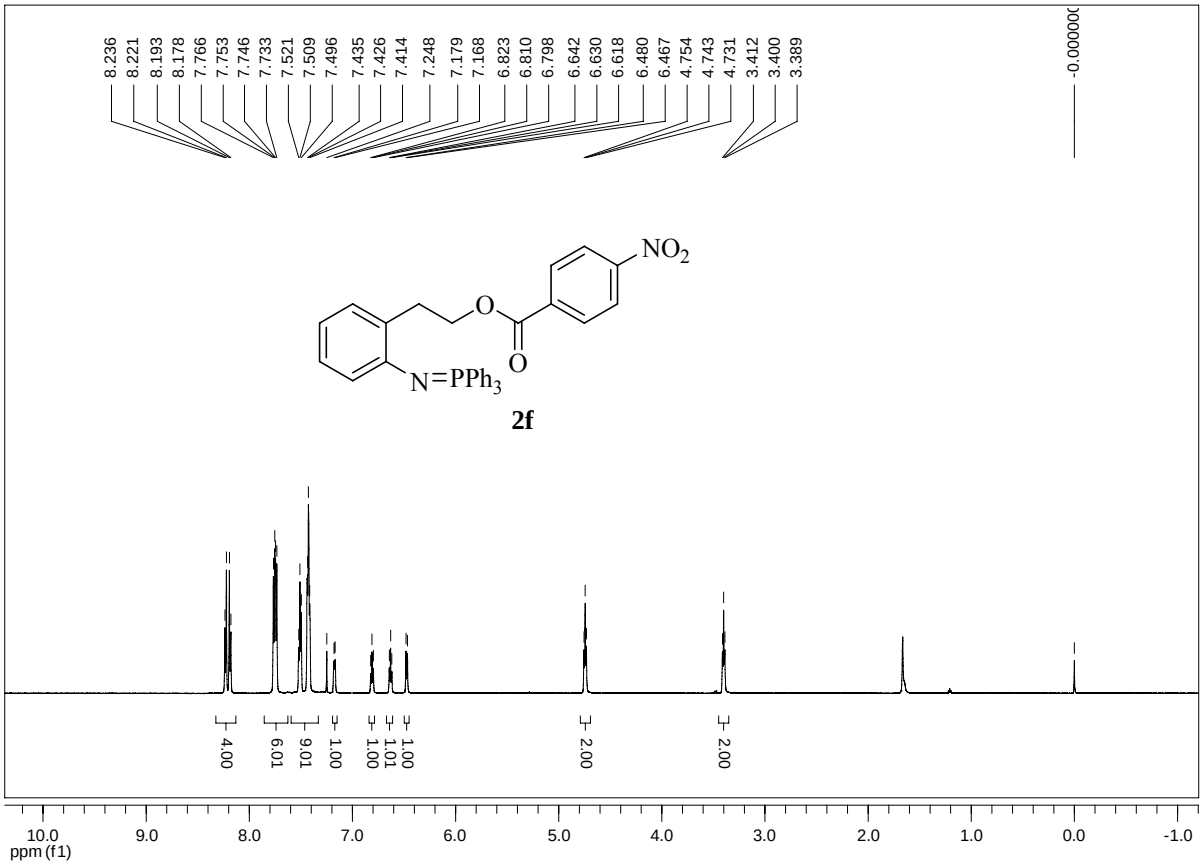
11.10
1.00
1.00
1.00
1.00
1.97
1.98
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
ppm (f1)

2e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7.733
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7.509
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7.435
7.426
7.414
7.248
7.179
7.168
6.823
6.810
6.798
6.642
6.630
6.618
6.480
6.467
4.754
4.743
4.731
3.412
3.400
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O
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1.00
1.01
1.00
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2.00
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7.0
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4.0
3.0
2.0
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0.0
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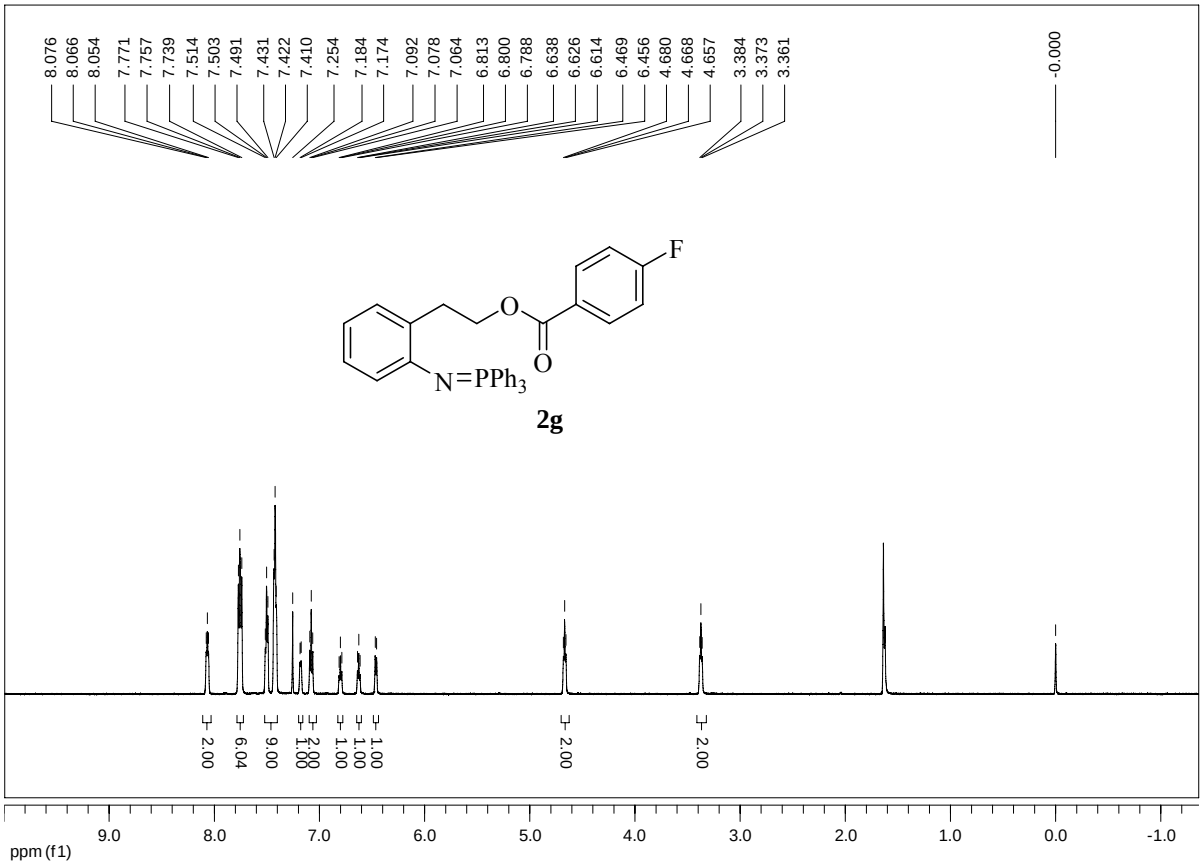
ppm (f1)

2f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7.514
7.503
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7.422
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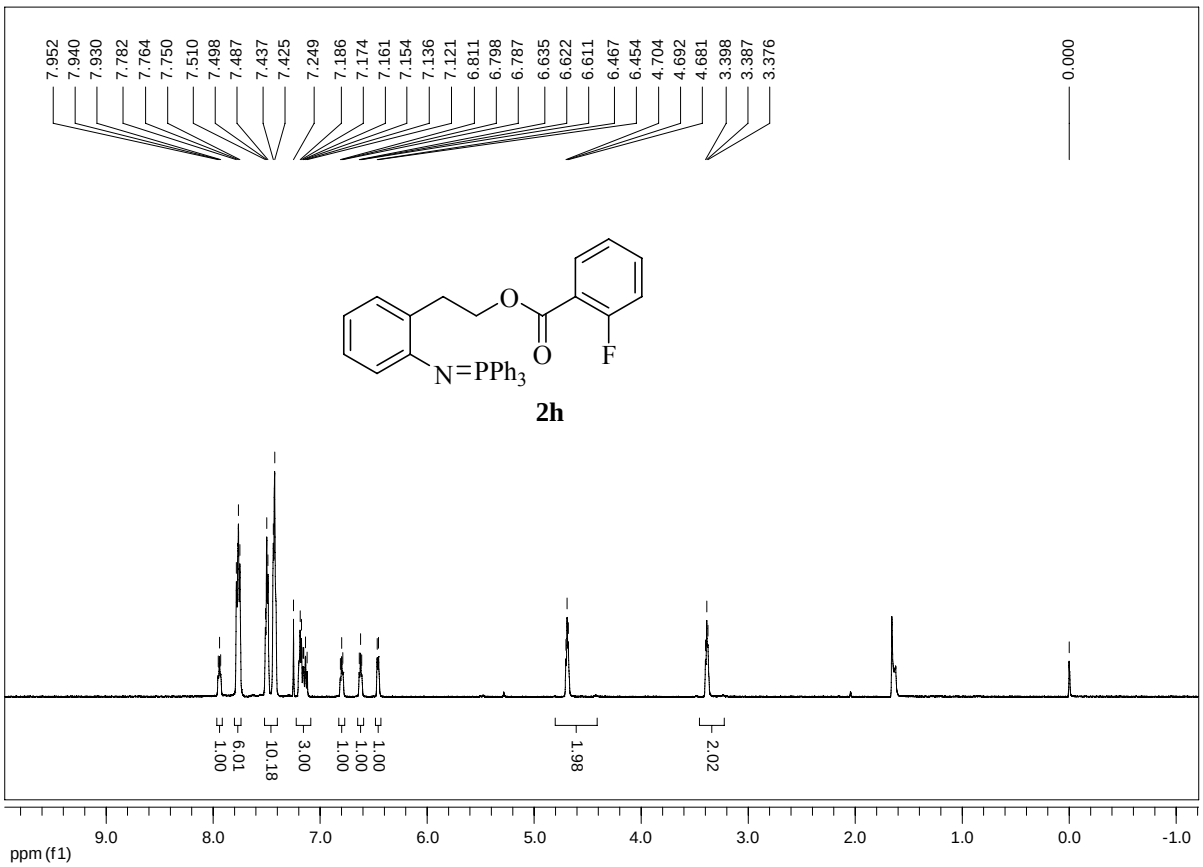
7.184
7.174
7.092
7.078
7.064
6.813
6.800
6.788
6.638
6.626
6.614
6.469
6.456
4.680
4.668
4.657
3.384
3.373
3.361
-0.000
F
O
O
N=PPh3
2.00
6.04
9.00
2.00
1.00
1.00
1.00
2.00
2.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
ppm (f1)

2g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7.174
7.161
7.154
7.136
7.121
6.811
6.798
6.787
6.635
6.622
6.611
6.467
6.454
4.704
4.692
4.681
3.398
3.387
3.376
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O
F
N=PPh3
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3.00
1.00
1.00
1.00
1.98
2.02
9.0
8.0
7.0
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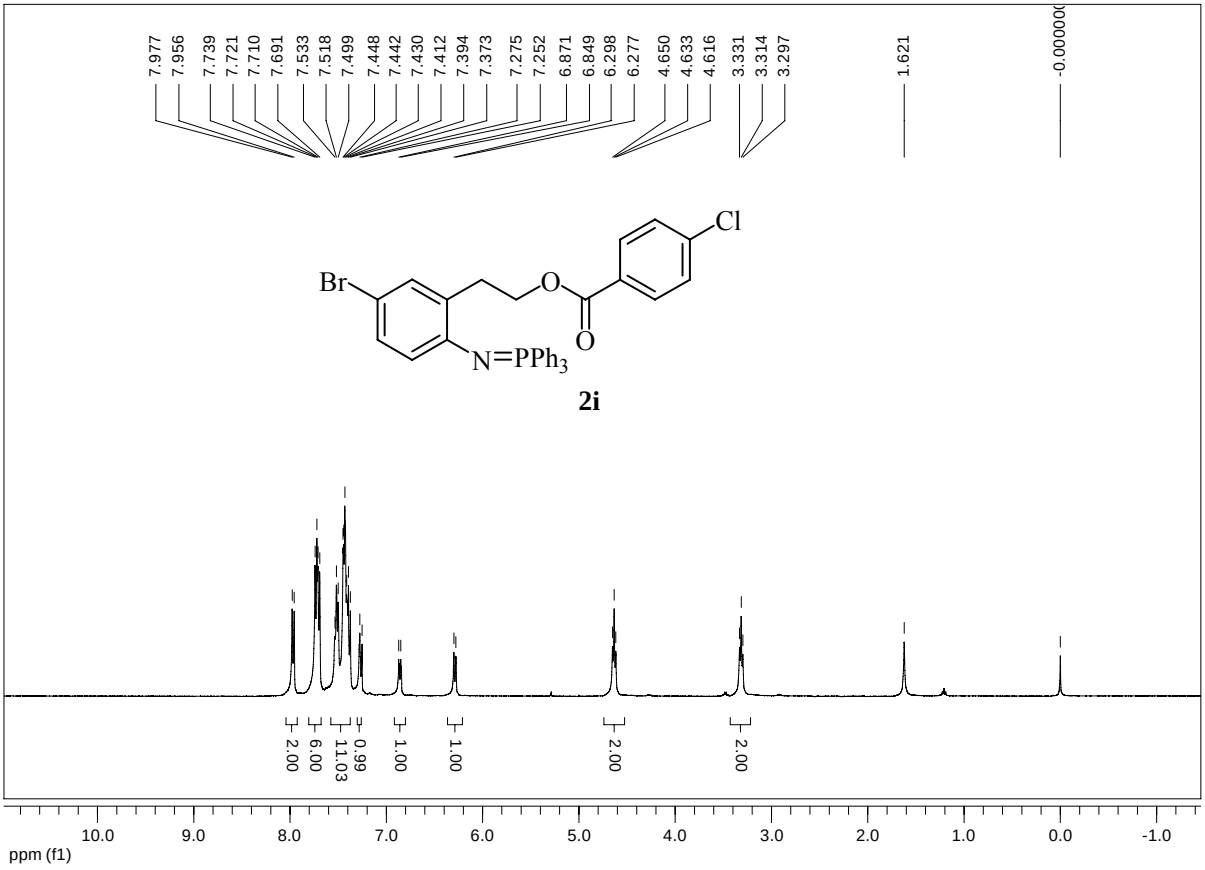
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
ppm (f1)

2h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7.430
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7.373
7.275
7.252
6.871
6.849
6.298
6.277
4.650
4.633
4.616
3.331
3.314
3.297
1.621
-0.000000
Cl
Br
O
O
N=PPh3
2.00
6.00
11.03
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1.00
1.00
2.00
2.00
10.0
9.0
8.0
7.0
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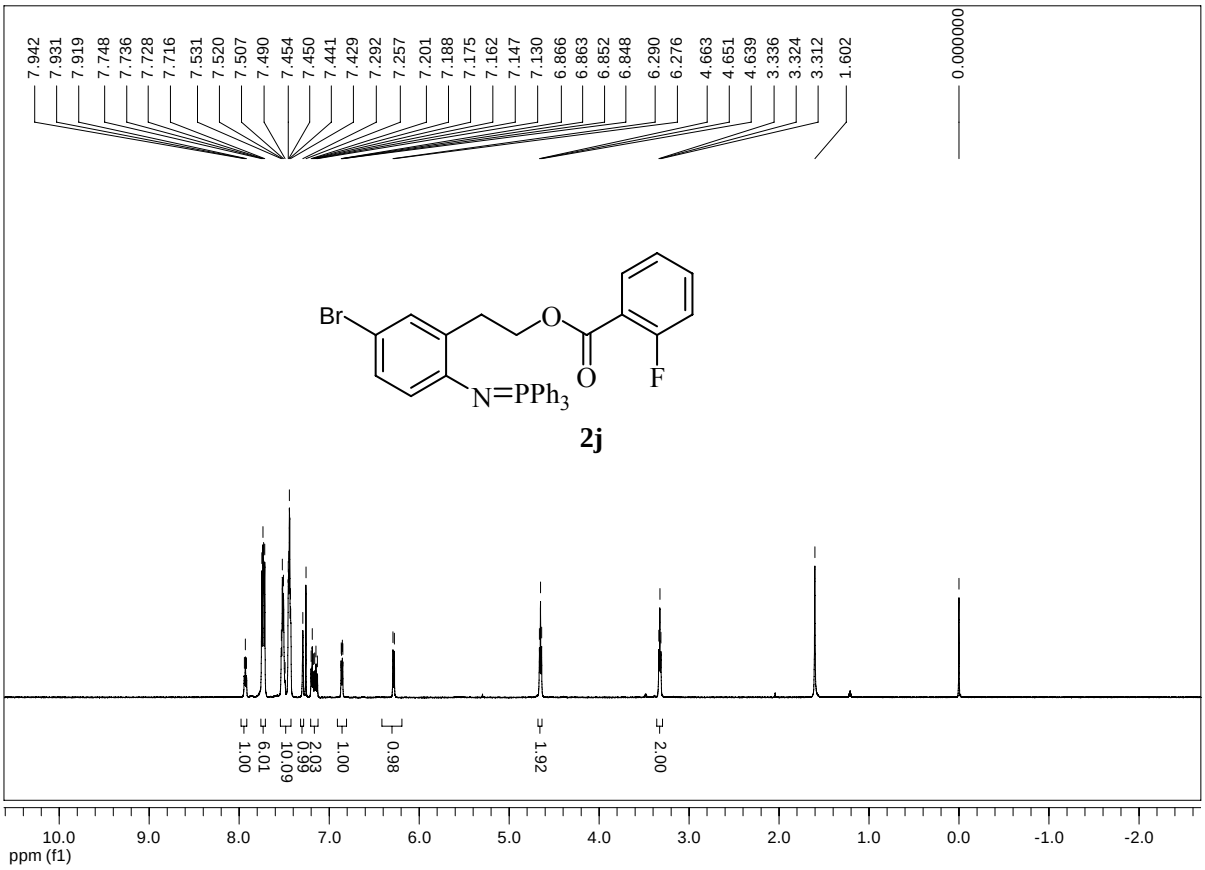
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
ppm (f1)

2i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7.454
7.450
7.441
7.429
7.292
7.257
7.201
7.188
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6.848
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3.324
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O
F
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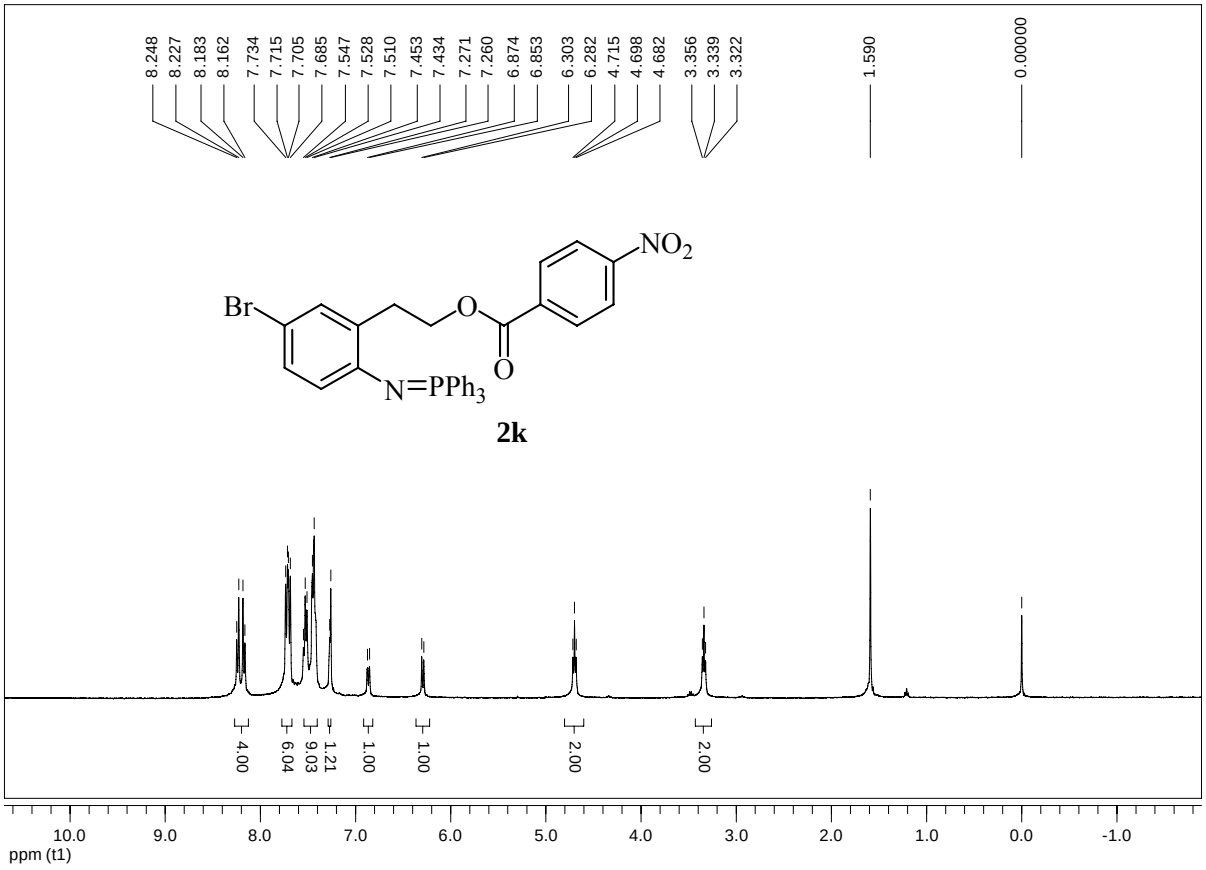
6.01
10.09
2.03
0.99
1.00
0.98
1.92
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
ppm (f1)

2j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7.528
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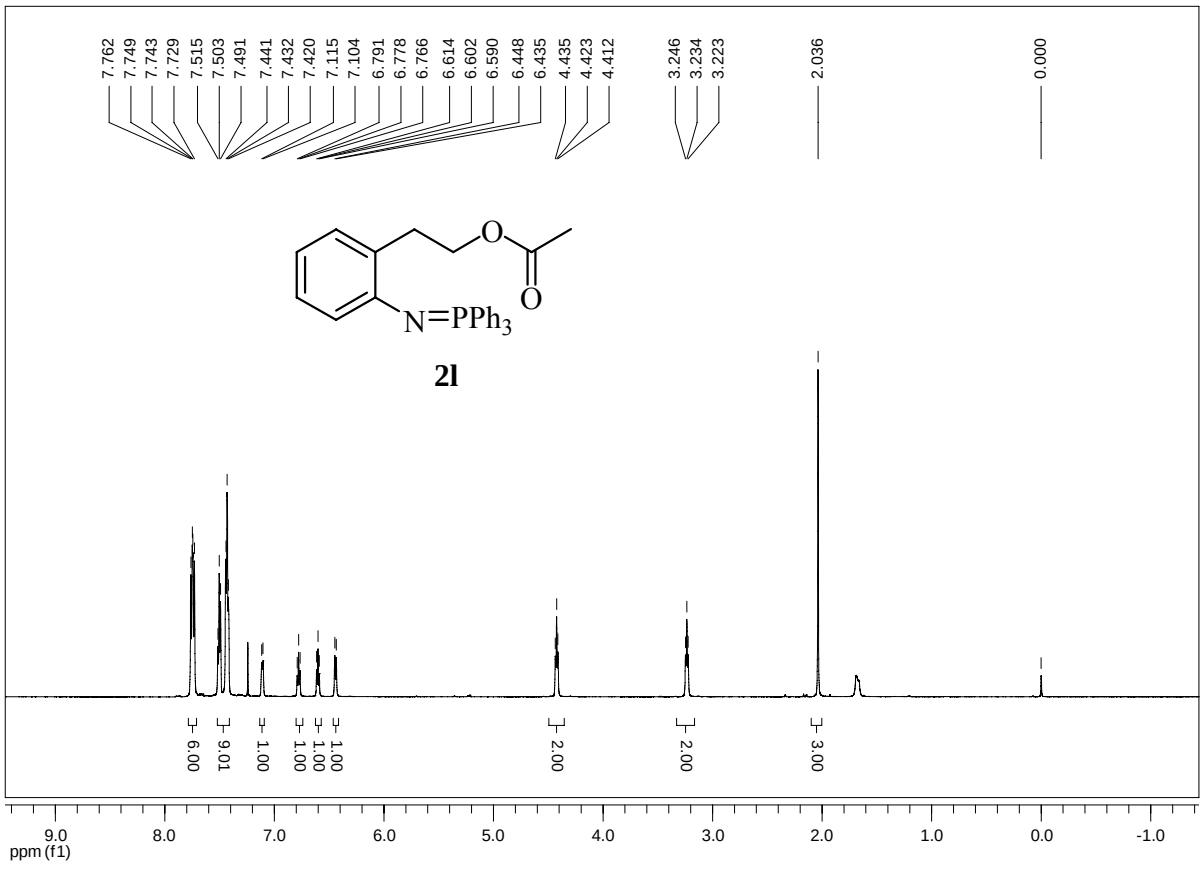
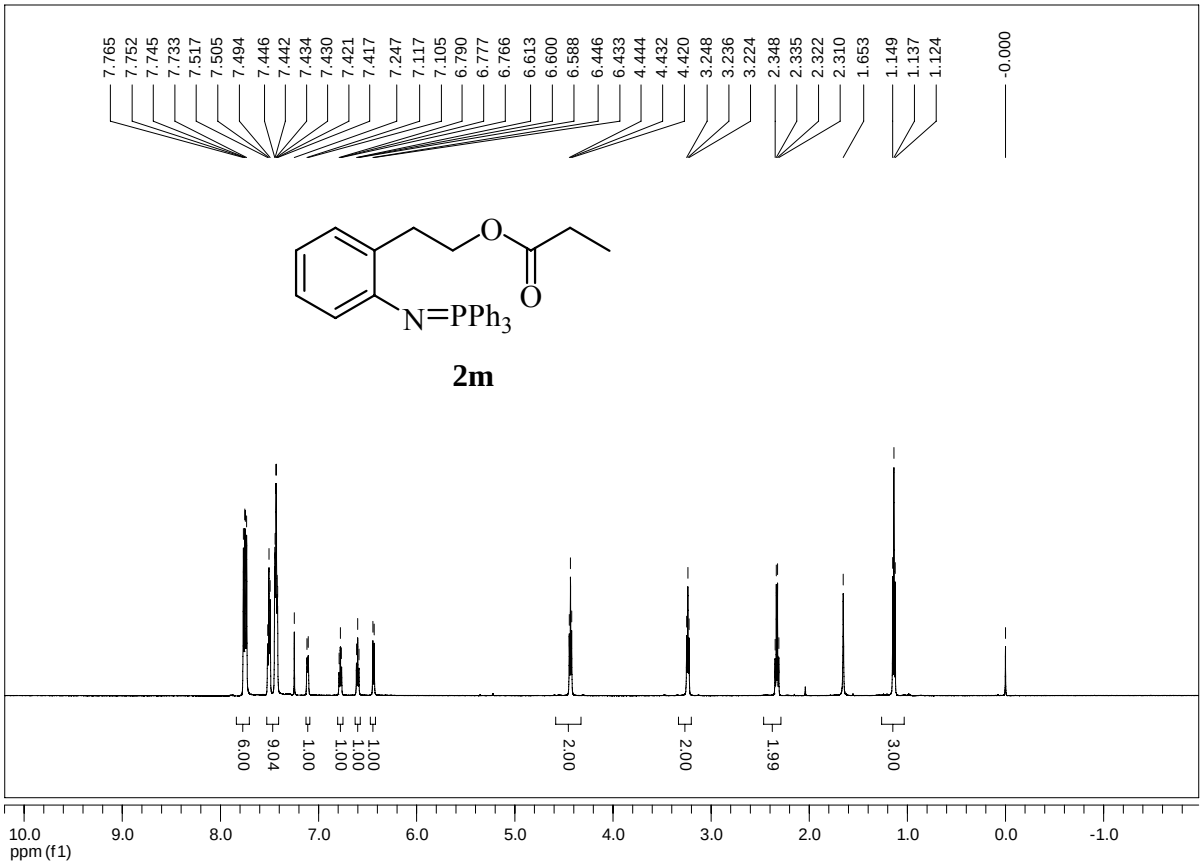
7.453
7.434
7.271
7.260
6.874
6.853
6.303
6.282
4.715
4.698
4.682
3.356
3.339
3.322
1.590
0.00000
NO2
Br
O
O
N=PPh3
4.00
9.04
6.03
1.21
1.00
1.00
2.00
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
ppm (t1)

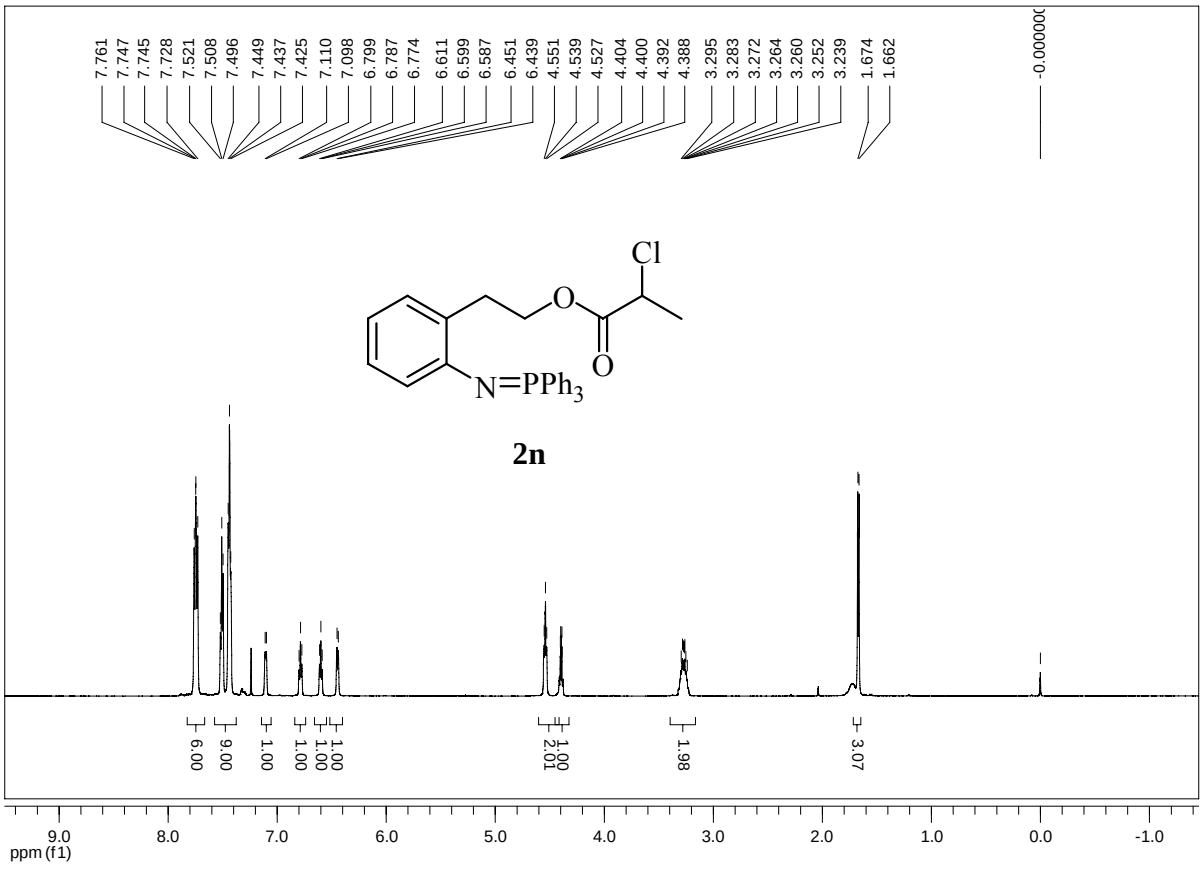
2k


7.762
7.749
7.743
7.729
7.515
7.503
7.491
7.441
7.432
7.420
7.115
7.104
6.791
6.778
6.766
6.614
6.602
6.590
6.448
6.435
4.435
4.423
4.412
3.246
3.234
3.223
2.036
0.000
O
O
N=PPh3
6.00
9.01
1.00
1.00
1.00
2.00
2.00
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
ppm (f1)

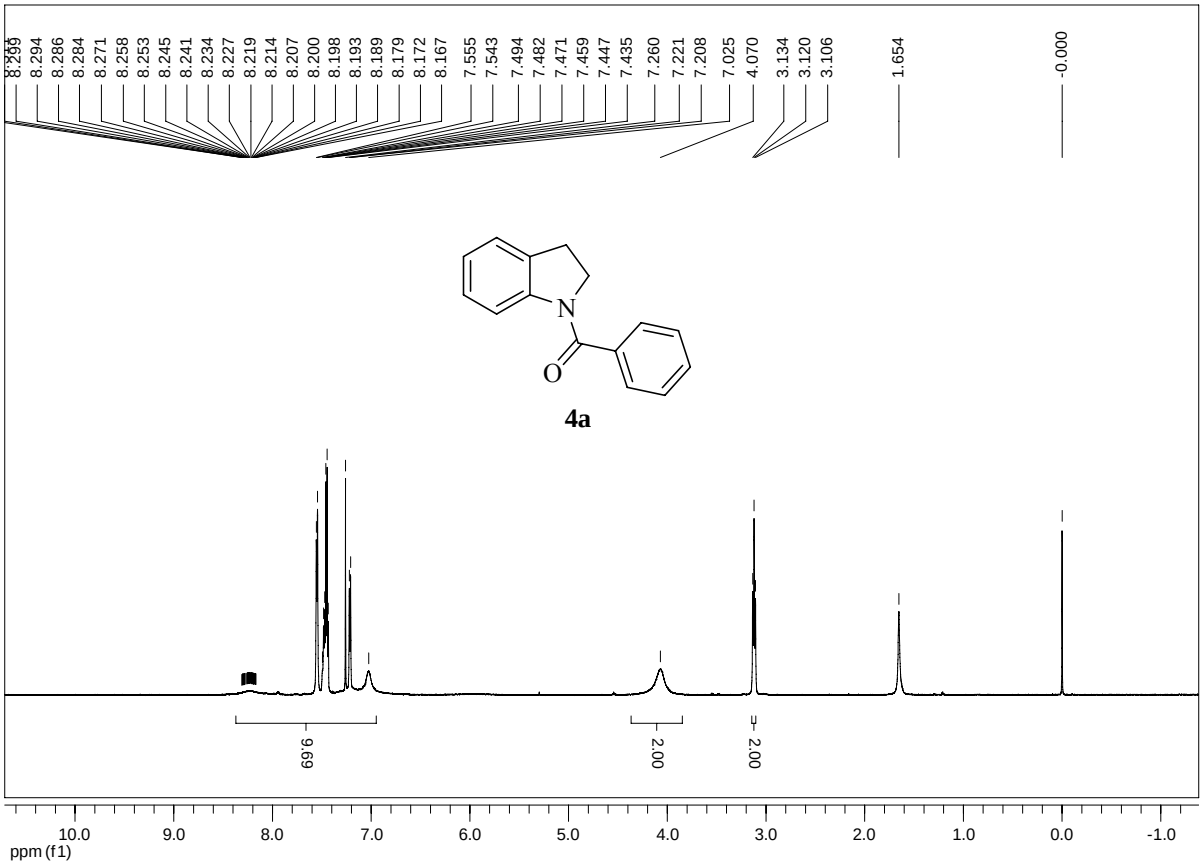
2l


7.765
7.752
7.745
7.733
7.517
7.505
7.494
7.446
7.442
7.434
7.430
7.421
7.417
7.247
7.117
7.105
6.790
6.777
6.766
6.613
6.600
6.588
6.446
6.433
4.444
4.432
4.420
3.248
3.236
3.224
2.348
2.335
2.322
2.310
1.653
1.149
1.137
1.124
-0.000
O
O
N=PPh3
6.00
9.04
1.00
1.00
1.00
1.00
2.00
2.00
1.99
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
ppm (f1)

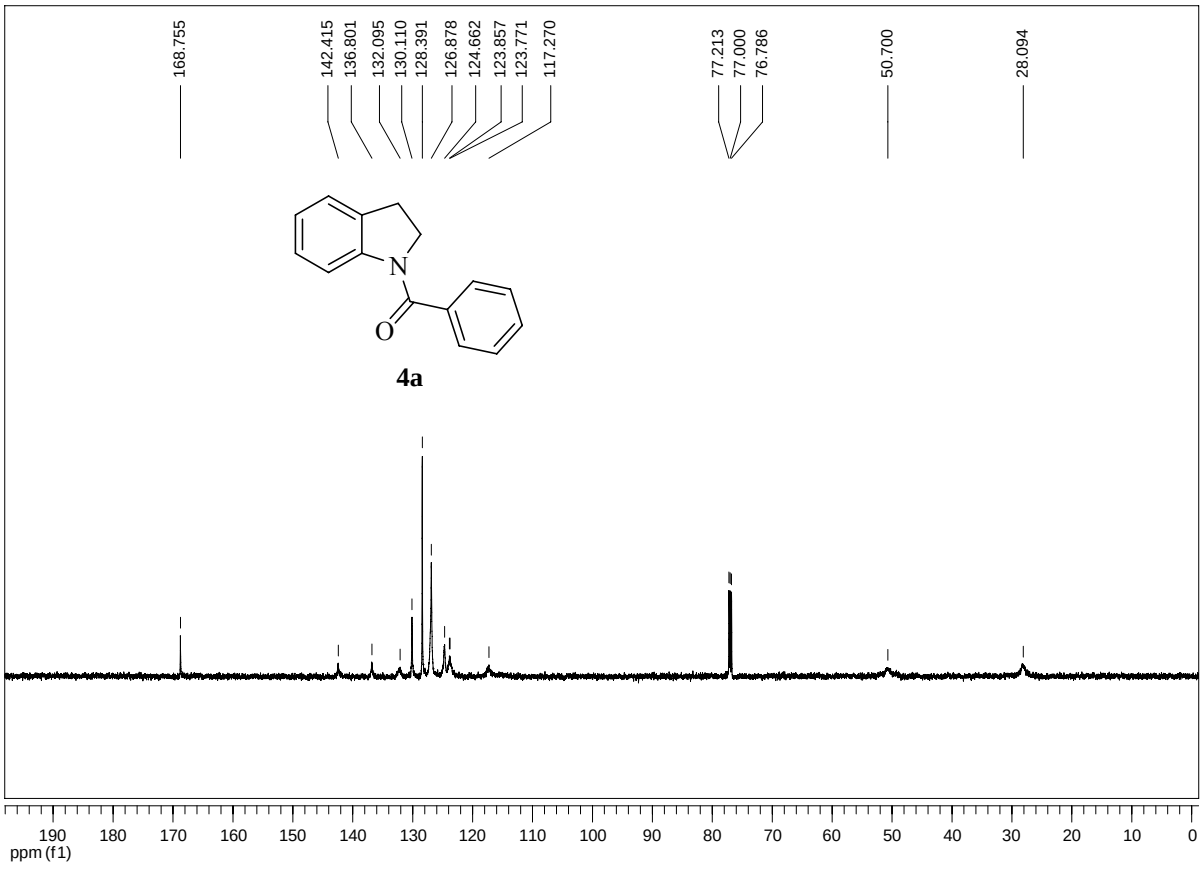
2m


7.761
7.747
7.745
7.728
7.521
7.508
7.496
7.449
7.437
7.425
7.110
7.098
6.799
6.787
6.774
6.611
6.599
6.587
6.451
6.439
4.551
4.539
4.527
4.404
4.400
4.392
4.388
3.295
3.283
3.272
3.264
3.260
3.252
3.239
1.674
1.662
-0.000000
Cl
O
O
N=PPh3
6.00
9.00
1.00
1.00
1.00
1.00
1.00
2.01
1.98
3.07
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
ppm (f1)

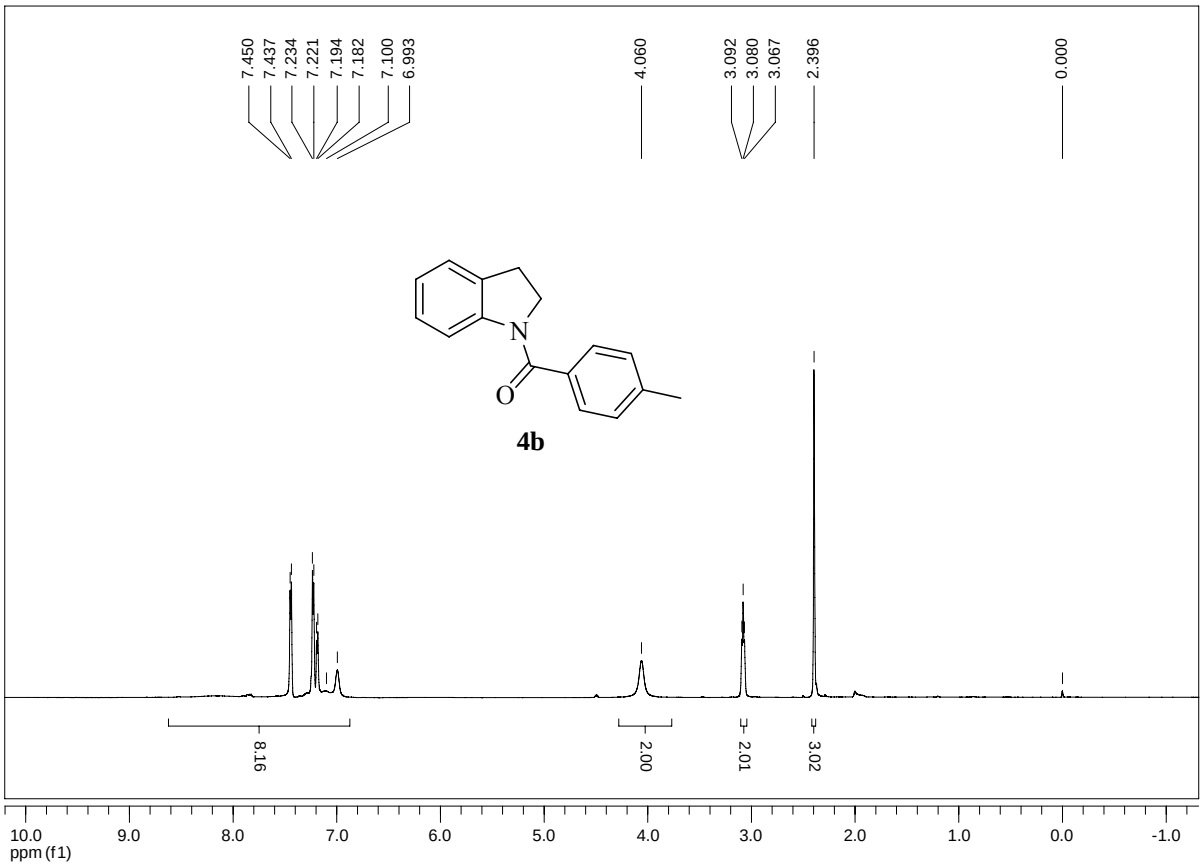
2n


8.299
8.294
8.286
8.284
8.271
8.258
8.253
8.245
8.241
8.234
8.227
8.219
8.214
8.207
8.200
8.198
8.193
8.189
8.179
8.172
8.167
7.555
7.543
7.494
7.482
7.471
7.459
7.447
7.435
7.260
7.221
7.208
7.025
4.070
3.134
3.120
3.106
1.654
-0.000
N
O
9.69
2.00
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
ppm (f1)

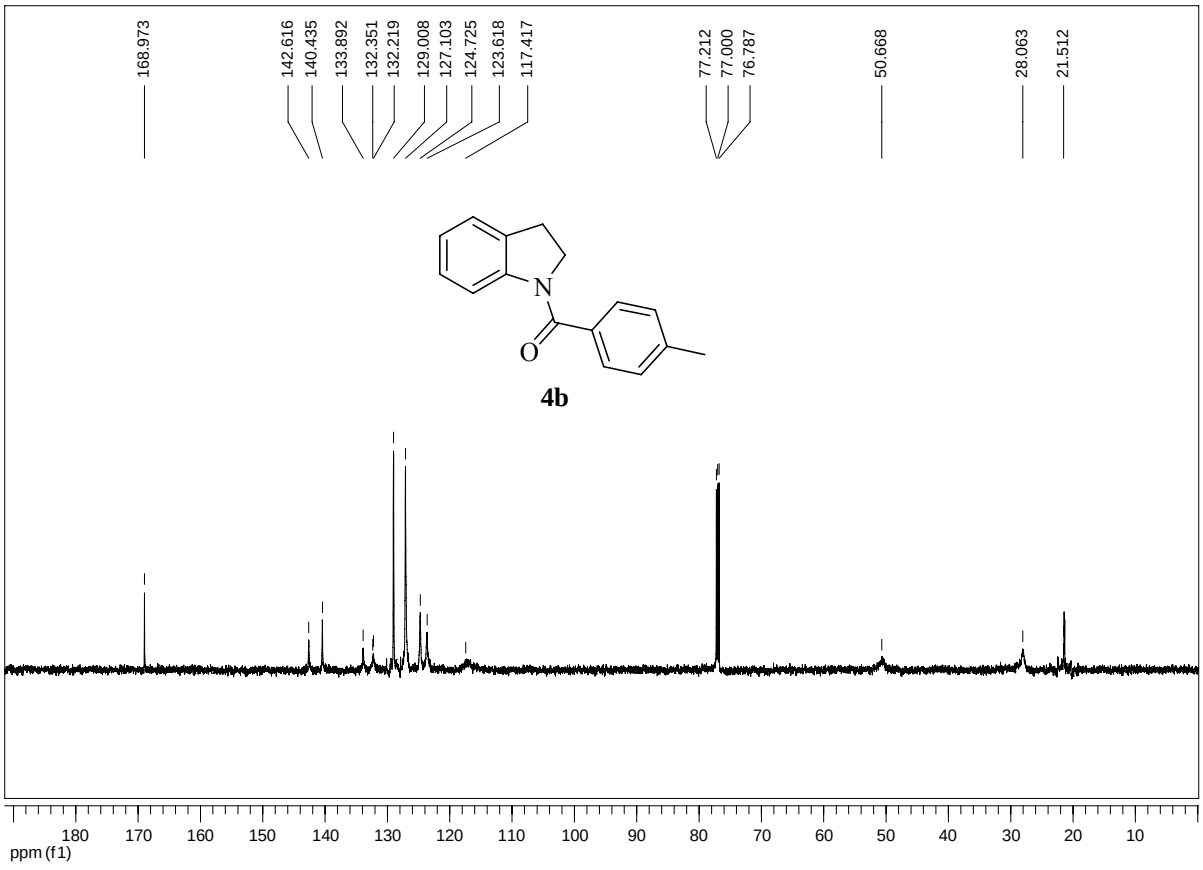
4a


168.755
142.415
136.801
132.095
130.110
128.391
126.878
124.662
123.857
123.771
117.270
77.213
77.000
76.786
50.700
28.094
N
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (f1)

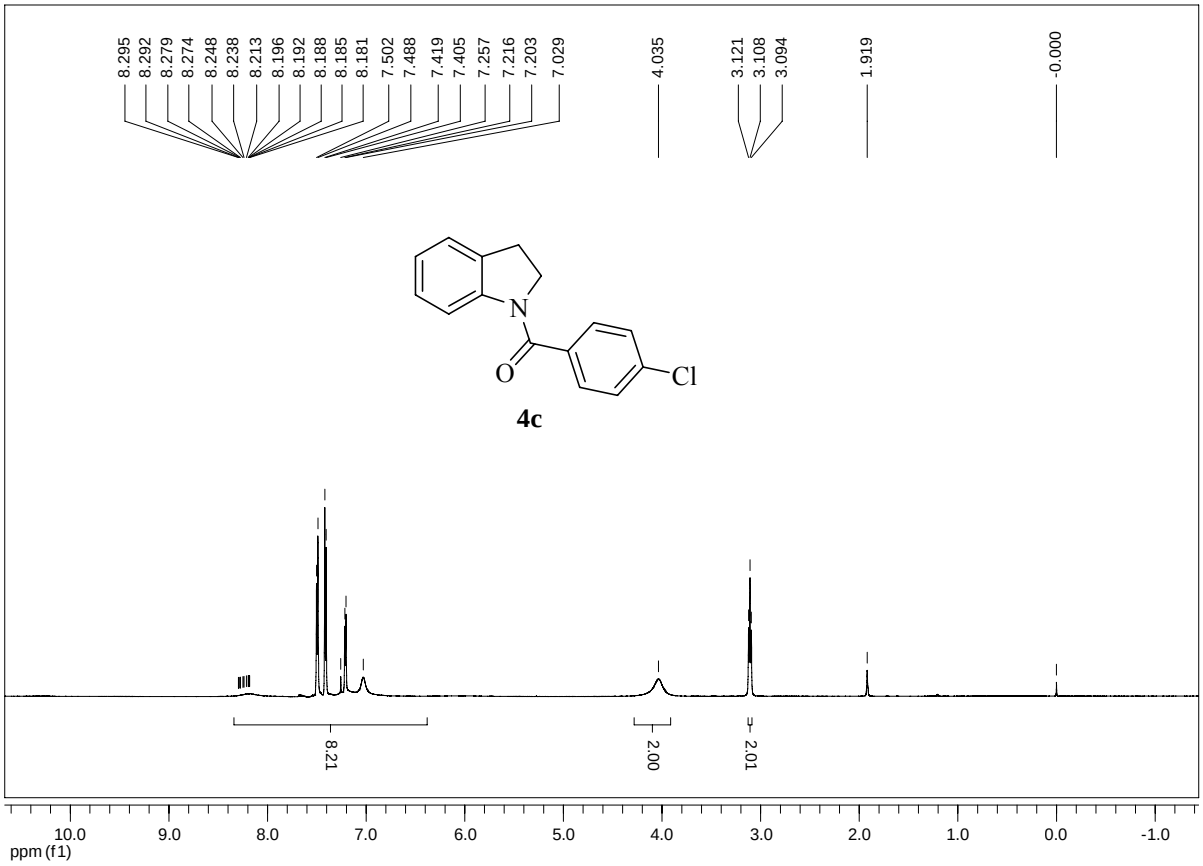
4a


7.450
7.437
7.234
7.221
7.194
7.182
7.100
6.993
4.060
3.092
3.080
3.067
2.396
0.000
8.16
2.00
2.01
3.02
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
ppm (f1)

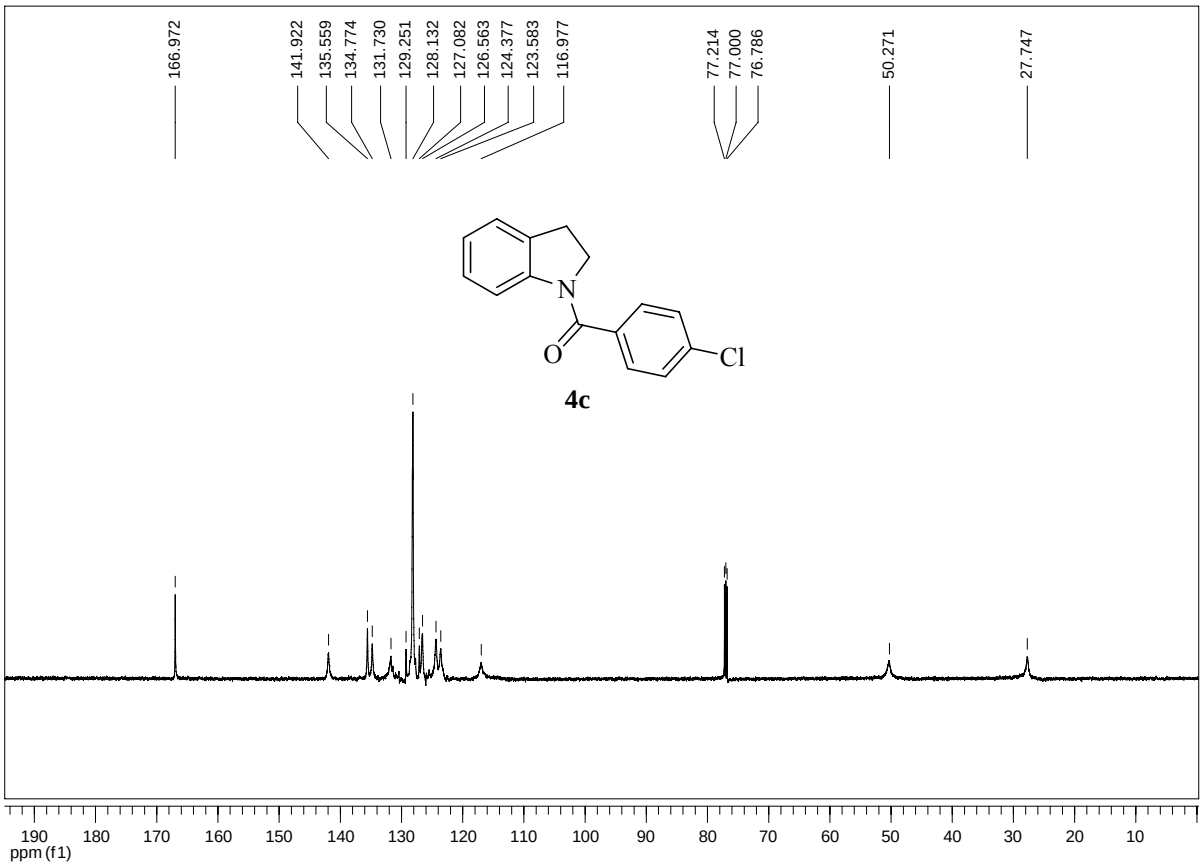
4b


168.973
142.616
140.435
133.892
132.351
132.219
129.008
127.103
124.725
123.618
117.417
77.212
77.000
76.787
50.668
28.063
21.512
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)

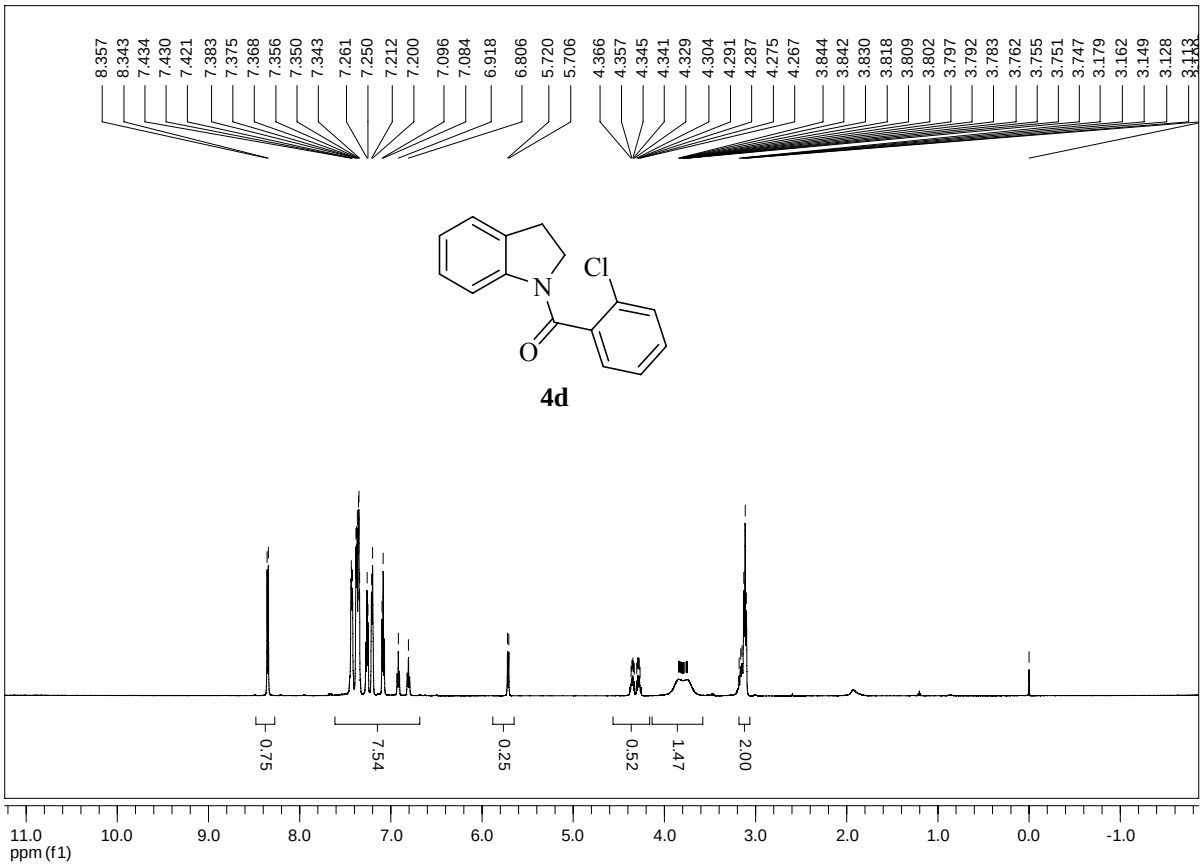
4b


8.295
8.292
8.279
8.274
8.248
8.238
8.213
8.196
8.192
8.188
8.185
8.181
7.502
7.488
7.419
7.405
7.257
7.216
7.203
7.029
4.035
3.121
3.108
3.094
1.919
-0.000
N
O
Cl
8.21
2.00
2.01
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
ppm (f1)

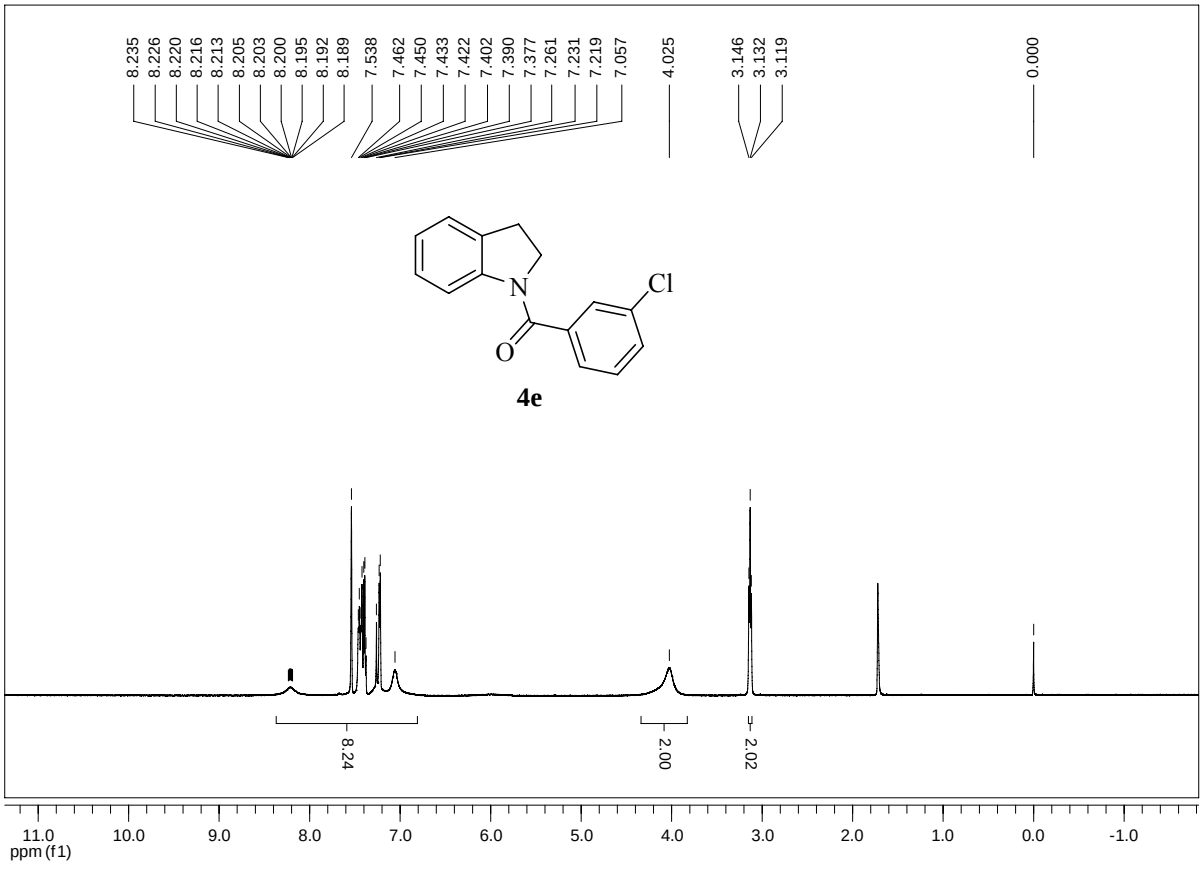
4c


166.972
141.922
135.559
134.774
131.730
129.251
128.132
127.082
126.563
124.377
123.583
116.977
77.214
77.000
76.786
50.271
27.747
N
O
Cl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)

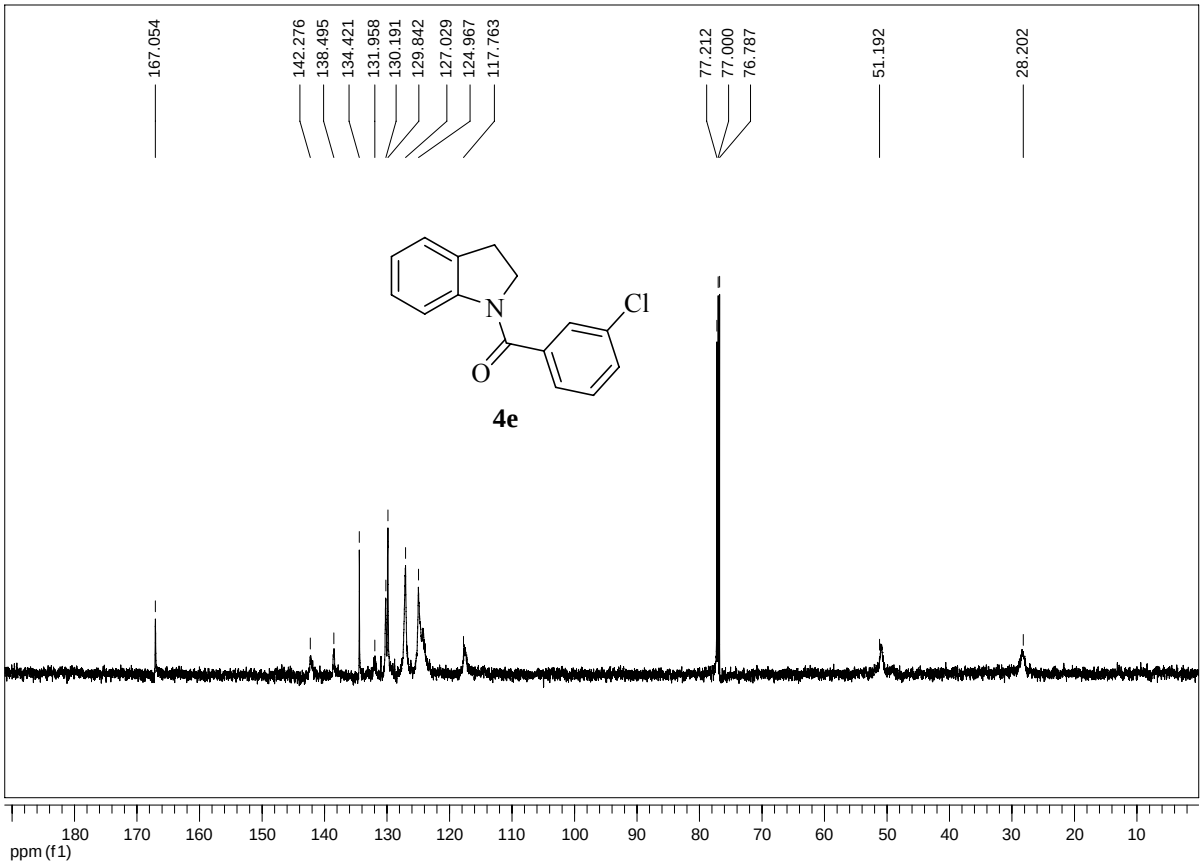
4c


8.357
8.343
7.434
7.430
7.421
7.383
7.375
7.368
7.356
7.350
7.343
7.261
7.250
7.212
7.200
7.096
7.084
6.918
6.806
5.720
5.706
4.366
4.357
4.345
4.341
4.329
4.304
4.291
4.287
4.275
4.267
3.844
3.842
3.830
3.818
3.809
3.802
3.797
3.792
3.783
3.762
3.755
3.751
3.747
3.179
3.162
3.149
3.128
Cl
N
O
0.75
7.54
0.25
0.52
1.47
2.00
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
ppm (f1)

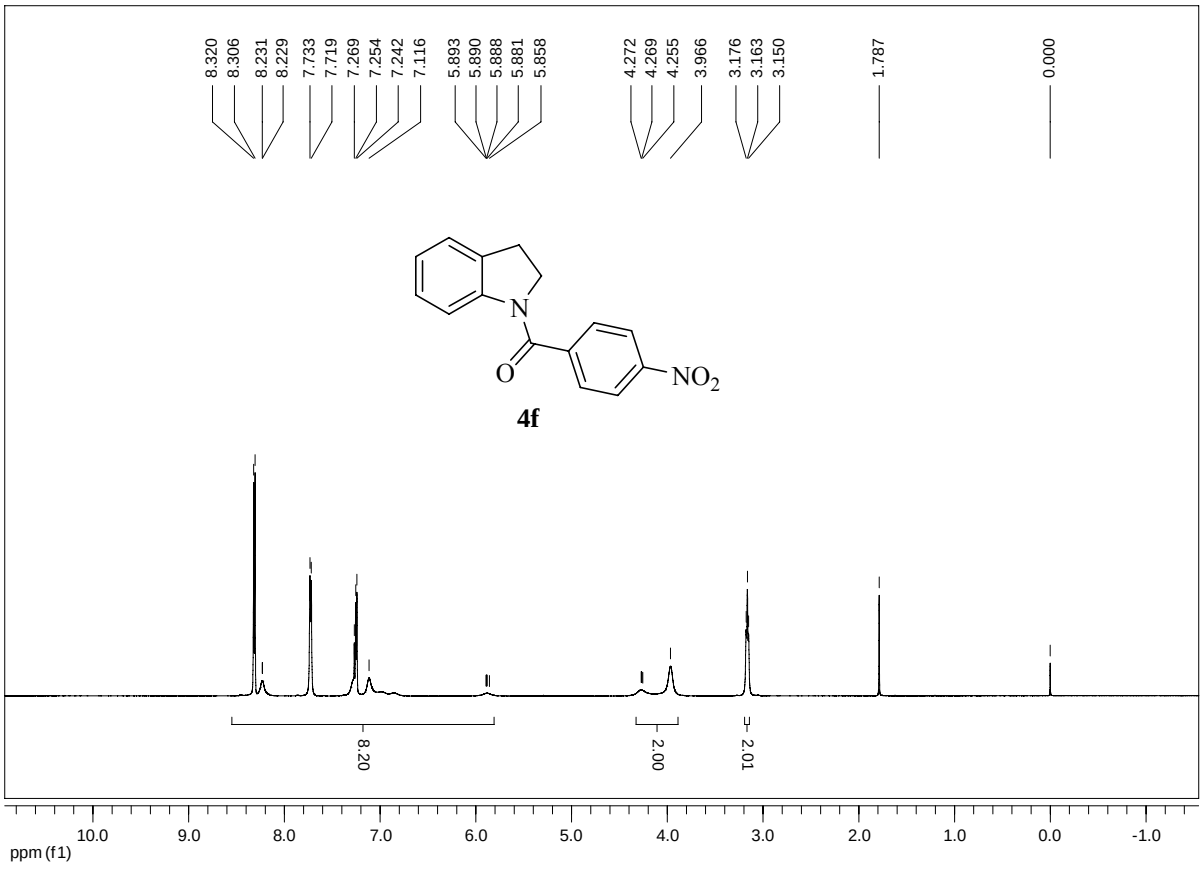
4d


8.235
8.226
8.220
8.216
8.213
8.205
8.203
8.200
8.195
8.192
8.189
7.538
7.462
7.450
7.433
7.422
7.402
7.390
7.377
7.261
7.231
7.219
7.057
4.025
3.146
3.132
3.119
0.000
Cl
N
O
8.24
2.00
2.02
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
ppm (f1)

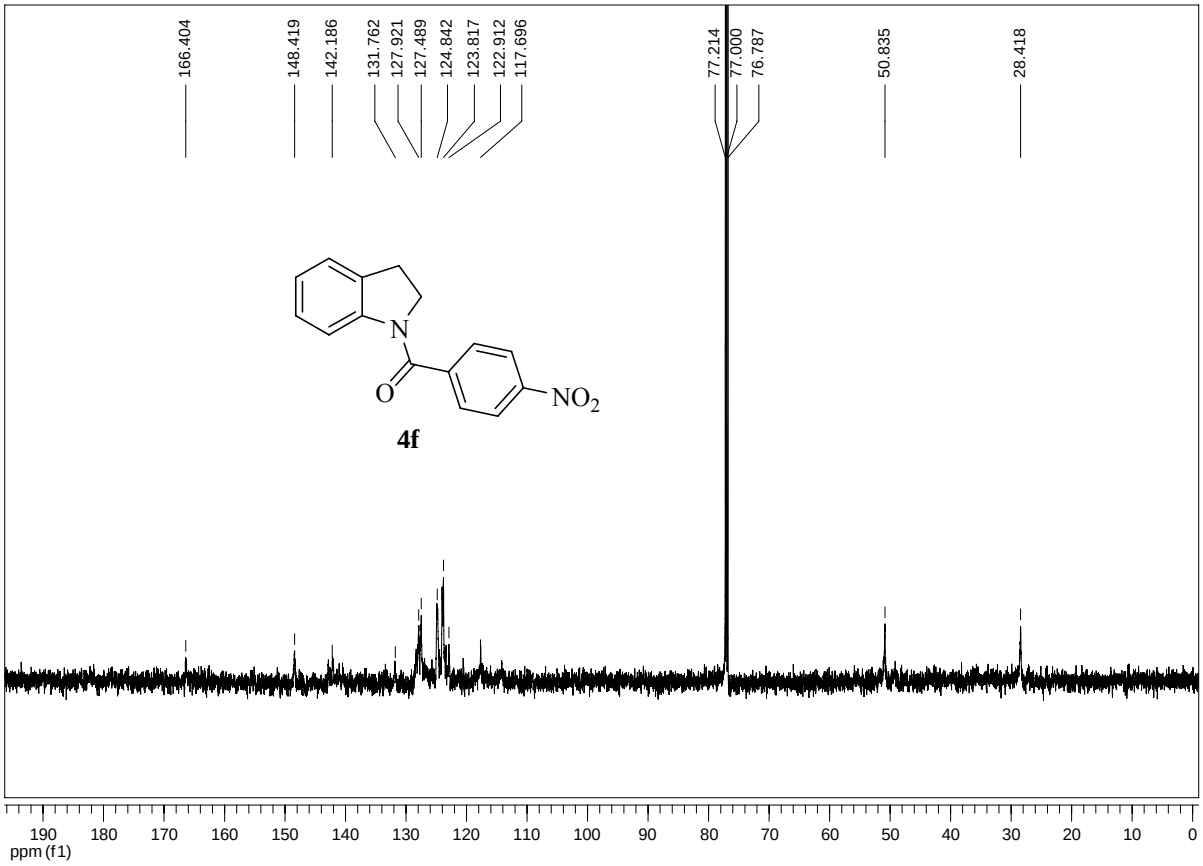
4e


167.054
142.276
138.495
134.421
131.958
130.191
129.842
127.029
124.967
117.763
77.212
77.000
76.787
51.192
28.202
N
O
Cl
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm (f1)

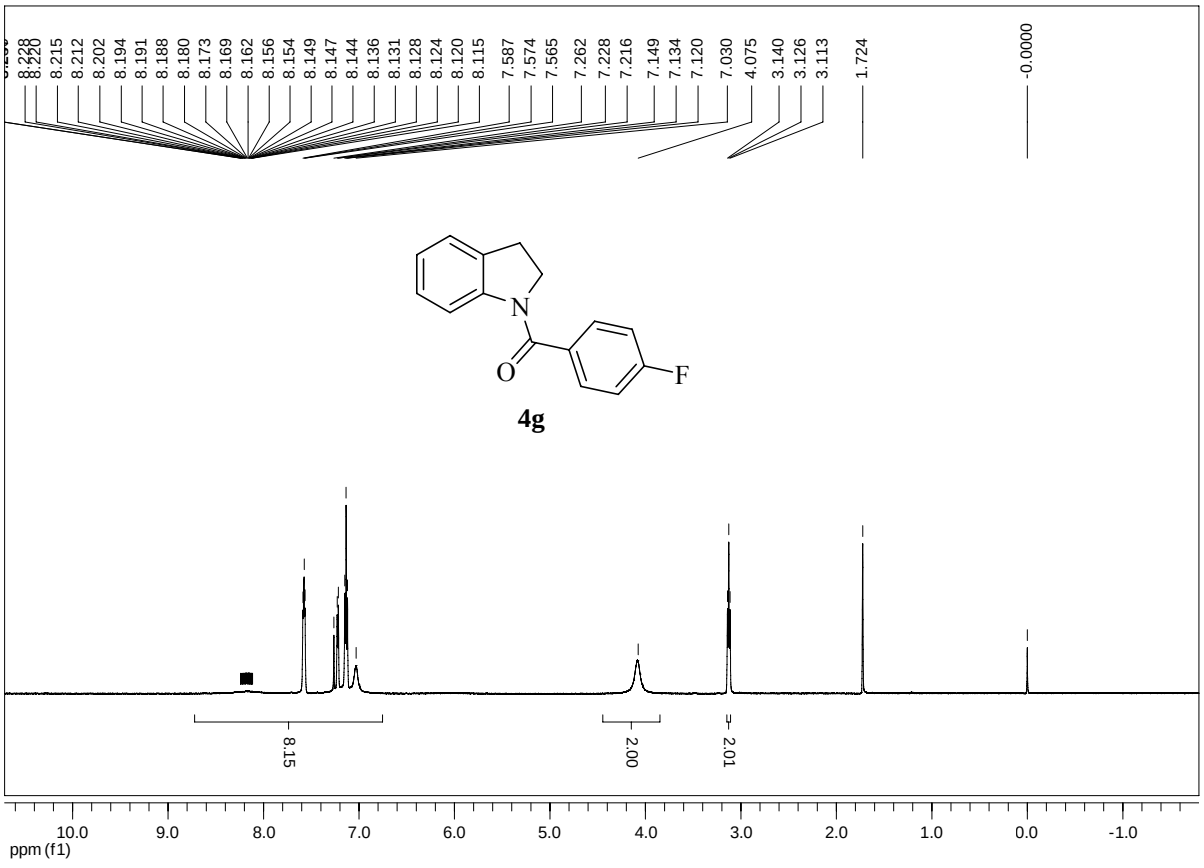
4e


8.320
8.306
8.231
8.229
7.733
7.719
7.269
7.254
7.242
7.116
5.893
5.890
5.888
5.881
5.858
4.272
4.269
4.255
3.966
3.176
3.163
3.150
1.787
0.000
N
O
NO2
8.20
2.00
2.01
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
ppm (f1)

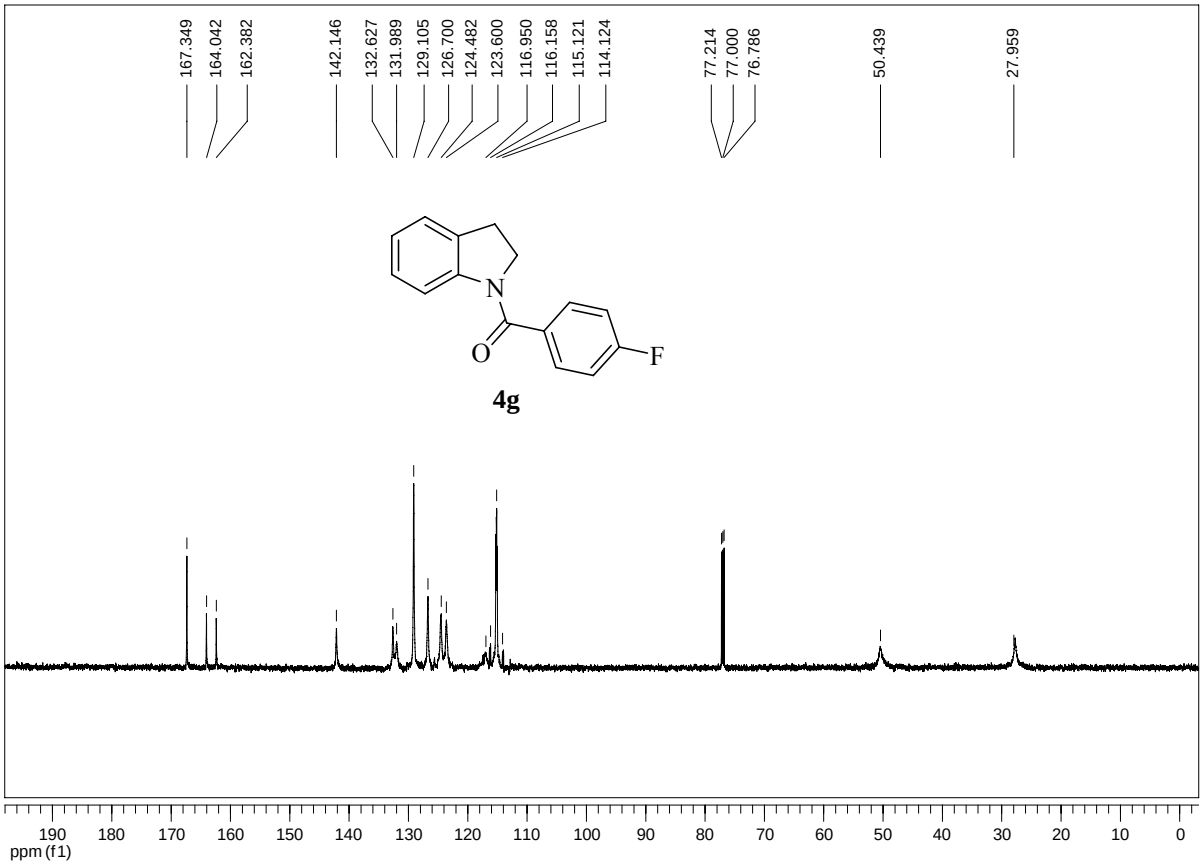
4f

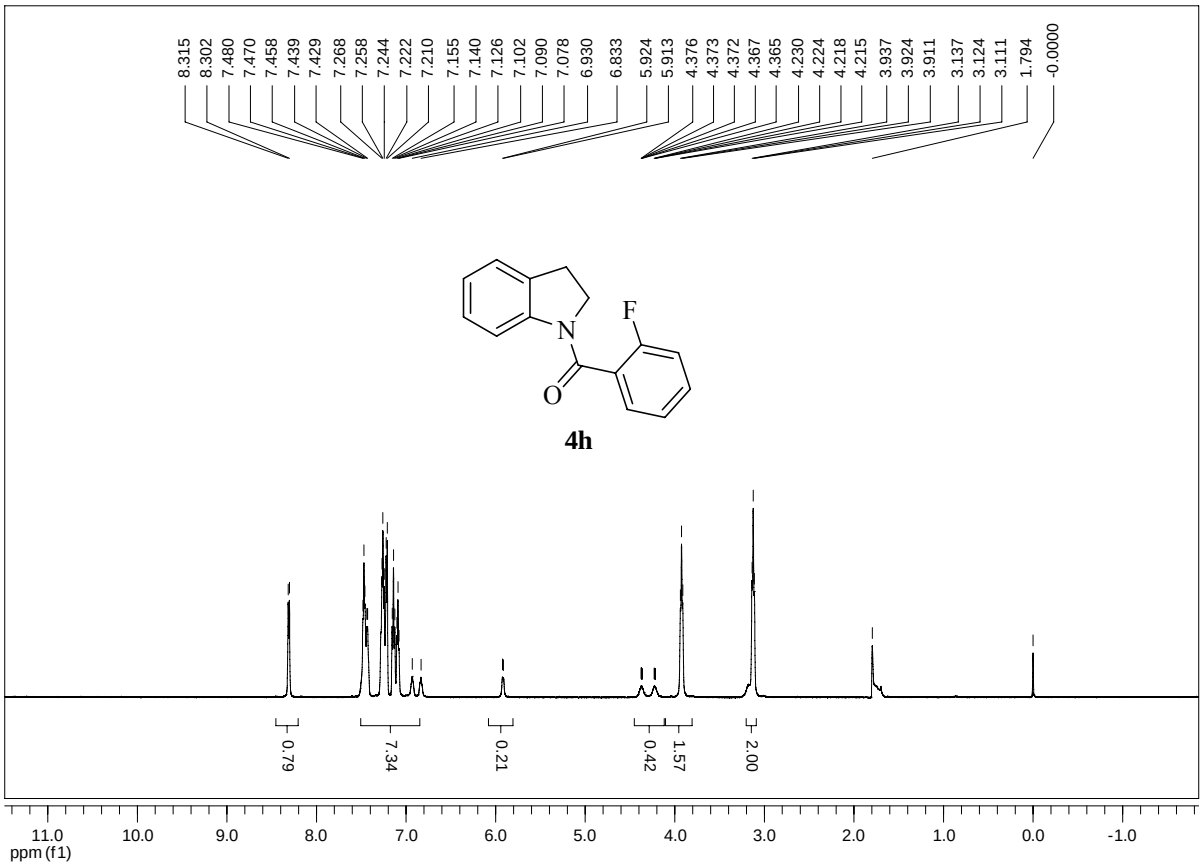

166.404
148.419
142.186
131.762
127.921
127.489
124.842
123.817
122.912
117.696
77.214
77.000
76.787
50.835
28.418
N
O
NO2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (f1)

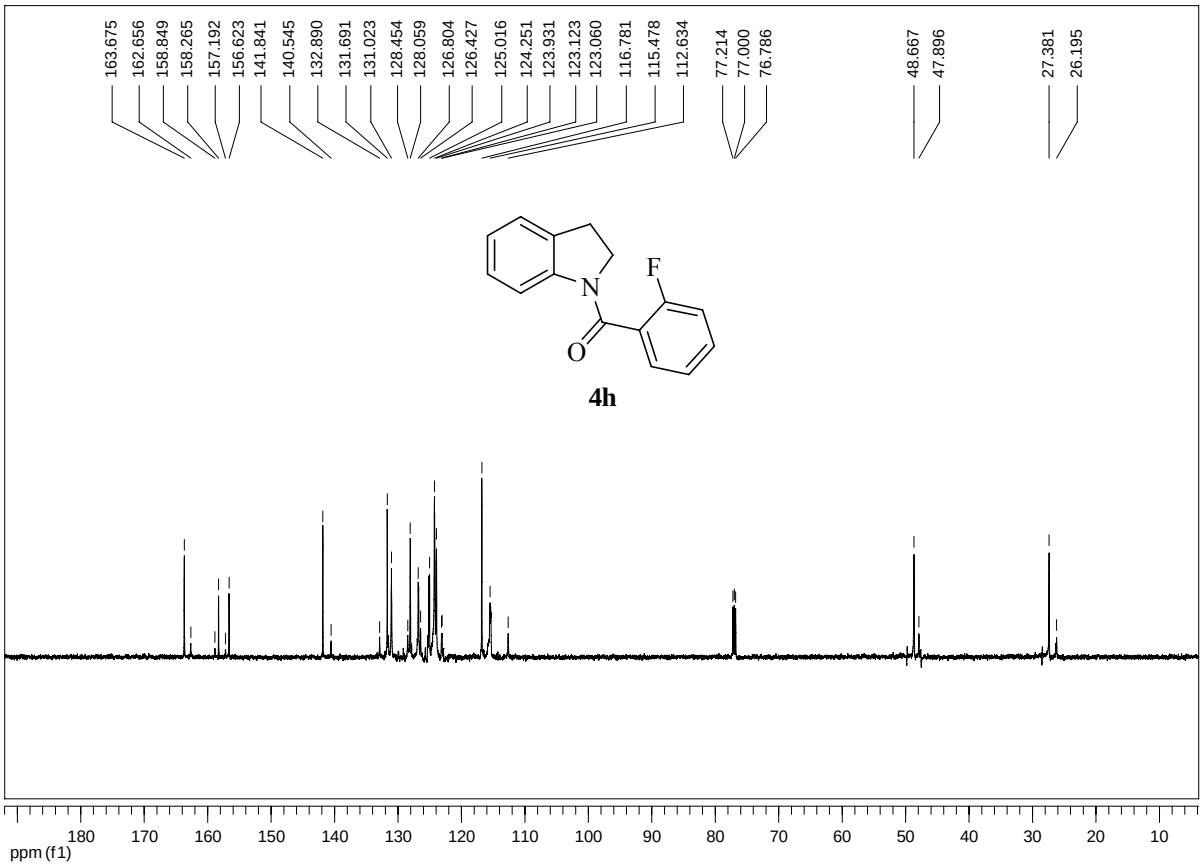
4f


8.228
8.220
8.215
8.212
8.202
8.194
8.191
8.188
8.180
8.173
8.169
8.162
8.156
8.154
8.149
8.147
8.144
8.136
8.131
8.128
8.124
8.120
8.115
7.587
7.574
7.565
7.262
7.228
7.216
7.149
7.134
7.120
7.030
4.075
3.140
3.126
3.113
1.724
-0.0000
N
O
F
8.15
2.00
2.01
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
ppm (f1)

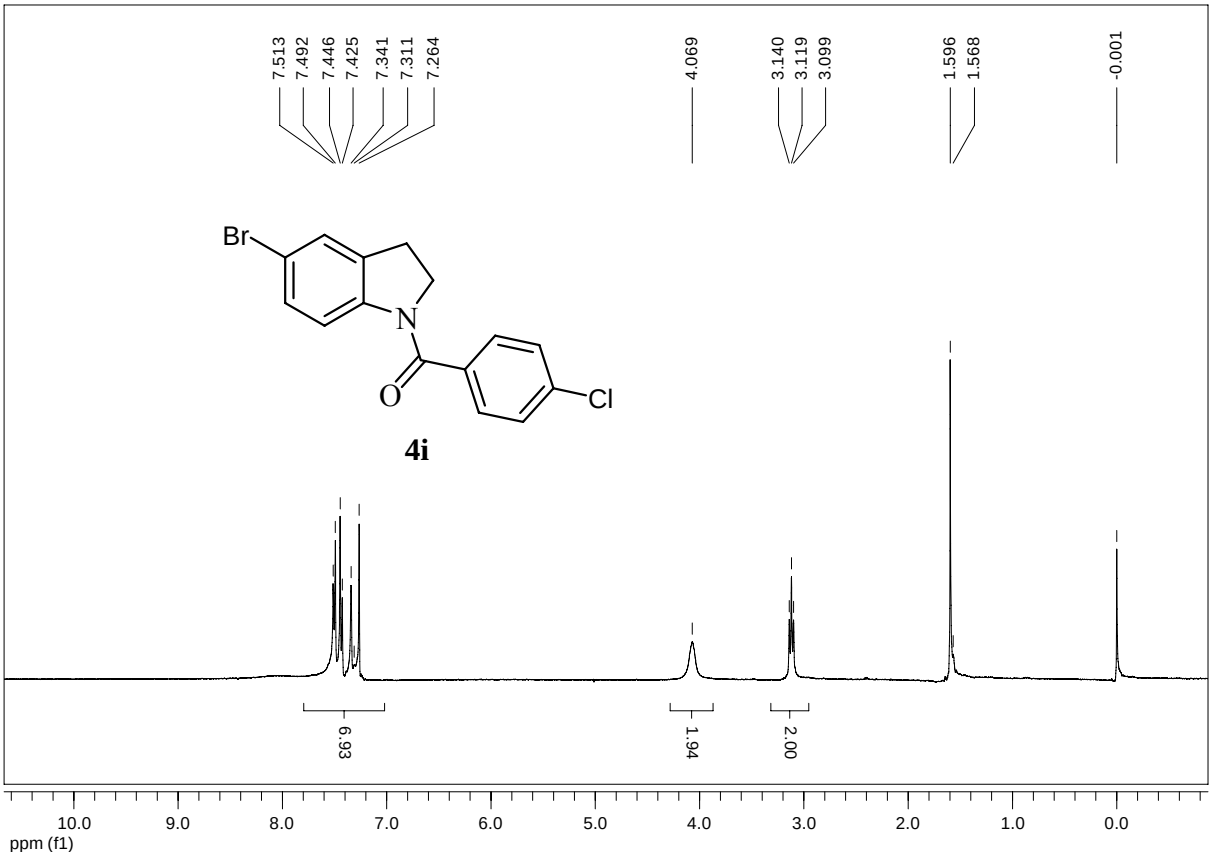
4g


167.349
164.042
162.382
142.146
132.627
131.989
129.105
126.700
124.482
123.600
116.950
116.158
115.121
114.124
77.214
77.000
76.786
50.439
27.959
N
O
F
4g
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (f1)

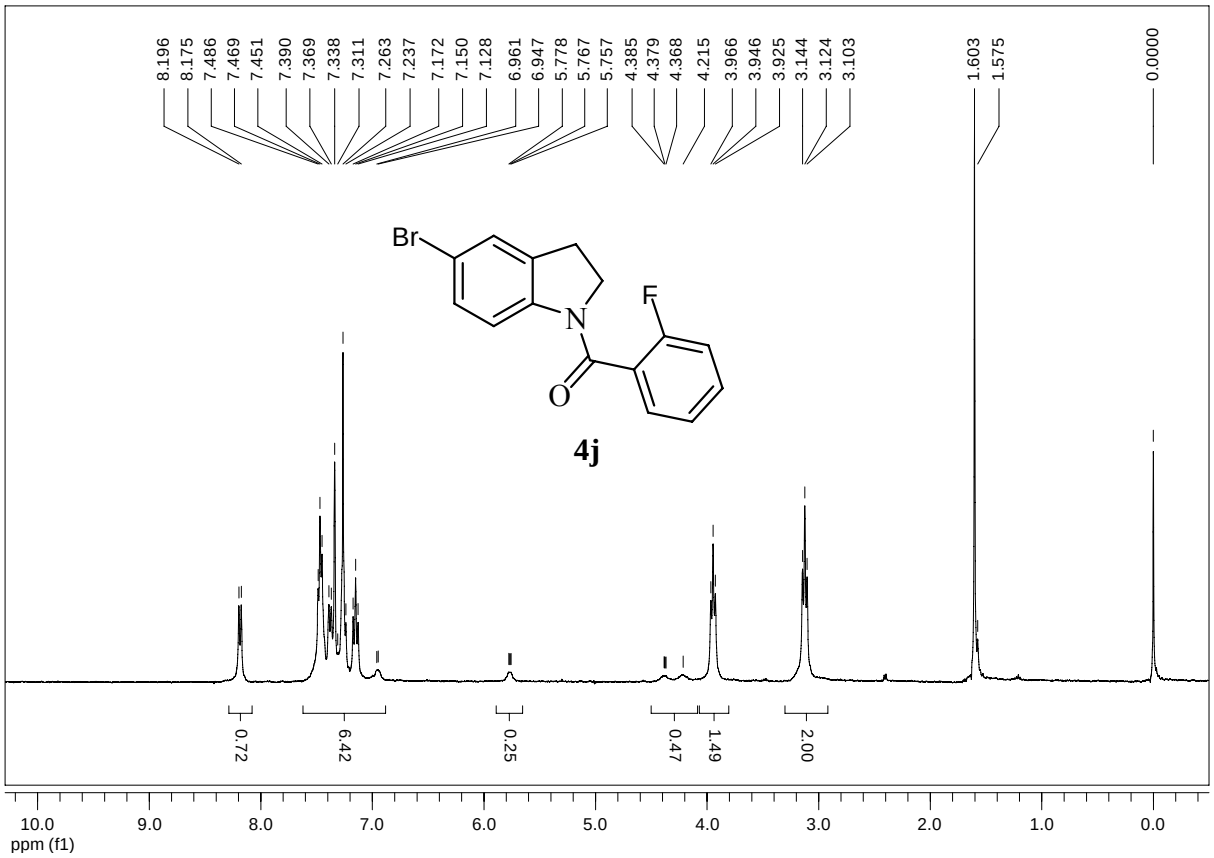

8.315
8.302
7.480
7.470
7.458
7.439
7.429
7.268
7.258
7.244
7.222
7.210
7.155
7.140
7.126
7.102
7.090
7.078
6.930
6.833
5.924
5.913
4.376
4.373
4.372
4.367
4.365
4.230
4.224
4.218
4.215
3.937
3.924
3.911
3.137
3.124
3.111
1.794
-0.0000
N
F
O
4h
0.79
7.34
0.21
0.42
1.57
2.00
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
ppm (f1)


163.675
162.656
158.849
158.265
157.192
156.623
141.841
140.545
132.890
131.691
131.023
128.454
128.059
126.804
126.427
125.016
124.251
123.931
123.123
123.060
116.781
115.478
112.634
77.214
77.000
76.786
48.667
47.896
27.381
26.195
F
N
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)

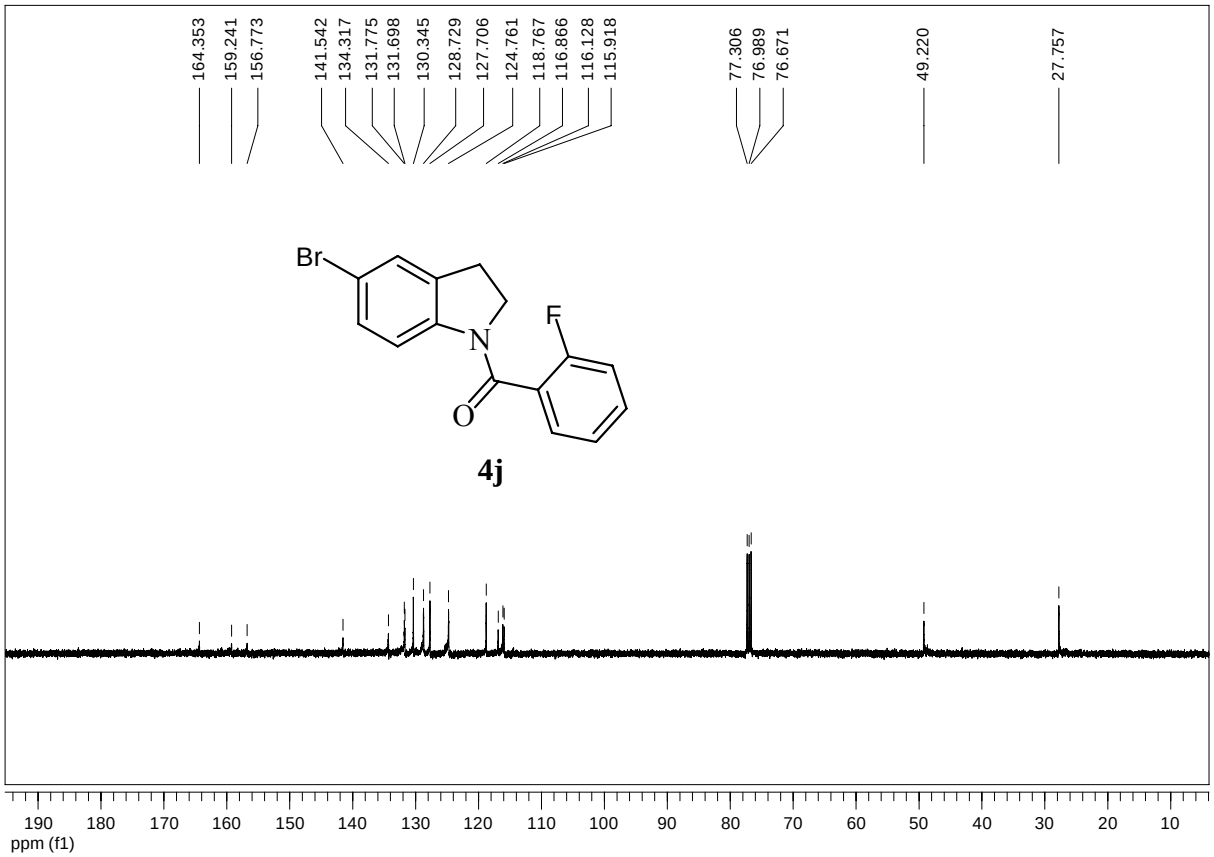
4h


7.513
7.492
7.446
7.425
7.341
7.311
7.264
4.069
3.140
3.119
3.099
1.596
1.568
-0.001
Br
N
O
Cl
6.93
1.94
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

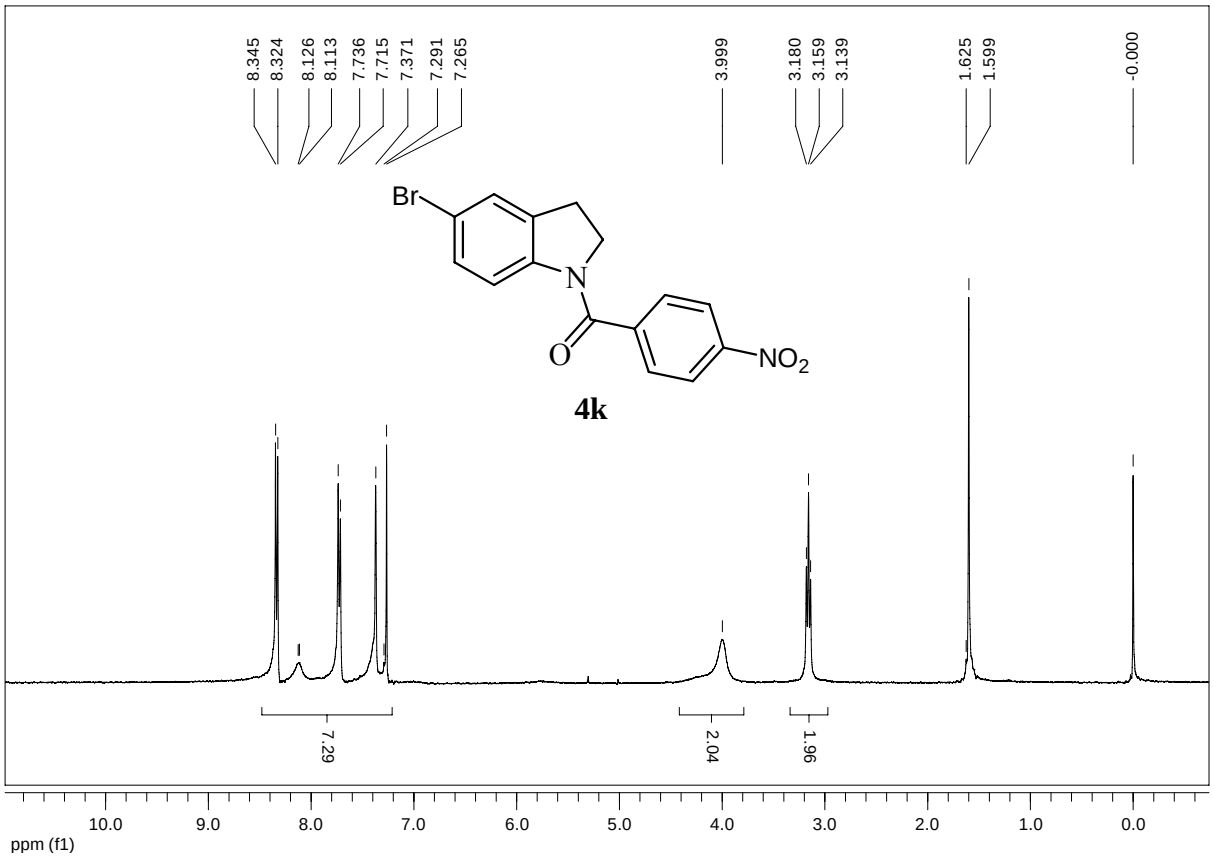
4i

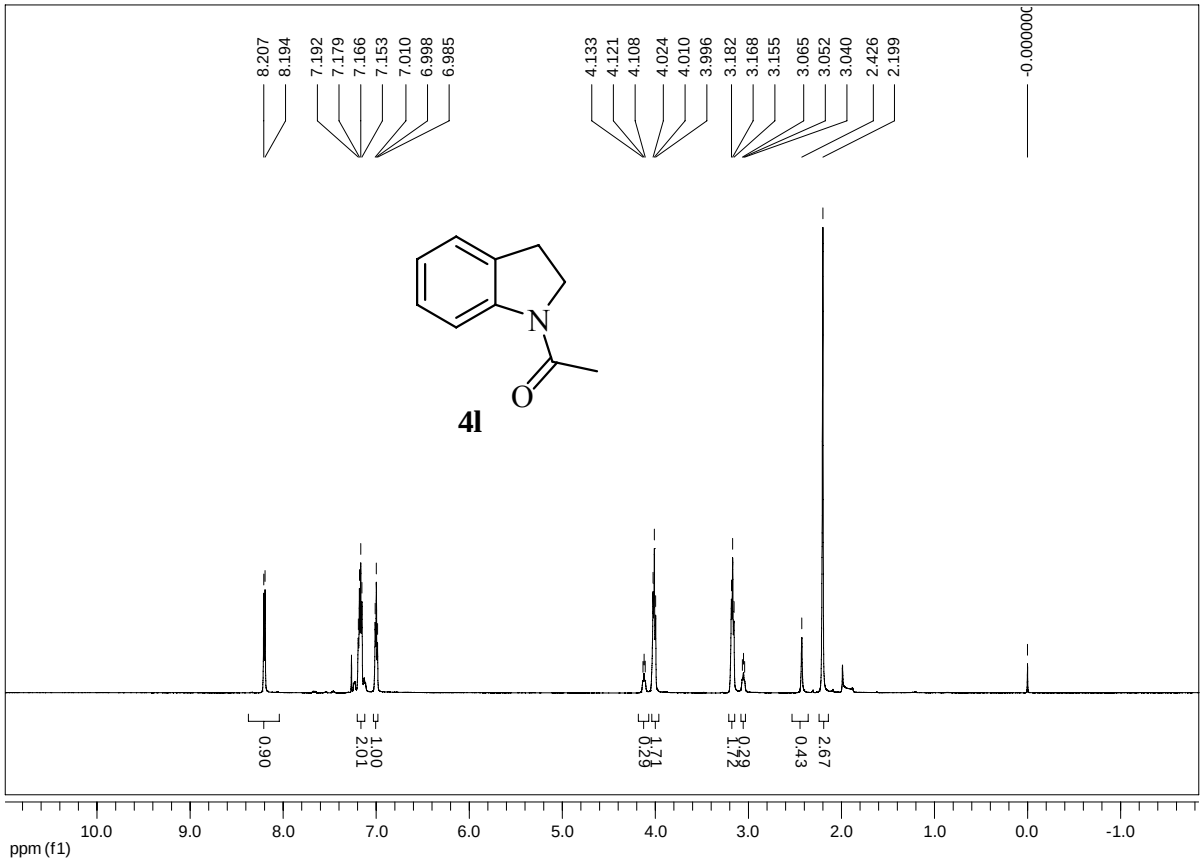

8.196
8.175
7.486
7.469
7.451
7.390
7.369
7.338
7.311
7.263
7.237
7.172
7.150
7.128
6.961
6.947
5.778
5.767
5.757
4.385
4.379
4.368
4.215
3.966
3.946
3.925
3.144
3.124
3.103
1.603
1.575
0.0000
Br
F
N
O
0.72
6.42
0.25
0.47
1.49
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

4j


164.353
159.241
156.773
141.542
134.317
131.775
131.698
130.345
128.729
127.706
124.761
118.767
116.866
116.128
115.918
77.306
76.989
76.671
49.220
27.757
Br
F
N
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)

4j


8.345
8.324
8.126
8.113
7.736
7.715
7.371
7.291
7.265
3.999
3.180
3.159
3.139
1.625
1.599
-0.000
Br
N
O
NO2
4k
7.29
2.04
1.96
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


8.207
8.194
7.192
7.179
7.166
7.153
7.010
6.998
6.985
4.133
4.121
4.108
4.024
4.010
3.996
3.182
3.168
3.155
3.065
3.052
3.040
2.426
2.199
-0.000000
N
O
4l
0.90
2.01
1.00
0.29
1.71
0.29
1.72
0.43
2.67
10.0
9.0
8.0
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6.0
5.0
4.0
3.0
2.0
1.0
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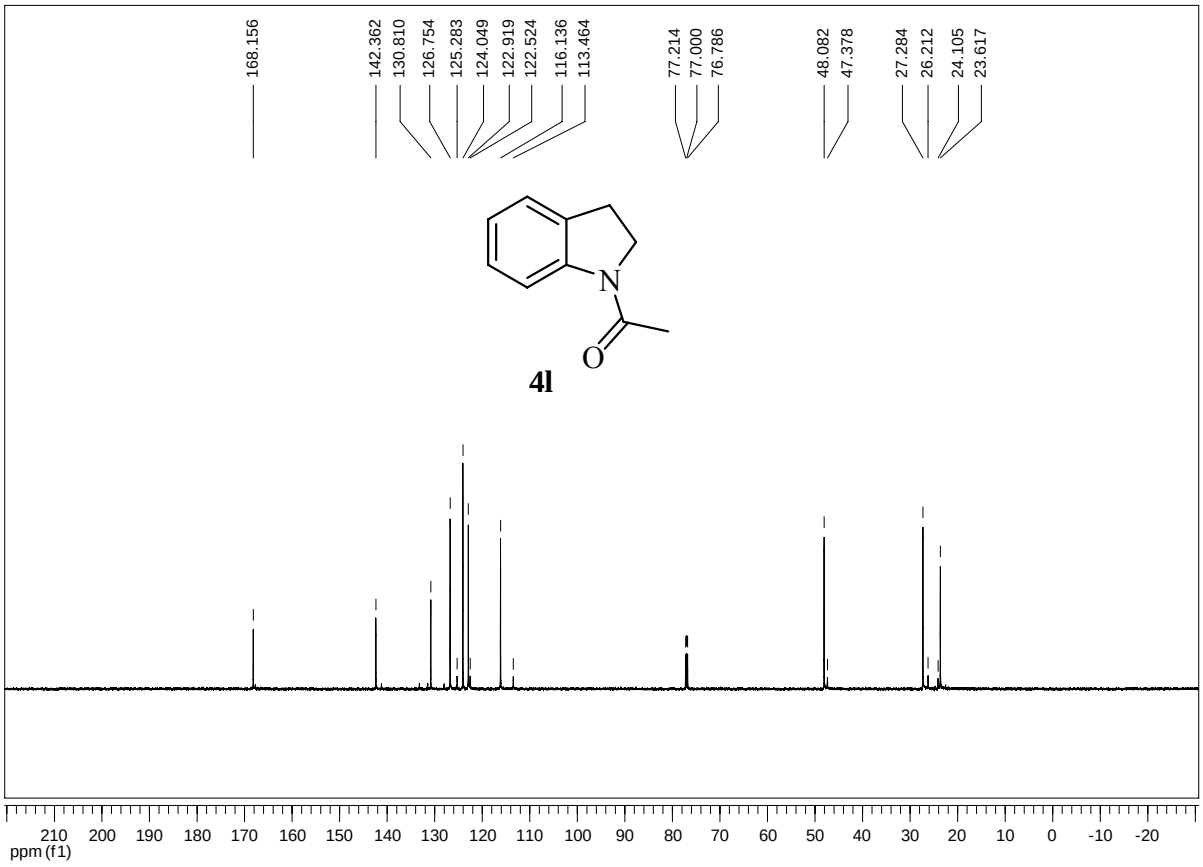
-1.0
ppm (f1)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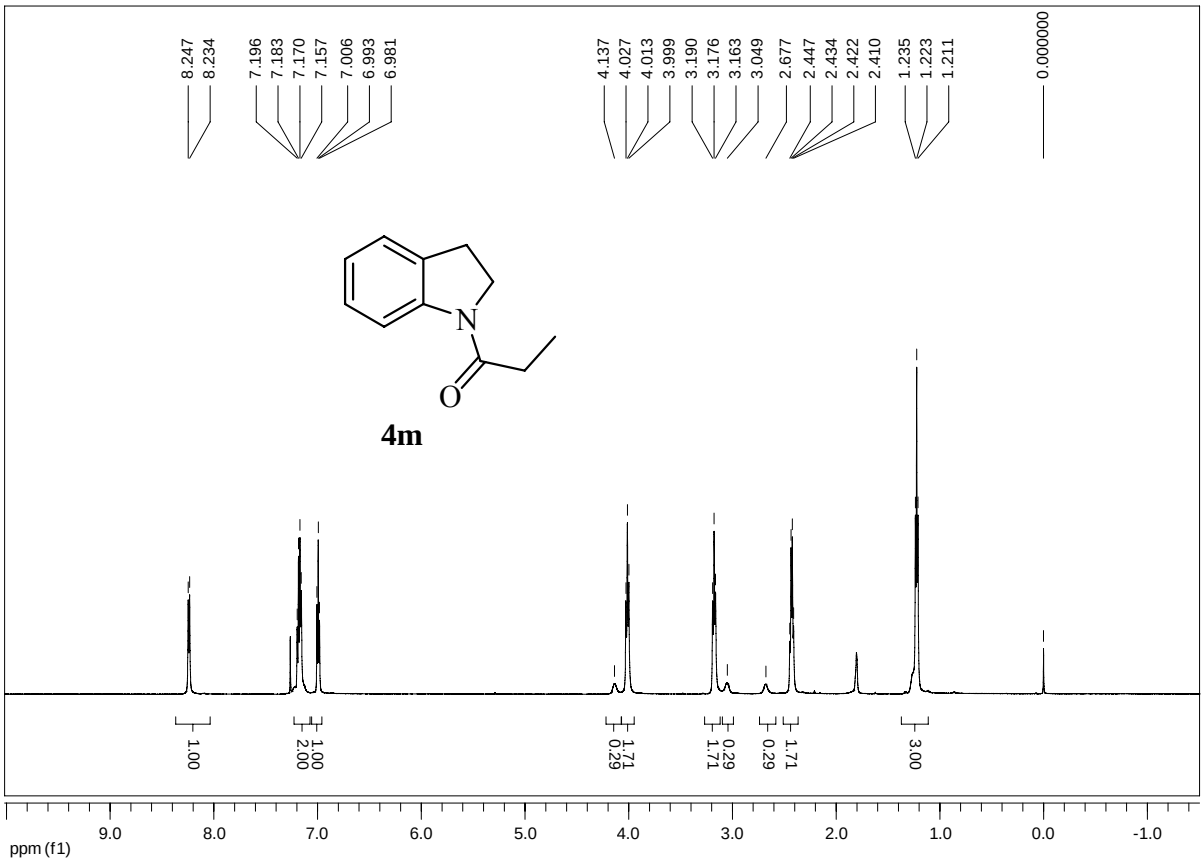
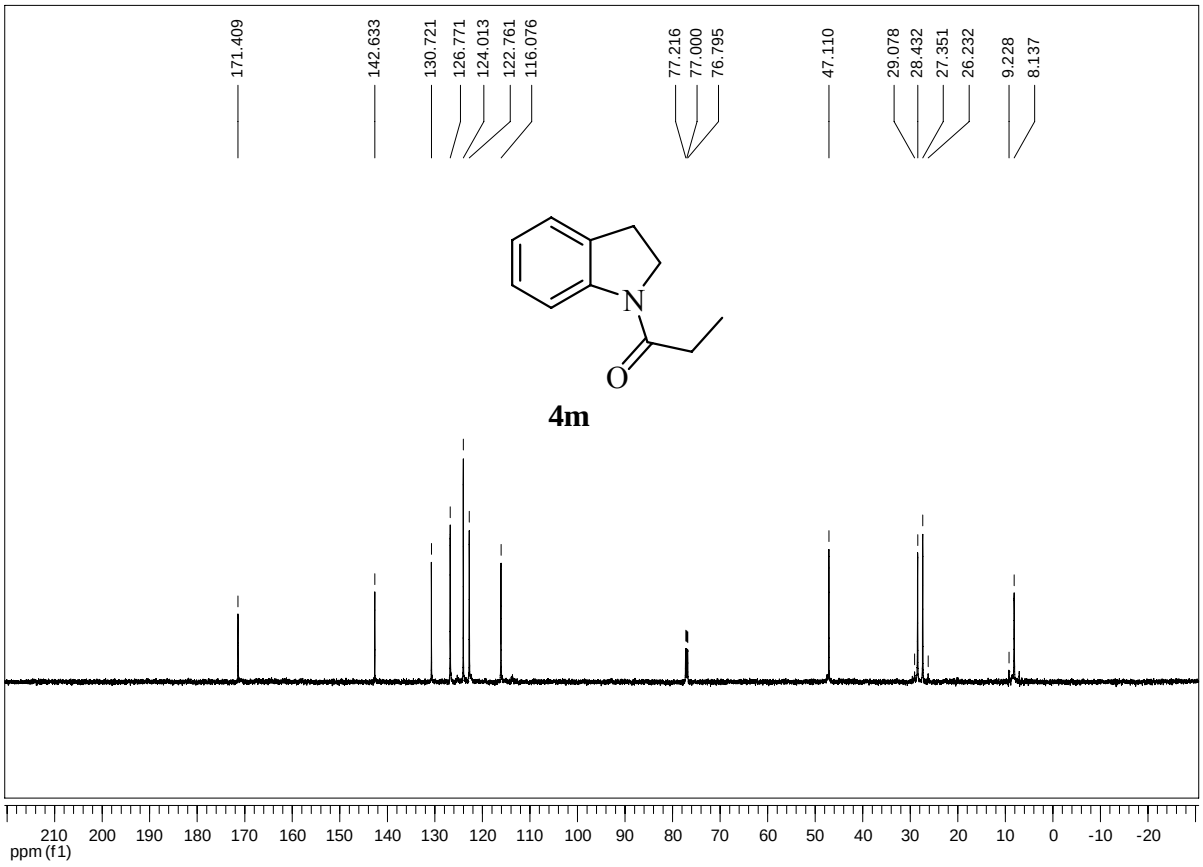
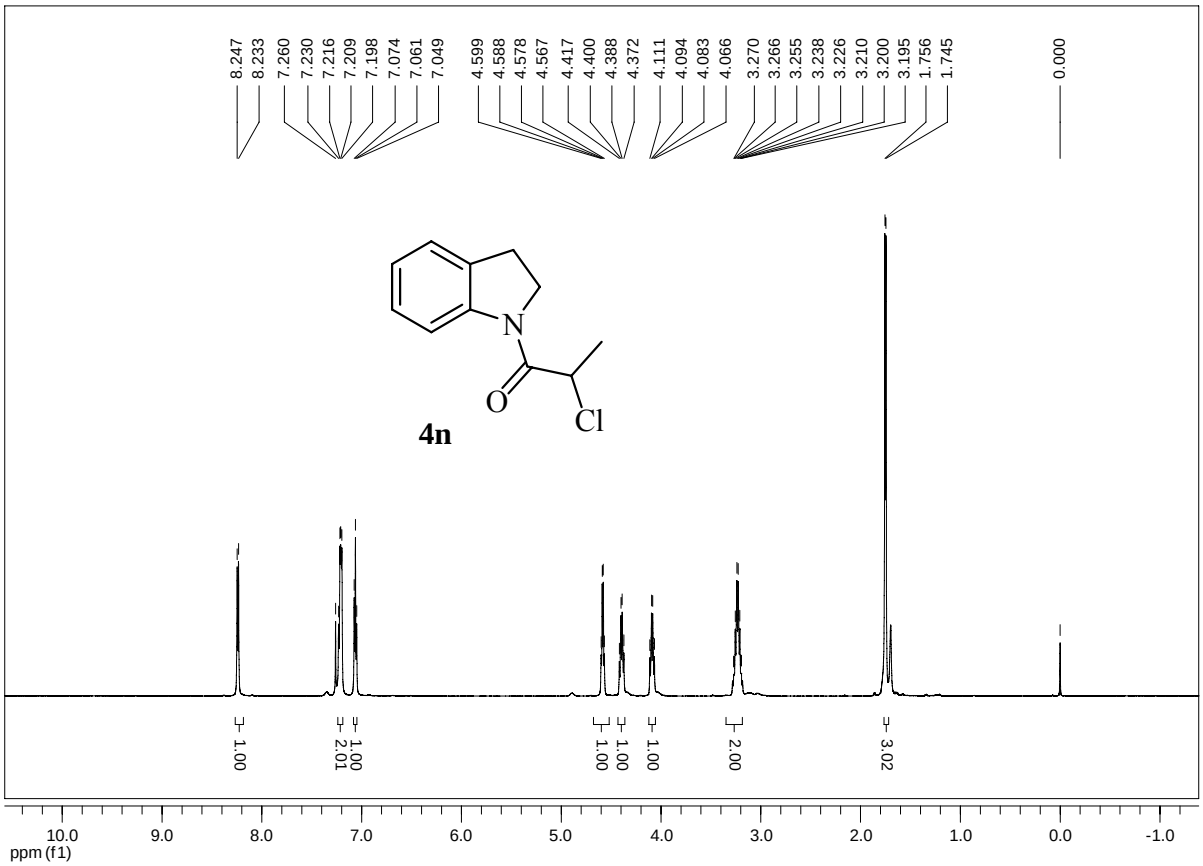
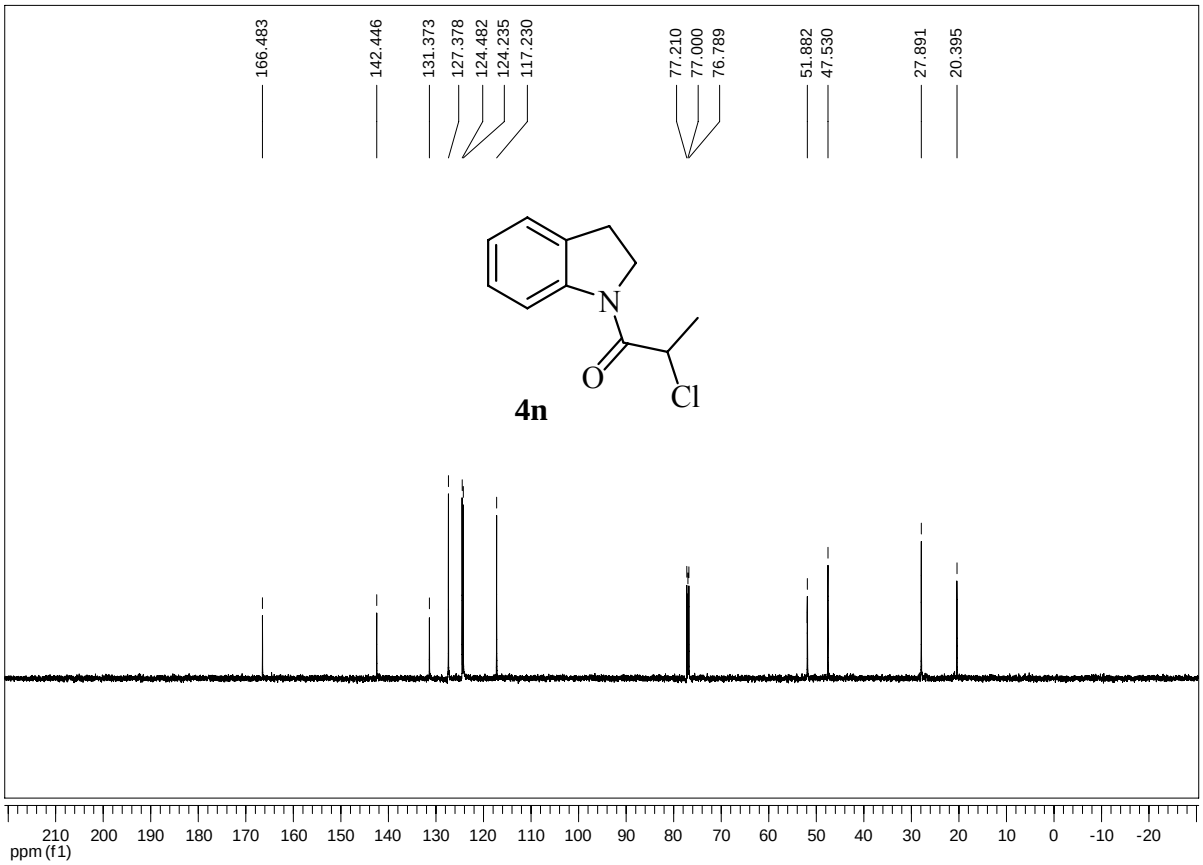
142.362
130.810
126.754
125.283
124.049
122.919
122.524
116.136
113.464
77.214
77.000
76.786
48.082
47.378
27.284
26.212
24.105
23.617
N
O
4l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
ppm (f1)


8.247
8.234
7.196
7.183
7.170
7.157
7.006
6.993
6.981
4.137
4.027
4.013
3.999
3.190
3.176
3.163
3.049
2.677
2.447
2.434
2.422
2.410
1.235
1.223
1.211
0.000000
N
O
4m
1.00
2.00
1.00
0.29
1.71
1.71
0.29
0.29
1.71
3.00
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
ppm (f1)


171.409
142.633
130.721
126.771
124.013
122.761
116.076
77.216
77.000
76.795
47.110
29.078
28.432
27.351
26.232
9.228
8.137
N
O
4m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
ppm (f1)


8.247
8.233
7.260
7.230
7.216
7.209
7.198
7.074
7.061
7.049
4.599
4.588
4.578
4.567
4.417
4.400
4.388
4.372
4.111
4.094
4.083
4.066
3.270
3.266
3.255
3.238
3.226
3.210
3.200
3.195
1.756
1.745
0.000
N
O
Cl
4n
1.00
2.01
1.00
1.00
1.00
1.00
2.00
3.02
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
ppm (f1)


166.483
142.446
131.373
127.378
124.482
124.235
117.230
77.210
77.000
76.789
51.882
47.530
27.891
20.395
N
O
Cl
4n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
ppm (f1)