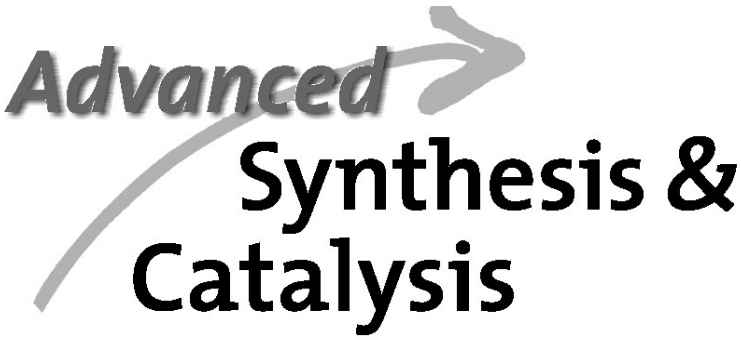

Supporting Information

Modular Synthesis of Functionalizable Alkoxy-Tethered *N*-Heterocyclic Carbene Ligands and an Active Catalyst for Buchwald-Hartwig Aminations

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Supporting Information

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GC method for GC-FID and GC-MS experiments

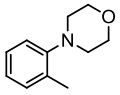
The GC-FID method used consisted of: Column; Agilent HP-5, 30 m × 250 μm. Inlet; temp. = 250 °C, pressure = 100.0 kPa, 16:1 split, total flow = 25.0 mL/min, helium carrier. Detector; temp. = 275 °C, hydrogen flow = 40.0 mL/min, air flow 450.0 mL/min, makeup flow (helium) = 45.0 mL/min. Oven; initial temp. = 45 °C (5 min), ramp = 10 °C/min to 250 °C, hold at 250 °C for 5 min. The GC-MS measurements were performed in scan mode with a 4 min solvent delay.

Procedures and characterization data for isolated Buchwald-Hartwig reaction products

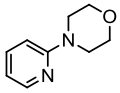
General procedure

In a drybox, a 5 mL screw topped vial was charged with a stir bar, precatalyst **19** (3.0 mg, 0.0025 mmol, 0.005 equiv.), ^{t}BuOK (84 mg, 0.75 mmol, 1.5 equiv.) and amine if solid, capped with a septum cap and removed to the bench top. The appropriate amine (0.55 mmol, 1.1 equiv.) and solvent (0.5 mL) were added *via* syringe, and the mixture was allowed to stand for a few minutes. The aryl halide (0.5 mmol, 1.0 equiv.) was then added *via* syringe, immediately after which the vial was placed in a shallow oil bath atop a thermo-regulated hot plate and stirred at 400-500 rpm. The reaction was quenched with water (2 mL) and extracted with DCM (4 times with 1 mL), passing the DCM extracts through a small plug of silica gel. The silica plug was then washed with DCM (2 mL), and the combined extracts evaporated *in vacuo.*

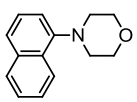
Additional information specific to each reaction



N-(o-tolyl)morpholine (**23a**). The reaction vial was charged with 59 μL 2-chlorotoluene (**21a**) and 48 μL morpholine (**22a**), and heated at 30 °C for 30 min. The product was obtained as a colorless oil (83 mg, 94%) after silica-gel chromatography using hexane then 50:1 hexane/EtOAc as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (ddd, J = 11.1, 10.6, 8.4, 2H), 7.08-6.88 (m, 2H), 3.98-3.76 (m, 4H), 3.03-2.80 (m, 4H), 2.33 (s, 3H). The ^{1}H NMR spectrum of the purified product matches that reported previously[1] and is reproduced below, as is the GC trace and mass spectrum.

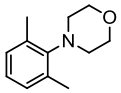


N-(2-pyridyl)morpholine (**23b-c**). **23b**: The reaction vial was charged with 48 μL 2-bromopyridine (**21b**) and 48 μL morpholine (**22a**), and heated at 30 °C for 15 min. **23c**: The reaction vial was charged with 47 μL 2-chloropyridine (**21c**) and 48 μL morpholine (**22a**) and heated at 30 °C for 15 min. In both cases the product was obtained as a low-melting solid (76 mg, 93%; 79 mg, 96%) after silica-gel chromatography using 4:1 hexane/EtOAc as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (ddd, J = 4.9, 2.0, 0.9 Hz, 1H), 7.50 (ddd, J = 8.6, 7.2, 2.0 Hz, 1H), 6.76-6.49 (m, 2H), 3.99-3.64 (m, 4H), 3.64-3.37 (m, 4H). The ^{1}H NMR spectrum of the purified product matches that reported previously[2] and is reproduced below, as is the GC trace and mass spectrum.

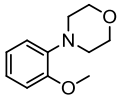


N-(1-naphthyl)morpholine (**23d**). The reaction vial was charged with 68 μL technical grade (~10% 2-chloro isomer) 1-Chloronaphthalene (**21d**) and 48 μL morpholine (**22a**), and heated at 30 °C for 15 min. The product was obtained as a white solid (99 mg, 93% combined yield) after silica-gel chromatography using hexane then 50:1 hexane/EtOAc as eluent. Pure *N*-(1-naphthyl)morpholine (92 mg) was the first to elute, followed by 7 mg of an isomeric mixture containing *N*-(2-

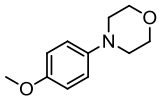
naphthyl)morpholine. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30-8.06 (m, 1H), 7.95-7.73 (m, 1H), 7.58 (d, J = 8.2 Hz, 1H), 7.54-7.37 (m, 3H), 7.11 (d, J = 7.1 Hz, 1H), 4.12-3.80 (m, 4H), 3.25-2.93 (m, 4H). The ^{1}H NMR spectrum of the purified product matches that reported previously[3] and is reproduced below, as is the GC trace and mass spectrum.



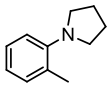
N-(2,6-dimethylphenyl)morpholine (**23e**). The reaction vial was charged with 66 μL 2-chloro-1,3-dimethylbenzene (**21e**) and 48 μL morpholine (**22a**), and heated at 40 °C for 90 min. The product was obtained as a white solid (88 mg, 92%) after silica-gel chromatography using 50:1 hexane/EtOAc as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11-6.83 (m, 3H), 3.97-3.63 (m, 4H), 3.19-2.99 (m, 4H), 2.36 (s, 6H). The ^{1}H NMR spectrum of the purified product matches that reported previously[4] and is reproduced below, as is the GC trace and mass spectrum.



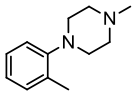
N-(2-methoxyphenyl)morpholine (**23f**). The reaction vial was charged with 64 μL 2-chloroanisole (**21f**) and 48 μL morpholine (**22a**), and heated at 50 °C for 4 h. The product was obtained as a yellow oil (44 mg, 45% or 82 mg, 84% at 1 mol% cat. loading) after silica-gel chromatography using 20:1 then 10:1 hexane/EtOAc as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06-6.98 (m, 1H), 6.94 (d, J = 4.0 Hz, 2H), 6.88 (d, J = 7.9 Hz, 1H), 3.92-3.88 (m, 4H), 3.87 (s, 3H), 3.21-2.91 (m, 4H). The ^{1}H NMR spectrum of the purified product matches that reported previously[1] and is reproduced below, as is the GC trace and mass spectrum.



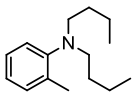
N-(4-methoxyphenyl)morpholine (**23g**). The reaction vial was charged with 61 μL 4-chloroanisole (**21g**) and 48 μL morpholine (**22a**), and heated at 50 °C for 30 min. The product was obtained as a white solid (94 mg, 97%) after silica-gel chromatography using 20:1 then 10:1 hexane/EtOAc as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ T6.93-6.91 (m, 2H), 6.88-6.83 (m, 2H), 3.90-3.84 (m, 4H), 3.78 (s, 3H), 3.09-3.05 (m, 4H). The ^{1}H NMR spectrum of the purified product matches that reported previously[1] and is reproduced below, as is the GC trace and mass spectrum.



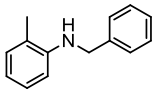
N-(o-tolyl)pyrrolidine (**23h**). The reaction vial was charged with 59 μL 2-chlorotoluene (**21a**) and 46 μL pyrrolidine (**22b**), and heated at 50 °C for 30 min. The product was obtained as a colorless oil (68 mg, 84%) after silica-gel chromatography using hexane then 50:1 hexane/EtOAc as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15-7.09 (m, 2H), 6.92-6.81 (m, 2H), 3.20 (t, J = 6.5 Hz, 4H), 2.33 (s, 3H), 1.96-1.91 (m, 4H). The ^{1}H NMR spectrum of the purified product matches that reported previously[5] and is reproduced below, as is the GC trace and mass spectrum.



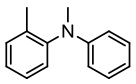
N-methyl-N'-(o-tolyl)piperazine **(23i)**. The reaction vial was charged with 59 μL 2-chlorotoluene (**21a**) and 61 μL *N*-methylpiperazine (**22c**), and heated at 50 °C for 30 min. The product was obtained as a yellow oil (86 mg, 90%) after silica-gel chromatography using 25:1 then 10:1 EtOAc/MeOH as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19-7.14 (m, 2H), 7.06-6.96 (m, 2H), 2.96 (t, J = 4.8 Hz, 4H), 2.60 (br s, 4H), 2.37 (s, 3H), 2.30 (s, 3H). The ^{1}H NMR spectrum of the purified product matches that reported previously[6] and is reproduced below, as is the GC trace and mass spectrum.



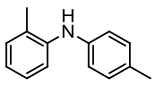
N,N-dibutyl-2-methylaniline (**23j**). The reaction vial was charged with 59 μL 2-chlorotoluene (**21a**) and 93 μL dibutylamine (**22d**), and heated at 60 °C for 90 min. The product was obtained as a colorless oil (95 mg, 86%) after silica-gel chromatography using hexane then 50:1 hexane/EtOAc as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19-7.11 (m, 2H), 7.08 (dd, J = 8.0, 1.5 Hz, 1H), 6.99-6.94 (m, 1H), 2.92-2.87 (m, 4H), 2.29 (s, 3H), 1.43-1.35 (m, 4H), 1.32-1.21 (m, 4H), 0.86 (t, J = 7.3 Hz, 6H). The ^{1}H NMR spectrum of the purified product matches that reported previously[7] and is reproduced below, as is the GC trace and mass spectrum.



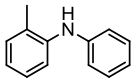
N-benzyl-2-methylaniline (**23k**). The reaction vial was charged with 59 μL 2-chlorotoluene (**21a**) and 60 μL benzylamine (**22e**), and heated at 60 °C for 60 min. The product was obtained as a white solid (90 mg, 91%) after silica-gel chromatography using hexane then 50:1 hexane/EtOAc as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.33 (m, 4H), 7.32-7.27 (m, 1H), 7.14-7.07 (m, 2H), 6.72-6.62 (m, 2H), 4.39 (s, 2H), 2.18 (s, 3H). The ^{1}H NMR spectrum of the purified product matches that reported previously[8] and is reproduced below, as is the GC trace and mass spectrum.



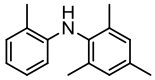
N,2-dimethyl-N-phenylaniline (**23l**). The reaction vial was charged with 59 μL 2-chlorotoluene (**21a**) and 60 μL *N*-methylaniline (**22f**), and heated at 60 °C for 60 min. The product was obtained as a colorless oil (89 mg, 90%) after silica-gel chromatography using hexane then 50:1 hexane/EtOAc as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.14 (m, 6H), 6.74-6.68 (m, 1H), 6.56-6.52 (m, 2H), 3.23 (s, 3H), 2.15 (s, 3H). The ^{1}H NMR spectrum of the purified product matches that reported previously[8] and is reproduced below, as is the GC trace and mass spectrum.



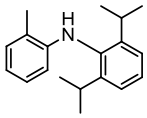
2-methyl-N-(p-tolyl)aniline (**23m**). The reaction vial was charged with 59 μL 2-chlorotoluene (**21a**) and 59 mg *p*-toluidine (**22g**), and heated at 50 °C for 4 h. Only trace product was observed by GC-FID/MS, and was not isolated.



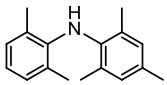
2-methyl-N-phenylaniline (**23n**). The reaction vial was charged with 59 μL 2-chlorotoluene (**21a**) and 50 μL aniline (**22h**), and heated at 50 °C for 4 h. Only trace product was observed by GC-FID/MS, and was not isolated.



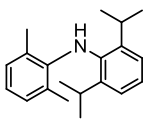
2,4,6-trimethyl-N-(o-tolyl)aniline (**23o**). The reaction vial was charged with 59 μL 2-chlorotoluene (**21a**) and 77 μL mesidine (**22i**), and heated at 50 °C for 30 min. The product was obtained as a white solid (110 mg, 97%) after silica-gel chromatography using hexane then 100:1 hexane/EtOAc as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (dd, J = 7.4, 0.5 Hz, 1H), 6.99-6.93 (m, 3H), 6.71-6.66 (m, 1H), 6.13 (dd, J = 8.1, 1.2 Hz, 1H), 4.87 (br s, 1H), 2.32 (s, 3H), 2.31 (s, 3H), 2.15 (s, 6H). The ^{1}H NMR spectrum of the purified product matches that reported previously[9] and is reproduced below, as is the GC trace and mass spectrum.



2,6-diisopropyl-N-(o-tolyl)aniline (**23p**). The reaction vial was charged with 59 μL 2-chlorotoluene (**21a**) and 115 μL (90% technical grade) 2,6-diisopropylaniline (**22j**), and heated at 50 °C for 2 h. The product was obtained as a colorless oil (132 mg, 98%) after silica-gel chromatography using hexane then 100:1 hexane/EtOAc as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (dd, J = 8.6, 6.5 Hz, 1H), 7.24-7.21 (m, 2H), 7.13 (dd, J = 7.3, 0.5 Hz, 1H), 6.98-6.93 (m, 1H), 6.70-6.65 (m, 1H), 6.12 (dd, J = 8.1, 1.0 Hz, 1H), 4.91 (s, 1H), 3.11 (sept, J = 6.9 Hz, 2H), 2.35 (s, 3H), 1.18 (d, J = 6.9 Hz, 6H), 1.12 (d, J = 6.9 Hz, 6H). The ^{1}H NMR spectrum of the purified product matches that reported previously[10] and is reproduced below, as is the GC trace and mass spectrum.



N-(2,6-dimethylphenyl)-2,4,6-trimethylaniline (**24a**). The reaction vial was charged with 66 μL 2-chloro-1,3-dimethylbenzene (**21e**) and 77 μL mesidine (**22i**), and heated at 50 °C for 30 min. The product was obtained as a white solid (119 mg, 99%) after silica-gel chromatography using hexane then 100:1 hexane/EtOAc as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97-6.94 (m, 2H), 6.82-6.76 (m, 3H), 4.70 (br s, 1H), 2.25 (s, 3H), 1.99 (s, 6H), 1.99 (s, 6H). The ^{1}H NMR spectrum of the purified product matches that reported previously[9,11] and is reproduced below, as is the GC trace and mass spectrum.



N-(2,6-diisopropylphenyl)-2,6-dimethylaniline (**24b**). The reaction vial was charged with 66 μL 2-chloro-1,3-dimethylbenzene (**21e**) and 115 μL (90% technical grade) 2,6-diisopropylaniline (**22j**), and heated at 60 °C for 60 min. The product was obtained as a colorless oil (139 mg, 99%) after silica-gel chromatography using hexane then 100:1 hexane/EtOAc as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17-7.09 (m, 3H), 6.94 (d, J = 7.5 Hz, 2H), 6.72 (t, J = 7.4 Hz, 1H), 4.79 (s, 1H), 3.15 (sept, J = 6.9

Hz, 2H), 1.98 (s, 6H), 1.12 (d, J = 6.9 Hz, 12H). The ^{1}H NMR spectrum of the purified product matches that reported previously[11] and is reproduced below, as is the GC trace and mass spectrum.

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NMR spectra of new compounds

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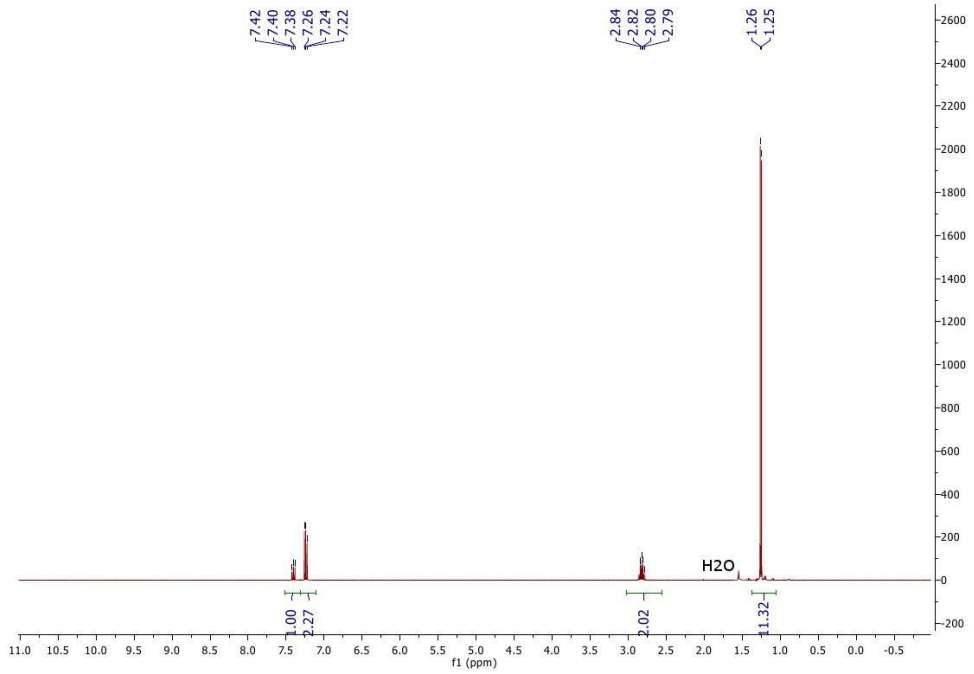

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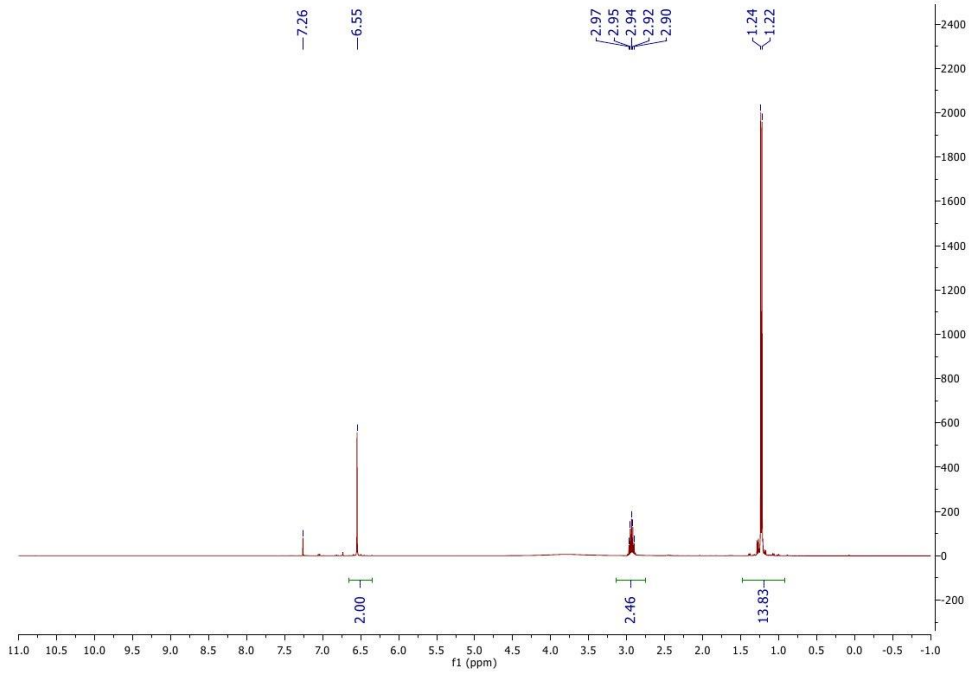

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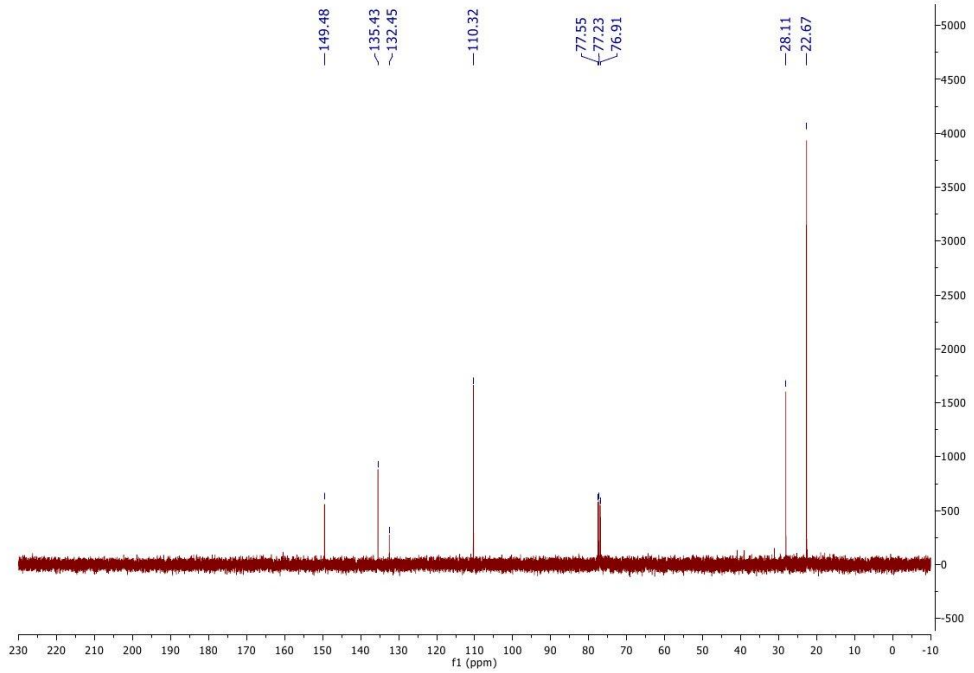

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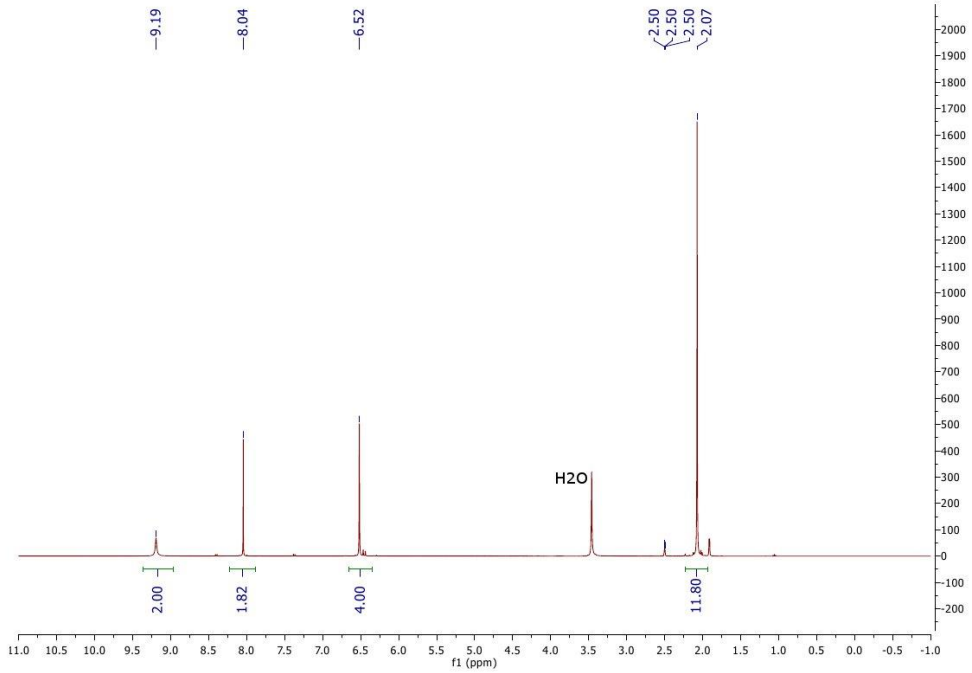
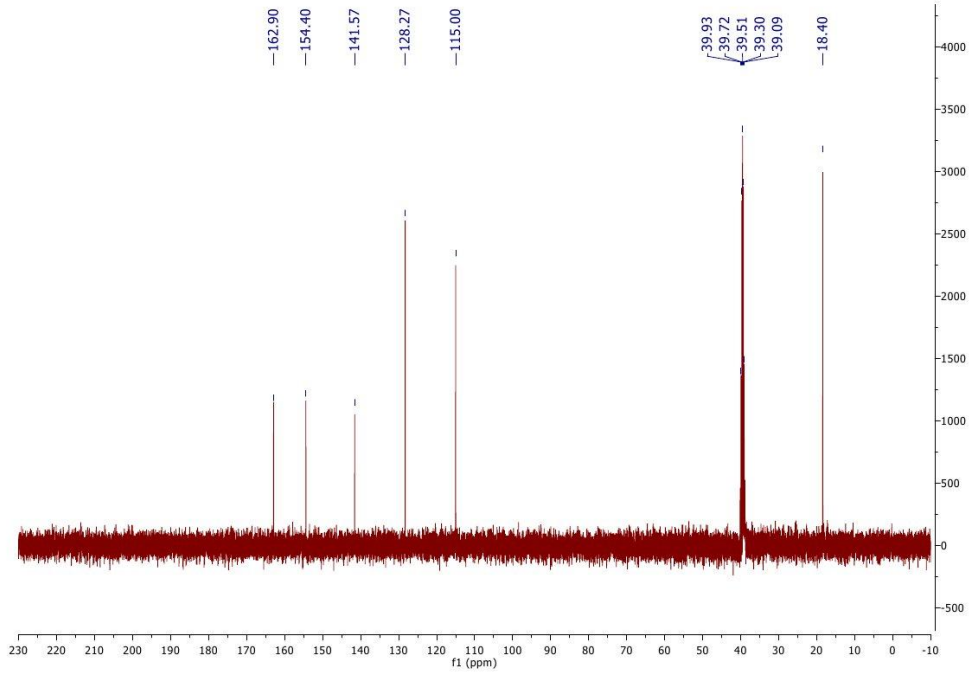
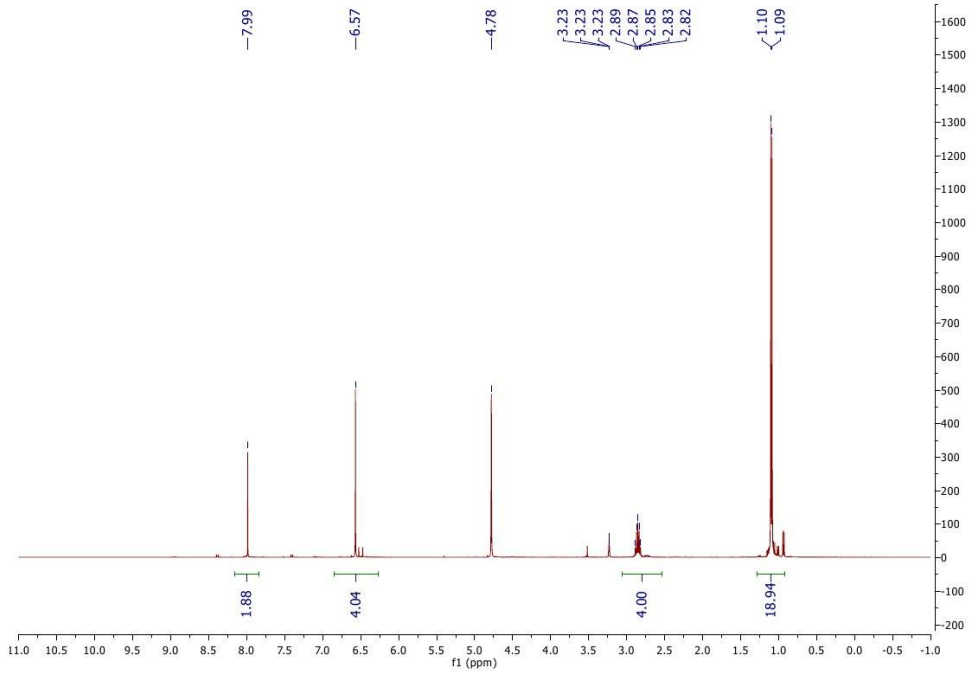


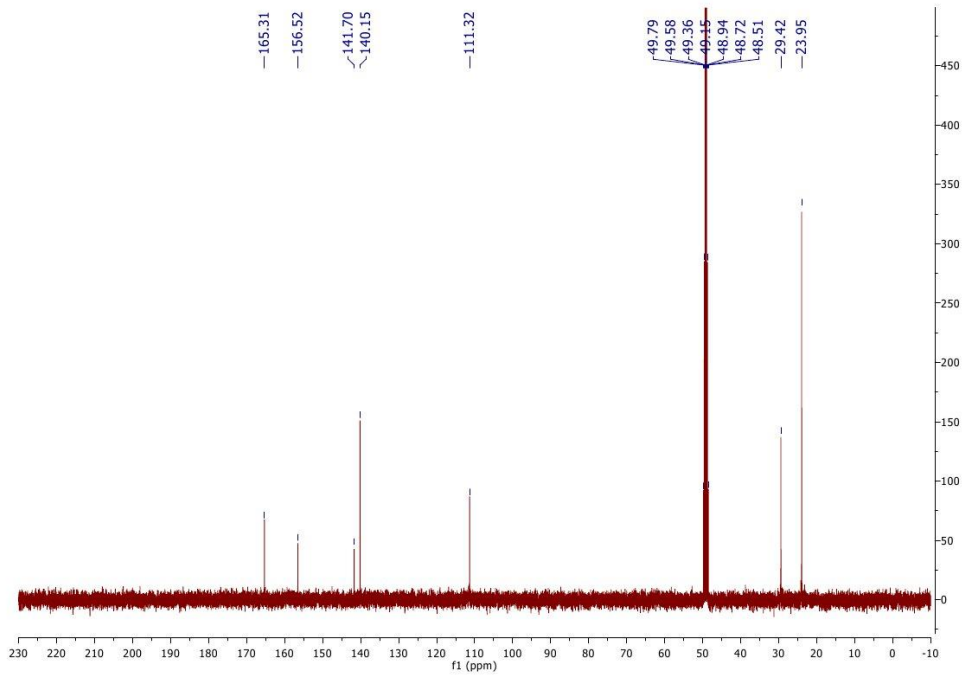
^{13}C{^{1}H} NMR spectrum (100 MHz) of **5a** in DMSO-d_6:



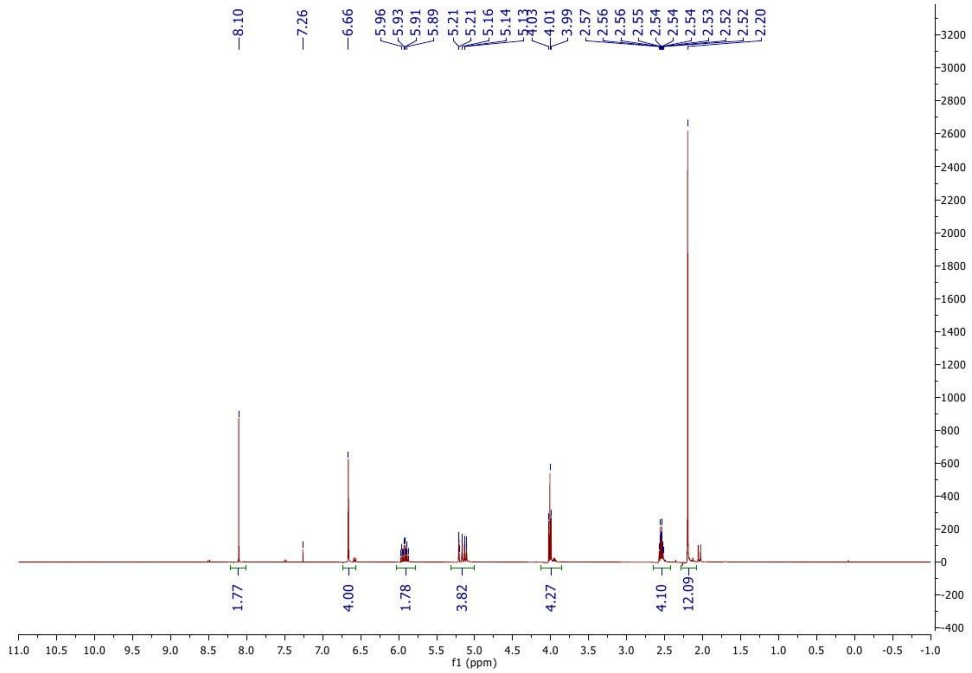
^{1}H NMR spectrum (400 MHz) of **5b** in CD_3OD:



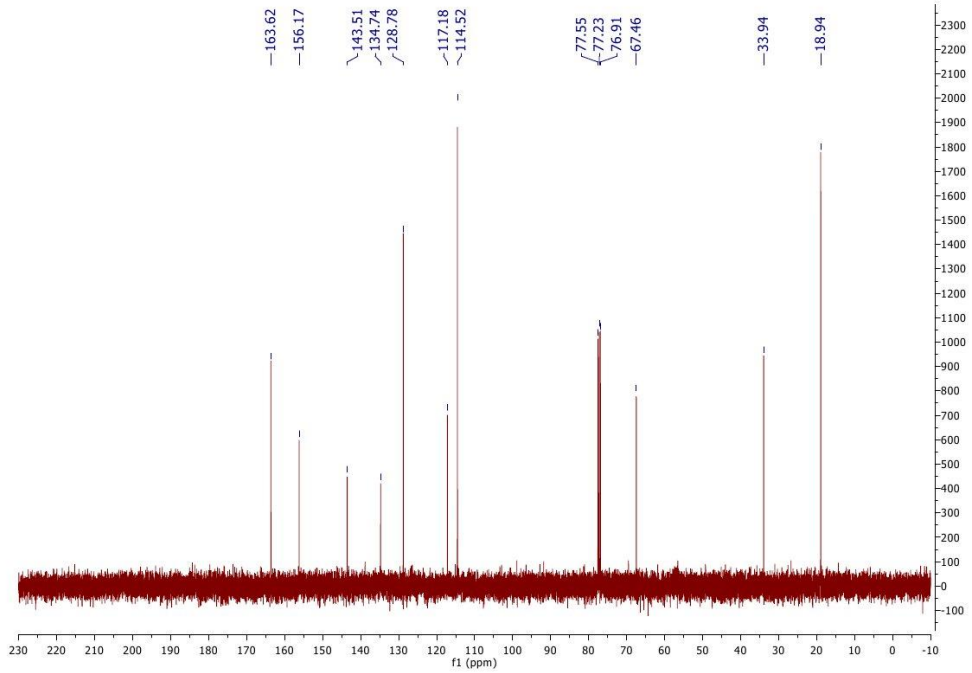
^{13}C{^{1}H} NMR spectrum (100 MHz) of **5b** in CD_3OD:



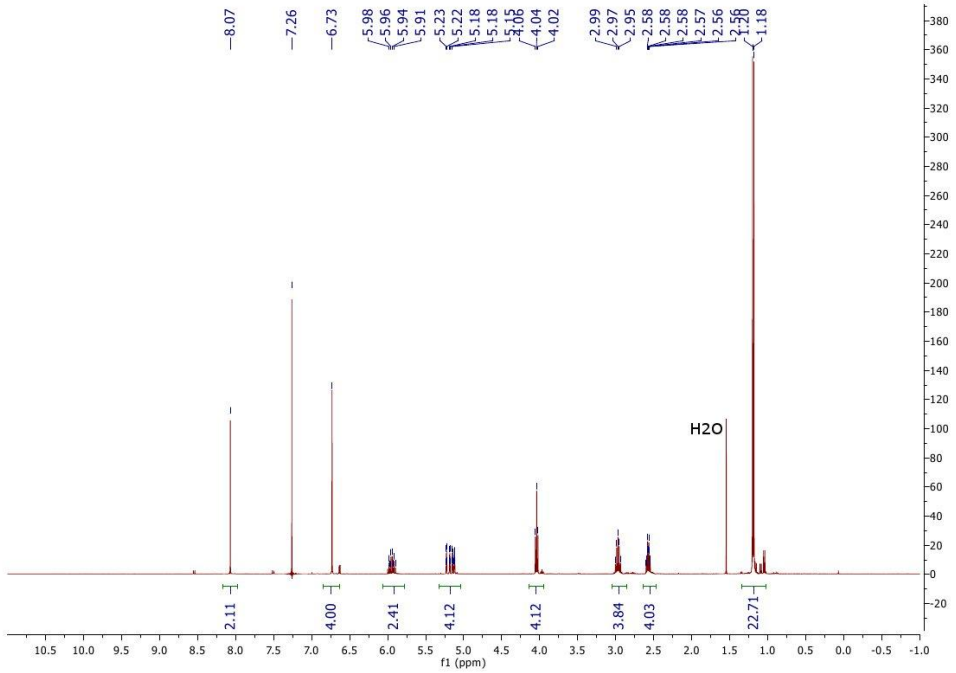
^{1}H NMR spectrum (400 MHz) of **6a** in $CDCl_3$:



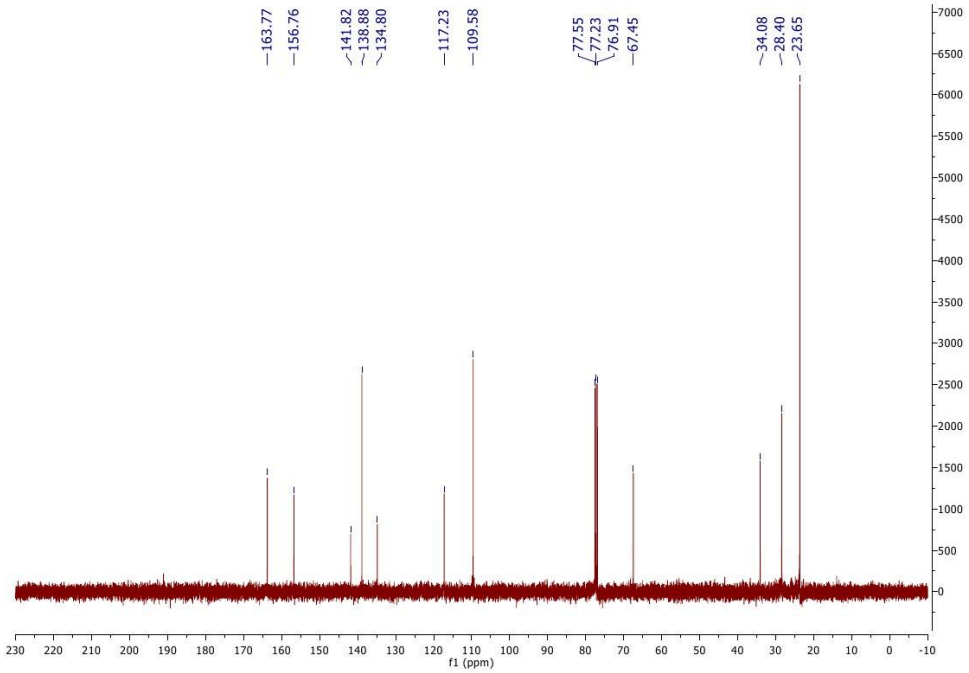
^{13}C{^{1}H} NMR spectrum (100 MHz) of **6a** in $CDCl_3$:



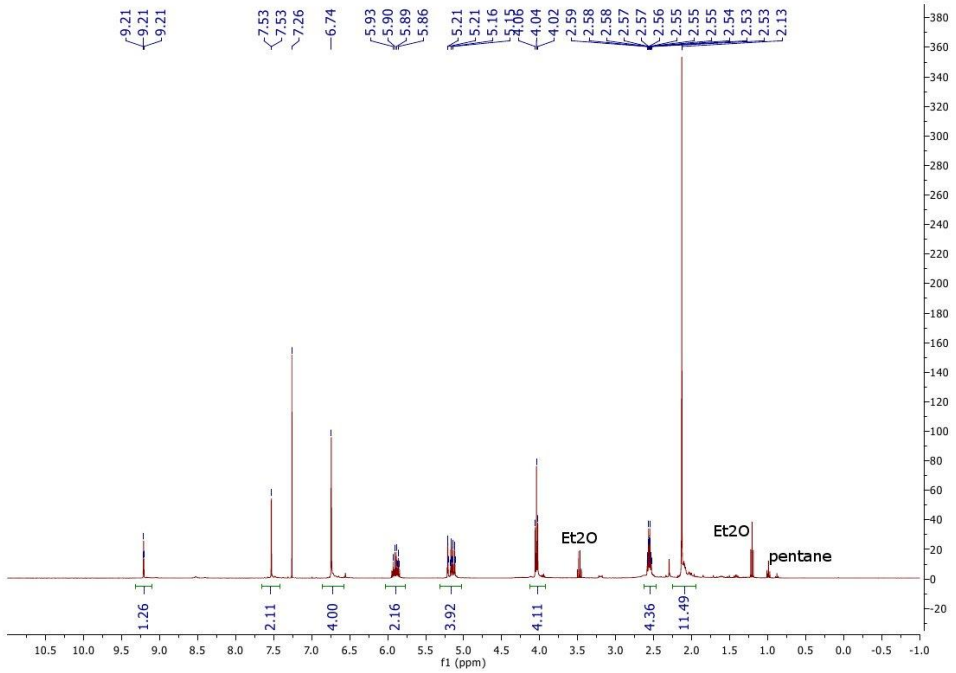
^{1}H NMR spectrum (400 MHz) of **6b** in $CDCl_3$:



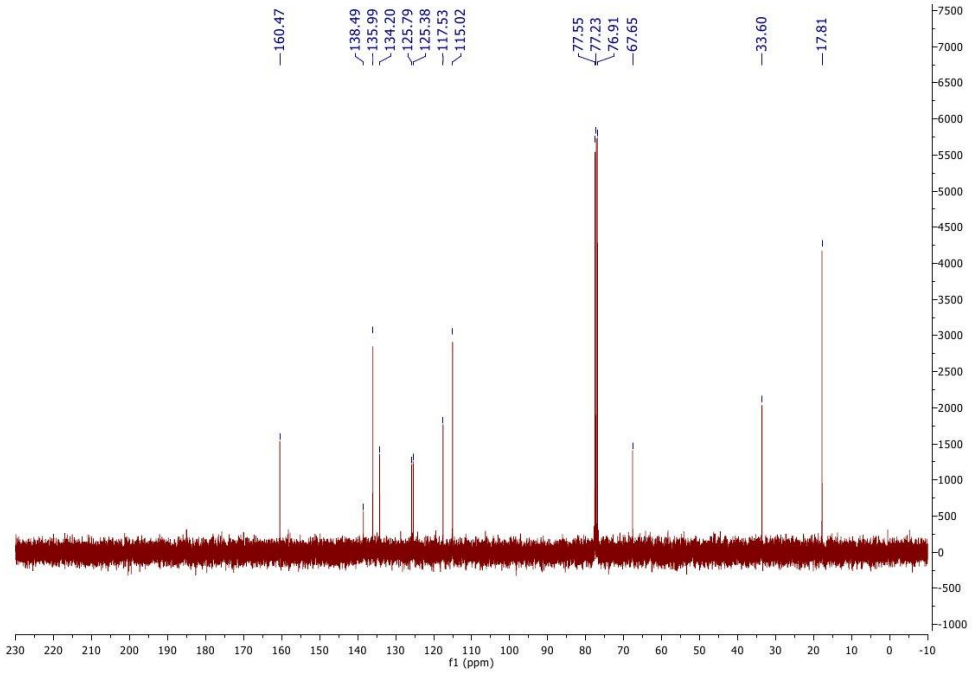
^{13}C{^{1}H} NMR spectrum (100 MHz) of **6b** in $CDCl_3$:



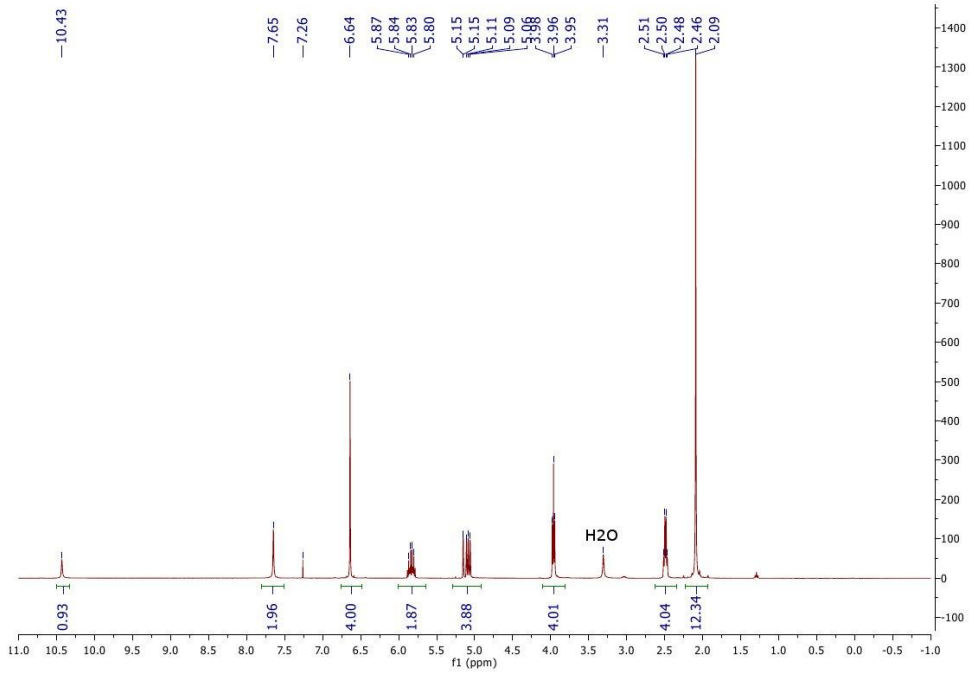
^{1}H NMR spectrum (400 MHz) of **7a** in $CDCl_3$:



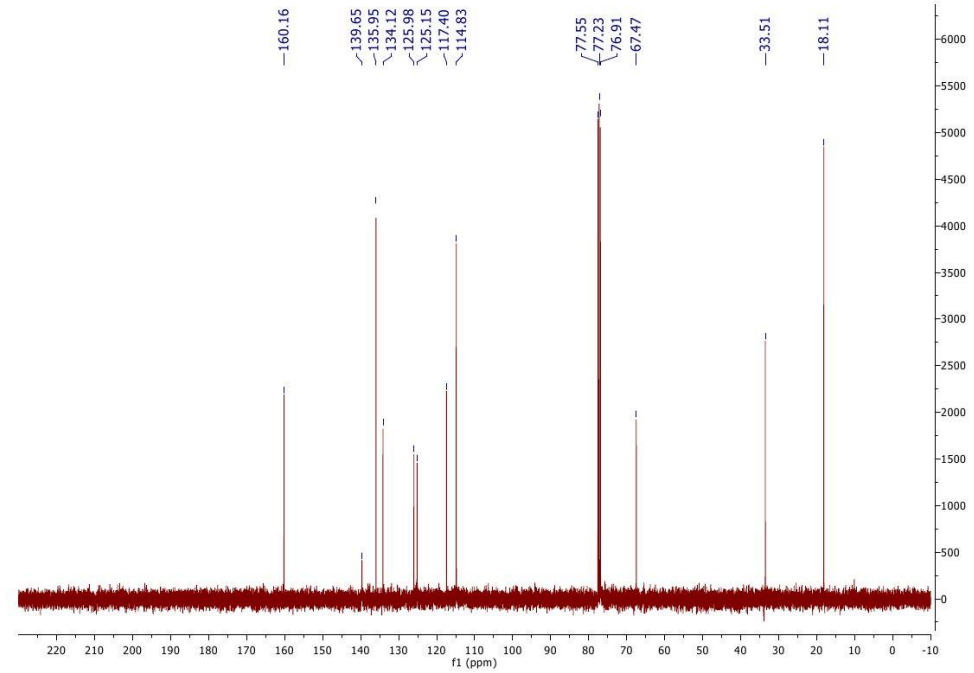
^{13}C{^{1}H} NMR spectrum (100 MHz) of **7a** in $CDCl_3$:



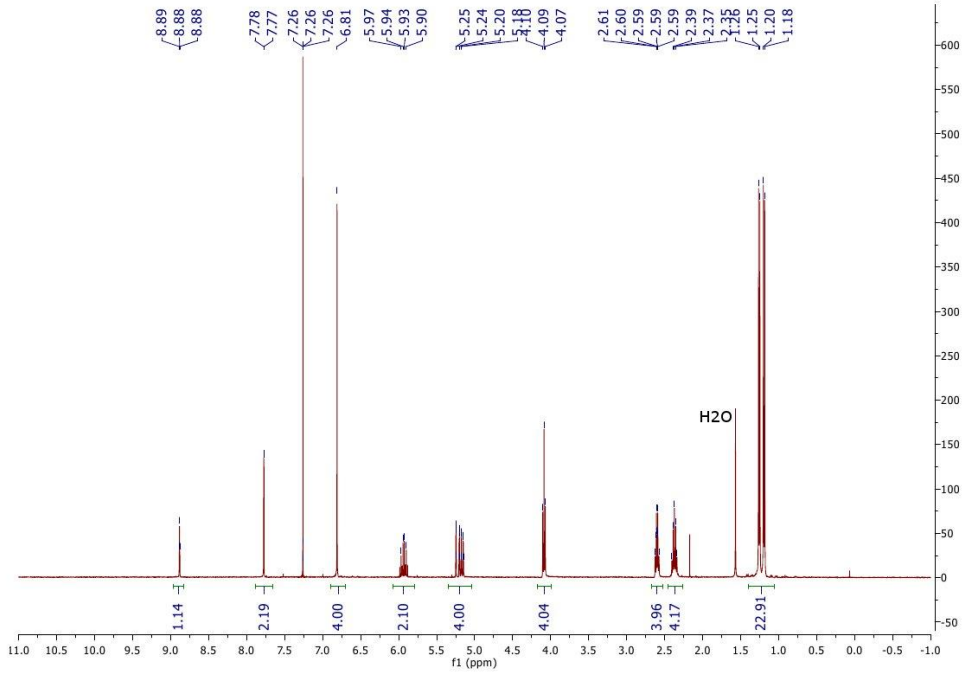
^{1}H NMR spectrum (400 MHz) of **7b** in $CDCl_3$:



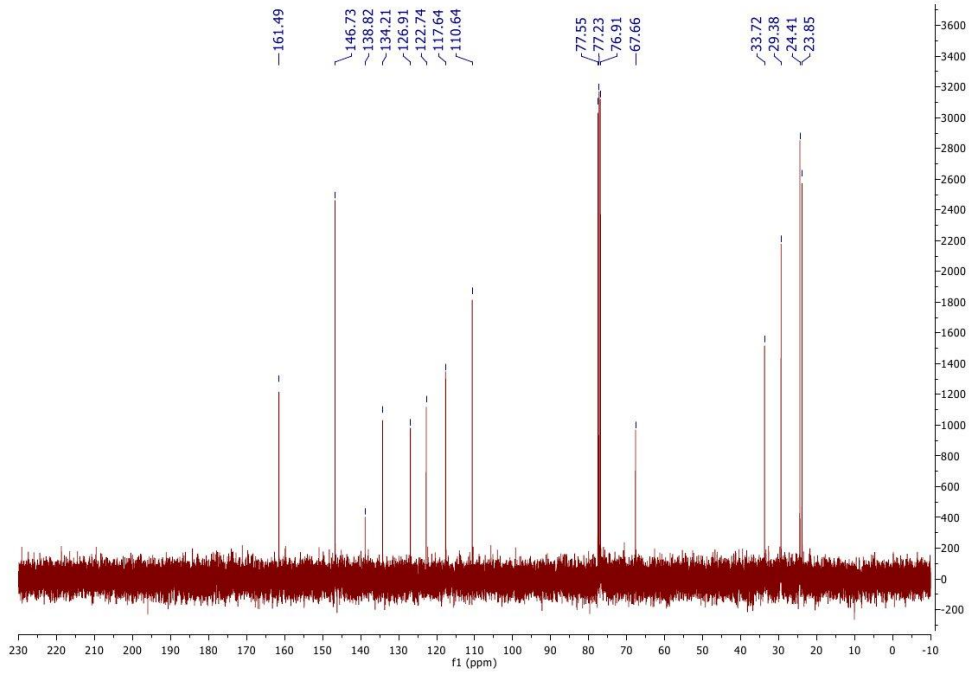
^{13}C{^{1}H} NMR spectrum (100 MHz) of **7b** in CDCl3:



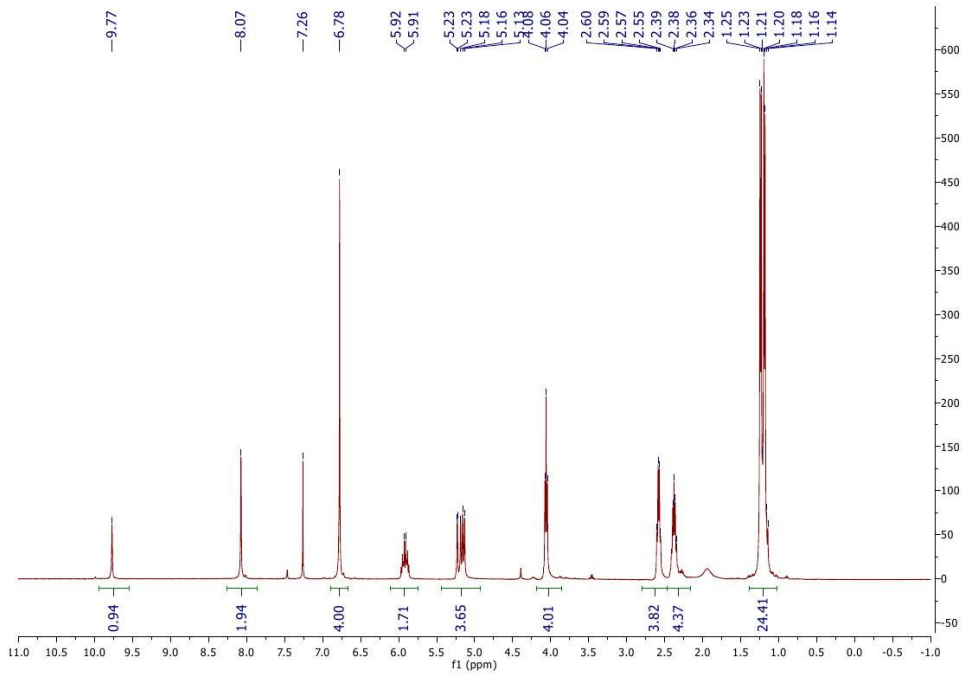
^{1}H NMR spectrum (400 MHz) of **8a** in $CDCl_3$:



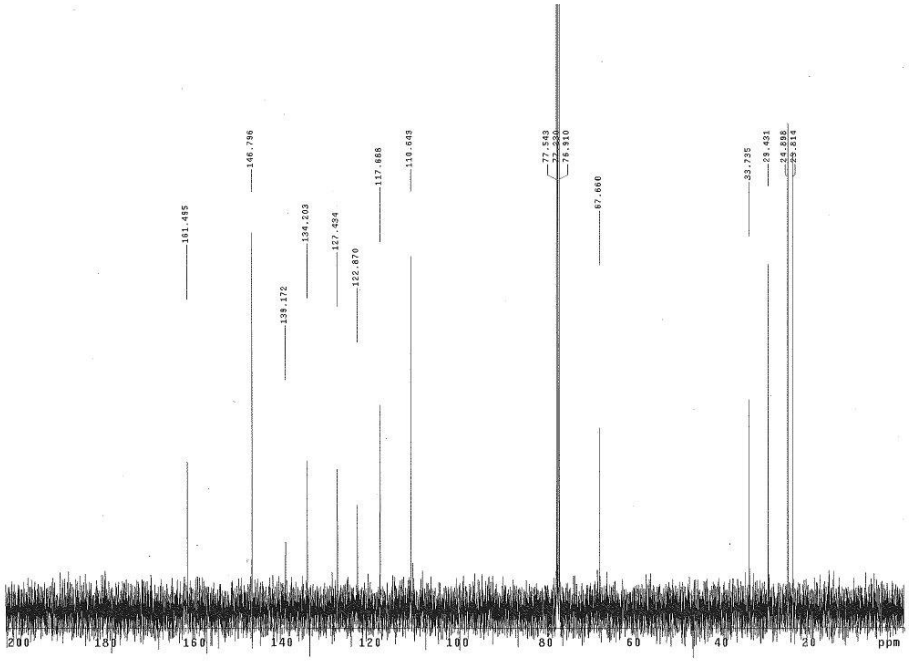
^{13}C{^{1}H} NMR spectrum (100 MHz) of **8a** in $CDCl_3$:



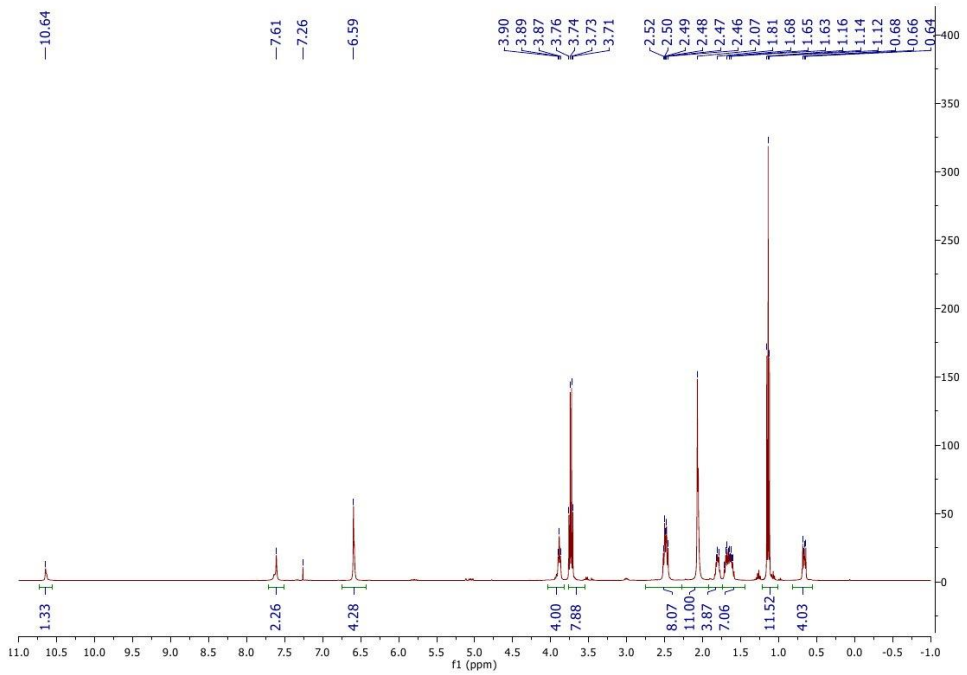
^{1}H NMR spectrum (400 MHz) of **8b** in $CDCl_3$:



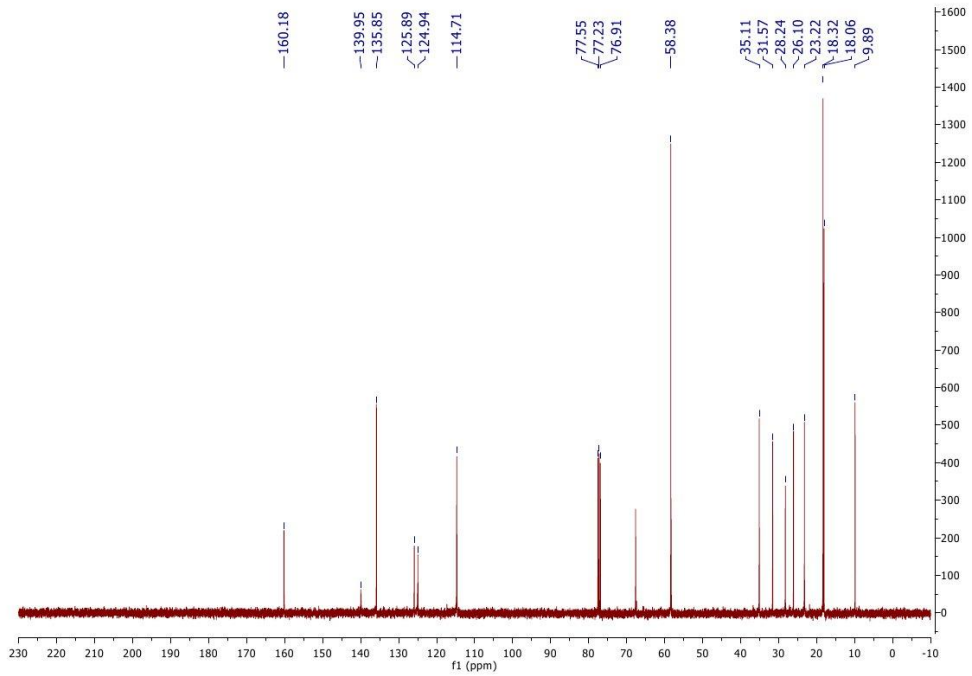
^{13}C{^{1}H} NMR spectrum (100 MHz) of **8b** in $CDCl_3$:



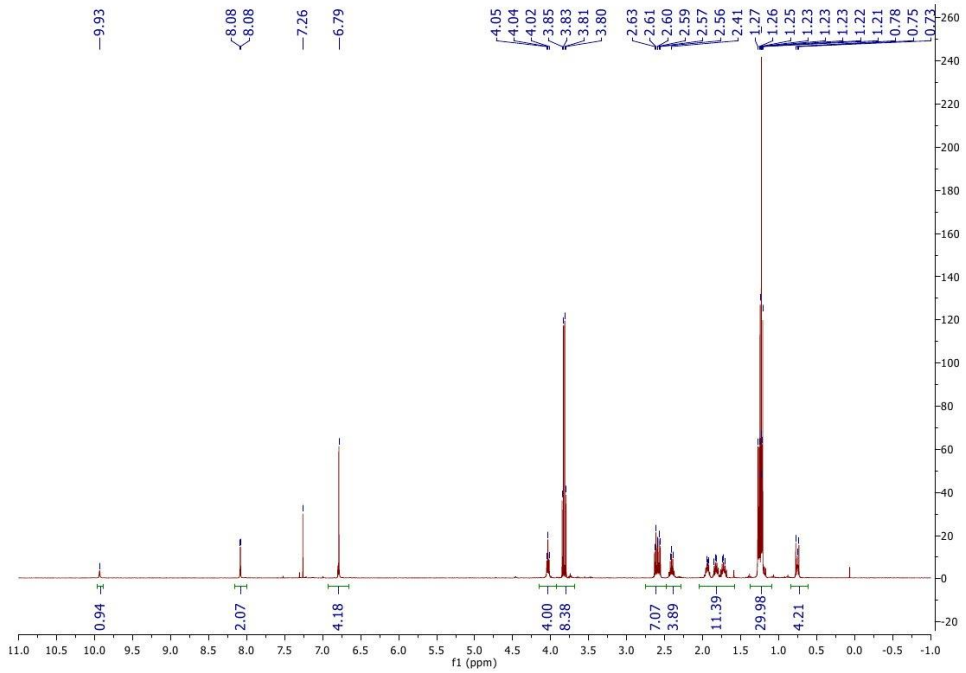
^{1}H NMR spectrum (400 MHz) of **9a** in $CDCl_3$:



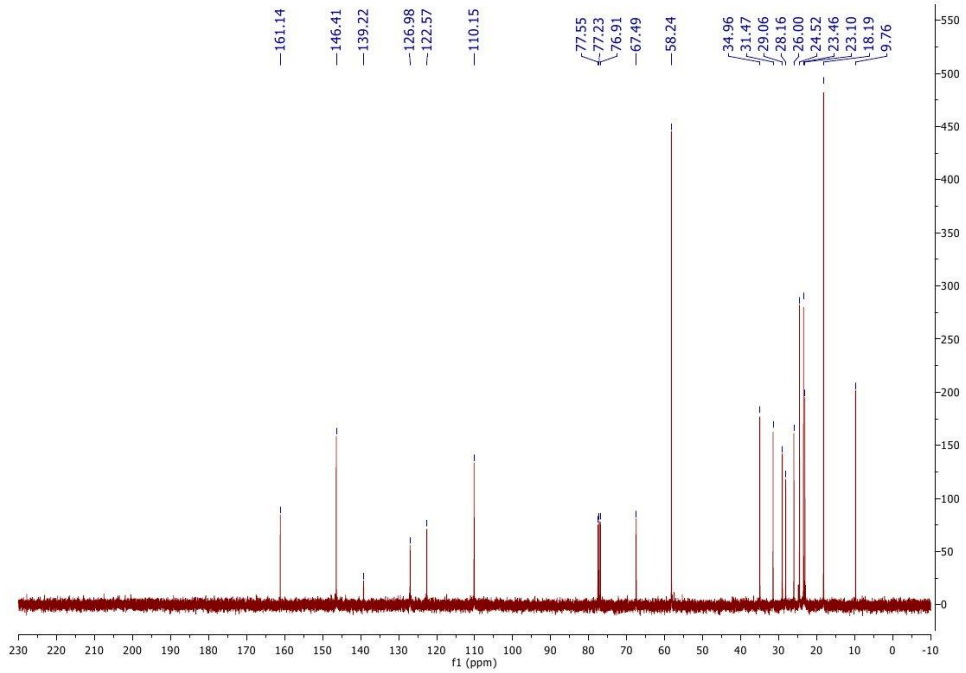
^{13}C{^{1}H} NMR spectrum (100 MHz) of **9a** in $CDCl_3$:



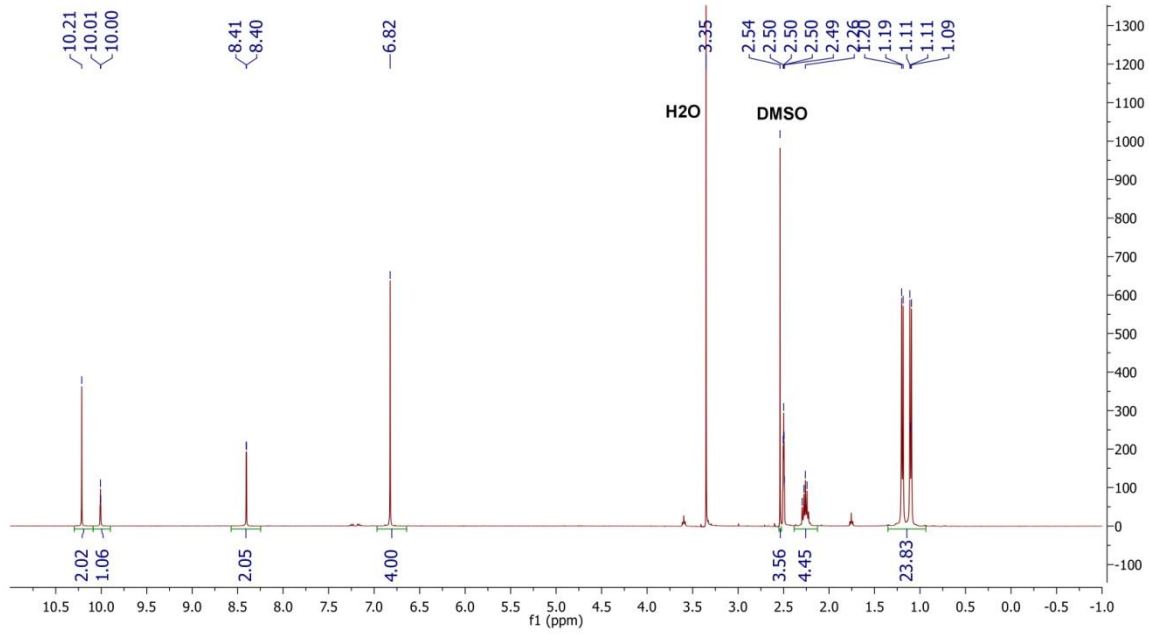
^{1}H NMR spectrum (400 MHz) of **9b** in $CDCl_3$:



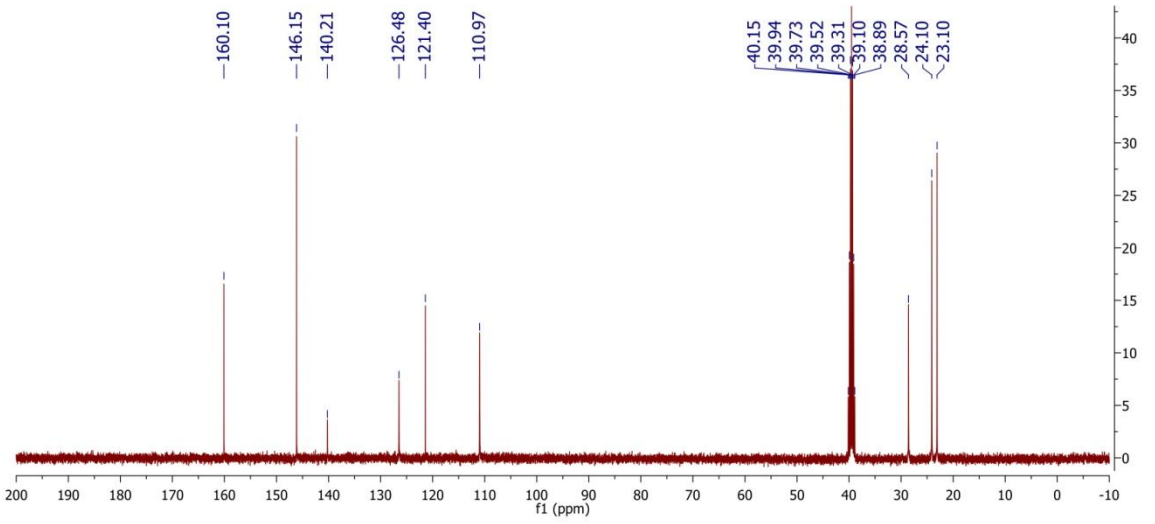
^{13}C{^{1}H} NMR spectrum (100 MHz) of **9b** in $CDCl_3$:



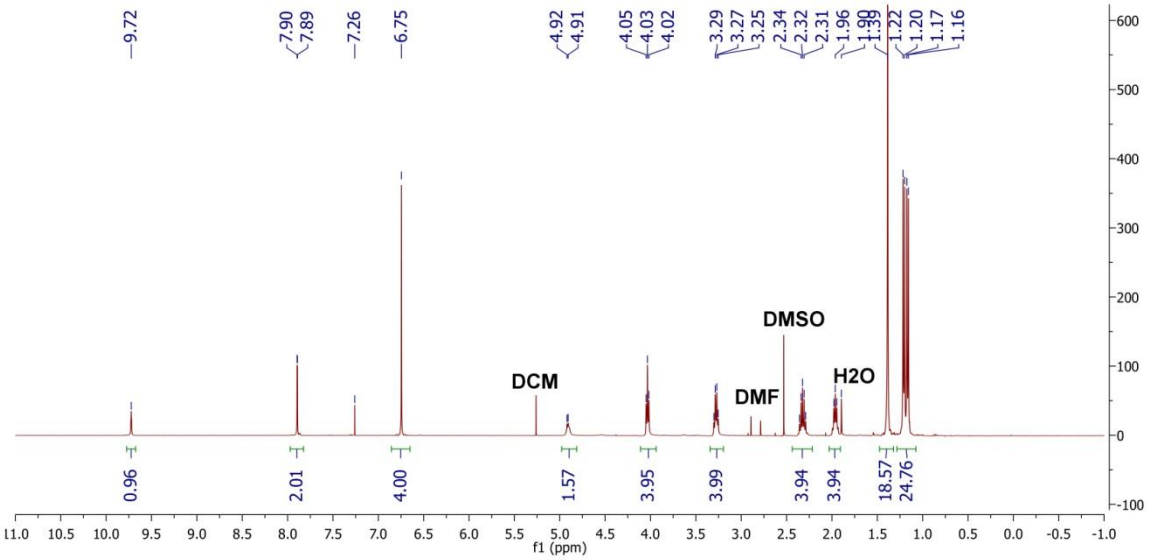
^{1}H NMR spectrum (400 MHz) of **10** in DMSO-d_6:



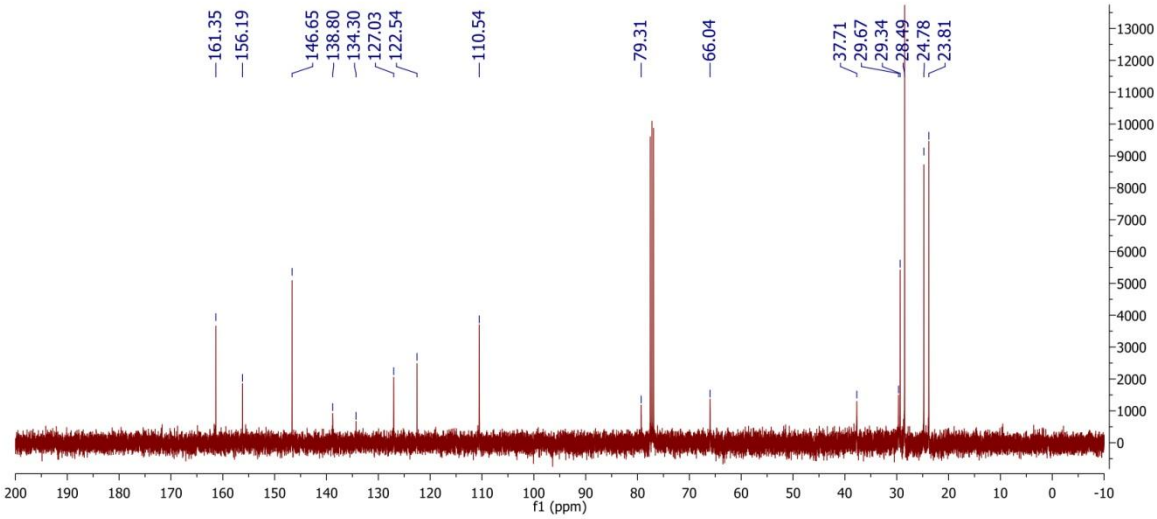
^{13}C{^{1}H} NMR spectrum (100 MHz) of **10** in DMSO-d_6:



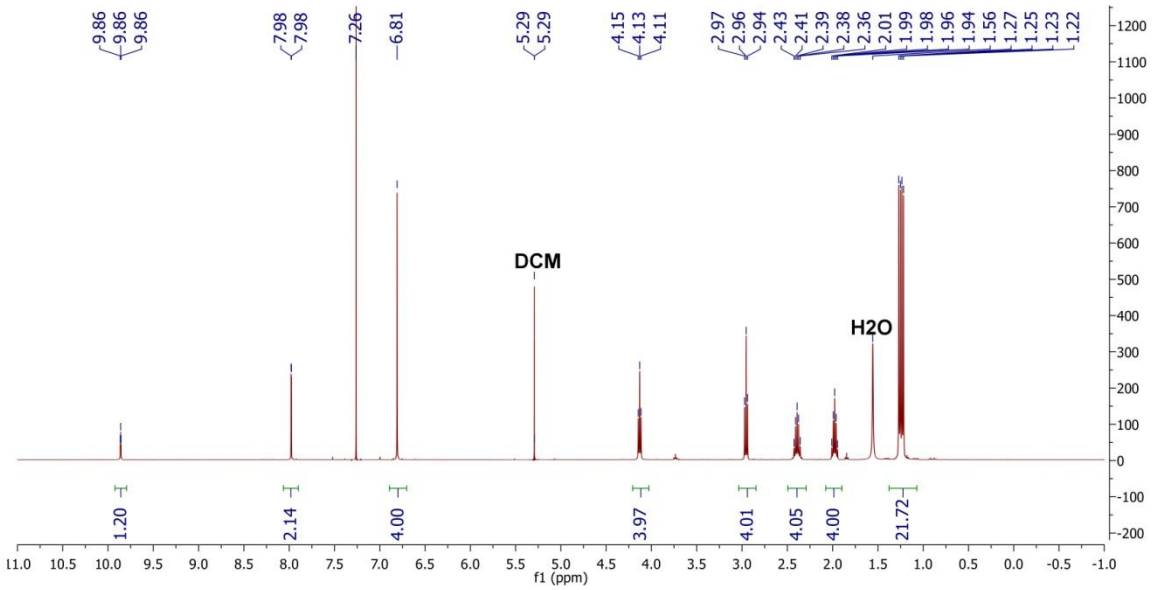
^{1}H NMR spectrum (400 MHz) of **12** in $CDCl_3$:



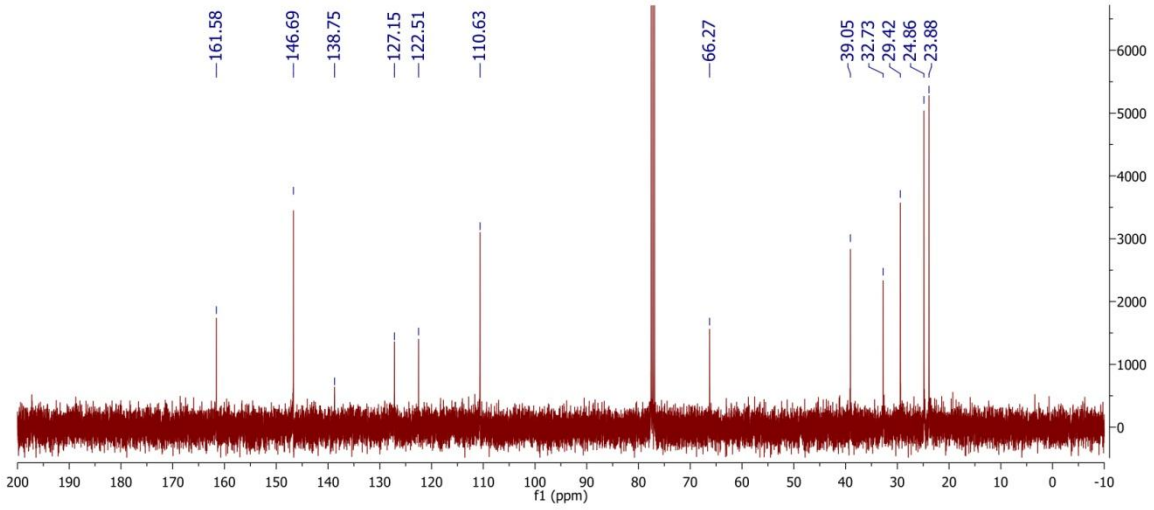
^{13}C{^{1}H} NMR spectrum (100 MHz) of **12** in $CDCl_3$:



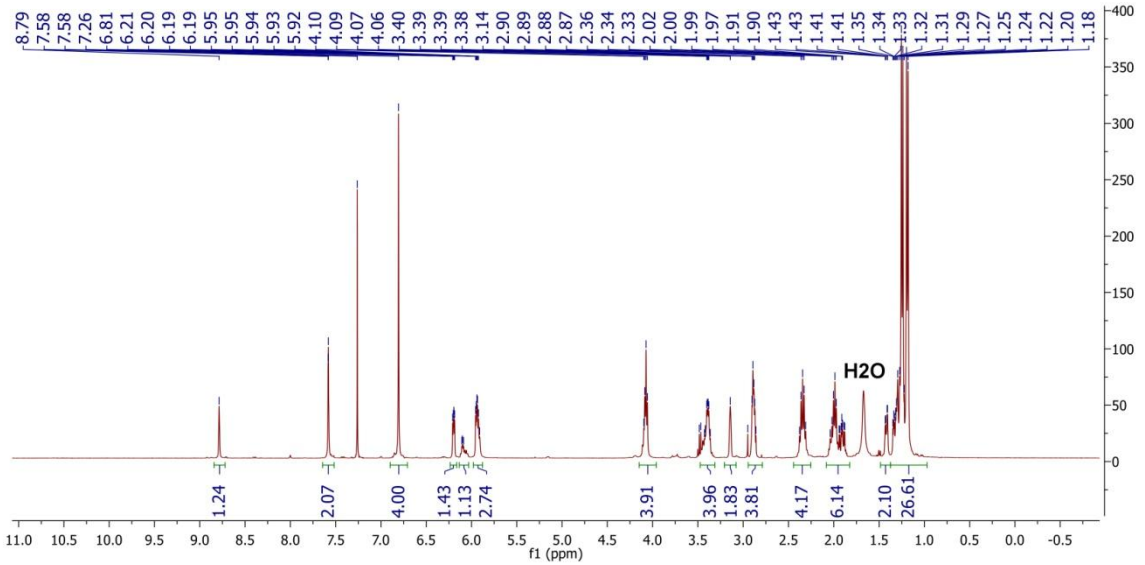
^{1}H NMR spectrum (400 MHz) of **13** in $CDCl_3$:



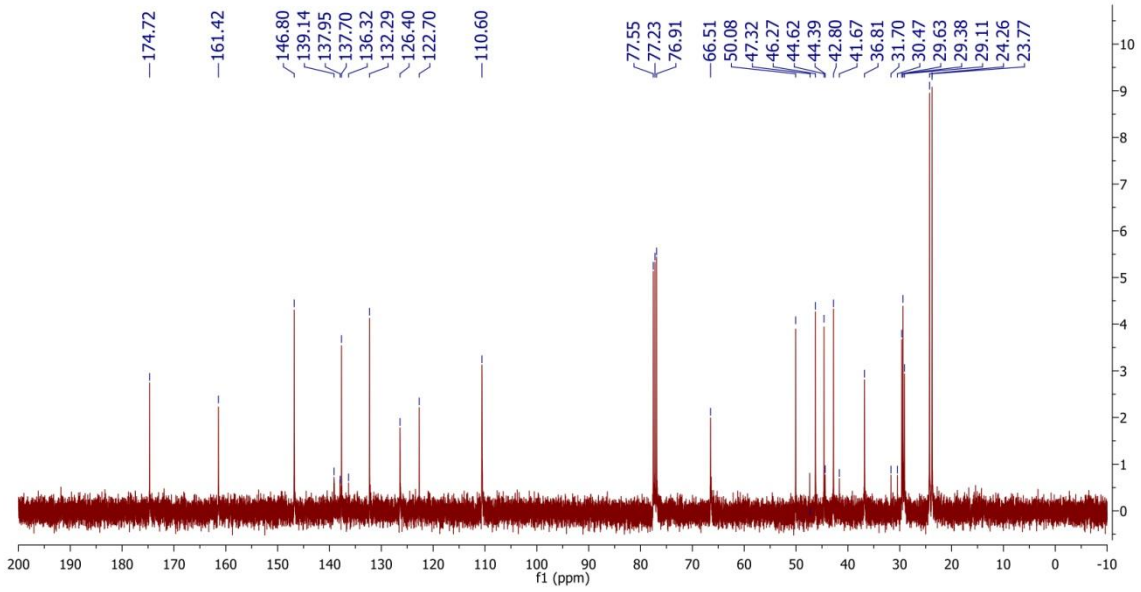
^{13}C{^{1}H} NMR spectrum (100 MHz) of **13** in $CDCl_3$:



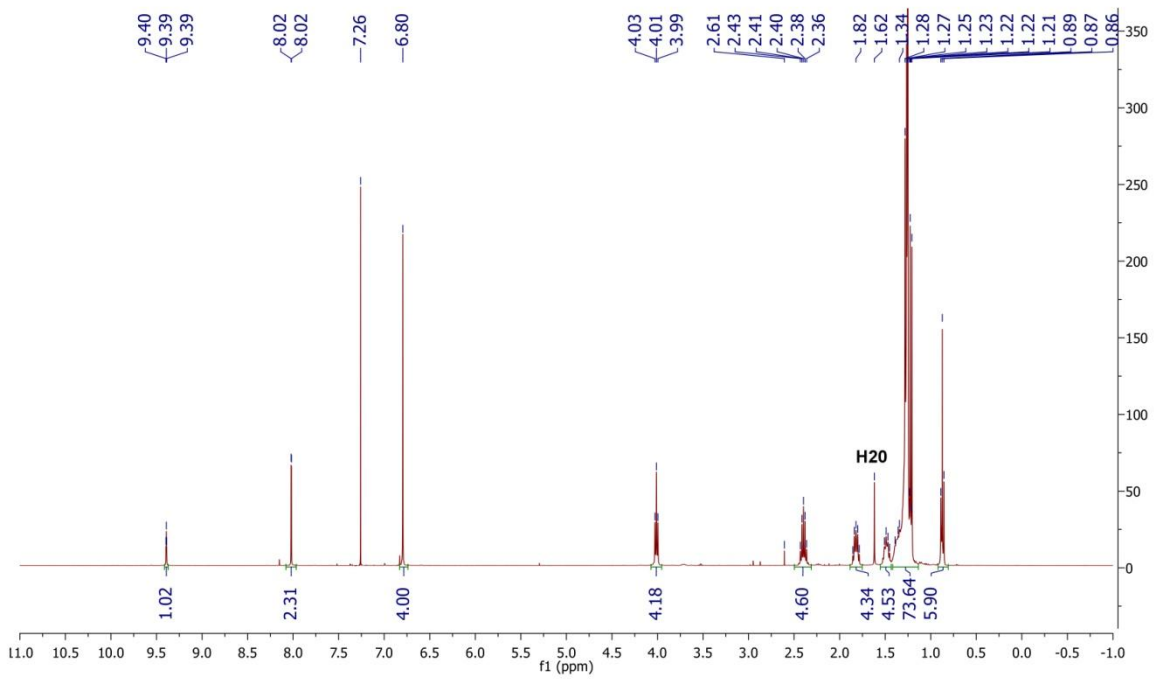
^{1}H NMR spectrum (400 MHz) of **15** in $CDCl_3$:



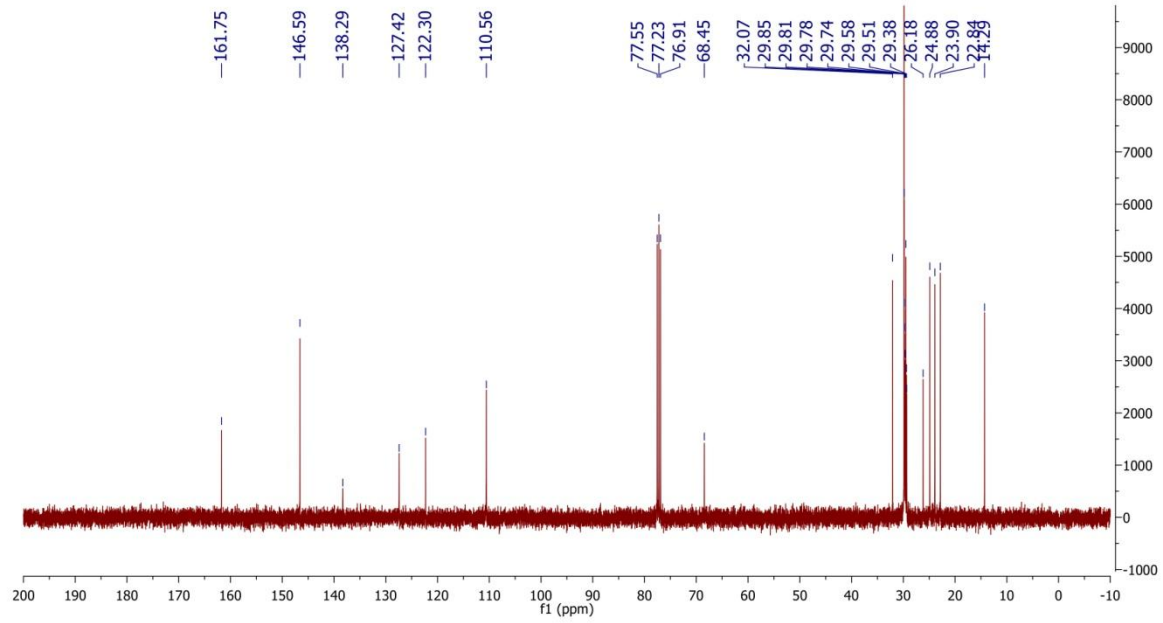
^{13}C{^{1}H} NMR spectrum (100 MHz) of **15** in $CDCl_3$:



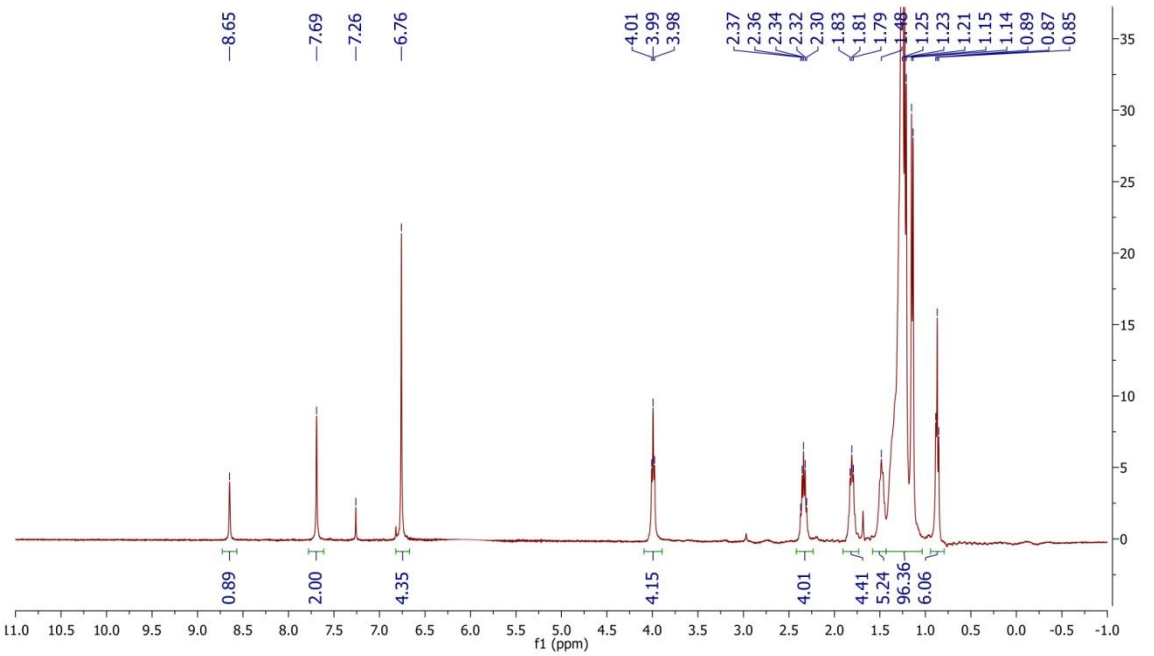
^{1}H NMR spectrum (400 MHz) of **16** in $CDCl_3$:



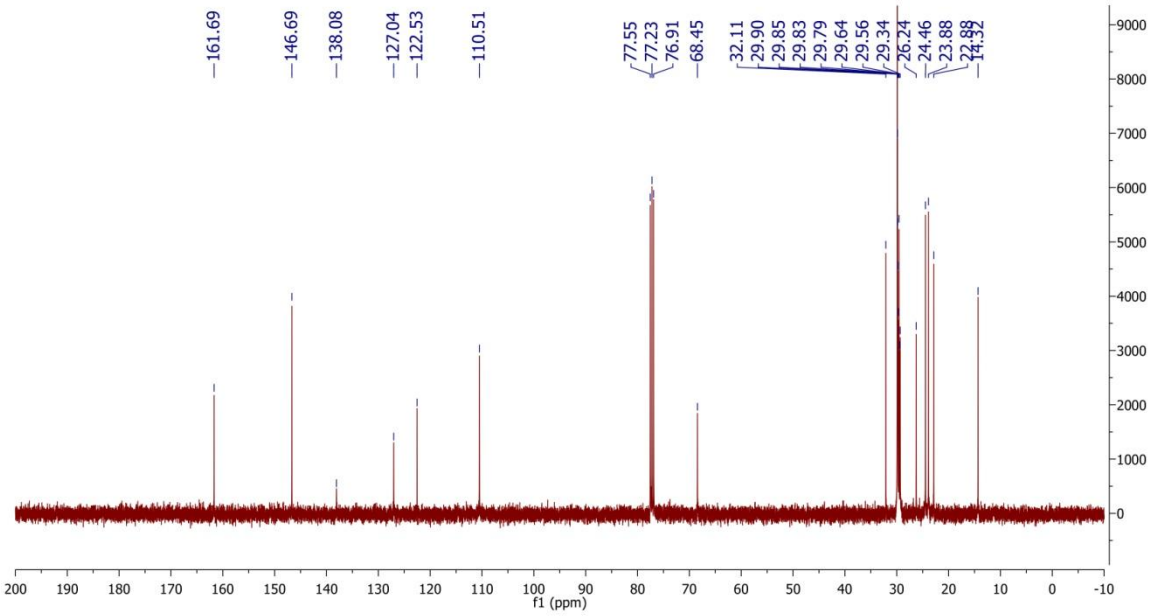
^{13}C{^{1}H} NMR spectrum (100 MHz) of **16** in $CDCl_3$:



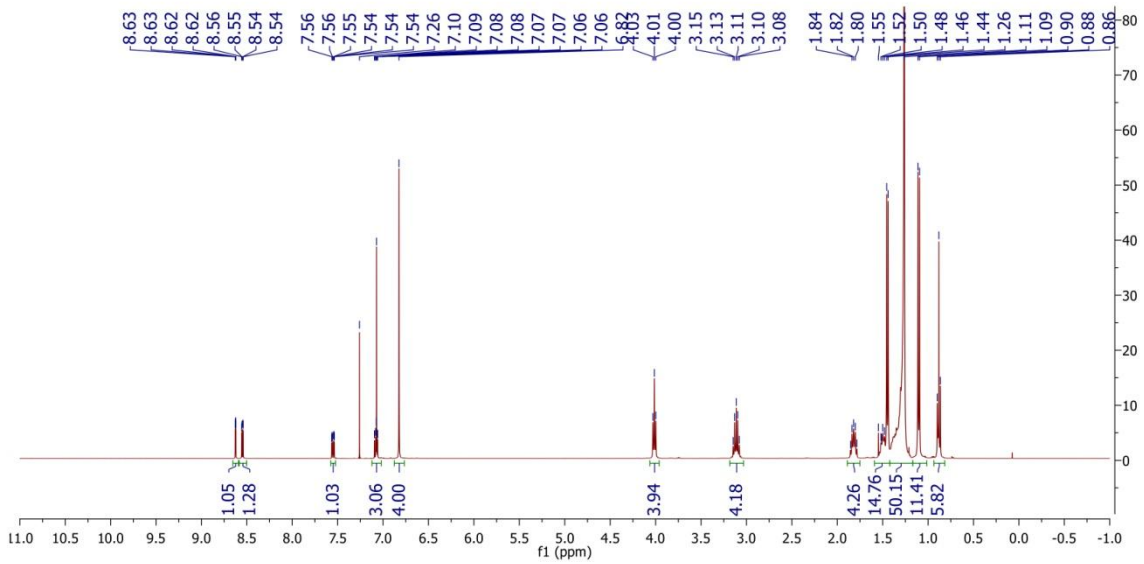
^{1}H NMR spectrum (400 MHz) of **17** in $CDCl_3$:



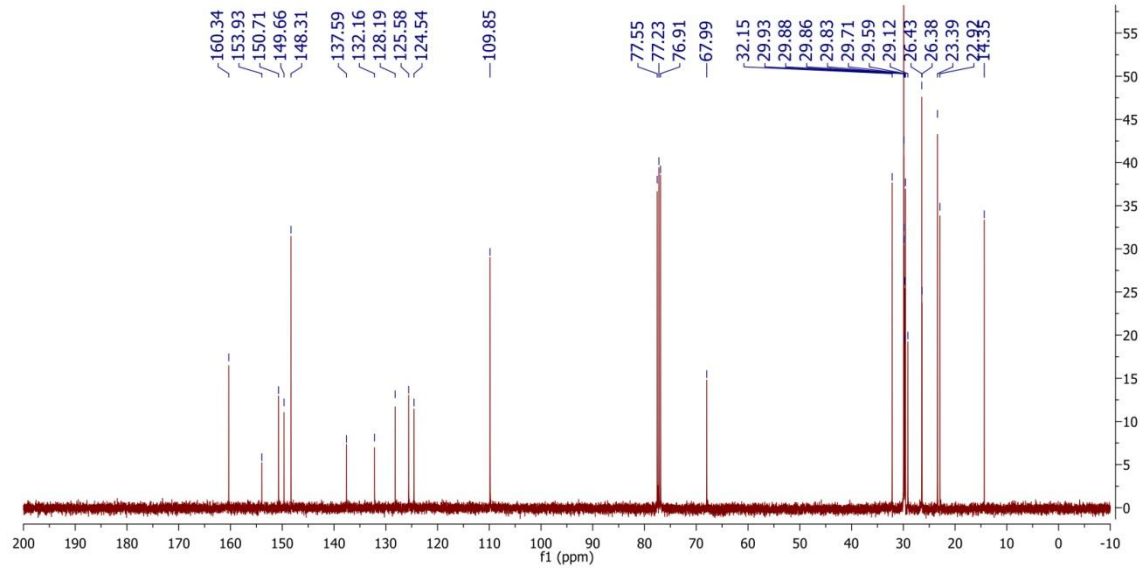
^{13}C{^{1}H} NMR spectrum (100 MHz) of **17** in $CDCl_3$:



^{1}H NMR spectrum (400 MHz) of **19** in $CDCl_3$:

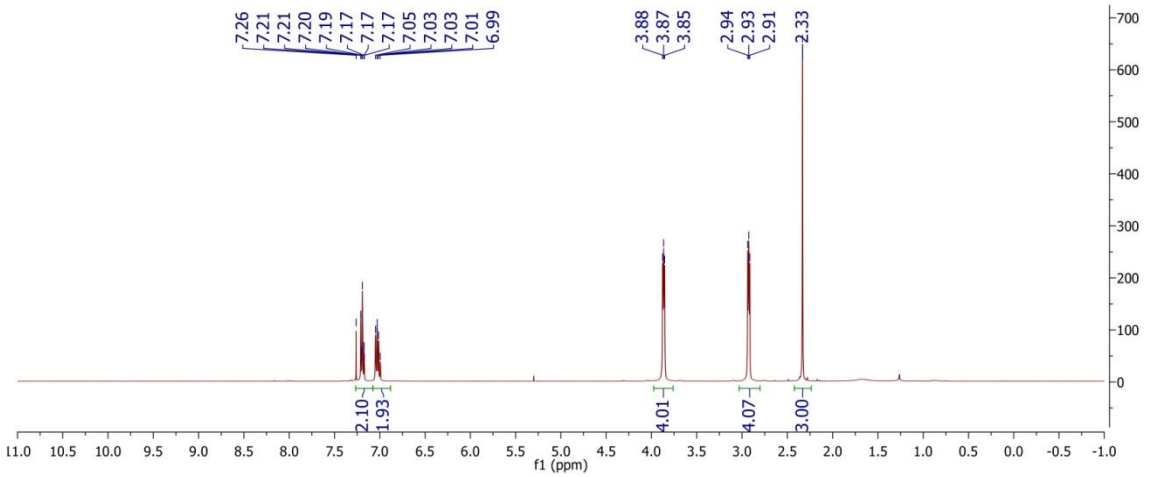


^{13}C{^{1}H} NMR spectrum (100 MHz) of **19** in $CDCl_3$:

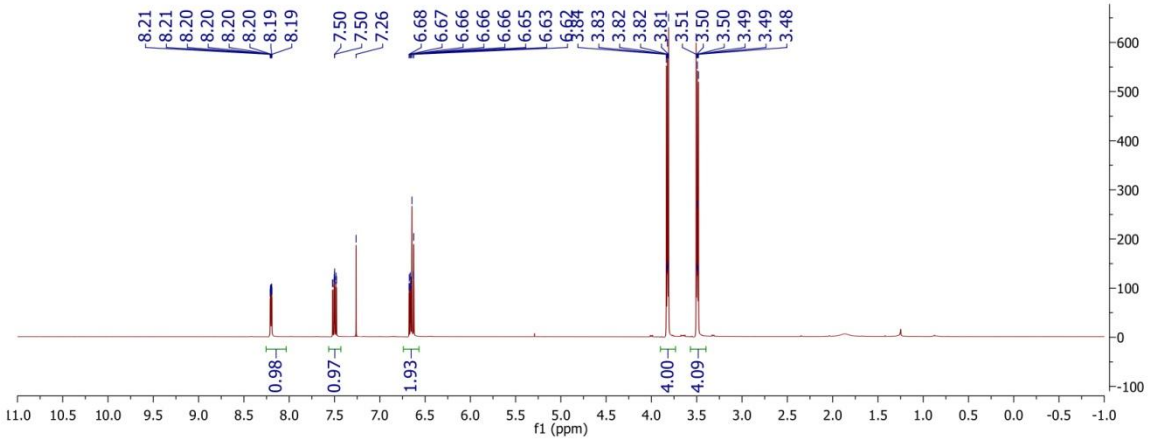


NMR spectra of Buchwald-Hartwig reaction products

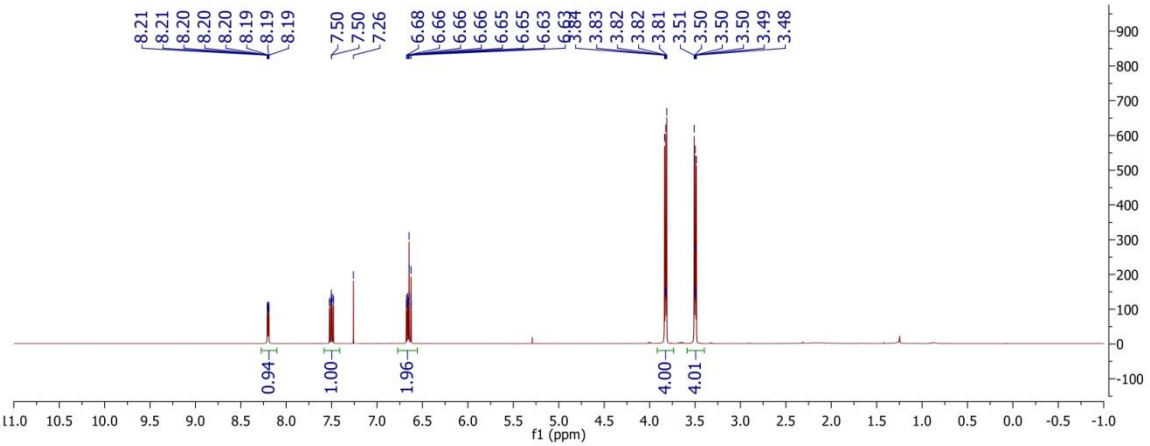
^{1}H NMR spectrum (400 MHz) of **23a** in $CDCl_3$:



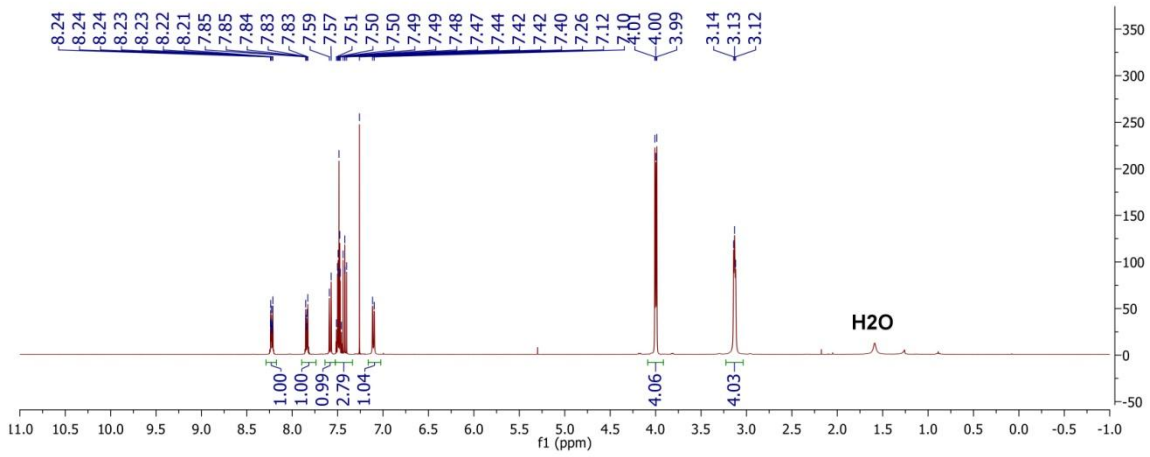
^{1}H NMR spectrum (400 MHz) of **23b** in $CDCl_3$:



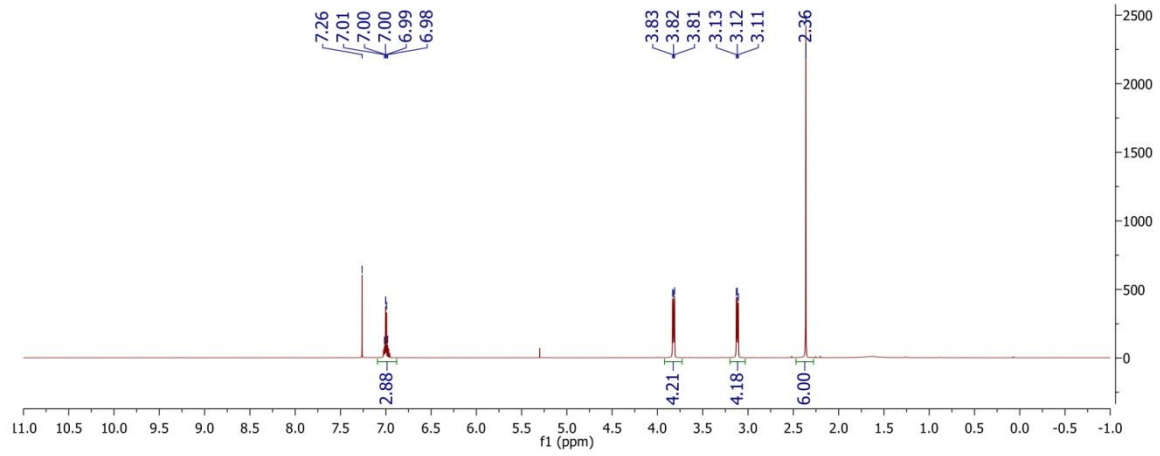
^{1}H NMR spectrum (400 MHz) of **23c** in $CDCl_3$:



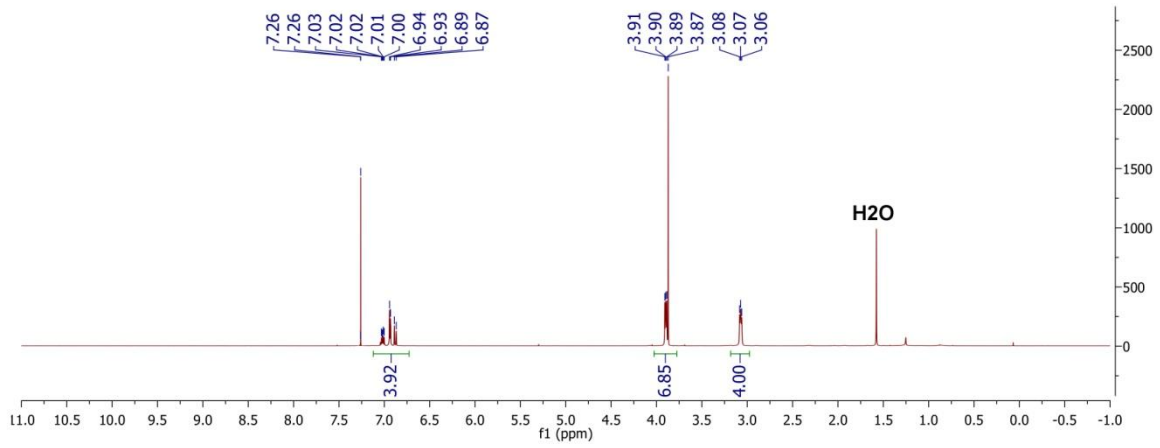
^{1}H NMR spectrum (400 MHz) of **23d** in $CDCl_3$:



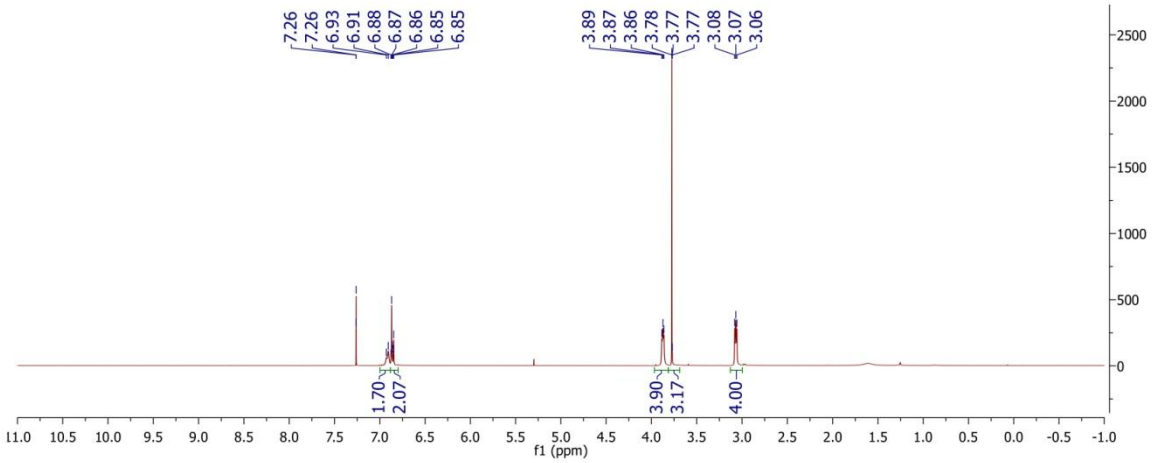
^{1}H NMR spectrum (400 MHz) of **23e** in $CDCl_3$:



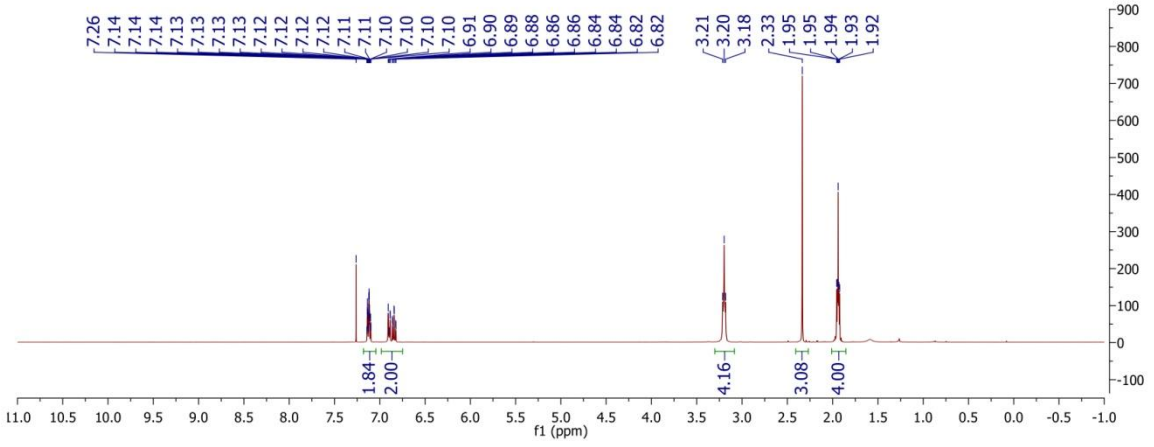
^{1}H NMR spectrum (400 MHz) of **23f** in $CDCl_3$:



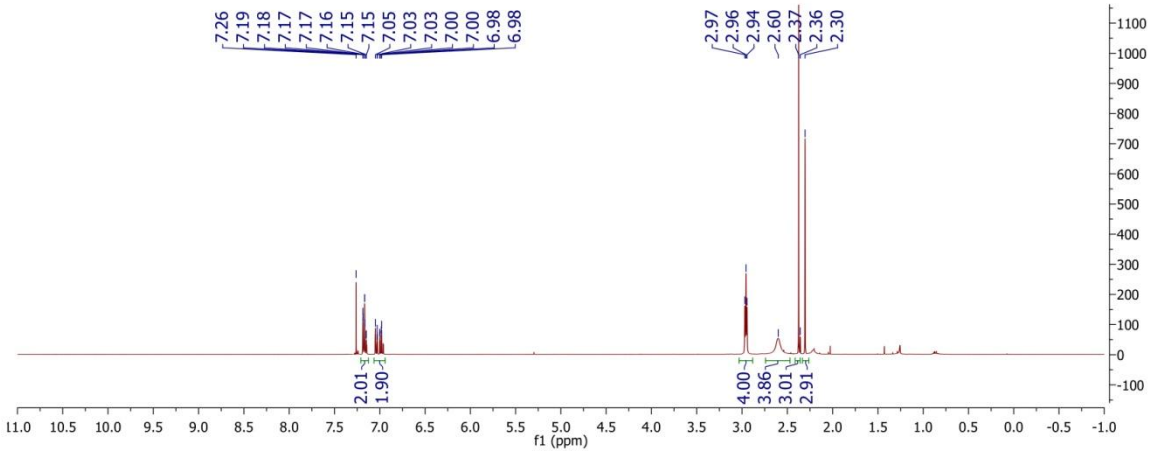
^{1}H NMR spectrum (400 MHz) of **23g** in $CDCl_3$:



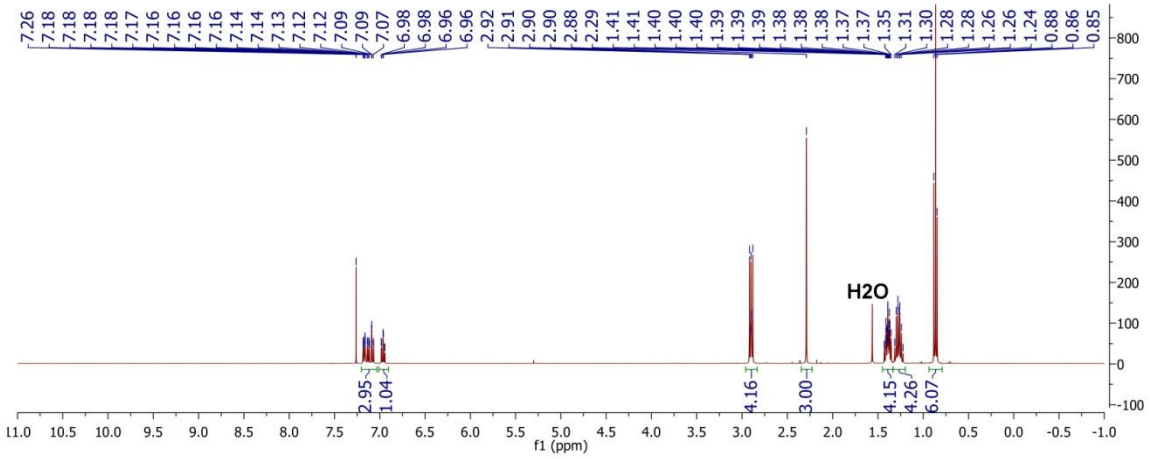
^{1}H NMR spectrum (400 MHz) of **23h** in $CDCl_3$:



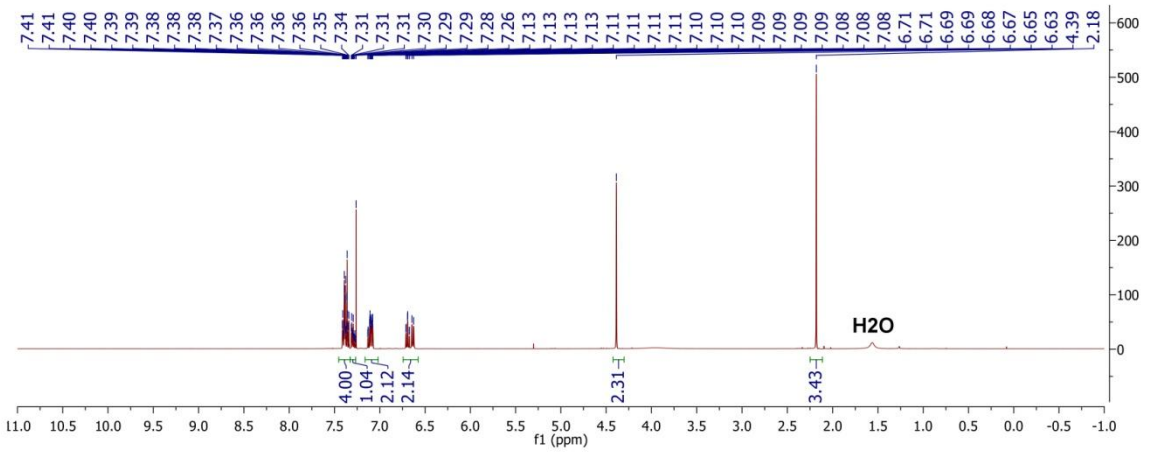
^{1}H NMR spectrum (400 MHz) of **23i** in $CDCl_3$:



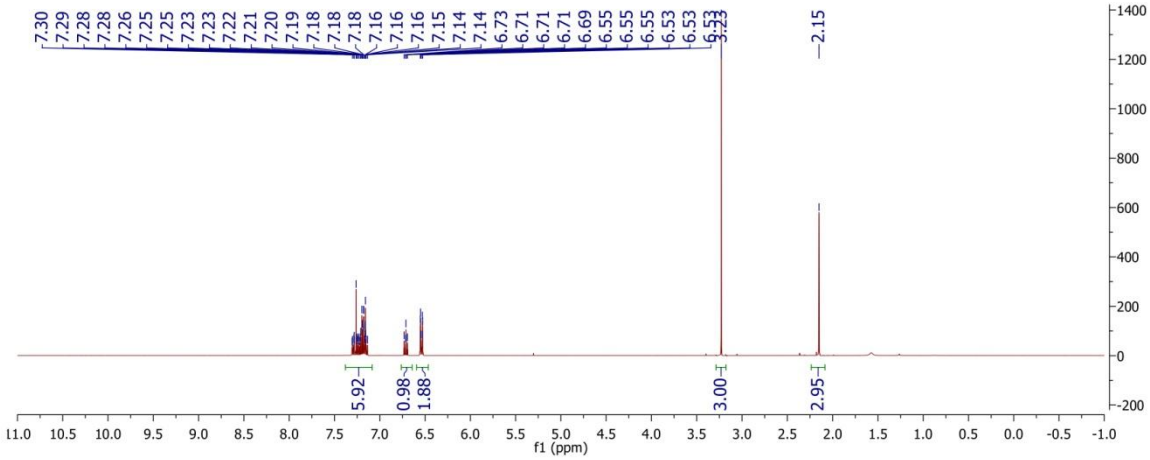
^{1}H NMR spectrum (400 MHz) of **23j** in $CDCl_3$:



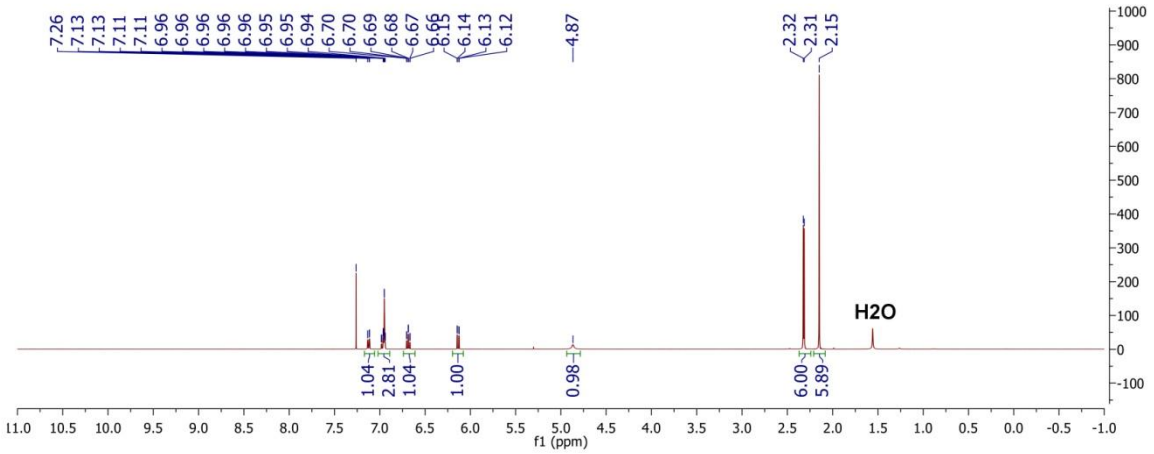
^{1}H NMR spectrum (400 MHz) of **23k** in $CDCl_3$:



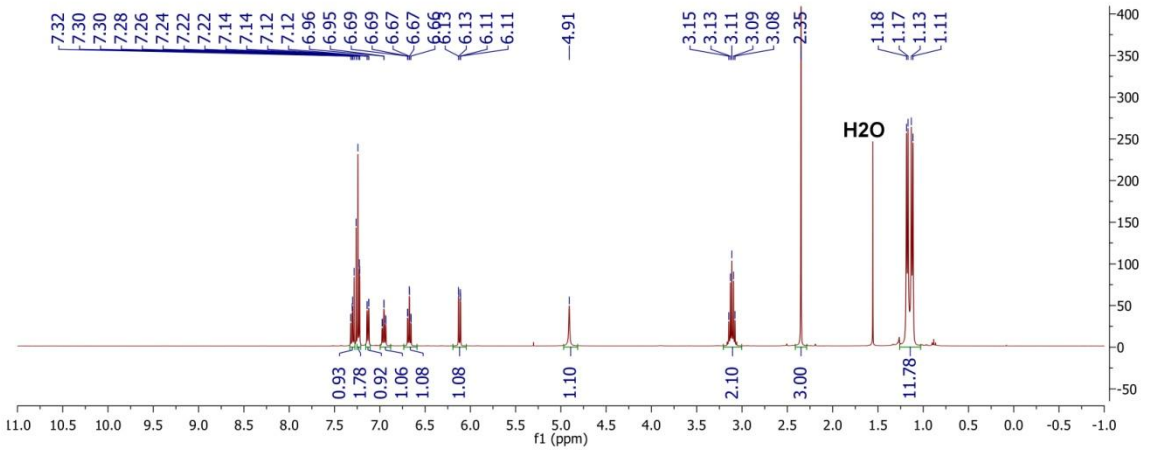
^{1}H NMR spectrum (400 MHz) of **23l** in $CDCl_3$:



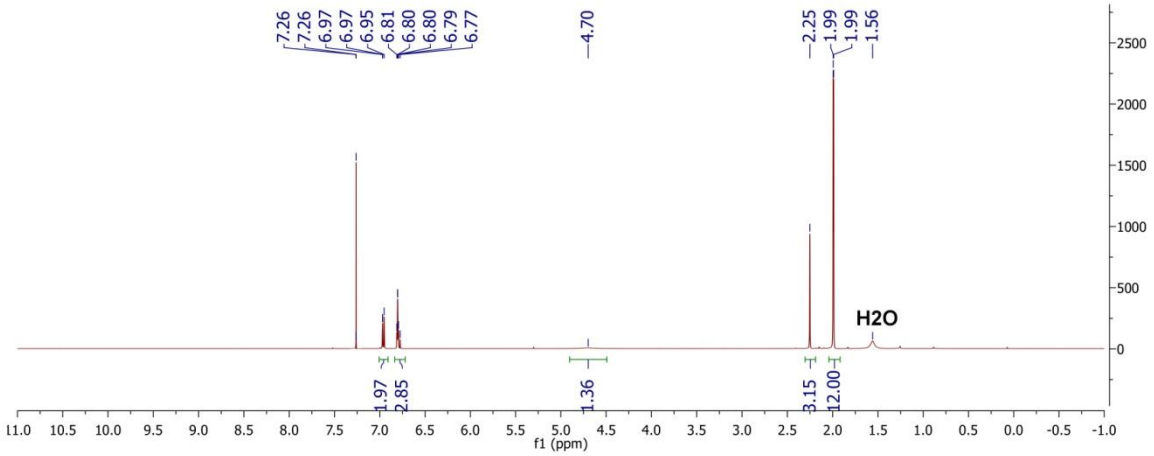
^{1}H NMR spectrum (400 MHz) of **23o** in $CDCl_3$:



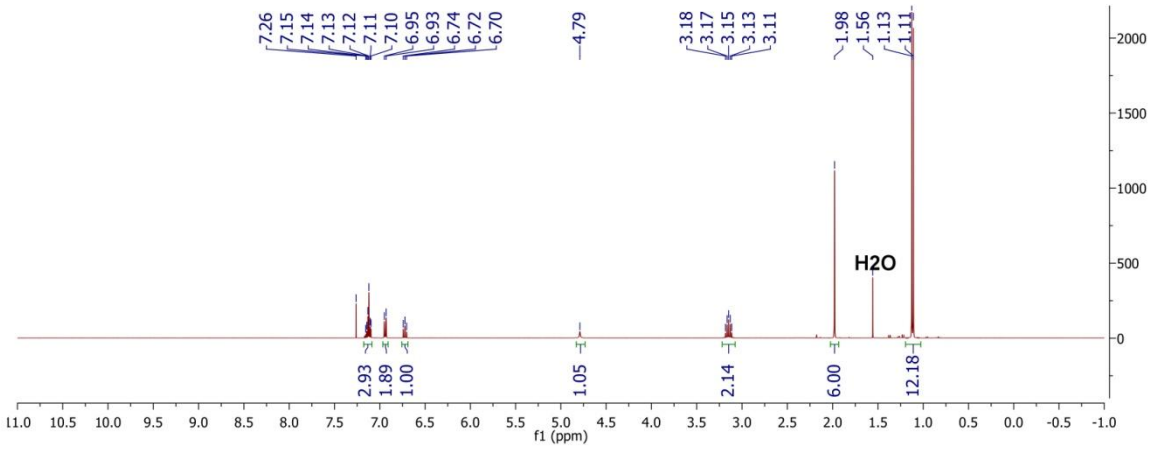
^{1}H NMR spectrum (400 MHz) of **23p** in $CDCl_3$:



^{1}H NMR spectrum (400 MHz) of **24a** in $CDCl_3$:

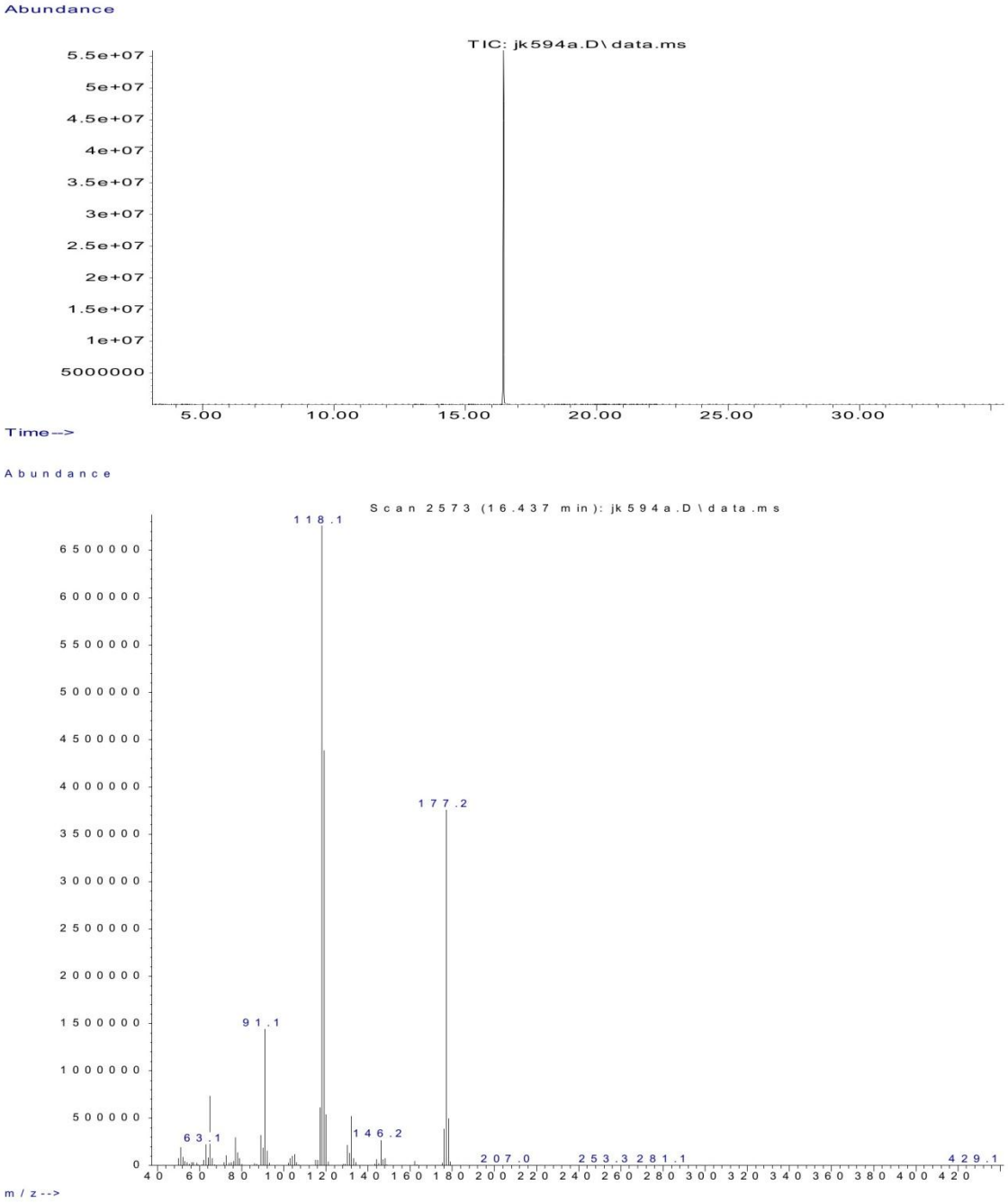


^{1}H NMR spectrum (400 MHz) of **24b** in $CDCl_3$:

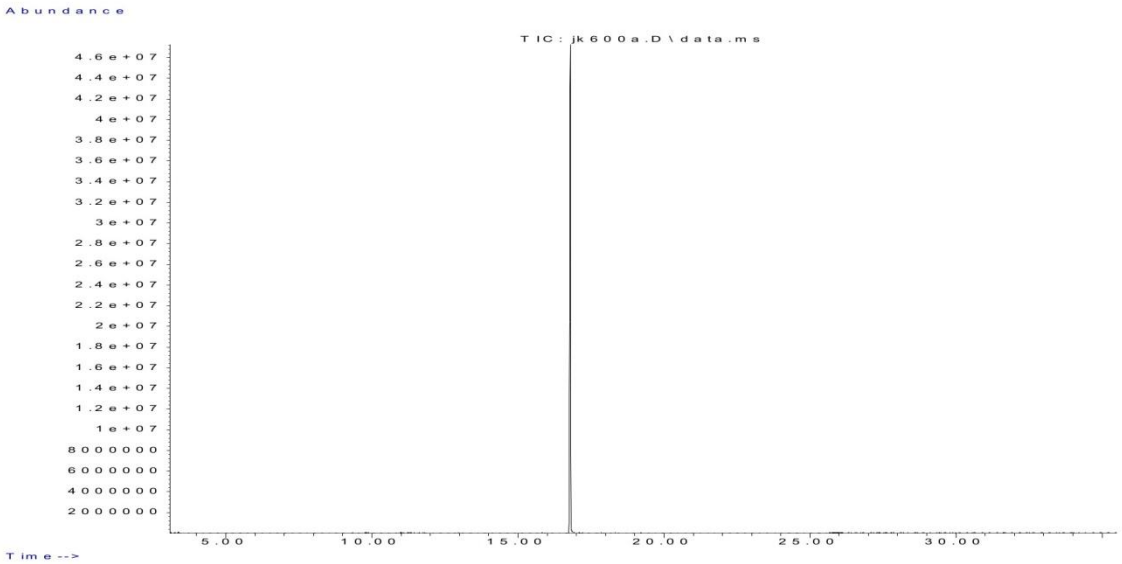


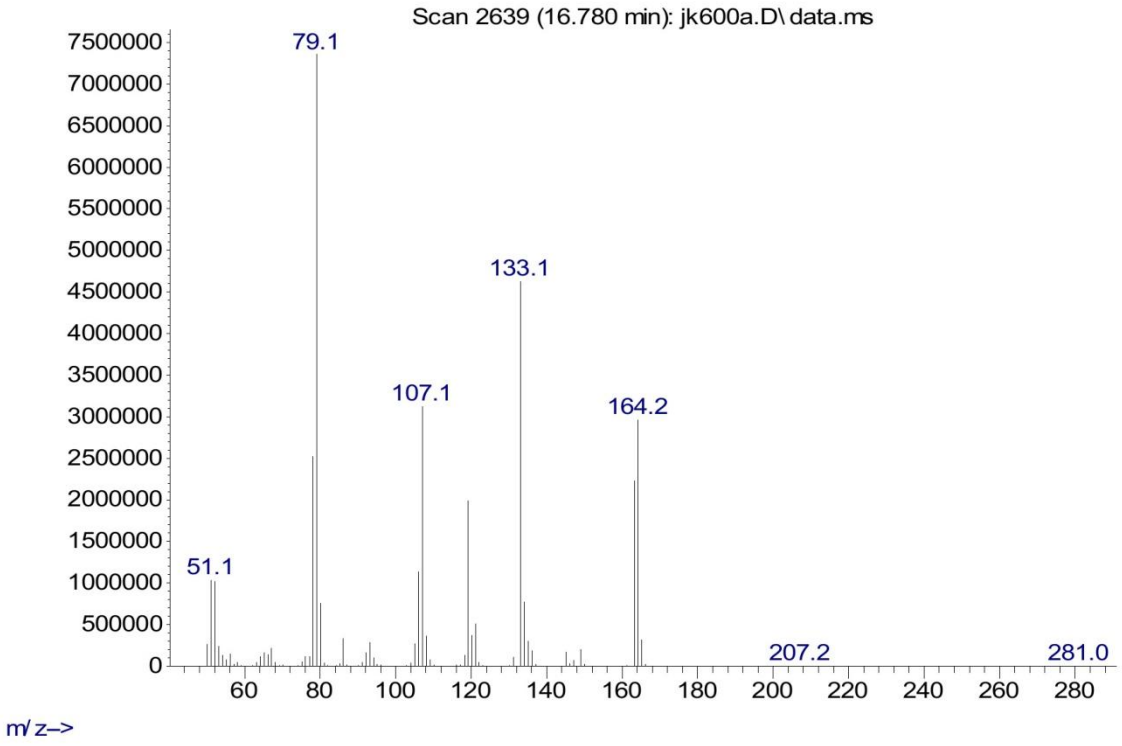
GC traces and mass spectra of Buchwald-Hartwig reaction products

GC trace and mass spectrum of **23a**:

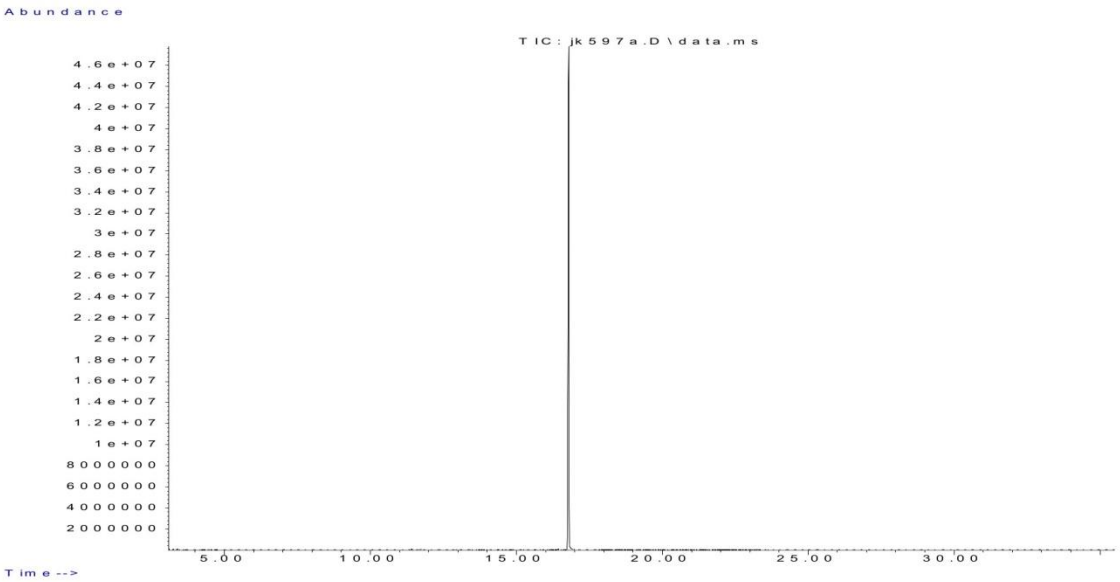


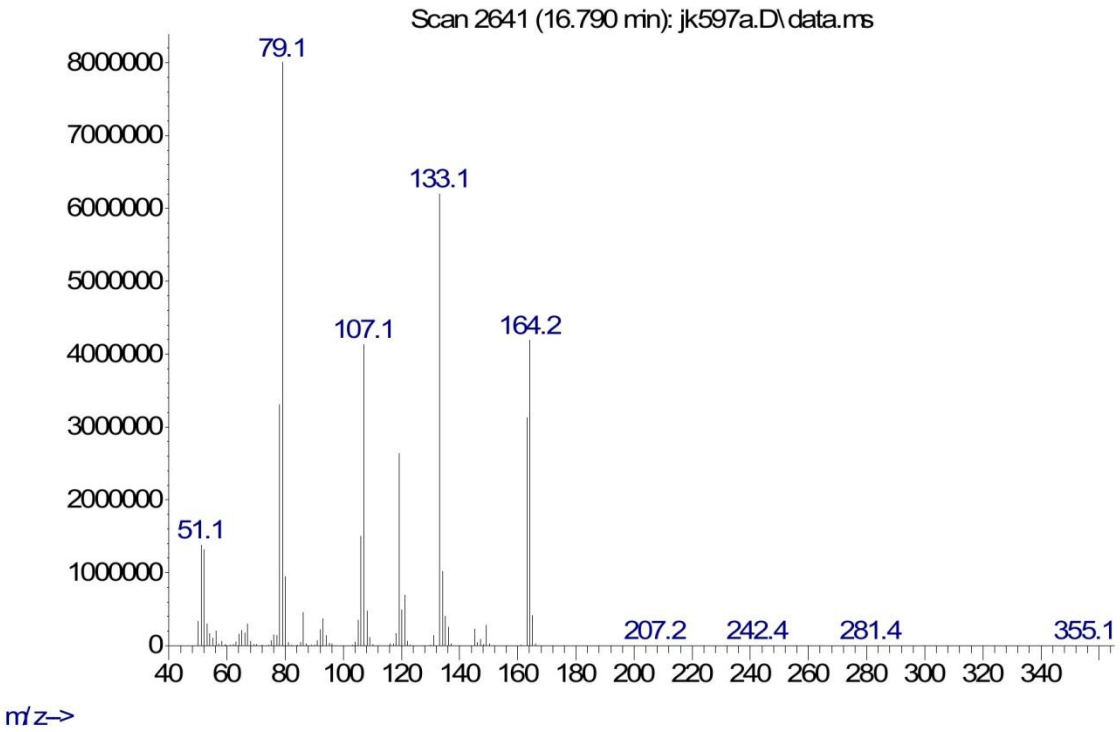
GC trace and mass spectrum of **23b**:



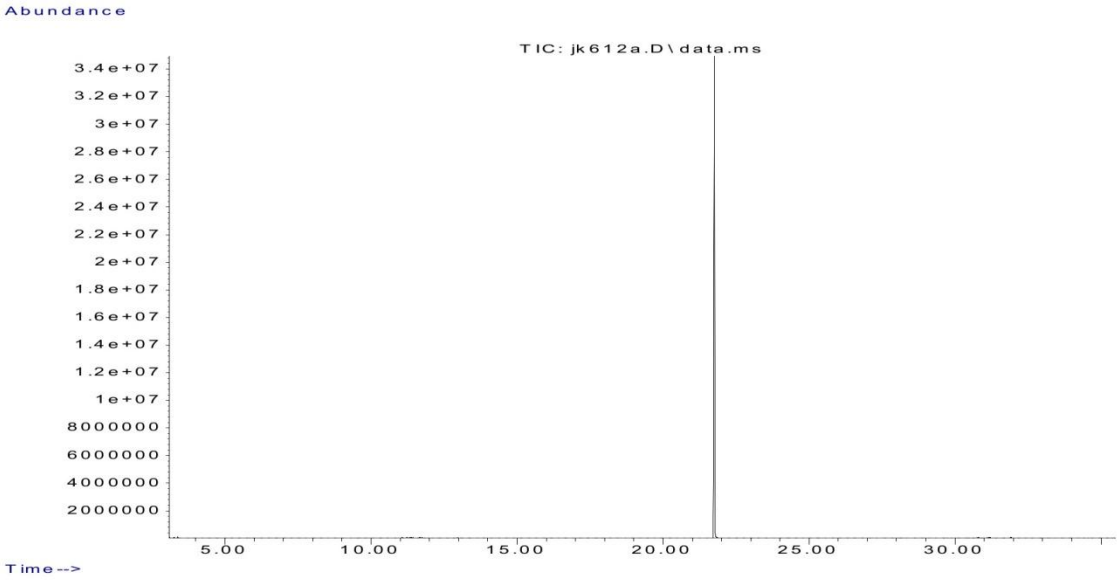


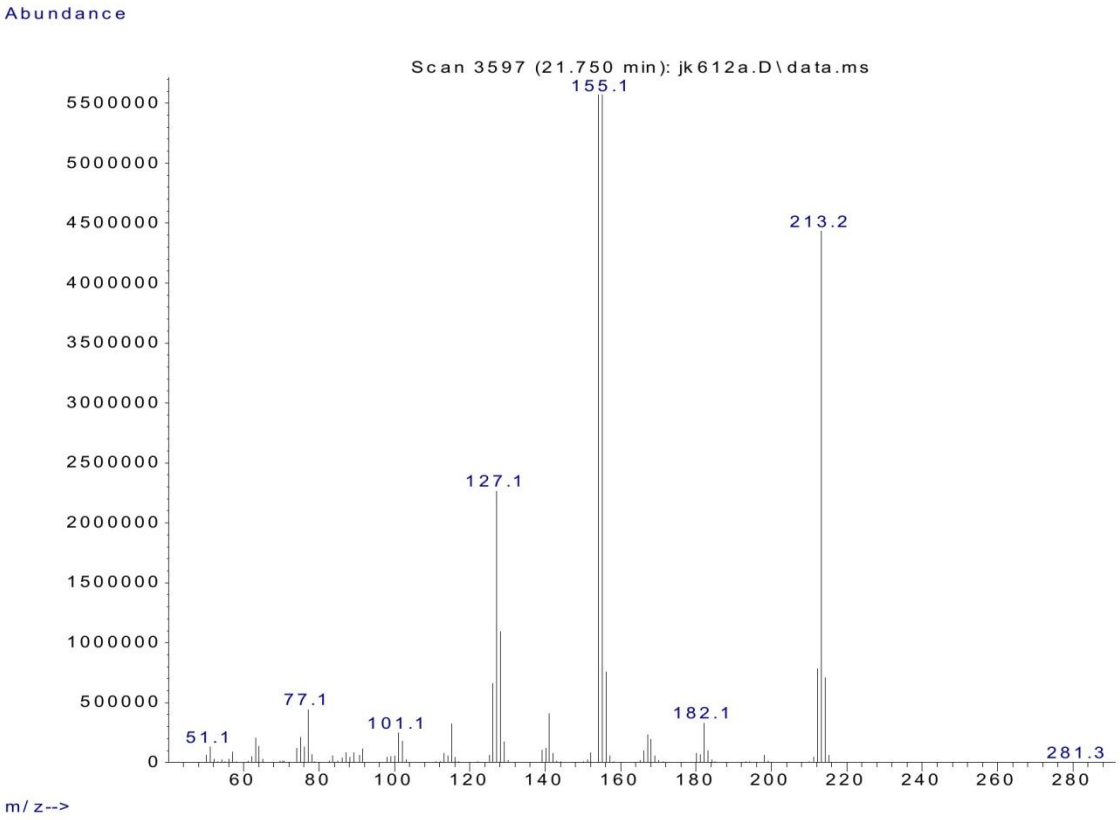
GC trace and mass spectrum of **23c**:



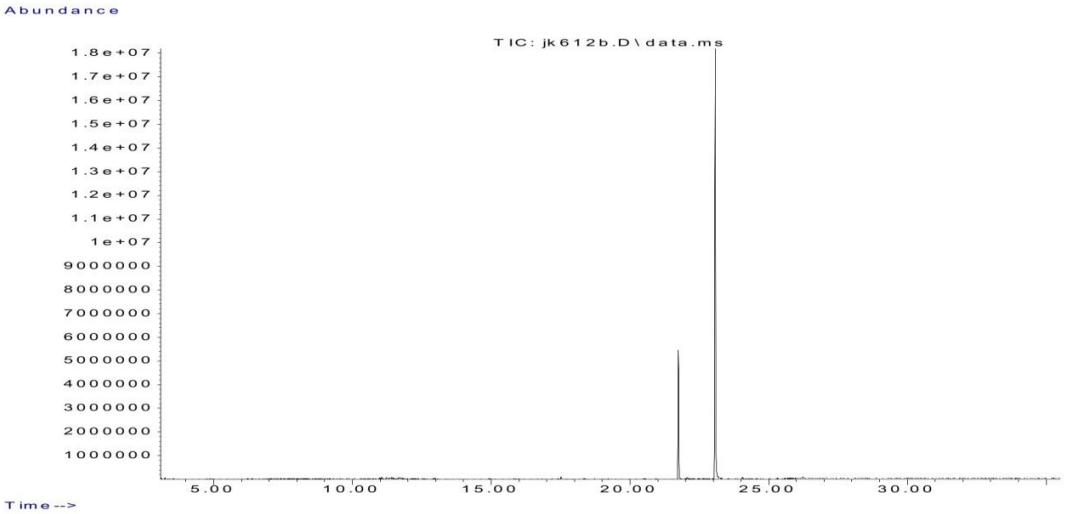


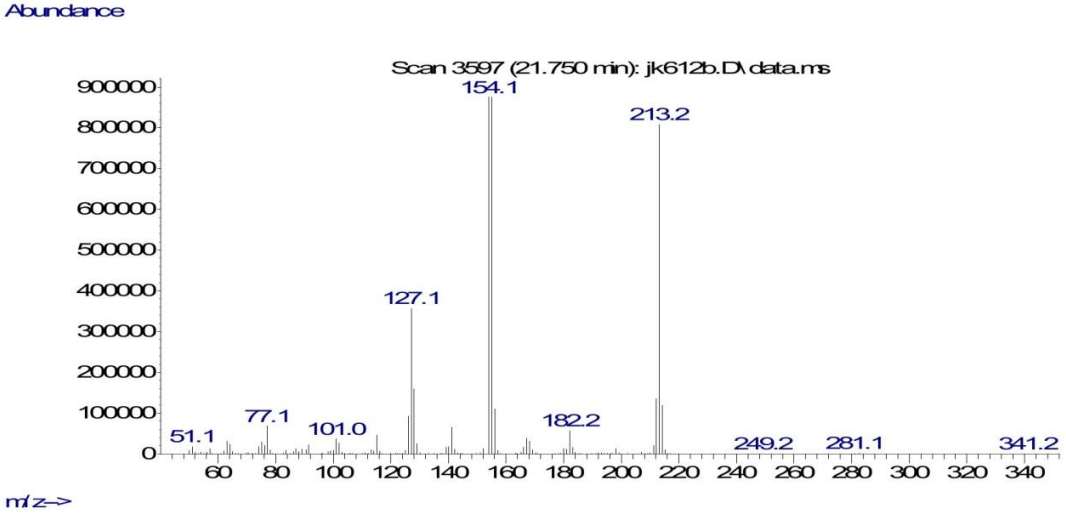
GC trace and mass spectrum of **23d**, pure 1-naphthyl isomer:

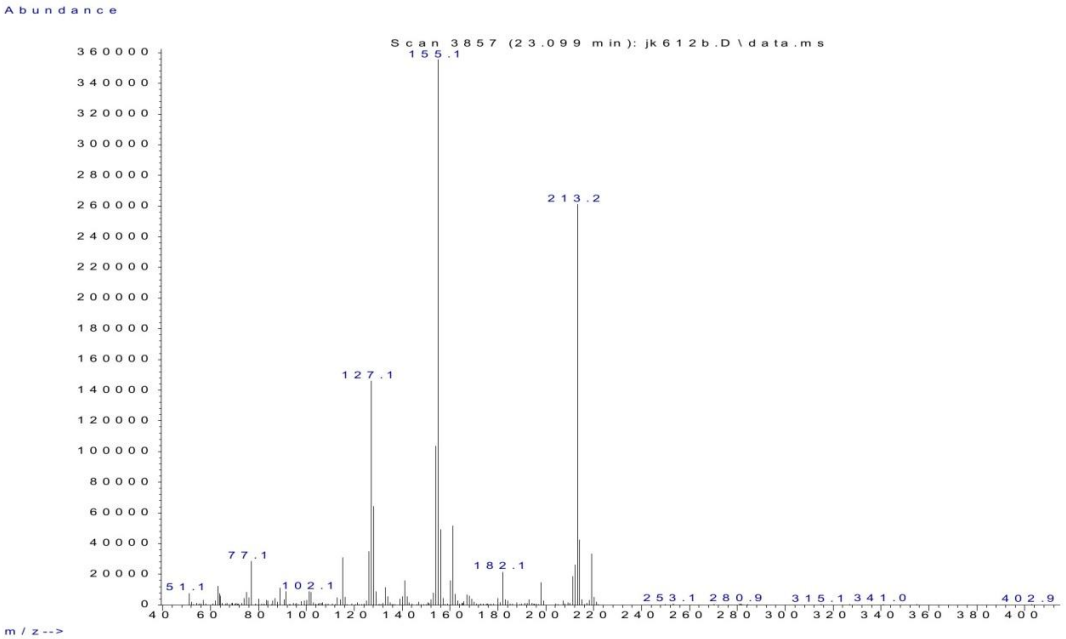




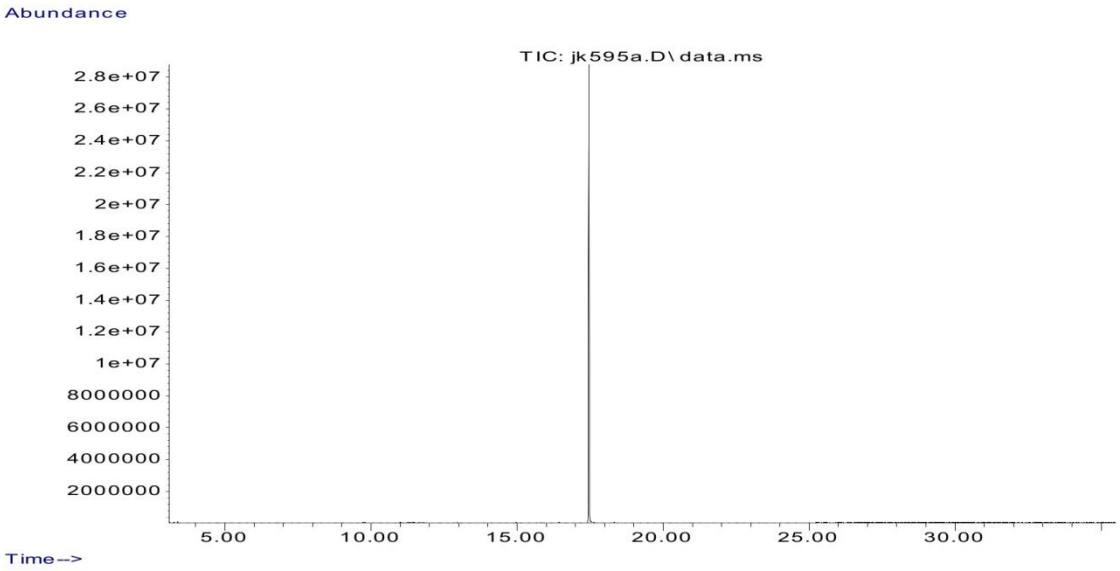
GC trace and mass spectrum of **23d**, 1 and 2-naphthyl isomers:

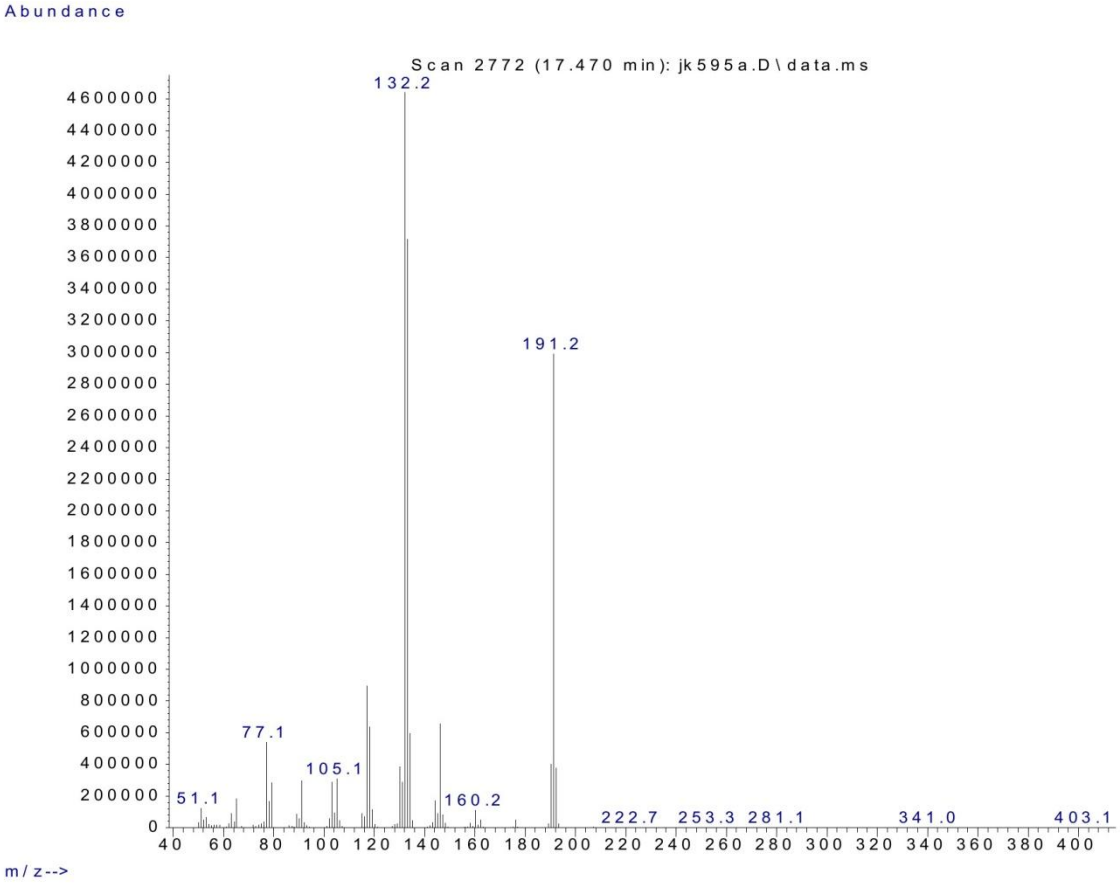




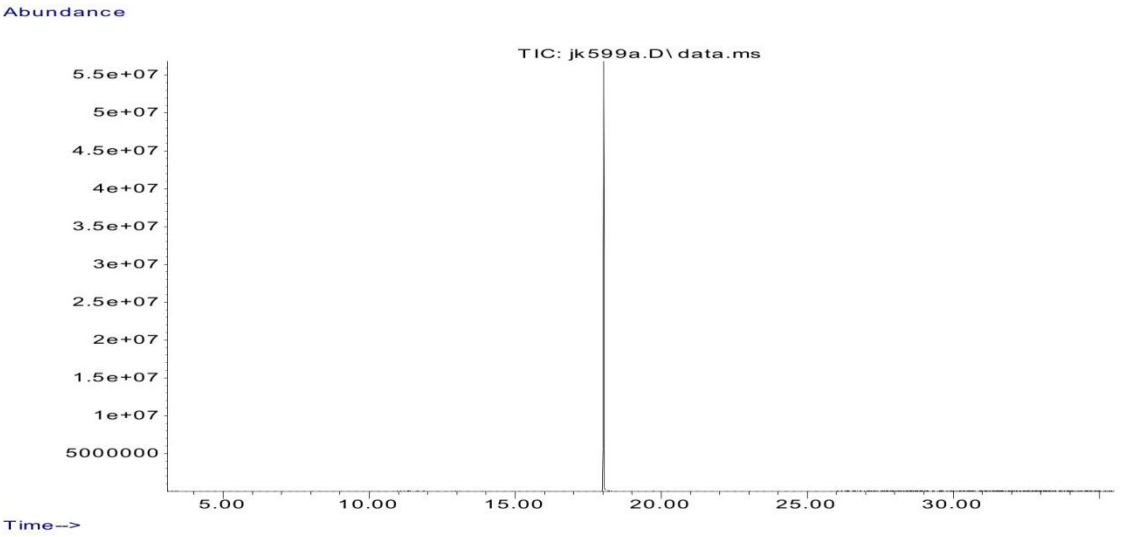


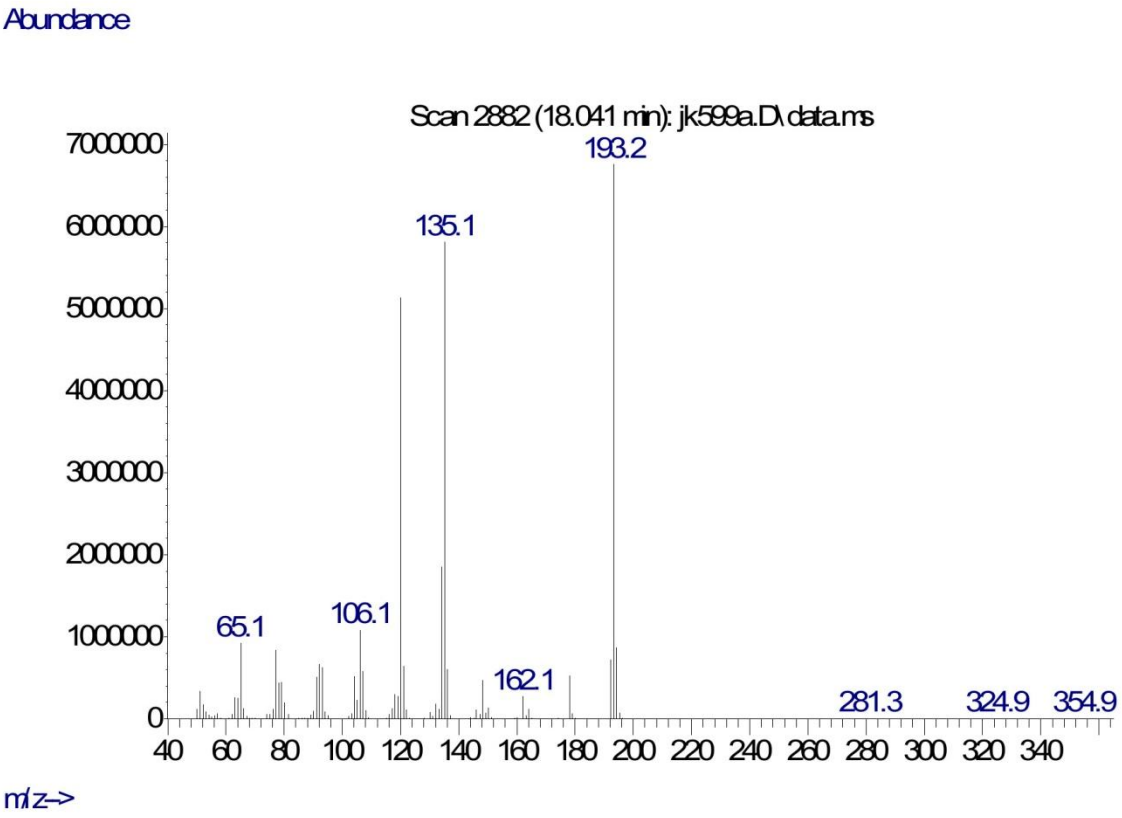
GC trace and mass spectrum of **23e**:



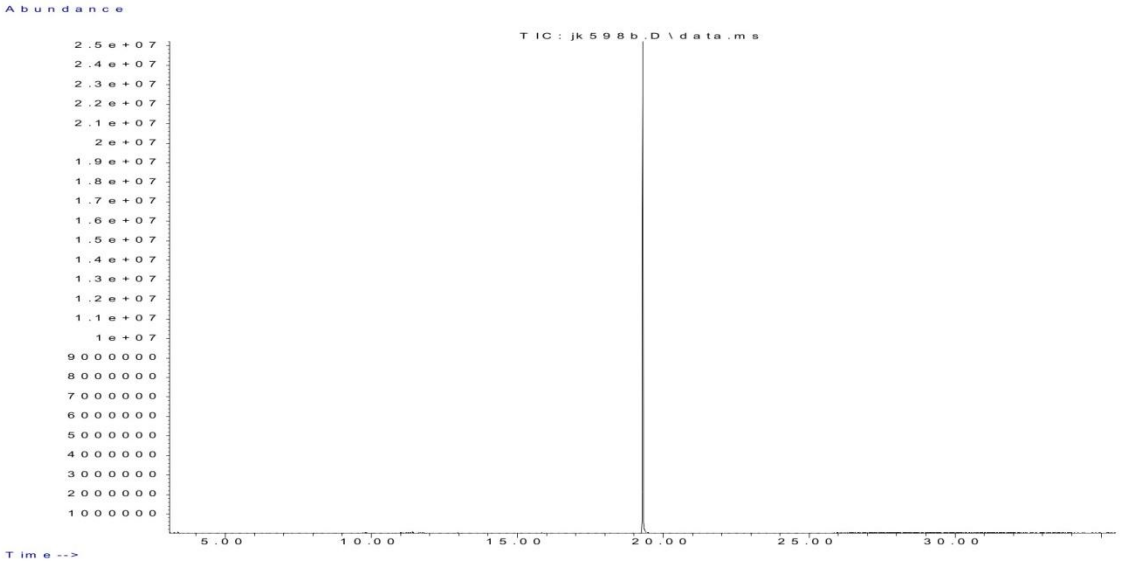


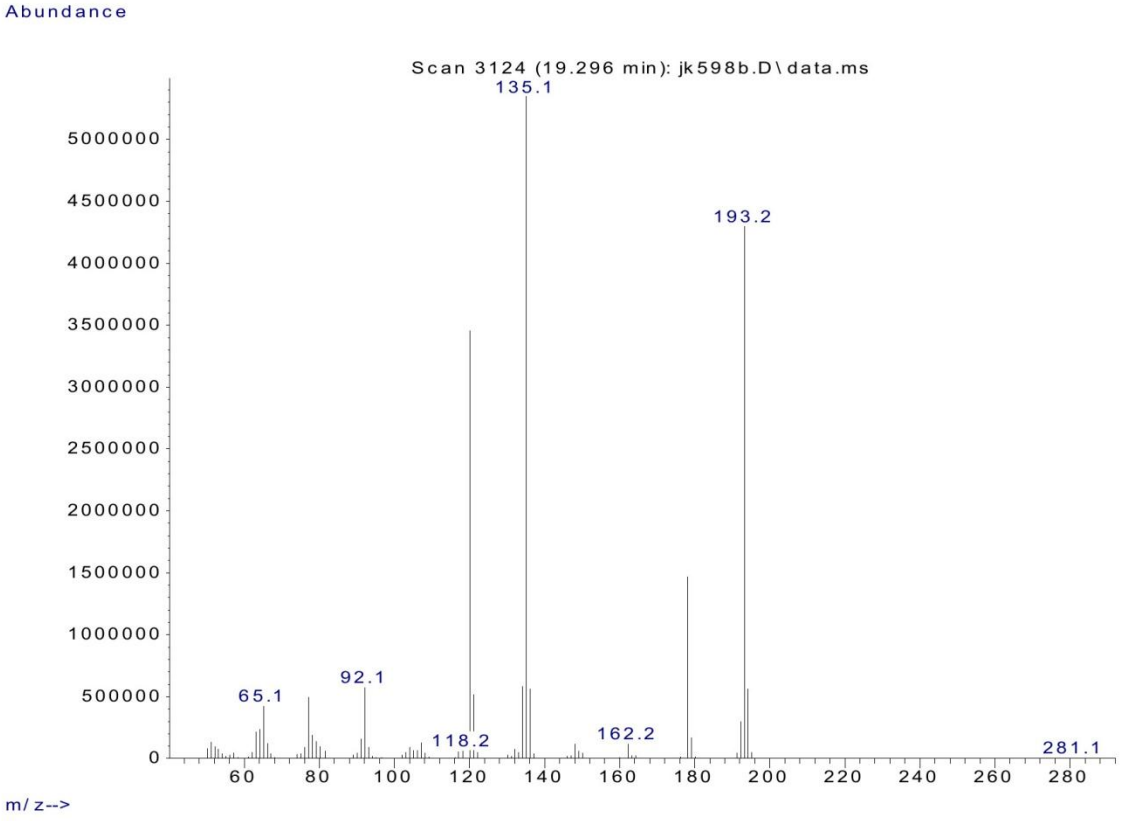
GC trace and mass spectrum of **23f**:



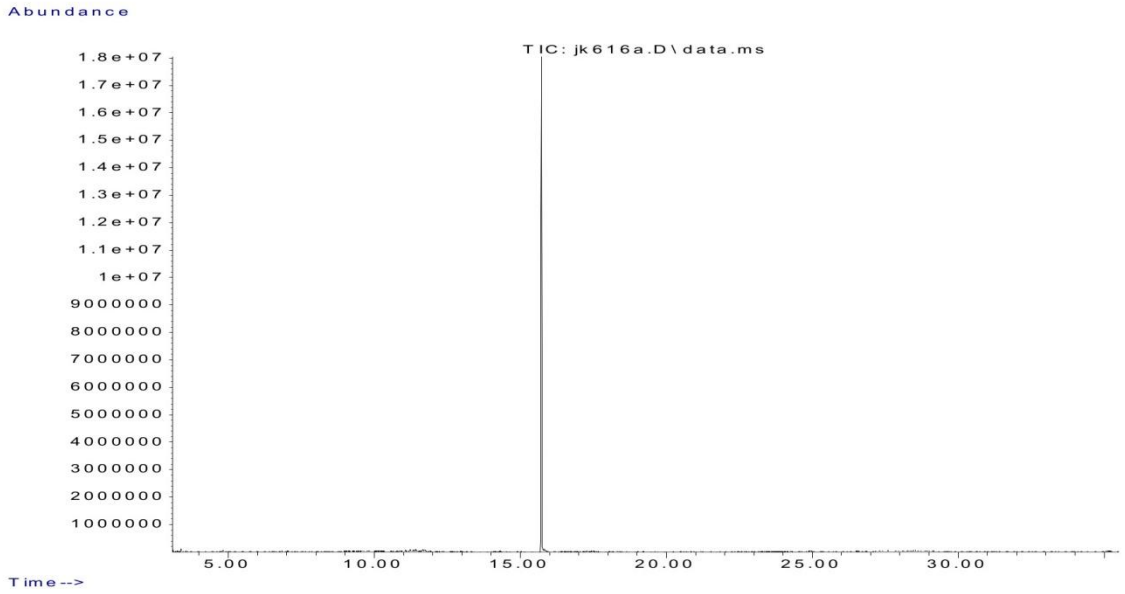


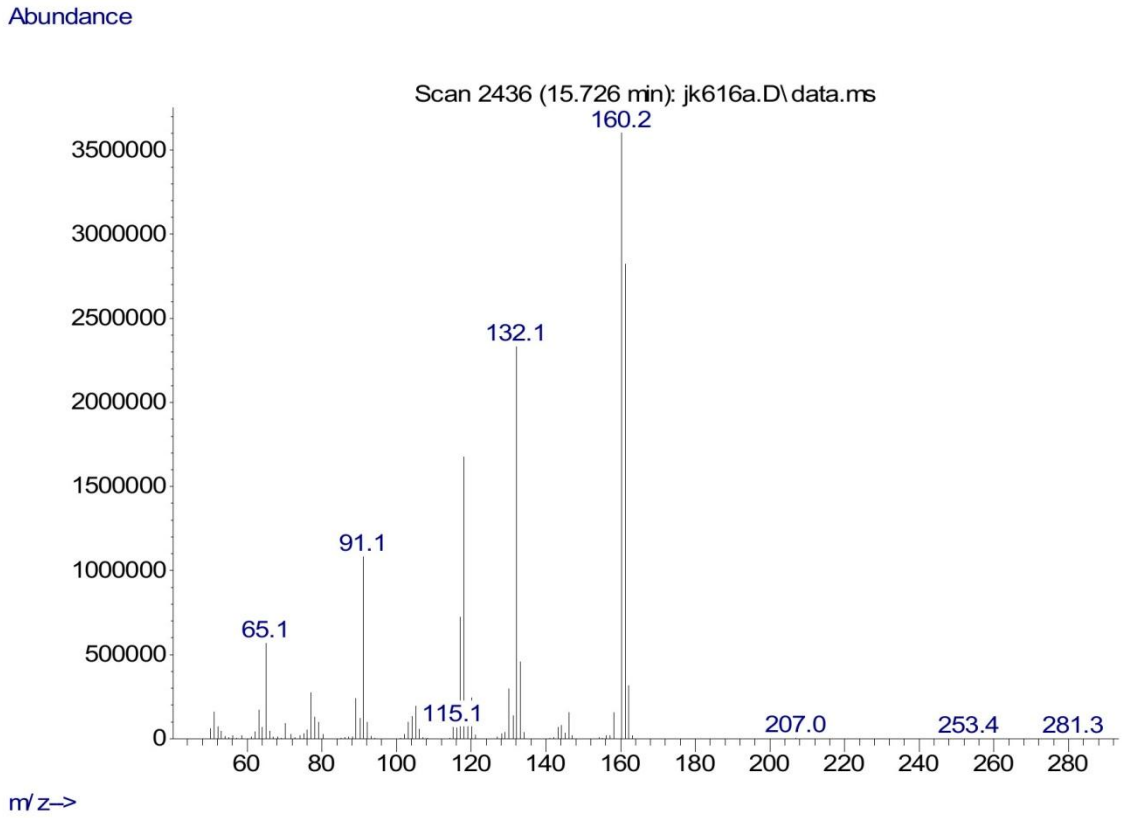
GC trace and mass spectrum of **23g**:



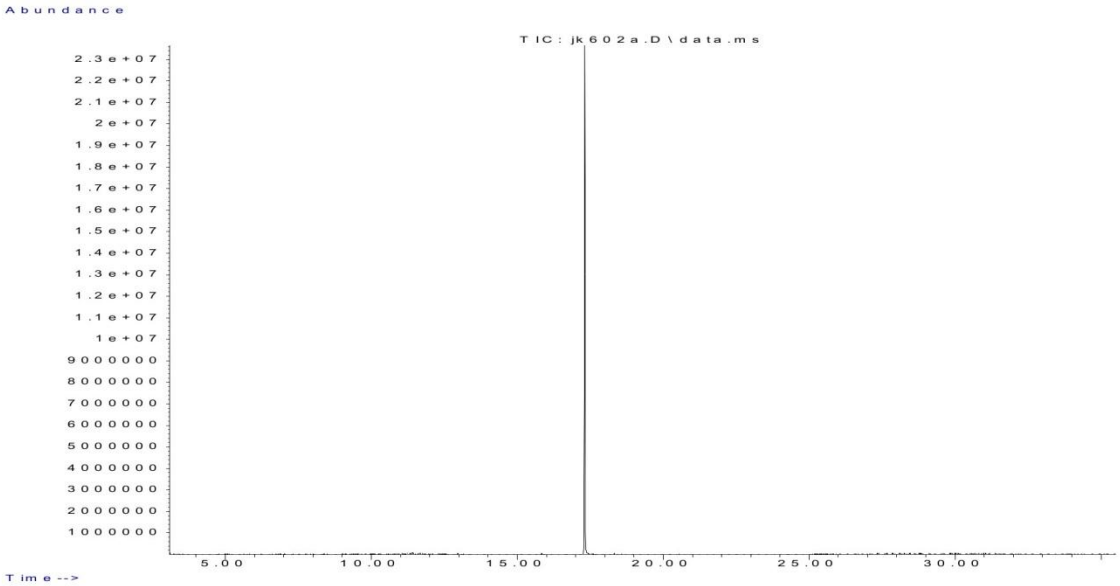


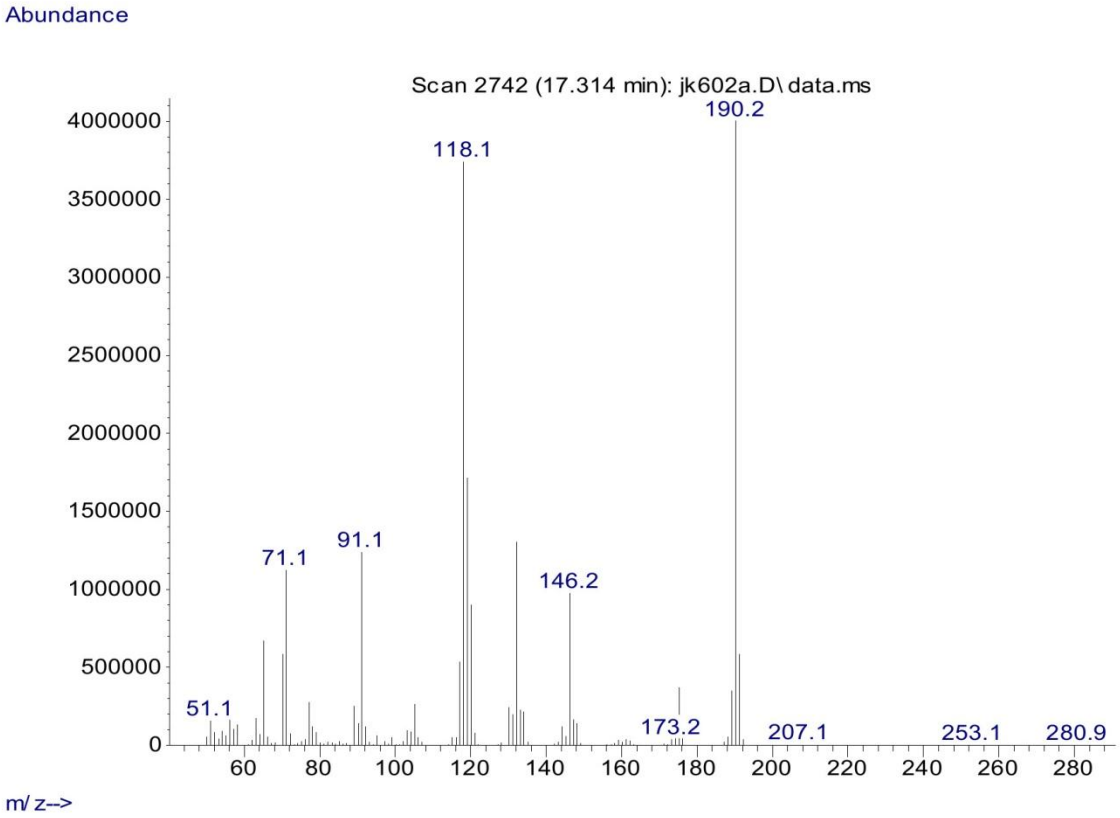
GC trace and mass spectrum of **23h**:



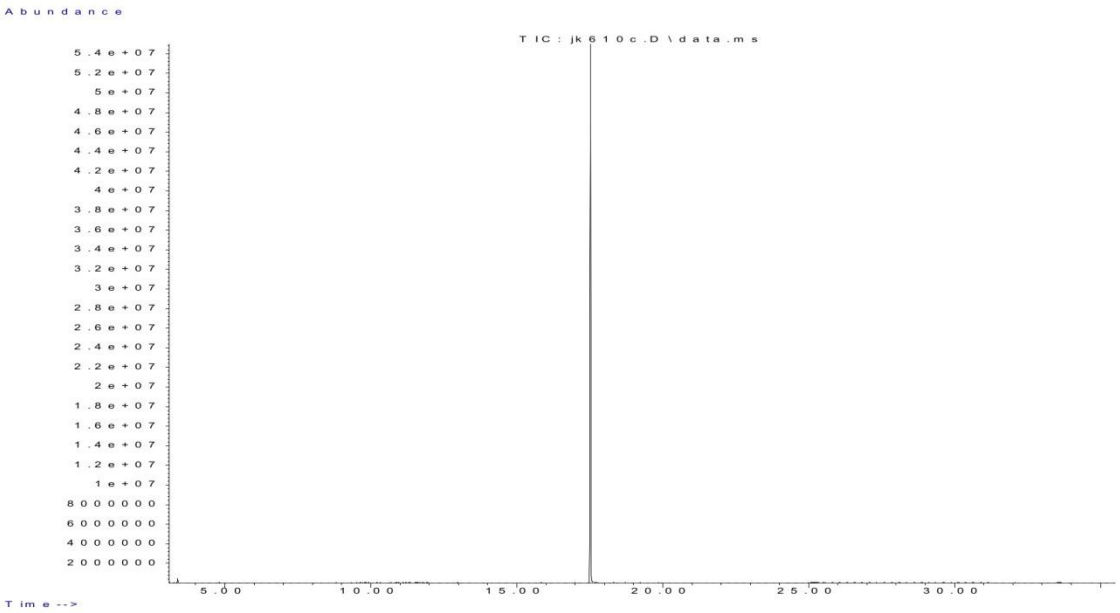


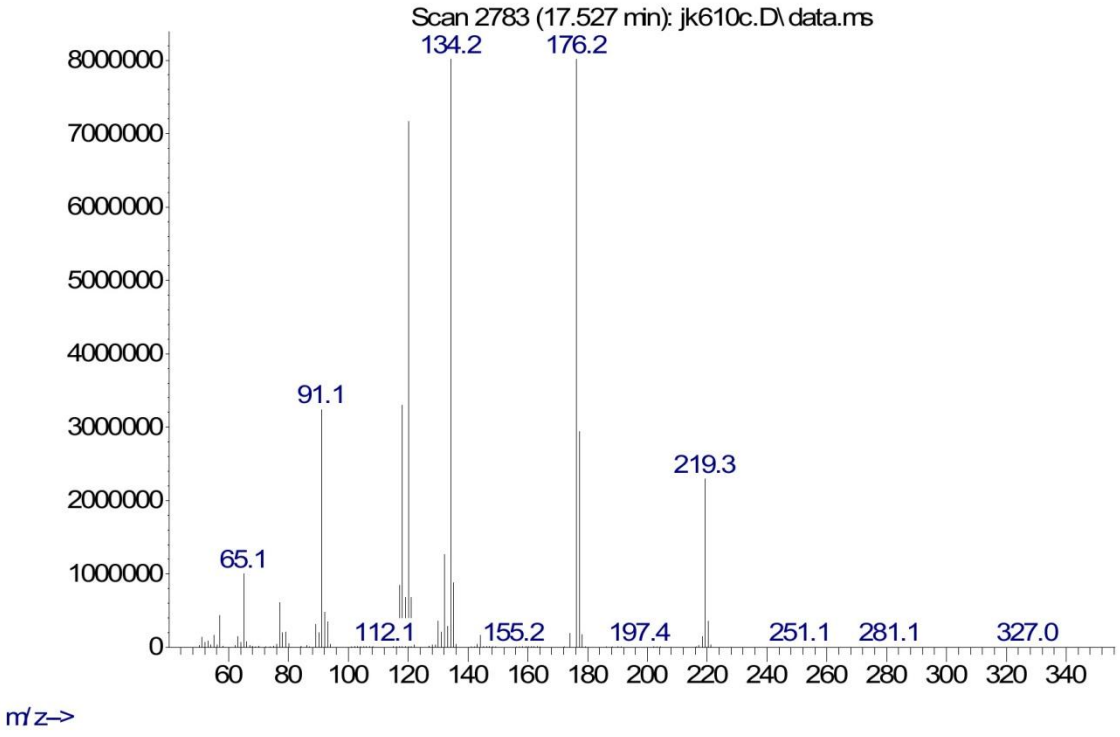
GC trace and mass spectrum of **23i**:



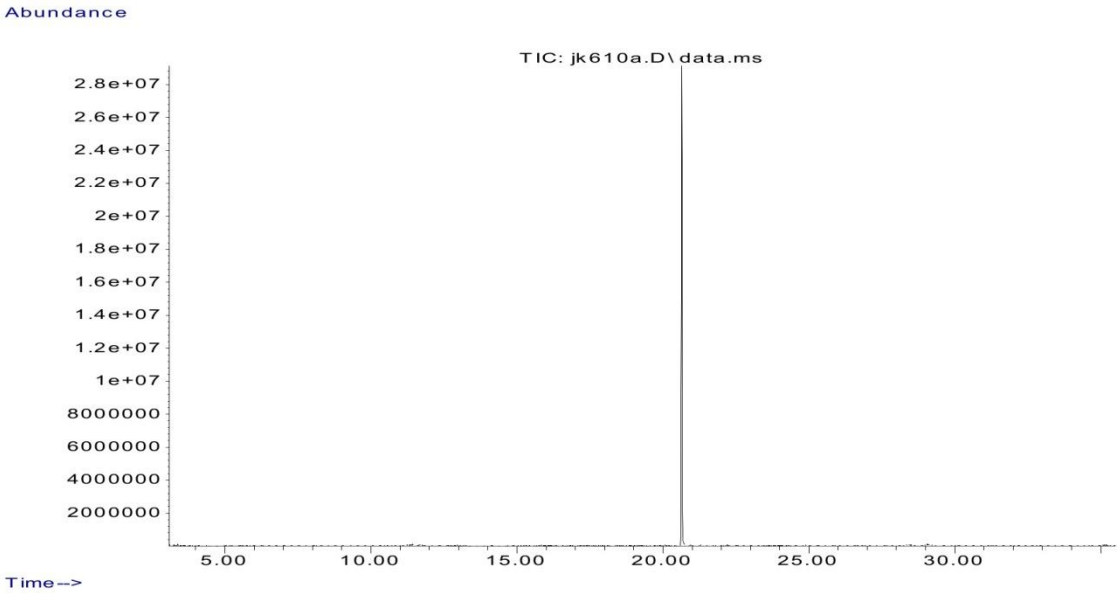


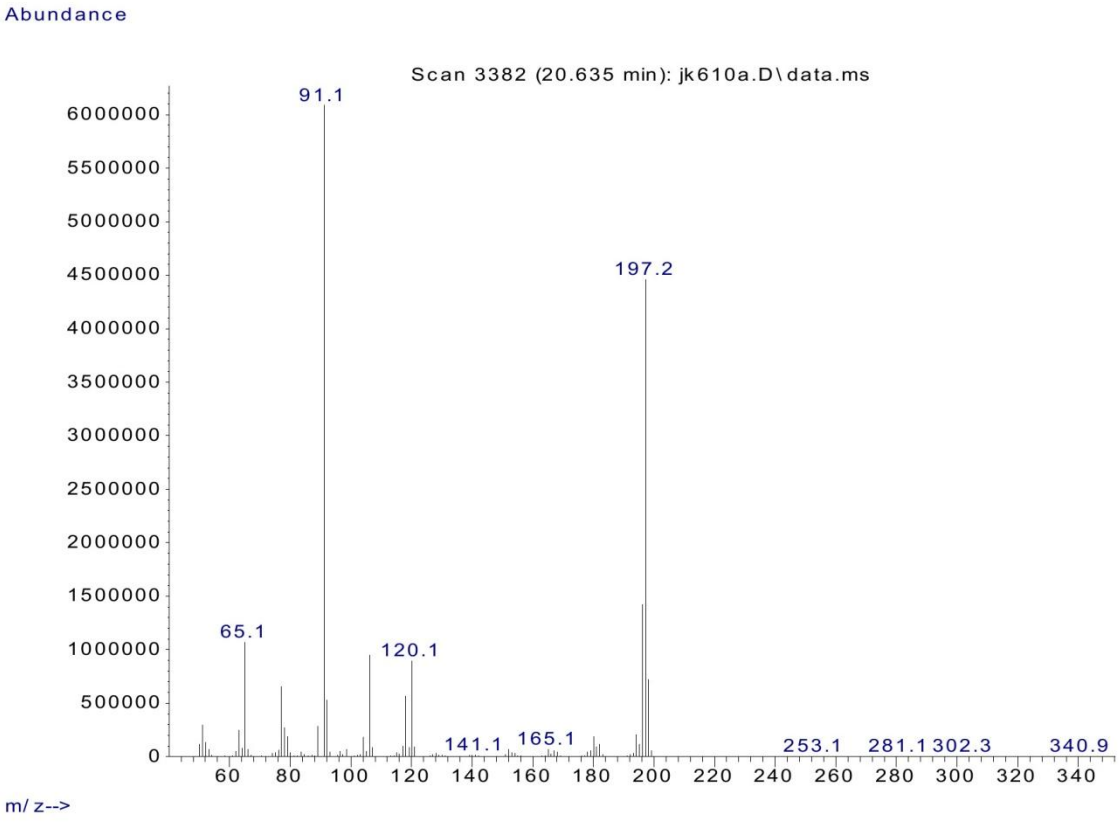
GC trace and mass spectrum of **23j**:



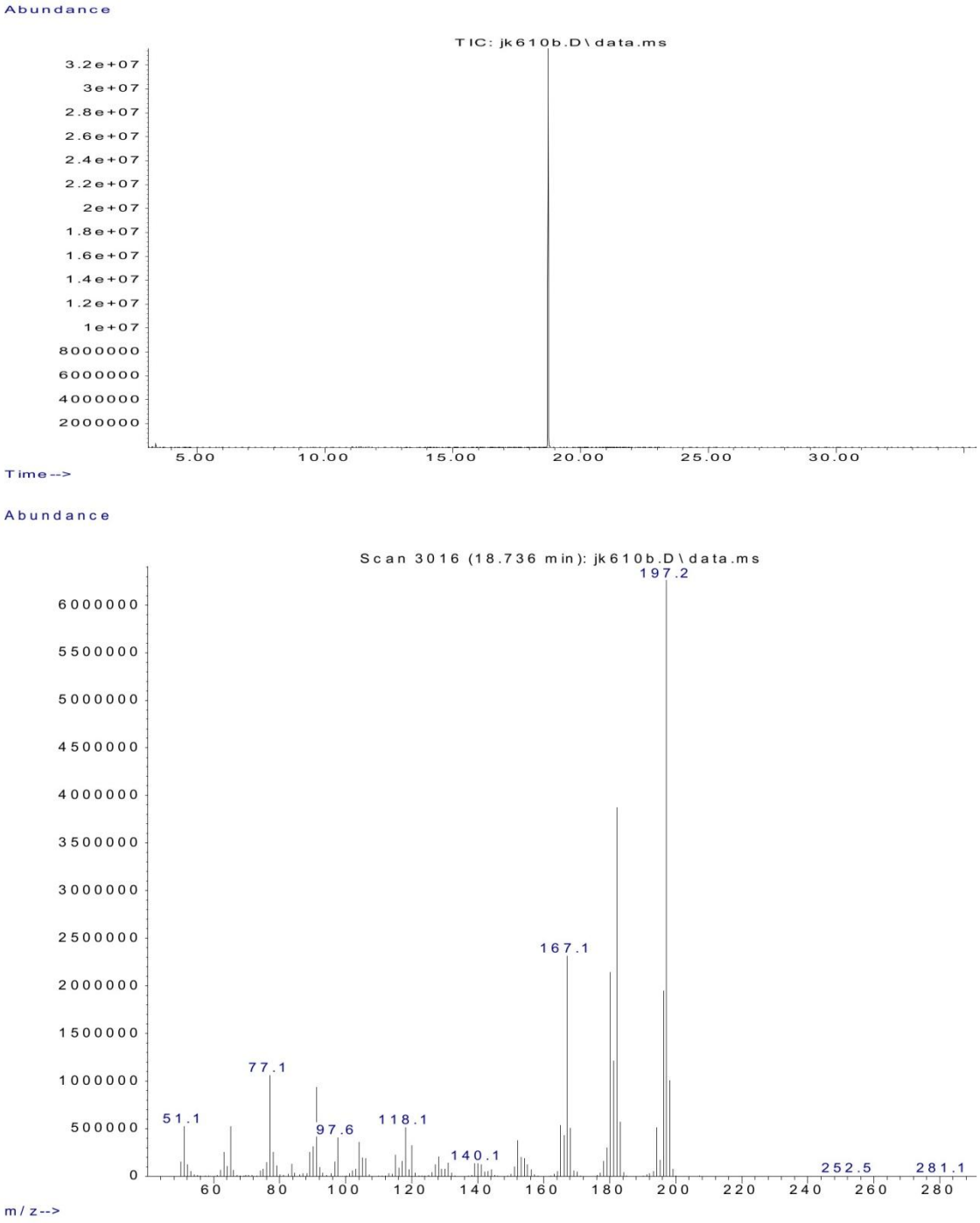


GC trace and mass spectrum of **23k**:

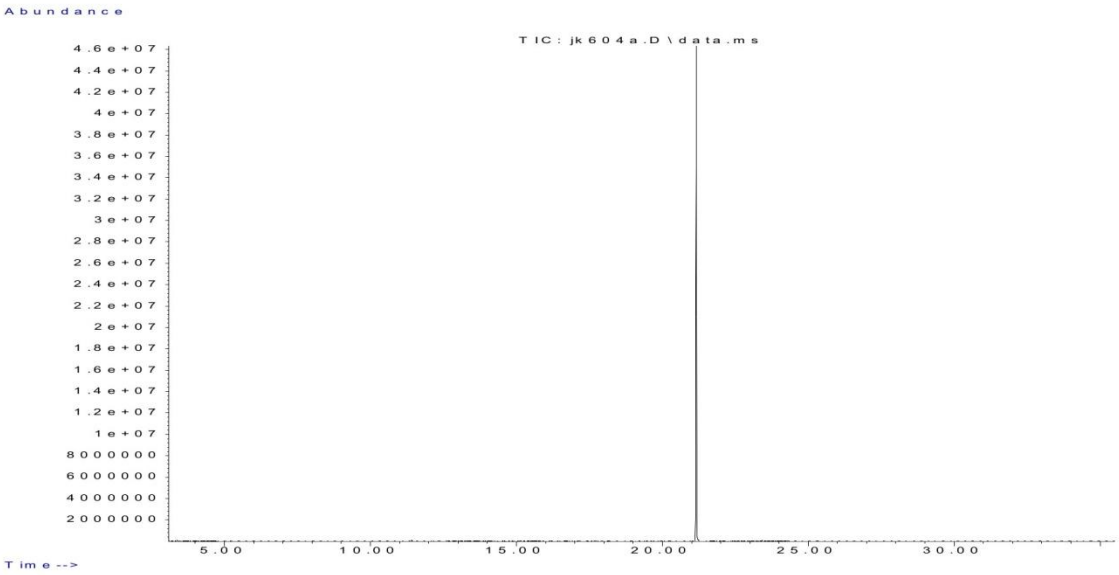


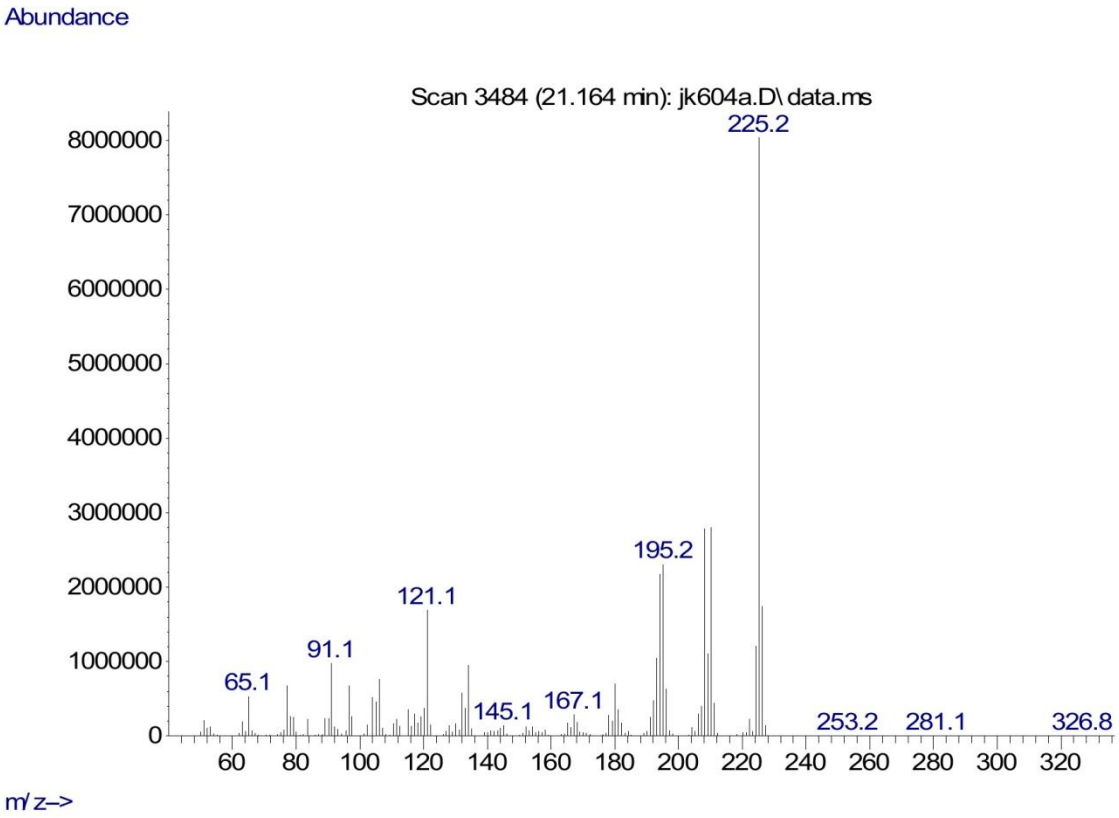


GC trace and mass spectrum of **23l**:

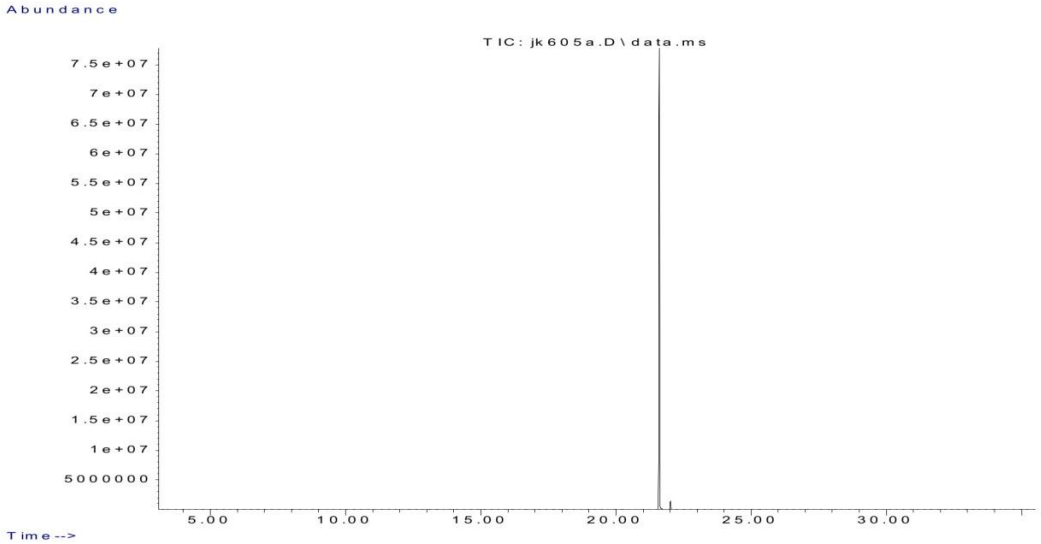


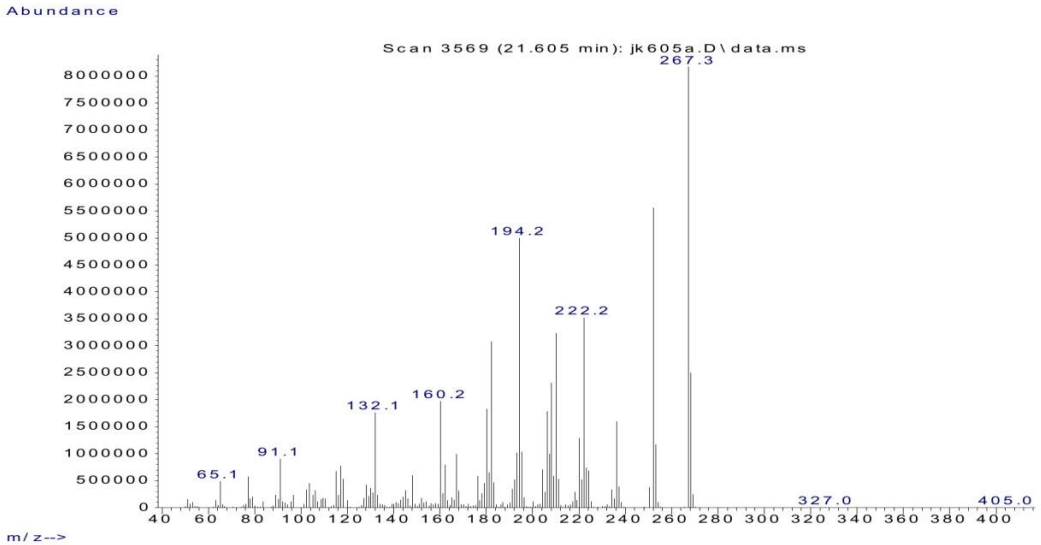
GC trace and mass spectrum of **23o**:

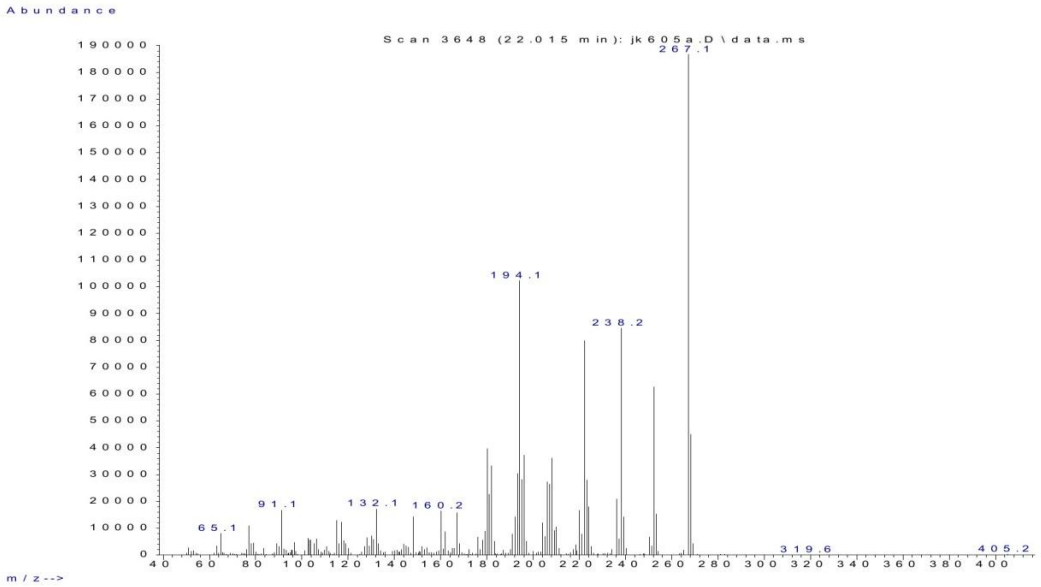




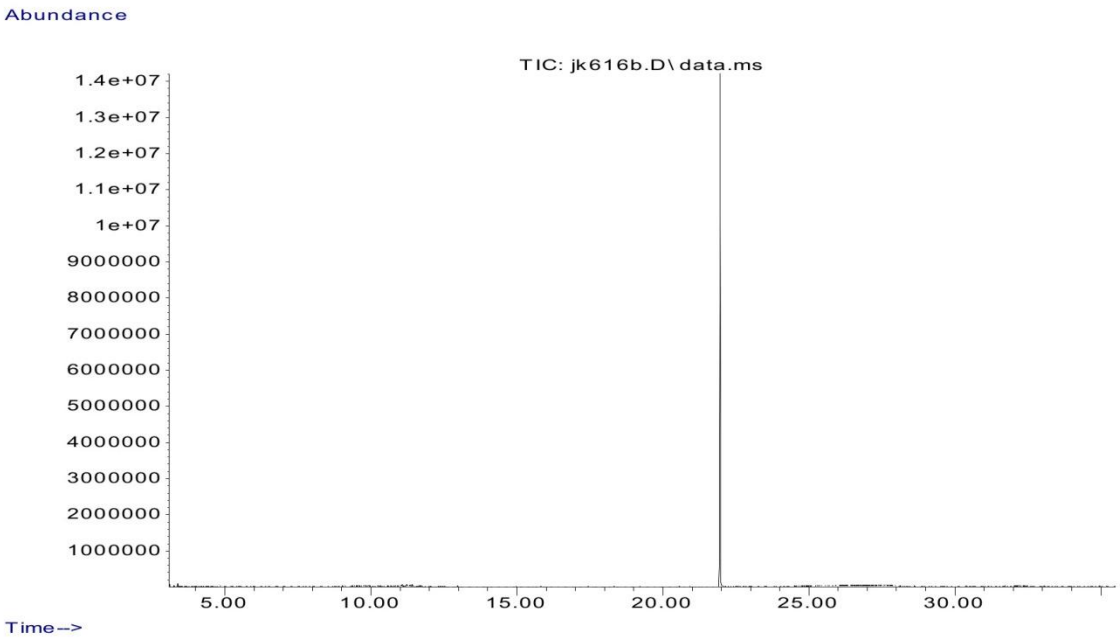
GC trace and mass spectrum of **23p**:

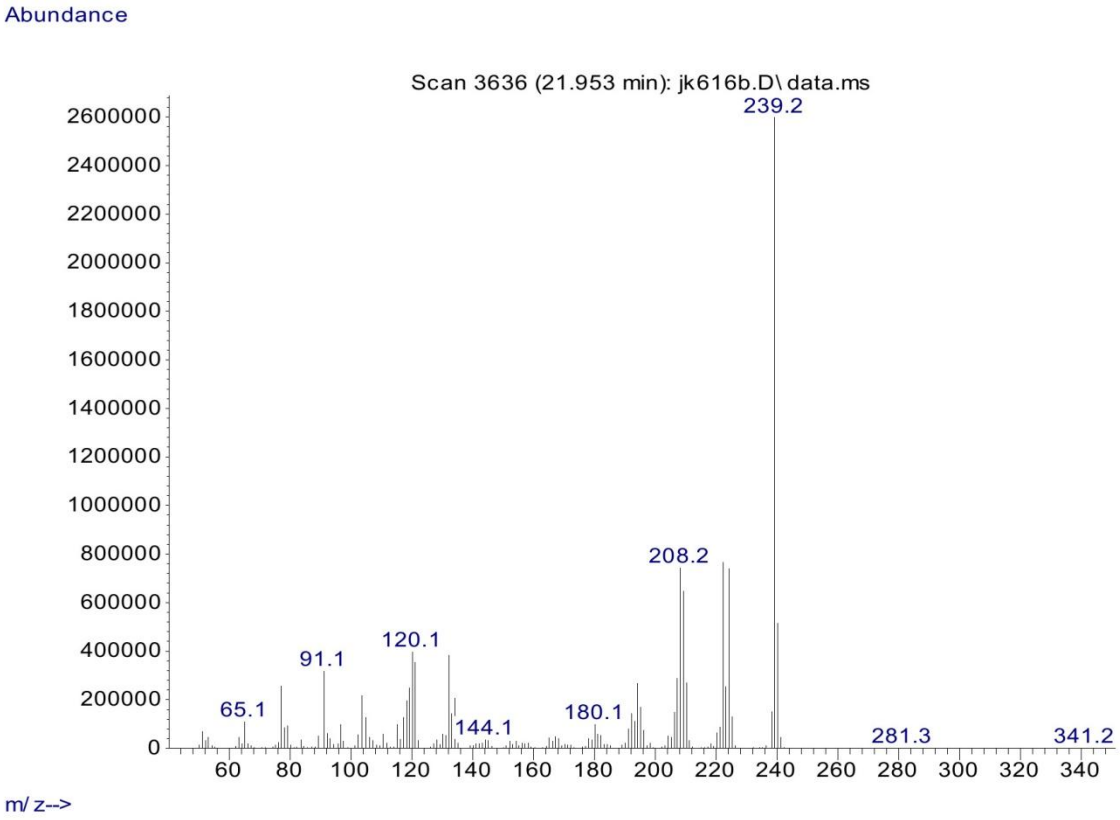




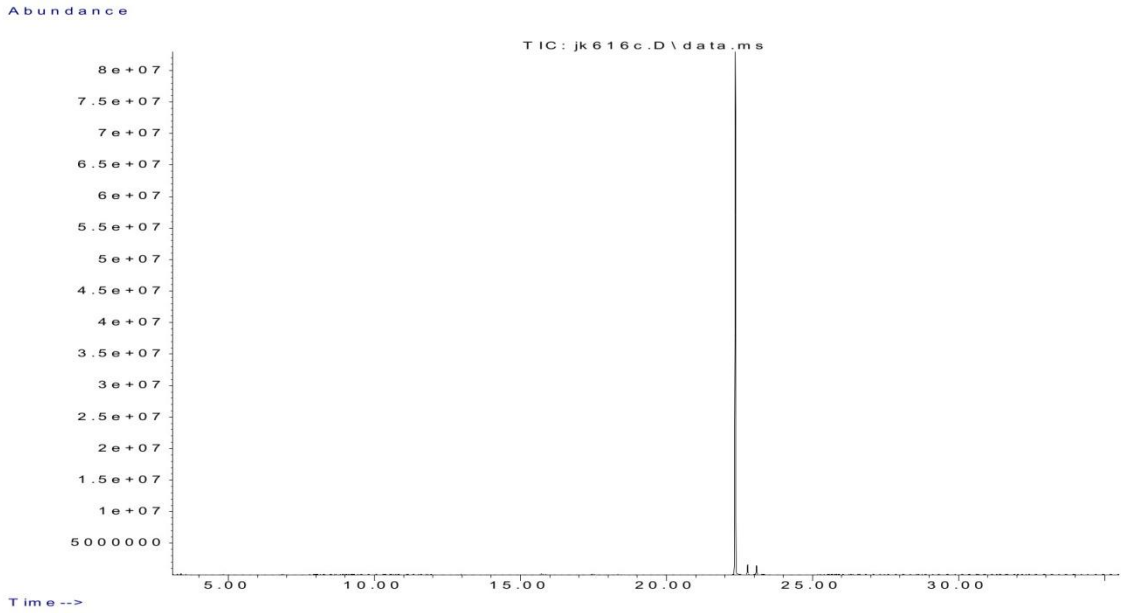


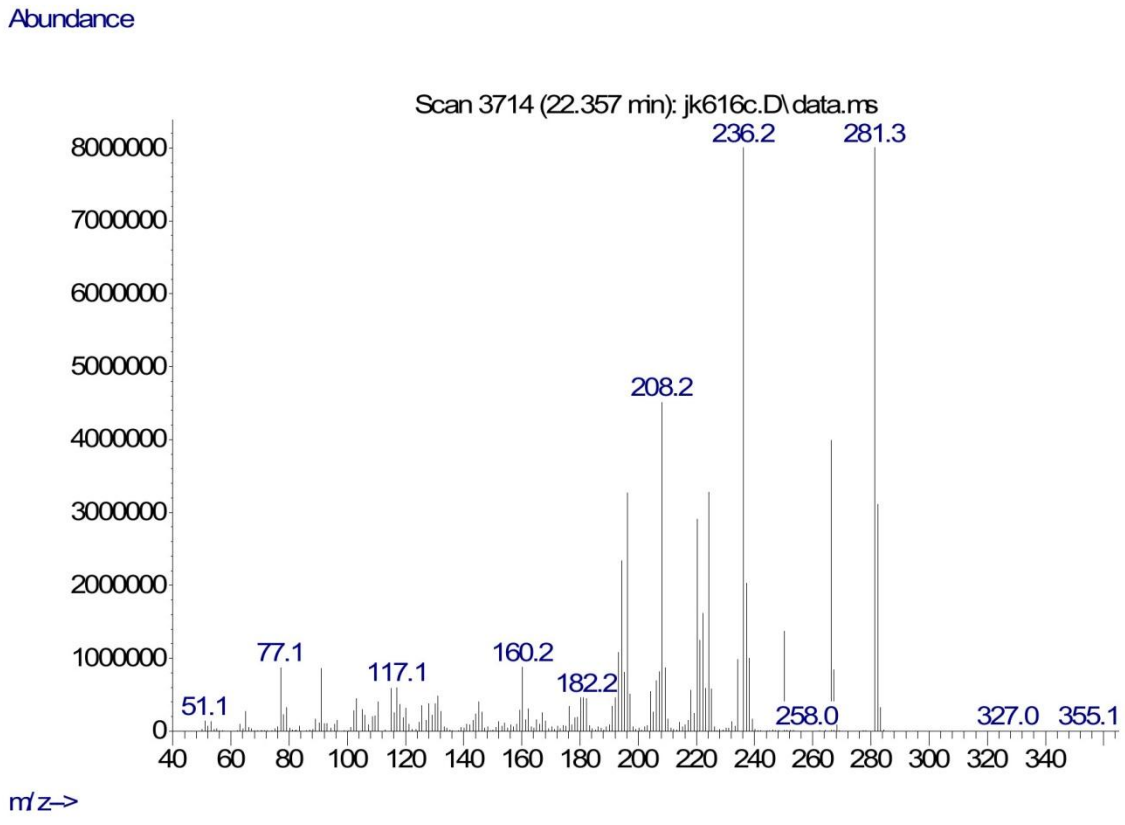
GC trace and mass spectrum of **24a**:





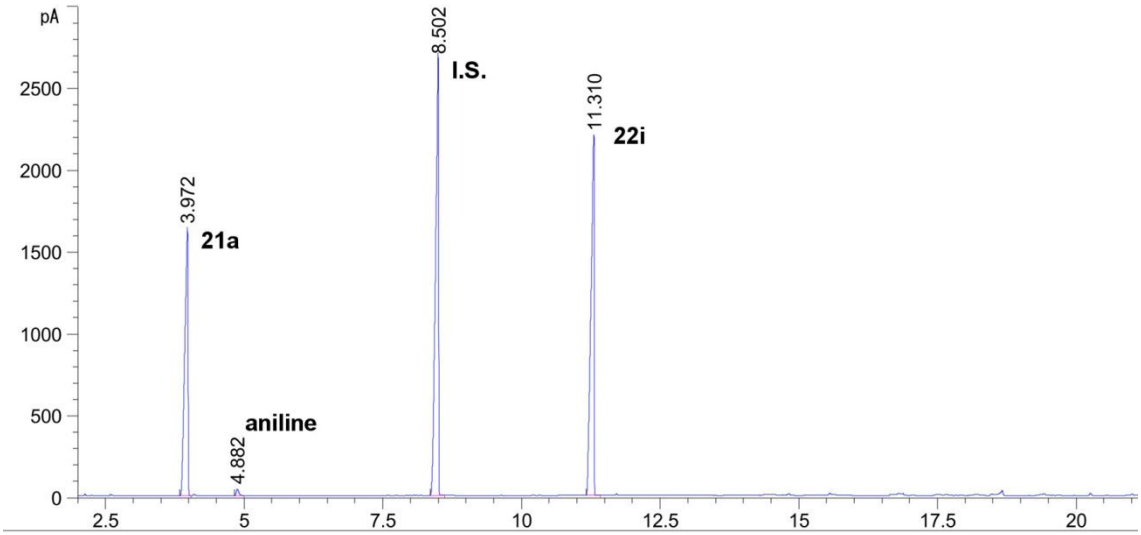
GC trace and mass spectrum of **24b**:





GC-FID traces for the reaction of 21a with 22i, with added aniline 22h

GC-FID trace after 30 min reaction time:



GC-FID trace after 120 min reaction time: