Electronic Supplementary Information

Strong Lewis acid of air-stable cationic titanocene perfluoroalkyl(aryl)sulfonate complexes as highly efficient and recyclable catalysts for C-C bond forming reactions

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Experiment Section

Typical procedure for the Strecker reaction of benzaldehyde(5a) with aniline (6a) and trimethylsilyl cyanide (7a) catalyzed by 1·THF: A mixture of PhCHO (106 mg, 1.0 mmol), $PhNH_2$ (93 mg, 1.0 mmol), trimethylsilylcyanide (119 mg, 1.2 mmol) and Catalyst **1**·THF (9 mg, 0.01 mol) was stirred at room temperature until the reaction was complete. It was subject to evaporation in vacuum at room temperature, the residue was dissolved in CH_2Cl_2 (10 ml × 3) and the catalyst was collected by means of filtration for the next cycle of reaction. To the filtrate, after evaporation of the solvent a pale yellow solid mixture was obtained. The products **8a** were isolated by silica gel column chromatography on silica gel (petroleum ether:EtOAc = 8:1) in yield 96% (199 mg) as pale yellow solid. Aldehydes and amines and nucleophiles trimethylsilyl cyanide are commercially available. **8a-8l, 8n-8p** are known compounds [S1-S4] and **8m** is new compound. The spectra data are summarized as follows:

***2-Anilino-2-phenylacetonitrile (8a)*:** Light-yellow solid, mp: 85-86 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 5.6 Hz, 2H, ArH), 7.43 (d, *J* = 3.0 Hz, 3H, ArH), 7.25 (t, *J* = 8.0 Hz, 2H, ArH), 6.88 (t, *J* = 7.2 Hz, 1H, ArH), 6.75 (d, *J* = 7.6 Hz, 2H, ArH), 5.39 (d, *J* = 8.4 Hz, 1H, CH), 4.06 (d, *J* = 8.4 Hz, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.74, 133.98, 129.62, 129.59, 129.38, 127.31, 120.29, 118.31, 114.21, 50.21; MS(70 ev): m/z = 208.1 [M^+].

***2-Anilino-2-(p-methylphenyl)acetonitrile (8b)*:** Light-yellow solid, mp: 77-78 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.0 Hz, 2H, ArH), 7.27 (t, *J* = 7.8 Hz, 4H, ArH), 6.89 (t, *J* = 7.4 Hz, 1H, ArH), 6.77 (d, *J* = 8.0 Hz, 2H, ArH), 5.38 (d, *J* = 8.0 Hz, 1H, CH), 3.99 (d, *J* = 8.4 Hz, 1H, NH), 2.39 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.76, 139.62, 131.03, 129.99, 129.58, 127.19, 120.21, 118.37, 114.11, 49.99, 21.20; MS(70 ev): m/z = 222.2 [M^+].

***2-Anilino-2-(p-methoxyphenyl)acetonitrile (8c)*:** Light-yellow solid, mp: 94-95 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.8 Hz, 2H, ArH), 7.27 (t, *J* = 8.0 Hz, 2H, ArH), 6.96 (d, *J* = 8.8 Hz, 2H, ArH), 6.90 (t, *J* = 7.4 Hz, 1H, ArH), 6.77 (d, *J* = 8.0 Hz, 2H, ArH), 5.36 (d, *J* = 8.4 Hz, 1H, CH), 4.00 (s, 1H, NH), 3.83 (s, 3H, OCH_3); ^{13}C

NMR (100 MHz, $CDCl_3$): δ 160.45, 144.78, 129.58, 128.66, 125.98, 120.19, 118.49, 114.66, 114.13, 55.46, 49.67; MS(70 ev): m/z = 238.1 [M^+].

***2-Anilino-2-(o-fluorinephenyl)acetonitrile (8d)*:** Light-yellow solid, mp: 116-117 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.61 (t, *J* = 7.4 Hz, 1H, ArH), 7.44-7.39 (m, 1H, ArH), 7.28-7.20 (m, 3H, ArH), 7.14 (t, *J* = 9.2 Hz, 1H, ArH), 6.89 (t, *J* = 7.2 Hz, 1H, ArH), 6.77 (d, *J* = 8.0 Hz, 2H, ArH), 5.60 (d, *J* = 8.4 Hz, 1H, CH), 4.09 (d, *J* = 8.4 Hz, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.36, 158.88, 144.48, 131.72, 129.62, 129.01, 125.09, 121.69, 120.53, 117.70, 116.36, 114.42, 44.73; MS(70 ev): m/z = 226.1 [M^+].

***2-Anilino-2-(p-chlorinephenyl)acetonitrile (8e)*:** Light-yellow solid, mp: 96-98 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.6 Hz, 2H, ArH), 7.38 (d, *J* = 8.4 Hz, 2H, ArH), 7.24 (t, *J* = 7.2 Hz, 2H, ArH), 6.89 (t, *J* = 7.4 Hz, 1H, ArH), 6.73 (d, *J* = 8.0 Hz, 2H, ArH), 5.37 (d, *J* = 8.4 Hz, 1H, CH), 4.09 (d, *J* = 8.4 Hz, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.46, 135.55, 132.49, 129.65, 129.54, 128.64, 120.55, 117.97, 114.37, 49.62; MS(70 ev): m/z = 242.1 [M^+].

***2-Anilino-2-(p-brominephenyl)acetonitrile (8f)*:** Light-yellow solid, mp: 86-88 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.8 Hz, 2H, ArH), 7.46 (d, *J* = 8.4 Hz, 2H, ArH), 7.26 (t, *J* = 7.8 Hz, 2H, ArH), 6.91 (t, *J* = 7.4 Hz, 1H, ArH), 6.74 (d, *J* = 8.0 Hz, 2H, ArH), 5.38 (d, *J* = 8.4 Hz, 1H, CH), 4.06 (d, *J* = 8.4 Hz, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.38, 132.98, 132.52, 129.64, 128.89, 123.74, 120.60, 117.81, 114.34, 49.72; MS(70 ev): m/z = 286.0 [M^+].

2-(N-Anilino)-2-cinnamyl acetonitrile (8g): Pale yellow solid, mp 109-110 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.0 Hz, 2H, ArH), 7.39-7.25 (m, 5H, ArH), 7.05 (d, *J* = 16.0 Hz, 1H, ArH), 6.91 (t, *J* = 7.4 Hz, 1H, ArH), 6.78 (d, *J* = 8.0 Hz, 2H, ArH), 6.28 (dd, *J* = 16.0 Hz, 4.8 Hz, 1H, ArH), 5.07 (q, *J* = 8.4 Hz, 1H, CH), 3.91 (d, *J* = 9.2 Hz, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.46, 135.16, 134.93, 129.64, 128.98, 128.88, 126.97, 120.97, 120.44, 117.70, 114.42, 47.80; MS(70 ev): m/z = 234.0 [M^+].

2-(furan-2-yl)-2-(phenylamino)acetonitrile(8h): Pale brown solid, mp 69-70 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.48 (s, 1H, ArH), 7.28 (t, *J* = 7.6 Hz, 2H, ArH), 6.92 (t, *J* = 7.4 Hz, 1H, ArH), 6.78 (d, *J* = 8.0 Hz, 2H, ArH), 6.58 (s, 1H, ArH), 6.42 (d, *J* = 1.2 Hz, 1H, ArH), 5.48 (d, *J* = 9.2 Hz, 1H, CH), 4.22 (d, *J* = 7.6 Hz, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.08, 144.11, 144.02, 129.63, 120.70, 116.57, 114.53, 110.97, 109.69, 44.39.

***2-(phenylamino)pentanenitrile (8i)*:** Colorless oil, ^1H NMR (400 MHz, $CDCl_3$): δ 7.25 (t, *J* = 7.0 Hz, 2H, ArH), 6.87 (t, *J* = 7.0 Hz, 1H, ArH), 6.71 (d, *J* = 7.6 Hz, 2H, ArH), 4.21 (t, *J* = 6.8 Hz, 1H, CH), 3.65 (s, 1H, NH), 1.95-1.88 (m, 2H, CH_2), 1.66-1.58 (m, 2H, CH_2), 1.03 (d, *J* = 7.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.84, 129.57, 119.92, 119.61, 114.03, 45.63, 35.48, 18.96, 13.45; MS(70 ev): m/z = 174.1 [M^+].

***2-phenyl-2-(p-methyl-phenylamino)acetonitrile (8j)*:** Light-yellow solid, mp: 82-83 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 6.8 Hz, 2H, ArH), 7.42 (d, *J* = 5.6 Hz, 3H, ArH), 7.06 (d, *J* = 7.6 Hz, 2H, ArH), 6.67 (d, *J* = 7.6 Hz, 2H, ArH), 5.36 (s, 1H, CH), 3.92 (s, 1H, NH), 2.26 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.45, 134.16, 130.09, 129.73, 129.48, 129.32, 127.29, 118.43, 114.52, 50.67, 20.52; MS(70 ev): m/z = 222.2 [M^+].

***2-phenyl-2-(p-chlorinephenylamino)acetonitrile (8k)*:** Light-yellow solid, mp: 107-109 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (t, *J* = 3.6 Hz, 2H, ArH), 7.42(t, *J* = 3.2 Hz, 3H, ArH), 7.18 (d, *J* = 8.8 Hz, 2H, ArH), 6.66 (d, *J* =

8.8 Hz, 2H, ArH), 5.35 (s, 1H, CH), 4.14 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.29, 133.54, 129.70, 129.48, 129.43, 127.24, 125.07, 118.03, 115.44, 50.26; MS(70 ev): m/z = 242.1 [M^+].

***2-phenyl-2-(8-quinolinylamino)acetonitrile (8l)*:** Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (s, 1H, ArH), 8.06 (d, *J* = 8.0 Hz, 1H, ArH), 7.65 (d, *J* = 7.2 Hz, 2H, ArH), 7.42 (t, *J* = 7.2 Hz, 4H, ArH), 7.35 (q, *J* = 8.4 Hz, 1H, ArH), 7.32 (t, *J* = 7.8 Hz, 1H, ArH), 7.22 (d, *J* = 8.0 Hz, 1H, ArH), 6.90 (d, *J* = 7.6 Hz, 1H, ArH), 6.66 (d, *J* = 8.0 Hz, 1H, CH), 5.62 (d, *J* = 8.0 Hz, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.69, 141.36, 138.39, 136.20, 133.87, 133.39, 129.53, 129.41, 128.59, 127.38, 121.87, 118.10, 117.28, 107.06, 49.61; MS(70 ev): m/z = 259.1 [M^+].

***2-(p-brominephenyl)-2-(p-trifluoromethoxyphenylamino)acetonitrile (8m)*:** Light-yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.6 Hz, 1H, ArH), 7.66 (d, *J* = 7.6 Hz, 1H, ArH), 7.43 (t, *J* = 7.6 Hz, 1H, ArH), 7.32(t, *J* = 7.8 Hz, 1H, ArH), 7.13 (d, *J* = 8.4 Hz, 2H, ArH), 6.76 (d, *J* = 8.4 Hz, 2H, ArH), 5.67 (d, *J* = 8.0 Hz, 1H, CH), 4.13 (d, *J* = 7.6 Hz, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.28, 142.64, 133.88, 132.90, 131.45, 129.21, 128.53, 123.61, 122.71, 117.55, 114.84, 50.56; MS(70 ev): m/z = 370.0 [M^+]; HRMS Calcd for $C_{15}H_{10}BrF_3N_2O$: 369.9929, $[M]^+$: Found: 369.9925.

***2-Anilino-2-phenylpropanenitrile (8n)*:** Yellow solid, 140-142 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 7.2 Hz, 2H, ArH), 7.42-7.33 (m, 3H, ArH), 7.11 (t, *J* = 7.6 Hz, 2H, ArH), 6.80 (t, *J* = 7.6 Hz, 1H, ArH), 6.54 (d, *J* = 8.0 Hz, 2H, ArH), 4.30 (s, 1H, NH), 1.94 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.47, 139.90, 129.26, 129.04, 128.61, 124.89, 120.73, 119.99, 115.77, 57.12, 33.43; MS(70 ev): m/z = 222.1 [M^+].

1-Anilino-Cyclohexanecarbonitrile (8o): White solid, 69-71 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ7.23 (t, *J* = 7.2 Hz, 2H, ArH), 6.90 (t, *J* = 9.4 Hz, 3H, ArH), 3.67 (s, 1H, NH), 2.32 (t, *J* = 11.6 Hz, 2H, CH_2), 1.76 (s, 2H, CH_2), 1.72-1.59 (m, 5H, CH_2), 1.31 (s, 1H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.62, 129.26, 121.22, 120.53, 117.52, 54.39, 36.64, 24.92, 22.24; MS(70 ev): m/z = 200.1 [M^+].

1-Anilino-(4-methylcyclohexane)carbonitrile (8p): White solid, mp: 86-88 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ7.24 (t, *J* = 7.4 Hz, 2H, ArH), 6.92-6.86 (m, 3H, ArH), 3.63 (s, 1H, NH), 2.28 (d, *J* = 14.0 Hz, 2H, CH_2), 1.93 (t, *J* = 13.0 Hz, 2H, CH_2), 1.64-1.48 (m, 3H, CH_2), 1.32-1.24 (m, 2H, CH_2), 0.92 (d, *J* = 6.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.64, 129.28, 122.37, 120.26, 116.99, 51.79, 36.96, 34.03, 28.36, 21.27; MS(70 ev): m/z = 214.1 [M^+].

Typical procedure for the Mannich-type reaction of benzaldehyde (5a) with aniline (6a) and trimethyl(1-phenyl-vinyloxy)silane (9b) catalyzed by 3: Complex **3** (7 mg, 0.01 mmol), PhCHO (106 mg 1.0 mmol), $PhNH_2$ (93 mg, 1.0 mmol) and trimethyl(1-phenyl-vinyloxy)silane (230 mg, 1.2 mmol) were placed in a 50 mL round-bottomed flask. Then the mixture was stirred at room temperature until the reaction was complete as indicated by TLC. Then the solvents of the resulting mixture were removed by evaporation in vacuum, the residue was dissolved CH_2Cl_2 and the catalyst was collected by means of filtration for the next cycle of reaction. The filtrate was subject to volatilization and the crude product was obtained, the products **10a** were isolated by silica gel column chromatography on silica gel (petroleum ether : EtOAc = 30:1) in yield 94% (283mg) as white solid. Aldehydes and amines and nucleophiles ketene silyl acetals (**9a)** and enol silyl ethers (**9b**) are commercially available. **10a-10l** are known compounds[S5-S6] and the spectra data are summarized as follows:

***1,3-diphenyl--3-(N-phenylamino)propan-1-one (10a)*:** White solid, mp.: 169-171 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.4 Hz, 2H, ArH), 7.55 (t, *J* = 7.0 Hz, 1H, ArH), 7.45-7.08 (m, 9H, ArH), 6.65 (t, *J* = 7.4 Hz, 1H, ArH), 6.55 (d, *J* = 8.0 Hz, 2H, ArH), 5.00 (dd, *J* = 7.6 Hz, 5.2 Hz, 1H, CH), 4.55 (s, 1H, NH), 3.50 (dd, *J* = 16.0 Hz, 5.2 Hz, 1H, CH_2), 3.41 (dd, *J* = 16.0 Hz, 7.6 Hz, 1H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.30, 147.00, 142.99, 136.70, 133.45, 129.13, 128.85, 128.72, 128.23, 127.38, 126.39, 117.80, 113.83, 54.80, 46.33; Ms(70 ev): m/z = 301.1 [M^+].

***3-(4-methylphenyl)-1-phenyl-3-(N-phenylamino)propan-1-one (10b)*:** White solid, mp.: 129-130 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 6.8 Hz, 2H, ArH), 7.57-7.06 (m, 9H, ArH), 6.65 (t, *J* = 7.4 Hz, 1H, ArH), 6.55 (d, *J* = 8.8 Hz, 2H, ArH), 4.97 (t, *J* = 6.4 Hz, 1H, CH), 4.50 (s, 1H, NH), 3.49 (dd, *J* = 16.4 Hz, 5.2 Hz, 1H, CH_2), 3.39 (dd, *J* = 16.0 Hz, 7.6 Hz, 1H, CH_2), 2.30 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.36, 147.08, 139.97, 136.96, 136.77, 133.38, 129.51, 129.10, 128.69, 128.22, 126.28, 117.73, 113.82, 54.53, 46.37, 21.07; Ms(70 ev): m/z = 315.1 [M^+].

***3-(4-methoxylphenyl)-1-phenyl-3-(N-phenylamino)propan-1-one (10c)*:** White solid, mp.: 137-138 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.0 Hz, 2H, ArH), 7.55-6.84 (m, 9H, ArH), 6.66 (t, *J* = 7.0 Hz, 1H, ArH), 6.56 (d, *J* = 8.4 Hz, 2H, ArH), 4.96 (t, *J* = 6.4 Hz, 1H, CH), 3.76 (s, 3H, OCH_3), 3.48 (dd, *J* = 16.4 Hz, 5.2 Hz, 1H, CH_2), 3.40 (dd, *J* = 16.0 Hz, 7.2 Hz, 1H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.47, 158.82, 146.97, 136.77, 134.89, 133.40, 129.12, 128.70, 128.21, 127.49, 117.81, 114.20, 113.90, 55.26, 54.30, 46.31; Ms(70 ev): m/z = 331.1 [M^+].

***3-(2-fluorophenyl)-1-phenyl-3-(N-phenylamino)propan-1-one (10d)*:** White solid, mp.: 139-140 ^{o}C; IR (KBr): 3450, 3389, 1668 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.6 Hz, 2H, ArH), 7.55 (t, *J* = 7.4 Hz, 1H, ArH), 7.45 (d, *J* = 7.6 Hz, 3H, ArH), 7.20 (d, *J* = 6.4 Hz, 1H, ArH), 7.11-6.56 (m, 8H, ArH), 5.27 (t, *J* = 6.2 Hz, 1H, CH), 3.60 (dd, *J* = 15.6 Hz, 4.8 Hz, 1H, CH_2), 3.41 (dd, *J* = 16.0 Hz, 8.0 Hz, 1H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.28, 161.76, 159.33, 146.43, 136.50, 133.51, 129.18, 128.95, 128.73, 128.56, 128.28, 124.49, 118.15, 115.69, 115.47, 113.83, 49.64, 44.39; Ms(70 ev): m/z = 319.1 [M^+]; HRMS Calcd for $C_{20}H_{18}FNO$: 319.1372, $[M]^+$: Found: 319.1368.

***3-(4-chlorophenyl)-1-phenyl-3-(N-phenylamino)propan-1-one (10e)*:** White solid, mp.: 114-115 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.0 Hz, 2H, ArH), 7.56 (t, *J* = 7.4 Hz, 1H, ArH), 7.44 (t, *J* = 7.8 Hz, 2H, ArH), 7.37 (d, *J* = 8.4 Hz, 2H, ArH), 7.26 (d, *J* = 8.0 Hz, 2H, ArH), 7.09 (t, *J* = 7.8 Hz, 2H, ArH), 6.68 (t, *J* = 7.4 Hz, 1H, ArH), 6.54 (d, *J* = 8.0 Hz, 2H, ArH), 4.97 (t, *J* = 6.2 Hz, 1H, CH), 3.47 (dd, *J* = 16.4 Hz, 5.2 Hz, 1H, CH_2), 3.41 (dd, *J* = 16.4 Hz, 7.2 Hz, 1H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.94, 146.56, 141.41, 136.58, 133.60, 133.03, 129.18, 128.98, 128.77, 128.19, 127.88, 118.22, 113.99, 54.32, 46.05; Ms(70 ev): m/z = 335.1 [M^+].

***3-(4-bromophenyl)-1-phenyl-3-(N-phenylamino)propan-1-one (10f)*:** White solid, mp.: 127-128 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.0 Hz, 2H, ArH), 7.56 (t, *J* = 7.4 Hz, 1H, ArH), 7.44 (t, *J* = 8.2 Hz, 4H, ArH), 7.34 - 6.68 (m, 5H, ArH), 6.53 (d, *J* = 7.6 Hz, 2H, ArH), 4.96 (t, *J* = 6.4 Hz, 1H, CH), 3.46 (dd, *J* = 16.4 Hz, 5.6 Hz, 1H, CH_2), 3.40 (dd, *J* = 16.4 Hz, 7.2 Hz, 1H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.90, 146.63, 142.04, 136.58, 133.60, 131.93, 129.19, 128.78, 128.25, 128.19, 121.10, 118.18, 113.94, 54.31, 46.05; Ms(70 ev): m/z = 379.1 [M^+].

***3-(3-nitrophenyl)-1-phenyl-3-(N-phenylamino)propan-1-one (10g)*:** White solid, mp.: 140-141 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (s, 1H, ArH), 8.06 (d, *J* = 8.0 Hz, 1H, ArH), 7.89 (d, *J* = 8.0 Hz, 2H, ArH), 7.81 (d, *J* = 7.6

Hz, 1H, ArH), 7.56 (t, *J* = 7.2 Hz, 1H, ArH), 7.48-7.09 (m, 5H, ArH), 6.69 (t, *J* = 7.4 Hz, 1H, ArH), 6.54 (d, *J* = 8.0 Hz, 2H, ArH), 5.12 (t, *J* = 6.2 Hz, 1H, CH), 3.51 (d, *J* = 6.0 Hz, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.35, 148.71, 146.33, 145.52, 136.40, 133.78, 133.02, 129.77, 129.30, 128.85, 128.17, 122.50, 121.51, 118.47, 113.90, 54.10, 45.84; Ms(70 ev): m/z = 346.1 [M^+].

3-(2-naphthyl)-1-phenyl-3-(N-phenylamino)propan-1-one (10h): White solid, mp.: 133-135 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.0 Hz, 3H, ArH), 7.82-7.78 (m, 3H, ArH), 7.58-7.51 (m, 2H, ArH), 7.41 (t, *J* = 7.2 Hz, 4H, ArH), 7.06 (t, *J* = 7.2 Hz, 2H, ArH), 6.66-6.58 (m, 3H, ArH), 5.15 (t, *J* = 6.2 Hz, 1H, CH), 4.62 (s, 1H, NH), 3.57 (dd, *J* = 16.0 Hz, 4.8 Hz, 1H, CH_2), 3.46 (dd, *J* = 16.0 Hz, 8.0 Hz, 1H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.21, 147.08, 140.56, 136.66, 133.52, 132.91, 129.16, 128.76, 128.26, 127.72, 126.20, 125.83, 125.16, 124.58, 117.91, 113.96, 55.05, 46.40; Ms(70 ev): m/z = 353.1 [M^+].

***3-(phenyl)-1-phenyl-3-(N-4-methylphenylamino)propan-1-one (10i)*:** White solid, mp.: 168-169 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 7.2 Hz, 2H, ArH), 7.51-7.19 (m, 8H, ArH), 6.88 (t, *J* = 8.8 Hz, 2H, ArH), 6.47 (d, *J* = 8.4 Hz, 2H, ArH), 4.96 (t, *J* = 6.4 Hz, 1H, CH), 4.39 (s, 1H, NH), 3.41 (dd, *J* = 16.4 Hz, 5.2 Hz, 1H, CH_2), 3.36 (dd, *J* = 16.0 Hz, 7.6 Hz, 1H, CH_2), 2.17 (s, 3H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.35, 144.74, 143.19, 136.79, 133.38, 129.62, 128.81, 128.69, 128.22, 127.30, 127.01, 126.42, 114.04, 55.11, 46.38, 20.37; Ms(70 ev): m/z = 315.2 [M^+].

***3-(phenyl)-1-phenyl-3-(N-4-chlorophenylamino)propan-1-one (10j)*:** White solid, 308 mg, yield 92%, mp.: 168-169 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.0 Hz, 2H, ArH), 7.46- 7.22 (m, 8H, ArH), 7.00 (t, *J* = 10.0 Hz, 1H, ArH), 6.47 (d, *J* = 6.8 Hz, 2H, ArH), 4.93 (t, *J* = 6.2 Hz, 1H, CH), 3.48 (dd, *J* = 16.4 Hz, 4.8 Hz, 1H, CH_2), 3.41 (dd, *J* = 16.0 Hz, 7.2 Hz, 1H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.20, 145.42, 142.37, 136.62, 133.55, 128.94, 128.92, 128.74, 128.20, 127.55, 126.33, 122.64, 115.11, 55.09, 46.14; Ms(70 ev): m/z = 335.1 [M^+].

Methyl 2,2-dimethyl-3-(N-phenylamino)-3-phenylpropanoate (10k) : White solid, mp.: 169-171 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.28-7.22 (m, 5H, ArH), 7.03 (t, *J* = 7.9 Hz, 2H, ArH), 6.59 (t, *J* = 7.4 Hz, 1H, ArH), 6.50 (d, *J* = 8.0 Hz, 2H, ArH), 4.80 (d, *J* = 8.0 Hz, 1H, CH), 4.49 (d, *J* = 7.6 Hz, 1H, NH), 3.65 (s, 3H, OCH_3), 1.27 (s, 3H, CH_3), 1.16 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.01, 146.89, 139.18, 128.98, 128.24, 127.96, 127.40, 117.22, 113.34, 64.31, 52.06, 46.96, 24.52, 20.66; Ms(70 ev): m/z = 283.1 [M^+].

Methyl 2,2-dimethyl-3-(N-phenylamino)-3-(4-chlorophenyl)propanoate (10l) : White solid, mp.: 108-110 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.26-7.20 (m, 4H, ArH), 7.04 (t, *J* = 7.4 Hz, 2H, ArH), 6.61 (t, *J* = 7.2 Hz, 1H, ArH), 6.46 (d, *J* = 8.0 Hz, 2H, ArH), 4.79 (d, *J* = 6.4 Hz, 1H, CH), 4.45 (d, *J* = 6.4 Hz, 1H, NH), 3.64 (s, 3H, OCH_3), 1.27 (s, 3H, CH_3), 1.15 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.82, 146.64, 137.97, 133.24, 129.64, 129.13, 128.31, 117.60, 113.42, 63.90, 52.24, 46.91, 24.54, 20.84; Ms(70 ev): m/z = 317.1 [M^+]

Typical procedure for the Mukaiyama-aldol reaction of benzaldehyde (5a) with ketene silyl acetals (9a) catalyzed by $2{\cdot}H_2O{\cdot}$THF: Complex $2{\cdot}H_2O{\cdot}$THF (45 mg, 0.05 mmol), and ketene silyl acetal (**9a**) (208 mg, 1.2 mmol) were added to a solution of PhCHO (**4a**) (106 mg, 1.0 mmol) in THF (3.0 mL) at 0 °C. Then the temperature was raised to room temperature slowly. After the mixture was stirred at room temperature for 4 h and monitored by TLC, it was subject to evaporation in vacuum at room temperature, the residue was dissolved in *n*-hexane (10 mL×3) and the catalyst was collected by means of filtration for the next cycle of reaction. To the combined hexane solution, MeOH and HCl(aq) were added and the mixture was stirred for 15 minutes. $NaHCO_3$ (aq) was added for neutralization. The mixture was subject to evaporation, and the solids thus obtained were

dissolved in AcOEt and water. After extraction with AcOEt (three times), the organic layer was washed with NaCl (aq) and dried over $MgSO_4$. After evaporation, the residue was subject to silica gel column chromatography (petroleum ether : ethyl acetate = 10:1), colourless crystals of (**11a**) were obtained, (196 mg, isolated yield 95%). Aldehydes and nucleophiles enol silyl ethers and ketene silyl acetals are commercially available. **11a–11e, 11h-p** are known compounds[S7-S9] and **11f, 11g** are new compound. The spectra data are summarized as follows:

***Methyl 3-hydroxy-2,2-dimethyl-3-phenylpropanoate (11a)*:** White solid, 58-60 ^oC, ^1H NMR (400MHz, $CDCl_3$): δ 7.33-7.25 (m, 5H, ArH), 4.88 (d, *J* = 3.6 Hz, 1H, CH), 3.71 (s, 3H, OCH_3), 3.14 (d, *J* = 4.0 Hz, 1H, OH), 1.14 (s, 3H, CH_3), 1.09 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.21, 140.00, 127.76, 127.66, 78.68, 52.11, 47.74, 23.01, 19.06; Ms(70 ev): m/z = 208.1 [M^+].

***Methyl 3-hydroxy-2,2-dimethyl-3-p-tolylpropanoate(11b)*:** White solid, 70-73 ^oC; ^1H NMR (400MHz, $CDCl_3$): δ 7.18 (d, *J* = 8.0 Hz, 2H, ArH), 7.11 (d, *J* = 8.0 Hz, 2H, ArH), 4.84 (d, *J* = 3.2 Hz, 1H, CH), 3.70 (s, 3H, OCH_3), 3.08 (d, *J* = 4.0 Hz, 1H, OH), 2.33 (s, 3H, CH_3), 1.13 (s, 3H, CH_3), 1.09 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.24, 137.36, 137.05, 128.46, 127.53, 78.56, 52.07, 47.76, 22.98, 21.11, 19.08; Ms(70 ev): m/z = 222.1 [M^+].

***Methyl 3-(4-chlorophenyl)-3-hydroxy-2,2-dimethylpropanoate (11c)*:** White solid, 65-66 ^oC; ^1H NMR (400MHz, $CDCl_3$): δ 7.28 (d, *J* = 8.4 Hz, 2H, ArH), 7.22 (d, *J* = 8.4 Hz, 2H, ArH), 4.85 (d, *J* = 4.0 Hz, 1H, CH), 3.71 (s, 3H, OCH_3), 3.29 (d, *J* = 3.6 Hz, 1H, OH), 1.12 (s, 3H, CH_3), 1.08 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.07, 138.46, 133.50, 129.00, 127.93, 77.95, 52.20, 47.65, 22.84, 19.03; Ms(70 ev): m/z = 226.1 [M^+].

***(E)-Methyl 3-hydroxy-2,2-dimethyl-5-phenylpent-4-enoate (11d)*:** Colorless oil, ^1H NMR (400MHz, $CDCl_3$): *δ* 7.38 (d, *J* = 7.4 Hz, 2H, ArH), 7.32 (t, *J* = 7.4 Hz, 2H, ArH), 7.24 (t, *J* = 6.8 Hz, 1H, ArH), 6.63 (d, *J* = 16.0 Hz, 1H, CH=), 6.20 (dd, *J* = 16.0 Hz, 7.2 Hz, 1H, CH=), 4.35 (d, *J* = 6.8 Hz, 1H, CH), 3.72 (s, 3H, OCH_3), 2.85 (br, 1H, OH), 1.24 (s, 3H, CH_3), 1.23 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.91, 136.60, 132.96, 128.59, 127.82, 127.42, 126.58, 77.85, 52.09, 47.23, 22.81, 20.01; Ms(70 ev): m/z = 234.1 [M^+].

***(E)-Methyl 3-hydroxy-2,2-dimethyl-5-(2-tolyl)pent-4-enoate (11e)*:** Colorless oil, ^1H NMR (400MHz, $CDCl_3$): *δ* 7.36 (s, 1H, ArH), 7.27-7.22 (m, 3H, ArH), 6.84 (d, *J* = 15.6 Hz, 1H, CH=), 6.07 (dd, *J* = 15.6 Hz, 7.2 Hz, 1H, CH=), 4.37 (t, *J* = 6.0 Hz, 1H, CH), 3.72 (s, 3H, OCH_3), 2.80 (d, *J* = 5.6 Hz, 1H, OH), 2.34 (s, 3H, CH_3), 1.25 (s, 3H, CH_3), 1.24 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.83, 138.49, 134.54, 131.48, 129.81, 129.01, 127.72, 126.40, 124.58, 77.54, 52.15, 47.18, 22.80, 20.08; Ms(70 ev): m/z = 248.1 [M^+].

***(E)-Methyl 3-hydroxy-2,2-dimethyl-5-(4-methoxylphenyl)pent-4-enoate (11f)*:** Colorless oil, ^1H NMR (400MHz, $CDCl_3$): *δ* 7.31 (d, *J* = 8.8 Hz, 2H, ArH), 6.85 (d, *J* = 8.8 Hz, 2H, ArH), 6.56 (d, *J* = 15.6 Hz, 1H, CH=), 6.06 (dd, *J* = 15.6 Hz, 7.2 Hz, 1H, CH=), 4.32 (t, *J* = 6.2 Hz, 1H, CH), 3.80 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 2.76 (d, *J* = 5.6 Hz, 1H, OH), 1.23 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.92, 159.39, 132.53, 129.38, 127.77, 125.16, 113.99, 55.30, 52.03, 47.24, 22.80, 19.98; FT-IR (neat, cm^{-1}): 3389, 3009, 2958, 2846, 1718, 1610, 1435, 1299, 1128, 1016, 958; Ms(70 ev): m/z: = 264.1 [M^+]; HRMS Calcd for $C_{15}H_{20}O_4$: 264.1362, [M^+] : Found: 264.1359.

***(E)-Methyl 3-hydroxy-2,2-dimethyl-5-(3-fluorinephenyl)pent-4-enoate (11g)*:** Colorless oil, ^1H NMR (400MHz, $CDCl_3$): *δ* 7.27 (q, *J* = 7.2 Hz, 1H, ArH), 7.14 (d, *J* = 7.6 Hz, 1H, ArH), 7.08 (d, *J* = 10.0 Hz, 1H, ArH), 6.94 (t, *J* = 8.4 Hz, 1H, ArH), 6.61 (d, *J* = 15.6 Hz, 1H, CH=), 6.22 (dd, *J* = 16.0 Hz, 6.8 Hz, 1H, CH=), 4.35 (t, *J* = 5.6 Hz,

1H, CH), 3.73 (s, 3H, OCH_3), 2.88 (d, *J* = 5.6 Hz, 1H, OH), 1.25 (s, 3H, CH_3), 1.23 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.84, 164.30, 161.86, 138.93, 131.72, 130.03, 128.87, 122.49, 114.70, 114.48, 113.08, 112.86, 52.14, 47.18, 29.70, 22.80, 20.07; FT-IR (neat, cm^{-1}): 3472, 3135, 2928, 1756, 1592, 1438, 1266, 1130, 1112, 1025, 949, 876; Ms(70 ev): m/z = 252.1 [M^+]; HRMS Calcd for $C_{14}H_{17}FO_3$: 252.1162, [M^+]: Found: 252.1158.

***(E)-Methyl 3-hydroxy-2,2-dimethyl-5-(3-chlorophenyl)pent-4-enoate (11h)*:** Colorless oil, ^1H NMR (400MHz, $CDCl_3$): *δ* 7.41 (d, *J* = 8.8 Hz, 1H, ArH), 7.18-7.16 (m, 3H, ArH), 6.58 (d, *J* = 16.0 Hz, 1H, CH=), 6.22 (dd, *J* = 16.0 Hz, 6.8 Hz, 1H, CH=), 4.34 (d, *J* = 6.8 Hz, 1H, CH), 3.73 (s, 3H, OCH_3), 2.90 (s, 1H, OH), 1.25 (s, 3H, CH_3), 1.23 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.83, 138.49, 134.54, 131.48, 129.81, 129.04, 127.72, 126.40, 124.84, 52.15, 47.18, 22.80, 20.08; Ms(70 ev): m/z = 268.1 [M^+].

***3-Hydroxy-1-phenyl-3-phenylpropan-1-one (11i)*:** Colorless oil. ^1H NMR (400MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.0 Hz, 2H, ArH), 7.61-7.28 (m, 8H, ArH), 5.35 (t, *J* = 5.8 Hz, 1H, CH), 3.60 (s, 1H, CH_2), 3.36 (d, *J* = 6.0 Hz, 1H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.24, 142.94, 136.56, 136.70, 128.74, 128.61, 128.18, 127.72, 125.78, 70.06, 47.41; Ms(70 ev): m/z = 226.1 [M^+].

***3-Hydroxy-1-phenyl-3-p-tolylpropan-1-one (11j)*:** Colorless oil. ^1H NMR (400MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.2 Hz, 2H, ArH), 7.59-7.19 (m, 7H, ArH), 5.32 (t, *J* = 5.8 Hz, 1H, CH), 3.57 (s, 1H, OH), 3.38 (s, 1H, CH_2), 3.36 (d, *J* = 5.2 Hz, 1H, CH_2), 2.36 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.33, 139.96, 137.43, 136.55, 133.70, 129.28, 128.75, 128.18, 125.73, 69.90, 47.42, 21.19; Ms(70 ev): m/z = 240.1 [M^+].

***3-Hydroxy-1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (11k)*:** White solid, mp: 101-102 ^oC; ^1H NMR (400MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.6 Hz, 2H, ArH), 7.65-7.46 (m, 7H, ArH), 5.41 (t, *J* = 4.8 Hz, 1H, CH), 3.75 (s, 1H, OH), 3.37 (d, *J* = 3.2 Hz, 1H, CH_2), 3.35 (s, 1H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.83, 146.90, 136.33, 133.90, 129.66, 128.81, 127.08 (q, *J* = 262.25 Hz), 125.59, 125.48, 69.47, 47.20; ^{19}F NMR (376 MHz, $CDCl_3$): δ ppm 62.43; Ms(70 ev): m/z = 294.1 [M^+].

3-(2-fluorophenyl)-3-hydroxy-1-phenylpropan-1-one (11l): Yellow solid, mp: 98-100 ^oC; ^1H NMR (400MHz, $CDCl_3$): δ 8.00-7.44 (m, 9H, ArH), 5.85 (t, *J* = 5.2 Hz, 1H, CH), 4.03 (s, 1H, OH), 3.70 (d, *J* = 16.4 Hz, 1H, CH_2), 3.21 (dd, *J* = 18.0 Hz, 9.6 Hz, 1H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.93, 147.29, 140.36, 138.60, 136.31, 133.85, 128.85, 128.80, 128.26, 124.46, 65.94, 46.48; Ms(70 ev): m/z = 244.1 [M^+].

***3-(4-chlorophenyl)-3-hydroxy-1-phenylpropan-1-one (11m)*:** White solid, mp.: 97-98 ^oC; ^1H NMR (400MHz, $CDCl_3$): δ 7.61-7.32 (m, 7H, ArH), 7.94 (d, *J* = 7.6 Hz, 2H, ArH), 5.32 (t, *J* = 5.0 Hz, 1H, CH), 3.68 (s, 1H, OH), 3.35 (s, 1H, CH_2), 3.33 (d, *J* = 3.6 Hz, 1H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.99, 141.46, 136.36, 133.82, 133.35, 128.78, 128.72, 128.16, 127.18, 69.42, 47.25; Ms(70 ev): m/z = 260.1 [M^+].

***3-(4-Bromophenyl)-3-hydroxy-1-phenylpropan-1-one (11n)*:** White solid, mp: 98-100 ^oC; ^1H NMR (400MHz; $CDCl_3$): δ 7.95 (d, *J* = 7.6 Hz, 2H, ArH), 7.60-7.31 (m, 7H, ArH), 5.31 (t, *J* = 4.6 Hz, 1H, CH), 3.74 (s, 1H, OH), 3.35 (s, 1H, CH_2), 3.33 (d, *J* = 3.6 Hz, 1H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.01, 141.95, 136.35, 133.86, 131.67, 128.80, 128.17, 127.53, 121.45, 69.44, 47.23; Ms(70 ev): m/z = 304.1 [M^+].

***3-(2-Nitrophenyl)-3-hydroxy-1-phenylpropan-1-one (11o)*:** White solid, mp.: 108-109 ^oC; ^1H NMR (400MHz; $CDCl_3$): δ 7.95 (d, *J* = 7.6 Hz, 2H, ArH), 7.66-7.00 (m, 7H, ArH), 5.62 (t, *J* = 4.6 Hz, 1H, CH), 3.83 (s, 1H, OH), 3.50 (d, *J* = 16.8 Hz, 1H, CH_2), 3.23 (dd, *J* = 17.6 Hz, 9.2 Hz, 1H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.27,

160.60, 158.16, 136.44, 133.75, 128.19, 127.41, 124.44, 115.33, 115.12, 64.37, 45.83; Ms(70 ev): m/z = 271.1 [M^+].

***3-Hydroxy-1-phenyldecane-1-one* (*11p*):** Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.6 Hz, 2H, ArH), 7.59 (t, *J* = 7.4 Hz, 1H, ArH), 7.46 (t, *J* = 7.6 Hz, 2H, ArH), 4.22(s, 1H, OH), 3.28 (s, 1H, CH), 3.19 (d, *J* = 2.8 Hz, 1H, CH_2), 3.04 (dd, *J* = 17.6 Hz, 9.2 Hz, 1H, CH_2), 1.73-1.25 (m, 8H, CH_2), 0.90-0.87 (m, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.07, 136.81, 133.53, 128.69, 128.09, 67.78, 45.04, 36.56, 29.29, 25.57, 22.63, 14.11; Ms(70 ev): m/z: 234.1 (M^+).

Typical procedure for allylation of benzaldehyde (5a) with tetrallyltin (12a) catalyzed by 2·H_2O·THF

To a CH_3CN (3.0 mL) solution of benzaldehyde (106 mg, 1.0 mmol), **2**·H_2O·THF (45 mg, 0.05 mmol) was added. To the mixture was added tetrallyltin (0.3 mmol) at RT. After the mixture was stirred at RT for an hours and monitored by TLC, it was evaporated in vacuum at RT. To the residue, hexane (10 mL × 3) was added; the catalyst precipitated and was recovered by filtration for the next reaction cycle. The combined *n*-hexane solution was concentrated, and then MeOH and HCl (aq) was added and stirred for 15 mins. $NaHCO_3$ (aq) was added for neutralization. After the mixture was subject to evaporation, the as-obtained solids were dissolved in AcOEt and water. After extraction with AcOEt (three times), the organic layer was washed with NaClaq and dried over $MgSO_4$. After evaporation, GLC yield was measured. Otherwise, the residue was subject to silica gel column chromatography (petroleum ether : ethyl acetate = 8:1), colorless oil (**13a**) was obtained: 139 mg, isolated yield 95%. Aldehydes and tetrallyltin are commercially available. **13a-13c** are known compounds,[S6] and the spectra data are summarized as follows:

1-Phenyl-3-buten-1-ol (13a): Colorless oil , ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.27 (m, 5H, ArH), 5.83-5.76 (m, 1H, vinyl), 5.16-5.13 (m, 1H, 2 vinyls), 4.75-4.72 (m, 1H), 2.54-2.47 (m, 2H, CH_2), 2.11 (br, 1H, OH), ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.88, 134.51, 128.45, 127.60, 125.84, 118.50, 73.31, 43.87.

1-(p-methlphenyl)-3-buten-1-ol (13b): Colorless oil , ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 6.8 Hz, 2H, Ar), 7.16 (d, *J* = 8.0 Hz, 2H, Ar), 5.84-5.76 (m, 1H, vinyl), 5.15-5.12 (m, 2H, 2 vinyls), 4.71 (t, *J* = 6.6 Hz, 1H, CH), 2.52-2.49 (m, 2H, CH_2), 2.34 (s, 3H, CH_3), 2.18 (br, 1H, OH), ^{13}C NMR (100 MHz; $CDCl_3$) δ 140.90, 137.26, 134.61, 129.13, 125.78, 118.36, 73.18, 43.81, 21.14.

1-(p-chlorophenyl)-3-buten-1-ol(13c): Colorless oil , ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.26 (m, 4H, ArH), 5.81-5.73 (m, 1H, vinyl), 5.18-5.14 (m, 2H, 2 vinyls), 4.73-4.70 (m, 1H, CH), 2.52-2.41 (m, 2H, CH_2), 2.14 (d, *J* = 2.8 Hz, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 142.28, 133.99, 133.16, 128.55, 127.22, 118.94, 118.7, 72.54, 43.90.

Typical procedure for the Mukaiyama-aldol reaction of Benzaldehyde dimethyl acetal (14) with ketene silyl acetals or enol silyl ethers (9) catalyzed by 2·H_2O·THF: [The operation method is similar to Mukaiyama-aldol reaction of benzaldehyde(**5a**) with ketene silyl acetals (**9a**). The solvent was replaced with CH_3CN. Benzaldehyde dimethyl acetal (**14**) and nucleophiles ketene silyl acetals (**9a**) and enol silyl ethers (**9b**) are commercially available]. **15a,15b** are known compounds[S10] and the spectra data are summarized as follows:

Methyl 2,2-dimethyl-3-methoxy-3-phenylpropanoate(15a): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.18 (m, 5H, ArH), 4.41 (s, 1H, CH), 3.63 (s, 1H, OCH_3), 3.11 (s, 1H, OCH_3), 1.04 (s, 1H, CH_3), 0.93 (s, 1H,

CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.27, 137.33, 128.41, 127.78, 87.88, 57.38, 51.87, 47.96, 22.65, 18.67; Ms(70 ev): m/z: 222.1 (M^+).

1,3-Diphenyl-3-methoxy-1-propanone(15b): Colorless oil; ^1H NMR (400MHz; $CDCl_3$): δ 7.94 (d, *J* = 7.6 Hz, 2H, ArH), 7.54-7.25 (m, 8H, ArH), 4.90-4.87 (m, 1H, CH), 3.59 (dd, *J* = 16.4 Hz, 8.4 Hz, 1H, CH_2), 3.24 (s, 1H, OCH_3), 3.08 (d, *J* = 16.4 Hz, 8.4 Hz, 1H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.73, 141.46, 137.20, 133.12, 128.61, 128.57, 128.26, 127.89, 126.68, 79.58, 56.92, 47.17; Ms(70 ev): m/z: 240.1 (M^+).

Typical procedure for Friedel-Crafts acylation of anisole (16a) with acetic anhydride (17a) catalyzed by 2·H_2O·THF: To a 50 mL round-bottomed flask was added anisole (16a) (108 mg, 1.0 mmol), acetic anhydride (204 mg, 2.0 mmol) and catalyst (45 mg, 0.05 mmol). Then the mixture was stirred at room temperature until complete consumption of starting material as monitored by TLC or GC-MS analysis. The residue was dissolved *n*-hexane and the catalyst was collected by means of filtration for the next cycle of reaction. The filtrate was subject to volatilization and the crude product was obtained, After that, the resulting mixture was removed by evaporation in vacuum and was then subject subject to silica gel column chromatograph; the Friedel-Crafts acylation product (**18a**) was obtained: 131 mg, isolated yield 87%. Alkyl aryl ethers and anhydride are commercially available. **18a-18i** are known compounds[S11-S16] and the spectra data are summarized as follows:

1-(4-methoxyphenyl)ethanone(18a)**:** Oil, ^1H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.2 Hz, 2H, ArH), 6.93 (d, *J* = 7.2 Hz, 2H, ArH), 3.87 (s, 3H, OCH_3), 2.56 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.78, 167.52, 130.61, 130.24, 113.71, 55.47, 26.32; Ms(70 ev): m/z: 150.1 (M^+).

1-(4-ethoxyphenyl)ethanone(18b)**:** Oil, ^1H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 7.2 Hz, 2H, ArH), 6.91 (d, *J* = 7.2 Hz, 2H, ArH), 4.09 (q, *J* = 6.6 Hz, 2H, CH_2), 2.55 (s, 3H, CH_3), 1.44 (t, *J* = 5.6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.78, 162.96, 130.61, 130.24, 114.16, 63.77, 26.30, 14.68; Ms(70 ev): m/z: 164.1 (M^+).

1-(4-butoxyphenyl)ethanone(18c)**:** Oil, ^1H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.4 Hz, 2H, ArH), 6.92 (d, *J* = 8.8 Hz, 2H, ArH), 4.03 (t, *J* = 6.6 Hz, 2H, CH_2), 2.56 (s, 3H, OCH_3), 1.81-1.76 (m, 2H, CH_2), 1.53-1.46 (m, 2H, CH_2), 0.99 (t, *J* = 7.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.86, 163.14, 130.60, 130.10, 114.13, 67.95, 31.14, 26.35, 19.19, 13.82; Ms(70 ev): m/z: 192.1 (M^+).

1-(4-methoxy-2-methylphenyl)ethanone (18d): Oil, ^1H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.4 Hz, 1H, ArH), 7.77 (s, 1H, ArH), 6.84 (d, *J* = 7.6 Hz, 1H, ArH), 3.89 (s, 3H, OCH_3), 2.55 (s, 3H, CH_3), 2.24 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.16, 161.77, 130.89, 129.82, 128.50, 126.74, 109.15, 55.52, 26.33, 16.25; Ms(70 ev): m/z: 164.1 (M^+).

1-(4-methoxy-3-methylphenyl)ethanone (18e): Oil, ^1H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.0 Hz, 1H, ArH), 6.77-6.73 (m, 2H, ArH), 3.84 (s, 3H, OCH_3), 2.56 (s, 3H, CH_3), 2.54 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.50, 161.20, 142.19, 132.50, 121.49, 117.49, 110.60, 55.29, 29.05, 22.56; Ms(70 ev): m/z: 164.1 (M^+).

1-(4-methoxy-3,5-dimethylphenyl)ethanone (18f): Oil, ^1H NMR (400 MHz, $CDCl_3$): δ 6.55 (s, 2H, ArH), 3.78 (s, 3H, OCH_3), 2.45 (s, 3H, CH_3), 2.24 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.04, 159.46, 135.56, 134.53, 113.22, 55.16, 32.42, 19.64; Ms(70 ev): m/z: 178.1 (M^+).

1-(4-methoxy-2-chlorophenyl)ethanone (18g): Oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (s, 1H, ArH), 7.78 (d, *J* = 8.4 Hz, 1H, ArH), 6.89 (d, *J* = 9.0 Hz, 1H, ArH), 3.90 (s, 3H, OCH_3), 2.48(s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.71, 157.76, 129.82, 129.65, 127.74, 121.85, 110.25, 55.36, 25.25; Ms(70 ev): m/z: 184.0 (M^+).

1-(4-methoxy-2-bromophenyl)ethanone (18h): Oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 3.6 Hz, 1H, ArH), 7.91 (t, *J* = 5.8 Hz, 1H, ArH), 6.93 (t, *J* = 7.2 Hz, 1H, ArH), 3.96 (s, 3H, OCH_3), 2.54 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.65, 159.60, 143.01, 133.87, 131.16, 129.50, 110.68, 56.50, 26.33; Ms(70 ev): m/z: 228.0 (M^+).

***1-(4-methoxyphenyl)propanone(18i)*:** Oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.8 Hz, 2H, ArH), 6.93 (d, *J* = 8.8 Hz, 2H, ArH), 3.87 (s, 3H, OCH_3), 2.95 (q, *J* = 7.2 Hz, 2H, CH_2), 1.21 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.55, 163.30, 130.23, 130.04, 113.67, 55.46, 31.43, 8.46; Ms(70 ev): m/z: 164.1 (M^+).

Typical procedure for the aza-Friedel-Crafts of benzaldehyde (5a) with indole (19a) and *N,N*-dimethylaniline (50a) catalyzed by complex 3: To a 50 mL round-bottomed flask was added benzaldehyde (106 mg, 1.0 mmol), indole (117 mg, 1.0 mmol) and *N,N*-dimethylaniline (133 mg, 1.1 mmol), CH_2ClCH_2Cl (3 mL) and catalyst **3** (14 mg, 0.02 mol). Then the mixture was stirred at 100 °C until complete consumption of starting material as monitored by TLC. Then the reaction mixture was evaporated in vacuum, CH_2Cl_2 (3×10 ml) was added to the reaction mixture and the catalyst was filtered for the next cycle of reaction. The combined CH_2Cl_2 solution was removed by evaporation in vacuum and was then subject to silica gel column chromatograph; the one-pot three-component aza-Friedel-Crafts product (**21a**) was obtained, whie solid, 235.0 mg, isolated yield 72%. Aldehydes and indoles such as and nucleophiles ***N,N*-**dialkylaniline are commercially available. **21a-21c, 21e, 21h-21k** are known compounds[S17-S18] and **21d, 21f, 21g**, **21i** are new compound. The spectra data are summarized as follows:

***4-((1H-indol-3-yl)(phenyl)methyl)-N,N-dimethylaniline*(21a)**: White solid, mp 159-161 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (s, 1H, NH), 7.30-7.07 (m, 10H, ArH), 6.96 (t, *J* = 6.8 Hz, 1H, ArH), 6.65 (t, *J* = 8.4 Hz, 2H, ArH), 6.52 (s, 1H, ArH), 5.57 (s, 1H, CH), 2.89 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.02, 144.68, 136.66, 132.19, 129.52, 128.89, 128.12, 127.05, 125.91, 123.93, 121.88, 120.54, 119.20, 112.58, 110.93, 47.79, 40.71; Ms(70 ev): m/z: 326.2 (M^+).

***4-((1H-indol-3-yl)(p-tolyl)methyl)-N,N-dimethylaniline*(21b)**: White solid, mp 163-165 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 1H, NH), 7.32 (d, *J* = 8.4 Hz, 1H, ArH), 7.25 (d, *J* = 5.2 Hz, 2H, ArH), 7.16-7.05 (m, 7H, ArH), 6.97 (t, *J* = 7.4 Hz, 1H, ArH), 6.66 (d, *J* = 8.4 Hz, 2H, ArH), 6.58 (s, 1H, ArH), 5.54 (s, 1H, CH), 2.90 (s, 6H, CH_3), 2.31 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.72, 136.73, 135.35, 129.52, 128.88, 128.80, 128.16, 123.90, 121.92, 120.83, 120.12, 119.24, 112.68, 119.30, 110.93, 110.90, 47.42, 40.83, 21.07; Ms(70 ev): m/z: 340.2 (M^+).

***4-((1H-indol-3-yl)(p-methoxyphenyl)methyl)-N,N-dimethylaniline*(21c)**: White solid, mp 160-162 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 1H, NH), 7.33 (d, *J* = 8.0 Hz, 1H, ArH), 7.24 (d, *J* = 6.4 Hz, 2H, ArH), 7.13 (d, *J* = 8.0 Hz, 2H, ArH), 7.07 (d, *J* = 8.0 Hz, 2H, ArH), 6.97 (d, *J* = 7.4 Hz, 1H, ArH), 6.80 (d, *J* = 7.6 Hz, 2H, ArH), 6.67 (d, *J* = 8.0 Hz, 2H, ArH), 6.57 (s, 1H, ArH), 5.53 (s, 1H, CH), 3.77 (s, 3H, OCH_3), 2.91 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.78, 149.03, 136.97, 136.76, 132.61, 129.83, 129.48, 127.12, 123.87, 121.93, 121.02, 120.13, 119.24, 113.53, 112.65, 110.94, 55.22, 44.99, 40.80; Ms(70 ev): m/z: 356.2 (M^+).

***4-((1H-indol-3-yl)(o-fluorophenyl)methyl)-N,N-dimethylaniline*(21d)**: White solid, mp 184-186 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (s, 1H, NH), 7.32 (d, *J* = 8.0 Hz, 1H, ArH), 7.24 (d, *J* = 7.2 Hz, 1H, ArH), 7.19-7.02 (m, 6H, ArH), 6.98 (d, *J* = 7.6 Hz, 2H, ArH), 6.67 (d, *J* = 8.0Hz, 2H, ArH), 6.59 (s, 1H, ArH), 5.89 (s, 1H, CH), 2.91 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.93, 159.48, 149.20, 136.78, 131.58 (*J* = 14.4 Hz), 130.80, 130.48 (*J* = 4.2 Hz), 129.46, 127.68, 126.94, 124.01, 123.78 (*J* = 3.4 Hz), 122.05, 119.91, 119.32 (*J* = 5.4 Hz), 115.20 (*J* = 22.0 Hz), 112.62, 111.03, 40.74, 40.18 (*J* = 3.4 Hz); Ms(70 ev): m/z: 344.2 (M^+); HRMS Calcd for $C_{23}H_{21}FN_2$: 344.1689, [M^+] : Found: 344.1692.

***4-((1H-indol-3-yl)(p-chlorophenyl)methyl)-N,N-dimethylaniline*(21e)**: White solid, mp 130-132 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (s, 1H, NH), 7.34 (d, *J* = 8.0 Hz, 1H, ArH), 7.22 (d, *J* = 8.0 Hz, 3H, ArH), 7.15 (d, *J* = 8.4 Hz, 3H, ArH), 7.05 (d, *J* = 8.0 Hz, 2H, ArH), 6.99 (t, *J* = 7.4 Hz, 1H, ArH), 6.66 (d, *J* = 8.0 Hz, 2H, ArH), 6.57 (s, 1H, ArH), 5.55 (s, 1H, CH), 2.92 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.20, 143.29, 136.75, 131.66, 131.58, 130.30, 129.50, 128.31, 126.93, 123.98, 122.12, 120.19, 119.97, 119.41, 112.62, 111.06, 55.20, 47.25, 40.72; Ms(70 ev): m/z: 360.1 (M^+).

***4-((1H-indol-3-yl)(o-bromophenyl)methyl)-N,N-dimethylaniline*(21f)**: White solid, mp 176-178 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (s, 1H, NH), 7.56 (d, *J* = 8.0 Hz, 1H, ArH), 7.31 (d, *J* = 8.0 Hz, 1H, ArH), 7.21 (d, *J* = 8.0 Hz, 1H, ArH), 7.16-6.96 (m, 7H, ArH), 6.66 (d, *J* = 8.4 Hz, 2H, ArH), 6.52 (s, 1H, ArH), 5.98 (s, 1H, CH), 2.91 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.14, 143.61, 136.78, 132.88, 130.79, 130.41, 129.85, 127.70, 127.21, 126.98, 125.11, 124.24, 122.09, 119.95, 119.82, 119.38, 112.55, 111.03, 47.01, 40.72; Ms(70 ev): m/z: 404.1 (M^+); HRMS Calcd for $C_{23}H_{21}BrN_2$: 404.0888, [M^+] : Found: 404.0885.

***4-((1H-indol-3-yl)(o-nitrophenyl)methyl)-N,N-dimethylaniline*(21g)**: White solid, mp 156-158 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (s, 1H, NH), 7.80 (d, *J* = 8.0 Hz, 1H, ArH), 7.40-7.27 (m, 4H, ArH), 7.21 (d, *J* = 8.4 Hz, 1H, ArH), 7.14 (d, *J* = 7.6 Hz, 1H, ArH), 7.04 (d, *J* = 8.0 Hz, 2H, ArH), 6.98 (d, *J* = 7.6 Hz, 1H, ArH), 6.64 (d, *J* = 8.0 Hz, 2H, ArH), 6.53 (s, 1H, ArH), 6.30 (s, 1H, CH), 2.90 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.74, 149.32, 138.78, 136.79, 132.33, 131.42, 129.82, 129.70, 127.08, 126.75, 124.40, 124.34, 122.26, 119.71, 119.56, 118.96, 112.61, 111.19, 42.29, 40.66; Ms(70 ev): m/z: 371.1 (M^+); HRMS Calcd for $C_{23}H_{21}O_2N_3$: 371.1634, [M^+] : Found: 371.1630.

***4-((1H-2-methyl-indol-3-yl)(phenyl)methyl)-N,N-dimethylaniline*(21h)**: White solid, mp 87-89 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (s, 1H, NH), 7.26-7.16 (m, 6H, ArH), 7.05 (t, *J* = 7.4 Hz, 4H, ArH), 6.88 (t, *J* = 7.4 Hz, 1H, ArH), 6.65 (d, *J* = 8.0 Hz, 2H, ArH), 5.65 (s, 1H, CH), 2.90 (s, 6H, CH_3), 2.17 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.99, 144.71, 135.21, 132.01, 131.89, 129.77, 129.16, 128.58, 128.07, 125.81, 120.64, 119.71, 119.08, 114.64, 112.63, 110.03, 46.79, 40.83, 12.43; Ms(70 ev): m/z: 340.2 (M^+).

***4-((1H-7-methyl-indol-3-yl)(phenyl)methyl)-N,N-dimethylaniline*(21i)**: White solid, mp 84-85 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (s, 1H, NH), 7.28-7.22 (m, 4H, ArH), 7.18 (d, *J* = 8.0 Hz, 1H, ArH), 7.09 (t, *J* = 7.4 Hz, 3H, ArH), 6.95 (d, *J* = 6.8 Hz, 1H, ArH), 6.90 (d, *J* = 7.4 Hz, 1H, ArH), 6.66 (d, *J* = 8.4 Hz, 2H, ArH), 6.58 (s, 1H, ArH), 5.57 (s, 1H, CH), 2.91 (s, 6H, CH_3), 2.45 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.06, 144.77, 136.28, 132.27, 129.58, 128.96, 128.16, 126.67, 125.93, 123.64, 122.54, 121.21, 120.08, 119.51, 117.84, 112.61, 47.95, 40.77, 16.62; Ms(70 ev): m/z: 340.2 (M^+).

***4-((1H-6-fluoro-indol-3-yl)(phenyl)methyl)-N,N-dimethylaniline*(21j)**: White solid, mp 181-183 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (s, 1H, NH), 7.26-7.06 (m, 8H, ArH), 7.00 (d, *J* = 9.6 Hz, 1H, ArH), 6.73 (t, *J* = 9.2 Hz,

1H, ArH), 6.67 (d, *J* = 8.4 Hz, 2H, ArH), 6.54 (s, 1H, ArH), 5.53 (s, 1H, CH), 2.93 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.11, 149.13, 144.47, 136.70, 136.58, 131.87, 129.51, 128.88, 128.23, 126.08, 124.23, 123.72, 120.83 (d, *J* = 10 Hz), 112.60, 108.03 (d, *J* = 24.3 Hz), 97.25 (d, *J* = 25.8 Hz), 47.83, 40.74; Ms(70 ev): m/z: 344.2 (M^+).

***4-((1H-5-chloro-indol-3-yl)(phenyl)methyl)-N,N-dimethylaniline*(21k)**: White solid, mp 165-166 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 7.94 (s, 1H, NH), 7.28-7.17 (m, 7H, ArH), 7.05 (d, *J* = 8.0 Hz, 3H, ArH), 6.66 (d, *J* = 8.0 Hz, 2H, ArH), 6.59 (s, 1H, ArH), 5.51 (s, 1H, CH), 2.91 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.17, 144.33, 135.06, 131.73, 129.49, 128.86, 128.28, 128.22, 126.15, 125.32, 125.00, 122.34, 120.47, 119.40, 112.68, 112.01, 47.61, 40.76; Ms(70 ev): m/z: 360.1 (M^+).

***4-((1H-indol-3-yl)(phenyl)methyl)-N,N-dimethylaniline*(21i)**: White solid, mp 78-80 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 7.90 (s, 1H, NH), 7.32 (d, *J* = 8.0 Hz, 1H, ArH), 7.27-7.23 (m, 5H, ArH), 7.14 (t, *J* = 7.6 Hz, 2H, ArH), 7.04 (d, *J* = 8.0 Hz, 2H, ArH), 6.97 (d, *J* = 7.8 Hz, 1H, ArH), 6.62-6.58 (m, 3H, ArH), 5.56 (s, 1H, CH), 3.30 (q, *J* = 6.8 Hz, 4H, CH_2), 1.13 (t, *J* = 6.8 Hz, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.32, 144.88, 136.73, 130.91, 129.72, 128.97, 128.15, 127.17, 125.91, 123.98, 121.92, 120.80, 120.13, 119.24, 111.77, 110.95, 47.81, 44.33, 12.68; Ms(70 ev): m/z: 354.2 (M^+).

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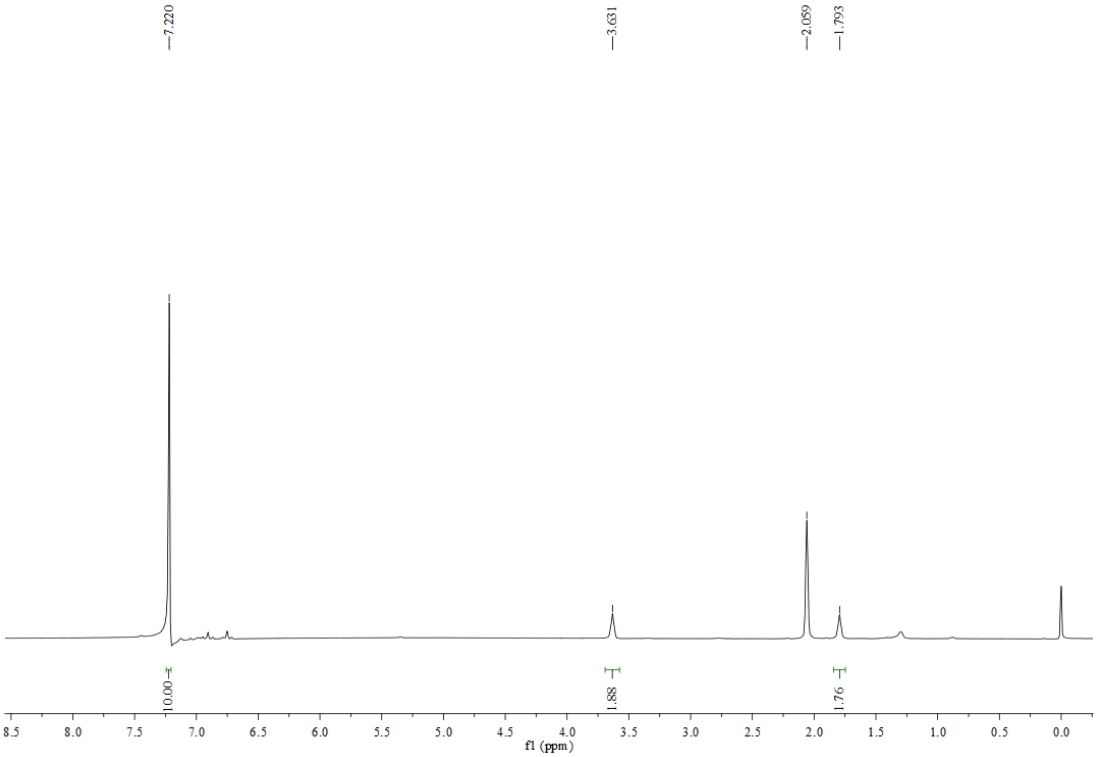
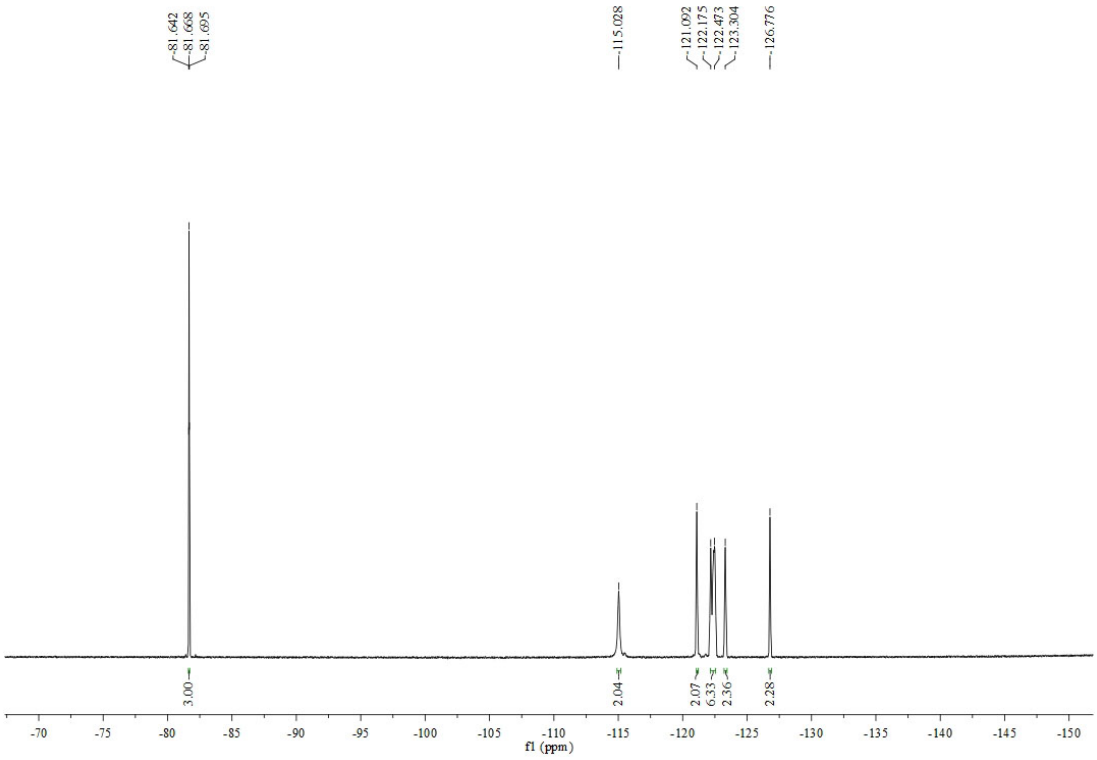
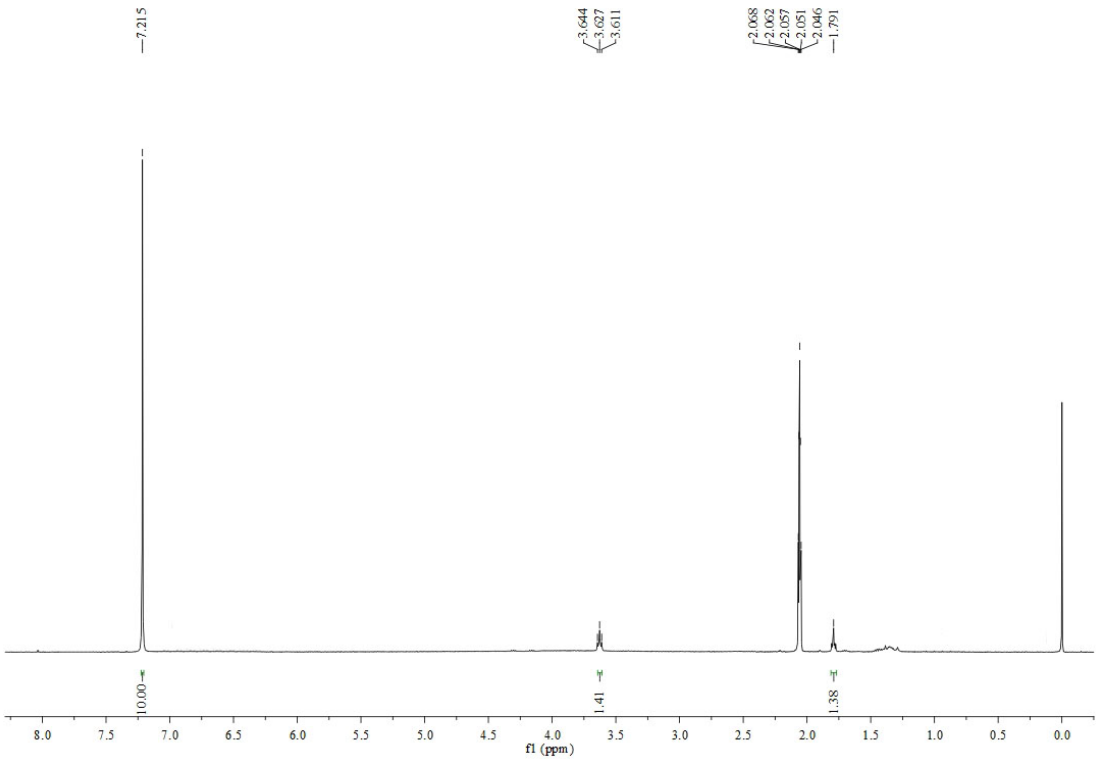


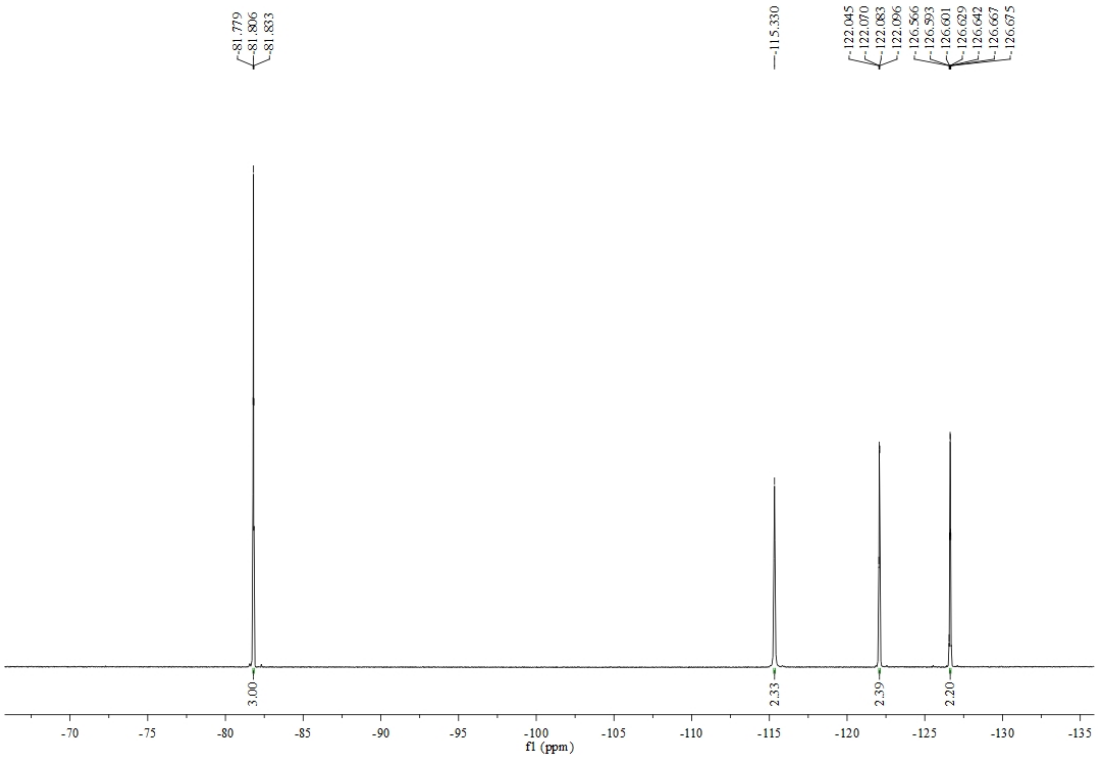
^{1}H NMR of **$Cp_2Ti(OH_2)_2(OSO_2C_8F_{17})\cdot THF$** in Acetone-[$D_6$]



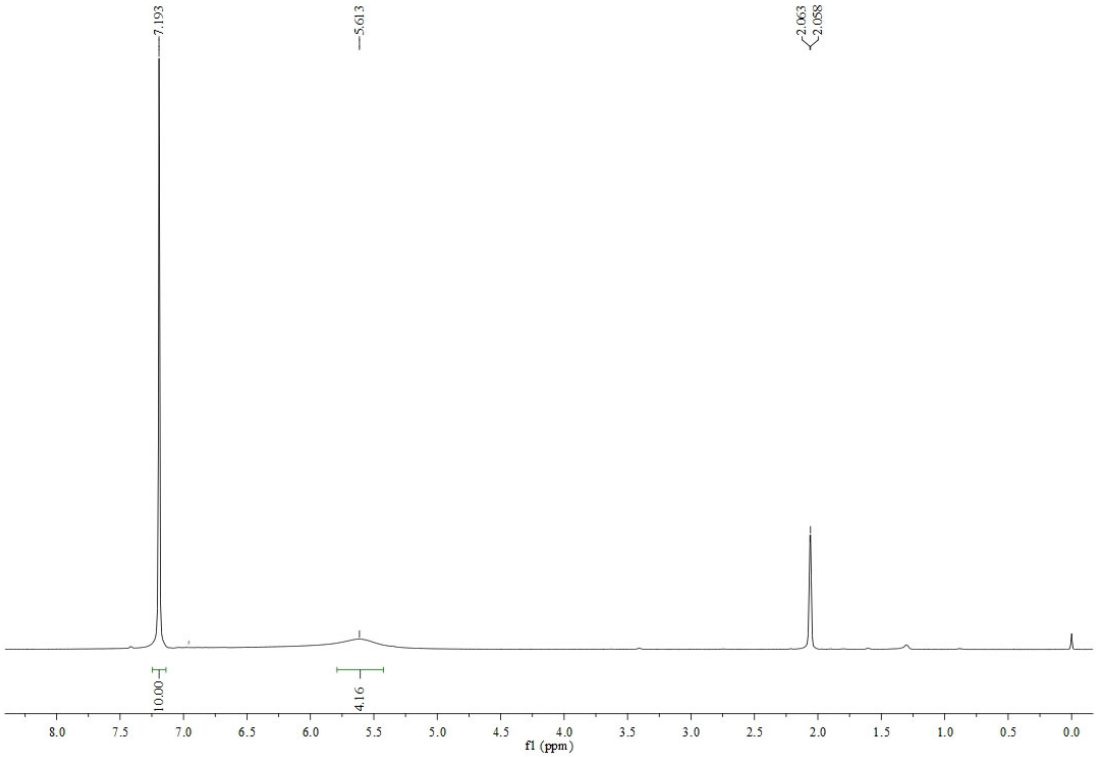
^{19}F NMR of **$Cp_2Ti(OH_2)_2(OSO_2C_8F_{17})\cdot THF$** in Acetone-[$D_6$]



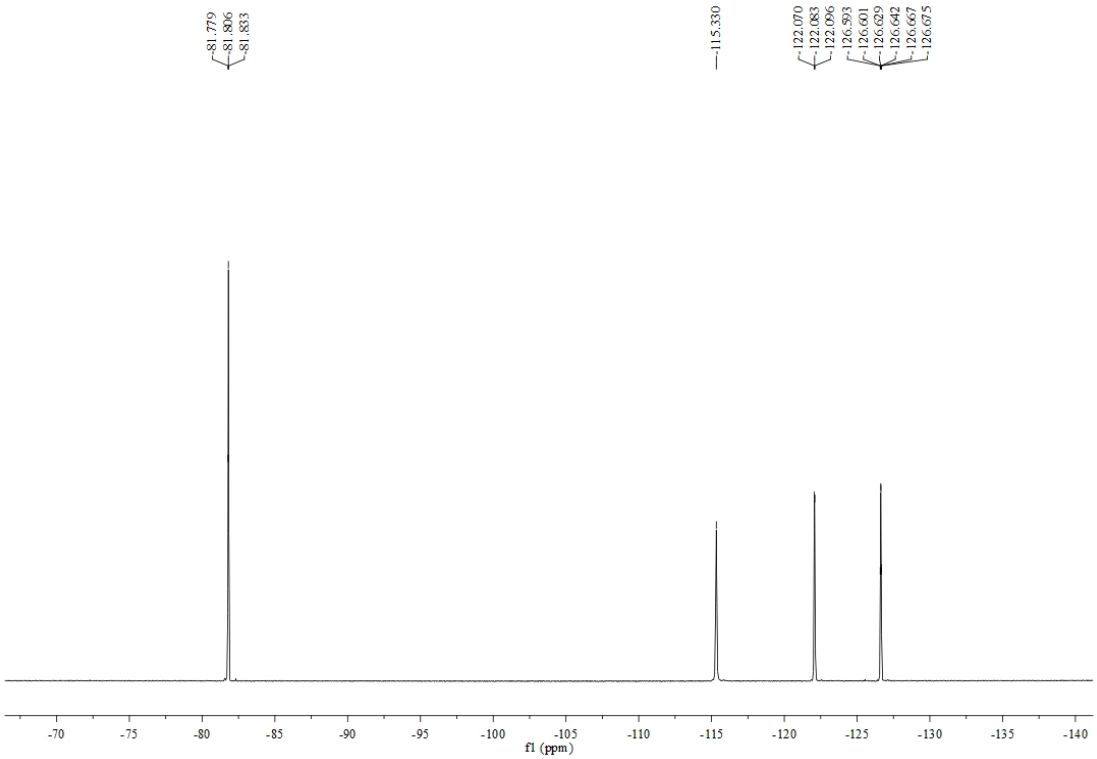
^{1}H NMR of **$Cp_2Ti(OH_2)_2(OSO_2C_4F_9)\cdot H_2O\cdot THF$** in Acetone-[$D_6$]



^{19}F NMR of **$Cp_2Ti(OH_2)_2(OSO_2C_4F_9)\cdot H_2O\cdot THF$** in Acetone-[$D_6$]

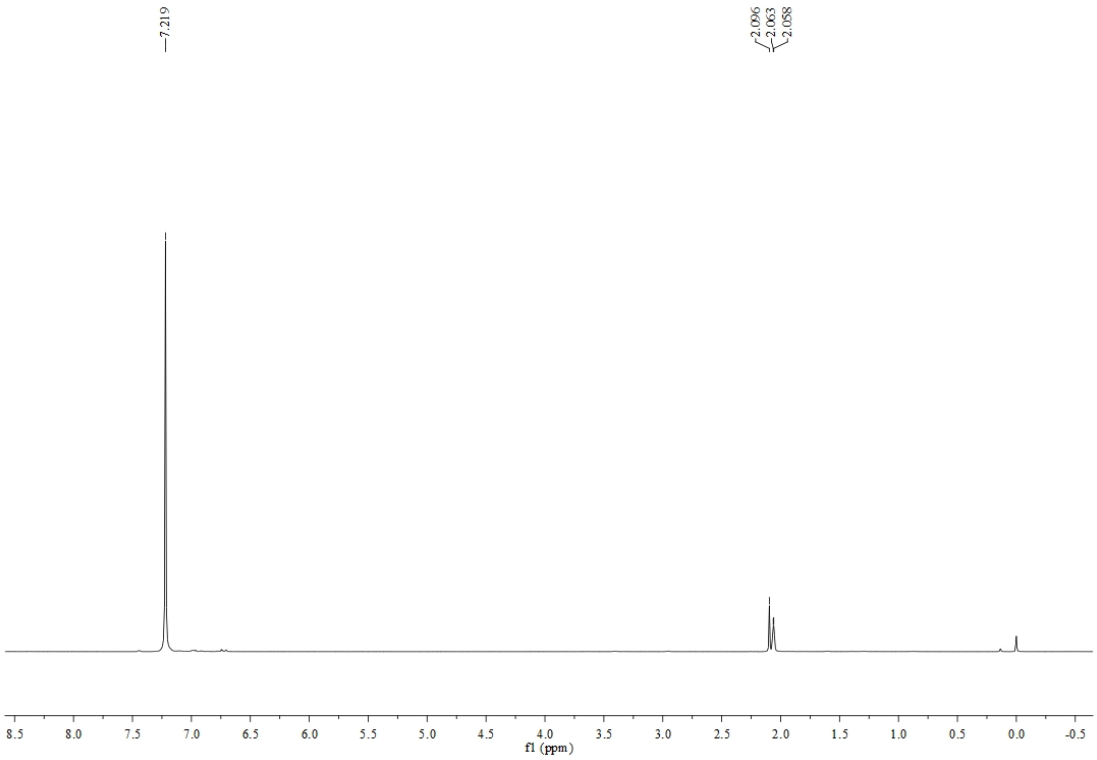


^{1}H NMR of **$[(Cp)_2Ti(H_2O)_2][OSO_2C_4F_9]_2$** in Acetone-[$D_6$]

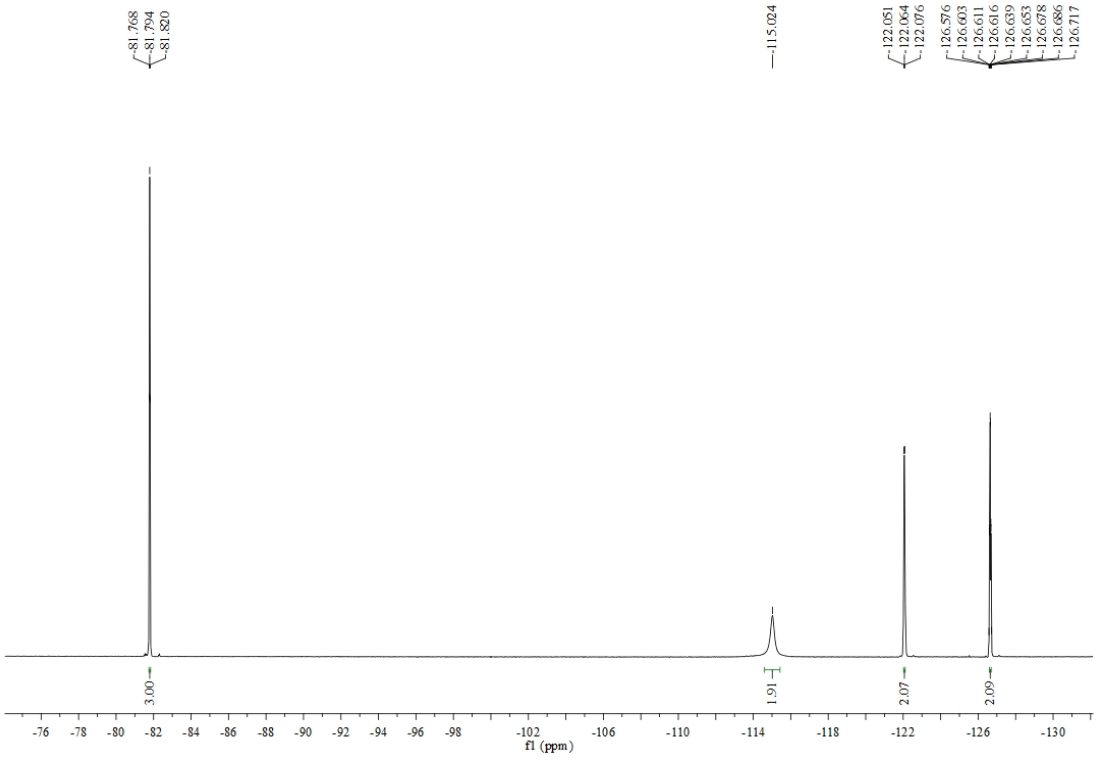


^{19}F NMR of **$[(Cp)_2Ti(H_2O)_2][OSO_2C_4F_9]_2$** in Acetone-[$D_6$]

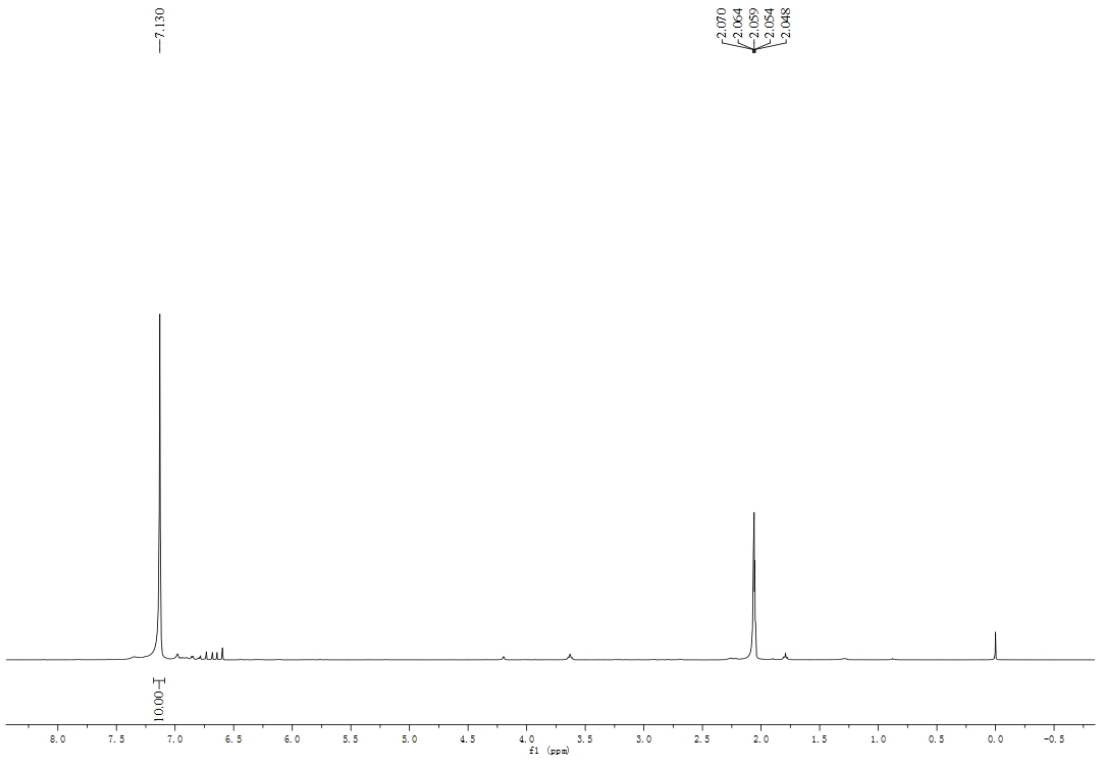
^{1}H and ^{19}F NMR Spectra of cauterant sample of complex **$[(Cp)_2Ti(H_2O)_2][OSO_2C_4F_9]_2$**·$H_2O$·THF after heating at 180 ˚C for two days in nitrogen atmosphere.



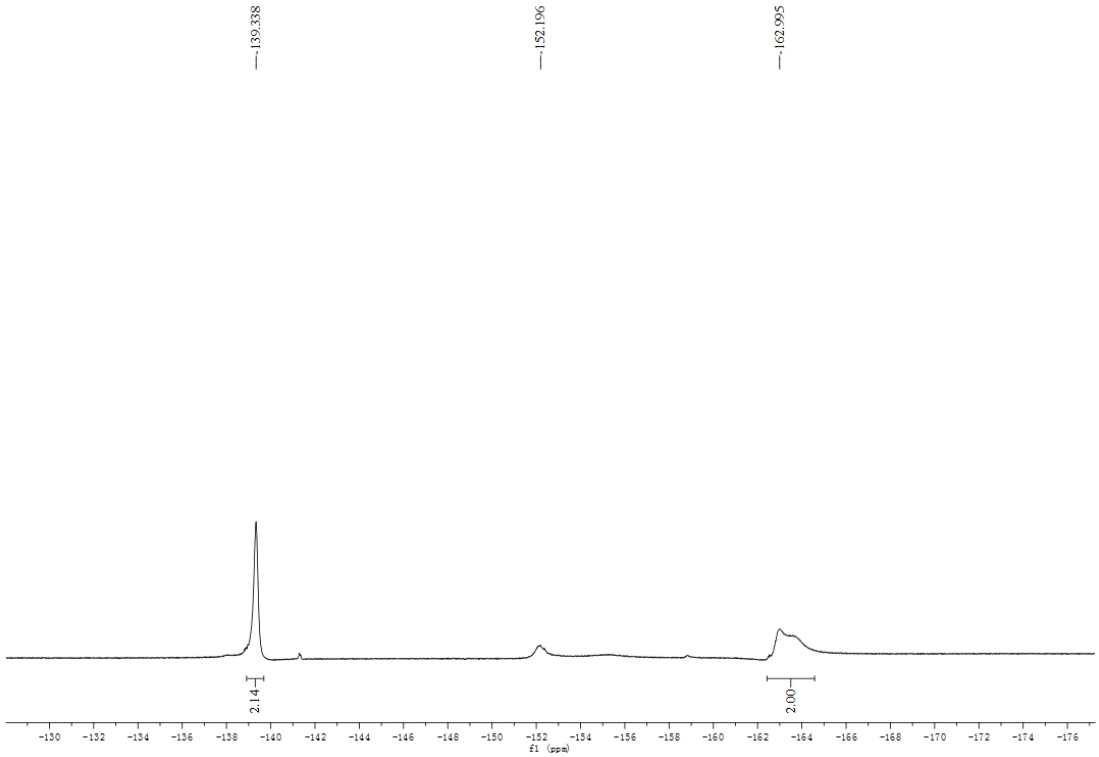
^{1}H NMR of **$Cp_2Ti(OSO_2C_4F_9)_2$** in Acetone-[D_6]



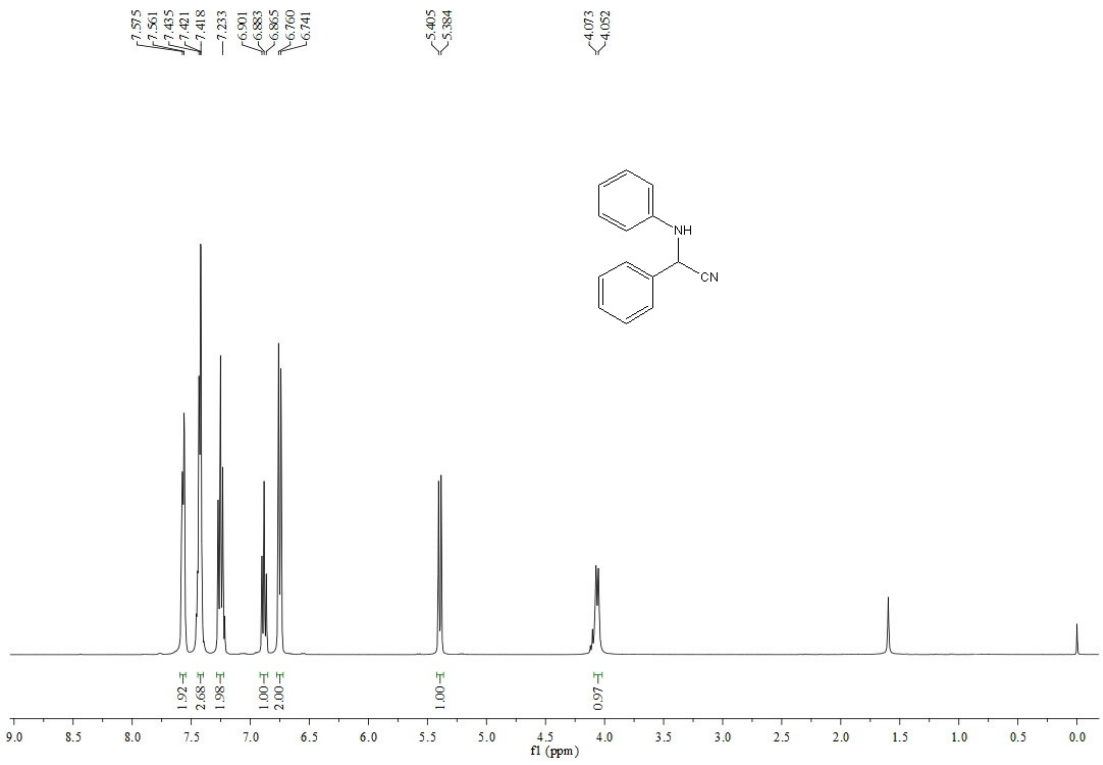
^{19}F NMR of **$Cp_2Ti(OSO_2C_4F_9)_2$** in Acetone-[D_6]



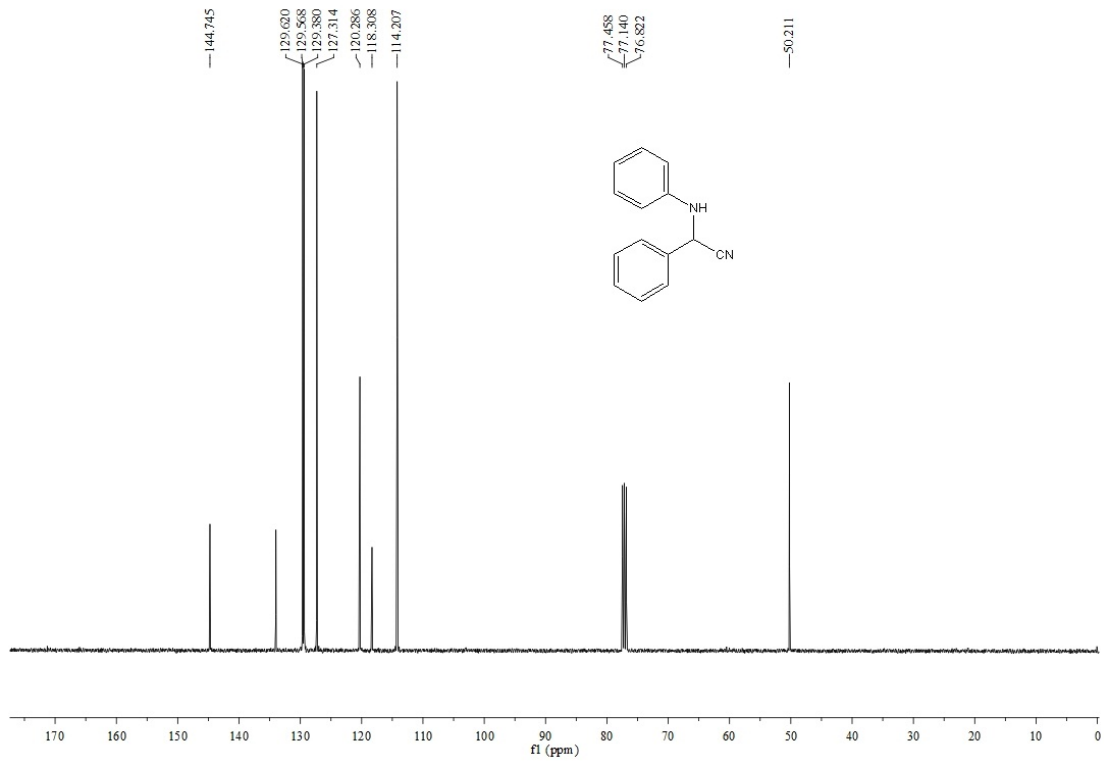
^{1}H NMR of **$[(Cp)_2Ti(H_2O)_2][OSO_2C_6F_5]_2$** in Acetone-[$D_6$]



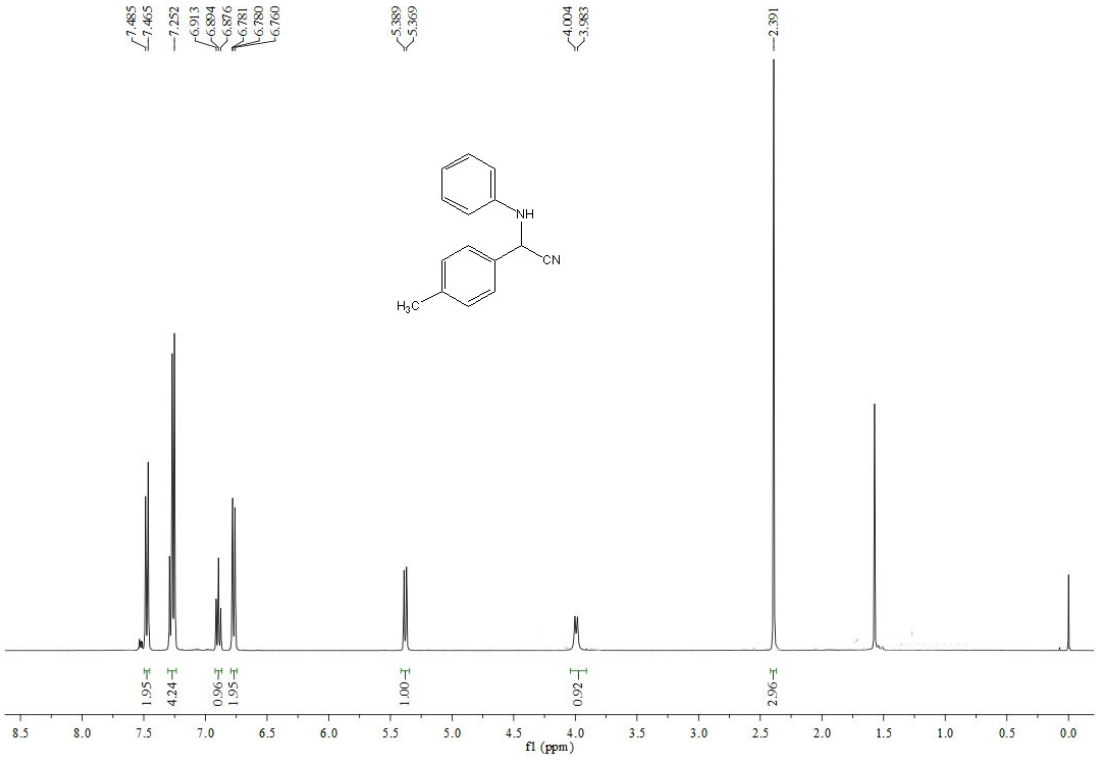
^{19}F NMR of **$[(Cp)_2Ti(H_2O)_2][OSO_2C_6F_5]_2$** in Acetone-[$D_6$]



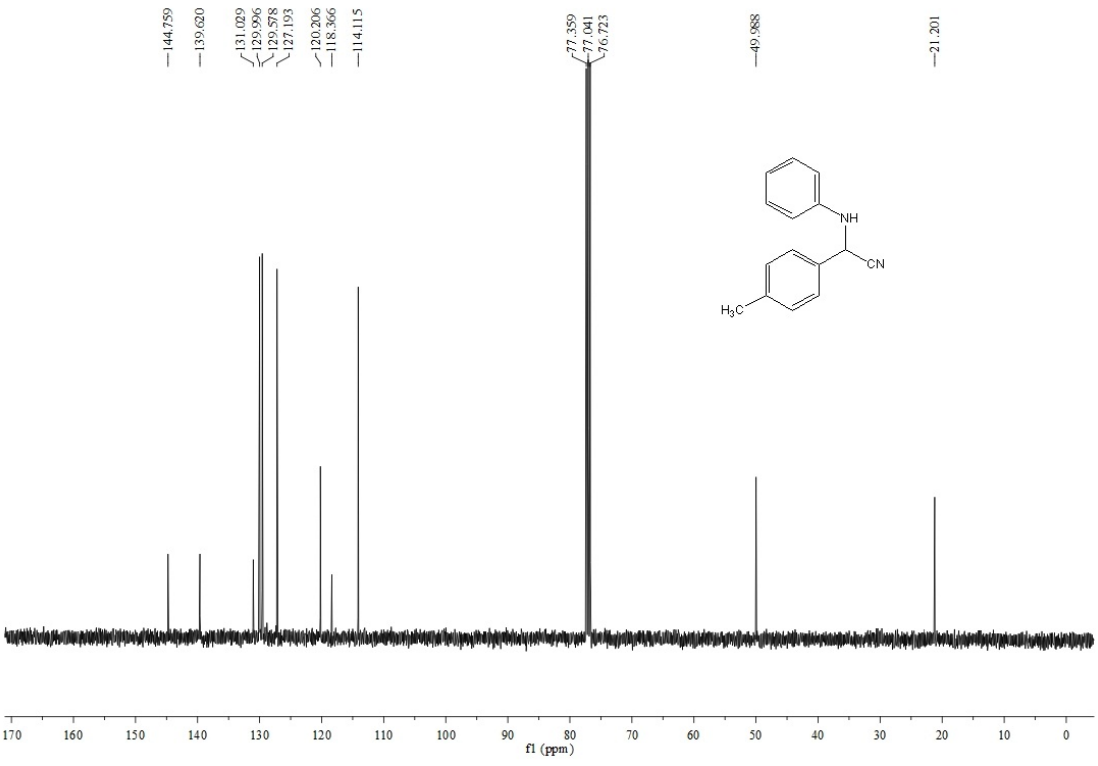
^{1}H NMR of **8a** in $CDCl_3$



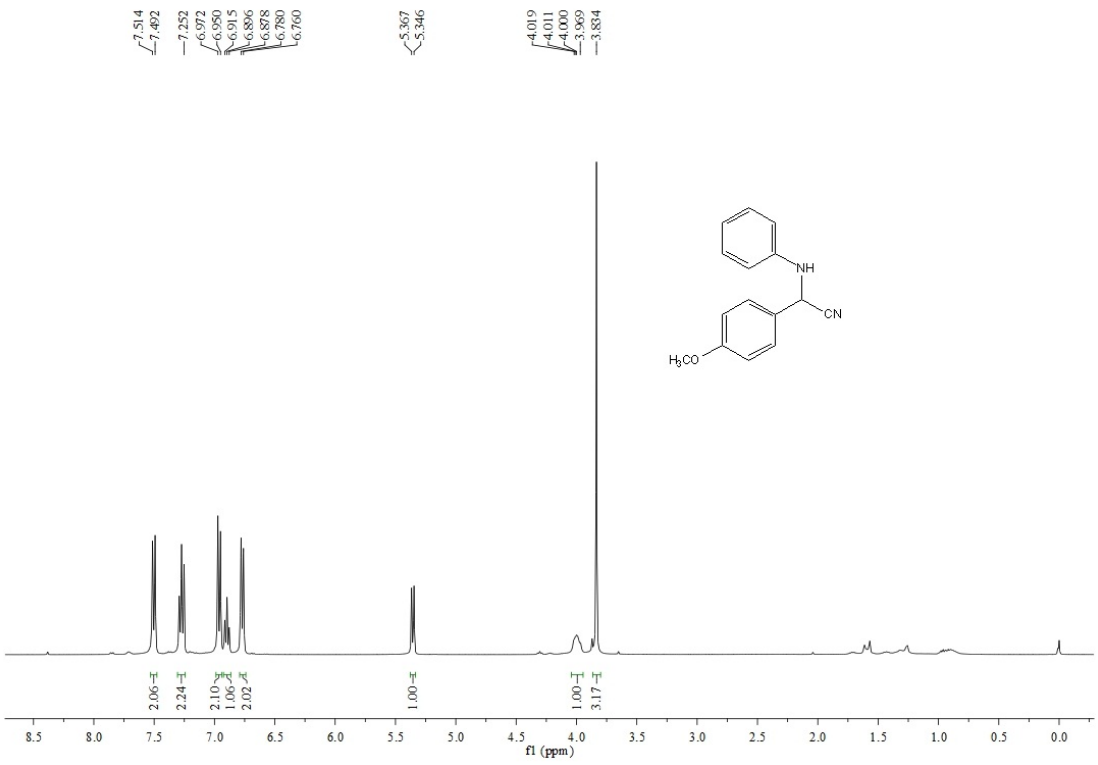
^{13}C NMR of **8a** in $CDCl_3$



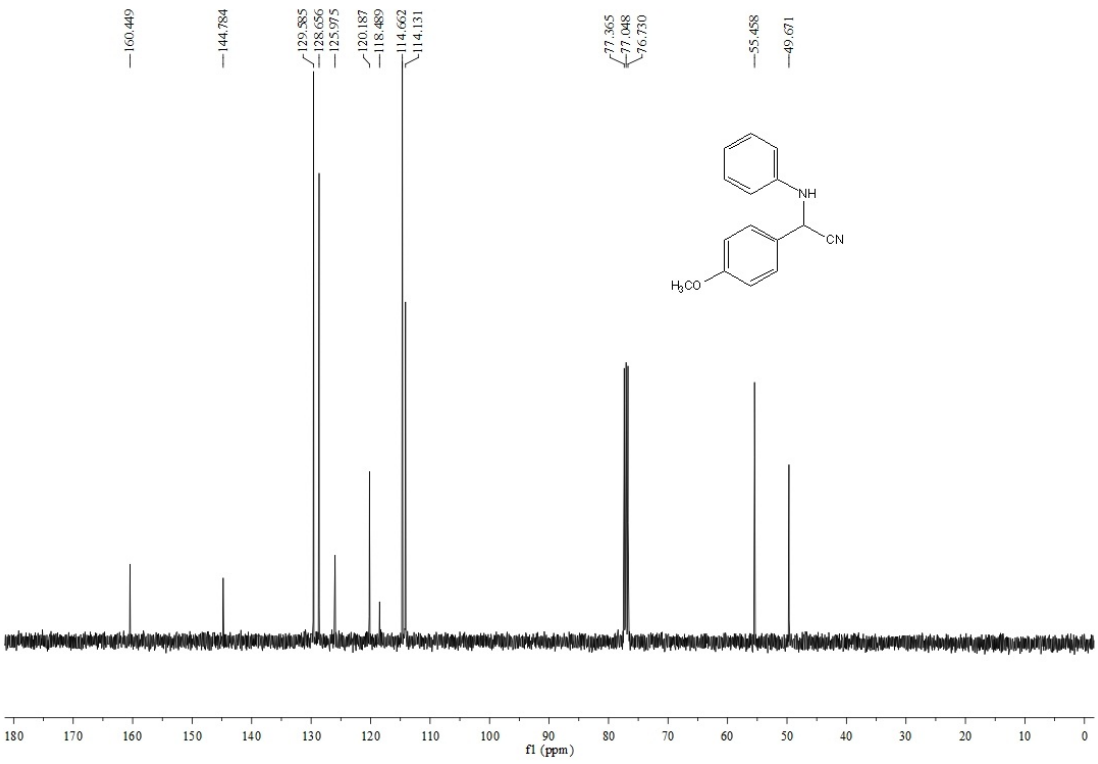
^{1}H NMR of **8b** in $CDCl_3$



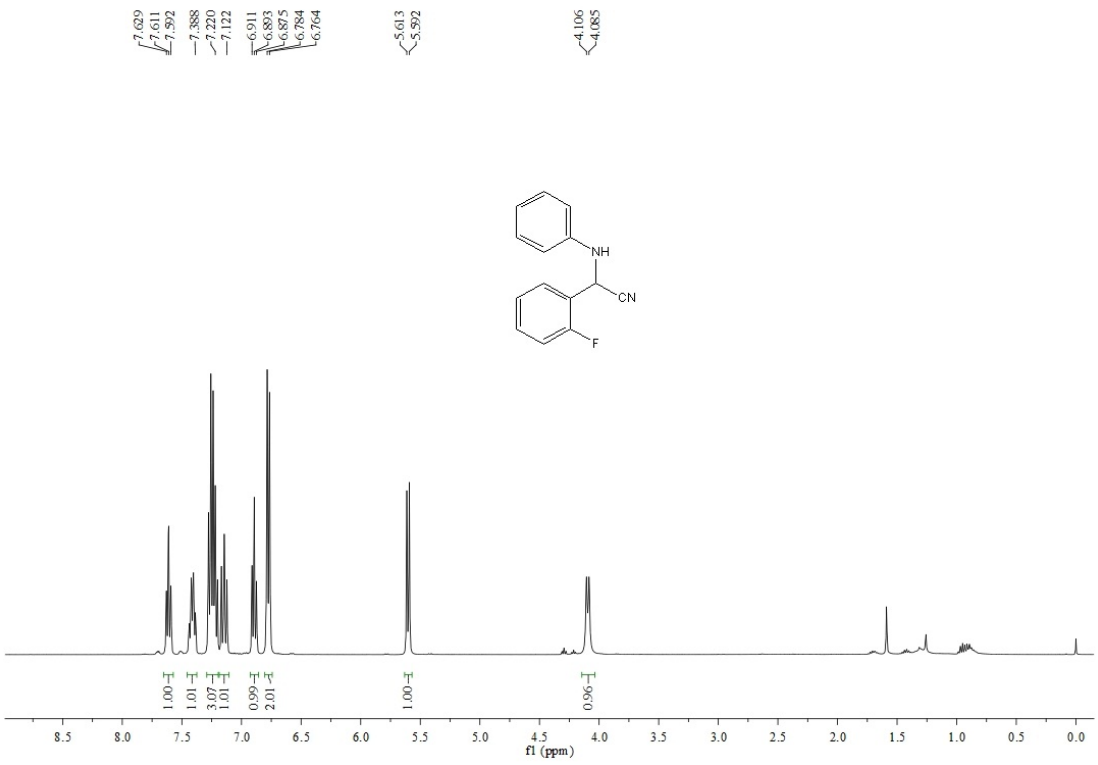
^{13}C NMR of **8b** in $CDCl_3$



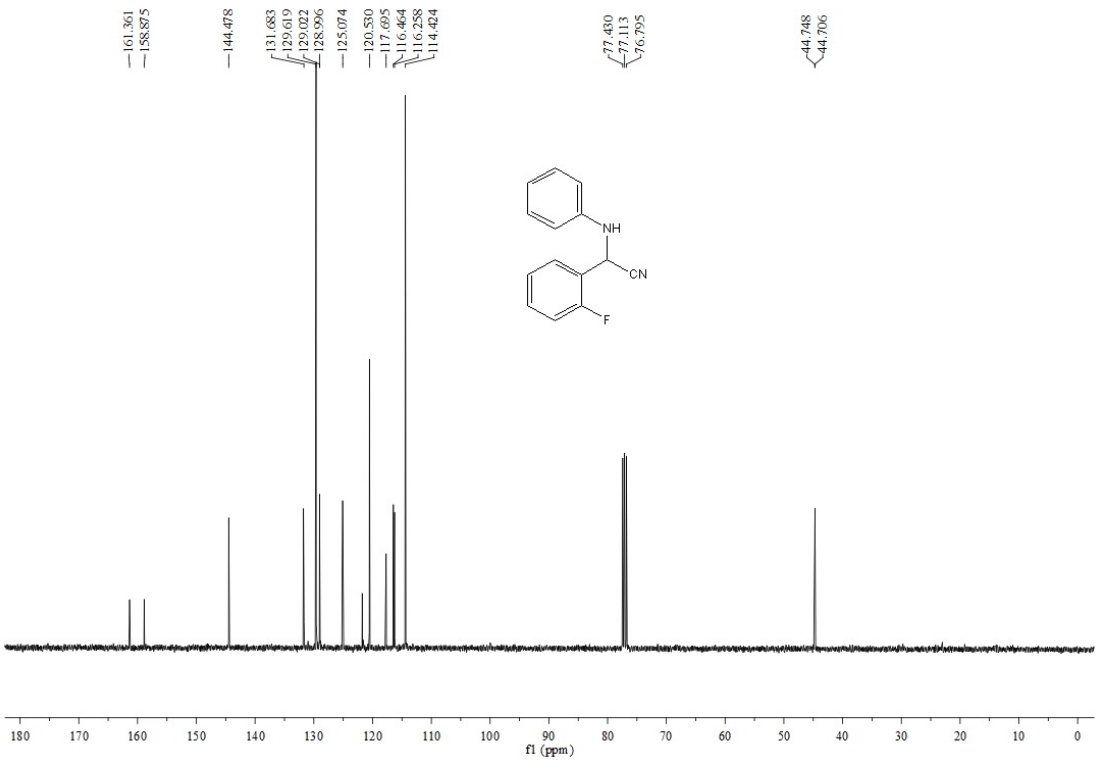
^{1}H NMR of **8c** in $CDCl_3$



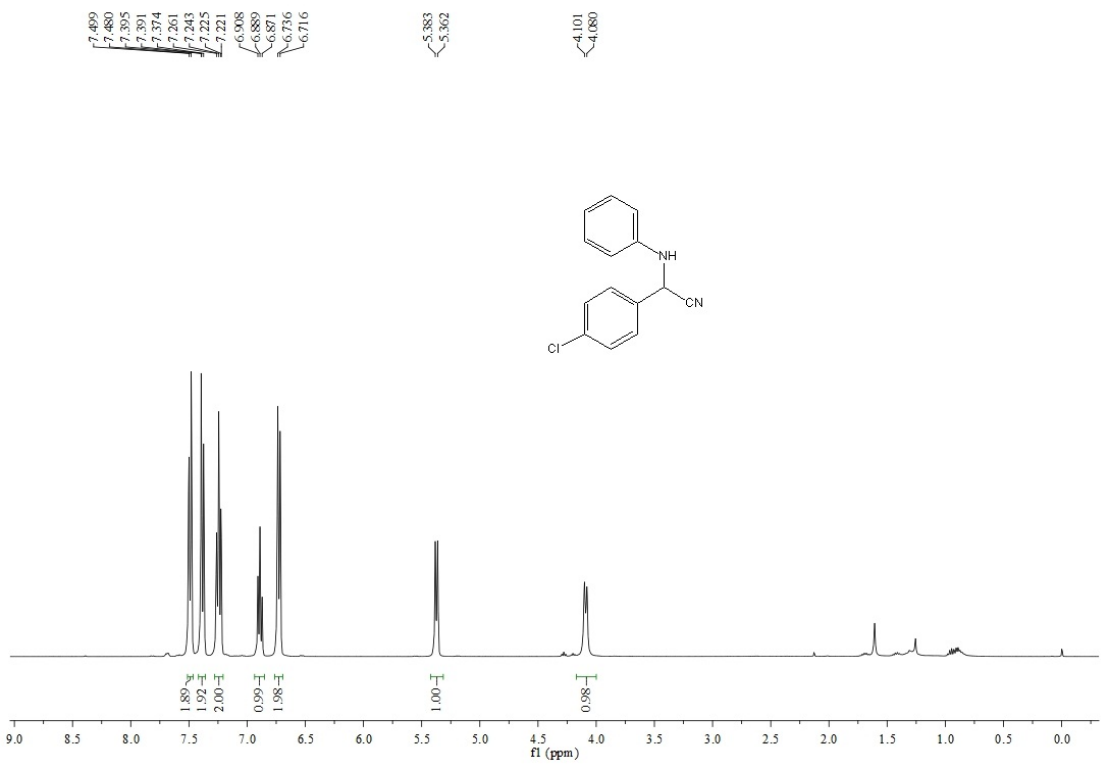
^{13}C NMR of **8c** in $CDCl_3$



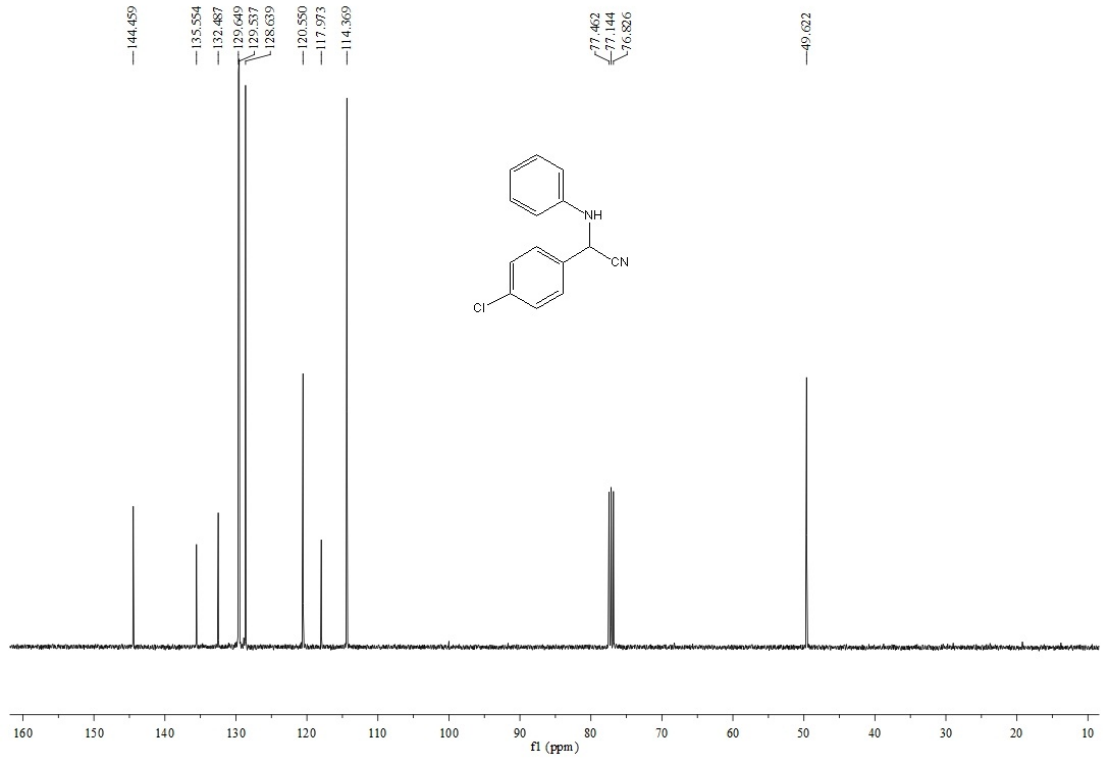
^{1}H NMR of **8d** in $CDCl_3$



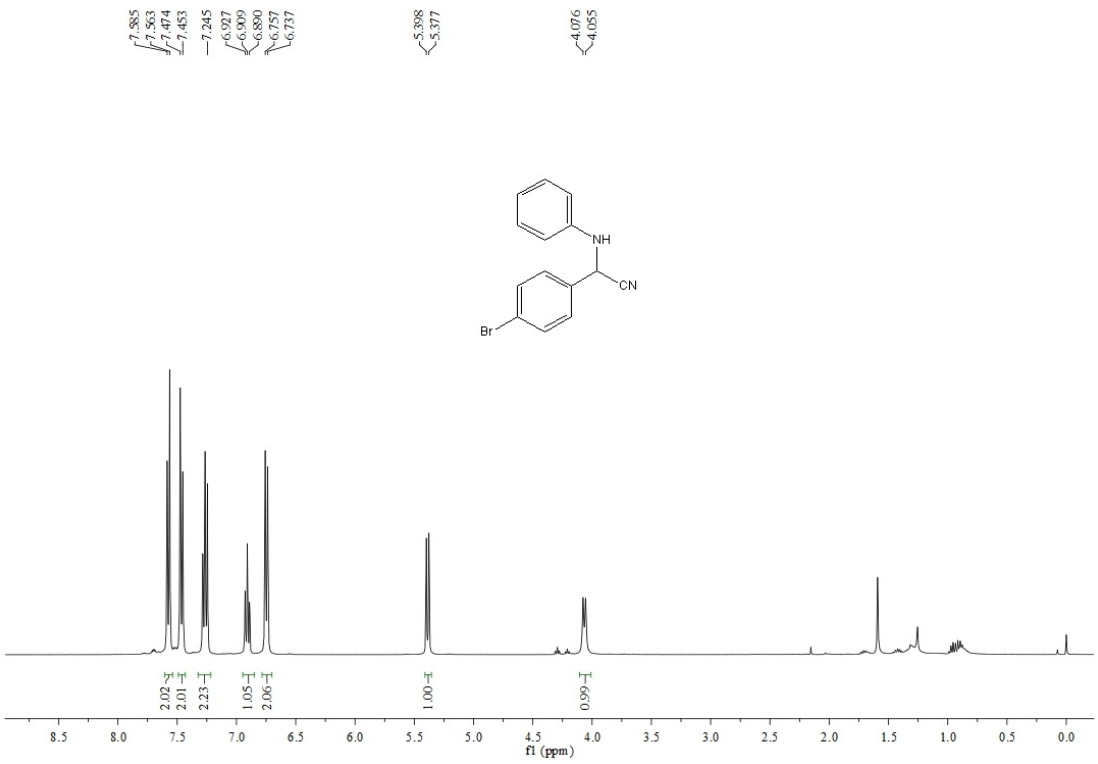
^{13}C NMR of **8d** in $CDCl_3$



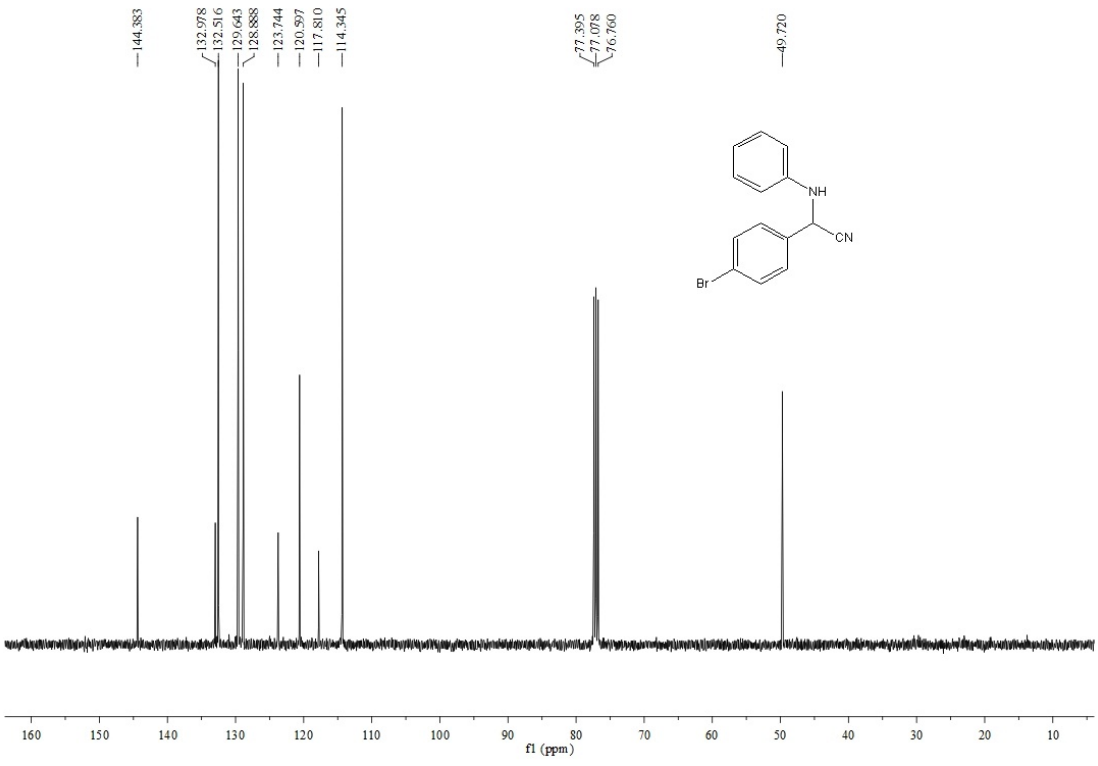
^{1}H NMR of **8e** in $CDCl_3$



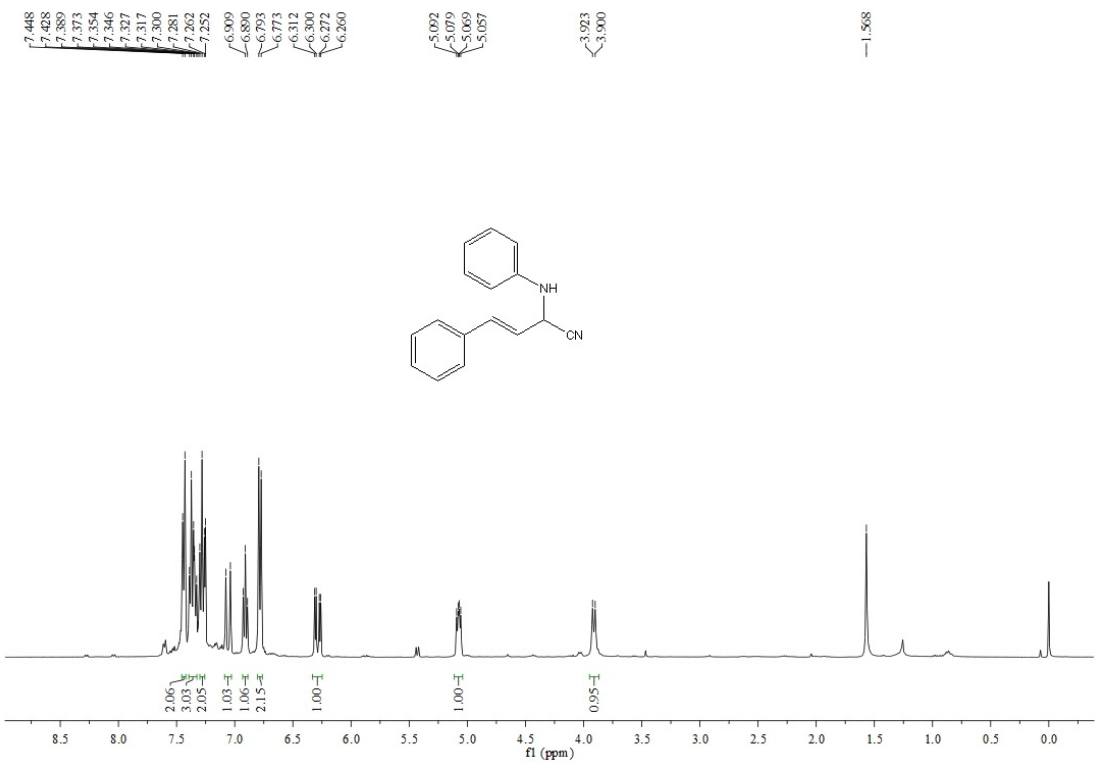
^{13}C NMR of **8e** in $CDCl_3$



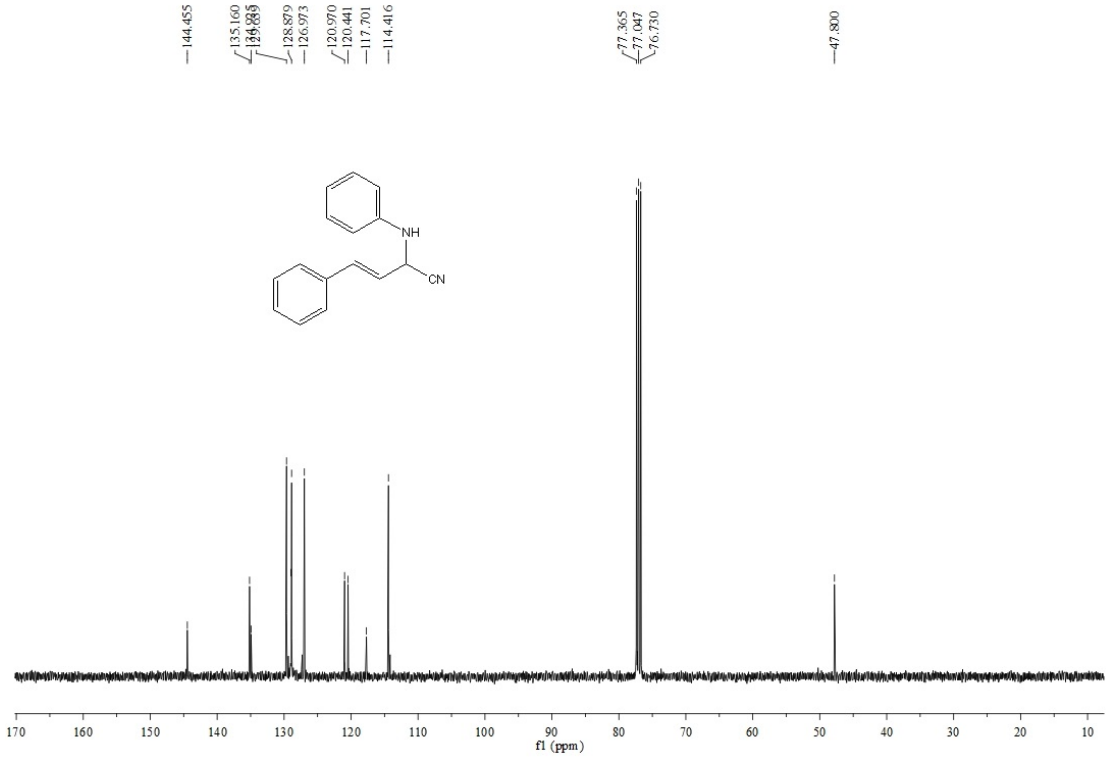
^{1}H NMR of **8f** in $CDCl_3$



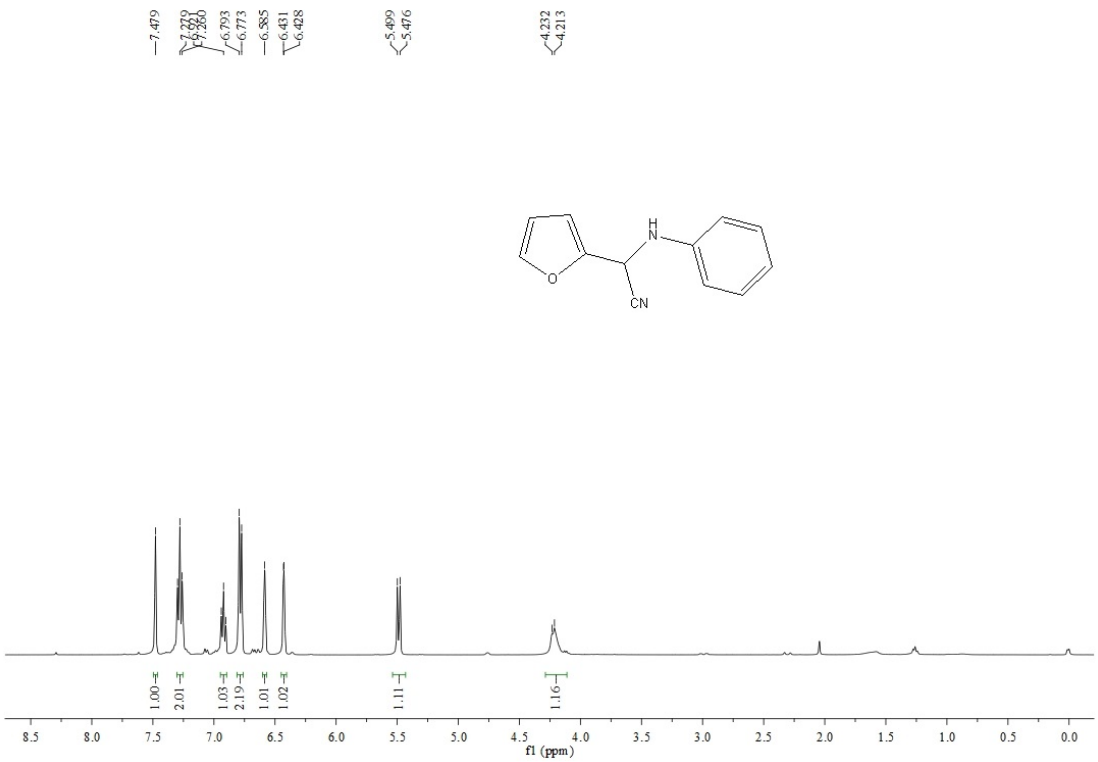
^{13}C NMR of **8f** in $CDCl_3$



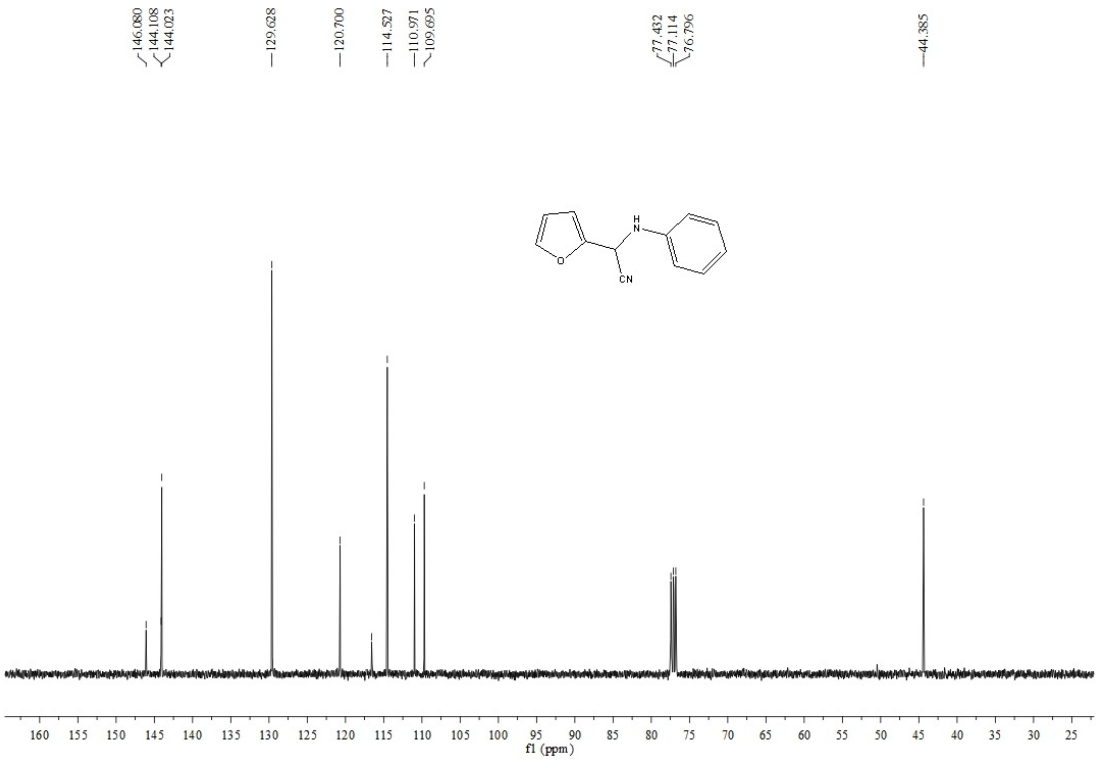
^{1}H NMR of **8g** in $CDCl_3$



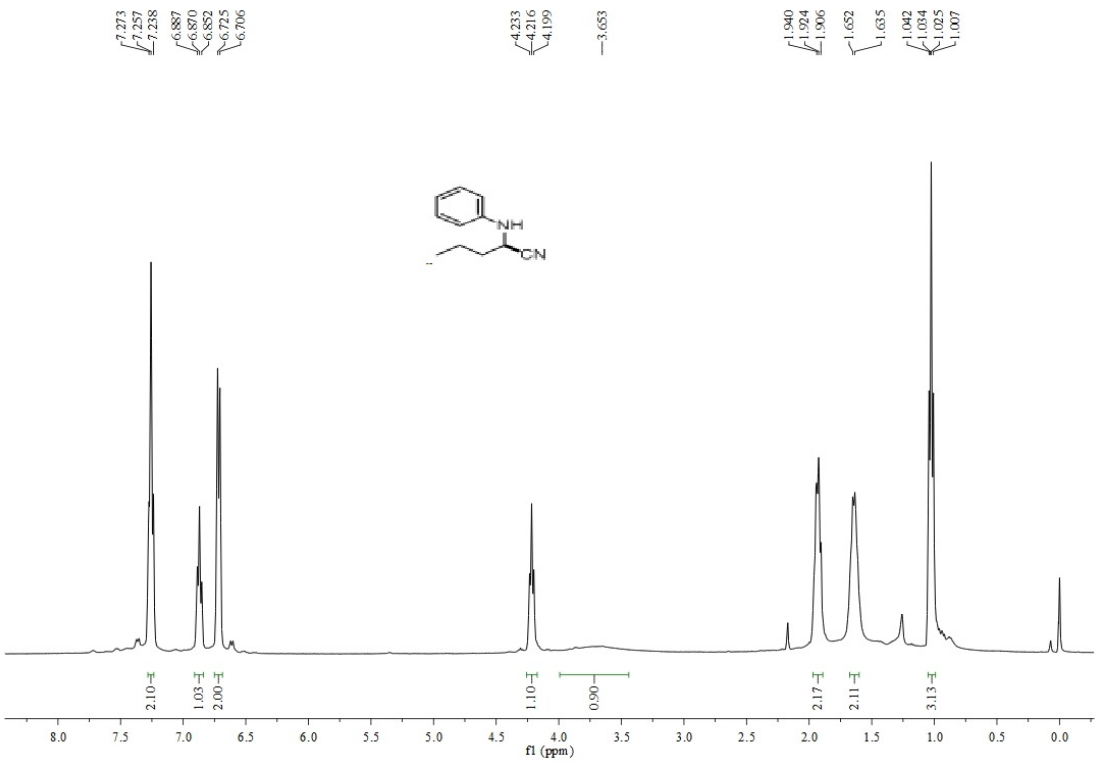
^{13}C NMR of **8g** in $CDCl_3$



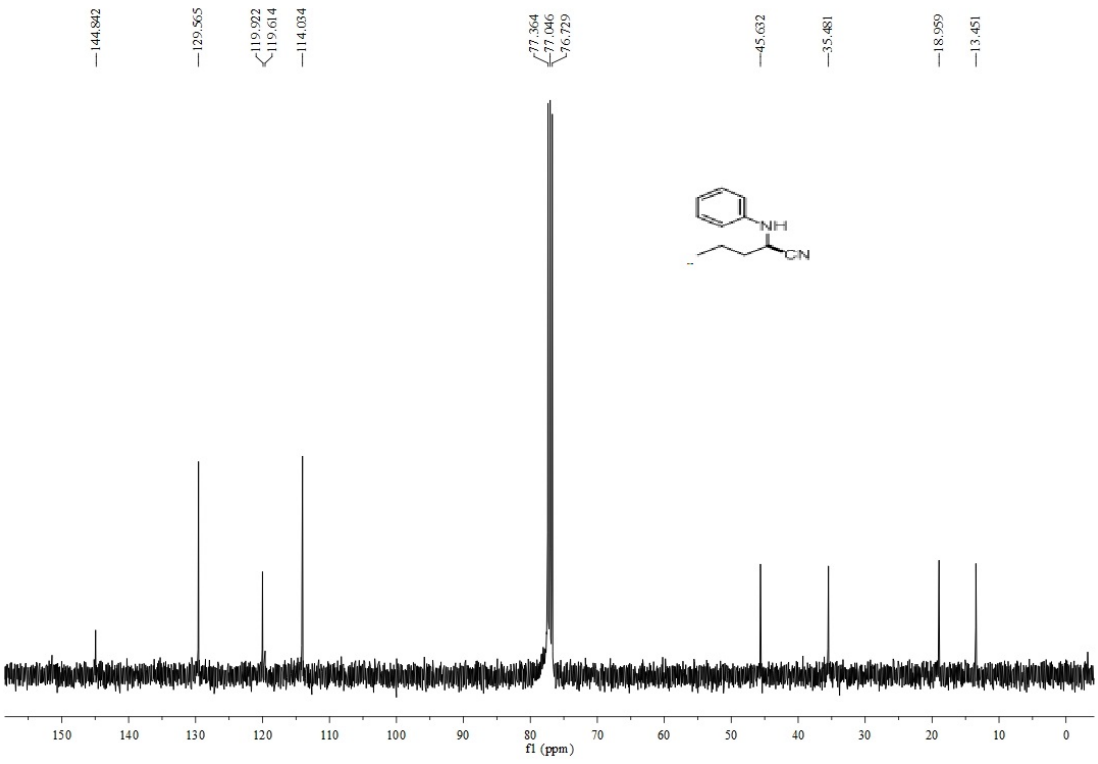
^{1}H NMR of **8h** in $CDCl_3$



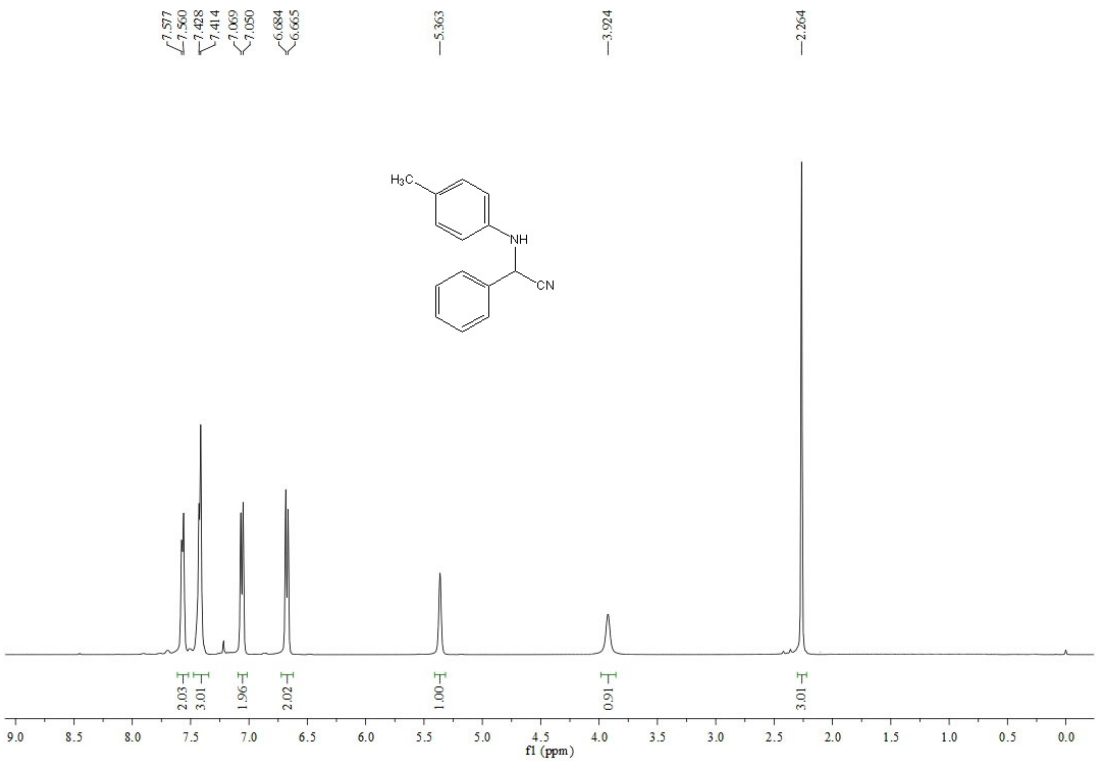
^{13}C NMR of **8h** in $CDCl_3$



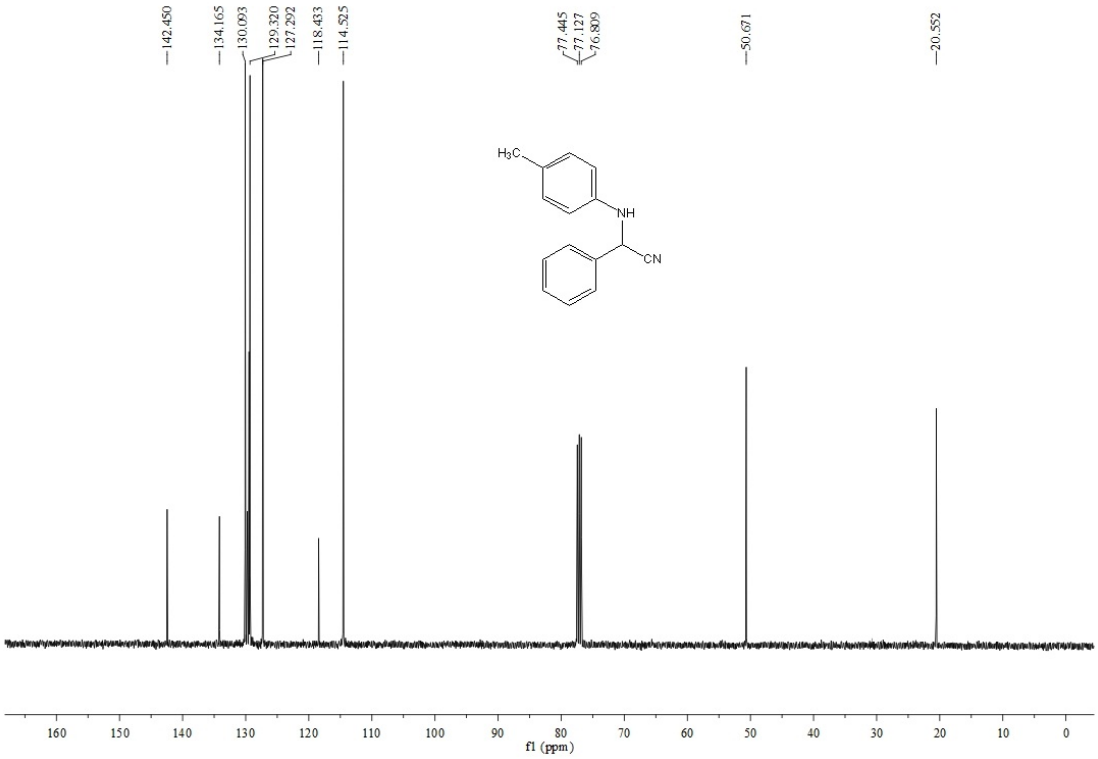
^{1}H NMR of **8i** in $CDCl_3$



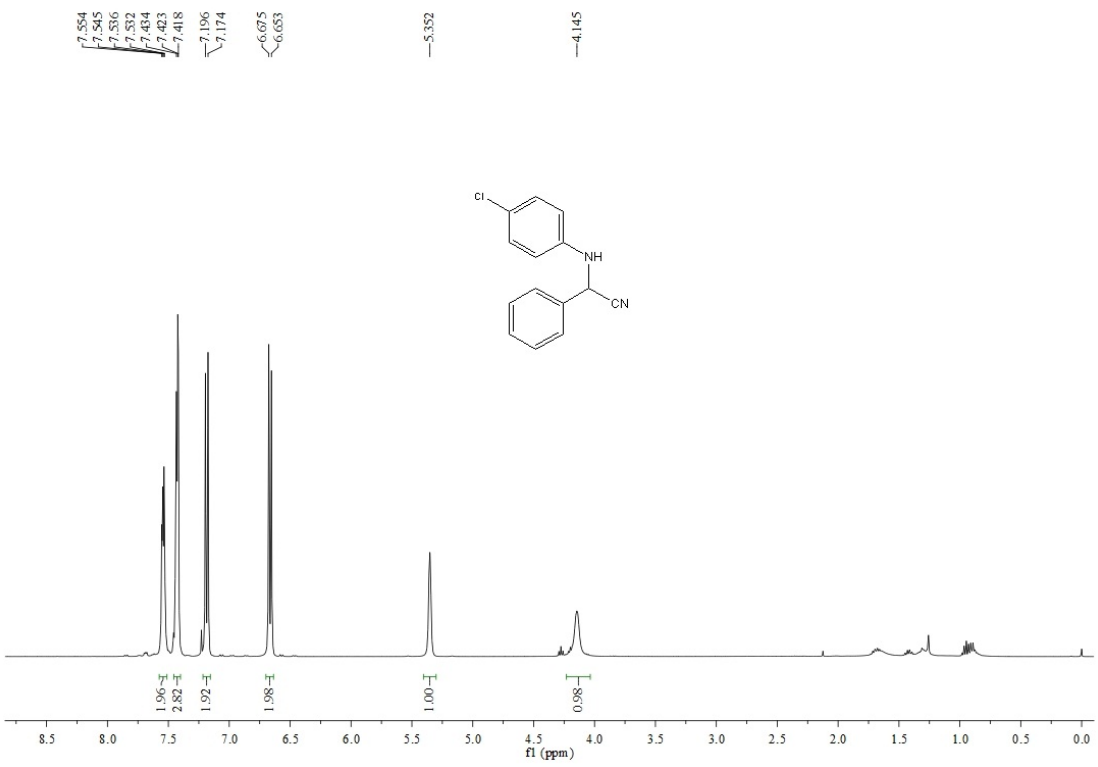
^{13}C NMR of **8i** in $CDCl_3$



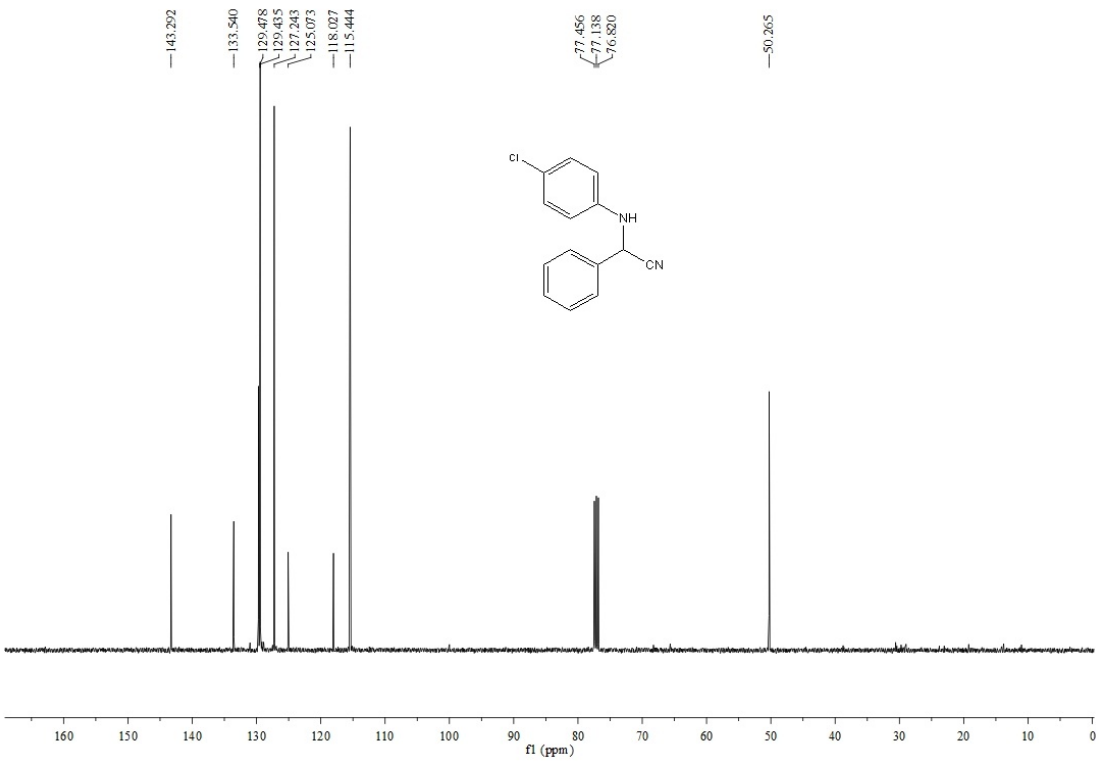
^{1}H NMR of **8j** in $CDCl_3$



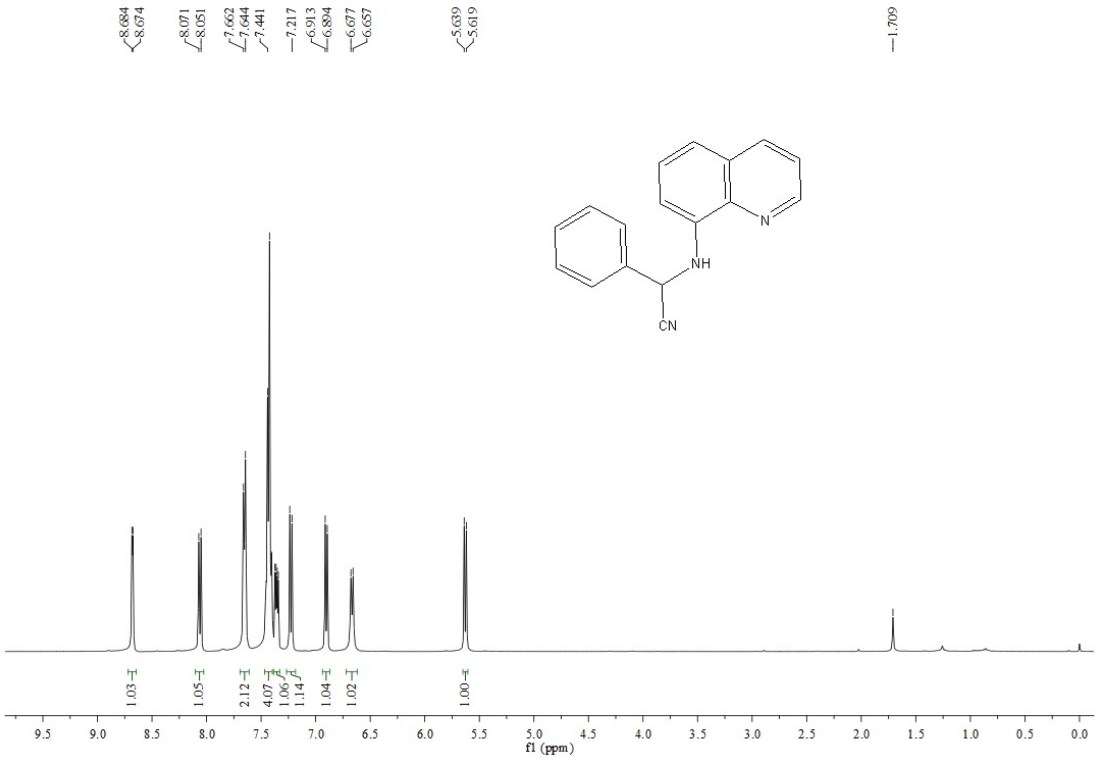
^{13}C NMR of **8j** in $CDCl_3$



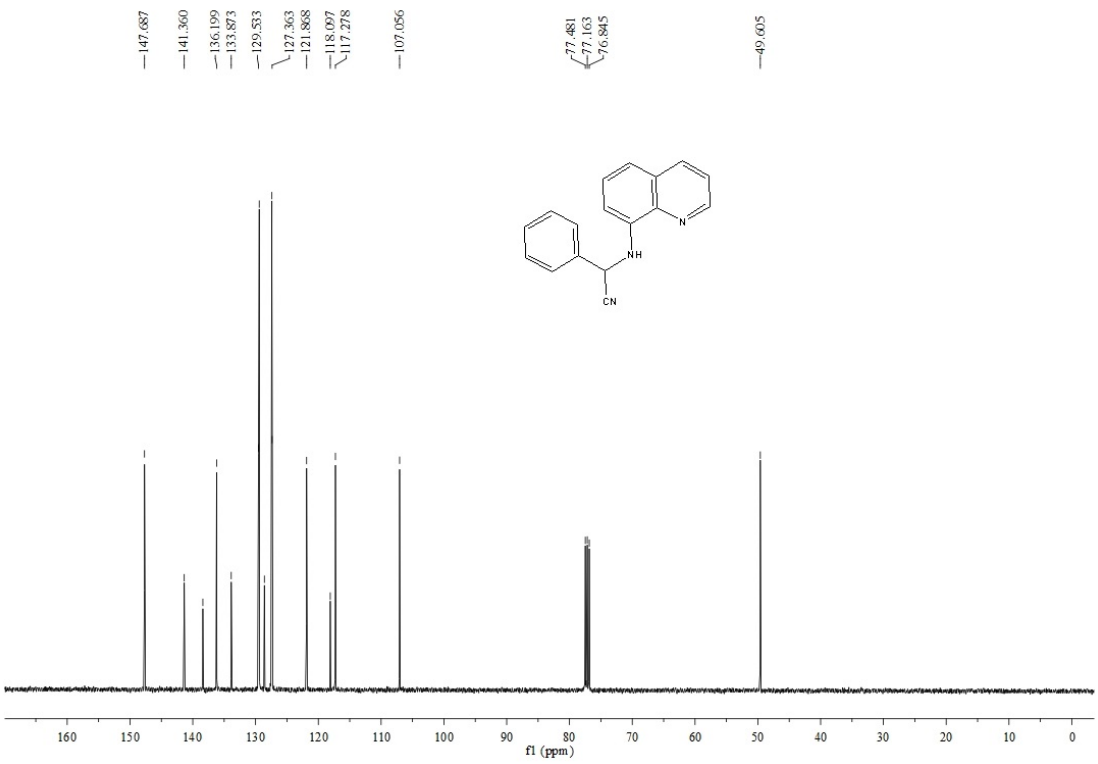
^{1}H NMR of **8k** in $CDCl_3$



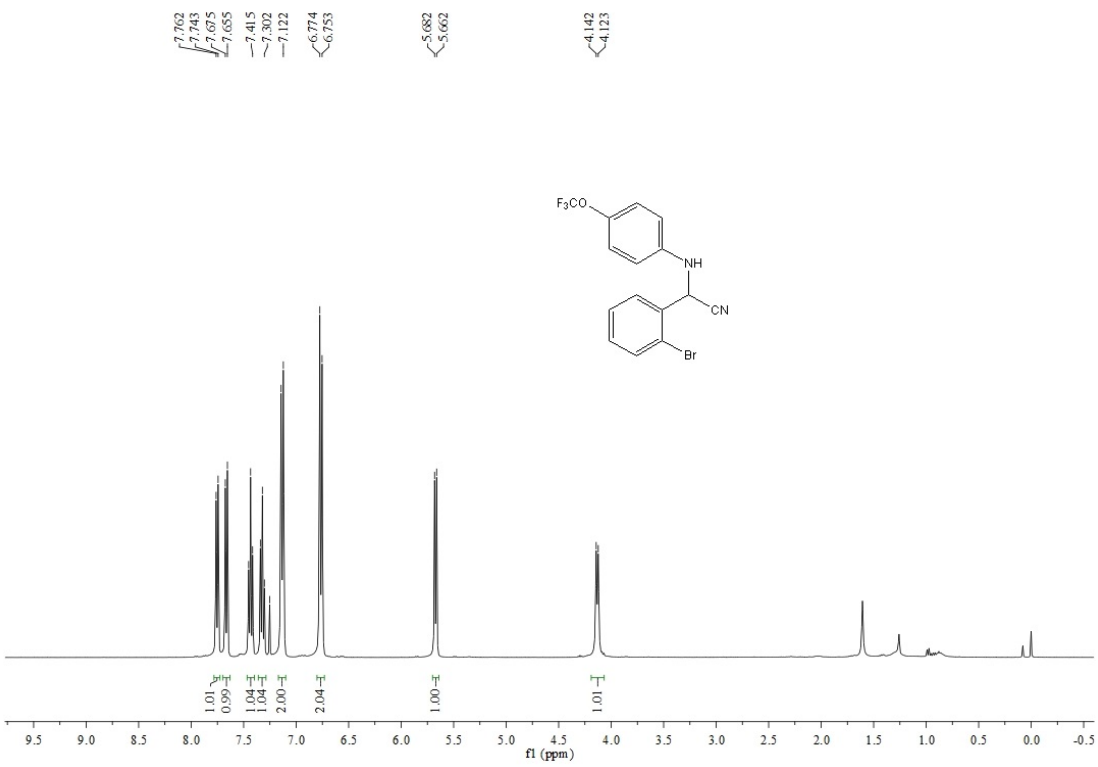
^{13}C NMR of **8k** in $CDCl_3$



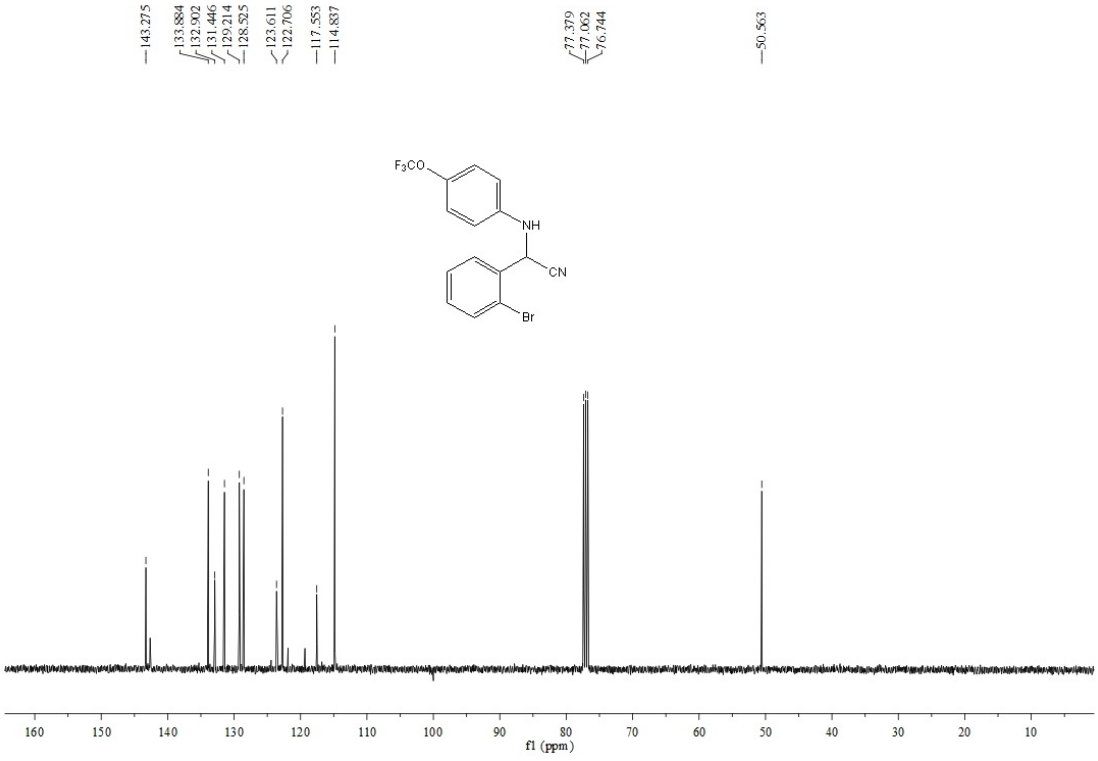
^{1}H NMR of **8l** in $CDCl_3$



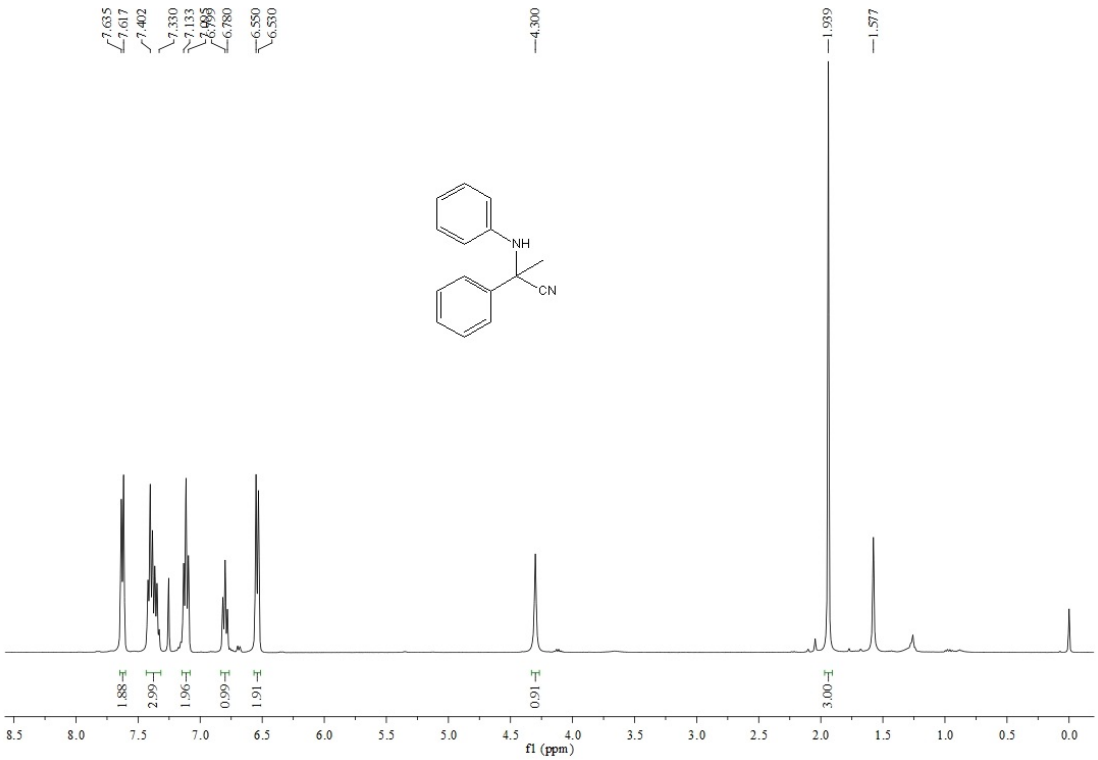
^{13}C NMR of **8l** in $CDCl_3$



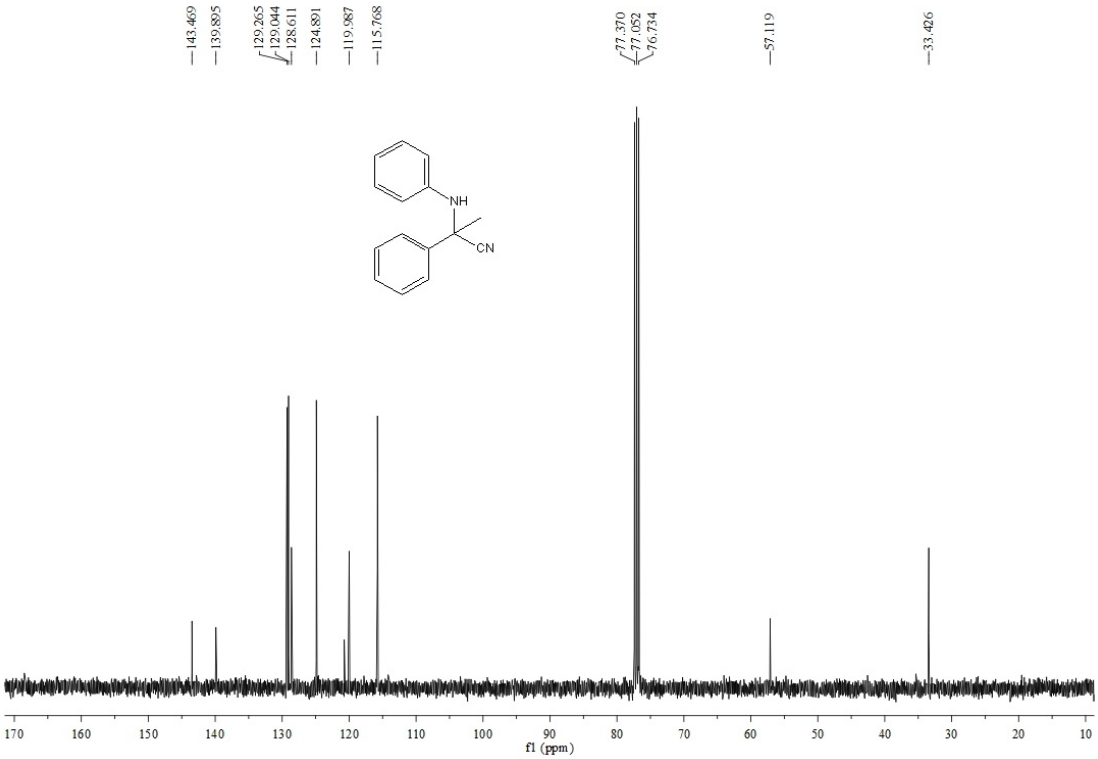
^{1}H NMR of **8m** in $CDCl_3$



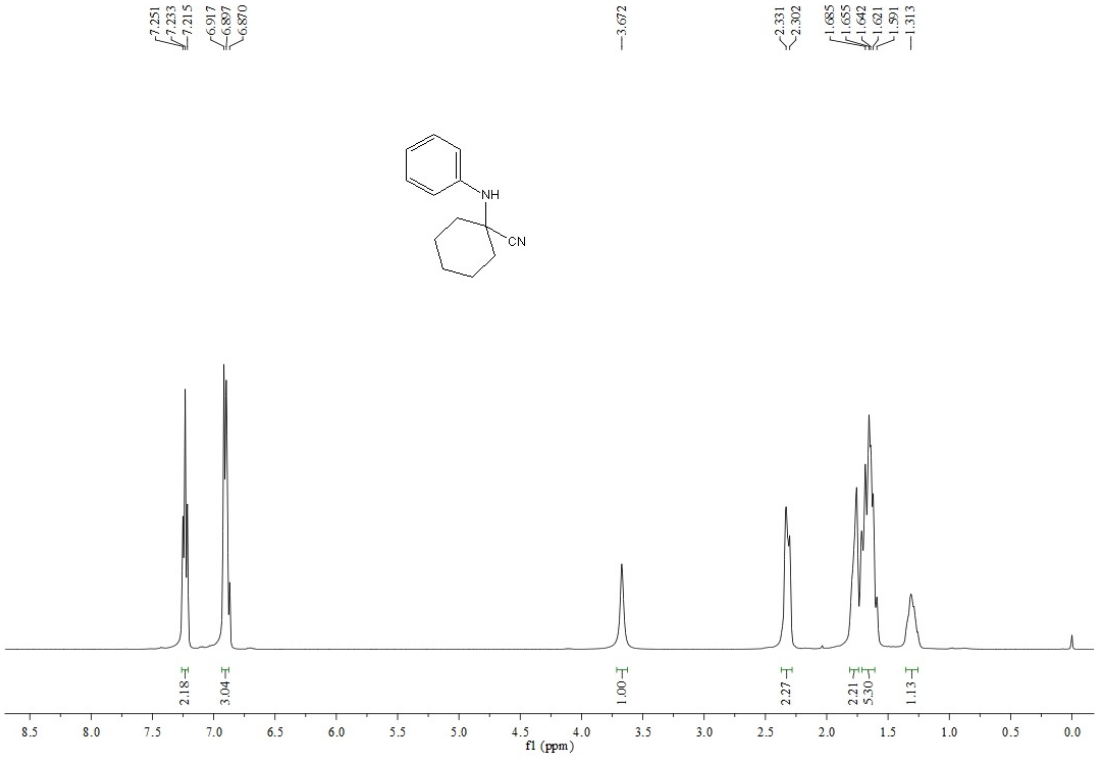
^{13}C NMR of **8m** in $CDCl_3$



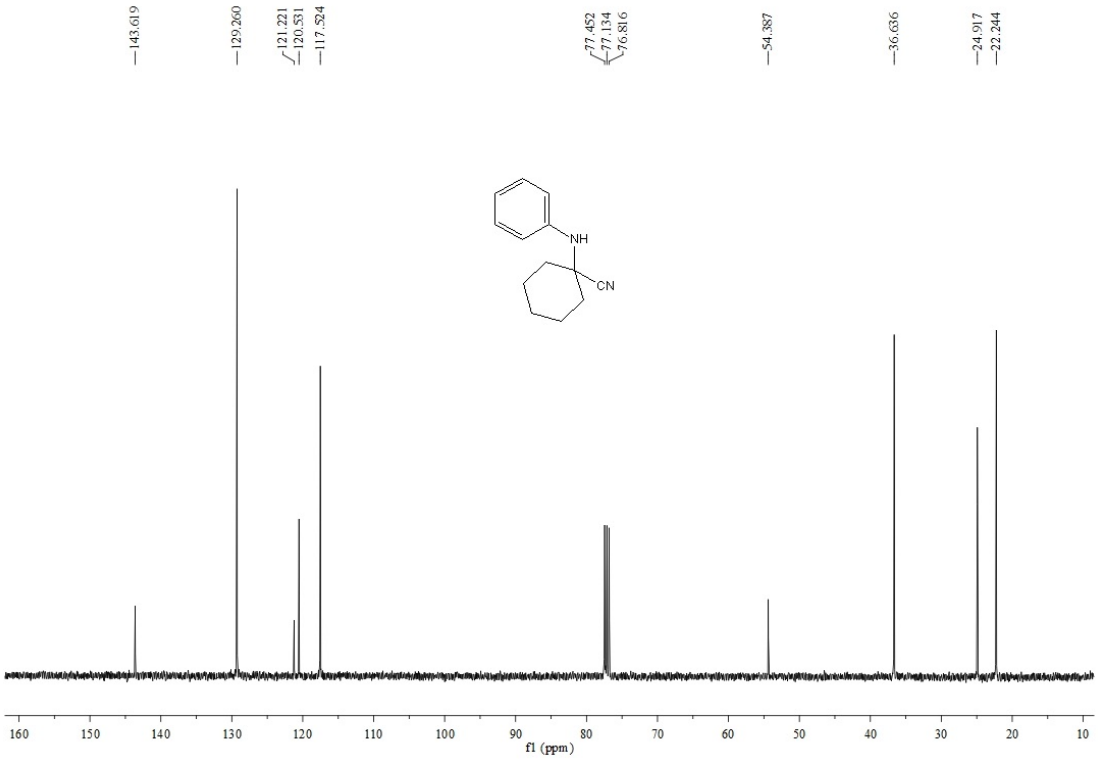
^{1}H NMR of **8n** in $CDCl_3$



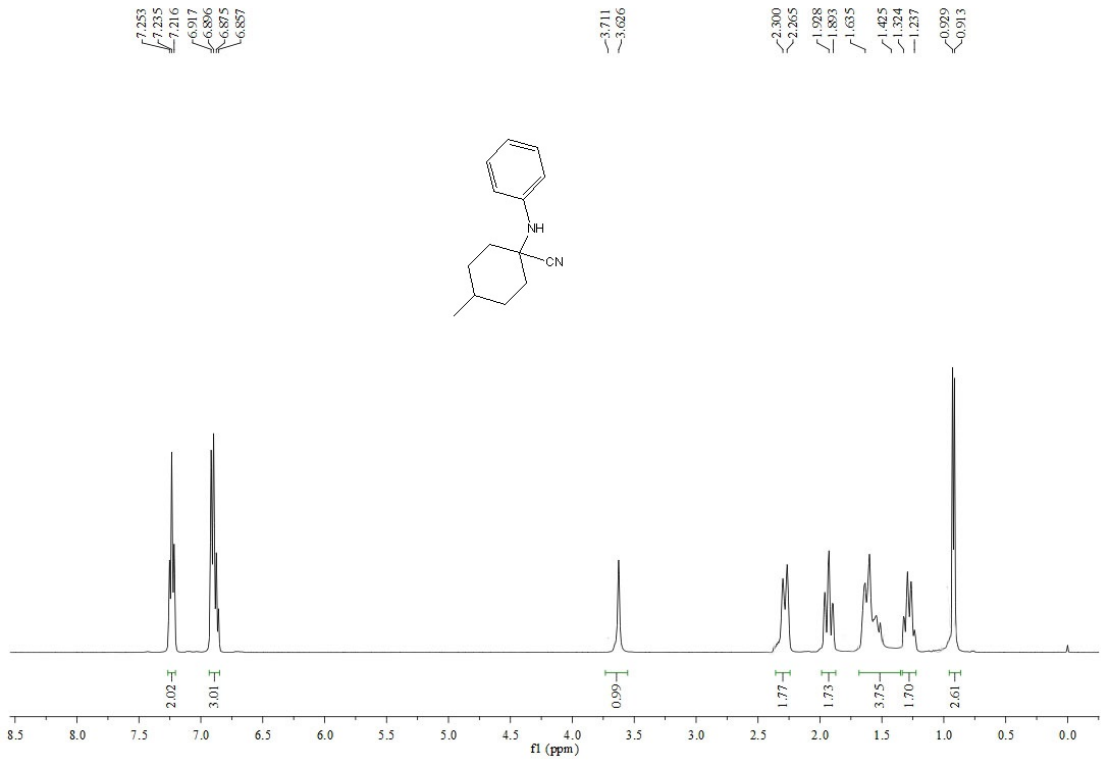
^{13}C NMR of **8n** in $CDCl_3$



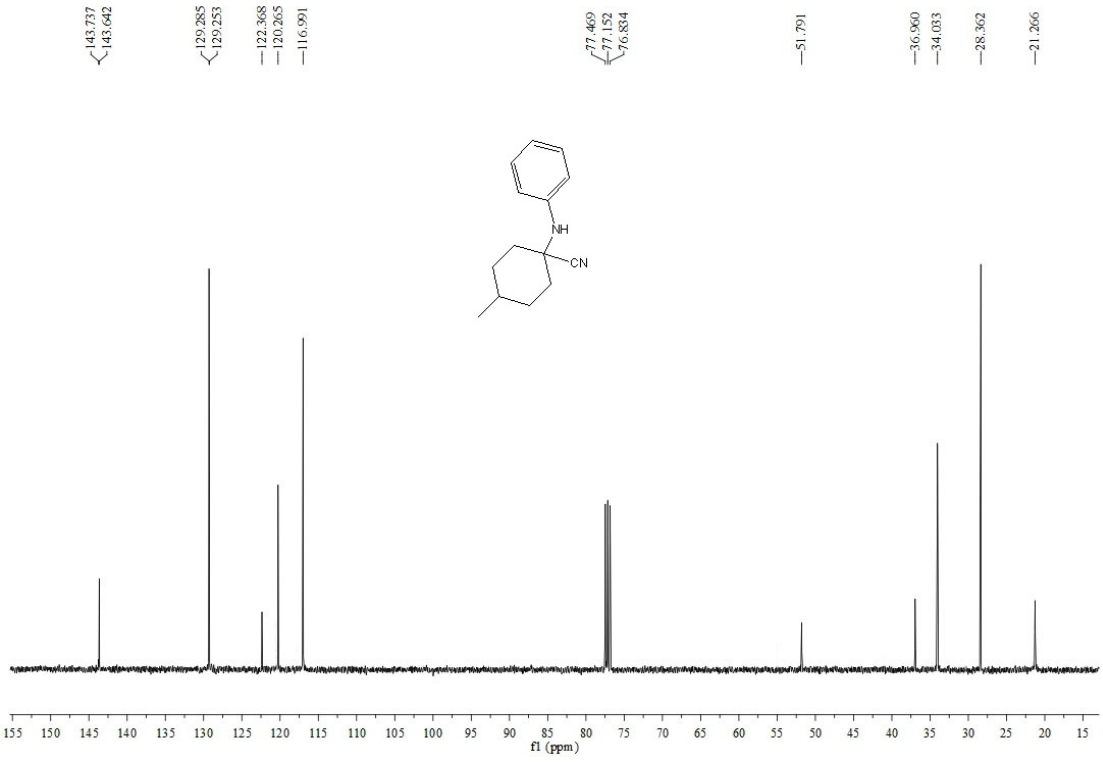
^{1}H NMR of **8o** in $CDCl_3$



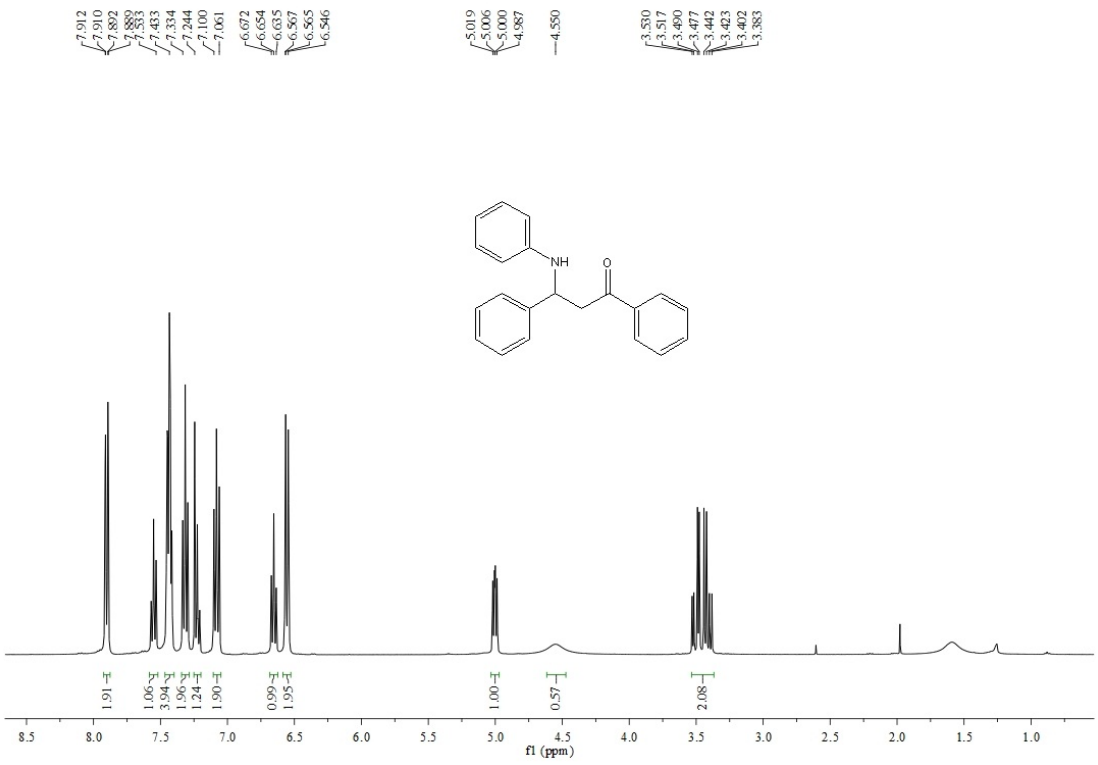
^{13}C NMR of **8o** in $CDCl_3$



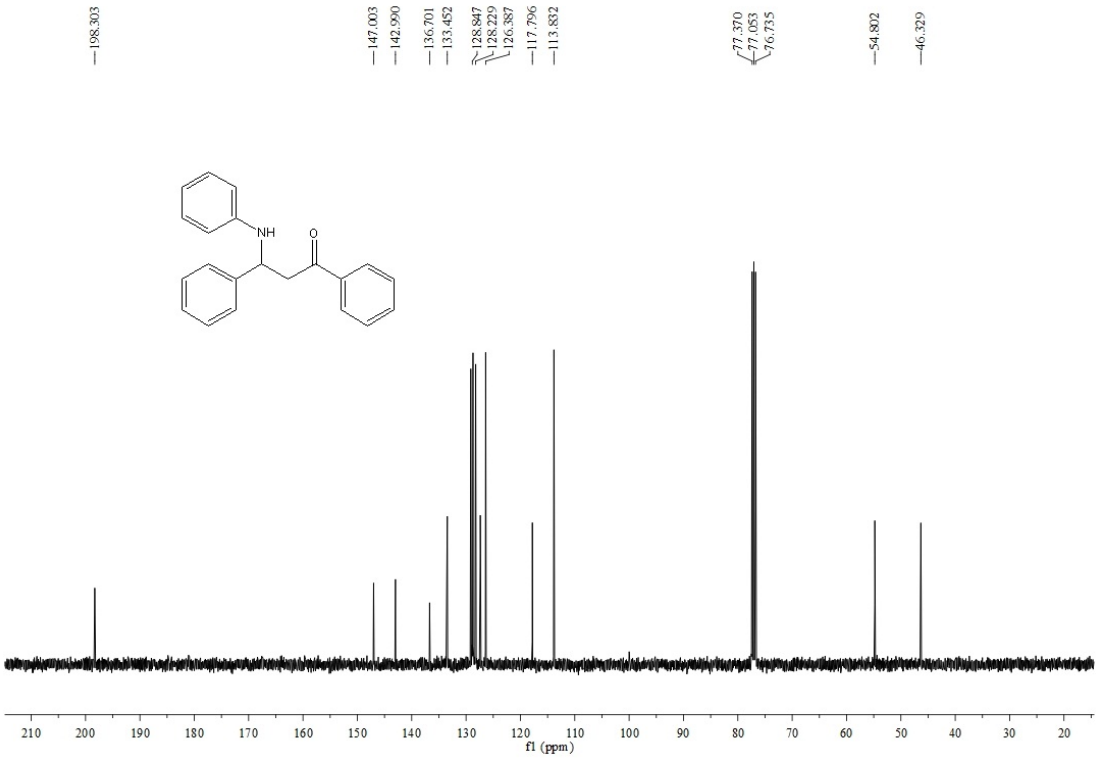
^{1}H NMR of **8p** in $CDCl_3$



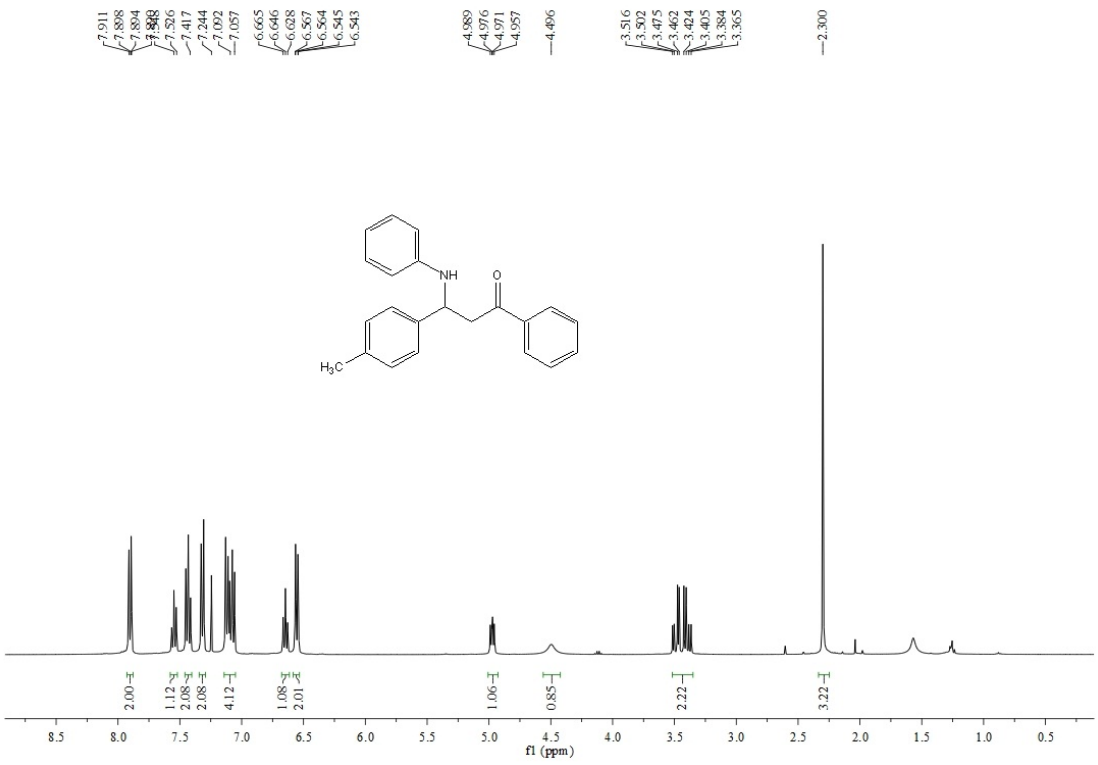
^{13}C NMR of **8p** in $CDCl_3$



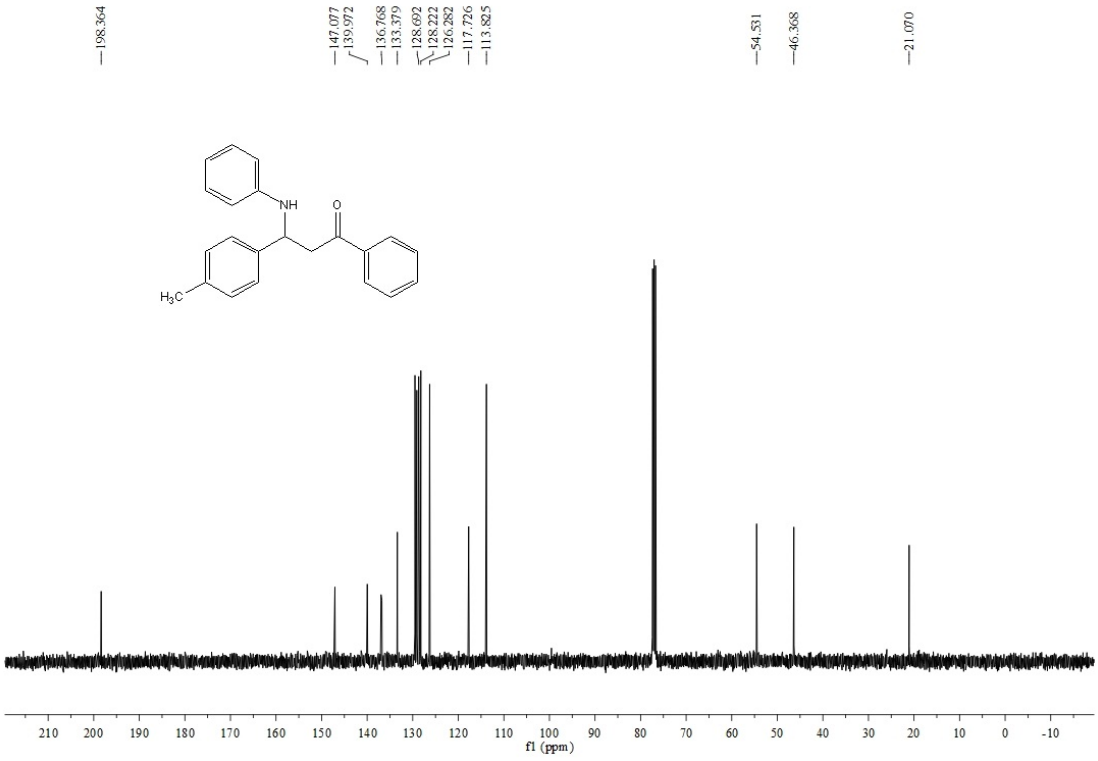
^{1}H NMR of **10a** in $CDCl_3$



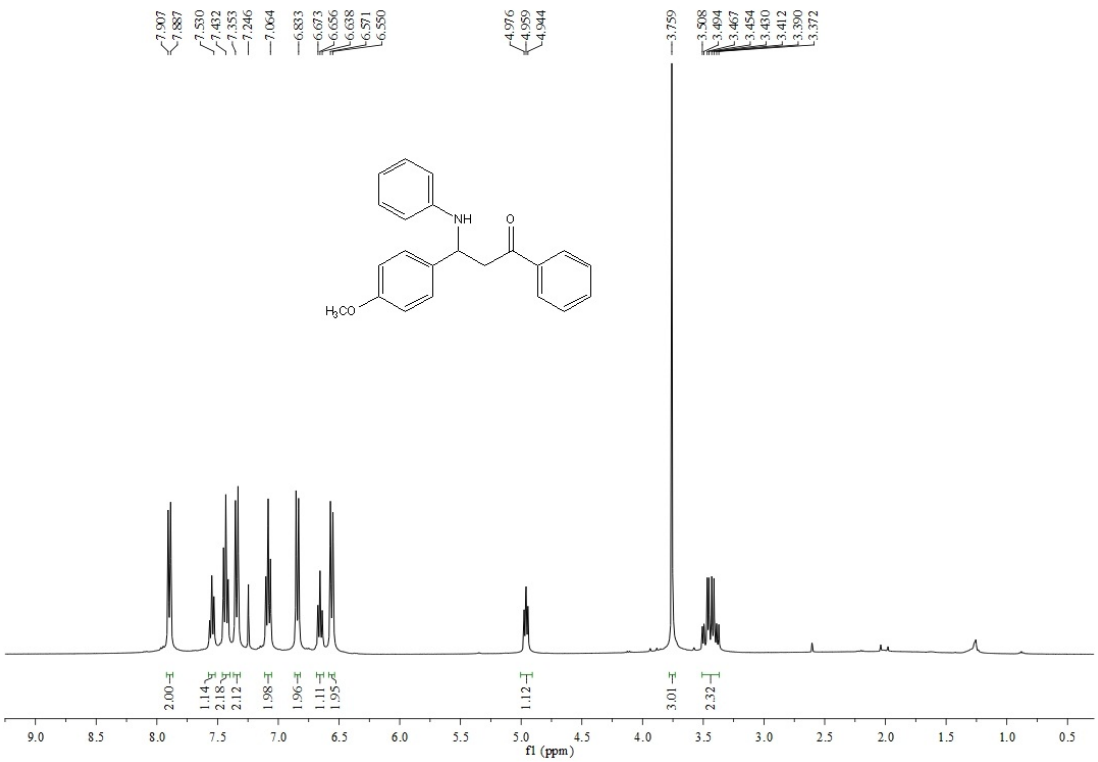
^{13}C NMR of **10a** in $CDCl_3$



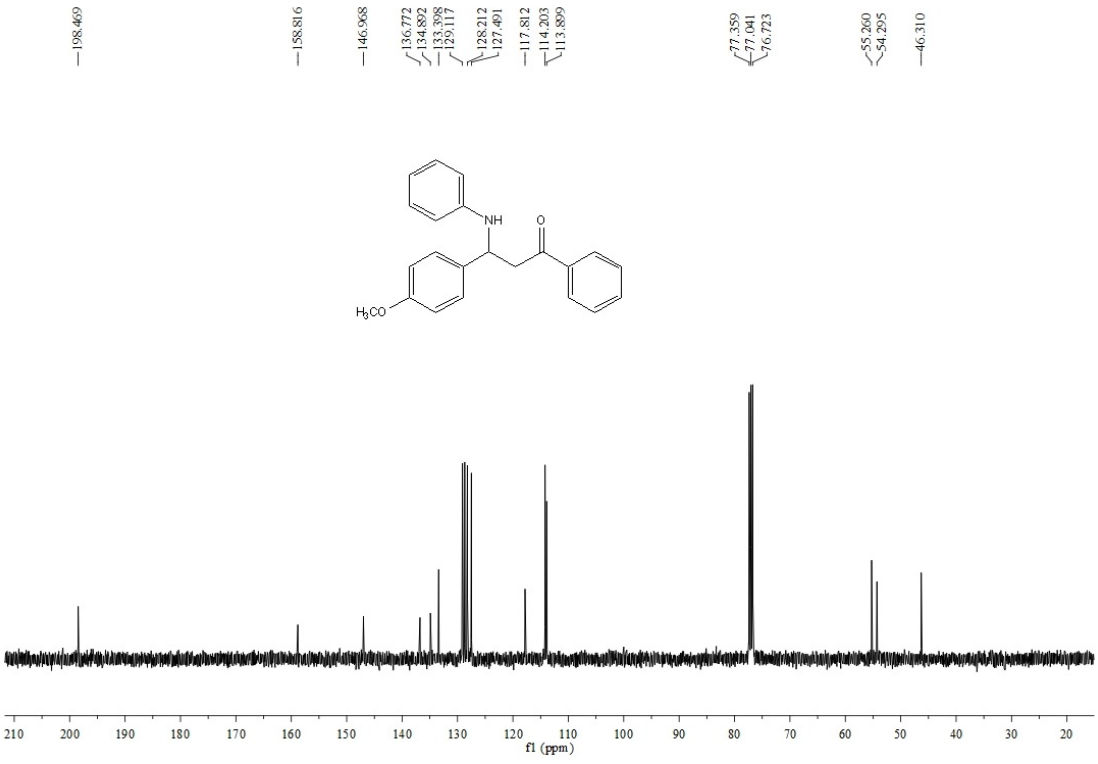
^{1}H NMR of **10b** in $CDCl_3$



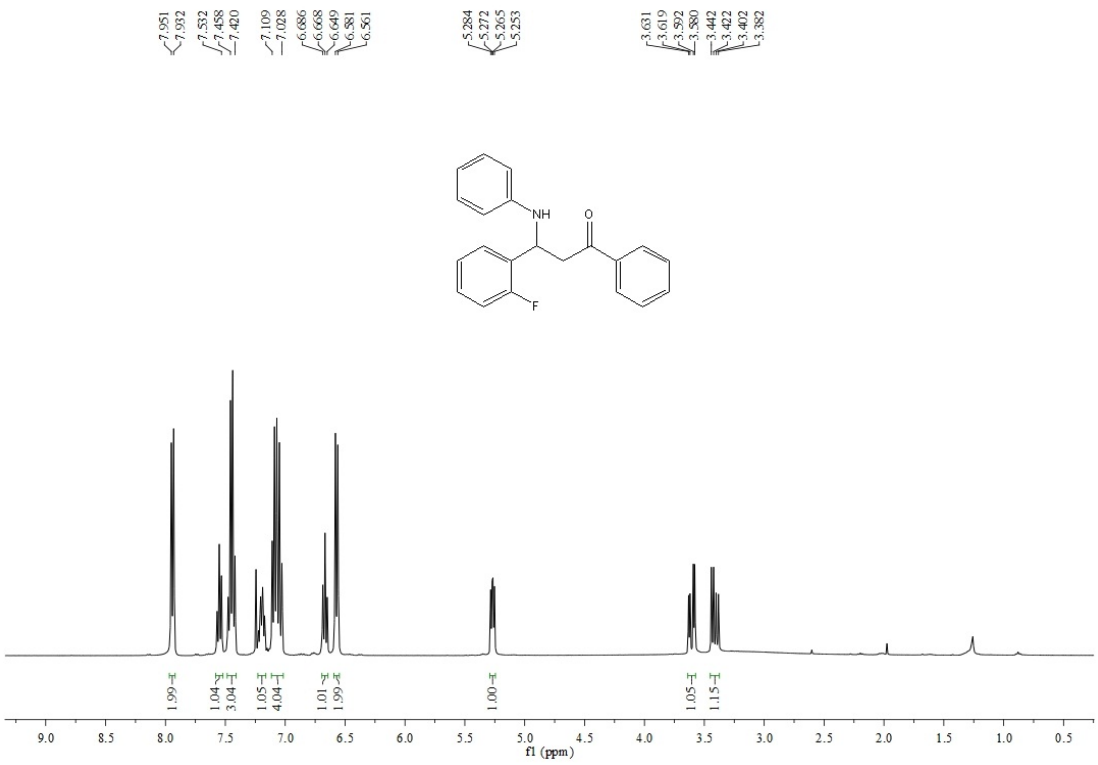
^{13}C NMR of **10b** in $CDCl_3$



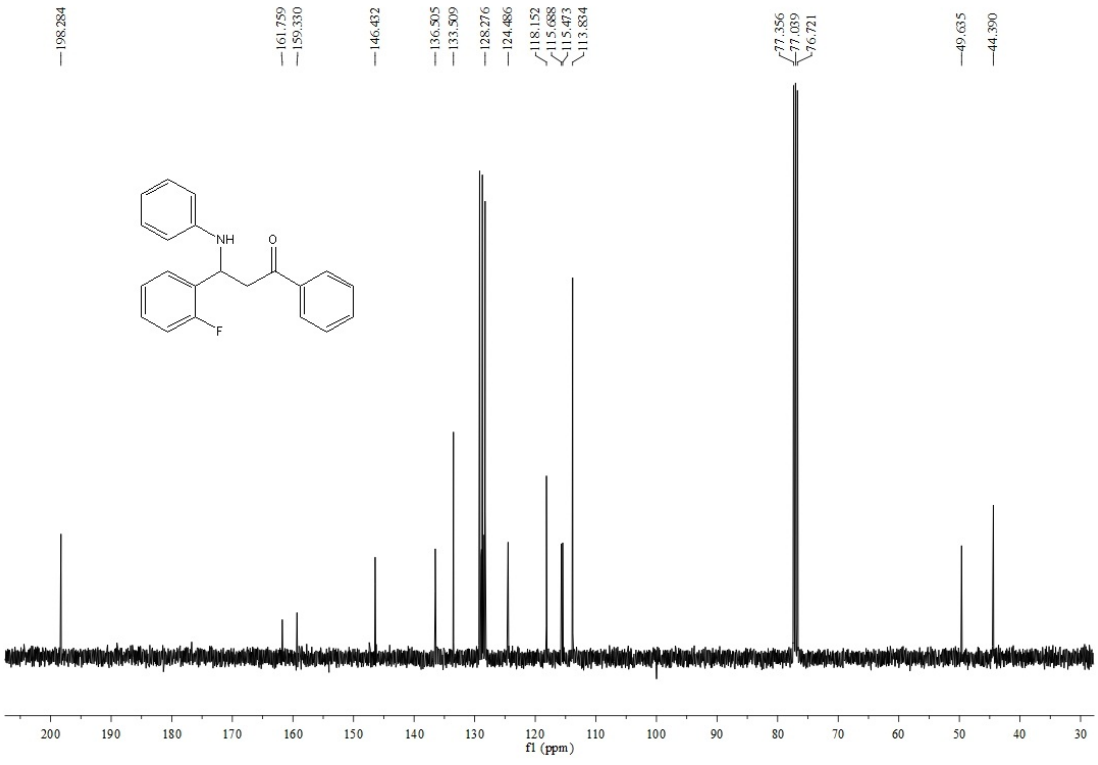
^{1}H NMR of **10c** in $CDCl_3$



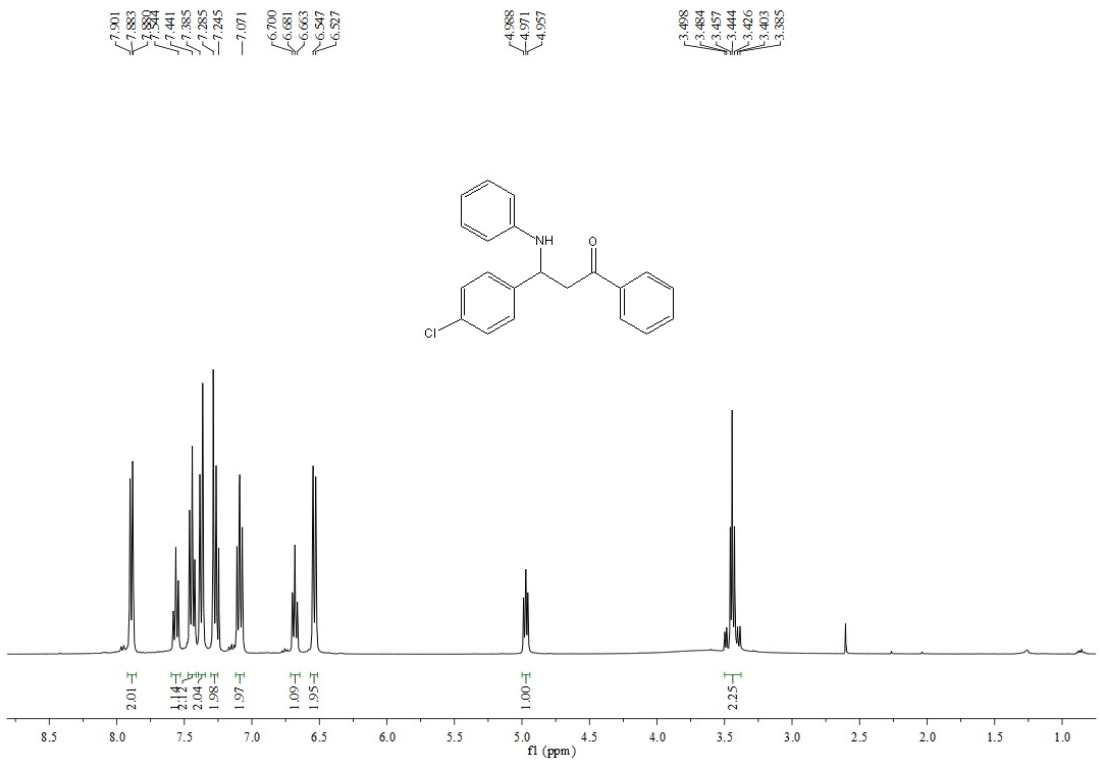
^{13}C NMR of **10c** in $CDCl_3$



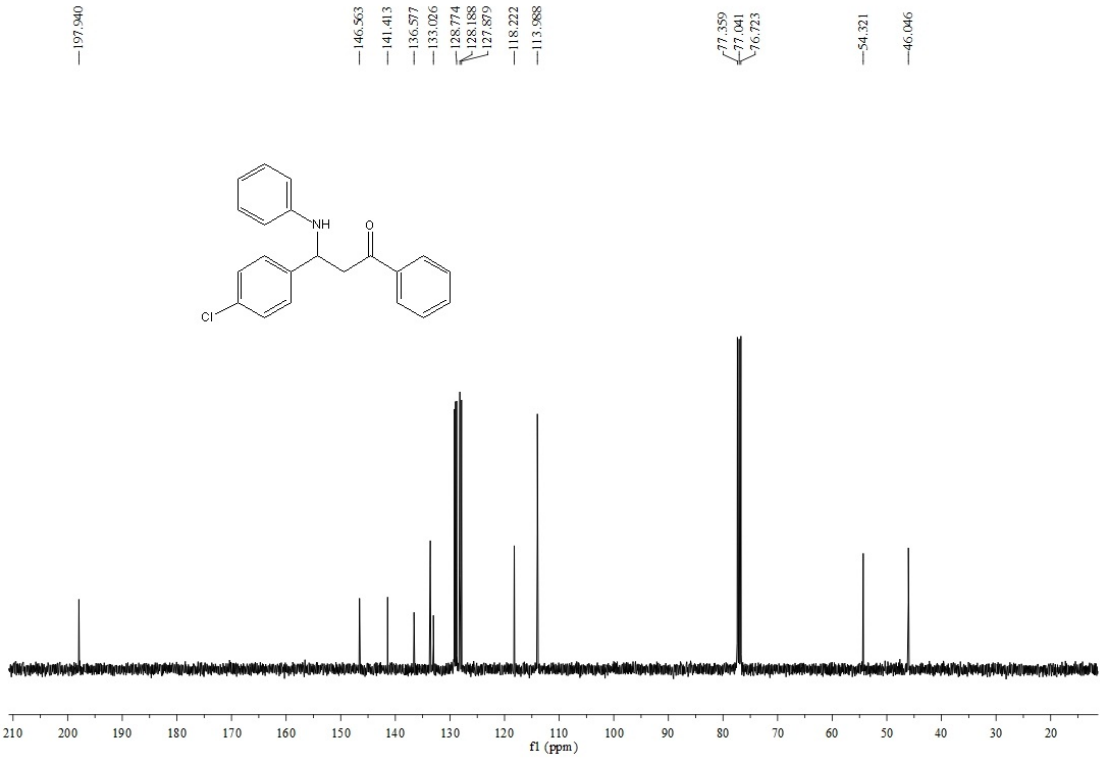
^{1}H NMR of **10d** in $CDCl_3$



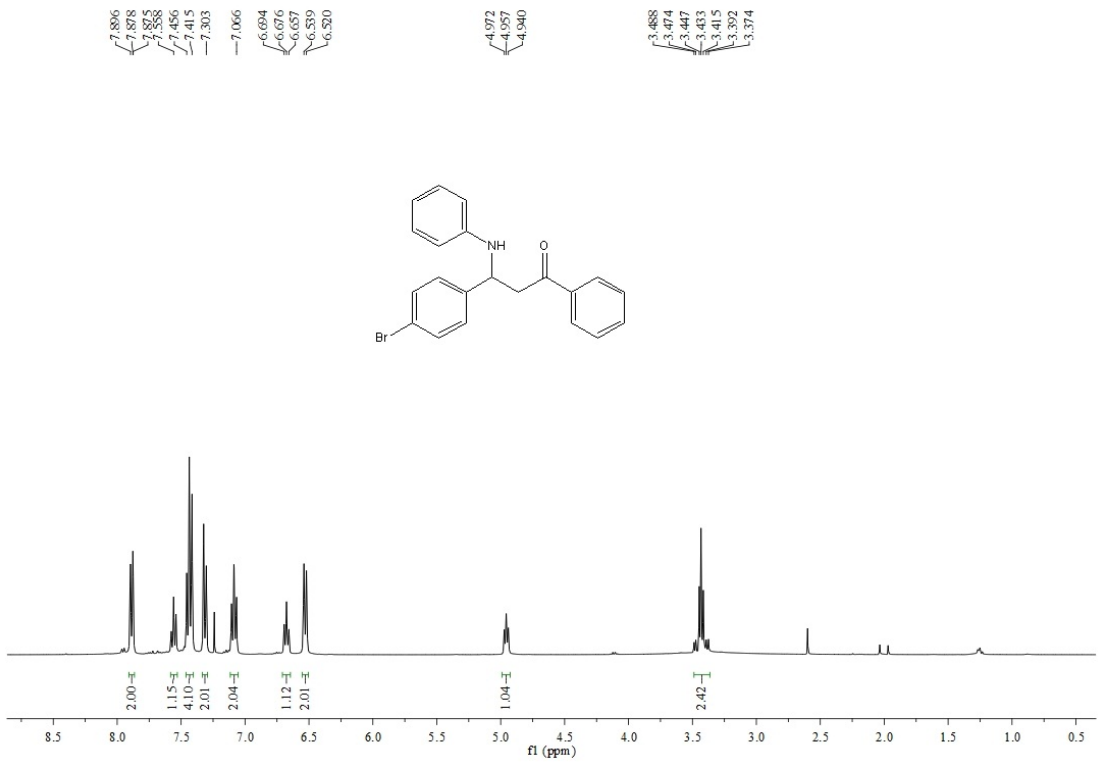
^{13}C NMR of **10d** in $CDCl_3$



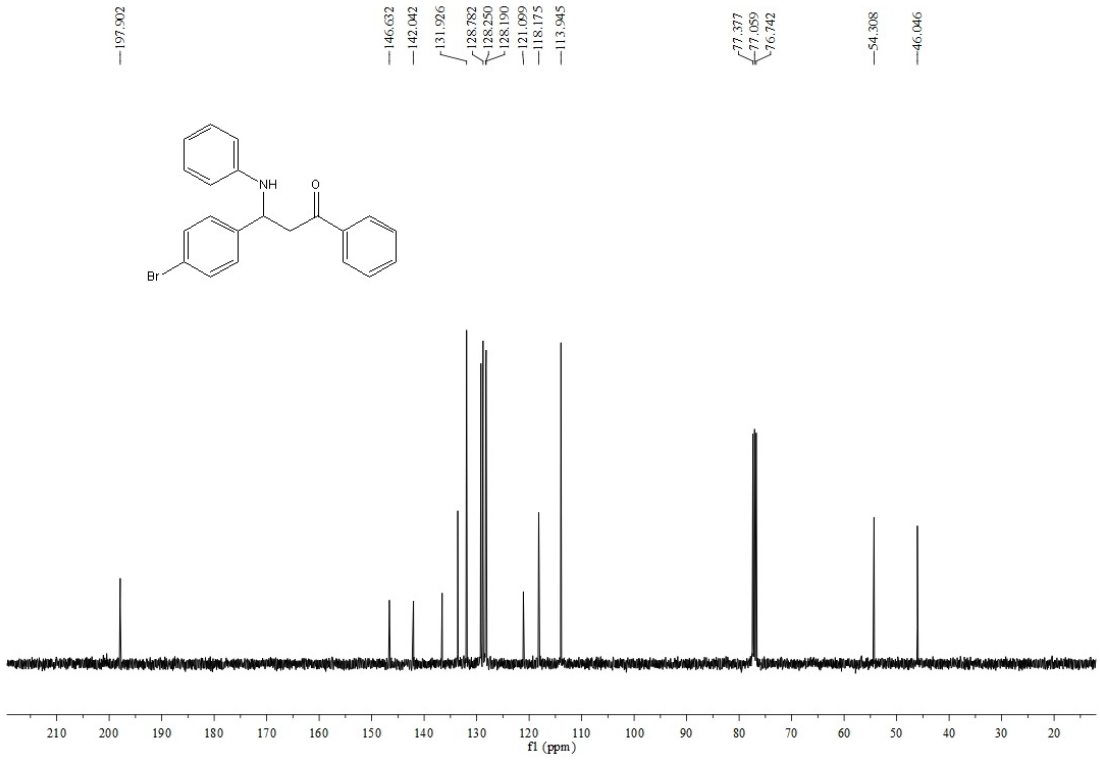
^{1}H NMR of **10e** in $CDCl_3$



^{13}C NMR of **10e** in $CDCl_3$

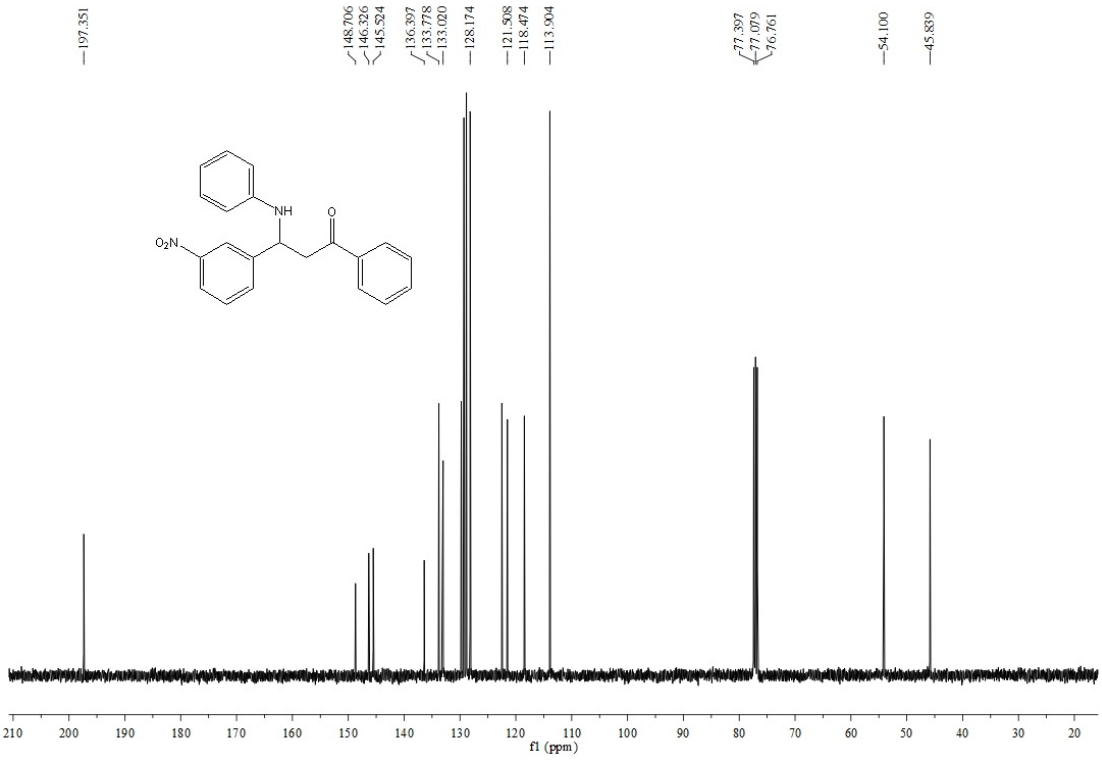


^{1}H NMR of **10f** in $CDCl_3$

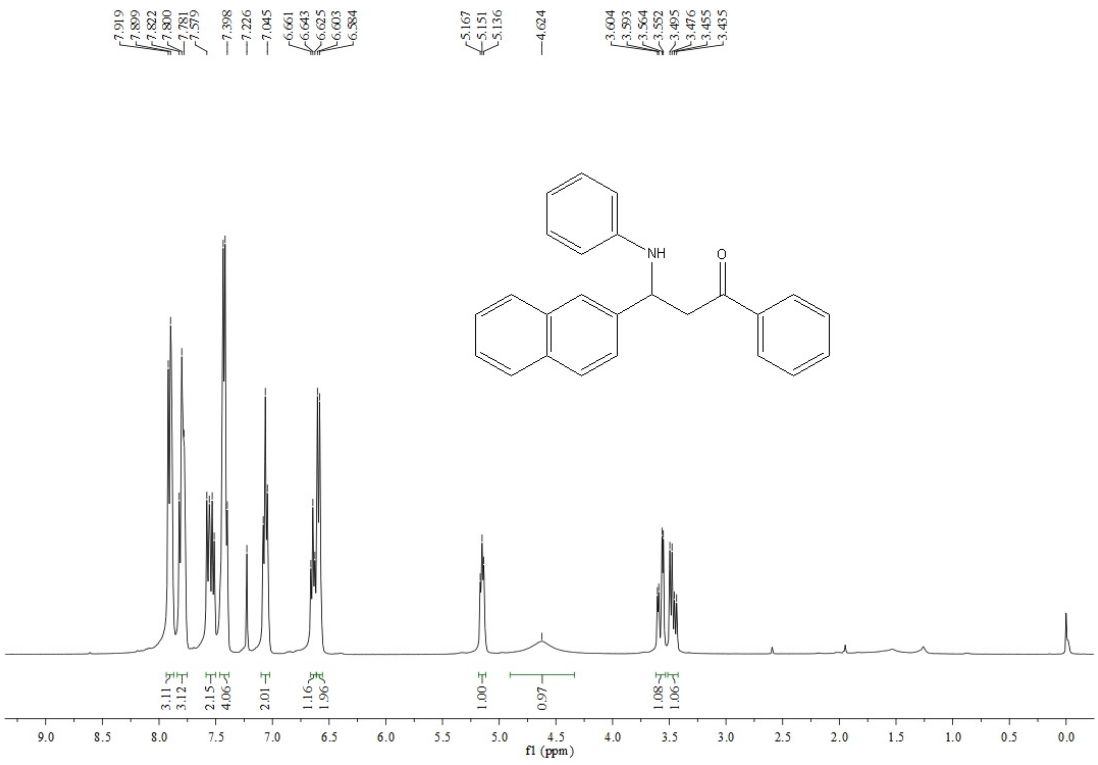


^{13}C NMR of **10f** in $CDCl_3$

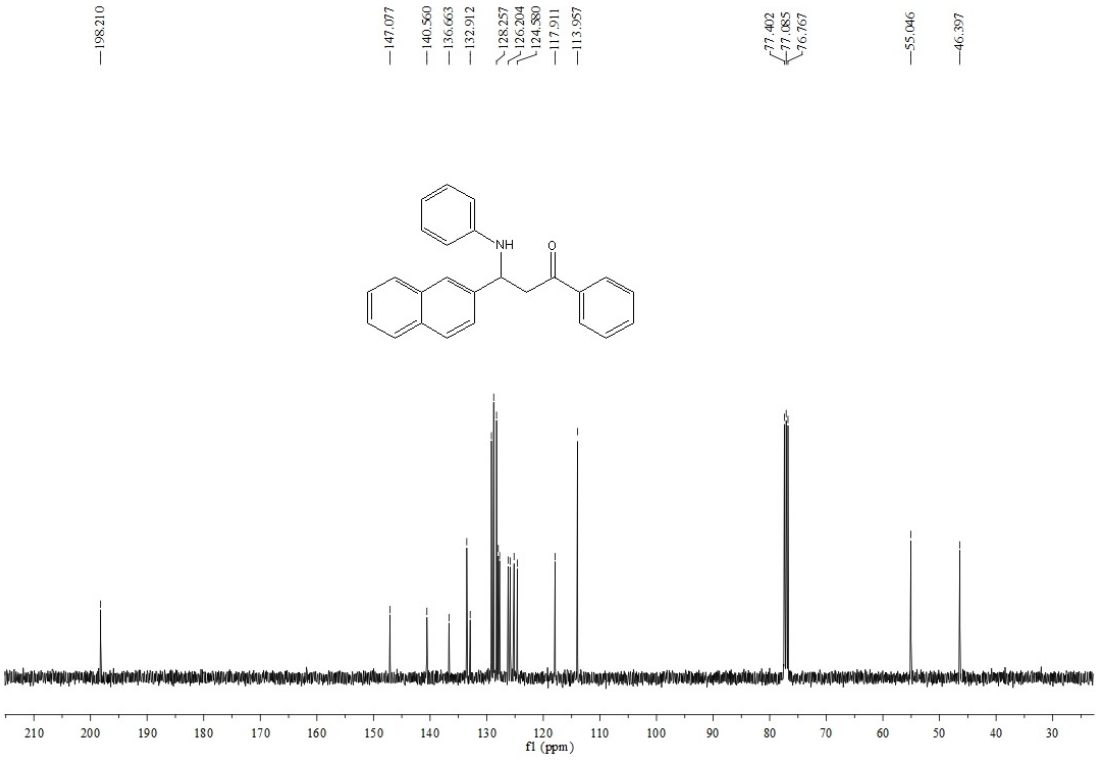
^{1}H NMR of **10g** in $CDCl_3$



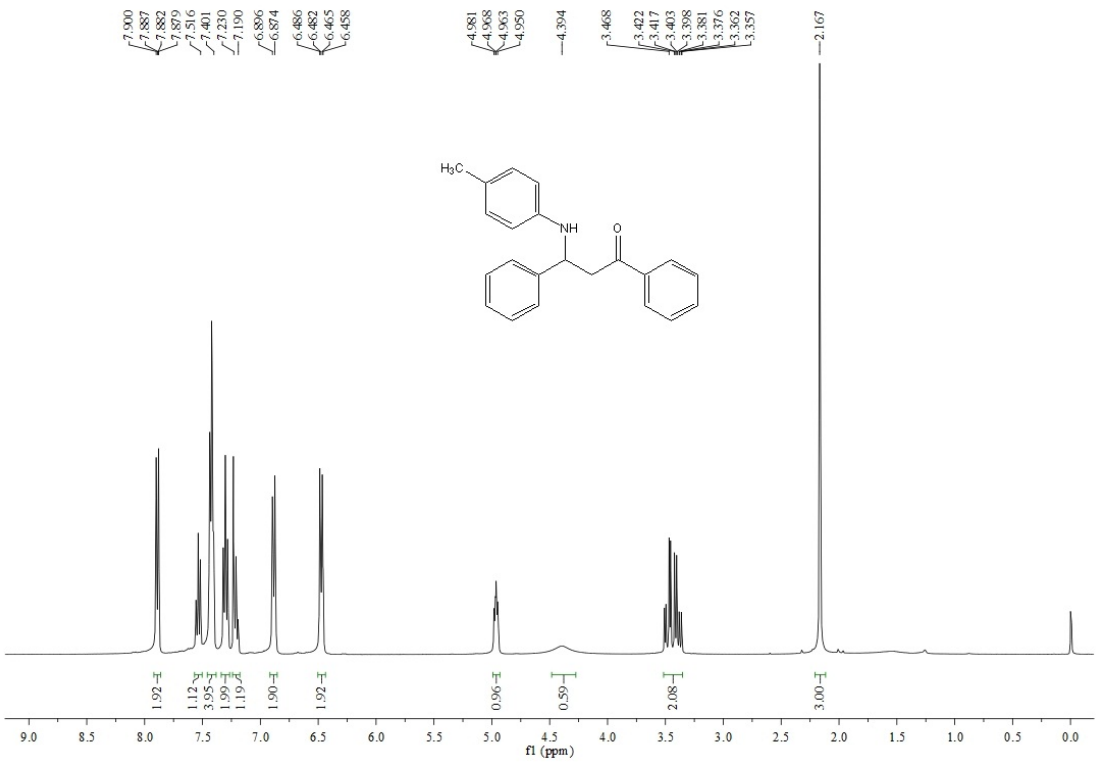
^{13}C NMR of **10g** in $CDCl_3$



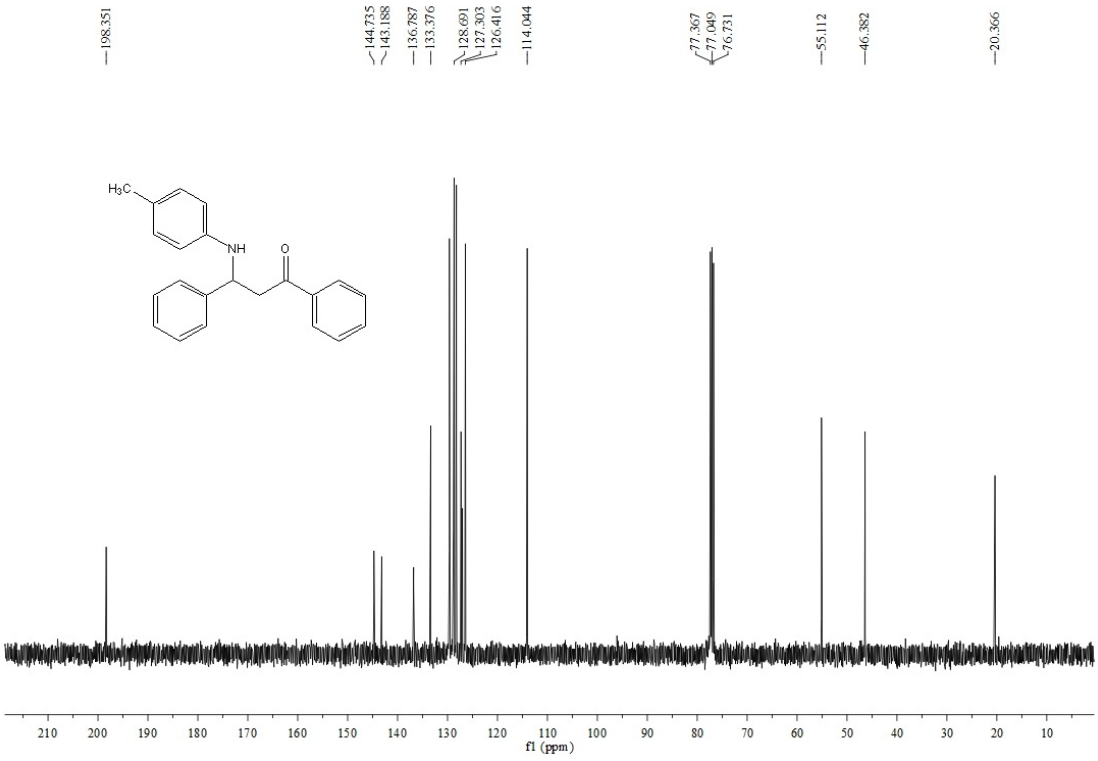
^{1}H NMR of **10h** in $CDCl_3$



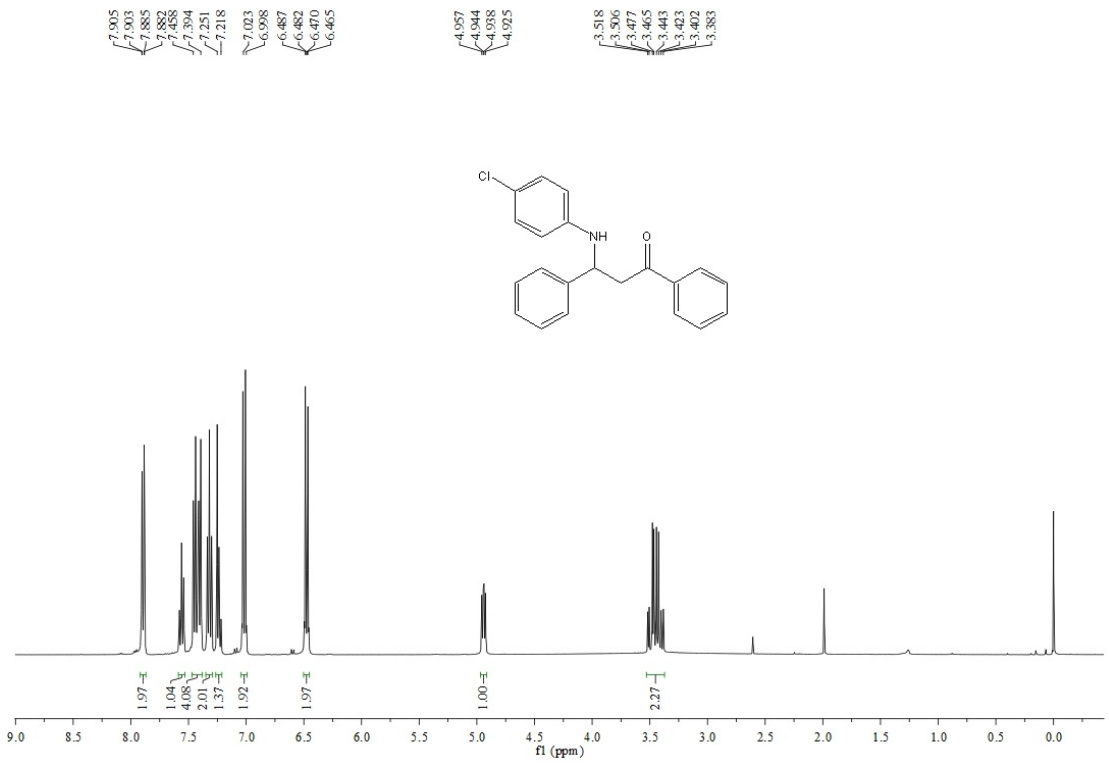
^{13}C NMR of **10h** in $CDCl_3$



^{1}H NMR of **10i** in $CDCl_3$



^{13}C NMR of **10i** in $CDCl_3$



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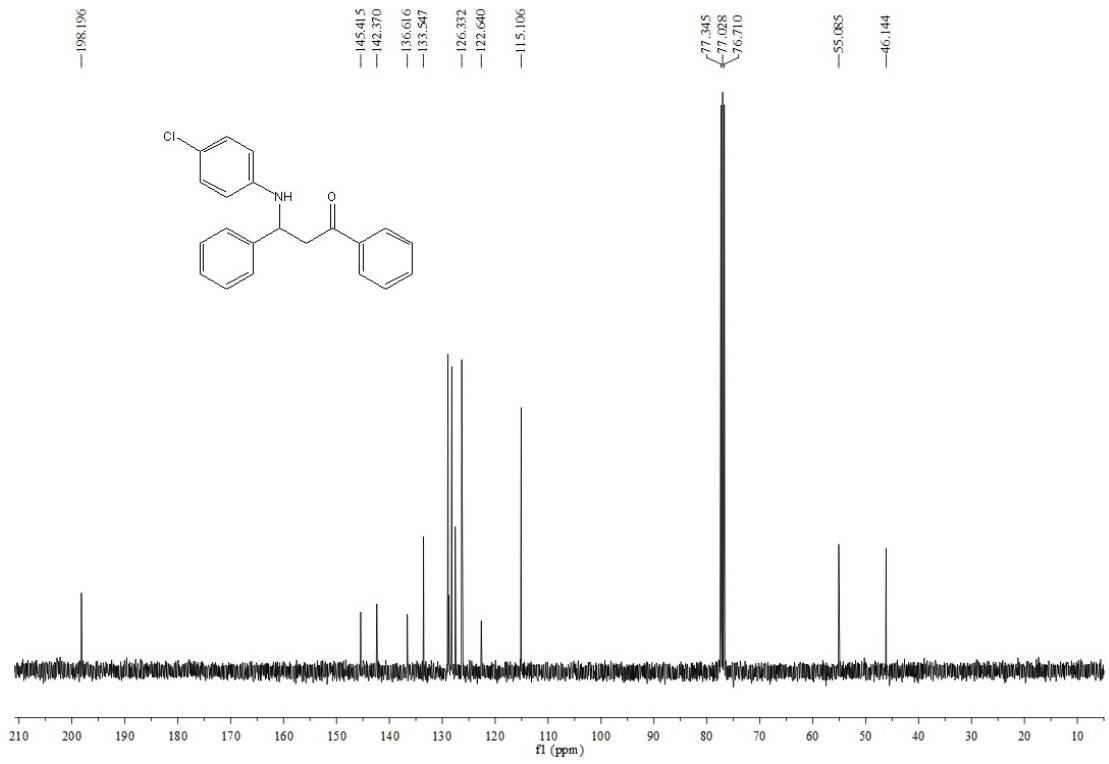
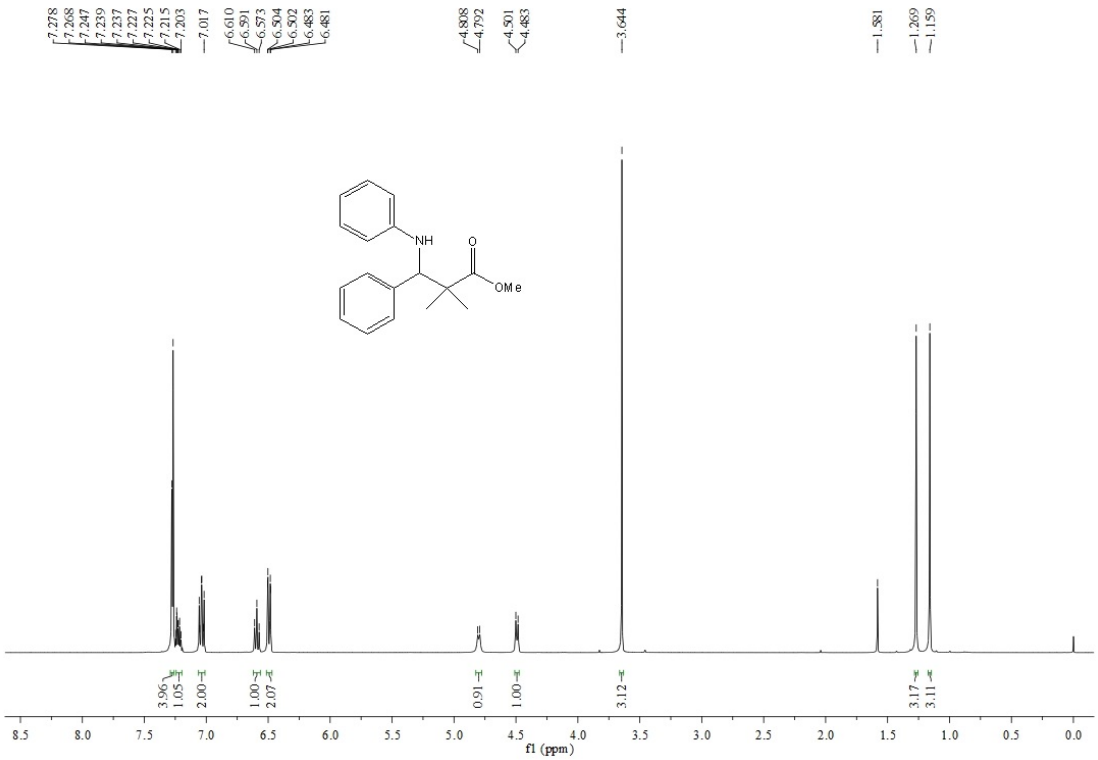
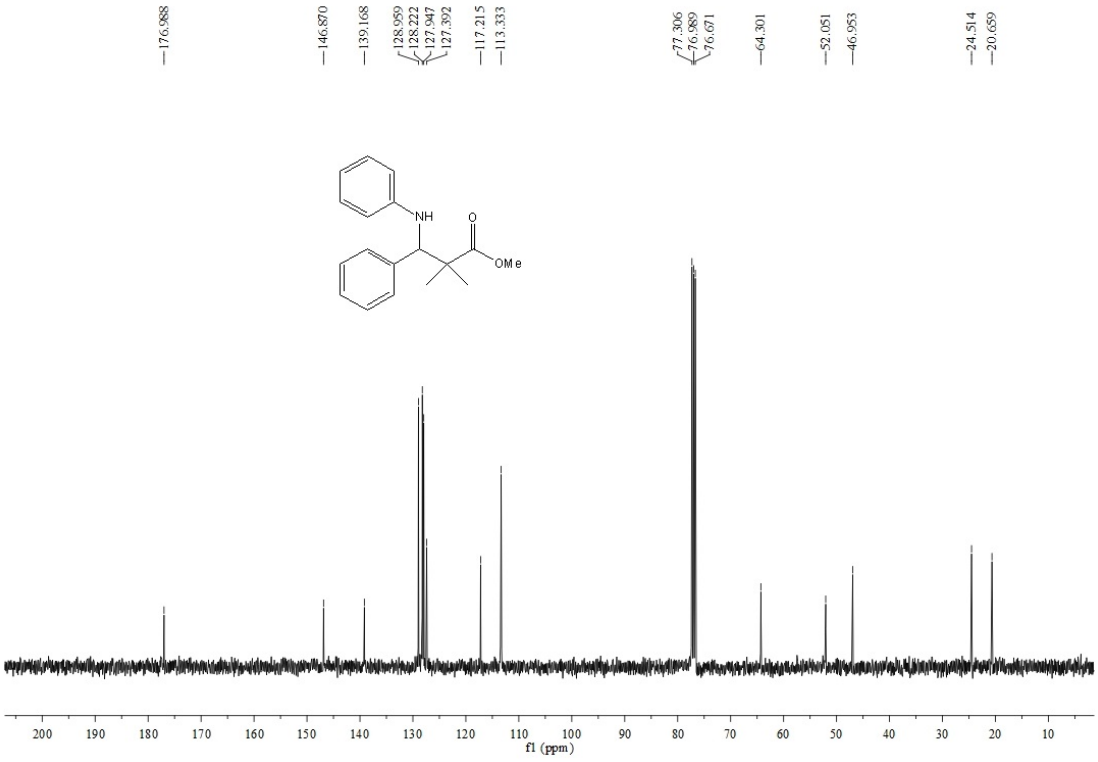


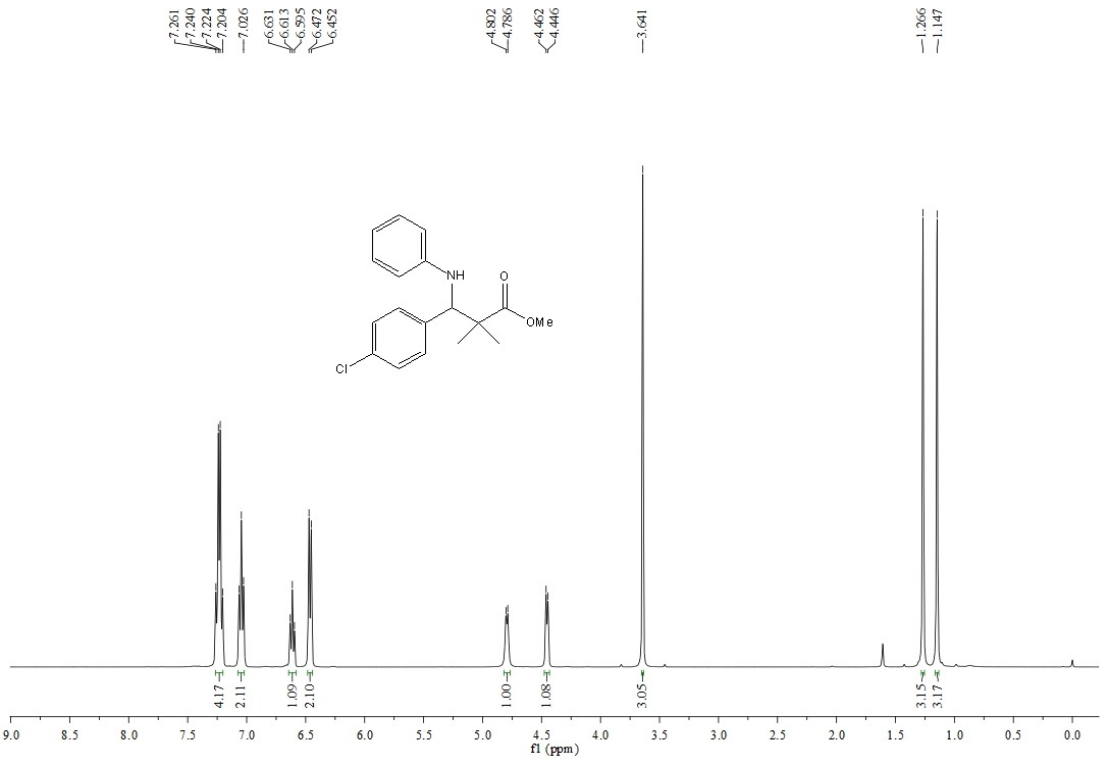
^{13}C NMR of **10j** in $CDCl_3$



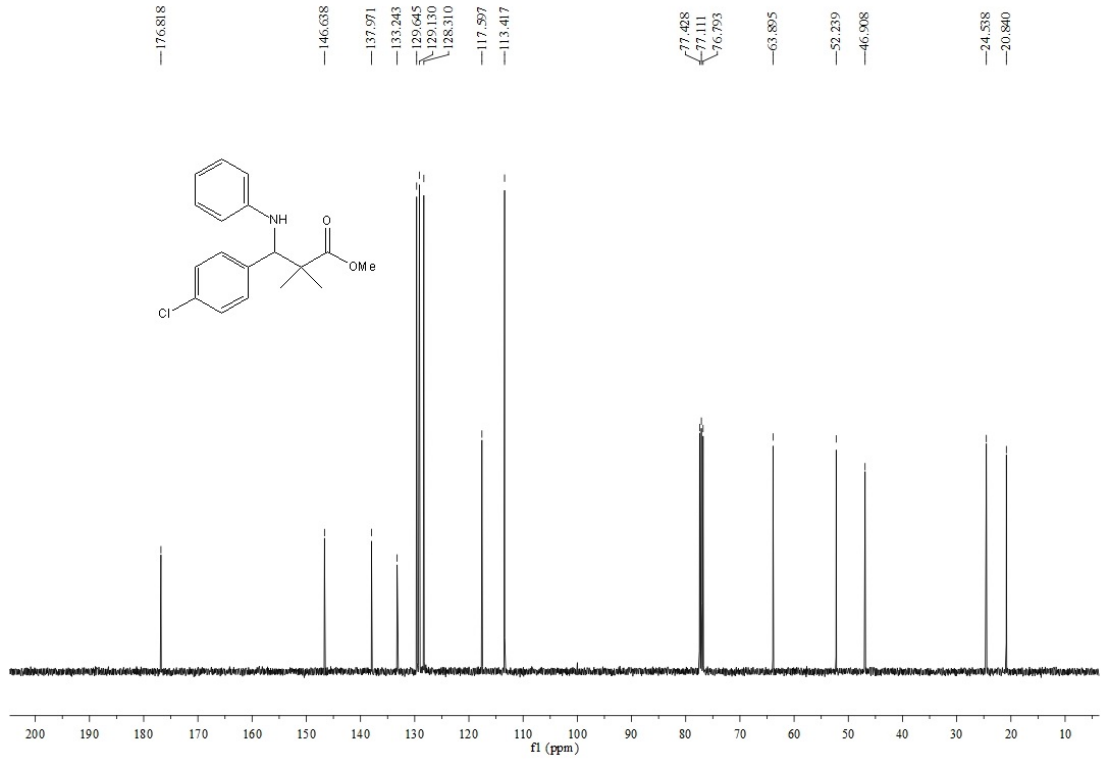
^{1}H NMR of **10k** in $CDCl_3$



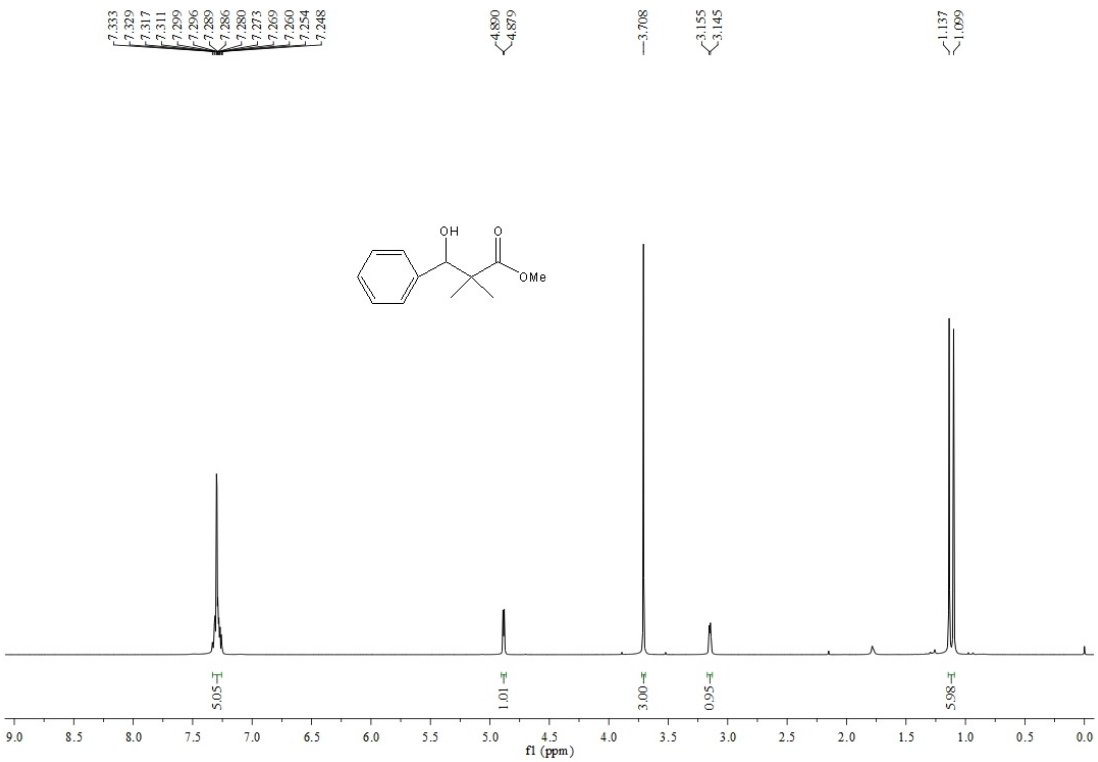
^{13}C NMR of **10k** in $CDCl_3$



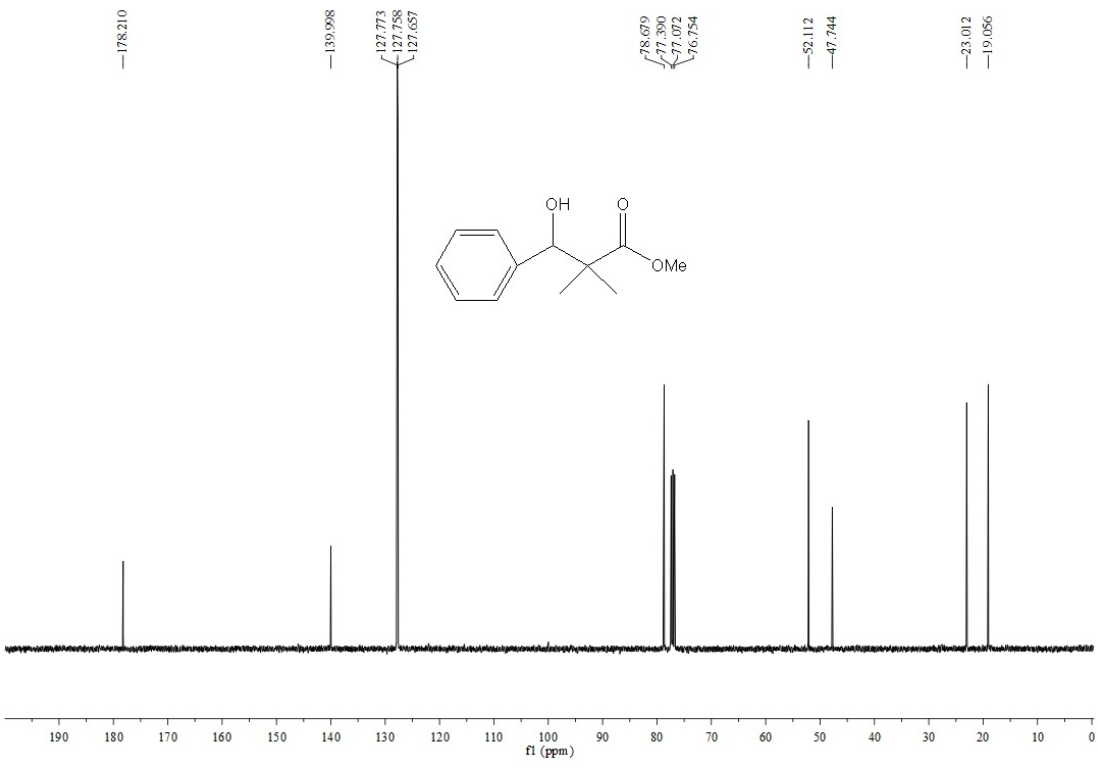
^{1}H NMR of **10l** in $CDCl_3$



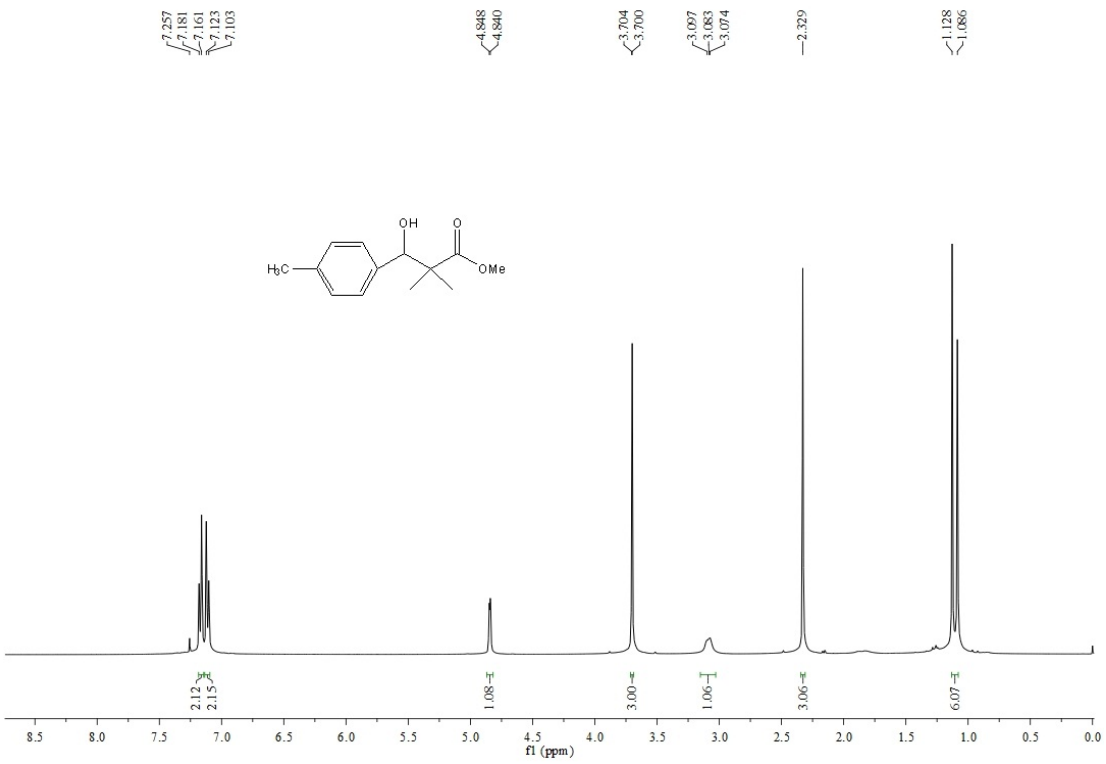
^{13}C NMR of **10l** in $CDCl_3$



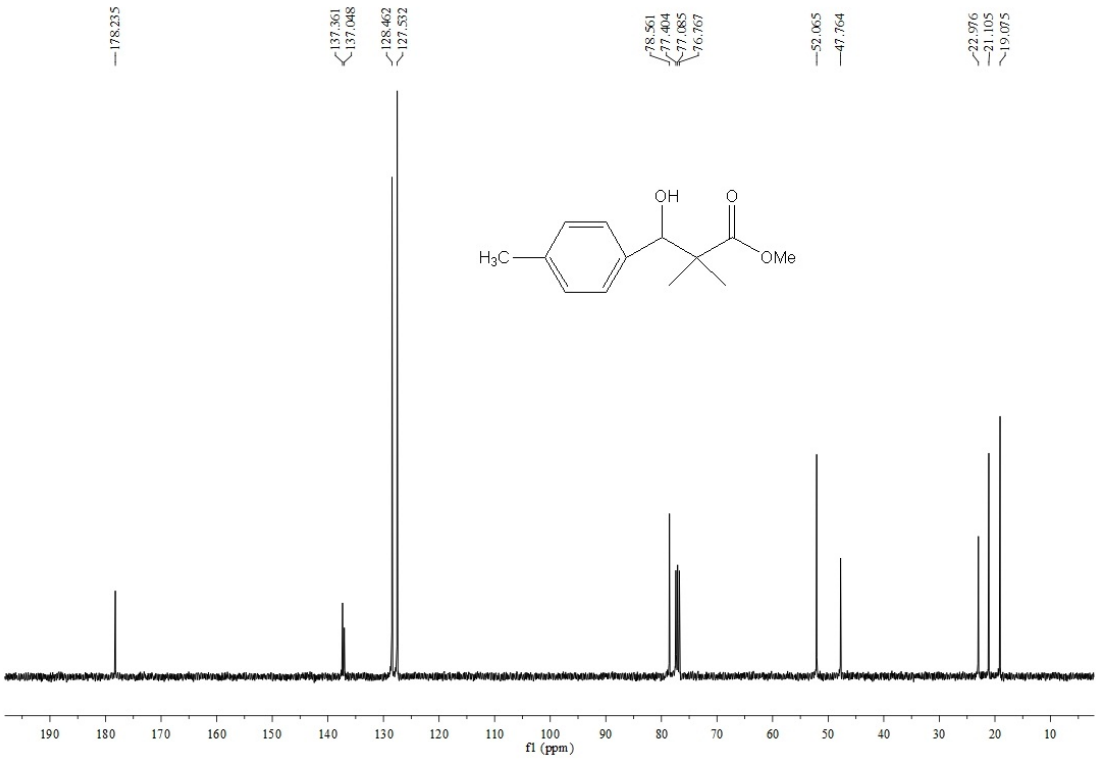
^{1}H NMR of **11a** in $CDCl_3$



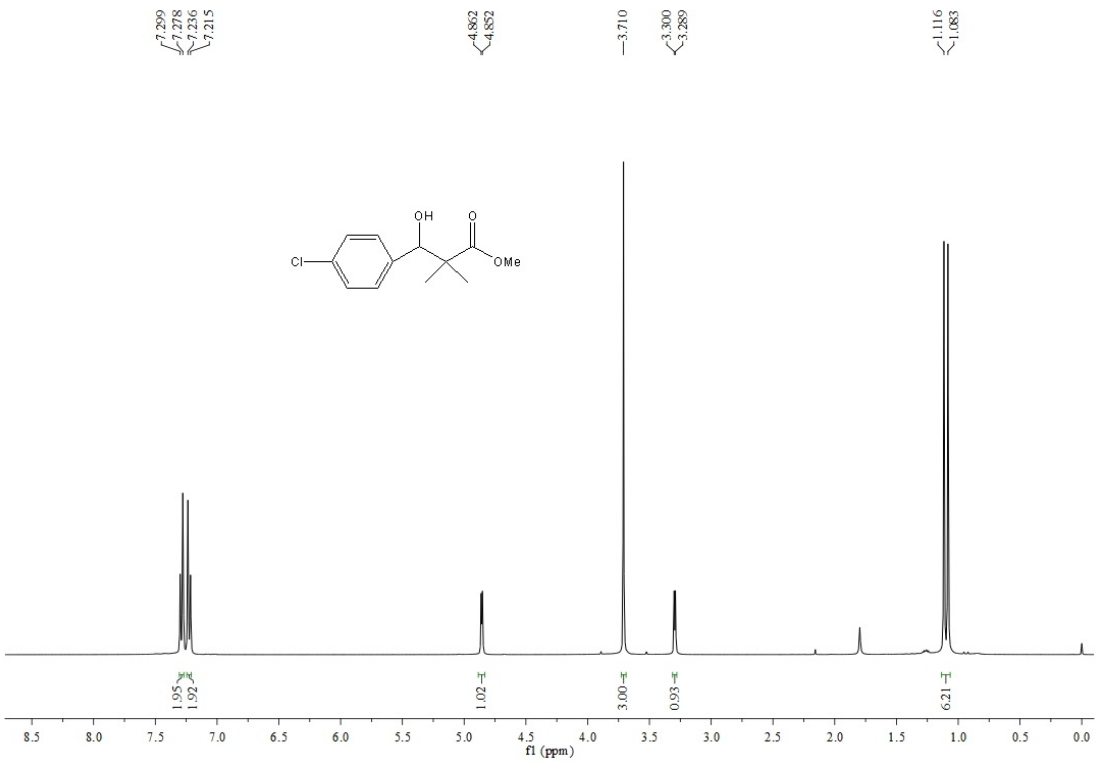
^{13}C NMR of **11a** in $CDCl_3$



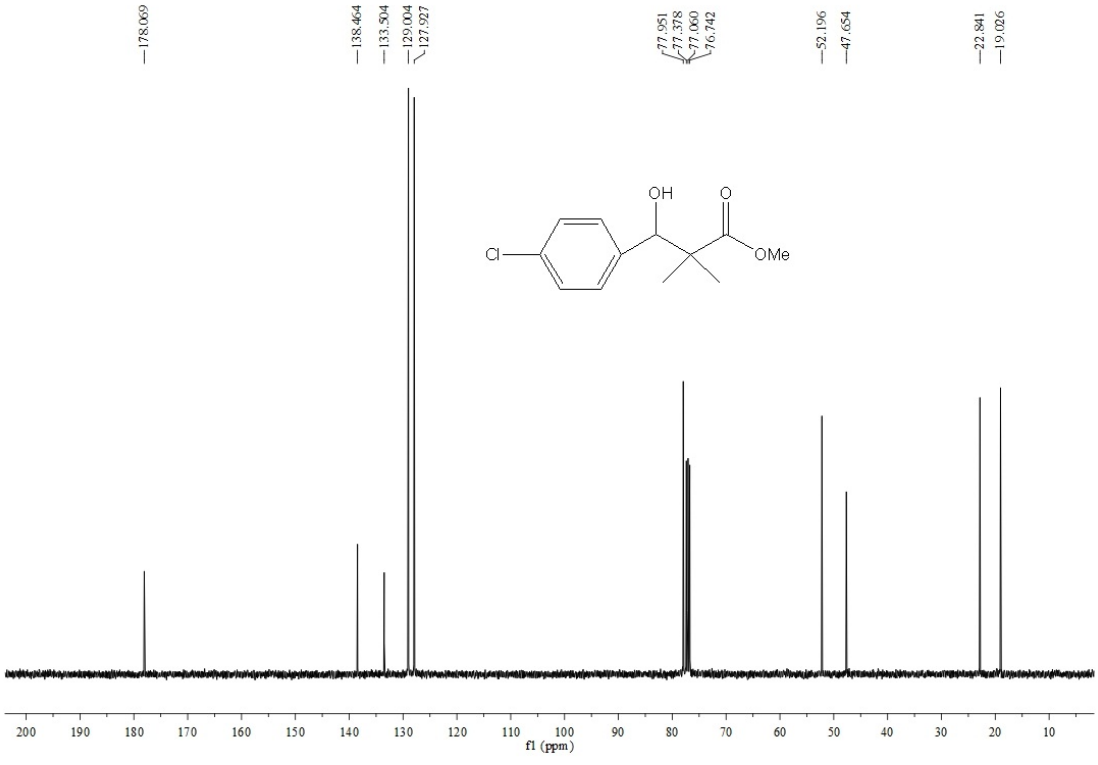
^{1}H NMR of **11b** in $CDCl_3$



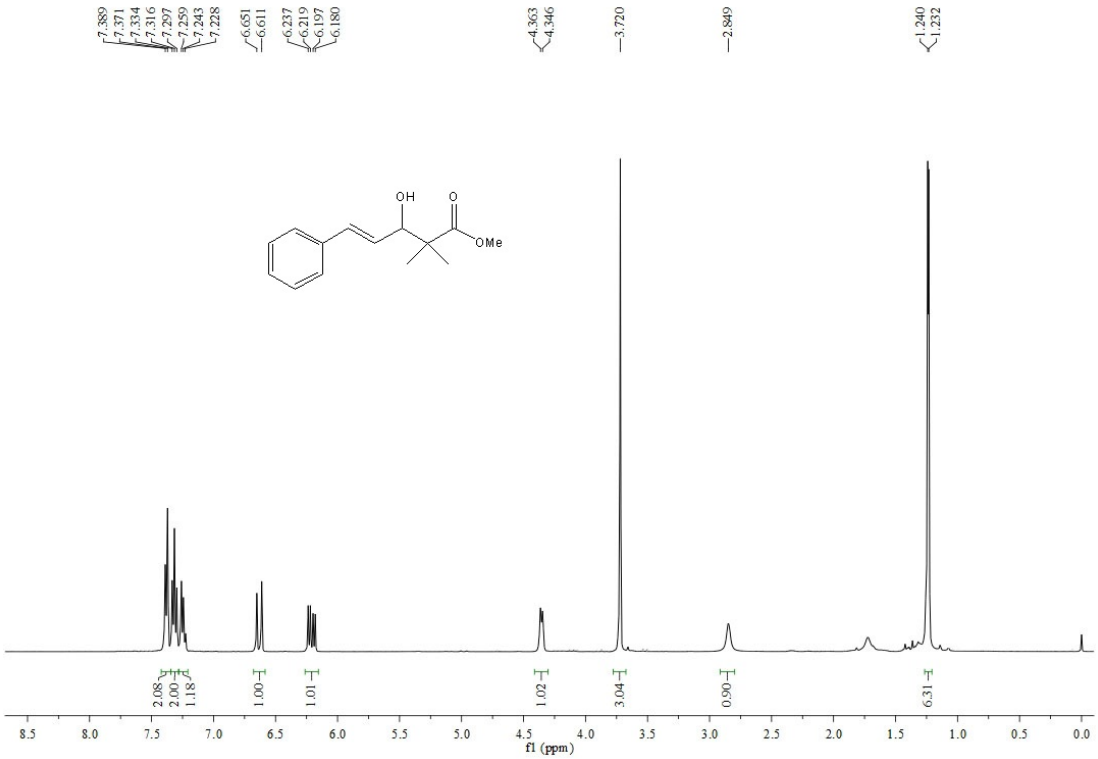
^{13}C NMR of **11b** in $CDCl_3$



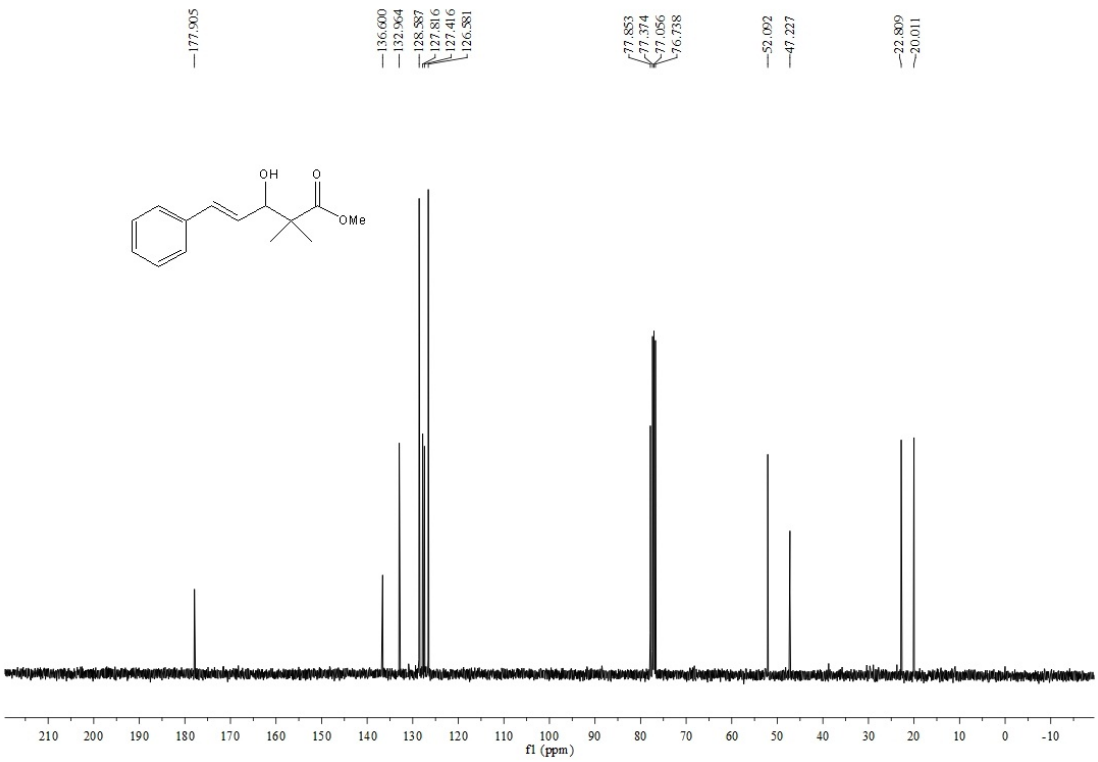
^{1}H NMR of **11c** in $CDCl_3$



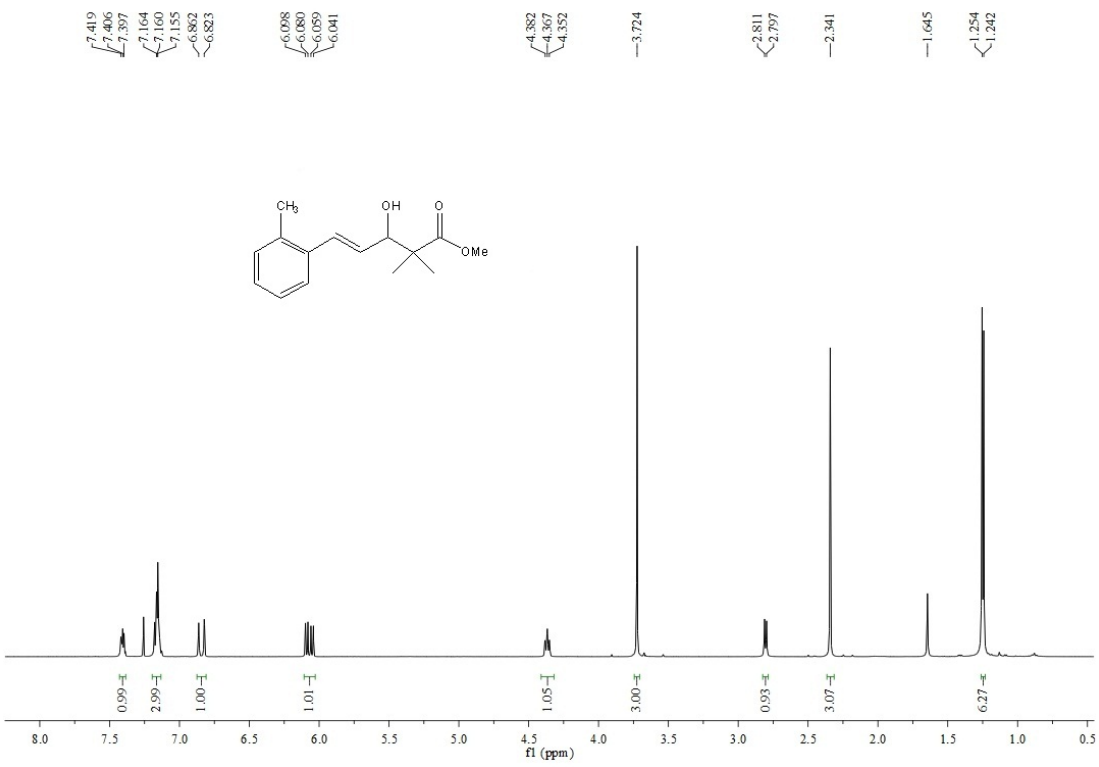
^{13}C NMR of **11c** in $CDCl_3$



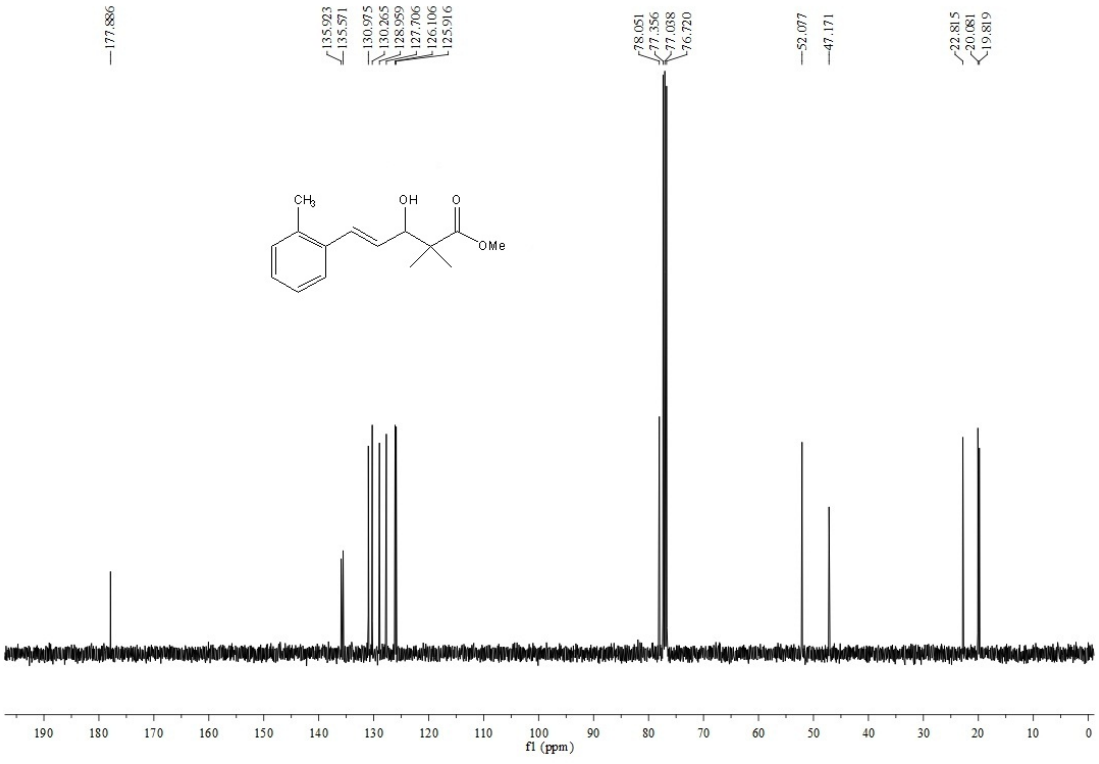
^{1}H NMR of **11d** in $CDCl_3$



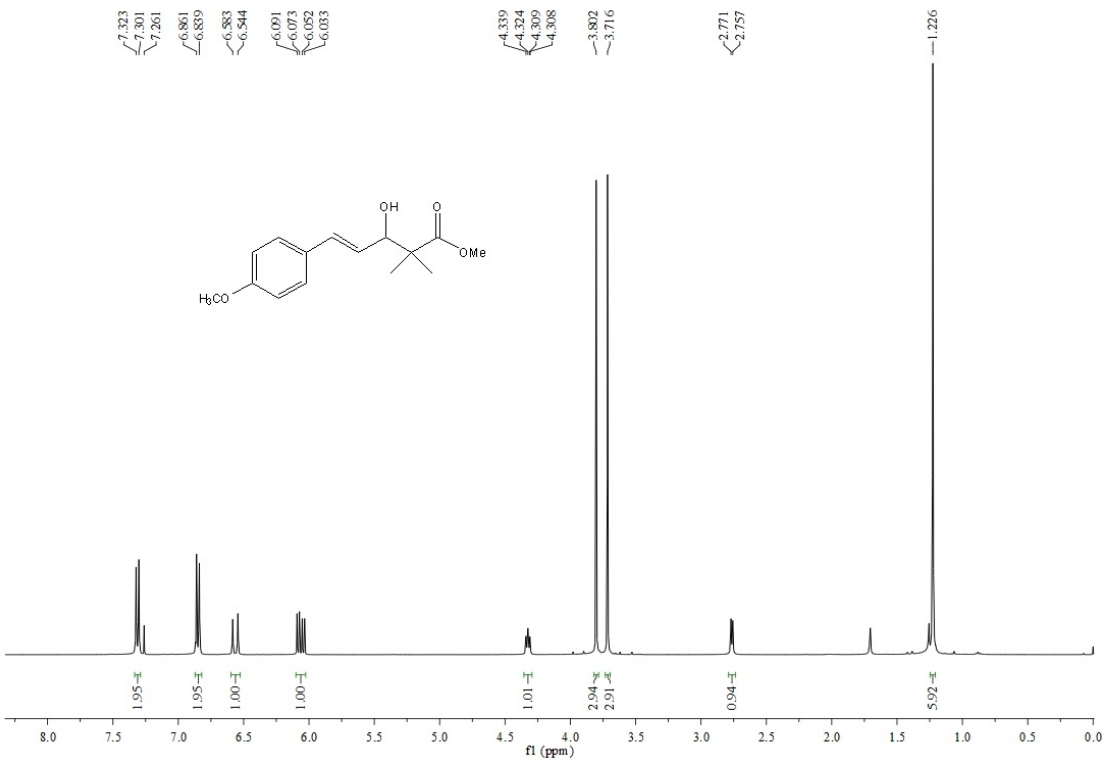
^{13}C NMR of **11d** in $CDCl_3$



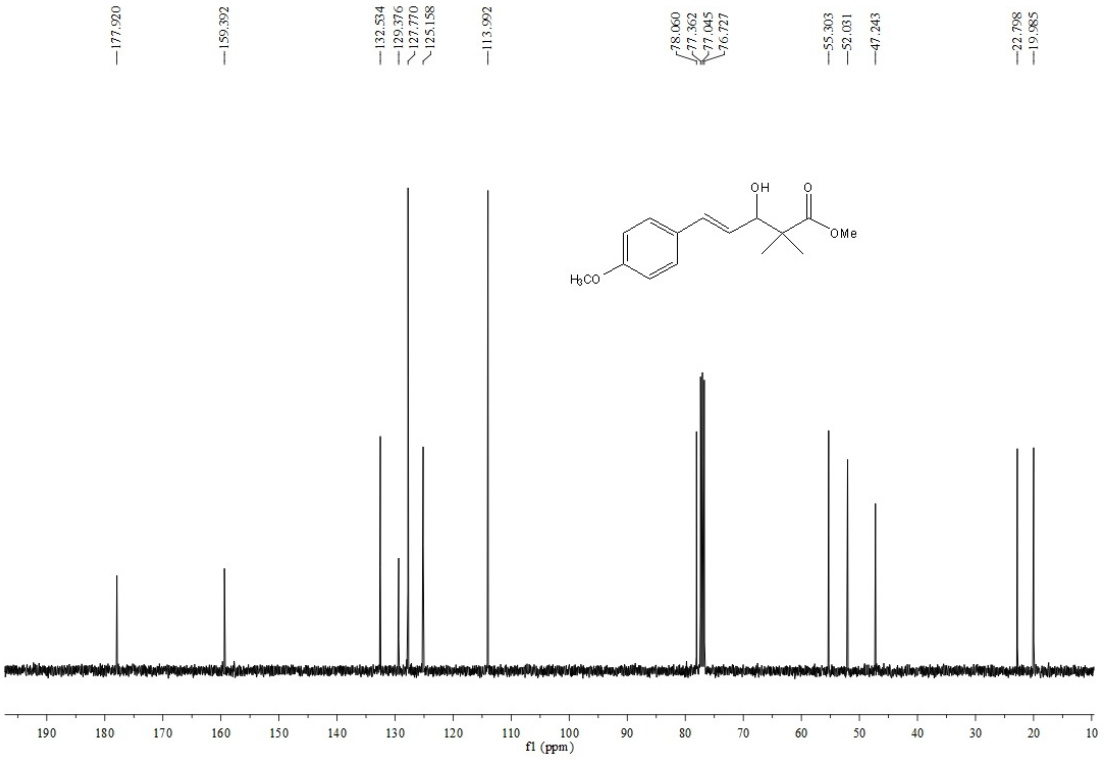
^{1}H NMR of **11e** in $CDCl_3$



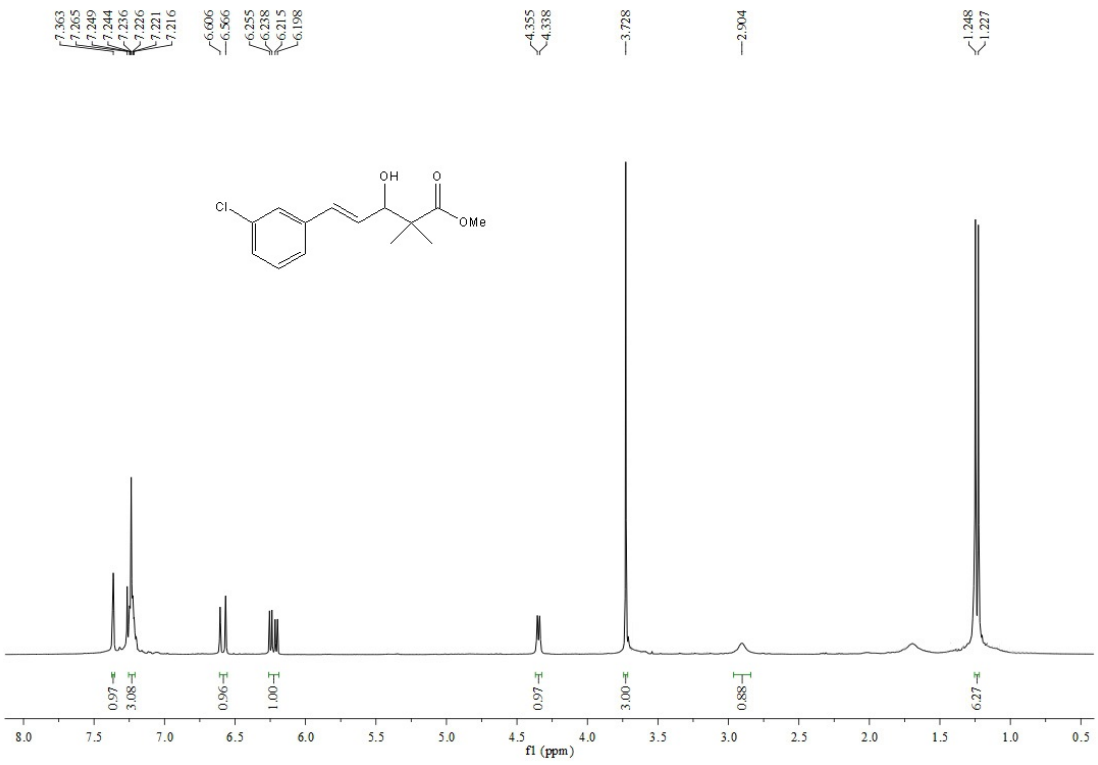
^{13}C NMR of **11e** in $CDCl_3$



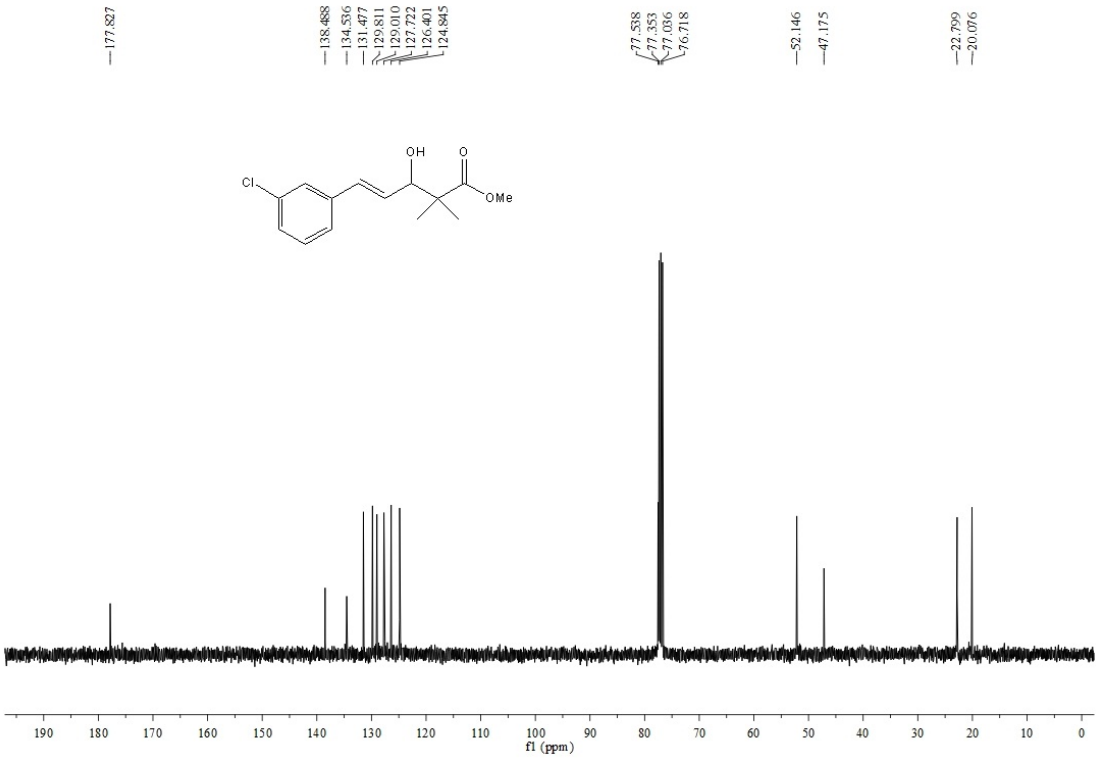
^{1}H NMR of **11f** in $CDCl_3$



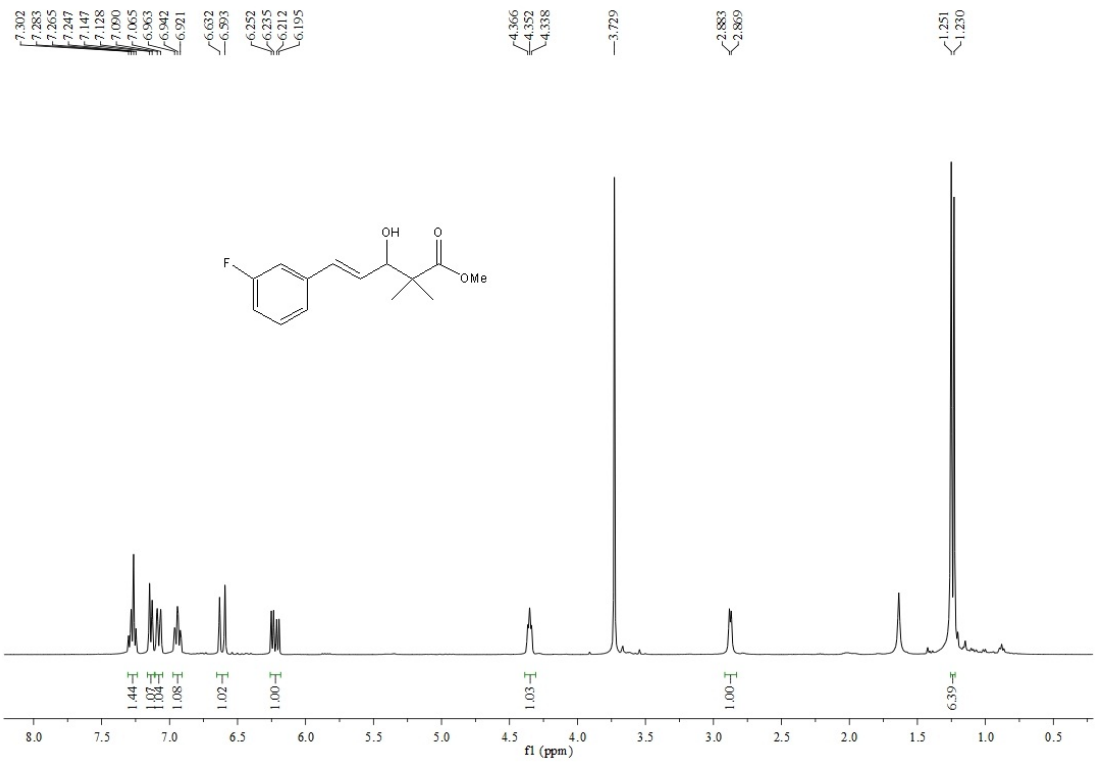
^{13}C NMR of **11f** in $CDCl_3$



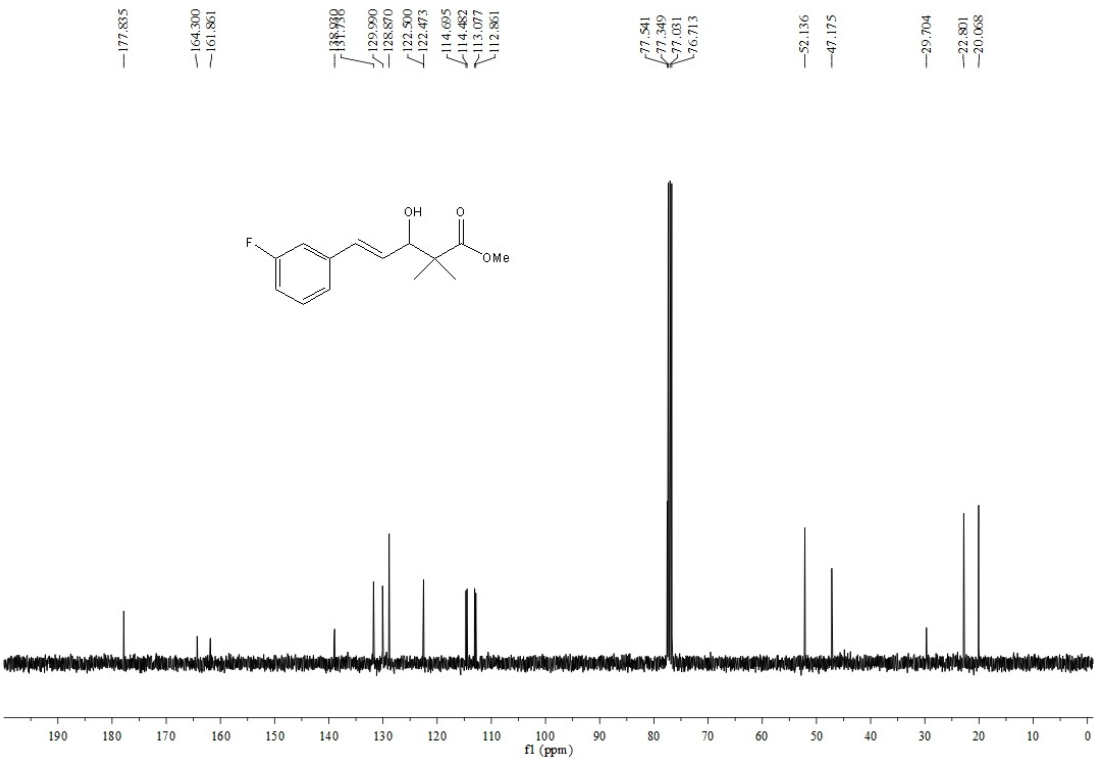
^{1}H NMR of **11g** in $CDCl_3$



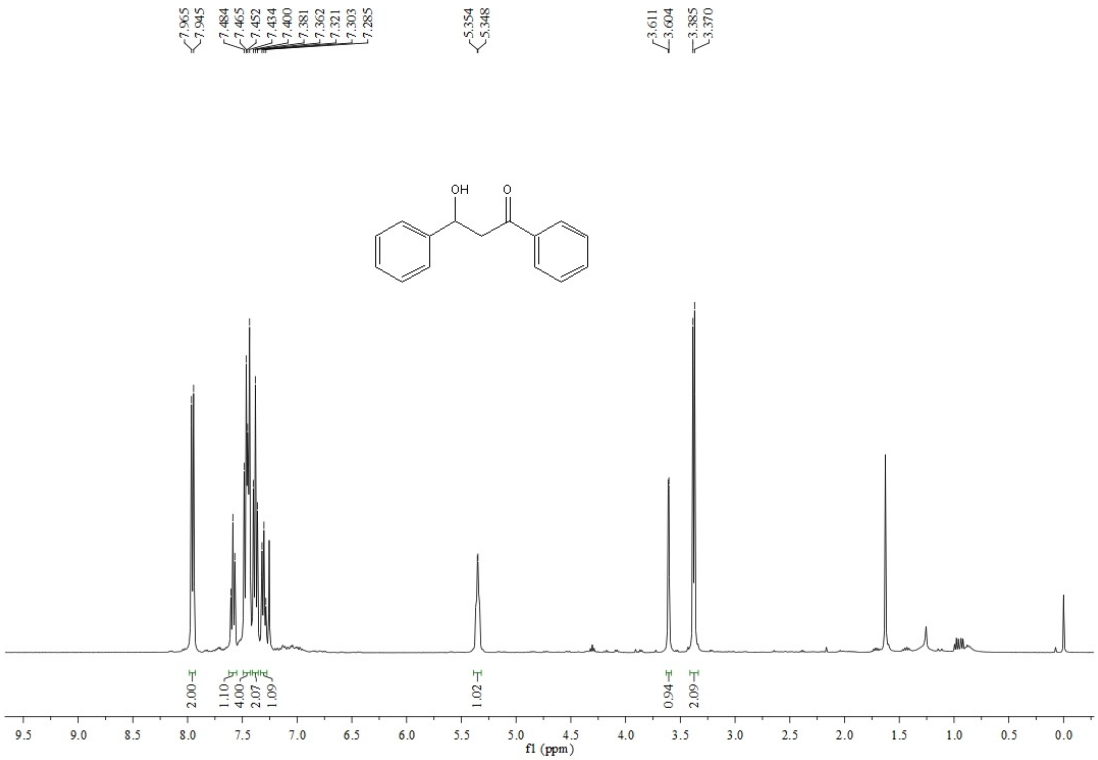
^{13}C NMR of **11g** in $CDCl_3$



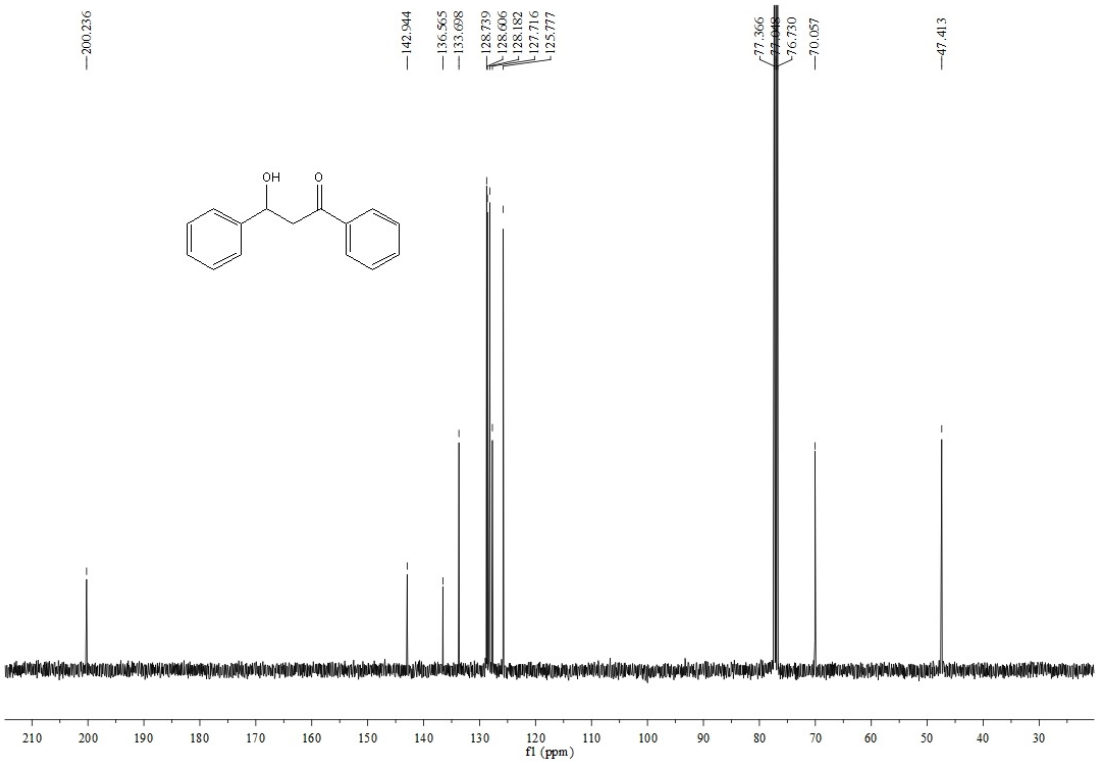
^{1}H NMR of **11h** in $CDCl_3$



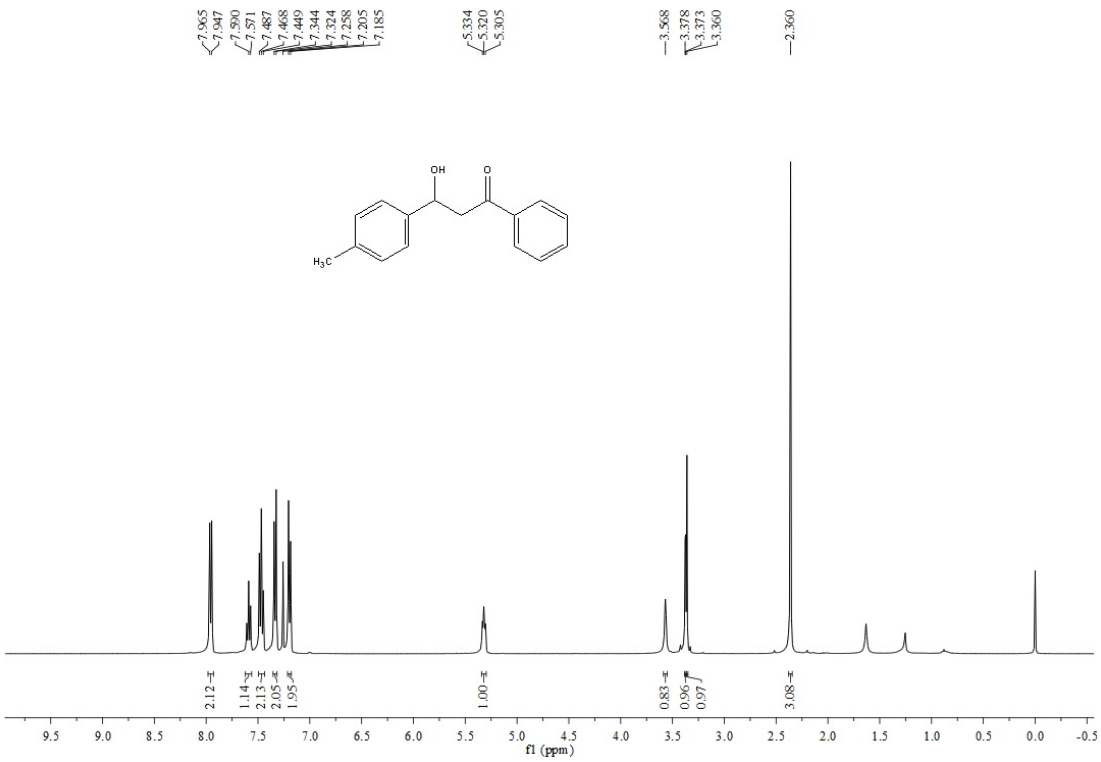
^{13}C NMR of **11h** in $CDCl_3$



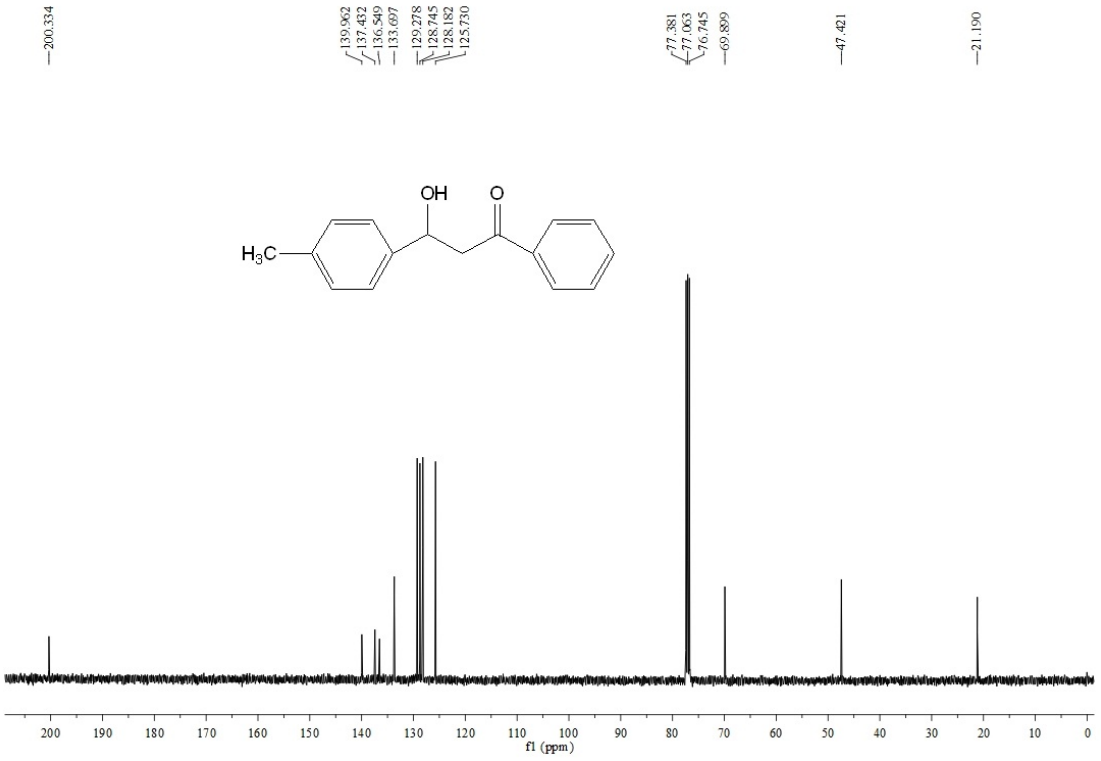
^{1}H NMR of **11i** in $CDCl_3$



^{13}C NMR of **11i** in $CDCl_3$

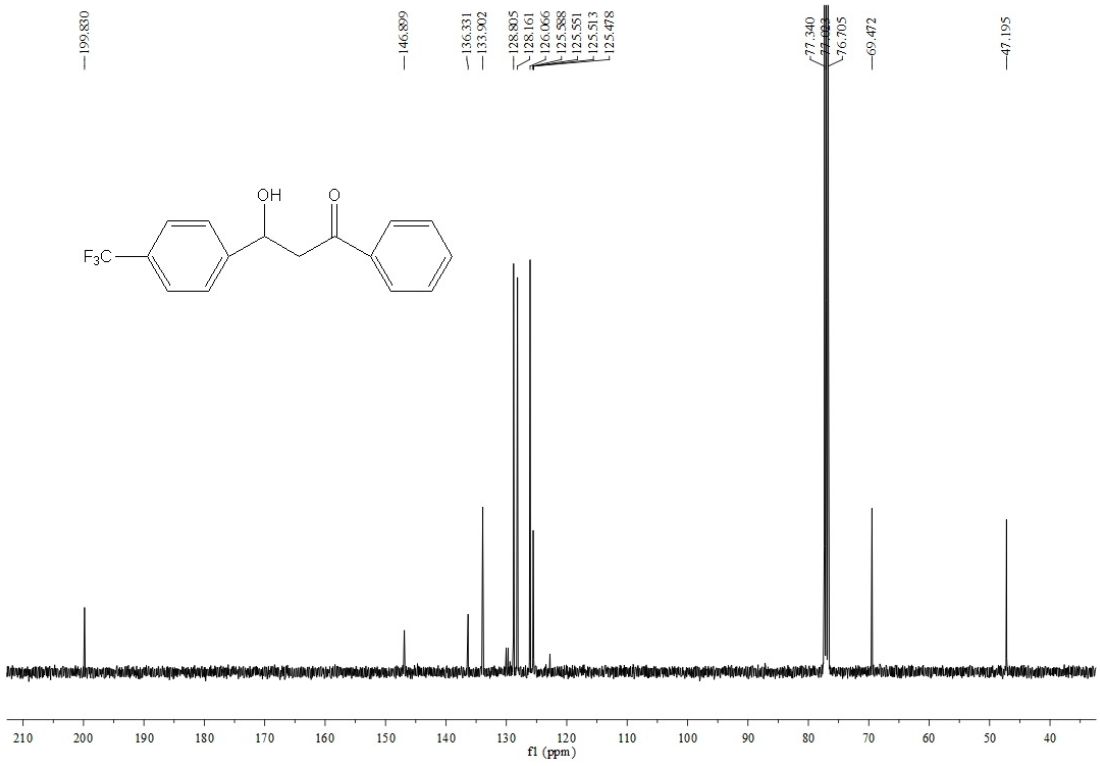


^{1}H NMR of **11j** in $CDCl_3$



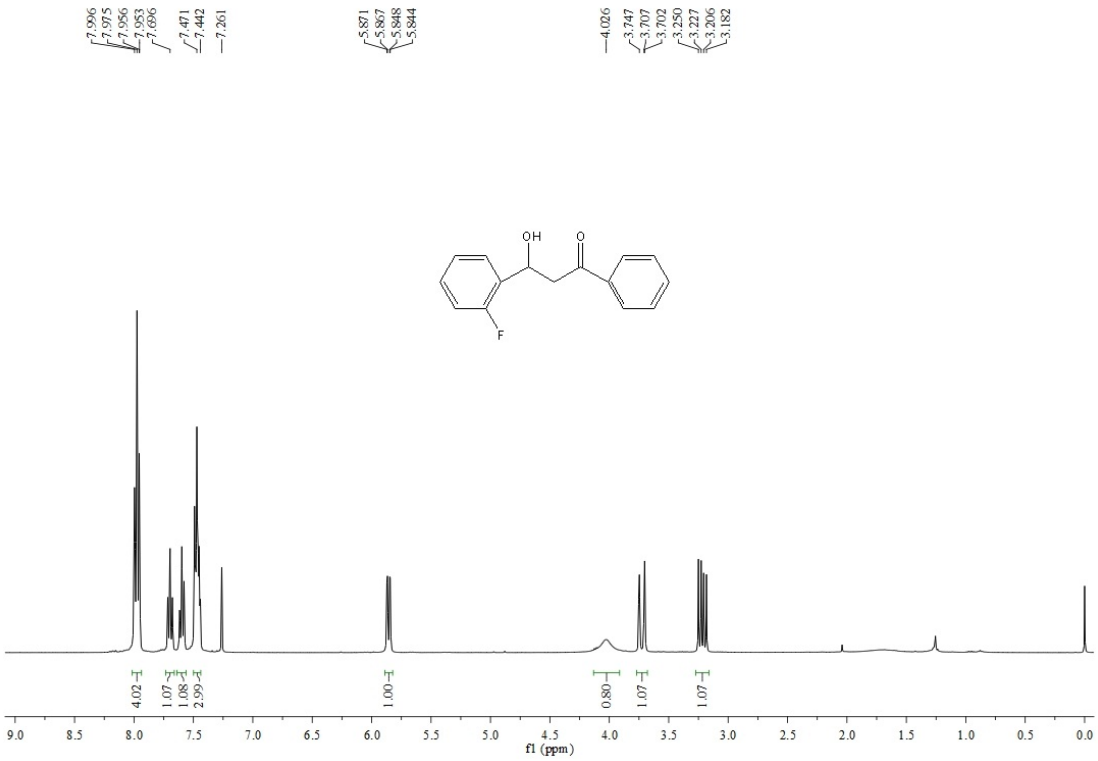
^{13}C NMR of **11j** in $CDCl_3$

^{1}H NMR of **11k** in $CDCl_3$

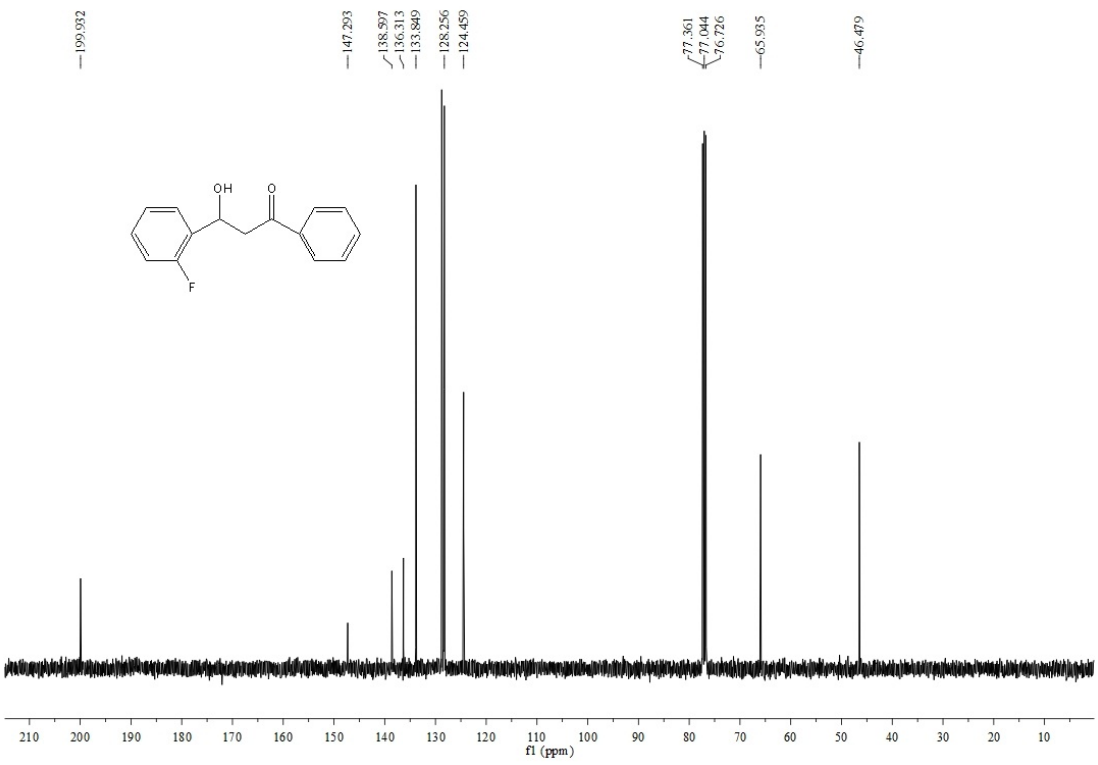


^{13}C NMR of **11k** in $CDCl_3$

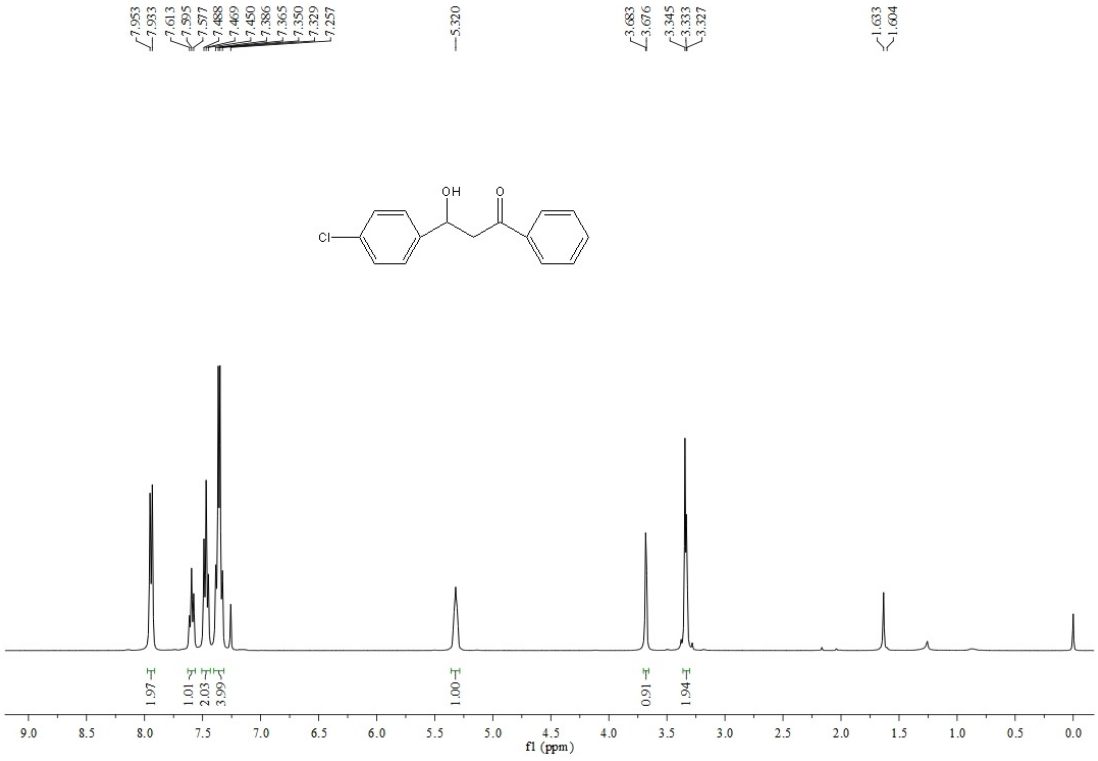
^{19}F NMR of **11k** in $CDCl_3$



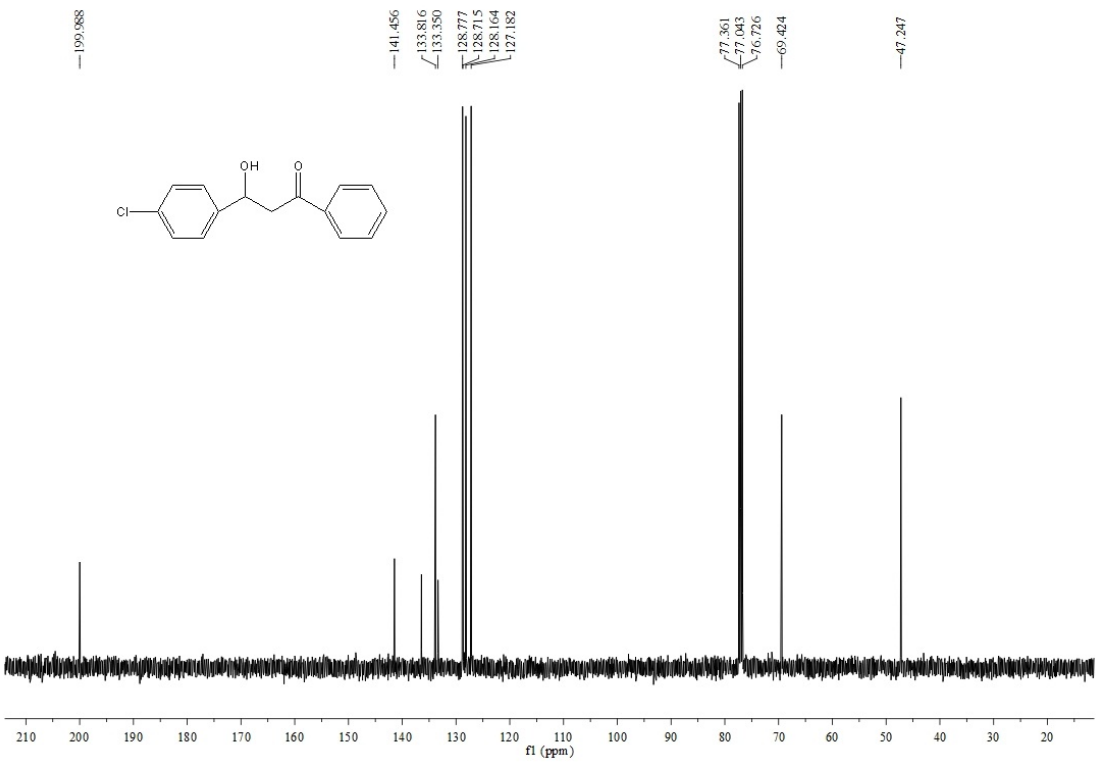
^{1}H NMR of **11l** in $CDCl_3$



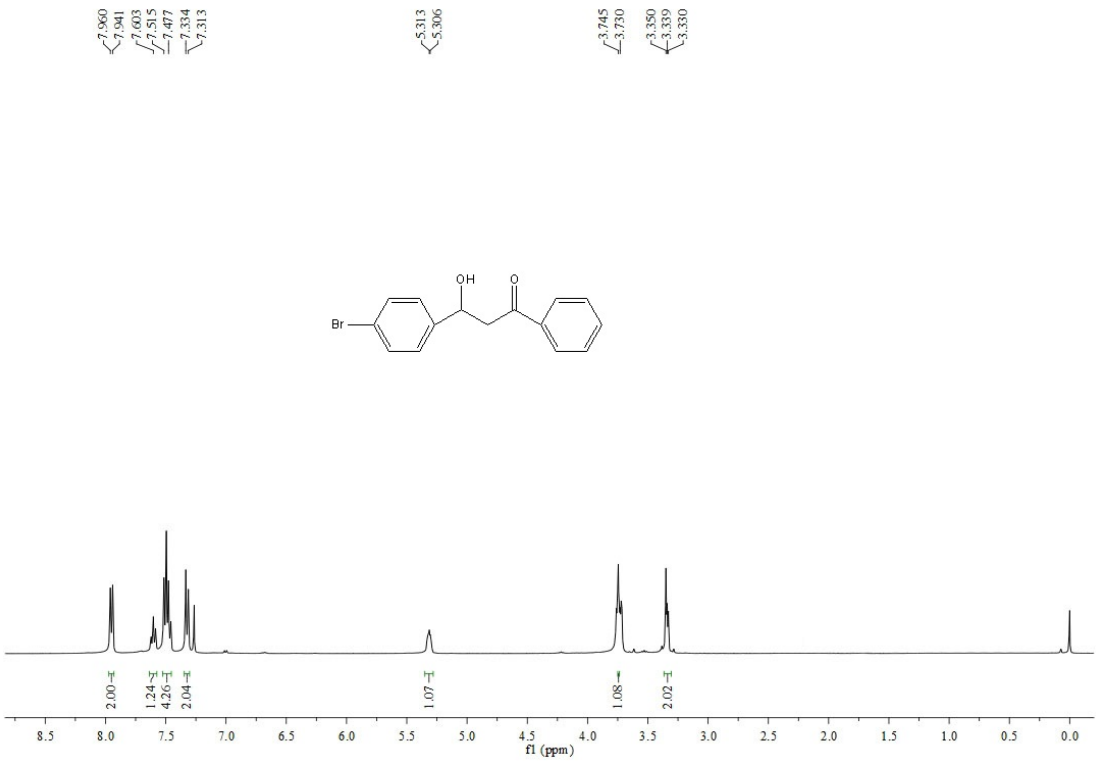
^{13}C NMR of **11l** in $CDCl_3$



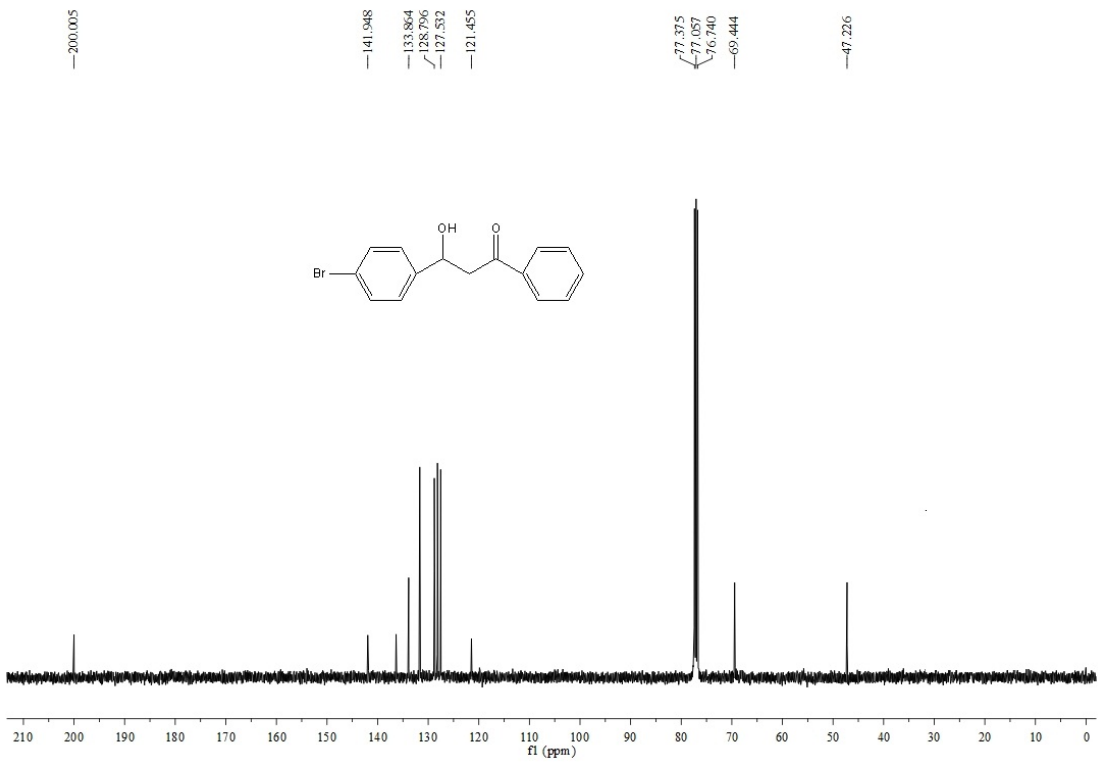
^{1}H NMR of **11m** in $CDCl_3$



^{13}C NMR of **11m** in $CDCl_3$



^{1}H NMR of **11n** in $CDCl_3$



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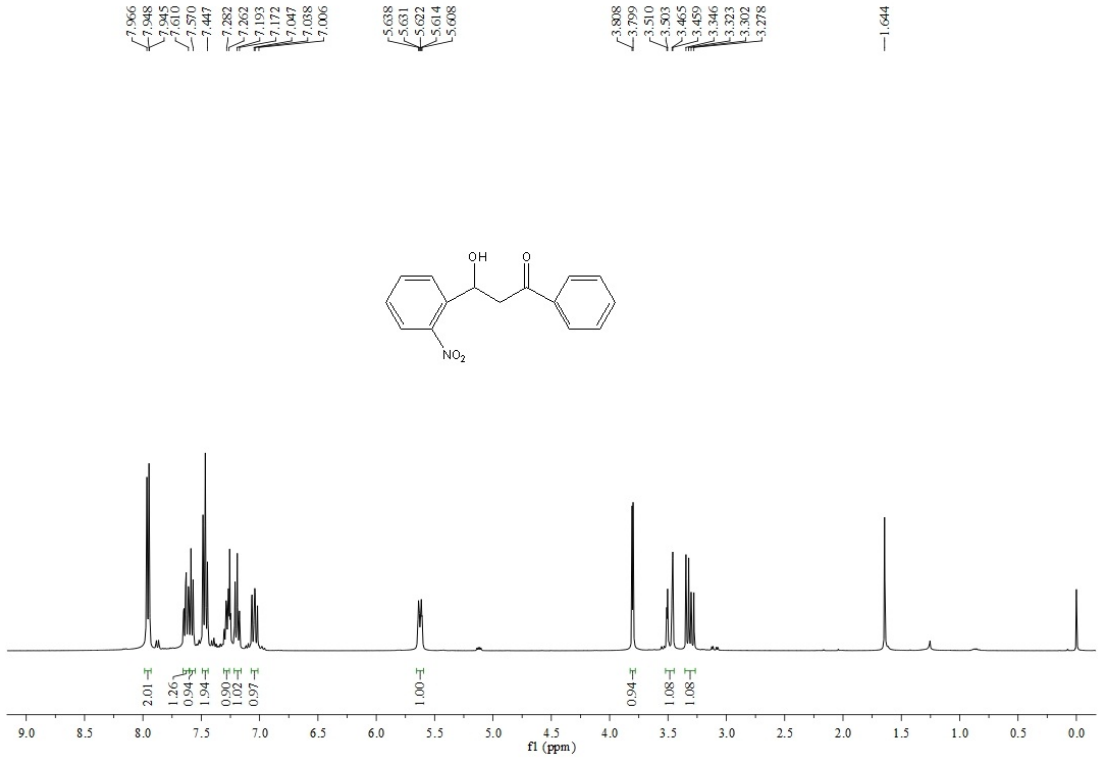
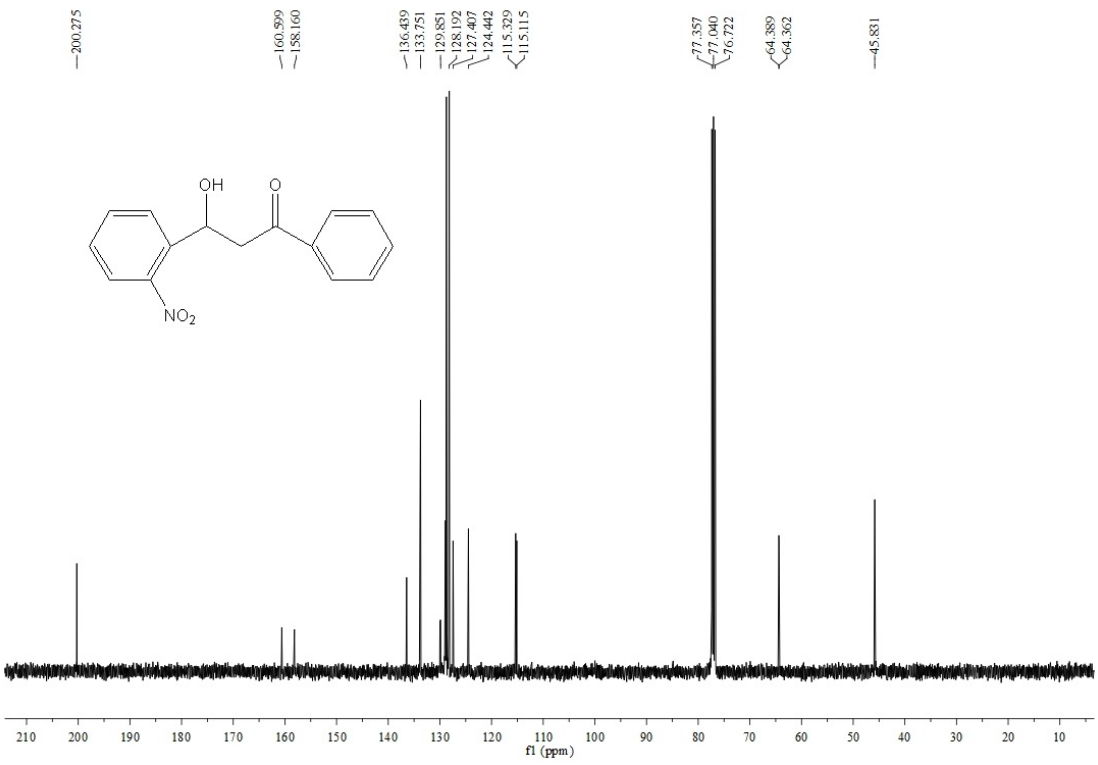
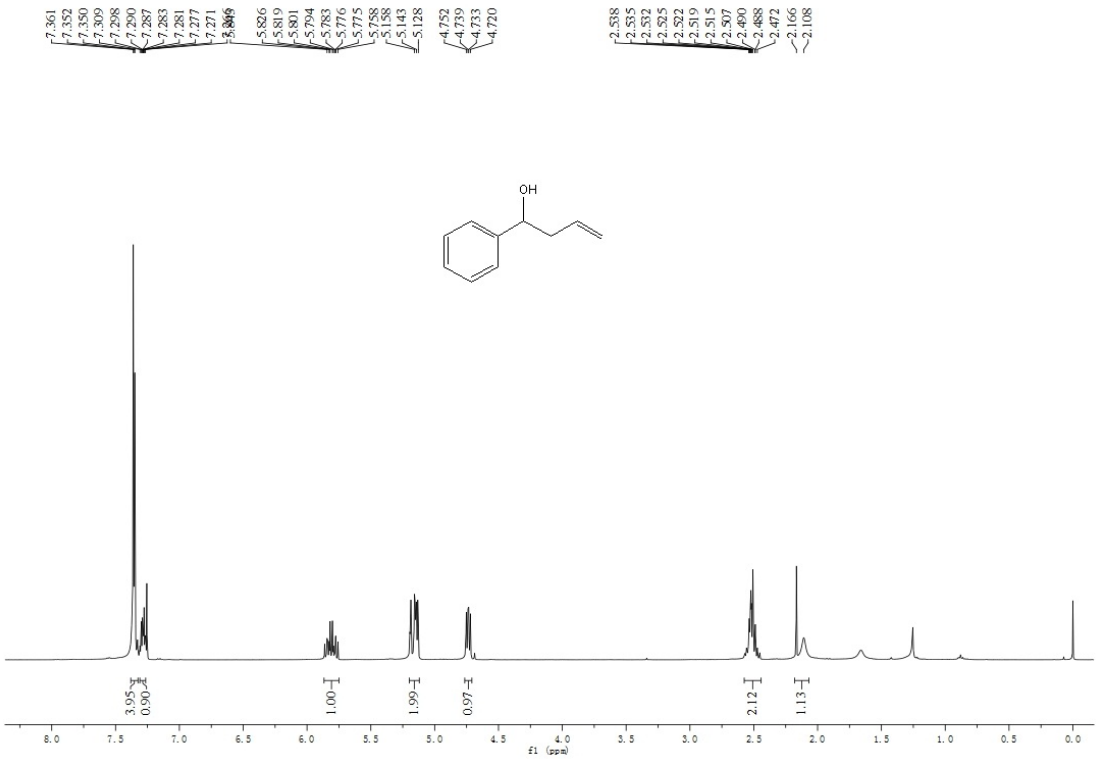


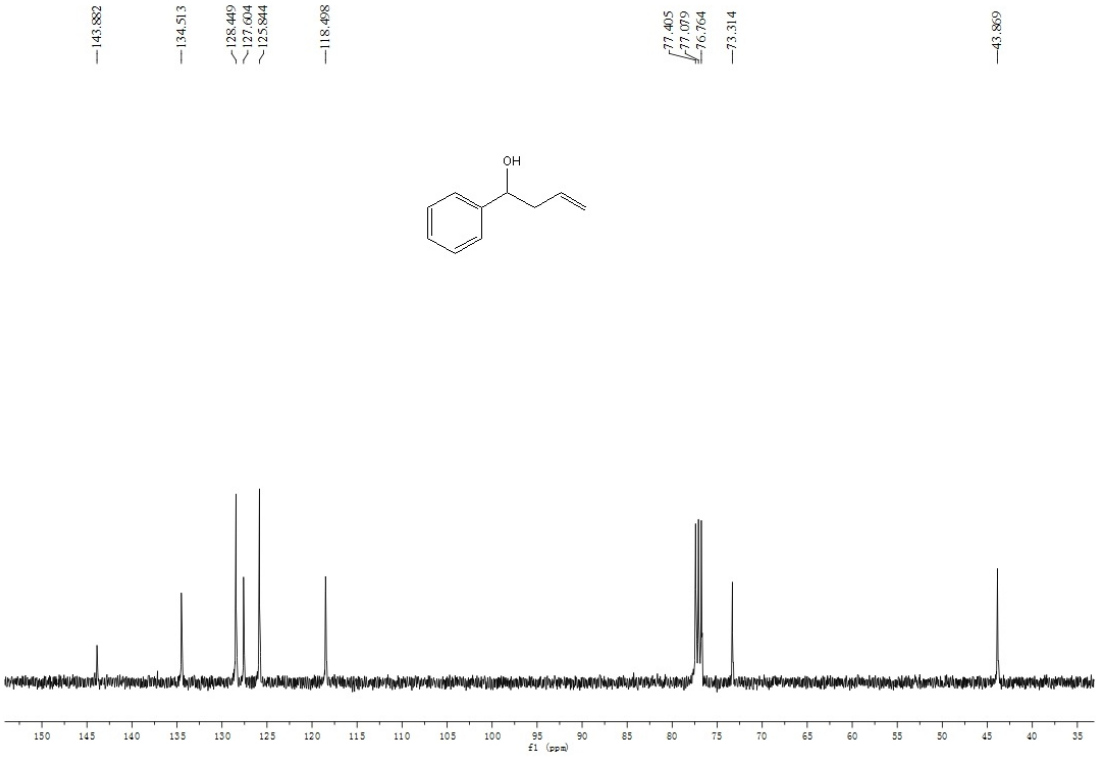
^{1}H NMR of **11o** in $CDCl_3$



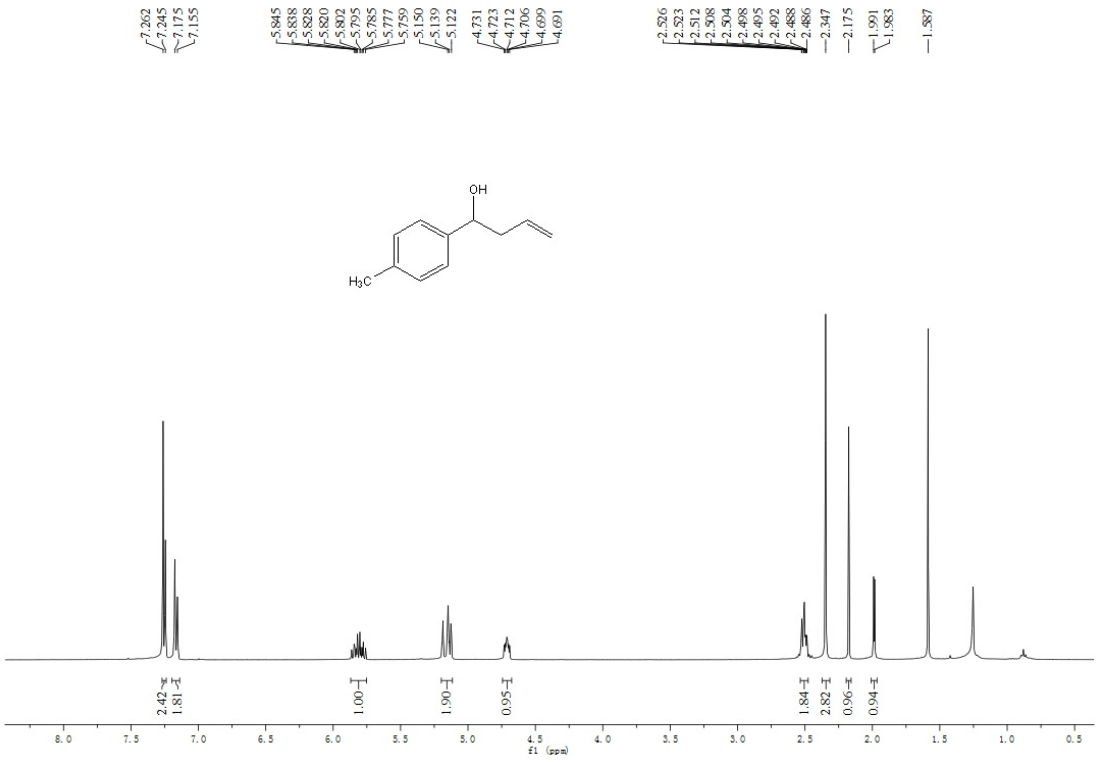
^{13}C NMR of **11o** in $CDCl_3$



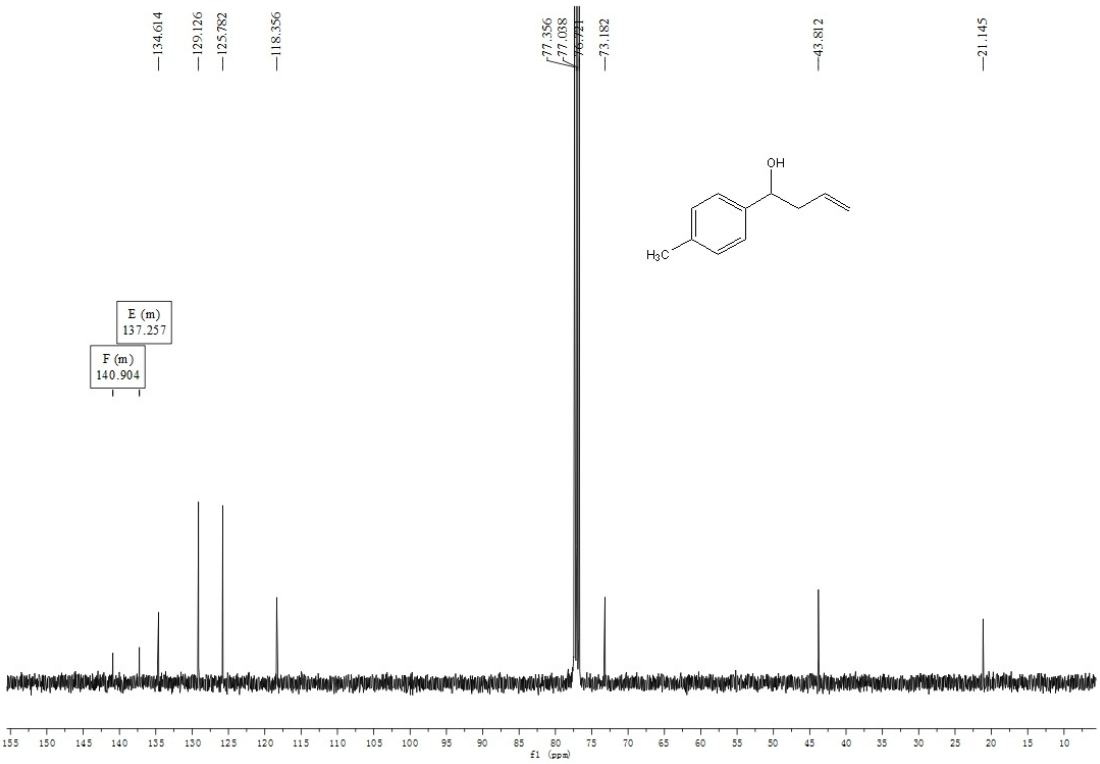
^{1}H NMR of **13a** in $CDCl_3$



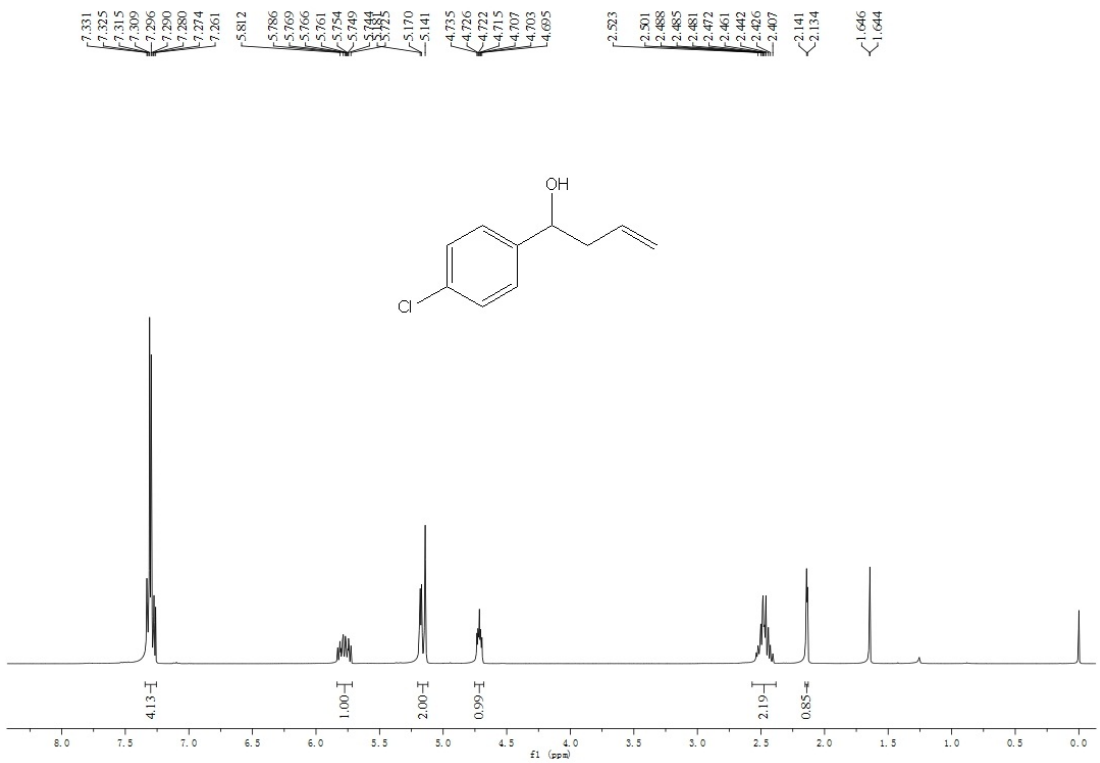
^{13}C NMR of **13a** in $CDCl_3$



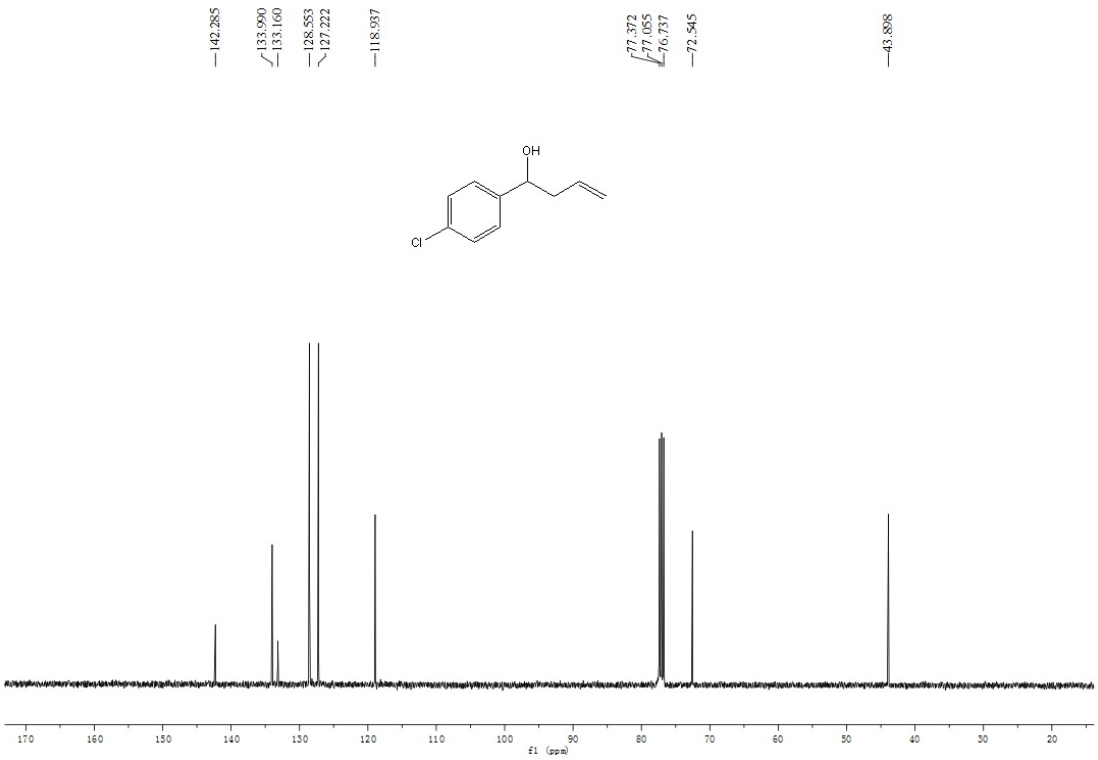
^{1}H NMR of **13b** in $CDCl_3$



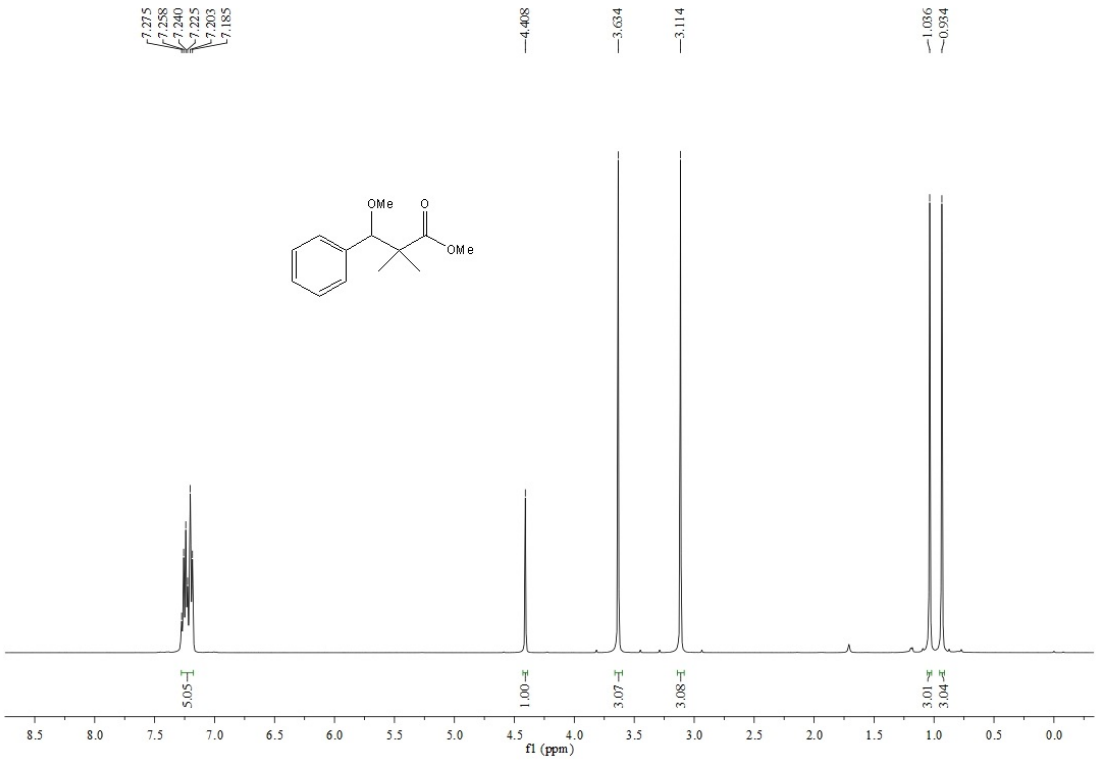
^{13}C NMR of **13b** in $CDCl_3$



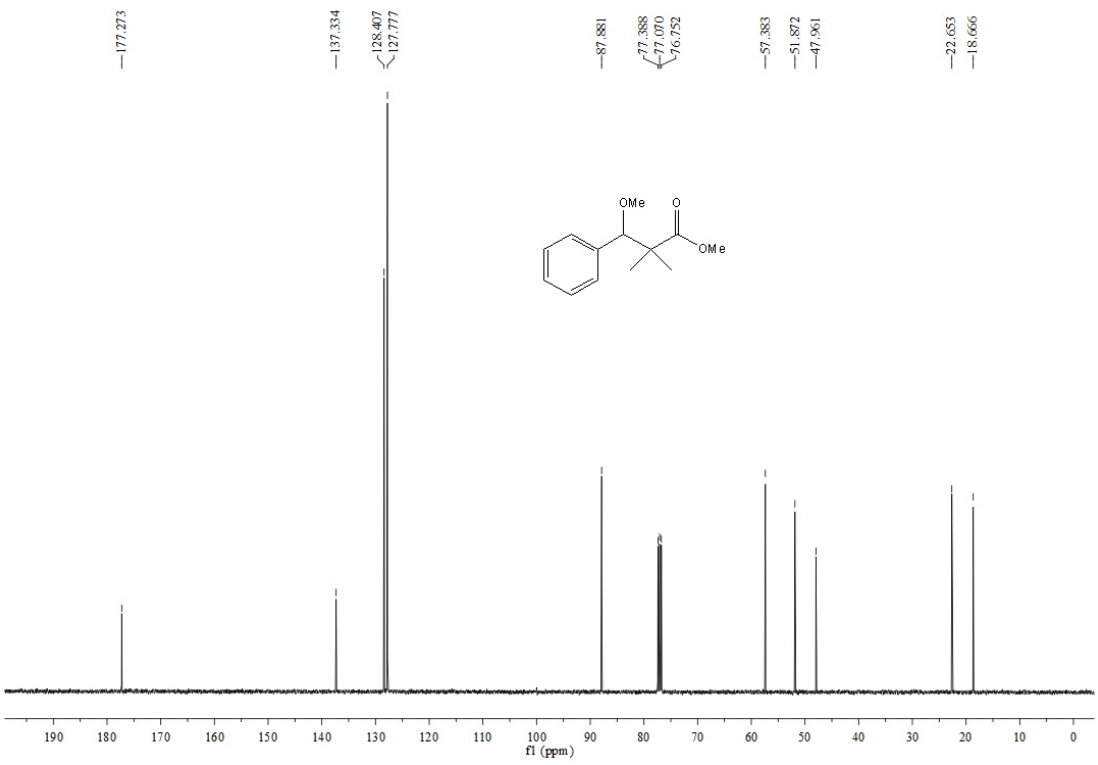
^{1}H NMR of **13c** in $CDCl_3$



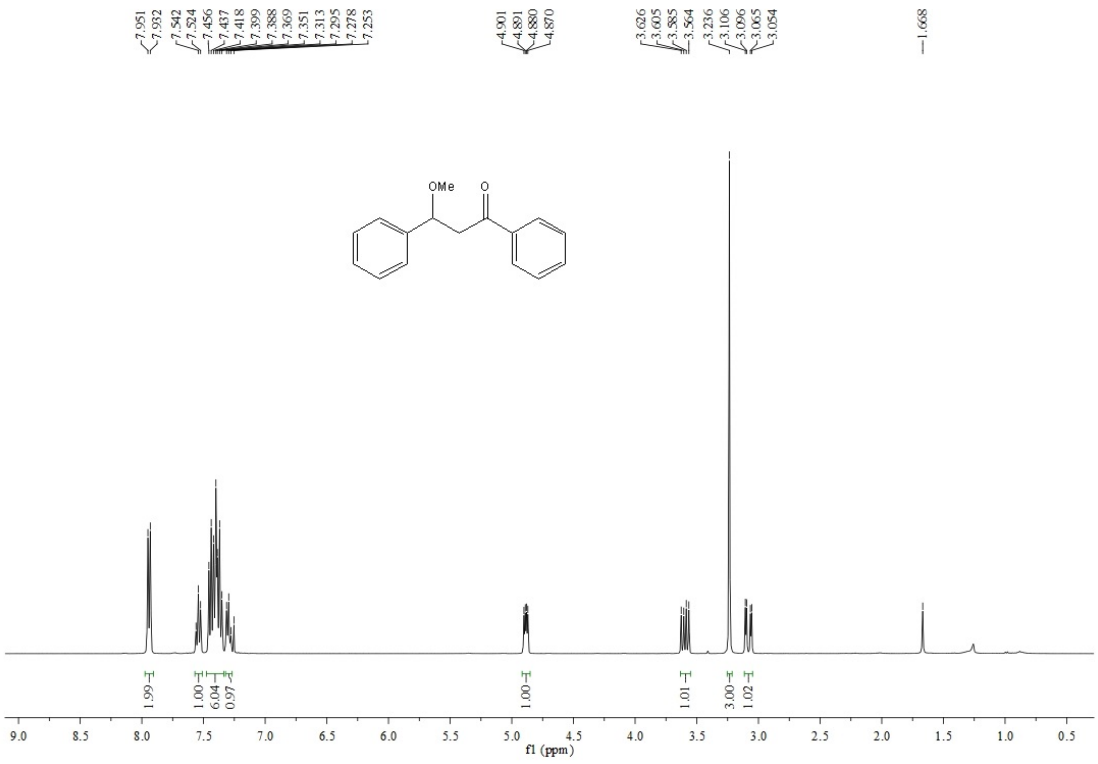
^{13}C NMR of **13c** in $CDCl_3$



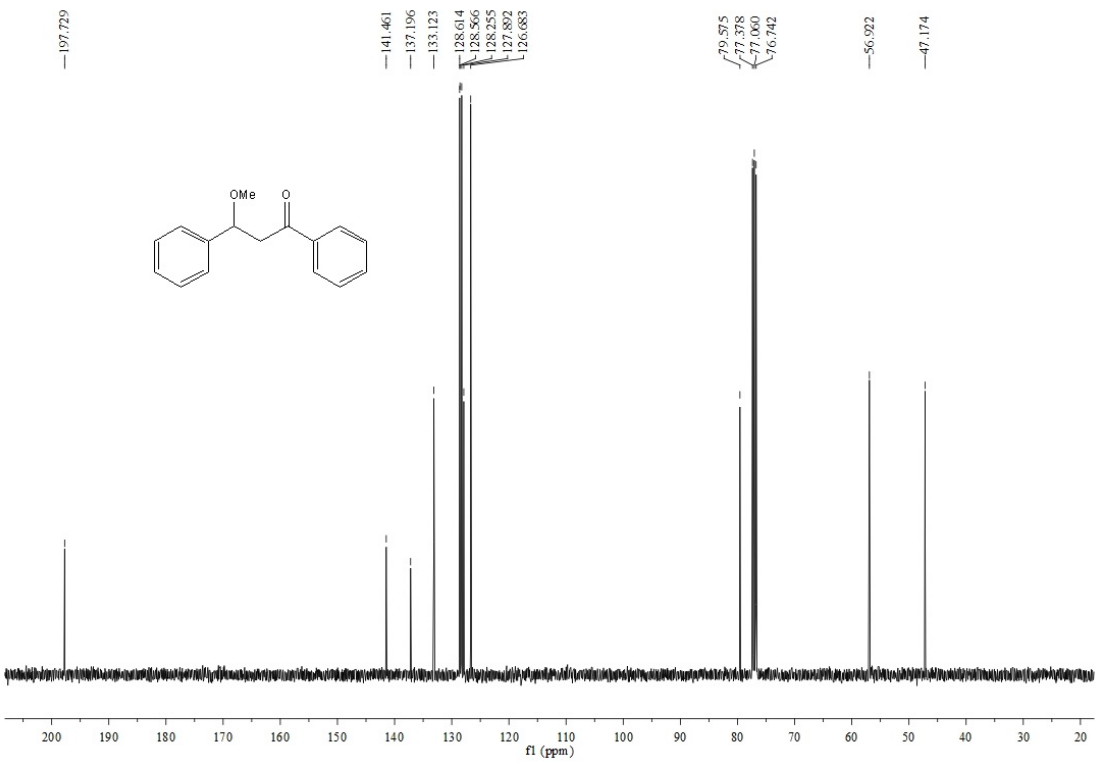
^{1}H NMR of **15a** in $CDCl_3$



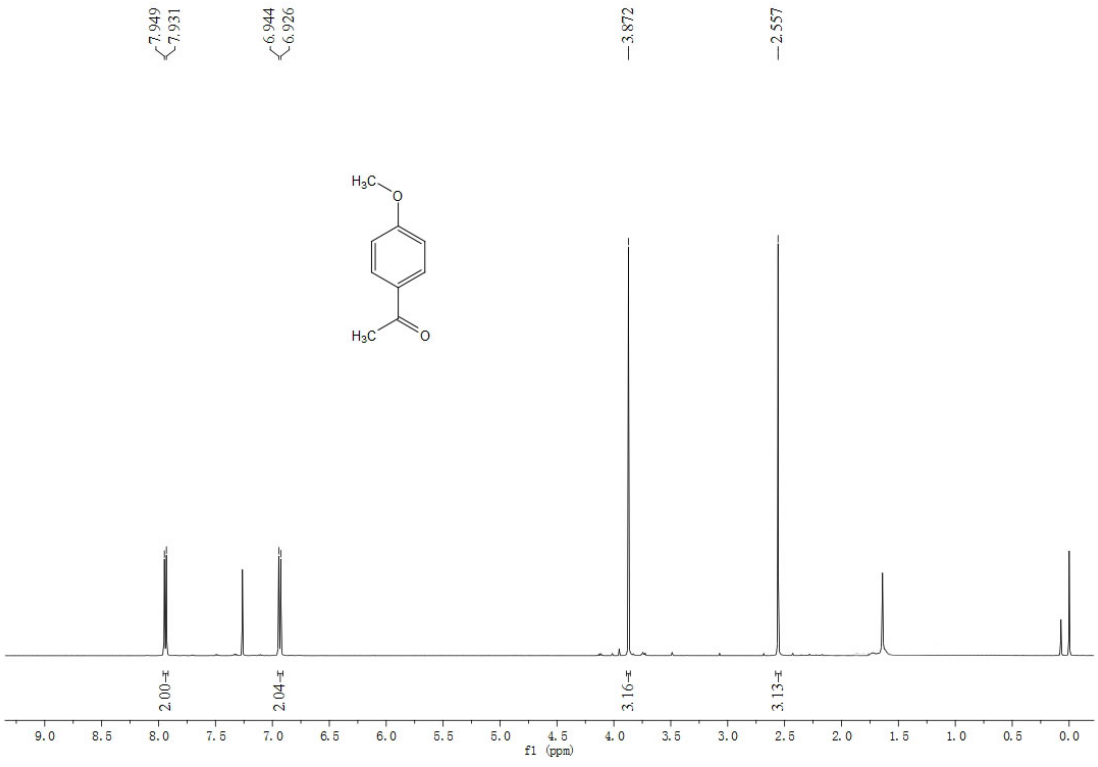
^{13}C NMR of **15a** in $CDCl_3$



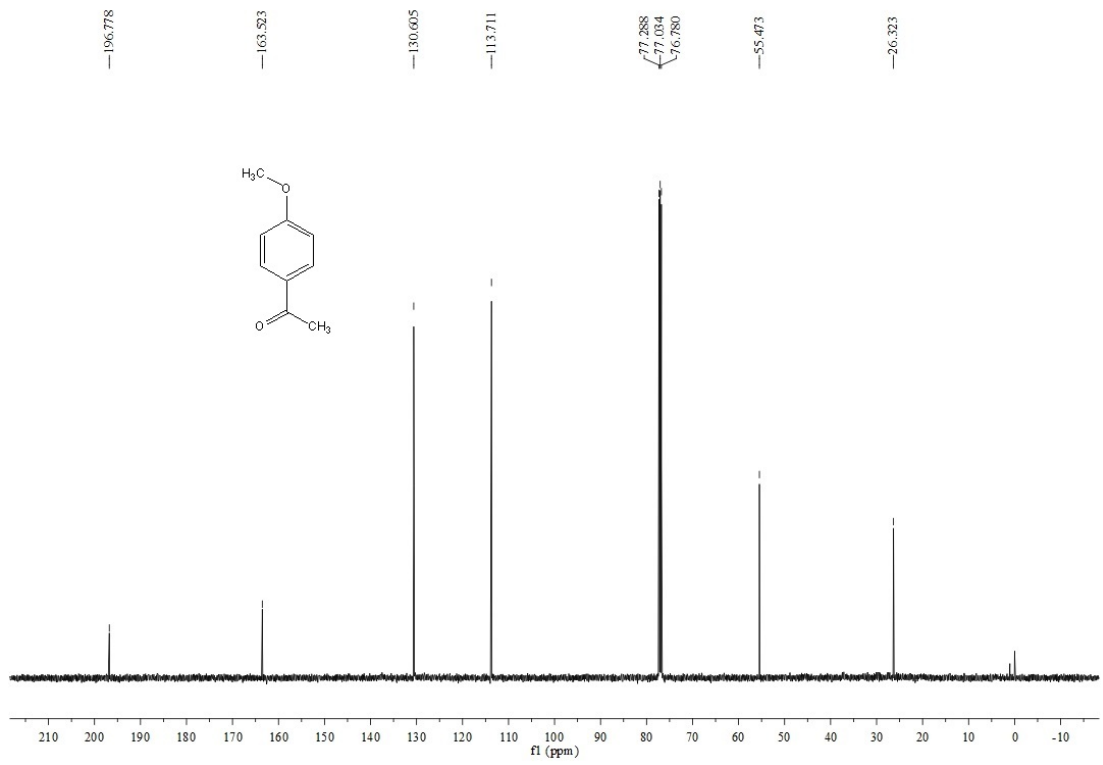
^{1}H NMR of **15b** in $CDCl_3$



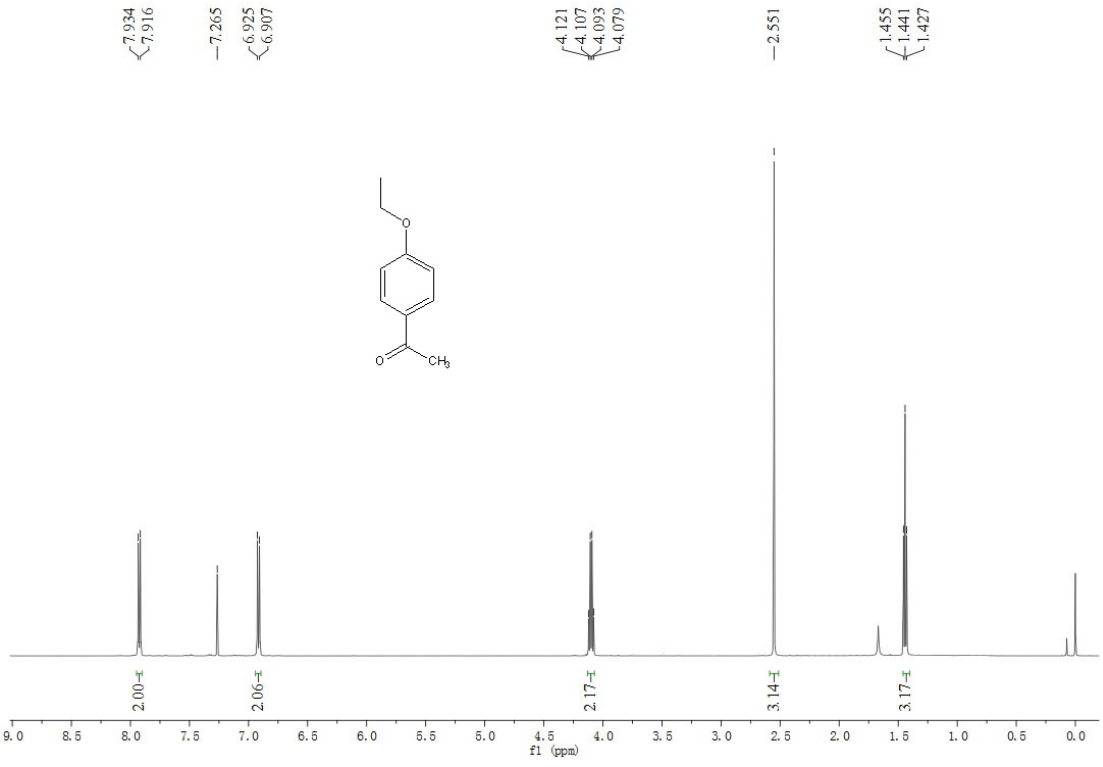
^{13}C NMR of **15b** in $CDCl_3$



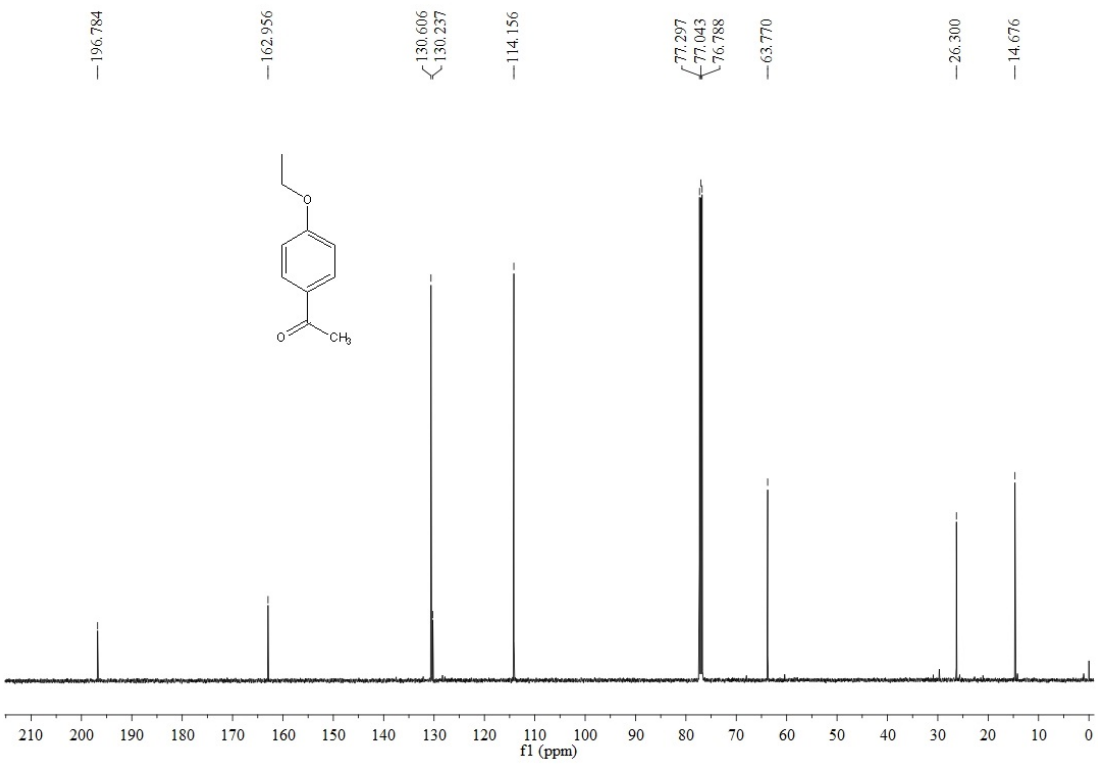
^{1}H NMR of **18a** in $CDCl_3$



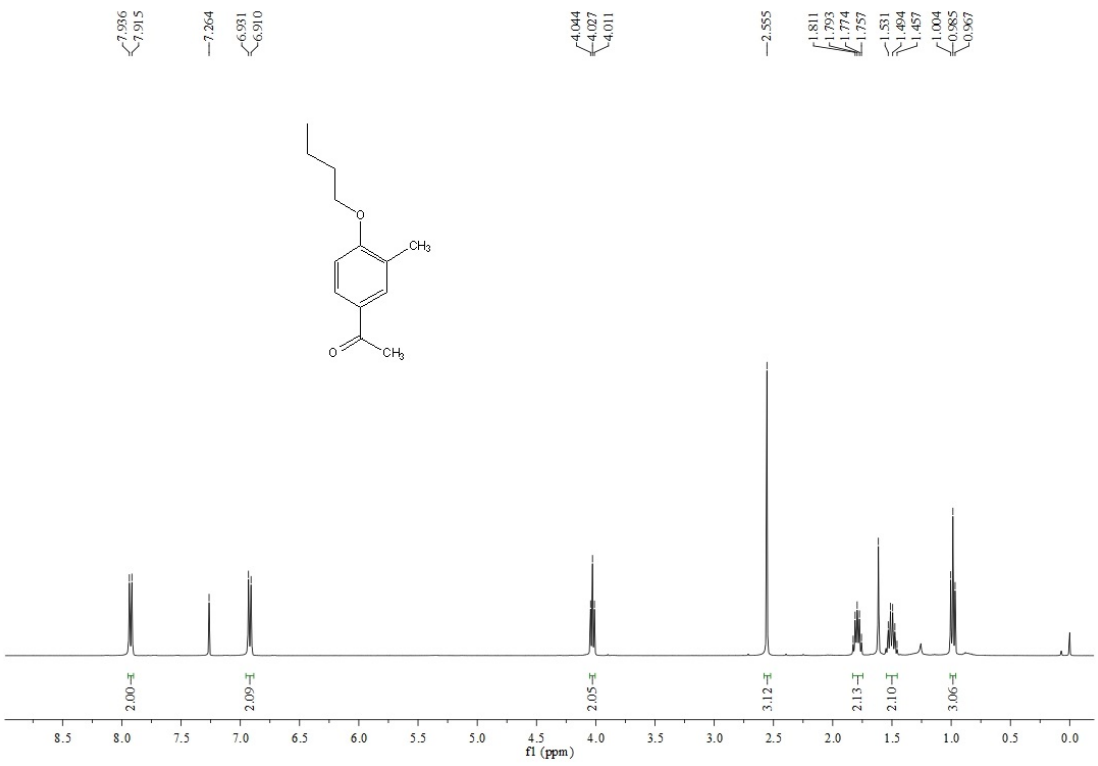
^{13}C NMR of **18a** in $CDCl_3$



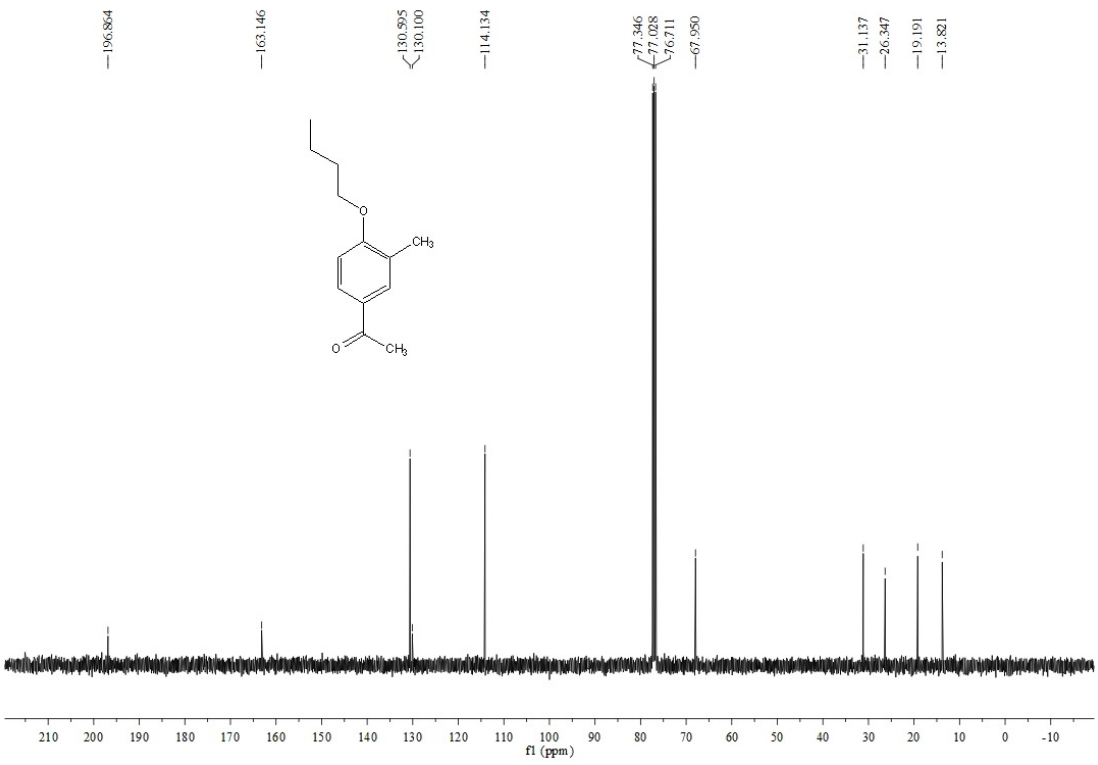
^{1}H NMR of **18b** in $CDCl_3$



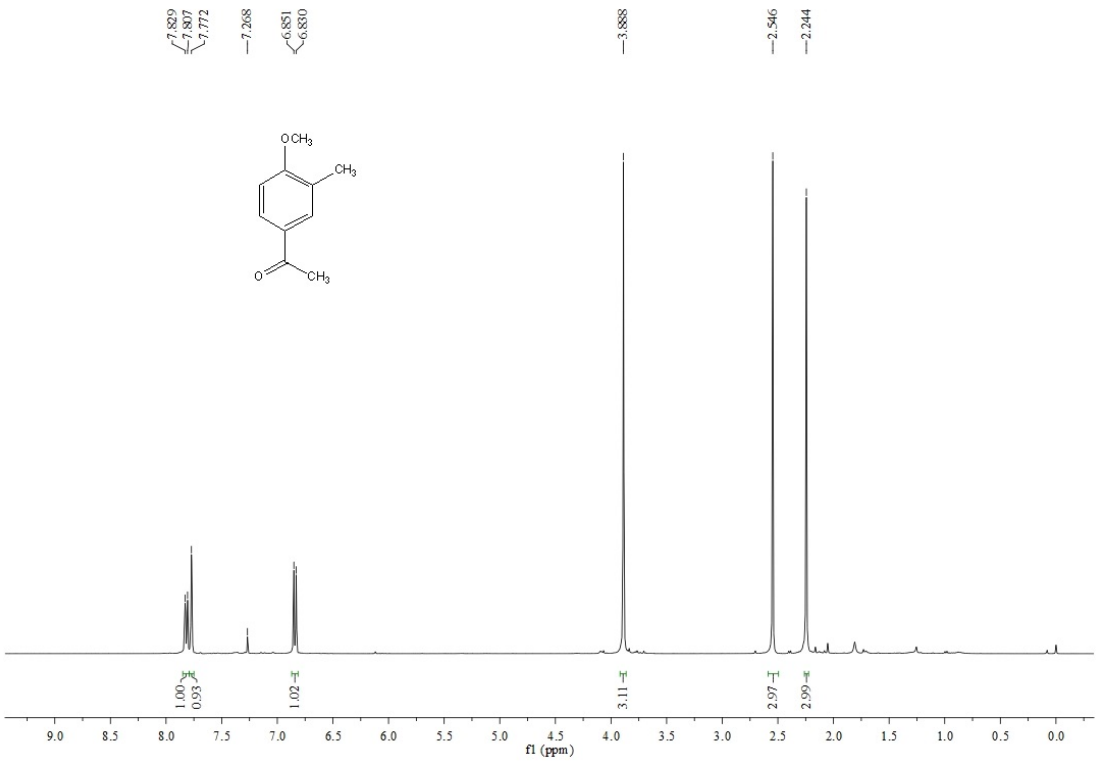
^{13}C NMR of **18b** in $CDCl_3$



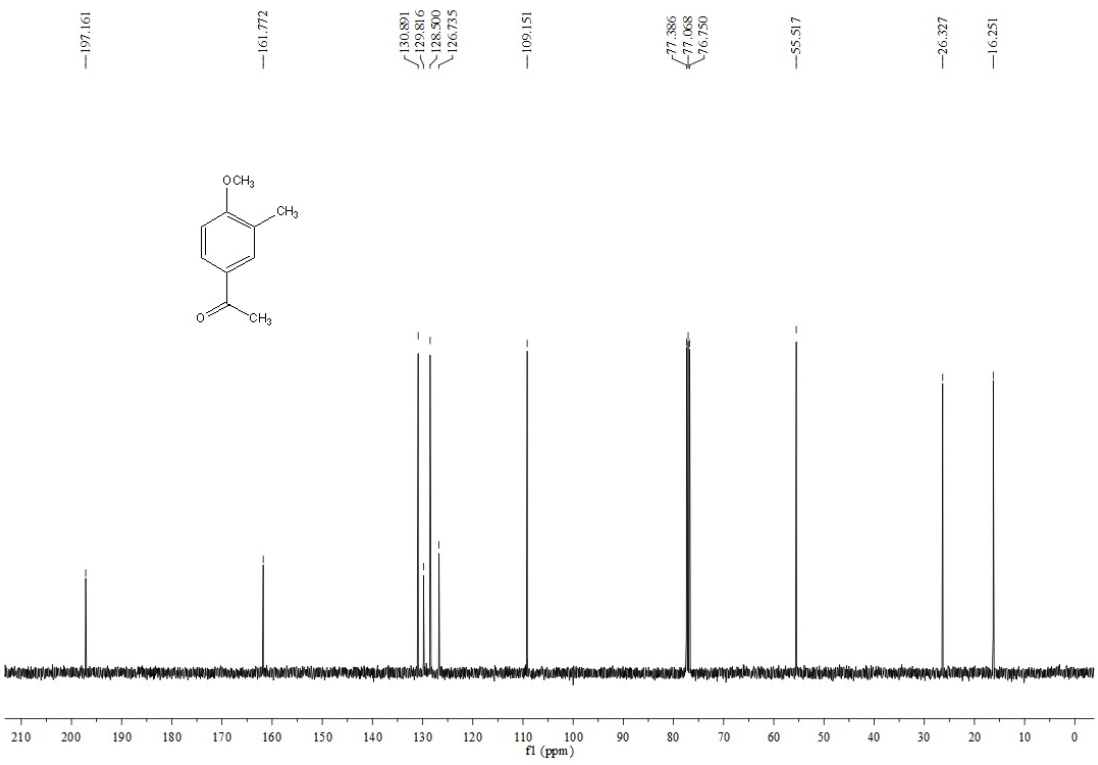
^{1}H NMR of **18c** in $CDCl_3$



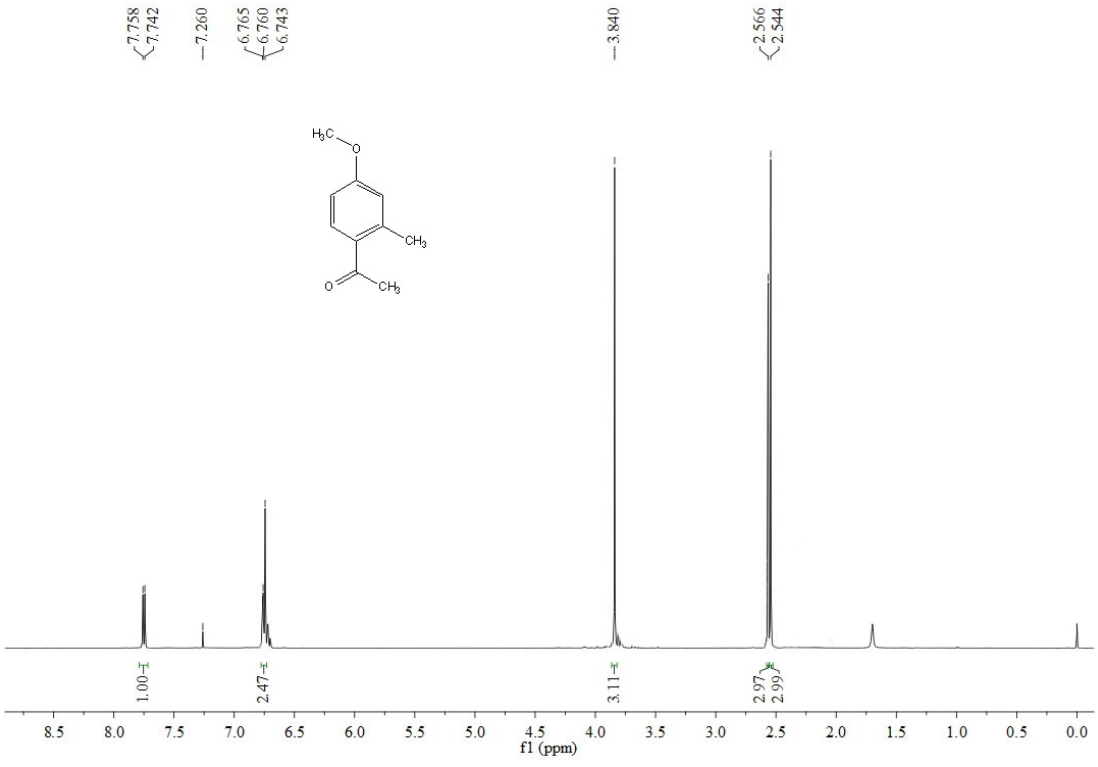
^{13}C NMR of **18c** in $CDCl_3$



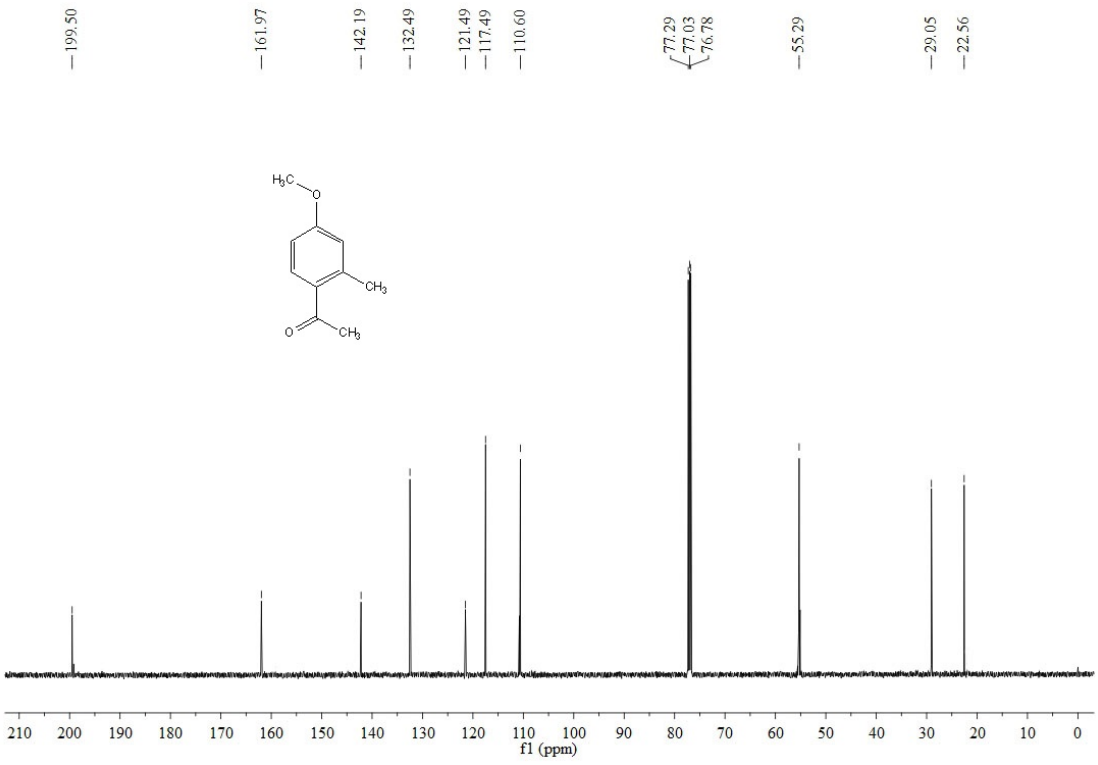
^{1}H NMR of **18d** in $CDCl_3$



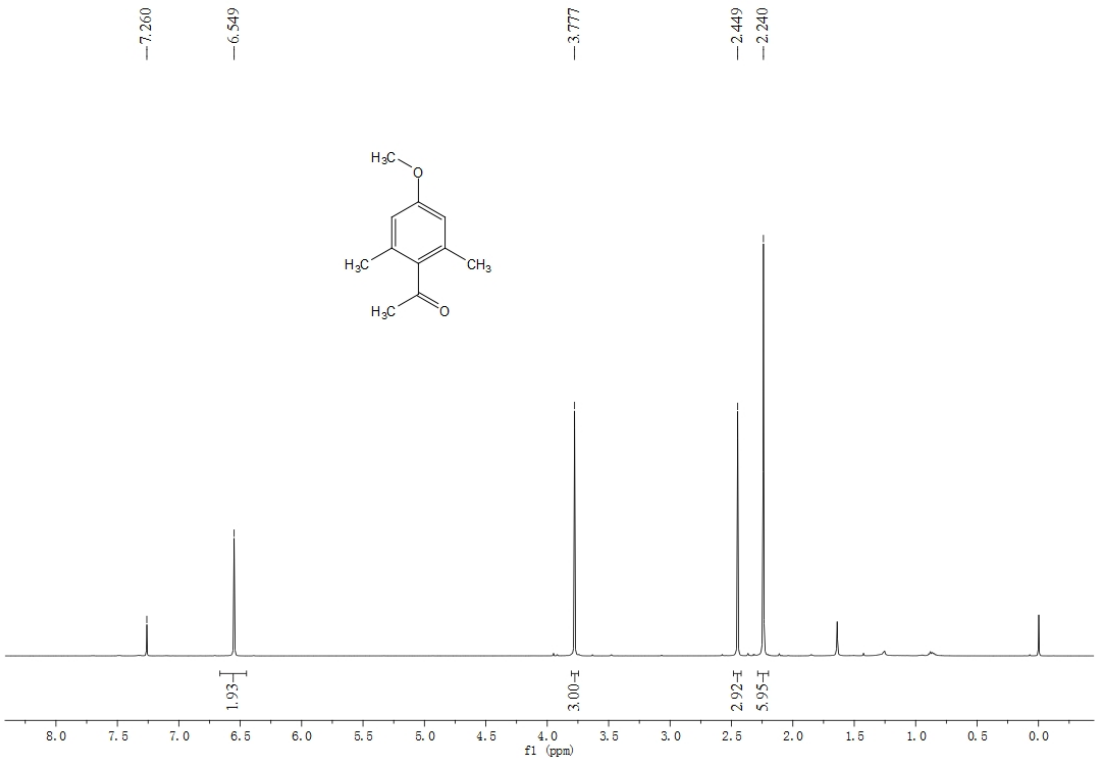
^{13}C NMR of **18d** in $CDCl_3$



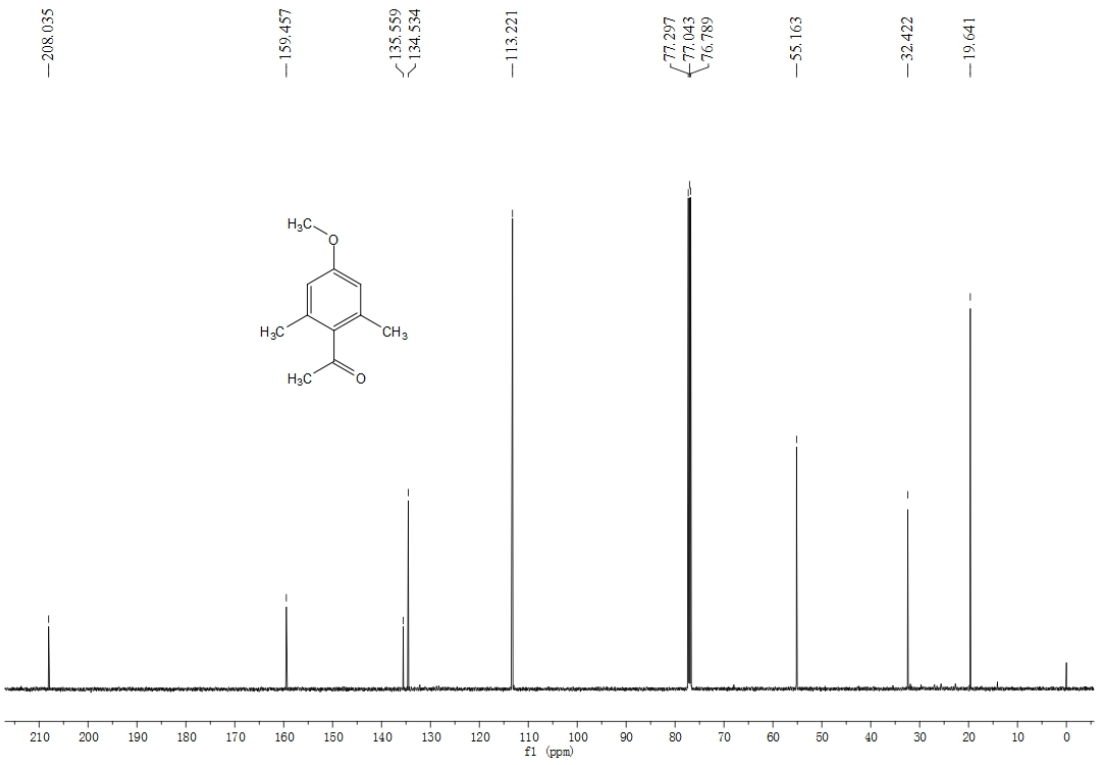
^{1}H NMR of **18e** in $CDCl_3$



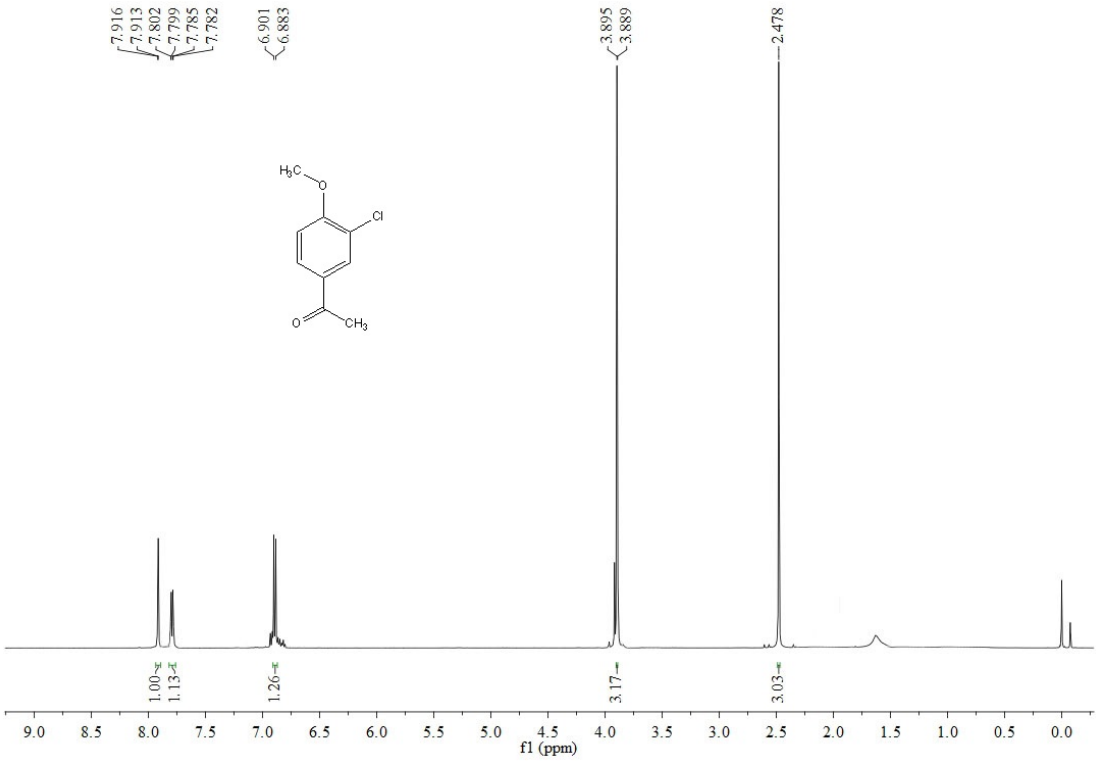
^{13}C NMR of **18e** in $CDCl_3$



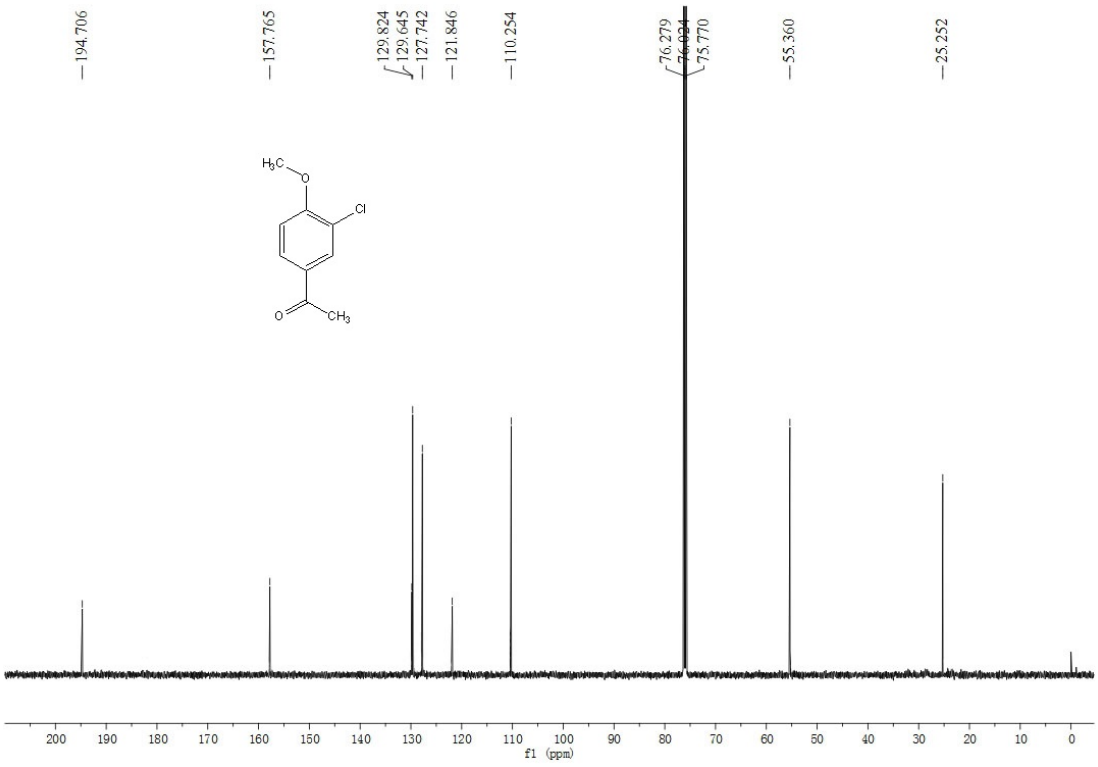
^{1}H NMR of **18f** in $CDCl_3$



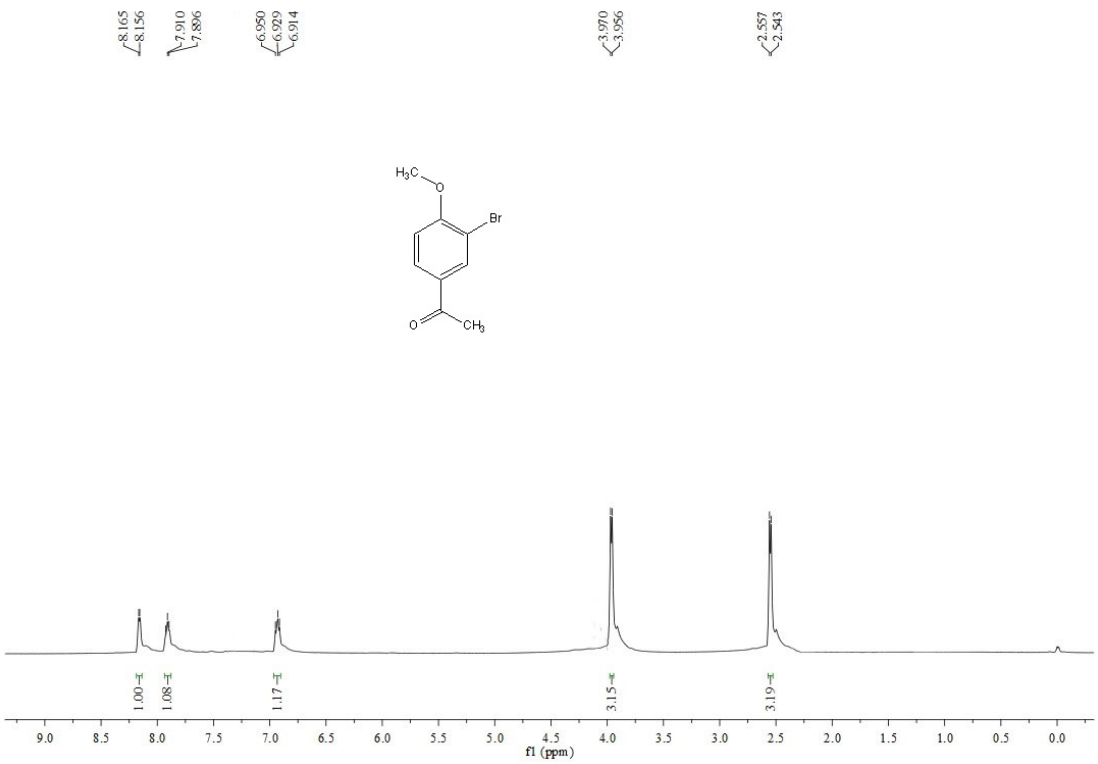
^{13}C NMR of **18f** in $CDCl_3$



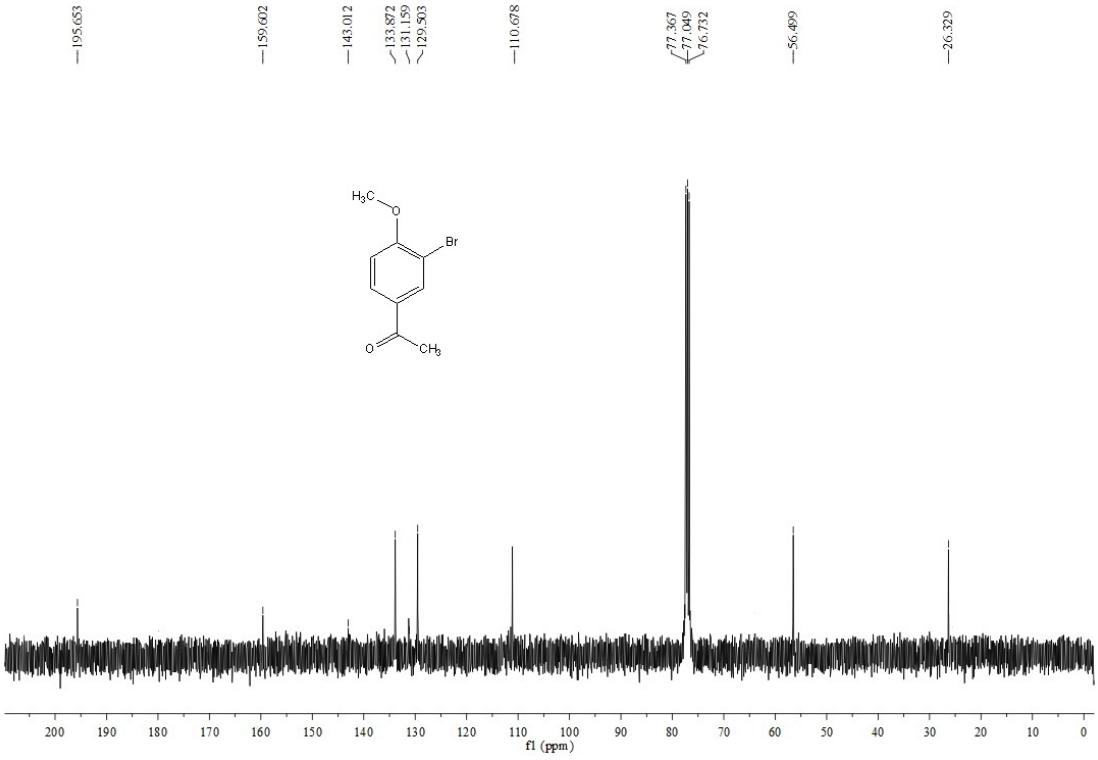
^{1}H NMR of **18g** in $CDCl_3$



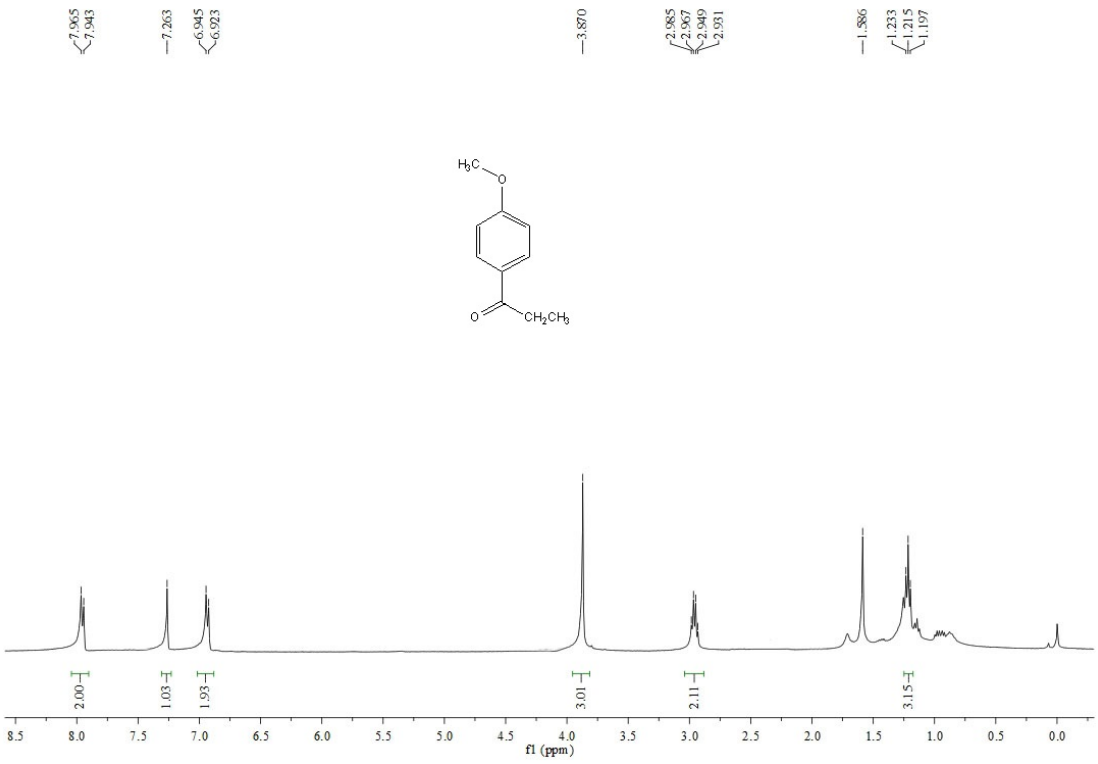
^{13}C NMR of **18g** in $CDCl_3$



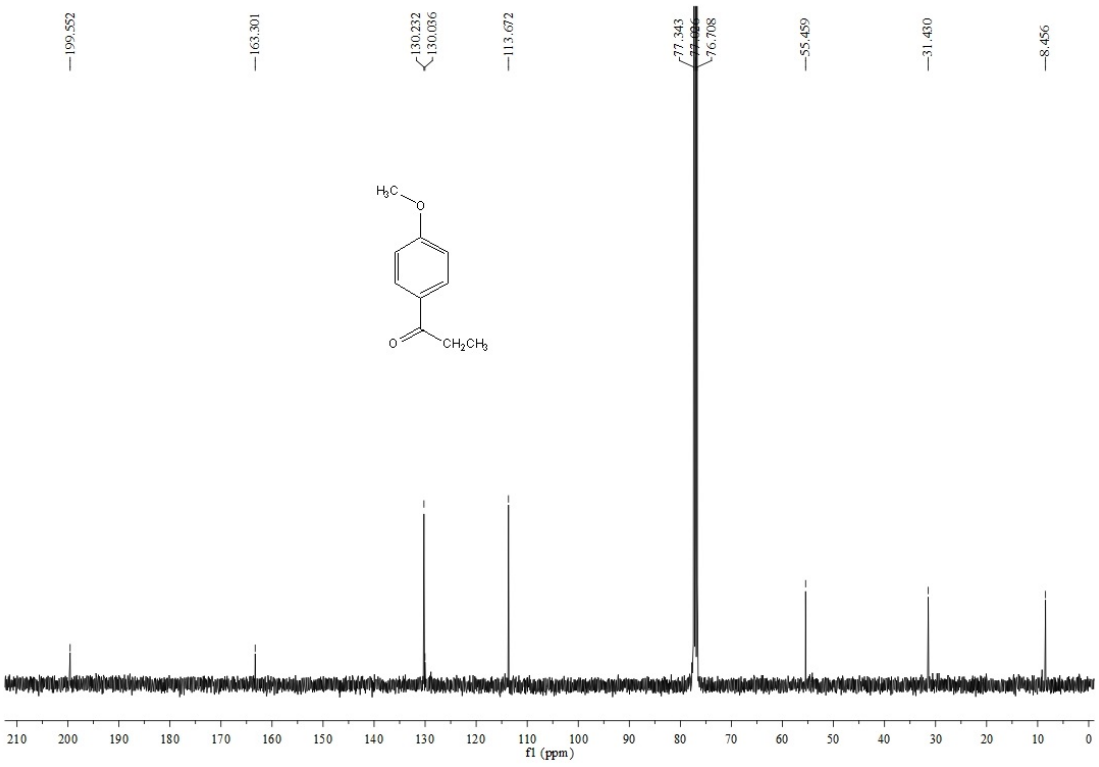
^{1}H NMR of **18h** in $CDCl_3$



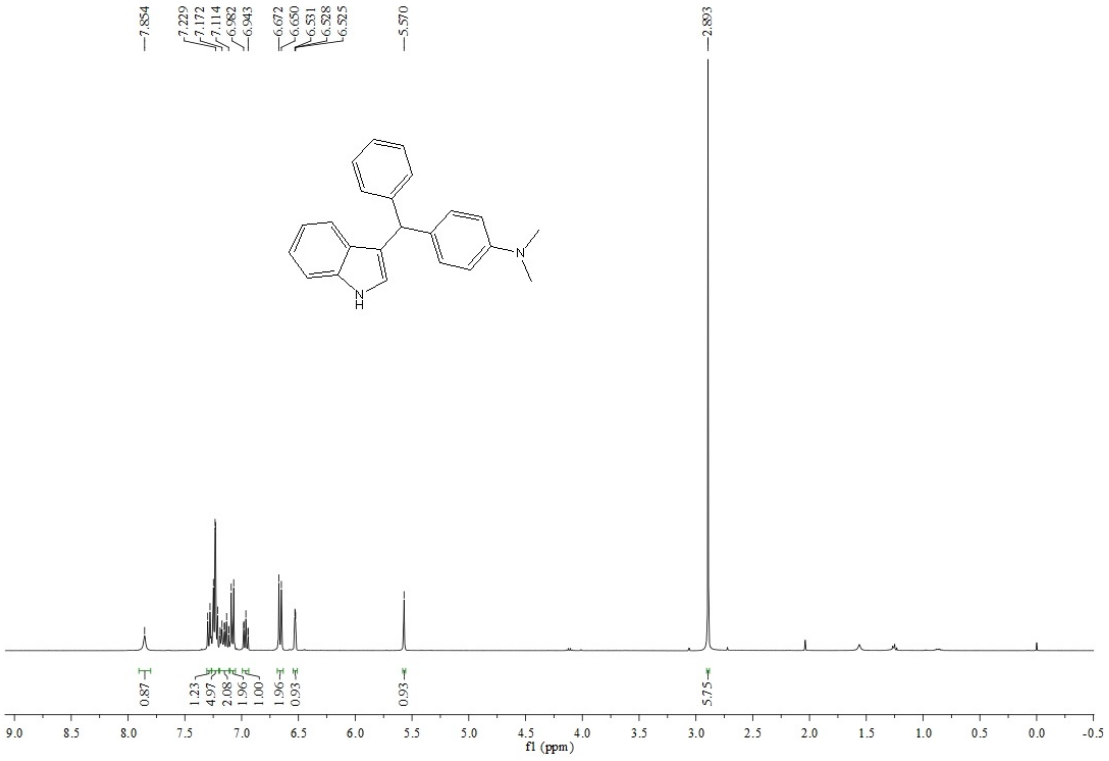
^{13}C NMR of **18h** in $CDCl_3$



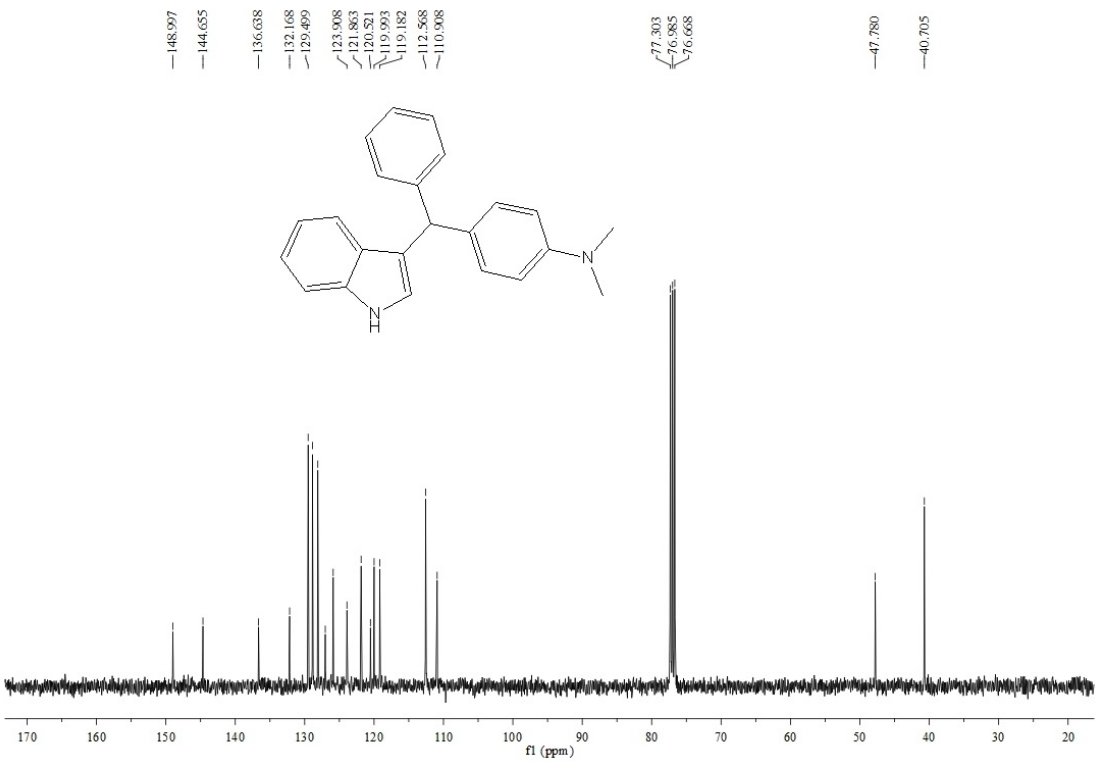
^{1}H NMR of **18i** in $CDCl_3$



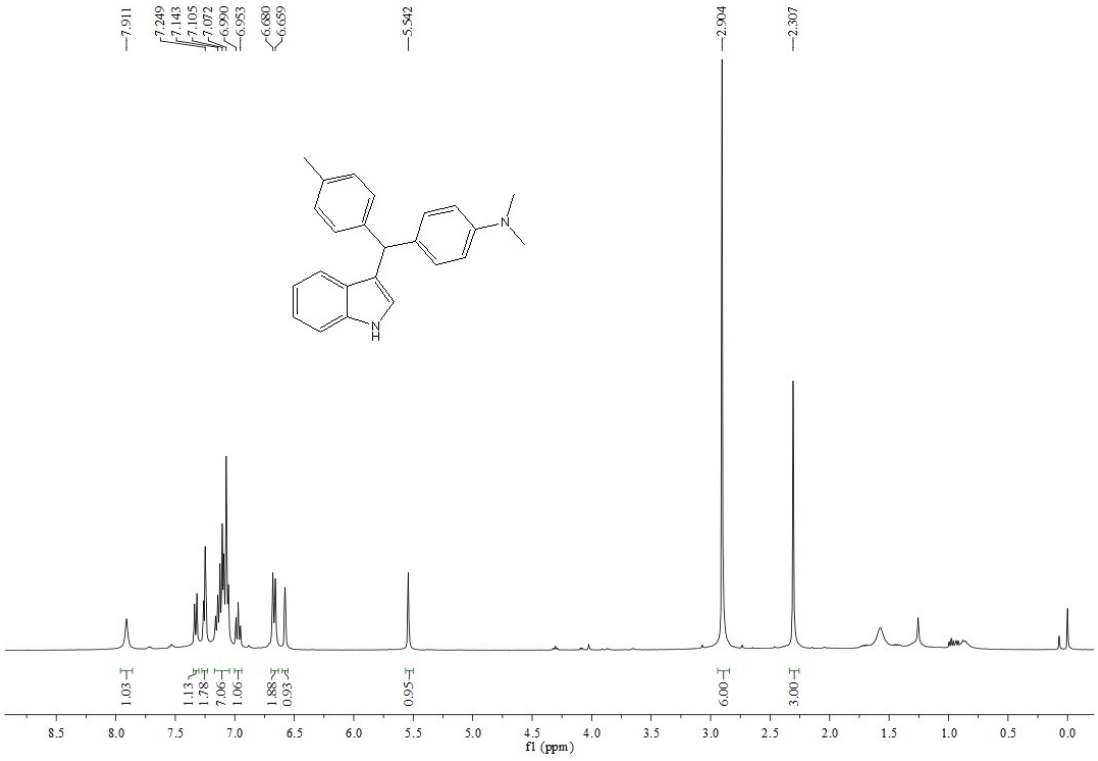
^{13}C NMR of **18i** in $CDCl_3$



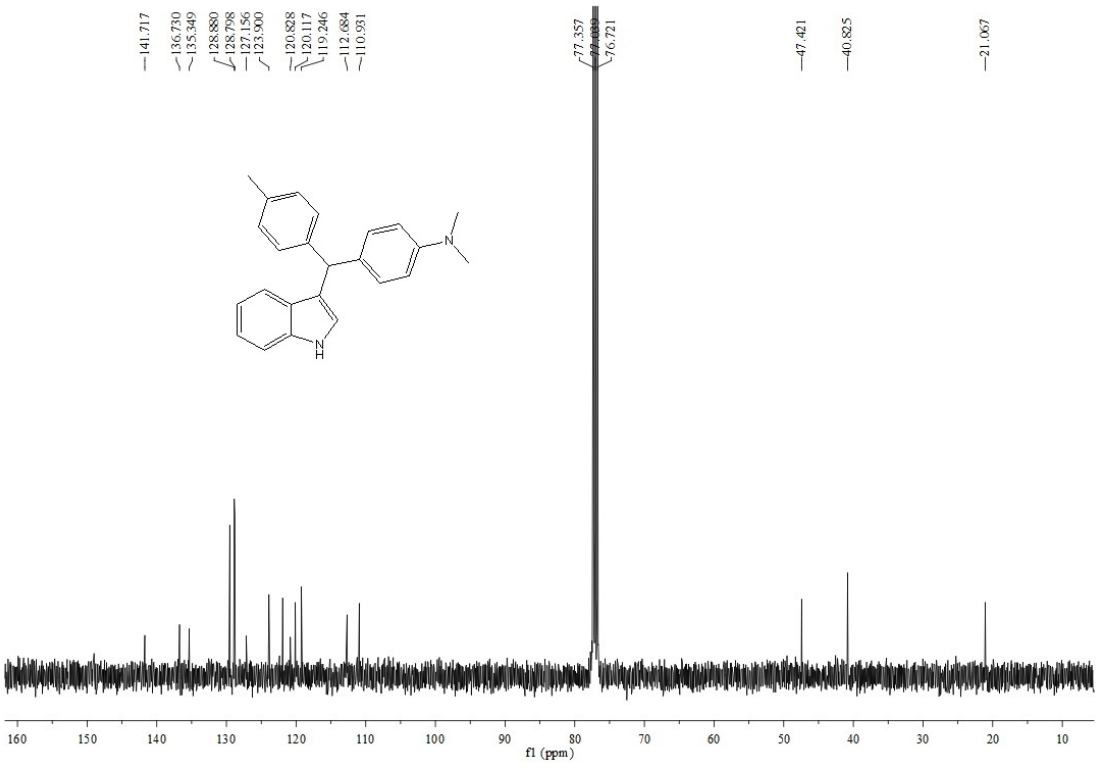
^{1}H NMR of **21a** in $CDCl_3$



^{13}C NMR of **21a** in $CDCl_3$



^{1}H NMR of **21b** in $CDCl_3$



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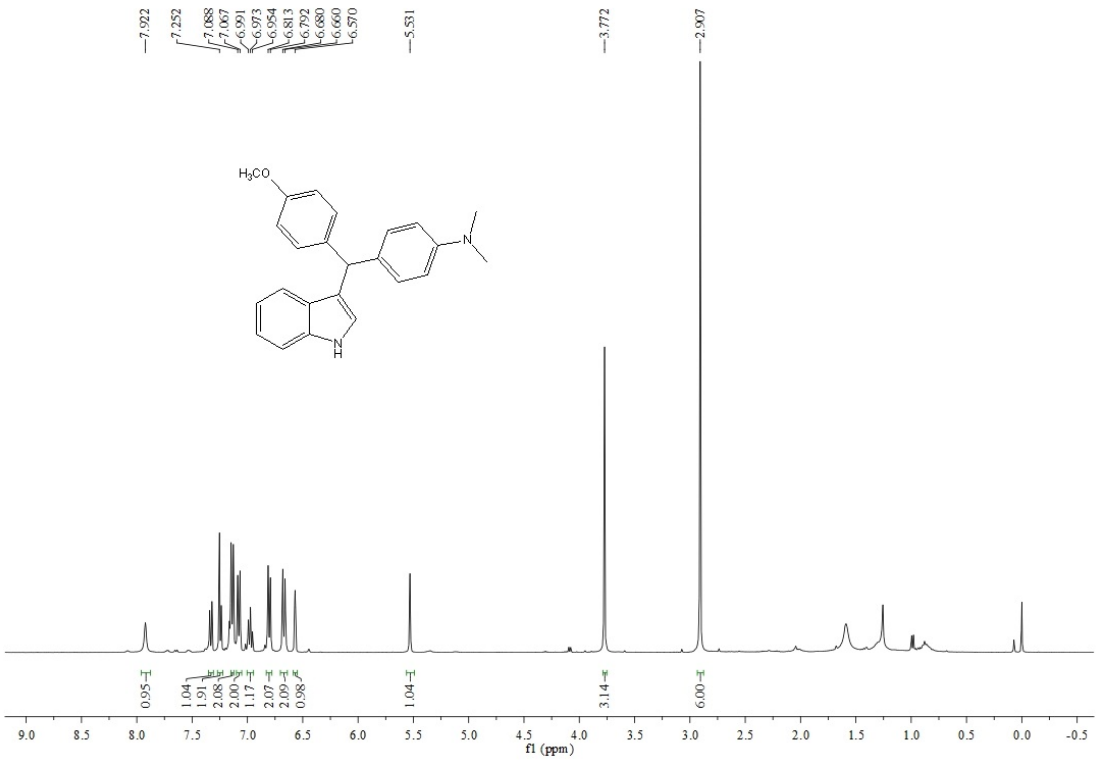

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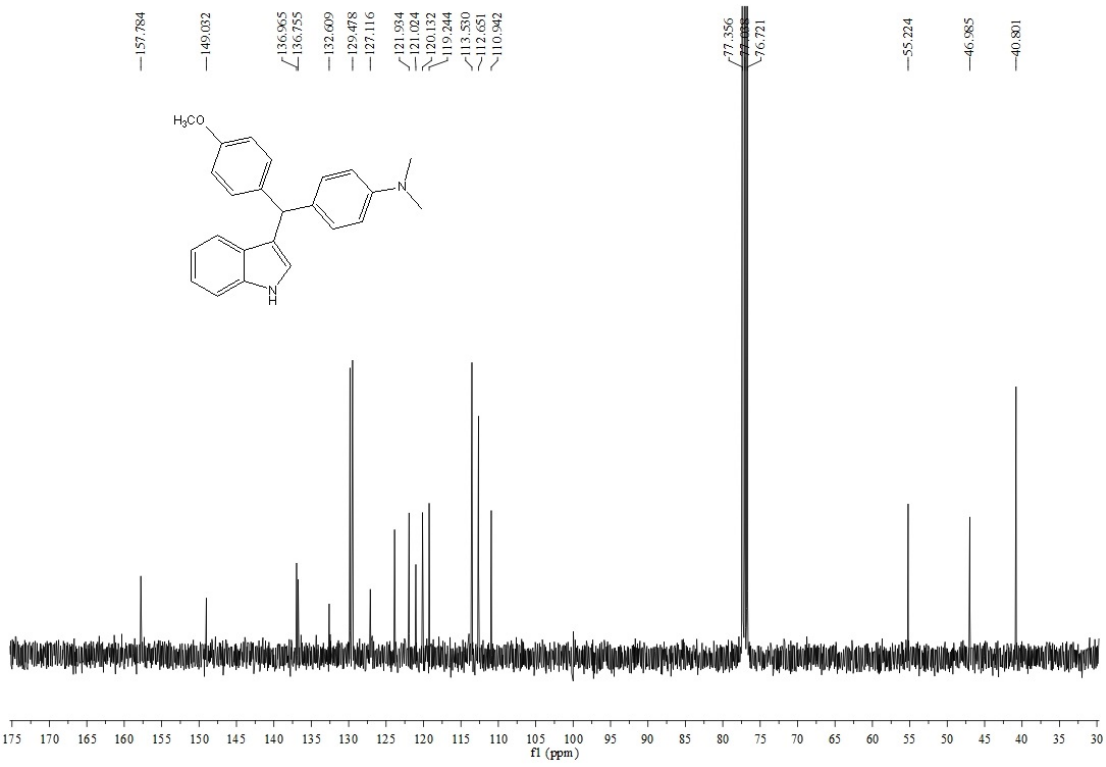
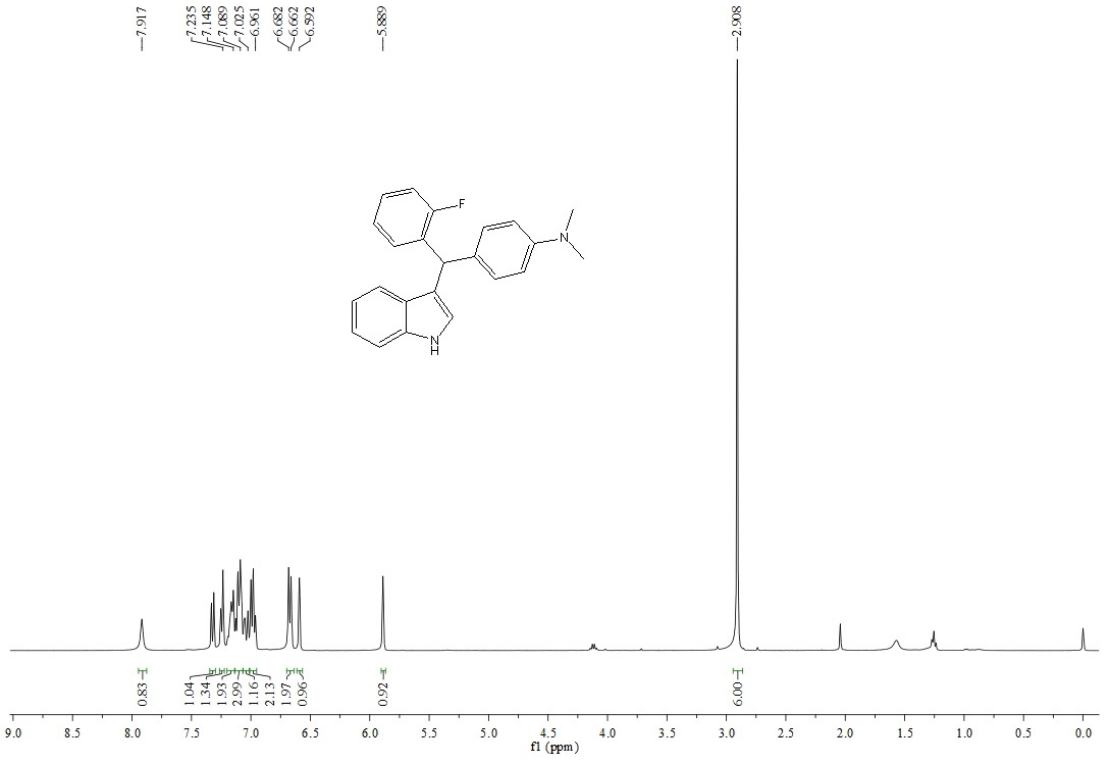
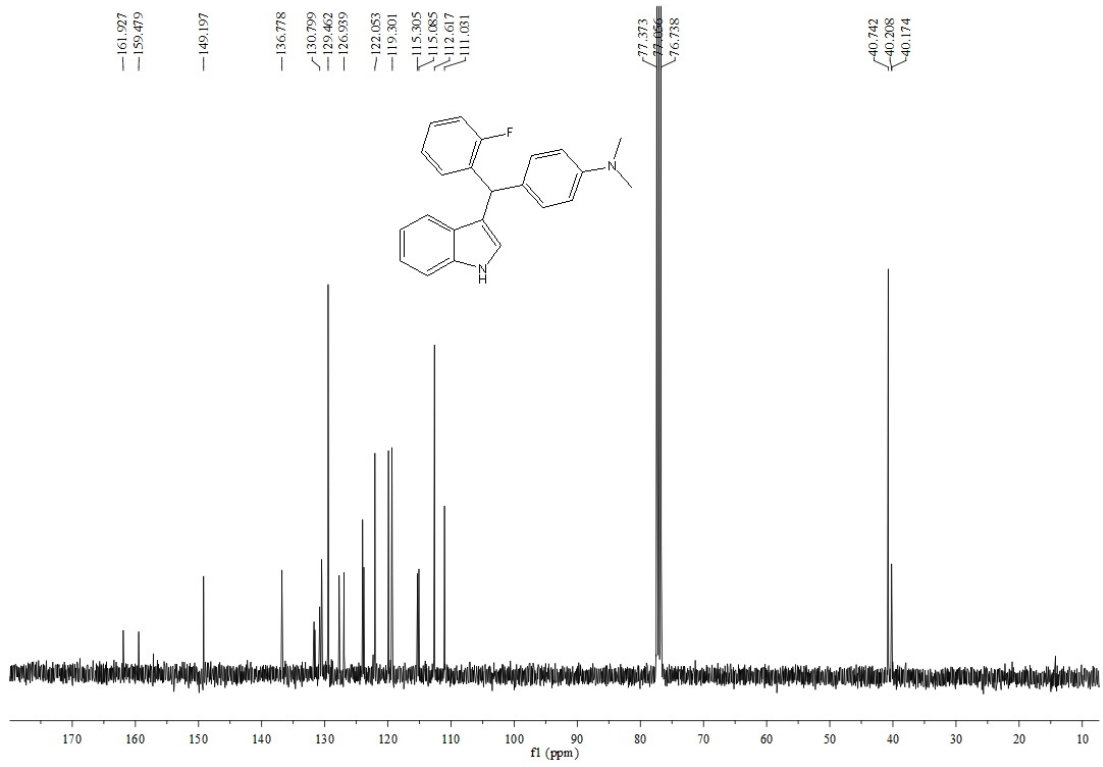


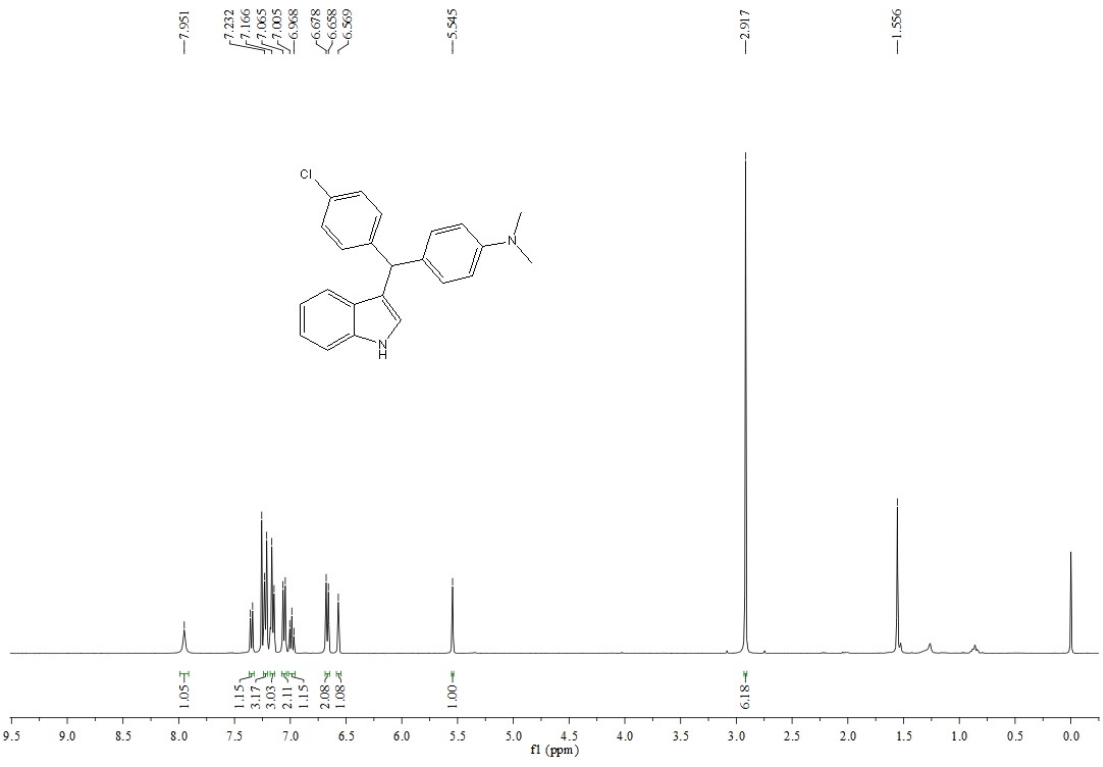
^{13}C NMR of **21c** in $CDCl_3$



^{1}H NMR of **21d** in $CDCl_3$



^{13}C NMR of **21d** in $CDCl_3$



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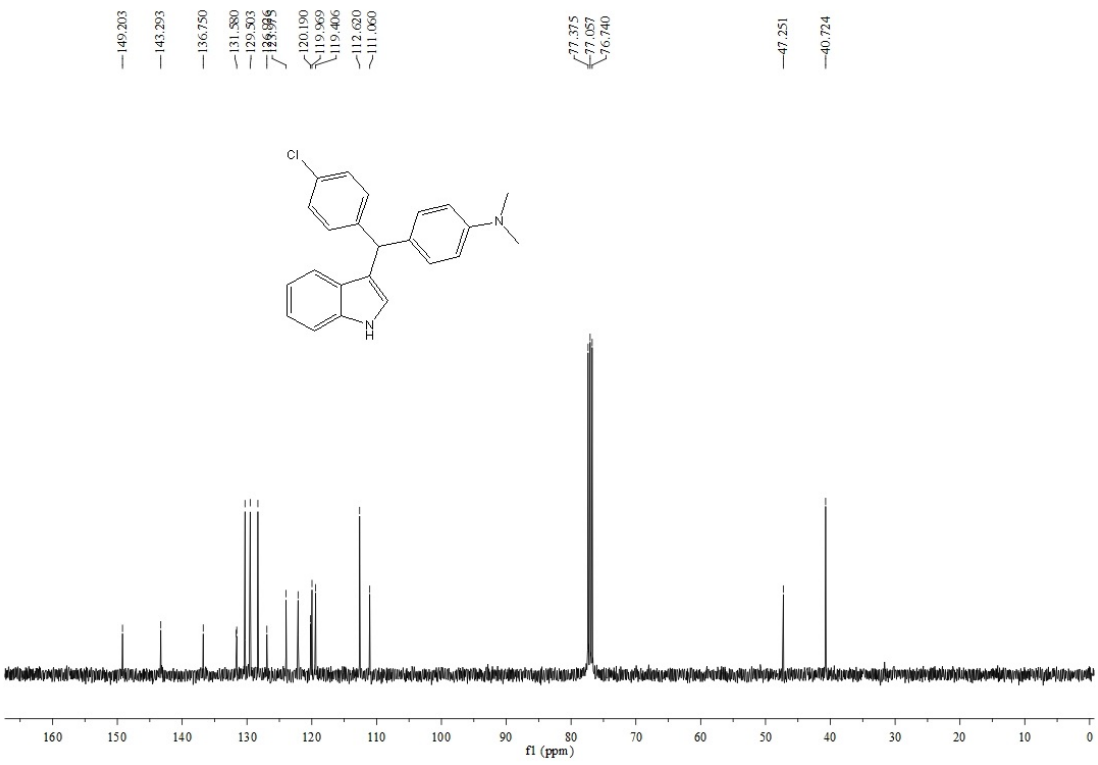

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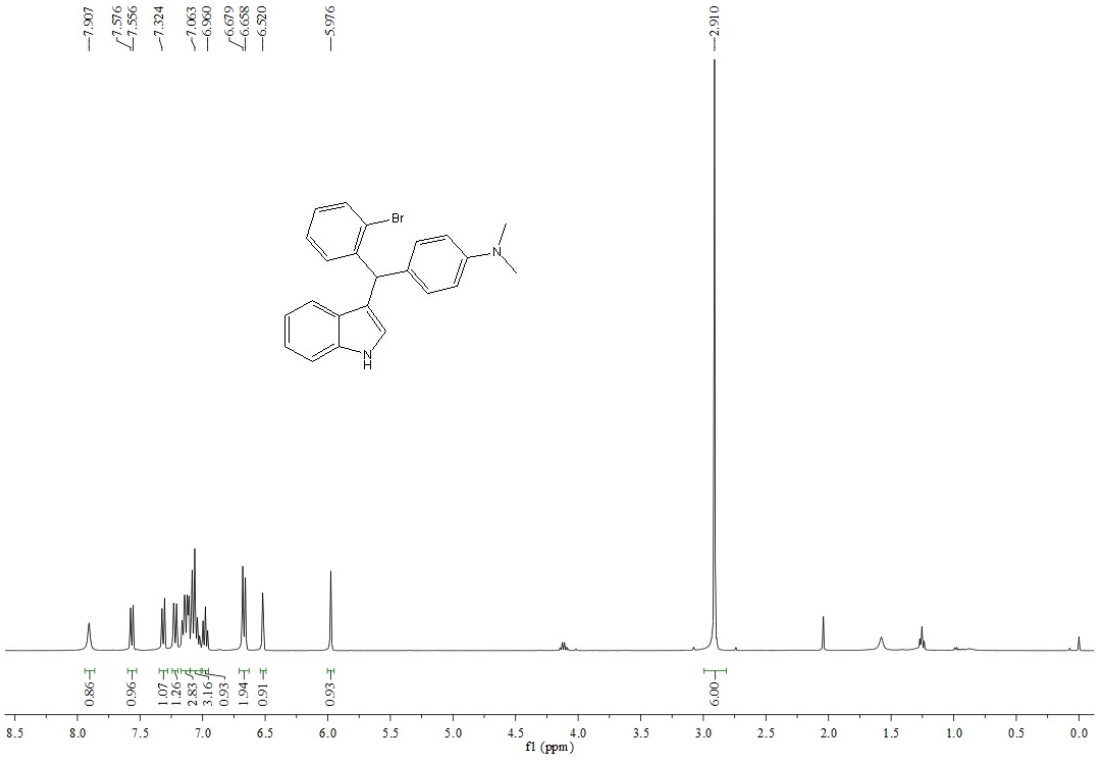
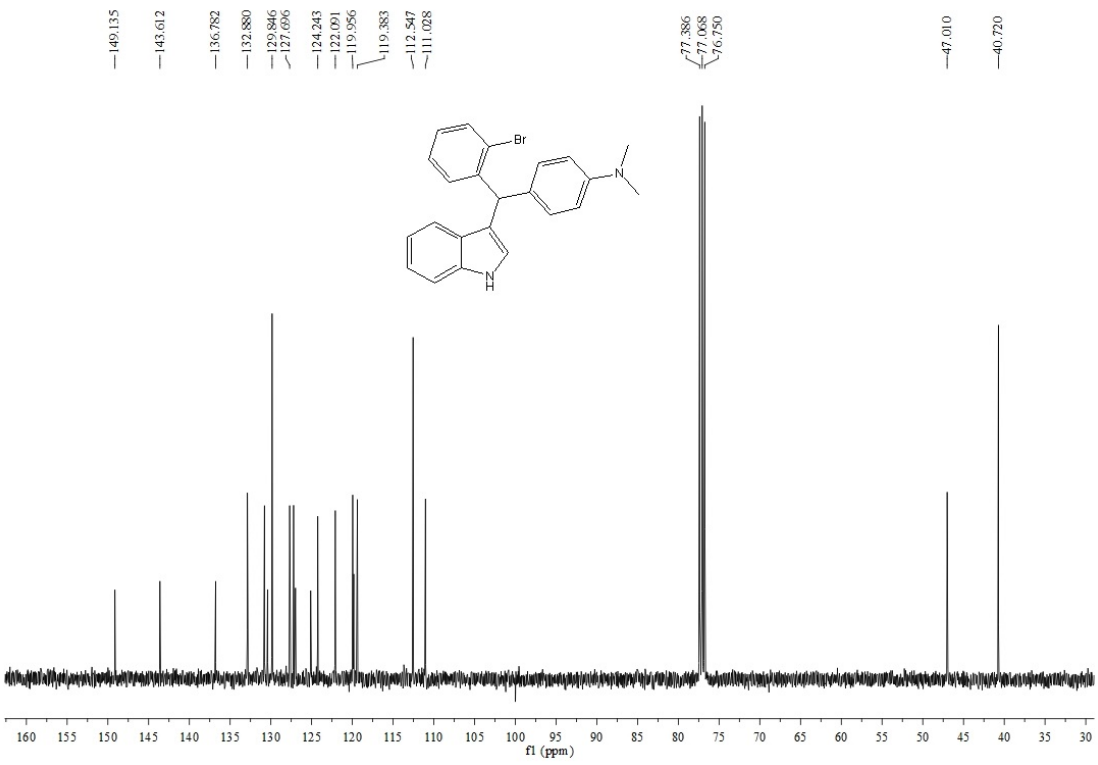
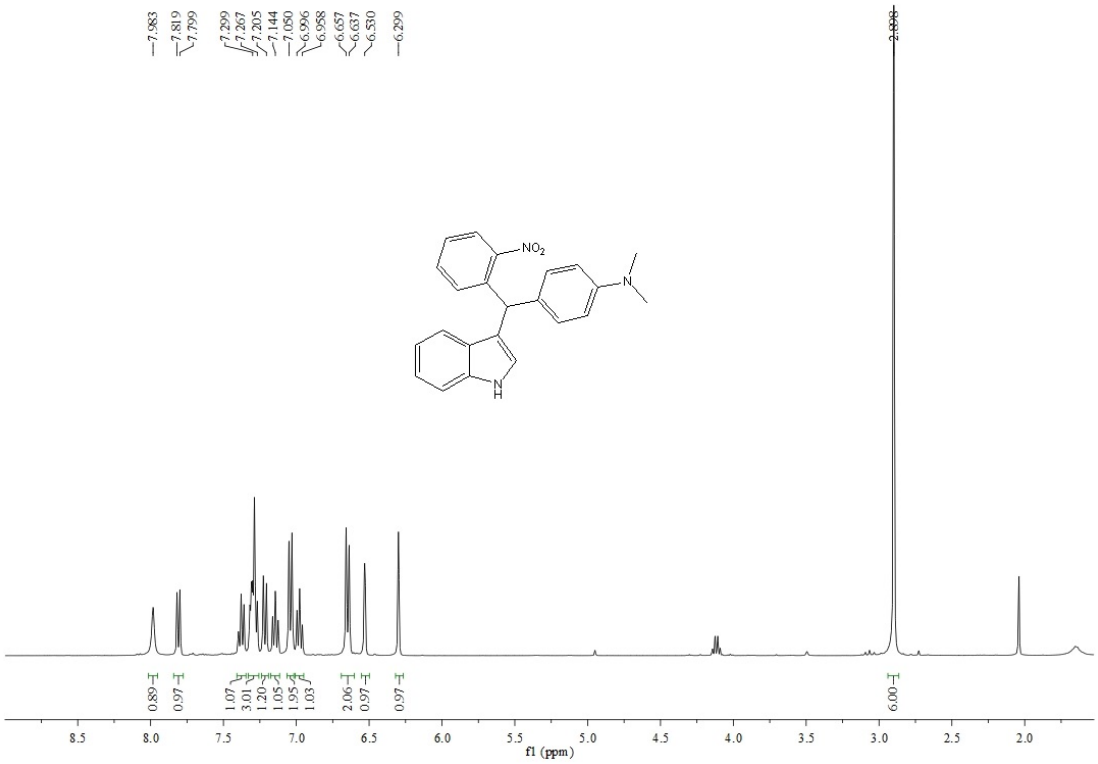


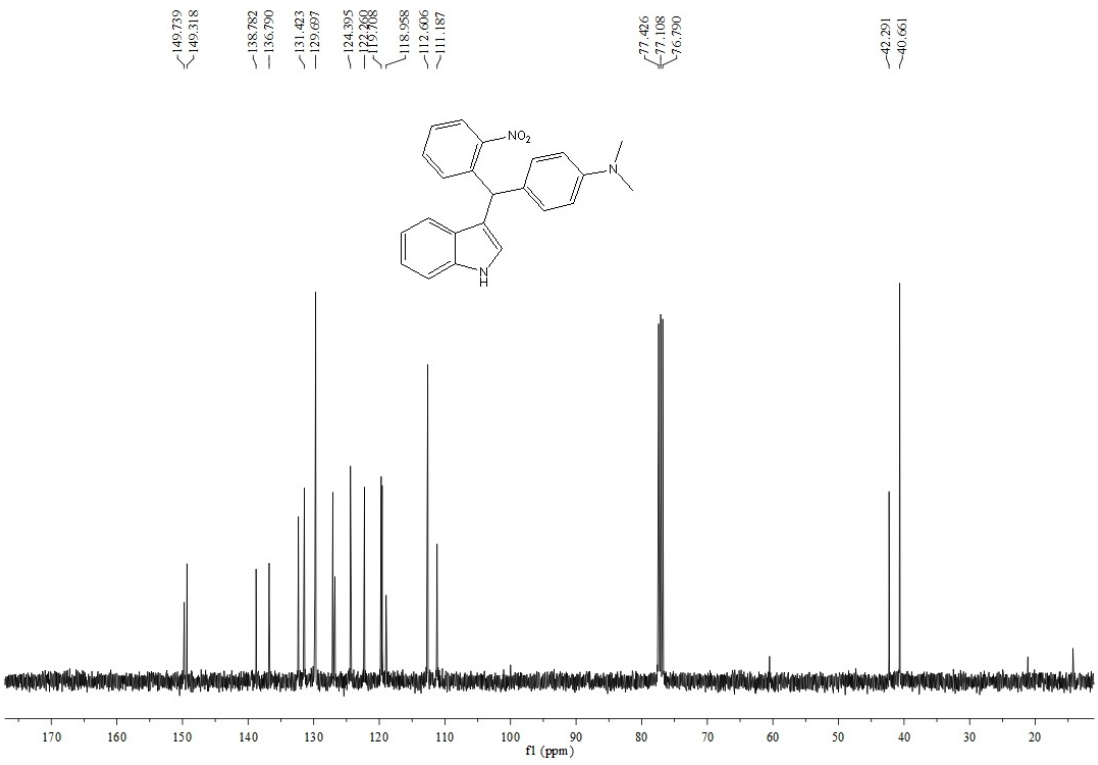
^{1}H NMR of **21f** in $CDCl_3$



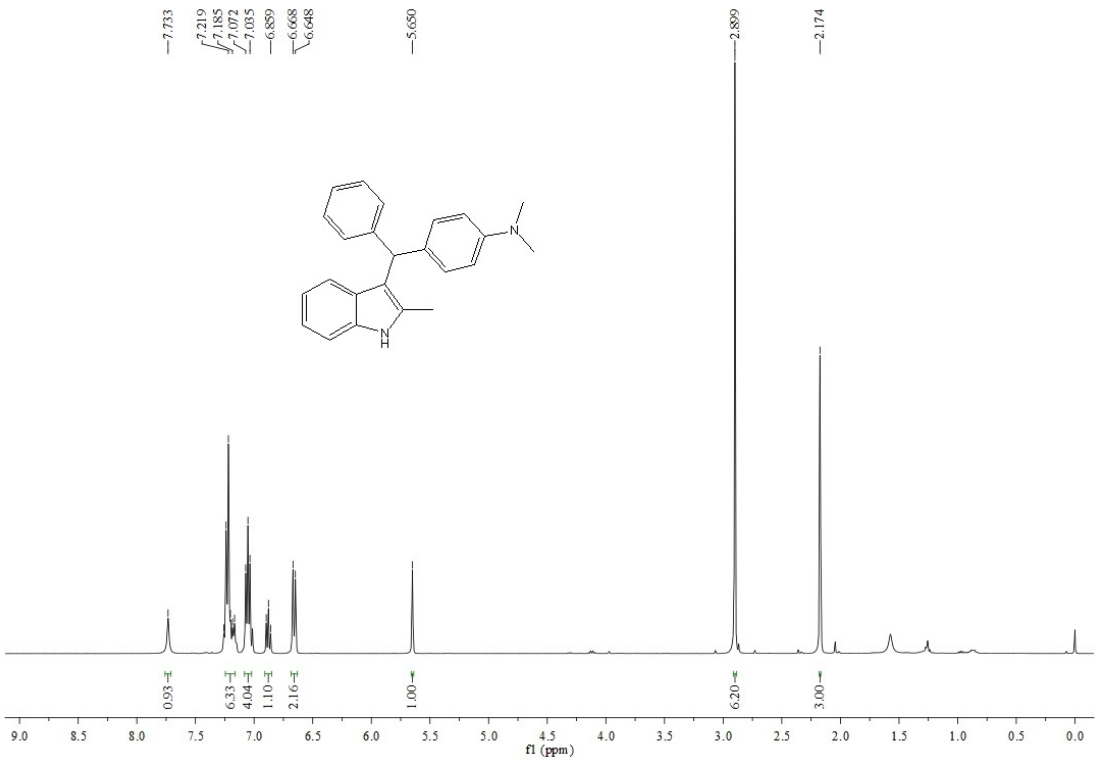
^{13}C NMR of **21f** in $CDCl_3$



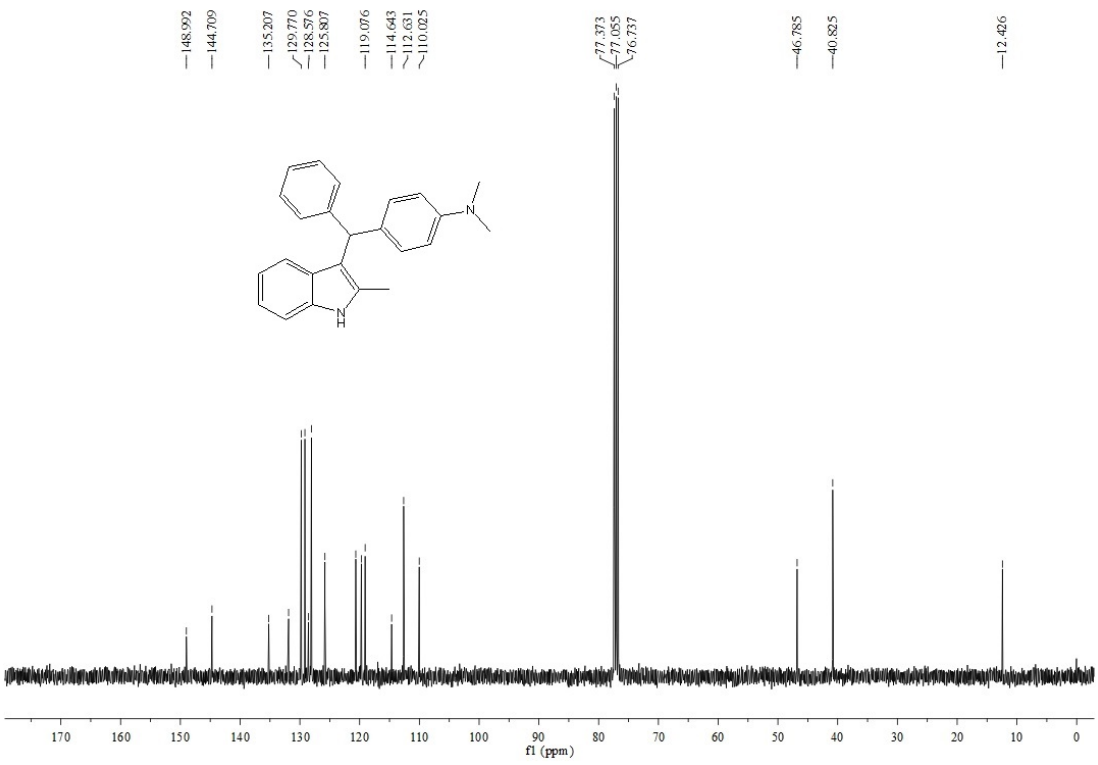
^{1}H NMR of **21g** in $CDCl_3$



^{13}C NMR of **21g** in $CDCl_3$



^{1}H NMR of **21h** in $CDCl_3$



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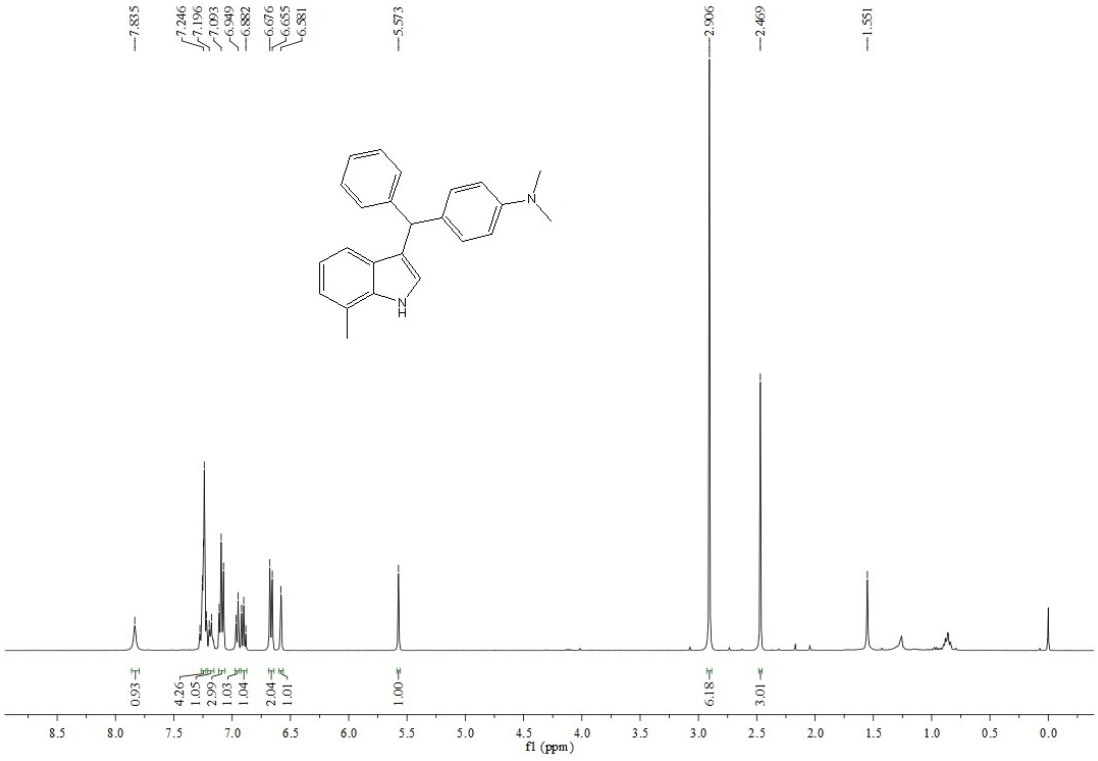

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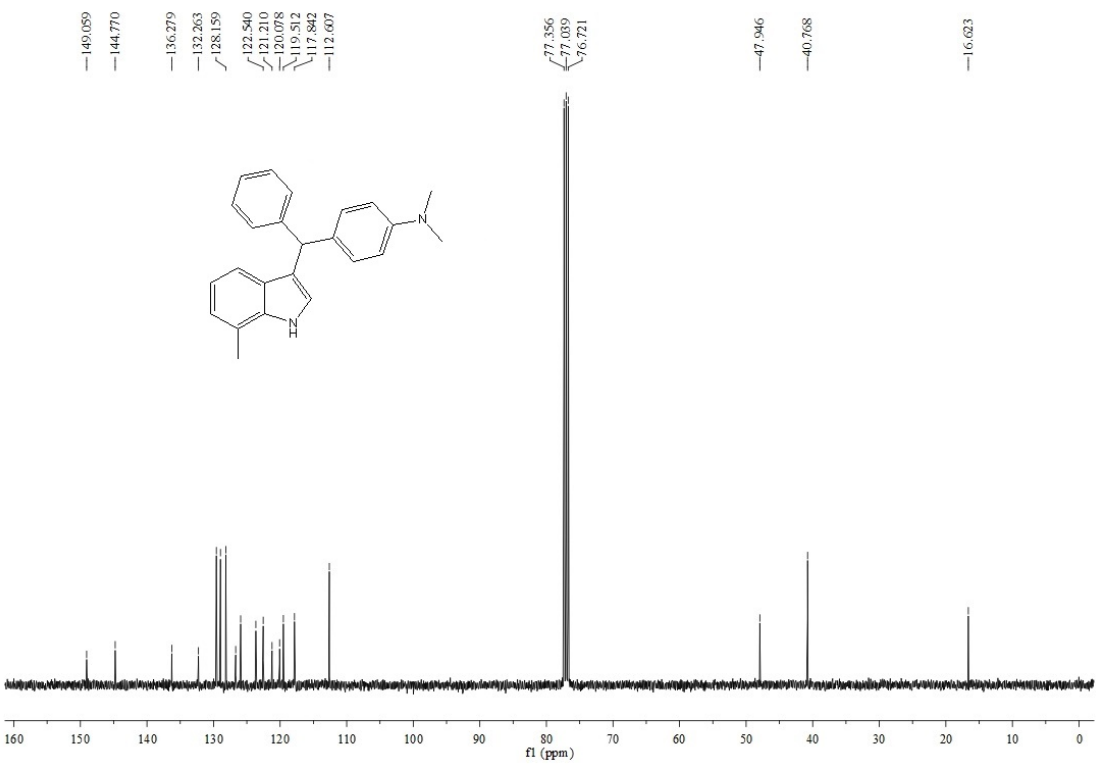
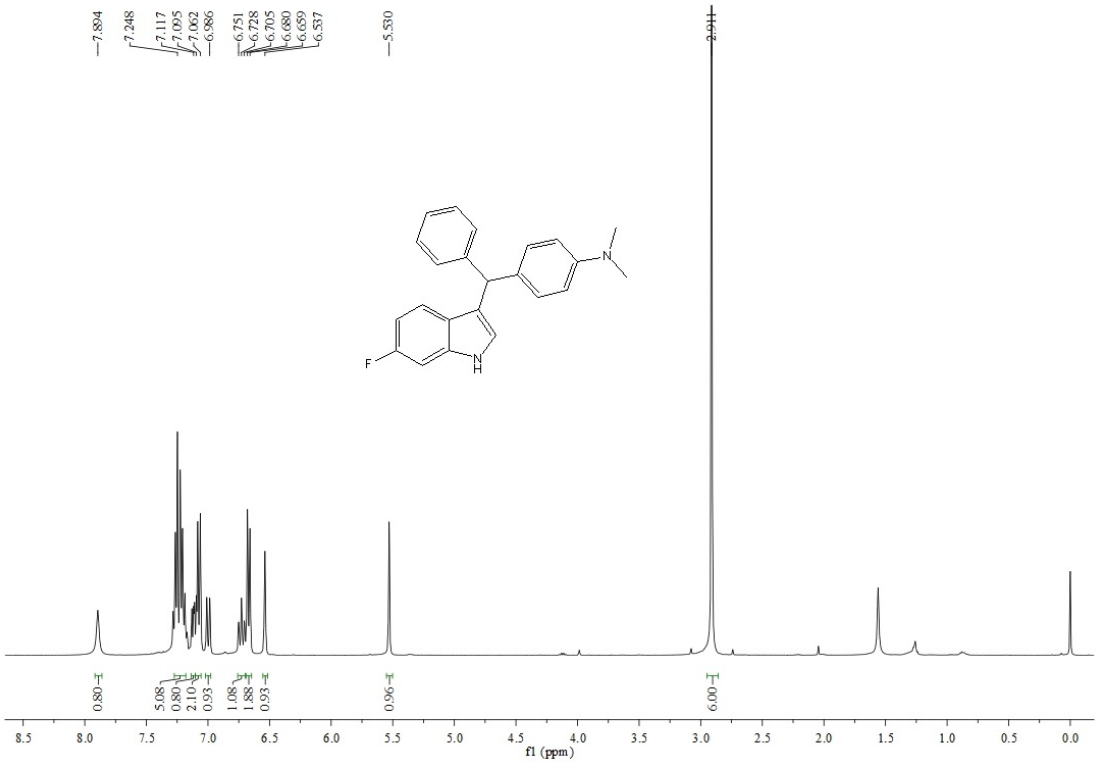


^{13}C NMR of **21i** in $CDCl_3$



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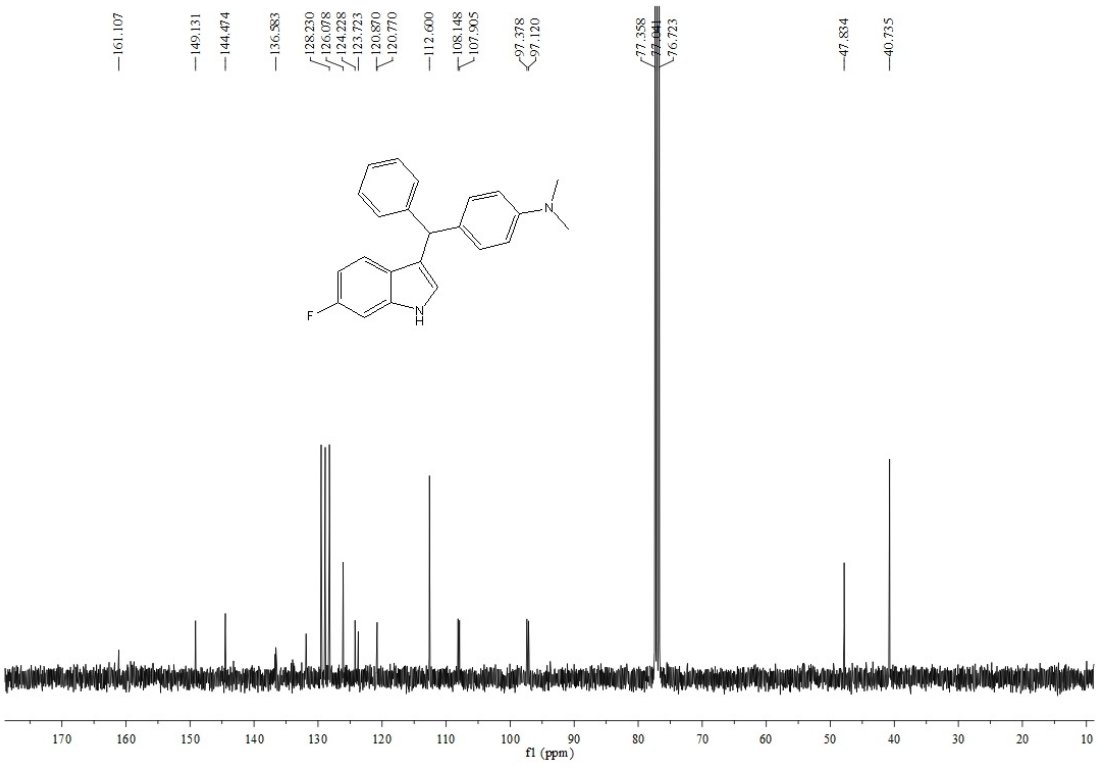

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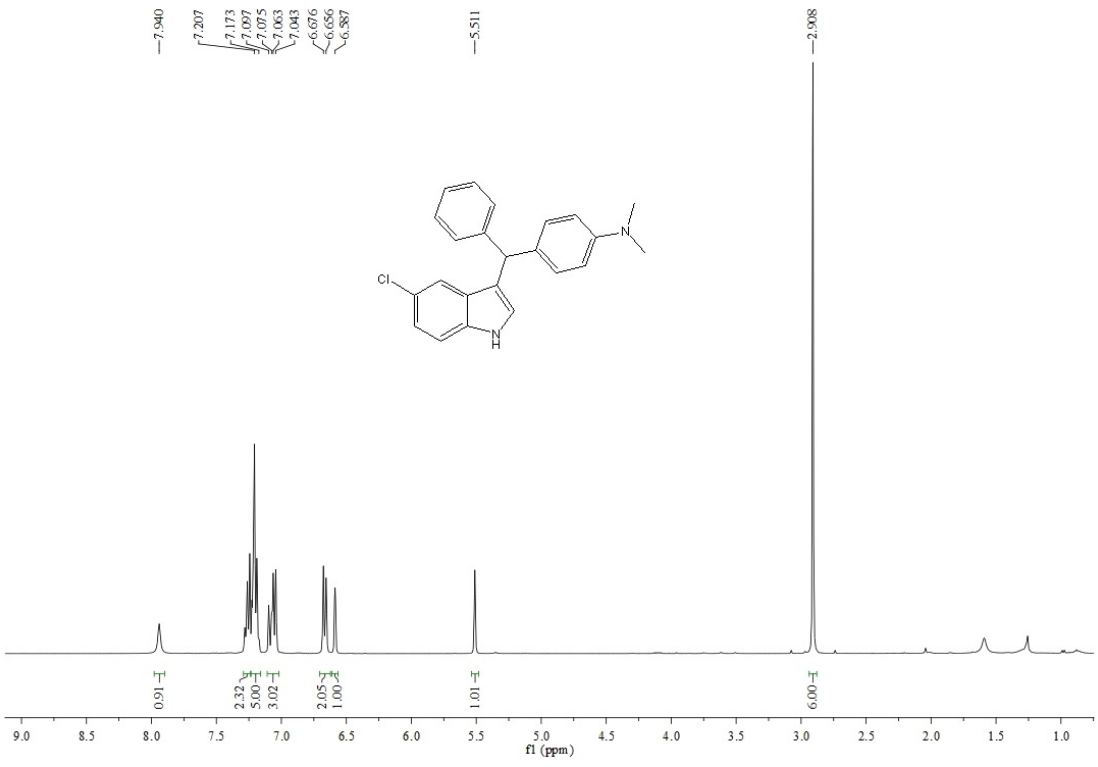
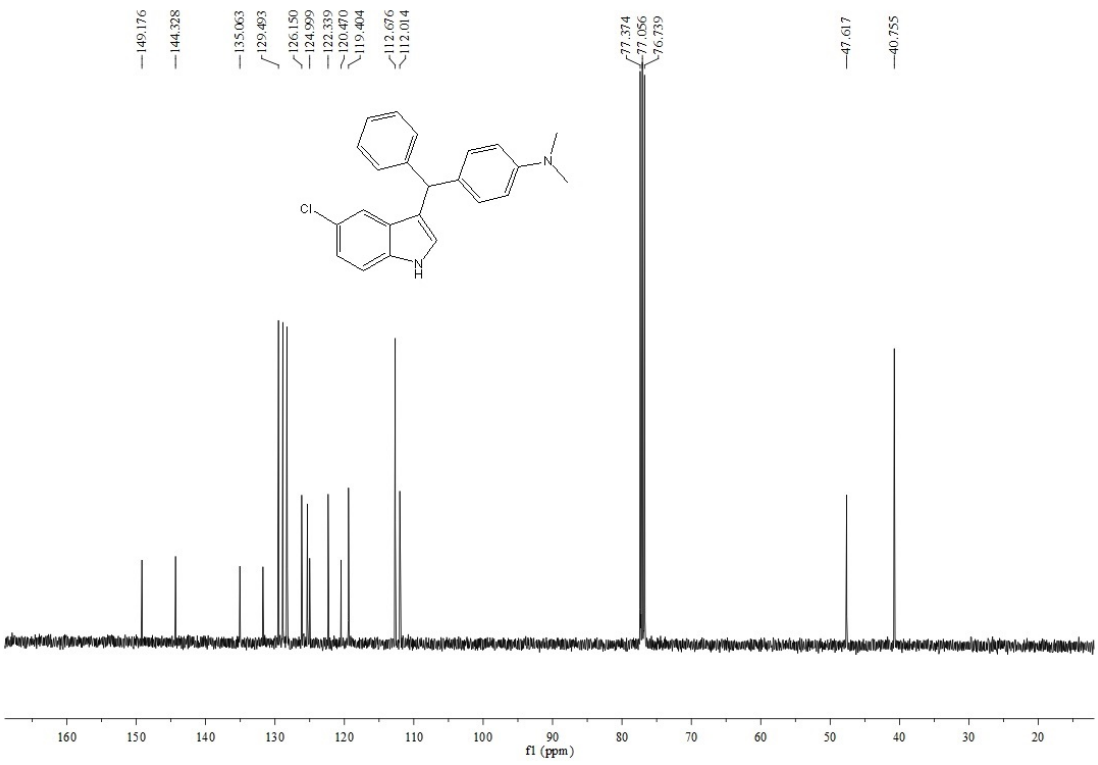


^{1}H NMR of **21k** in $CDCl_3$



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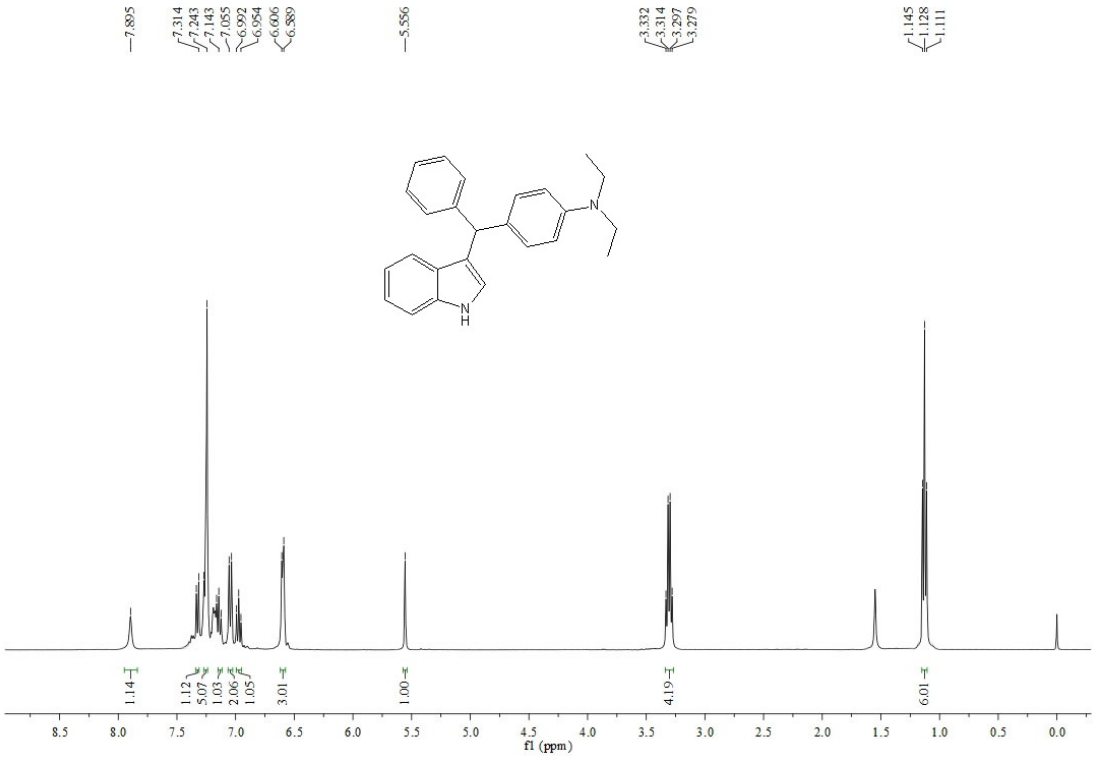
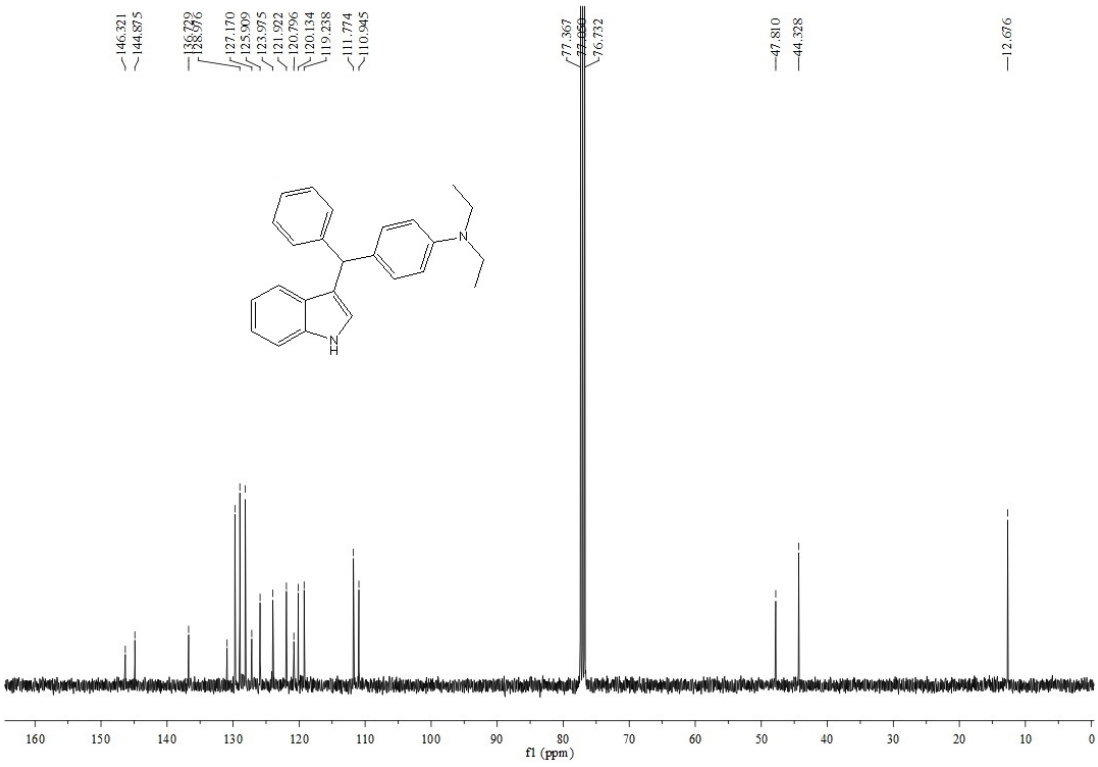


^{1}H NMR of **21i** in $CDCl_3$



^{13}C NMR of **21i** in $CDCl_3$