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Electronic Supplementary Information

Synthesis of Trisubstituted Hydrazine *via* MnO_2-Promoted Oxidative Coupling of *N,N*-Disubstituted Hydrazine and Boronic Ester

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General Information

Reagents and solvents

In general, all reagents were obtained commercially and used without further purification unless otherwise noted. Solvents for extractions and columns such as dichloromethane, methanol, n-hexane and ethyl acetate were technical grade. Solvents for reactions were dried over 4Å sieves. Deuterated solvents were purchased from Cambridge Stable Isotopes and used as received.

Characterization

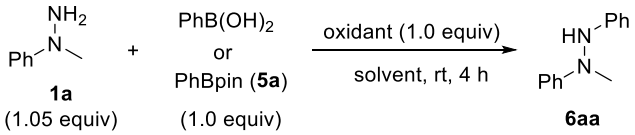
All ^{1}H and ^{13}C spectra are recorded on the Bruker AVANCE spectrometer, operating at 300 MHz, 400 MHz or 500 MHz for ^{1}H NMR, 75 MHz or 100 MHz for ^{13}C NMR. Chemical shifts are reported in parts per million (ppm). Chemical shifts are reported downfield from $CDCl_3$ (δ 7.27 ppm) for ^{1}H NMR. Chemical shifts of ^{13}C NMR are reported in the scale relative to the solvent of $CDCl_3$ (δ 77.0 ppm) used as an internal reference. Multiplicities are recorded as follows: s (singlet), d (doublet), t (triplet), dd (doublet of doublet), dt (doublet of triplet), m (multiplet), brs (broad singlet), qd (quartet of double), Coupling constants are reported in Hertz (Hz).

Mass spectra were in general recorded on an AMD 402/3 or a HP 5989A mass selective detector.

Experimental techniques

Unless otherwise stated, all reactions and reaction work-ups were carried out in air. Column chromatography was performed using silica gel (200-300 mesh ASTM).

Optimization of Reaction Conditions



Entry	boron	oxidant	solvent	Yield(%)[b]
1	PhB $(OH)_2$	MnO_2	CH_2Cl_2	23
2	$PhB(OH)_2$	MnO_2	THF	31
3	$PhB(OH)_2$	MnO_2	CH_3CN	37
4	$PhB(OH)_2$	MnO_2	DMF	44
5	$PhB(OH)_2$	MnO_2	DMSO	57
6	PhBpin	MnO_2	DMSO	85
7	PhBpin	NaOCl	DMSO	ND[c]
8	PhBpin	^{t}BuOCl	DMSO	ND[c]
9	PhBpin	$PhI(OAc)_2$	DMSO	34
10	PhBpin[d]	$PhI(OAc)_2$[d]	DMSO	71
11	PhBpin	O_2	DMSO	NR[c]
12	PhBpin	*m*-CPBA	DMSO	ND[c]

[a] Reaction conditions: hydrazine **1a** (0.21 mmol, 1.05 equiv), $PhB(OH)_2$ or PhBpin (0.2 mmol, 1.0 equiv) and oxidant (0.2 mmol, 1.0 equiv) in the indicated solvent (2 mL). [b] Isolated yield. [c] NR = no reaction, ND = not detected. [d] PhBpin (0.4 mmol) and $PhI(OAc)_2$ (0.4 mmol) were used.

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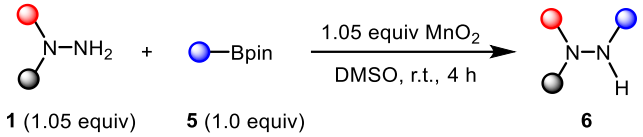
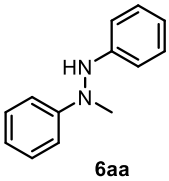


General Procedure:

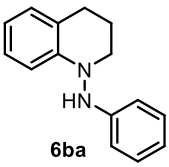
In a 25 mL Schlenk tube, the mixture of **1** (0.21 mmol, 1.05 equiv), **5** (0.2 mmol, 1.00 equiv), and MnO_2 (0.21 mmol, 18.3 mg, 1.05 equiv) were dissolved in anhydrous DMSO (2 mL). The mixture was stirred at r.t. for 4 hours. After completion of the reaction (monitored by TLC), water (10 mL) was added to the reaction mixture, and EtOAc was used for extraction (10 mL X 3). The combined organics were dried over anhydrous Na_2SO_4, and the solvent was evaporated to dryness. The crude product was purified by flash chromatography (petroleum ether/ethyl acetate as eluent) to give the desired product **6.**

Characterization Data



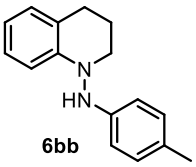
6aa

Yield = 85%, 33.7 mg, yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.37 (m, 4H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.89-6.96 (m, 4H), 5.50 (s, 1H), 3.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.9, 147.6, 129.5, 129.3, 119.9, 119.0, 113.0, 112.6, 39.8. HRMS (ESI) Calcd for $C_{13}H_{15}N_2^+$ ($M+H^+$) 199.1230, found 199.1231.



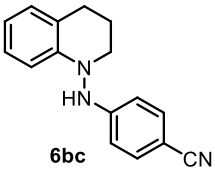
6ba

Yield = 60%, 26.9 mg, yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.28 (m, 2H), 7.01-7.09 (m, 3H), 6.85-6.89 (m, 3H), 6.75 (t, *J* = 7.2 Hz, 1H), 5.38 (s, 1H), 3.42 (s, 2H), 2.86 (t, *J* = 6.4 Hz, 2H), 2.14-2.19 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 147.1, 129.5, 129.1, 127.2, 122.8, 119.7, 118.6, 112.8, 112.3, 50.9, 27.3, 22.7. HRMS (ESI) Calcd for $C_{15}H_{16}N_2Na^+$ ($M+Na^+$) 247.1206, found 247.1208.



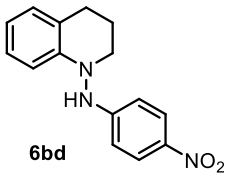
6bb

Yield = 35%, 16.7 mg, yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02-7.08 (m, 5H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.71-6.75 (m, 1H), 5.28 (s, 1H), 3.41 (t, *J* = 5.2 Hz, 2H), 2.85 (t, *J* = 6.4 Hz, 2H), 2.30 (s, 3H), 2.12-2.18 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.2, 145.2, 129.9, 129.0, 127.2, 122.6, 118.5, 112.7, 112.5, 50.8, 27.3, 22.7, 20.5. HRMS (ESI) Calcd for $C_{16}H_{19}N_2^+$ ($M+H^+$) 239.1543, found 239.1545.



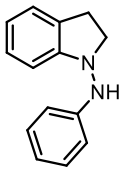
6bc

Yield = 74%, 36.9 mg, yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.8 Hz, 2H), 7.06-7.09 (m, 2H), 6.86 (t, *J* = 8.0 Hz, 3H), 6.81 (t, *J* = 7.2 Hz, 1H), 5.85 (s, 1H), 3.30-3.51 (m, 2H), 2.86 (s, 2H), 2.17 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.4, 146.1, 134.0, 129.4, 127.3, 123.4, 120.1, 119.7, 112.8, 111.7, 101.4, 51.3, 27.1, 22.7. HRMS (ESI) Calcd for $C_{16}H_{15}N_3Na^+$ ($M+Na^+$) 272.1158, found 272.1161.



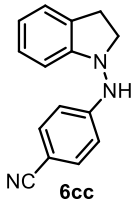
6bd

Yield = 81%, 43.6 mg, yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.16 (d, *J* = 5.4 Hz, 2H), 7.06-7.09 (m, 2H), 6.81-6.88 (m, 4H), 6.06 (s, 1H), 3.42 (d, *J* = 70.2 Hz, 2H), 2.86-2.88 (m, 2H), 2.16-2.25 (m, 2H). ^{13}C NMR (75MHz, $CDCl_3$): δ 153.3, 145.9, 140.1, 129.5, 127.3, 126.6, 123.6, 120.1, 113.0, 110.7, 51.5, 27.0, 22.7. HRMS (ESI) Calcd for $C_{15}H_{15}N_3O_2Na^+$ ($M+Na^+$) 292.1056, found 292.1057.



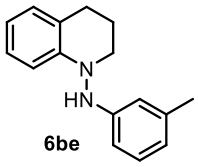
6ca

Yield = 63%, 26.5 mg, yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.32 (m, 2H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.88-6.93 (m, 2H), 6.81 (d, *J* = 7.6 Hz, 1H), 5.13 (s, 1H), 3.55 (t, *J* = 7.6 Hz, 2H), 3.08 (t, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 148.4, 129.4, 128.1, 127.5, 124.8, 120.6, 119.9, 112.8, 109.9, 57.0, 27.9. HRMS (ESI) Calcd for $C_{14}H_{15}N_2^+$ ($M+H^+$) 211.1230, found 211.1230.



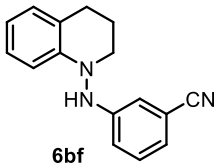
6cc

Yield = 87%, 40.9 mg, yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.92 (t, *J* = 7.2 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 5.54 (s, 1H), 3.53-3.54 (m, 2H), 3.08 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0, 151.7, 133.9, 128.1, 127.6, 125.1, 121.5, 120.1, 112.1, 109.9, 101.6, 57.1, 27.8. HRMS (ESI) Calcd for $C_{15}H_{14}N_3^+$ ($M+H^+$) 236.1182, found 236.1185.



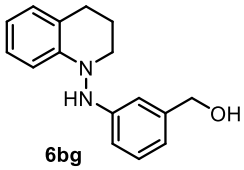
6be

Yield = 76%, 36.2 mg, yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (t, *J* = 7.6 Hz, 1H), 7.08-7.16 (m, 3H), 6.82 (t, *J* = 7.2 Hz, 1H), 6.73-6.77 (m, 3H), 5.35 (s, 1H), 3.46 (s, 2H), 2.92 (t, *J* = 6.4 Hz, 2H), 2.40 (s, 3H), 2.20-2.25 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 147.3, 139.4, 129.4, 129.1, 127.3, 122.8, 120.7, 118.7, 113.0, 112.9, 109.6, 50.9, 27.4, 22.8, 21.8. HRMS (ESI) Calcd for $C_{16}H_{18}N_2Na^+$ ($M+Na^+$) 261.1362, found 261.1364.



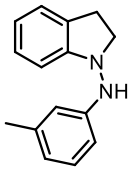
6bf

Yield = 78%, 38.9 mg, yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (t, *J* = 8.0 Hz, 1H), 7.06-7.13 (m, 5H), 6.91-6.93 (m, 1H), 6.80-6.84 (m, 1H), 5.64 (s, 1H), 3.40 (s, 2H), 2.89 (t, *J* = 6.0 Hz, 2H), 2.19-2.20 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 146.5, 130.3, 129.4, 127.3, 123.4, 123.1, 119.5, 116.5, 114.9, 113.2, 112.8, 51.1, 27.1, 22.7. HRMS (ESI) Calcd for $C_{16}H_{15}N_3Na^+$ ($M+Na^+$) 272.1158, found 272.1160.



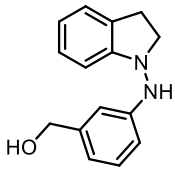
6bg

Yield = 55%, 28.0 mg, yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.2 Hz, 2H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.86 (t, *J* = 7.6 Hz, 2H), 6.75-6.82 (m, 2H), 5.45 (s, 1H), 4.64 (s, 2H), 3.42 (s, 2H), 2.87 (t, *J* = 6.0 Hz, 2H), 2.15-2.20 (m, 2H), 2.03 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 147.1, 142.5, 129.7, 129.1, 127.2, 122.9, 118.8, 118.2, 112.8, 111.6, 110.7, 65.4, 51.0, 27.3, 22.8. HRMS (ESI) Calcd for $C_{16}H_{18}N_2ONa^+$ ($M+Na^+$) 277.1311, found 277.1314.



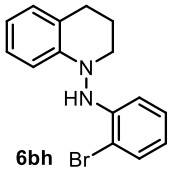
6ce

Yield = 70%, 31.4 mg, yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11-7.19 (m, 3H), 6.86-6.88 (m, 2H), 6.80 (t, *J* = 8.0 Hz, 2H), 6.71 (d, *J* = 7.6 Hz, 1H), 5.07 (s, 1H), 3.53 (t, *J* = 7.6 Hz, 2H), 3.06 (t, *J* = 8.0 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 148.4, 139.3, 129.2, 128.1, 127.5, 124.8, 120.8, 120.5, 113.4, 110.0, 109.9, 57.1, 27.9, 21.7. HRMS (ESI) Calcd for $C_{15}H_{16}N_2Na^+$ ($M+Na^+$) 247.1206, found 247.1207.



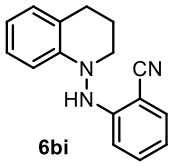
6cg

Yield = 58%, 27.9 mg, yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (t, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.03 (s, 1H), 6.93 (dd, *J* =8.0 Hz, *J* = 5.6 Hz, 1H), 6.88 (t, *J* = 7.6 Hz, 2H), 6.77 (d, *J* = 7.6 Hz, 1H), 5.18 (s, 1H), 4.65 (s, 2H), 3.52 (t, *J* = 7.2 Hz, 2H), 3.06 (t, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8, 148.8, 142.3, 129.6, 128.1, 127.5, 124.9, 120.7, 118.4, 112.1, 111.2, 109.9, 65.4, 57.1, 27.9. HRMS (ESI) Calcd for $C_{15}H_{16}N_2ONa^+$ ($M+Na^+$) 263.1155, found 263.1157.



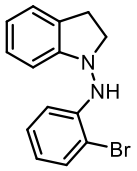
6bh

Yield = 53%, 32.0 mg, yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.06-7.10 (m, 2H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.72-6.80 (m, 2H), 6.03 (s, 1H), 3.44 (s, 2H), 2.88 (d, *J* = 5.2 Hz, 2H), 2.18-2.19 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.7, 144.1, 132.6, 129.2, 128.7, 127.3, 123.1, 120.3, 119.1, 113.2, 112.8, 107.3, 51.3, 27.2, 22.8. HRMS (ESI) Calcd for $C_{15}H_{16}BrN_2^+$ ($M+H^+$) 303.0491, found 303.0493.



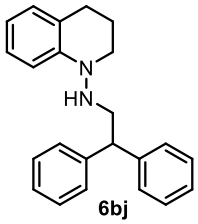
6bi

Yield = 70%, 34.9 mg, yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 (dd, *J* = 4.8 Hz, *J* = 0.9 Hz, 1H), 7.46 (t, *J* = 4.8 Hz, 1H), 7.10-7.13 (m, 3H), 6.93 (d, *J* = 4.8 Hz,1H), 6.83-6.89 (m, 2H), 6.30 (s, 1H), 3.46 (d, *J* = 39.9 Hz, 2H), 2.90(s, 2H), 2.22 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.4, 146.1, 134.7, 132.9, 129.4, 127.3, 123.5, 119.8, 119.0, 117.2, 112.9, 112.0, 94.2, 51.5, 27.1, 22.7. HRMS (ESI) Calcd for $C_{16}H_{15}N_3Na^+$ ($M+Na^+$) 272.1158, found 272.1158.



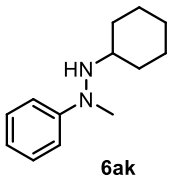
6ch

Yield = 35%, 20.2 mg, yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.27-7.29 (m, 1H), 7.22-7.25 (m, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 6.93 (t, *J* = 7.2 Hz, 1H), 6.75-6.80 (m, 2H), 5.80 (s, 1H), 3.59 (s, 2H), 3.10 (t, *J* = 7.6 Hz, 2H),. ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 145.1, 132.4, 128.7, 128.2, 127.6, 124.9, 121.0, 120.4, 114.0, 110.0, 107.4, 57.4, 27.9. HRMS (ESI) Calcd for $C_{14}H_{14}BrN_2^+$ ($M+H^+$) 289.0335, found 289.0335.



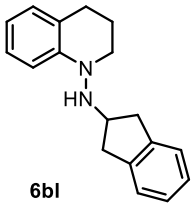
6bj

Yield = 52%, 34.1 mg, yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 3.6 Hz, 8H), 7.27-7.28 (m, 2H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.68 (t, *J* = 7.2 Hz, 1H), 4.27 (t, *J* = 7.6 Hz,1H), 3.62 (d, *J* = 7.6 Hz, 2H), 3.31 (t, *J* = 5.6 Hz, 2H), 2.77 (t, *J* = 6.0 Hz, 2H), 2.03-2.09 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.4, 143.1, 128.9, 128.8, 128.7, 128.6, 128.2, 126.9, 126.6, 122.7, 117.7, 113.0, 52.1, 50.0, 49.8, 27.4, 22.7. HRMS (ESI) Calcd for $C_{23}H_{24}N_2Na^+$ ($M+Na^+$) 351.1832, found 351.1833.



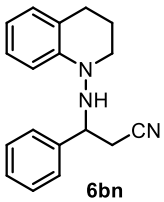
6ak

Yield = 32%, 13.1 mg, yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.29 (m, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.79 (t, *J* = 7.2 Hz, 1H), 3.10 (s, 3H), 2.94-2.99 (m, 1H), 1.82 (t, *J* = 12.8 Hz, 4H), 1.67 (d, *J* = 4.8 Hz, 1H), 1.24-1.33 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2, 128.9, 117.6, 112.9, 56.1, 40.1, 31.7, 26.3, 24.6. HRMS (ESI) Calcd for $C_{13}H_{20}N_2Na^+$ ($M+Na^+$) 227.1519, found 227.1522.



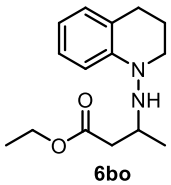
6bl

Yield = 54%, 28.5 mg, yellow oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31-7.32 (m, 2H), 7.25-7.27 (m, 2H), 7.06-7.11 (m, 2H), 7.03 (d, *J* = 7.0 Hz, 1H), 6.73 (t, *J* = 7.0 Hz, 1H), 4.18-4.22 (m, 1H), 3.44 (t, *J* = 5.5 Hz, 2H), 3.16 (dd, *J* = 16.0 Hz, *J* = 6.5 Hz, 2H), 2.94 (dd, *J* = 15.5 Hz, *J* = 3.5 Hz, 2H), 2.86 (t, *J* = 6.5 Hz, 2H), 2.13-2.18 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.7, 142.1, 128.9, 126.9, 126.4, 124.8, 122.3, 117.7, 113.1, 57.4, 50.4, 38.5, 27.4, 22.7. HRMS (ESI) Calcd for $C_{18}H_{20}N_2Na^+$ ($M+Na^+$) 287.1519, found 287.1522.



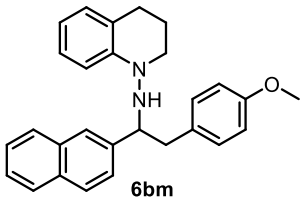
6bn

Yield = 58%, 32.1 mg, yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57-7.58 (m, 2H), 7.42-7.50 (m, 3H), 7.36 (d, *J* = 4.8 Hz, 1H), 7.18 (t, *J* = 4.5 Hz, 1H), 7.05 (d, *J* = 4.2 Hz, 1H), 6.79-6.80 (m, 1H), 4.44 (dd, *J* = 4.2 Hz, *J* = 2.7 Hz, 1H), 3.58-3.62 (m, 1H), 3.50 (s, 1H), 3.13-3.17 (m, 1H), 2.78-2.92 (m, 4H), 2.11-2.15 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.0, 138.6, 129.2, 129.1, 127.5, 127.0, 123.5, 119.0, 118.1, 113.3, 58.7, 50.7, 27.1, 24.6, 22.7. HRMS (ESI) Calcd for $C_{18}H_{20}N_3^+$ ($M+H^+$) 278.1652, found 278.1653.



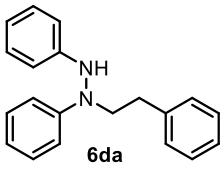
6bo

Yield = 80%, 41.9 mg, yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, *J* = 8.0 Hz, 1H), 7.10 (t, *J* =8.0 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.68 (t, *J* = 7.6 Hz, 1H), 4.11(q, *J* = 6.8 Hz, 2H), 3.62-3.70 (m, 1H), 3.35-3.40 (m, 1H), 3.25-3.30 (m, 1H), 2.77 (t, *J* = 6.4 Hz, 2H), 2.57 (dd, *J* = 15.6 Hz, *J* = 7.2 Hz,1H), 2.38 (dd, *J* = 15.6 Hz, *J* = 5.6 Hz, 1H), 2.02-2.08 (m, 2H), 1.27-1.29 (m, 1H), 1.21(t, *J* = 7.2 Hz, 3H), 1.16 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.6, 148.5, 128.9, 126.9, 122.6, 117.9, 113.3, 60.4, 50.7, 49.3, 40.5, 27.4, 22.6, 19.1, 14.2. HRMS (ESI) Calcd for $C_{15}H_{22}N_2O_2Na^+$ ($M+Na^+$) 285.1573, found 285.1575.



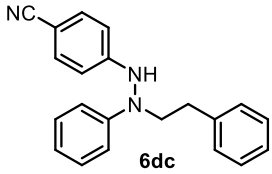
6bm

Yield = 77%, 62.9 mg, yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86-7.87 (m, 1H), 7.84-7.85 (m, 1H), 7.81-7.83 (m, 1H), 7.78 (s, 1H), 7.64 (dd, *J* = 5.1 Hz, *J* = 0.9 Hz, 1H), 7.48-7.50 (m, 2H), 7.09 (d, *J* = 5.1 Hz, 2H), 7.03 (t, *J* = 4.5 Hz, 1H), 6.93 (d, *J* = 4.8 Hz, 2H), 6.82 (d, *J* = 5.1 Hz, 2H), 6.65 (t, *J* =4.5 Hz, 1H), 4.42 (t, *J* = 4.2 Hz, 1H), 3.80 (s, 3H), 3.22-3.27 (m, 1H), 3.14-3.18 (m, 1H), 3.09-3.13 (m, 1H), 3.00-3.05 (m, 1H), 2.62-2.72 (m, 2H), 1.83-1.88 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.2, 147.9, 140.2, 133.3, 133.1, 130.6, 130.4, 128.9, 127.9, 127.7, 127.0, 126.8, 126.0, 125.9, 125.6, 122.8, 117.5, 113.8, 112.1, 64.2, 55.3, 50.9, 41.5, 27.3, 22.5. HRMS (ESI) Calcd for $C_{28}H_{28}N_2ONa^+$ ($M+Na^+$) 431.2094, found 431.2095.



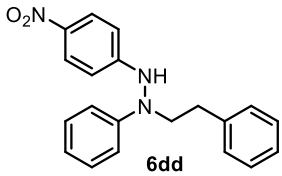
6da

Yield = 53%, 30.5 mg, yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.39 (m, 10H), 6.99 (d, *J* =8.4 Hz, 2H), 6.88 (t, *J* = 7.2 Hz, 2H), 6.74 (d, *J* = 8.4 Hz, 2H), 5.41 (s, 1H), 3.85 (t, *J* = 6.4 Hz, 2H), 3.05 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 147.4, 139.6, 129.4, 128.9, 128.8, 126.5, 119.7, 118.6, 112.7, 112.4, 53.1, 32.7. HRMS (ESI) Calcd for $C_{20}H_{20}N_2Na^+$ ($M+Na^+$) 311.1519, found 311.1521.



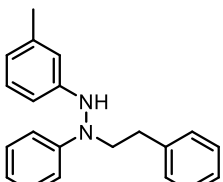
6dc

Yield = 78%, 48.9 mg, yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.8 Hz, 2H), 7.28-7.38 (m, 5H), 7.23 (d, *J* = 7.2 Hz, 2H), 6.91-6.94 (m, 3H), 6.71 (d, *J* = 8.4 Hz, 2H), 5.85 (s, 1H), 3.83 (s, 2H), 3.02 (t, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.2, 148.4, 139.3, 134.0, 129.6, 128.9, 128.8, 126.7, 120.1, 119.7, 113.2, 111.9, 101.4, 53.8, 32.6. HRMS (ESI) Calcd for $C_{21}H_{19}N_3Na^+$ ($M+Na^+$) 336.1471, found 336.1474.



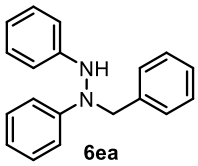
6dd

Yield = 51%, 34.0 mg, yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 9.2 Hz, 2H), 7.28-7.38 (m, 5H), 7.22 (d, *J* = 6.8 Hz, 2H), 6.90-6.95 (m, 3H), 6.69 (d, *J* = 8.8 Hz, 2H), 5.94 (s, 1H), 3.73-3.94 (m, 2H), 3.00-3.07 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 148.1, 140.1, 139.2, 129.6, 128.9, 128.8, 126.8, 126.4, 120.1, 113.3, 110.8, 54.0, 32.6. HRMS (ESI) Calcd for $C_{20}H_{20}N_3O_2^+$ ($M+H^+$) 334.1550, found 334.1551.



6de

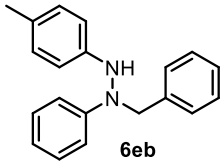
Yield = 60%, 36.3 mg, yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.39 (m, 7H), 7.14 (t, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.88 (t, *J* = 7.2 Hz, 1H), 6.70 (d, *J* = 7.2 Hz, 1H), 6.54-6.58 (m, 2H), 5.37 (s, 1H), 3.85 (t, *J* = 6.0 Hz, 2H), 3.05 (t, *J* = 7.6 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.4, 147.4, 139.7, 139.4, 129.4, 129.3, 128.9, 128.8, 126.5, 120.7, 118.5, 113.0, 112.7, 109.6, 53.1, 32.6, 21.7. HRMS (ESI) Calcd for $C_{21}H_{22}N_2Na^+$ ($M+Na^+$) 325.1675, found 325.1678.



6ea

Yield = 45%, 24.7 mg, colorless oil

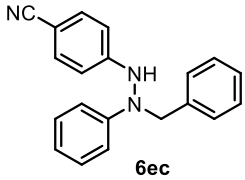
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.37 (m, 3H), 7.24-7.31 (m, 6H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.86-6.90 (m, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 5.71 (s, 1H), 4.80 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.9, 146.9, 136.8, 129.5, 129.4, 128.8, 127.8, 127.5, 120.0, 118.7, 112.9, 112.8, 54.2. HRMS (ESI) Calcd for $C_{19}H_{18}N_2Na^+$ (M+Na$^+$) 297.1362, found 297.1364.



6eb

Yield = 25%, 14.4 mg, yellow oil.

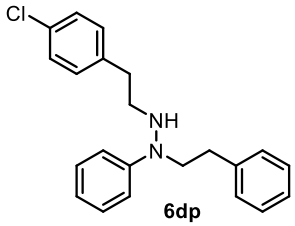
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.37 (m, 8H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.85 (t, *J* = 7.6 Hz, 1H),6.71 (d, *J* = 7.6 Hz, 1H), 6.61-6.65 (m, 2H), 5.67 (s, 1H), 4.80 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.0, 146.9, 139.4, 136.8, 129.3, 128.8, 127.8, 127.4, 120.9, 118.6, 113.5, 112.7, 110.1, 54.1, 21.7. HRMS (ESI) Calcd for $C_{20}H_{20}N_2Na^+$ (M+Na$^+$) 311.1519, found 311.1522.



6ec

Yield = 75%, 44.9 mg, yellow oil.

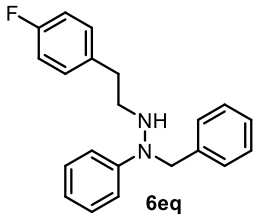
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.26-7.37 (m, 7H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.92 (t, *J* = 7.2 Hz,1H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.08 (s, 1H), 4.76 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.9, 149.0, 136.0, 134.0, 129.6, 128.9, 128.1, 127.8, 120.0, 119.9, 113.4, 112.2, 101.7, 55.5. HRMS (ESI) Calcd for $C_{20}H_{17}N_3Na^+$ (M+Na$^+$) 322.1315, found 322.1316.



6dp

Yield = 65%, 45.5 mg, yellow oil.

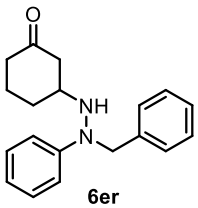
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.37 (m, 7H), 7.23 (d, *J* = 7.2 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.84 (t, *J* = 7.2 Hz, 1H), 3.69 (t, *J* = 7.6 Hz, 2H), 3.12 (t, *J* = 6.8 Hz, 2H), 2.90 (t, *J* = 8.0 Hz, 2H), 2.82 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.5, 139.8, 138.4, 132.0, 130.2, 129.3, 128.8, 128.7, 128.6, 126.3, 118.1, 113.3, 53.4, 49.4, 34.0, 32.5. HRMS (ESI) Calcd for $C_{22}H_{23}ClN_2Na^+$ (M+Na$^+$) 373.1442, found 373.1444.



6eq

Yield = 35%, 22.4 mg, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.27 (m, 7H), 7.16 (m, 2H), 6.98-7.04 (m, 4H), 6.84 (t, *J* = 7.6 Hz, 1H), 4.69 (s, 2H), 3.16 (t, *J* = 7.2 Hz, 2H), 2.82 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.5 (d, *J* = 145.4 Hz), 150.5, 137.6, 135.5 (d, *J* = 1.7 Hz), 130.1 (d, *J* = 4.5 Hz), 129.1, 128.7, 127.6, 127.3, 118.1, 115.2 (d, *J* = 12.7 Hz), 113.4, 55.2, 49.1, 33.8. HRMS (ESI) Calcd for $C_{21}H_{21}FN_2Na^+$ (M+Na$^+$) 343.1581, found 343.1584.

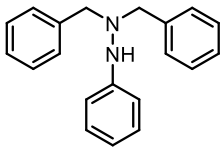


6er

Yield = 58%, 34.1 mg, yellow oil.

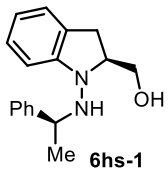
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21-7.33 (m, 7H), 7.03 (d, *J* = 7.6Hz, 2H), 6.82 (t, *J* = 6.8 Hz, 1H), 4.68 (q, *J* = 16.0 Hz, 2H), 3.47-3.49 (m, 2H), 2.52-2.55 (m, 1H), 2.35 (t, *J* = 6.8 Hz, 3H), 2.04-2.12 (m, 1H), 1.94-1.97 (m, 1H), 1.66-1.76 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 210.3, 150.9, 137.1,

129.1, 128.7, 127.7, 127.3, 118.6, 113.9, 56.2, 55.2, 46.1, 41.3, 29.1, 21.9. HRMS (ESI) Calcd for $C_{19}H_{23}N_2O^+$ ($M+H^+$) 295.1805, found 295.1808.



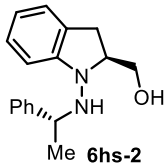
6fa

Yield = 7%, 4.0 mg, colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, J = 7.5 Hz, 2H), 7.37-7.39 (m, 2H), 7.29-7.36 (m, 9H), 7.23-7.26 (m, 2H), 4.58 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.7, 137.0, 131.9, 128.6, 128.5, 127.7, 127.2, 125.6, 57.9. HRMS (ESI) Calcd for $C_{20}H_{20}N_2Na^+$ ($M+Na^+$) 311.1519, found 311.1520.



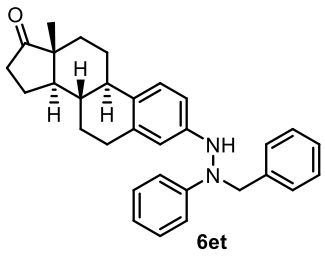
6hs-1

Yield = 30%, 16.1 mg, yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46-7.48 (m, 2H), 7.42 (t, J = 4.5 Hz, 2H), 7.36-7.39 (m, 1H), 7.21 (t, J = 4.5 Hz, 1H), 7.11 (d, J = 4.2 Hz, 1H), 6.87 (t, J = 4.5 Hz, 1H), 6.84 (d, J = 4.8 Hz, 1H) 4.43 (q, J = 3.9 Hz, 1H), 3.55 (d, J = 7.2 Hz, 1H), 3.49 (t, J = 5.1 Hz, 1H), 3.32 (d, J = 6.0 Hz, 1H), 2.78-2.89 (m, 2H), 1.54 (d, J = 3.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.1, 143.7, 128.7, 128.2, 127.9, 127.5, 124.9, 120.6, 108.2, 108.1, 71.2, 61.4, 59.7, 29.5, 20.7. HRMS (ESI) Calcd for $C_{17}H_{20}N_2ONa^+$ ($M+Na^+$) 291.1468, found 291.1469.



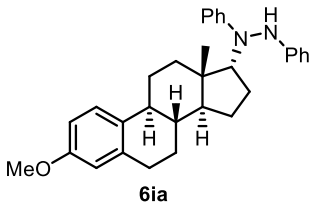
6hs-2

Yield = 30%, 16.1 mg, yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44-7.45 (m, 2H), 7.40 (t, J = 4.5 Hz, 2H), 7.34 (t, J = 4.2 Hz, 1H), 7.14 (t, J = 4.5 Hz, 1H), 7.10 (d, J = 4.2 Hz, 1H), 6.84 (t, J = 4.5 Hz, 1H), 6.73 (d, J = 4.5 Hz, 1H), 4.46 (q, J = 3.9 Hz, 1H), 3.94-4.00 (m, 2H), 3.65-3.71 (m, 1H), 2.89 (dd, J = 9.3 Hz, J = 5.1 Hz, 1H), 2.72 (dd, J = 9.0 Hz, J = 6.3 Hz, 1H), 1.57 (d, J = 3.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 128.8, 128.7, 128.2, 128.0, 127.9, 127.6, 127.5, 127.3, 124.9, 120.7, 64.9, 59.1, 30.4, 21.6. HRMS (ESI) Calcd for $C_{17}H_{20}N_2ONa^+$ ($M+Na^+$) 291.1468, found 291.1471.



6et

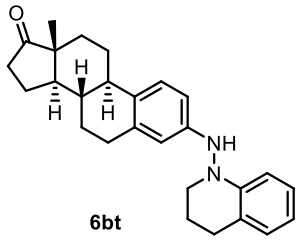
Yield = 56%, 50.4 mg, yellow oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31-7.36 (m, 3H), 7.24-7.27 (m, 4H), 7.18 (d, J = 8.5 Hz, 1H), 7.05 (d, J = 8.0 Hz, 2H), 6.83 (t, J = 7.5 Hz, 1H), 6.63 (dd, J = 8.5 Hz, J = 2.5 Hz, 1H), 6.58 (d, J = 2.0 Hz, 1H), 5.63 (s, 1H), 2.85-2.89 (m, 2H), 2.50-2.56 (m, 1H), 2.38-2.42 (m, 1H), 2.25-2.30 (m, 1H), 2.12-2.20 (m, 1H), 1.95-2.03 (m, 2H), 1.60-1.67 (m, 4H), 1.50-1.57 (m, 4H), 1.36 (s, 2H), 0.93 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.0, 144.7, 137.7, 136.8, 131.5, 129.3, 128.8, 127.7, 127.4, 126.4, 118.5, 112.9, 112.7, 110.8, 53.9, 50.4, 48.1, 44.1, 38.4, 35.9, 31.6, 29.7, 26.6, 25.9, 24.8, 21.6, 13.9. HRMS (ESI) Calcd for $C_{31}H_{34}N_2ONa^+$ ($M+Na^+$) 473.2563, found 473.2565.



6ia

Yield = 50%, 45.2 mg, yellow oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40-7.45 (m, 2H), 7.22-7.33 (m, 6H), 7.09 (d, J = 8.0 Hz, 1H), 7.01 (t, J =7.5 Hz, 1H), 6.87 (t, J = 7.0 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 6.68 (s, 1H), 3.82 (d, J = 5.0 Hz, 3H), 2.90 (s, 2H), 2.23-2.34 (m, 2H), 2.15 (q, J = 15.5 Hz, 1H), 1.87-1.94 (m, 2H), 1.77-1.84 (m, 1H), 1.63-1.68 (m, 1H), 1.48-1.54

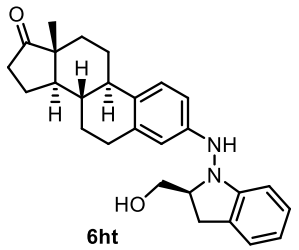
(m, 1H), 1.27 (d, J = 15.0 Hz, 6H), 0.60 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.5, 148.1, 138.0, 132.7, 129.3, 129.2, 129.1, 126.4, 126.3, 119.1, 114.6, 113.8, 112.2, 111.5, 55.2, 51.9, 51.4, 43.9, 39.1, 38.5, 38.2, 29.9, 27.4, 26.3, 23.4, 23.1, 12.1. HRMS (ESI) Calcd for $C_{31}H_{36}N_2ONa^+$ ($M+Na^+$) 475.2720, found 475.2721.



6bt

Yield = 62%, 49.6 mg, yellow oil.

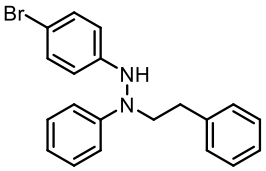
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, J = 8.4 Hz, 1H), 7.02-7.07 (m, 3H), 6.71-6.75 (m, 1H), 6.68 (dd, J = 8.0 Hz, J = 2.0 Hz, 1H), 6.63 (d, J = 2.0 Hz, 1H), 5.28 (s, 1H), 3.39-3.40 (m, 4H), 2.83-2.90 (m, 4H), 2.49-2.56 (m, 1H), 2.35-2.43 (m, 1H), 2.24-2.30 (m, 1H), 2.12-2.18 (m, 3H), 2.05-2.09 (m, 1H), 2.03-2.04 (m, 1H), 1.98-2.01 (m, 1H), 1.48-1.62 (m, 6H), 0.93 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.2, 145.5, 137.7, 131.2, 129.0, 127.2, 126.4, 122.7, 118.5, 112.8, 112.4, 110.3, 50.8, 50.4, 48.1, 44.1, 38.5, 35.9, 31.6, 29.7, 27.3, 26.6, 25.9, 22.7, 21.6, 13.9. HRMS (ESI) Calcd for $C_{27}H_{33}N_2O^+$ ($M+H^+$) 401.2587, found 401.2589.



6ht

Yield = 34%, 28.3 mg, yellow oil.

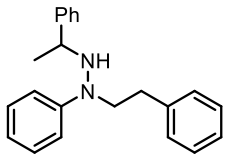
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (t, J = 8.8 Hz, 2H), 7.09 (t, J = 7.6 Hz, 1H), 6.88 (t, J = 7.2 Hz, 1H), 6.76-6.80 (m, 2H), 6.68 (d, J = 7.6 Hz, 1H), 5.25 (s, 1H), 3.97 (dd, J = 11.6 Hz, J = 3.2 Hz, 1H), 3.85 (dd, J = 11.6 Hz, J = 4.4 Hz, 1H), 3.75 (s, 1H), 2.98-3.13 (m, 2H), 2.87-2.91 (m, 2H), 2.49-2.56 (m, 1H), 2.39-2.43 (m, 1H), 2.24-2.29 (m, 1H), 2.14-2.21 (m, 1H), 2.09-2.12 (m, 1H), 2.06-2.08 (m, 1H), 2.03-2.04 (m, 1H), 1.98-2.01 (m, 1H), 1.60-1.68 (m, 2H), 1.56-1.57 (m, 1H), 1.44-1.51 (m, 2H), 0.94 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.9, 137.9, 132.0, 127.6, 127.5, 126.5, 126.3, 124.9, 121.3, 112.8, 110.6, 110.0, 63.1, 50.4, 48.1, 44.1, 38.4, 35.9, 31.6, 30.2, 29.7, 26.6, 25.9, 24.9, 21.6, 13.9. HRMS (ESI) Calcd for $C_{27}H_{32}N_2O_2Na^+$ ($M+Na^+$) 439.2356, found 439.2360.



6du

Yield = 76%, 13.9g, yellow oil

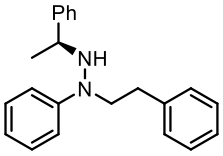
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.37 (m, 2H), 7.26-7.31 (m, 6H), 7.22-7.24 (m, 2H), 6.91-6.94 (m, 2H), 6.86 (t, J = 7.6 Hz, 1H), 6.56-6.60 (m, 2H), 5.35 (s, 1H), 3.80 (s, 1H), 3.00 (t, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.9, 146.5, 139.5, 132.1, 129.4, 128.8, 126.5, 119.0, 114.0, 112.8, 111.2, 53.2, 32.6. HRMS (ESI) Calcd for $C_{20}H_{20}BrN_2^+$ ($M+H^+$) 367.0804, found 367.0806.



(±)6ds

Yield = 87%, 55.0 mg, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 7.2 Hz, 2H), 7.37 (t, J = 7.2 Hz, 2H), 7.28-7.34 (m, 5H), 7.20-7.25 (m, 3H), 6.99 (d, J = 8.4 Hz, 2H), 6.83 (t, J = 7.2 Hz, 1H), 4.17 (q, J = 6.8 Hz, 1H), 3.58-3.73 (m, 2H), 2.75-2.90 (m, 2H), 1.38 (d, J = 6.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) : δ 149.8, 144.1, 139.9, 129.2, 128.8, 128.6, 128.4, 127.4, 127.4, 126.2, 117.8, 113.2, 57.3, 54.6, 32.1, 21.5. HRMS (ESI) Calcd for $C_{22}H_{25}N_2^+$ ($M+H^+$) 317.2012, found 317.2014.

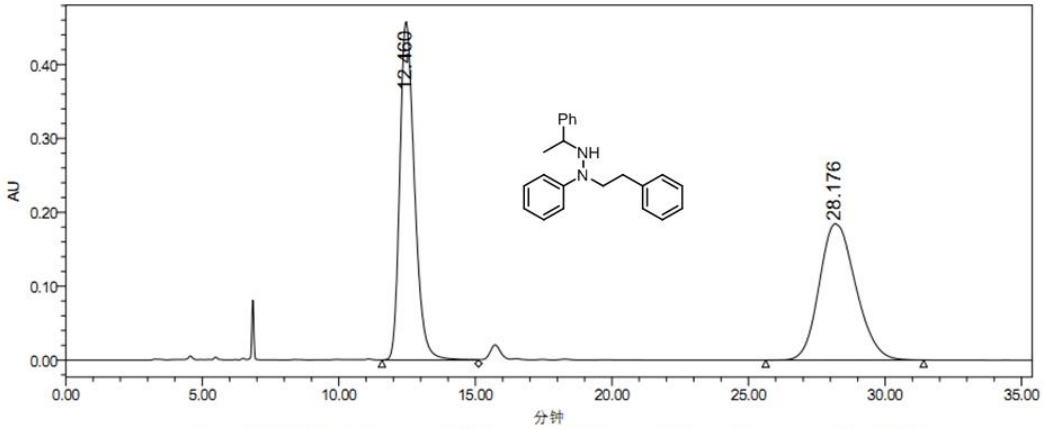


(*S*)-6ds

Yield = 95%, 60.1 mg, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.47 (m, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.32-7.35 (m, 5H), 7.21-7.27 (m, 3H), 7.01 (d, J = 8.4 Hz, 2H), 6.84 (t, J = 7.2 Hz, 1H), 4.19 (q, J = 6.4 Hz, 1H), 3.60-3.74 (m, 2H), 2.77-2.91 (m, 2H), 1.39 (d, J = 6.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.8, 144.1, 139.9, 129.2, 128.8, 128.6, 128.5, 127.4, 127.4, 126.2, 117.8, 113.2, 57.3, 54.6, 32.1, 21.5. HRMS (ESI) Calcd for $C_{22}H_{25}N_2^+$ ($M+H^+$) 317.2012, found 317.2013. $[\alpha]^{25}_D$ = +181.6 (c = 0.5 in CH_2Cl_2); 92% ee [Chiralcel OJ column, hexane / i-PrOH = 90:10, 1.0 mL/min, λ_{max} 254 nm, t_R = 11.97 min and 27.71 min].

HPLC of (*S*)-6ds



Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

	Channel Description	RT (min)	Area (礦*sec)	% Area	Height (礦)
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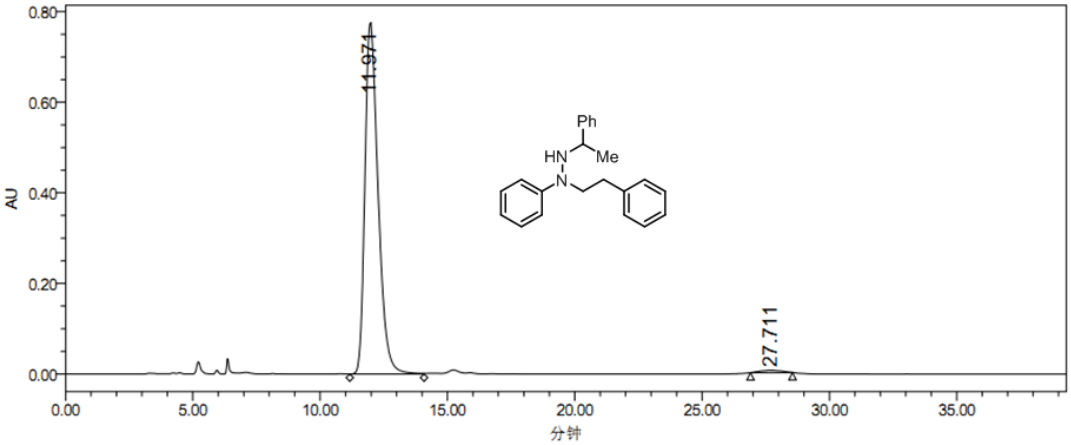
2	W2489 ChA 254nm	28.176	17138859	49.96	184429

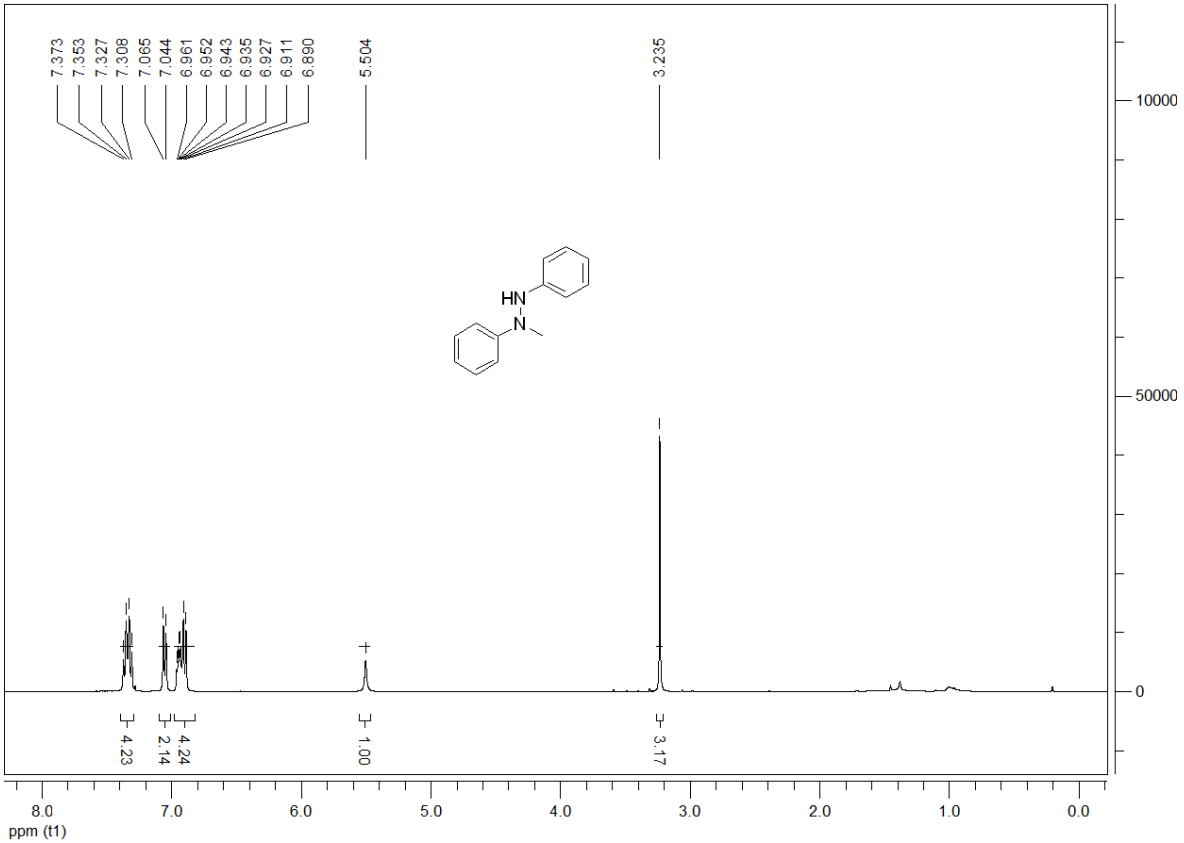


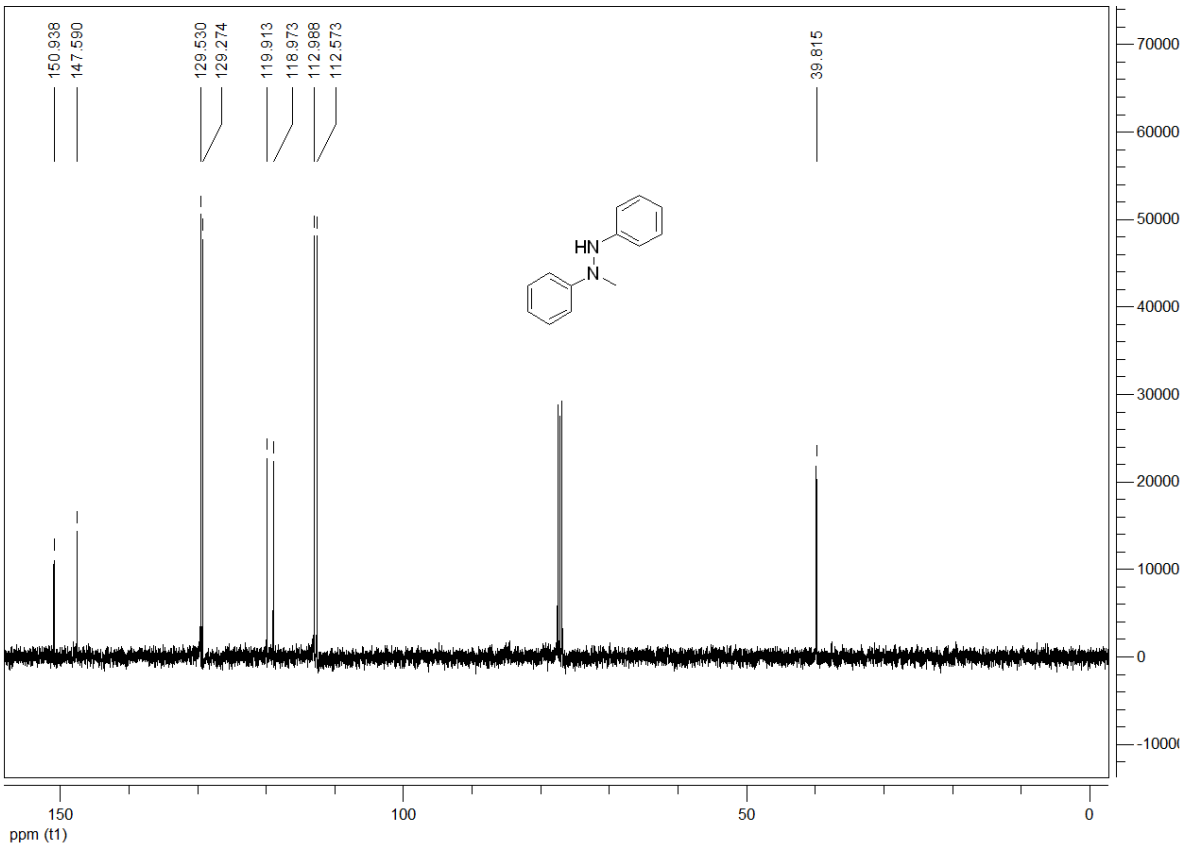
Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

	Channel Description	RT (min)	Area (礦*sec)	% Area	Height (礦)
1	W2489 ChA 254nm	11.971	27792623	98.93	775090
2	W2489 ChA 254nm	27.711	301219	1.07	4984

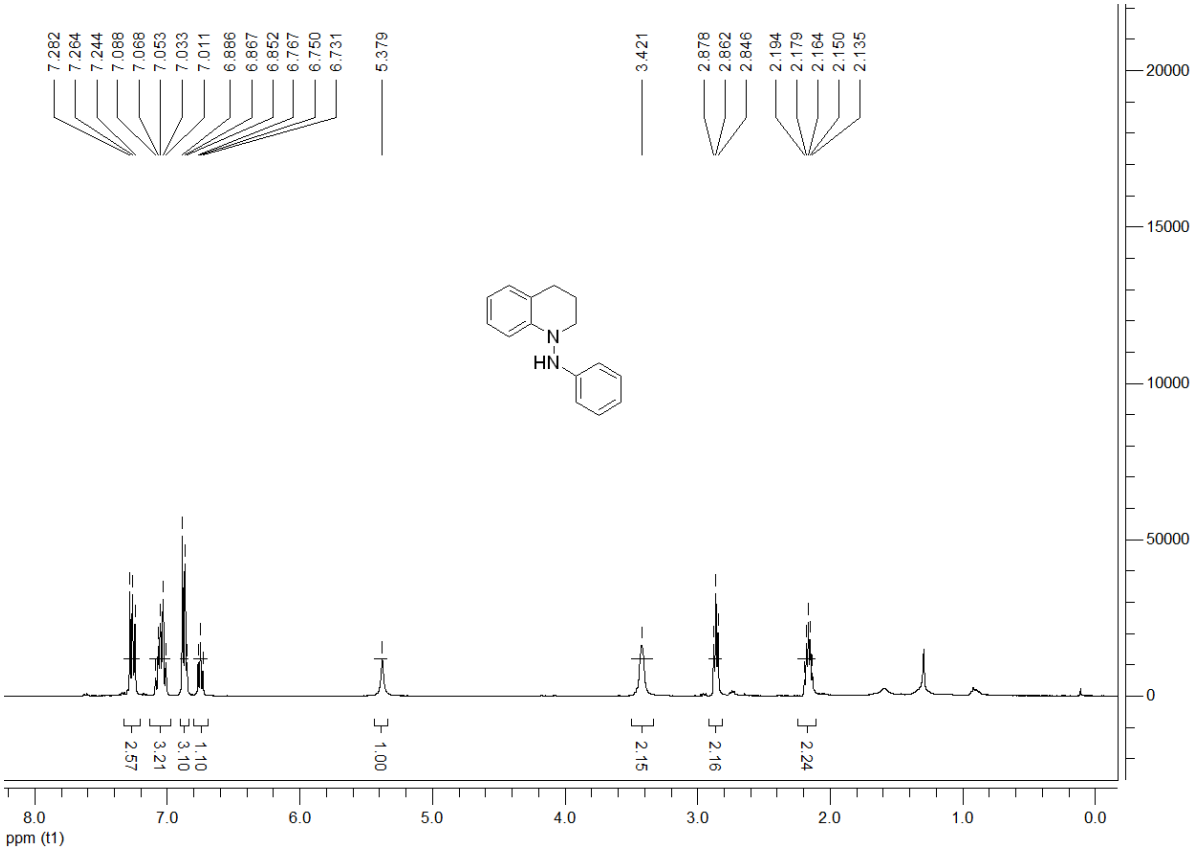
^{1}H and ^{13}C NMR spectra of products

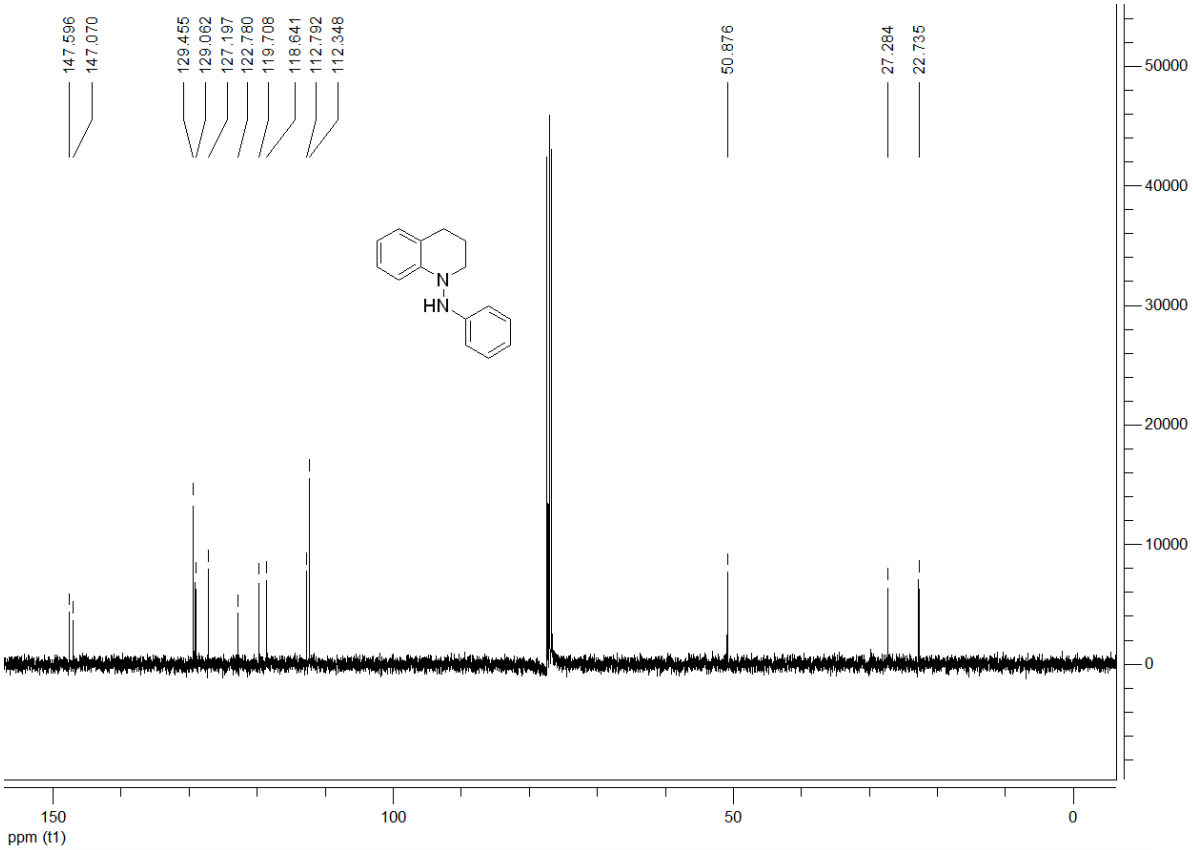
^{1}H and ^{13}C NMR of **6aa**



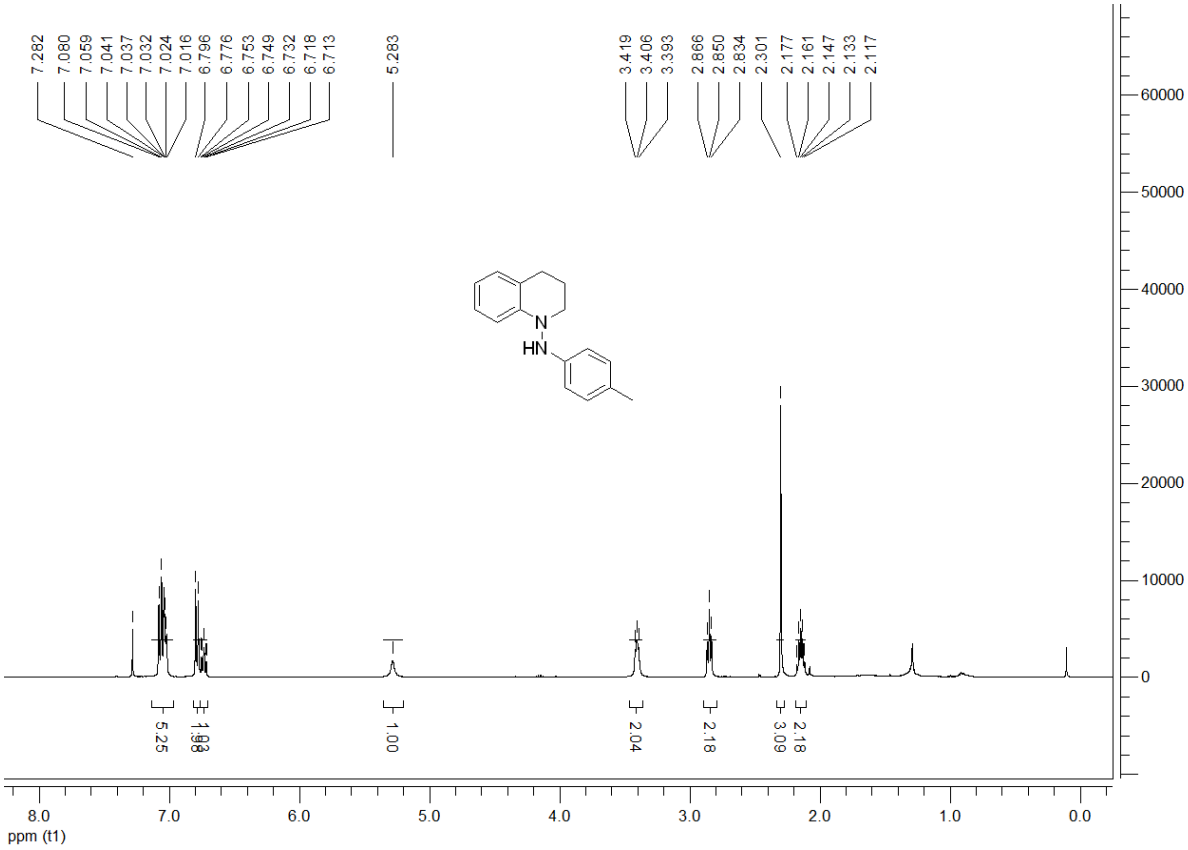


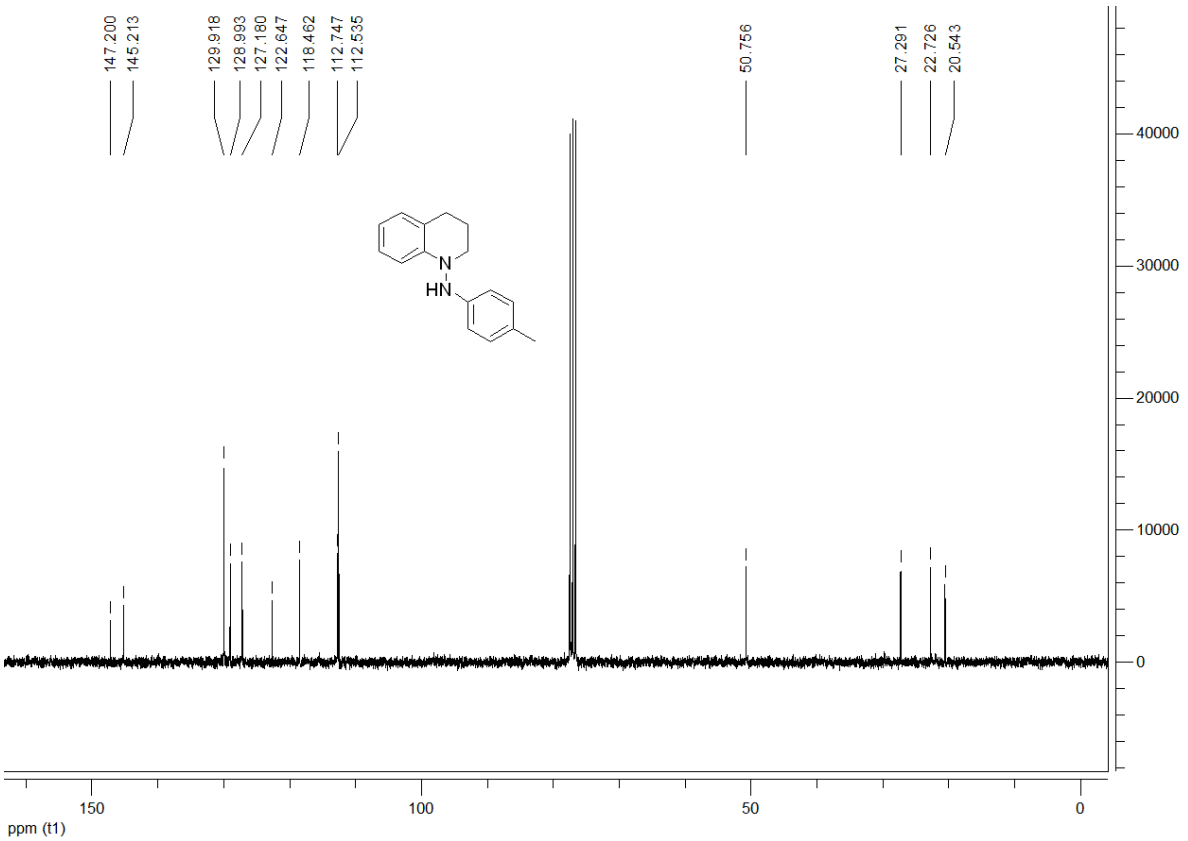
^{1}H and ^{13}C NMR of **6ba**



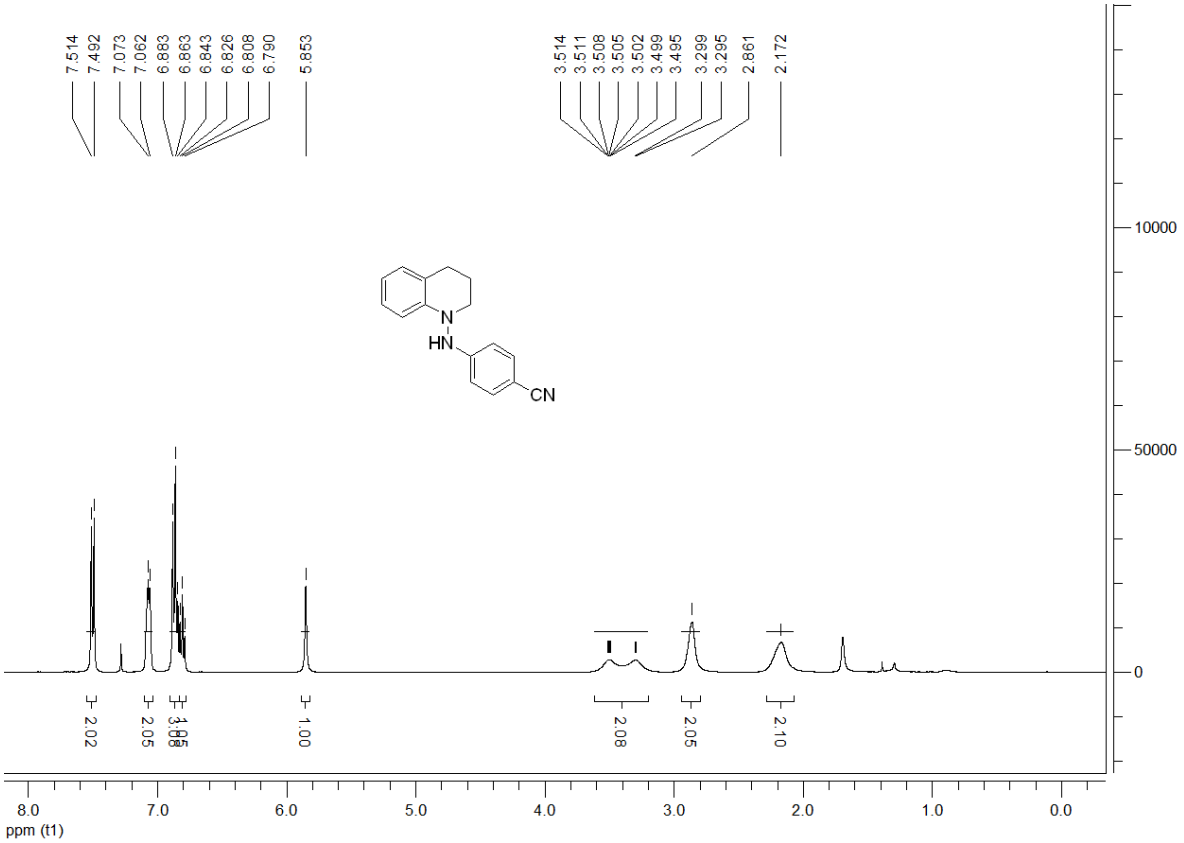


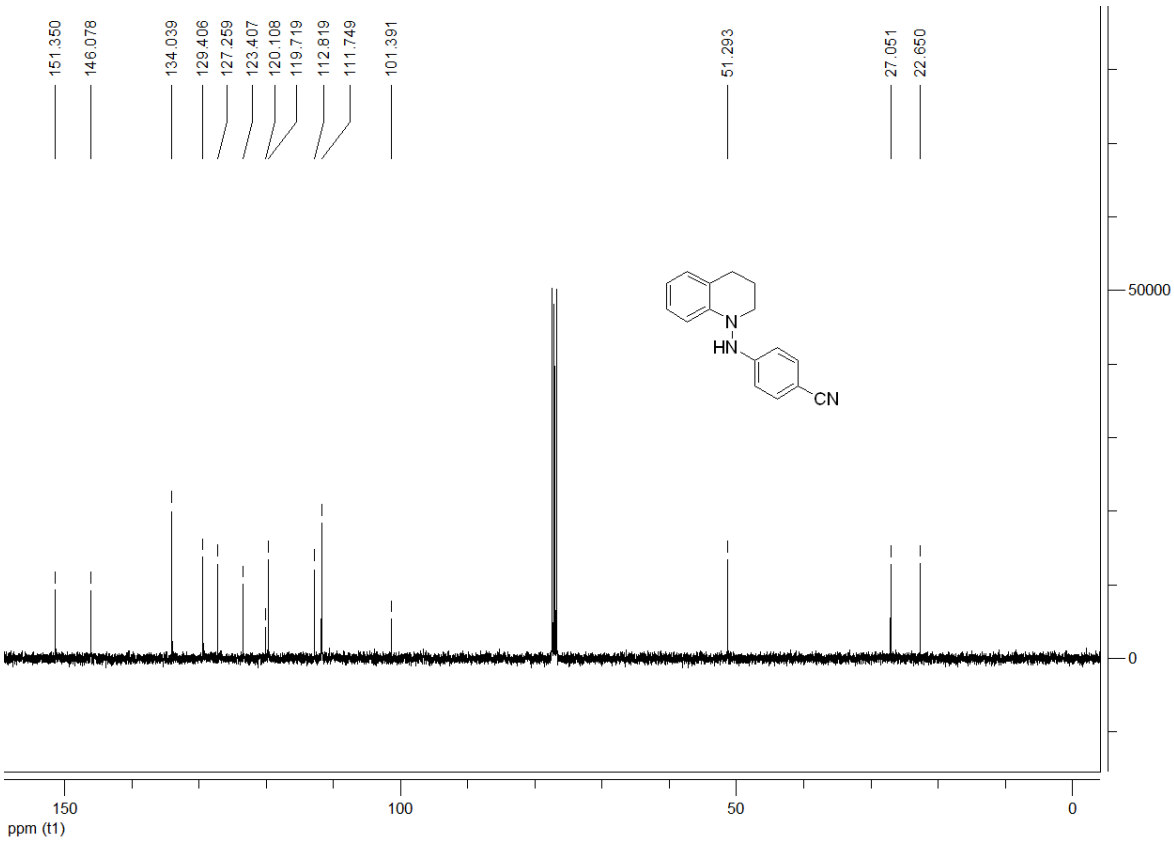
^{1}H and ^{13}C NMR of **6bb**



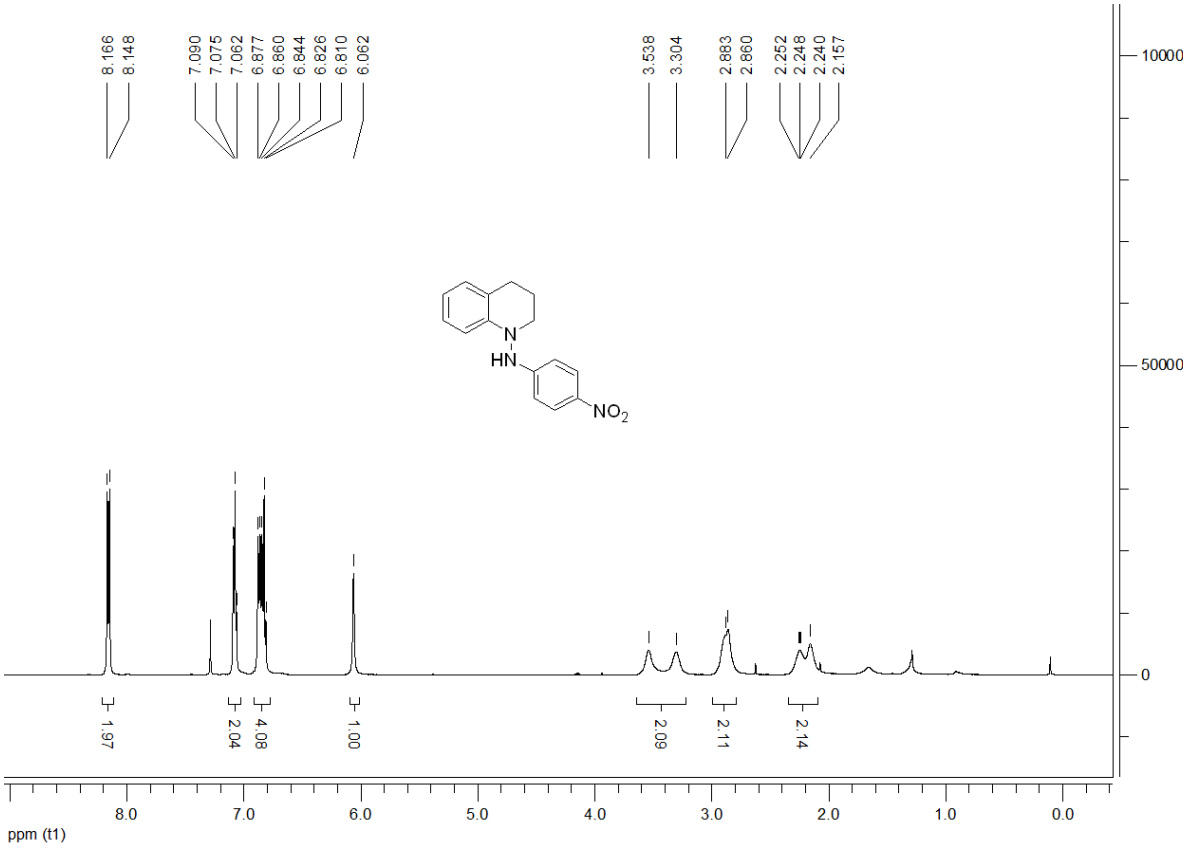


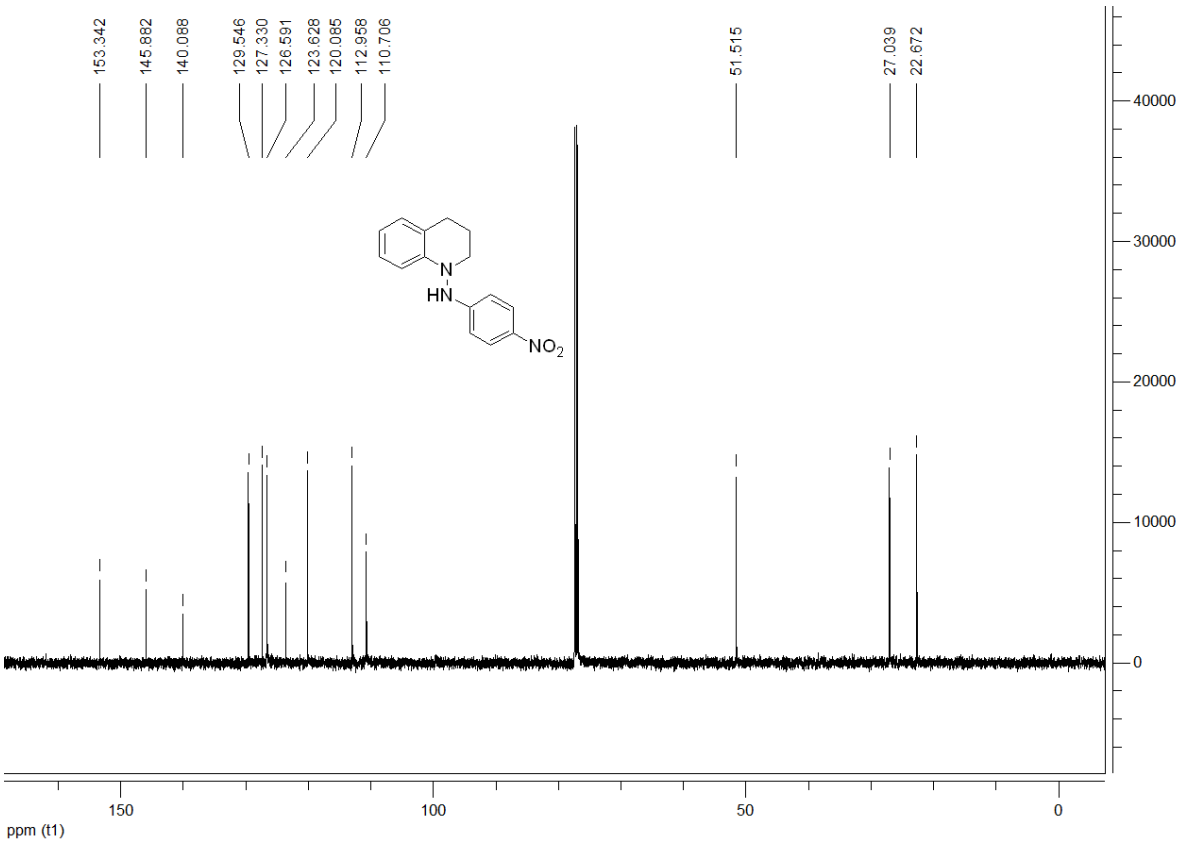
^{1}H and ^{13}C NMR of **6bc**



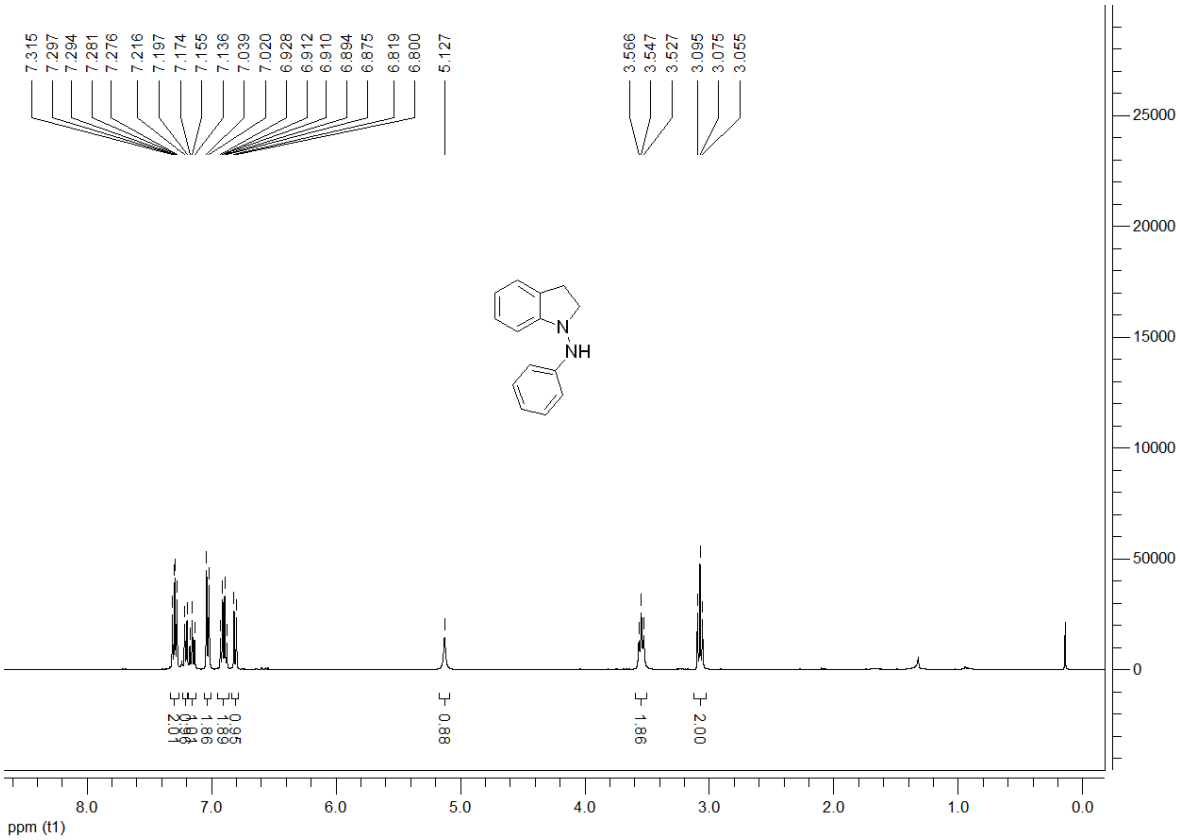


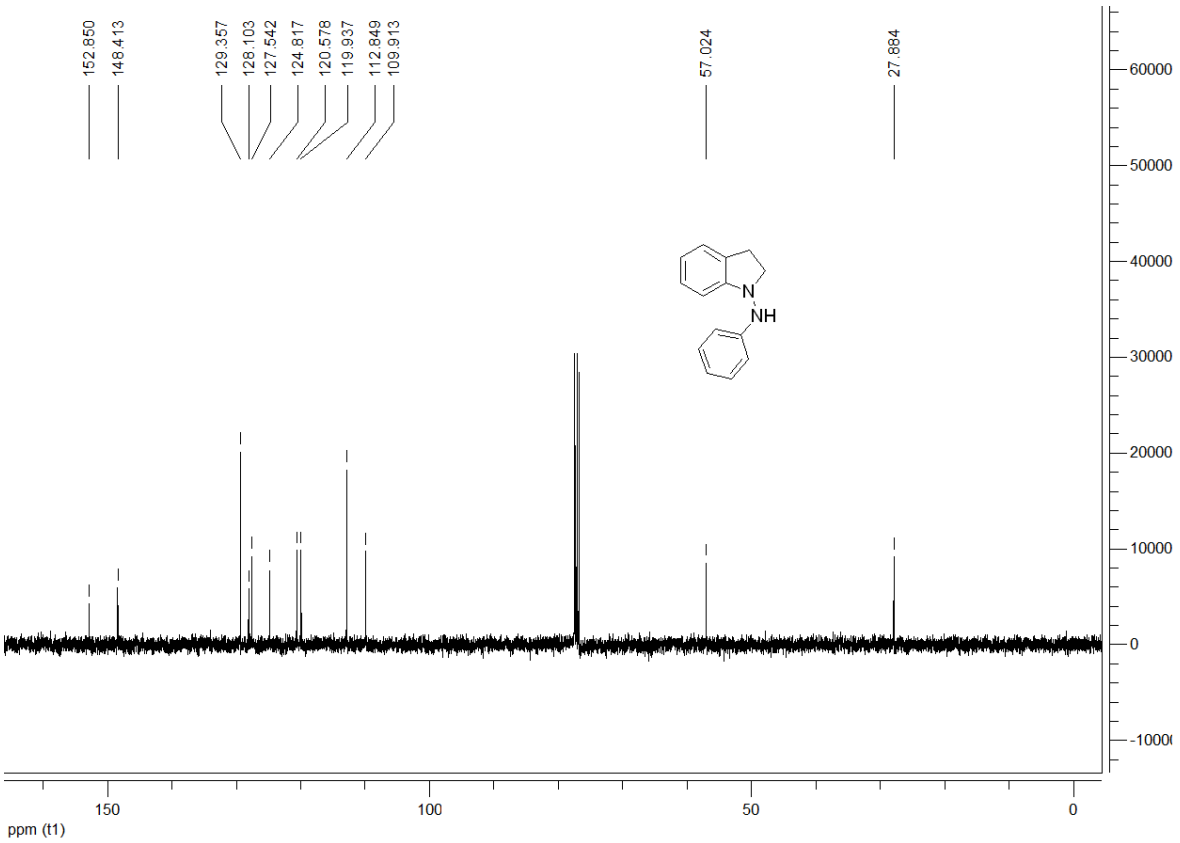
^{1}H and ^{13}C NMR of **6bd**



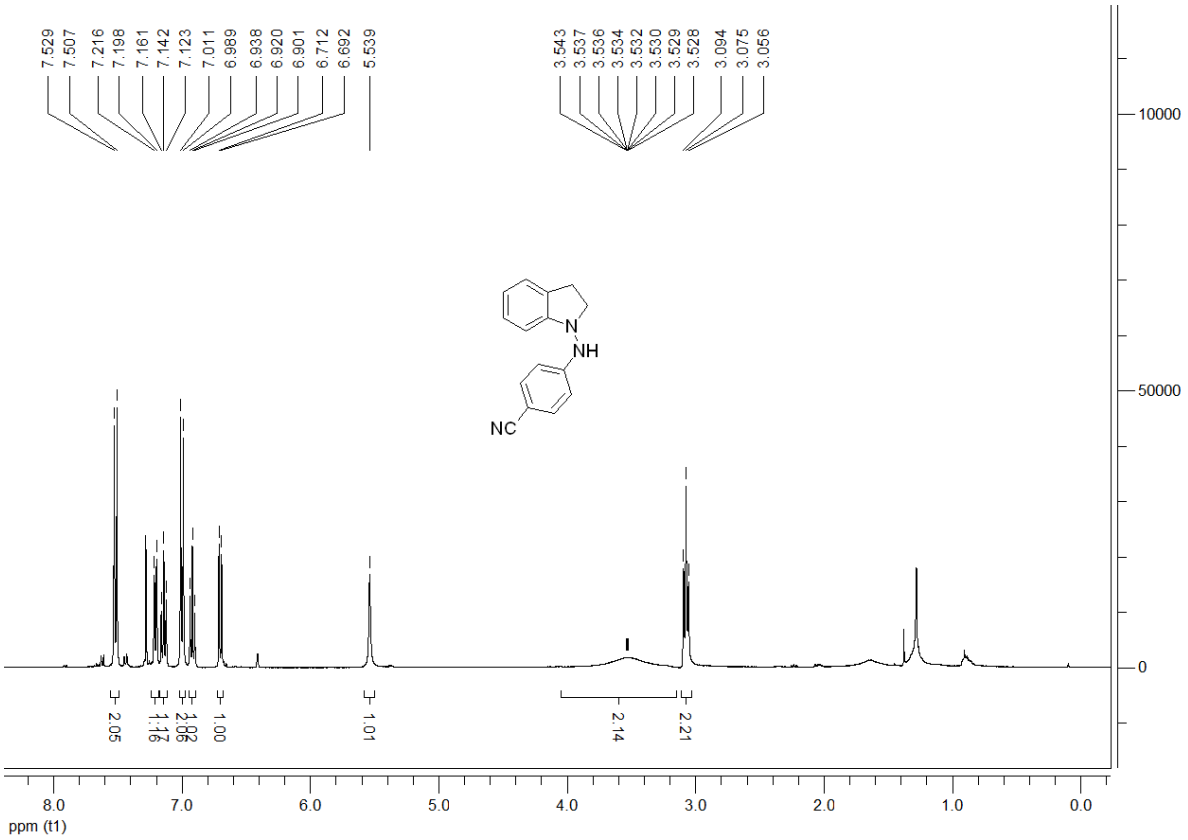


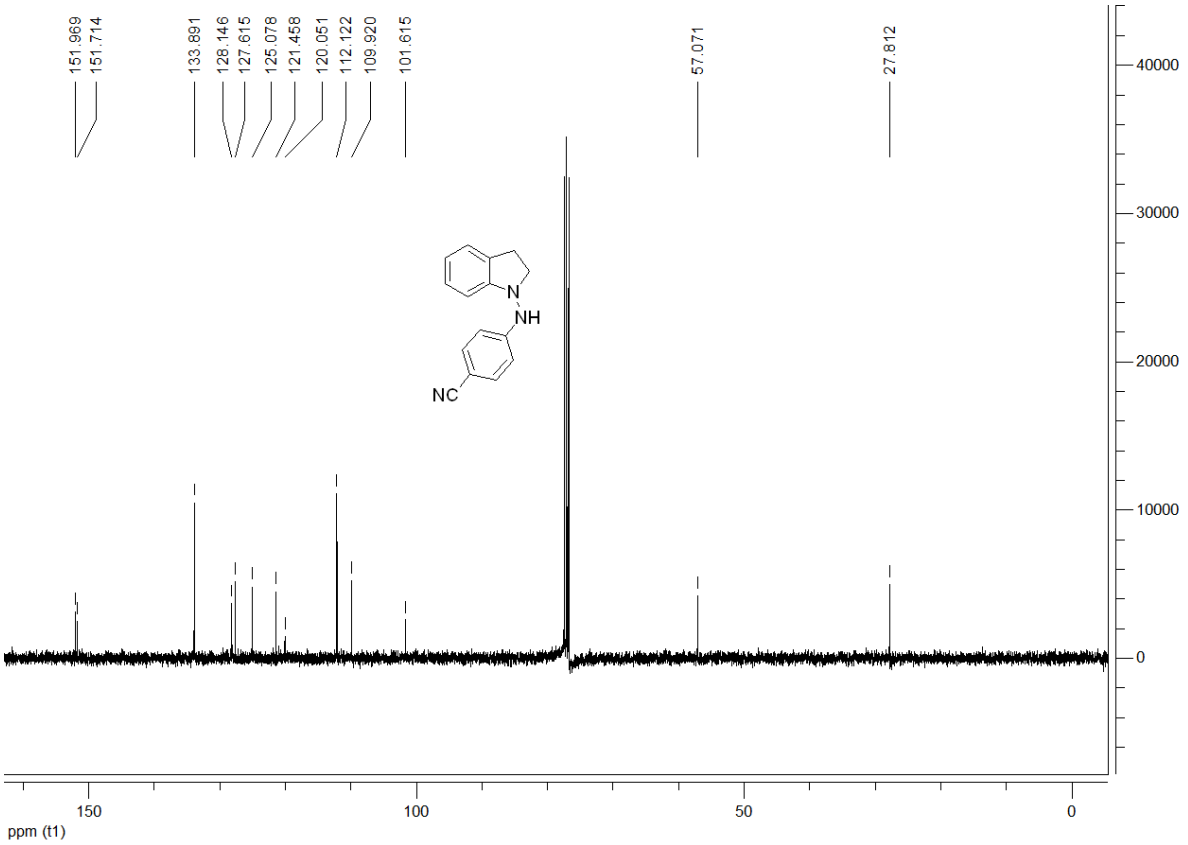
^{1}H and ^{13}C NMR of **6ca**



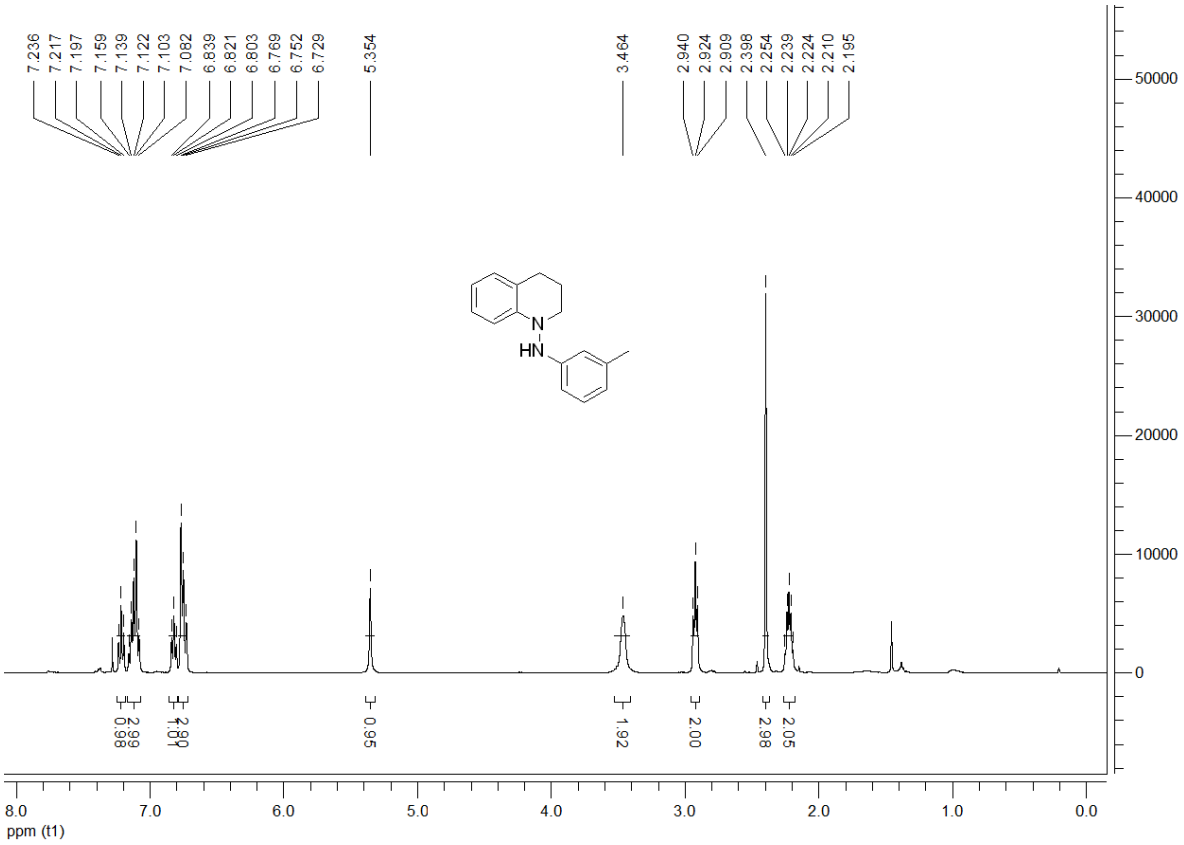


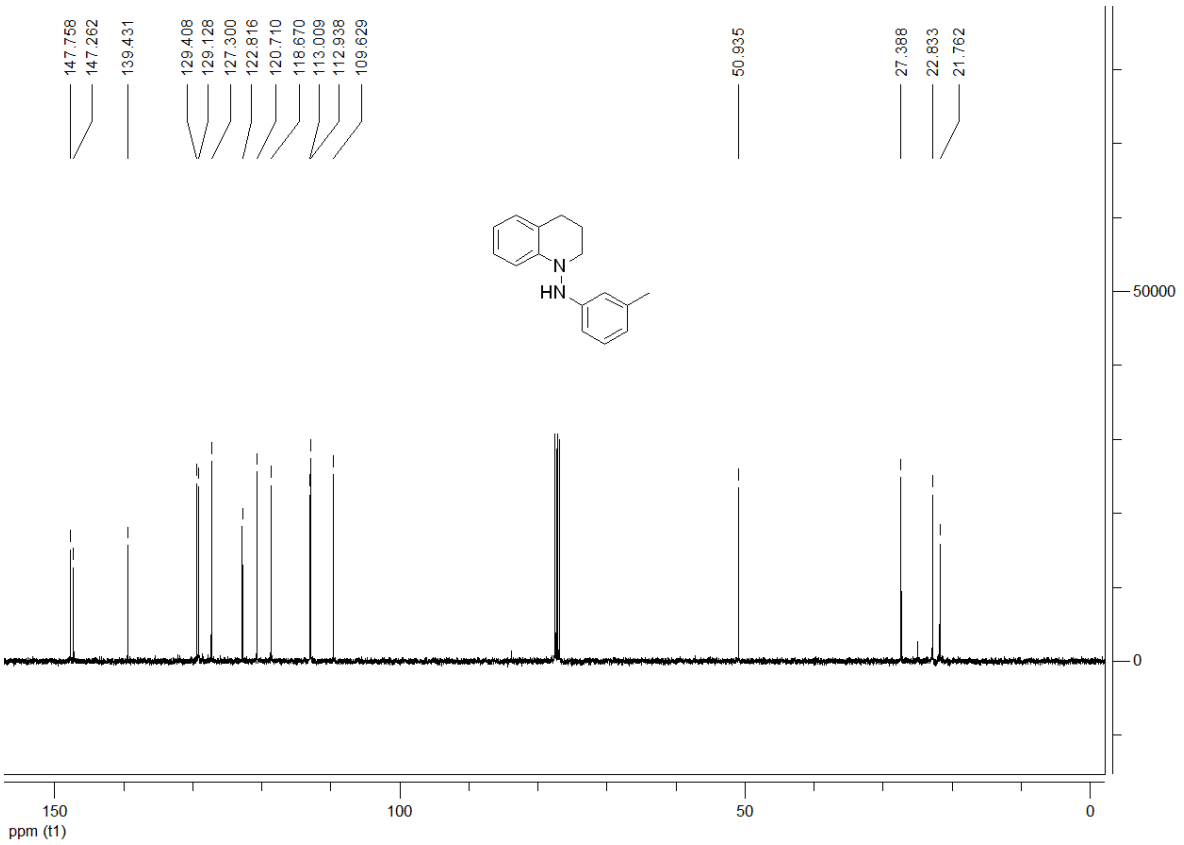
^{1}H and ^{13}C NMR of **6cc**



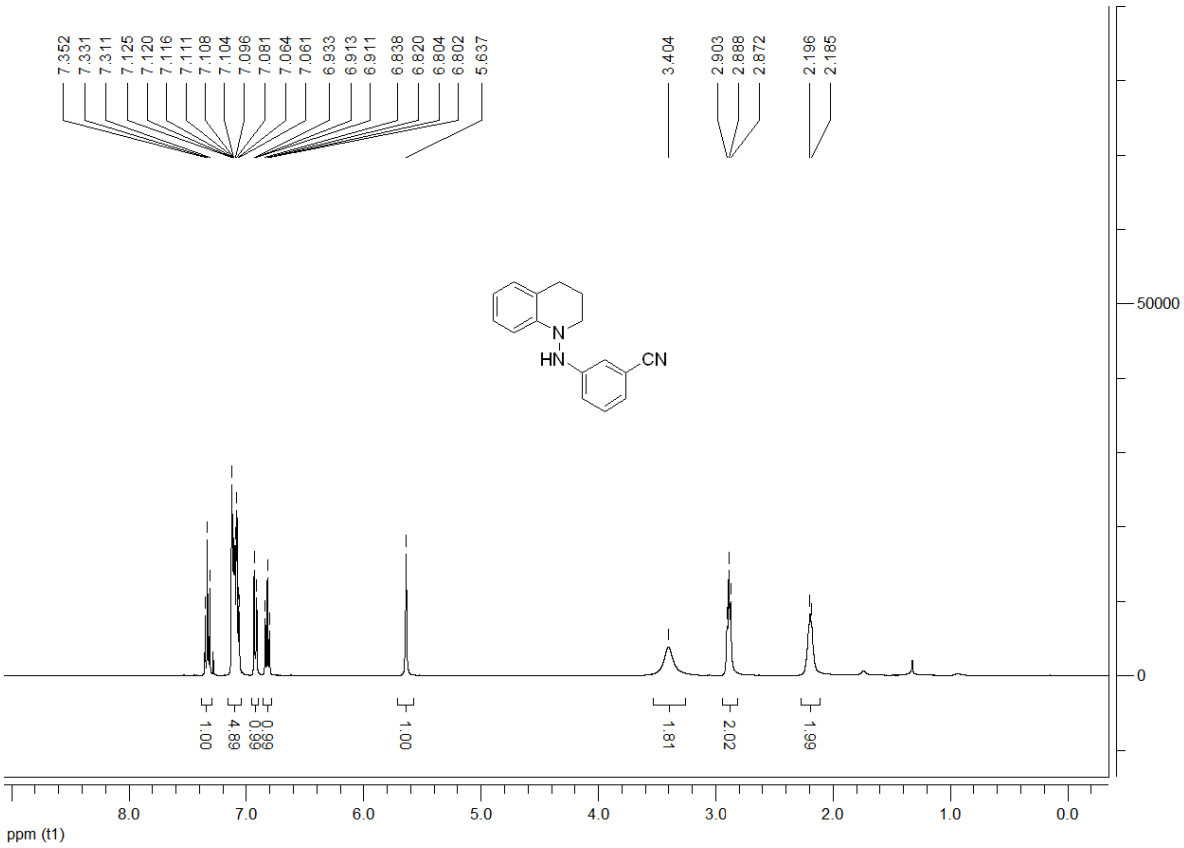


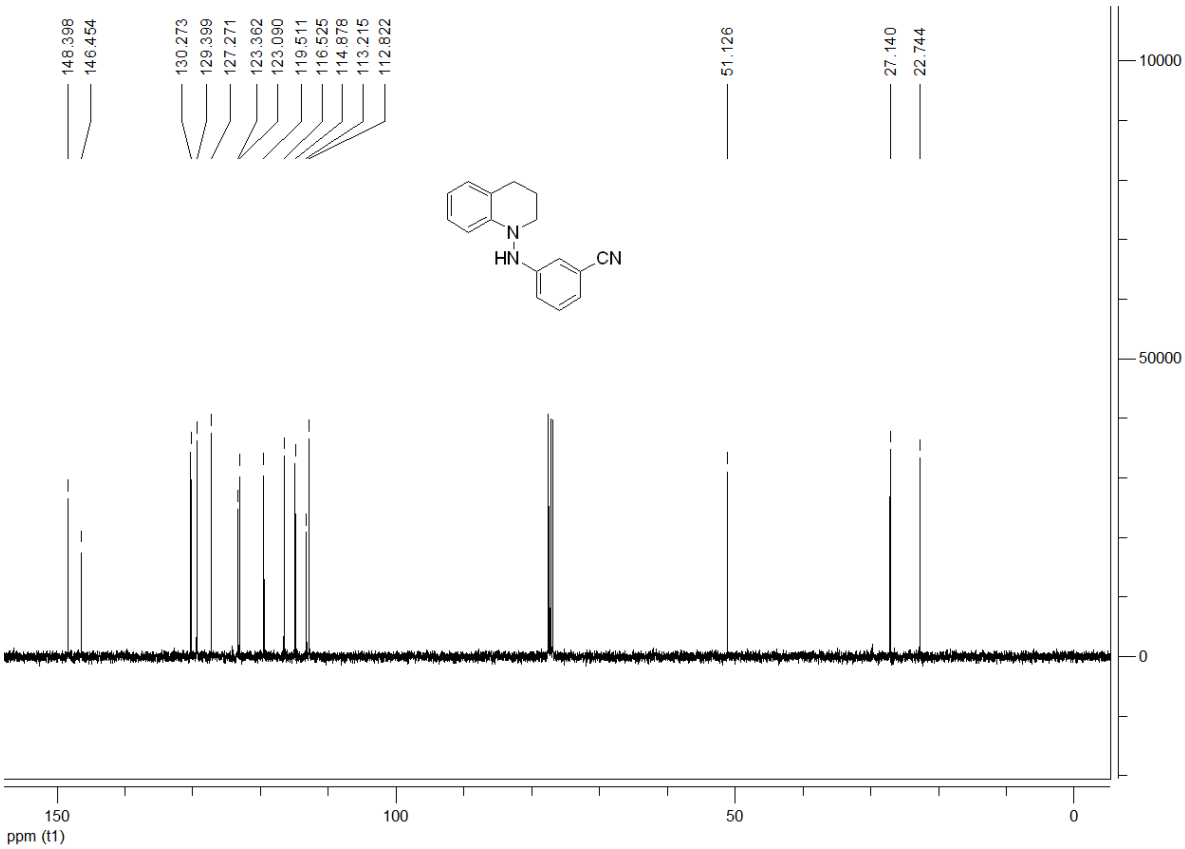
^{1}H and ^{13}C NMR of **6be**



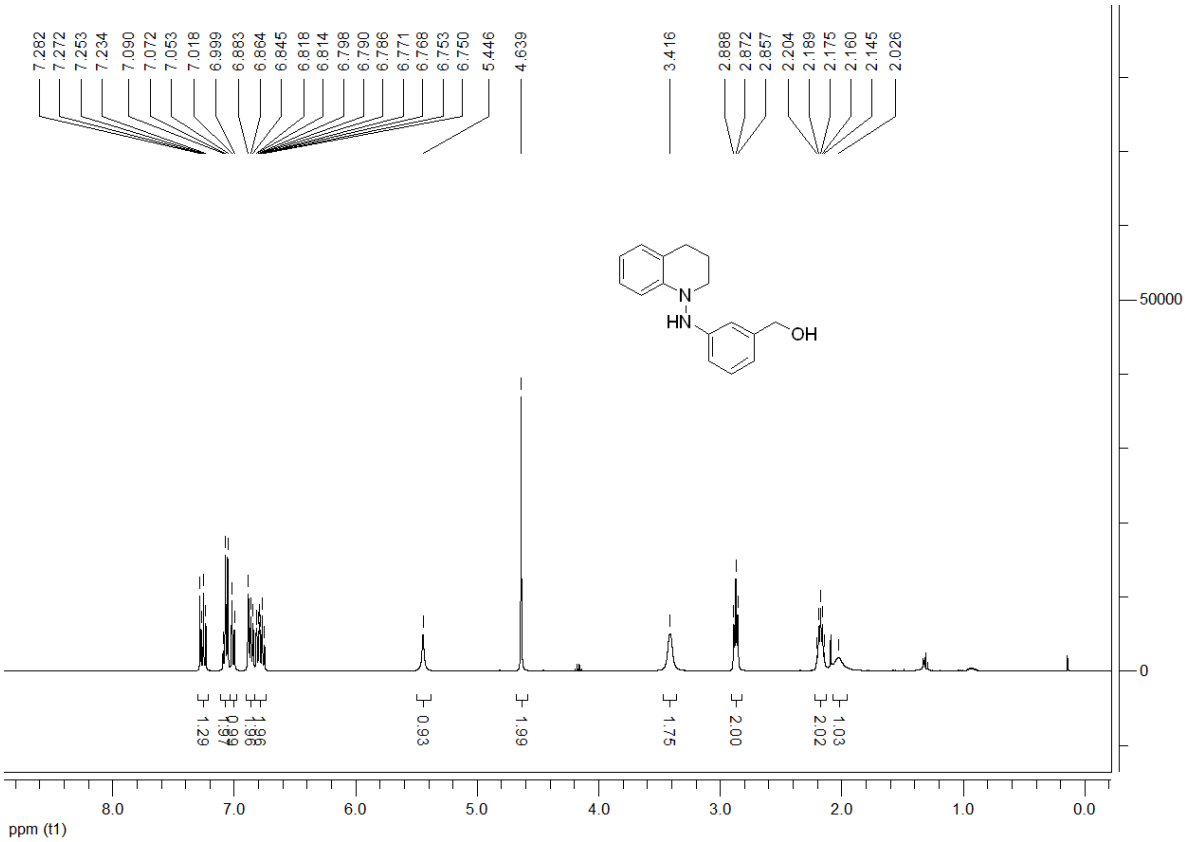


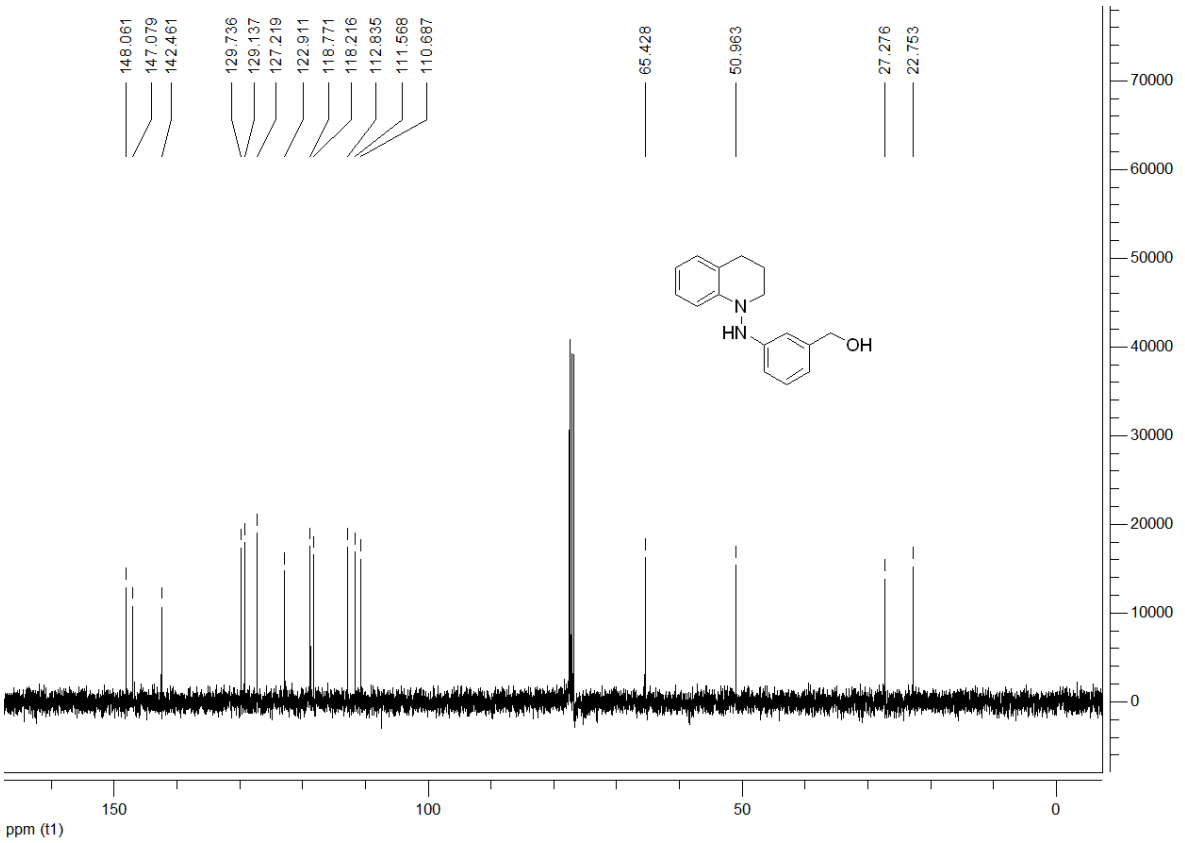
^{1}H and ^{13}C NMR of **6bf**



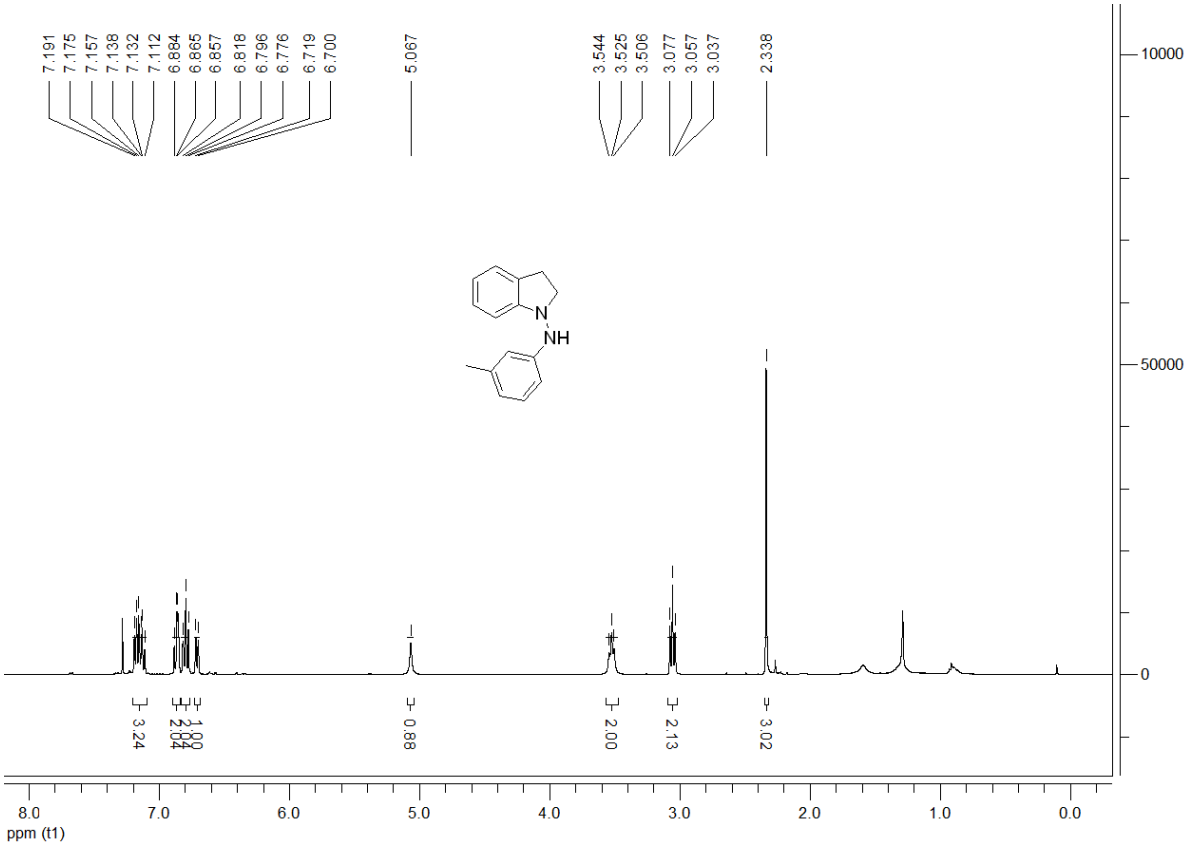


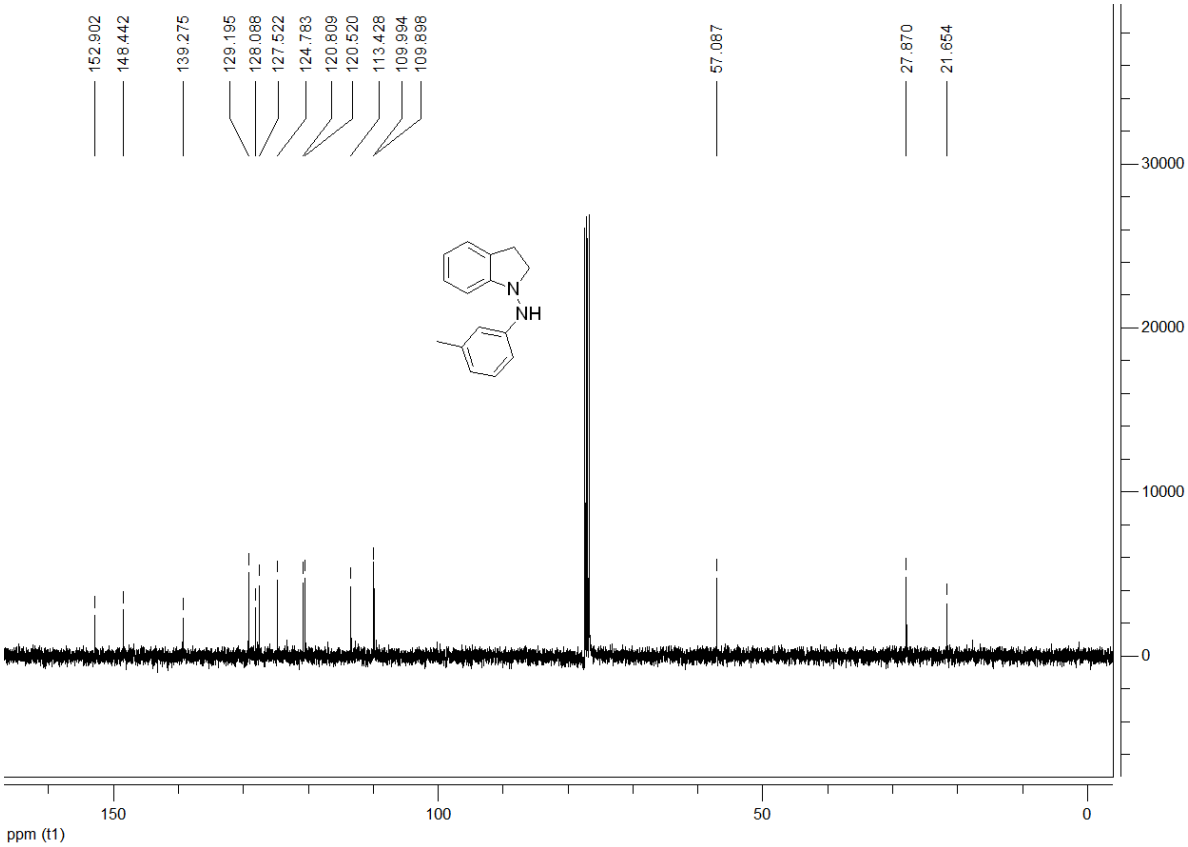
^{1}H and ^{13}C NMR of **6bg**



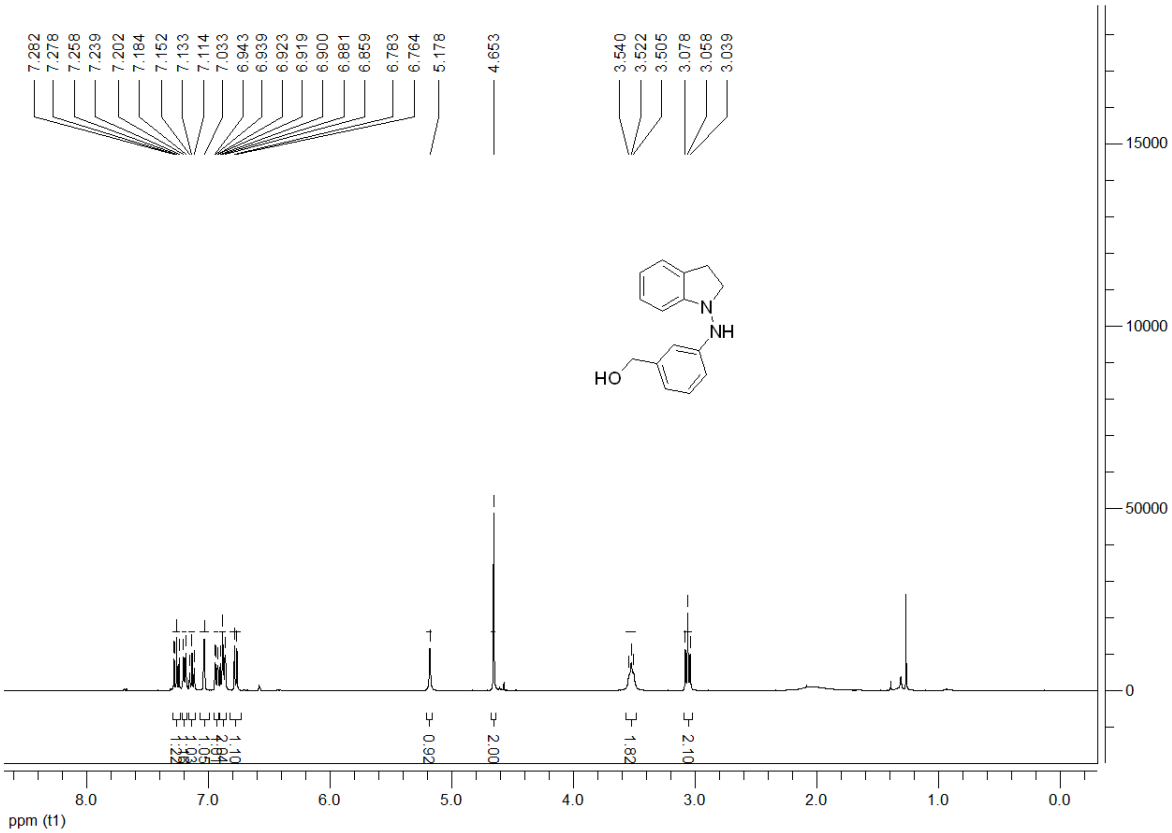


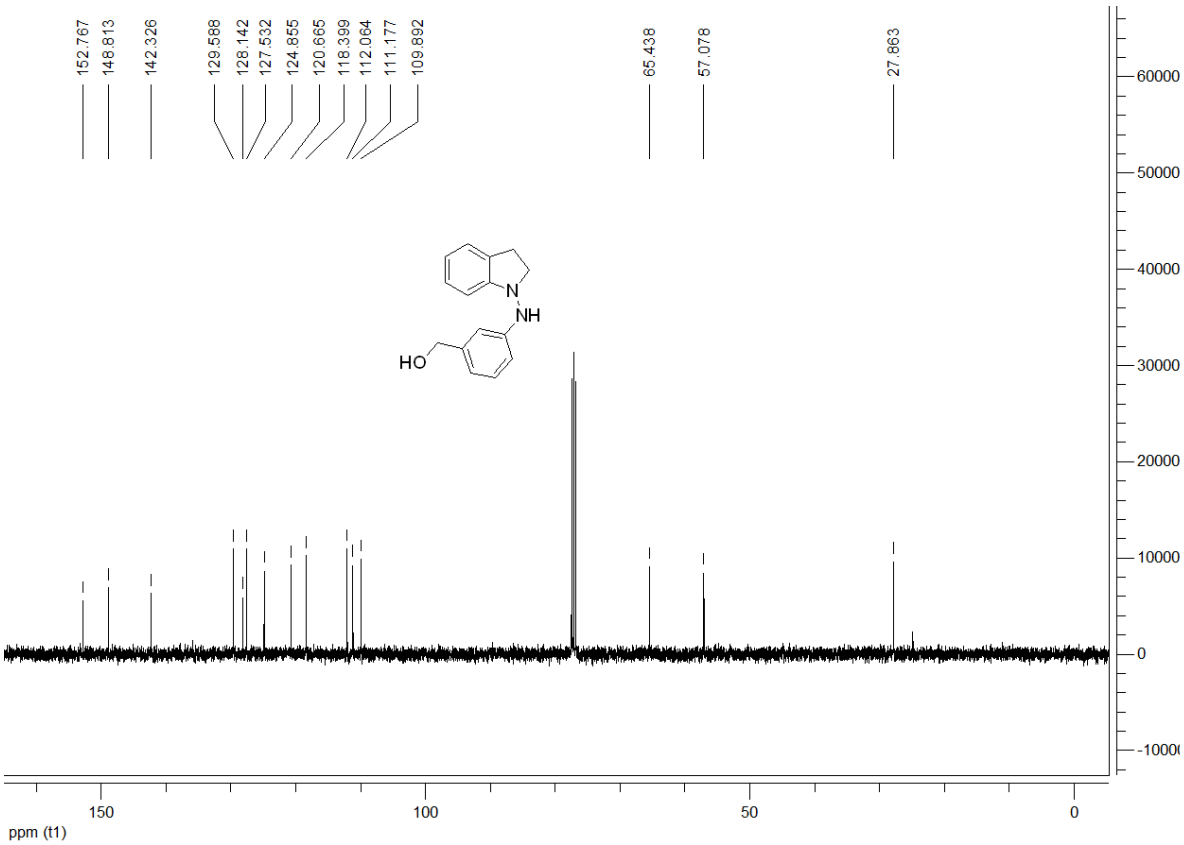
^{1}H and ^{13}C NMR of **6ce**



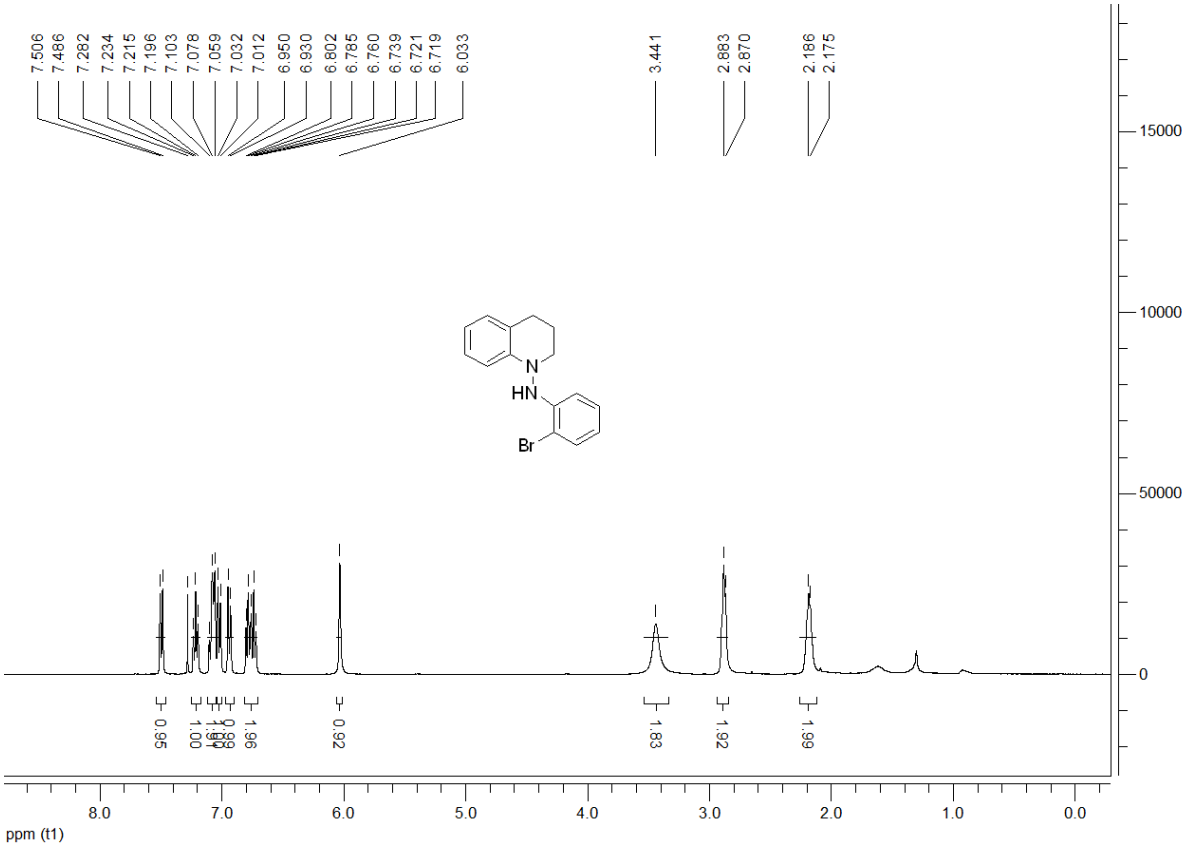


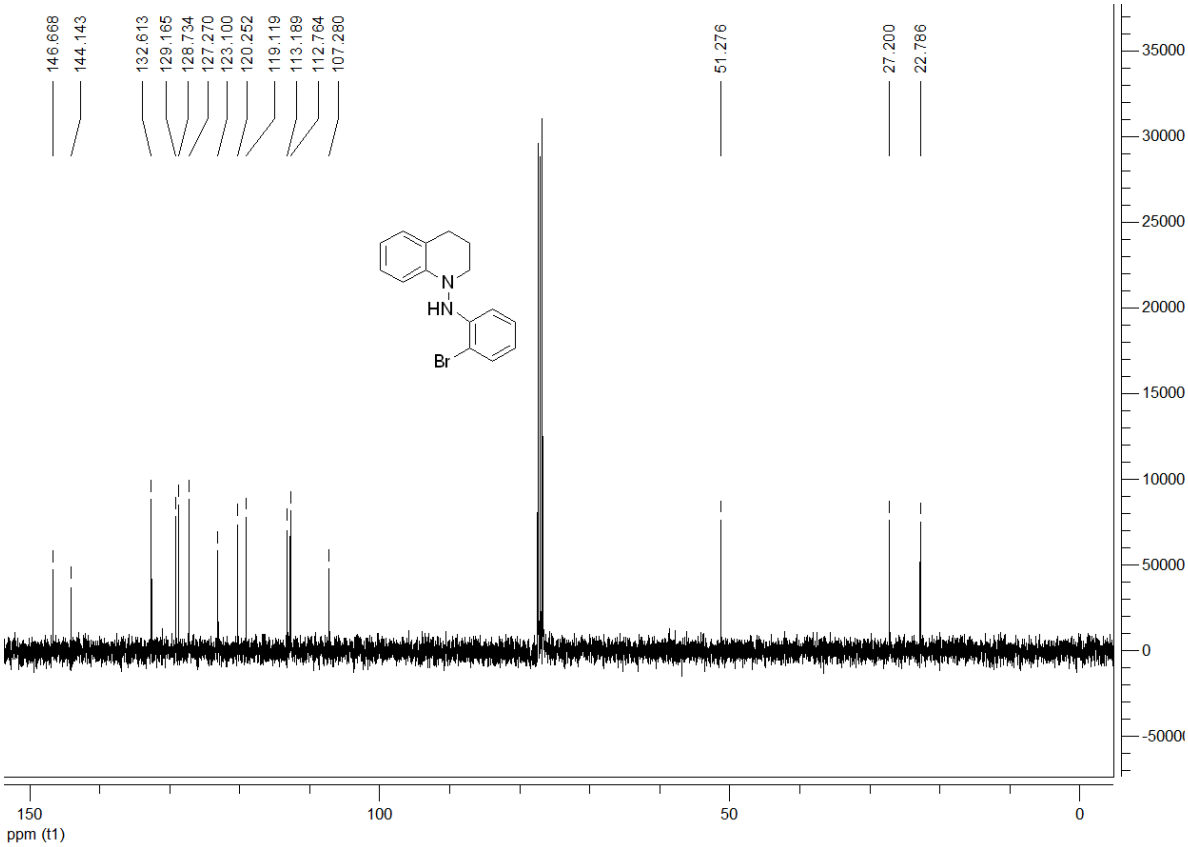
^{1}H and ^{13}C NMR of **6cg**



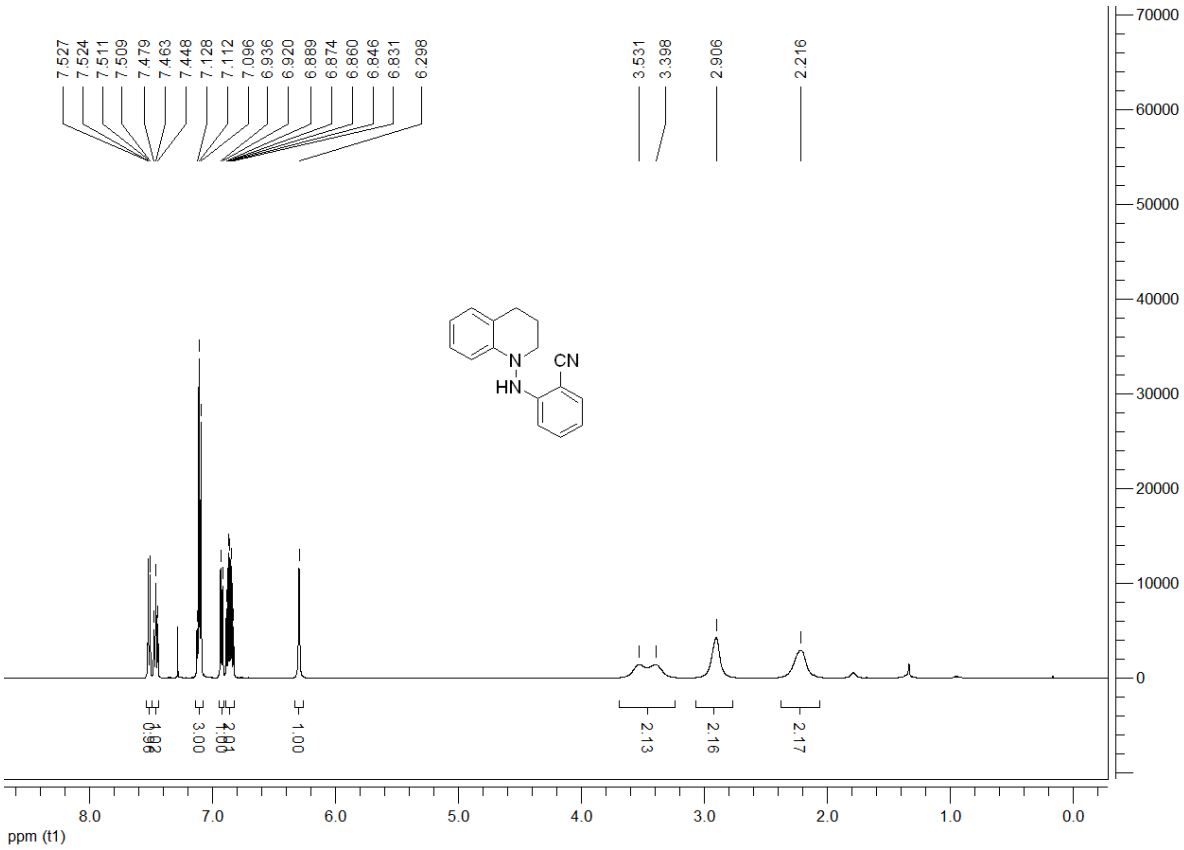


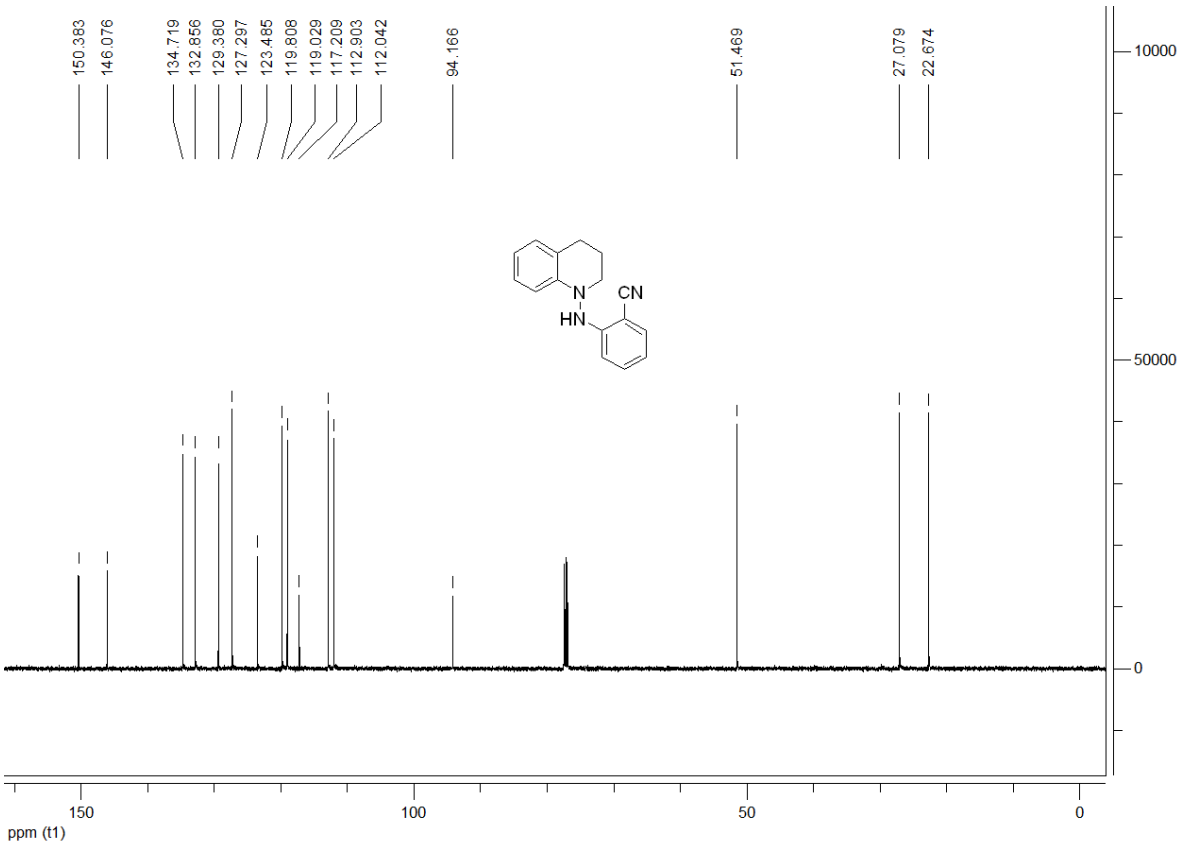
^{1}H and ^{13}C NMR of **6bh**



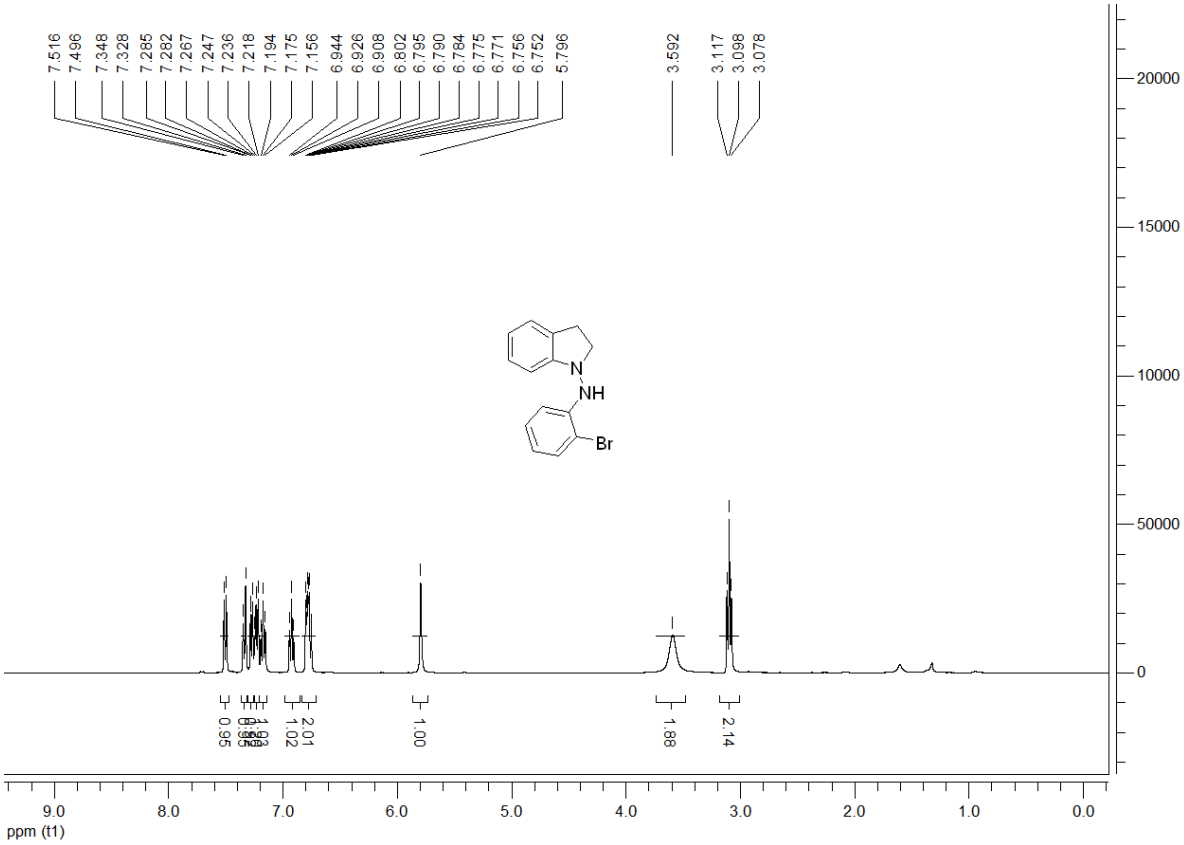


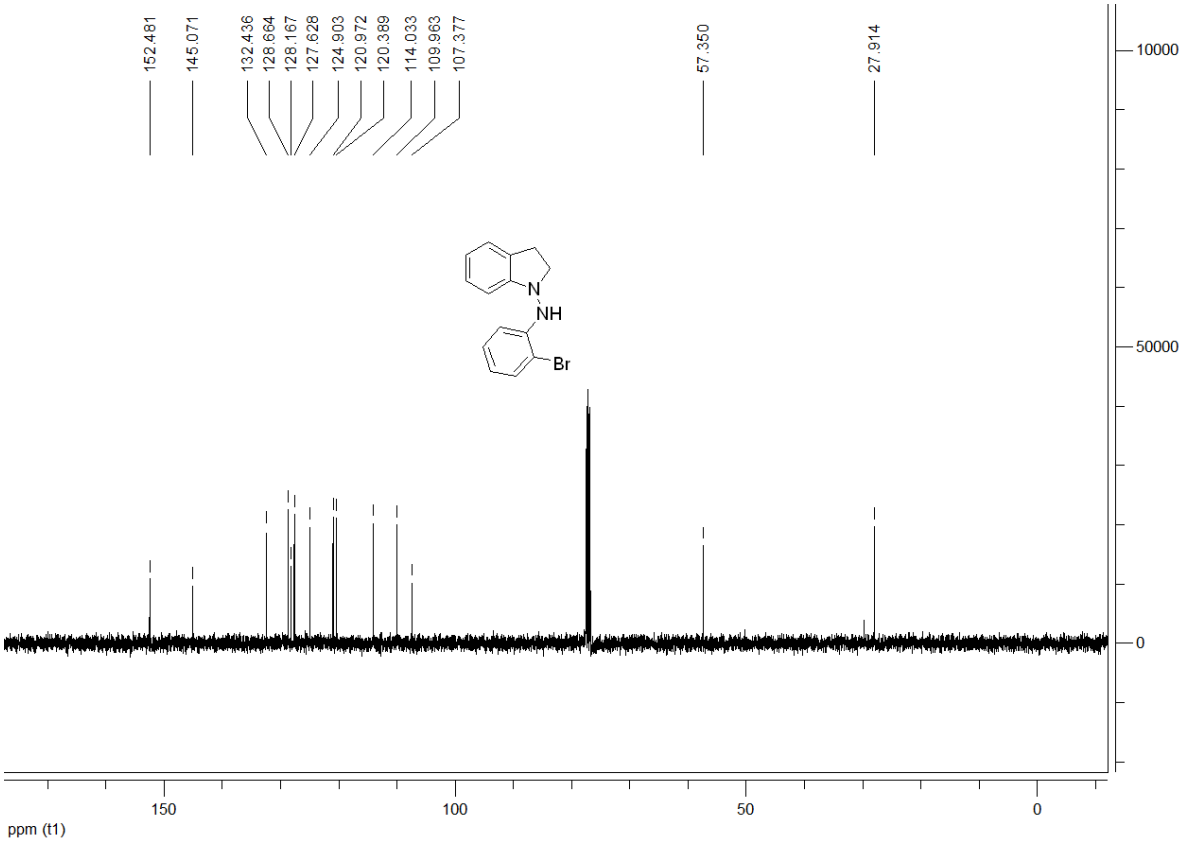
^{1}H and ^{13}C NMR of **6bi**



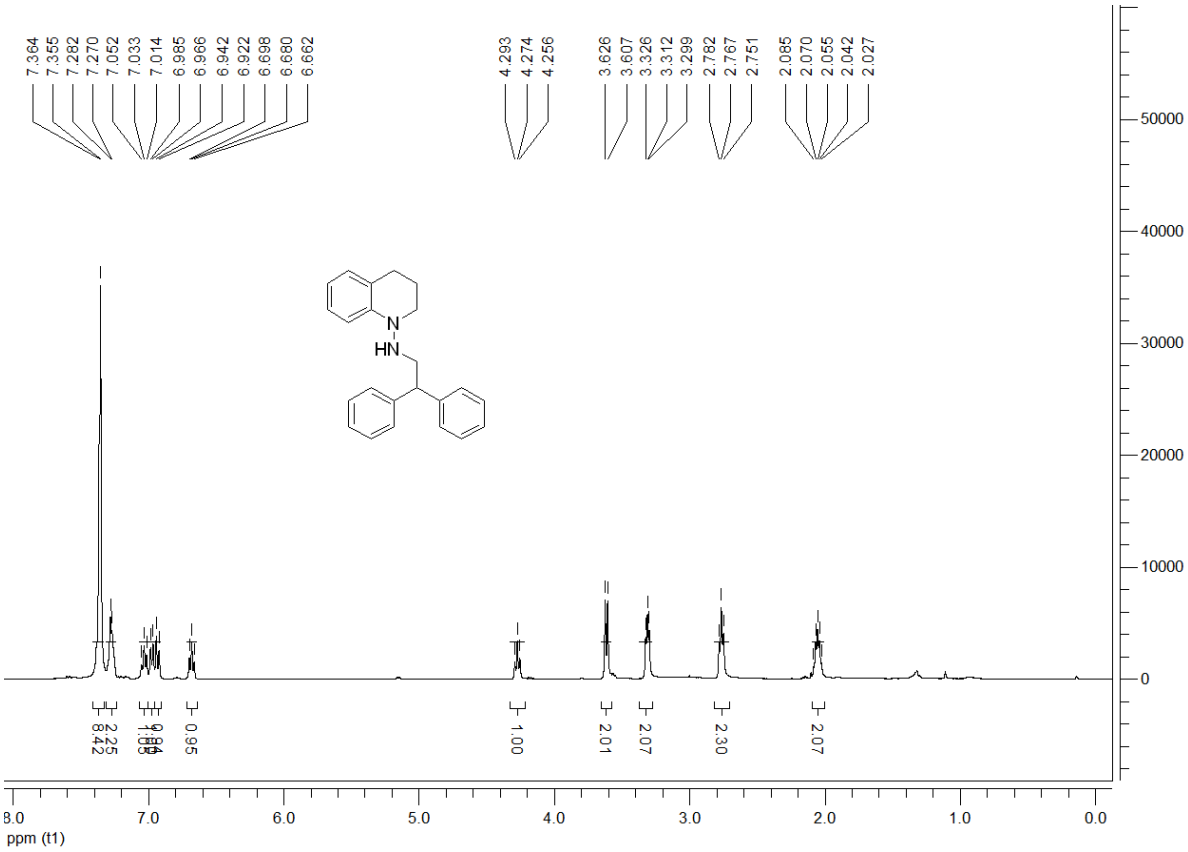


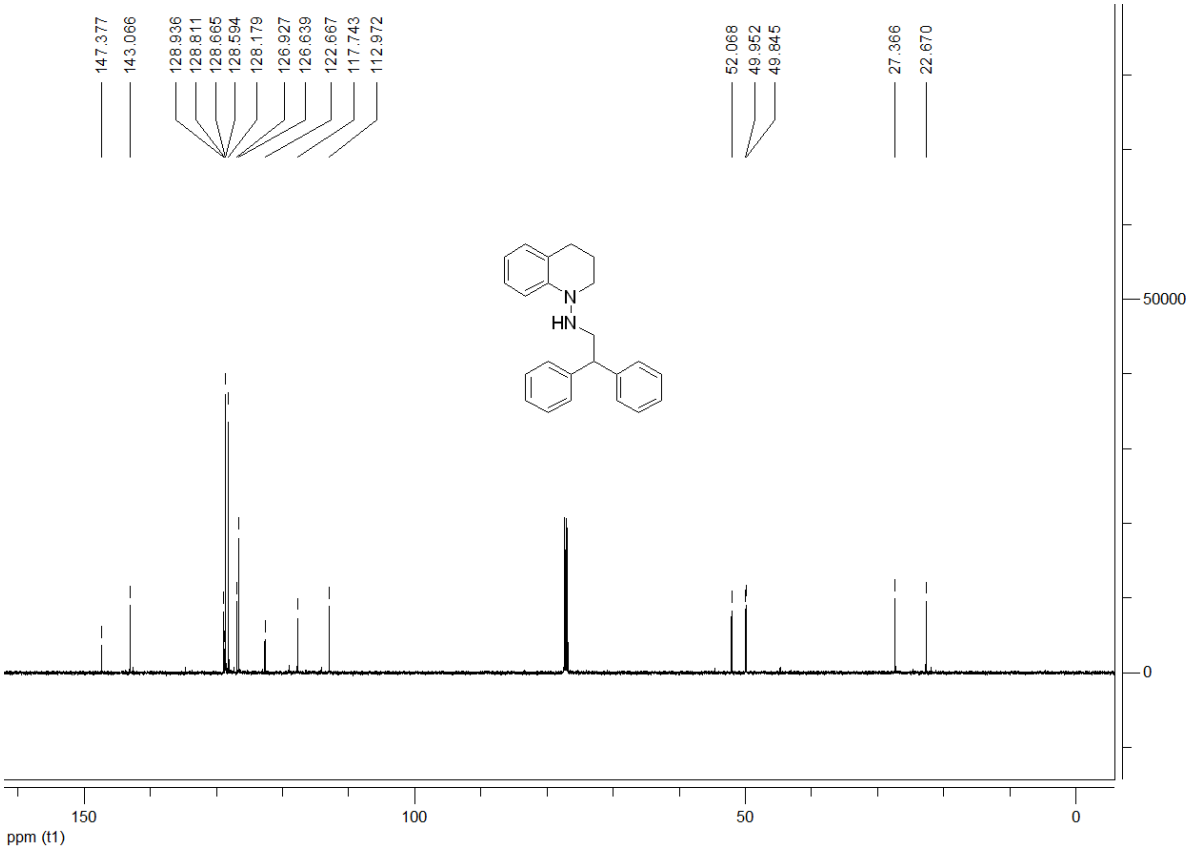
^{1}H and ^{13}C NMR of **6ch**



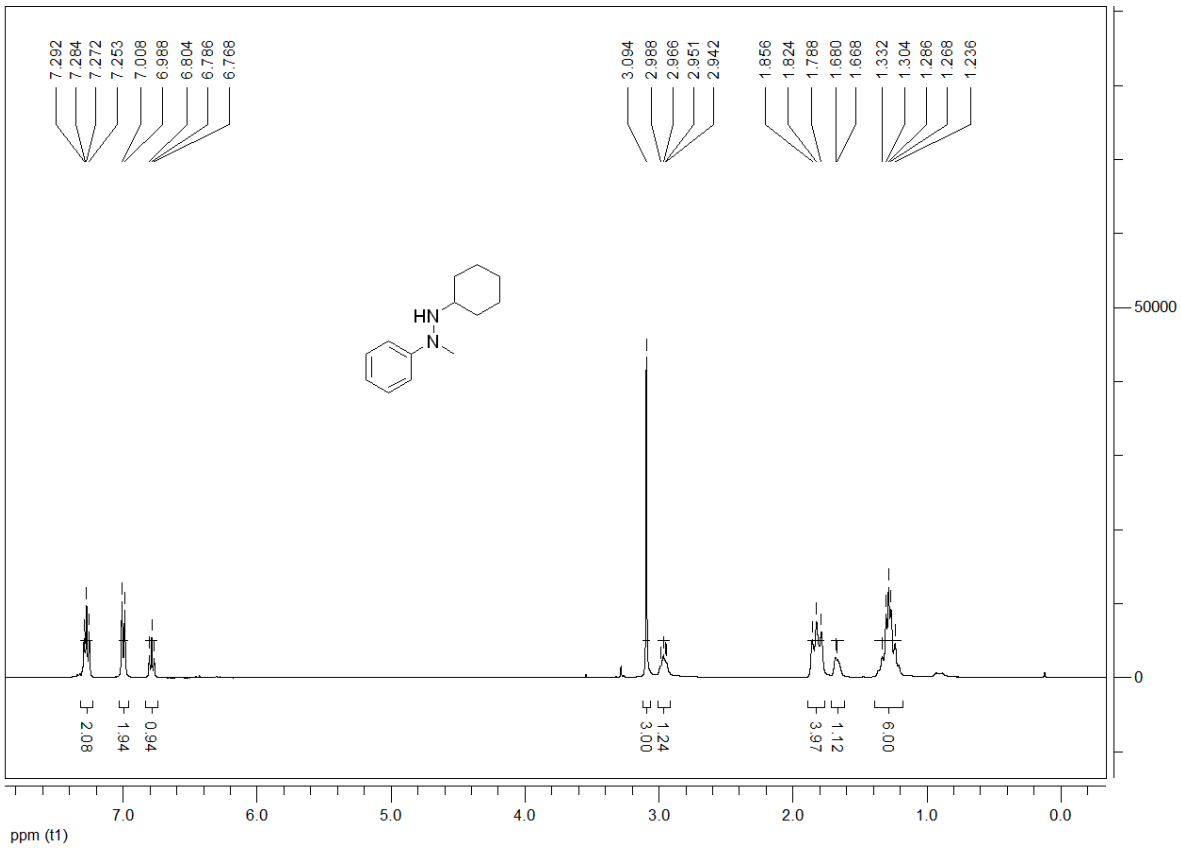


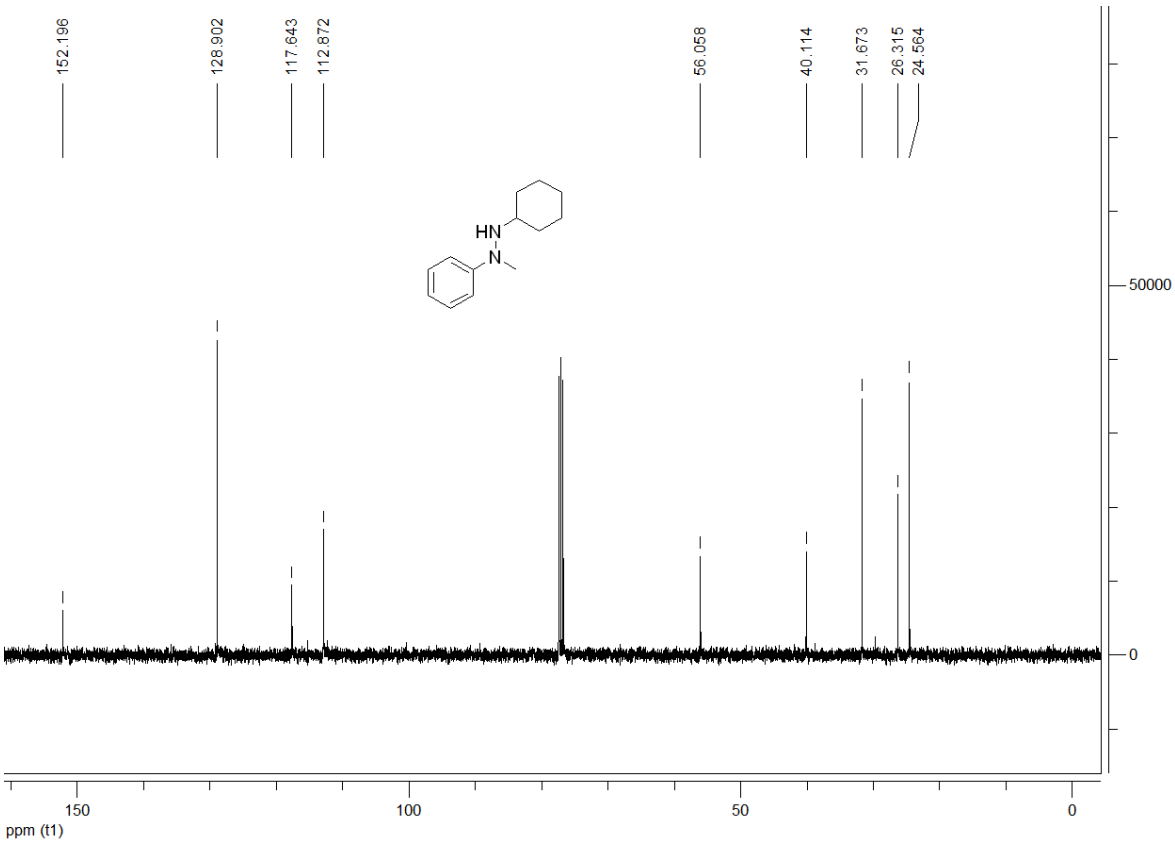
^{1}H and ^{13}C NMR of **6bj**



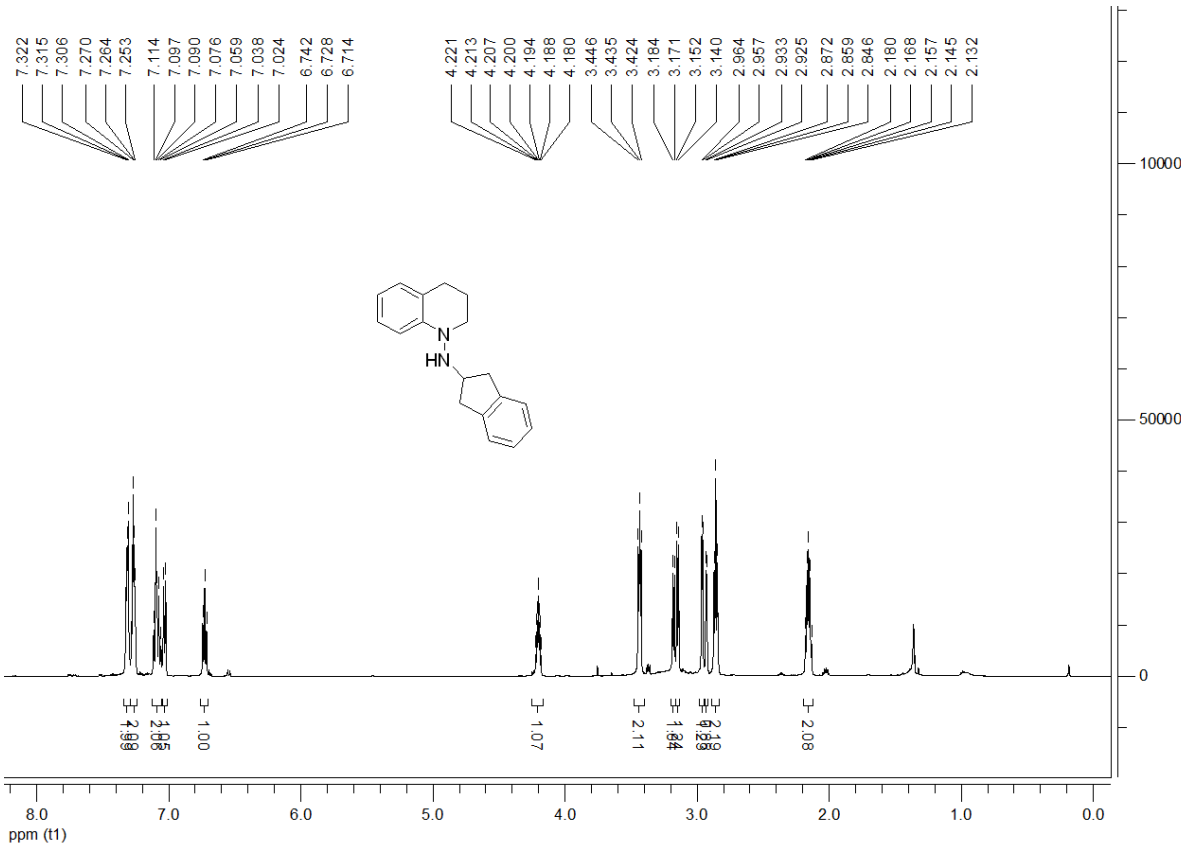


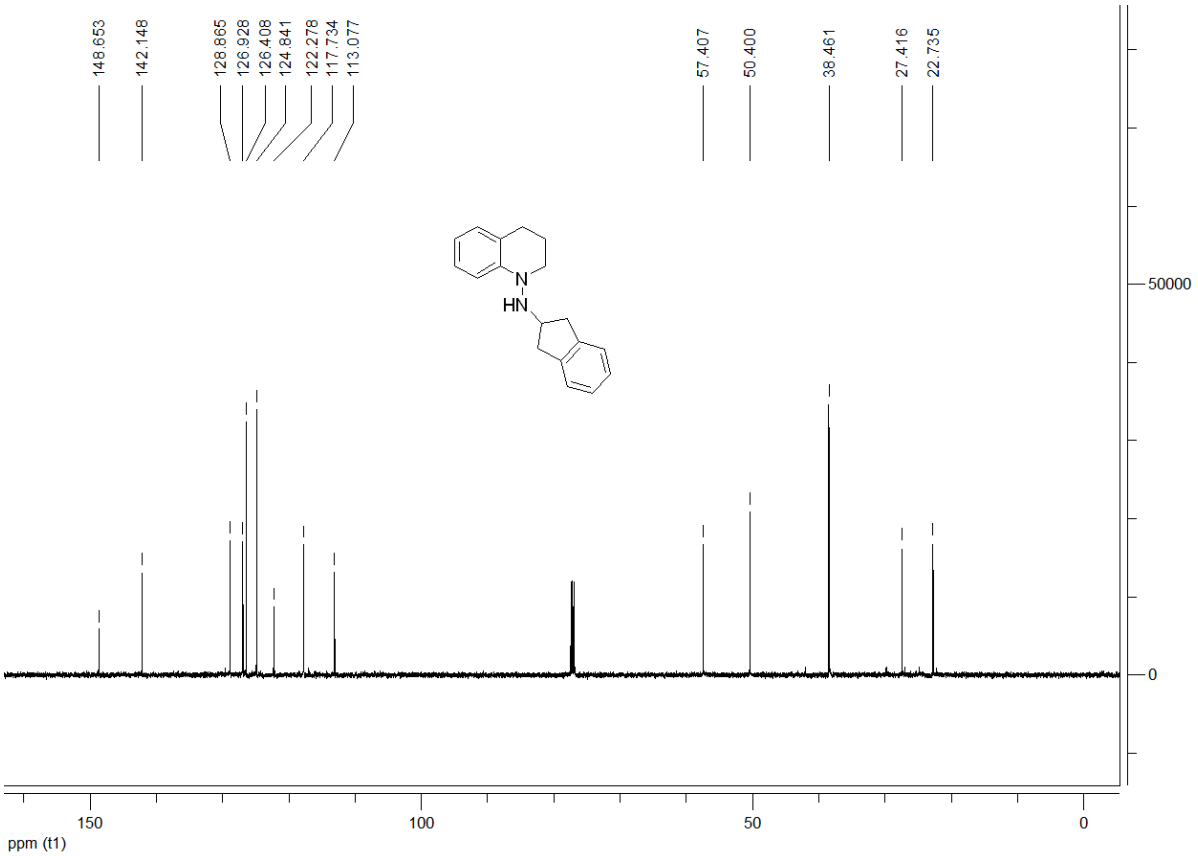
^{1}H and ^{13}C NMR of **6ak**



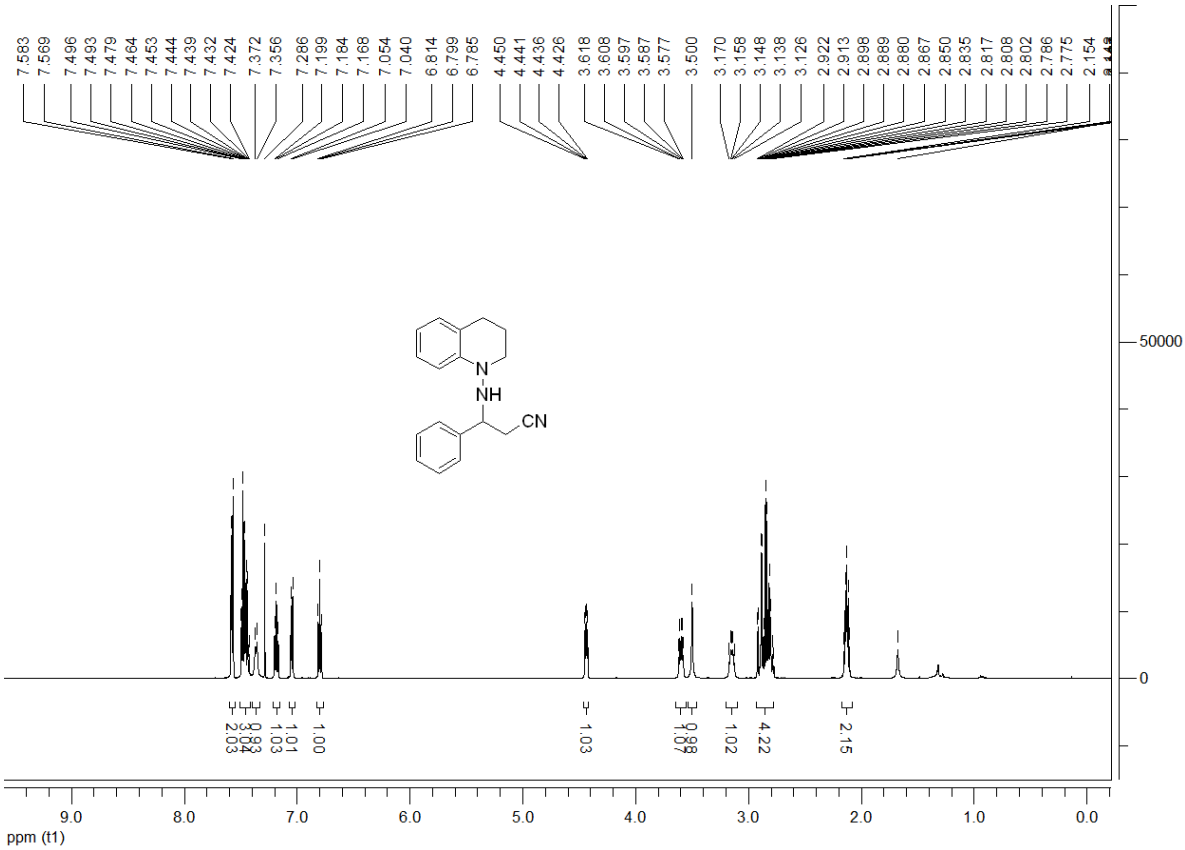


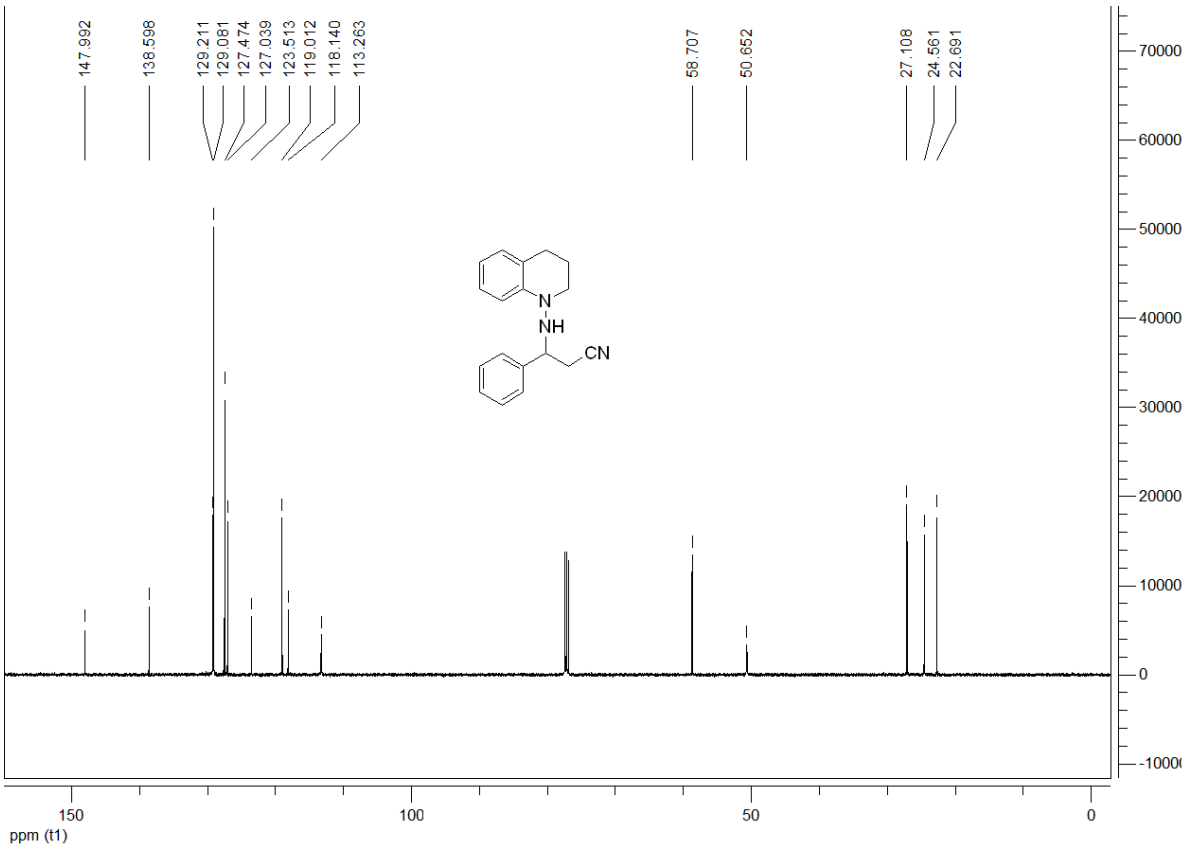
^{1}H and ^{13}C NMR of **6bl**



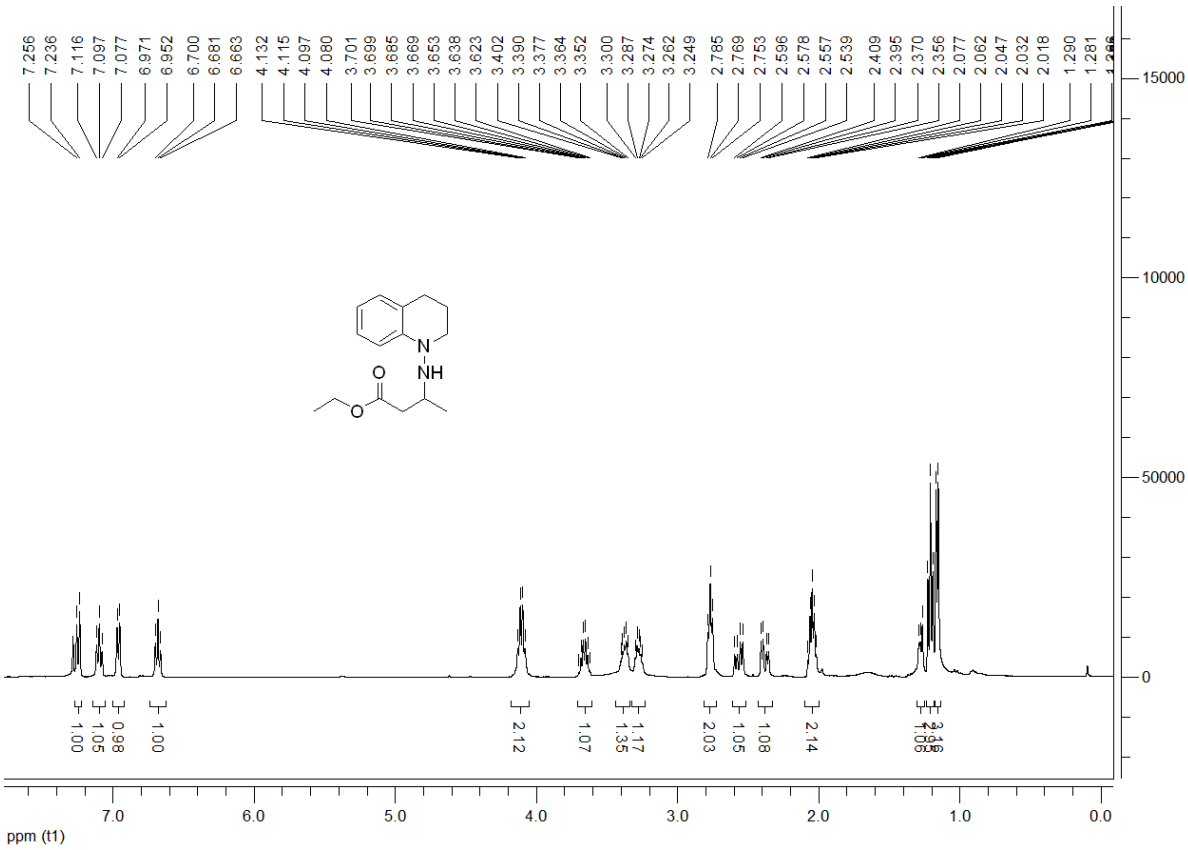


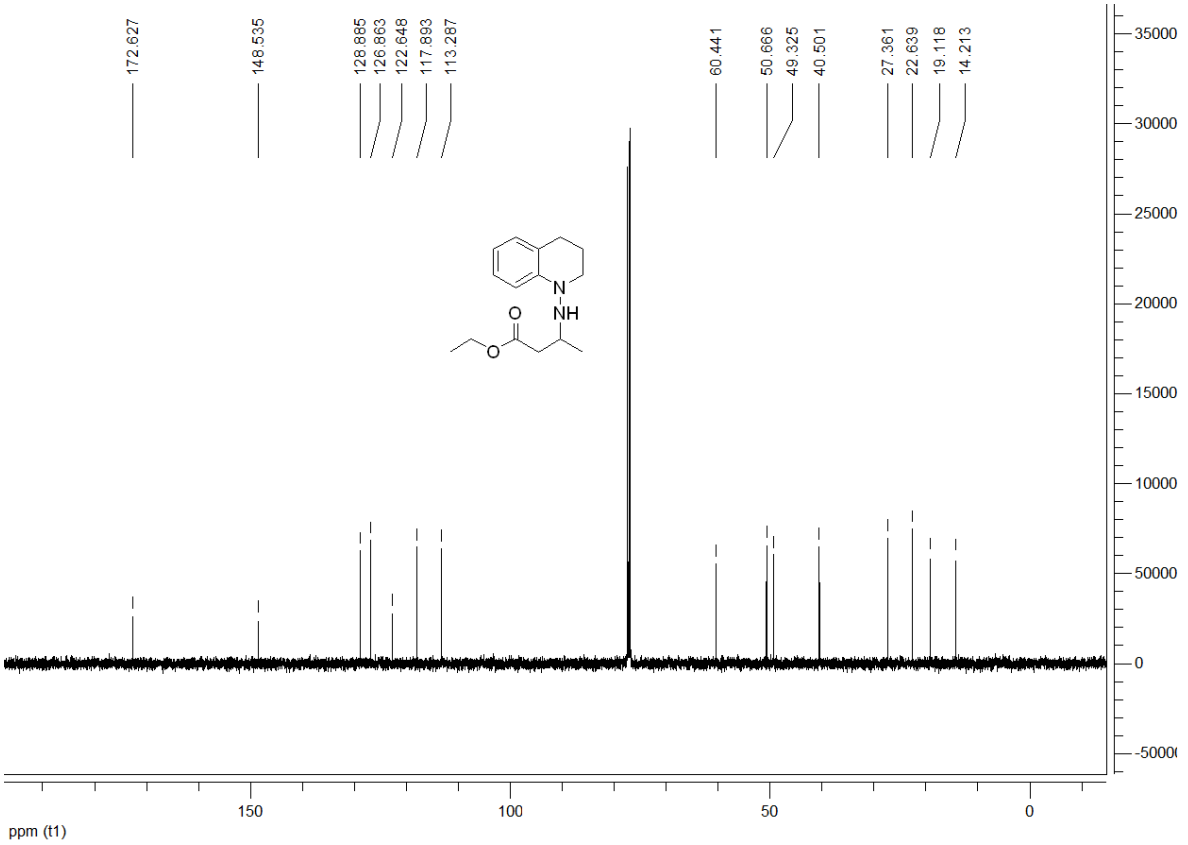
^{1}H and ^{13}C NMR of **6bn**



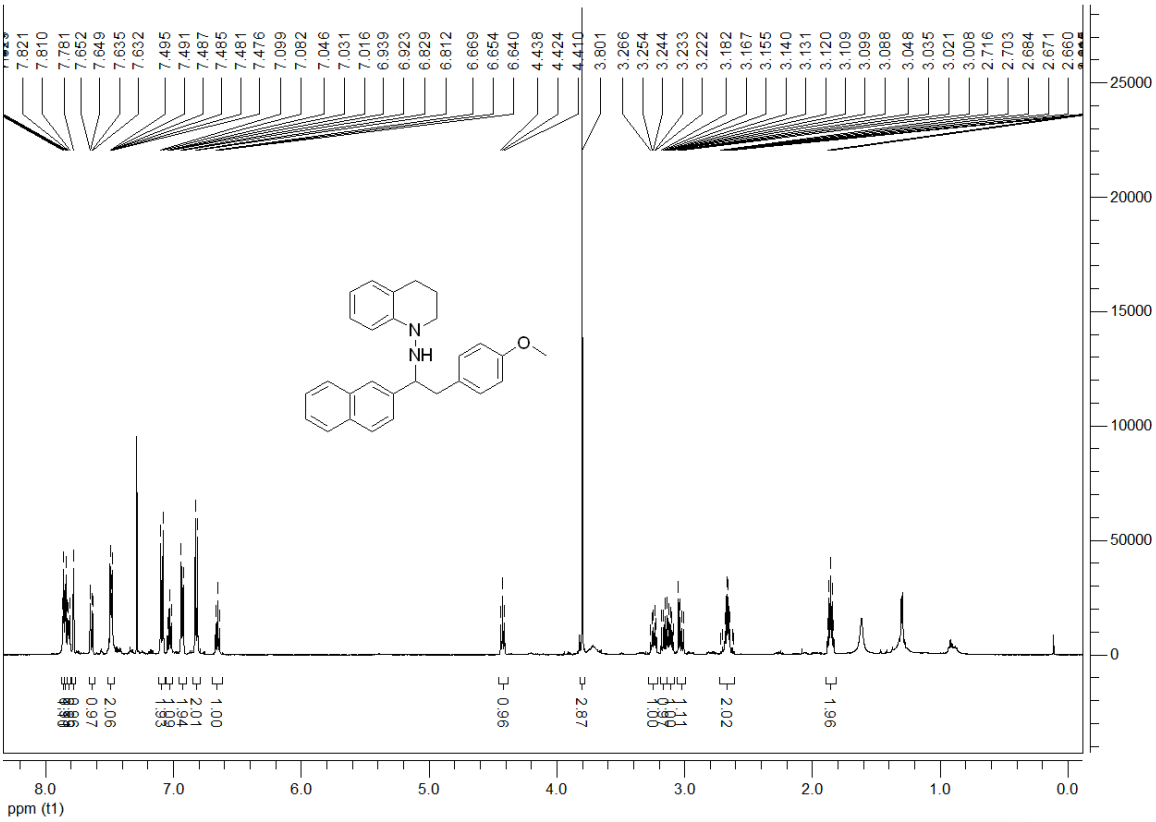


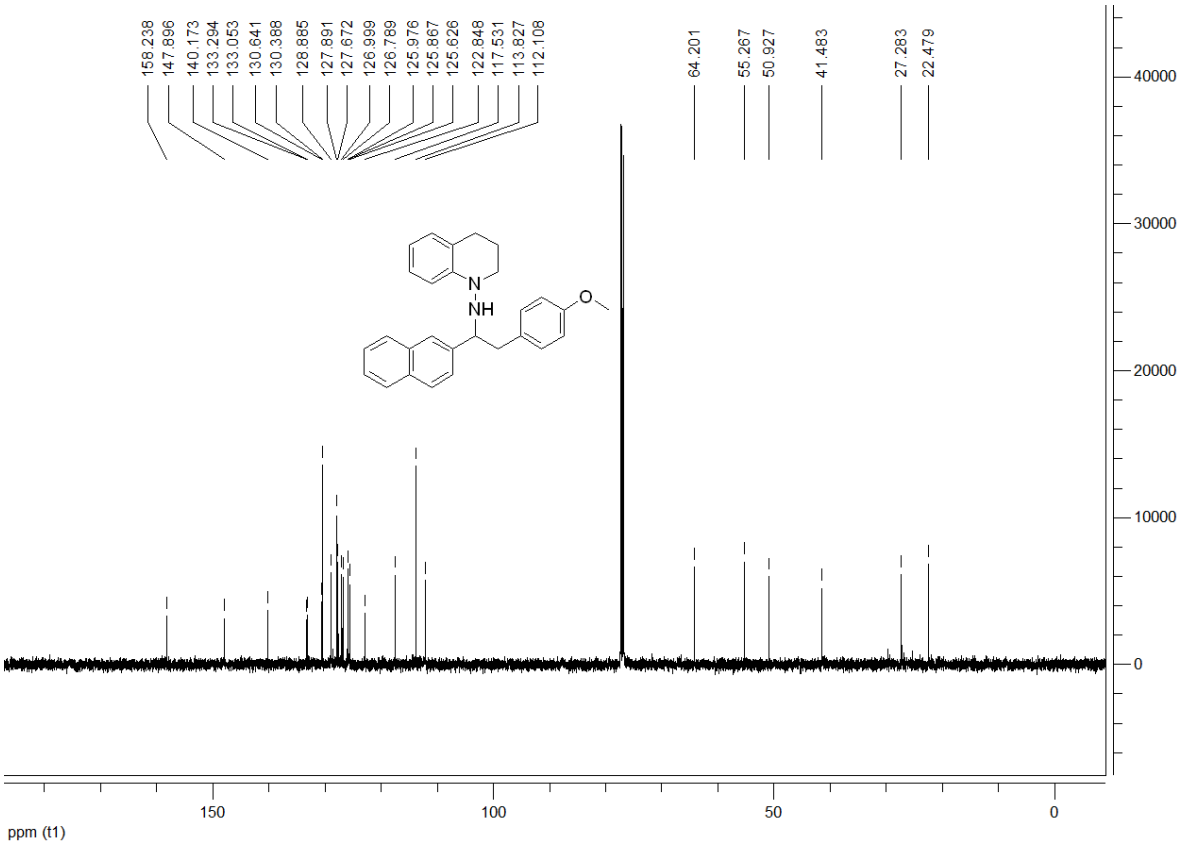
^{1}H and ^{13}C NMR of **6bo**



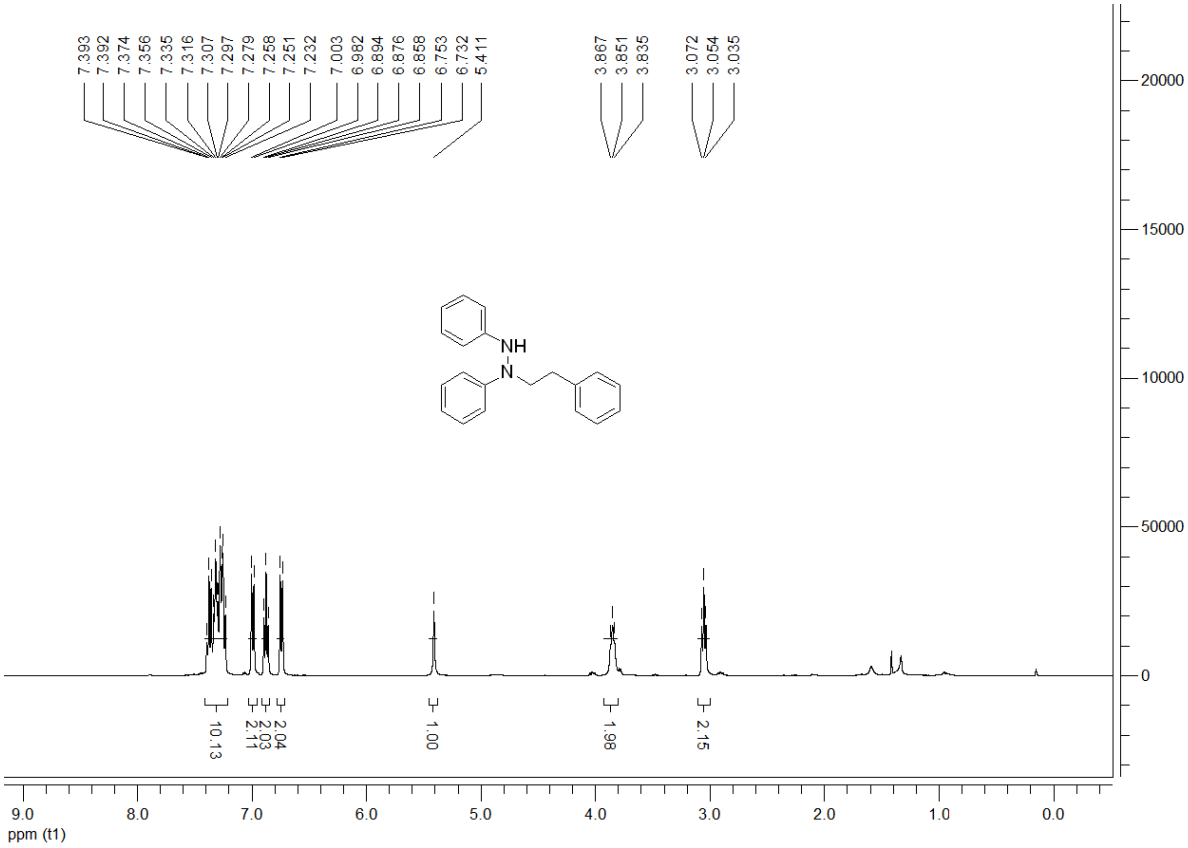


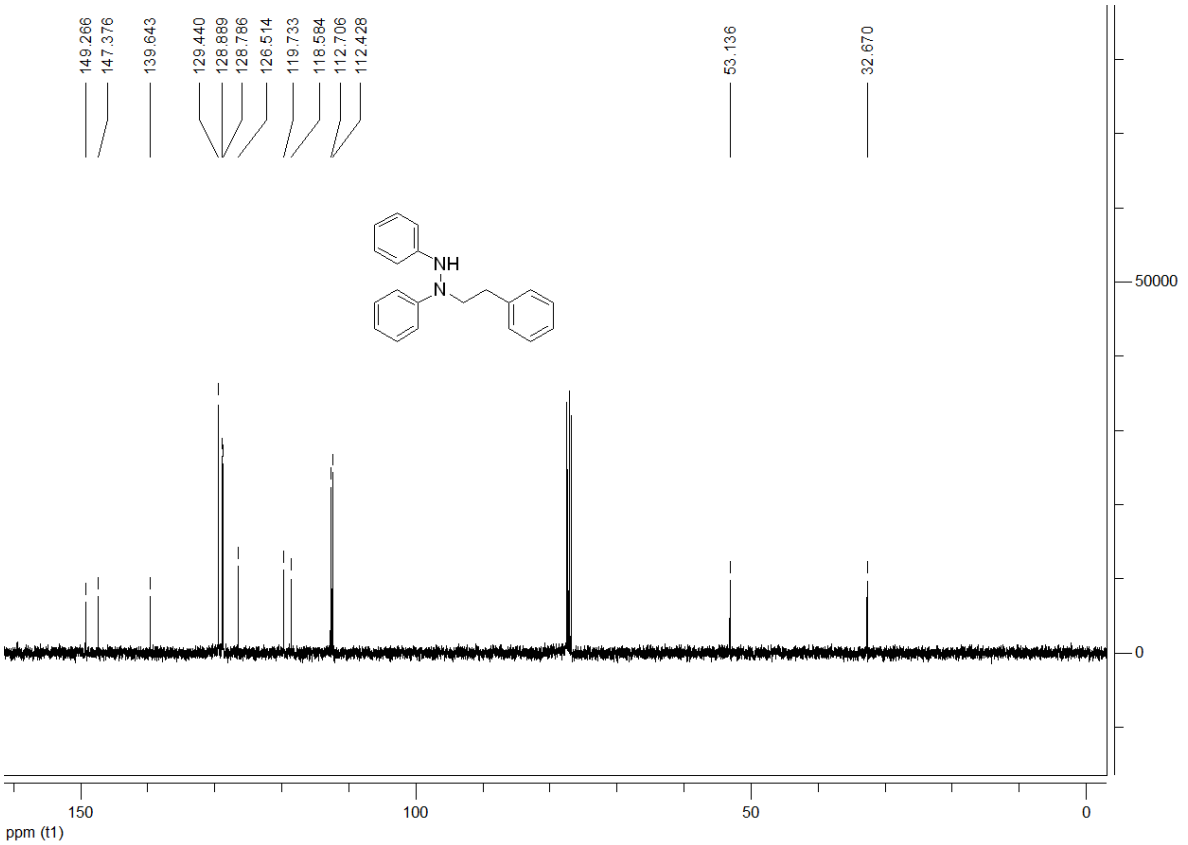
^{1}H and ^{13}C NMR of **6bm**



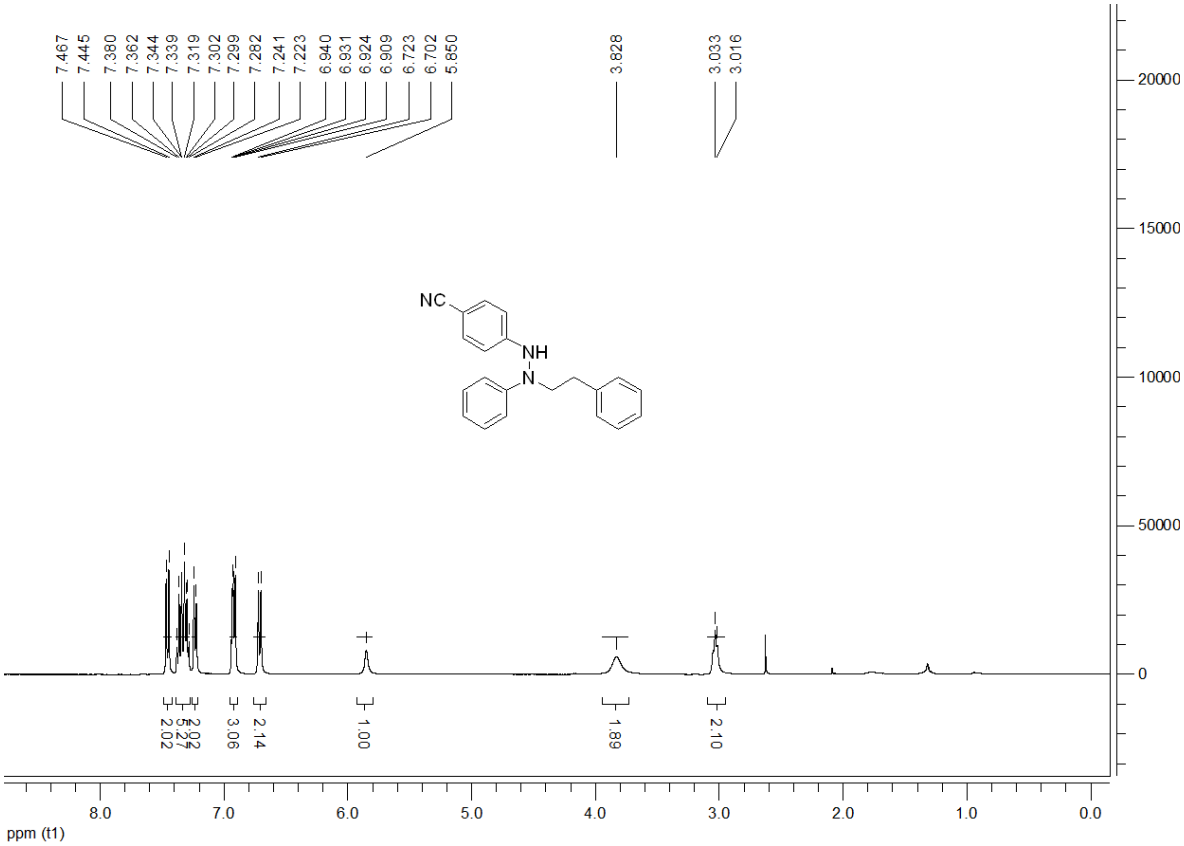


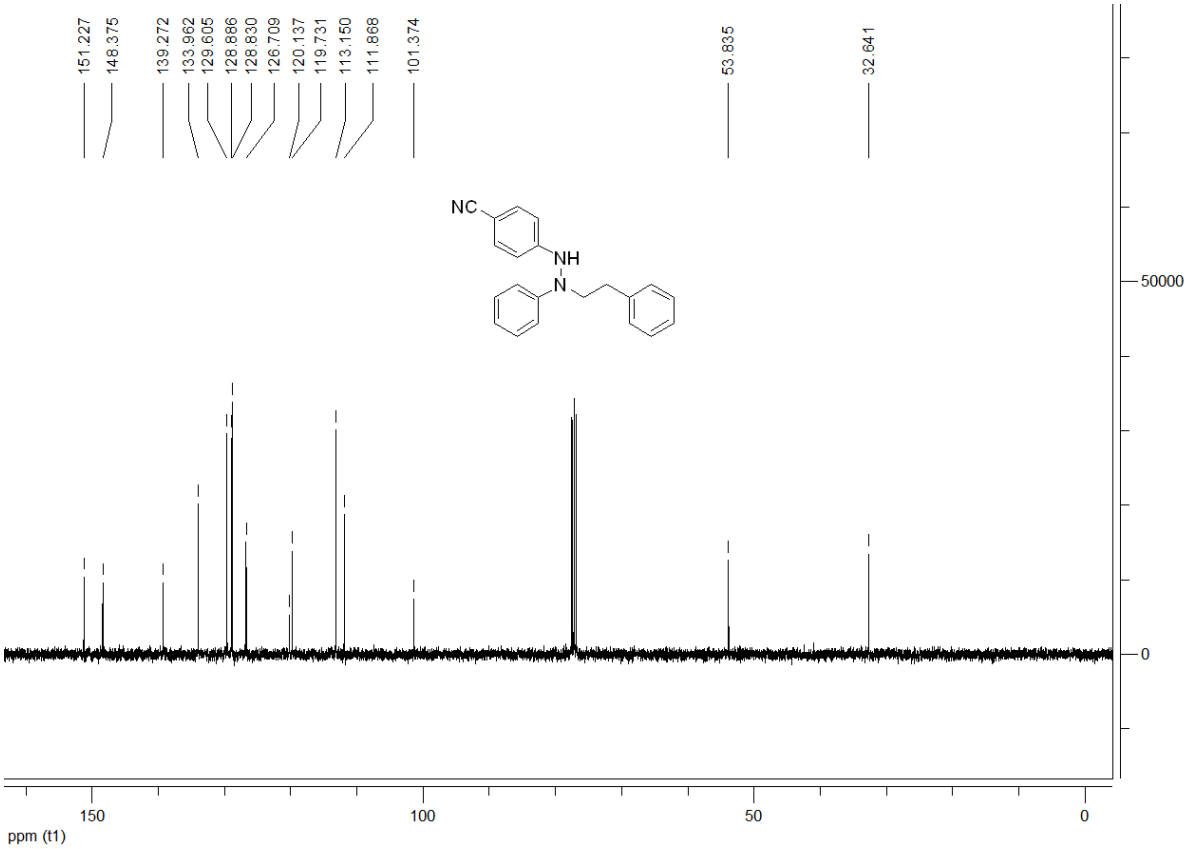
^{1}H and ^{13}C NMR of **6da**



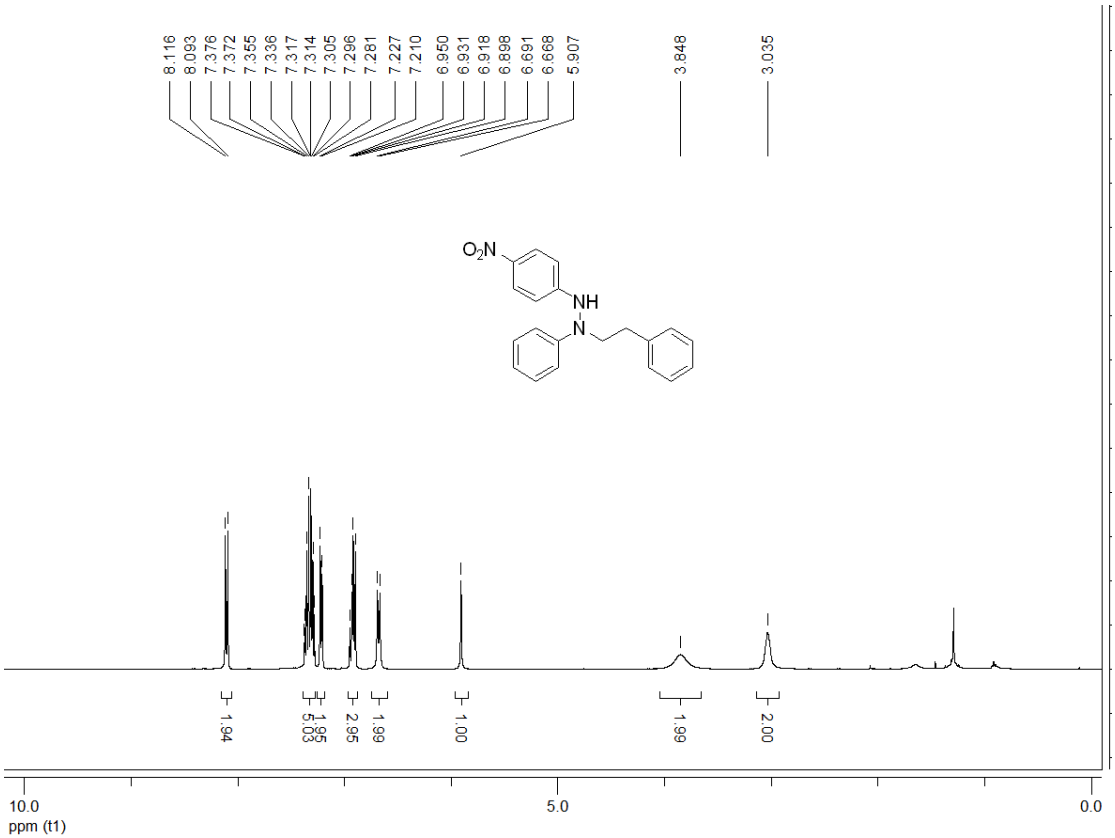


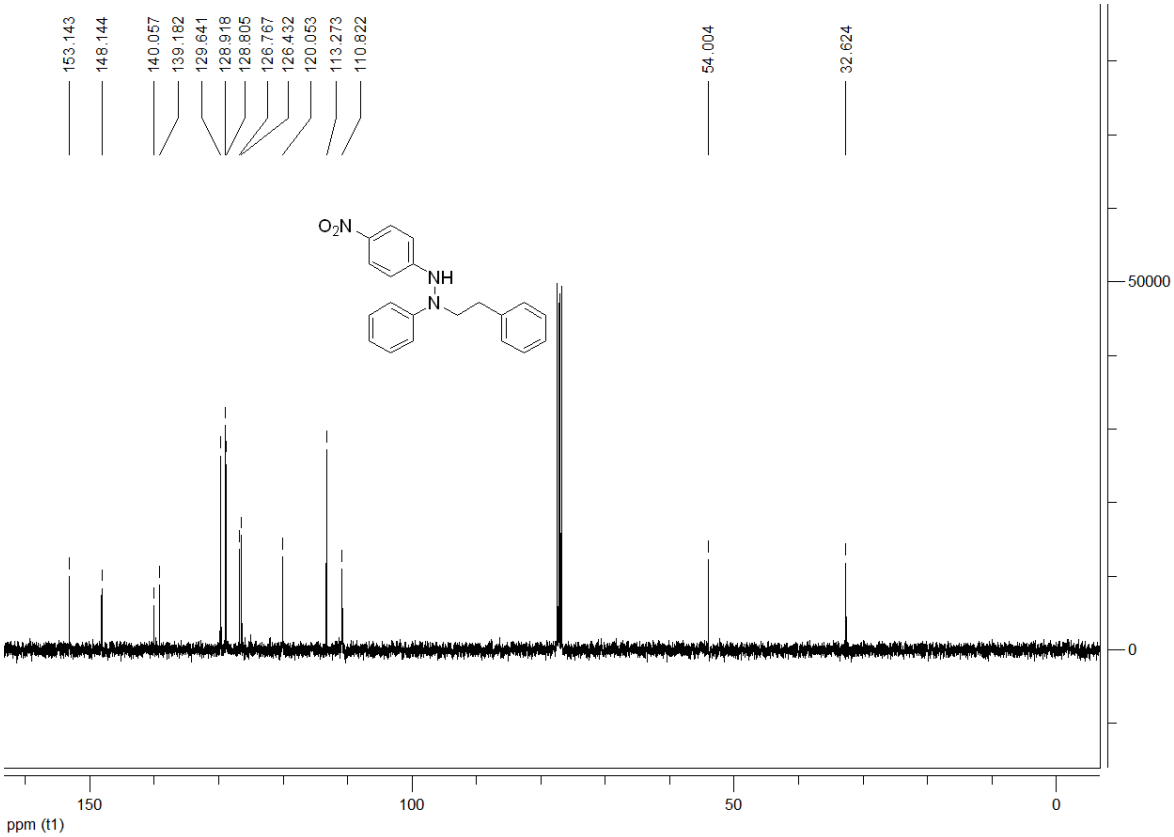
^{1}H and ^{13}C NMR of **6dc**



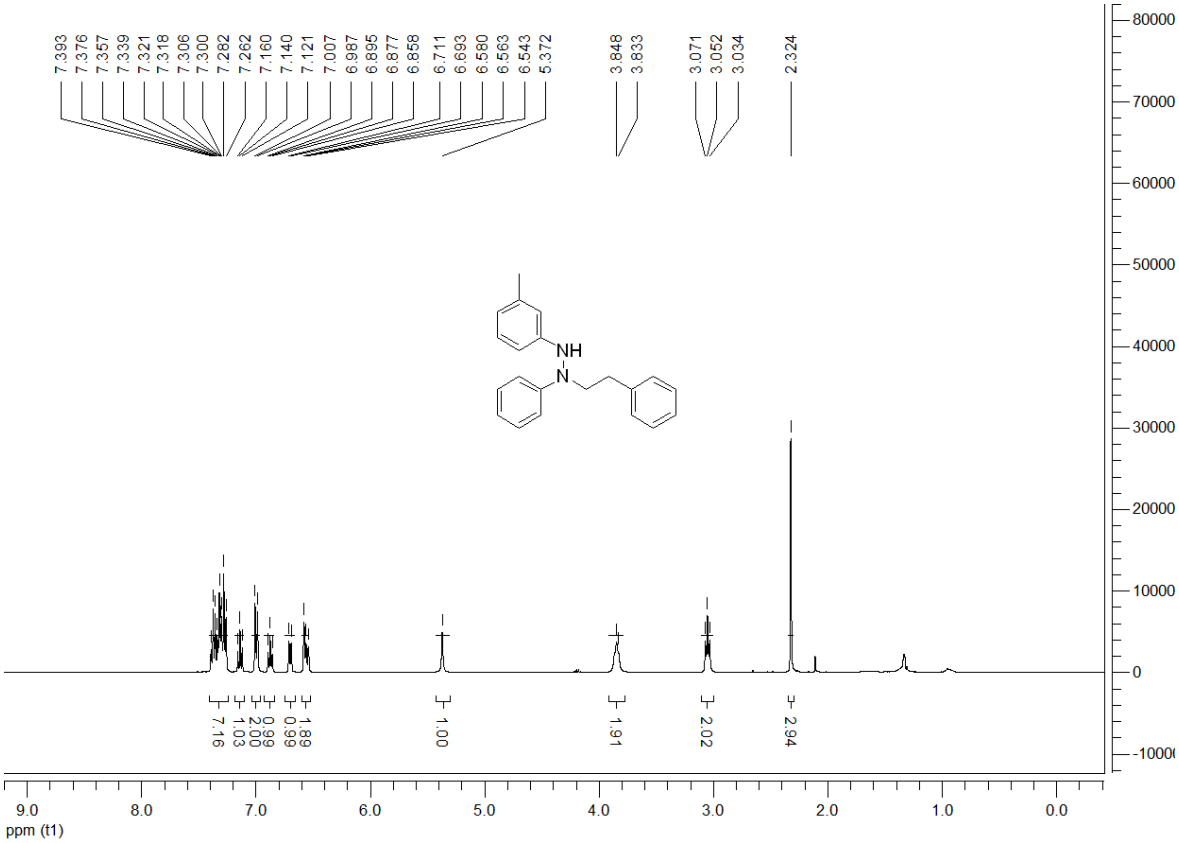


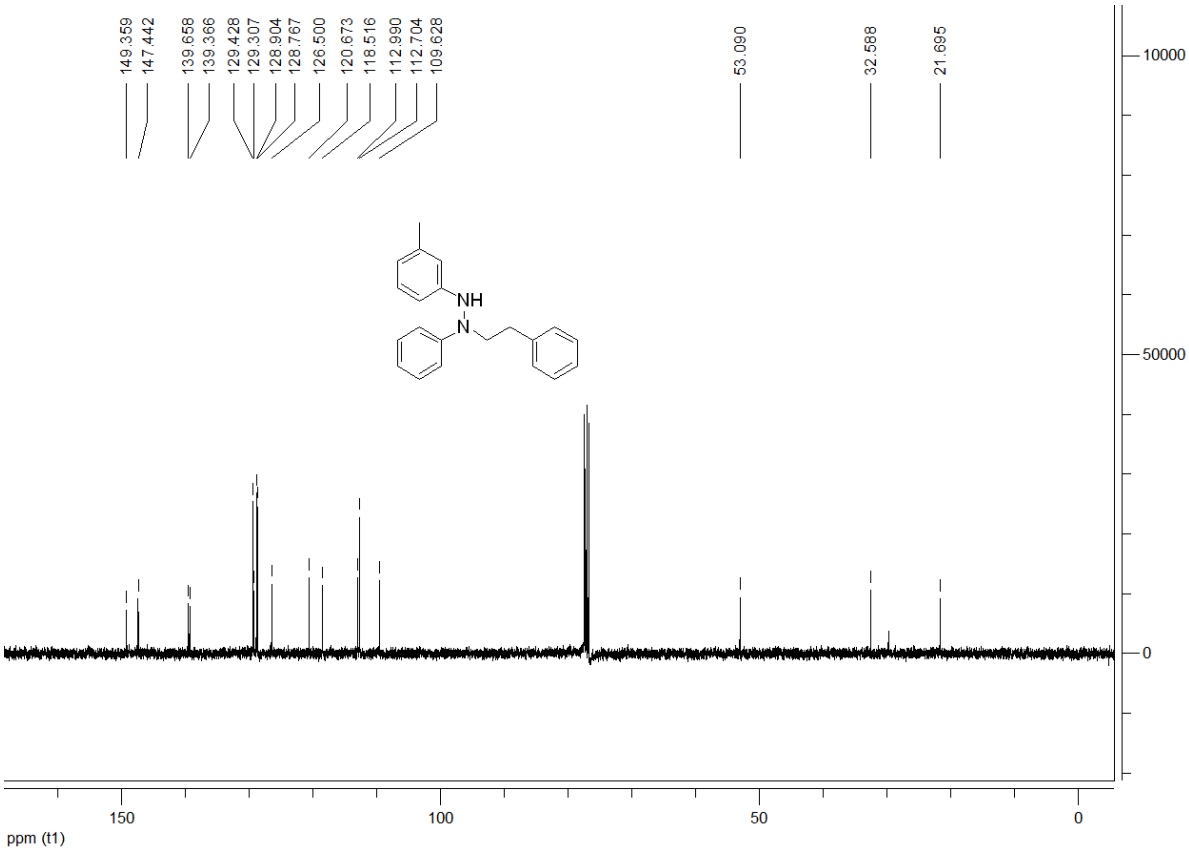
^{1}H and ^{13}C NMR of **6dd**



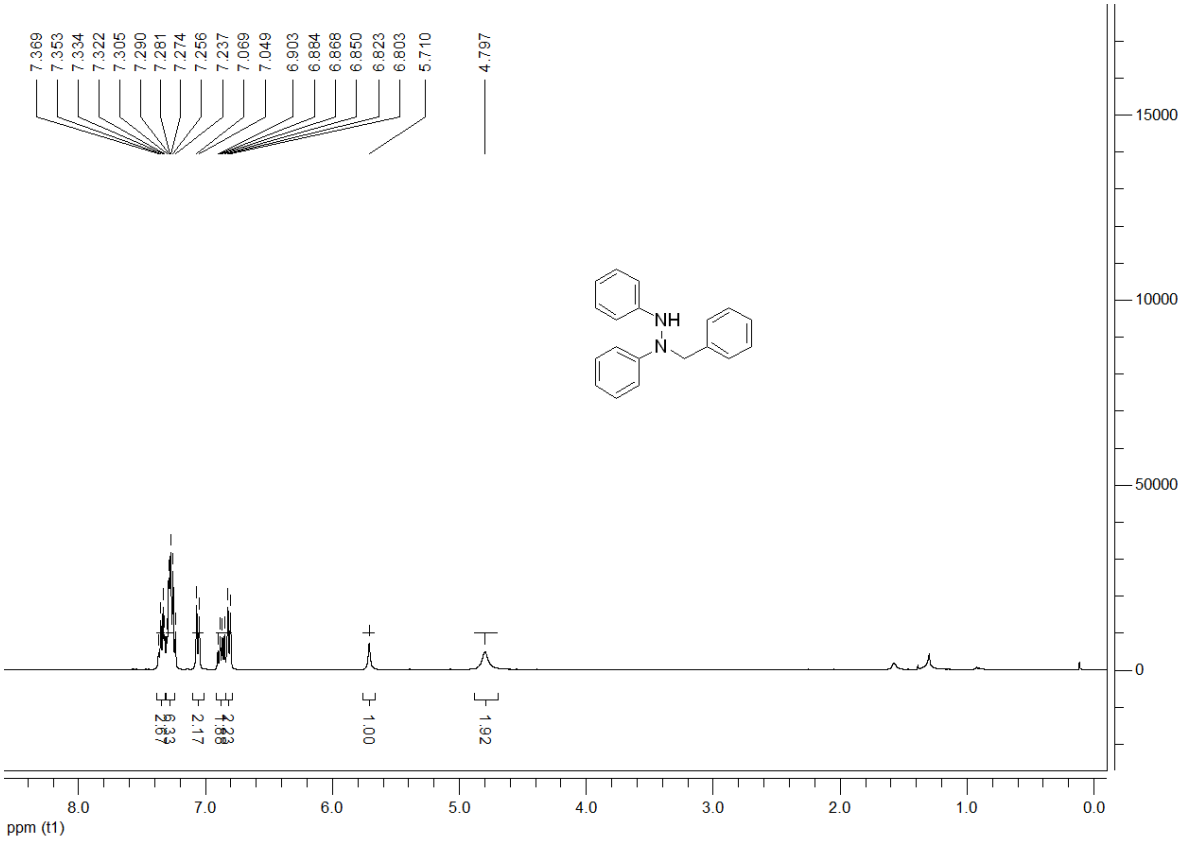


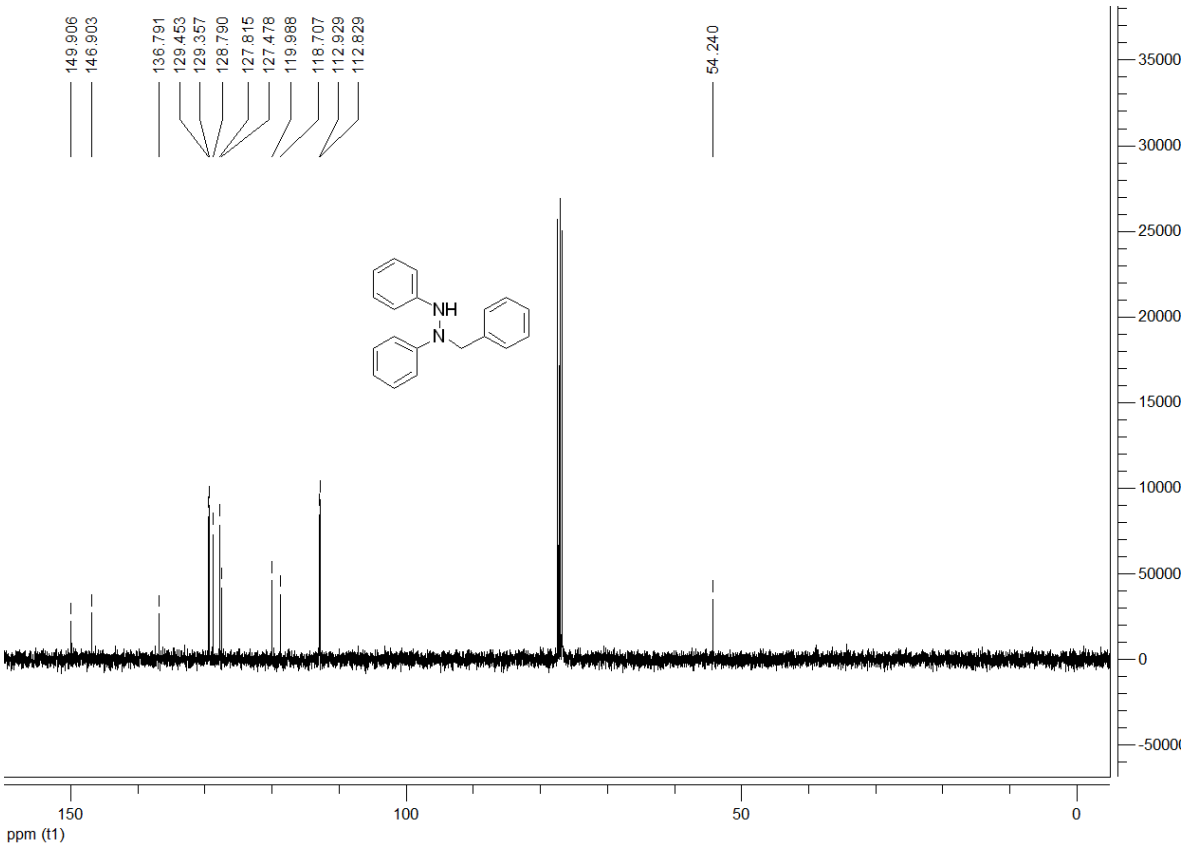
^{1}H and ^{13}C NMR of **6de**



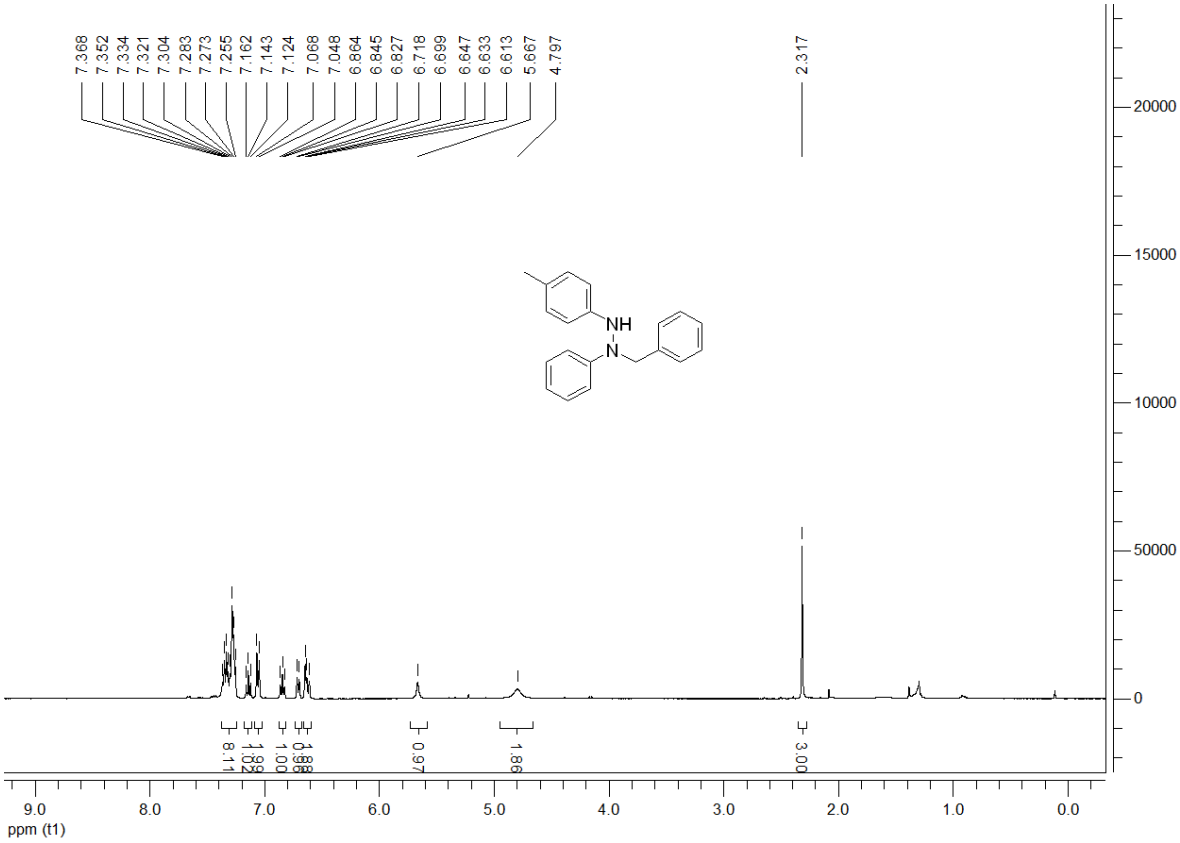


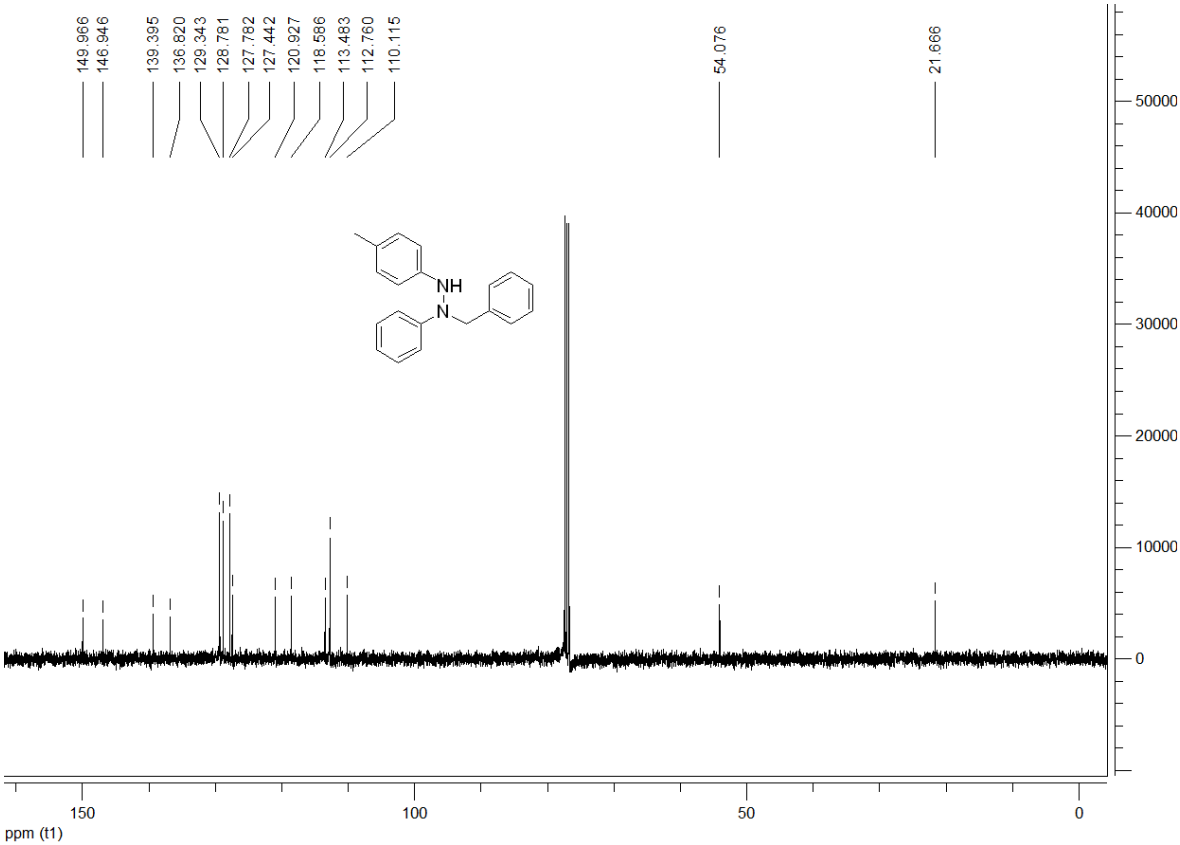
^{1}H and ^{13}C NMR of **6ea**



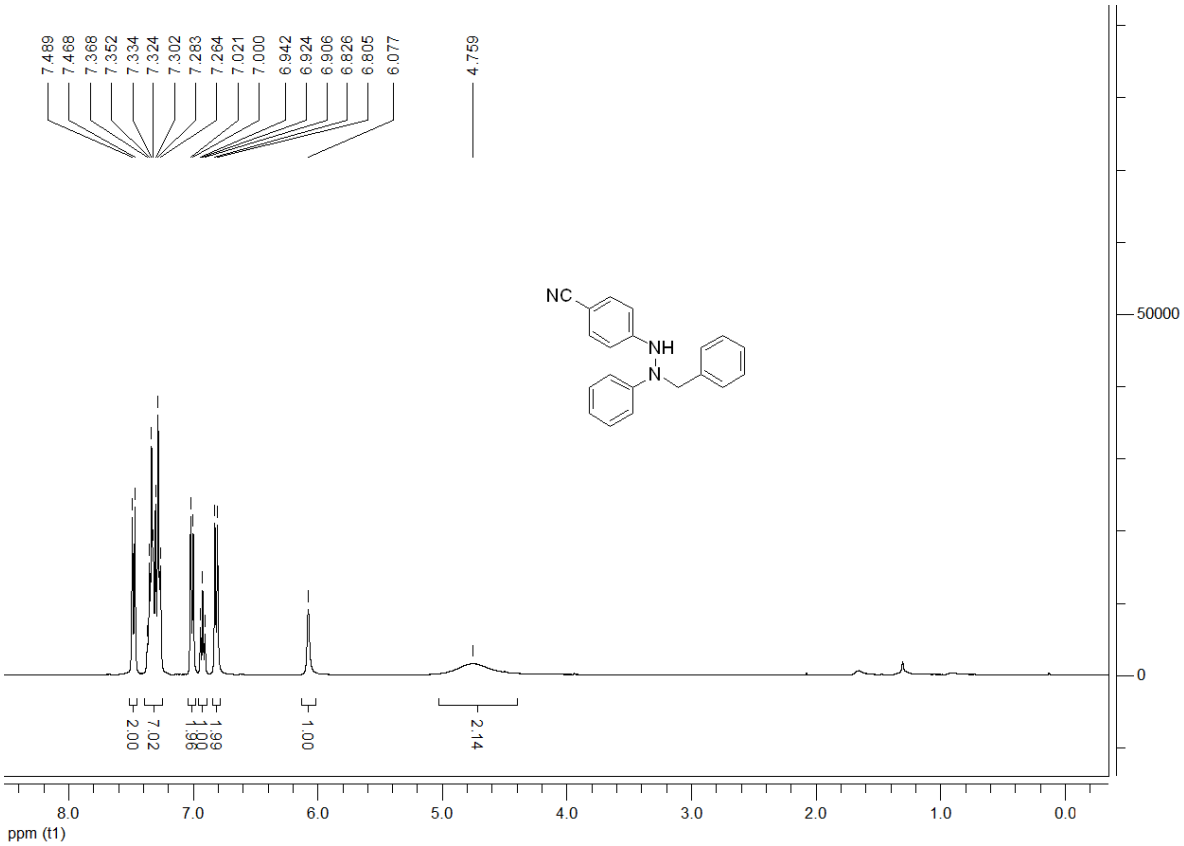


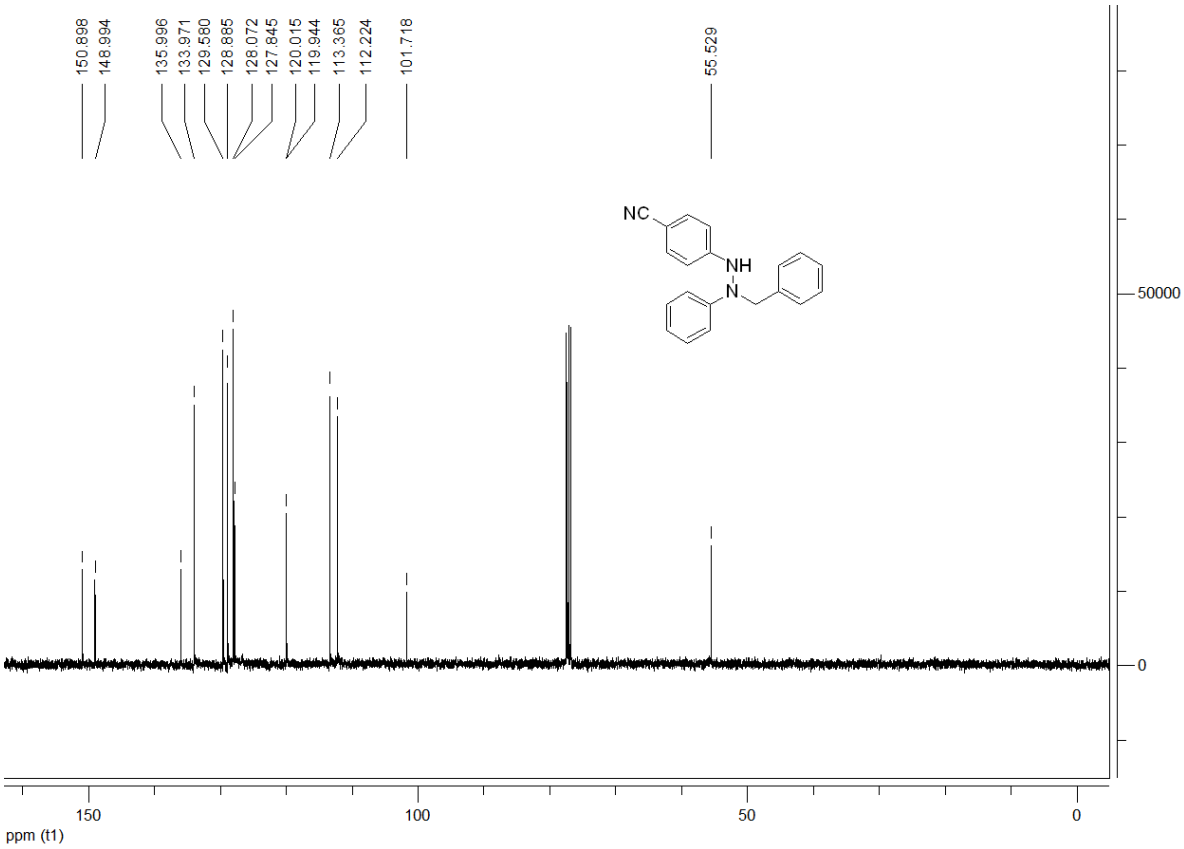
^{1}H and ^{13}C NMR of **6eb**



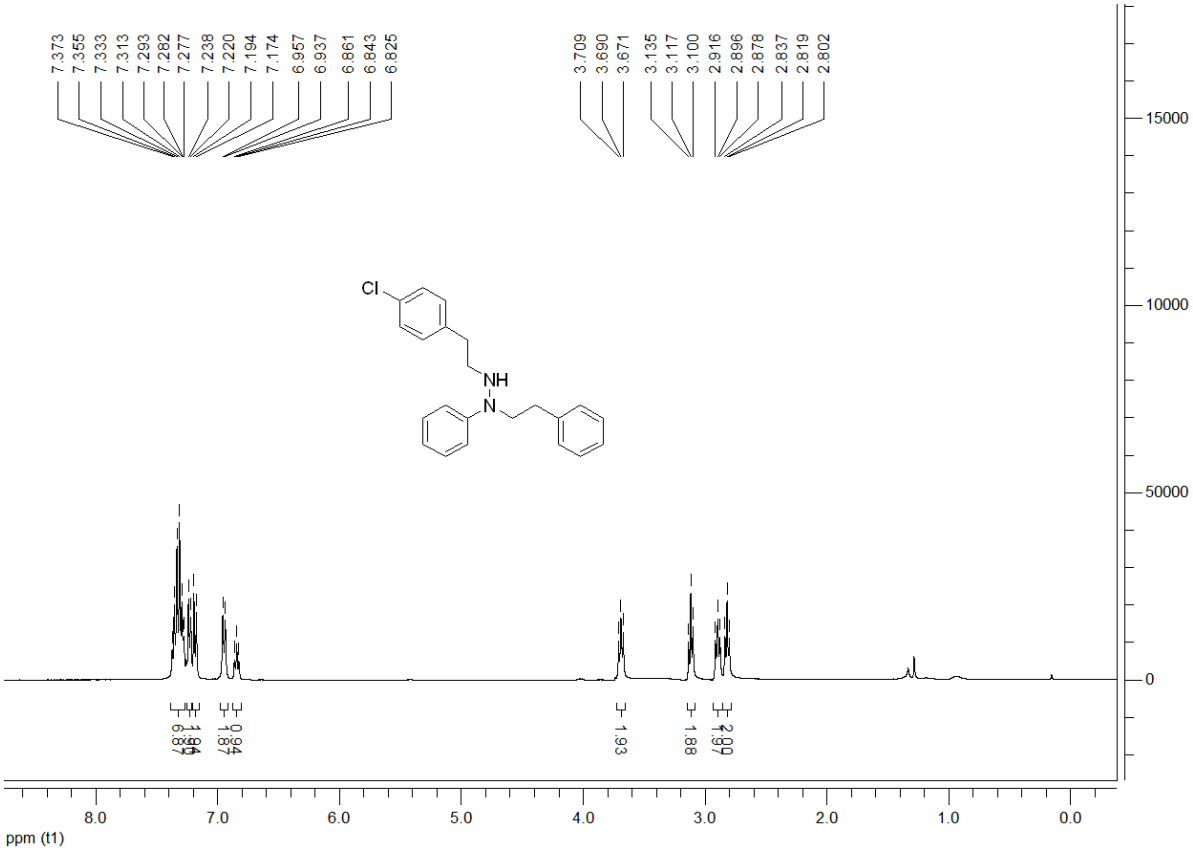


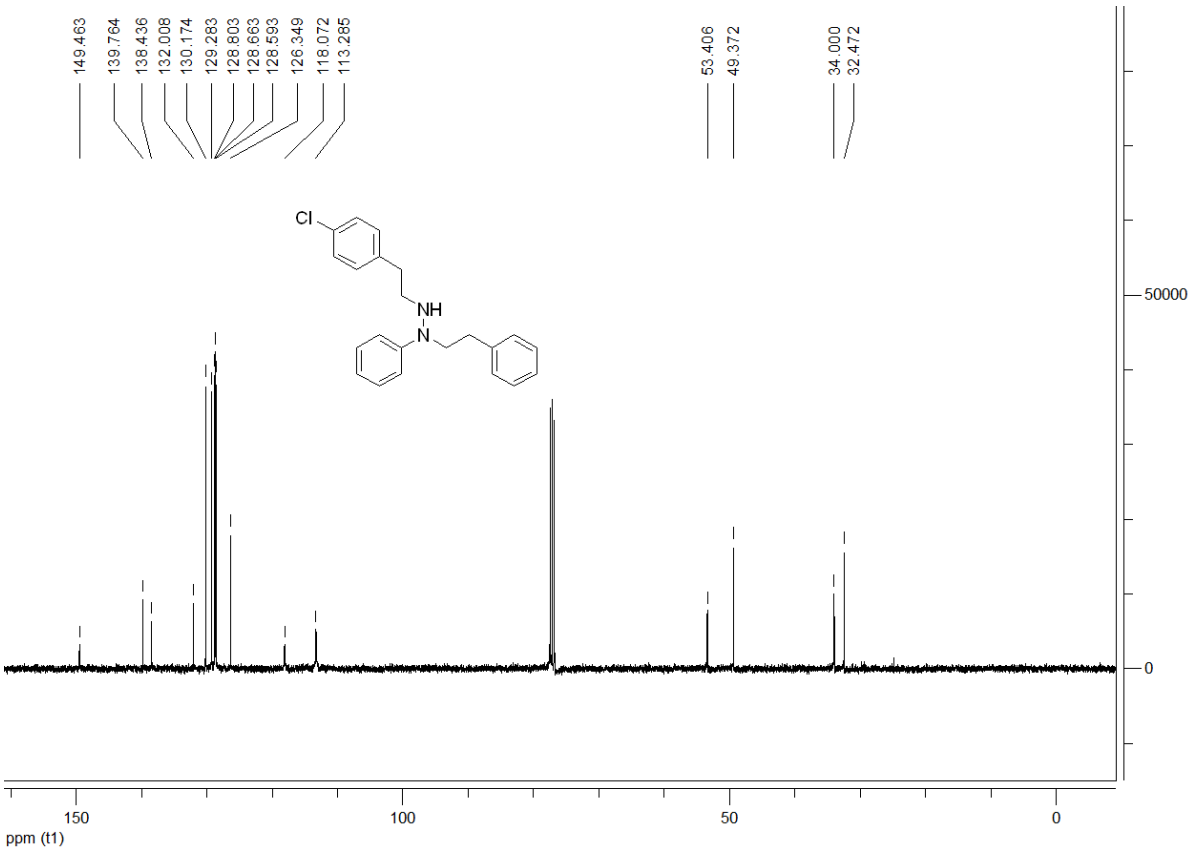
^{1}H and ^{13}C NMR of **6ec**



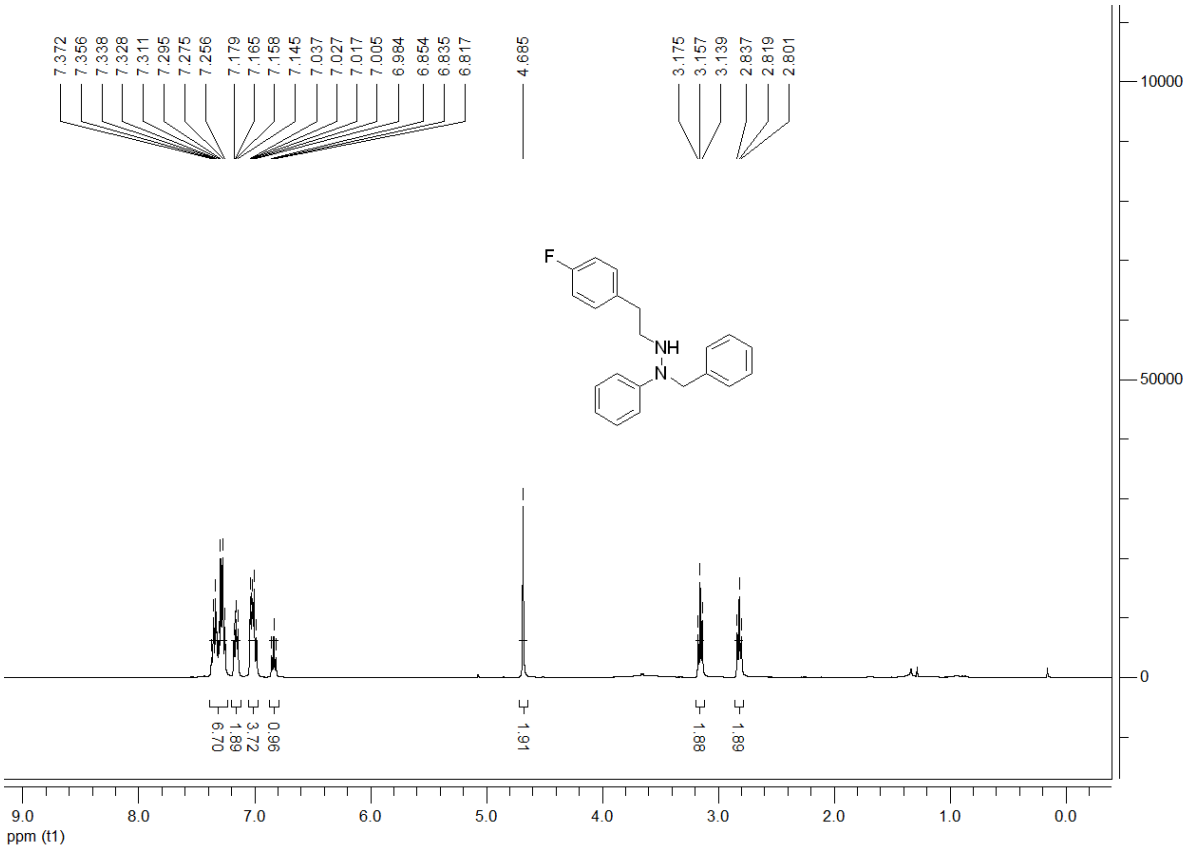


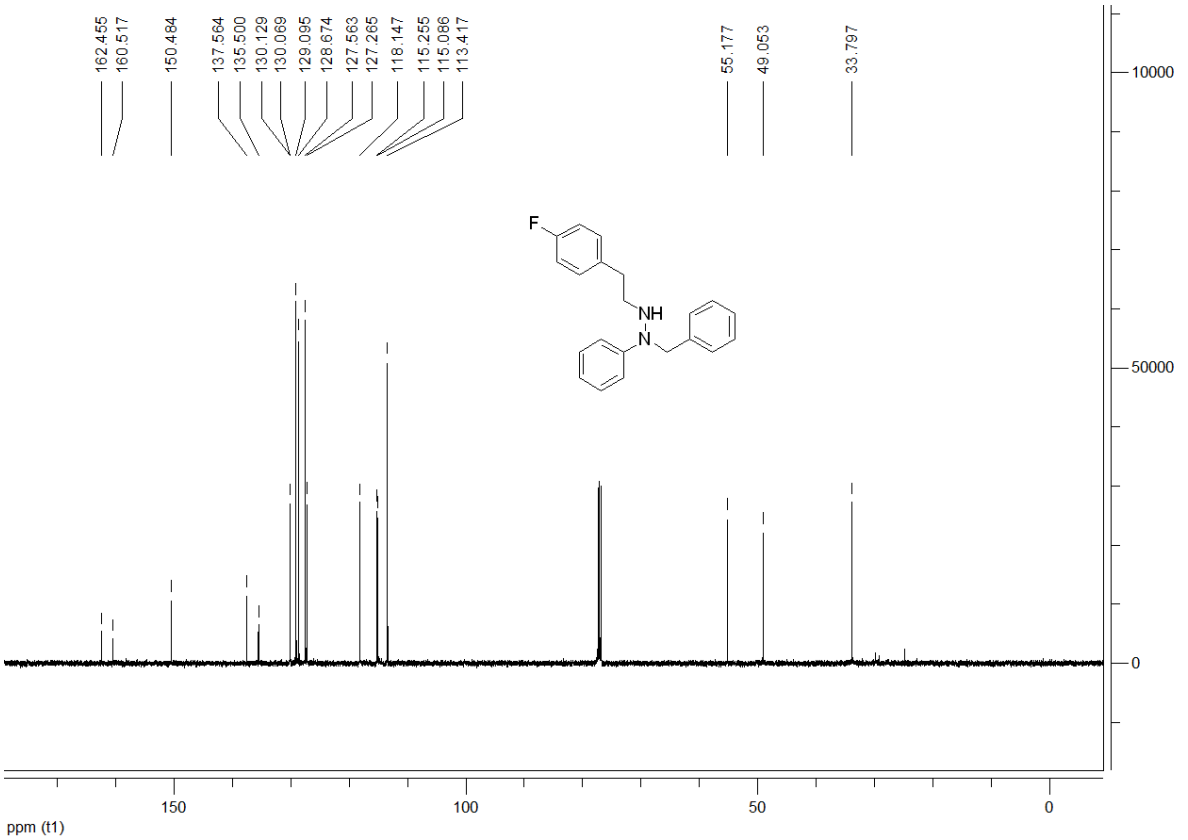
^{1}H and ^{13}C NMR of **6dp**



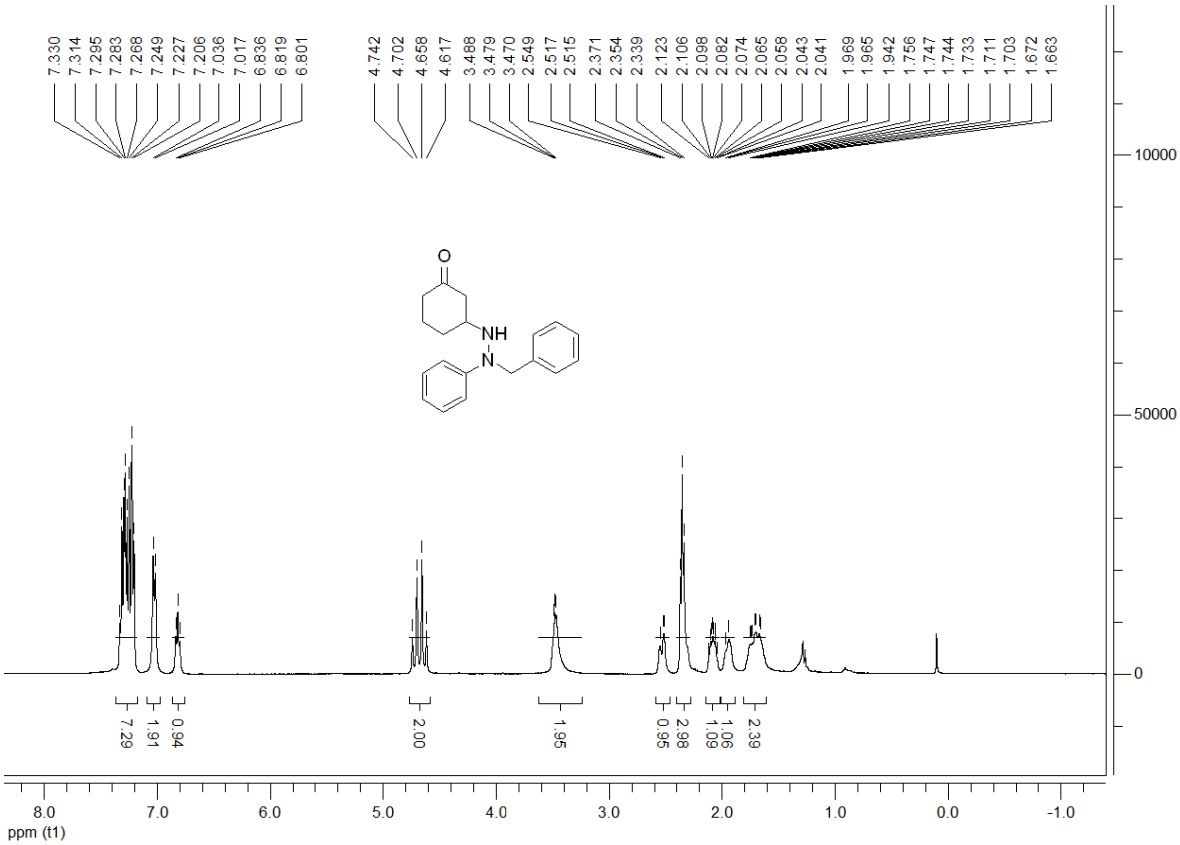


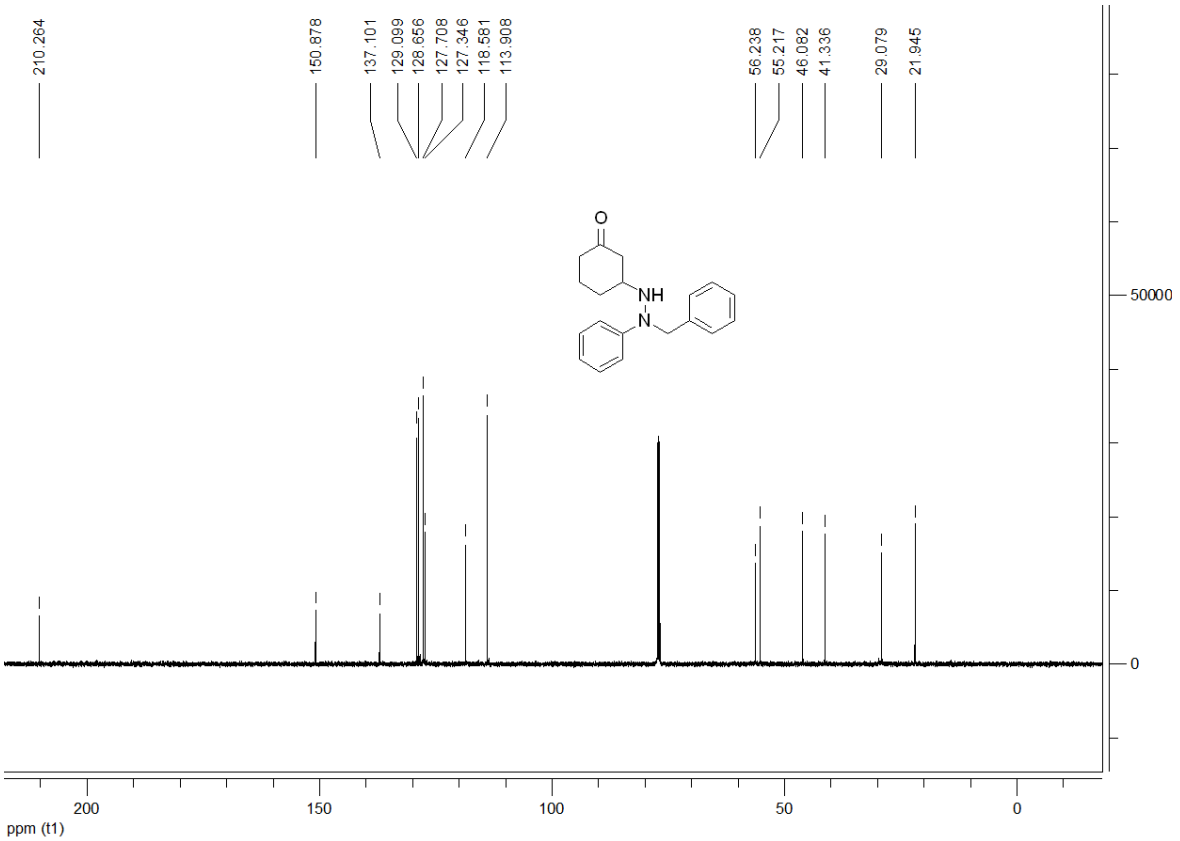
^{1}H and ^{13}C NMR of **6eq**



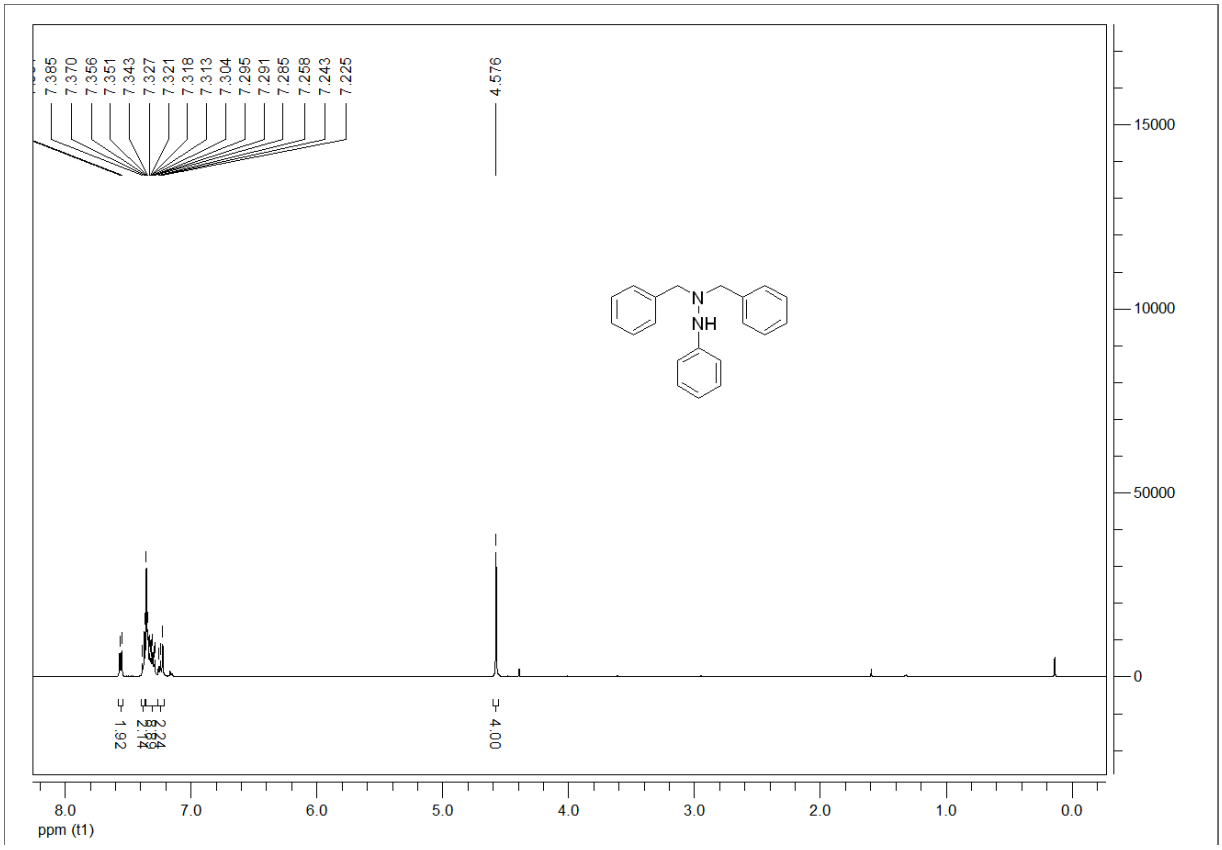


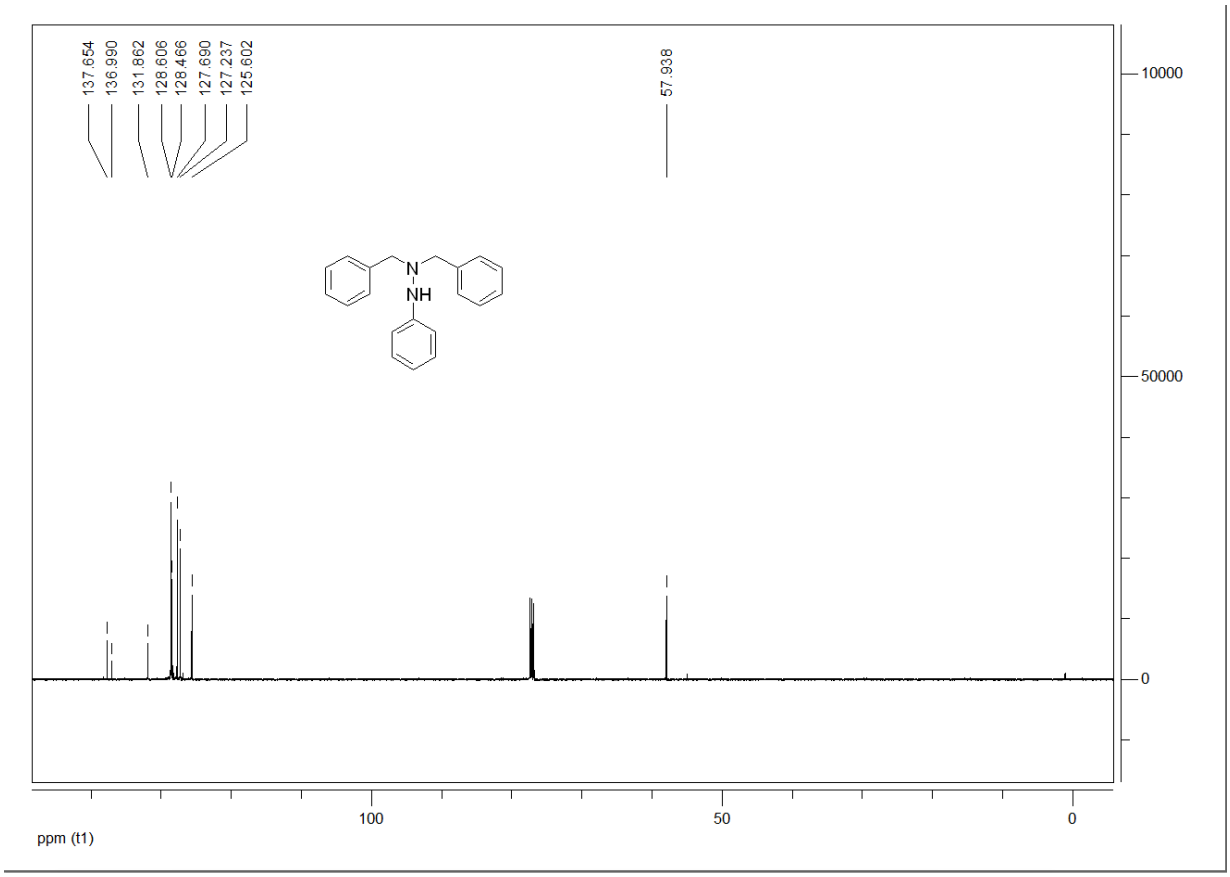
^{1}H and ^{13}C NMR of **6er**



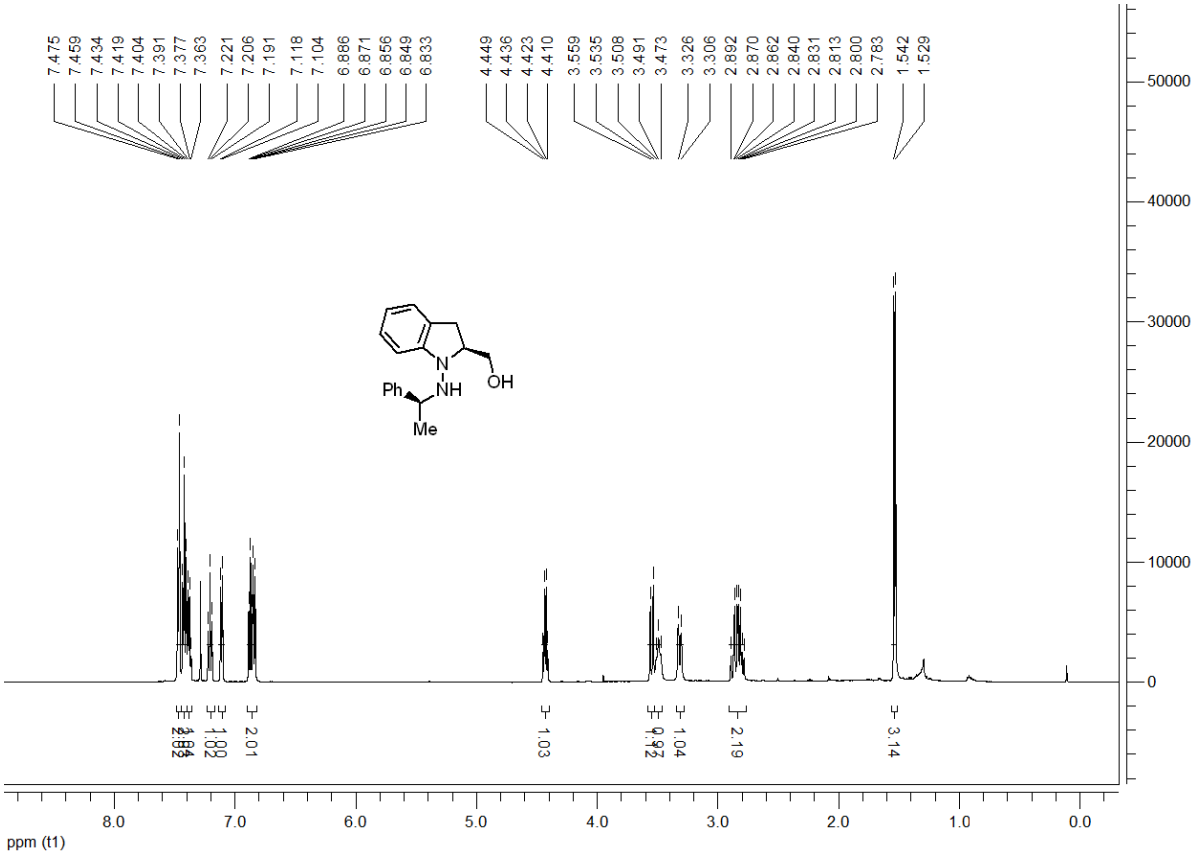


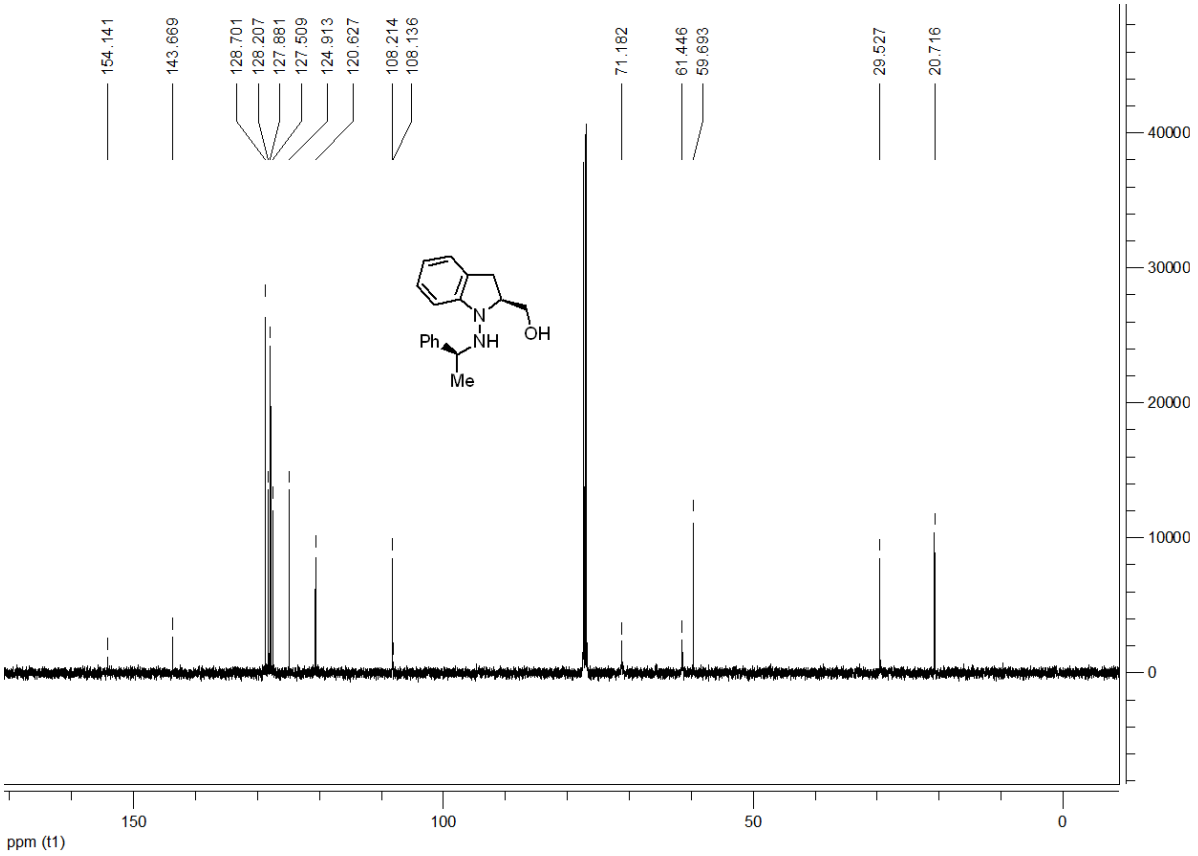
^{1}H and ^{13}C NMR of **6fa**



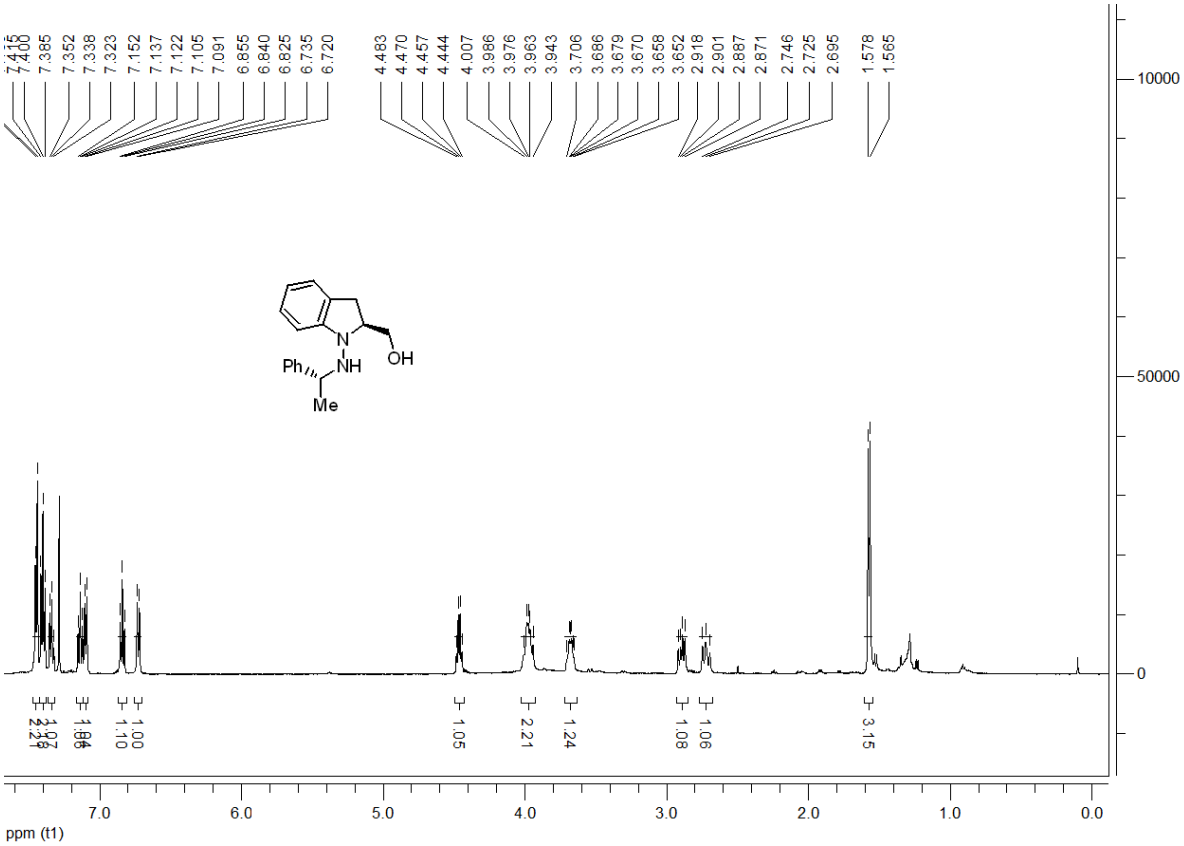


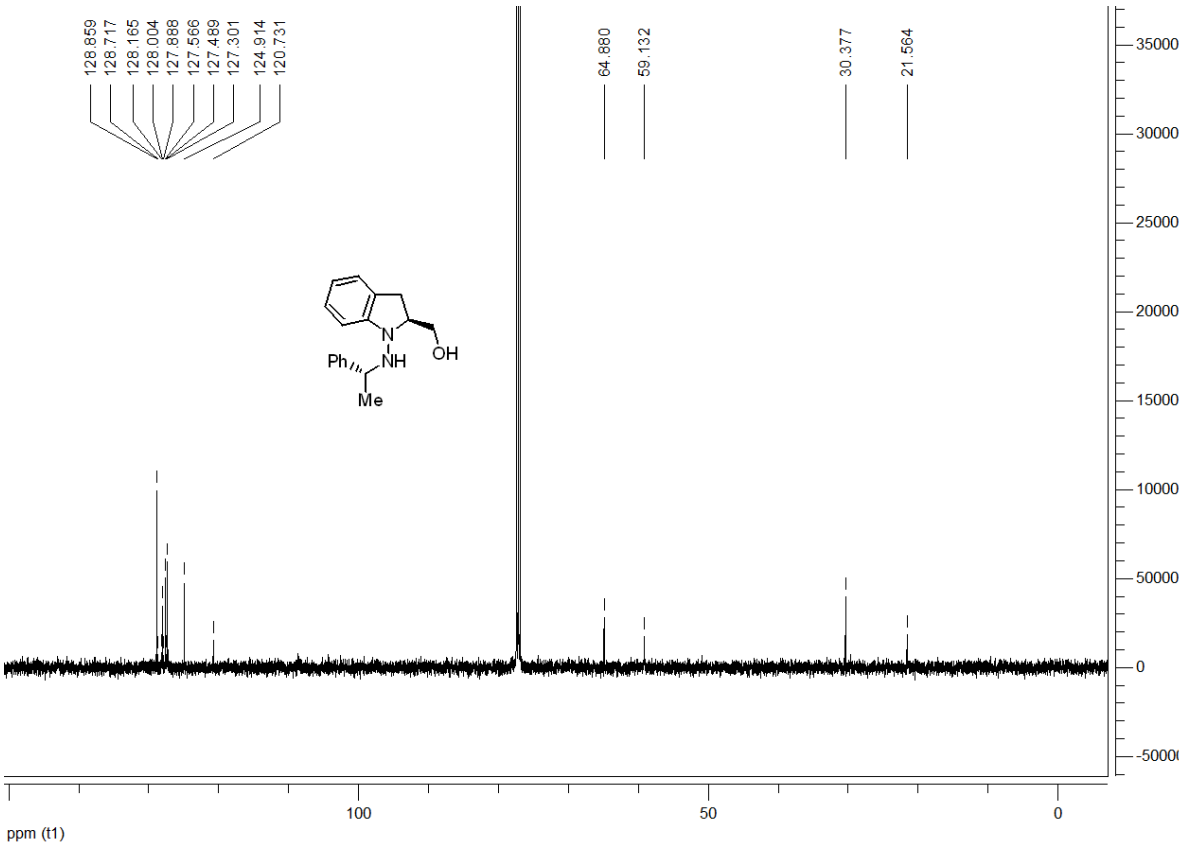
^{1}H and ^{13}C NMR of **6hs-1**



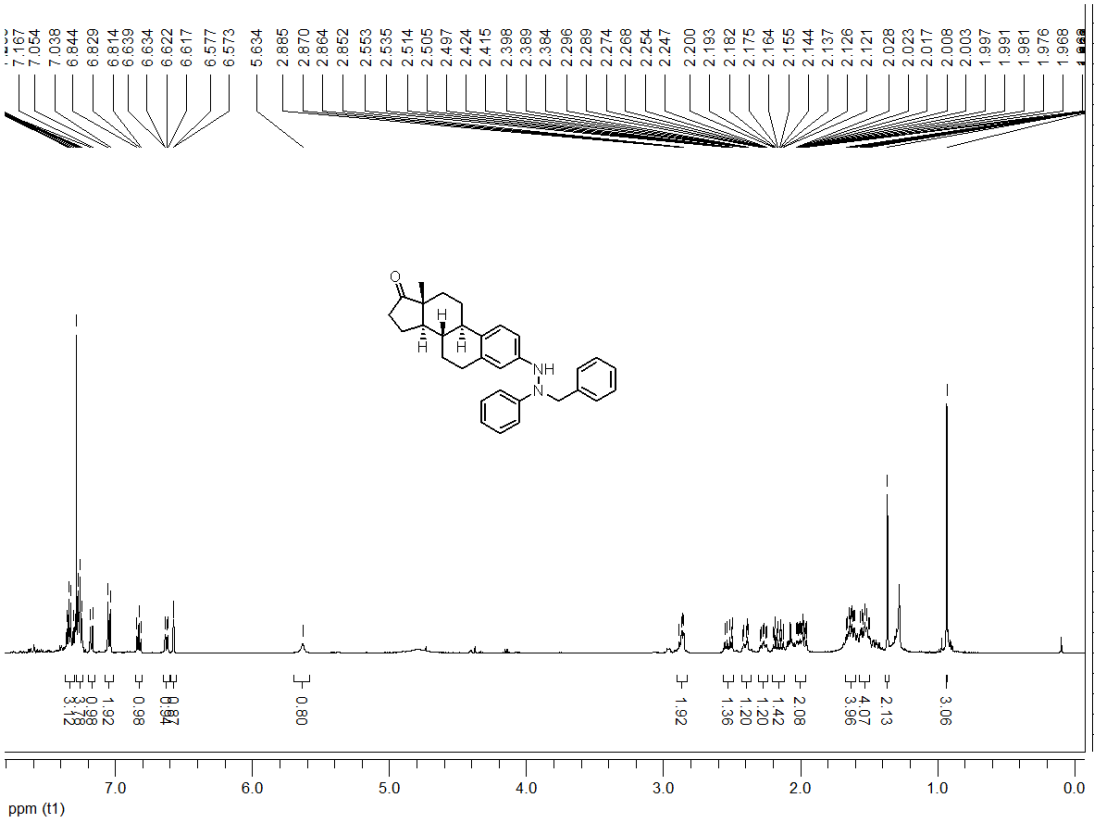


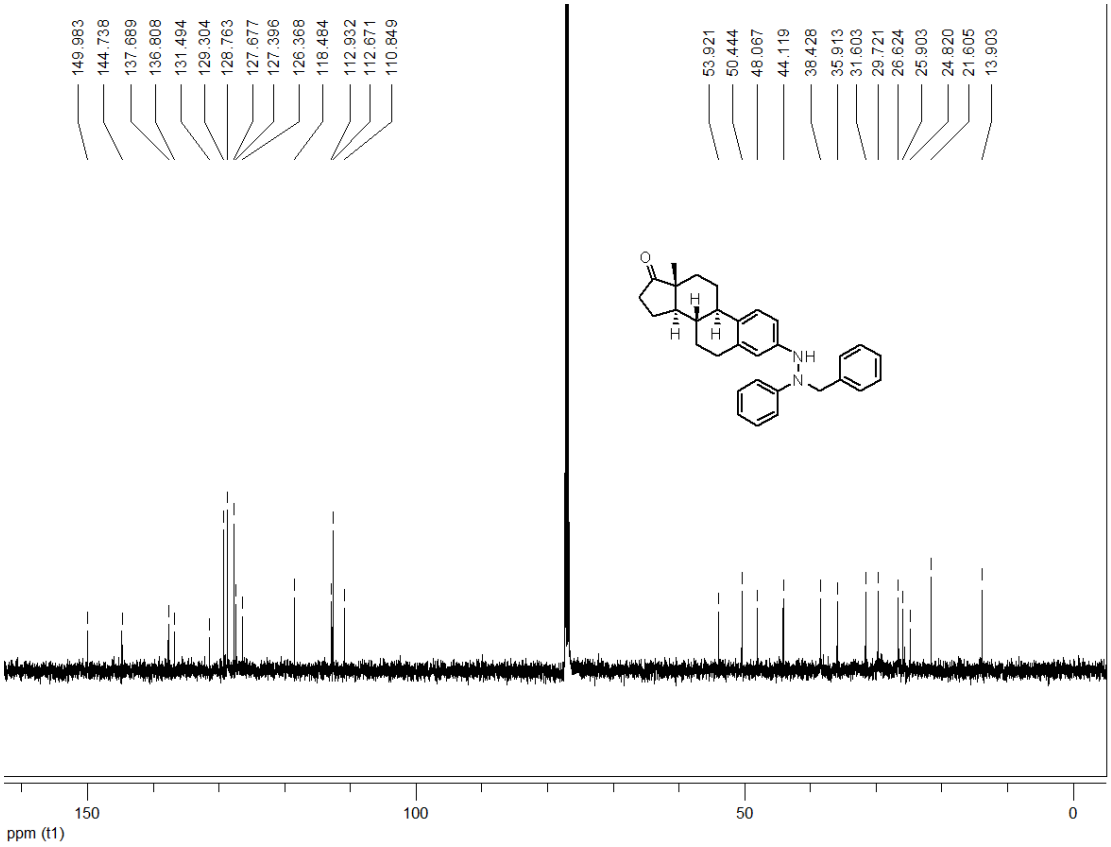
^{1}H and ^{13}C NMR of **6hs-2**



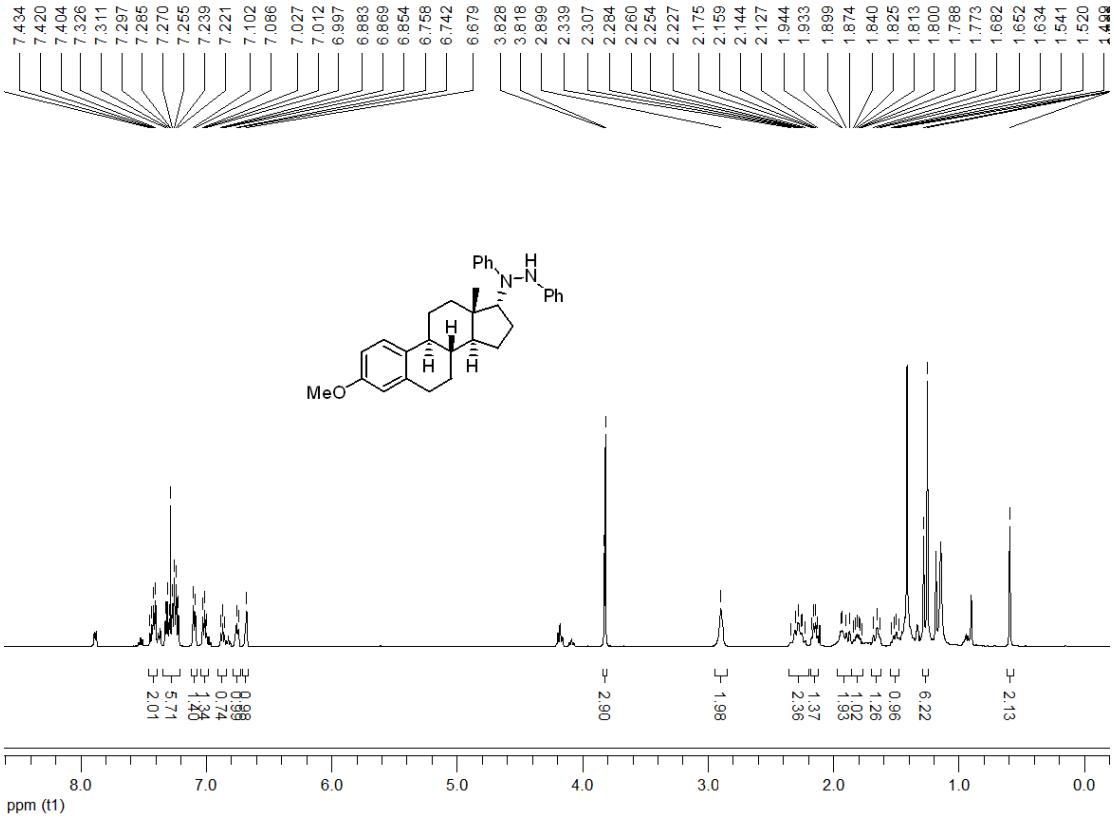


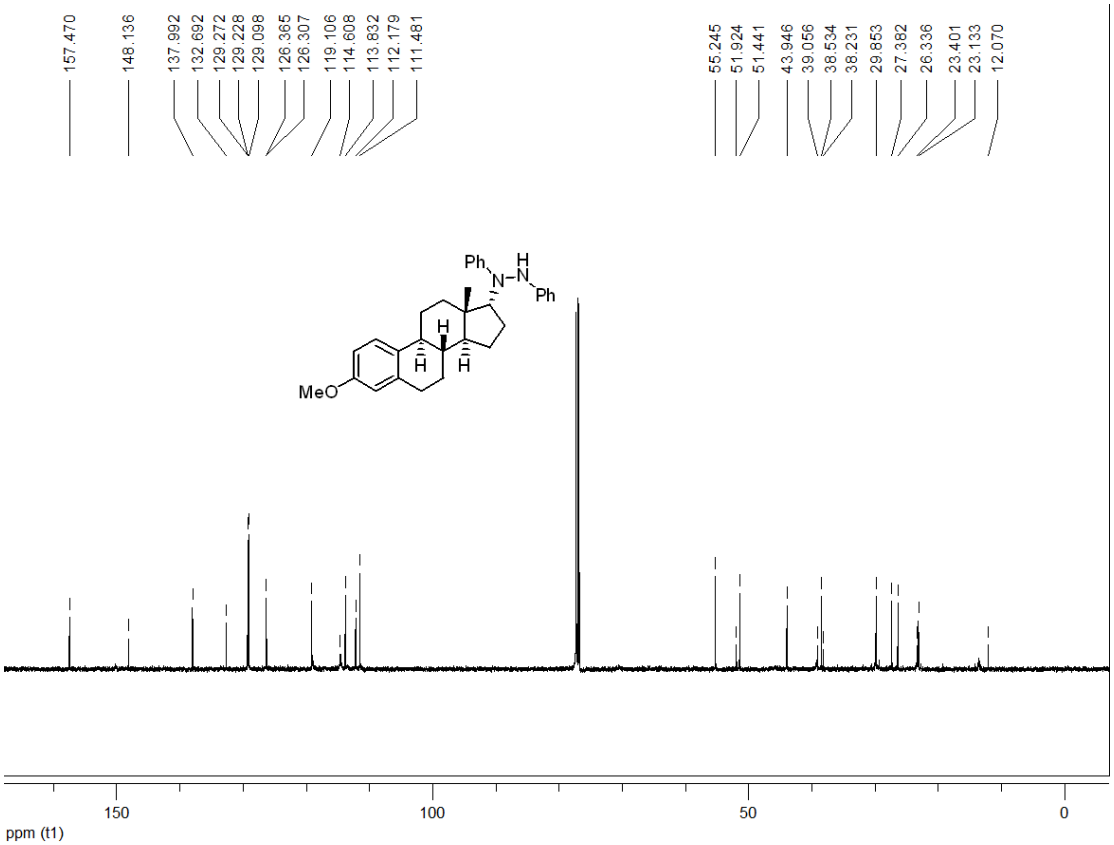
^{1}H and ^{13}C NMR of **6et**



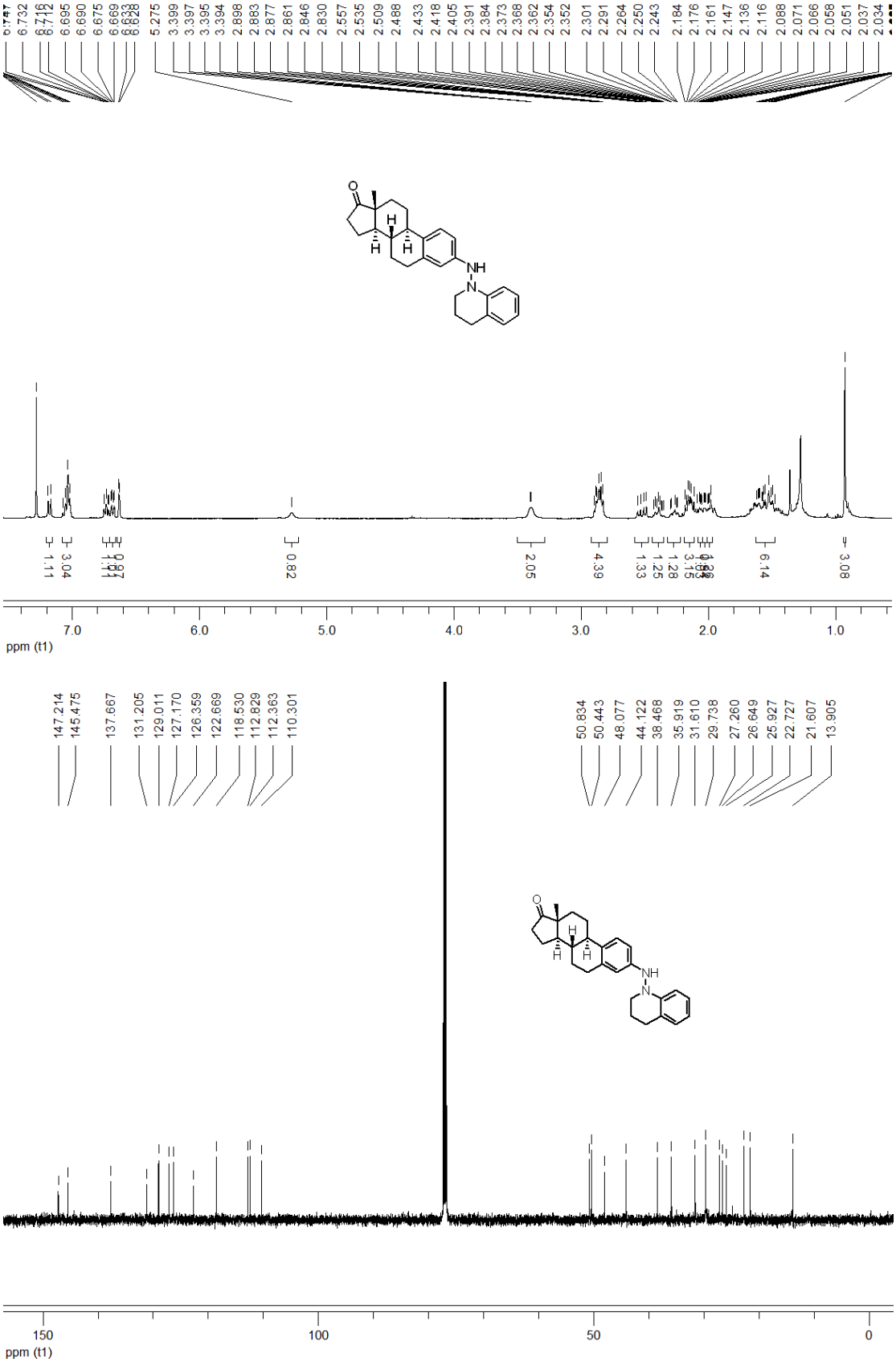


^{1}H and ^{13}C NMR of **6ia**

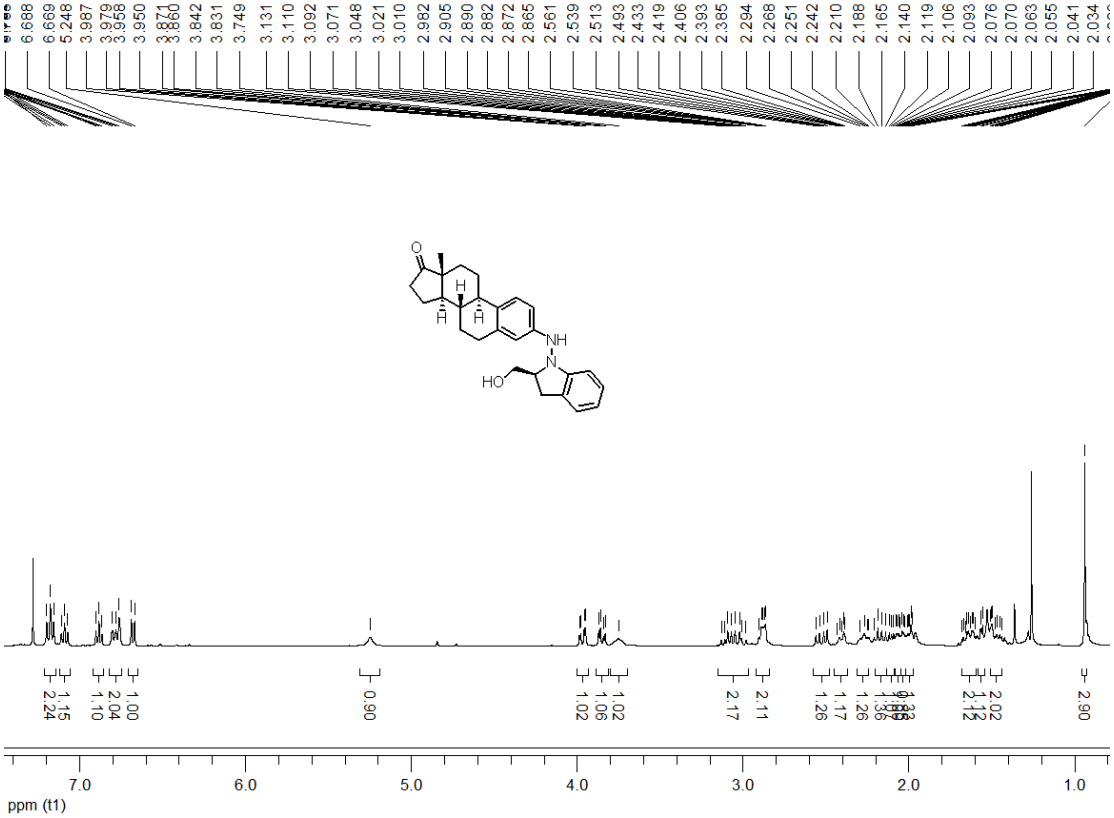


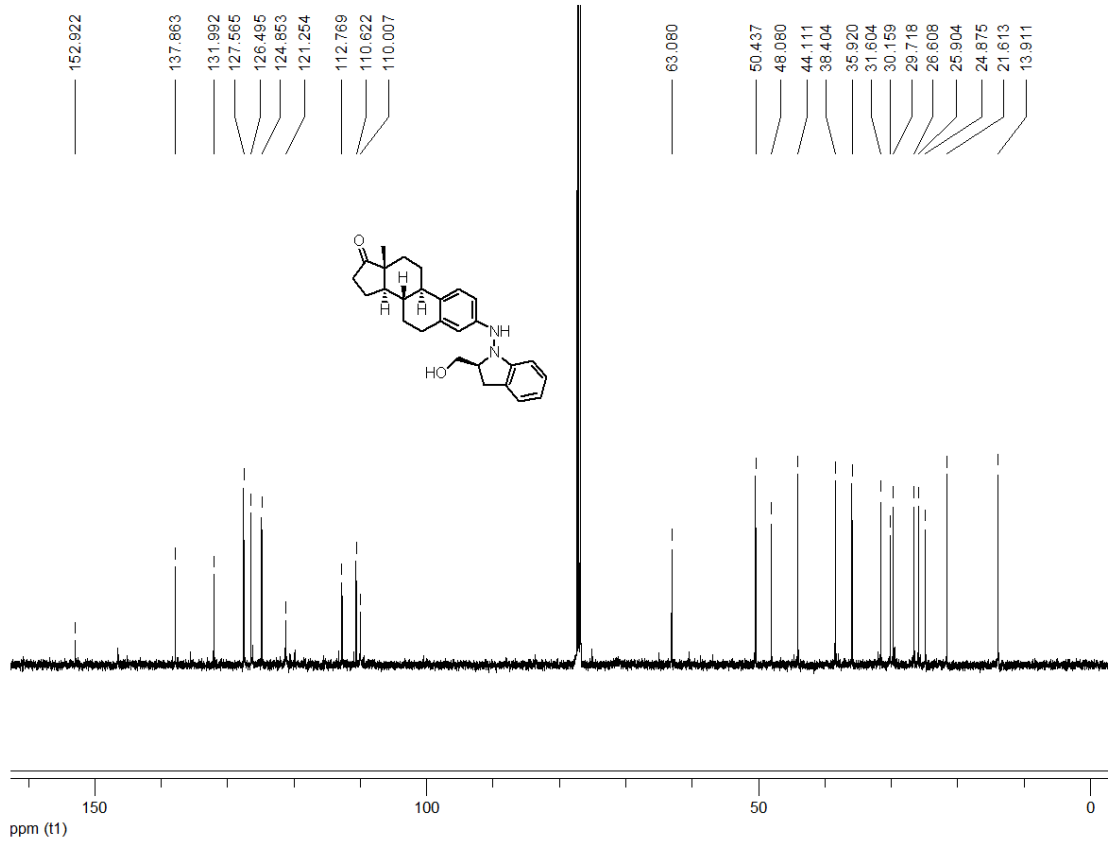


^{1}H and ^{13}C NMR of **6bt**

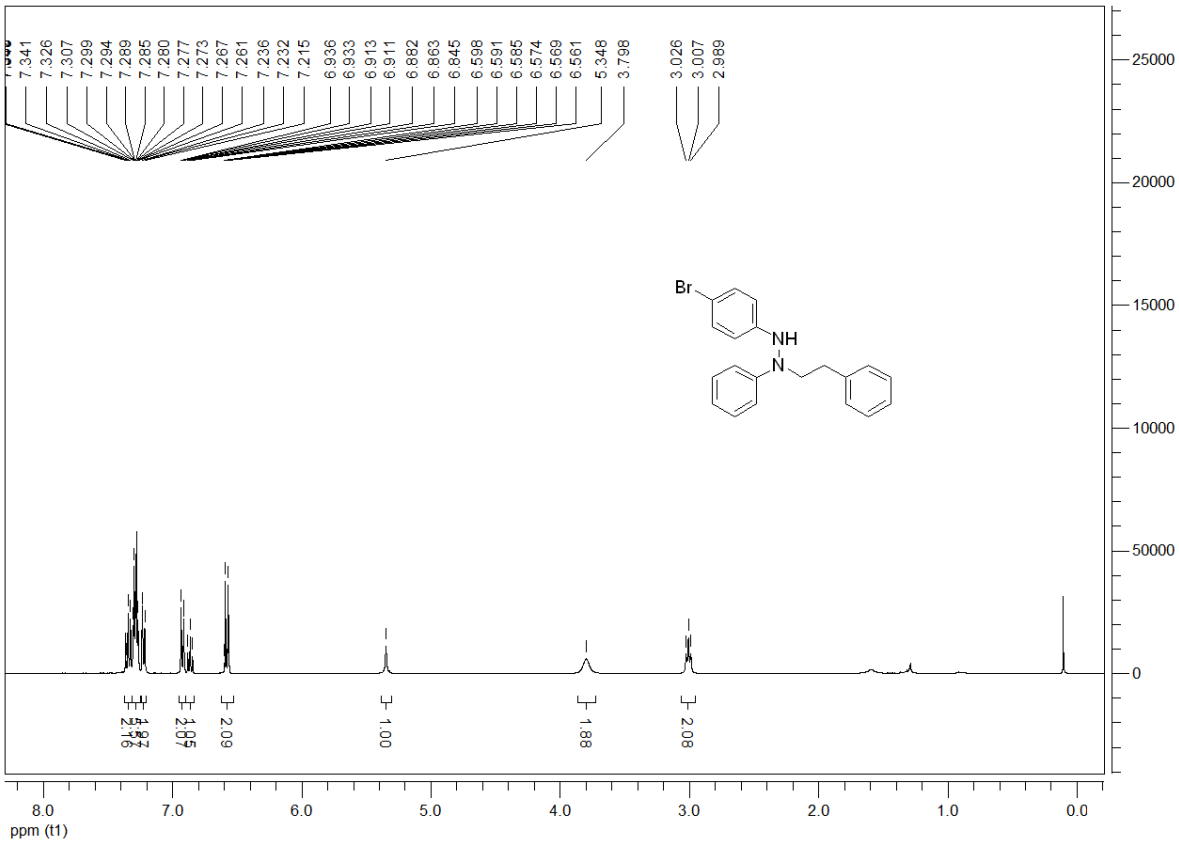


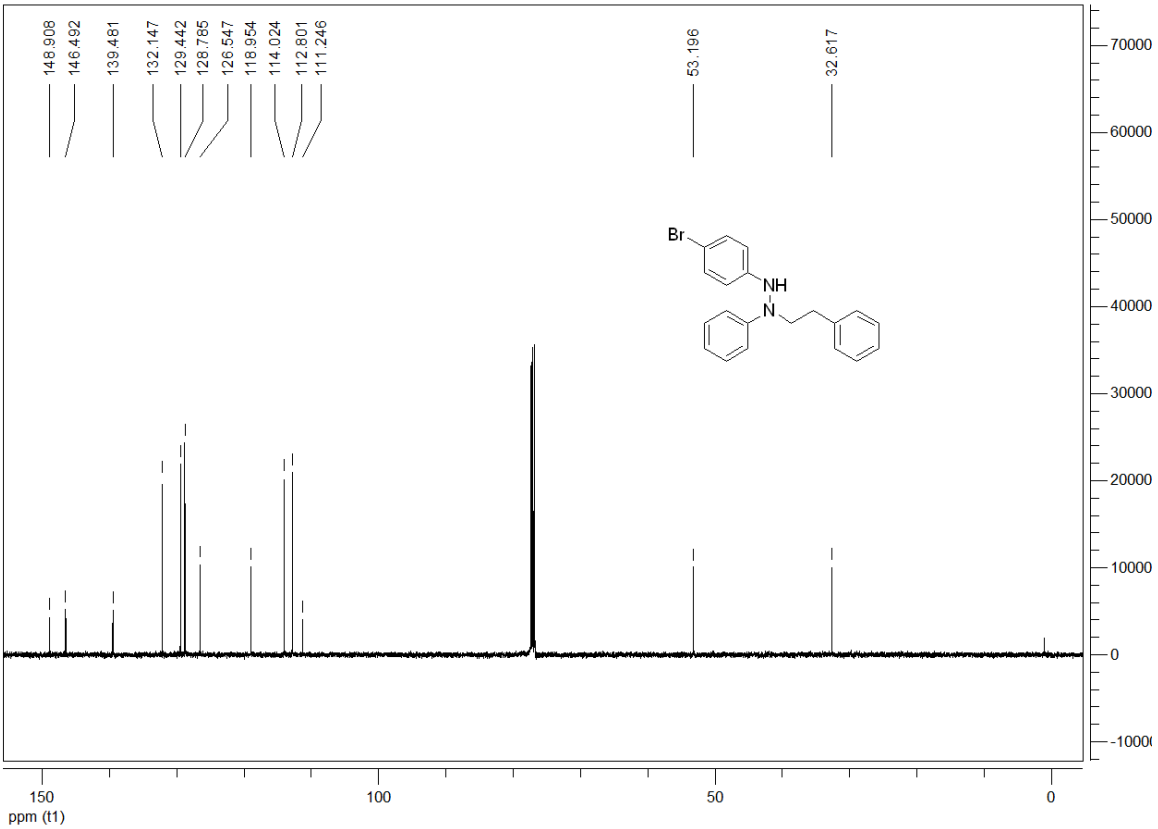
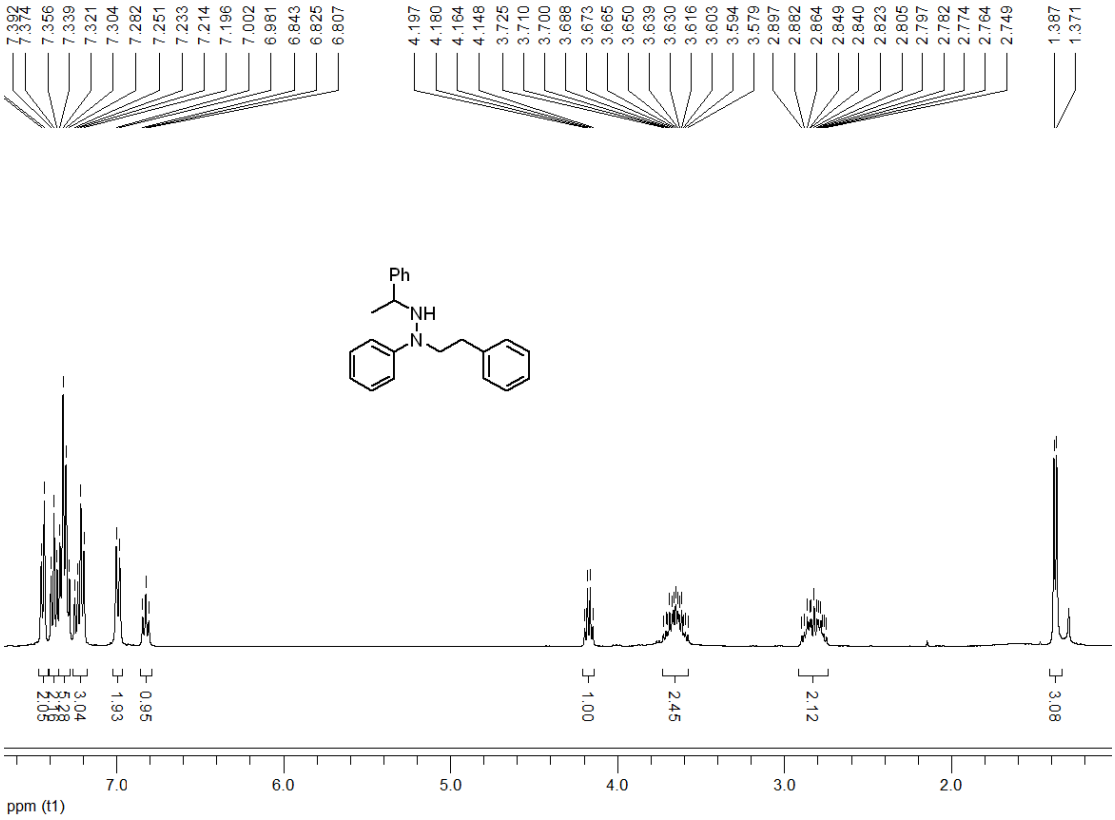
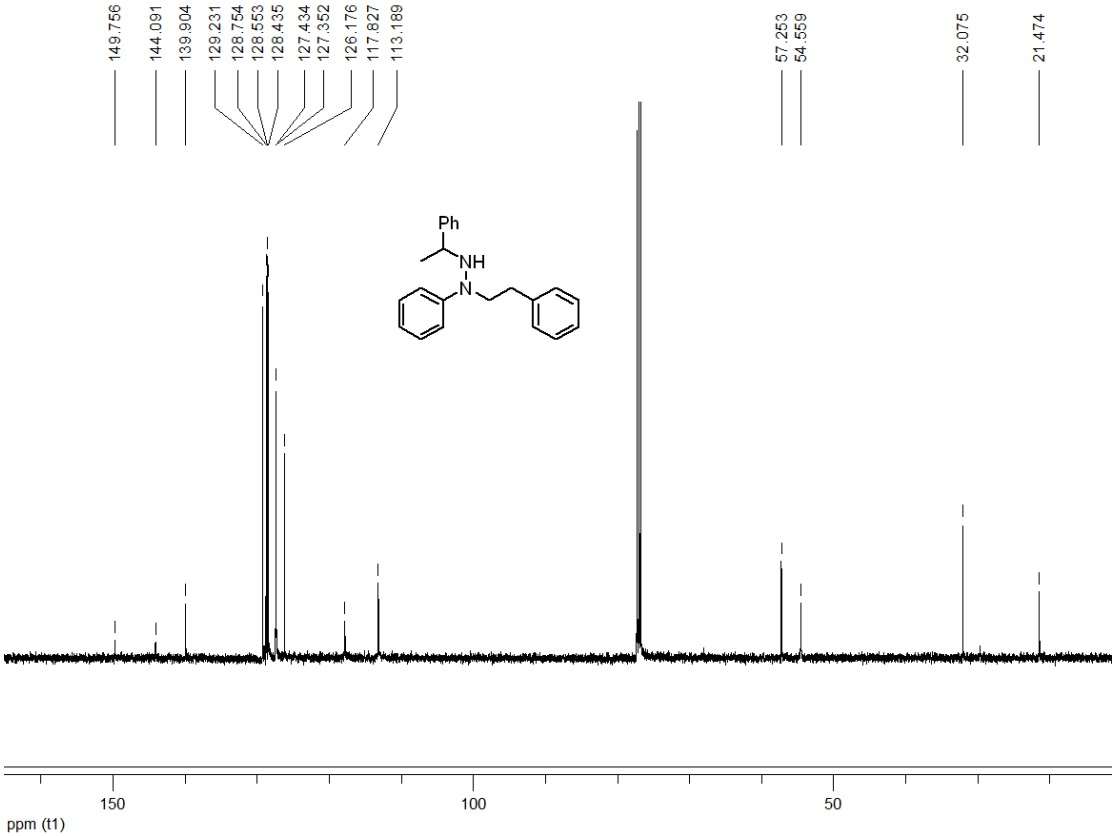
^{1}H and ^{13}C NMR of **6ht**





^{1}H and ^{13}C NMR of **6du**





^{1}H and ^{13}C NMR of **6ds**