Supporting Information for

Metal-free Direct Amination/aromatisation of 2-Cyclohexenones to Iodo-*N*-Arylanilines and *N*-Arylanilines promoted by iodine †

M. Teresa Barros,[a] Suvendu S. Dey,[a] Christopher D. Maycock,[b,c*] Paula Rodrigues [b]

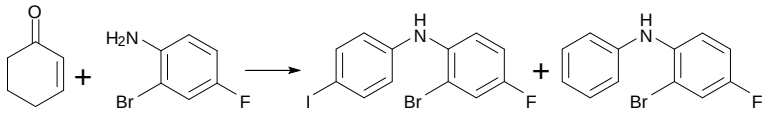
[a] Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Monte da Caparica,

[b] Instituto de Tecnologia Química e Biologia, Universidade Nova de Lisboa, 2780-157 Oeiras, Portugal.

[c] Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa Portugal.

Contents:

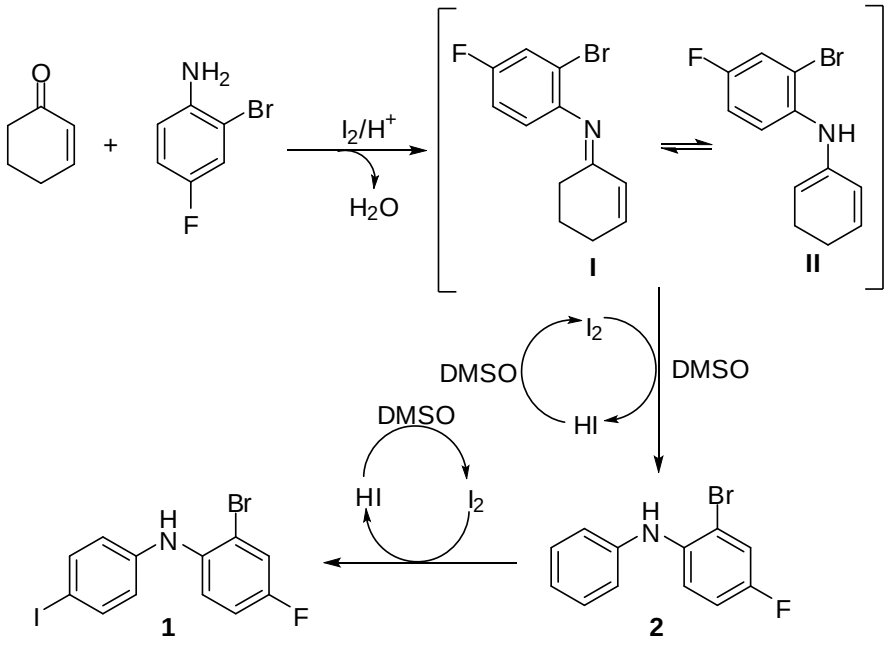
Table SA Optimization of aromatization of 2-cyclohexenone[a]



Entry	Reagent (mol%)	Temp (^{o}C)	Solvent	Time (h)	**1:2**	Yield (%)[b]
1	I_2 (110) + *p*-TsOH (10)	90	DMSO	1	25:75[c]	78
2	**I_2 (110) + *p*-TsOH (10)**	**90**	**DMSO**	**4**	**100:00**	**89**
3	**I_2 (50) + *p*-TsOH (10)**	**90**	**DMSO**	**1**	**00:100**	**91**
4	I_2 (30) + *p*-TsOH (10)	90	DMSO	5	00:100	45
5	I_2 (50) + *p*-TsOH (10)	50	DMSO	1.5	00:100	79
6	I_2 (50) + *p*-TsOH (10)	rt	DMSO	12	00:100	40
7	I_2 (110)	90	DMSO	4	100:00	79
8	I_2 (110) + *p*-TsOH (10)	75	EtOH	12	00:100	55
9	I_2 (110) + *p*-TsOH (10)	65	THF	12	00:100	45
10	I_2 (110) + *p*-TsOH (10)	80	CH_3CN	12	00:100	72
11	NIS (110) + *p*-TsOH (10)	75	EtOH	12	00:100	69
12	NIS (110) + *p*-TsOH (10)	65	THF	12	00:100	56
13	NIS (110) + *p*-TsOH (10)	40	CH_2Cl_2	12	00:100	49
14	NIS (110) + *p*-TsOH (10)	90	DMSO	18	10:90[c]	77
15	NIS (220) + *p*-TsOH (10)	90	DMSO	18	100:00	75

[a]Mixture of 0.33 mmol of 2-cylchexenone, 0.25 mmol of amine in 0.5 ml of solvent was studied; [b]Isolated Yield; [c]Isolated ratio, separated by preparative TLC.

Scheme SB: Plausible mechanism



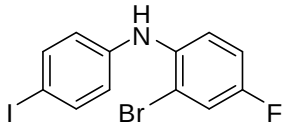
Experimental Procedures:

All chemicals used were of reagent grade. All solvents were freshly distilled before use. Flash chromatography was performed on Kieselgel 60, particle size 0.032-0.063 mm. NMR spectra were obtained at 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR) using $CDCl_3$ as solvent unless noted otherwise. Chemical shifts are reported in ppm relative to TMS. Infrared (IR) spectra were obtained using a Perkin-Elmer 1600 FT-IR spectrophotometer and are in cm^{-1}; *para*-toluenesulfonic acid monohydrate = *p*-TsOH; trace amounts of solvents such as CH_2Cl_2, EtOAc, H_2O (from $CDCl_3$) are found to be present in a few ^{1}H-NMR-spectra.

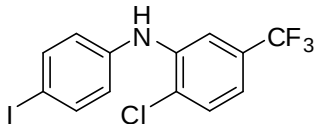
2-Cyclohexen-1-one and 3-methyl-2-cyclohexen-1-one were purchased commercially. Syntheses of 6-Carbethoxy-5-methyl-2-cyclohexen-1-one[1], 4-methyl-2-cyclohexen-1-one[2], 4-phenyl-2-cyclohexen-1-one[2], 4-*tert*-butyl-2-cyclohexen-1-one[2], 4-Carbethoxy-3-methyl-5-phenyl-2-cyclohexen-1-one[3] and 4-Carbethoxy-5-(4-chlorophenyl)-3-methyl-2-cyclohexen-1-one[3] were carried following literature procedures.

General Experimental procedure for the synthesis of mono-iodo-*N*-phenylanilines:

In a screw capped vessel, a solution of 2-cyclohexenones (0.33 mmol), amines (0.25 mmol), iodine (70 mg, 110 mol%) and *p*-TsOH (4.7 mg, 10 mol%) in 0.50 ml of DMSO was heated at 90 ^{o}C for the required time to complete the reaction (TLC). After cooling, 40 ml of dichloromethane was added. The solution was washed with 20 ml of 20% sodium thiosulfate followed by 10 ml of brine. The organic extract was dried over sodium sulfate. Evaporation of the organic layer and purification through a short silica gel column (eluted with hexanes/ethyl acetate) afforded the titled products.

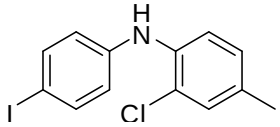


2-Bromo-4-fluoro-*N*-(4-iodophenyl)aniline (1): Brownish white solid (87 mg, 89%), m.p. = 75 ^{o}C; IR (υ_{max}): 3390, 3058, 3016, 1583, 1502, 1466, 1315, 1023, 806, 749, 665; ^{1}H NMR: δ 7.55 (m, 2H), 7.31 (dd, J = 7.9, 2.9 Hz, 1H), 7.19 (dd, J = 9.0, 5.2 Hz, 1H), 6.95 (ddd, J = 9.0, 7.9, 2.9 Hz, 1H), 6.80 (m, 2H), 5.79 (s, 1H); ^{13}C NMR: δ 157.1 (d, J_{C-F} = 253.5 Hz), 142.3, 138.3 (2C), 136.9 (d, J_{C-F} = 2.7 Hz), 120.4 (2C), 120.1 (d, J_{C-F} = 25.4 Hz), 118.7 (d, J = 11.1 Hz), 115.2 (d, J_{C-F} = 22.3 Hz), 113.8 (d, J_{C-F} = 9.3 Hz), 83.9. HRMS (ESI-FIA-TOF) Calcd. for $C_{12}H_9BrFIN$ $[M+H]^+$ requires m/z = 391.8947; Found: m/z = 391.8942.

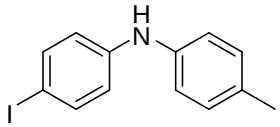


2-Chloro-*N*-(4-iodophenyl)-5-(trifluoromethyl)aniline (1a): White solid (84 mg, 85%), m.p. = 82 ^{o}C; IR (υ_{max}): 3401, 3063, 3024, 1597, 1502, 1484, 1460, 1440, 1315, 1221, 1055, 1012, 808, 749, 678; ^{1}H NMR: δ 7.66 (m, 2H), 7.46 (d, J = 8.2 Hz, 1H), 7.40 (d, J

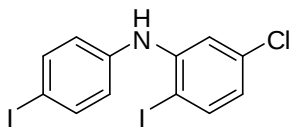
= 1.8 Hz, 1H), 7.05 (dd, J = 8.2 Hz, 1.8 Hz, 1H), 6.94 (m, 2H), 6.17 (s, 1H); ^{13}C NMR: δ 140.4, 140.2, 138.7 (2C), 130.3, 130.1 (q, J_{C-F} = 32.4 Hz), 126.7 (q, J_{C-F} = 271.3 Hz), 124.6 (broad), 122.7 (2C), 116.9 (q, J_{C-F} = 3.8 Hz), 111.5 (q, J_{C-F} = 3.9 Hz), 86.4. Anal. Calcd for $C_{13}H_8ClF_3IN$: C, 39.27; H, 2.03; N, 3.52. Found: C, 39.31; H, 1.82; N, 3.63.



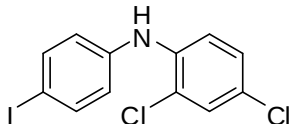
2-Chloro-*N*-(4-iodophenyl)-4-methylaniline (1b): Brownish white solid (78 mg, 91%), m.p. = 73 ^{o}C; IR (υ_{max}): 3401, 3052, 3017, 1587, 1501, 1489, 1469, 1443, 1317, 1222, 1051, 1038, 1002, 809, 745, 682; ^{1}H NMR: δ 7.53 (d, J = 8.6 Hz, 2H), 7.19 (s, 1H), 7.16 (d, J = 8.2 Hz, 1H), 6.95 (d, J = 8.2 Hz, 1H), 6.83 (d, J =8.6 Hz, 2H), 5.88 (s, 1H), 2.27 (s, 3H); ^{13}C NMR: δ 142.3, 138.1 (2C), 136.5, 131.7, 130.2, 128.0, 122.9, 120.3 (2C), 117.5, 83.3, 20.4. Anal. Calcd for $C_{13}H_{11}ClIN$: C, 45.44; H, 3.23; N, 4.08. Found: C, 45.64; H, 3.05; N, 4.18.



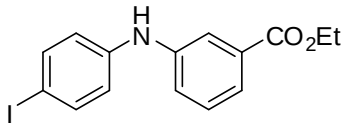
4-Iodo-*N*-p-tolylaniline (1c): White solid (17 mg, 22%), m.p. = 99 ^{o}C; IR (υ_{max}): 3390, 3024, 2914, 2856, 1604, 1578, 1535, 1507, 1482, 1320, 1269, 1176, 1109, 1060, 999, 854, 709, 563; ^{1}H NMR: δ 7.47 (m, 2H), 7.09 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 6.75 (m, 2H), 5.58 (broad s, 1H), 2.30 (s, 3H); ^{13}C NMR: δ 143.9, 139.4, 138.0 (2C), 131.9, 129.9 (2C), 119.7 (2C), 118.4 (2C), 81.2, 20.7. Anal. Calcd for $C_{13}H_{12}IN$: C, 50.51; H, 3.91; N, 4.53. Found: C, 50.52; H, 3.95; N, 4.56.



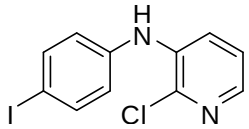
5-Chloro-2-iodo-*N*-(4-iodophenyl)aniline (1d): White solid (103 mg, 91%), m.p. = 117 ^{o}C; IR (υ_{max}): 3401, 3062, 3027, 1587, 1502, 1484, 1459, 1440, 1315, 1221, 1055, 1031, 1012, 808, 749, 678; ^{1}H NMR: δ 7.68 – 7.59 (m, 3H), 7.08 (d, J = 2.4 Hz, 1H), 6.90 (m, 2H), 6.63 (dd, J = 8.5, 2.4 Hz, 1H), 5.87 (s, 1H); ^{13}C NMR: δ 144.5, 140.8, 140.1, 138.5 (2C), 135.3, 122.5 (2C), 122.1, 115.2, 85.9, 85.4. Anal. Calcd for $C_{12}H_8ClI_2N$: C, 31.64; H, 1.77; N, 3.08. Found: C, 31.74; H, 1.62; N, 3.23.



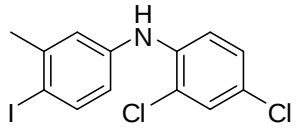
2,4-Dichloro-*N*-(4-iodophenyl)aniline (1e): White solid (84 mg, 92%), m.p. = 88 ^{o}C; IR (υ_{max}): 3405, 3048, 1592, 1504, 1467, 1390, 1315, 1220, 1099, 1049, 808, 773, 740, 694, 549; ^{1}H NMR: δ 7.59 (m, 2H), 7.36 (d, J = 2.2 Hz, 1H), 7.15 (d, J = 8.8 Hz, 1H), 7.10 (dd, J = 8.8, 2.2 Hz, 1H), 6.88 (m, 2H), 5.95 (broad s, 1H); ^{13}C NMR: δ 141.1, 138.4 (2C), 138.3, 129.5, 127.6, 125.1, 122.5, 121.8 (2C), 116.7, 85.1. Anal. Calcd for $C_{12}H_8Cl_2IN$: C, 39.59; H, 2.22; N, 3.85. Found: C, 39.77; H, 2.06; N, 4.00.



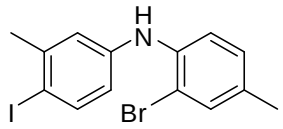
Ethyl 3-(4-iodophenylamino)benzoate (1f): Grey solid (68 mg, 75%), m.p. = 78 ^{o}C; IR (υ_{max}): 3368, 2977, 2931, 1716, 1683, 15181, 1506, 1484, 1465, 1299, 1251, 1228, 1174, 1112, 1078, 1002, 813, 775, 698, 543; ^{1}H NMR: δ 7.71 (s, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.54 (m, 2H), 7.33 (t, J = 8.0 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 6.84 (m, 2H), 5.82 (s, 1H), 4.36 (q, J = 7.1 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H); ^{13}C NMR: δ 166.5, 142.6, 142.5, 138.4 (2C), 132.1, 129.6, 122.6, 122.1, 119.8 (2C), 118.9, 83.1, 61.1, 14.3. Anal. Calcd for $C_{15}H_{14}INO_2$: C, 49.07; H, 3.84; N, 3.81. Found: C, 49.16; H, 3.62; N, 3.88.



2-Chloro-*N*-(4-iodophenyl)pyridin-3-amine (1g): Yellow solid (58 mg, 70%), m.p. = 110 ^{o}C; IR (υ_{max}): 3359, 3248, 3060, 1567, 1492, 1417, 1313, 1263, 1070, 1006, 809, 734; ^{1}H NMR: δ 7.92 (dd, J = 4.6, 1.6 Hz, 1H), 7.66 (m, 2H), 7.51 (dd, J = 8.1, 1.6 Hz, 1H), 7.14 (dd, J = 8.1, 4.6 Hz, 1H), 6.95 (m, J = 8.8 Hz, 2H), 6.13 (broad s, 1H); ^{13}C NMR: δ 139.9, 139.8, 138.6 (2C), 136.9, 123.2, 122.5 (2C), 121.9, 86.3. Anal. Calcd for $C_{11}H_8ClIN_2$: C, 39.97; H, 2.44; N, 8.47. Found: C, 39.88; H, 2.32; N, 8.63.

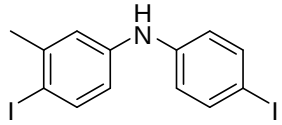


2,4-Dichloro-*N*-(4-iodo-3-methylphenyl)aniline (1h): Yellow viscous liquid (76 mg, 80%); IR (υ_{max}): 3405, 3047, 1592, 1510, 1467, 1390, 1314, 1225, 1099, 1051, 808, 777, 742, 695, 546; ^{1}H NMR: δ 7.69 (d, J = 8.4 Hz, 1H), 7.36 (d, J = 2.3 Hz, 1H), 7.15 (d, J = 8.8 Hz, 1H), 7.09 (dd, J = 8.8, 2.3 Hz, 1H), 7.00 (d, J = 2.6 Hz, 1H), 6.68 (dd, J = 8.4, 2.6 Hz, 1H), 5.95 (s, 1H), 2.39 (s, 3H); ^{13}C NMR: δ 142.6, 141.5, 139.6, 138.5, 129.4, 127.6, 124.8, 122.3, 121.2, 119.0, 116.7, 92.2, 28.1. Anal. Calcd for $C_{13}H_{10}Cl_2IN$: C, 41.30; H, 2.67; N, 3.71. Found: C, 41.54; H, 2.60; N, 3.73.

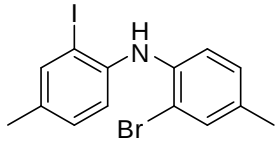


2-Bromo-*N*-(4-iodo-3-methylphenyl)-4-methylaniline (1i): Yellow viscous liquid (85 mg, 85%); IR (υ_{max}): 3390, 3060, 3011, 1583, 1502, 1453, 1318, 1022, 806, 747, 669; ^{1}H NMR: δ 7.63 (d, J = 8.4 Hz, 1H), 7.36 (d, J = 0.9 Hz, 1H), 7.15 (d, J = 8.2 Hz, 1H), 7.00 (dd, J = 8.2, 0.9 Hz, 1H), 6.96 (d, J = 2.7 Hz, 1H), 6.63 (dd, J = 8.4, 2.7 Hz, 1H), 5.83 (s,

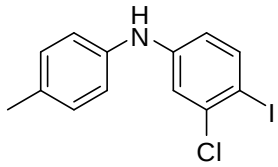
1H), 2.37 (s, 3H), 2.27 (s, 3H); ^{13}C NMR: δ 142.9, 142.3, 139.4, 137.9, 133.4, 132.0, 128.8, 119.9, 117.8, 117.7, 113.6, 90.5, 28.2, 20.4. HRMS (ESI-FIA-TOF) Calcd. for $C_{14}H_{14}BrIN$ $[M+H]^+$ requires m/z = 401.9354; Found: m/z = 401.9349.



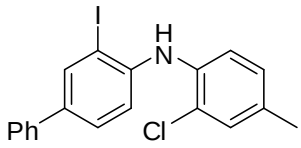
4-Iodo-*N*-(4-iodophenyl)-3-methylaniline (1j): Brown viscous liquid (26 mg, 24%); IR (υ_{max}): 3389, 3021, 2914, 2856, 1604, 1577, 1535, 1511, 1482, 1320, 1266, 1178, 1109, 1065, 999, 854, 709, 567; ^{1}H NMR: δ 7.63 (d, J = 8.5 Hz, 1H), 7.53 (m, 2H), 6.94 (d, J = 2.7 Hz, 1H), 6.80 (d, m, 2H), 6.61 (dd, J = 8.5, 2.7 Hz, 1H), 5.61 (s, 1H), 2.36 (s, 3H); ^{13}C NMR: δ 142.7, 142.4, 142.3, 139.5, 138.2 (2C), 119.9 (2C), 119.4, 117.4, 90.4, 82.9, 28.2. Anal. Calcd for $C_{13}H_{11}I_2N$: C, 35.89; H, 2.55; N, 3.22. Found: C, 35.82; H, 2.40; N, 3.06.



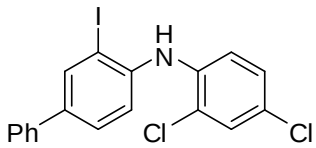
2-Bromo-*N*-(2-iodo-4-methylphenyl)-4-methylaniline (1k): White solid (75 mg, 75%), m.p. = 53 ^{o}C; IR (υ_{max}): 3402, 3071, 3021, 1573, 1502, 1446, 1325, 1022, 811, 748, 665; ^{1}H NMR: δ 7.65 (s, 1H), 7.38 (s, 1H), 7.14 – 6.93 (m, 4H), 6.05 (s, 1H), 2.27 (s, 3H), 2.26 (s, 3H); ^{13}C NMR: δ 140.6, 139.8, 138.4, 133.3, 133.2, 131.8, 129.7, 128.7, 118.4, 117.5, 113.6, 91.3, 20.3, 20.1. Anal. Calcd for $C_{14}H_{13}BrIN$: C, 41.82; H, 3.26; N, 3.48. Found: C, 42.09; H, 3.40; N, 3.58.



3-Chloro-4-iodo-*N*-p-tolylaniline (1l): Brown gummy solid (36 mg, 42%); IR (υ_{max}): 3400, 3050, 2898, 1587, 1510, 1481, 1469, 1443, 1317, 1222, 1051, 1028, 809, 745, 682; ^{1}H NMR: δ 7.59 (d, J = 8.7 Hz, 1H), 7.13 (d, J = 8.2 Hz, 2H), 7.09 (d, J = 2.6 Hz, 1H), 7.00 (d, J = 8.2 Hz, 2H), 6.59 (dd, J = 8.7, 2.6 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR: δ 145.8, 140.2, 138.9, 138.4, 132.9, 130.1 (2C), 120.6 (2C), 116.2, 116.0, 84.0, 20.8. Anal. Calcd for $C_{13}H_{11}ClIN$: C, 45.44; H, 3.23; N, 4.08. Found: C, 45.35; H, 3.34; N, 3.92.

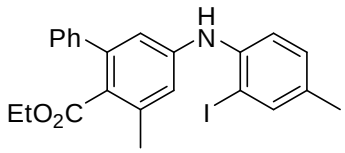


***N*-(2-Chloro-4-methylphenyl)-3-iodobiphenyl-4-amine (1m):** White solid (76 mg, 73%), m.p. = 49 ^{o}C; IR (υ_{max}): 3401, 3052, 3018, 1601, 1587, 1501, 1489, 1469, 1443, 1317, 1222, 1051, 1038, 1002, 809, 745, 682; ^{1}H NMR: δ 8.05 (d, J = 2.1 Hz, 1H), 7.52 (m, 2H), 7.45 (dd, J = 8.5, 2.1 Hz, 1H), 7.41 (m, 2H), 7.31 (m, 1H), 7.25 (d, J = 1.8 Hz, 1H), 7.21 (d, J = 8.2 Hz, 1H), 7.19 (d, J = 8.5 Hz, 1H). 7.01 (dd, J = 8.2, 1.8 Hz, 1H), 6.23 (broad s, 1H), 2.31 (s, 3H); ^{13}C NMR: δ 142.4, 139.3, 137.9, 136.3, 135.7, 132.6, 130.4, 128.8 (2C), 128.1, 127.7, 127.1, 126.6 (2C), 124.2, 119.1, 116.6, 90.2, 20.5. Anal. Calcd for $C_{13}H_{11}ClIN$: C, 54.37; H, 3.60; N, 3.34. Found: C, 54.35; H, 3.61; N, 3.18.

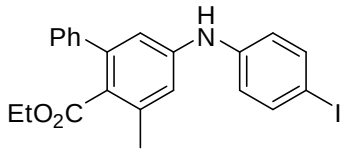


***N*-(2,4-Dichlorophenyl)-3-iodobiphenyl-4-amine (1n):** White solid (77 mg, 70%), m.p. = 92 ^{o}C; IR (υ_{max}): 3400, 3052, 3017, 1591, 1587, 1501, 1489, 1469, 1443, 1317, 1222, 1051, 1038, 1002, 809, 748, 680; ^{1}H NMR: δ 8.08 (d, J = 1.9 Hz, 1H), 7.53 (d, J = 7.6

Hz, 2H), 7.50 (dd, J = 8.2, 1.9 Hz, 1H), 7.47 – 7.38 (m, 3H), 7.34 (t, J = 7.6 Hz, 1H), 7.26 (d, J = 8.2 Hz, 1H), 7.17 (d, J = 8.7 Hz, 1H), 7.13 (dd, J = 8.7, 2.0 Hz, 1H), 6.28 (s, 1H); ^{13}C NMR: δ 141.2, 139.0, 138.2, 138.1, 137.2, 129.6, 128.9 (2C), 127.8, 127.6, 127.4, 126.6 (2C), 125.8, 123.5, 118.5, 117.8, 91.9. Anal. Calcd for $C_{18}H_{12}Cl_2IN$: C, 49.12; H, 2.75; N, 3.18. Found: C, 49.17; H, 2.66; N, 2.93.

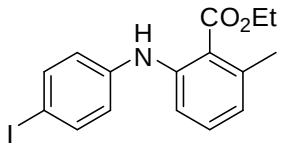


Ethyl-5-(2-iodo-4-methylphenylamino)-3-methylbiphenyl-2-carboxylate (1o): Yellow viscous liquid (61 mg, 52%); (υ_{max}): 3407, 3357, 3060, 2980, 2933, 1718, 1512, 1494, 1455, 1294 1176, 1129, 1046, 867, 770, 741, 695, 548; ^{1}H NMR: δ 7.64 (d, J = 1.4 Hz, 1H), 7.39 -7.28 (m, 5H), 7.24 (d, J = 8.2 Hz, 1H), 7.08 (dd, J = 8.2, 1.4 Hz, 1H), 6.82 (d, J = 2.0 Hz, 1H), 6.80 (d, J = 2.0 Hz, 1H), 3.99 (q, J = 7.2 Hz, 2H), 2.38 (s, 3H), 2.27 (s, 3H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR: δ 169.6, 144.1, 142.5, 141.4, 139.9, 139.8, 137.9, 133.8, 129.9, 128.1 (4C), 127.2, 125.6, 119.4, 117.2, 115.5, 91.8, 60.6, 20.2 (2C), 13.6. Anal. Calcd for $C_{23}H_{22}INO_2$: C, 58.61; H, 4.70; N, 2.97. Found: C, 58.27; H, 4.75; N, 2,89.

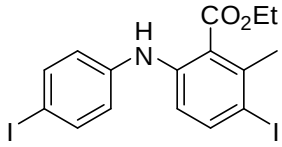


Ethyl-5-(4-iodophenylamino)-3-methylbiphenyl-2-carboxylate (1p): White solid (67 mg, 59%), m.p. = 144 ^{o}C; IR (υ_{max}): 3407, 3357, 3060, 2983, 2933, 1716, 1519, 1506, 1494, 1455, 1298 1176, 1128, 1043, 867, 773, 738, 694, 546; ^{1}H NMR: δ 7.55 (d, J = 8.6 Hz, 2H), 7,38 – 7.28 (m, 5H), 6.93 – 6.77 (m, 4H), 3.99 (q, J = 7.2 Hz, 2H), 2.37 (s, 3H),

0.90 (t, J = 7.2 Hz, 3H); ^{13}C NMR: δ 169.6, 143.5, 142.5, 141.8, 141.2, 138.2 (2C), 137.9, 128.2 (2C), 128.0 (2C), 127.3, 125.7, 120.7 (2C), 117.3, 115.6, 83.6, 60.7, 20.1, 13.6. Anal. Calcd for $C_{22}H_{20}INO_2$: C, 57.78; H, 4.41; N, 3.06. Found: C, 57.84; H, 4.45; N, 3.23.



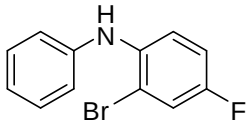
Ethyl-2-(4-iodophenylamino)-6-methylbenzoate (1q): Yellow liquid (64 mg, 67%); IR (υ_{max}): 3366, 2979, 2931, 1716, 1683, 1519, 1506, 1494, 1465, 1297, 1251, 1228, 1174, 1112, 1078, 1002, 813, 775, 701, 549; ^{1}H NMR: δ 7.54 (m, 2H), 7.18 – 7.11 (m, 2H), 6.88 (m, 2H), 6.73 (dd, J = 6.7, 1.2 Hz, 1H), 4.38 (q, J = 7.2 Hz, 2H), 2.45 (s, 3H), 1.39 (t, J = 7.2 Hz, 3H); ^{13}C NMR: δ 169.2, 143.8, 142.0, 139.5, 138.1 (2C), 131.4, 123.0, 121.6 (2C), 119.1, 114.4, 83.7, 61.1, 22.4, 14.2. Anal. Calcd for $C_{16}H_{16}INO_2$: C, 50.41; H, 4.23; N, 3.67. Found: C, 50.70; H, 4.36; N, 3.72.



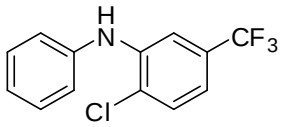
Ethyl-3-iodo-6-(4-iodophenylamino)-2-methylbenzoate (1r): White solid (17 mg, 17%), m.p. = 104 ^{o}C; IR (υ_{max}): 3366, 2979, 2931, 1716, 1683, 1519, 1506, 1494, 1465, 1297, 1251, 1228, 1174, 1112, 1078, 1002, 813, 775, 701, 549; ^{1}H NMR: δ 7.68 (d, J = 8.8 Hz, 1H), 7.55 (m, 2H), 6.87 (d, J = 8.8 Hz, 1H), 6.83 (m, 2H), 4.39 (q, J = 7.2 Hz, 2H), 2.48 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H); ^{13}C NMR: δ 168.5, 142.4, 141.5, 141.3, 140.4, 138.2(2C), 122.5, 121.4 (2C), 116.4, 91.4, 84.2, 61.7, 27.4, 14.1. Anal. Calcd for $C_{16}H_{15}I_2NO_2$: C, 37.90; H, 2.98; N, 2.76. Found: C, 38.08; H, 2.95; N, 2.94.

General Experimental procedure for the synthesis of *N*-phenylanilines:

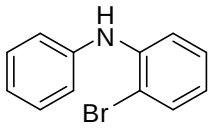
In a screw capped vessel, a solution of 2-cyclohexenones (0.33 mmol), amines (0.25 mmol), iodine (32 mg, 50 mol%) and *p*-TsOH (4.7 mg, 10 mol%) in 0.50 ml of DMSO was heated at 90 ^{o}C for the required time to complete the reaction (TLC). After cooling, 30 ml of dichloromethane was added. The solution was washed with 10 ml of 20% sodium thiosulfate followed by 10 ml of brine. The organic extract was dried over sodium sulfate. Evaporation of organic layer and purification through short silica gel column chromatography (eluted with hexanes/ethylacetate) afforded the titled products.



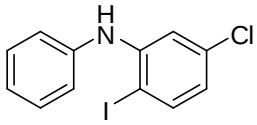
2-Bromo-4-fluoro-*N*-phenylaniline (2)[4]: (61 mg**,** 91%); ^{1}H NMR: δ 7.35 – 7.25 (m, 3H), 7.21 (dd, J = 9.0, 5.2 Hz, 1H), 7.06 (dd, J = 7.7, 0.8 Hz, 2H), 7.01 (td, J = 7.4, 0.8 Hz, 1H), 6.92 (m, 1H), 5.85 (broad s, 1H); ^{13}C NMR: δ 156.5 (d, J_{C-F} = 241.6 Hz), 142.2, 137.9 (d, J_{C-F} = 2.8 Hz), 129.5 (2C), 122.3, 119.9 (J_{C-F} = 25.3 Hz), 119.3 (2C), 117.6 (d, J_{C-F} = 7.8 Hz), 115.0 (d, J_{C-F} = 21.9 Hz), 112.7 (d, J_{C-F} = 10.7 Hz).



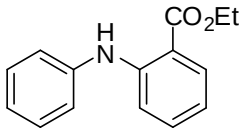
2-Chloro-*N*-phenyl-5-(trifluoromethyl)aniline (2a)[5]: (59 mg, 87%); ^{1}H NMR: δ 7.47 – 7.41 (m, 2H), 7.43 (s, 1H), 7.31 (t, J = 7.7 Hz, 2H), 7.18 (d, J = 7.7 Hz, 2H), 7.13 (t, J = 7.7 Hz, 1H), 7.01 (d, J = 8.2 Hz, 1H), 6.24 (s, 1H); ^{13}C NMR: δ 141.2, 140.2, 130.0 (q, J_{C-F} = 32.5 Hz), 130.1, 129.8 (2C), 124.0, 123.8 (q, J_{C-F} = 271.1 Hz), 121.4 (2C), 116.2 (q, J_{C-F} = 3.7 Hz), 110.9 (q, J_{C-F} = 3.7 Hz).



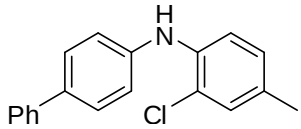
2-Bromo-*N*-phenylaniline (2b)[6]: (56 mg, 91%) ; ^{1}H NMR: δ 7.52 (dd, J = 7.6, 1.5 Hz, 1H), 7.31 (dd, J = 7.5, 7.4 Hz, 2H), 7.24 (dd, J = 8.2, 1.5 Hz, 1H), 7.19 – 7.11 (m, 3H), 7.03 (t, J = 7.4 Hz, 1H), 6.73 (ddd, J = 8.6, 8.2, 1.5 Hz, 1H), 6.08 (broad s, 1H); ^{13}C NMR: δ 141.6, 141.4, 132.9, 129.4 (2C), 128.1, 122.7, 120.9, 120.3 (2C), 115.8, 112.2.



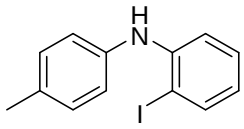
5-Chloro-2-iodo-*N*-phenylaniline (2c): Yellow viscous liquid (72 mg, 88%); IR (υ_{max}): 3401, 3062, 3027, 1587, 1502, 1484, 1459, 1440, 1315, 1220, 1051, 1035, 1002, 809, 746, 688; ^{1}H NMR: δ 7.62 (d, J = 8.4 Hz, 1H), 7.34 (m, 2H), 7.17 – 7.04 (m, 4H), 6.57 (dd, J = 8.4, 2.4 Hz, 1H), 5.92 (broad s, 1H); ^{13}C NMR: δ 145.4, 140.8, 139.9, 135.3, 129.7 (2C), 123.7, 121.3, 121.2 (2C), 114.5, 84.6. Anal. Calcd for $C_{12}H_9ClIN$: C, 43.73; H, 2.75; N, 4.25. Found: C, 43.52; H, 2.78; N, 4.20.



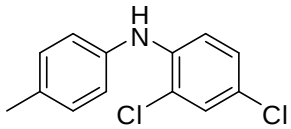
Ethyl 2-(phenylamino)benzoate (2d): Colourless liquid (54 mg, 89%); IR (υ_{max}): 3337, 2981, 2911, 1703, 1678, 1590, 1529, 1339, 1279, 1174, 758, 695; ^{1}H NMR: δ 9.50 (broad s, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.42 – 7.21 (m, 6H), 7.08 (t, J = 7.3 Hz, 1H), 6.73 (t, J = 8.0 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H); ^{13}C NMR: δ 168.5, 147.9, 140.8, 133.9, 131.6, 129.3 (2C), 123.5, 122.4 (2C), 117.1, 114.1, 112.3, 60.6, 14.3. Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81. Found: C, 74.65; H, 6.20; N, 5.72.



***N*-(2-Chloro-4-methylphenyl)biphenyl-4-amine (2e):** Pale yellow solid (107 mg, 73%), mp = 81 ^{o}C; IR (υ_{max}): 3407, 3056, 2919, 2856, 1606, 1523, 1409, 840, 740; ^{1}H NMR: δ 7.56 (d, J = 7.4 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H), 7.41 (t, J = 7.4 Hz, 2H), 7.29 (t, J = 7.4 Hz, 1H), 7.25 (d, J = 8.3 Hz, 1H), 7.20 (s, 1H), 7.15 (d, J = 8.5 Hz, 2H), 6.96 (d, J = 8.3 Hz, 1H), 6.01 (br s, 1H), 2.28 (s, 3H); ^{13}C NMR: δ 141.8, 140.8, 137.2, 134.7, 131.1, 130.2, 128.8 (2C), 128.1, 128.0 (2C), 126.8, 126.6 (2C), 122.4, 119.0 (2C), 117.1, 20.4. Anal. Calcd for $C_{19}H_{16}ClN$: C, 77.68; H, 5.49; N, 4.77. Found: C, 77.50; H, 5.48; N, 4.69.

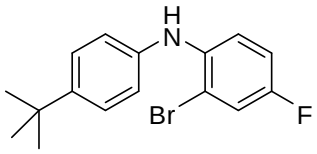


2-Iodo-*N*-*p*-tolylaniline (2f): Yellow liquid (59 mg, 76%); IR (υ_{max}): 3380, 3023, 291, 2861, 1587, 1513, 1450, 1309, 1008, 808, 744, 534; ^{1}H NMR: δ 7.74 (d, J = 7.9 Hz, 1H), 7.20 – 7.01 (m, 6H), 6.57 (t, J = 7.4 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR: δ 144.6, 139.4, 139.2, 129.9 (2C), 129.0, 121.2, 121.2 (2C), 114.9, 87.8, 20.8. Anal. Calcd for $C_{13}H_{12}IN$: C, 50.51; H, 3.91; N, 4.53. Found: C, 50.41; H, 3.90; N, 4.43.

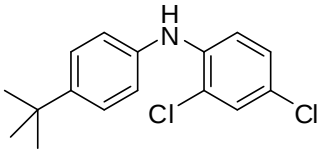


2,4-Dichloro-*N*-p-tolylaniline (2g): Colourless Liquid (47 mg, 75%); IR (υ_{max}): 3405, 3048, 1592, 1504, 1467, 1390, 1315, 1099, 1049, 808, 773, 740, 694, 549; ^{1}H NMR: δ 7.33 (s, 1H), 7.14 (d, J = 8.2 Hz, 2H), 7.06 – 7.01 (m, 4H), 5.96 (broad s, 1H), 2.33 (s, 3H); ^{13}C NMR: δ 140.0, 138.2, 133.2, 130.1 (2C), 129.1, 127.5, 123.4, 121.6 (2C), 121.0,

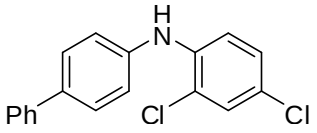
115.2, 20.8. Anal. Calcd for $C_{13}H_{11}C_{l2}N$: C, 61.93; H, 4.40; N, 5.56. Found: C, 61.78; H, 4.41; N, 5.45.



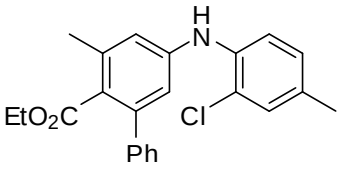
2-Bromo-*N*-(4-tert-butylphenyl)-4-fluoroaniline (2h): White solid (60 mg, 75%), m.p. = 95 ^{o}C; ^{1}H NMR: δ 7.32 (d, J = 8.5 Hz, 2H), 7.27 (dd, J = 7.9, 2.8 Hz, 1H), 7.16 (dd, J = 9.0, 5.2 Hz, 1H), 7.02 (d, J = 8.5 Hz, 2H), 6.89 (m, 1H), 1.31 (s, 9H); ^{13}C NMR: δ 156.1 (d, J_{C-F} = 241.0 Hz), 145.6, 139.4, 138.4 (d, J_{C-F} = 2.4 Hz), 126.3 (2C), 119.7 (d, J_{C-F} = 25.5 Hz), 119.6 (2C), 116.7 (d, J_{C-F} = 8.0 Hz), 114.9 (d, J_{C-F} = 11.8 Hz), 111.8 (d, J_{C-F} = 10.9Hz), 34.3, 31.4 (2C). Anal. Calcd for $C_{16}H_{17}BrFN$: C, 59.64; H, 5.32; N, 4.35. Found: C, 59.52; H, 5.35; N, 4.41.



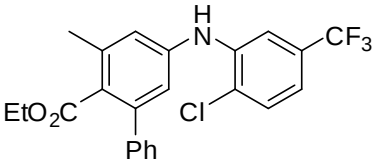
***N*-(4-Tert-butylphenyl)-2,4-dichloroaniline (2i):** Colourless liquid (58 mg, 79%); IR (υ_{max}): 3405, 3048, 1597, 1508, 1466, 1390, 1325, 1097, 1049, 818, 777, 741, 694; ^{1}H NMR: δ 7.37 – 7.31 (m, 3H), 7.14 – 7.02 (m, 4H), 5.96 (broad, 1H), 1.32 (s, 9H); ^{13}C NMR: δ 146.4, 139.7, 138.2, 129.2, 127.5, 126.4 (2C), 123.5, 121.1, 120.8 (2C), 115.5, 34.3, 31.4 (3C). Anal. Calcd for $C_{16}H_{17}C_{l2}N$: C, 65.32; H, 5.82; N, 4.76. Found: C, 65.43; H, 5.96; N, 4.80.



***N*-(2,4-Dichlorophenyl)biphenyl-4-amine (2j):** White solid (58 mg, 74%), m.p. = 80 ^{o}C; ^{1}H NMR: δ 7.61 – 7.54 (m, 4H), 7.43 (m, 2H), 7.37 (d, J = 2.4 Hz, 1H), 7.33 (m, J = 7.6 Hz, 1H), 7.23 (d, J = 8.8 Hz, 1H), 7.19 (m, 2H), 7.11 (dd, J = 8.8, 2.4 Hz, 1H), 6.10 (broad s, 1H); ^{13}C NMR: δ 140.5, 140.4, 139.0, 135.9, 129.3, 128.8 (2C), 128.2 (2C), 127.6, 126.9, 126.7 (2C), 124.4, 121.9, 120.4 (2C), 116.3. HRMS (ESI-FIA-TOF) Calcd. for $C_{18}H_{14}Cl_2N$ $[M+H]^+$ requires m/z = 314.0503; Found: m/z = 314.0503.

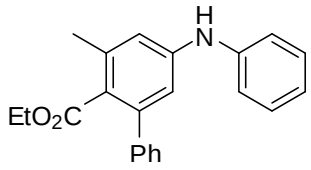


Ethyl-5-(2-chloro-4-methylphenylamino)-3-methylbiphenyl-2-carboxylate (2k): White solid (81 mg, 86%), m.p. = 95 ^{o}C; IR (υ_{max}): 3359, 2981, 2901, 1721, 1589, 1510, 1376, 1355, 1085, 1014, 833, 746, 547; ^{1}H NMR: δ 7.39 – 7.31 (m, 5H), 7.29 (d, J = 8.2 Hz, 1H), 6.99 (dd, J = 8.2, 1.4 Hz, 1H), 6.87 (two d, J = 2.0 Hz, 2H), 3.99 (q, J = 7.2 Hz, 2H), 2.39 (s, 3H), 2.28 (s, 3H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C NMR: δ 169.6, 143.6, 142.5, 141.4, 137.9, 136.1, 132.2, 130.3, 128.1 (3C), 128.1 (2C), 127.3, 125.9, 123.6, 118.8, 117.7, 115.9, 60.7, 20.5, 20.2, 13.6. Anal. Calcd for $C_{23}H_{22}ClNO_2$: C, 72.72; H, 5.84; N, 3.69. Found: C, 72.54; H,5.88; N,3.52.

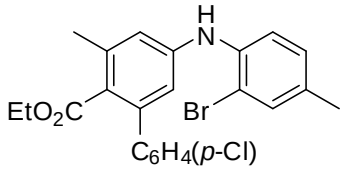


Ethyl-5-{2-chloro-4-(trifluoromethyl)phenylamino}-3-methylbiphenyl-2-carboxylate (2l): Yellow viscous liquid (86 mg, 79%); IR (υ_{max}): 3407, 3357, 3060, 2983, 2933, 1714, 1594, 1523, 1436, 1332, 1268, 1170, 1128, 1081, 863, 771, 738, 701, 647; ^{1}H NMR: δ 7.60 (d, J = 1.5 Hz, 1H), 7.46 (d, J = 8.2 Hz, 1H), 7.41 – 7.31 (m, 5H), 7.07 (dd, J = 8.2,

1.5 Hz, 1H), 7.00 (d, J = 2.4 Hz, 1H), 6.99 (d, J = 2.4 Hz, 1H), 6.28 (s, 1H), 4.04 (q, J = 7.8 Hz, 2H), 2.42 (s, 3H), 0.94 (t, J = 7.8 Hz, 3H); ^{13}C NMR: δ 169.3, 142.6, 141.3, 140.7, 140.1, 138.1, 130.3, 130.1 (q, J_{C-F} = 32.7 Hz), 128.3 (2C), 128.2, 128.1 (2C), 127.6, 125.1 (broad), 124.0 (q, J_{C-F} = 270.5 Hz), 120.2, 118.6, 117.2 (q, J_{C-F} = 3.9 Hz), 112.6 (q, J_{C-F} = 3.9 Hz), 60.9, 20.0, 13.6. Anal. Calcd for $C_{23}H_{19}ClF_3NO_2$: C, 63.67; H, 4.41; N, 3.23. Found: C, 63.78; H, 4.44; N, 3.05.

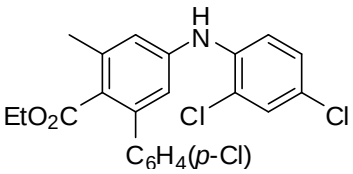


Ethyl-3-methyl-5-(phenylamino)biphenyl-2-carboxylate (2m): White solid (54 mg, 65%), m.p. = 125 ^{o}C; IR (υ_{max}): 3360, 2977, 2931, 2902, 1716, 1581, 1506, 1465, 1299, 1251, 1228, 1112, 1078, 813, 775; ^{1}H NMR: δ 7.40 – 7.26 (m, 7H), 7.16 (d, J = 7.7 Hz, 2H), 7.00 (t, J = 7.7 Hz, 1H), 6.87 (s, 2H), 3.99 (q, J = 7.1 Hz, 2H), 2.38 (s, 3H), 0.89 (t, J = 7.1 Hz, 3H); ^{13}C NMR: δ 169.6, 144.1, 142.5, 141.6, 141.5, 137.9, 129.5 (2C), 128.2 (2C), 128.1 (2C), 127.2, 125.5, 122.4, 119.5 (2C), 117.0, 115.3, 60.7, 20.2, 13.6. Anal. Calcd for $C_{22}H_{21}NO_2$: C, 79.73; H, 6.39; N, 4.23. Found: C, 79.59; H,6.18; N,4.30.

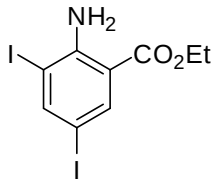


Ethyl-5-(2-bromo-4-methylphenylamino)-4'-chloro-3-methylbiphenyl-2-carboxylate (2n): Yellow viscous liquid (99 mg, 87%); IR (υ_{max}): 3359, 2981, 2821, 1720, 1579, 1509, 1376, 1353, 1085, 1014, 831, 736, 547; ^{1}H NMR: δ 7.39 (d, J = 1.5 Hz, 1H), 7.33 (m, 2H), 7.29 – 7.23 (m, 3H), 7.04 (dd, J = 8.3, 1.5 Hz, 1H), 6.87 (d, J = 2.1 Hz, 1H), 6.79 (d, J = 2.1 Hz, 1H), 4.03 (q, J = 7.2 Hz, 2H), 2.37 (s, 3H), 2.28 (s, 3H), 0.97 (t, J =

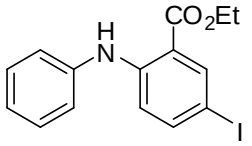
7.2 Hz, 3H); ^{13}C NMR: δ 169.3, 143.9, 141.2, 139.8, 138.1, 137.1, 133.5, 133.4, 133.0, 129.5 (2C), 128.9, 128.3 (2C), 125.7, 119.3, 117.8, 115.6, 114.7, 60.8, 20.4, 20.2, 13.7. HRMS (ESI-FIA-TOF) Calcd. for $C_{23}H_{22}BrClNO_2$ $[M+H]^+$ requires m/z = 458.0522; Found: m/z = 458.0516.



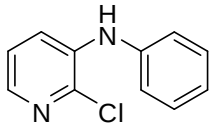
Ethyl-4'-chloro-5-(2,4-dichlorophenylamino)-3-methylbiphenyl-2-carboxylate (2o): Yellow viscous liquid (90 mg, 83%); IR (υ_{max}): 3407, 3357, 3060, 2983, 2933, 1716, 1590, 1523, 1437, 1332, 1269, 1176, 1128, 1043, 867, 773, 738, 694, 647; ^{1}H NMR: δ 7.38 (d, J = 2.4 Hz, 1H), 7.34 (m, 2H), 7.30 – 7.24 (m, 3H), 7.13 (dd, J = 8.6, 2.4 Hz, 1H), 6.92 (d, J = 2.0 Hz, 1H), 6.85 (d, J = 2.0 Hz, 1H), 4.05 (q, J = 7.2 Hz, 2H), 2.39 (s, 3H), 0.99 (t, J = 7.2 Hz, 3H); ^{13}C NMR: δ 169.2, 142.5, 141.2, 139.4, 138.2, 137.8, 133.6, 129.6, 129.5 (2C), 128.4 (2C), 127.7, 126.9, 125.8, 123.4, 119.1, 118.0, 116.9, 60.9, 20.1, 13.7. Anal. Calcd for $C_{22}H_{18}C_{l3}NO_2$: C, 60.78; H, 4.17; N, 3.22. Found: C, 60.62; H,4.18; N,3.30.



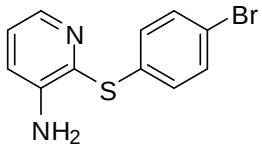
Ethyl-2-amino-3,5-diiodobenzoate (3): Yellow solid (72 mg, 69%), m.p. = 102 ^{o}C; ^{1}H NMR: δ 8.15 (d, J = 2.4 Hz, 1H), 8.02 (d, J = 2.4 Hz, 1H), 6.44 (broad s, 1H), 4.34 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H); ^{13}C NMR: δ 166.2, 150.5, 149.2, 139.9, 112.9, 87.1, 75.7, 61.2, 14.3. Anal. Calcd for $C_9H_9I_2NO_2$: C, 25.92; H, 2.18; N, 3.36. Found: C, 25.95; H, 2.07; N, 3.44.



Ethyl-5-iodo-2-(phenylamino)benzoate (4): Yellow gummy solid (14 mg, 15%); IR (υ_{max}): 3364, 2980, 2930, 1714, 1684, 1519, 1501, 1498, 1465, 1292, 1250, 1228, 1176, 1111, 1075, 1008, 813, 775, 701, 551; ^{1}H NMR: δ 9.48 (s, 1H), 8.23 (d, J = 3.5 Hz, 1H), 7.51 (dd, J = 8.8, 3.5 Hz, 1H), 7.35 (t, J = 7.6 Hz, 2H), 7.21 (d, J = 7.6 Hz, 2H), 7.12 (t, J = 7.6 Hz, 1H), 7.00 (d, J = 8.8 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H); ^{13}C NMR: δ 167.3, 147.6, 142.2, 140.1, 139.8, 129.5 (2C), 124.2, 122.9 (2C), 116.2, 114.2, 76.9, 61.0, 14.3. Anal. Calcd for $C_{15}H_{14}INO_2$: C, 49.07; H, 3.84; N, 3.81. Found: C, 49.05; H, 3.67; N, 3.76.

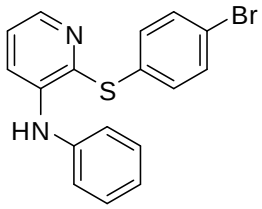


2-Chloro-*N*-phenylpyridin-3-amine (7)[7]**.** White solid (84 mg, 82%): mp = 71-75 ^{o}C; ^{1}H NMR: δ 7.87 (dd, J = 4.4, 1.6 Hz, 1H), 7.49 (dd, J = 8.0, 1.6 Hz, 1H), 7.36 (t, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.14 – 7.06 (m, 2H), 6.14 (br s, 1H); ^{13}C NMR: δ 140.0, 139.1, 138.5, 137.7, 129.7 (2C), 123.9, 123.1, 121.2, 121.1 (2C).

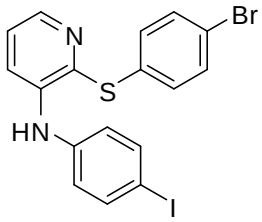


2-(4-Bromophenylthio)pyridin-3-amine (8): Brownish white solid - crude; ^{1}H NMR: δ 8.02 (dd, J = 4.4, 1.6 Hz, 1H), 7.38 (d, J = 8.3 Hz, 2H), 7.16 (d, J = 8.3 Hz, 2H), 7.14 –

7.06 (m, 2H), 4.11 (broad s, 1H); ^{13}C NMR: δ 144.1, 140.4, 138.3, 133.2, 132.2 (2C), 131.0 (2C), 124.5, 122.3, 120.7.



2-(4-Bromophenylthio)-*N*-phenylpyridin-3-amine (9): Yellowish white solid (59 mg, 67%), m.p. = 77-80 ^{o}C; IR (υ_{max}): 3359, 3248, 3060, 1567, 1493, 1313, 1070, 1006, 809, 734; ^{1}H NMR: δ 8.07 (dd, J = 4.5, 1.4 Hz, 1H), 7.49 (dd, J = 8.2, 1.4 Hz, 1H), 7.42 (m, 2H), 7.32 (m, 2H), 7.24 (m, 2H), 7.13 – 7.03 (m, 4H), 6.35 (s, 1H); ^{13}C NMR: δ 142.2, 141.3, 141.2, 140.6, 132.3 (2C), 132.1 (2C), 129.6 (2C), 123.6, 123.4, 121.8, 121.4, 120.6 (2C). Anal. Calcd for $C_{17}H_{13}BrN_2S$: C, 57.15; H, 3.67; N, 7.84. Found: C, 57.38; H, 3.71; N, 7.96.

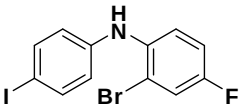


2-(4-Bromophenylthio)-*N*-(4-iodophenyl)pyridin-3-amine (10): Yellow gummy solid (67 mg, 56%); IR (υ_{max}): 3359, 3248, 3060, 1567, 1493, 1313, 1070, 1006, 809, 734; ^{1}H NMR: δ 8.07 (dd, J = 4.6, 1.5 Hz, 1H), 7.59 (d, J = 8.7, 2H), 7.42 (m, 2H), 7.49 (dd, J = 8.2, 1.5 Hz, 1H), 7.43 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 8.5 Hz, 2H), 7.12 (dd, J = 8.2, 4.6 Hz, 1H), 6.82 (d, J = 8.7, 2H), 6.26 (broad s, 1H); ^{13}C NMR: δ 143.3, 141.7, 140.6, 140.1, 138.5 (2C), 132.7 (2C), 132.4 (2C), 131.5, 123.5, 122.9, 121.9, 121.8 (2C), 85.6.

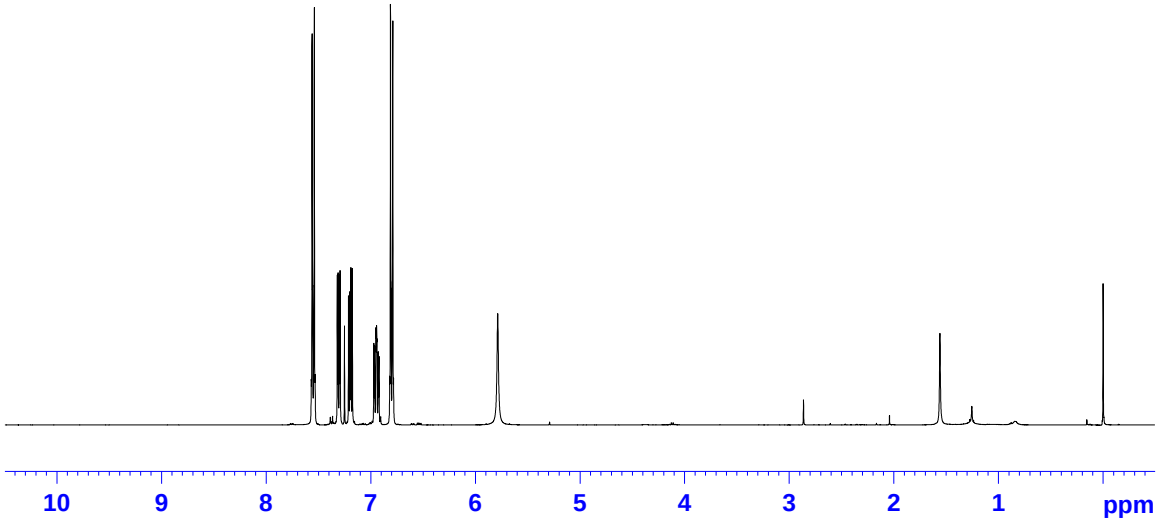
Anal. Calcd for $C_{17}H_{12}BrIN_2S$: C, 42.26; H, 2.50; N, 5.80. Found: C,42.22; H,2.44; N, 5.68.

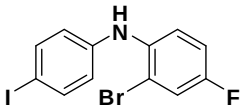
References:

1. B.-D. Chong, Y.-I. Ji, S.-S. Oh, J.-D. Yang, W. Baik and S. Koo, *J. Org. Chem.*, 1997, **62**, 9323.
2. M. Uyanik, M. Akakura and K. Ishihara, *J. Am. Chem. Soc.*, 2009 , **131**, 251.
3. D. B. Ramachary, K. Ramakumar and V. V. Narayana, *J. Org. Chem.*, 2007, **72**, 1458.
4. N. Barbero, M. Carril, R. SanMartin and E. Dominguez, *Tetrahedron*, 2008 , **64**, 7283.
5. L.-C. Campeau, P. Thansandote and K. Fagnou, *Org. Lett.*, 2005, **7**, 1857.
6. M. E. Buden, V. A. Vaillard, E. M. Sandra and R. A. Rossi, *J. Org. Chem.*, 2009, **74**, 4490.
7. J. T. Kuethe, A. Wong and I. W. Davies, *J. Org. Chem.*, 2004**, 69**, 7752.

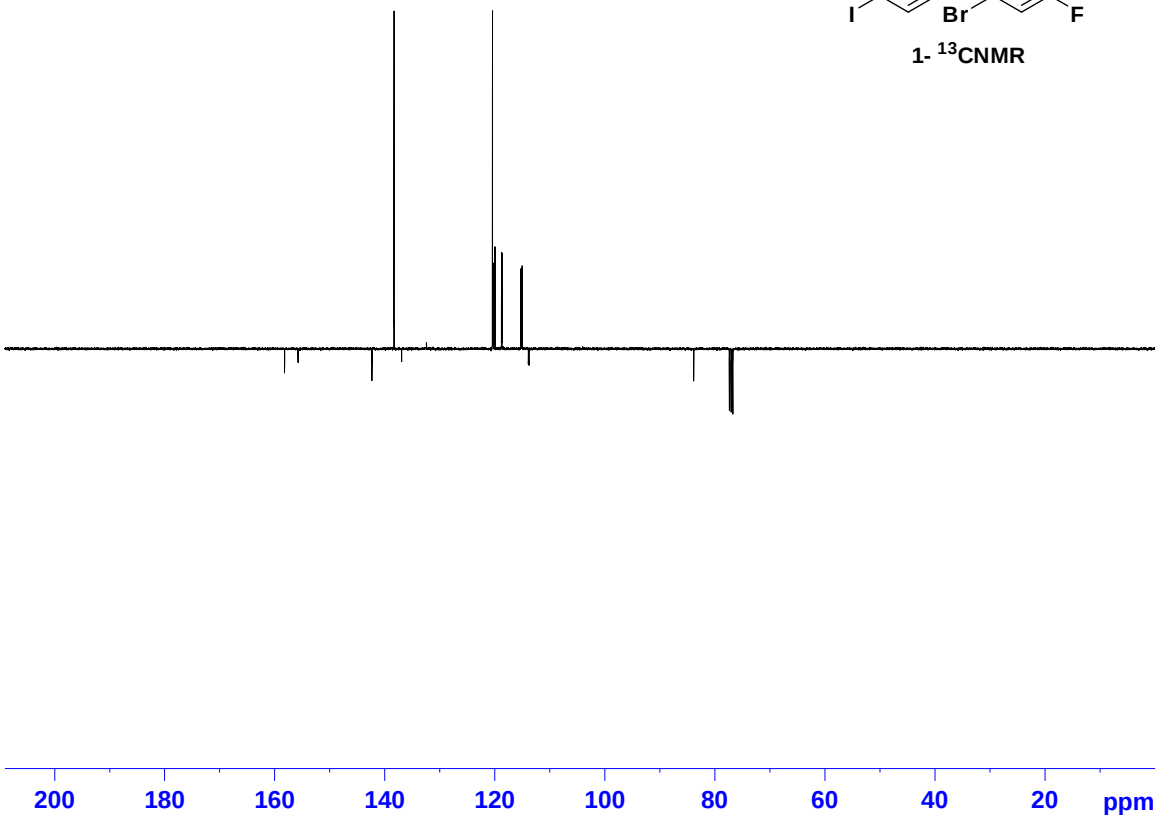


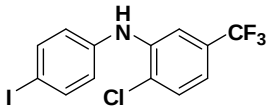
1- ^{1}HNMR



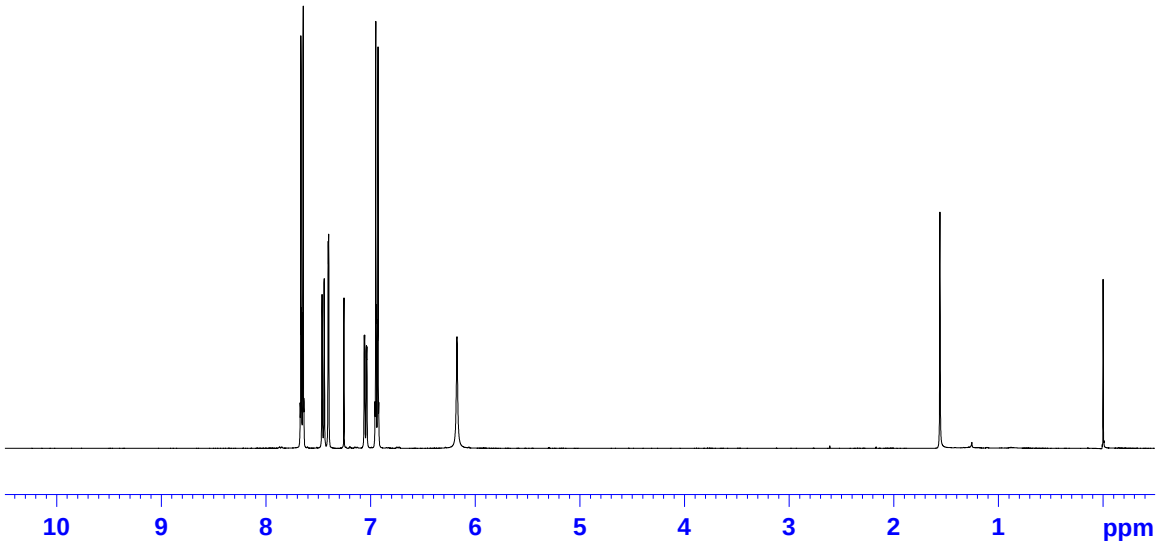


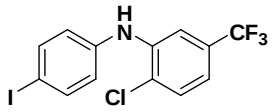
1- ^{13}CNMR



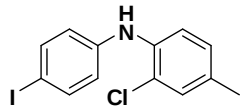


1a- ^{1}HNMR

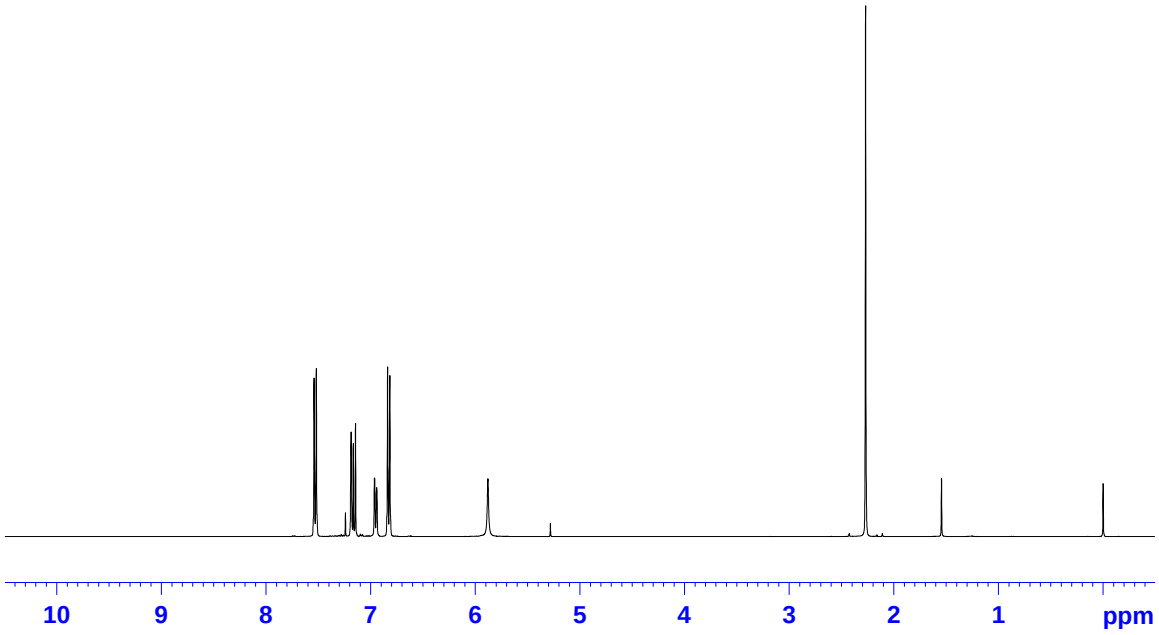


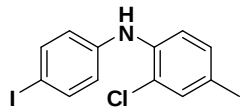


1a- ^{13}CNMR

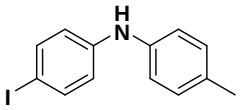


1b- ^{1}HNMR

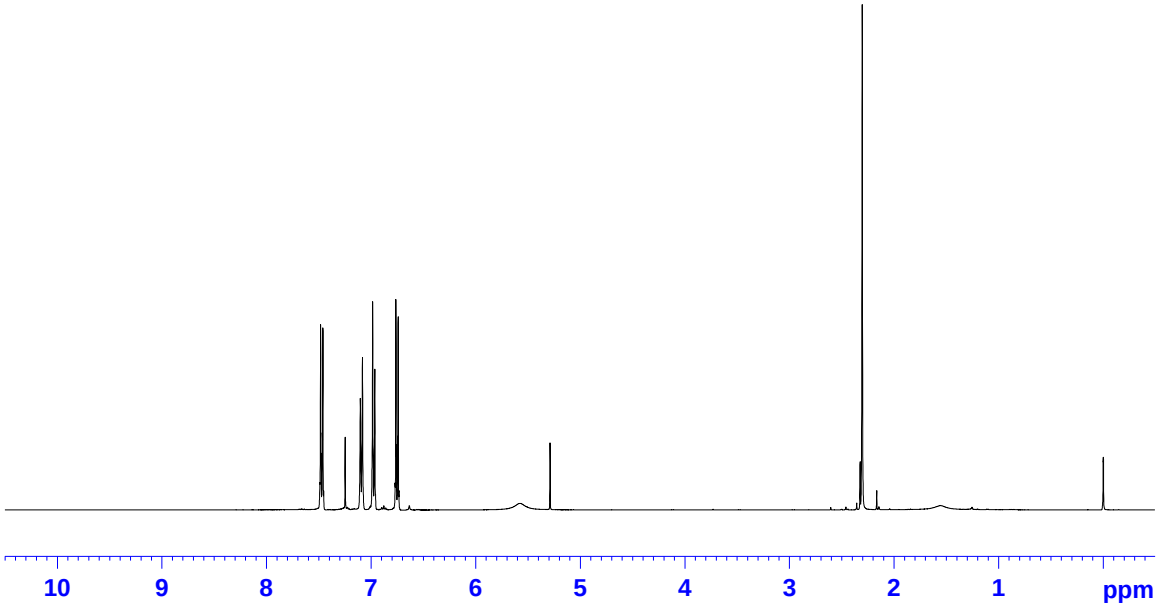


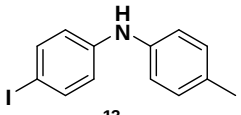


1b- ^{13}CNMR

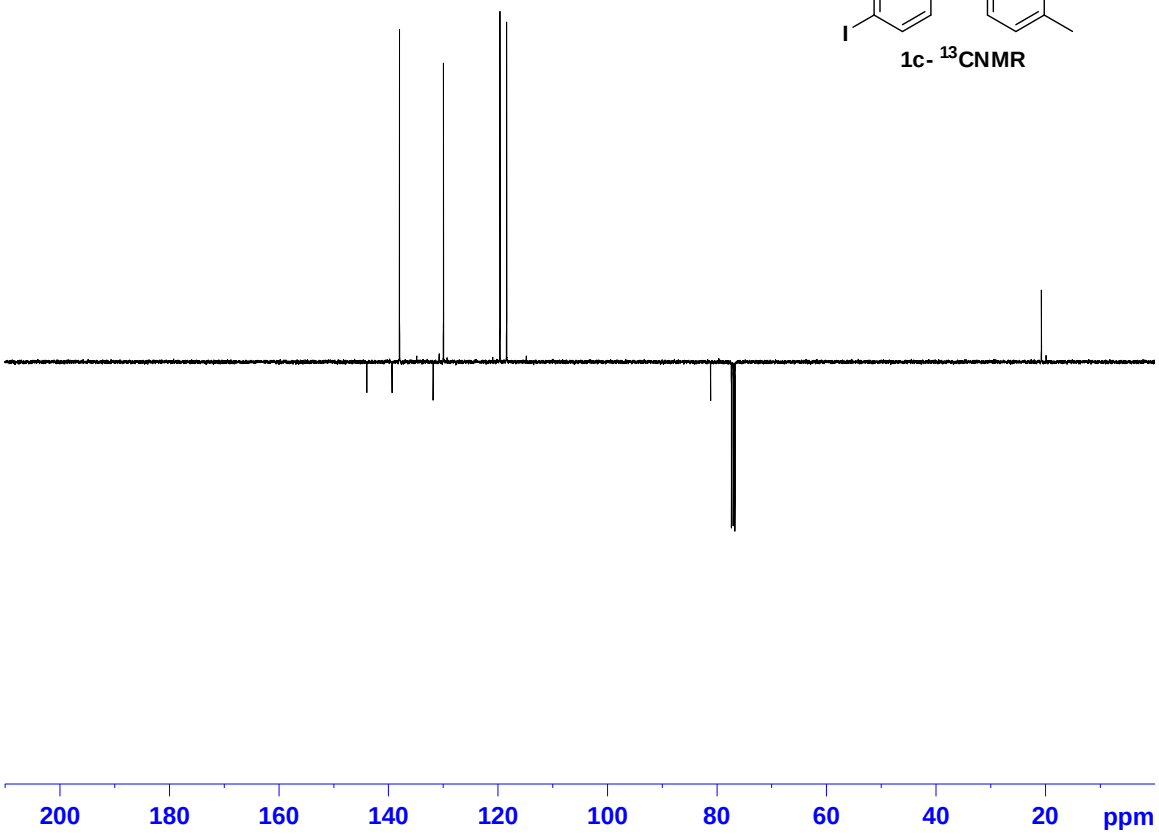


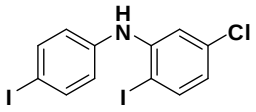
1c- ^{1}HNMR



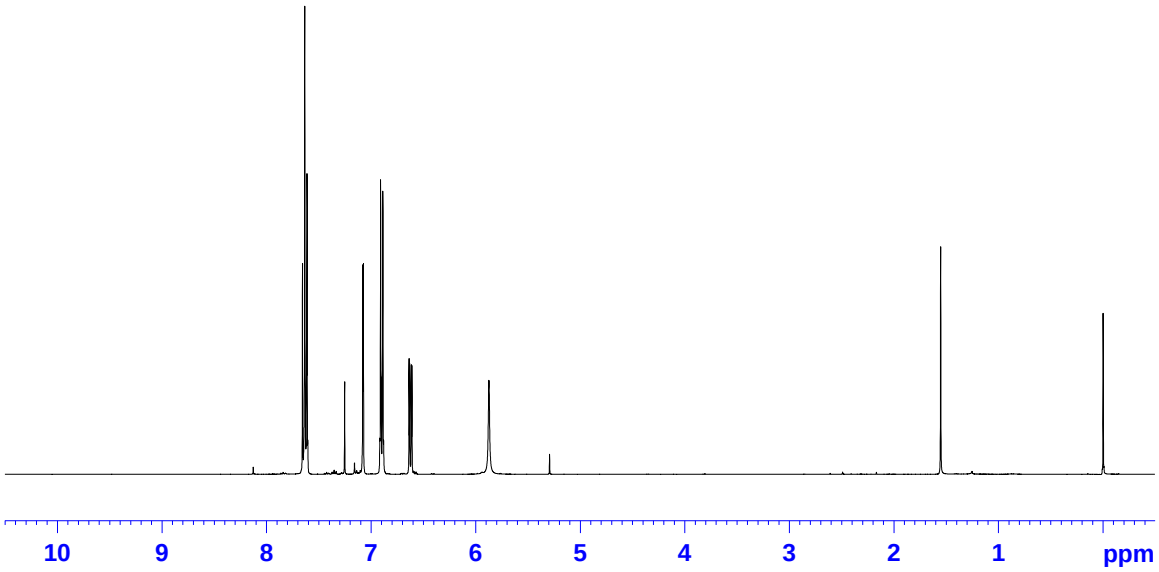


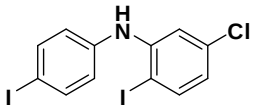
1c- ^{13}CNMR



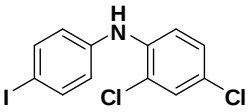


1d- ^{1}HNMR

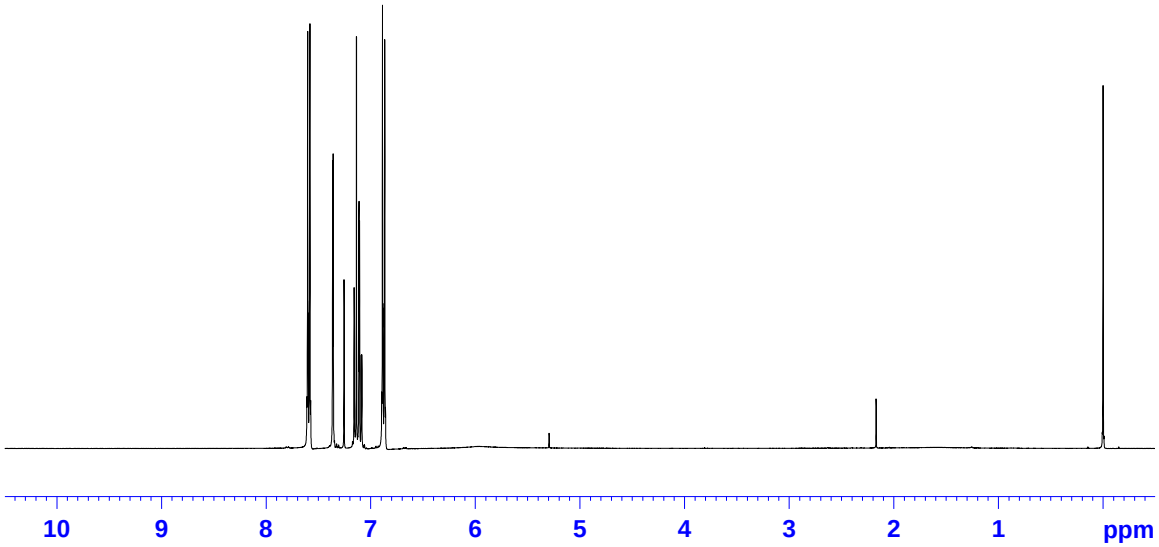


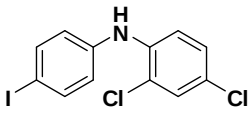


1d- ^{13}CNMR

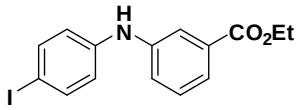


1e- ^{1}HNMR

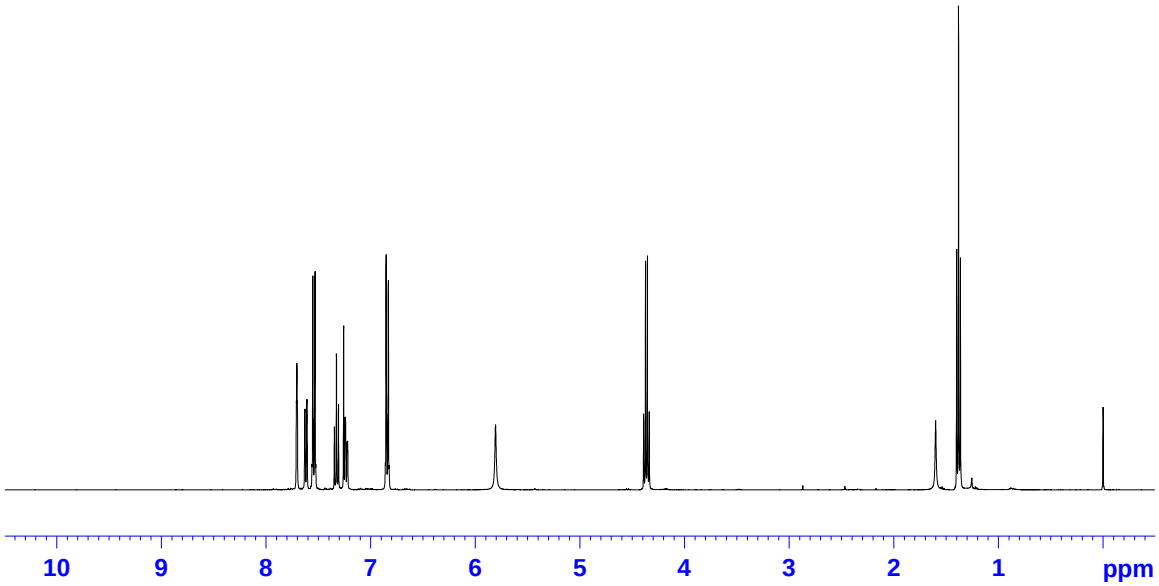


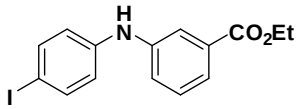


1e- ^{13}CNMR

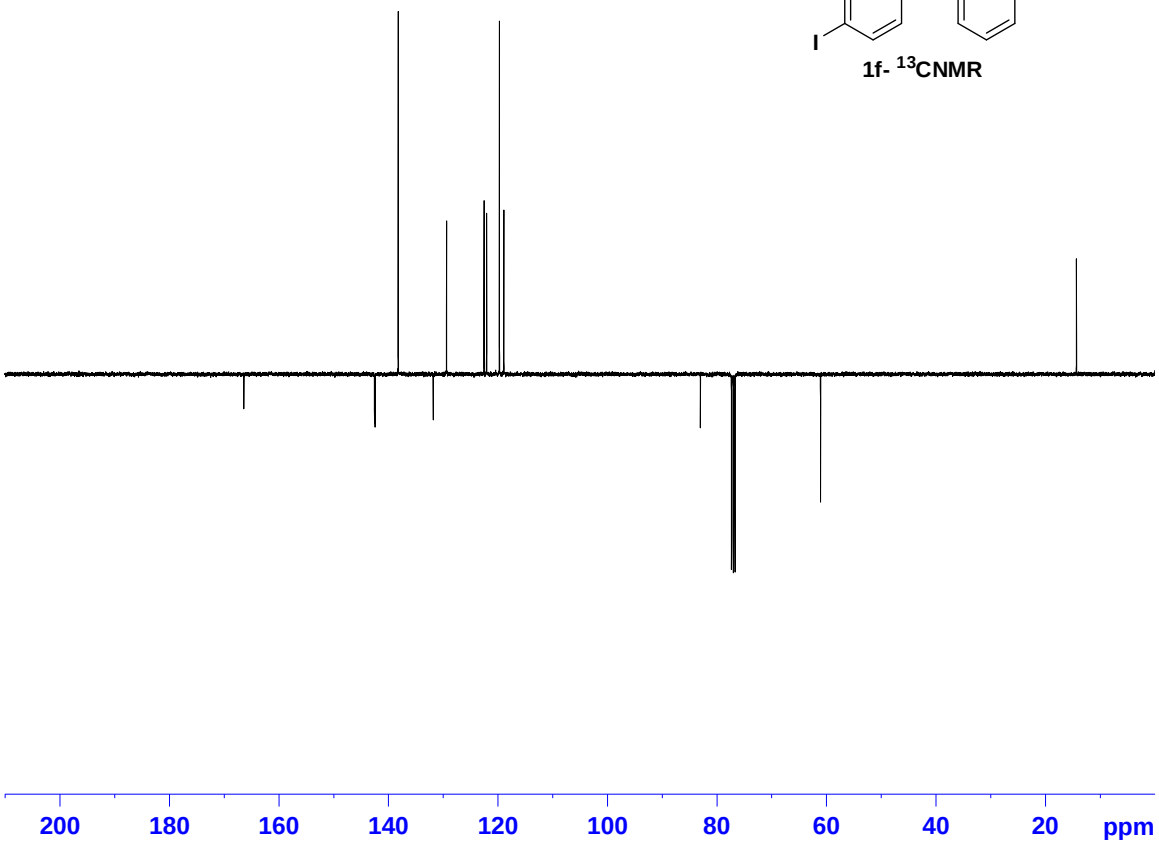


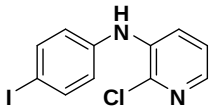
1f- ^{1}HNMR



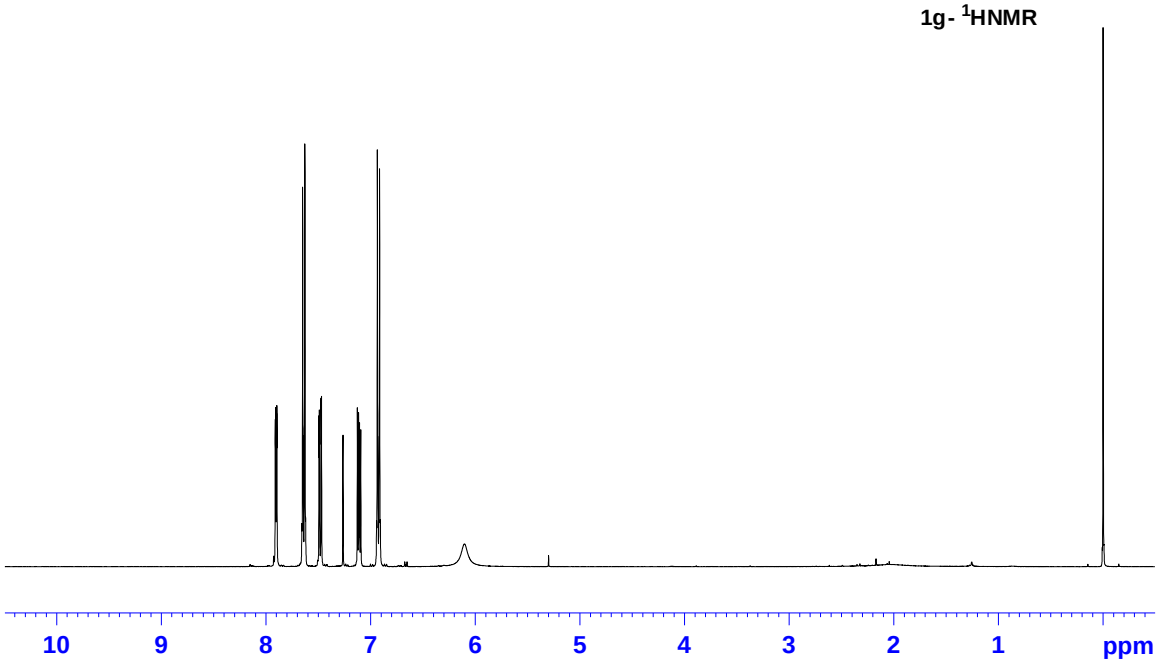


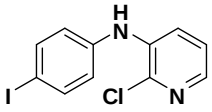
1f- ^{13}CNMR



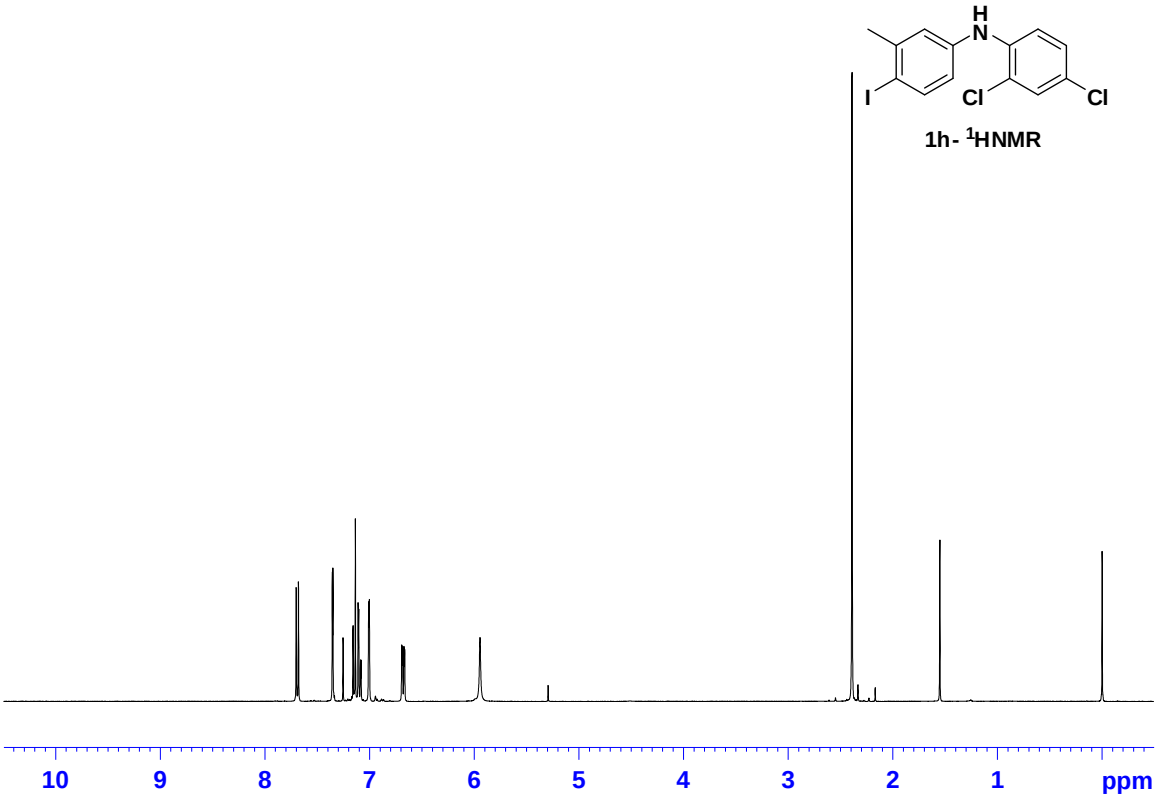


1g- ^{1}HNMR

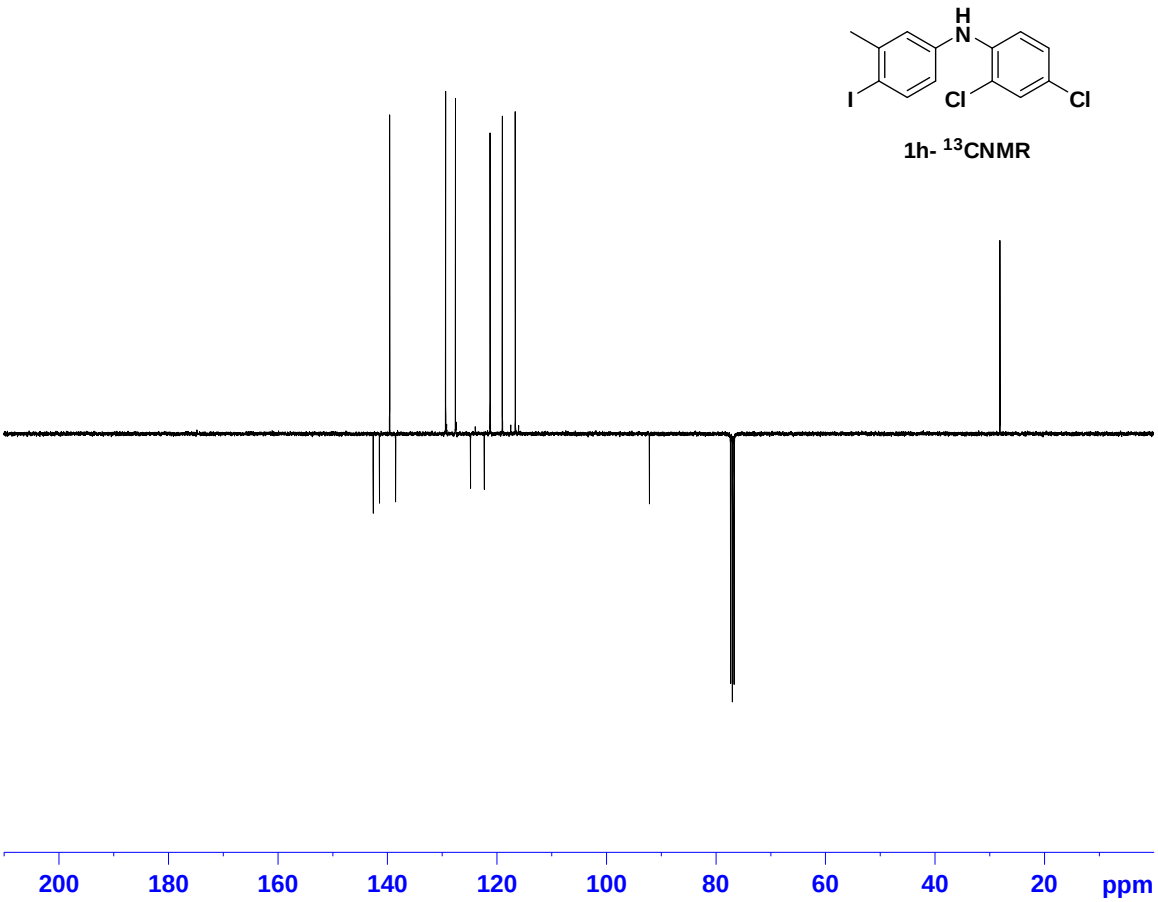




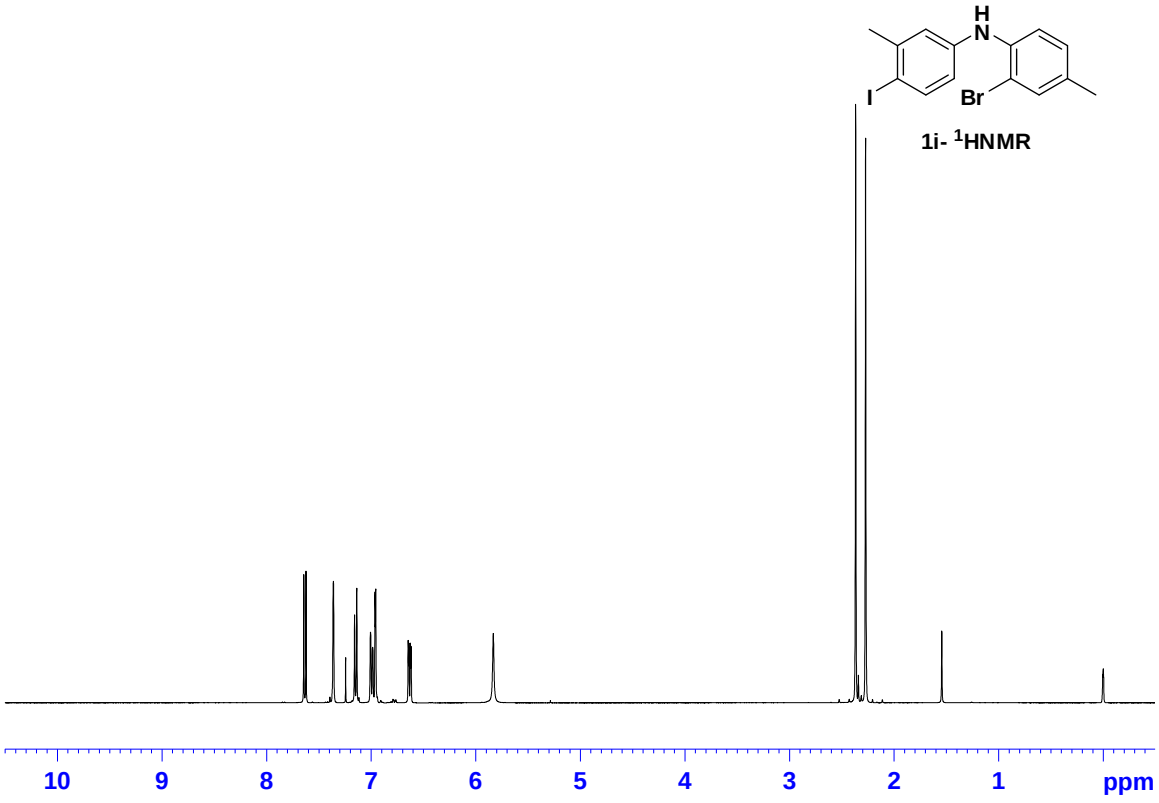
1g- ^{13}CNMR

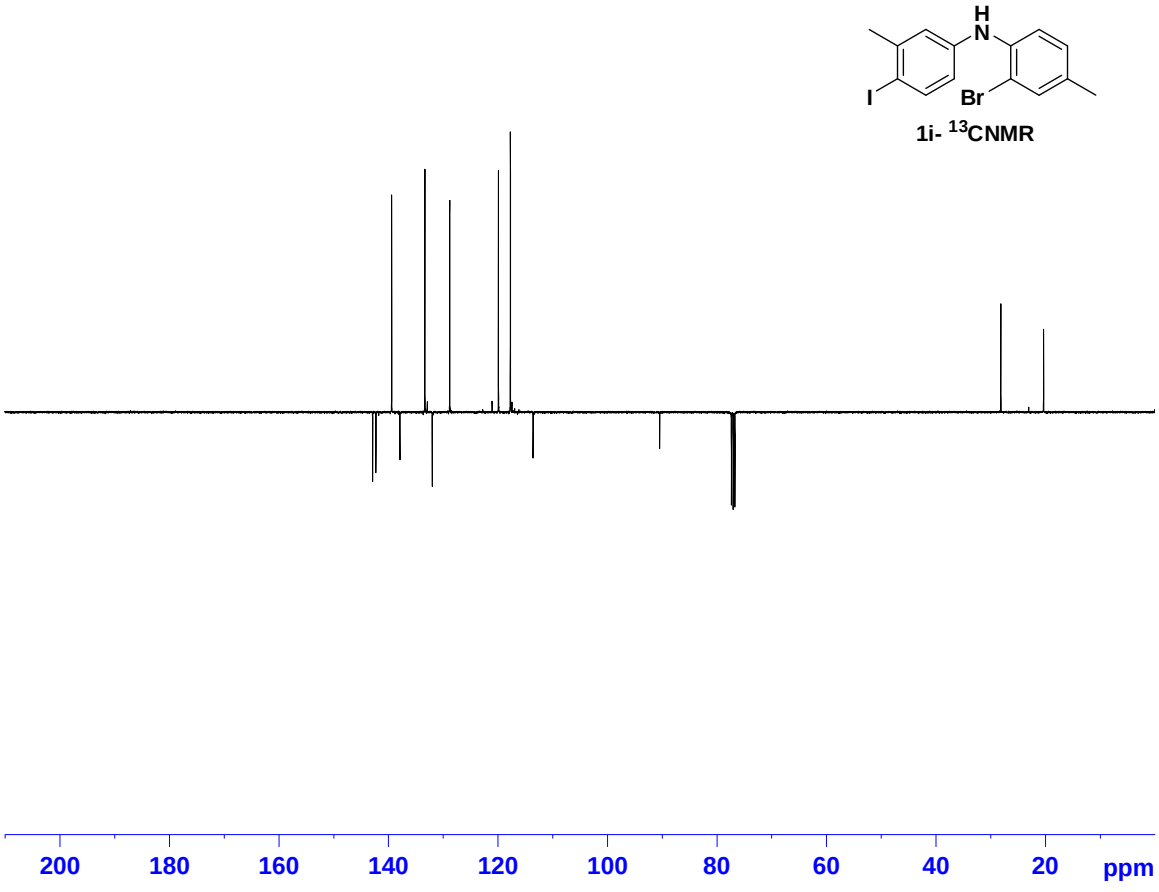


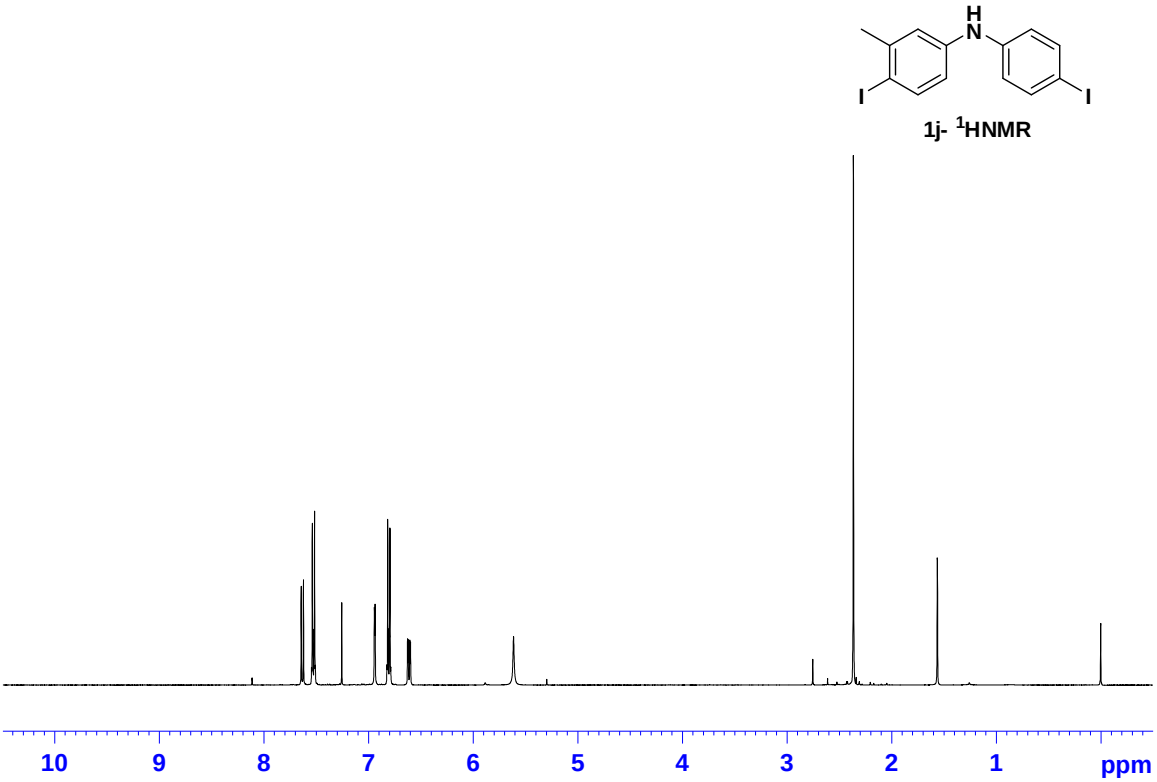
1h- ^{1}HNMR



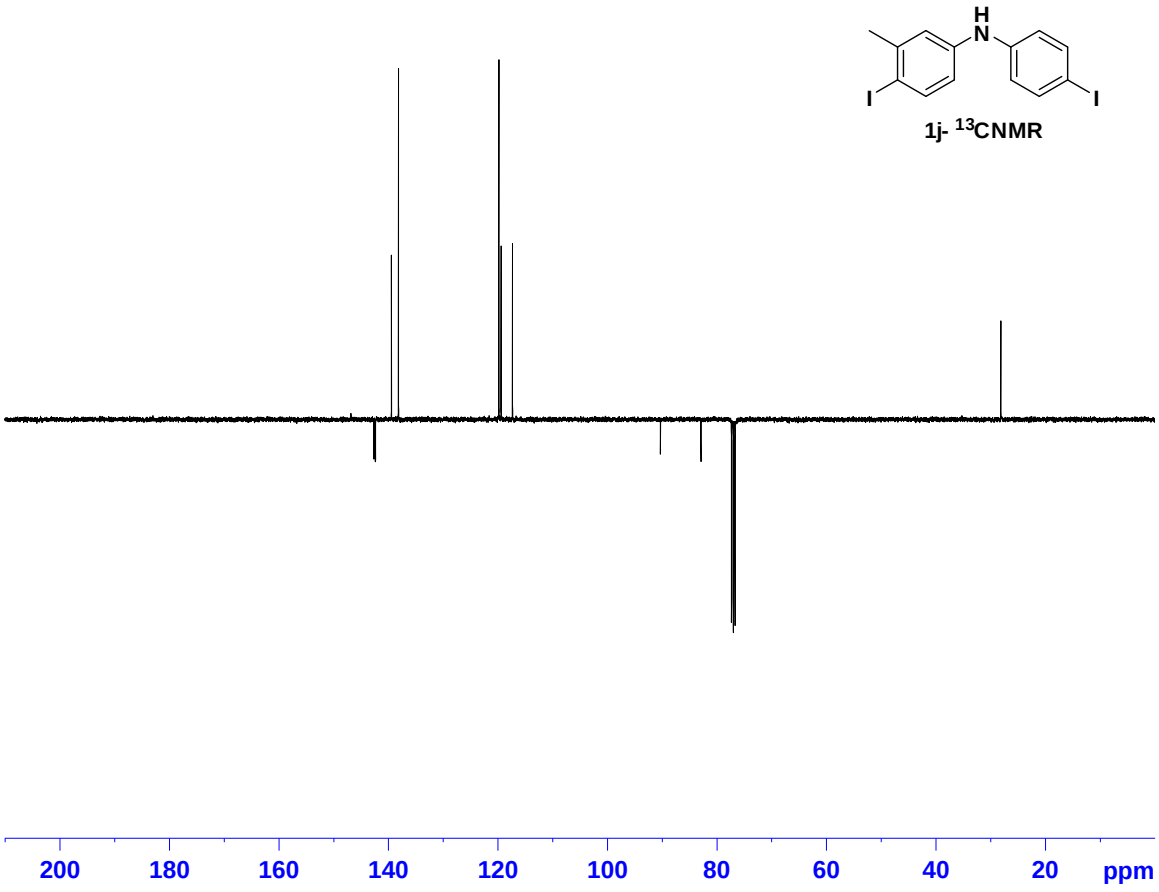
1h- ^{13}CNMR



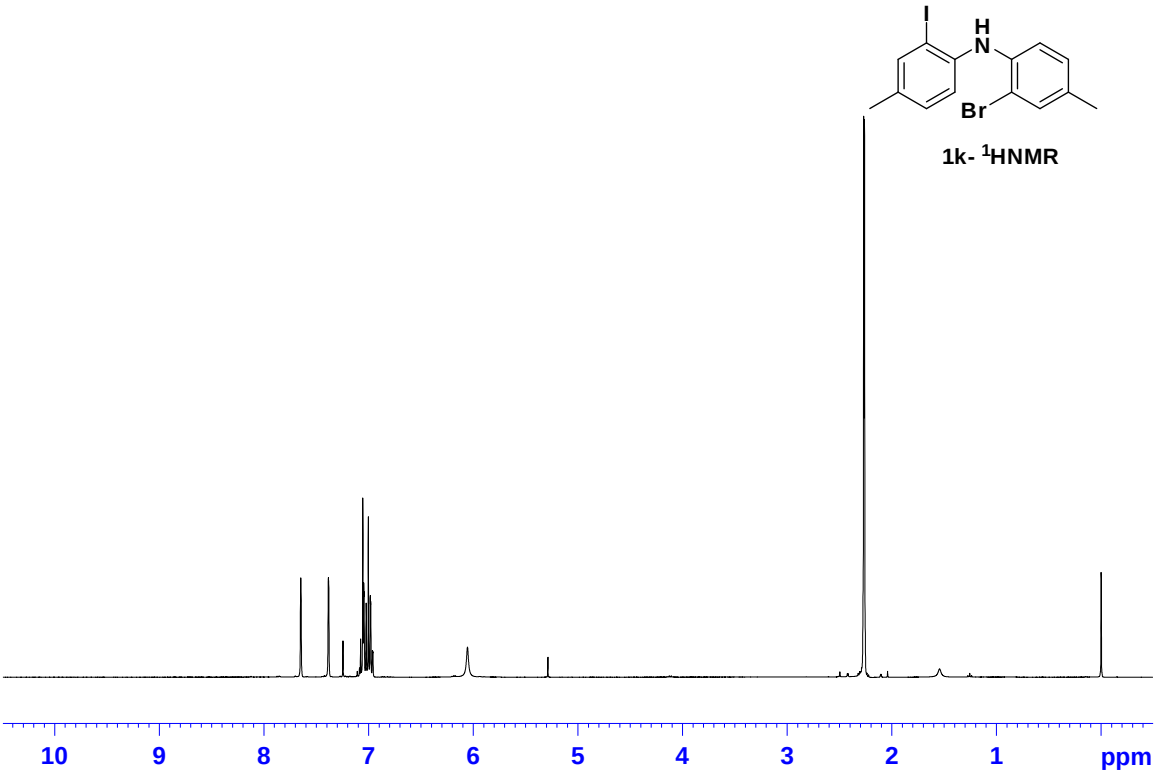




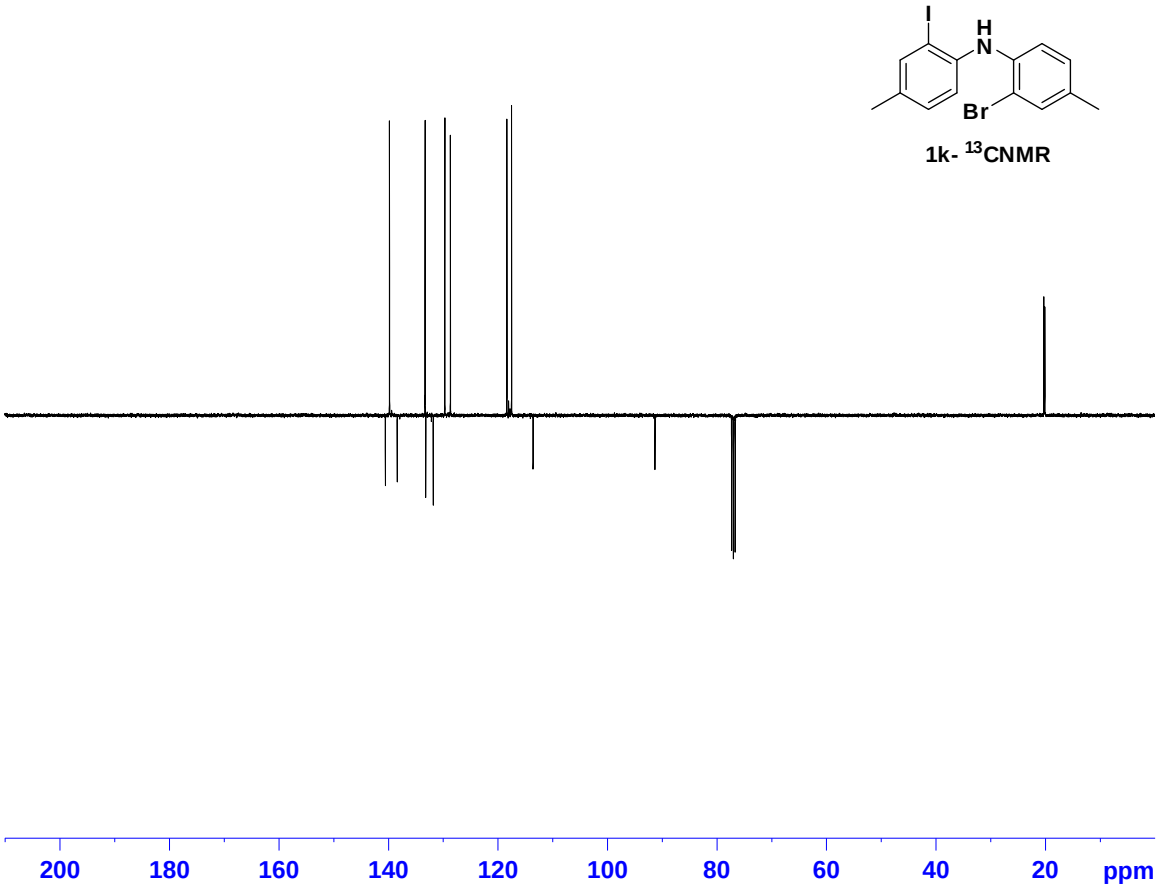
1j- ^{1}HNMR



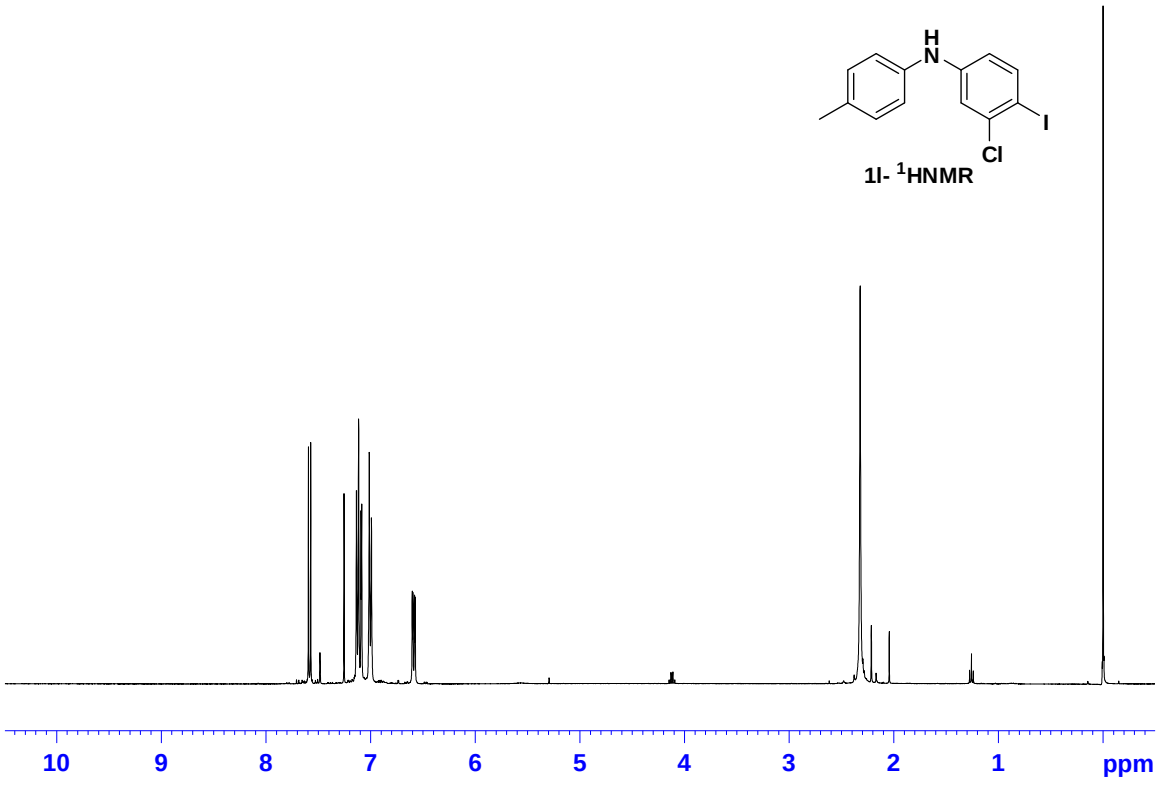
1j- ^{13}CNMR

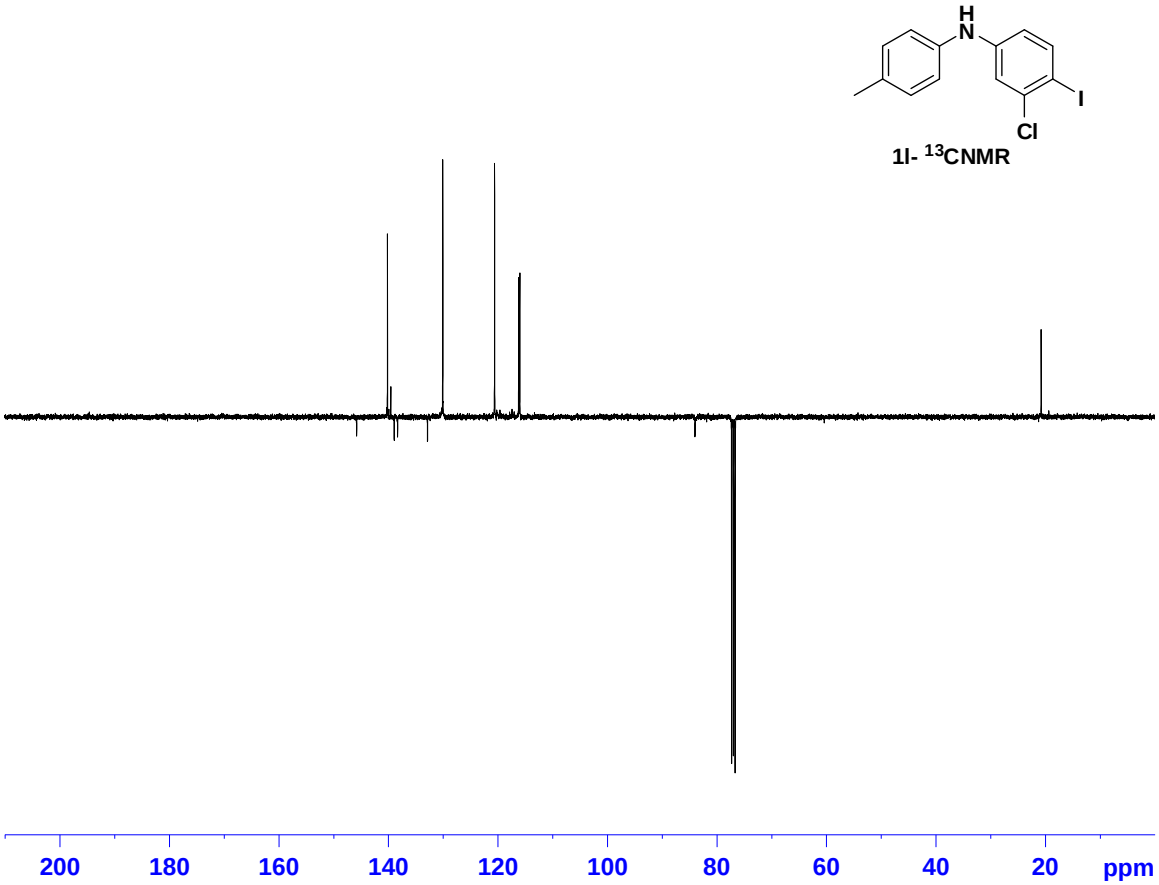


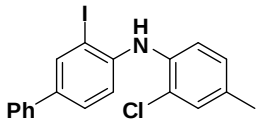
1k- ^{1}HNMR



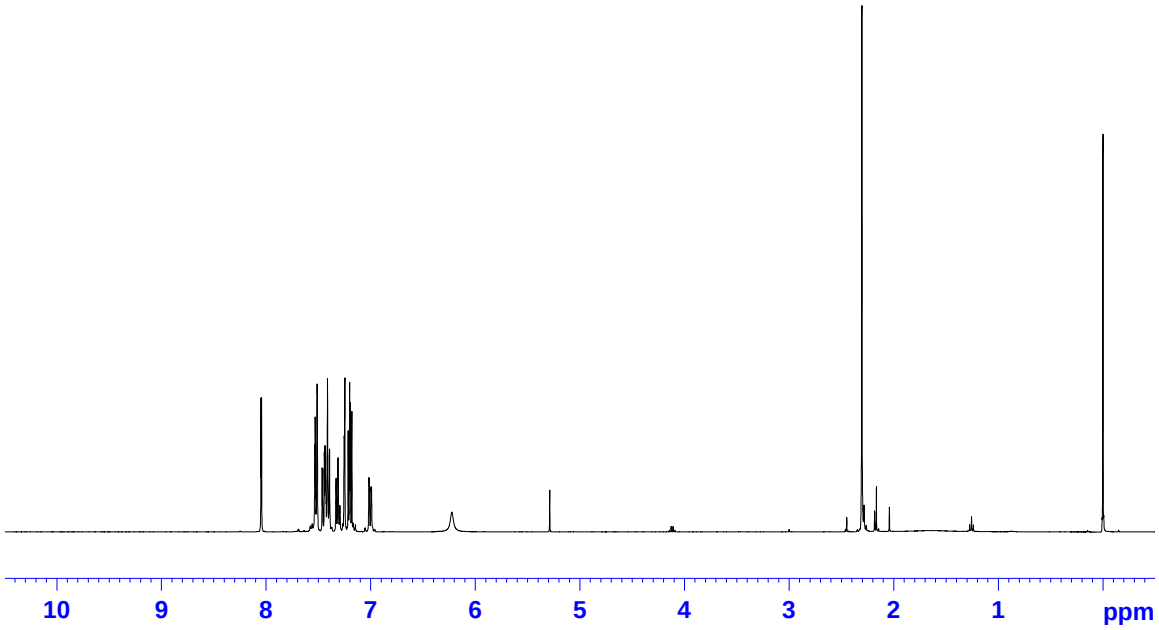
1k- ^{13}CNMR

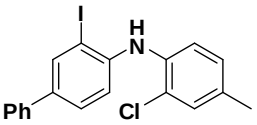

H
N
I
Cl
1l- 1HNMR
10
9
8
7
6
5
4
3
2
1
ppm


H
N
I
Cl
1l- 13CNMR
200
180
160
140
120
100
80
60
40
20
ppm

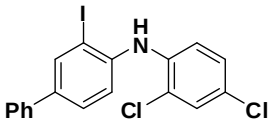


1m- ^{1}HNMR

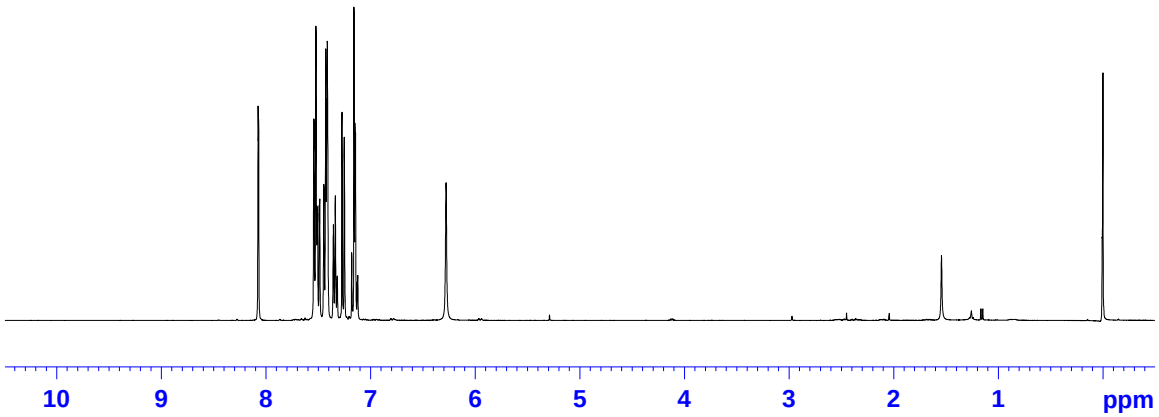


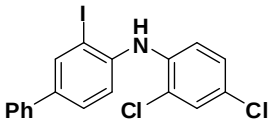


1m- ^{13}CNMR

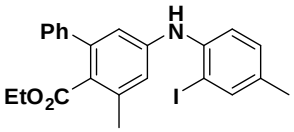


1n- ^{1}HNMR

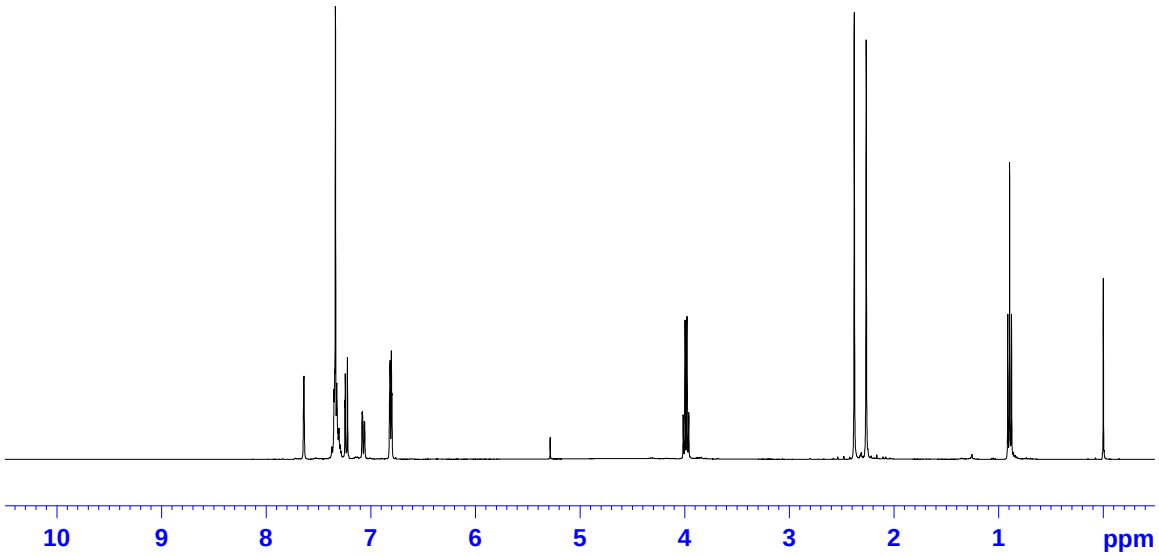


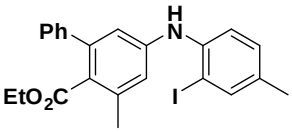


1n- ^{13}CNMR

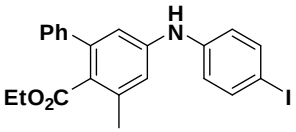


1o- ^{1}HNMR

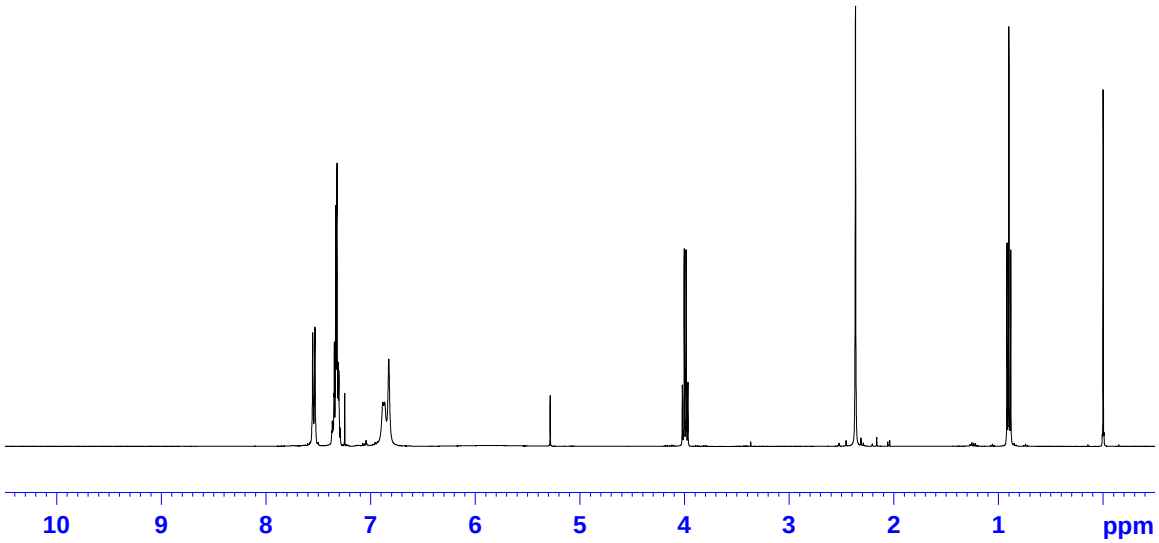


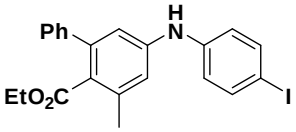


1o- ^{13}CNMR

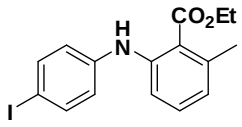


1p- ^{1}HNMR

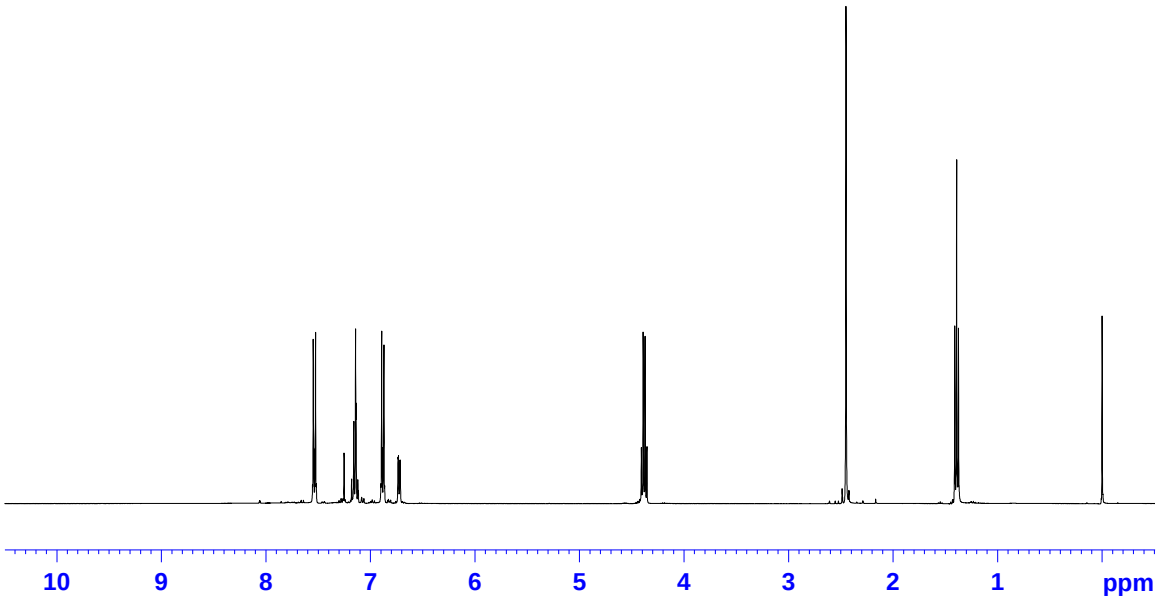


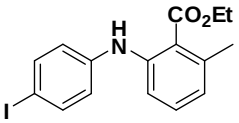


1p- ^{13}CNMR

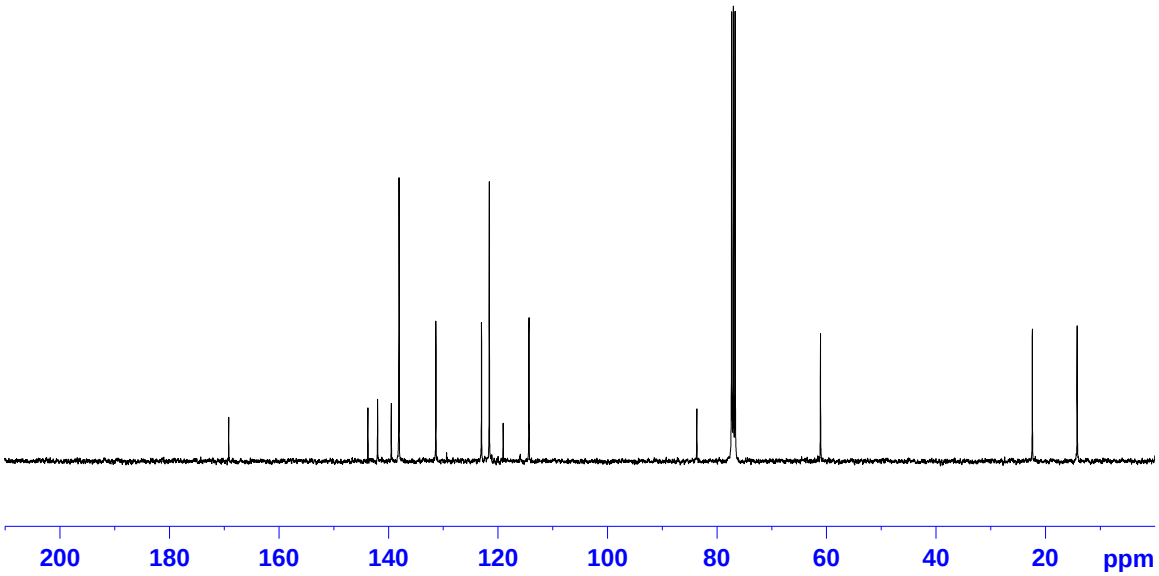


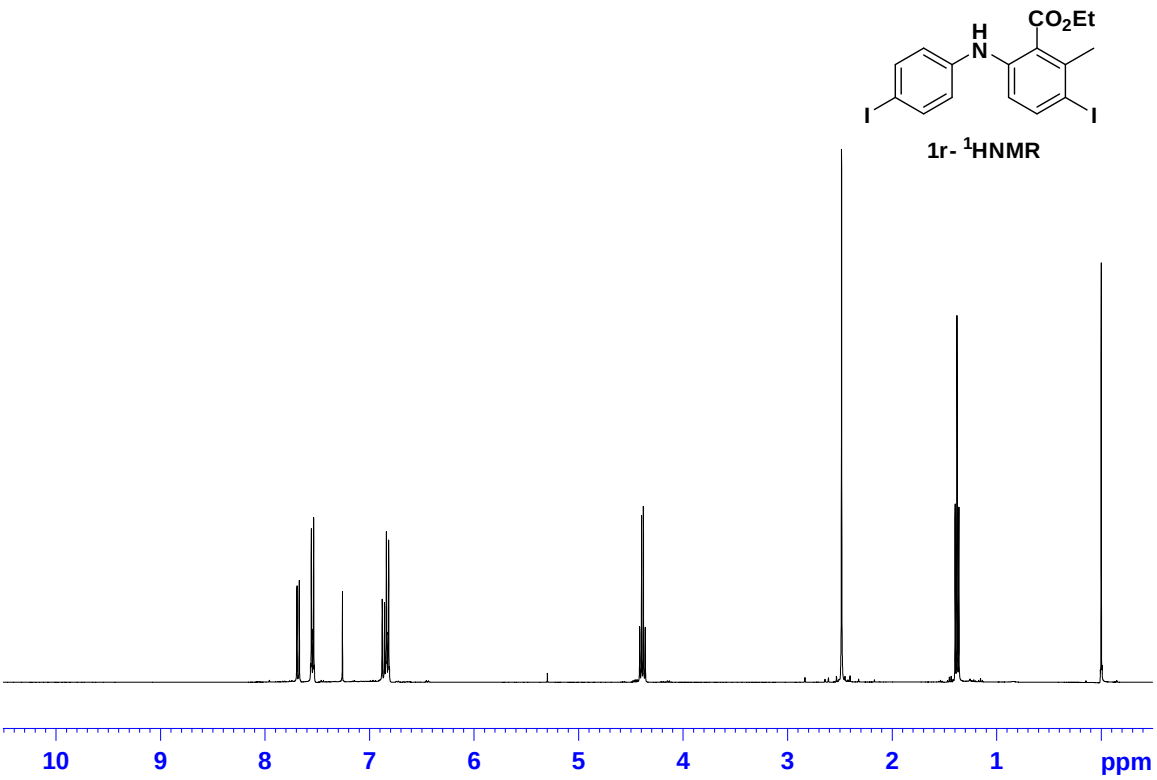
1q- ^{1}HNMR

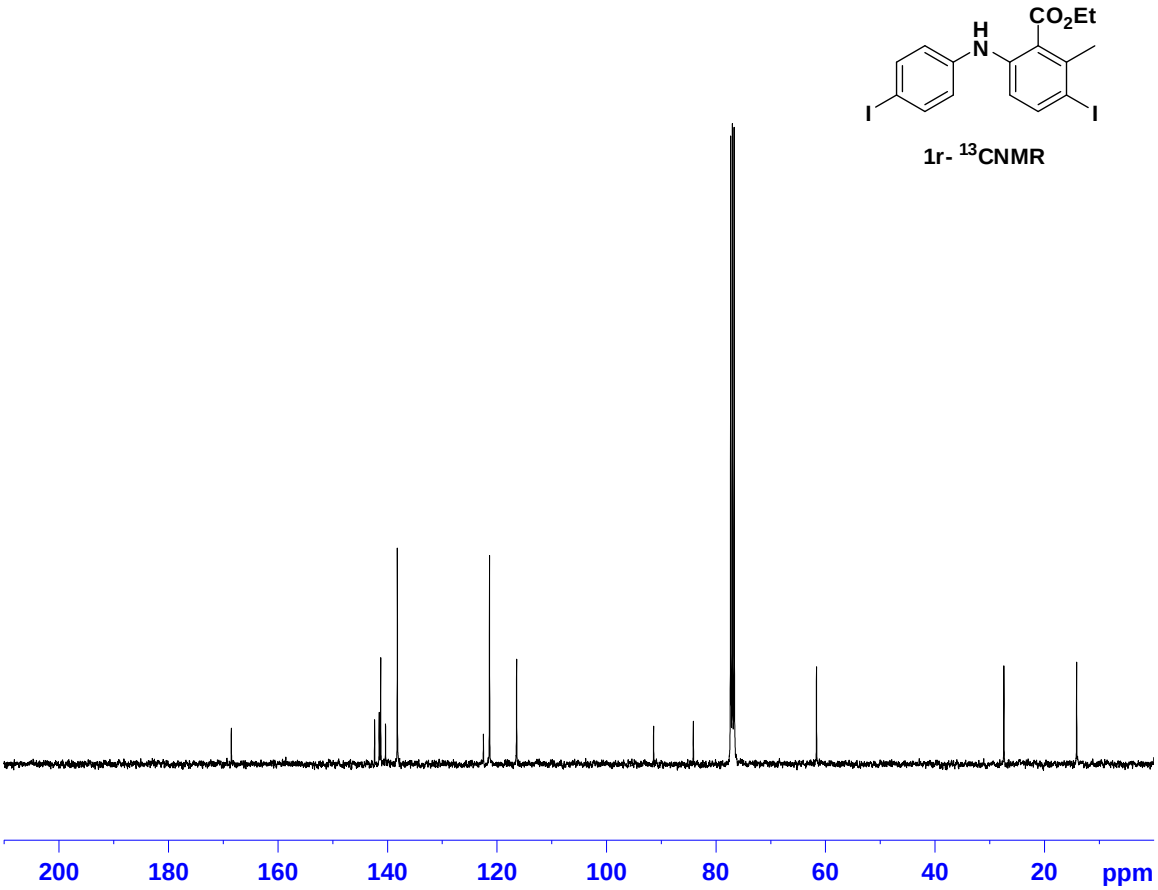


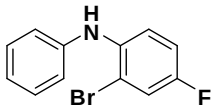


1q- ^{13}CNMR

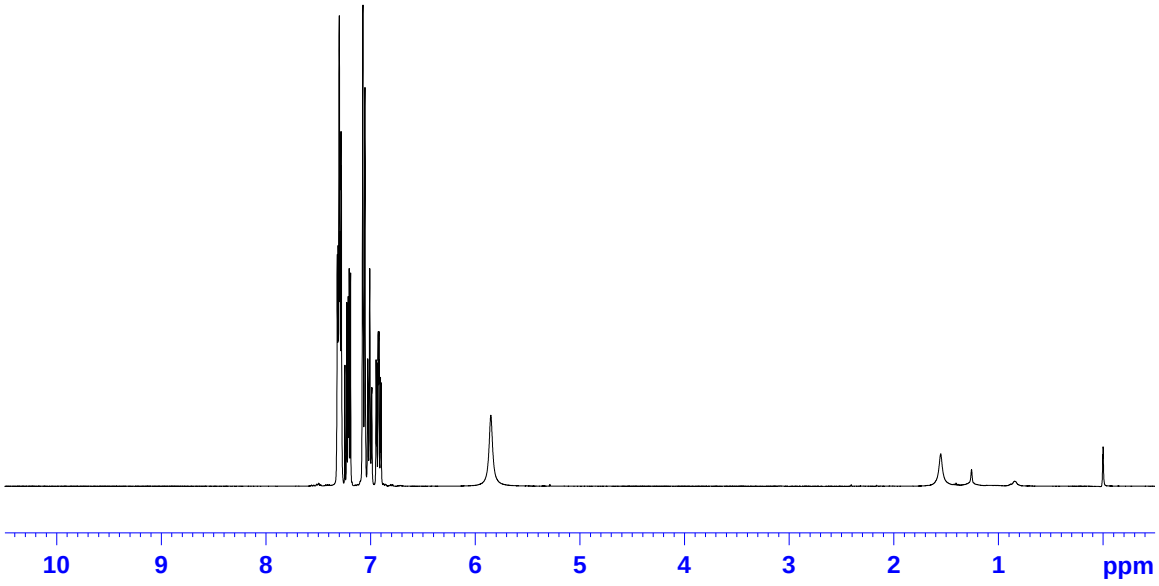


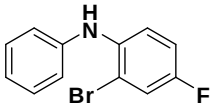

CO2Et
H
N
I
I
1r- 1HNMR
10
9
8
7
6
5
4
3
2
1
ppm


CO2Et
H
N
I
I
1r- 13CNMR
200
180
160
140
120
100
80
60
40
20
ppm

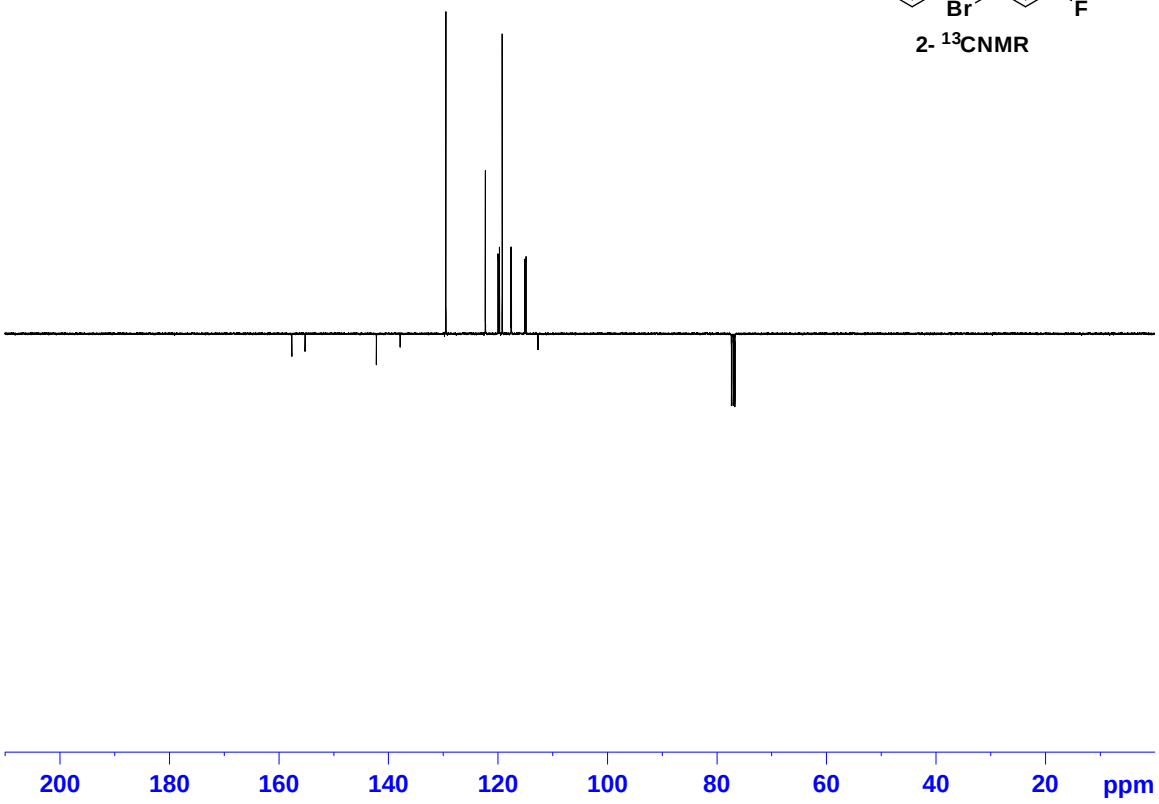


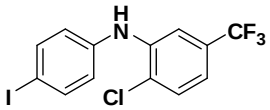
2- ^{1}HNMR



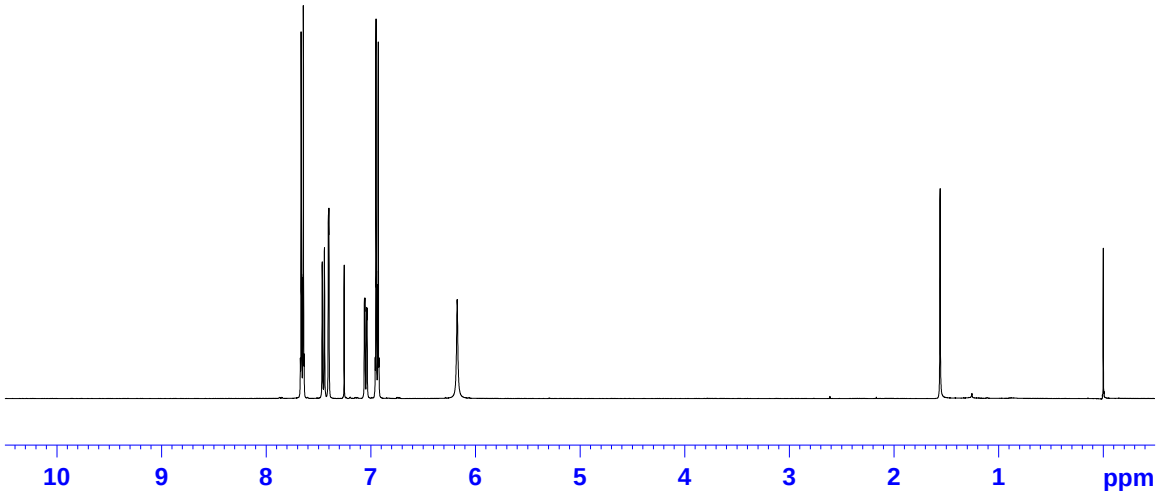


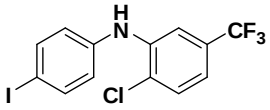
2- ^{13}CNMR



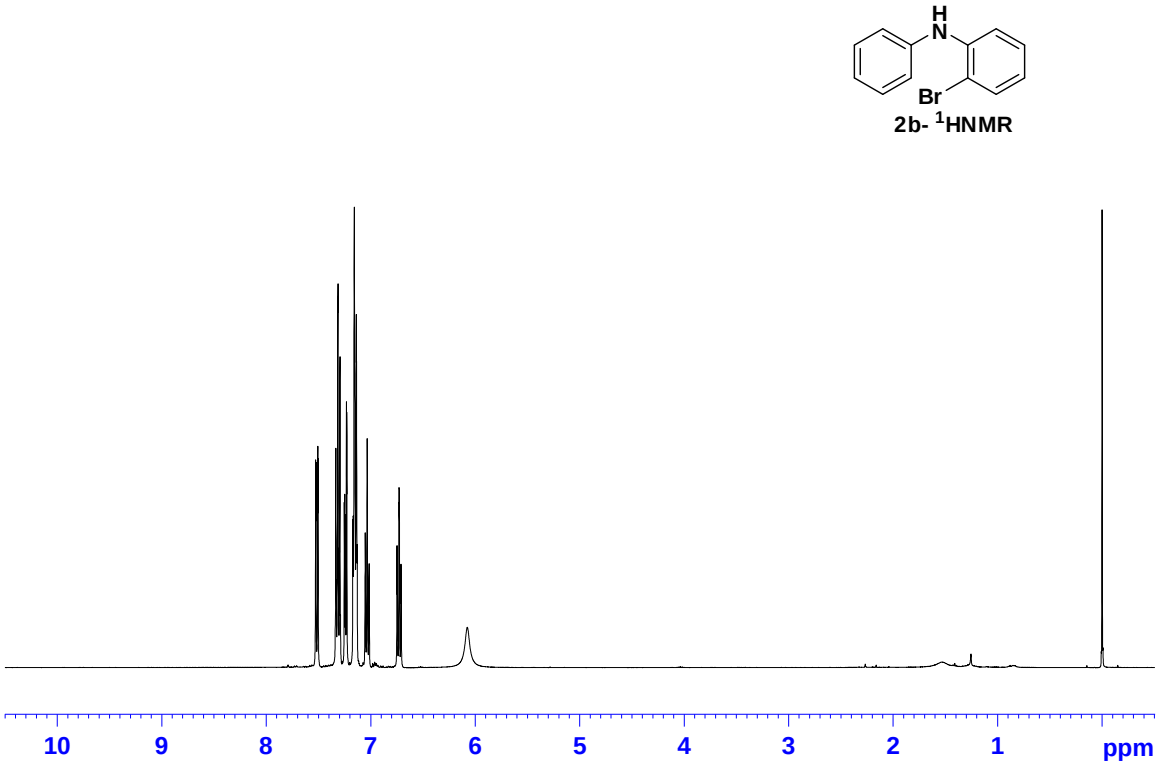


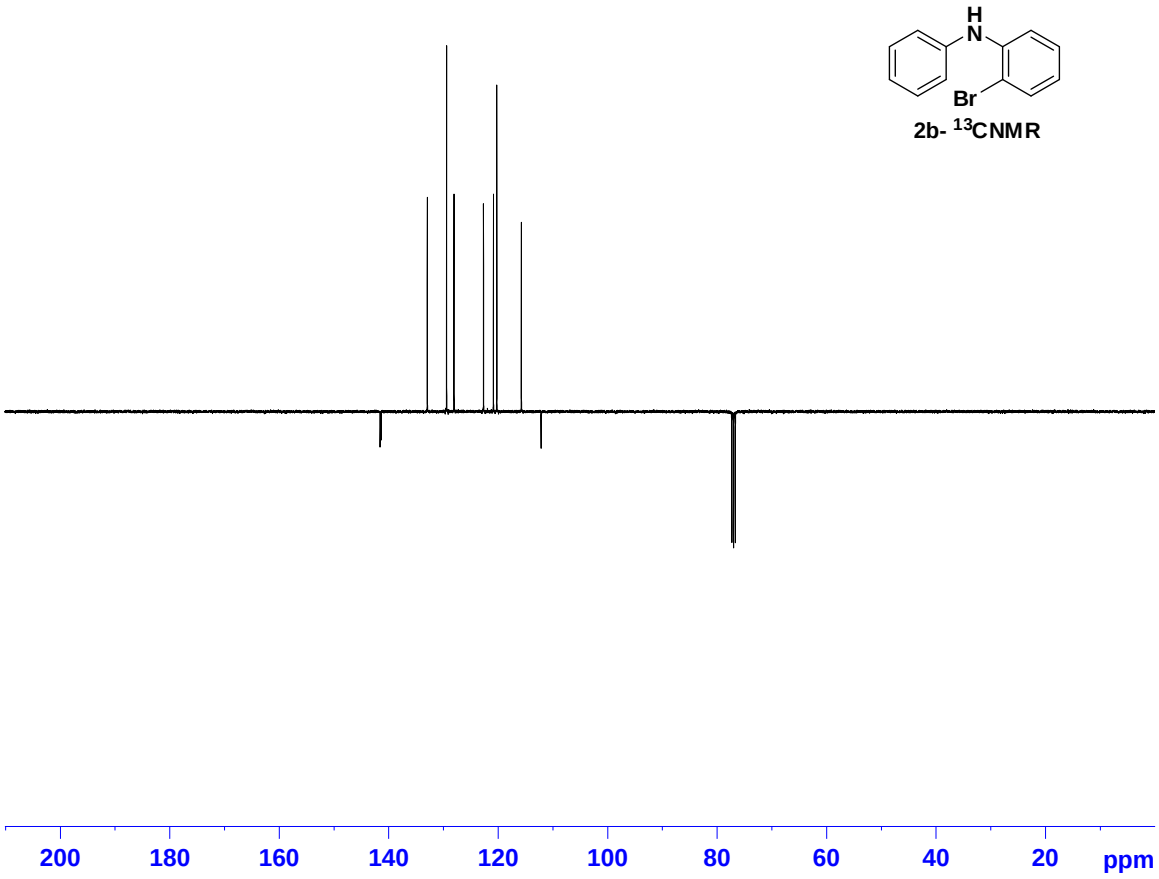
2a- ^{1}HNMR

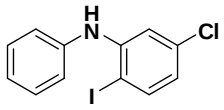




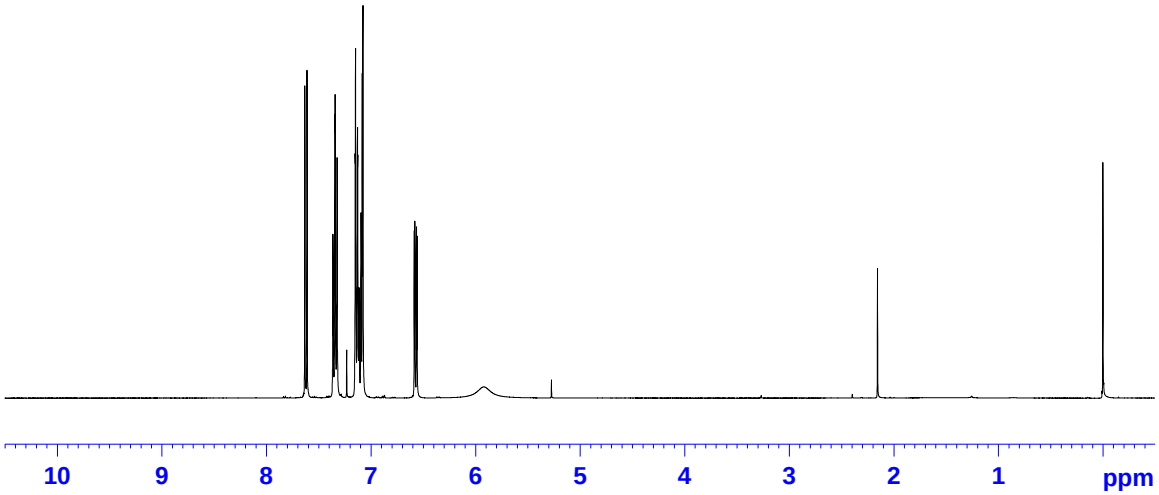
2a- ^{13}CNMR

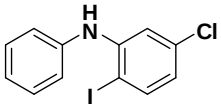

H
N
Br
2b- 1HNMR
10
9
8
7
6
5
4
3
2
1
ppm


H
N
Br
2b- 13CNMR
200
180
160
140
120
100
80
60
40
20
ppm

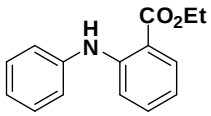


2c- ^{1}HNMR

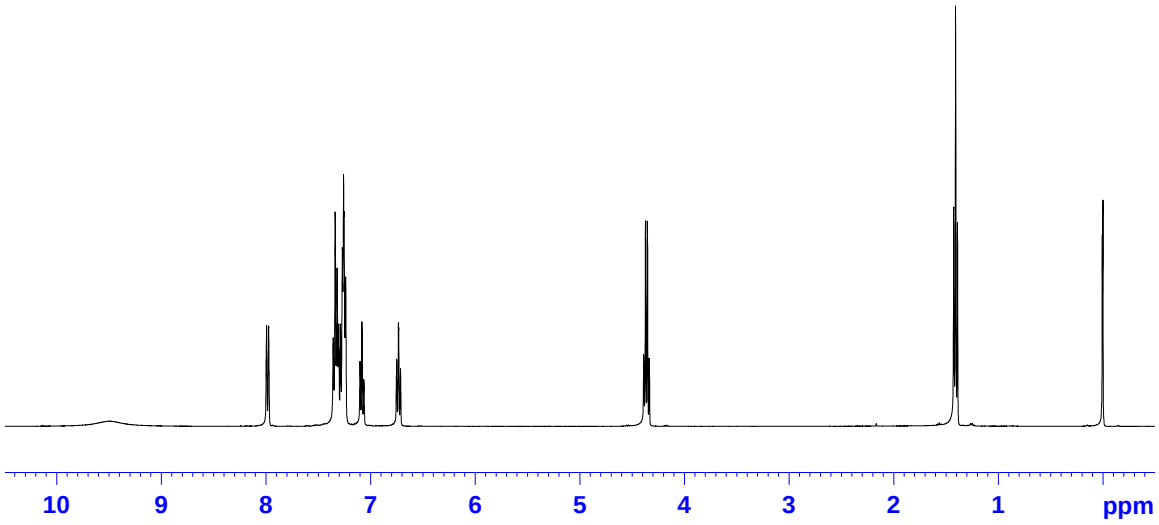


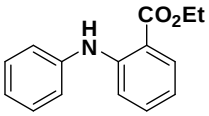


2c- ^{13}CNMR

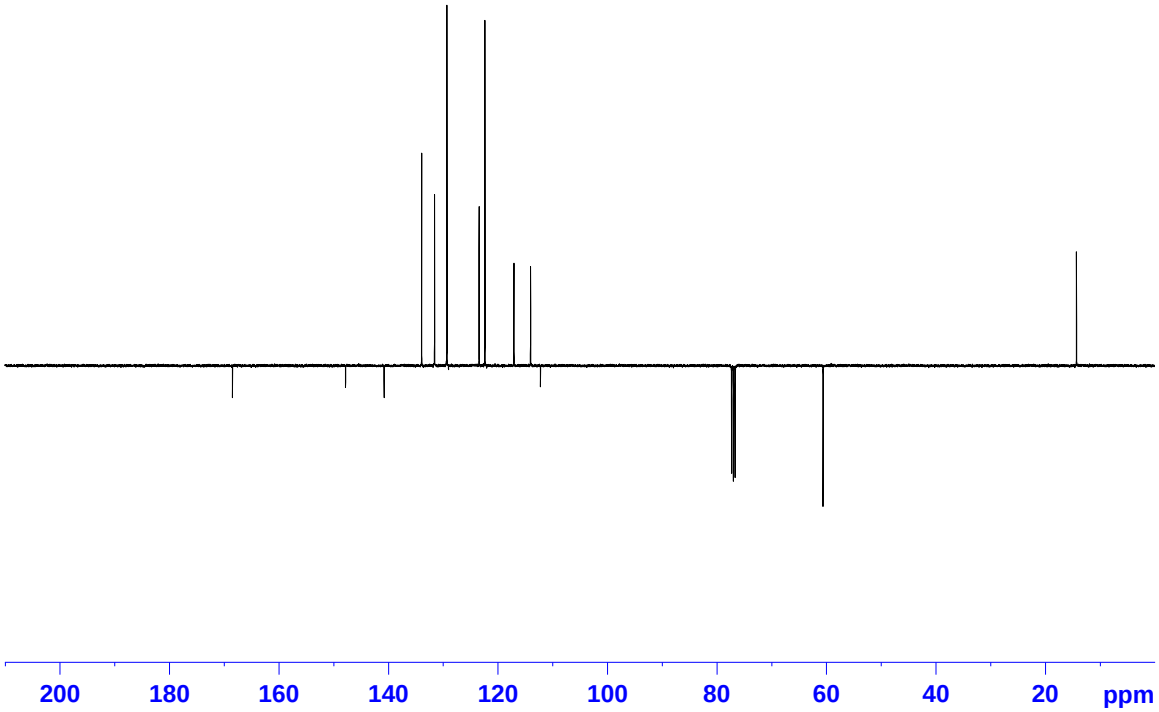


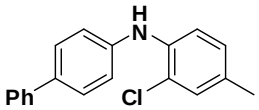
2d- ^{1}HNMR



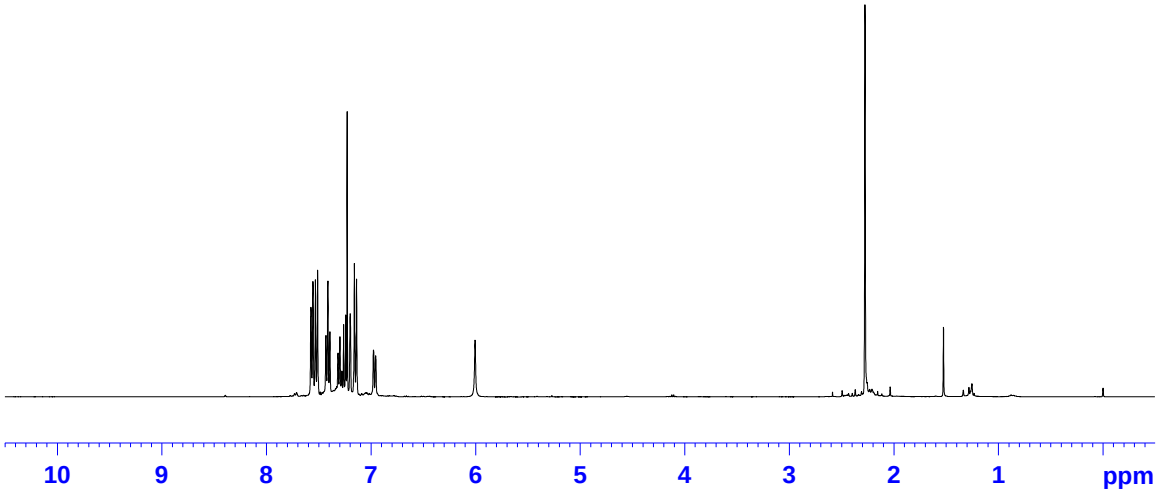


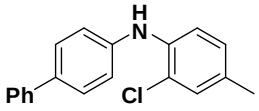
2d- ^{13}CNMR



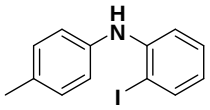


2e- ^{1}HNMR

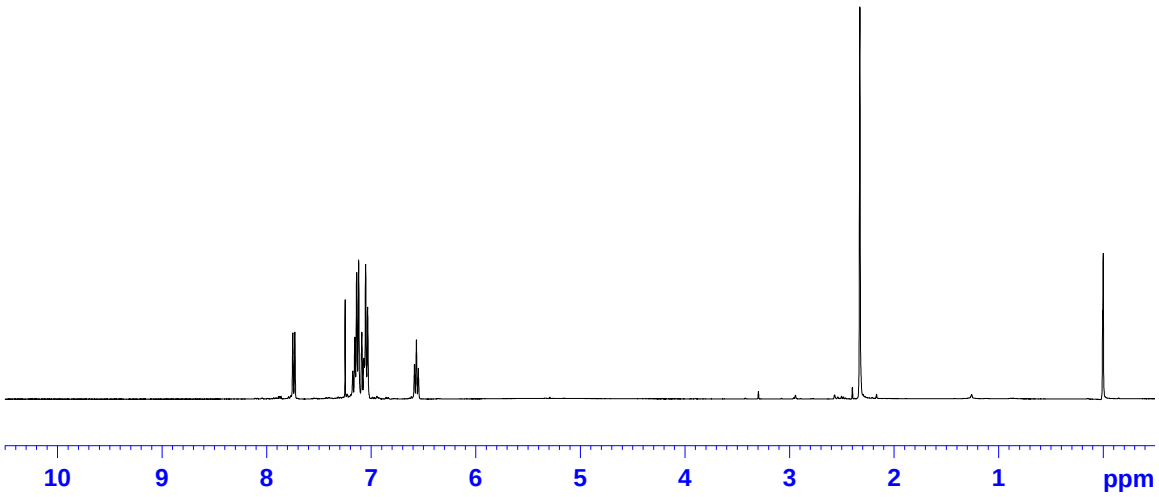


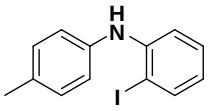


2e- ^{13}CNMR

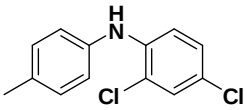


2f- ^{1}HNMR

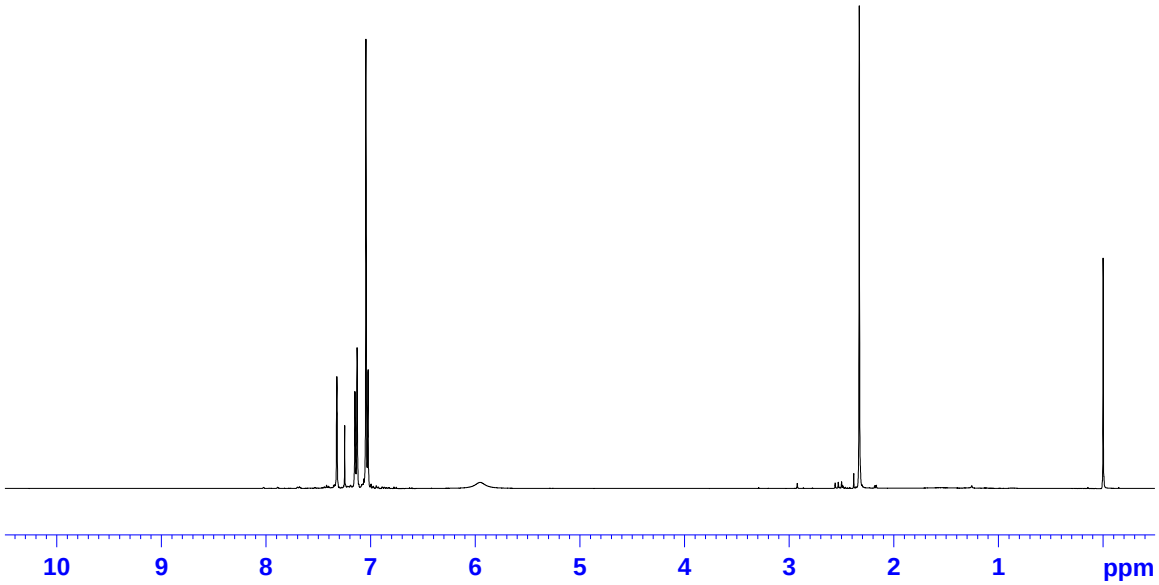


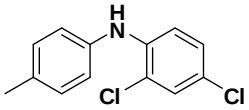


2f- ^{13}CNMR

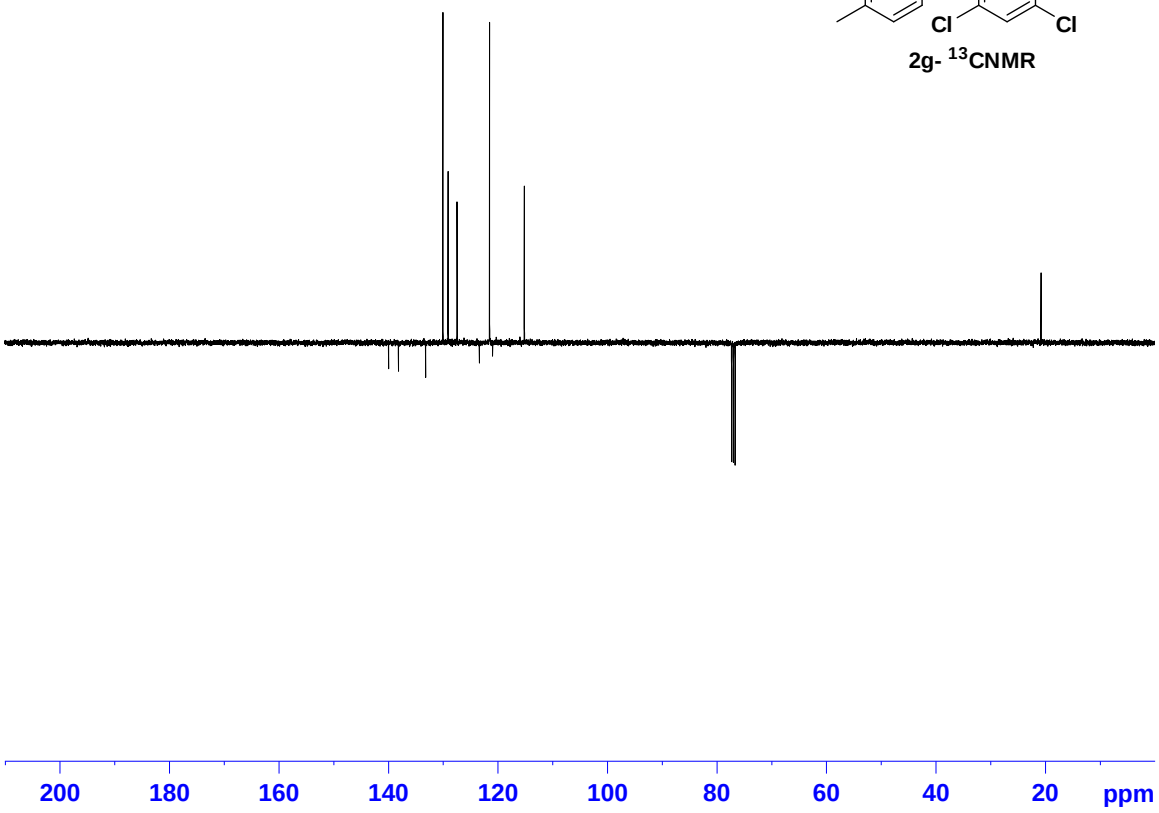


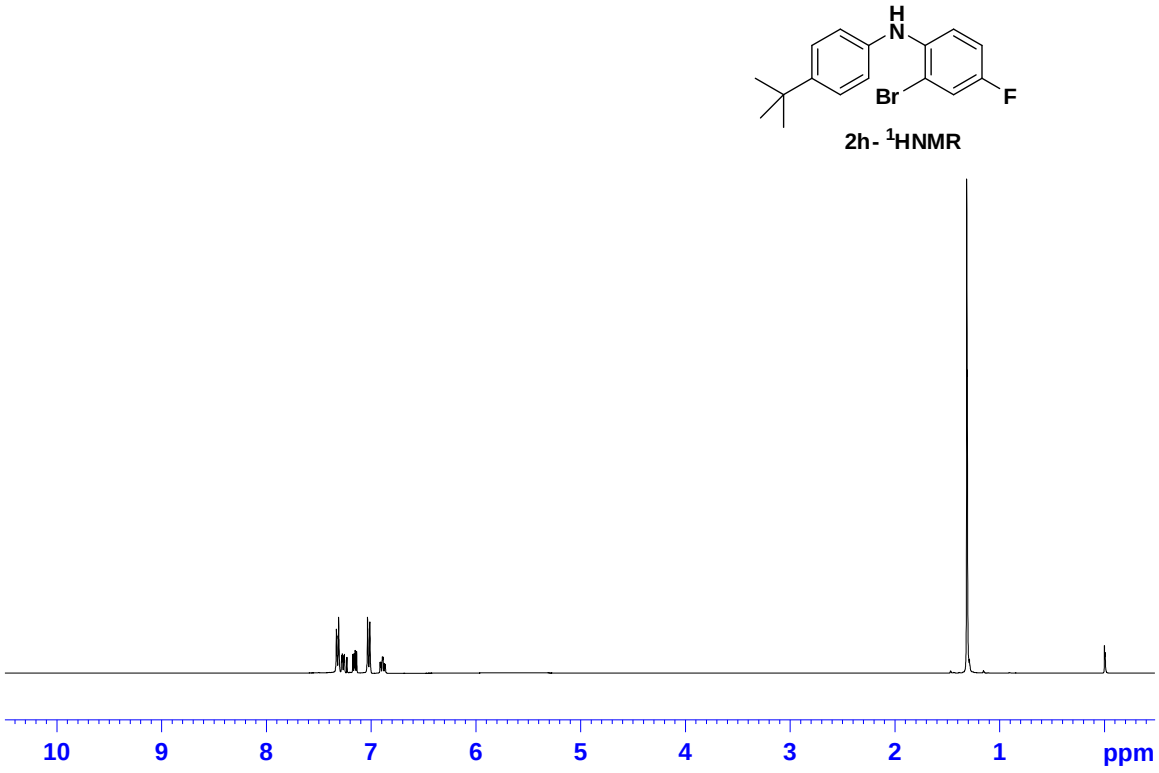
2g- ^{1}HNMR

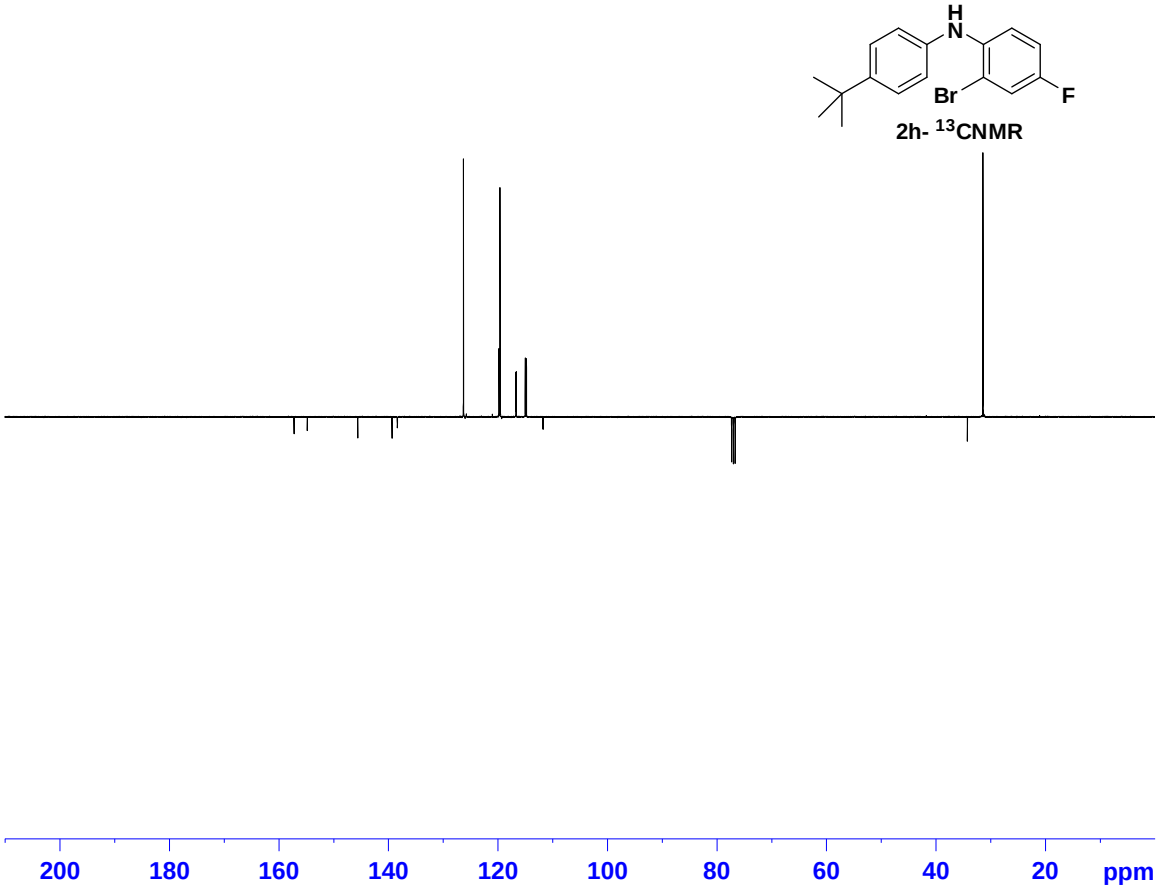


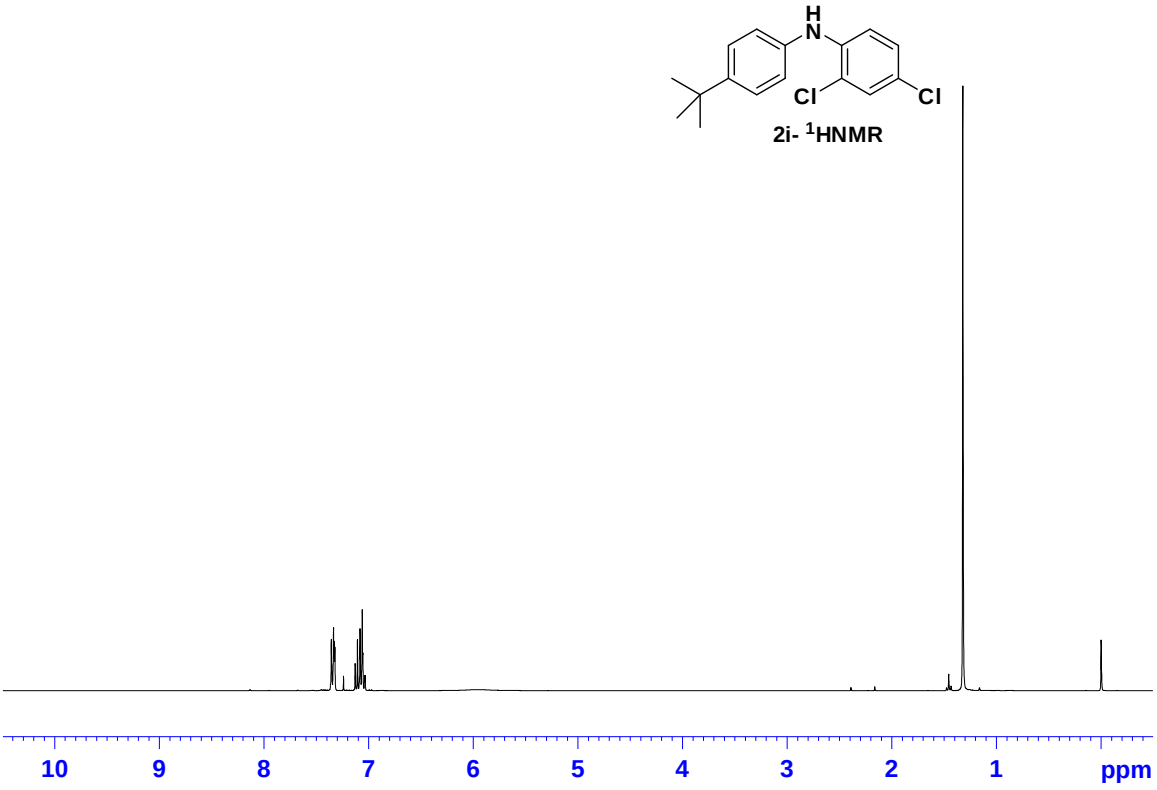


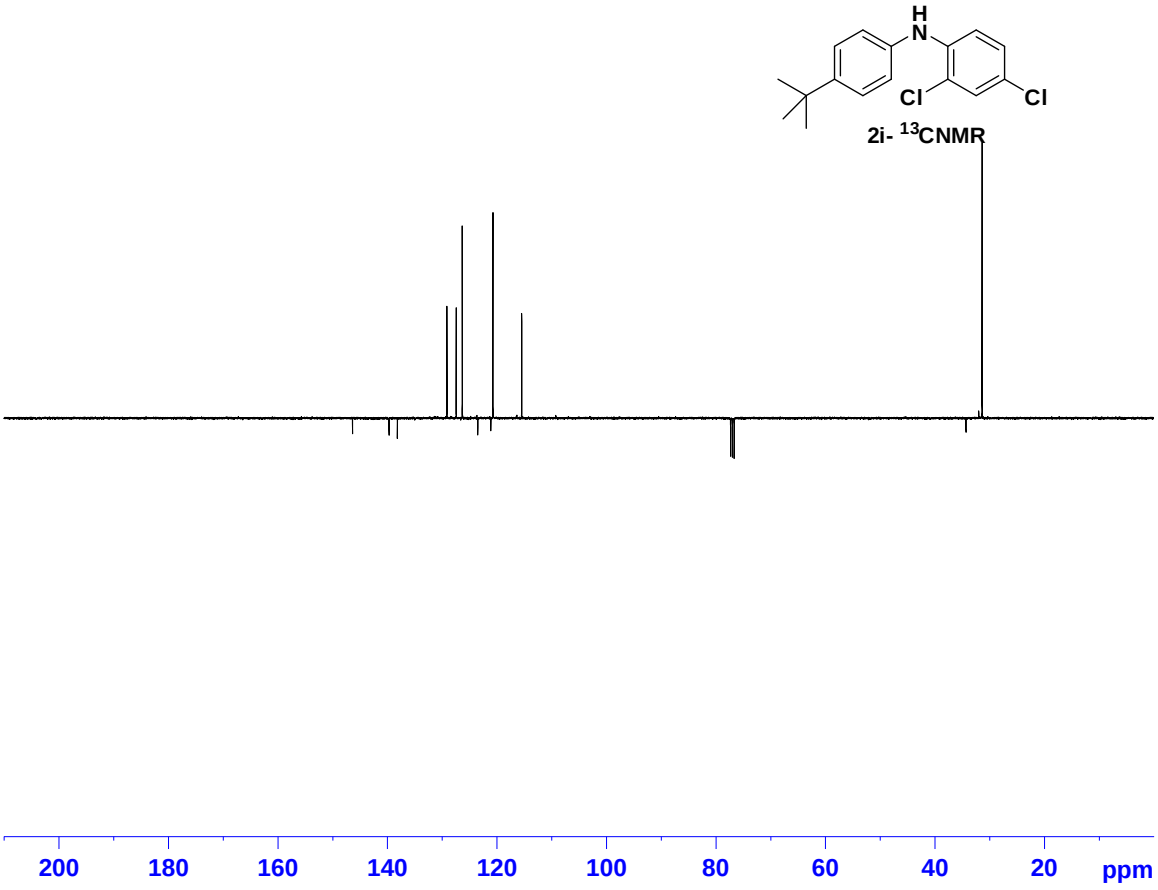
2g- ^{13}CNMR

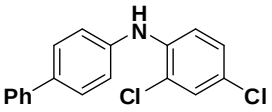




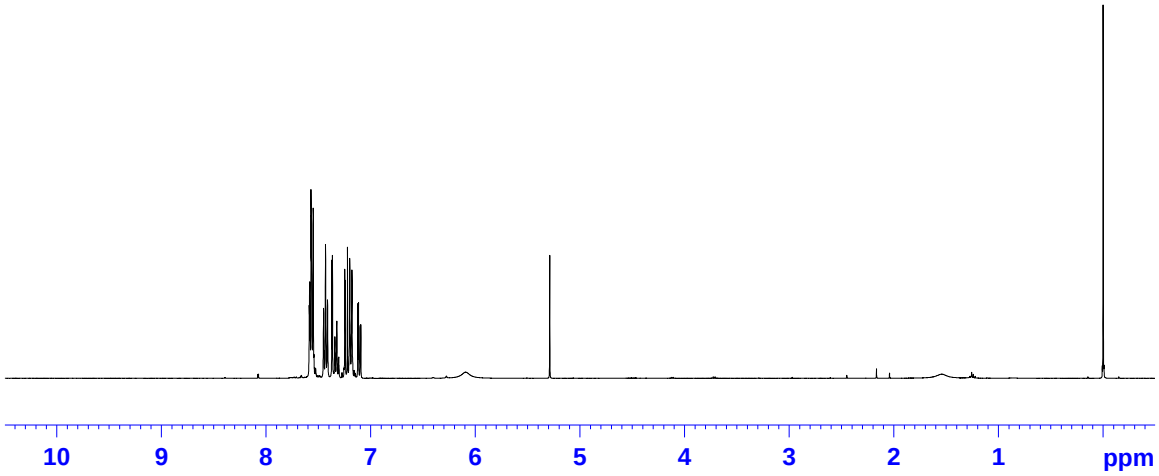


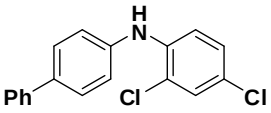

H
N
Cl
Cl
2i- 1HNMR
10
9
8
7
6
5
4
3
2
1
ppm


H
N
Cl
Cl
2i- 13CNMR
200
180
160
140
120
100
80
60
40
20
ppm

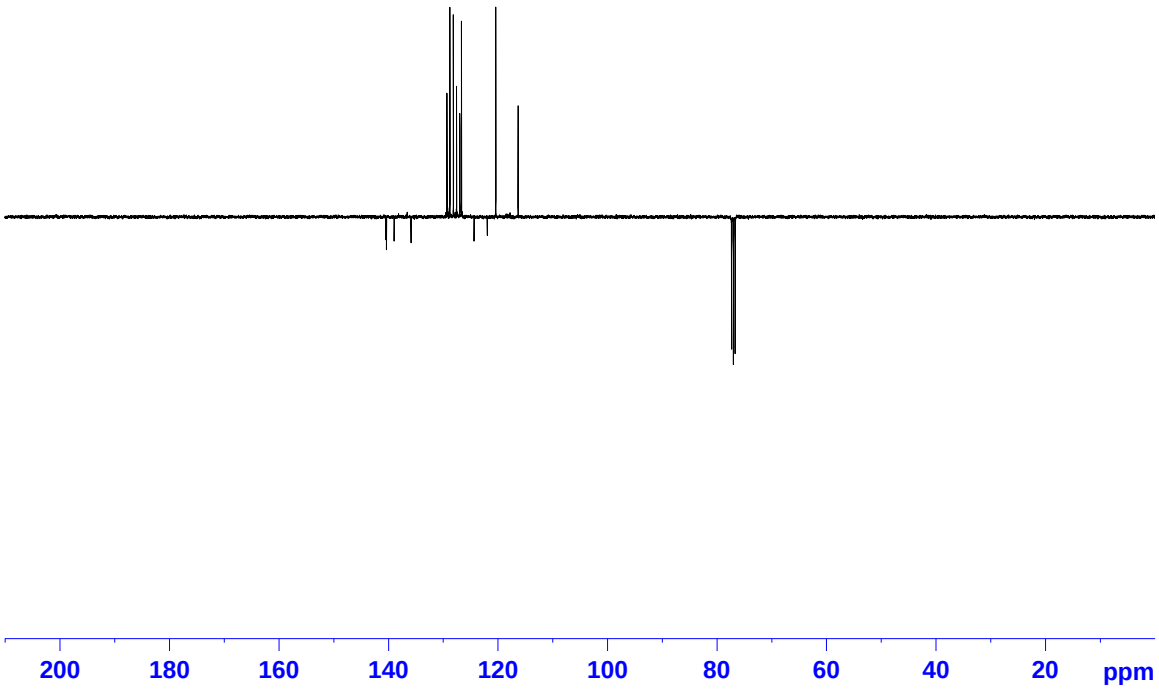


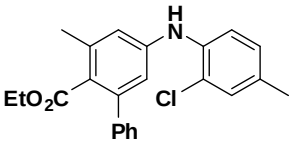
2j- ^{1}HNMR



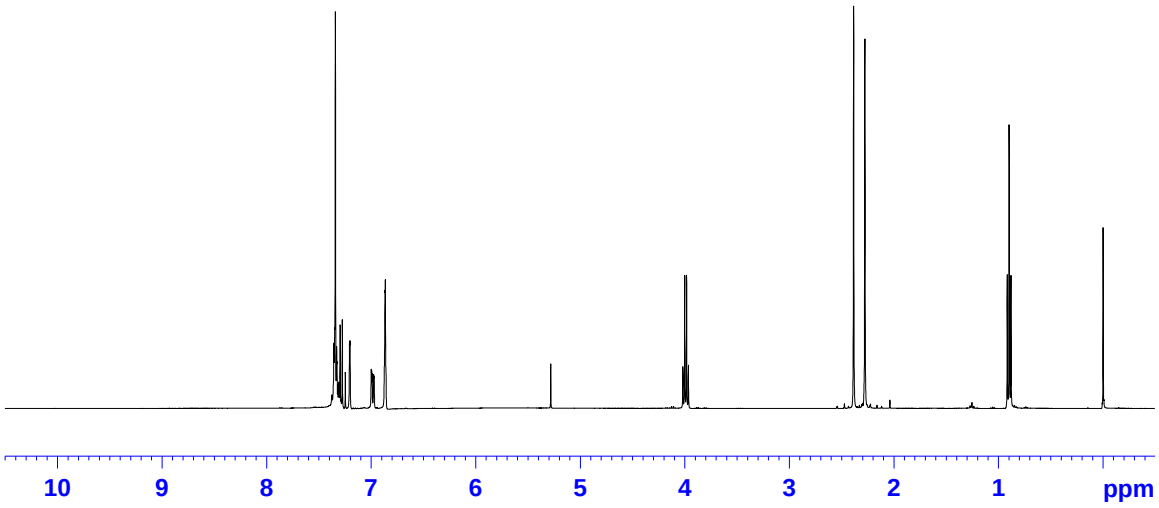


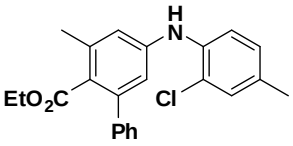
2j- ^{13}CNMR



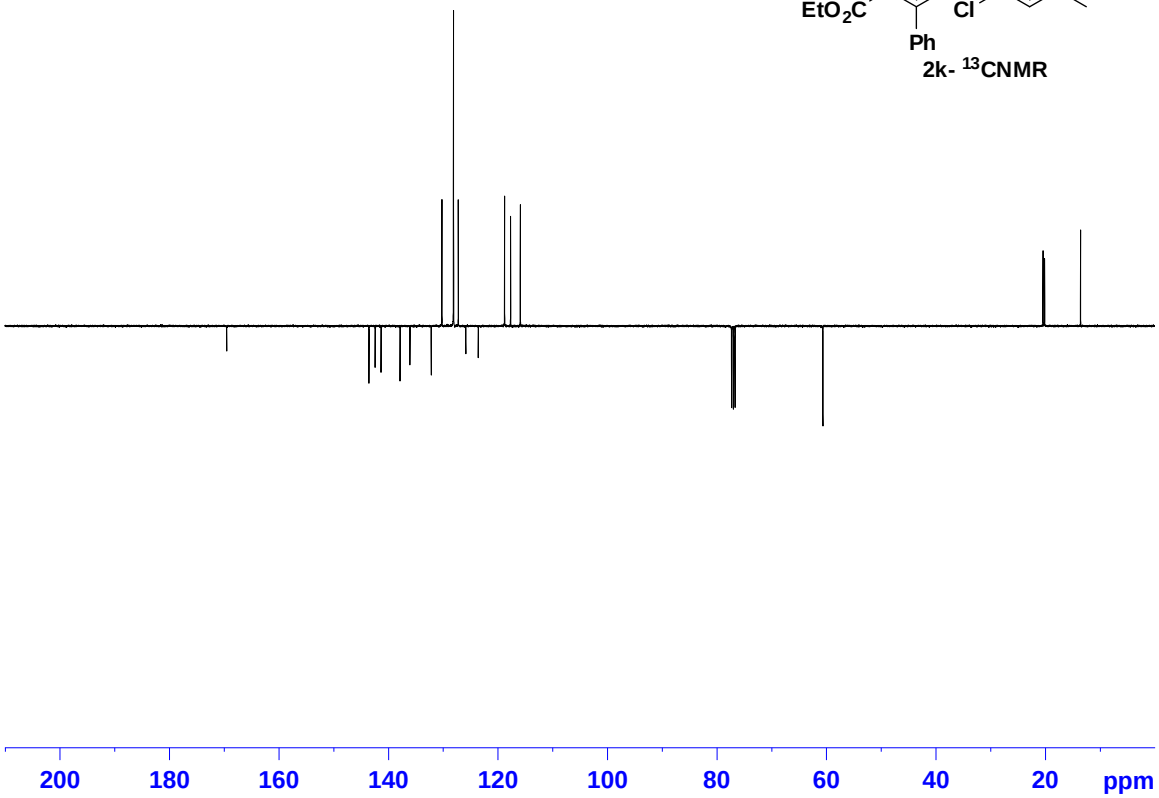


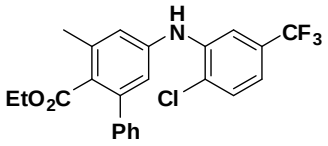
2k- ^{1}HNMR



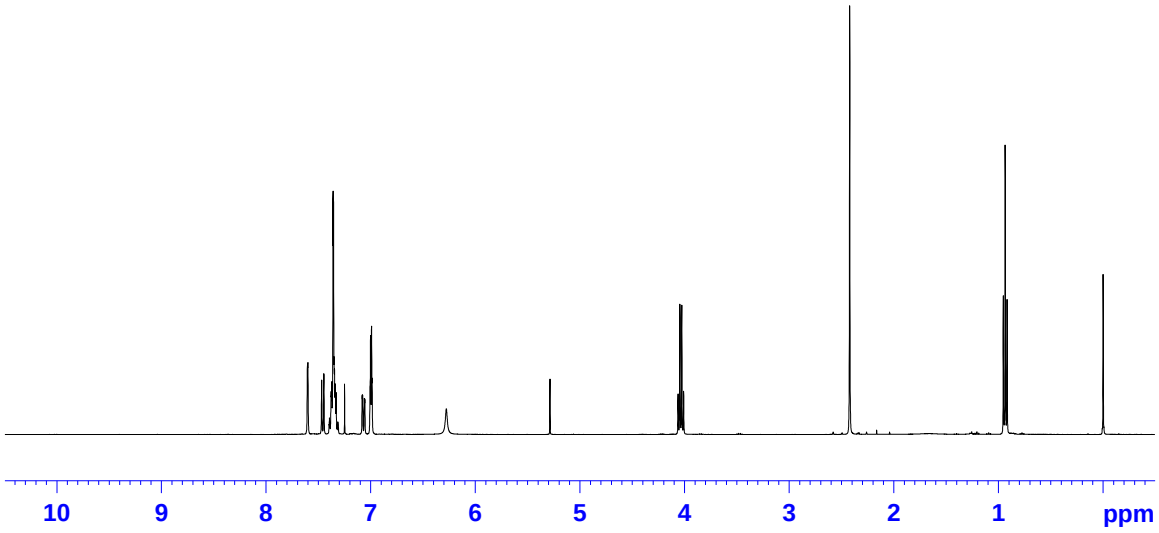


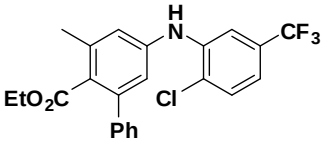
2k- ^{13}CNMR



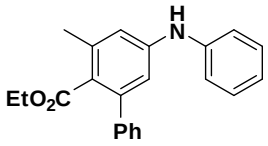


2l- ^{1}HNMR

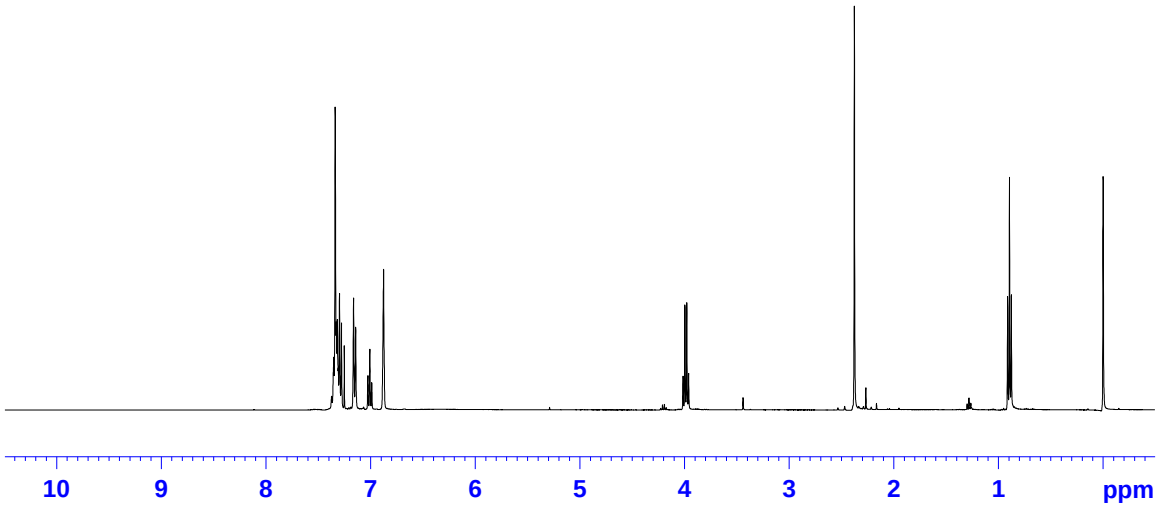


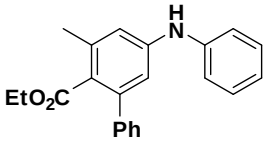


2l- ^{13}CNMR



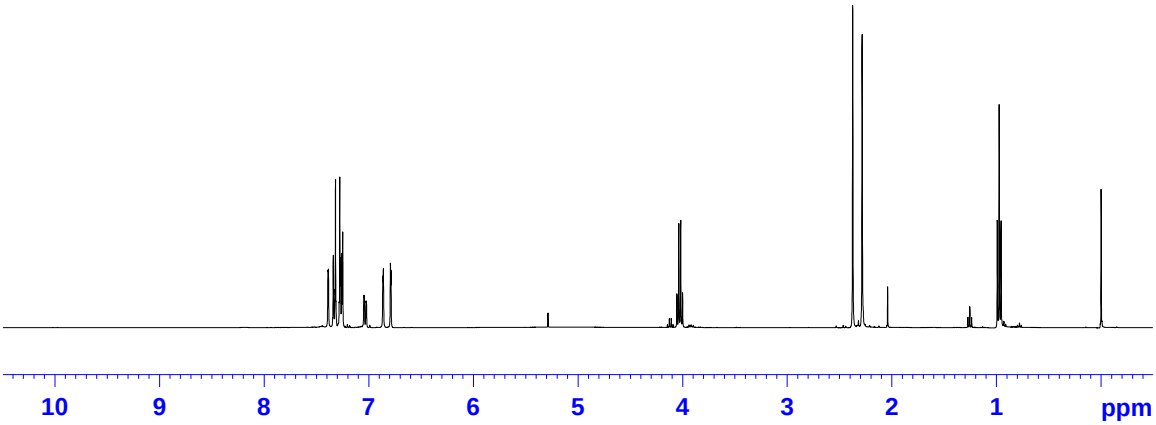
2m- ^{1}HNMR

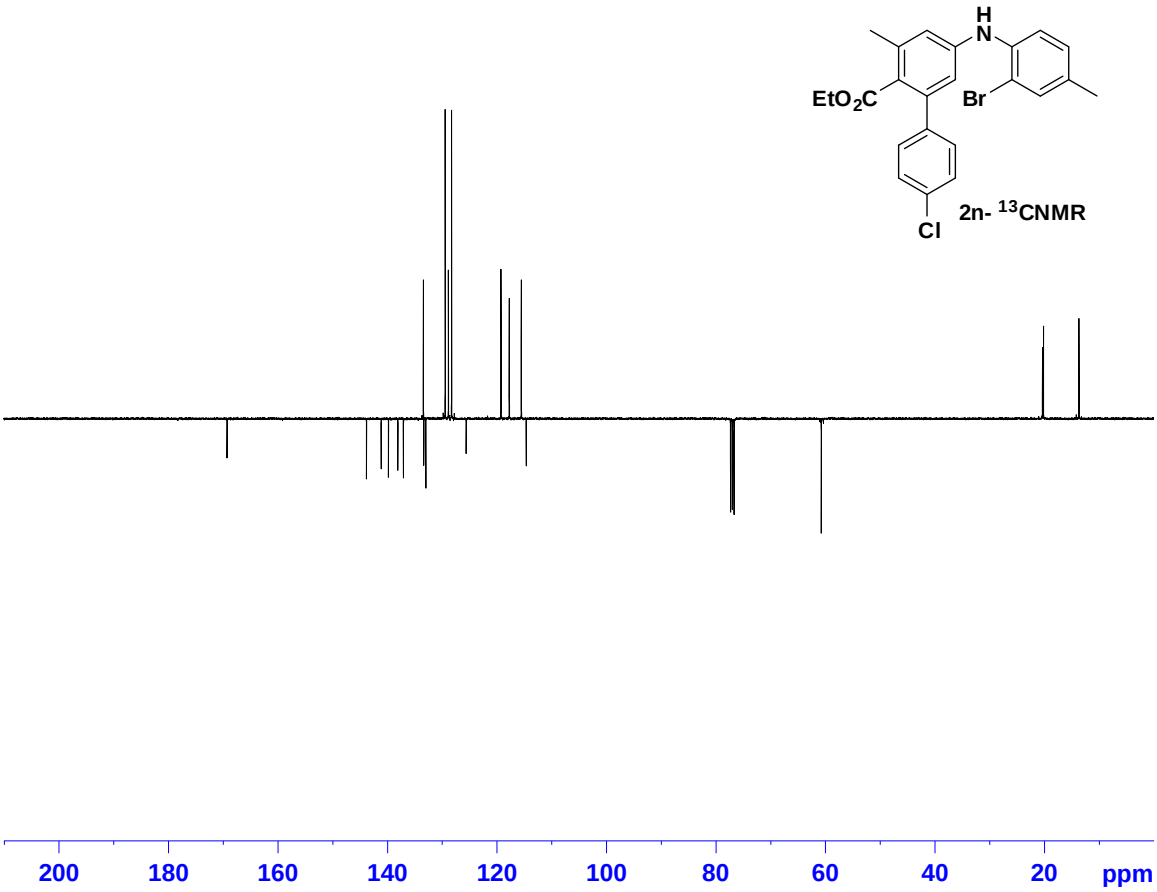


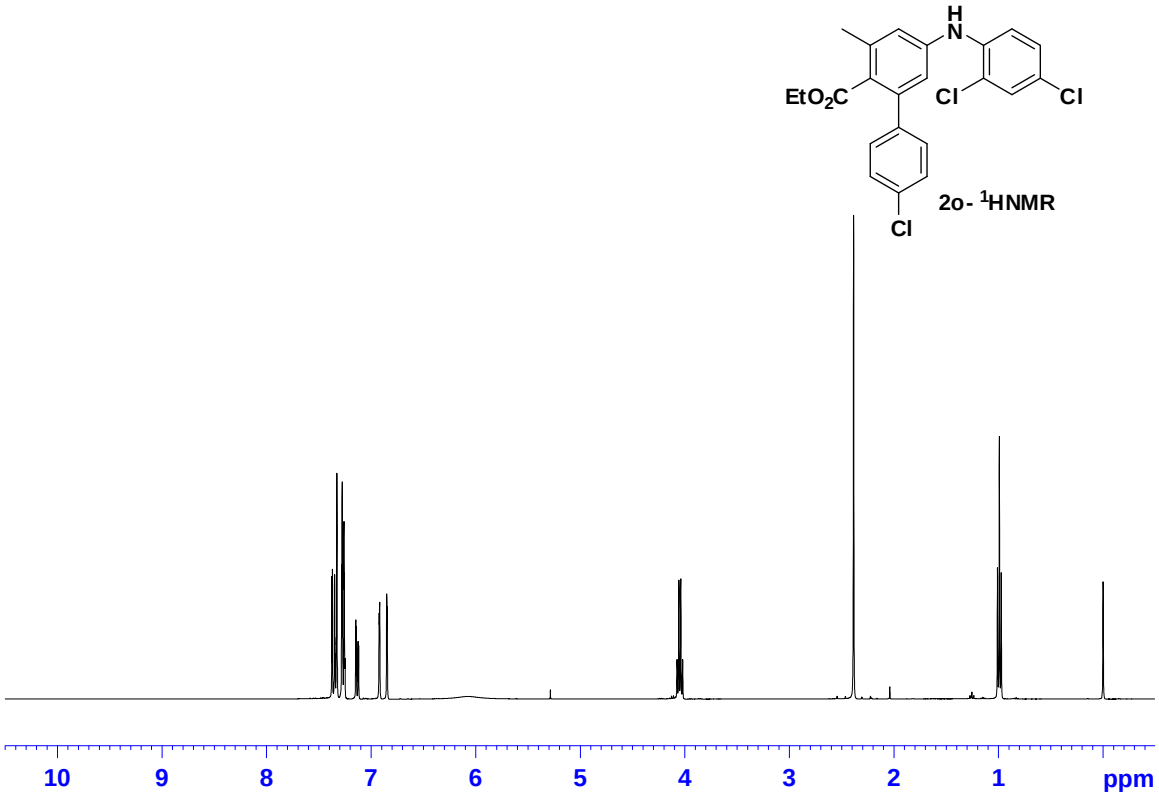


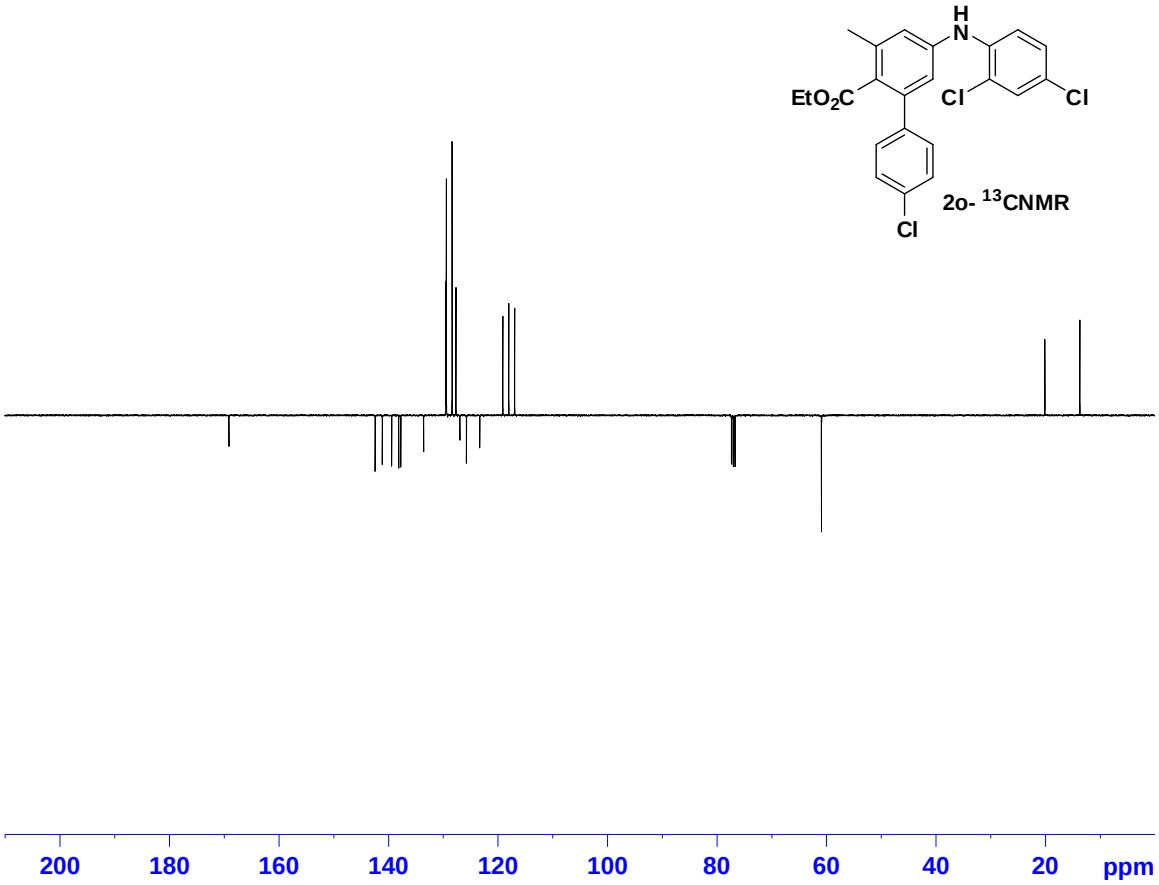
2m- ^{13}CNMR

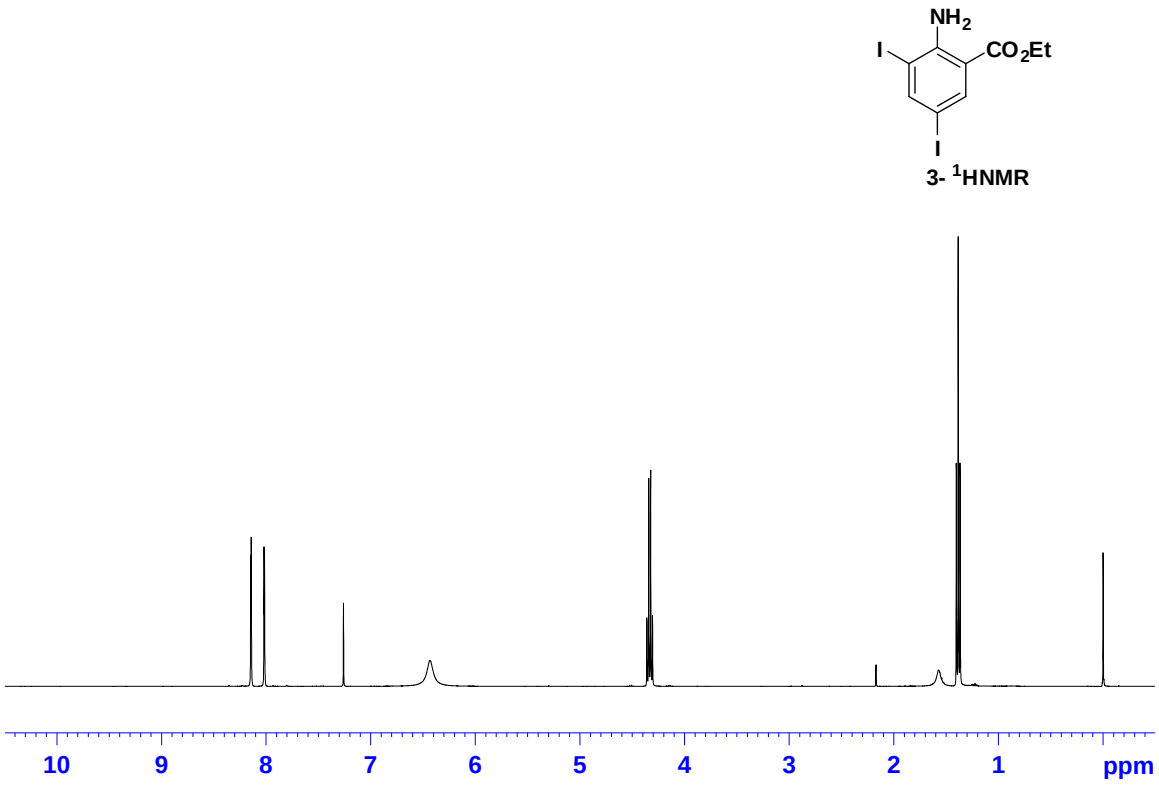

H
N
EtO2C
Br
Cl
2n- 1HNMR

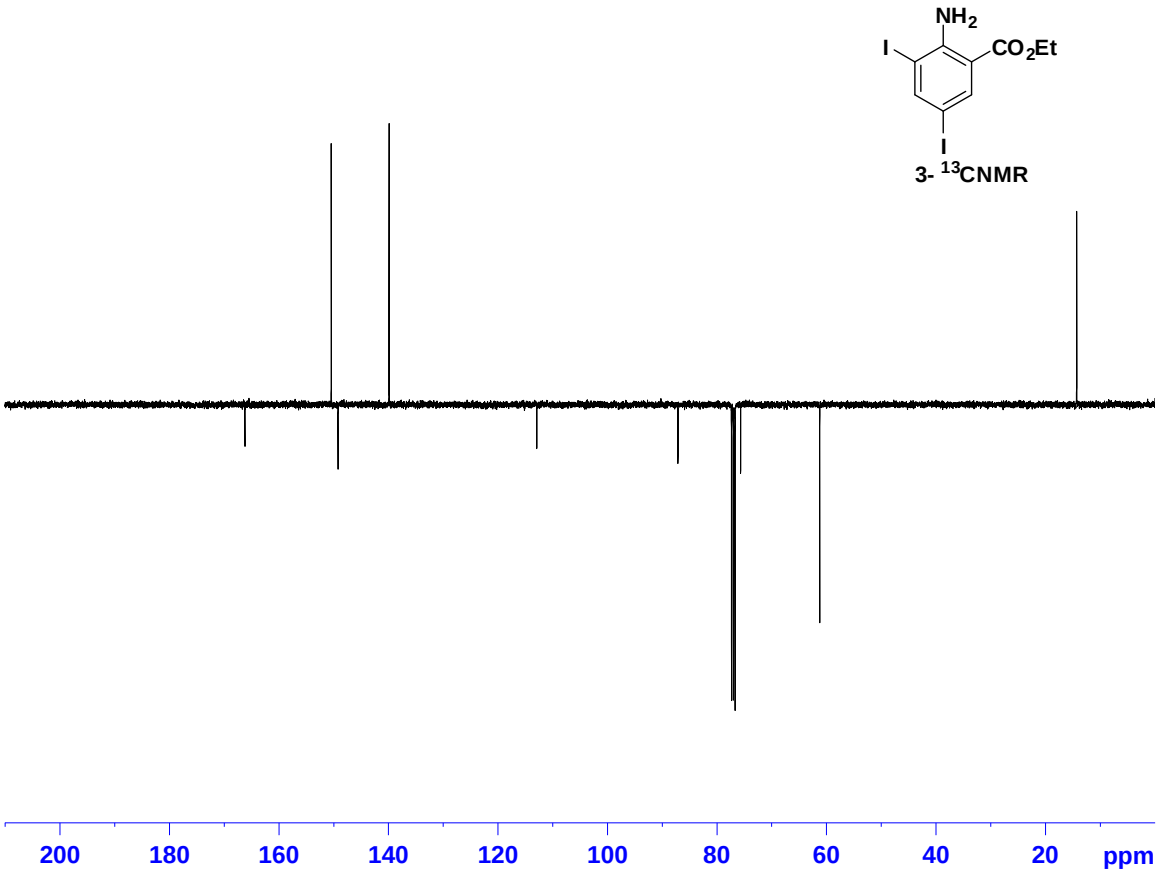

10
9
8
7
6
5
4
3
2
1
ppm

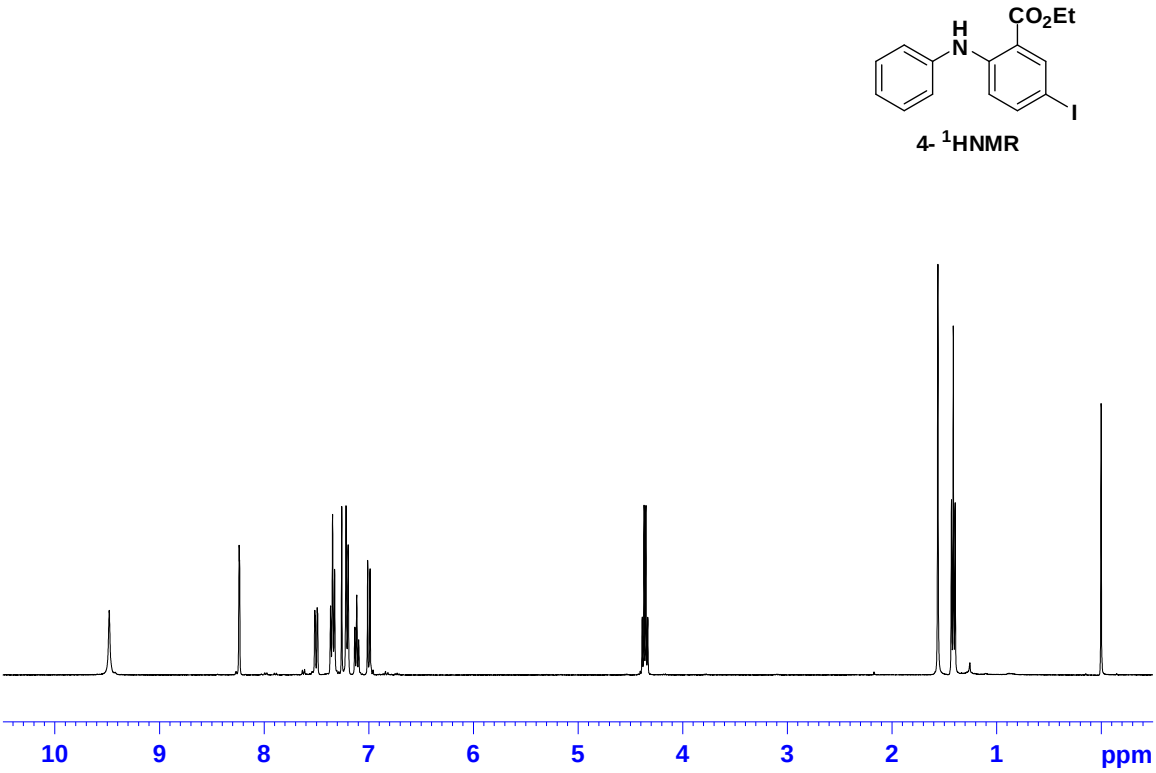

H
N
EtO2C
Br
Cl
2n- 13CNMR
200
180
160
140
120
100
80
60
40
20
ppm


H
N
EtO2C
Cl
Cl
Cl
2o- 1HNMR
10
9
8
7
6
5
4
3
2
1
ppm

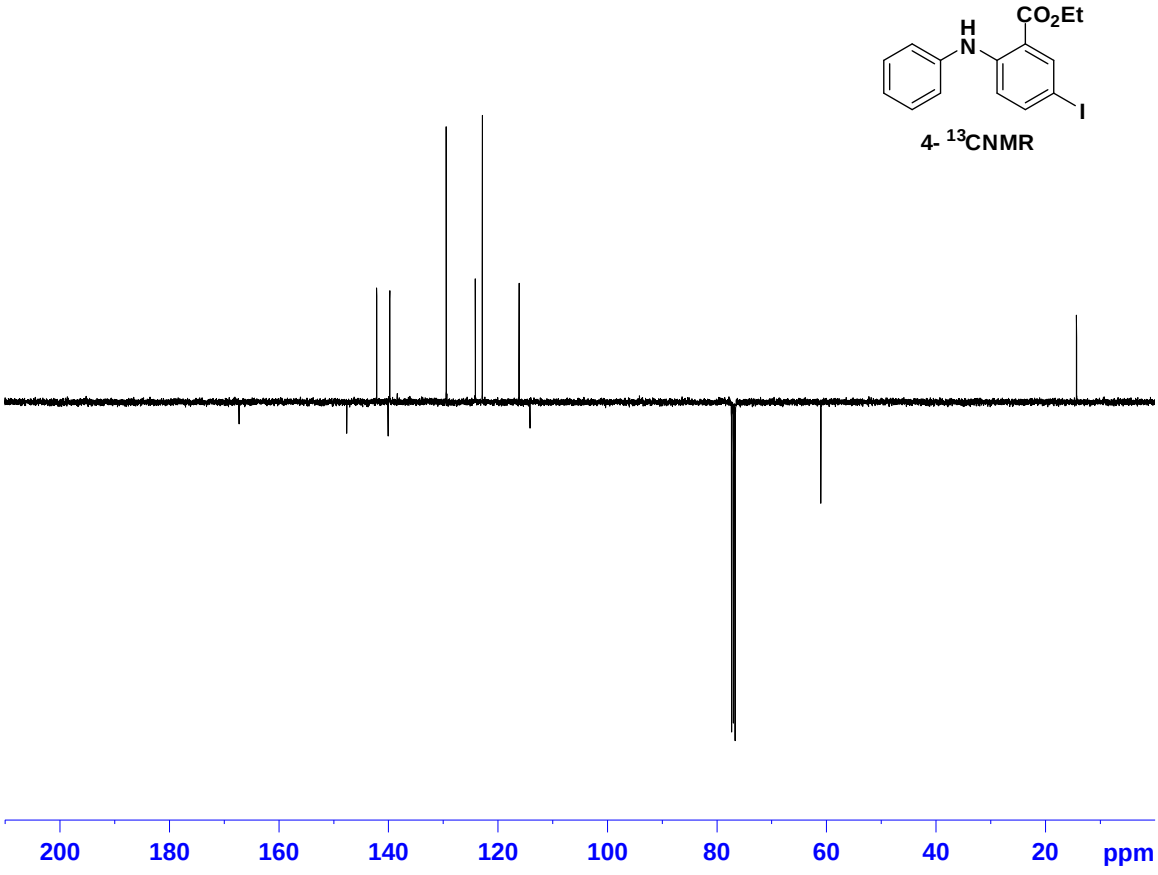

H
N
EtO2C
Cl
Cl
Cl
2o- 13CNMR
200
180
160
140
120
100
80
60
40
20
ppm



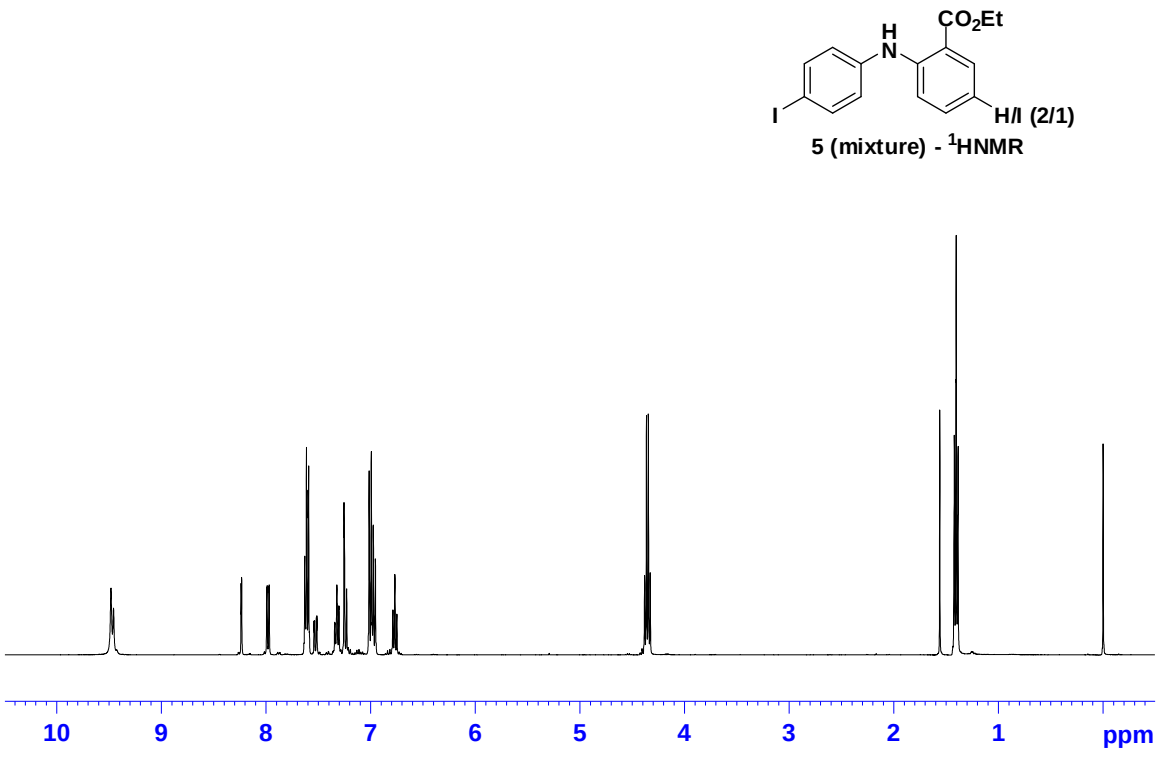


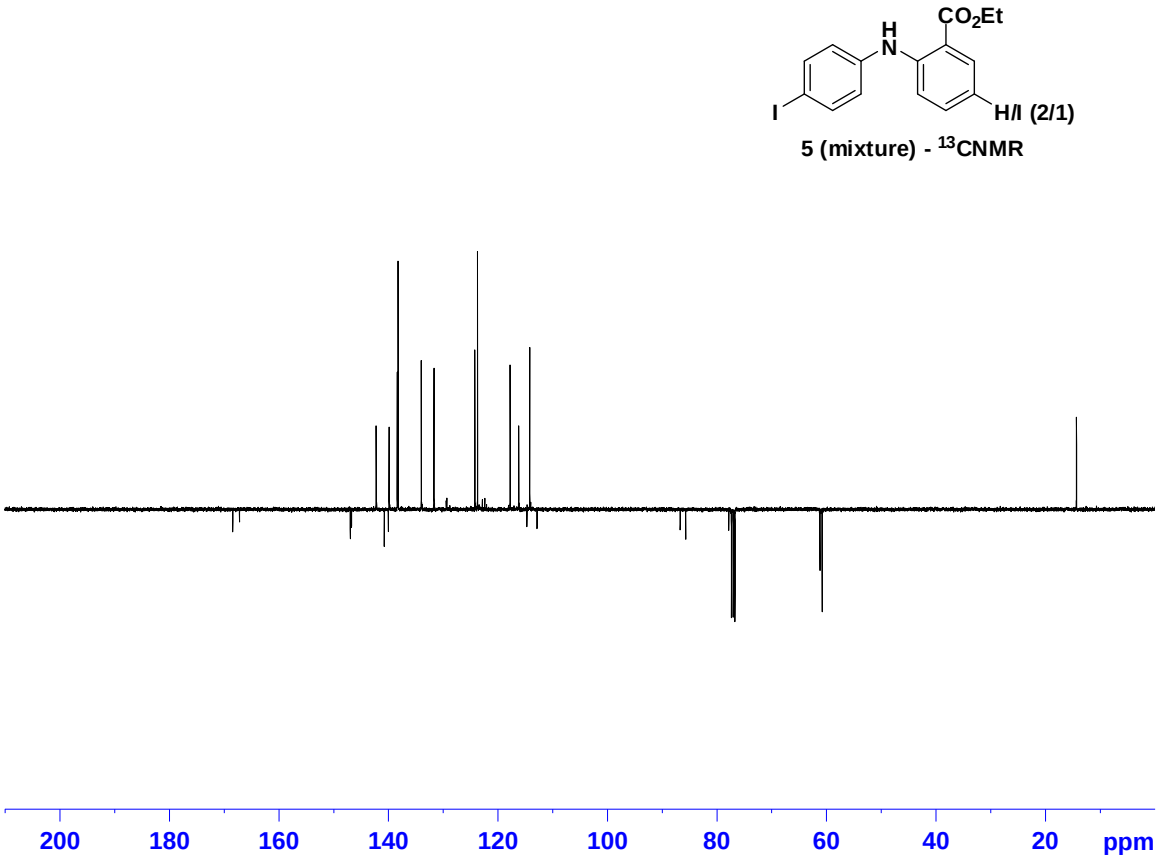


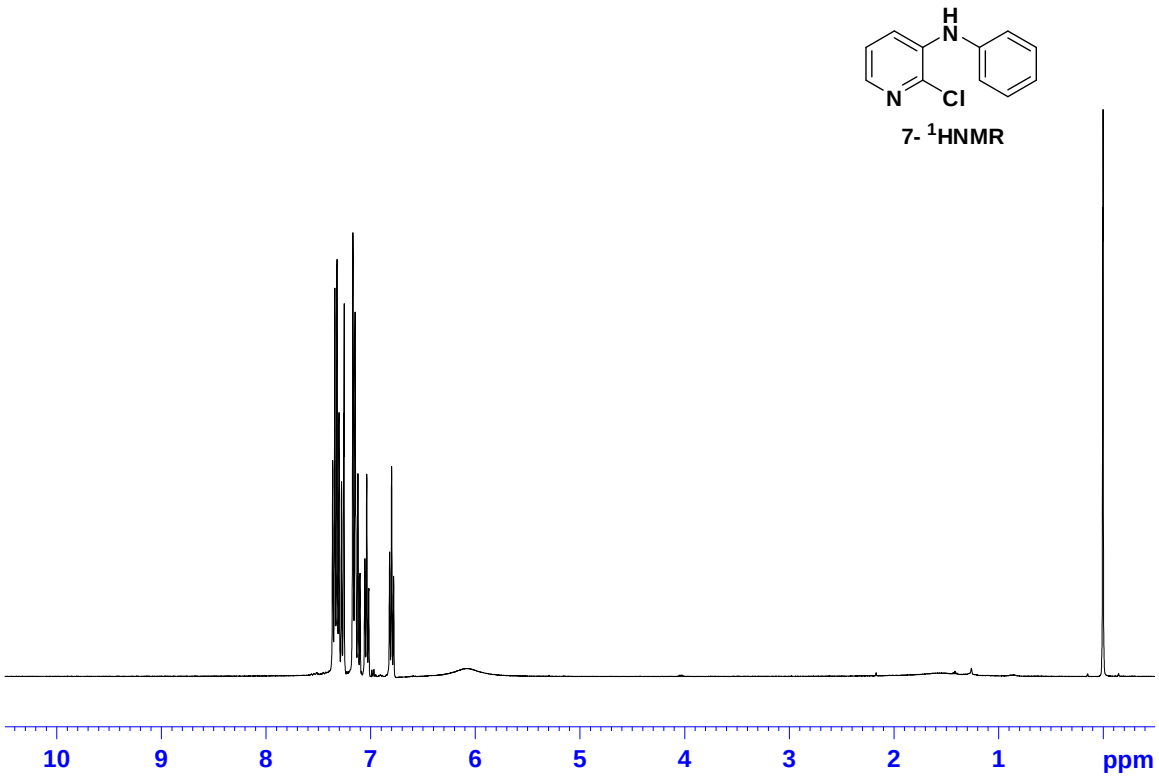
4- ^{1}HNMR



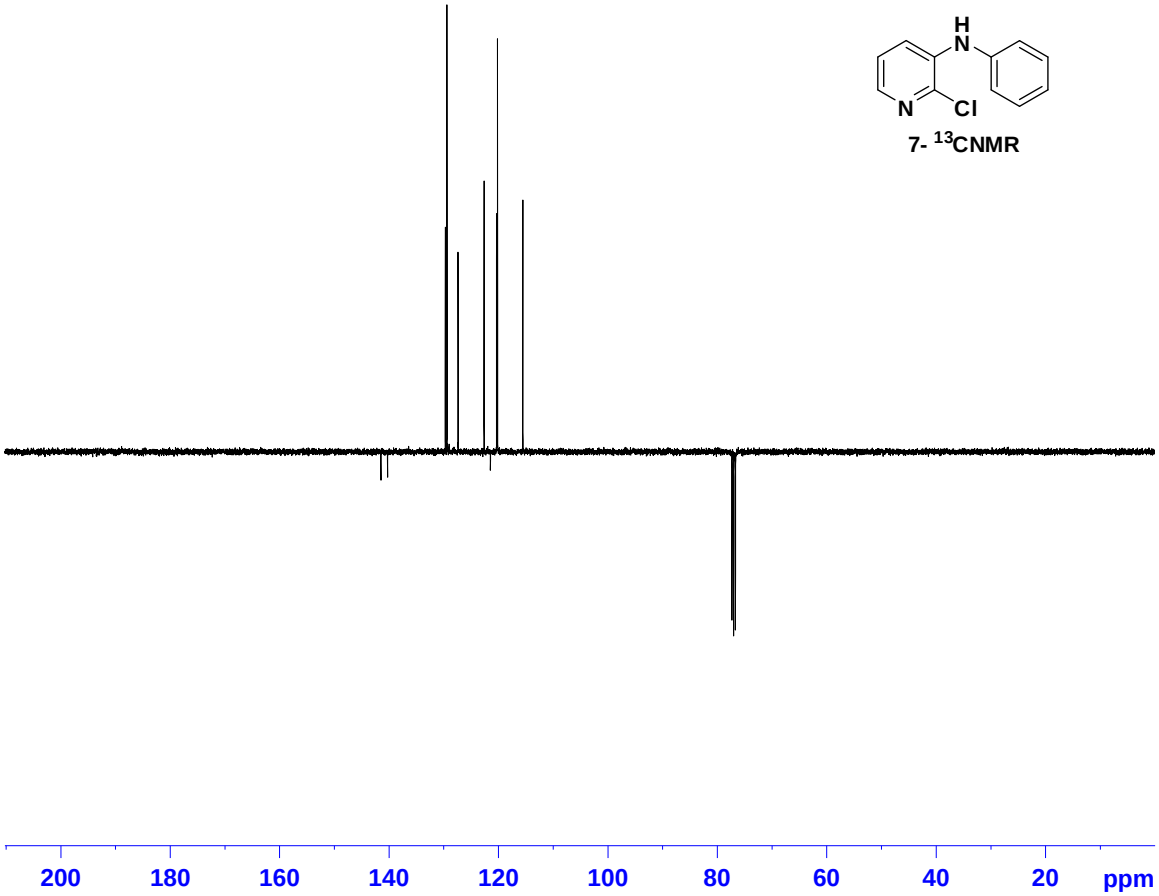
4- ^{13}CNMR



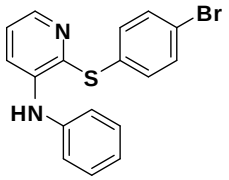




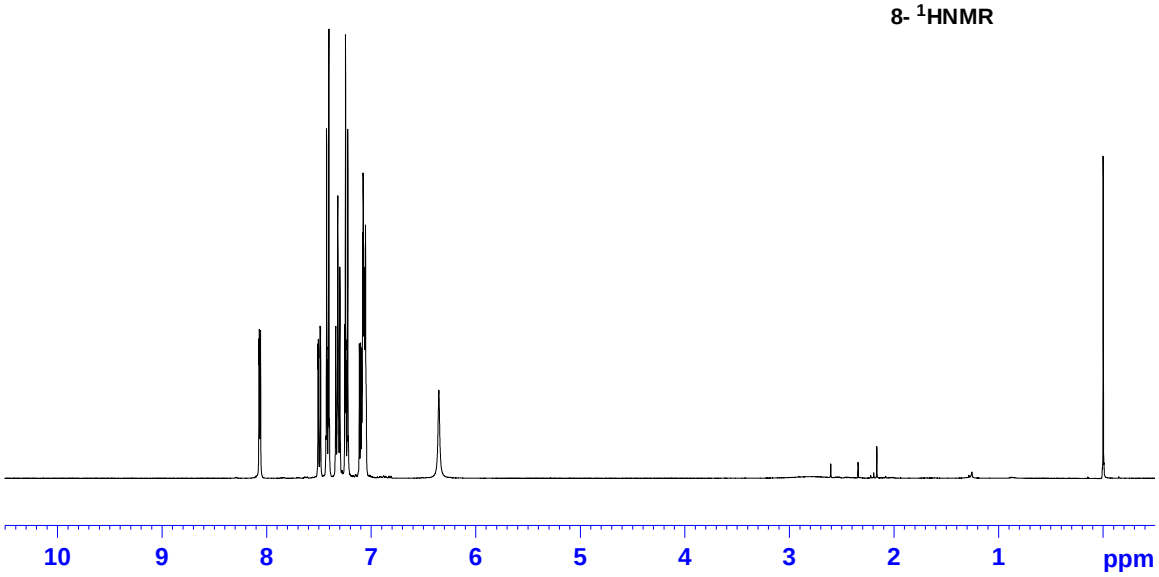
7- ^{1}HNMR

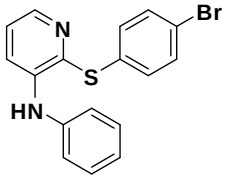


7- ^{13}CNMR

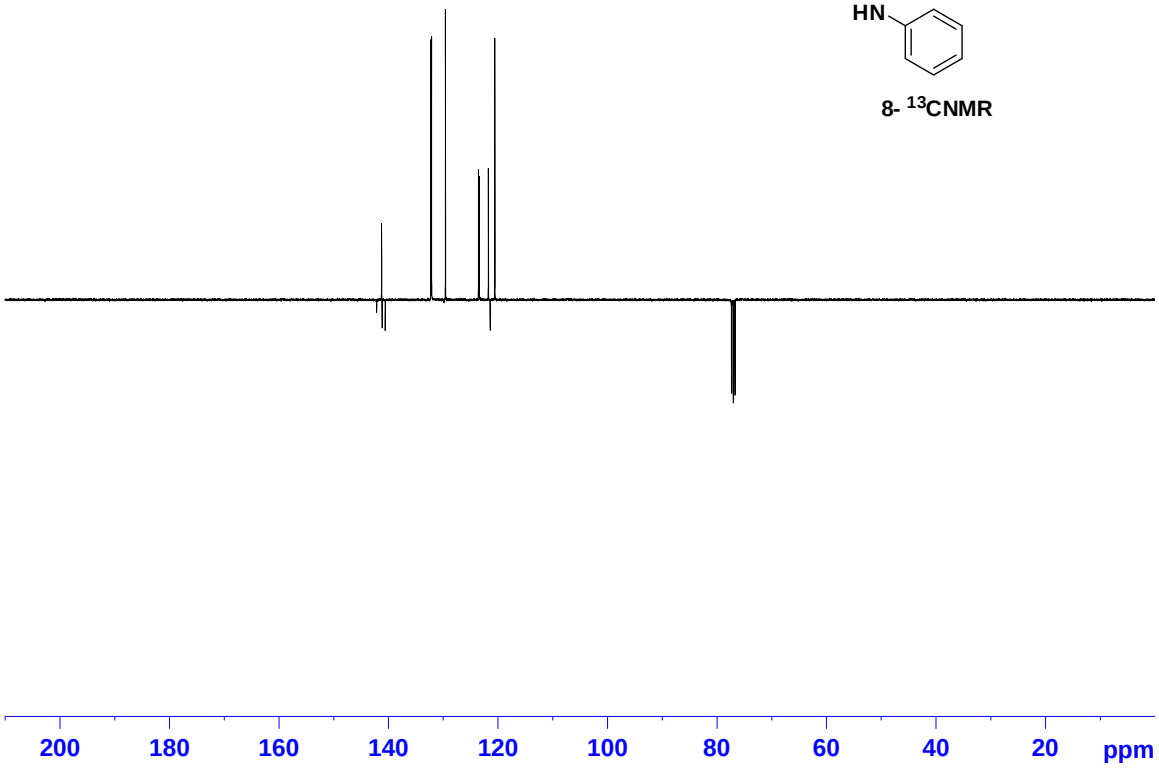


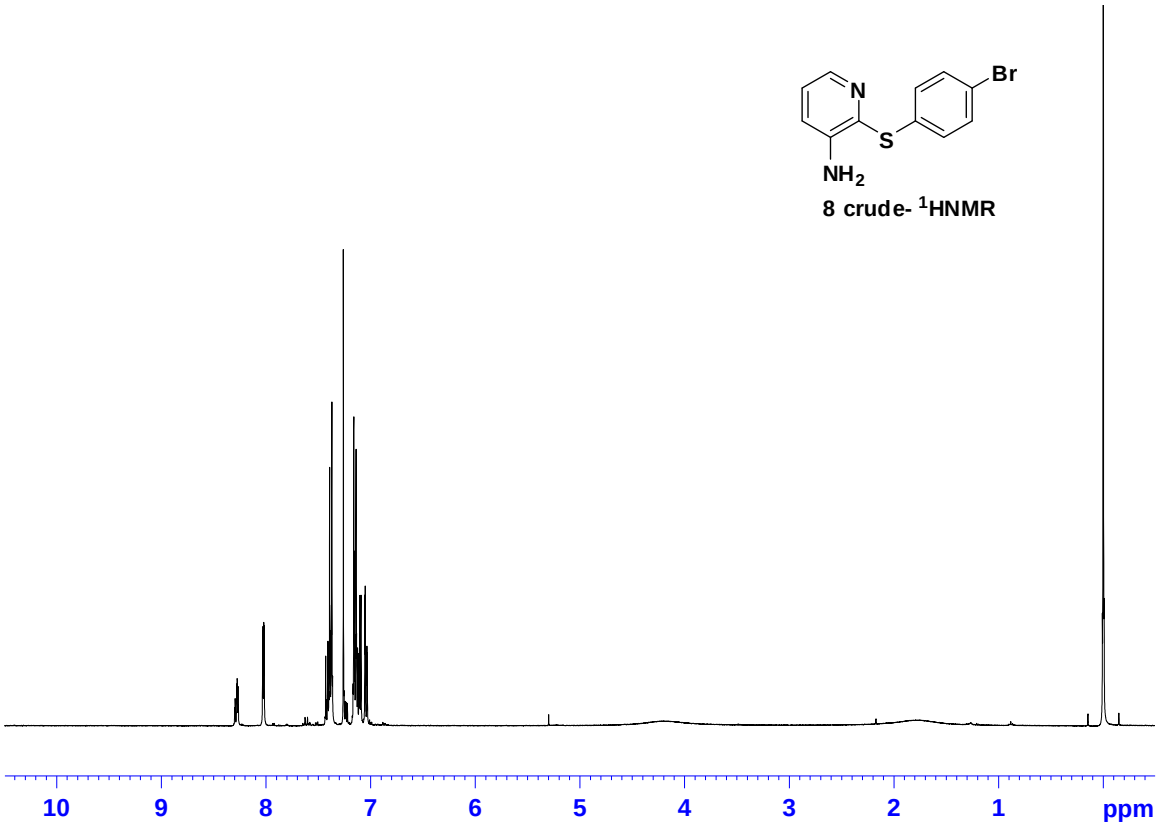
8- ^{1}HNMR

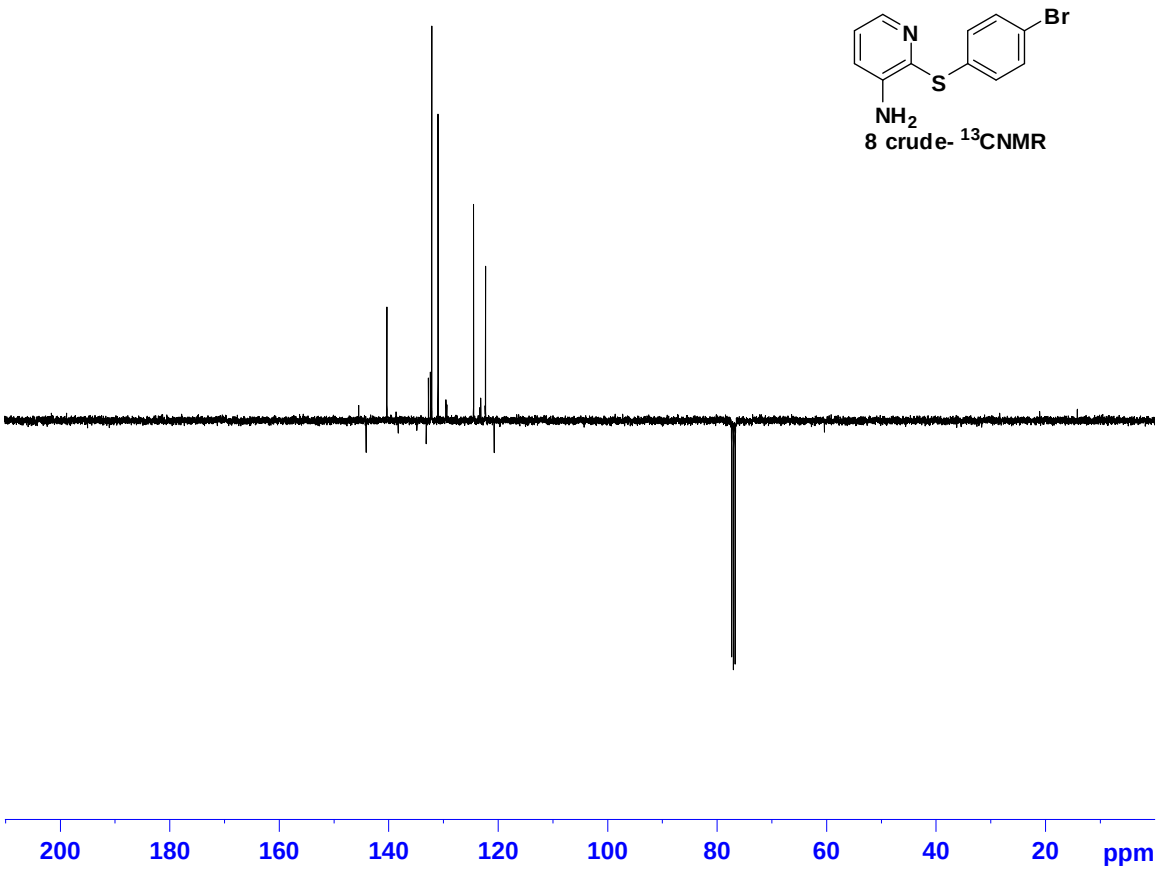


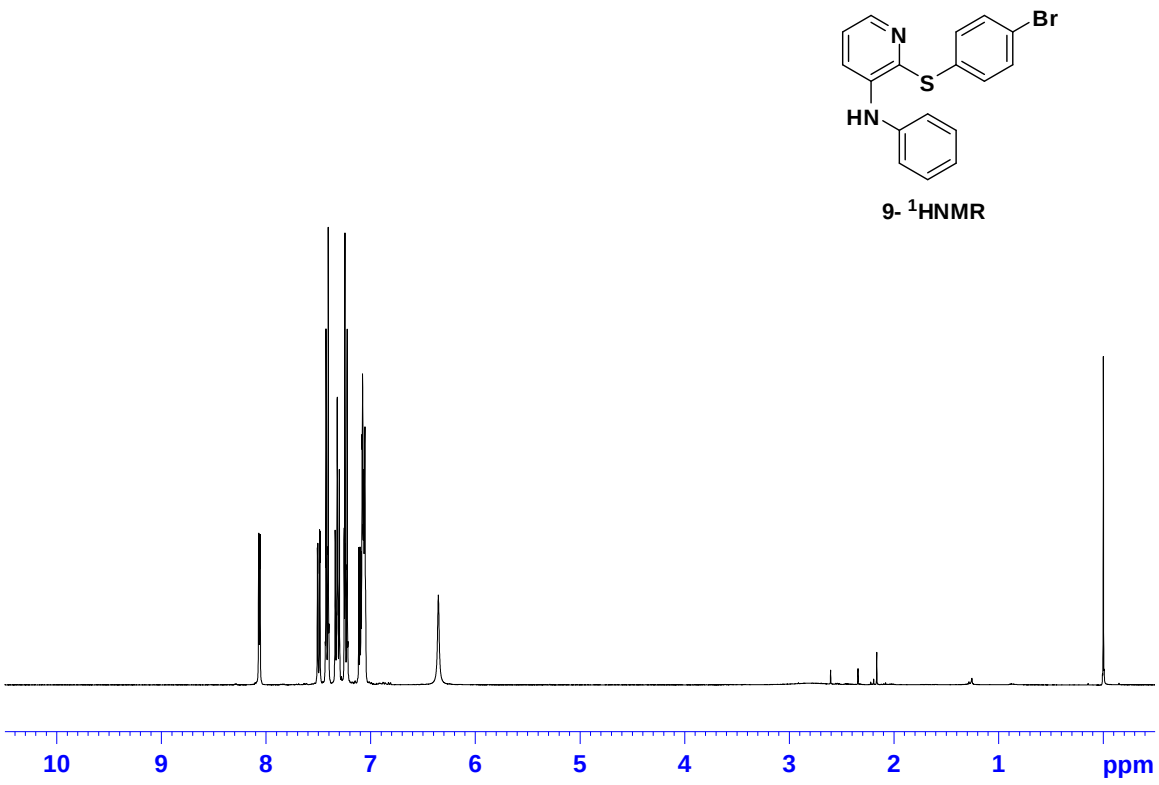


8- ^{13}CNMR

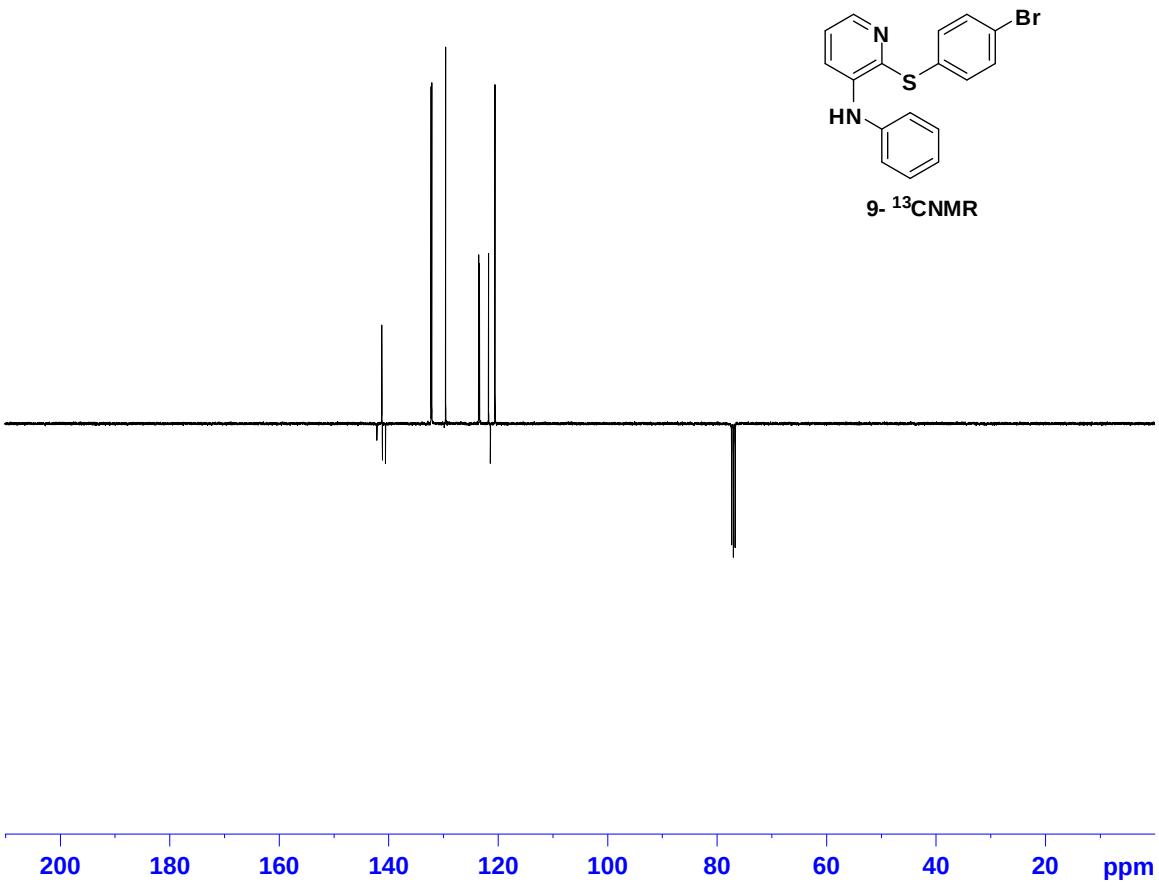



N
Br
S
NH2
8 crude- 1HNMR
10
9
8
7
6
5
4
3
2
1
ppm

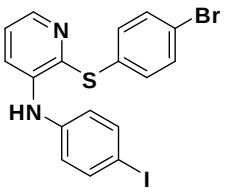

N
Br
S
NH2
8 crude- 13CNMR
200
180
160
140
120
100
80
60
40
20
ppm



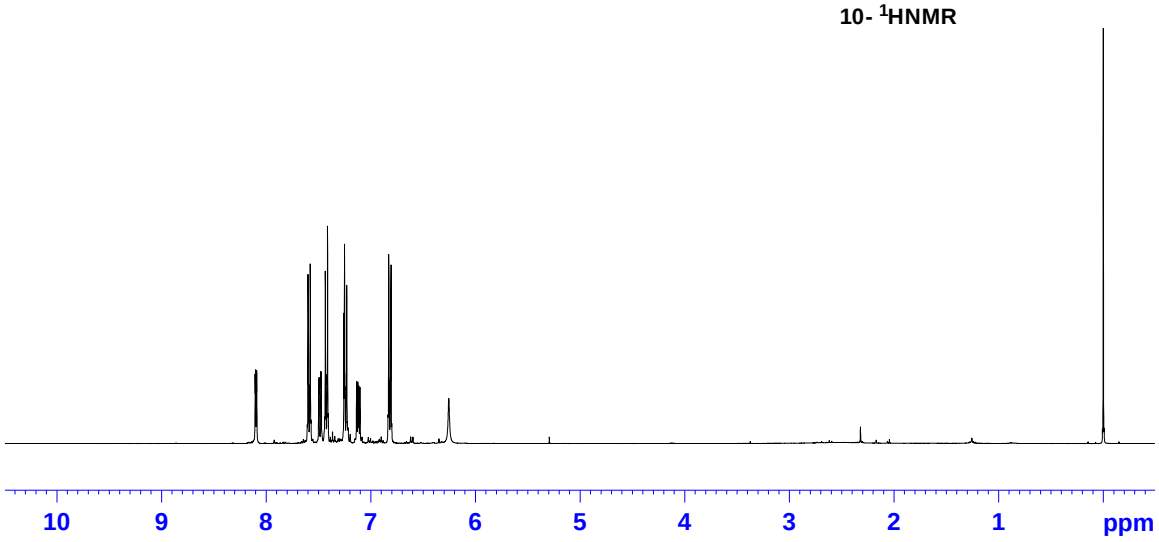
9- ^{1}HNMR

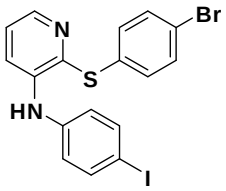


9- ^{13}CNMR



10- ^{1}HNMR





10- ^{13}CNMR