Supporting Information

Nickel-catalyzed alkene *ipso*-selective reductive hydroamination with nitroarenes

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Materials and methods

The following chemicals were purchased and used as received: nickel(II) bromide 2-methoxyethyl ether complex (CAS: 312696-09-6, Aldrich, 459674-5G); triethoxysilane (CAS: 998-30-1, TCI, T1040); diethoxymethylsilane (CAS: 27176-10-9, Adamas, 35415E); tetrahydrofuran (CAS: 109-99-9, Energy Chemical, W3100755000); 1,4-dioxane (CAS: 123-91-1, Adamas, 01375906); methanol (CAS: 67-56-1, Sinopharm, 10014118); *N*,*N*-dimethylacetamide (CAS: 127-19-5, Adamas, 011342855); potassium fluoride (CAS: 7789-23-3, Acros, 01163384); sodium carbonate anhydrous (CAS: 497-19-8, Sinopharm, 10019260).

^{1}H NMR, ^{13}C NMR, ^{11}B NMR and ^{19}F NMR spectra were recorded on Bruker 400 MHz spectrometer and Bruker 500 MHz spectrometer at 295 K in $CDCl_3$ unless otherwise noted. Data for ^{1}H NMR were reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. Data for ^{13}C NMR were reported as follows: chemical shift (δ ppm), multiplicity, and coupling constant (Hz); Data for ^{11}B NMR were reported as follows: chemical shift (δ ppm), multiplicity, and coupling constant (Hz). Data for ^{19}F NMR were reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz). Chemical shifts were reported using the residual solvent $CHCl_3$ as the internal reference for ^{1}H NMR (δ = 7.260 ppm) and $CDCl_3$ peak as the internal reference for ^{13}C NMR (δ = 77.160 ppm). High-resolution mass spectral analysis (HRMS) data were acquired on Water XEVO G2 Q-TOF (Waters Corporation). Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2010 plus Series GC system equipped with a flame-ionization detector. Organic solutions were concentrated under reduced pressure on Buchi rotary evaporator. Column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (300-400 mesh).

General procedure

In air, a 10 mL screw-cap test tube equipped with a magnetic stirrer was charged with L8 (0.03 mmol, 15 mol%), $NiBr_2$(diglyme) (0.02 mmol, 10 mol%), Na_2CO_3 (0.6 mmol, 3.0

equiv), TBAI (0.1 mmol, 0.5 equiv), Mg powder (0.1 mmol, 0.5 equiv) (if the nitroarene or the alkenes were solid, they were added at this step). The test tube was evacuated and backfilled with argon three times. Then, solvent (1,4-dioxane : MeOH = 5:1, 1.20 mL) was added, followed by the alkene (0.4 mmol, 2.0 equiv) and nitroarene (0.2 mmol, 1.0 equiv). Then, DEMS (2.0 mmol, 10.0 equiv) was added dropwise via a syringe, and the solution was stirred for 5 min at 25 °C, followed by stirring at 50 °C for 12 h. The reaction mixture was diluted with H_2O followed by extraction with EtOAc, dried with anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to obtain the target product. The yield represents the isolated yield of the major product. The reaction regioselectivity was determined by GC analysis of the reaction mixture. In a few cases, the reaction regioselectivity could not be determined by GC analysis; ^{1}H NMR determined regioisomeric ratios shown in the table after chromatography purification.

Supplementary Figures

N-hexylaniline (**3**): Following standard conditions, **3** was obtained as a light yellow oil (24.8 mg, 70% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 7.14 (m, 2H), 6.74 – 6.66 (m, 1H), 6.65 – 6.56 (m, 2H), 3.46 (brs, 1H), 3.11 (t, *J* = 7.1 Hz, 2H), 1.62 (p, *J* = 7.1 Hz, 2H), 1.47 – 1.29 (m, 6H), 0.93 – 0.89 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.6, 129.4, 117.3, 112.9, 44.2, 31.8, 29.7, 27.0, 22.8, 14.2. The NMR data were consistent with those reported in previous literature.[1] Regioselectivity was determined to be 6.3:1.0 *l*:*b* by GC analysis of the reaction mixture.

N-octylaniline (**5**): Following standard conditions, **5** was obtained as a light yellow oil (26.7 mg, 65% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.25 – 7.13 (m, 2H), 6.73 – 6.66 (m, 1H), 6.65 – 6.55 (m, 2H), 3.71 (brs, 1H), 3.11 (t, *J* = 7.2 Hz, 2H), 1.66 – 1.57 (m, 2H), 1.45 – 1.24 (m, 10H), 0.90 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.5, 129.3, 117.2, 112.9, 44.2, 31.9, 29.6, 29.5, 29.4, 27.3, 22.8, 14.2. The NMR data were consistent with those reported in previous literature.[2] Regioselectivity was determined to be 5.5:1.0 *l*:*b* by GC analysis of the reaction mixture.

N-(5-(naphthalen-2-yloxy)pentyl)aniline (**6**): Following standard conditions, **6** was obtained

as a colorless oil (34.8 mg, 57% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.68 (m, 3H), 7.50 – 7.43 (m, 1H), 7.39 – 7.29 (m, 1H), 7.23 – 7.10 (m, 4H), 6.78 – 6.67 (m, 1H), 6.67 – 6.57 (m, 2H), 4.10 (t, *J* = 6.4 Hz, 2H), 3.72 (brs, 1H), 3.18 (t, *J* = 6.9 Hz, 2H), 1.98 – 1.84 (m, 2H), 1.81 – 1.53 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.0, 148.4, 134.6, 129.4, 129.3, 128.9, 127.7, 126.8, 126.4, 123.6, 119.0, 117.3, 112.8, 106.5, 67.8, 44.0, 29.4, 29.1, 23.9. HRMS (ESI) calcd for $C_{21}H_{23}NONa^{+}$ [(M+Na)$^{+}$] 328.1672, found 328.1685. Regioselectivity was determined to be 7.4:1.0 *l*:*b* by GC analysis of the reaction mixture.

N-(4-(cyclohexyloxy)butyl)aniline (**7**): Following standard conditions, **7** was obtained as a light yellow oil (19.8 mg, 40% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.11 (m, 2H), 6.78 – 6.67 (m, 1H), 6.67 – 6.59 (m, 2H), 3.49 (t, *J* = 5.9 Hz, 2H), 3.27 – 3.18 (m, 1H), 3.15 (t, *J* = 6.5 Hz, 2H), 2.00 – 1.85 (m, 2H), 1.80 – 1.64 (m, 6H), 1.60 – 1.48 (m, 2H), 1.35 – 1.02 (m, 4H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 129.3, 128.0, 117.6, 113.2, 77.7, 67.6, 44.3, 32.5, 27.9, 26.4, 25.9, 24.3. HRMS (ESI) calcd for $C_{16}H_{26}NO^{+}$ [(M+H)$^{+}$] 248.2009, found 248.2014. Regioselectivity could not be determined by GC analysis. Regioisomeric ratio was determined to be >20:1.0 *l:b* by ^{1}H NMR after chromatography purification.

N-(4-(methyldiphenylsilyl)butyl)aniline (**8**): Following standard conditions, **8** was obtained as a light yellow oil (34.0 mg, 47% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.75 – 7.49 (m, 4H), 7.49 – 7.36 (m, 6H), 7.25 – 7.09 (m, 2H), 6.80 – 6.67 (m, 1H), 6.67 – 6.51 (m, 2H), 3.74 (t, *J* = 5.8 Hz, 2H), 3.10 (t, *J* = 6.6 Hz, 2H), 1.79 – 1.56 (m, 4H), 0.65 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 136.1, 134.4, 134.1, 130.0, 129.3, 128.0, 117.7, 113.2, 63.2, 44.2, 30.2, 25.9, 0.1. HRMS (ESI) calcd for $C_{23}H_{27}NOSiNa^{+}$ [(M+Na)$^{+}$] 384.1754, found 384.1763. Regioselectivity was determined to be 16:1.0 *l*:*b* by GC analysis of the reaction mixture.

4-(phenylamino)butyl benzoate (**9**): Following standard conditions, **9** was obtained as a light yellow oil (40.4 mg, 75% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 8.01 (m, 2H), 7.60 – 7.51 (m, 1H), 7.49 – 7.38 (m, 2H), 7.24 – 7.13 (m, 2H), 6.77 – 6.68 (m, 1H), 6.67 – 6.60 (m, 2H), 4.38 (t, *J* = 6.4 Hz, 2H), 3.21 (t, *J* = 7.0 Hz, 2H), 1.95 – 1.73 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7, 148.1, 133.0, 130.3, 129.6, 129.4, 128.5, 117.6, 113.0, 64.7, 43.7, 26.5, 26.2. The NMR data were consistent with those reported in

previous literature.[3] Regioselectivity could not be determined by GC analysis. Regioisomeric ratio was determined to be >20:1.0 *l*:*b* by ^{1}H NMR after chromatography purification.

4-(4-((5-(phenylamino)pentyl)oxy)phenyl)butan-2-one (**10**): Following standard conditions, **10** was obtained as a light yellow oil (38.1 mg, 54% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.13 (m, 2H), 7.13 – 7.07 (m, 2H), 6.84 – 6.80 (m, 2H), 6.75 – 6.68 (m, 1H), 6.67 – 6.57 (m, 2H), 3.95 (t, *J* = 6.4 Hz, 2H), 3.15 (t, *J* = 7.0 Hz, 2H), 2.95 – 2.63 (m, 4H), 2.14 (s, 3H), 1.91 – 1.51 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 208.4, 157.5, 148.3, 133.0, 129.3, 129.3, 117.4, 114.5, 112.9, 67.8, 45.5, 44.0, 30.2, 29.3, 29.2, 29.0, 23.8. HRMS (ESI) calcd for $C_{21}H_{27}NO_2Na^+$ [(M+Na)$^+$] 348.1934, found 348.1943. Regioselectivity was determined to be 7.3:1.0 *l*:*b* by GC analysis of the reaction mixture.

N-(6-(phenylamino)hexyl)pivalamide (**11**): Following standard conditions, **11** was obtained as a yellow oil (22.1 mg, 40% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 7.13 (m, 2H), 6.74 – 6.66 (m, 1H), 6.66 – 6.55 (m, 2H), 5.62 (brs, 1H), 3.30 – 3.16 (m, 2H), 3.10 (t, *J* = 7.1 Hz, 2H), 1.69 – 1.31 (m, 8H), 1.19 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.5, 148.3, 129.3, 117.4, 112.9, 44.0, 39.4, 38.7, 29.7, 29.4, 27.7, 26.8, 26.7. HRMS (ESI) calcd for $C_{17}H_{29}N_2O^+$ [(M+H)$^+$] 277.2274, found 277.2293. Regioselectivity was determined to be 7.1:1.0 *l*:*b* by GC analysis of the reaction mixture.

2-(4-(phenylamino)butyl)isoindoline-1,3-dione (**12**): Following standard conditions, **12** was obtained as a yellow oil (44.2 mg, 75% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.80 (m, 2H), 7.77 – 7.63 (m, 2H), 7.17 – 7.12 (m, 2H), 6.76 – 6.65 (m, 1H), 6.64 – 6.56 (m, 2H), 3.74 (t, *J* = 7.1 Hz, 2H), 3.16 (t, *J* = 7.0 Hz, 2H), 1.91 – 1.58 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.5, 148.1, 134.0, 132.1, 129.3, 123.3, 117.4, 112.9, 43.6, 37.7, 26.7, 26.3. HRMS (ESI) calcd for $C_{18}H_{18}N_2O_2Na^+$ [(M+Na)$^+$] 317.126, found 317.1272. Regioselectivity was determined to be 6.6:1.0 *l*:*b* by GC analysis of the reaction mixture.

5-(phenylamino)pentyl furan-2-carboxylate (**13**): Following standard conditions, **13** was obtained as a light yellow oil (19.2 mg, 35% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.56 (m, 1H), 7.20 – 7.15 (m, 3H), 6.75 – 6.66 (m, 1H), 6.66 – 6.59 (m, 2H), 6.58 – 6.47 (m, 1H), 4.33 (t, *J* = 6.6 Hz, 2H), 3.80 (brs, 1H), 3.14 (t, *J* = 7.1 Hz, 2H), 1.90 – 1.45 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.9, 148.2, 146.4, 144.8, 129.3, 117.9,

117.5, 112.9, 111.9, 64.9, 44.0, 29.2, 28.6, 23.6. HRMS (ESI) calcd for $C_{16}H_{19}NO_3Na^+$ [$(M+Na)^+$] 296.1257, found 296.1361. Regioselectivity could not be determined by GC analysis. Regioisomeric ratio was determined to be >20:1.0 *l*:*b* by ^{1}H NMR after chromatography purification.

N-(5-(1H-indol-1-yl)pentyl)aniline (**14**): Following standard conditions, **14** was obtained as a yellow oil (36.2 mg, 65% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.73 – 7.62 (m, 1H), 7.41 – 7.30 (m, 1H), 7.24 – 7.16 (m, 3H), 7.15 – 7.07 (m, 2H), 6.81 – 6.68 (m, 1H), 6.66 – 6.57 (m, 2H), 6.54 – 6.41 (m, 1H), 4.15 (t, *J* = 7.0 Hz, 2H), 3.09 (t, *J* = 7.0 Hz, 2H), 1.98 – 1.83 (m, 2H), 1.74 – 1.57 (m, 2H), 1.55 – 1.34 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.1, 136.0, 129.4, 128.7, 127.9, 121.5, 121.1, 119.3, 117.6, 113.0, 109.4, 101.1, 46.3, 44.0 (d, *J* = 2.6 Hz), 30.1, 29.2, 24.6. HRMS (ESI) calcd for $C_{19}H_{23}N_2^+$ [$(M+H)^+$] 279.1856, found 279.1859. Regioselectivity was determined to be 6.7:1.0 *l*:*b* by GC analysis of the reaction mixture.

1-(1-(5-(phenylamino)pentyl)-1H-pyrrol-2-yl)ethan-1-one (**15**): Following standard conditions, **15** was obtained as a light yellow oil (37.3 mg, 69% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.21 – 7.11 (m, 2H), 7.01 – 6.96 (m, 1H), 6.90 – 6.81 (m, 1H), 6.75 – 6.66 (m, 1H), 6.66 – 6.56 (m, 2H), 6.19 – 6.10 (m, 1H), 4.33 (t, *J* = 7.3 Hz, 2H), 3.10 (t, *J* = 7.1 Hz, 2H), 2.44 (s, 3H), 1.85 – 1.75 (m, 2H), 1.72 – 1.62 (m, 2H), 1.49 – 1.34 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 188.3, 148.4, 130.3, 130.1, 129.3, 120.4, 117.3, 112.9, 108.0, 49.7, 43.9, 31.3, 29.1, 27.4, 24.2. HRMS (ESI) calcd for $C_{17}H_{23}N_2O^+$ [$(M+H)^+$] 271.1805, found 271.1812. Regioselectivity was determined to be 8.6:1.0 *l*:*b* by GC analysis of the reaction mixture.

N-cyclohexylaniline (**16**): Following standard conditions, use **L1** instead of **L8** as ligand, **16** was obtained as a light yellow oil (28.8 mg, 82% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 – 7.12 (m, 2H), 6.72 – 6.63 (m, 1H), 6.63 – 6.56 (m, 2H), 3.71 (brs, 1H), 3.26 (tt, *J* = 10.1, 3.8 Hz, 1H), 2.11 – 2.01 (m, 2H), 1.82 – 1.72 (m, 2H), 1.71 – 1.61 (m, 1H), 1.45 – 1.31 (m, 2H), 1.29 – 1.23 (m, 1H), 1.21 – 1.09 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.4, 129.4, 117.0, 113.3, 51.8, 33.6, 26.0, 25.1. The NMR data were consistent with those reported in previous literature.[4]

N-cyclopentylaniline (**17**): Following standard conditions, use **L1** instead of **L8** as ligand,

17 was obtained as a light yellow oil (26.5 mg, 82% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 7.12 (m, 2H), 6.75 – 6.66 (m, 1H), 6.66 – 6.54 (m, 2H), 3.87 – 3.64 (m, 1H), 2.09 – 1.92 (m, 2H), 1.78 – 1.41 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.9, 129.3, 117.2, 113.4, 54.9, 33.6, 24.1. The NMR data were consistent with those reported in previous literature.[5]

N-phenylbicyclo[2.2.1]heptan-2-amine (**18**): Following standard conditions, use **L1** instead of **L8** as ligand, **18** was obtained as a light yellow oil (30.3 mg, 81% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 7.12 (m, 2H), 6.73 – 6.64 (m, 1H), 6.63 – 6.50 (m, 2H), 3.66 (brs, 1H), 3.24 (dd, *J* = 7.9, 3.5 Hz, 1H), 2.46 – 2.14 (m, 2H), 1.99 – 1.68 (m, 1H), 1.62 – 1.39 (m, 3H), 1.36 – 0.97 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.6, 129.3, 117.0, 113.3, 56.7, 41.3, 41.2, 35.7, 35.4, 28.5, 26.5. The NMR data were consistent with those reported in previous literature.[6]

N-cyclohexyl-4-methylaniline (**19**): Following standard conditions, use **L1** instead of **L8** as ligand, **19** was obtained as a light yellow oil (29.9 mg, 79% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.10 – 6.88 (m, 2H), 6.73 – 6.30 (m, 2H), 3.22 (tt, *J* = 9.8, 3.9 Hz, 1H), 2.23 (s, 3H), 2.10 – 1.99 (m, 2H), 1.81 – 1.60 (m, 3H), 1.42 – 1.07 (m, 5H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 145.2, 129.8, 126.2, 113.6, 52.1, 33.6, 26.1, 25.1, 20.4. The NMR data were consistent with those reported in previous literature.[7]

N-cyclohexyl-3-methylaniline (**20**): Following standard conditions, use **L1** instead of **L8** as ligand, **20** was obtained as a light yellow oil (29.2 mg, 77% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.05 (td, *J* = 7.2, 1.8 Hz, 1H), 6.49 (d, *J* = 7.5 Hz, 1H), 6.42 (d, *J* = 6.8 Hz, 2H), 3.24 (tt, *J* = 10.3, 3.8 Hz, 1H), 2.27 (s, 3H), 2.17 – 1.94 (m, 2H), 1.89 – 1.56 (m, 3H), 1.53 – 0.94 (m, 5H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 147.4, 139.1, 129.2, 118.0, 114.1, 110.5, 51.8, 33.6, 26.0, 25.1, 21.7. The NMR data were consistent with those reported in previous literature.[8]

N-cyclohexyl-2-fluoro-5-methylaniline (**21**): Following standard conditions, use **L1** instead of **L8** as ligand, **21** was obtained as a light yellow oil (33.2 mg, 80% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.94 – 6.65 (m, 1H), 6.62 – 6.47 (m, 1H), 6.47 – 6.20 (m, 1H), 3.76 (brs, 1H), 3.25 (tt, *J* = 10.1, 3.8 Hz, 1H), 2.27 (s, 3H), 2.17 – 1.97 (m, 2H), 1.85 – 1.64 (m, 3H), 1.53 – 1.06 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.0 (d, *J* = 234.9 Hz),

135.5, 134.0 (d, *J* = 3.3 Hz), 116.4 (d, *J* = 6.6 Hz), 114.2 (d, *J* = 18.7 Hz), 113.4 (d, *J* = 3.4 Hz), 51.6, 33.5, 26.0, 25.1, 21.4. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -141.5. HRMS (ESI) calcd for $C_{13}H_{19}FN^+$ [(M+H)$^+$] 208.1496, found 208.1503.

2-chloro-*N*-cyclohexyl-4-methylaniline (**22**): Following standard conditions, use **L1** instead of **L8** as ligand, **22** was obtained as a light yellow oil (25.1 mg, 56% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.11 – 7.04 (m, 1H), 6.98 – 6.88 (m, 1H), 6.68 – 6.55 (m, 1H), 4.15 (brs, 1H), 3.27 (tt, *J* = 9.9, 3.7 Hz, 1H), 2.21 (s, 3H), 2.13 – 1.89 (m, 2H), 1.82 – 1.52 (m, 3H), 1.46 – 1.06 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 129.8, 129.6, 128.4, 128.3, 52.0, 33.3, 26.0, 25.0, 20.2. HRMS (ESI) calcd for $C_{13}H_{19}ClN^+$ [(M+H)$^+$] 224.1201, found 224.1206.

3-bromo-*N*-cyclohexyl-5-methylaniline (**23**): Following standard conditions, use **L1** instead of **L8** as ligand, **23** was obtained as a light yellow oil (41.7 mg, 78% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.11 – 7.01 (m, 1H), 6.56 – 6.46 (m, 1H), 6.45 – 6.38 (m, 2H), 3.24 (tt, *J* = 10.2, 3.8 Hz, 1H), 2.27 (s, 3H), 2.08 – 1.99 (m, 2H), 1.82 – 1.72 (m, 2H), 1.71 – 1.57 (m, 1H), 1.46 – 1.31 (m, 2H), 1.29 – 1.08 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.3, 139.1, 129.2, 118.0, 114.1, 110.4, 51.8, 33.6, 26.0, 25.1, 21.7. HRMS (ESI) calcd for $C_{13}H_{19}BrN^+$ [(M+H)$^+$] 268.0696, found 268.0705.

methyl 3-(cyclohexylamino)benzoate (**24**): Following standard conditions, use **L1** instead of **L8** as ligand, **24** was obtained as a light yellow oil (35.4 mg, 76% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.29 (m, 1H), 7.27 – 7.23 (m, 1H), 7.22 – 7.17 (m, 1H), 6.80 – 6.72 (m, 1H), 3.88 (s, 3H), 3.53 (brs, 1H), 3.30 (tt, *J* = 10.2, 3.8 Hz, 1H), 2.12 – 1.94 (m, 2H), 1.81 – 1.58 (m, 3H), 1.46 – 1.02 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.7, 147.4, 131.1, 129.3, 118.0, 117.7, 113.8, 52.1, 51.7, 33.4, 25.9, 25.0. The NMR data were consistent with those reported in previous literature.[9]

1-(3-(cyclohexylamino)phenyl)ethan-1-one (**25**): Following standard conditions, use **L1** instead of **L8** as ligand, **25** was obtained as a light yellow oil (32.1 mg, 74% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.20 (m, 2H), 7.19 – 7.13 (m, 1H), 6.81 – 6.74 (m, 1H), 3.79 (brs, 1H), 3.31 (tt, *J* = 10.2, 3.8 Hz, 1H), 2.56 (s, 3H), 2.16 – 1.93 (m, 2H), 1.85 – 1.60 (m, 3H), 1.50 – 1.03 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.9, 147.5, 138.2, 129.4, 118.0, 117.4, 112.0, 51.7, 33.3, 26.8, 25.9, 25.0. The NMR data were consistent

with those reported in previous literature.[10]

1-(4-(cyclohexylamino)phenyl)propan-2-one (**26**): Following standard conditions, use **L1** instead of **L8** as ligand, **26** was obtained as a light yellow oil (19.4 mg, 42% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.07 – 6.86 (m, 2H), 6.65 – 6.45 (m, 2H), 3.54 (s, 2H), 3.23 (tt, *J* = 10.2, 3.8 Hz, 1H), 2.11 (s, 3H), 2.08 – 1.96 (m, 2H), 1.86 – 1.60 (m, 3H), 1.50 – 1.07 (m, 5H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 207.8, 146.4, 130.3, 122.4, 113.5, 51.9, 50.4, 33.5, 29.0, 26.0, 25.1. HRMS (ESI) calcd for $C_{15}H_{21}NONa^{+}$ [(M+Na)$^{+}$] 254.1515, found 254.1523.

N-cyclohexyl-4-(methylthio)aniline (**27**): Following standard conditions, use **L1** instead of **L8** as ligand, **27** was obtained as a light yellow oil (23.1 mg, 52% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.17 (m, 2H), 6.60 – 6.46 (m, 2H), 3.22 (tt, *J* = 10.2, 3.8 Hz, 1H), 2.40 (s, 3H), 2.13 – 1.95 (m, 2H), 1.86 – 1.70 (m, 2H), 1.71 – 1.58 (m, 1H), 1.43 – 1.29 (m, 2H), 1.28 – 1.02 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.3, 131.9, 123.5, 113.8, 51.8, 33.4, 25.9, 25.1, 19.5. HRMS (ESI) calcd for $C_{13}H_{20}NS^{+}$ [(M+H)$^{+}$] 222.1311, found 222.1317.

2-(4-(cyclohexylamino)phenyl)acetonitrile (**28**): Following standard conditions, use **L1** instead of **L8** as ligand, **28** was obtained as a light yellow oil (32.1 mg, 75% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.14 – 7.02 (m, 2H), 6.65 – 6.48 (m, 2H), 3.68 (brs, 1H), 3.61 (s, 2H), 3.24 (tt, *J* = 10.2, 3.7 Hz, 1H), 2.12 – 2.00 (m, 2H), 1.83 – 1.59 (m, 3H), 1.47 – 0.96 (m, 5H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 147.1, 129.0, 118.8, 117.5, 113.5, 51.8, 33.4, 25.9, 25.0, 22.8. HRMS (ESI) calcd for $C_{14}H_{19}FN_{2}^{+}$ [(M+H)$^{+}$] 215.1543, found 215.1550.

N-cyclohexyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (**29**): Following standard conditions, use **L1** instead of **L8** as ligand, **29** was obtained as a light yellow oil (48.8 mg, 81% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.51 (m, 2H), 6.67 – 6.42 (m, 2H), 3.30 (tt, *J* = 10.1, 3.8 Hz, 1H), 2.14 – 1.94 (m, 2H), 1.82 – 1.57 (m, 3H), 1.53 – 1.02 (m, 17H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.5, 112.4, 83.2, 51.5, 33.3, 25.9, 25.0, 24.9. ^{11}B NMR (160 MHz, Chloroform-*d*) δ 31.1. HRMS (ESI) calcd for $C_{18}H_{29}BNO_{2}^{+}$ [(M+H)$^{+}$] 302.2286, found 302.2294.

4-(cyclohexylamino)phenyl trifluoromethanesulfonate (**30**): Following standard conditions,

use **L1** instead of **L8** as ligand, **30** was obtained as a light yellow oil (46.5 mg, 72% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.10 – 6.89 (m, 2H), 6.70 – 6.37 (m, 2H), 3.83 (brs, 1H), 3.21 (tt, *J* = 9.9, 3.9 Hz, 1H), 2.13 – 1.84 (m, 2H), 1.83 – 1.58 (m, 3H), 1.45 – 1.04 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.1, 140.4, 122.2, 118.9 (q, *J* = 321.1 Hz), 113.2, 51.9, 33.2, 25.8, 25.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -72.8. HRMS (ESI) calcd for $C_{13}H_{17}F_3NO_3S^+$ [(M+H)$^+$] 324.0876, found 324.0875.

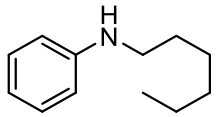
2-(4-(cyclohexylamino)phenyl)ethan-1-ol (**31**): Following standard conditions, use **L1** instead of **L8** as ligand, **31** was obtained as a light yellow oil (9.7 mg, 22% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.13 – 6.90 (m, 2H), 6.70 – 6.31 (m, 2H), 3.78 (t, *J* = 6.5 Hz, 2H), 3.22 (tt, *J* = 10.2, 3.8 Hz, 1H), 2.74 (t, *J* = 6.5 Hz, 2H), 2.26 – 1.93 (m, 2H), 1.87 – 1.51 (m, 3H), 1.48 – 1.01 (m, 5H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 145.8, 130.0, 126.7, 113.8, 64.0, 52.2, 38.3, 33.5, 26.0, 25.1. The NMR data were consistent with those reported in previous literature.[11]

4-(phenylamino)butyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (**41**): Following standard conditions, **41** was obtained as a light yellow oil (38.4 mg, 38% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.70 – 7.59 (m, 2H), 7.49 – 7.42 (m, 2H), 7.22 – 7.13 (m, 2H), 7.00 – 6.95 (m, 1H), 6.93 – 6.81 (m, 1H), 6.75 – 6.64 (m, 2H), 6.61 – 6.53 (m, 2H), 4.22 – 4.06 (m, 2H), 3.82 (s, 3H), 3.67 (s, 2H), 3.24 – 2.83 (m, 2H), 2.39 (s, 3H), 1.84 – 1.53 (m, 4H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.0, 168.5, 156.1, 146.9, 139.4, 136.1, 133.9, 132.9, 131.3, 129.8, 129.4, 129.2, 128.8, 117.7, 115.1, 113.0, 111.6, 101.5, 64.8, 55.8, 43.7, 30.5, 26.3, 26.0, 13.5. Regioselectivity could not be determined by GC analysis. Regioisomeric ratio was determined to be >20:1.0 *l:b* by ^{1}H NMR after chromatography purification.

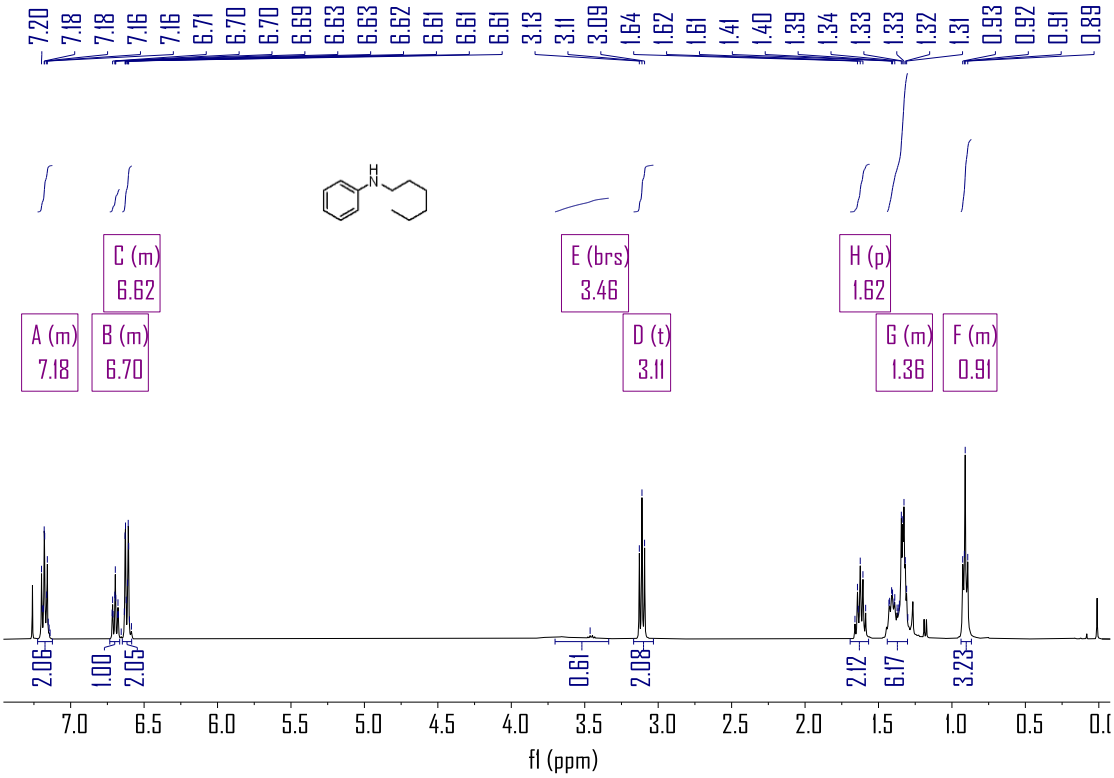
4-(phenylamino)butyl 2-(6-chloro-9*H*-carbazol-2-yl)propanoate (**42**): Following standard conditions, **42** was obtained as a light yellow oil (37.9 mg, 45% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.03 (brs, 1H), 7.99 – 7.90 (m, 2H), 7.39 – 7.33 (m, 2H), 7.30 – 7.27 (m, 1H), 7.19 – 7.13 (m, 3H), 6.75 – 6.70 (m, 1H), 6.61 – 6.49 (m, 2H), 4.18 – 4.00 (m, 2H), 3.91 – 3.81 (m, 1H), 3.14 – 2.91 (m, 2H), 1.73 – 1.45 (m, 7H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 174.8, 140.4, 139.5, 138.2, 131.8, 129.5, 125.9, 125.1, 124.4, 121.7, 120.7, 120.1, 119.7, 118.0, 113.2, 111.7, 109.7, 64.5, 46.1, 43.8, 26.2, 25.9, 18.8. Regioselectivity

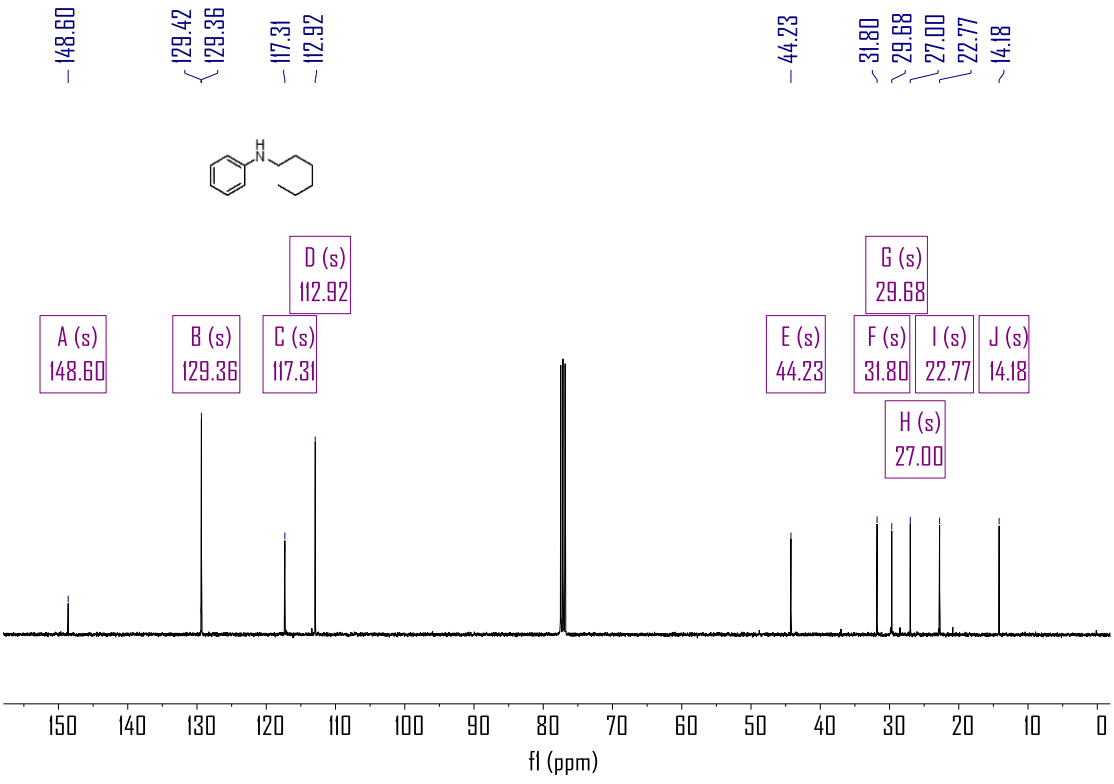
could not be determined by GC analysis. Regioisomeric ratio was determined to be >20:1.0 *l:b* by ^{1}H NMR after chromatography purification.

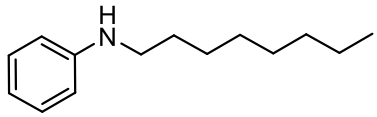
4-(phenylamino)butyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (**43**): Following standard conditions, **43** was obtained as a light yellow oil (22.7 mg, 30% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.83 – 7.62 (m, 3H), 7.53 – 7.35 (m, 1H), 7.18 – 7.06 (m, 4H), 6.81 – 6.66 (m, 1H), 6.60 – 6.50 (m, 2H), 4.16 – 4.04 (m, 2H), 3.91 (s, 3H), 3.87 – 3.80 (m, 1H), 3.06 – 3.00 (m, 2H), 1.80 – 1.46 (m, 7H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 174.8, 157.7, 135.8, 133.8, 129.4, 129.3, 129.0, 127.2, 126.3, 126.0, 119.2, 117.8, 113.2, 105.7, 64.4, 55.4, 45.6, 43.8, 26.3, 25.8, 18.5. Regioselectivity could not be determined by GC analysis. Regioisomeric ratio was determined to be >20:1.0 *l:b* by ^{1}H NMR after chromatography purification.



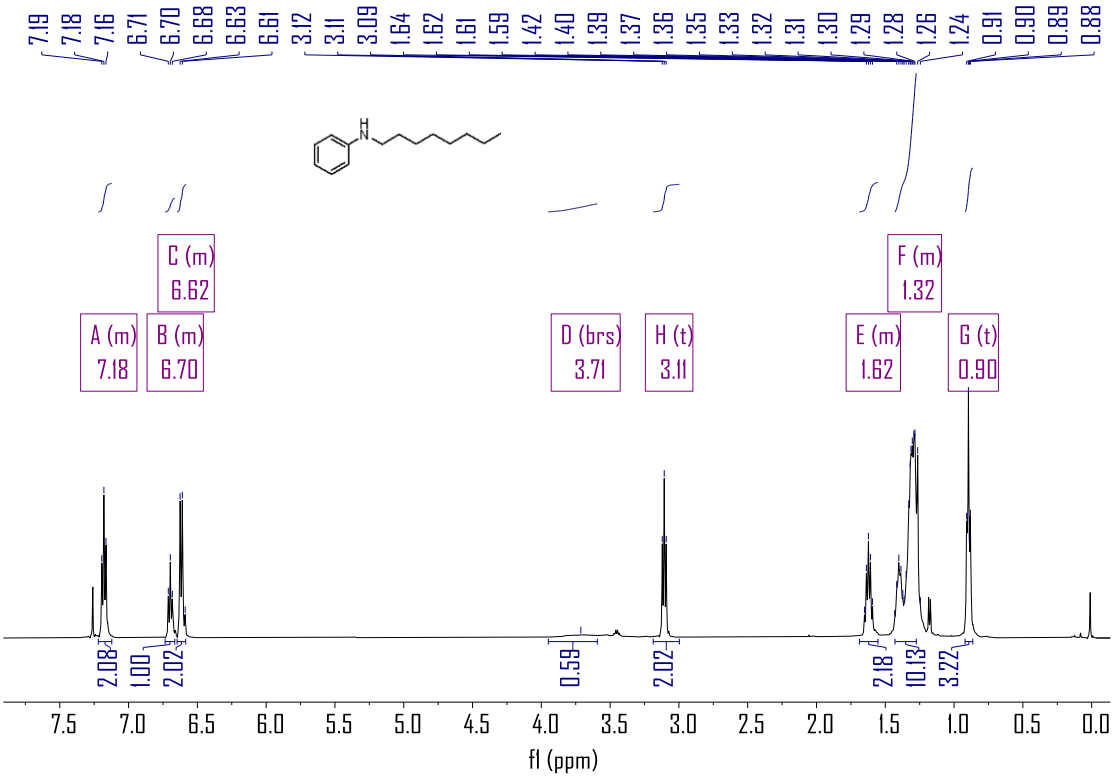
N-hexylaniline **(3)**

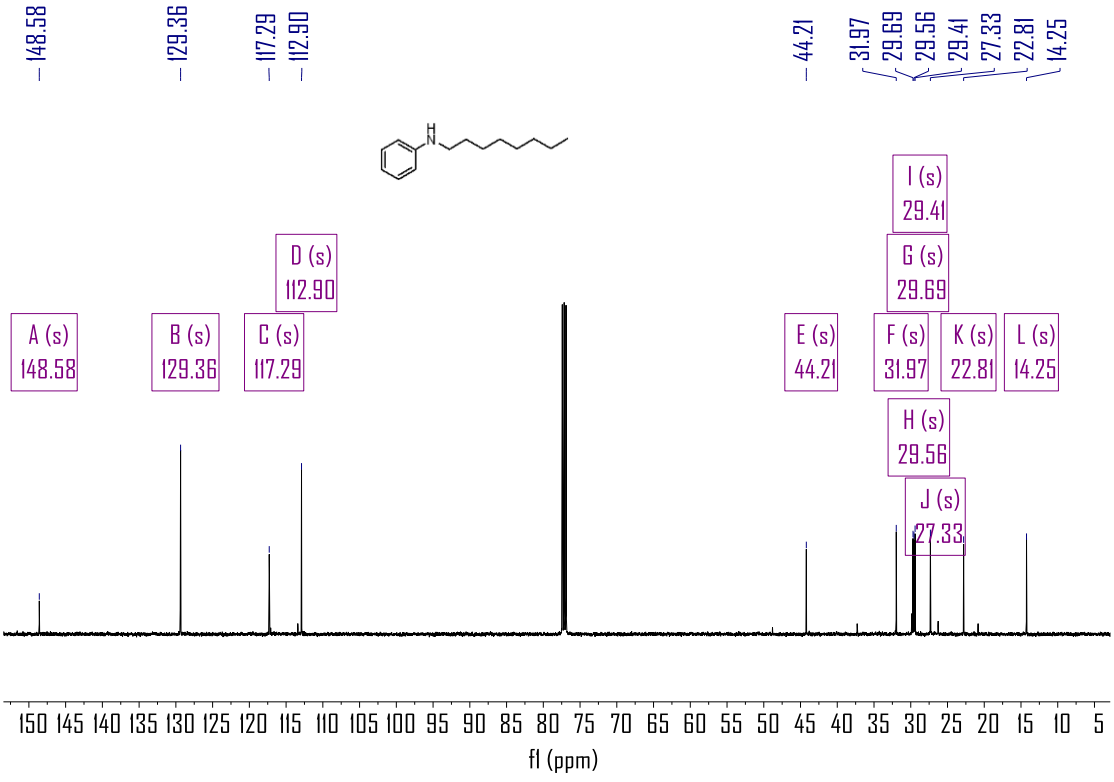


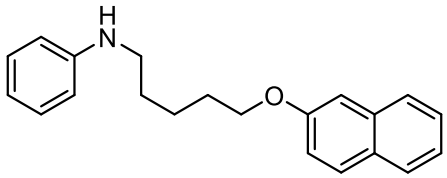




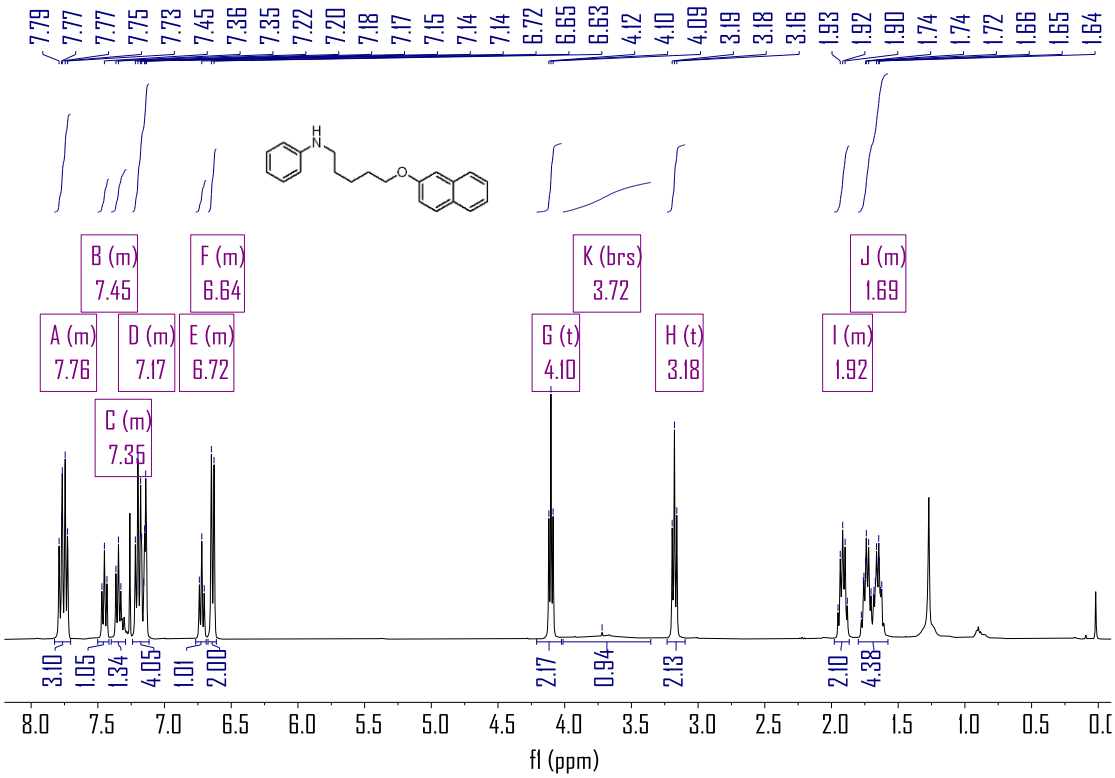
N-octylaniline **(5)**

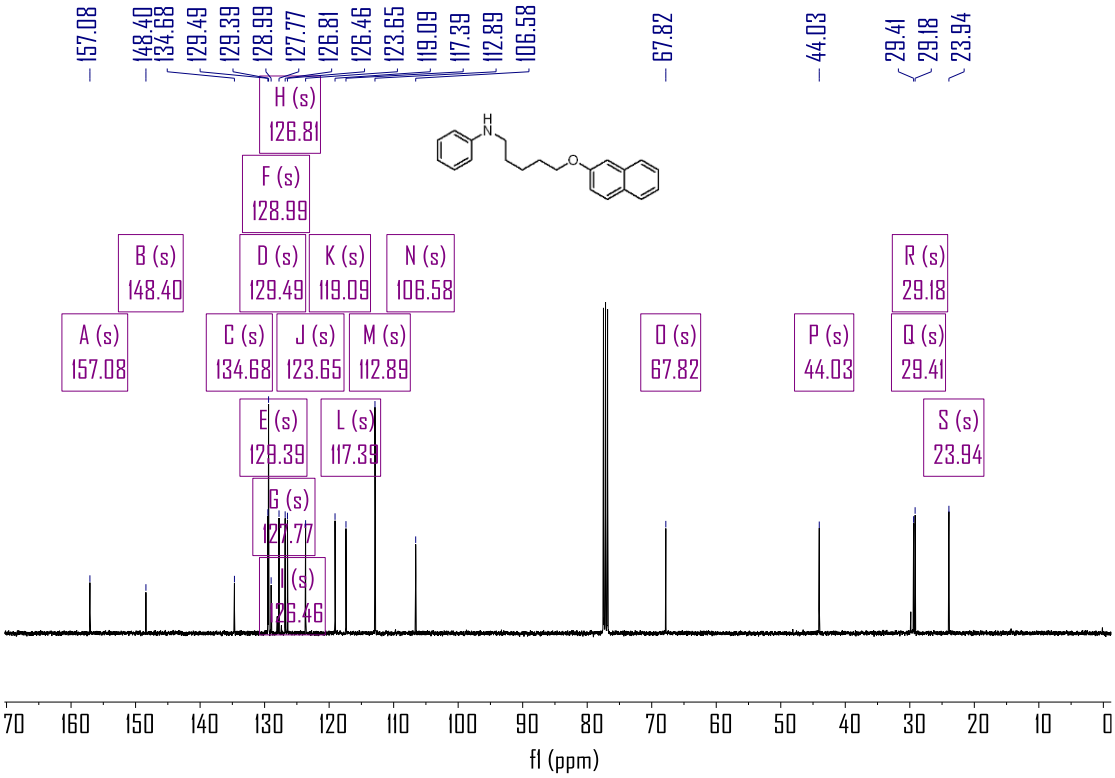


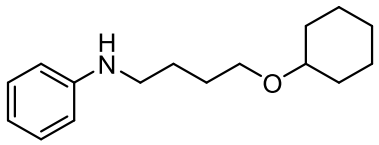




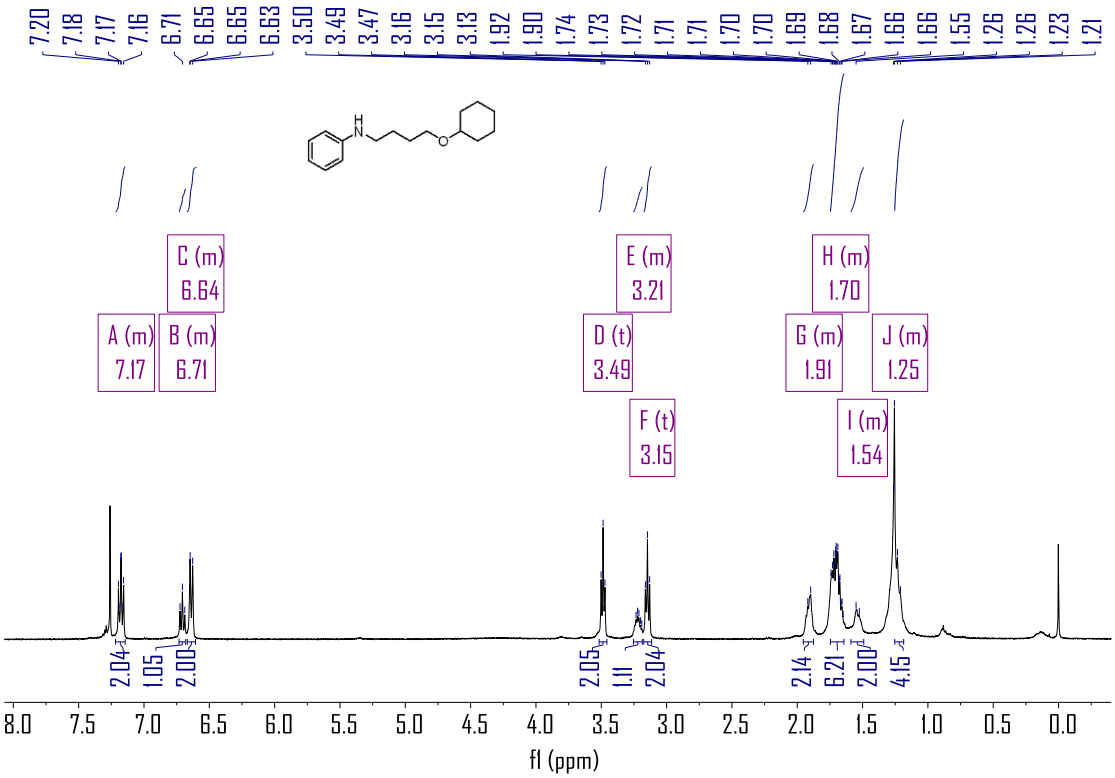
N-(5-(naphthalen-2-yloxy)pentyl)aniline **(6)**

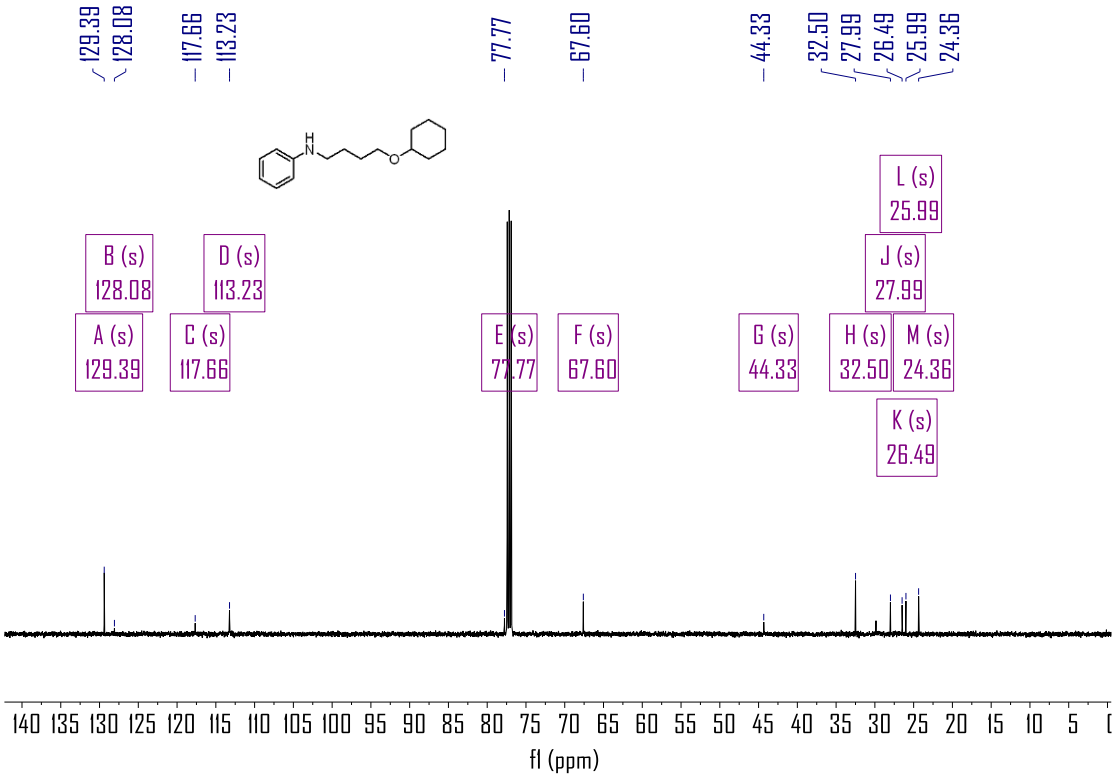


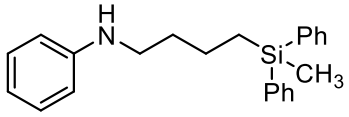




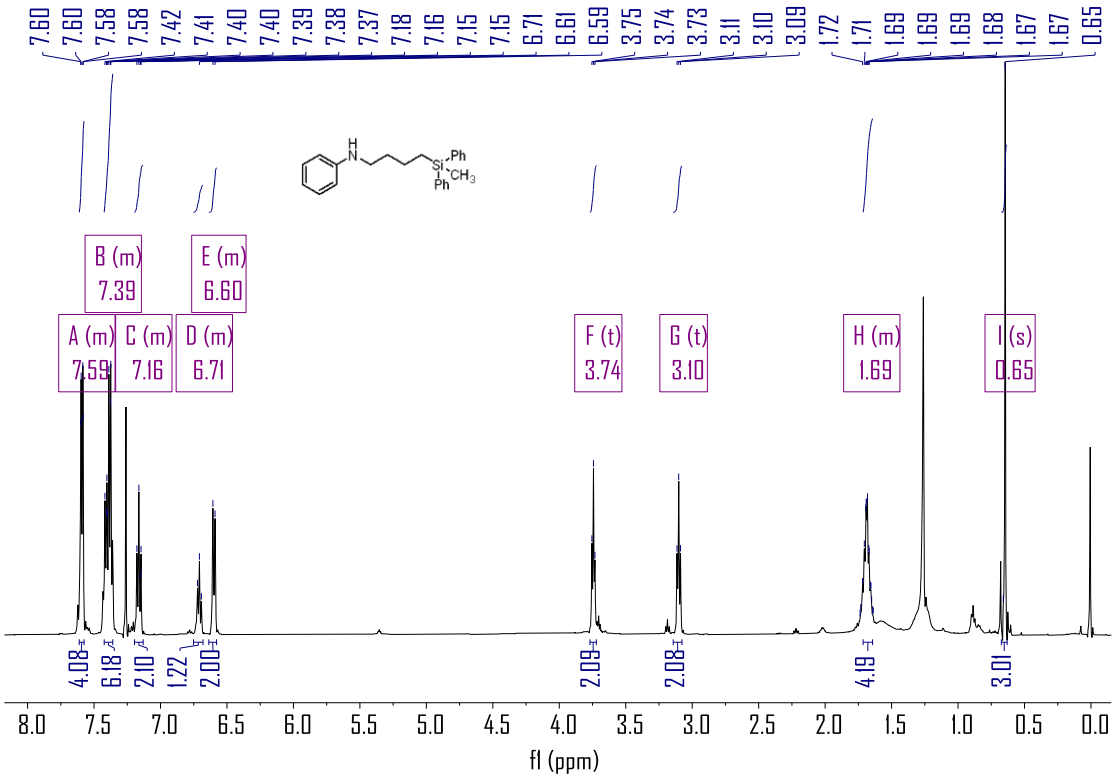
N-(4-(cyclohexyloxy)butyl)aniline **(7)**

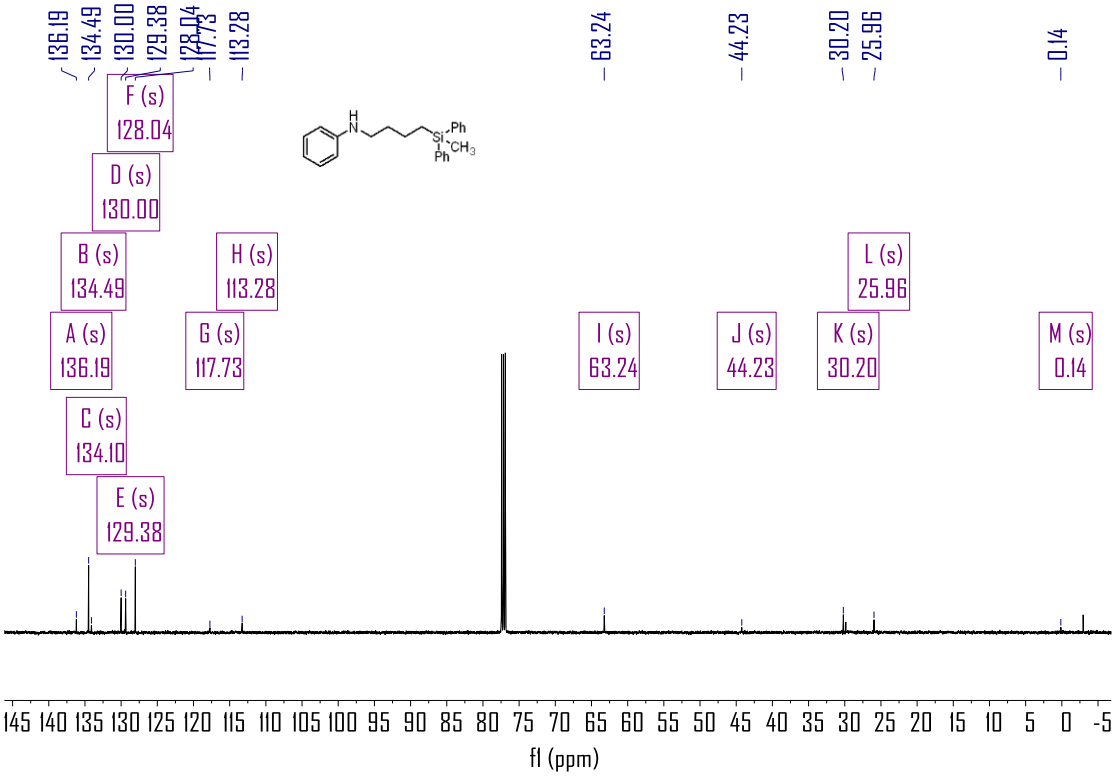


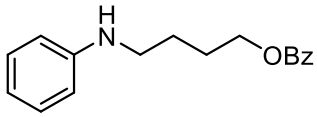




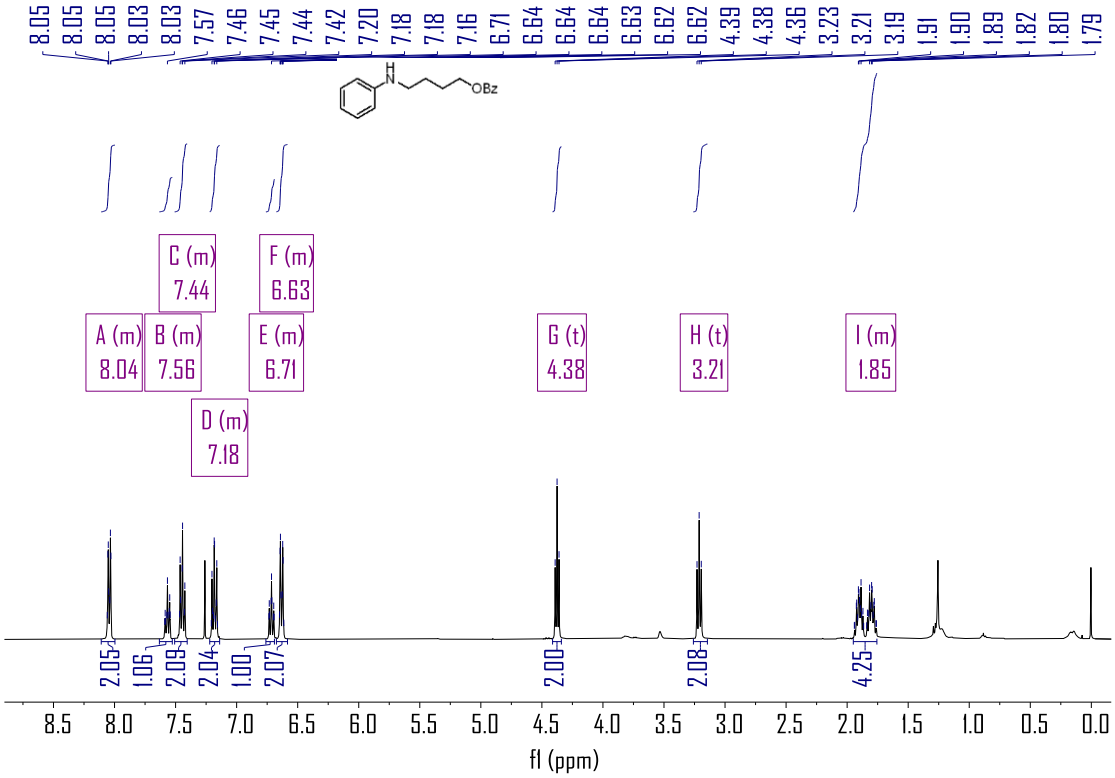
N-(4-(methyldiphenylsilyl)butyl)aniline **(8)**

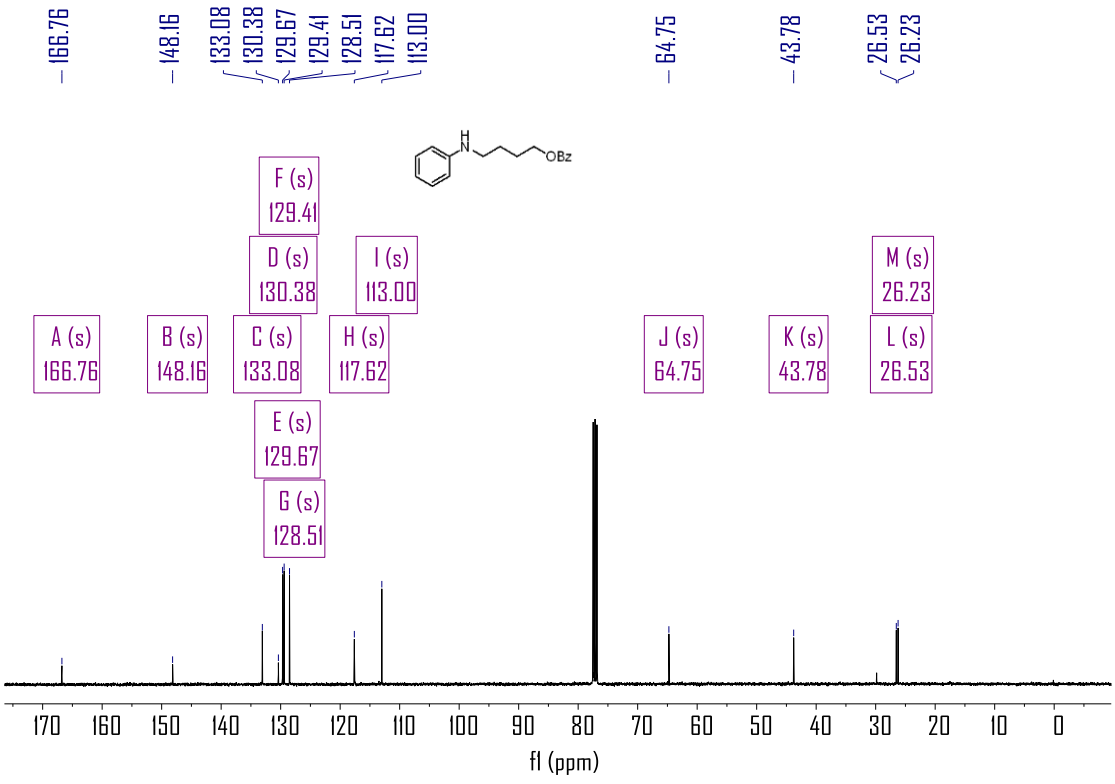


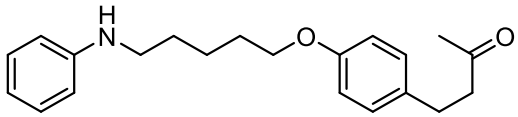




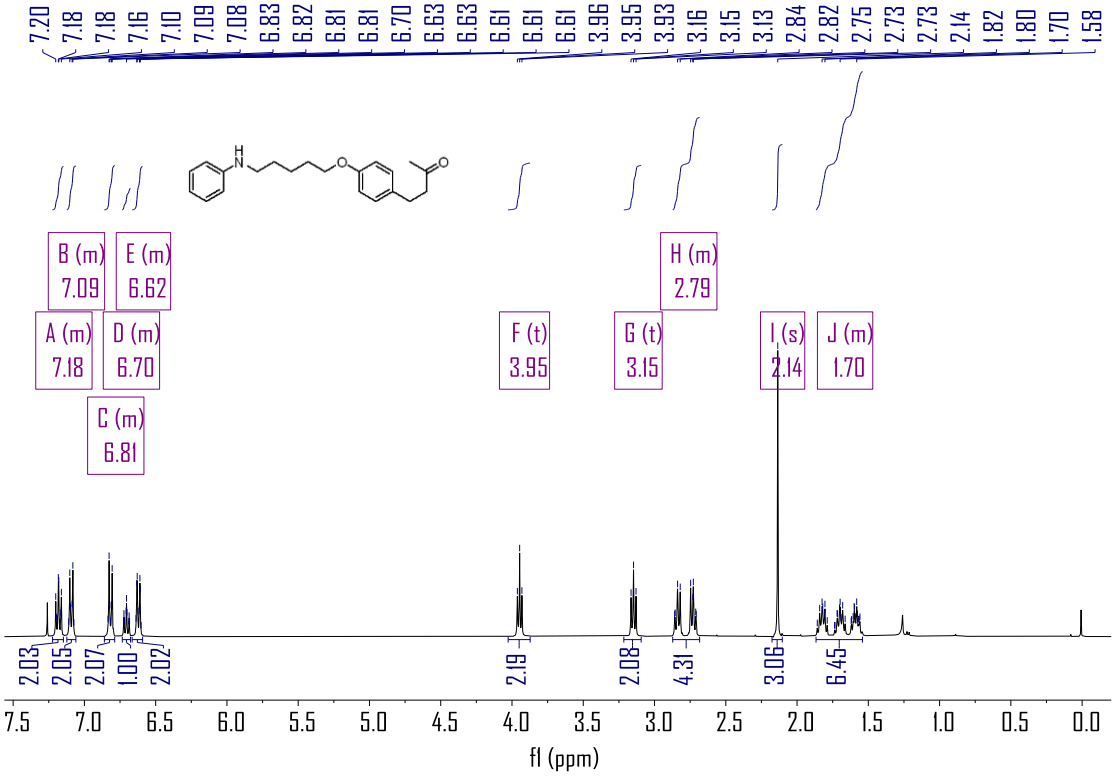
4-(phenylamino)butyl benzoate **(9)**

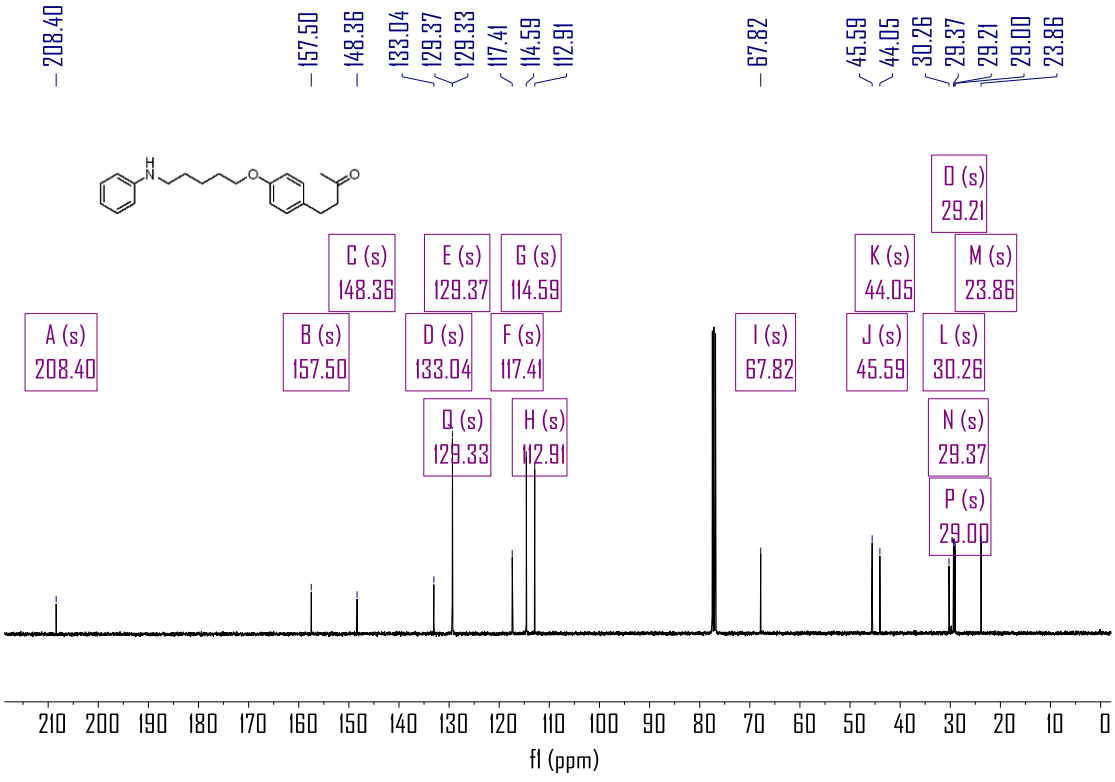


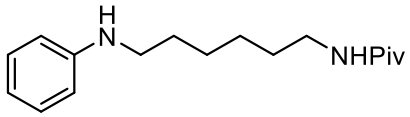




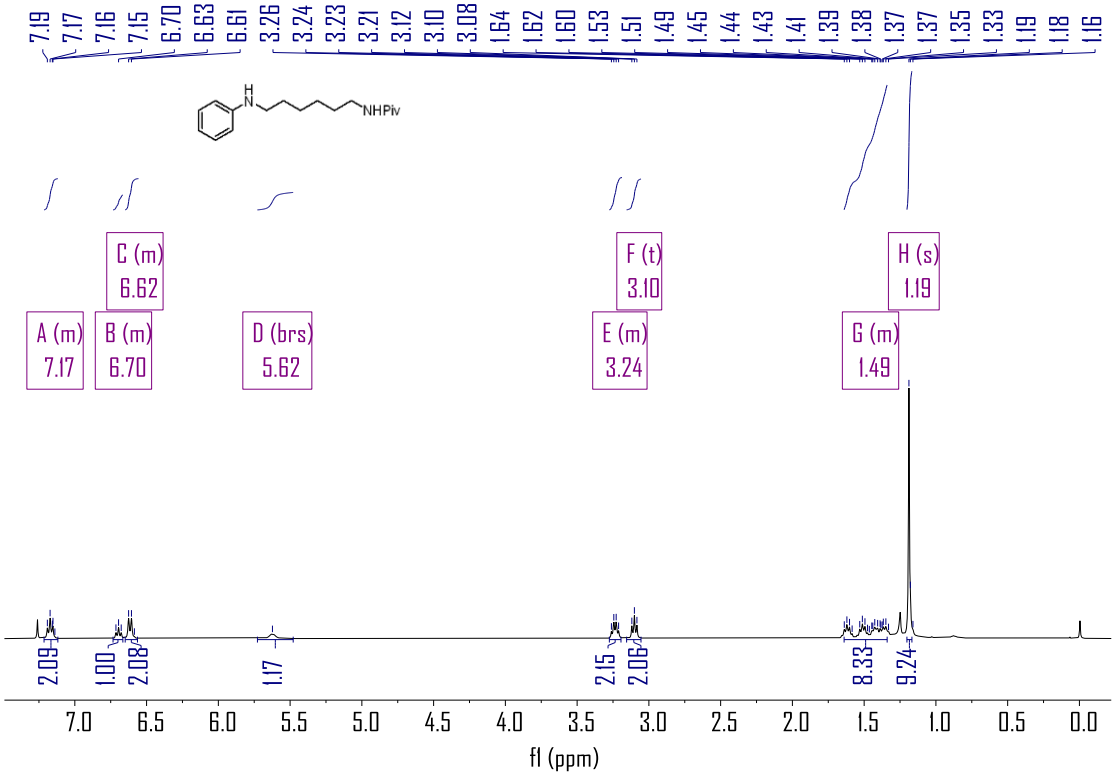
4-(4-((5-(phenylamino)pentyl)oxy)phenyl)butan-2-one **(10)**

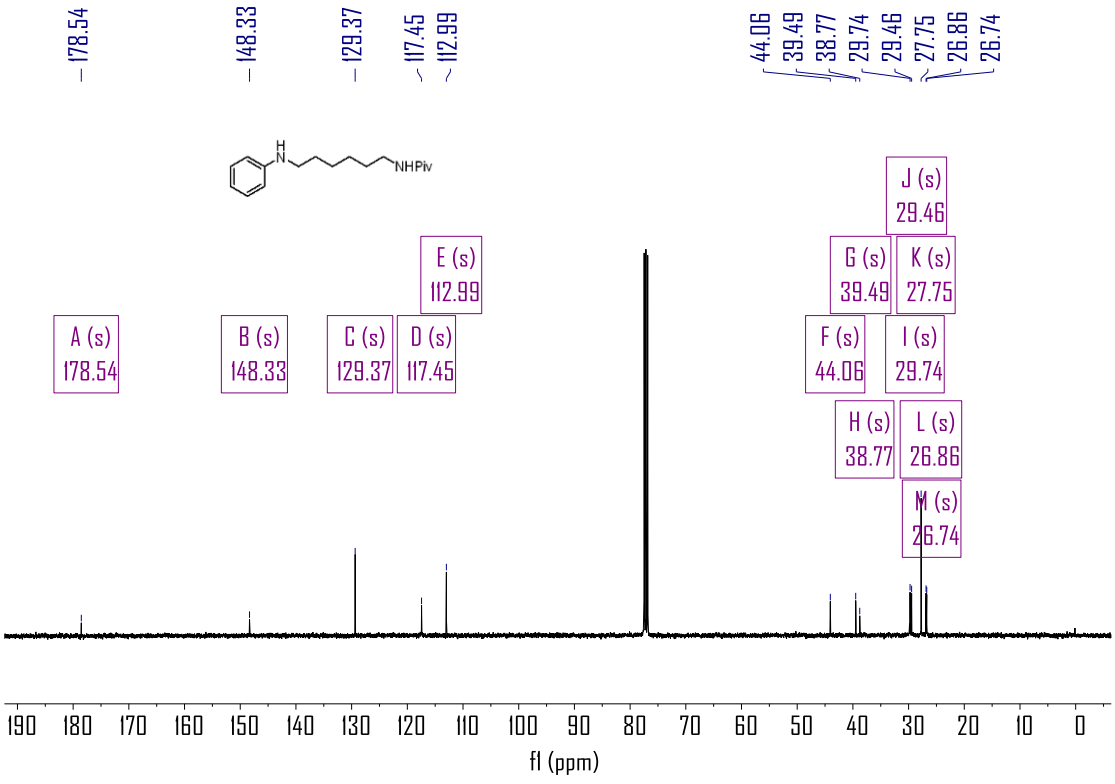


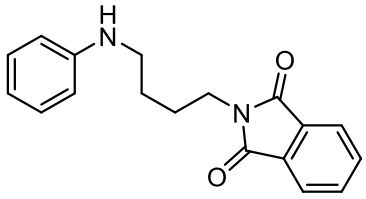




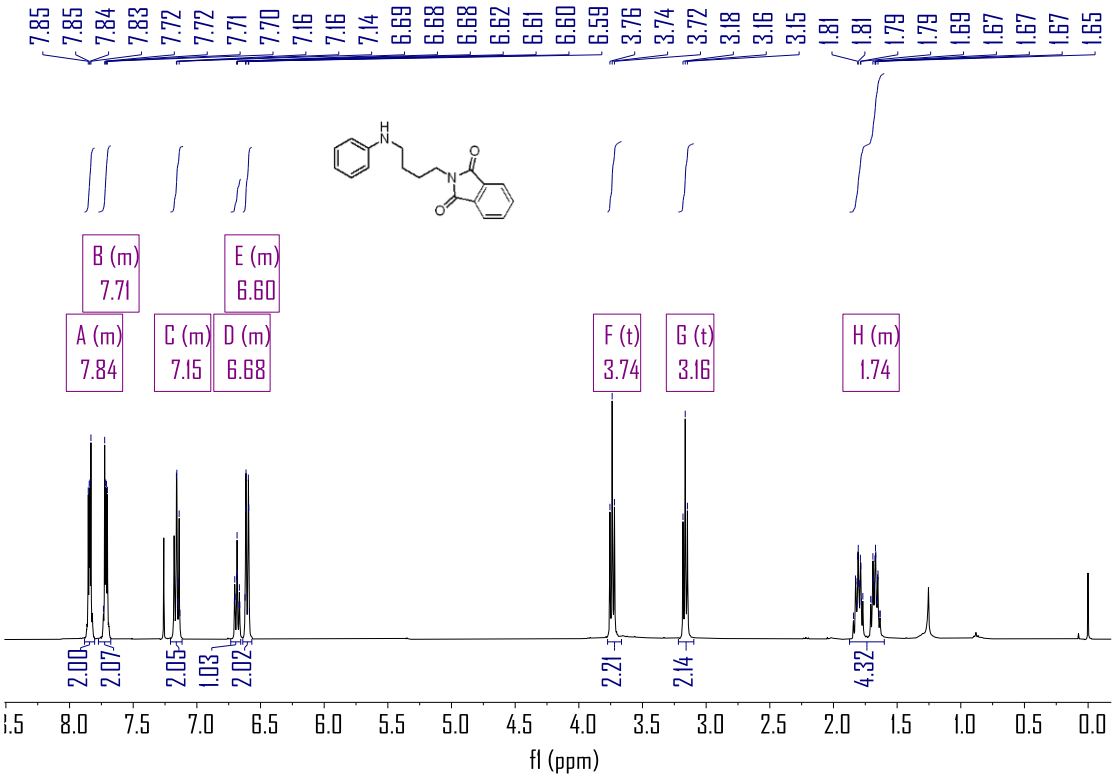
N-(6-(phenylamino)hexyl)pivalamide **(11)**

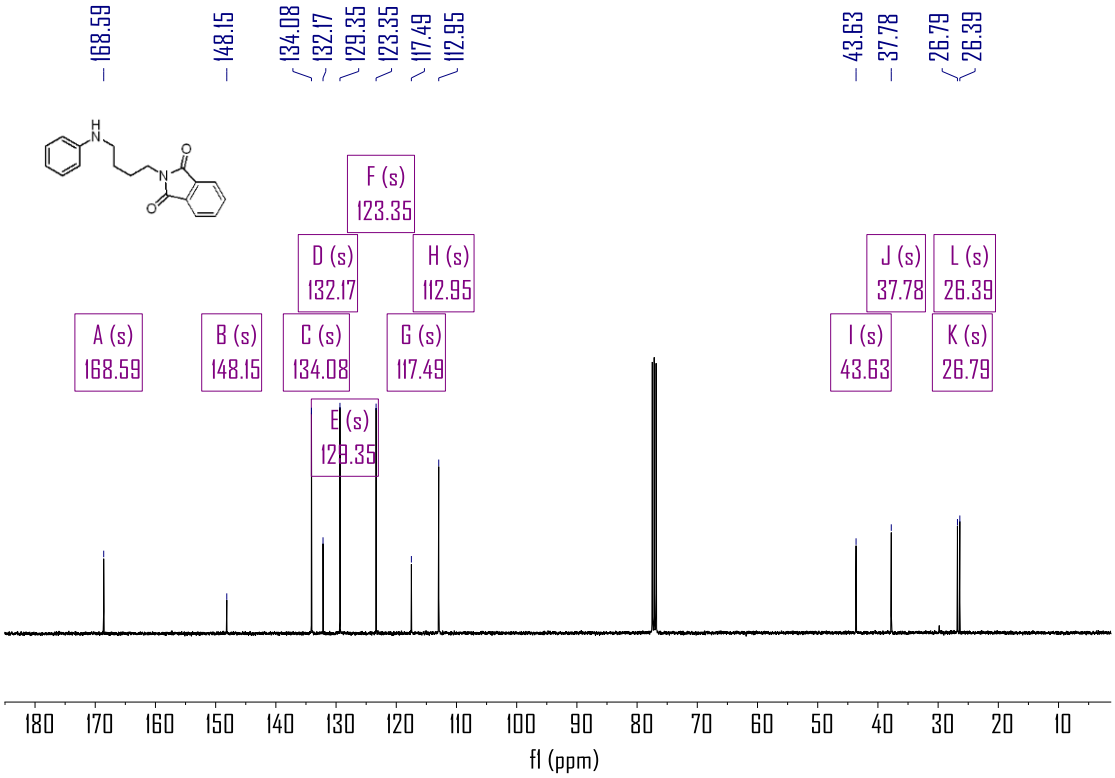


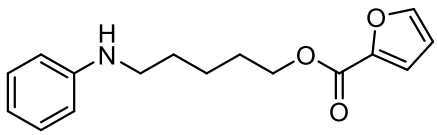




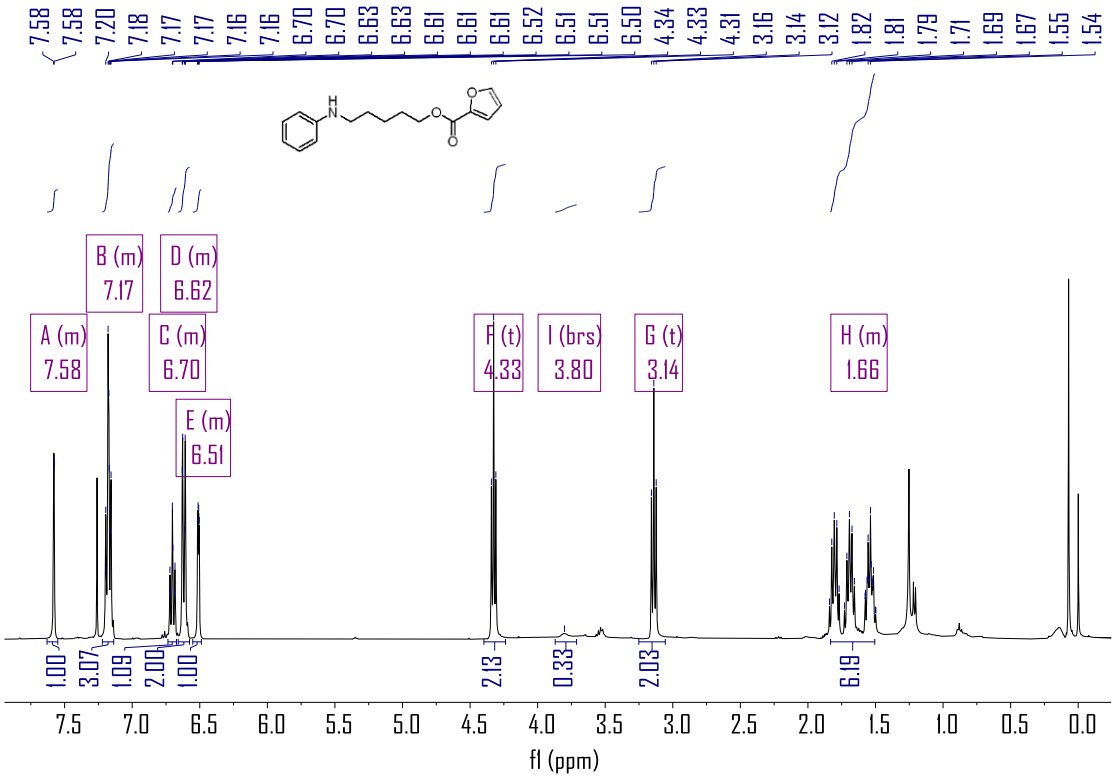
2-(4-(phenylamino)butyl)isoindoline-1,3-dione **(12)**

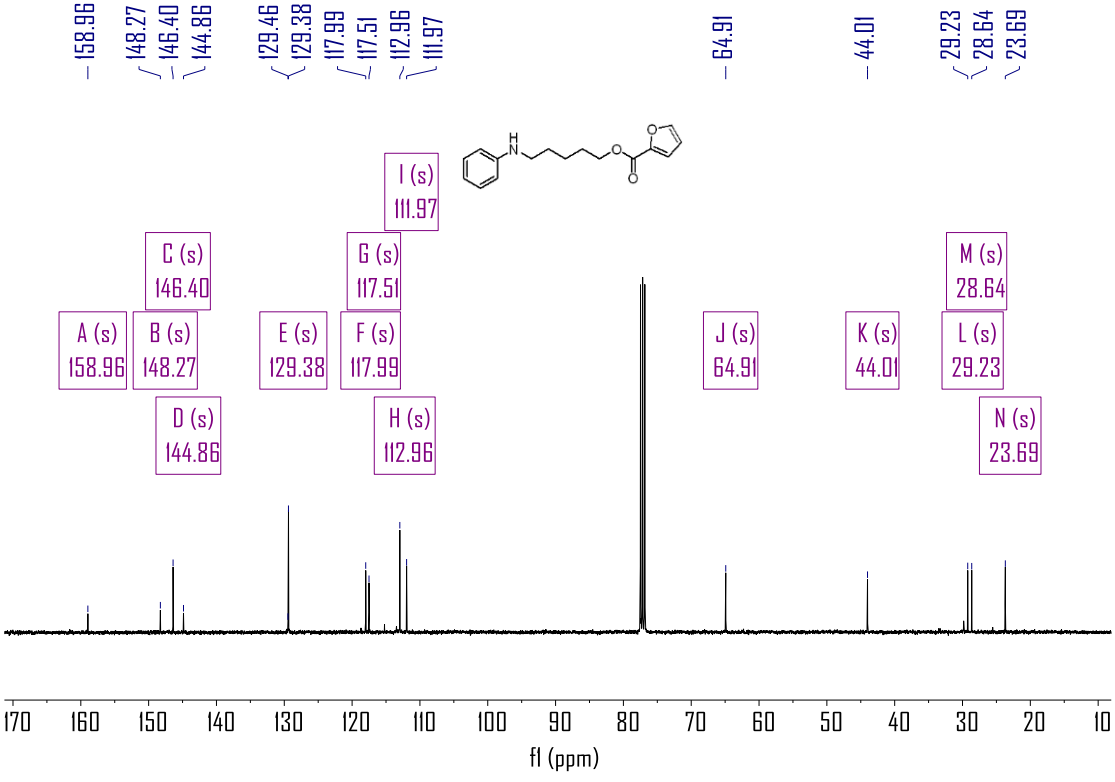


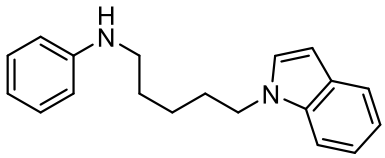




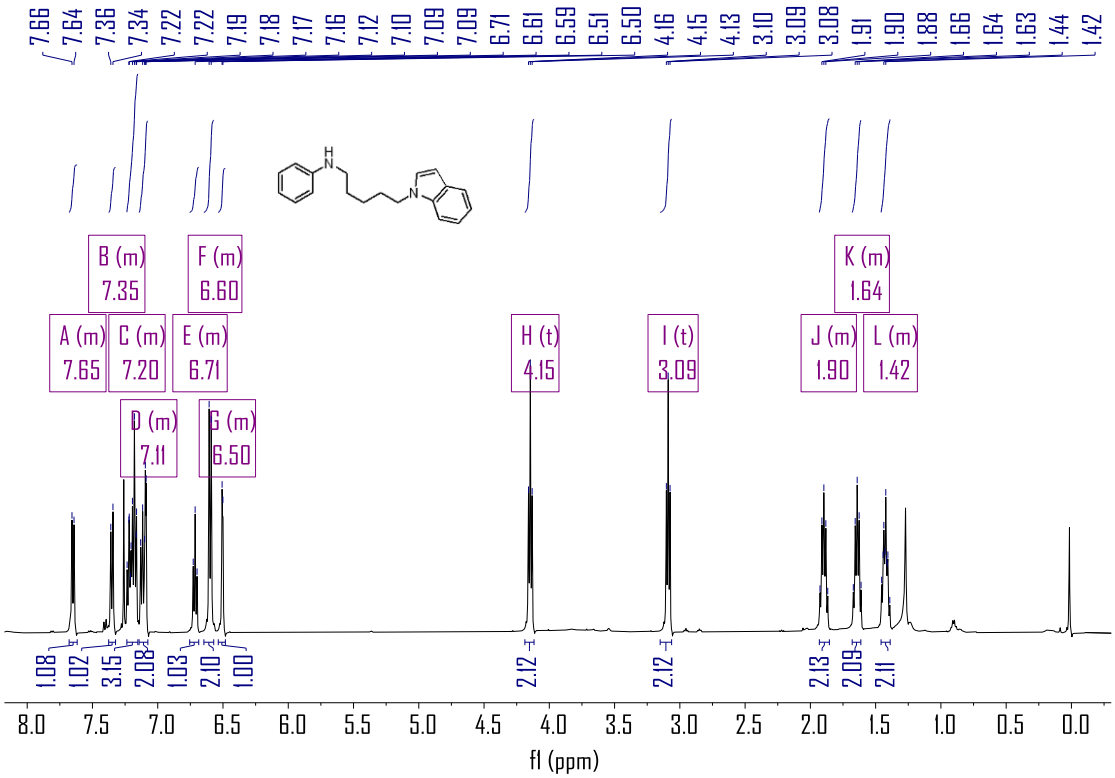
5-(phenylamino)pentyl furan-2-carboxylate **(13)**

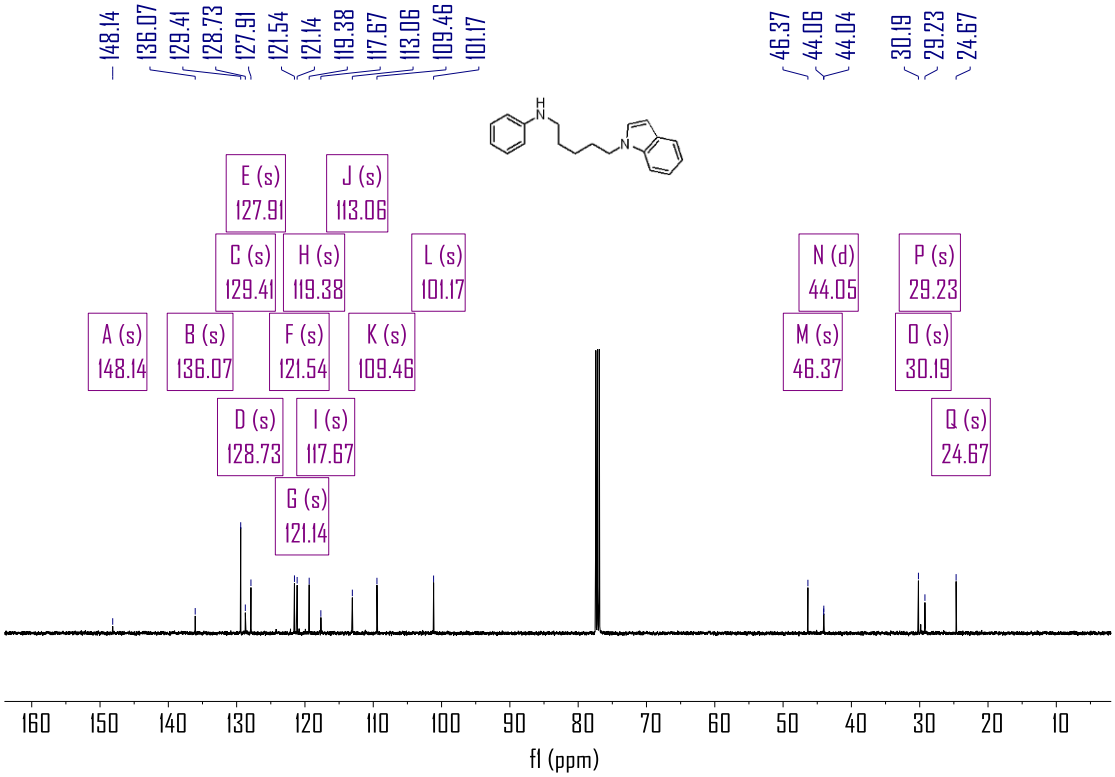


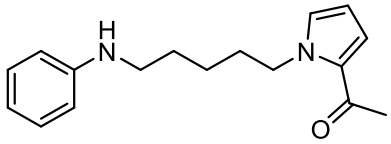




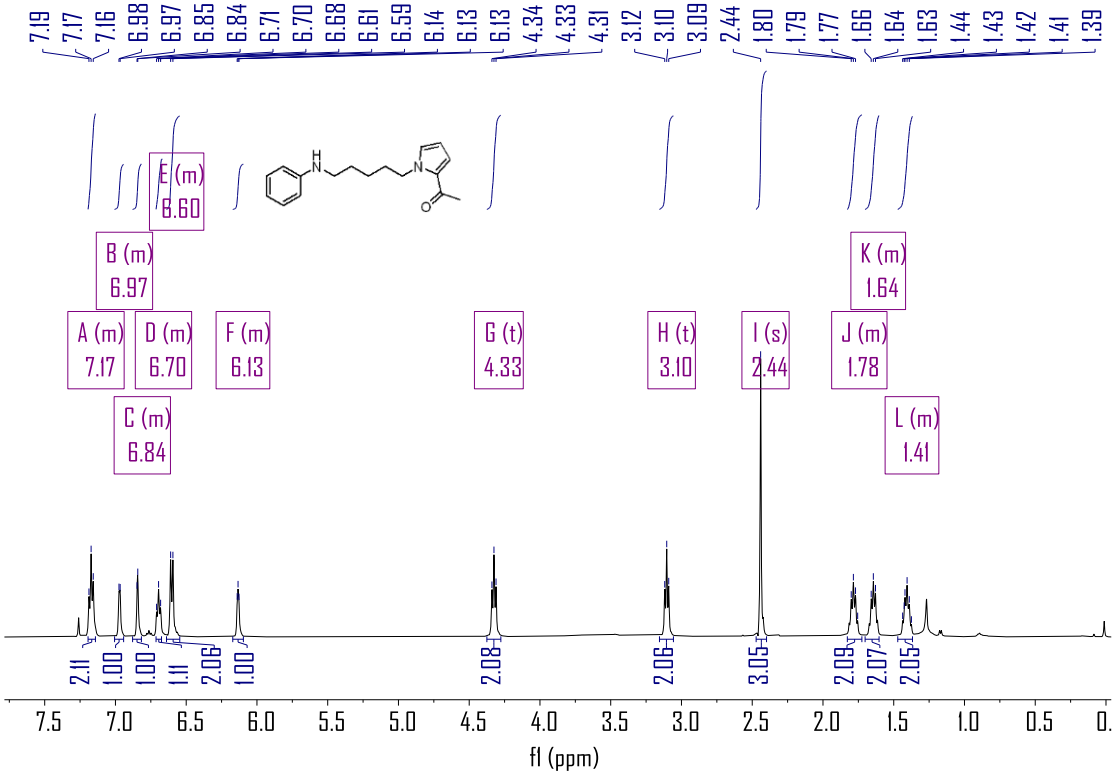
N-(5-(1H-indol-1-yl)pentyl)aniline **(14)**

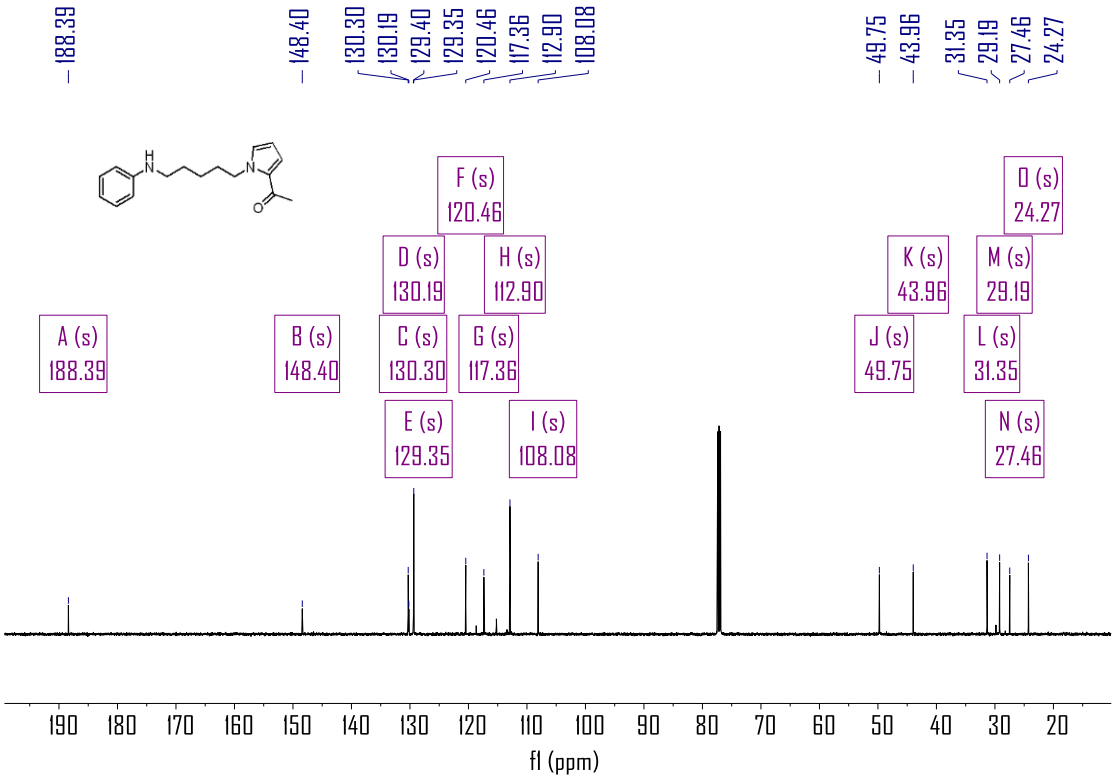


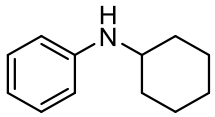




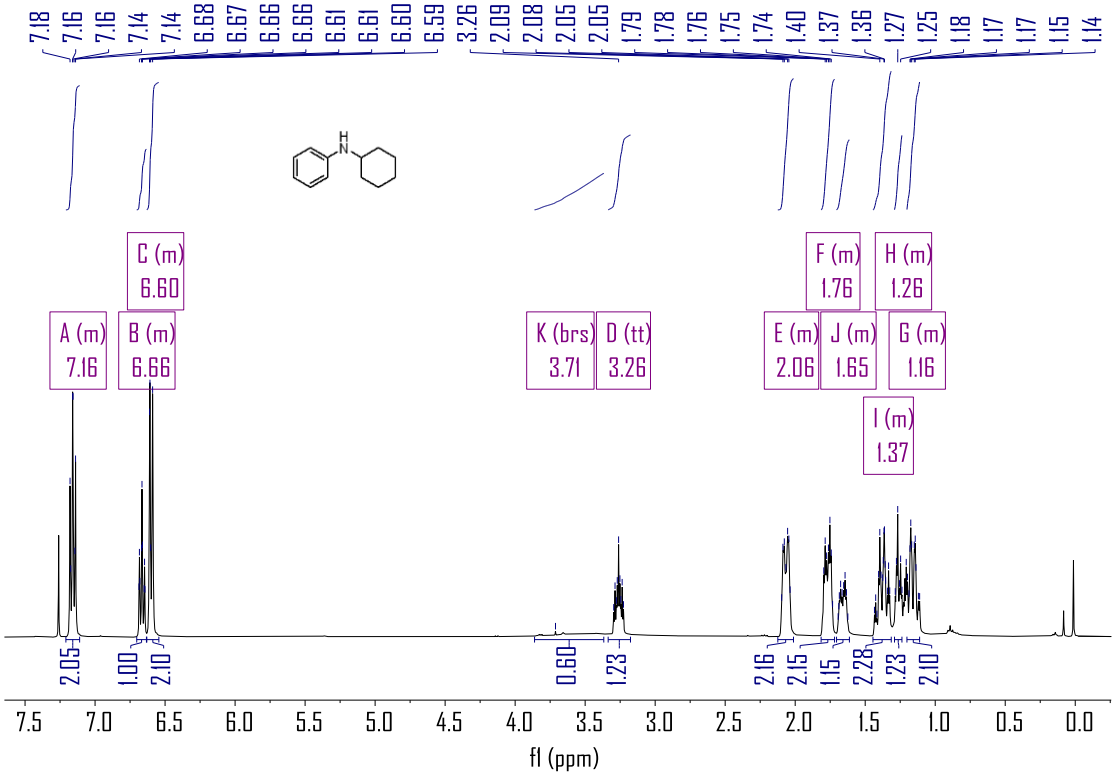
1-(1-(5-(phenylamino)pentyl)-1H-pyrrol-2-yl)ethan-1-one **(15)**

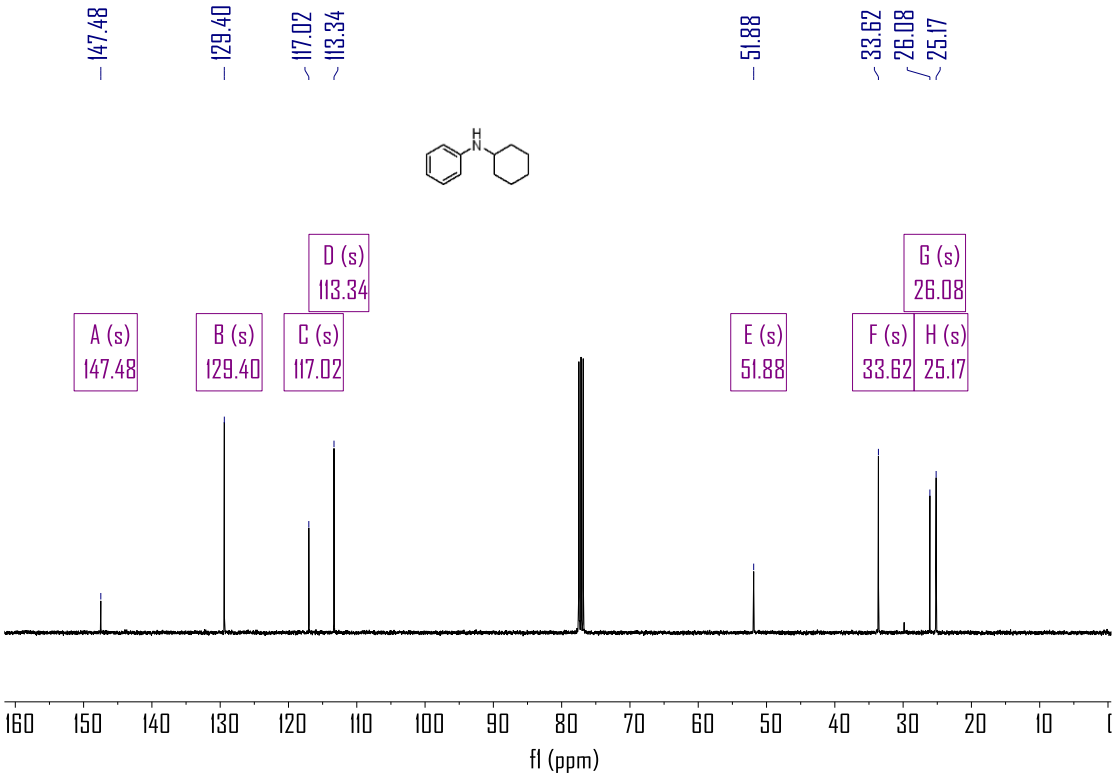


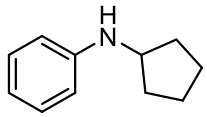




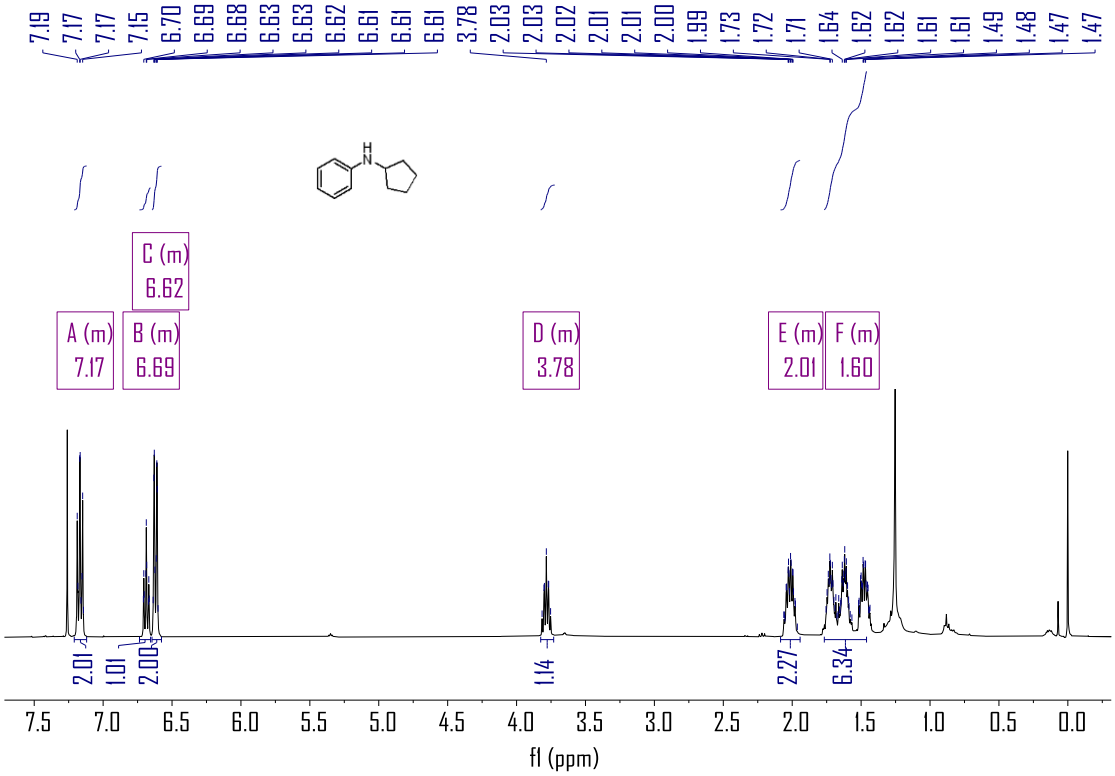
N-cyclohexylaniline **(16)**

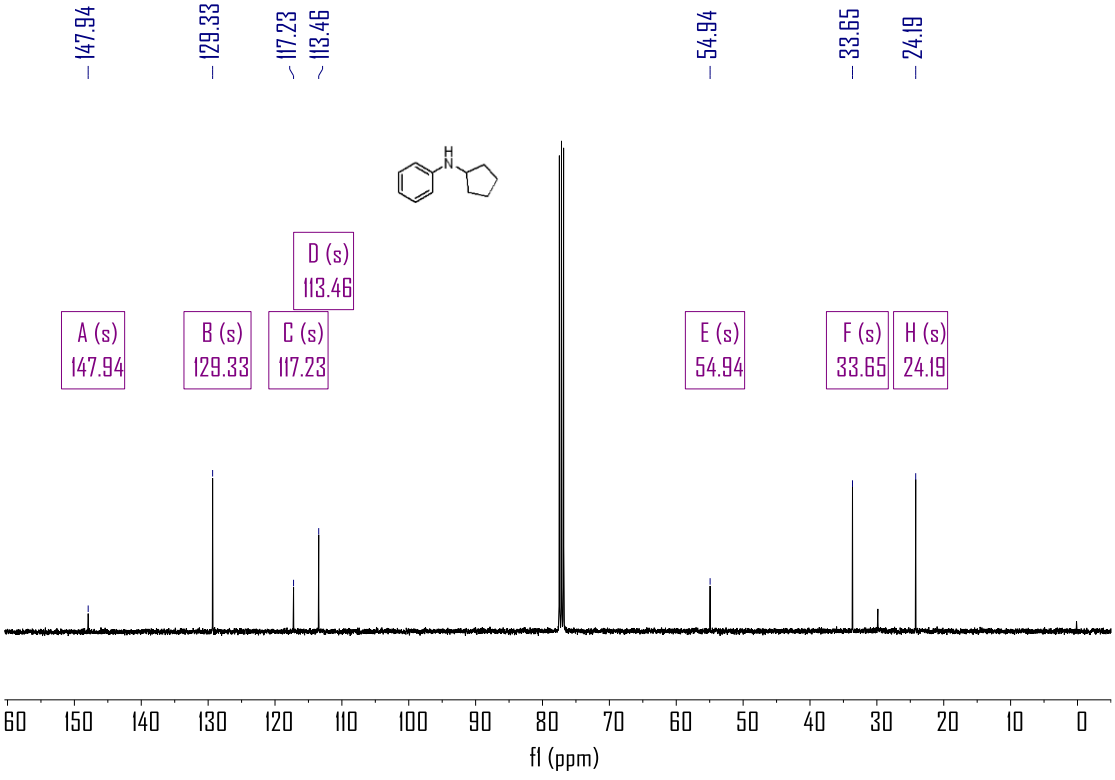


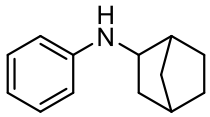




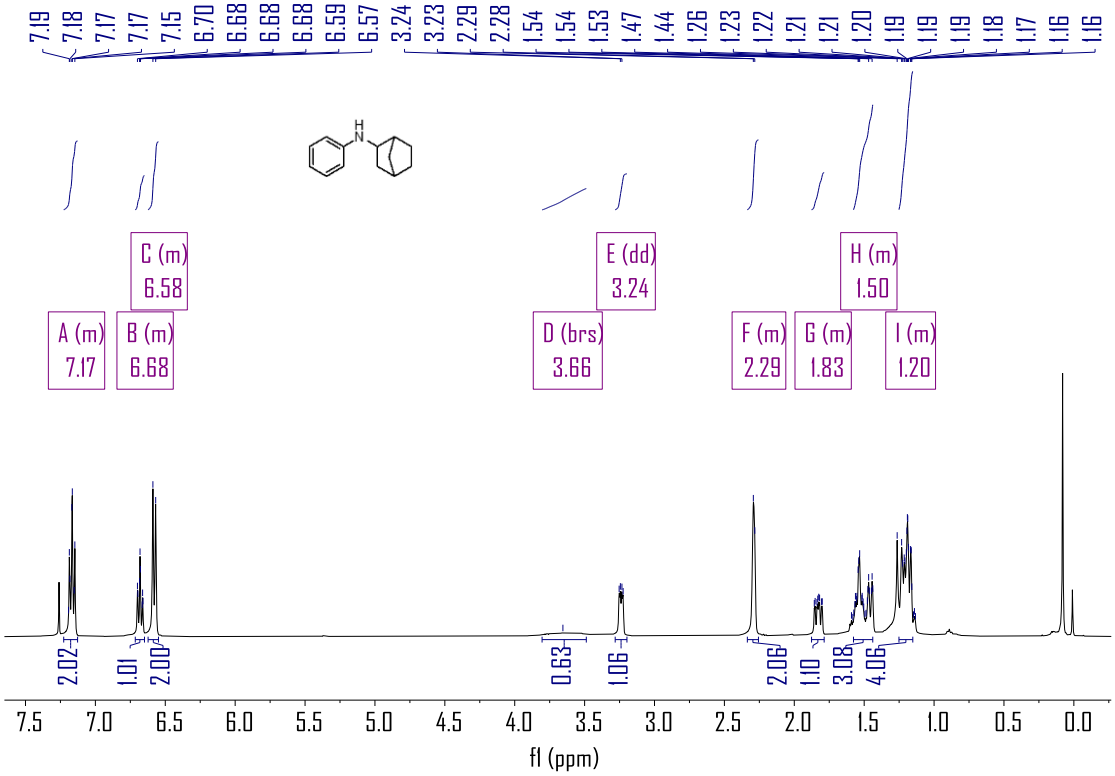
N-cyclopentylaniline **(17)**

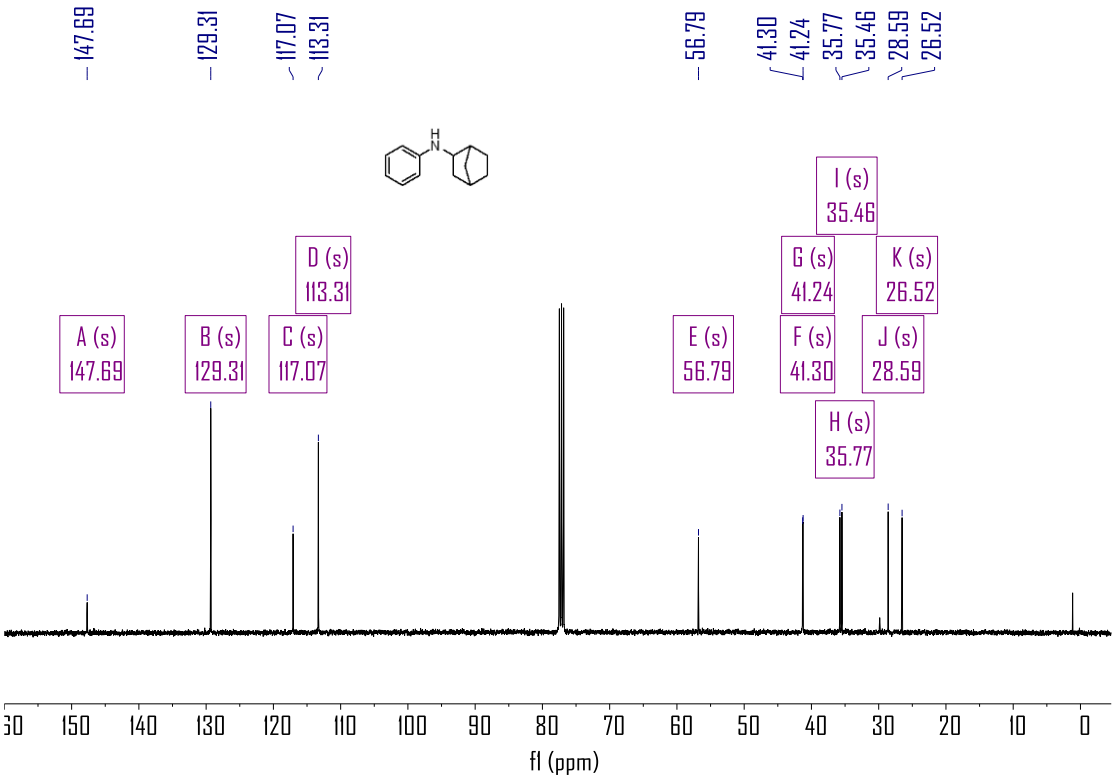


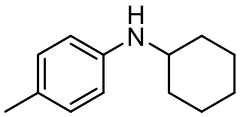




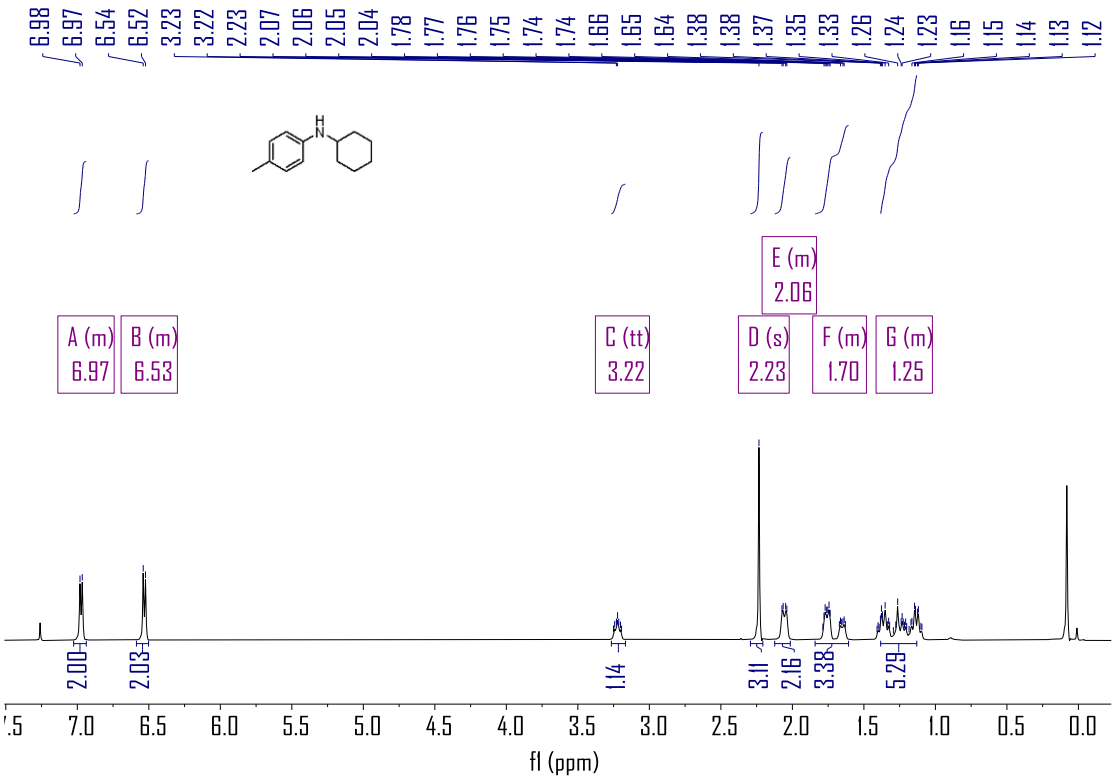
N-phenylbicyclo[2.2.1]heptan-2-amine **(18)**

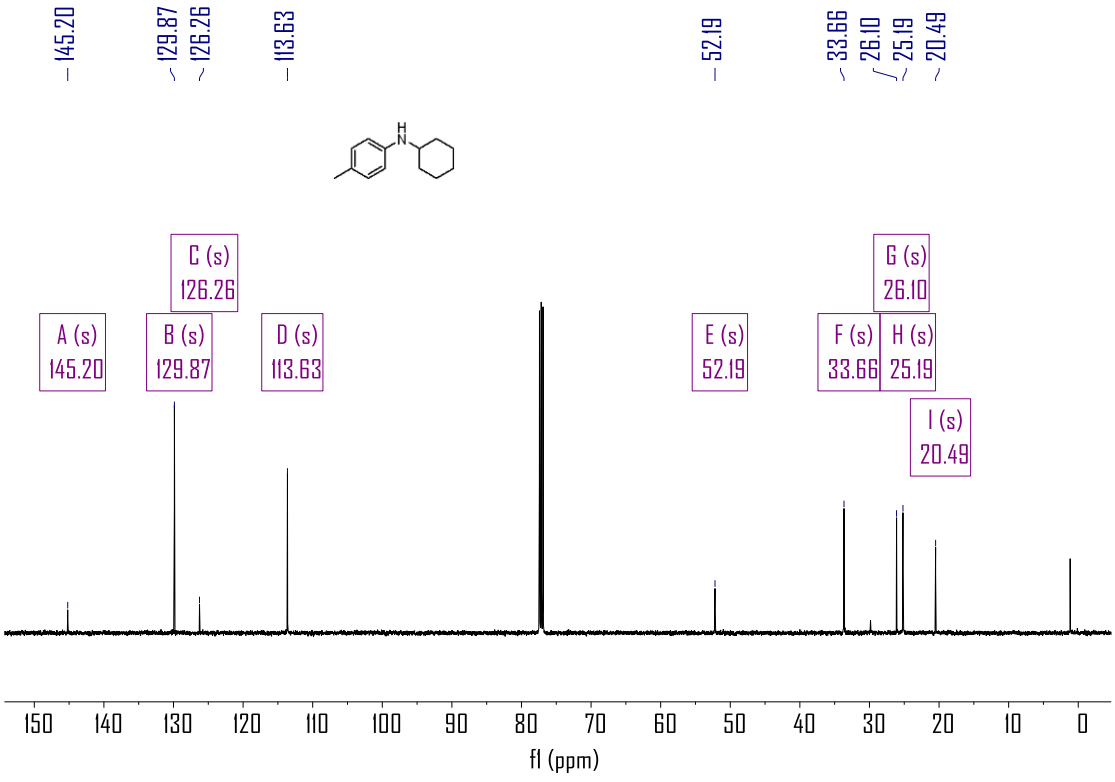


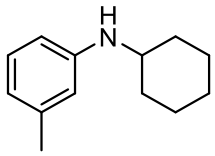




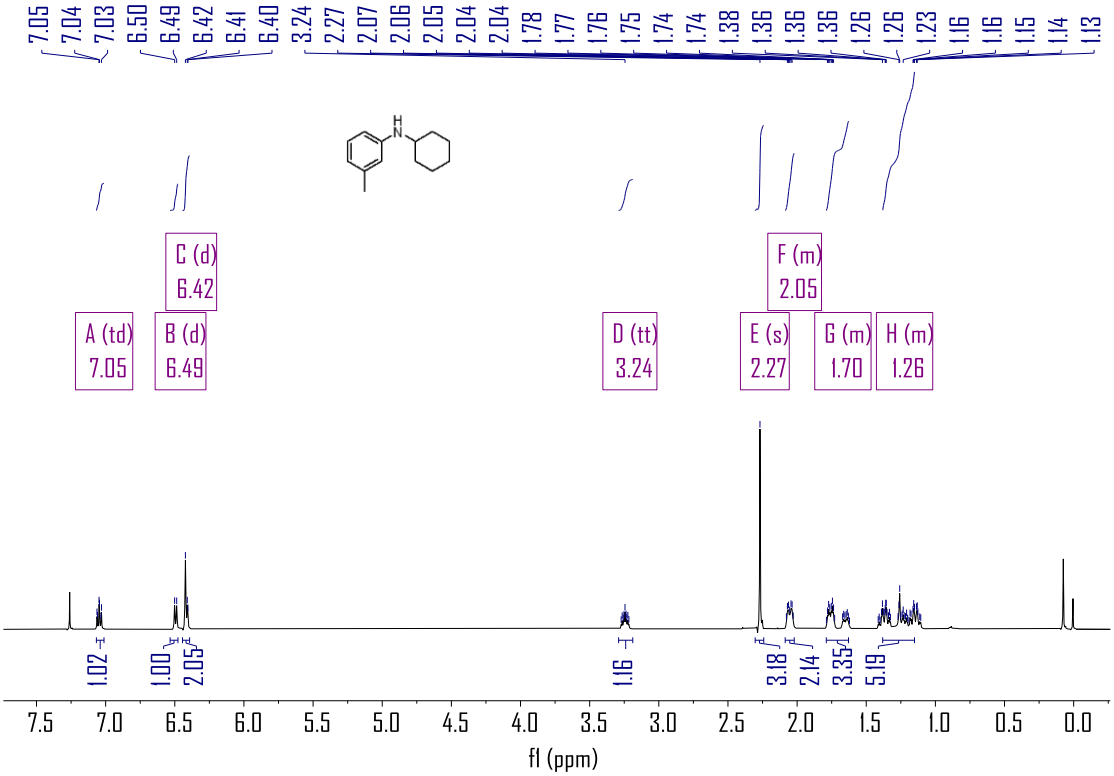
N-cyclohexyl-4-methylaniline **(19)**

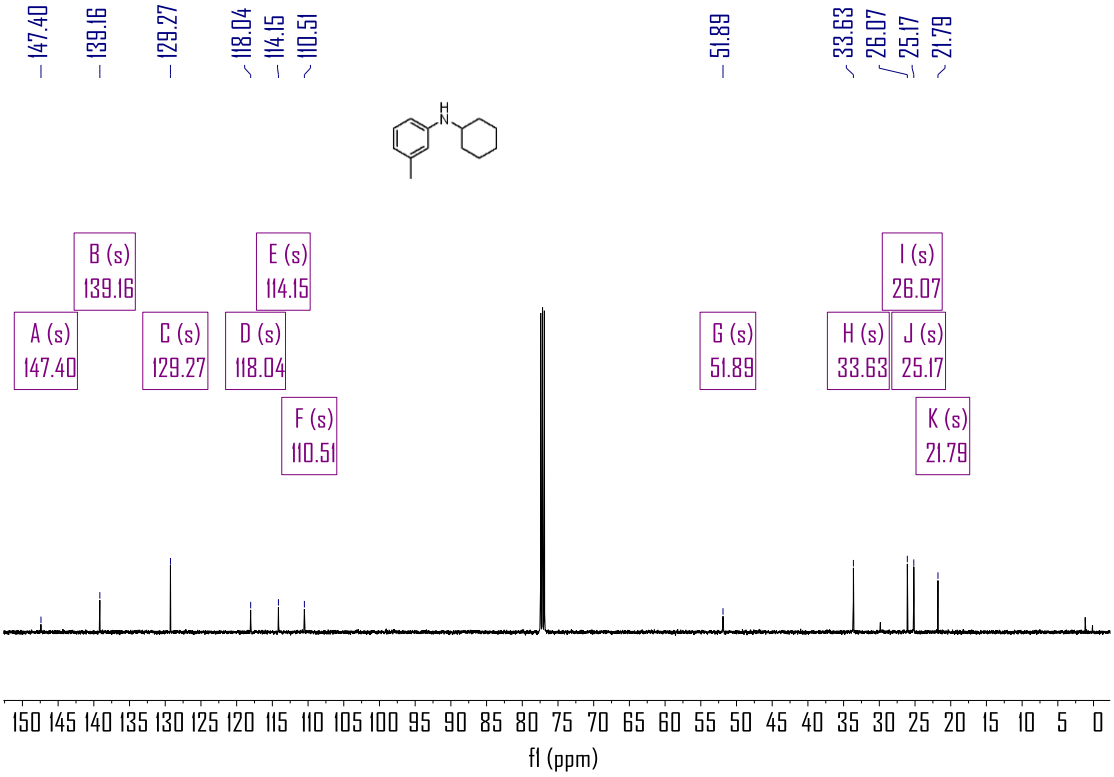


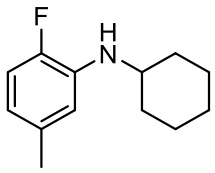




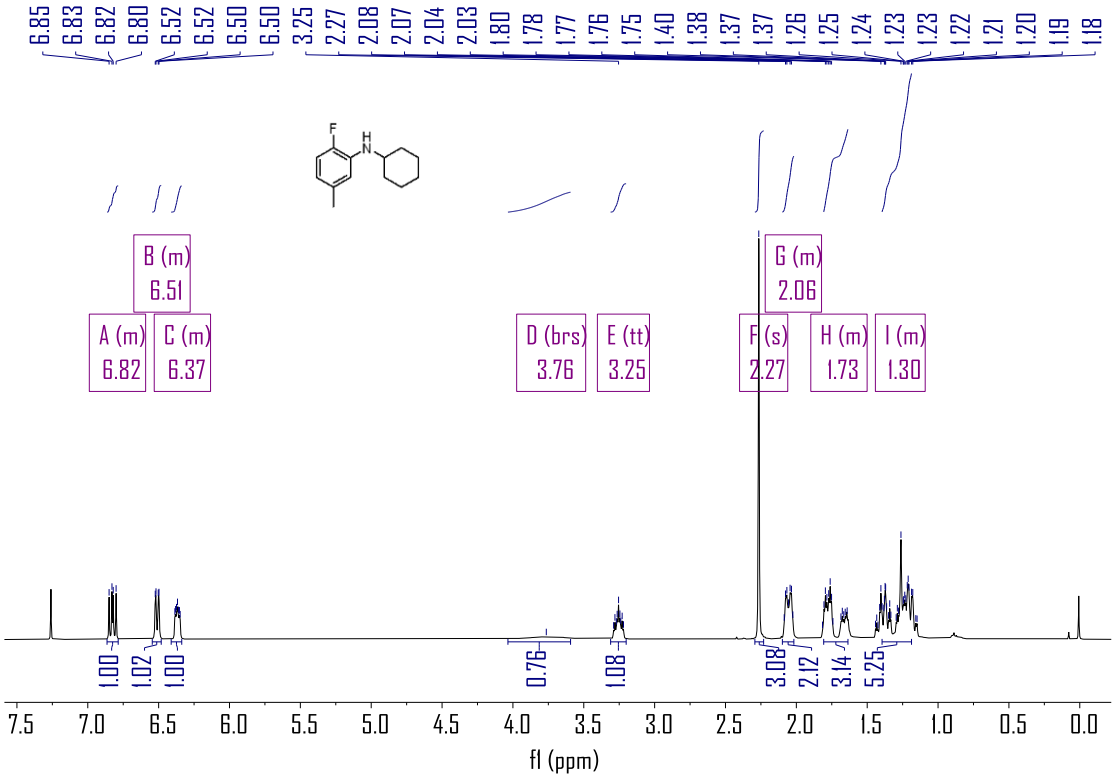
N-cyclohexyl-3-methylaniline **(20)**

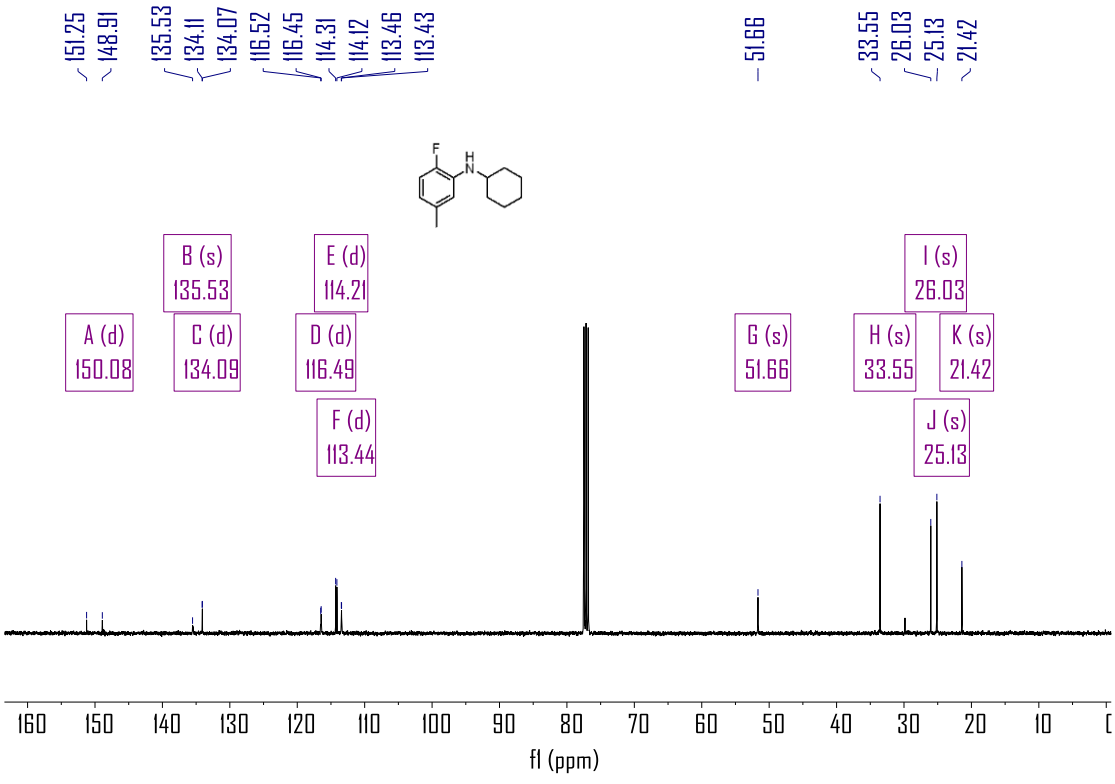


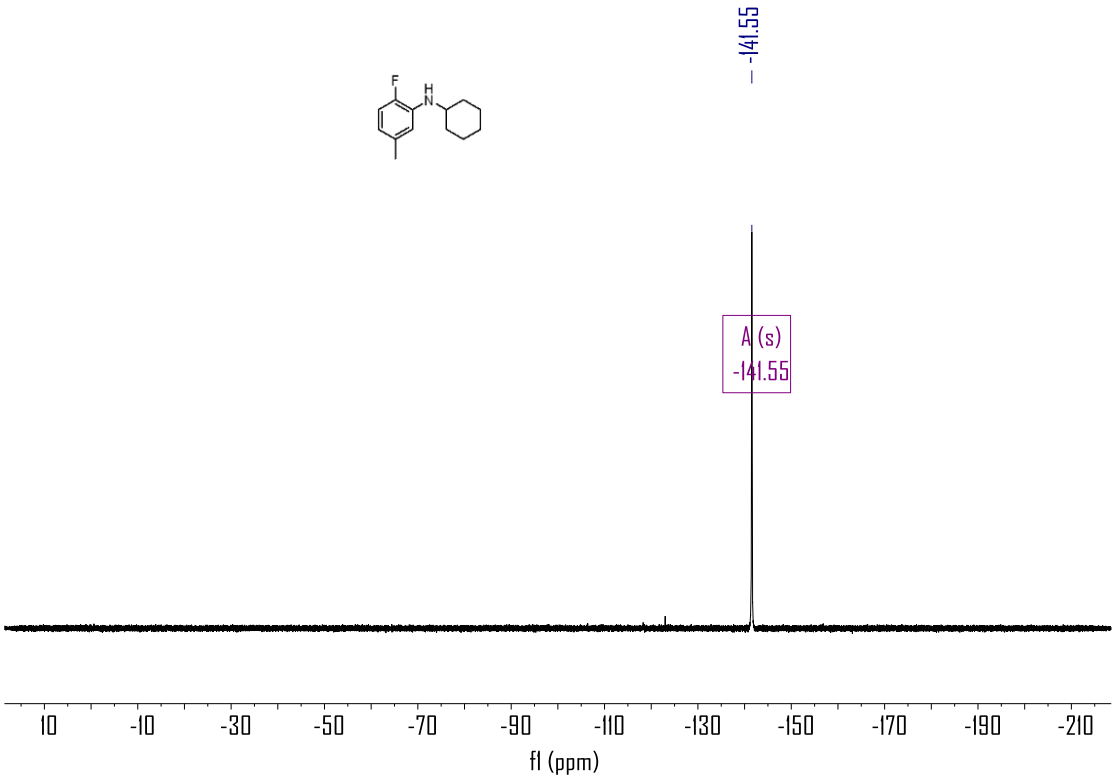


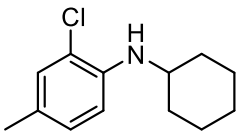


N-cyclohexyl-2-fluoro-5-methylaniline **(21)**

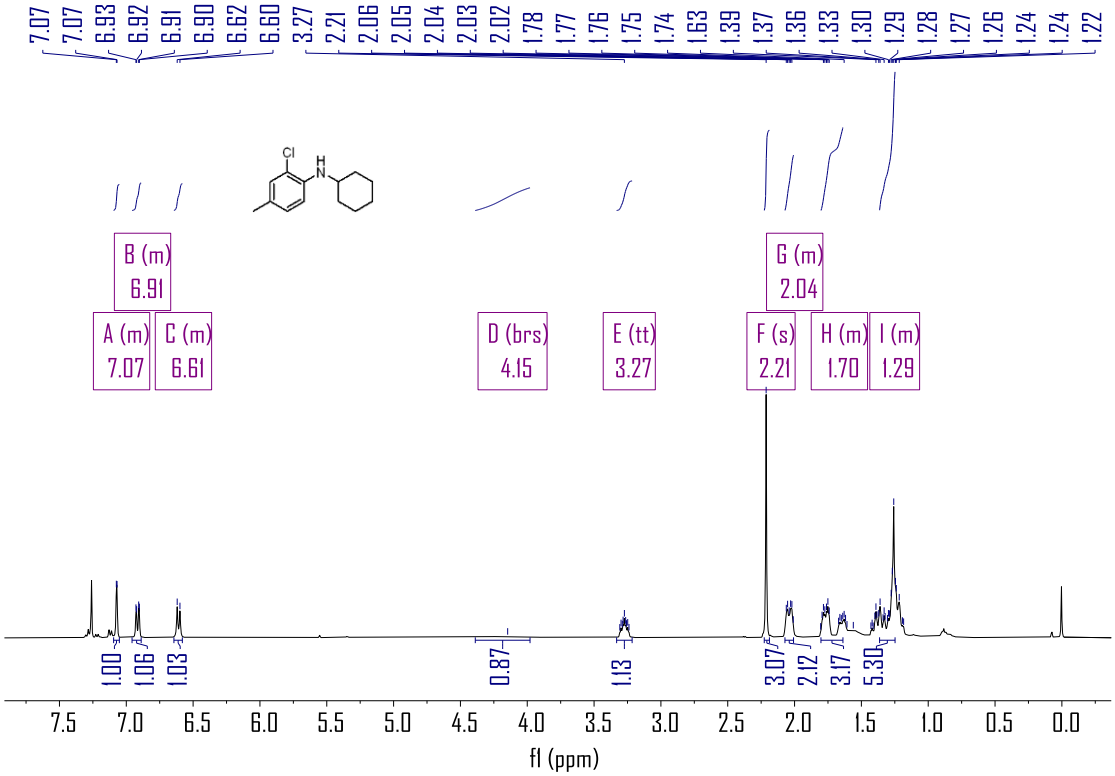


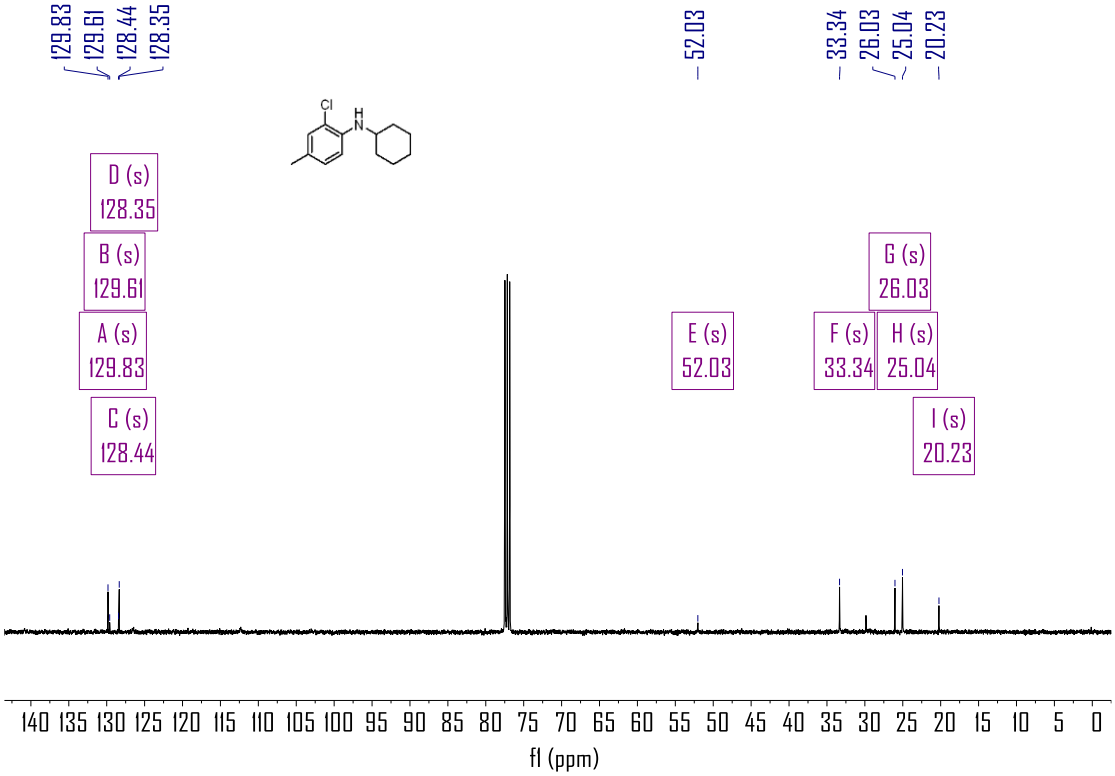


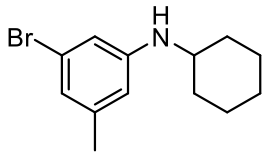

F
H
N
-141.55
A (s)
-141.55
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)



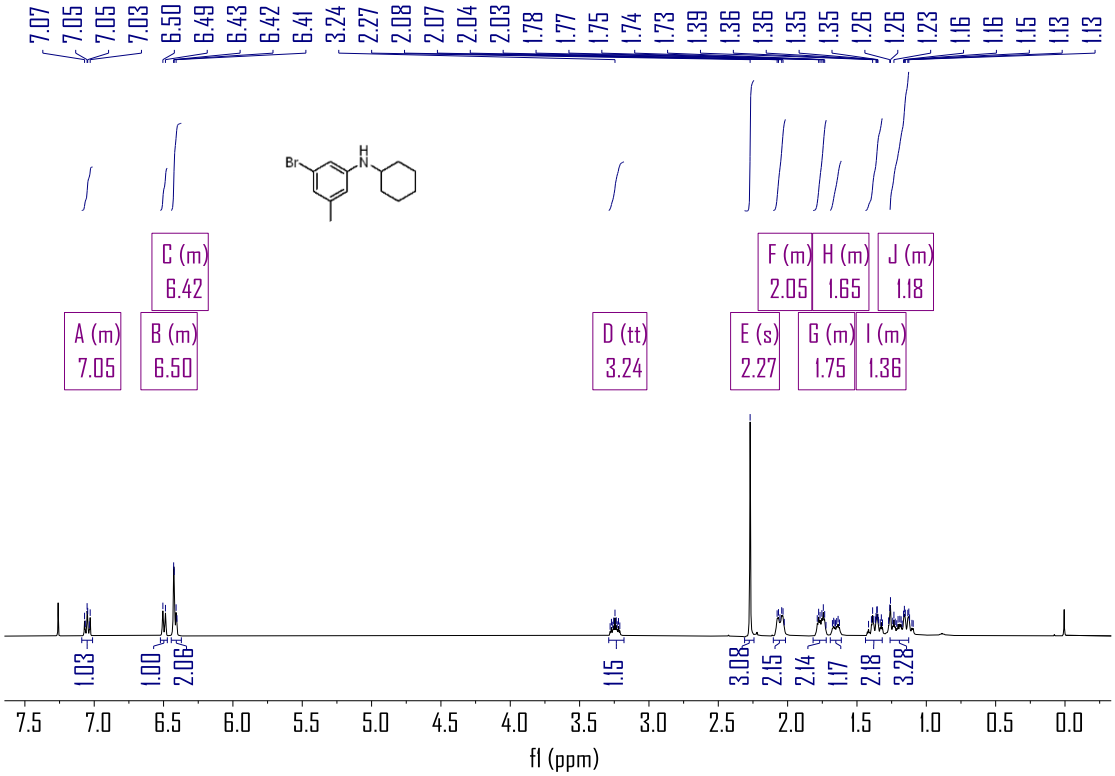
2-chloro-*N*-cyclohexyl-4-methylaniline **(22)**

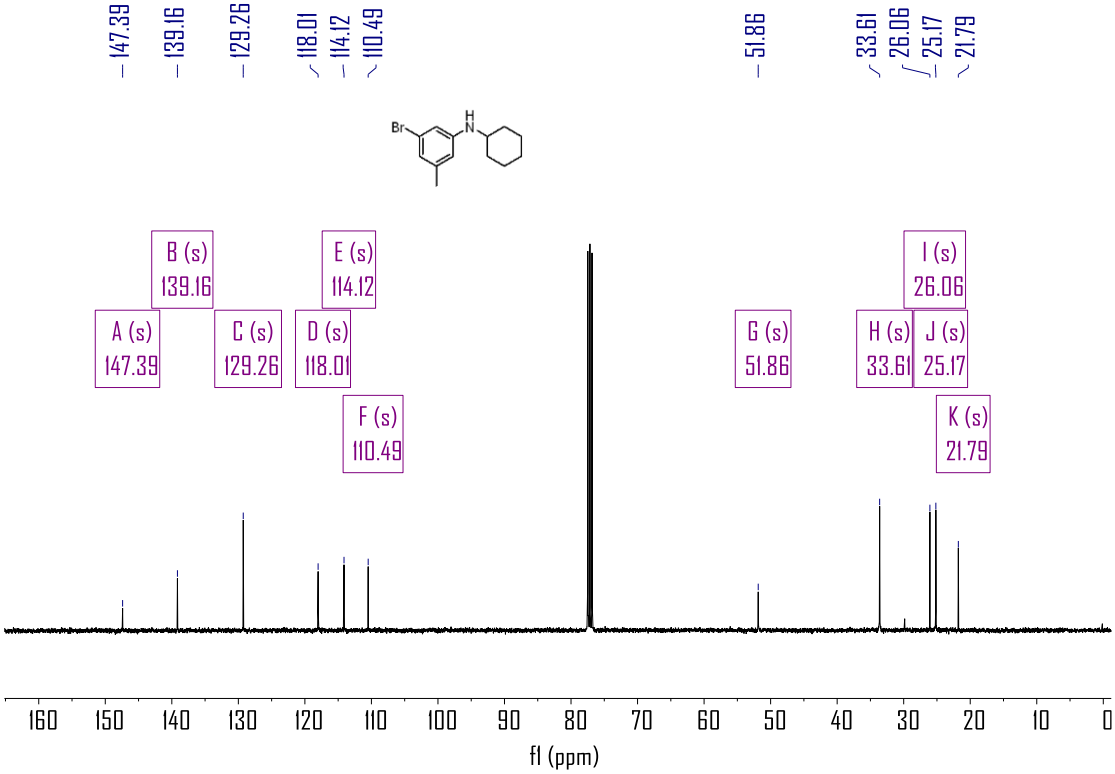


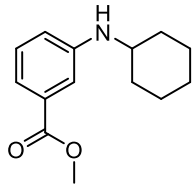




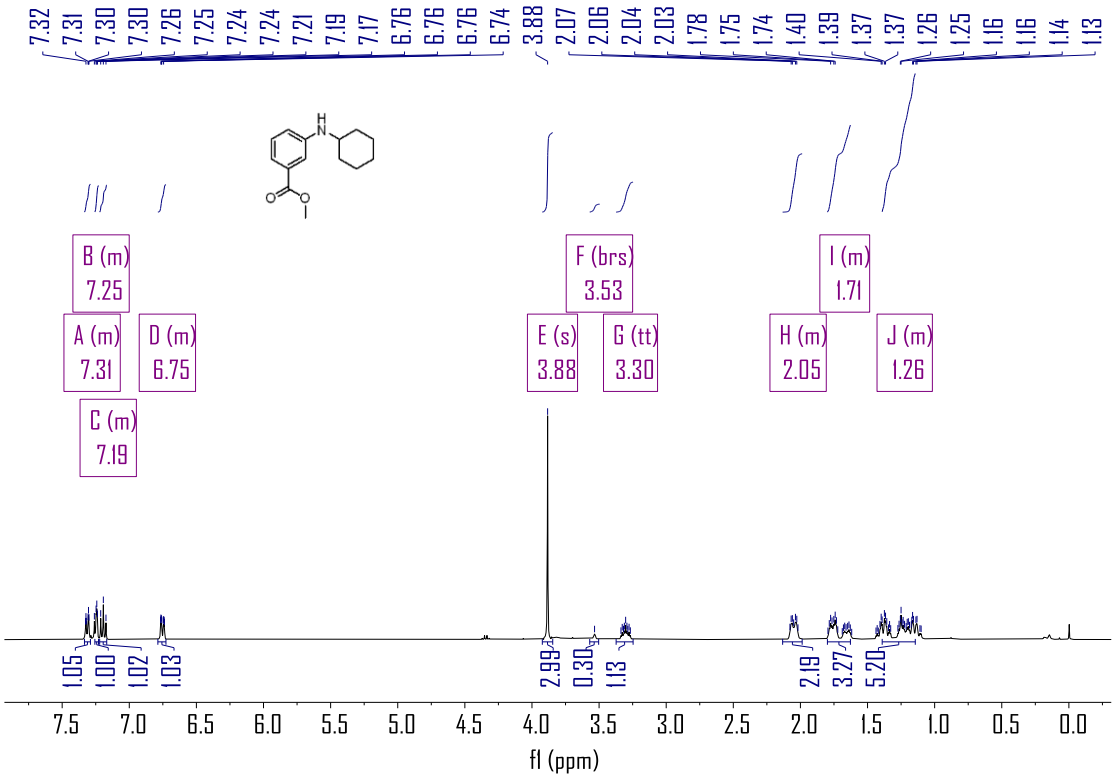
3-bromo-*N*-cyclohexyl-5-methylaniline **(23)**

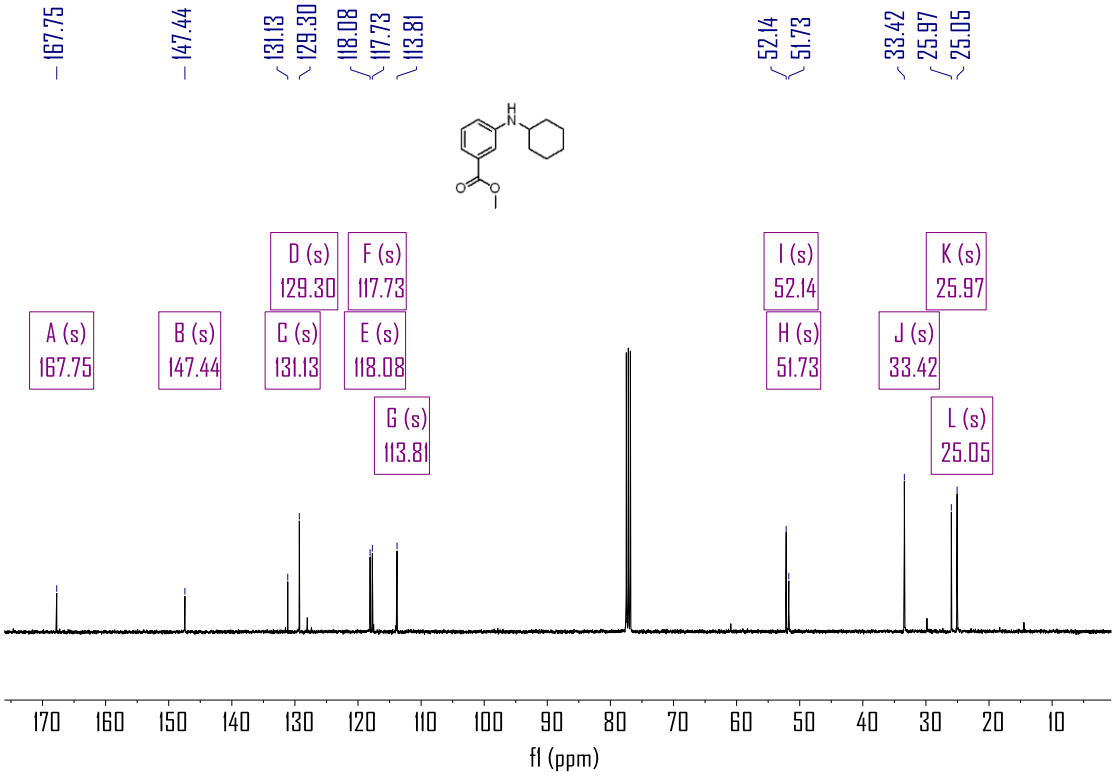


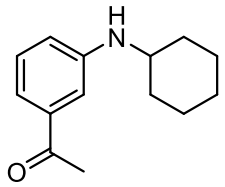




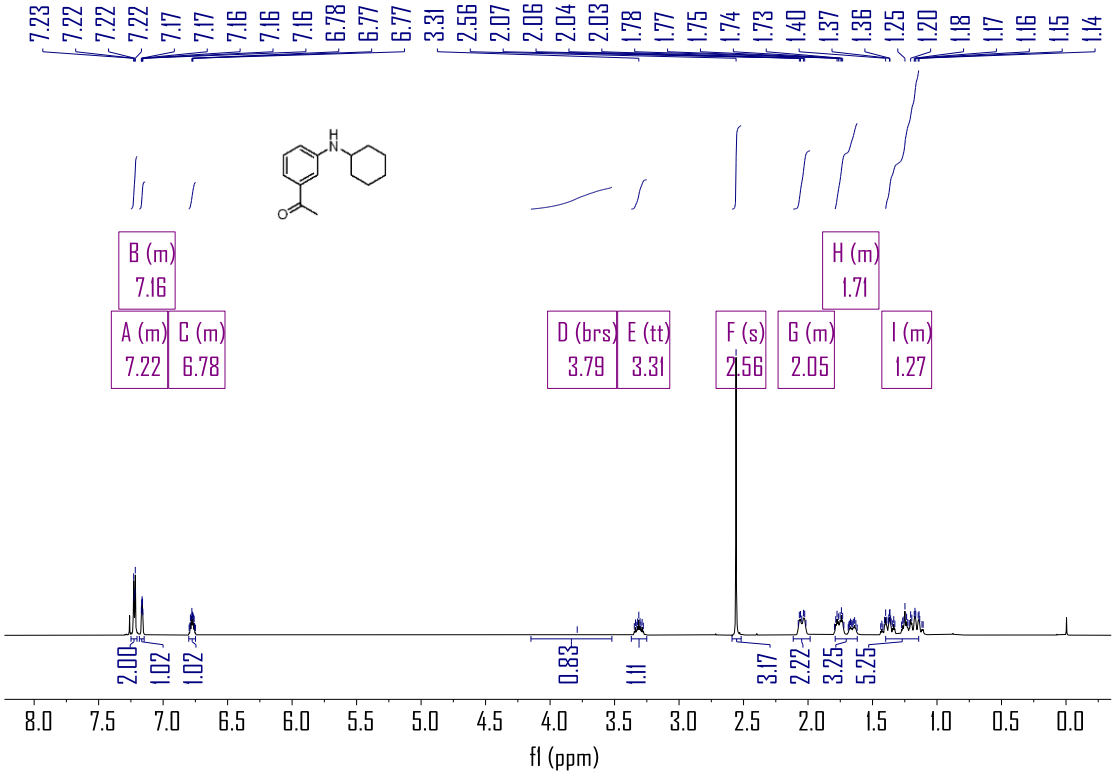
methyl 3-(cyclohexylamino)benzoate **(24)**

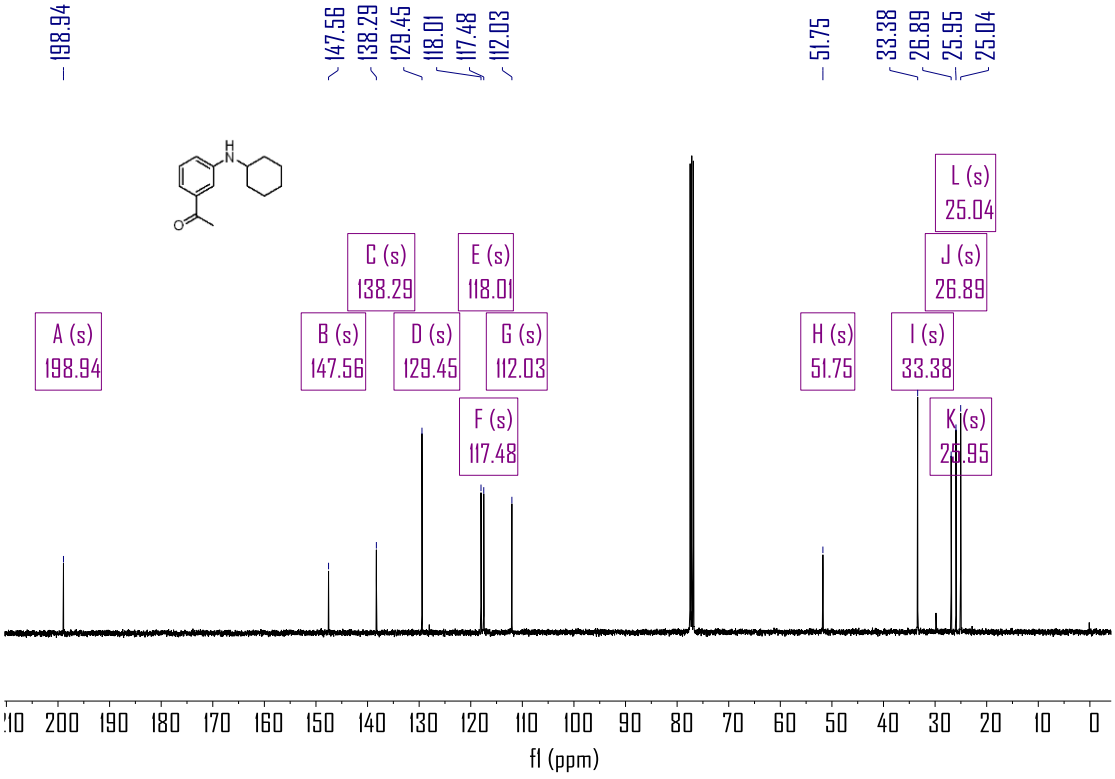


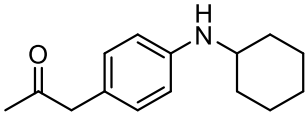




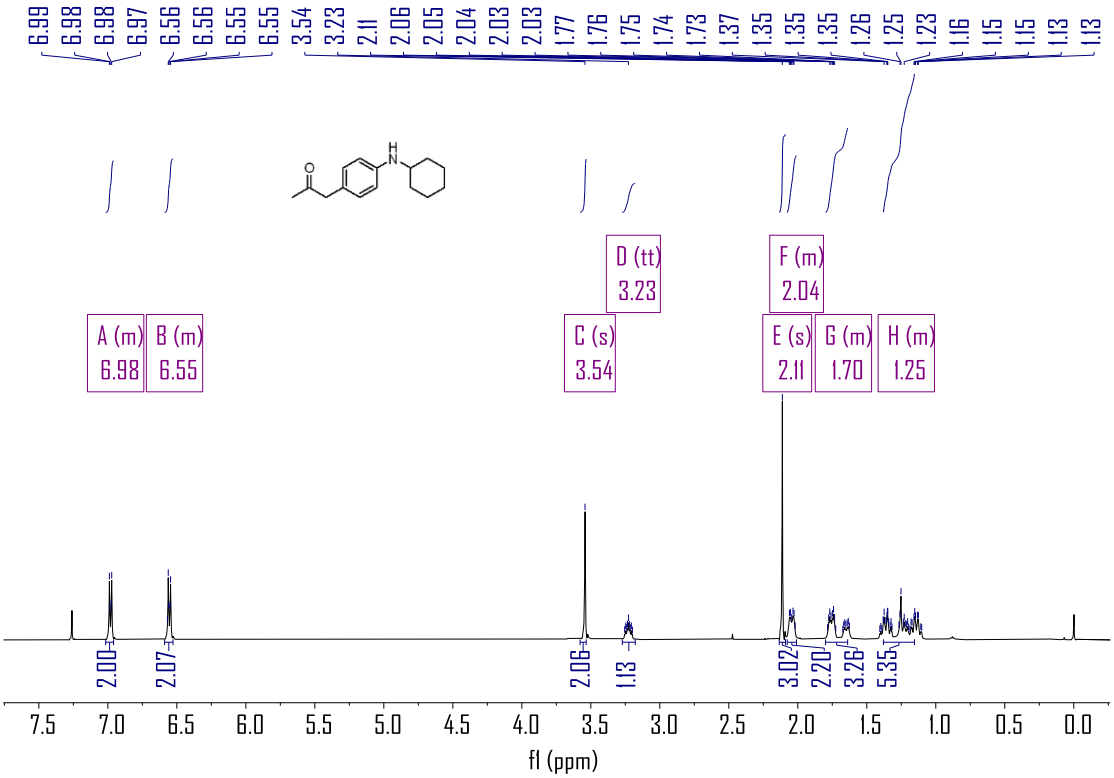
1-(3-(cyclohexylamino)phenyl)ethan-1-one **(25)**

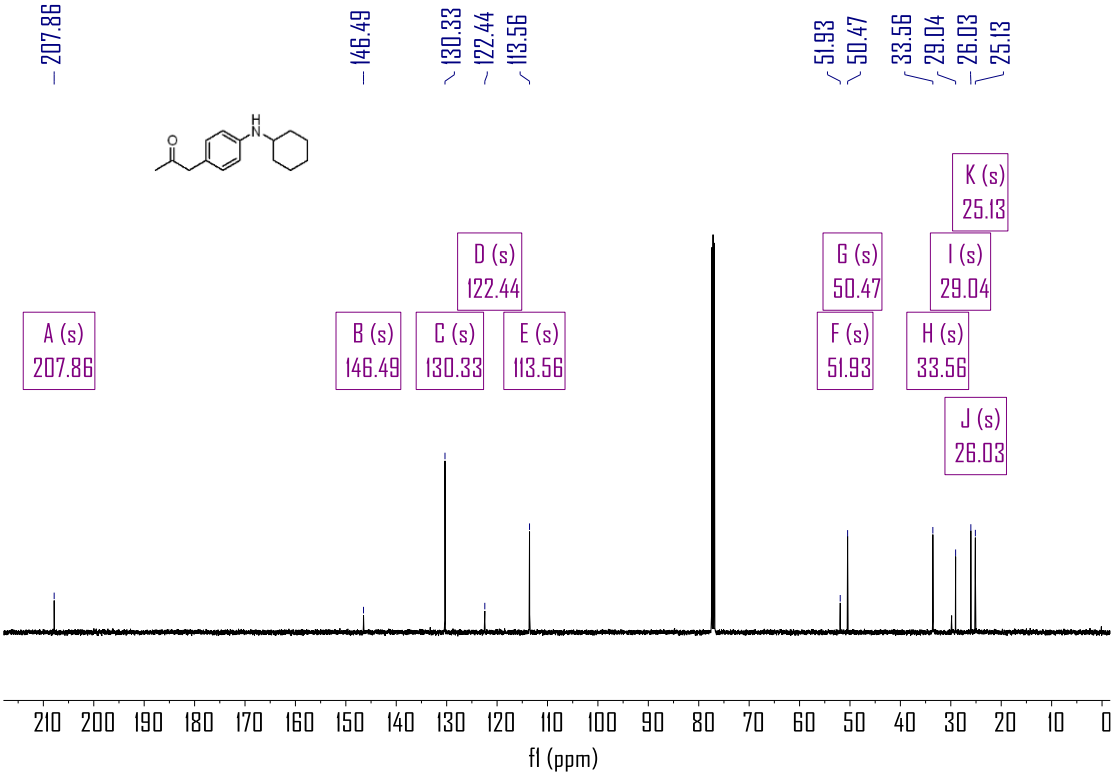


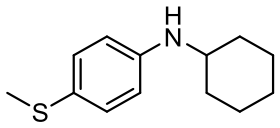




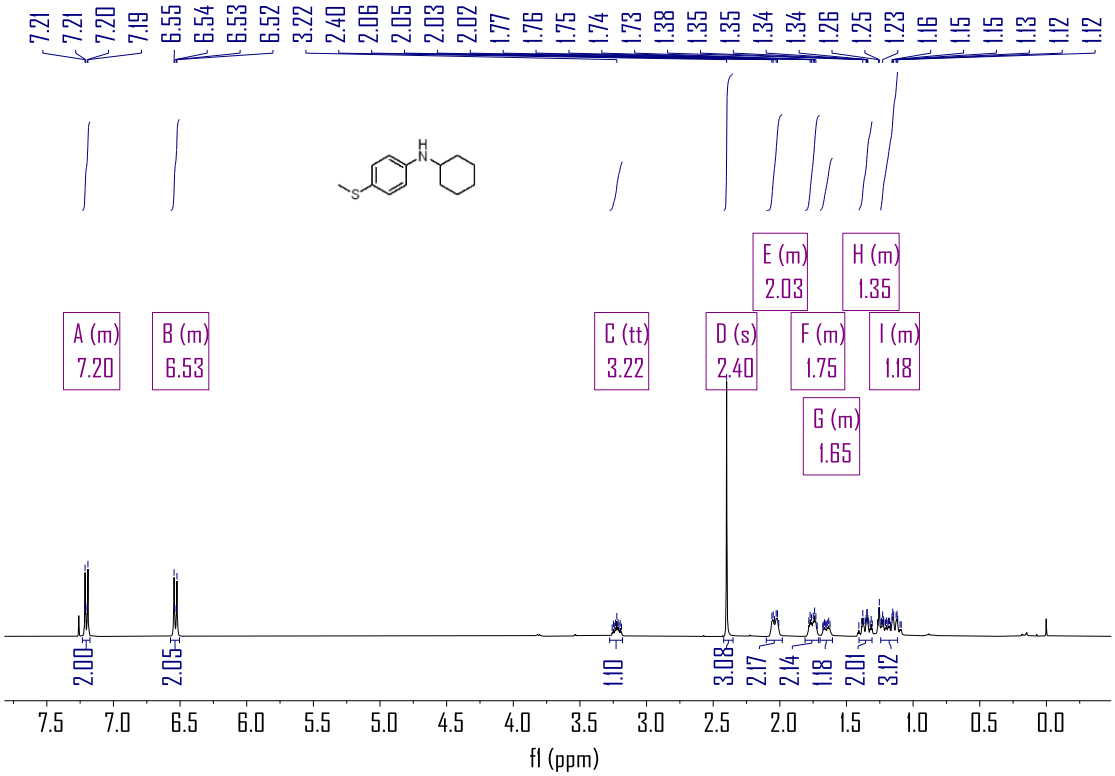
1-(4-(cyclohexylamino)phenyl)propan-2-one **(26)**

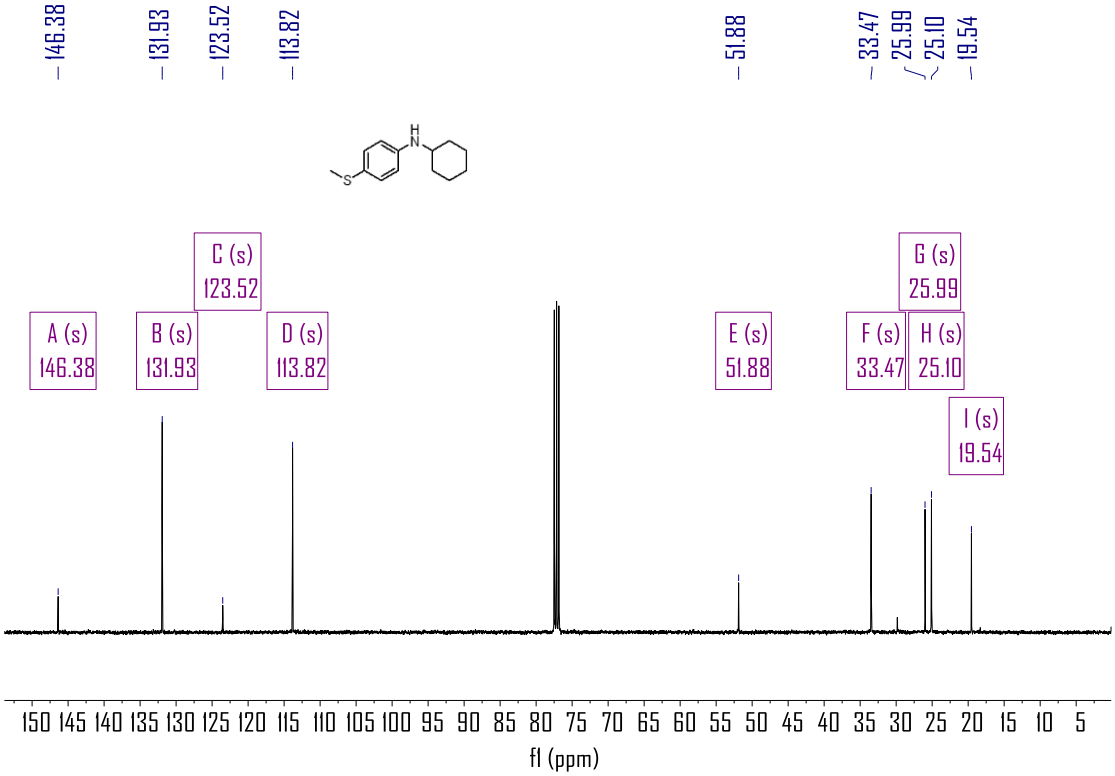


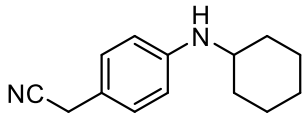




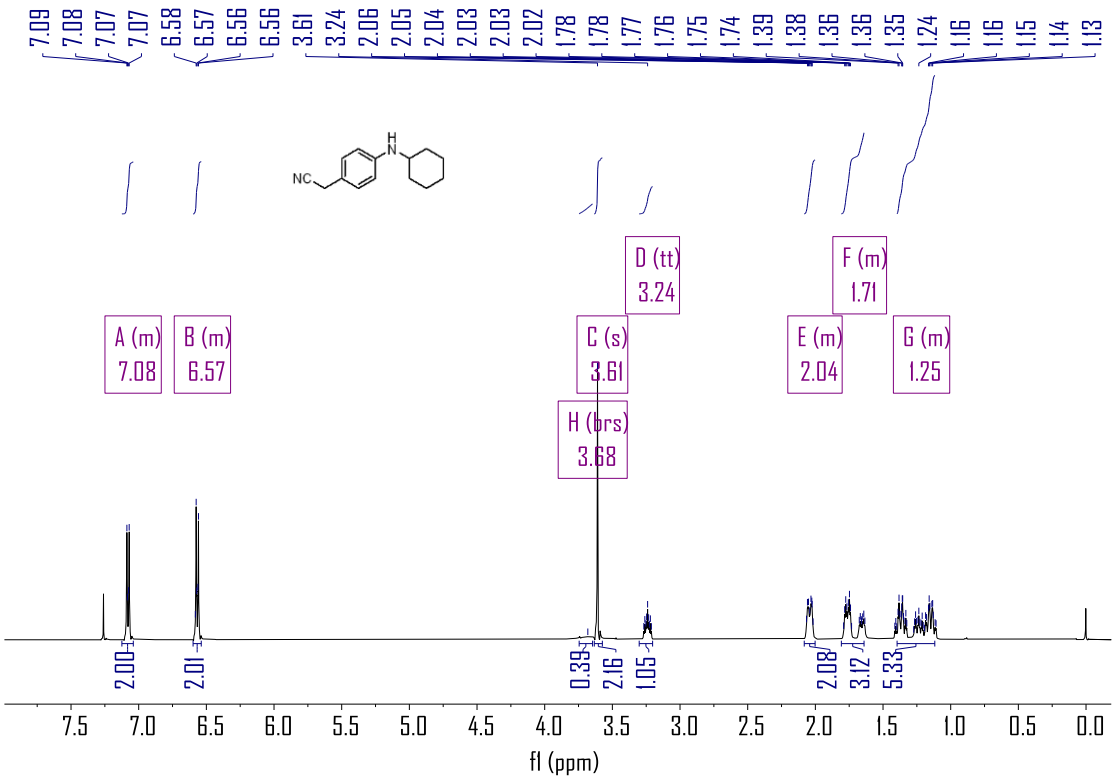
N-cyclohexyl-4-(methylthio)aniline **(27)**

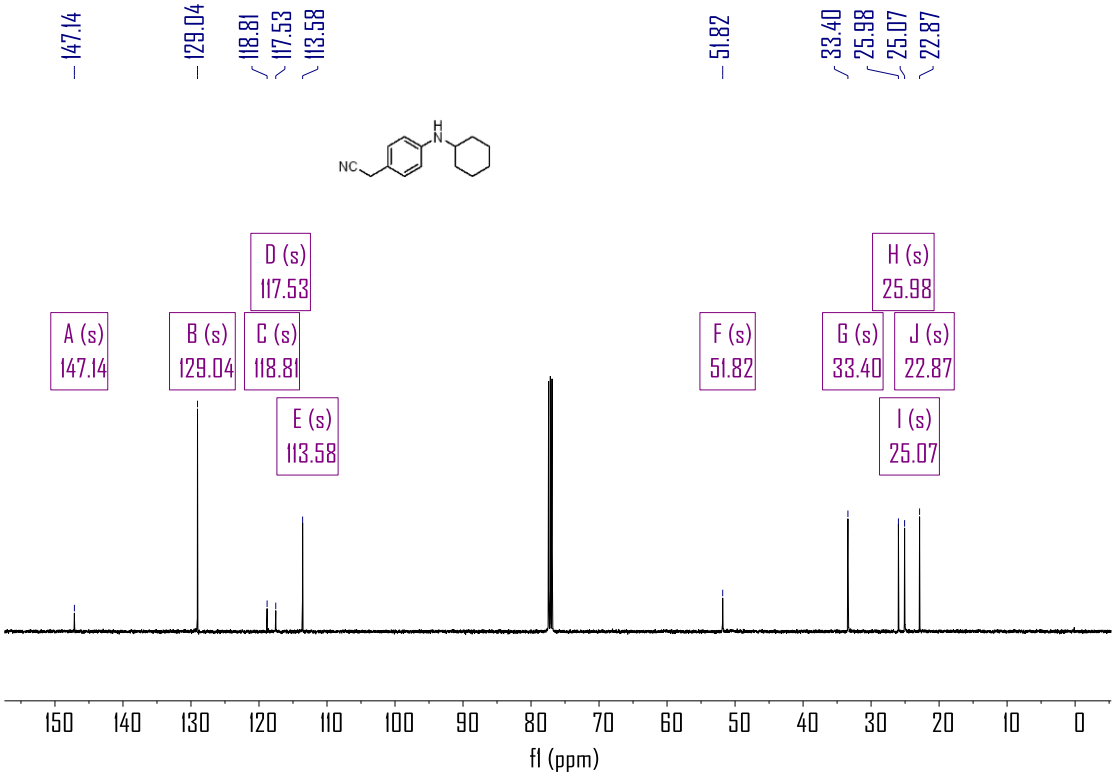


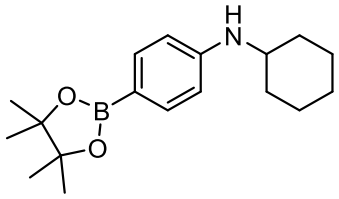




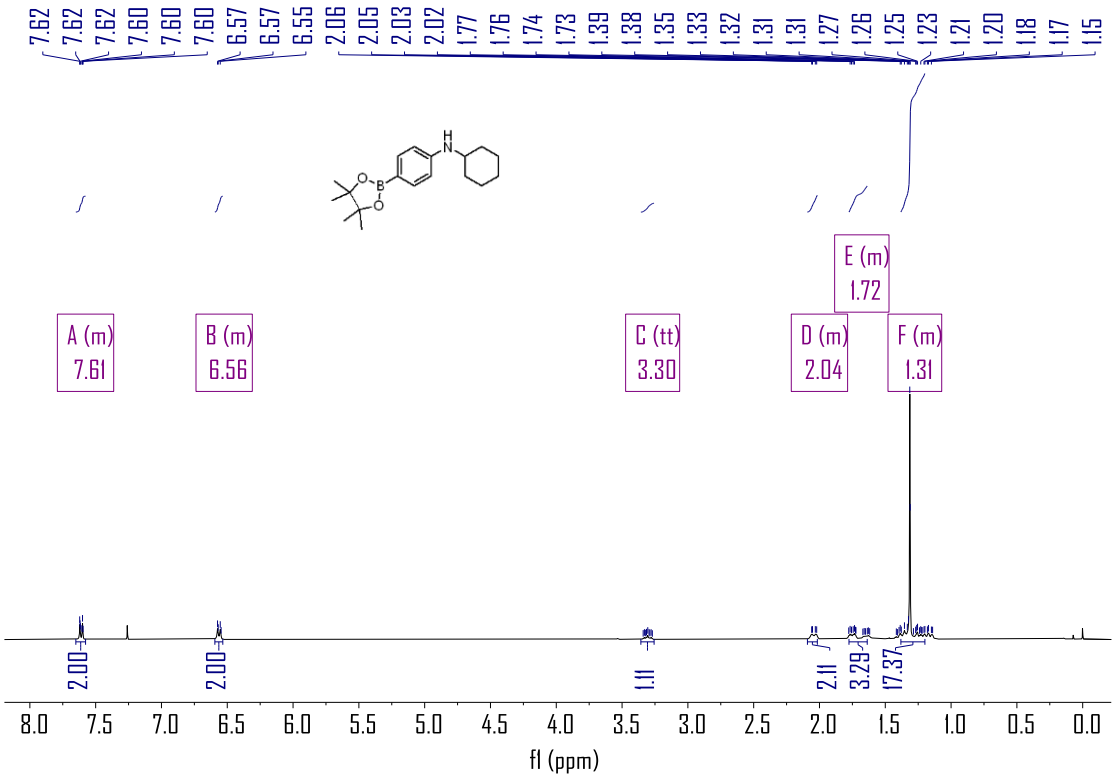
2-(4-(cyclohexylamino)phenyl)acetonitrile **(28)**

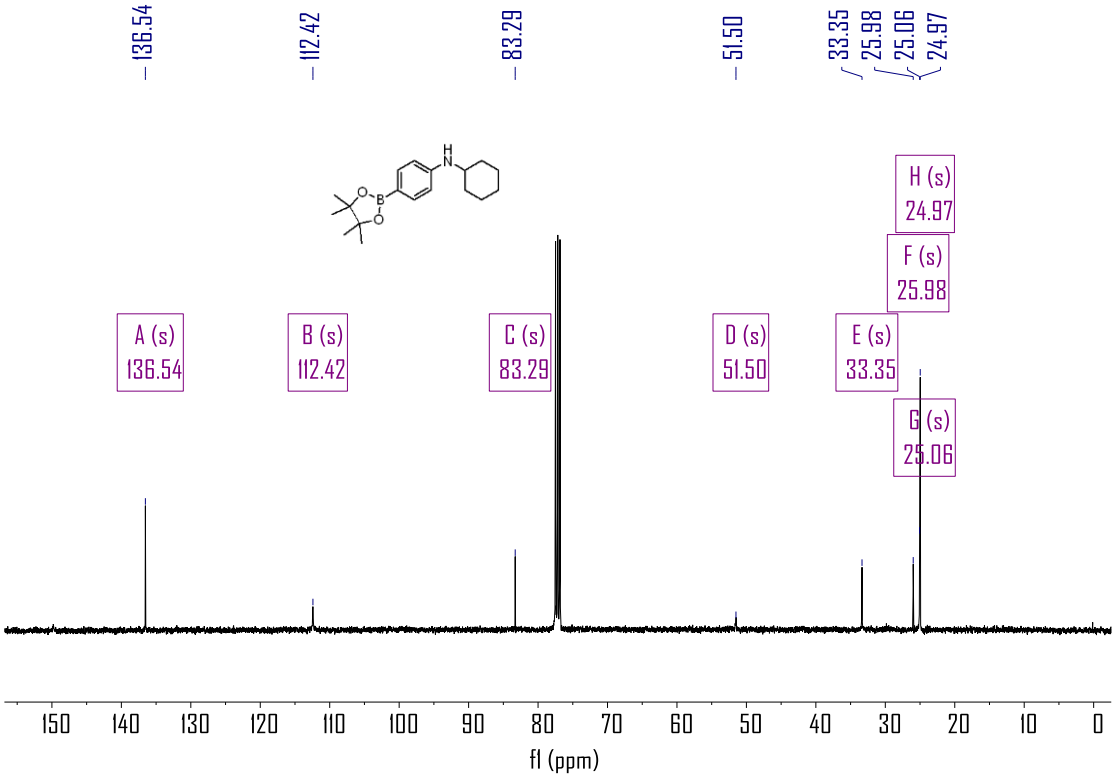


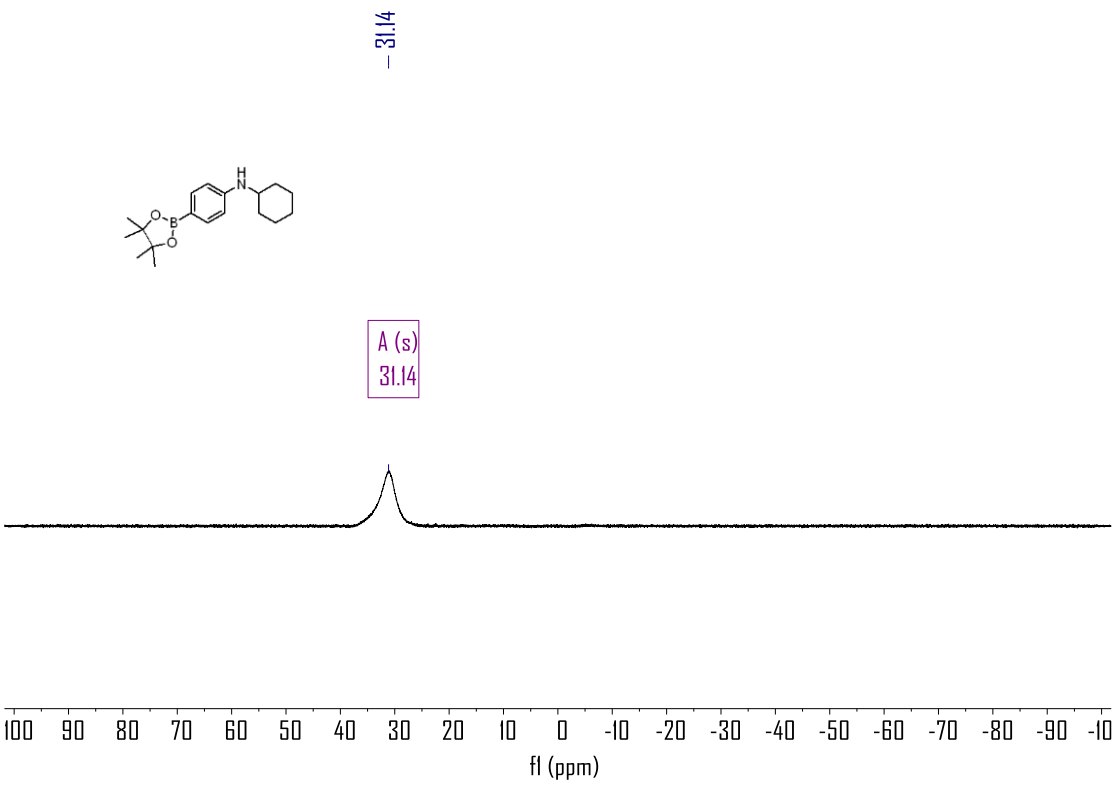


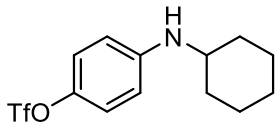


N-cyclohexyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline **(29)**

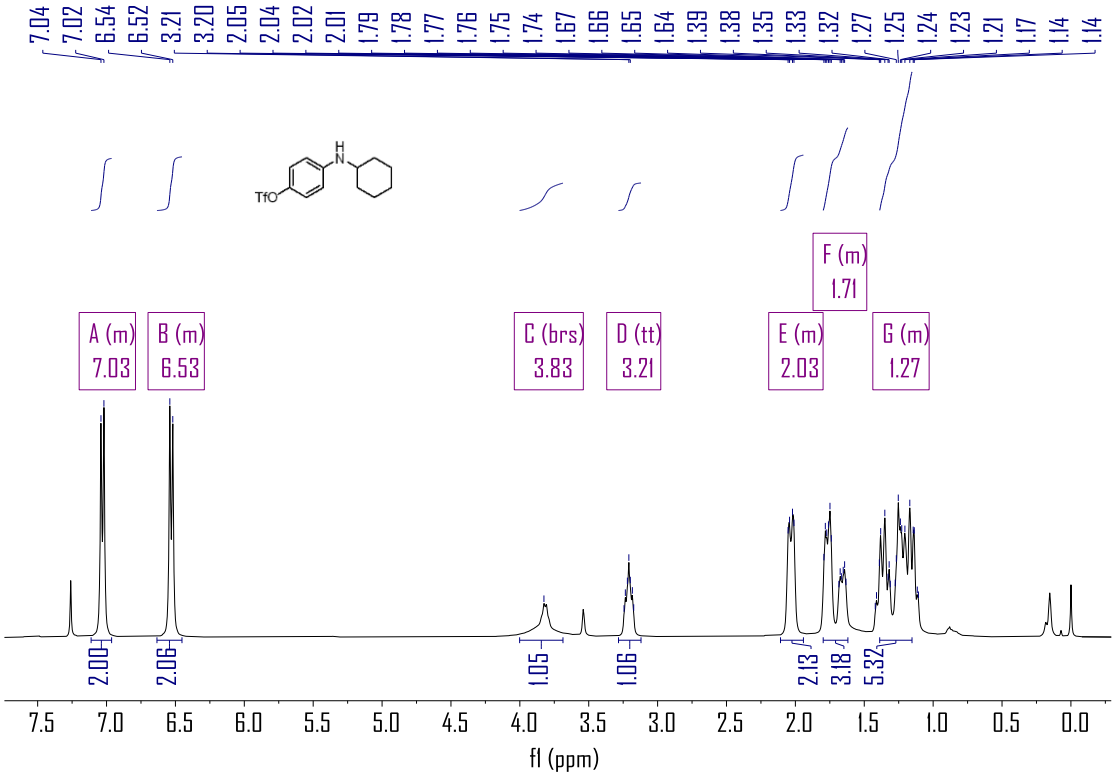


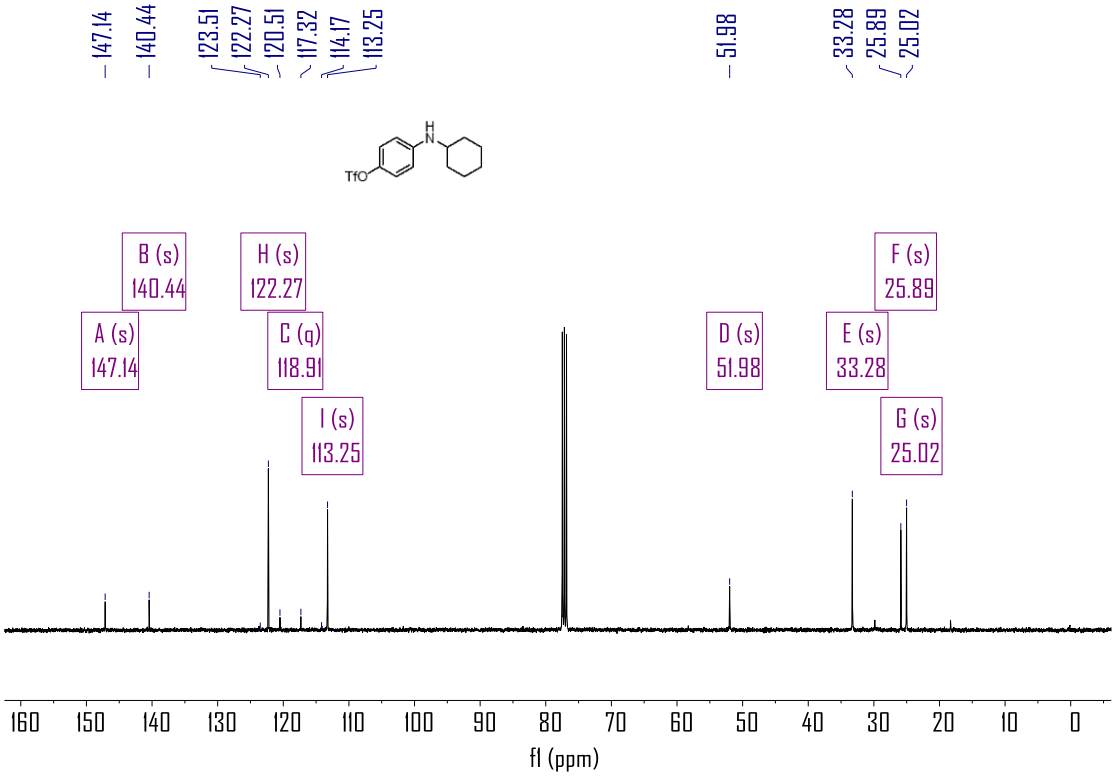


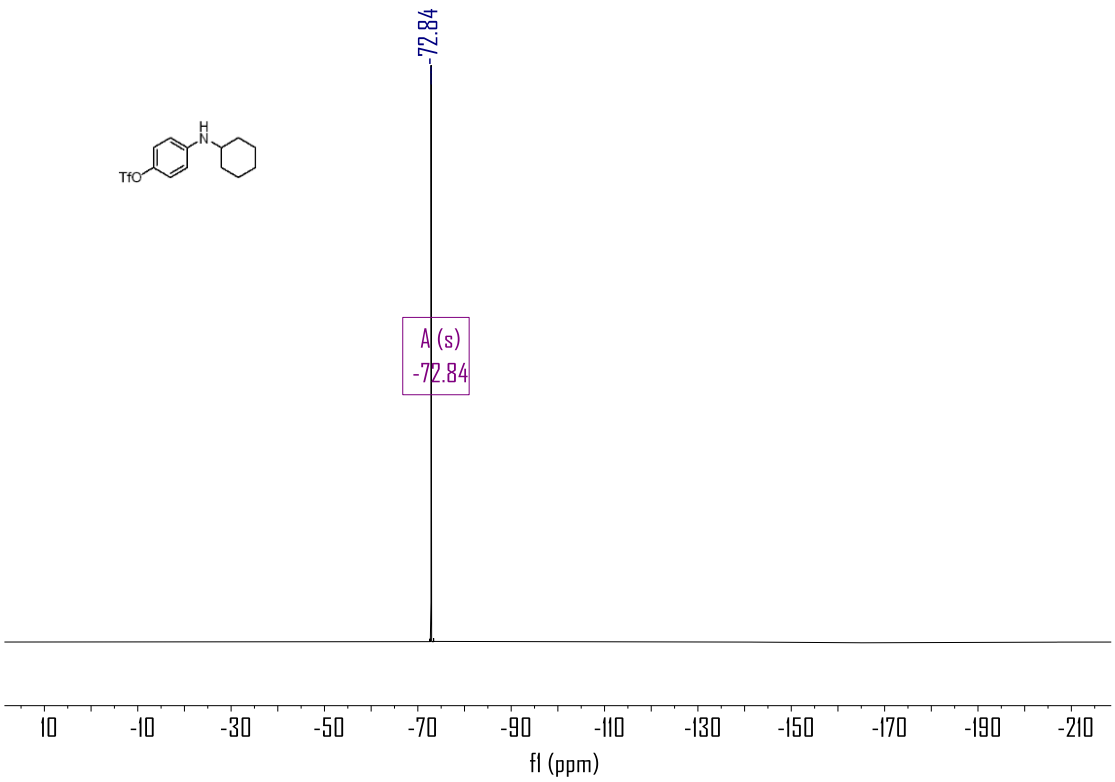

31.14
A (s)
31.14
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -10
f1 (ppm)

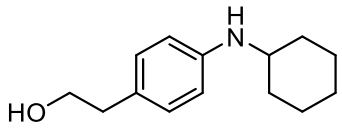


4-(cyclohexylamino)phenyl trifluoromethanesulfonate **(30)**

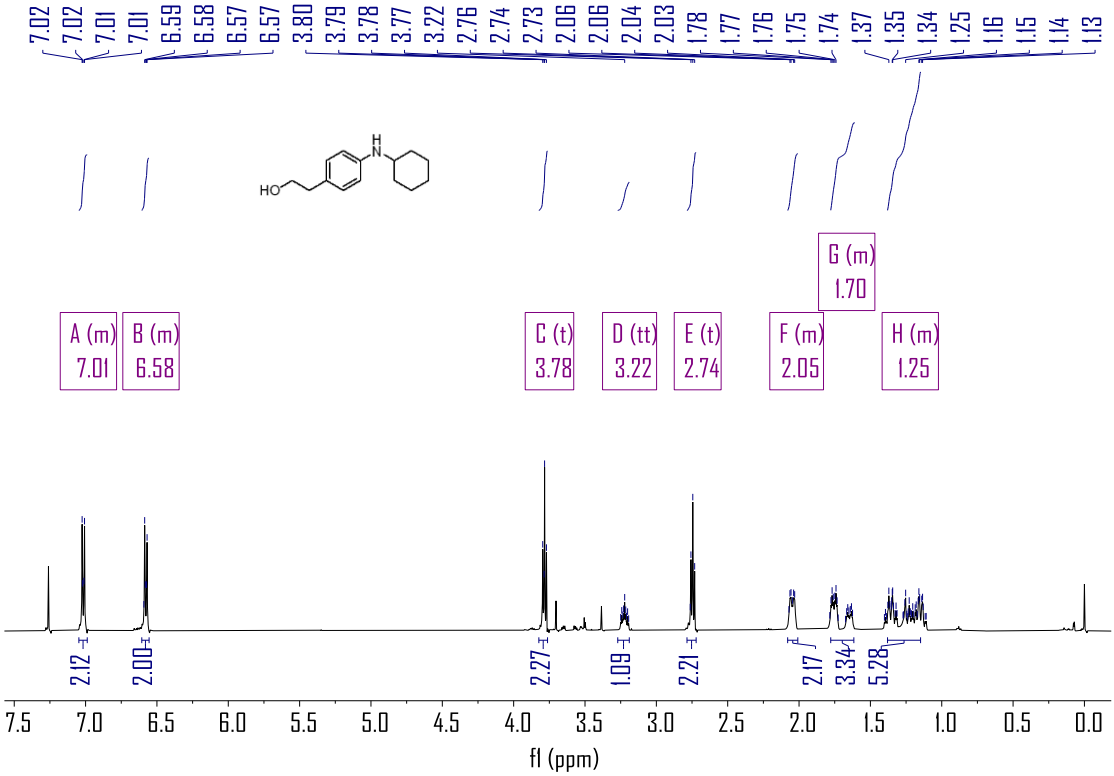


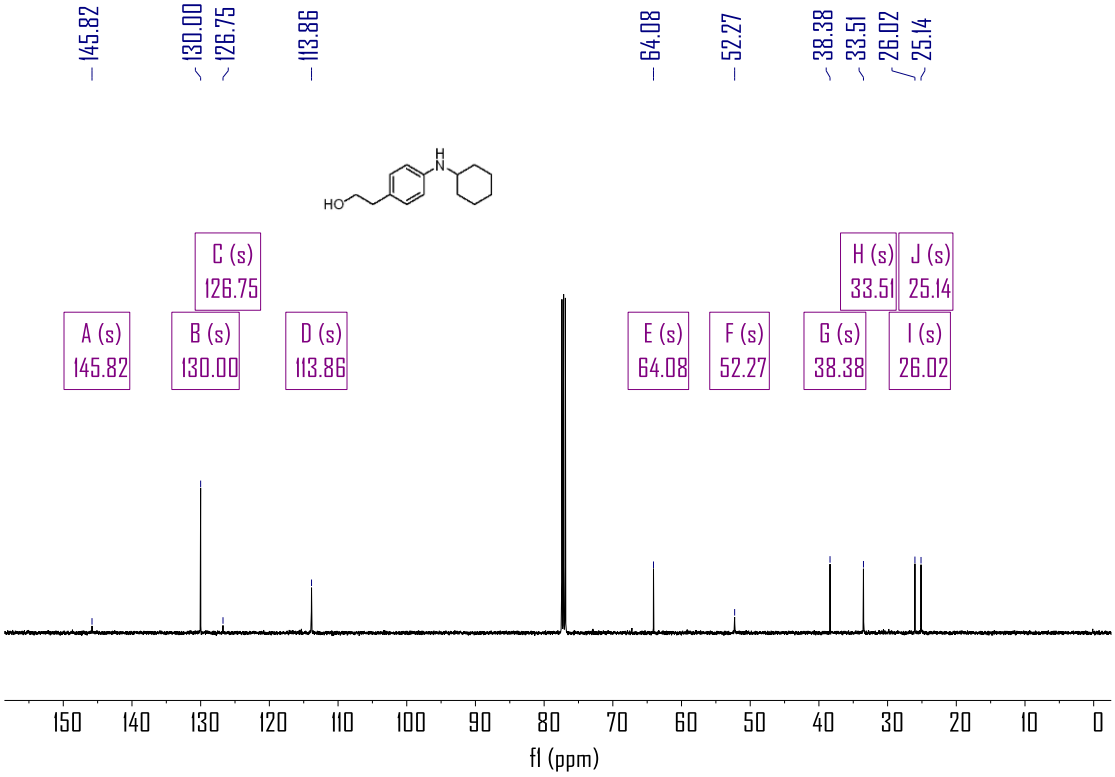


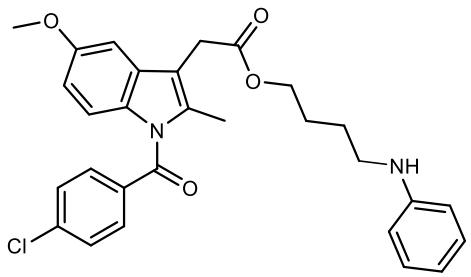

-72.84
TfO
H
N
A (s)
-72.84
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)



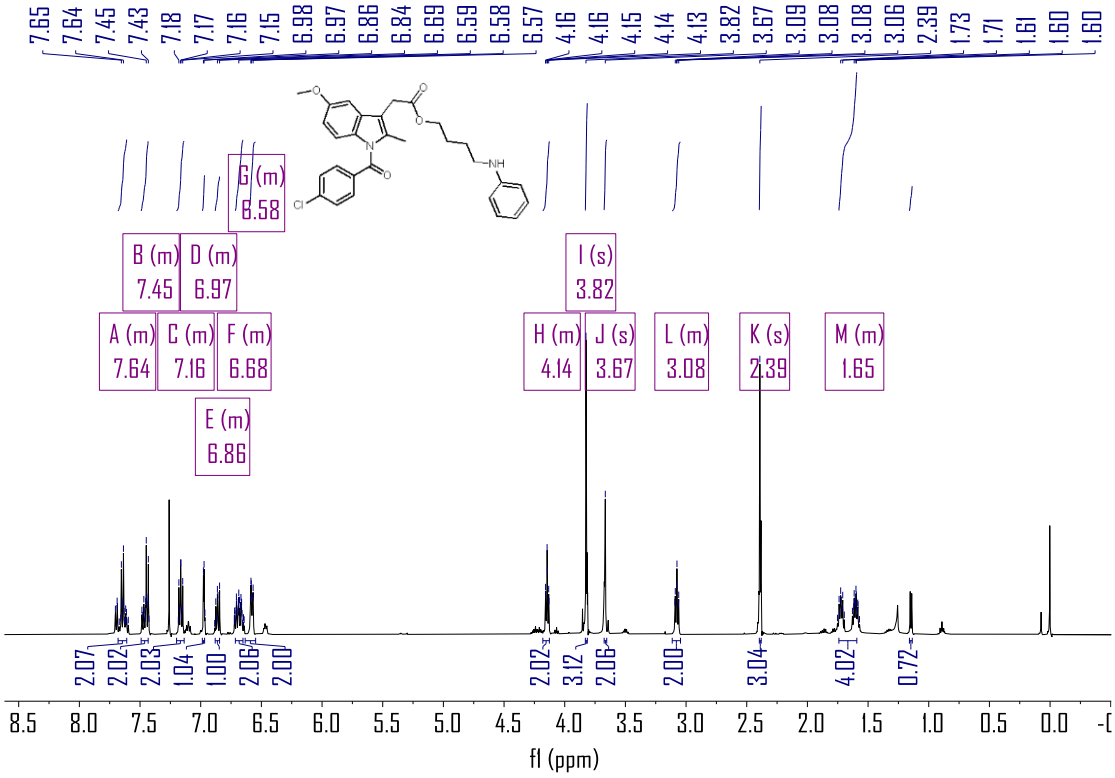
2-(4-(cyclohexylamino)phenyl)ethan-1-ol **(31)**

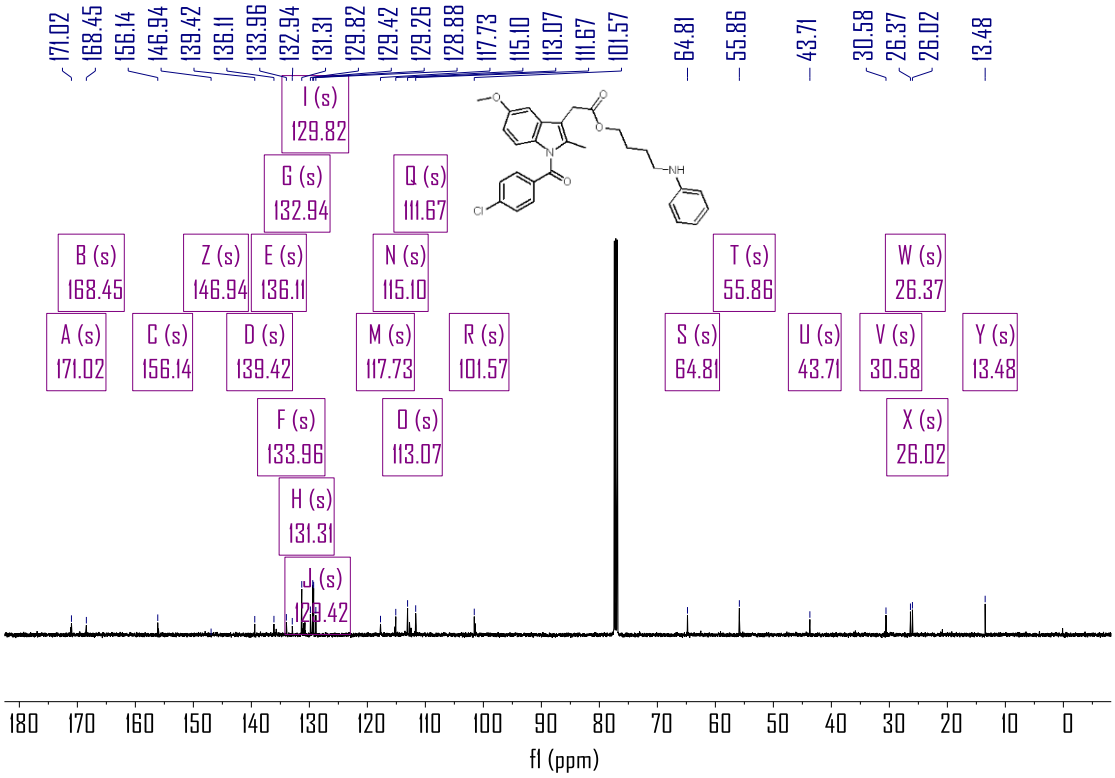


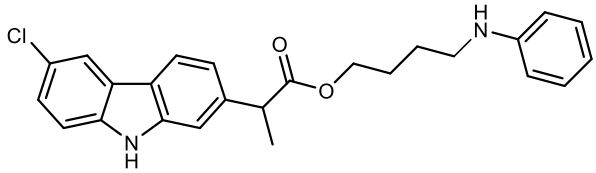




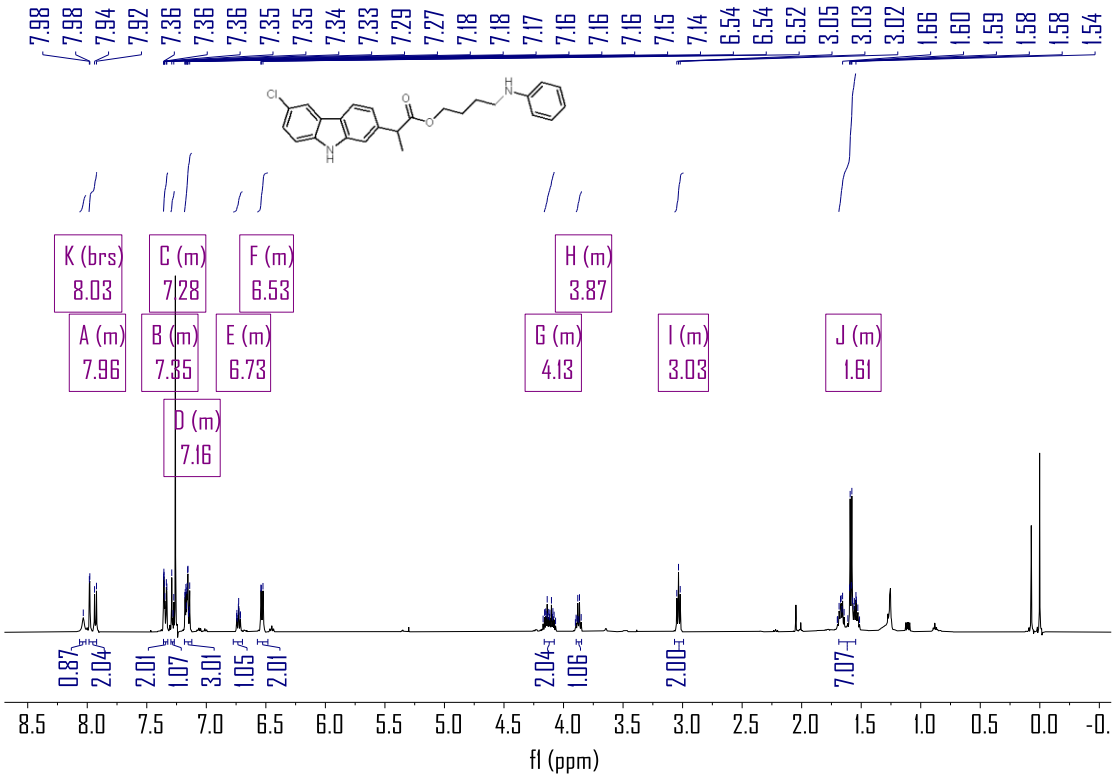
4-(phenylamino)butyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate **(41)**

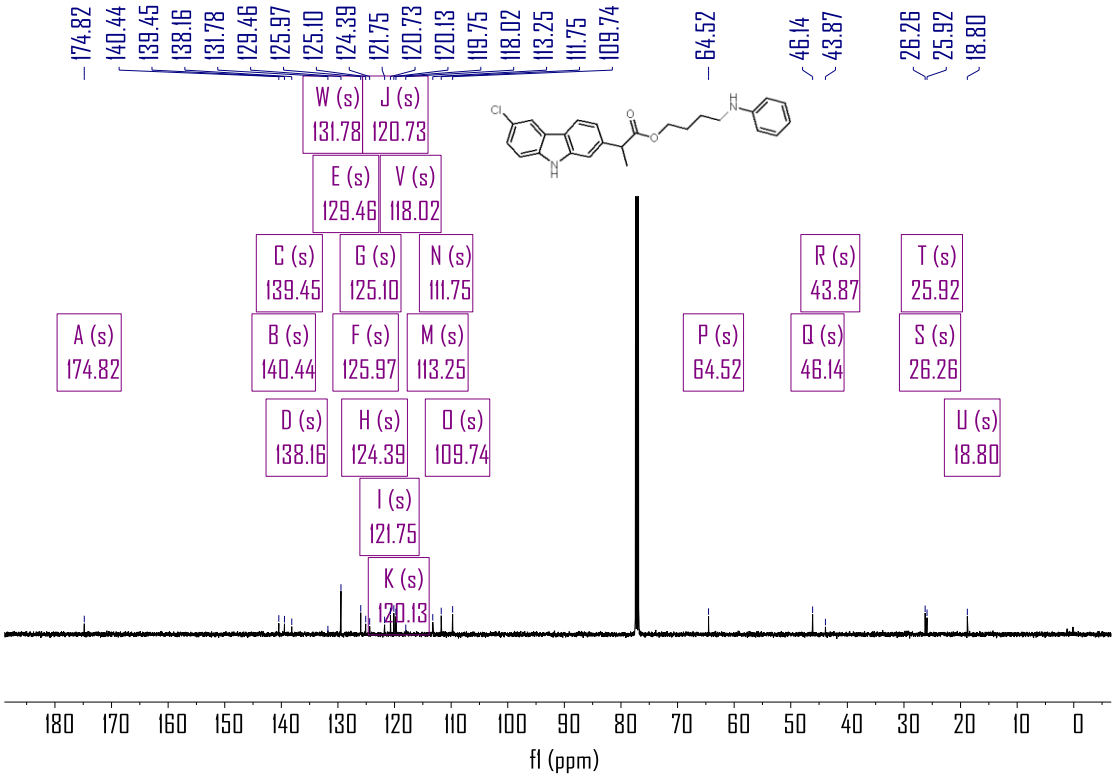


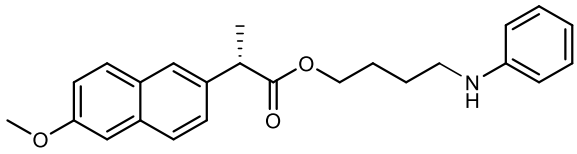

171.02
168.45
156.14
146.94
139.42
136.11
133.96
132.94
131.31
129.82
129.42
129.26
128.88
117.73
115.10
113.07
111.67
101.57
64.81
55.86
43.71
30.58
26.37
26.02
13.48
I (s)
129.82
G (s)
132.94
Q (s)
111.67
B (s)
168.45
Z (s)
146.94
E (s)
136.11
N (s)
115.10
T (s)
55.86
W (s)
26.37
A (s)
171.02
C (s)
156.14
D (s)
139.42
M (s)
117.73
R (s)
101.57
S (s)
64.81
U (s)
43.71
V (s)
30.58
Y (s)
13.48
F (s)
133.96
O (s)
113.07
X (s)
26.02
H (s)
131.31
J (s)
129.42
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



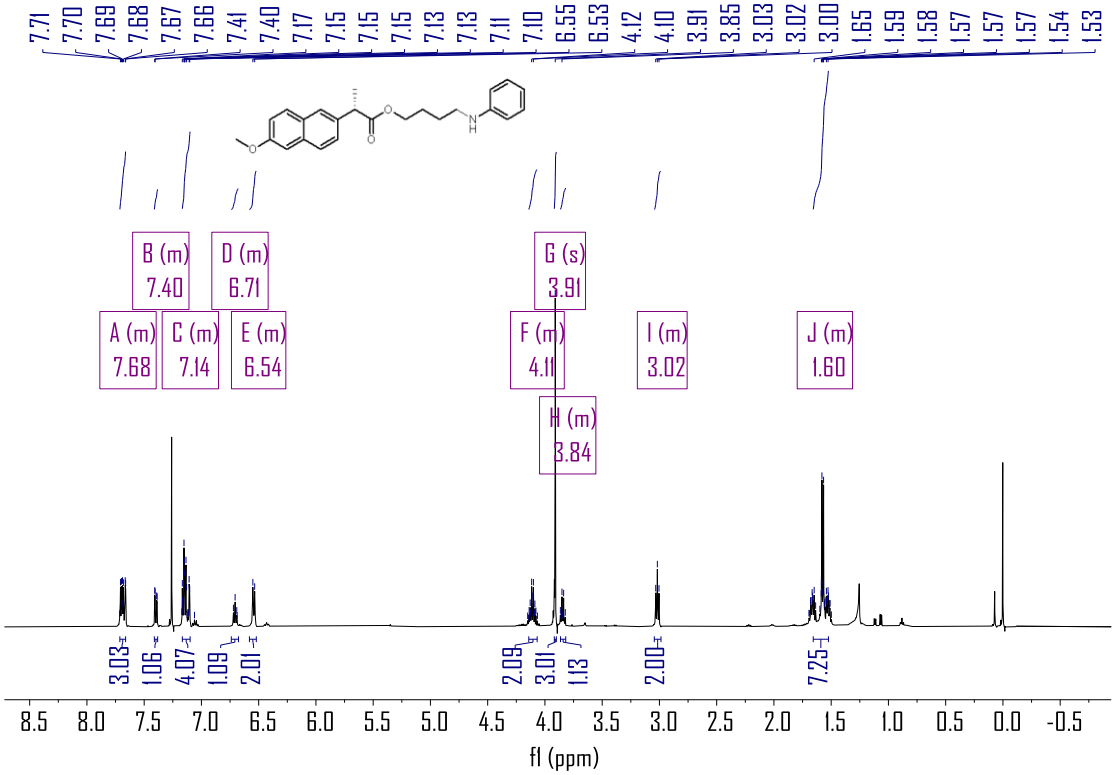
4-(phenylamino)butyl 2-(6-chloro-9*H*-carbazol-2-yl)propanoate **(42)**

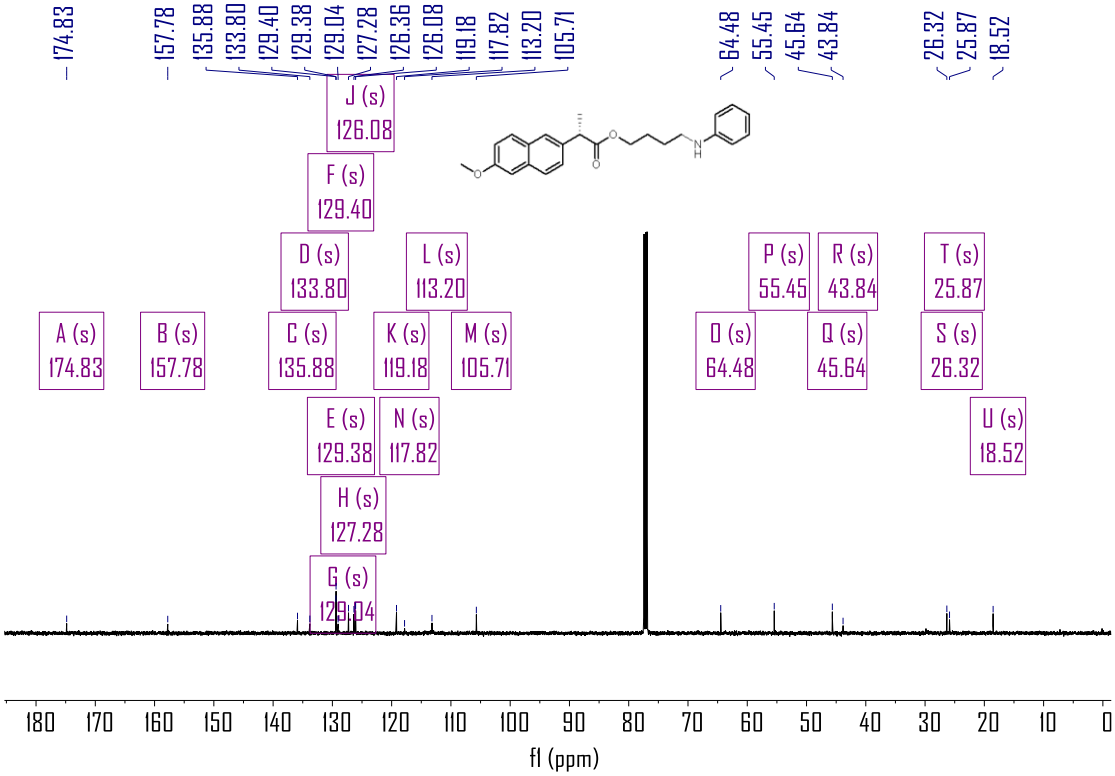






4-(phenylamino)butyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate **(42)**





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