Supporting Information for

Aluminium complex as an efficient catalyst for chemo-selective reduction of amides to amines

Suman Das,[a] Himadri Karmakar,[a] Jayeeta Bhattacharjee,[a] Tarun K. Panda*[a]

Department of Chemistry, Indian Institute of Technology Hyderabad, Kandi – 502 285, Sangareddy, Telangana, India.

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X-ray crystallographic analyses:

Single crystals of complexes **1a, 1b** and **2b** were grown from a concentrated solution of toluene or toluene/THF (3:1) in an argon-filled atmosphere at -35 °C. A crystal of suitable dimensions of complexes **1a, 1b** and **2b** were mounted on a CryoLoop (Hampton Research Corp.) with a layer of light mineral oil. All the crystals **1a**, **1b,** and **2b** were measured at 293 K. All measurements were made on a Rigaku Supernova X-calibur Eos CCD detector with graphite monochromatic Mo-Kα (0.71073 Å) radiation. Crystal data and structure refinement parameters of complexes **1a, 1b** and **2b** are summarized in Table TS1. The structures were solved by direct methods (SIR2004)[1] and refined on F^2 by full-matrix least-squares methods, using SHELXL-2016/6.[2] Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\sum w(Fo^2 - Fc^2)^2]$ ($w = 1 / [\sigma^2(Fo^2) + (aP)^2 + bP]$), where $P = (\mathrm{Max}(Fo^2,0) + 2Fc^2) / 3$ with $\sigma^2(Fo^2)$ from counting statistics. The function $R1$ and $wR2$ were $(\Sigma||Fo| - |Fc||) / \Sigma|Fo|$ and $[\Sigma w(Fo^2 - Fc^2)^2 / \Sigma(wFo^4)]^{1/2}$, respectively. The ORTEP-3 program was used to draw the molecules of **1a, 1b,** and **2b**. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1912620 (**1a**), 1912619 (**1b**) 1912621 (**2b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: + (44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

Table TS1. Crystallography table of metal complexes **1a, 1b,** and **2b.**

Crystal Parameters	**1a**	**1b**	**2b**
Identification code	8421	8494	8524
CCDC No.	1912620	1912619	1912621
Empirical formula	$C_{21}H_{17}N_2PS$	$C_{21}H_{17}N_2PSe$	$C_{27}H_{30}AlN_2PSe$
Formula weight	360.40	407.30	535.44
T (K)	293(2) K	293(2) K	293(2) K
λ (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P\,2_1/n$	$P\,2_1/n$	P -1
a(Å)	9.6363(4)	9.6733(4)	9.8019(13)
b (Å)	15.4223(6)	15.4600(8)	10.1178(13)
c(Å)	12.3931(4)	12.4870(5)	13.5450(19)
α (°)	90	90	89.947(11)
β (°)	104.016(4)	103.385(4)	83.892(11)
γ (°)	90	90	81.113(11)
V(Å^3)	1786.95(12)	1816.70(14)	1319.5(3)
Z	4	4	2
D_{calc} g cm^{-3}	1.340	1.489	1.348
μ (mm^{-1})	0.276	2.160	1.538
F(000)	752	824	552
Theta range for data collection	3.138 to 29.100 deg	3.030 to 29.121 deg.	2.998 to 29.082 deg
Limiting indices	-13<=h<=10, -19<=k<=20, -14<=l<=16	-12<=h<=13, -21<=k<=17, -17<=l<=16	-12<=h<=13, -13<=k<=13, -17<=l<=17
Reflections collected / unique	8530 / 4124 [R(int) = 0.0420]	13856 / 4328 [R(int) = 0.0525]	10966 / 6005 [R(int) = 0.0490]
Completeness to theta	99.8 %	99.8 %	99.8 %
Absorption correction	Multi-scan	Multi-scan	Multi-scan
Max. and min. transmission	1.00000 and 0.91324	1.00000 and 0.24268	1.00000 and 0.93571
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4124 / 0 / 226	4328 / 0 / 226	6005 / 0 / 300
Goodness-of-fit on F^2	1.064	1.028	1.047
Final R indices [I>2sigma(I)]	R1 = 0.0550, wR2 = 0.1066	R1 = 0.0485, wR2 = 0.0957	R1 = 0.0729, wR2 = 0.1764
R indices (all data)	R1 = 0.1010, wR2 = 0.1370	R1 = 0.0963, wR2 = 0.1175	R1 = 0.1274, wR2 = 0.2092

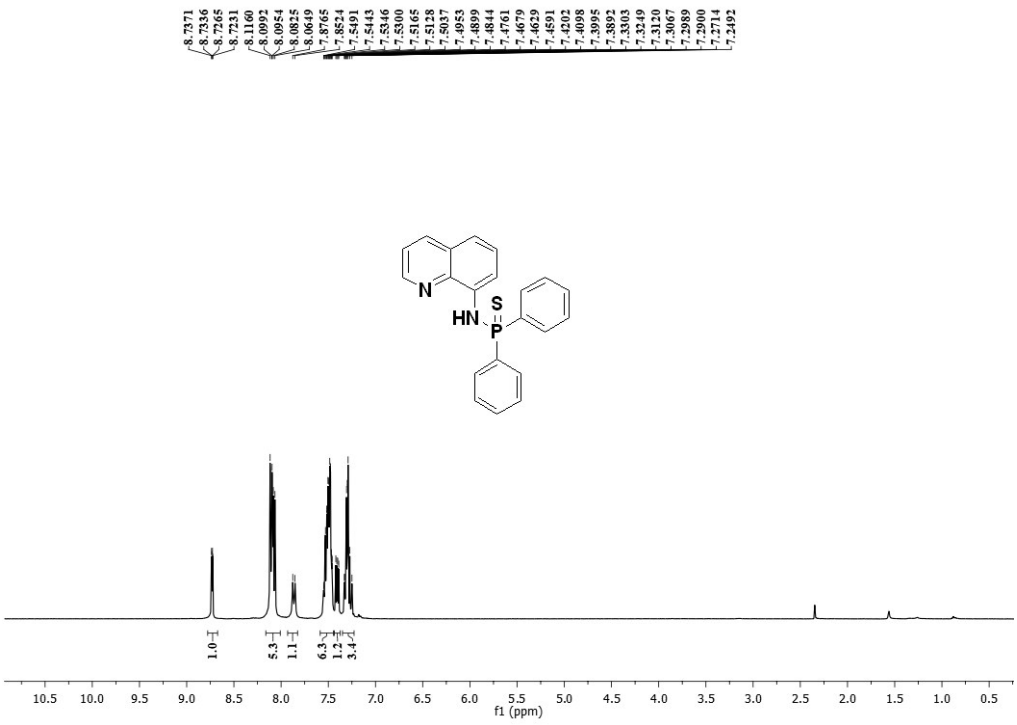


Figure FS1. [1]H NMR spectra of complex **1a**.

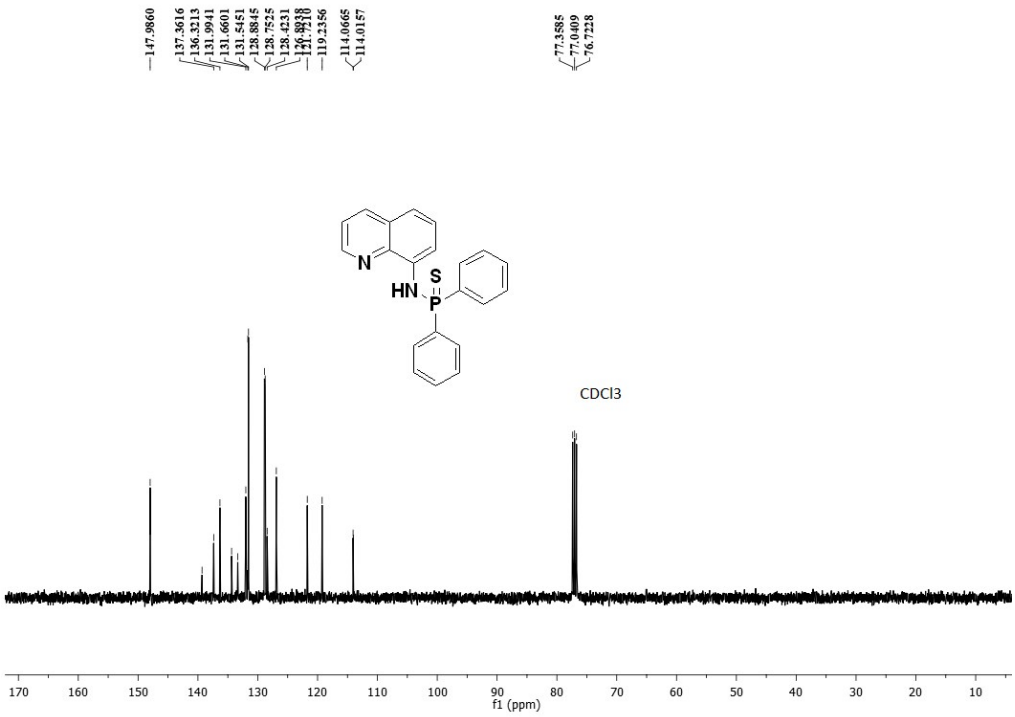


Figure FS2. [13]C NMR spectra of complex **1a**.

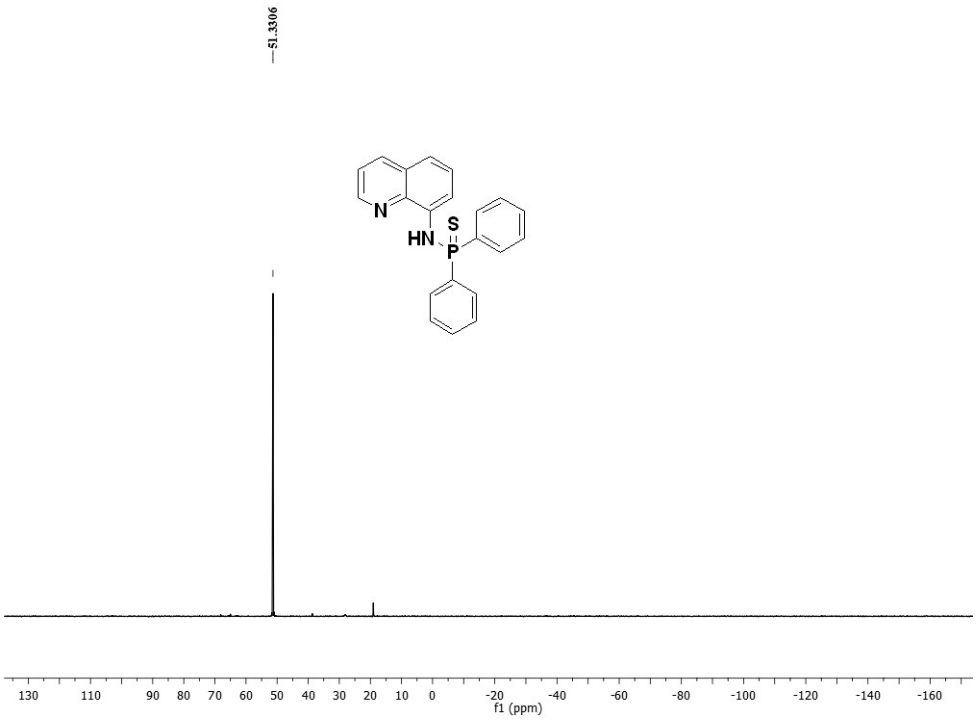


Figure FS3. ^{13}P NMR spectra of complex **1a**.

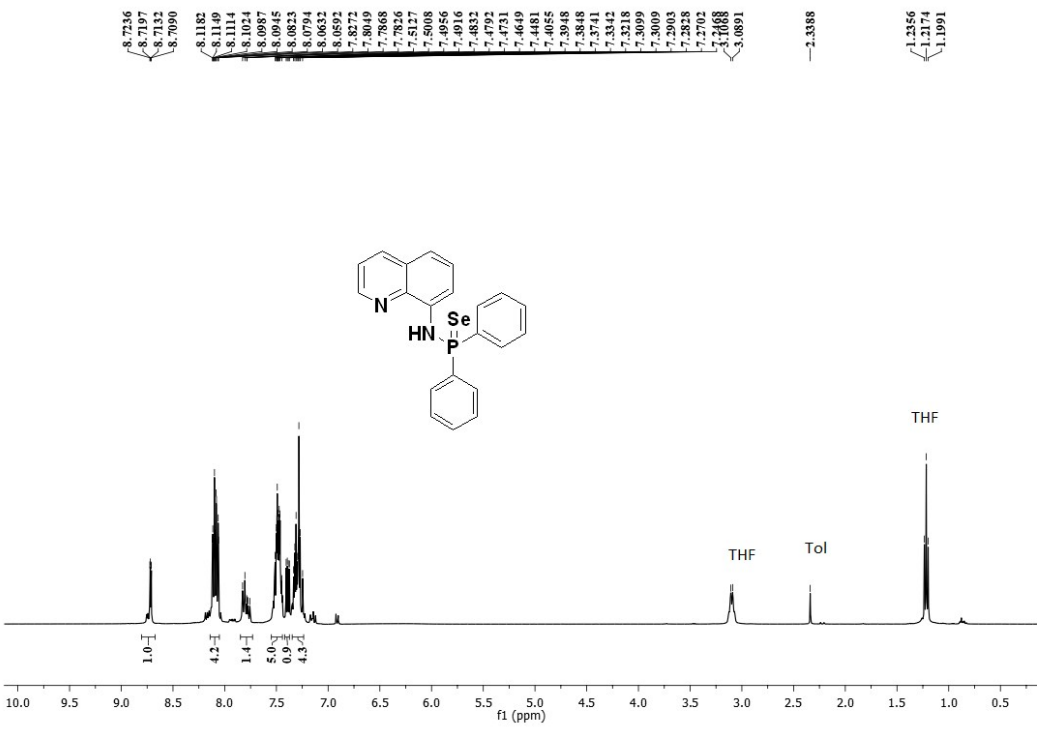


Figure FS4. ^{1}H NMR spectra of complex **1b**.

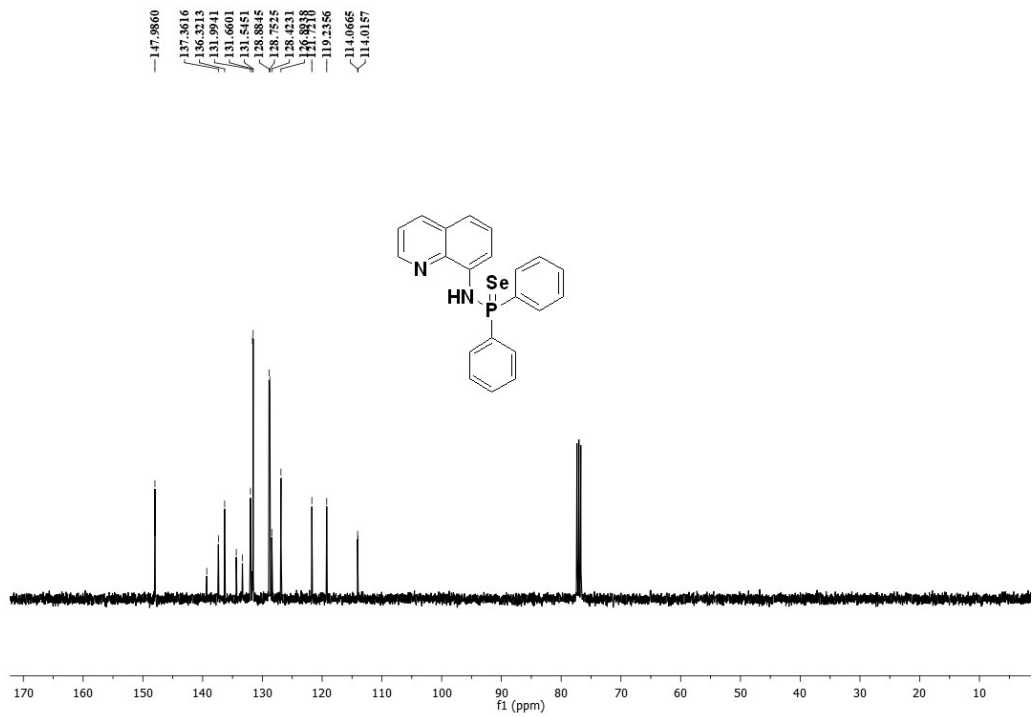


Figure FS5. ^{13}C NMR spectra of complex **1b**.

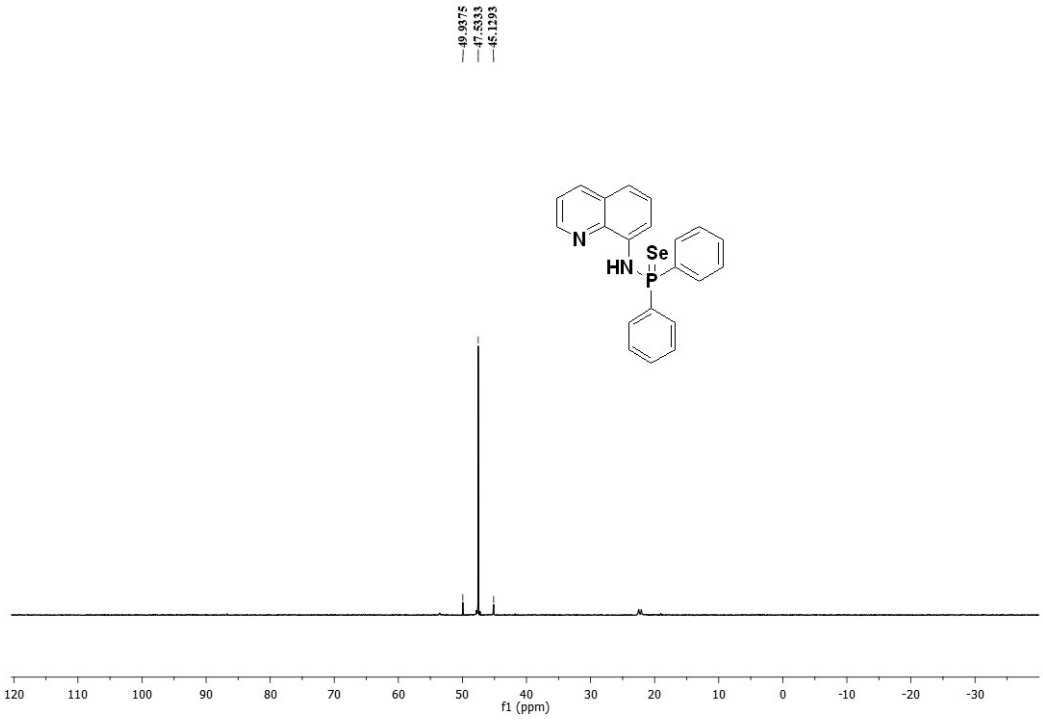


Figure FS6. ^{13}P NMR spectra of complex **1b**.

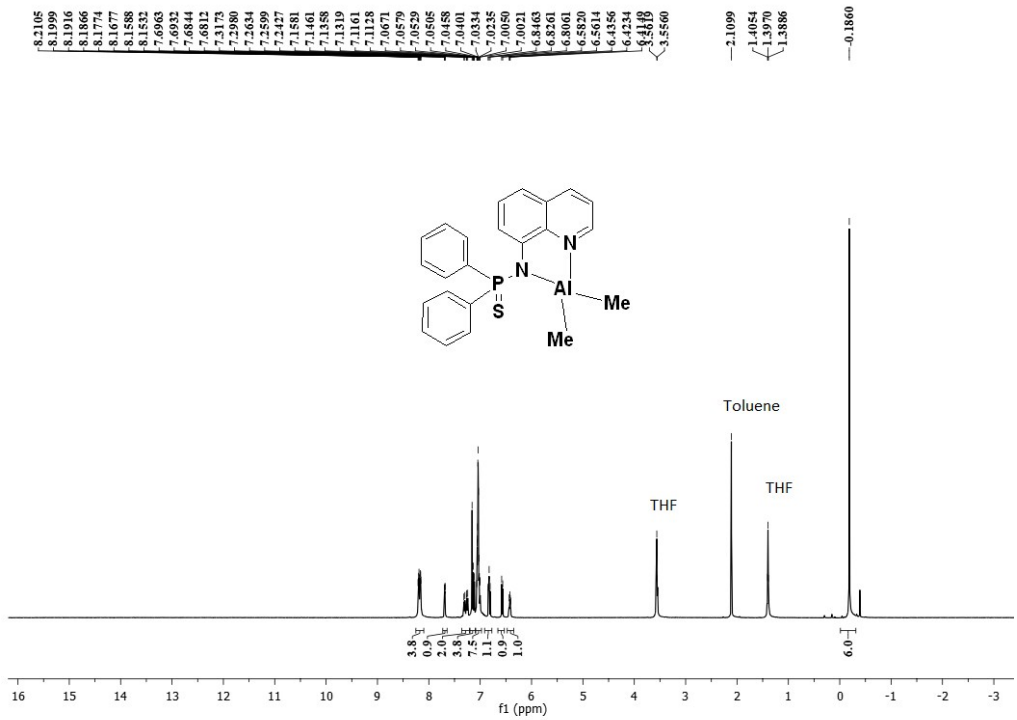


Figure FS7. ^{1}H NMR spectra of complex **2a**.

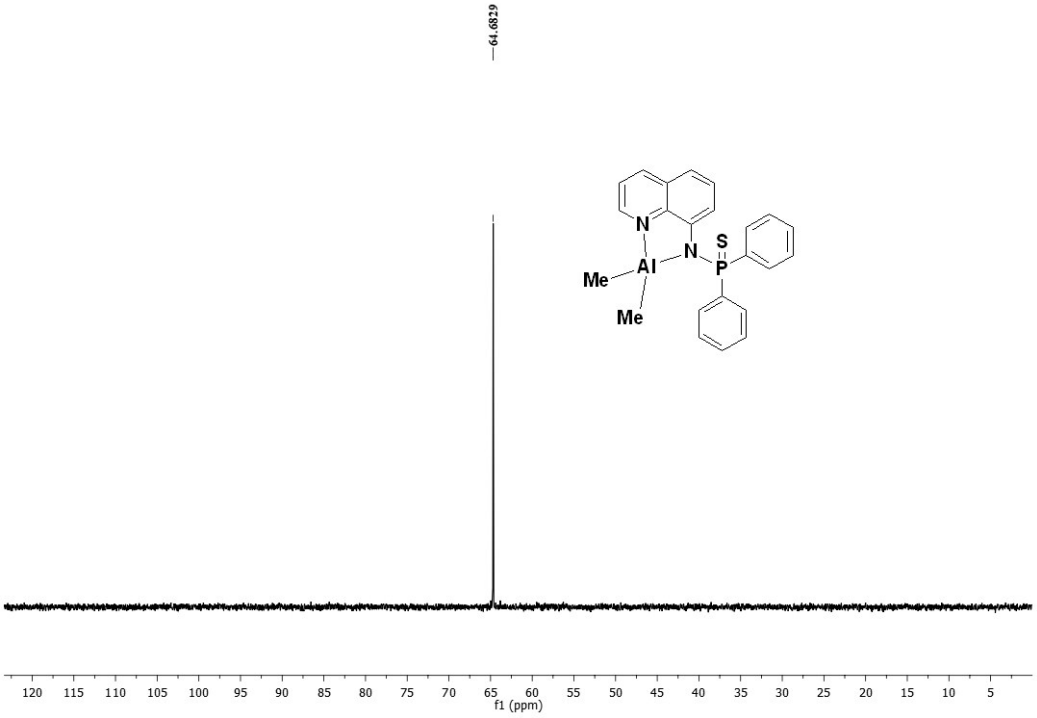


Figure FS8. ^{13}P NMR spectra of complex **2a**.

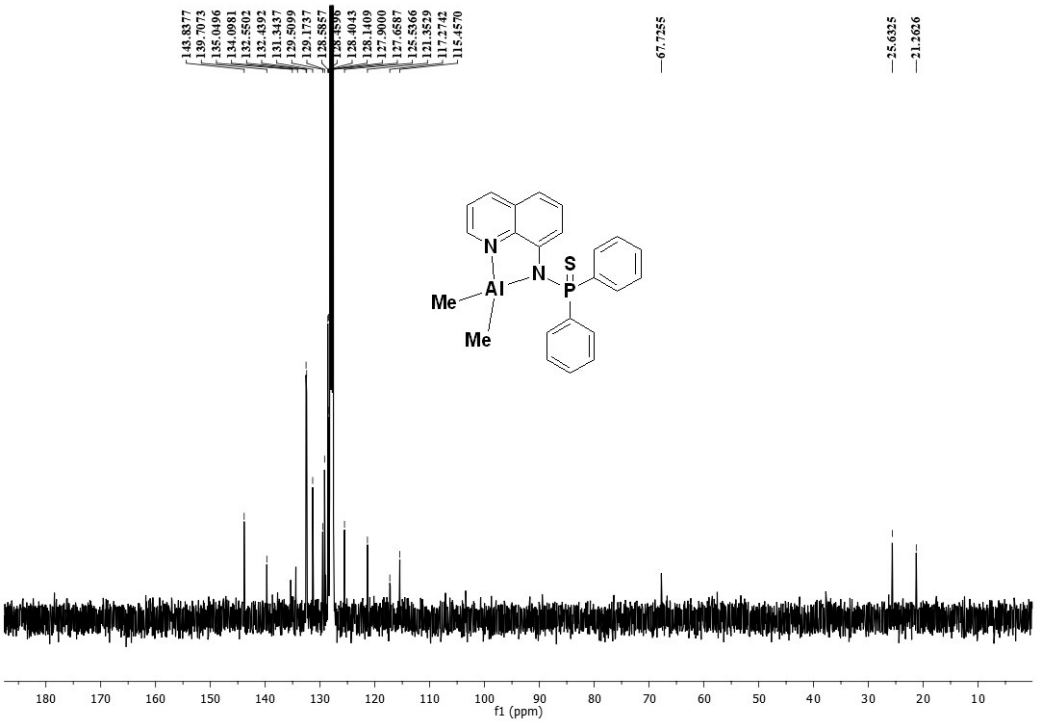


Figure FS9. ^{13}C NMR spectra of complex **2a**.

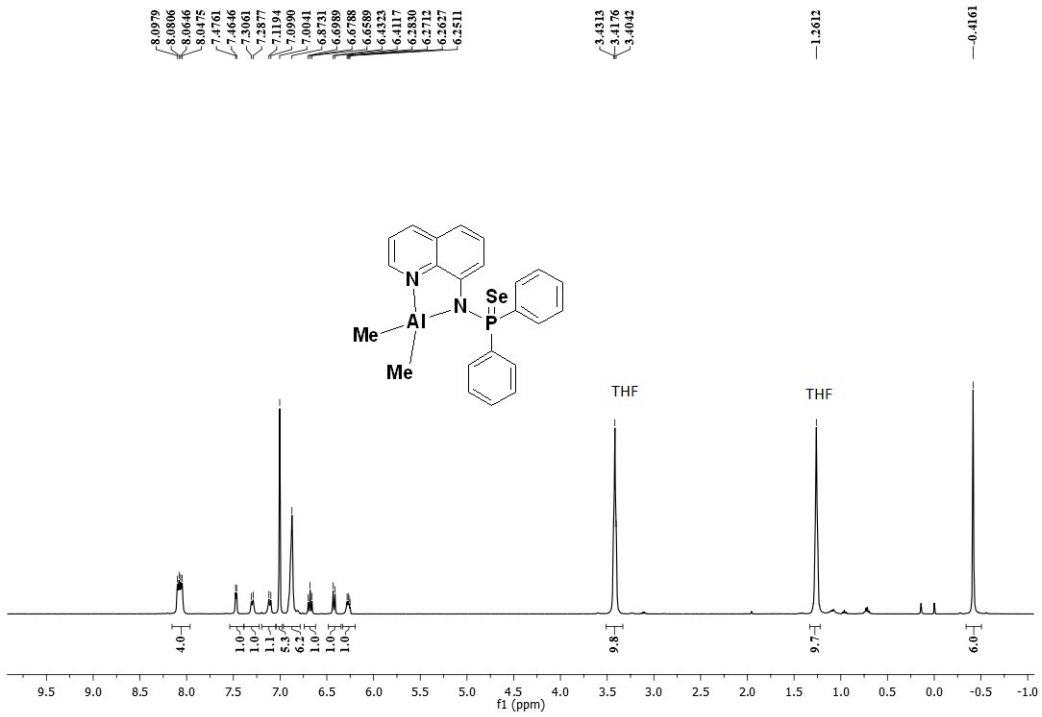


Figure FS10. ^{1}H NMR spectra of complex **2b**.

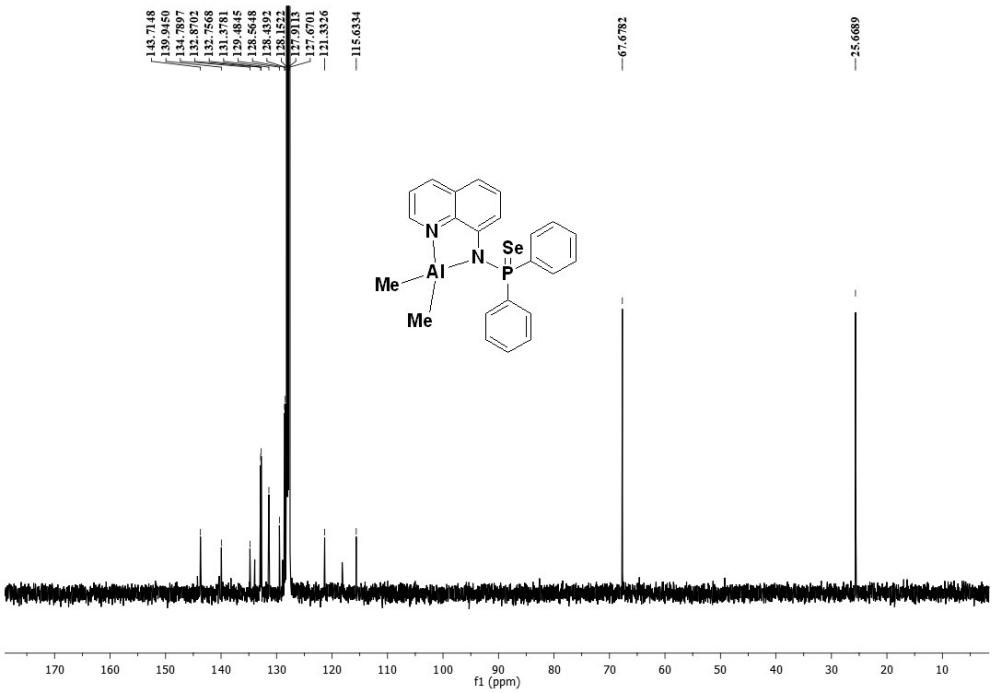


Figure FS11. ^{13}C NMR spectra of complex **2b**.

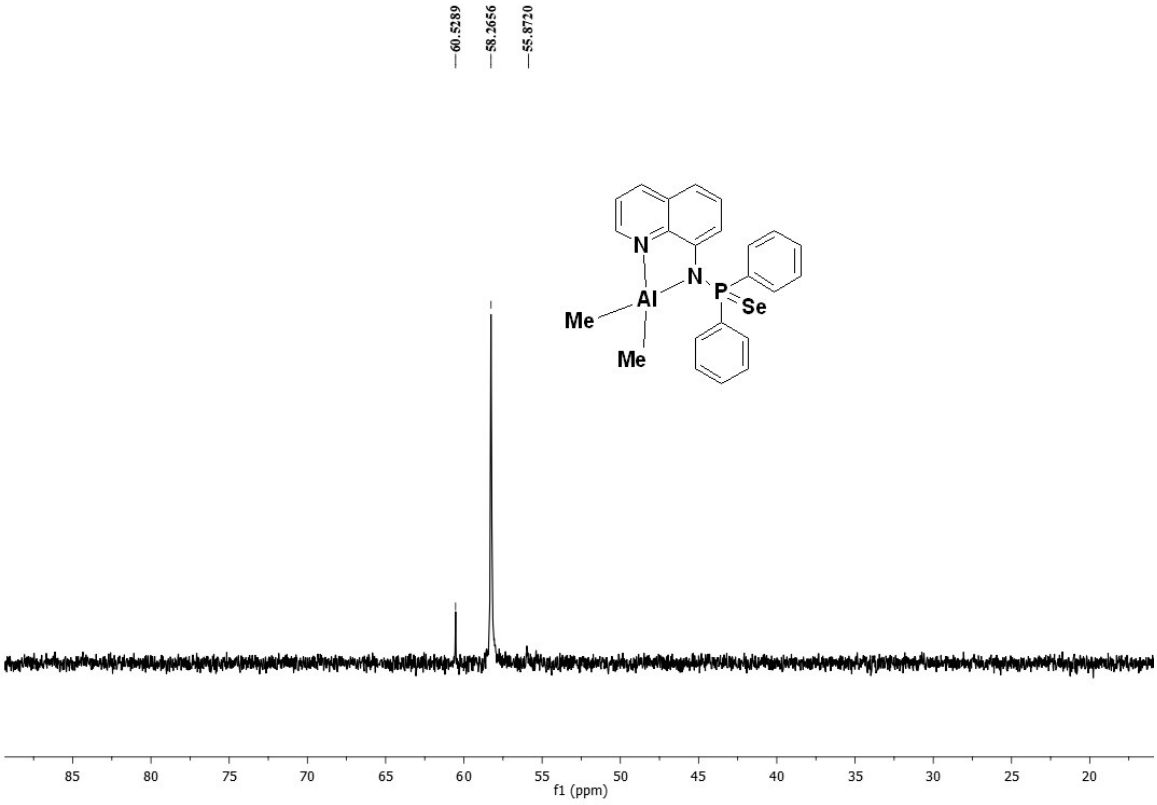
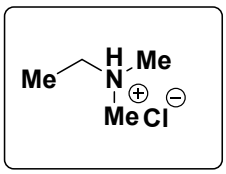


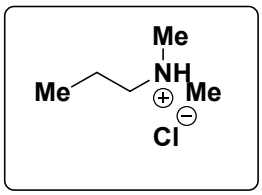
Figure FS12. ^{13}P NMR spectra of complex **2b**.

Catalytic aluminium complex as an efficient catalyst for selective reduction of amides to amines

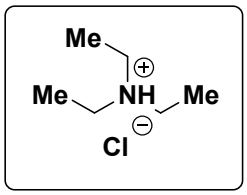
<u>Characterisation Data</u>: (reduction of amides to amines).



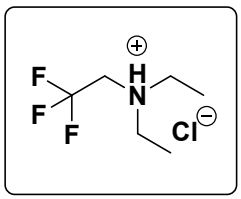
Isolated yield (**3a**) (39.6 mg, 96%). ^{1}H NMR (400 MHz, D_2O): δ 3.13 - 3.07 (q, 2H, CH_2), 2.78 (s, 6H, CH_3), 2.64 (s, 1H, N*H*), 1.24 - 1.20 (t, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 83.7, 75.5, 38.3, 35.6, 34.5, 23.7, 19.9 ppm.



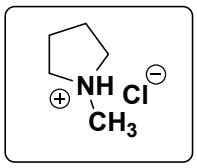
Isolated yield (**3b**) (46.2 mg, 94%). ^{1}H NMR (400 MHz, D_2O): δ 2.91 (s, 1H, CH_2), 2.83 (s, 1H, CH_2), 2.63 (s, 2H, CH_2), 2.35-2.30 (s, 2H, CH_2), 1.29 - 1.27 (d, 6H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 83.9, 75.6, 37.4, 35.4, 34.6, 26.2, 23.8, 8.8 ppm.



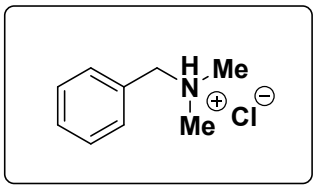
Isolated yield (**3c**) (51.4 mg, 90%). ^{1}H NMR (400 MHz, D_2O): δ 3.27 – 3.16 (m, 6H, CH_2), 1.96 (s, 1H, N*H*), 0.94 – 0.91 (s, 1H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 83.9, 75.6, 37.4, 35.4, 34.6, 26.2, 23.8, 8.8 ppm.



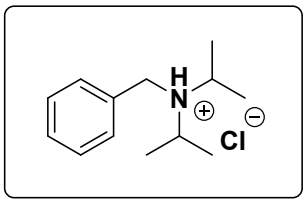
Isolated yield (**3d**) (63.1 mg, 88%). ^{1}H NMR (400 MHz, D_2O): δ 3.06 (s, 2H, CH_2), 1.69 – 1.63 (m, 2H, CH_2), 1.57- 1.53 (m, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 75.6, 44.7, 23.9, 22.2, 21.5, ppm. ^{19}F NMR (376 MHz, D_2O): δ – 64.8 ppm.



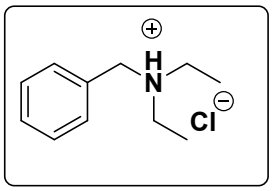
Isolated yield (**3e**) (44.2 mg, 92%). ^{1}H NMR (400 MHz, D_2O): δ 3.33 – 3.30 (m, 2H, CH_2), 2.64 (s, 3H, CH_3), 2.26 – 2.22 (m, 2H, CH_2), 1.89 – 1.83 (m, 2H, CH_2) ppm. ^{13}C NMR (100 MHz, D_2O): δ 75.5, 50.2, 30.6, 29.4, 23.7, 16.8 ppm.



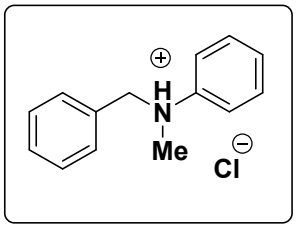
Isolated yield (**3f**) (70.2 mg, 92%). ^{1}H NMR (400 MHz, D_2O): δ 7.41 - 7.35 (m, 5H, Ar*H*), 4.24 (s, 2H, CH_2), 3.03 - 2.65 (m, 1H, N*H*), 1.14 (s, 6H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 130.8, 130.1, 129.3, 128.6, 126.6, 75.6, 42.1, 39.6, 35.2, 34.5, ppm.



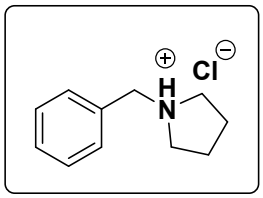
Isolated yield (**3g**) (101.5 mg, 964%). ^{1}H NMR (400 MHz, D_2O): δ 7.41 (s, 5H, Ar*H*), 4.21 (s, 2H, CH_2), 3.73 – 3.67 (m, 2H, CH_2), 1.35 - 1.33 (d, 6H, CH_3), 1.12 (s, 6H, N(CH_3)$_2$), 1.01- 0.97(m, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 130.6, 130.4, 129.6, 129.2, 75.6, 54.6, 50.1, 23.8, 18.0, 17.2 ppm.



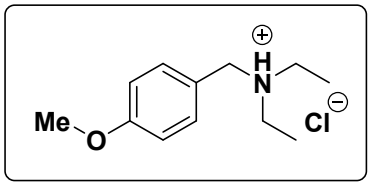
Isolated yield (**3h**) (88.4 mg, 96%). ^{1}H NMR (400 MHz, D_2O): δ 7.41 - 7.36 (m, 5H, Ar*H*), 4.18 (s, 2H, CH_2), 3.12-3.02 (q, 4H, CH_2), 1.21 - 1.17 (t, 1H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 130.7, 130.0, 129.3, 129.1, 83.9, 75.6, 55.8, 46.7, 23.7, 8.1 ppm.



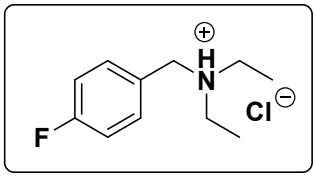
Isolated yield (**3i**) (103.5 mg, 93%). ^{1}H NMR (400 MHz, D_2O): δ 7.46 - 7.41 (m, 1H, Ar*H*), 7.37 - 7.35 (m, 2H, Ar*H*), 7.29 - 7.25 (m, 2H, Ar*H*), 7.22 - 7.18 (m, 2H, Ar*H*), 7.11 - 7.09 (m, 2H, Ar*H*) 4.5 (s, 2H, CH_2), 3.17 (s, 3H, CH_3), 2.91 (s, 1H, N*H*) ppm. ^{13}C NMR (100 MHz, D_2O): δ 139.2, 130.9, 130.3, 130.0, 129.9, 128.9, 121.7, 121.4, 75.6, 63.8, 44.0, 36.9, 23.8 ppm.



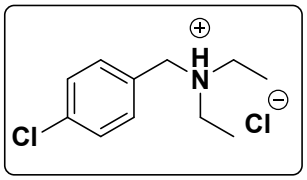
Isolated yield (**3j**) (81.9 mg, 90%). ^{1}H NMR (400 MHz, D_2O): δ 7.45 - 7.40 (m, 2H, Ar*H*), 7.32 - 7.31 (m, 2H, Ar*H*), 7.23 - 7.21 (m, 1H, Ar*H*), 3.50 (s, 2H, CH_2), 2.86 – 2.83 (m, 2H, CH_2). 1.71 – 1.47 (m, 2H, CH_2) ppm. ^{13}C NMR (100 MHz, D_2O): δ 133.8, 130.7, 129.8, 129.2, 122.9, 55.5, 47.6, 27.3, 23.7, 20.5 ppm.



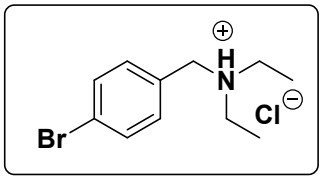
Isolated yield (**3k**) (97.1 mg, 89%). ^{1}H NMR (400 MHz, D_2O): δ 7.26 - 7.24 (d, *J* = 8.6 Hz 1H, Ar*H*), 6.95 – 6.92 (d, *J* = 8.67 Hz 1H, Ar*H*), 4.22 (s, 2H, CH_2), 3.83 (s, 3H, OCH_3), 3.48 - 3.45 (q, 2H, CH_3). 3.28 – 3.15 (q, 2H, CH_3), 1.13 - 1.02 (t, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 159.9, 128.3, 127.9, 114.0, 75.6, 55.5, 44.4, 40.1, 23.9, 19.8, 13.6, 12.3 ppm.



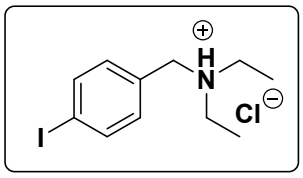
Isolated yield (**3l**) (83.8 mg, 82%). ^{1}H NMR (400 MHz, D_2O): δ 7.38 - 7.34 (m, Hz 2H, Ar*H*), 7.19 – 7.15 (m, 2H, Ar*H*), 4.25 (s, 2H, CH_2), 3.46 – 3.45 (q, 2H, CH_3), 3.23 – 3.21 (q, 2H, CH_3), 1.321-1.34 (t, 3H, CH_3), 1.06 – 1.00 (t, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 133.3, 128.1, 116.3, 115.8, 83.9, 75.6, 55.1, 46.7, 42.3 23.7, 13.2, 12.1 ppm.



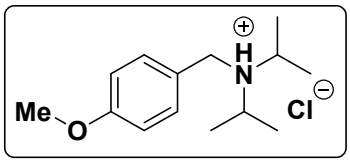
Isolated yield (**3m**) (93.5 mg, 84%). ^{1}H NMR (400 MHz, D_2O): δ 7.61 - 7.59 (m, Hz 2H, Ar*H*), 7.34 – 7.32 (m, 2H, Ar*H*), 4.22 (s, 2H, CH_2), 3.15 – 3.10 (q, 2H, CH_3), 3.09 – 2.98 (q, 2H, CH_3), 1.25 - 1.17 (t, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 132.4, 129.4, 128.9, 127.6, 75.7, 46.8, 23.8, 8.2 ppm.



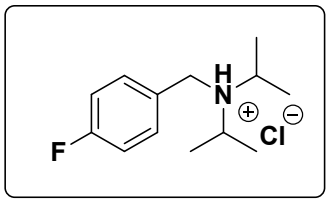
Isolated yield (**3n**) (116.2 mg, 85%). ^{1}H NMR (400 MHz, D_2O): δ 7.54 - 7.51 (m, Hz, 2H, Ar*H*), 7.26 – 7.24 (m, 1H, Ar*H*), 7.17 – 7.15 (m, 1H, Ar*H*), 4.15 (s, 2H, CH_2), 3.37 - 3.36 (q, 3H, CH_3), 3.13 - 3.02 (q, 3H, CH_3), 1.13 – 1.07 (q, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 133.3, 128.1, 116.3, 115.8, 83.9, 75.6, 55.1, 46.7, 42.3 23.7, 13.2, 12.1 ppm.



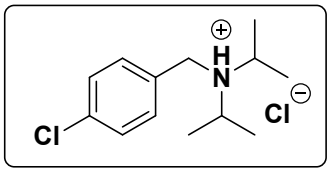
Isolated yield (**3o**) (142.0 mg, 87%). ^{1}H NMR (400 MHz, D_2O): δ 7.36 - 7.32 (m, Hz, 2H, Ar*H*), 7.16 – 7.12 (m, 2H, Ar*H*), 4.14 (s, 2H, CH_2), 3.46 - 3.41 (q, 3H, CH_3), 3.23 - 3.12 (q, 3H, CH_3), 1.12 – 1.17 (t, 3H, CH_3) 1.03 – 1.00 (t, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 131.8, 128.1, 115.8, 115.6, 75.7, 44.4, 42.3, 40.2, 23.7, 13.2, 12.1, 10.5 ppm.



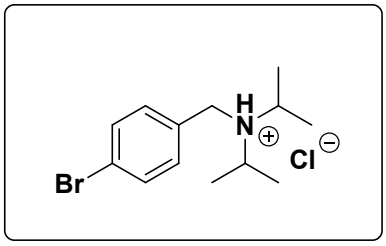
Isolated yield (**3p**) (117.4 mg, 94%). ^{1}H NMR (400 MHz, D_2O): δ 7.31 - 7.29 (d, *J* = 8.6 Hz, 1H, Ar*H*), 7.18 – 7.16 (d, *J* = 8.6 Hz 1H, Ar*H*), 6.90 – 6.88 (d, *J* = 8.6 Hz 1H, Ar*H*), 4.12 (s, 2H, CH_2), 3.70 - 3.63 (s, 3H, OCH_3), 3.62 – 3.57 (m, 2H, CH_3) 1.28 – 1.26 (d, 6H, CH_3), 1.22 – 1.21 (d, 6H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 159.6, 132.1, 127.3, 122.8, 114.6, 83.4, 75.6, 55.5, 54.2, 49.6, 23.9, 19.8, 18.05, 17.3 ppm.



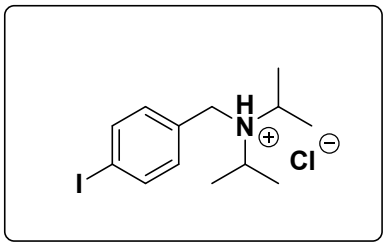
Isolated yield (**3q**) (100.4 mg, 85%). ^{1}H NMR (400 MHz, D_2O): δ 7.51 - 7.49 (d, *J* = 8.3 Hz, 2H, Ar*H*), 7.26 – 7.24 (d, *J* = 8.3 Hz 2H, Ar*H*), 4.16 (s, 2H, CH_2), 3.65 – 3.62 (t, 2H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 132.3, 132.1, 129.3, 123.1, 83.9, 75.6, 54.8, 46.7, 23.7, 17.6 ppm.



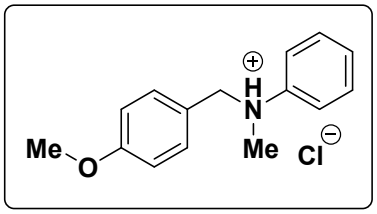
Isolated yield (**3r**) (111.9 mg, 88%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.19 (s, 1H, N*H*), 7.07 – 7.67 (m, 2H, Ar*H*), 7.25 – 7.20 (m, 2H, Ar*H*), 4.32 (s, 2H, CH_2), 3.63 - 3.61 (m, 2H, CH_2), 1.35 – 1.33 (d, 6H, CH_3) 1.31 – 1.29 (d, 6H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 163.4, 161.0, 133.1, 127.1, 115.5, 115.3, 81.4, 54.1, 48.8, 24.3, 20.2, 18.2, 17.3 ppm.



Isolated yield (**3s**) (135.2 mg, 89%). ^{1}H NMR (400 MHz, D_2O): δ 7.57 - 7.55 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.34 - 7.32 (d, *J* = 8.4 Hz, 2H, Ar*H*), 4.22 (s, 2H, CH_2), 3.57 – 3.68 (m, 2H, C*H*), 1.36 - 1.34 (d, 6H, CH_3), 1.30 - 1.28 (d, 6H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 132.2, 131.5, 129.7, 129.1, 123.3, 83.9, 75.6, 54.6, 49.4, 23.7, 17.9, 17.1 ppm.

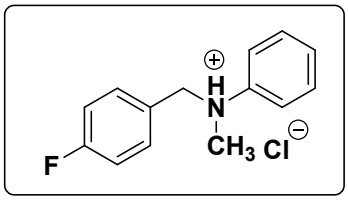


Isolated yield (**3t**) (163.2 mg, 90%). ^{1}H NMR (400 MHz, D_2O): δ 7.83 - 7.81 (d, *J* = 8 Hz, 2H, Ar*H*), 7.24 - 7.22 (d, *J* = 8 Hz, 2H, Ar*H*), 4.27 (s, 2H, CH_2), 3.77 – 3.37 (m, 1H, C*H*), 3.18 - 3.13 (m, 1H, C*H*), 1.33 - 1.29 (d, 6H, CH_3) 1.26 - 1.22 (d, 6H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 140.8, 134.9, 78.2, 57.2, 26.3, 20.9, 10.9 ppm.

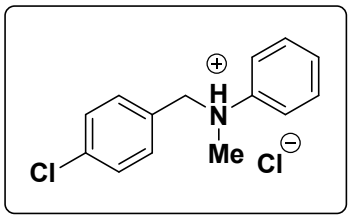


Isolated yield (**3u**) (141.4 mg, 95%). ^{1}H NMR (400 MHz, D_2O): δ 7.52 - 7.46 (m, 6H, Ar*H*), 7.06 – 7.03 (d, *J* = 8.6 Hz 1H, Ar*H*), 6.76 – 6.74 (d, *J* = 8.67 Hz 1H, Ar*H*), 4.7 (s, 2H, CH_2), 3.64 (s,

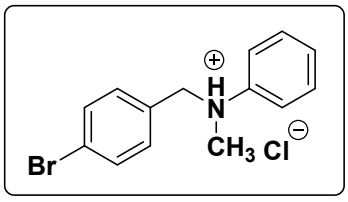
3H, OCH_3), 2.94 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 159.6, 132.1, 127.3, 122.8, 114.6, 83.4, 75.6, 55.5, 54.2, 49.6, 23.9, 19.8, 18.05, 17.3 ppm.



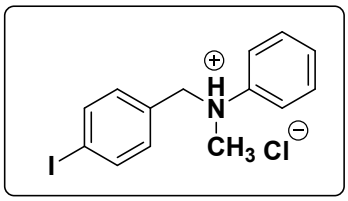
Isolated yield (**3v**) (110.4 mg, 86%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.51 - 7.45 (m, 4H, Ar*H*), 7.44 – 7.42 (m, 1H, Ar*H*), 7.28 – 7.26 (m, 1H, Ar*H*), 7.14 – 7.10 (m, 1H, Ar*H*), 7.01 - 6.99 (m, 1H, Ar*H*), 3.34 (s, 2H, CH_2), 2.91 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 137.3, 130.6, 128.3, 116.8, 122.0, 114.7, 81.9, 36.1, 24.3 ppm.



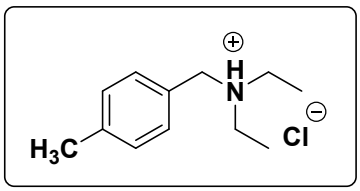
Isolated yield (**3w**) (133.2 mg, 89%). ^{1}H NMR (400 MHz, D_2O): δ 7.44 - 7.41 (m, 3H, Ar*H*), 7.36 – 7.34 (m, 3H, Ar*H*), 7.25 – 7.16 (m, 1H, Ar*H*), 7.02 – 7.0 (m, 1H, Ar*H*), 3.23 (s, 2H, CH_2), 2.96 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 136.3, 132.4, 130.4, 129.7, 121.7, 75.6, 63.0, 43.9, 36.9, 23.7 ppm.



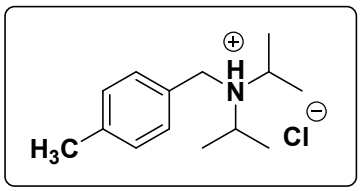
Isolated yield (**3x**) (128.2 mg, 90%). ^{1}H NMR (400 MHz, D_2O): δ 7.43 - 7.40 (m, 3H, Ar*H*), 7.35 – 7.32 (m, 3H, Ar*H*), 7.22 – 7.21 (m, 1H, Ar*H*), 6.94 – 6.92 (m, 1H, Ar*H*), 3.22 (s, 2H, CH_2), 2.94 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 130.3, 129.8, 121.7, 83.9, 75.6, 36.9, 23.7 ppm.



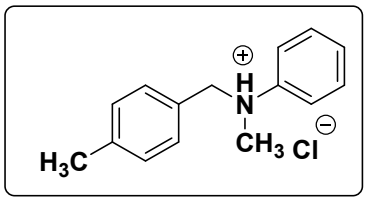
Isolated yield (**3y**) (142.3 mg, 92%). ^{1}H NMR (400 MHz, D_2O): δ 7.46 - 7.41 (m, 3H, Ar*H*), 7.36 – 7.34 (m, 3H, Ar*H*), 7.25 – 7.23 (m, 1H, Ar*H*), 7.18 – 7.16 (m, 1H, Ar*H*), 7.02 - 7.00 (m, 1H, Ar*H*), 3.23 (s, 2H, CH_2), 2.96 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 132.6, 131.9 130.6, 129.8, 121.7, 121.4, 75.4, 36.8, 23.7 ppm.



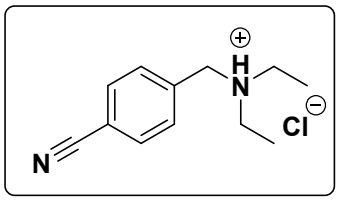
Isolated yield (**3z**) (136.2 mg, 90%). ^{1}H NMR (400 MHz, D_2O): δ 7.20 - 7.09 (m, 4H, Ar*H*), 4.09 (s, 2H, CH_2), 3.35 - 3.31 (q, 2H, CH_3). 3.11 – 3.08 (q, 2H, CH_3), 2.20 (s, 3H, CH_3), 1.20 - 1.13 (t, 3H, CH_3). 0.94 – 0.89 (t, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 140.3, 132.7, 129.9, 125.9, 83.0, 75.6, 46.6, 44.3, 40.0, 23.9, 20.5, 13.6, 12.3 ppm.



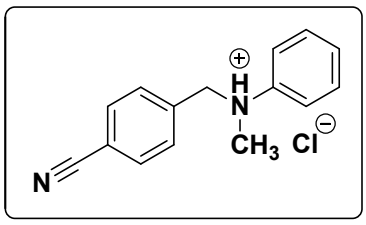
Isolated yield (**3za**) (145.6 mg, 94%). ^{1}H NMR (400 MHz, D_2O): δ 7.27 - 7.25 (d, *J* = 8.1 Hz, 2H, Ar*H*), 7.20 – 7.18 (d, *J* = 8.0 Hz, 2H, Ar*H*), 4.17 (s, 2H, CH_2). 3.67 – 3.64 (m, 2H, C*H*), 2.23 (s, 3H, CH_3), 1.31 - 1.29 (d, *J* = 6.7 Hz, 6H CH_3), 1.25 - 1.23 (d, *J* = 6.7 Hz, 6H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 140.3, 130.4, 129.7, 125.9, 83.9, 75.6, 54.6, 44.3, 40.0, 23.9, 20.3, 17.9,17.2 ppm.



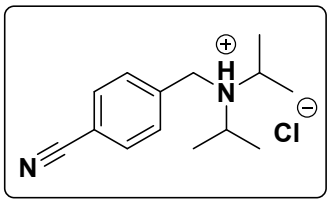
Isolated yield (**3zb**) (140.3 mg, 94%). ^{1}H NMR (400 MHz, D_2O): δ 7.46 - 7.42 (m, 2H, Ar*H*), 7.39 - 7.35 (m, 3H, Ar*H*), 7.27 - 7.25 (m, 1H, Ar*H*), 7.01 - 6.94 (m, 4H, Ar*H*), 3.22 (s, 2H, CH_2), 2.97 (s, 3H, CH_3), 2.12 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 172.0, 130.5, 130.3, 129.5,121.9, 121.6, 83.0, 75.6, 37.1, 23.9, 20.5 ppm.



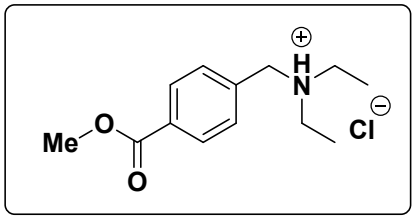
Isolated yield (**4a**) (91.3 mg, 86%). ^{1}H NMR (400 MHz, D_2O): δ 7.38 - 7.37 (d, *J* = 8.6 Hz, 1H, Ar*H*), 7.20 - 7.18 (d, *J* = 8.6 Hz 1H, Ar*H*), 4.02 (s, 2H, CH_2), 3.28 - 3.26 (q, 2H, CH_3), 3.02 – 2.97 (q, 2H, CH_3), 1.10 - 1.07 (t, 3H, CH_3). 0.86 – 0.82 (t, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 172.3, 136.3, 134.0, 129.3, 126.9, 83.6, 75.6, 55.5, 44.4, 42.7, 40.1, 23.9, 13.6,12.3 ppm.



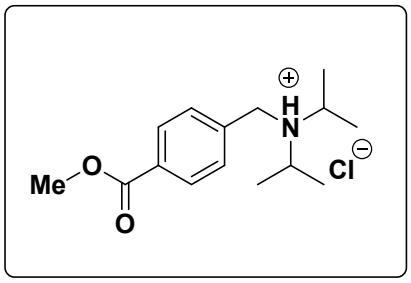
Isolated yield (**4b**) (125.4 mg, 88%). ^{1}H NMR (400 MHz, D_2O): δ 7.14 - 7.69 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.37 – 7.35 (d, *J* = 8.0 Hz, 1H, Ar*H*), 4.19 (s, 2H, CH_2), 3.74 – 3.65 (s, 2H, C*H*), 1.44 – 1.43 (d, *J* = 6.8 Hz, 6H, CH_3), 1.11 – 1.09 (d, *J* = 6.8 Hz, 6H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 138.2, 133.6, 129.4, 126.0, 83.9, 75.7, 52.3, 46.1, 42.8, 23.9, 19.8 ppm.



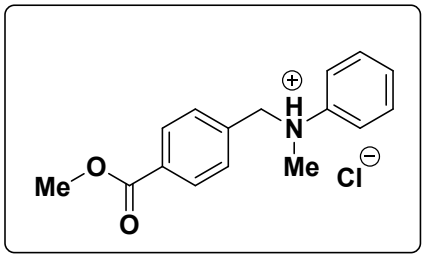
Isolated yield (**4c**) (107.6 mg, 90%). ^{1}H NMR (400 MHz, D_2O): δ 7.51 - 7.49 (d, 2H, Ar*H*), 6.92 – 6.90 (d, *J* = 8.6 Hz 1H, Ar*H*), 4.37 (s, 2H, CH_2), 3.74 (s, 2H, CH_2), 2.97 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 159.9, 128.3, 127.9, 114.0, 75.6, 55.5, 44.4, 40.1, 23.9, 19.8, 13.6, 12.3 ppm.



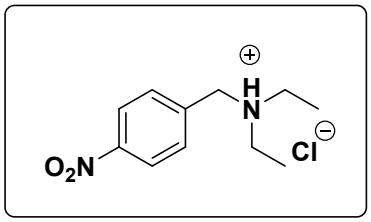
Isolated yield (**4d**) (124.9 mg, 88%). ^{1}H NMR (400 MHz, D_2O): δ 7.98 - 7.95 (d, *J* = 8.6 Hz 1H, Ar*H*), 7.39 - 7.37 (d, *J* = 7.8 Hz 1H, Ar*H*), 4.29 (s, 2H, CH_2), 3.28 - 3.26 (q, 2H, CH_3). 3.02 – 2.97 (q, 2H, CH_3), 1.10 - 1.07 (t, 3H, CH_3). 0.86 – 0.82 (t, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 169.9, 130.9, 130.4, 129.3, 126.1, 75.6, 63.3, 55.2, 52.7, 46.9, 44.1, 40.1, 23.9, 13.0, 11.9, 8.0 ppm.



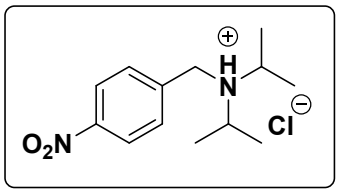
Isolated yield (**4e**) (126.6 mg, 90%). ^{1}H NMR (400 MHz, D_2O): δ 7.90 - 7.88 (m, 1H, Ar*H*), 7.49 - 7.47 (m,1H, Ar*H*), 7.37 - 7.32 (m, 2H, Ar*H*), 7.21 - 7.20 (m, 1H, Ar*H*), 4.29 (s, 2H, CH_2), 3.81 (s, 3H, OCH_3), 3.69 – 3.67 (m, 1H, C*H*), 3.10 - 3.04 (m, 1H, C*H*), 1.35 – 1.31 (d, *J* = 6.7 Hz, 6H, CH_3), 1.26 – 1.24 (d, *J* = 6.6 Hz, 6H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 130.7, 130.4, 127.8, 125.3, 83.9, 75.6, 63.3, 54.9, 52.7, 46.9, 44.6, 23.9, 19.7, 17.9, 17.1 ppm.



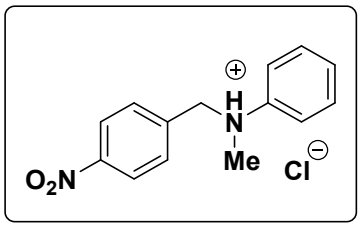
Isolated yield (**4f**) (135.4 mg, 94%). ^{1}H NMR (400 MHz, D_2O): δ 7.70 - 7.68 (d, *J* = 8.3 Hz 1H, Ar*H*), 7.44 - 7.38 (m, 3H, Ar*H*), 7.34 - 7.28 (m, 3H, Ar*H*), 7.28 - 7.20 (m, 2H, Ar*H*), 7.22 - 7.14 (m, 3H, Ar*H*), 4.66 (s, 2H, CH_2), 3.22 (s, 3H, OCH_3), 2.97 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 169.9, 142.5, 138.9, 136.4, 130.4, 129.3, 127.4, 126.1, 83.7, 75.6, 63.3, 57.2, 52.5, 46.9, 23.9, 8.4 ppm.



Isolated yield (**4g**) (94.05 mg, 80%). ^{1}H NMR (400 MHz, D_2O): δ 7.92 - 7.90 (d, *J* = 6.8 Hz, 2H, Ar*H*), 7.24 - 7.12 (m,2H, Ar*H*), 4.10 (s, 2H, CH_2), 3.16 - 3.11 (m, 2H, CH_2), 2.90 – 2.85 (m, 2H, CH_2), 0.86 - 0.81 (t, 3H, CH_3). 0.72 – 0.69 (t, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 135.9, 130.3, 129.7, 121.7, 83.5 75.4, 63.5, 44.3, 37.1, 23.9 ppm.



Isolated yield (**4h**) (112.05 mg, 84%). ^{1}H NMR (400 MHz, D_2O): δ 7.72 - 7.70 (d, *J* = 8.3 Hz 2H, Ar*H*), 7.12 -7.10 (d, *J* = 8 Hz 2H, Ar*H*), 4.15 (s, 2H, CH_2), 3.66 - 3.62 (m, 1H, C*H*), 3.06 – 3.01 (m, 1H, C*H*), 1.27 - 1.21 (d, *J* = 6.7 Hz 6H, CH_3), 1.21 - 1.19 (d, *J* = 6.6 Hz 6H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 137.2, 130.5, 126.9, 123.8, 83.4, 75.4, 52.7, 46.9, 23.9, 13.0, 19.7 ppm.



Isolated yield (**4i)** (117.6 mg, 86%). ^{1}H NMR (400 MHz, D_2O): δ 7.76 - 7.73 (d, *J* = 8.6 Hz, 1H, Ar*H*), 7.28 - 7.18 (m, 5H, Ar*H*), 7.06 - 6.99 (m, 4H, Ar*H*), 6.95 - 6.86 (m, 2H, Ar*H*), 4.67 (s, 2H, CH_2), 3.13 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ 147.9, 138.7, 135.0, 132.1, 130.3, 129.8, 126.8, 122.9, 121.7, 83.5, 75.4, 61.7, 45.1, 38.1, 37.0, 23.9 ppm.

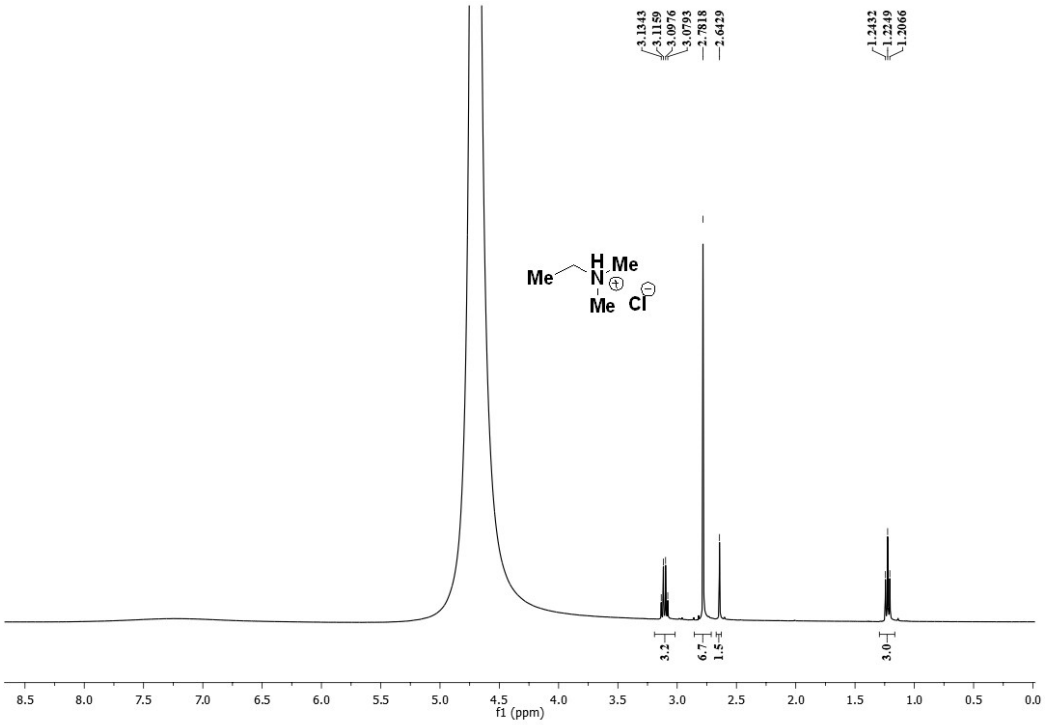


Figure FS13. ^{1}H NMR spectra of compound **(3a)**.

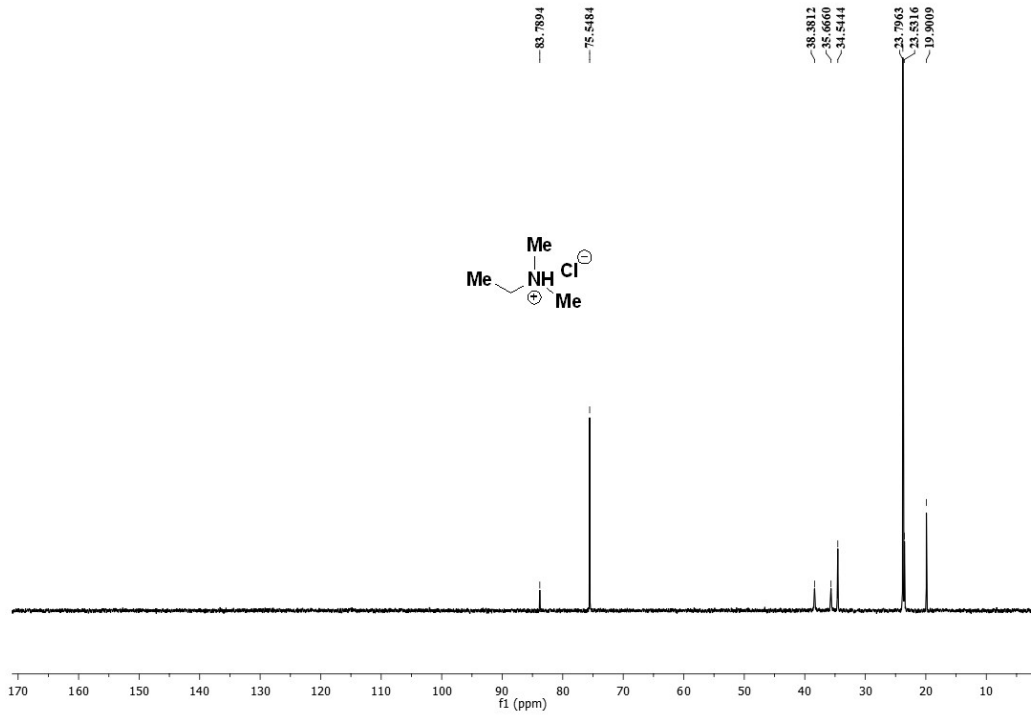


Figure FS14. ^{13}C NMR spectra of compound **(3a)**.

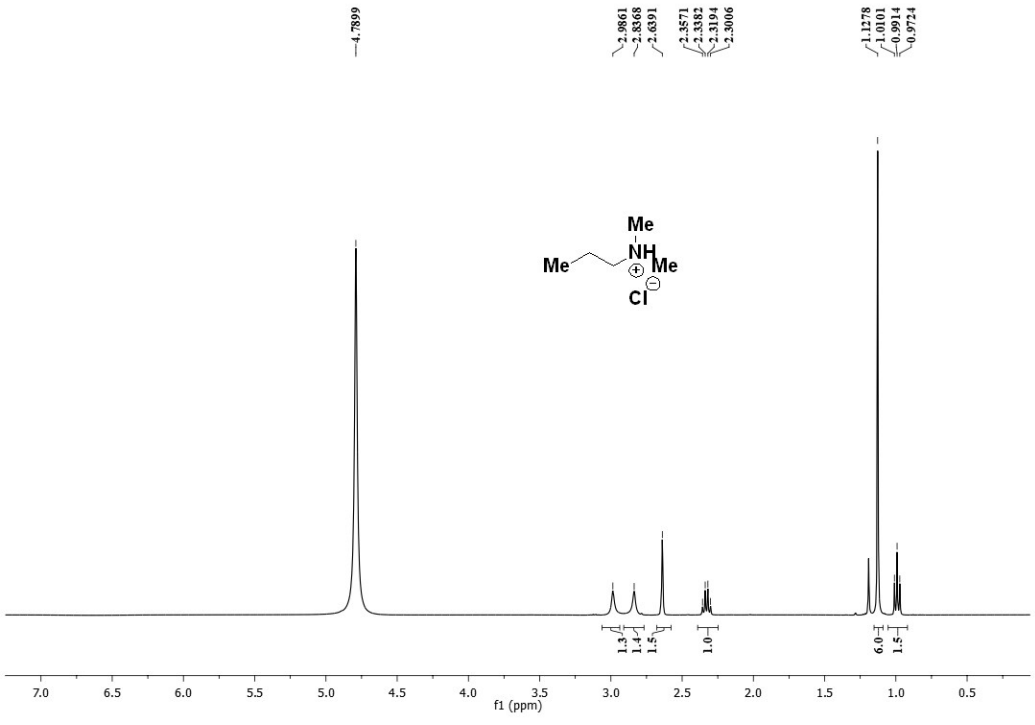


Figure FS15. ^{1}H NMR spectra of compound **(3b)**.

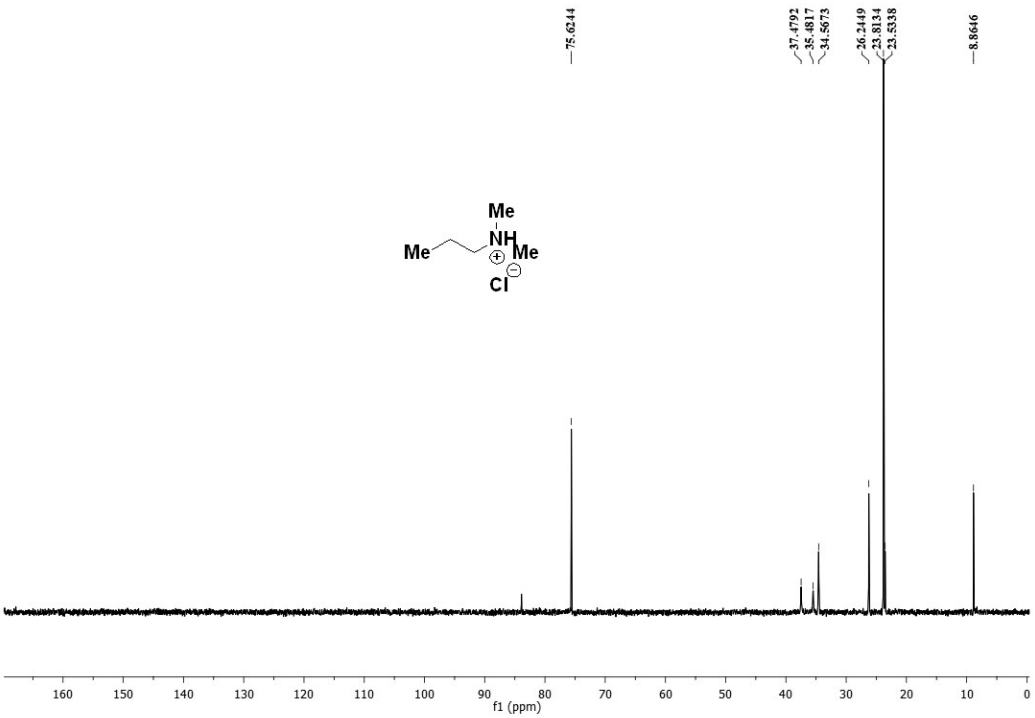


Figure FS16. ^{13}C NMR spectra of compound **(3b)**.

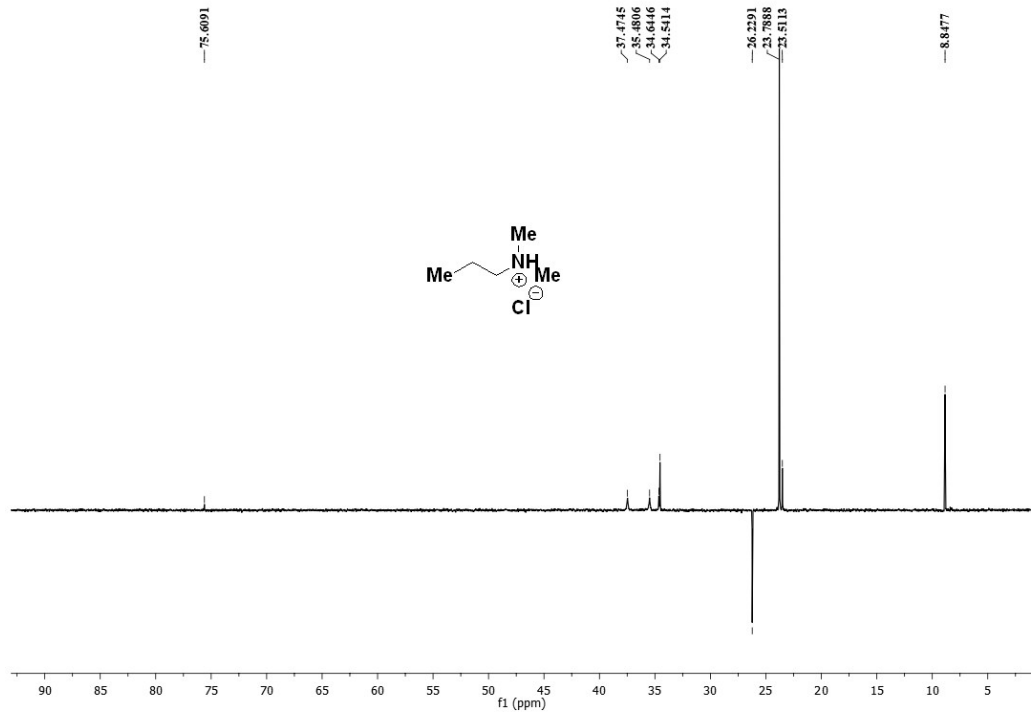


Figure FS17. ^{13}C -DEPT NMR spectra of compound **(3b)**.

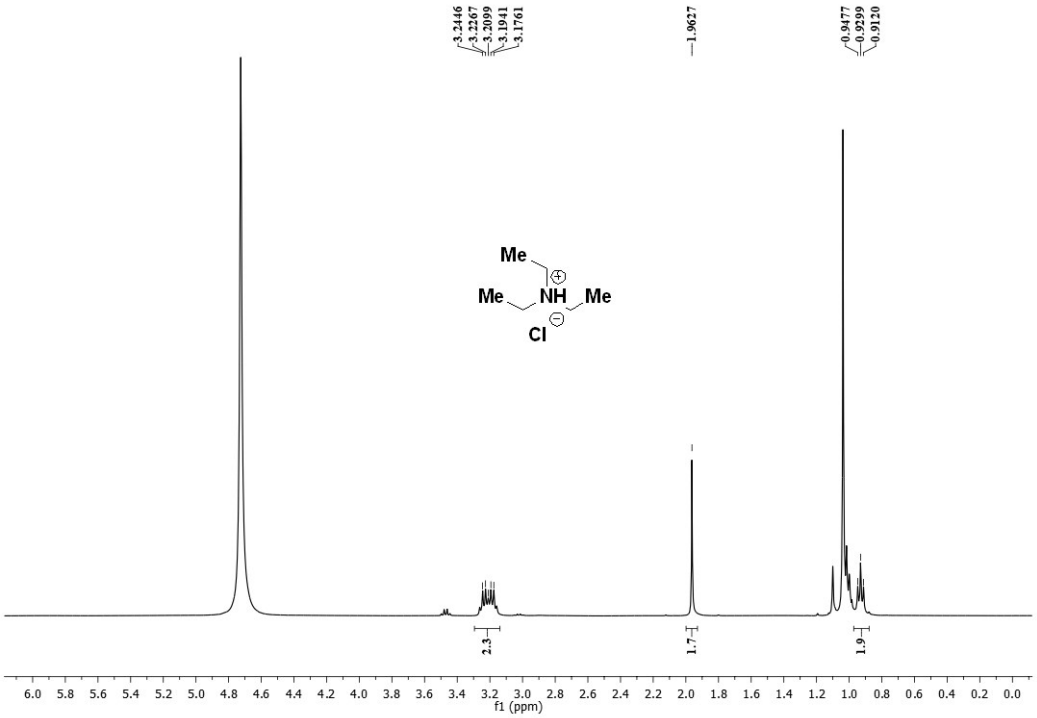


Figure FS18. [1]H NMR spectra of compound **(3c)**.

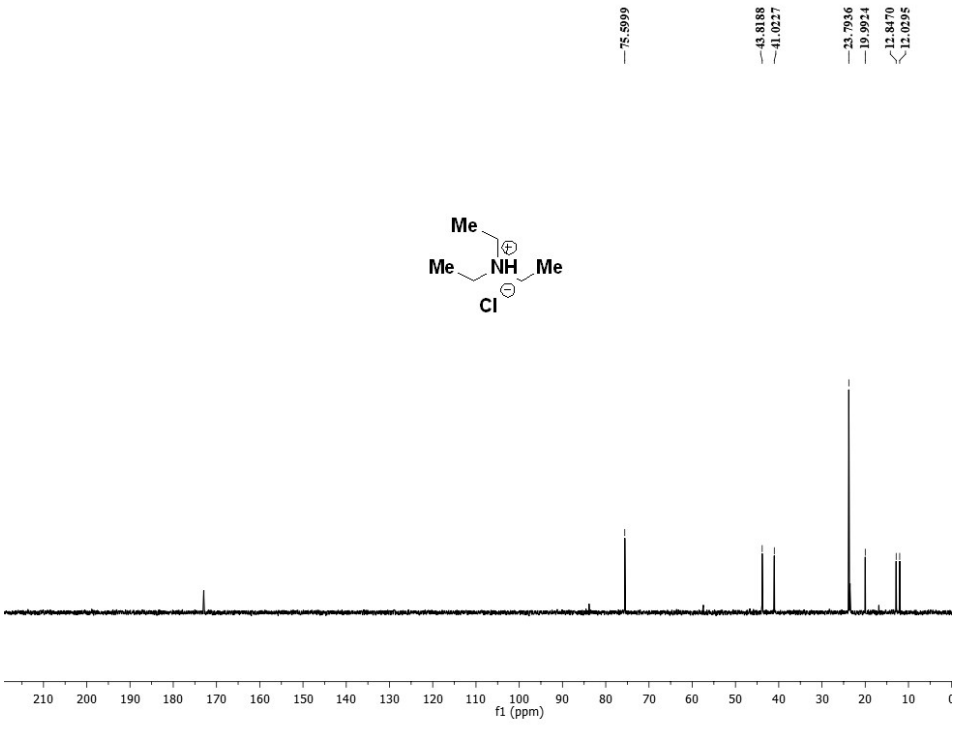


Figure FS19. [13]C NMR spectra of compound **(3c)**.

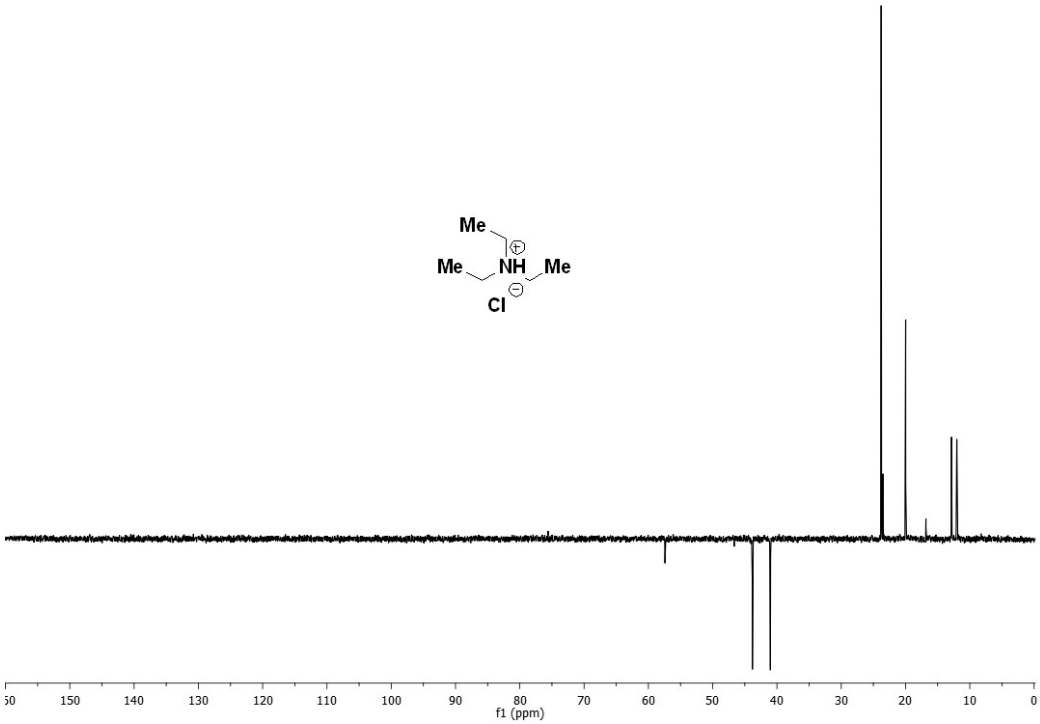


Figure FS20. ^{13}C -DEPT NMR spectra of compound **(3b)**.

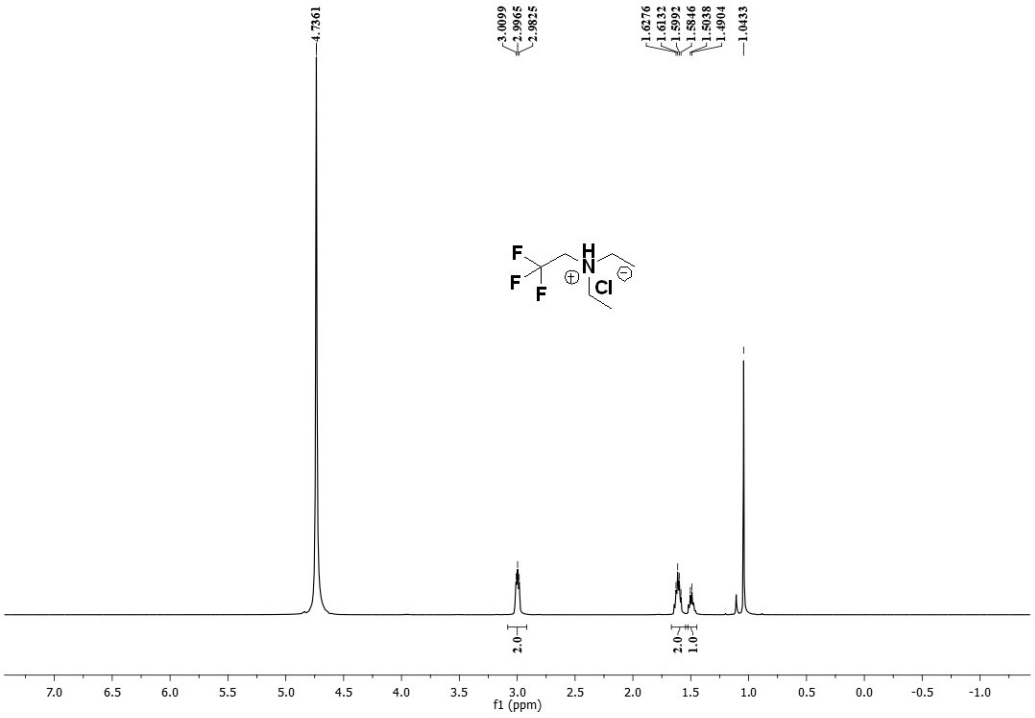


Figure FS21. ^{1}H NMR spectra of compound **(3d)**.

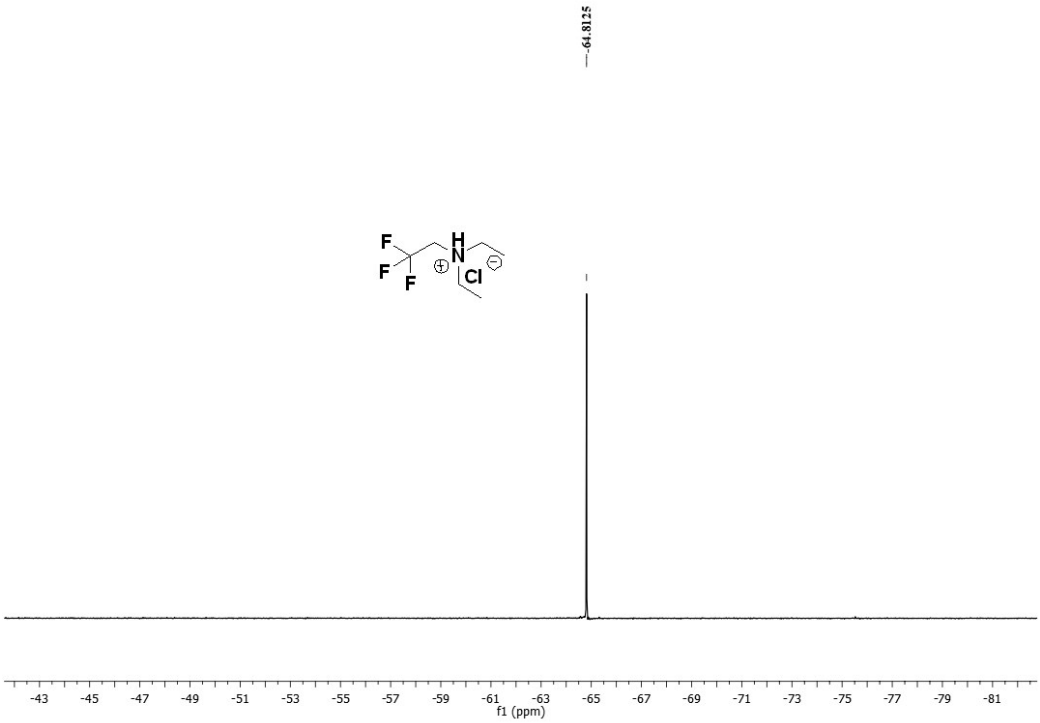


Figure FS22. ^{19}F NMR spectra of compound **(3d)**.

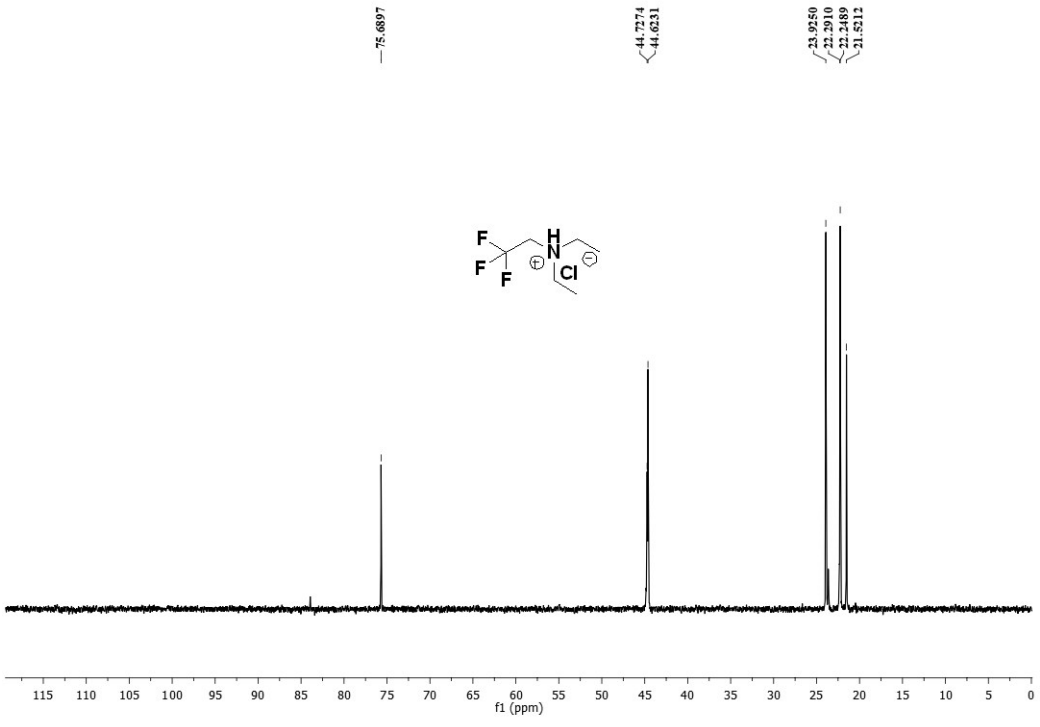


Figure FS23. ^{13}C NMR spectra of compound **(3d)**.

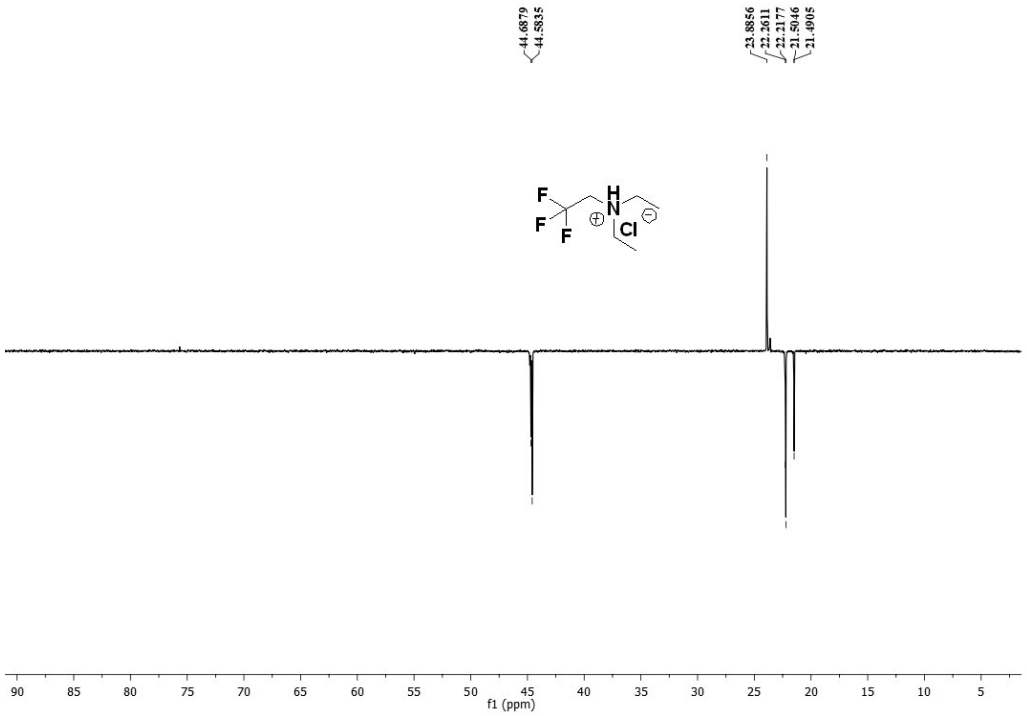


Figure FS24. ^{13}C-DEPT NMR spectra of compound **(3d)**.

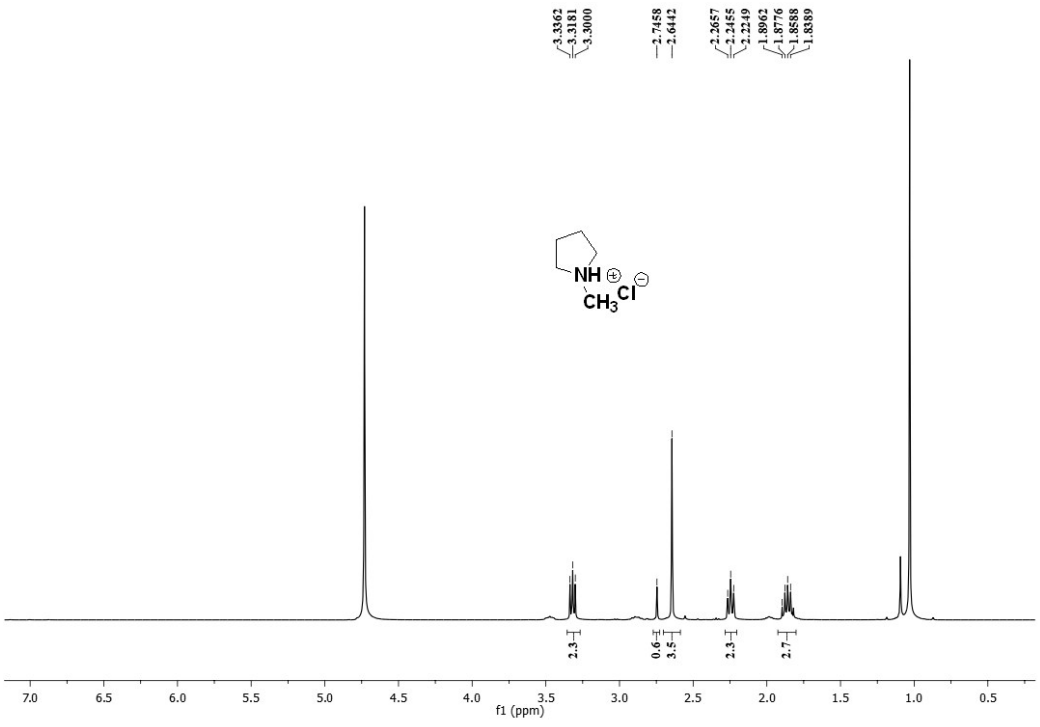


Figure FS25. ^{1}H NMR spectra of compound **(3e)**.

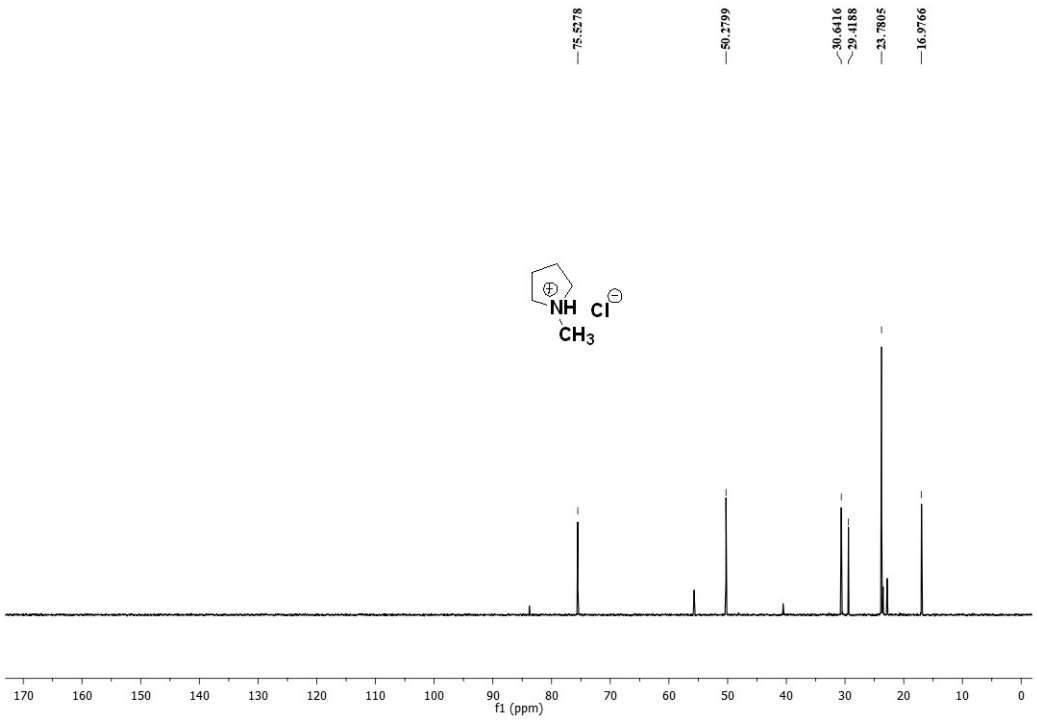


Figure FS26. ^{13}C NMR spectra of compound **(3e)**.

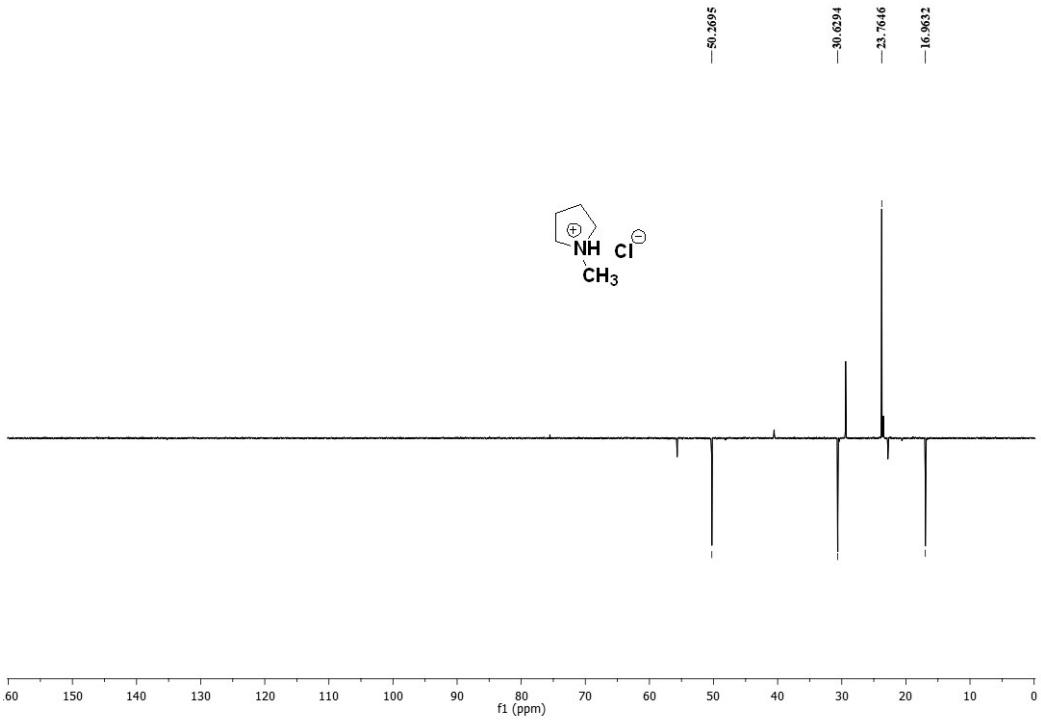


Figure FS27. ^{13}C-DEPT NMR spectra of compound **(3e)**.

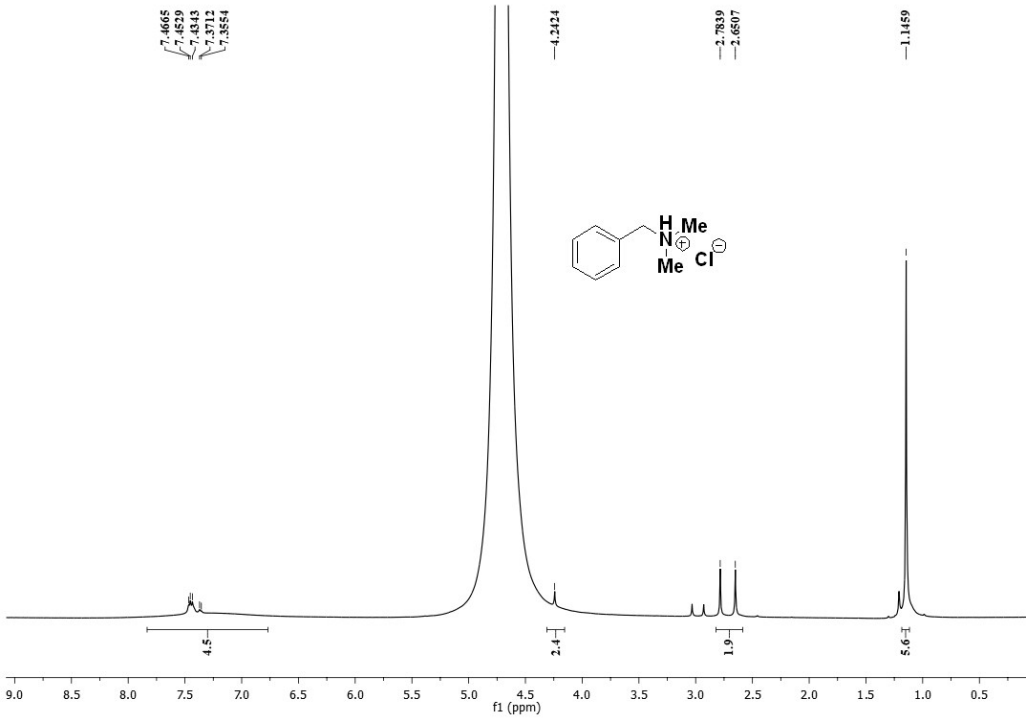


Figure FS28. ^{1}H NMR spectra of compound **(3f)**.

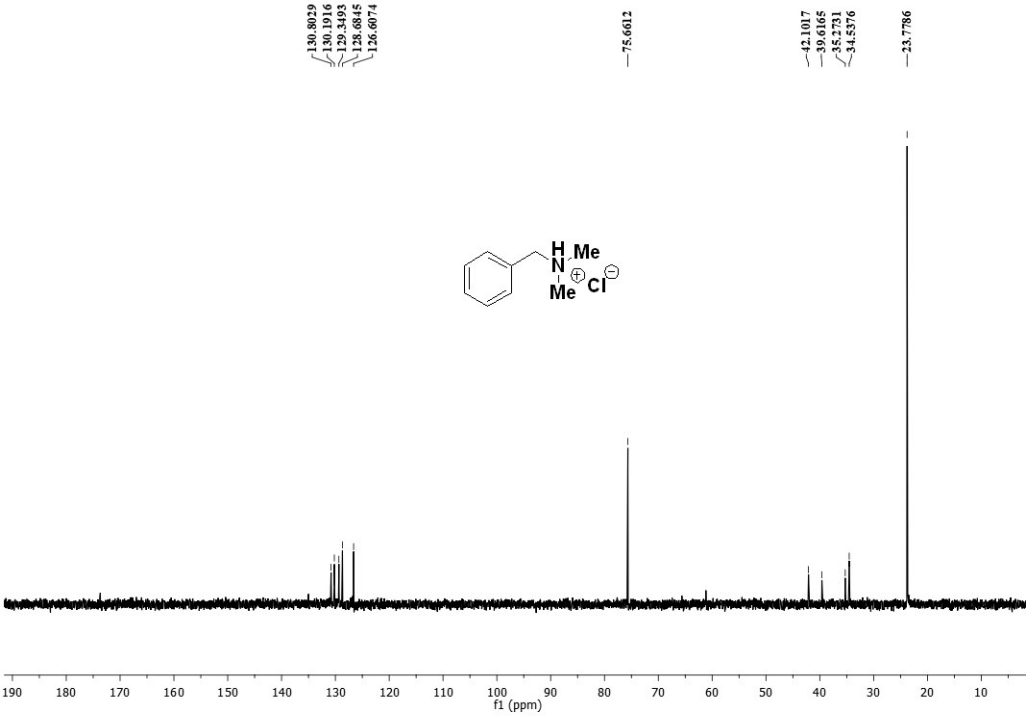


Figure FS29. ^{13}C NMR spectra of compound **(3e)**.

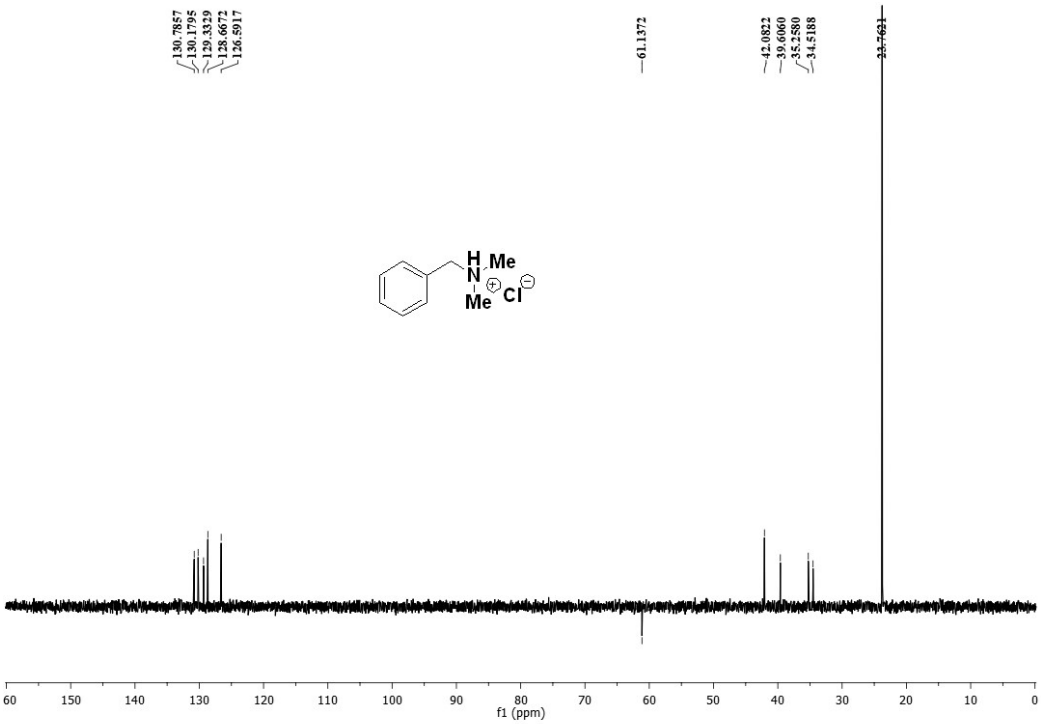


Figure FS30. ^{13}C-DEPT NMR spectra of compound **(3e)**.

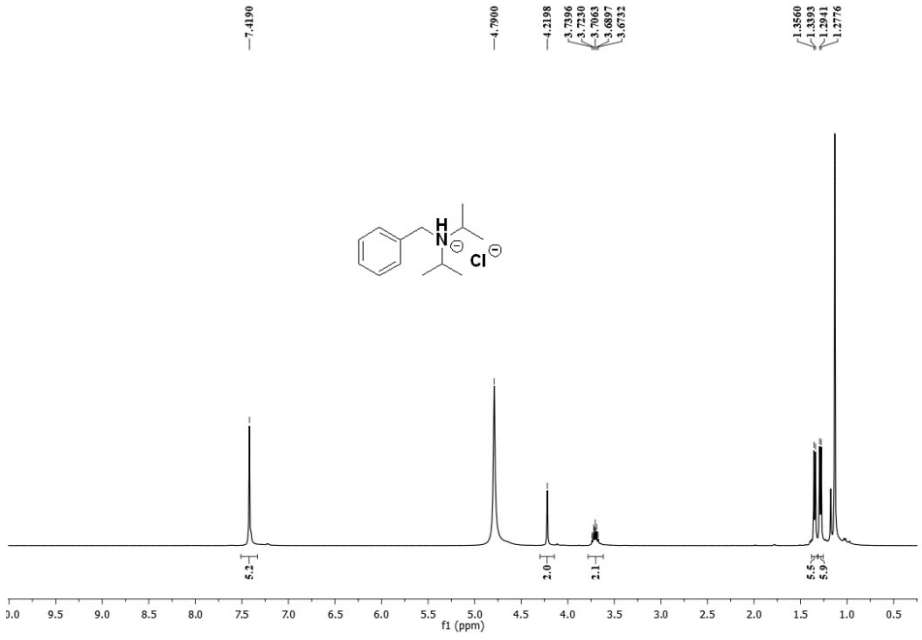


Figure FS31. ^{1}H NMR spectra of compound **(3g)**.

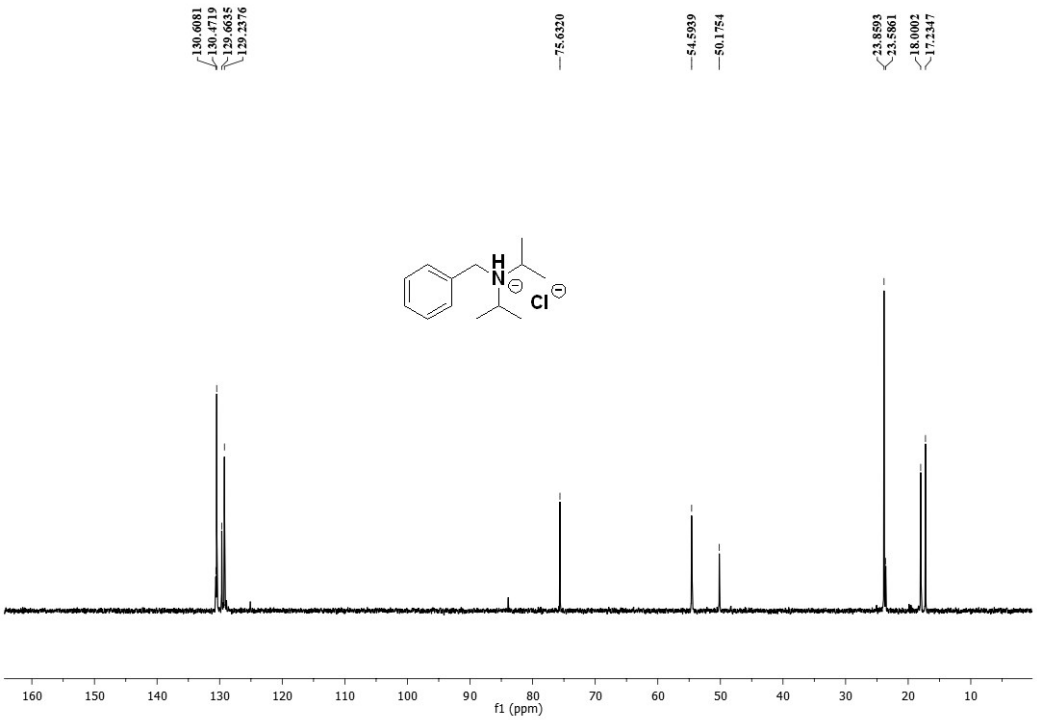


Figure FS32. ^{13}C NMR spectra of compound **(3g)**.

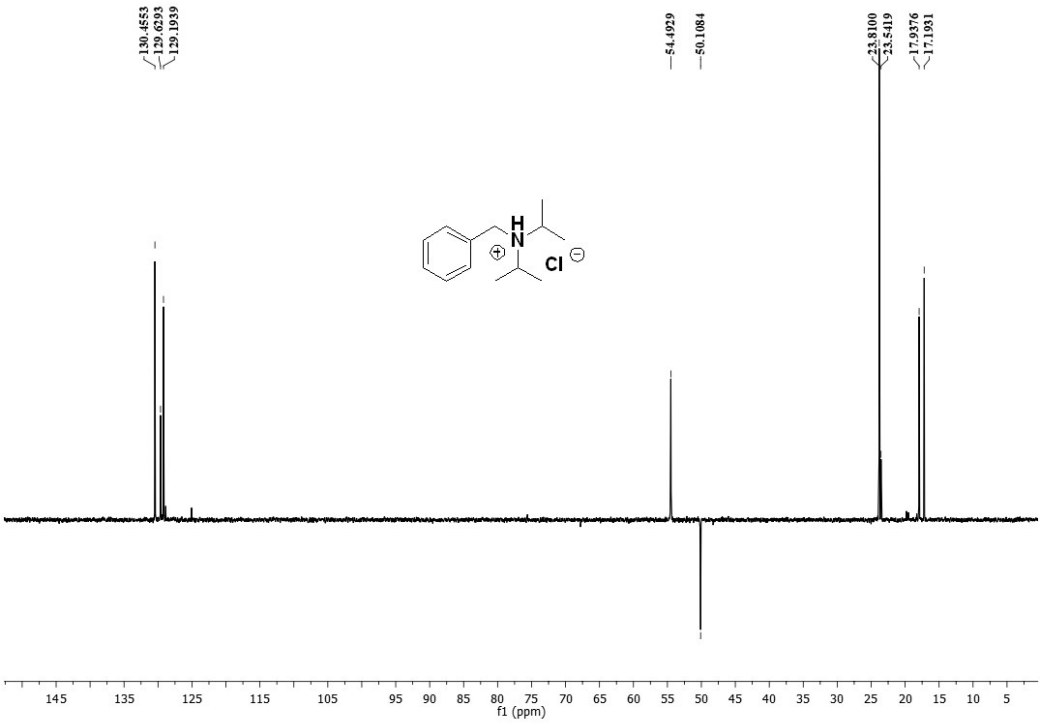


Figure FS33. ^{13}C-DEPT NMR spectra of compound **(3g)**.

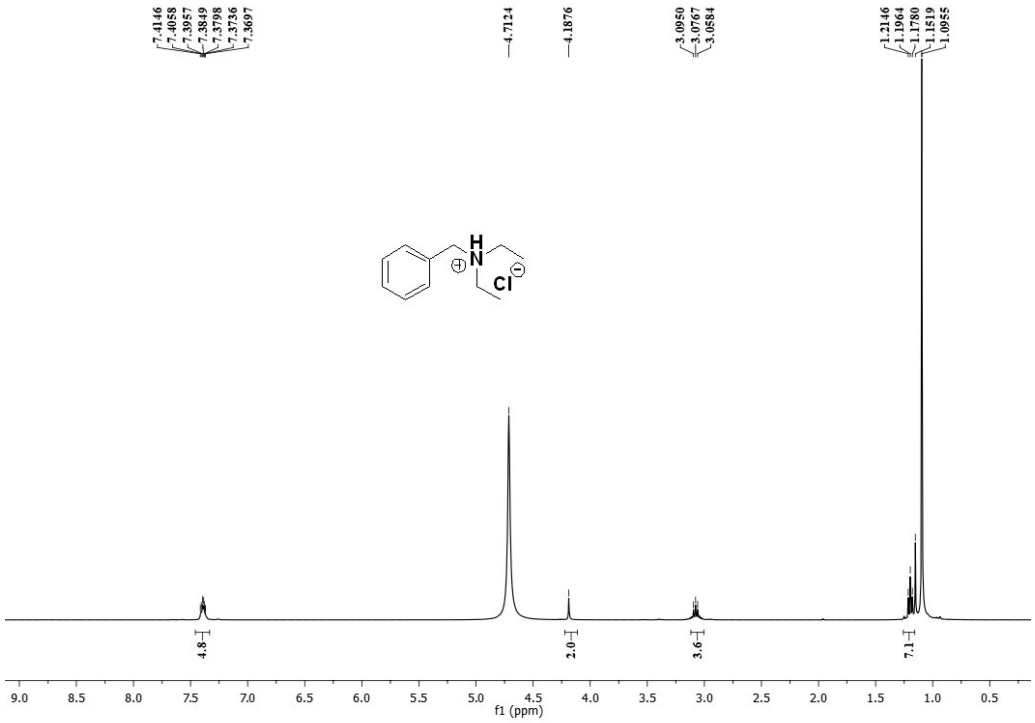


Figure FS34. ^{1}H NMR spectra of compound **(3h)**.

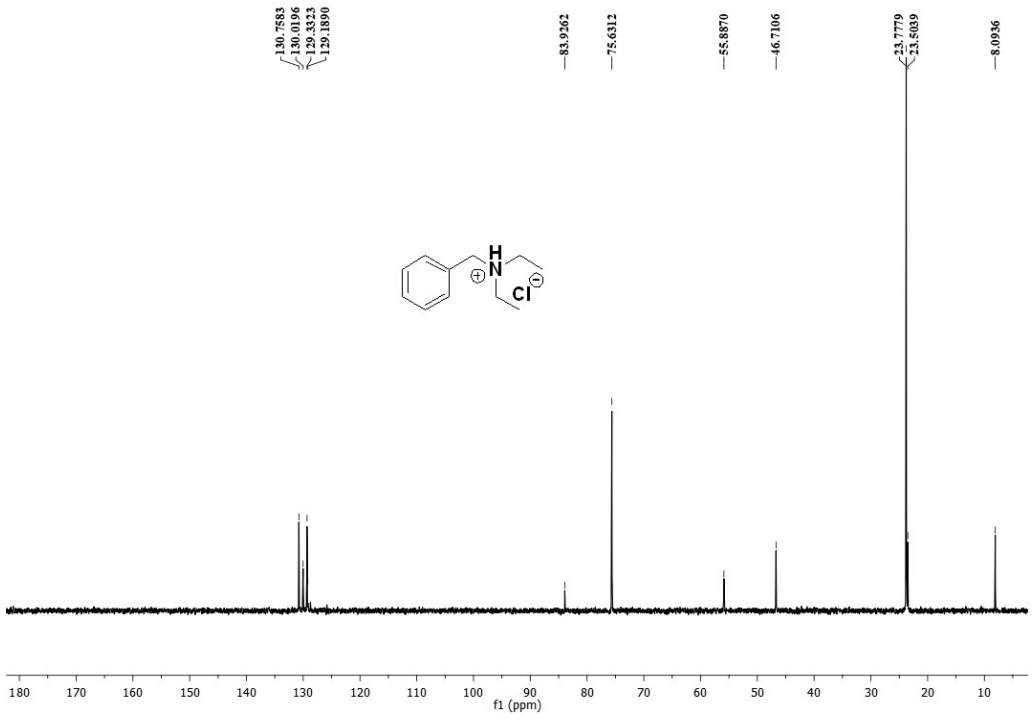


Figure FS35. ^{13}C NMR spectra of compound **(3h)**.

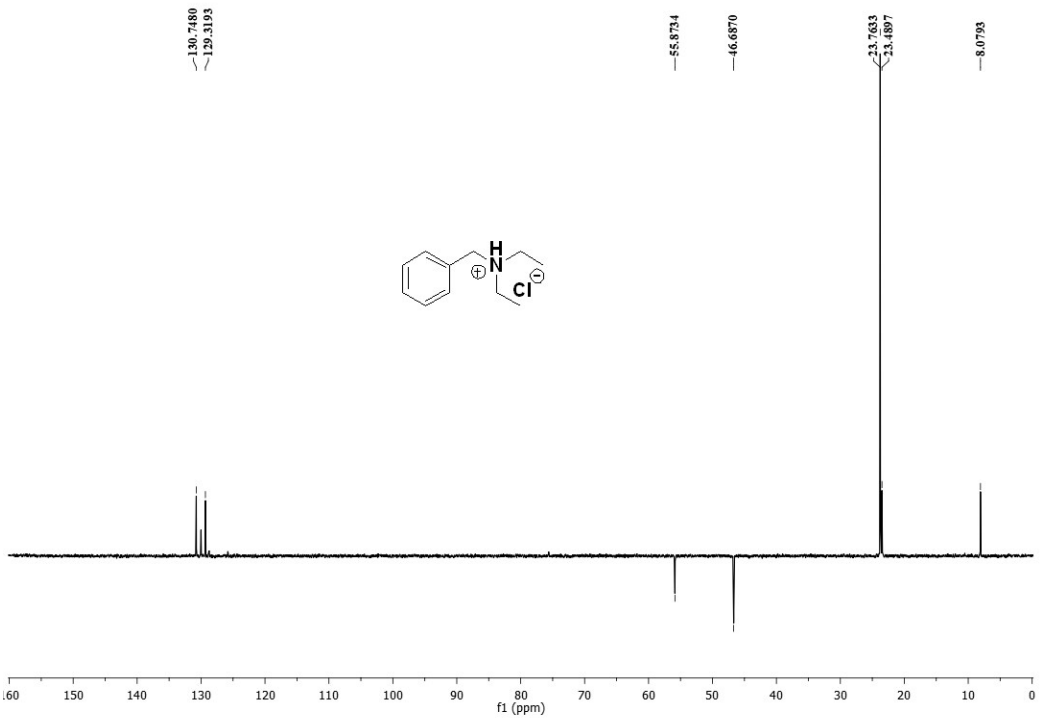


Figure FS36. ^{13}C-DEPT NMR spectra of compound **(3h)**.

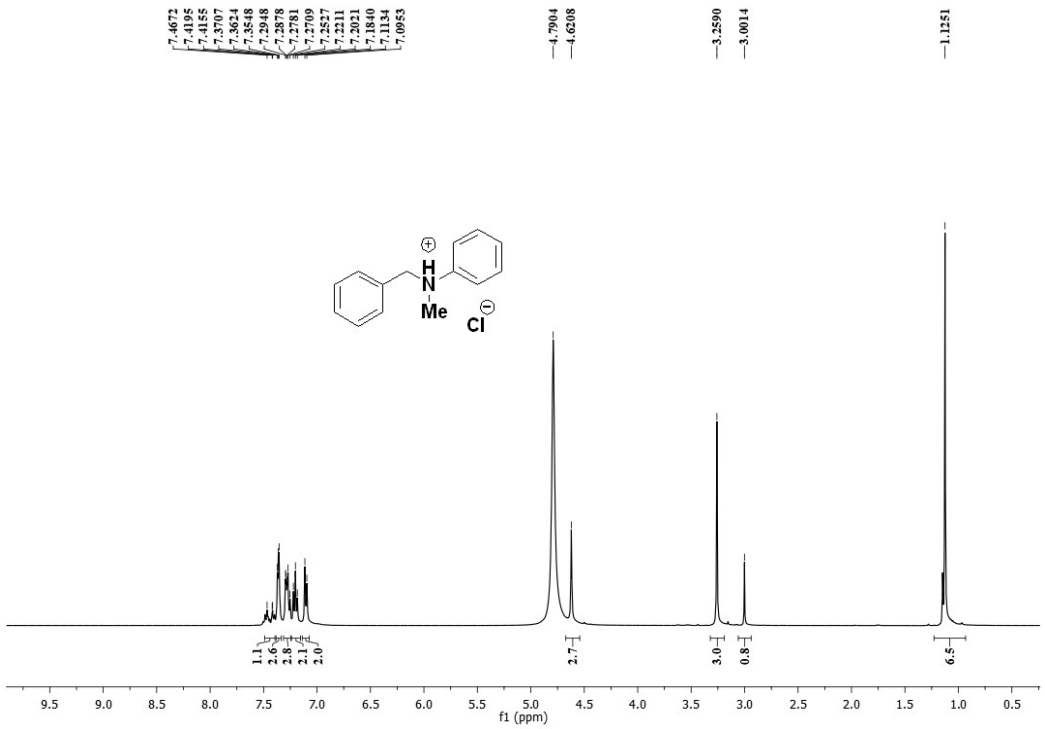


Figure FS37. ^{1}H NMR spectra of compound **(3i)**.

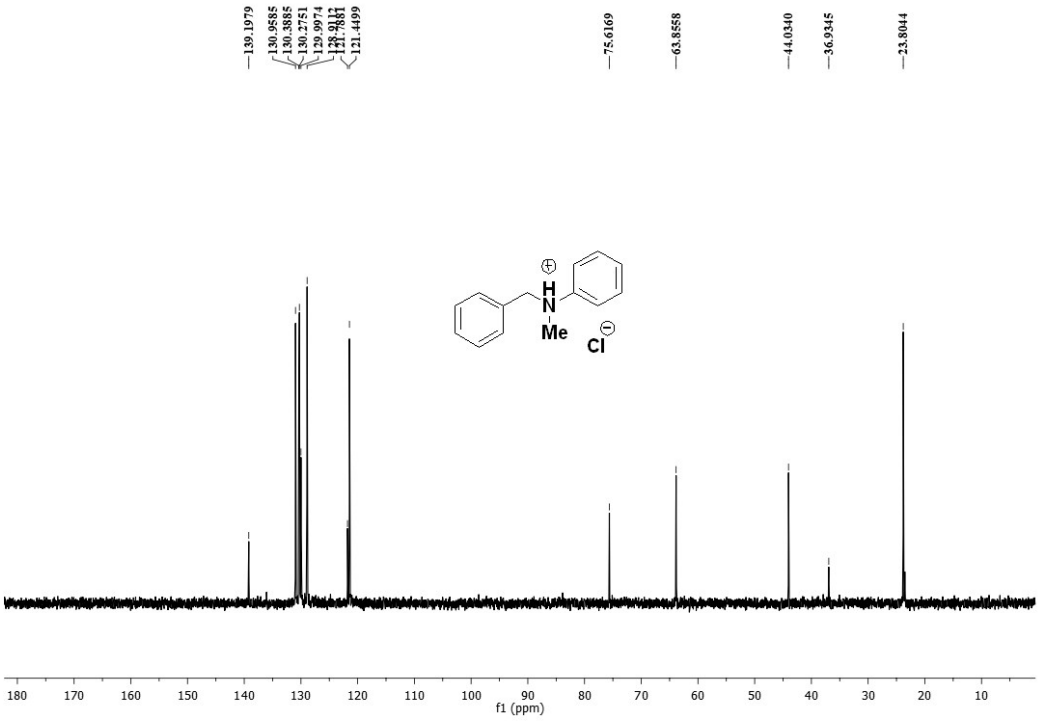


Figure FS38. ^{13}C NMR spectra of compound **(3i)**.

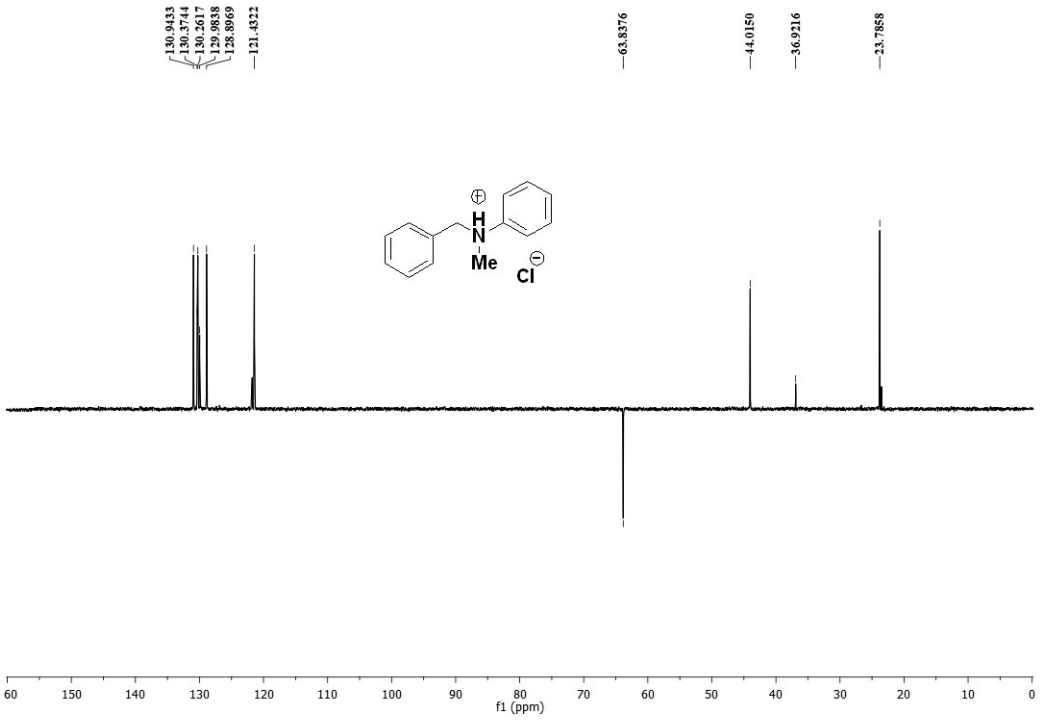


Figure FS39. ^{13}C- DEPT NMR spectra of compound **(3i)**.

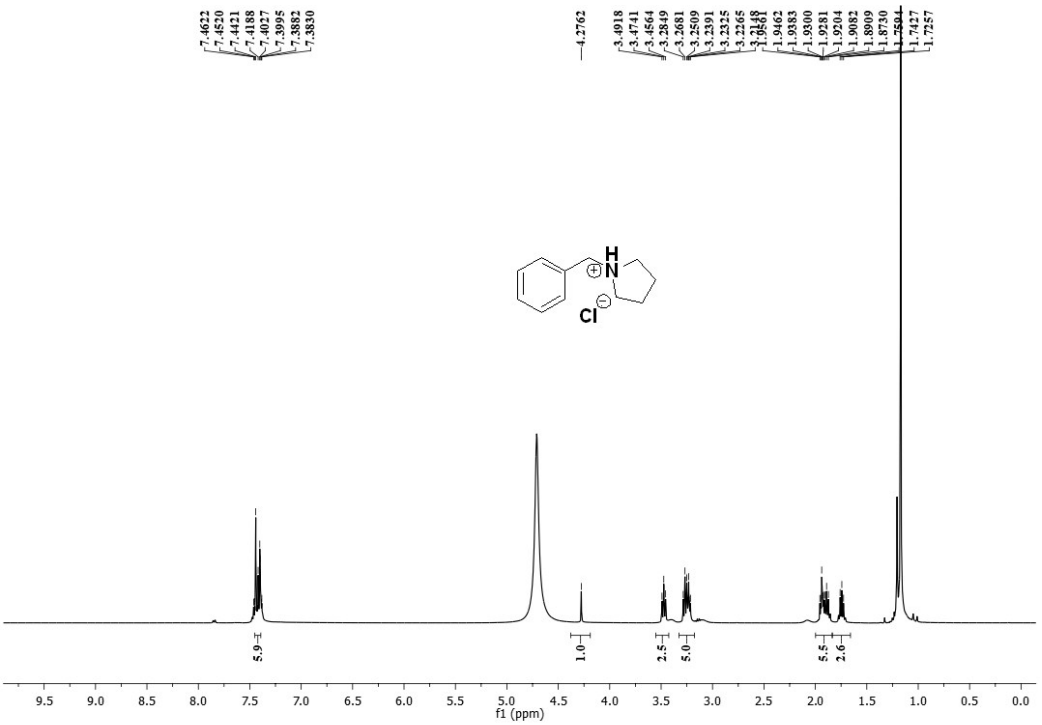


Figure FS40. [1]H NMR spectra of compound **(3i)**.

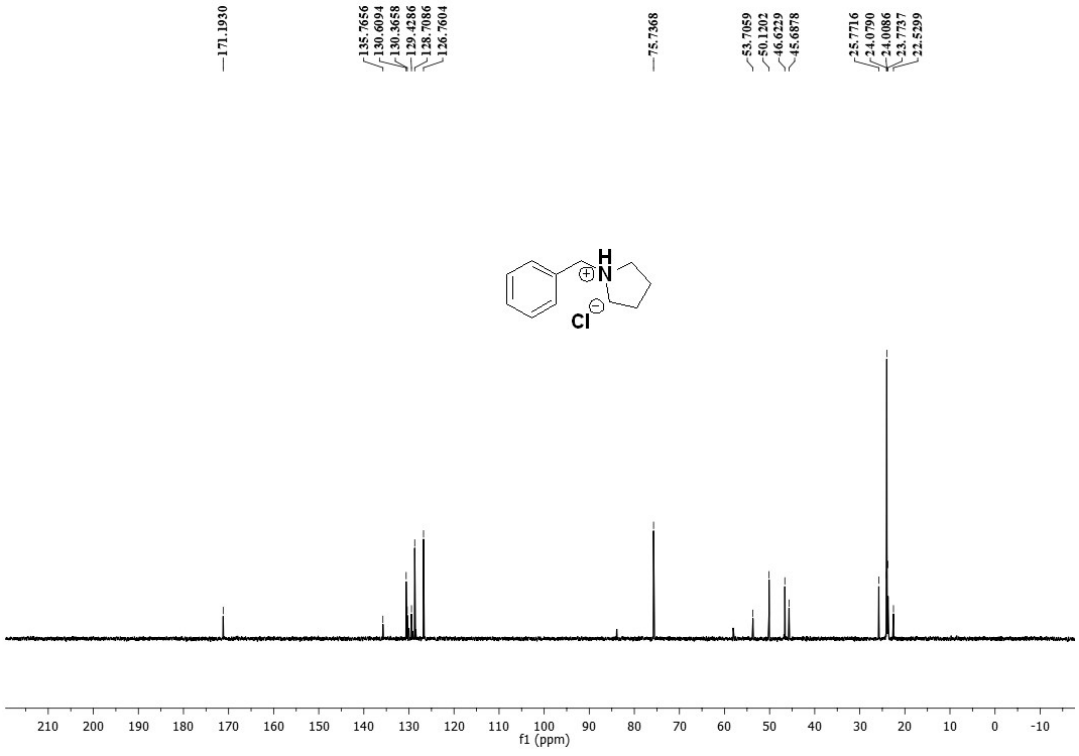


Figure FS41. [13]C NMR spectra of compound **(3i)**.

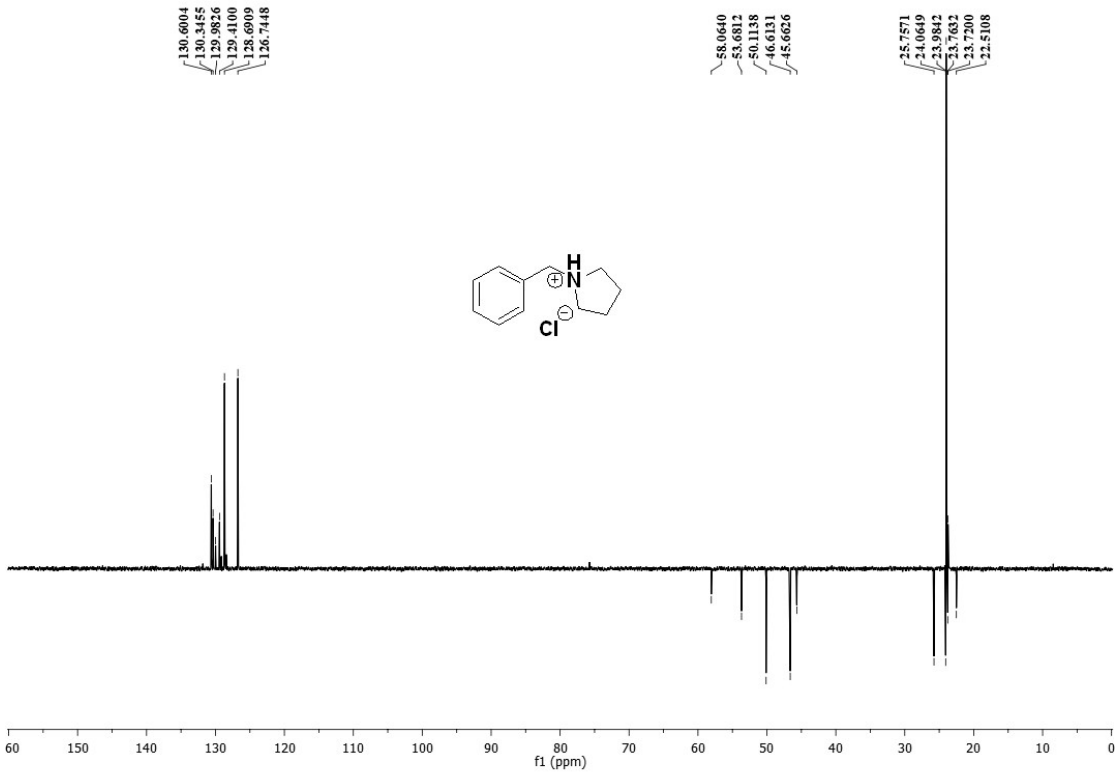


Figure FS42. ^{13}C- DEPT NMR spectra of compound **(3i)**.

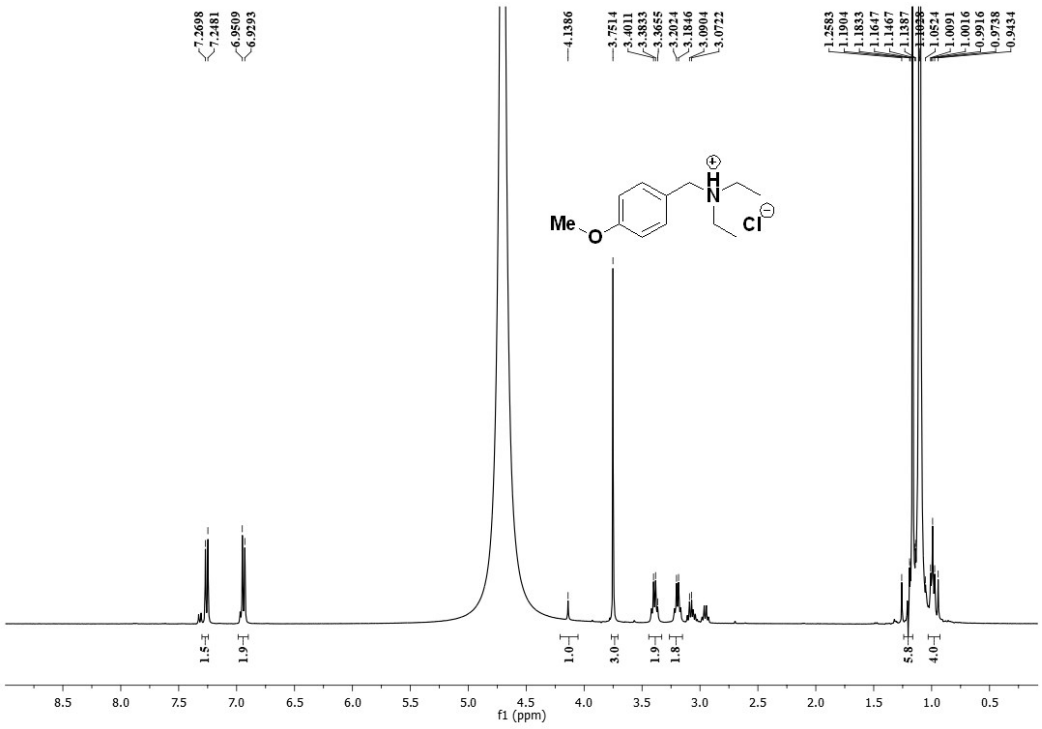


Figure FS43. ^{1}H NMR spectra of compound **(3k)**.

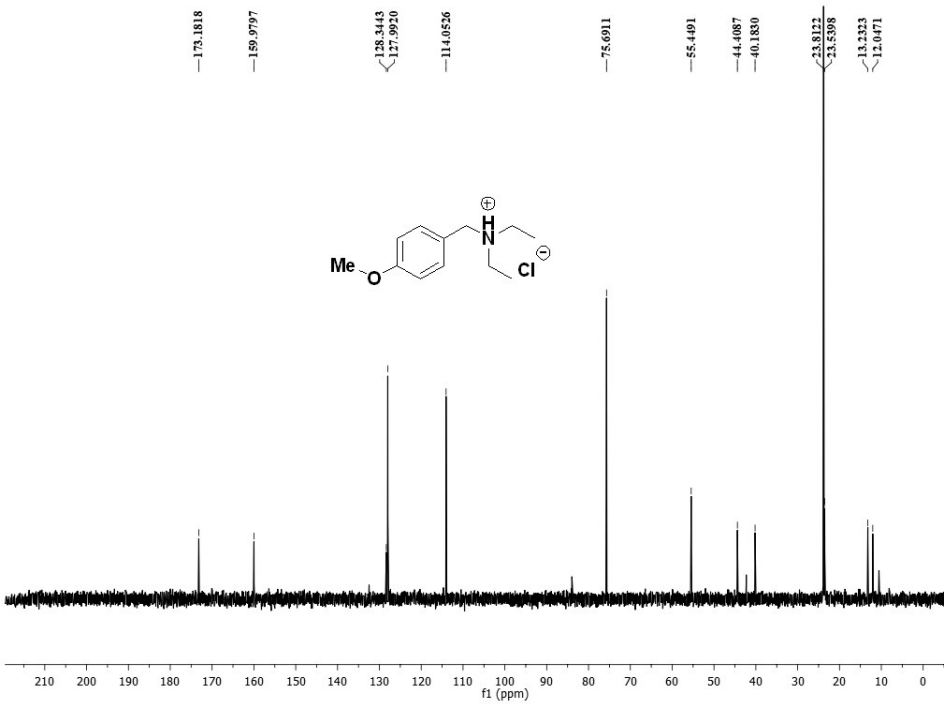


Figure FS44. ^{13}C NMR spectra of compound **(3k)**.

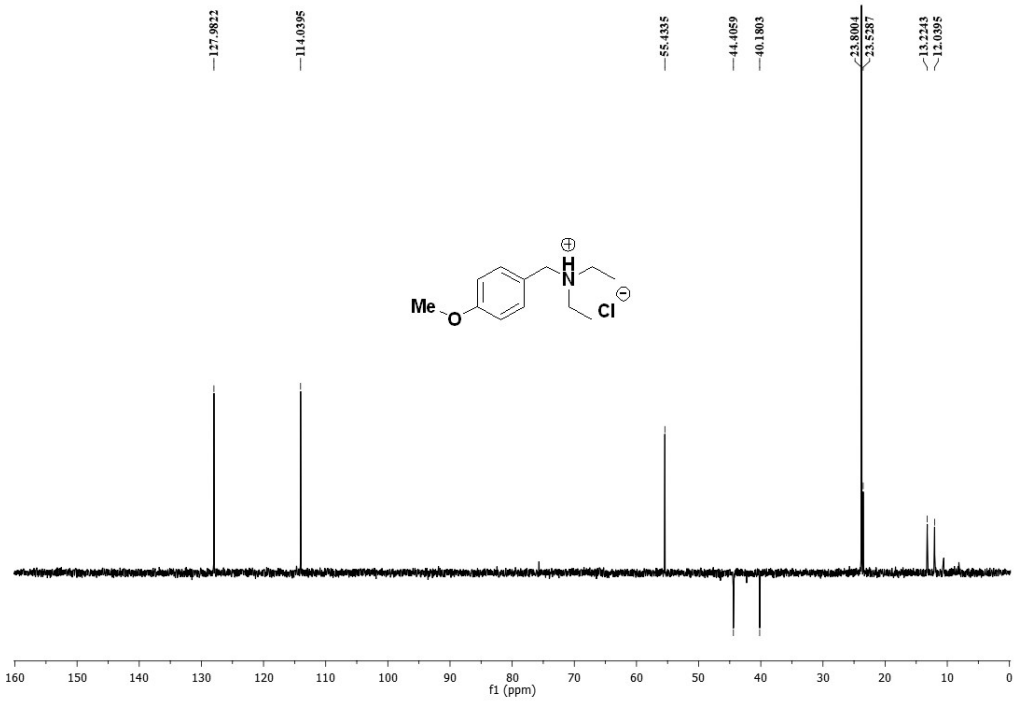


Figure FS45. ^{13}C-DEPT NMR spectra of compound **(3k)**.

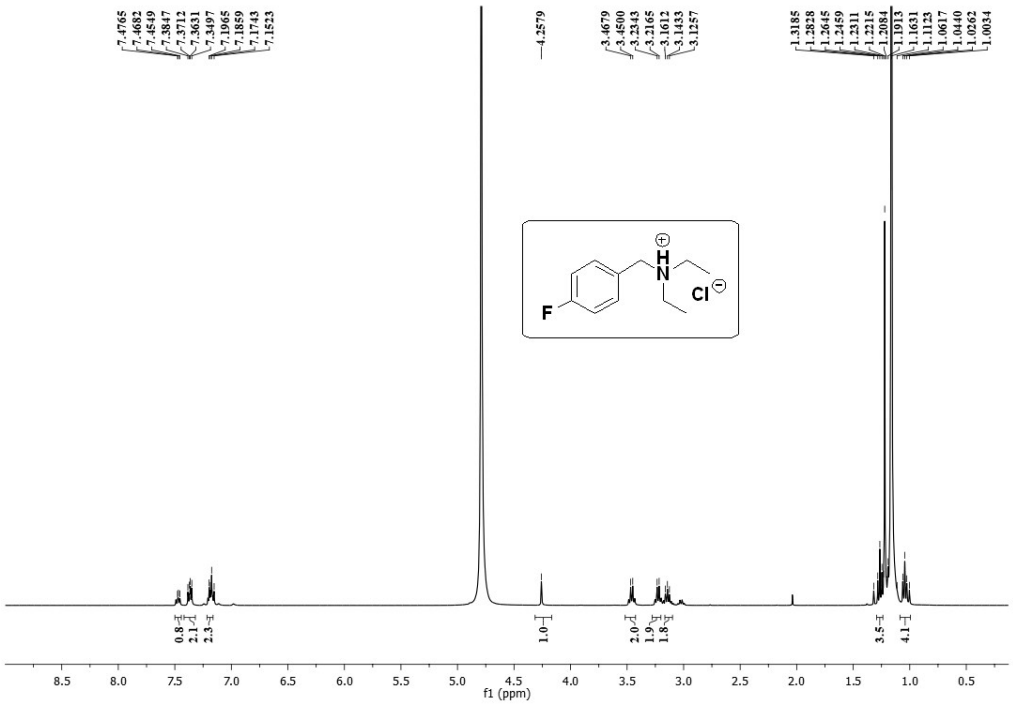


Figure FS46. ^{1}H NMR spectra of compound **(3l)**.

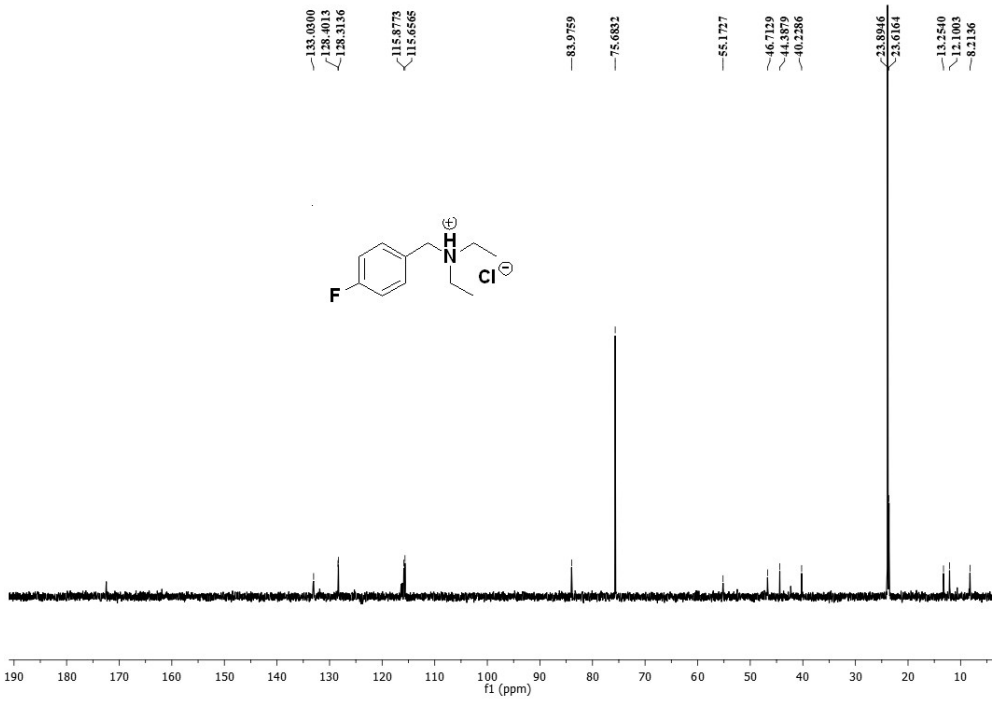


Figure FS47. ^{13}C NMR spectra of compound **(3l)**.

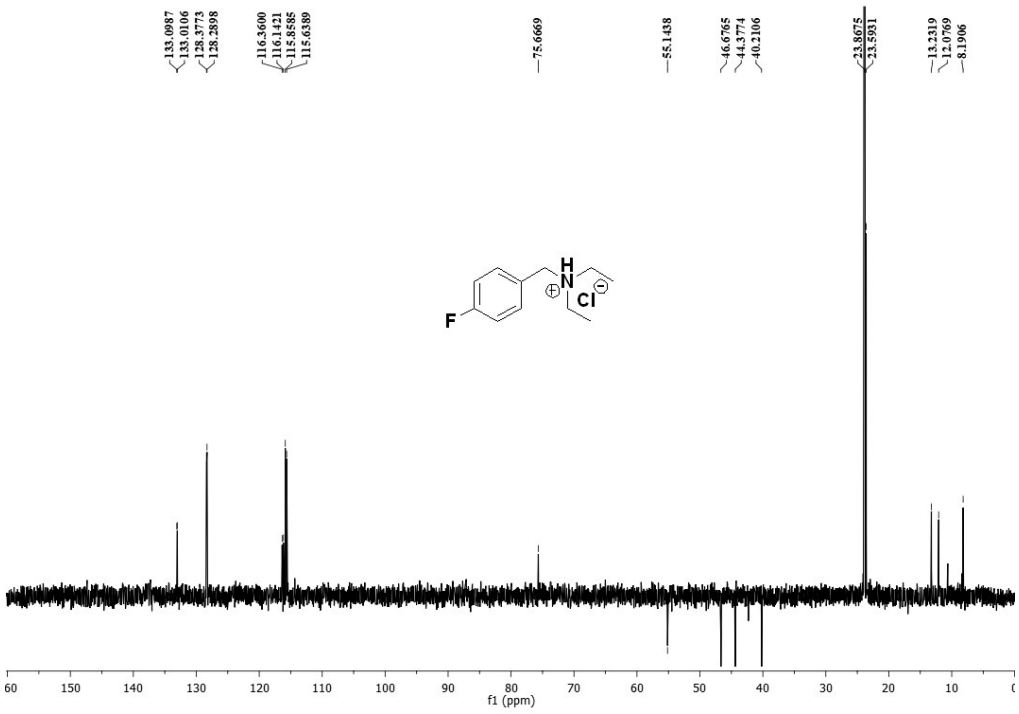


Figure FS48. ^{13}C- DEPT NMR spectra of compound **(3l)**.

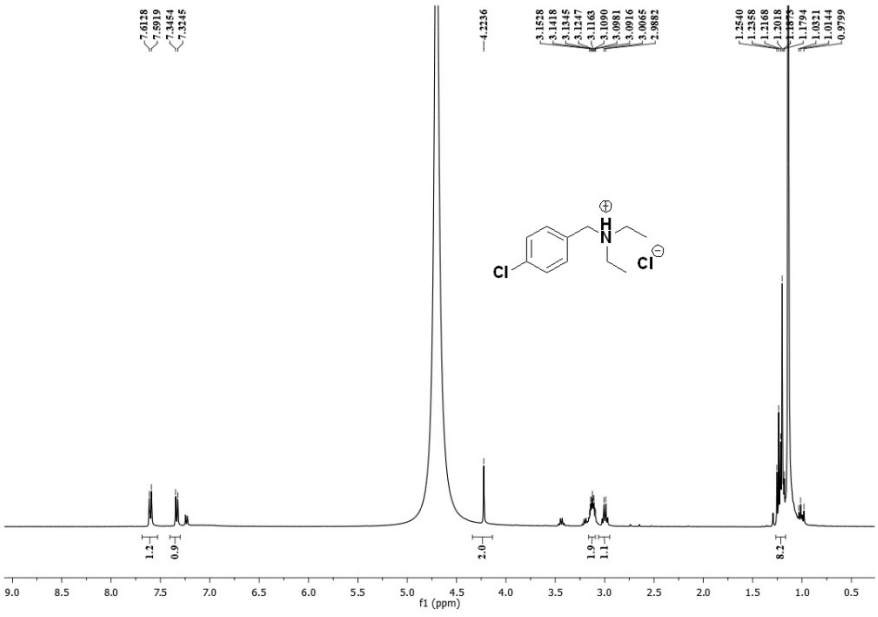


Figure FS49. ^{1}H NMR spectra of compound **(3m)**.

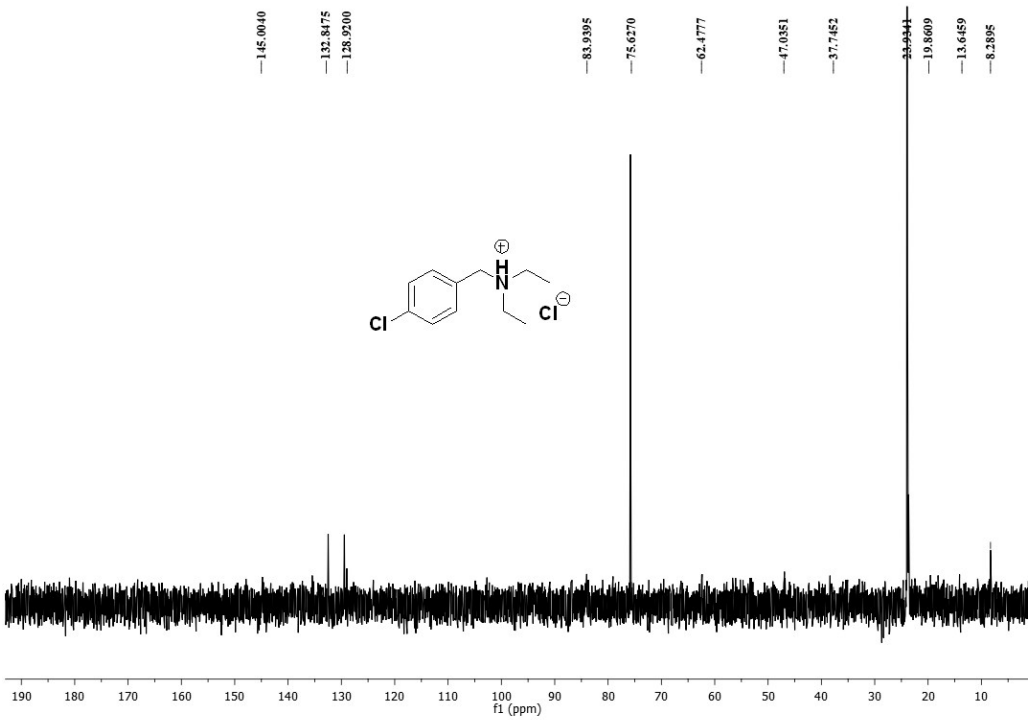


Figure FS50. ^{13}C NMR spectra of compound **(3m**).

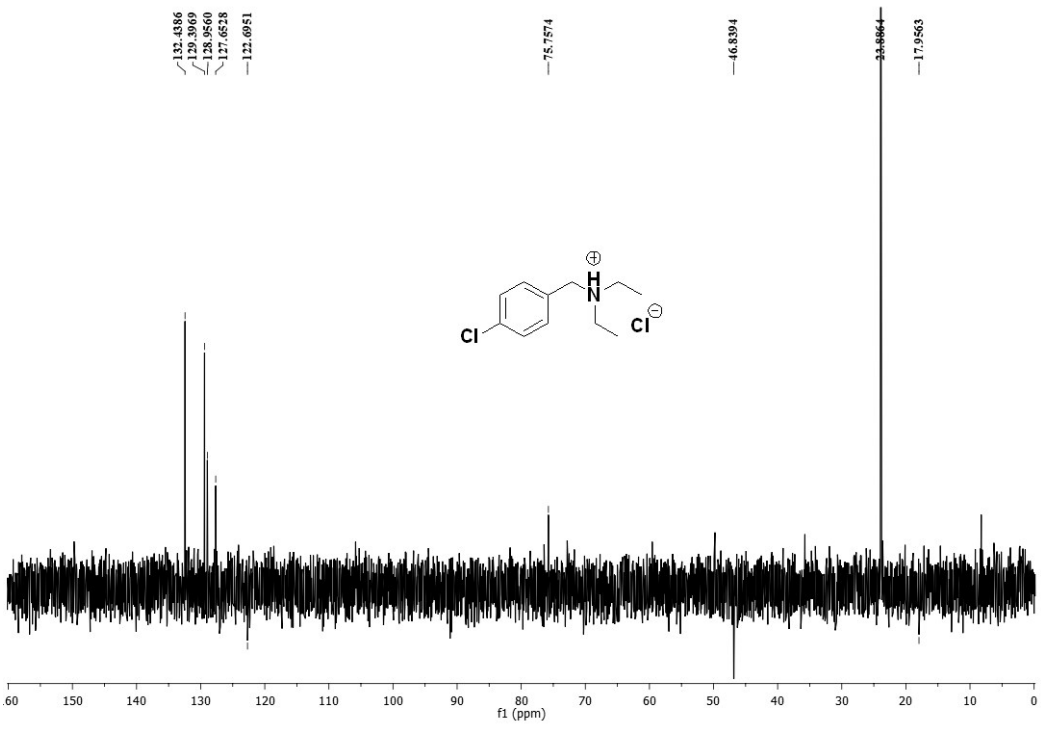


Figure FS51. ^{13}C –DEPT NMR spectra of compound (**3m**).

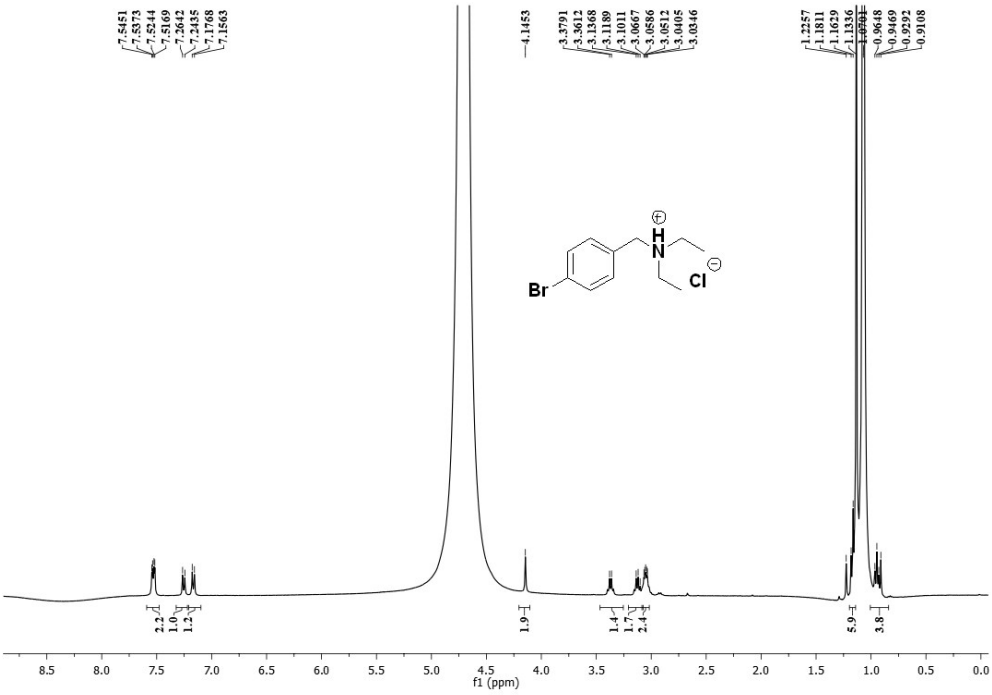


Figure FS52. [1]HNMR spectra of compound **(3n)**.

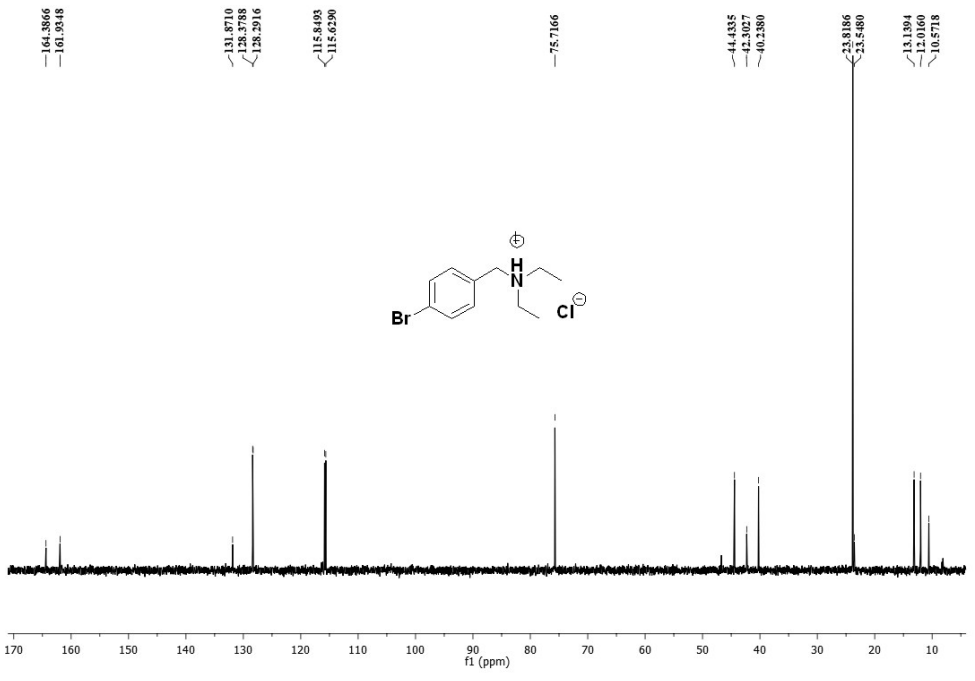


Figure FS53. [13]C NMR spectra of compound **(3n)**.

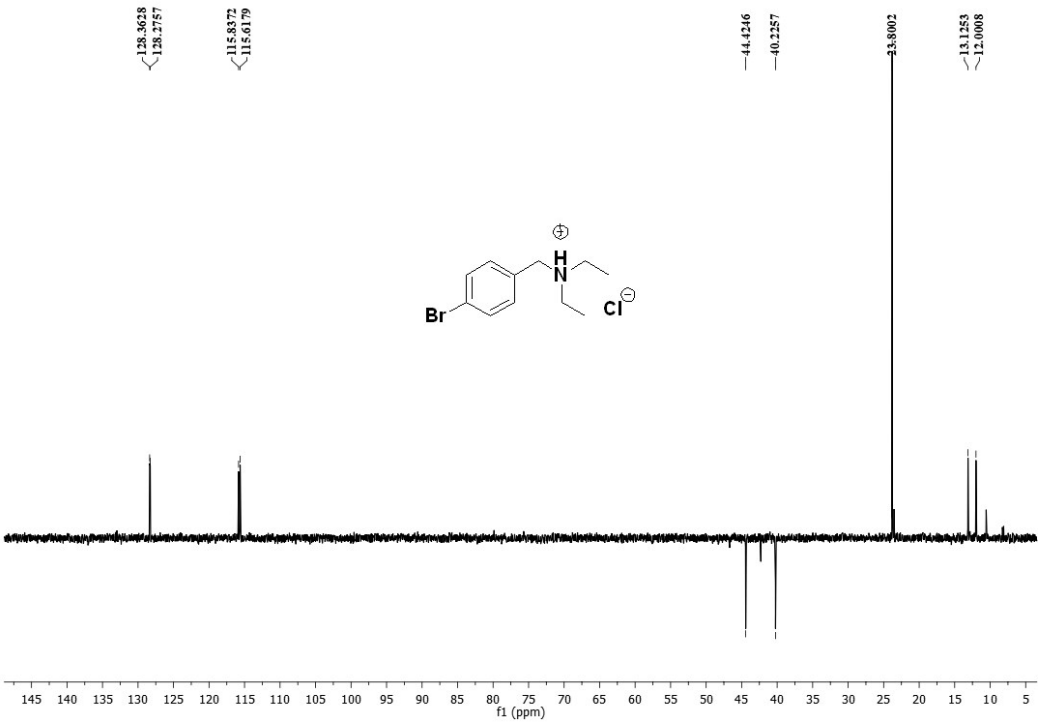


Figure FS54. ^{13}C-DEPT NMR spectra of compound **(3n)**.

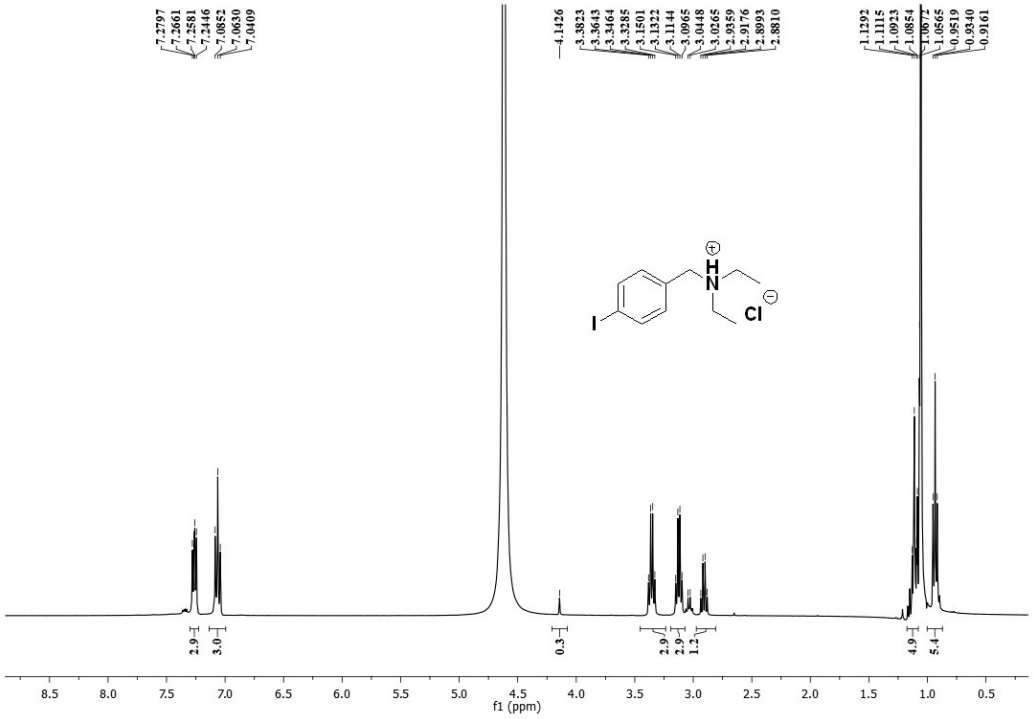


Figure FS55. ^{1}H NMR spectra of compound **(3o)**.

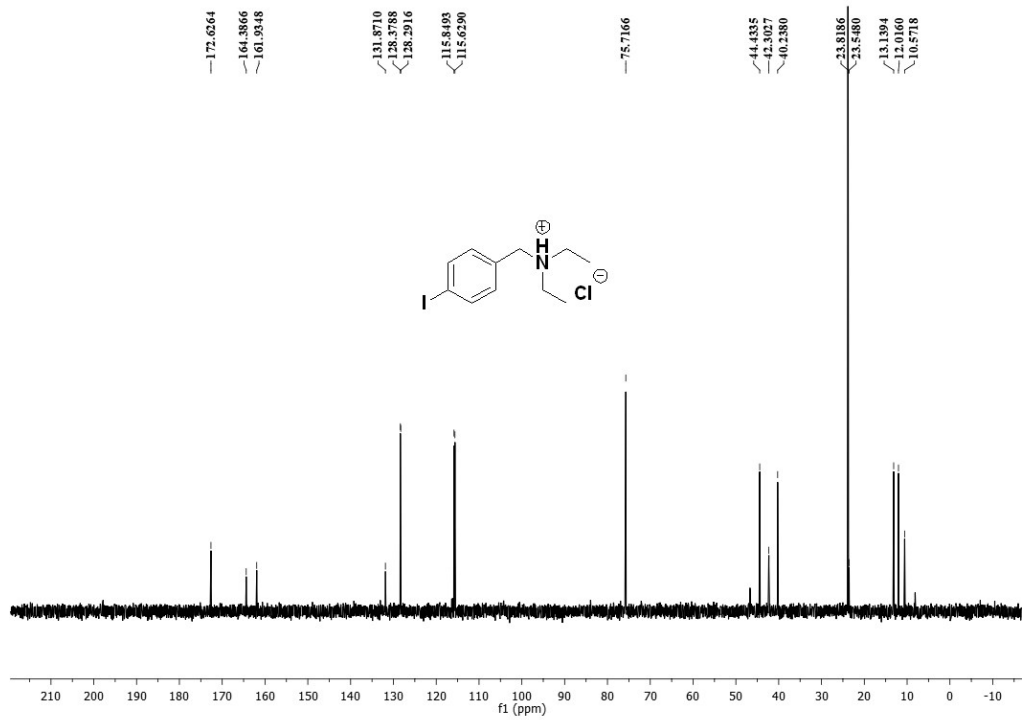


Figure FS56. ^{13}C NMR spectra of compound **(3o)**.

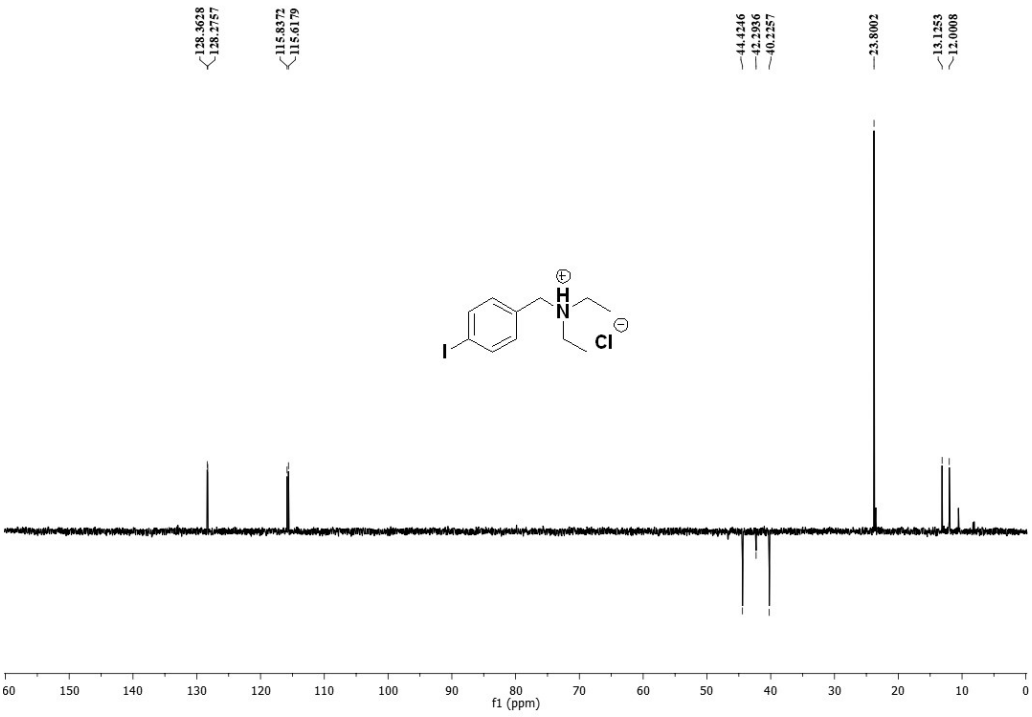


Figure FS57. ^{13}C-DEPT NMR spectra of compound **(3o)**.

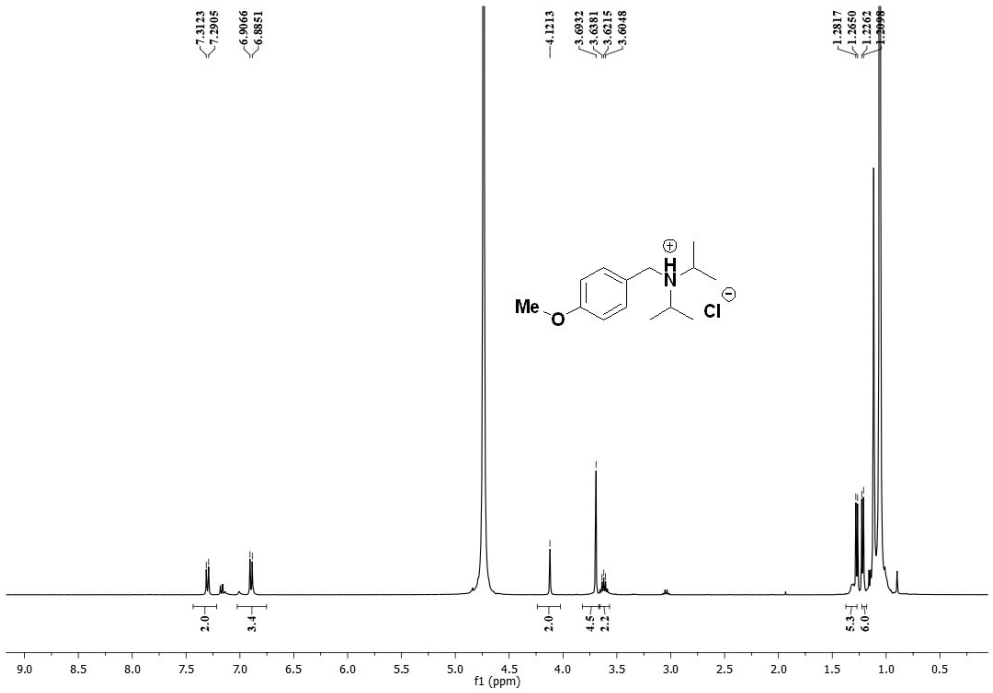


Figure FS58. ^{1}H NMR spectra of compound **(3p)**.

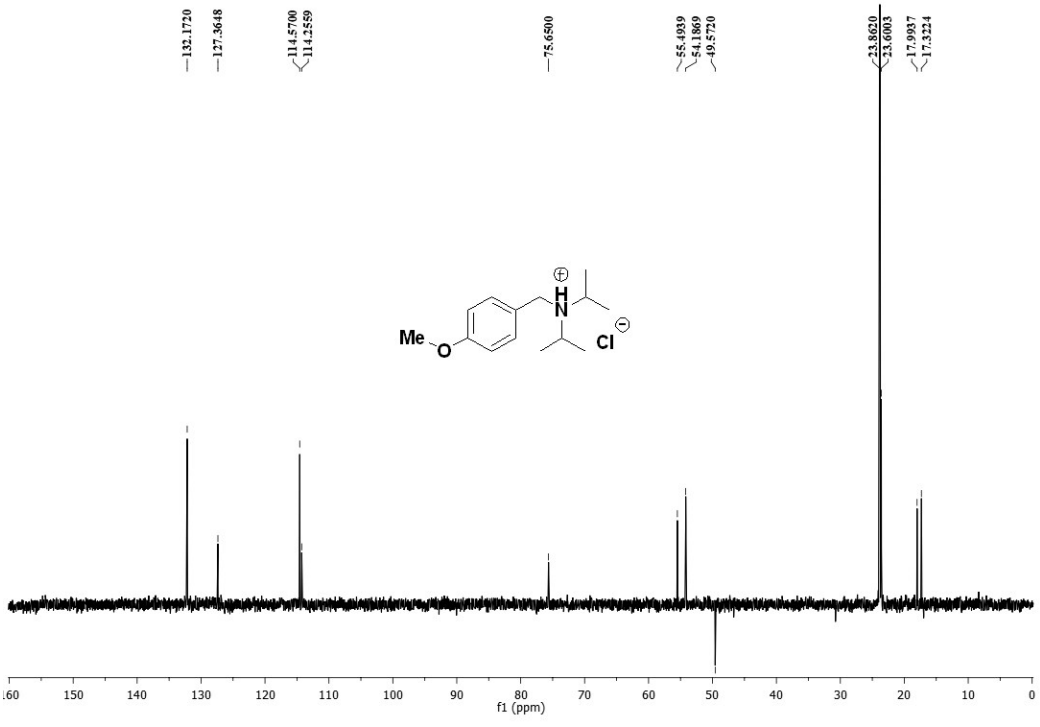


Figure FS59. ^{13}C NMR spectra of compound **(3p)**.

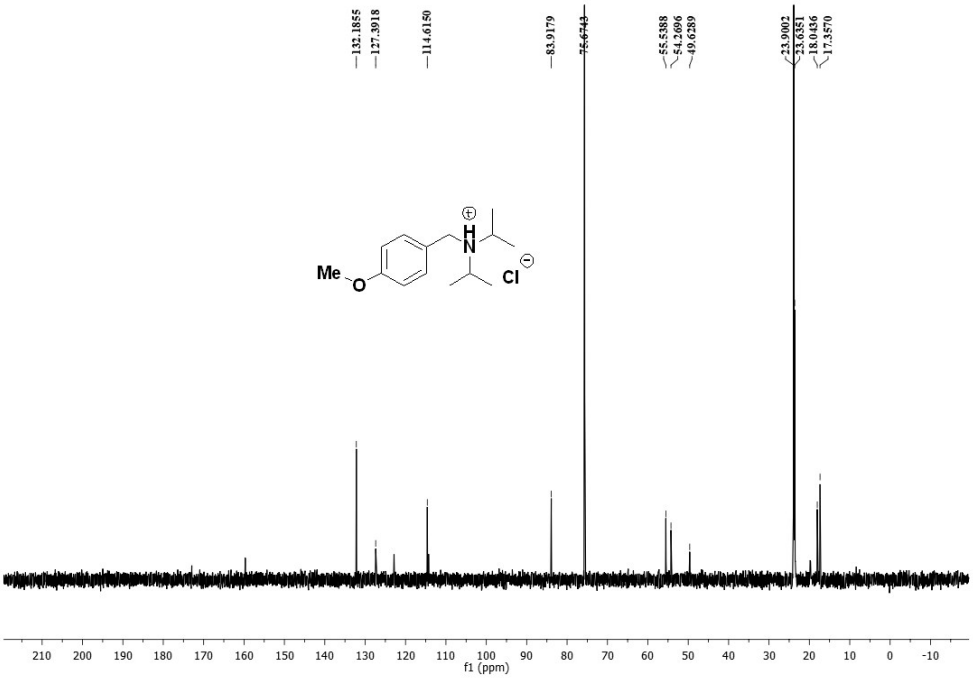


Figure FS60. ^{13}C-DEPT NMR spectra of compound **(3p)**.

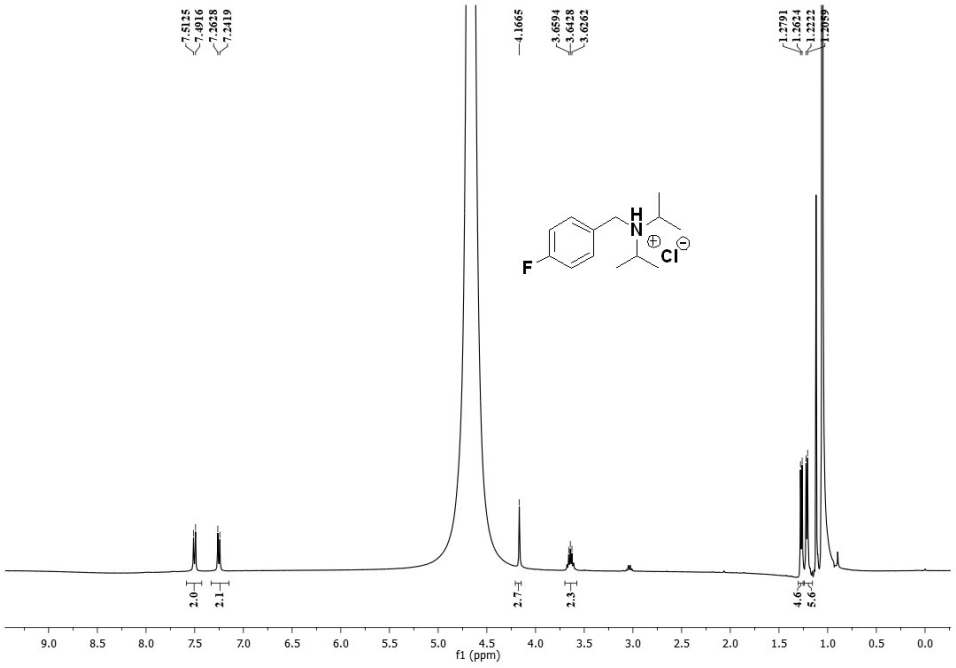


Figure FS61. ^{1}H NMR spectra of compound **(3q)**.

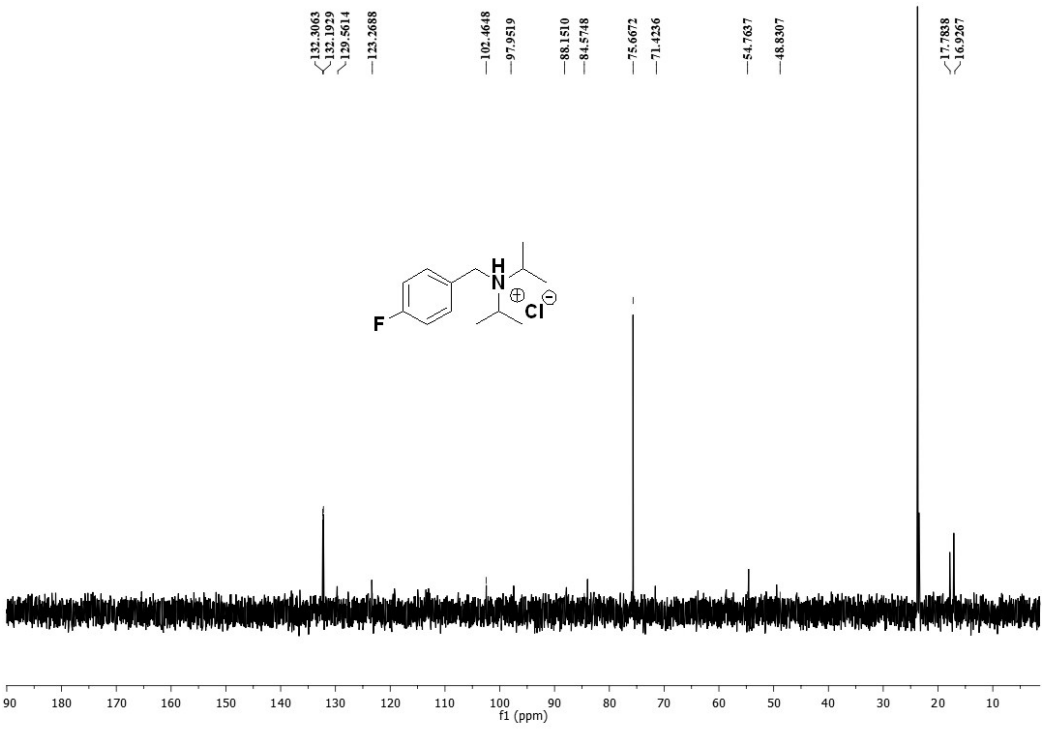


Figure FS62. ^{13}C NMR spectra of compound **(3q)**.

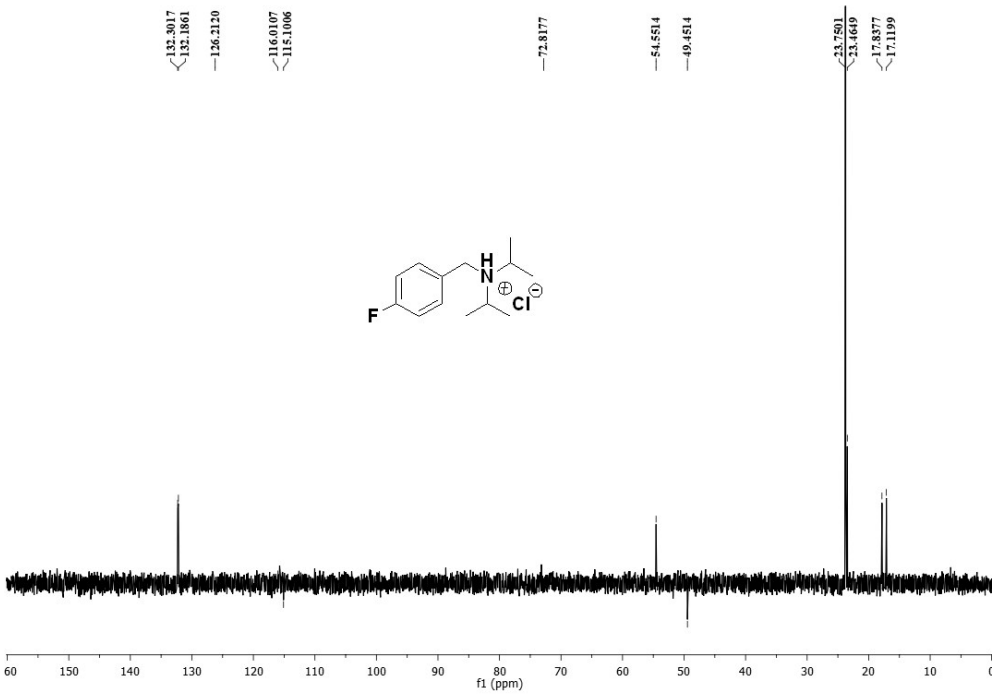


Figure FS63. ^{13}C-DEPT NMR spectra of compound **(3q)**.

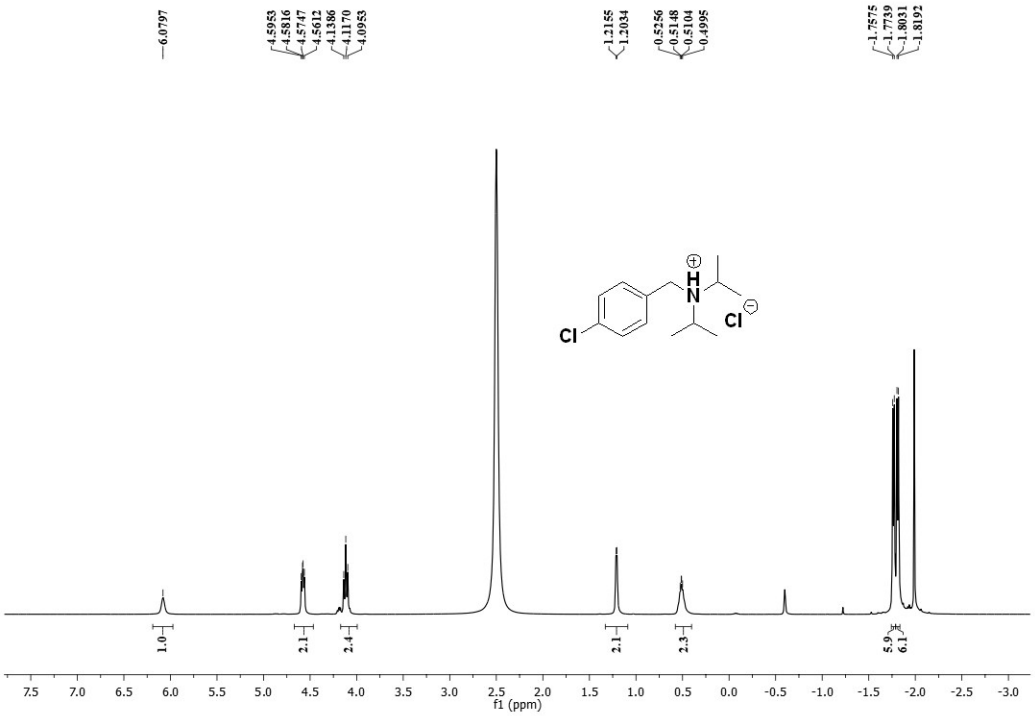


Figure FS64. ^{1}H NMR spectra of compound **(3r)**.

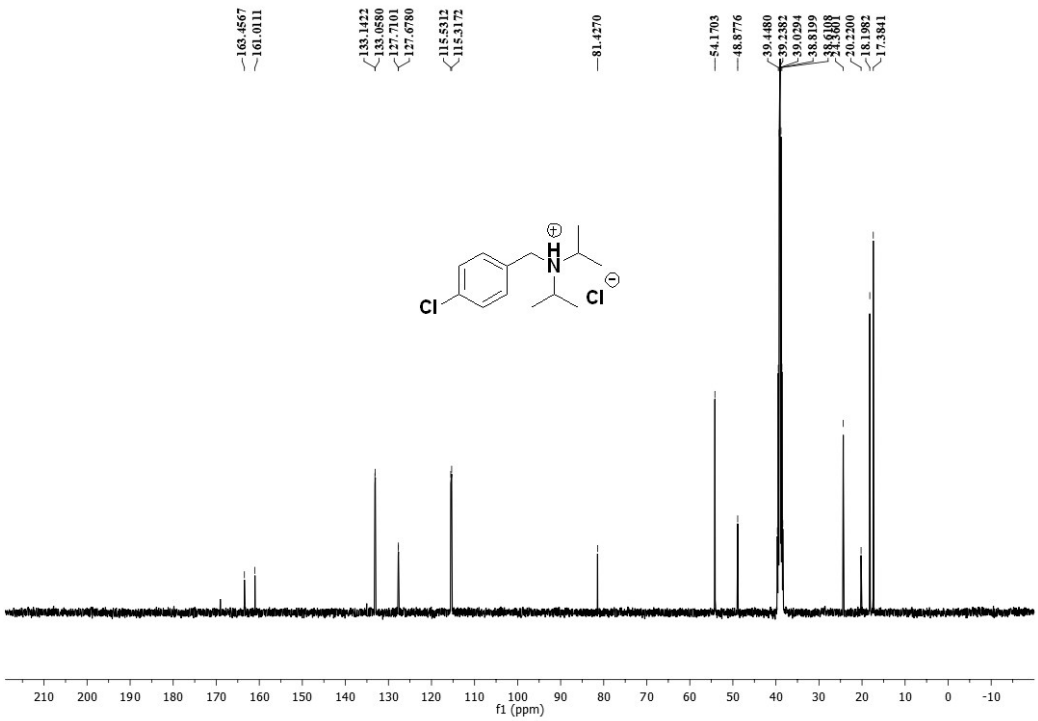


Figure FS65. ^{13}C NMR spectra of compound **(3r)**.

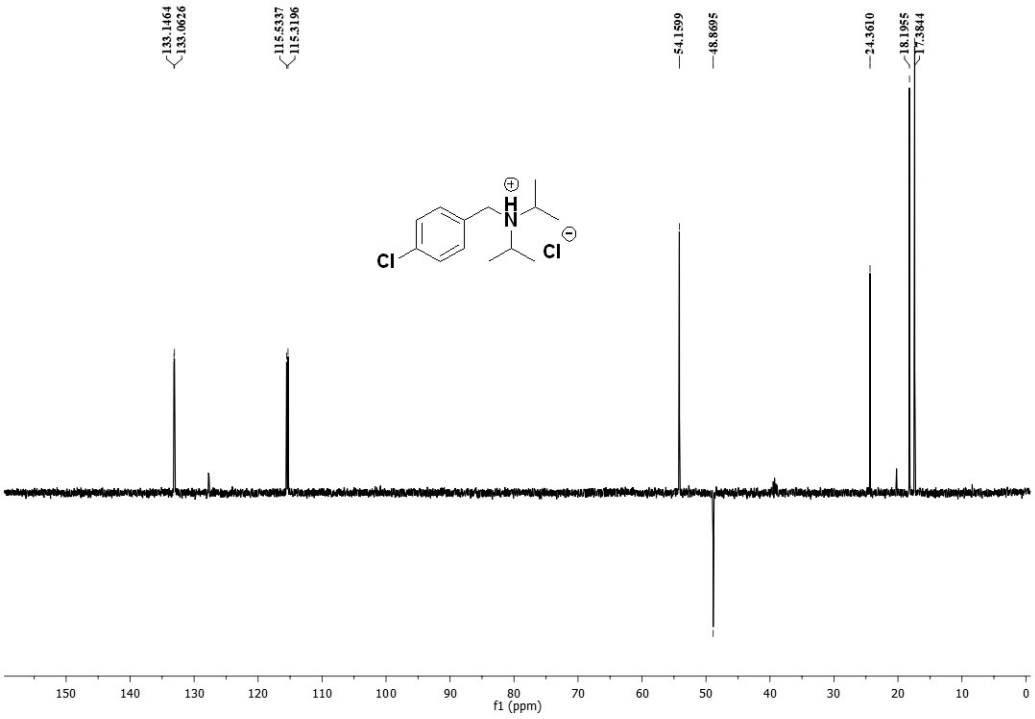


Figure FS66. ^{13}C- DEPT NMR spectra of compound **(3r)**.

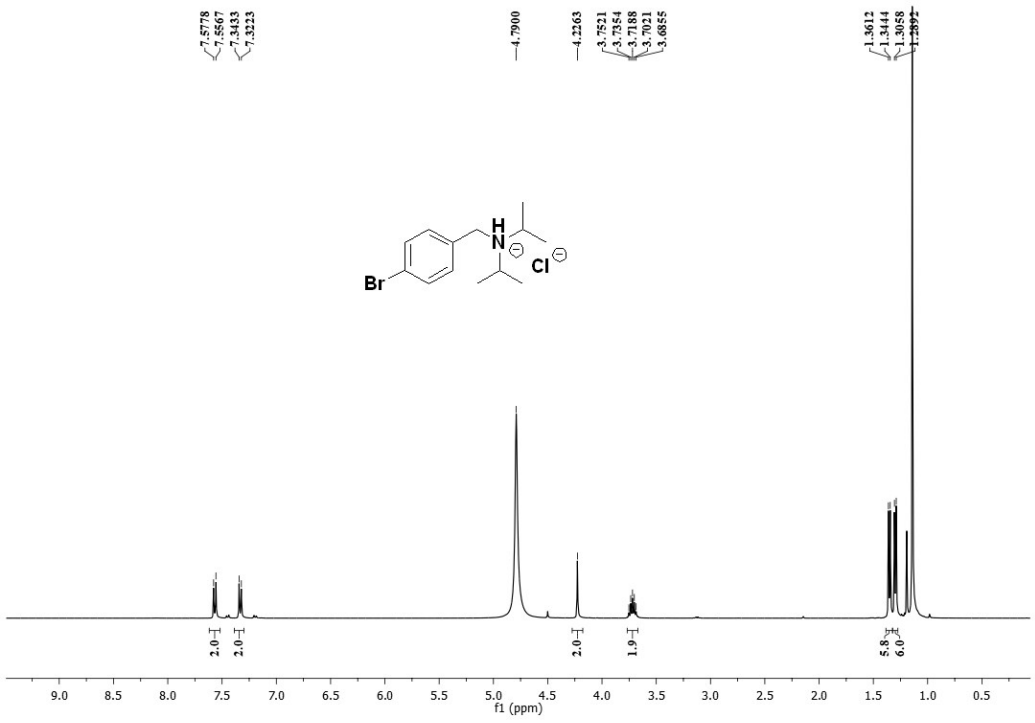


Figure FS67. ^{1}H NMR spectra of compound **(3s)**.

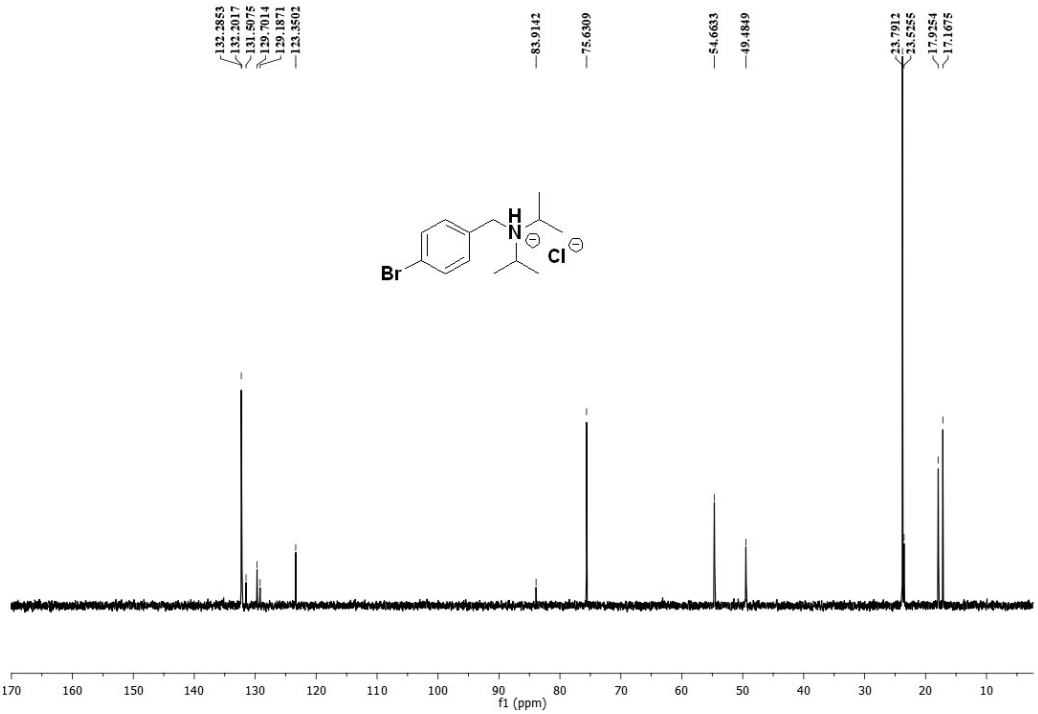


Figure FS68. ^{13}C NMR spectra of compound **(3s)**.

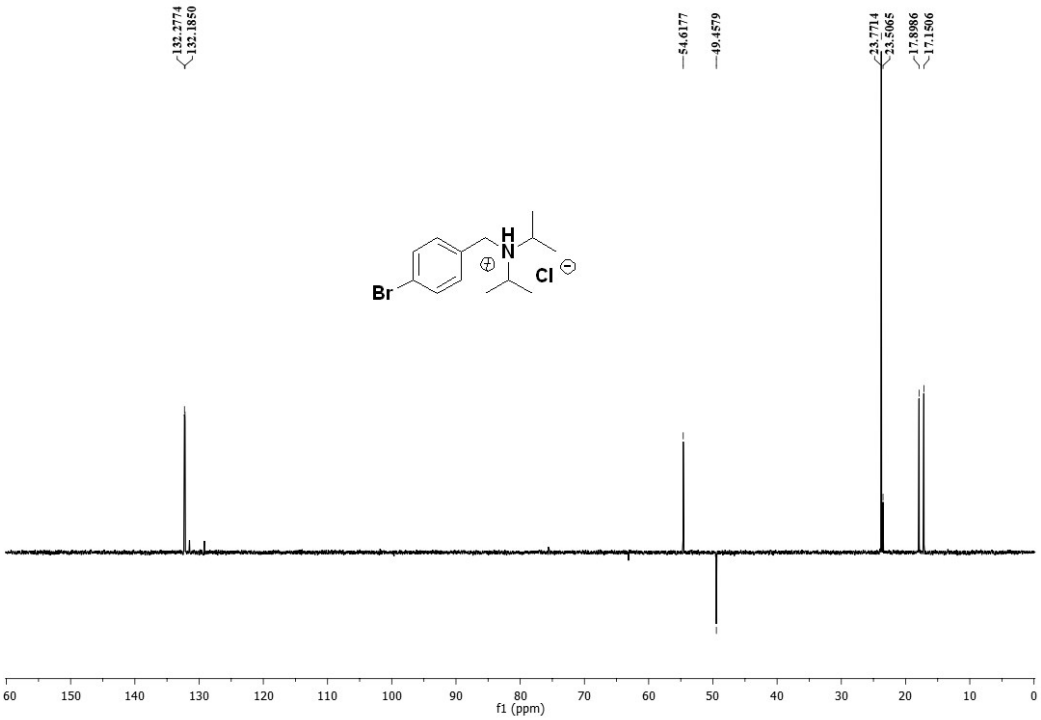


Figure FS69. ^{13}C-DEPT NMR spectra of compound **(3s)**.

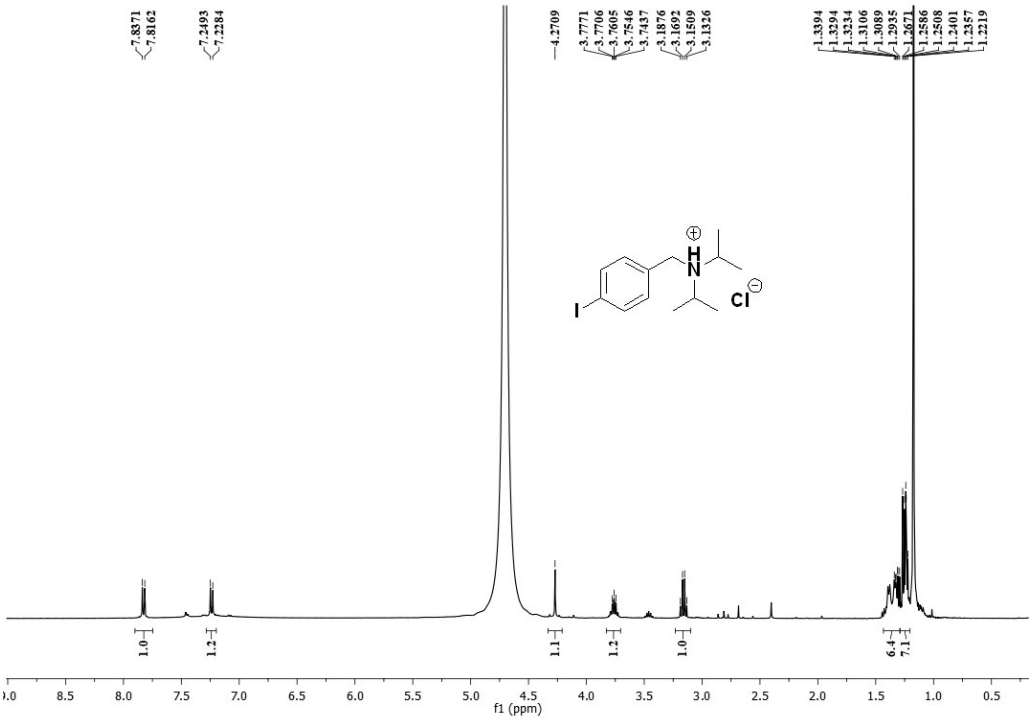


Figure FS70. [1]H NMR spectra of compound **(3t)**.

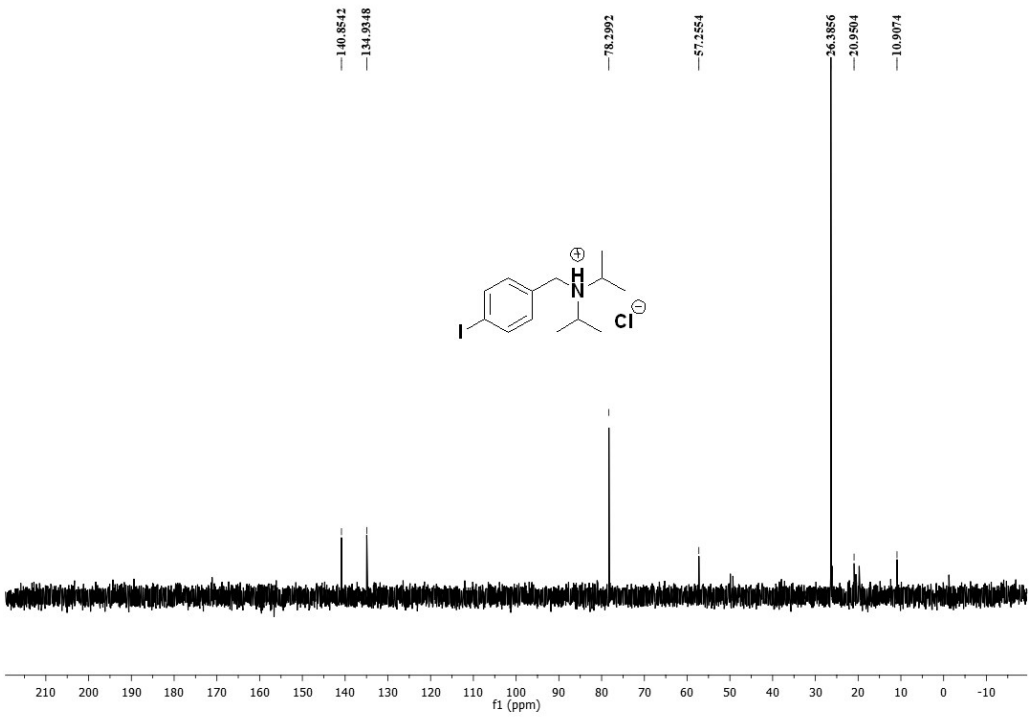


Figure FS71. [13]C NMR spectra of compound **(3t)**.

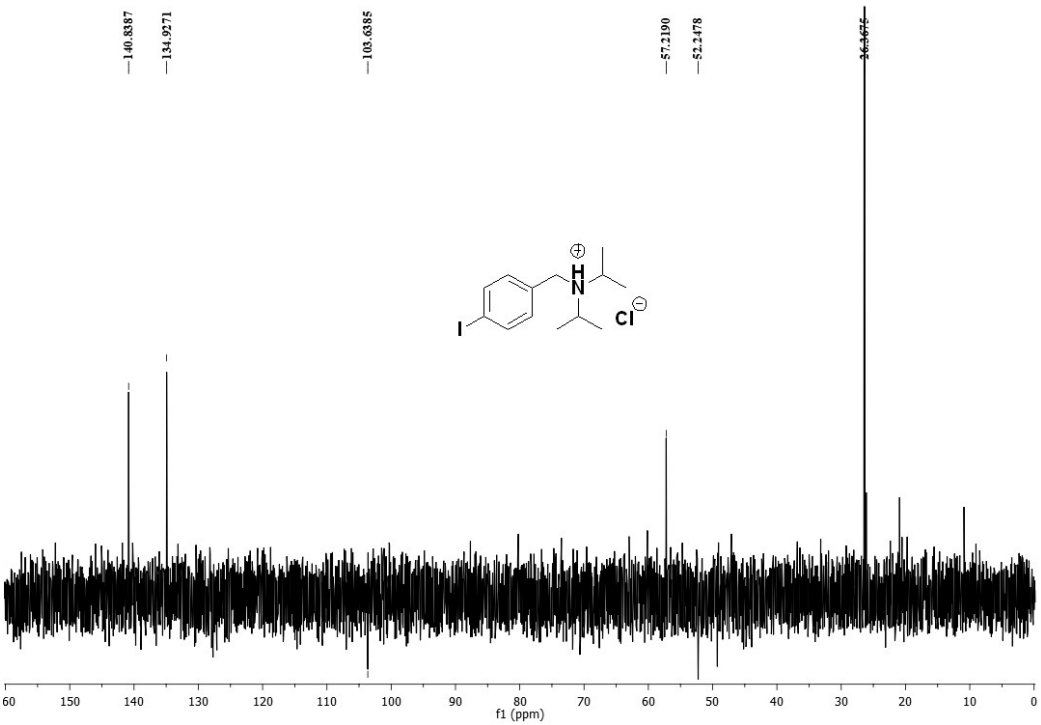


Figure FS72. ^{13}C-DEPT NMR spectra of compound **(3t)**.

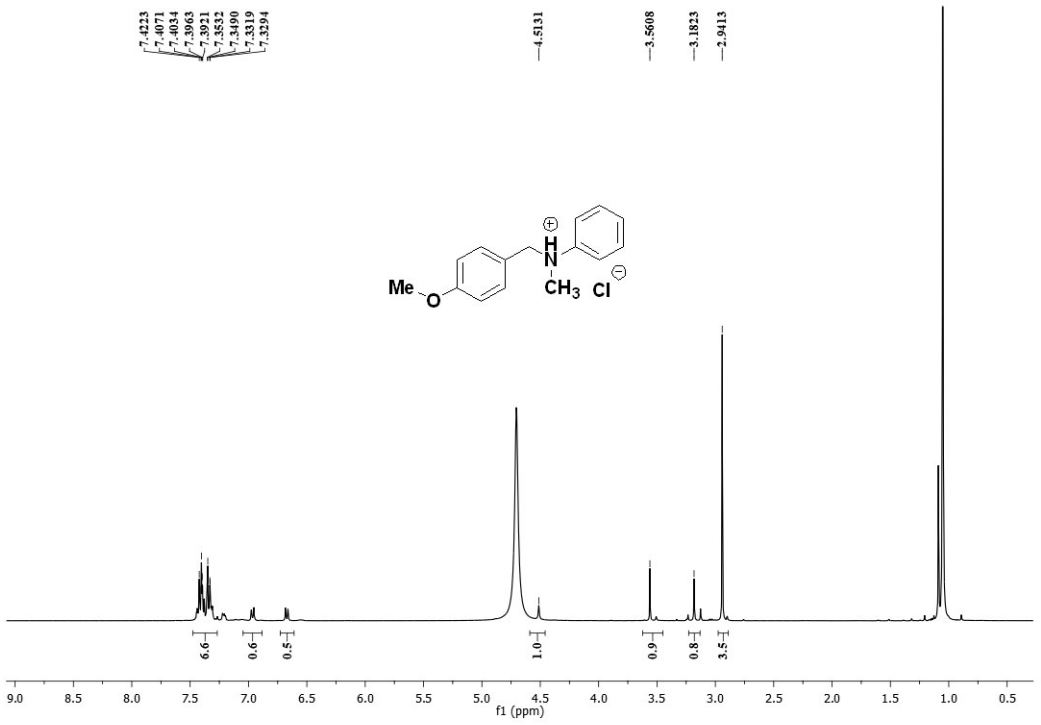


Figure FS73. ^{1}H NMR spectra of compound **(3u)**.

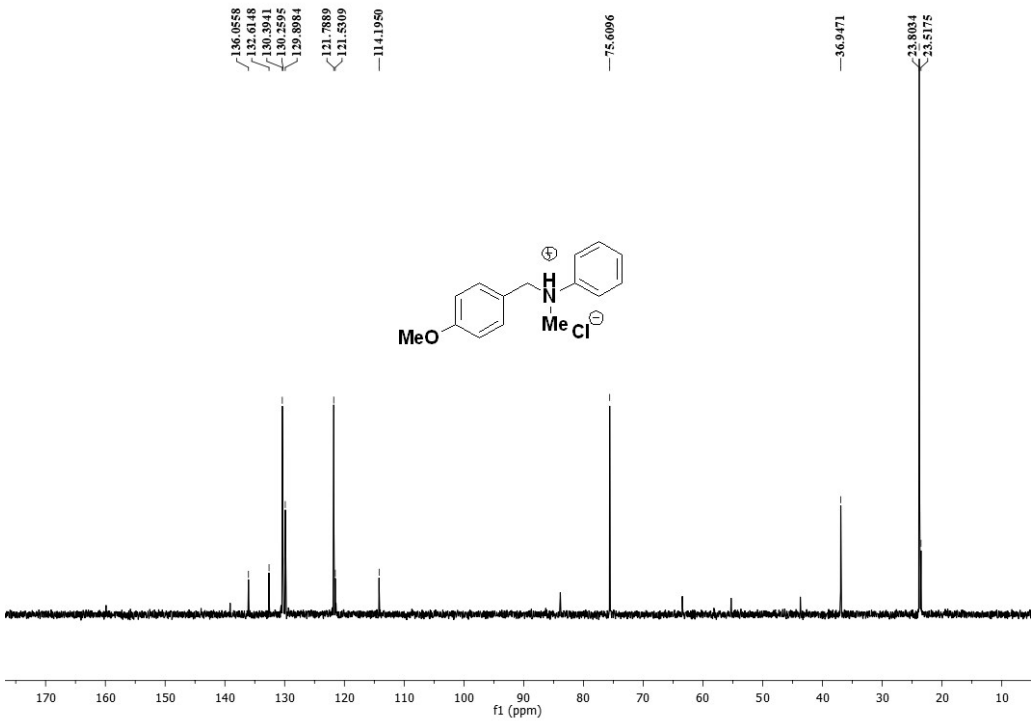


Figure FS74. ^{13}C NMR spectra of compound **(3u)**.

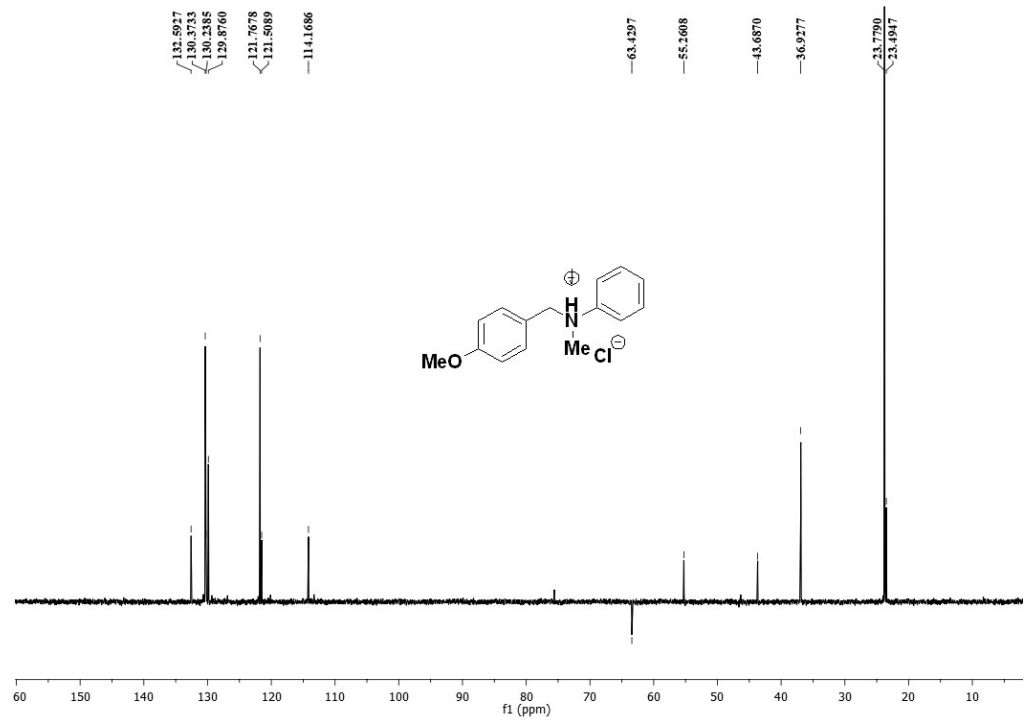


Figure FS75. ^{13}C-DEPT NMR spectra of compound **(3u)**.

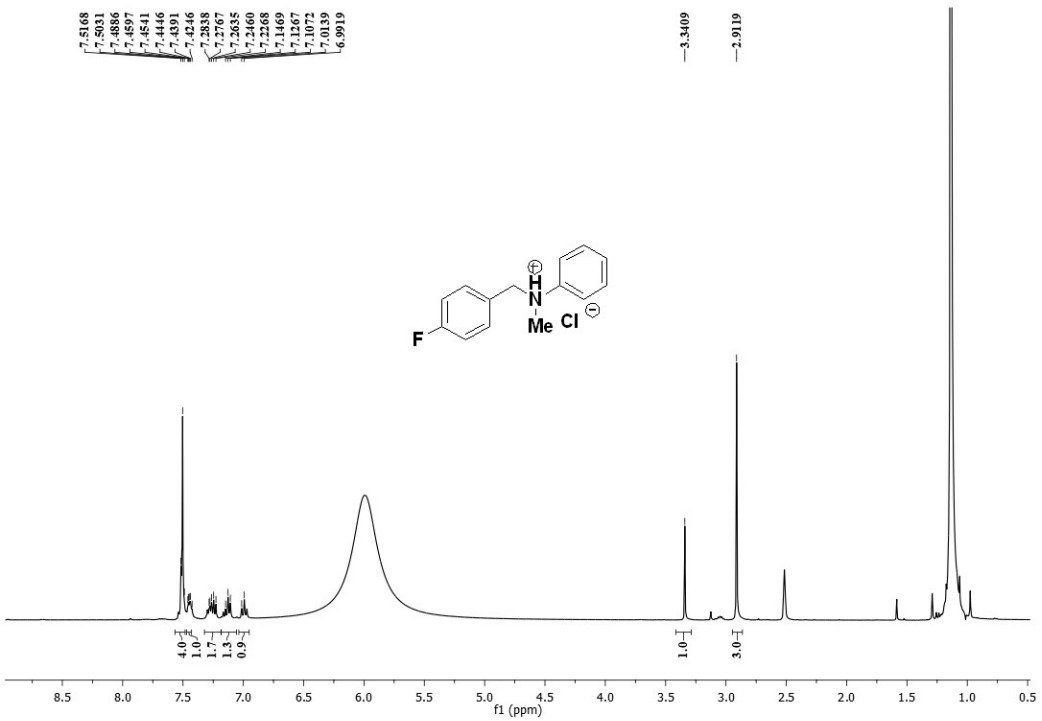


Figure FS76. [1]H NMR spectra of compound **(3v)**.

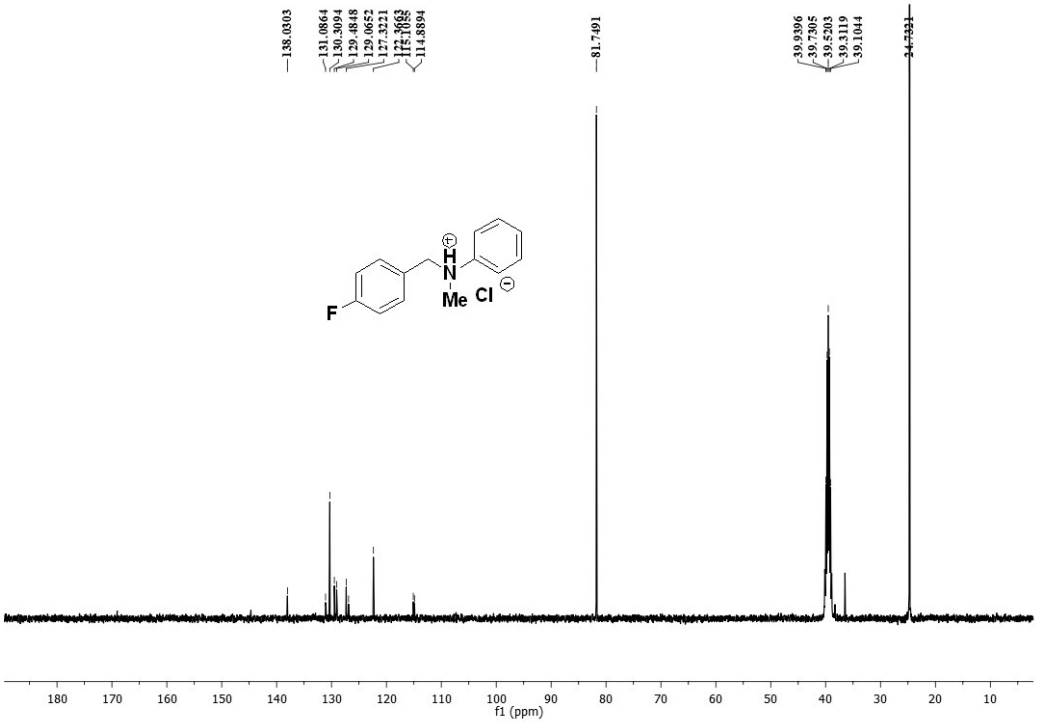


Figure FS77. [13]C NMR spectra of compound **(3v)**.

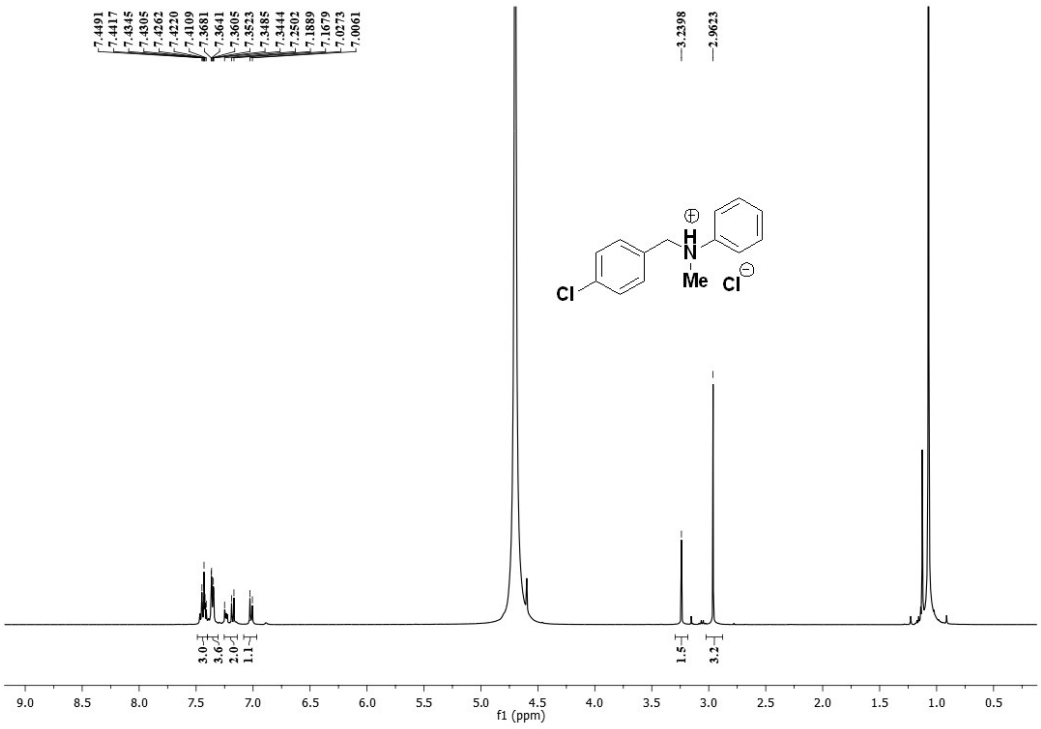


Figure FS78. [1]H NMR spectra of compound **(3w)**.

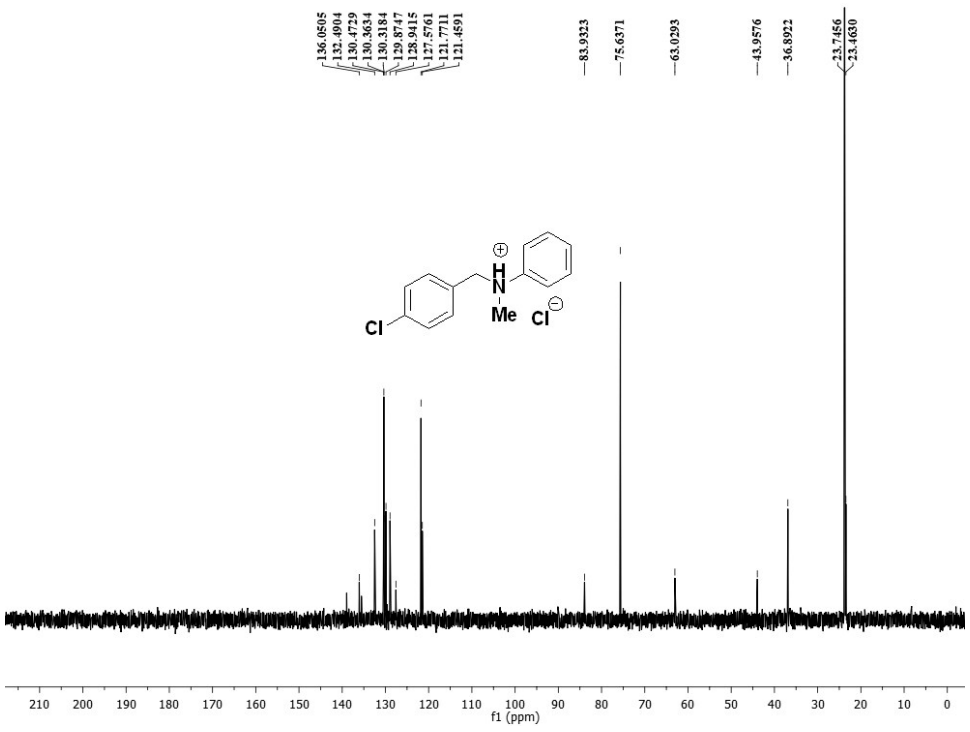


Figure FS79. [13]C NMR spectra of compound **(3w)**.

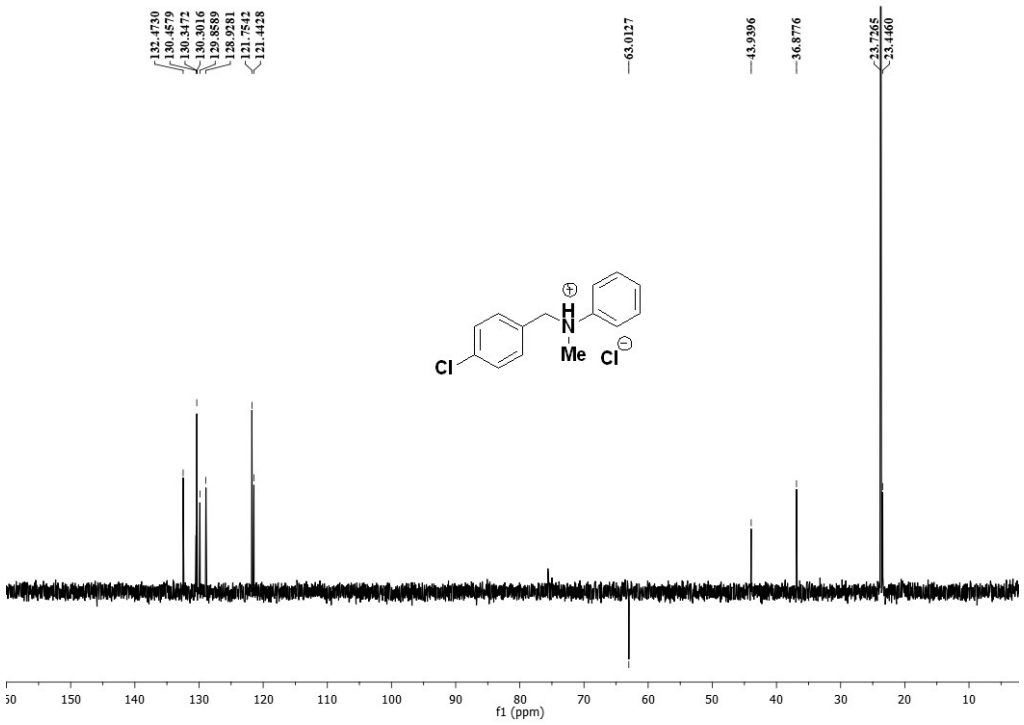


Figure FS80. ^{13}C-DEPT NMR spectra of compound **(3w)**.

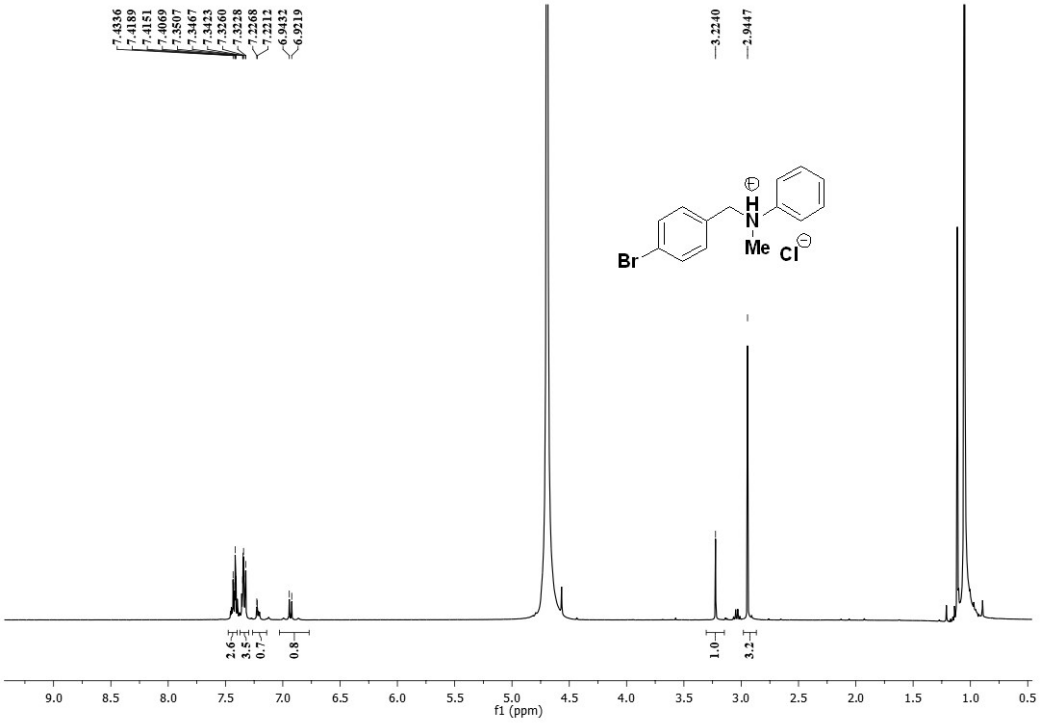


Figure FS81. ^{1}H NMR spectra of compound **(3x)**.

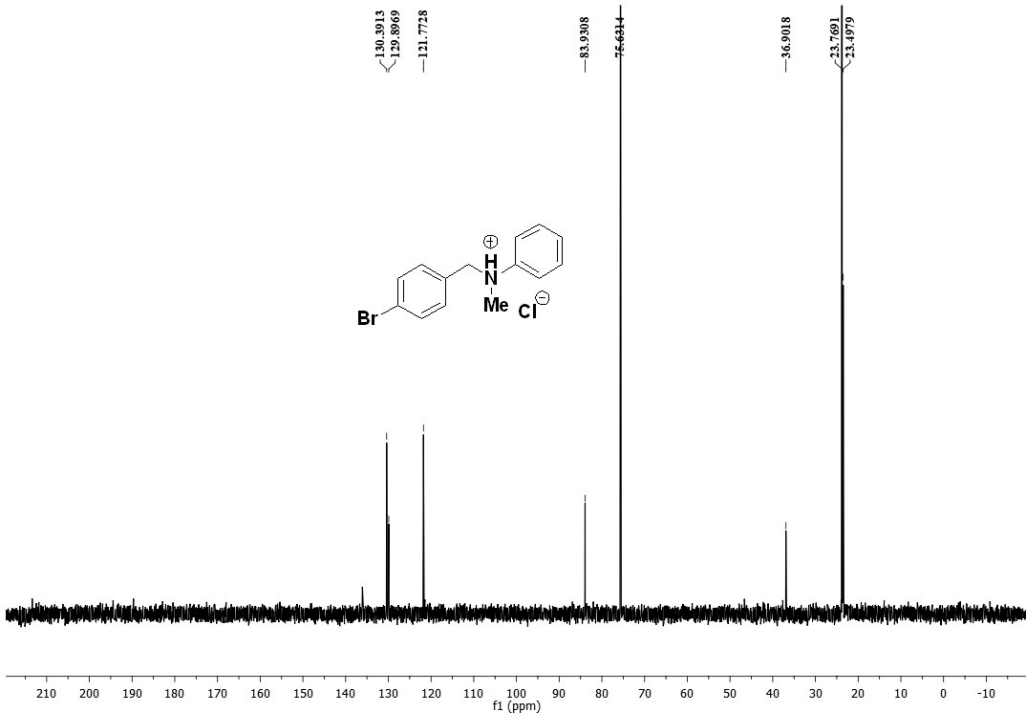


Figure FS82. ^{13}C NMR spectra of compound **(3x)**.

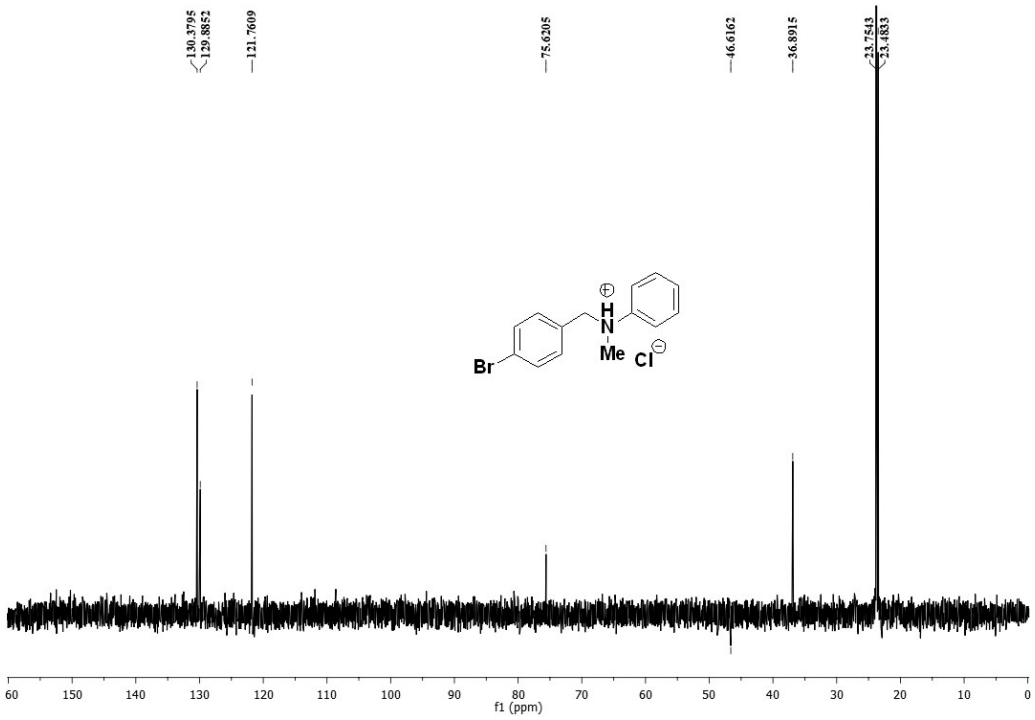


Figure FS83. ^{13}C-DEPT NMR spectra of compound **(3x)**.

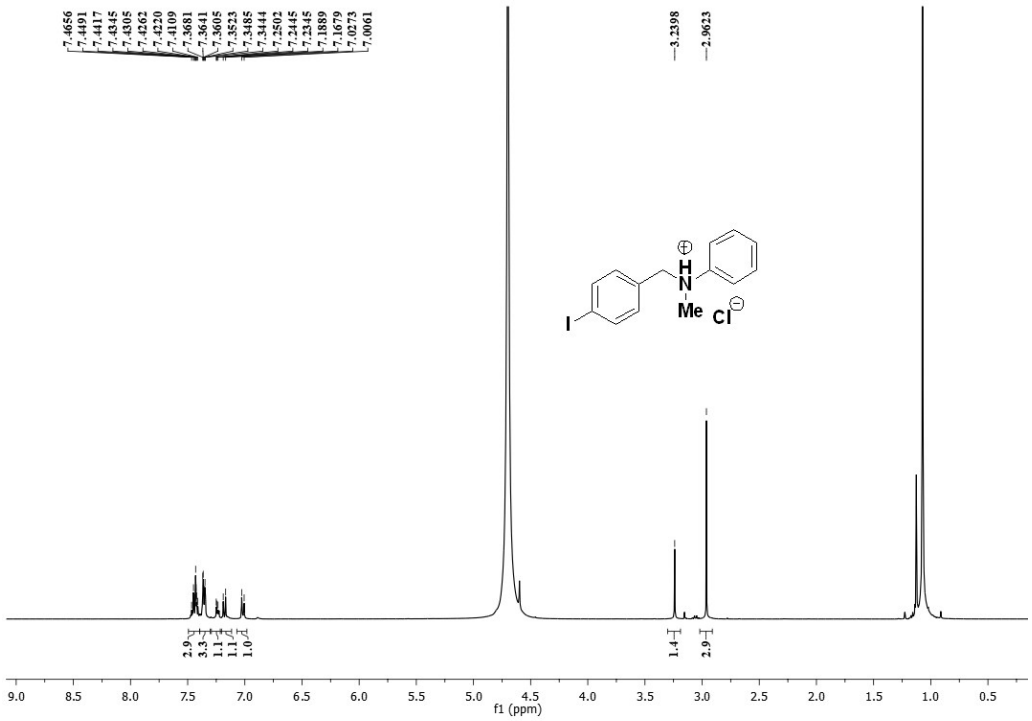


Figure FS84. [1]H NMR spectra of compound **(3y)**.

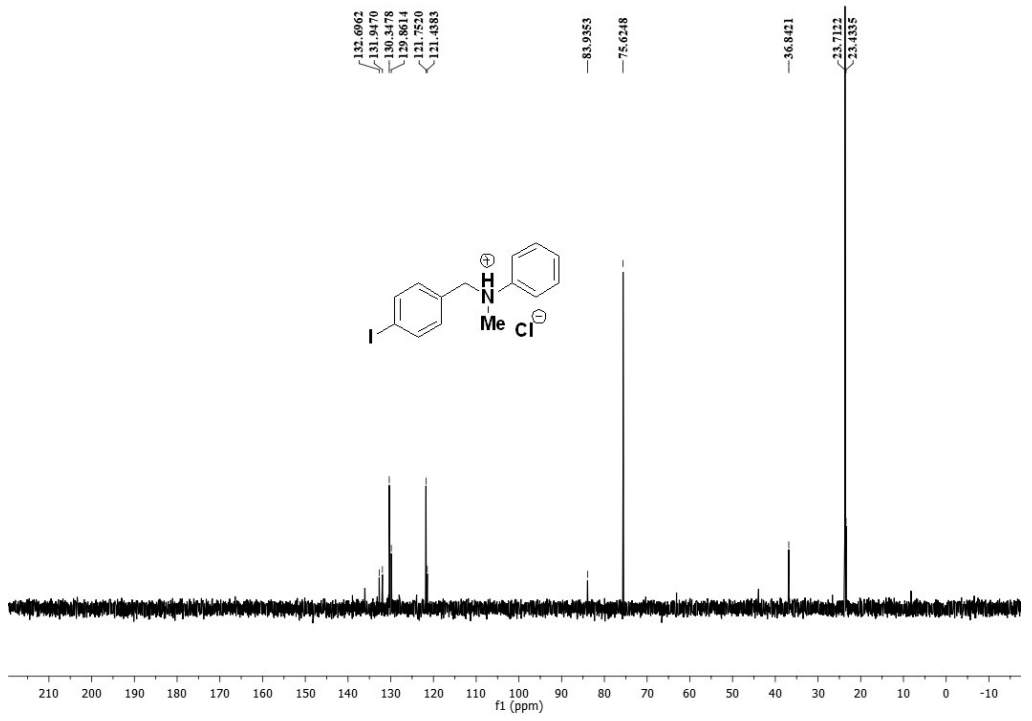


Figure FS85. [13]C NMR spectra of compound **(3y)**.

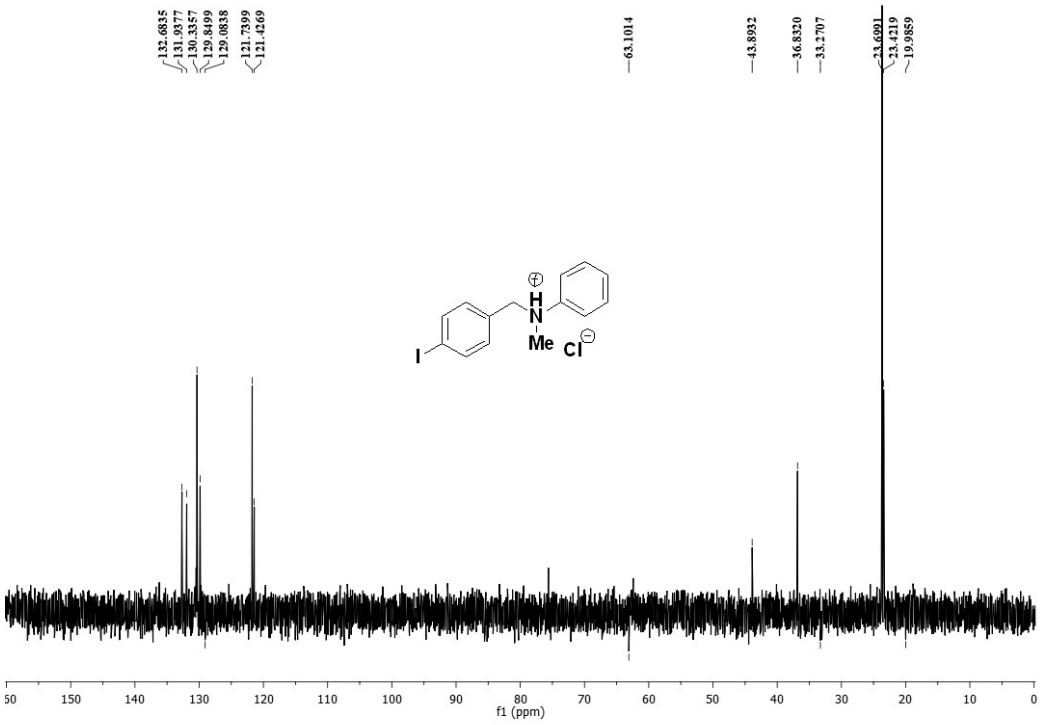


Figure FS86. ^{13}C NMR spectra of compound **(3y)**.

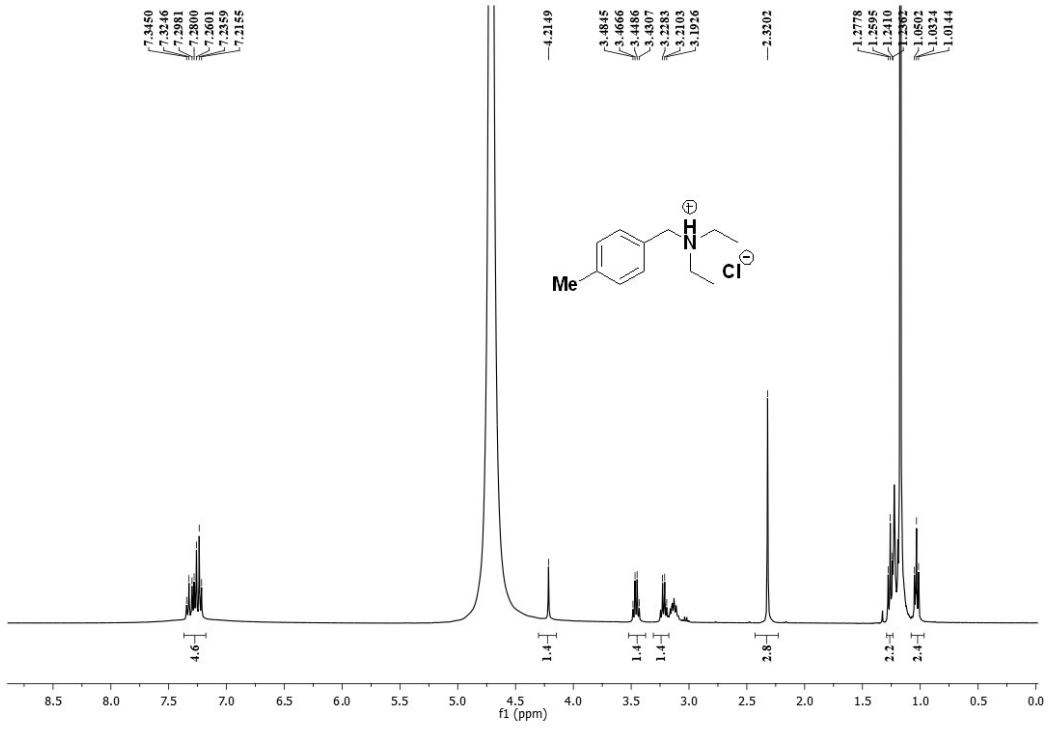


Figure FS87. ^{1}H NMR spectra of compound **(3z)**.

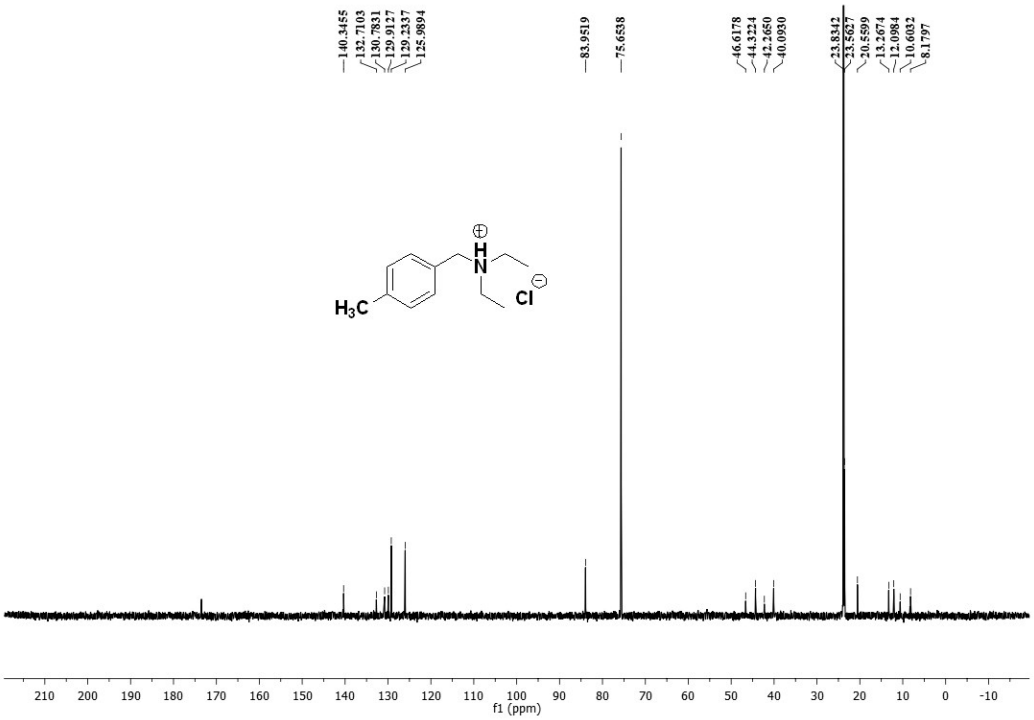


Figure FS88. ^{13}C NMR spectra of compound **(3z)**.

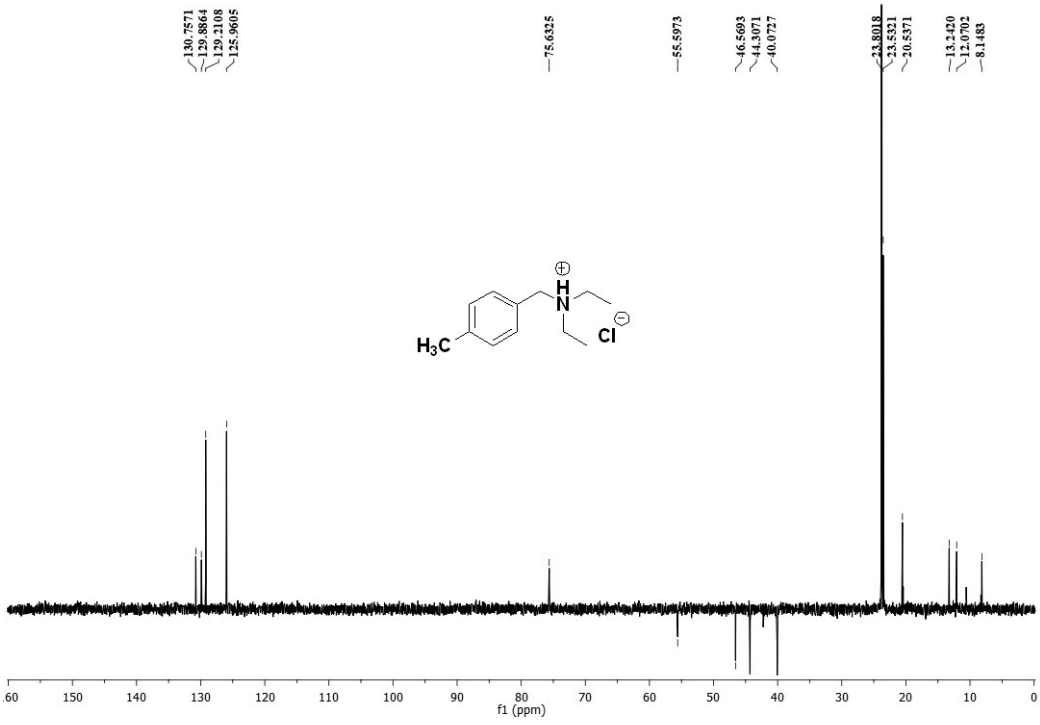


Figure FS89. ^{13}C-DEPT NMR spectra of compound **(3z)**.

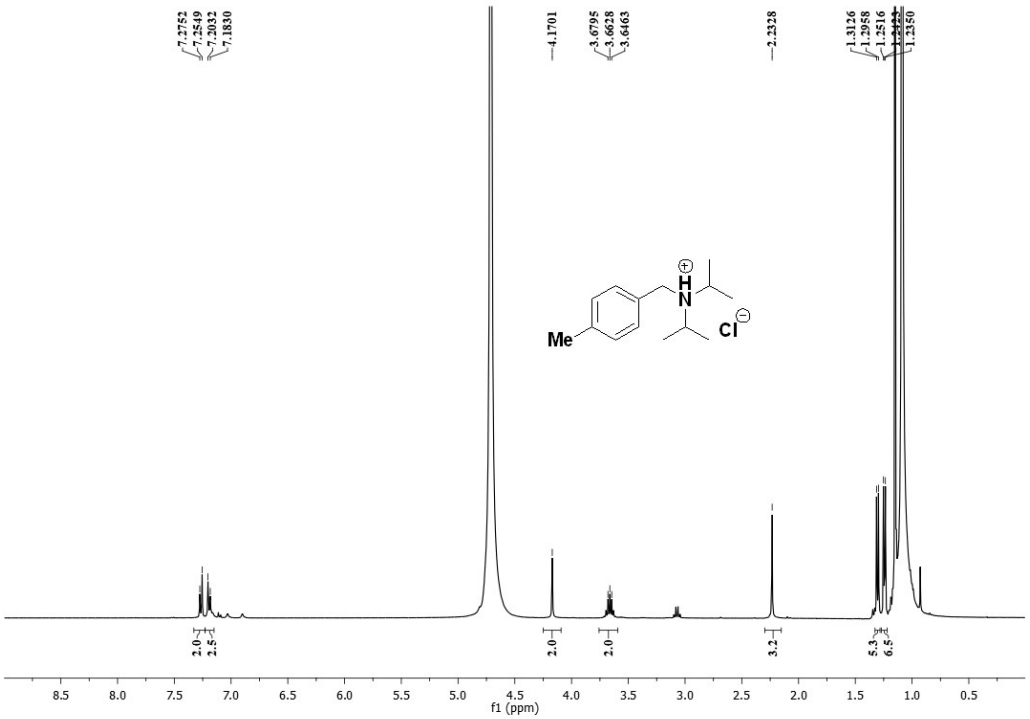


Figure FS90. [1]H NMR spectra of compound **(3za)**.

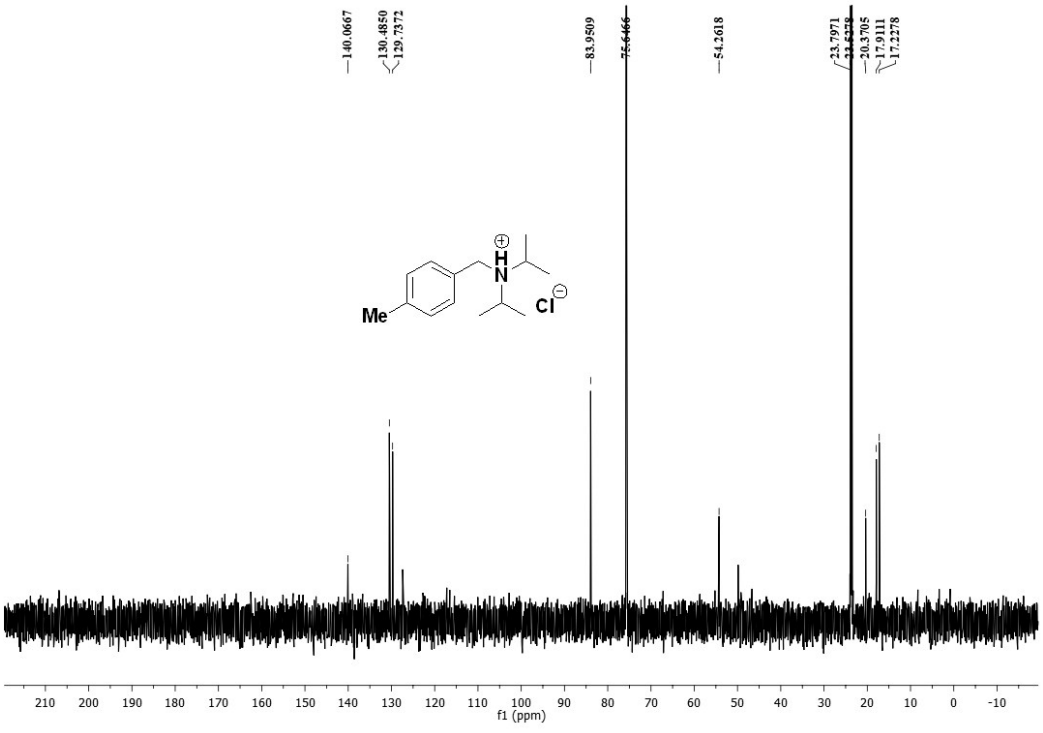


Figure FS91. [13]C NMR spectra of compound **(3za)**.

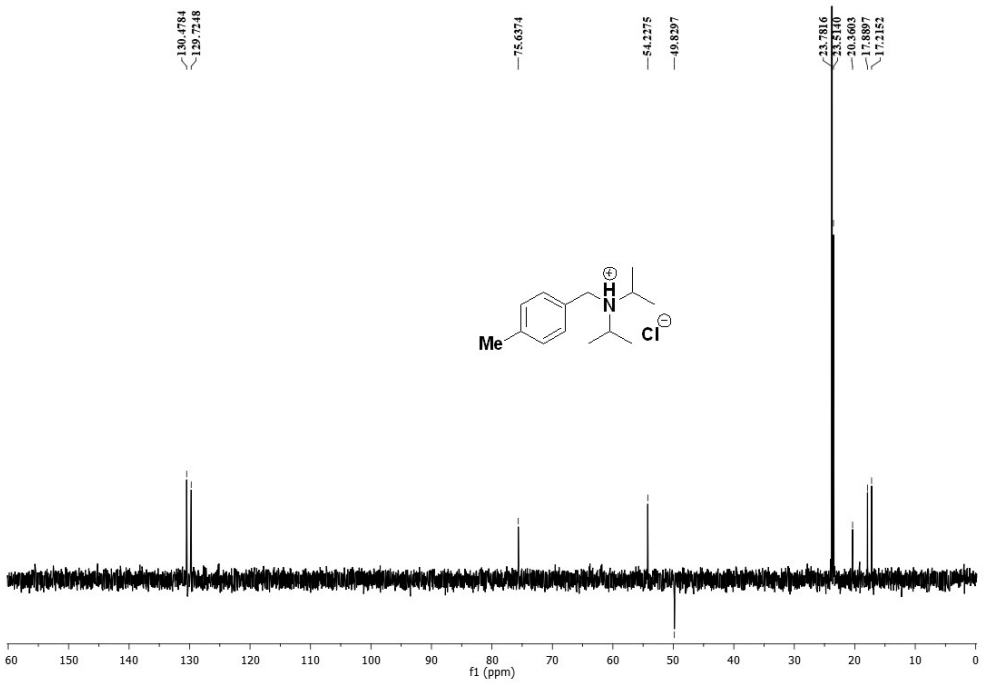


Figure FS92. ^{13}C-DEPT NMR spectra of compound **(3za)**.

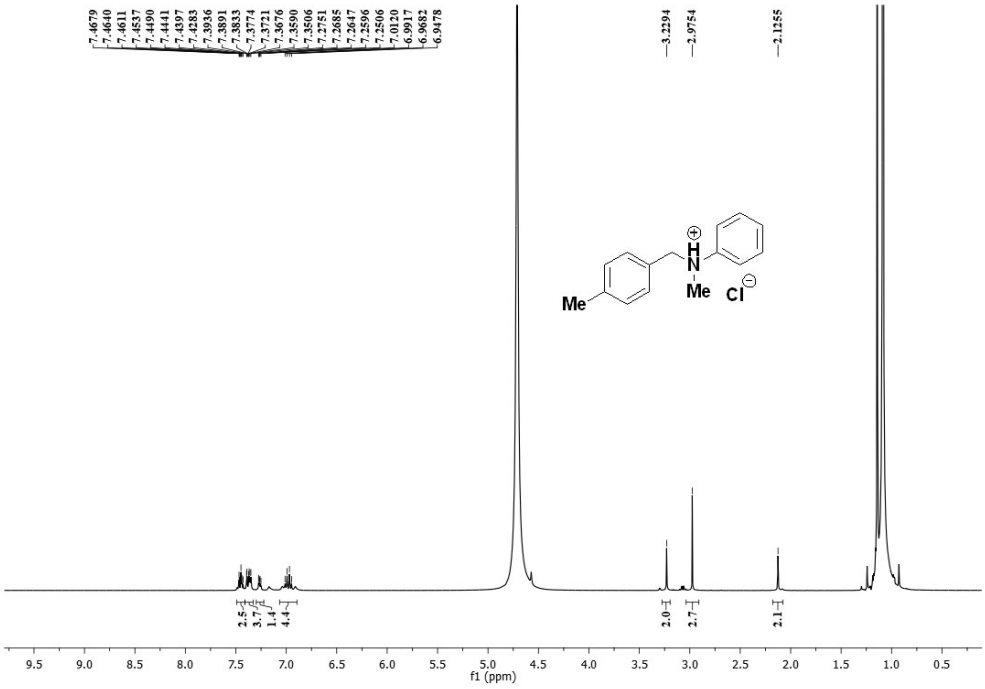


Figure FS93. ^{1}H NMR spectra of compound **(3zb)**.

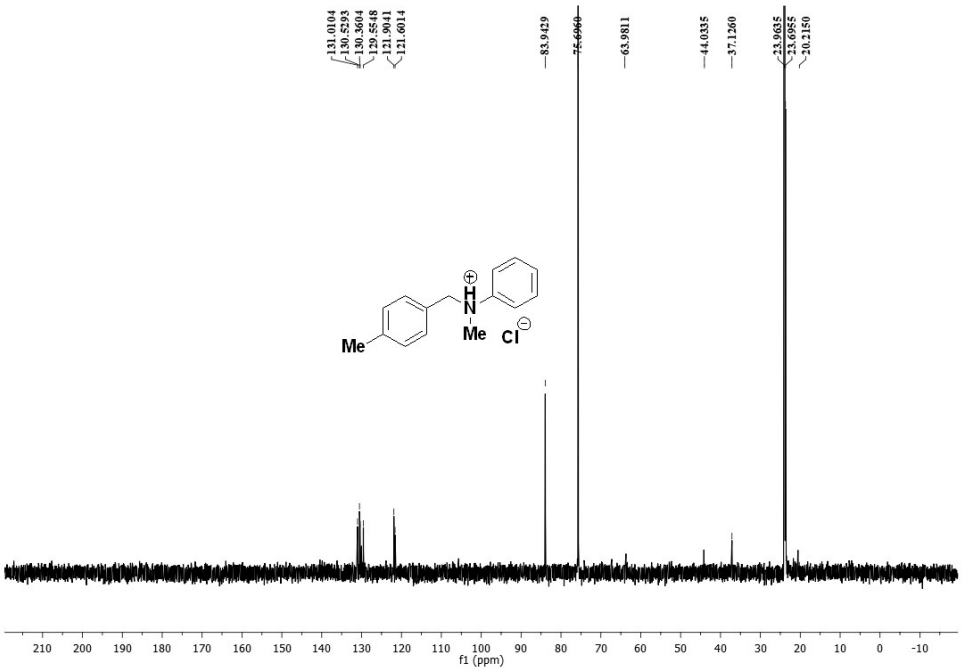


Figure FS94. ^{13}C NMR spectra of compound **(3zb)**.

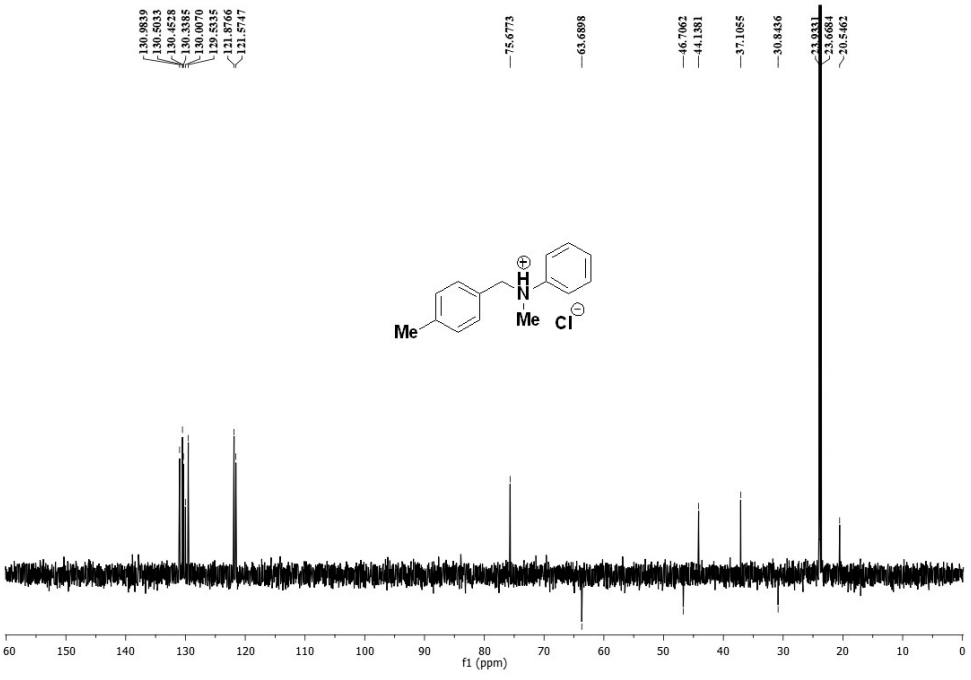


Figure FS95. ^{13}C-DEPT NMR spectra of compound **(3zb)**.

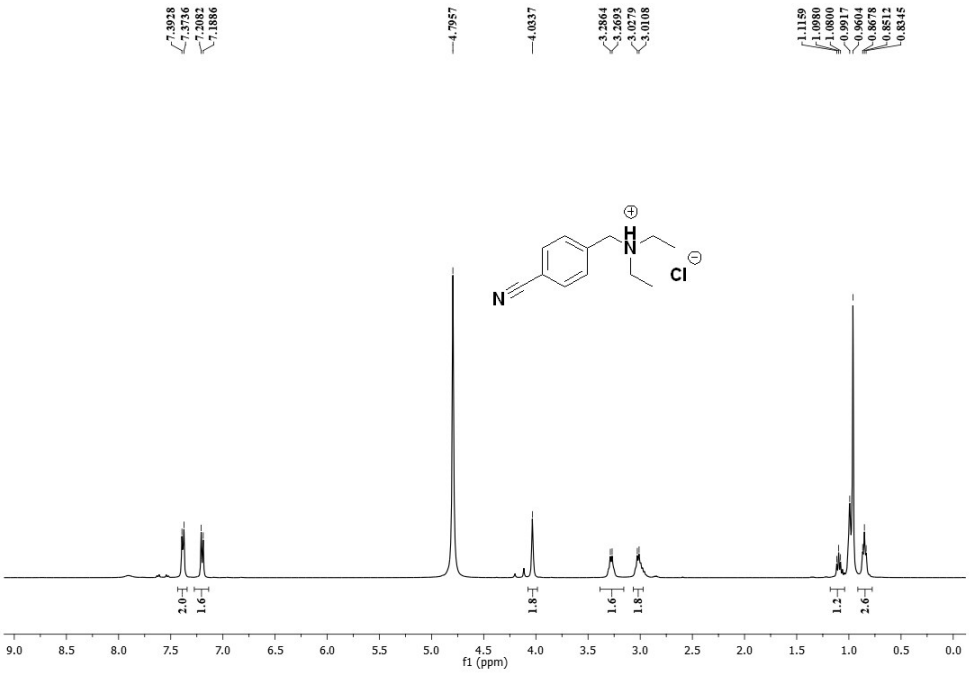


Figure FS96. ^{1}H NMR spectra of compound **(4a)**.

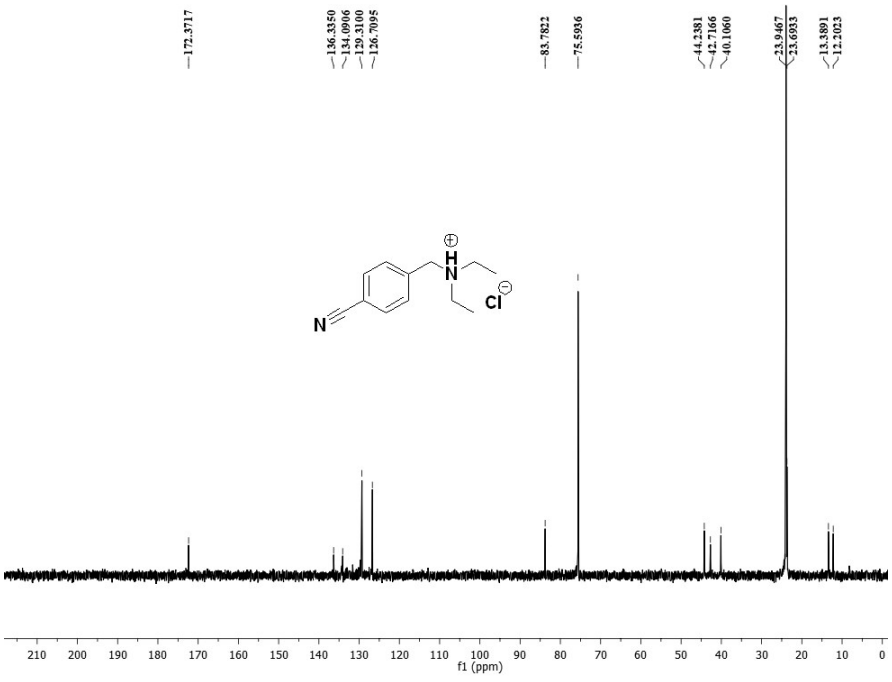


Figure FS97. ^{13}C NMR spectra of compound **(4a)**.

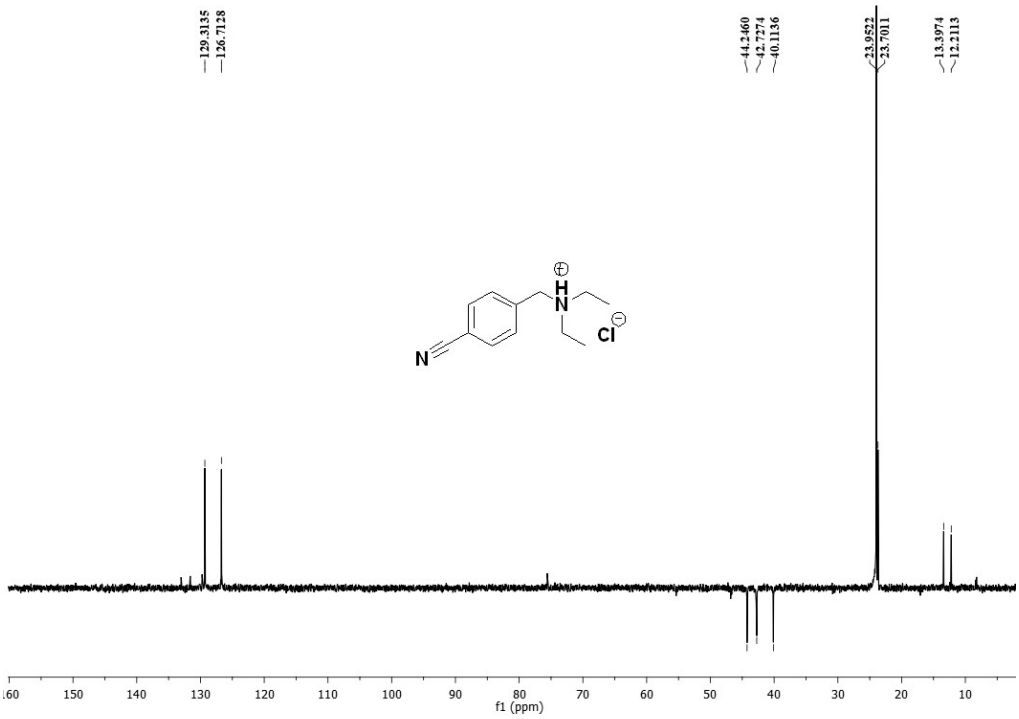


Figure FS98. ^{13}C-DEPT NMR spectra of compound **(4a)**.

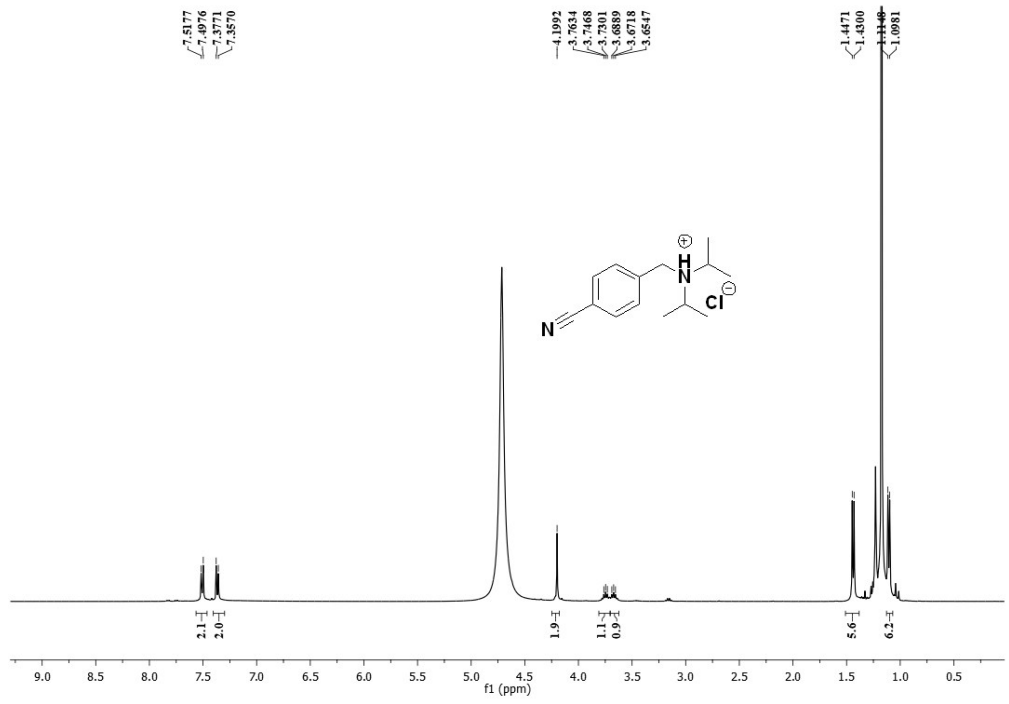


Figure FS99. ^{1}H NMR spectra of compound **(4b)**.

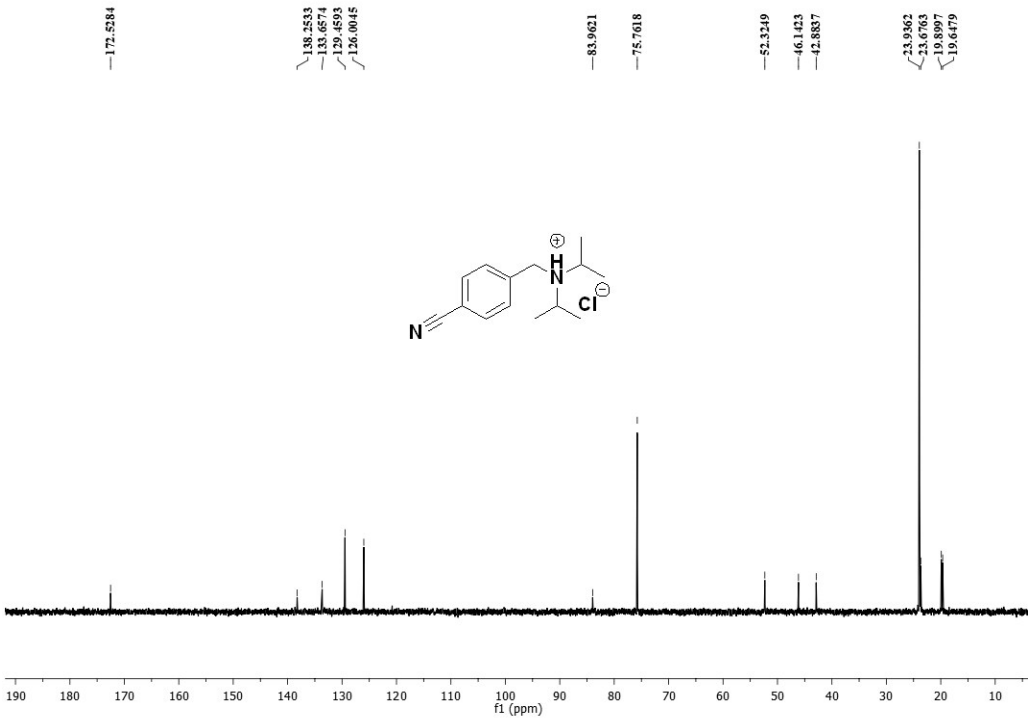


Figure FS100. ^{13}C NMR spectra of compound **(4b)**.

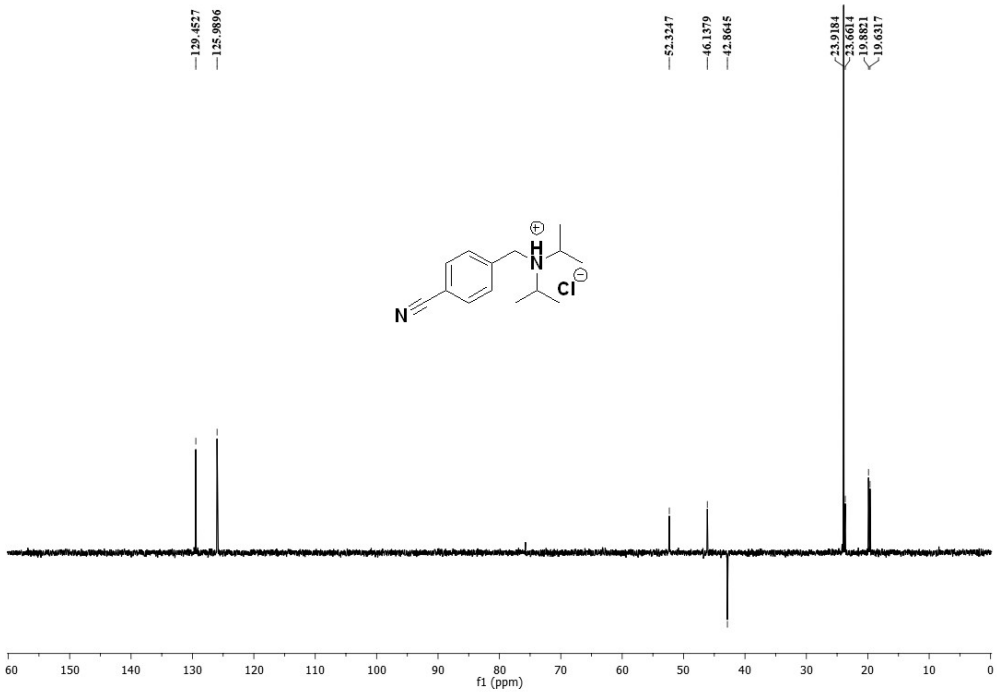


Figure FS101. ^{13}C-DEPT spectra of compound **(4b)**.

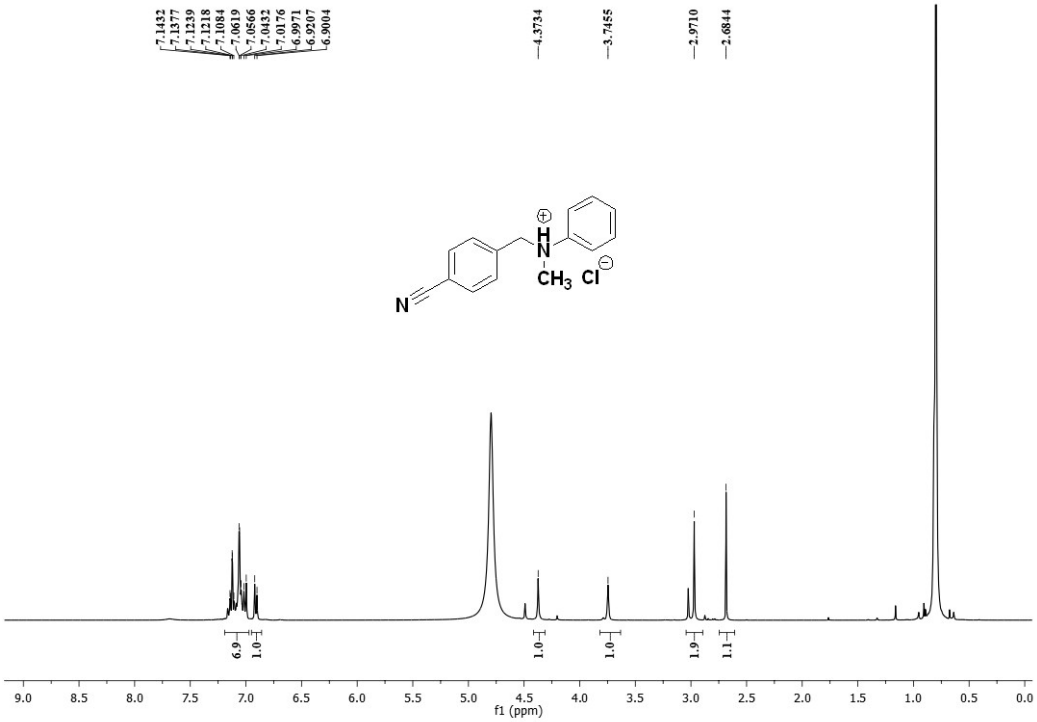


Figure FS102. ^{1}H NMR spectra of compound **(4c)**.

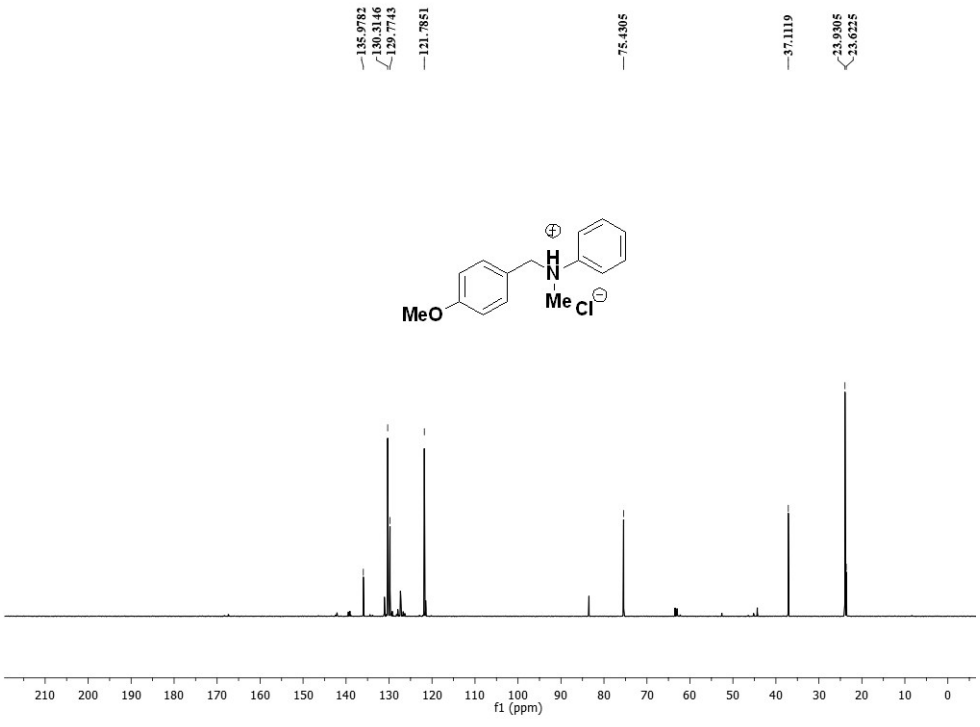


Figure FS103. ^{13}C NMR spectra of compound **(4c)**.

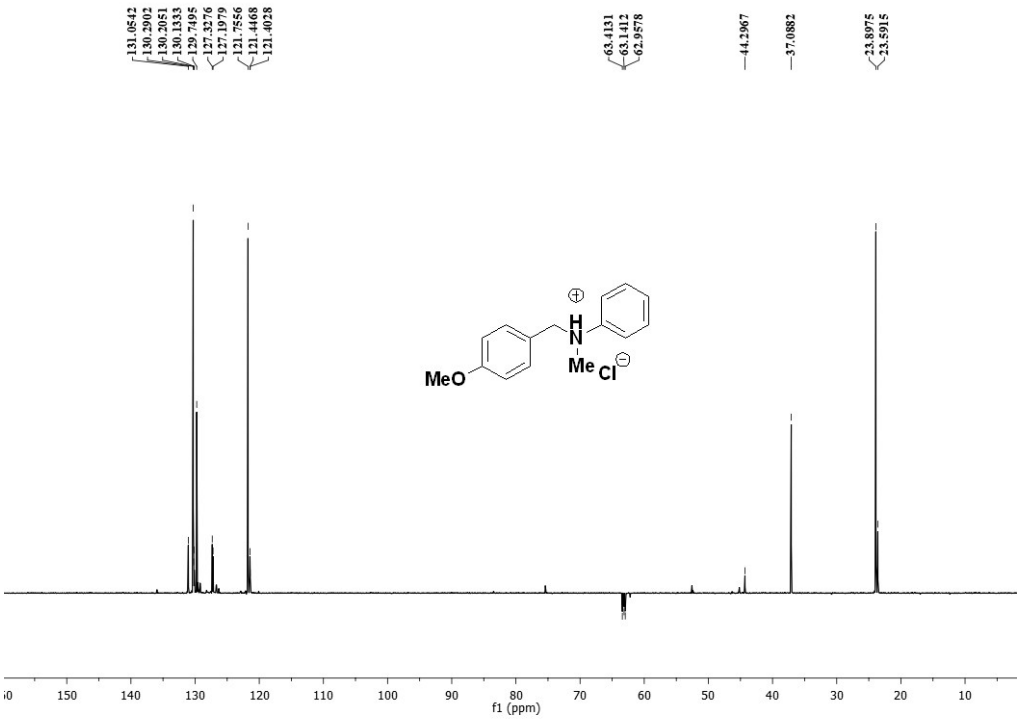


Figure FS104. ^{13}C-DEPT NMR spectra of compound **(4c)**.

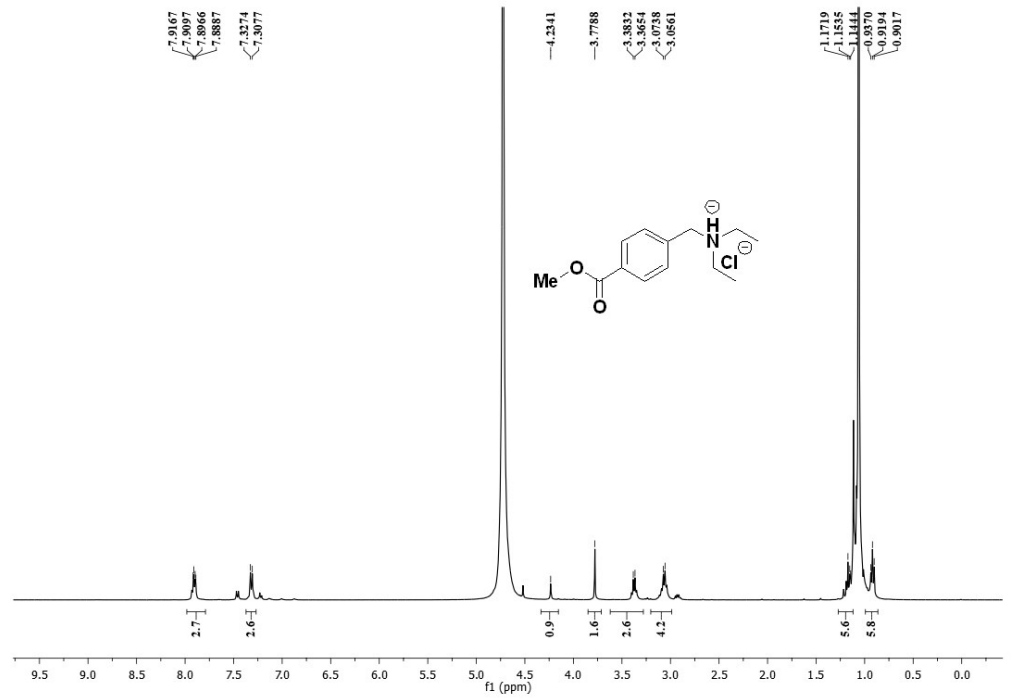


Figure FS105. ^{1}H NMR spectra of compound **(4d)**.

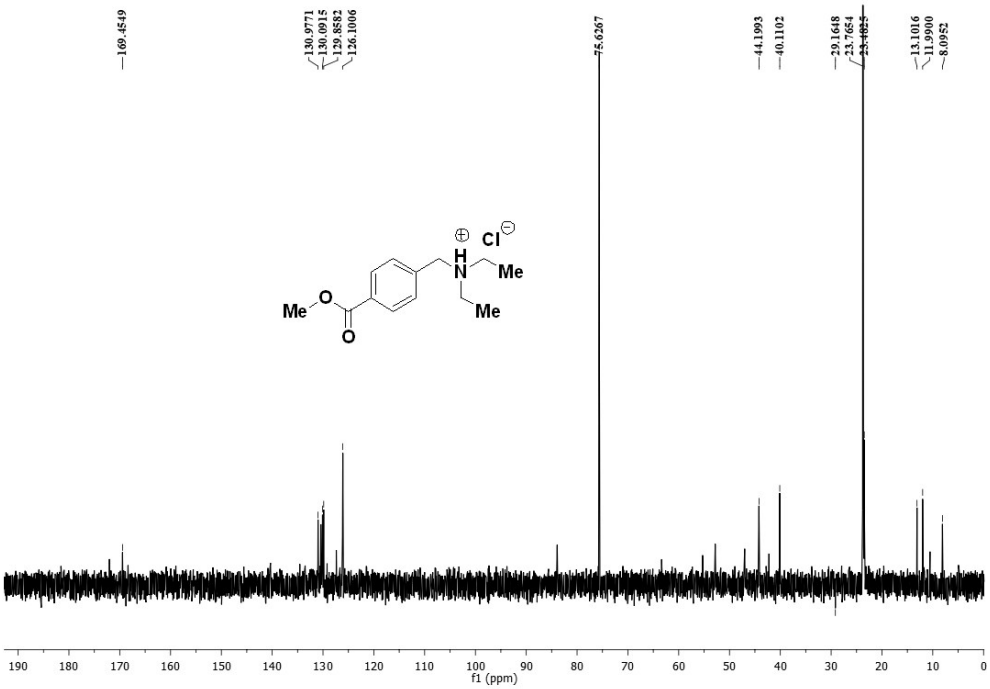


Figure FS106. ^{13}C NMR spectra of compound **(4d)**.

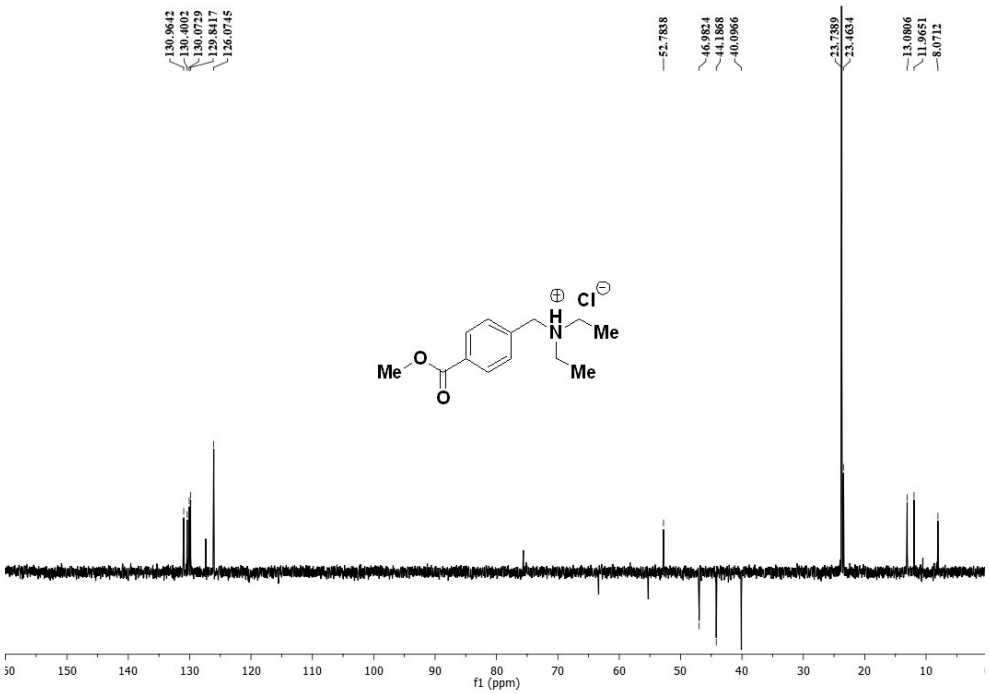


Figure FS107. ^{13}C-DEPT NMR spectra of compound **(4d)**.

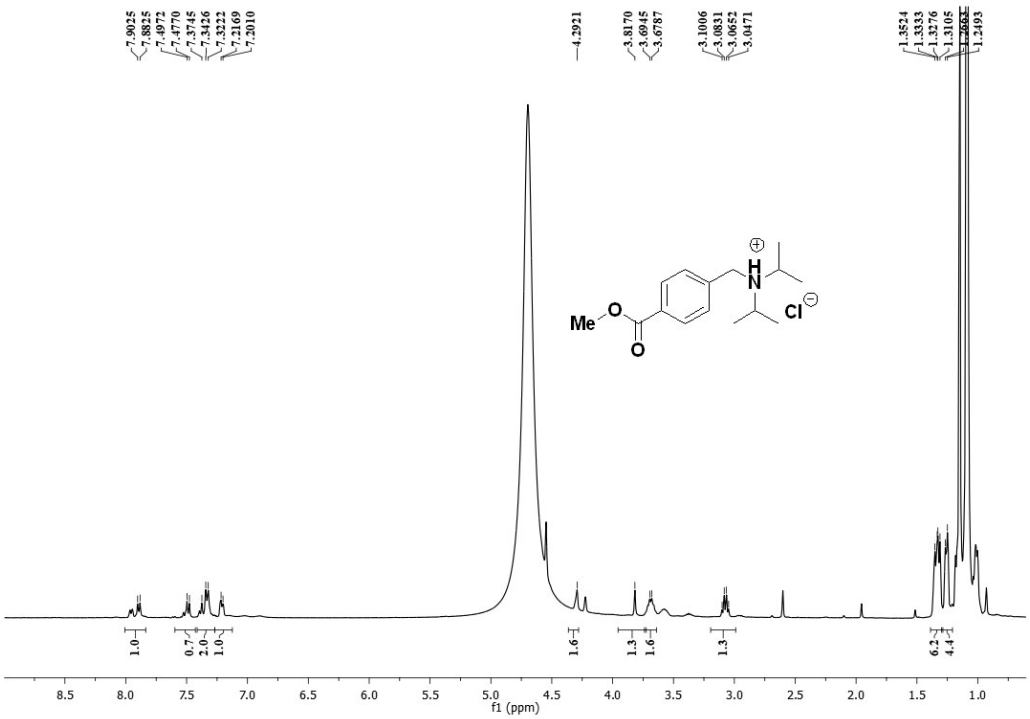


Figure FS108. ^{1}H NMR spectra of compound **(4e)**.

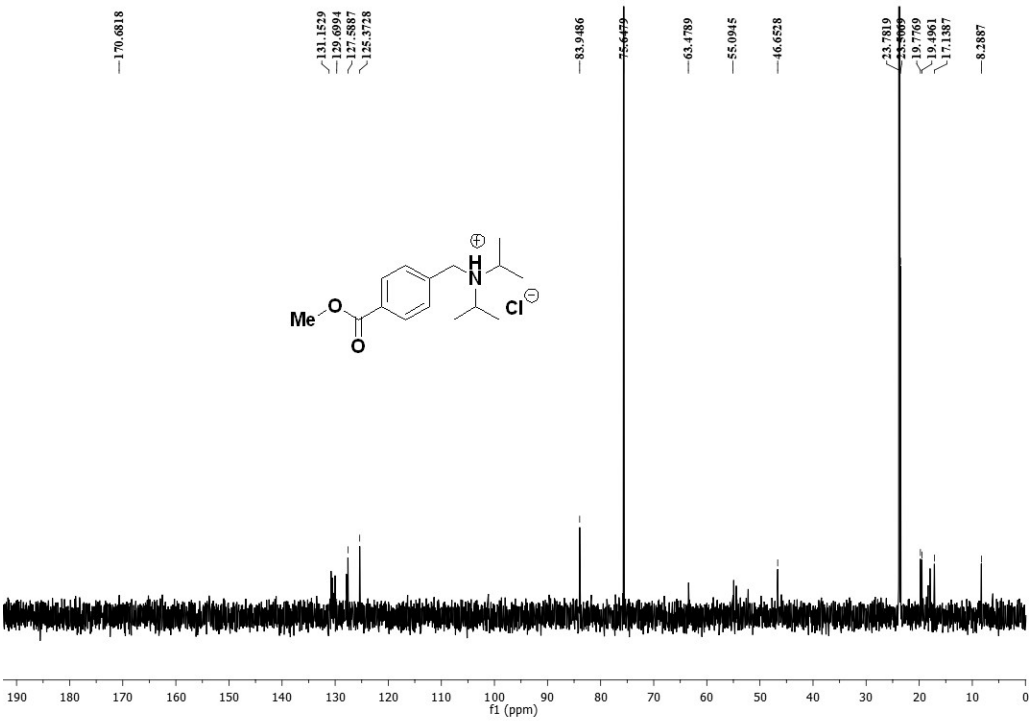


Figure FS109. ^{13}C NMR spectra of compound **(4e)**.

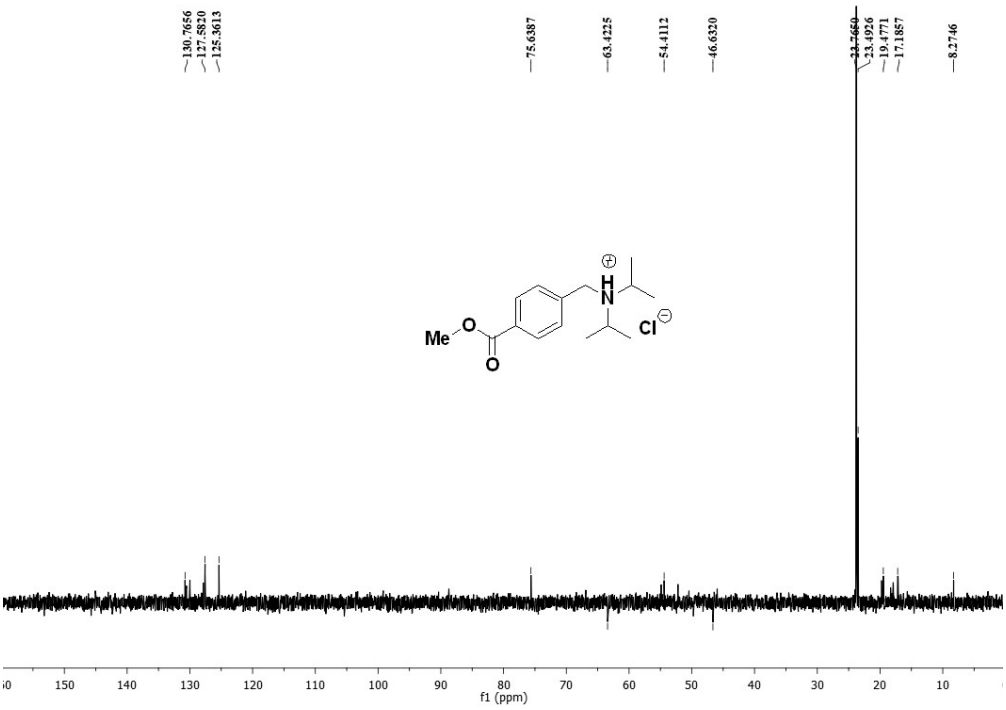


Figure FS110. ^{13}C-DEPT NMR spectra of compound **(4e)**.

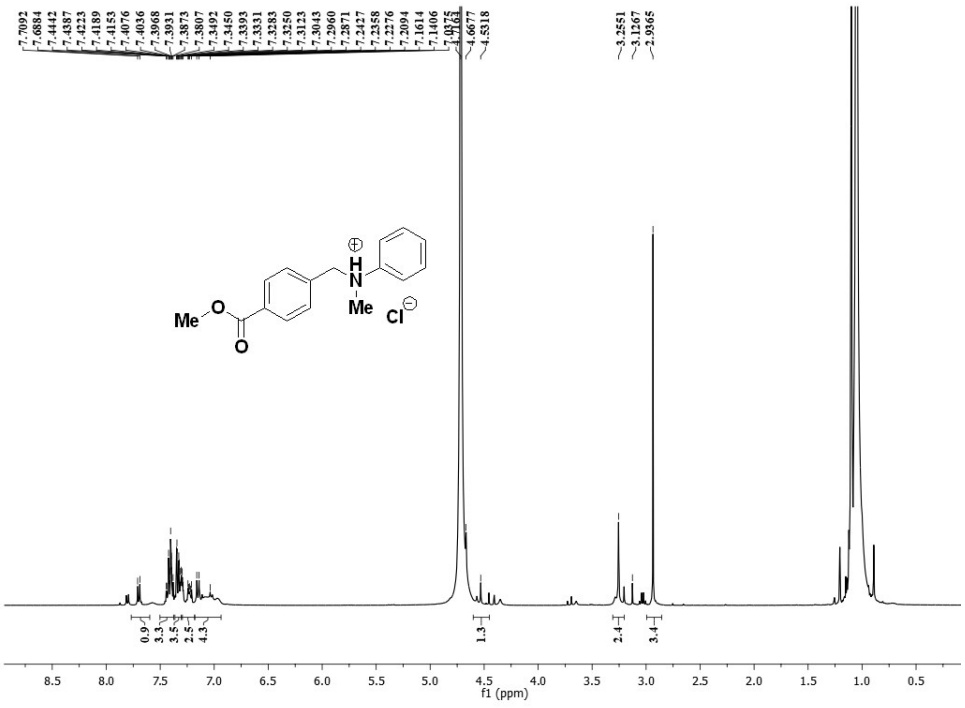


Figure FS111. ^{1}H NMR spectra of compound **(4f)**.

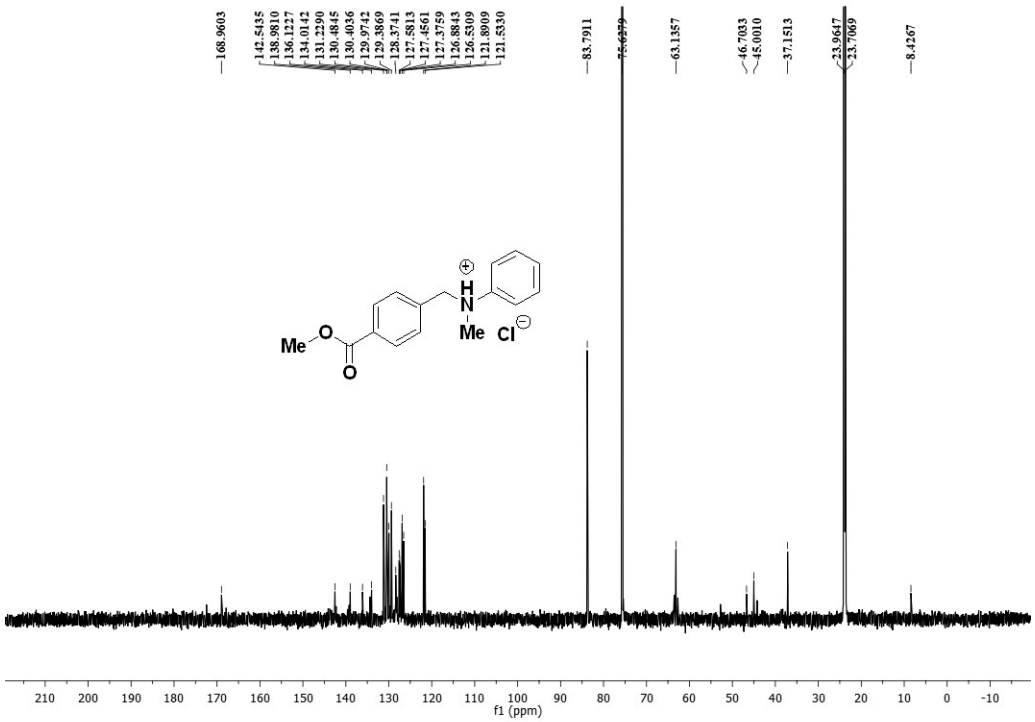


Figure FS112. ^{13}C NMR spectra of compound **(4f)**.

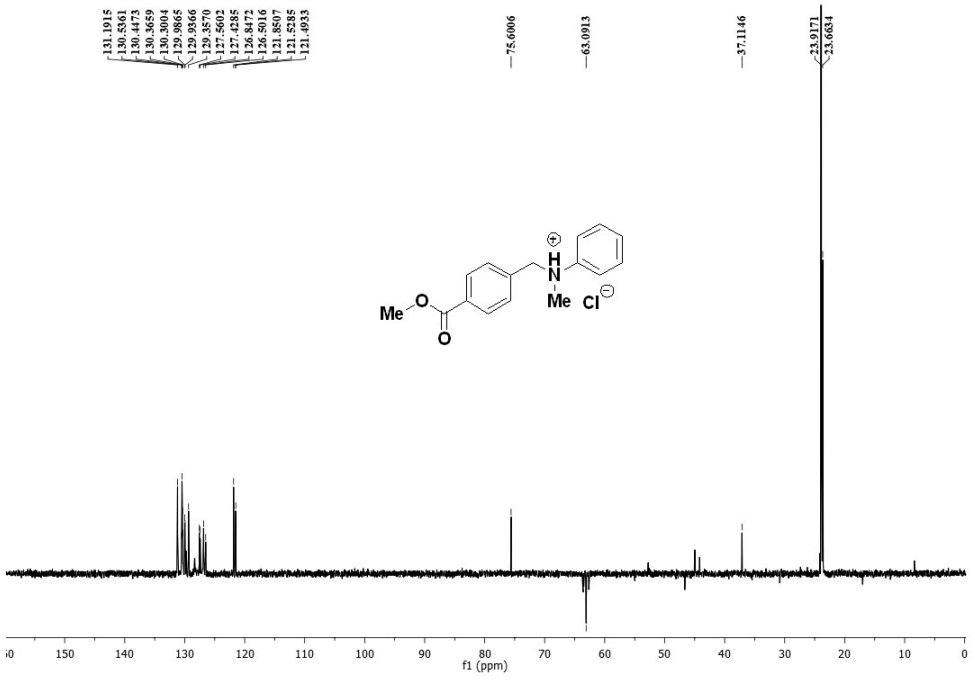


Figure FS113. ^{13}C-DEPT NMR spectra of compound **(4f)**.

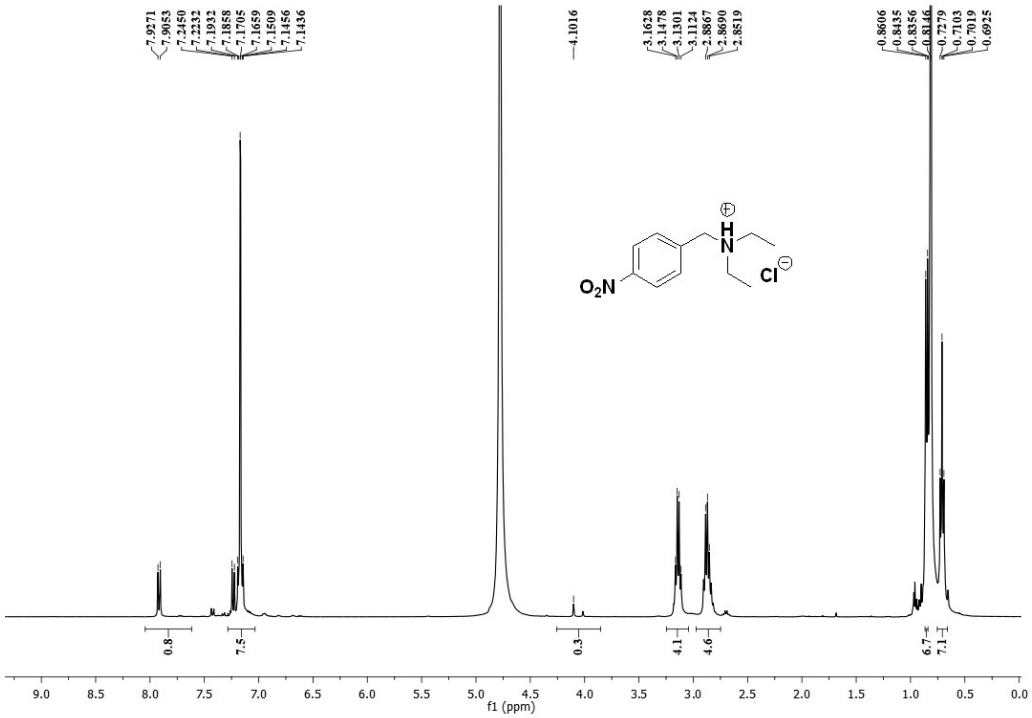


Figure FS114. [1]H NMR spectra of compound **(4g)**.

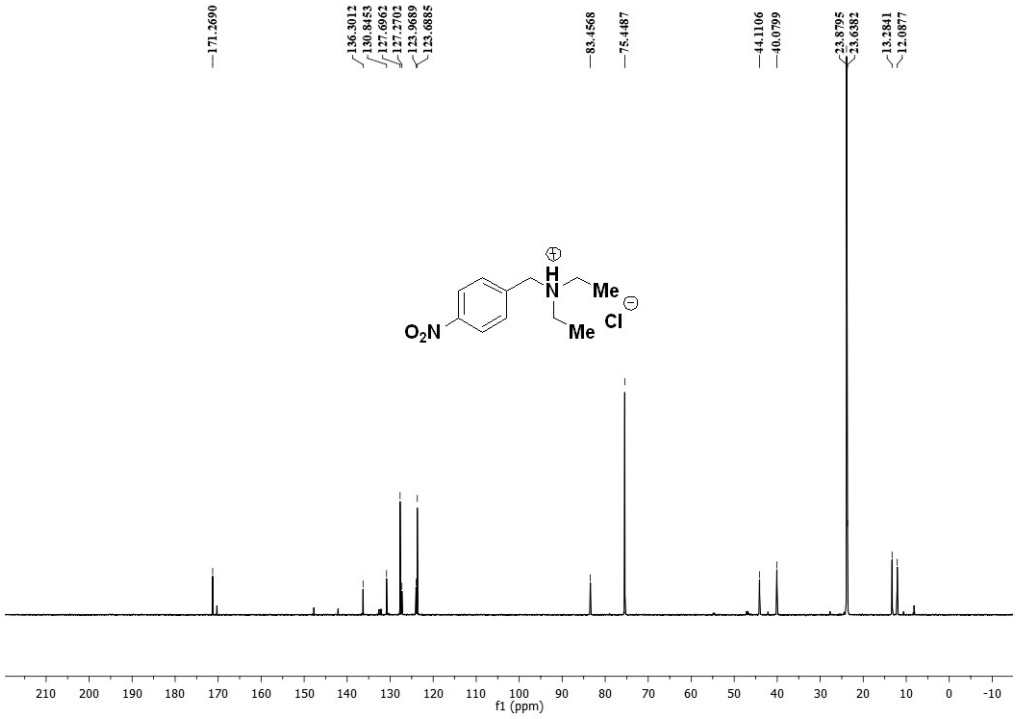


Figure FS115. [13]C NMR spectra of compound **(4g)**.

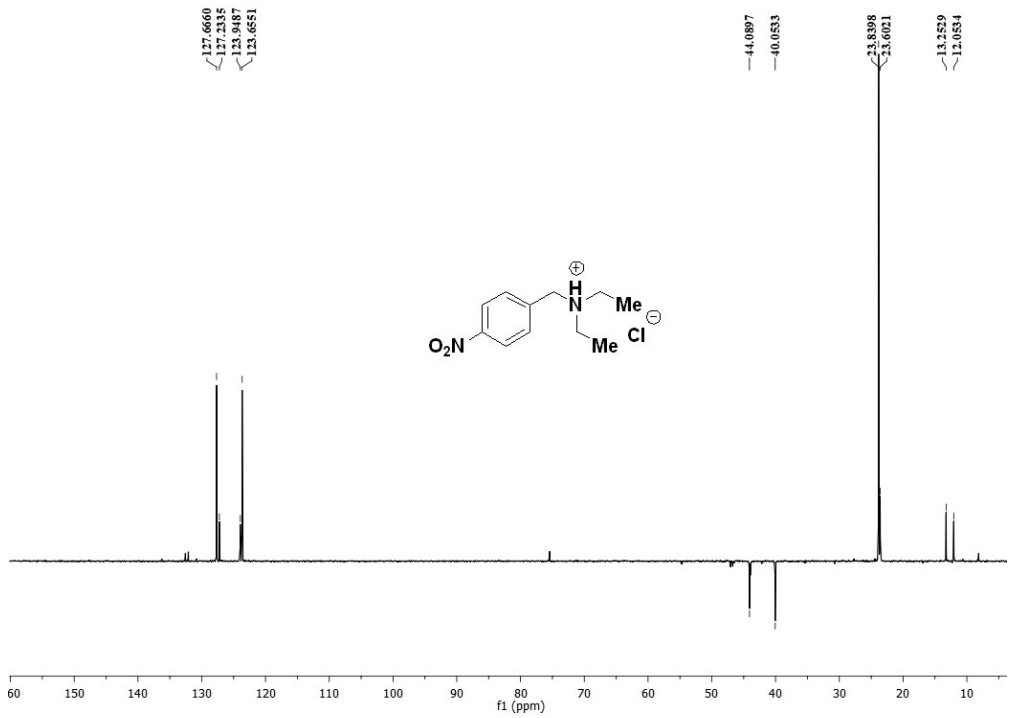


Figure FS116. ^{13}C-DEPT NMR spectra of compound **(4g)**.

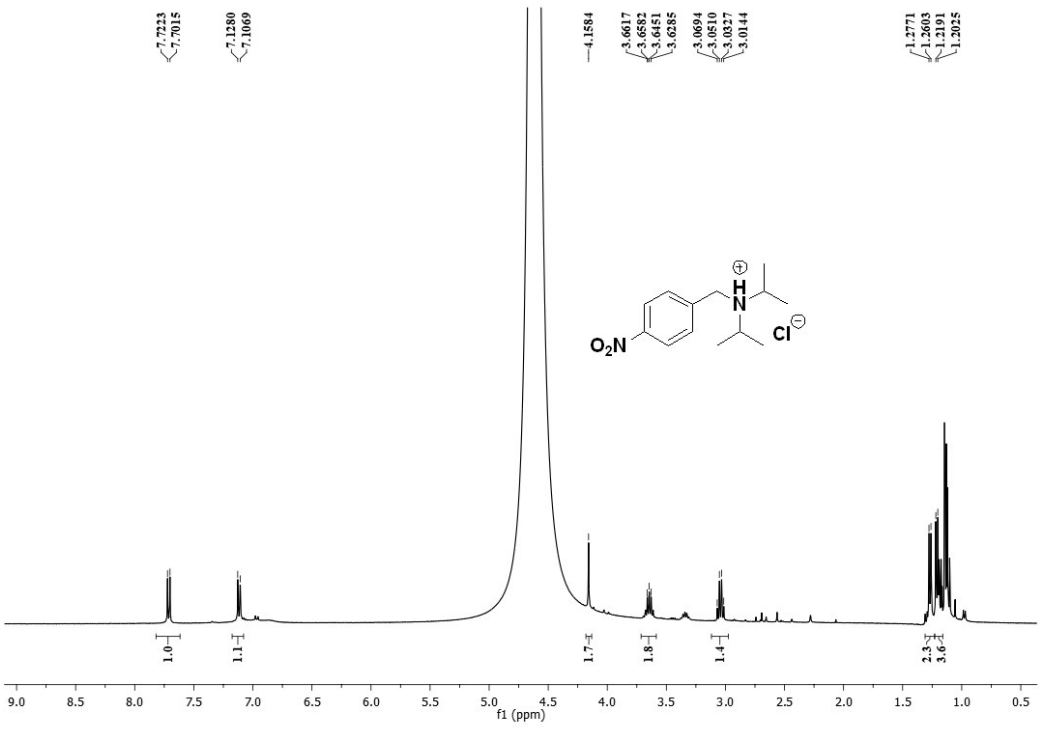


Figure FS117. ^{1}H NMR spectra of compound **(4h)**.

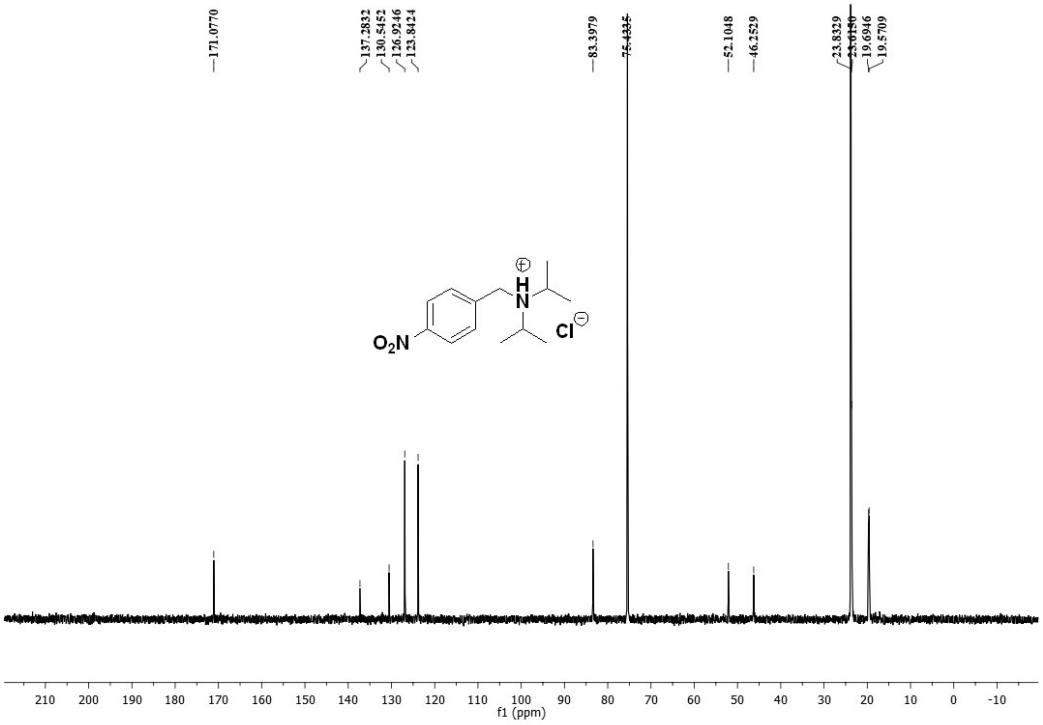


Figure FS118. ^{13}C NMR spectra of compound **(4h)**.

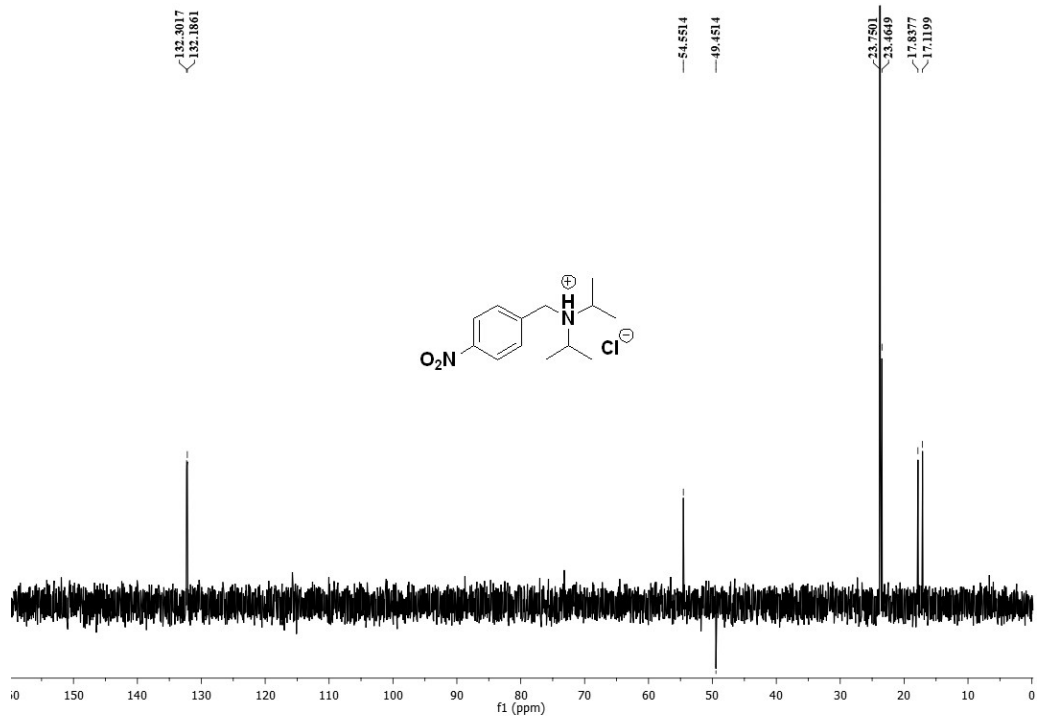


Figure FS119. ^{13}C-DEPT NMR spectra of compound **(4h)**.

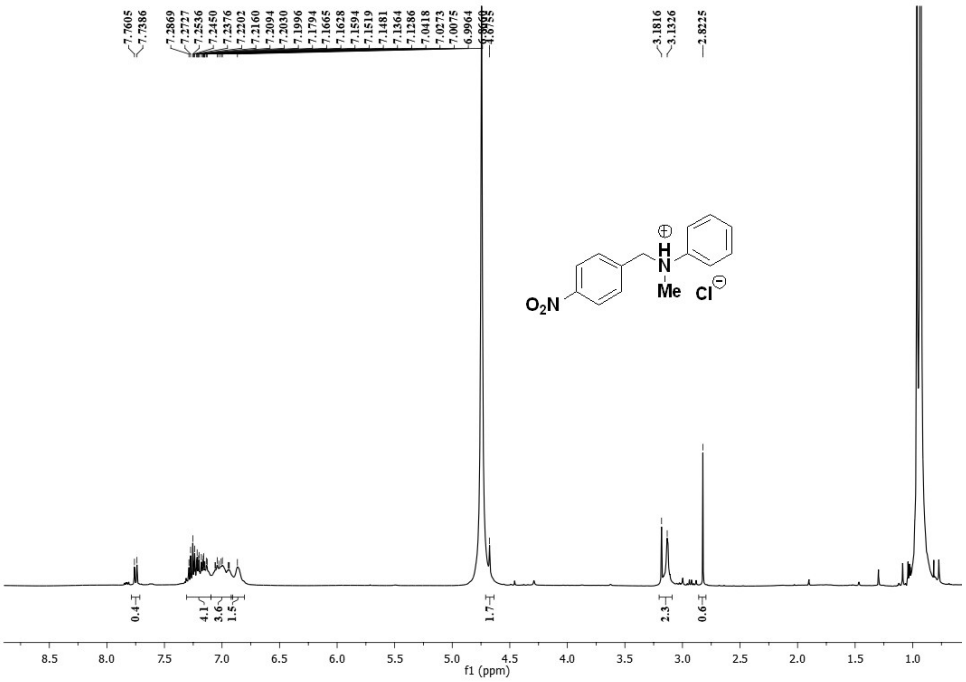


Figure FS120. [1]H NMR spectra of compound **(4i)**.

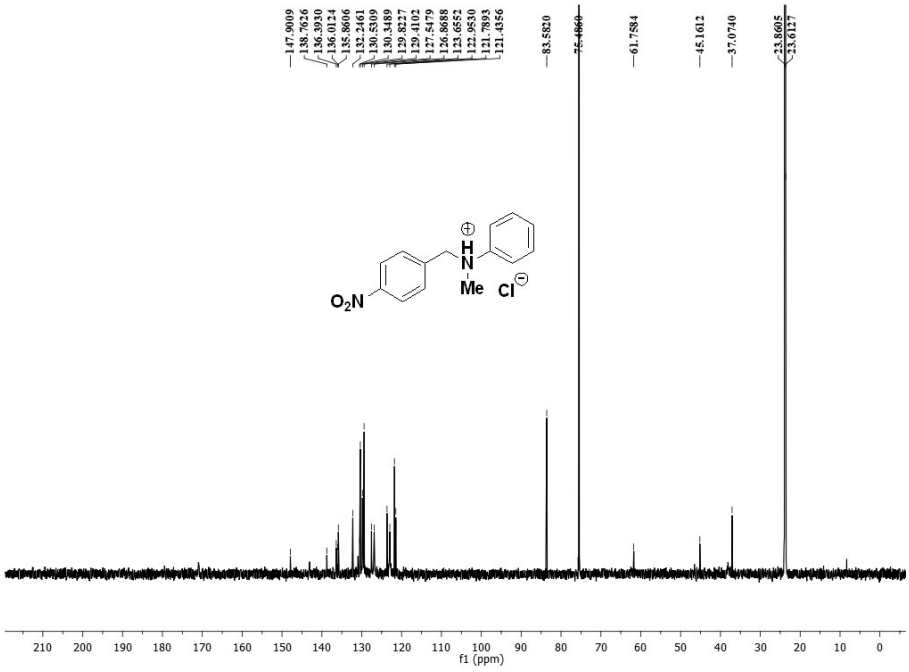


Figure FS121. [13]C NMR spectra of compound **(4i)**.

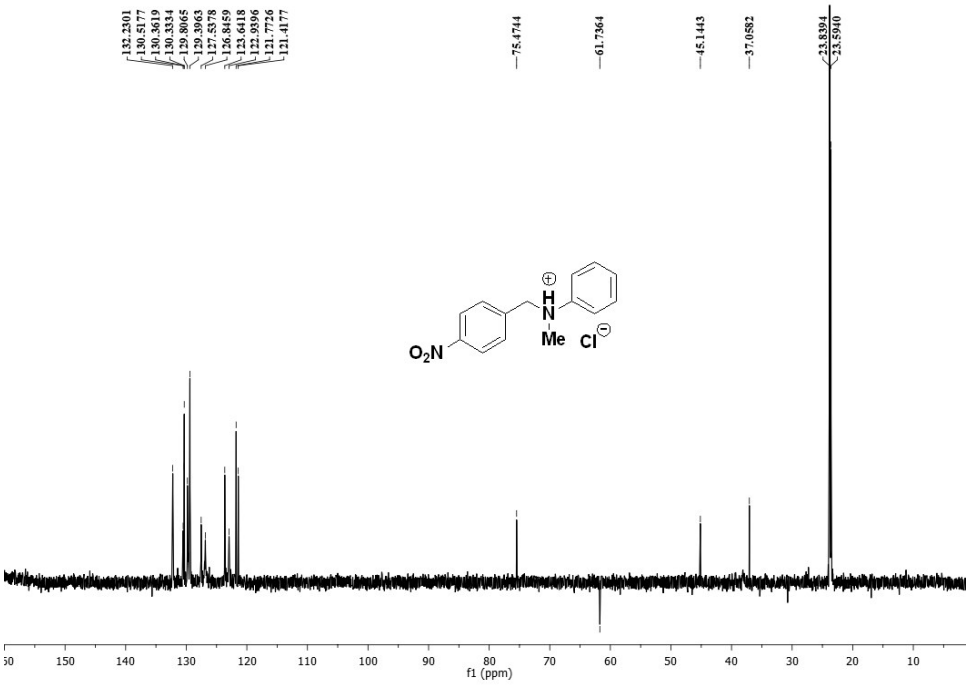


Figure FS122. ^{13}C- DEPT NMR spectra of compound **(4i)**.

Kinetic studies

Typical NMR-Scale Reaction for determining Kinetic Study by ^{1}H-NMR Arrays.

In a glove box, the respective amount of complex **2b** (0.001, 0.0015, 0.002, 0.025, 0.03 M), N,N-dimethyl benzamide (7.4 mg, 0.05 M), HBpin (12.8 mg, 0.1 M), and the internal standard, hexamethylbenzene (8.0 mg, 0.05 M), were added in a vial and after that C_6D_6 (1 mL) was added to these reaction mixture. From this stock solution, 0.5 mL aliquot was taken out and it was added to rubber septum-sealed NMR tube, wrapped with parafilm, and removed from the box. The solution was set in the NMR tube at 60^{o}C. After that, the tube was shaken and reinserted into the instrument again and scanning was begun. Single (^{1}H NMR) scans were collected at regular intervals. Substrate and/or product concentrations were determined relative to the intensity of the internal standard resonance plotted versus time.

Kinetic Analysis. Kinetic analysis of the NMR-scale reactions described above was carried out by collecting multiple (>10) data points early in the reaction (<20% conversion). Under these conditions, the reaction can be approximated as pseudo-zero-order with respect to the substrate

concentrations. The product concentration was measured from the area of the $C_6H_4CH_2NMe_2$ peak formed with respect to their starting material peak standardized to the methyl peak area of the C_6Me_6 internal standard.

General Procedure for Kinetic NMR Experiments.

As expected, plots of $\ln[PhCONMe_2]/\ln[PhCONMe_2]_0$ vs. time for a wide range of catalyst $[Ph_2P(Se)NC_9H_6NAl(Me)_2]$ are linear (Figure FS120, Table S2). A plot of $\boldsymbol{k_{obs}}$ vs. $[Ph_2P(Se)NC_9H_6NAl(Me)_2]$ (Figure FS121, Table S3) is also linear, with slope 0.8 which indicate the rate law of the reaction follow first order dependence with respect to catalyst $[Ph_2P(Se)NC_9H_6NAl(Me)_2]$. The same experiment also conducted varying wide range of concentration of $[PhCONMe_2]$/ (0.03-0.07 M) and HBpin (0.1-0.5 M) which were also linear and follows first-order dependence with respect to $[PhCONMe_2]$ and HBpin (Figure FS123, Table S4, Figure FS125, Table S4).

Table TS2. Table for formation rates of $C_6H_4CH_2NMe_2$ vs time at various concentration of catalyst $[Ph_2P(Se)NC_9H_6NAl(Me)_2]$ (**2b**).

S.No	**$[PhCONMe_2]$/ Cat**	Time (h:m)	Conversion[a] (%)	**$[PhCONMe_2]^t$**	**$\ln([PhCONMe_2]_t/[PhCONMe_2]_0)$**
1	100/2	00.00	0	0	0
2	100/2	01.00	23	0.0385	-.261
3	100/2	02.00	35	0.0325	-.430
4	100/2	03.00	44	0.028	-.579
5	100/2	04.00	52	0.024	-.734
6	100/2	05.00	61	0.0195	-0.942
7	100/2	06.00	70	0.015	-1.20
8	100/2	07.00	73	0.0135	-1.31
9	100/3	00.00	0	0	0
10	100/3	01.00	25	0.0379	-0.277
11	100/3	02.00	42	0.029	-0.534
12	100/3	03.00	55	0.0227	-0.788
13	100/3	04.00	64	0.0182	-1.01
14	100/3	05.00	72	0.0139	-1.28
15	100/3	06.00	81	0.00105	-1.56
16	100/3	07.00	88	0.0066	-2.02
17	100/4	00.00	0	0	0
18	100/4	01.00	27.5	0.0362	-0.322

19	100/4	02.00	46	0.027	-0.616
20	100/4	03.00	62.5	0.01875	-0.975
21	100/4	04.00	70	0.015	-1.20
22	100/4	05.00	80	0.010	-1.61
23	100/4	06.00	87	0.0065	-2.04
24	100/4	07.00	91	0.0045	-2.41
25	100/5	00.00	0	0	0
26	100/5	01.00	29	0.0355	-0.342
27	100/5	02.00	48	0.026	-0.654
28	100/5	03.00	64	0.018	-1.02
29	100/5	04.00	74	0.013	-1.35
30	100/5	05.00	84	0.008	-1.83
31	100/5	06.00	89.5	0.00525	-2.25
32	100/5	07.00	93	0.0035	-2.66
33	100/6	00.00	0	0	0
34	100/6	01.00	24	0.0379	-0.473
35	100/6	02.00	60	0.0197	-0.93
36	100/6	03.00	73	0.0136	-1.3
37	100/6	04.00	81	0.0095	-1.66
38	100/6	05.00	88	0.0058	-2.15
39	100/6	06.00	93	0.0035	-2.65
40	100/6	07.00	95	0.0024	-2.98

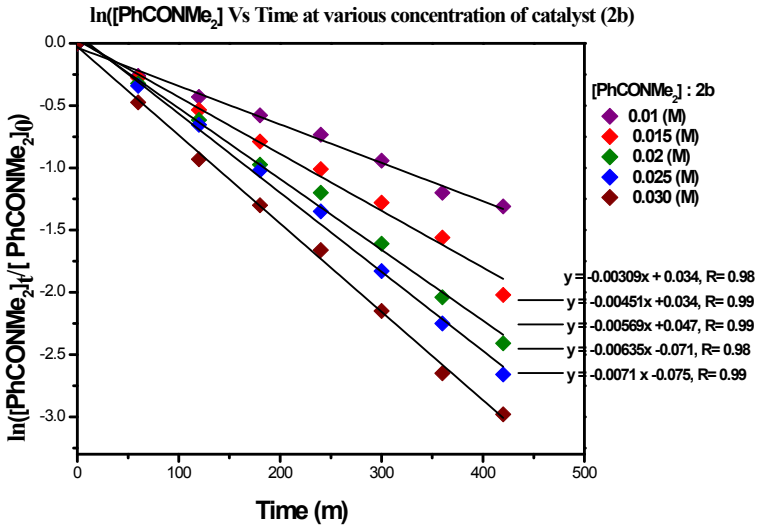


Figure FS123. Plots of ln[$PhCONMe_2$] versus time for the Aluminium complex (**2b**) catalysed reaction of $PhCONMe_2$ and HBpin at 60°C in C_6D_6 (0.5 ML). The catalyst concentration was varied from 1 mM to 3 mM.

Table TS3. Table for formation rates of $C_6H_4CH_2NMe_2$ vs $[Ph_2P(Se)NC_9H_6NAl(Me)_2]$ for the reaction of $[PhCONMe_2]$ with [HBpin] in presence of catalyst (**1**) $[Ph_2P(Se)NC_9H_6NAl(Me)_2]$. Reaction conditions: [HBpin] = 0.1 M and $[PhCONMe_2]$ = 0.05 M, $[Ph_2P(Se)NC_9H_6NAl(Me)_2]$ = [1 mM to 3 mM] in C_6D_6 (0.5 mL).

S.NO.	$[Ph_2P(Se)NC_9H_6NAl(Me)_2]$	k_{obs}
1	0.001	0.00309
2	0.0015	0.0045
3	0.002	0.00569
4	0.0025	0.00635
5	0.003	0.0071

S.NO.	$\ln[Ph_2P(Se)NC_9H_6NAl(Me)_2]$	$\ln k_{obs}$
1	-6.90	-5.77
2	-6.50	-5.4
3	-6.21	-5.16
4	-5.99	-5.05
5	-5.81	-4.94

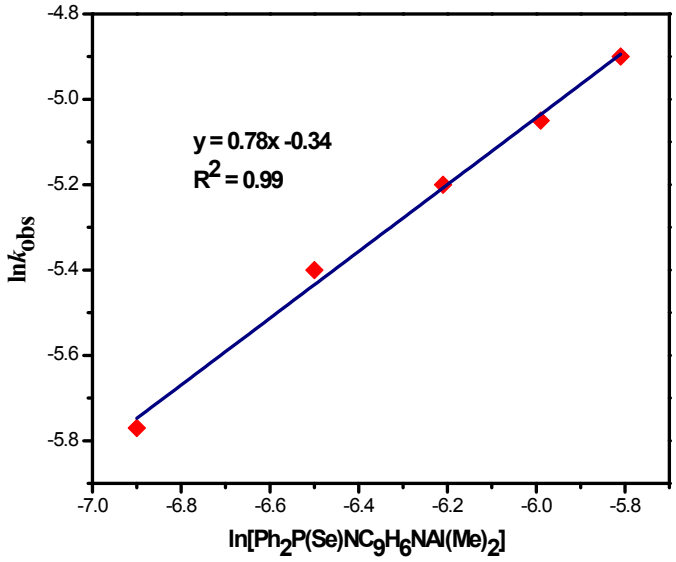


Figure FS124. Kinetics plots of $\ln k_{obs}$ vs $\ln[Ph_2P(Se)NC_9H_6NAl(Me)_2]$ for the reaction of $[PhCONMe_2]$ with [HBpin] in presence of catalyst (**2b**) $[Ph_2P(Se)NC_9H_6NAl(Me)_2]$ Reaction conditions: [HBpin] = 0.1 M and $[PhCONMe_2]$ = 0.05 M, $[Ph_2P(Se)NC_9H_6NAl(Me)_2]$] = [1 mM to 3 mM] in C_6D_6 (0.4 mL).

Table TS4. Table for Formation rates of $C_6H_4CH_2NMe_2$ versus the ratios of $PhCONMe_2$ / HBPin in C_6D_6 at 298 K, indicating a linear dependence. Conditions: $Ph_2P(Se)NC_9H_6NAl(Me)_2]$ = 0.0020(M), [HBPin] = 0.1 M and $[PhCONMe_2]$ [0.03 M to 0.07 M] in C_6D_6 (0.4 mL).

S.NO.	$[PhCONMe_2]$ x 10^{-1}	K_{obs}
1	0.3	0.0094
2	0.4	0.0151
3	0.5	0.0185
4	0.6	0.0215
5	0.7	0.0262

S.NO.	$\ln[PhCONMe_2]$	$\ln k_{obs}$
1	-3.51	-4.65
2	-3.21	-4.19
3	-2.99	-3.98
4	-2.81	-3.84
5	-2.65	-3.63

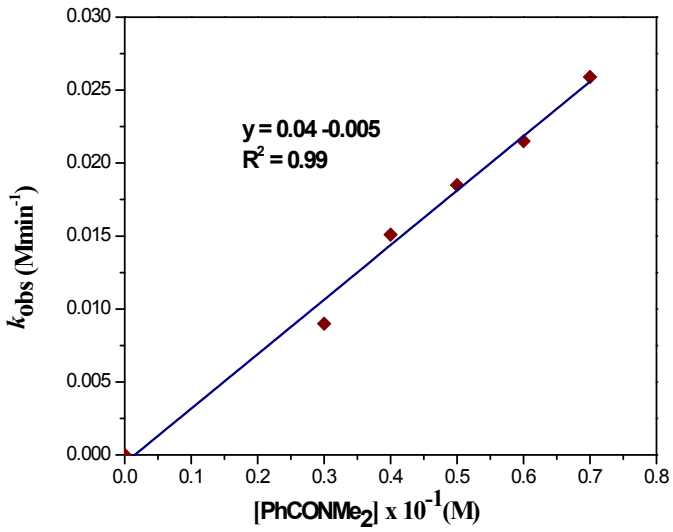


Figure FS125. Kinetics plots of k_{obs} vs $[PhCONMe_2]$ for the reaction of $[PhCONMe_2]$ with [HBpin] in presence of catalyst (**2b**) $[Ph_2P(Se)NC_9H_6NAl(Me)_2]$. Reaction conditions: $Ph_2P(Se)NC_9H_6NAl(Me)_2]$ = 0.002 (M), [HBpin] = 0.1 M and $[PhCONMe_2]$ [0.003 M to 0.007 M] in C_6D_6 (0.4 mL).

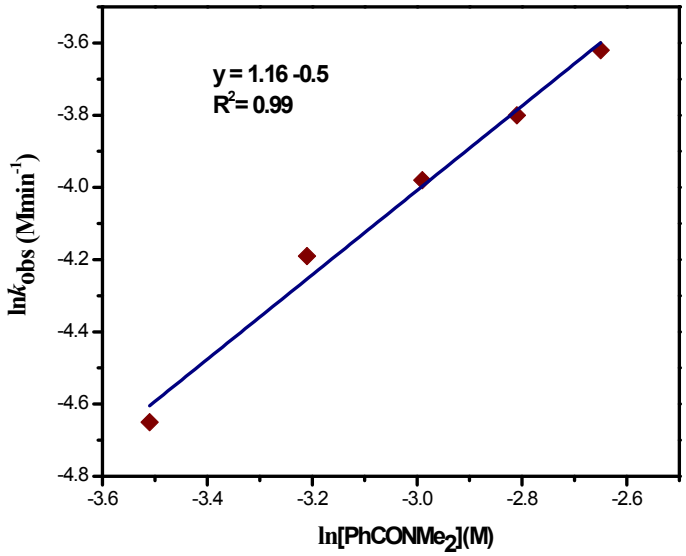


Figure FS126. Kinetics plots of $\ln k_{obs}$ vs $\ln[PhCONMe_2]$ for the reaction of $[PhCONMe_2]$ with [HBpin] in presence of catalyst (**2b**) $[Ph_2P(Se)NC_9H_6NAl(Me)_2]$. Reaction conditions: $Ph_2P(Se)NC_9H_6NAl(Me)_2]$ = 0.002 (M), [HBpin] = 0.1 M and $[PhCONMe_2]$ [0.03 M to 0.07 M] in C_6D_6 (0.4 mL).

Table TS5. Table for Formation rates of $C_6H_4CH_2NMe_2$ versus the ratios of $PhCONMe_2$ / HBpin in C_6D_6 at 60°C, indicating a linear dependence. Conditions: $[Ph_2P(Se)NC_9H_6NAl(Me)_2]$ = 0.002(M), $[PhCONMe_2]$ = 0.05 M and [HBpin] [0.1 M to 0.5 M] in C_6D_6 (0.4 mL).

S.NO.	[HBpin]	k_{obs}
1	0.1	0.011
2	0.2	0.0141
3	0.3	0.0195
4	0.4	0.0225
5	0.5	0.0249

S.NO.	ln[HBpin]	$ln\ k_{obs}$
1	-2.30	-4.51
2	-1.61	-4.2
3	-1.203	-3.94
4	-0.916	-3.79
5	-0.693	-3.69

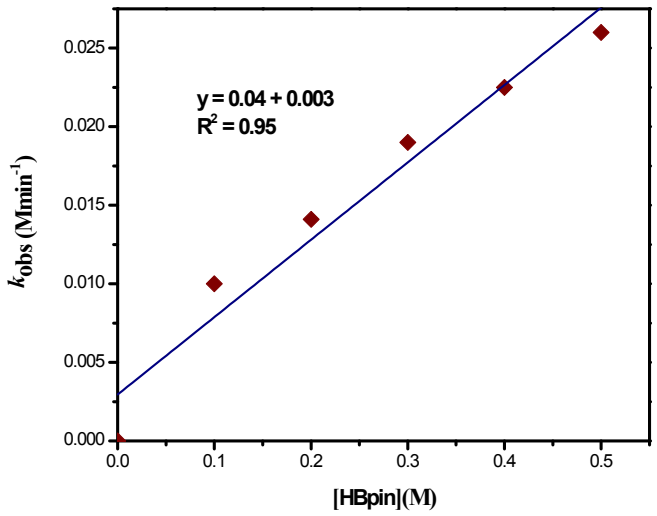


Figure FS127. Kinetics plots of k_{obs} vs [HBpin] for the reaction of [$PhCONMe_2$] with [HBpin] in presence of catalyst (**2b**) [$Ph_2P(Se)NC_9H_6NAl(Me)_2$]. Reaction conditions: $Ph_2P(Se)NC_9H_6NAl(Me)_2$] = 0.02 (M), [$PhCONMe_2$] = 0.05 M and [HBpin] = 0.1 M to 0.5 M] in C_6D_6 (0.4 mL).

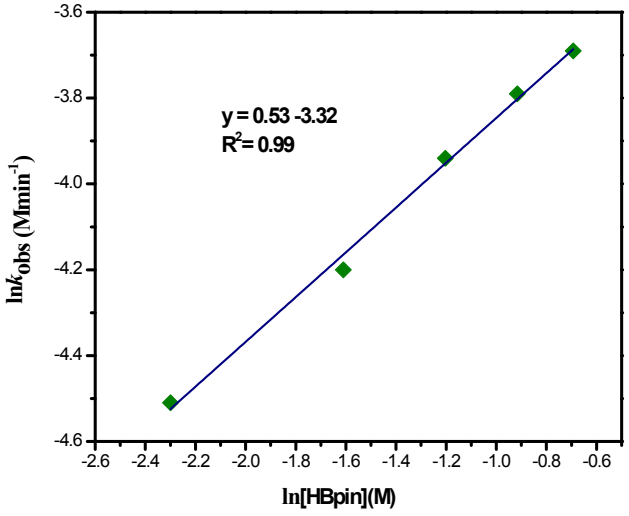


Figure FS128. Kinetics plots of lnk_{obs} vs ln[HBpin] for the reaction of [$PhCONMe_2$] with [HBpin] in presence of catalyst (**2b**) [$Ph_2P(Se)NC_9H_6NAl(Me)_2$]. Reaction conditions: [$Ph_2P(Se)NC_9H_6NAl(Me)_2$]. = 0.002 (M), [$PhCONMe_2$] = 0.05 M and [HBpin] = 0.1 M to 0.5 M] in C_6D_6 (0.4 mL).

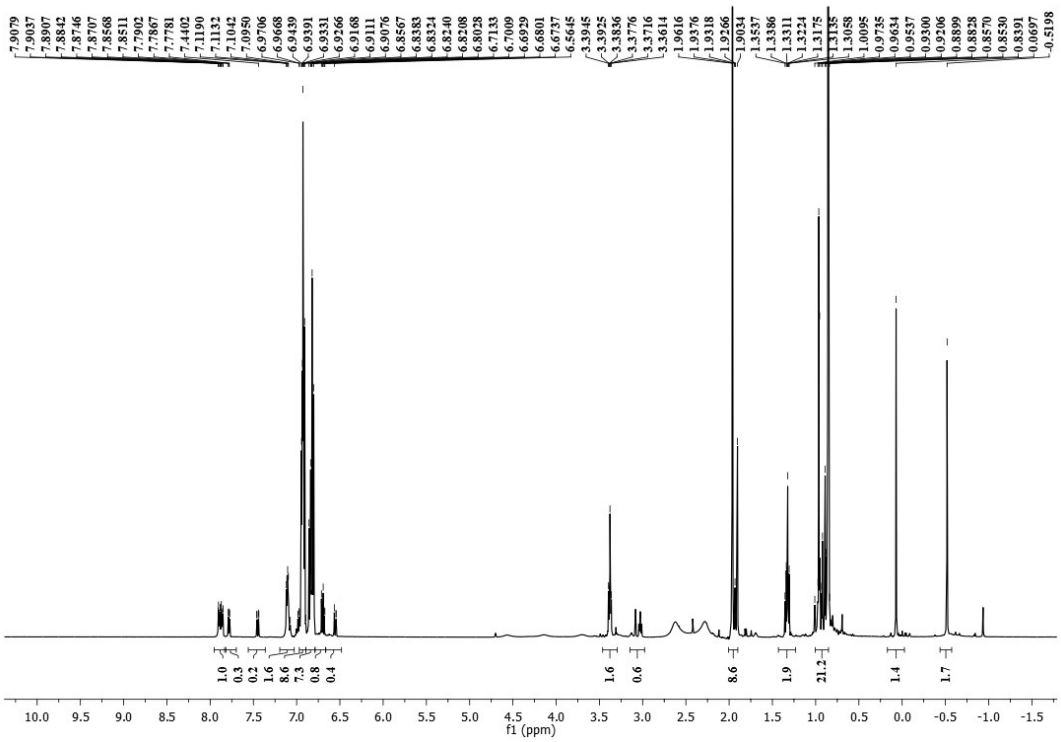


Figure FS129 : ^{1}H NMR spectrum of N, N dimethylbenzamide + HBpin + aluminium complex (**2a**) (1:1:1) reaction mixture in Tol-d_8 solvent.

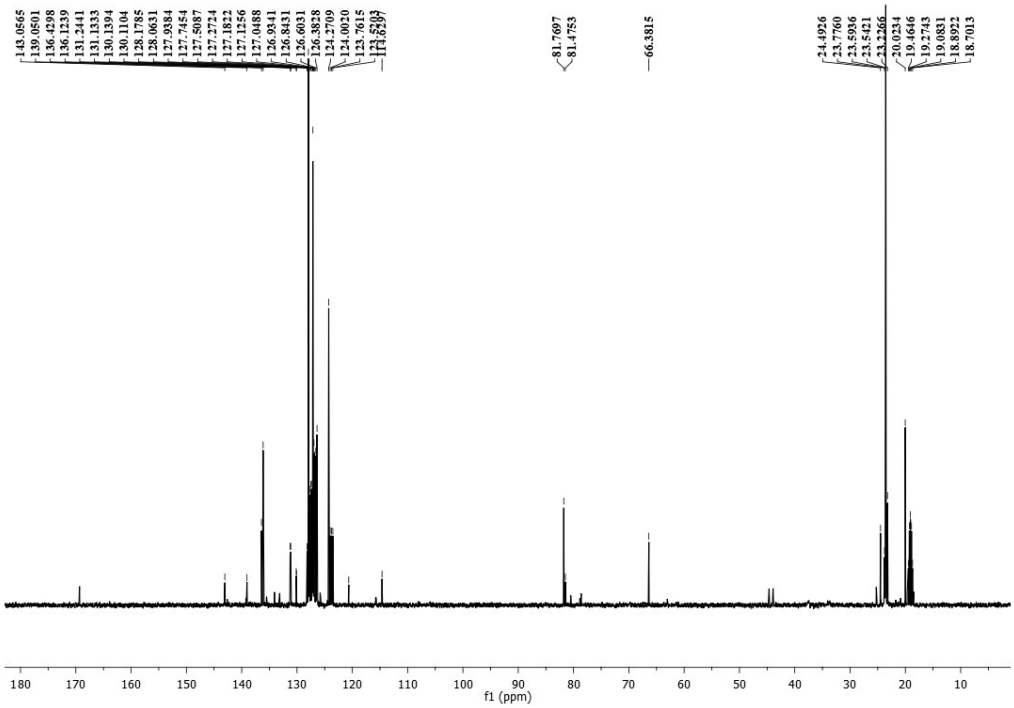


Figure FS130. ^{13}C NMR spectrum of N, N dimethylbenzamide + HBpin + aluminium complex (**2a**) (1:1:1) reaction mixture in Tol-d_8 solvent.

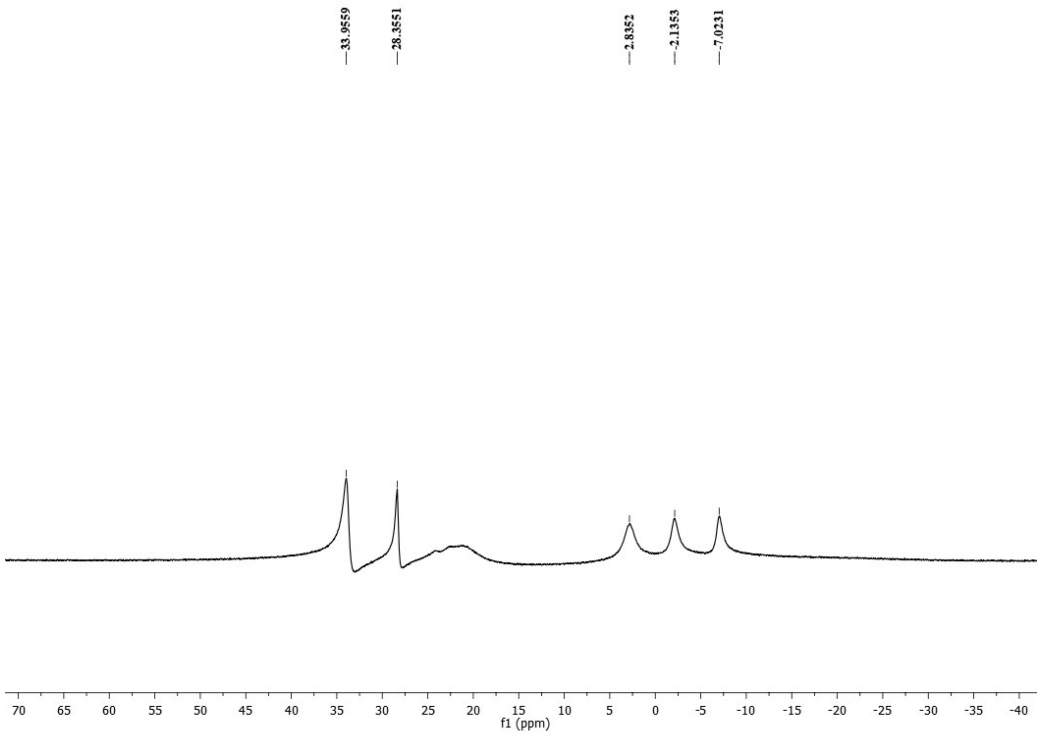


Figure FS131. ^{11}B NMR spectrum of N, N dimethylbenzamide + HBpin + aluminium complex (**2a**) (1:1:1) reaction mixture in Tol-d_8 solvent.

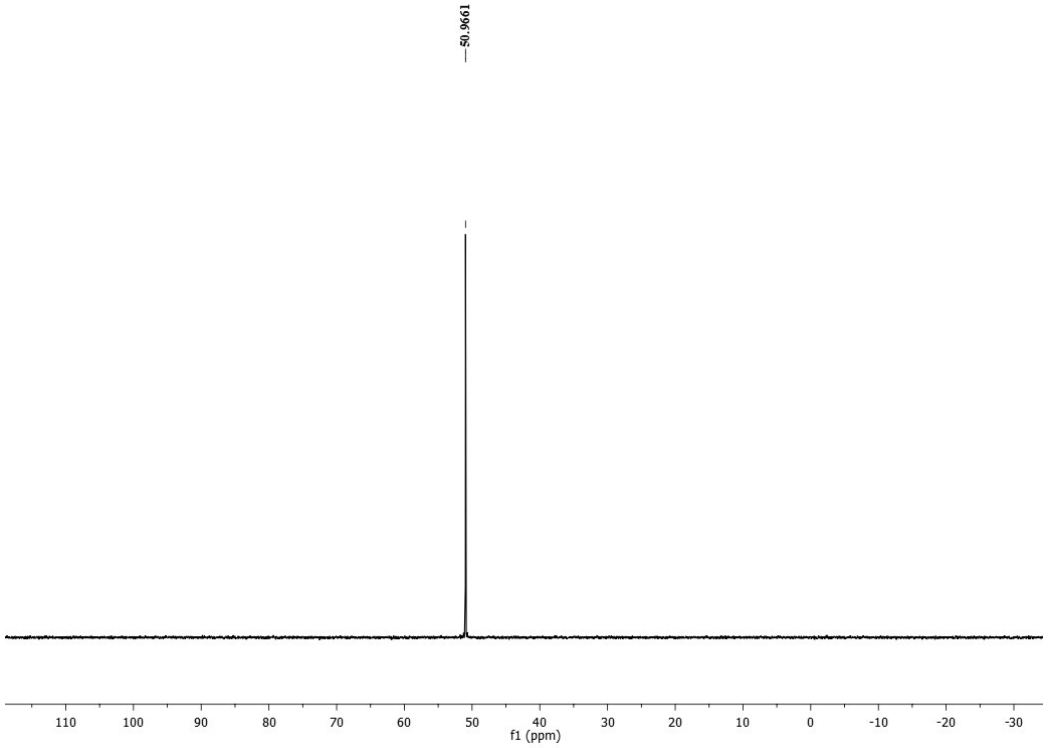


Figure FS132. ^{31}P NMR spectrum of N, N dimethylbenzamide + HBpin + aluminium complex (**2a**) (1:1:1) reaction mixture in Tol-d_8 solvent.

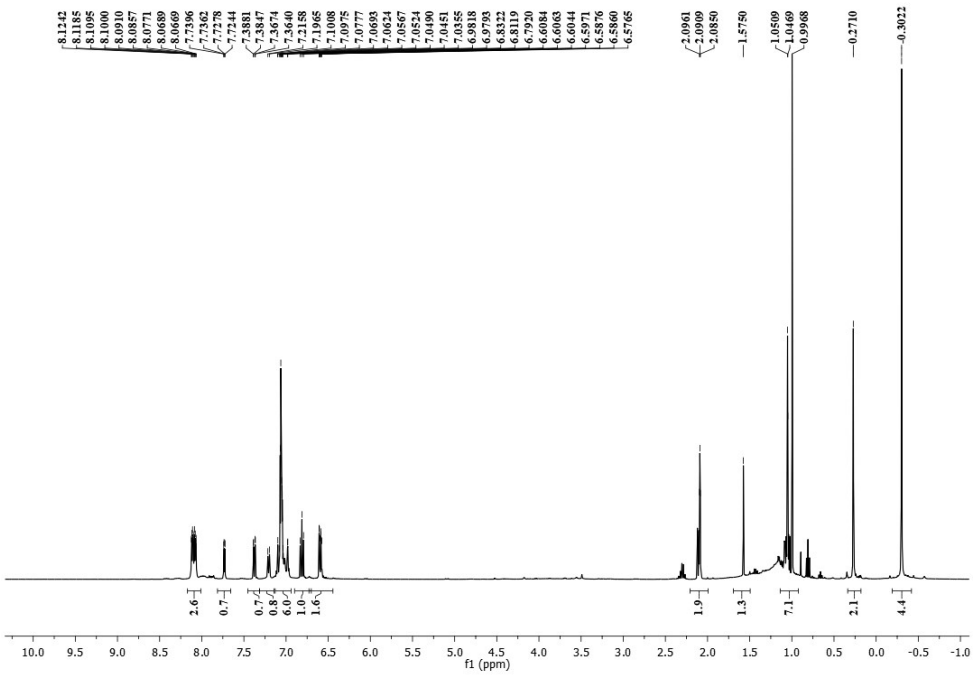


Figure FS133. ^{1}H NMR spectrum of aluminium complex (**2a**) and HBpin (1:1) reaction mixture in Tol-d_8 solvent.

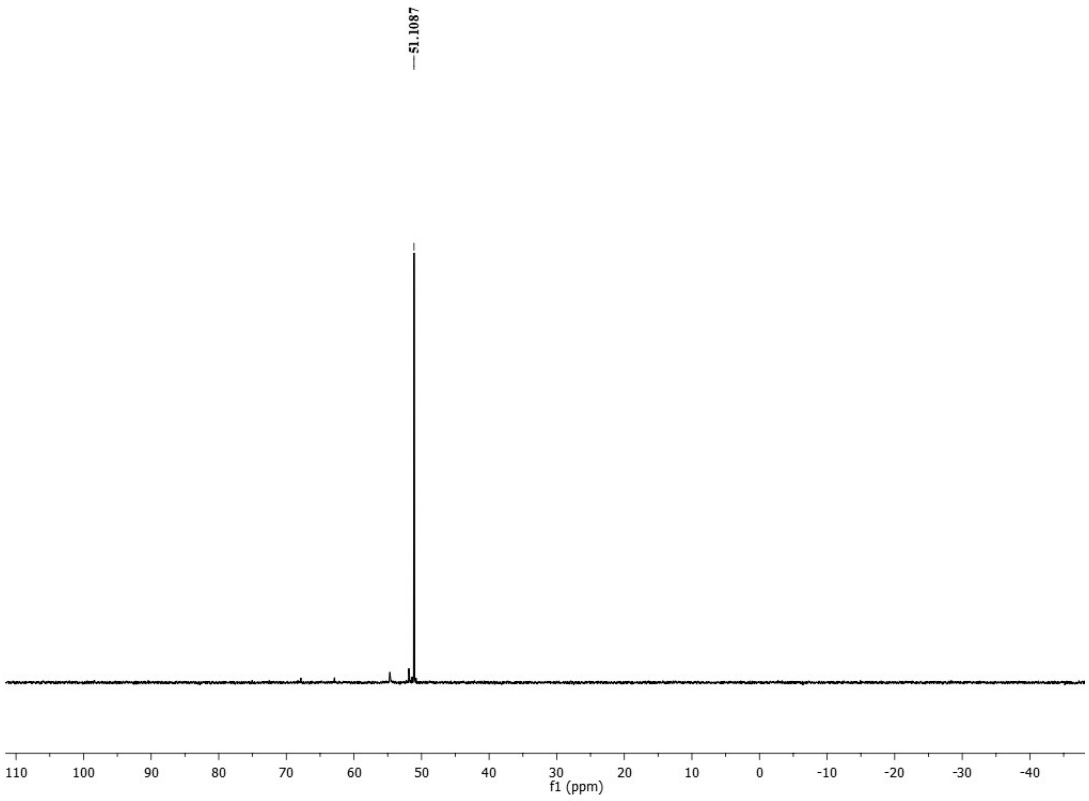


Figure FS134. ^{31}P NMR spectrum of aluminium complex (**2a**) and HBpin (1:1) reaction mixture in Tol-d_8 solvent.

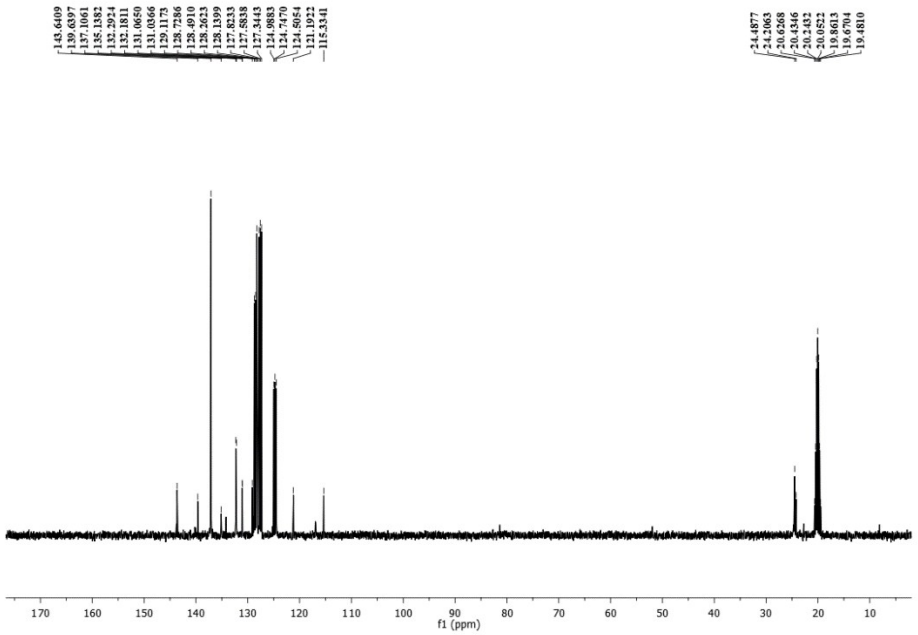


Figure FS135. ^{13}C NMR spectrum of aluminium complex (**2a**) and HBpin (1:1) reaction mixture in Tol-d_8 solvent.

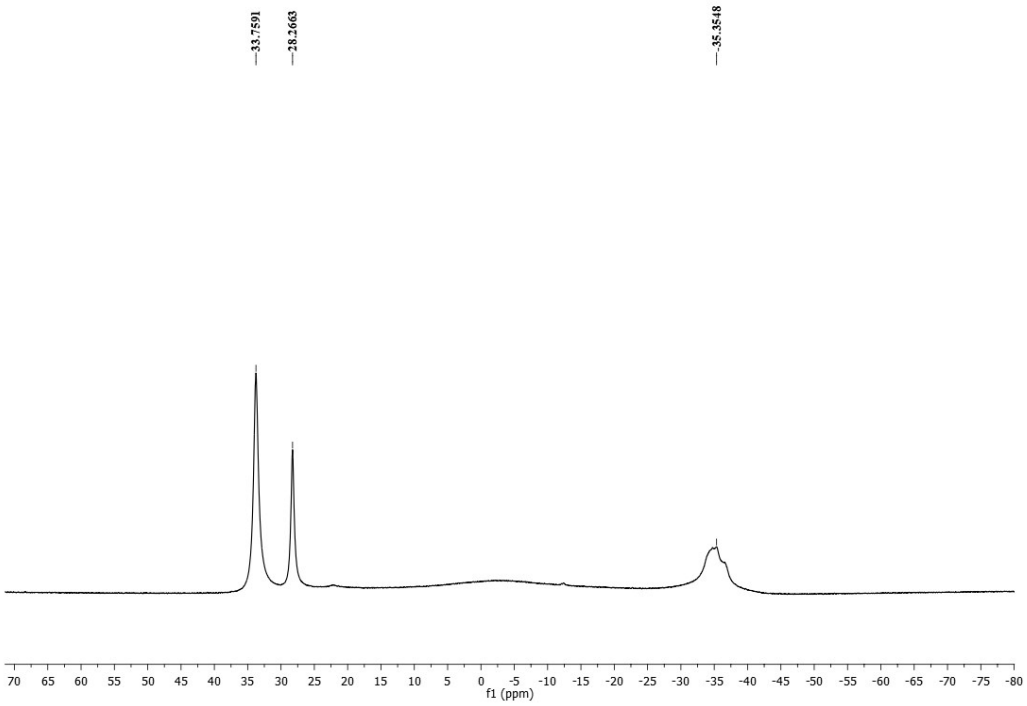


Figure FS136. ^{11}B NMR spectrum of aluminium complex (**2a**) and HBpin (1:1) reaction mixture in Tol-d_8 solvent.

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