Electronic Supplementary Material (ESI) for Chemical Science.
This journal is © The Royal Society of Chemistry 2020

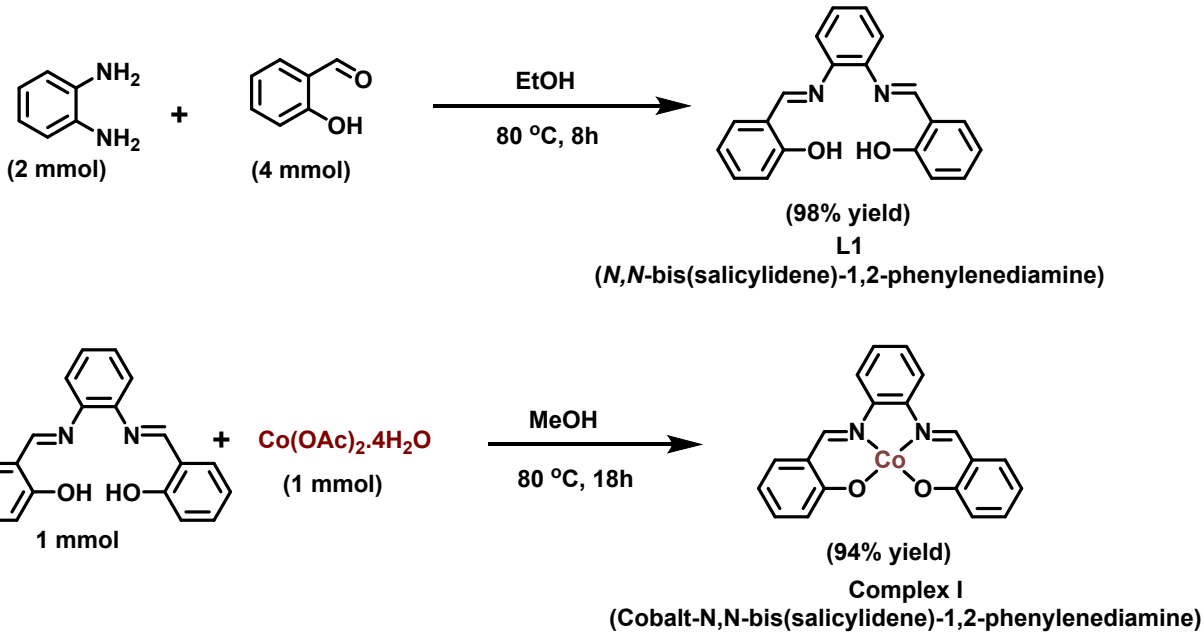
Supporting Information

Ultra-small Cobalt Nanoparticles from Molecularly-defined Co-Salen Complexes for Catalytic Synthesis of Amines

Thirusangumurugan Senthamarai, Vishwas G. Chandrashekhar, Manoj B. Gawande, Narayana V. Kalevaru, Radek Zbořil, Paul C. J. Kamer, Rajenahally V. Jagadeesh,* and Matthias Beller*

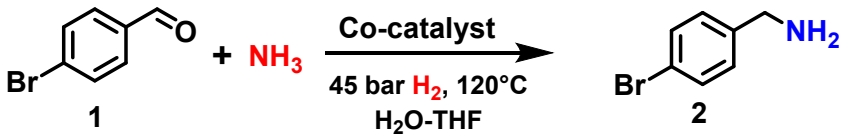
*Corresponding authors e-mail: jagadeesh.rajenahally@catalysis.de; matthias.beller@catalysis.de

Preparation of Co-salen complexes (ref 13)



Scheme S1. Preparation of salen ligand and Co-salen complex.

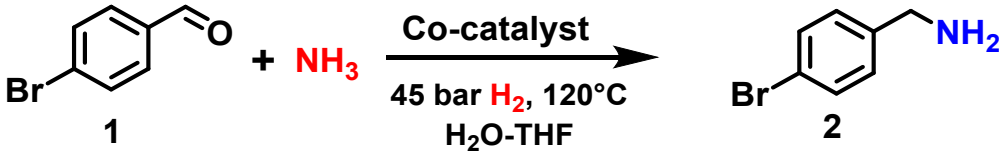
Table S1. Cobalt catalyzed reductive amination of benzaldehyde with ammonia in presence of molecular hydrogen: activity of different catalysts

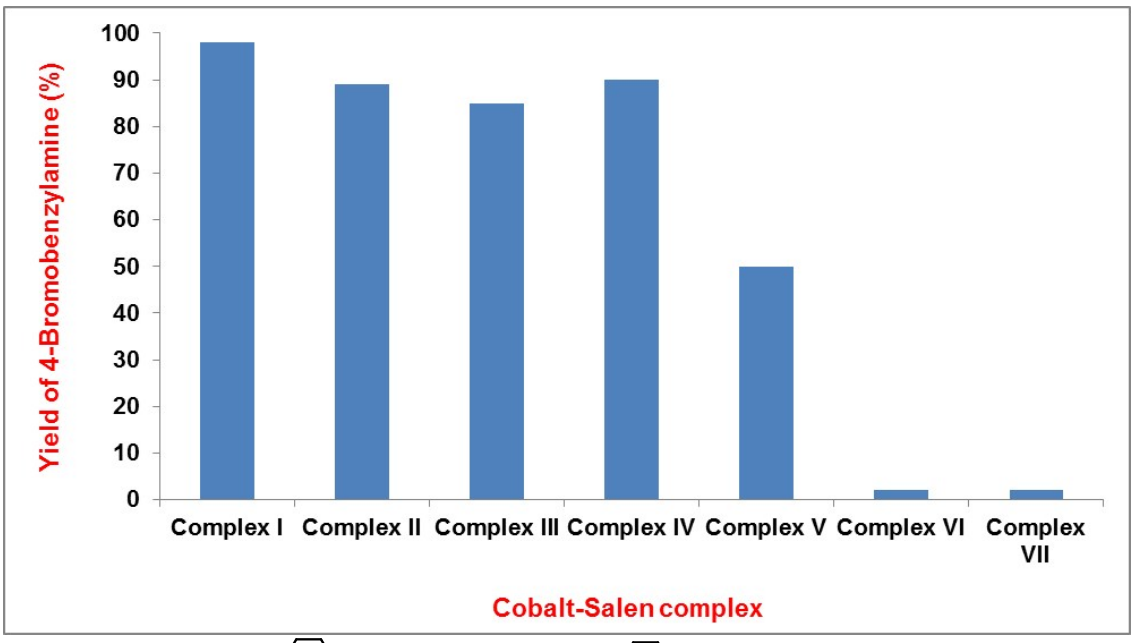


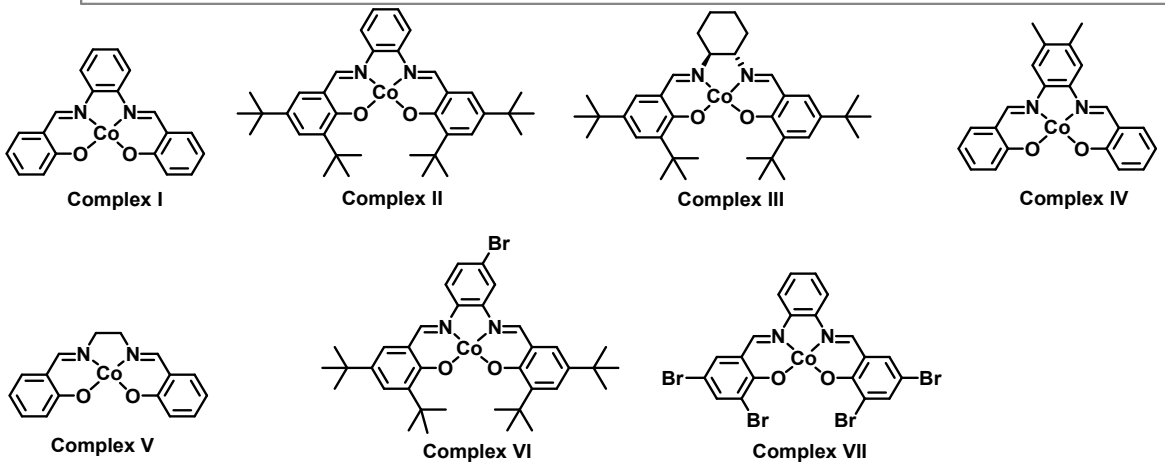
Entry	Catalyst	Yield of 4-bromobenzylamine
1	Complex **I** + Carbon (40 mg)	<1
2	Complex **I** + SiO_2 (40 mg)	<1
3	Immobilization of complex **I** on carbon and pyrolysis at 800 °C under Ar for 2h	40
4	Immobilization of complex **I** on SiO_2 and pyrolysis at 800 °C under Ar for 2h	50
5	Cobalt nanoparticles prepared by reported method (ref 11)	<1
6	Cobalt nanoparticles prepared by reported method (ref 11)	<1

Reaction conditions: 0.5 mmol 4-bromobenzaldehyde, 6 mol% Co-complex (weight of nanoparticles equivalent to 6 mol% Co), 5-7 bar NH_3, 45 bar H_2, 2.5 mL H_2O-THF (1.5:1), 120 °C, 24 h, GC yields using n-hexadecane as standard.

Figure S1. Co-catalyzed reductive amination of 4-bromobenzaldehyde: activity of different cobalt-salen complexes.







Reaction conditions: 0.5 mmol 4-bromobenzaldehyde, 6 mol% Co-complex, 5 bar NH_3, 45 bar H_2, 2.5 mL H_2O-THF (1.5:1), 120 °C, 24 h, GC yields using n-hexadecane standard.

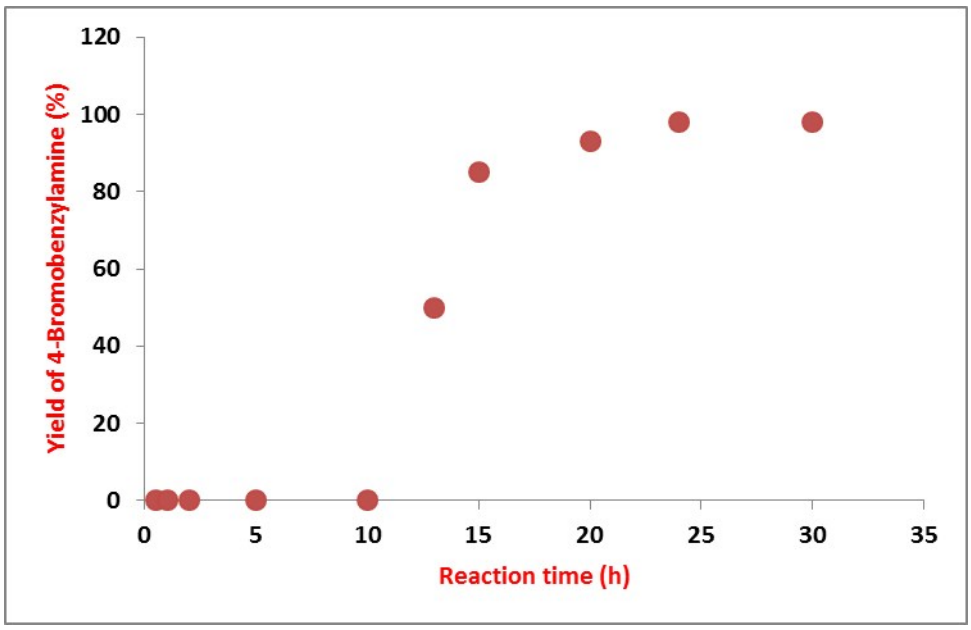


Figure S2. Reaction progress for the reductive amination of 4-bromobenzaldehyde at different interval of time. Reaction conditions: 0.5 mmol 4-bromobenzaldehyde, 6 mol% complex **I** (11 mg), 5-7 bar NH_3, 45 bar H_2, 2.5 mL H_2O-THF (1.5:1), 120 ^oC, GC yields using n-hexadecane standard.

Isolated *in situ* generated cobalt nanoparticles

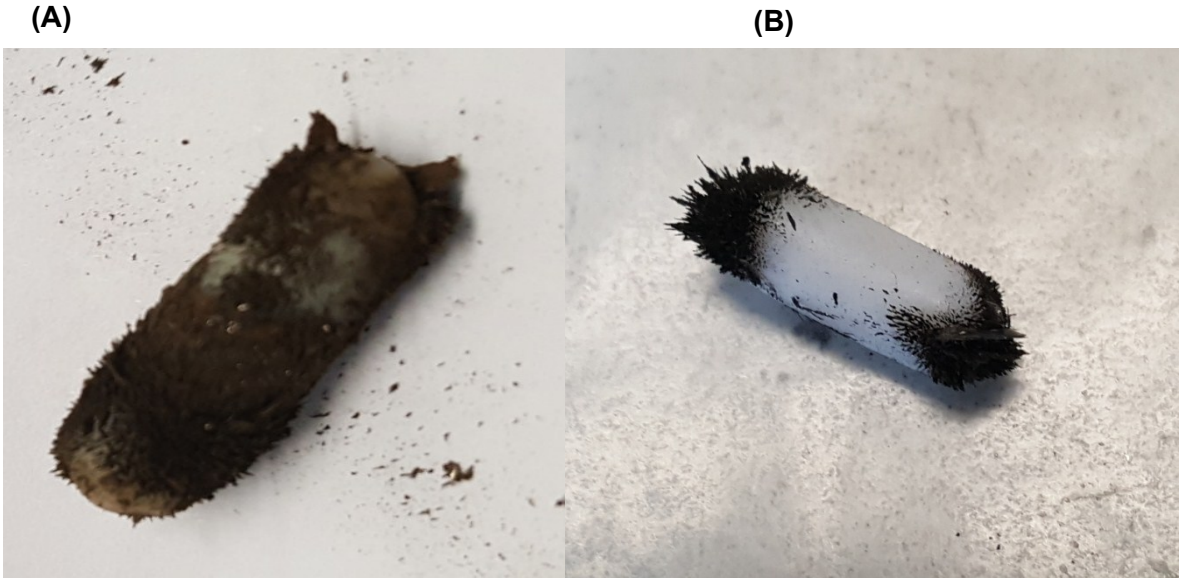
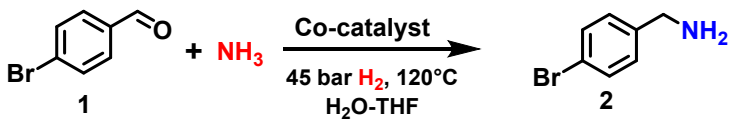


Figure S3. (A) Co NPs attached to magnetic stir bar after the reaction. **(B)** Isolated and washed Co NPs attached to magnetic stir bar.

Stability studies of *in situ* generated cobalt nanoparticles



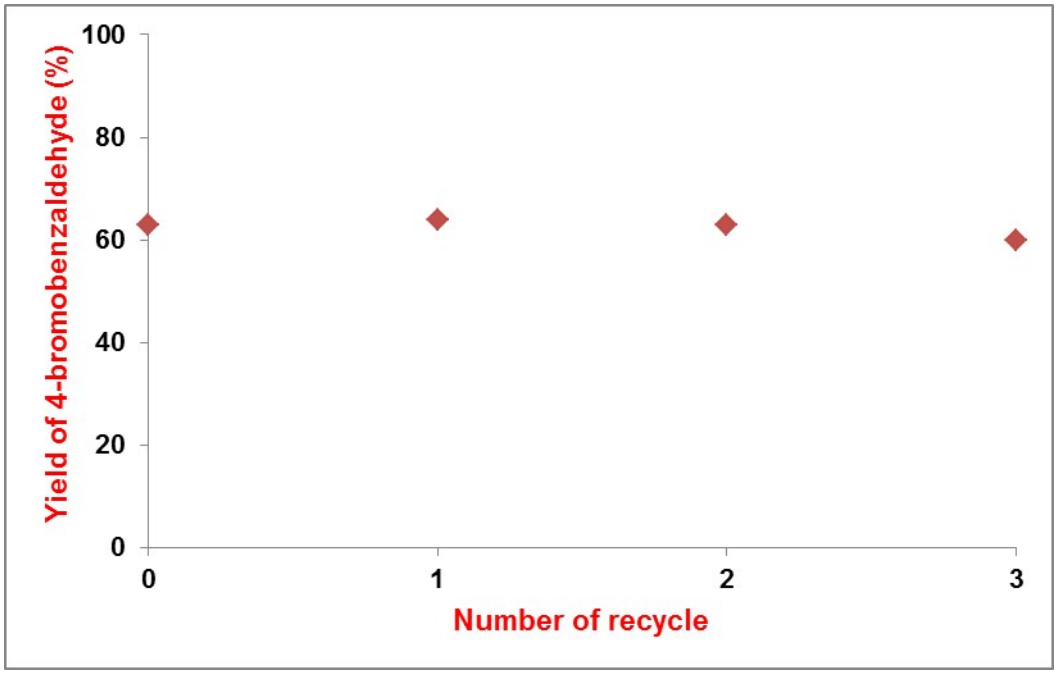


Figure S4. Stability studies of Co-NPs. Reaction condition: 2 mmol 4-bromobenzaldehyde, 8 mg Co NPs (6.5 mol%), 5-7 bar NH_3, 45 bar H_2, 10 mL H_2O-THF (1.5:1), 120°C, 10 h, yield were determined GC

Characterization of *in situ* generated cobalt nanoparticles

(a) TEM analysis and data

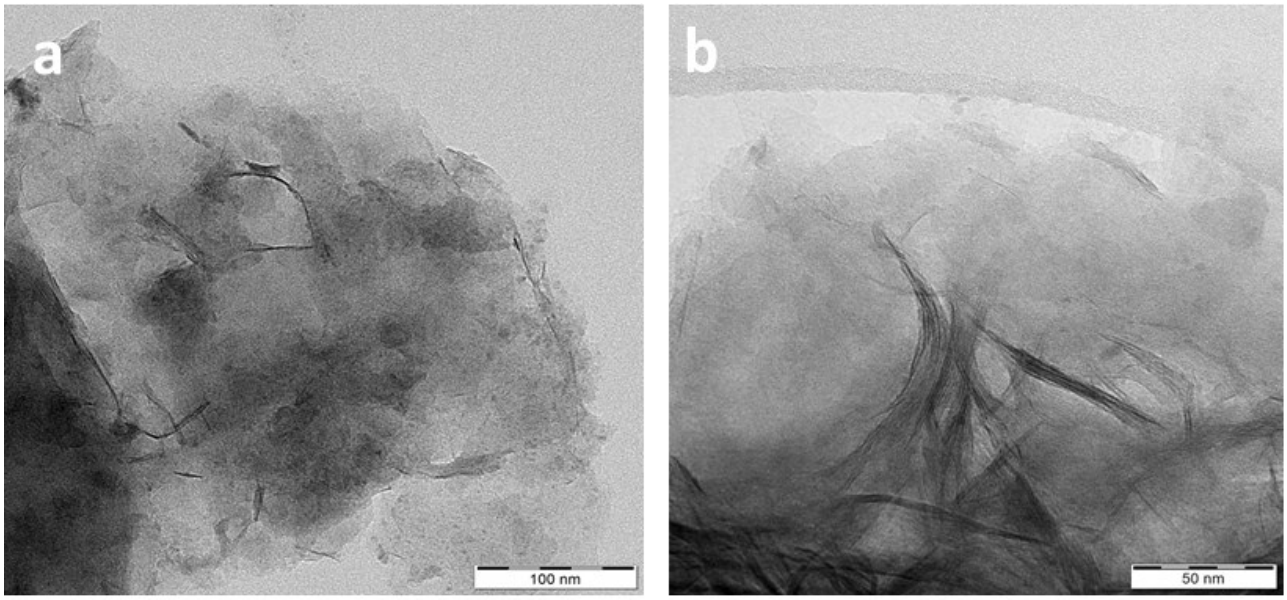


Figure S5. TEM images of in situ generated cobalt nanoparticles.

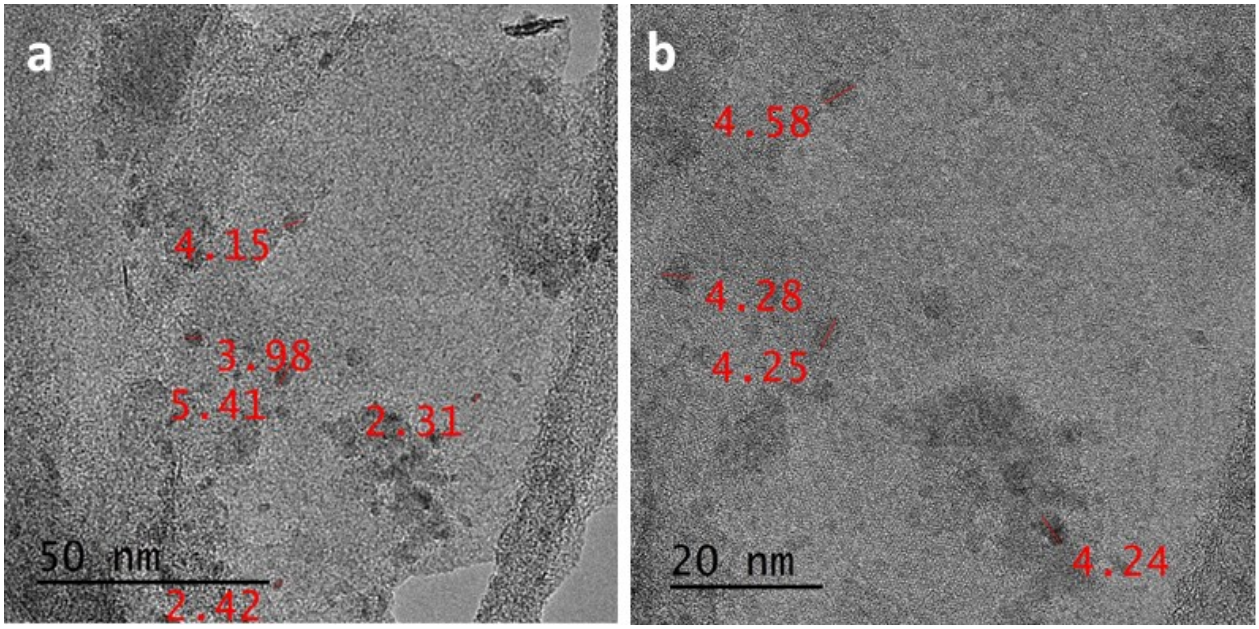


Figure S6. HRTEM images of in situ generated cobalt nanoparticles.

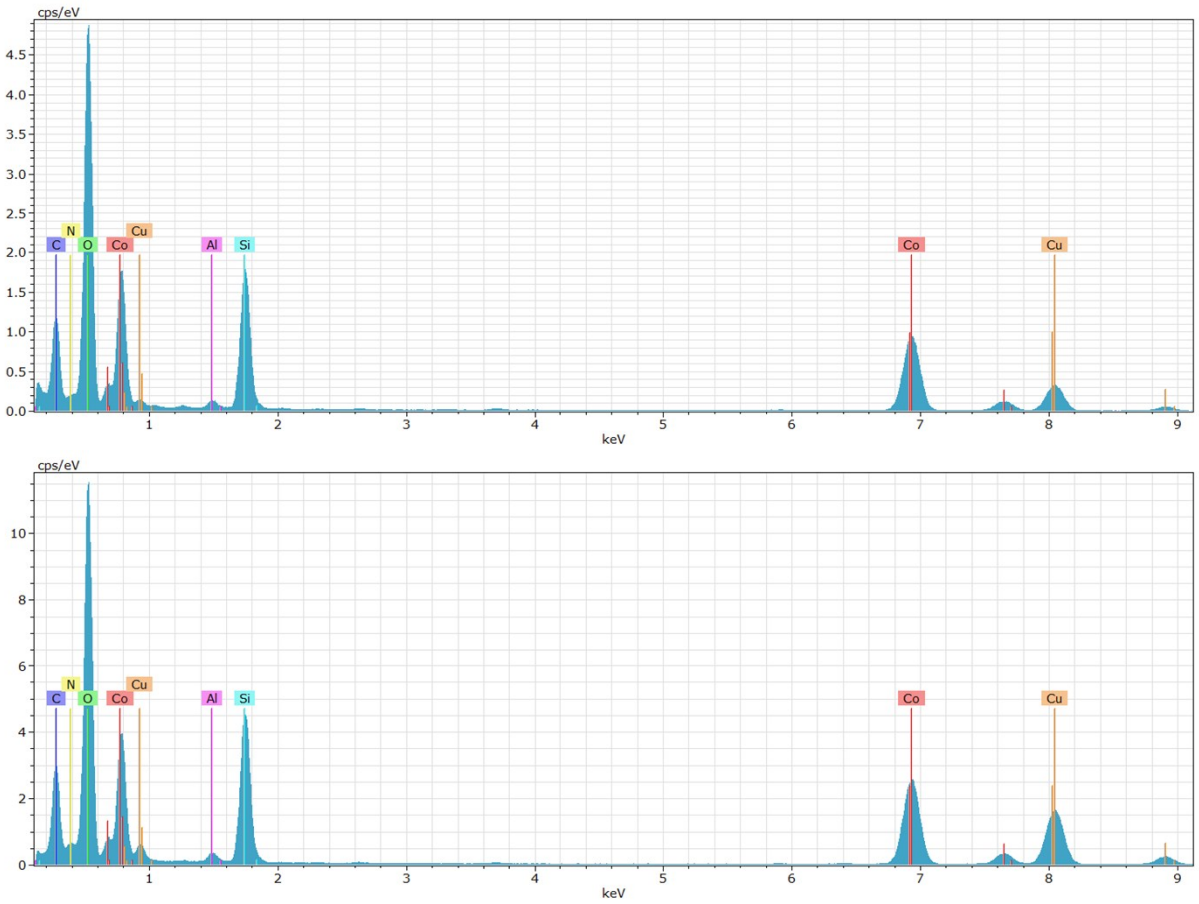


Figure S7. EDX spectra of *in situ* generated cobalt nanoparticles.

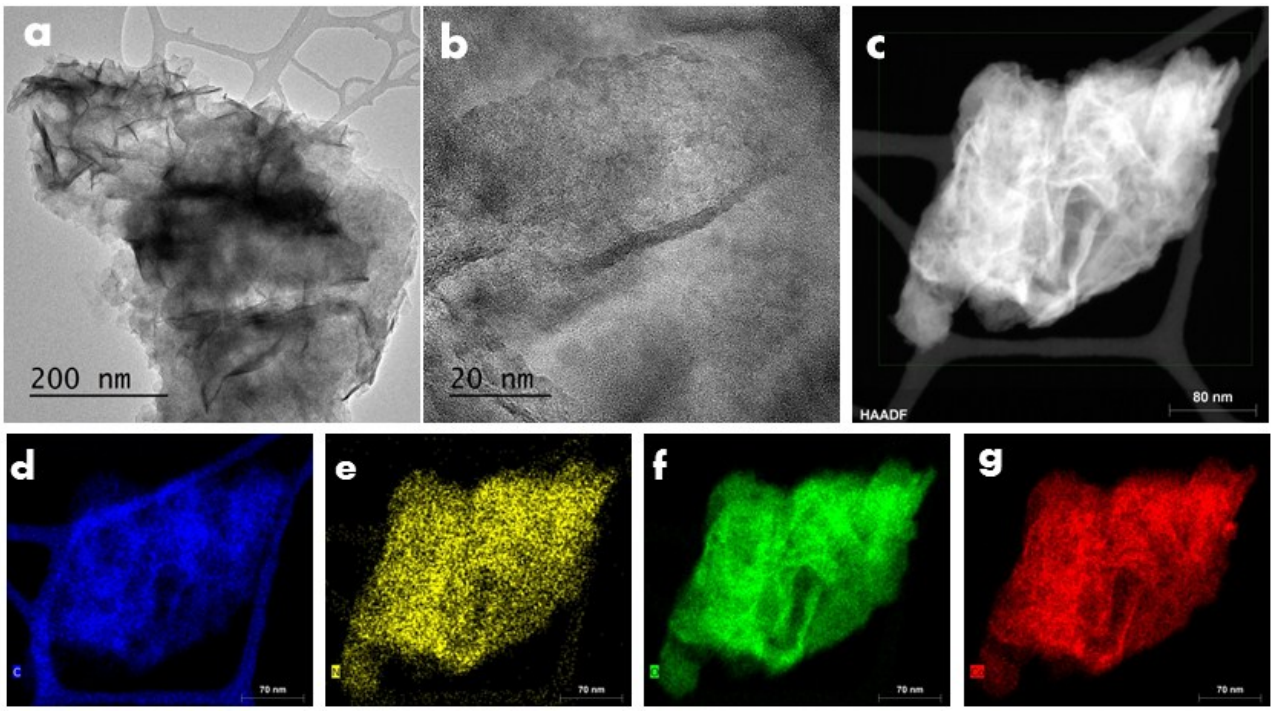


Figure S8. HRTEM and HAADF elemental mapping of recycled cobalt nanoparticles.

(*b) XRD analysis and data*

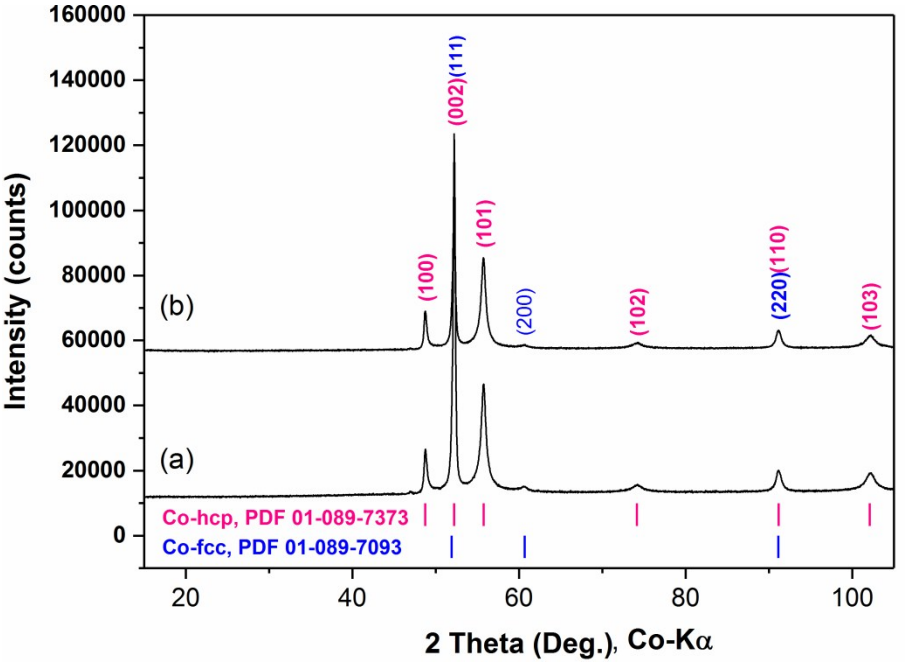


Figure S9. XRD patterns of samples (a) *in situ* generated Co nanoparticles and (b) recycled Co nanoparticles.

(c) XPS analysis and data

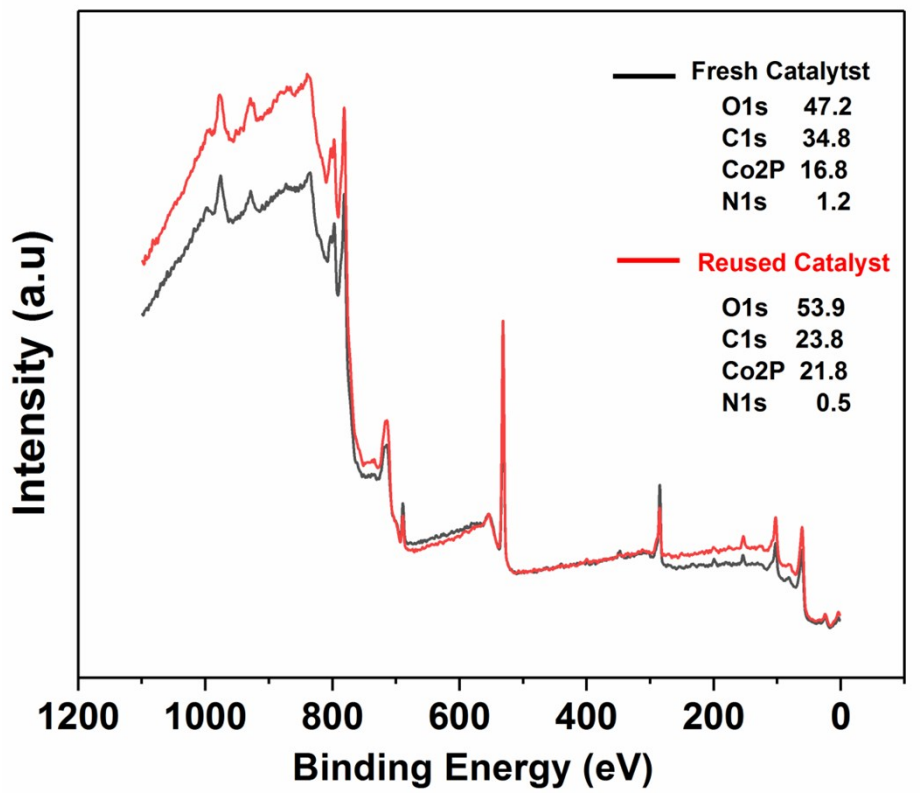


Figure S10. XPS survey scan of *in situ* generated and recycled Co nanoparticles.

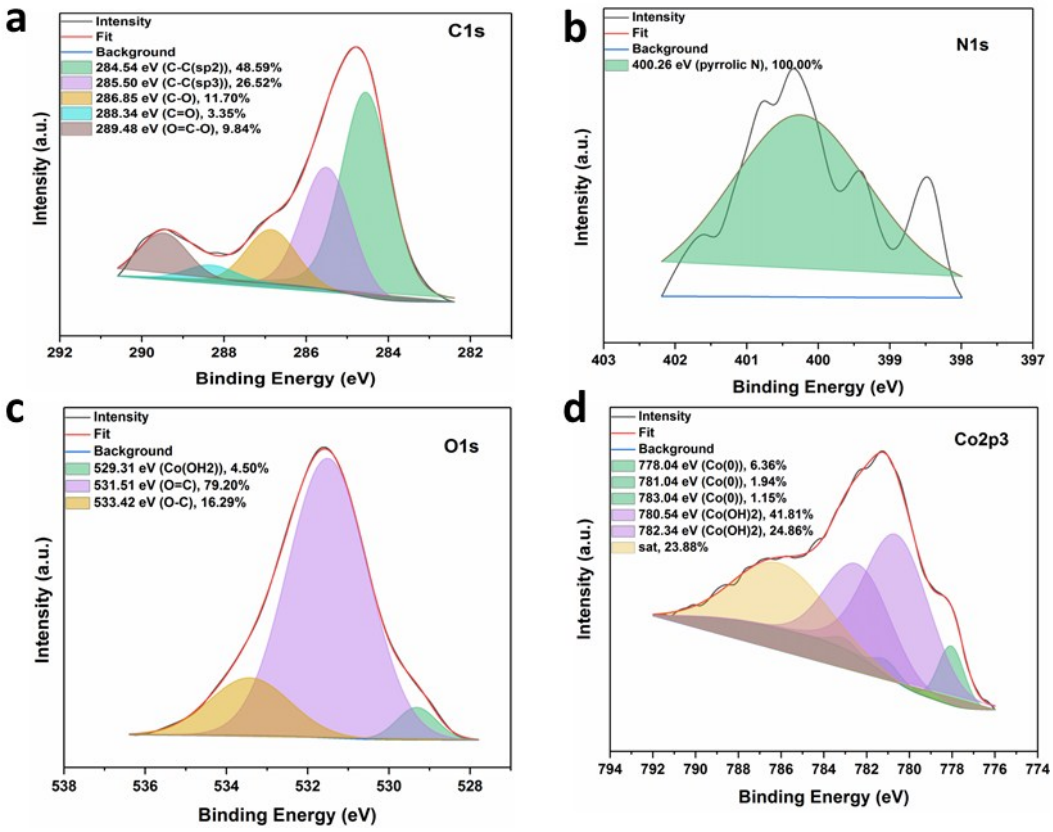


Figure S11. HR-XPS spectra of recycled cobalt nanoparticles.

(d) Magnetization measurements and data

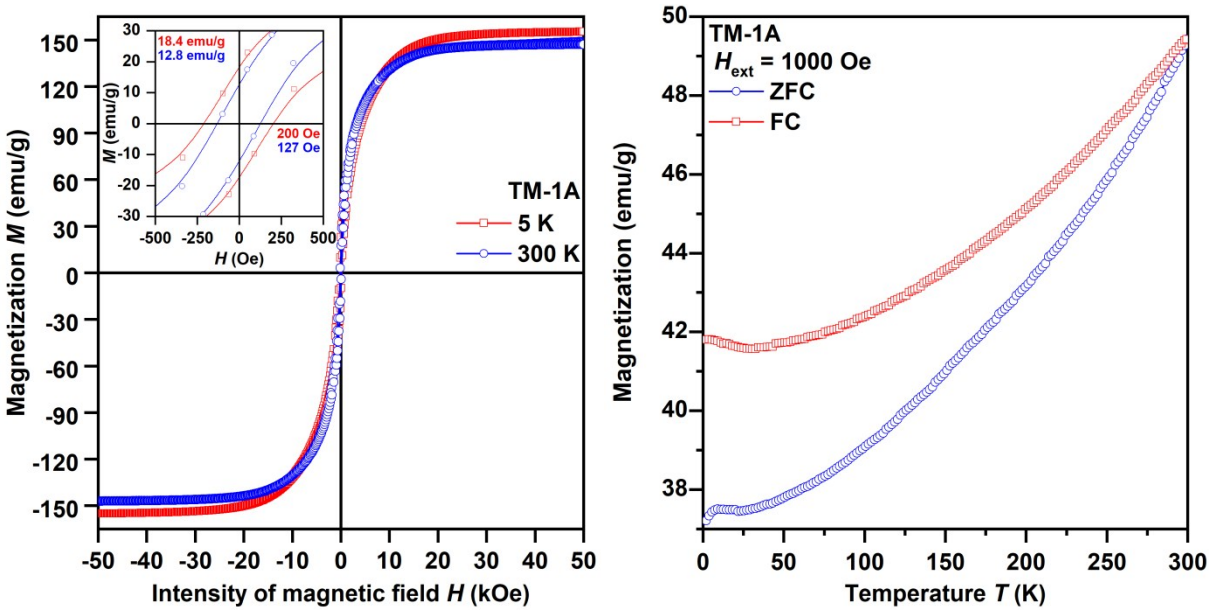
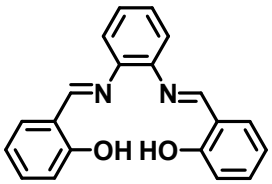


Figure S12. Magnetization results of in situ generated cobalt nanoparticles. Left: Hysteresis loops of the cobalt-nanoparticles, recorded at a temperature of 5 and 300 K. Right= Zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves of the cobalt-nanoparticles, measured under an external magnetic field of 1 kOe.

NMR spectral data

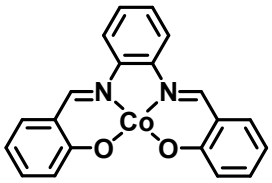
2,2'-((1E,1'E)-(1,2-phenylenebis(azanylylidene))bis(methanylylidene))diphenol (L1)



1H NMR (300 MHz, DMSO-d6) δ 12.97 (d, J = 1.8 Hz, 2H), 8.94 (s, 2H), 7.67 (dd, J = 7.9, 1.7 Hz, 2H), 7.54 – 7.27 (m, 6H), 7.12 – 6.83 (m, 4H).

13C NMR (75 MHz, DMSO) δ 164.49, 160.84, 142.71, 133.89, 132.92, 128.26, 120.20, 119.94, 119.54, 117.13.

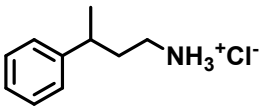
Cobalt (II)-N,N-bis(salicylidene)-1,2-phenylenediamine) (Complex I)



^{1}H NMR (300 MHz, DMSO-d_6) δ 9.04 – 8.69 (m, 2H), 8.65 – 8.21 (m, 2H), 8.08 – 6.95 (m, 8H), 6.85 – 6.39 (m, 2H).

^{13}C NMR (75 MHz, DMSO) δ 176.77, 168.42, 160.24, 146.54, 136.11, 135.40, 127.77, 123.01, 119.62, 116.95, 114.61.

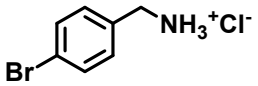
Product-26



1H NMR (300 MHz, DMSO-d6) δ 8.21 (br s, 3H), 7.57 – 7.00 (m, 5H), 2.87 – 2.61 (m, 2H), 2.60 – 2.44 (m, 1H), 1.86 (q, J = 7.7 Hz, 2H), 1.18 (d, J = 6.9 Hz, 3H).

13C NMR (75 MHz,DMSO-d6) δ 146.33 , 128.96 , 127.29 , 126.72 , 37.78 , 36.88 , 35.49 , 22.54.

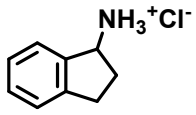
Product-2



1H NMR (300 MHz, DMSO-d6) δ 8.60 (br s, 3H), 7.61 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.5 Hz, 2H), 3.98 (s, 2H).

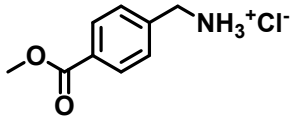
13C NMR (75 MHz, DMSO-d6) δ 134.03 , 131.87 , 131.81 , 122.16 , 41.90.

Product-37



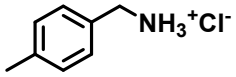
1H NMR (300 MHz, DMSO-d6) δ 8.65 (br s, 3H), 7.69 (d, J = 7.0 Hz, 1H), 7.51 – 7.10 (m, 3H), 4.88-4.50 (m, 1H), 3.20-3.04 (m, 1H), 3.00 – 2.82 (m, 1H), 2.53 – 2.41 (m, 1H), 2.16 –1.95 (m, 1H).
13C NMR (75 MHz, DMSO-d6) δ 144.40, 139.90, 129.41, 127.101, 125.56, 125.36, 55.01, 30.81, 30.34 .

Product-22



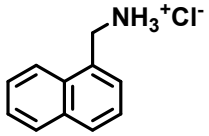
1H NMR (300 MHz, DMSO-d6) δ 8.76 (br s, 3H), 7.98 (d, J = 8.5 Hz, 2H), 7.68 (d, J = 8.8 Hz, 2H), 4.10 (s, 2H), 3.87 (s, 3H).
13C NMR (75 MHz, DMSO-d6) δ 166.36 , 139.92 , 129.92 , 129.69 , 52.71 , 42.16 . White solid.

Product-5



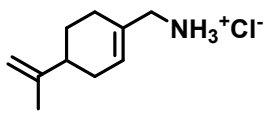
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.58 (brs, 3H), 7.46 – 7.30 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.7 Hz, 2H), 3.94 (s, 2H), 2.28 (s, 3H).
^{13}C NMR (101 MHz, DMSO) δ 138.12, 131.44, 129.47, 129.46, 42.35, 21.23.

Product-7



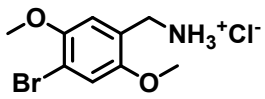
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.59 (brs, 3H), 8.18 – 8.12 (m, 1H), 8.00 (ddt, *J* = 9.3, 8.3, 1.1 Hz, 2H), 7.69 – 7.54 (m, 4H), 4.52 (s, 2H).
^{13}C NMR (101 MHz, DMSO) δ 133.66, 131.09, 130.33, 129.54, 129.11, 127.75, 127.24, 126.72, 125.83, 123.89, 40.51.

Product-27



1H NMR (400 MHz, DMSO-d6): δ 8.39 (br s, 3H), 5.94 – 5.60 (m, 1H), 4.71 (s, 2H), 3.29 (s, 2H), 2.21 – 2.01 (m, 4H), 1.71 (s, 3H), 1.56 – 1.51 (m, 2H).
13C NMR (101 MHz, DMSO): δ 149.31, 131.23, 125.94, 109.47, 48.98, 44.07, 30.29, 27.22, 27.01, 21.02.

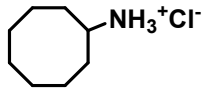
Product-20



^{1}H NMR (400 MHz, DMSO-d_6): δ 8.63 (br s, 3H), 7.54 (s, 2H), 3.95 (s, 2H), 3.68 (s, 6H).

^{13}C NMR (101 MHz, DMSO): δ 151.71, 149.67, 122.51, 116.31, 115.58, 111.18, 57.29, 56.87, 37.33.

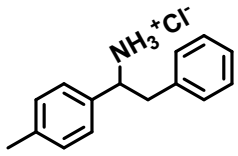
Product -40



^{1}H NMR (400 MHz, DMSO-d_6): δ 8.21 (br s, 3H), 3.23 – 2.97 (m, 1H), 1.91- 1.84 (m, 2H), 1.63-1.58 (m, 4H), 1.49-1.36 (m, 8H).

^{13}C NMR (101 MHz, DMSO): δ 51.36, 30.30, 26.72, 25.30, 23.30. Brown solid.

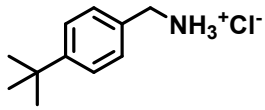
Product-35



^{1}H NMR (300 MHz, DMSO-d_6): δ 8.10 (br s, 3H), 7.35-7.29 (m, 2H), 7.24-7.19 (m, 2H), 6.97 – 6.78 (m, 5H), 4.36 (dd, *J* = 10.5, 4.7 Hz, 1H), 3.34 (dd, *J* = 13.3, 4.8 Hz, 1H), 3.09 – 2.88 (m, 1H). 2.11 (s, 3H).

^{13}C NMR (75 MHz, DMSO): δ 137.21, 135.96, 133.44, 129.47, 129.26, 128.92, 128.85, 128.36, 56.39, 40.46, 21.05. Off-White solid.

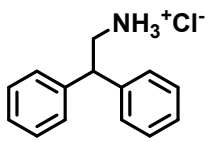
Product-6



^{1}H NMR (400 MHz, DMSO-d_6): δ 8.68 (br s, 3H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H),3.94 (s, 2H), 1.25 (s, 9H).

^{13}C NMR (101 MHz, DMSO): δ 151.24, 131.58, 129.29, 125.67, 42.21, 34.76, 31.53. pale Brown solid.

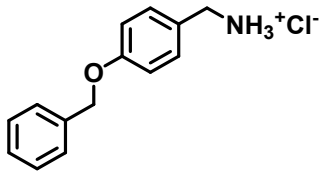
Product-25



^{1}H NMR (300 MHz, DMSO-d_6): δ 8.24 (br s, 3H), 7.42 – 7.19 (m, 10H), 4.44 (t, *J* = 7.8 Hz, 1H), 3.57 (d, *J* = 6.3 Hz, 2H).

^{13}C NMR (75 MHz, DMSO): δ 141.53, 129.24, 128.29, 127.47, 48.90, 42.90. Off-White solid.

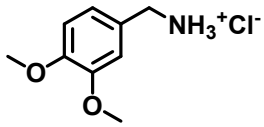
Product-18



^{1}H NMR (400 MHz, DMSO-d_6): δ 8.53 (br s, 3H), 7.65 – 7.18 (m, 7H), 7.10 – 6.87 (m, 2H), 5.13 (s, 2H), 4.11 (s, 2H).

^{13}C NMR (101 MHz, DMSO): δ 158.76, 137.41, 131.04, 128.90, 128.29, 128.08, 126.68, 115.25, 69.61, 42.06. Off-White solid.

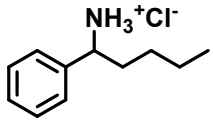
Product-15



^{1}H NMR (300 MHz, DMSO-d_6): δ 8.63 (br s, 3H), 7.30 (s, 1H), 7.13 (d, *J* = 8.3 Hz, 2H), 3.92 (s, 2H), 3.76 (s, 6H).

^{13}C NMR (75 MHz, DMSO): δ 149.26, 149.04, 126.79, 121.93, 113.52, 112.00, 56.09, 56.06, 42.50. White solid.

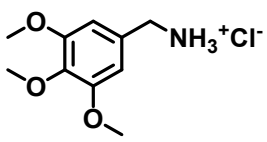
Product-34



^{1}H NMR (300 MHz, DMSO-d_6): δ 8.77 (br s, 3H), 7.64 – 7.50 (m, 2H), 7.39 – 7.29 (m, 3H).4.35 – 3.93 (m, 1H), 2.24 – 1.63 (m, 2H), 1.40 – 0.89 (m, 4H), 0.78 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (75 MHz, DMSO): δ 138.53, 129.07, 128.83, 128.03, 55.00, 34.38, 27.67, 22.12, 14.19. Off-White solid.

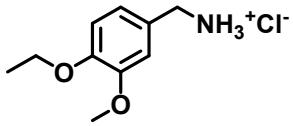
Product-16



^{1}H NMR (300 MHz, DMSO-d_6): δ 8.71 (br s, 3H), 6.98 (s, 2H), 4.02 (s, 2H), 3.78 (s, 6H), 3.64 (s, 3H).

^{13}C NMR (75 MHz, DMSO): δ 153.22, 137.73, 130.06, 107.10, 60.48, 56.52, 42.86. Off-White solid.

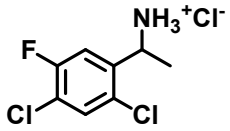
Product-17



^{1}H NMR (300 MHz, DMSO-d_6) δ 8.57 (brs, 3H), 7.28 (d, *J* = 1.9 Hz, 1H), 7.07 – 6.79 (m, 2H), 4.00 (q, *J* = 6.9 Hz, 2H), 3.91 (s, 2H), 3.80 (s, 3H), 1.31 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, DMSO) δ 149.22, 149.13, 148.44, 126.75, 121.89, 113.58, 113.07, 64.19, 56.03, 42.50, 15.16.

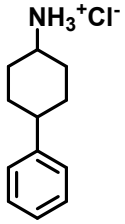
Product-32



^{1}H NMR (300 MHz, DMSO-d_6): δ 8.88 (br s, 3H), 8.16 (s, 2H), 4.65 (q, *J* = 6.7 Hz, 1H), 1.51 (d, *J* = 6.7 Hz, 3H).

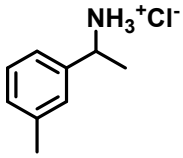
^{13}C NMR (75 MHz, DMSO): δ 156.81(d, *J*=243.2 Hz), 138.49(d, *J* =6.3 Hz), 131.71(d, *J* =19.4 Hz), 128.00(d, *J* =3.1Hz), 120.91(d, *J* =18.6 Hz), 116.45(d, *J* =39.4 Hz), 47.29, 20.03. Brown solid.

Product-39 diasterreomeric mixture (60:40)



^{1}H NMR (300 MHz, DMSO-d_6) δ 8.34 (brs, 3H), 7.44 – 6.97 (m, 5H), 2.60 – 2.38 (m, 2H), 2.19 – 1.85 (m, 3H), 1.85 – 1.41 (m, 5H).

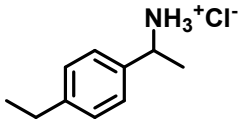
Product-30



^{1}H NMR (300 MHz, DMSO-d_6) δ 8.70 (brs, 3H), 7.36 (dd, *J* = 6.9, 1.5 Hz, 2H), 7.28 (dd, *J* = 8.4, 7.1 Hz, 1H), 7.16 (d, *J* = 7.3 Hz, 1H), 4.30 (q, *J* = 6.7 Hz, 1H), 2.31 (s, 3H), 1.52 (d, *J* = 6.7 Hz, 3H).

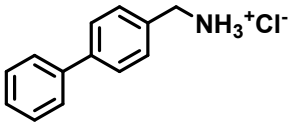
^{13}C NMR (75 MHz, DMSO) δ 139.91, 138.21, 129.28, 129.00, 127.94, 124.35, 50.52, 21.51, 21.34.

Product-29



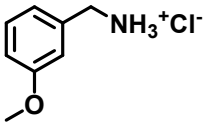
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.65 (brs, 3H), 7.55 – 7.35 (m, 2H), 7.24 (d, *J* = 7.8 Hz, 2H), 4.50 – 4.19 (m, 1H), 2.60 (q, *J* = 7.6 Hz, 2H), 1.51 (d, *J* = 6.7 Hz, 3H), 1.16 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (75 MHz, DMSO) δ 144.41, 137.19, 128.43, 127.34, 50.27, 28.32, 21.23, 16.13.

Product-4



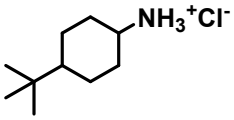
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.70 (brs, 3H), 7.75 – 7.59 (m, 6H), 7.51 – 7.44 (m, 2H), 7.41 – 7.35 (m, 1H), 4.06 (d, *J* = 5.6 Hz, 2H).
^{13}C NMR (75 MHz, DMSO) δ 140.62, 140.00, 133.74, 130.10, 129.45, 128.13, 127.20, 127.15, 42.27.

Product-14



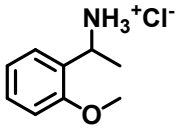
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.73 (brs, 3H), 7.29 (dd, *J* = 8.3, 7.5 Hz, 1H), 7.21 (dd, *J* = 2.7, 1.5 Hz, 1H), 7.12 – 7.03 (m, 1H), 6.91 (ddd, *J* = 8.3, 2.6, 1.0 Hz, 1H), 3.99 (s, 2H), 3.75 (s, 3H).
^{13}C NMR (75 MHz, DMSO) δ 159.72, 135.96, 130.06, 121.45, 114.97, 114.40, 55.69, 42.54.

Product-38 (Diastereomeric mixture 50:50)



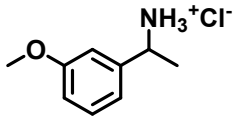
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.18 (brs, 3H), 3.35 – 2.75 (m, 1H), 2.17 – 1.69 (m, 3H), 1.56 – 1.23 (m, 4H), 1.09 – 0.90 (m, 2H), 0.82 (dd, *J* = 3.6, 1.4 Hz, 9H).

Product-33



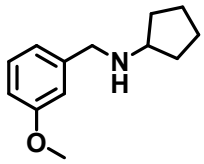
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.81 (brs, 3H), 7.56 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.33 (ddd, *J* = 8.2, 7.3, 1.6 Hz, 1H), 7.14 – 6.83 (m, 2H), 4.57 (q, *J* = 6.8 Hz, 1H), 3.82 (s, 3H), 1.49 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (75 MHz, DMSO) δ 156.43, 130.00, 127.49, 127.33, 120.98, 111.63, 56.10, 44.93, 19.95.

Product-31



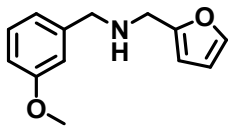
^{1}H NMR (300 MHz, DMSO-*d*$_6$) δ 8.81 (brs, 3H), 7.47 – 7.17 (m, 2H), 7.10 (dt, *J* = 7.8, 1.3 Hz, 1H), 6.89 (ddd, *J* = 8.2, 2.5, 0.9 Hz, 1H), 4.34 (d, *J* = 6.7 Hz, 1H), 3.76 (s, 3H), 1.65 – 1.25 (m, 3H).
^{13}C NMR (75 MHz, DMSO) δ 159.85, 141.49, 130.17, 119.39, 114.23, 113.05, 55.73, 50.58, 21.36.

Product-50



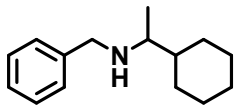
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.19 – 7.10 (m, 1H), 6.85 – 6.78 (m, 2H), 6.74 – 6.66 (m, 1H), 3.72 (s, 3H), 3.66 (d, *J* = 0.7 Hz, 2H), 3.03 (tt, *J* = 6.8, 6.3 Hz, 1H), 1.82 – 1.69 (m, 2H), 1.64 – 1.57 (m, 2H), 1.50 – 1.37 (m, 2H), 1.35 – 1.20 (m, 2H).
^{13}C NMR (75 MHz, CDCl$_3$) δ 159.73, 159.73, 142.30, 129.34, 120.50, 113.72, 112.33, 59.11, 55.18, 52.66, 33.13, 24.14, 24.11.

Product-49



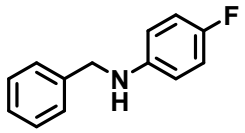
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.40 (dd, *J* = 1.9, 0.9 Hz, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 6.94 (dddd, *J* = 4.8, 1.7, 1.3, 0.7 Hz, 2H), 6.83 (ddd, *J* = 8.3, 2.6, 1.1 Hz, 1H), 6.35 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.22 (dq, *J* = 3.2, 0.8 Hz, 1H), 3.82 (s, 3H), 3.82 – 3.81 (m, 2H), 3.80 (s, 2H), 2.03 (d, *J* = 5.5 Hz, 1H).
^{13}C NMR (75 MHz, CDCl$_3$) δ 159.82, 153.83, 141.83, 141.54, 129.41, 120.56, 113.68, 112.65, 110.16, 107.10, 55.16, 52.73, 45.33, 31.26.

Product-52



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.78 – 6.92 (m, 5H), 3.89 – 3.42 (m, 2H), 2.41 (qd, *J* = 6.4, 5.0 Hz, 1H), 1.73 – 1.50 (m, 6H), 1.03 – 0.84 (m, 5H).
^{13}C NMR (75 MHz, CDCl$_3$) δ 141.00, 128.36, 128.15, 126.79, 57.12, 51.58, 42.98, 29.90, 28.13, 26.83, 26.72, 26.59, 16.73.

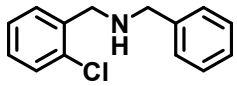
Product-42



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.48 – 7.22 (m, 5H), 7.07 – 6.81 (m, 2H), 6.70 – 6.50 (m, 2H), 4.33 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 155.66 (d, *J* = 254.3 Hz), 144.15, 139.02, 128.70, 127.61, 127.40, 115.67 (d, *J* = 21.4 Hz), 114.01 (d, *J* = 11.4 Hz), 49.15.

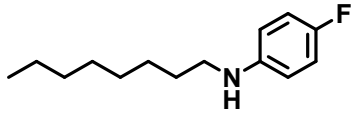
Product-48



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.38 – 7.31 (m, 1H), 7.30 – 7.06 (m, 8H), 3.83 (s, 2H), 3.73 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 139.81, 137.32, 133.81, 130.30, 129.52, 128.44, 128.40, 128.25, 127.09, 126.82, 53.02, 50.60.

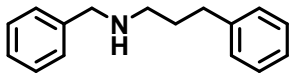
Product-57



^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.97 – 6.71 (m, 2H), 6.58 (ddd, *J* = 8.9, 4.4, 2.0 Hz, 2H), 2.98 (dd, *J* = 7.4, 1.8 Hz, 2H), 2.77 (s, 1H), 1.53 (dd, *J* = 11.0, 4.0 Hz, 2H), 1.23 – 1.17 (m, 9H), 0.86 – 0.77 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 154.96 (d, *J* = 252.3 Hz), 143.48, 115.67 (d, *J* = 21.4 Hz), 114.01 (d, *J* = 11.4 Hz),45.55, 31.70, 29.27, 29.13, 28.97, 27.01, 22.54, 14.02.

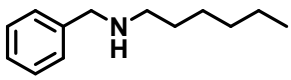
Product-54



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.51 – 7.19 (m, 10H), 3.89 (d, *J* = 3.0 Hz, 2H), 2.84 – 2.70 (m, 4H), 2.02 – 1.89 (m, 2H), 1.72 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.27, 140.54, 128.50, 128.50, 128.44, 128.25, 127.02, 125.87, 54.10, 48.99, 33.75, 31.82.

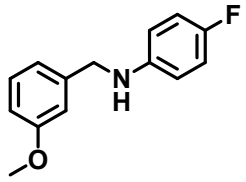
Product-55



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.43 – 7.06 (m, 5H), 3.72 (s, 2H), 2.71 – 2.46 (m, 2H), 2.34 – 1.89 (m, 2H), 1.51 – 1.36 (m, 2H), 1.29 – 1.14 (m, 6H), 0.85 – 0.76 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 139.97, 128.41, 128.24, 127.00, 53.91, 49.35, 31.76, 29.85, 27.03, 22.62, 14.05.

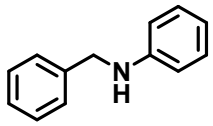
Product-44



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.44 – 7.16 (m, 1H), 7.04 – 6.75 (m, 4H), 6.68 – 6.47 (m, 2H), 4.29 (s, 2H), 3.83 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.95, 154.96 (d, *J* = 252.3 Hz), 144.50, 141.02, 129.69, 119.70, 115.67 (d, *J* = 22.4 Hz), 113.69 (d, *J* = 10.4 Hz), 113.05, 112.66, 55.22, 48.89.

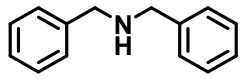
Product-41



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.62 – 7.30 (m, 5H), 7.30 – 7.18 (m, 2H), 6.88 – 6.59 (m, 3H), 4.39 (d, *J* = 1.4 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 148.13, 139.28, 129.31, 128.68, 127.59, 127.29, 117.73, 113.01, 48.45.

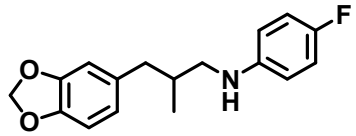
Product-46



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.63 – 7.14 (m, 10H), 3.90 (d, *J* = 1.7 Hz, 4H), 1.95 (d, *J* = 2.3 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 140.32, 128.49, 128.26, 127.05, 53.21.

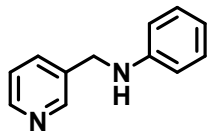
Product-56



^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.82 – 6.72 (m, 2H), 6.64 (dd, *J* = 7.9, 0.9 Hz, 1H), 6.57 – 6.47 (m, 2H), 6.43 – 6.33 (m, 2H), 5.82 (s, 2H), 3.37 (s, 1H), 2.92 (dd, *J* = 12.3, 6.0 Hz, 1H), 2.78 (dd, *J* = 12.3, 7.0 Hz, 1H), 2.56 (dd, *J* = 13.6, 6.5 Hz, 1H), 2.43 – 2.25 (m, 1H), 1.98 – 1.79 (m, 1H), 0.91 – 0.81 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 154.96 (d, *J* = 252.3 Hz), 147.60, 145.80, 144.72, 134.24, 121.93, 115.62 (d, *J* = 22.4 Hz), 113.59 (d, *J* = 10.4 Hz), 109.44, 108.10, 100.81, 50.51, 41.07, 35.13, 18.02.

Product-45

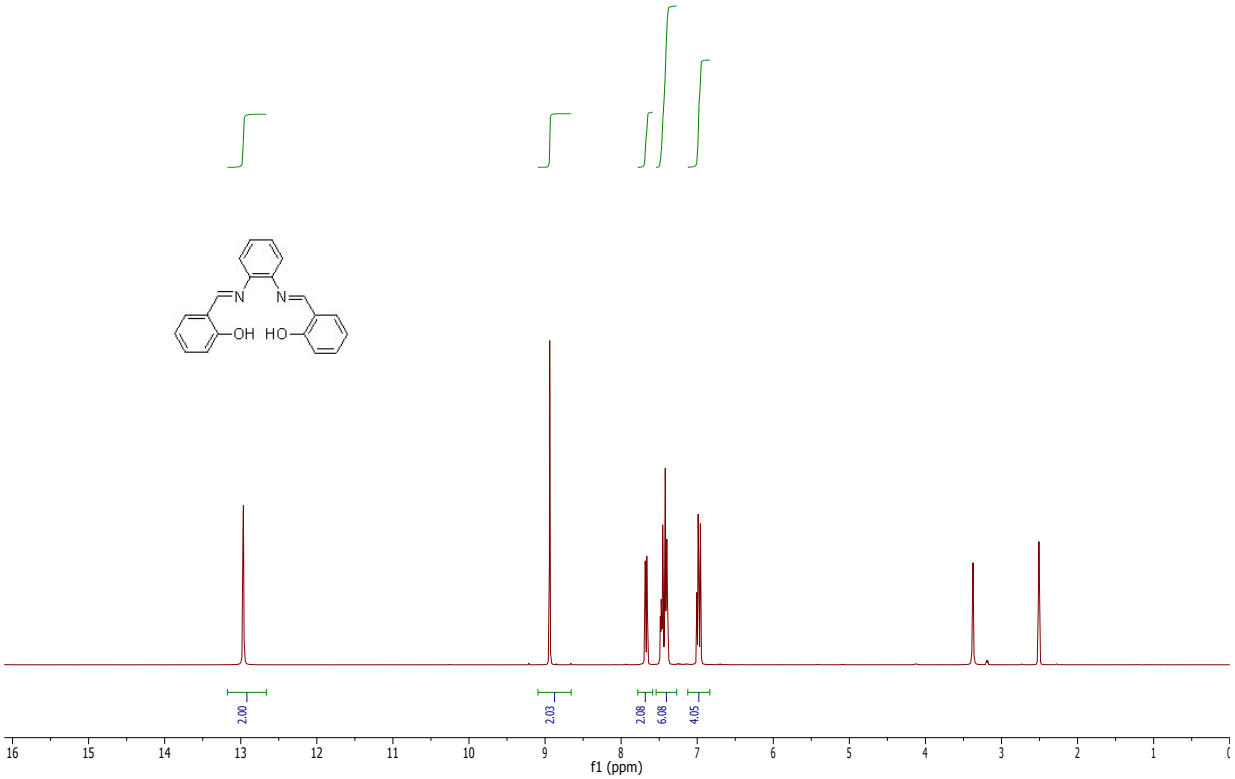


^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.92 – 8.29 (m, 2H), 7.72 (dq, *J* = 8.0, 1.4 Hz, 1H), 7.40 – 7.07 (m, 3H), 6.90 – 6.51 (m, 3H), 4.38 (s, 2H), 4.10 (d, *J* = 30.4 Hz, 1H).

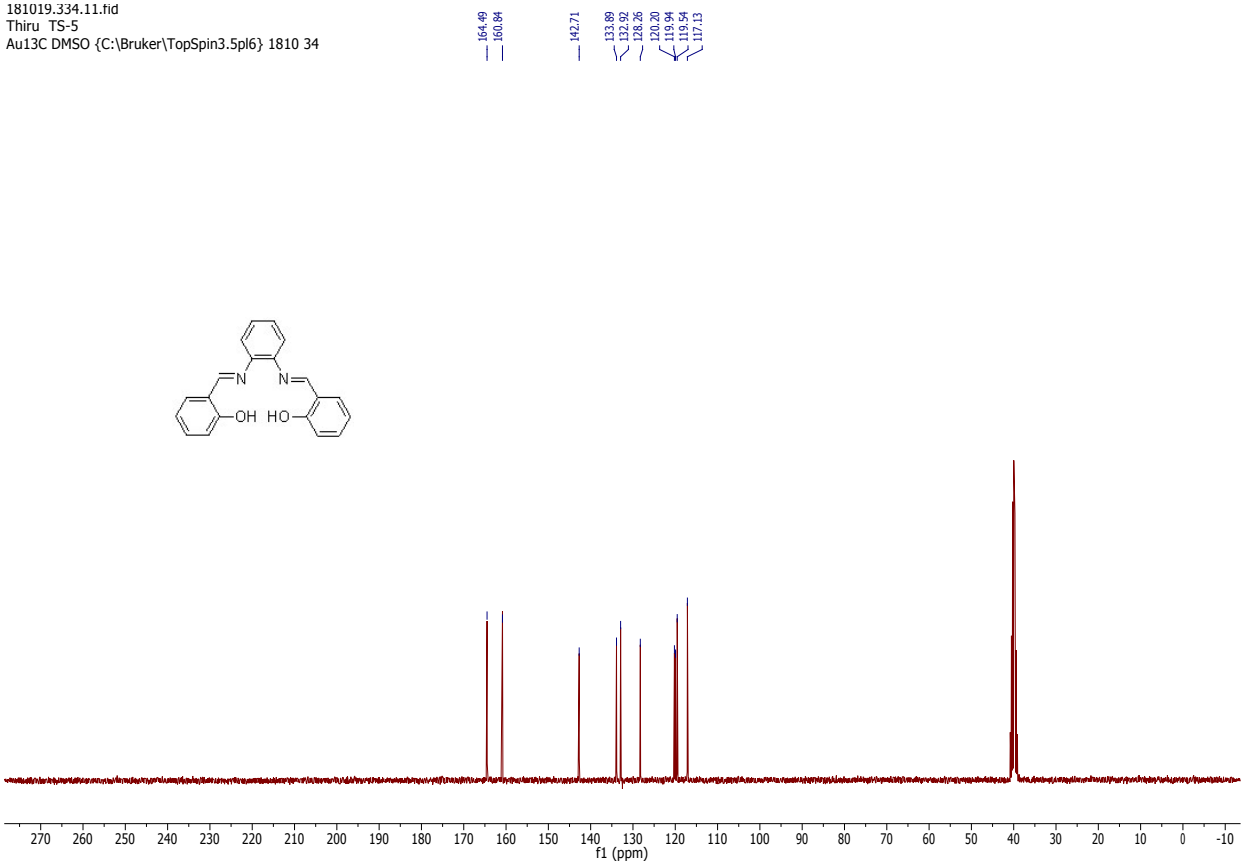
^{13}C NMR (75 MHz, $CDCl_3$) δ 149.07, 148.60, 147.65, 135.18, 135.03, 129.35, 123.60, 118.03, 112.97, 45.79.

NMR spectra

181019.334.10.fid
Thiru TS-5
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1810 34



181019.334.11.fid
Thiru TS-5
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1810 34



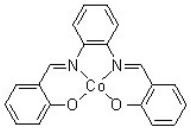
ESI-TOF Accurate Mass Report

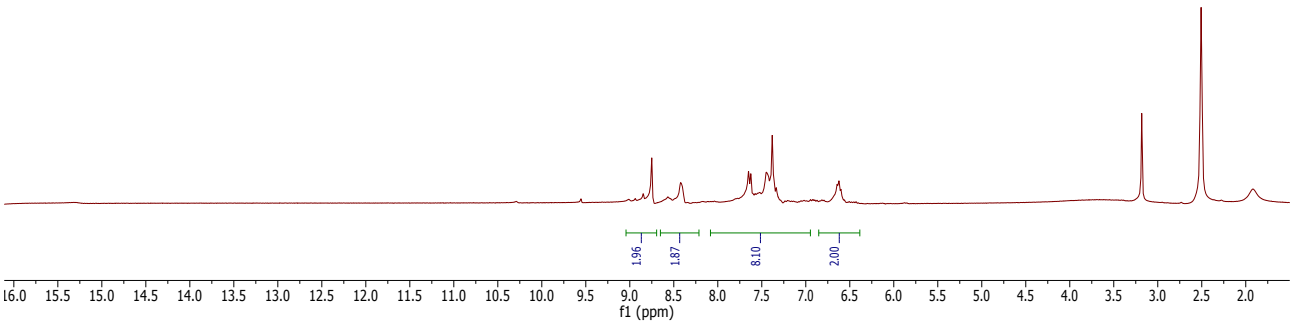
Results file: E:\Projects\1811.PRO\SampleDB\1811.rpt
Last modified: Thursday, November 08, 2018 13:23:19

Sample Summary:

Sample	File	Sample Name	User	Target	Formula	Expected Mass	Observed Mass	Error PPM	Error mDa
35	18110810	TS-5	Thiru	316.1212	C20H16O2N2	317.1290	317.1289	-0.3	-0.1

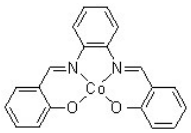
181019.336.10.fid
Thiru TS-5-2
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1810 36





181019.336.11.fid
Thiru TS-5-2
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1810 36

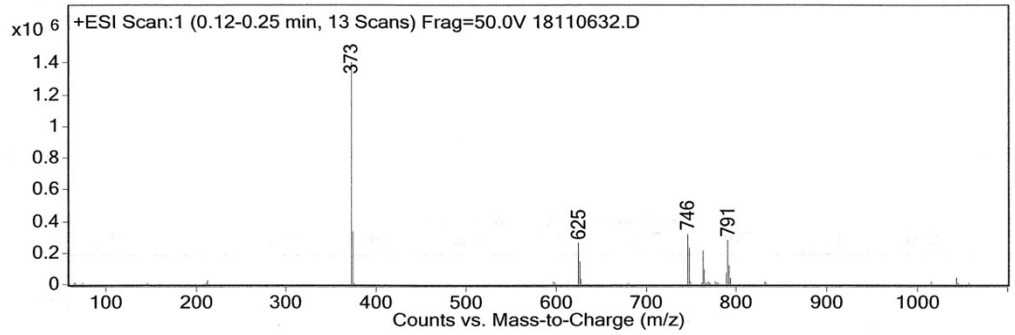
176.77
168.42
160.24
146.54
136.11
135.40
127.77
123.01
119.62
116.95
114.61



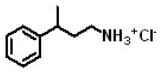
Qualitative Analysis Report

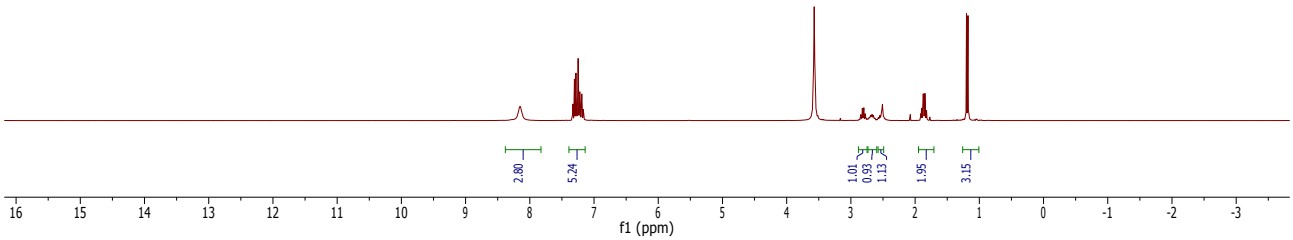
Instrument Name	LCMS	**Data Filename**	D:\Chem32\1\Data\1811\18110632.D
Acq Method	SCAN Pos_oS.M	**Sample Name**	TS-15
DA Method	HRMS.m	**Position**	Vial 27
User Name	SYSTEM	**Comment**	MeOH/0.1%HCOOH in H2O 90:10

User Spectra

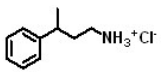


190128.f311.10.fid
Thiru TM7-915
PROTON DMSO {C:\Bruker\TopSpin3.6.0} 1901 11

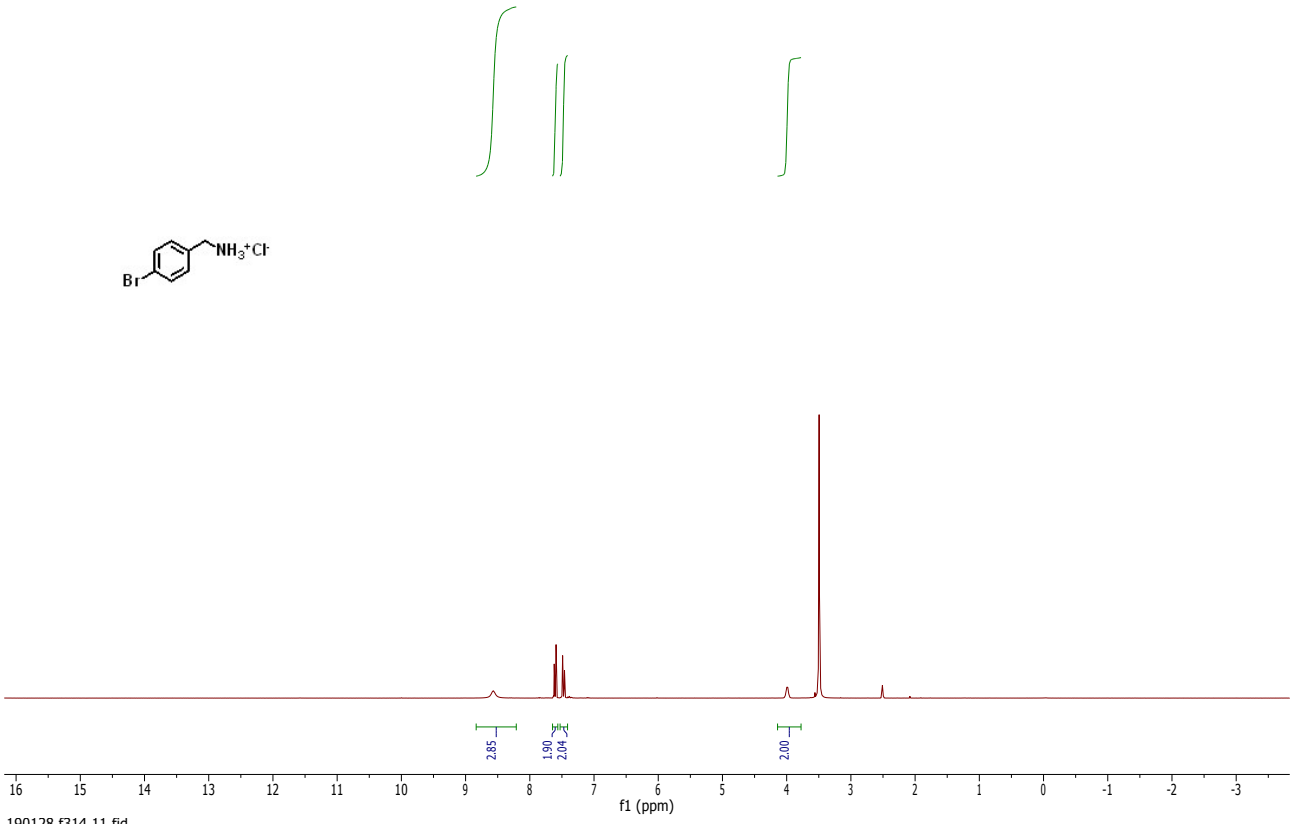




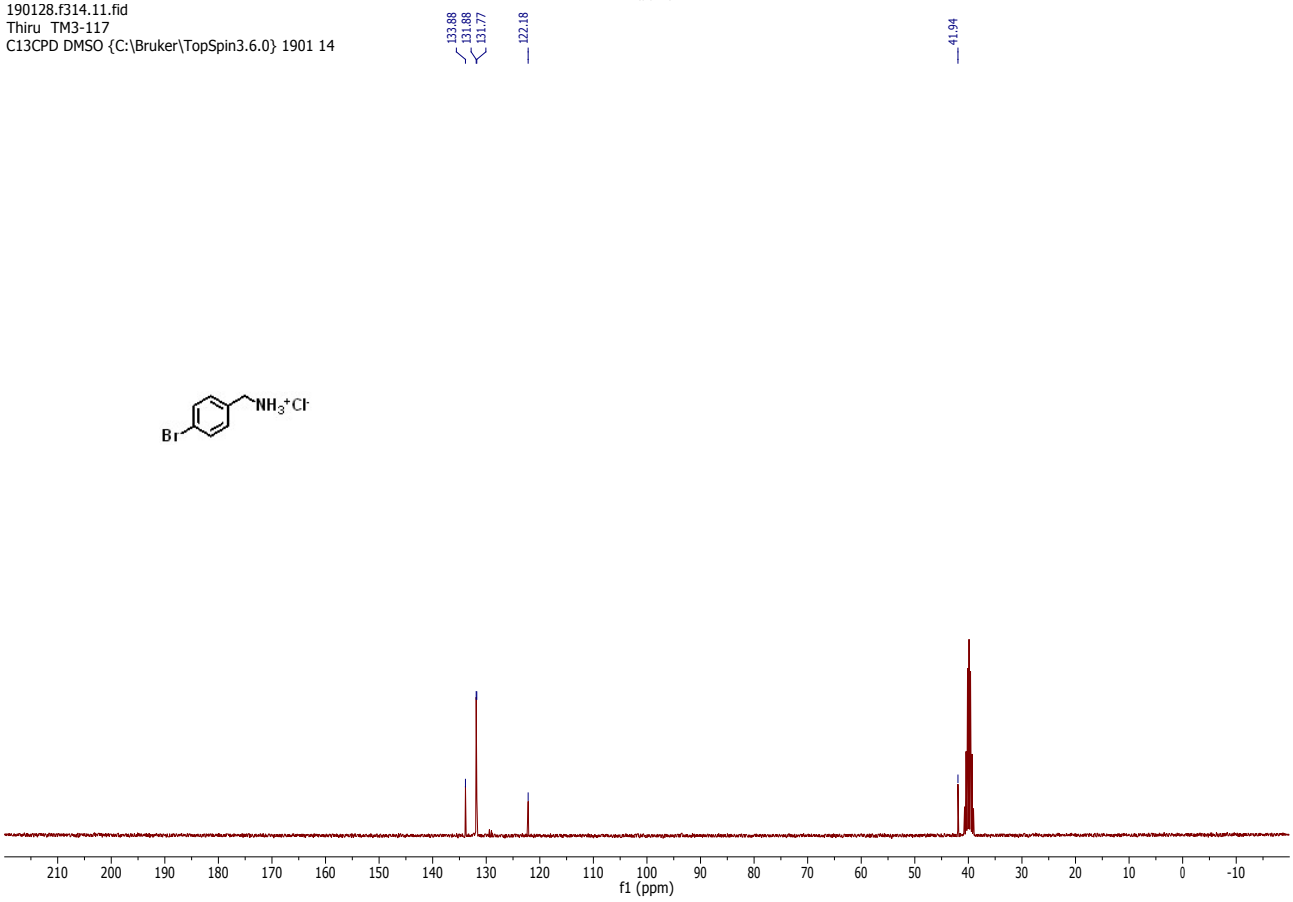
190128.f311.11.fid
Thiru TM7-915
C13CPD DMSO {C:\Bruker\TopSpin3.6.0} 1901 11



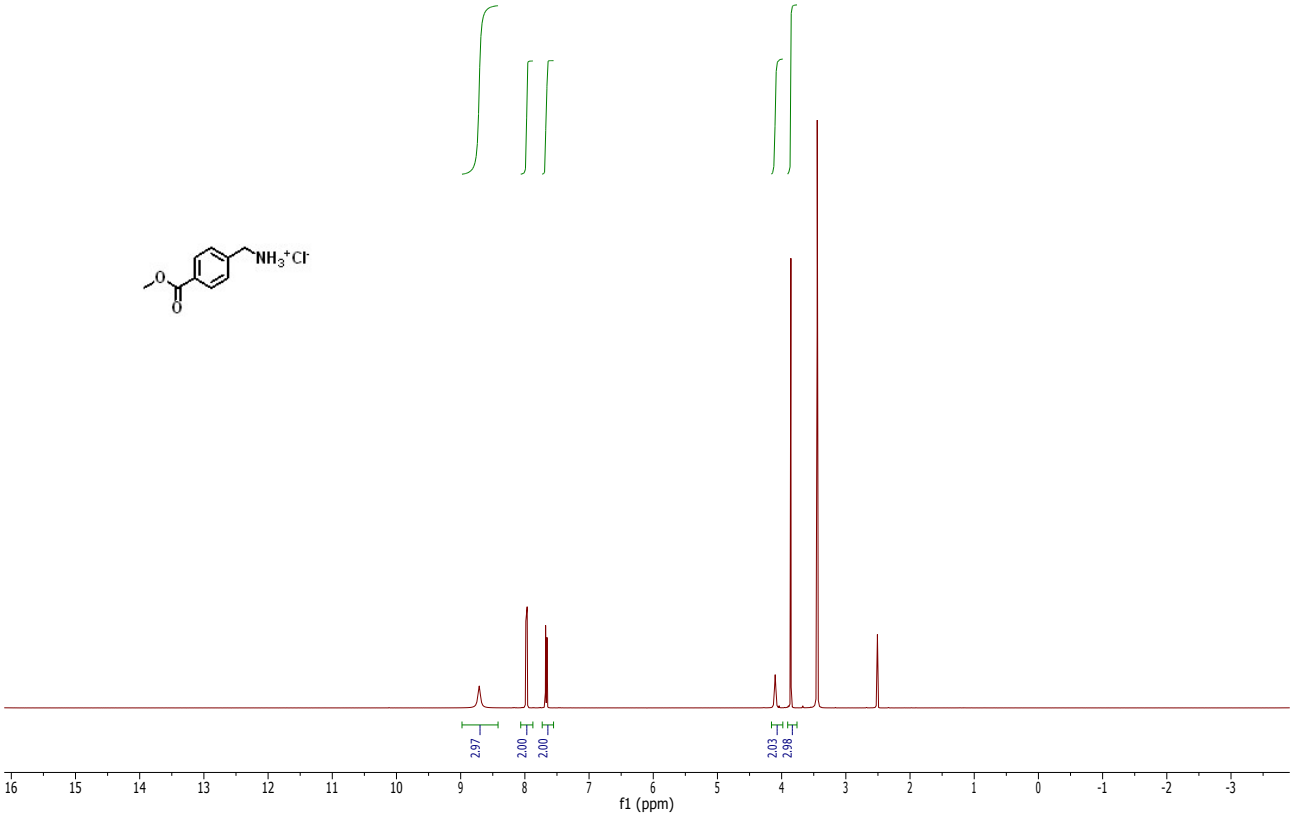
190128.f314.10.fid
Thiru TM3-117
PROTON DMSO {C:\Bruker\TopSpin3.6.0} 1901 14



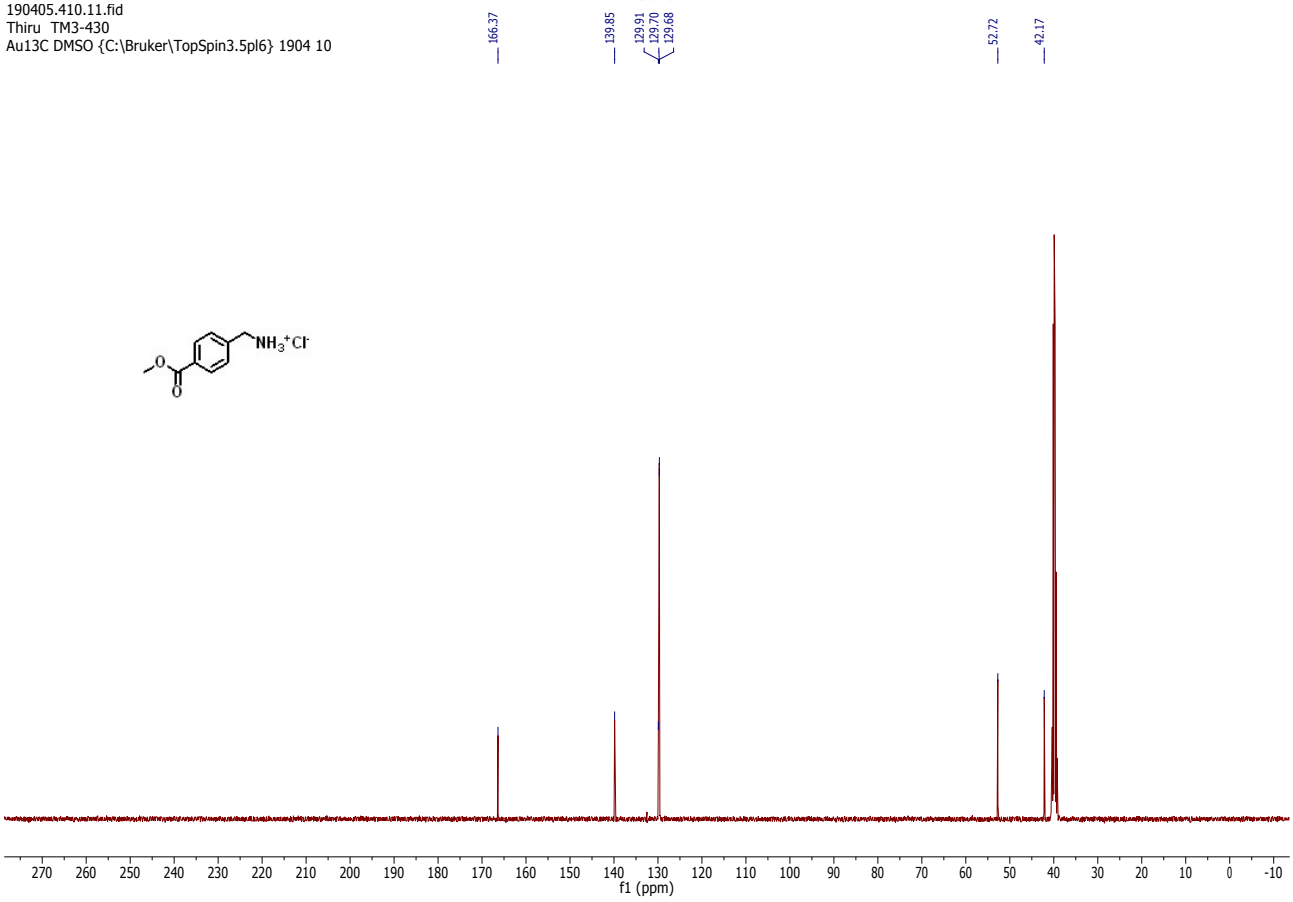
190128.f314.11.fid
Thiru TM3-117
C13CPD DMSO {C:\Bruker\TopSpin3.6.0} 1901 14



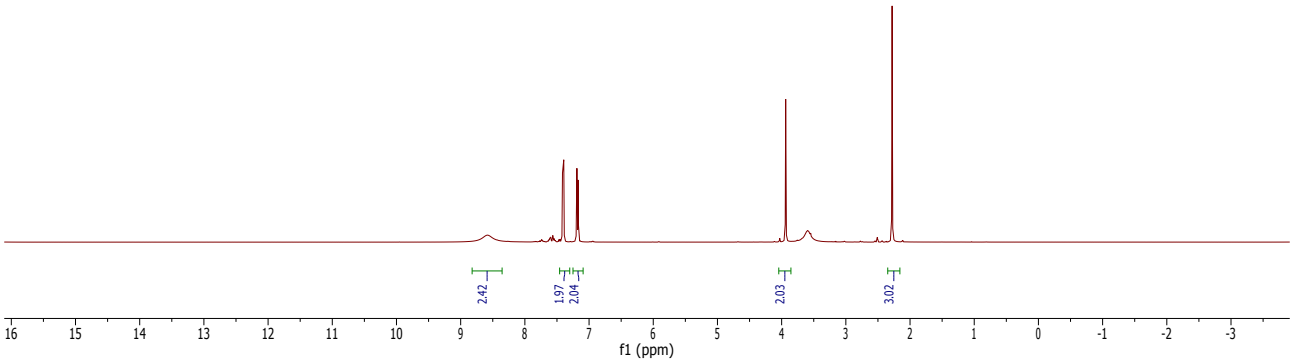
190405.410.10.fid
Thiru TM3-430
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1904 10



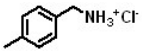
190405.410.11.fid
Thiru TM3-430
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1904 10



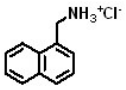
190405.412.10.fid
Thiru TM3-432
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1904 12



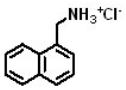
190405.412.11.fid
Thiru TM3-432
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1904 12



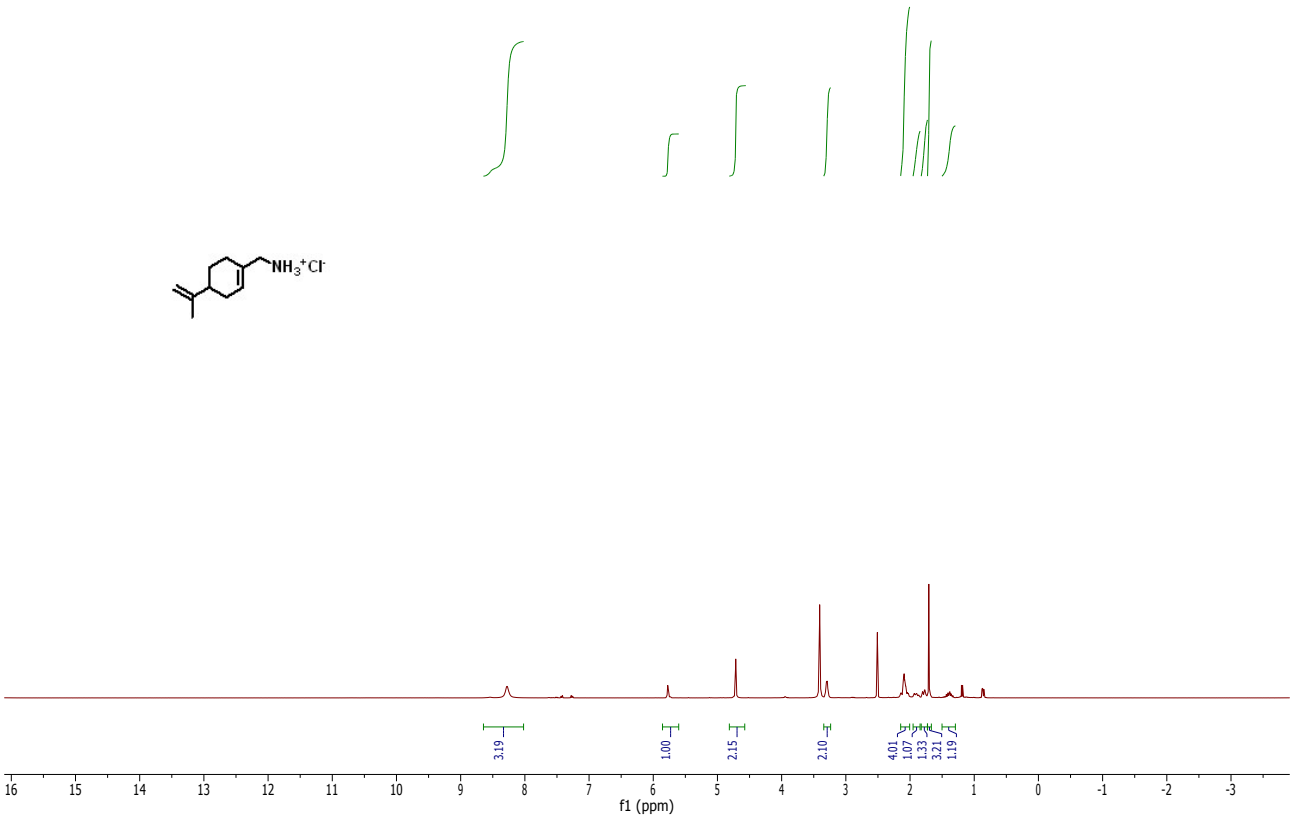
190405.414.10.fid
Thiru TM3-434
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1904 14



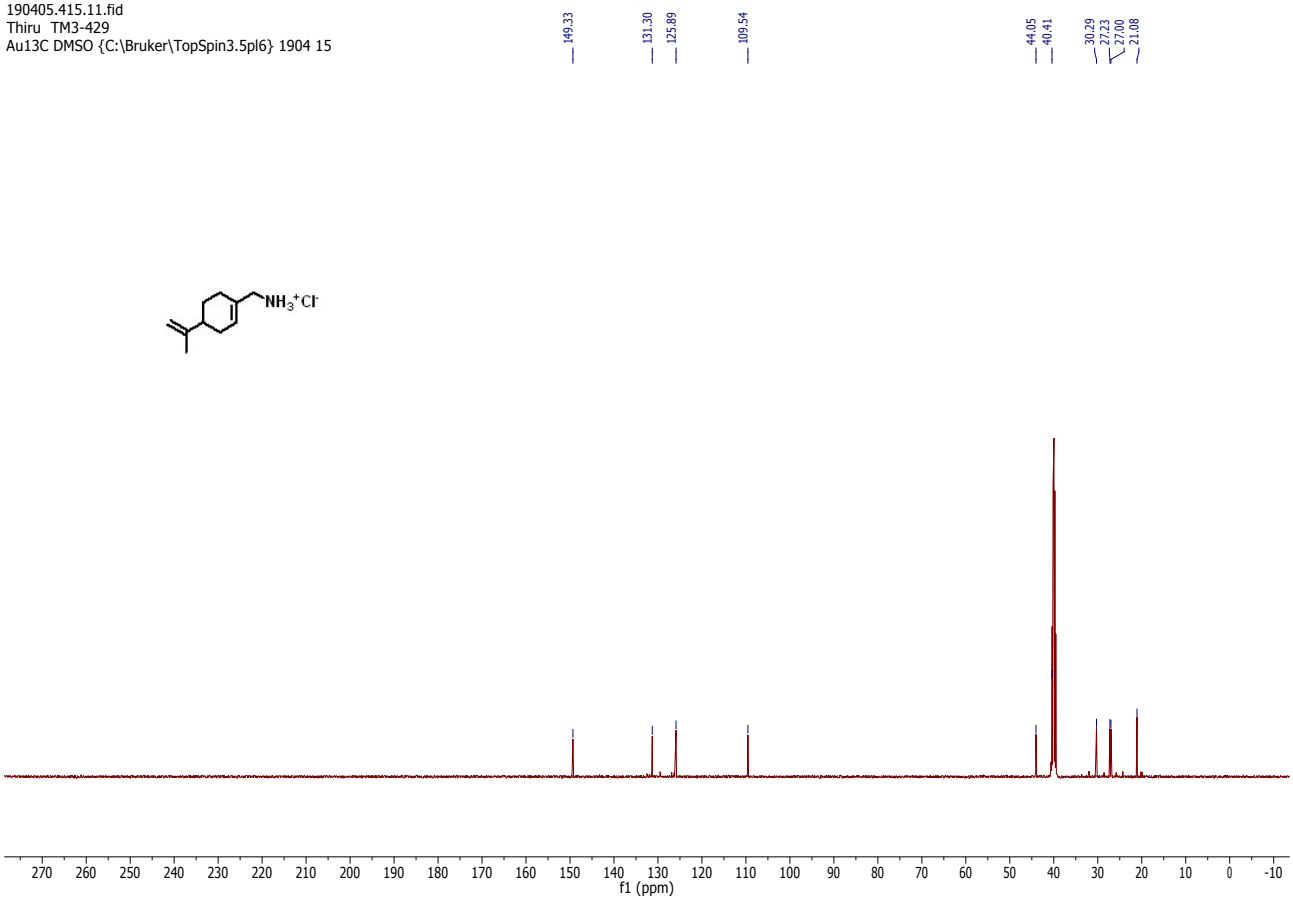
190405.414.11.fid
Thiru TM3-434
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1904 14



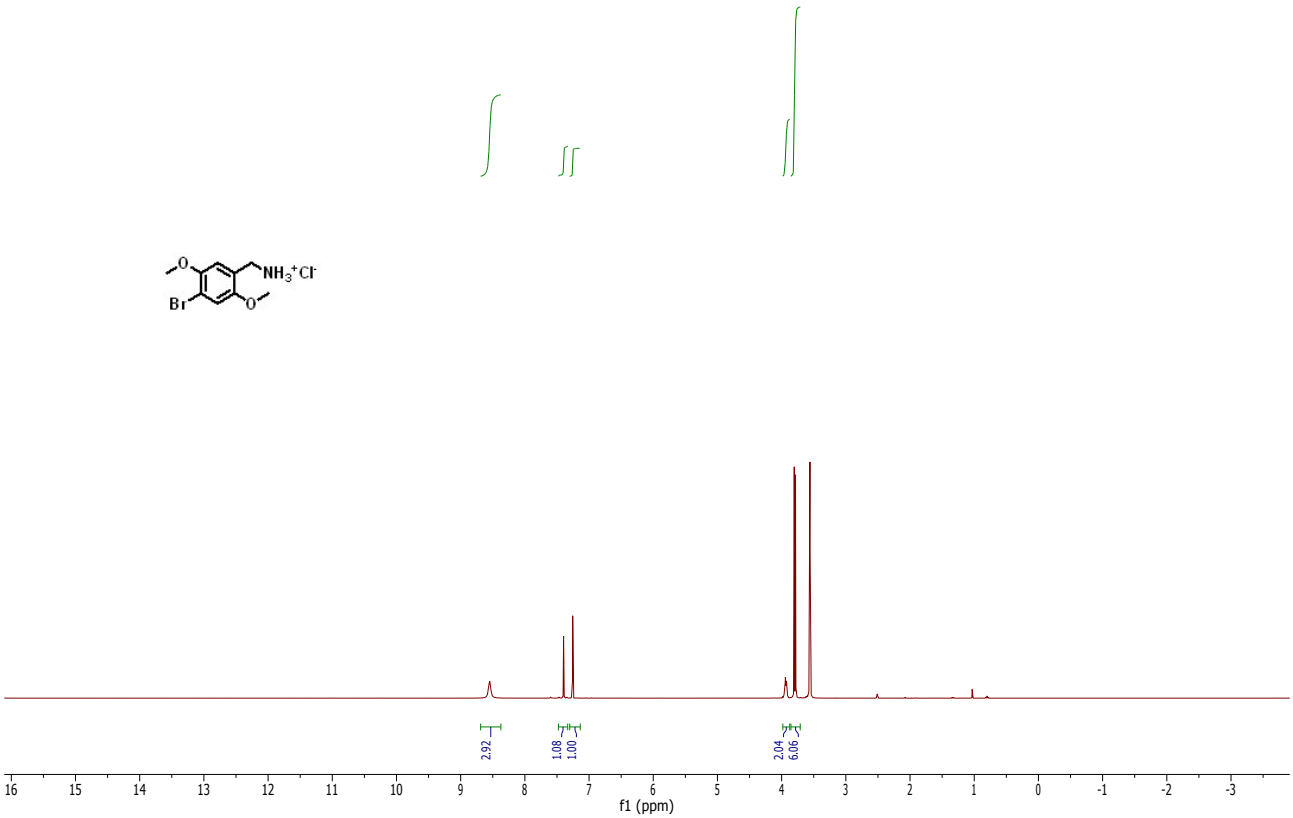
190405.415.10.fid
Thiru TM3-429
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1904 15



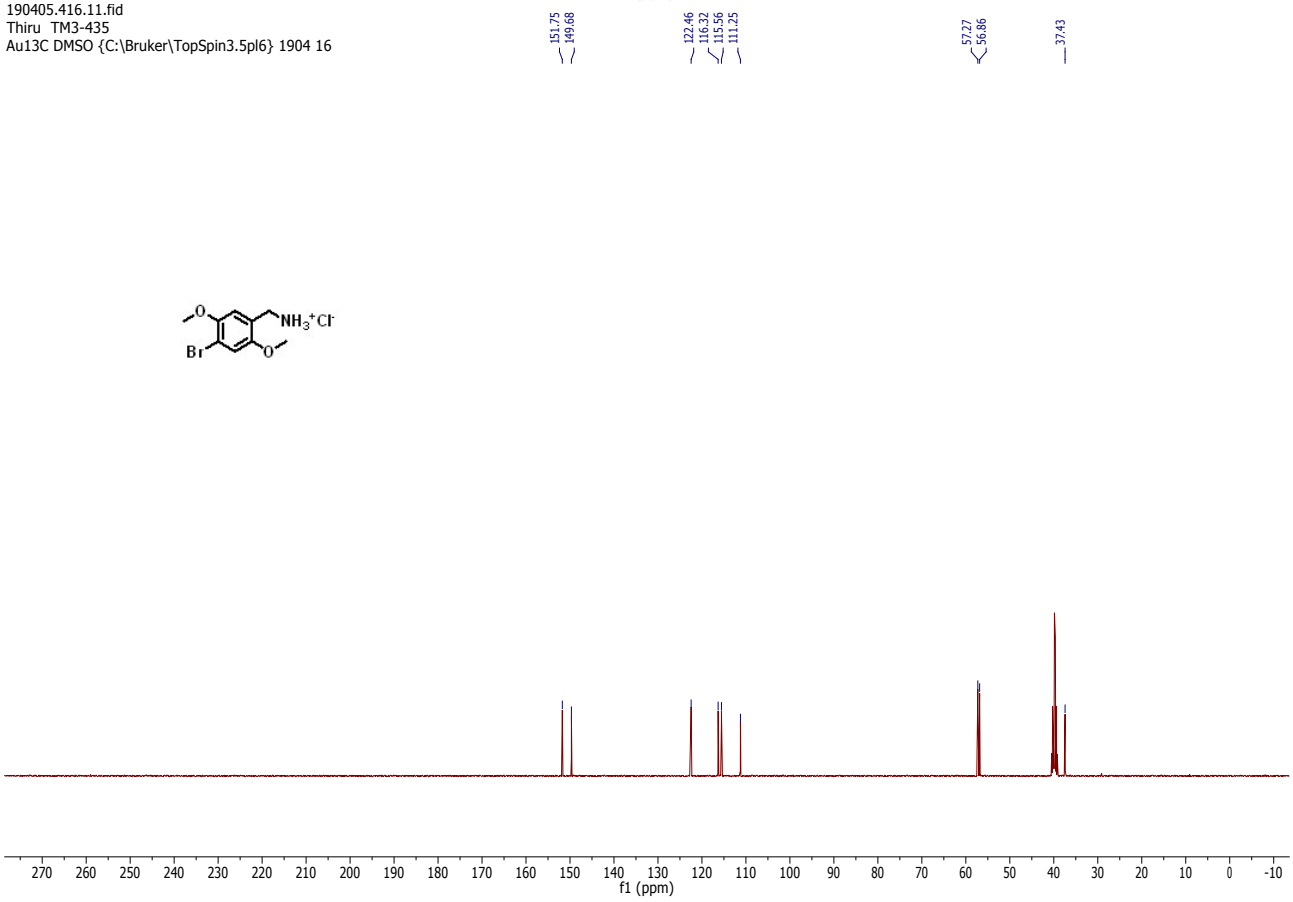
190405.415.11.fid
Thiru TM3-429
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1904 15



190405.416.10.fid
Thiru TM3-435
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1904 16



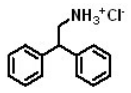
190405.416.11.fid
Thiru TM3-435
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1904 16

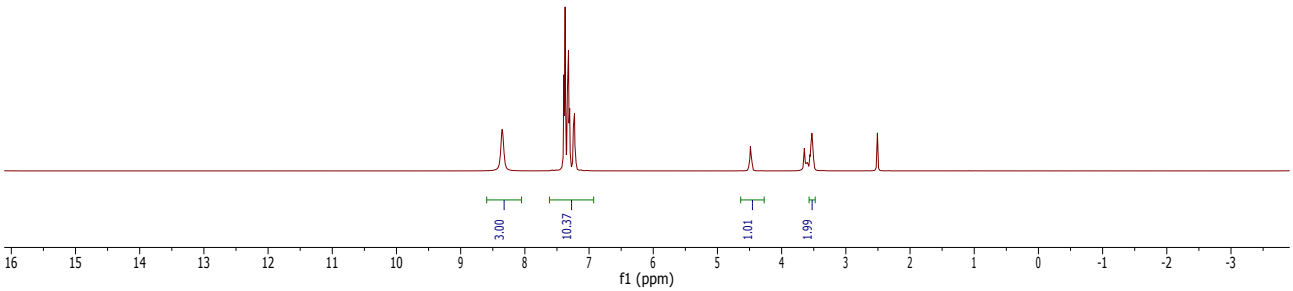


190405.426.10.fid
Thiru TM3-447
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1904 26

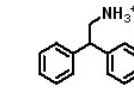
190405.426.11.fid
Thiru TM3-447
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1904 26

190405.427.10.fid
Thiru TM3-448
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1904 27

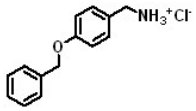




190405.427.11.fid
Thiru TM3-448
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1904 27

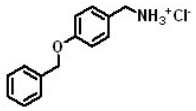


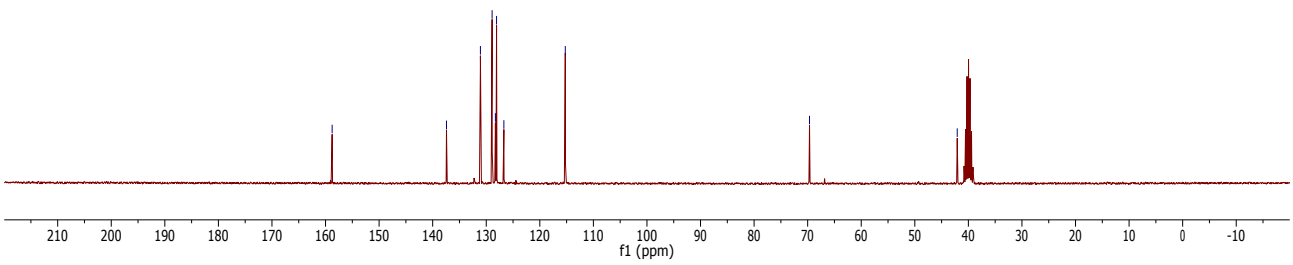
190704.f322.10.fid
Thiru TM3-597
PROTON DMSO {C:\Bruker\TopSpin3.6.0} 1907 22



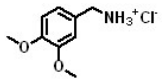
190704.f322.11.fid
Thiru TM3-597
C13CPD DMSO {C:\Bruker\TopSpin3.6.0} 1907 22

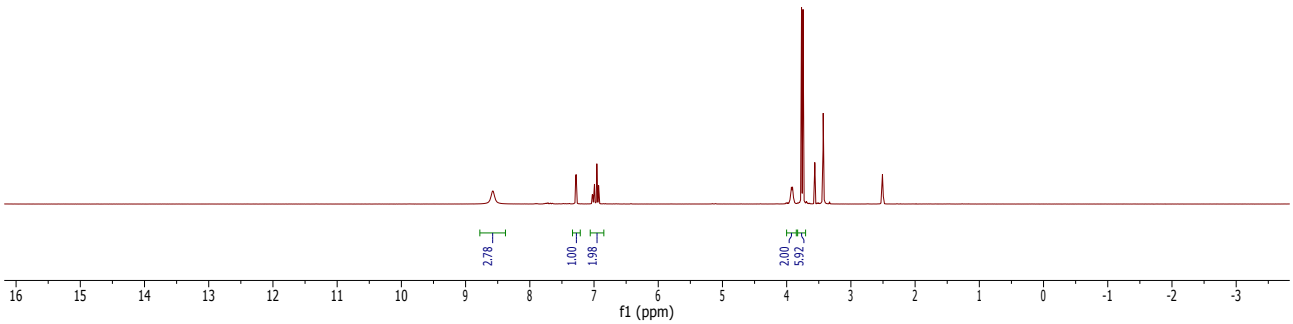
158.77
137.42
131.09
128.91
128.29
128.07
126.71
115.25
69.66
42.08





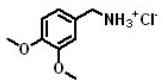
190704.f323.10.fid
Thiru TM3-431
PROTON DMSO {C:\Bruker\TopSpin3.6.0} 1907 23

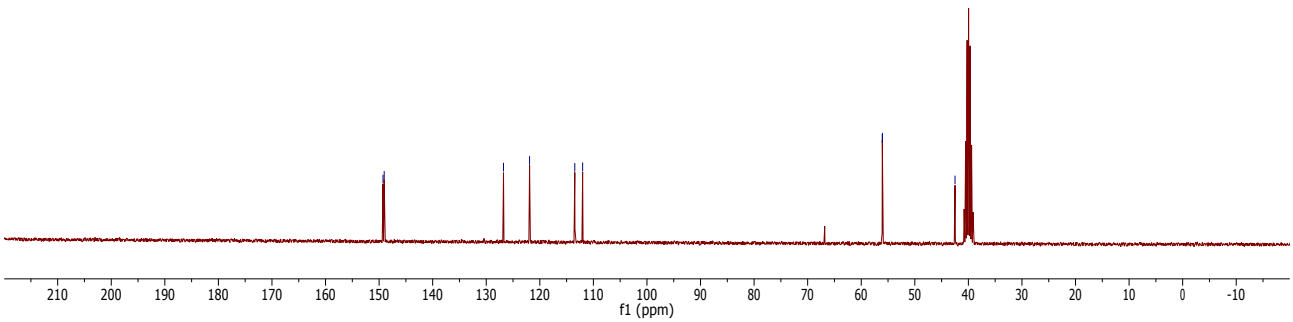




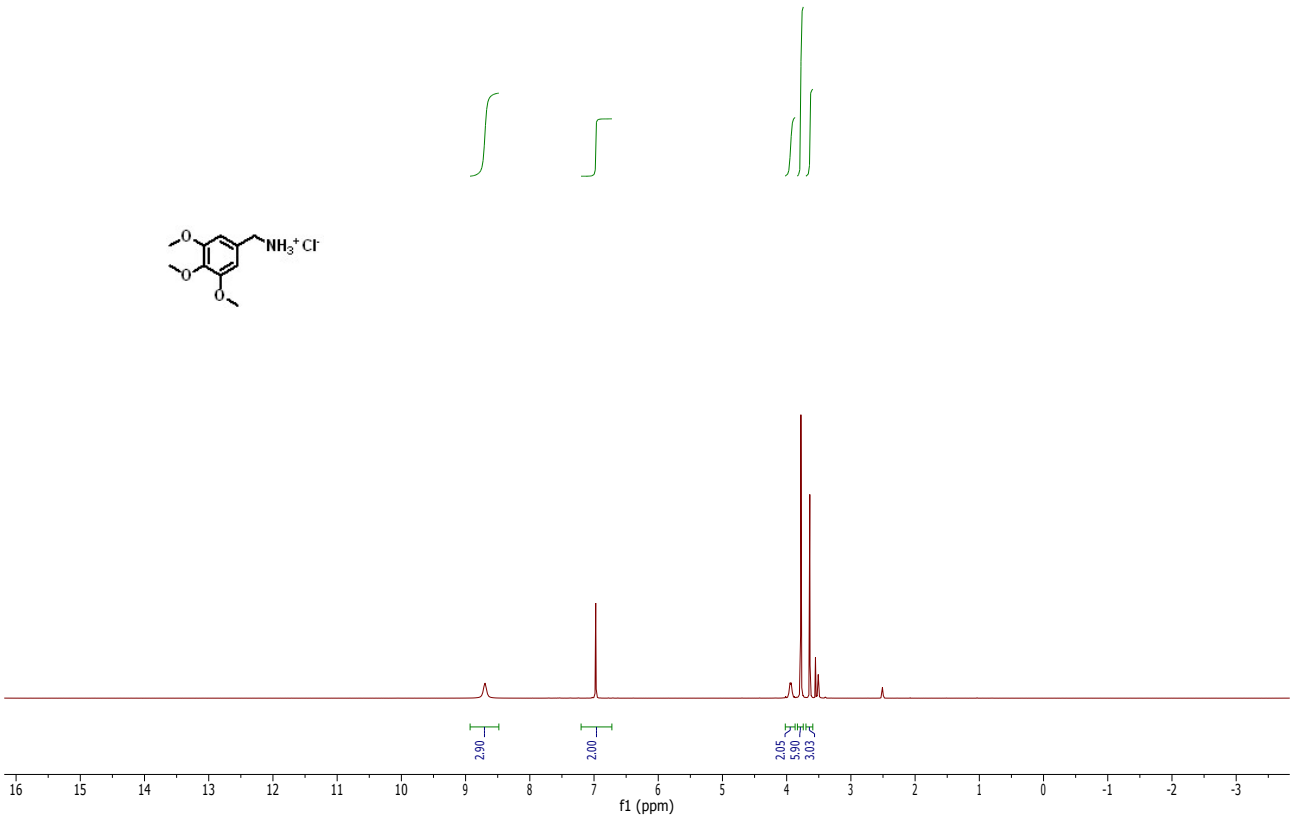
190704.f323.11.fid
Thiru TM3-431
C13CPD DMSO {C:\Bruker\TopSpin3.6.0} 1907 23

149.27
149.05
126.78
121.91
113.47
112.01
56.07
56.04
42.49

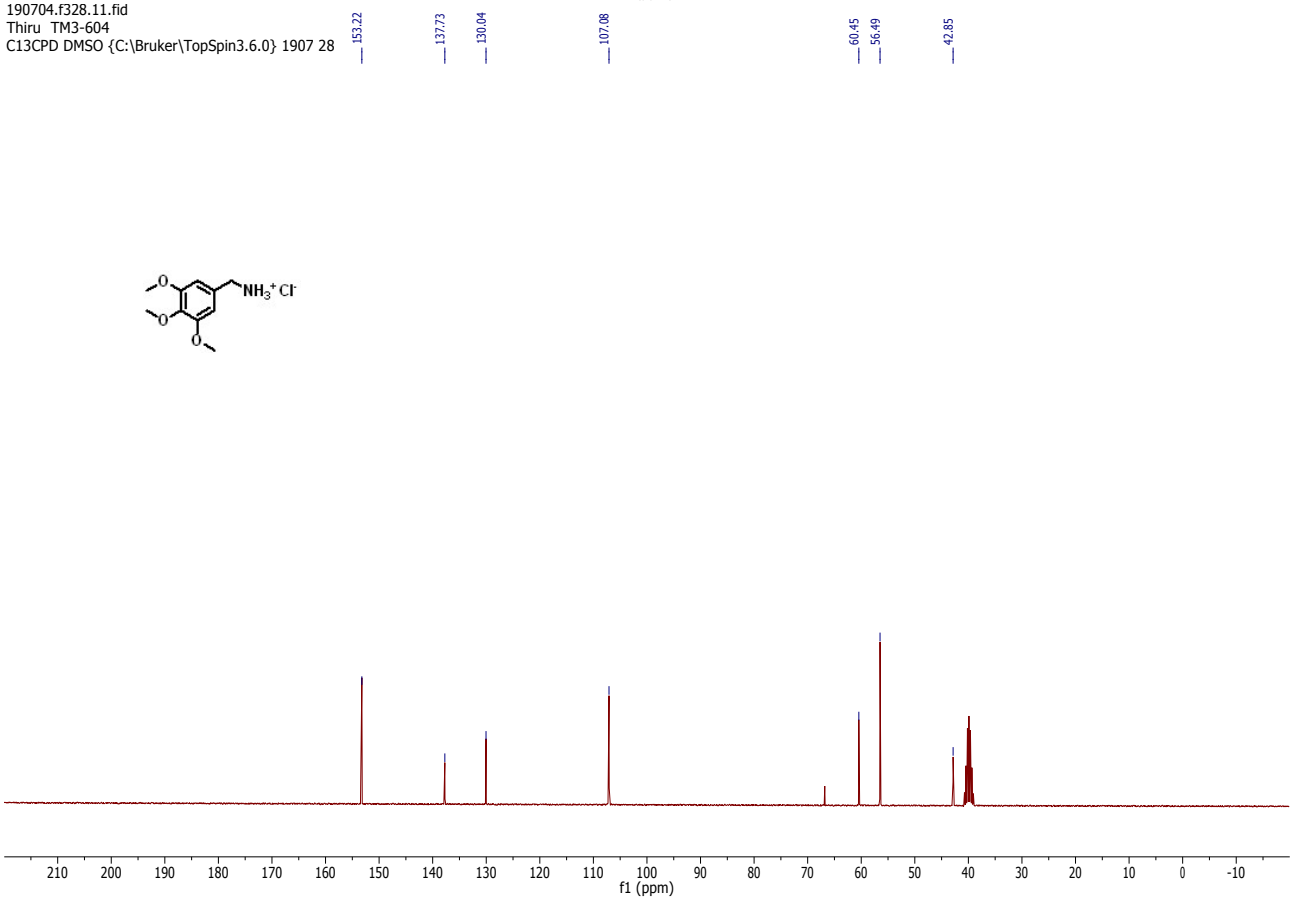




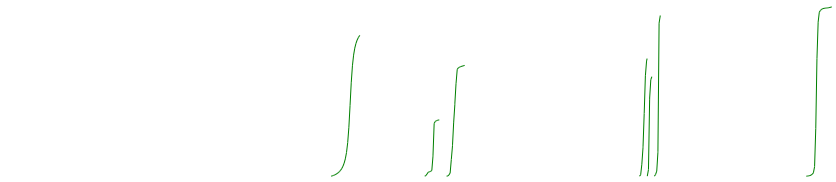
190704.f328.10.fid
Thiru TM3-604
PROTON DMSO {C:\Bruker\TopSpin3.6.0} 1907 28

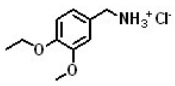


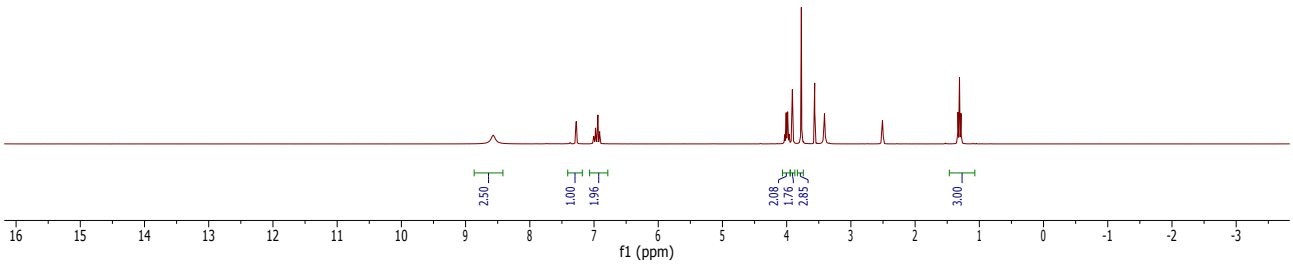
190704.f328.11.fid
Thiru TM3-604
C13CPD DMSO {C:\Bruker\TopSpin3.6.0} 1907 28



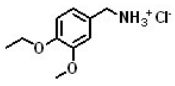
190704.f329.10.fid
Thiru TM3-603
PROTON DMSO {C:\Bruker\TopSpin3.6.0} 1907 29

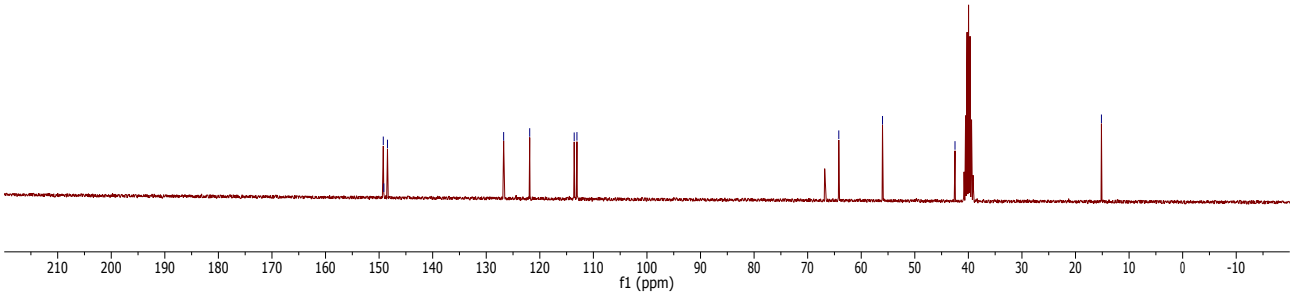




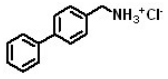


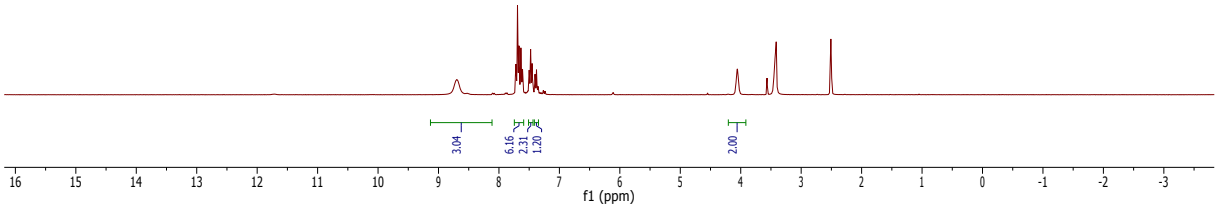
190704.f329.11.fid
Thiru TM3-603
C13CPD DMSO {C:\Bruker\TopSpin3.6.0} 1907 29



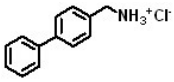


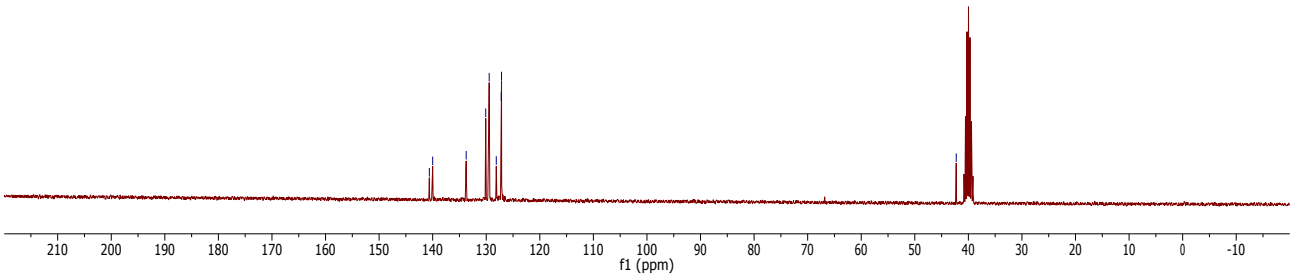
190712.f343.10.fid
Thiru TM3-598
PROTON DMSO {C:\Bruker\TopSpin3.6.0} 1907 43



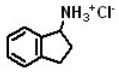


190712.f343.11.fid
Thiru TM3-598
C13CPD DMSO {C:\Bruker\TopSpin3.6.0} 1907 43

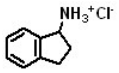




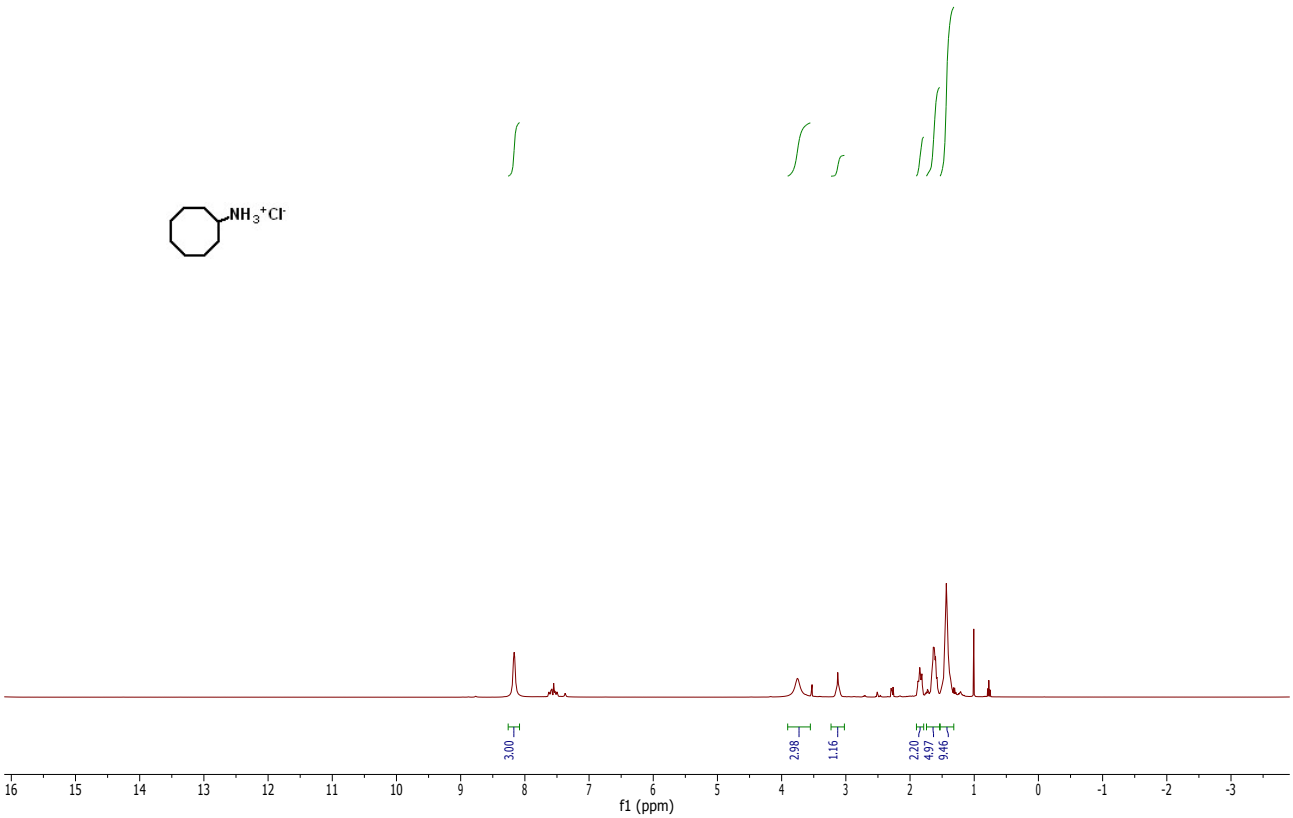
190128.f313.10.fid
Thiru TM7-847
PROTON DMSO {C:\Bruker\TopSpin3.6.0} 1901 13



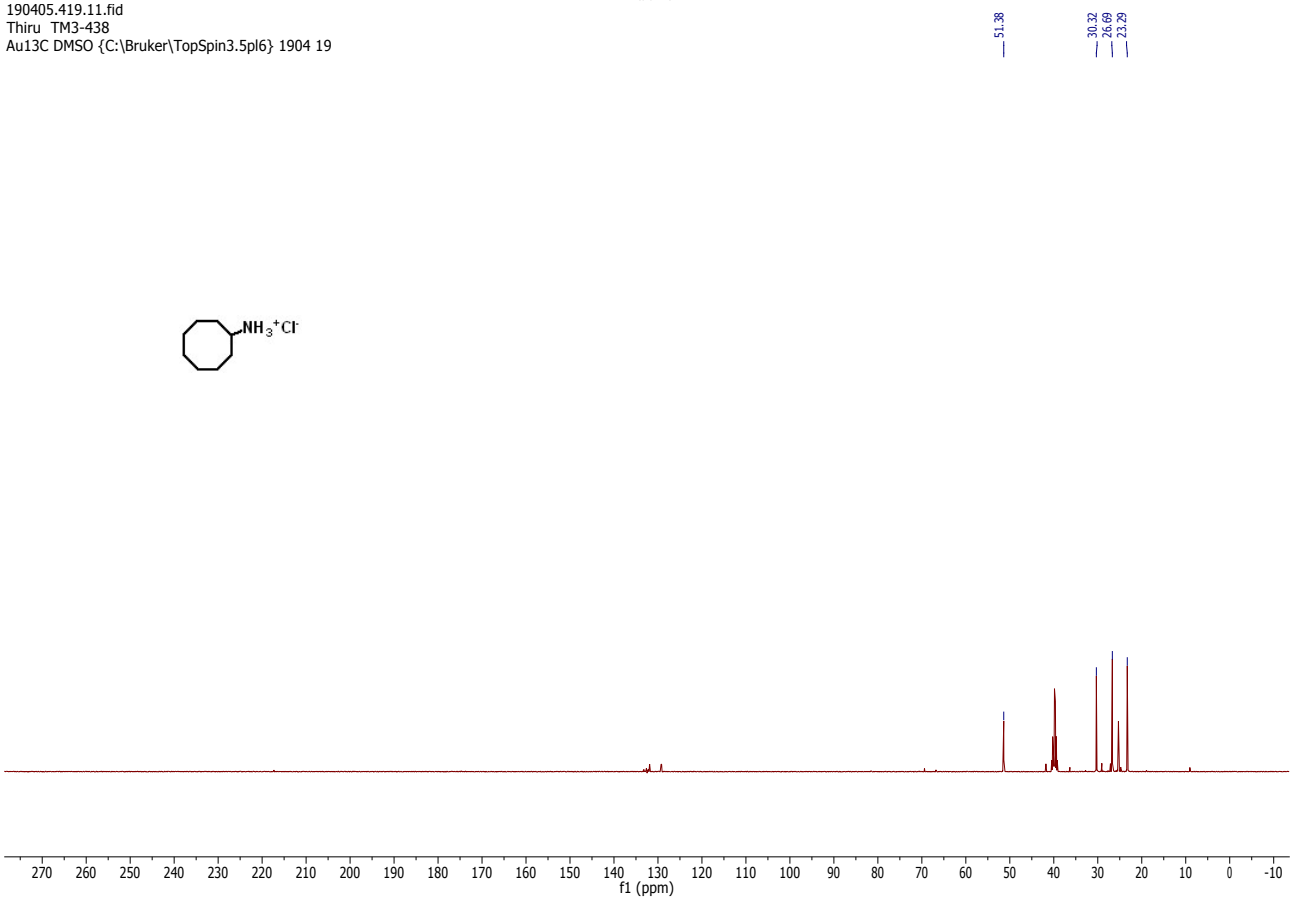
190128.f313.11.fid
Thiru TM7-847
C13CPD DMSO {C:\Bruker\TopSpin3.6.0} 1901 13



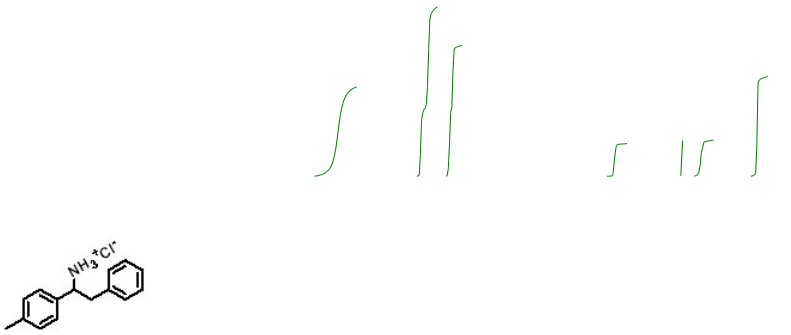
190405.419.10.fid
Thiru TM3-438
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1904 19

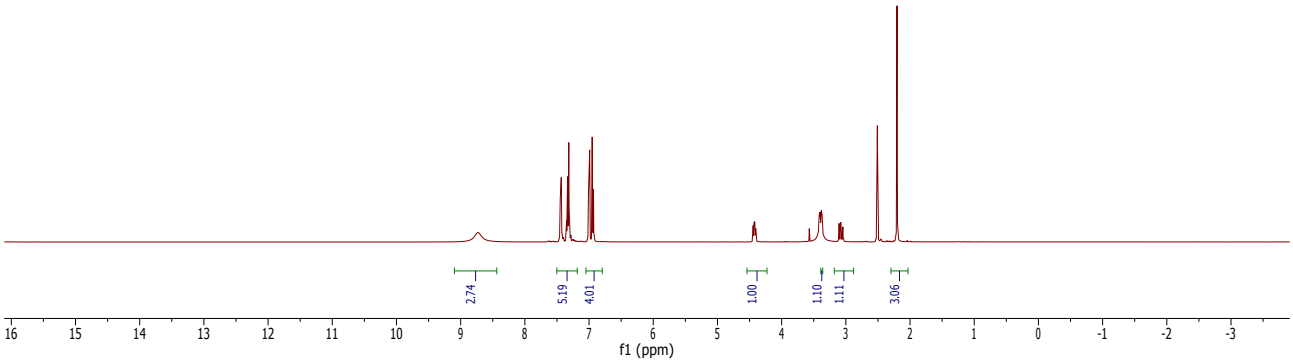


190405.419.11.fid
Thiru TM3-438
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1904 19

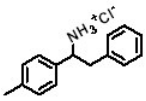


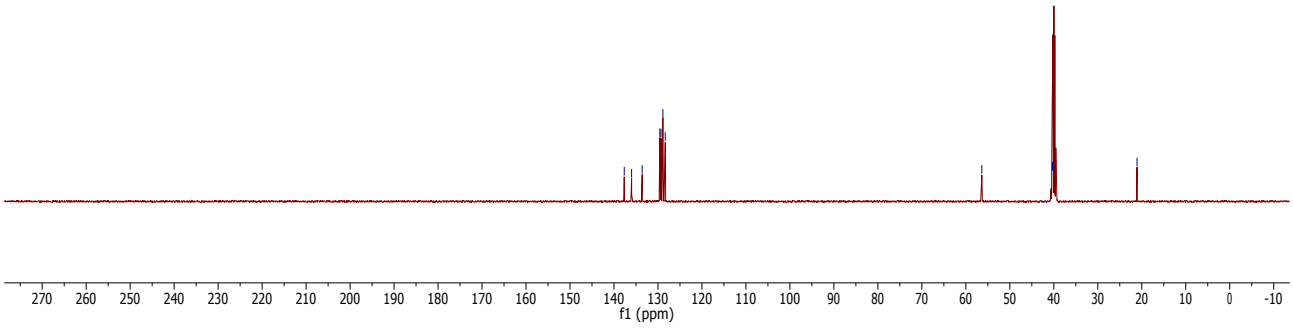
190405.424.10.fid
Thiru TM3-443
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1904 24



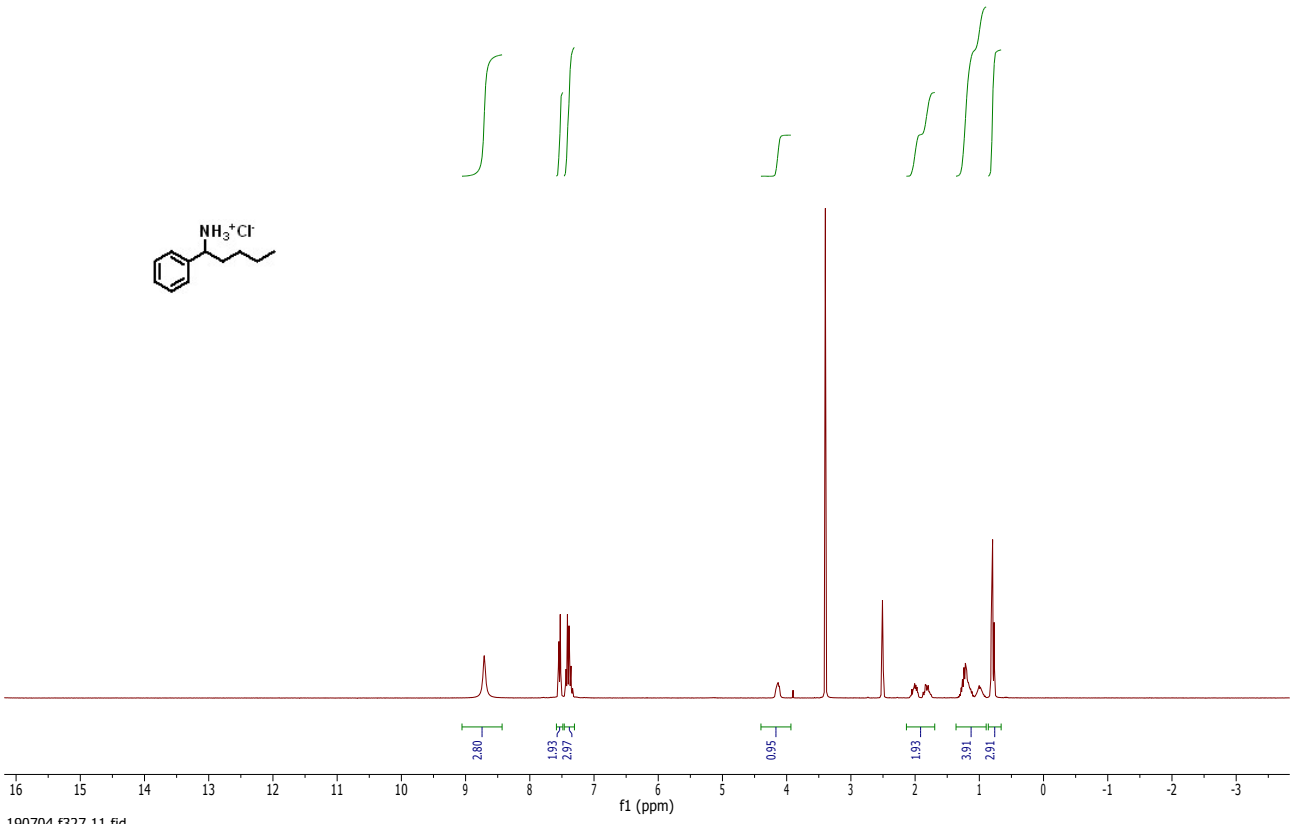


190405.424.11.fid
Thiru TM3-443
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1904 24

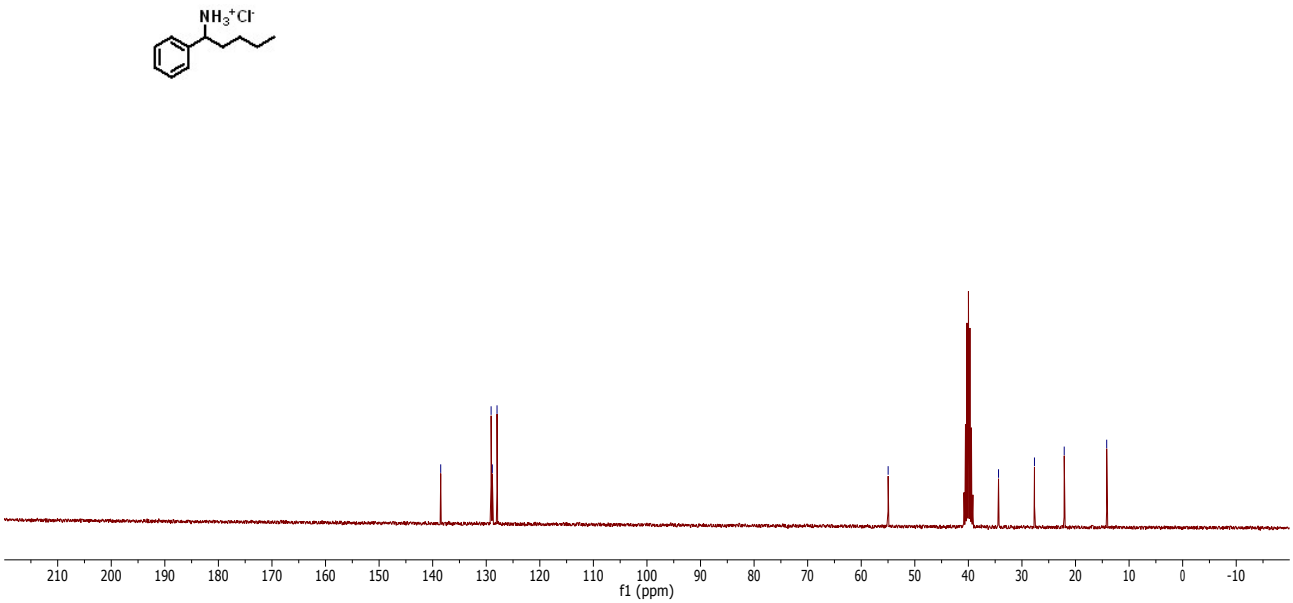




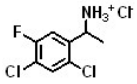
190704.f327.10.fid
Thiru TM3-444
PROTON DMSO {C:\Bruker\TopSpin3.6.0} 1907 27

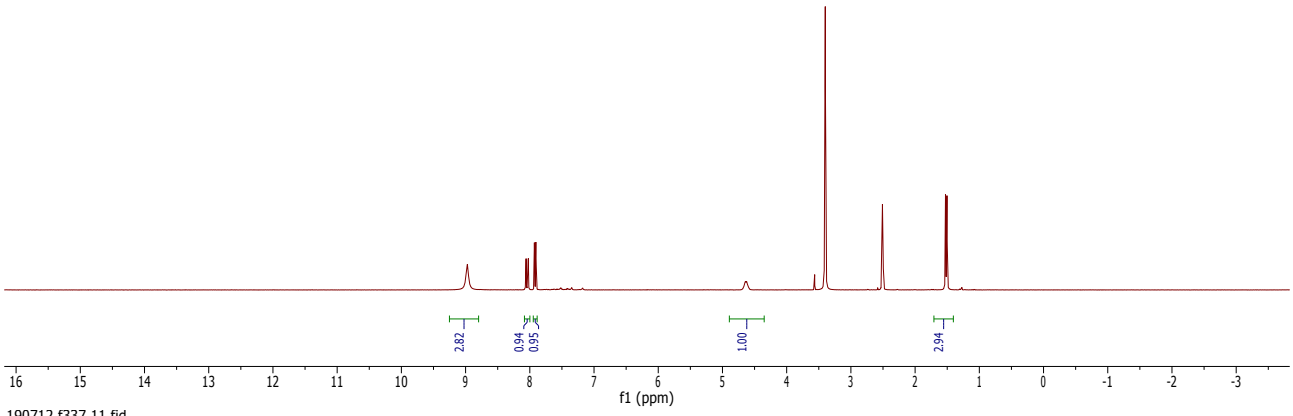


190704.f327.11.fid
Thiru TM3-444
C13CPD DMSO {C:\Bruker\TopSpin3.6.0} 1907 27



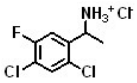
190712.f337.10.fid
Thiru TM3-440
PROTON DMSO {C:\Bruker\TopSpin3.6.0} 1907 37

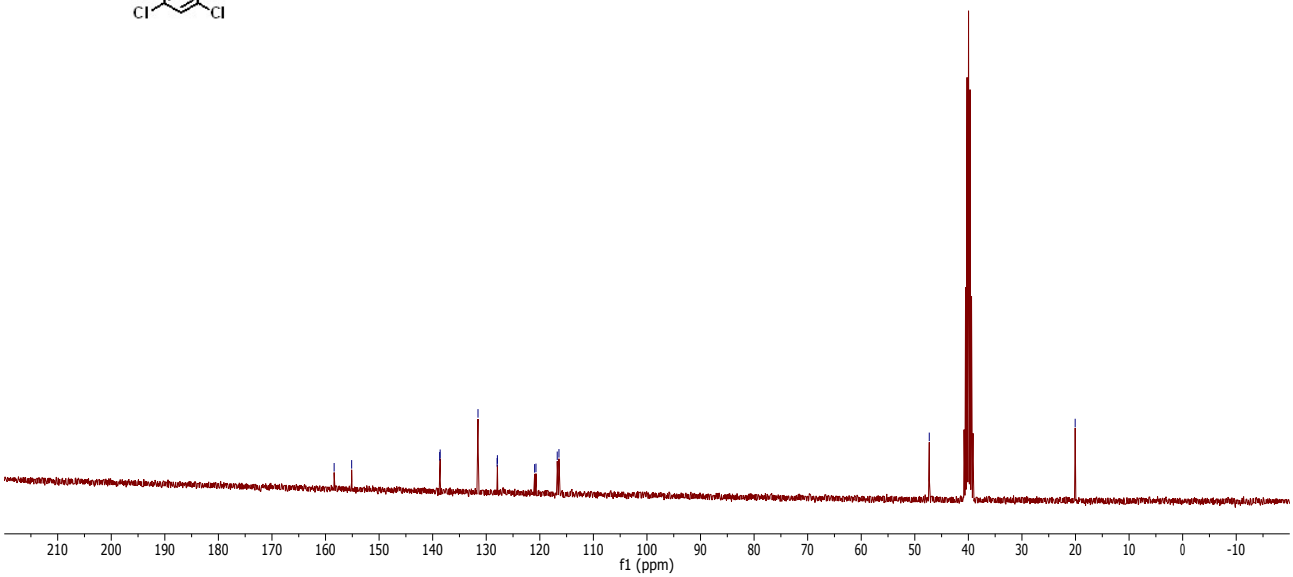




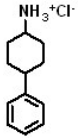
190712.f337.11.fid
Thiru TM3-440
C13CPD DMSO {C:\Bruker\TopSpin3.6.0} 1907 37

158.39
155.12
138.69
138.60
131.54
127.96
127.92
120.97
120.71
116.75
116.43
47.30
20.06

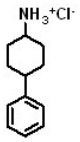


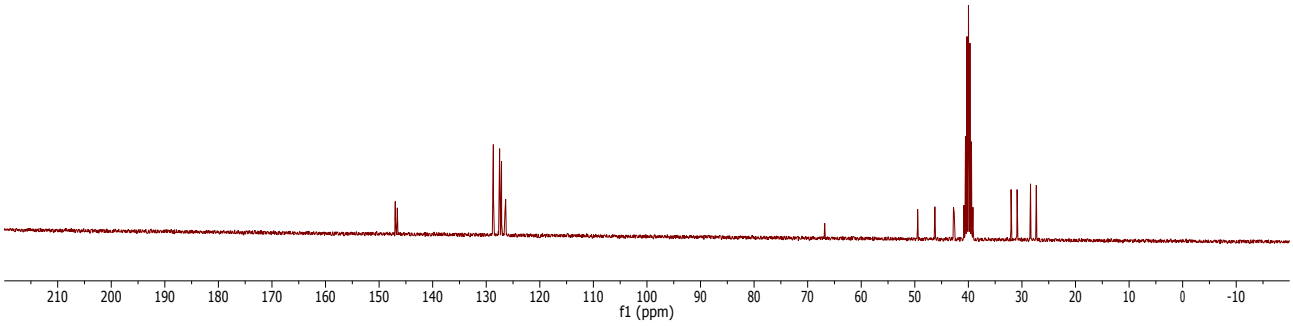


190712.f339.10.fid
Thiru TM3-599
PROTON DMSO {C:\Bruker\TopSpin3.6.0} 1907 39

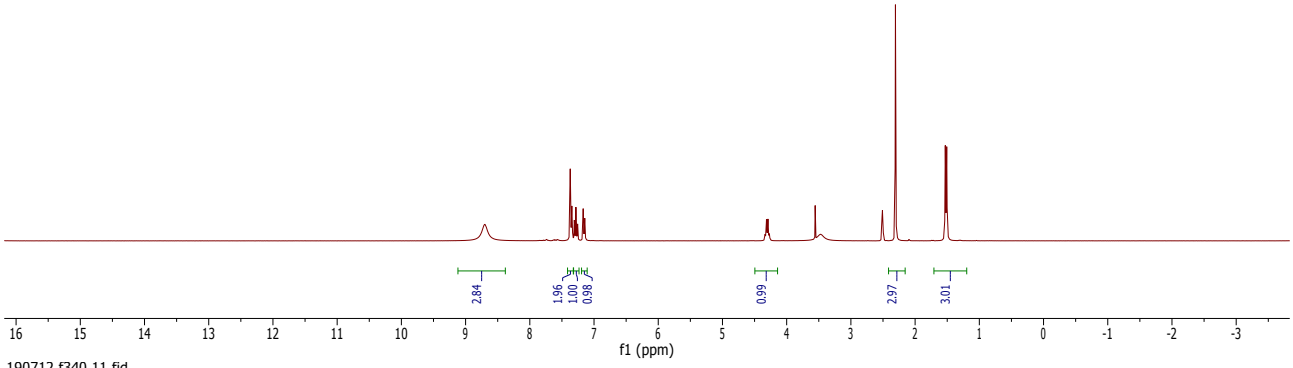


190712.f339.11.fid
Thiru TM3-599
C13CPD DMSO {C:\Bruker\TopSpin3.6.0} 1907 39



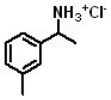


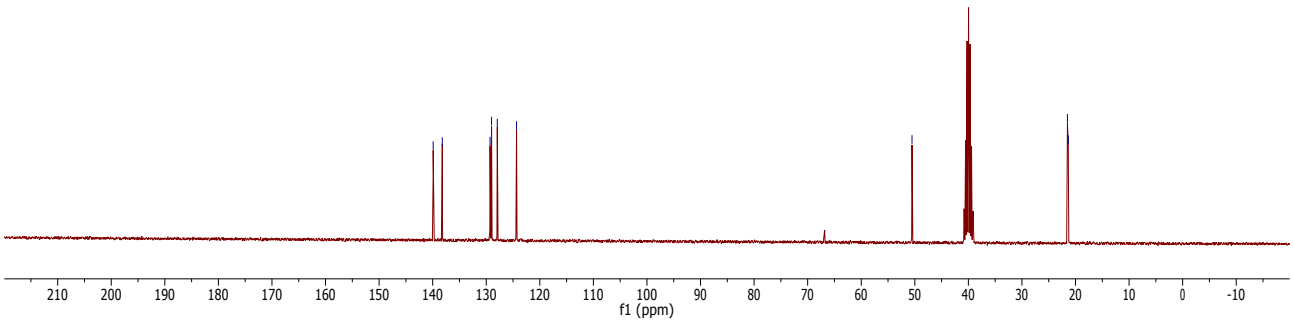
190712.f340.10.fid
Thiru TM3-600
PROTON DMSO {C:\Bruker\TopSpin3.6.0} 1907 40



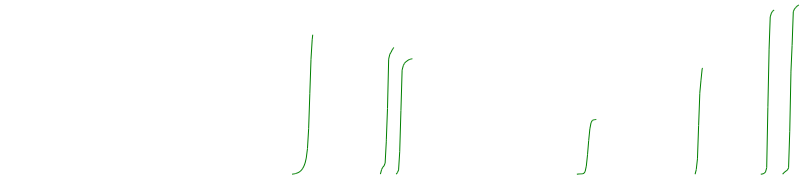
190712.f340.11.fid
Thiru TM3-600
C13CPD DMSO {C:\Bruker\TopSpin3.6.0} 1907 40

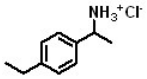
13C NMR (175 MHz, DMSO) δ 139.91, 138.21, 129.28, 129.00, 127.94, 124.35, 50.51, 21.34.

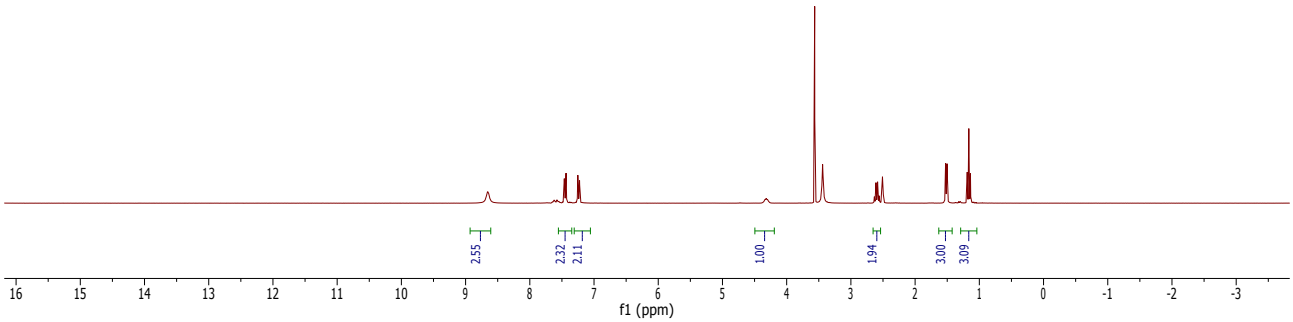




190712.f342.10.fid
Thiru TM3-602
PROTON DMSO {C:\Bruker\TopSpin3.6.0} 1907 42

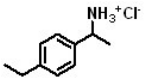


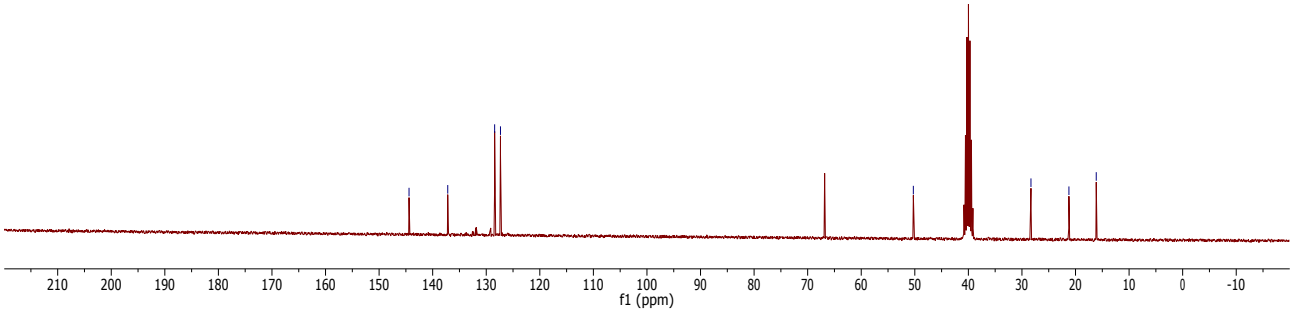




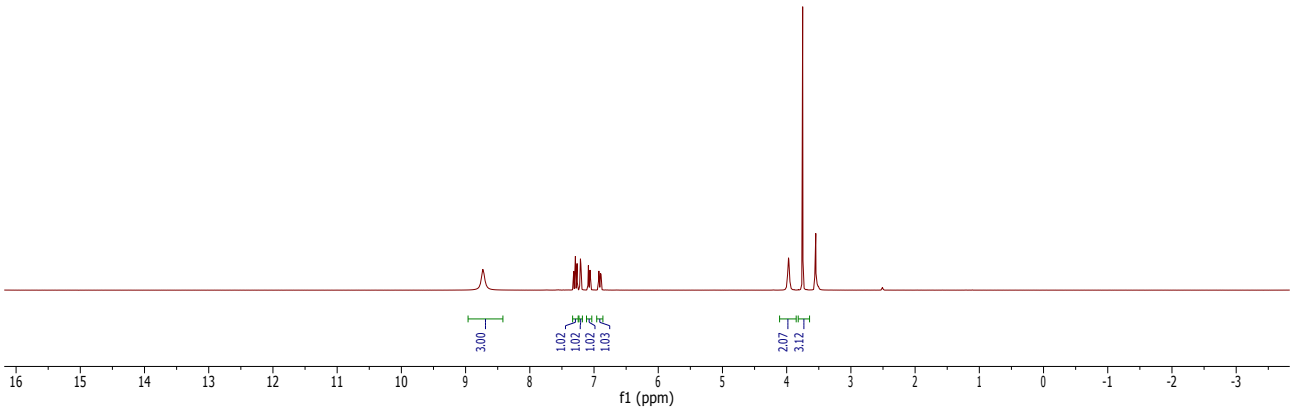
190712.f342.11.fid
Thiru TM3-602
C13CPD DMSO {C:\Bruker\TopSpin3.6.0} 1907 42

144.41
137.19
128.43
127.34
50.27
28.32
21.23
16.13



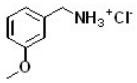


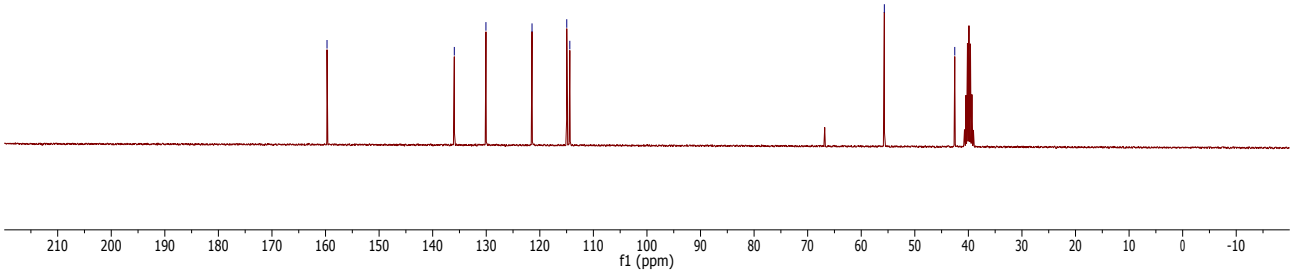
190905.f321.10.fid
Thiru TM3-339
PROTON DMSO {C:\Bruker\TopSpin3.6.0} 1909 21



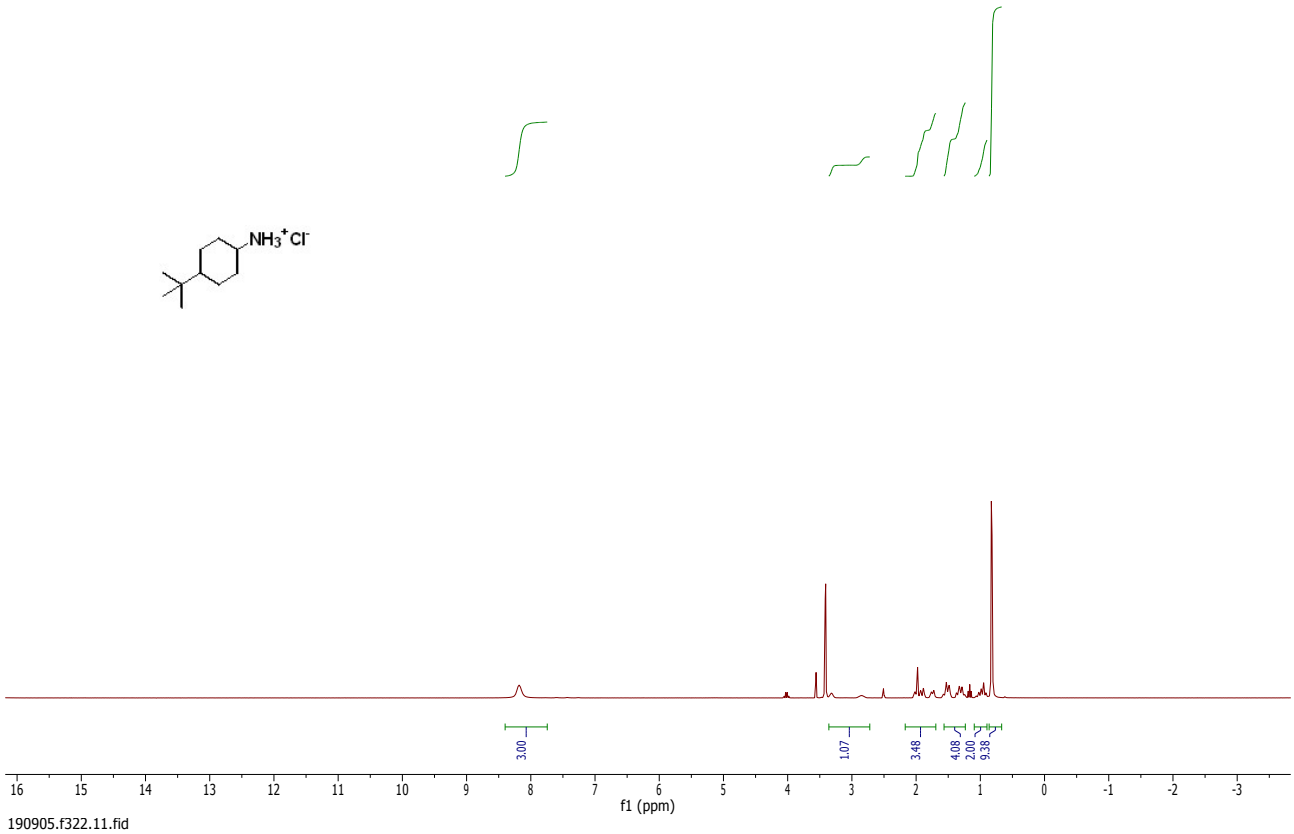
190905.f321.11.fid
Thiru TM3-339
C13CPD DMSO {C:\Bruker\TopSpin3.6.0} 1909 21

159.72
135.96
130.06
121.45
114.97
114.40
55.69
42.54

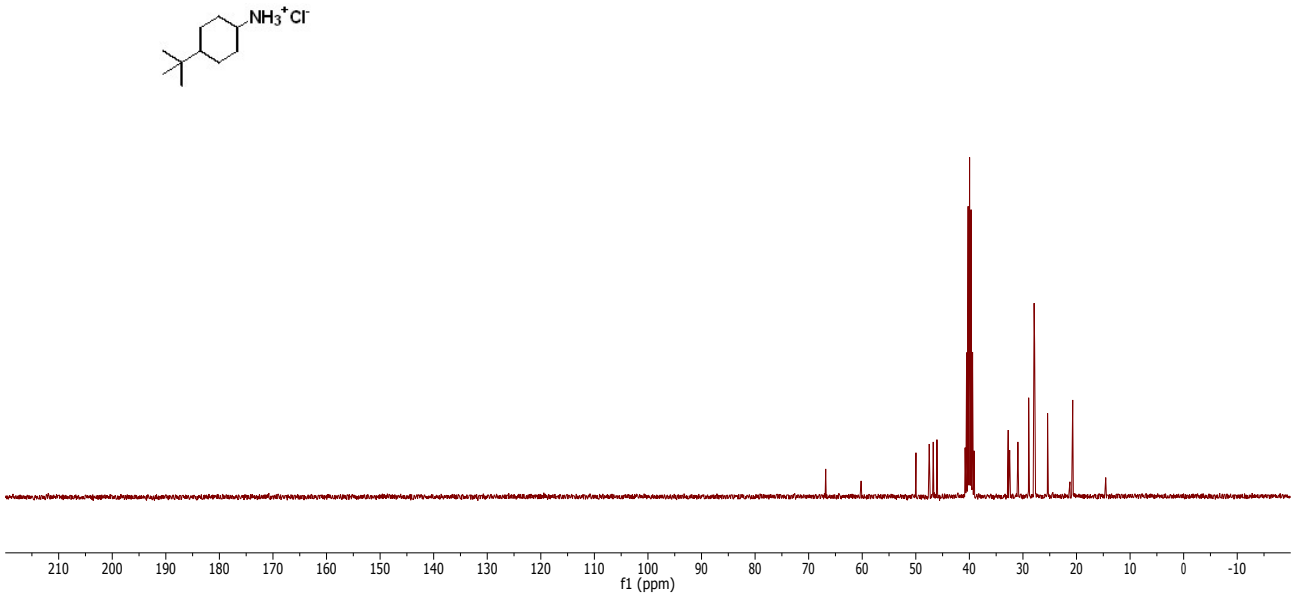




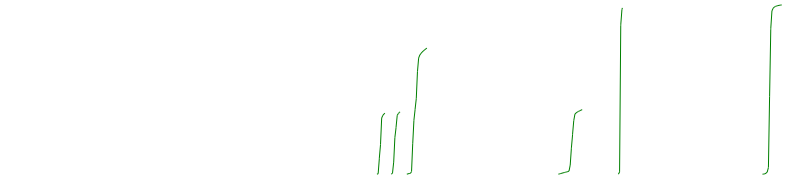
190905.f322.10.fid
Thiru TM3-398
PROTON DMSO {C:\Bruker\TopSpin3.6.0} 1909 22

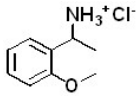


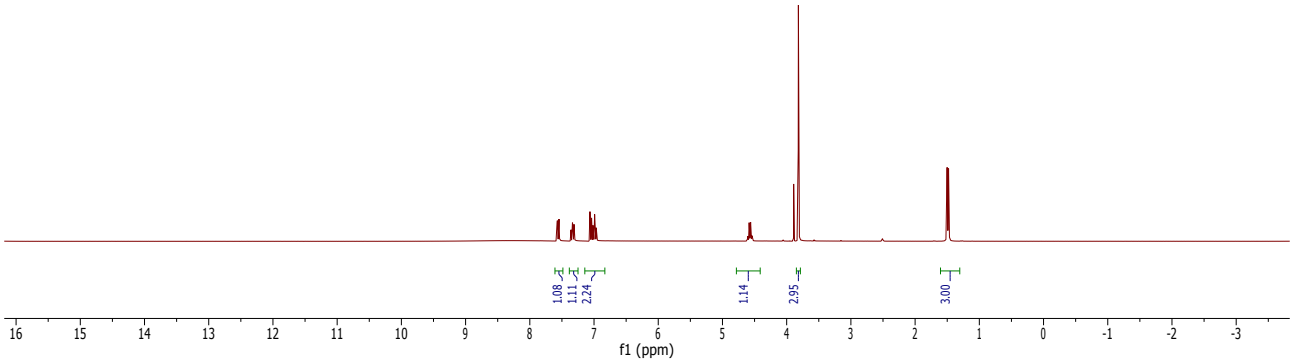
190905.f322.11.fid
Thiru TM3-398
C13CPD DMSO {C:\Bruker\TopSpin3.6.0} 1909 22



190905.f323.10.fid
Thiru TM3-442
PROTON DMSO {C:\Bruker\TopSpin3.6.0} 1909 23

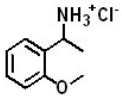


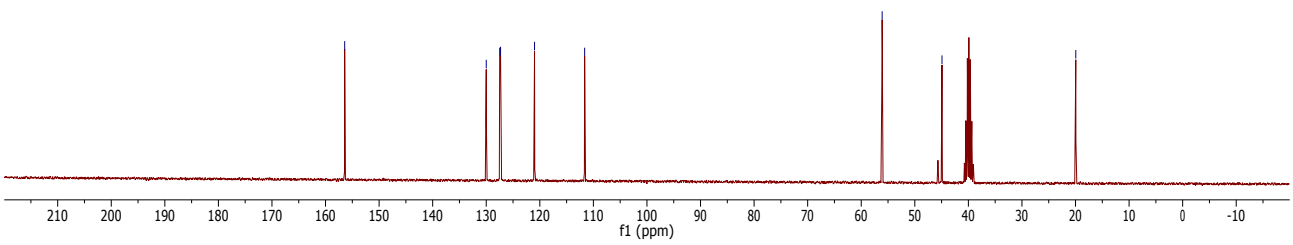




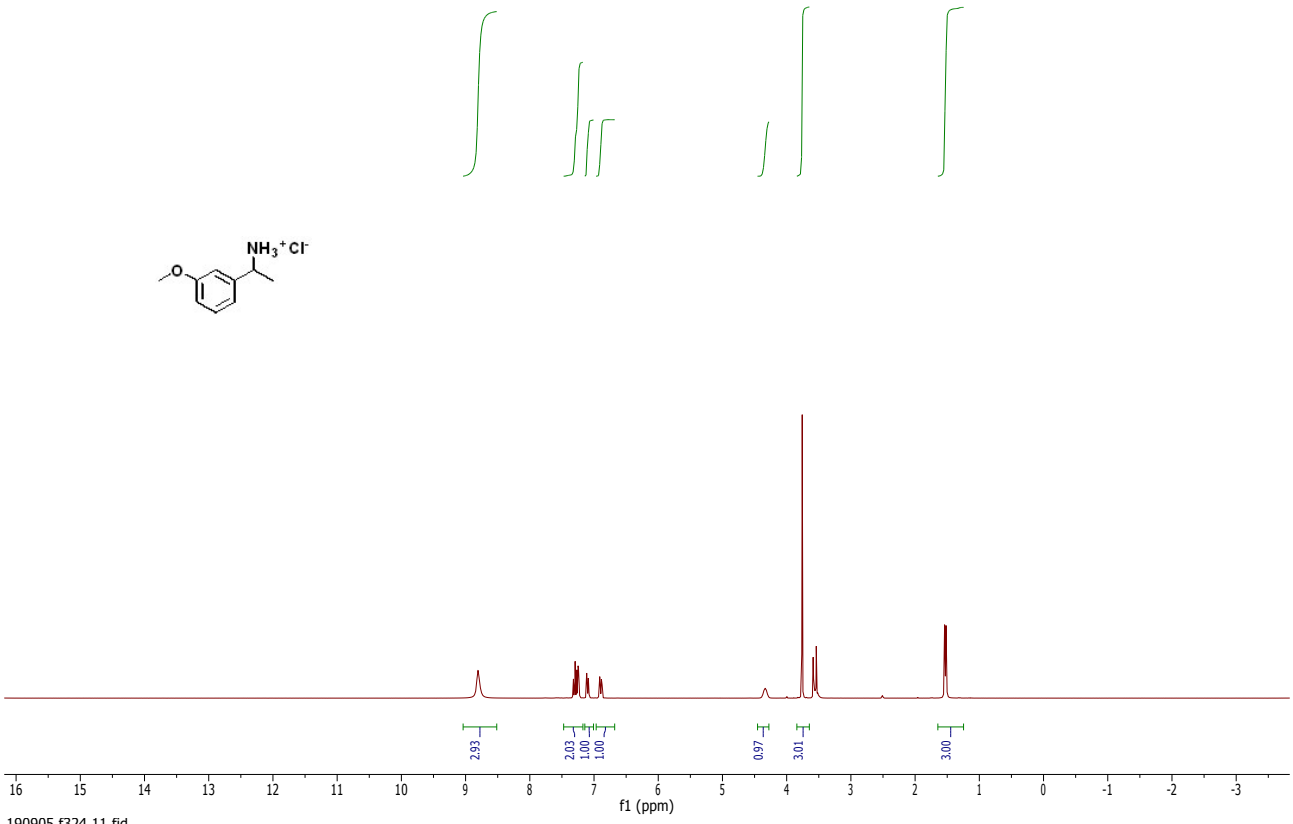
190905.f323.11.fid
Thiru TM3-442
C13CPD DMSO {C:\Bruker\TopSpin3.6.0} 1909 23

156.43
130.00
127.49
127.33
120.98
111.63
56.10
44.93
19.95

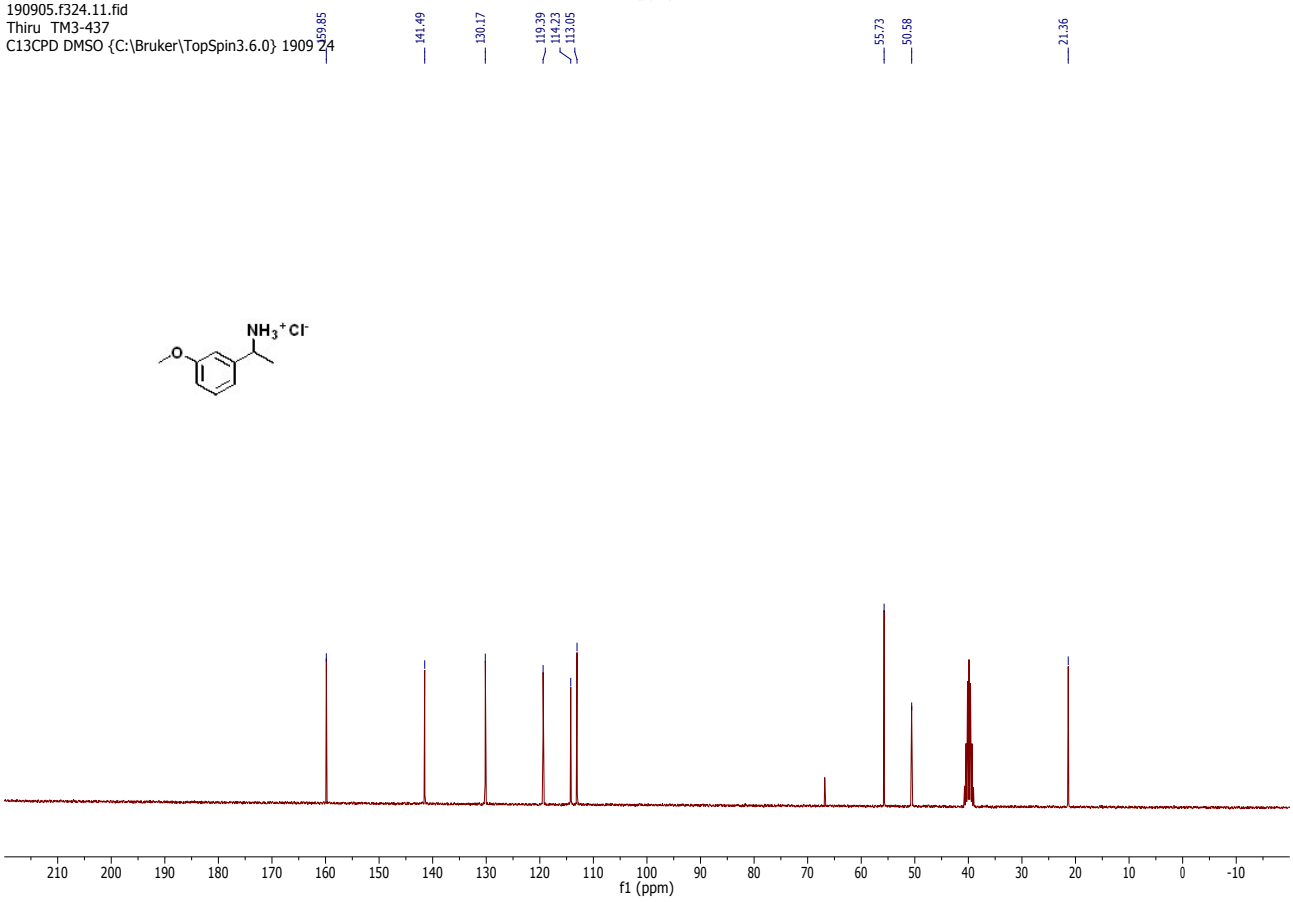




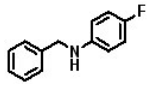
190905.f324.10.fid
Thiru TM3-437
PROTON DMSO {C:\Bruker\TopSpin3.6.0} 1909 24



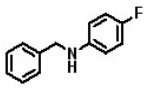
190905.f324.11.fid
Thiru TM3-437
C13CPD DMSO {C:\Bruker\TopSpin3.6.0} 1909 24



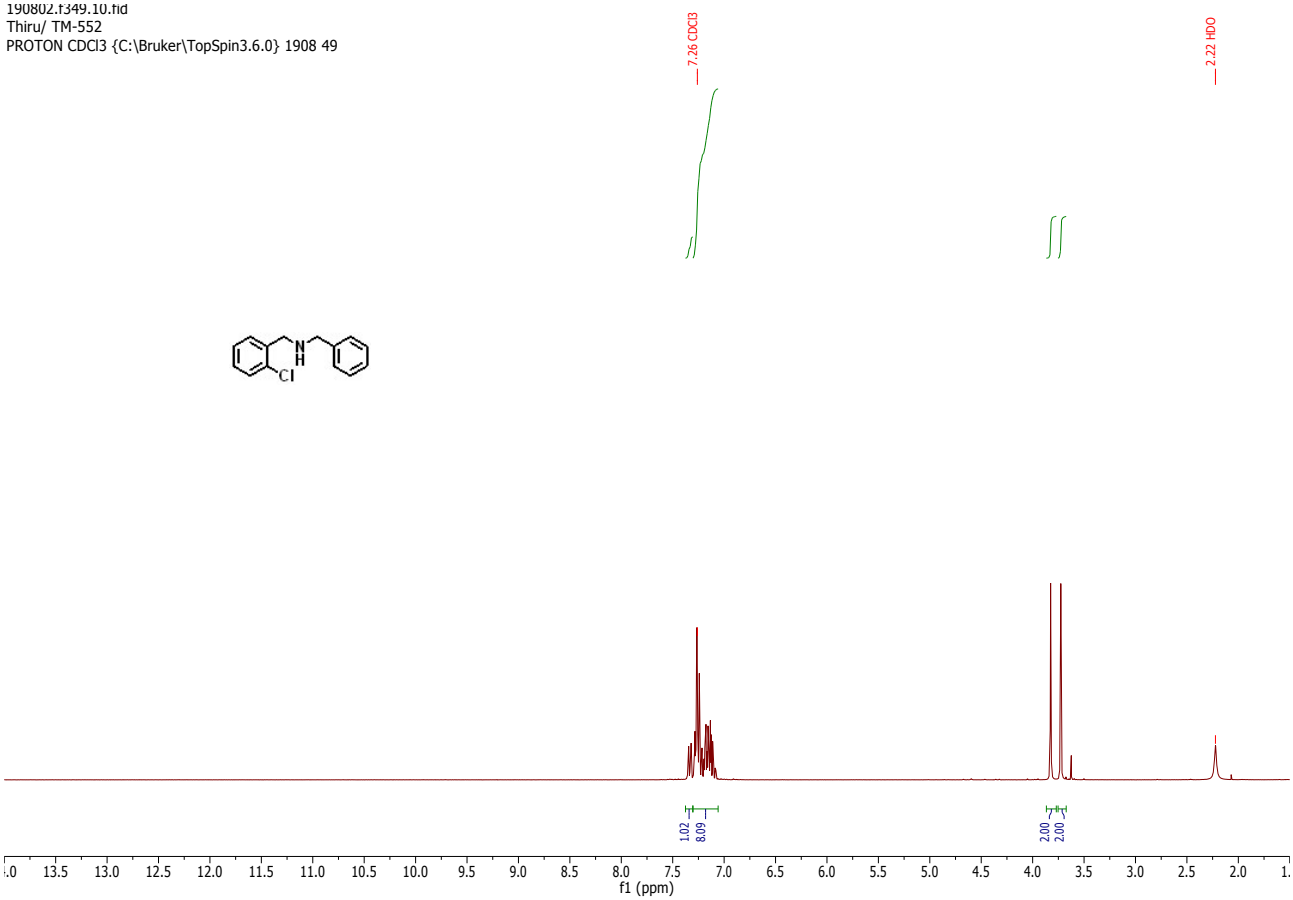
190726.f318.10.fid
Thiru TM3-549
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 1907 18



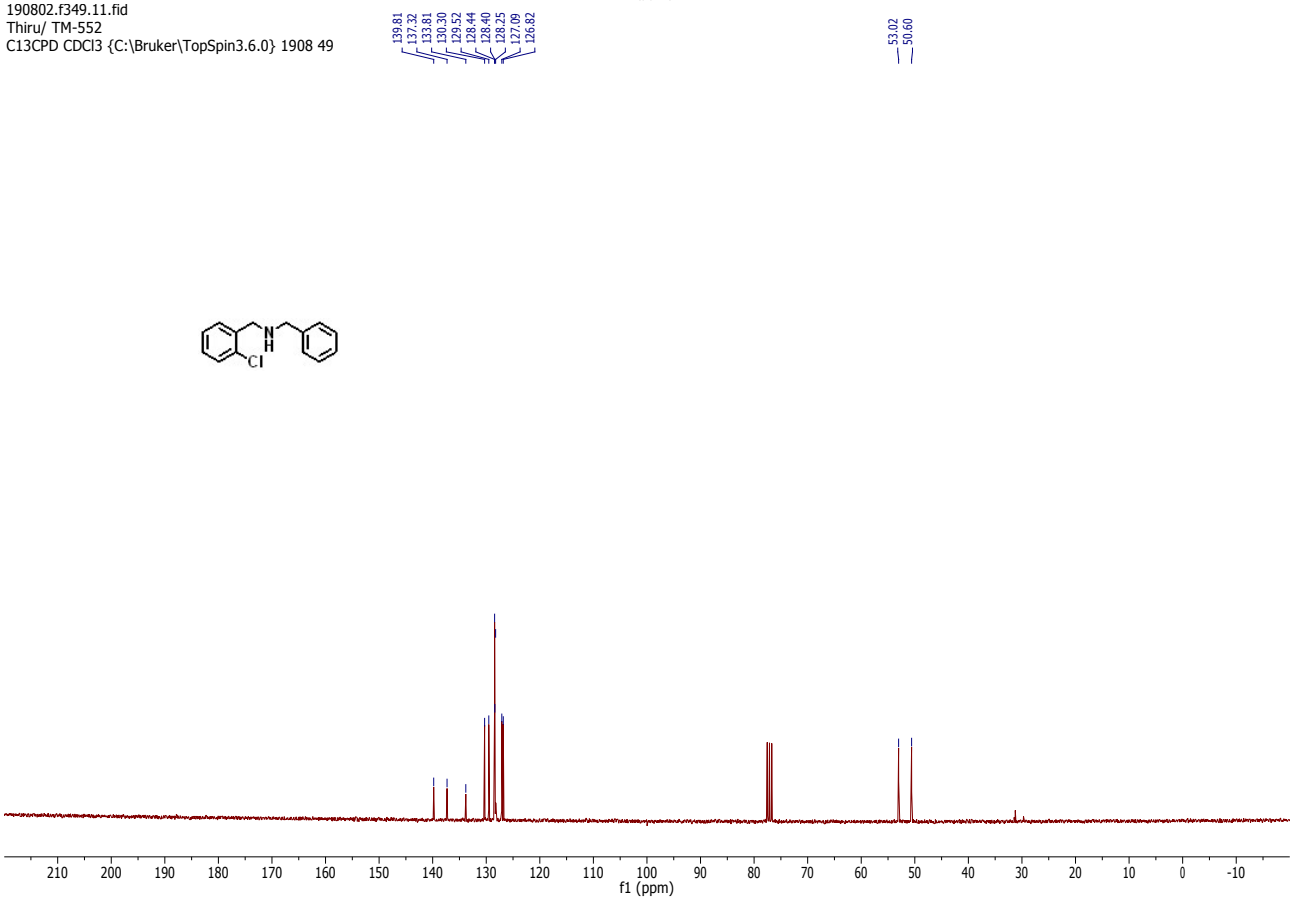
190726.f318.11.fid
Thiru TM3-549
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 1907 18



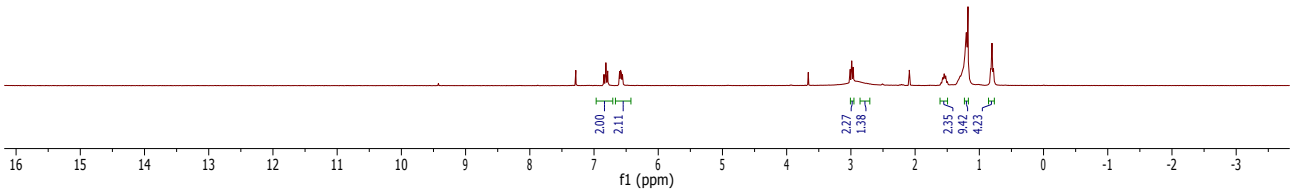
190802.f349.10.fid
Thiru/ TM-552
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 1908 49



190802.f349.11.fid
Thiru/ TM-552
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 1908 49

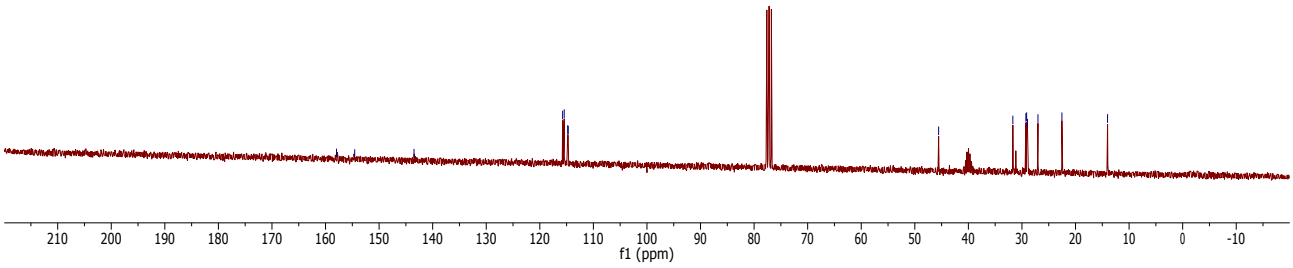


190802.f350.10.fid
Thiru/ TM-554
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 1908 50

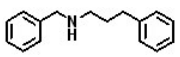


190802.f350.11.fid
Thiru/ TM-554
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 1908 50

157.95
154.56
143.48
115.74
115.45
114.80
114.69
45.55
31.70
29.27
29.13
28.97
27.01
22.54
14.02

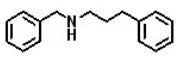


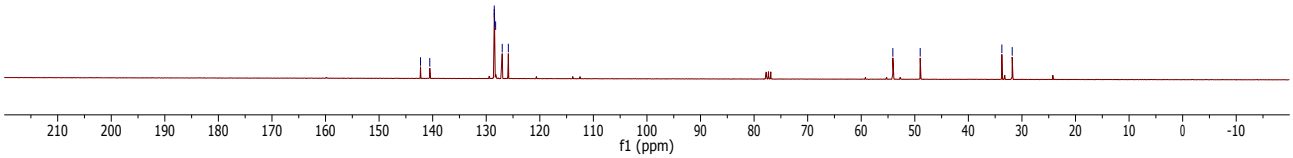
190802.f351.10.fid
Thiru/ TM-555
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 1908 51



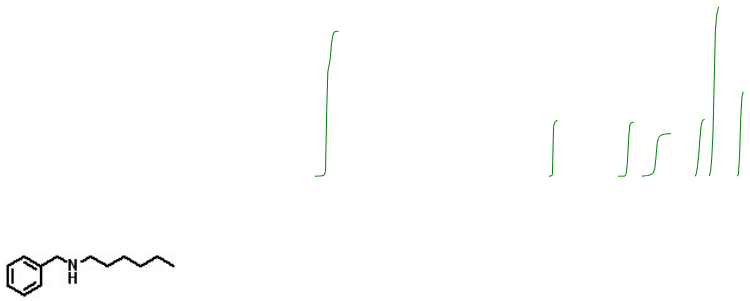
190802.f351.11.fid
Thiru/ TM-555
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 1908 51

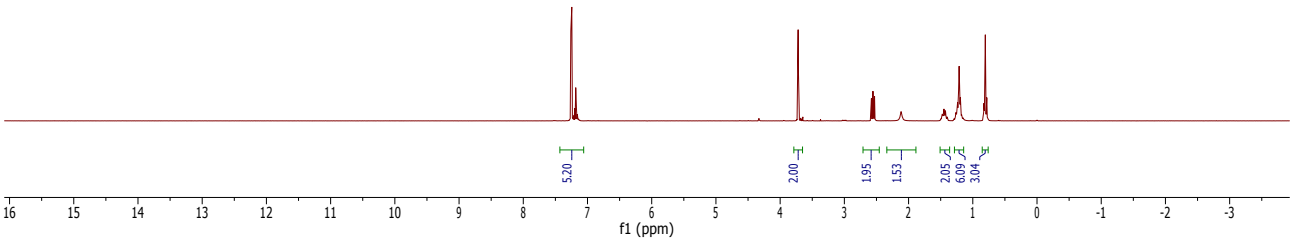
142.27
140.54
128.50
128.50
128.44
128.25
127.02
125.87
54.10
48.99
33.75
31.82



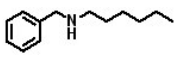


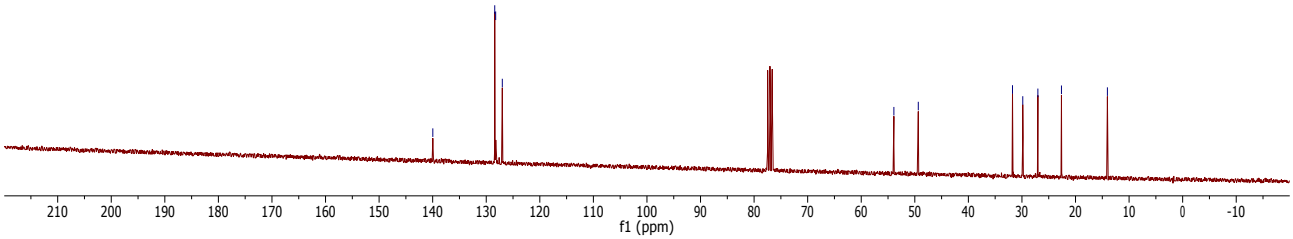
190802.f352.10.fid
Thiru/ TM-556
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 1908 52



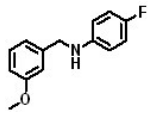


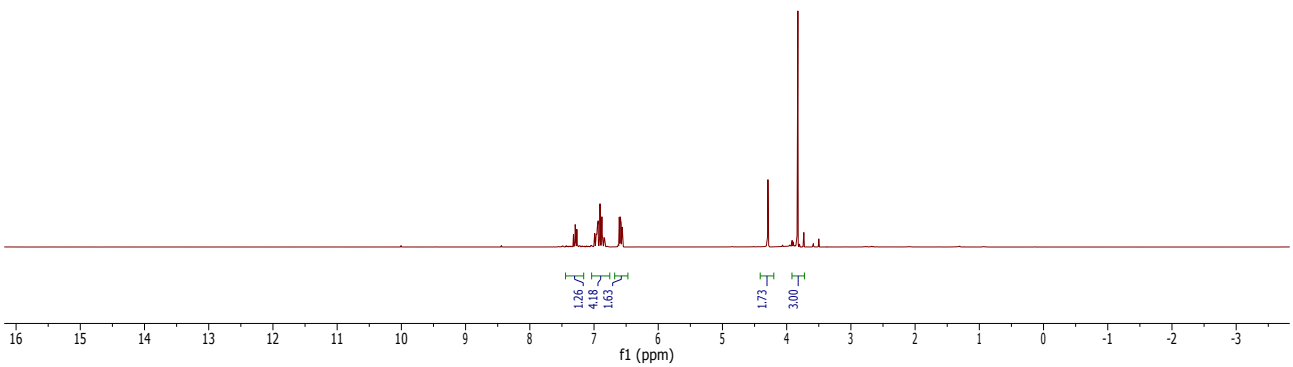
190802.f352.11.fid
Thiru/ TM-556
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 1908 52





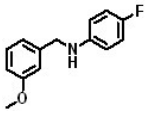
190802.f353.10.fid
Thiru/ TM-551
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 1908 53

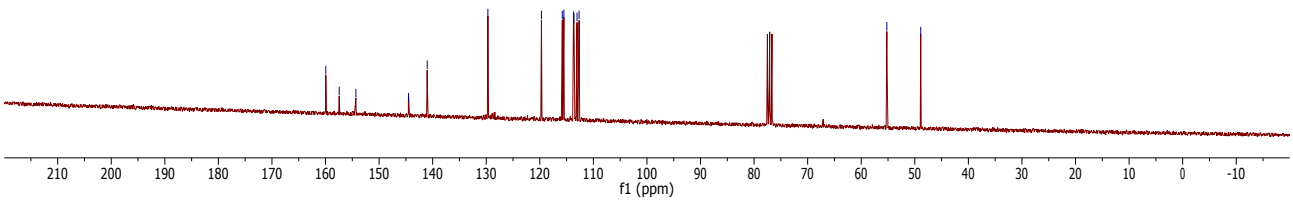




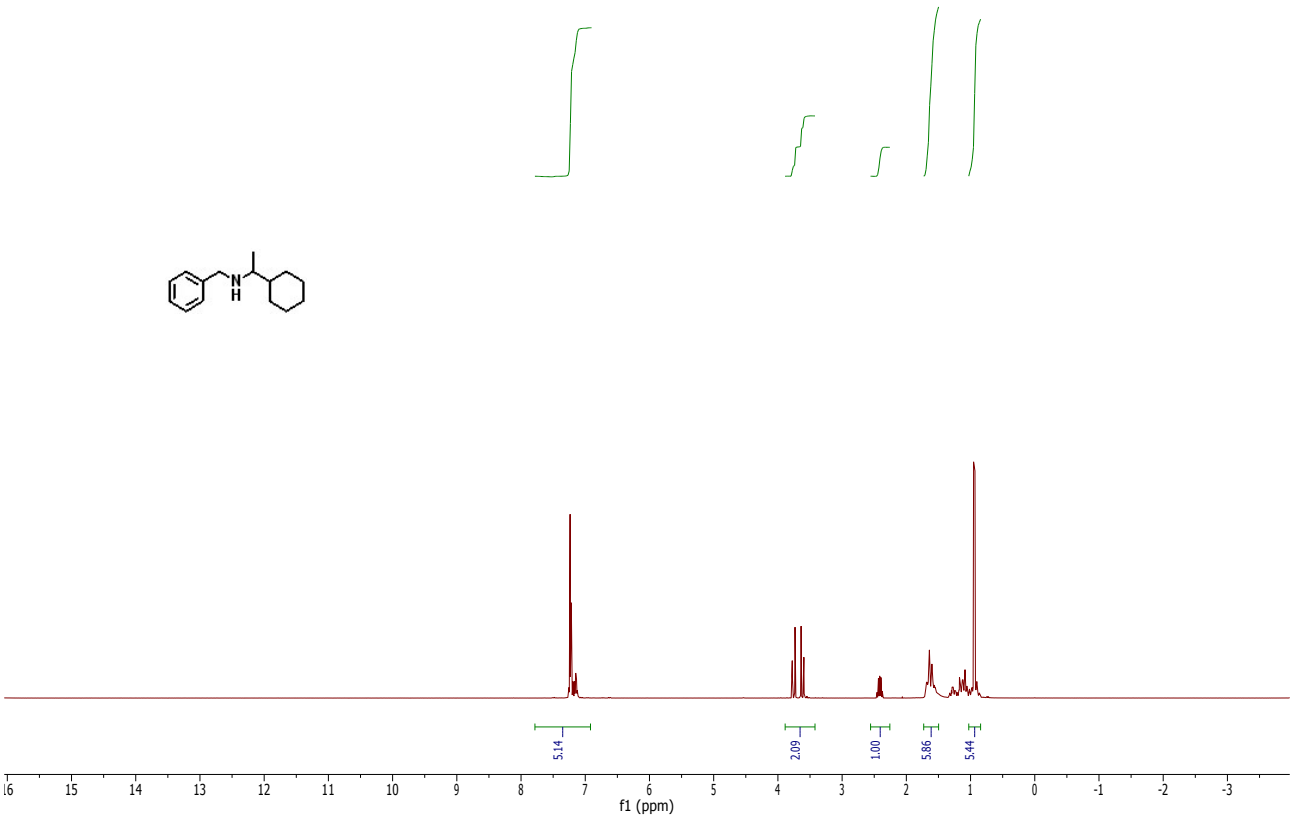
190802.f353.11.fid
Thiru/ TM-551
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 1908 53

159.95
157.45
154.34
144.50
141.02
129.69
119.70
115.80
115.51
113.72
113.62
113.05
112.66
55.22
48.89

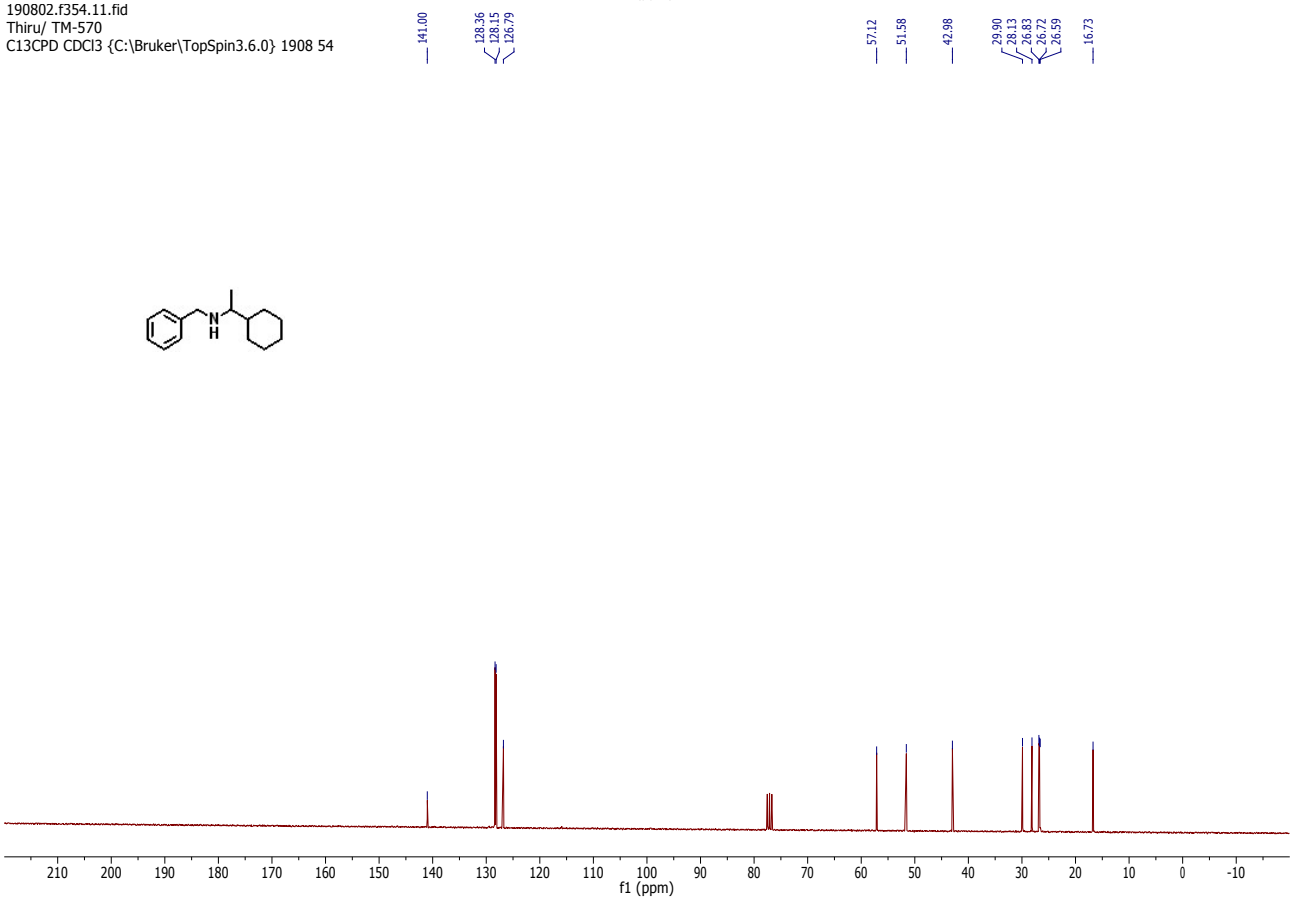




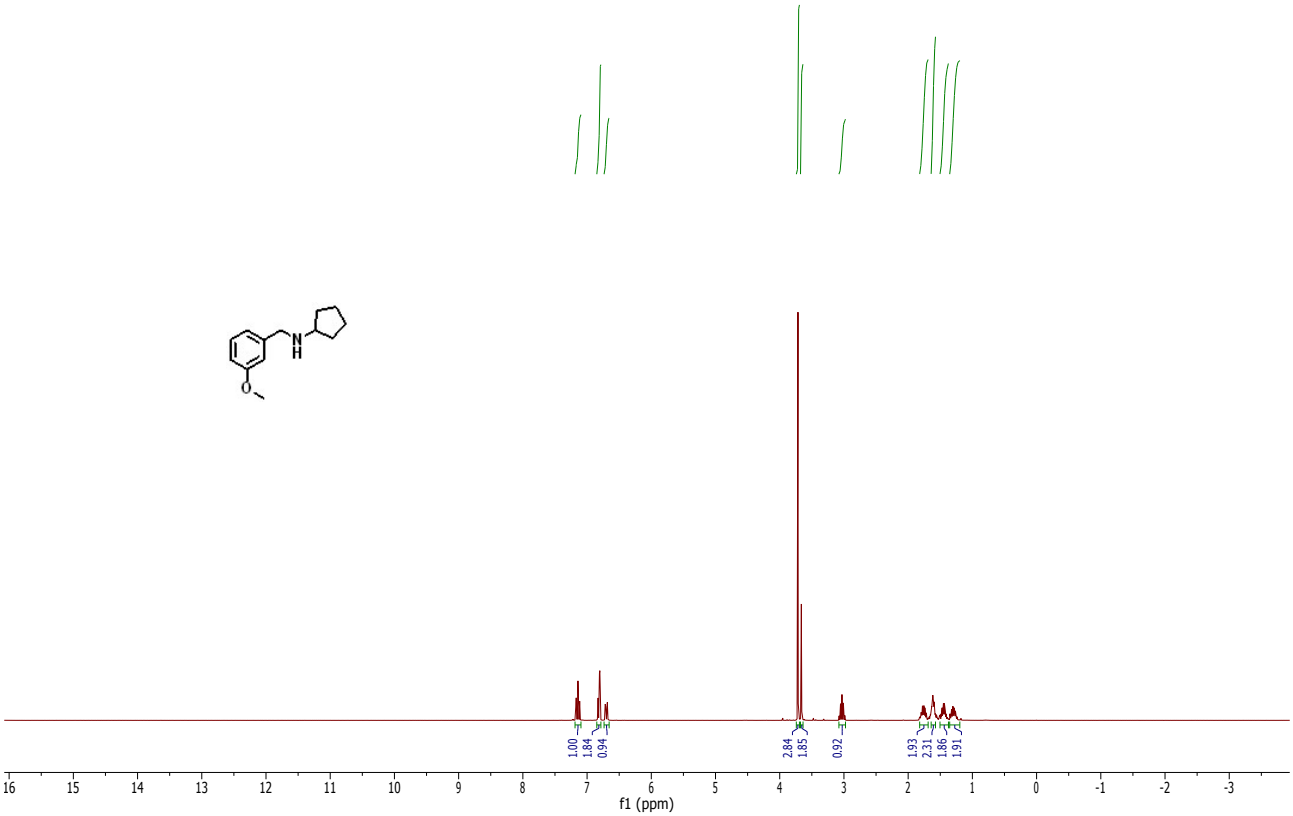
190802.f354.10.fid
Thiru/ TM-570
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 1908 54



190802.f354.11.fid
Thiru/ TM-570
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 1908 54

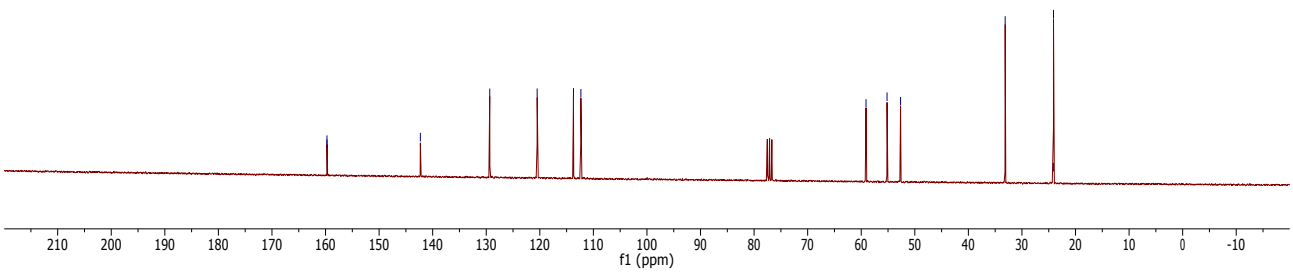


190802.f355.10.fid
Thiru/ TM-567
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 1908 55

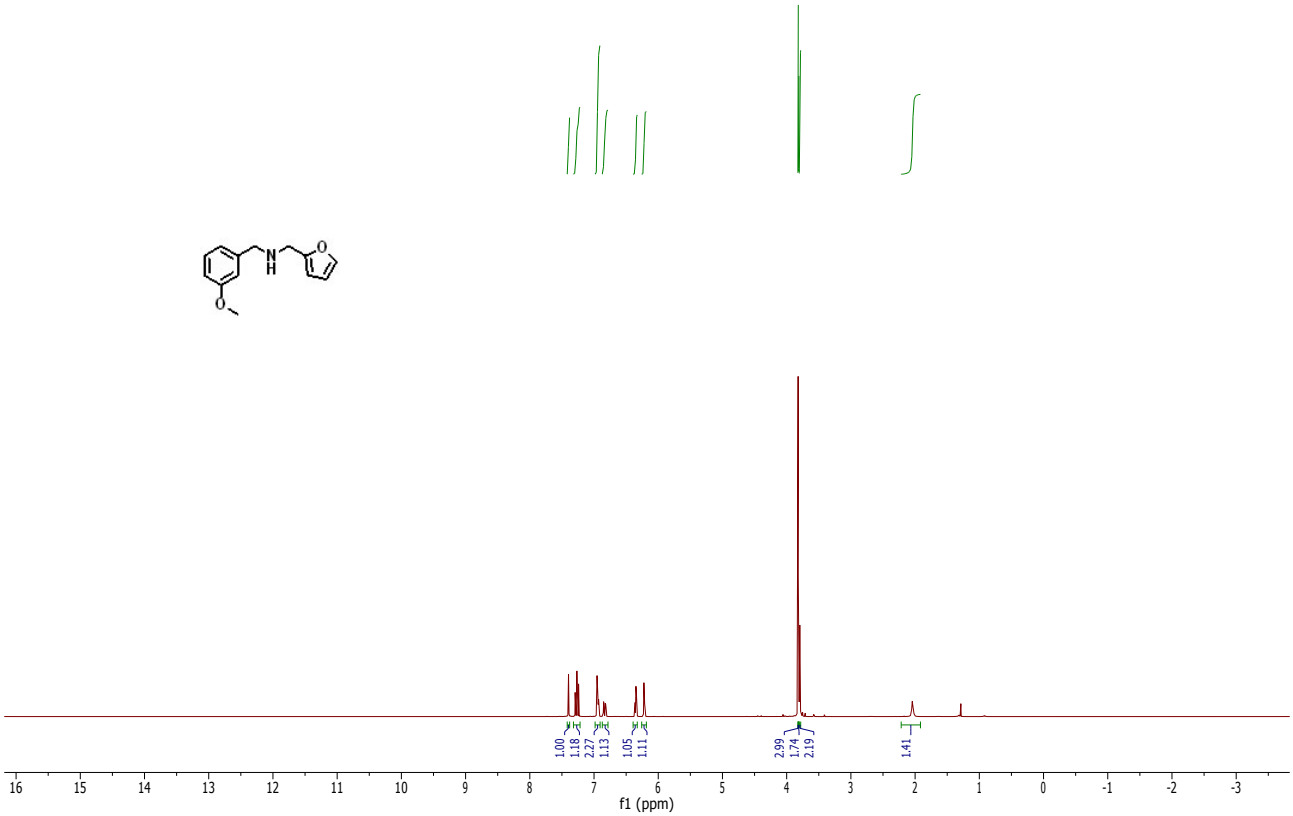


190802.f355.11.fid
Thiru/ TM-567
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 1908 55

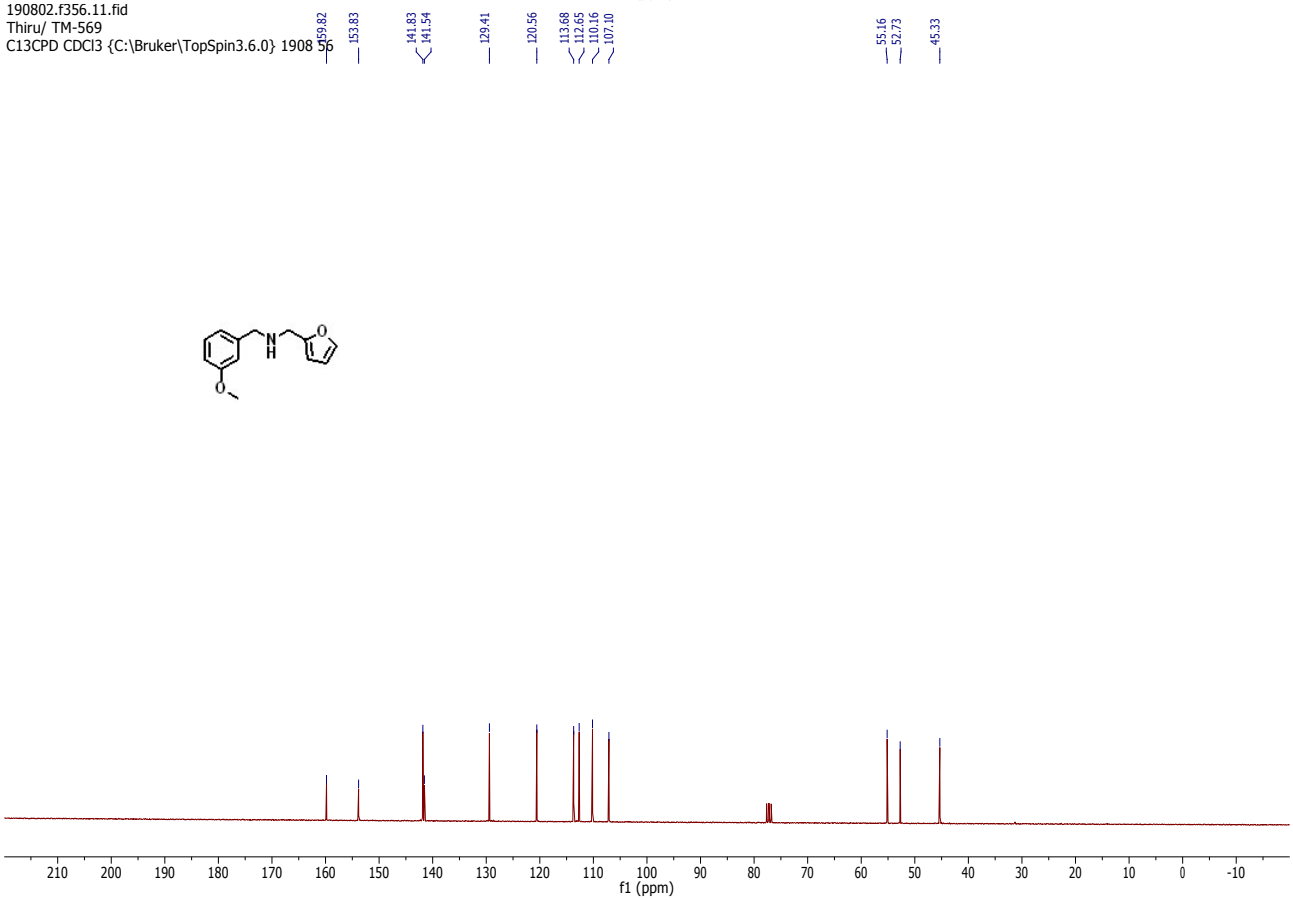
159.73
159.73
142.30
129.34
120.50
113.72
112.33
59.11
55.18
52.66
33.13
24.14
24.11



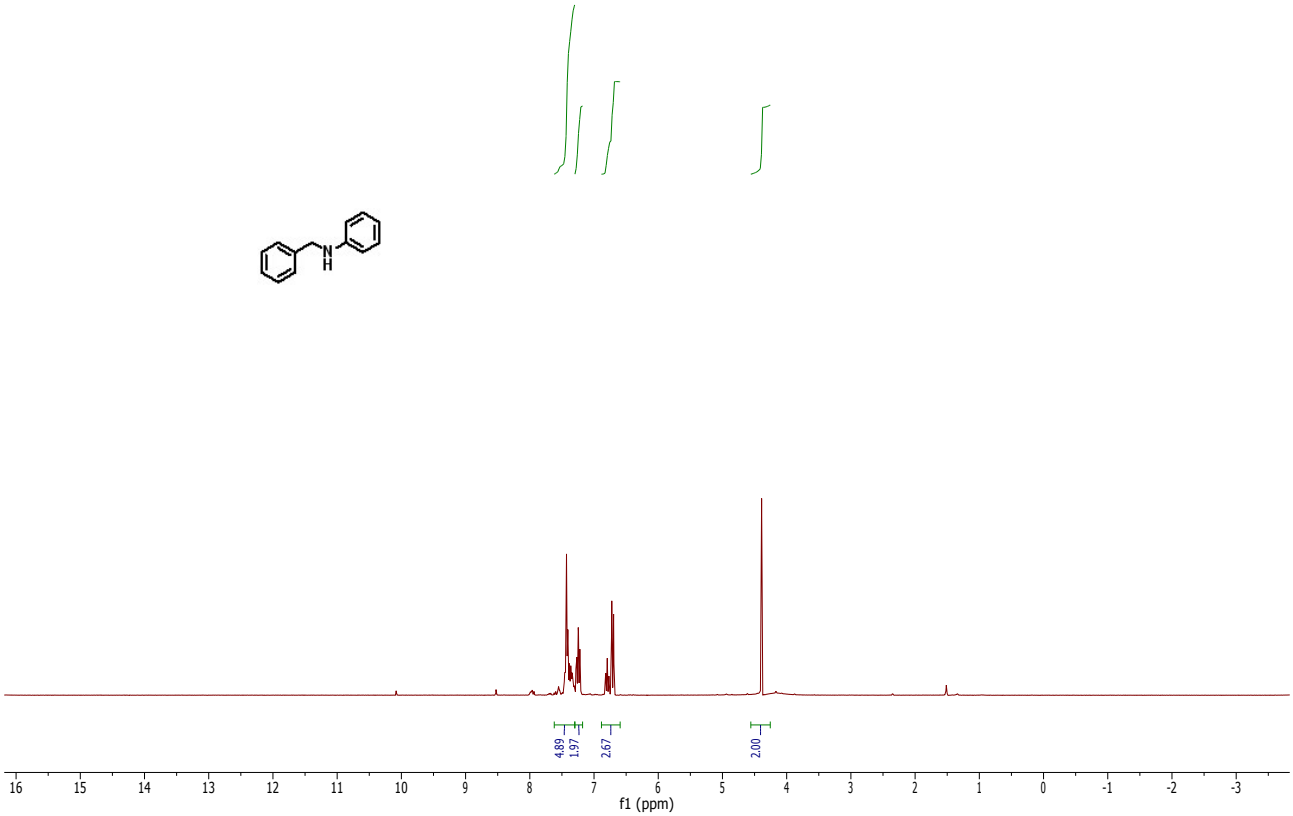
190802.f356.10.fid
Thiru/ TM-569
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 1908 56



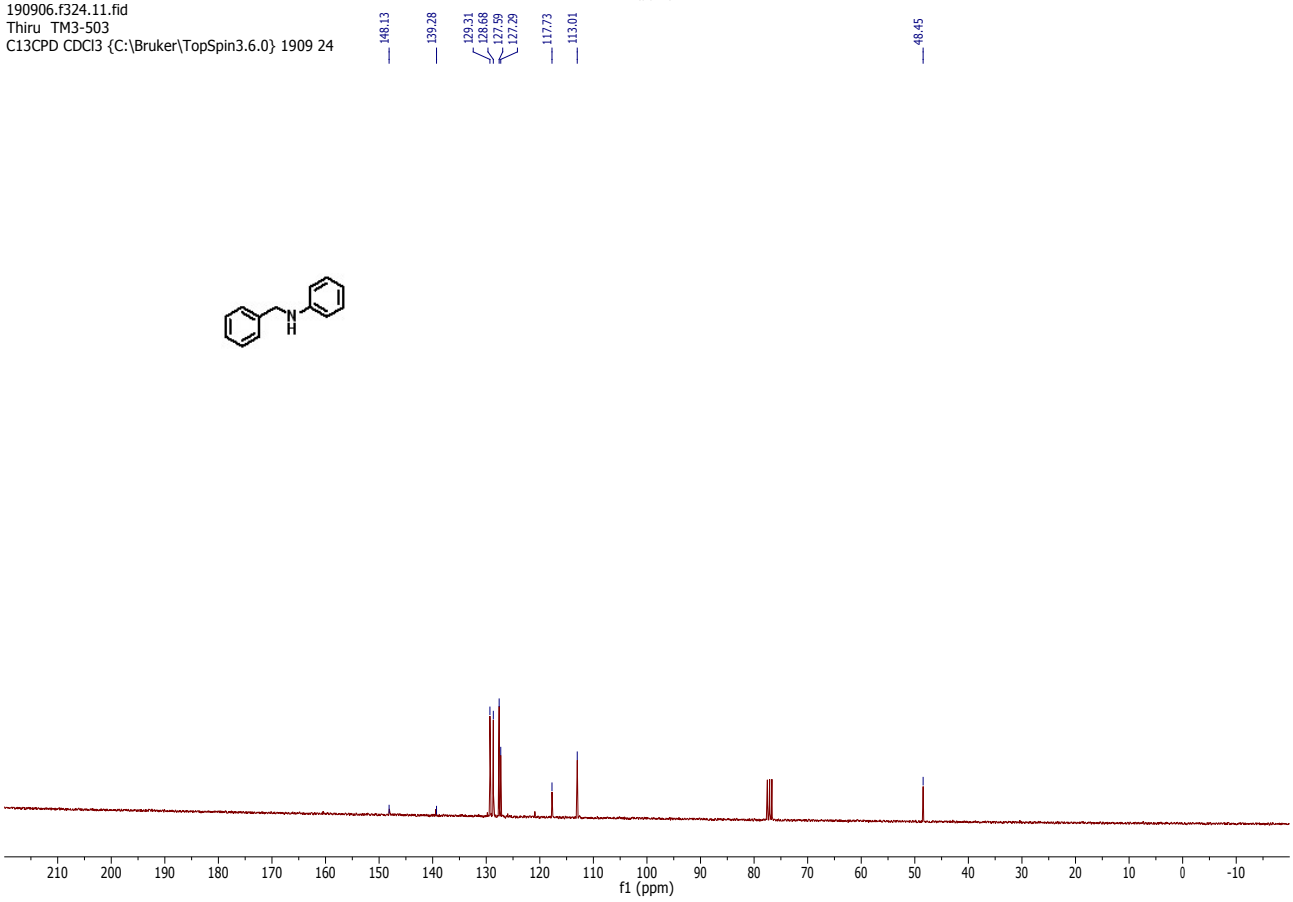
190802.f356.11.fid
Thiru/ TM-569
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 1908 56



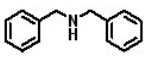
190906.f324.10.fid
Thiru TM3-503
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 1909 24



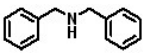
190906.f324.11.fid
Thiru TM3-503
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 1909 24



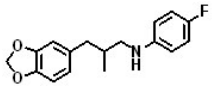
190906.f325.10.fid
Thiru TM3-509
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 1909 25

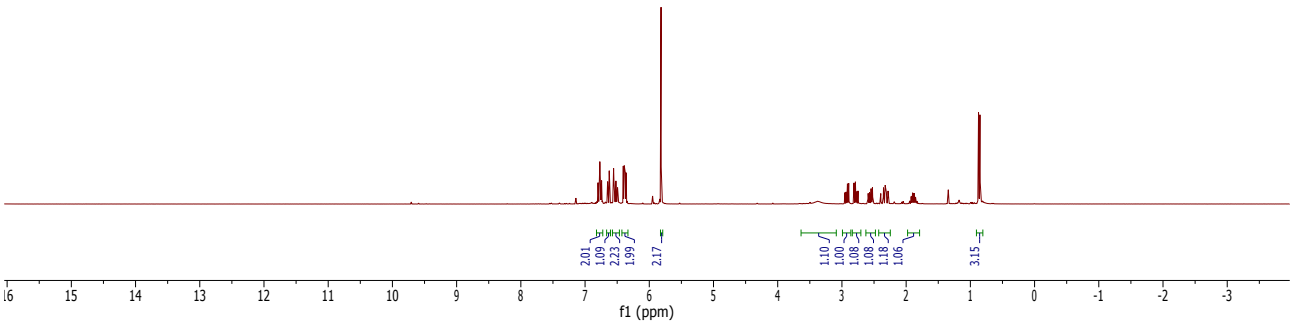


190906.f325.11.fid
Thiru TM3-509
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 1909 25



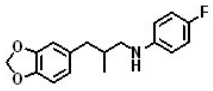
190906.f326.10.fid
Thiru TM3-553
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 1909 26

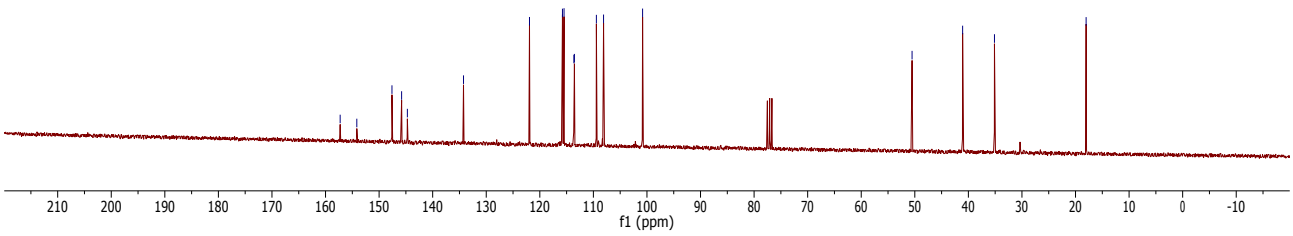




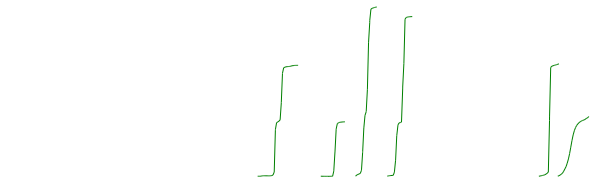
190906.f326.11.fid
Thiru TM3-553
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 1909 26

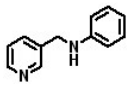
157.27
154.16
147.60
145.80
144.72
134.24
121.93
115.77
115.48
113.64
113.54
109.44
108.10
100.81
50.51
41.07
35.13
18.02

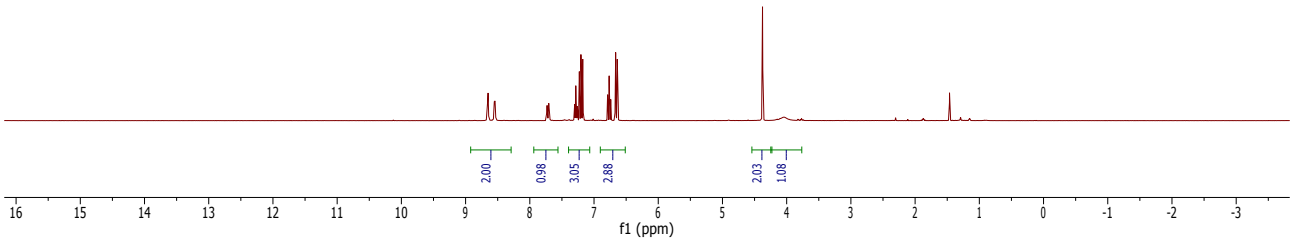




190906.f328.10.fid
Thiru TM3-572
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 1909 28







190906.f328.11.fid
Thiru TM3-572
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 1909 28

149.07
148.60
147.65
135.18
135.03
129.35
123.60
118.03
112.97
45.79