Electronic Supplementary Information (ESI) for

NHC-based Coordination Polymers as Solid Molecular Catalysts for Reductive Amination of Biomass Levulinic Acid

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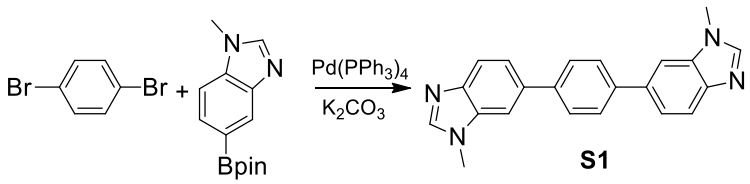
1. General

All commercial reagents were used directly without further purification, unless otherwise stated. Dry *N*,*N*-dimethylformamide (DMF), N-methylpyrrolidinone and pyridine were purchased from Alfa Aesar, stored over 4 Å molecular sieves, and handled under N_2. All reaction vials (50 mL) were purchased from Beijing Synthware Glass. $CDCl_3$ was purchased from Cambridge Isotope Laboratories.^{1}H, ^{13}C NMR were recorded on Jeol ECA-400 and Bruker 400 DRX spectrometers. The chemical shifts (δ) for ^{1}H NMR are given in parts per million (ppm) referenced to the residual proton signal of the deuterated solvent ($CHCl_3$ at δ 7.26 ppm); coupling constants are expressed in hertz (Hz). ^{13}C NMR spectra were referenced to the carbon signal of $CDCl_3$ (77.0 ppm). The following abbreviations are used to describe NMR signals: s = singlet, d = doublet, t = triplet, m = mulitplet, dd = doublet of doublets, q = quartet. GC-MS spectra were recorded on Agilent echnologies 1890A GC system and 5975C inert MSD with Triple-Axis Detector. ESI-MS spectra were recorded on a Bruker micrOTOF II instrument. IR spectra were recorded on AVATAR FT-IR 360 instrument. Powder XRD were recorded on a Bruker AXS D8. SEM were recorded on a FEI Nova NanoSEM 450.

2. Synthesis of NHC-based coordination polymers

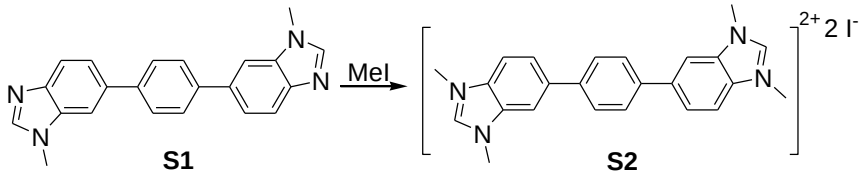
2.1 Synthesis of ditopic ligands



Scheme S1. Synthesis of **S1.**

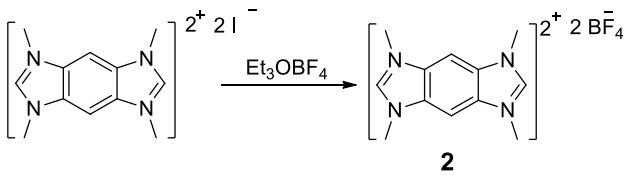
Under N_2, potassium carbonate (1.5 mmol), $Pd(PPh_3)_4$ (5 mol%), 1,4-dibromobenzen(1.5 mmol) and aryl boronic acid (3.1 mmol) were added into a 50 mL glass vial which was sealed with a septum and purged with N_2 for three times.

Dioxane (6 mL) and degased H_2O (2 mL) was then injected via syringe. At this time, the reaction stirred for 36 h at 80 ℃. Water phase was separated from the resulting mixture, the organic phase was diluted with 10 mL MeOH and filetered. The filtrate was purified in a Soxhlet apparatus with EtOH as a pale yellow solid (**S1**): 330 mg, 65%, ^{1}H NMR (400 MHz, 298 K, DMSO-d_6) δ = 8.23 (s, 2H), 7.97 (s, 2H), 7.81 (s, 4H), 7.68 (d, J = 8.5 Hz, 4H), 3.88 (s, 6H). ^{13}C NMR (101 MHz, 298 K, DMSO-d_6) δ = 145.79, 139.82, 134.72, 134.17, 131.95, 127.78, 121.91, 117.51, 111.04, 31.20. HRMS (ESI/TOF) *m/z*: Calcd. for $C_{22}H_{19}N_4$ $[M+H]^+$ 339.1610; Found: 339.1610.



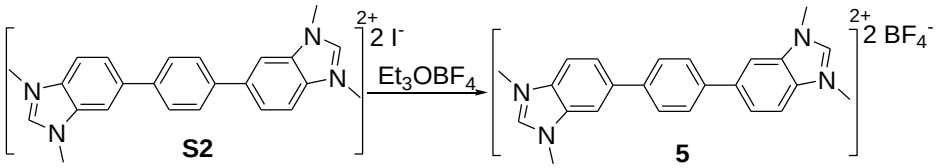
Scheme S2. Synthesis of bis-benzimidazolium salt S**2.**

A Schlenk tube was charged with **S1** (169 mg, 0.5 mmol), iodomethane (211 mg, 1.5 mmol), dry CH_2Cl_2 (5 mL), methanol (3 mL) and sealed with a Teflon-lined cap. After stirring 12 hours at ambient temperature, the resulting reaction mixture was poured into excess diethyl ether (50 mL). After precipitation completed, the solids were collected via filtration and dried under reduced pressure to afford the desired salts as a white powder (**S2**): 310 mg, 99%; ^{1}H NMR (400 MHz, 298 K, DMSO-d_6) δ = 9.67 (s, 2H), 8.43 (s, 2H), 8.13 (s, 4H), 8.05 (s, 4H), 4.16 (s, 6H), 4.12 (s, 6H). ^{13}C NMR (101 MHz, 298 K, DMSO-d_6) δ = 144.23, 139.08, 138.75, 133.00, 128.50, 125.95, 114.46, 111.81, 54.90, 33.85. HRMS (ESI/TOF) *m/z*: Calcd. for $C_{24}H_{24}N_4$ $[M-2I]^+$ 368.2001; Found: 368.1996.



Scheme S3. Synthesis of bis-benzimidazolium salt **2.**[S1]

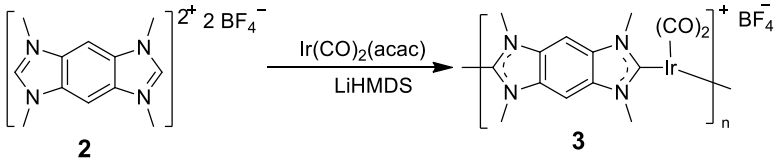
A Schlenk tube was charged with benzobisimidazolium dihalides (0.260 mmol), triethyloxonium tetrafluoroborate (117 mg, 1.04 mmol), dry CH_2Cl_2 (5 mL), and sealed with a Teflon-lined cap. After stirring 12 hours at ambient temperature, methanol (3 mL) was then added. The resulting reaction mixture was stirred for an additional hour and then poured into excess diethyl ether (50 mL). After precipitation completed, the solids were collected via filtration and dried under reduced pressure to afford the desired salts as a white powder. **2**: pale white powder, 96% yield; ^{1}H NMR (400 MHz, 298 K, DMSO-d_6) δ = 9.88 (s, 2H), 8.79 (s, 2H), 4.17 (s, 12H); ^{19}F NMR (376 MHz, 298 K, DMSO-d_6) δ = -148.3; ^{13}C NMR (100 MHz, 298 K, DMSO-d_6) δ = 147.09, 131.14, 98.71, 34.07.



Scheme S4. Synthesis of bis-benzimidazolium salt **5.**

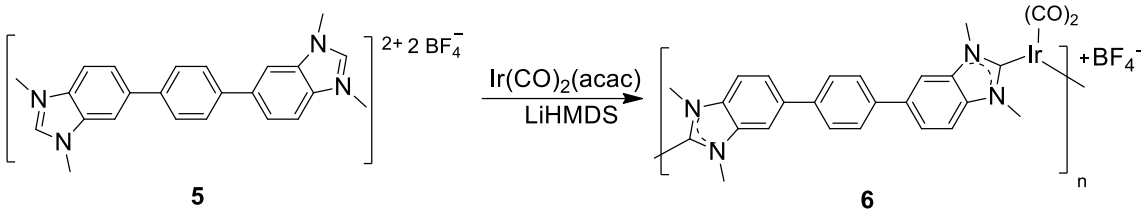
A Schlenk tube was charged with **S2** (0.260 mmol), triethyloxonium tetrafluoroborate (117 mg, 1.04 mmol), dry CH_2Cl_2 (5 mL), and sealed with a Teflon-lined cap. After stirring 12 hours at ambient temperature, methanol (3 mL) was then added. The resulting reaction mixture was stirred for an additional hour and then poured into excess diethyl ether (50 mL). After precipitation completed, the solids were collected via filtration and dried under reduced pressure to afford the desired salts as a white powder. **5**: 135 mg, 96%, ^{1}H NMR (400 MHz, 298 K, DMSO-d_6) δ = 9.67 (s, 2H), 8.43 (s, 2H), 8.13 (s, 4H), 8.05 (s, 4H), 4.14 (d, J = 15.4 Hz, 12H). ^{13}C NMR (101 MHz, 298 K, DMSO-d_6) δ = 144.24, 139.09, 138.75, 133.01, 128.51, 125.96, 114.52, 111.81, 54.91, 33.86. ^{19}F NMR (376 MHz, 298 K, DMSO-d_6) δ = -148.26. HRMS (ESI/TOF) *m/z*: Calcd. for $C_{24}H_{24}N_4$ $[M\text{-}2\ BF_4]^+$ 368.2001; Found: 368.1991.

2.2 Synthesis of NHC-based coordination polymers



Scheme S5. Synthesis of polymeric catalyst **3.**[S2]

Bis-benzimidazolium salt **2** (0.5 mmol) and the iridium precursor (0.5 mmol) were dissolved in DMF under N_2 at room temperature, LiHMDS solution in THF (1 M, 1 mL) was added in dropwise. The resulting mixture was stirred at 80 ^oC for 24 h. The dark brown solids were isolated after filtration and washed with deionized water for three times. The polymer solids were then dried over under vacuum. **3:** dark-brown solid, 93% yield; IR (KBr pellet) *v* 418.22, 424.01, 599.84, 1084.05, 1257.84, 1383.96, 465.51, 1629.09, 2273.14, 3443.20 (cm^{-1}); Elemental analysis (%) Calcd. for $(C_{12}H_{12}BF_4IrN_4O_2•1.5\ DMF)_n$: C, 30.99; H, 4.03; N, 11.31; found: C, 31.35; H, 3.60; N, 11.94 .



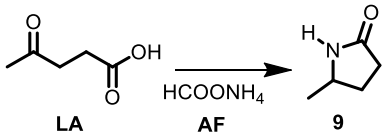
Scheme S6. Synthesis of polymeric catalyst **6.**

To the solution of bis-benzimidazolium salt **5** (0.5 mmol) and $[Ir(CO)_2acac]$ (0.5 mmol) in DMF, LiHMDS solution in THF (1M, 1 mL) was added in dropwise under N_2 at room temperature. The resulting mixture was stirred at 80 ^oC for 24 h. The solids were isolated after filtration and washed with deionized water for three times. The polymer solids were then dried over under vacuum to afford polymer **6** as dark-brown solid: 90% yield; IR (KBr pellet) *v* 3418.06, 2945.99, 2235.31, 1940.41, 1693.63, 1658.78, 1651.15, 1621.21, 1556.76, 1537.46, 1463.35, 1440.73, 1382.60, 1344.71, 1252.80, 1105.47, 1083.08, 867.97, 827.99, 584.41, 533.08, Elemental

analysis (%) Calcd. for $(C_{26}H_{22}BF_4IrN_4O_2 \bullet DMF)_n$: C, 44.97; H, 3.77; N, 9.04; found: C,44.61; H, 4.30; N, 8.93 .

3. Procedures for the Reductive Amination reactions of LA.

Table S1 condition screening[a]



LA AF 9

Entry	[cat.] (mol%)	t (h)	T (^{o}C)	Yield(%)
1	**7** (0.15)	48	80	53
2	**7** (0.15)	48	60	22
3	**7** (0.15)	48	40	ND
4	**7** (0.1)	24	120	82
5	**7** (0.03)	24	120	36
6	**7** (0.01)	24	120	29
7	**3** (0.03)	48	120	58
8	$RuCl_3$ (0.03)	48	120	46

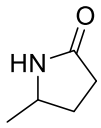
[a]10 mmol scale; Yield was determined with GC-MS.

Stepwise procedure for reductive amination:

Levulinic acid (232 mg, 2 mmol) and ammonium formate (132 mg, 2.1 mmol) were added in a test tube equipped with a stirring bar at room temperature To the resulting mixture, solid **7** (2.1 mg, 0.15 mol%) was added. The resulting mixture was stirred at 80 ^{o}C for 4 h. After cooling to room temperature, methanol (2 mL) was added to dissolve the product; the catalyst was separated with centrifuge and washed with methanol for 2 times. The methanol solution was combined and evaporated to dry.

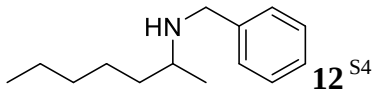
The obtained thick oil was stirred at 120 ^{o}C for additional 20 h. and the yield of product **9** was determined by GC-MS with N-methyl-2-pyrrolidone as an internal stander. The separated catalyst was then washed with Et_2O for three times and could be used in the next run without further activation.

4. Data for products.



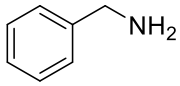
9 S3

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ = 6.81 (s, 1H), 3.89 – 3.78 (m, 1H), 2.42 – 2.32 (m, 2H), 2.32 – 2.20 (m, 1H), 1.73 – 1.57 (m, 1H), 1.23 (d, *J* = 6.1, 3H). MS (ESI) *m/z*: Calcd. for : $[M]^+$ C_5H_9NO 99.1; Found: 99.0.



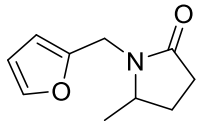
12 S4

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ = 7.36 – 7.28 (m, 4H), 7.26 – 7.21 (m, 1H), 3.78 (dd, *J* = 37.2, 12.9 Hz, 2H), 2.67 (dd, *J* = 12.1 Hz, 6.0, 1H), 1.55 – 1.40 (m, 1H), 1.39 – 1.19 (m, 8H), 1.08 (d, *J* = 6.3, 3H), 0.88 (t, *J* = 7.0, 3H). ^{13}C NMR (101 MHz, 298 K, $CDCl_3$) δ = 140.93, 128.36, 128.11, 126.77, 52.52, 51.44, 37.09, 32.08, 25.66, 22.67, 20.34, 14.08.



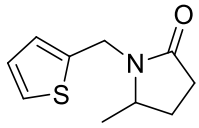
13 S5

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ = 7.38 – 7.17 (m, 5H), 3.82 (s, 2H). ^{13}C NMR (101 MHz, 298 K, $CDCl_3$) δ = 143.01, 128.08, 126.63, 126.30, 46.08.



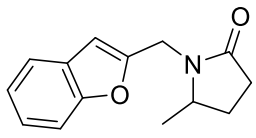
14

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ = 7.34 (d, *J* = 1.1, 1H), 6.32 – 6.29 (m, 1H), 6.23 (d, *J* = 3.1 Hz, 1H), 4.87 (d, *J* = 15.6 Hz, 1H), 4.05 (d, *J* = 15.6 Hz, 1H), 3.64 – 3.53 (m, 1H), 2.46 – 2.30 (m, 2H), 2.20 – 2.09 (m, 1H), 1.62 – 1.54 (m, 1H), 1.22 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, 298 K, $CDCl_3$) δ = 174.74, 142.36, 142.17, 110.33, 108.11, 53.25, 36.77, 30.14, 26.66, 19.56. HRMS (ESI/TOF) *m/z*: Calcd. for $C_{10}H_{14}NO_2$ $[M+H]^+$ 180.1025; Found: 180.1019.



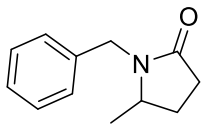
15

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ = 7.17 (dd, *J* = 4.9 Hz, 1.2, 1H), 6.95 – 6.86 (m, 2H), 5.04 (d, *J* = 15.4 Hz, 1H), 4.16 (d, *J* = 15.4 Hz, 1H), 3.64 – 3.52 (m, 1H), 2.46 – 2.25 (m, 2H), 2.19 – 2.07 (m, 1H), 1.65 – 1.49 (m, 1H), 1.19 (d, *J*=6.3, 3H). ^{13}C NMR (101 MHz, 298 K, $CDCl_3$) δ = 174.57, 139.29, 126.68, 126.33, 125.14, 52.54, 38.37, 30.14, 26.60, 19.54. HRMS (ESI/TOF) *m/z*: Calcd. for $C_{10}H_{14}NOS$ $[M+H]^+$ 196.0796; Found: 196.0796.



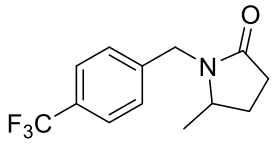
16

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ = 7.51 (d, *J* = 7.4 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 6.61 (s, 1H), 5.02 (d, *J* = 15.7 Hz, 1H), 4.19 (d, *J* = 15.7 Hz, 1H), 3.70 – 3.61 (m, 1H), 2.54 – 2.33 (m, 2H), 2.21 – 2.09 (m, 1H), 1.67 – 1.55 (m, 1H), 1.26 (d, *J* = 6.1, 3H). ^{13}C NMR (101 MHz, 298 K, $CDCl_3$) δ = 174.89, 154.89, 153.11, 128.17, 124.11, 122.78, 120.85, 111.21, 104.89, 53.35, 37.32, 30.09, 26.69, 19.62. HRMS (ESI/TOF) *m/z*: Calcd. for $C_{14}H_{16}NO_2$ $[M+H]^+$ 230.1181; Found: 230.1188.



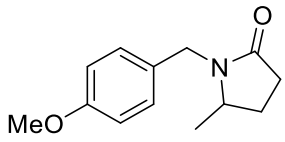
17a [S3]

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ = 7.36 – 7.23 (m, 5H), 4.97 (d, *J* = 15.0 Hz, 1H), 3.99 (d, *J* = 15.0 Hz, 1H), 3.60 – 3.50 (m, 1H), 2.53 – 2.39 (m, 2H), 2.19 – 2.10 (m, 1H), 1.66 – 1.54 (m, 1H), 1.16 (d, *J*=6.3, 3H). MS (ESI) *m/z*: Calcd. for : $[M]^+$ $C_{12}H_{15}NO$ 189.1; Found: 189.0.



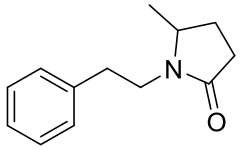
17b

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ = 7.57 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.91 (d, *J* = 15.3 Hz, 1H), 4.12 (d, *J* = 15.3 Hz, 1H), 3.58 – 3.47 (m, 1H), 2.57 – 2.34 (m, 2H), 2.23 – 2.16 (m, 1H), 1.68 – 1.57 (m, 1H), 1.15 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, 298 K, $CDCl_3$) δ = 175.12, 141.11, 128.09, 125.53, 125.50, 122.66, 53.10, 43.57, 30.05, 26.67, 19.61. ^{19}F NMR (376 MHz, 298 K, $CDCl_3$) δ = -62.53. HRMS (ESI/TOF) *m/z*: Calcd. for $C_{13}H_{15}F_3NO$ $[M+H]^+$ 258.1106; Found: 258.1108.



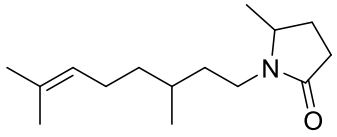
17c

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ = 7.12 (d, *J* = 8.3 Hz, 2H), 6.82 – 6.74 (m, 2H), 4.86 (d, *J* = 14.8 Hz, 1H), 3.87 (d, *J* = 14.8 Hz, 1H), 3.74 (d, *J* = 1.1 Hz, 3H), 3.49 – 3.40 (m, 1H), 2.46 – 2.28 (m, 2H), 2.13 – 2.03 (m, 1H), 1.61 – 1.47 (m, 1H), 1.14 – 1.04 (m, 3H). ^{13}C NMR (101 MHz, 298 K, $CDCl_3$) δ = 174.74, 158.86, 129.19, 128.86, 113.90, 55.15, 52.59, 43.16, 30.25, 26.55, 19.52. HRMS (ESI/TOF) *m/z*: Calcd. for $C_{13}H_{18}NO_2$ $[M+H]^+$ 220.1338; Found: 220.1342.



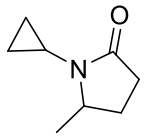
18 [S6]

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ = 7.29 (dd, *J* = 9.1 Hz, 5.6, 2H), 7.24 – 7.14 (m, 3H), 3.92 – 3.79 (m, 1H), 3.58 – 3.46 (m, 1H), 3.21 – 3.08 (m, 1H), 2.90 – 2.86 (m, 1H), 2.82 – 2.72 (m, 1H), 2.44 – 2.23 (m, 2H), 2.14 – 2.09 (m, 1H), 1.58 – 1.52 (m, 1H), 1.16 (d, *J*=6.3, 3H). ^{13}C NMR (101 MHz, 298 K, $CDCl_3$) δ = 174.69, 138.88, 128.64, 128.39, 126.31, 53.63, 41.63, 33.80, 30.14, 26.70, 19.63.



19

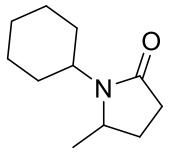
^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ = 5.10 – 5.01 (m, 1H), 3.74 – 3.55 (m, 3H), 2.94 – 2.82 (m, 1H), 2.43 – 2.24 (m, 2H), 2.20 – 2.08 (m, 1H), 1.93 (dd, *J* = 13.7, 7.9 Hz, 3H), 1.65 (s, 3H), 1.58 (s, 3H), 1.40 (dd, *J* = 9.8, 4.4 Hz, 2H), 1.19 – 1.15 (m, 2H), 0.90 (d, *J* = 2.7 Hz, 3H), 0.89 (d, *J*=3.6, 3H). ^{13}C NMR (101 MHz, 298 K, $CDCl_3$) δ = 174.57, 131.24, 130.83, 128.74, 124.57, 74.85, 72.79, 53.30, 52.92, 44.56, 38.33, 37.08, 36.67, 34.00, 31.30, 30.55, 30.30, 29.96, 27.03, 26.74, 26.70, 25.64, 25.37, 23.64, 21.92, 19.64, 19.45, 19.24, 17.58. HRMS (ESI/TOF) *m/z*: Calcd. for $C_{15}H_{27}NO$ $[M]^+$ 237.2093; Found: 237.2098.



20a [S6]

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ = 3.56 – 3.38 (m, 1H), 2.27 (d, *J* = 4.6 Hz, 2H), 2.22 – 2.11 (m, 1H), 2.06 – 1.93 (m, 1H), 1.55 – 1.38 (m, 1H), 1.20 – 1.07 (m, 3H), 0.89 – 0.65 (m, 2H), 0.60 – 0.38 (m, 2H). ^{13}C NMR (101 MHz, 298 K, $CDCl_3$) δ = 175.69, 54.86, 30.57, 26.17, 22.88, 19.93, 7.29, 4.04.

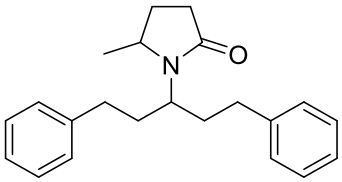
(Note: With (1-ethoxycyclopropoxy)trimethylsilane as starting material)



20b [S6]

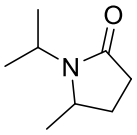
^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ = 3.77 (d, *J* = 4.6 Hz, 1H), 3.78 – 3.60 (m, 1H),

2.55 – 2.37 (m, 1H), 2.34 – 2.19 (m, 1H), 2.17 – 2.09 (m, 1H), 1.87 – 1.72 (m, 3H), 1.70 – 1.64 (m, 3H), 1.61 – 1.48 (m, 2H), 1.45 – 1.30 (m, 2H),1.24 (d, *J*=6.2, 3H), 1.16 – 1.00 (m, 1H). MS (ESI) *m/z*: Calcd. for: $[M]^+$ $C_{11}H_{19}NO$ 181.1; Found: 181.0.



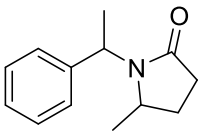
21

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ = 7.27 – 7.25 (m, 2H), 7.23 – 7.09 (m, 8H), 3.99 – 3.89 (m, 1H), 3.81 – 3.64 (m, 1H), 2.68 – 2.62 (m, 2H), 2.57 – 2.47 (m, 2H), 2.37 – 2.25 (m, 1H), 2.17 – 1.92 (m, 4H), 1.90 – 1.80 (m, 1H), 1.78 – 1.67 (m, 1H), 1.60 – 1.49 (m, 1H), 1.24 (d, *J* = 6.3, 3H). ^{13}C NMR (101 MHz, DMSO) δ = 170.84, 137.16, 136.80, 123.65, 123.62, 123.54, 123.51, 121.21, 121.09, 48.68, 48.25, 31.43, 29.12, 28.60, 27.20, 25.70, 22.89, 17.14. HRMS (ESI/TOF) *m/z*: Calcd. for $C_{22}H_{28}NO$ $[M+H]^+$ 322.2171; Found: 322.2175.



22 [S7]

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ = 4.20 – 4.09 (m, 1H), 3.83 – 3.70 (m, 1H), 2.51 – 2.39 (m, 1H), 2.35 – 2.28 (m, 1H), 2.20 – 2.07 (m, 1H), 1.61 – 1.54 (m, 1H), 1.28 – 1.20 (m, 9H). MS (ESI) *m/z*: Calcd. for : $[M]^+$ $C_8H_{15}NO$ 141.1; Found: 140.9.



23 [S6]

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ = 7.39 – 7.27 (m, 4H), 7.24 (dd, *J* = 8.4, 6.0, 1H), 5.49 – 5.38 (m, 1H), 3.85 – 3.78 (m, 0.4 H), 3.41 – 3.30 (m, 0.6H), 2.58 – 2.42 (m, 1H), 2.40 – 2.26 (m, 1H), 2.22 – 1.93 (m, 1.3H), 1.65 – 1.62 (m, 2H), 1.58 – 1.48 (s, 1.7H), 1.15 (d, *J* = 6.3 Hz, 1.6H), 0.77 (d, *J* = 6.3 Hz, 1.4H). MS (ESI) *m/z*: Calcd. for : $[M]^+$ $C_{13}H_{17}NO$ 203.1; Found: 203.0.

5. Time-dependent NMR spectra for the reductive amination.

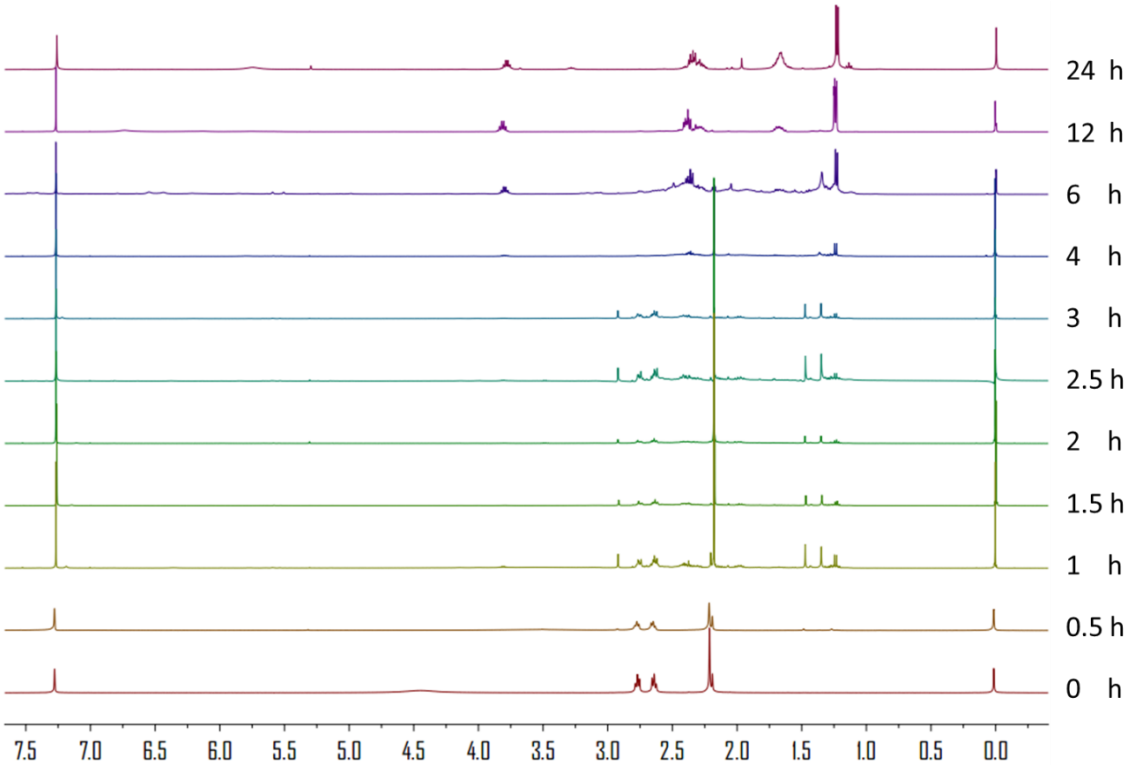


Fig. S1 ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) monitor for the reductive amination (The reaction was carried out with LA (10 mmol), AF (10 mmol) and solid **7** (0.15 mol%) at 120 ^{o}C.)

6. Profiles for the catalyst recycling in the Reductive Amination of LA by AF.

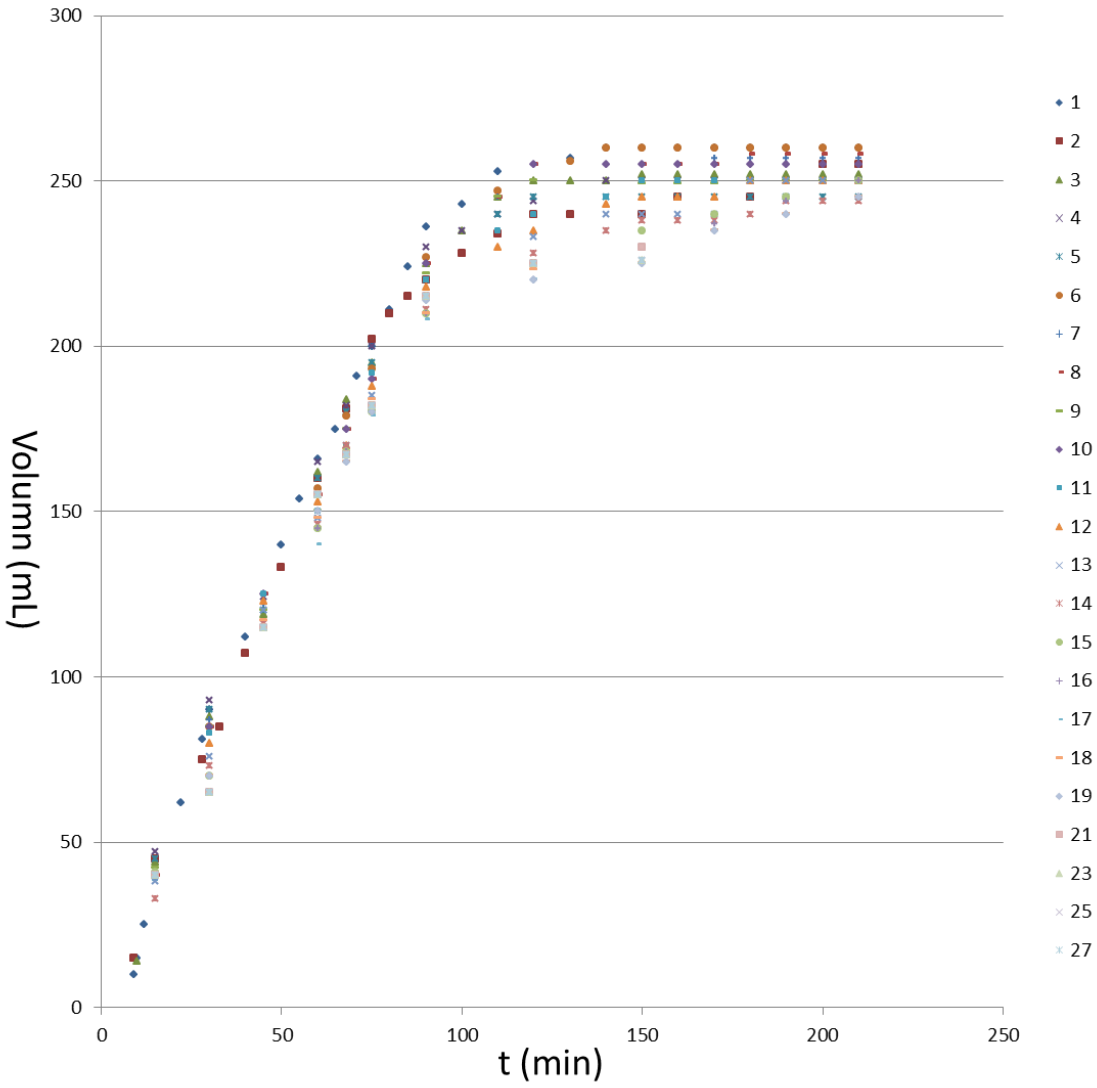


Fig. S2 The recycling experiment was carried out in 10 mmol scale with polymeric catalyst **7** under standard condition**.** The valume of the evaluated CO_2 was measured with a gas burette filled with saturated $NaHCO_3$ solution.

7. Powder XRD spectra for polymeric catalysts **3**, **6** and **7**.

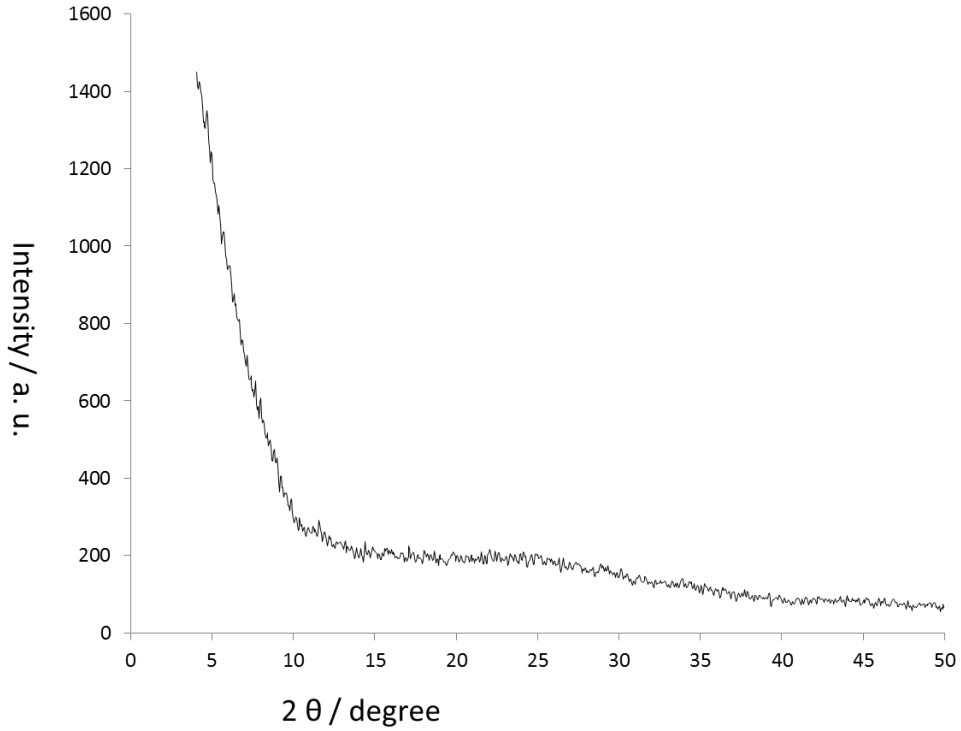


Fig. S3 The XRD spectrum of freshly prepared polymeric solid **7**.

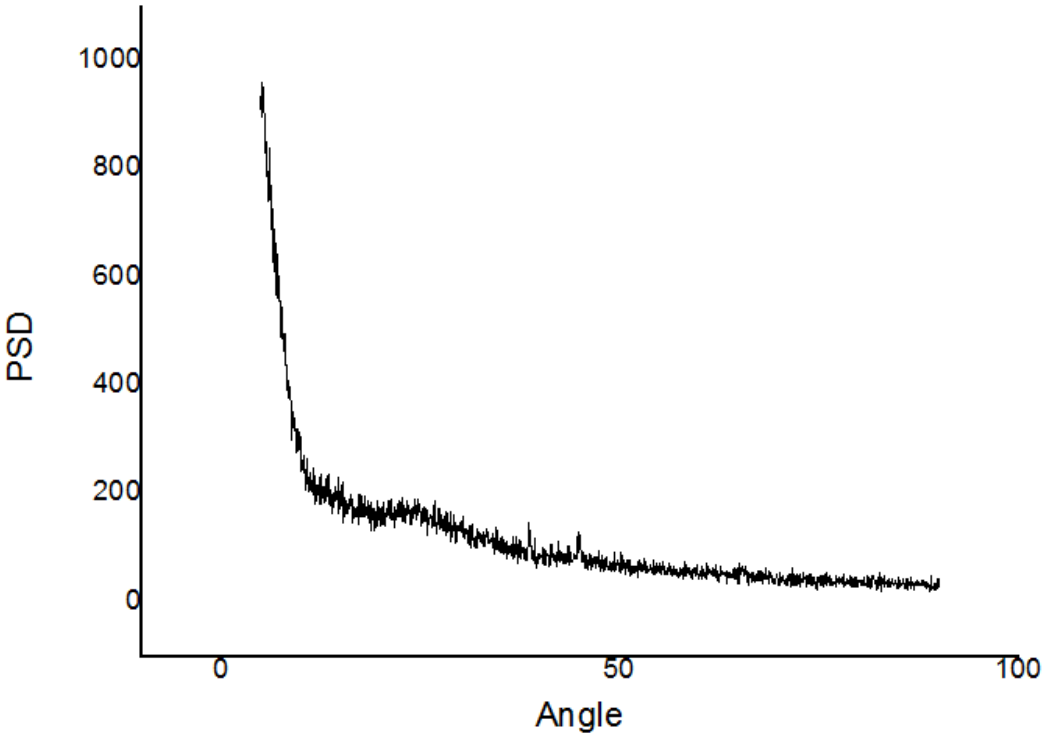


Fig. S4 The XRD spectrum of polymeric solid **7** after the 37th. runs.

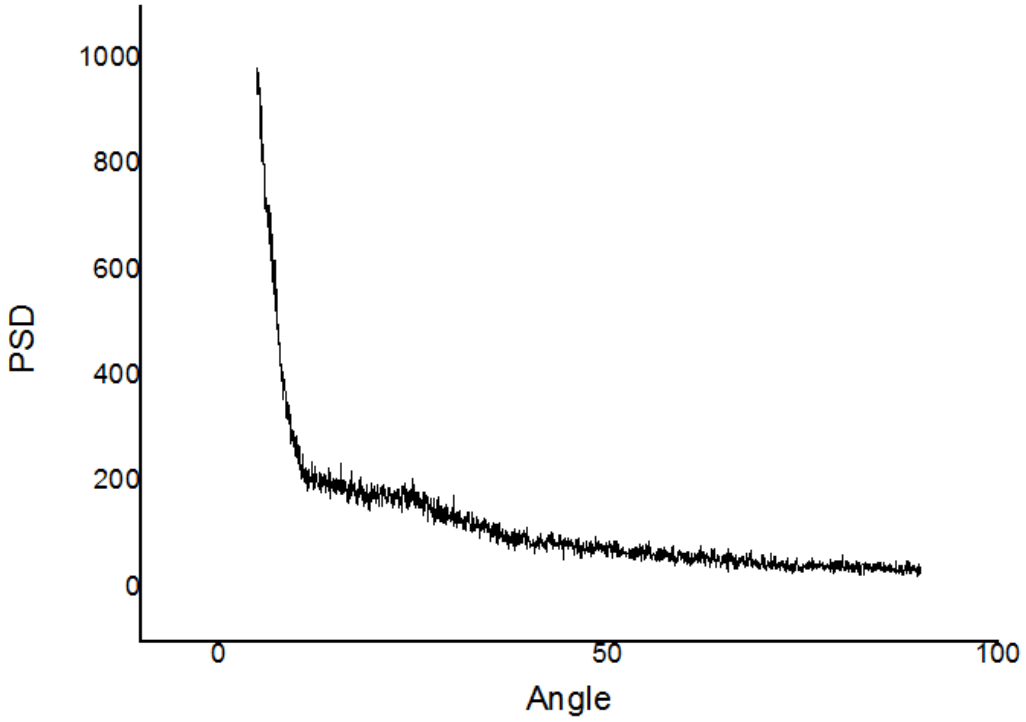


Fig. S5 The XRD spectrum of freshly prepared polymeric solid **3**.

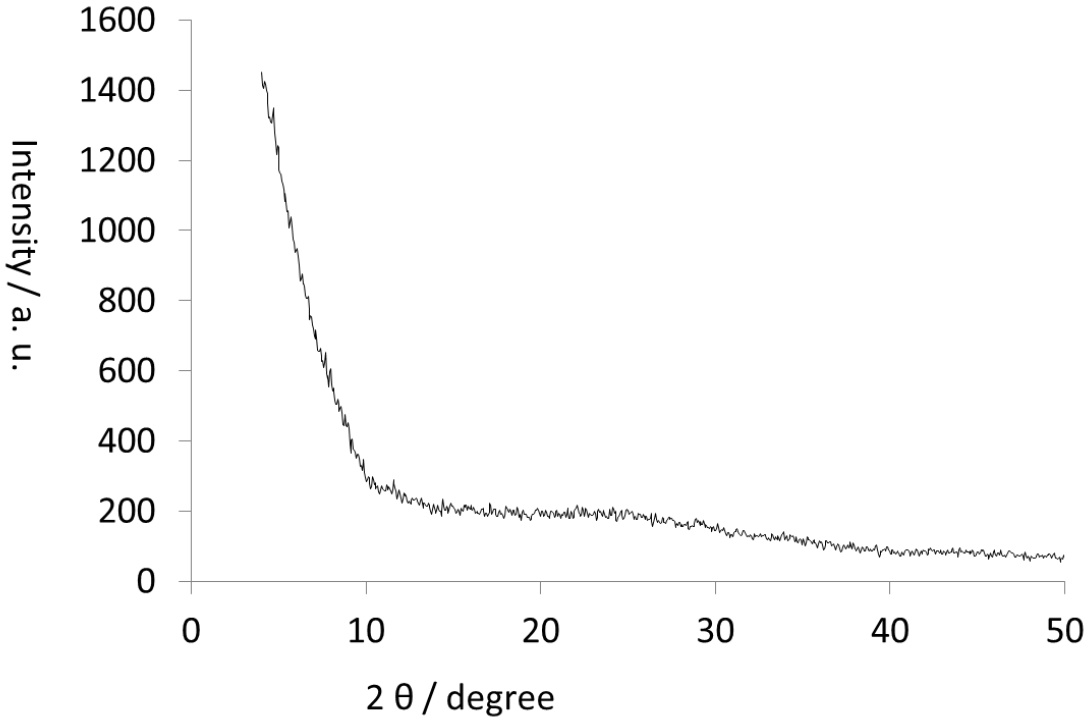


Fig. S6 The XRD spectrum of freshly prepared polymeric solid **6**.

8. SEM morphologies for polymeric catalysts **3**, **6** and **7**.

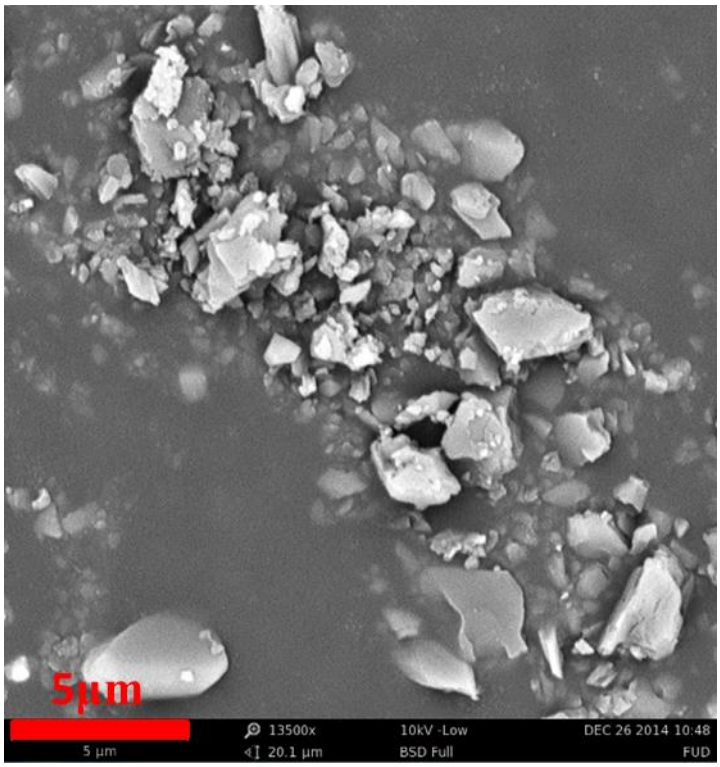


Fig. S7 SEM morphology of freshly prepared polymeric solid **7**.

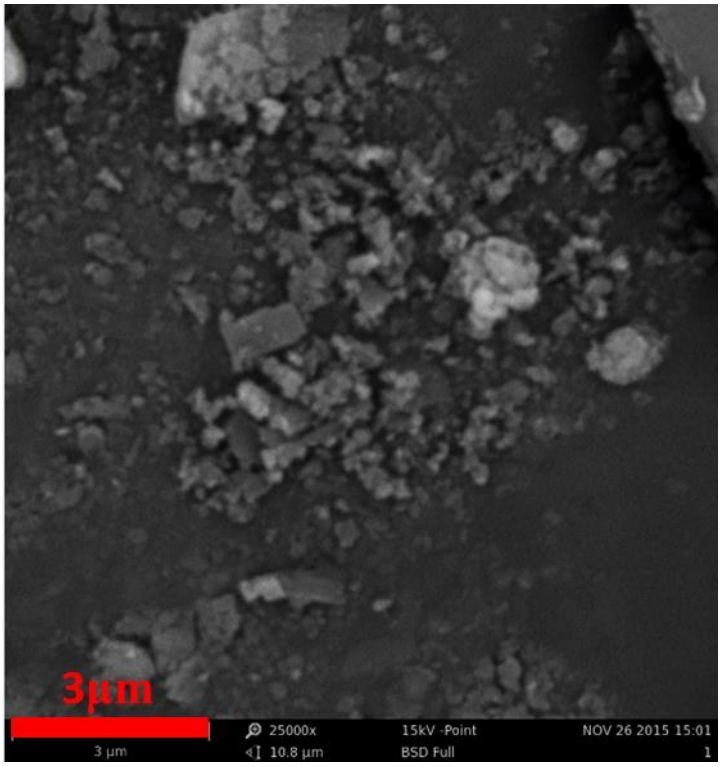


Fig. S8 SEM morphology of solid **7** after the 20th. runs with one-step procedure.

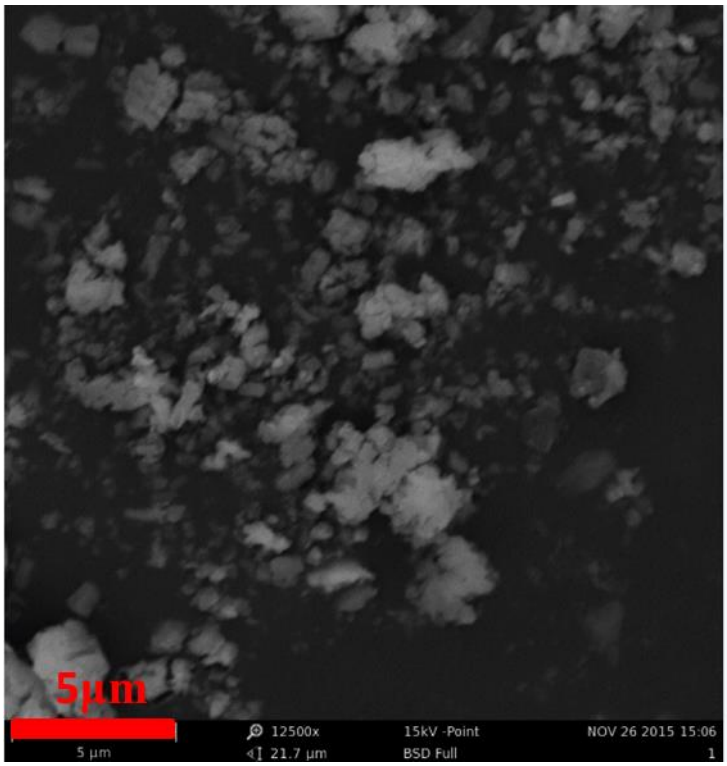


Fig. S9 SEM morphology of solid **7** after the 37th. runs with stepwise procedure.

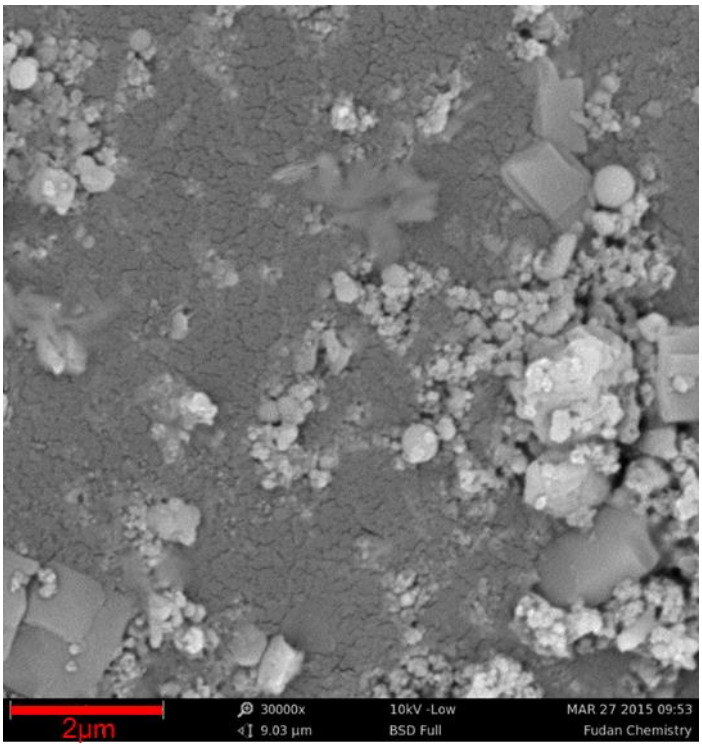


Fig. S10 SEM morphology of freshly prepared polymeric solid **3**.

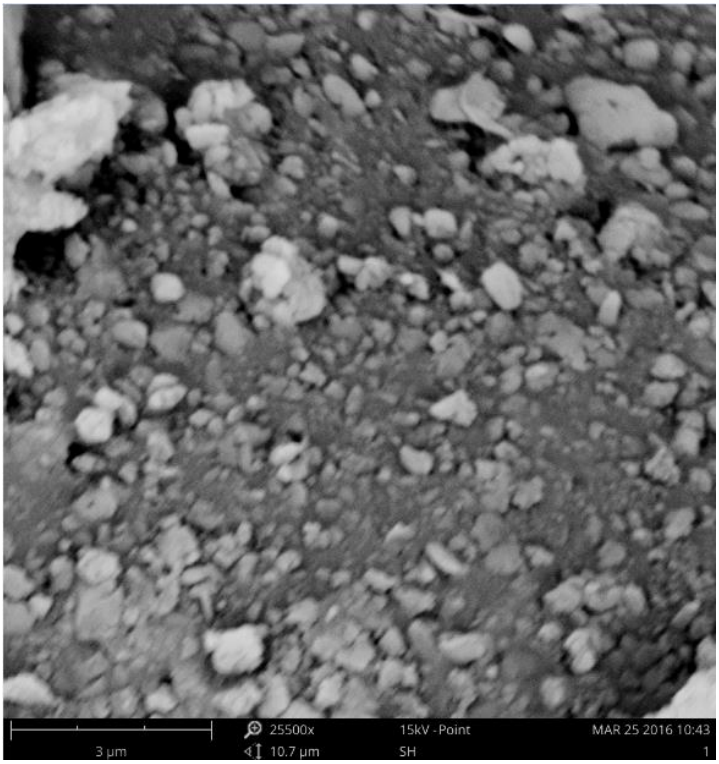


Fig. S11 SEM morphology of freshly prepared polymeric solid **6**.

9. TEM morphologies for polymeric catalysts **3**, **6** and **7**.

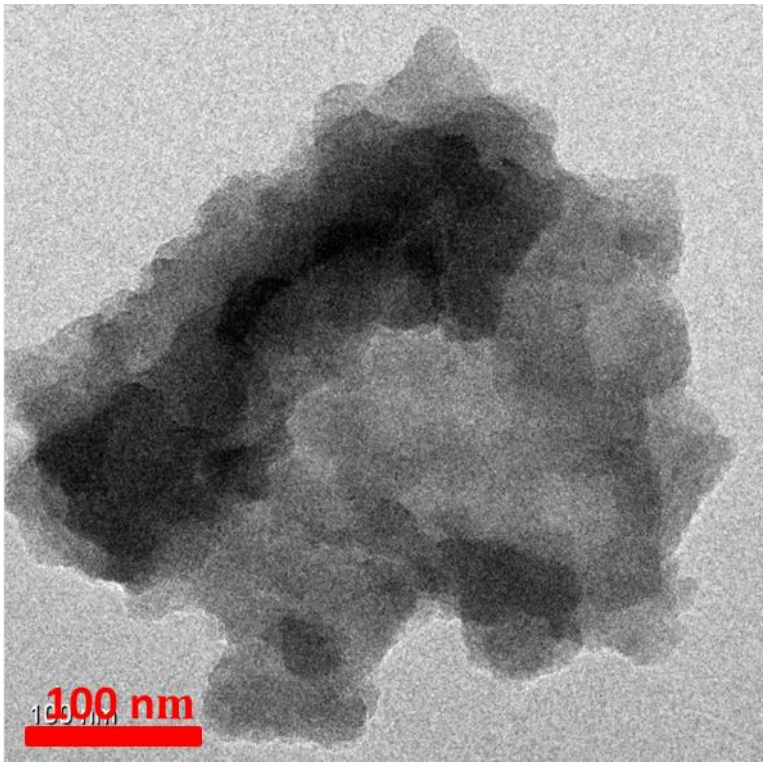


Fig. S12 TEM morphology of freshly prepared polymeric solid **7**.

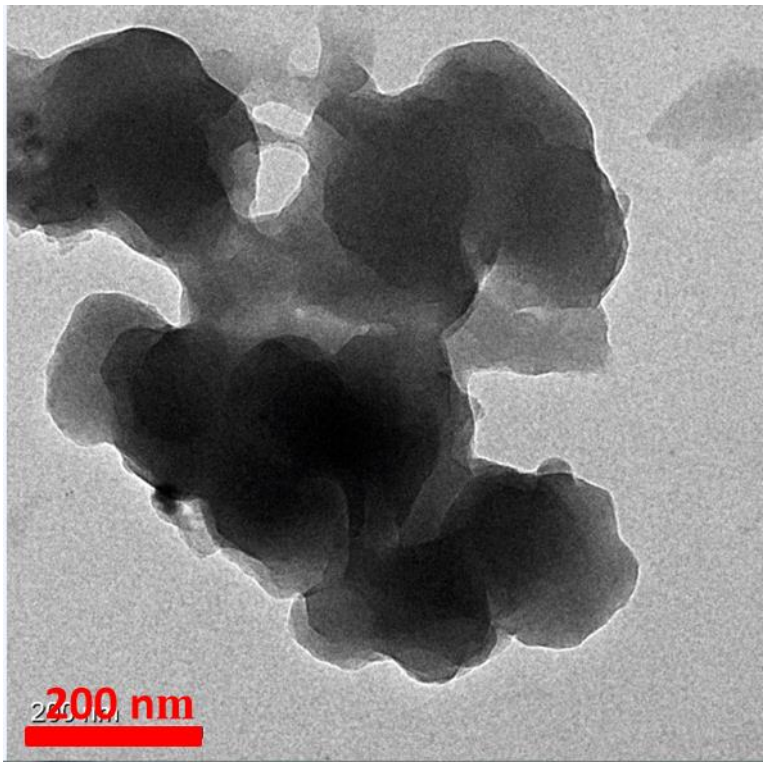


Fig. S13 TEM morphology of solid **7** after the 37th. runs with stepwise procedure.

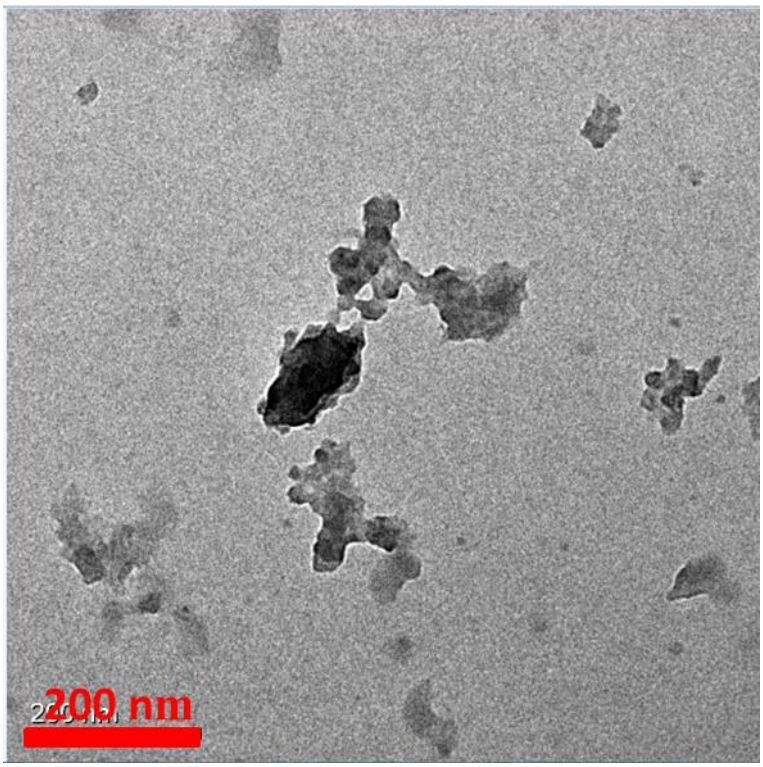


Fig. S14 TEM morphology of freshly prepared polymeric solid **6**.

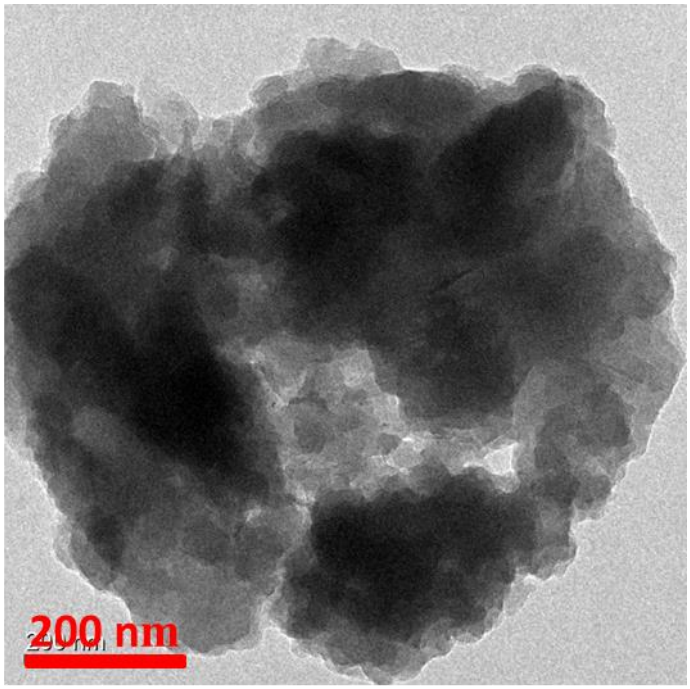


Fig. S15 TEM morphology of freshly prepared polymeric solid **3**.

10. EDX pattern of polymeric catalysts **3**, **6** and**7**.

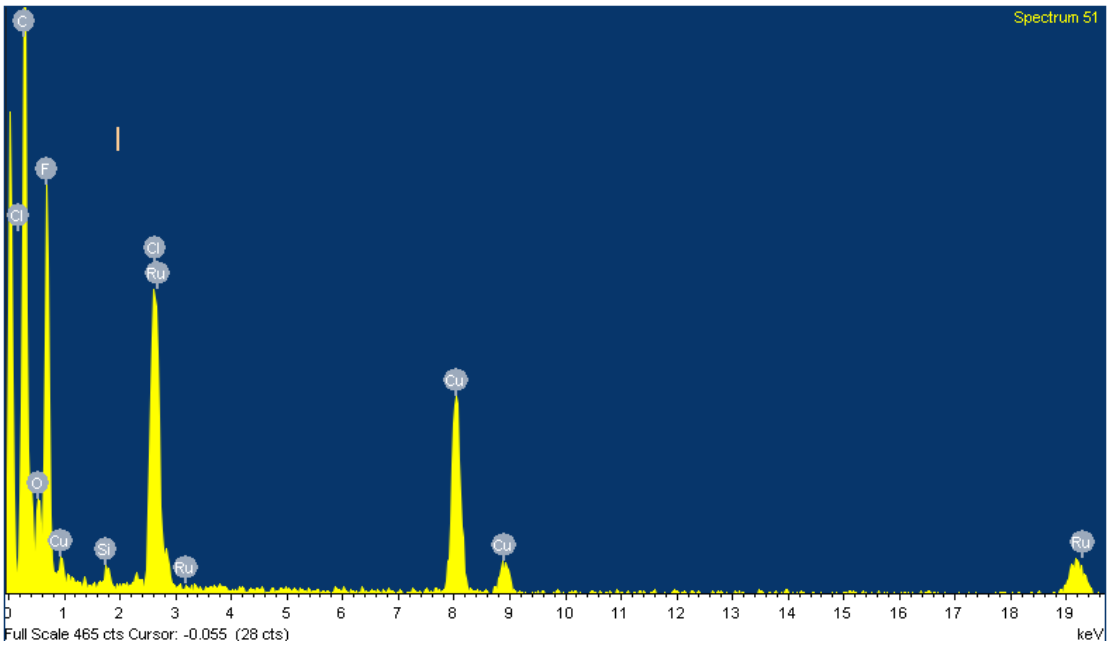


Fig. S16 EDX spectrum of freshly prepared polymeric solid **7**.

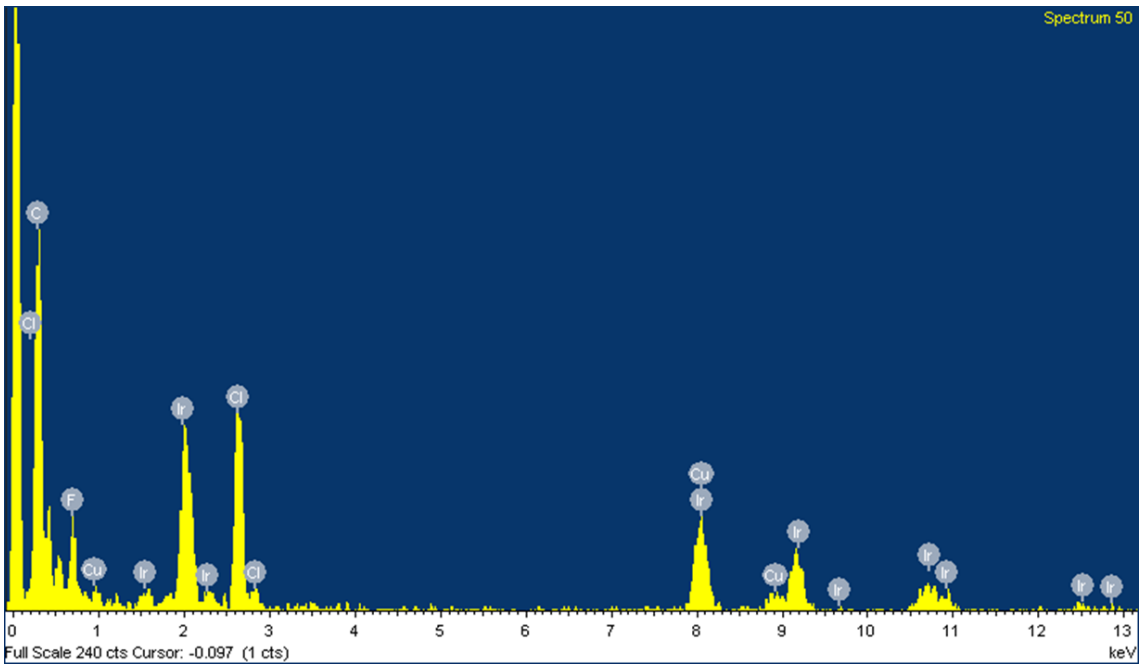


Fig. S17 EDX spectrum of freshly prepared polymeric solid **6**.

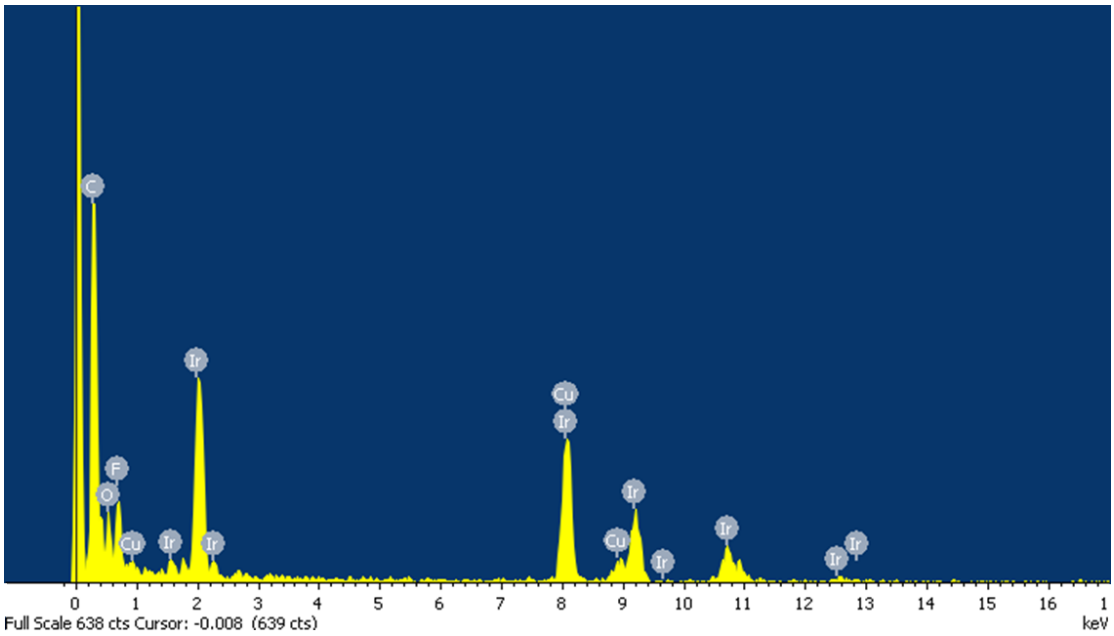


Fig. S18 EDX spectrum of freshly prepared polymeric solid **3**.

11. Metal-leaching measurements with the filtrates after each run by ICP-AES.

11.1 ICP-AES measurements of the clear filtrate after centrifugation with one-step procedure for the reductive amination and cyclization.

Table S2 The concentration of Ru in the filtrate for each runs after centrifugation with one-step procedure measured by the ICP-AES.[a]

Entry	Elementary	Concentration(mg/L)
1	Ru	4.08
2	Ru	1.43
3	Ru	0.283
4	Ru	0.076
5	Ru	0.063
6	Ru	0.033
7	Ru	0.021
8	Ru	0.023
9	Ru	0.014
10	Ru	0.012
11	Ru	0.016
12	Ru	0.012
13	Ru	<0.002
14	Ru	<0.002
15	Ru	<0.002
16	Ru	<0.002
17	Ru	<0.002
18	Ru	<0.002
19	Ru	<0.002
20	Ru	<0.002

[a] 1 mg/L is equal to 0.4% of initially input of [Ru] in the NHC-Ru polymeric catalyst **7**.

11.2 ICP-AES results of the clear filtrate after centrifugation with the stepwise procedure for the reductive amination and cyclization.

Table S3 The concentration of Ru in the filtrate for each runs after centrifugation with the stepwise procedure measured by the ICP-AES.[a]

Entry	Elementary	Concentration(mg/L)
1	Ru	4.28
2	Ru	0.23
3	Ru	0.083
4	Ru	0.026
5	Ru	0.003
6	Ru	0.001
7	Ru	<0.002
8	Ru	<0.002
9	Ru	<0.002
10	Ru	<0.002
11	Ru	<0.002
12	Ru	<0.002
13	Ru	<0.002
14	Ru	<0.002
15	Ru	<0.002
16	Ru	<0.002
17	Ru	<0.002
18	Ru	<0.002
19	Ru	<0.002
20	Ru	<0.002
21	Ru	<0.002
22	Ru	<0.002
23	Ru	<0.002
24	Ru	<0.002
25	Ru	<0.002
26	Ru	<0.002
27	Ru	<0.002
28	Ru	<0.002
29	Ru	<0.002
31	Ru	<0.002
32	Ru	<0.002
33	Ru	<0.002
34	Ru	<0.002
35	Ru	<0.002
36	Ru	<0.002
37	Ru	<0.002

[a] 1 mg/L is equal to 0.4% of initially input of [Ru] in the NHC-Ru polymeric catalyst **7.**

12. TGA spectra of polymeric catalysts **3**, **6** and **7**.

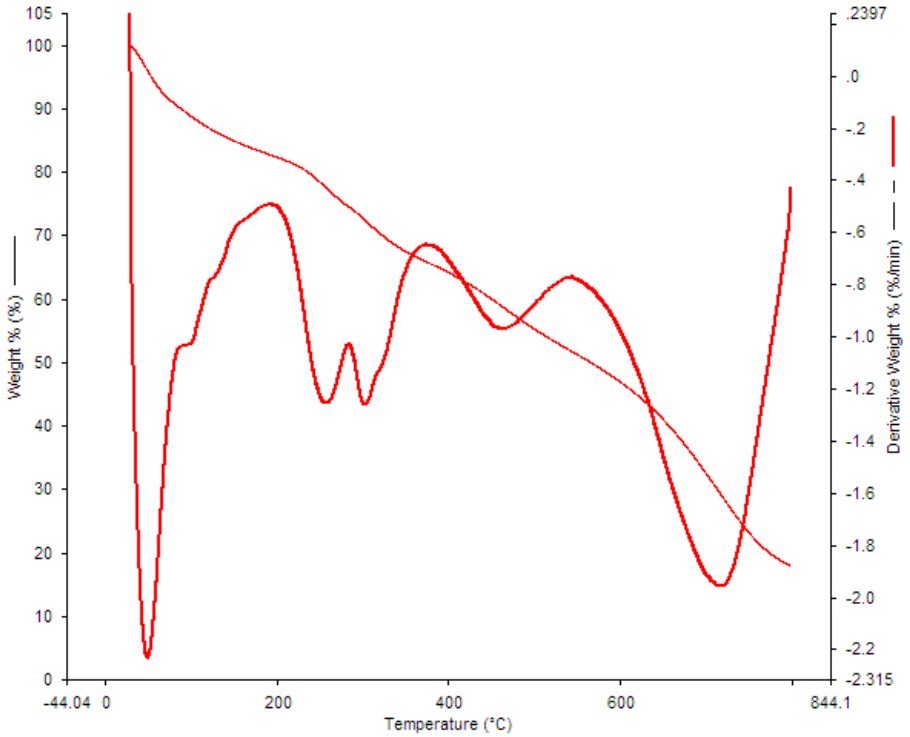


Fig. S19 TGA spectrum of freshly prepared polymeric solid **7**.

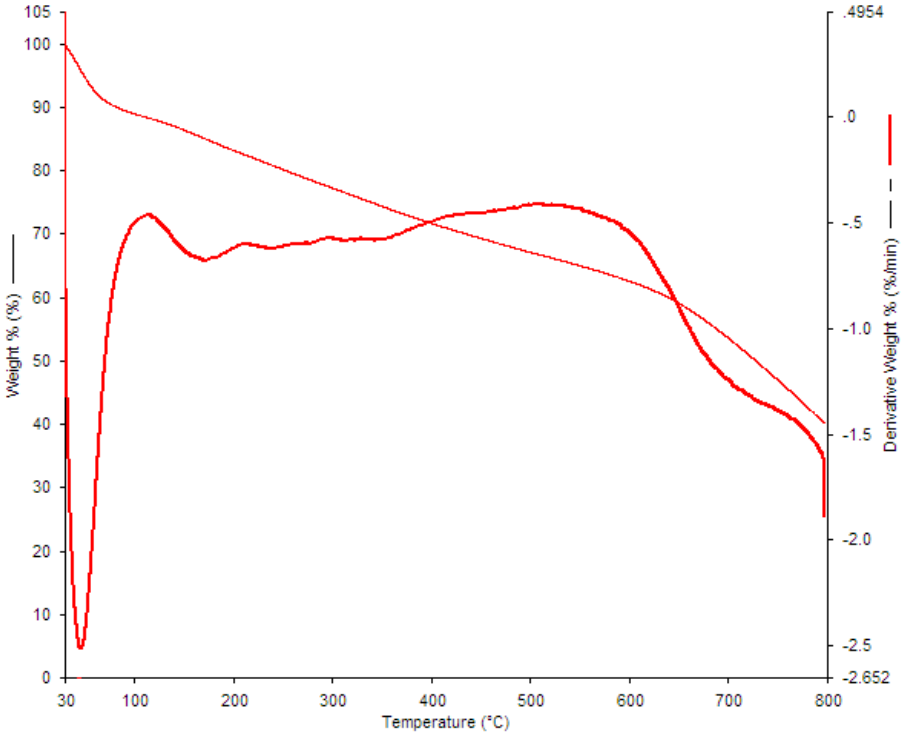


Fig. S20 TGA spectrum of freshly prepared polymeric solid **3**.

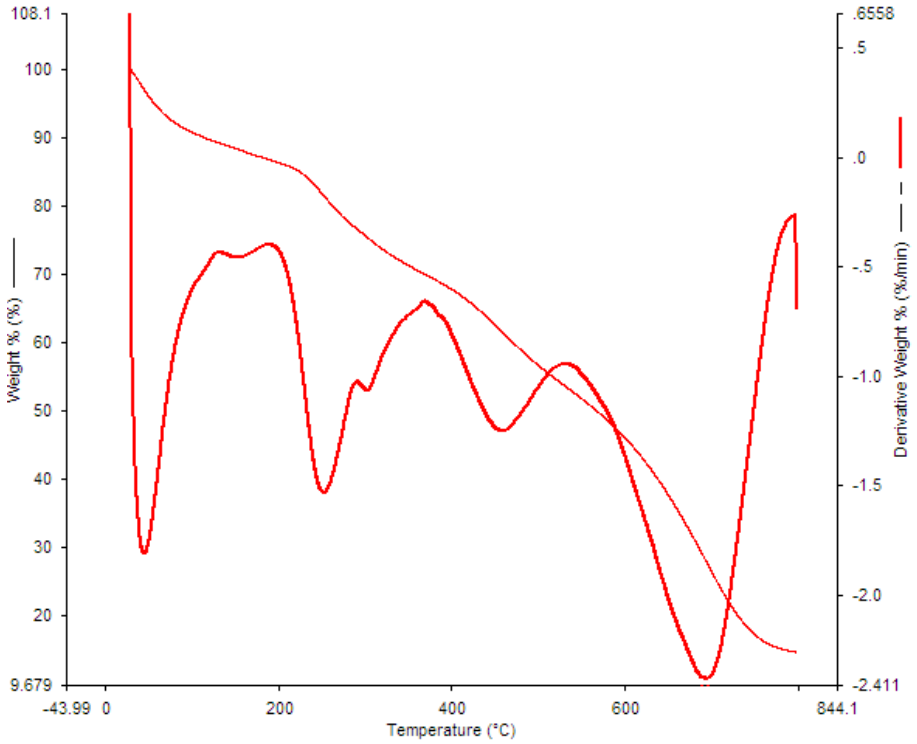


Fig. S21 TGA spectrum of freshly prepared polymeric solid **6**.

13. ^{1}H, ^{13}C and ^{19}F NMR spectra for important compounds.

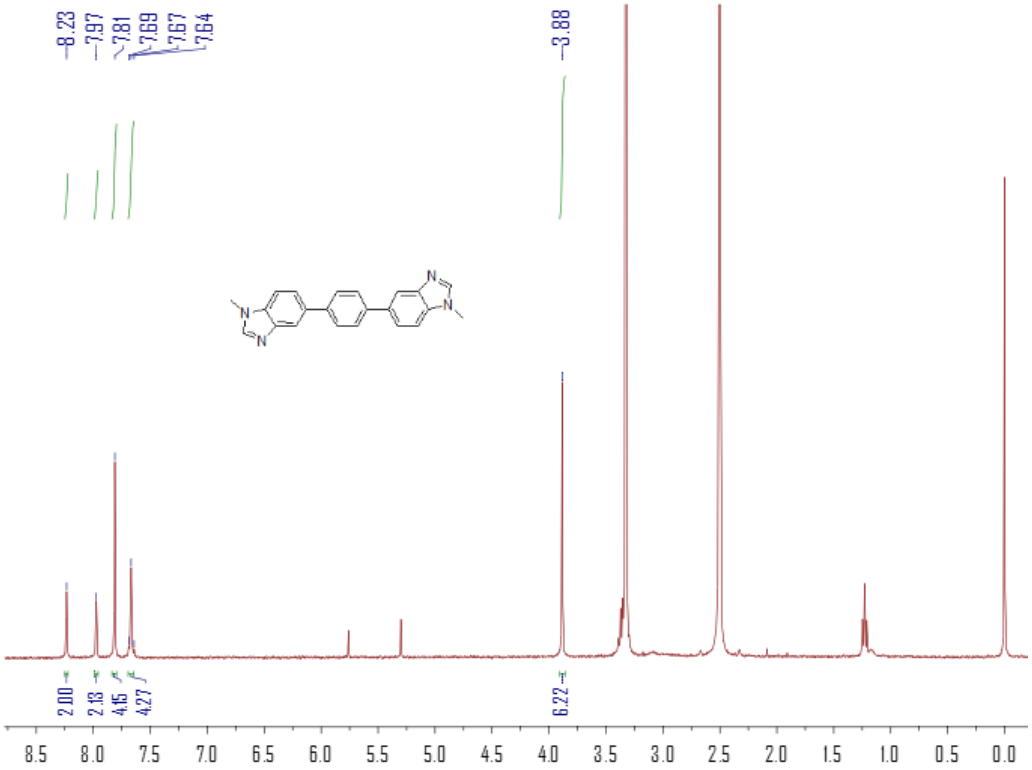


Fig. S22 ^{1}H NMR spectrum of compound **S1**.

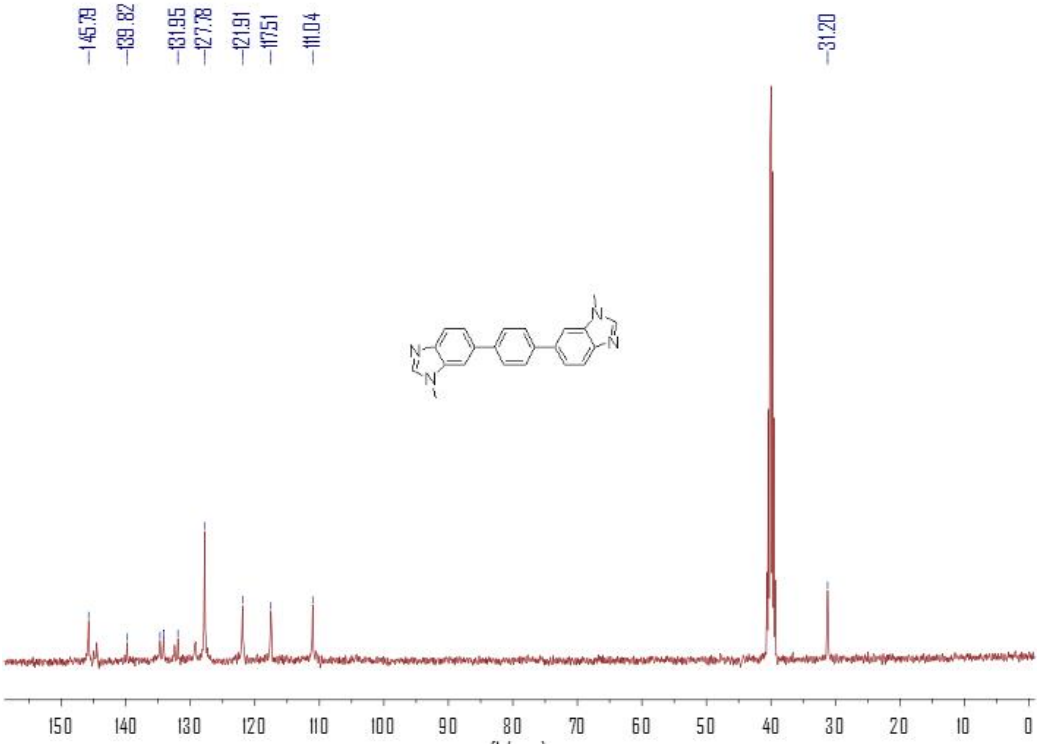


Fig. S23 ^{13}C NMR spectrum of compound **S1**.

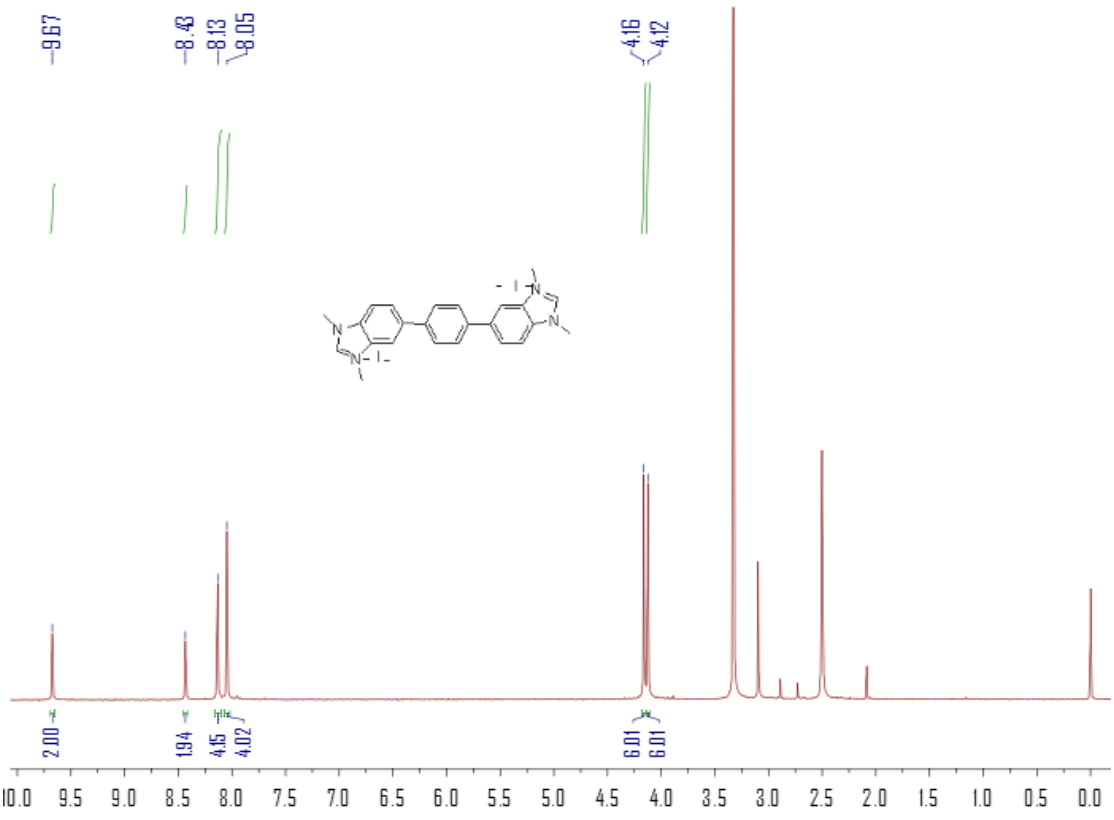


Fig. S24 ^{1}H NMR spectrum of compound **S2**.

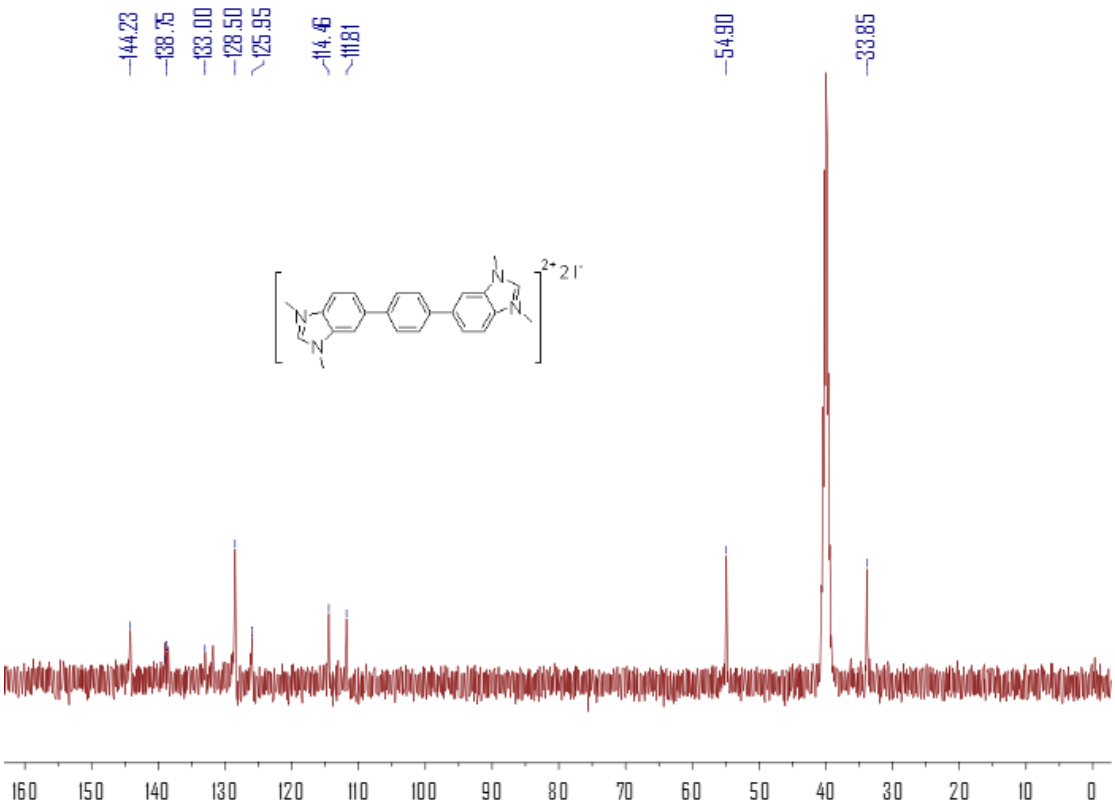


Fig. S25 ^{13}C NMR spectrum of compound **S2**.

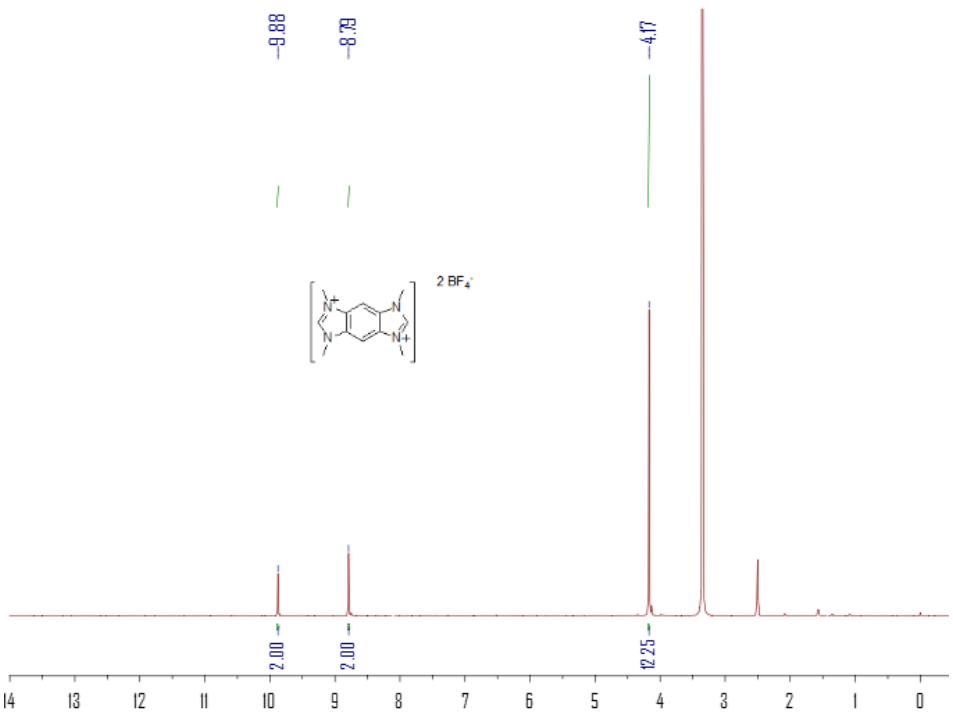


Fig. S26 ^{1}H NMR spectrum of compound **3**.

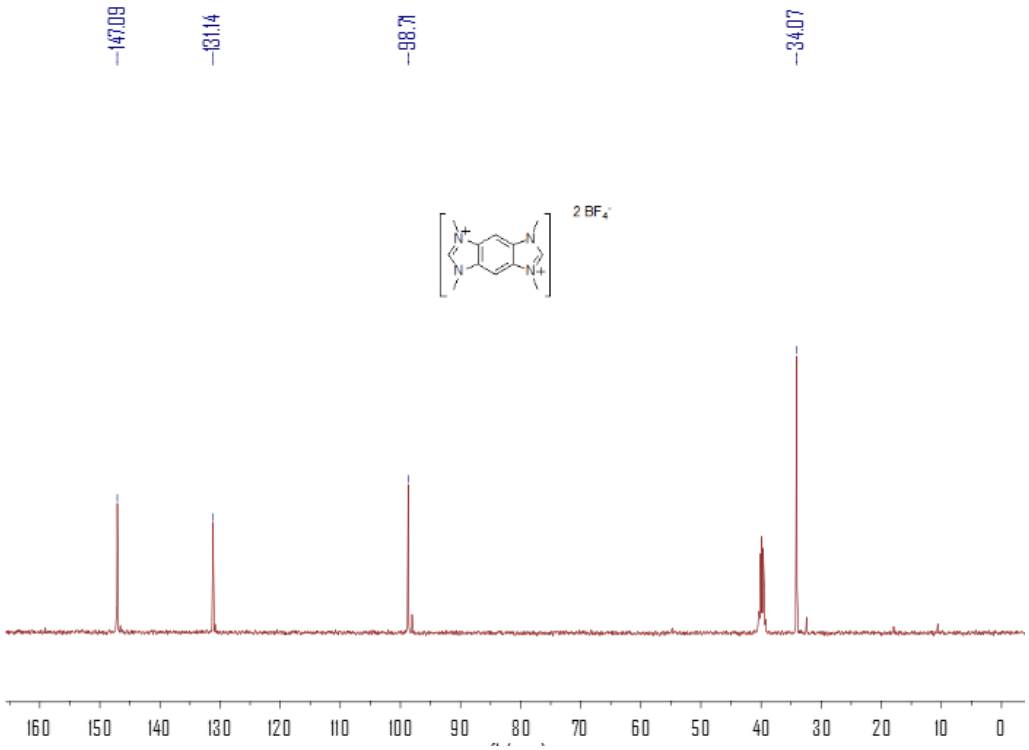


Fig. S27 ^{13}C NMR spectrum of compound **3**.

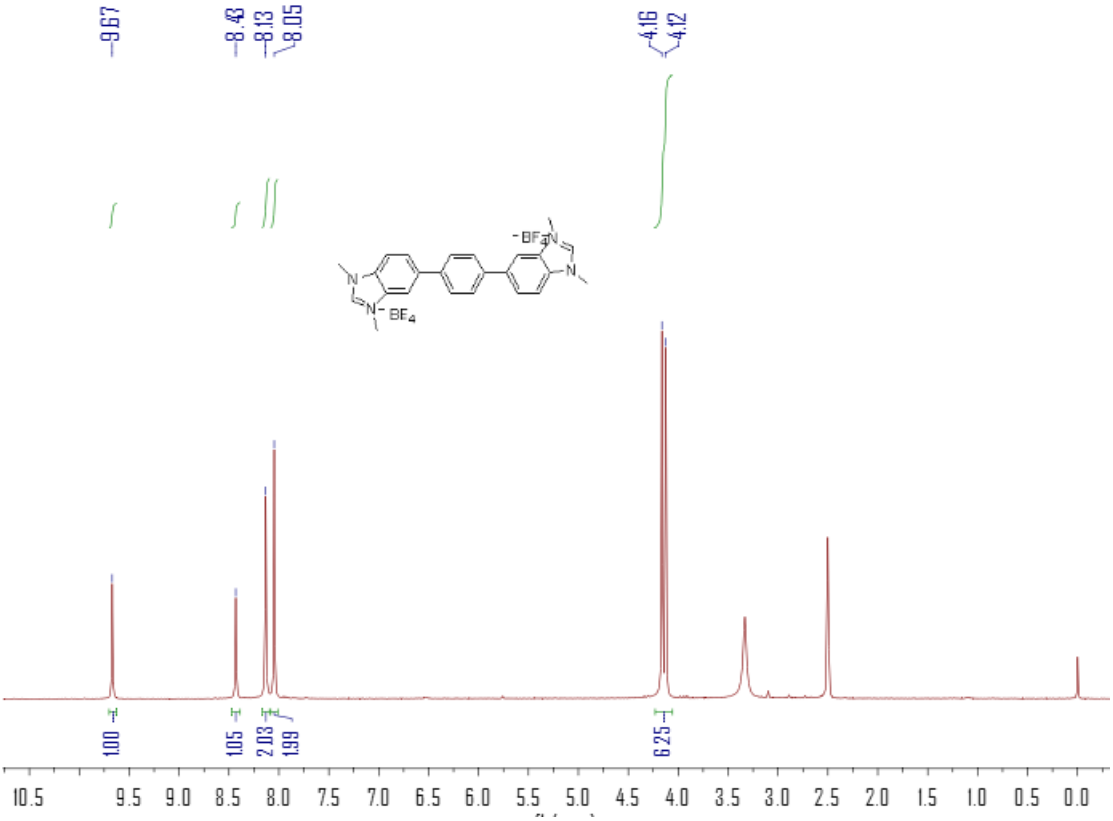


Fig. S28 ^{1}H NMR spectrum of compound **5**.

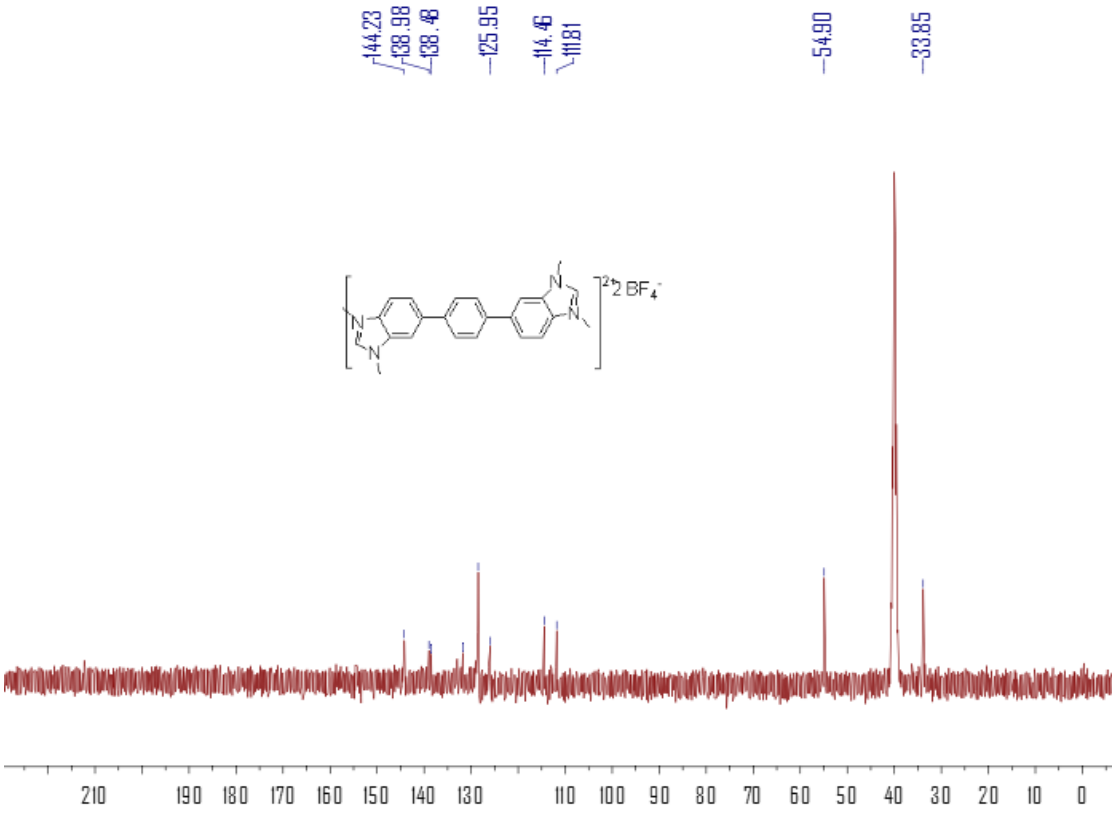


Fig. S29 ^{13}C NMR spectrum of compound **5**.

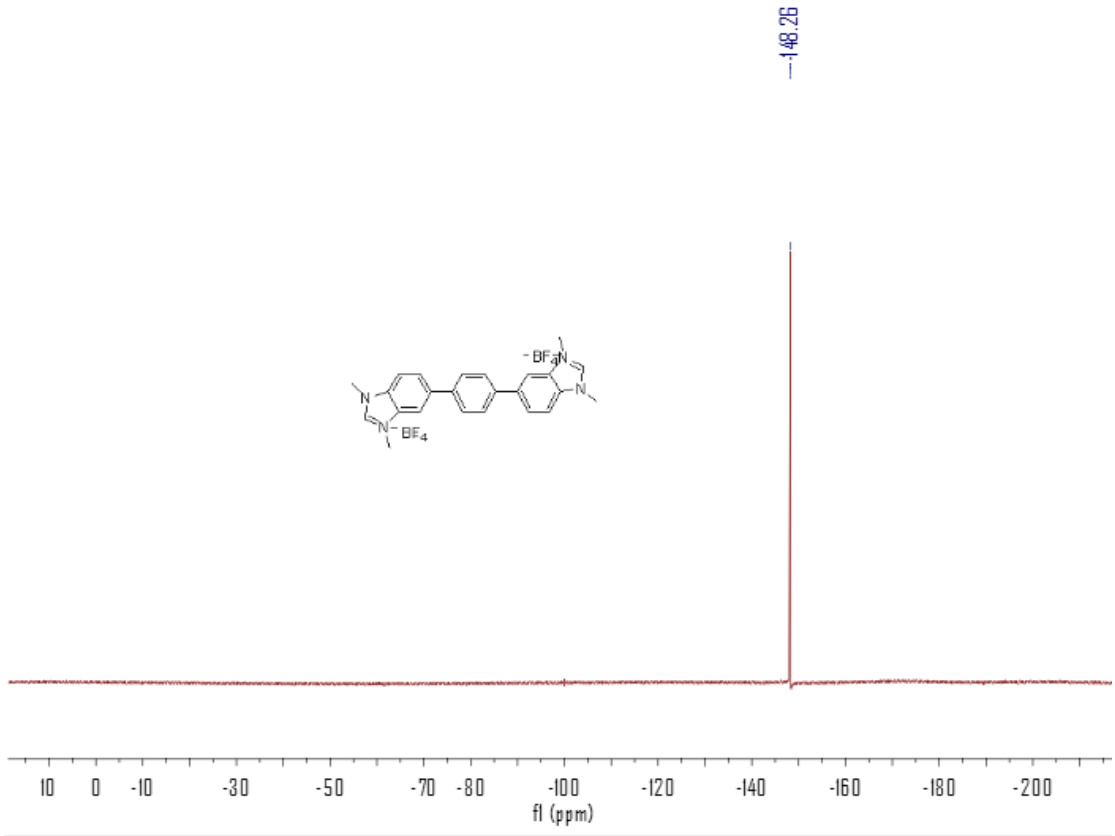


Fig. S30 ^{19}F NMR spectrum of compound **5**.

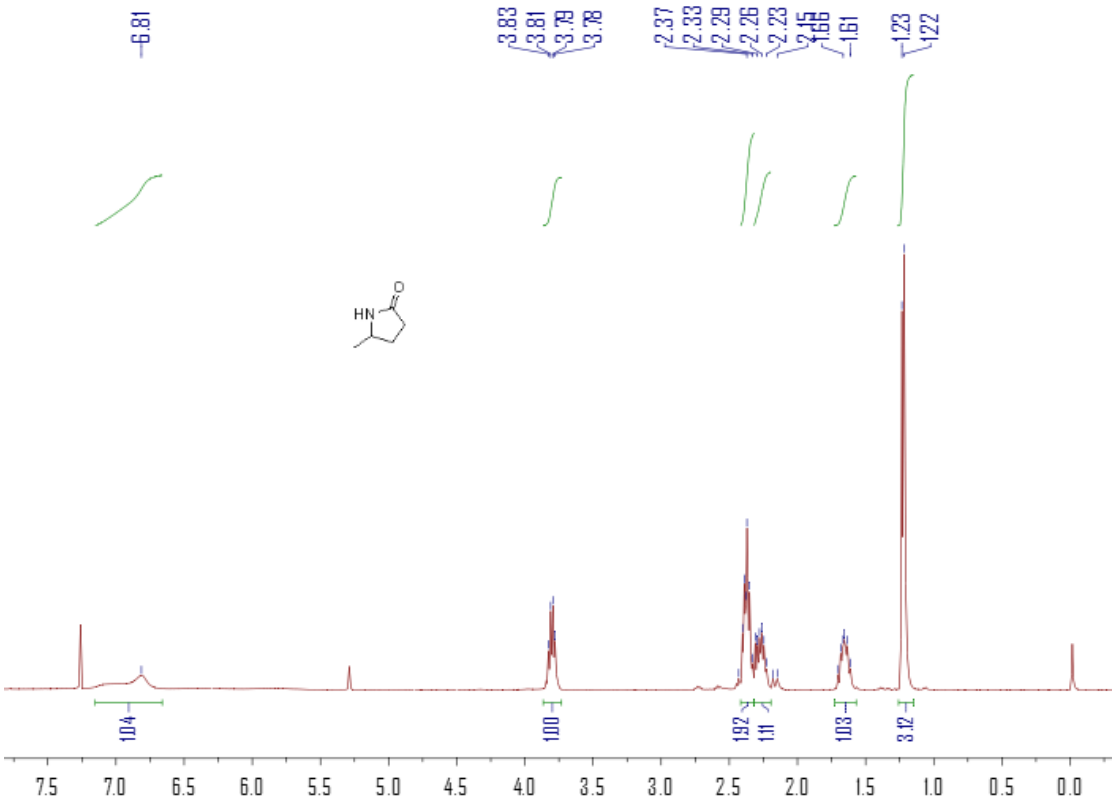


Fig. S31 ^{1}H NMR spectrum of compound **9**.

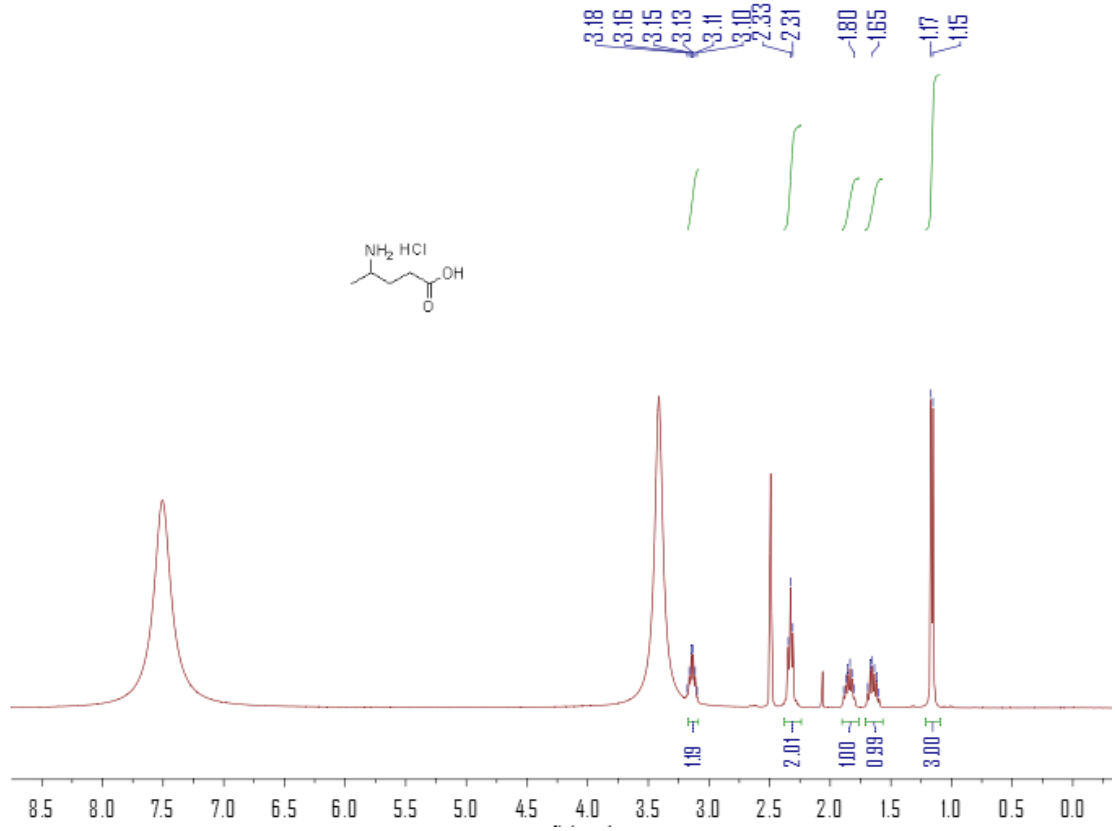


Fig. S32 ^{1}H NMR spectrum of compound **10**.

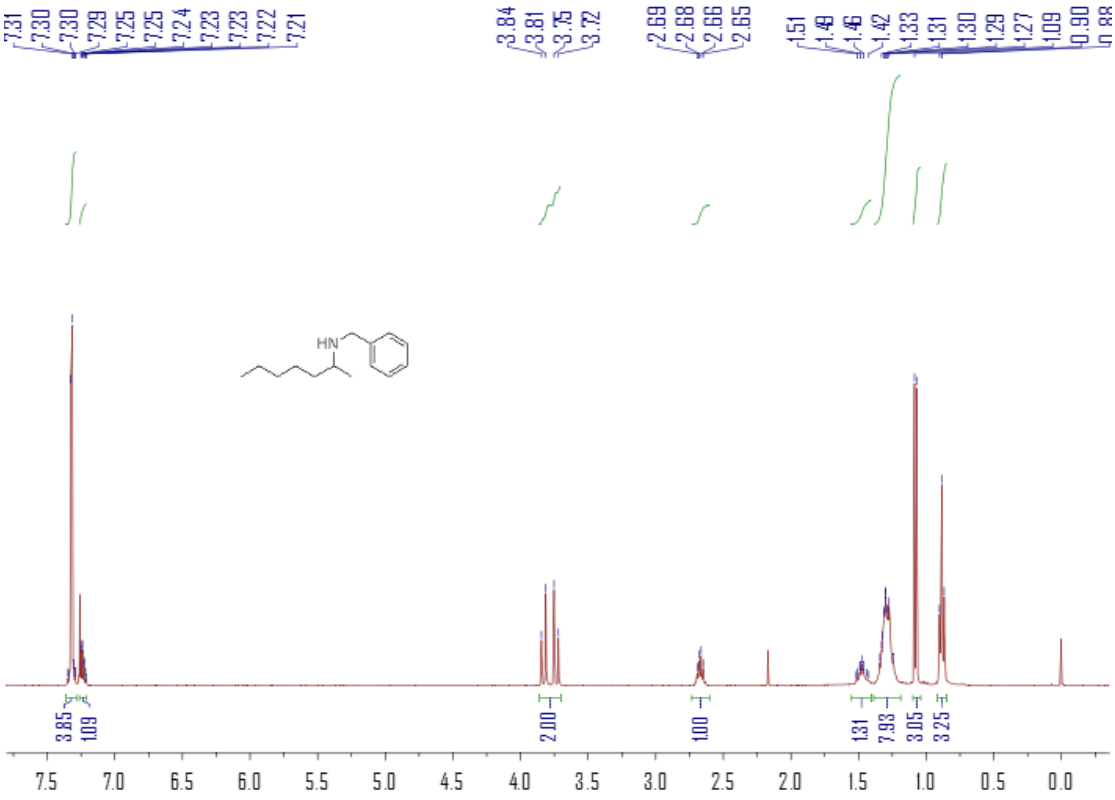


Fig. S33 ^{1}H NMR spectrum of compound **12**.

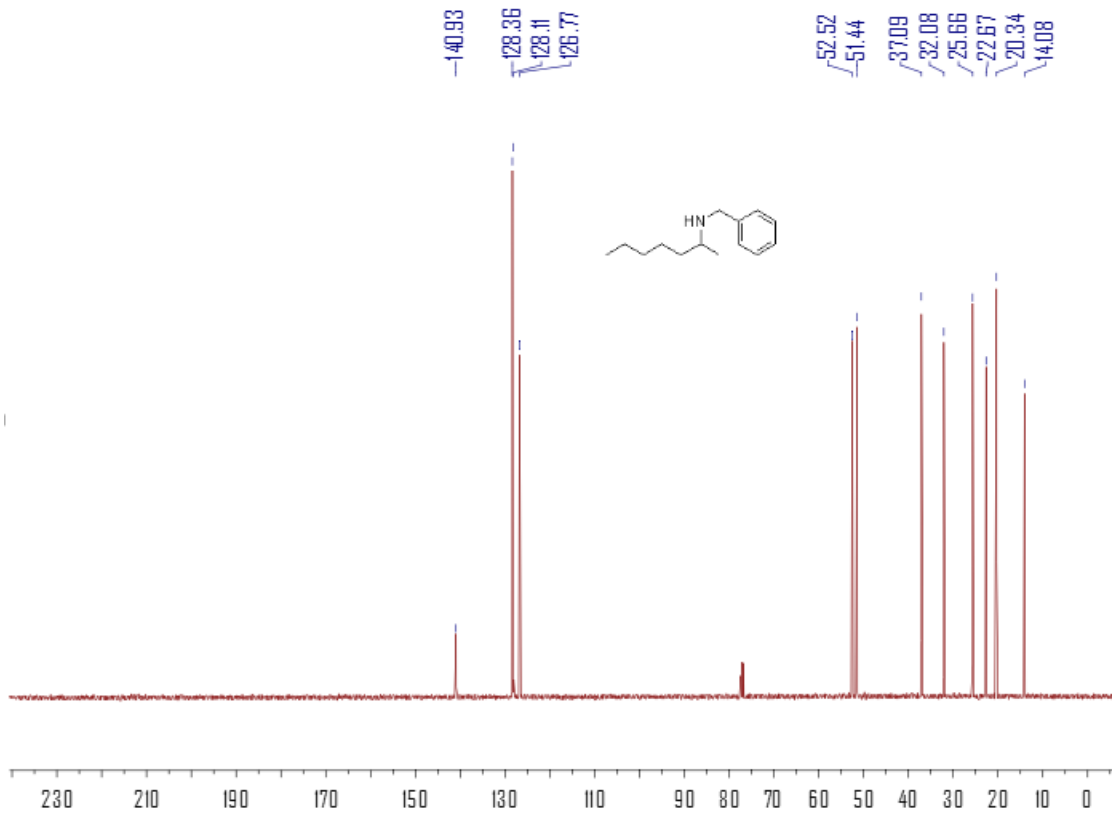


Fig. S34 ^{13}C NMR spectrum of compound **12**.

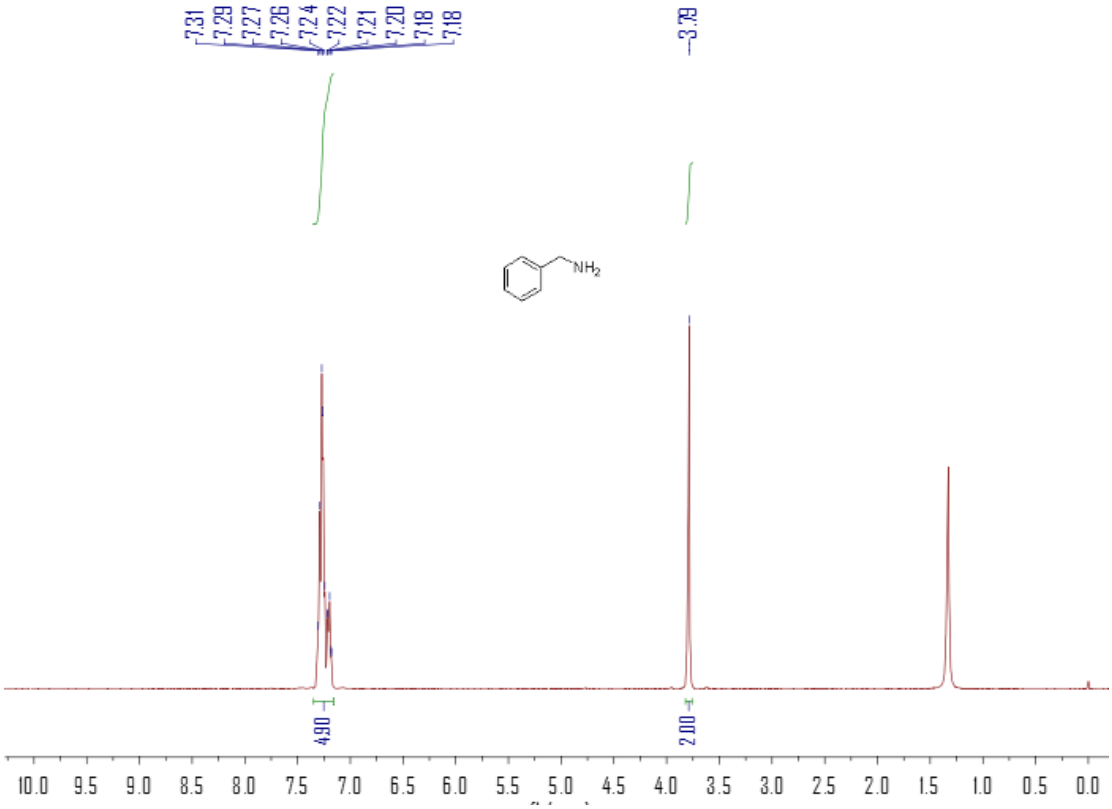


Fig. S35 ^{1}H NMR spectrum of compound **13**.

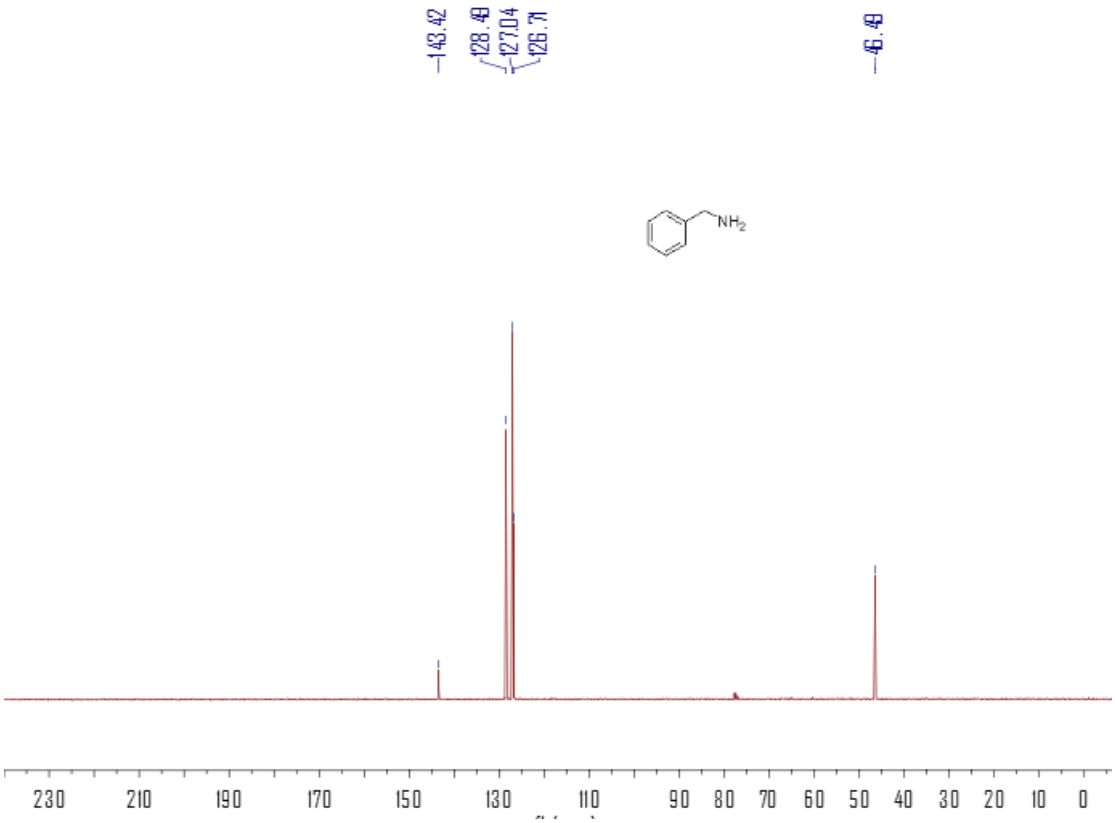


Fig. S36 ^{13}C NMR spectrum of compound **13**.

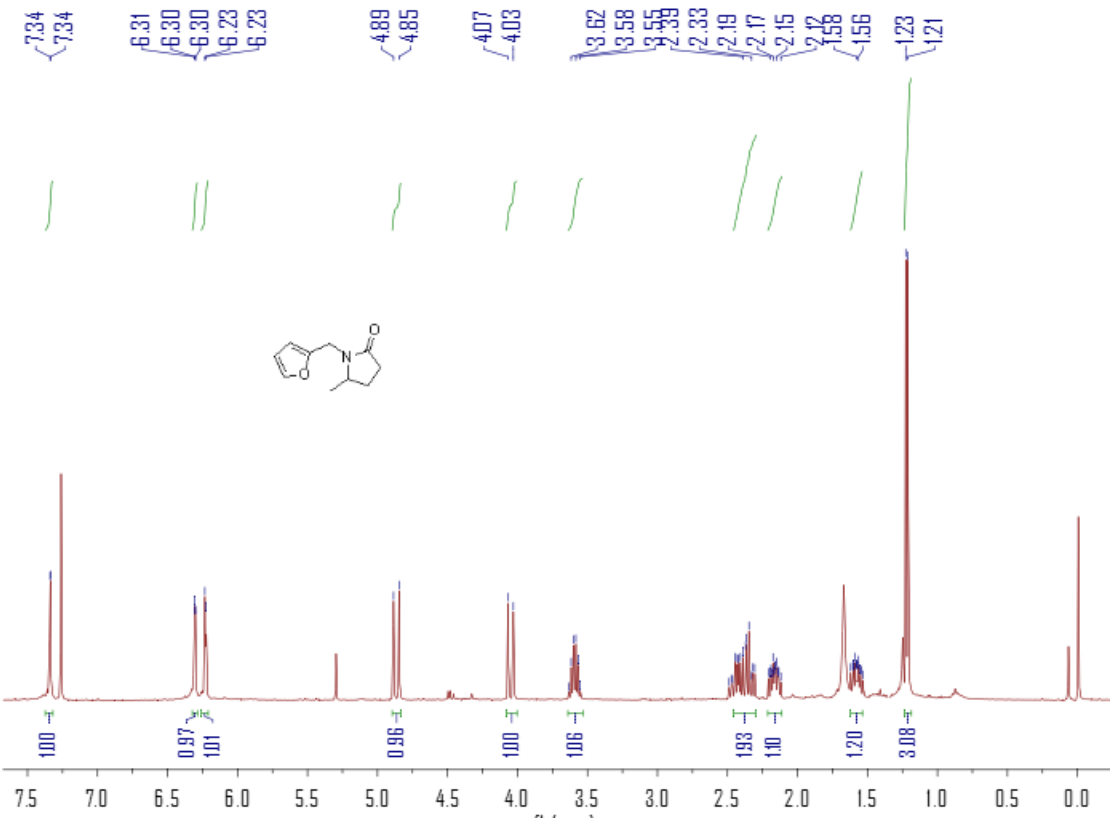


Fig. S37 ^{1}H NMR spectrum of compound **14**.

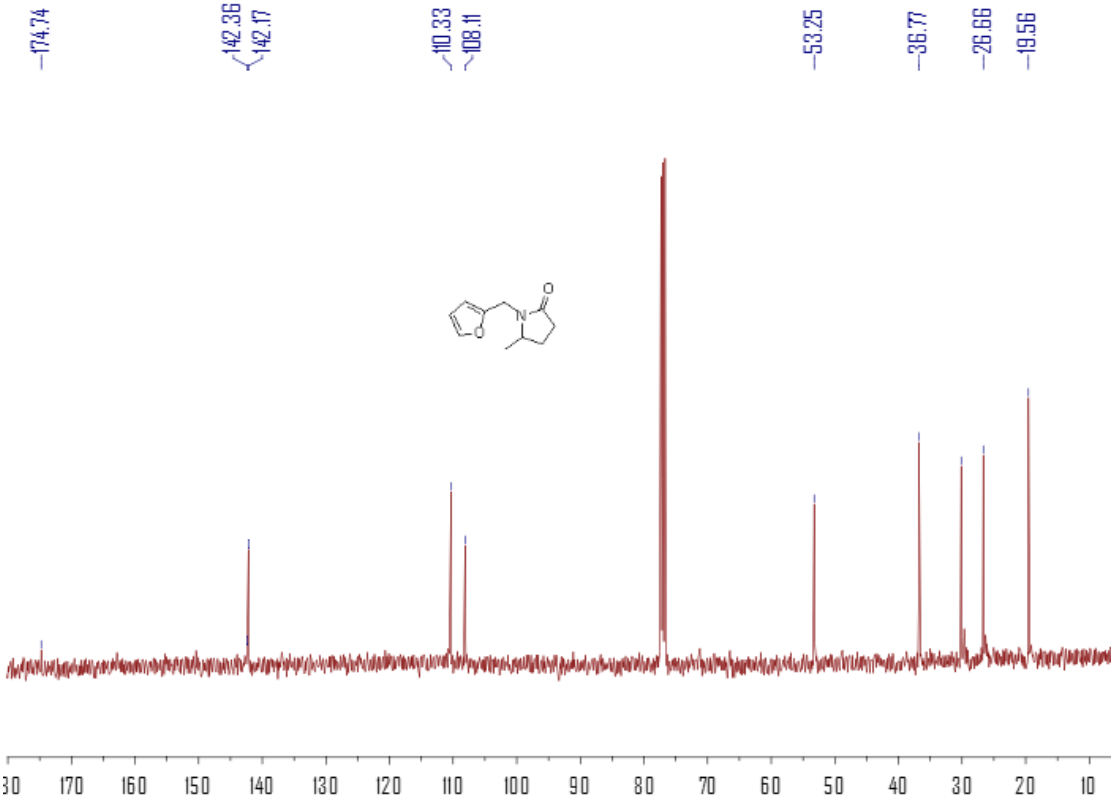


Fig. S38 ^{13}C NMR spectrum of compound **14**.

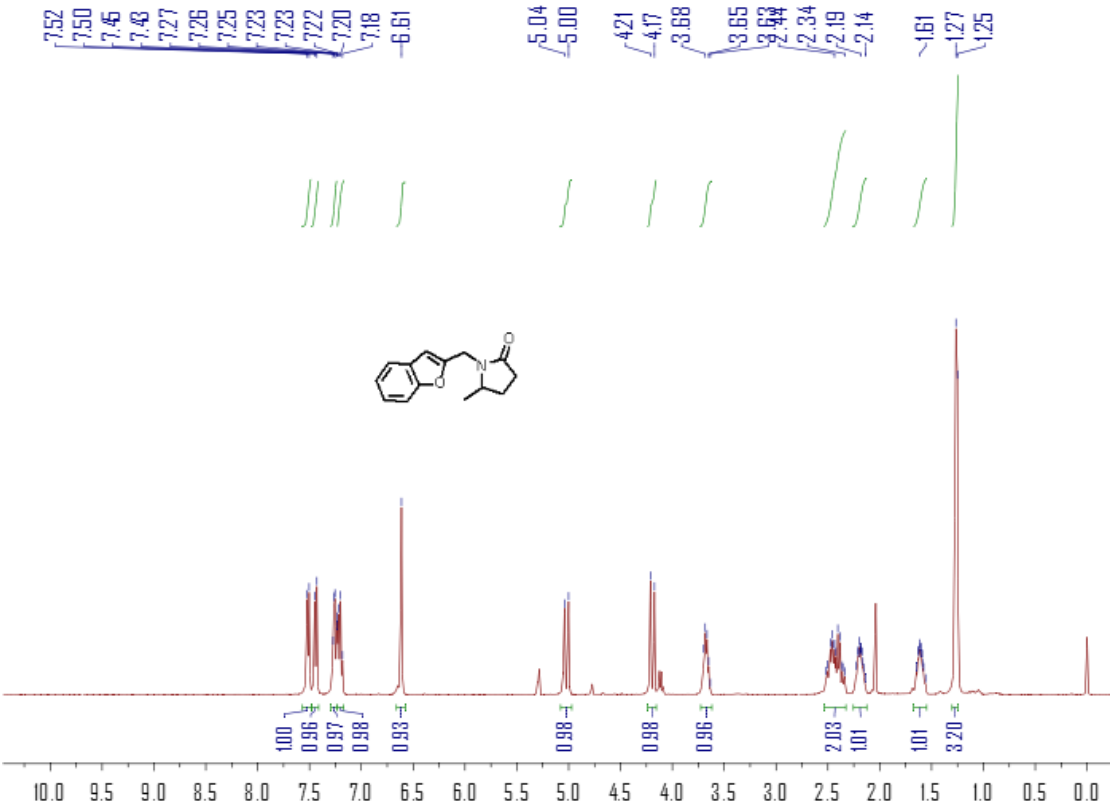


Fig. S39 ^{1}H NMR spectrum of compound **15**.

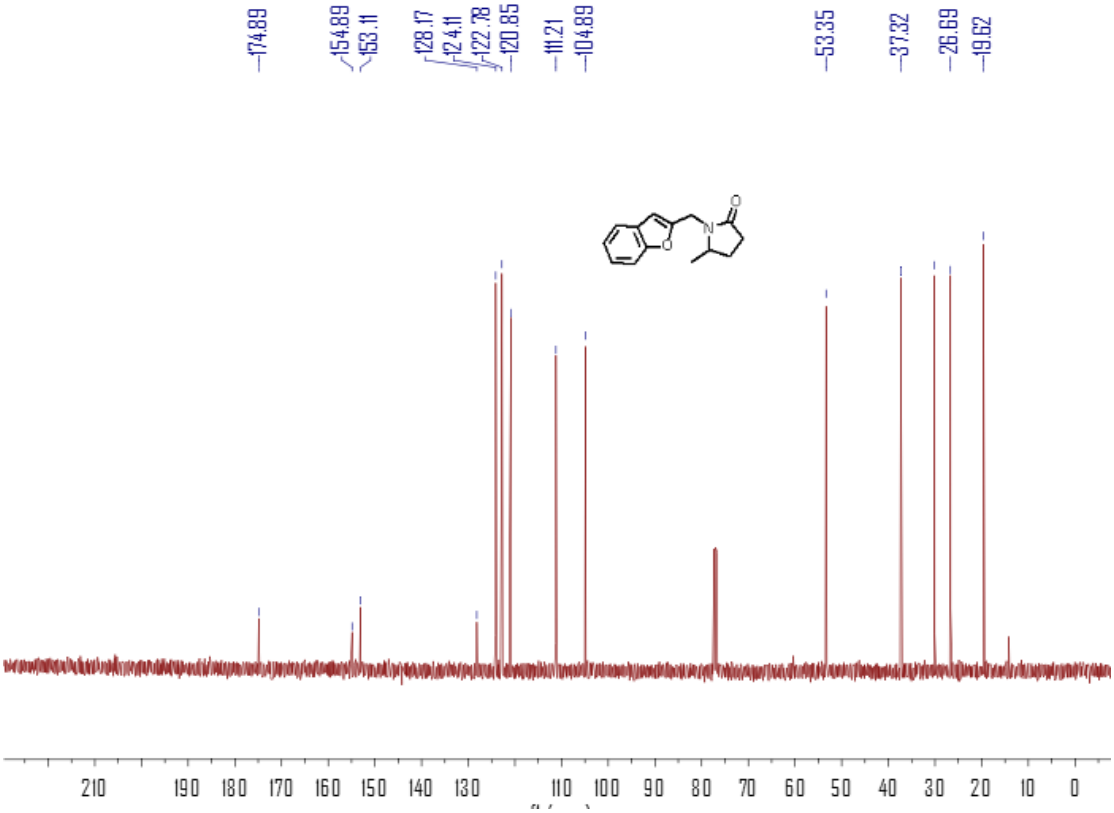


Fig. S40 ^{13}C NMR spectrum of compound **15**.

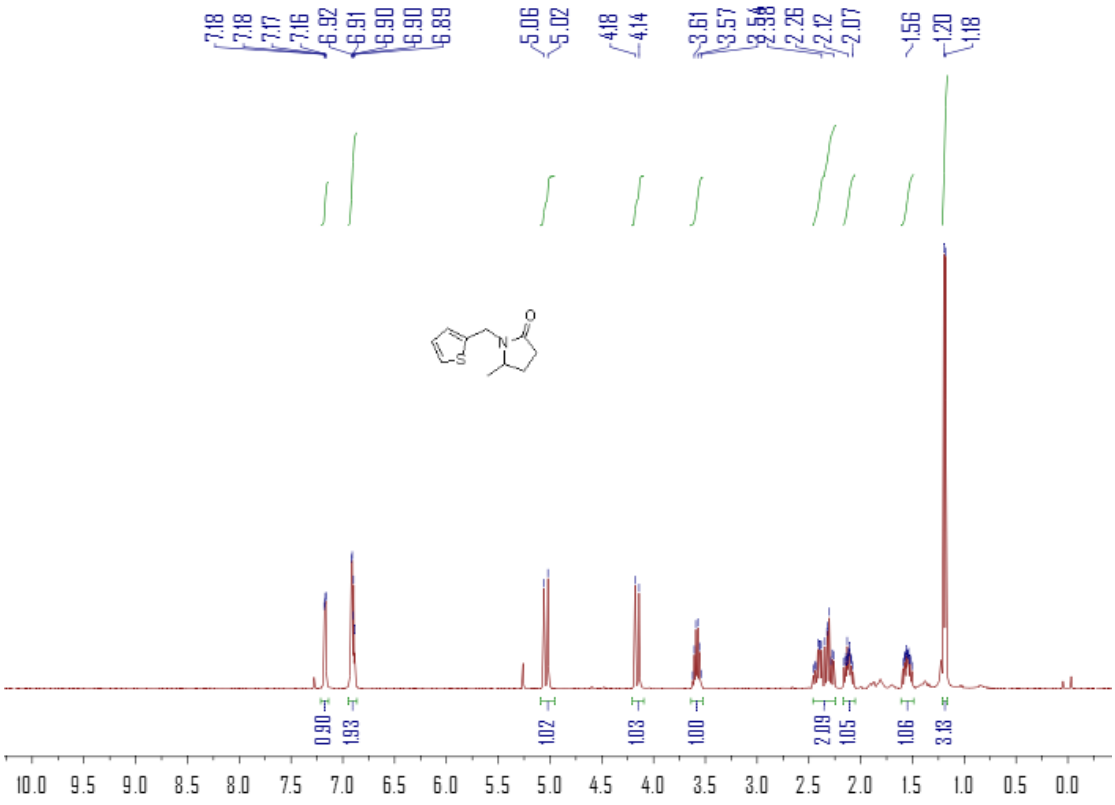


Fig. S41 ^{1}H NMR spectrum of compound **16**.

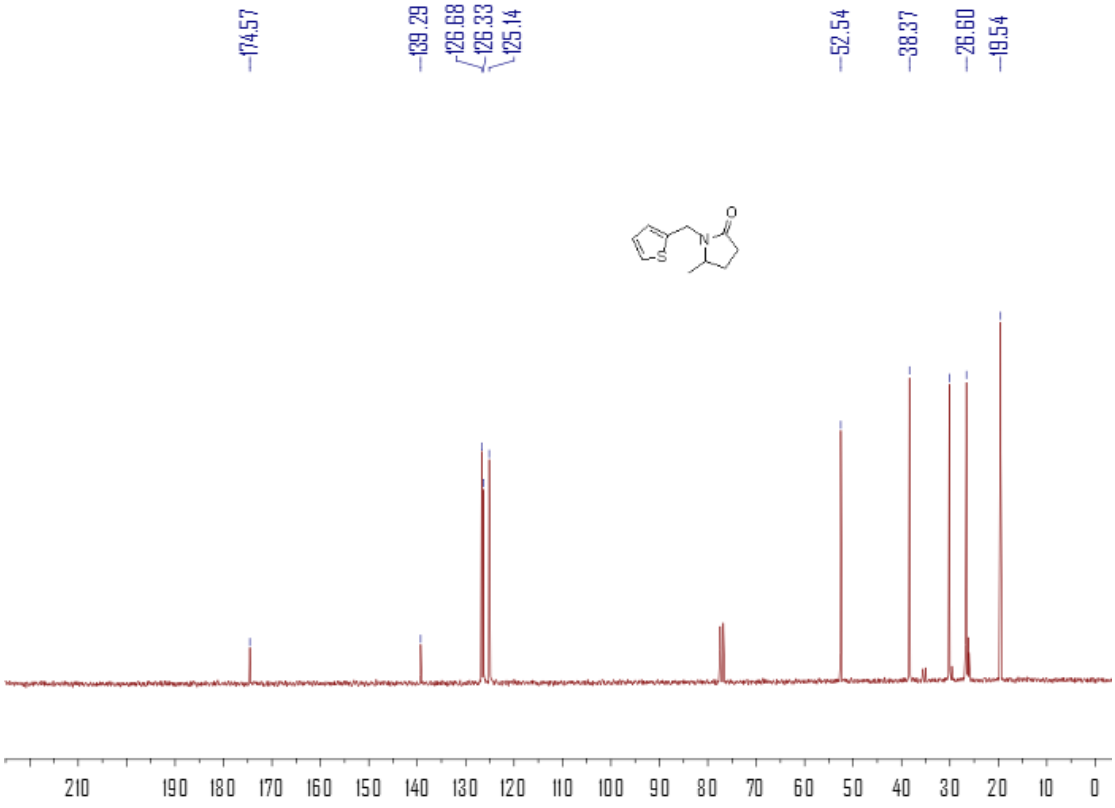


Fig. S42 ^{13}C NMR spectrum of compound **16**.

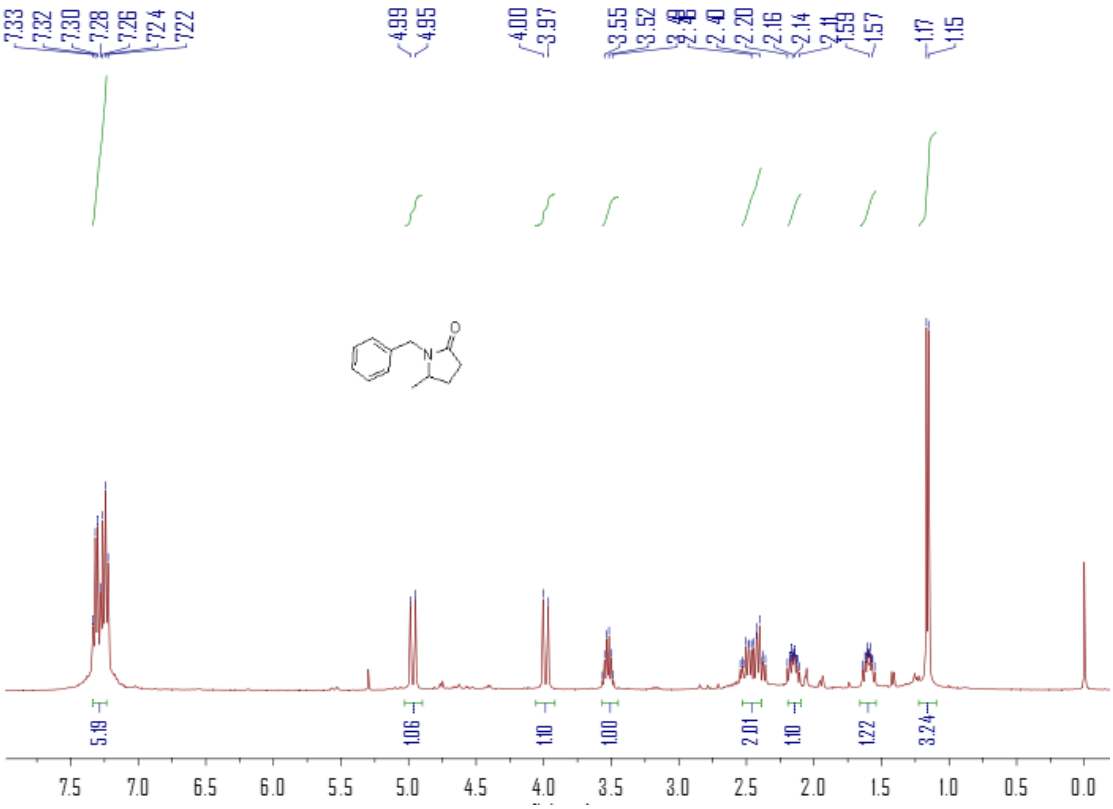


Fig. S43 ^{1}H NMR spectrum of compound **17a**.

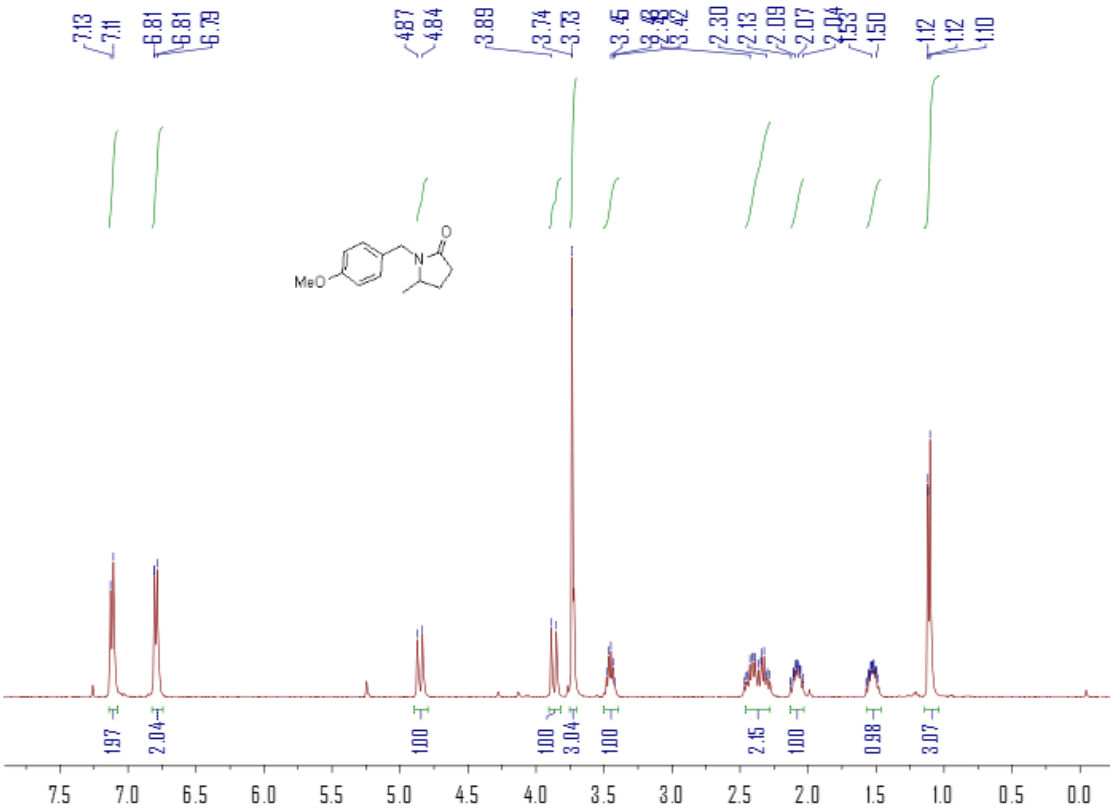


Fig. S44 ^{1}H NMR spectrum of compound **17b**.

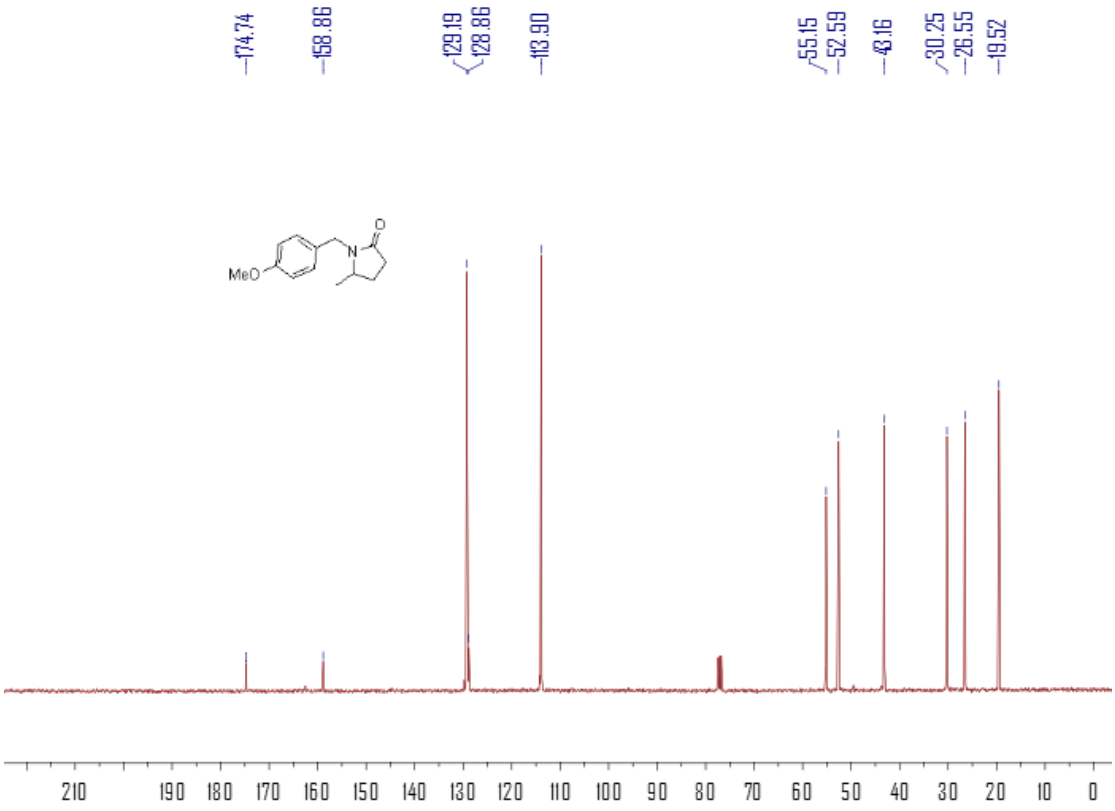


Fig. S45 ^{13}C NMR spectrum of compound **17b**.

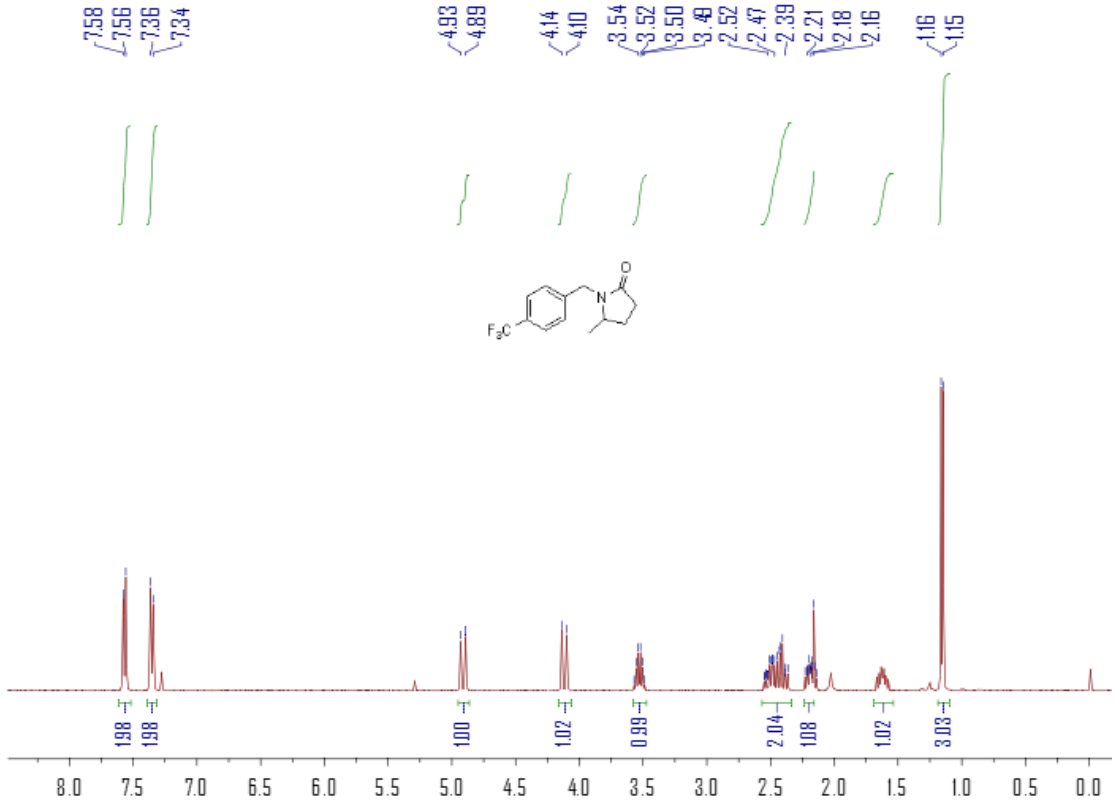


Fig. S46 ^{1}H NMR spectrum of compound **17c**.

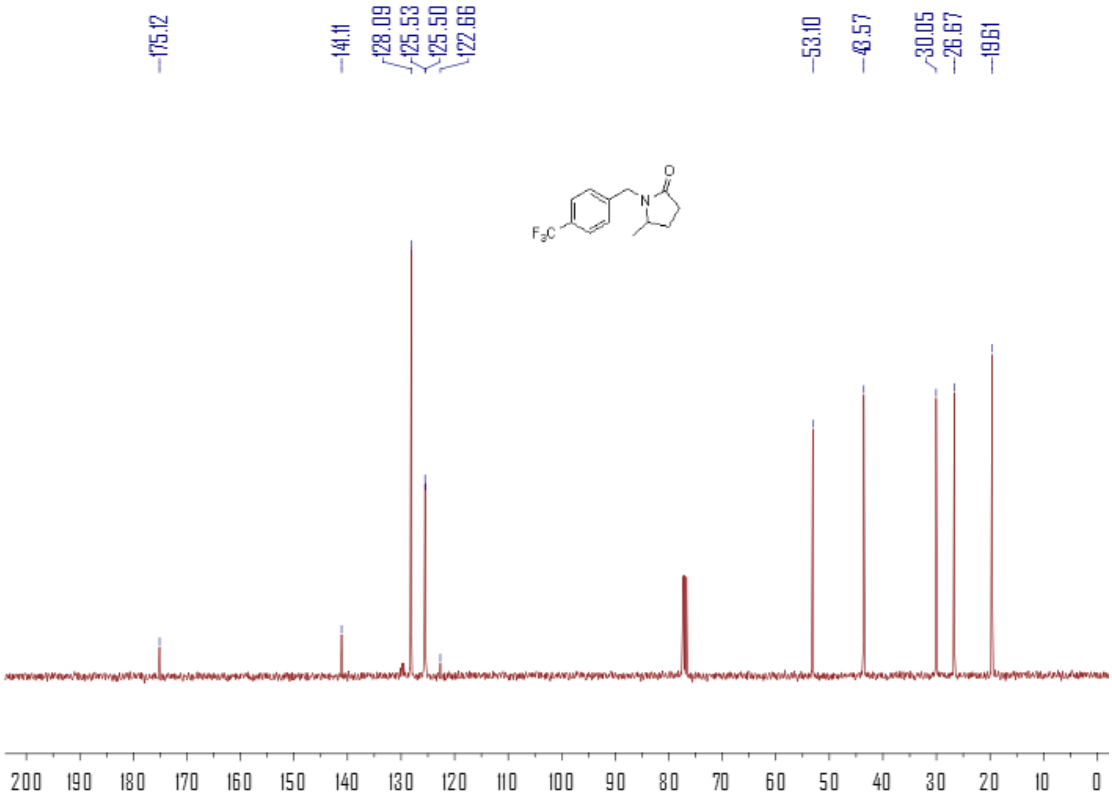


Fig. S47 ^{13}C NMR spectrum of compound **17c**.

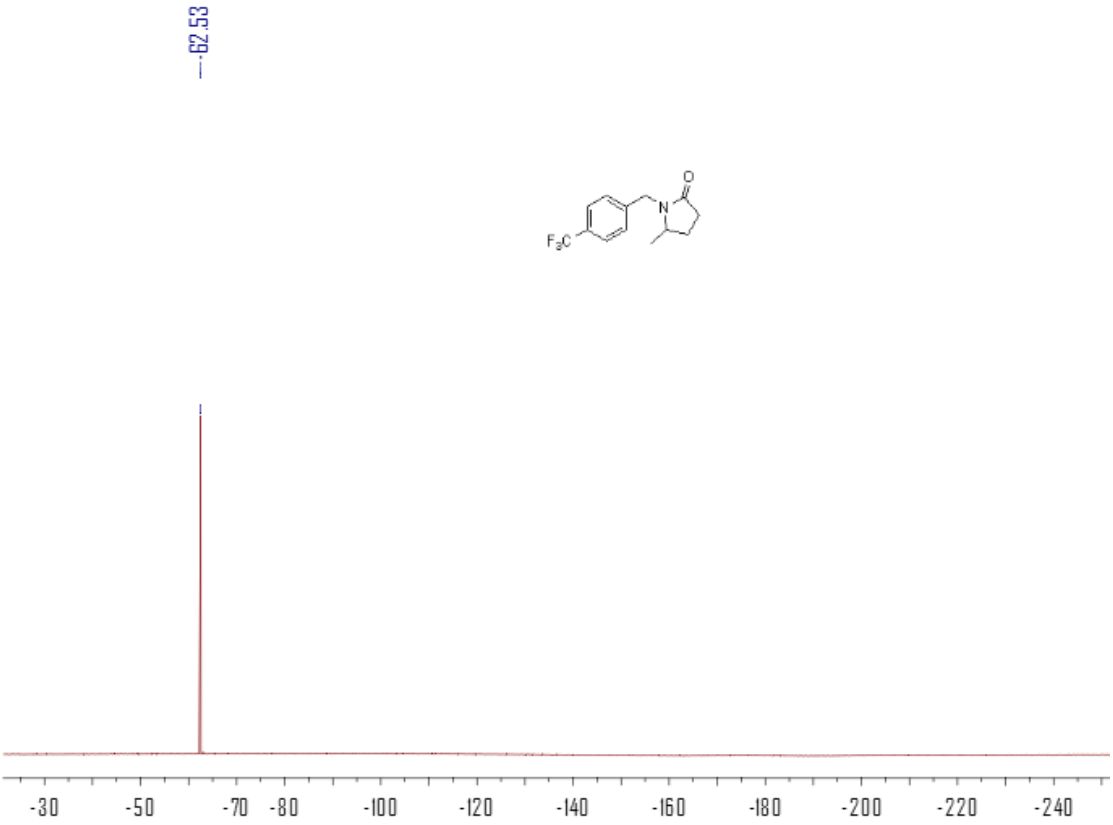


Fig. S48 ^{19}F NMR spectrum of compound **17c**.

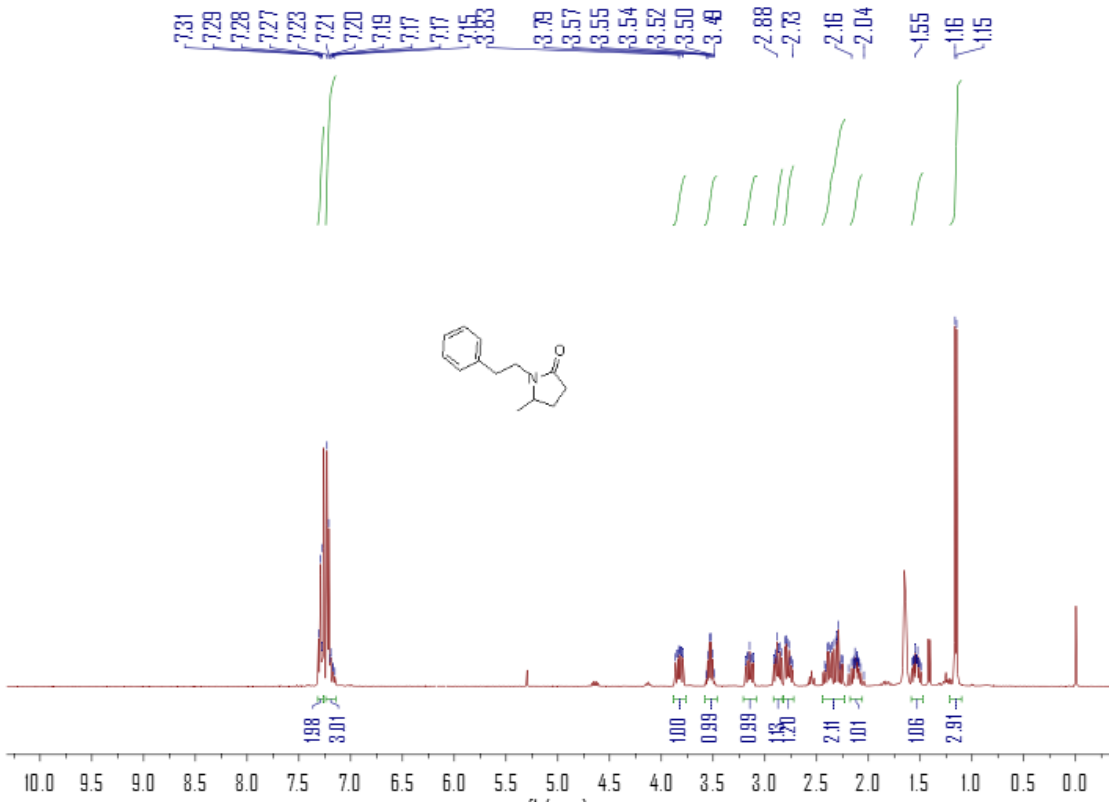


Fig. S49 ^{1}H NMR spectrum of compound **18**.

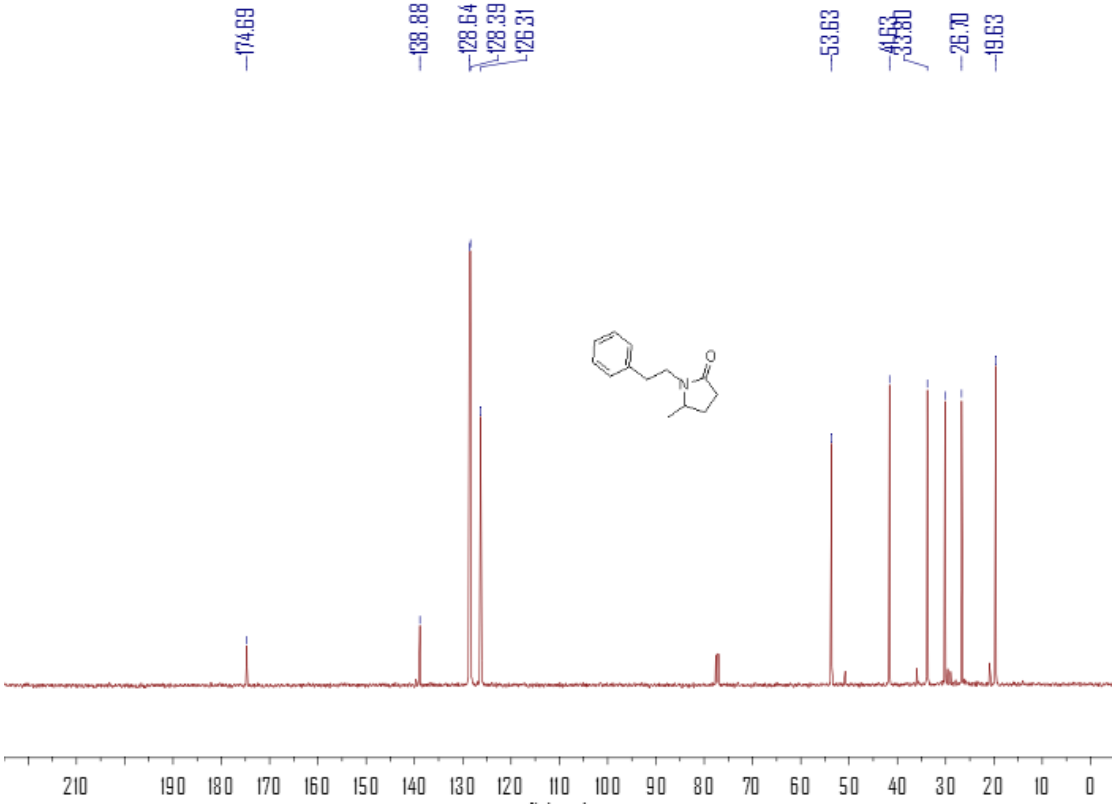


Fig. S50 ^{13}C NMR spectrum of compound **18**.

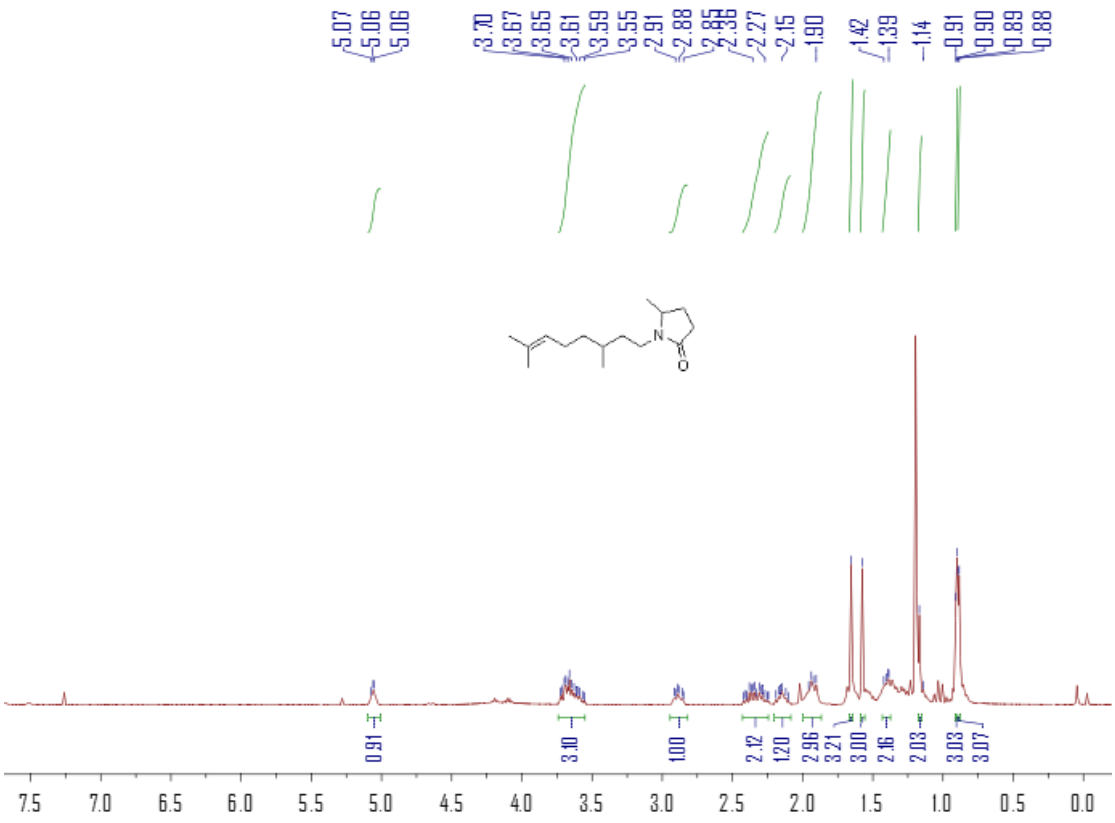


Fig. S51 ^{1}H NMR spectrum of compound **19**.

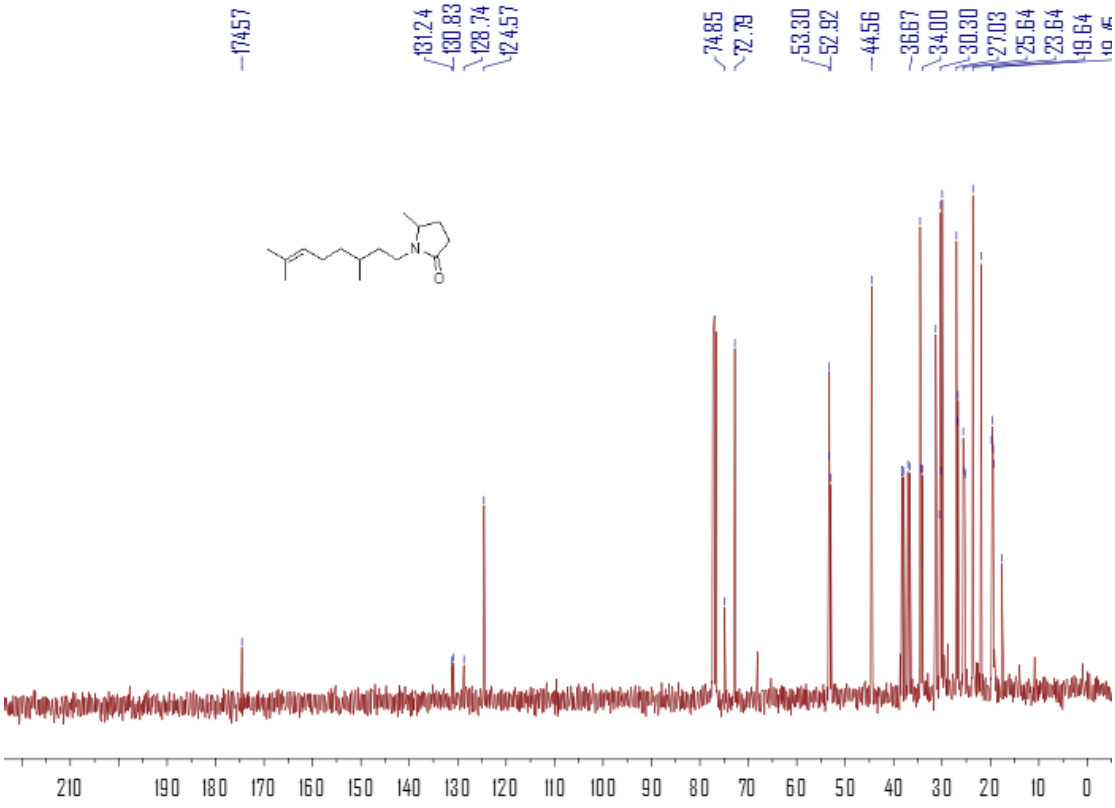


Fig. S52 ^{13}C NMR spectrum of compound **19**.

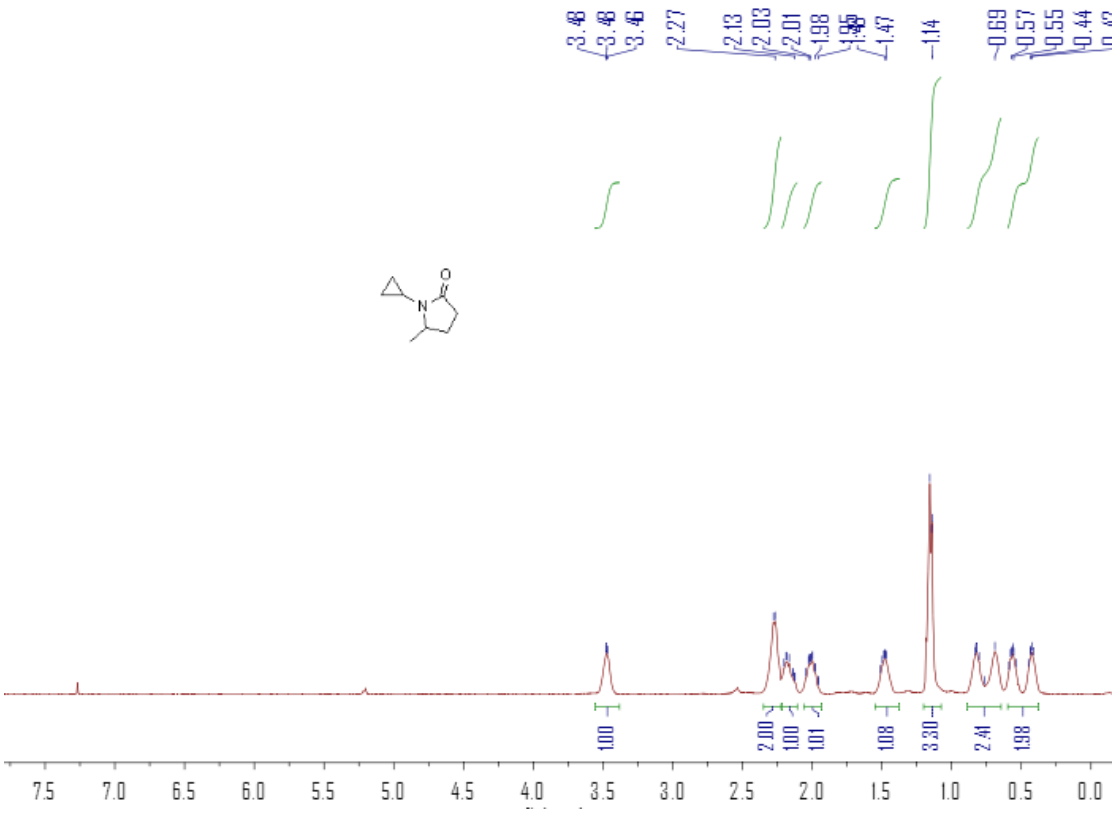


Fig. S53 ^{1}H NMR spectrum of compound **20a**.

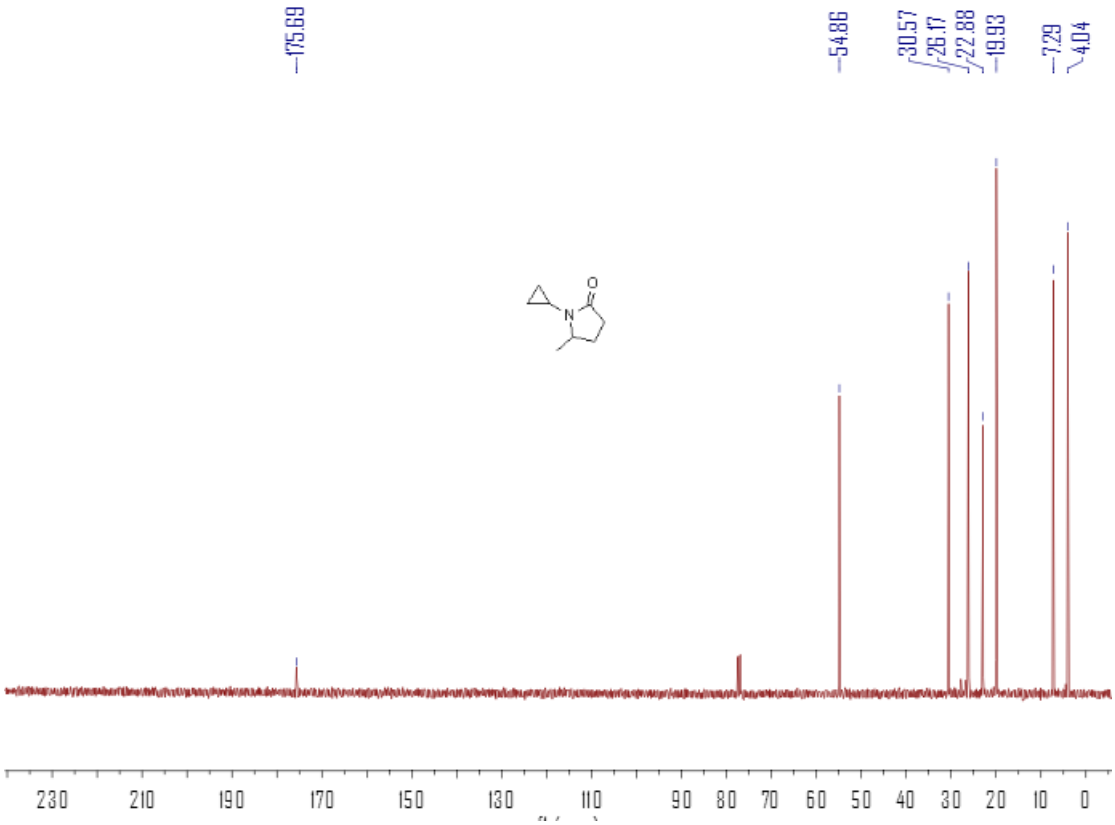


Fig. S54 ^{13}C NMR spectrum of compound **20a**.

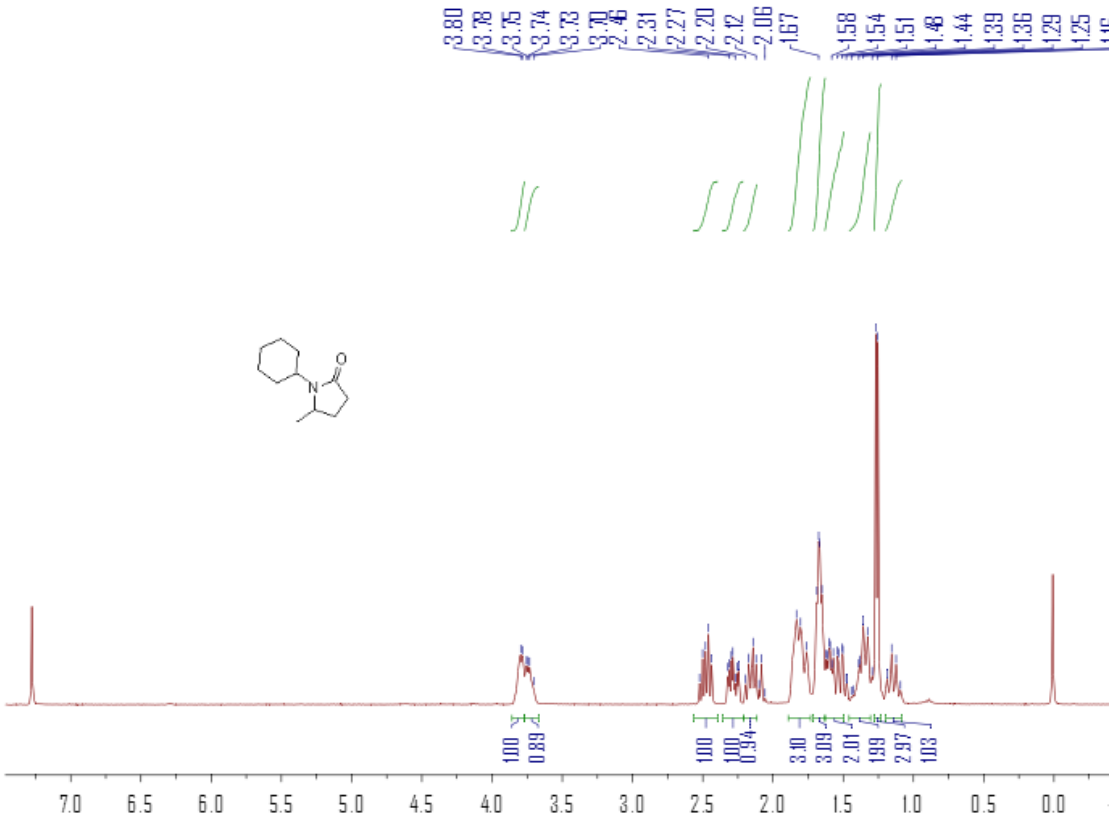


Fig. S55 ^{1}H NMR spectrum of compound **20b**.

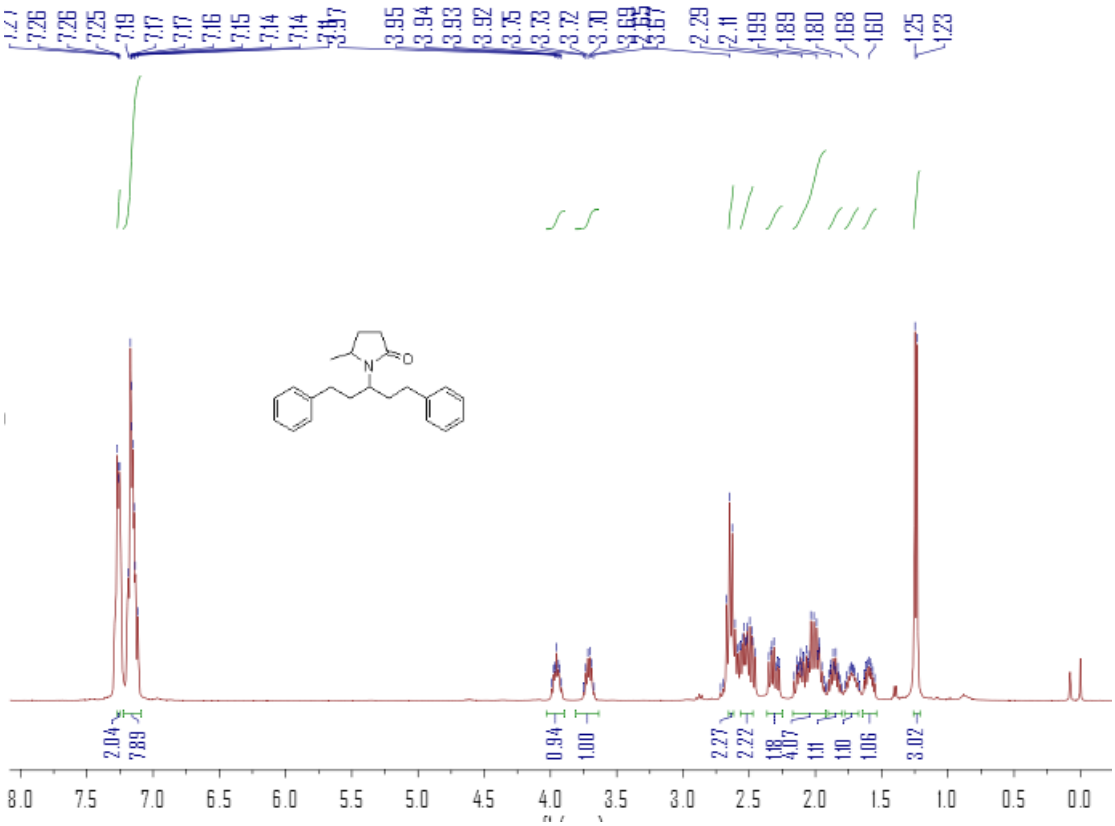


Fig. S56 ^{1}H NMR spectrum of compound **21**.

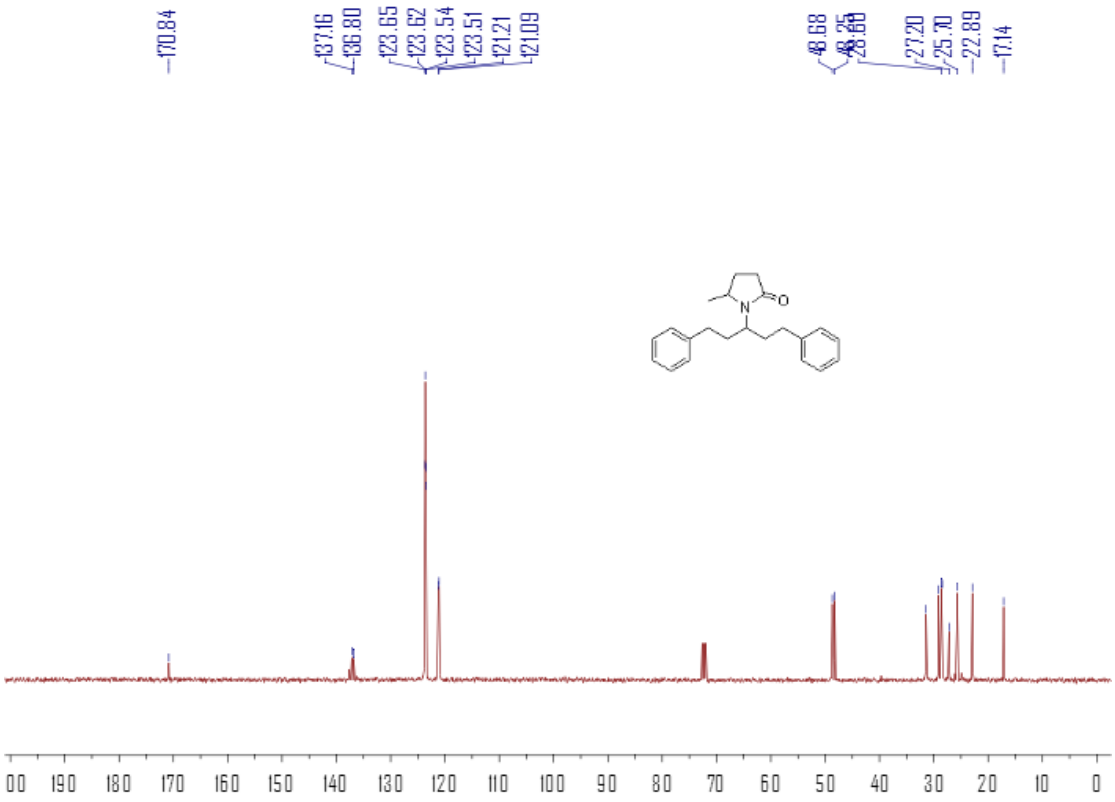


Fig. S57 ^{13}C NMR spectrum of compound **21**.

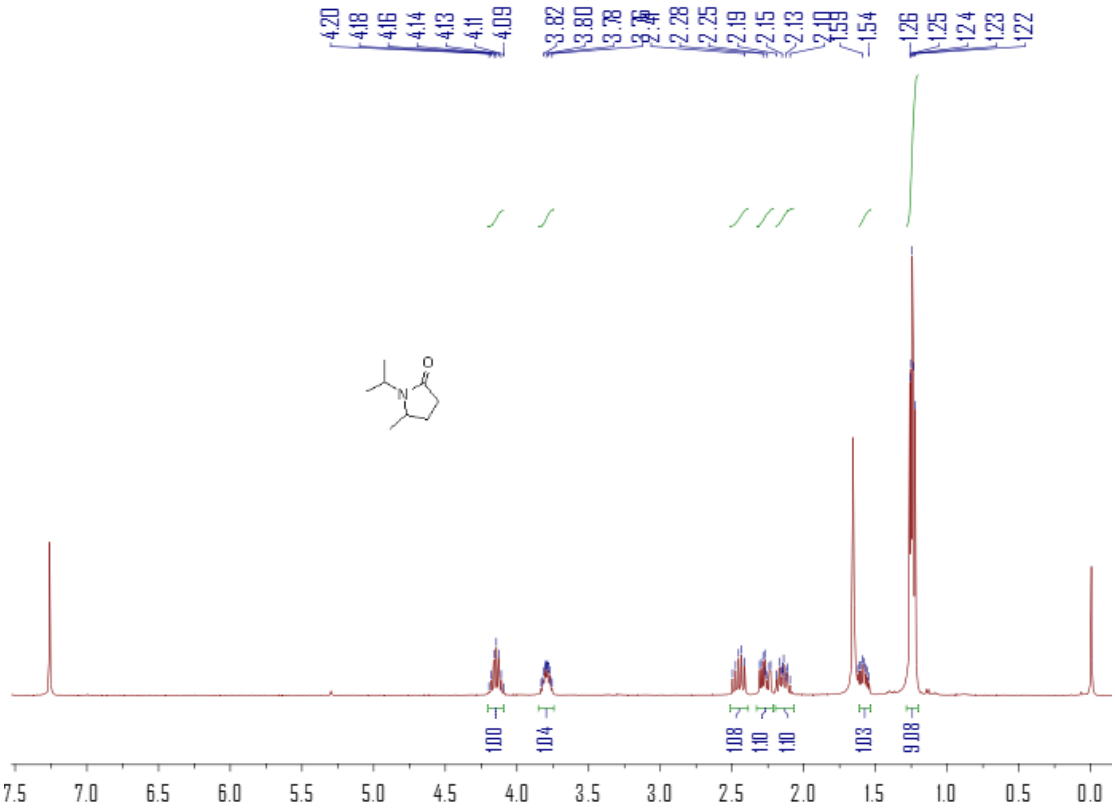


Fig. S58 ^{1}H NMR spectrum of compound **22**.

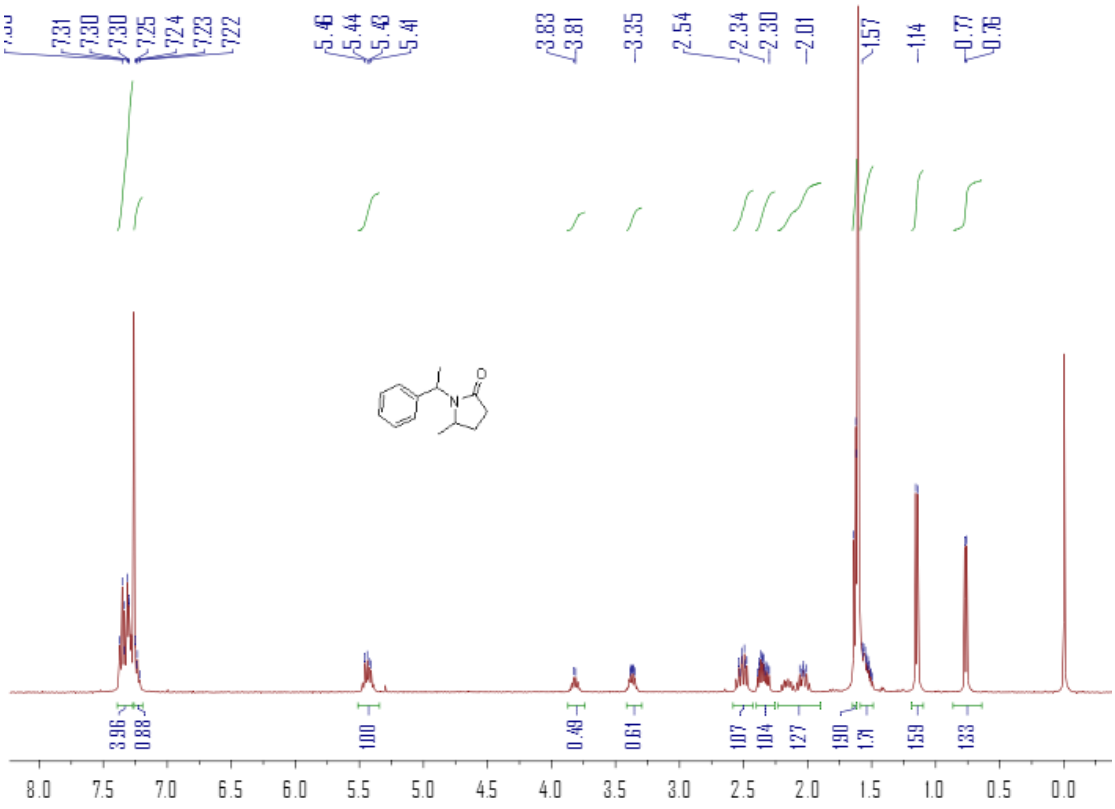


Fig. S59 ^{1}H NMR spectrum of compound **23**.

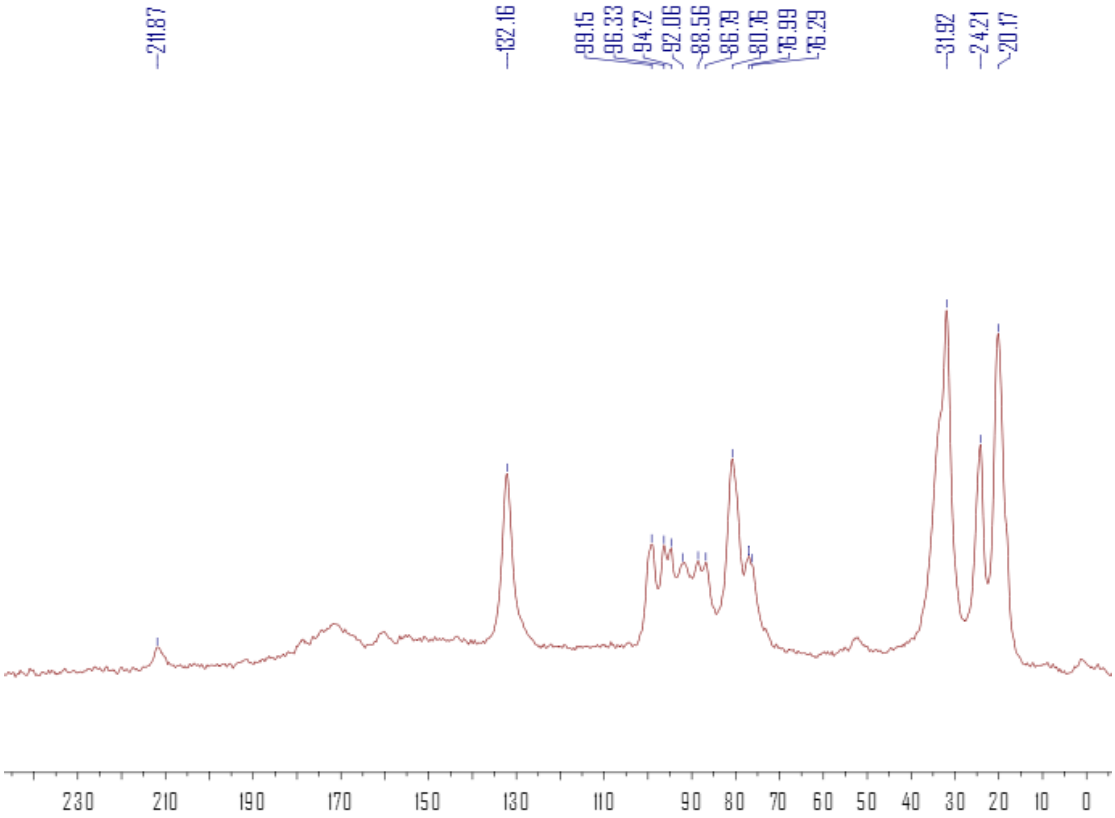


Fig. S60 Solid ^{13}C NMR spectrum of compound **7**.

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