Electronic Supplementary Information

Base-free transfer hydrogenation of aldehydes and ketones catalyzed by imidazoline-2-iminato actinide complexes

Hemanta Deka,[a] Natalia Fridman,[a] Marvin Koneczny, [b] Matthias Tamm[b] and Moris S. Eisen,*[a]

[a.] *Schulich Faculty of Chemistry, Technion – Israel Institute of Technology, Technion City, Haifa, 3200008, Israel. E-mail: chmoris@technion.ac.il.*
[b.] *Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Hagenring 30, 38106 Brauschweig, Germany.*

E-mail: chmoris@technion.ac.il
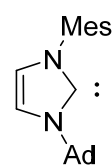
Fax: + 972-4-8295703; Tel: + 972-4-8292680

Table of Contents

1.   Synthetic procedure and characterization of ligand L₁H and L₂H[S1]

1.1.   (Adamantyl)-3-(2,4,6-trimethylphenyl)-imidazolin-2ylidene (Im$^{Ad, Mes}$ Carbene)
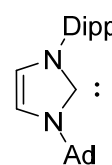
The compound was synthesized based on a procedure by MAUDUIT, where the carbene was not isolated, but instead used *in situ*.[S2, S3]

A suspension of KO^{t}Bu (1.99 g, 22.3 mmol, 1.1 eq.) in 10 mL THF is added to a solution of [Im$^{Ad, Mes}$H][Cl] (5.76 g, 16.1 mmol, 1 eq.) in 100 mL THF. The mixture is stirred for 3 h at room temperature and the solvent is subsequently removed under high vacuum. The residue is dissolved in 80 mL of hot toluene and filtered through Celite® and the frit is washed two times with ca. 10 mL of hot toluene. After removal of all volatiles under a high vacuum an offwhite solid is obtained. The solid is layered with 20 mL of *n*-hexane, and the suspension is stirred for 5 minutes at 60 °C and placed to cool in an ice bath. The supernatant solution is removed *via* a syringe and the remaining solvent is evaporated under a high vacuum to obtain the product (**Im$^{Ad, Mes}$ Carbene)** as a colorless crystalline powder (4.58 g, 14.3 mmol, 89%).

¹H NMR (500 MHz, C₆D₆): δ= 6.88 (d, $^3J_{HH}$ = 1.6 Hz, 1H, C*H*-backbone), 6.83-6.79 (m, 2H, *m*-Mes), 6.50 (d, $^3J_{HH}$ = 1.8 Hz, 1H, CH-backbone), 2.28 (d, $^3J_{HH}$ = 2.8 Hz, 6H, C*H₂*-Ad), 2.15 (s, 3H, *p*-C*H₃*), 2.13 (s, 6H, *o*-C*H₃*), 2.02 (br. s, 3H, C*H*-Ad), 1.66-1.52 (br. m, 6H, C*H₂*-Ad). **¹³C NMR** (126 MHz, C₆D₆): δ= 216.1 (s, N-*C*-N), 140.0 (s, *i*-Mes), 136.9 (s, *p*-Mes), 135.5 (s, *o*-Mes), 129.0 (s, *m*-Mes), 119.4 (s, *C*H-backbone), 114.8 (s, *C*H-backbone), 56.2 (s, Cq-Ad), 44.9 (s, *C*H₂-Ad), 36.6 (s, *C*H₂-Ad), 30.3 (s, *C*H-Ad), 21.0 (s, *p*-*C*H₃), 18.2 (s, *o*-*C*H₃). **Elemental analysis** (%) calc. for C₂₂H₂₈N₂ (320 g/mol): C 82.45, H 8.81, N 8.74; found: C 82.57, H 8.893, N 8.74.

1.2.   (Adamantyl)-3-(2,6-diisopropylphenyl)-imidazolin-2ylidene (Im$^{Ad, Dipp}$ Carbene)

The compound was synthesized based on a procedure by MAUDUIT, where the carbene was not isolated, but instead used *in situ*.

A suspension of KO^{t}Bu (5.22 g, 46.5 mmol, 1.1 eq.) in 25 mL THF is added to a solution of [I$^{Ad, Dipp}$H][Cl] (16.97 g, 42.3 mmol, 1 eq.) in 150 mL THF. The mixture is stirred for 40 min at room temperature and the solvent is subsequently removed under high vacuum. The residue is dissolved in 350 mL of hot toluene and filtered through Celite® and the frit is washed two times with ca. 10 mL of hot toluene. After removal of all volatiles under a high vacuum an offwhite solid is obtained. The solid is layered with 30 mL of *n*-hexane, and the suspension is stirred for 5 minutes at 60 °C and placed to cool in an ice bath. The supernatant

solution is removed *via* a syringe and the remaining solvent is evaporated under a high vacuum to obtain the product **Im$^{Ad, Dipp}$ Carbene** as a colorless crystalline powder (12.46 g, 34.4 mmol, 81%).

^{1}H NMR (300 MHz, C$_6$D$_6$): δ= 7.29-7.22 (m, 1H, *p*-Dipp), 7.16-7.11 (m, 2H, *m*-Dipp), 6.84 (d, $^3J_{HH}$ = 1.6 Hz, 1H, C*H*-backbone), 6.63 (d, $^3J_{HH}$ = 1.6 Hz, 1H, CH-backbone), 2.84 (sept., $^3J_{HH}$ = 7.0 Hz, 2H, C*H*(CH$_3$)$_2$), 2.22 (m, 6H, C*H$_2$*-Ad), 1.97 (br. s, 3H, C*H*-Ad), 1.54 (br. s, 6H, C*H$_2$*-Ad), 1.22 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H$_3$*)$_2$), 1.11 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H$_3$*)$_2$). **^{13}C NMR** (75 MHz, C$_6$D$_6$): δ= 217.0 (s, N-*C*-N), 146.4 (s, *o*-Dipp), 139.9 (s, *i*-Dipp), 128.7 (s, *p*-Dipp), 123.6 (s, *m*-Dipp), 120.6 (s, *C*H-backbone), 114.6 (s, *C*H-backbone), 56.2 (s, *C*q-Ad), 44.8 (s, *C*H$_2$-Ad), 36.6 (s, *C*H$_2$-Ad), 30.3 (s, *C*H-Ad), 28.6 (s, *C*H(CH$_3$)$_2$), 24.6 (s, CH(*C*H$_3$)$_2$), 24.0 (s, CH(*C*H$_3$)$_2$). **Elemental analysis** (%) calc. for C$_{25}$H$_{34}$N$_2$ (363 g/mol): C 82.82, H 9.45, N 7.73; found: C 82.67, H 9.481, N 7.21.

1.3. 1-(adamantan-1-yl)-3-mesityl-N-(trimethylsilyl)-1,3-dihydro-2H-imidazol-2-imine **(Im$^{Ad, Mes}$ N-TMS)**
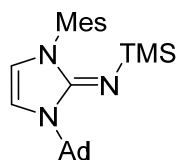
A solution of Carbene **Im$^{Ad, Mes}$ Carbene** (4.58 g, 14.3 mmol, 1 eq.) in 70 mL toluene is slowly treated with trimethylsilylazide (2.64 mL, 20 mmol, 1.4 eq.) at room temperature. The mixture is heated to reflux for 72 h, during which the formation of an offwhite solid can be observed. After cooling to room temperature the suspension is filtered and all volatiles are removed under a high vacuum. The resulting yellow viscous residue is purified with a bulb to bulb distillation at a high vacuum (5·10^{-2} mbar) with the aid of two heat guns. The obtained residue can be crystallized from hot *n*-hexane to obtain product **Im$^{Ad, Mes}$ N-TMS** as a light yellow crystalline solid (4.60 g, 11.3 mmol, 79%). For further purification, the product can be sublimed at 1·10^{-3} mbar and 165 °C.

^{1}H NMR (500 MHz, C$_6$D$_6$): δ= 6.79-6.77 (m, 2H, *m*-Mes), 6.16 (d, $^3J_{HH}$ = 3.0 Hz, 1H, C*H*-backbone), 5.66 (d, $^3J_{HH}$ = 3.1 Hz, 1H, CH-backbone), 2.36 (d, $^3J_{HH}$ = 2.7 Hz, 6H, C*H$_2$*-Ad), 2.13 (s, 6H, *o*-CH$_3$), 2.10 (s, 3H, *p*-CH$_3$), 2.03 (br. s., 3H, C*H*-Ad), 1.71-1.55 (br. m, 6H, C*H$_2$*-Ad), 0.09 (s, 9H, C*H$_3$*-TMS). **^{13}C NMR** (126 MHz, C$_6$D$_6$): δ= 141.2 (s, N-*C*-N), 138.1 (s, *p*-Mes), 137.7 (s, *o*-Mes), 134.8 (s, *i*-Mes), 129.3 (s, *m*-Mes), 110.2 (s, *C*H-backbone), 109.3 (s, *C*H-backbone), 55.7 (s, *C*q-Ad), 39.7 (s, *C*H$_2$-Ad), 36.7 (s, *C*H$_2$-Ad), 30.2 (s, *C*H-Ad), 21.1 (s, *p*-*C*H$_3$), 18.3 (s, *o*-*C*H$_3$), 3.5 (s, *C*H$_3$-TMS). **Elemental analysis** (%) calc. for C$_{25}$H$_{37}$N$_3$Si (408 g/mol): C 73.66, H 9.15, N 10.31; found: C 73.95, H 9.032, N 10.00.

1.4. **Im$^{Ad, Dipp}$ N-TMS**
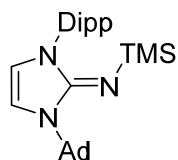
A solution of Carbene **Im$^{Ad, Dipp}$ Carbene** (4.00 g, 11.0 mmol, 1 eq.) in 100 mL toluene is slowly treated with trimethylsilylazide (2.18 mL, 16.5 mmol, 1.5 eq.) at room temperature. The mixture is heated to reflux for 72 h, during which the

formation of an offwhite solid can be observed. After cooling to room temperature, the suspension is filtered and all volatiles are removed under a high vacuum. The resulting yellow viscous residue is purified with bulb-to-bulb distillation at a high vacuum ($5\cdot10^{-2}$ mbar) with the aid of two heat guns. The obtained residue is washed with low amounts of *n*-hexane to obtain product **Im$^{Ad, Dipp}$ N-TMS** as a light-yellow solid (1.91 g, 4.2 mmol, 38%).

^{1}H NMR (400 MHz, C$_6$D$_6$): δ= 7.24-7.19 (m, 1H, *p*-Dipp), 7.13-7.10 (m, 2H, *m*-Dipp), 6.19 (d, $^3J_{HH}$ = 3 Hz, 1H, C*H*-backbone), 5.89 (d, $^3J_{HH}$ = 3 Hz, 1H, C*H*-backbone), 3.01 (sept, $^3J_{HH}$ = 6.89 Hz, 2H, C*H*(CH$_3$)$_2$), 2.33 (d, $^3J_{HH}$ = 2.7 Hz, 6H, C*H$_2$*-Ad), 2.01 (br. s, 3H, C*H*-Ad), 1.69-1.53 (br. m., 6H, C*H$_2$*-Ad); 1.33 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(C*H$_3$*)$_2$), 1.11 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(C*H$_3$*)$_2$), 0.07 (s, 9H, C*H$_3$*-TMS).**^{13}C NMR** (100 MHz, C$_6$D$_6$): δ= 148.3 (s, *o*-Dipp), 141.0 (N-*C*-N), 135.5 (s, *i*-Dipp), 129.5 (s, *p*-Dipp), 124.2 (s, *m*-Dipp), 112.3 (s, *C*H-backbone), 108.7 (s, *C*H-backbone),55.7 (s, *C*q-Ad), 39.8 (s, *C*H$_2$-Ad), 36.7 (s, *C*H$_2$-Ad), 30.2 (s, *C*H-Ad), 28.7(s, *C*H(CH$_3$)$_2$), 25.0 (s, CH(*C*H$_3$)$_2$), 23.1 (s, CH(*C*H$_3$)$_2$), 3.5 (s, *C*H$_3$-TMS). **Elemental analysis** (%) calc. for C$_{28}$H$_{43}$N$_3$Si (450 g/mol): C 74.78, H 9.64, N 9.34, found: C 75.27, H 9.481, N 9.29.

1.5. 1-(adamantan-1-yl)-3-mesityl-1,3-dihydro-2H-imidazol-2-imine (**L$_1$H**)
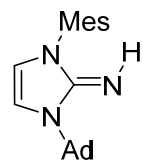
TMS-Imine **Im$^{Ad, Mes}$ N-TMS** (3.00 g, 7.36 mmol, 1 eq.) is treated with 40 mL methanol and the resulting solution is stirred for 2 h at room temperature. The solvent is removed under a high vacuum and the resulting offwhite solid is crystallized from hot *n*-hexane. The crystalline solid is washed three times with low amounts of *n*-hexane and the residual solvent is removed under a high vacuum. Subsequent sublimation at $1\cdot10^{-3}$ mbar and 130-140 °C yields product **L1H** as a colorless powder (1.00 g, 2.98 mmol, 40%).

^{1}H NMR (400 MHz, C$_6$D$_6$): δ= 6.71 (m, 2H, *m*-Mes), 6.16 (d, $^3J_{HH}$ = 2.9 Hz, 1H,C*H*-backbone), 5.66 (d, $^3J_{HH}$ = 2.8 Hz, 1H, C*H*-backbone), 4.46 (s, 1H, N-*H*), 2.53 (br.s, 6H, C*H$_2$*-Ad), 2.09 (s, 6H, *o*-C*H$_3$*), 2.07 (s, 3H, *p*-C*H$_3$*), 2.03 (br. s., 3H, C*H*-Ad),1.72-1.52 (br. m, 6H, C*H$_2$*-Ad). **^{13}C NMR** (100 MHz, C$_6$D$_6$): δ= 153.1 (s, N-*C*-N), 138.2 (s, *p*-Mes), 138.0 (s, *o*-Mes), 132.9 (s, *i*-Mes), 129.7 (s, *m*-Mes), 109.9 (s, *C*H-backbone), 109.4 (s, *C*H-backbone),55.9 (s, *C*q-Ad), 39.7 (s, *C*H$_2$-Ad), 36.7 (s, *C*H$_2$-Ad), 30.2 (s, *C*H-Ad), 21.0(s, *p*-*C*H$_3$), 18.0 (s, *o*-*C*H$_3$). **Elemental analysis** (%) calc. for C$_{22}$H$_{29}$N$_3$ (336 g/mol): C 78.76, H 8.71, N 12.53; found: C 78.94, H 8.774, N 12.46.

1.6. 1-(adamantan-1-yl)-3-(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-imine (**L$_2$H**)
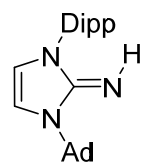
TMS-Imine **Im$^{Ad, Dipp}$ N-TMS** (0.40 g, 0.88 mmol, 1 eq.) is treated with 12 mL methanol and the resulting solution is stirred for 30 min at room temperature. The solvent volume is reduced to ca. 1/3 under a high vacuum and 5 mL *n*-hexane is added to the solution. After stirring for an additional 30 min the volatiles are removed under a high vacuum. The resulting slightly yellow solid is purified by sublimation at

2·10^{-3} mbar and 140 °C to yield product **L2H** as a colorless powder (0.30 g, 0.79 mmol, 90%). Alternatively, the product can be purified by crystallisation from hot *n*-hexane.

¹H NMR (400 MHz, C$_6$D$_6$): δ= 7.23-7.18 (m, 1H, *p*-Dipp), 7.12-7.08 (m, 2H, *m*-Dipp), 6.19 (d, $^3J_{HH}$ = 2.8 Hz, 1H, C*H*-backbone), 5.82 (d, $^3J_{HH}$ = 2.8 Hz, 1H, C*H*-backbone), 4.38 (br. s, 1H, N-*H*), 3.04 (sept, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 2.51 (br. s, 6H, C*H*$_2$-Ad), 2.01 (br. s, 3H, C*H*-Ad), 1.70-1.49 (br. m, 6H, C*H*$_2$-Ad), 1.23 (d, $^3J_{HH}$= 6.9Hz, 6H, CH(C*H*$_3$)$_2$), 1.12 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$).**¹³C NMR** (100 MHz, C$_6$D$_6$): δ= 154.4 (s, N-*C*-N), 149.3 (s, *o*-Dipp), 133.0 (s, *i*-Dipp), 129.9 (s, *p*-Dipp), 124.6 (s, *m*-Dipp), 111.4 (s, *C*H-backbone), 109.3 (s, *C*H-backbone), 55.9 (s, Cq-Ad), 39.7 (s, *C*H$_2$-Ad), 36.7 (s, *C*H$_2$-Ad), 30.2 (s, *C*H-Ad), 28.8 (s, *C*H(CH$_3$)$_2$), 24.3 (s, CH(*C*H$_3$)$_2$), 23.9 (s, CH(*C*H$_3$)$_2$). **Elemental analysis** (%) calc. for C$_{25}$H$_{35}$N$_3$ (378 g/mol): C 79.53, H 9.34, N 11.13, found: C 79.66, H 9.353, N 10.48.

2.   Table S1: Crystallographic data of complexes

	3	4	5	6	9	10	11	12
CCDC No.	2171322	2171323	2171324	2171325	2171326	2171327	2171328	2171322
Formulae	C$_{40}$H$_{82}$N$_6$Si$_6$Th	C$_{43}$H$_{88}$N$_6$Si$_6$Th	C$_{40}$H$_{82}$N$_6$Si$_6$U	C$_{43}$H$_{88}$N$_6$Si$_6$U	C$_{43}$H$_{58}$N$_3$Th. C$_7$H$_8$	C$_{46}$H$_{67}$N$_3$Th.	C$_{43}$H$_{61}$N$_3$U. C$_7$H$_8$	C46 N3 U [+ Hydrogens]
Molecular weight	1047.70	1089.77	1053.68	1095.76	941.09	894.06	950.11	
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1	P-1	P-1	Cc	P-1	P-1
Temperature/K	200	200	200	200	200	200	200	100
Wavelength	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
a/Å	11.5815(6)	11.288(2)	11.5471(15)	11.2306(12)	10.5397(6)	22.443(4)	10.5224(10)	10.538(3)
b/Å	12.1471(6)	11.846(3)	12.0762(15)	11.8646(13)	13.0967(7)	10.753(2)	13.0578(12)	10.555(3)
c/Å	21.0110(11)	22.347(5)	21.015(3)	22.222(2)	17.5453(9)	19.704(4)	17.5789(17)	22.881(6)
α/°	99.3760(10)	97.652(8)	99.923(3)	97.759(2)	77.6940(10)	90	77.589(2)	99.554(4)
β/°	94.752(2)	93.506(6)	94.541(3)	93.070(3)	82.0850(10)	118.318(3)	82.483(3)	93.279(5)
γ/°	115.875(3)	116.283(5)	116.066(3)	116.034(4)	71.0080(10)	90	71.767(4)	100.776(6)
V/ Å^3	2584.2(2)	2630.9(11)	2553.0(6)	2615.0(5)	2231.3(2)	4186.1(14)	2235.2(4)	2455.4(11)
Z	2	2	2	2	2	4	2	2
Density/gcm^{-1}	1.346	1.376	1.371	1.392	1.401	1.419	1.412	1.126
Absorption Coefficient	3.056	3.005	3.352	3.275	3.377	3.596	3.667	3.330
Absorption Correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
F(000)	1076	1124	1080	1128	954	1816	964	778
Total no of reflections	9168	9047	9116	9123	7917	7276	7850	8655
Reflections, *I>2σ(I)*	8027	6421	7805	8181	7032	6353	6456	6473
Max. 2θ/°	25.107	25.241	25.197	25.054	25.082	25.099	25.048	25.159
Complete to 2θ(%)	99.7	94.9	99.4	98.4	99.7	99.1	99.1	98.4
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goof (*F^2*)	0.976	0.956	1.000	1.019	1.012	1.022	0.986	1.022
R indices [*I>2σ(I)*]	0.0277	0.0601	0.0356	0.0308	0.0312	0.0423	0.0328	0.0698
R Indices (all data)	0.0346	0.1011	0.0460	0.0381	0.0364	0.0536	0.0482	0.1741
wR2	0.0577	0.1151	0.0813	0.0585	0.0675	0.0902	0.0648	0.1664

3. Spectroscopic data for transfer hydrogenation of aldehydes and ketones[2]

2a)
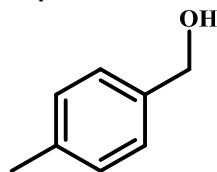
^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.22 (*d*, J= 6 Hz. 2H, Ar−C*H*), 7.00 (*d*, J= 6 Hz, 2H, Ar−C*H*), 4.52 (*d*, J= 6 Hz. 2H, C*H$_2$*) 3.34 (*s*, 1H, O*H*), 2.11 (*s*, 3H, C*H$_3$*). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 139.3, 136.7, 129.6 127.2 (Ar−*C*H), 64.7 (*C*H$_2$), 21.1 (*C*H$_3$).

2b)
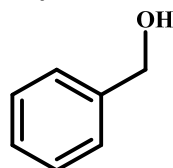
^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.29 (*d*, J= 6 Hz. 2H, Ar−C*H*), 7.18-7.14 (*m*, 1H, Ar−C*H*), 7.08-7.05 (*m*, 1H, C*H$_3$*), 4.52 (*s*, 2H, C*H$_2$*). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): 143.2,128.6, 127.5, 127.1 (Ar−*C*H), 64.7 (*C*H$_2$).

2c)
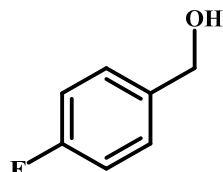
^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.11-7.09 (*m*, 2H, Ar-C*H*), 7.08-6.81 (*m*, 2H, Ar−C*H*), 4.41 (*s*, 2H, C*H$_2$*). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 163.7-161.2 (*d*, *J* = 180 Hz, Ar-*C*), 138.0-137.9 (*d*, *J* = 2.8 Hz, Ar-*C*), 128.8-128.7 (*d*, *J* = 6 Hz, Ar-*C*), 115.4-115.1 (*d*, *J* = 16 Hz, Ar-*C*), 63.8 (*C*H$_2$).

2d)
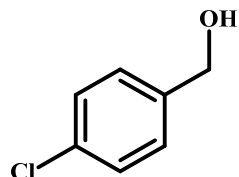
^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.11 (*d*, J=6 Hz. 2H, Ar−C*H*), 6.98 (*d*, J= 6 Hz, 2H, Ar−C*H*), 4.31 (*s*, 2H, C*H$_2$*),3.16 (*s*, 1H, O*H*). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 140.7, 133.0, 128.6, (Ar−*C*H), 63.8(*C*H$_2$).

2e)
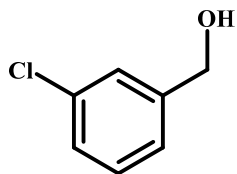
^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.33 (s, 1H, Ar–CH), 7.03 (m, 2H, Ar–CH), 6.87 (m, 1H, Ar-CH), 4.37 (s, 2H, CH$_2$), 3.94 (s, 1H, OH). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 144.5, 134.5, 129.8, 127.3, 127.1, 125.0 (Ar–CH), 63.7 (CH$_2$).

2f)
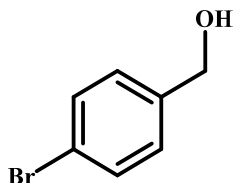
^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.28 (d, J= 6 Hz. 2H, Ar–CH), 6.99 (d, J= 6, 2H, Ar–CH), 4.83 (s, 2H, CH$_2$), 4.09 (s, 1H, OH). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 141.3, 131.6, 128.7, 121.1 (Ar–CH), 63.7 (CH$_2$).

2g)
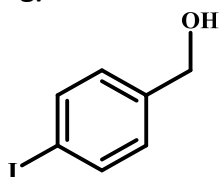
^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.47 (d, J=6 Hz. 2H, Ar–CH), 6.86 (d, J= 6 Hz, 2H, Ar–CH), 4.37 (s, 2H, CH$_2$). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 141.9, 137.6, 128.9, 92.5 (Ar–CH), 63.8 (CH$_2$).

2h)
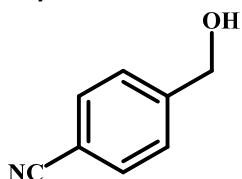
^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.08 (d, J=6 Hz. 2H, Ar–CH), 7.00 (d, J=6 Hz, 2H, Ar–CH), 4.37 (s, 2H, CH2), 4.09 (s, 1H, OH). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 147.4, 132.1, 126.9, 119.1, (Ar–CH), 111.0 (CN), 63.47(CH$_2$).

2i)
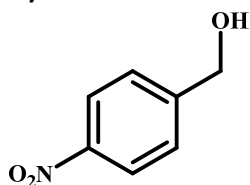
^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.90 (*d*, J=6 Hz, 2H, Ar–C*H*), 7.08 (*d*, J= 6 Hz, 2H, Ar–C*H*), 4.42 (*s*, 2H, *CH$_2$*). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 149.5, 147.3, 126.9, 123.5 (Ar–C*H*), 63.3 (*CH$_2$*).

2j)
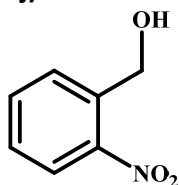
^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.63-7.68 (*m*, 2H, Ar–C*H*), 7.05 (*t*, J= 6 Hz, 1H, Ar–C*H*), 6.74 (*t*, J= 6 Hz, 1H, Ar–C*H*), 4.84 (*s*, 2H, *CH$_2$*), 3.69 (*s*, 1H, O*H*). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 147.4, 138.3, 133.5, 128.8, 127.6, 124.6 (Ar–C*H*), 61.6 (CH$_2$).

2k)
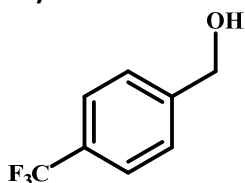
^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.36 (*d*, J=6 Hz, 2H, Ar–C*H*), 7.15 (*d*, J= 6 Hz, 2H, Ar–C*H*), 4.42 (*s*, 2H, *CH$_2$*). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 146.7, 126.9 (Ar-C*H*), 125.5-125.4 (q, J = 22 Hz, *C*F$_3$), 63.8 (*CH$_2$*).

2l)
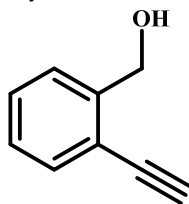
^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.57 (*d*, J = 9, 1H, Ar-C*H*) , 7.38 (*d*, J= 9 Hz, 1H, Ar–C*H*), 7.08 (t, , J= 9 Hz, 1H, Ar–C*H*) 6.88 (*t*, J= 9.0 Hz, 1H, Ar–C*H*), 4.89 (*s*, 2H, *CH$_2$*), 3.02 (*s*, 1H, CC*H*). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 144.7, 132.7, 129.2, 127.0, 126.9, 120.1 (Ar–C*H*), 82.6, 81.5 (*C*C*H*), 62.9 (CH$_2$).

2m)
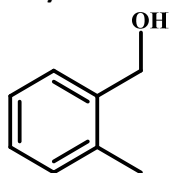
^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.45 (*d*, J = 6, 1H, Ar-C*H*) , 7.12-7.01 (*m*, 3H, Ar–C*H*), 4.54 (*s*, 2H, *CH$_2$*), 2.15 (C*H$_3$*). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 139.9, 135.9, 130.3,127.5, 126.2 (Ar–C*H*), 63.0 (CH$_2$), 18.6 (*CH$_3$*).

2n)
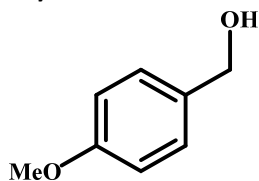
^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.22 (*d*, J=6 Hz. 2H, Ar−C*H*), 6.78 (*d*, J=6 Hz. 2H, Ar−C*H*), 4.50 (*s*, 2H, *CH2*), 3.40 (*s*, 1H, O*H*), 3.31 (*s*, 3H, OC*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 159.1, 133.9, 128.3, 113.7 (Ar−*C*H), 64.1(*C*H$_2$), 54.4 (O*C*H$_3$).

2o)
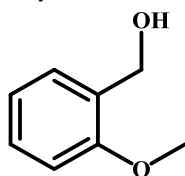
^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.34 (*d*, J= 6 Hz, 1H, Ar−C*H*), 7.08 (*t*, J= 6 Hz, 1H, Ar−C*H*), 6.87 (*t*, J= 6 Hz, 1H, Ar−C*H*), 6.48 (*d*, J= 6 Hz, 1H, Ar−C*H*), 4.74 (*s*, 2H, C*H*$_2$), 3.21 (s, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 157.4, 130.4, 128.5, 128.4, 120.9, 110.5 (Ar-*C*), 61.3 (*C*H$_2$), 54.7 (O*C*H$_3$).

2q)
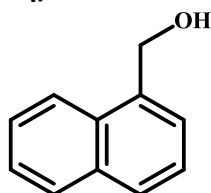
^{1}H NMR (300 MHz, C$_6$D$_6$): δ 8.03 (*d*, *J* = 6 Hz, 1H, Ar−C*H*), 7.65 (*d*, *J* = 6 Hz, 1H, Ar−C*H*), 7.57 (*d*, *J* = 6 Hz, 1H, Ar−C*H*), 7.52 (*d*, *J* = 6 Hz, 1H, Ar−C*H*), 7.32-7.24 (*m*, 3H, Ar−C*H*), 4.99 (*s*, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 137.6, 134.2, 131.8, 128.6, 128.2, 126.2, 125.9, 125.7, 125.0, 124.2 (Ar-*C*), 62.9 (*C*H$_2$).

2r)
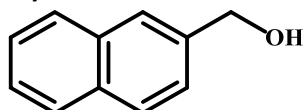
^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.75 (*s*, 1H, Ar-C*H*), 7.67 (*d*, *J* = 6 Hz, 1H, Ar−C*H*), 7.63 (*d*, *J* = 6 Hz, 2H, Ar−C*H*), 7.42 (*d*, *J* = 6 Hz, 1H, Ar−C*H*), 7.28-7.22 (*m*, 2H, Ar−C*H*), 4.71 (*s*, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 139.8, 134.0, 133.4, 128.2, 126.4, 125.8, 125.6, 125.5 (Ar-*C*), 64.7 (*C*H$_2$).

2s)
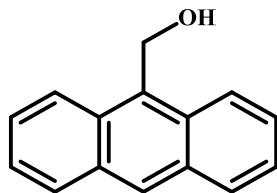
¹H NMR (300 MHz, C₆D₆): δ 8.36 (*d*, *J* = 6 Hz, 2H, Ar–C*H*), 8.15 (*s*, 1H, Ar–C*H*), 7.79 (*d*, *J* = 6 Hz, 5H, Ar–C*H*), 7.32-7.22 (*m*, 4H, Ar–C*H*), 5.40 (*s*, 2H, C*H₂*), 3.15 (*b*, 1H, O*H*). ¹³C{¹H} NMR (75 MHz, C₆D₆): δ 132.5, 132.1, 130.9, 129.2, 126.2, 125.2, 125.0 (Ar-*C*), 57.0 (*C*H₂).

2t)
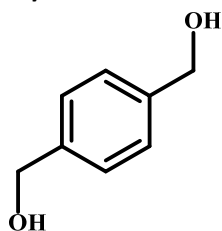
¹H NMR (300 MHz, C₆D₆): δ 7.30 (*s*, 4H, Ar–C*H*), 4.56 (*s*, 4H, C*H₂*). ¹³C{¹H} NMR (75 MHz, C₆D₆): δ 141.1, 127.1 (Ar-*C*), 64.5 (*C*H₂).

2u)
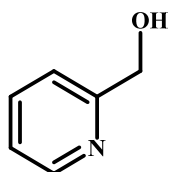
¹H NMR (300 MHz, C₆D₆): δ 8.30 (*d*, *J* = 3.6 Hz, 1H, Ar-C*H*), 7.04 (*t*, *J* = 6 Hz, 1H, Ar–C*H*), 6.99 (*d*, *J* = 6 Hz, 2H, Ar–C*H*), 7.58 (*t*, *J* = 4 Hz, 1H, Ar–C*H*), 4.73 (*s*, 2H, C*H₂*), 4.62 (*b*, 1H, O*H*). ¹³C{¹H} NMR (75 MHz, C₆D₆): δ 149.7, 148.5, 136.4, 122.0, 120.7 (Ar-C), 64.6 (*C*H₂).

2v)
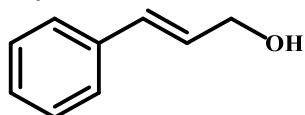
¹H NMR (300 MHz, C₆D₆): δ 7.26 (*d*, J= 6 Hz. 2H, Ar–C*H*), 7.12 (*t*, J= 6 Hz, 2H, Ar–C*H*), 7.04 (*t*, J= 6 Hz, 1H, Ar–C*H*), 6.55 (*d*, J= 12 Hz. 1H, C*H*), 6.27-6.21 (*m*, 1H, C*H*), 4.16 (*d*, J= 6 Hz. 2H, C*H₂*). ¹³C{¹H} NMR (75 MHz, C₆D₆): δ 137.6, 130.4 (Ar-*C*), 129.7 (*C*H), 128.8 (Ar-*C*), 127.6 (*C*H), 126.8 (Ar–*C*H), 63.1 (*C*H₂).

2w)
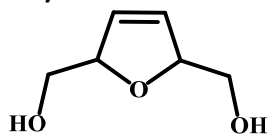
^{1}H NMR (300 MHz, C$_6$D$_6$): δ 6.01 (*s*, 4H, Ar−C*H*), 4.42 (*s*, 4H, C*H*$_2$), 4.05 (*b*, 2H, O*H*). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 154.9, 108.4 (Ar-*C*), 57.2 (*C*H$_2$).

2x)
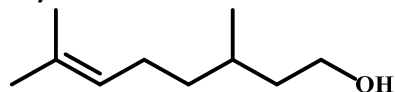
^{1}H NMR (300 MHz, C$_6$D$_6$): δ 5.19 (ddd, *J* = 7.1, 4.3, 1.4 Hz, 1H, C*H*), 3.58 (ddd, *J* = 17.8, 8.2, 3.1 Hz, 2H, C*H*$_2$OH), 2.08 − 1.98 (m, 4H, C*H*$_2$), 1.86 (s, 1H, O*H*), 1.67 (s, 3H, CH3), 1.45 − 1.27 (m, 3H, CH, CH$_2$), 0.88 (d, *J* = 6.6 Hz, 3H, CHC*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 130.9(*C*), 125.4 (*C*H), 60.6 (*C*H$_2$), 40.3 (*C*H$_2$), 37.7 (*C*H$_2$), 29.6 (*C*H), 26.0 (*C*H$_2$), 25.9 (*C*H$_3$), 19.7 (*C*H$_3$), 17.7 (*C*H$_3$).

4a)
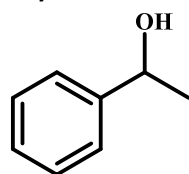
^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.30 (*d*, *J* = 6 Hz, 2H, Ar-C*H*), 7.24 (*t*, *J* = 6 Hz, 2H, Ar−C*H*), 7.16 (*t*, *J* = 6 Hz, 1H, Ar−C*H*), 4.61 (*q*, *J* = 6 Hz, 1 H, CH), 1.35 (*d*, *J* = 6 Hz, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 146.8, 128.6, 127.4, 125.7, 70.2 (Ar-*C*H), 70.2 (*C*H), 25.7 (*C*H$_3$).

4b)
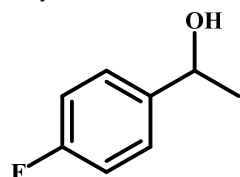
^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.05-7.01 (*m*, 2H, Ar−C*H*), 6.84-6.79 (*m*, 2H, Ar−C*H*), 4.48 (*q*, *J* = 6 Hz, 1 H, CH), 1.23 (*d*, *J* = 6 Hz, 3H, C*H*$_3$).. ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 161.2, 131.1-131.0 (*d*, *J* = 6.7 Hz, Ar-*C*), 127.4-127.3 (*d*, *J* = 6 Hz, Ar-*C*), 115.6-115.1 (*d*, *J* = 37 Hz, Ar-*C*) 69.4 (*C*H), 26.0 (*C*H$_3$).

4c)
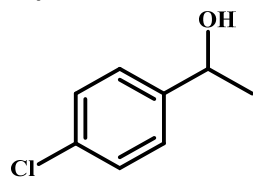
^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.15 (*d*, *J* = 6 Hz, 2H, Ar−C*H*), 7.09 (*d*, *J* = 6 Hz, 2H, Ar−C*H*), 4.62 (*q*, *J* = 6 Hz, 1 H, CH), 1.31 (*d*, *J* = 6 Hz, 3H, C*H*$_3$).. ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 145.7, 132.8, 128.6, 127.3 (Ar-*C*) 69.2 (*C*H), 25.8 (*C*H$_3$).

4d)
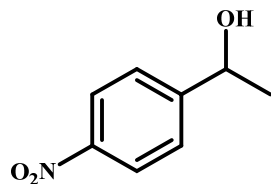
^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.89 (*d*, *J* = 6 Hz, 2H, Ar−C*H*), 7.10 (*d*, *J* = 6 Hz, 2H, Ar−C*H*), 4.60 (*q*, *J* = 6 Hz, 1 H, C*H*), 3.96 (*b*, 1H, O*H*) 1.26 (*d*, *J* = 6 Hz, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 154.2, 147.3, 126.2, 123.6 (Ar-*C*) 69.0 (*C*H), 25.6 (*C*H$_3$).

4e)
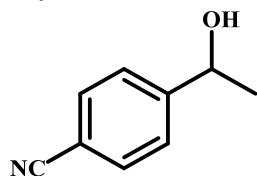
^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.14-7.08 (*m*, 4H, Ar−C*H*), 4.64 (*q*, *J* = 5 Hz, 1 H, C*H*), 1.26 (*d*, *J* = 6 Hz, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 152.5, 132.12, 126.3, (Ar-*C*), 119.2 (*C*N), 110.9 (Ar-*C*), 69.5 (*C*H), 25.8 (*C*H$_3$).

4f)
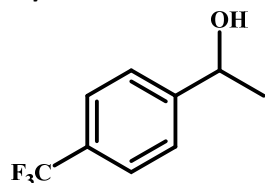
^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.38 (*d*, *J* = 6 Hz, 2H, Ar−C*H*), 7.18 (*d*, *J* = 6 Hz, 2H, Ar−C*H*), 4.61 (*q*, *J* = 6 Hz, 1 H, C*H*), 3.70 (*b*, 1H, O*H*) 1.27 (*d*, *J* = 6 Hz, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 151.2, 129.3 (*q*, *J* = 24 Hz, Ar-*C*), 129.3 (*q*, *J* = 24 Hz, Ar-*C*) 126.1 (Ar-*C*), 125.4 (*q*, *J* = 3 Hz, Ar-*C*) 125.1 (*q*, *J* = 202 Hz, *C*F$_3$) 69.3 (*C*H), 25.7(*C*H$_3$).

4g)
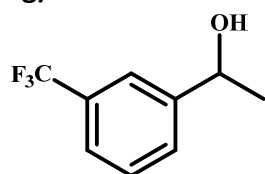
^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.71 (*s*, 2H, Ar−C*H*), 7.31 (*t*, *J* = 6 Hz, 2H, Ar−C*H*), 7.01 (*t*, *J* = 6 Hz, 2H, Ar−C*H*), 4.66 (*q*, *J* = 6 Hz, 1 H, C*H*), 1.29 (*d*, *J* = 6 Hz, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 148.4, 130.7 (*q*, *J* = 24, Ar-*C*), 129.2, 129.0 (Ar-*C*), 125.2 (*q*, *J* = 202 Hz, CF$_3$) 123.9 (*q*, *J* = 3 Hz, Ar-*C*) 122.6 (*q*, *J* = 3, Ar-*C*), 69.3 (*C*H), 25.7 (*C*H$_3$).

4h)
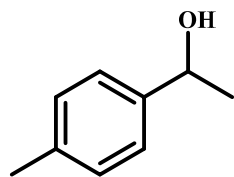
^{1}H NMR (300 MHz, CDCl$_3$): δ 7.27 (*d*, *J* = 6 Hz, 2H, Ar–C*H*), 7.16 (*d*, *J* = 6 Hz, 2H, Ar–C*H*), 4.88 (*q*, *J* = 6 Hz, 1 H, CH) 2.35 (*s*, 3H, C*H*$_3$), 1.59 (*d*, *J* = 6 Hz, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 143.0, 137.3, 129.3, 125.5 (Ar-*C*) 70.4 (*C*H), 25.2 (*C*H$_3$) 21.2 (*C*H$_3$).

4i)
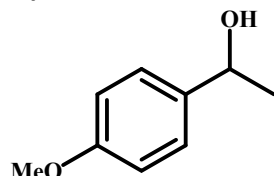
^{1}H NMR (300 MHz, CDCl$_3$): δ 7.31 (*d*, *J* = 6 Hz, 2H, Ar–C*H*), 6.89 (*d*, *J* = 6 Hz, 2H, Ar–C*H*), 4.87 (*q*, *J* = 6 Hz, 1 H, CH), 3.81 (*s*, 3H, C*H*$_3$), 1.72 (*b*, 1H, OH), 1.49 (*d*, *J* = 6 Hz, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 159.0, 138.0, 126.7, 113.9 (Ar-*C*), 70.1 (*C*H), 55.3 (*C*H$_3$) 25.1 (*C*H$_3$).

4j)
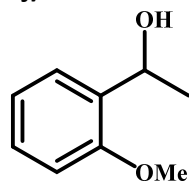
^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.60 (*d*, *J* = 6 Hz, 1H, Ar–C*H*), 7.07 (*t*, *J* = 6 Hz, 1H, Ar–C*H*), 6.92 (t, *J* = 6 Hz, 1H, Ar–C*H*), 6.52 (*d*, *J* = 6 Hz, 2H, Ar–C*H*), 5.31 (*q*, *J* = 6 Hz, 1 H, CH), 3.68 (*b*, 1H, OH), 3.29 (*s*, 3H, C*H*$_3$), 1.54 (*d*, *J* = 6 Hz, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 156.4, 135.2, 126.4, 121.1, 110.4 (Ar-*C*), 65.3 (*C*H), 65.3 (*C*H), 54.8 (*C*H$_3$), 25.1 (*C*H$_3$).

4k)
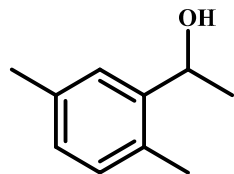
^{1}H NMR (300 MHz, CDCl$_3$): δ 7.33 (*s*, 1H, Ar–C*H*), 7.04-6.97 (*m*, 2H, Ar–C*H*), 5.12 (*q*, *J* = 6 Hz, 1 H, CH), 2.33 (*s*, 3H, C*H*$_3$), 2.30 (*s*, 3H, C*H*$_3$), 3.68 (*b*, 1H, OH), 3.29 (*s*, 3H, C*H*$_3$), 1.69 (*b*, 1H, OH), 1.54 (*d*, *J* = 6 Hz, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 143.7, 135.9, 131.1, 130.4, 127.9, 125.2, (Ar-*C*), 66.9 (*C*H), 24.0 (*C*H$_3$), 21.2 (*C*H$_3$), 18.5 (*C*H$_3$).

4l)
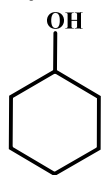
^{1}H NMR (300 MHz, CDCl$_3$): δ 3.58 – 3.48 (m, 1H, CH), 1.85 (m, 2H, CH_2), 1.69 – 1.60 (m, 2H, CH_2), 1.39 (m, 2H, CH_2), 1.33 – 1.23 (m, 2H, CH_2), 1.20 – 1.14 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 70.0 (CH), 35.9 (CH$_2$), 26.0 (CH$_2$), 24.5 (CH$_2$).

4m)
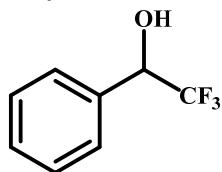
^{1}H NMR (300 MHz, CDCl$_3$): δ 7.48 (d, J = 6 Hz, 2H, Ar–CH), 7.14-7.07 (m, 3H, Ar–CH), 4.89 (q, J = 6 Hz, 1 H, CH). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 135.9, 129.1, 128.5 (Ar-C), 125.6 (q, J = 210 Hz, CF$_3$), 72.5 (q, J = 23 Hz, CH).

4n)
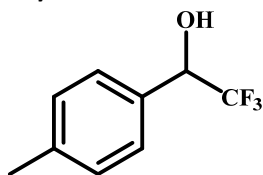
^{1}H NMR (300 MHz, CDCl$_3$): δ 7.41 (d, J = 6 Hz, 2H, Ar–CH), 6.96 (d, J = 6 Hz, 2H, Ar–CH), 4.92 (q, J = 6 Hz, 1 H, CH), 2.05 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 138.8, 133.1, 129.3, 128.0 (Ar-C) 125.7 (q, J = 210 Hz, CF$_3$), 72.50 (q, J = 23 Hz, CH), 21.1 (CH$_3$).

4o)
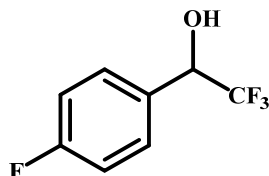
^{1}H NMR (300 MHz, CDCl$_3$): δ 732-729 (m, 2H, Ar–CH), 688-6-75 (m, 2H, Ar–CH), 4.85 (q, J = 6 Hz, 1 H, CH). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 163.5 (d, J = 183 Hz, Ar-C), 131.8 (Ar-C), 129.9 (d, J = 6 Hz, Ar-C), 125.4 (q, J = 210 Hz, CF$_3$), 71.9 (q, J = 22 Hz, CH).

4p)
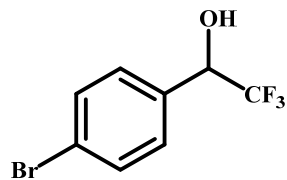
^{1}H NMR (300 MHz, CDCl$_3$): δ 7.21 (*d*, *J* = 6 Hz, 2H, Ar−C*H*), 7.15 (*d*, *J* = 6 Hz, 2H, Ar−C*H*), 4.78 (*q*, *J* = 6 Hz, 1 H, CH), 2.05 (*s*, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 135.0, 131.7, 129.7 (Ar-*C*), 125.3 (*q*, *J* = 210 Hz, *C*F$_3$), 123.4 (Ar-*C*), 71.89 (*q*, *J* = 23 Hz, *C*H).

4. Characterization of Ligands
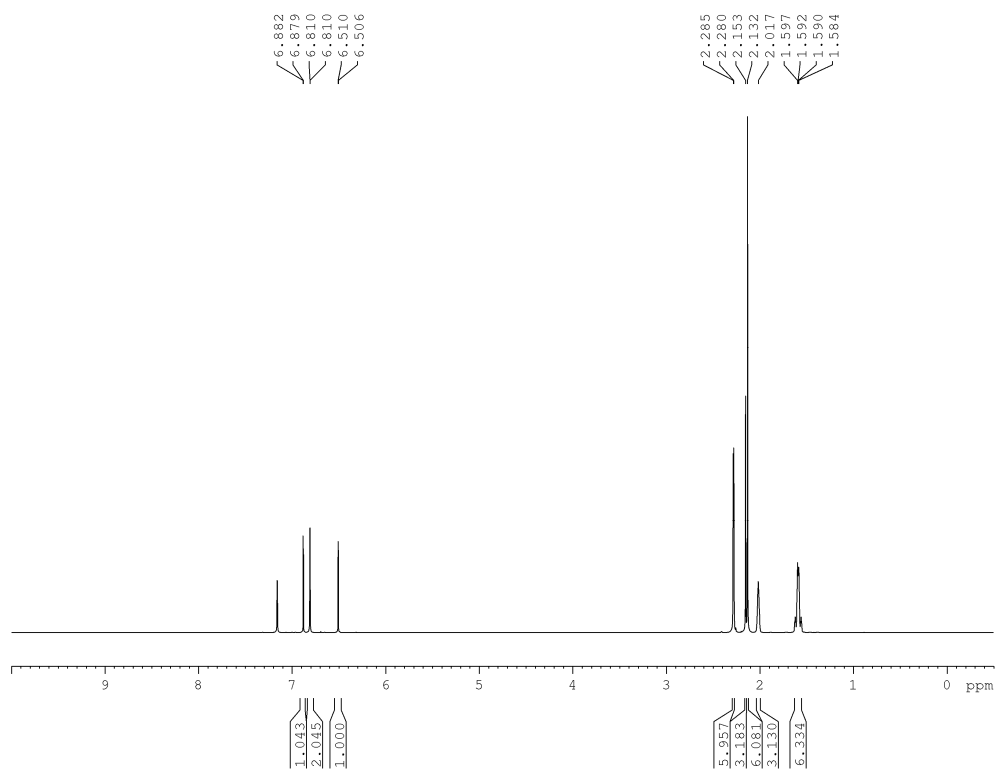
Figure S1: ^{1}H NMR spectrum of **Im$^{Ad, Mes}$ Carbene** in C$_6$D$_6$.
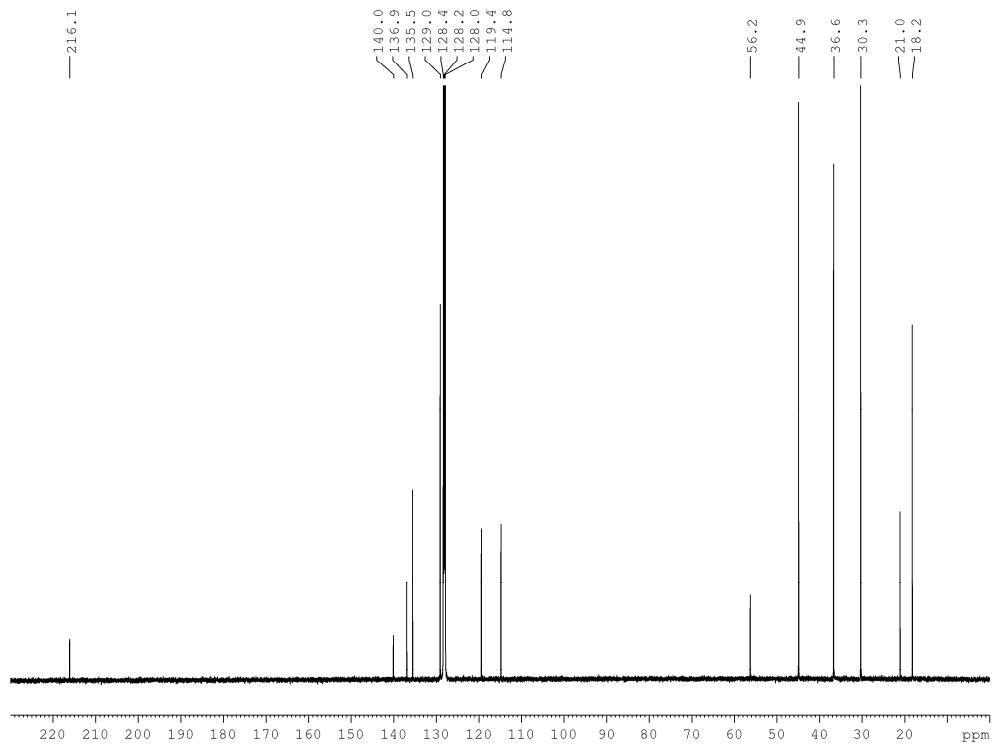
Figure S2: ^{13}C NMR spectrum of **Im$^{Ad, Mes}$ Carbene** in C_6D_6.
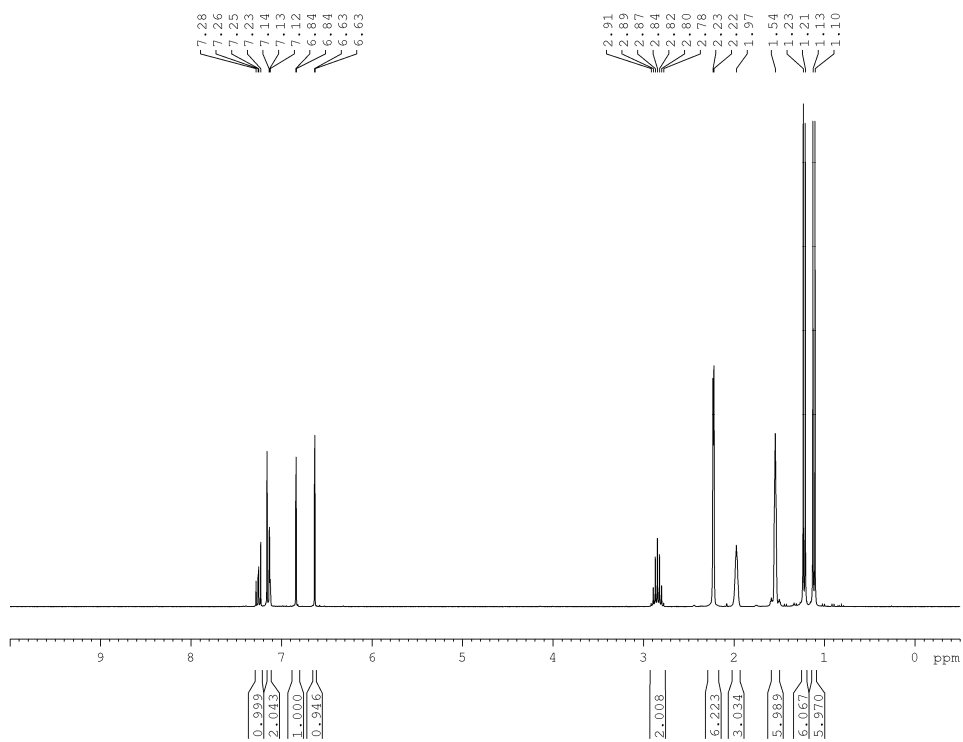
Figure S3: ^{1}H NMR spectrum of **Im$^{Ad, Dipp}$ Carbene** in C_6D_6.
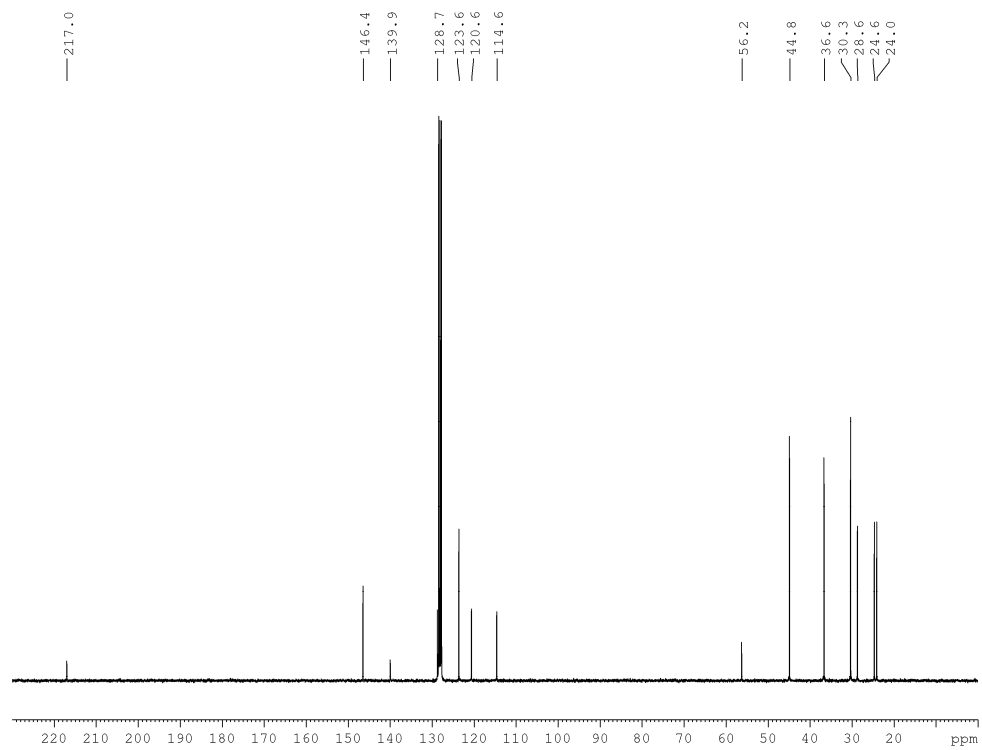
Figure S4: ^{13}C NMR spectrum of **Im$^{Ad, Dipp}$ Carbene** in C_6D_6.
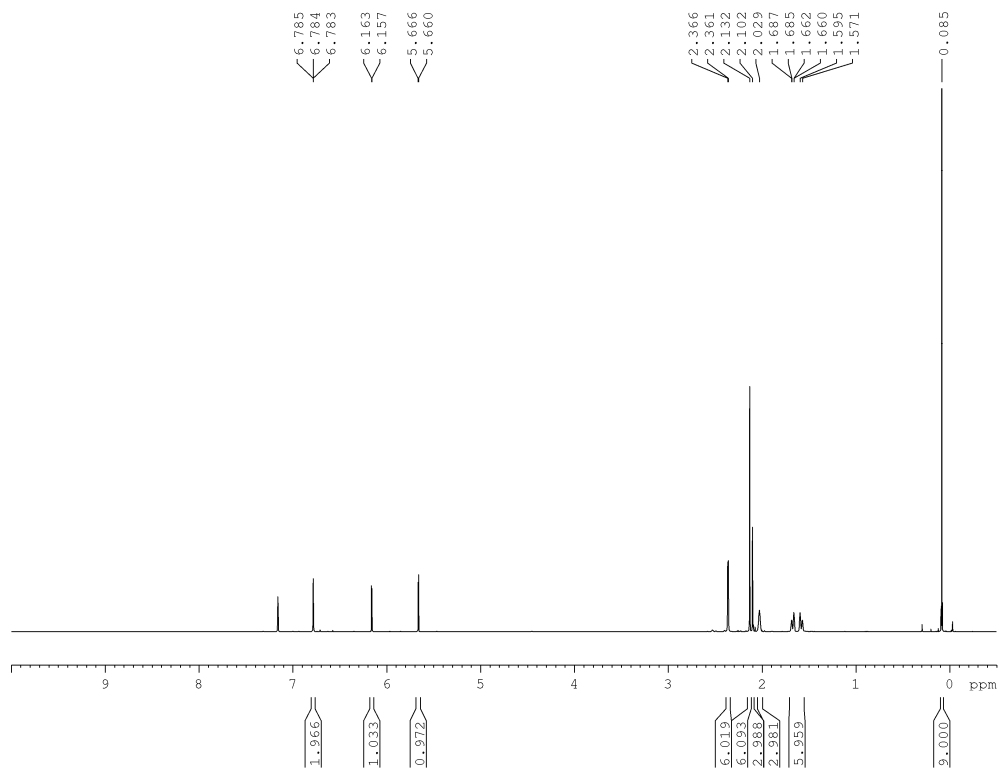
Figure S5: ^1H NMR spectrum of **Im$^{Ad, mes}$ N-TMS** in C_6D_6.
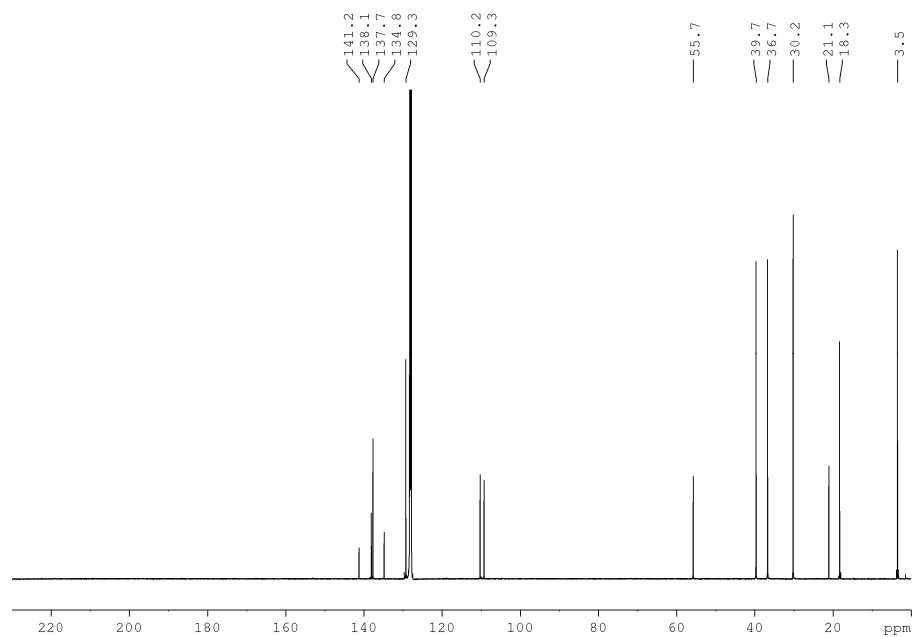
Figure S6: ^{13}C NMR spectrum of **Im$^{Ad, mes}$ N-TMS** in C_6D_6.
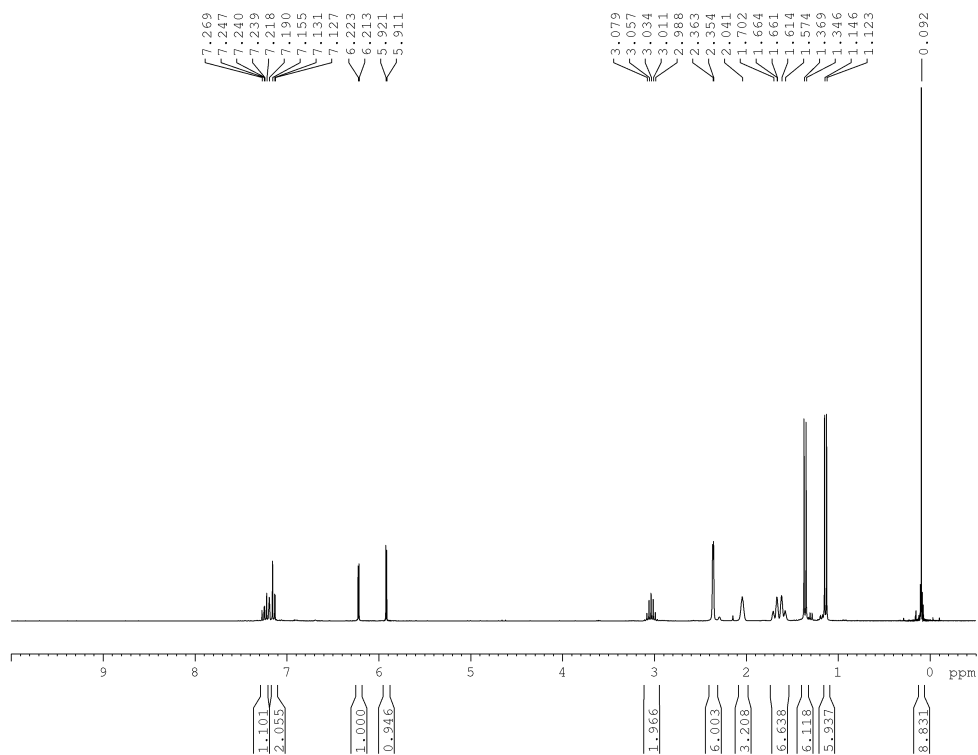
Figure S7: ^1H NMR spectrum of **Im$^{Ad, Dipp}$ N-TMS** in C_6D_6.
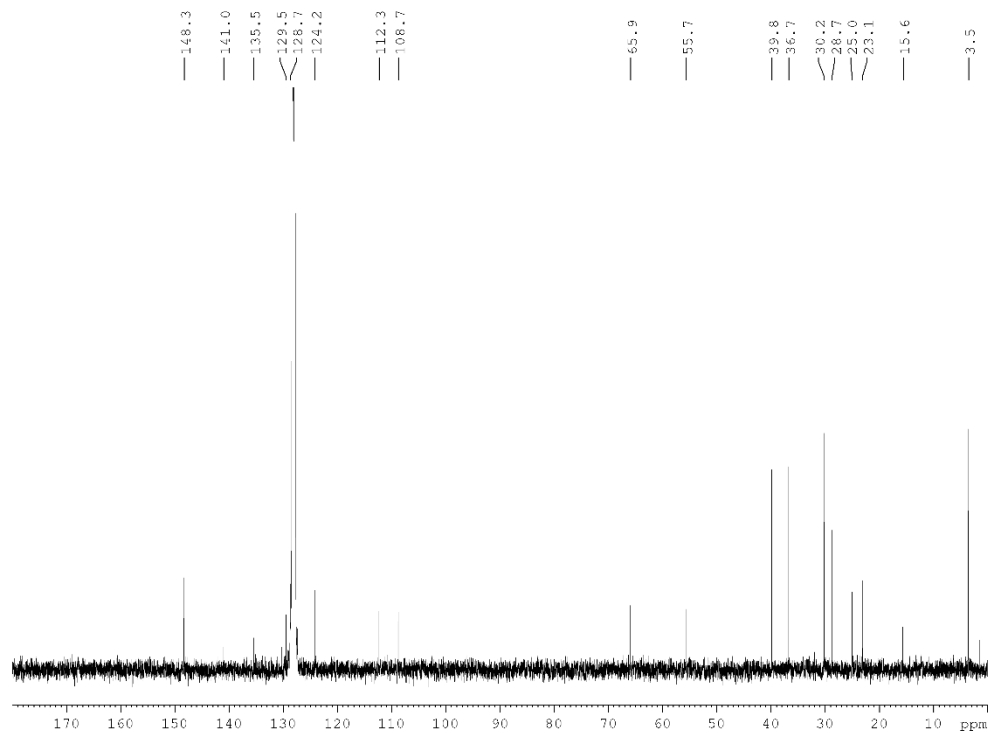
Figure S8: ^{13}C NMR spectrum of $Im^{Ad, Dipp}$ **N-TMS** in C_6D_6.
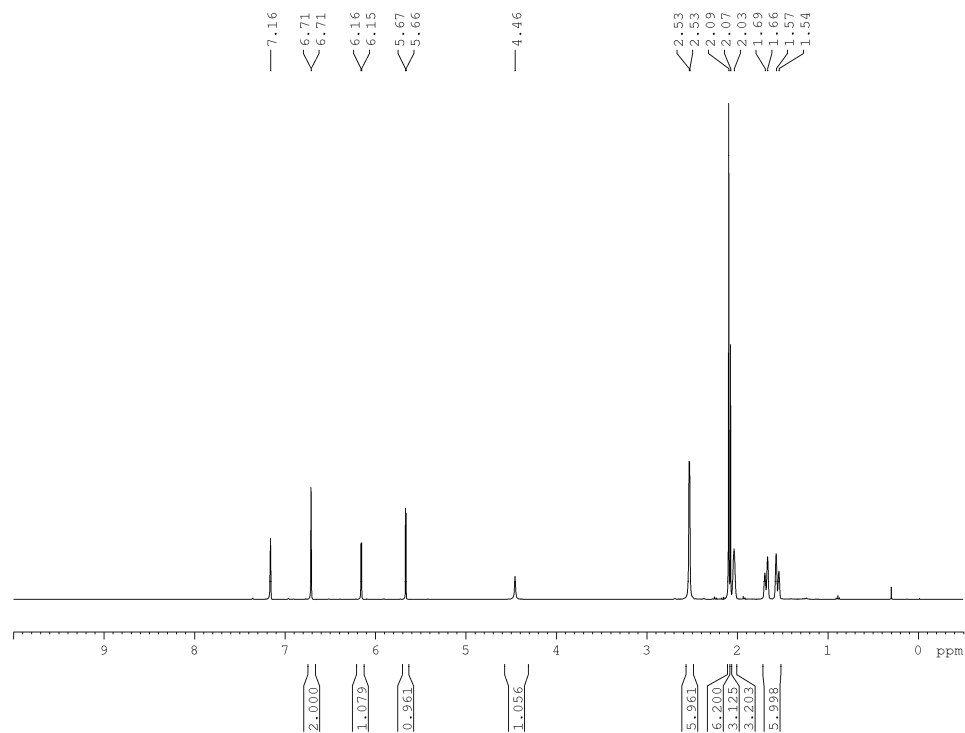
Figure S9: ^{1}H NMR spectrum of **L₁H** in C_6D_6.
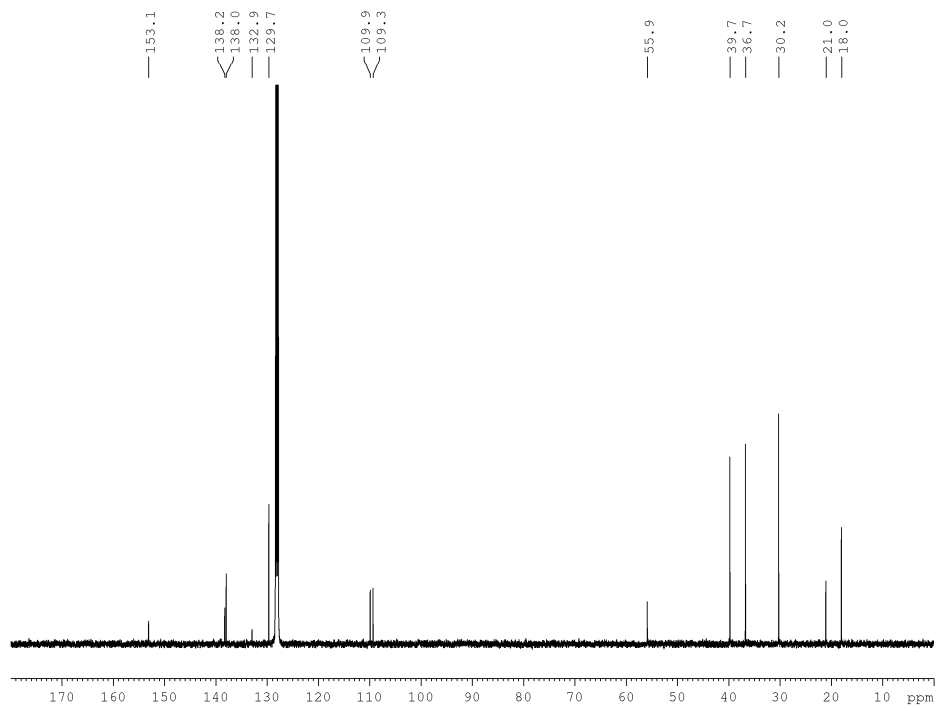
Figure S10: ^{13}C NMR spectrum of **L₁H** in C_6D_6.
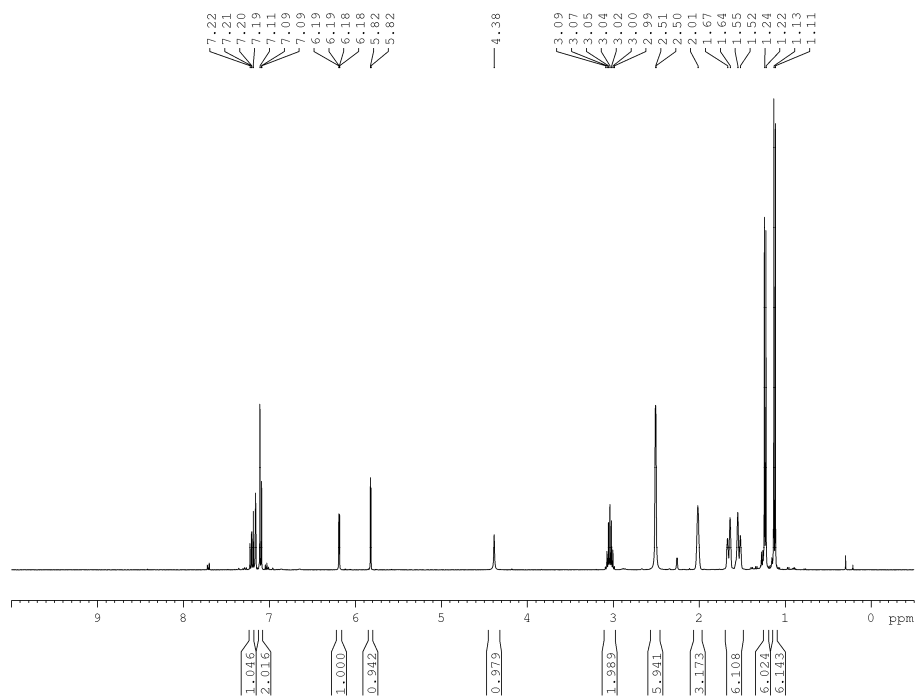
Figure S11: ^1H NMR spectrum of **L₂H** in C_6D_6.
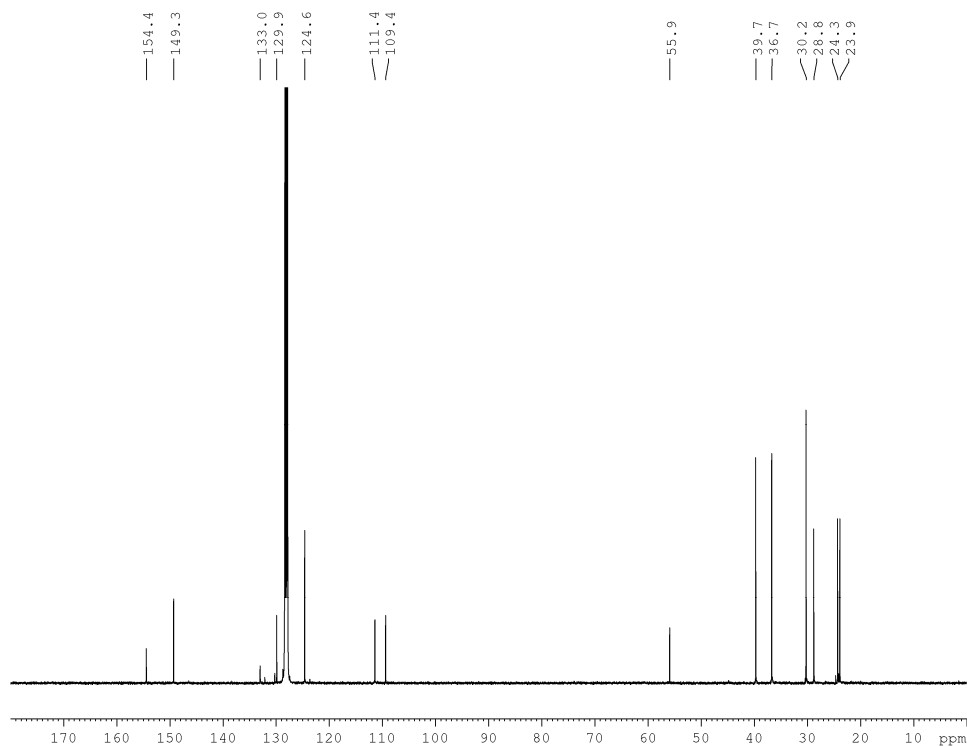
Figure S12: ^{13}C NMR spectrum of **L$_2$H** in C_6D_6.

4.1 Crystallographic data of **Im$^{Ad,\,Mes}$ Carbene**

Identification code	mk31mk
Empirical formula	$C_{22}H_{28}N_2$
Formula weight	320.46
Temperature	100(2) K
Wavelength	0.71073 Å
Instrument (scan mode)	XtaLAB Synergy, Single source HyPix (⬚ scan)
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 13.5173(4) Å ⬚= 90°
	b = 10.3836(2) Å ⬚= 95.869(2)°
	c = 12.8450(4) Å ⬚ = 90°
Volume	1793.45(8) Å^3
Z	4
Density (calculated)	1.187 Mg/m^3
Absorption coefficient	0.069 mm^{-1}
F(000)	696

Crystal habitus	plate (colourless)
Crystal size	0.279 x 0.211 x 0.143 mm^3
Theta range for data collection	2.478 to 44.855°
Index ranges	-26<=h<=26, -20<=k<=20, -25<=l<=25
Reflections collected	134137
Independent reflections	14658 [R(int) = 0.0485]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.88245
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14658 / 0 / 220
Goodness-of-fit on F^2	1.066
Final R indices [I>2sigma(I)]	R1 = 0.0441, wR2 = 0.1296
R indices (all data)	R1 = 0.0624, wR2 = 0.1381
Largest diff. peak and hole	0.606 and -0.314 e.Å^{-3}
Crystallisation Details:	Toluol/n-Hexan -40°C

Solution: SHELXT-2014/5 (G. M. Sheldrick, Acta Cryst., 2015, A71, 3-8)

Refinement: SHELXL-2018/3 (G. M. Sheldrick, Acta Cryst. (2008), A64, 112-122)

Interface: OLEX2 v1.2 (O. V. Dolomanov et al., J. Appl. Cryst., 2009, 42, 339-341)

4.2 Crystallographic data of **Im$^{Ad, Dipp}$ Carbene**

Identification code	mk28mk	
Empirical formula	C$_{25}$H$_{34}$N$_2$	
Formula weight	362.54	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Instrument (scan mode)	XtaLAB Synergy, Single source, HyPix (⬚ scan)	
Crystal system	Orthorhombic	
Space group	*Pnma*	
Unit cell dimensions	a = 10.4134(2) Å	⬚= 90°
	b = 12.3697(2) Å	⬚= 90°
	c = 16.5809(2) Å	⬚ = 90°
Volume	2135.80(6) Å^3	
Z	4	
Density (calculated)	1.127 Mg/m^3	
Absorption coefficient	0.490 mm^{-1}	

F(000)	792
Crystal habitus	plate (colourless)
Crystal size	0.347 x 0.100 x 0.089 mm^3
Theta range for data collection	4.460 to 77.393°
Index ranges	-11<=h<=13, -15<=k<=15, -20<=l<=20
Reflections collected	39788
Independent reflections	2337 [R(int) = 0.0431]
Completeness to theta = 67.684°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.47134
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2337 / 0 / 141
Goodness-of-fit on F^2	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0398, wR2 = 0.0995
R indices (all data)	R1 = 0.0417, wR2 = 0.1013
Largest diff. peak and hole	0.216 and -0.194 e.Å^{-3}
Crystallisation Details:	toluene/*n*-hexane -30 °C

Solution: SHELXT-2014/5 (G. M. Sheldrick, Acta Cryst., 2015, A71, 3-8)

Refinement: SHELXL-2018/3 (G. M. Sheldrick, Acta Cryst., 2008, A64, 112-122)

Interface: OLEX2 v1.2 (O. V. Dolomanov et al., J. Appl. Cryst., 2009, 42, 339-341)

4.3 Crystallographic data of Im$^{Ad, Mes}$ N-TMS

Identification code	mk17mk	
Empirical formula	C$_{25}$H$_{37}$N$_3$Si	
Formula weight	407.66	
Temperature	103(1) K	
Wavelength	0.71073 Å	
Instrument (scan mode)	Oxford Diffraction Xcalibur, Eos (⬚ scan)	
Crystal system	Monoclinic	
Space group	*P*2$_1$/*n*	
Unit cell dimensions	a = 9.7011(4) Å	⬚= 90°
	b = 24.1407(8) Å	⬚= 99.776(4)°
	c = 10.2311(4) Å	⬚ = 90°
Volume	2361.24(16) Å^3	
Z	4	
Density (calculated)	1.147 Mg/m^3	

Absorption coefficient	0.115 mm^{-1}	
F(000)	888	
Crystal habitus	irregular (colourless)	
Crystal size	0.701 x 0.591 x 0.469 mm^3	
Theta range for data collection	2.291 to 36.316°	
Index ranges	-16<=h<=16, -40<=k<=40, -17<=l<=17	
Reflections collected	121520	
Independent reflections	11433 [R(int) = 0.0726]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.961 and 0.942	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11433 / 0 / 268	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0457, wR2 = 0.1173	
R indices (all data)	R1 = 0.0601, wR2 = 0.1258	
Largest diff. peak and hole	0.671 and -0.236 e.Å^{-3}	
Crystallisation Details:	*n*-hexane at -27 °C	

Solution: SHELXT-2014/5 (G. M. Sheldrick, Acta Cryst., 2015, A71, 3-8)

Refinement: SHELXL-2018/3 (G. M. Sheldrick, Acta Cryst. (2008), A64, 112-122)

Interface: OLEX2 v1.2 (O. V. Dolomanov et al., J. Appl. Cryst., 2009, 42, 339-341)

4.4 Crystallographic data of **L₁H**

Identification code	mk18mk	
Empirical formula	C$_{22}$H$_{29}$N$_3$	
Formula weight	335.48	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Instrument (scan mode)	XtaLAB Synergy, Single source, HyPix (scan)	
Crystal system	Orthorhombic	
Space group	*Pbca*	
Unit cell dimensions	a = 16.6873(2) Å	= 90°
	b = 11.37240(10) Å	= 90°
	c = 19.4505(2) Å	= 90°
Volume	3691.21(7) Å^3	
Z	8	

Density (calculated)	1.207 Mg/m^3
Absorption coefficient	0.545 mm^{-1}
F(000)	1456
Crystal habitus	fragment of trapezoid (colourless)
Crystal size	0.108 x 0.101 x 0.099 mm^3
Theta range for data collection	4.547 to 77.613°
Index ranges	-21<=h<=21, -14<=k<=11, -24<=l<=24
Reflections collected	41369
Independent reflections	3865 [R(int) = 0.0255]
Completeness to theta = 67.684°	100.0 %
Absorption correction	Gaussian
Max. and min. transmission	1.000 and 0.793
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3865 / 0 / 233
Goodness-of-fit on F^2	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0408, wR2 = 0.1015
R indices (all data)	R1 = 0.0429, wR2 = 0.1038
Largest diff. peak and hole	0.280 and -0.283 e.Å^{-3}
Crystallisation Details:	cooling of hot *n*-hexane solution to room temperature

Solution: SHELXT-2014/5 (G. M. Sheldrick, Acta Cryst., 2015, A71, 3-8)

Refinement: SHELXL-2018/3 (G. M. Sheldrick, Acta Cryst., 2008, A64, 112-122)

Interface: OLEX2 v1.2 (O. V. Dolomanov et al., J. Appl. Cryst., 2009, 42, 339-341)

4.5 Crystallographic data of **L₁H**

Identification code	mk15mk	
Empirical formula	C$_{25}$H$_{35}$N$_3$	
Formula weight	377.56	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Instrument (scan mode)	XtaLAB Synergy, Single source, HyPix (◻ scan)	
Crystal system	Monoclinic	
Space group	*P*2$_1$/*c*	
Unit cell dimensions	a = 13.8605(1) Å	◻= 90°
	b = 6.5130(1) Å	◻= 98.599(1)°
	c = 24.0076(2) Å	◻ = 90°
Volume	2142.89(4) Å^3	

Z	4
Density (calculated)	1.170 Mg/m^3
Absorption coefficient	0.521 mm^{-1}
F(000)	824
Crystal habitus	lath (colourless)
Crystal size	0.352 x 0.067 x 0.039 mm^3
Theta range for data collection	3.225 to 77.449°
Index ranges	-17<=h<=17, -6<=k<=8, -30<=l<=30
Reflections collected	47042
Independent reflections	4470 [R(int) = 0.0319]
Completeness to theta = 67.684°	100.0 %
Absorption correction	Gaussian
Max. and min. transmission	1.000 and 0.784
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4470 / 0 / 261
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0378, wR2 = 0.0967
R indices (all data)	R1 = 0.0401, wR2 = 0.0998
Largest diff. peak and hole	0.265 and -0.212 e.Å^{-3}
Crystallisation Details:	*n*-hexane -40 °C

Solution: SHELXT-2014/5 (G. M. Sheldrick, Acta Cryst., 2015, A71, 3-8)

Refinement: SHELXL-2018/3 (G. M. Sheldrick, Acta Cryst., 2008, A64, 112-122)

Interface: OLEX2 v1.2 (O. V. Dolomanov et al., J. Appl. Cryst., 2009, 42, 339-341)
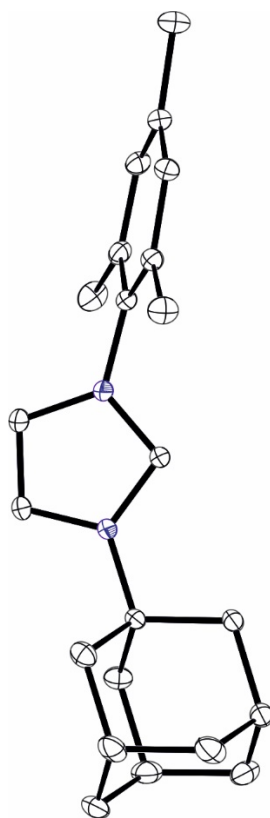
Figure S13: Molecular structure of **Im**[Ad, Mes] **Carbene** with thermal displacement parameters drawn at 50% probability. All hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-N1 1.3739(5), C1-N2 1.3651(5), N1-C4 1.4313(5), N2-C13 1.4711(6), N1-C1-N2 102.05(3).
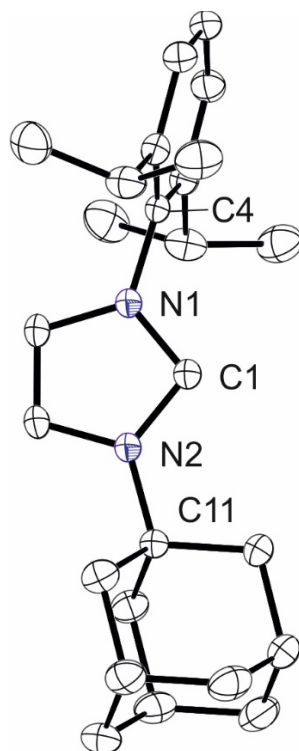
Figure S14: Molecular structure of **Im$^{Ad, Dipp}$ Carbene** with thermal displacement parameters drawn at 50% probability. All hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-N1 1.3709(18), C1-N2 1.3627(18), N1-C4 1.4352(17), N2-C11 1.4765(17), N1-C1-N2 101.48(11).
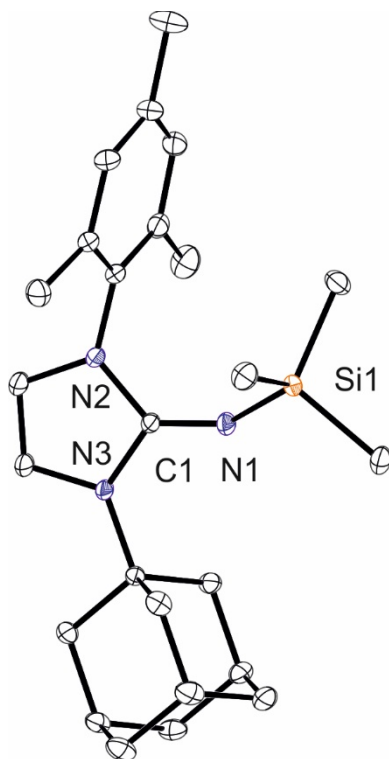
Figure S15: Molecular structure of **Im$^{Ad, Mes}$ N-TMS** with thermal displacement parameters drawn at 50% probability. All hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-N1 1.2782(10), N1-Si1 1.6823(7), N2-C1-N3 103.99(6), C1-N1-Si1142.68(7).
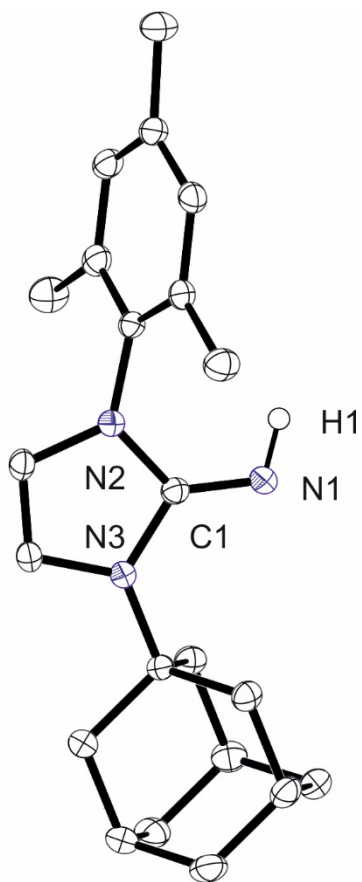
Figure S16: Molecular structure of **L₁H** with thermal displacement parameters drawn at 50% probability. All hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-N1 1.2966(14), N2-C1-N3 104.55(9).
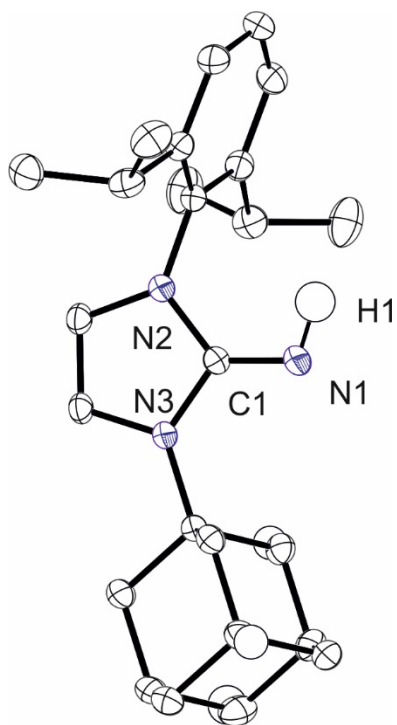
Figure S17: Molecular structure of **L₂H** with thermal displacement parameters drawn at 50% probability. All hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-N1 1.2891(13), N2-C1-N3 104.78(8).

5. Characterization of Complexes
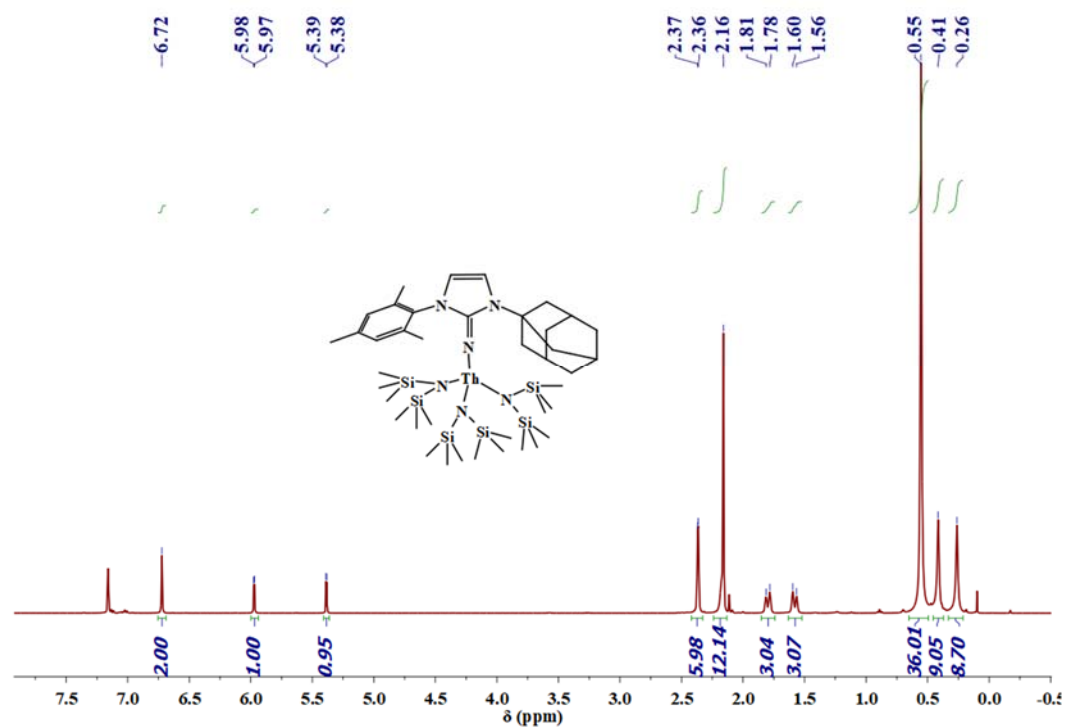
Figure S18: ^{1}H NMR spectrum of **3** in C$_6$D$_6$.
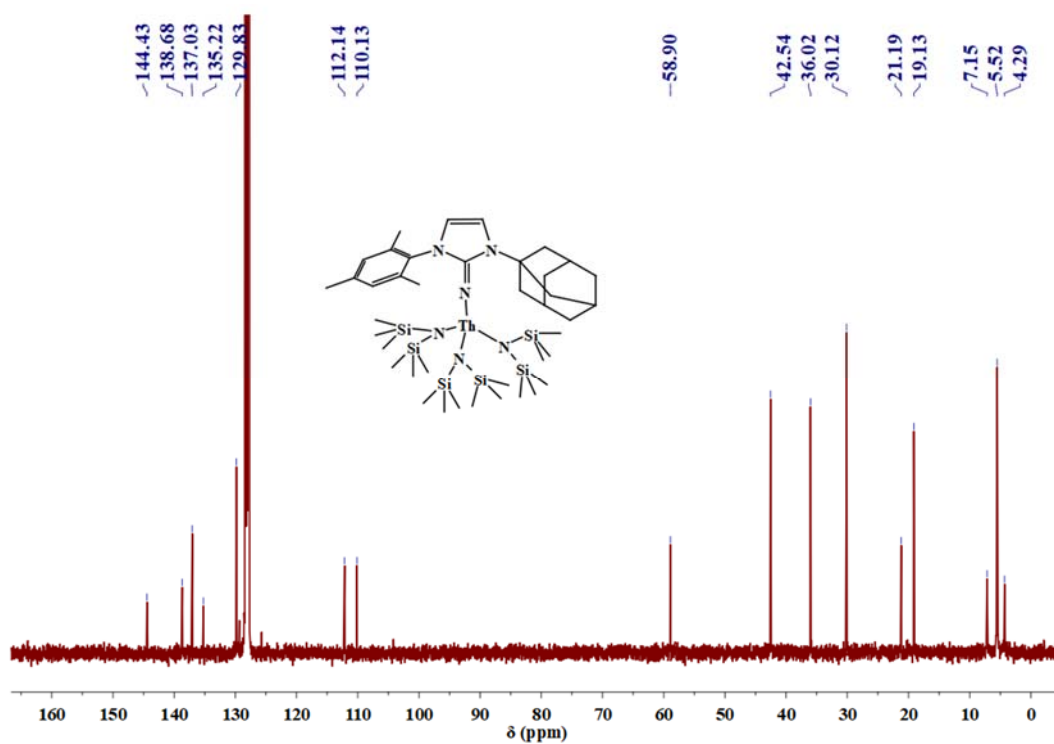
Figure S19: ^{13}C NMR spectrum of **3** in C$_6$D$_6$
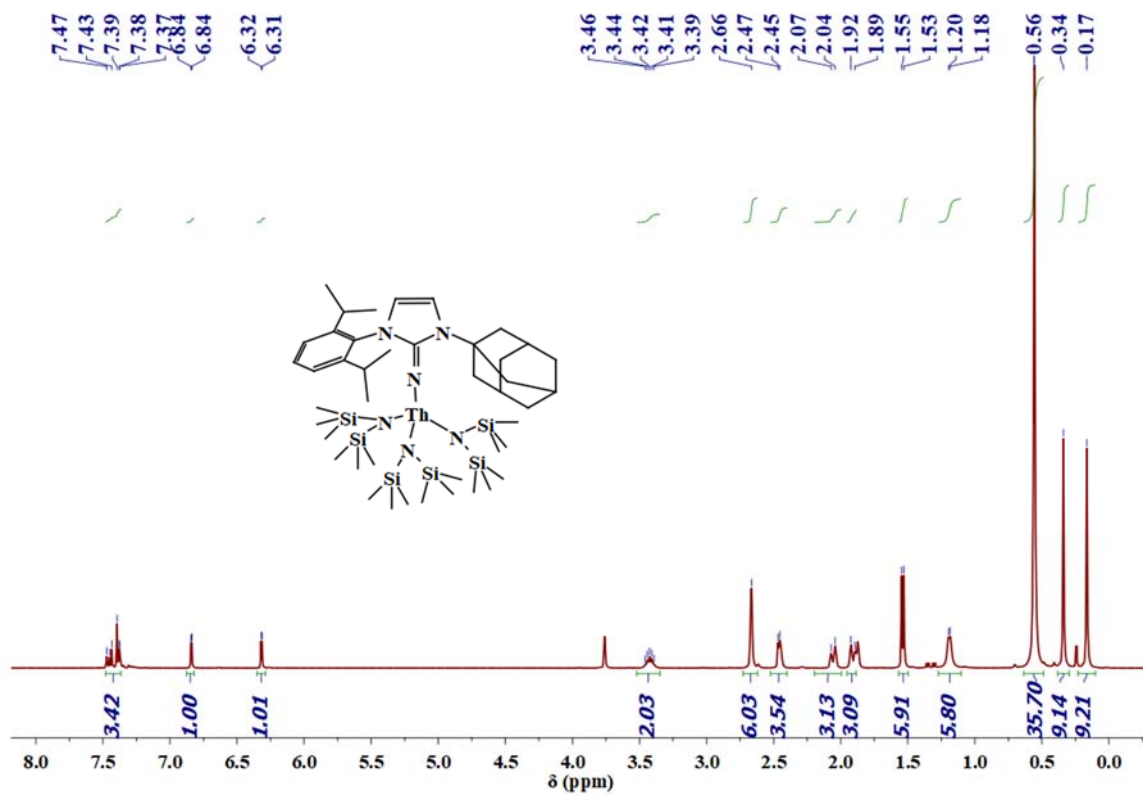
Figure S20: ^{1}H NMR spectrum of **4** in THF-d8.
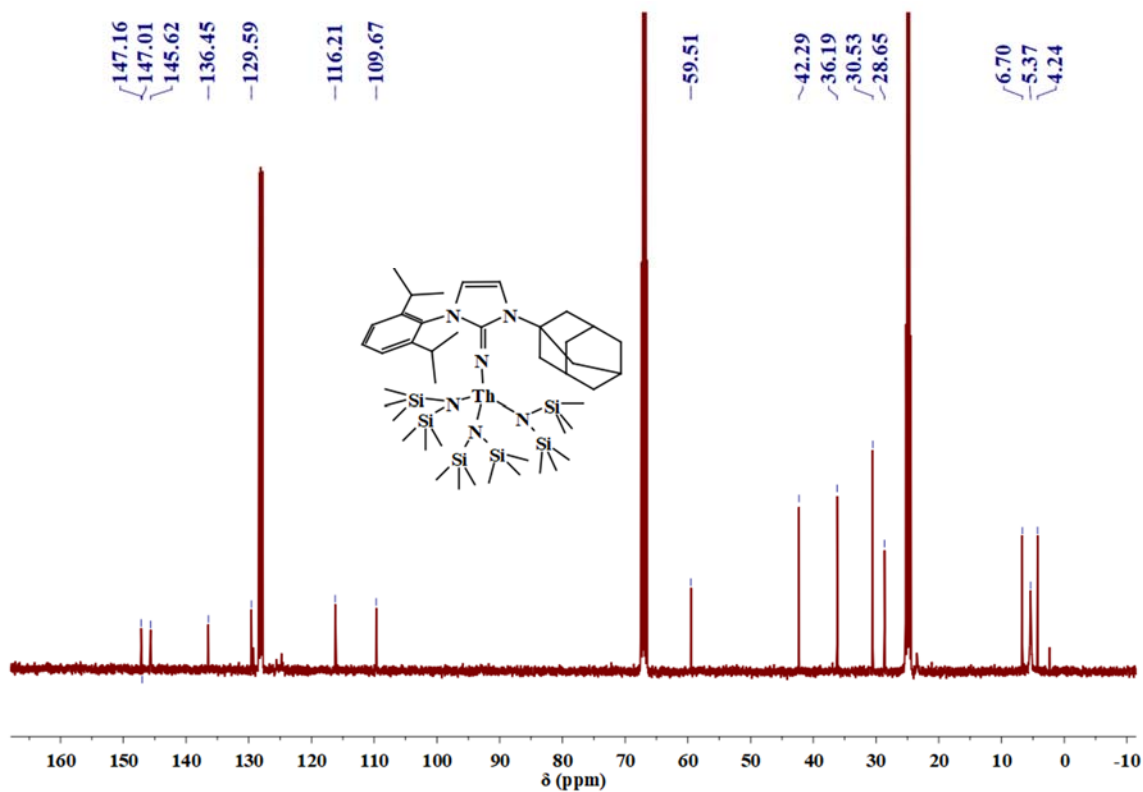
Figure S21: ^{13}C NMR spectrum of **4** in THF-d8 and C_6D_6 mixture.
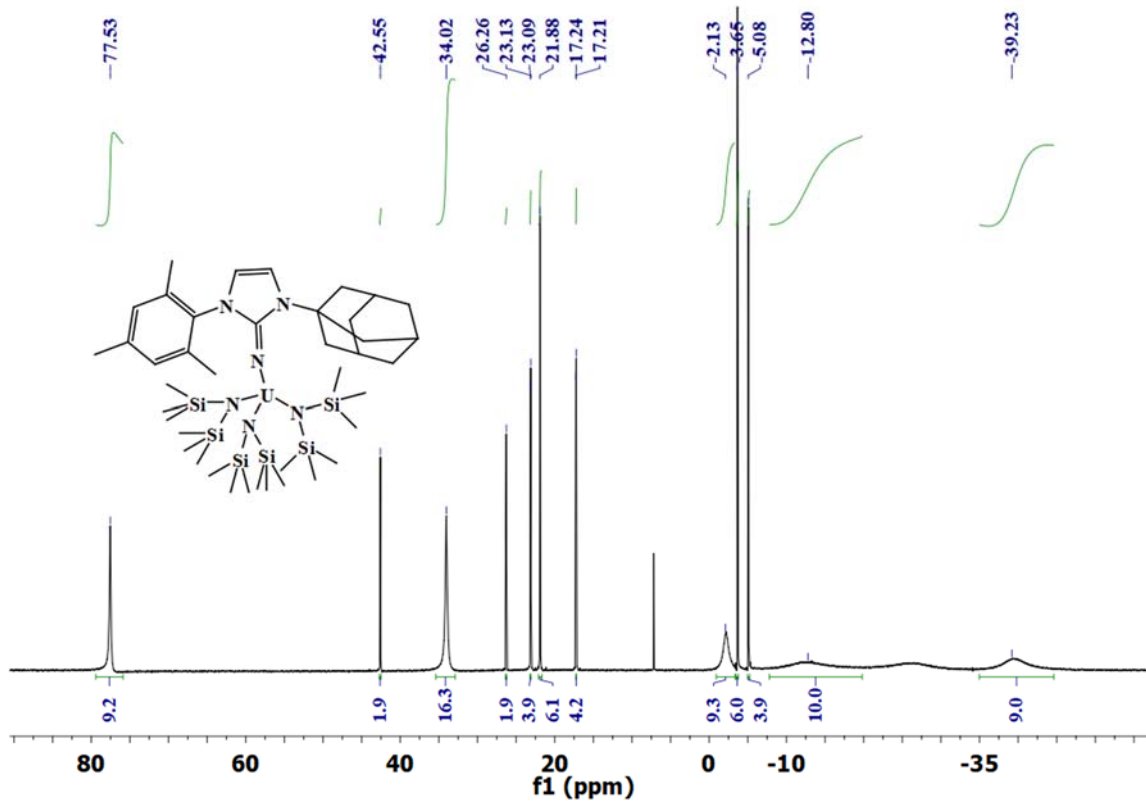
Figure S22: ^1H NMR spectrum of **5** in C_6D_6.
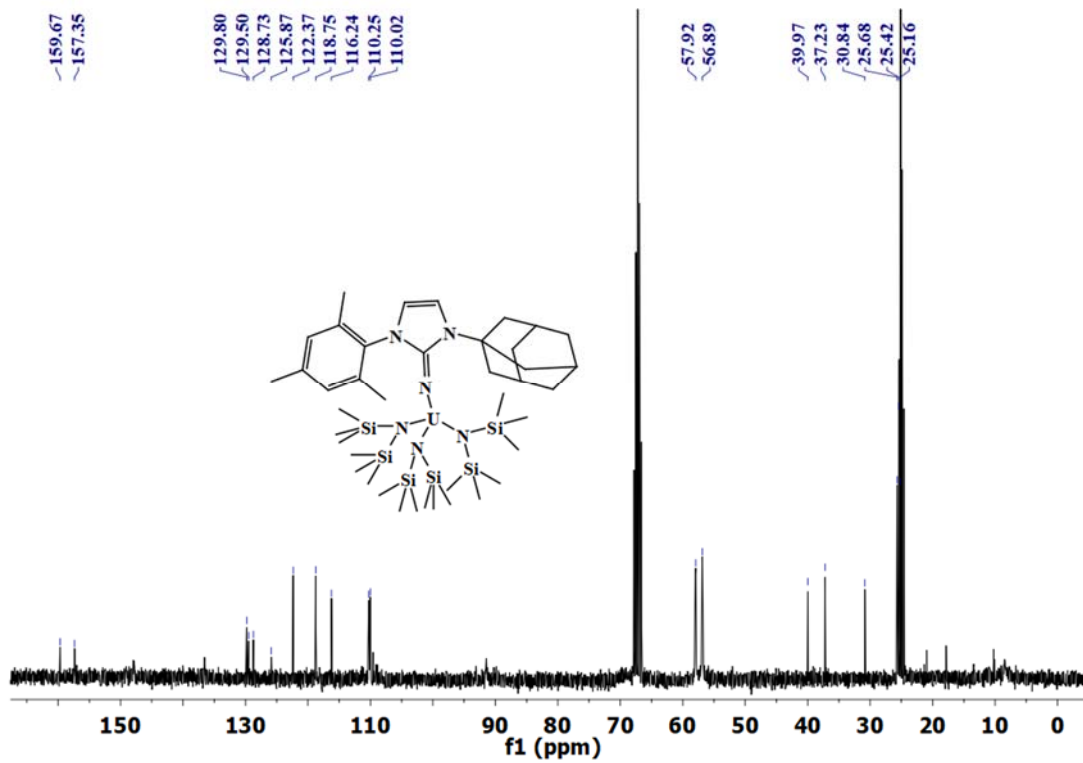
Figure S23: ^{13}C NMR spectrum of **5** in THF-d_8.
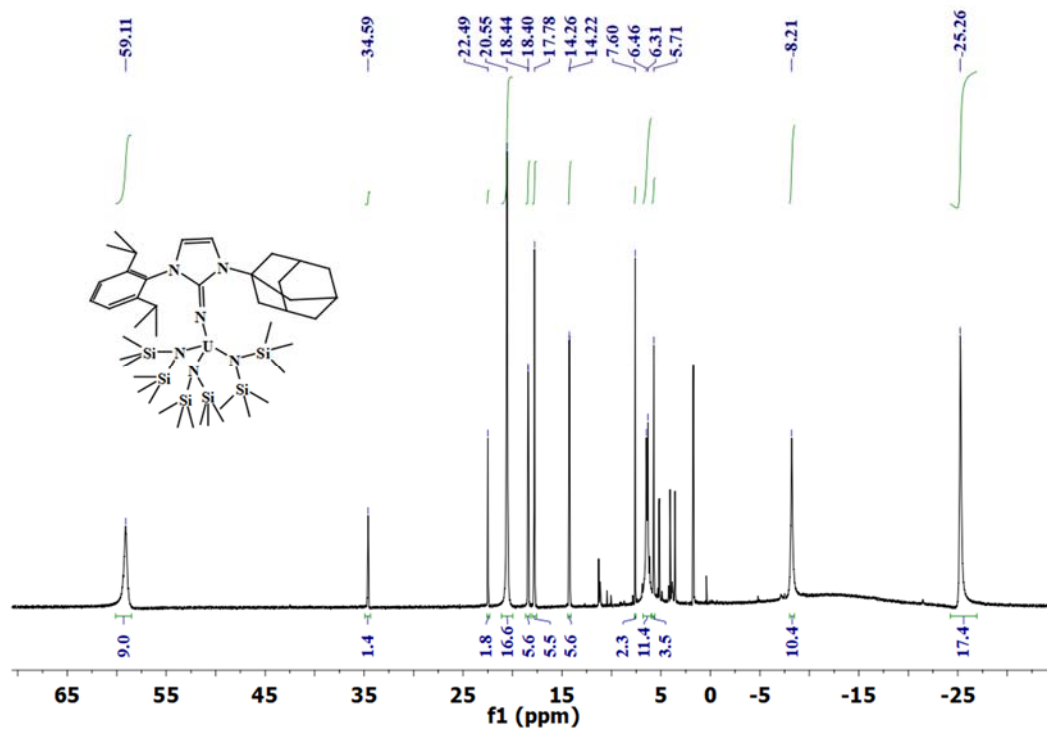
Figure S24: ^{1}H NMR spectrum of **6** in THF-d$_8$.
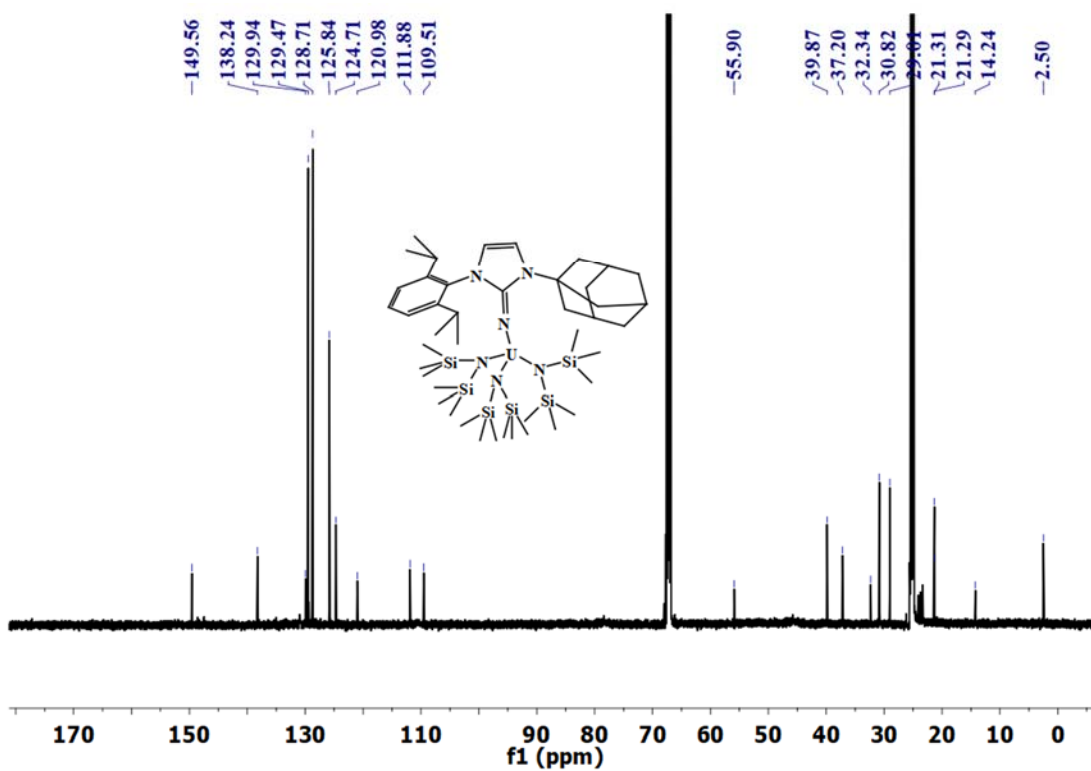
Figure S25: ^{13}C NMR spectrum of **6** in THF-d$_8$.
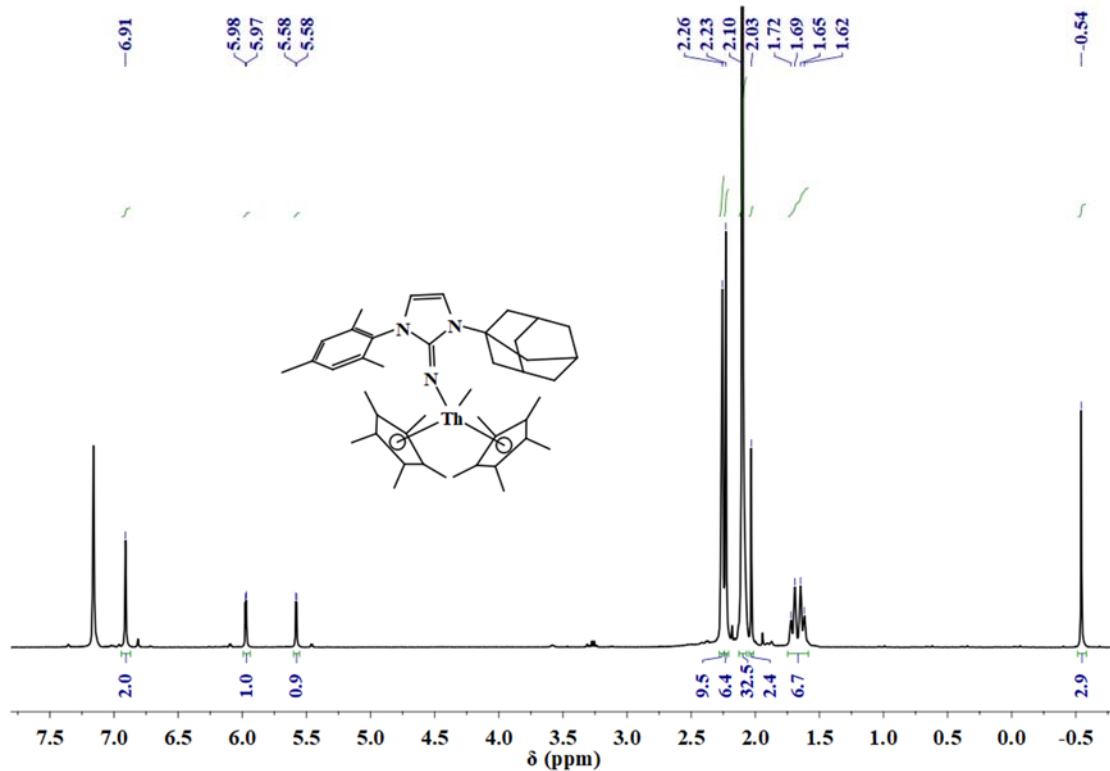
Figure S26: ^{1}H NMR spectrum of **9** in C_6D_6.
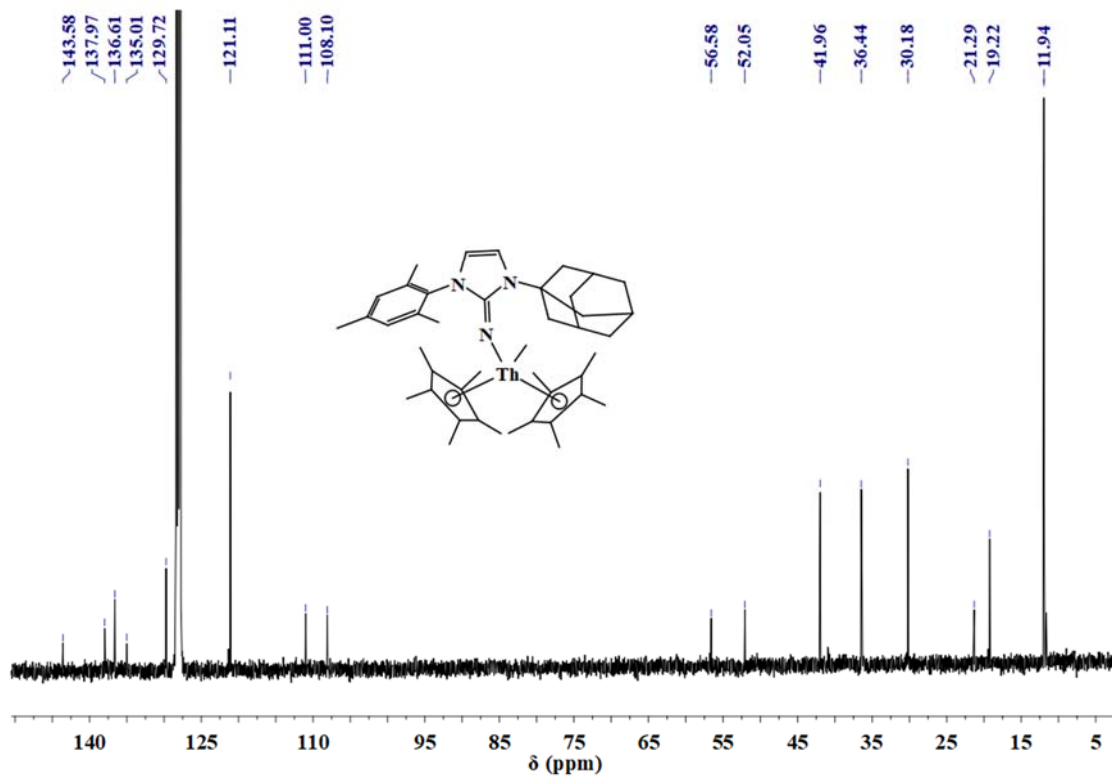
Figure S27: ^{13}C NMR spectrum of **9** in C_6D_6.
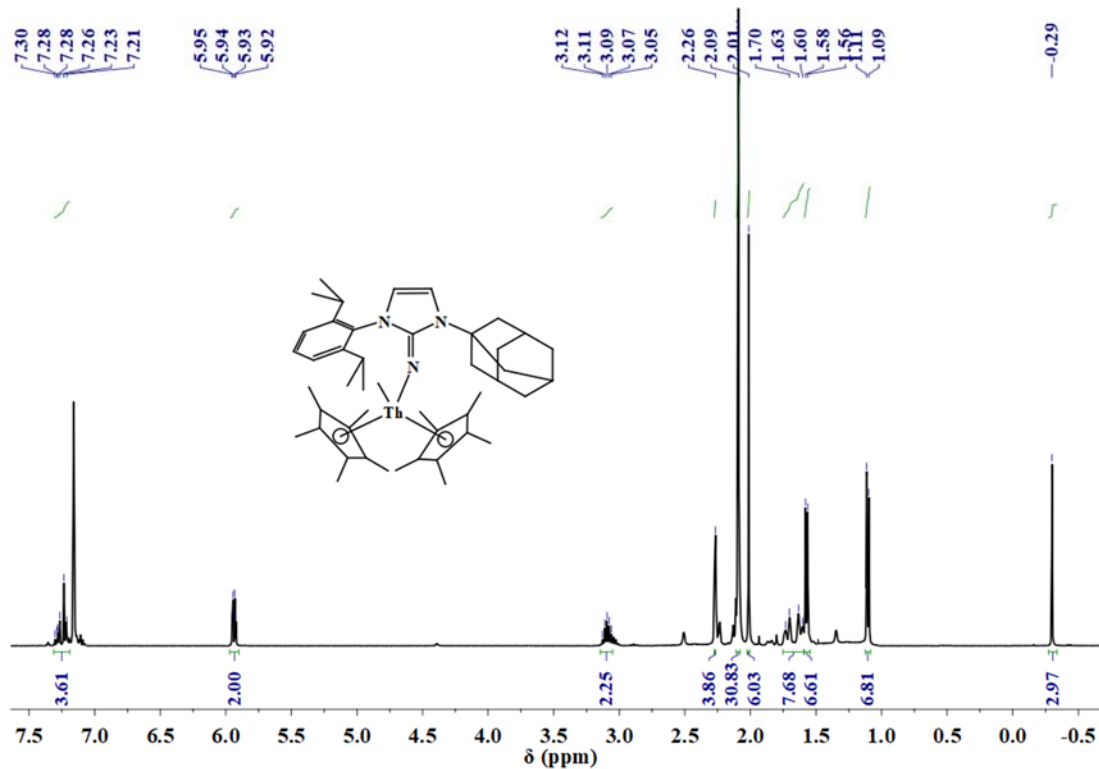
Figure S28: ^{1}H NMR spectrum of **10** in C_6D_6.
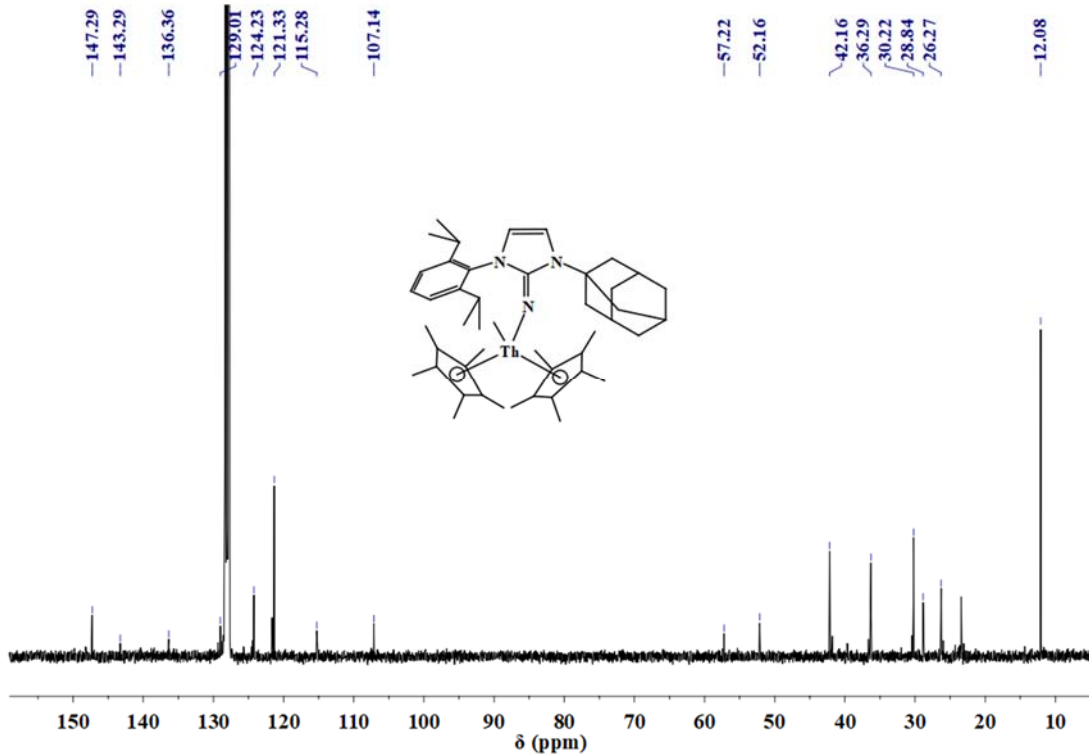
Figure S29: ^{13}C NMR spectrum of **10** in C_6D_6.
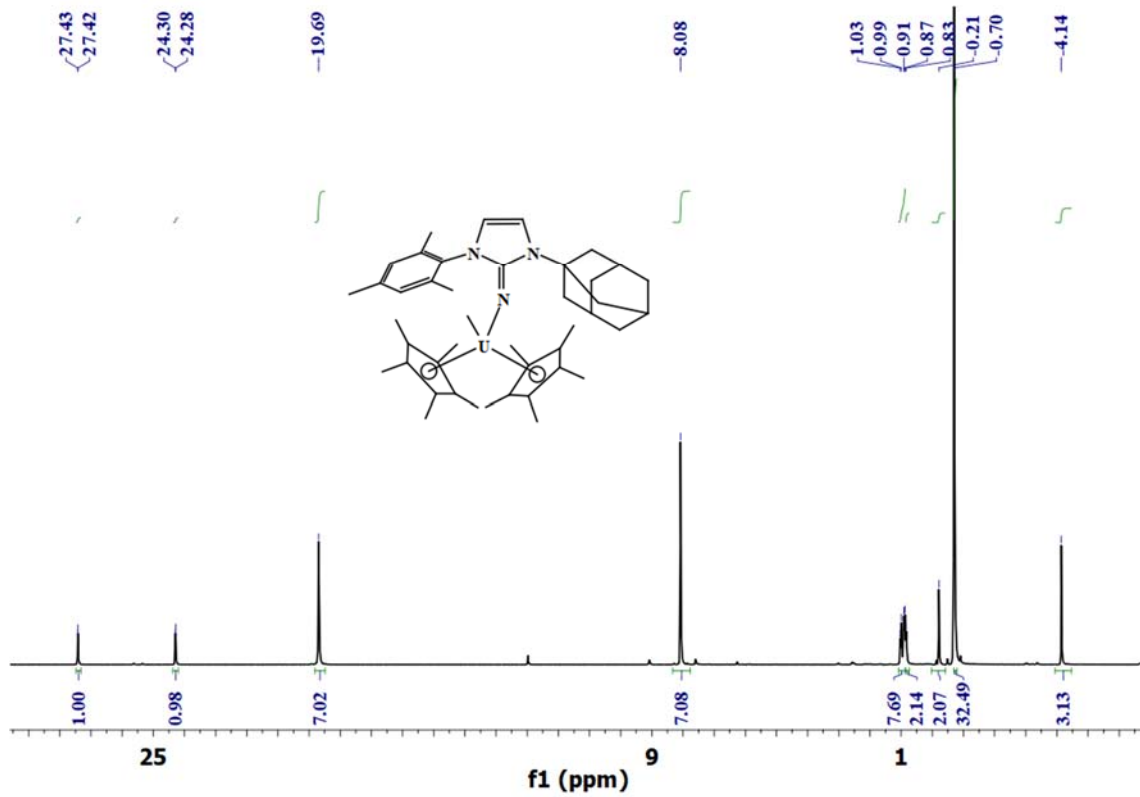
Figure S30: ^1H NMR spectrum of **11** in C_6D_6.
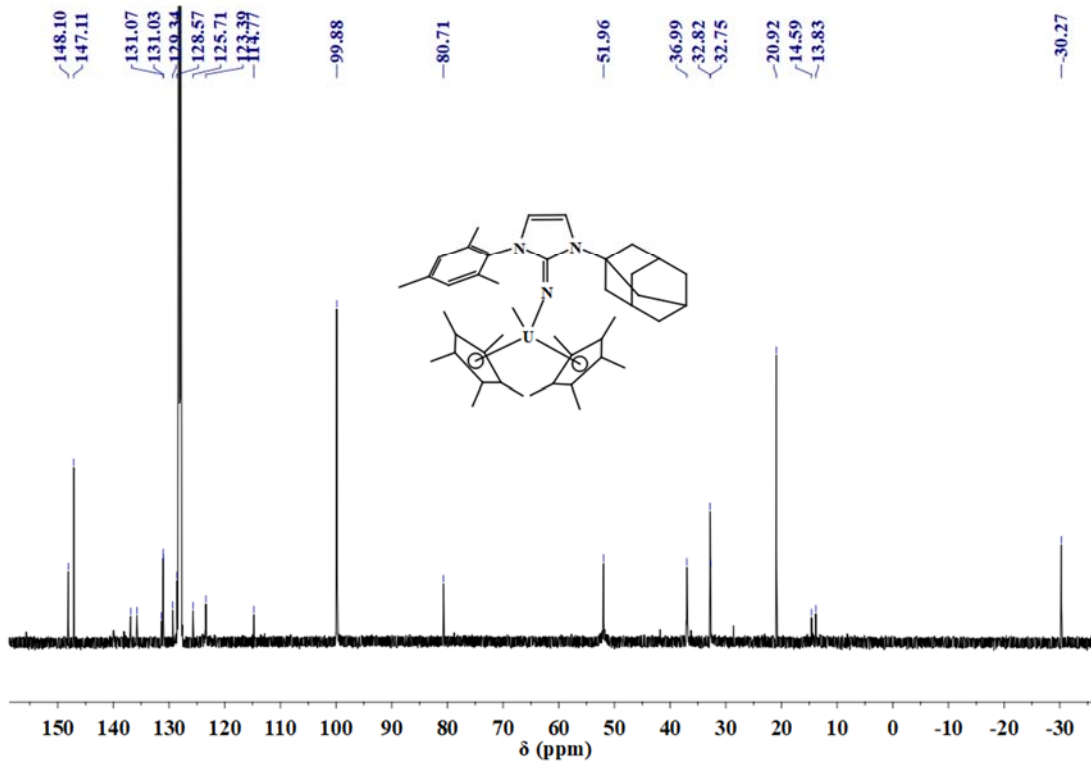
Figure S31: ^{13}C NMR spectrum of **11** in C_6D_6.
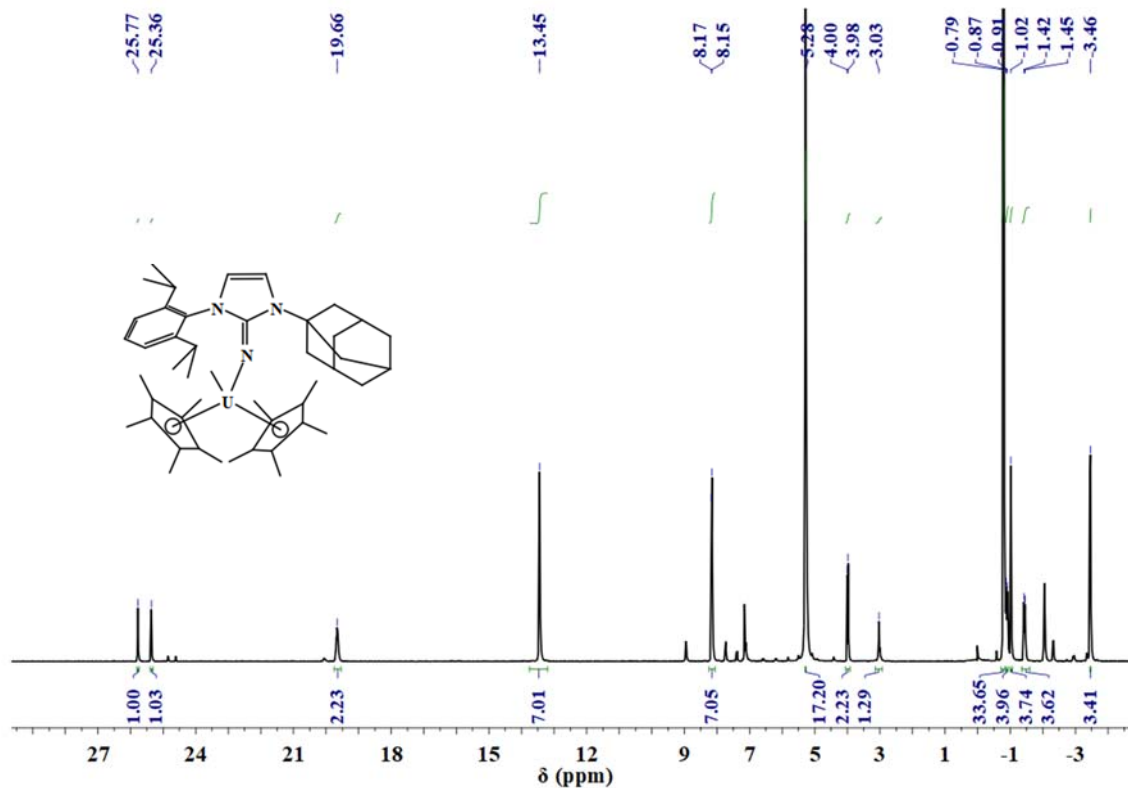
Figure S32: ^{1}H NMR spectrum of **12** in C_6D_6.
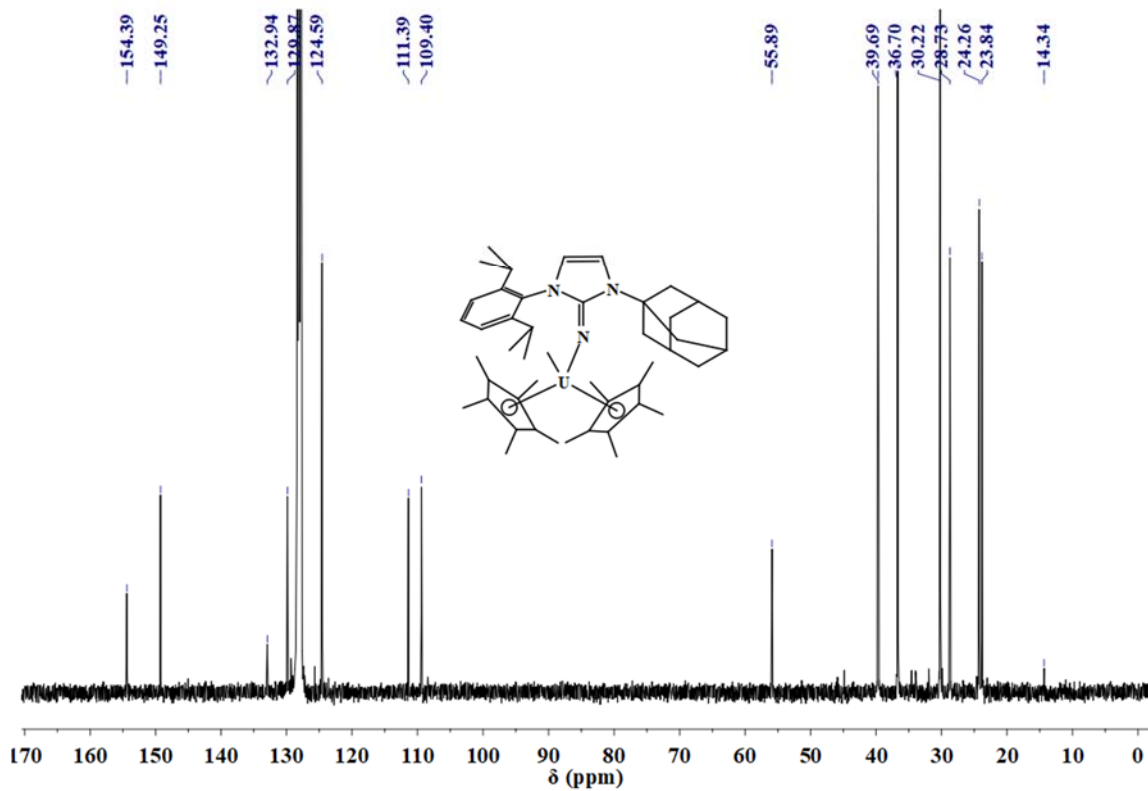
Figure S33: ^{13}C NMR spectrum of **12** in C_6D_6.
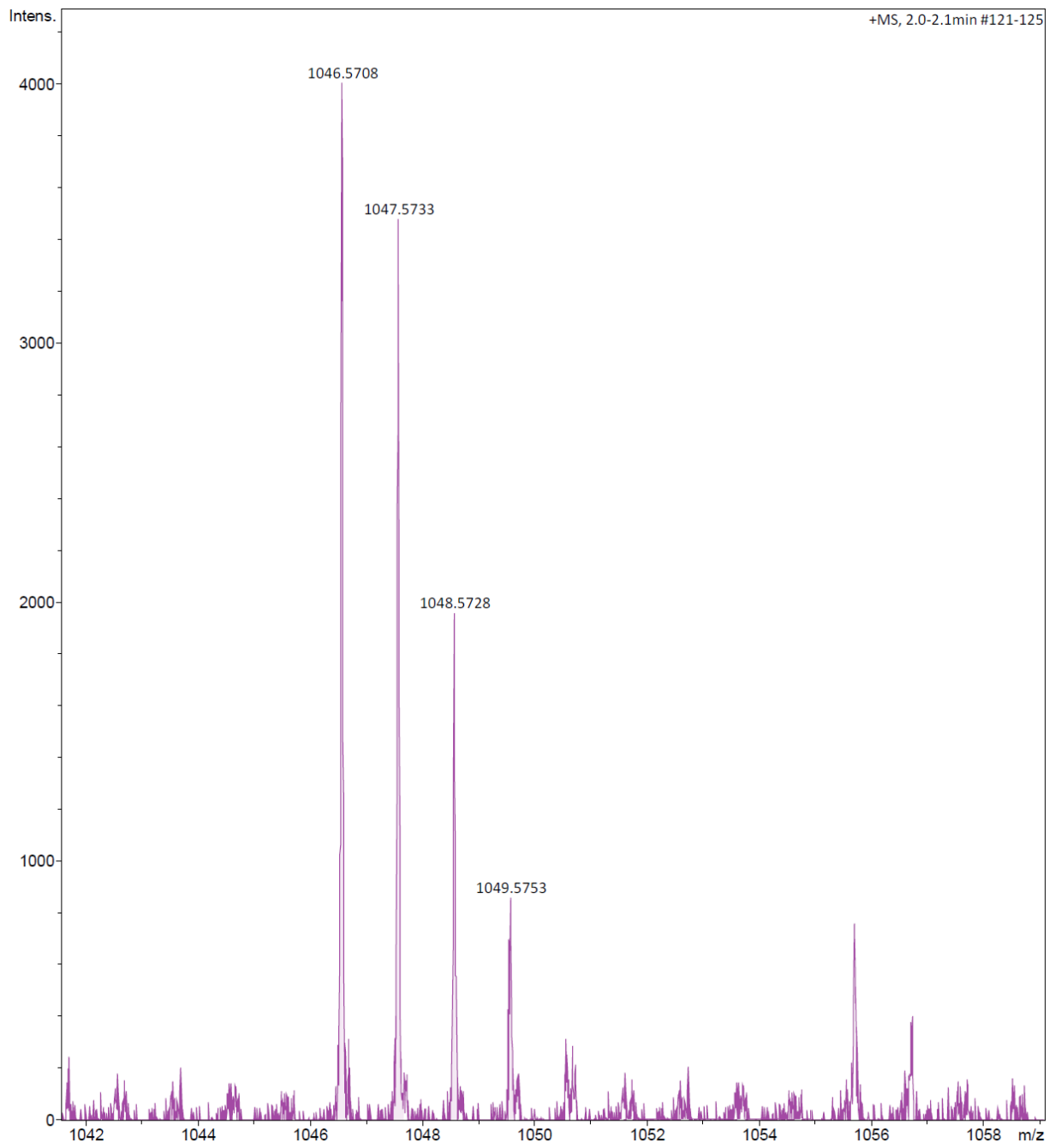
Figure S34: APCI mass spectrum of **3.**
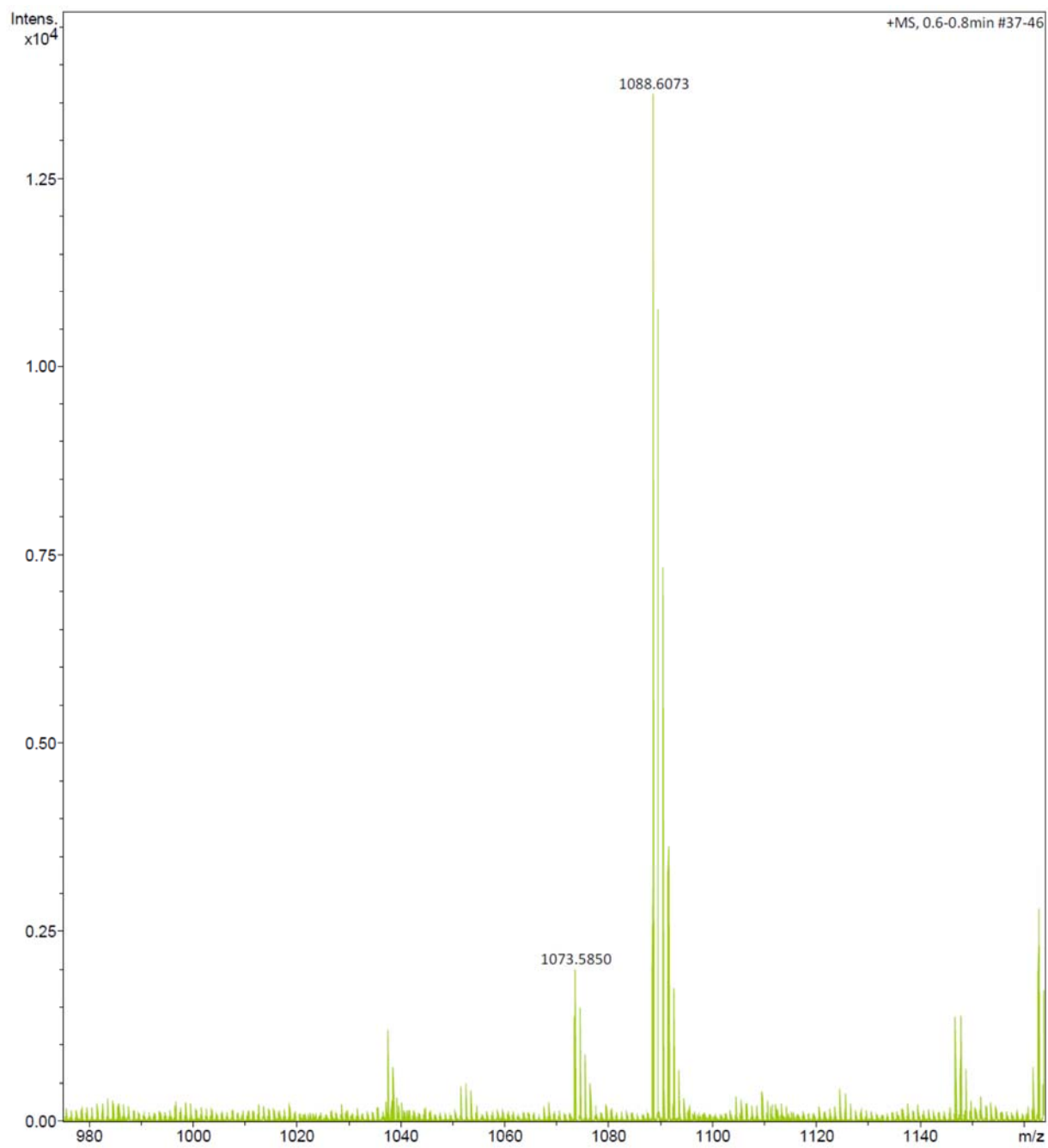
Figure S35: APCI mass spectrum of **4.**
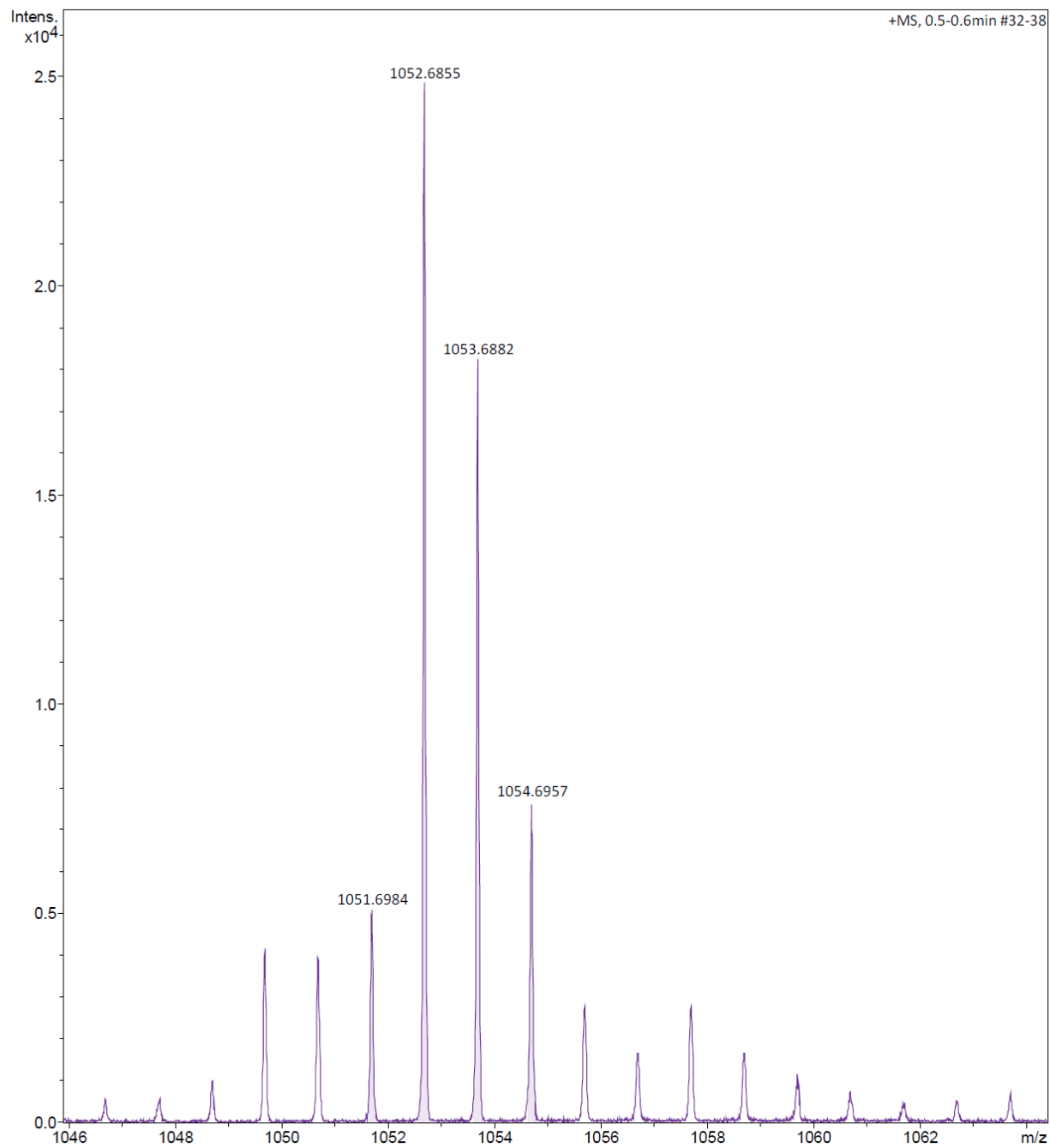
Figure S36: APCI mass spectrum of **5.**
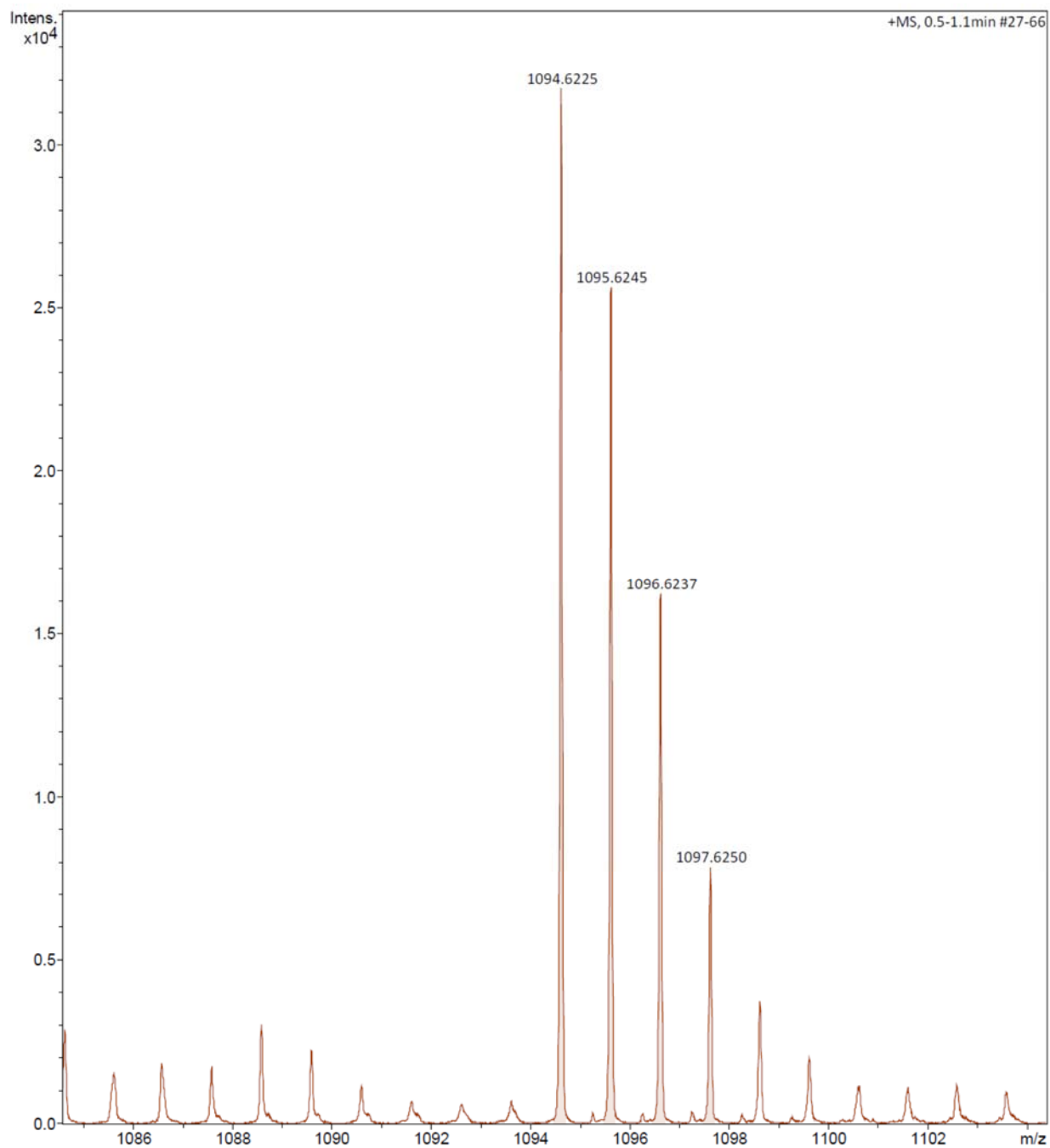
Figure S37: APCI mass spectrum of **6**.
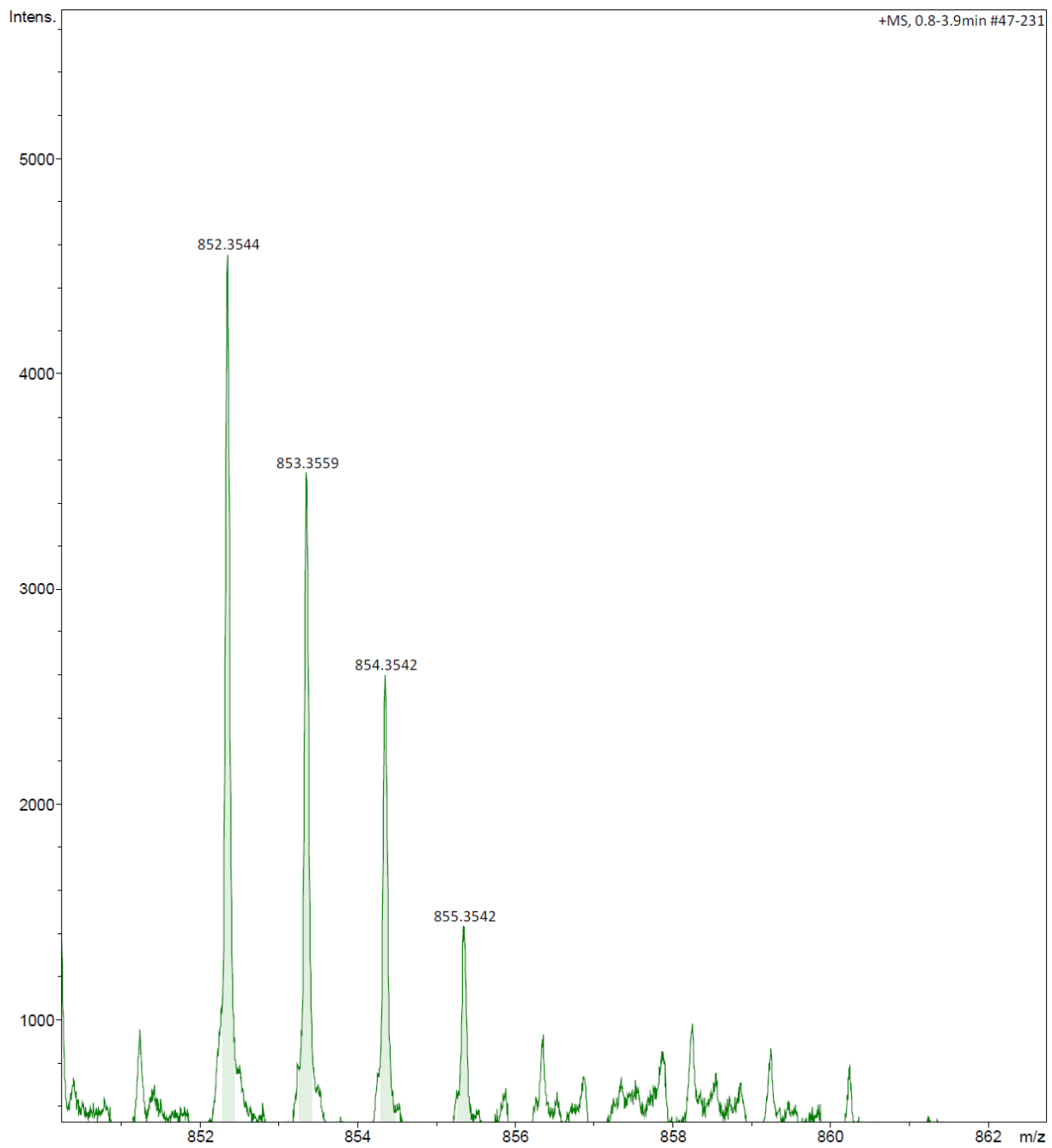
Figure S38: APCI mass spectrum of **9**.
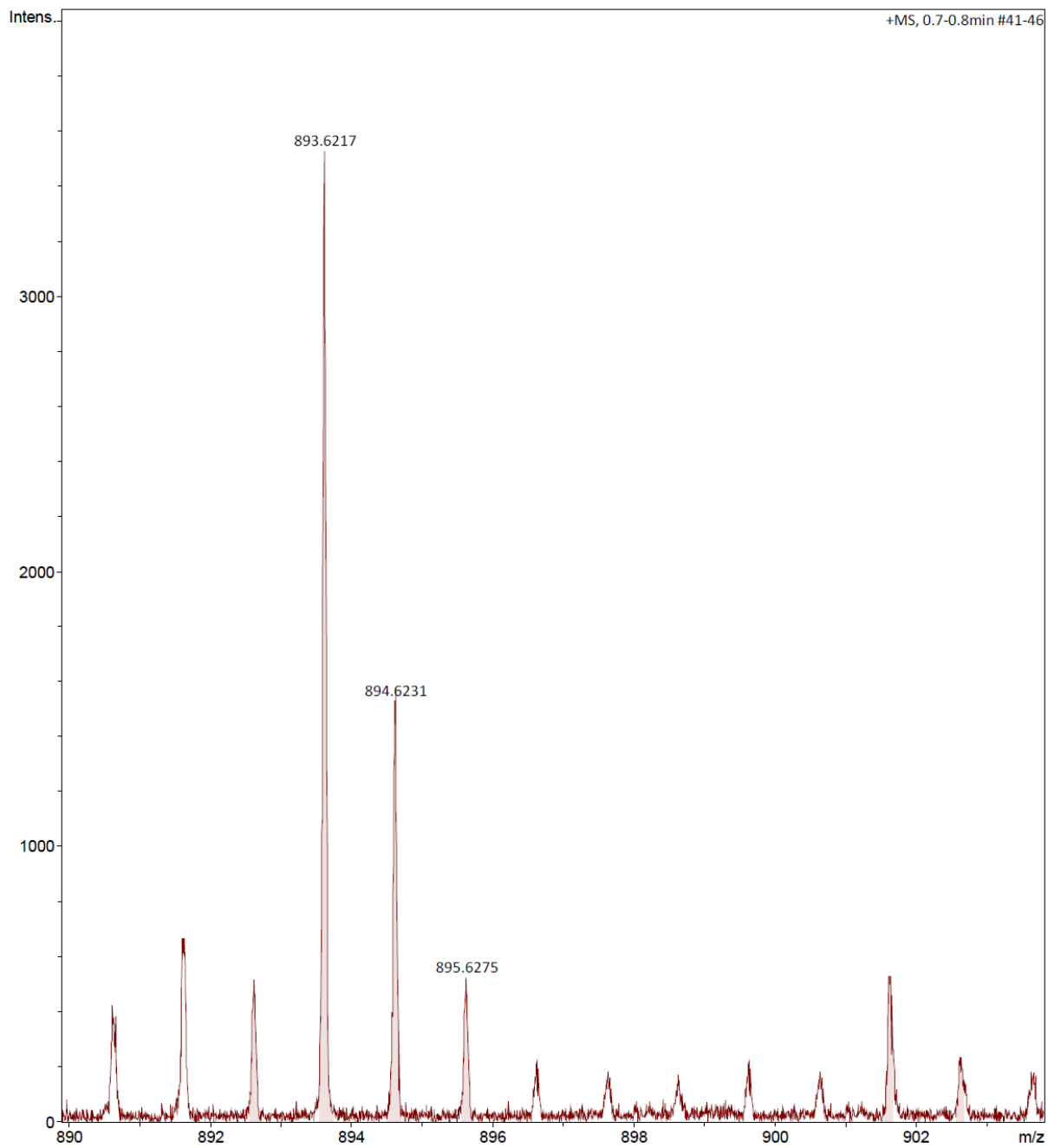
Figure S39: APCI mass spectrum of **10**.
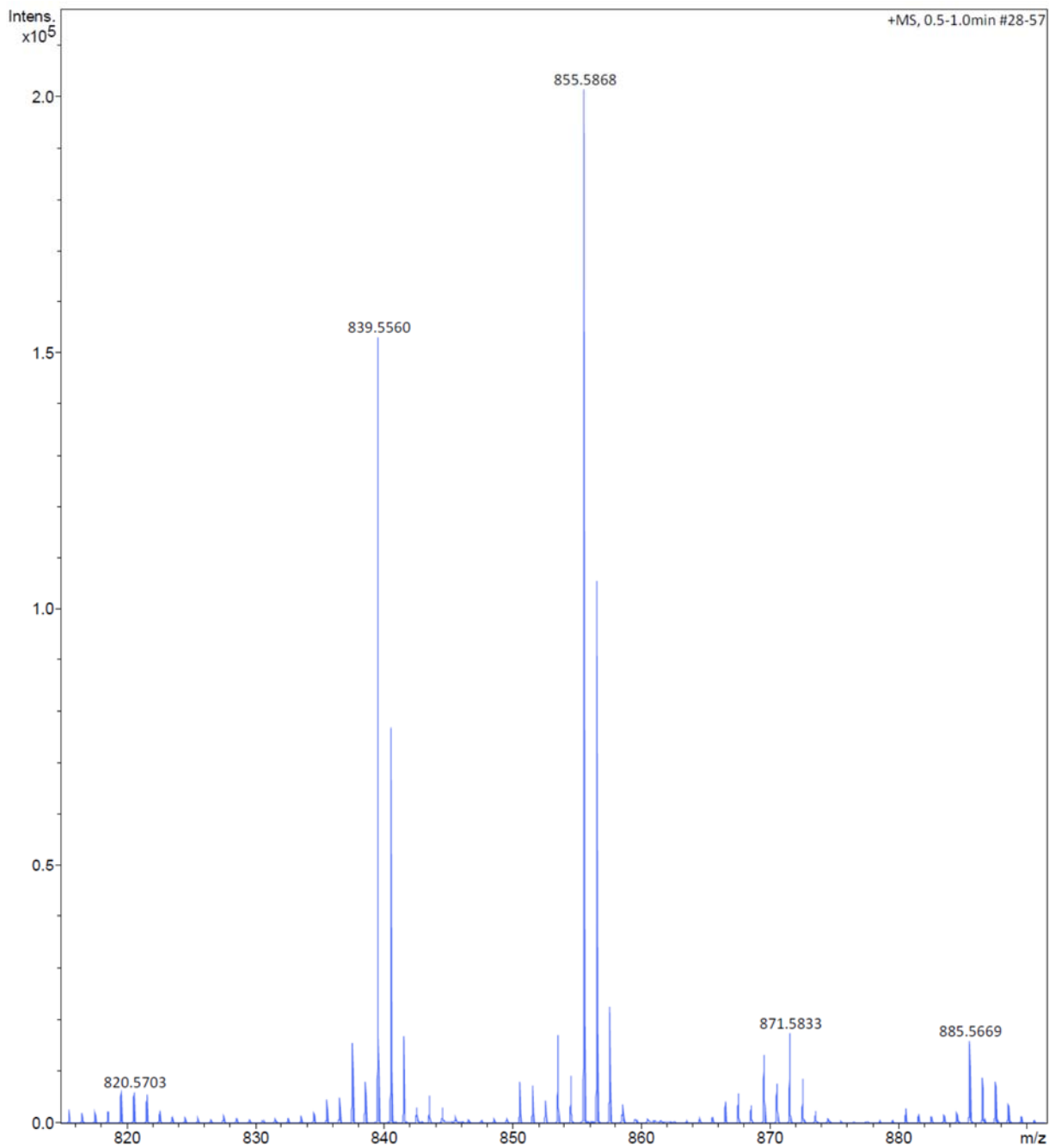
Figure S40: APCI mass spectrum of **11**.
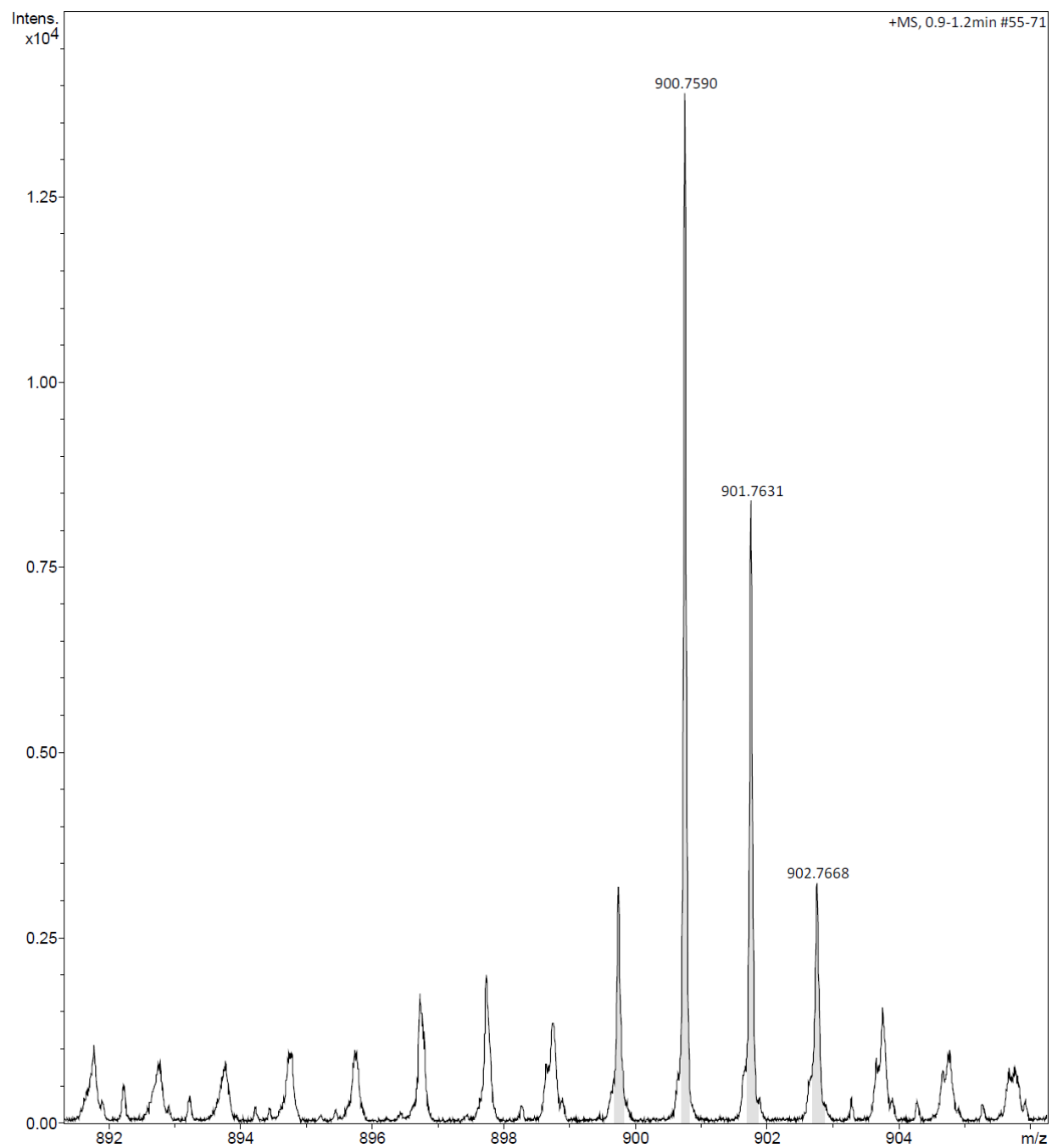
Figure S41: APCI mass spectrum of **12**.

6. ^{1}H and ^{13}C NMR of catalytic transfer hydrogenation products.
* Indicates Isopropanol, # Indicates Acetone
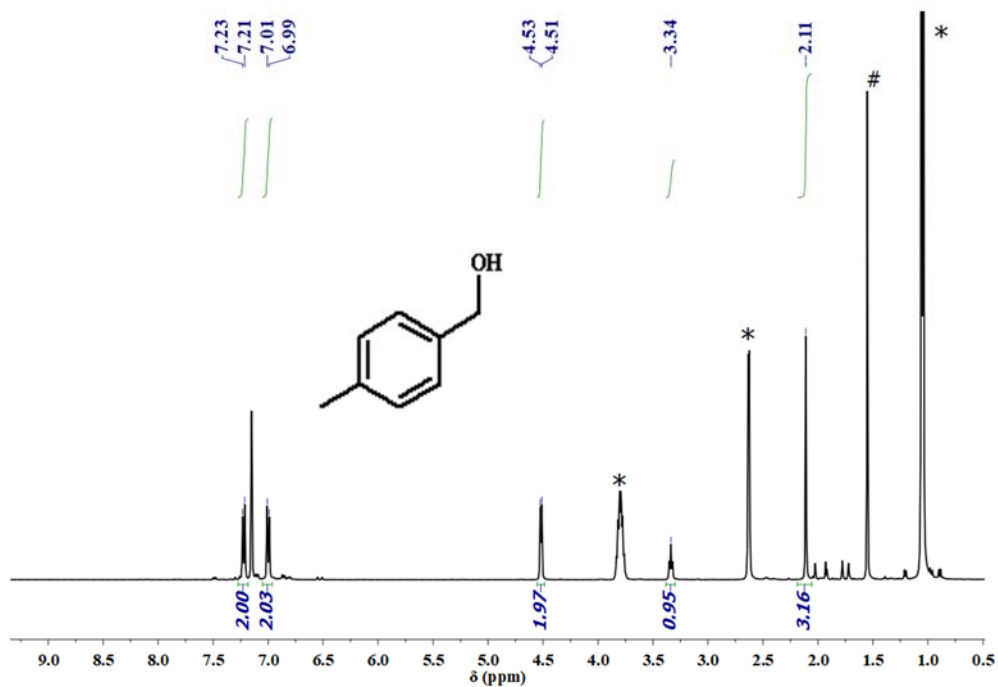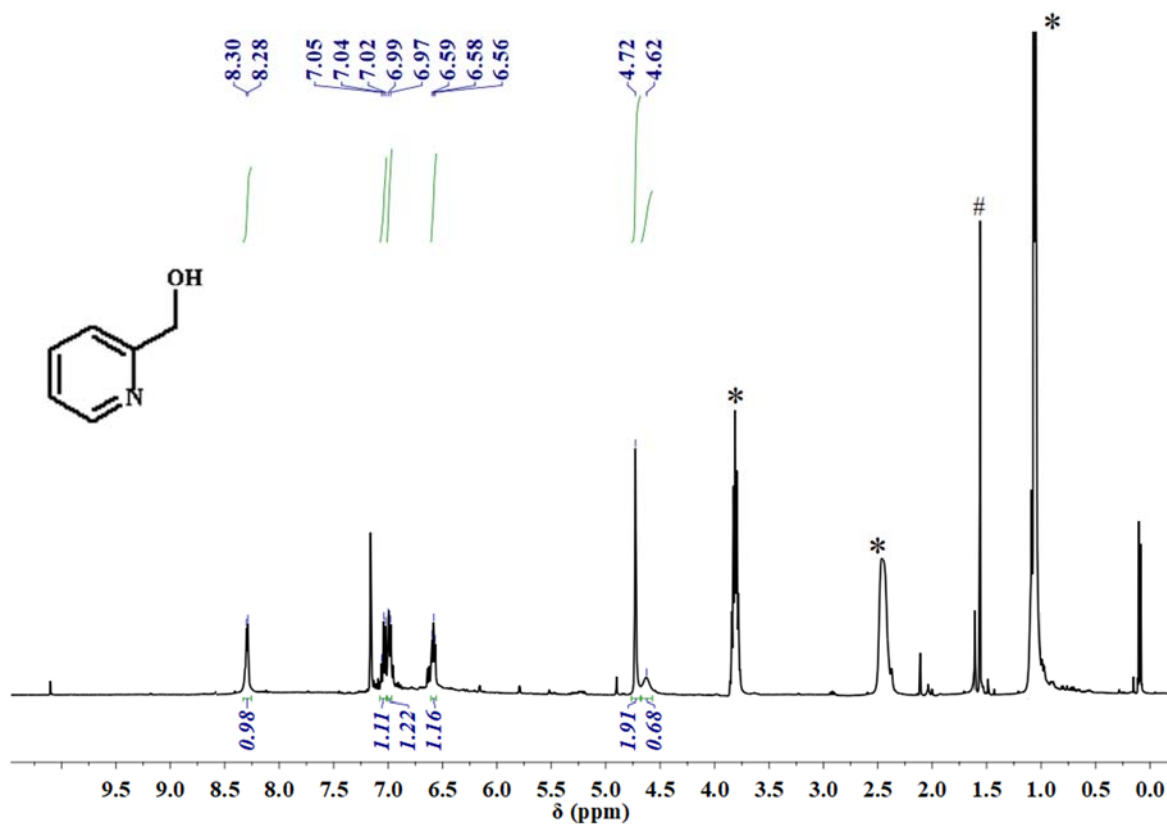

Figure S42: ^{1}H NMR spectrum of **2a** in C$_6$D$_6$ in the reaction mixture.
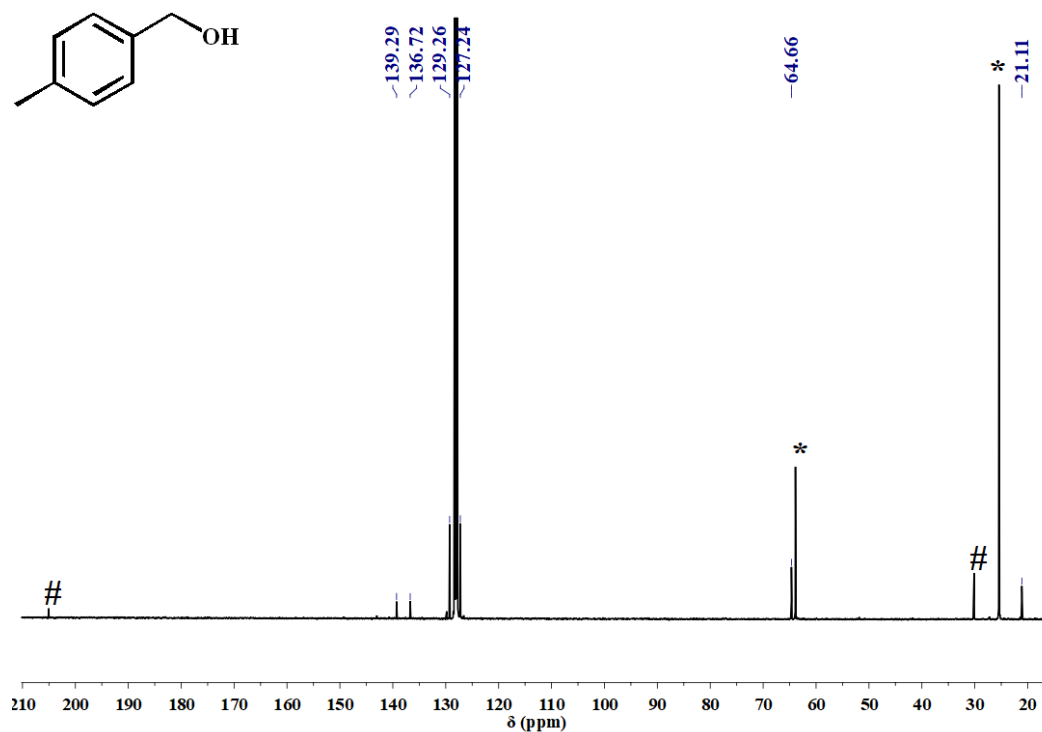
Figure S43: ^{13}C NMR spectrum of **2a** in C$_6$D$_6$ in the reaction mixture.
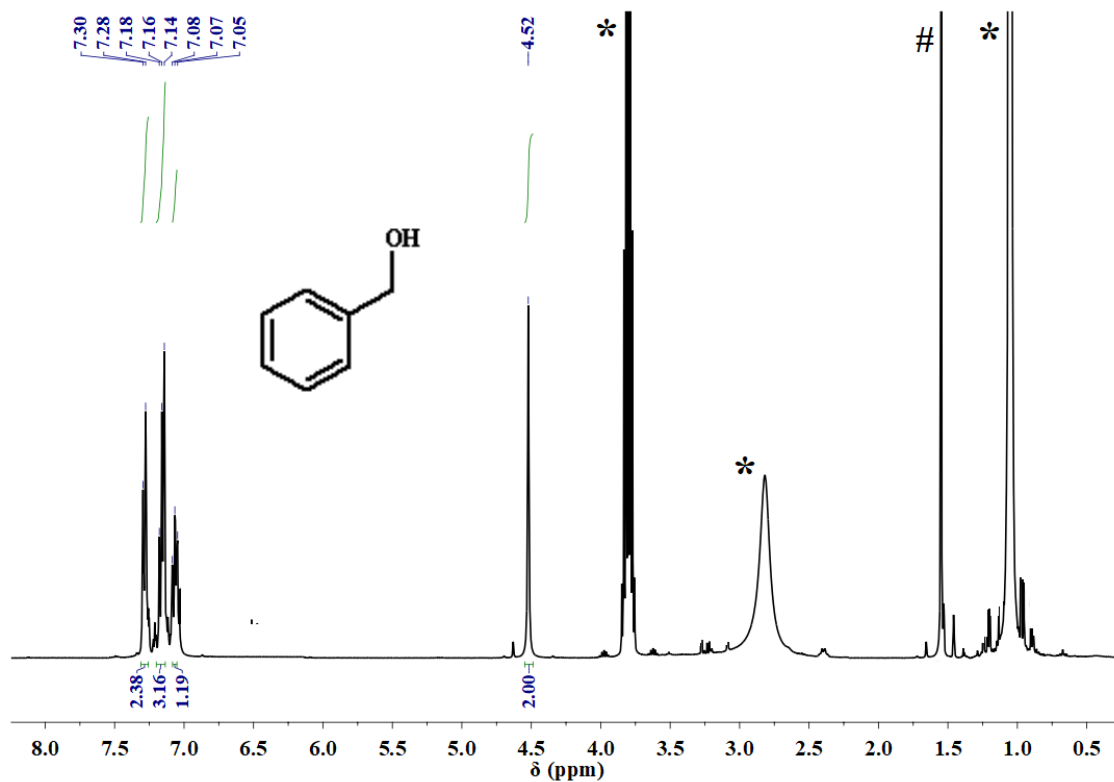
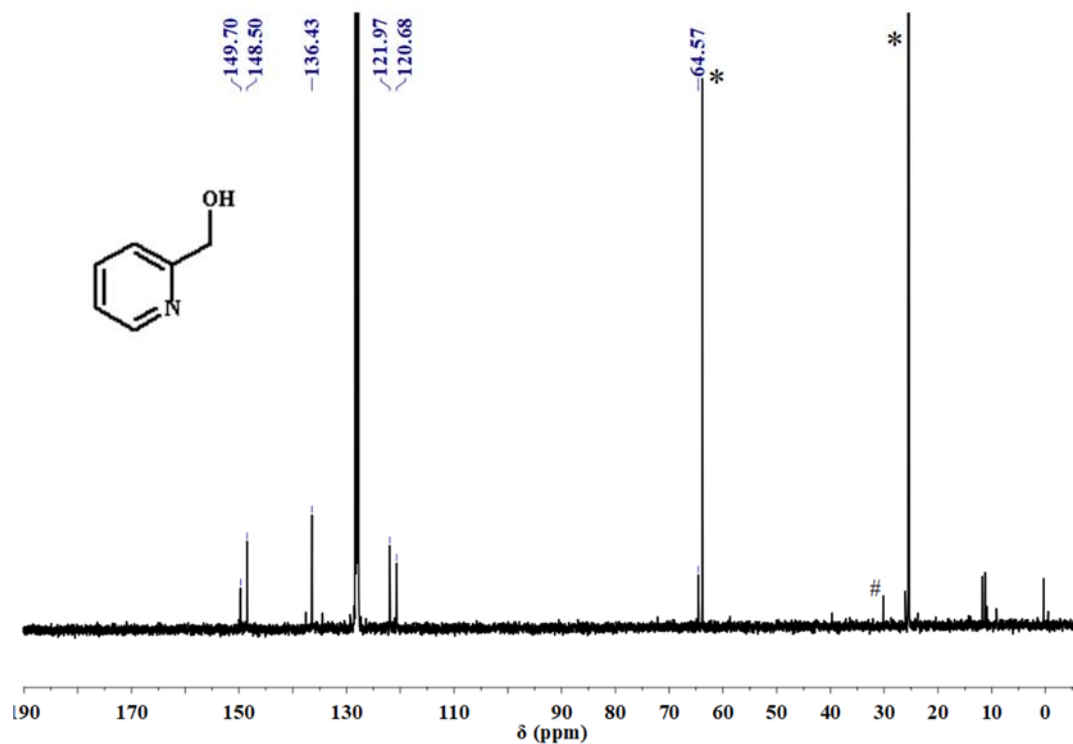**Figure S44**: ^1H NMR spectrum of **2b** in C_6D_6 in the reaction mixture.
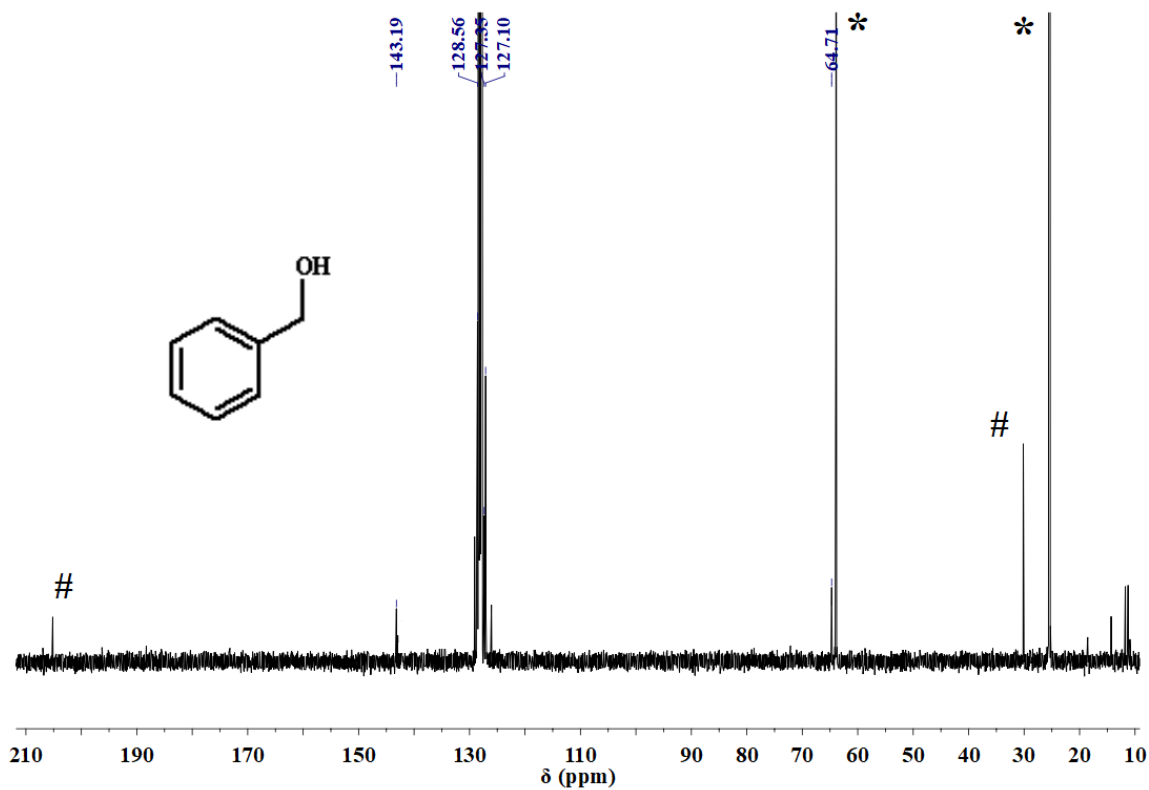
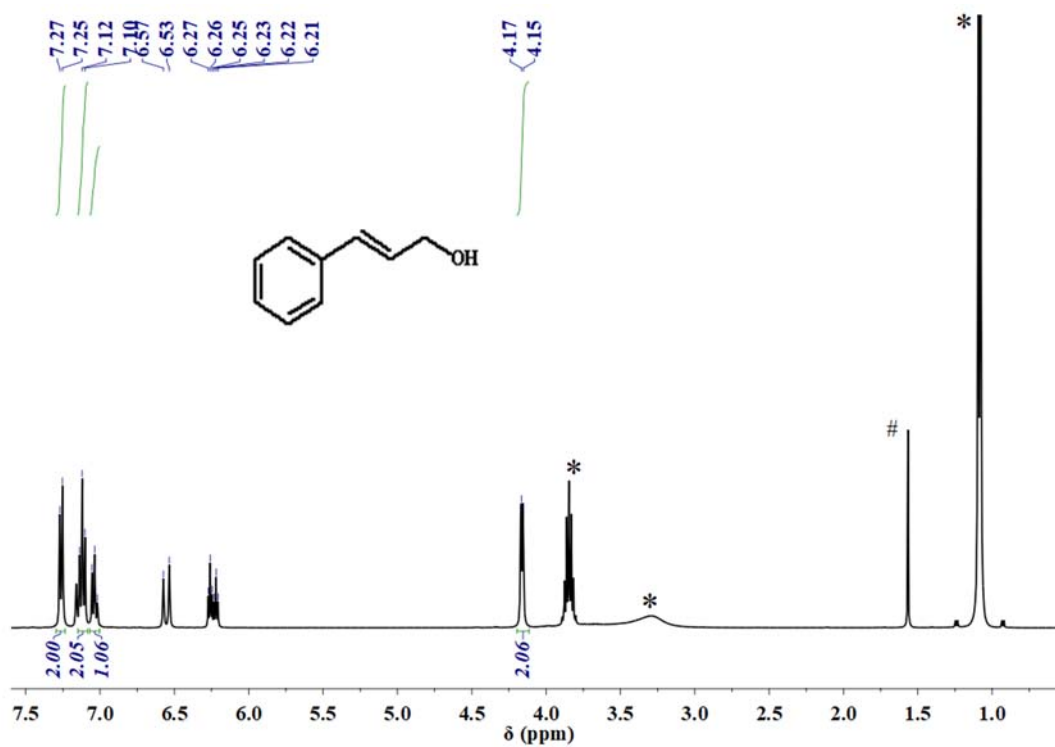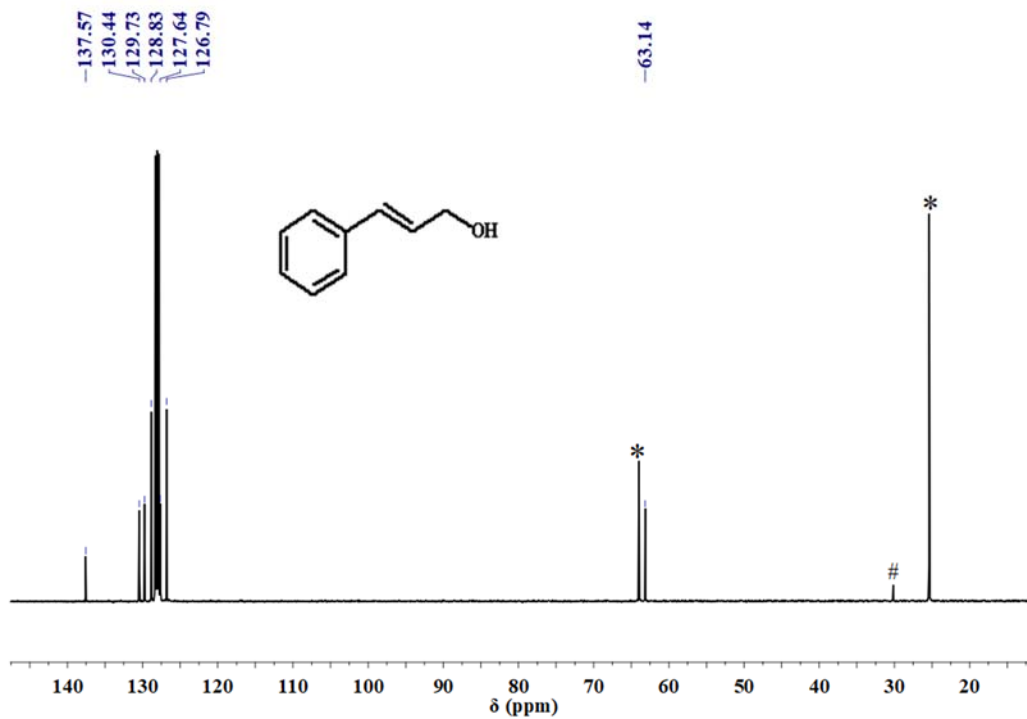**Figure S45**: ^{13}C NMR spectrum of **2b** in C_6D_6 in the reaction mixture.
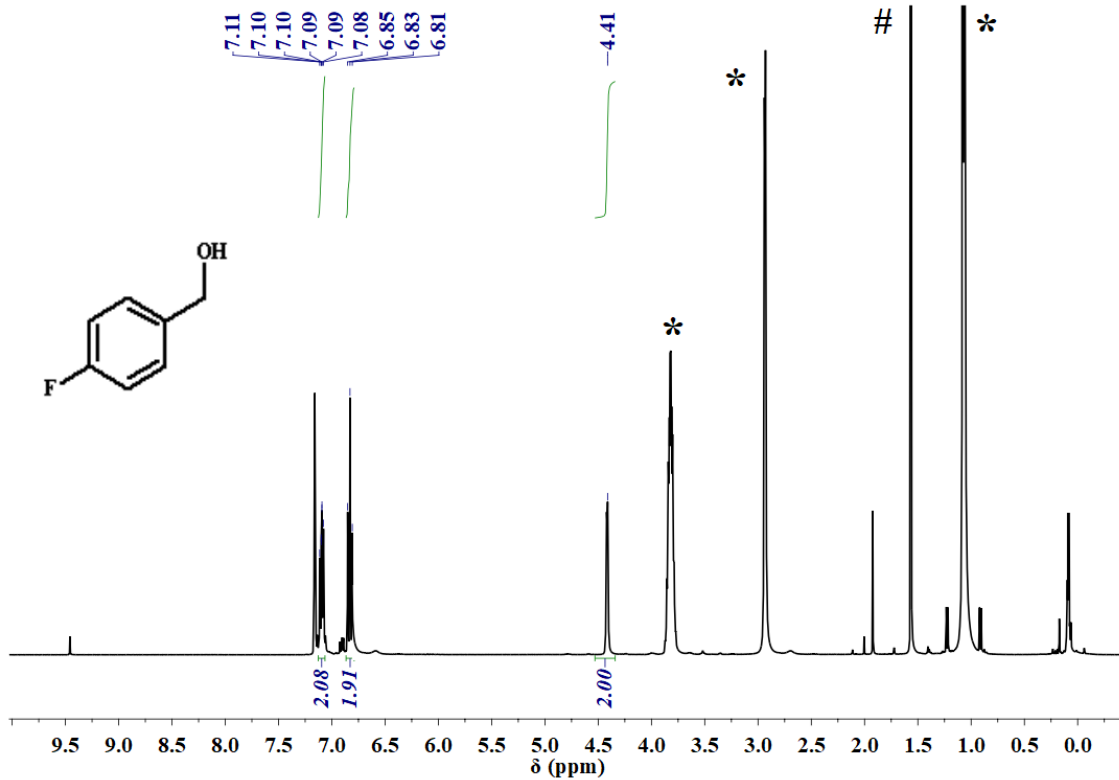
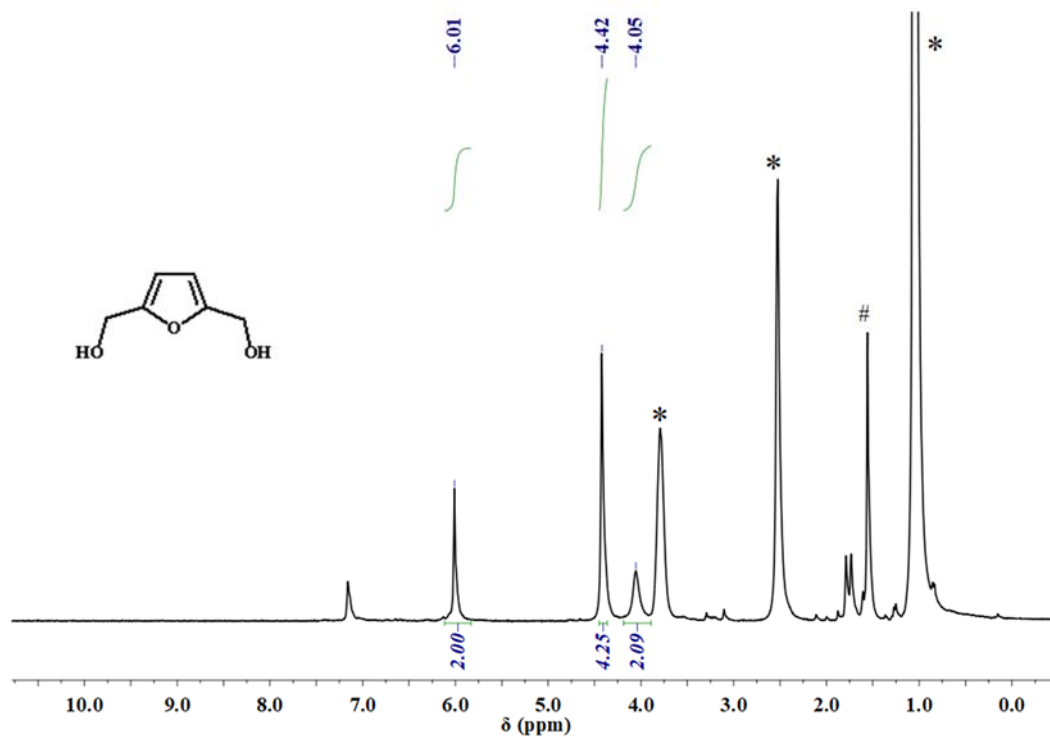**Figure S46**: ^{1}H NMR spectrum of **2c** in C_6D_6 in the reaction mixture.
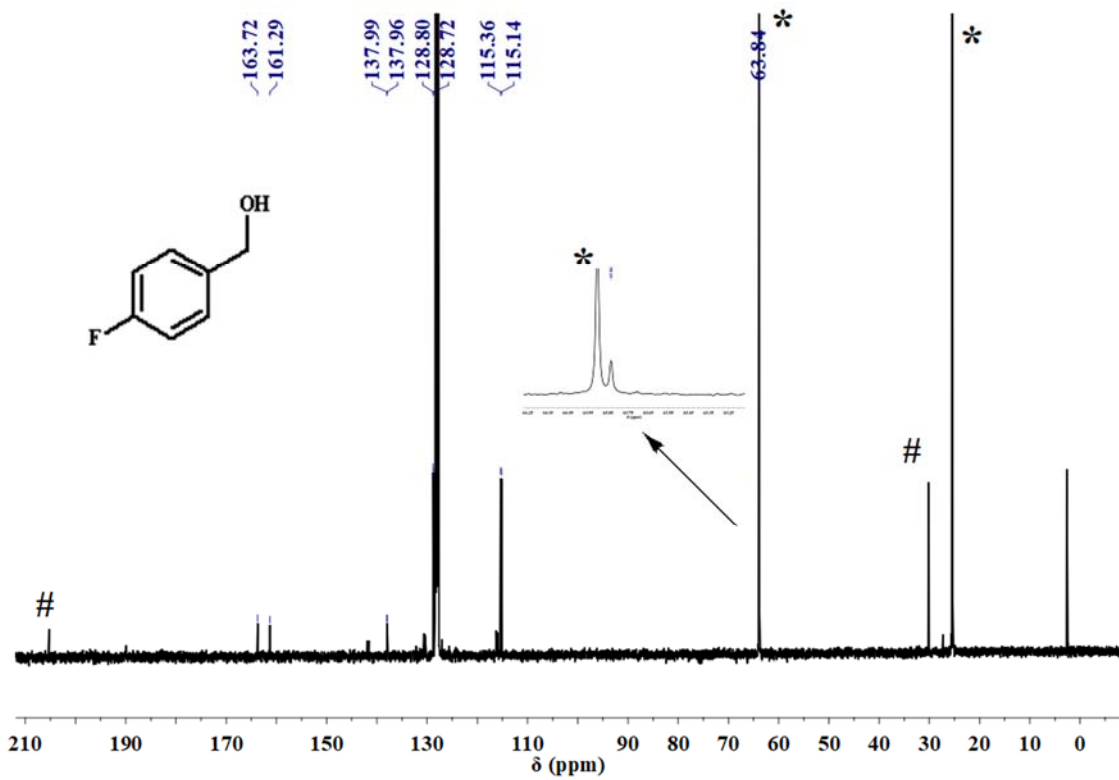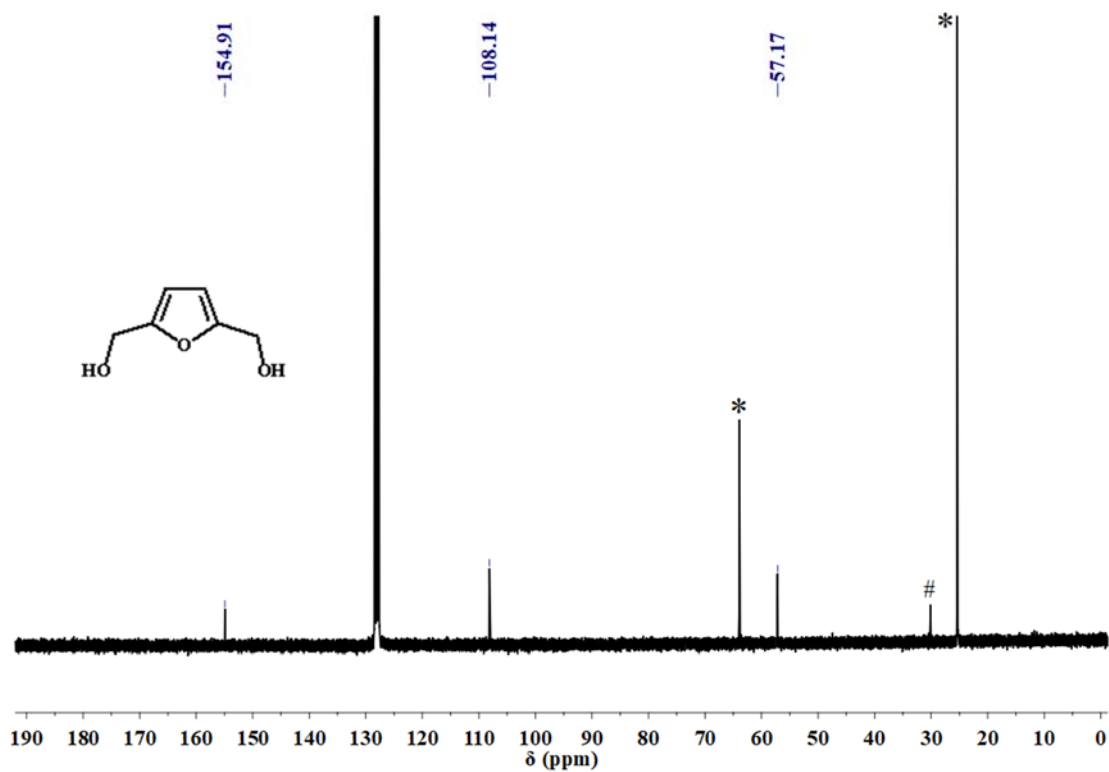

Figure S47: ^{13}C NMR spectrum of **2c** in C_6D_6 in the reaction mixture.
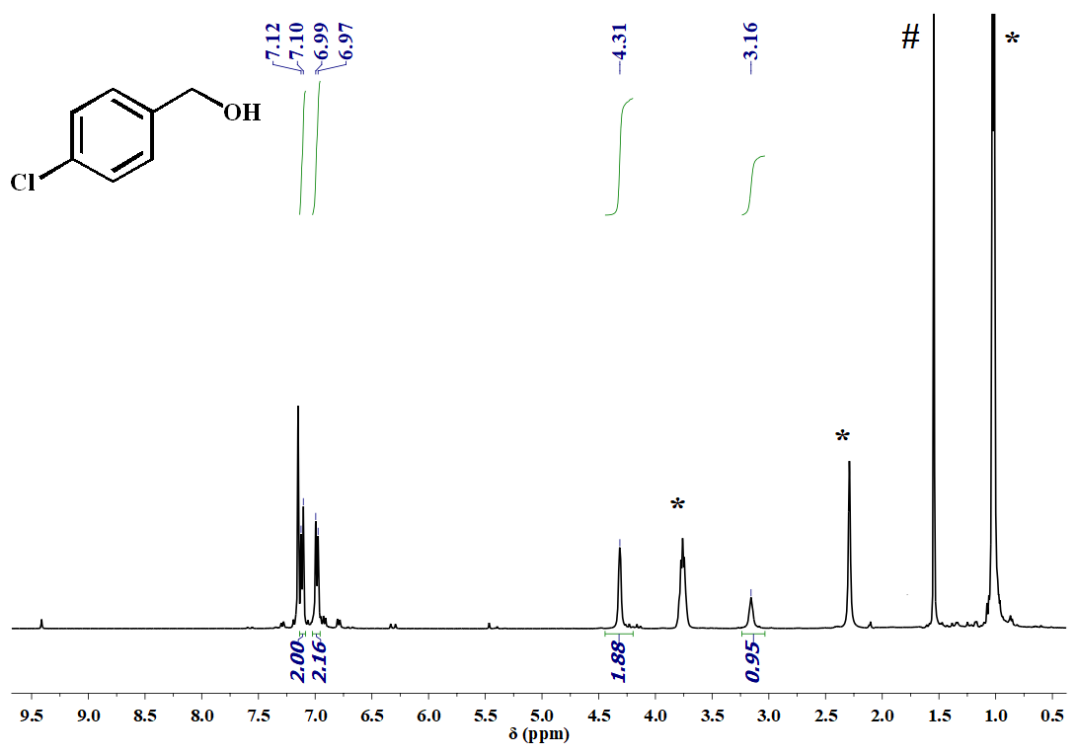
Figure S48: ^{1}H NMR spectrum of **2d** in C$_6$D$_6$ in the reaction mixture.
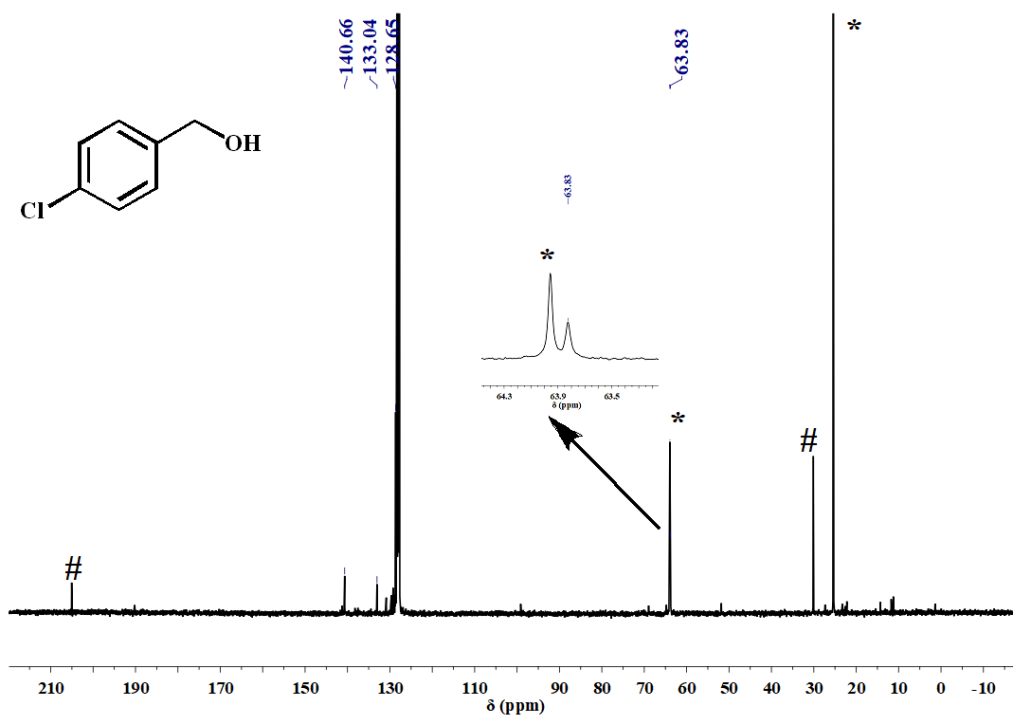
Figure S49: ^{13}C NMR spectrum of **2d** in C$_6$D$_6$ in the reaction mixture.
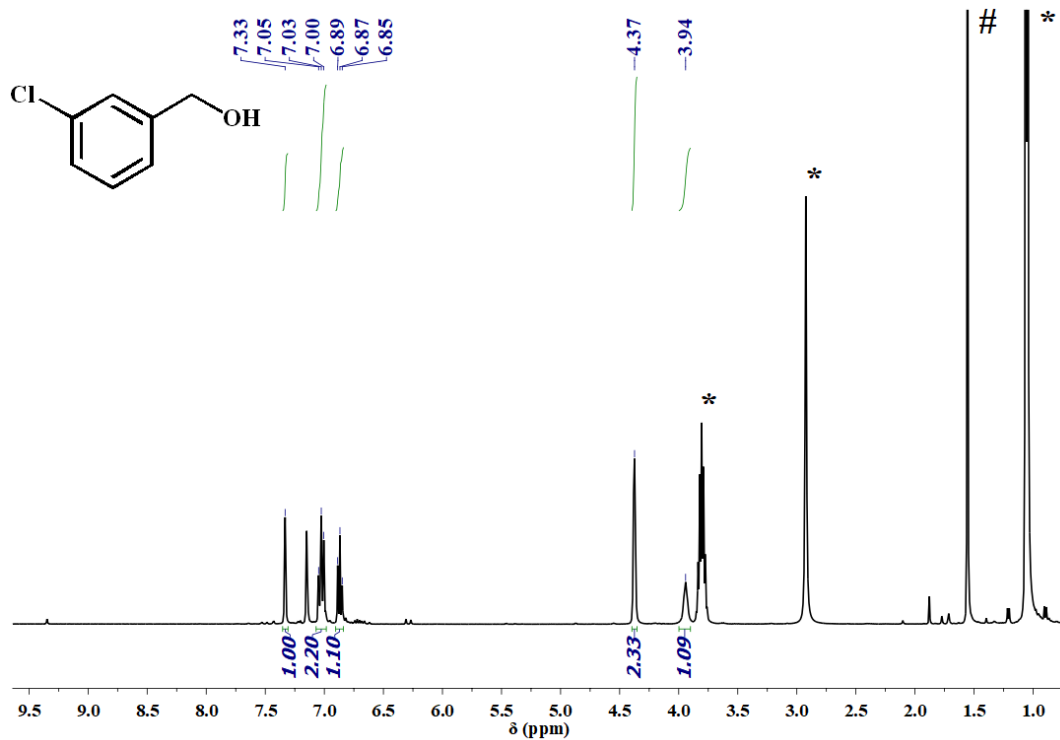
Figure S50: ^{1}H NMR spectrum of **2e** in C_6D_6 in the reaction mixture.
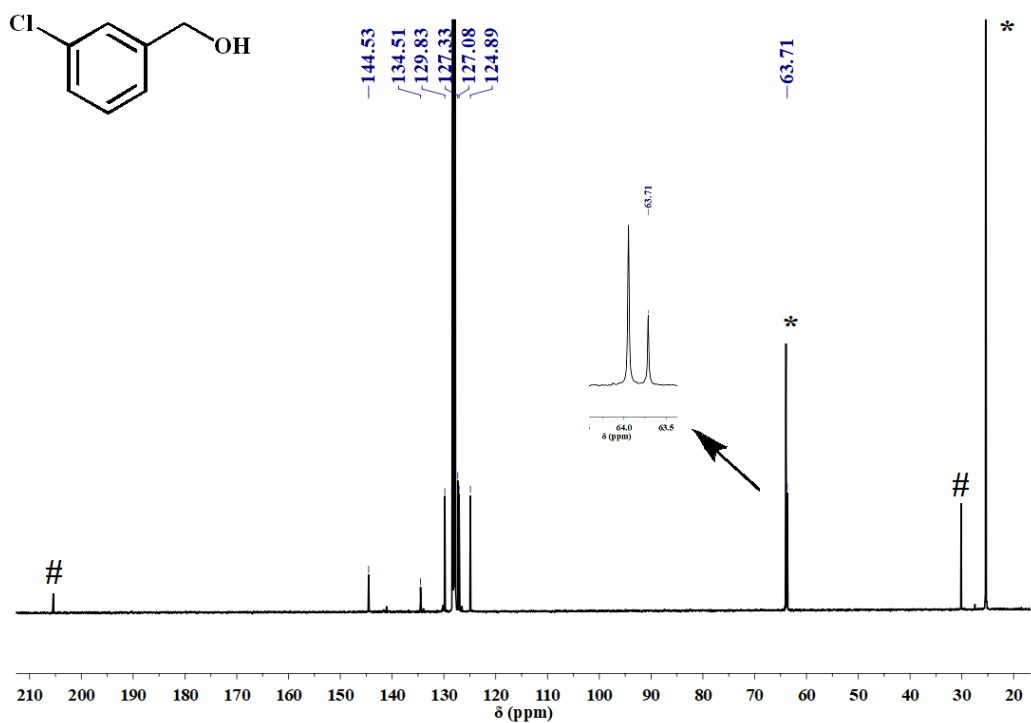
Figure S51: ^{13}C NMR spectrum of **2e** in C_6D_6 in the reaction mixture.
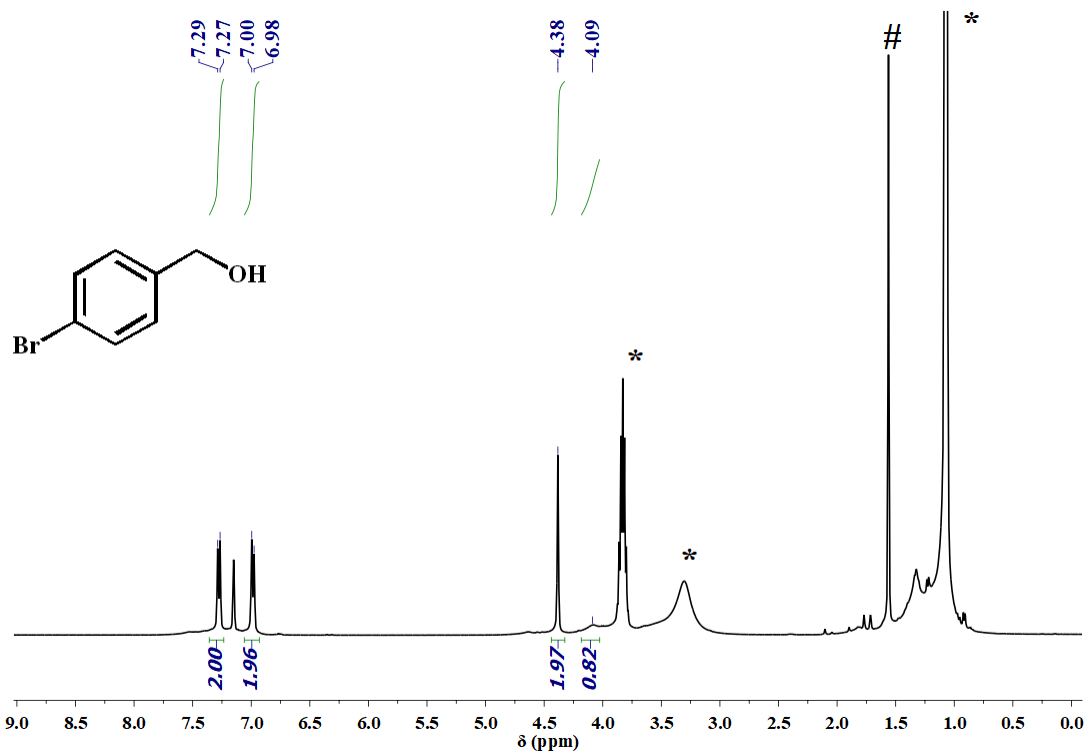
Figure S52: ^{1}H NMR spectrum of **2f** in C_6D_6 in the reaction mixture.
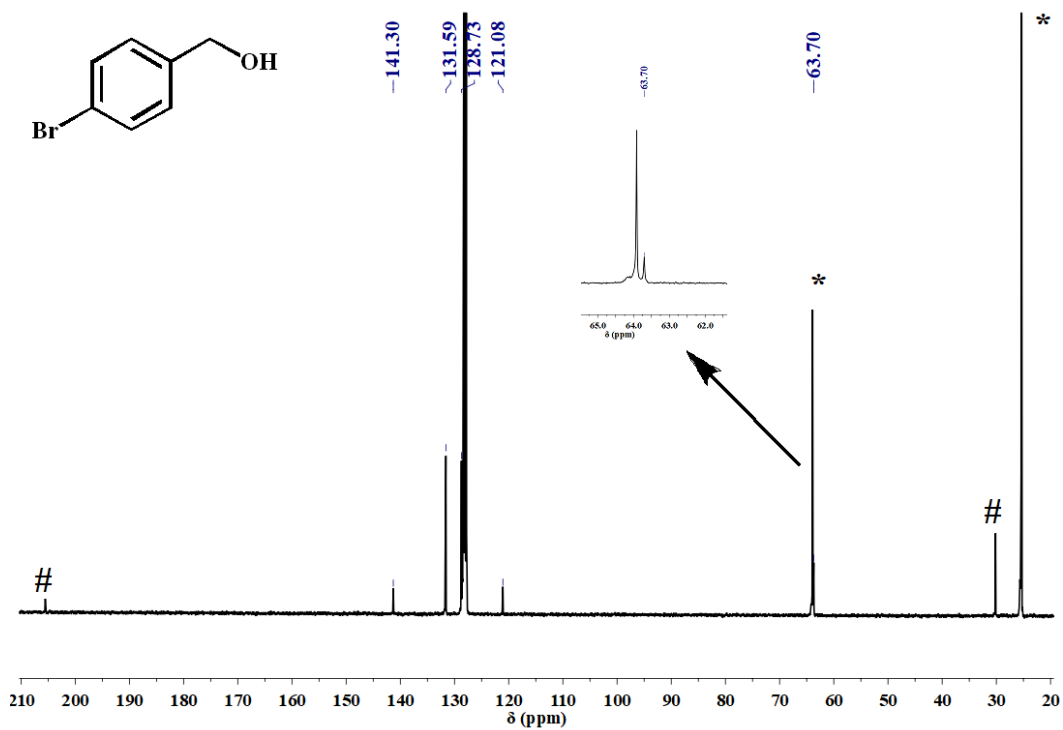
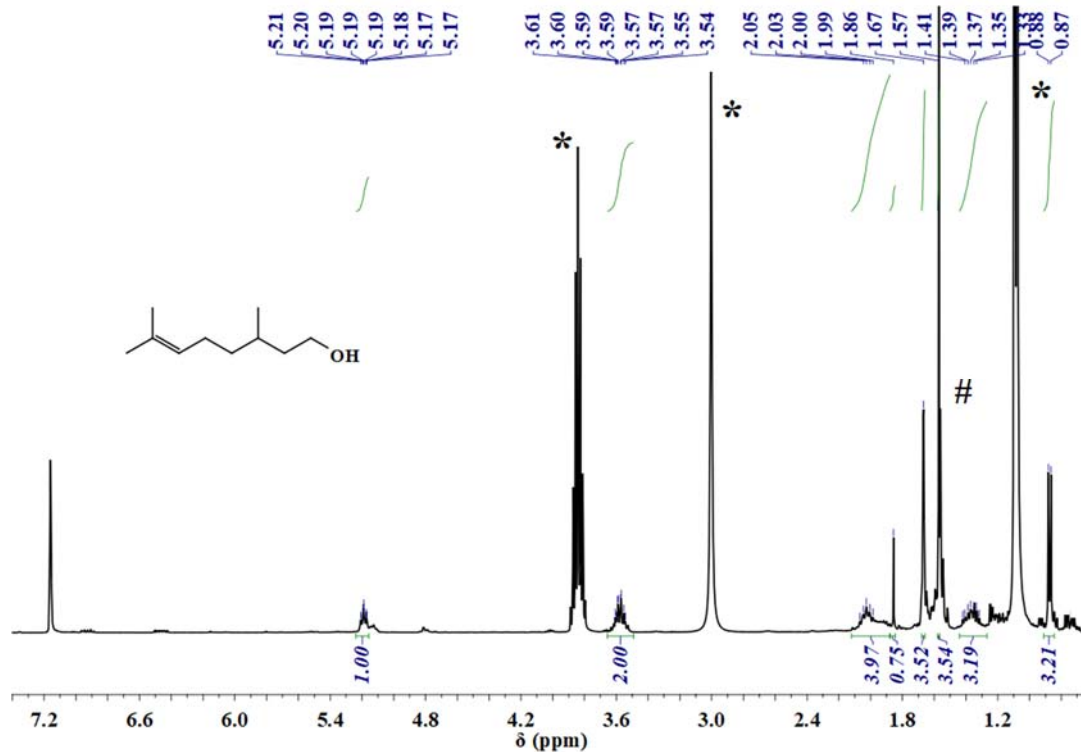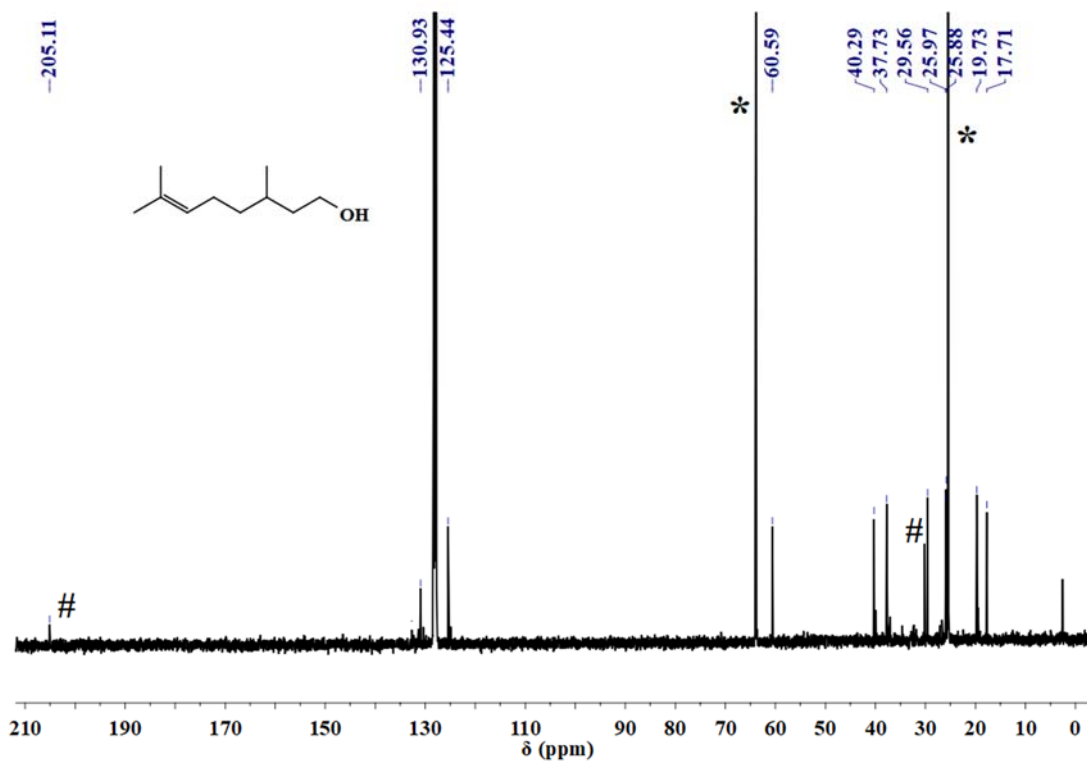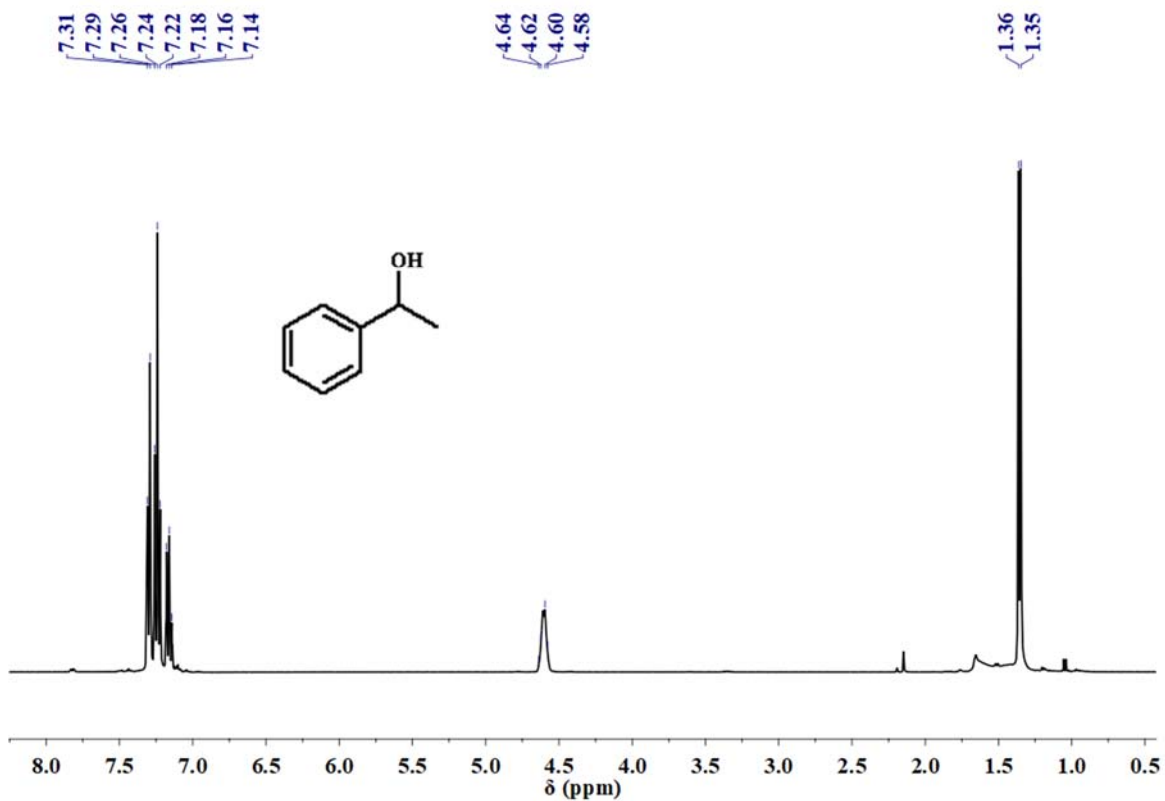**Figure S53**: ^{13}C NMR spectrum of **2f** in C_6D_6 in the reaction mixture.
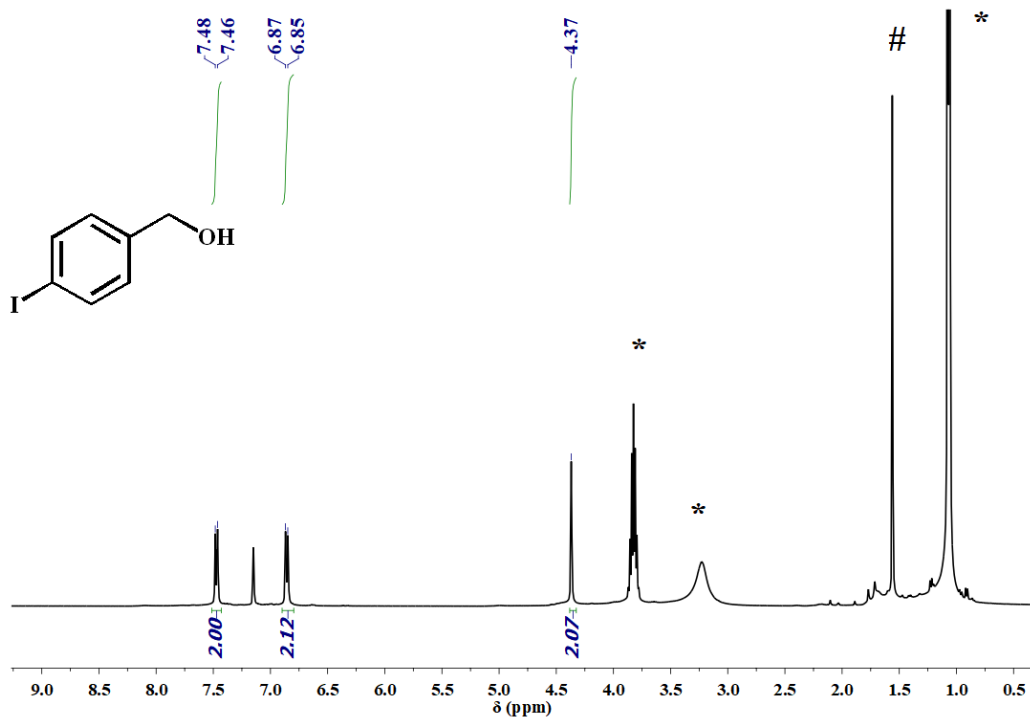
Figure S54: ^{1}H NMR spectrum of **2g** in C$_6$D$_6$ in the reaction mixture.
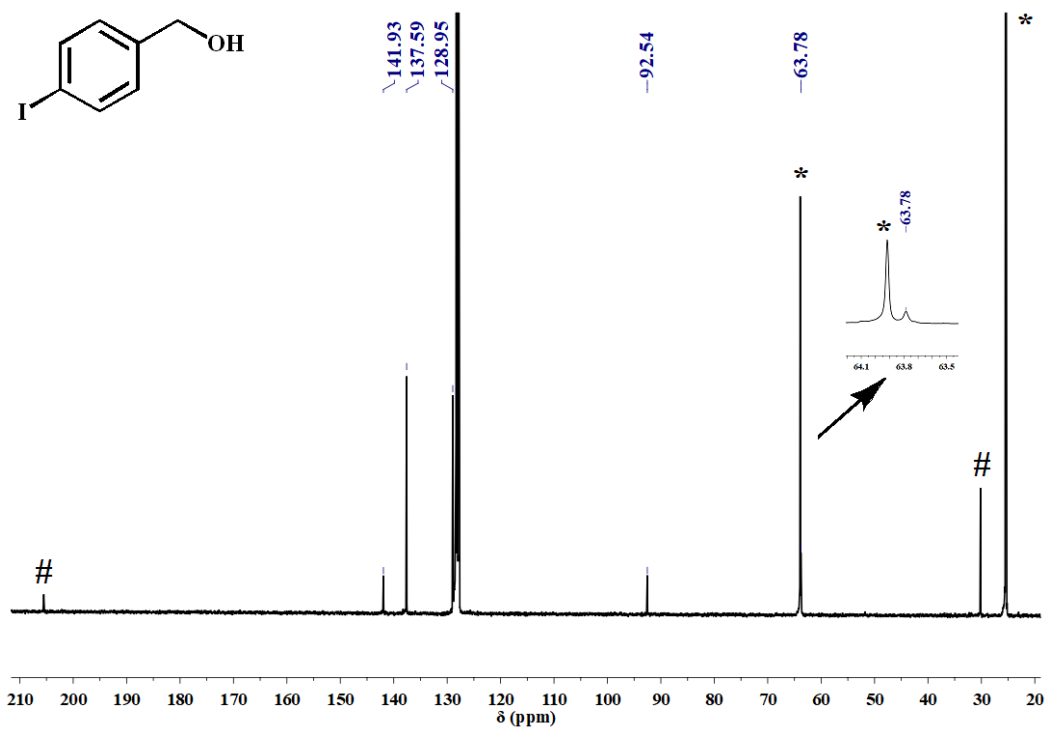
Figure S55: ^{13}C NMR spectrum of **2g** in C$_6$D$_6$ in the reaction mixture.
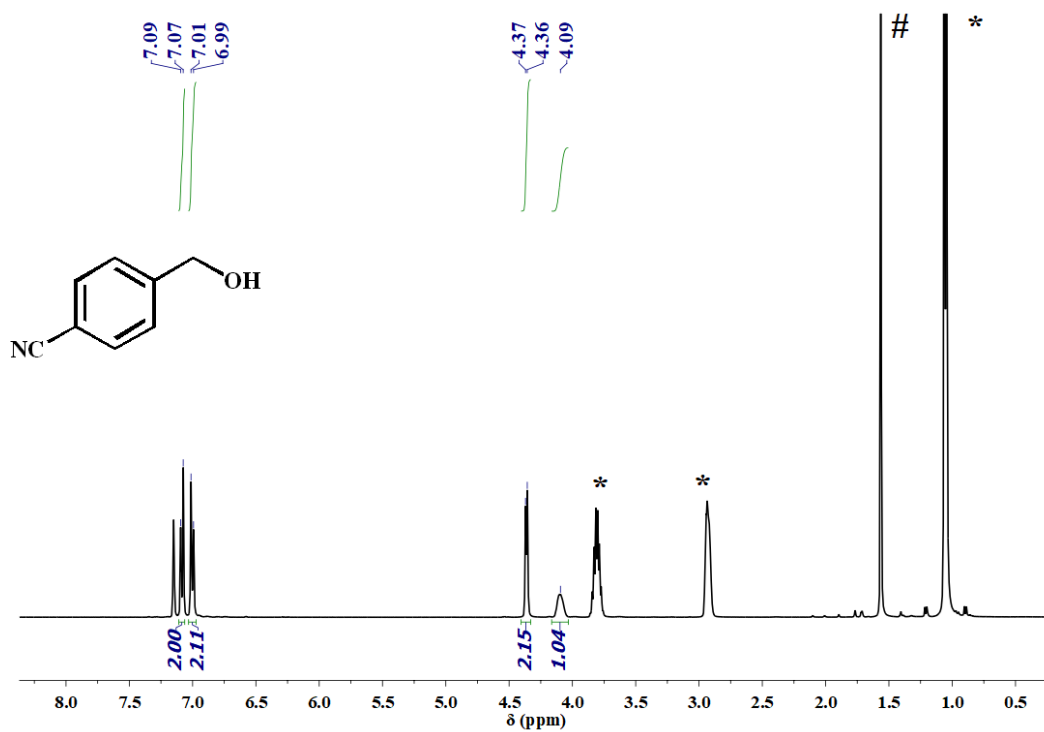
Figure S56: ^{1}H NMR spectrum of **2h** in C$_6$D$_6$ in the reaction mixture.
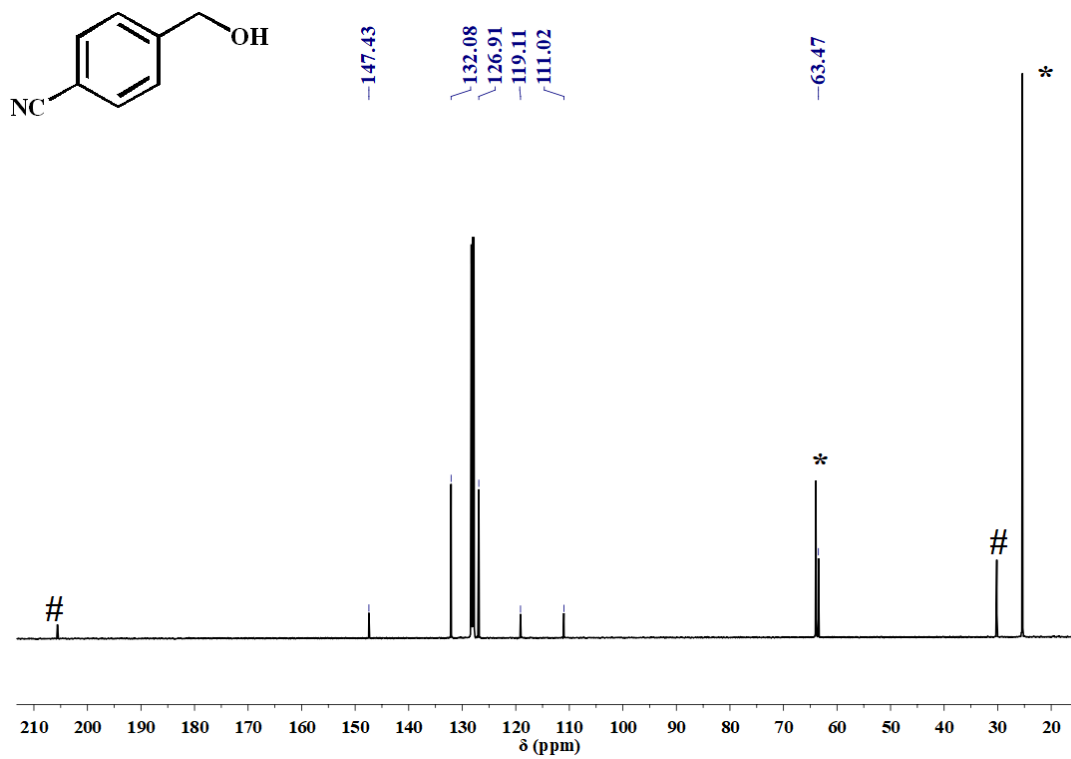
Figure S57: ^{13}C NMR spectrum of **2h** in C$_6$D$_6$ in the reaction mixture.

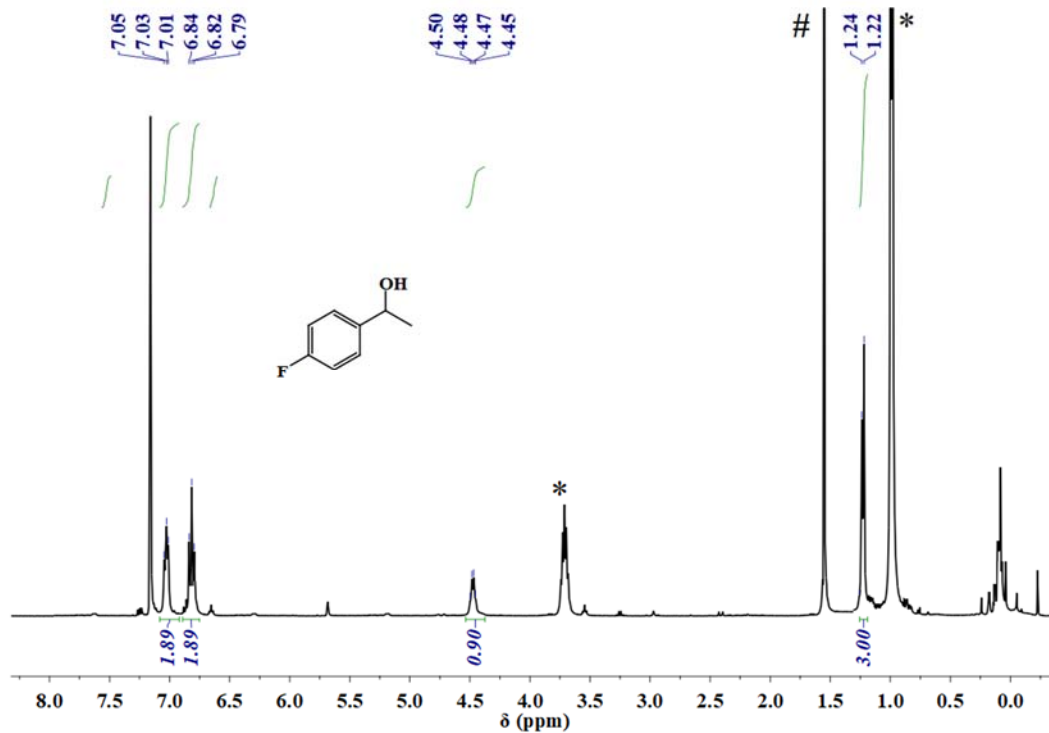55
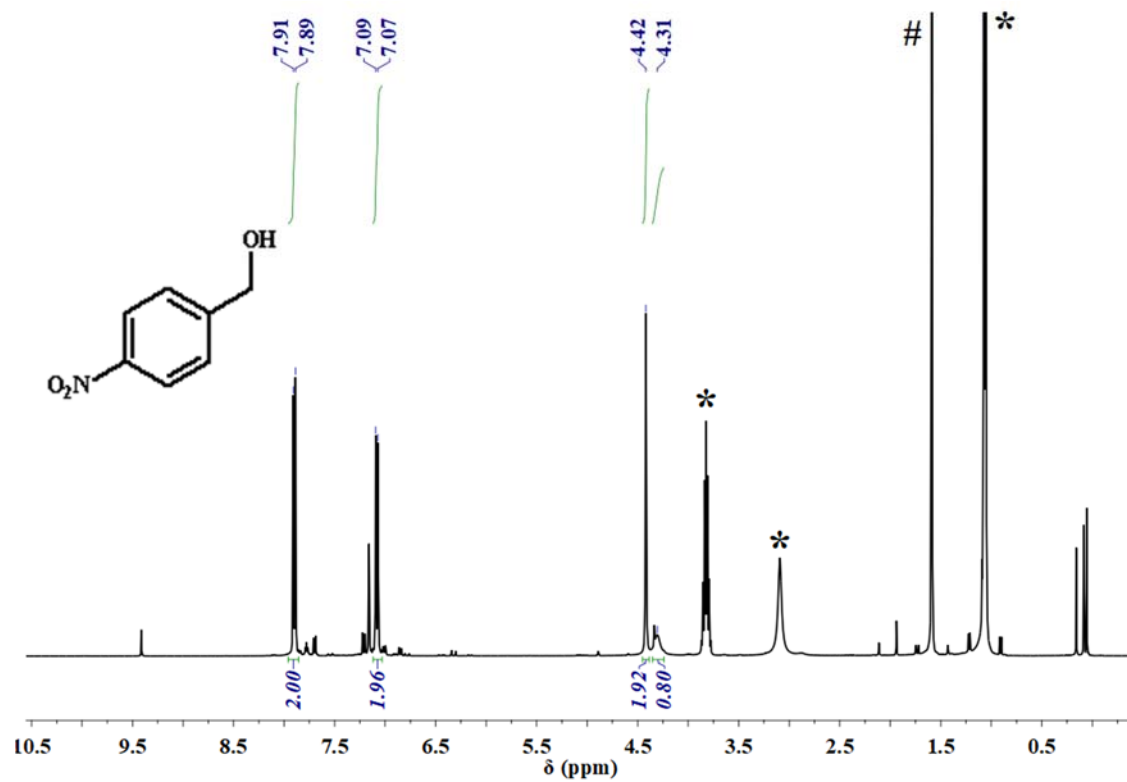
Figure S58: ^{1}H NMR spectrum of **2i** in C_6D_6 in the reaction mixture.
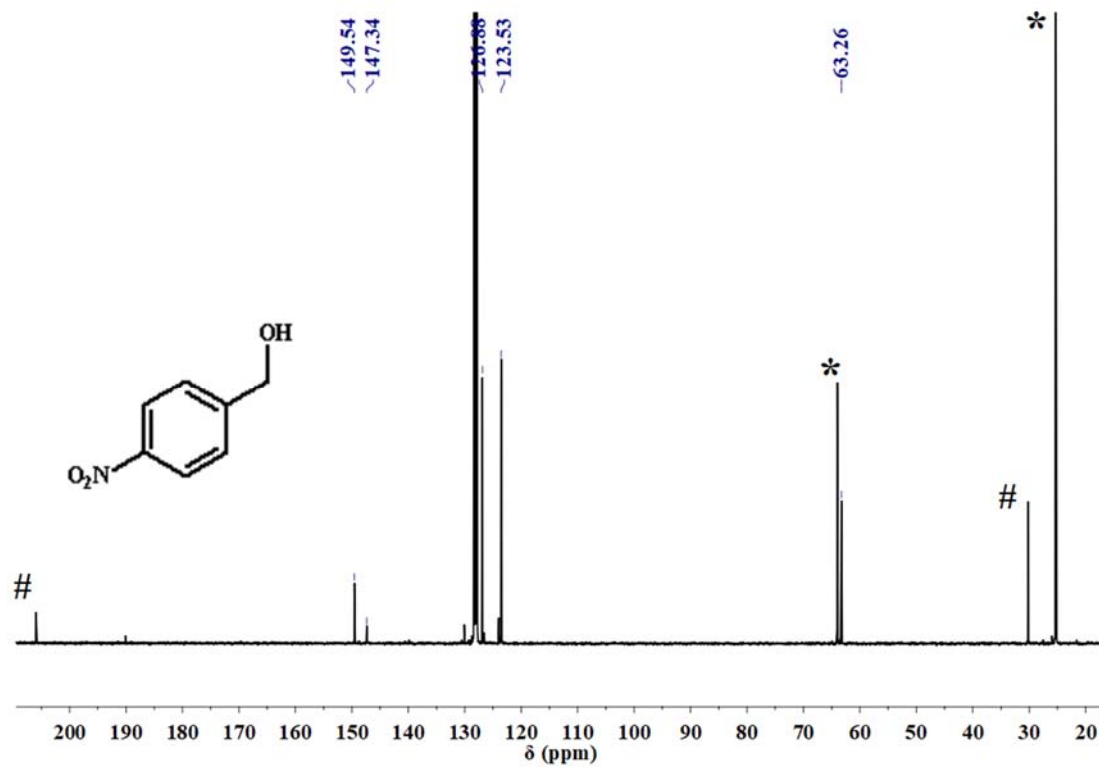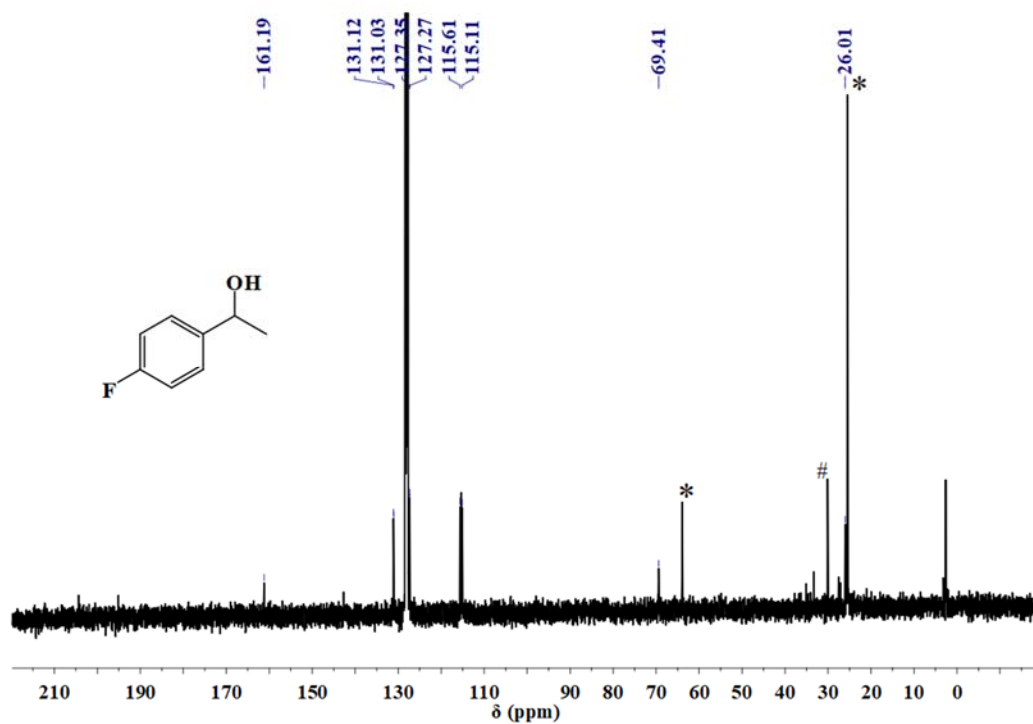

Figure S59: ^{13}C NMR spectrum of **2i** in C_6D_6 in the reaction mixture.

56
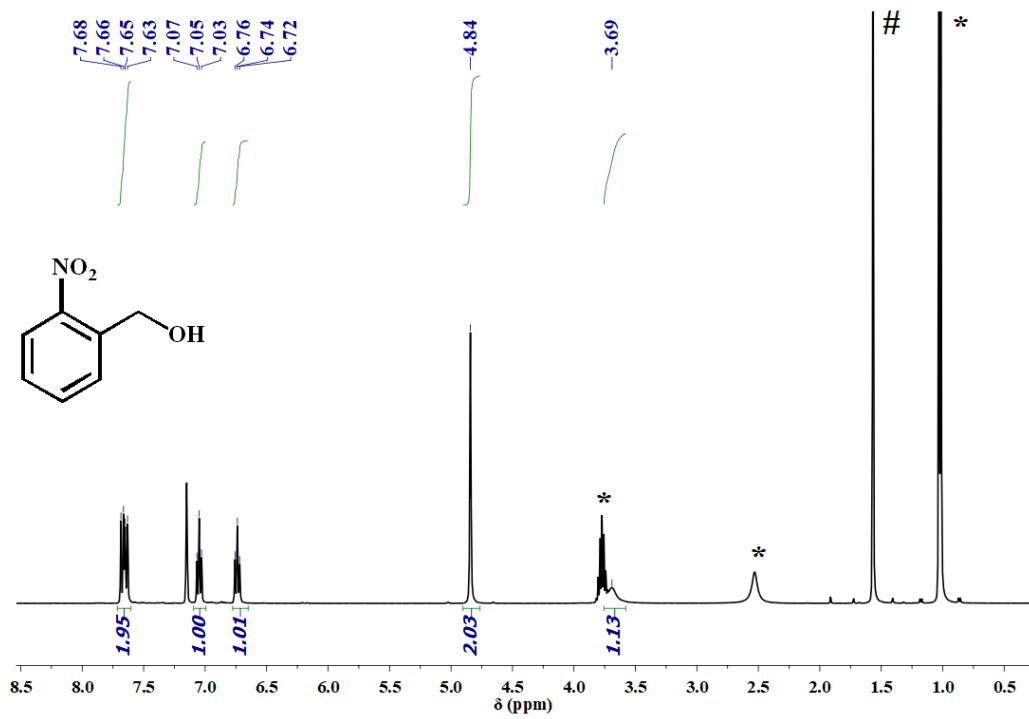
Figure S60: ^{1}H NMR spectrum of **2j** in C_6D_6 in the reaction mixture.
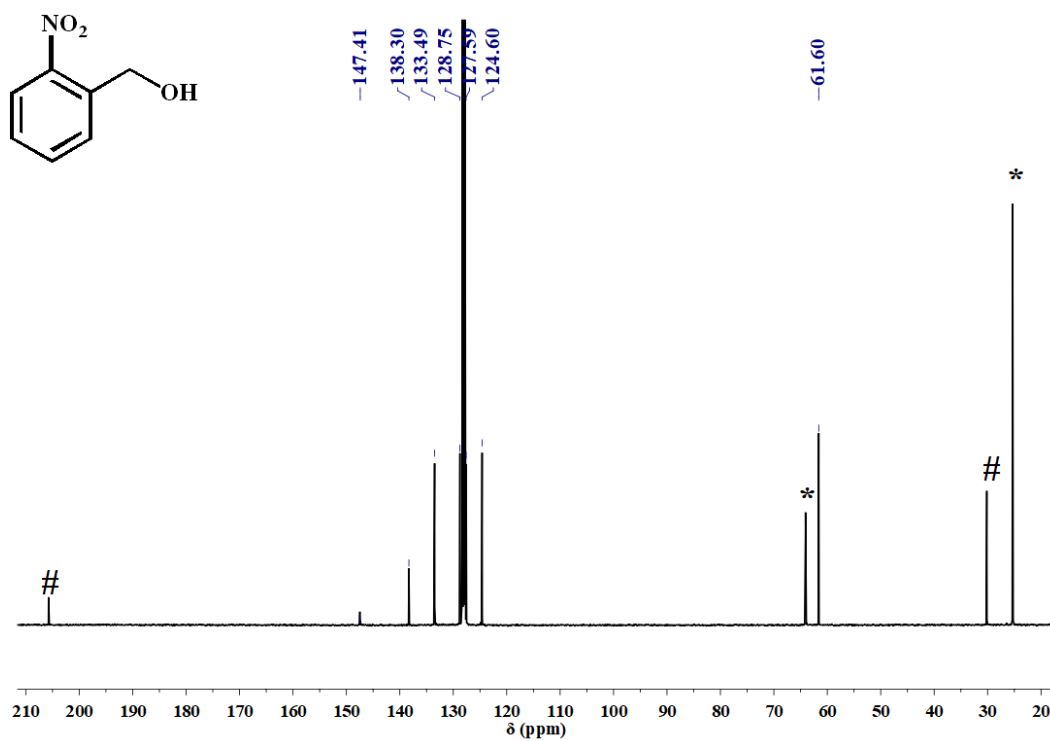
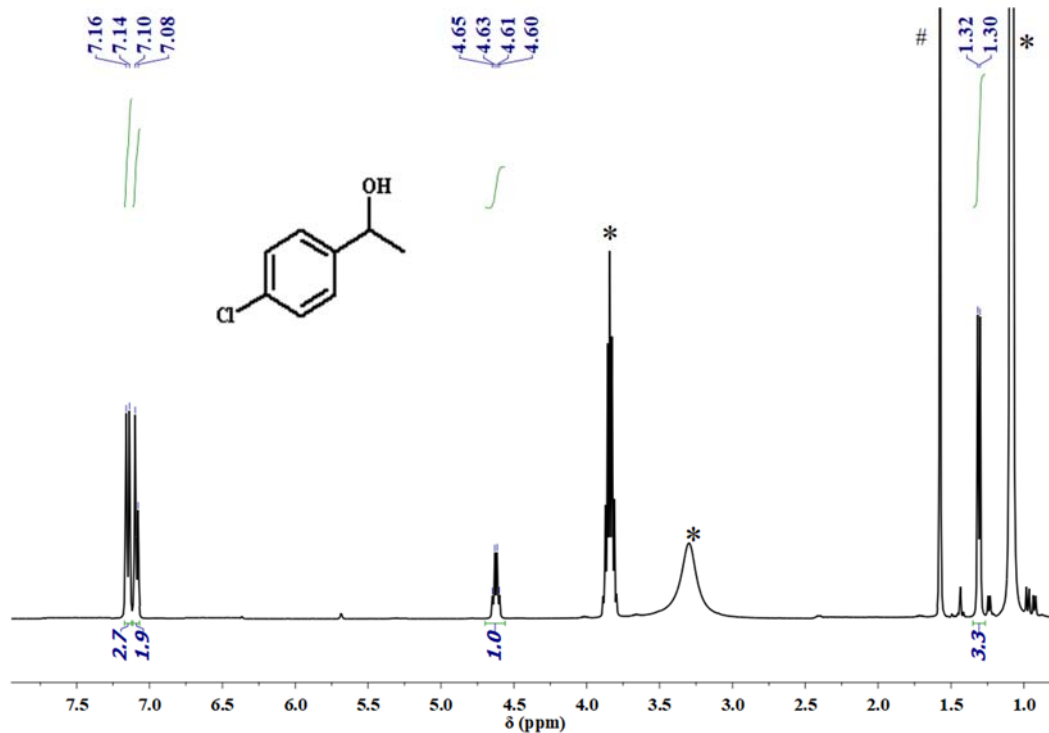**Figure S61**: ^{13}C NMR spectrum of **2j** in C_6D_6 in the reaction mixture.

57
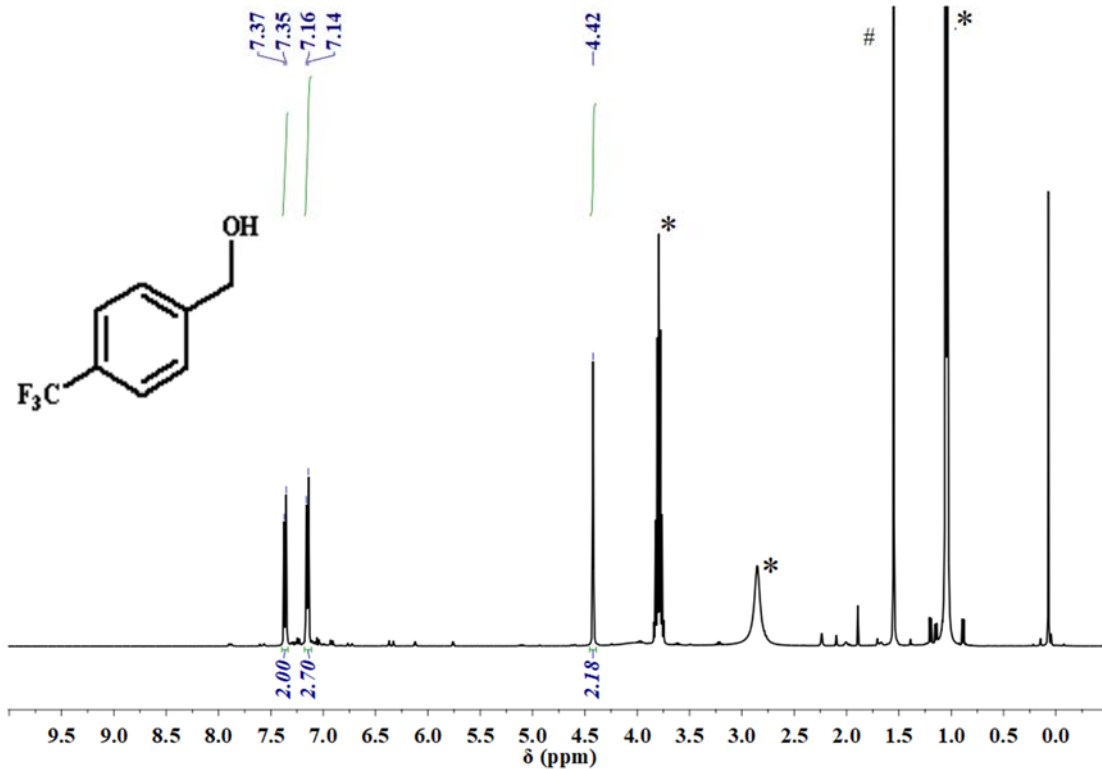
Figure S62: ^{1}H NMR spectrum of **2k** in C$_6$D$_6$ in the reaction mixture.
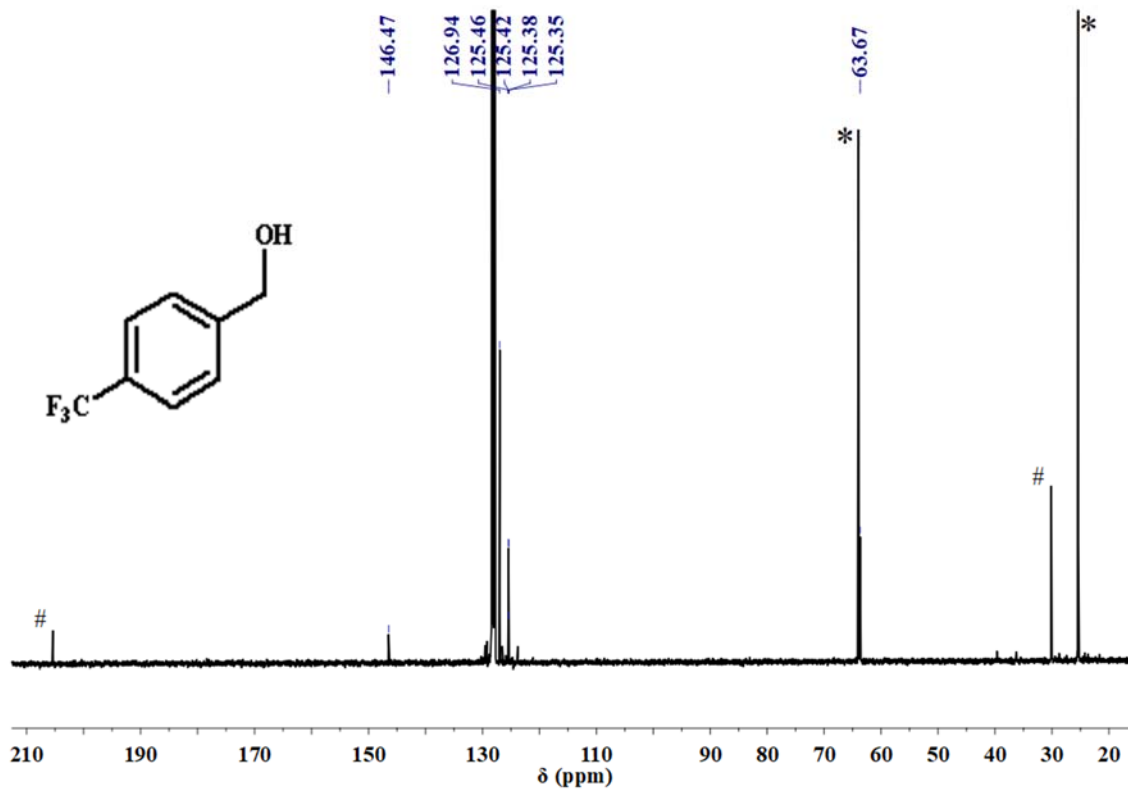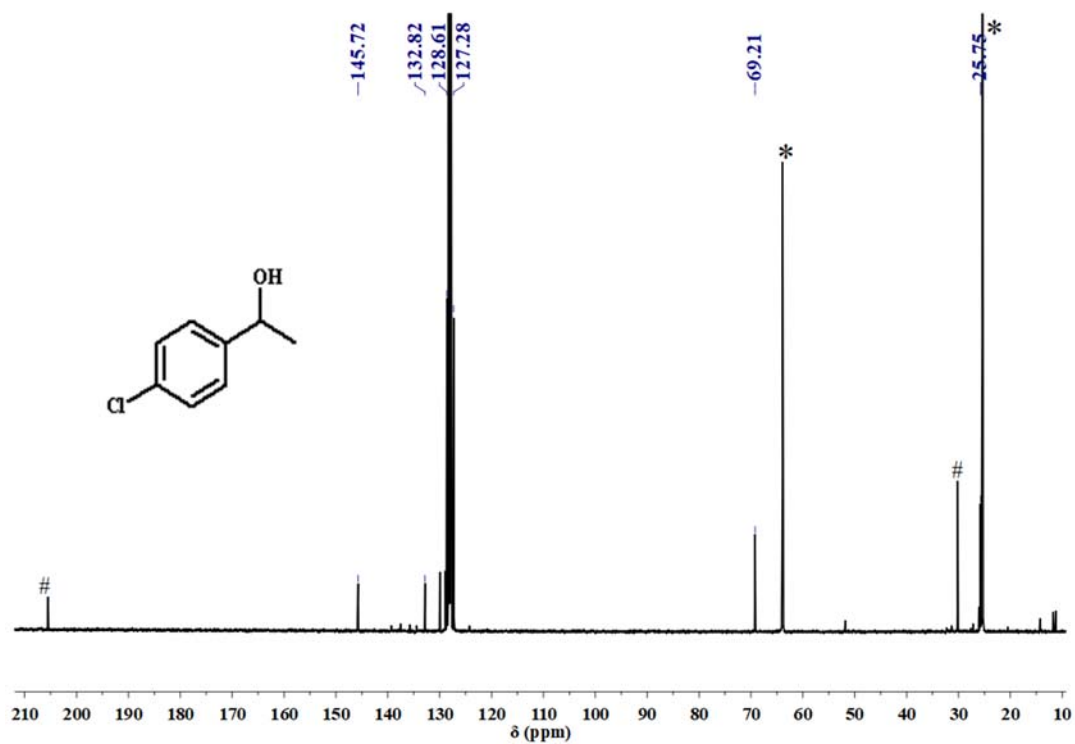

Figure S63: ^{13}C NMR spectrum of **2k** in C$_6$D$_6$ in the reaction mixture.
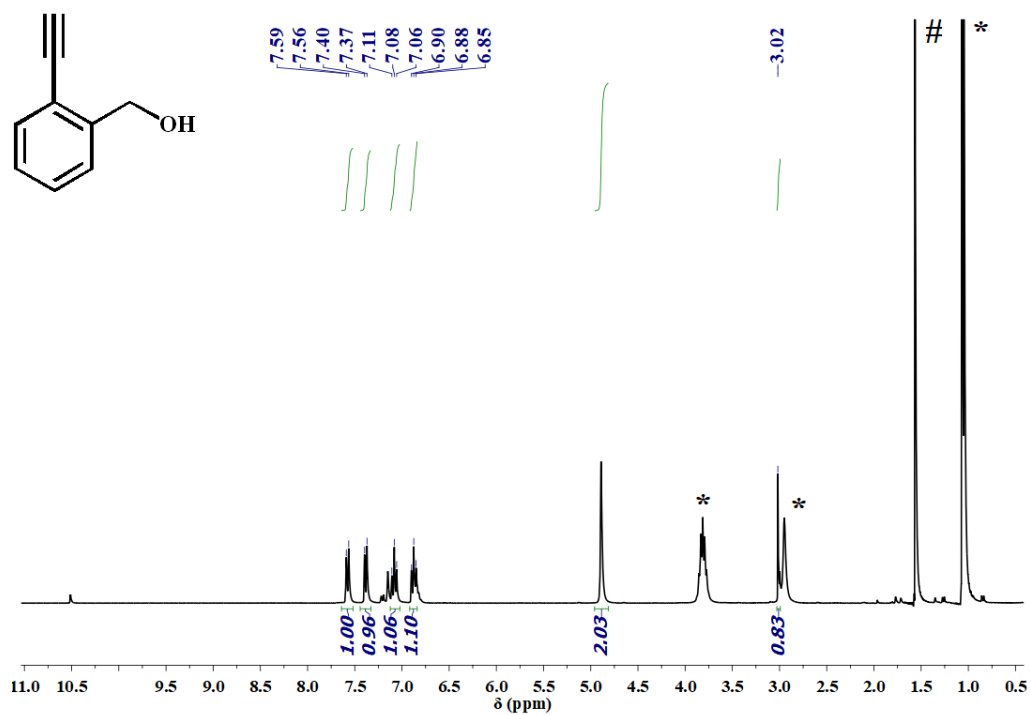
Figure S64: ^{1}H NMR spectrum of **2l** in C_6D_6 in the reaction mixture.
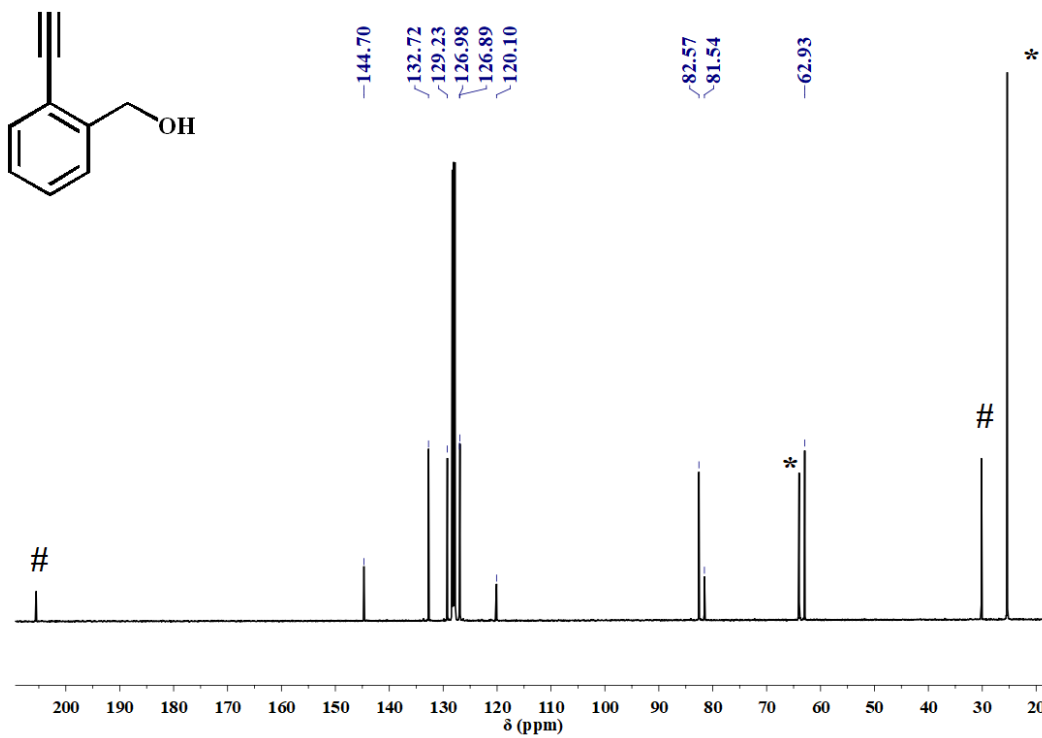
Figure S65: ^{1}H NMR spectrum of **2l** in C_6D_6 in the reaction mixture.
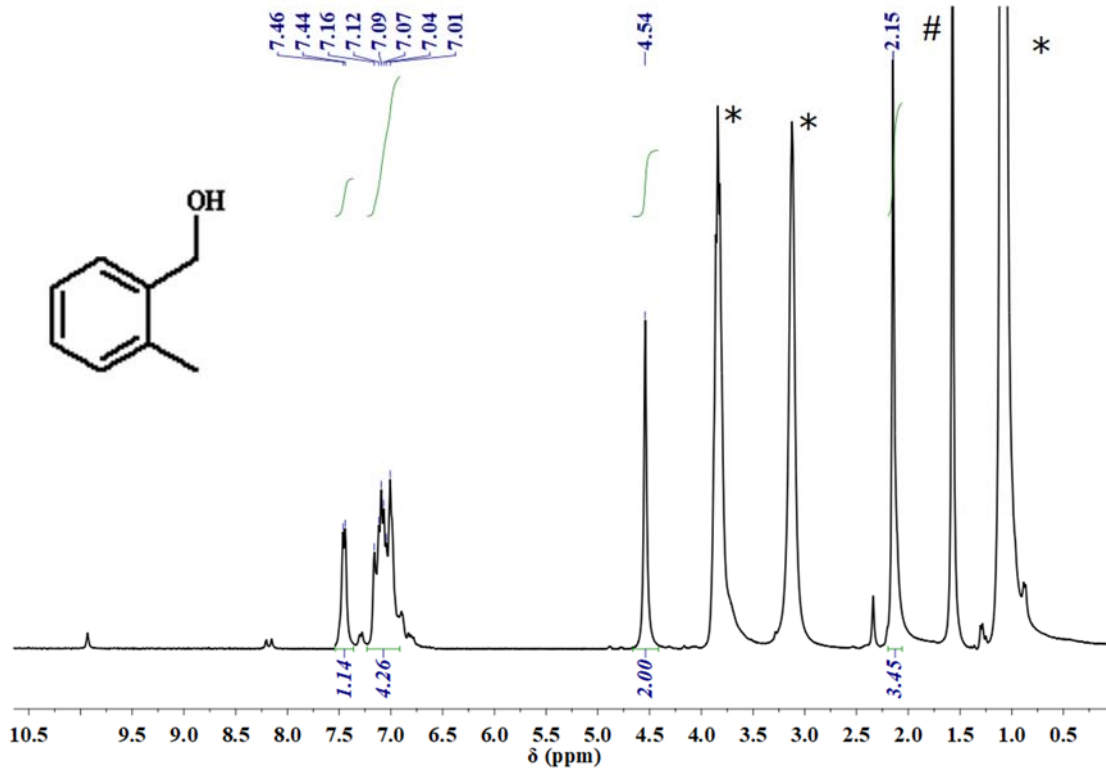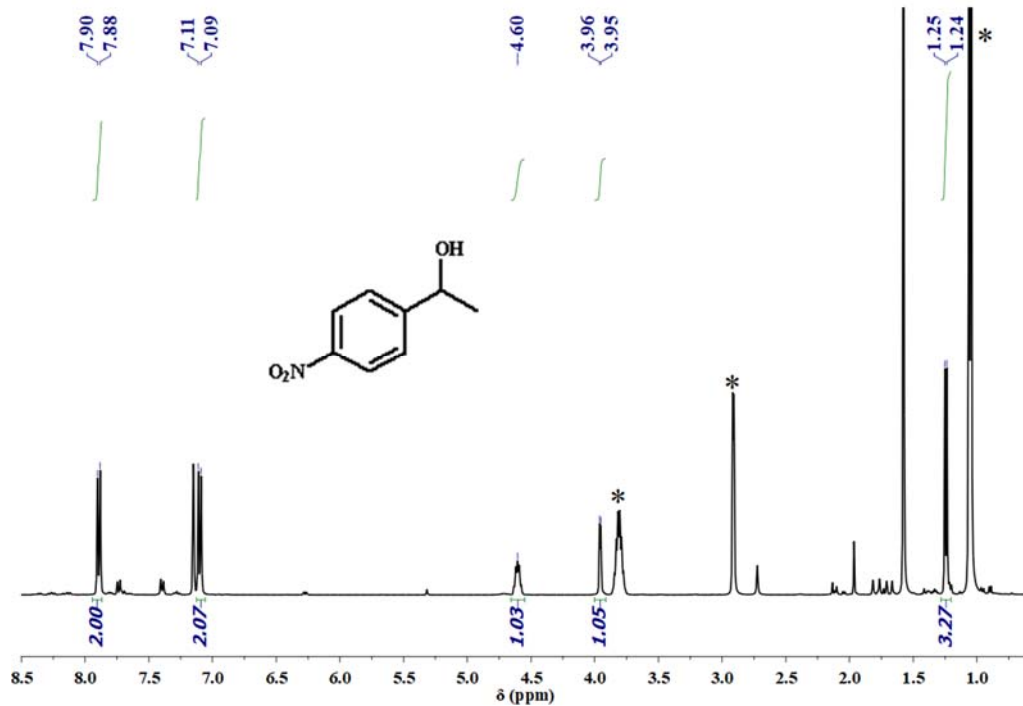
Figure S66: ^{1}H NMR spectrum of **2m** in C_6D_6 in the reaction mixture.
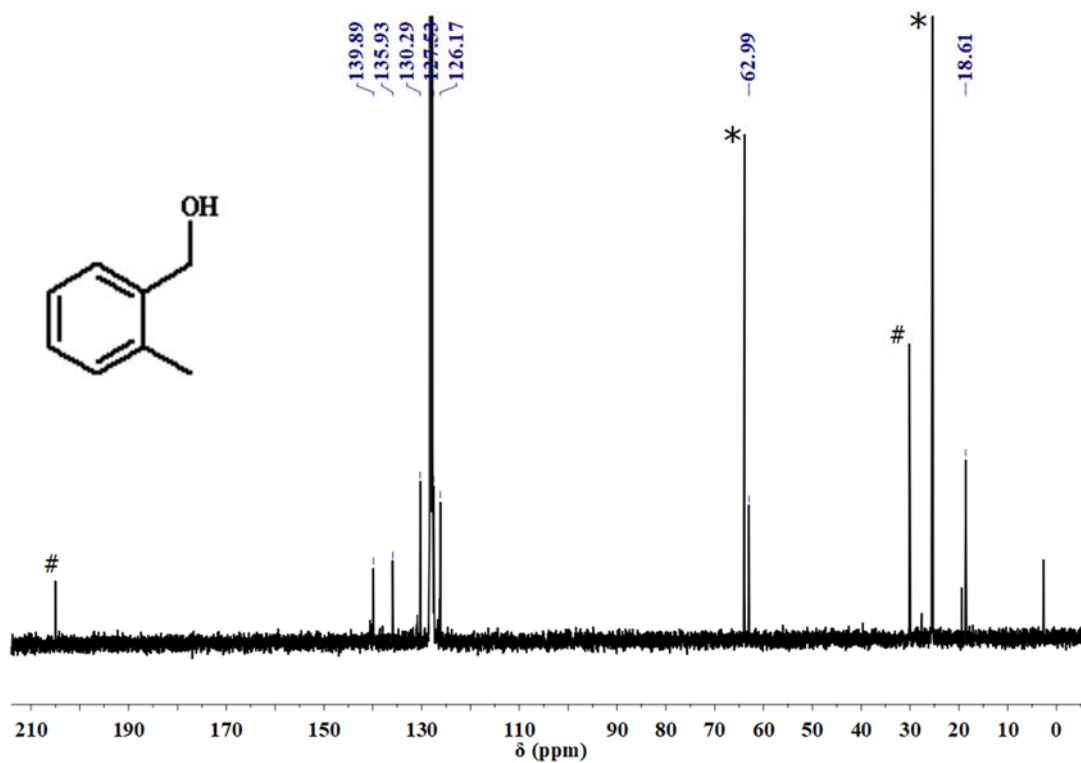
Figure S67: ^{13}C NMR spectrum of **2m** in C_6D_6 in the reaction mixture.
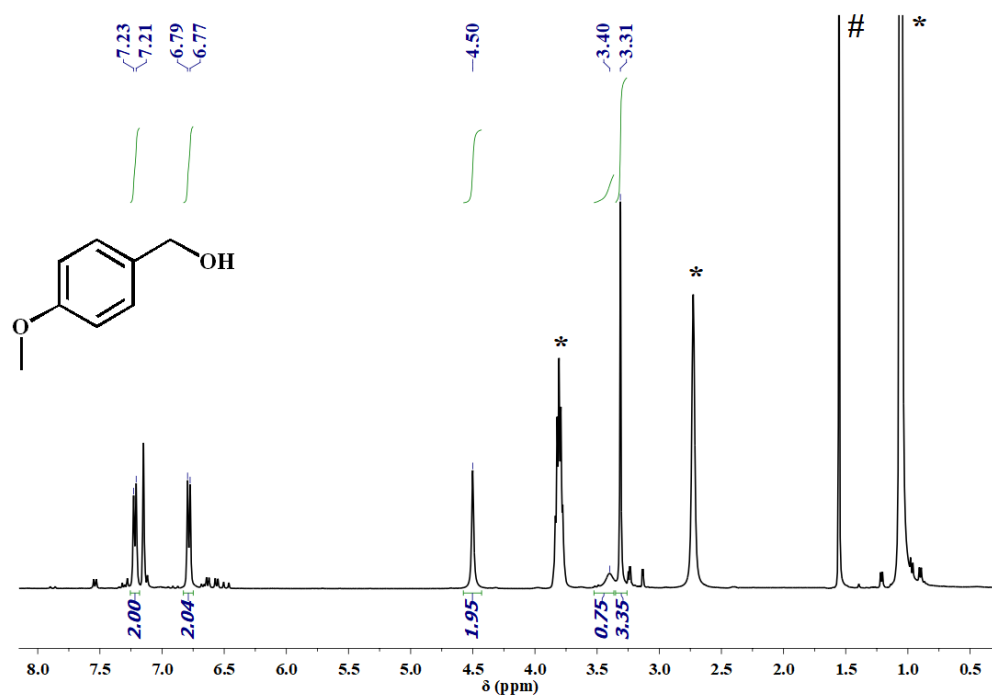
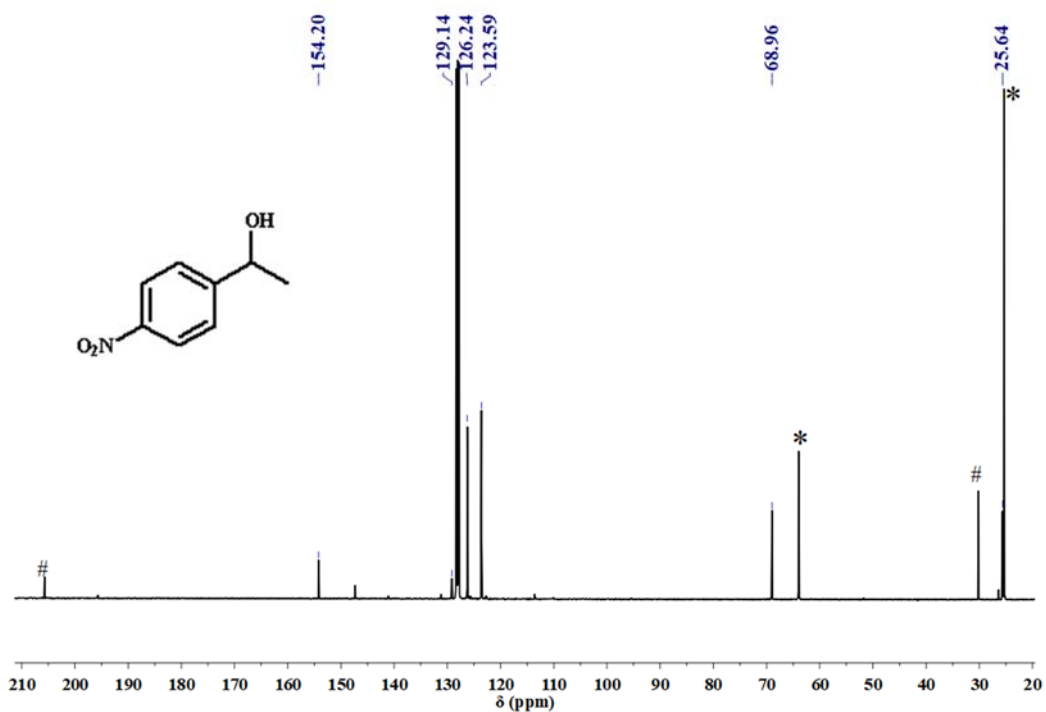**Figure S68**: ^{1}H NMR spectrum of **2n** in C_6D_6 in the reaction mixture.
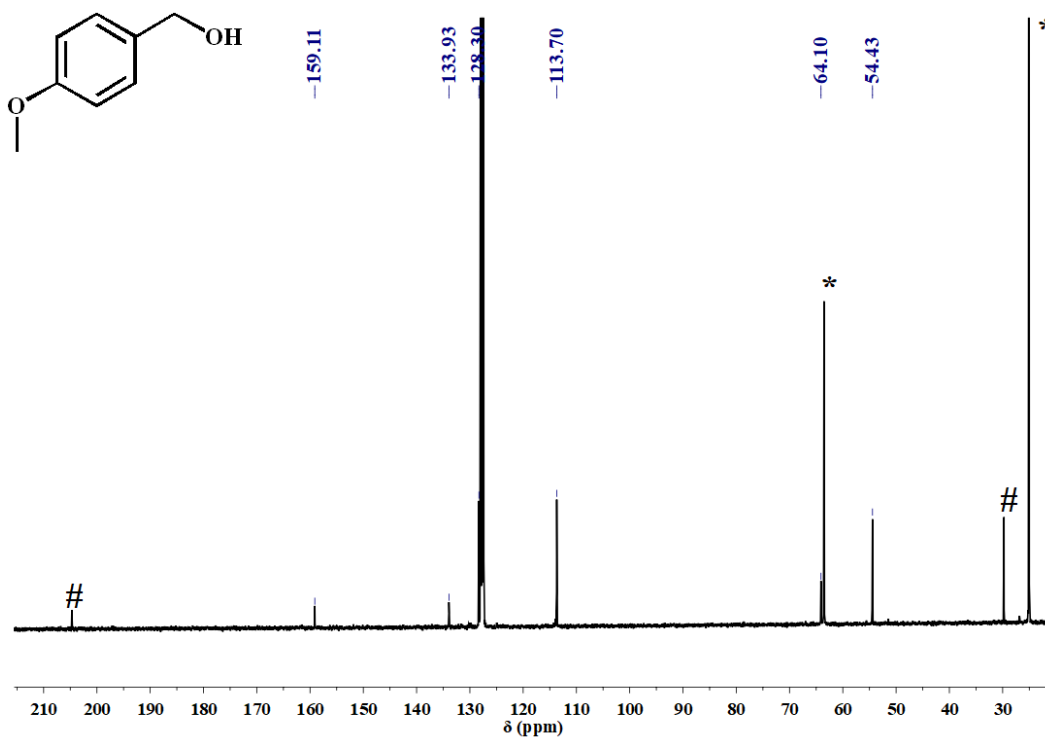
Figure S69: ^{1}H NMR spectrum of **2n** in C_6D_6 in the reaction mixture.
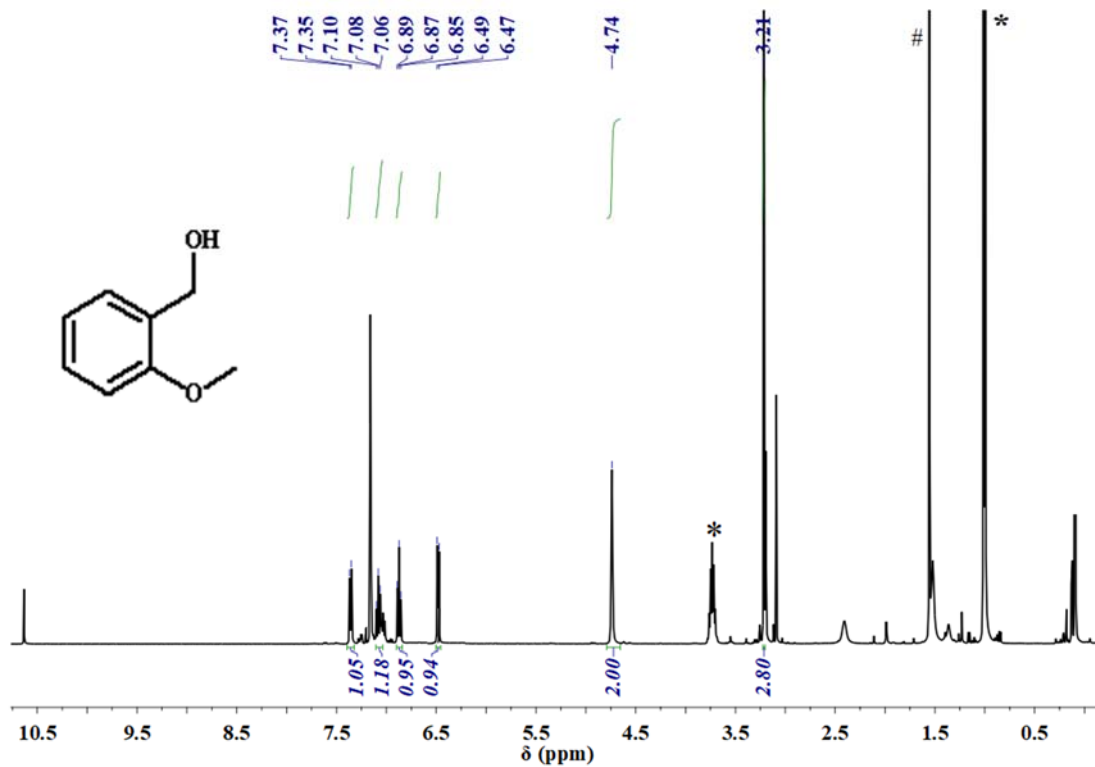
Figure S70: ^1H NMR spectrum of **2o** in C_6D_6 in the reaction mixture.
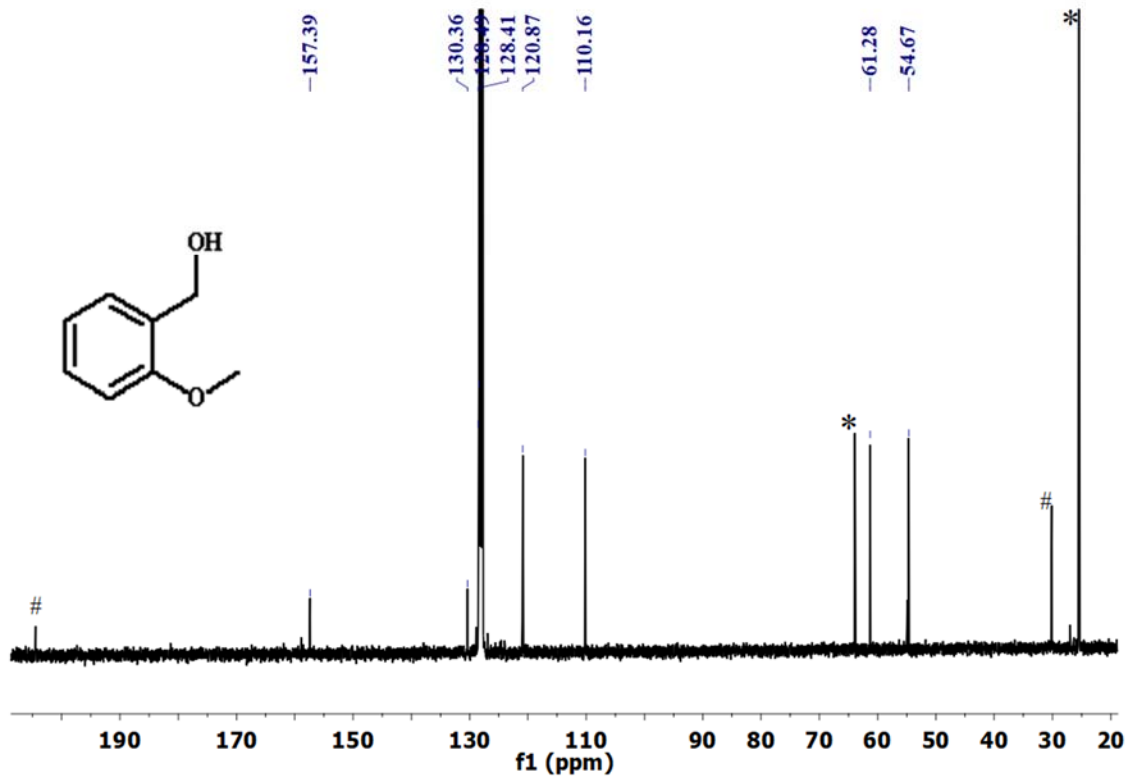
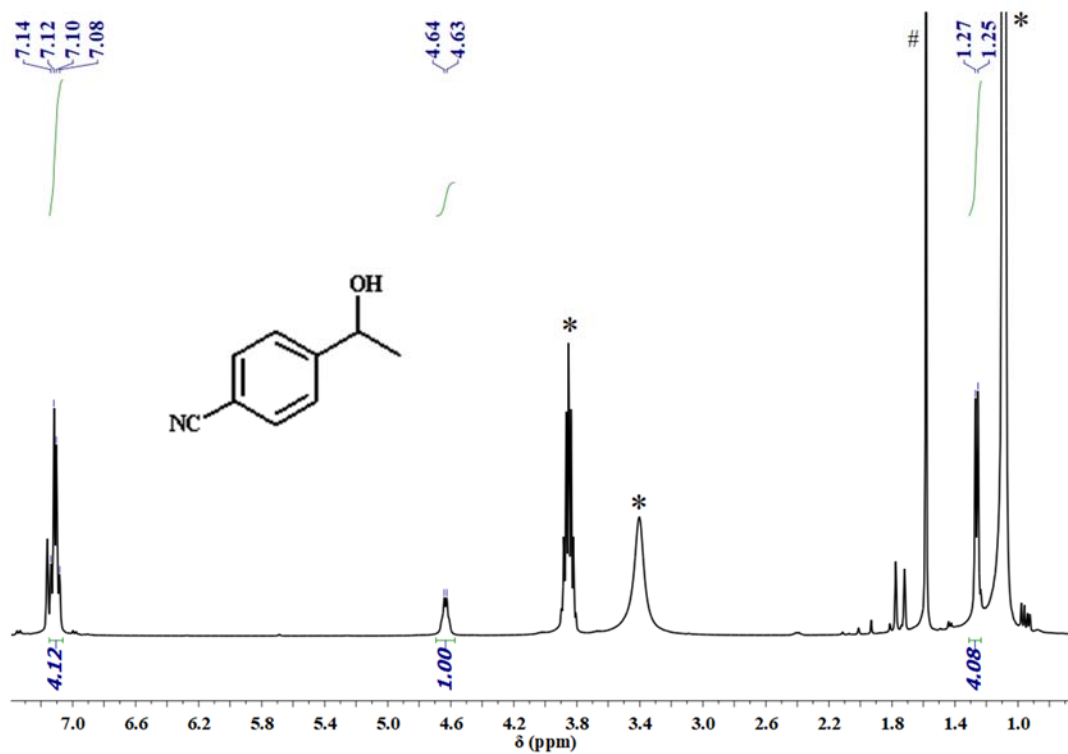**Figure S71**: ^{13}C NMR spectrum of **2o** in C_6D_6 in the reaction mixture.
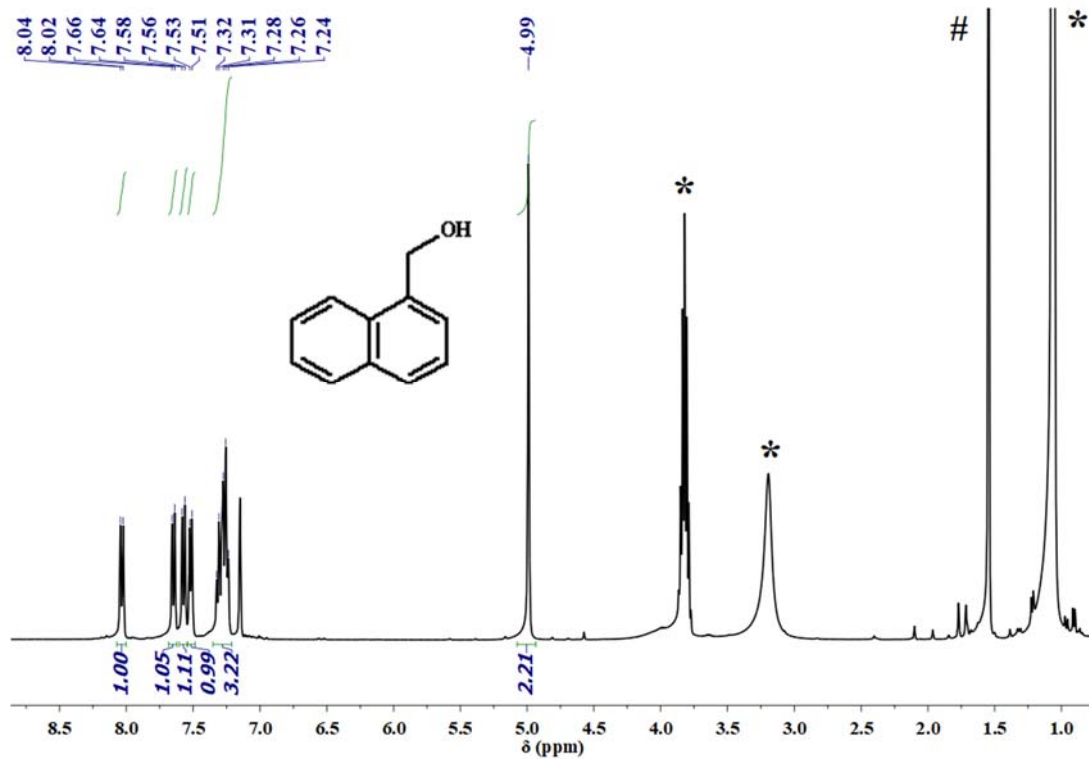
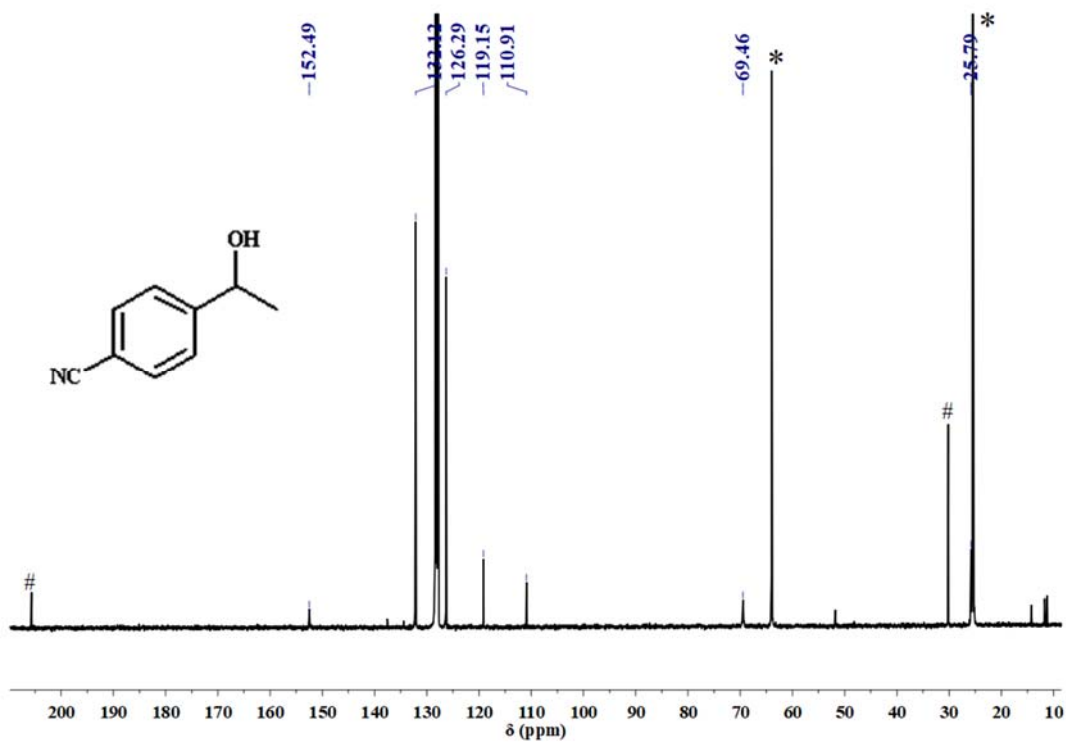**Figure S72**: ^1H NMR spectrum of **2q** in C_6D_6 in the reaction mixture.
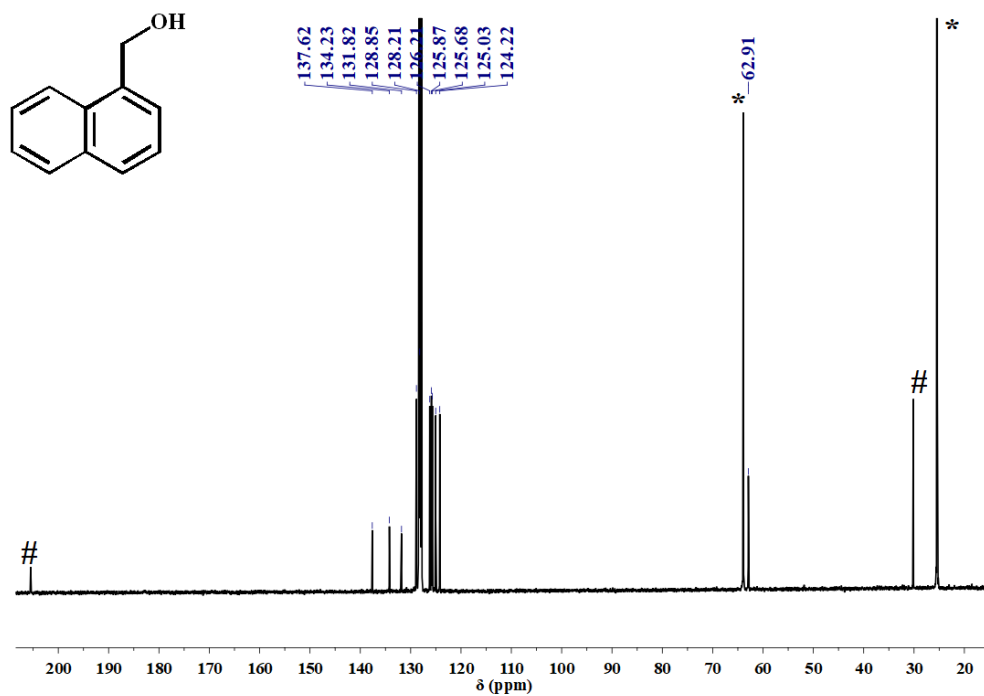
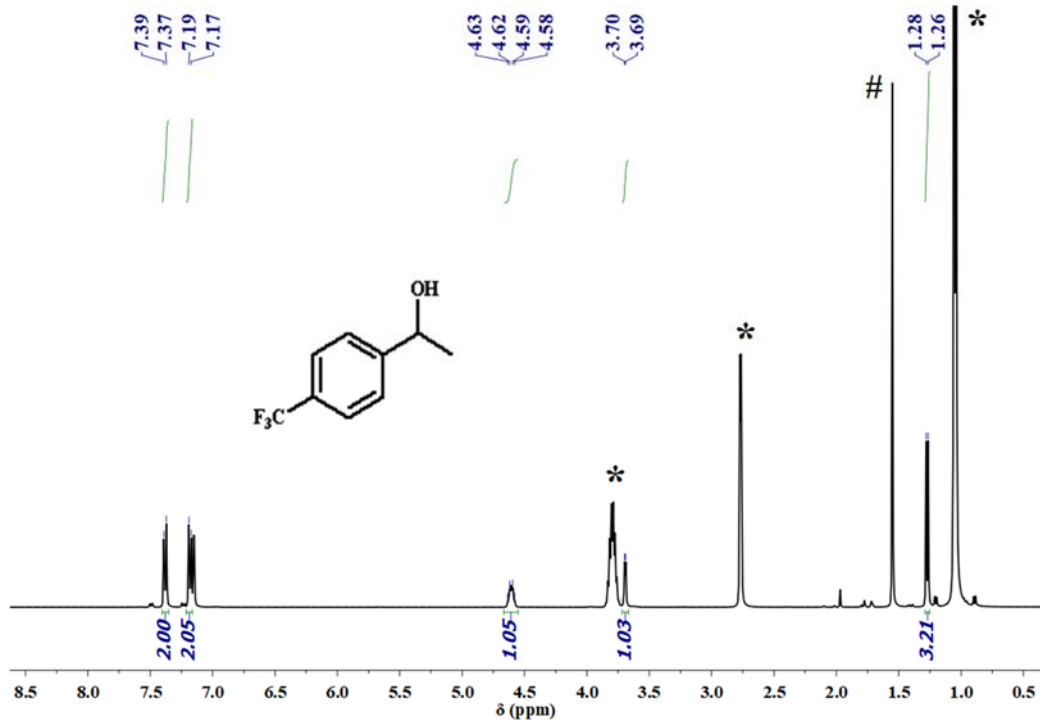**Figure S73**: ^{13}C NMR spectrum of **2q** in C_6D_6 in the reaction mixture.
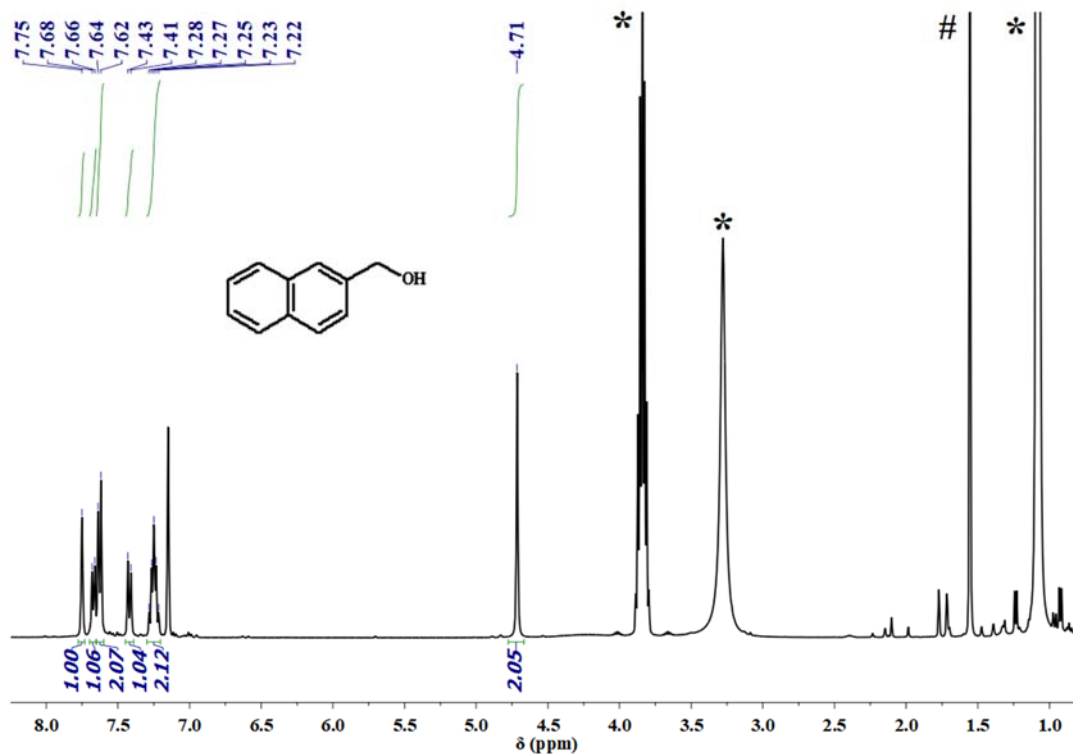
Figure S74: ^1H NMR spectrum of **2r** in C_6D_6 in the reaction mixture.
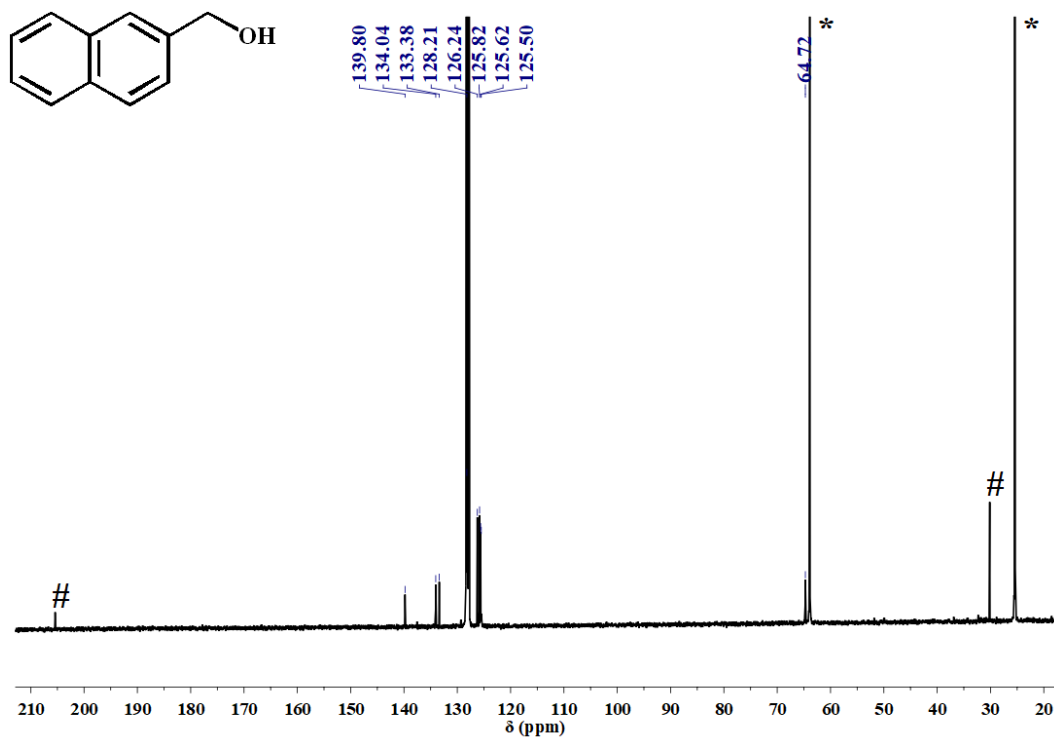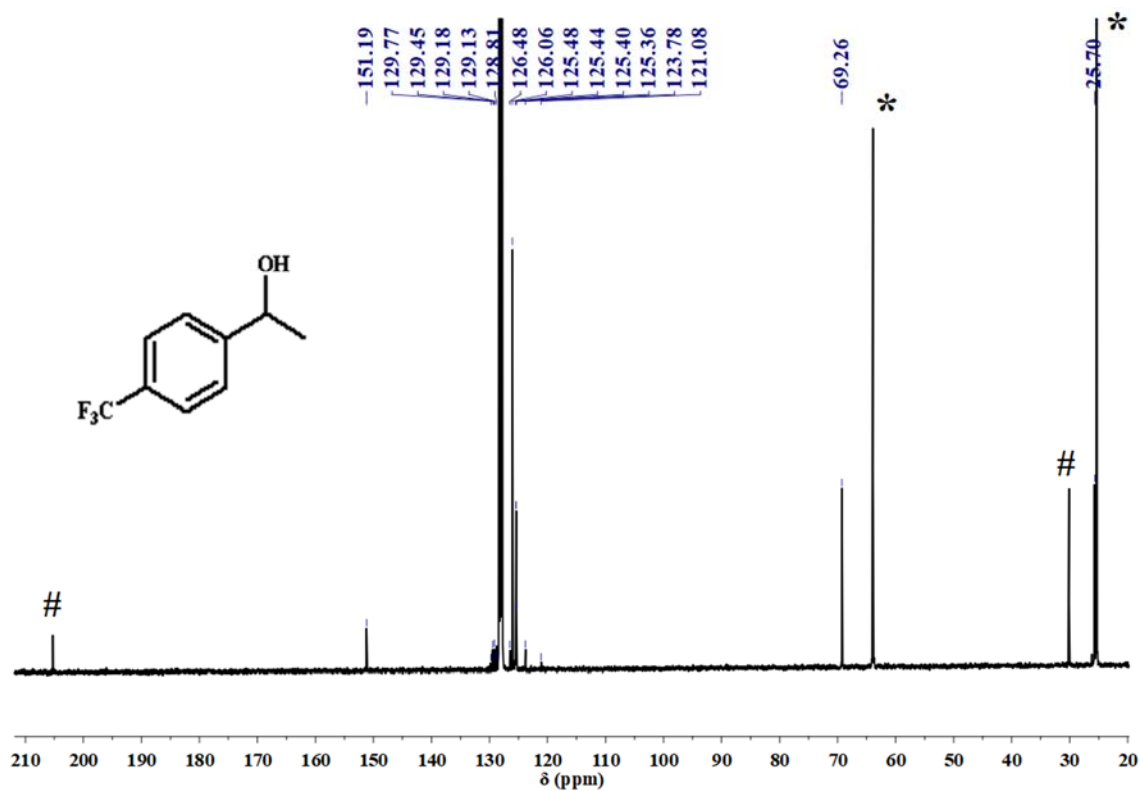

Figure S75: ^{13}C NMR spectrum of **2r** in C_6D_6 in the reaction mixture.
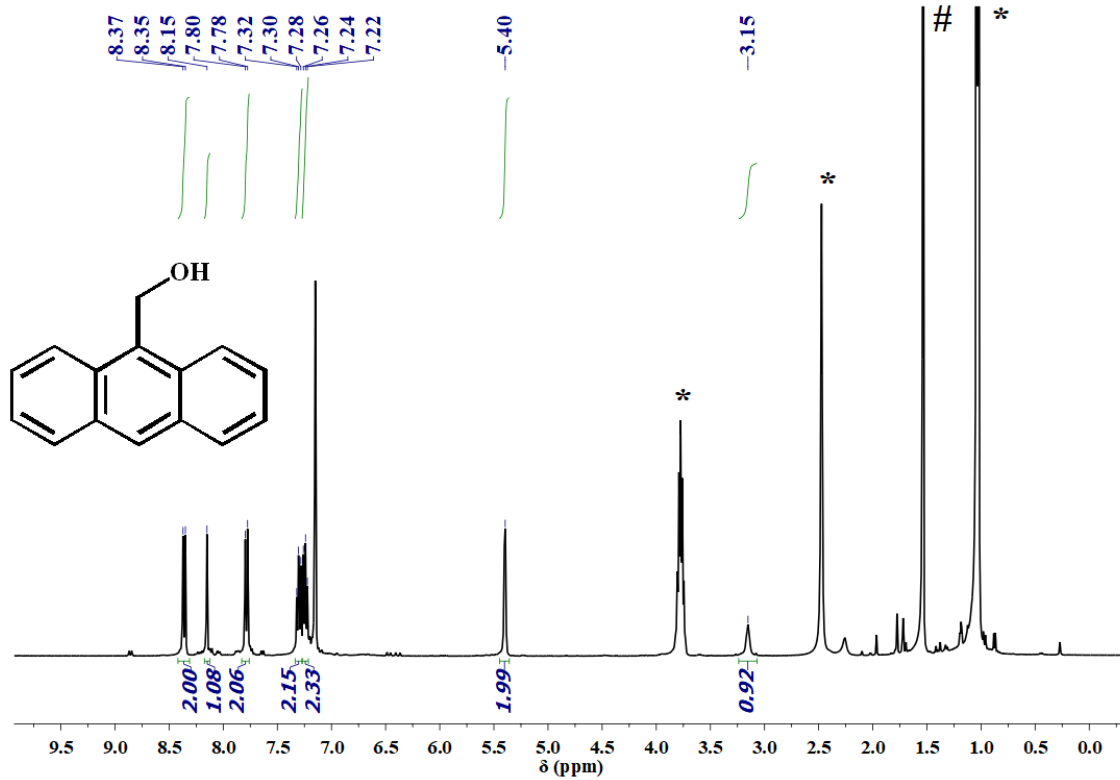
Figure S76: ^1H NMR spectrum of **2s** in C_6D_6 in the reaction mixture.
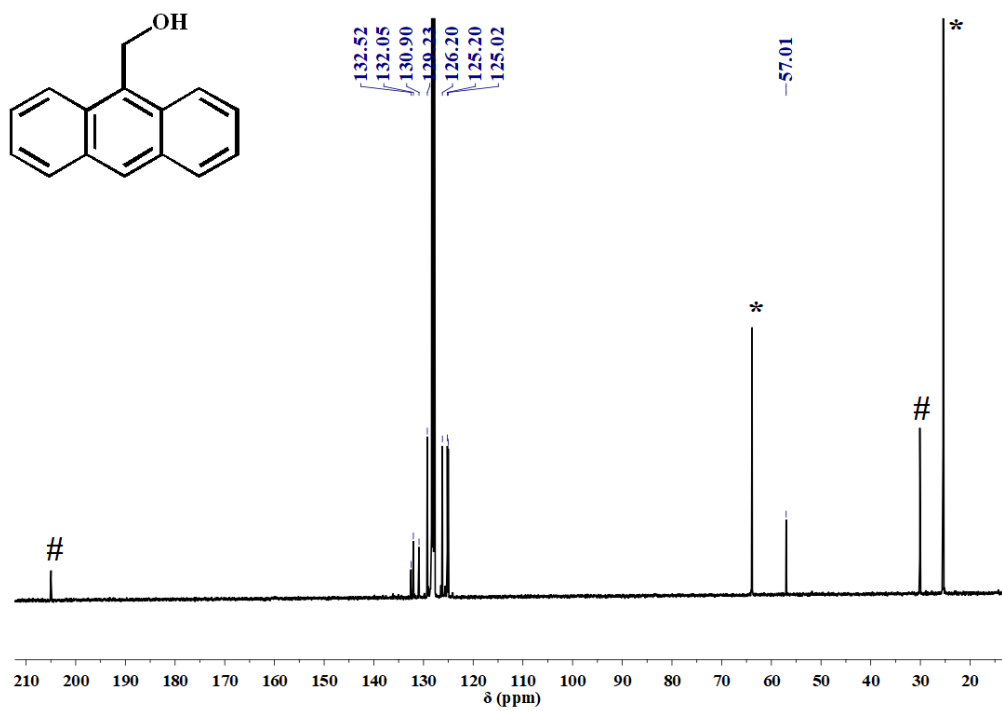
Figure S77: ^{13}C NMR spectrum of **2s** in C_6D_6 in the reaction mixture.
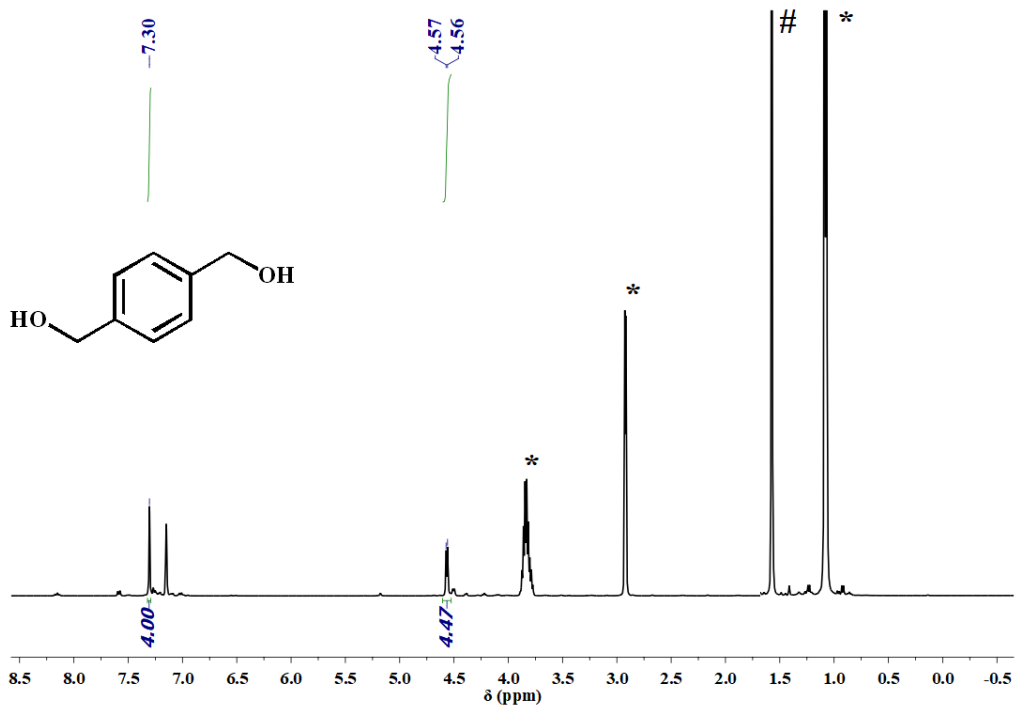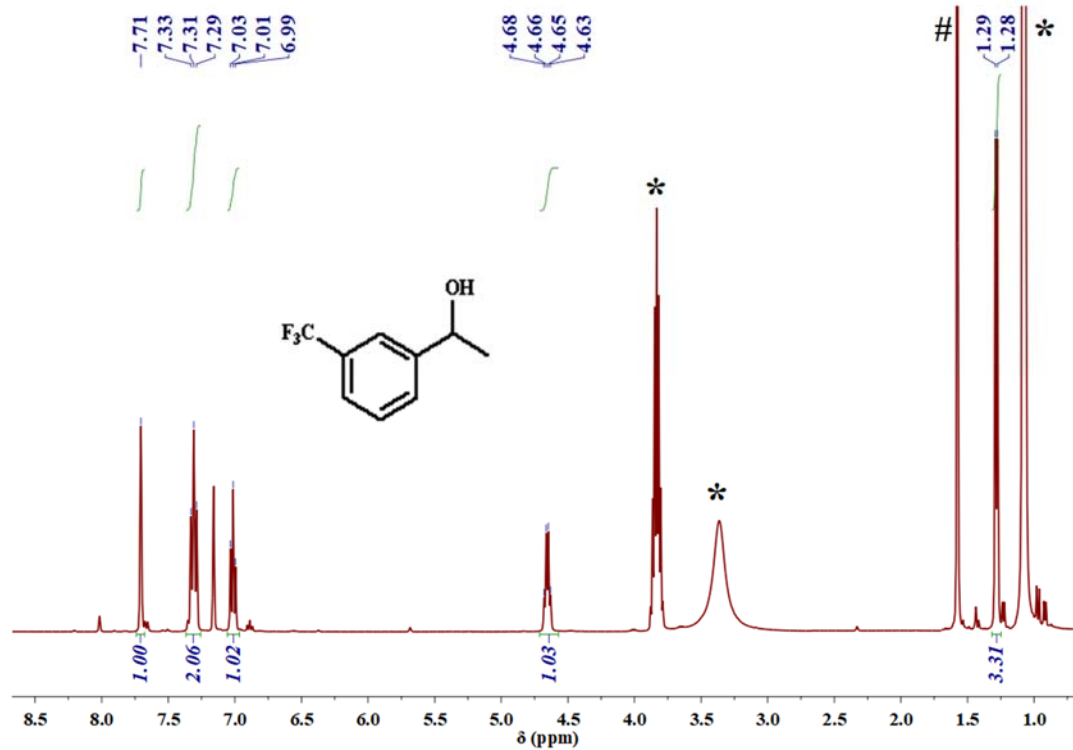
Figure S78: ^{1}H NMR spectrum of **2t** in C$_6$D$_6$ in the reaction mixture.
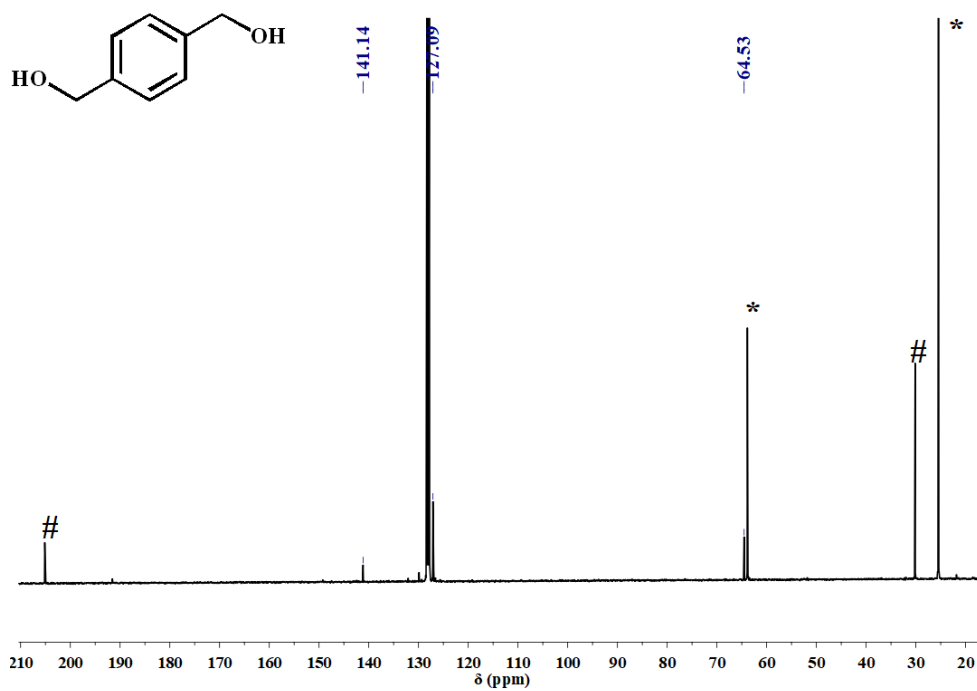
Figure S79: ^{13}C NMR spectrum of **2t** in C$_6$D$_6$ in the reaction mixture.

66

Figure S80: ^{1}H NMR spectrum of **2u** in C$_6$D$_6$ in the reaction mixture.

Figure S81: ^{13}C NMR spectrum of **2u** in C$_6$D$_6$ in the reaction mixture.

Figure S82: ^{1}H NMR spectrum of **2v** in C_6D_6 in the reaction mixture.

Figure S83: ^{13}C NMR spectrum of **2v** in C_6D_6 in the reaction mixture.

Figure S84: ^{1}H NMR spectrum of **2w** in C_6D_6 in the reaction mixture.

Figure S85: ^{13}C NMR spectrum of **2w** in C_6D_6 in the reaction mixture.

Figure S86: ^{1}H NMR spectrum of **2x** in C_6D_6 in the reaction mixture.

Figure S87: ^{13}C NMR spectrum of **2x** in C_6D_6 in the reaction mixture.

Figure S88: ^1H NMR spectrum of **4a** in C_6D_6.
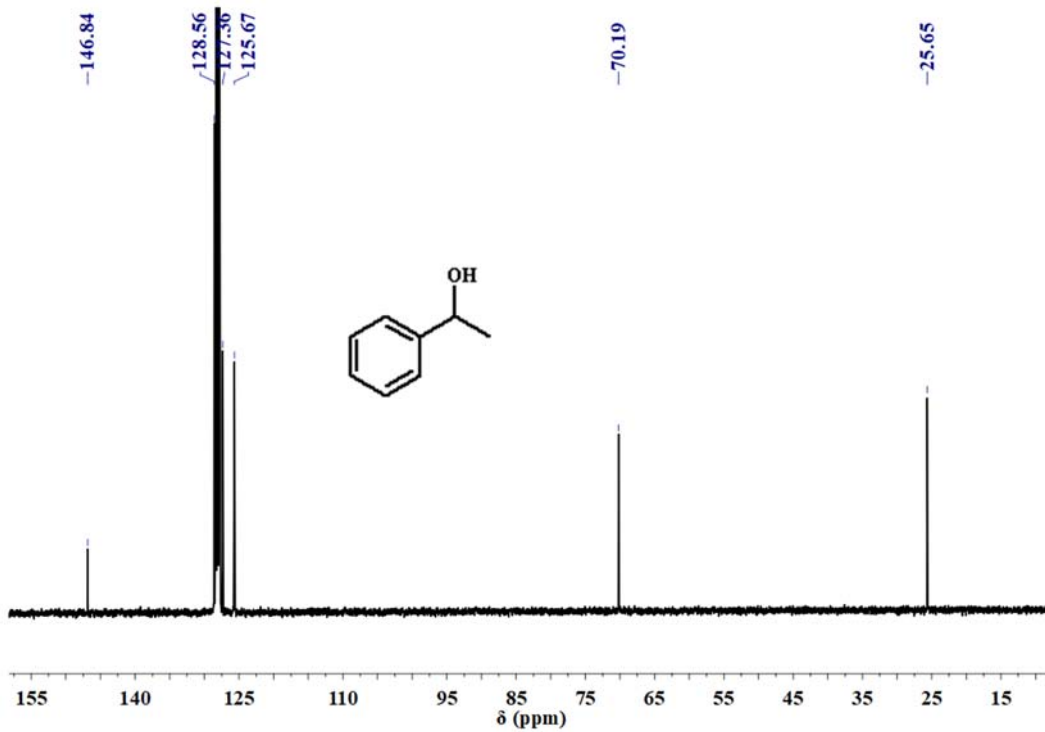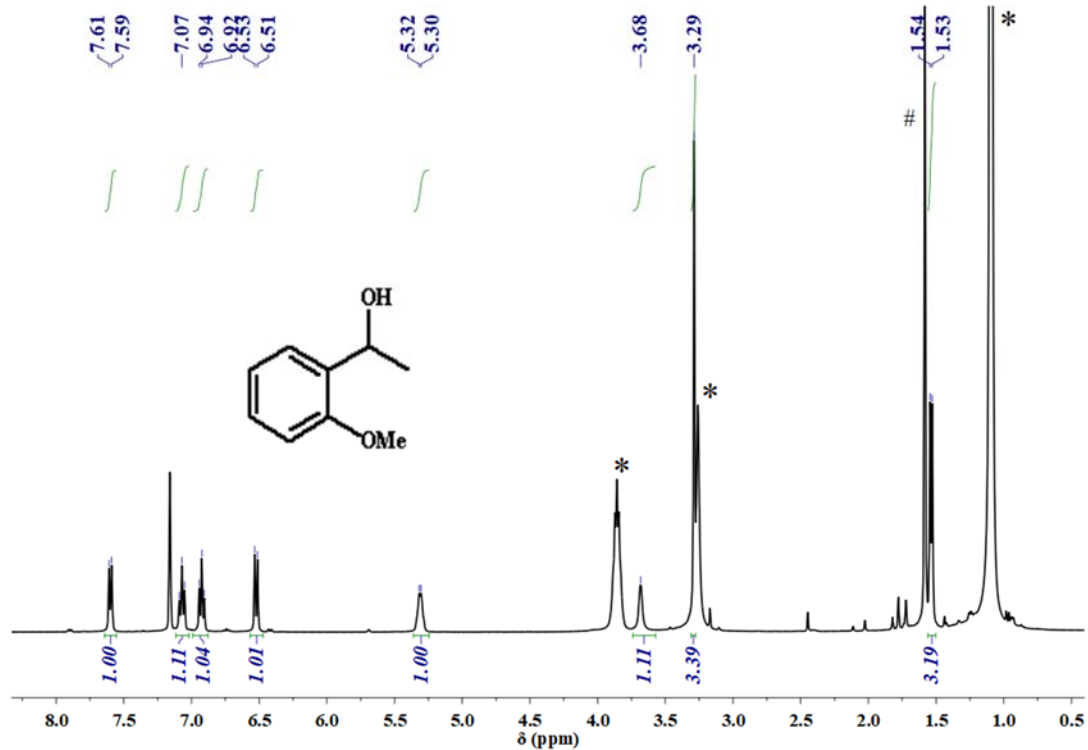

Figure S89: ^{13}C NMR spectrum of **4a** in C_6D_6.

Figure S90: ^{1}H NMR spectrum of **4b** in C$_6$D$_6$ in the reaction mixture.

Figure S91: ^{13}C NMR spectrum of **4b** in C$_6$D$_6$ in the reaction mixture.

Figure S92: ^{1}H NMR spectrum of **4c** in C_6D_6 in the reaction mixture.

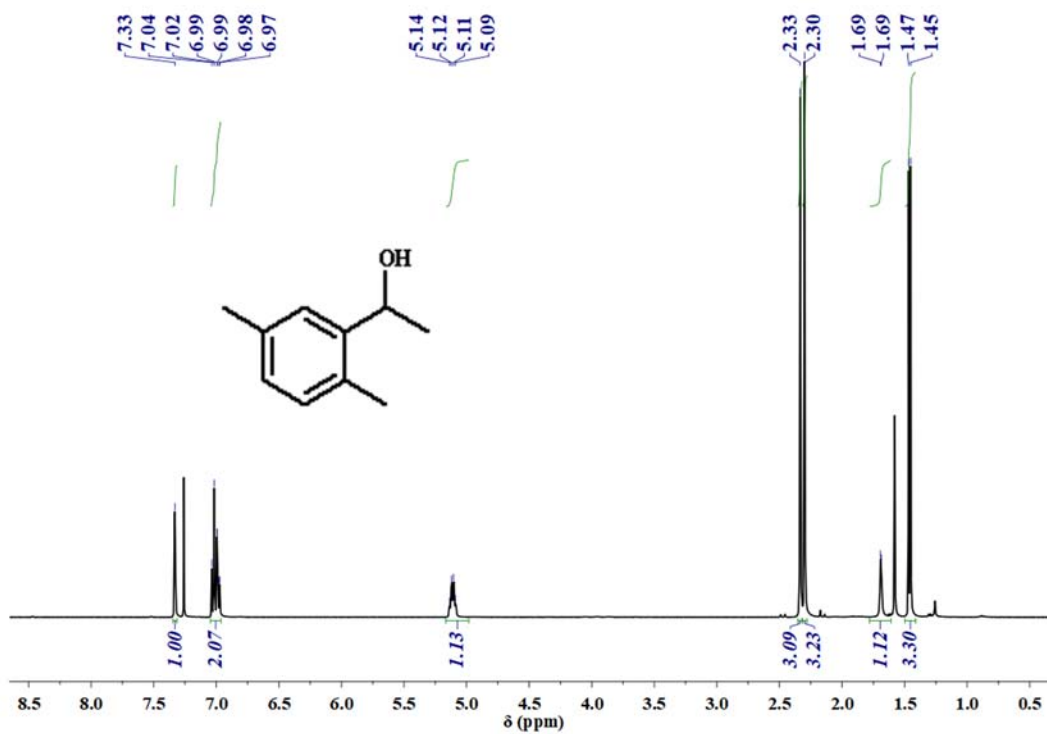**Figure S93**: ^{13}C NMR spectrum of **4c** in C_6D_6 in the reaction mixture.

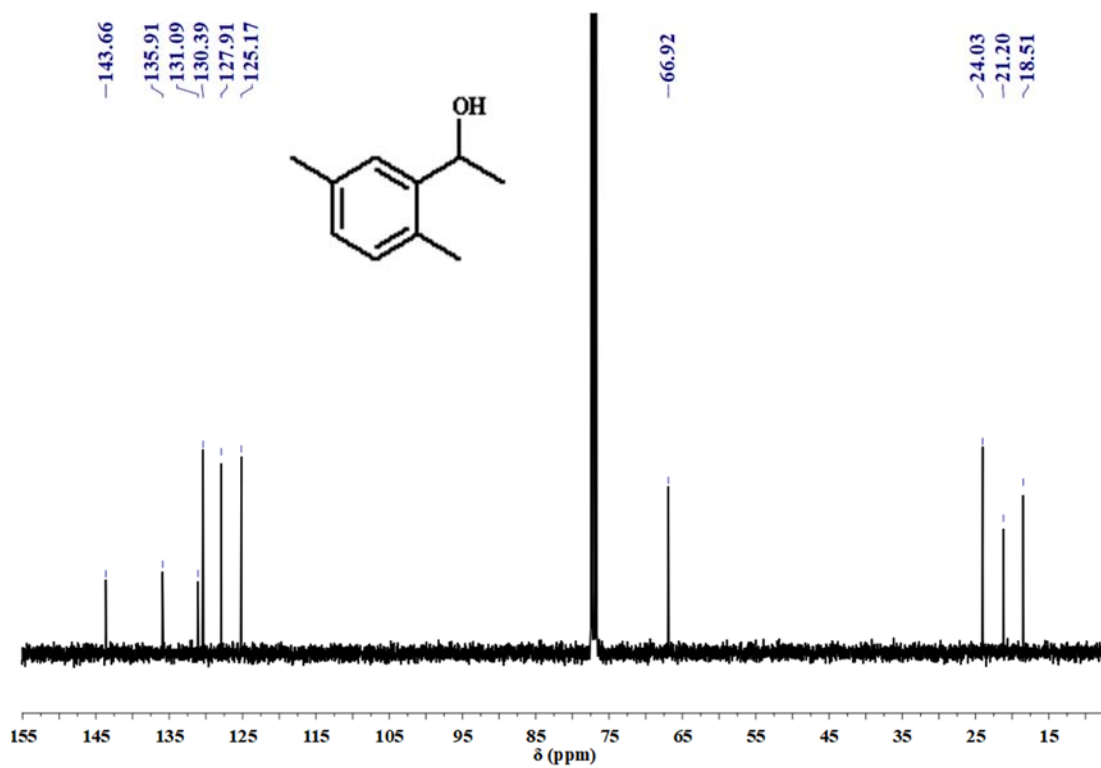**Figure S94**: ^{1}H NMR spectrum of **4d** in C_6D_6 in the reaction mixture.

Figure S95: ^{13}C NMR spectrum of **4d** in C_6D_6 in the reaction mixture.

Figure S96: ^{1}H NMR spectrum of **4e** in C$_6$D$_6$ in the reaction mixture.

Figure S97: ^{13}C NMR spectrum of **4e** in C$_6$D$_6$ in the reaction mixture.

Figure S98: ^{1}H NMR spectrum of **4f** in C$_6$D$_6$ in the reaction mixture.

Figure S99: ^{13}C NMR spectrum of **4f** in C$_6$D$_6$ in the reaction mixture.
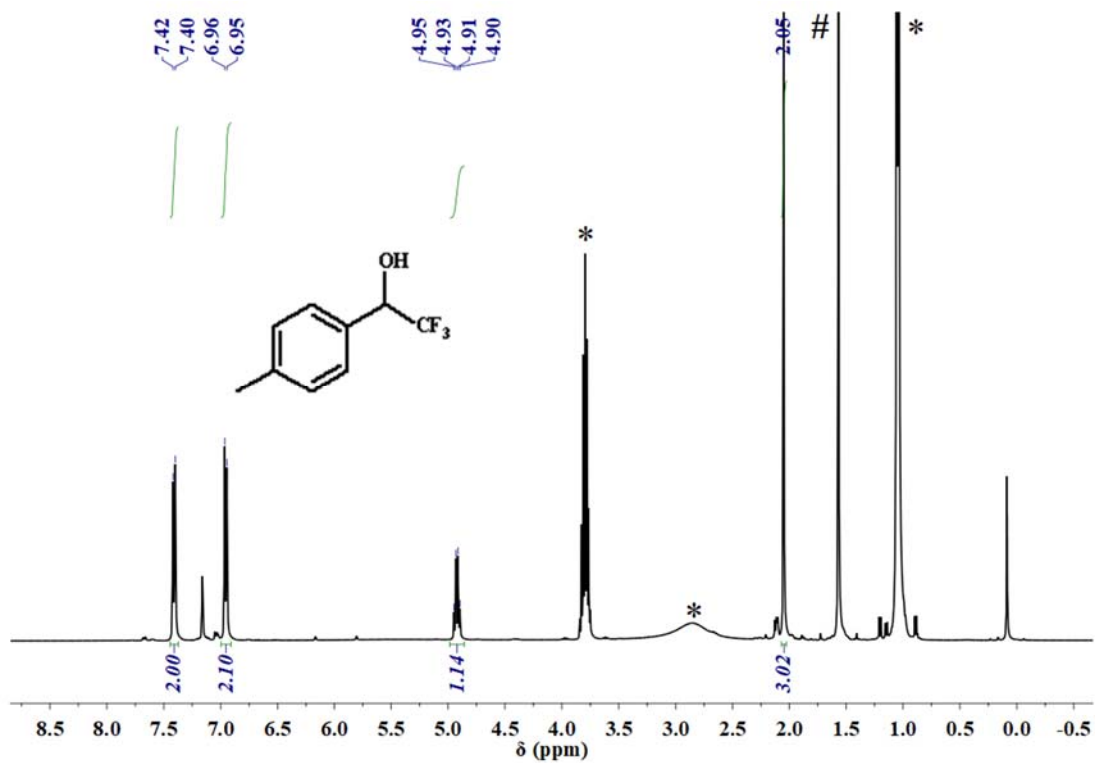
76

Figure S100: ^1H NMR spectrum of **4g** in C_6D_6 in the reaction mixture.
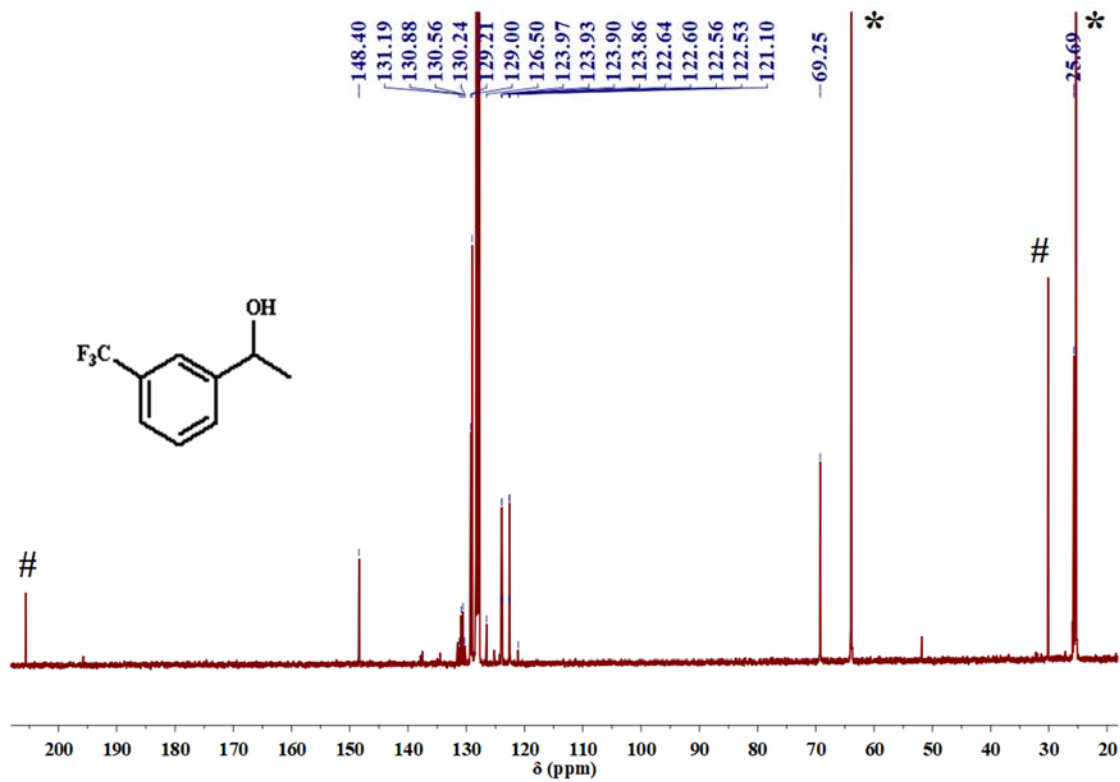
Figure S101: ^{13}C NMR spectrum of **4g** in C_6D_6 in the reaction mixture.
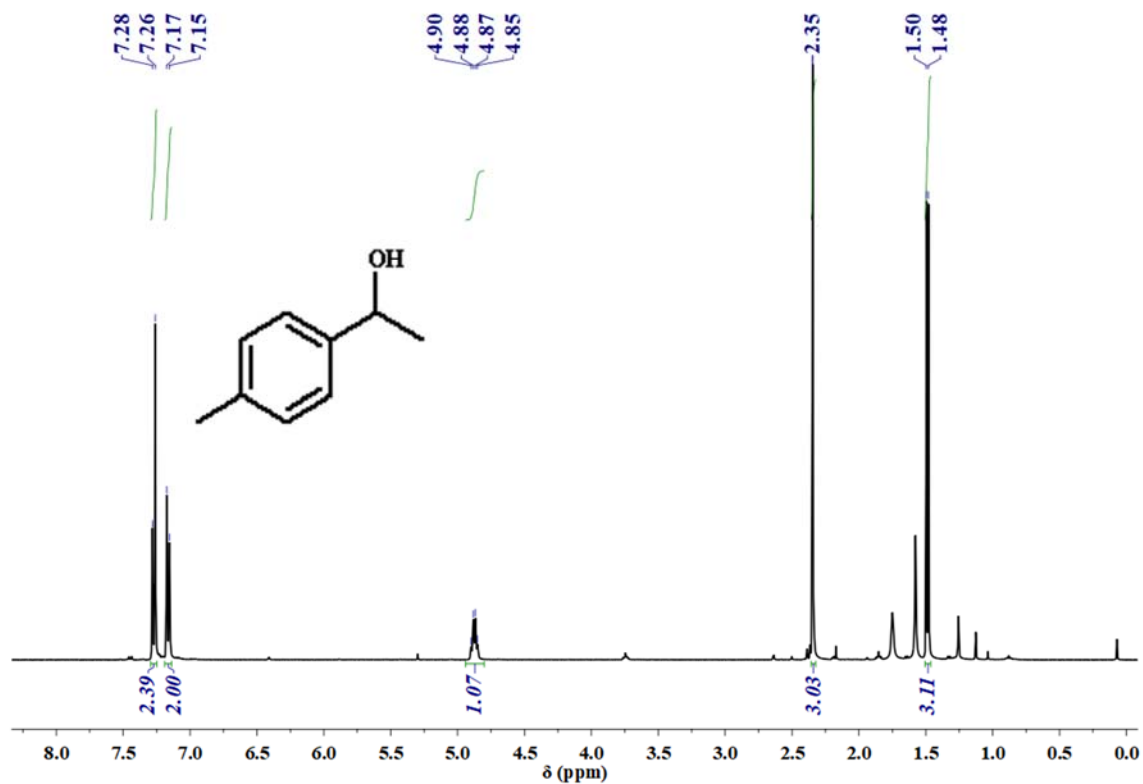
Figure S102: ^1H NMR spectrum of **4h** in CDCl$_3$.
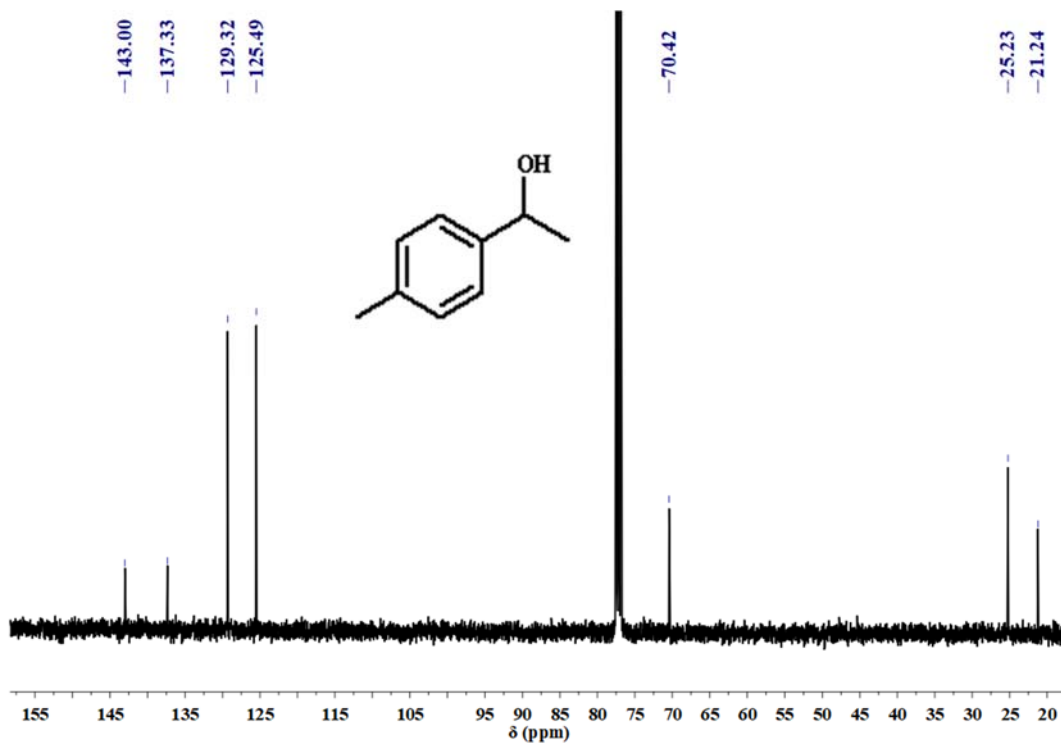
Figure S103: ^{13}C NMR spectrum of **4h** in CDCl$_3$.

78
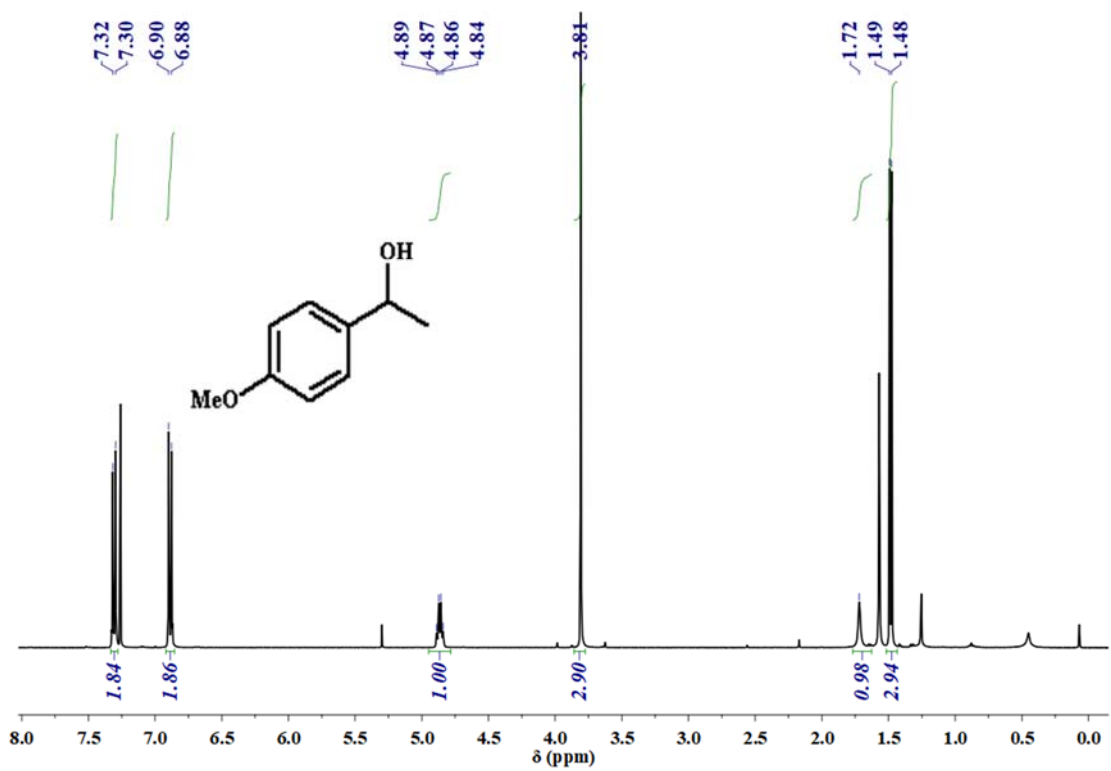
Figure S104: ^{1}H NMR spectrum of **4i** in CDCl$_3$.
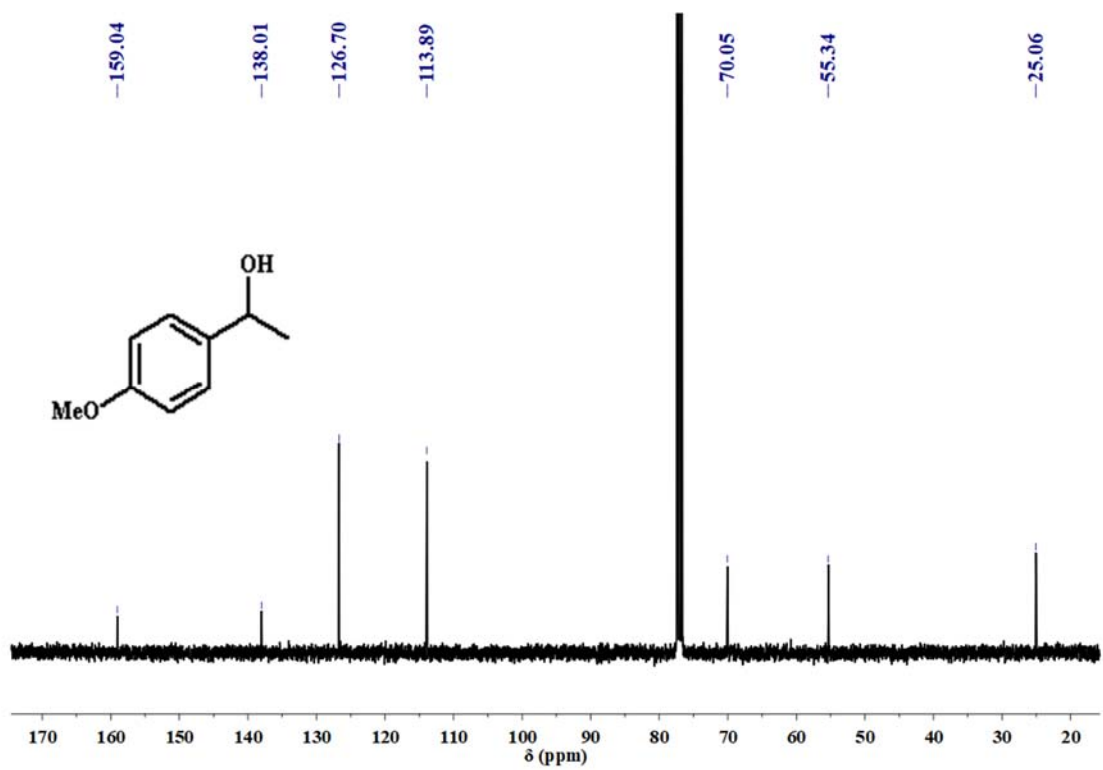
Figure S105: ^{13}C NMR spectrum of **4i** in CDCl$_3$.

Figure S106: ^{1}H NMR spectrum of **4j** in C$_6$D$_6$ in the reaction mixture.
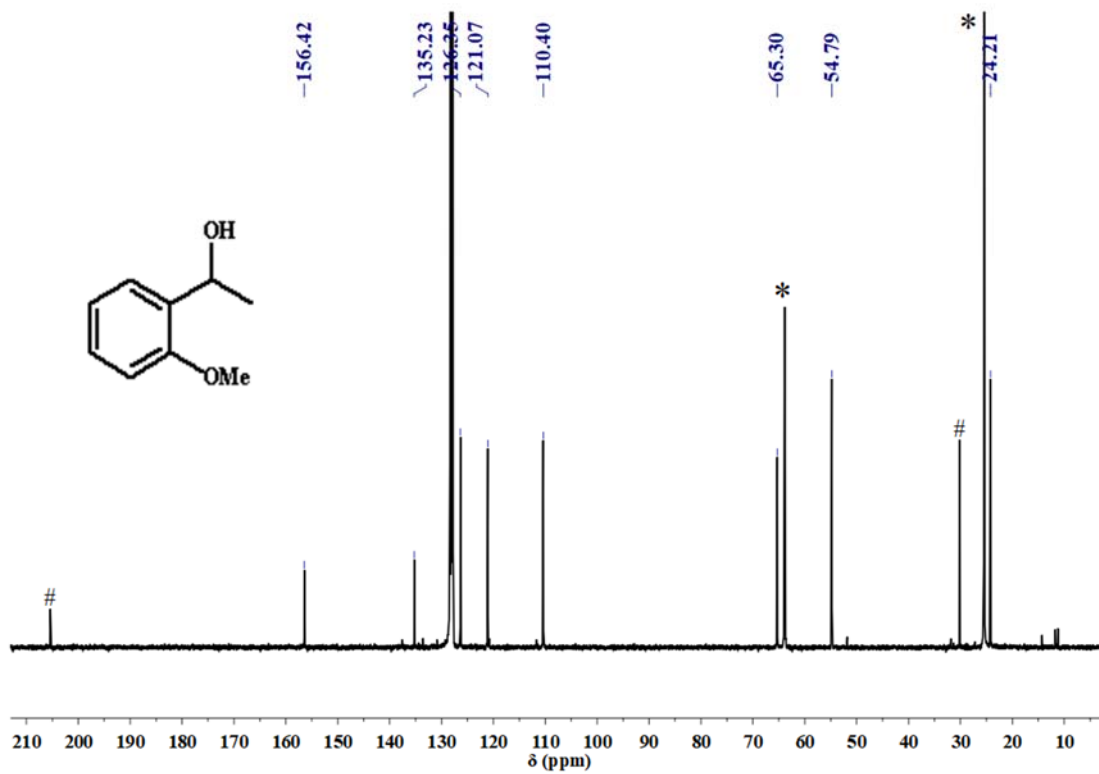
Figure S107: ^{13}C NMR spectrum of **4j** in C$_6$D$_6$ in the reaction mixture.
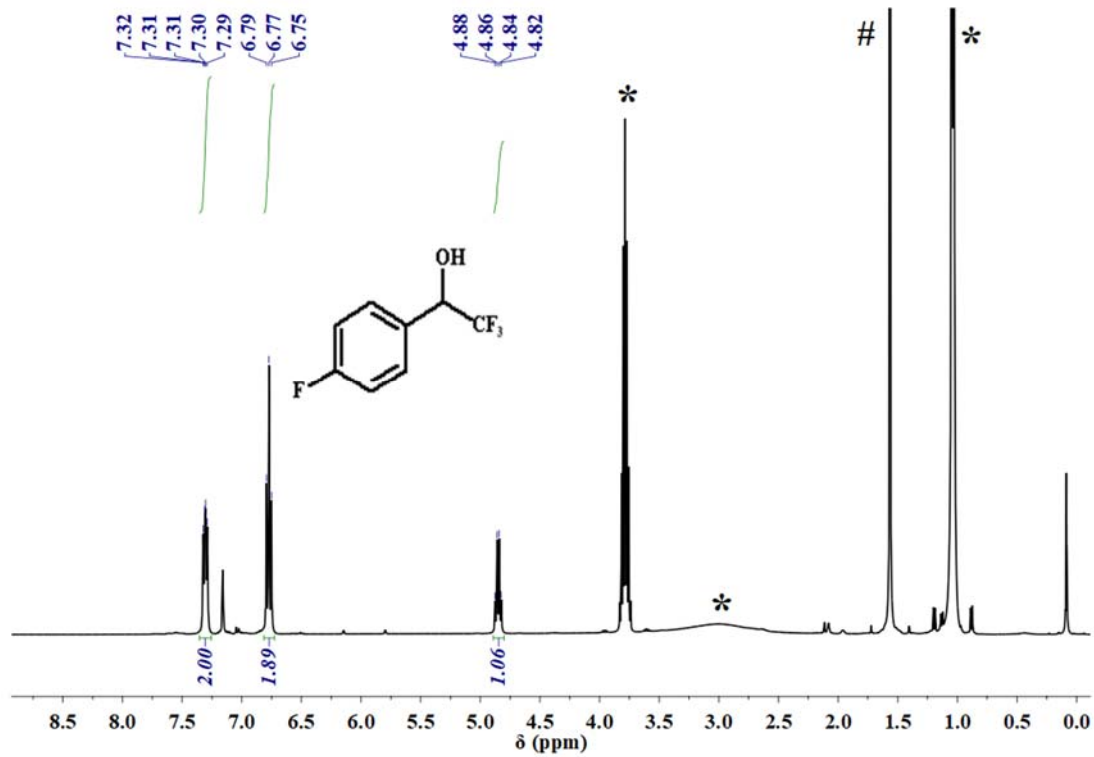
Figure S108: ^{1}H NMR spectrum of **4k** in CDCl$_3$.

Figure S109: ^{13}C NMR spectrum of **4k** in CDCl$_3$.
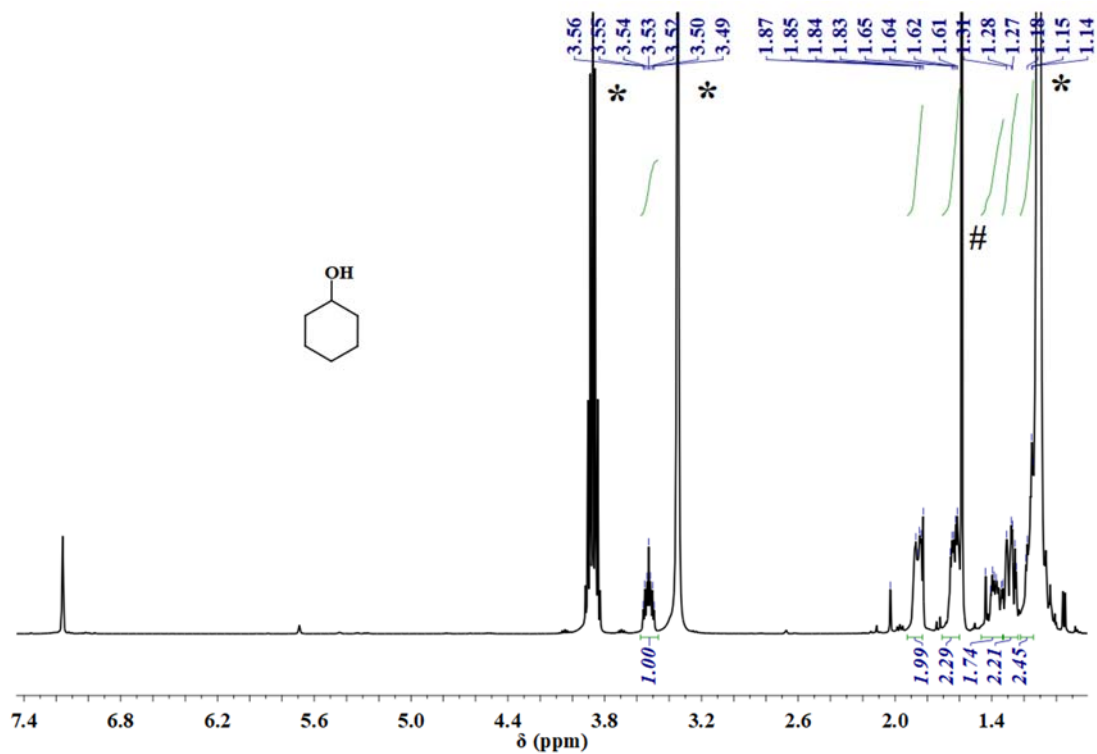
Figure S1110: ^{1}H NMR spectrum of **4l** in CDCl$_3$.
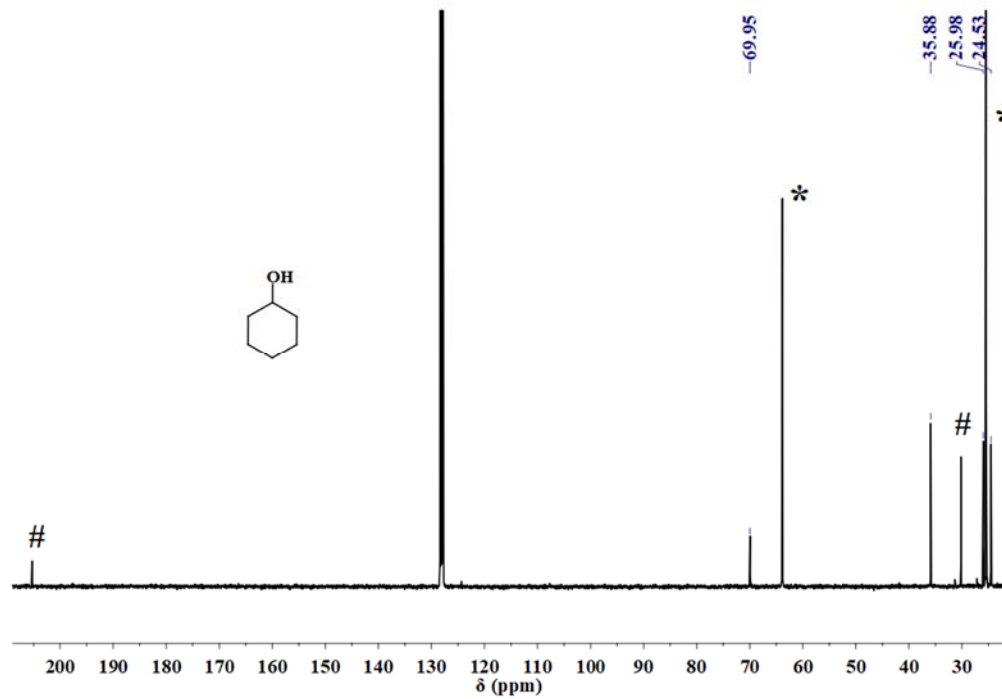
Figure S1111: ^{13}C NMR spectrum of **4l** in CDCl$_3$.
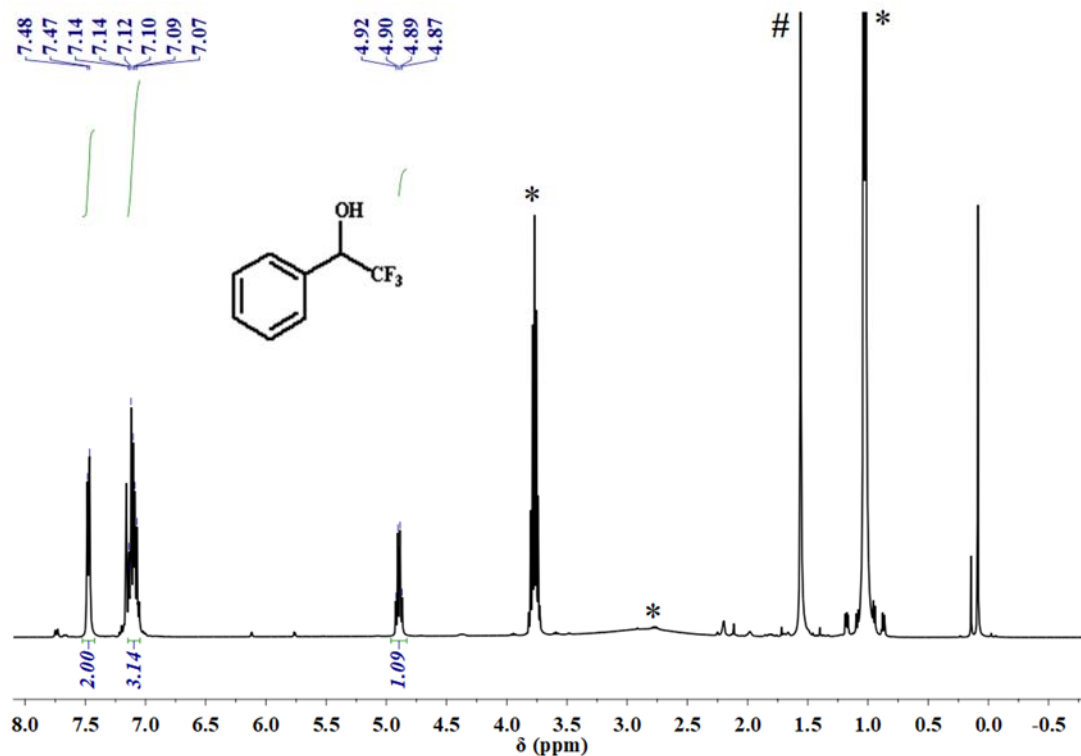
Figure S112: ^1H NMR spectrum of **4m** in C_6D_6 in the reaction mixture.
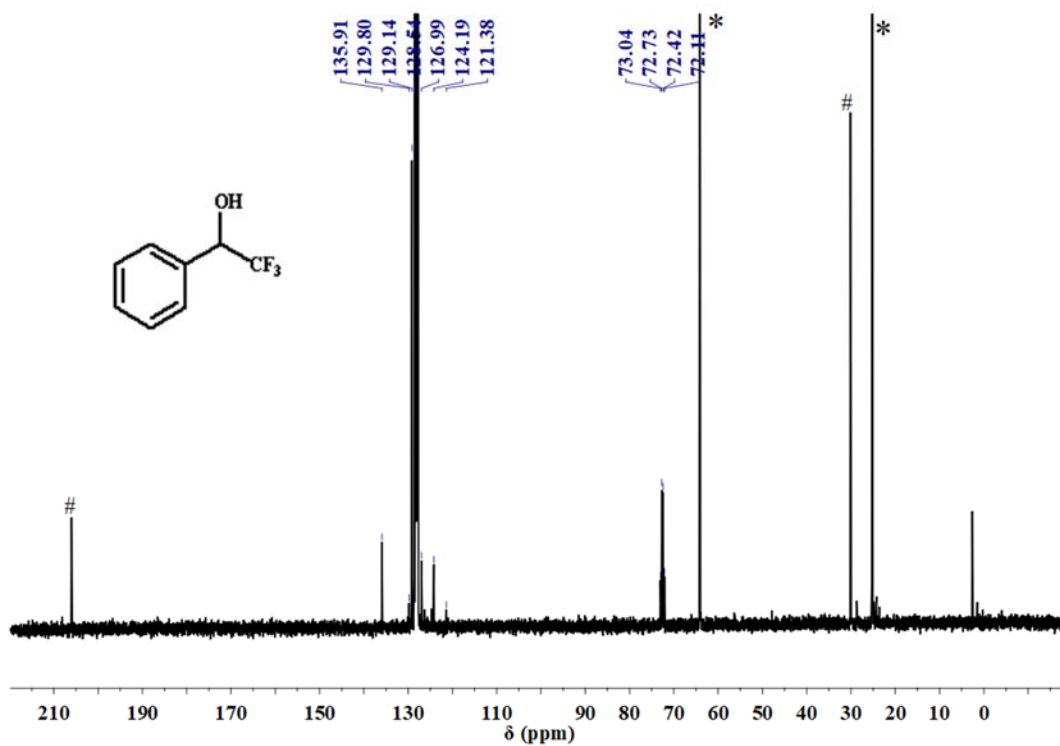
Figure S113: ^{13}C NMR spectrum of **4m** in C_6D_6 in the reaction mixture.

Figure S114: ^{1}H NMR spectrum of **4n** in C$_6$D$_6$ in the reaction mixture.
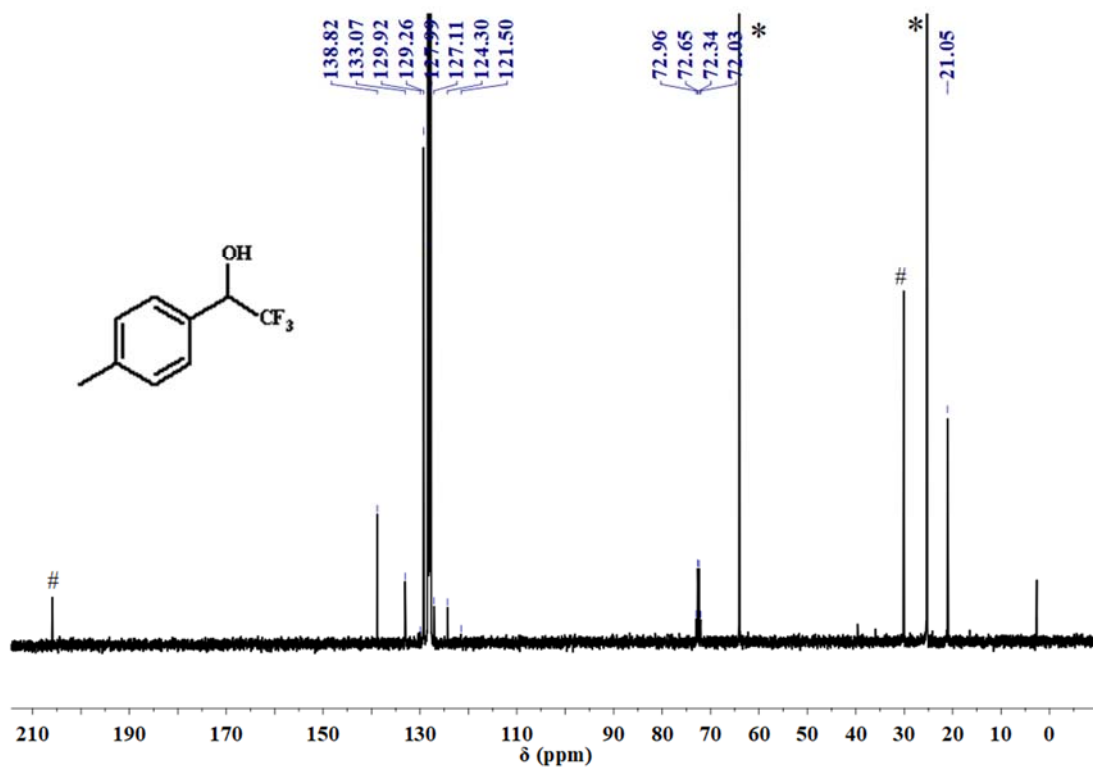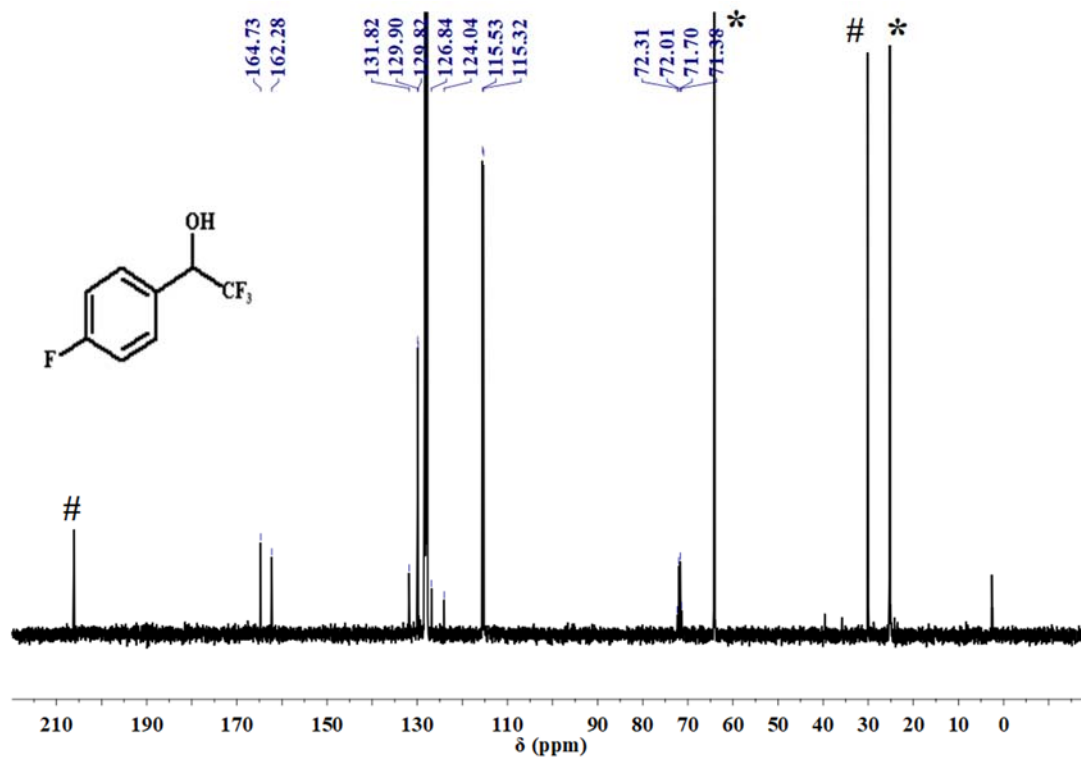

Figure S115: ^{1}H NMR spectrum of **4n** in C$_6$D$_6$ in the reaction mixture.

Figure S116: ^1H NMR spectrum of **4o** in C_6D_6 in the reaction mixture.

Figure S117: ^{13}C NMR spectrum of **4o** in C_6D_6 in the reaction mixture.
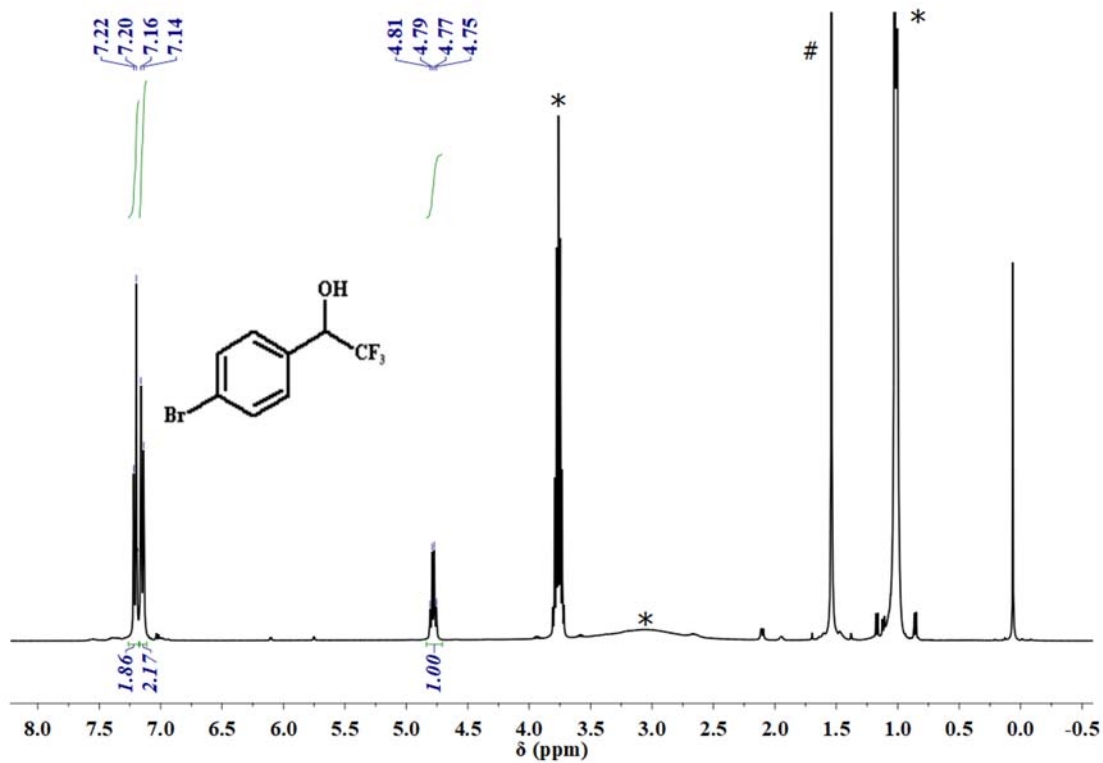
Figure S118: ^{1}H NMR spectrum of **4p** in C_6D_6 in the reaction mixture.
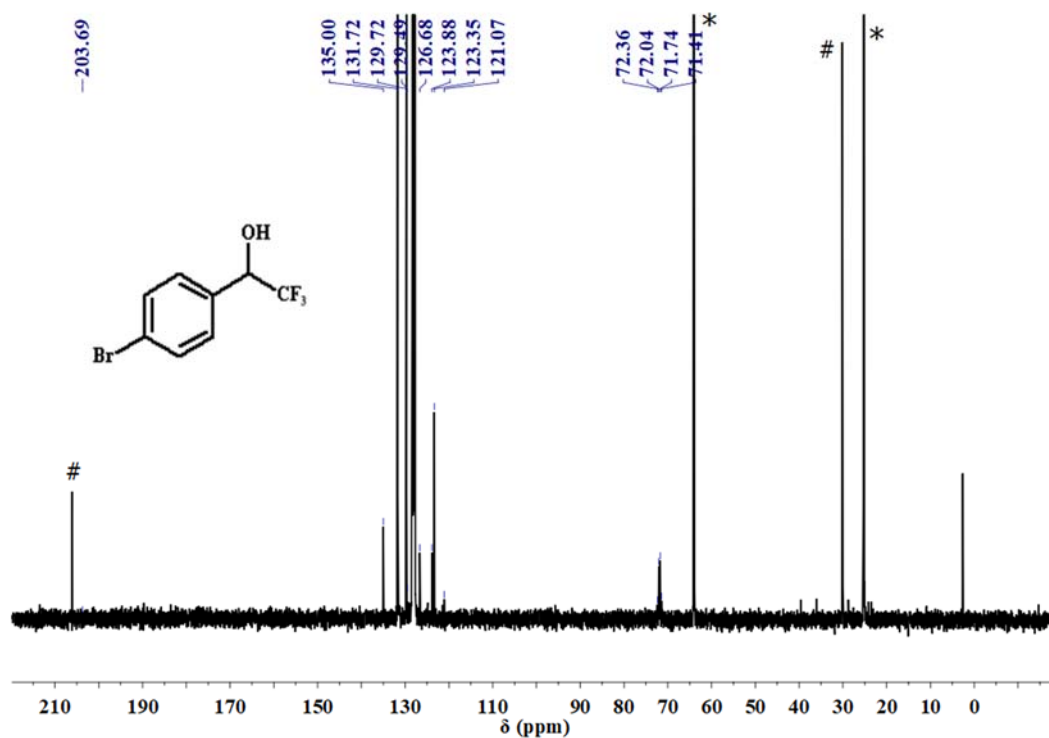
Figure S119: ^{13}C NMR spectrum of **4p** in C_6D_6 in the reaction mixture.
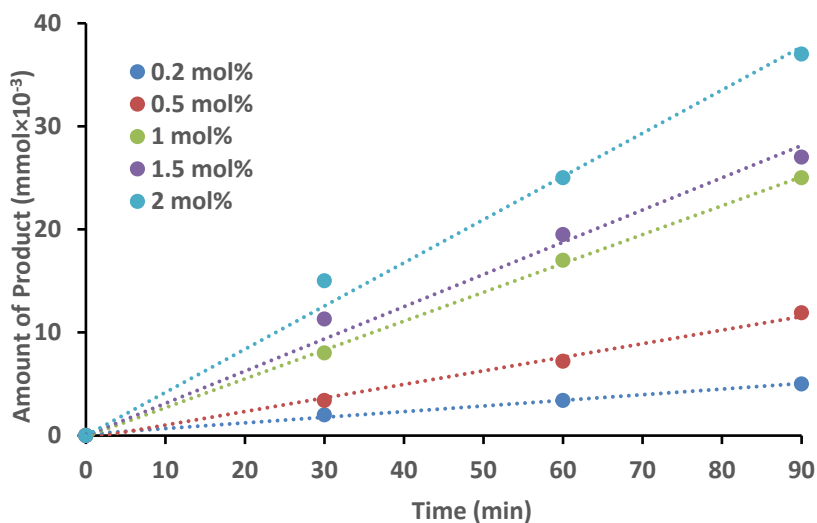
7. Kinetic and thermodynamic study

Figure S120. Plot of the amount of product (mmol X10^{-3}) vs. time (min) at different concentrations of complex **4** in the reaction of acetophenone (0.1 mmol) and ^{i}PrOH (50 µL) catalyzed the complex at 80 °C.

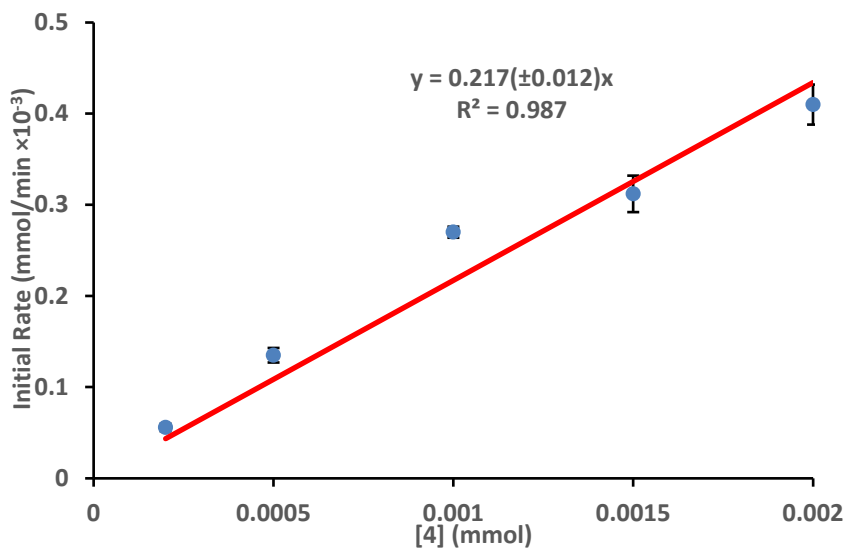| [4] (mmol)×10^{-3}	Initial Rate (mmol/min)×10^{-3} (Standard error)	ln[4]	ln(Initial Rate)
0.2	0.055(±0.004)	-8.517	-9.80(±0.07)
0.5	0.135(±0.008)	-7.600	-8.91(±0.06)
1	0.27(±0.006)	-6.907	-8.22(±0.02)
1.5	0.31(±0.02)	-6.502	-8.07 (±0.06)
2	0.41(±0.02)	-6.214	-7.80(±0.05)

Figure S121. Plot of Initial Rate vs. [**4**] in the reaction of acetophenone (0.1 mmol) and ^{i}PrOH (50 µL) catalyzed by complex **4** at 80 °C.
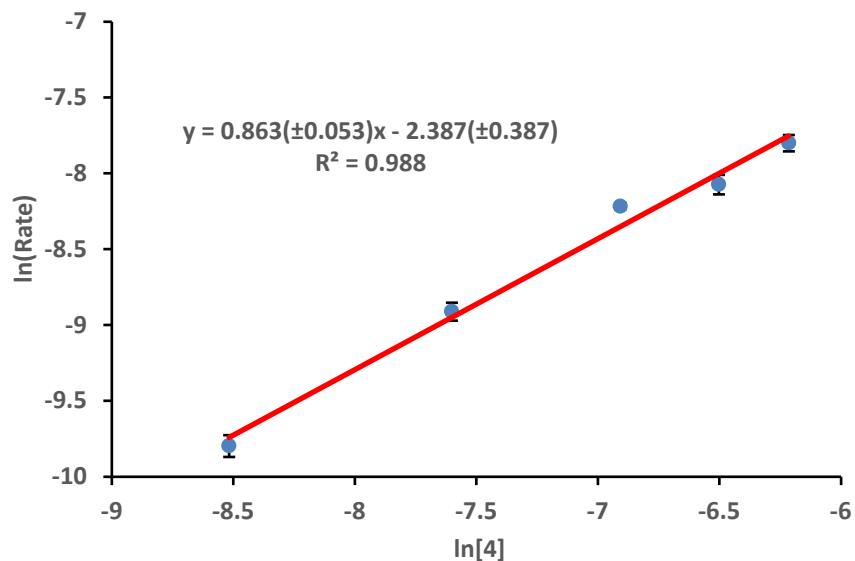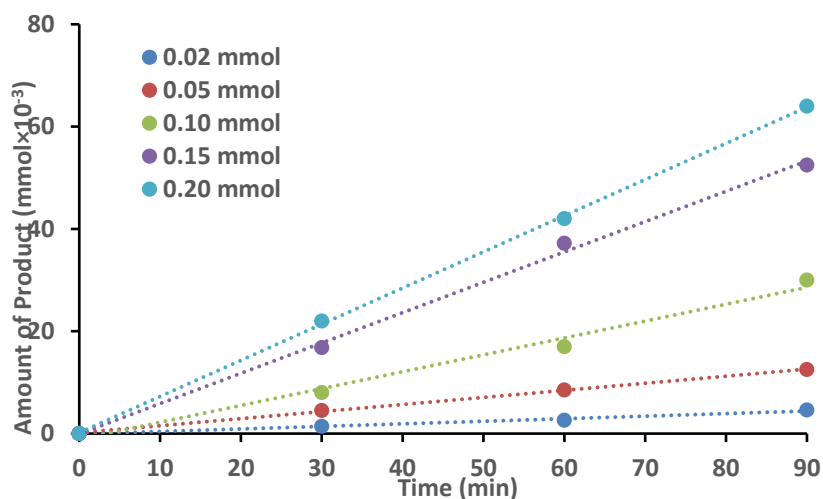
Figure S122. The plot of ln(Initial Rate) vs. ln[**4**].

Figure S123. Plot of Amount of product (mmol X10^{-3}) vs. time (min) at different concentrations of Acetophenone in the reaction of acetophenone and ^{i}PrOH (50 μL) catalyzed by complex **4** (0.001 mmol) at 80 °C.

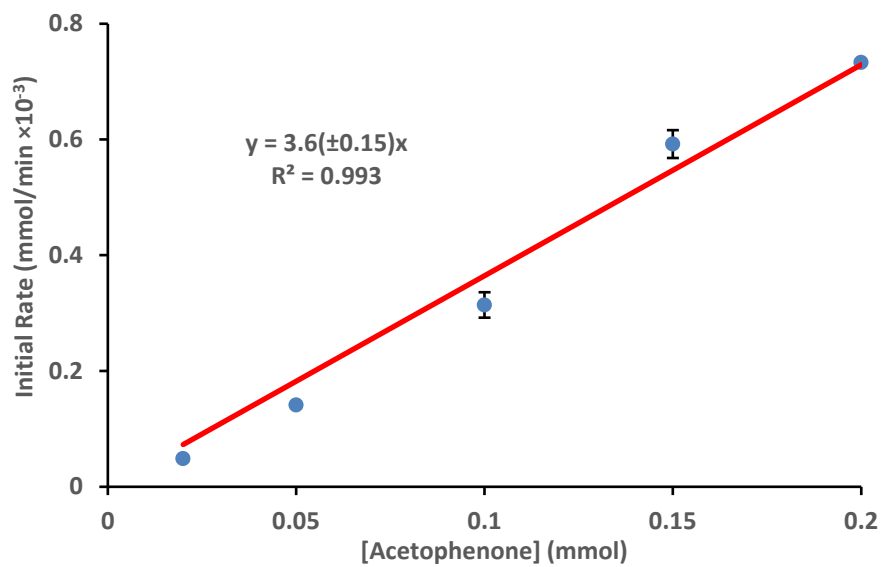| [Acetophenone] (mmol	Initial Rate (mmol/min) $\times 10^{-3}$ (Standard error)	ln[Acetophenone]	ln(Initial Rate)
0.02	0.048(±0.004)	-3.91202	-9.93(±0.08)
0.05	0.141(±0.003)	-2.99573	-8.87(±0.08)
0.1	0.31(±0.02)	-2.30259	-8.07(±0.07)
0.15	0.59(±0.02)	-1.89712	-7.43(±0.04)
0.2	0.733(±0.005)	-1.60944	-7.218(±0.007)

Figure S124. The plot of Initial Rate vs. [Acetophenone] in the reaction of acetophenone and ^{i}PrOH (50 μL) catalyzed by complex **4** (0.001 mmol) at 80 °C.
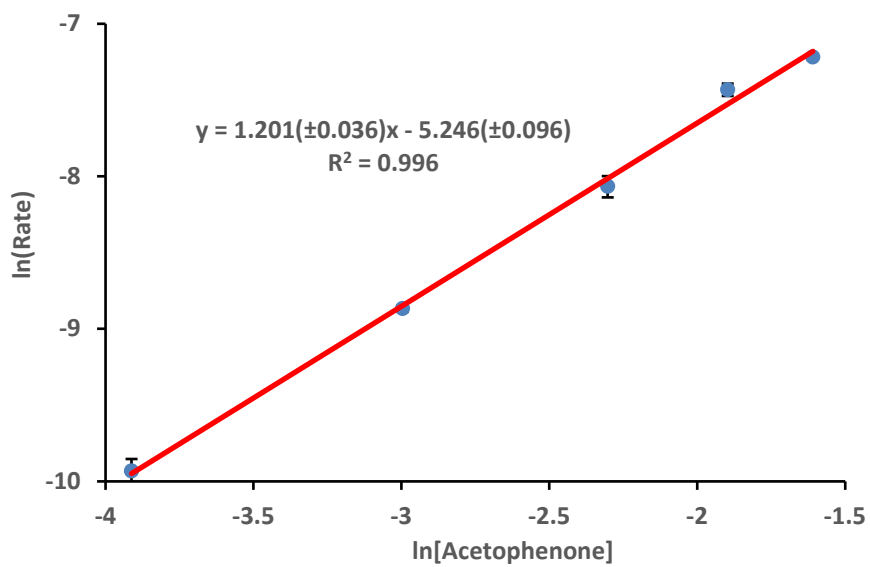

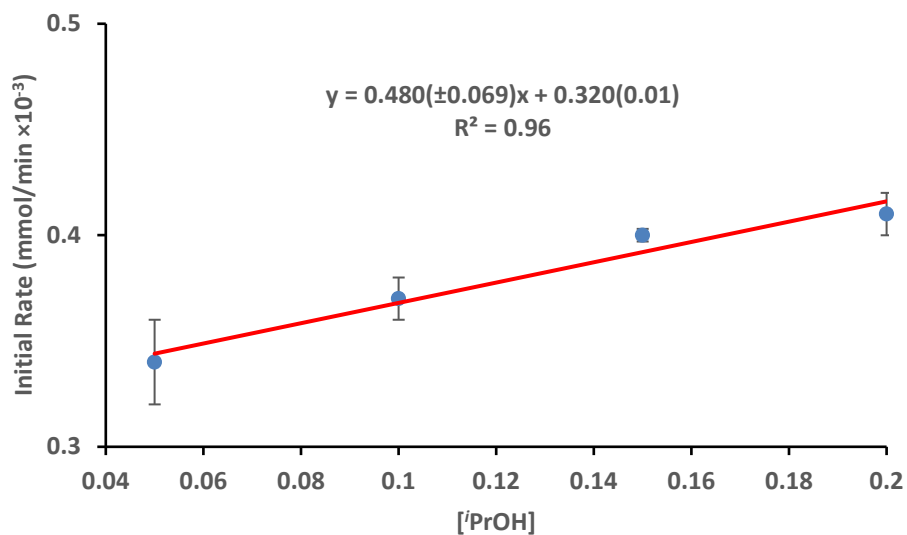**Figure S125**. Plot of ln(Initial Rate) vs. ln[Acetophenone].

Figure S126. Plot of Initial Rate vs. [^{i}PrOH] in the reaction of acetophenone (0.2 mmol) and ^{i}PrOH catalyzed by complex **4** (0.001 mmol) at 80 °C.
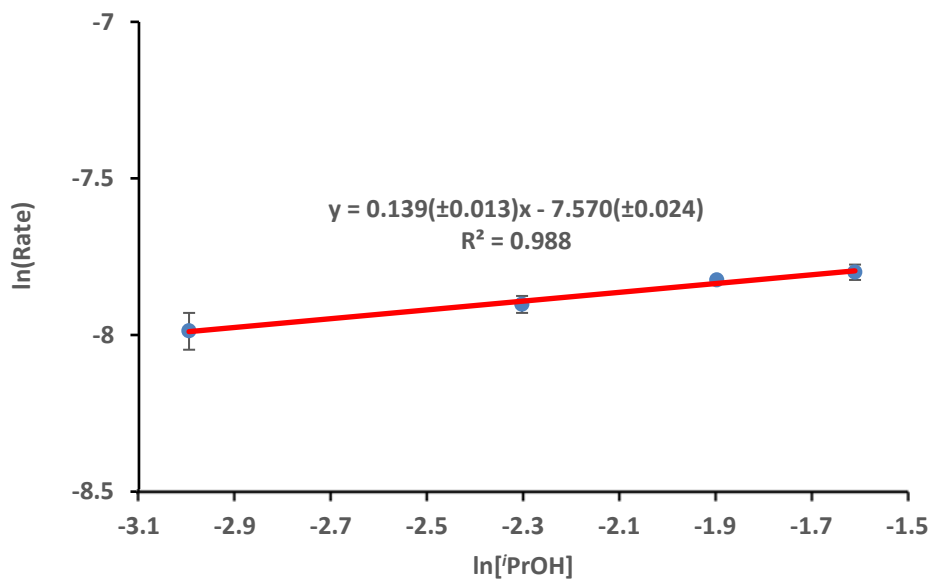

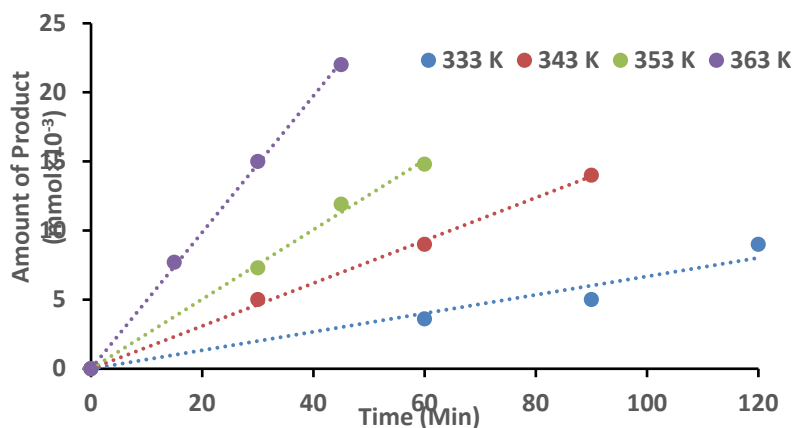**Figure S127**. Plot of ln(Initial Rate) vs. ln[^{i}PrOH].

Figure S128. Plot of Amount of product (mmol X10^{-3}) vs. time (min) at different temperatures in the reaction of acetophenone (0.1 mmol) and ^{i}PrOH (50 µL) catalyzed by complex **4** (0.001 mmol).

Temperature (K)	Initial Rate (mmol/min)×10^{-3}(Standard error)	1/T (K^{-1})	k/T	lnk	ln(k/T)
333	0.067(±0.005)	0.003003	2.012E-07	-9.61082	-15.419
343	0.155(±0.002)	0.002915	4.518E-07	-8.77209	-14.6098
353	0.252(±0.005)	0.002833	7.138E-07	-8.28608	-14.1525
363	0.494(±0.004)	0.002755	1.360E-06	-7.61298	-13.5074

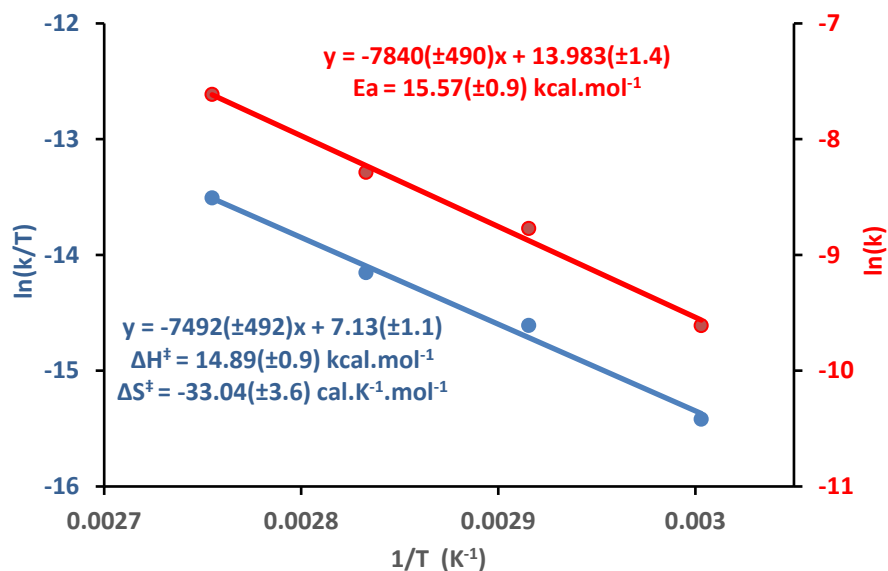**Figure S129**. Eyring plot (blue line) of ln(k/T) vs 1/T and Arrhenius plot (red line) of ln(k) vs 1/T for the reaction of acetophenone (0.1 mmol) and ^{i}PrOH (50 µL) catalyzed by complex **4** (0.001 mmol).
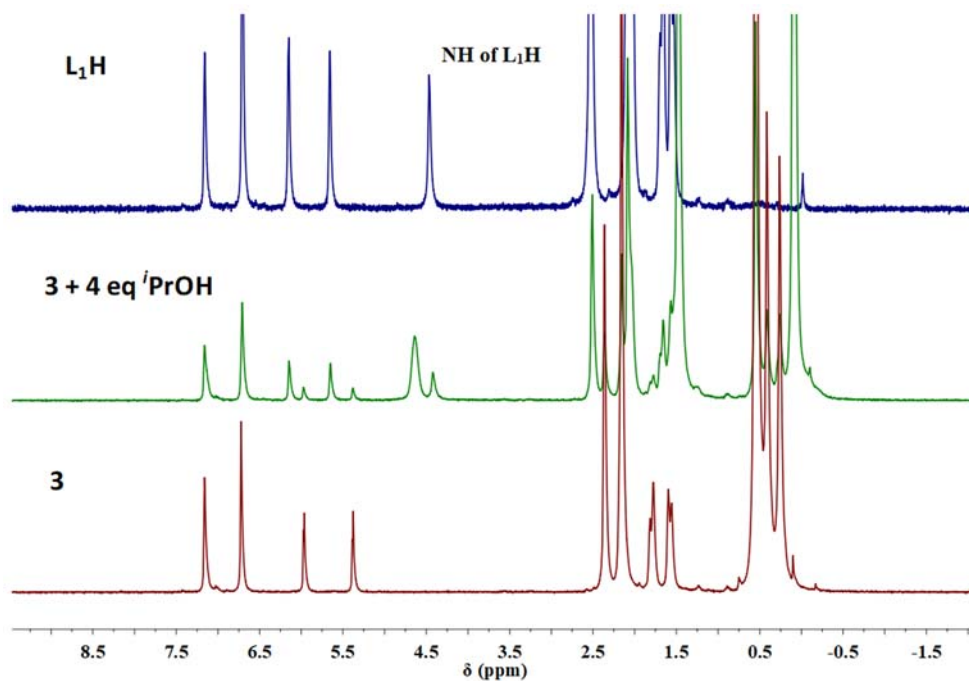
8. Stoichiometric study

Figure S130. ^{1}H NMR study of 1:4 mixture of **3** and ^{i}PrOH in C$_6$D$_6$. The green line shows the formation of ligand L$_1$H and Th(O^{i}Pr)$_4$.
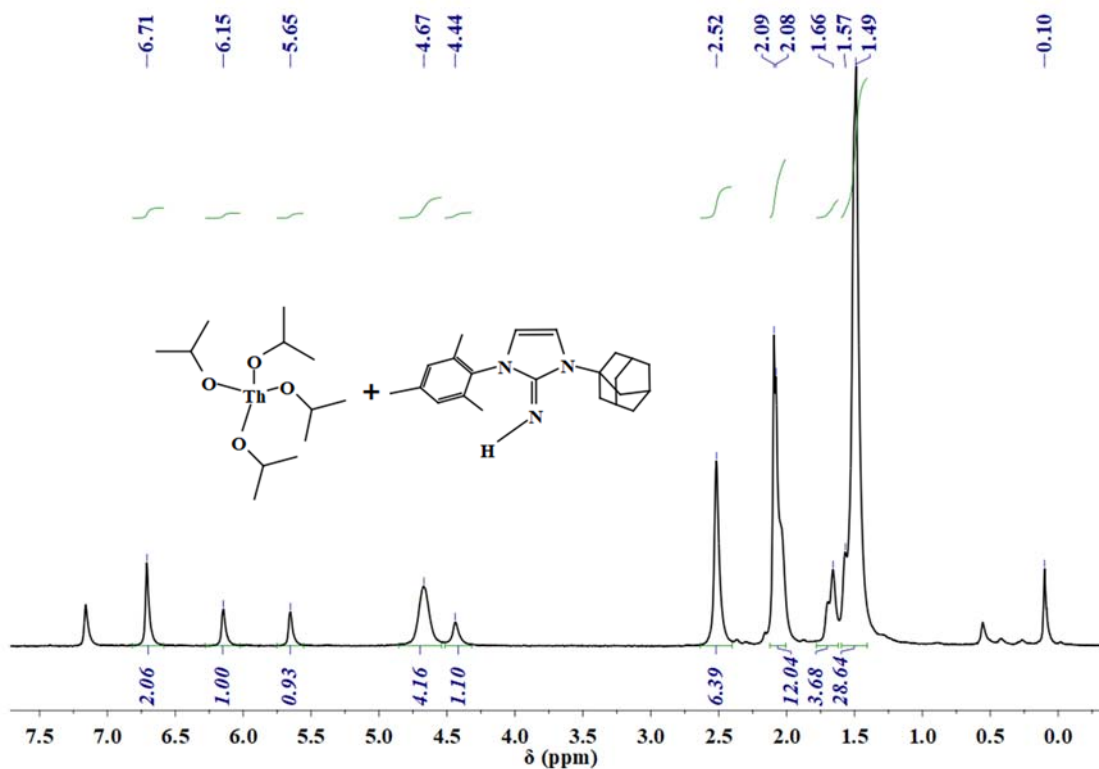
Figure S131. ^{1}H NMR of L$_1$H and Th(O^{i}Pr)$_4$ formed by the reaction of **3** and ^{i}PrOH.
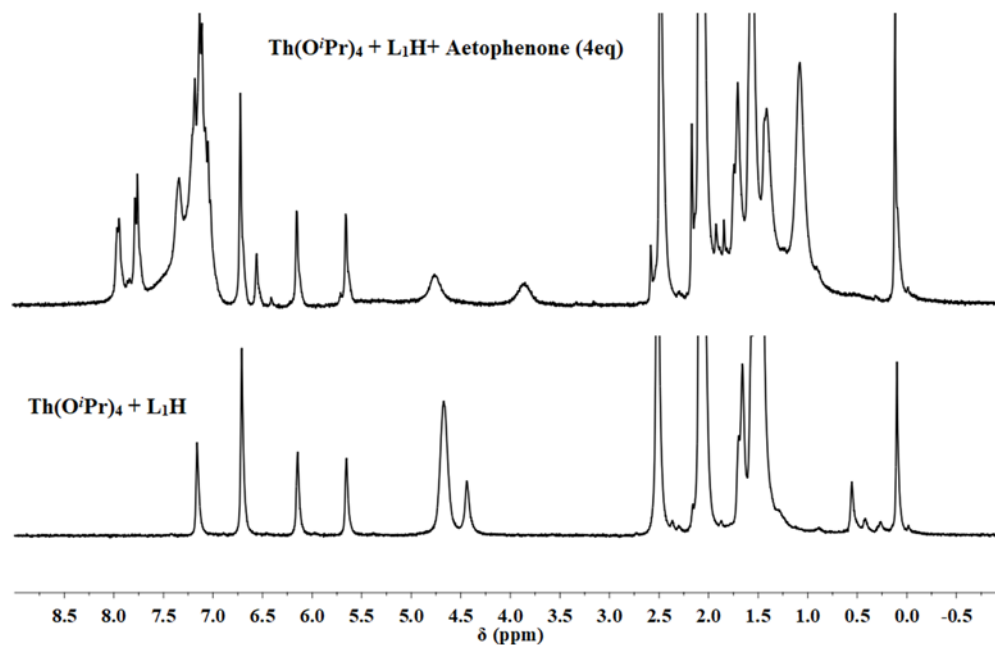
Figure S132. ^{1}H NMR study of product formed by the reaction of and ^{i}PrOH in C$_6$D$_6$ ((Th(O^{i}Pr)$_4$ + L$_1$H) (bottom line) and 4 equivalent of acetophenone (top line).
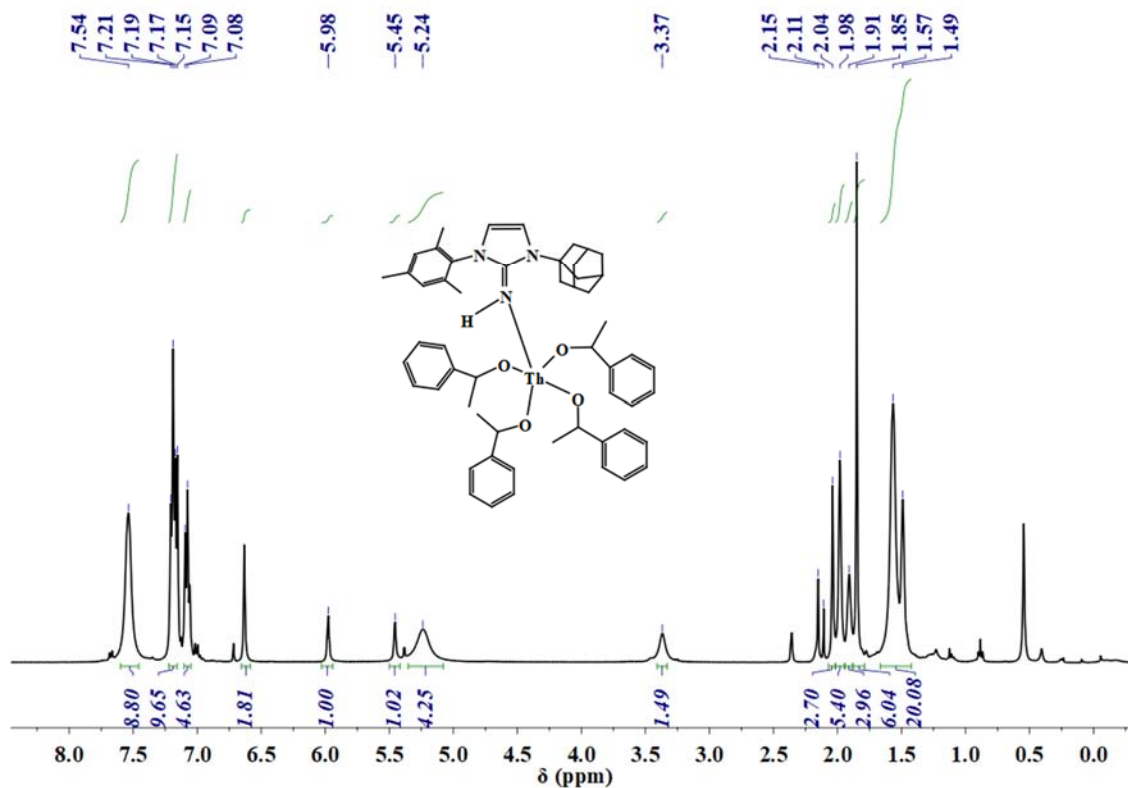
Figure S133. ^{1}H NMR of Th(L$_1$H)(O(CH)(CH$_3$)Ph)$_4$ (**A**) formed by the reaction of **3** and ^{i}PrOH and then acetophenone.
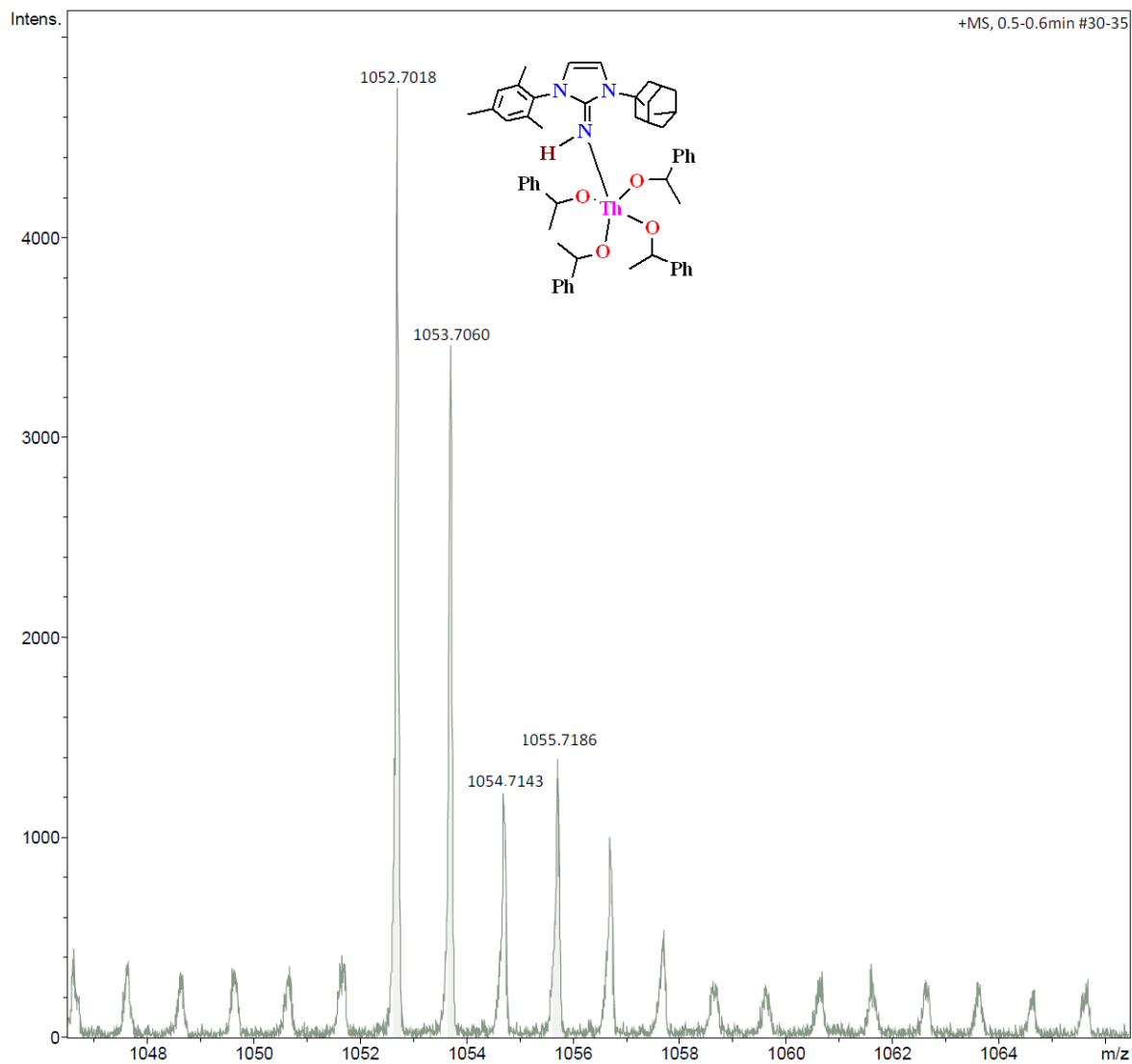
Figure S134. APCI mass analysis of product formed by the reaction of **3** and ^{i}PrOH (Excess) in C_6D_6 and 4 equivalent of acetophenone.
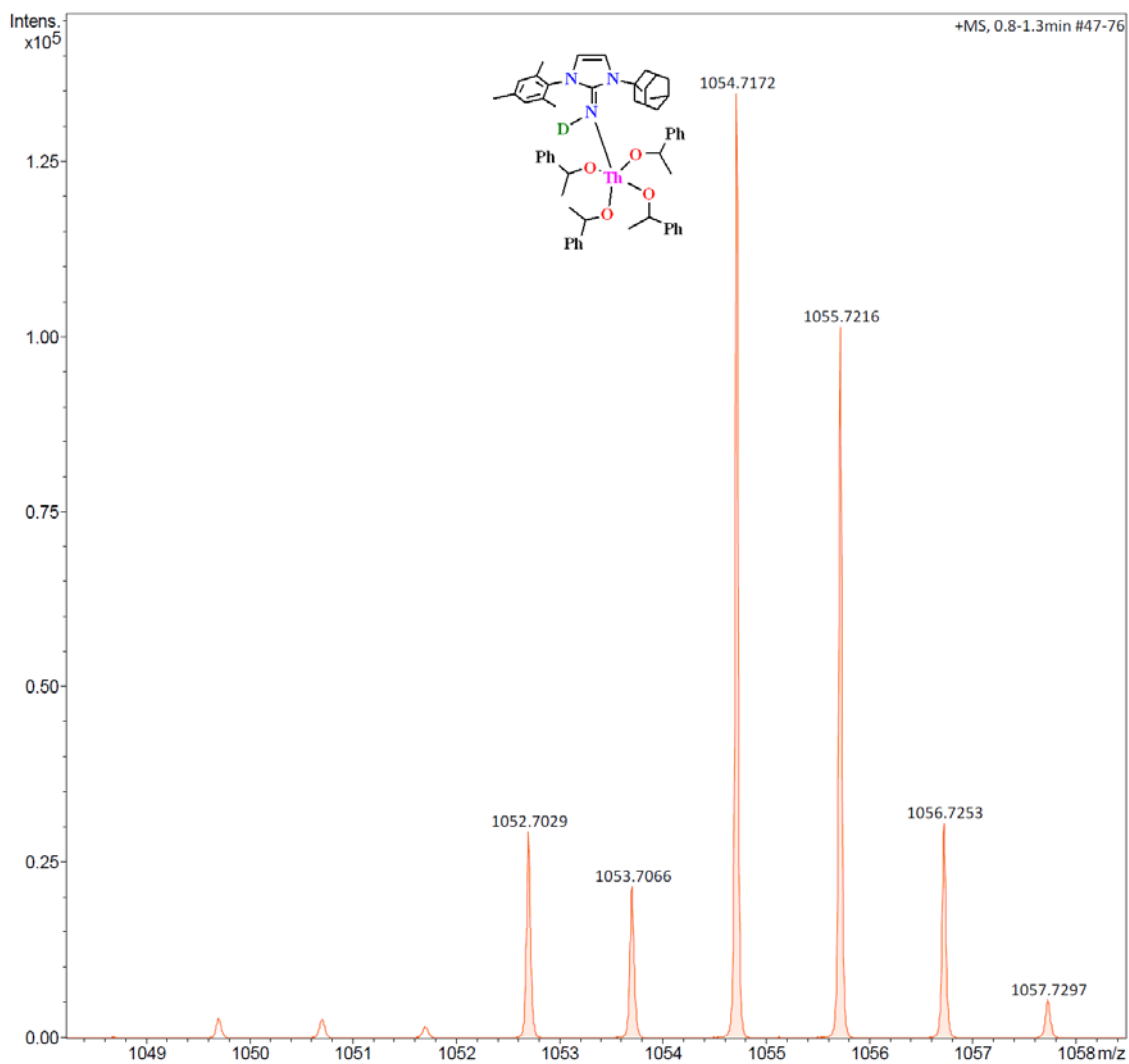
Figure S135. APCI mass analysis of product formed by the reaction of **3** and ^{i}PrOD (Excess) in C_6D_6 and 4 equivalent of acetophenone.
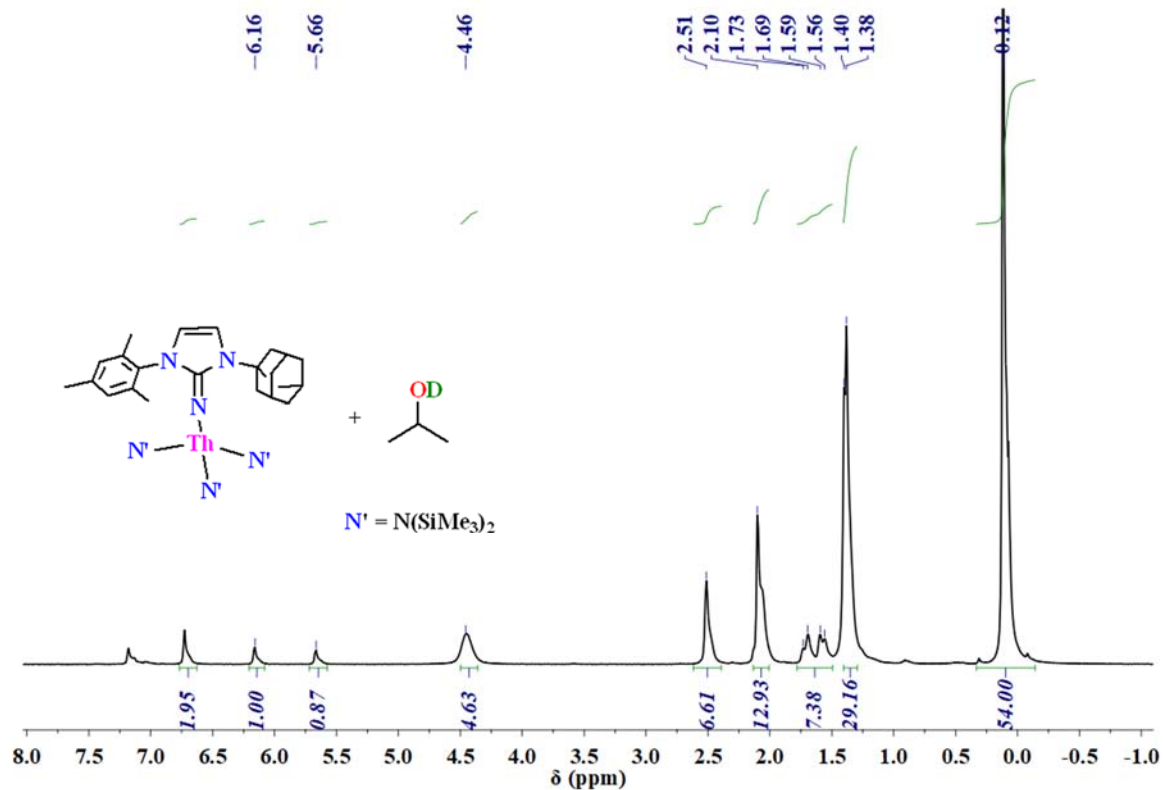
Figure S133. ^{1}H NMR of reaction of **3** and ^{i}PrOD.

9. References

S1. M. Koneczny, A. B. Erol, M. Mauduit, M. S. Eisen and M. Tamm, *Dalton Trans.*, 2022, **51**, 11448-11456

S2. P. Queval, C. Jahier, M. Rouen, I. Artur, J.-C. Legeay, L. Falivene, L. Toupet, C. Crévisy, L. Cavallo, O. Baslé et al., *Angew. Chem. Int. Ed.* 2013, **52**, 14103.

S3. R. Tarrieu, A. Dumas, J. Thongpaen, T. Vives, T. Roisnel, V. Dorcet, C. Crévisy, O. Baslé, M. Mauduit, *J. Org. Chem.* 2017, **82**, 1880.