Electronic Supplementary Information

Bis(*N*-heterocyclic carbene)-Borylene-Mediated Heteroallene Activation

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S1. Experimental Section

General procedure. All operations were carried out under an inert atmosphere of argon gas by standard Schlenk techniques. [(IMe)$_2$BMes] (**1**) was synthesized according to literature.[1] All other chemicals were purchased from Sigma-Aldrich and used directly without further purification. All solvents were dried over K metal or CaH_2 prior to use. The ^{1}H, ^{11}B{^{1}H}, ^{19}F and ^{13}C{^{1}H} NMR spectra were recorded on a JEOL ECA 400 spectrometer or Bruker Avance III 400. The NMR spectra were recorded in deuterated solvents, and the chemical shifts are relative to $SiMe_4$ for ^{1}H and ^{13}C; $BF_3.Et_2O$ for ^{11}B and ^{19}F, respectively. The following abbreviations are used to describe signal multiplicities: s = singlet, d = doublet, t = triplet, sept = septet, dd = doublet of doublet, m = multiplet, brs = broad singlet. Coupling constants J are given in Hertz (Hz). HRMS spectra were obtained at the Mass Spectrometry Laboratory in the School of Chemistry, Chemical Engineering and Biotechnology, Nanyang Technological University. Melting points were measured with an OptiMelt automated melting point system.

Synthesis of 2

The 30 mL toluene solution of $DippN_3$ (0.3 mmol, 0.06 g) was added into a 100 mL Schlenk flask containing MesB(IMe)$_2$ (0.3 mmol, 0.11 g) at room temperature. After which, the reaction mixture was then stirred for four hours. The resulting yellow solution was then filtered. The filtrate was concentrated and kept at room temperature to obtain **2** as yellow single crystals (0.10 g, 76% yield). M.p.: 231 °C. ^{1}H NMR (399.5 MHz, C_6D_6, 25 °C): δ 7.33 (d, 2H, Ar-*H* (Dipp), $^3J_{H,H}$ = 7.5 Hz), 7.00 (t, 1H, Ar-*H* (Dipp), J_{HH} = 7.5 Hz), 6.78 (s, 2H, Ar-*H* (Mes)), 3.91 (sept, 2H, C*H*(CH$_3$)$_2$, J_{HH} = 6.8 Hz), 3.20 (s, 6H, N-C*H*$_3$), 2.29 (s, 6H, Ar-C*H*$_3$), 2.23 (s, 3H, Ar-C*H*$_3$), 1.43 (d, 6H, CH(C*H*$_3$)$_2$, $^3J_{H,H}$ = 6.8 Hz), 1.28 (d, 6H, CH(C*H*$_3$)$_2$, $^3J_{H,H}$ = 7.0 Hz), 1.12 (s, 6H, C-C*H*$_3$). ^{11}B{^{1}H} NMR (128.2 MHz, C_6D_6, 25 °C): δ 23.2 (br). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 25 °C): δ 153.7 (Ar-*C* (Dipp)), 140.3 (Ar-*C* (Mes)), 135.6 (Ar-*C* (Mes)), 134.1 (Ar-*C* (Mes)), 124.0 (*C*=*C*), 122.7 (Ar-*C* (Dipp)), 116.3 (Ar-*C* (Dipp)), 32.1 (N*C*H$_3$), 28.1 (*C*H(CH$_3$)$_2$), 25.2 (Ar-*C*H$_3$), 23.3 (CH(*C*H$_3$)$_2$), 22.8 (CH(*C*H$_3$)$_2$), 21.3 (Ar-*C*H$_3$), 7.6 (*C*H$_3$). HRMS (ESI): *m/z* calcd for. $C_{28}H_{41}BN_3$: 430.3394 [(*M* + *H*)]$^+$; found: 430.3395.

General procedure for the catalytic cyclotrimerization of isocyanates

Compound **1** (0.0013 g, 0.003 mmol, catalytic loading: 3 mol%) was added into a J-Young NMR tube and washed down with 0.2 mL of C_6D_6. Isocyanate substrates (0.30 mmol, 1 equiv.) were then added and washed down with 0.2 mL of C_6D_6, Subsequently, the J-Young NMR tube was shaken for solvation of all compounds. The reactions were followed by NMR spectroscopy and cyclohexane or 1,3,5-trimethoxybenzene was used as an internal standard to determine their yields. The chemical shifts of the products are in good agreement with the reported values in the literature.[2]

Isolation of products **4a**-**4d**

Upon solvation of compound **1** and substrates, the corresponding isocyanurates precipitated out as colorless crystals. The mother liquid was removed, and the crystals were washed with hexane and dried under vacuum to obtain the isocyanurates.

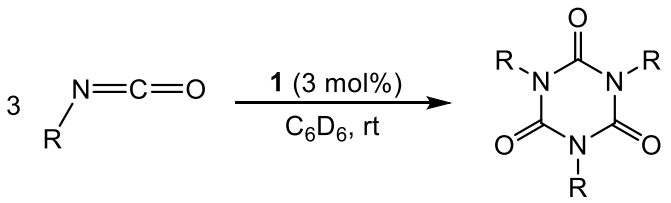
Isolation of products **4e** and **4j**

Upon conversion of the isocyanate substrates to the corresponding isocyanurates, the reaction mixture was dried in vacuo. The resulting solids were washed with hexane, then dried under vacuum to obtain the isocyanurates.

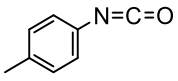
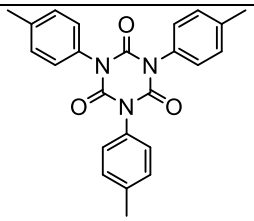
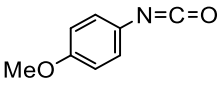
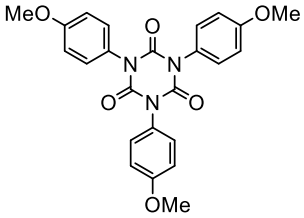
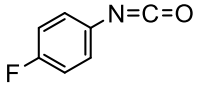
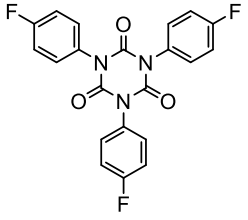
Mechanistic Studies: Regeneration of the catalyst

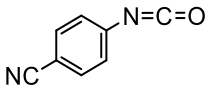
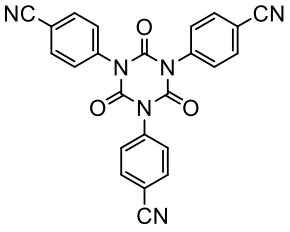
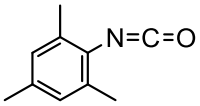
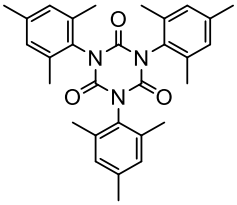
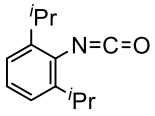
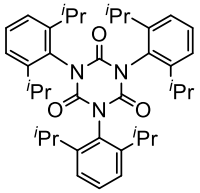
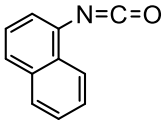
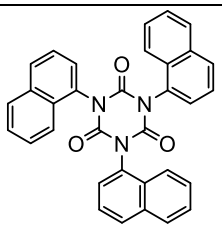
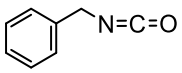
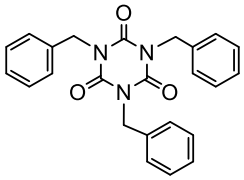
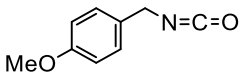
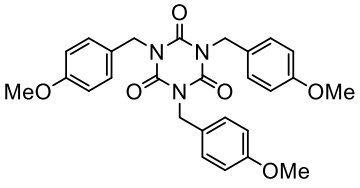
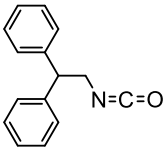
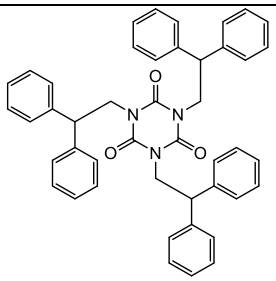
Compound **1** (0.0169 g, 0.04 mmol, catalytic loading: 20 mol%) was added into a J-Young NMR tube and washed down with 0.2 mL of C_6D_6. *p*-tolyl isocyanate (0.0266g, 0.20 mmol) was then added and washed down with 0.2 mL of C_6D_6, Subsequently, the J-Young NMR tube was shaken for solvation of all compounds. The solution was then filtered to remove the isocyanurate precipitate. The $^{11}B\{^1H\}$ NMR spectrum obtained from the crude reaction mixture showed the presence of complex **1** (Figure S4).

Table S1. Catalytic table for cyclotrimerization of isocyanates. Isolated yields are in parentheses.

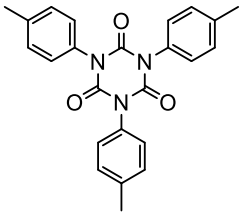


3 **4**

Entry	Isocyanate	Product	T (°C)	t (min)	Yield (%)	TOF (h^{-1})
1		 **4a**	24	5	>99 (87)	348
2		 **4b**	24	5	>99 (94)	376
3		 **4c**	24	5	>99 (93)	372

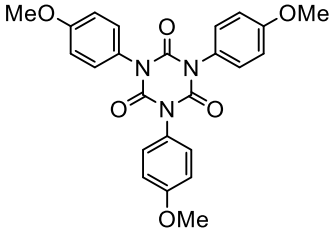
4		 **4d**	24	5	>99 (64)	256
5		 **4e**	24	7200	>99 (95)	0.26
6		 **4f**	24	2520	>99 (87)	0.69
7		 **4g**	24	30	>99 (94)	63
8		 **4h**	24	5	>99 (93)	372
9		 **4i**	24	4140	>99 (96)	0.46
10		 **4j**	24	690	>99 (57)	1.65

Characterization of compound 4a



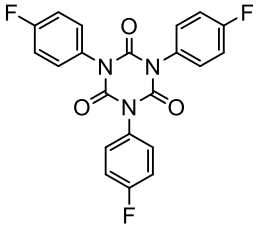
^{1}H NMR (399.5 MHz, 25 °C, $CDCl_3$, ppm): δ = 7.29-7.24 (m, 12H, [overlap with $CDCl_3$], Ar-*H*), 2.39 (s, 9H, Ar-C*H*$_3$). ^{13}C{^{1}H} NMR (100.4 MHz, 25 °C, $CDCl_3$, ppm): δ = 149.0 (N*C*(=O)N), 139.4 (Ar-*C*), 131.2 (Ar-*C*), 130.1 (Ar-*C*), 128.2 (Ar-*C*), 21.4 (Ar-*C*H$_3$).

Characterization of compound 4b



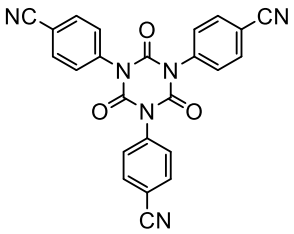
^{1}H NMR (399.5 MHz, 25 °C, $CDCl_3$, ppm): δ = 7.31-7.27 (m, 6H, Ar-*H*), 7.00-6.96 (m, 6H, Ar-*H*), 3.83 (s, 9H, O-C*H*$_3$). ^{13}C{^{1}H} NMR (100.4MHz, 25 °C, $CDCl_3$, ppm): δ = 160.1 (Ar-*C*), 149.3 (N*C*(=O)N), 129.6 (Ar-*C*), 126.5 (Ar-*C*), 114.7 (Ar-*C*), 55.6 (O-*C*H$_3$).

Characterization of compound 4c



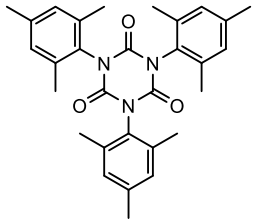
^{1}H NMR (399.5 MHz, 25 °C, $CDCl_3$, ppm): δ = 7.39-7.34 (m, 6H, Ar-*H*), 7.22-7.16 (m, 6H, Ar-*H*). ^{13}C{^{1}H} NMR (100.4 MHz, 25 °C, $CDCl_3$, ppm): δ = 163.0 (d, Ar-*C*), 148.7 (N*C*(=O)N), 130.4 (d, Ar-*C*), 129.4 (d, Ar-*C*), 116.7 (d, Ar-*C*). ^{19}F NMR (376.0 MHz, 25 °C, $CDCl_3$, ppm): δ = -111.0 (m).

Characterization of compound 4d



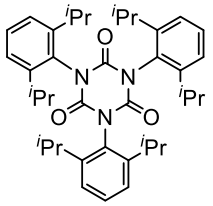
^{1}H NMR (399.5 MHz, 25 °C, CD_3CN, ppm): δ = 7.90 (d, 6H, Ar-*H*, $^{3}J_{H,H}$ = 8.5 Hz), 7.60 (d, 6H, Ar-*H*, $^{3}J_{H,H}$ = 8.5 Hz). ^{13}C{^{1}H} NMR (100.4 MHz, 25 °C, CD_3CN, ppm): δ = 149.3 (N*C*(=O)N), 139.2 (Ar-*C*), 134.5 (Ar-*C*), 130.9 (Ar-*C*), 118.3 (Ar-*C*N), 114.1 (Ar-*C*).

Characterization of compound 4e



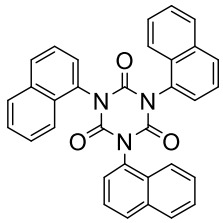
^{1}H NMR (399.5 MHz, 25 °C, C_6D_6, ppm): δ = 6.74 (s, 6H, Ar-*H*), 2.26 (s, 18H, Ar-C*H*$_3$), 2.04 (s, 9H, Ar-C*H*$_3$). ^{13}C{^{1}H} NMR (100.4 MHz, 25 °C, C_6D_6, ppm): δ 147.9 (N*C*(=O)N), 139.1 (Ar-*C*), 135.7 (Ar-*C*), 130.7 (Ar-*C*), 129.8 (Ar-*C*), 21.0 (Ar-*C*H$_3$), 17.7 (Ar-*C*H$_3$).

Characterization of compound 4f



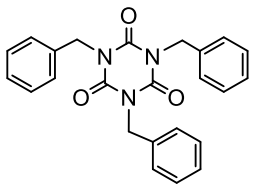
^{1}H NMR (399.5 MHz, 25 °C, $CDCl_3$, ppm): δ = 7.26 (m, 9H, Ar-*H* [overlap with $CDCl_3$]), 3.63 (sept, 6H, C*H*(CH$_3$)$_2$, $^{3}J_{H,H}$ = 6.8 Hz), 1.42 (d, 36H, CH(C*H*$_3$)$_2$, $^{3}J_{H,H}$ = 6.9 Hz). ^{13}C{^{1}H} NMR (100.4 MHz, 25 °C, $CDCl_3$, ppm): δ = 143.2 (N*C*(=O)N), 126.2 (Ar-*C*), 123.5 (Ar-*C*), 122.9 (Ar-*C*), 118.7 (Ar-*C*), 29.7 (Ar-*C*H), 23.0 (CH-*C*H$_3$).

Characterization of compound 4g



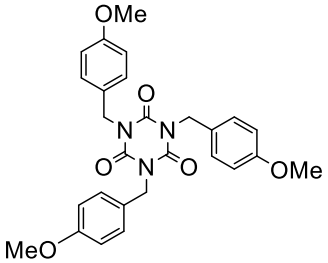
^{1}H NMR (399.5 MHz, 25 °C, $CDCl_3$, ppm): δ = 8.08 – 7.95 (m, 9H, Ar-*H*), 7.79 – 7.71 (m, 6H, Ar-*H*), 7.63 – 7.56 (m, 6H, Ar-*H*). ^{13}C{^{1}H} NMR (100.4 MHz, 25 °C, $CDCl_3$, ppm): δ = 148.9 (N*C*(=O)N), 134.6 (Ar-*C*), 130.4 (Ar-*C*), 130.1 (Ar-*C*), 130.0 (Ar-*C*), 129.1 (Ar-*C*), 127.8 (Ar-*C*), 127.4 (Ar-*C*), 126.7 (Ar-*C*), 125.5 (Ar-*C*), 120.9 (Ar-*C*).

Characterization of compound 4h



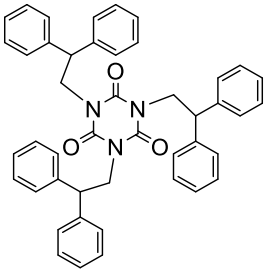
^{1}H NMR (399.5 MHz, 25 °C, $CDCl_3$, ppm): δ = 7.48 – 7.46 (m, 6H, Ar-*H*), 7.36 – 7.28 (m, 9H, Ar-*H*), 5.05 (s, 6H, Ar-C*H*$_2$). ^{13}C{^{1}H} NMR (100.4 MHz, 25 °C, $CDCl_3$, ppm): δ = 149.2 (N*C*(=O)N), 135.9 (Ar-*C*), 129.2 (Ar-*C*), 128.7 (Ar-*C*), 128.3 (Ar-*C*), 46.4 (Ar-*C*H$_2$).

Characterization of compound 4i



^{1}H NMR (399.5 MHz, 25 °C, $CDCl_3$, ppm): δ = 7.45-7.42 (m, 6H, Ar-*H*), 6.87-6.84 (m, 6H, Ar-*H*), 4.97 (s, 6H, Ar-C*H*$_2$), 3.79 (s, 9H, O-C*H*$_3$). ^{13}C{^{1}H} NMR (100.4 MHz, 25 °C, $CDCl_3$, ppm): δ = 159.5 (Ar-*C*), 149.2 (N*C*(=O)N), 130.8 (Ar-*C*), 128.2 (Ar-*C*), 114.0 (Ar-*C*), 55.3 (O-*C*H$_3$), 45.7 (Ar-*C*H$_2$).

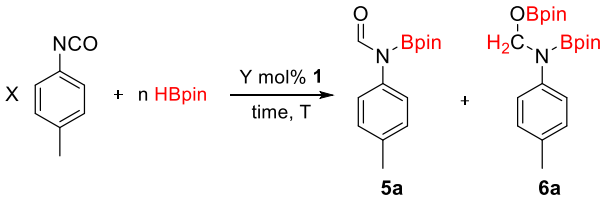
Characterization of compound 4j



^{1}H NMR (399.5 MHz, 25 °C, $CDCl_3$, ppm): δ = 7.30 – 7.22 (m, 18 H, [overlap with $CDCl_3$], Ar-*H*), 7.17 – 7.14 (m, 12H, Ar-*H*), 4.37 (d, 6H, N-C*H*$_2$, $^{3}J_{H,H}$ = 7.1 Hz), 4.30 (t, 3H, Ph$_2$C*H*, $^{3}J_{H,H}$ = 8.0 Hz). ^{13}C{^{1}H} NMR (100.4 MHz, 25 °C, $CDCl_3$, ppm): δ = 148.7 (N*C*(=O)N), 141.0 (Ar-*C*), 128.6 (Ar-*C*), 128.5 (Ar-*C*), 127.0 (Ar-*C*), 48.7 (N-*C*H$_2$), 46.8 (Ph$_2$*C*H).

Optimization for the catalytic hydroboration of *p*-tolyl isocyanate using HBpin:
Catalyst **1** (Y mmol), HBpin (n equivalent), *p*-tolyl isocyanate (X mmol) and C_6D_6 (0.4 mL) were added into a J-Young NMR tube. The J-Young NMR tube was shaken for solvation of all compounds, then placed on a rotating spinner and spun at room temperature. The reaction conditions are indicated in Table S2. The reaction was monitored by ^{1}H NMR spectroscopy to confirm the formation of the *N*-boryl formamide product based on the NC(=O)H signal and the *N*-,*O*-bis(boryl)hemiaminal product based on the NCH_2OBpin signal. The yields of the products were reported according to the integration of ^{1}H NMR signals of NC(=O)H at 8.96 ppm and NCH_2OBpin at 5.48 ppm. The catalytic studies were repeated in triplicate.

Table S2. Catalytic optimization for the hydroboration of *p*-tolyl isocyanate with HBpin.

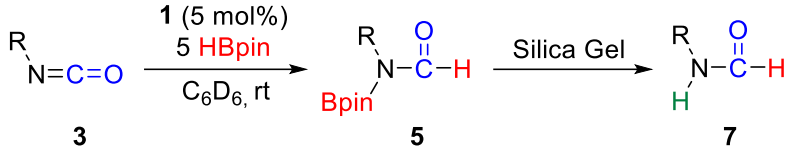


Entry	X (mmol)	Y (mol%)	n (eq.)	T (°C)	Time (h)	Yield (%)	
						5a[a]	**6a**[b]
1	0.3	1	1	25	8	<1	<1
2	0.3	1	5	25	5	19	6
3	0.3	3	5	25	6	93	7
4[c]	0.3	5	5	25	6	96	6
5	0.3	5	5	60	4	0	4
6	0.1	3	5	25	2	70	2
7	0.1	5	5	25	2	96	4

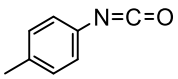
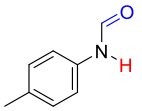
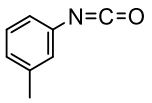
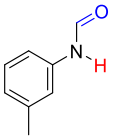
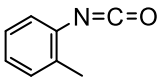
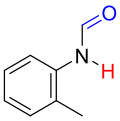
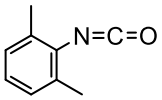
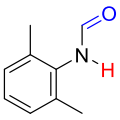
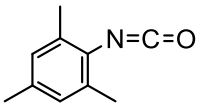
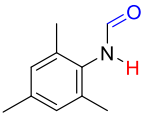
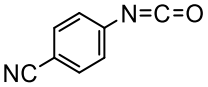
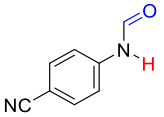
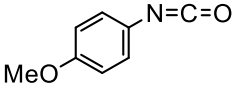
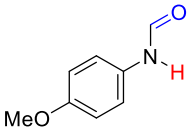
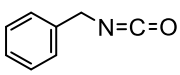
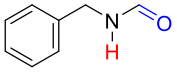
Reaction conditions: Required amounts of isocyanate substrates (0.10, 0.30 mmol), required amounts of **1** (1, 3 or 5 mol%), required amounts of HBpin (0.30, 0.50 or 1.50 mmol) and C_6D_6 (0.40 mL) in a J-Young NMR tube. [a]NMR yield of *N*-borylated formamide **5a** was determined by ^{1}H NMR spectroscopy on the basis of isocyanate consumption and appearance of NC(=O)H signal. [b]NMR yield of *N*-,*O*-bis(boryl)hemiaminal **6b** was determined by ^{1}H NMR spectroscopy on the basis of *N*-borylated formamide consumption and appearance of NCH_2OBpin signal. The catalytic trials were repeated in triplicate. [c]Optimized condition.

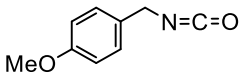
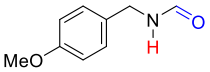
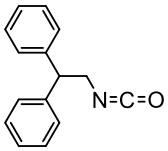
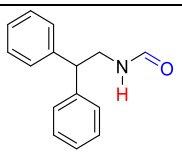
General procedures for the catalytic hydroboration of isocyanates using 1 as the catalyst:
Compound **1** (0.0066 g, 0.015 mmol, catalytic loading: 5 mol%) was added into a J-Young NMR tube and washed down with 0.2 mL of C_6D_6. HBpin (1.50 mmol, 5 equiv.) was then added and washed down with 0.1 mL of C_6D_6, followed by isocyanate substrates (0.30 mmol, 1 equiv.) and another wash with 0.2 mL of C_6D_6. Subsequently, the J-Young NMR tube was shaken for solvation of all compounds. The reactions were followed by NMR spectroscopy and the NMR yields were reported based on consumption of isocyanate. The resulting formamides were isolated by flash column chromatography using ethyl acetate/hexane as the eluents. The chemical shifts of the products are in good agreement with the reported values in the literature.[3]

Table S3. Catalytic table for hydroboration of isocyanates using HBpin for the formation of *N*-boryl formamides. Isolated yields are in parentheses.

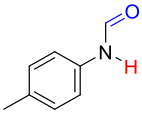


3 5 7

Entry	Isocyanate	Product	T (°C)	t (h)	Yield (%)	TOF (h^{-1})
1		 **7a**	24	2	96 (62)	9.6
2		 **7b**	24	1.5	96 (70)	12.8
3		 **7c**	24	2	98 (69)	9.8
4		 **7d**	24	2	94 (80)	9.4
5		 **7e**	24	2	98 (90)	9.8
6		 **7f**	24	3	85 (81)	5.67
7		 **7g**	24	1.5	96 (92)	12.8
8		 **7h**	24	0.5	99 (86)	39.6

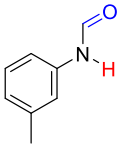
9		 **7i**	24	1.3	99 (96)	15.2
10		 **7j**	24	5	99 (88)	3.96

Characterization of compound 7a



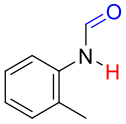
50:50 mixture of rotamers. ^{1}H NMR (399.5 MHz, 25 °C, $CDCl_3$, ppm): δ = 8.61 (d, 1H, C*H*O, $^{3}J_{H,H}$ = 11.5 Hz), 8.36 (s, 1H, C*H*O), 7.53 (brs, 1H, N*H*), 7.42 (d, 2H, Ar-*H*, $^{3}J_{H,H}$ = 8.4 Hz), 7.15 (t, 4H, Ar-*H*, $^{3}J_{H,H}$ = 8.6 Hz), 6.97 (d, 2H, Ar-*H*, $^{3}J_{H,H}$ = 8.3 Hz), 2.34 (s, 3H, Ar-C*H*$_3$), 2.32 (s, 3H, Ar-C*H*$_3$). ^{13}C{^{1}H} NMR (125.7 MHz, 25 °C, $CDCl_3$, ppm): δ = 162.6 (*C*HO), 158.9 (*C*HO), 135.4 (Ar-*C*), 134.7 (Ar-*C*), 134.4 (Ar-*C*), 134.1 (Ar-*C*), 130.4 (Ar-*C*), 129.8 (Ar-*C*), 120.1 (Ar-*C*), 119.5 (Ar-*C*), 21.0 (Ar-*C*H$_3$), 20.9 (Ar-*C*H$_3$).

Characterization of compound 7b



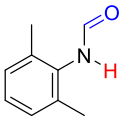
49:51 mixture of rotamers. ^{1}H NMR (399.5 MHz, 25 °C, $CDCl_3$, ppm): δ = 8.68 (d, 1H, C*H*O, $^{3}J_{H,H}$ = 11.5 Hz), 8.37 (d, 1H, C*H*O, $^{3}J_{H,H}$ = 1.8 Hz), 7.78 (brs, 1H, N*H*), 7.40 (s, 1H, Ar-*H*), 7.30 (d, 1H, Ar-*H*, $^{3}J_{H,H}$ = 8.3 Hz), 7.25 – 7.19 (m, 2H, Ar-*H*), 7.01 (d, 1H, Ar-*H*, $^{3}J_{H,H}$ = 7.6 Hz), 6.96 (d, 1H, Ar-*H*, $^{3}J_{H,H}$ = 7.5 Hz), 6.90 – 6.86 (m, 2H, Ar-*H*), 2.36 (s, 3H, Ar-C*H*$_3$), 2.35 (s, 3H, Ar-C*H*$_3$). ^{13}C{^{1}H} NMR (125.7 MHz, 25 °C, $CDCl_3$, ppm): δ = 162.5 (*C*HO), 159.0 (*C*HO), 140.1 (Ar-*C*), 139.3 (Ar-*C*), 136.9 (Ar-*C*), 136.7 (Ar-*C*), 129.7 (Ar-*C*), 129.1 (Ar-*C*), 126.3 (Ar-*C*), 125.8 (Ar-*C*), 120.7 (Ar-*C*), 119.7 (Ar-*C*), 117.1 (Ar-*C*), 116.0 (Ar-*C*), 21.6 (Ar-*C*H$_3$), 21.5 (Ar-*C*H$_3$).

Characterization of compound 7c



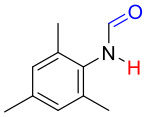
63:37 mixture of rotamers. ^{1}H NMR (399.5 MHz, 25 °C, $CDCl_3$, ppm): δ = 8.54 (d, 1H, C*H*O, $^{3}J_{H,H}$ = 11.3 Hz), 8.44 (s, 1H, C*H*O), 7.90 (d 1H, Ar-*H*, $^{3}J_{H,H}$ = 8.4 Hz), 7.81 (brs, 1H, N*H*), 7.24 – 7.07 (m, 7H, Ar-*H*), 2.30 (s, 3H, Ar-C*H*$_3$), 2.28 (s, 3H, Ar-C*H*$_3$). ^{13}C{^{1}H} NMR (125.7 MHz, 25 °C, $CDCl_3$, ppm): δ = 163.3 (*C*HO), 159.2 (*C*HO), 135.1 (Ar-*C*), 134.7 (Ar-*C*), 131.4 (Ar-*C*), 130.7 (Ar-*C*), 129.7 (Ar-*C*), 128.6 (Ar-*C*), 127.3 (Ar-*C*), 127.0 (Ar-*C*), 126.2 (Ar-*C*), 125.7 (Ar-*C*), 123.1 (Ar-*C*), 120.7 (Ar-*C*), 17.9 (Ar-*C*H$_3$), 17.8 (Ar-*C*H$_3$).

Characterization of compound 7d



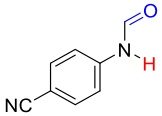
49:51 mixture of rotamers. ^{1}H NMR (399.5 MHz, 25 °C, $CDCl_3$, ppm): δ = 8.40 (s, 1H, C*H*O), 8.09 (d, 1H, C*H*O, $^{3}J_{H,H}$ = 11.9 Hz), 7.18 – 7.06 (m, 6H, Ar-*H*), 6.85 (brs, 1H, N*H*), 2.31 (s, 6H, Ar-C*H*$_3$), 2.26 (s, 6H, Ar-C*H*$_3$). ^{13}C{^{1}H} NMR (125.7 MHz, 25 °C, $CDCl_3$, ppm): δ = 164.9 (*C*HO), 159.4 (*C*HO), 135.4 (Ar-*C*), 133.2 (Ar-*C*), 132.5 (Ar-*C*), 128.9 (Ar-*C*), 128.4 (Ar-*C*), 127.9 (Ar-*C*), 127.9 (Ar-*C*), 18.9 (Ar-*C*H$_3$), 18.7 (Ar-*C*H$_3$).

Characterization of compound 7e



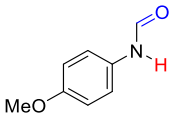
47:53 mixture of rotamers. ^{1}H NMR (399.5 MHz, 25 °C, $CDCl_3$, ppm): δ = 8.36 (s, 1H, C*H*O), 8.04 (d, 1H, C*H*O, $^{3}J_{H,H}$ = 12.0 Hz), 7.09 (brs, 1H, N*H*), 6.93 (s, 2H, Ar-*H*), 6.89 (s, 2H, Ar-*H*), 2.29 (s, 3H, Ar-C*H*$_3$), 2.25 (s, 9H, Ar-C*H*$_3$ [overlap with Ar-C*H*$_3$ of other rotamer]), 2.20 (s, 6H, Ar-C*H*$_3$). ^{13}C{^{1}H} NMR (125.7 MHz, 25 °C, $CDCl_3$, ppm): δ = 165.2 (*C*HO), 159.7 (*C*HO), 137.7 (Ar-*C*), 137.6 (Ar-*C*), 135.3 (Ar-*C*), 135.1 (Ar-*C*), 130.6 (Ar-*C*), 129.8 (Ar-*C*), 129.5 (Ar-*C*), 129.1 (Ar-*C*), 21.0 (Ar-*C*H$_3$), 21.0 (Ar-*C*H$_3$), 18.7 (Ar-*C*H$_3$), 18.6 (Ar-*C*H$_3$).

Characterization of compound 7f



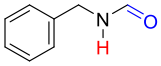
29:71 mixture of rotamers. ^{1}H NMR (399.5 MHz, 25 °C, $CDCl_3$, ppm): δ = 8.84 (d, 1H, C*H*O, $^{3}J_{H,H}$ = 11.0 Hz), 8.45 (s, 1H, C*H*O), 7.91 (brs, 1H, N*H*), 7.71 – 7.61 (m, 7H, Ar-*H*), 7.43 (brs, 1H, N*H*), 7.17 (d, 1H, Ar-*H*, $^{3}J_{H,H}$ = 8.3 Hz). ^{13}C{^{1}H} NMR (125.7 MHz, 25 °C, $CDCl_3$, ppm): δ = 161.2 (*C*HO), 159.0 (*C*HO), 140.9 (Ar-*C*), 134.2 (Ar-*C*), 133.6 (Ar-*C*), 119.9 (Ar-*C*), 118.0 (Ar-*C*), 108.1 (Ar-*C*≡N).

Characterization of compound 7g



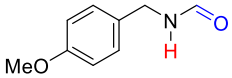
50:50 mixture of rotamers. ^{1}H NMR (399.5 MHz, 25 °C, $CDCl_3$, ppm): δ = 8.50 (d, 1H, C*H*O, $^{3}J_{H,H}$ = 11.5 Hz), 8.32 (d, 1H, C*H*O, $^{3}J_{H,H}$ = 1.9 Hz), 7.88 (brs, 1H, N*H*), 7.47 – 7.42 (m, 2H, Ar-*H*), 7.27 (brs, 1H, N*H* [overlap with $CDCl_3$ signal]), 7.06 – 7.00 (m, 2H, Ar-*H*), 6.92-6.84 (m, 4H, Ar-*H*), 3.80 (s, 3H, O-C*H*$_3$), 3.79 (s, 3H, O-C*H*$_3$). ^{13}C{^{1}H} NMR (125.7 MHz, 25 °C, $CDCl_3$, ppm): δ = 163.1 (*C*HO), 159.0 (*C*HO), 157.8 (Ar-*C*), 156.9 (Ar-*C*), 130.0 (Ar-*C*), 129.6 (Ar-*C*), 121.9 (Ar-*C*), 121.9 (Ar-*C*), 115.0 (Ar-*C*), 114.4 (Ar-*C*), 55.7 (O-*C*H$_3$), 55.6 (O-*C*H$_3$).

Characterization of compound 7h



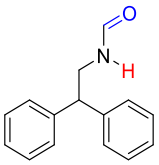
15:85 mixture of rotamers. ^{1}H NMR (399.5 MHz, 25 °C, $CDCl_3$, ppm): δ = 8.27 (s, 1H, C*H*O), 8.19 (d, 1H, C*H*O, $^{3}J_{H,H}$ = 12.0 Hz), 7.41 – 7.21 (m, 10H, Ar-*H* [overlap with $CDCl_3$ signal]), 5.86 (brs, 2H, N*H*), 4.49 (d, 2H, Ar-C*H*$_2$, $^{3}J_{H,H}$ = 5.9 Hz), 4.42 (d, 2H, Ar-C*H*$_2$, $^{3}J_{H,H}$ = 6.5 Hz). ^{13}C{^{1}H} NMR (125.7 MHz, 25 °C, $CDCl_3$, ppm): δ = 164.7 (*C*HO), 161.1 (*C*HO), 137.7 (Ar-*C*), 137.6 (Ar-*C*), 129.1 (Ar-*C*), 128.9 (Ar-*C*), 128.9 (Ar-*C*), 128.1 (Ar-*C*), 128.0 (Ar-*C*), 127.9 (Ar-*C*), 127.1 (Ar-*C*), 45.8 (Ar-*C*H$_2$), 42.4 (Ar-*C*H$_2$).

Characterization of compound 7i



16:84 mixture of rotamers. ^{1}H NMR (399.5 MHz, 25 °C, $CDCl_3$, ppm): δ = 8.23 (s, 1H, C*H*O), 8.17 (d, 1H, CHO, $^{3}J_{H,H}$ = 12.0 Hz), 7.23 – 6.84 (m, 8H, Ar-*H*), 5.86 (brs, 2H, N*H*), 4.41 (d, 2H, Ar-C*H*$_2$, $^{3}J_{H,H}$ = 5.8 Hz), 4.34 (d, 2H, Ar-C*H*$_2$, $^{3}J_{H,H}$ = 6.4 Hz), 3.80 (s, 3H, O-C*H*$_3$), 3.79 (s, 3H, O-C*H*$_3$). ^{13}C{^{1}H} NMR (125.7 MHz, 25 °C, $CDCl_3$, ppm): δ = 164.6 (*C*HO), 161.0 (*C*HO), 159.5 (Ar-*C*), 159.3 (Ar-*C*), 129.8 (Ar-*C*), 129.6 (Ar-*C*), 129.3 (Ar-*C*), 128.4 (Ar-*C*), 114.4 (Ar-*C*), 114.3 (Ar-*C*), 55.4, (O-*C*H$_3$), 45.3 (Ar-*C*H$_2$), 41.8 (Ar-*C*H$_2$).

Characterization of compound 7j



15:85 mixture of rotamers. ^{1}H NMR (399.5 MHz, 25 °C, $CDCl_3$, ppm): δ = 8.08 (s, 1H, C*H*O), 7.98 (d, 1H, C*H*O, $^{3}J_{H,H}$ = 11.9 Hz), 7.35 – 7.31 (m, 8H, Ar-*H*), 7.26 – 7.22 (m, 12H, Ar-*H* [overlap with $CDCl_3$ signal]), 5.52 (brs, 1H, N*H*), 4.20 (t, 1H, Ar-C*H*, $^{3}J_{H,H}$ = 8.0 Hz), 4.08 (d, 1H, Ar-C*H*, $^{3}J_{H,H}$ = 7.8 Hz), 3.95 (dd, 2H, N-C*H*$_2$, $^{3}J_{H,H}$ = 8.0, 6.0 Hz), 3.83 (d, 2H, N-C*H*$_2$, $^{3}J_{H,H}$ = 7.2 Hz). ^{13}C{^{1}H} NMR (125.7 MHz, 25 °C, $CDCl_3$, ppm): δ = 164.3 (*C*HO), 161.2 (*C*HO), 141.6 (Ar-*C*), 141.0 (Ar-*C*), 129.1 (Ar-*C*), 129.0 (Ar-*C*), 128.1 (Ar-*C*), 128.0 (Ar-*C*), 127.4 (Ar-*C*), 127.1 (Ar-*C*), 52.8 (Ar-*C*H), 50.7 (Ar-*C*H), 46.5 (Ar-*C*H$_2$), 42.4 (Ar-*C*H$_2$).

S2. NMR Spectra of Isolated Compounds

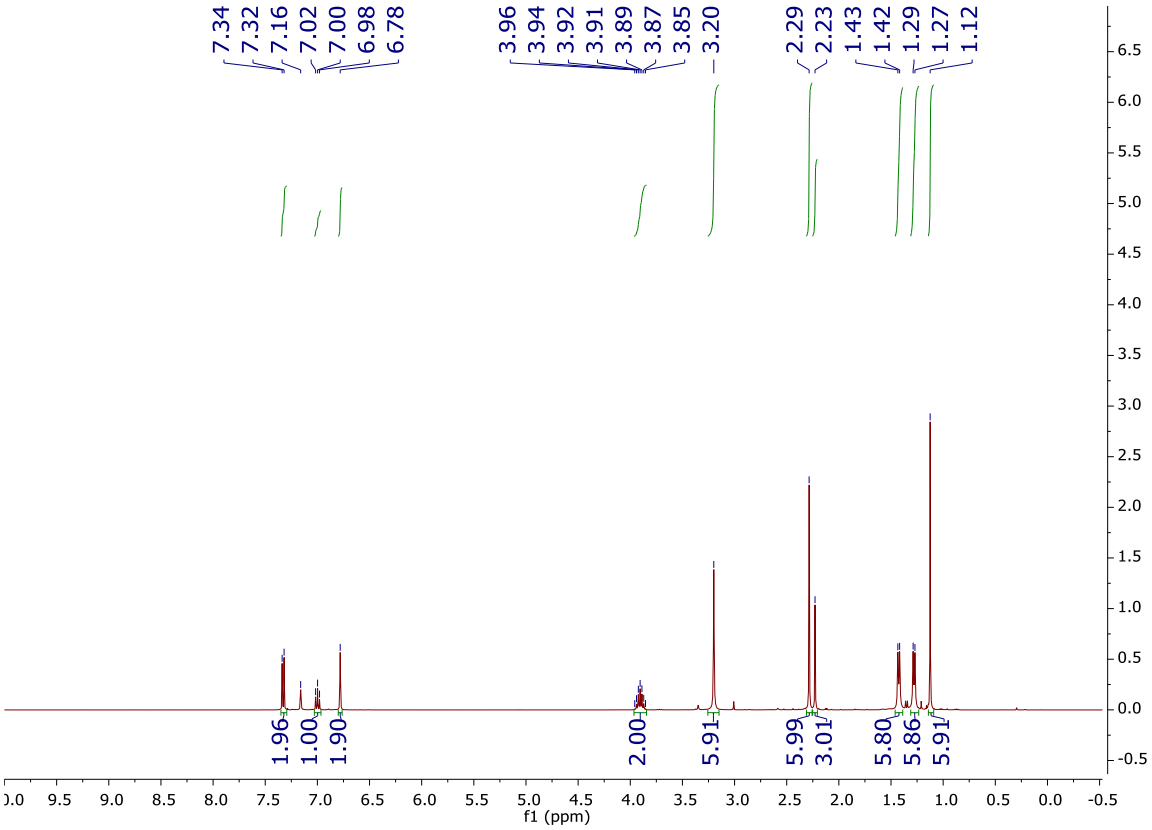


Figure S1. ^{1}H NMR spectrum of compound **2** (in C_6D_6).

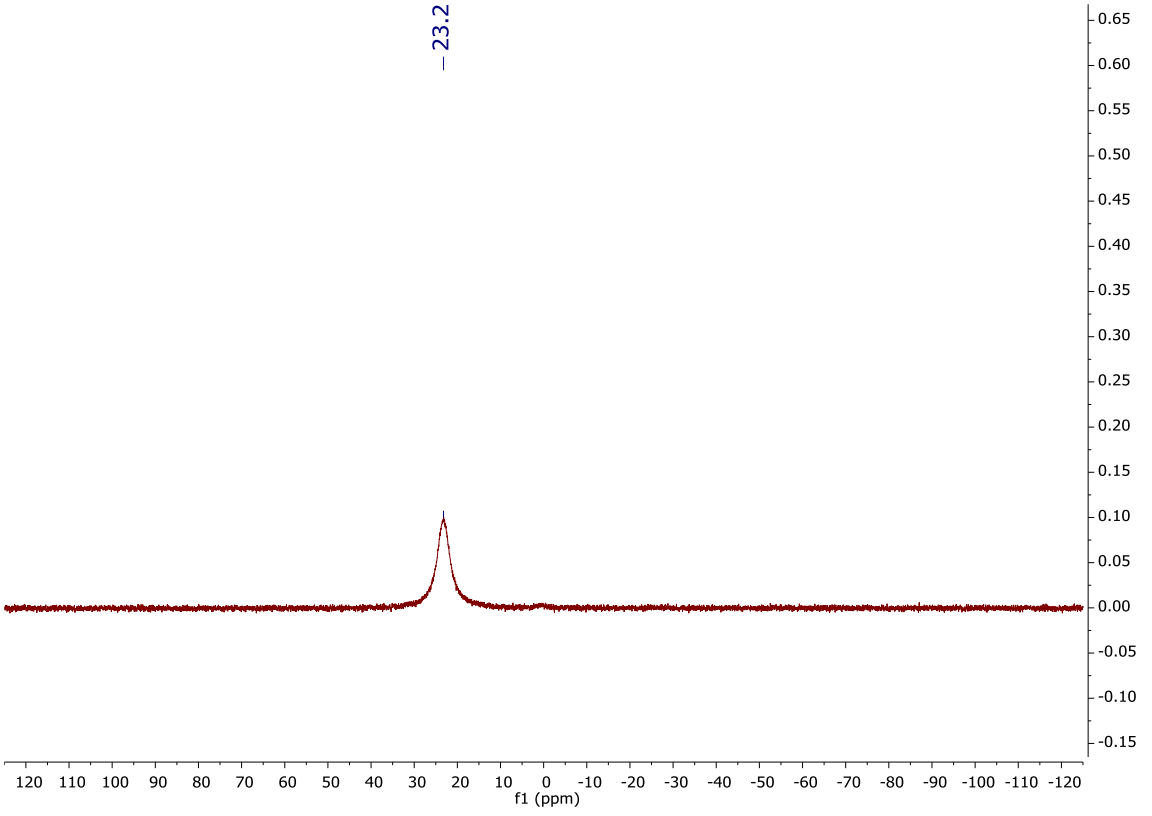


Figure S2. $^{11}B\{^{1}H\}$ NMR spectrum of compound **2** (in C_6D_6).

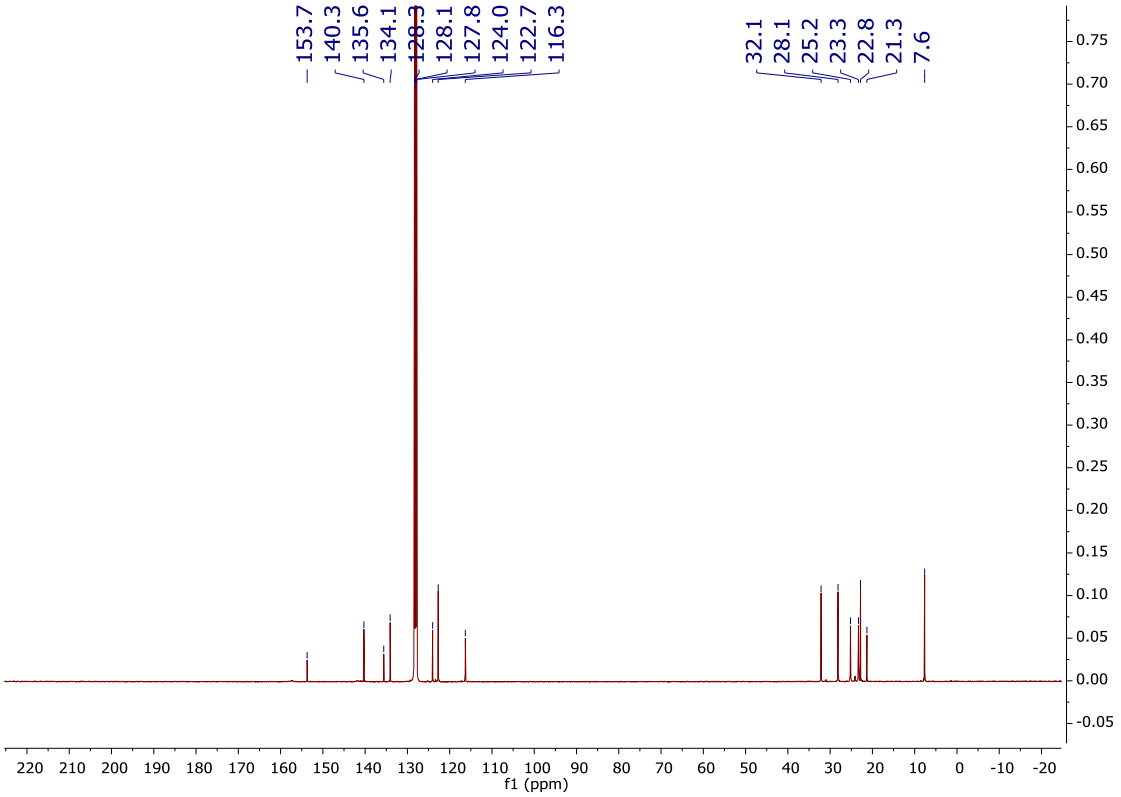


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2** (in C_6D_6).

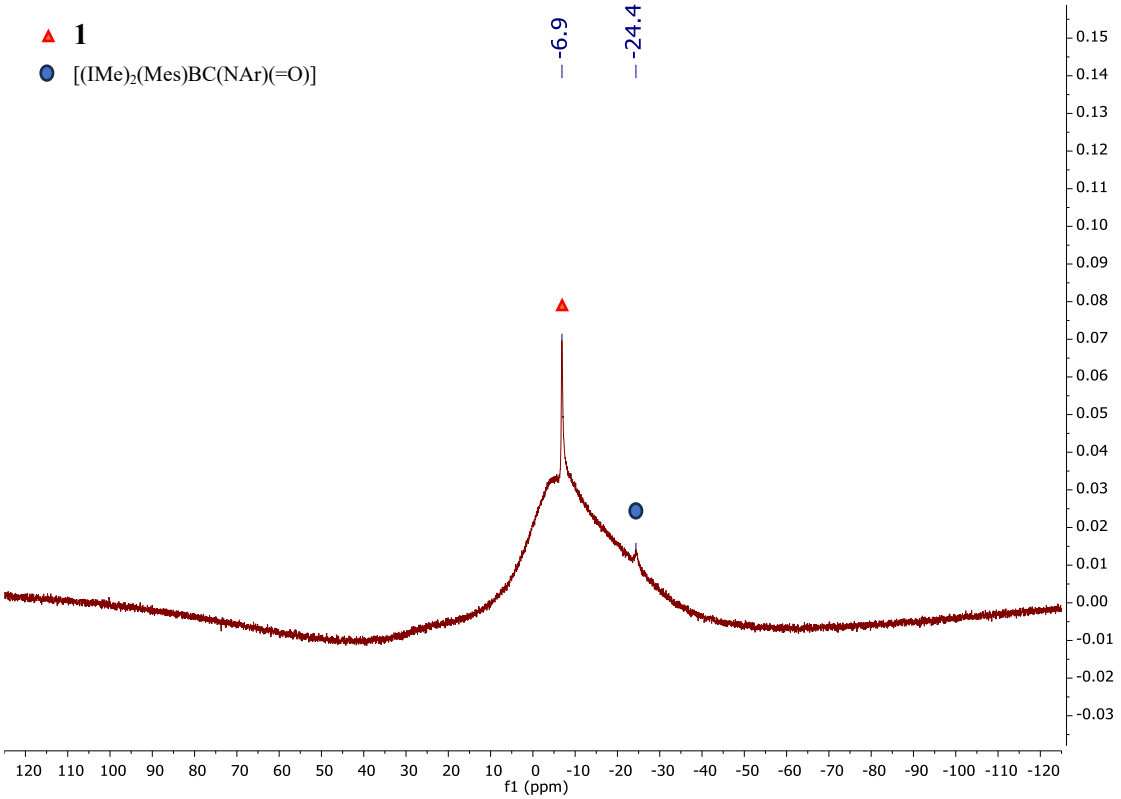


Figure S4. Crude $^{11}B\{^{1}H\}$ NMR spectrum after the catalytic reaction between **1** and *p*-tolyl isocyanate **(**in C_6D_6).

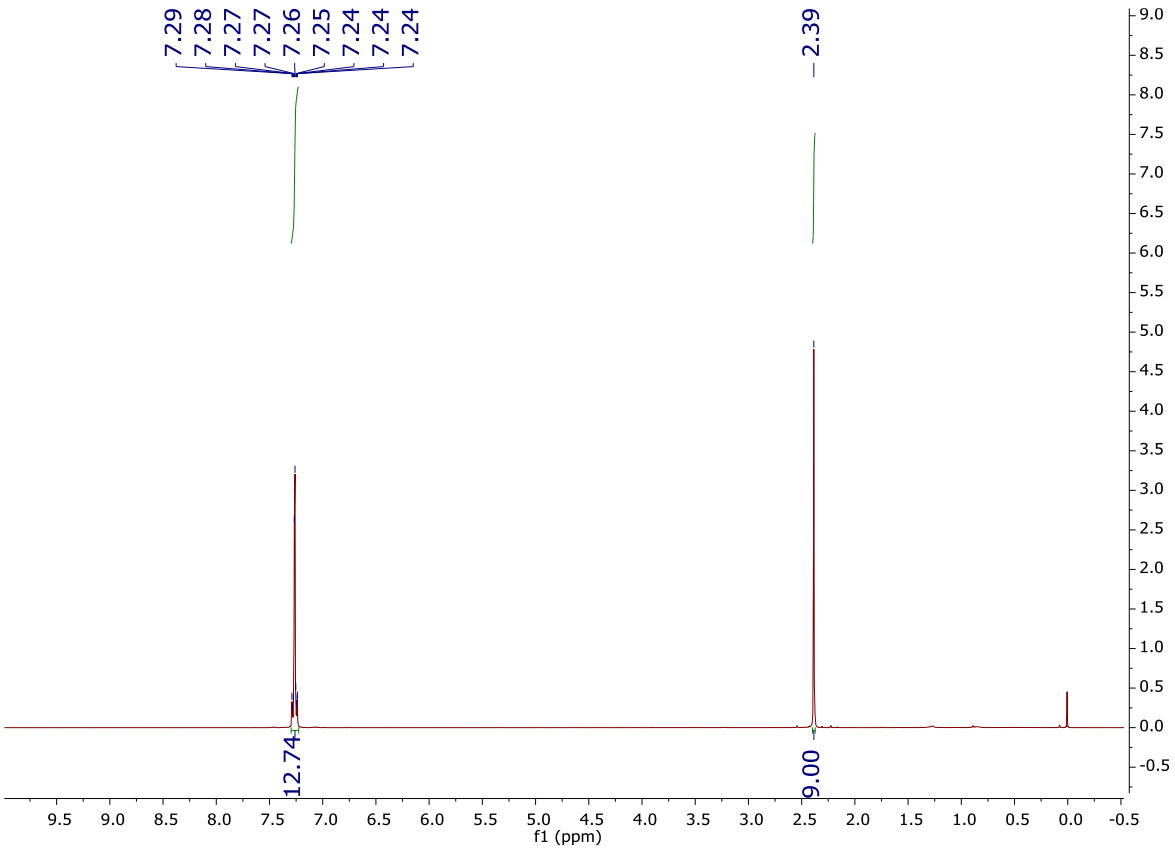


Figure S5. ^{1}H NMR spectrum of compound **4a (**in $CDCl_3$).

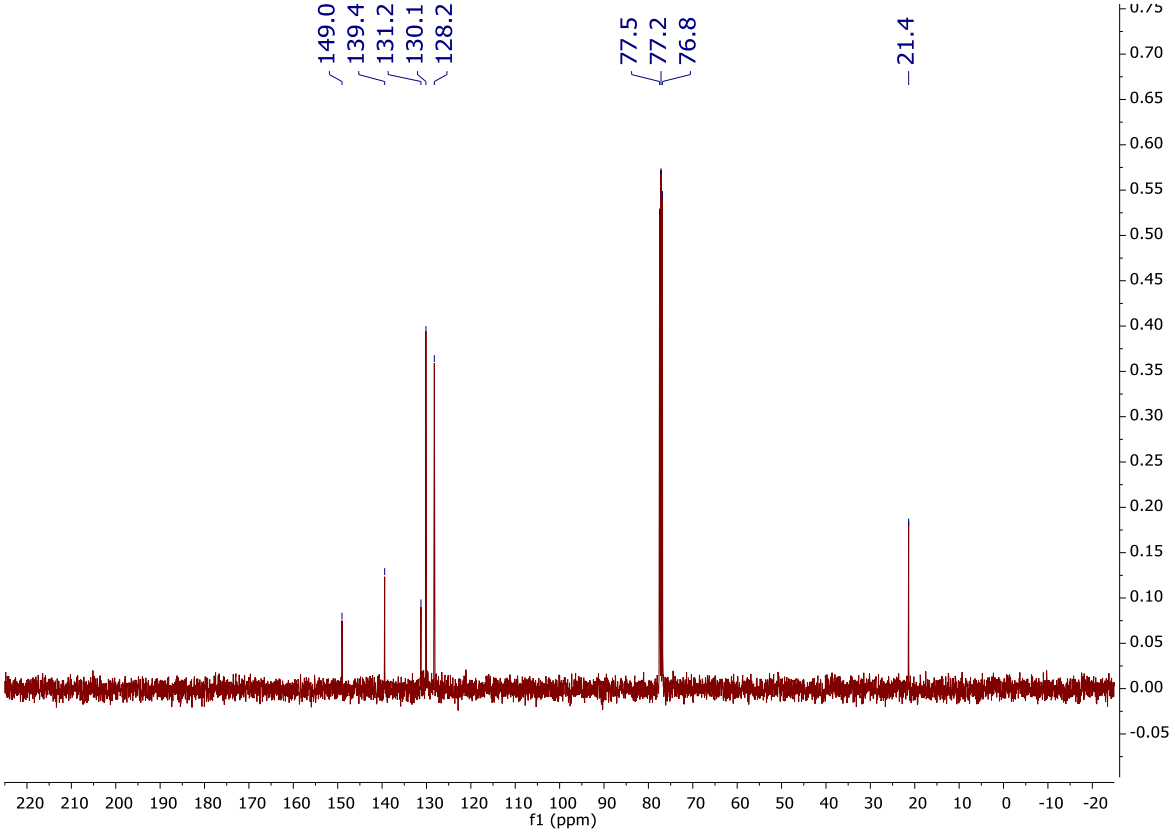


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4a (**in $CDCl_3$).

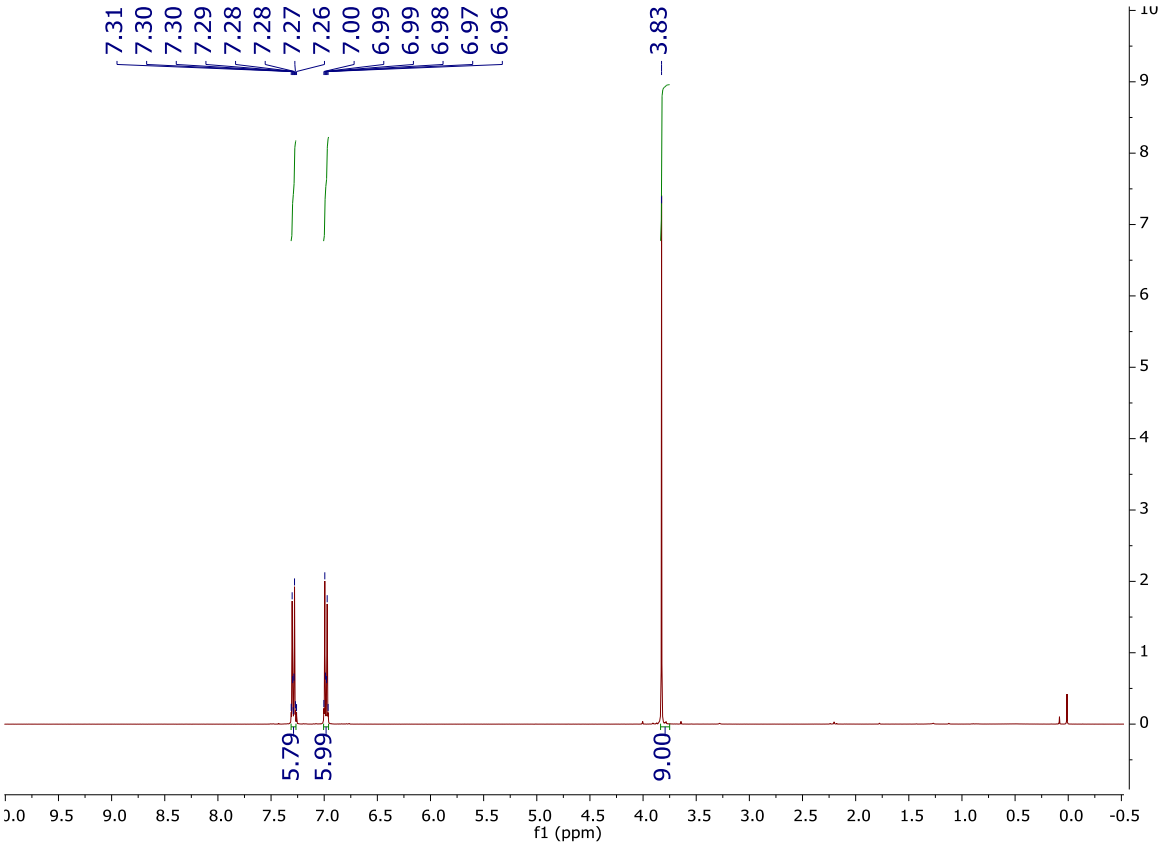


Figure S7. ^{1}H NMR spectrum of compound **4b (**in $CDCl_3$).

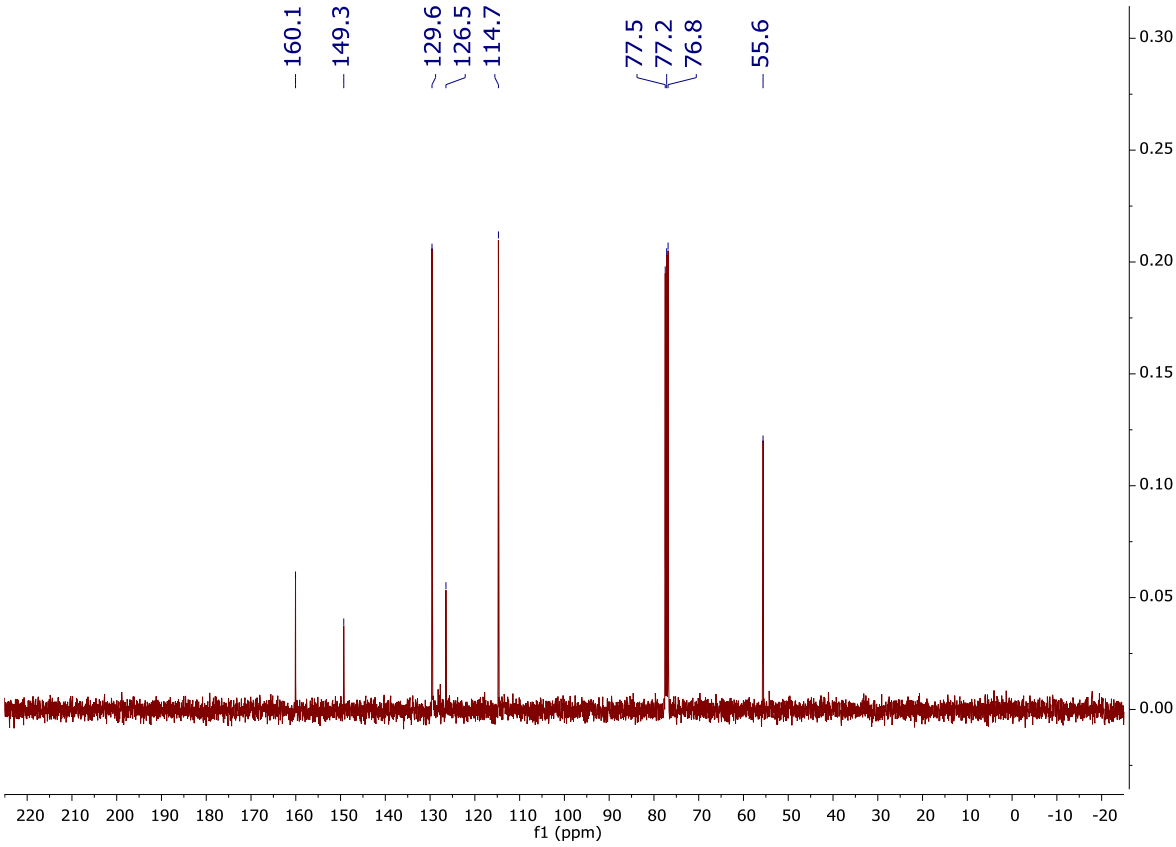


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4b (**in $CDCl_3$).

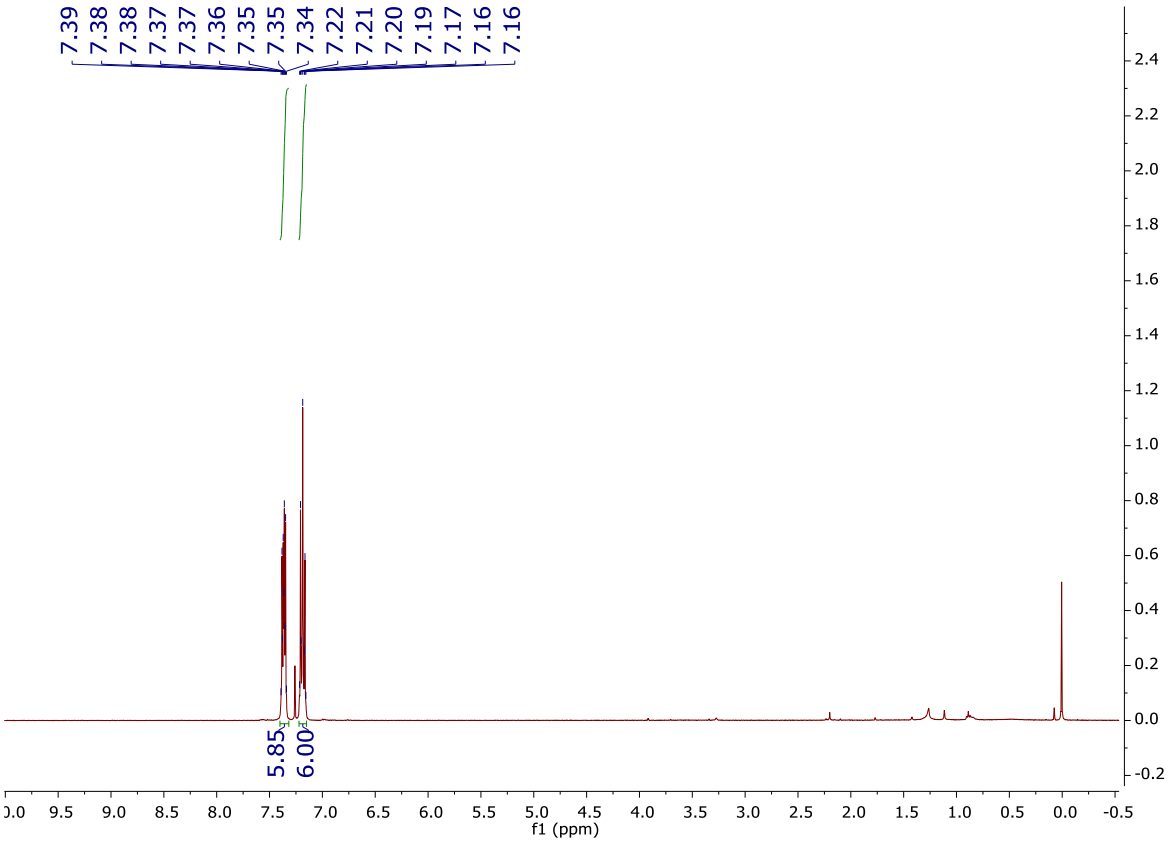


Figure S9. ^{1}H NMR spectrum of compound **4c** (in $CDCl_3$).

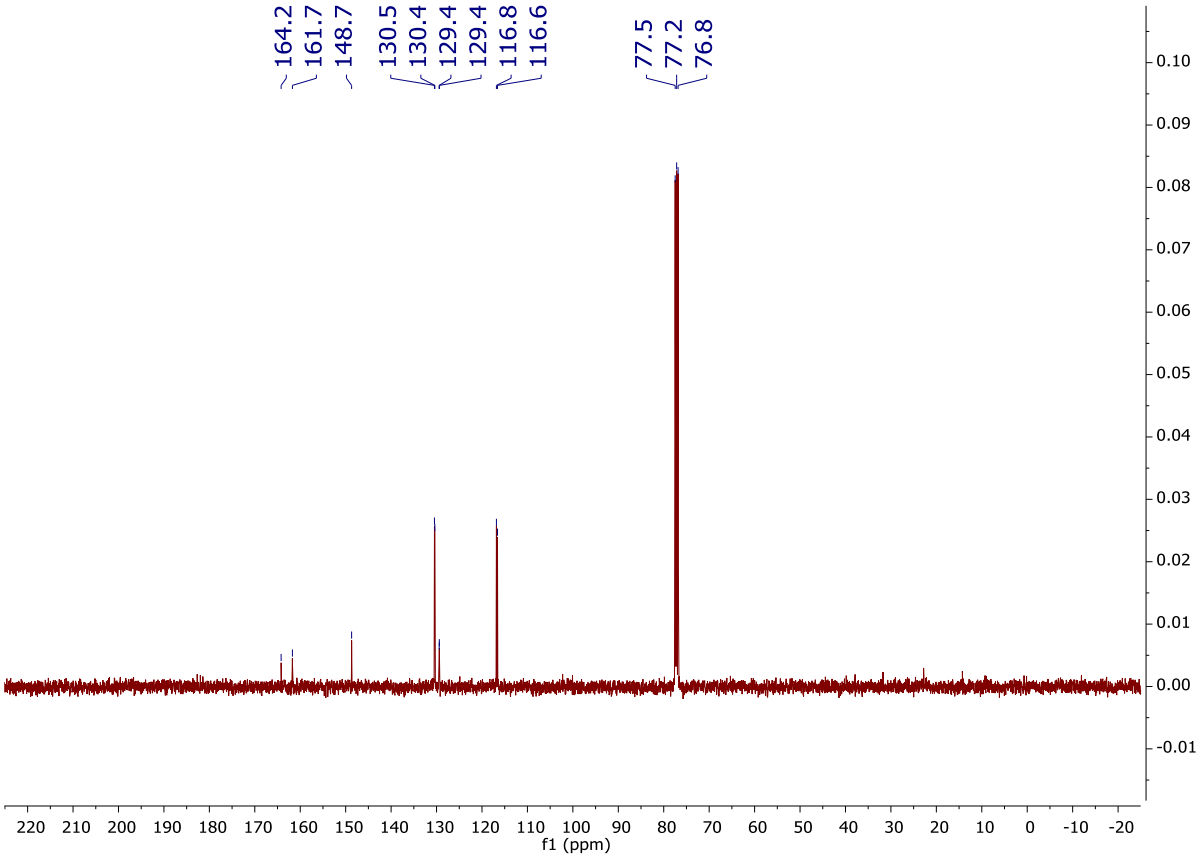


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4c** (in $CDCl_3$).

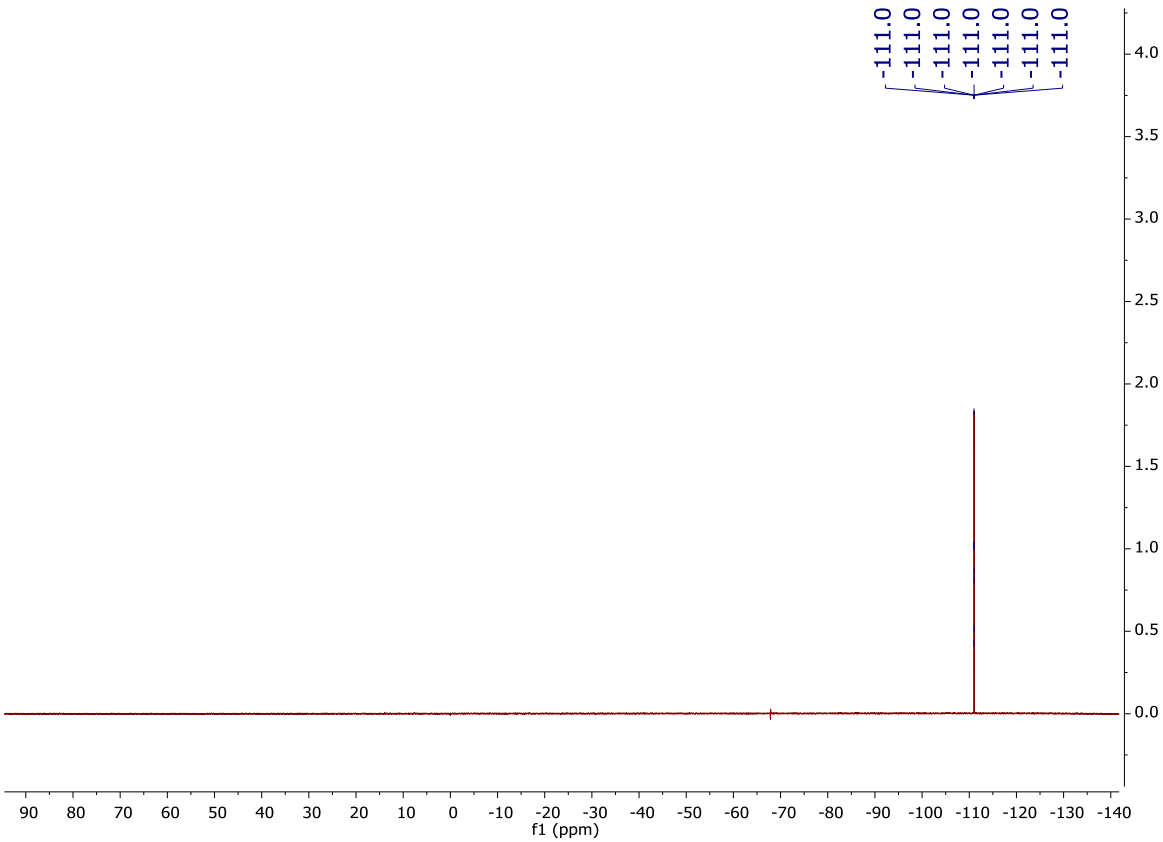


Figure S11. ^{19}F NMR spectrum of compound **4c (**in $CDCl_3$).

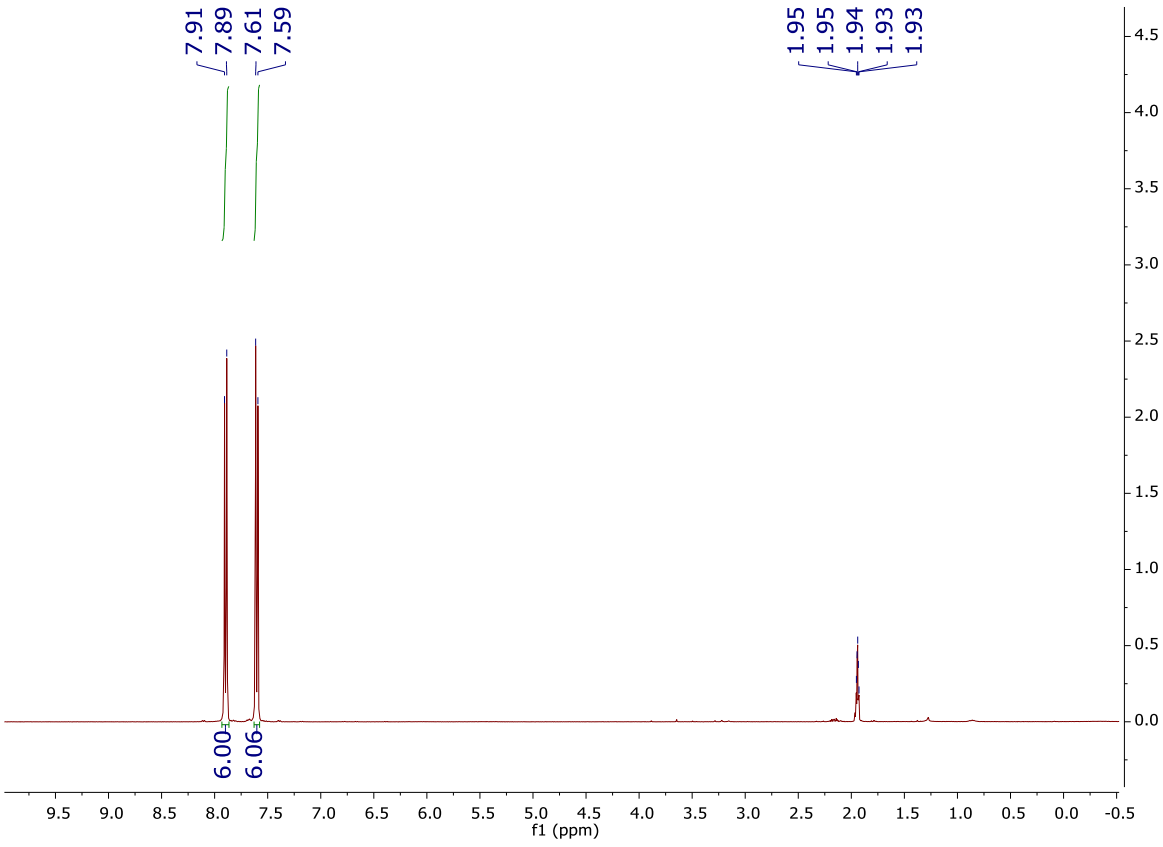


Figure S12. ^{1}H NMR spectrum of compound **4d (**in CD_3CN).

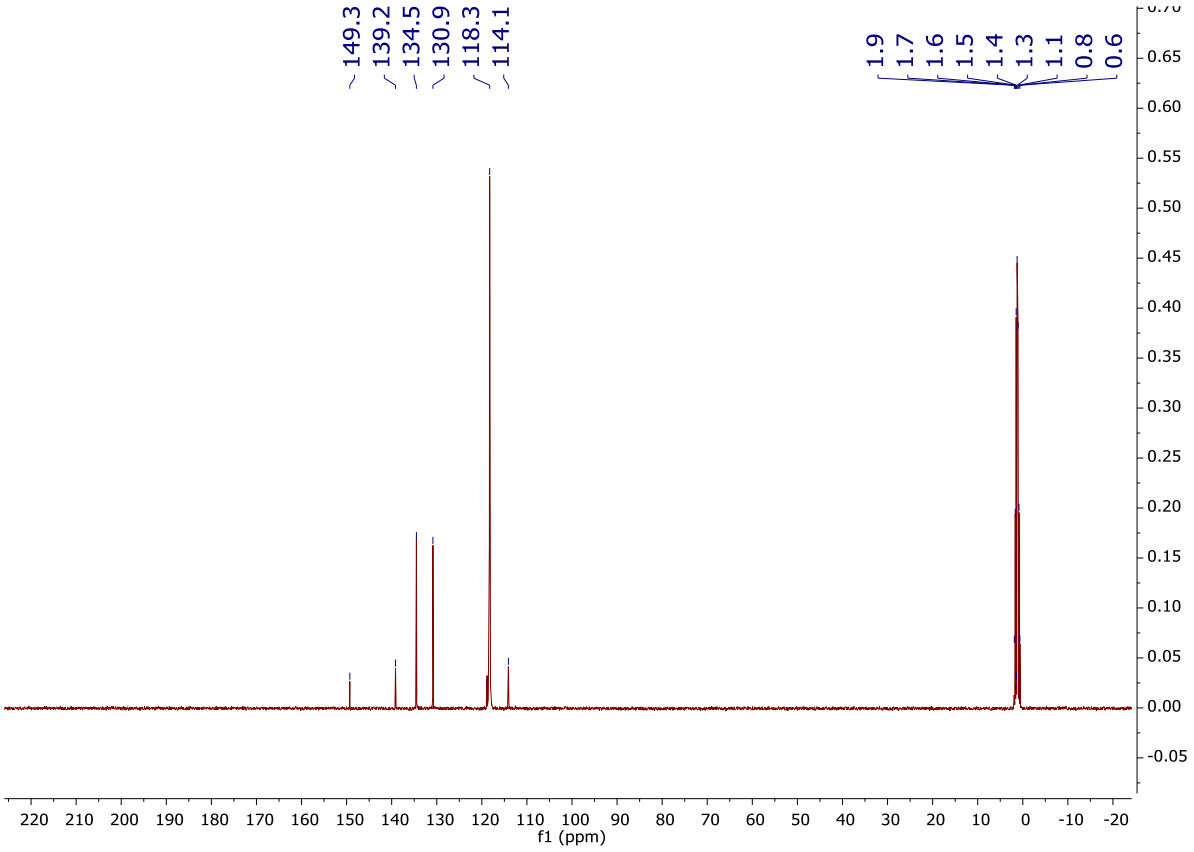


Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4d (**in CD_3CN).

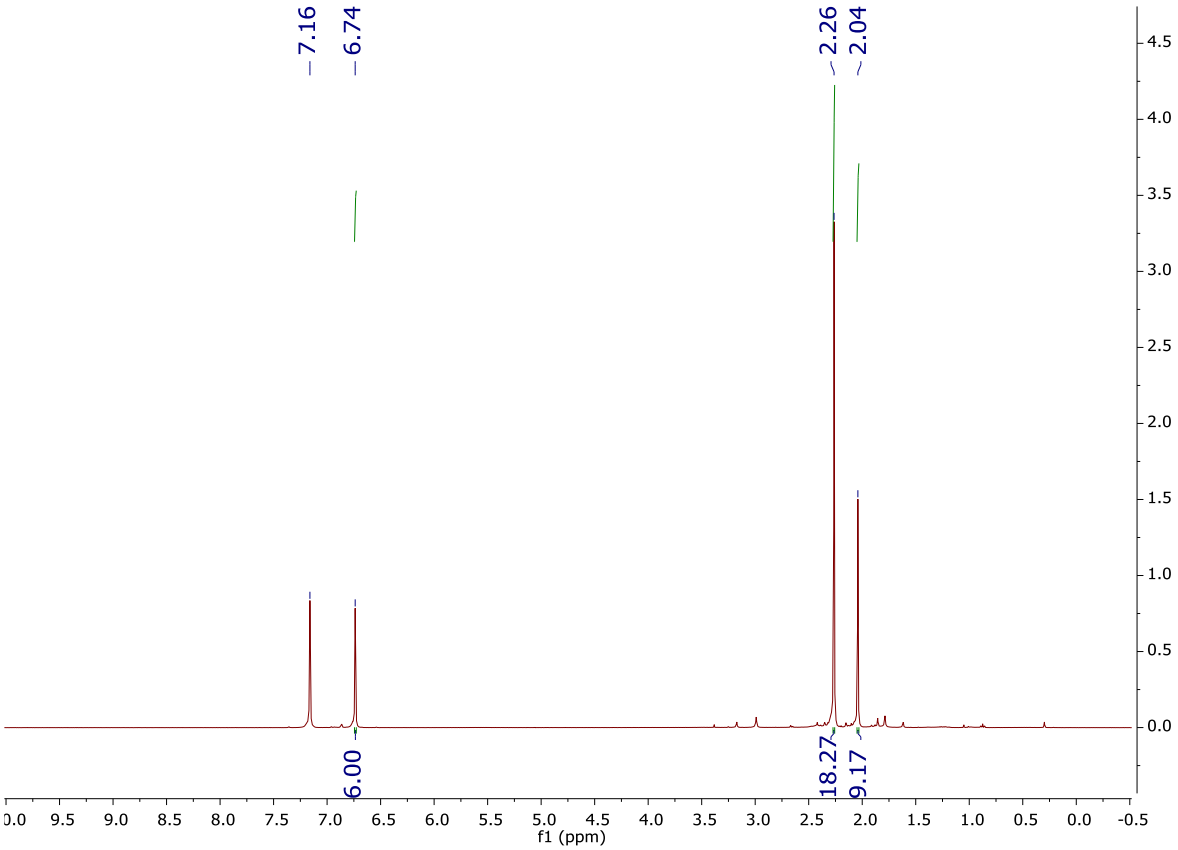


Figure S14. ^{1}H NMR spectrum of compound **4e (**in C_6D_6).

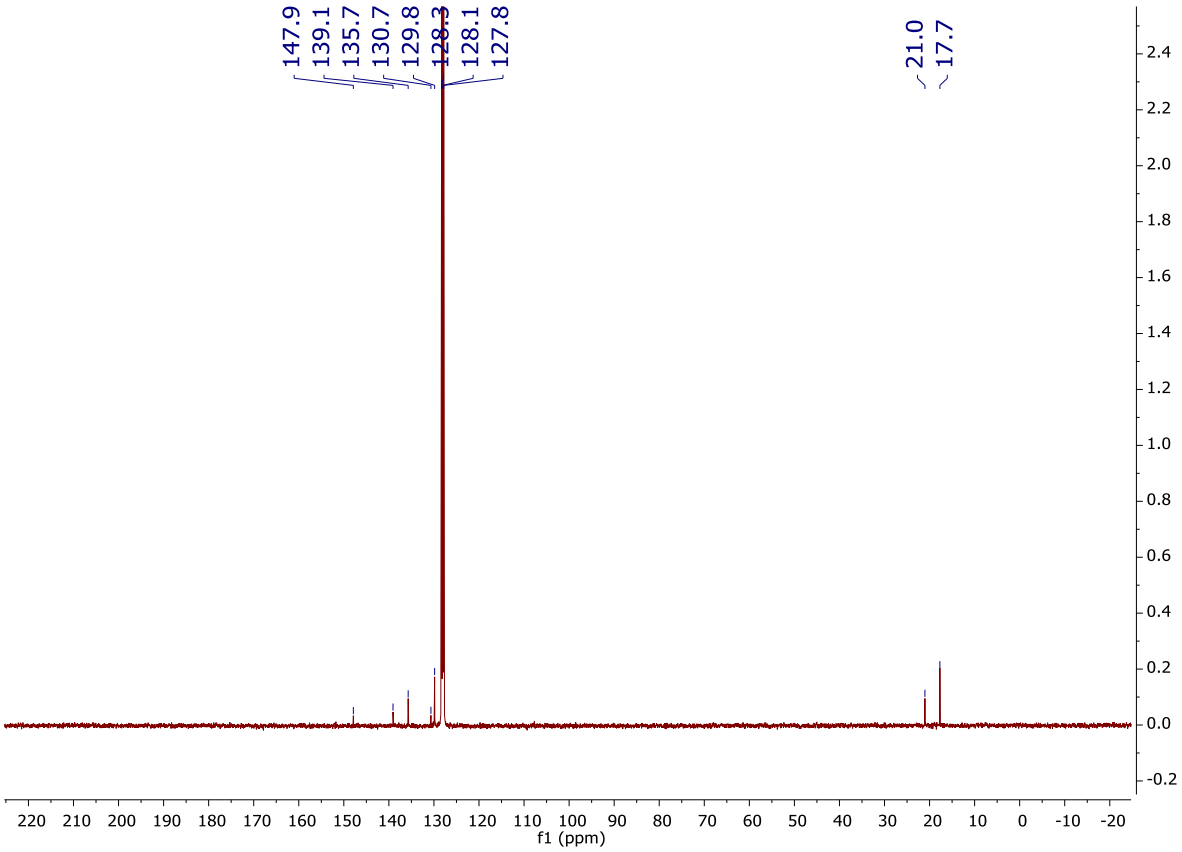


Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4e (**in C_6D_6).

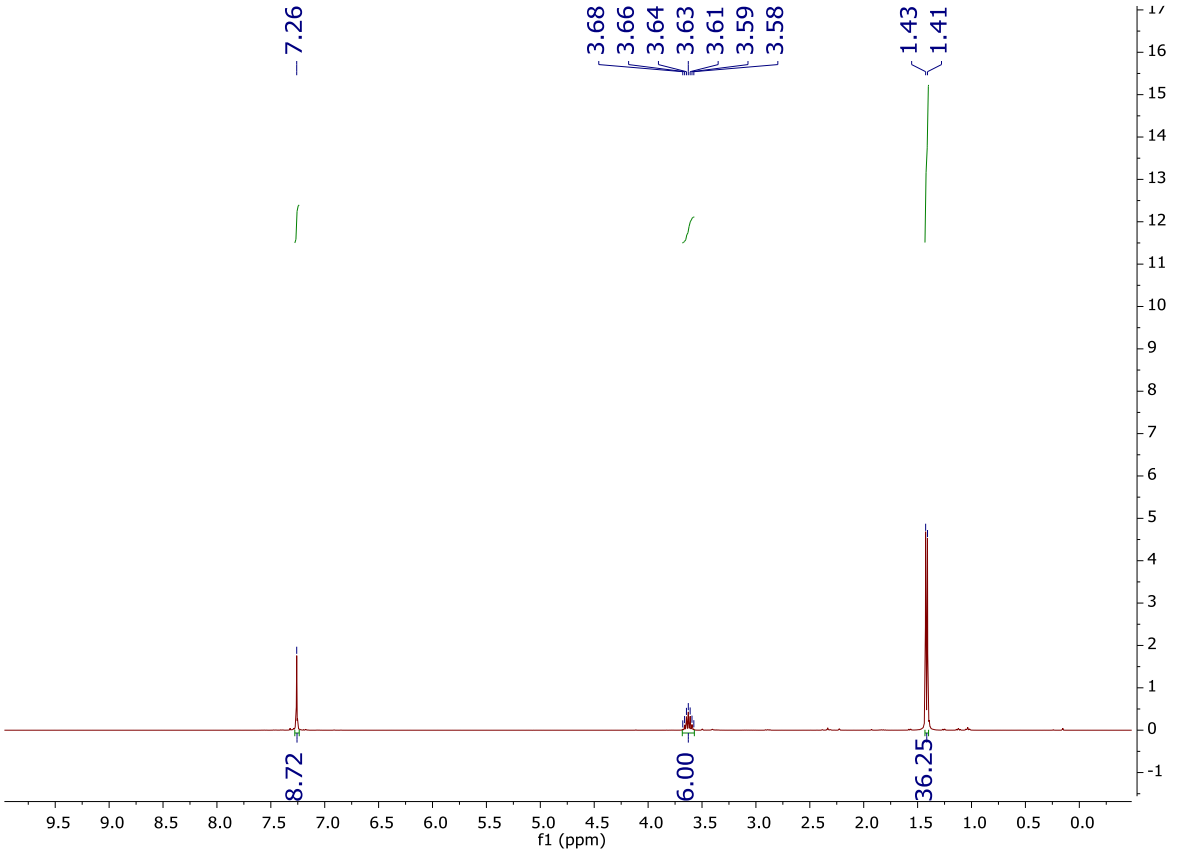


Figure S16. ^{1}H NMR spectrum of compound **4f (**in $CDCl_3$).

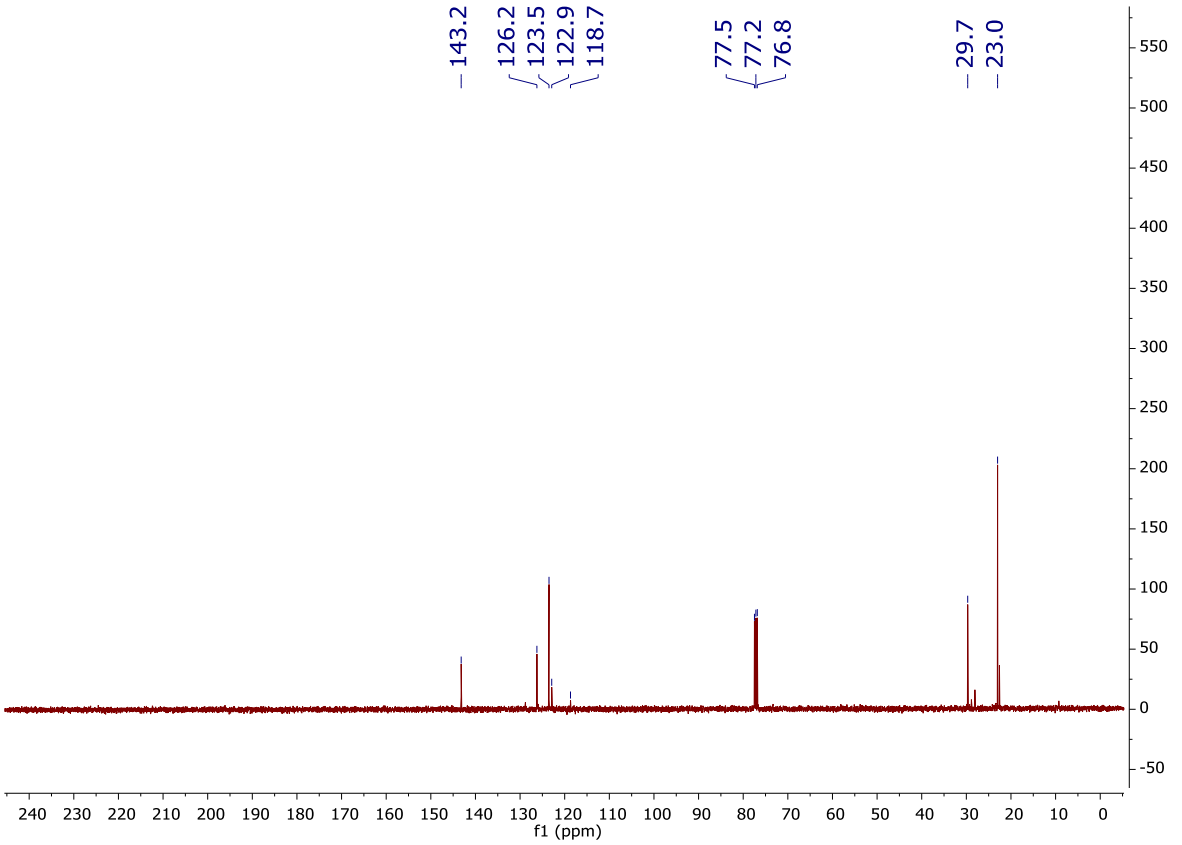


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4f (**in $CDCl_3$).

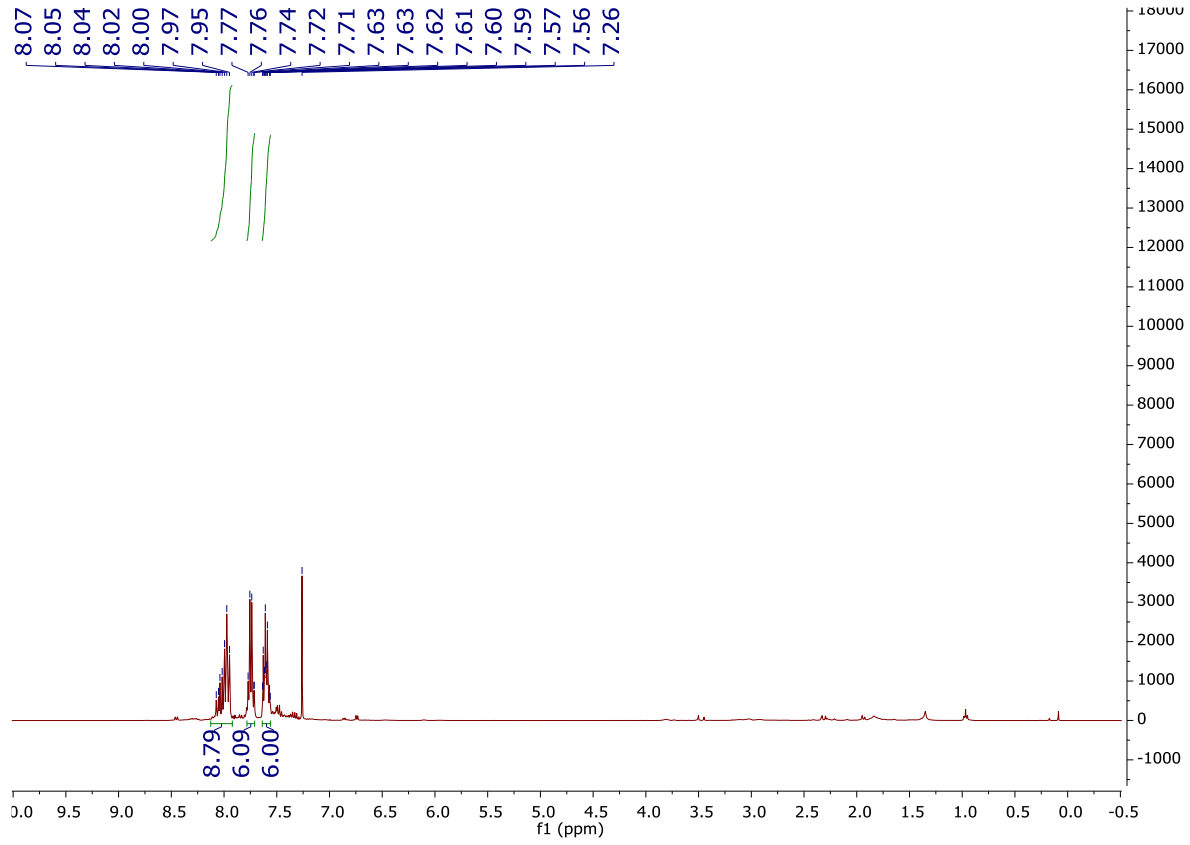


Figure S18. ^{1}H NMR spectrum of compound **4g (**in $CDCl_3$).

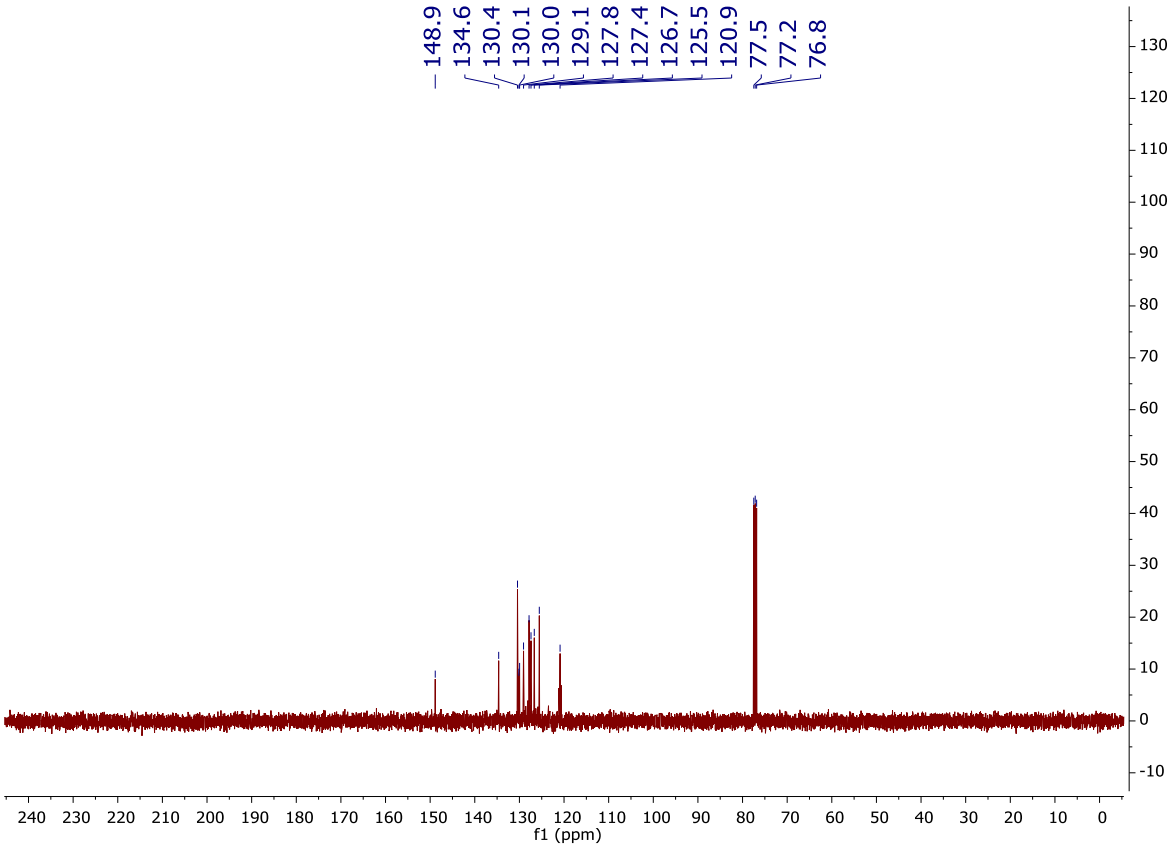


Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4g (**in $CDCl_3$).

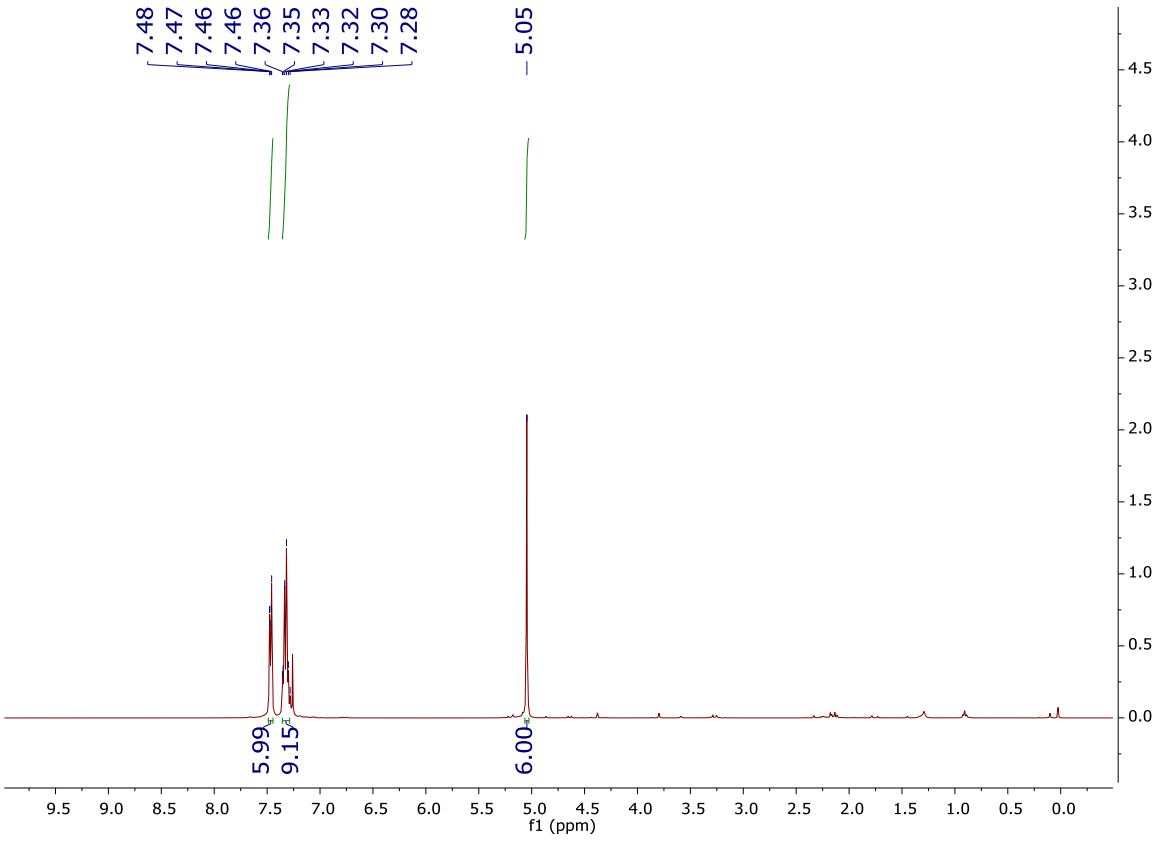


Figure S20. ^{1}H NMR spectrum of compound **4h (**in $CDCl_3$).

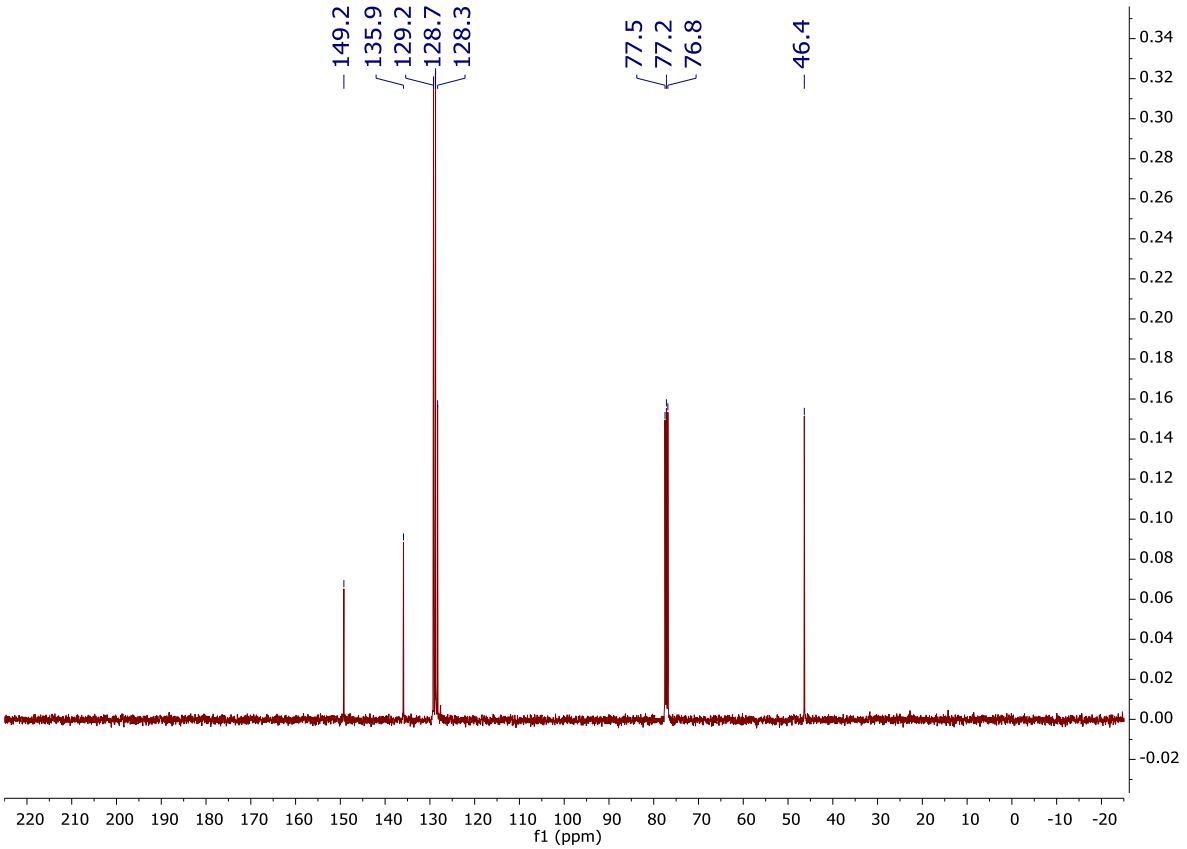


Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4h (**in $CDCl_3$).

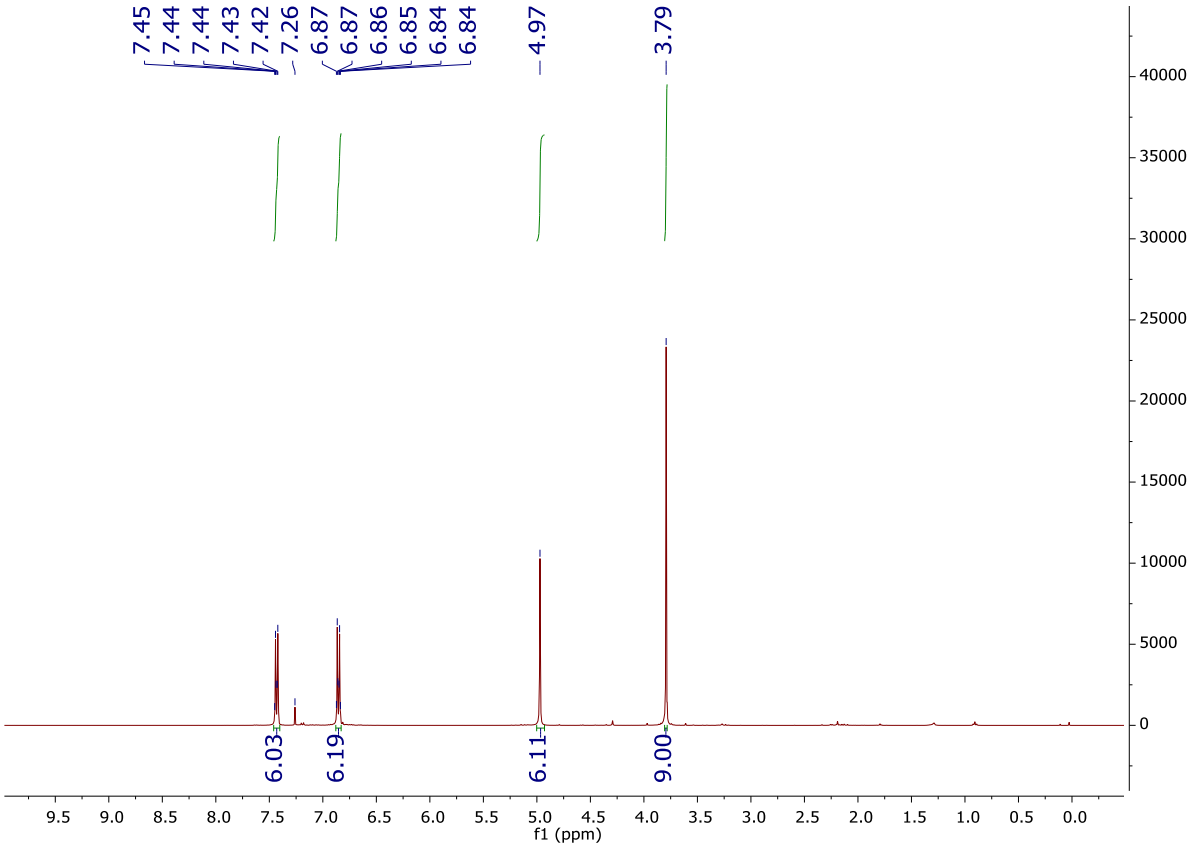


Figure S22. ^{1}H NMR spectrum of compound **4i (**in C_6D_6).

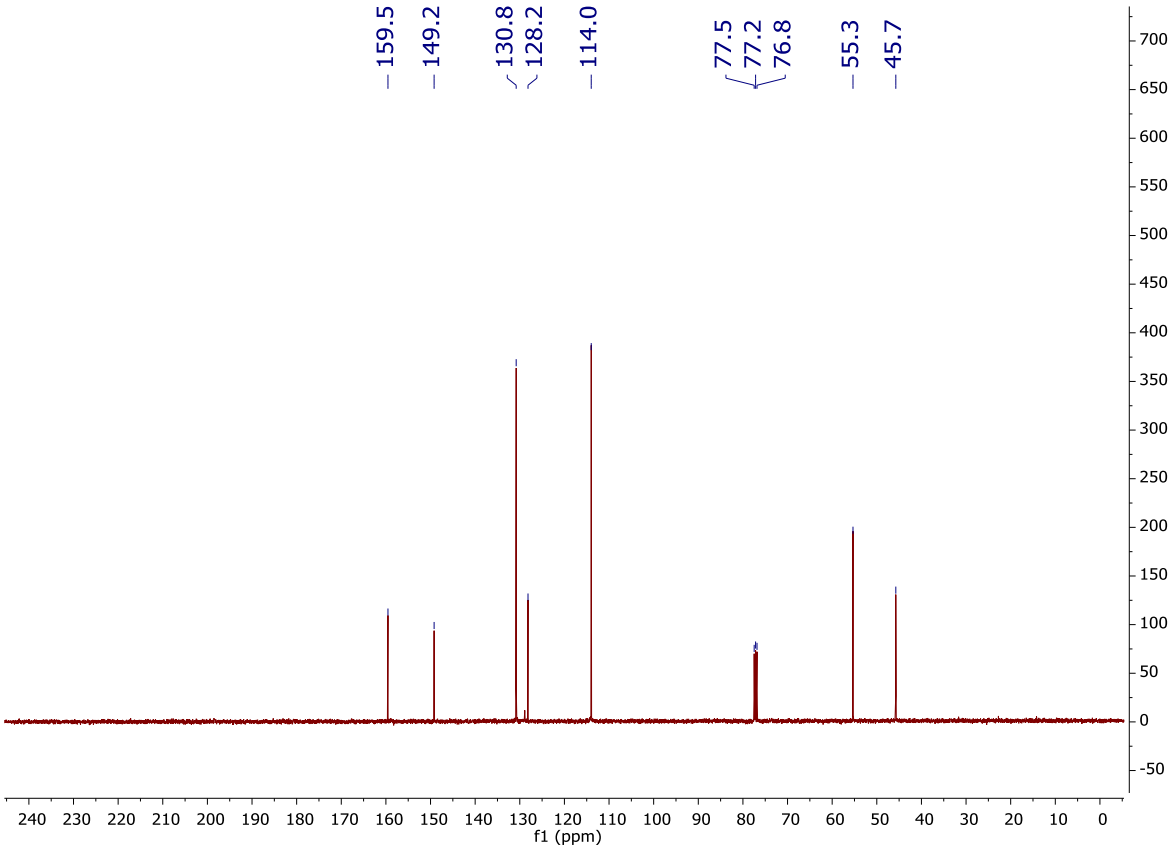


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4i (**in $CDCl_3$).

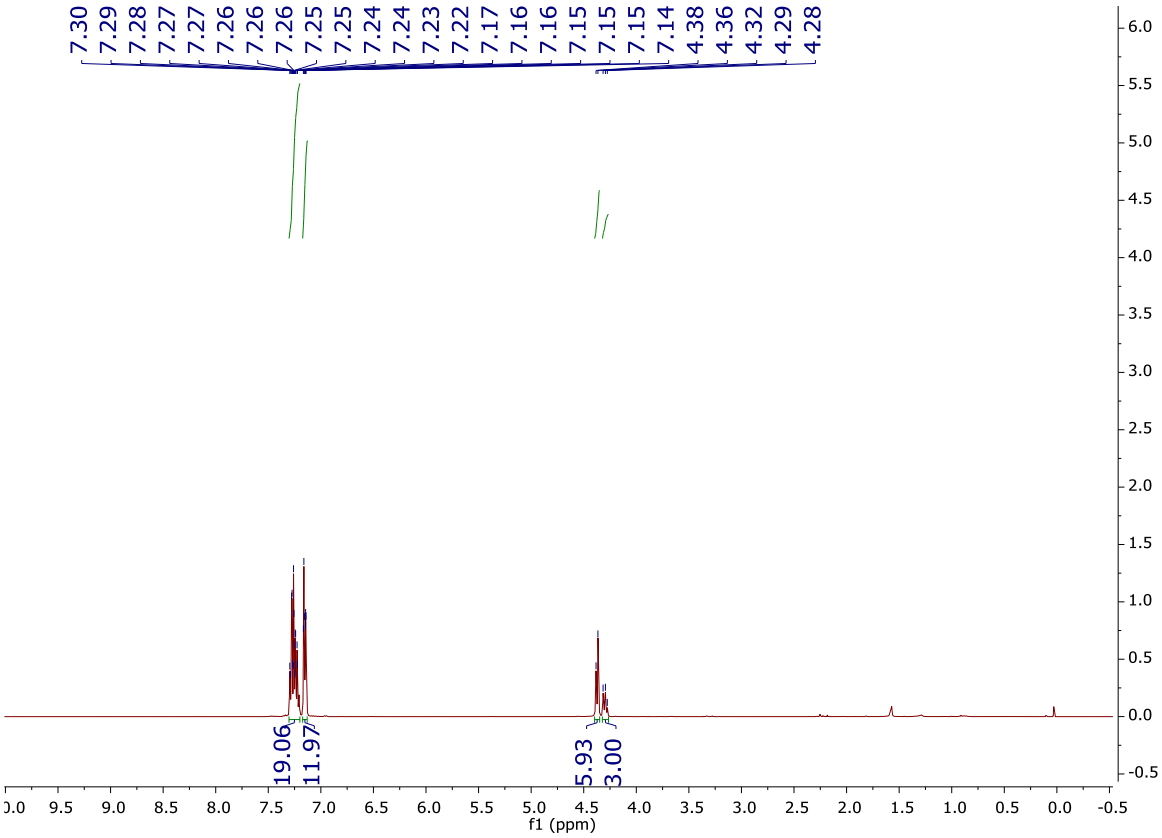


Figure S24. ^{1}H NMR spectrum of compound **4j (**in $CDCl_3$).

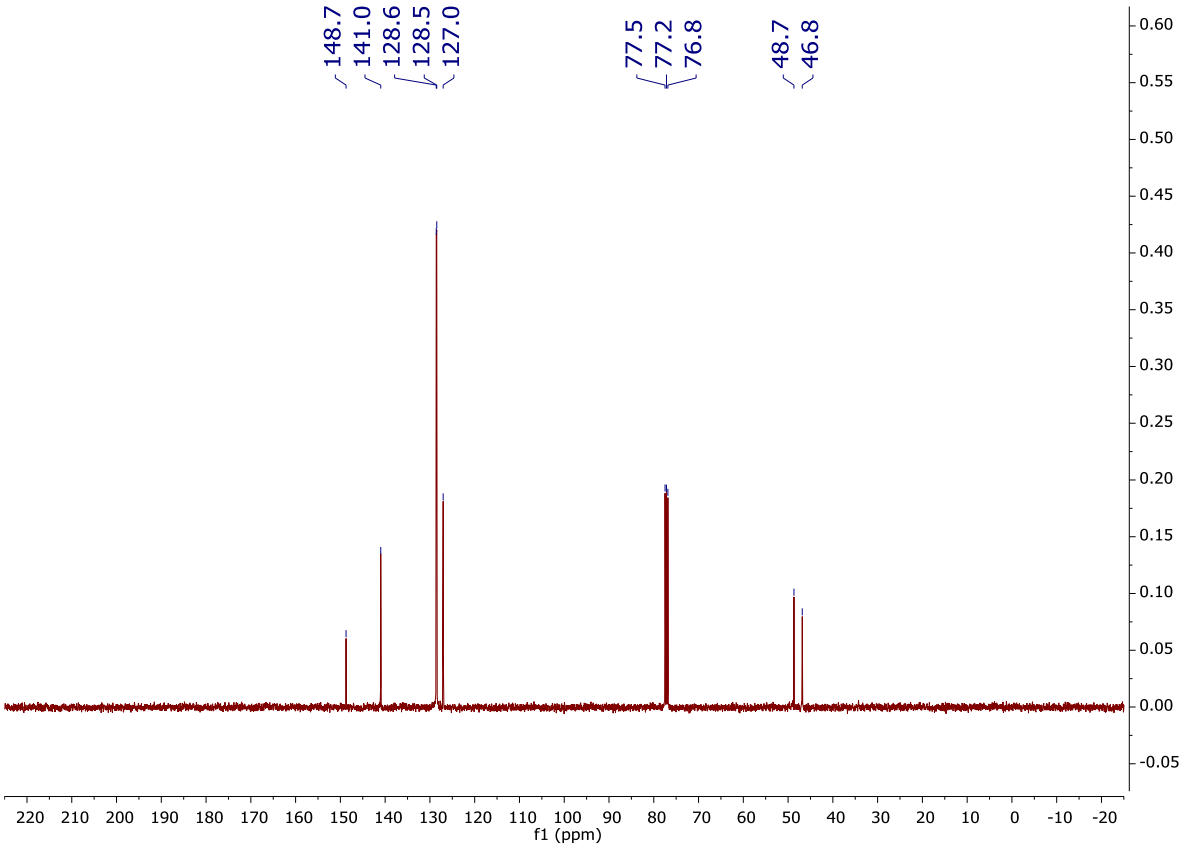


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4j (**in $CDCl_3$).

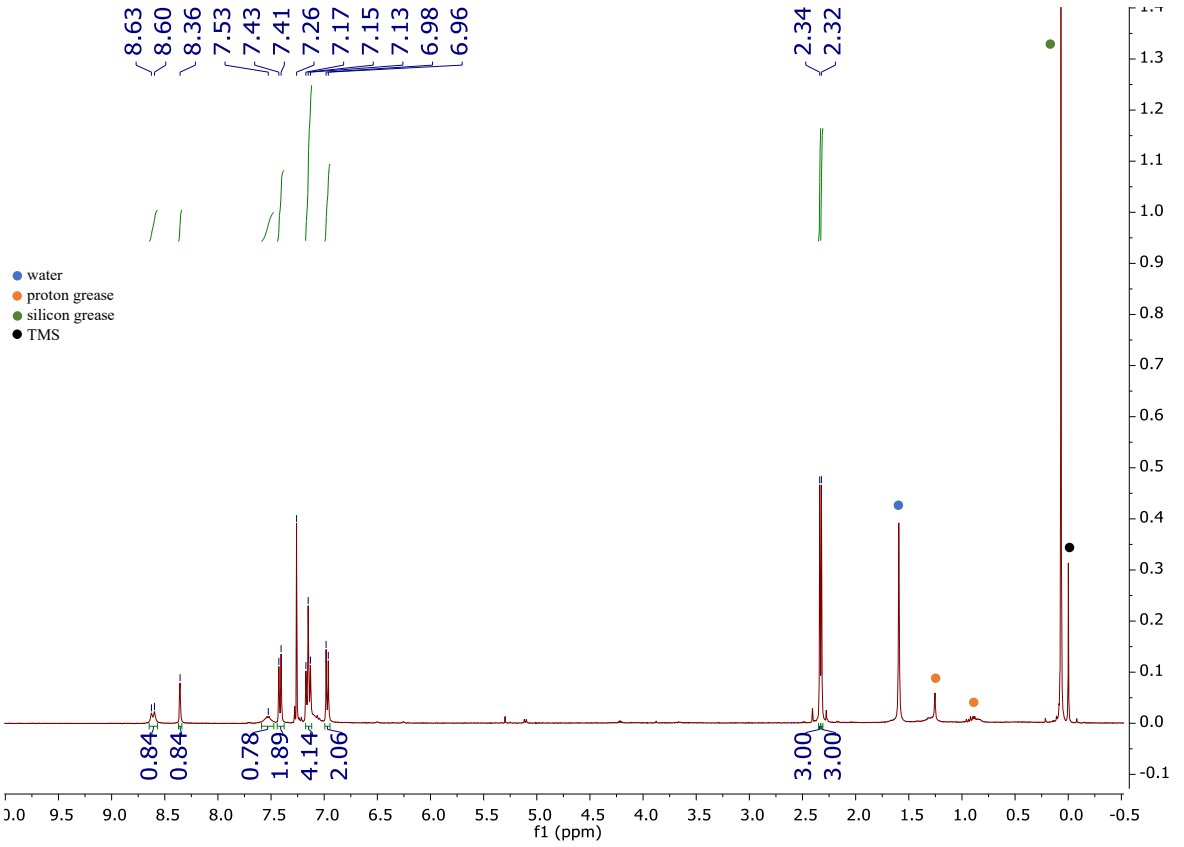


Figure S26. ^{1}H NMR spectrum of compound **7a (**in $CDCl_3$).

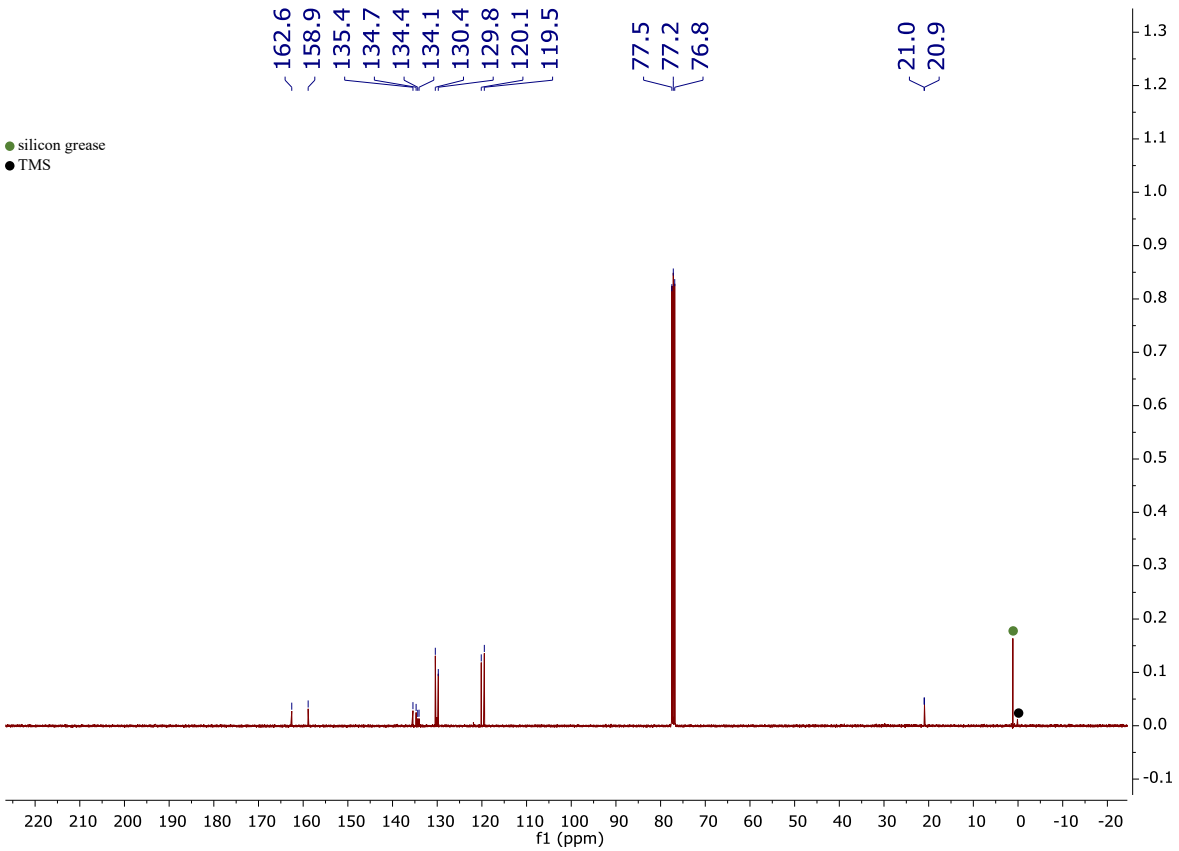


Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7a (**in $CDCl_3$).

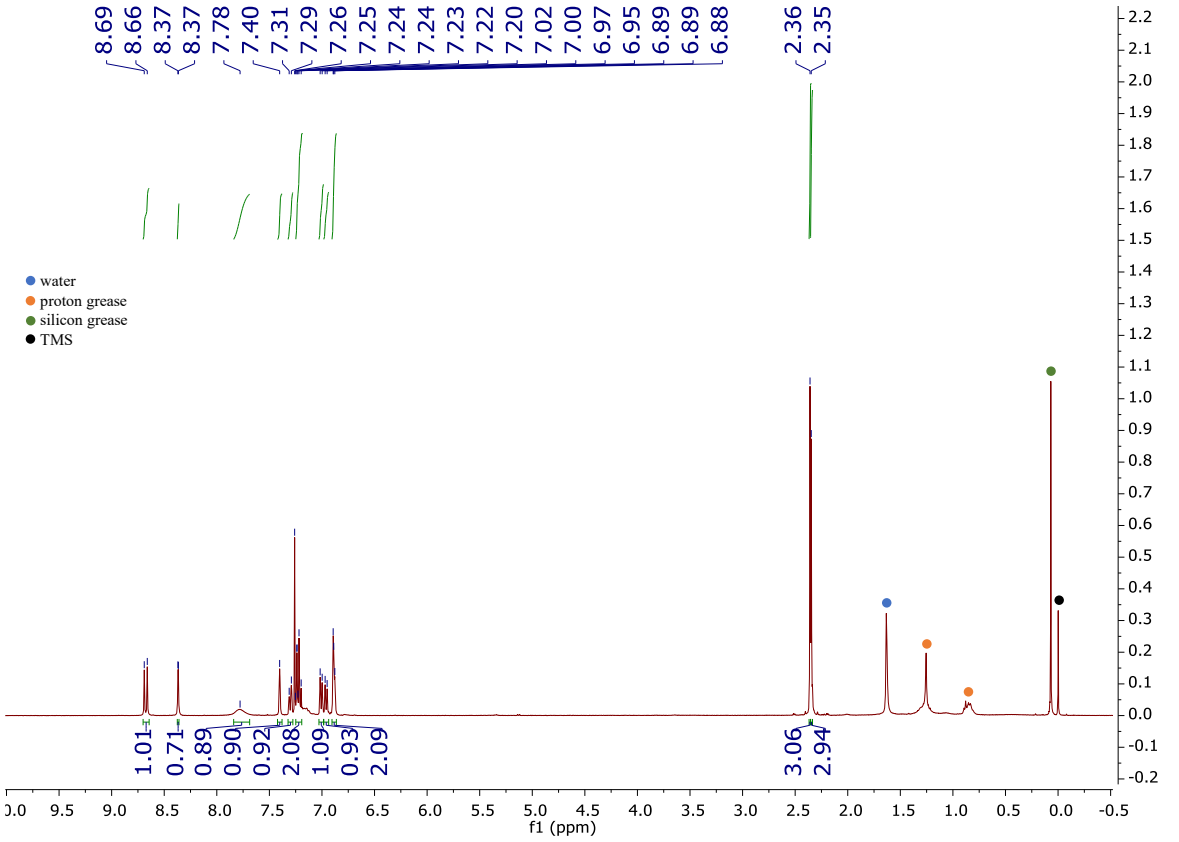


Figure S28. ^{1}H NMR spectrum of compound **7b (**in $CDCl_3$).

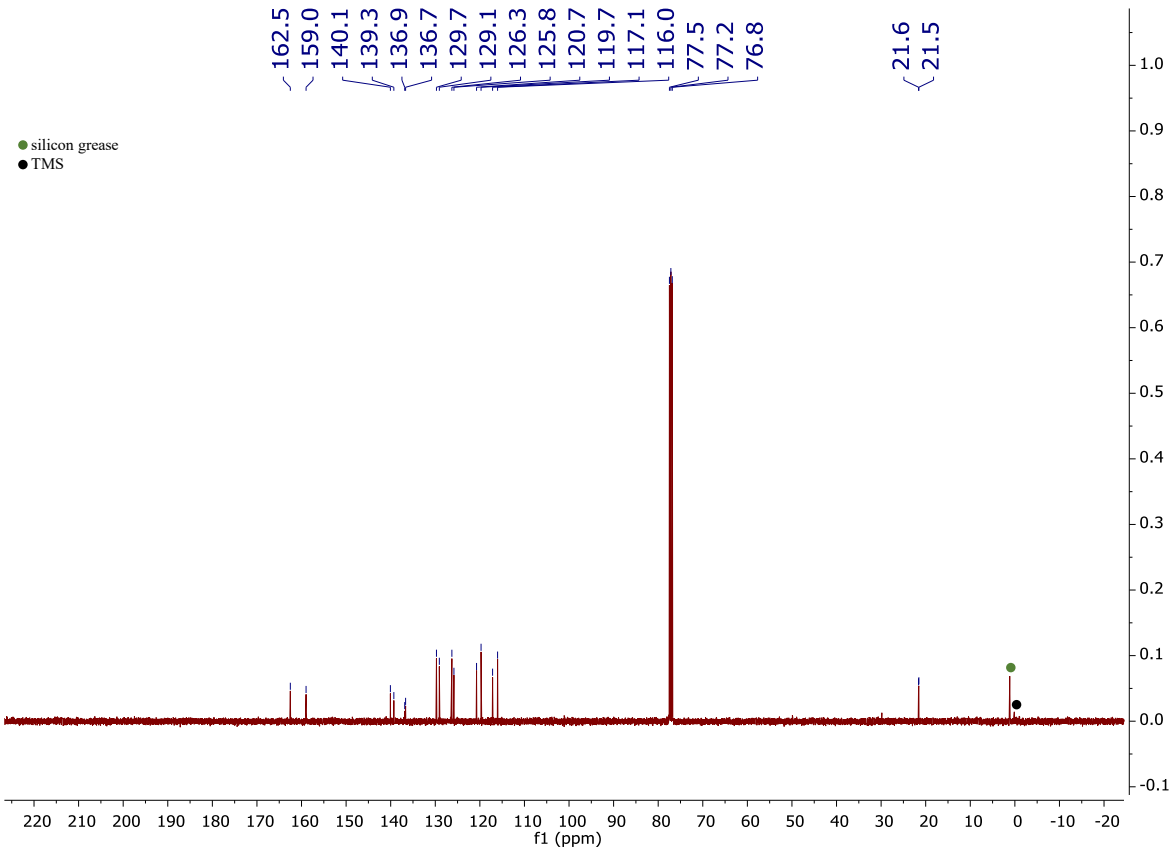


Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7b (**in $CDCl_3$).

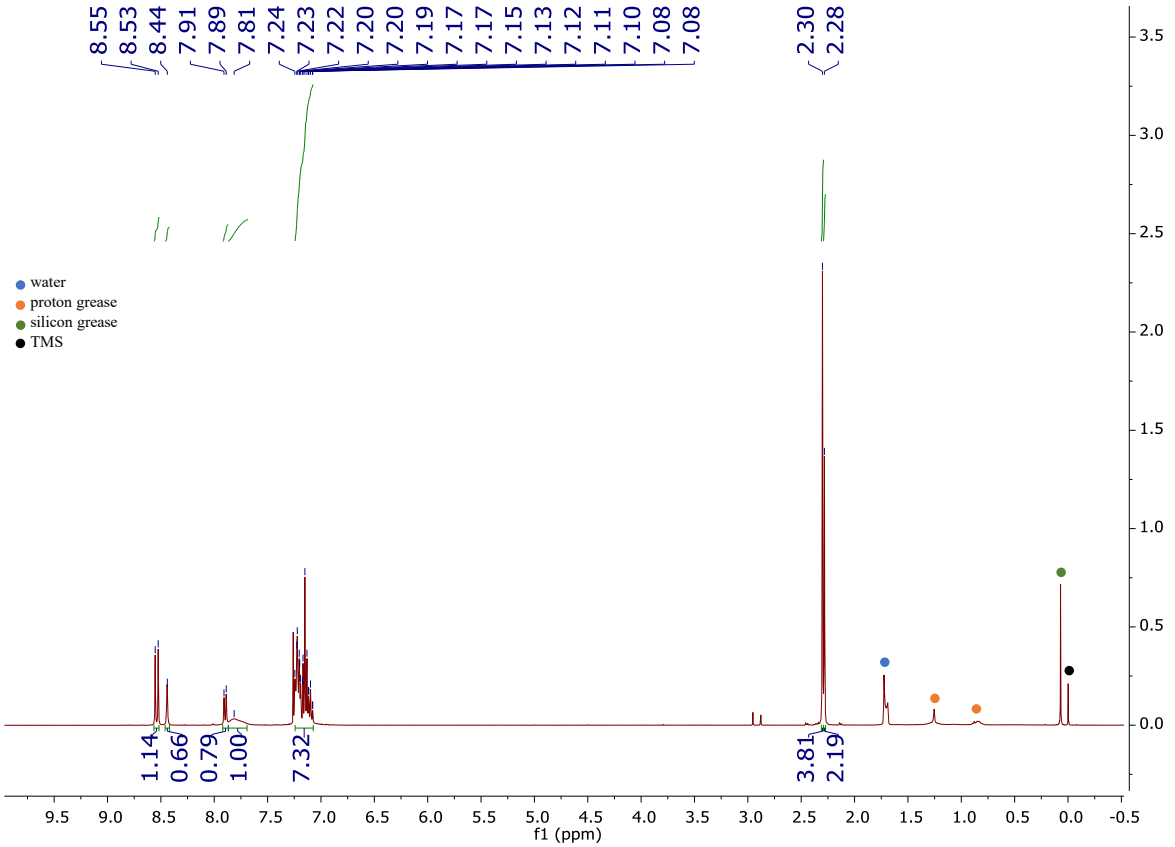


Figure S30. ^{1}H NMR spectrum of compound **7c (**in $CDCl_3$).

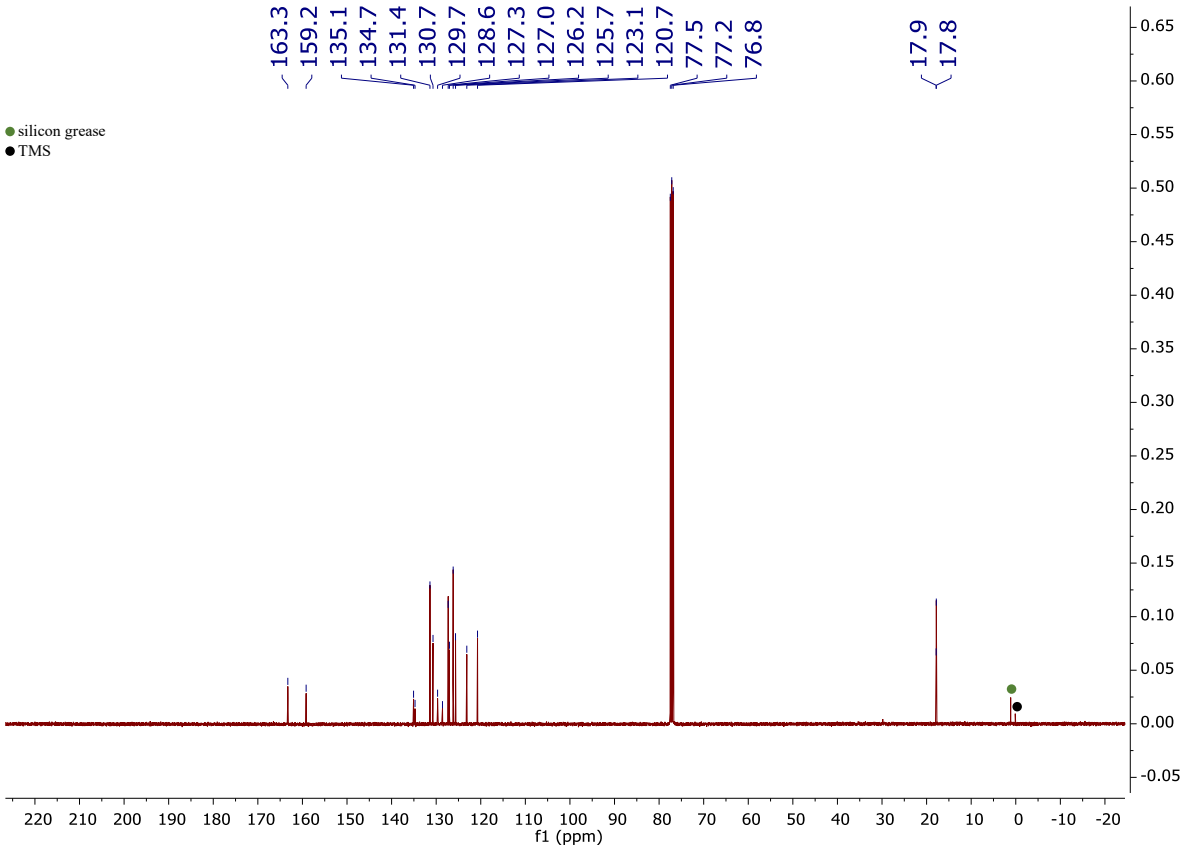


Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7c (**in $CDCl_3$).

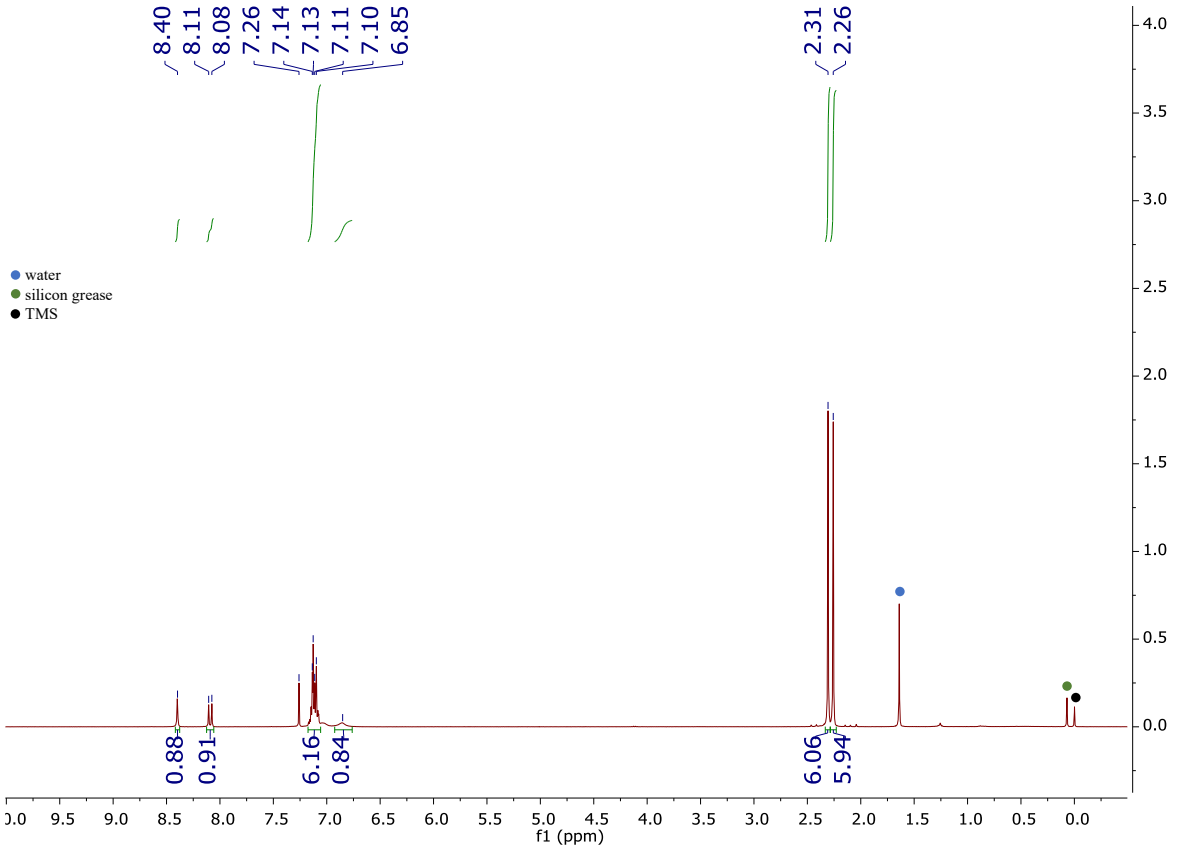


Figure S32. ^{1}H NMR spectrum of compound **7d (**in $CDCl_3$).

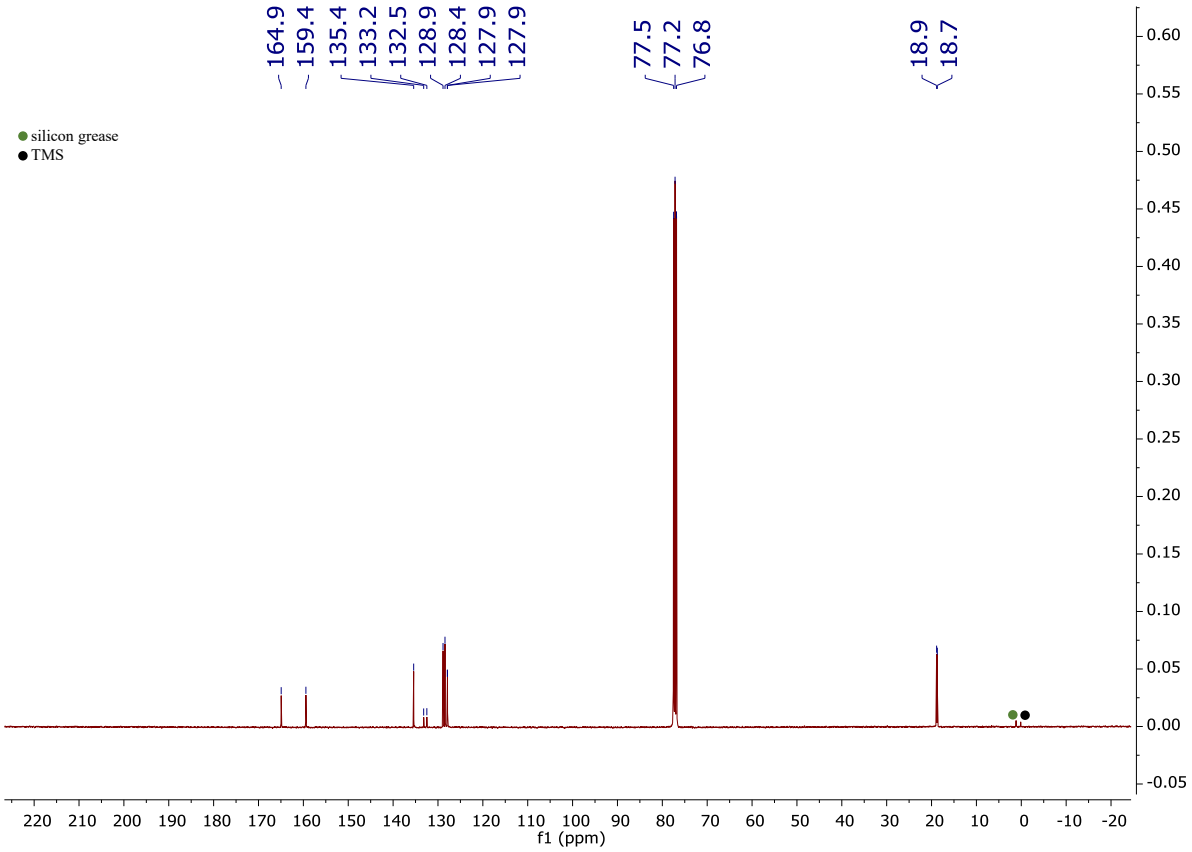


Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7d** (in $CDCl_3$).

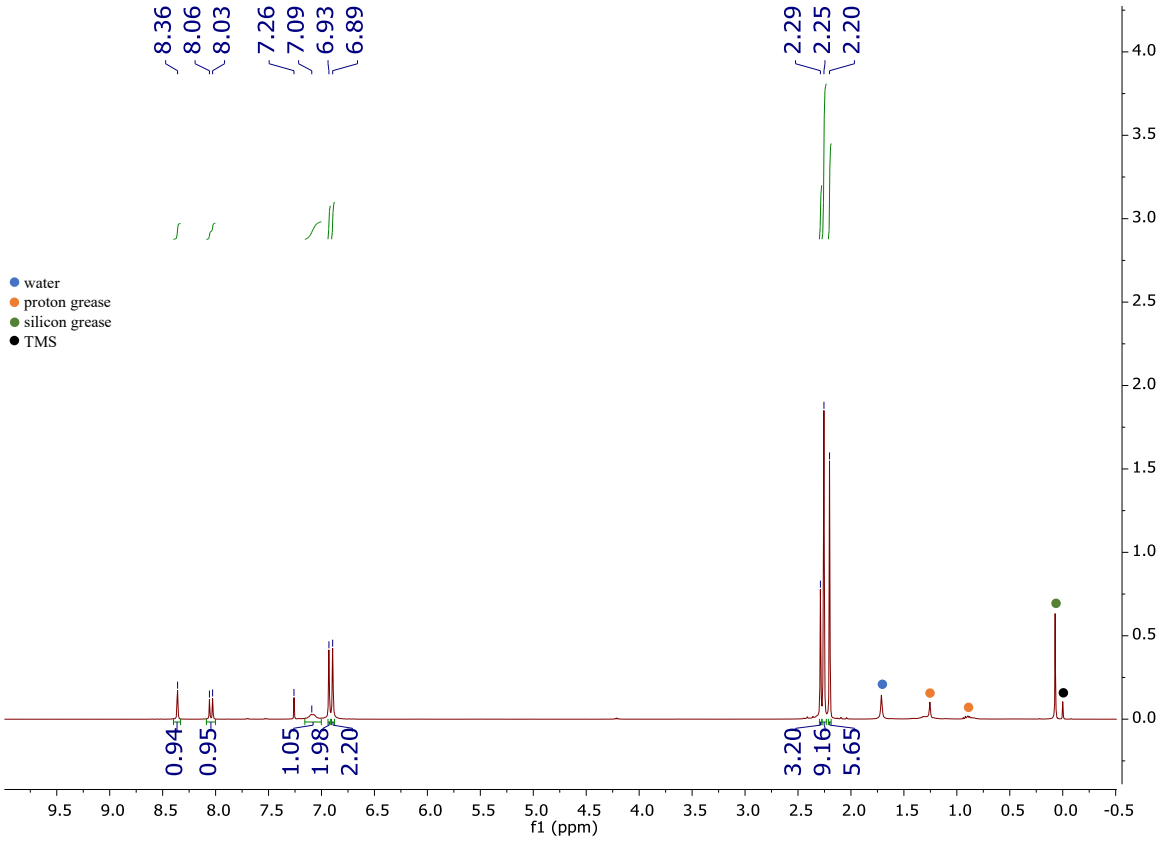


Figure S34. ^{1}H NMR spectrum of compound **7e** (in $CDCl_3$).

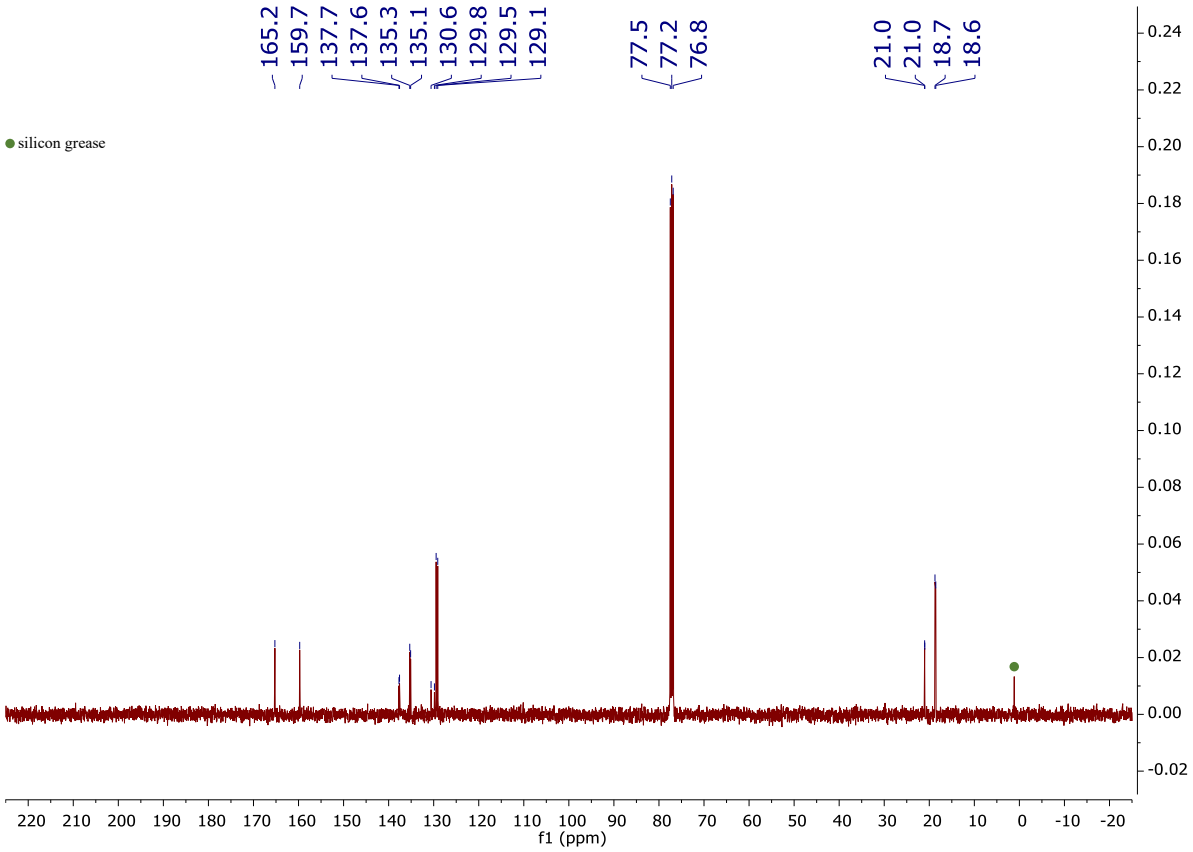


Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7e (**in $CDCl_3$).

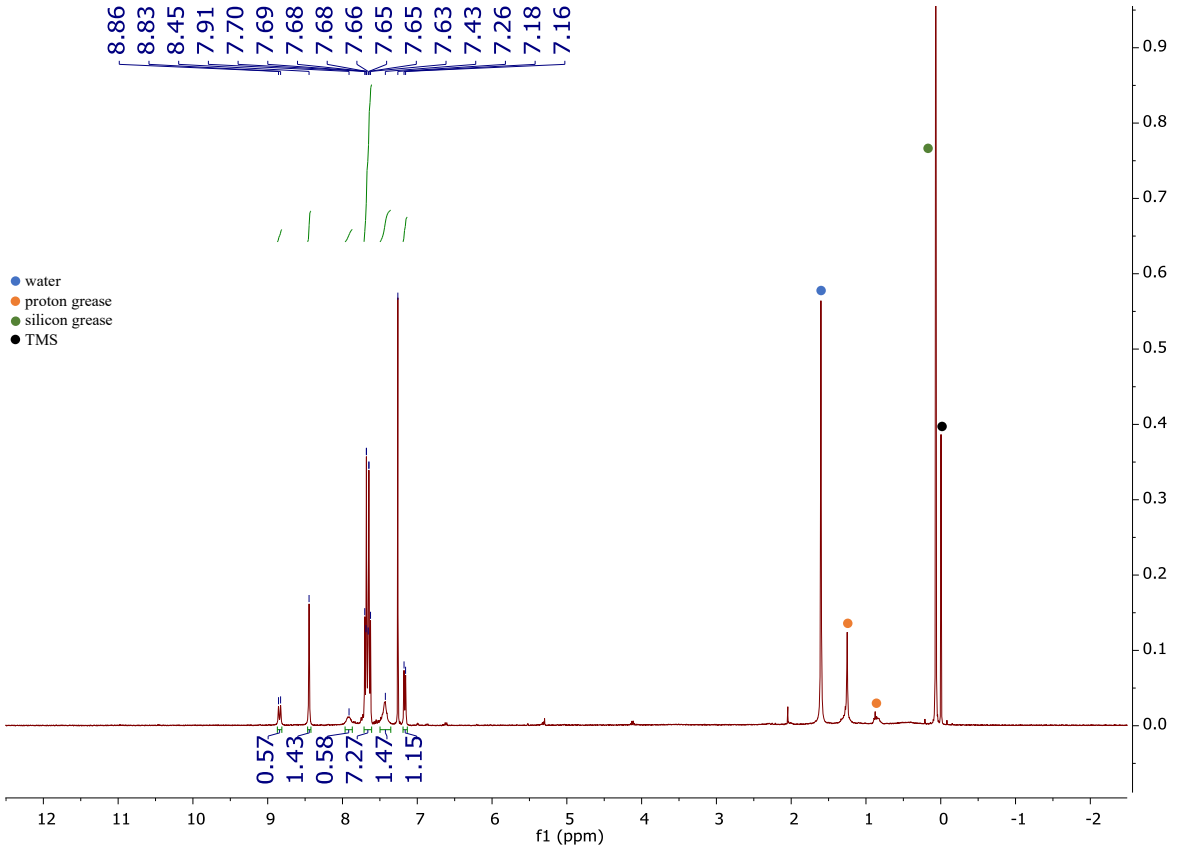


Figure S36. ^{1}H NMR spectrum of compound **7f (**in $CDCl_3$).

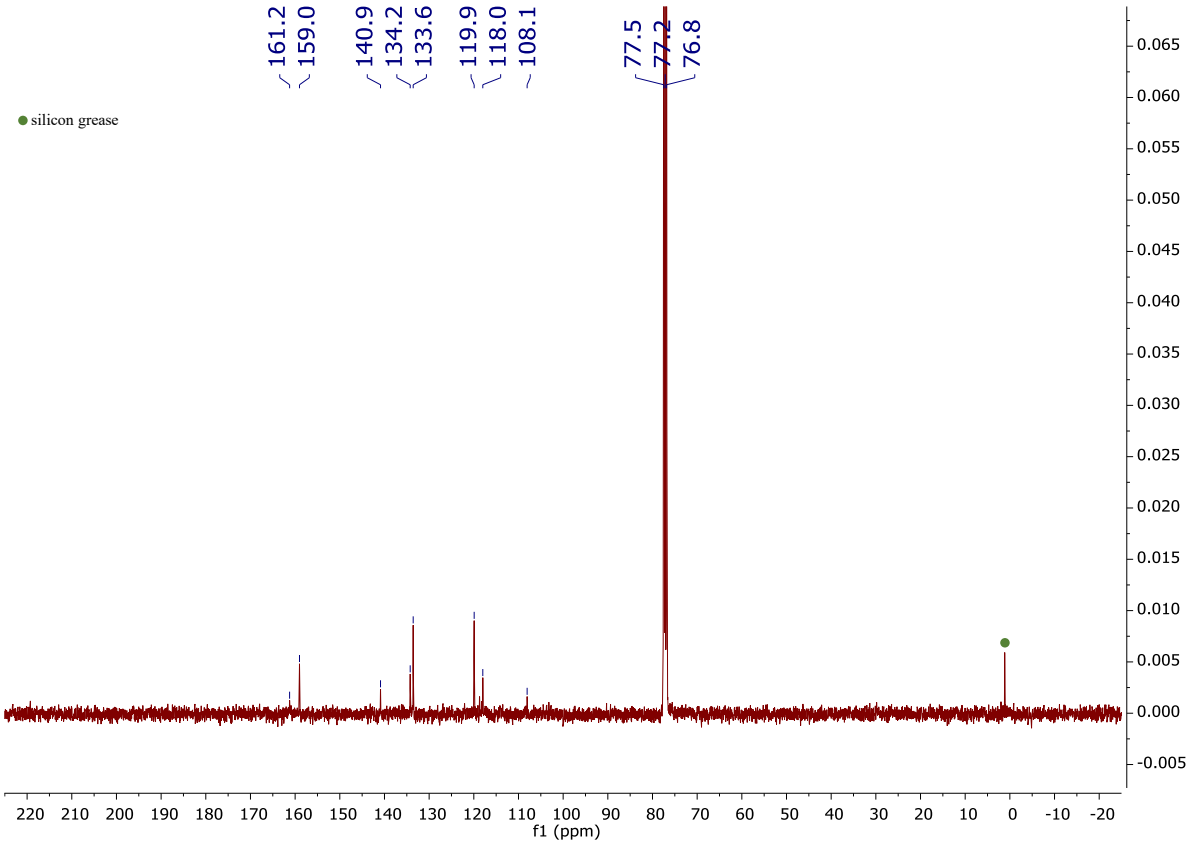


Figure S37. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7f (**in $CDCl_3$).

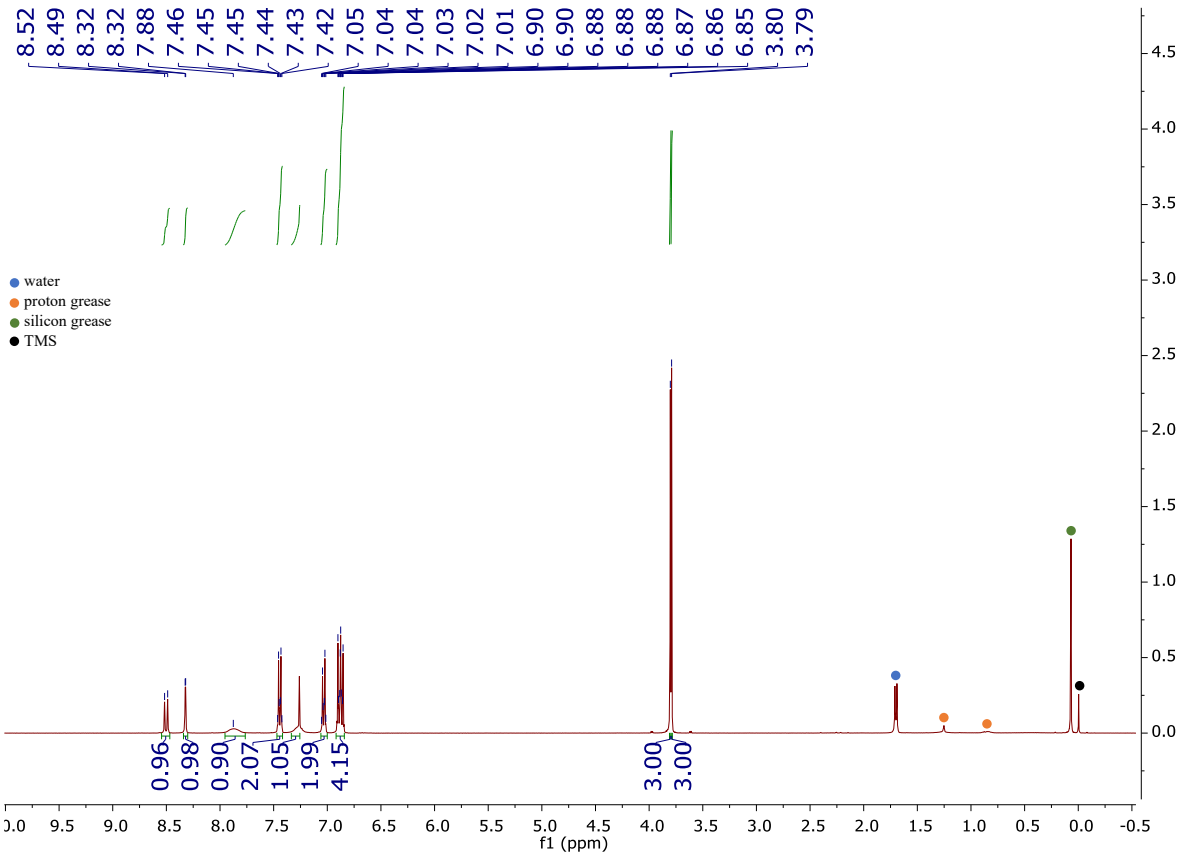


Figure S38. ^{1}H NMR spectrum of compound **7g (**in $CDCl_3$).

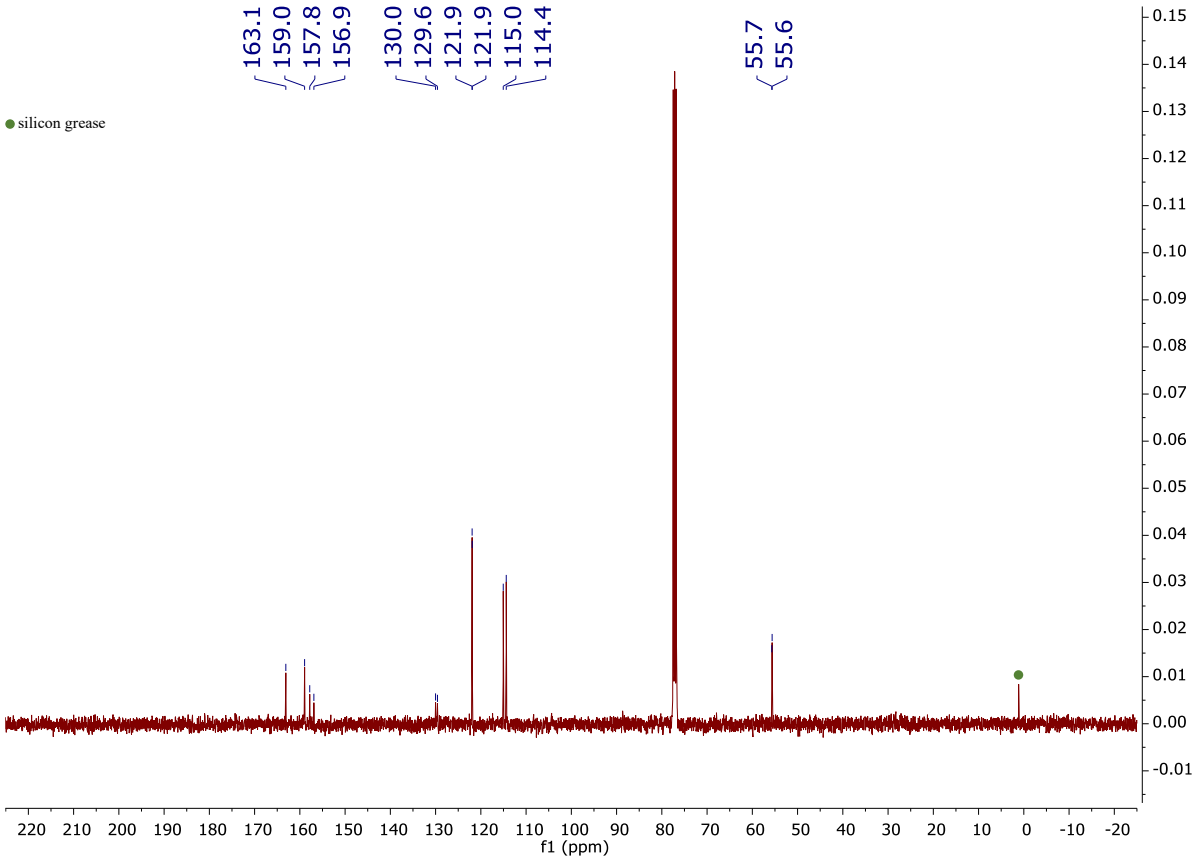


Figure S39. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7g** (in $CDCl_3$).

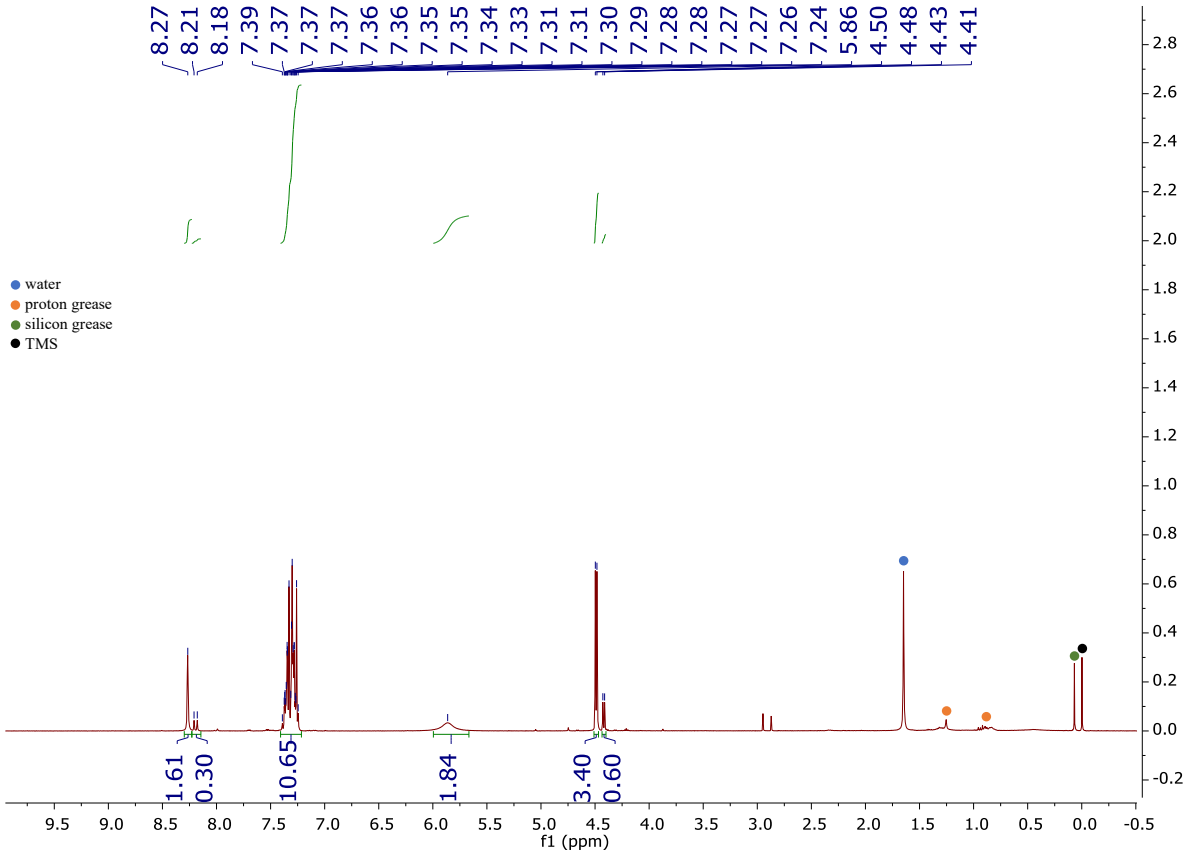


Figure S40. ^{1}H NMR spectrum of compound **7h** (in $CDCl_3$).

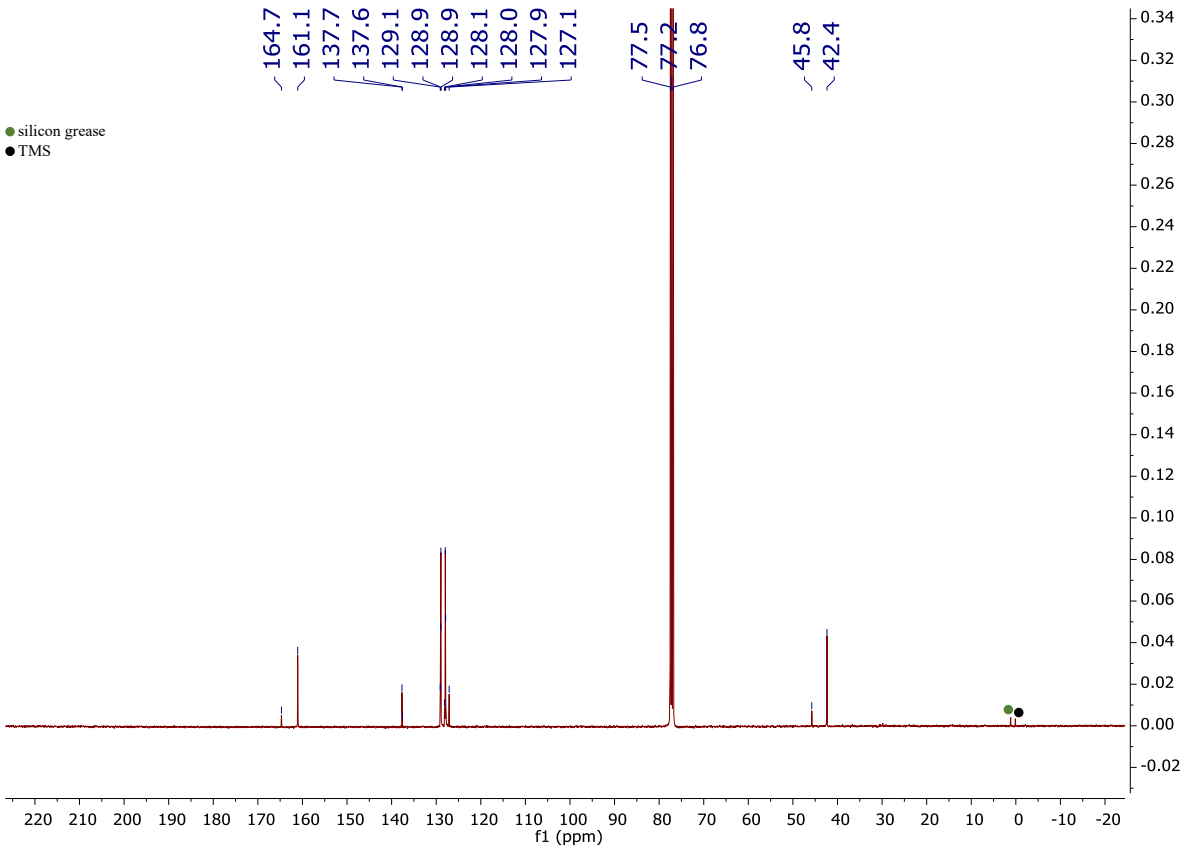


Figure S41. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7h (**in $CDCl_3$).

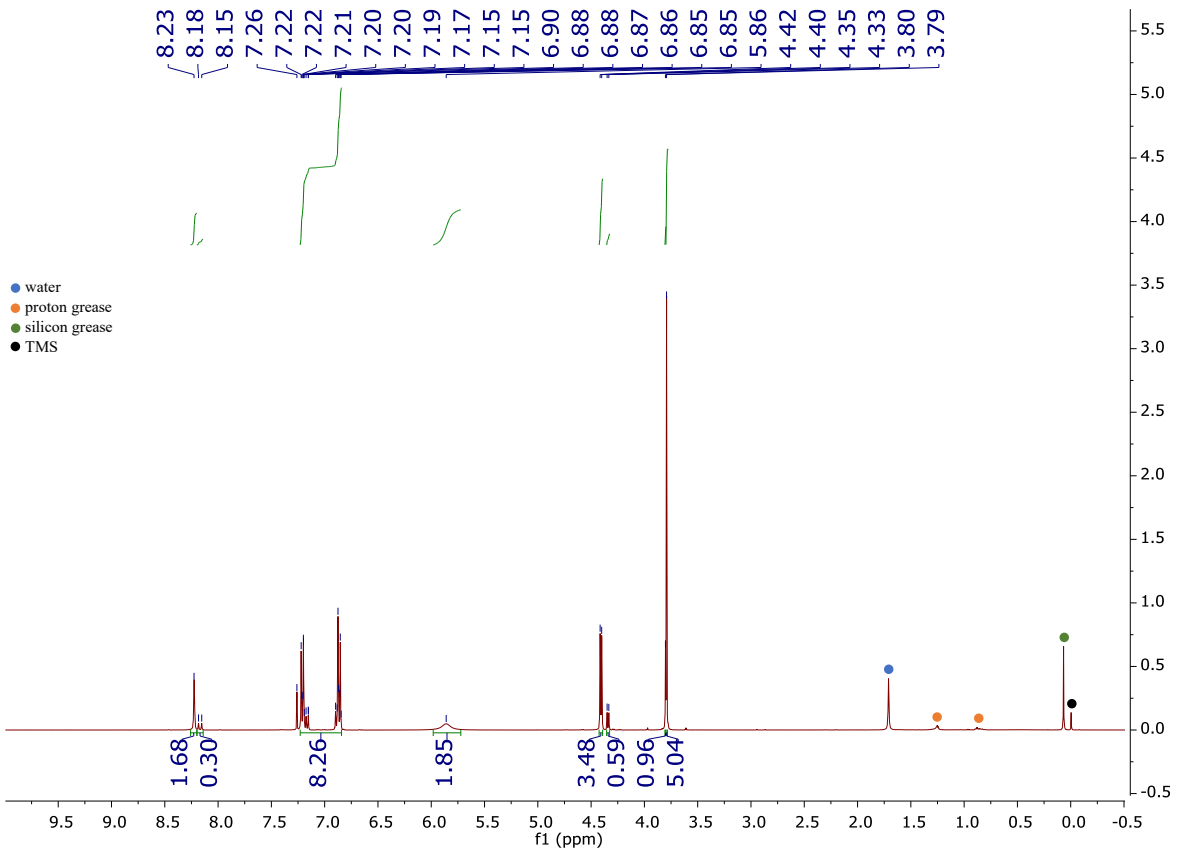


Figure S42. ^{1}H NMR spectrum of compound **7i (**in $CDCl_3$).

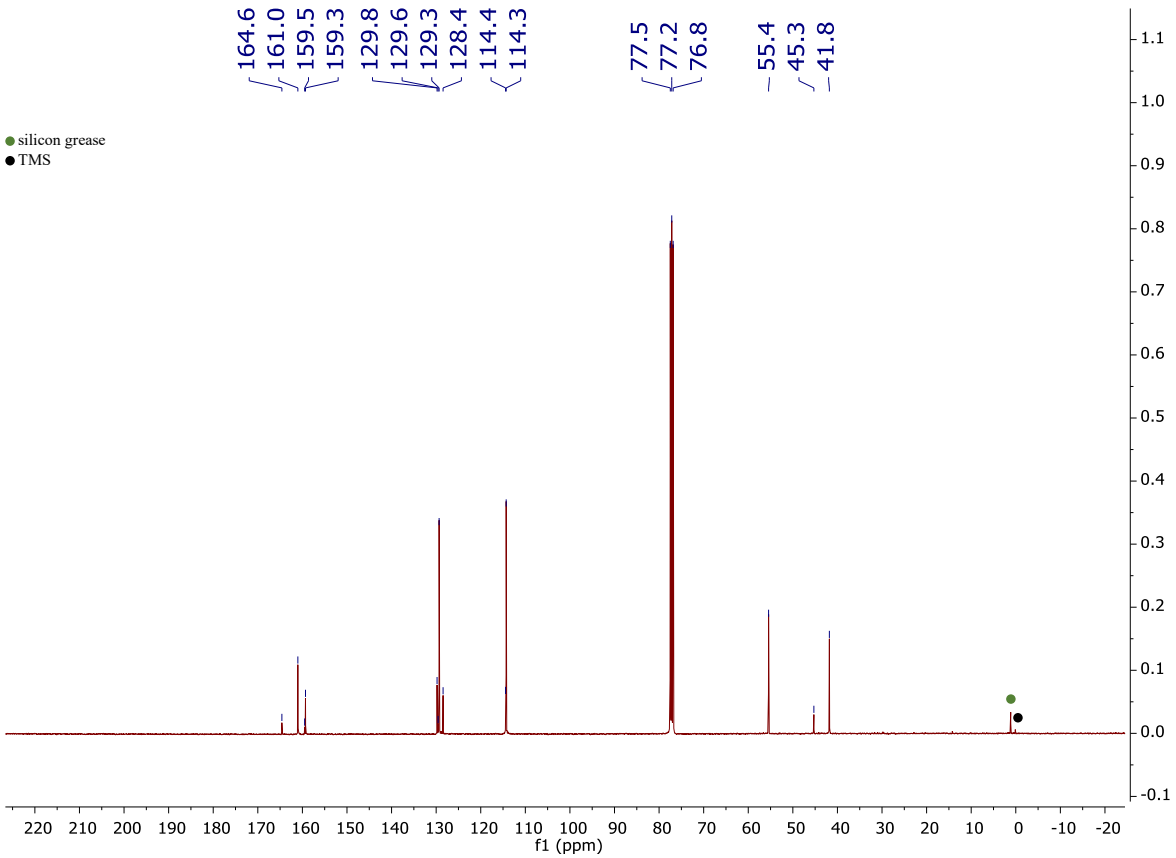


Figure S43. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7i (**in $CDCl_3$).

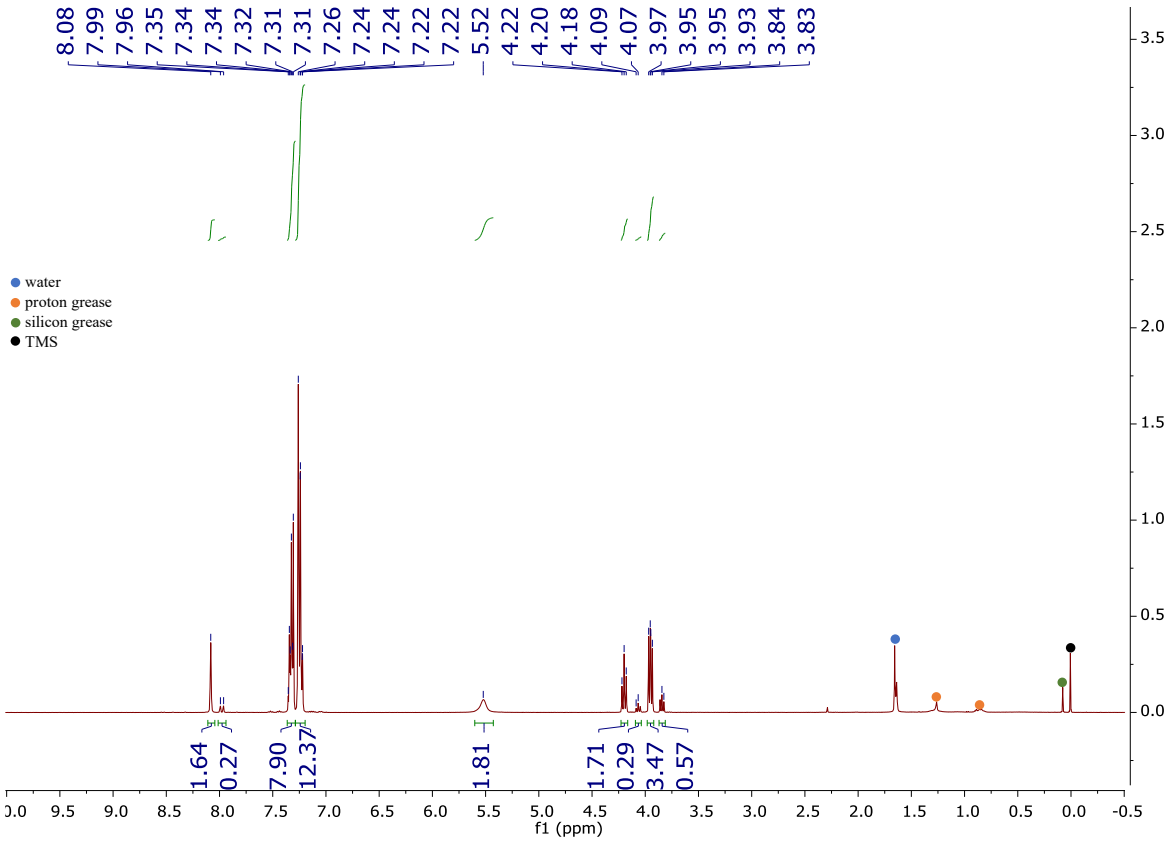


Figure S44. ^{1}H NMR spectrum of compound **7j (**in $CDCl_3$).

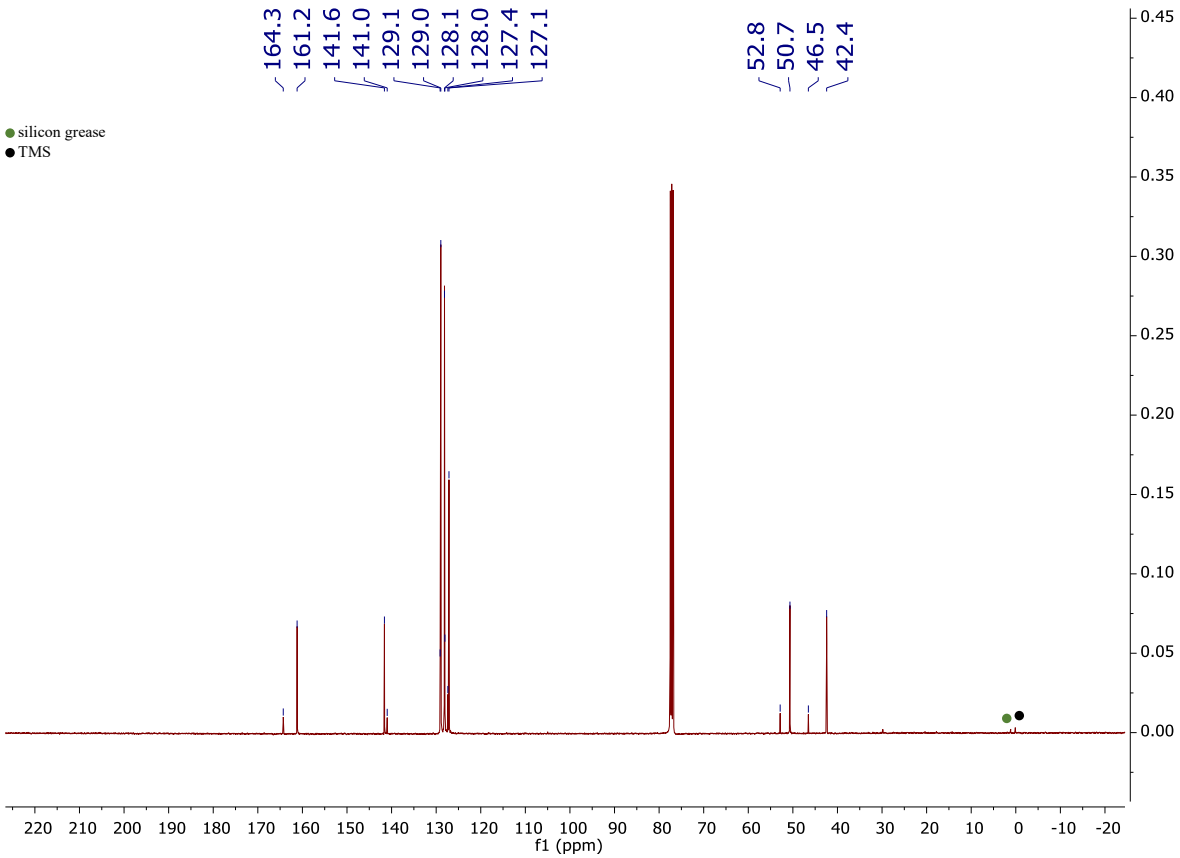


Figure S45. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7j (**in $CDCl_3$).

S3. X-Ray Data Collection and Structural Refinement

The X-ray diffraction intensity data were measured at 100 K with a Bruker APEX II diffractometer equipped with a CCD detector, employing Mo K α radiation (λ = 0.71073 Å), with the SMART suite of programs.[2] All data were processed and corrected for Lorentz and polarization effects with SAINT and for absorption effects with SADABS. Structural solution and refinement were carried out with the SHELXTL suite of programs.[3] The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. Details of the crystallographic data and a summary of the intensity data collection parameters for **2**, **4a-e**, **4h** and **4j** are listed in Tables S4-S6. CCDC-2270478 **2**, CCDC-2257721 **4a**, CCDC-2257722 **4b**, CCDC-2257723 **4c**, CCDC-2257724 **4d**, CCDC-2257725 **4e**, CCDC-2257726 **4h**, CCDC-2517514 **4j** contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data_request/cif.

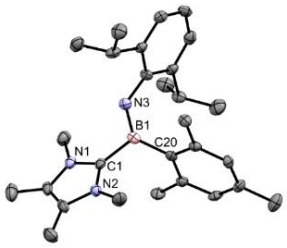


Figure S46. X-ray crystal structure of **2** with thermal ellipsoids shown at 50% probability. All hydrogen atoms are removed for clarity. Selected bond lengths (Å) and angles (deg): B1-N3 1.355(5), B1-C1 1.616(5), C1-N1 1.362(4), C1-N2 1.346(4), C1-B1-N3 114.1(3), C20-B1-N3 129.8(3), C1-B1-C20 116.0(3). CCDC deposition number 2270478.

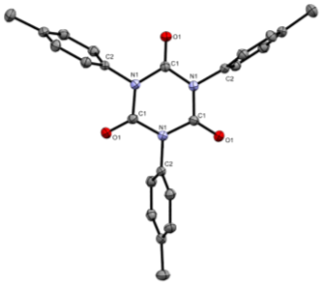


Figure S47. X-ray crystal structure of **4a** with thermal ellipsoids shown at 50% probability. All hydrogen atoms are removed for clarity. Selected bond lengths (Å) and angles (deg): C1-O1 1.204(3), C1-N1 1.393(3), C2-N1 1.454(3); O1-C1-N1 122.8(2), N1-C1-N1 114.9(2), C1-N1-C2 117.22(18). CCDC deposition number 2257721.

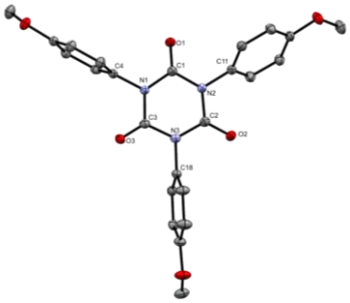


Figure S48. X-ray crystal structure of **4b** with thermal ellipsoids shown at 50% probability. All hydrogen atoms are removed for clarity. Selected bond lengths (Å) and angles (deg): C1-O1 1.211 (3), C1-N1 1.395(3), C4-N1 1.447(3); O1-C1-N1 122.1(2), N2-C1-N1 115.0(2), C1-N1-C4 117.5(2). CCDC deposition number 2257722.

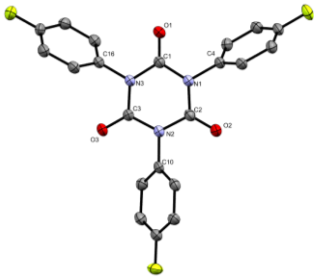


Figure S49. X-ray crystal structure of **4c** with thermal ellipsoids shown at 50% probability. All hydrogen atoms are removed for clarity. Selected bond lengths (Å) and angles (deg): C1-O1 1.209(3), C1-N1 1.384(3), C4-N1 1.452(3); O1-C1-N1 122.6(2), N1-C1-N3 115.1(2), C1-N1-C4 117.6(2). CCDC deposition number 2257723.

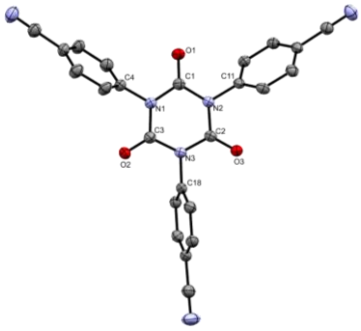


Figure S50. X-ray crystal structure of **4d** with thermal ellipsoids shown at 50% probability. All hydrogen atoms are removed for clarity. Selected bond lengths (Å) and angles (deg): C1-O1 1.210(3), C1-N1 1.383(3), C4-N1 1.448(3); O1-C1-N1 122.3(2), N1-C1-N2 115.40(18), C1-N1-C4 116.76(17). CCDC deposition number 2257724.

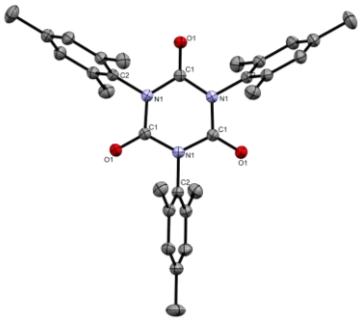


Figure S51. X-ray crystal structure of **4e** with thermal ellipsoids shown at 50% probability. All hydrogen atoms are removed for clarity. Selected bond lengths (Å) and angles (deg): C1-O1 1.207(2), C1-N1 1.3905(11), C2-N1 1.451(2); O1-C1-N1 122.41(8), N1-C1-N1 115.18(16), C1-N1-C2 117.59(8). CCDC deposition number 2257725.

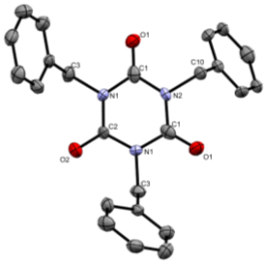


Figure S52. X-ray crystal structure of **4h** with thermal ellipsoids shown at 50% probability. All hydrogen atoms are removed for clarity. Selected bond lengths (Å) and angles (deg): C1-O1 1.209(11), C1-N1 1.387(11), C3-N1 1.491(11); O1-C1-N2 122.2(11), N1-C1-N2 116.0(10), C1-N1-C3 117.1(8). CCDC deposition number 2257726.

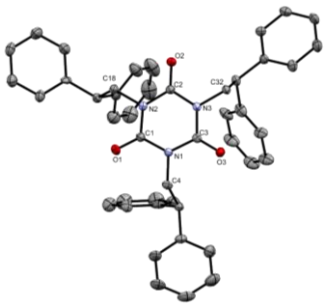


Figure S53. X-ray crystal structure of **4j** with thermal ellipsoids shown at 50% probability. All hydrogen atoms are removed for clarity. Selected bond lengths (Å) and angles (deg): C1-O1 1.210(2), C1-N1 1.391(2), C4-N1 1.4751(19); O1-C1-N1 122.82(15), N1-C1-N2 115.54(14), C1-N1-C4 118.17(13). CCDC deposition number 2517514.

Table S4. X-Ray data for compounds **4a, 4b** and **4c.**

	4a	**4b**	**4c**
Formula	$C_{30}H_{27}N_3O_3$	$C_{25}H_{23}Cl_3N_3O_{6.50}$	$C_{27}H_{18}F_3N_3O_3$
Fw	477.54	575.81	489.44
T/K	100(2)	100(2)	100(2)
cryst system	trigonal	orthorhombic	monoclinic
space group	*R* 3 *c*	*P n a* 21	*P* 1 21/*c* 1
a (Å)	12.8280 (7)	12.3523 (11)	17.8460 (15)
b (Å)	12.8280 (7)	13.3248 (10)	16.4283 (14)
c (Å)	25.5324 (19)	15.9694 (12)	7.7056 (7)
α (deg)	90	90	90
β (deg)	90	90	94.458 (3)
γ (deg)	120	90	90
V (Å^3)	3638.6 (5)	2628.4 (4)	2252.3 (3)
Z	6	4	4
d_{calcd} (g cm^{-3})	1.308	1.455	1.443
μ (mm^{-1})	0.085	0.397	0.112
F(000)	1512	1188	1008
cryst size (mm)	0.04 x 0.12 x 0.14	0.20 x 0.22 x 0.24	0.18 x 0.20 x 0.22
2*θ* range (deg)	4.86 < 2*θ* < 62.39	5.17 < 2*θ* < 66.81	4.959 < 2*θ* < 53.00
index range	-18 ≤ *h* ≤ 18, -18 ≤ *k* ≤ 18, -37 ≤ *l* ≤ 37	-20 ≤ *h* ≤ 20, -22 ≤ *k* ≤ 19, -25 ≤ l ≤ 26	-22 ≤ *h* ≤ 19, -20 ≤ *k* ≤ 20 -9 ≤ *l* ≤ 9
no. of rflns collected	16707	68598	22948
no. of indep rflns	2707	12674	4785
*R*1, *wR*2 (*I* > 2*σ*(*I*))	0.0501, 0.1074	0.0543, 0.1034	0.0576, 0.1177
*R*1, *wR*2 (all data)	0.0691, 0.1179	0.1022, 0.1239	0.1184, 0.1451
goodness of fit, F^2	1.038	1.018	1.029
no. of data/restraints/params	2707 / 1 / 110	12674 / 1 / 341	4785 / 0 / 326
largest diff peak and hole, eÅ^{-3}	0.223 / -0.275	0.451 / -0.458	0.300 / -0.337

Table S5. X-Ray data for compounds **4d, 4e**, **4h.**

	4d	**4e**	**4h**
Formula	$C_{24}H_{13}N_6O_{3.50}$	$C_{30}H_{33}N_3O_3$	$C_{24}H_{21}N_3O_3$
Fw	441.40	483.59	399.44
T/K	100(2)	100(2)	103(2)
cryst system	triclinic	trigonal	orthorhombic
space group	*P* -1	*R* -3 *c*	*P m n* 21
a (Å)	10.2262 (7)	15.9830 (5)	18.741 (10)
b (Å)	12.4749 (9)	15.9830 (5)	4.507 (3)
c (Å)	17.7971 (11)	18.6933 (10)	11.291 (7)
α (deg)	102.205 (2)	90	90
β (deg)	92.512 (2)	90	90
γ (deg)	104.981 (2)	120	90
V (Å^3)	2132.0 (3)	4135.5 (3)	953.7 (9)
Z	4	6	2
d_{calcd} (g cm^{-3})	1.375	1.165	1.391
μ (mm^{-1})	0.097	0.076	0.093
F(000)	908	1548	420
cryst size (mm)	0.04 x 0.14 x 0.26	0.06 x 0.10 x 0.12	0.02 x 0.20 x 0.22
2*θ* range (deg)	$4.624 < 2\theta < 54.20$	$5.097 < 2\theta < 61.72$	$7.217 < 2\theta < 44.70$
index range	$-13 \le h \le 13$, $-15 \le k \le 15$, $-22 \le l \le 19$	$-22 \le h \le 23$, $-22 \le k \le 23$, $-26 \le l \le 27$	$-18 \le h \le 22$, $-5 \le k \le 4$, $-13 \le l \le 13$
no. of rflns collected	50209	16216	4704
no. of indep rflns	9392	1472	1725
*R*1, *wR*2 ($I > 2\sigma(I)$)	0.0551, 0.1342	0.0473, 0.1142	0.0728, 0.1387
*R*1, *wR*2 (all data)	0.0882, 0.1541	0.0771, 0.1420	0.1985, 0.1860
goodness of fit, F^2	1.047	1.019	0.917
no. of data/restraints/params	9392 / 0 / 604	1472 / 0 / 59	1725 / 1 / 134
largest diff peak and hole, eÅ^{-3}	0.266 / -0.752	0.282 / -0.265	0.325 / -0.251

Table S6. X-Ray data for compound **4j.**

	4j
Formula	$C_{46}H_{40}Cl_3N_3O_3$
Fw	789.16
T/K	100(2)
cryst system	triclinic
space group	*P* -1
a (Å)	12.4889 (11)
b (Å)	13.5583 (12)
c (Å)	13.6320 (11)
α (deg)	61.128 (2)
β (deg)	78.860 (3)
γ (deg)	85.886 (3)
V (Å^3)	1982.7 (3)
Z	2
d_{calcd} (g cm^{-3})	1.322
μ (mm^{-1})	0.277
F(000)	824
cryst size (mm)	0.18 x 0.20 x 0.22
2*θ* range (deg)	$4.348 < 2\theta < 62.04$
index range	$-18 \le h \le 18$, $-19 \le k \le 19$, $-19 \le l \le 17$
no. of rflns collected	66357
no. of indep rflns	12605
*R*1, *wR*2 ($I > 2\sigma(I)$)	0.0719, 0.1840
*R*1, *wR*2 (all data)	0.1032, 0.2092
goodness of fit, F^2	1.030
no. of data/restraints/params	12605 / 836 / 625
largest diff peak and hole, eÅ^{-3}	1.050 / -0.593

S4. Theoretical Studies

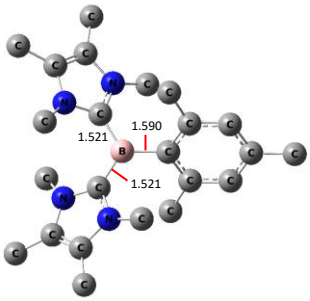
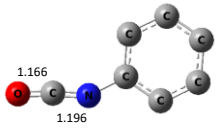
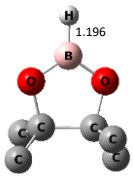
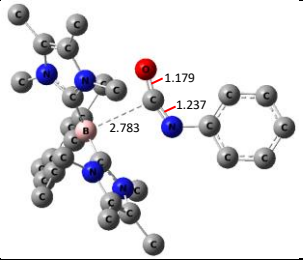
The mechanism for the hydroboration of phenyl isocyanate using HBpin catalyzed by borylene **1** was performed at the M06-2X[6]/def2-SVP[7] level of theory using the Gaussian 16 B.01 software.[8] All structures were optimized until the maximum force fell below 0.000450 Hartree/Bohr, with stationary states having zero imaginary frequencies and transition states having one imaginary frequency. The Gibbs free energy was calculated at 298.15 K and 1 atm.

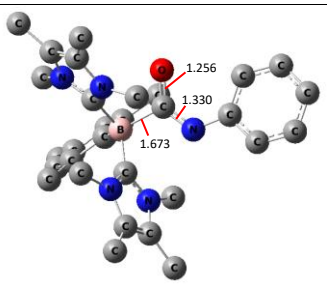
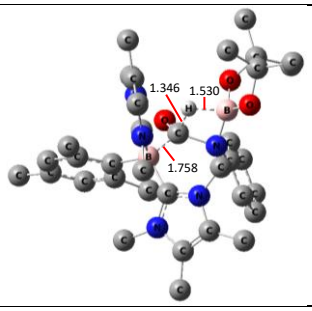
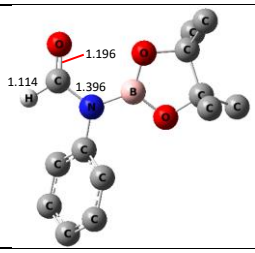
List of abbreviations used in theoretical studies.

Abbreviation	Definition
Cpd	Compound
HBpin	Pinacolborane
Int	Intermediate
TS	Transition state
Prod	Product

List of color coded atom used in optimized structures.

Color	Definition
White	Hydrogen
Grey	Carbon
Blue	Nitrogen
Red	Oxygen
Pink	Boron

	
Cpd1	Reactant
	
HBpin	TS1

	
Int1	TS2
	
Prod1	

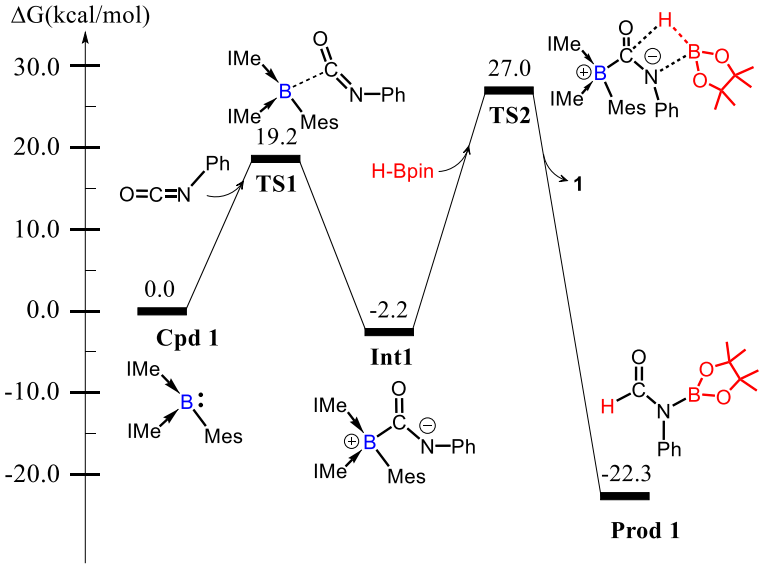


Figure S54. DFT-calculated free energy profile (kcal·mol^{-1}) at M06-2X/def2-SVP level for the proposed mechanism of **1**-catalyzed hydroboration of phenyl isocyanate using HBpin.

Table S7
Cpd 1 (M06-2X/Def2-SVP)
G = -1139.555142 Hartree

Atomic Number	Coordinates (Angstroms) X	Y	Z
N	2.29955100	0.98492600	-0.70855500
C	1.09053000	1.05524700	-0.03836700
N	1.08583000	2.31531000	0.52280800
C	2.25509700	3.00221400	0.21105800
C	3.01670800	2.17474200	-0.55141600
C	4.36064800	2.38664300	-1.15857000
H	4.32111500	2.42597600	-2.25869200
H	5.05495200	1.57852800	-0.88023000
H	4.78846100	3.33385400	-0.80882700
C	2.52705700	4.38417200	0.69793100
H	2.61015000	4.42649100	1.79524600
H	1.72584100	5.07643300	0.39788300
H	3.46871500	4.75557200	0.27664500
C	2.59490500	-0.01579700	-1.70280700
H	2.99165400	-0.94812700	-1.26962900
H	3.32394600	0.38054800	-2.41979900
H	1.65535500	-0.27369800	-2.21952700
C	0.07727900	2.76362400	1.45254800
H	-0.21643200	1.91373500	2.08656400
H	-0.83085900	3.12037300	0.94188500
H	0.48537600	3.56881500	2.07546600
B	-0.02463000	0.02066400	0.00691600
N	1.51883800	-2.05230700	0.41245400
C	0.36996200	-1.44695700	-0.06708900
N	-0.38151700	-2.49100900	-0.56551500
C	0.28168300	-3.70316900	-0.40113700
C	1.46867800	-3.43378900	0.20260200
C	2.57270200	-4.34703500	0.61104400
H	2.68314900	-4.40676500	1.70539700
H	3.53765700	-4.01413000	0.19793600
H	2.38029000	-5.36164600	0.24209300
C	-0.29109800	-4.99930400	-0.86238300
H	0.36459600	-5.82819800	-0.57061400
H	-0.40831000	-5.03269900	-1.95689900
H	-1.28114600	-5.17788900	-0.41613200
C	2.44024000	-1.40091100	1.30904700
H	3.20064300	-0.80138600	0.78311400
H	2.94651700	-2.15196700	1.92734700
H	1.86641600	-0.70813900	1.94700100
C	-1.60021700	-2.30143200	-1.31464600

H	-2.47161800	-2.14494000	-0.65969600
H	-1.77681500	-3.17494300	-1.95393400
H	-1.49224100	-1.39978800	-1.93591800
C	-1.54900100	0.45926100	0.12735400
C	-4.29775600	1.25606400	0.34918500
C	-2.10125900	1.47175600	-0.70307500
C	-2.42477400	-0.13787900	1.07511500
C	-3.76278300	0.25889600	1.16658500
C	-3.44175300	1.85293700	-0.57688900
H	-4.40660700	-0.21493700	1.91459000
H	-3.83478400	2.63466900	-1.23469600
C	-1.27063700	2.14943000	-1.76618100
H	-1.90468200	2.72106500	-2.45806900
H	-0.69288600	1.40496100	-2.33562900
H	-0.52950700	2.84435600	-1.33750500
C	-1.93177400	-1.19198700	2.03687500
H	-1.74393700	-2.15712700	1.53774600
H	-2.66167200	-1.36673300	2.83949800
H	-0.97073700	-0.88901900	2.48063000
C	-5.74958500	1.64920300	0.44474000
H	-6.38203000	0.99590200	-0.17777200
H	-5.90721400	2.68147800	0.10244800
H	-6.11706100	1.57083600	1.47786400

Table S8

PhNCO (M06-2X/Def2-SVP)

G = -399.201253 Hartree

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z

C	-2.42626100	1.21924100	1.26874400
N	-1.63121300	0.64258600	0.58611700
O	-3.12380000	1.81422600	1.98991500
C	-1.35467600	-0.17641400	-0.50091000
C	-0.02451700	-0.51046600	-0.77562100
C	-2.38288000	-0.66648100	-1.31667300
C	-2.07357700	-1.48511500	-2.39869700
C	-0.74810300	-1.82038800	-2.67574300
C	0.27198700	-1.33019000	-1.86092100
H	1.31105600	-1.58759200	-2.07077800
H	0.76049500	-0.11896100	-0.12887300
H	-2.87798300	-1.86407300	-3.03071500
H	-0.51152400	-2.46222200	-3.52494000
H	-3.41729400	-0.40080100	-1.09459500

Table S9
HBpin (M06-2X/Def2-SVP)
G = -411.218899 Hartree

Atomic Number	Coordinates (Angstroms) X	Y	Z
C	-3.82627200	0.92783400	0.29409600
C	-2.32561200	0.92221800	0.01382400
H	-4.04226100	0.67444500	1.34116900
H	-4.34885300	0.21282400	-0.35719000
H	-4.21862700	1.93220300	0.08524500
C	-1.71931100	-0.52379100	-0.01227200
C	-1.61139000	1.89578400	0.93552700
O	-2.15284200	1.34851000	-1.35082400
H	-1.64881900	1.54033800	1.97594300
H	-2.10645100	2.87523800	0.88669800
H	-0.56338900	2.02827800	0.64170300
C	-2.41158300	-1.52105700	0.90081400
C	-0.21226300	-0.53691200	0.23108000
O	-1.92540700	-0.91454100	-1.38299200
H	-2.34896700	-1.19261700	1.94886800
H	-1.91837200	-2.49886900	0.81470900
H	-3.46644000	-1.64590200	0.62899100
H	0.02949500	-0.31224700	1.27907800
H	0.29481900	0.19543100	-0.41314900
H	0.17404100	-1.53529100	-0.01452800
B	-2.04834400	0.22671700	-2.11900800
H	-2.06322400	0.24215700	-3.31511300

Table S10
TS1 (M06-2X/Def2-SVP)
G = -1538.725748 Hartree

Atomic Number	Coordinates (Angstroms) X	Y	Z
N	-0.32211700	-0.19347200	2.89441200
C	-0.31583600	-0.54536300	1.56267400
N	0.31351000	-1.75968500	1.53243800
C	0.69908600	-2.15216600	2.80702500
C	0.31439500	-1.16858400	3.66363900
C	0.48319800	-1.04637100	5.13901100
H	-0.47612600	-1.11115100	5.67619800
H	0.95315700	-0.08820400	5.40823600
H	1.12604200	-1.85253100	5.51226300
C	1.41093900	-3.43527600	3.06555300
H	2.39240800	-3.46804800	2.56755100
H	0.82732100	-4.29433500	2.70240300
H	1.57457000	-3.56791000	4.14150100
C	-1.17257200	0.83555200	3.44585800
H	-0.69544000	1.82501700	3.46585500
H	-1.45721600	0.56260700	4.46934100
H	-2.07419700	0.91228900	2.81930900
C	0.49977400	-2.56815300	0.34747600
H	0.55797400	-1.90650100	-0.52117400
H	-0.34540300	-3.26220000	0.20491000
H	1.43779700	-3.13105800	0.43288400
B	-0.92764100	0.18413500	0.35653200
N	-0.35145600	2.68969700	1.00794900
C	-1.12664800	1.71303400	0.41276300
N	-2.09837700	2.42847300	-0.25293200
C	-1.90837500	3.80046300	-0.10323200
C	-0.82057300	3.96185500	0.69025300
C	-0.14364400	5.19585400	1.17730100
H	0.89538300	5.25676600	0.81982800
H	-0.11973900	5.23635100	2.27735300
H	-0.67583800	6.08544300	0.82047300
C	-2.79717700	4.81388200	-0.73797900
H	-2.39227300	5.82003100	-0.57654000
H	-3.81686000	4.79339000	-0.32264500
H	-2.87458400	4.65058800	-1.82330600
C	0.92331600	2.51537800	1.66919700
H	0.91207200	2.98084500	2.66558500
H	1.72333600	2.97590300	1.07139400
H	1.14382000	1.45029300	1.78122000
C	-3.28278500	1.85701400	-0.85911400
H	-3.10278800	1.52325200	-1.89128200

H	-4.08081400	2.60893600	-0.85624000
H	-3.60304100	0.98407400	-0.27783000
C	-1.73999600	-0.73764900	-0.68352700
C	-3.21975200	-2.42846900	-2.48083300
C	-2.62853700	-1.74237400	-0.20825900
C	-1.63809000	-0.60471200	-2.09392000
C	-2.37065300	-1.42730900	-2.95425400
C	-3.33323700	-2.56277300	-1.09877600
H	-2.26672500	-1.28603700	-4.03473800
H	-4.01419600	-3.31869000	-0.69538900
C	-2.90541200	-1.94433300	1.26557600
H	-3.82154100	-2.53374400	1.40918300
H	-3.02426200	-0.97757000	1.77747600
H	-2.08871700	-2.47275100	1.78432800
C	-0.70845600	0.40292700	-2.72039700
H	-0.72434600	1.37732100	-2.21431500
H	-0.94675800	0.54829900	-3.78373700
H	0.33413000	0.05110700	-2.65930000
C	-3.96961300	-3.32945200	-3.42732500
H	-4.35941100	-2.76824100	-4.28871900
H	-4.81566600	-3.81917000	-2.92580500
H	-3.31500700	-4.12171100	-3.82389200
C	1.64791300	0.75179900	-0.53394600
N	2.26770100	-0.20419400	-0.04743400
O	1.47921300	1.78552400	-1.07688500
C	3.63896400	-0.43390600	-0.26600300
C	4.25790900	-1.44561200	0.47840600
C	4.39873700	0.29666700	-1.19223700
C	5.60996200	-1.72424300	0.30202300
C	5.75075300	0.01036900	-1.36397300
C	6.36399000	-0.99903500	-0.62120900
H	3.64998900	-1.99397700	1.19965500
H	3.92034700	1.08798400	-1.77253000
H	6.33161000	0.58383000	-2.08858900
H	7.42299500	-1.21891100	-0.76130600
H	6.07963700	-2.51429900	0.89062800

Table S11

Int1 (M06-2X/Def2-SVP)

G = -1538.759945 Hartree

Atomic Number	Coordinates (Angstroms) X	Y	Z
N	2.08769900	1.17705300	-0.63225400
C	1.15487900	1.09567100	0.35126900
N	1.10365600	2.33172800	0.88373500
C	2.01543500	3.17862400	0.27859000
C	2.64193100	2.45308200	-0.68674300
C	3.70907000	2.83042700	-1.65563600
H	3.34921600	2.81664400	-2.69595600
H	4.57386600	2.15400700	-1.58763400
H	4.06168000	3.84584900	-1.44024700
C	2.20192600	4.59031600	0.71480400
H	2.48070000	4.64006700	1.77737700
H	1.28254400	5.17882200	0.58126300
H	2.99745300	5.06567300	0.12925700
C	2.44422000	0.16910900	-1.61207400
H	3.40261100	-0.30739900	-1.36028300
H	2.53268700	0.64479300	-2.59693000
H	1.66903400	-0.59707000	-1.66790400
C	0.30953300	2.77009600	2.02120900
H	-0.38502600	1.98288100	2.30863700
H	-0.24724000	3.67339500	1.73549700
H	0.97517000	2.95697000	2.87140500
B	0.24322200	-0.14680800	0.93656700
N	1.74905700	-2.21845300	0.24215700
C	0.54963000	-1.59699600	0.20751700
N	-0.29351600	-2.48482000	-0.36601000
C	0.37363200	-3.66350100	-0.68485400
C	1.66667100	-3.49098100	-0.29264100
C	2.83218400	-4.41803300	-0.33804200
H	3.23023500	-4.59853600	0.67108800
H	3.64936200	-4.01799700	-0.95683300
H	2.53064200	-5.38327100	-0.76063200
C	-0.28646900	-4.84280700	-1.31410200
H	0.46310500	-5.61609800	-1.51843000
H	-0.76921500	-4.58371800	-2.26770500
H	-1.04805800	-5.28408400	-0.65409700
C	2.93255000	-1.75915500	0.95649900
H	3.82956300	-2.05828800	0.39991500
H	2.92363000	-2.19930800	1.96418300
H	2.90481900	-0.67312000	1.08794000
C	-1.73337300	-2.33259600	-0.54689600
H	-2.19431200	-1.98553000	0.38263200

H	-2.14755600	-3.30915000	-0.81488600
H	-1.96109900	-1.61356800	-1.34240000
C	-1.33785100	0.32116700	0.82238000
C	-4.07089100	1.15280800	0.50287200
C	-1.83453700	0.81559700	-0.41005300
C	-2.25897500	0.27471600	1.90512300
C	-3.58740800	0.67980200	1.72169900
C	-3.16924200	1.21325500	-0.55553500
H	-4.27096800	0.62299300	2.57374800
H	-3.51396600	1.57405500	-1.52932400
C	-0.97837000	0.90417500	-1.65631800
H	-1.61022800	0.99488000	-2.55062000
H	-0.34433800	0.01422700	-1.78422700
H	-0.31049600	1.78055900	-1.63937500
C	-1.88554400	-0.19403300	3.29084000
H	-1.50436900	-1.22247100	3.28567500
H	-2.75194400	-0.12239500	3.96121700
H	-1.06862800	0.40908000	3.71690100
C	-5.50078200	1.60215900	0.35314500
H	-6.19090100	0.90482400	0.84890500
H	-5.78755700	1.67806400	-0.70445700
H	-5.65185600	2.59152900	0.81224400
C	0.86479900	-0.51579100	2.44611700
N	1.63721400	0.41751100	2.99704600
O	0.65254500	-1.68638300	2.84990100
C	2.30567100	0.22440500	4.19549300
C	3.25587500	1.21498800	4.54617100
C	2.13316700	-0.84295800	5.11297000
C	3.98597600	1.15772000	5.72573600
C	2.86862600	-0.88778300	6.29733800
C	3.79836000	0.09998600	6.61976800
H	3.39964300	2.03489400	3.83758400
H	1.41699600	-1.62291200	4.87097300
H	2.70763900	-1.72122500	6.98604400
H	4.36688600	0.04901400	7.54983300
H	4.70899700	1.94481100	5.95354700

Table S12
TS2 (M06-2X/Def2-SVP)
G = -1949.932226 Hartree

Atomic Number	Coordinates (Angstroms) X	Y	Z
N	1.65279700	0.76998500	0.71944100
C	1.69741700	-0.58922000	0.76640400
N	2.97608200	-0.87939800	1.09252400
C	3.71710000	0.26852600	1.30254400
C	2.87857100	1.31752200	1.07339700
C	3.12155500	2.78427200	1.17999300
H	2.39702400	3.26096300	1.85586000
H	3.05915600	3.28890000	0.20404700
H	4.12527700	2.96222900	1.58324600
C	5.14046700	0.22679200	1.73997800
H	5.78507300	-0.25351200	0.98902000
H	5.24518300	-0.33683100	2.67869600
H	5.51525500	1.24327400	1.90650700
C	0.53833600	1.61785600	0.31101900
H	-0.04881900	1.12308100	-0.46618300
H	0.95044400	2.55405500	-0.08108800
H	-0.12377200	1.83365500	1.15877400
C	3.58475000	-2.19384700	1.19680100
H	2.87143900	-2.96712200	0.90934100
H	3.85994600	-2.40714300	2.23355500
H	4.47126800	-2.22701600	0.54451100
B	0.46956800	-1.66842600	0.58948500
N	1.78487900	-2.73200000	-1.54422800
C	0.83140600	-2.75403100	-0.58071500
N	0.22507800	-3.95014400	-0.71012200
C	0.80314600	-4.69486800	-1.72362900
C	1.79303500	-3.92473700	-2.25833000
C	2.75052500	-4.19976100	-3.36647600
H	3.79187700	-4.04724800	-3.04678600
H	2.56543900	-3.55812500	-4.24158900
H	2.64932700	-5.24131800	-3.69306700
C	0.35303200	-6.07457500	-2.05905300
H	1.01957100	-6.51705100	-2.80855000
H	-0.66824100	-6.08050700	-2.46776000
H	0.36457800	-6.71747500	-1.16687400
C	2.59309100	-1.58855200	-1.92722200
H	2.74019000	-1.60921400	-3.01364300
H	3.57413400	-1.59893900	-1.43282500
H	2.07006300	-0.66303400	-1.66486100
C	-0.92441700	-4.41505000	0.06140800
H	-1.44546900	-3.55901300	0.50420400

H	-0.59439700	-5.03791700	0.90603600
H	-1.58395000	-4.97864000	-0.60911800
C	-0.99346800	-0.95847300	0.32172600
C	-3.63002900	0.15531200	0.04299300
C	-1.67905000	-0.96339000	-0.92046300
C	-1.64653300	-0.30056500	1.39994400
C	-2.92936400	0.23032800	1.24503500
C	-2.97041000	-0.42596700	-1.03429700
H	-3.39418000	0.72879800	2.10139000
H	-3.46843900	-0.45120000	-2.00797800
C	-1.08249200	-1.45740800	-2.22717600
H	-1.04961400	-2.55442300	-2.30780000
H	-0.05876000	-1.08774500	-2.37925500
H	-1.68513700	-1.09320500	-3.06972700
C	-1.00071600	-0.05566100	2.74296800
H	0.09376500	-0.12167400	2.71617700
H	-1.32717700	-0.81338400	3.46649800
H	-1.27571100	0.94163600	3.12127400
C	-5.03324200	0.68747500	-0.08094400
H	-5.76053600	-0.03017400	0.32971300
H	-5.30161800	0.86960700	-1.13062300
H	-5.15413800	1.62771600	0.47558700
C	0.33417200	-2.64495900	2.04610500
N	1.45315200	-2.53121800	3.08399800
O	-0.82891100	-2.84607200	2.45485300
C	1.17408300	-1.92731400	4.32814000
C	1.90318900	-0.79151700	4.71159600
C	0.17950100	-2.41161700	5.19595200
C	1.65105000	-0.14733900	5.92139500
C	-0.07365100	-1.76075800	6.40252000
C	0.65662700	-0.63005400	6.77248700
H	2.66835700	-0.41974600	4.02369300
H	-0.38978400	-3.28492000	4.88052900
H	-0.85429900	-2.14122000	7.06481800
H	0.45322800	-0.12883300	7.72052700
H	2.23056800	0.73493200	6.20171400
C	2.79710000	-5.95564100	2.72430900
C	4.13092200	-6.58352100	3.09891700
C	2.35695000	-6.44598200	1.34002400
O	2.93958400	-4.54575300	2.66969000
C	1.66649000	-6.12369700	3.79572800
C	0.81352400	-7.37279800	3.62466300
O	0.86879900	-4.97284800	3.58285200
C	2.21632800	-6.05105800	5.22151500
H	0.28699600	-7.36213900	2.66160100
H	0.05645600	-7.40792500	4.42045300
H	1.42744000	-8.28456000	3.68891400
H	3.08741200	-6.09571700	0.59455500

H	1.37525000	-6.02055300	1.08260100
H	2.29643800	-7.54291500	1.28916500
H	4.85454200	-6.42722400	2.28553200
H	4.02385600	-7.66660100	3.26293400
H	4.53586400	-6.12370300	4.00865900
H	2.78553200	-6.95162400	5.49551800
H	1.36943400	-5.94141500	5.91287300
H	2.86148000	-5.16779500	5.33507300
B	1.65526000	-3.98135500	2.94171600
H	0.93759800	-3.76574100	1.60736500

Table S13
Prod1 (M06-2X/Def2-SVP)
G = -810.455675 Hartree

Atomic Number	Coordinates (Angstroms) X	Y	Z
C	0.24789500	-0.01734700	3.02049400
N	1.27027100	0.92955300	3.10427000
O	-0.68916200	0.03408600	2.27791400
C	2.39090600	0.62035300	3.93134200
C	2.84623100	1.54167800	4.88005200
C	3.03160300	-0.61615300	3.81020900
C	3.92737500	1.22518000	5.69634800
C	4.10295600	-0.93522100	4.64370400
C	4.55597200	-0.01604100	5.58687400
H	2.34672700	2.50693100	4.96695100
H	2.69861200	-1.32186400	3.04724800
H	4.59322900	-1.90447500	4.54223700
H	5.39908900	-0.26290300	6.23317600
H	4.27643500	1.95160900	6.43164900
H	0.39963400	-0.85065700	3.74418400
B	1.21842200	2.19112400	2.38457700
O	0.12734200	2.68563700	1.74079800
O	2.30663300	3.01979000	2.33193700
C	0.56777800	3.83802900	0.99987500
C	1.84585500	4.27396800	1.79695600
C	-0.54898600	4.86662800	0.97537800
C	0.89081100	3.36416600	-0.41445300
C	1.51785700	5.17255300	2.98679100
C	2.94590800	4.88991400	0.95087700
H	0.70808000	4.73975100	3.59262900
H	1.21369700	6.17749300	2.66336000
H	2.41336400	5.26241100	3.61717800
H	3.30406000	4.18589100	0.19057900
H	3.79473000	5.16078800	1.59351100
H	2.58340800	5.80109200	0.45251900
H	1.71559700	2.63716700	-0.40497600
H	1.16722000	4.20324100	-1.06779300
H	0.00242300	2.86852100	-0.82774400
H	-0.90580300	5.09216800	1.98738700
H	-1.39455500	4.47228700	0.39589400
H	-0.20537400	5.79730200	0.49998900

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