

Supplementary Information

Synthesis and Characterization of New Diazenecarboxamide Ligands Using a Selective Adduct Formation with $B(C_6F_5)_3$

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Experimental

General remarks

All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk-line techniques. All reagents were used as received from Aldrich unless otherwise specified. All solvents were dried with molecular sieves. The starting compounds (2,6-diisopropylphenyl)isocyanate^{1,2} and *trans*-chloro(phenyl)bis(triphenylphosphine) nickel(II)³ was synthesized according to literature procedure. NMR spectra were obtained using 400 Bruker Advance spectrometer (400.133 MHz for ¹H, 100.16 MHz for ¹³C, 200 MHz for ¹⁹F and 160.984 MHz for ³¹P) using deuterated solvent with tetramethylsilane (TMS) as an internal standard. FTIR spectra were recorded on a Bruker Vector-22 spectrophotometer using KBr pellets.

Synthesis of ligands

N,2-Diphenyldiazenecarboxamide (L₁)

Phenyl isocyanate (1.38 g; 11.6 mmol) was added to a solution of phenyl hydrazine (1.25 g; 11.6 mmol) in anhydrous acetonitrile (40 mL). The mixture was stirred for 1 h. The white precipitated is formed. The solvent was evaporated under vacuum to obtain (2.39 g; 10.5 mmol) of intermediate product $C_6H_5NHNHCONHC_6H_5$. Then, crude product was suspended in a mixture of

CH_2Cl_2/CH_3CH_2OH (5:1) and pyridine (0.83 g; 10.5 mmol). The solution was cooled by water, and (1.91 g; 10.7 mmol) *N*-bromosuccinimide was added dropwise during 5 min with stirring. The solution changed its color to deep red. The resulting solution is left stirring for 10 min at room temperature and was washed in turn with water (2 × 15 mL), then 10% NaOH (10 mL) and water (2 × 15 mL). The solution was dried over $MgSO_4$, filtered and evaporated under vacuum. The crude product was dissolved in minimum amounts of methanol and recrystallized and orange solid was washed with cool hexane. Yield 2.07 g (79.5 %). Anal. calcd. for $C_{13}H_{11}N_3O$: C, 69.32; H, 4.92; N, 18.66; found: C, 69.27; H, 4.56; N, 18.81.

X-ray crystal structure analysis of L₁

Formula $C_{13}H_{11}N_3O$; M 225.25; orange crystal; 0.47 × 0.35 × 0.25 mm; a 11.4783(2), b 13.1911(2), c 15.8362(3) Å; β 103.823(1)°; V 2328.34(7) Å³; ρ_{calc} 1.285 g cm⁻³; μ 0.085 mm⁻¹; empirical absorption correction (0.961 ≤ T ≤ 0.979); Z 8; monoclinic; space group P2₁/c (No. 14); λ 0.71073 Å; T 223(2) K, ω and φ scans, 17780 reflections collected (±h, ±k, ±l); 4655 independent (R_{int} 0.042) and 4029 observed reflections [*I* > 2σ(*I*)]; 315 refined parameters; R 0.044; wR² 0.107; max. (min) residual electron density 0.15 (-0.15) e Å⁻³; the hydrogen atoms at N1A and N1B were refined freely; others were calculated and refined as riding atoms.

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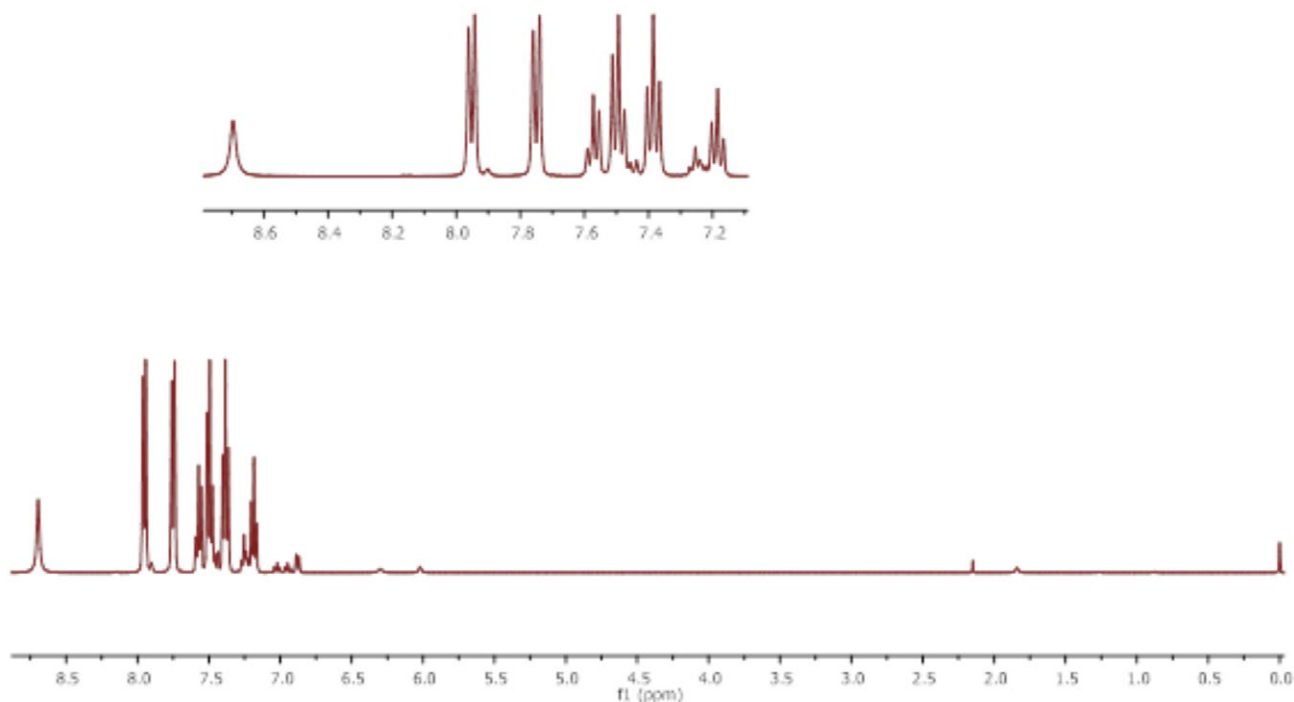


Figure S1. ^1H NMR spectrum (400 MHz, CDCl_3) of L_1 .

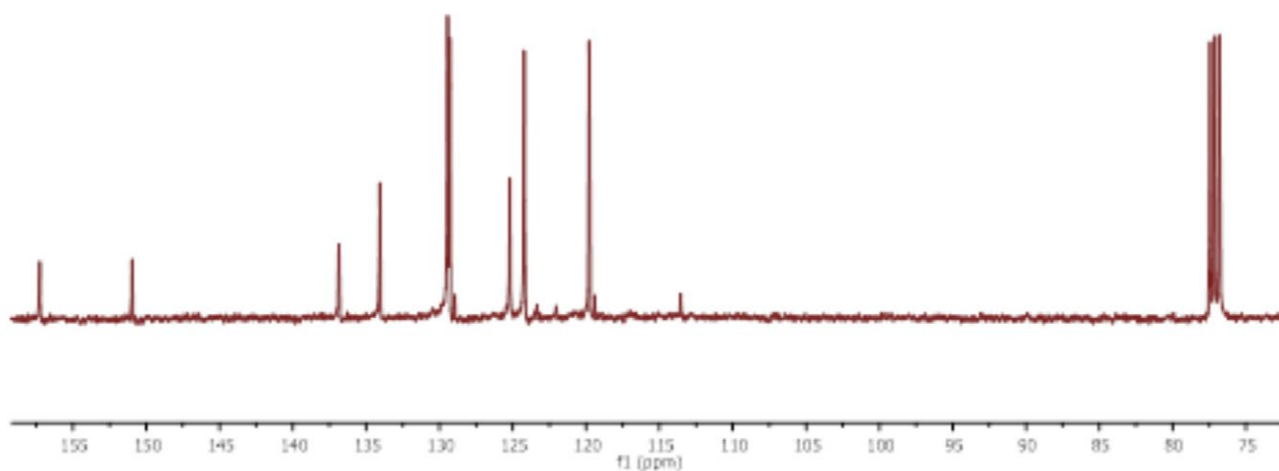


Figure S2. ^{13}C NMR spectrum (100 MHz, CDCl_3) of L_1 .

N-(2,6-Diisopropylphenyl)-2-phenyldiazenecarboxamide (L_2)

(2,6-Diisopropylphenyl)isocyanate (0.79 g; 3.91 mmol) was added to a solution of phenylhydrazine (0.42 g; 3.91 mmol) in anhydrous acetonitrile (40 mL). The mixture was stirred for 1 h. The solvent was evaporated under vacuum to obtain (0.84 g; 2.71 mmol) of white solid product $\text{C}_6\text{H}_5\text{NHNHCONH}$ 2,6-*i*Pr $_2$ C $_6$ H $_3$. Then, crude product was suspended in a mixture of $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CH}_2\text{OH}$ (5:1) and

pyridine (0.21 g; 2.71 mmol). The solution was cooled by water, and (0.49 g; 2.75 mmol) *N*-bromosuccinimide was added dropwise during 5 min with stirring. The solution changed its color to deep orange. The resulting solution is left stirring for 10 min at room temperature and was washed in turn with water (2×15 mL), then 10% NaOH (10 mL) and water (2×15 mL). The solution was dried over MgSO_4 , filtered and evaporated under vacuum. The crude product was dissolved in minimum amounts of methanol and recrystallized and orange solid was washed with cool

hexane. Yield 0.63 g (52%). Anal. calcd. for $C_{19}H_{23}N_3O$: C, 73.76; H, 7.49; N, 13.58; found: C, 73.47; H, 7.51; N, 13.68.

X-ray crystal structure analysis of L_2

Formula $C_{19}H_{23}N_3O$; M 309.40; pale yellow crystal; $0.33 \times 0.17 \times 0.03$ mm; a 8.2918(2), b 24.6137(8), c 8.9360(3) Å; β 109.400(2)°; V 1720.22(9) Å³; ρ_{calc} 1.195 g cm⁻³; μ 0.075 mm⁻¹; empirical absorption

correction ($0.975 \leq T \leq 0.997$); Z 4, monoclinic; space group $P2_1/n$ (No. 14); λ 0.71073 Å; T 223(2) K, ω and ϕ scans; 5367 reflections collected ($\pm h, \pm k, \pm l$); 3471 independent (R_{int} 0.042) and 2426 observed reflections [$I > 2\sigma(I)$]; 216 refined parameters; R 0.073; wR^2 0.155; max. (min) residual electron density 0.21 (−0.28) e Å⁻³; the hydrogen atom at N1 was refined freely; others were calculated and refined as riding atoms.

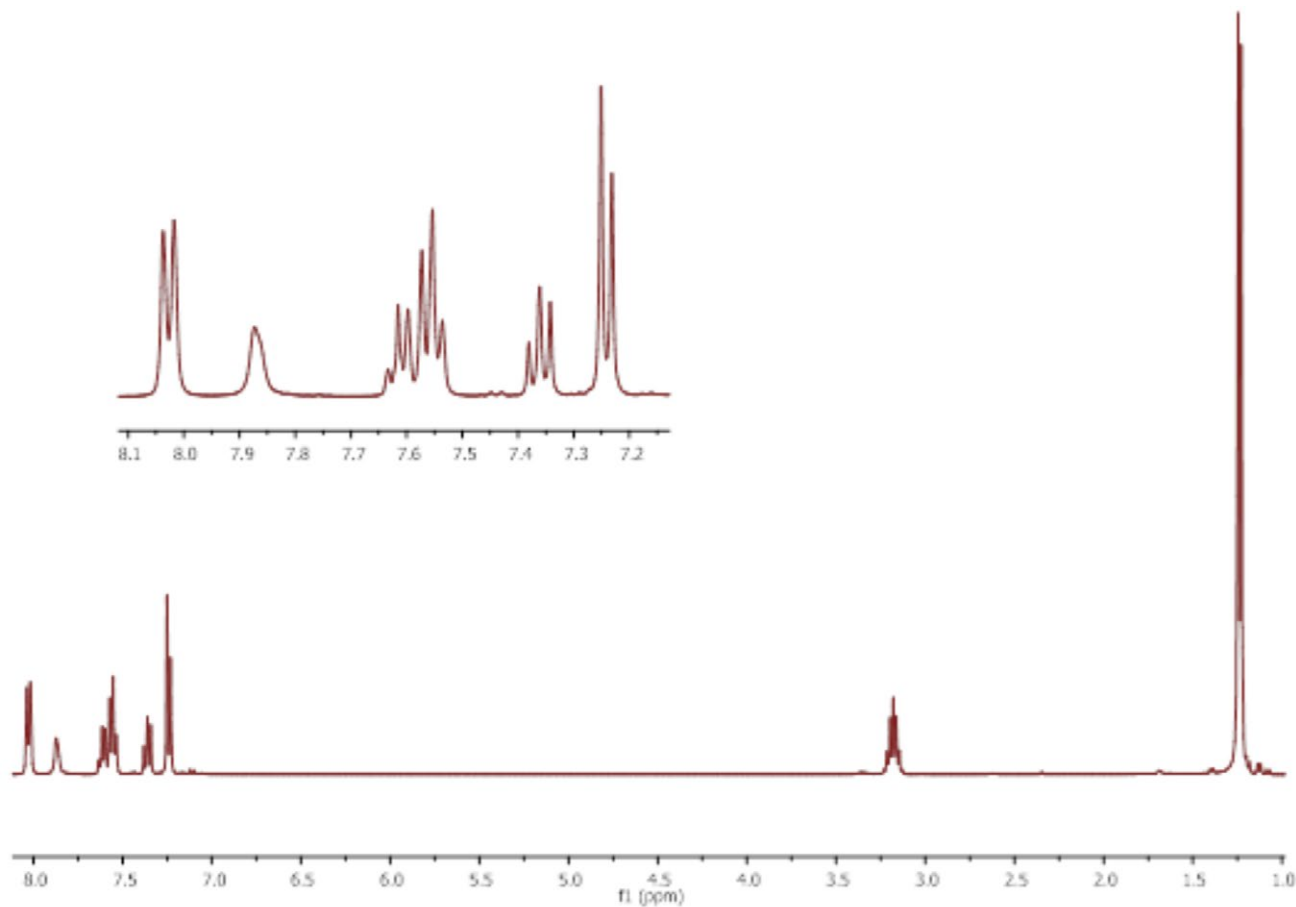


Figure S3. ¹H NMR spectrum (400 MHz, CDCl₃) of L_2 .

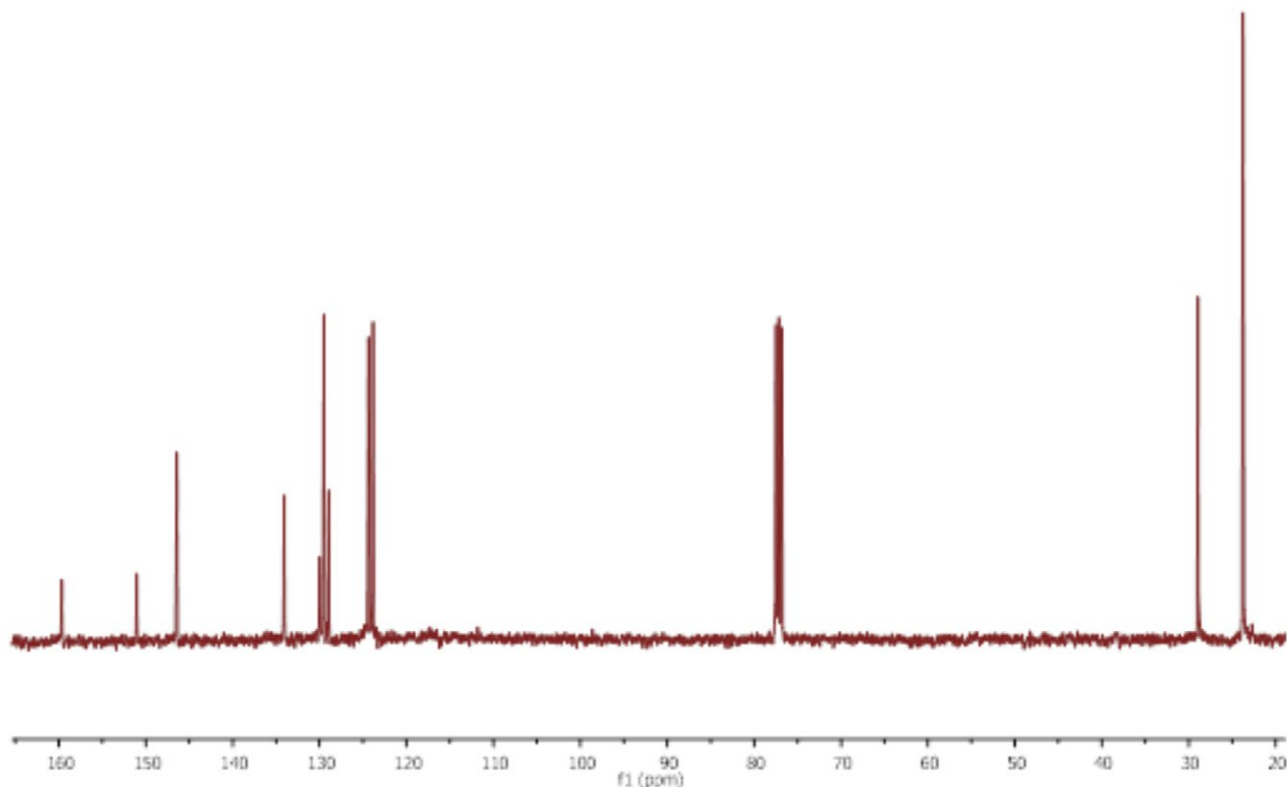


Figure S4. ^{13}C NMR spectrum (100 MHz, CDCl_3) of L_2 .

N-(2,6-Diisopropylphenyl)-2-(perfluorophenyl) diazenecarboxamide (L_3)

(2,6-Diisopropylphenyl)isocyanate (1.50 g; 7.4 mmol) was added to a solution of pentafluorophenyl hydrazine (1.4 g; 7.4 mmol) in anhydrous acetonitrile (40 mL). The mixture was stirred for 1 h. The white precipitated is formed. The solvent was evaporated under vacuum to obtain (2.7 g; 6.7 mmol) of intermediate product $\text{C}_6\text{F}_5\text{NHNHCONH}$ 2,6-*i*Pr $_2\text{C}_6\text{H}_3$. Then, crude product was suspended in a mixture of $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CH}_2\text{OH}$ (5:1) and pyridine (0.53 g; 6.7 mmol). The solution was cooled by water, and (1.24 g; 6.9 mmol) *N*-bromosuccinimide was added dropwise during 5 min with stirring. The solution changed its color to deep red. The resulting solution is left stirring for 10 min at room temperature and was washed in turn with water (2 \times 15 mL), then 10% NaOH (10 mL) and water (2 \times 15 mL). The solution was dried over MgSO_4 , filtered and evaporated under vacuum. The crude product was dissolved in minimum amounts of methanol and recrystallized and orange solid was washed with cool hexane. Yield 1.43 g (49%). Anal. calcd. for $\text{C}_{19}\text{H}_{18}\text{F}_5\text{N}_3\text{O}$: C, 57.14; H, 4.54; N, 10.52; found: C, 57.25; H, 4.08; N, 10.64.

X-ray crystal structure analysis of L_3

Formula $\text{C}_{19}\text{H}_{18}\text{F}_5\text{N}_3\text{O}$; M 399.36; orange crystal; 0.20 \times 0.13 \times 0.07 mm; a 9.0620(4), b 25.6197(9), c 17.2406(4) Å; β 102.693(2) $^\circ$; V 3905.7(2) Å 3 ; ρ_{calc} 1.358 g cm $^{-3}$; μ 1.031 mm $^{-1}$; empirical absorption correction (0.820 \leq T \leq 0.931); Z 8; monoclinic; space group P2 $_1$ /n (No. 14); λ 1.54178 Å; T 223(2) K; ω and ϕ scans, 31228 reflections collected (\pm h, \pm k, \pm l); 6767 independent (R_{int} 0.053) and 5098 observed reflections [$I > 2\sigma(I)$]; 521 refined parameters; R 0.049; wR 2 0.128, max. (min) residual electron density 0.14 (−0.22) e Å $^{-3}$; the hydrogen atoms at N1A and N1B were refined freely; others were calculated and refined as riding atoms.

Synthesis of diazenecarboxamide- $\text{B}(\text{C}_6\text{F}_5)_3$ adduct

N,2-Diphenyldiazenecarboxamide- $\text{B}(\text{C}_6\text{F}_5)_3$ adduct (A_1)

A solution of $\text{B}(\text{C}_6\text{F}_5)_3$ (0.11 g; 0.13 mmol) in anhydrous dichloromethane was added to L_1 (0.05 g; 0.13 mmol) previously dissolved in anhydrous dichloromethane. The mixture was stirred for 2 h at room temperature. The solution was filtered and evaporated to dryness. The solid

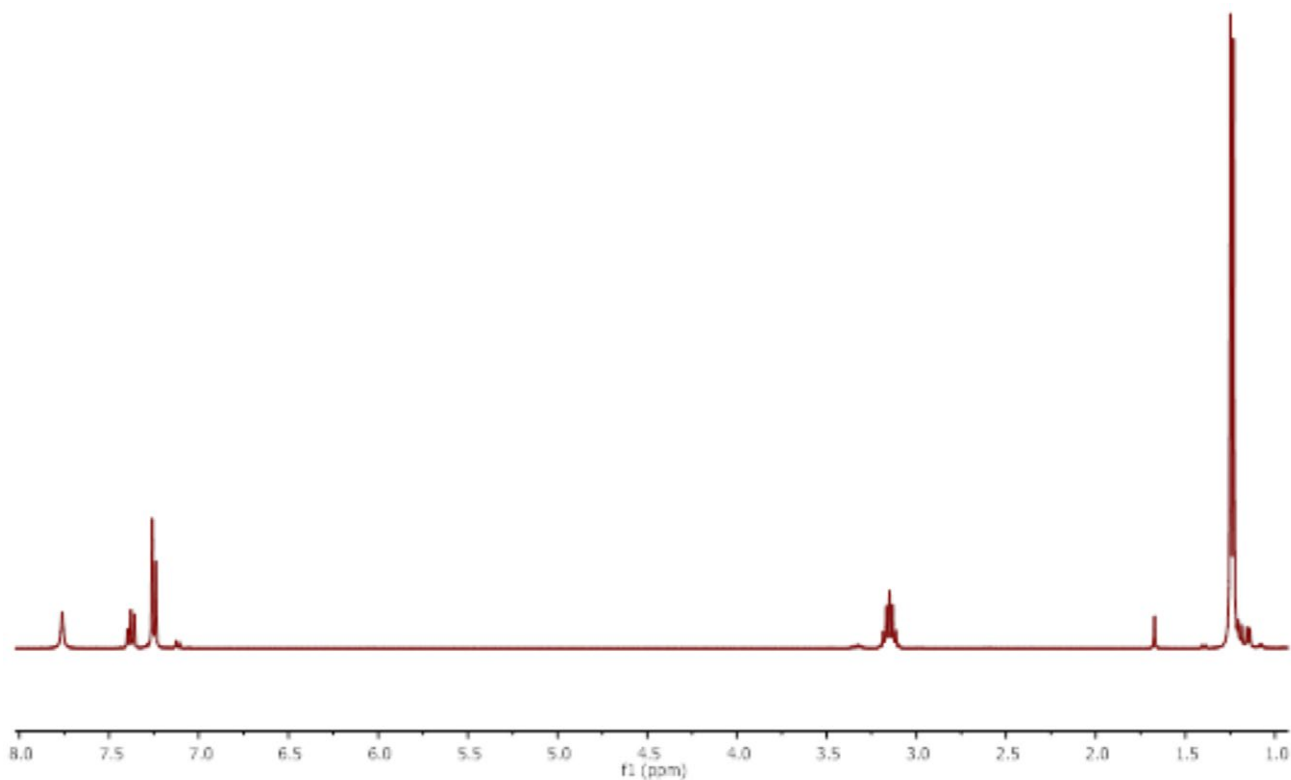


Figure S5. ^1H NMR spectrum (400 MHz, CDCl_3) of L_3 .

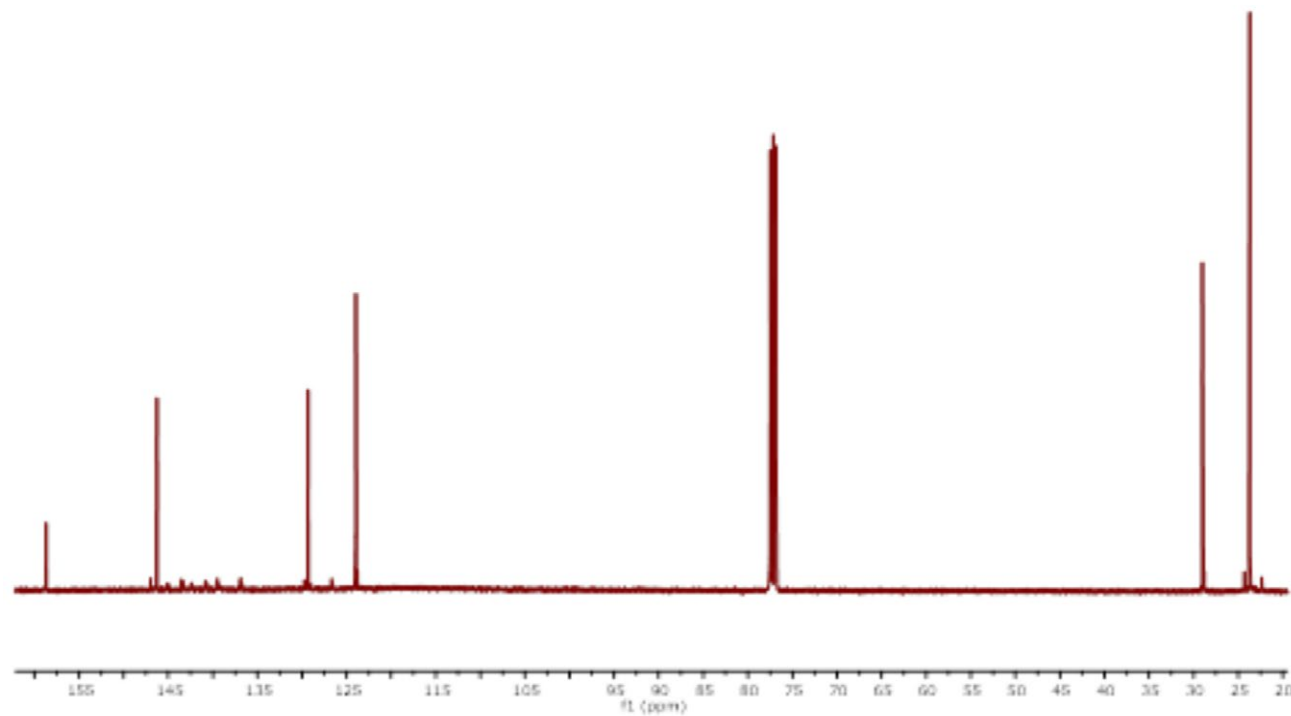


Figure S6. ^{13}C NMR spectrum (100 MHz, CDCl_3) of L_3 .

was washed twice with anhydrous pentane and dry in vacuum to obtain A_1 like a red solid in quantitative yield. Single red crystals of A_1 suitable for X-ray crystal structure

analysis were obtained from dichloromethane/pentane by the diffusion method. Anal. calcd. for $\text{C}_{31}\text{H}_{11}\text{BF}_{15}\text{N}_3\text{O}$: C, 50.50; H, 1.50; N, 5.70; found: C, 50.30; H, 1.56; N, 5.87.

X-ray crystal structure analysis of A_1

Formula $C_{31}H_{11}BF_{15}N_3O$; M 737.24; red crystal; $0.18 \times 0.12 \times 0.04$ mm; a 32.4585(8), b 9.2877(2), c 19.5857(6) Å; β 93.985(1)°; V 5890.1(3) Å³; ρ_{calc} 1.663 g cm⁻³; μ 0.168 mm⁻¹; empirical absorption correction ($0.970 \leq T \leq 0.993$); Z 8; monoclinic; space

group $C2/c$ (No. 15); λ 0.71073 Å; T 223(2) K, ω and ϕ scans; 32876 reflections collected ($\pm h, \pm k, \pm l$); 7200 independent (R_{int} 0.057) and 4676 observed reflections [$I > 2\sigma(I)$]; 464 refined parameters; R 0.054; wR^2 0.126; max. (min) residual electron density 0.21 (−0.19) e Å⁻³; the hydrogen atom at N1 was refined freely; others were calculated and refined as riding atoms.

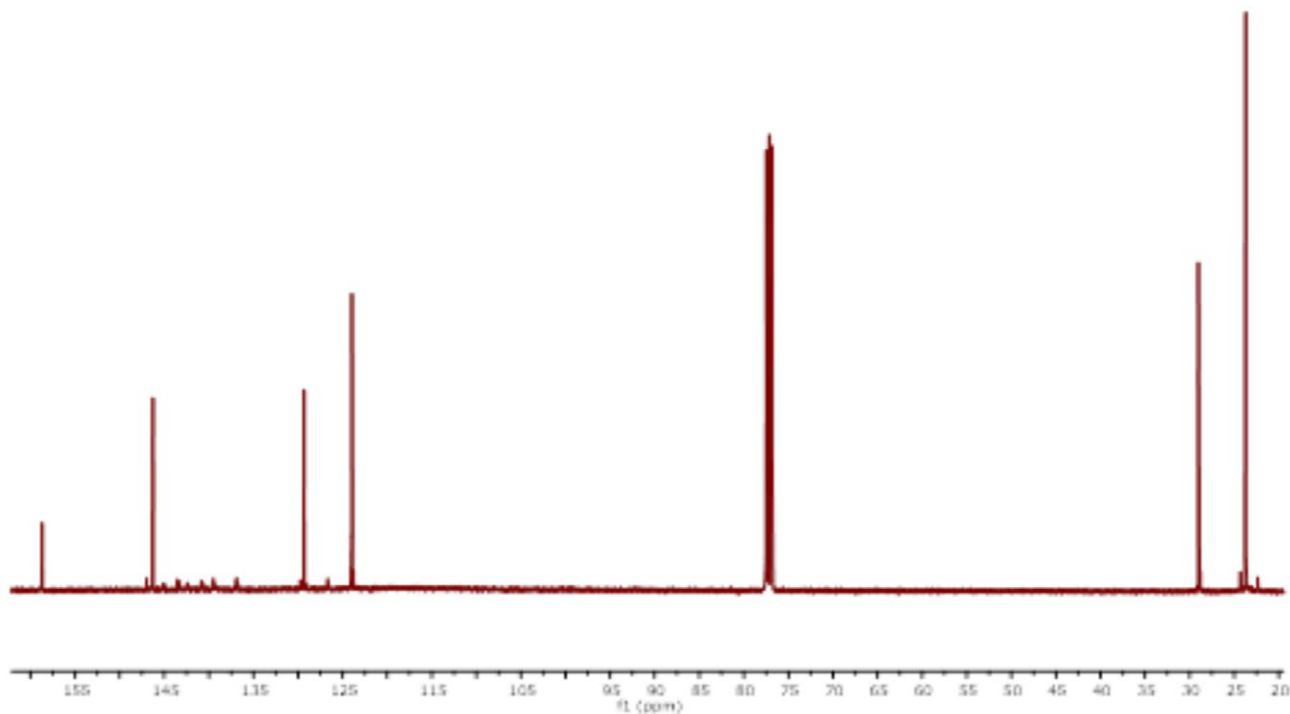


Figure S7. ¹H NMR spectrum (400 MHz, CD₂Cl₂) of A_1 .

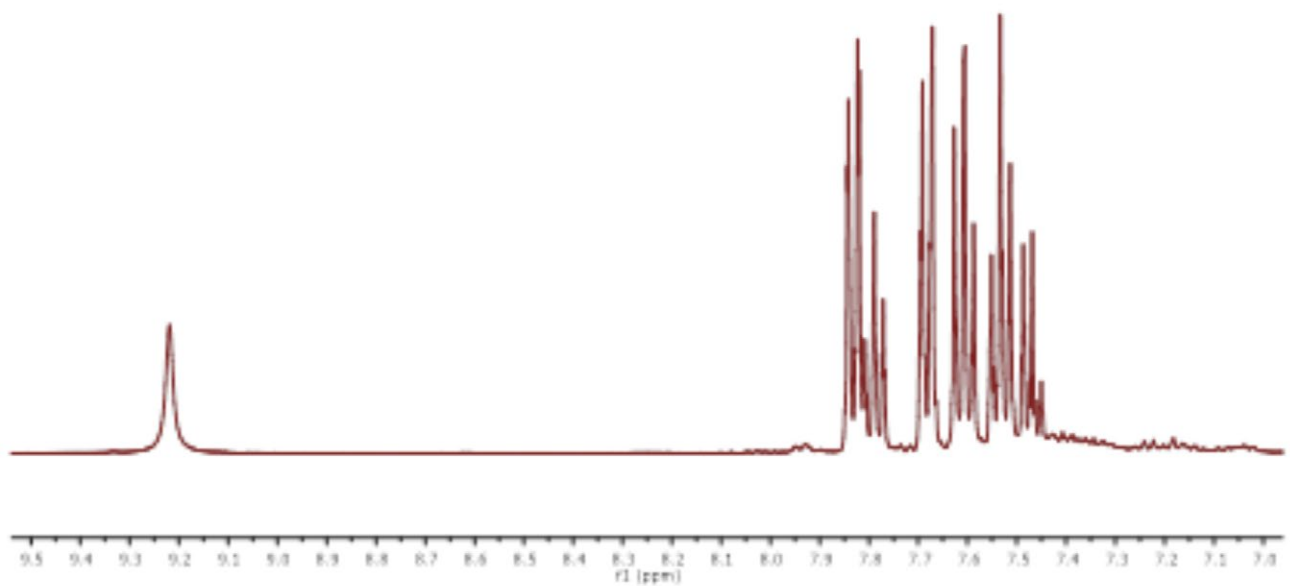


Figure S8. ¹³C NMR spectrum (100 MHz, CD₂Cl₂) of A_1 .

N-(2,6-Diisopropylphenyl)-2-phenyldiazene-carboxamide- $B(C_6F_5)_3$ adduct (A_2)

A solution of $B(C_6F_5)_3$ (0.09 g; 0.17 mmol) in $B(C_6F_5)_3$ in anhydrous dichloromethane was added to L_2 (0.05 g; 0.17 mmol) previously dissolved in anhydrous dichloromethane. The mixture was stirred for 2 h at room temperature. The solution was filtered and evaporated to dryness. The solid was washed twice with anhydrous pentane and dry in vacuum to obtain A_1 like a red solid in quantitative yield. Single red crystals of A_2 suitable for X-ray crystal structure analysis were obtained from dichloromethane/pentane by the diffusion method. Anal. calcd. for $C_{37}H_{23}BF_{15}N_3O$: C, 54.10; 2.82; N, 5.12; found: C, 53.80; 3.00; N, 5.23.

X-ray crystal structure analysis of A_2

Formula $C_{37}H_{23}BF_{15}N_3O$; M 821.39; red crystal; $0.30 \times 0.20 \times 0.15$ mm; a 10.7352(1), b 17.8758(3), c 18.2497(3) Å; β 97.113(1)°; V 3475.2(1) Å³; ρ_{calc} 1.570 g cm⁻³; μ 0.151 mm⁻¹; empirical absorption correction ($0.956 \leq T \leq 0.977$); Z 4; monoclinic; space group $P2_1/n$ (No. 14); λ 0.71073 Å; T 223(2) K, ω and ϕ scans, 20532 reflections collected ($\pm h, \pm k, \pm l$); 6016 independent (R_{int} 0.037) and 4950 observed reflections [$I > 2\sigma(I)$]; 522 refined parameters; R 0.045; wR^2 0.097; max. (min) residual electron density 0.18 (−0.18) e Å⁻³; the hydrogen atom at N1 was refined freely; others were calculated and refined as riding atoms.

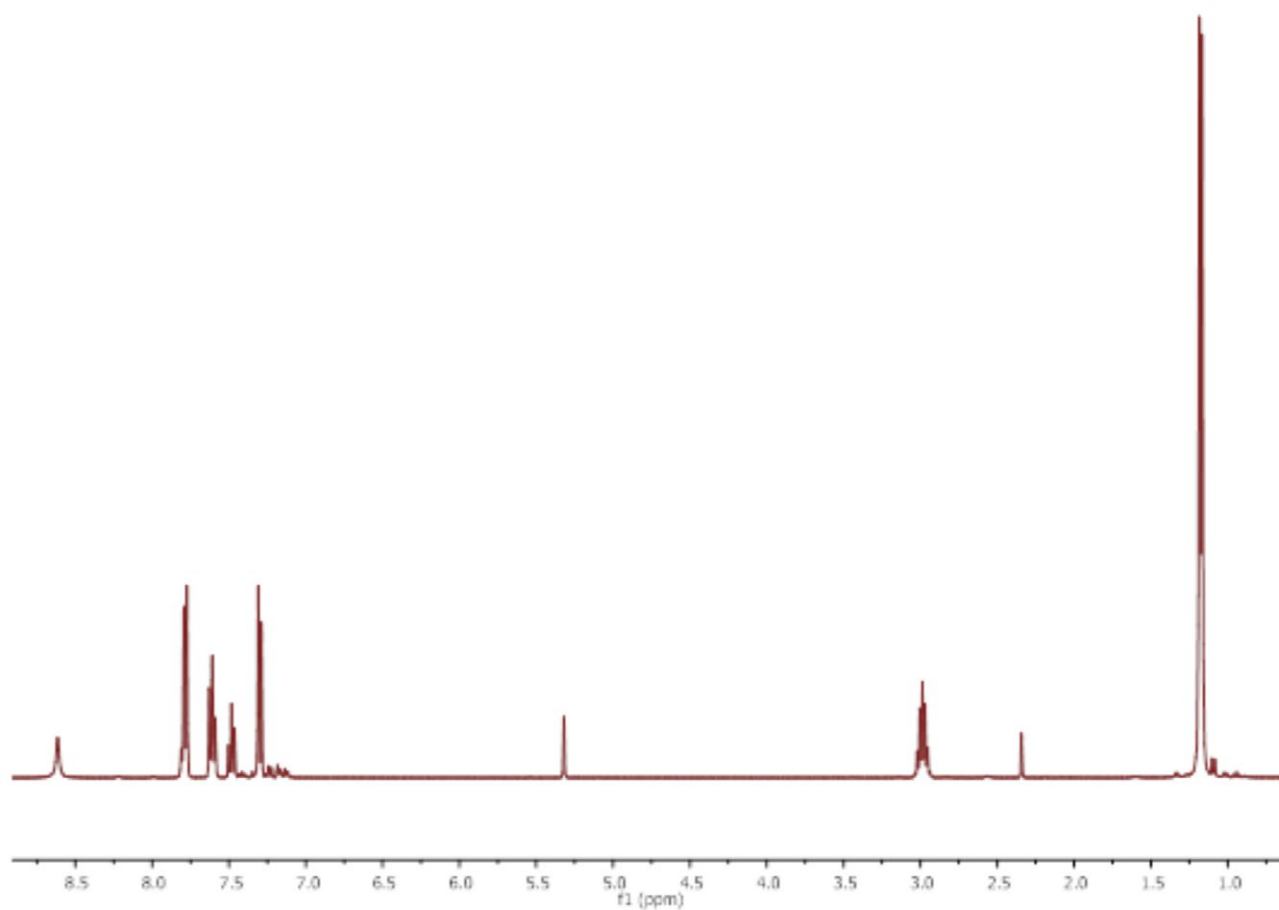


Figure S9. ¹H NMR spectrum (400 MHz, CD_2Cl_2) of A_2 .

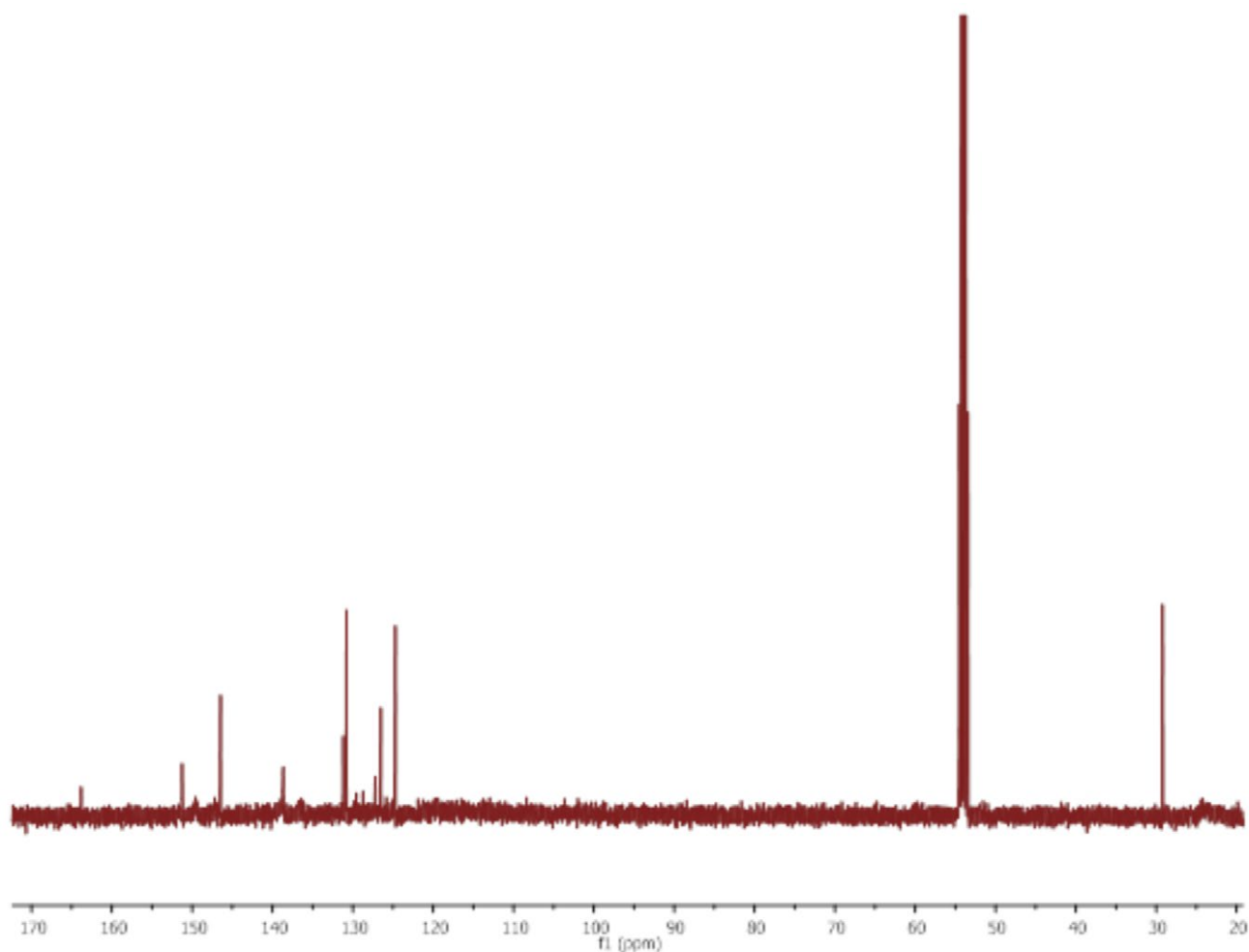


Figure S10. ^{13}C NMR spectrum (100 MHz, CD_2Cl_2) of A_2 .

N-(2,6-Diisopropylphenyl)-2-(perfluorophenyl)diazene-carboxamide- $\text{B}(\text{C}_6\text{F}_5)_3$ adduct (A_3)

A solution of $\text{B}(\text{C}_6\text{F}_5)_3$ (0.06 g; 0.13 mmol) in anhydrous dichloromethane was added to L_3 (0.05 g; 0.13 mmol) previously dissolved in anhydrous dichloromethane. The mixture was stirred for 2 h at room temperature. The solution was filtered and evaporated to dryness. The solid was washed twice with anhydrous pentane and dry in vacuum to obtain A_1 like a red solid in quantitative yield. Single red crystals of A_3 , suitable for X-ray crystal structure analysis were obtained from dichloromethane/pentane by the diffusion method. Anal. calcd. for $\text{C}_{37}\text{H}_{18}\text{BF}_{20}\text{N}_3\text{O}$: C, 48.76; H, 1.99; N, 4.61; found: C, 49.01; H, 2.15; N, 4.67.

X-ray crystal structure analysis of A_3

Formula $\text{C}_{37}\text{H}_{18}\text{BF}_{20}\text{N}_3\text{O}$; M 911.35; orange crystal; $0.23 \times 0.20 \times 0.05$ mm; a 21.3600(4), b 18.5923(3), c 20.9253(4) Å; β 117.711(1)°; V 7357.0(2) Å³; ρ_{calc} 1.646 g cm⁻³; μ 0.170 mm⁻¹; empirical absorption correction (0.961 ≤ T ≤ 0.991); Z 8; monoclinic; space group $\text{P}2_1/c$ (No. 14); λ 0.71073 Å; T 223(2) K; ω and ϕ scans; 45360 reflections collected ($\pm h, \pm k, \pm l$); 12737 independent (R_{int} 0.057) and 8671 observed reflections [$I > 2\sigma(I)$]; 1133 refined parameters; R 0.071; wR^2 0.178, max. (min) residual electron density 0.46 (−0.24) e Å⁻³; the hydrogen atoms at N1A and N1B were refined freely; others were calculated and refined as riding atoms.

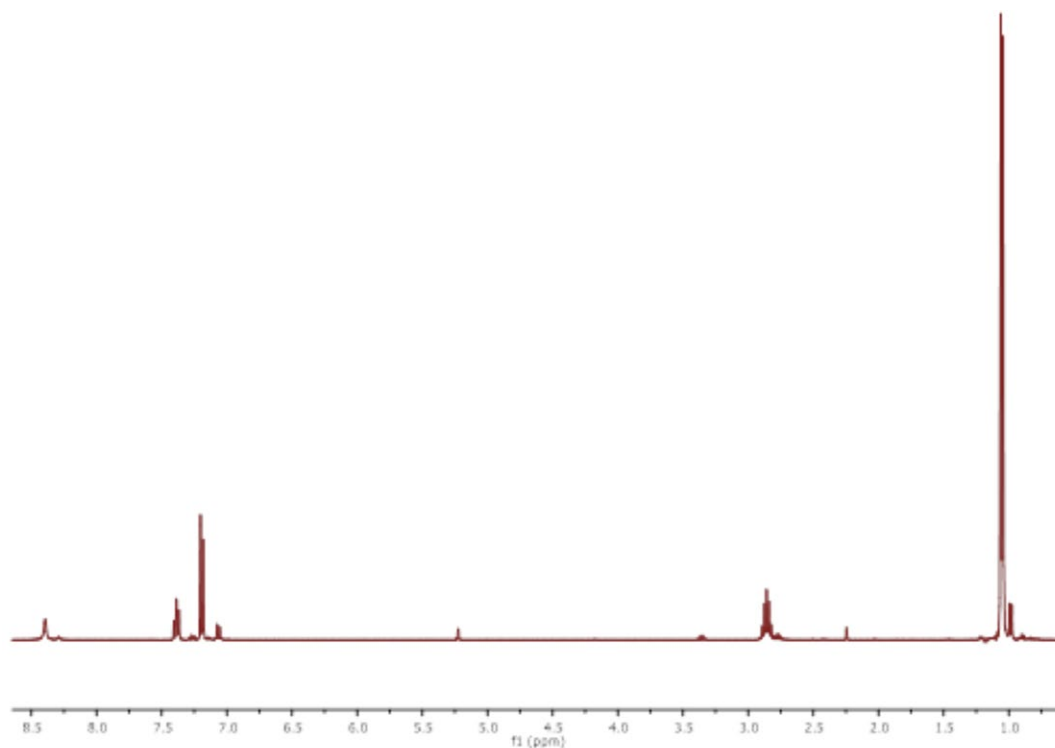


Figure S11. ^1H NMR spectrum (400 MHz, CD_2Cl_2) of A_3 .

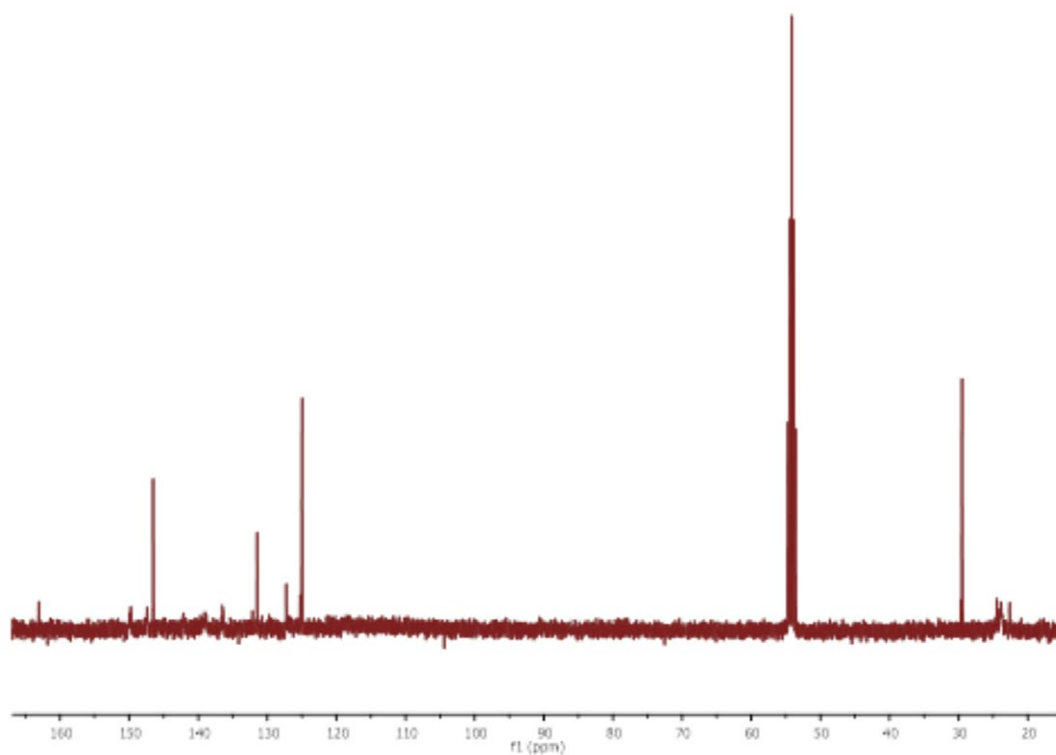


Figure S12. ^{13}C NMR spectrum (100 MHz, CD_2Cl_2) of A_3 .

References

1. Pieters, L.; Kosmrlj, J.; Lenarsic, R.; Kocivar, M.; Polanc, S.; *Arkivoc* **2001**, v, 42.
2. Wang, Y. L.; Wang, X. Y.; Li, J. P.; Ian, D.; Wang, H.; *Synth. Commun.* **1997**, *27*, 1737.
3. Hidai, M.; Kashiwagi, T.; Ikeuchi, T.; Uchida, Y.; *J. Organomet. Chem.* **1971**, *30*, 279.