Single electron reduction of NHC-CO_2-borane compounds

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Supporting Information

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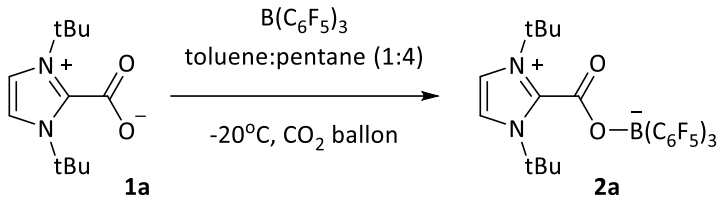
1 General procedures

Manipulations were carried out following standard Schlenk line and glove box techniques using argon as the inert gas. Solvents were dried using a MBraun SPS column. Deuterated solvents were freeze-pump-thaw degassed and stored under Ar over 4Å molecular sieves. Quick Pressure Valve NMR tubes, a balloon fitted with a long needle adapter and Fisher-Porter flasks were used for the reactions with CO_2. NMR spectra were collected on Bruker machine: Avance III 40. All chemical shifts for ^{1}H and ^{13}C are relative to TMS. Chemical shifts are given in ppm, coupling constants in Hz. The following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet sept, septet; m, multiplet.

Voltammetric measurements were carried out with a potentiostat Autolab PGSTAT100 (ECO Chemie, The Netherlands) controlled by GPES 4.09 software. Experiments were performed in a homemade Schlenk three–electrode cell. The cell was prepared under argon in order to avoid the presence of moisture and air. The reference electrode consisted of a saturated calomel electrode (SCE) separated from the solution by a bridge compartment. The counter electrode was a platinum wire of ca 1cm² apparent surface. The working electrode was glassy carbon microdisk (1.0 mm of diameter, Bio-logic SAS). The supporting electrolyte (n-Bu_4N)[PF_6] (Fluka, 99% puriss electrochemical grade). The reduction potentials of the redox couple, $Fc^{+/0}$ is 0.46 V versus SCE in the presence of this supporting electrolyte. It was dried under vacuum at 50°C for 12 h. Dichloromethane was dried on MBraun SPS column. ^{Cy}CAAC-CO_2 was synthesized following a reported procedure [1]. $B(C_6F_5)_3$ was purchased from Sigma Aldridge without any further purification. EPR measurements were carried out at room temperature using a Bruker E500 spectrometer operating at X-band (9.77 GHz), rectangular cavity (ER4102000), with 100 KHz modulation frequency. The instrument settings were as follows: microwave power; 0.8162 - 5.146 mW; modulation amplitude; 2 G. Hyperfine coupling constants a and g values were obtained with a simulation of experimental spectra using easyspin (Matlab toolbox).

2 Synthesis and characterisation of compounds (2a-d, [2b•⁻] and [2d•⁻])

2.1 I^{t}Bu-CO_2-$B(C_6F_5)_3$ (2a)



Compound **2a** was synthesized following the procedure reported by Tamm et *al.*[1]

^{1}H NMR (400 MHz, 298 K, CD_2Cl_2) δ 7.30 (s, 2H, CH) 1.61 (s, 18H, CH3). ^{11}B NMR (128 MHz, 298 K, CD_2Cl_2) δ -4.0 (s). $^{13}C\{^1H\}$ NMR (100 MHz, 298 K, CD_2Cl_2) δ = 156.0 (CCO_2), 148.5 (dm, $^1J_{CF}$ = 242.6 Hz, ortho-C_6F_5) 140.0 (N_2CCO_2) 139.8 (dm, $^1J_{CF}$= 254.5 Hz, para-C_6F_5) 137.1 (dm, $^1J_{CF}$ = 247.4 Hz, meta-C_6F_5) 120.9 (BC_{ipso}) 118.8 ($N_2(CH)_2$) 64.8 ($C(CH_3)_3$) 30.0 (CH_3). ^{19}F NMR (376 MHz, 298 K, CD_2Cl_2): δ −131.2 (m, $^3J_{FF}$= 20.2Hz, 6F, ortho-C_6F_5) −160.3 (t, $^3J_{FF}$= 20.4Hz, 3F, para-C_6F_5) −166.3 (m, 6F, meta-C_6F_5). $E_{p,exp}^{red}$ (vs. $Fc^{+/0}$) = -2.30 V.

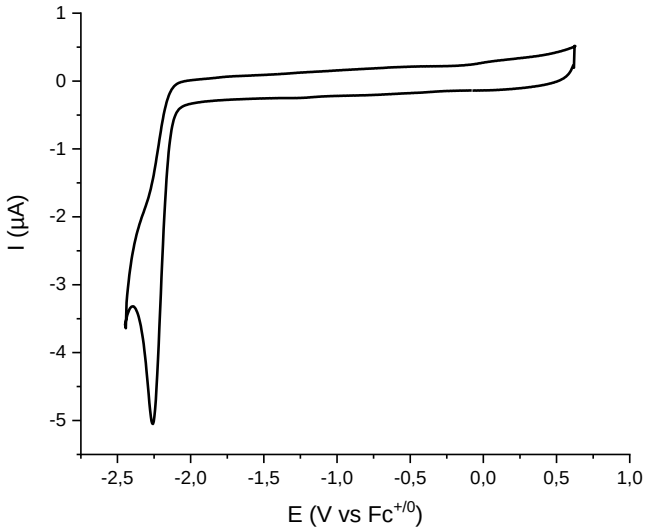


Figure S1. Cyclic voltammogram at reducing potentials of **2a** (5 mM) on GC microdisk in 0.1 M $[nBu_4N][PF_6]$/ CH_2Cl_2 media under Ar atmosphere. scan rate: 0.2 V/s.

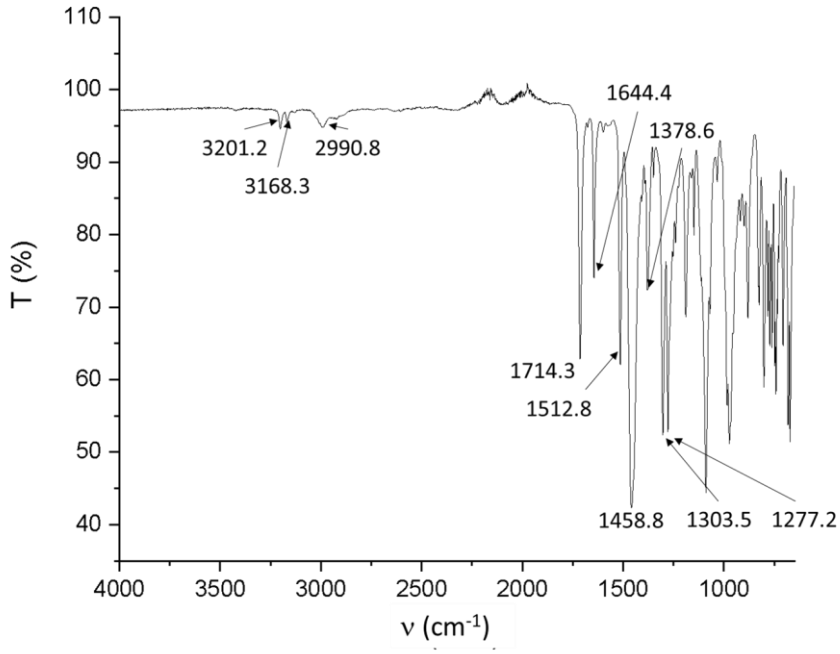
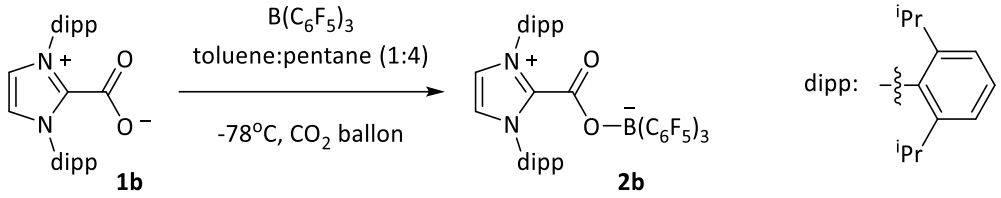


Figure S2. FTIR (solid state) of **2a** at 298 K.

Table S1. Theoretical and experimental IR frequencies for **2a**

Experimental	**Theoretical**	**Assignation**
1714.3	1738.6	C=O
1644.4	1647.1-1622.2	C=C (BCF)
1512.8	1514.2-1511.7	C-F
1458.0	1469.8-1404.3	C(sp^3)-H torsion
1378.6	1388.4-1342.1	C(sp^3)-H torsion
1303.5;1277.2	1307.1-1269.8	C-O

2.2 IPr-CO_2-$B(C_6F_5)_3$ (**2b**)



1b (200 mg, 0.46 mmol) and $B(C_6F_5)_3$ (236.8 mg, 0.46 mmol) were placed in a Schlenk flask under argon. The flask was flushed with CO_2 via a balloon charged with this gas for 1 min. 10 mL of a toluene-pentane (1:4) solution was then added and the flask placed at -78 °C under CO_2. The resulting white suspension was stirred for 1 h at -78 °C, after which the suspension was filtered and washed with pentane (3x5 mL) at room temperature. The resulting white residue was purified via crystallisation from a saturated solution of pentane-CH_2Cl_2. After filtration and drying under vacuum, the expected product **2b** was isolated as a white powder in 28% yield (122 mg).

^{1}H NMR (400.2 MHz, 298 K, CD_2Cl_2) δ 7.57 (t, $^3J_{HH}$ = 7.8 Hz, 2H, p-Ar) 7.36 (s, 2H, C_2H_2) 7.31 (d, $^3J_{HH}$ = 7.8 Hz, 4H, m-Ar) 2.40 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*$(CH_3)_2$) 1.15 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(C*H*$_3)_2$) 1.11 (d, $^3J_{HH}$ = 6.7 Hz, 12H, CH(C*H*$_3)_2$). ^{11}B NMR (128.4 MHz, 298 K, CD_2Cl_2) δ -3.4 (s). ^{13}C{^{1}H} NMR (100.6 MHz, 298 K, CD_2Cl_2) δ = 152.8 (NHC-*C*O_2), 148.1 (d, $^1J_{CF}$ = 241.0 Hz, m-C_6F_5) 144.5 (o-Ar) 139.5 (d, $^1J_{CF}$ = 247.3 Hz, p-C_6F_5) 139.3 (N_2C) 136.2 (d, $^1J_{CF}$ = 245.8 Hz, o-C_6F_5), 132.3 (ipso-Ar), 132.2 (p-Ar), 126.6 (C_2H_2), 125.0 (m-Ar), 120.0 (BC-ipso) 29.8 (*C*H$(CH_3)_2$) 25.4 (CH(*C*$H_3)_2$) 22.2 (CH(C*H*$_3)_2$). ^{19}F NMR (376.5 MHz, 298 K, CD_2Cl_2): δ −134.1 (d, $^3J_{FF}$ = 24.2 Hz, 6F, o-C_6F_5), −161.4 (t, $^3J_{FF}$ = 20.7 Hz, 3F, p-C_6F_5) −166.4 (t, $^3J_{FF}$ = 21.6 Hz, 6F, m-C_6F_5). HRMS (ESI+) m/z: Calcd for $C_{46}H_{37}BF_{15}N_2O_2$ [M+H$^+$]: 945.2620 found 945.2614. Anal (%): Calcd for $C_{46}H_{36}BF_{15}N_2O_2$: C, 58.49; H, 3.84; N, 2.97. Found: C, 58.41; H, 3.53; N, 2.83. FTIR (solid state): $\nu_{C=O}$=1717 cm^{-1}. $E_{1/2,exp}^{red}$ (vs. $Fc^{+/0}$) = -2.08 V.

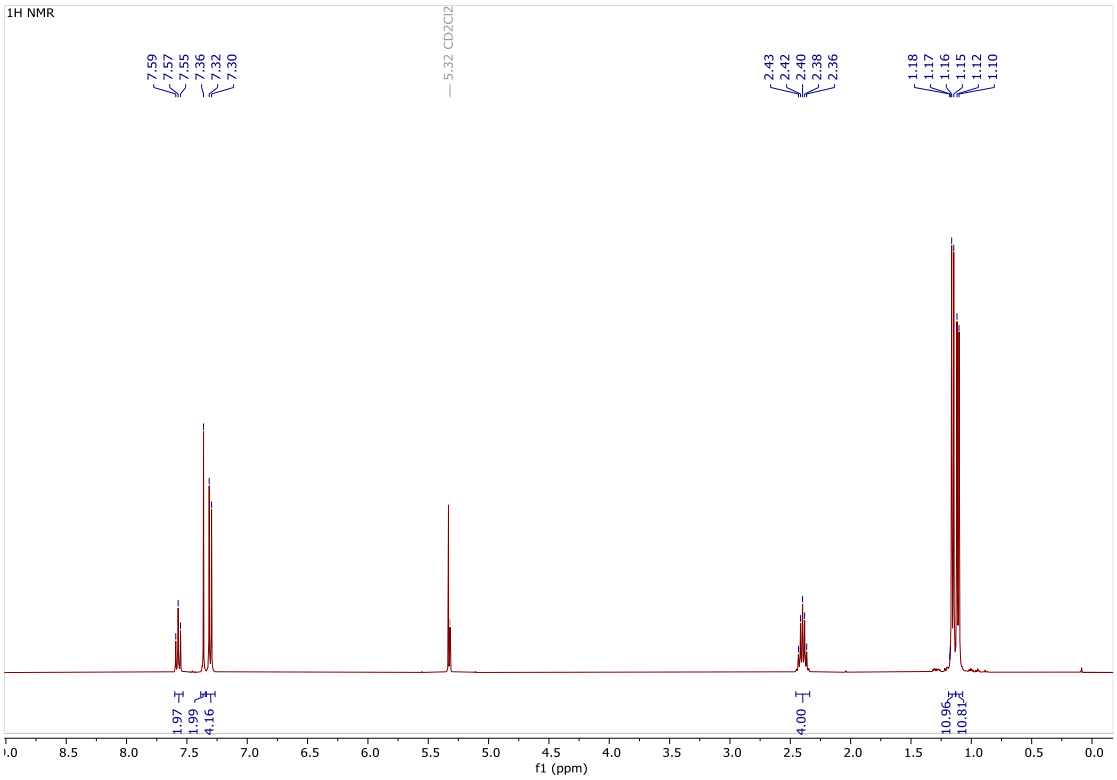


Figure S3. ^{1}H NMR spectrum of **2b** in CD_2Cl_2 at 298 K.

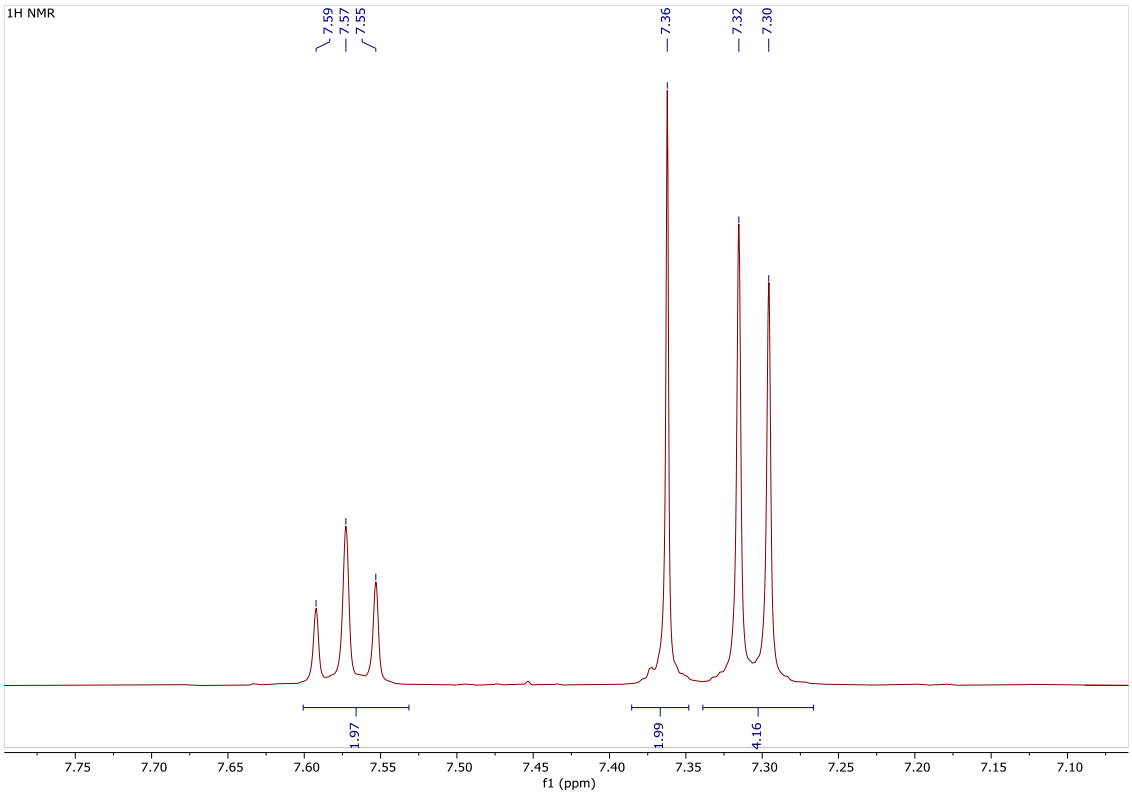


Figure S4. Zoom ^{1}H NMR spectrum of **2b** in CD_2Cl_2 at 298 K.

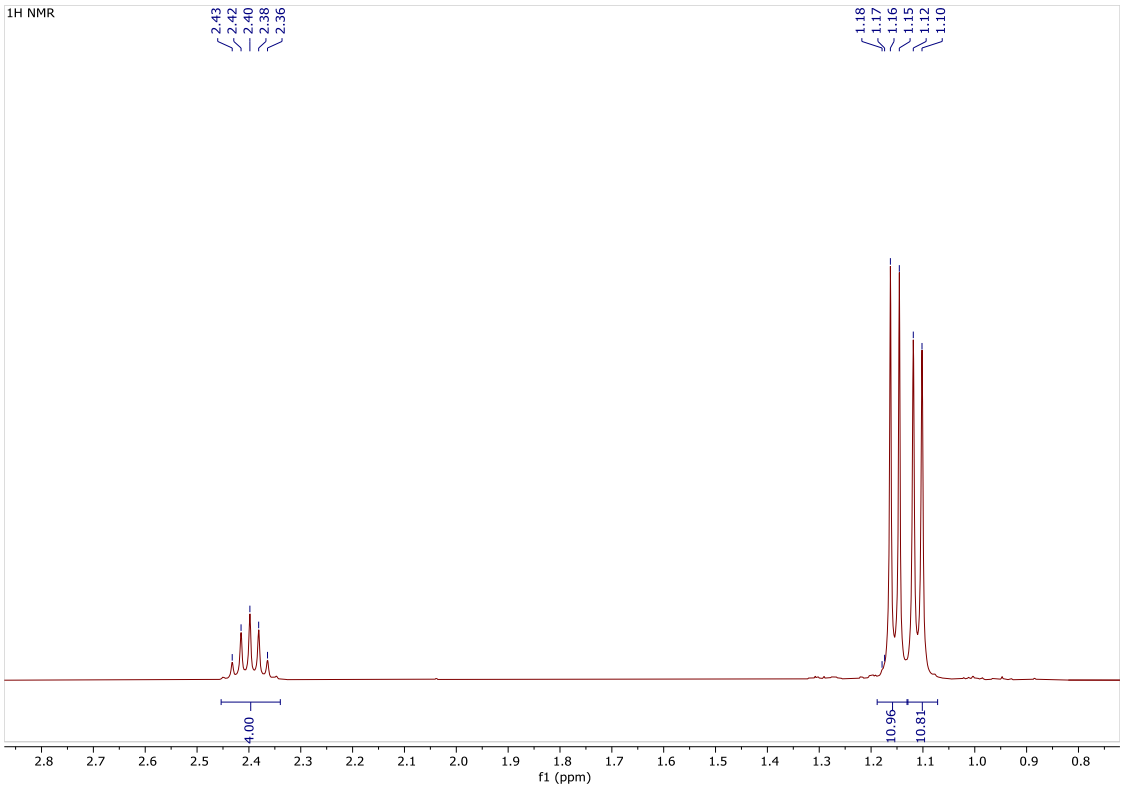


Figure S5. Zoom ^{1}H NMR spectrum of **2b** in CD_2Cl_2 at 298 K.

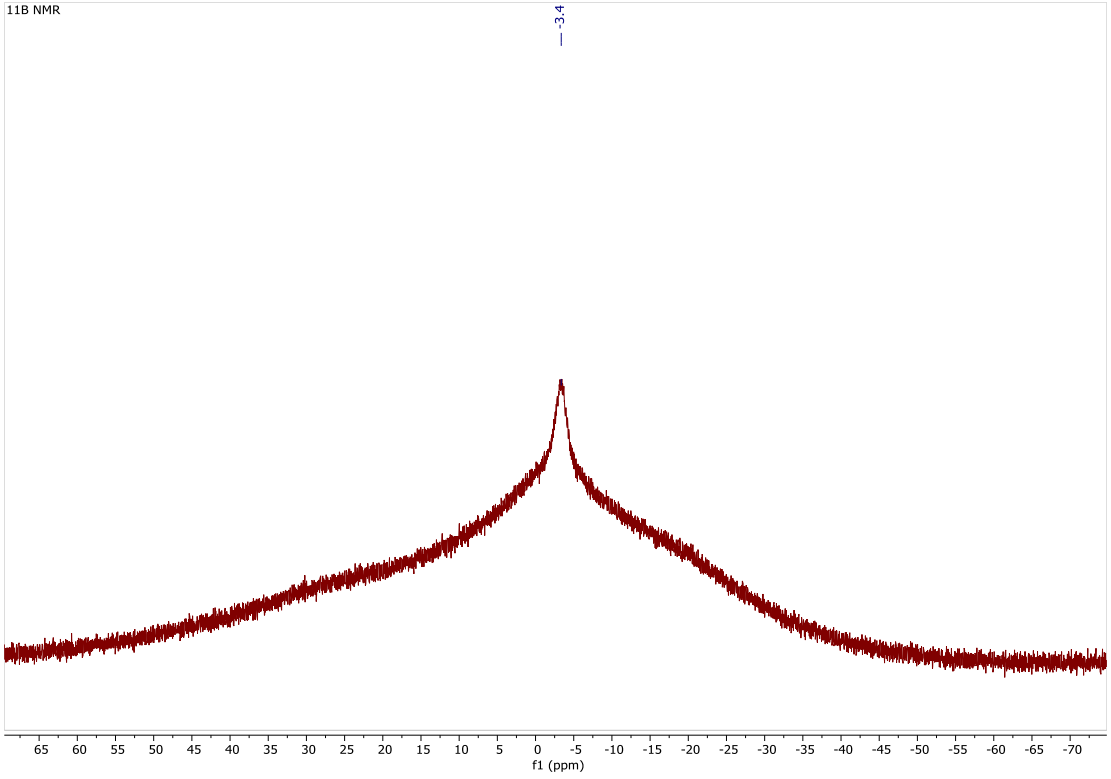


Figure S6. ^{11}B NMR spectrum of **2b** in CD_2Cl_2 at 298 K.

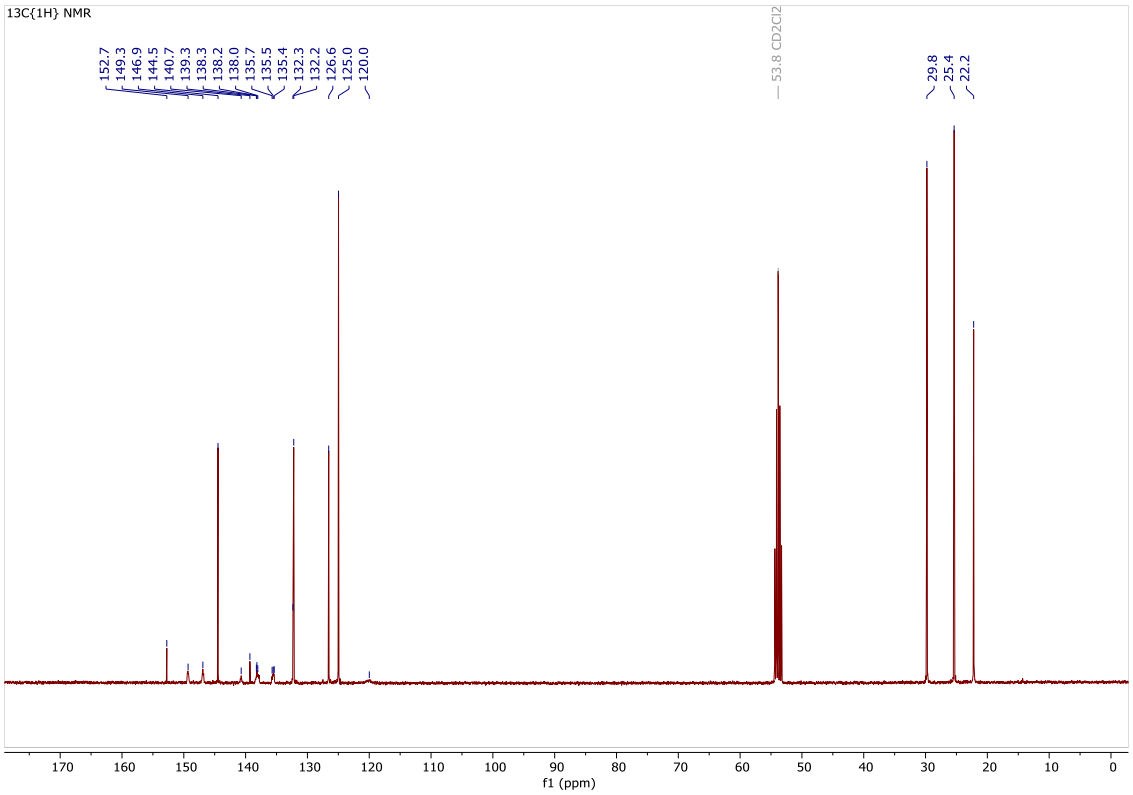


Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of **2b** in CD_2Cl_2 at 298 K.

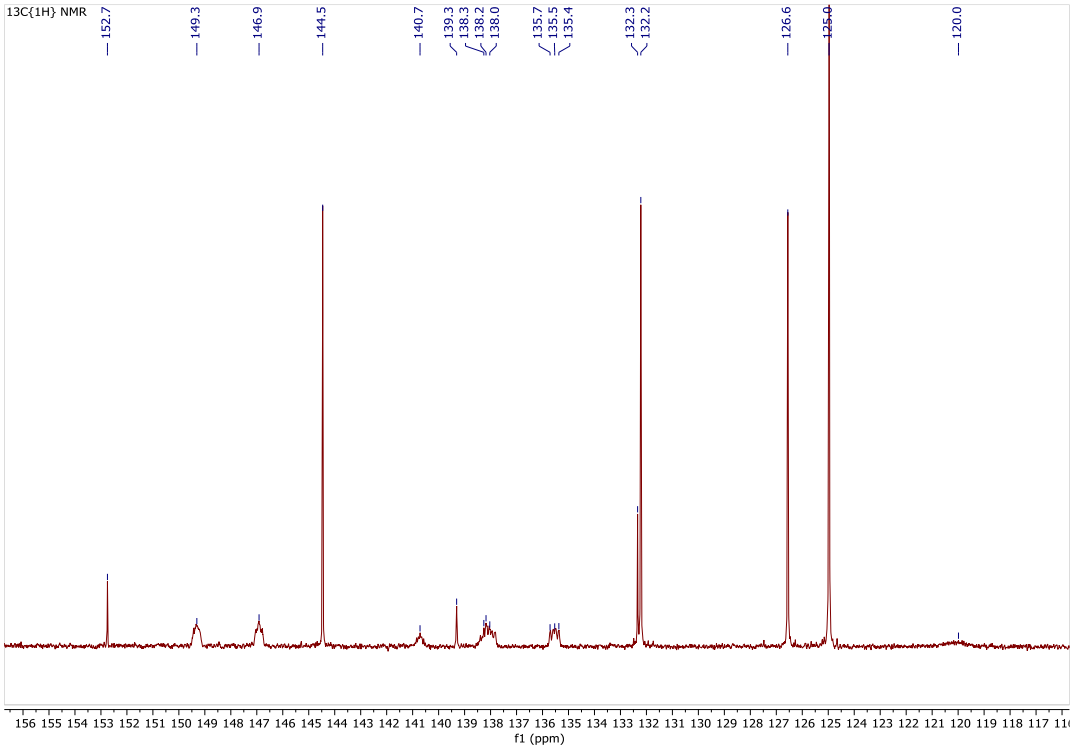


Figure S8. Zoom $^{13}C\{^{1}H\}$ NMR spectrum of **2b** in CD_2Cl_2 at 298 K.

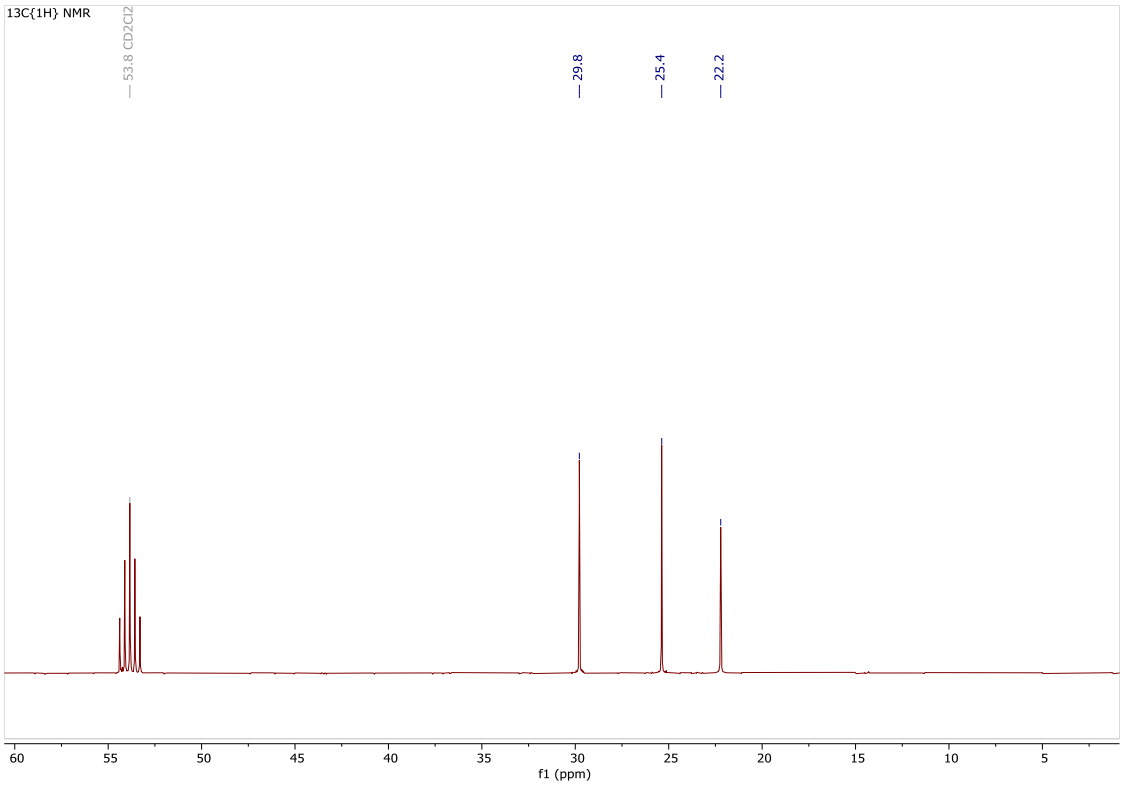


Figure S9. Zoom $^{13}C\{^{1}H\}$ NMR spectrum of **2b** in CD_2Cl_2 at 298 K

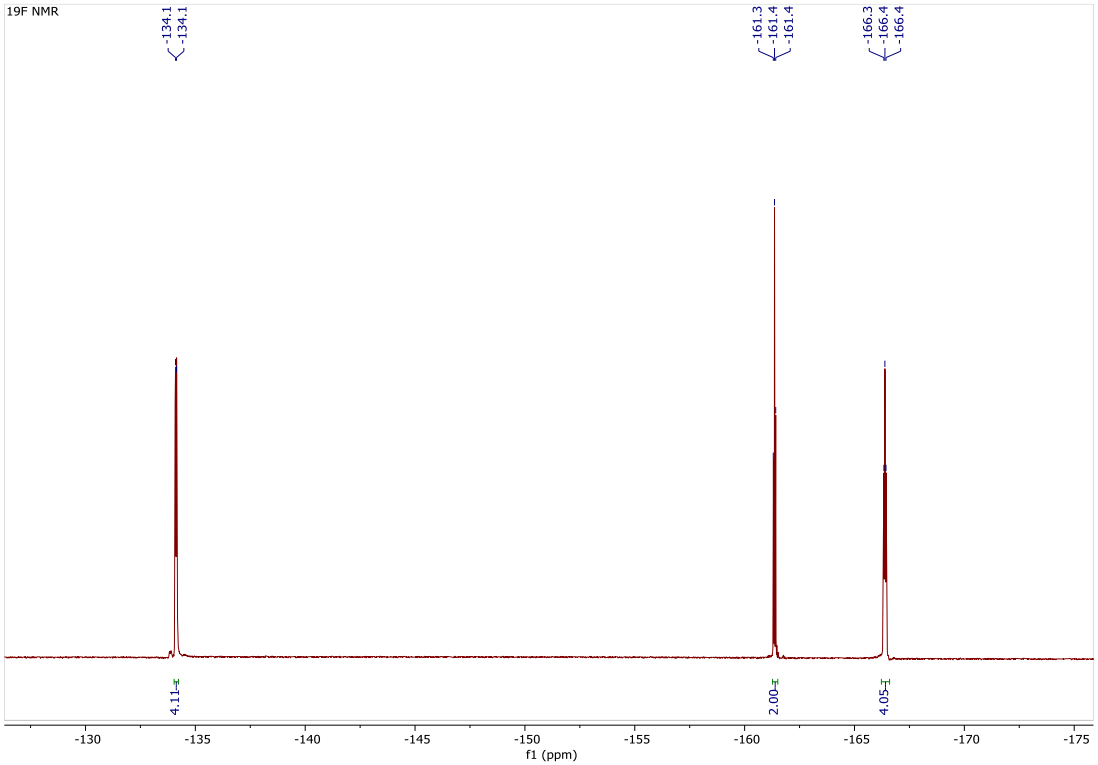


Figure S10. ^{19}F NMR spectrum of **2b** in CD_2Cl_2 at 298 K.

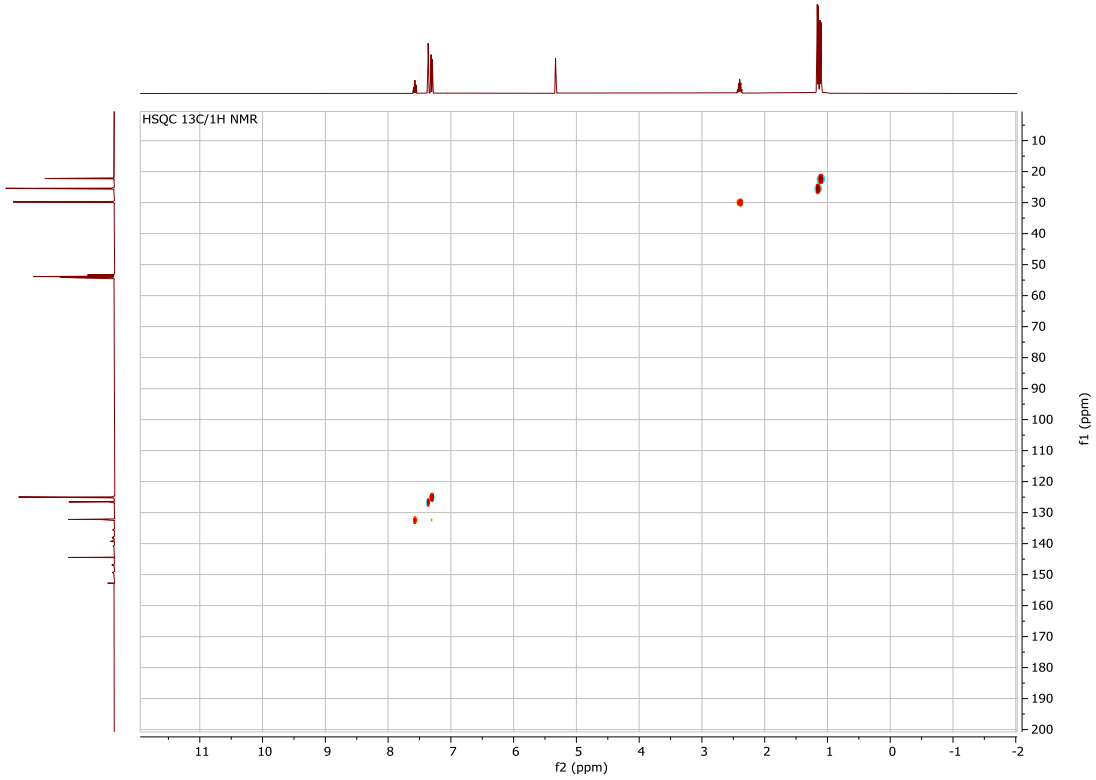


Figure S11. HSQC $^{13}C/^{1}H$ NMR spectrum of **2b** in CD_2Cl_2 at 298 K.

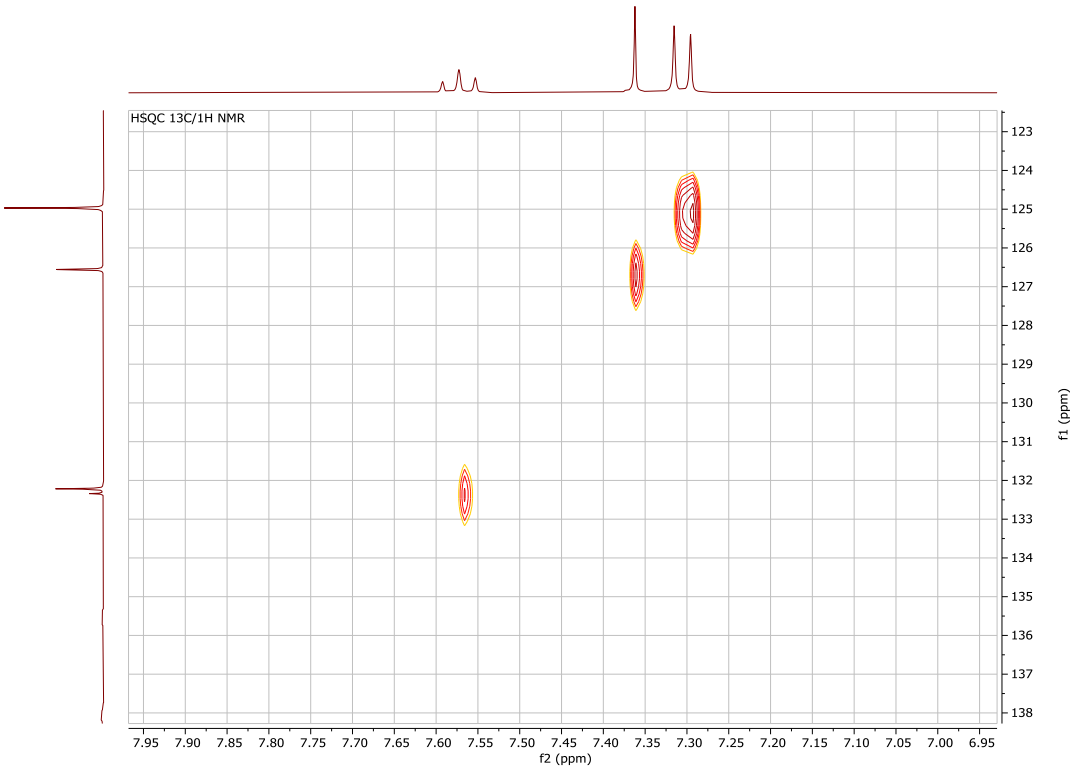


Figure S12. Zoom HSQC $^{13}C/^{1}H$ NMR spectrum of **2b** in CD_2Cl_2 at 298 K.

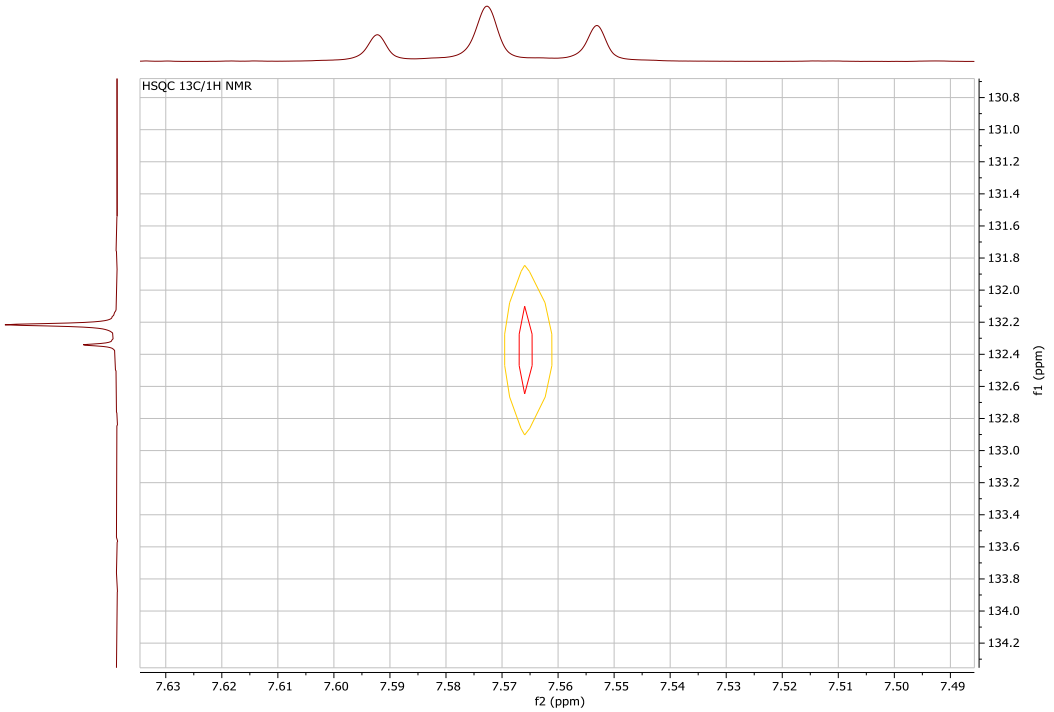


Figure S13. Zoom HSQC $^{13}C/^{1}H$ NMR spectrum of **2b** in CD_2Cl_2 at 298 K.

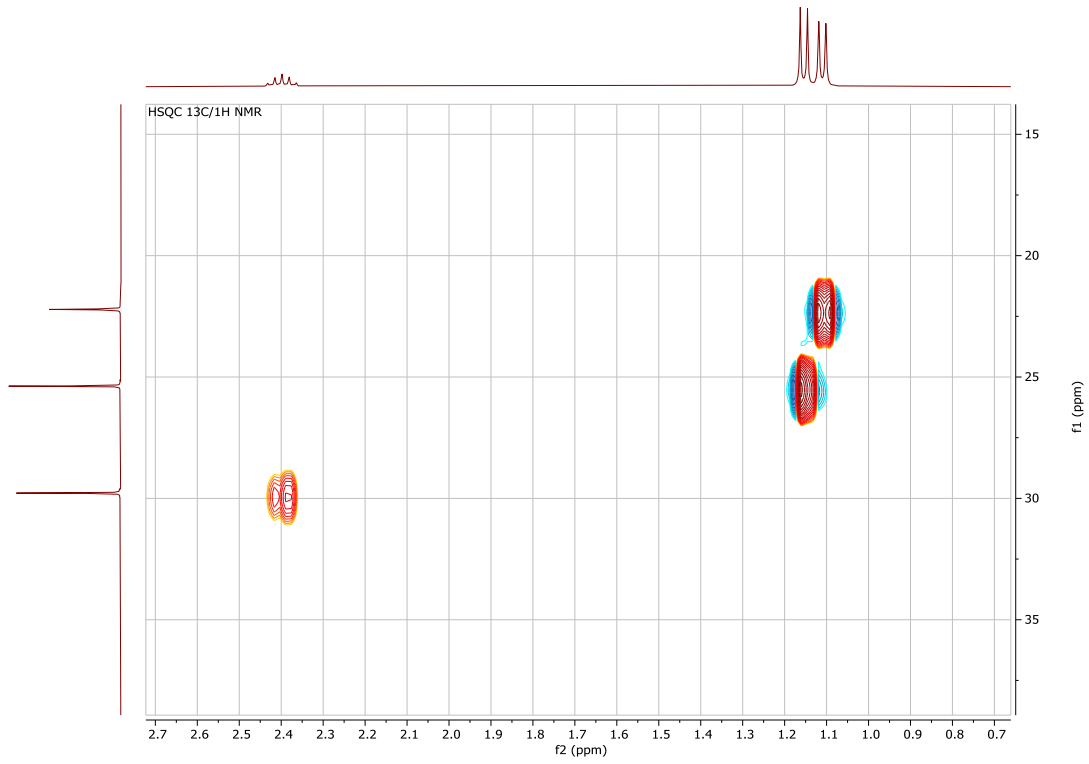


Figure S14. Zoom HSQC $^{13}C/^{1}H$ NMR spectrum of **2b** in CD_2Cl_2 at 298 K.

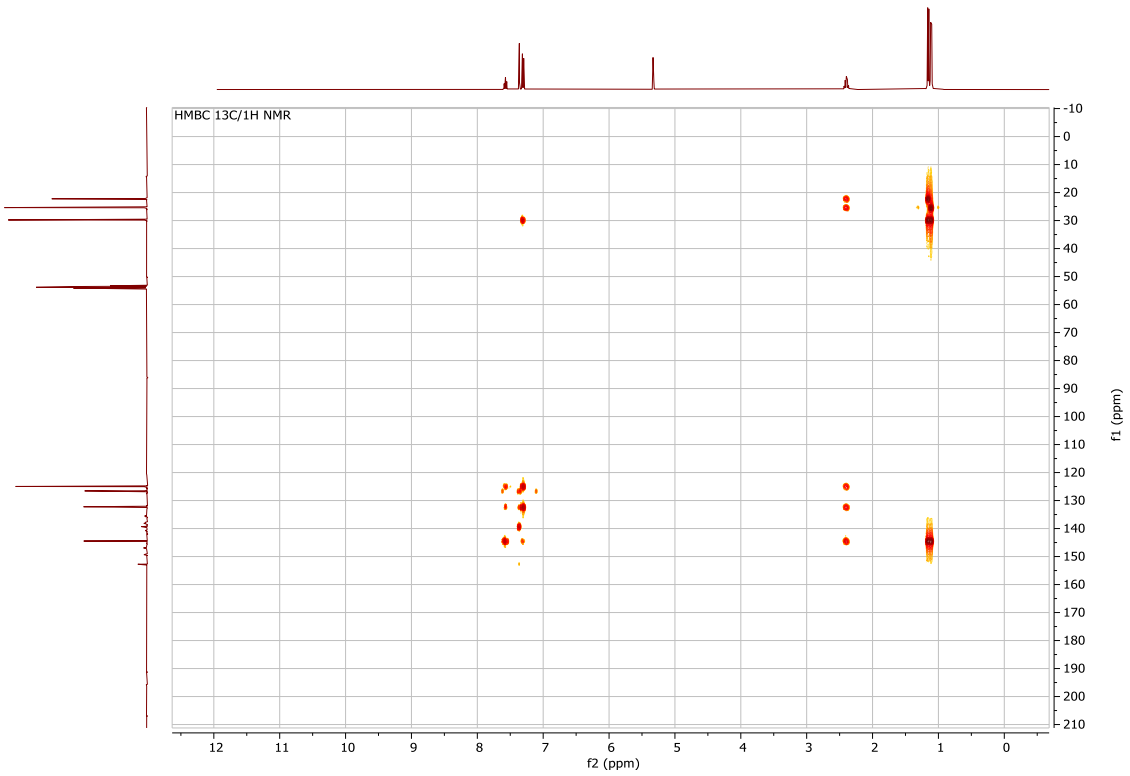


Figure S15. HMBC $^{13}C/^{1}H$ NMR spectrum of **2b** in CD_2Cl_2 at 298 K.

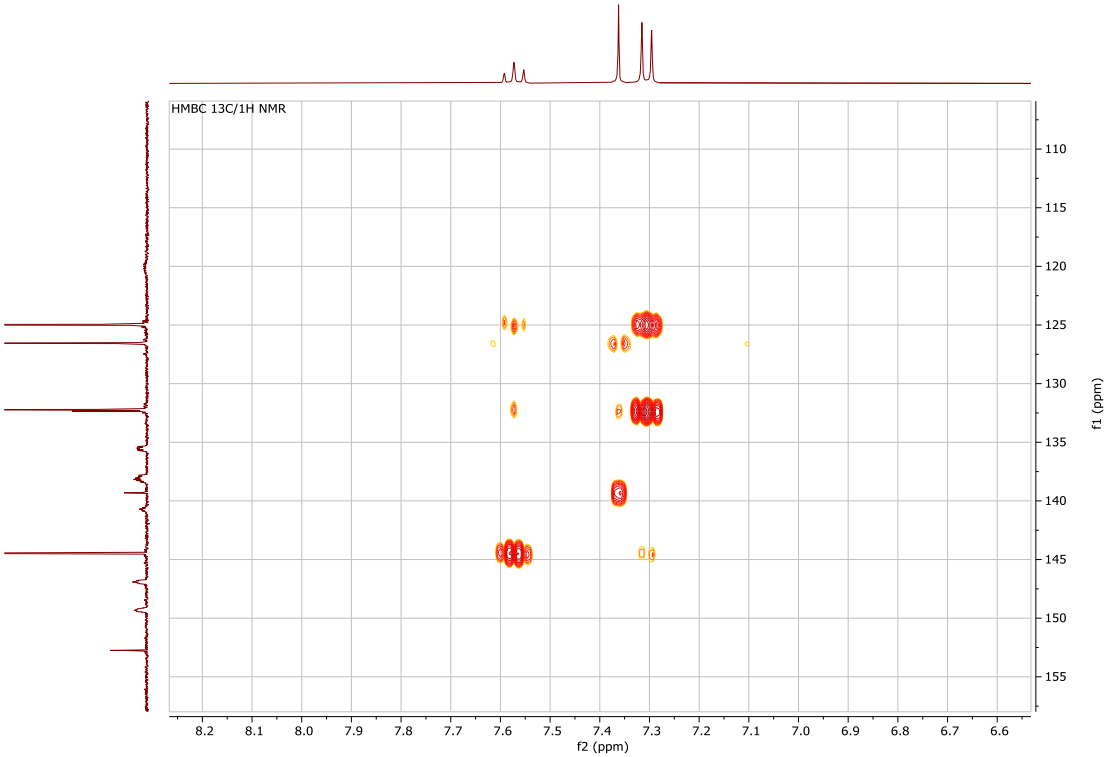


Figure S16. Zoom HMBC $^{13}C/^{1}H$ NMR spectrum of **2b** in CD_2Cl_2 at 298 K.

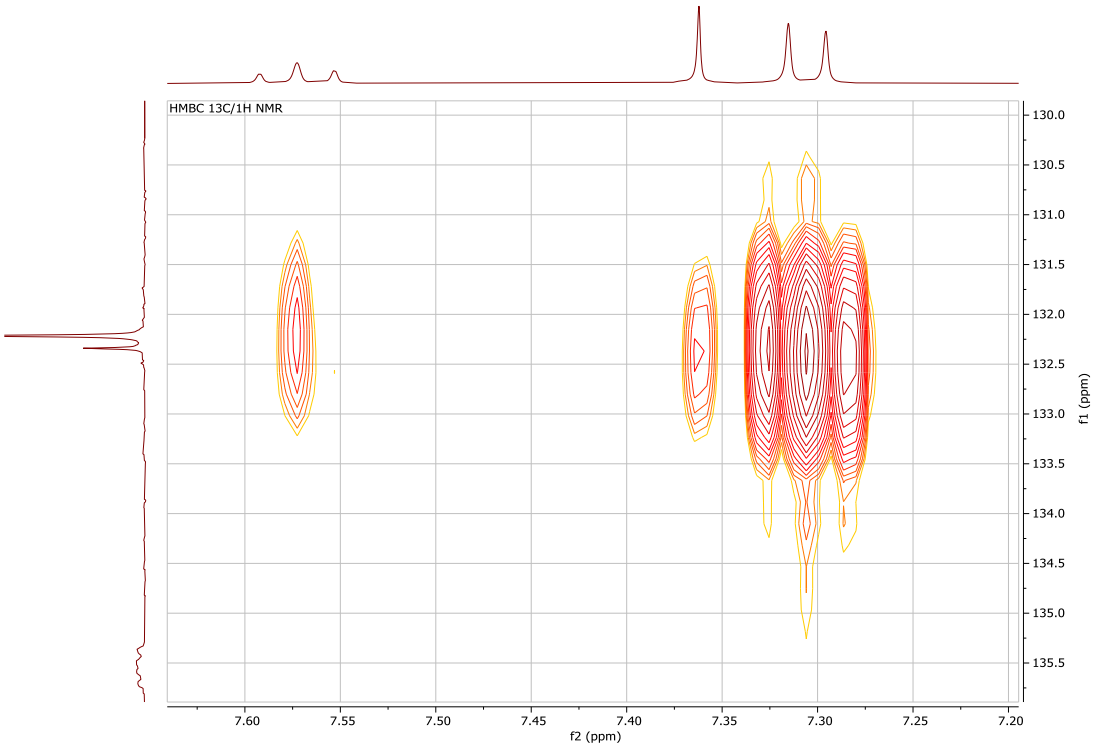


Figure S17. Zoom HMBC $^{13}C/^{1}H$ NMR spectrum of **2b** in CD_2Cl_2 at 298 K.

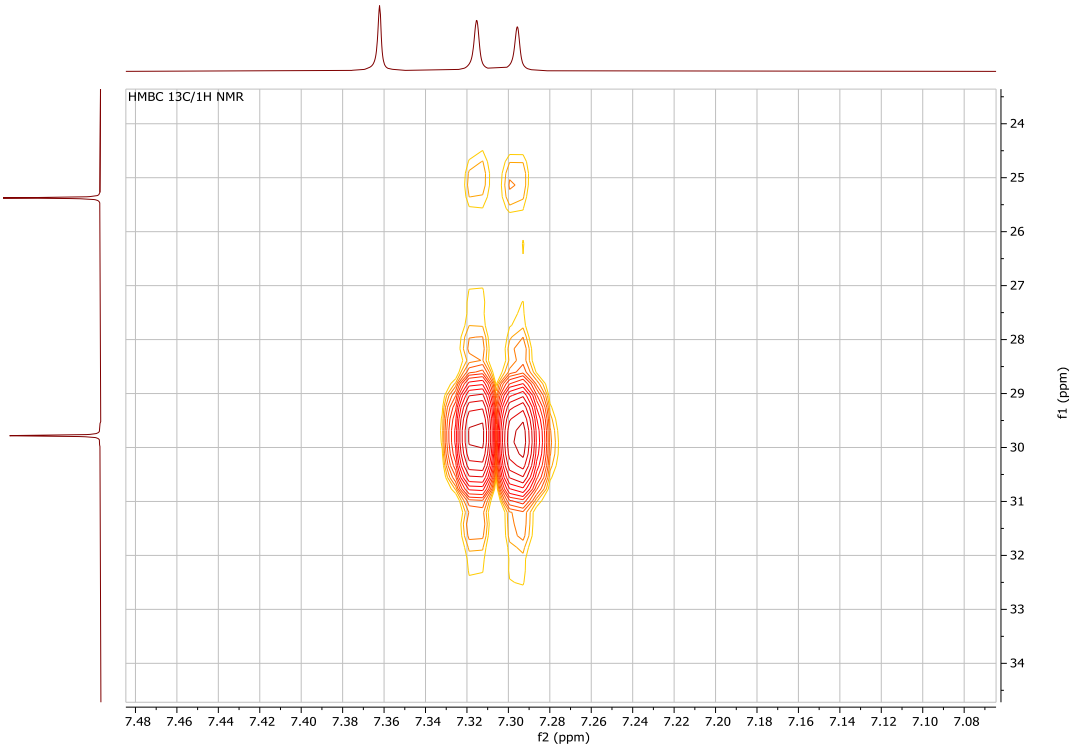


Figure S18. Zoom HMBC $^{13}C/^{1}H$ NMR spectrum of **2b** in CD_2Cl_2 at 298 K.

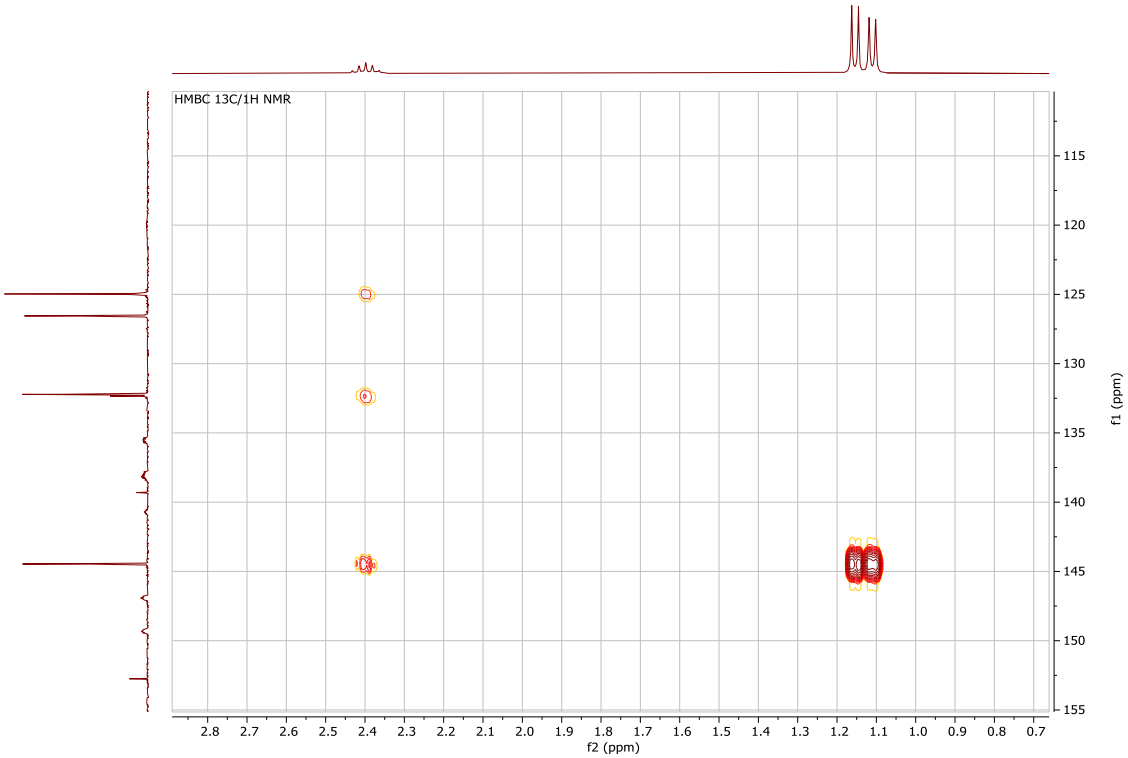


Figure S19. Zoom HMBC $^{13}C/^{1}H$ NMR spectrum of **2b** in CD_2Cl_2 at 298 K.

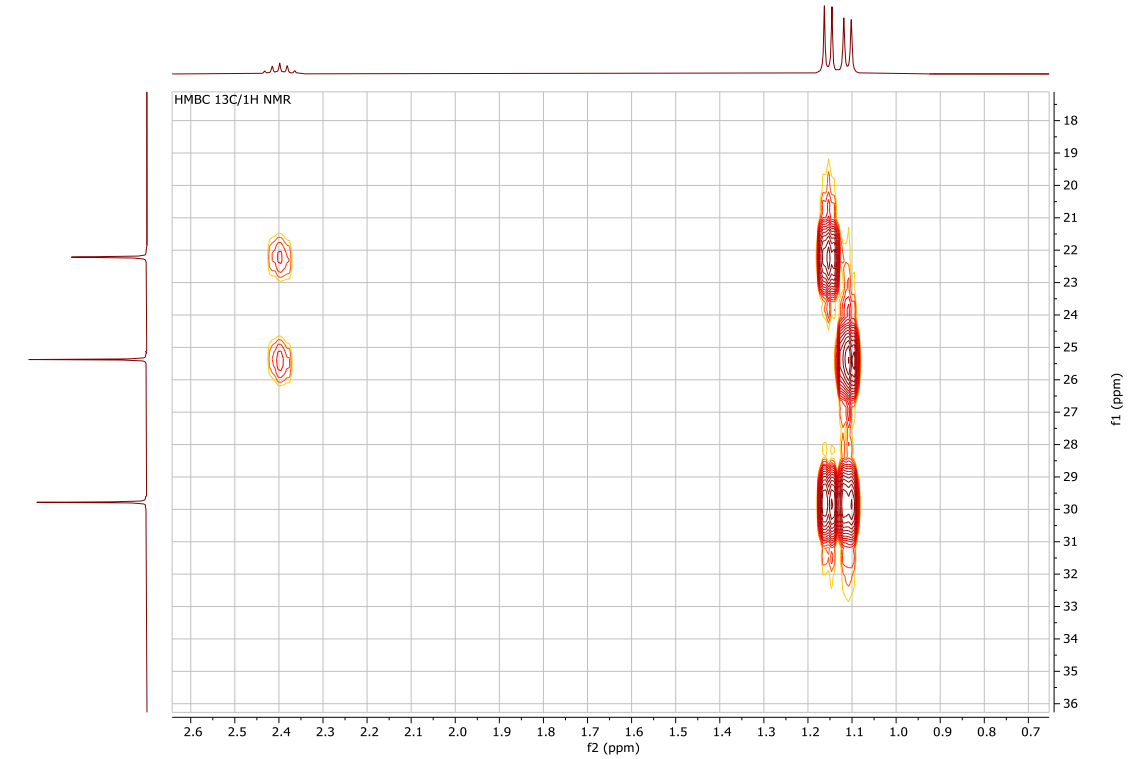


Figure S20. Zoom HMBC $^{13}C/^{1}H$ NMR spectrum of **2b** in CD_2Cl_2 at 298 K.

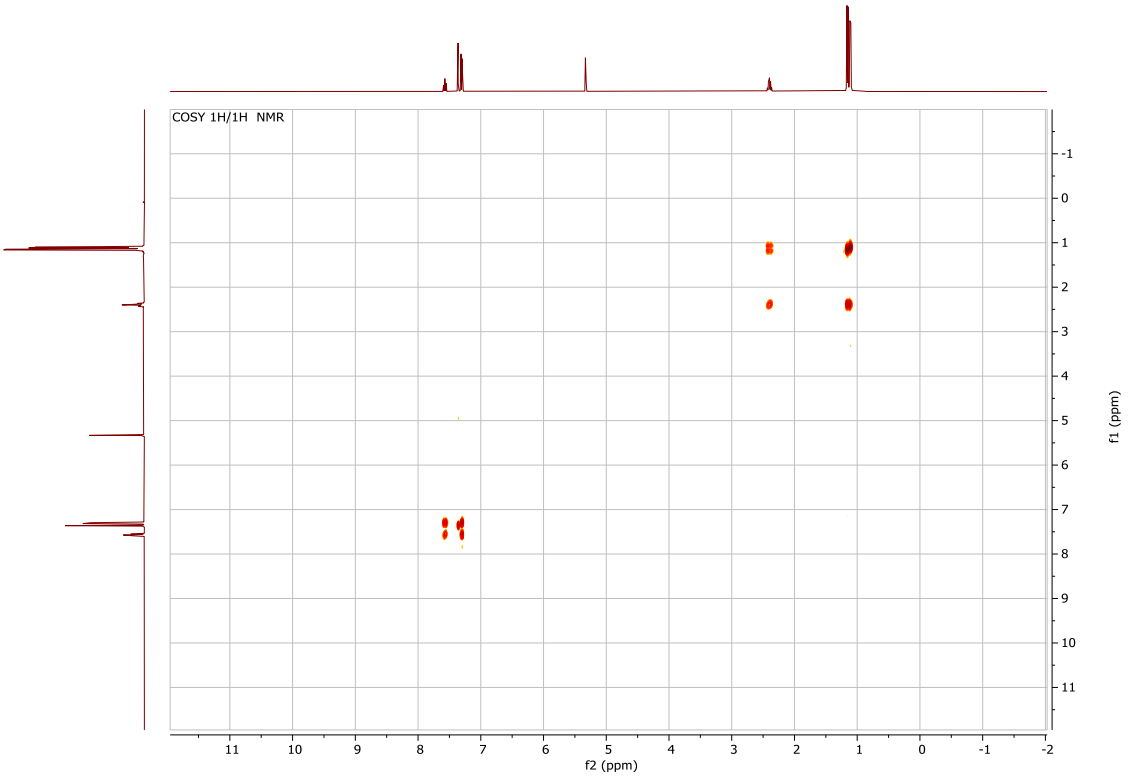


Figure S21. COSY $^{1}H/^{1}H$ NMR spectrum of **2b** in CD_2Cl_2 at 298 K.

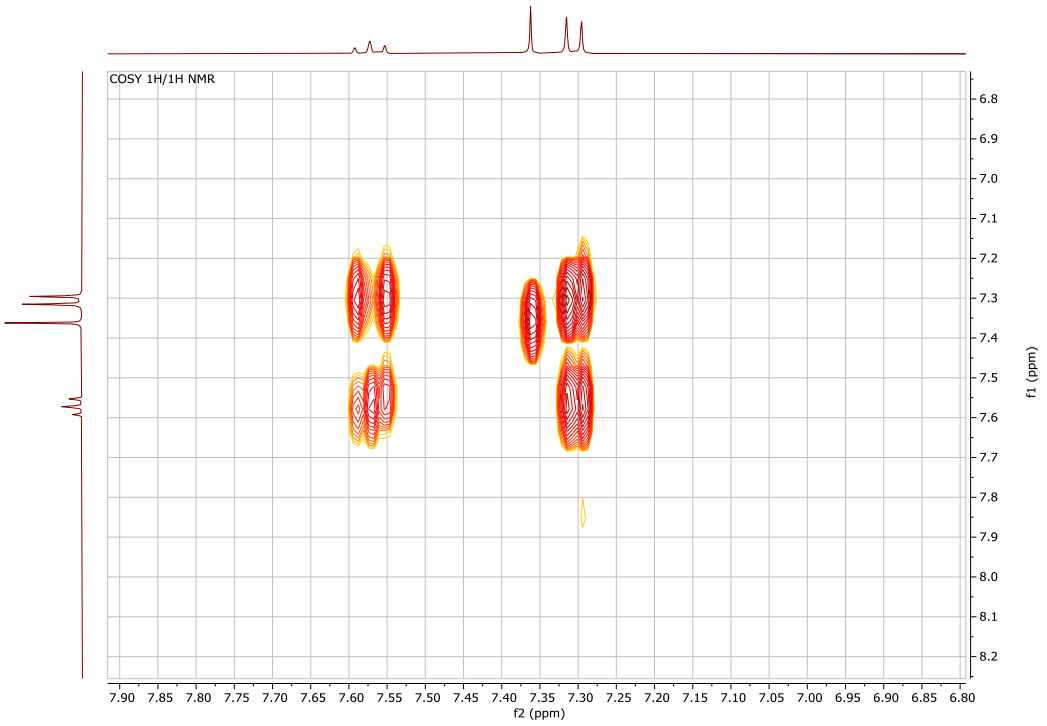


Figure S22. Zoom COSY $^{1}H/^{1}H$ NMR spectrum of **2b** in CD_2Cl_2 at 298 K.

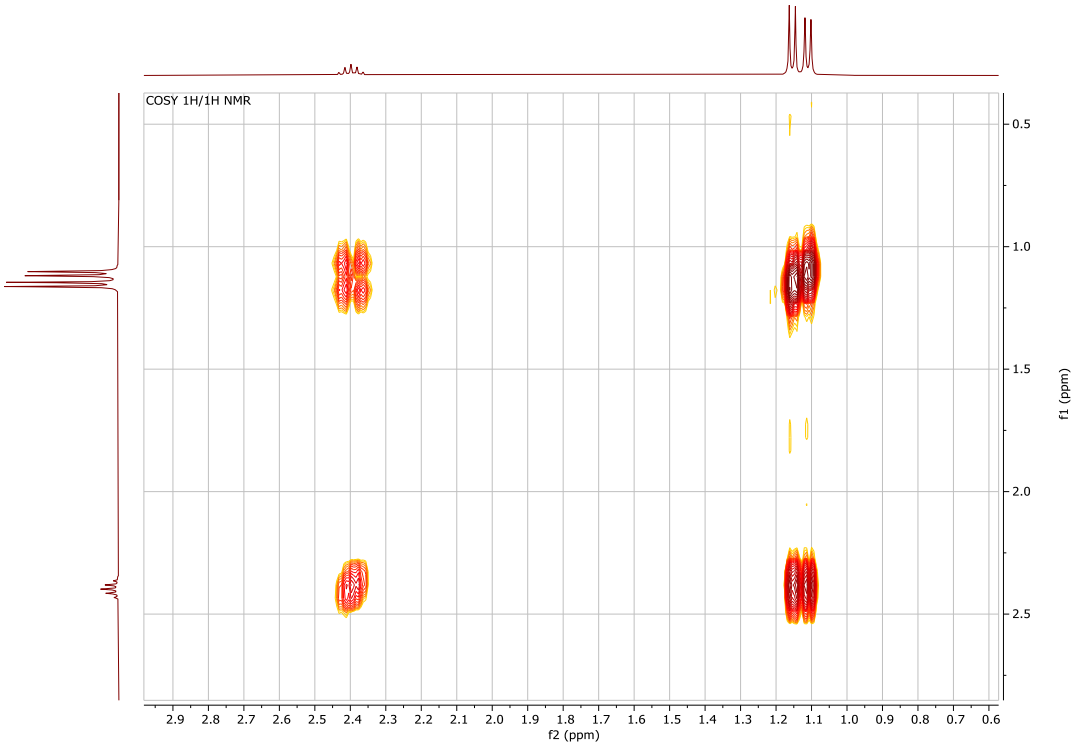


Figure S23. Zoom COSY $^{1}H/^{1}H$ NMR spectrum of **2b** in CD_2Cl_2 at 298 K.

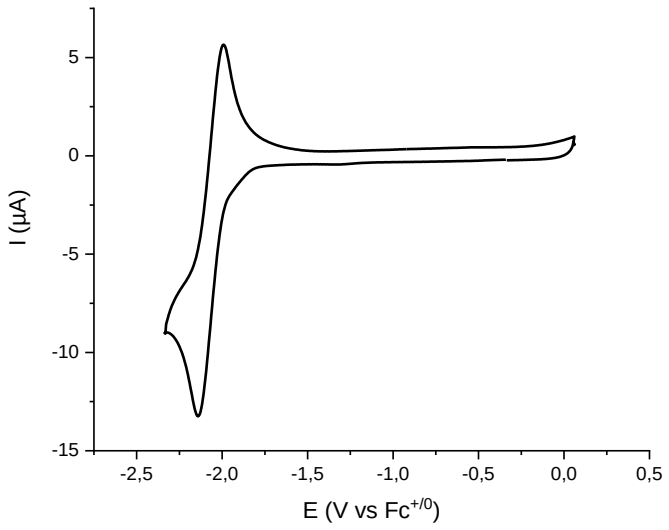


Figure S24. Cyclic voltammogram at reducing potentials of **2b** (5 mM) on GC microdisk in 0.1 M $[nBu_4N][PF_6]$/ CH_2Cl_2 media under Ar atmosphere. scan rate: 0.2 V/s.

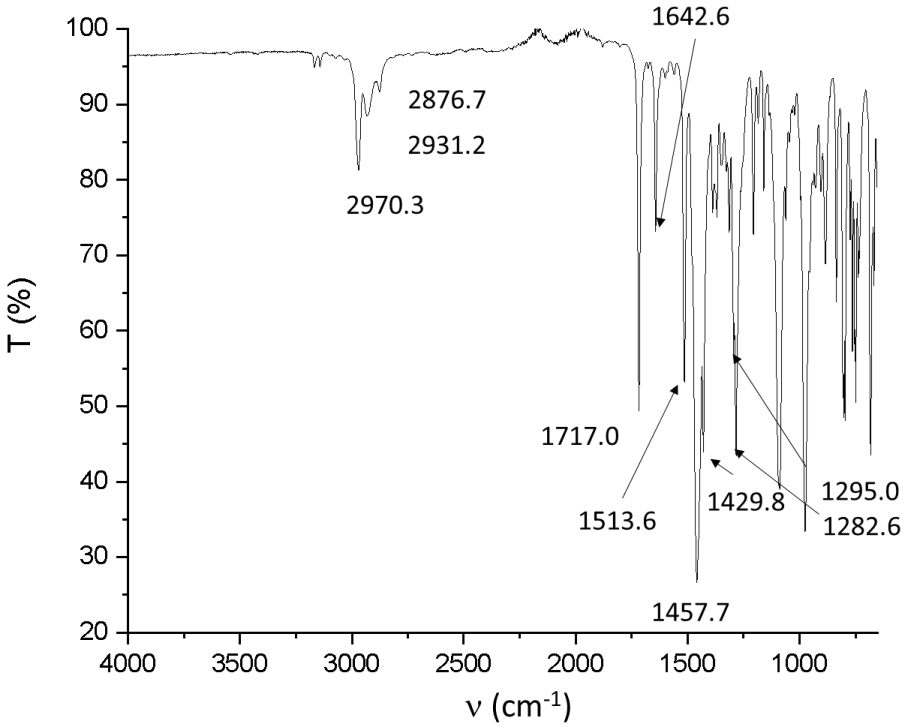
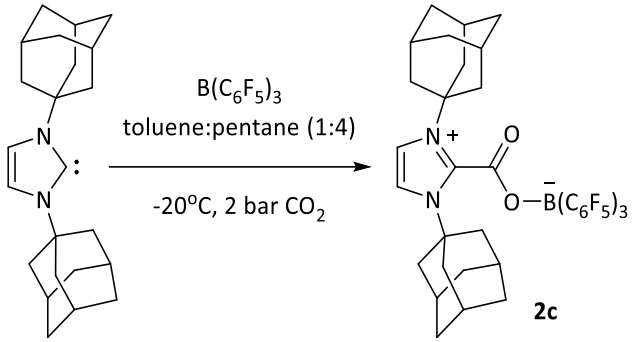


Figure S25. FTIR (solid state) of **2b** at 298 K.

Table S2. Theoretical and experimental IR frequencies for [**2b**]

Experimental	**Theoretical**	**Assignation**
1717.0	1734.9	C=O
1642.6	1647.5-1624.9	C=C (BCF)
1513.6	1513.4-1510.8	C-F
1457.7; 1429.8	1437.5-1406.8	C(sp^3)-H torsion
1295.0; 1282.6	1310.6-1289.9	C-O

2.3 IAd-CO_2-$B(C_6F_5)_3$ (**2c**)



IAd (150 mg, 0.45 mmol) and $B(C_6F_5)_3$ (236.8 mg, 0.44 mmol) were placed in a Fisher porter flask under argon. The flask was charged with 2 bar of CO_2 and three CO_2-vacuum cycles were performed. 10 mL of a toluene-pentane (1:4) solution was then added and the flask placed at -20 °C under CO_2. The resulting white suspension was stirred for 1 h at -20 °C, after which the suspension was filtered and washed with pentane (3x5 mL) at room temperature. The resulting white residue was dried under vacuum leading to the isolation of **2c** as a white powder in 66% yield (265.5 mg).

^{1}H NMR (400.1 MHz, 298 K, $CDCl_3$) δ 7.42 (s, 2H, C_2H_2), 2.29 (s, 6H, CH-Ad) 2.15 (s, 12H, CH_2-Ad) 1.77 (q, $^3J_{HH}$ = 14.3 Hz, 12H, CH_2-Ad). ^{11}B NMR (128.4 MHz, 298 K, $CDCl_3$) δ -3.8 (s). ^{13}C{^{1}H} NMR (100.6 MHz, 297.9 K, $CDCl_3$) δ = 161.9 (NHC-*C*O_2), 148.1 (d, $^1J_{CF}$ = 240.1 Hz, m-C_6F_5), 139.1 (d, $^1J_{CF}$ = 234.9 Hz, p-C_6F_5), 136.6 (d, $^1J_{CF}$ = 237.9 Hz, o-C_6F_5), 130.7 (N_2C), 121.0 (BC-ipso), 118.9 (C_2H_2), 61.1 (C-Ad), 42.8 (CH_2-Ad), 35.3 (CH_2-Ad), 29.5 (CH-Ad). ^{19}F NMR (376.5 MHz, 298 K, CD_2Cl_2): δ −133.9 (d, $^3J_{FF}$ = 20.0 Hz, 6F, o-C_6F_5), −161.1 (t, $^3J_{FF}$ = 20.9 Hz, 3F, p-C_6F_5), −166.0 (t, $^3J_{FF}$ = 23.8 Hz, 6F, m-C_6F_5). Anal (%): Calcd for $C_{42}H_{32}BF_{15}N_2O_2.C_6H_5CH_3$: C, 59.77; H, 4.09; N, 2.85. Found: C, 59.27; H, 4.15; N, 3.70. FTIR (solid state): $\nu_{C=O}$ = 1715 cm^{-1}. $E_{p,exp}^{red}$ (vs. $Fc^{+/0}$) = -2.44 V.

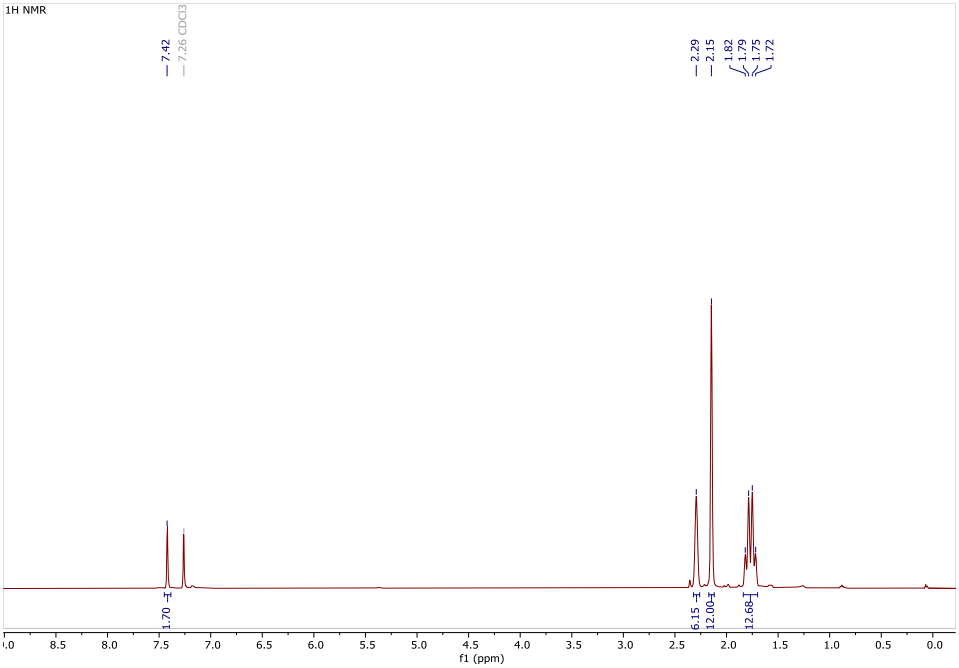


Figure S26. ^{1}H NMR spectrum of **2c** in $CDCl_3$ at 298 K.

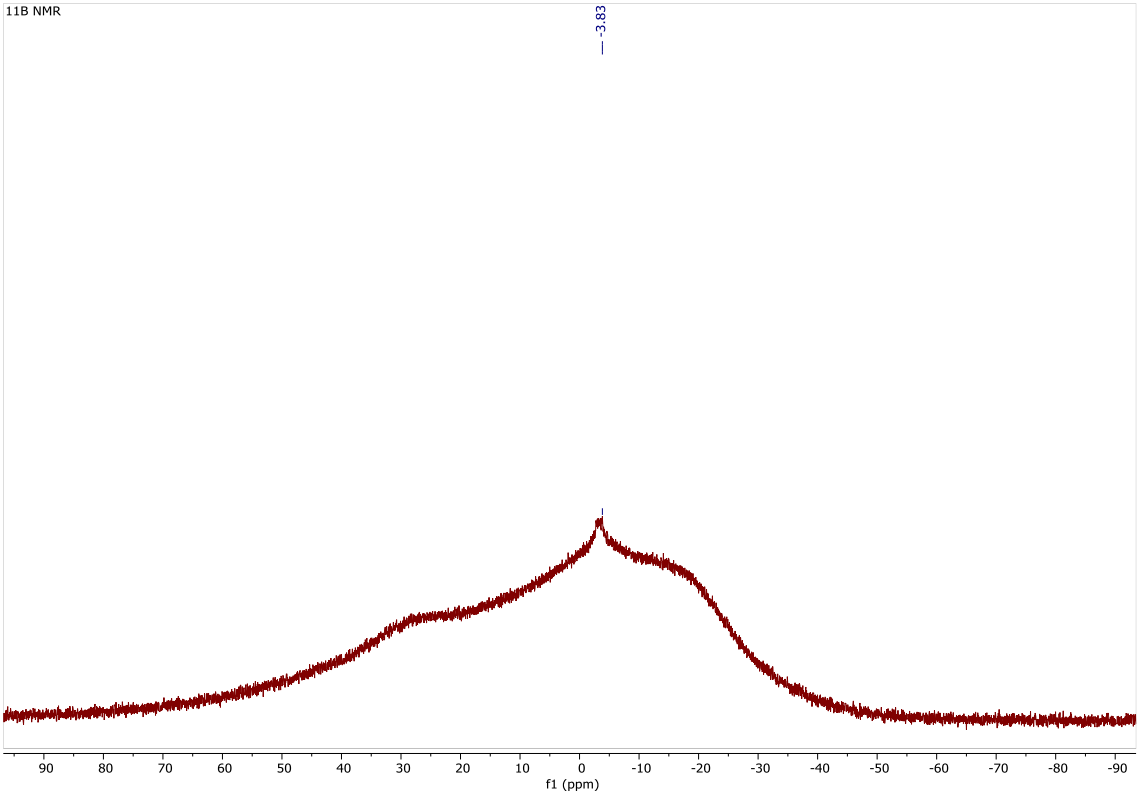


Figure S27. ^{11}B NMR spectrum of **2c** in $CDCl_3$ at 298 K.

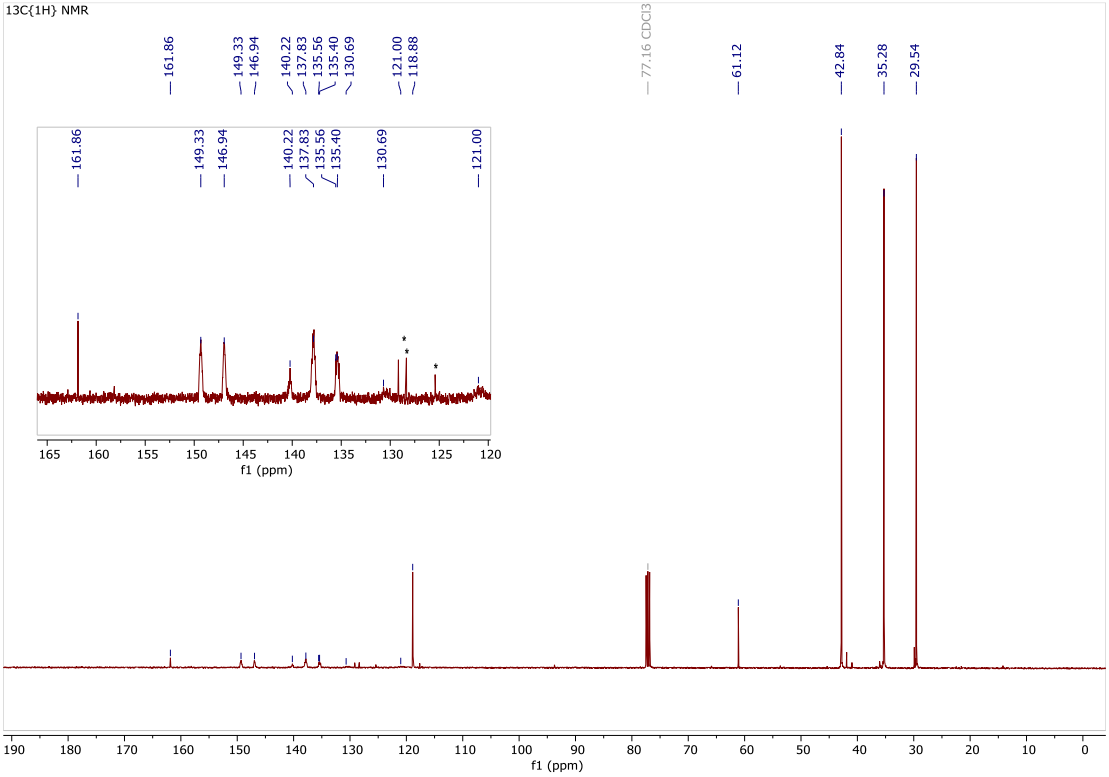


Figure S28. $^{13}C\{^1H\}$ NMR spectrum of **2c** in $CDCl_3$ at 298 K. (*$C_6H_5CH_3$), ns = 8249.

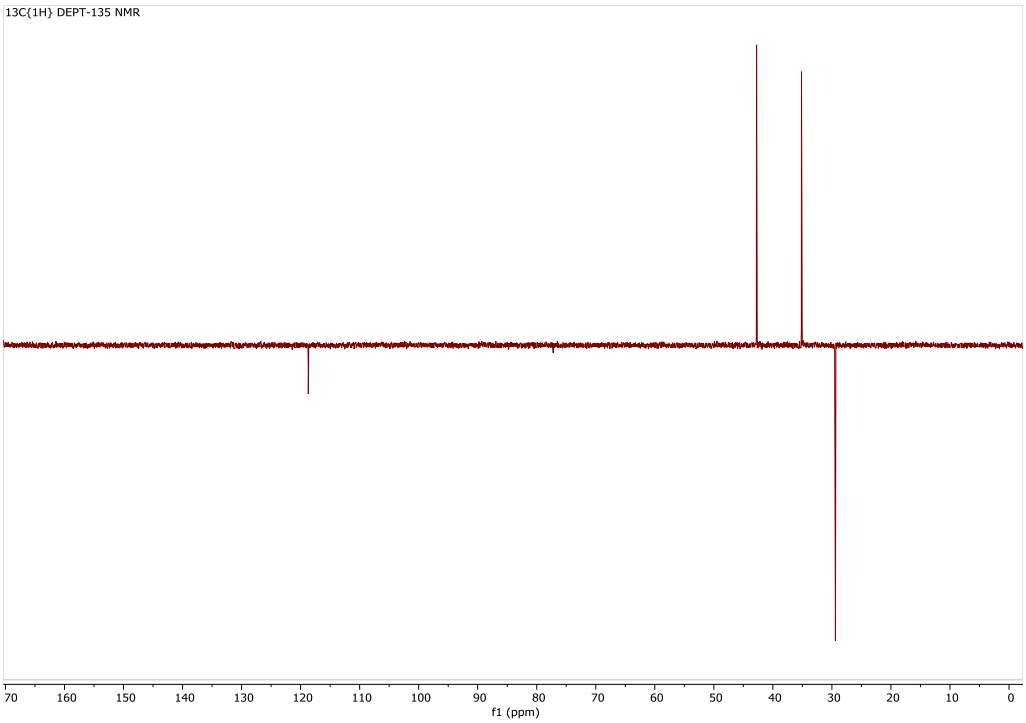


Figure S29. $^{13}C\{^{1}H\}$ DEPT-135 NMR spectrum of **2c** in $CDCl_3$ at 298 K.

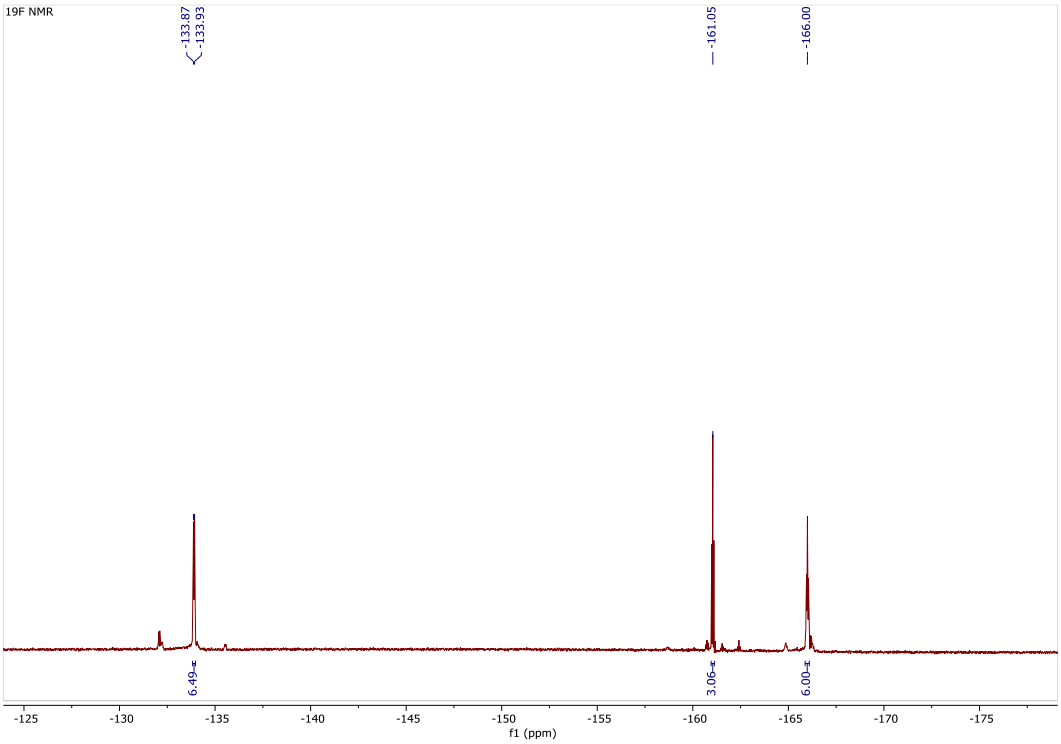


Figure S30. ^{19}F NMR spectrum of **2c** in $CDCl_3$ at 298 K.

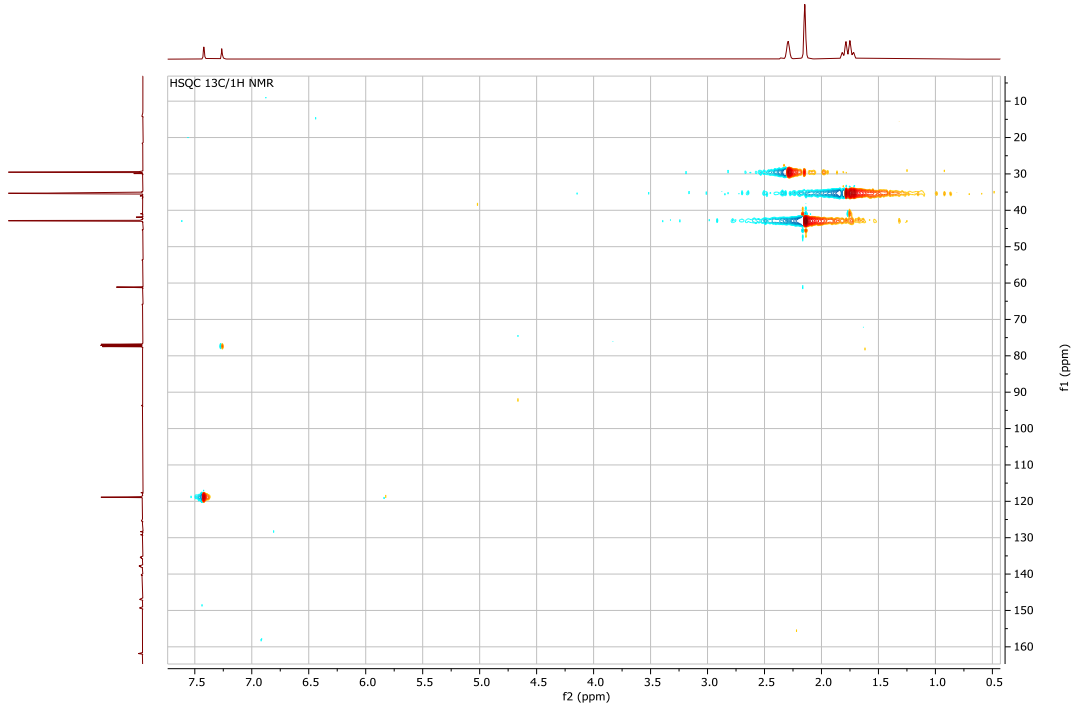


Figure S31. HSQC $^{13}C/^{1}H$ NMR spectrum of **2c** in $CDCl_3$ at 298 K.

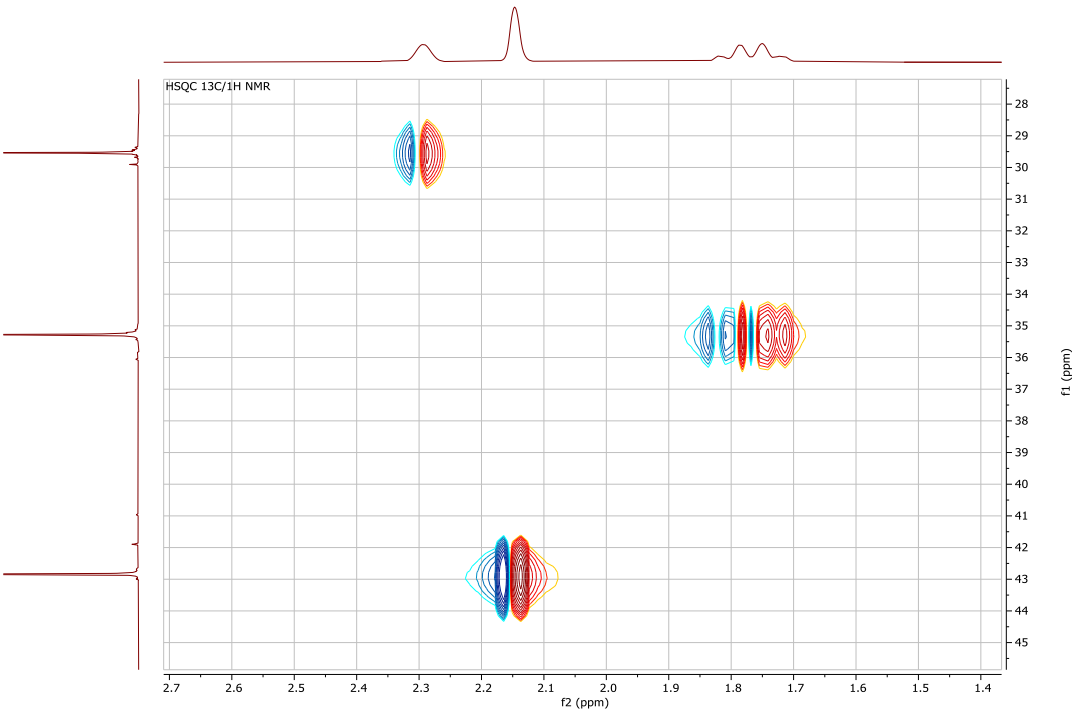


Figure S32. Zoom HSQC $^{13}C/^{1}H$ NMR spectrum of **2c** in $CDCl_3$ at 298.1 K.

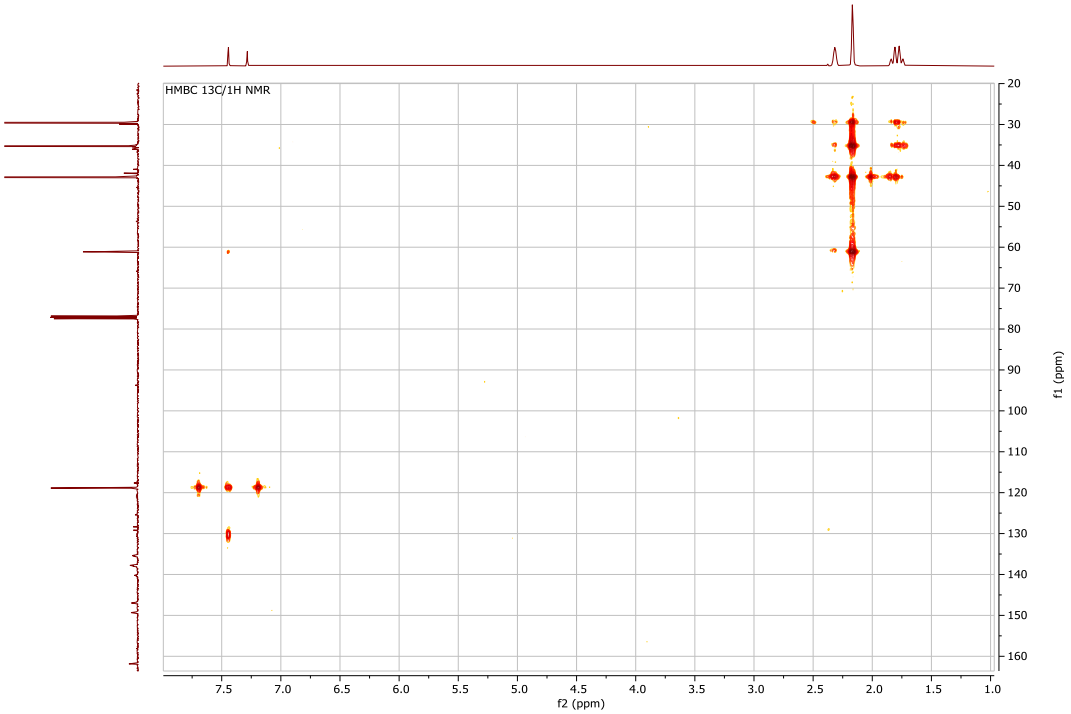


Figure S33. HMBC $^{13}C/^{1}H$ NMR spectrum of **2c** in $CDCl_3$ at 298.1 K.

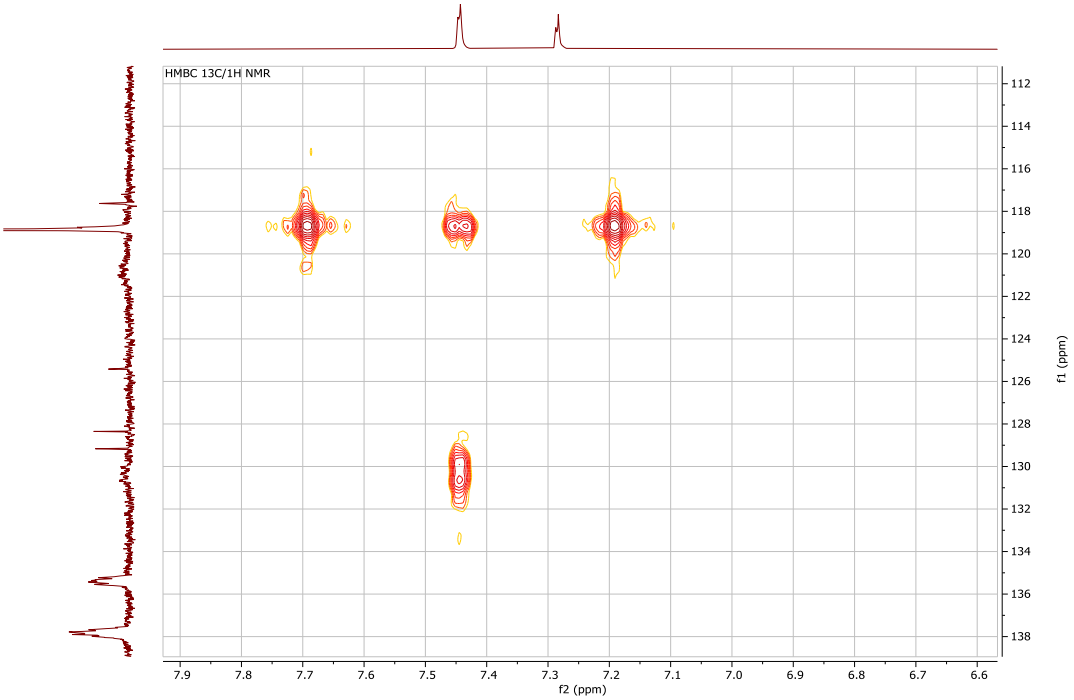


Figure S34. Zoom HMBC $^{13}C/^{1}H$ NMR spectrum of **2c** in $CDCl_3$ at 298.1 K.

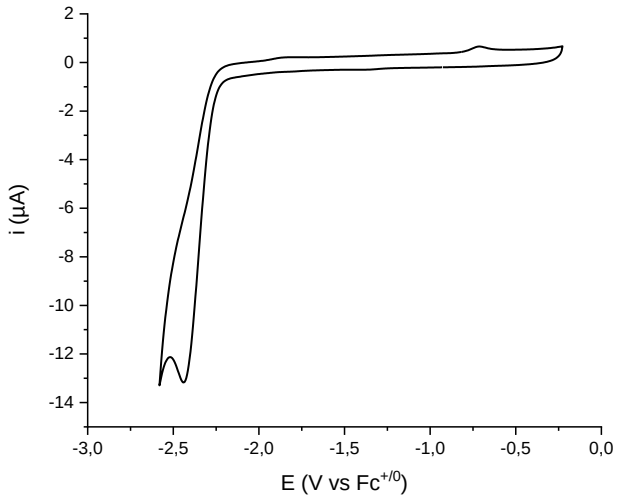


Figure S35. Cyclic voltammogram at reducing potentials of **2c** (5 mM) on GC microdisk in 0.1 M $[nBu_4N][PF_6]$/ CH_2Cl_2 media under Ar atmosphere. scan rate: 0.2 V/s.

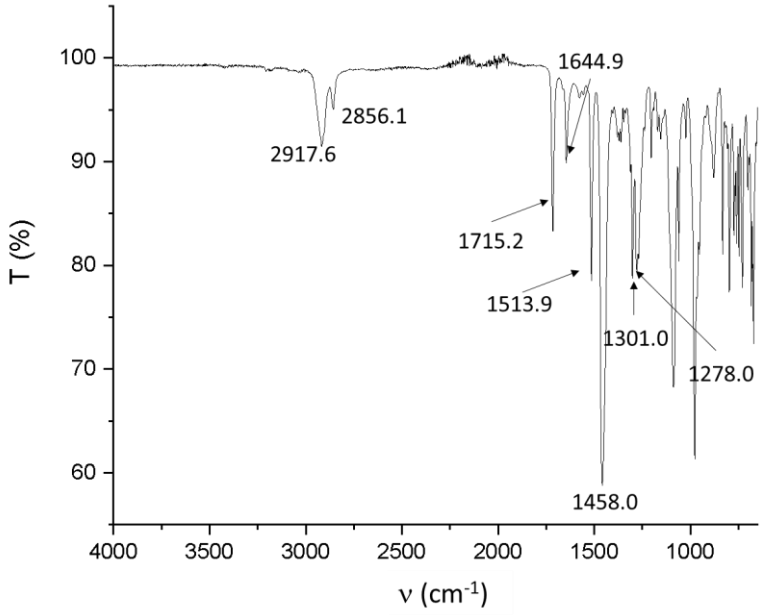
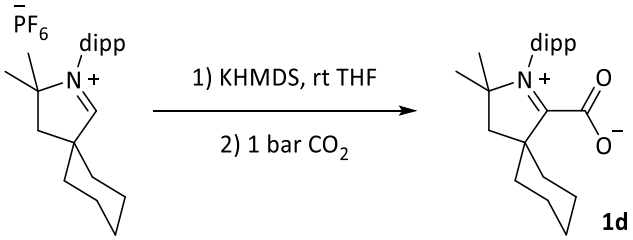


Figure S36. FTIR (solid state) of **2c** at 298 K.

Table S3. Theoretical and experimental IR frequencies for [**2c**]

Experimental	**Theoretical**	**Assignation**
1715.2	1735.7	C=O
1644.9	1651.1-1623.4	C=C (BCF)
1513.9	1515.2-1511.8	C-F
1458.0	1452.0-1405.4	C(sp^3)-H torsion
1301.0;1278.0	1300.8-1290.6	C-O

2.4 ^{Cy}CAAC-CO_2 (**1d**)



Compound **1d** was synthesized according to the reported procedure.[2]

^{1}H NMR (400 MHz, 298 K, CD_2Cl_2) δ 7.44 (t, $^3J_{HH}$ = 7.81 Hz, 2H, p-Ar), 7.29 (d, $^3J_{HH}$ = 7.6 , 2H, m-Ar), 2.74 (sept, $^3J_{HH}$ = 6.4 Hz, 2H, $CH(CH_3)_2$), 2.33 (s, 2H, $(CH_2)_{backbone}$), 2.16 (td, $^3J_{HH}$ = 13.8 Hz, $^4J_{HH}$ = 3.8 Hz, 2H, $(CH_2)_{Cy}$)), 1.86 (m, 4H, $(CH_2)_{Cy}$)) 1.73 (d, $^3J_{HH}$ = 11.0 Hz, 1H, $(CH_2)_{Cy}$)), 1.46 (s, 6H, $(CH_2)_{backbone}$), 1.43 (m, 1H, $(CH_2)_{Cy}$), 1.39 (m, 2H, $(CH_2)_{Cy}$) 1.32 (d, $^3J_{HH}$ = 6.5 Hz, 6H, $CH(CH_3)_2$), 1.29 ppm (d, $^3J_{HH}$= 6.7 Hz, 6H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100.6 MHz, 298 K, CD_2Cl_2) δ 158.6 (CO_2), 146.1 (o-Ar), 130.9 (p-Ar), 129.5 (ipso-Ar), 126.0 (m-Ar), 79.6 ($C_{backbone}$), 53.1 (C_{Cy}), 45.5 ($(CH_2)_{backbone}$), 36.2 ($(CH_2)_{Cy}$), 30.1 ($(CH(CH_3)_2)$), 29.6 ($(CH_3)_{backbone}$), 26.5 ($CH(CH_3)_2$), 25.0 ($CH(CH_3)_2$), 24.5 ($(CH_2)_{Cy}$) , 22.2 ($(CH_2)_{Cy}$). $E_{1/2}$ (vs. $Fc^{+/0}$) = -2.13 V. The carbenic carbon could not be assigned.

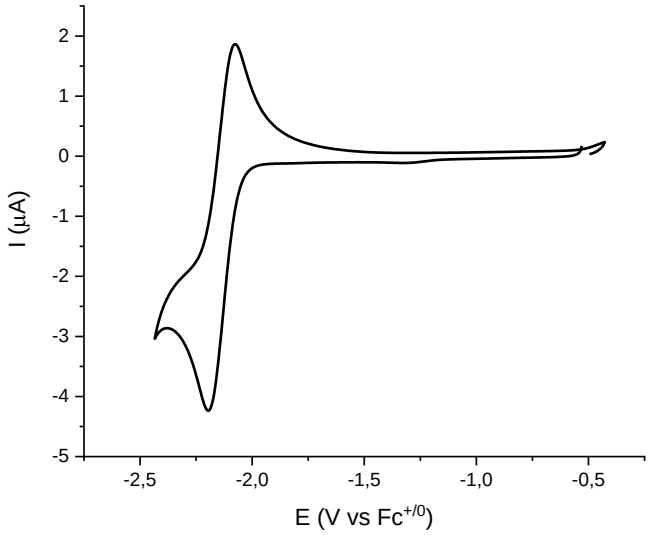
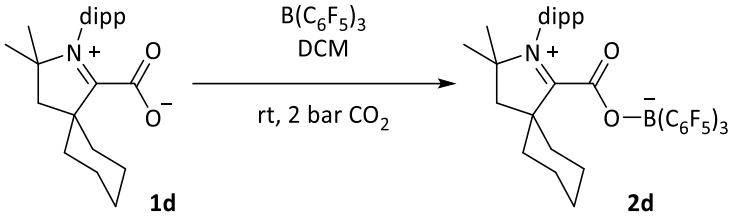


Figure S37. Cyclic voltammogram at reducing potentials of **1d** (5 mM) on GC microdisk in 0.1 M $[nBu_4N][PF_6]$/ CH_2Cl_2 media under Ar atmosphere. scan rate: 0.2 V/s.

2.5 ^{Cy}CAAC-CO_2-$B(C_6F_5)_3$ (2d)



1d **2d**

1d (200 mg, 0.54 mmol) and $B(C_6F_5)_3$ (277.08 mg, 0.54 mmol) were placed in a Fischer-Porter at room temperature. Under 1 bar CO_2, DCM (20 mL) was added and the solution was stirred up for 1h. The solvent was removed under reduced pressure yielding a white solid. The resulting white residue was purified via crystallisation from a saturated pentane-CH_2Cl_2 solution. After filtration and drying under vacuum, the expected product **2d** was isolated as a white powder in 37% yield (177 mg).

^{1}H NMR (400.2 MHz, 298 K, CD_2Cl_2) δ 7.53 (t, $^3J_{HH}$ = 7.7 Hz, 1H, p-Ar), 7.21 (d, $^3J_{HH}$ = 7.9 Hz, 2H, m-Ar) 2.48 (m, 6H, C*H*$(CH_3)_2$, $(CH_2)_{backbone}$, $(CH_2)_{Cy}$), 1.97 (m, 2H, $(CH_2)_{Cy}$), 1.86 (m, 3H, $(CH_2)_{Cy}$) 1.52 (s, 6H, $(CH_3)_{backbone}$), 1.47 (m, 3H, $(CH_2)_{Cy}$), 1.21 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3)_2$) 0.74 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3)_2$). ^{11}B NMR (128.4 MHz, 298 K, CD_2Cl_2) δ -2.9 (s). ^{13}C{^{1}H} NMR (100.6 MHz, 298 K, CD_2Cl_2) δ = 188.4 (N_2C), 158.0 (NHC-*C*O_2), 148.1 (d, $^1J_{CF}$ = 243.3 Hz, m-C_6F_5) 144.9 (o-Ar), 139.6 (d, $^1J_{CF}$ = 245.8 Hz, p-C_6F_5), 137.0 (d, $^1J_{CF}$ = 243.0 Hz, o-C_6F_5), 132.4 (p-Ar), 128.1 (ipso-Ar), 126.5 (m-Ar), 119.9 (BC-ipso), 83.5 ($C_{backbone}$), 55.7 (C_{Cy}), 46.1 ($(CH_2)_{backbone}$), 34.0 ($(CH_2)_{Cy}$), 30.1 (*C*H$(CH_3)_2$), 30.0 ($(CH_3)_{backbone}$), 25.0 (CH(*C*H$_3)_2$), 24.4 (CH(*C*H$_3)_2$), 24.4 ($(CH_2)_{Cy}$), 22.0 ($(CH_2)_{Cy}$). ^{19}F NMR (376.5 MHz, 298 K, CD_2Cl_2): δ −133.0 (d, $^3J_{FF}$ = 24.0 Hz, 6F, o-C_6F_5), −161.1 (t, $^3J_{FF}$ = 20.3 Hz, 3F, p-C_6F_5), −166.1 (td, $^3J_{FF}$ = 24.2 Hz, 6F, m-C_6F_5). HRMS (ESI+) m/z: Calcd for $C_{42}H_{35}BF_{15}N_2O_2$ [M+H$^+$]: 882.2594 found 882.2610. Anal (%): Calcd for $C_{42}H_{34}BF_{15}N_2O_2.CH_2Cl_2$: C, 53.44; H, 3.86; N, 1.47. Found: C, 54.32; H, 3.64; N, 1.47. FTIR (solid state): $\nu_{C=O}$ = 1709 cm^{-1}. $E_{1/2,exp}^{red}$ (vs. $Fc^{+/0}$) = -1.34 V.

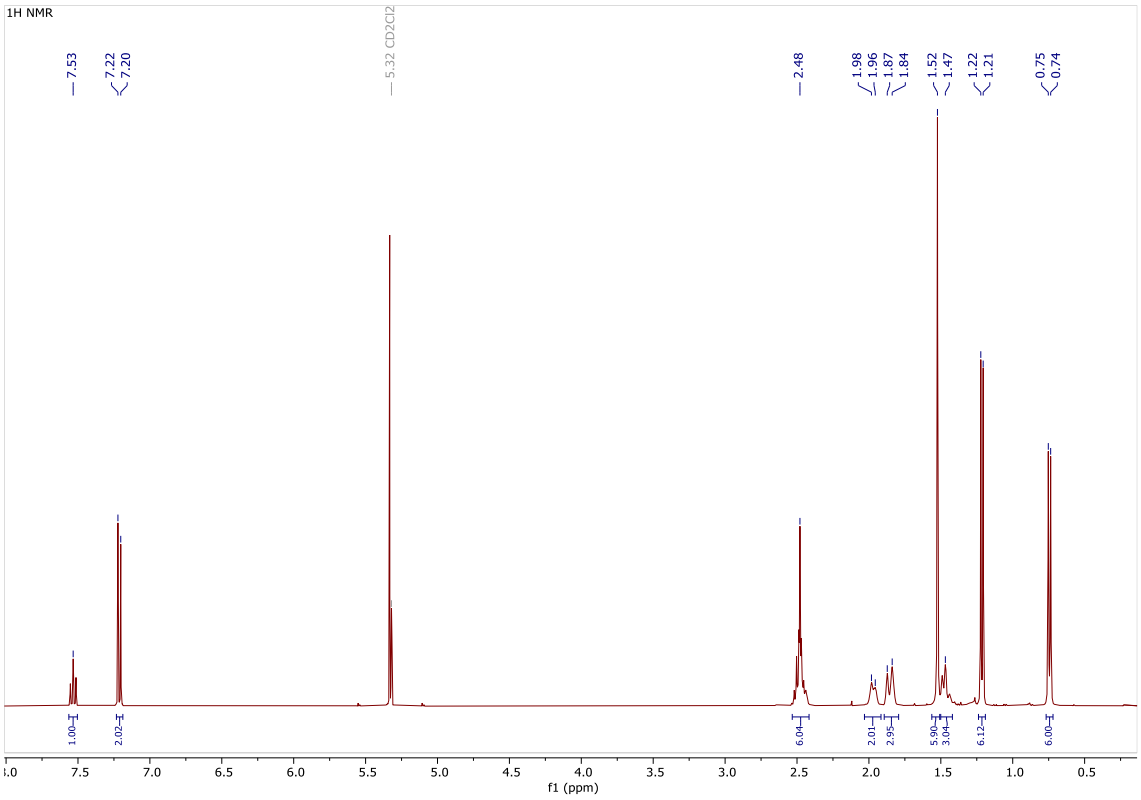


Figure S38. ^{1}H NMR spectrum of **2d** in CD_2Cl_2 at 298 K.

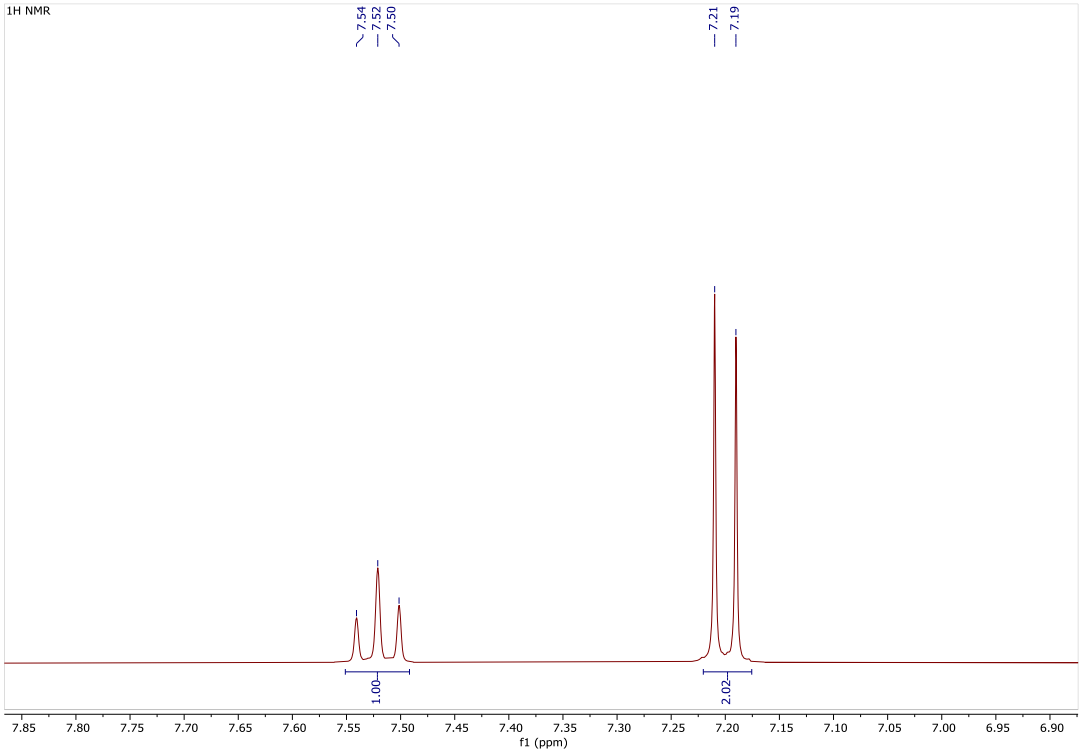


Figure S39. Zoom ^{1}H NMR spectrum of **2d** in CD_2Cl_2 at 298 K.

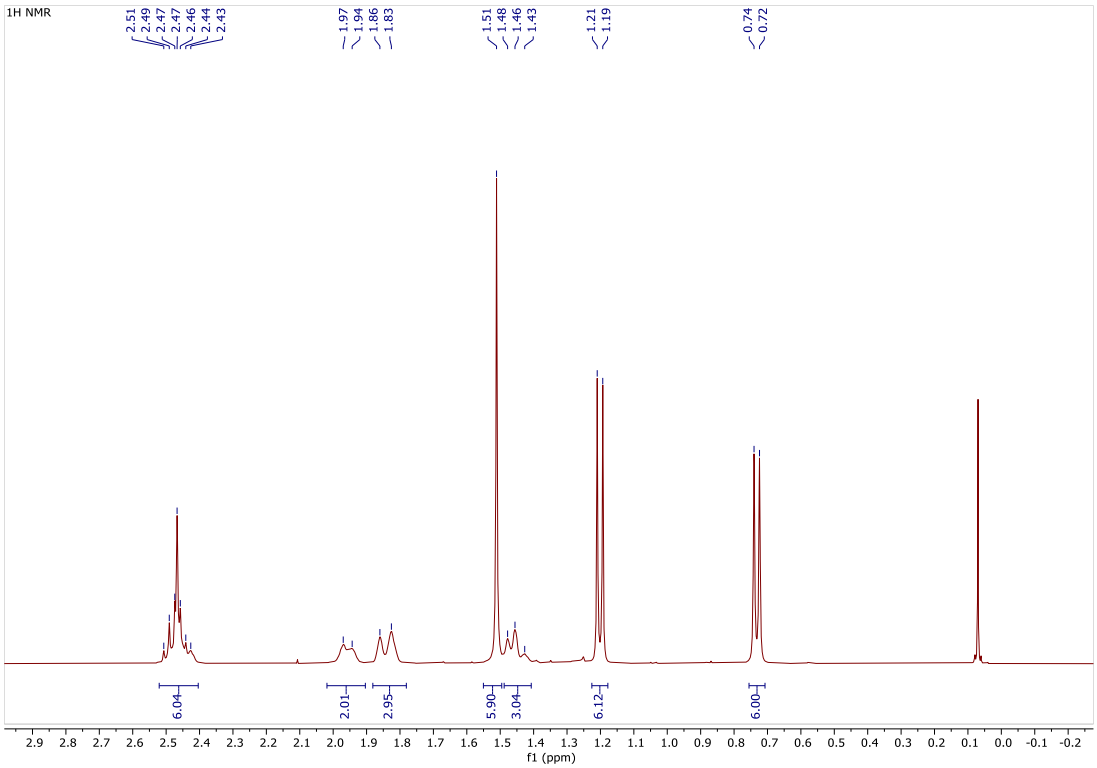


Figure S40. Zoom ^{1}H NMR spectrum of **2d** in CD_2Cl_2 at 298 K.

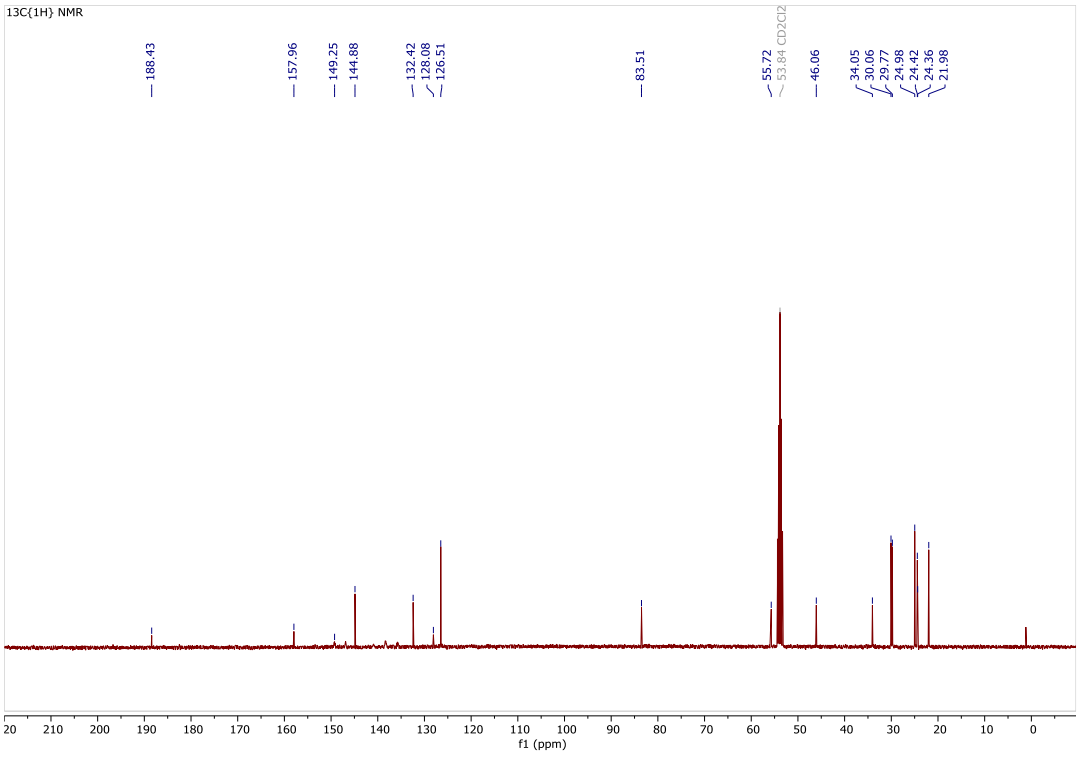


Figure S41. ^{13}C{^{1}H} NMR spectrum of **2d** in CD_2Cl_2 at 298 K.

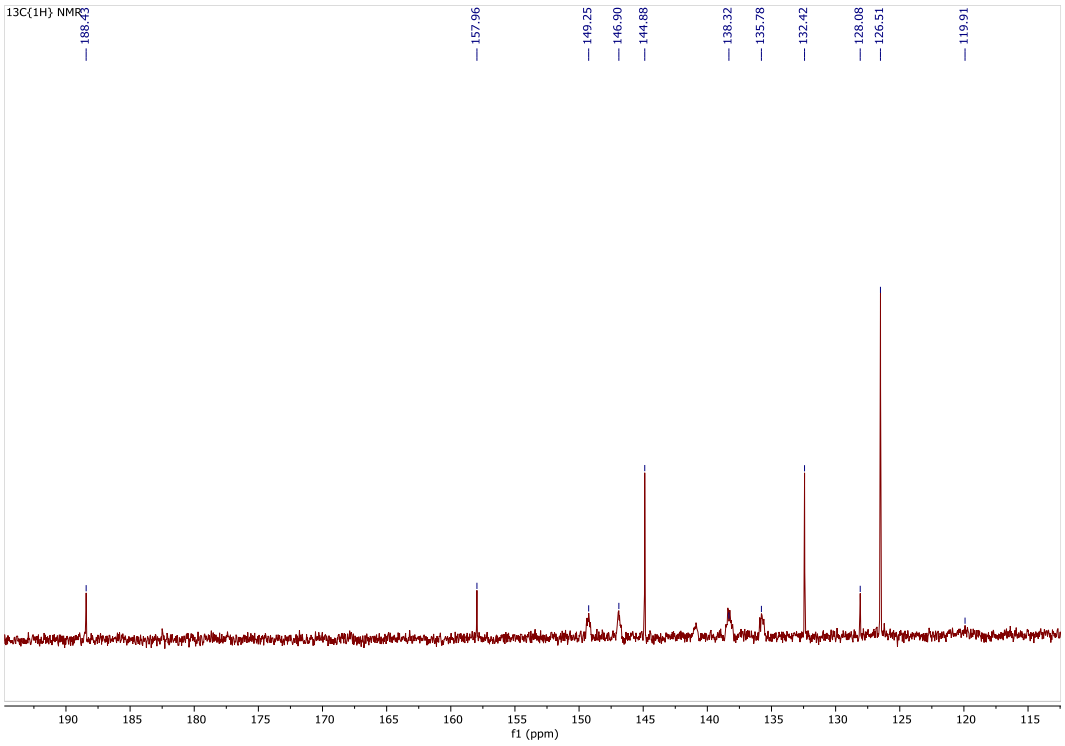


Figure S42. Zoom $^{13}C\{^{1}H\}$ NMR spectrum of **2d** in CD_2Cl_2 at 298 K between 190 and 115 ppm.

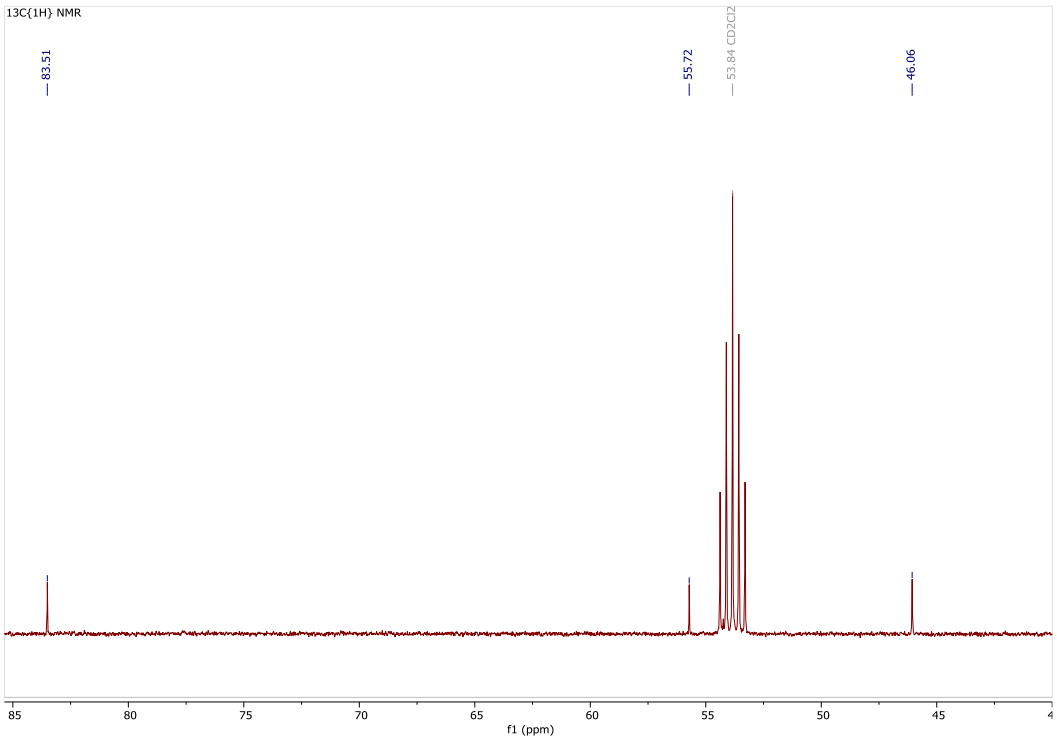


Figure S43. Zoom $^{13}C\{^{1}H\}$ NMR spectrum of **2d** in CD_2Cl_2 at 298 K between 85 and 45 ppm.

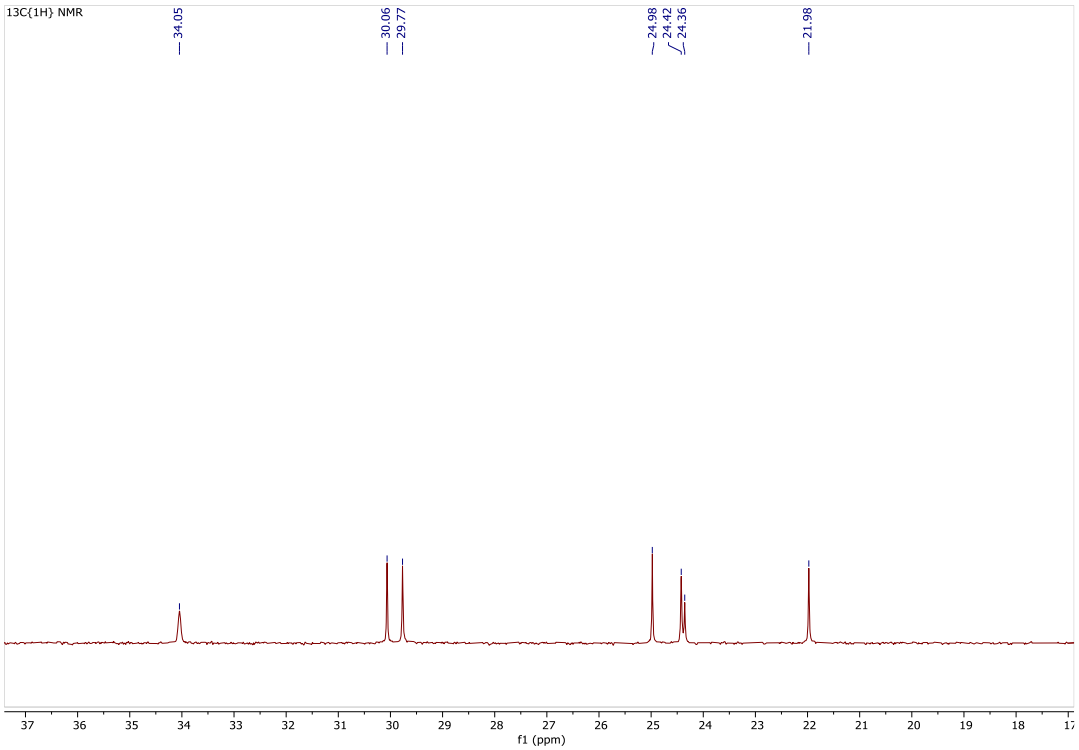


Figure S44. Zoom $^{13}C\{^{1}H\}$ NMR spectrum of **2d** in CD_2Cl_2 at 298 K between 36 and 18 ppm.

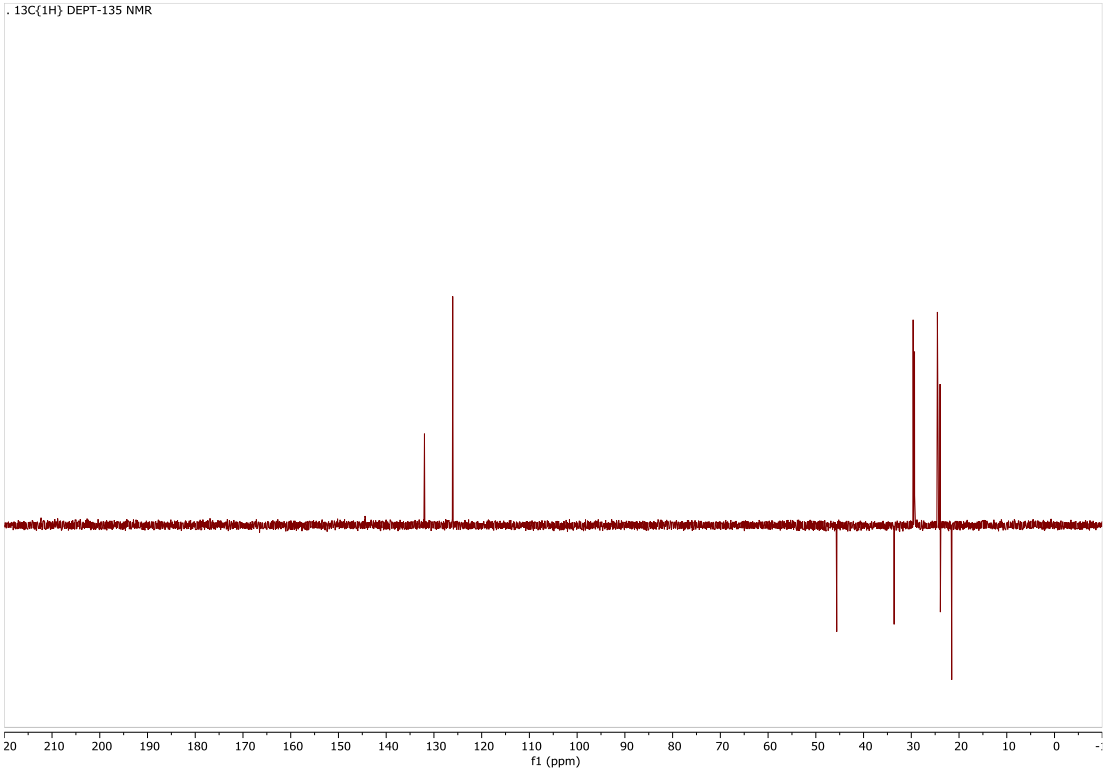


Figure S45. $^{13}C\{^{1}H\}$ DEPT-135 NMR spectrum of **2d** in CD_2Cl_2 at 298 K.

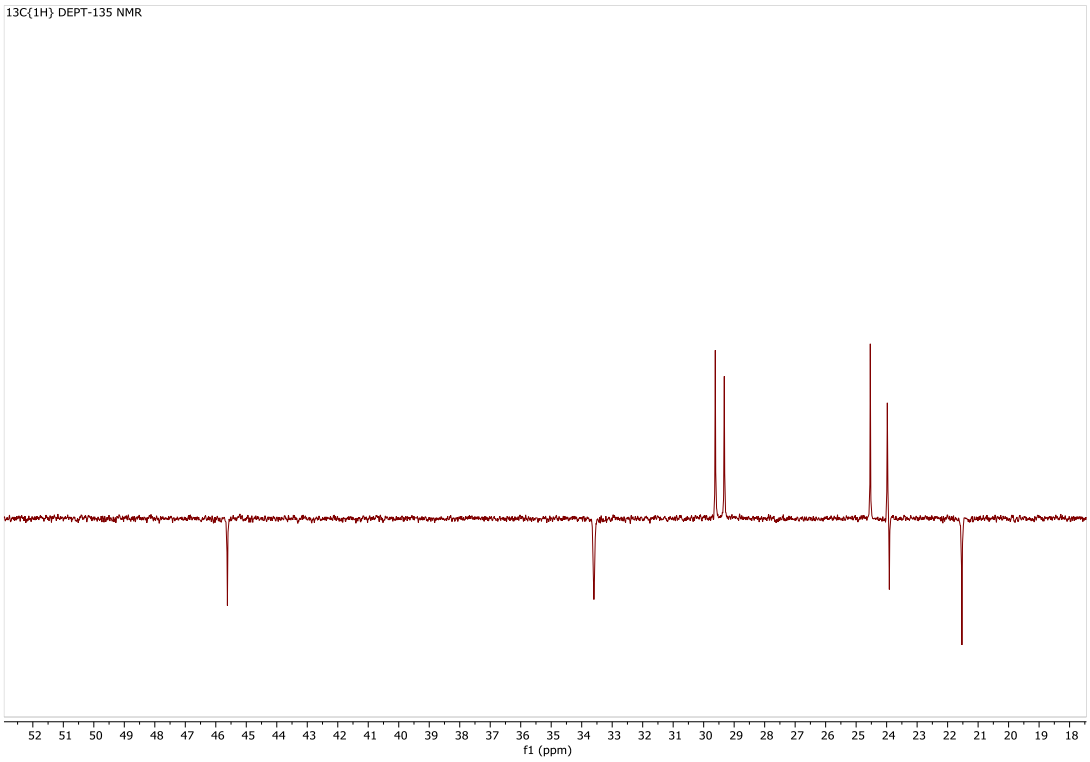


Figure S46. Zoom $^{13}C\{^{1}H\}$ DEPT-135 NMR spectrum of **2d** in CD_2Cl_2 at 298 K between 52 and 19 ppm.

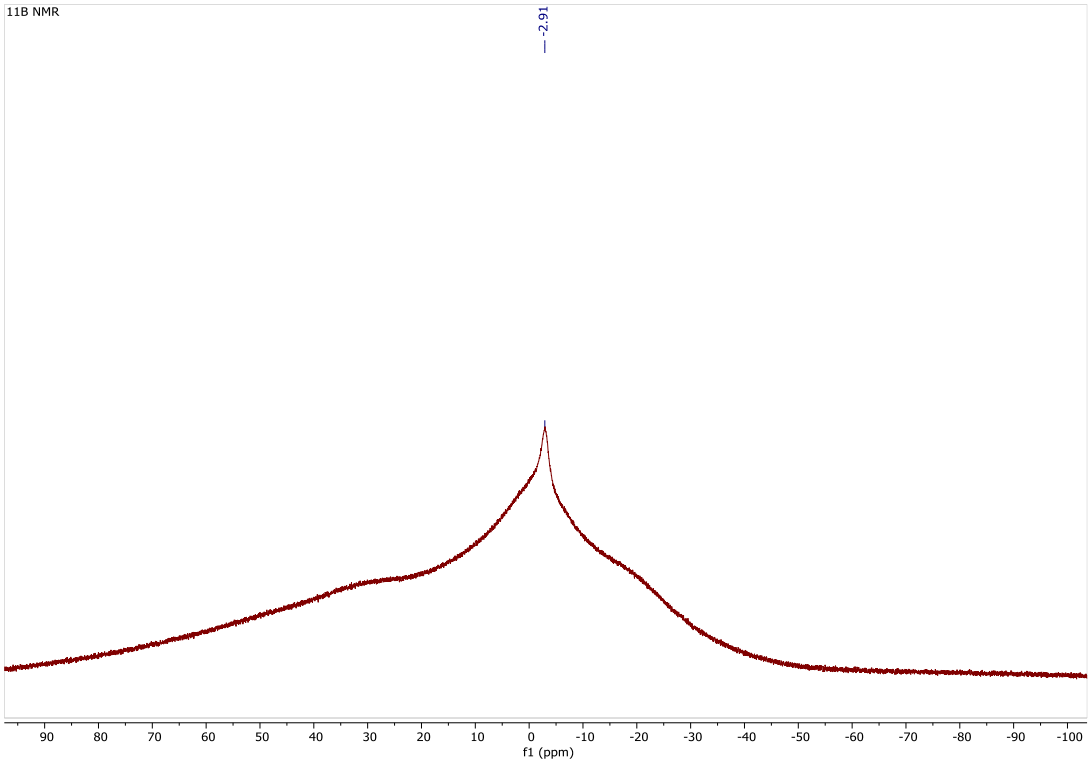


Figure S47. ^{11}B NMR spectrum of **2d** in CD_2Cl_2 at 298 K.

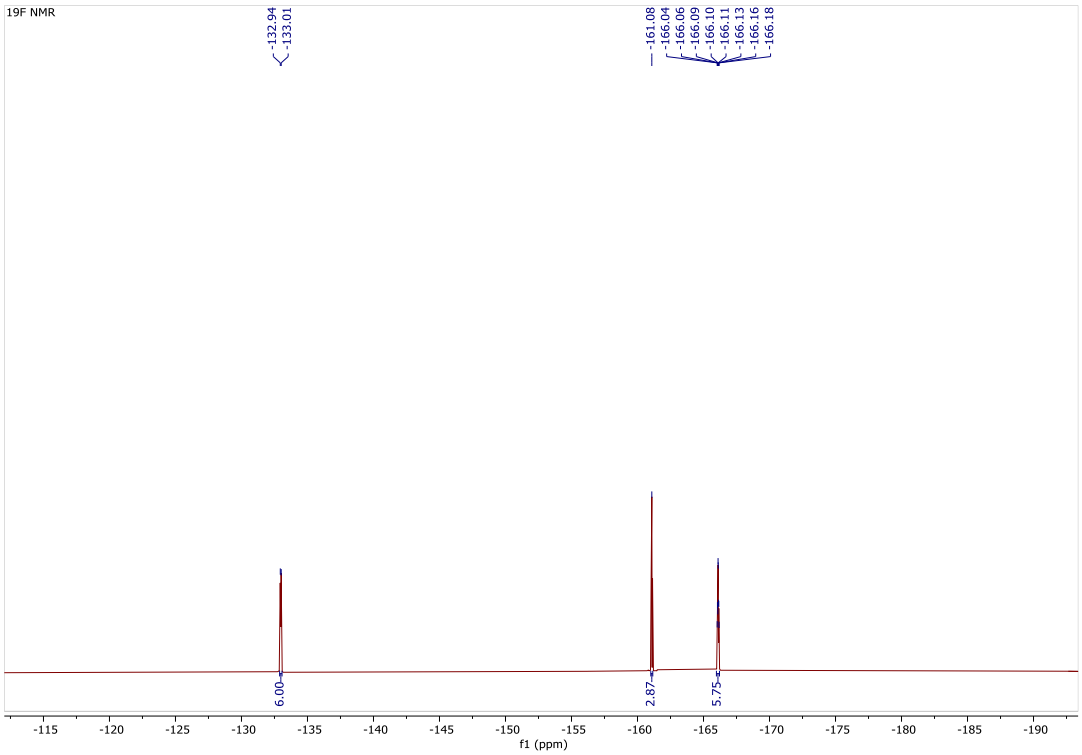


Figure S48. ^{19}F NMR spectrum of **2d** in CD_2Cl_2 at 298 K.

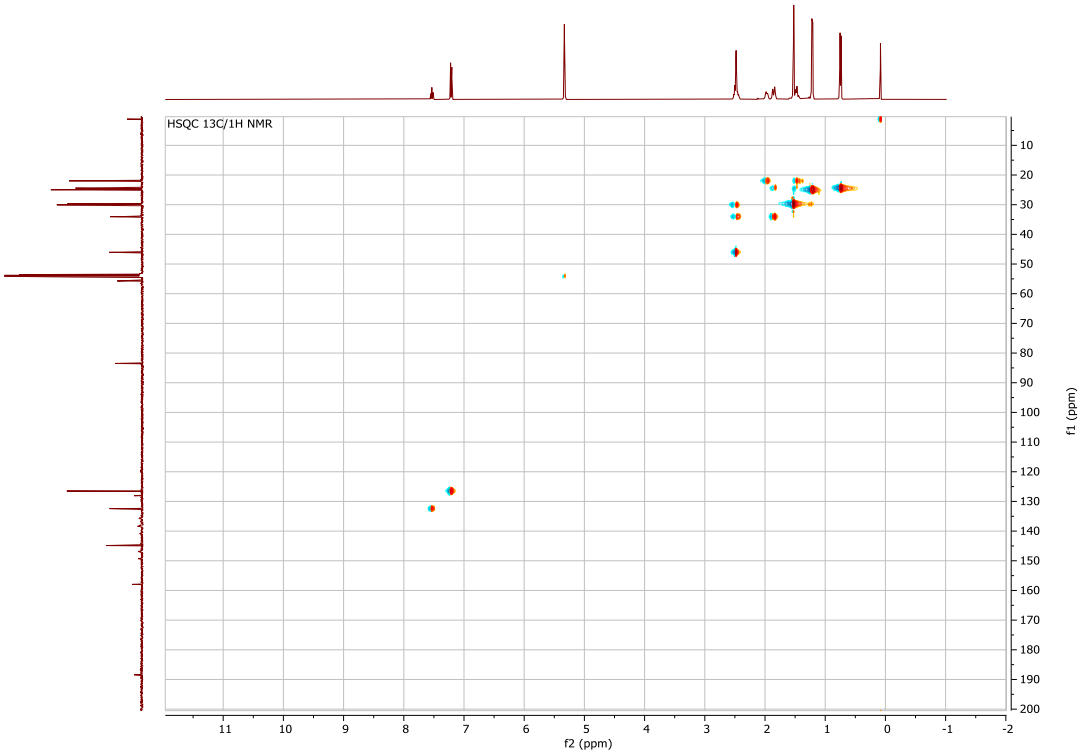


Figure S49. HSQC $^{13}C/^{1}H$ NMR spectrum of **2d** in CD_2Cl_2 at 298 K.

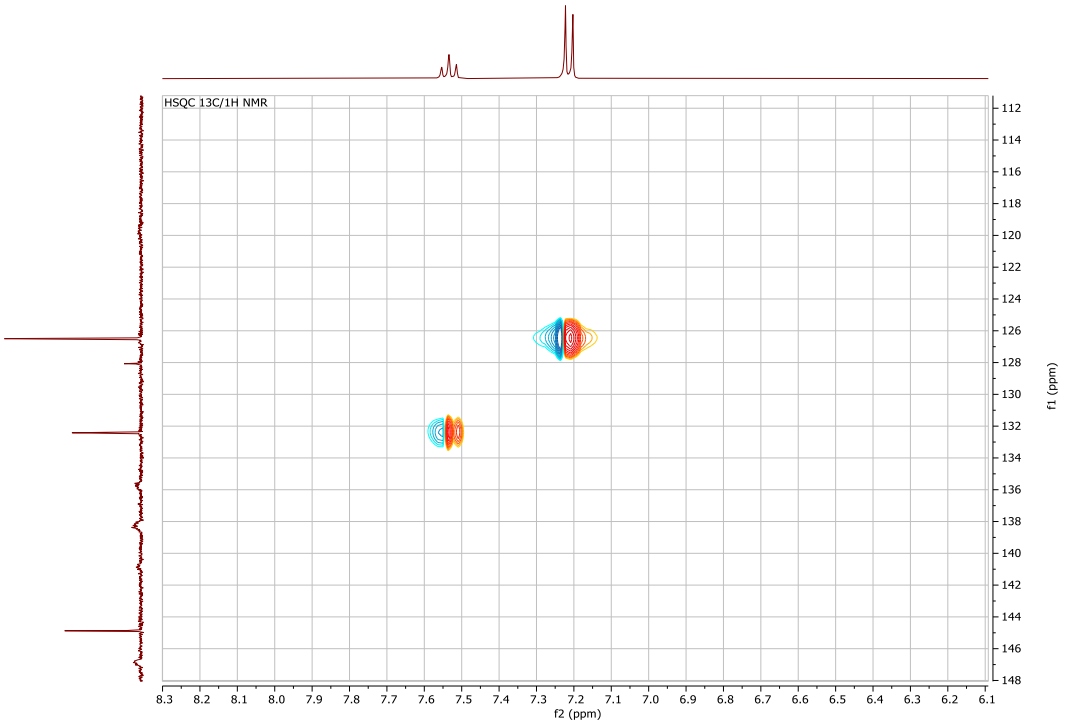


Figure S50. Zoom HSQC $^{13}C/^{1}H$ NMR spectrum of **2d** in CD_2Cl_2 at 298 K.

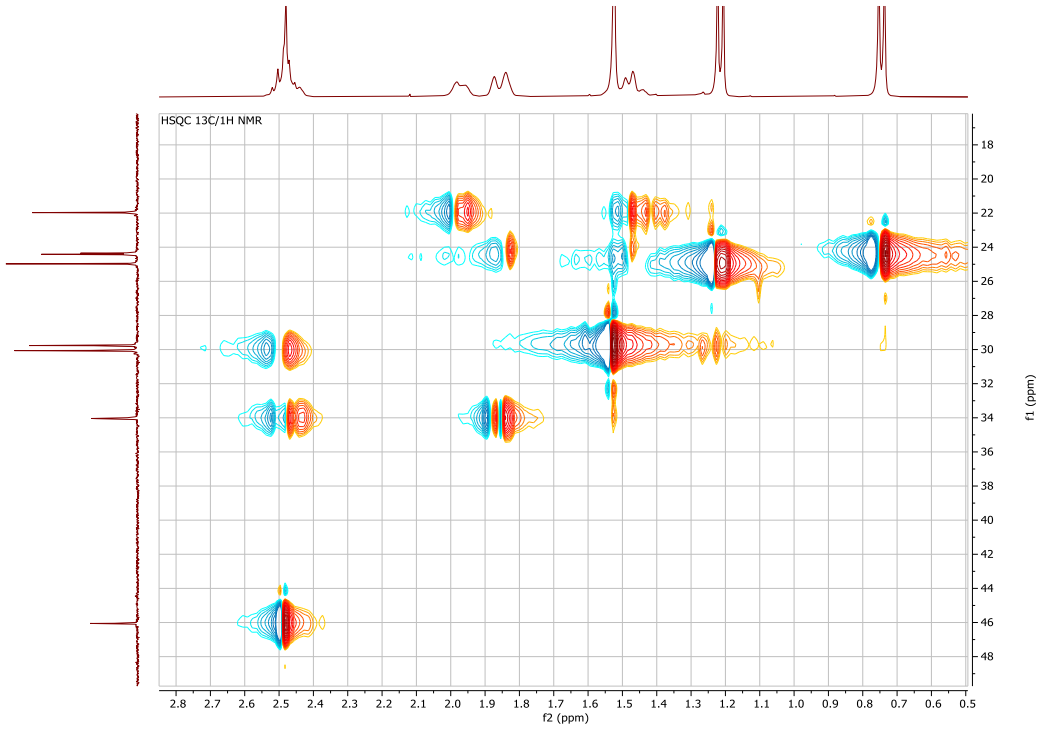


Figure S51. Zoom HSQC $^{13}C/^{1}H$ NMR spectrum of **2d** in CD_2Cl_2 at 298 K.

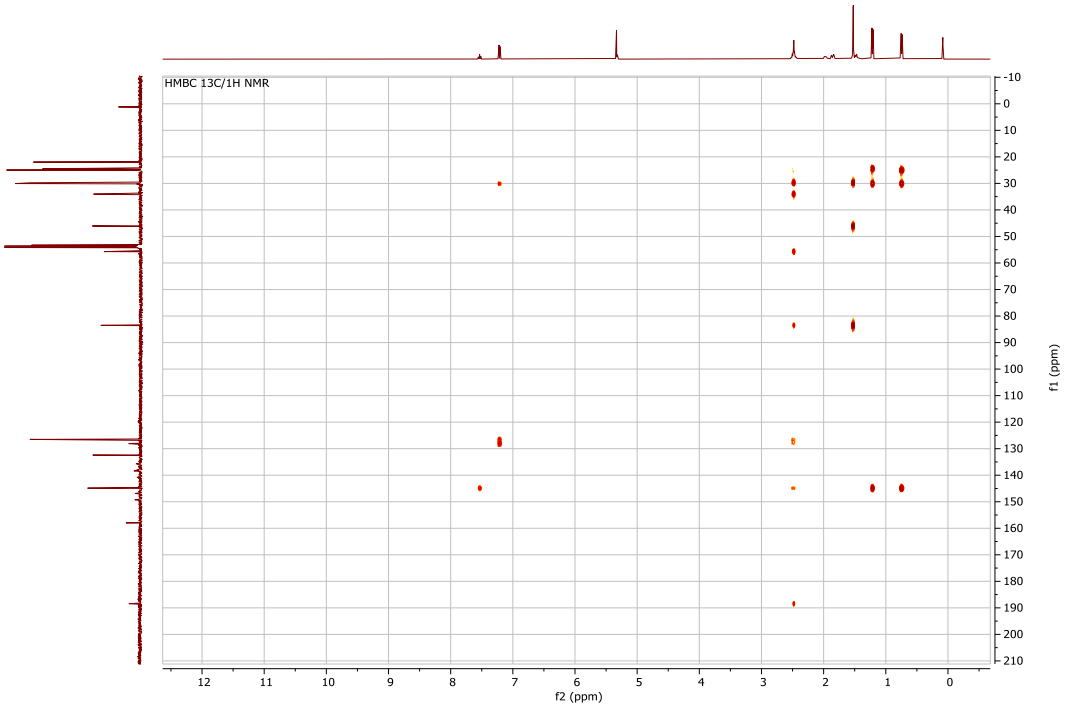


Figure S52. HMBC $^{13}C/^{1}H$ NMR spectrum of **2d** in CD_2Cl_2 at 298 K.

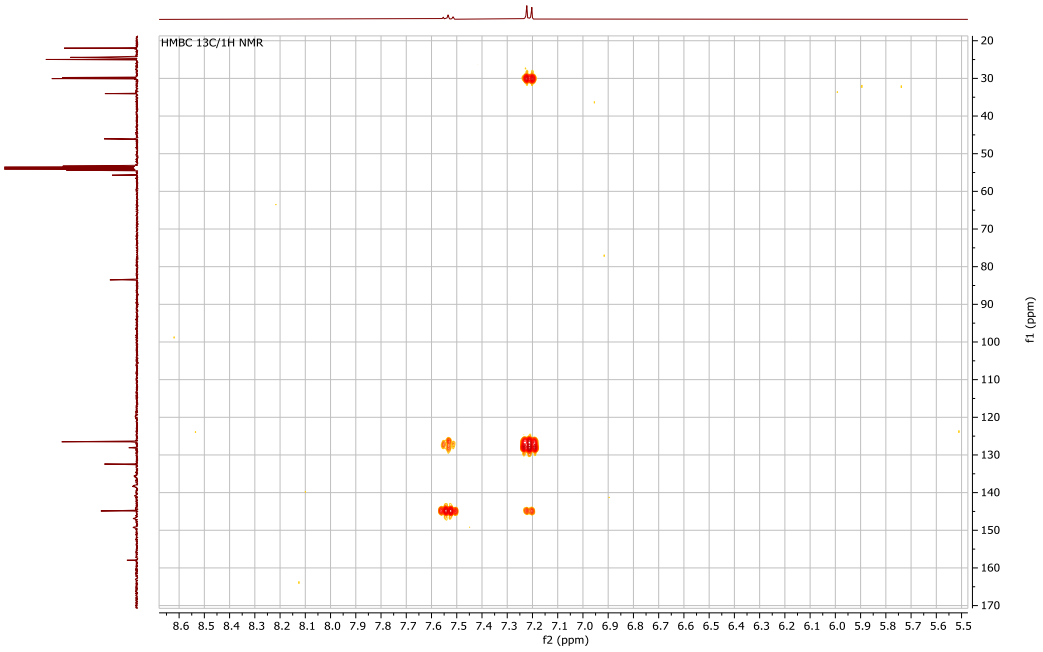


Figure S53. Zoom HMBC $^{13}C/^{1}H$ NMR spectrum of **2d** in CD_2Cl_2 at 298 K.

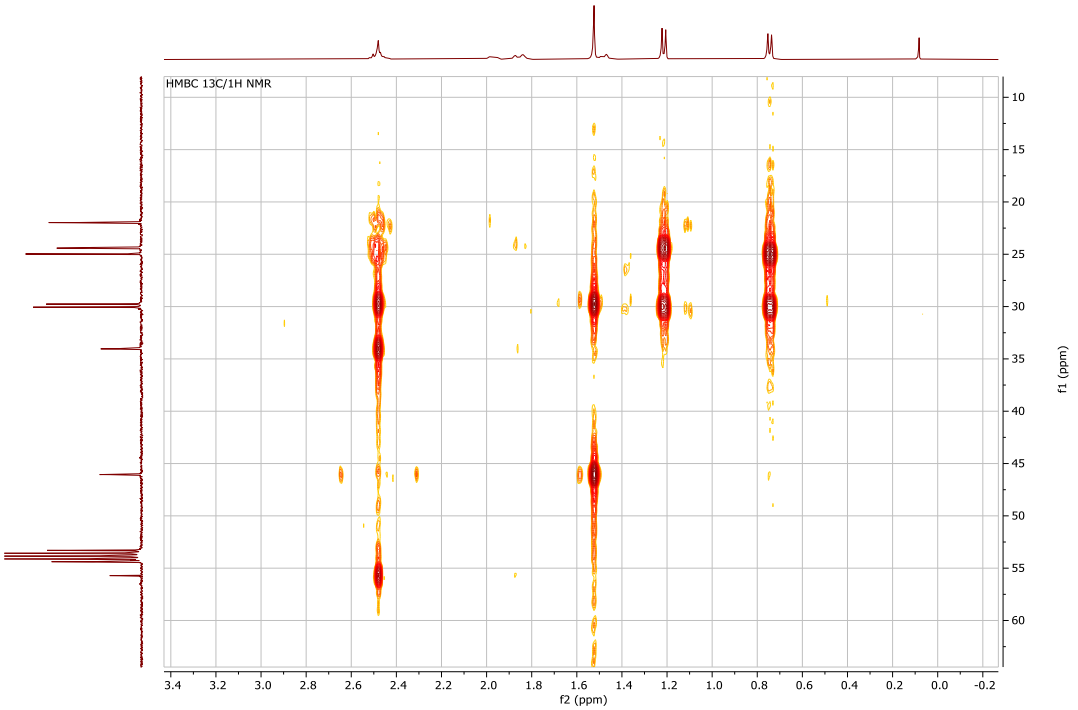


Figure S54. Zoom HMBC $^{13}C/^{1}H$ NMR spectrum of **2d** in CD_2Cl_2 at 298 K.

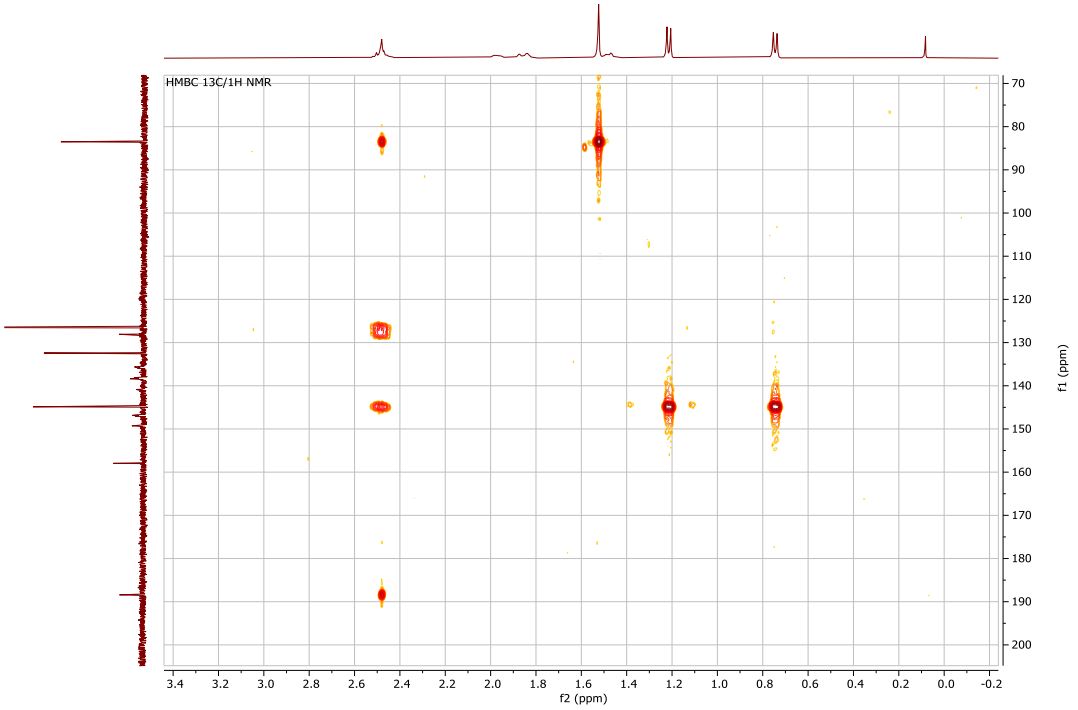


Figure S55. Zoom HMBC $^{13}C/^{1}H$ NMR spectrum of **2d** in CD_2Cl_2 at 298 K.

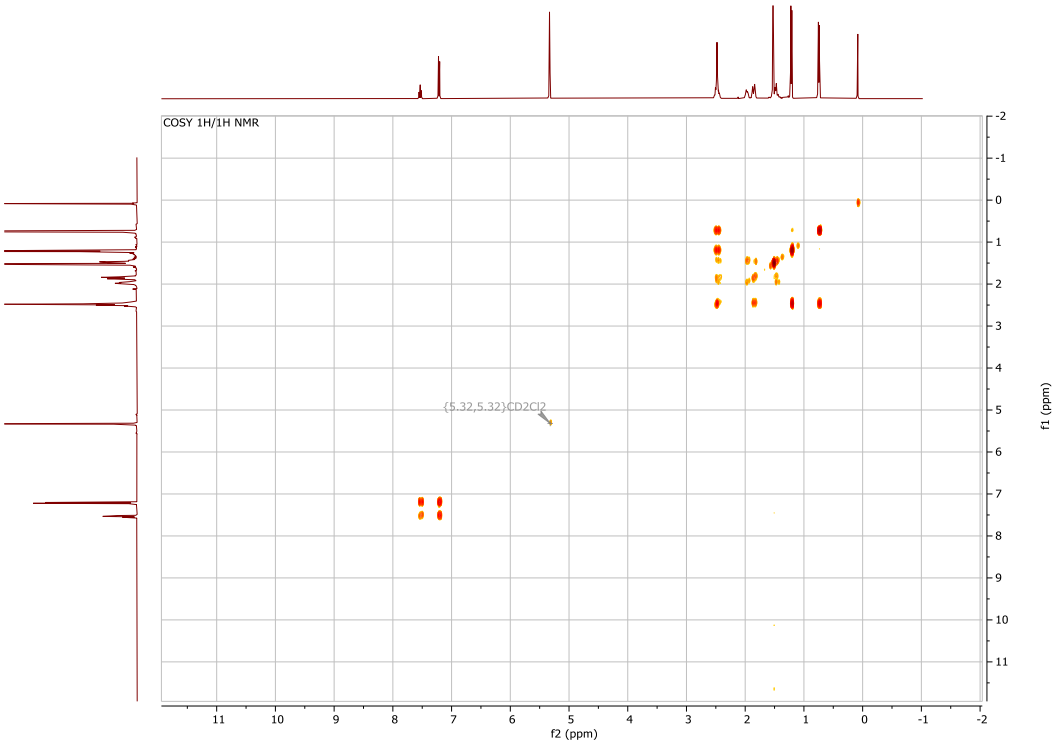


Figure S56. COSY $^{1}H/^{1}H$ NMR spectrum of **2d** in CD_2Cl_2 at 298 K.

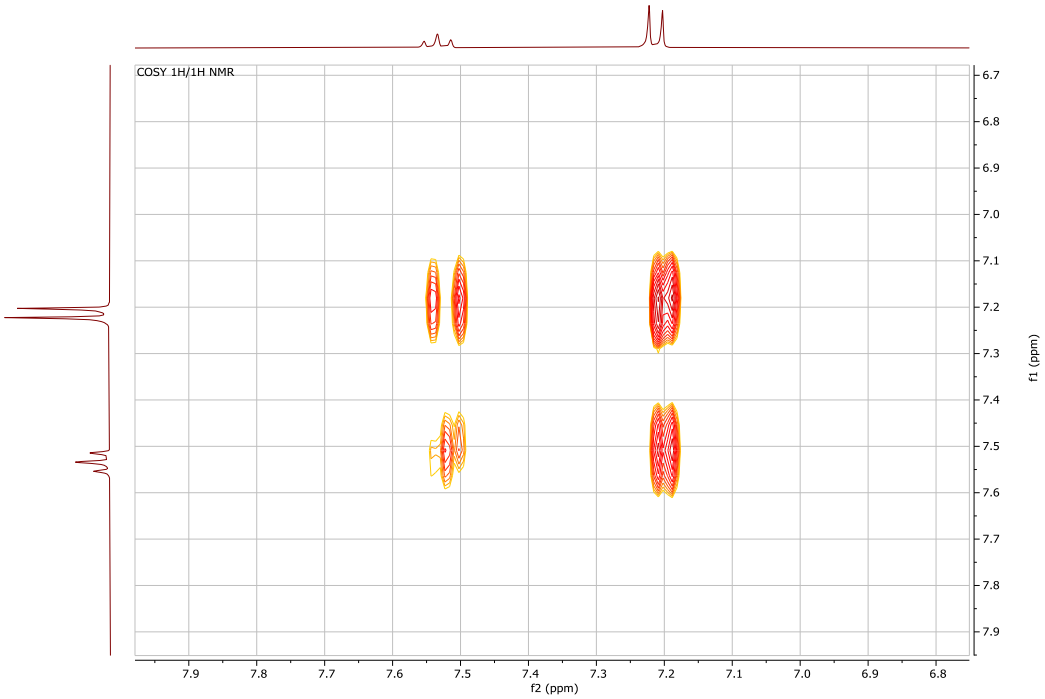


Figure S57. Zoom COSY $^{1}H/^{1}H$ NMR spectrum of **2d** in CD_2Cl_2 at 298 K.

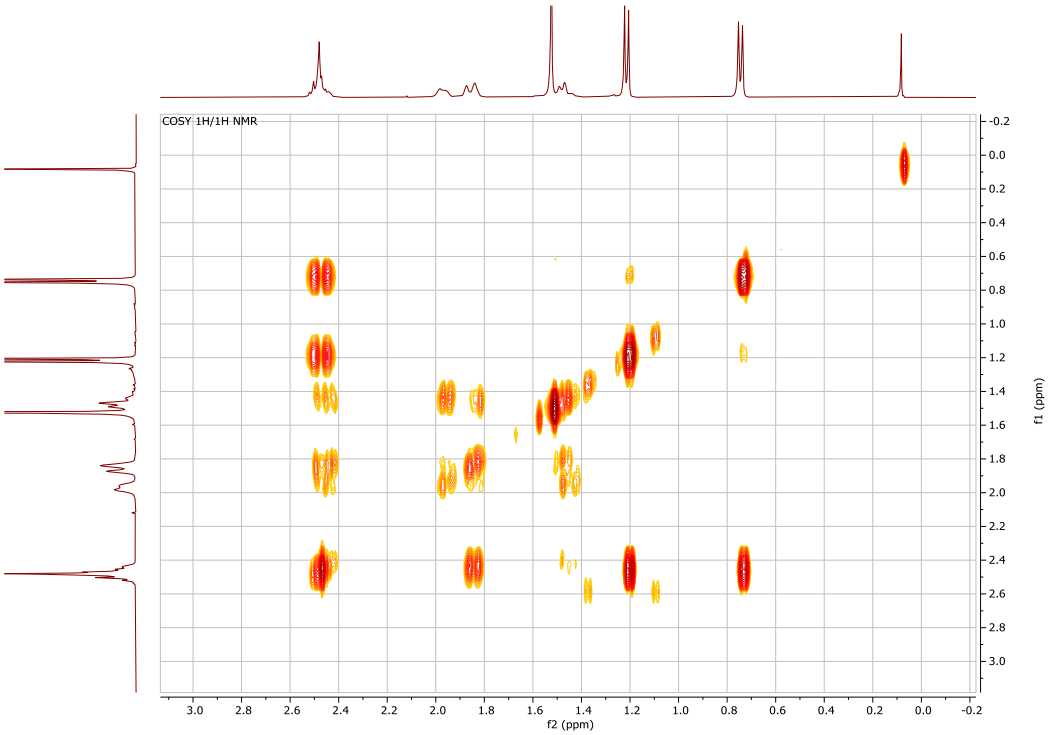


Figure S58. Zoom COSY $^{1}H/^{1}H$ NMR spectrum of **2d** in CD_2Cl_2 at 298 K.

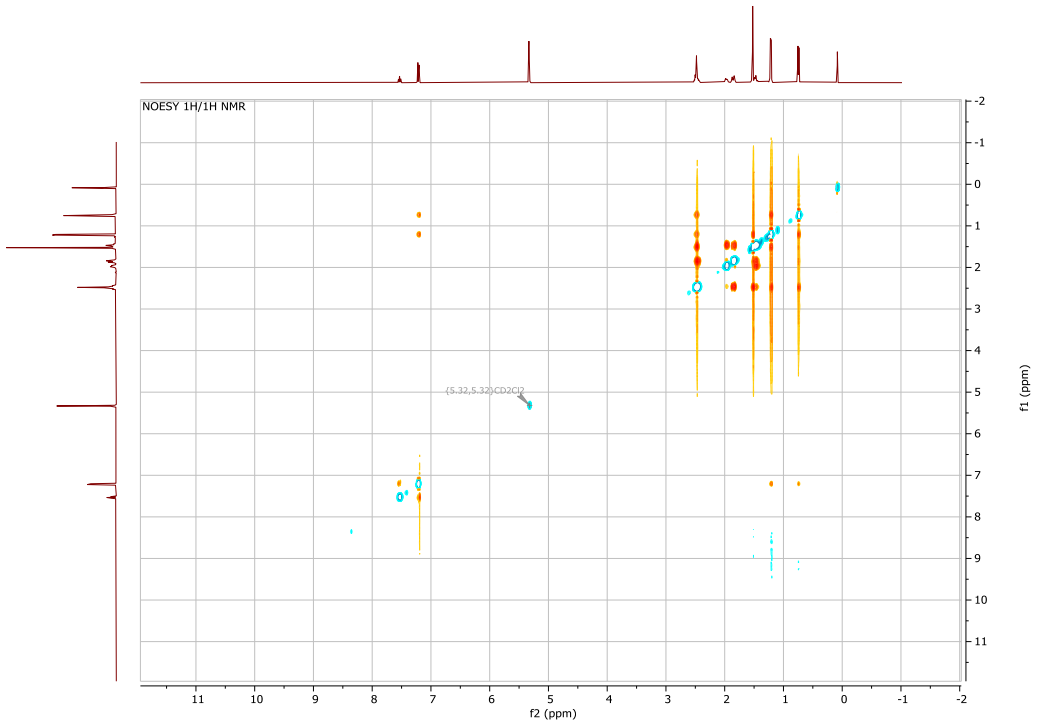


Figure S59. NOESY $^{1}H/^{1}H$ NMR spectrum of **2d** in CD_2Cl_2 at 298 K.

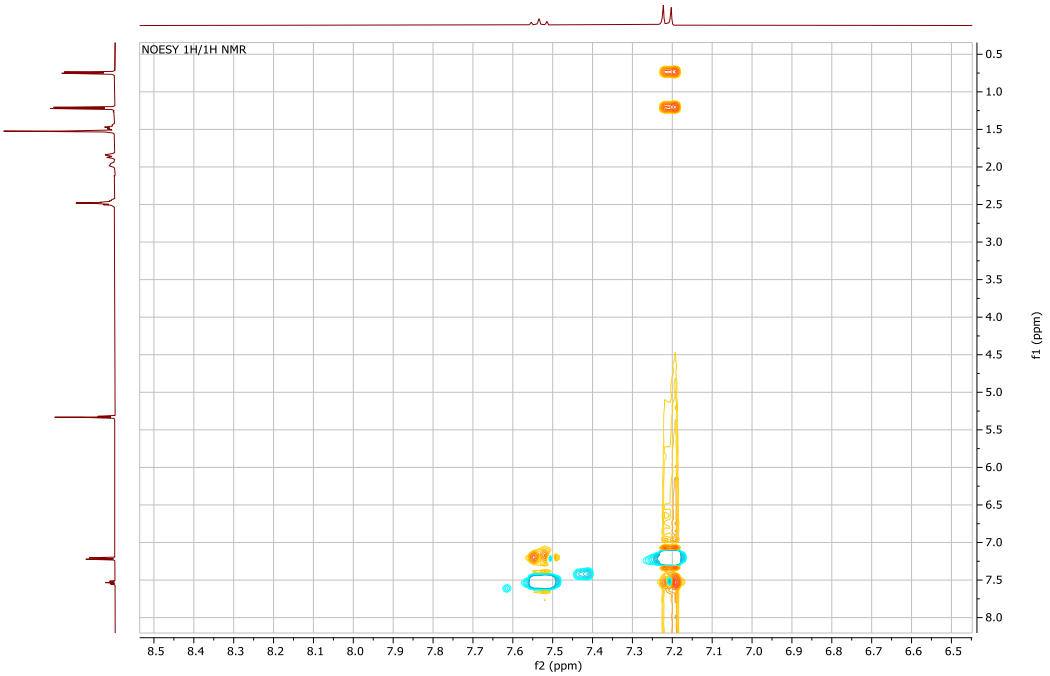


Figure S60. Zoom NOESY $^{1}H/^{1}H$ NMR spectrum of **2d** in CD_2Cl_2 at 298 K.

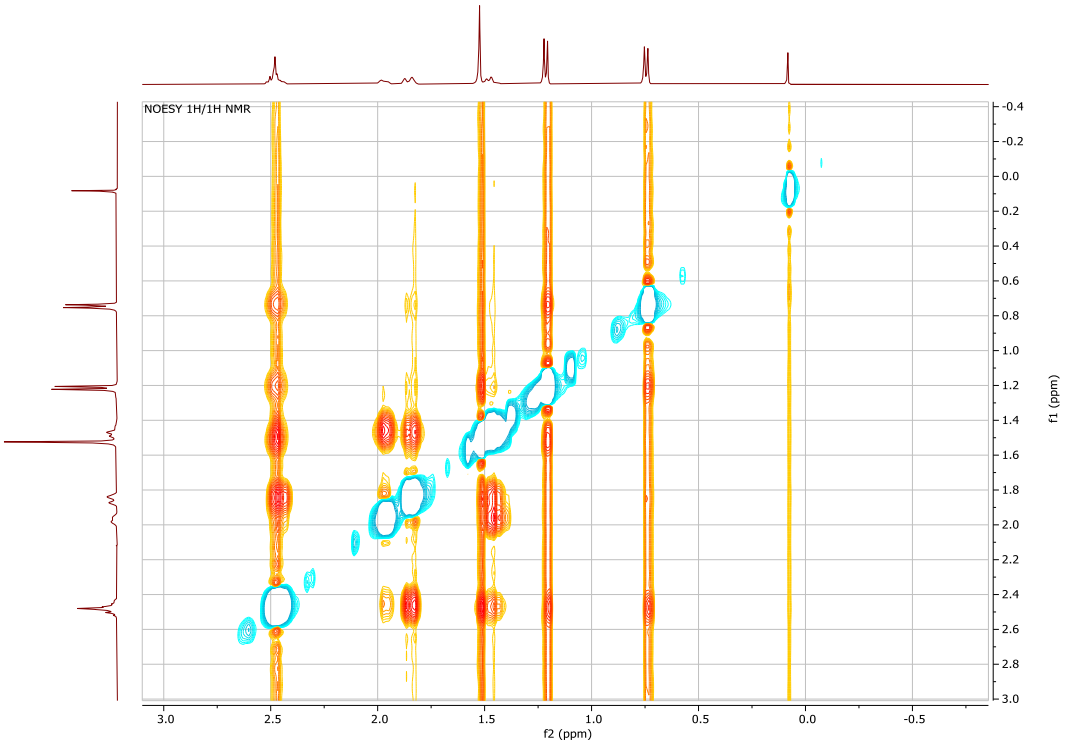


Figure S61. Zoom NOESY $^{1}H/^{1}H$ NMR spectrum of **2d** in CD_2Cl_2 at 298 K.

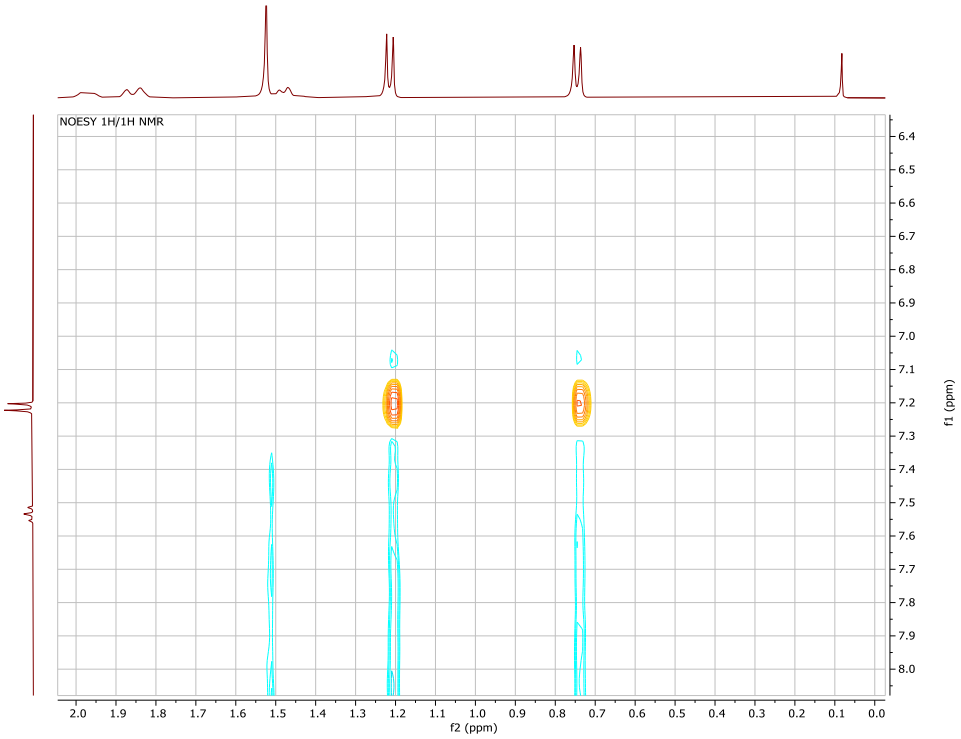


Figure S62. Zoom NOESY $^{1}H/^{1}H$ NMR spectrum of **2d** in CD_2Cl_2 at 298 K.

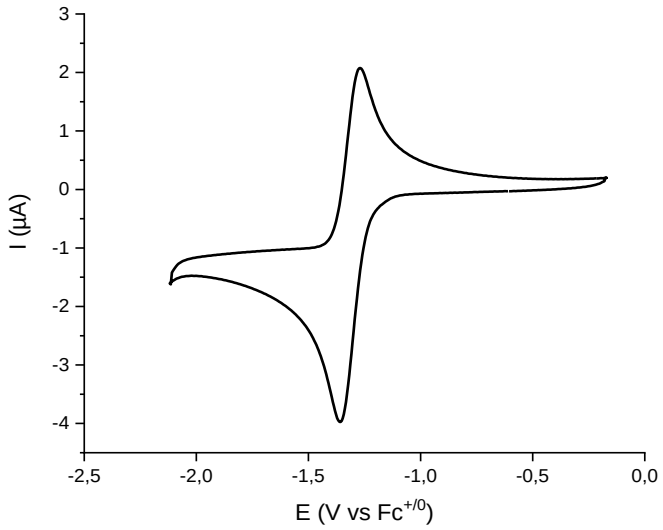


Figure S63. Cyclic voltammogram at reducing potentials of **2d** (5 mM) on GC microdisk in 0.1 M $[nBu_4N][PF_6]$/ CH_2Cl_2 media under Ar atmosphere. scan rate: 0.2 V/s.

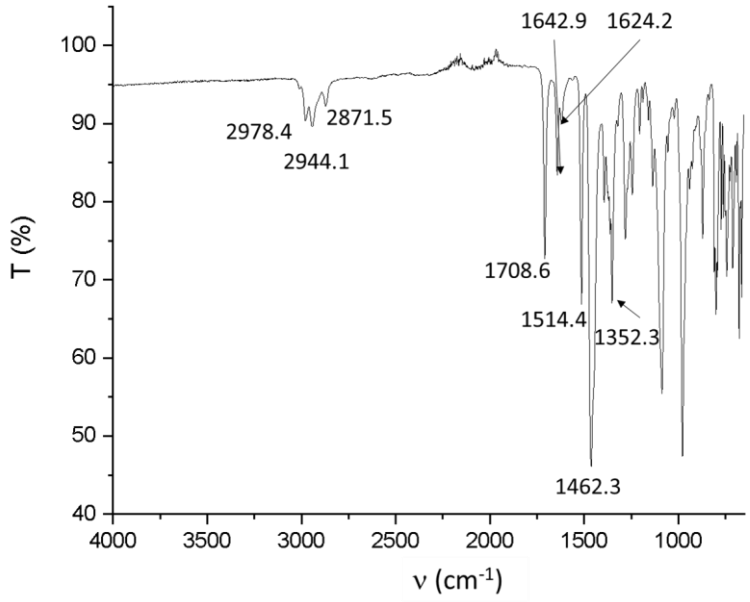
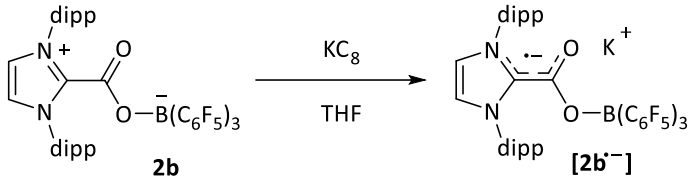


Figure S64. FTIR (solid state) of **2d** at 298 K.

Table S4. Theoretical and experimental IR frequencies for [**2d**]

Experimental	**Theoretical**	**Assignation**
1708.6	1733.5	C=O
1642.9	1656.9	C=N
1624.2	1649.4-1624.5	C=C(BCF)
1514.4	1514.5-1454.2	C-F
1462.3	1451.6-1407.6	$C(sp^3)$-H
1352.3	1364.5	C-O

2.6 KIPr-CO_2-$B(C_6F_5)_3$ ([**2b**$^{\bullet-}$])



Compound **2b** (24 mg, 0.03 mmol) and KC_8 (3.2 mg, 0.03 mmol) were placed in a 4 mL vial inside an argon glovebox. Then, 1 mL of THF was added to the vial and stirred for one minute. The resulting dark solution was transferred into another vial and the EPR and IR were performed. EPR (CW, X-band) g = 2.0026 (a_N = 4.6 G). IR (liquid state): $\nu_{C=O}$ = 1602 cm^{-1}.

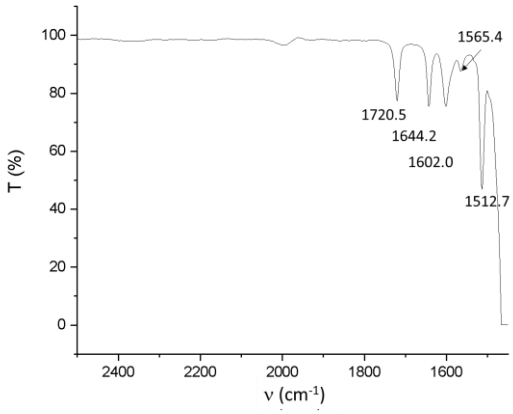


Figure S65. IR (liquid state) of [**2b**$^{\bullet-}$] at 298 K.

Table S5. Theoretical and experimental IR frequencies for [**2b**$^{\bullet-}$]

Experimental	**Theoretical with K^+**	**Theoretical without K^+**	**Assignation**
1720.5	-	-	C=O of **2b**
1644.2	1645.1-1640.9	1644.4-1623.2	C=C(BCF)
1602.0	1633.8	1617.4	C=O
1565.4	1590.3-1576.8 ;1552.9	1589.9-1579.8 ;1559.3	C=C(backbone) ;C=C(dipp)
1512.7	1494.8-1482.8	1512.2-1459.6	C-F

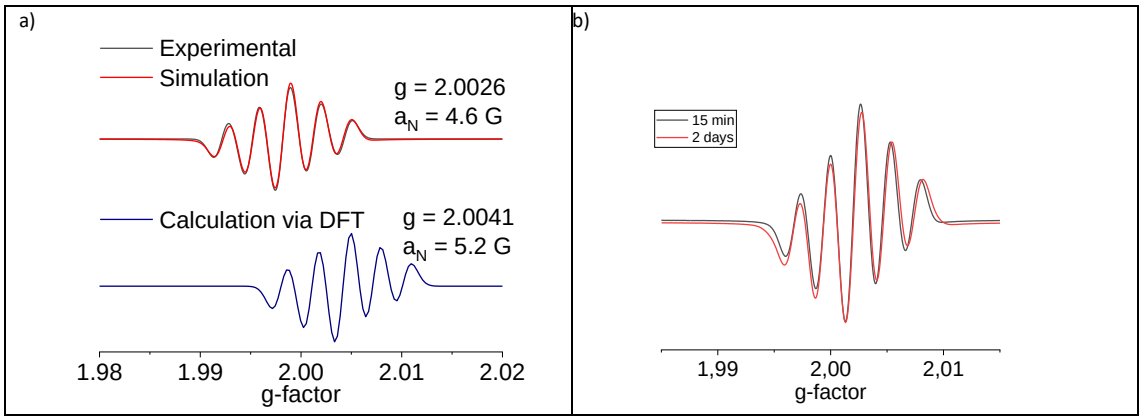
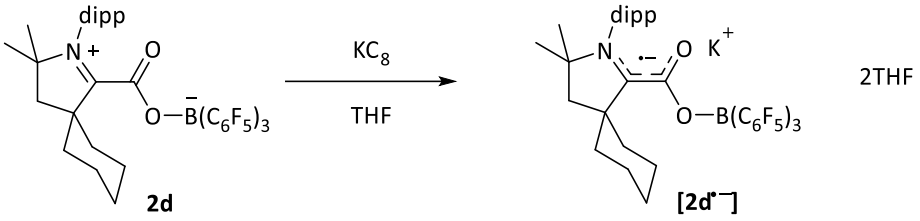


Figure S66. a) Continuous wave X-band EPR spectrum taken on a 3.0 mM [**2b**$^{\bullet-}$] THF solution at room temperature (black), simulation (red) and calculated by DFT (navy), b) experimental spectrum after 15 min from a) in black, superimposed with the spectrum in red taken 2 days later from the same batch kept at room temperature in an argon glove box and analysed in the same conditions.

2.7 K^{Cy}CAAC-CO_2-$B(C_6F_5)_3$.2THF ([**2d**$^{\bullet-}$])



Compound **2d** (50 mg, 0.06 mmol) and KC_8 (7.7 mg, 0.06 mmol) were placed in a 4 mL vial inside an argon glovebox. Then, 0.5 mL of THF were added to the vial and stirred for one minute. The resulting dark yellow solution was transferred into another vial. To the precedent solution, 2 mL of pentane were added forming a double-layered solution, which was placed at -36°C. The expected product [**2d**$^{\bullet-}$] was isolated as orange crystals in 22 % yield (11 mg). EPR (CW, X-band) g = 2.0026 (a_N = 6.1 G). Anal (%): Calcd for $C_{38}H_{32}BF_{15}KN_2O_4$: C, 57.04; H, 5.25; N, 1.28. Found: C, 56.80; H, 4.82; N, 1.47. FTIR (solid state): $\nu_{C=O}$ = 1596 cm^{-1}.

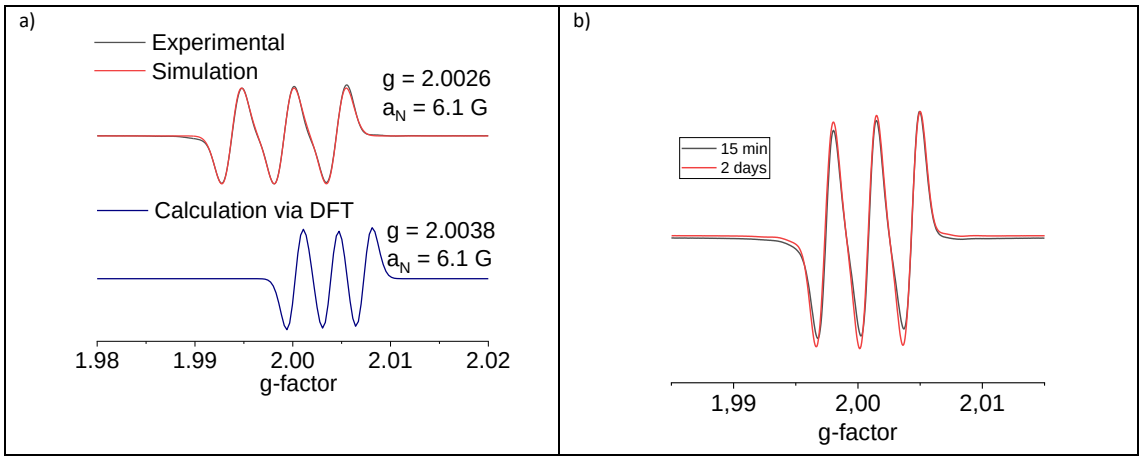


Figure S67. a) Continuous wave X-band EPR spectrum taken on a 3.7 mM [**2d**$^{\bullet-}$] THF solution at room temperature (black), simulation (red) and calculated by DFT (navy), b) experimental spectrum after 15 min from a) in black, superimposed with the spectrum in red taken 2 days later from the same batch kept at room temperature in an argon glove box and analysed in the same conditions.

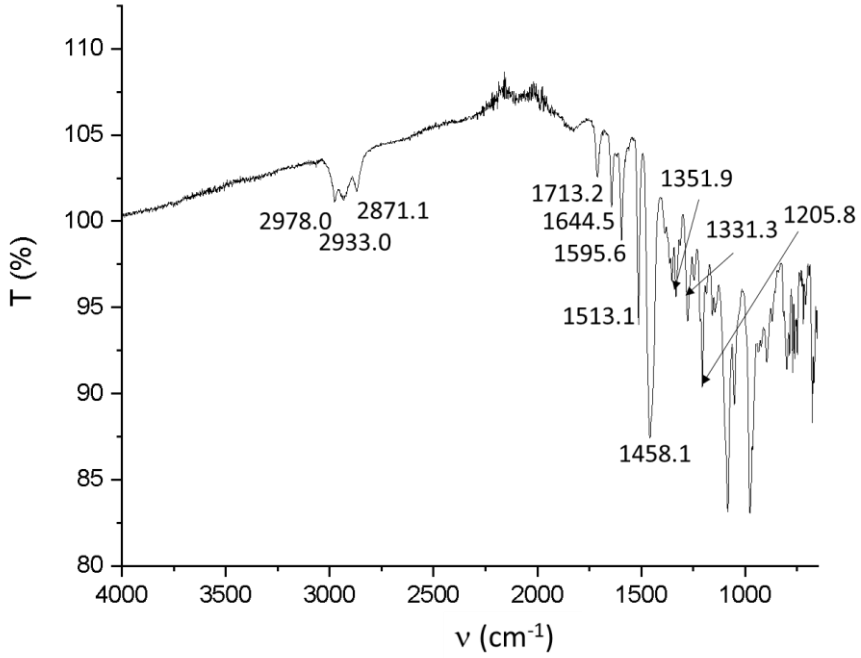
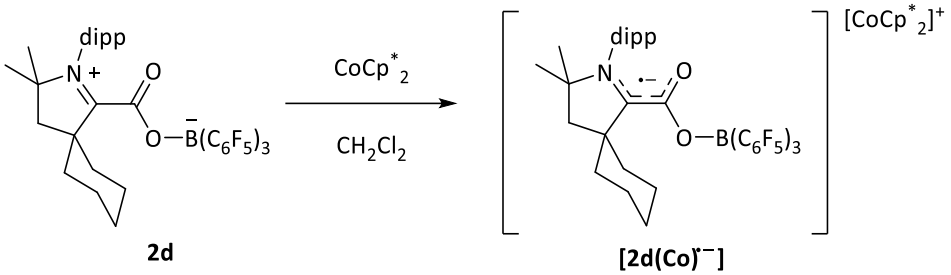


Figure S68. FTIR (solid state) of [**2d**$^{\bullet-}$] at 298 K.

Table S6. Theoretical and experimental IR frequencies for [**2d**$^{\bullet-}$]

Experimental	**Theoretical with K^+**	**Theoretical without K^+**	**Assignation**
1713.2	-		C=O of **2d**
1644.5	1643.1-1622.0	1644.3-1623.8	C=C(BCF)
1595.6	1603.1	1610.2	C=O
1513.1	1511.0-1507.0	1511.0-1507.0	C-F
1458.1	1478.4	1478.4	C=N
1351.9;1331.3	1352.1-1261.8	1352.1-1261.8	C(sp^3)-H torsion
1205.8	1173.5	1173.5	C-O

2.8 $[CoCp^*_2]^{Cy}$CAAC-CO_2-$B(C_6F_5)_3$ (**[2d(Co)$^{\bullet-}$]**)



Compound **2d** (13.4 mg, 0.02 mmol) and $CoCp^*_2$ (5 mg, 0.02 mmol) were placed in a 4 mL vial inside an argon glovebox. Then, 1 mL of DCM were added into the vial and stirred for one minute. The resulting dark yellow solution was transferred into another vial and diluted by a factor 10 to perform the EPR measurement. EPR (CW, X-band) g =2.0023 (a_N = 6.1G).

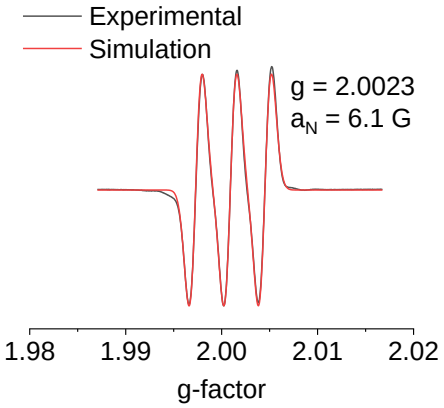
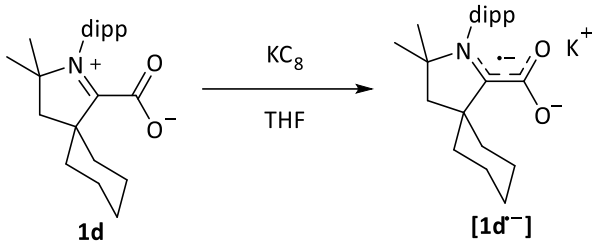


Figure S69. Continuous wave X-band EPR spectrum taken on a 6 mM **[2d(Co)$^{\bullet-}$]** THF solution at room temperature (black) and simulation (red).

2.9 K^{Cy}CAAC-CO_2 ([**1d**$^{\bullet-}$])



Compound **1d** (11.1 mg, 0.03 mmol) and KC_8 (4.1 mg, 0.03 mmol) were placed in a 4 mL vial inside an argon glovebox. Then, 1 mL of THF was added to the vial and the solution was stirred for 1 minute. The resulting orange solution was transferred into another vial and EPR was performed after dilution by 10. EPR (CW, X-band) g = 2.0035 (a_N = 5.1 G).

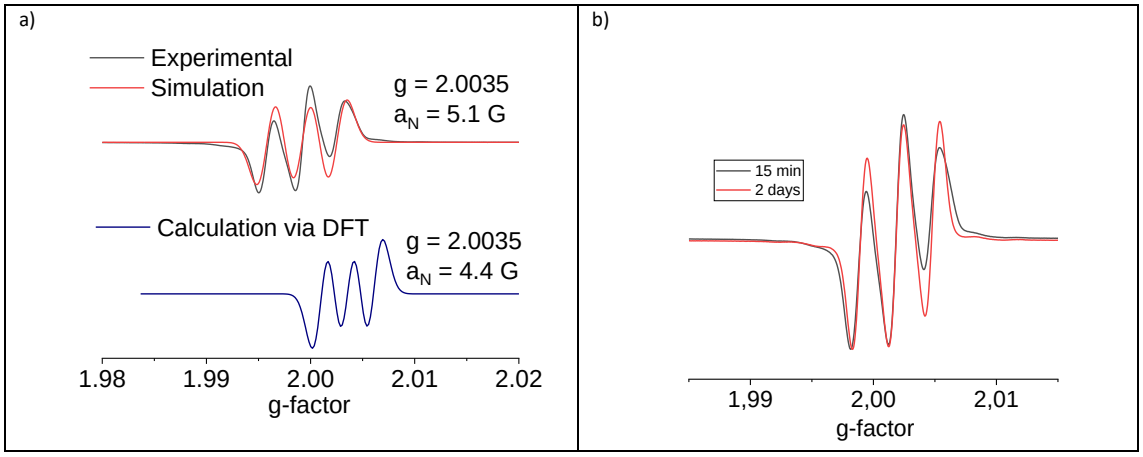


Figure S70. a) Continuous wave X-band EPR spectrum taken on a 3.0 mM **[1d$^{\bullet-}$]** THF solution at room temperature (black) and simulation (red) and calculated by DFT (navy), b) experimental spectrum after 15 min from a) in black, superimposed with the spectrum in red taken 2 days later from the same batch kept at room temperature in an argon glove box and analysed in the same conditions.

2.10 Reactivity toward DMPO

To a solution of **[1d]**$^{\bullet-}$, **[2d]**$^{\bullet-}$ or **[2b]**$^{\bullet-}$ (0.003 mmol, 0.03 M in THF) was added DMPO (0.015 mmol, 0.88 M in THF). After dilution by 10, EPR was performed after 65 hours for **[1d]**$^{\bullet-}$ and **[2d]**$^{\bullet-}$ and after 3 hours for **[2b]**$^{\bullet-}$.

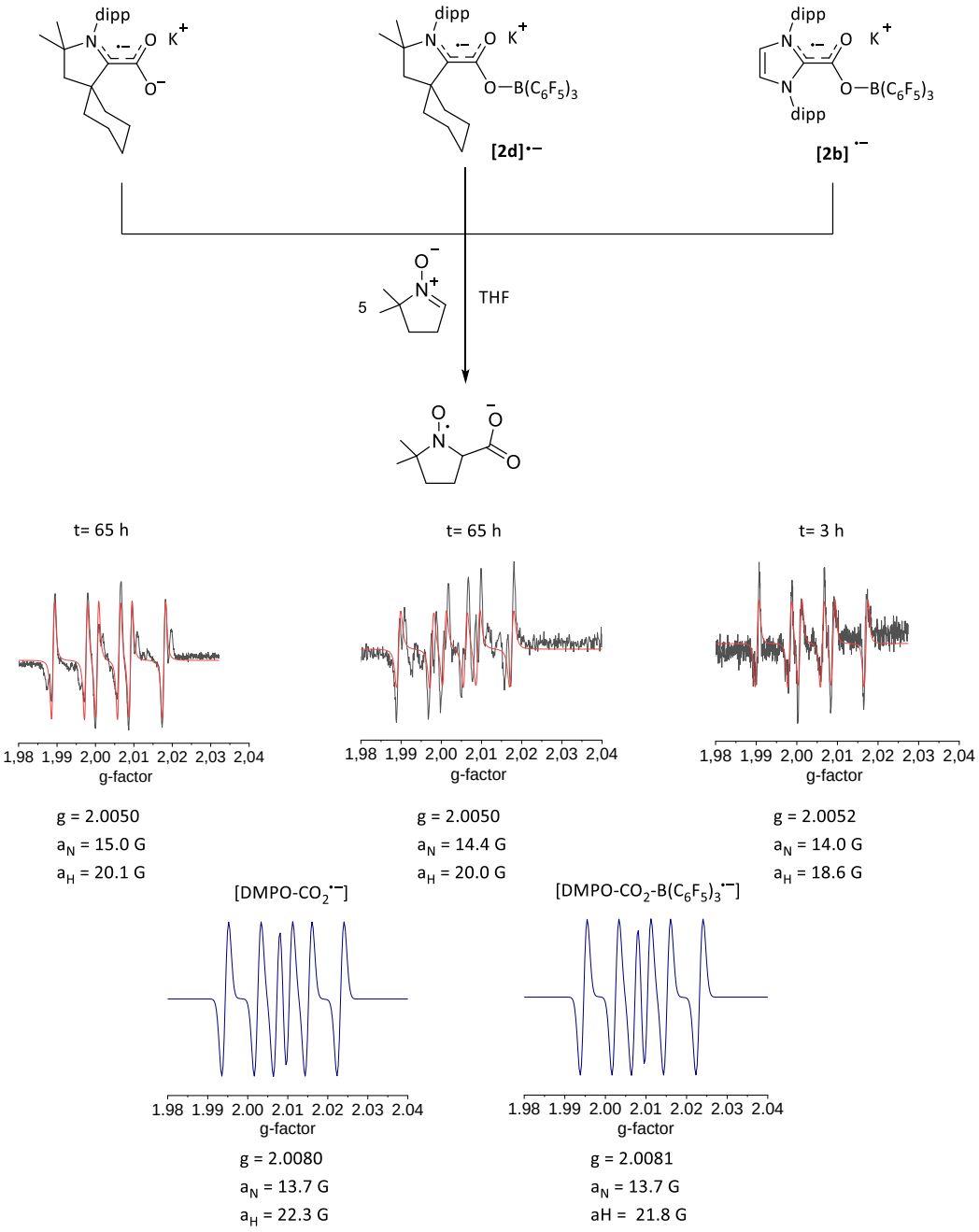


Figure S71. Continuous wave X-band EPR spectrum taken of reaction mixture of **[1d]**$^{\bullet-}$, **[2d]**$^{\bullet-}$ or **[2b]**$^{\bullet-}$ with 5 equivalents of DMPO in THF solution at room temperature (black), simulations (red) and calculated via DFT (navy).

3 X-Ray diffraction details

Data were collected at low temperature (100 K) either on a XtaLAB Synergy diffractometer using a Cu-Kα radiation (λ = 1.54184 Å) micro-source, or on a Bruker Kappa Apex II diffractometer using a Mo-Kα radiation (λ = 0.71073 Å) micro-source, both equipped with an Oxford Cryosystems Cooler Device. The structures have been solved using the new dual-space algorithm program SHELXT,[3] and refined by means of least-squares procedures using either SHELXL-2018[3] program included in the software package WinGX [4] version 1.639, or with the aid of the program CRYSTALS.[5] The Atomic Scattering Factors were taken from International Tables for X-Ray Crystallography.[6] Hydrogen atoms were placed geometrically and refined using a riding model. All non-hydrogen atoms were anisotropically refined.

AMA244B and AMA204F structures exhibit disorders (respectively one of the THF coordinated to the K atom, and the CH_2Cl_2 independent solvent molecule), which were handled by the 'Part' and 'EADP' options in Shelxl.

Ellipsoid plots in the figures of the crystallography section were generated using the software ORTEP-35.[7] The crystal structures have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 2306774-2306777 for AMA244B ([**2d**$^{\bullet-}$]), AMA198 (**2b**), AMA204F (**2d**) and AMA173 (**2c**), respectively

4 Computational Analysis

4.1 General computational details

The calculations were carried out using Gaussian16[8] software. Geometry optimizations were performed using the M06-2X functional[9] combined with the Grimme's D3 correction to consider dispersion effects.[10] The optimizations were carried out in solution (solvent = dichloromethane, DCM, ε = 8.93) using the SMD continuum model[11] with BS1 as a basis set. BS1 uses the 6-311-G++(d,p) basis set for the H, C, N, F and O atoms.[12] Frequencies calculations were performed with the aim at characterising the stationary points, either minima or transition states. All energies in solution were corrected by single-point calculations with a larger basis set (BS2) including def2TZVP basis set for all atoms.[13]

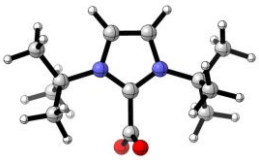
Gibbs energies in dichloromethane were calculated at 298.15 K adding the potential energies in dichloromethane, obtained with single-point calculations using BS2, the thermal and entropic corrections obtained from frequency calculations with BS1. To adjust the Gibbs energies from 1 atm to 1 mol·L^{-1} standard state in solution, a correction of RTln(c_s/c_g) was added ($\Delta G^{1\ atm \rightarrow 1\ M}$). The value 1.9 kcal·mol^{-1} was added to energies of all species, c_s is the standard molar concentration in solution (1 mol·L^{-1}), c_g is the standard molar concentration in gas phase (0.0446 mol·L^{-1}), and R is the gas constant (8.314 J·mol^{-1}·K^{-1}). All reported energies in the following discussion correspond to M062X-D3 energies in dichloromethane at 298.15K in kcal·mol^{-1}, if not otherwise specified, calculated using the formula:

$$G = E(BS2) + G(BS1) - E(BS1) + \Delta G^{1\ atm \rightarrow 1\ M}$$

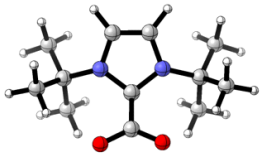
Structure visualization was performed with IboView software.[14] The orbital related calculations were performed using ORCA 5.0.4[15] with the functional M06-2X[2]. It was combined with Grimme's D3 correction considering the original damping function (D3ZERO)[10] including def2TZVP basis set for all atoms. The calculations were carried out in solution (dichloromethane) with SMD as solvation model. NPA charges from the optimised geometries were obtained using the keyword pop=NPA.

The EPR calculations were carried out using ORCA 5.0.4 suite of programmes[15] with the functional M06-2X[9] including a triple-zeta with a polarisation function basis set, 6-311G(d,p)[12] for all atoms in solution (solvent= tetrahydrofuran, ε = 7.4257) using the SMD as continuum solvent model. An additional keyword, SOMF(1X)[16], was included in order to accelerate the calculations of integrals in the spin-orbit coupling calculation part (prior to the formal calculation of EPR parameters). The optimised geometries employed as input for EPR calculations have been assessed using M06-2X-D3[9,10], BS1[12] and SMD (solvent= tetrahydrofuran, ε = 7.4257) as functional, basis set and solvent model, respectively. The EPR representations were performed by EasySpin, an open-source MATLAB toolbox.[17]

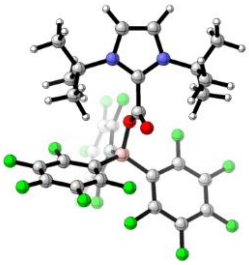
4.2 3D-views and absolute energies (hartrees) of every optimised species.



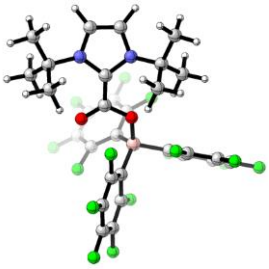
(1a)



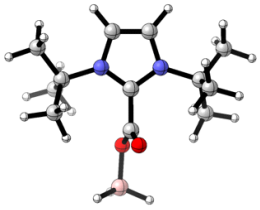
([1a]$^{\bullet-}$)



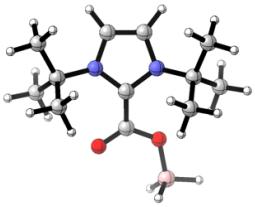
(2a)



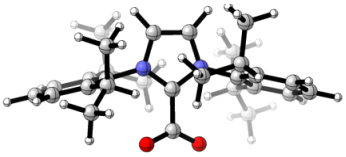
([2a]$^{\bullet-}$)



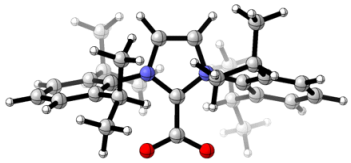
(2a-BH_3)



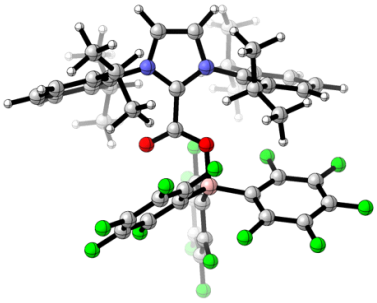
([2a-BH_3]$^{\bullet-}$)



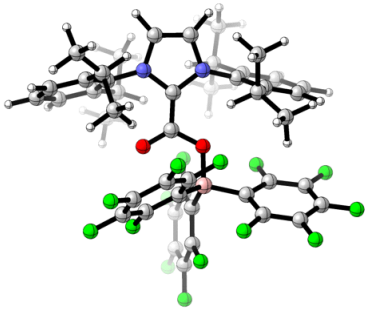
(1b)



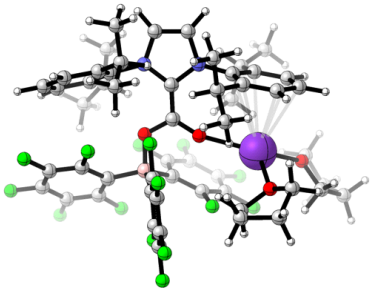
([1b]$^{\bullet-}$)



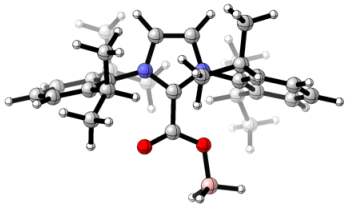
(2b)



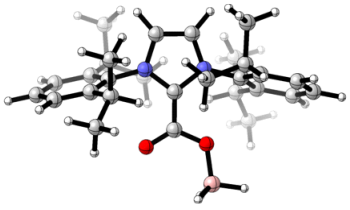
([2b]$^{\bullet-}$)



[2b$^{\bullet-}$][K^+]·$(THF)_2$



(2b-BH_3)



([2b-BH_3]$^{\bullet-}$)

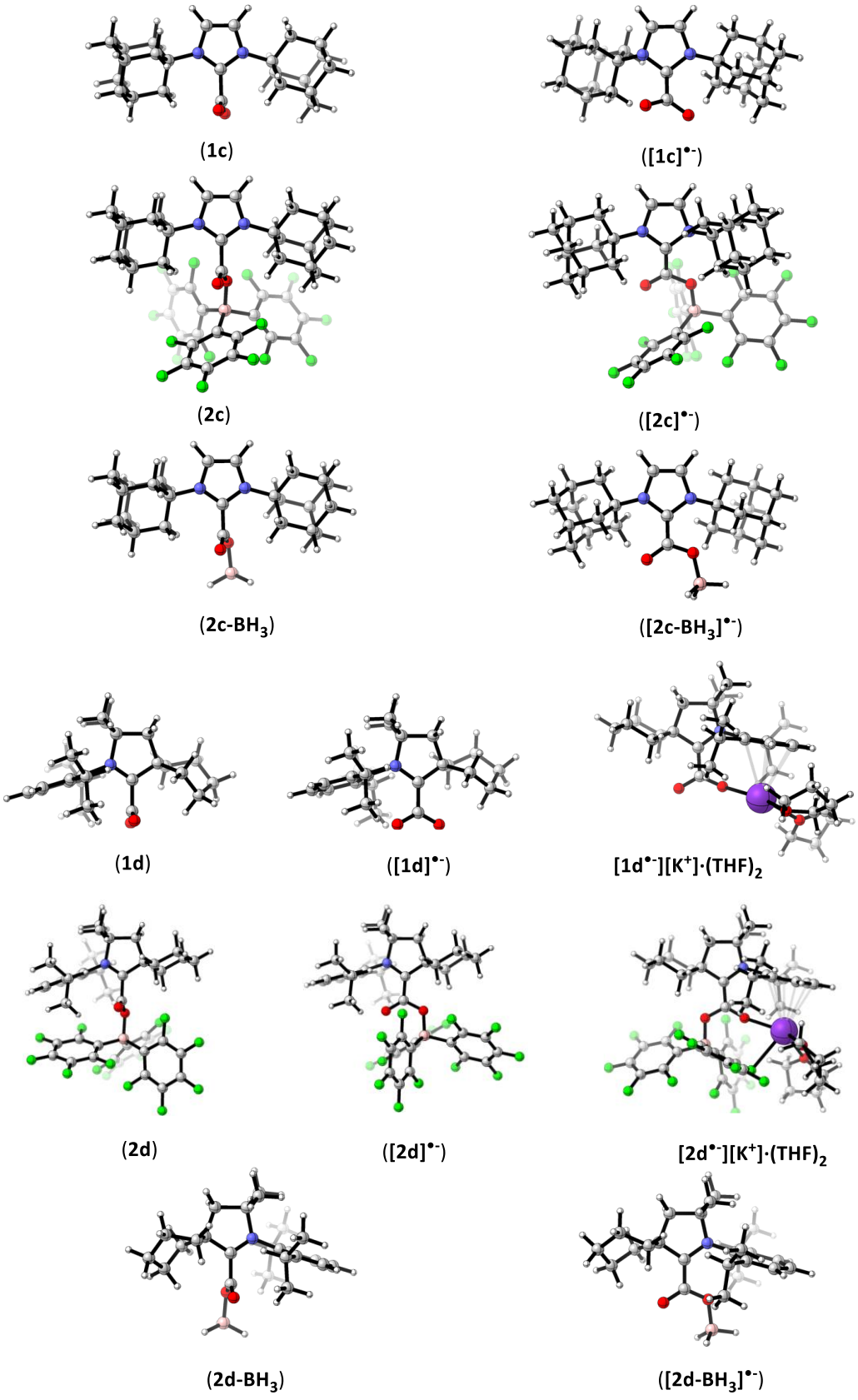


Figure S72. Studied adducts **1a**-**d**, **2a**-**d** and (**2(a**-**d)-BH$_3$**) and their corresponding monoreduced species ([(**1a**-**d**)]$^{\bullet-}$, [(**2a**-**d**)]$^{\bullet-}$ and [(**2(a**-**d)-BH$_3$**)]$^{\bullet-}$).

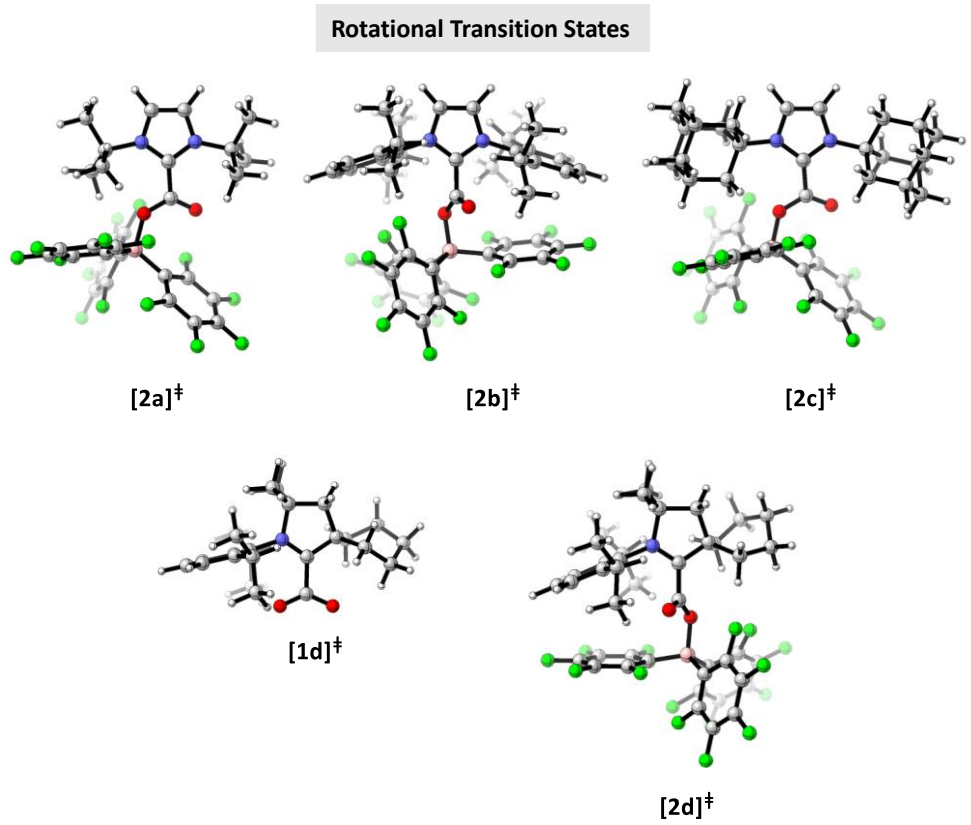


Figure S73. Rotational transition states **[2a-d]‡** and **[1d]‡**.

Table S7. Internal and Gibbs energies and thermal and entropic corrections (T,S correction) in dichloromethane of all the species. For transition states the imaginary frequency is also given (in cm^{-1}).

	E/BS1	T,S correction	G/BS1	E/BS2-nopt	G/BS2	Freq
Absolute Minima						
1a	-729,210380	0,270572	-728,939808	-729,282770	-729,012198	-
[1a]•⁻	-729,258488	0,265193	-728,993295	-729,327264	-729,062071	-
2a	-2937,503141	0,394868	-2937,108273	-2937,825703	-2937,430835	-
[2a]•⁻	-2937,592715	0,388719	-2937,203995	-2937,912045	-2937,523326	-
2a-BH_3	-755,858298	0,300922	-755,557376	-755,936068	-755,635146	-
[2a-BH_3]•⁻	-755,927351	0,295541	-755,631810	-756,002498	-755,706957	-
1b	-1348,463873	0,528675	-1347,935198	-1348,600276	-1348,071601	-
[1b]•⁻	-1348,527803	0,524875	-1348,002929	-1348,661845	-1348,136970	-
2b	-3556,782090	0,653866	-3556,128224	-3557,166904	-3556,513038	-
[2b]•⁻	-3556,882077	0,650292	-3556,231785	-3557,264004	-3556,613712	-
2b-BH_3	-1375,111585	0,558979	-1374,552606	-1375,253245	-1374,694266	-
[2b-BH_3]•⁻	-1375,198825	0,555091	-1374,643734	-1375,339013	-1374,783922	-
1c	-1193,701991	0,487443	-1193,214548	-1193,816880	-1193,329437	-
[1c]•⁻	-1193,750125	0,482487	-1193,267638	-1193,861017	-1193,378530	-
2c	-3402,000762	0,612962	-3401,387799	-3402,364388	-3401,751426	-
[2c]•⁻	-3402,084616	0,602991	-3401,481624	-3402,445673	-3401,842682	-
2c-BH_3	-1220,350261	0,517737	-1219,832524	-1220,470390	-1219,952653	-
[2c-BH_3]•⁻	-1220,421165	0,514199	-1219,906966	-1220,538675	-1220,024476	-
1d	-1140,700775	0,497025	-1140,203751	-1140,810188	-1140,313163	-
[1d]•⁻	-1140,786751	0,492647	-1140,294103	-1140,893848	-1140,401201	-
2d	-3349,015146	0,624165	-3348,390981	-3349,372830	-3348,748665	-
[2d]•⁻	-3349,138670	0,618181	-3348,520488	-3349,494953	-3348,876772	-
2d-BH_3	-1167,346612	0,526577	-1166,820034	-1167,461083	-1166,934506	-
[2d-BH_3]•⁻	-1167,457583	0,524006	-1166,933577	-1167,570450	-1167,046444	-
Rotational Transition States						
[1d]‡	-1140,691113	0,497911	-1140,193201	-1140,80034-7	-1140,302436	-54.0
[2a]‡	-2937,484588	0,396494	-2937,088094	-2937,80585-4	-2937,409360	-24.9
[2b]‡	-3556,775080	0,654056	-3556,121023	-3557,15974-8	-3556,505692	-9.5
[2c]‡	-3401,973975	0,612184	-3401,361791	-3402,33736-3	-3401,725179	-33.6
[2d]‡	-3348,992828	0,624368	-3348,368460	-3349,35068-8	-3348,726320	-261.7

4.3 Mulliken spin density values for adducts [(1a-d)$^{\bullet-}$], [(2a-d)$^{\bullet-}$] and [2(a-d)-$BH_3^{\bullet-}$].

Table S8. Mulliken spin density values for **[(1a-d)$^{\bullet-}$]**, **[(2a-d)$^{\bullet-}$]** and **[(2(a-d)-BH_3)$^{\bullet-}$]**.

Compounds	CO_2 moiety				NHC moiety		Borane moiety (BR_3)	
	C	O (C=O)	O (C-O)	Total Spin density (CO_2)	Carbenic C	N	B	R_3
Free [$CO_2^{\bullet-}$]	0.81	0.19		1.00	-	-	-	-
[1a$^{\bullet-}$]	-0.08	0.10		0.02	0.57	0.34	-	-
[2a$^{\bullet-}$]	0.13	0.14	0.04	0.31	0.30	0.33	0.33	-0.02
[2a-$BH_3^{\bullet-}$]	-0.02	0.11	0.11	0.20	0.60	0.34	0.00	0.00
[1b$^{\bullet-}$]	0.00	0.16		0.16	0.56	0.19	-	-
[2b$^{\bullet-}$]	0.42	0.14	-0.04	0.52	0.57	0.17	0.02	-0.05
[2b-$BH_3^{\bullet-}$]	0.06	0.15	0.03	0.24	0.44	0.22	0.00	0.01
[1c$^{\bullet-}$]	0.00	0.08		0.08	0.66	0.32	-	-
[2c$^{\bullet-}$]	0.01	0.11	0.05	0.17	0.35	0.33	-0.01	0.02
[2c-$BH_3^{\bullet-}$]	-0.09	0.12	0.02	0.04	0.51	0.33	0.01	0.00
[1d$^{\bullet-}$]	0.00	0.15		0.15	0.61	0.22	-	-
[2d$^{\bullet-}$]	0.33	0.12	0.00	0.45	0.69	0.23	0.04	-0.09
[2d-$BH_3^{\bullet-}$]	0.01	0.13	0.02	0.16	0.65	0.22	0.00	0.00

4.4 NPA charge population

Table S9. NPA charge population for adducts **1a**-**d**, **2a**-**d** and **2(a**-**d)-BH$_3$**.

Compounds	C	CO_2 moiety O (C=O)	CO_2 moiety O (C-O)	Total NPA charge (CO_2)	NHC moiety Carbenic C	NHC moiety N	Borane moiety (BR_3) B	Borane moiety (BR_3) R_3
Free CO_2	1.05		-1.05	0.00	-	-	-	-
1a	0.75		-1.48	-0.73	0.35	-0.62	-	-
2a	0.81	-0.60	-0.63	-0.42	0.34	-0.57	0.56	-1.00
2a-BH$_3$	0.79	-0.63	-0.62	-0.46	0.35	-0.58	-0.11	-0.28
1b	0.73		-1.46	-0.73	0.40	-0.67	-	-
2b	0.80	-0.60	-0.62	-0.42	0.35	-0.58	0.56	-0.96
2b-BH$_3$	0.77	-0.62	-0.61	-0.46	0.38	-0.62	-0.10	-0.28
1c	0.75		-1.48	-0.73	0.36	-0.63	-	-
2c	0.82	-0.61	-0.63	-0.42	0.35	-0.58	0.56	-0.99
2c-BH$_3$	0.79	-0.62	-0.63	-0.46	0.36	-0.59	-0.11	-0.28
1d	0.72		-1.46	-0.76	0.46	-0.33	-	-
2d	0.78	-0.60	-0.63	-0.45	0.46	-0.29	0.56	-0.99
2d-BH$_3$	0.76	-0.63	-0.62	-0.49	0.47	-0.30	-0.11	-0.27

Table S10. NPA charge population for adducts **[(1a**-**d)$^{\bullet-}$]**, **[(2a**-**d)$^{\bullet-}$]** and **[(2**(**a**-**d**)**-BH$_3$)$^{\bullet-}$]**.

Compounds	C	CO_2 moiety O (C=O)	CO_2 moiety O (C-O)	Total NPA charge (CO_2)	NHC moiety Carbenic C	NHC moiety N	Borane moiety (BR_3) B	Borane moiety (BR_3) R_3
Free [CO_2]$^{\bullet-}$	0.52		-1.52	-1.00	-	-	-	-
[1a]$^{\bullet-}$	0.70		-1.66	-0.96	0.09	-0.78	-	-
[2a]$^{\bullet-}$	0.69	-0.73	-0.69	-0.72	0.16	-0.72	0.57	-1.07
[2a-BH$_3$]$^{\bullet-}$	0.69	-0.74	-0.69	-0.74	0.14	-0.74	-0.09	-0.34
[1b]$^{\bullet-}$	0.65		-1.67	-1.02	0.17	-0.84	-	-
[2b]$^{\bullet-}$	0.66	-0.71	-0.68	-0.73	0.20	-0.76	0.56	-1.06
[2b-BH$_3$]$^{\bullet-}$	0.65	-0.74	-0.68	-0.77	0.21	-0.79	-0.08	-0.35
[1c]$^{\bullet-}$	0.71		-1.64	-0.93	0.10	-0.82	-	-
[2c]$^{\bullet-}$	0.73	-0.72	-0.68	-0.67	0.14	-0.75	0.56	-1.06
[2c-BH$_3$]$^{\bullet-}$	0.69	-0.74	-0.69	-0.74	0.14	-0.74	-0.09	-0.34
[1d]$^{\bullet-}$	0.68		-1.66	-0.98	0.09	-0.45	-	-
[2d]$^{\bullet-}$	0.70	-0.70	-0.68	-0.68	0.13	-0.39	0.56	-1.06
[2d-BH$_3$]$^{\bullet-}$	0.69	-0.72	-0.68	-0.71	0.12	-0.41	-0.09	-0.33

4.5 Frontier orbitals

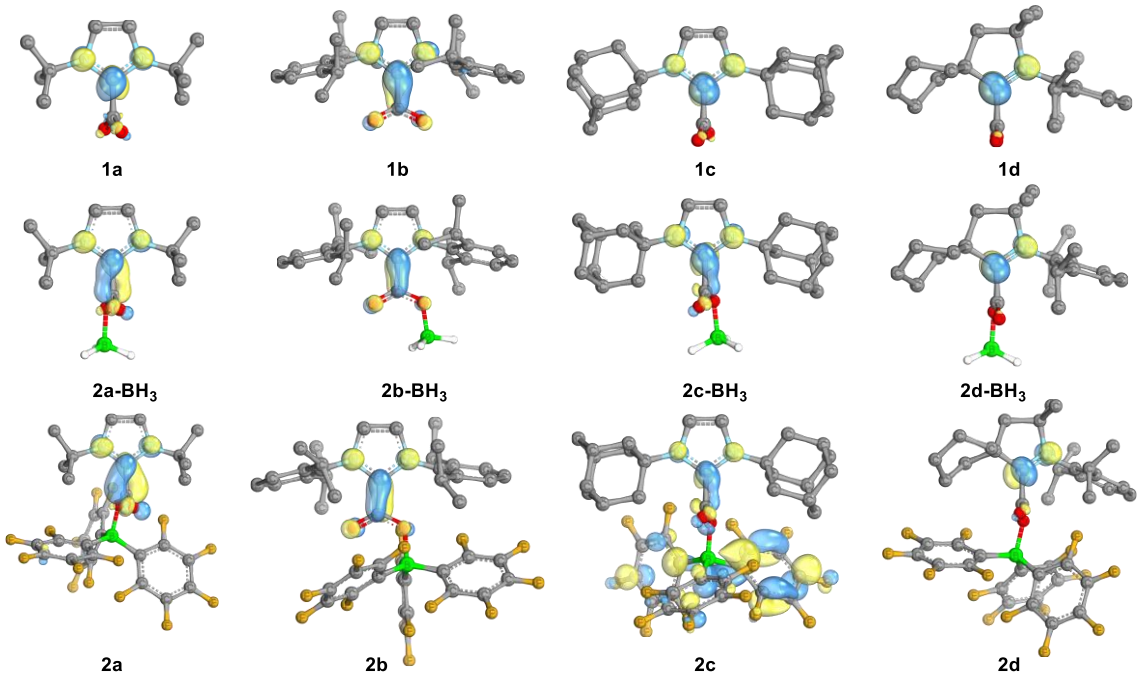


Figure S74. LUMO orbitals of the neutral adducts **1a-d**, **2(a-d)-BH_3** and **2a-d**. Visualization (IBOview,[14] Threshold = 45).

Table S11. Localisation of LUMO in **1d**, **2a-d**.

	2a	**2c**	**2b**	**2d**	**1d**
C_{NHC}	23%	6%	28%	56%	53%
C_{CO2}	35%	3%	18%	2%	2%
N	16%	4%	22%	23%	19%
O (C=O)	8%	1%	10%	2%	1%
O (C-O)	3%	<1%	4%	<1%	20%
B	4%	3%	<1%	1%	

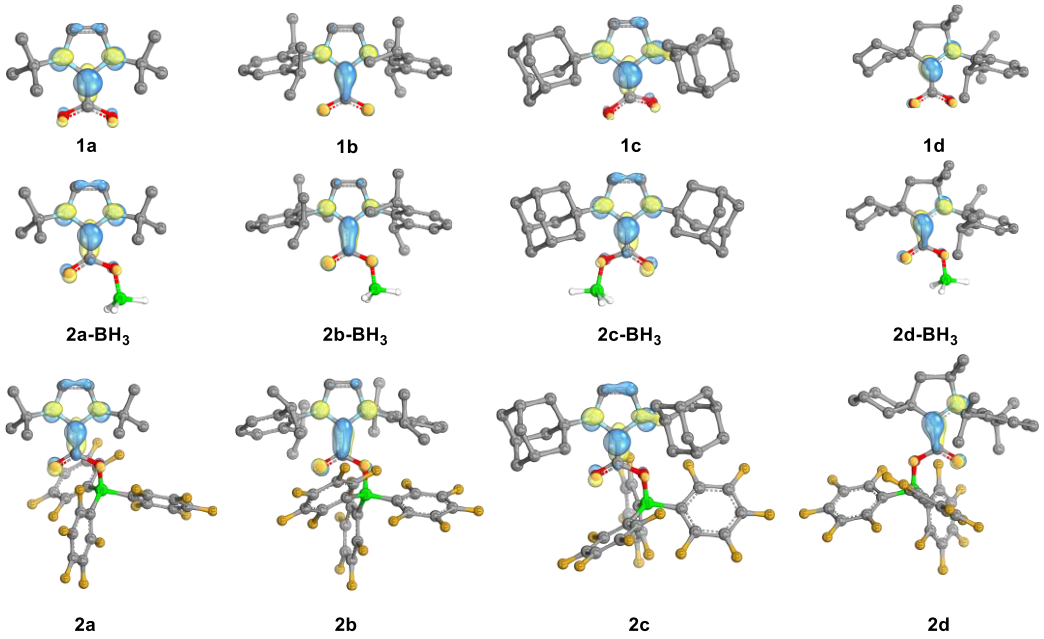


Figure S75. SOMO orbitals of the reduced adducts **[(1a-d)$^{\bullet-}$]**, [**(2a-d)$^{\bullet-}$**] and **[(2(a-d)-BH$_3$)$^{\bullet-}$]**. Visualization (IBOview,[14] Threshold = 45).

Table S12. Localisation of SOMO in [**1d$^{\bullet-}$**] and [**2a-d$^{\bullet-}$**].

		2a$^{\bullet-}$	**2c$^{\bullet-}$**	**2b$^{\bullet-}$**	**2d$^{\bullet-}$**	**1d$^{\bullet-}$**
SOMO	**C_{NHC}**	26%	28%	25%	41%	51%
	C_{CO2}	12%	8%	15%	11%	5%
	N	26%	27%	25%	20%	20%
	O (C=O)	3%	7%	10%	10%	7%
	O (C-O)	8%	3%	4%	5%	6%
	B	<1%	<1%	<1%	<1%	-

4.6 Relaxed potential energy surface scan for the CO_2 rotation relative to NHC in **1d** and **2a-d**.

Rotational energy profiles have been computed performing a geometry optimisation at each step while maintaining the scanned variable (torsion angle D(NHC)-CO_2) constant). These profiles are shown in Figure S76 combined with the energy of the LUMO.

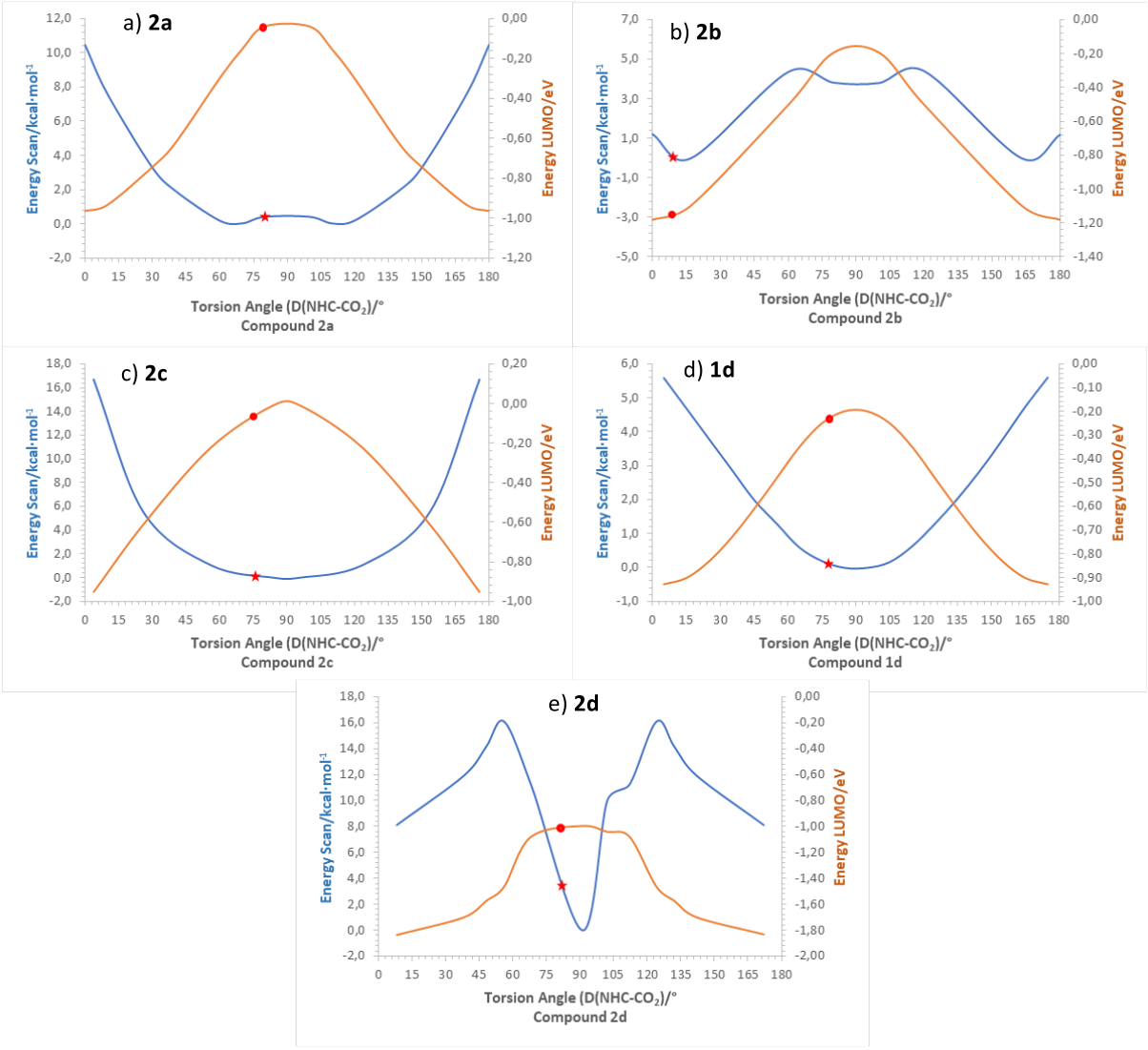
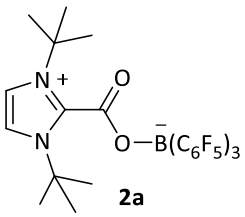


Figure S76. Relaxed potential energy surface scan and their LUMO energy in function of the dihedral angle, D(NHC-CO_2), for the CO_2 rotation relative to NHC in **1d** (e) and **2a-d** (a-d). Red dot (LUMO curve) and red star (Energy curve) correspond to the minimum for each adduct.

Table S13. Theoretical reduction potential ($E_{1/2}$) of all synthesized adducts (from transition state) versus $Fc^{+/0}$ redox couple.

Transition state	ΔG_{red} / kcal·mol^{-1}	$E^{1/2}$ / V
[2a]‡	-71.5	-1.68
[2c]‡	-73.7	-1.58
[2b]‡	-67.8	-1.84
[1d]‡	-62.0	-2.09
[2d]‡	-92.2	-0.78

4.7 Cartesian coordinates

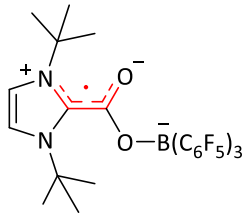


2a

C	4.894812000	1.695413000	1.153337000
C	4.928268000	0.369685000	1.423751000
H	5.598215000	2.464039000	1.415309000
H	5.673675000	-0.200642000	1.946259000
N	3.738067000	1.947698000	0.451672000
N	3.791401000	-0.193841000	0.889484000
C	3.077801000	0.787351000	0.309576000
C	3.373818000	3.308141000	-0.105586000
C	3.779795000	3.338687000	-1.578167000
C	1.880308000	3.554481000	0.083079000
C	4.151106000	4.366028000	0.675798000
H	4.850858000	3.149650000	-1.683159000
H	3.226460000	2.598606000	-2.156627000
H	3.562235000	4.331078000	-1.979419000
H	1.583137000	3.364678000	1.115534000
H	1.676964000	4.601978000	-0.147179000
H	1.267539000	2.957335000	-0.590506000
H	3.812315000	5.343553000	0.330469000
H	3.956845000	4.294998000	1.748567000
H	5.225196000	4.308114000	0.493045000
C	3.481416000	-1.676860000	0.928789000
C	2.344892000	-1.923244000	1.918932000
C	3.141467000	-2.145897000	-0.485573000
C	4.731761000	-2.417687000	1.398708000
H	2.626435000	-1.567232000	2.913023000
H	1.425517000	-1.427475000	1.616146000
H	2.161411000	-2.998673000	1.974551000
H	3.948832000	-1.895209000	-1.177756000
H	3.026888000	-3.231697000	-0.464734000
H	2.209403000	-1.728481000	-0.863296000

H	4.512974000	-3.485251000	1.351943000
H	5.588661000	-2.216922000	0.751936000
H	4.986594000	-2.176963000	2.432375000
C	1.771769000	0.615926000	-0.457003000
O	1.766309000	0.744650000	-1.655128000
O	0.782969000	0.340026000	0.329153000
B	-0.621626000	-0.123137000	-0.075721000
C	-1.483712000	1.076866000	-0.789466000
C	-2.394602000	0.939303000	-1.830630000
C	-1.452216000	2.345573000	-0.219389000
C	-3.138609000	1.995783000	-2.335022000
C	-2.169361000	3.428519000	-0.697125000
C	-3.015819000	3.253264000	-1.775877000
C	-1.407181000	-0.395485000	1.340734000
C	-2.678801000	-0.954996000	1.286706000
C	-0.979886000	-0.055263000	2.617690000
C	-3.474154000	-1.189768000	2.391299000
C	-1.748876000	-0.274345000	3.754271000
C	-3.000914000	-0.843979000	3.645032000
C	-0.406949000	-1.482647000	-0.975739000
C	-0.129239000	-1.464037000	-2.342755000
C	-0.306344000	-2.743189000	-0.392134000
C	0.233431000	-2.589713000	-3.066109000
C	0.050214000	-3.890650000	-1.082741000
C	0.330051000	-3.813920000	-2.432226000
F	-2.635821000	-0.251242000	-2.396266000
F	-3.982950000	1.805983000	-3.350431000
F	-3.721756000	4.275498000	-2.252261000
F	-2.072395000	4.624867000	-0.113680000
F	-0.729168000	2.559277000	0.891139000
F	0.213114000	0.513751000	2.847205000
F	-3.185811000	-1.310741000	0.093696000
F	-4.682205000	-1.740993000	2.265260000
F	-3.745217000	-1.053313000	4.728591000
F	-1.284767000	0.069608000	4.958134000
F	-0.203466000	-0.336539000	-3.055905000

F	0.491777000	-2.502199000	-4.371864000
F	0.682233000	-4.901067000	-3.112173000
F	0.144570000	-5.062451000	-0.450936000
F	-0.534581000	-2.924244000	0.919366000



[2a$^{\bullet-}$]

C	4.159756000	2.571500000	0.140531000
C	4.937722000	1.479188000	0.016584000
H	4.440693000	3.549298000	0.488583000
H	5.983837000	1.380577000	0.244743000
N	2.867120000	2.265637000	-0.265723000
N	4.177446000	0.428690000	-0.472646000
C	2.849185000	0.887628000	-0.565381000
C	1.941109000	3.325858000	-0.797277000
C	1.416054000	2.894783000	-2.168574000
C	0.811628000	3.593418000	0.201905000
C	2.720338000	4.633286000	-0.990711000
H	2.249981000	2.770994000	-2.865987000
H	0.851702000	1.968179000	-2.114124000
H	0.758551000	3.677501000	-2.555978000
H	1.230287000	3.946266000	1.149127000
H	0.153689000	4.374063000	-0.192152000
H	0.232406000	2.694451000	0.390024000
H	2.049019000	5.356511000	-1.458406000
H	3.054229000	5.061679000	-0.043456000
H	3.584075000	4.494970000	-1.645423000
C	4.791571000	-0.765083000	-1.139929000
C	4.697980000	-1.991678000	-0.227009000
C	4.109774000	-1.002214000	-2.490129000
C	6.274977000	-0.481340000	-1.409327000
H	5.199867000	-1.786363000	0.723011000
H	3.659435000	-2.251702000	-0.035510000

H	5.201516000	-2.838333000	-0.702434000
H	4.214306000	-0.118959000	-3.126833000
H	4.600297000	-1.842466000	-2.988035000
H	3.054588000	-1.238917000	-2.370576000
H	6.679033000	-1.318724000	-1.981593000
H	6.410914000	0.430897000	-1.995405000
H	6.855947000	-0.404629000	-0.487793000
C	1.714849000	0.014977000	-0.485252000
O	0.535092000	0.640333000	-0.328000000
O	1.789538000	-1.218379000	-0.546237000
B	-0.641539000	-0.153270000	0.103949000
C	-0.196252000	-0.929290000	1.489822000
C	0.238537000	-0.153302000	2.556849000
C	-0.039878000	-2.293800000	1.675405000
C	0.769342000	-0.666663000	3.726760000
C	0.484010000	-2.854267000	2.831158000
C	0.892238000	-2.036567000	3.866365000
C	-1.230989000	-1.144005000	-1.068836000
C	-2.330714000	-1.945859000	-0.797678000
C	-0.793614000	-1.186485000	-2.384300000
C	-2.942521000	-2.767464000	-1.725173000
C	-1.378039000	-1.995972000	-3.349639000
C	-2.455177000	-2.794685000	-3.019976000
C	-1.859919000	0.943856000	0.349882000
C	-2.669490000	1.065423000	1.470496000
C	-2.170928000	1.828940000	-0.677348000
C	-3.679049000	2.010273000	1.590342000
C	-3.163318000	2.790330000	-0.599134000
C	-3.925166000	2.885061000	0.550860000
F	-1.500978000	1.773519000	-1.839409000
F	-2.520015000	0.255615000	2.532488000
F	-4.416062000	2.081565000	2.702461000
F	-4.889949000	3.799079000	0.648778000
F	-3.400480000	3.617608000	-1.621383000
F	-0.371159000	-3.172294000	0.715797000
F	0.613343000	-4.180406000	2.947949000

F	1.400746000	-2.560102000	4.982906000
F	1.156820000	0.140035000	4.720198000
F	0.146329000	1.187862000	2.491738000
F	0.223353000	-0.425307000	-2.815803000
F	-0.913521000	-2.003408000	-4.603702000
F	-3.025535000	-3.574708000	-3.939626000
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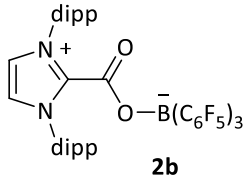
F	-2.847686000	-1.951331000	0.446157000



2b

F	2.439185000	-1.660483000	0.190388000
F	3.009971000	2.900094000	-0.933990000
F	0.715905000	2.018855000	-2.192620000
F	4.754094000	-2.226703000	-1.023142000
F	2.721634000	2.359957000	2.159571000
F	-0.053541000	2.831777000	2.404822000
F	6.182551000	-0.259314000	-2.227707000
F	5.280906000	2.301745000	-2.147971000
F	0.081281000	-1.563346000	1.992131000
F	-0.526484000	4.296435000	-2.786491000
F	-1.272294000	5.089338000	1.786173000
F	-1.536246000	5.866532000	-0.804415000
O	0.203959000	-0.158981000	-0.304991000
F	3.334912000	1.814553000	4.710753000
F	0.681579000	-2.062282000	4.510746000
F	2.312617000	-0.400957000	5.916181000
O	-1.601234000	0.417016000	0.905668000
N	-3.144791000	-1.276273000	-0.805201000
N	-1.336470000	-2.280440000	-1.452488000
C	-1.806692000	-1.245153000	-0.739178000
C	-1.038219000	-0.226355000	0.054544000
C	3.091649000	-0.655136000	-0.408197000
C	2.567672000	0.633455000	-0.363392000
C	-4.085655000	-0.365413000	-0.181122000

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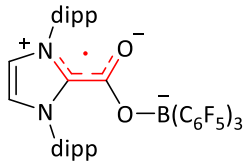

[2b$^{\bullet-}$]

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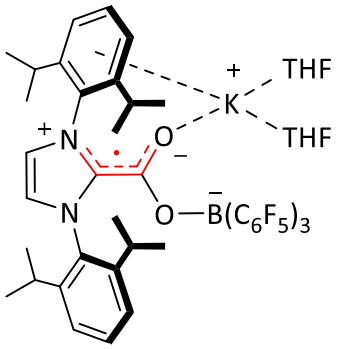

[2b$^{\bullet-}$][K$^+$]·(THF)$_2$

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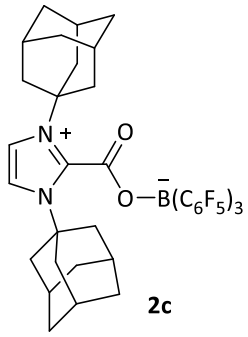

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F	-0.539834000	-2.654028000	5.597425000
F	2.495374000	-2.967883000	1.157856000
F	1.667905000	-1.277886000	4.797192000
F	-2.434164000	-3.331495000	3.768154000
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O	-0.426028000	1.098743000	2.029308000
F	4.878285000	-3.241894000	0.064995000
N	-1.682115000	3.161552000	-0.020673000
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C	-0.488663000	2.603047000	0.231597000
C	-0.271719000	1.224467000	0.841285000
C	-3.079310000	2.593898000	0.036924000
C	-3.641048000	2.609597000	-1.396243000
H	-3.623018000	3.630709000	-1.788760000
H	-3.011869000	1.988238000	-2.038143000
C	-3.109883000	1.166313000	0.596442000
H	-2.740926000	1.160879000	1.622557000
H	-2.486674000	0.504118000	-0.009810000
C	0.884547000	-1.322965000	2.568479000
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H	-3.518477000	3.484456000	1.956389000
H	-3.919895000	4.525513000	0.579861000
C	2.079797000	-0.947933000	-1.781828000
C	-1.460148000	4.450548000	-0.459530000
H	-2.263947000	5.108815000	-0.737990000
C	3.320633000	-1.101032000	-2.374995000
C	-1.629144000	-3.920509000	-2.044650000
C	-5.940957000	2.994554000	-0.485223000
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H	-6.978053000	2.644156000	-0.481978000
C	4.283834000	-1.862844000	-1.739137000
C	-0.859682000	-3.227120000	-1.131221000
C	-0.125097000	4.660804000	-0.460782000
H	0.426290000	5.541257000	-0.733374000

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C	-2.387334000	-3.211819000	-2.961618000
C	-1.552294000	-1.176758000	-2.009601000
C	-1.335386000	-2.678014000	3.383286000
C	-0.379358000	-2.335163000	4.315558000
C	-0.032420000	-1.664566000	1.580493000
C	1.730898000	-1.493356000	-0.548152000
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C	-2.343788000	-1.832762000	-2.944199000
C	3.970576000	-2.475280000	-0.541276000
C	2.713385000	-2.295430000	0.018035000
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H	4.197696000	1.693506000	-2.076340000
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C	-5.102464000	0.652112000	-0.845478000
H	-4.488380000	0.005977000	-1.483676000
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C	0.746845000	-1.641949000	3.902256000
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H	2.421974000	5.197998000	-0.908458000
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H	3.796979000	0.534553000	0.106180000
H	5.380894000	1.323034000	0.089964000
C	3.900851000	2.331297000	1.315940000

H	4.160459000	1.783084000	2.225216000
C	4.607750000	3.690000000	1.297858000
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H	2.094133000	3.038838000	-2.117452000
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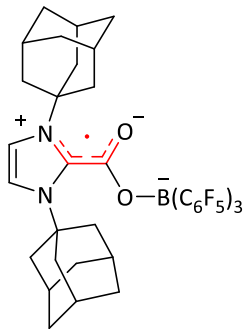

[2c$^{\bullet-}$]

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C	-0.970997000	-0.129156000	-0.563574000
C	-0.699876000	3.324249000	-0.833559000
C	-1.824831000	4.223932000	-0.280443000
H	-2.465655000	4.560080000	-1.101285000
H	-2.444167000	3.634969000	0.407013000
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H	0.987616000	2.246278000	-0.037550000
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C	0.172471000	4.133772000	-1.806508000
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H	-2.090019000	3.338897000	-3.223535000
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H	-4.168628000	1.657857000	-3.135963000
C	-1.229767000	5.443681000	0.439127000
H	-2.045051000	6.073191000	0.808499000
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H	1.380433000	5.919832000	-1.790140000
C	-4.209516000	-0.026311000	-0.864505000
C	-6.711956000	-0.098044000	-0.500726000
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C	-5.171826000	-0.837708000	1.319239000
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H	-5.736181000	0.686673000	-2.245317000
H	-5.522883000	1.701845000	-0.809224000
C	-5.191450000	-2.269459000	0.761356000
H	-4.239321000	-2.765965000	0.979381000
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C	-5.423999000	-2.230243000	-0.757283000
H	-5.444793000	-3.250127000	-1.152467000
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C	-4.027529000	-0.050508000	0.664683000
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F	6.178868000	2.357191000	0.140681000
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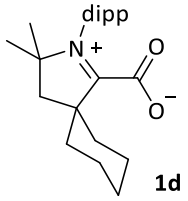

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C	3.024097000	-1.531187000	-0.076591000
C	3.966054000	-1.059522000	-1.181882000
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C	-4.149824000	0.621412000	-0.629070000
C	-3.701760000	-0.681344000	-0.467576000
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H	-3.111147000	-3.093681000	-1.771532000
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H	-1.892555000	3.707972000	-1.860985000
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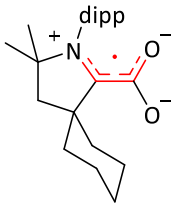

[1d$^{\bullet-}$]

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H	5.878093000	-0.936640000	0.333164000
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C	0.171033000	-0.566308000	1.804477000
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C	0.829505000	-0.334714000	-0.488911000
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C	-1.714058000	1.598078000	0.018393000
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H	-4.761458000	-0.777291000	-0.353896000
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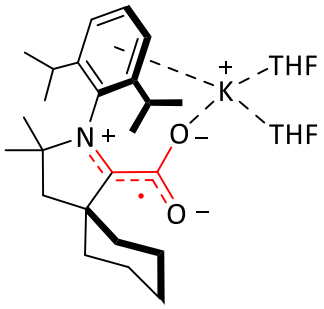

$[1d^{\bullet-}][K^+]\cdot(THF)_2$

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H	-7.670879000	1.429418000	-0.906395000

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H	-4.307237000	0.698626000	-2.432612000
H	-4.359528000	-1.043228000	-2.153207000
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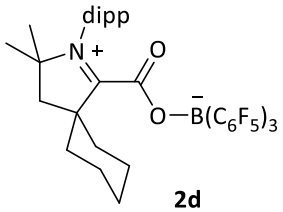

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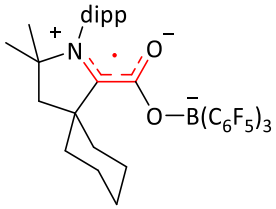

[2d$^{\bullet-}$]

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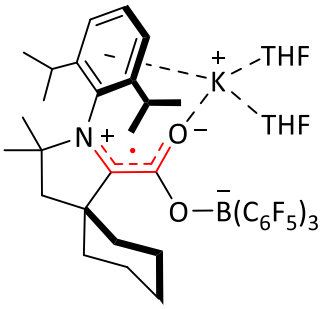

[2d$^{\bullet-}$][K^{+}]·(THF)$_2$

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C	-5.640018000	-0.628450000	-0.052321000
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H	2.555649000	5.532581000	-0.841207000
C	0.433776000	5.092559000	-2.488723000
H	1.403649000	4.917326000	-2.957390000

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C	2.174291000	3.108570000	1.783255000
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C	3.026080000	4.003114000	2.687480000
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H	3.342121000	4.914044000	2.173025000
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C	1.726956000	0.635930000	-3.490834000
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O	3.284532000	-2.261355000	-2.025132000
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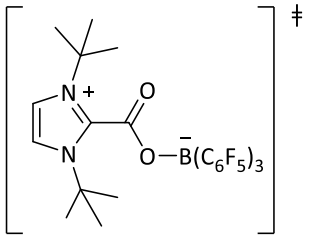

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C	-3.156520000	0.053097000	0.374340000
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C	2.738669000	-0.697948000	3.789675000
C	1.059835000	1.478328000	-0.797426000
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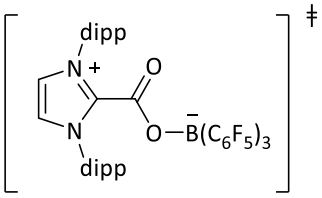

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F	2.324508000	-3.475552000	2.966261000
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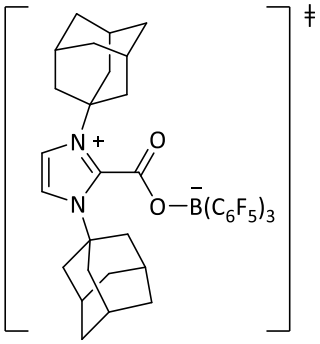

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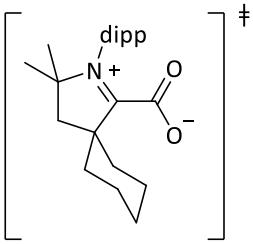

[1d]‡

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C	0.256484000	-0.099619000	1.906009000
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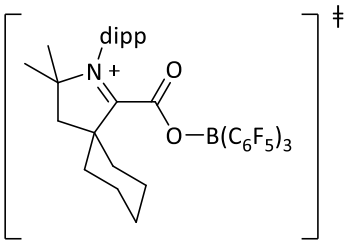

[2d]‡

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5 References

1. E. Theuergarten, T. Bannenberg, M. D. Walter, D. Holschumacher, M. Freytag, C. G. Daniliuc, P. G. Jones and M. Tamm, Computational and experimental investigations of CO_2 and N_2O fixation by sterically demanding N-heterocyclic carbenes (NHC) and NHC/borane FLP systems, *Dalton Trans.* **2014**, *43*, 1651-1662.
2. L. E. Lieske, L. A. Freeman, G. Wang, D. A. Dickie, R. J. Gilliard Jr. and C. W. Machan, Metal-Free Electrochemical Reduction of Carbon Dioxide Mediated by Cyclic(Alkyl)(Amino) Carbenes, *Chem. Eur. J.* **2019**, *25*, 6098-6101.
3. G. Sheldrick, SHELXT - Integrated space-group and crystal-structure determination, *Acta Crystallographica Section A* **2015**, *71*, 3-8.
4. L. Farrugia, WinGX suite for small-molecule single-crystal crystallography, *J. Appl. Crystallogr.* **1999**, *32*, 837-838.
5. P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout and D. J. Watkin, CRYSTALS version 12: software for guided crystal structure analysis, *J. Appl. Crystallogr.*, **2003**, *36*, 1487.
6. W. Schmitz, International Tables for X-ray Crystallography, vol. IV. The Kynoch Press, Birmingham, England, 1974., *Kristall und Technik* **1975**, *10*, K120-K120.
7. L. Farrugia, ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface (GUI), *J. Appl. Crystallogr.*, **1997**, *30*, 565.
8. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian16, Rev. B.01*; Gaussian, Inc., Wallingford CT, **2016**.
9. Y. Zhao and D. G. Truhlar, The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals, *Theor. Chem. Acc.* **2008**, *120*, 215-241.
10. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, *J. Chem. Phys.* **2010**, *132*, (15), 154104.
11. A. V. Marenich, C. J. Cramer and D. G. Truhlar, Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions, *The Journal of Physical Chemistry B* **2009**, *113*, 6378-6396.
12. R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions, *J. Chem. Phys.* **2008**, *72*, 650-654.

13. a) F. Weigend and R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305; b) K. A. Peterson, D. Figgen, E. Goll, H. Stoll and M. Dolg, Systematically convergent basis sets with relativistic pseudopotentials. II. Small-core pseudopotentials and correlation consistent basis sets for the post-d group 16–18 elements, *J. Chem. Phys.* **2003**, *119*, 11113-11123.
14. IboView - program for analysing molecular electronic structure, based on Intrinsic Atomic Orbitals (IAOs). http://www.iboview.org. G. Knizia, *J. Chem. Theory Comput.* **2013**, *9*, 4834–4843.
15. F. Neese, Software update: The ORCA program system—Version 5.0, *WIREs Computational Molecular Science* **2022**, *12*, e1606.
16. F. Neese, A. Hansen and D. G. Liakos, Efficient and Accurate Approximations to the Local Coupled Cluster Singles Doubles Method Using a Truncated Pair Natural Orbital Basis. *The Journal of Chemical Physics* **2009**, *131* (6), 064103.
17. S. Stoll and A. Schweiger, EasySpin, a Comprehensive Software Package for Spectral Simulation and Analysis in EPR. *Journal of Magnetic Resonance* **2006**, *178* (1), 42–55.