Heteroleptic copper(I) complexes [Cu(dmp)(N^P)]BF_4 for photoinduced atom-transfer radical addition reactions

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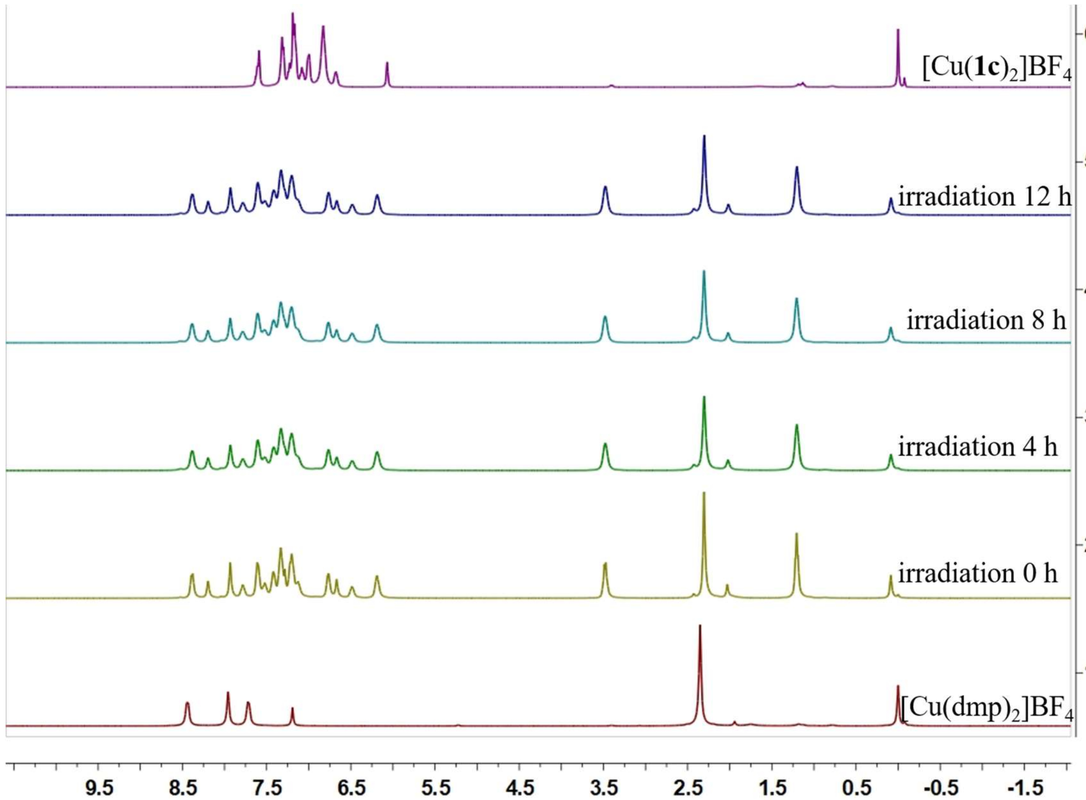


Fig. S1. ¹H NMR of compound **2c** in $CDCl_3$ with visible light irradiation time and ¹H NMR of $Cu(\mathbf{1c})_2BF_4$ and $Cu(dmp)_2BF_4$ in $CDCl_3$.

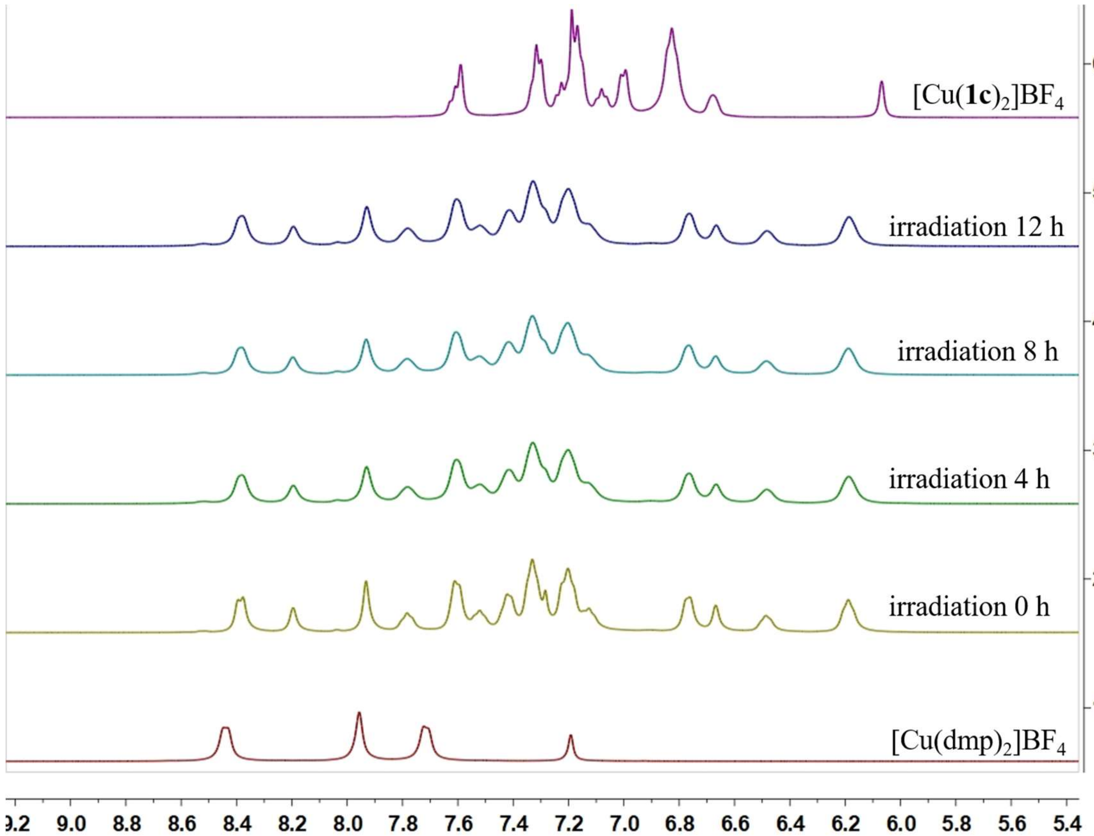


Fig. S2. Enlarge of aromatic area of **Fig. S1**.

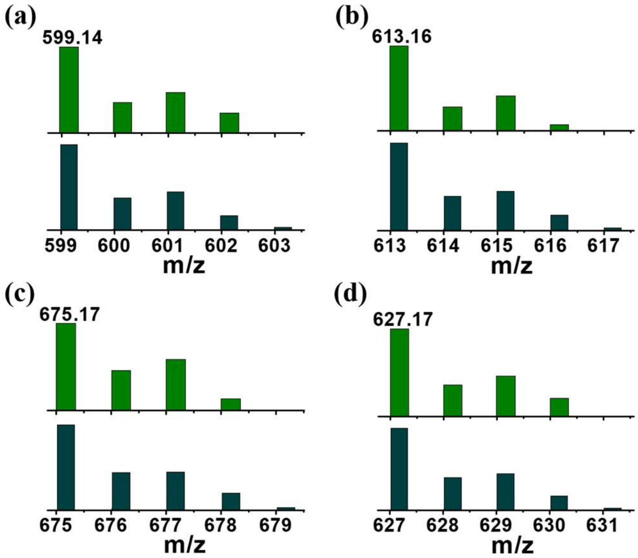


Fig. S3 The ESI-MS spectra of **2a** (a), **2b** (b), **2c** (c), **2d** (d). The calculated isotope patterns (lower) and observed patterns (upper) of $[M]^+$ for cations of **2a-2d**.

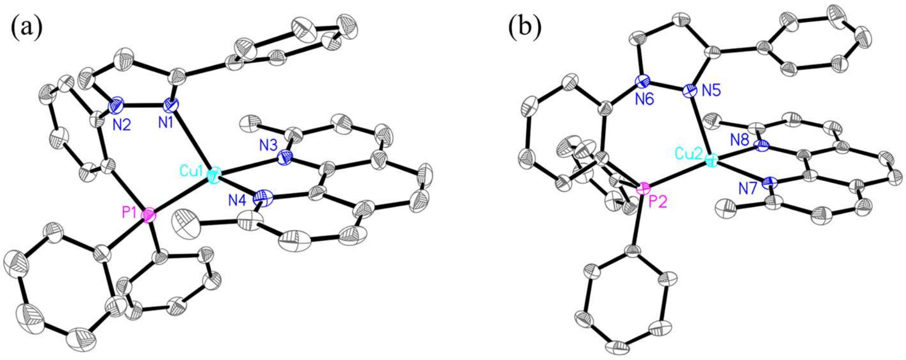


Fig. S4. View of two $[(PhC_3H_2N_2PPh_3)Cu(dmp)]^+$ cations (a and b) in **2c** with a labelling scheme and 30% thermal ellipsoids. All H atoms, uncoordinated molecules and BF_4^- anions are omitted for clarity.

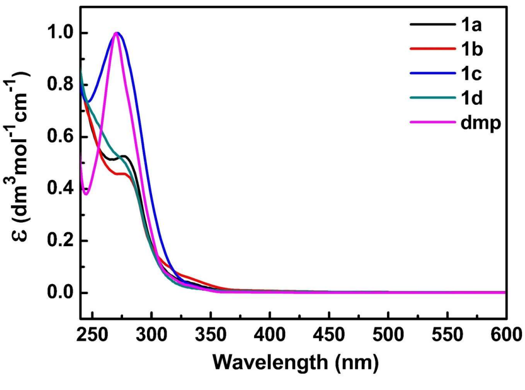


Fig. S5. UV/vis absorption spectrum of **1a-1d** and dmp in CH_2Cl_2 solution (c = 2 × 10^{-5} M) at room temperature.

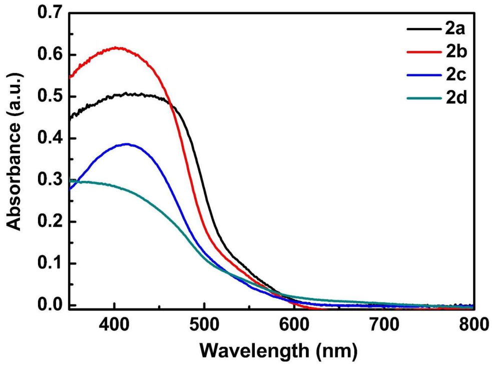


Fig. S6. UV/vis absorption spectrum of **2a-2d** in the solid state.

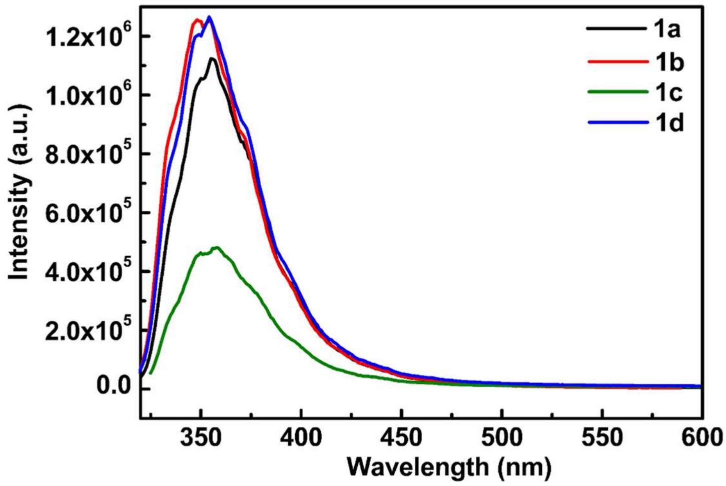


Fig. S7. Emission spectra of **1a-1d** measured in CH_2Cl_2 solution (c = 2 × 10^{-5} M) at room temperature (E_x = 305 nm).

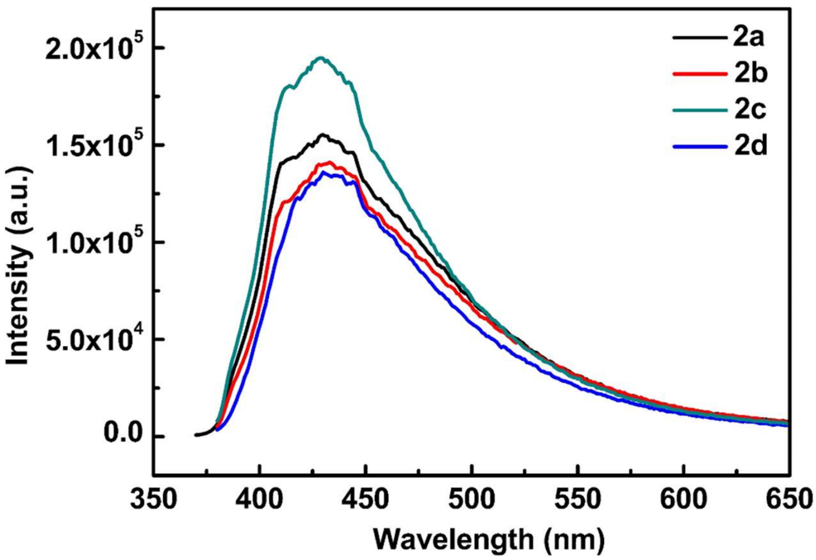


Fig. S8. Emission spectra of **2a-2d** measured in CH_2Cl_2 solution (c = 2 × 10^{-5} M) at room temperature (E_x = 400 nm).

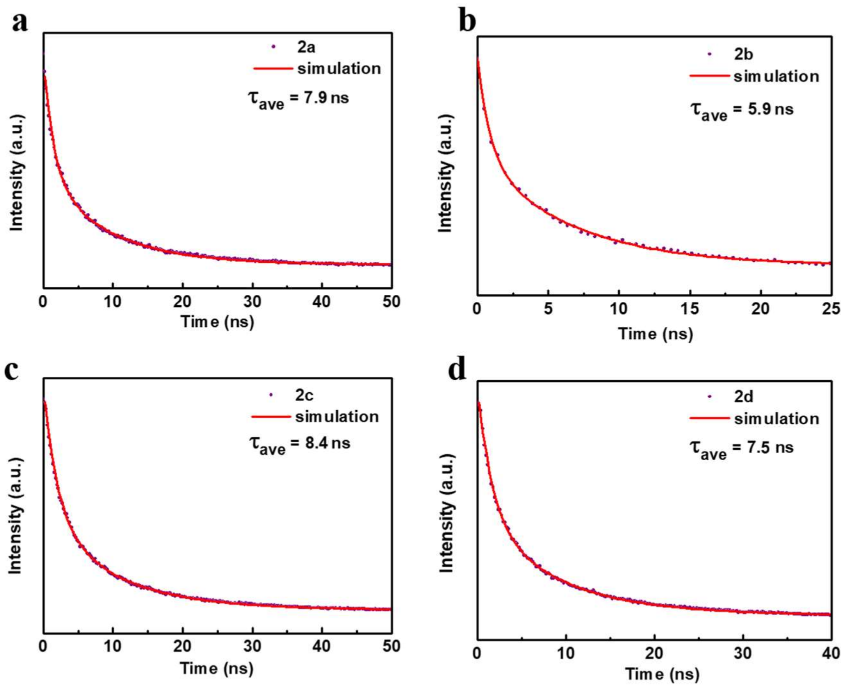


Fig. S9. Time dependences of the emission intensity of **2a** (a), **2b** (b), 2c (c) and **2d** (d) measured at room temperature (E_x = 400 nm) in CH_2Cl_2 solution (c = 2 × 10^{-5} M).

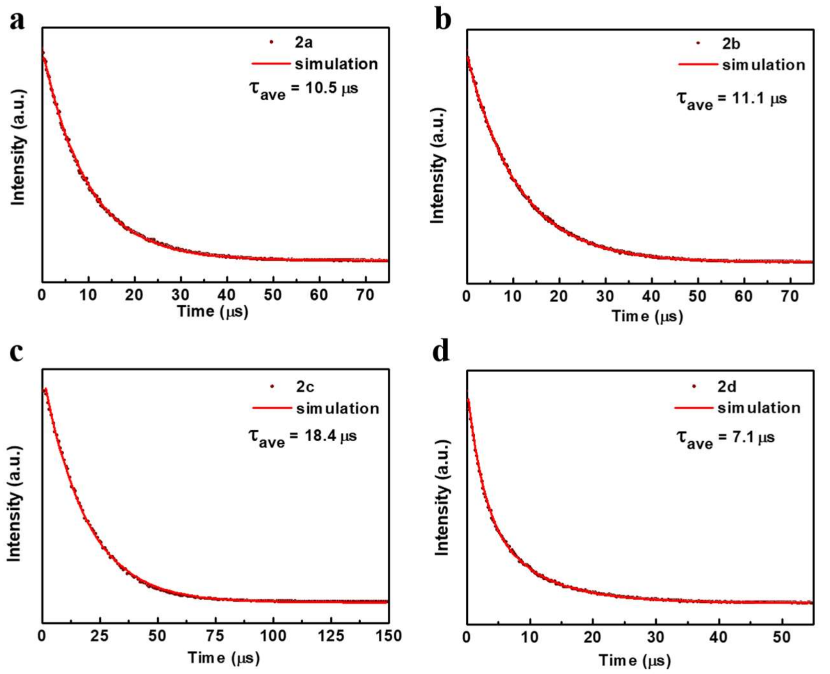


Fig. S10. Time dependences of the emission intensity of **2a** (a), **2b** (b), 2c (c) and **2d** (d) measured at room temperature (E_x = 400 nm) in solid state.

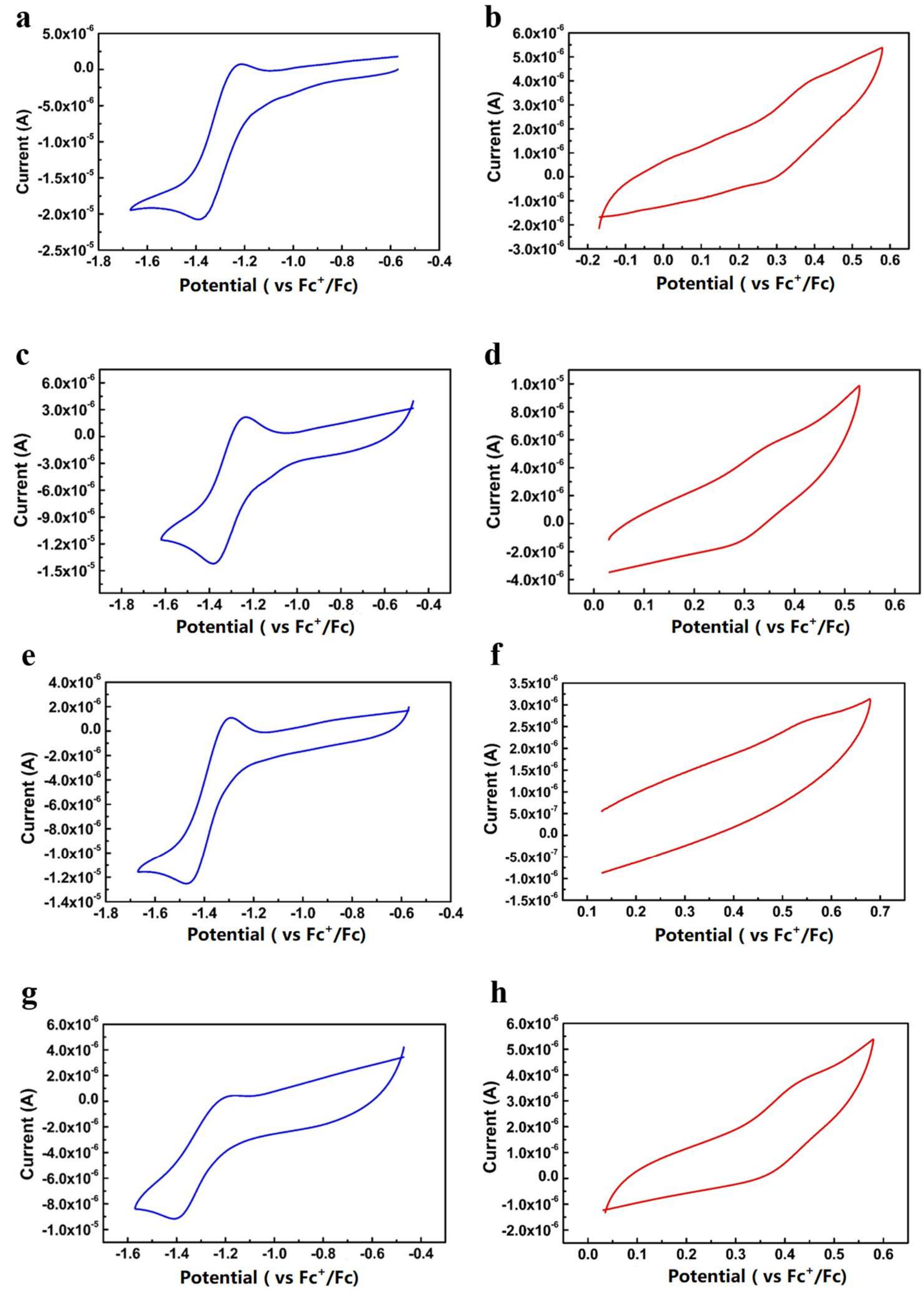


Fig. S11. Cyclic voltammograms of **2a** (a, b), **2b** (c, d), **2c** (e, f) and **2d** (g, h) (1 $mmol\cdot L^{-1}$) (0.10 $mol\cdot L^{-1}$ $^{n}Bu_4NPF_6/CH_2Cl_2$ electrolyte) at 100 mV/s scan rate under an argon atmosphere. Working electrode: glassy carbon electrode tip (3 mm diameter); Counter electrode: platinum wire. The excited-state energy E_{00} (1240/521.5 = 2.38 V (**2a**), 1240/519.5 = 2.39 V (**2b**), 1240/507.6 = 2.44 V (**2c**), 1240/528 = 2.35 V (**2d**)) was obtained from absorption spectra, respectively. The oxidation potential and reduction potential of *__2a__-*__2d__ were calculated, according to $E_{ox}^{*} = E_{ox} - E_{00}$.

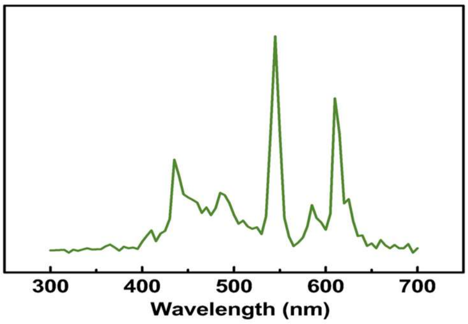


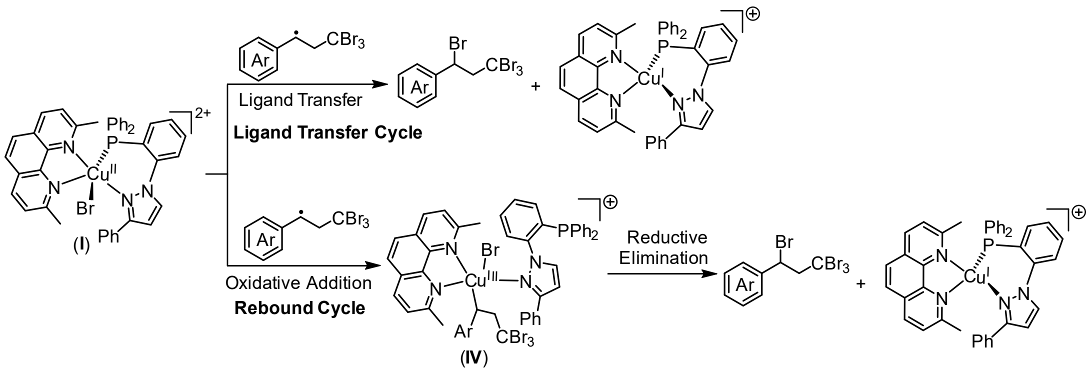
Fig. S12. Emission spectrum of 45 W CFL.

The reaction quantum yield[S1]

Φ = Mole number for product/Mole number for absorption of photons = 2.38

$$\phi = \frac{nN_A/t}{fP\lambda/hc}$$

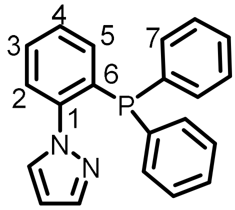
n: the mole number of the product 6; t: reaction time (1800 s); N_A: 6.02×10^{23}/mol; f: $1-10^{-A}$ (455 nm, A = 0.685); P: P = E*S (E: illumination intensity, E = 10.2 mW/cm^2 ; S: the area of irradiation S = 1 cm^2); λ: wavelength (λ = 4.55×10^{-7} m); h: planck constant (h = 6.626×10^{-34} J*s); c: velocity of light (c = 3×10^{8} m/s).



Scheme S1 Possible mechanistic pathways of ligand transfer cycle and rebound cycle.

Characterization Data

1-(2-(Diphenylphosphanyl)phenyl)-1H-pyrazole (1a)[S2]



Anal. Calcd. for $C_{21}H_{17}N_2P$: C, 76.82; H, 5.22; N, 8.53%. Found: C, 76.74; H, 5.31; N, 8.74%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.59 (m, 1H), 7.50 – 7.40 (m, 3H), 7.35 – 7.25 (m, 11H), 7.02 (dd, $^3J_{HH}$ = 7.3, $^4J_{HH}$ = 3.1 Hz, 1H, H5), 6.25 (m, 1H).

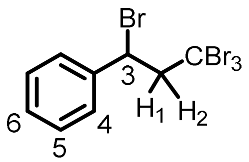
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, ppm): δ = 144.6 (d, $^2J_{CP}$ = 21.2 Hz, C1), 140.4, 136.6 (d, $^1J_{CP}$ = 11.2 Hz, C6), 134.8, 133.9 (d, $^2J_{CP}$ = 20.5 Hz, C7), 131.2 (d, $^3J_{CP}$ = 5.3 Hz, C2), 129.7, 128.9, 128.8, 128.6 (d, $^3J_{CP}$ = 7.2 Hz, C4), 128.2, 126.3 (d, $^4J_{CP}$ = 2.6 Hz, C3), 106.3.

^{31}P NMR (162 MHz, $CDCl_3$, ppm): δ = –14.5.

HRMS (ESI) *m/z* $[M + Na]^+$ Calcd for $C_{21}H_{17}N_2NaP^+$ 351.1022; Found 351.1062.

IR (KBr, *v*, selected peak, cm^{-1}): 1590, 1472, 1432, 1390, 1328, 1192, 1159, 1076, 1043, 1019, 932, 848, 745, 695.

(1,3,3,3-Tetrabromopropyl)benzene (5a)[S3]



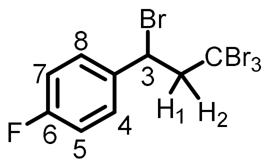
Following the general procedure, **5a** as a white solid was obtained from flash column chromatography using PE as an eluent. Yield: 78.6 mg, 91%. m.p. 62-64 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.49 (m, 2H), 7.37 (m, 2H), 7.31 (t, $^3J_{HH}$ = 7.2 Hz, 1H, H6), 5.33 (dd, $^3J_{HH}$ = 7.7, $^3J_{HH}$ = 4.1 Hz, 1H, H3), 4.12 (dd, $^2J_{HH}$ = 15.6, $^3J_{HH}$ = 4.1 Hz, 1H, H2), 4.05 (dd, $^2J_{HH}$ = 15.6, $^3J_{HH}$ = 7.7 Hz, 1H, H1).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, ppm): δ = 140.8, 129.0, 128. 9, 128.2, 66.5, 50.1, 35.0.

HRMS (ESI) *m/z* $[M]^+$ Calcd for $C_9H_8Br_4^+$ 431.7360; Found 431.7369.

1-Fluoro-4-(1,3,3,3-tetrabromopropyl)benzene (5b)[S3]



Following the general procedure, **5b** as a colorless oil was obtained from flash column chromatography using PE as an eluent. Yield: 62.1 mg, 69%.

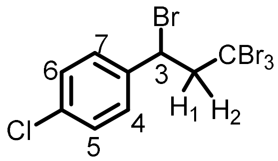
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.48 (dd, $^{3}J_{HH}$ = 8.7, $^{3}J_{FH}$ = 5.2 Hz, 2H, H5 or H7), 7.06 (m, 2H), 5.34 (dd, $^{3}J_{HH}$ = 8.4, $^{3}J_{HH}$ = 3.8 Hz, 1H, H3), 4.10 (dd, $^{2}J_{HH}$ = 15.5, $^{3}J_{HH}$ = 3.8 Hz, 1H, H2), 4.01 (dd, $^{2}J_{HH}$ = 15.5, $^{3}J_{HH}$ = 8.4 Hz, 1H, H1).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, ppm): δ = 162.8 (d, $^{1}J_{CF}$ = 248.9 Hz, C6), 136.6, 130.1 (d, $^{3}J_{CF}$ = 8.6 Hz, C4), 115.9 (d, $^{2}J_{CF}$ = 21.9 Hz, C5), 66.5, 49.1, 34.7.

^{9}F NMR (377 MHz, $CDCl_3$, ppm): δ = -112.0.

HRMS (ESI) *m/z* $[M]^+$ Calcd for $C_9H_7Br_4F^+$ 449.7265; Found 449.7272.

1-Chloro-4-(1,3,3,3-tetrabromopropyl)benzene (5c)[S3]



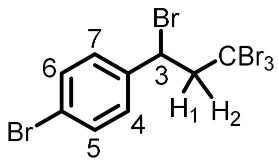
Following the general procedure, **5c** as a white solid was obtained from flash column chromatography using PE as an eluent. Yield: 83.5 mg, 90%. m.p. 69-74 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.43 (d, $^{3}J_{HH}$ = 8.5 Hz, 2H, H5 or H6), 7.34 (d, $^{3}J_{HH}$ = 8.5 Hz, 2H, H4 or H7), 5.31 (dd, $^{3}J_{HH}$ = 8.3, $^{3}J_{HH}$ = 3.8 Hz, 1H, H3), 4.10 (dd, $^{2}J_{HH}$ = 15.5, $^{3}J_{HH}$ = 3.8 Hz, 1H, H2), 4.01 (dd, $^{2}J_{HH}$ = 15.5, $^{3}J_{HH}$ = 8.3 Hz, 1H, H1).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, ppm): δ = 139.2, 134.8, 129.6, 129.1, 66.3, 48.9, 34.6.

HRMS (ESI) *m/z* $[M]^+$ Calcd for $C_9H_7Br_4Cl^+$ 465.6970; Found 465.6968.

1-Bromo-4-(1,3,3,3-tetrabromopropyl)benzene (5d)[S3]



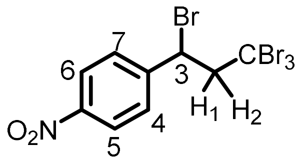
Following the general procedure, **5d** as a white solid was obtained from flash column chromatography using PE as an eluent. Yield: 50.5 mg, 50%. m.p. 88-95 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.43 (d, $^{3}J_{HH}$ = 8.5 Hz, 2H, H5 or H6), 7.34 (d, $^{3}J_{HH}$ = 8.5 Hz, 2H, H4 or H7), 5.31 (dd, $^{3}J_{HH}$ = 8.3, $^{3}J_{HH}$ = 3.8 Hz, 1H, H3), 4.10 (dd, $^{2}J_{HH}$ = 15.5, $^{3}J_{HH}$ = 3.8 Hz, 1H, H2), 4.01 (dd, $^{2}J_{HH}$ = 15.5, $^{3}J_{HH}$ = 8.3 Hz, 1H, H1).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, ppm): δ = 139.7, 132.1, 129.9, 123.0, 66.2, 48.9, 34.6.

HRMS (ESI) *m/z* $[M]^+$ Calcd for $C_9H_7Br_5^+$ 509.6465; Found 509.6469.

1-Nitro-4-(1,3,3,3-tetrabromopropyl)benzene (5g)[S4]



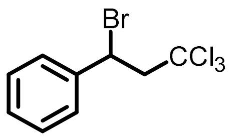
Following the general procedure, **5g** as a white solid was obtained from flash column chromatography using PE as an eluent. Yield: 26.7 mg, 28%. m.p. 88-91 °C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.24 (d, $^3J_{HH}$ = 8.7 Hz, 2H, H5 or H6), 7.68 (d, $^3J_{HH}$ = 8.7 Hz, 2H, H4 or H7), 5.38 (dd, $^3J_{HH}$ = 8.5, $^3J_{HH}$ = 3.7 Hz, 1H, H3), 4.15 (dd, $^2J_{HH}$ = 15.6, $^3J_{HH}$ = 3.7 Hz, 1H, H2), 4.05 (dd, $^2J_{HH}$ = 15.5, $^3J_{HH}$ = 8.5 Hz, 1H, H1).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, ppm): δ = 147.9, 147.5, 129.3, 124.2, 66.0, 47.4, 34.0.

HRMS (ESI) *m/z* $[M]^+$ Calcd for $C_9H_7Br_4NO_2^+$ 476.7210; Found 476.7218.

(1-Bromo-3,3,3-trichloropropyl)benzene (5k)[S5]



Following the general procedure, **5k** as a colorless oil was obtained from flash column chromatography using PE as an eluent. Yield: 37.2 mg, 62%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.47–7.43 (m, 2H), 7.39–7.33 (m, 2H), 7.31 (m, 1H), 5.37 (m, 1H), 3.75 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, ppm): δ = 140.8 128.9, 127.8, 127.4, 96.5, 62.6, 47.5.

HRMS (EI) m/z $[M]^+$ Calcd for $C_9H_8BrCl_3^+$ 299.8875; Found 299.8881.

References

S1 K. Zhang, L.-Q. Lu, Y. Jia, Y. Wang, F.-D. Lu, F. Pan and W.-J. Xiao, *Angew. Chem. Int. Ed.*, 2019, **58**, 13375−13379.

S2 J.-H. Jia, X.-L. Chen, J.-Z. Liao, D. Liang, M.-X. Yang, R. Yu and C.-Z. Lu, *Dalton Trans.*, 2019, **48**, 1418–1426.

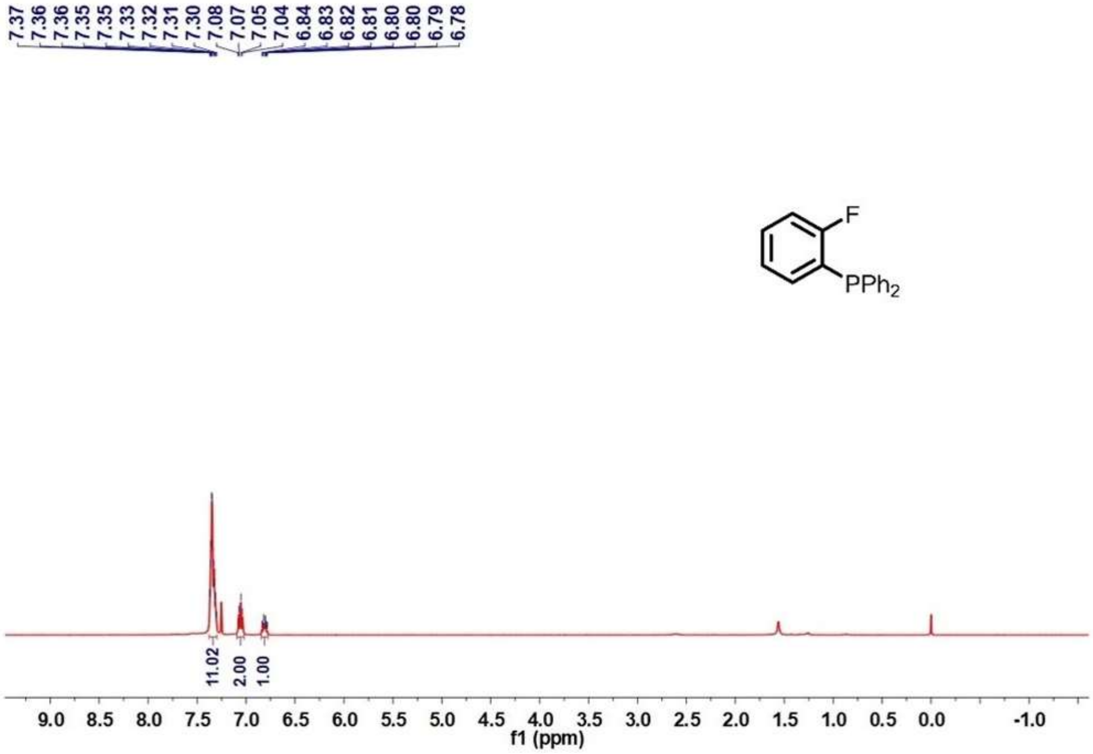
S3 K. Matsuo, E. Yamaguchi, A. Itoh, *J. Org. Chem.*, 2020, **85**, 10574-10583.

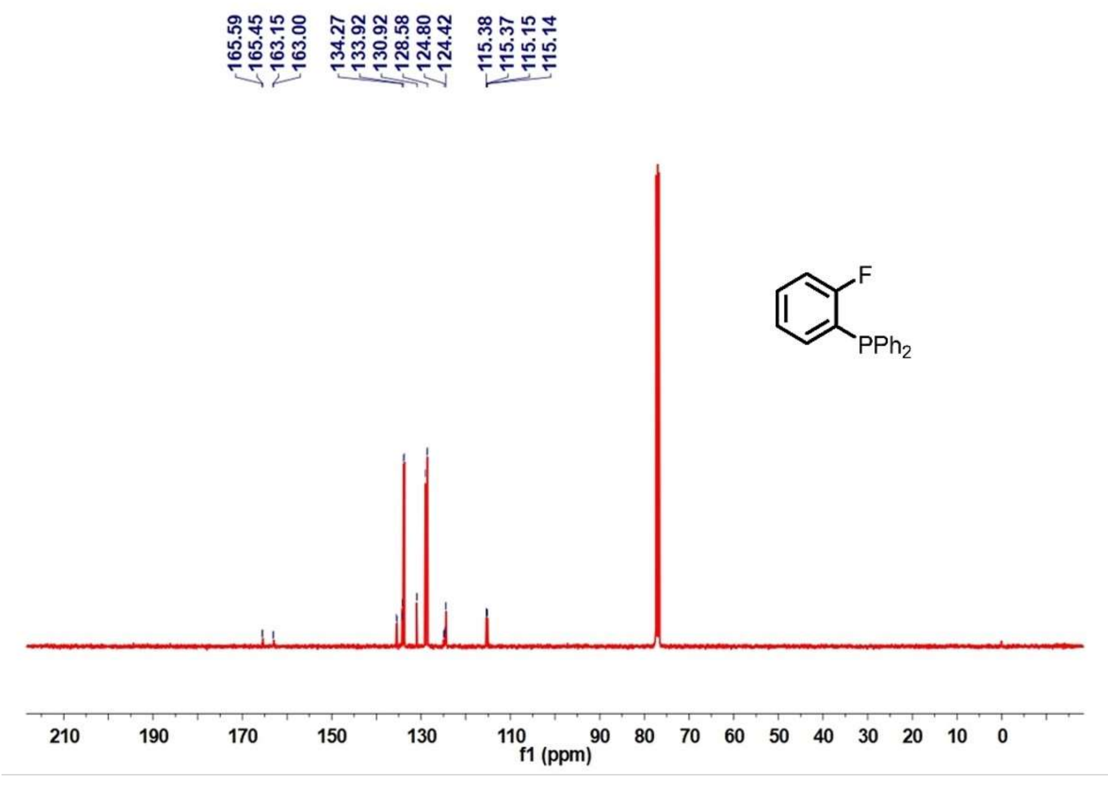
S4 C. X. Song, P. Chen and Y. Tang, *RSC Adv.*, 2017, **7**, 11233-112.

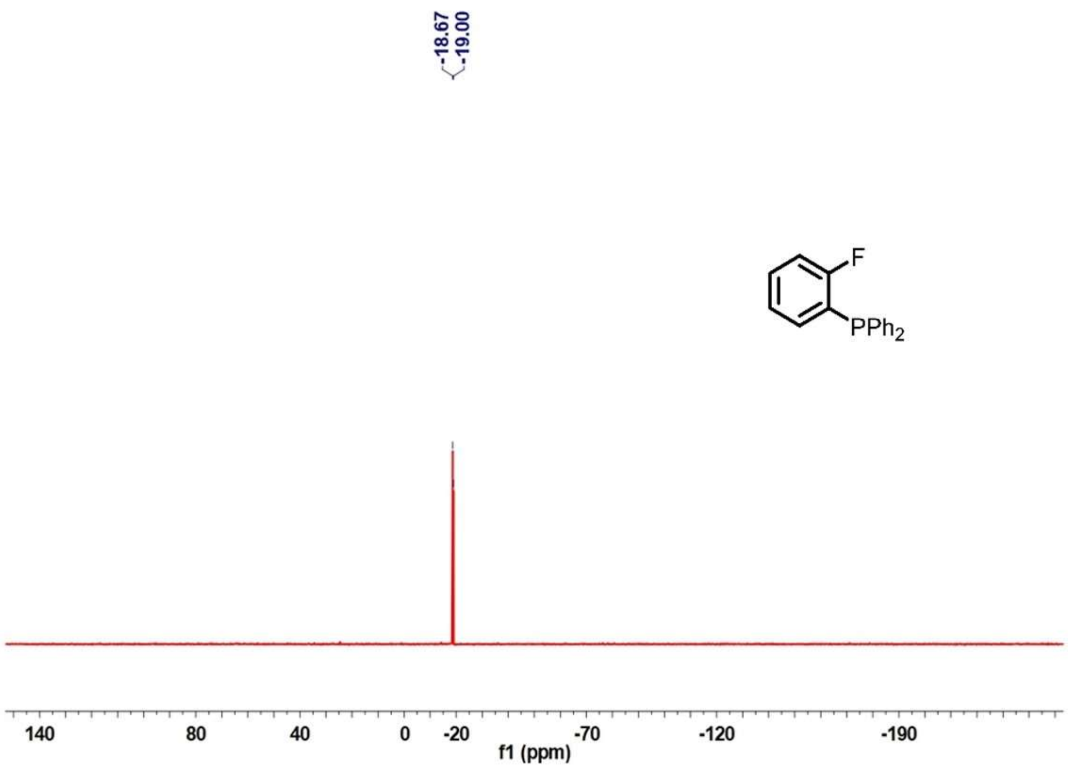
S6 Q. Yao and C. J. Li, *Chem. Commun.*, 2017, **53**, 11225-11228.

NMR spectra

Fig. S13. The ^{1}H (400 MHz), $^{13}C\{^{1}H\}$ (101 MHz), ^{31}P (162 MHz) and ^{19}F (377 MHz) NMR spectra for (2-fluorophenyl)diphenylphosphane in $CDCl_3$.






-18.67
-19.00
F
PPh2
140
80
40
0
-20
-70
-120
-190
f1 (ppm)

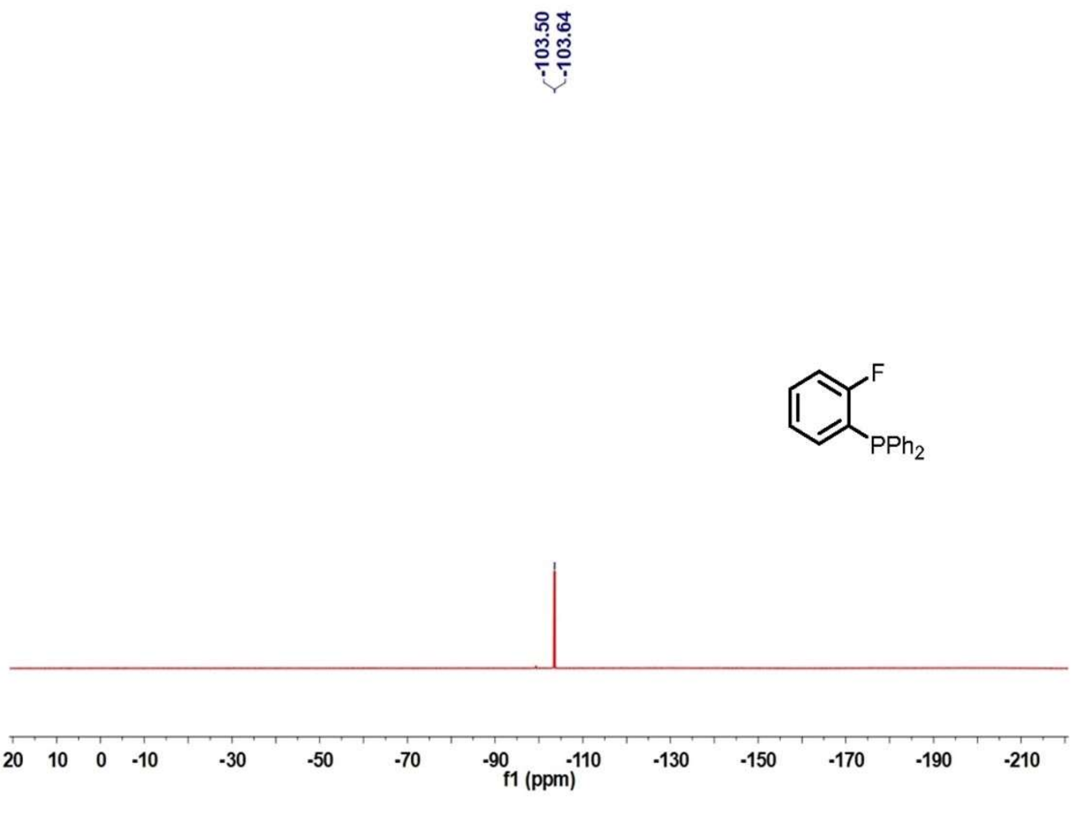
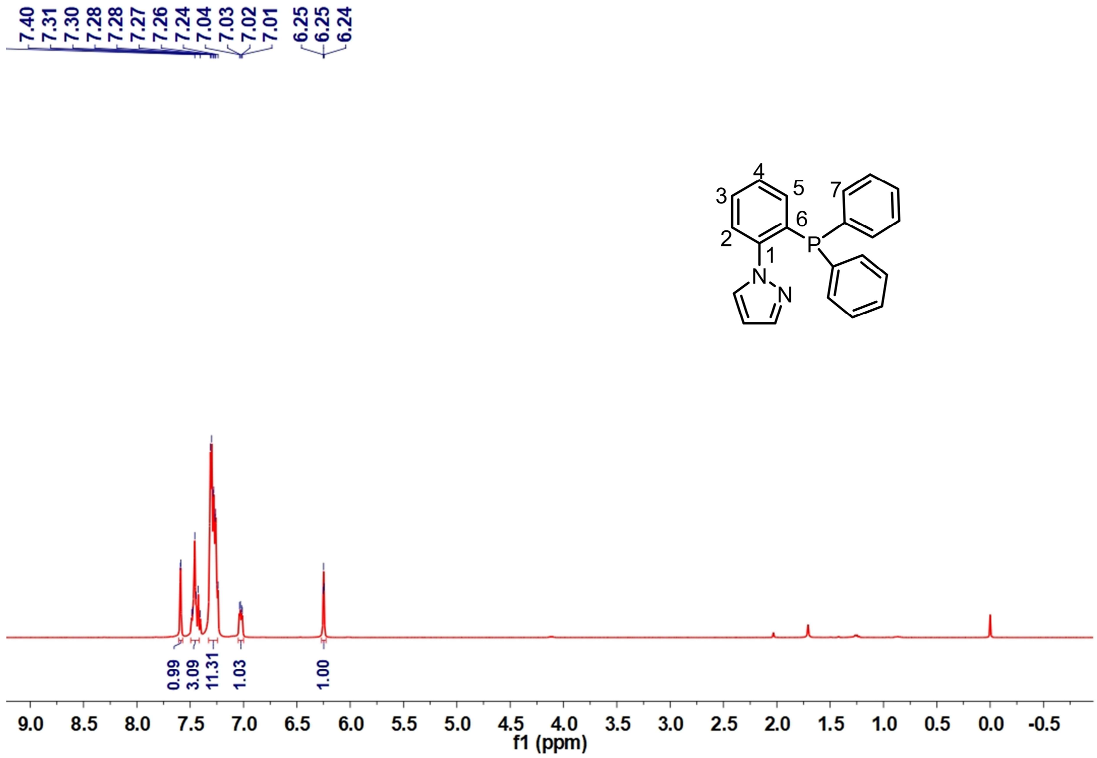
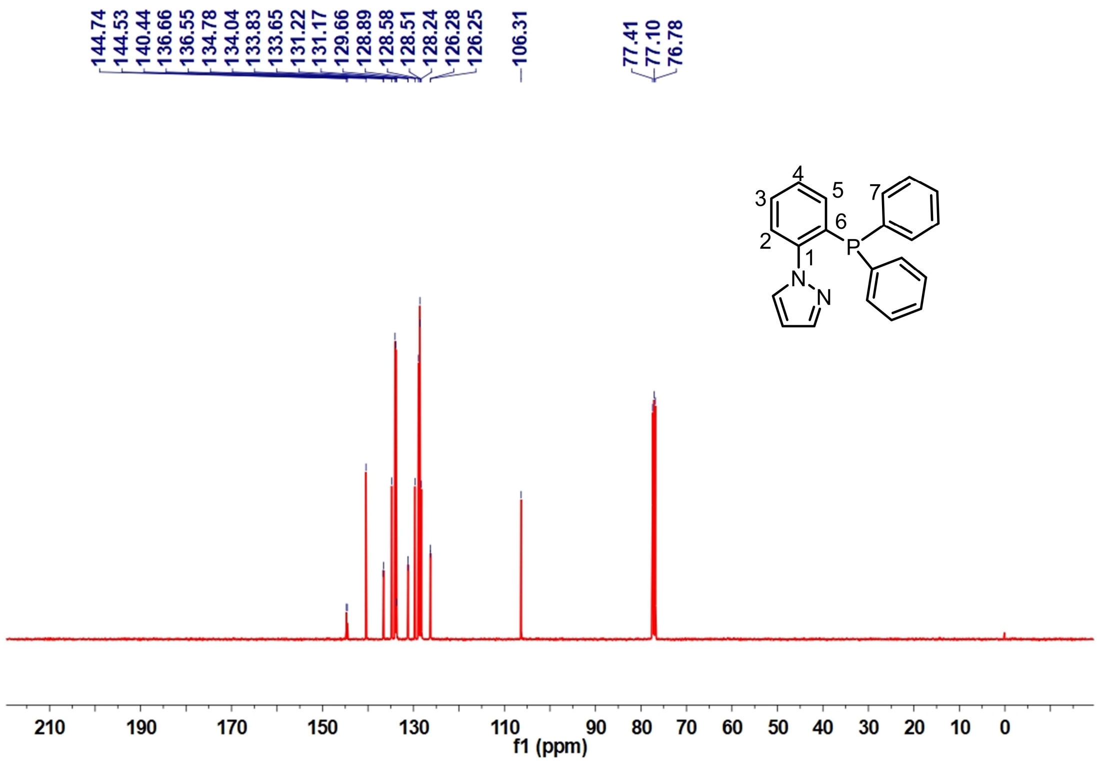
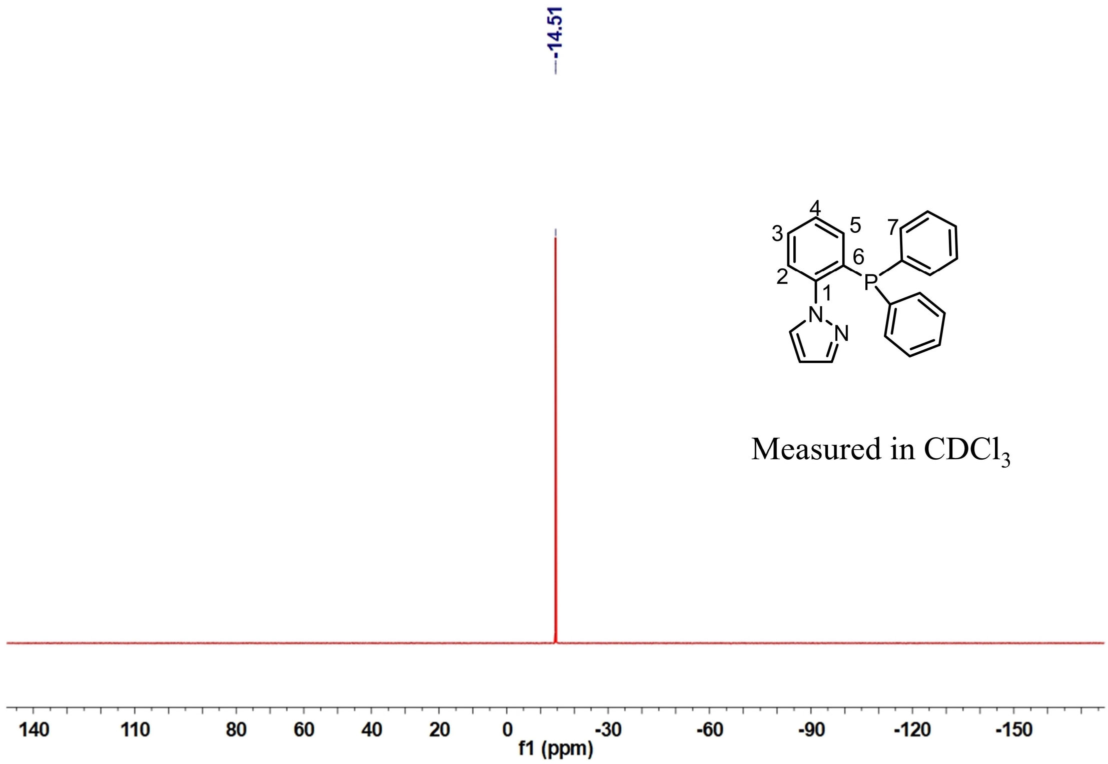

-103.50
-103.64
F
PPh2
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

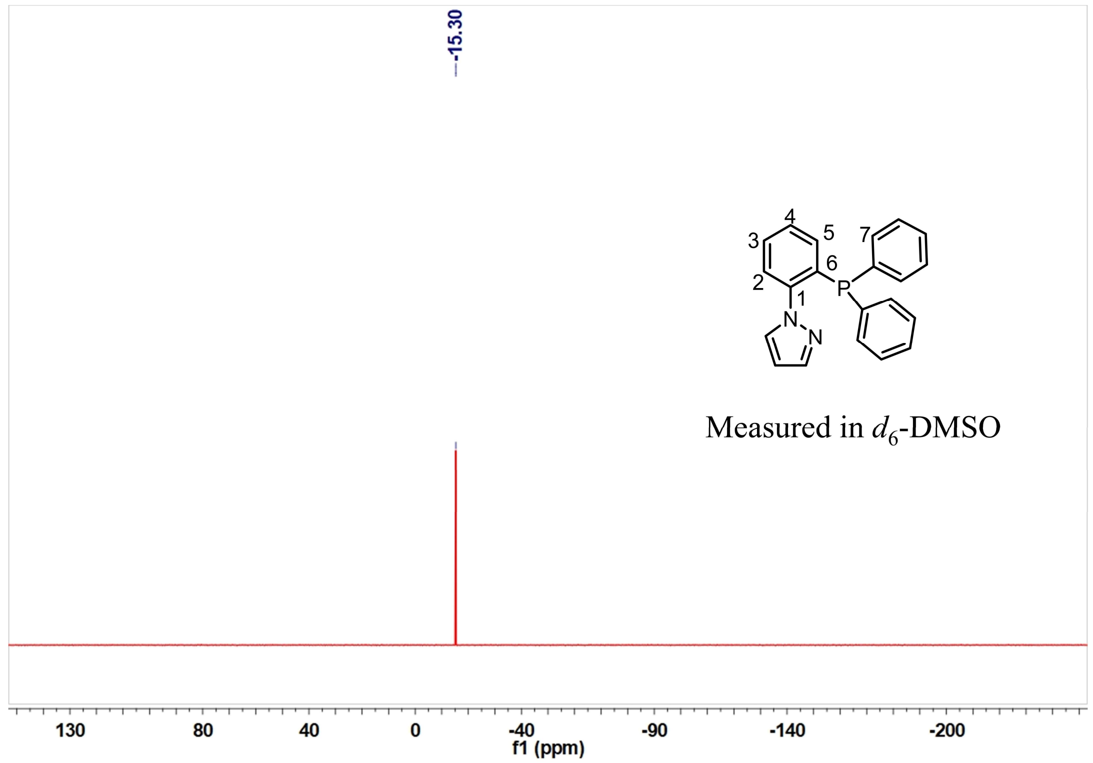
Fig. S14. The ^{1}H (400 MHz), $^{13}C\{^{1}H\}$ (101 MHz) and ^{31}P (162 MHz) NMR spectra for 1-(2-(diphenylphosphanyl)phenyl)-1H-pyrazole (**1a**) in $CDCl_3$ and ^{31}P (162 MHz) NMR spectra in d_6-DMSO.





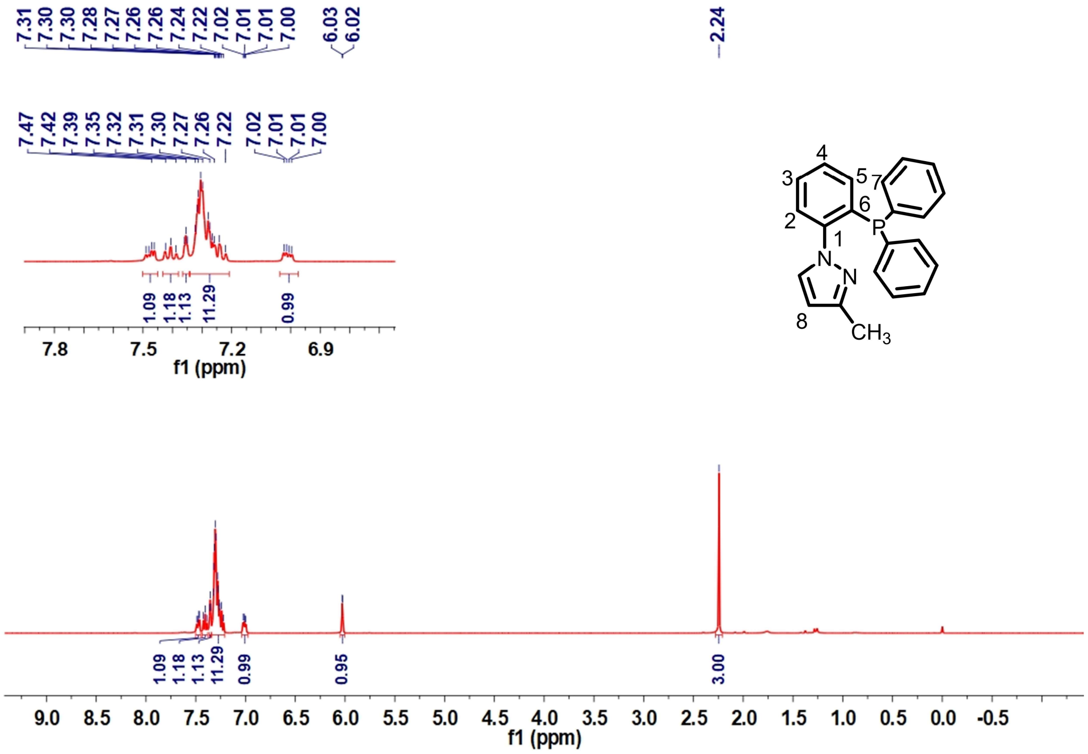


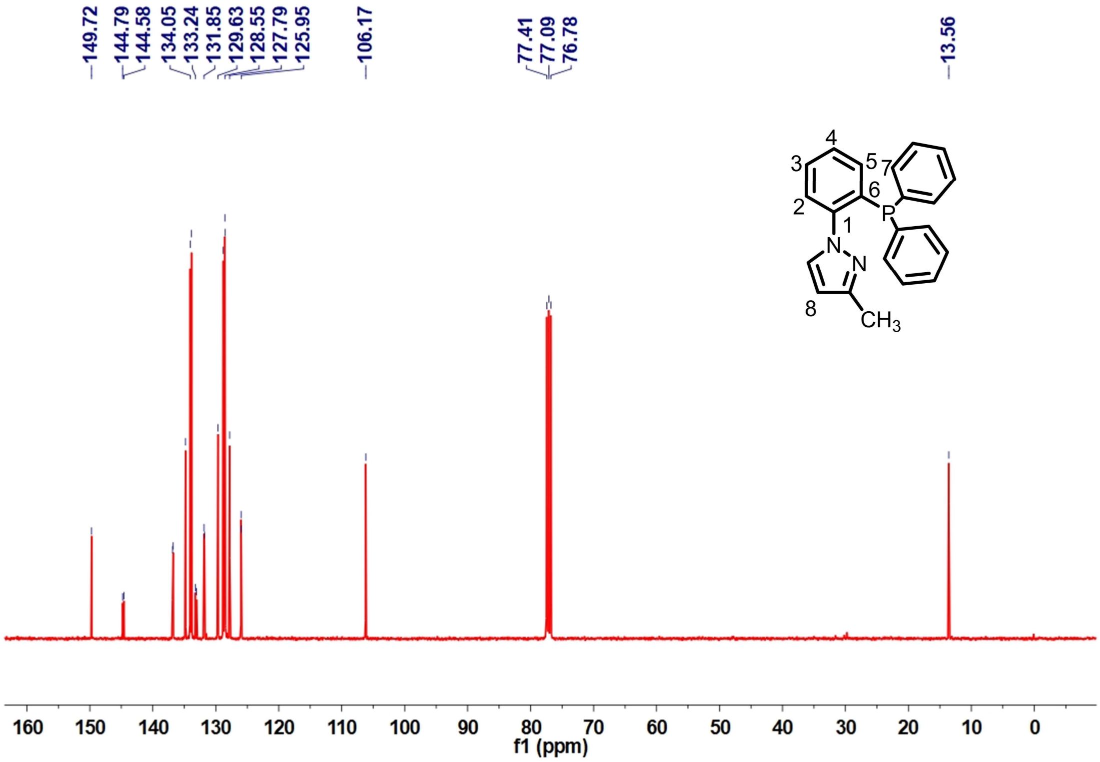
-14.51
4
3
5
7
6
2
P
1
N
N
Measured in CDCl3
140
110
80
60
40
20
0
-30
-60
-90
-120
-150
f1 (ppm)

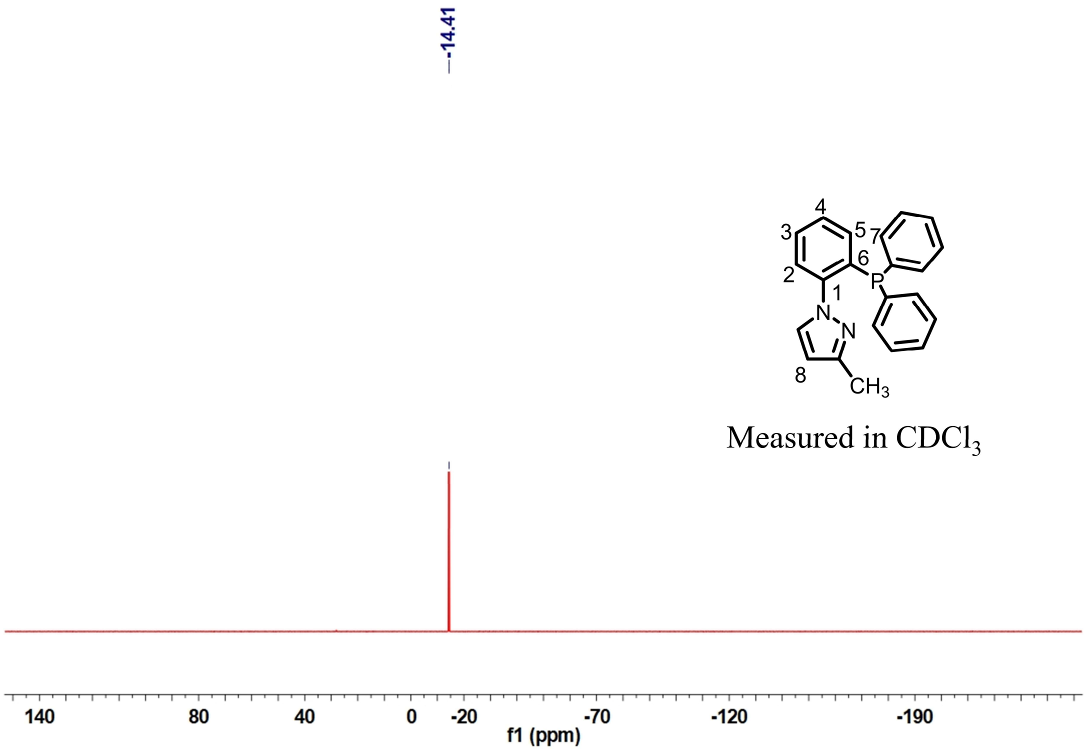


-15.30
4
3
5
7
6
2
P
1
N
N
Measured in d6-DMSO
130
80
40
0
-40
f1 (ppm)
-90
-140
-200

Fig. S15. The ^{1}H (400 MHz), $^{13}C\{^{1}H\}$ (101 MHz) and ^{31}P (162 MHz) NMR spectra for 1-(2-(diphenylphosphanyl)phenyl)-3-methyl-1H-pyrazole (**1b**) in $CDCl_3$ and ^{31}P (162 MHz) NMR spectra in d_6-DMSO.






-14.41
4
3
5
7
6
2
1
P
N
N
8
CH3
Measured in CDCl3
140
80
40
0
-20
-70
-120
-190
f1 (ppm)

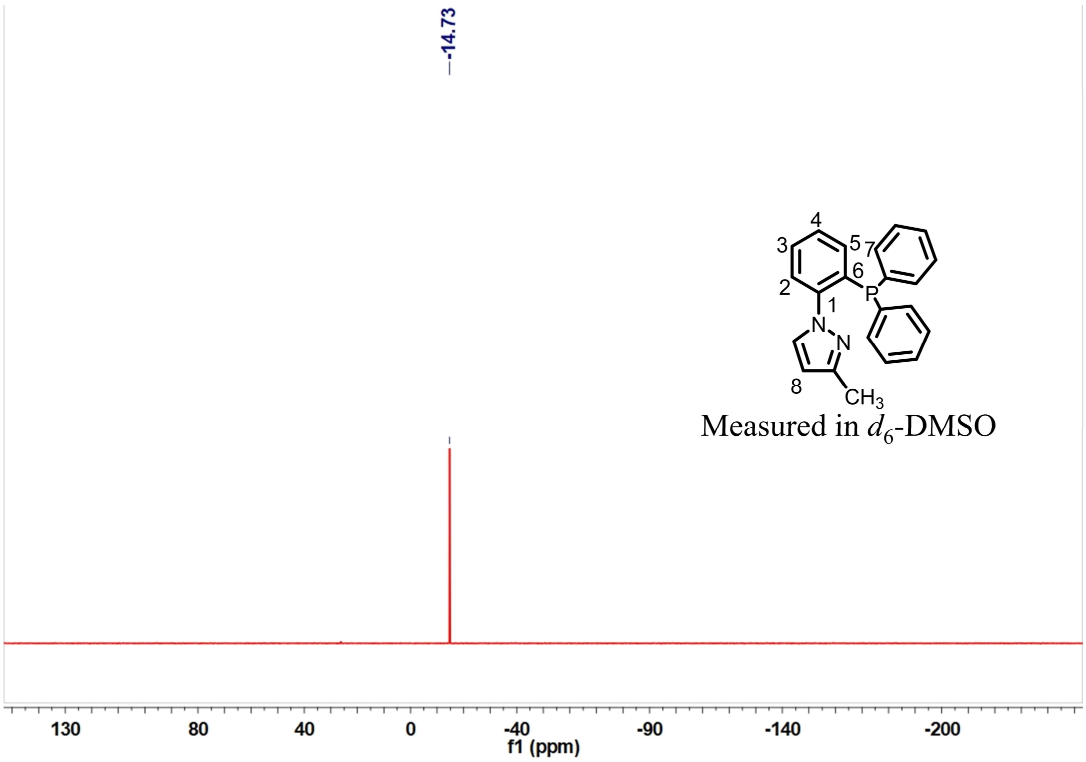
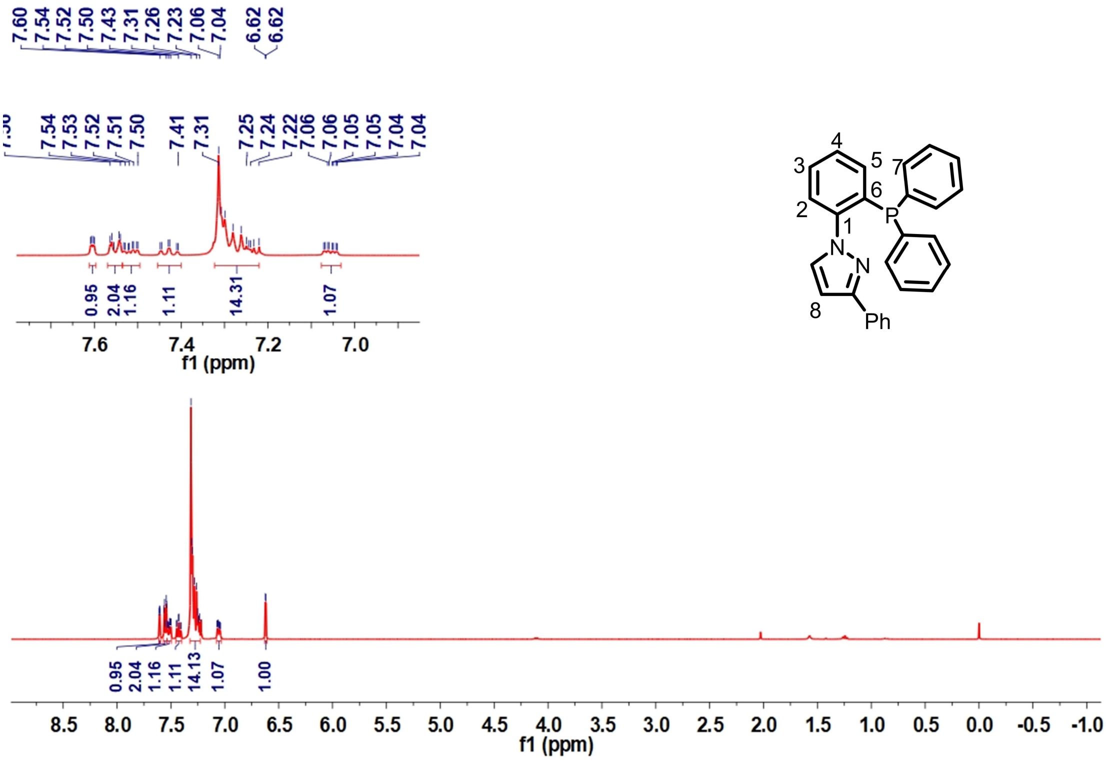
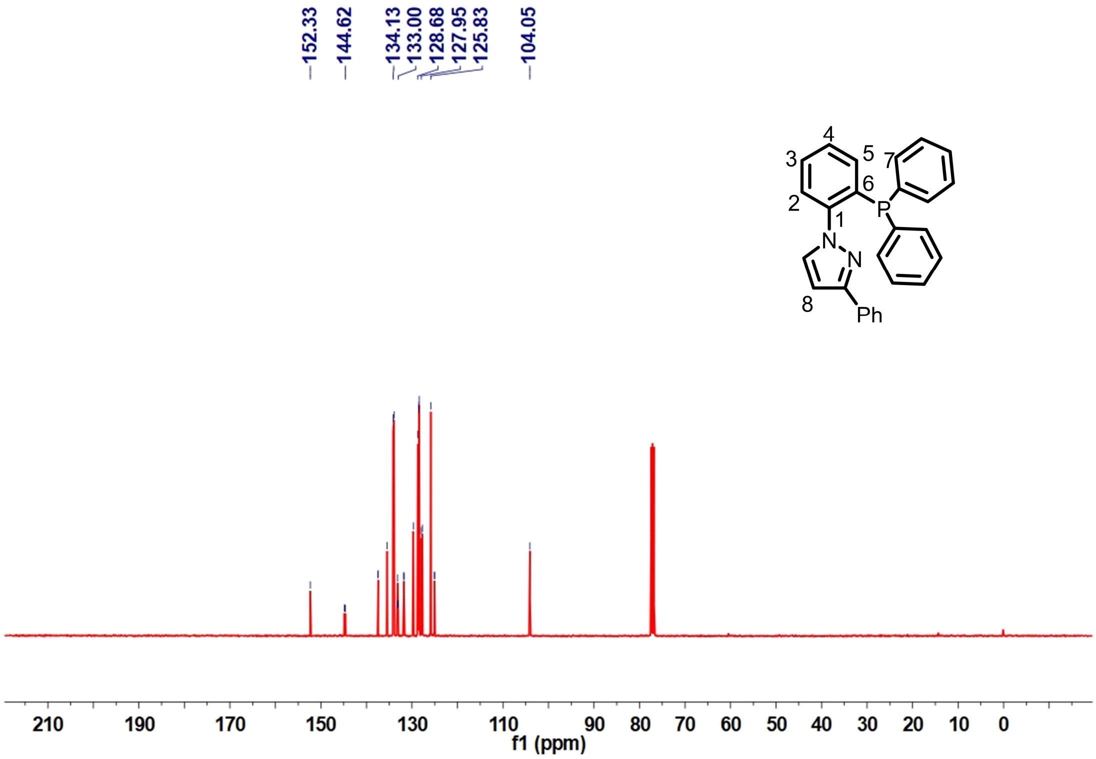
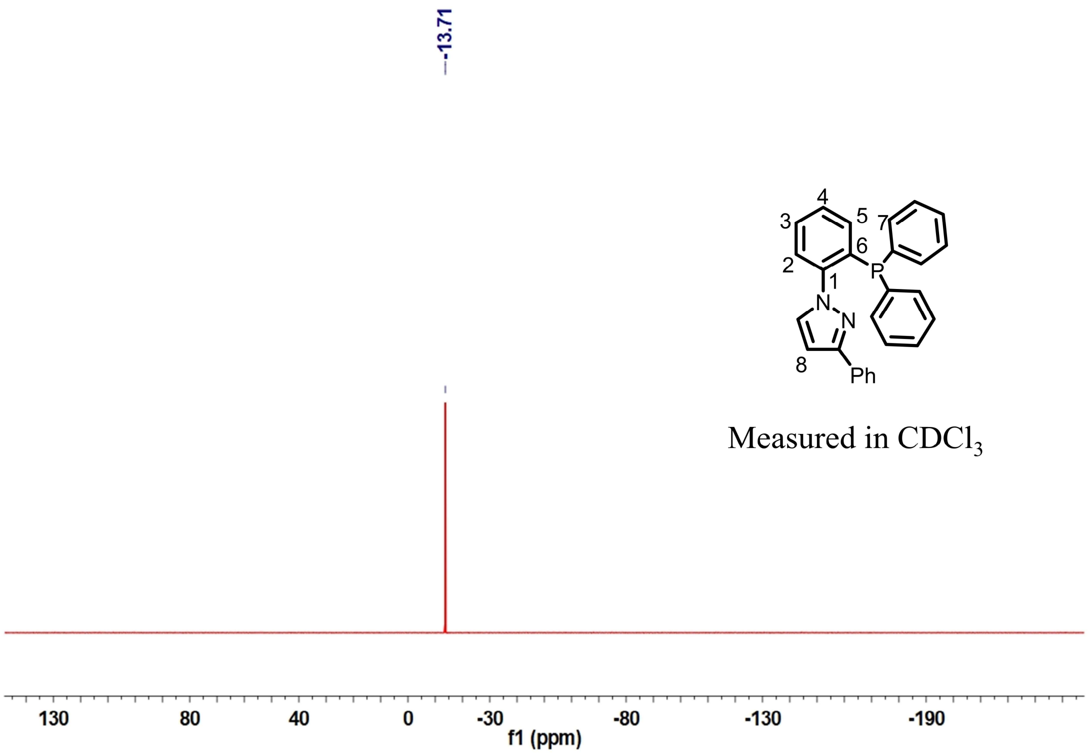

-14.73
4
3
5
7
6
2
1
P
N
N
8
CH3
Measured in d6-DMSO
130
80
40
0
-40
-90
-140
-200
f1 (ppm)

Fig. S16. The ^{1}H (400 MHz), $^{13}C\{^{1}H\}$ (101 MHz) and ^{31}P (162 MHz) NMR spectra for 1-(2-(diphenylphosphanyl)phenyl)-3-phenyl-1H-pyrazole (**1c**) in $CDCl_3$ and ^{31}P (162 MHz) NMR spectra in d_6-DMSO.






--13.71
Measured in $CDCl_3$
130
80
40
0
-30
-80
-130
-190
f1 (ppm)

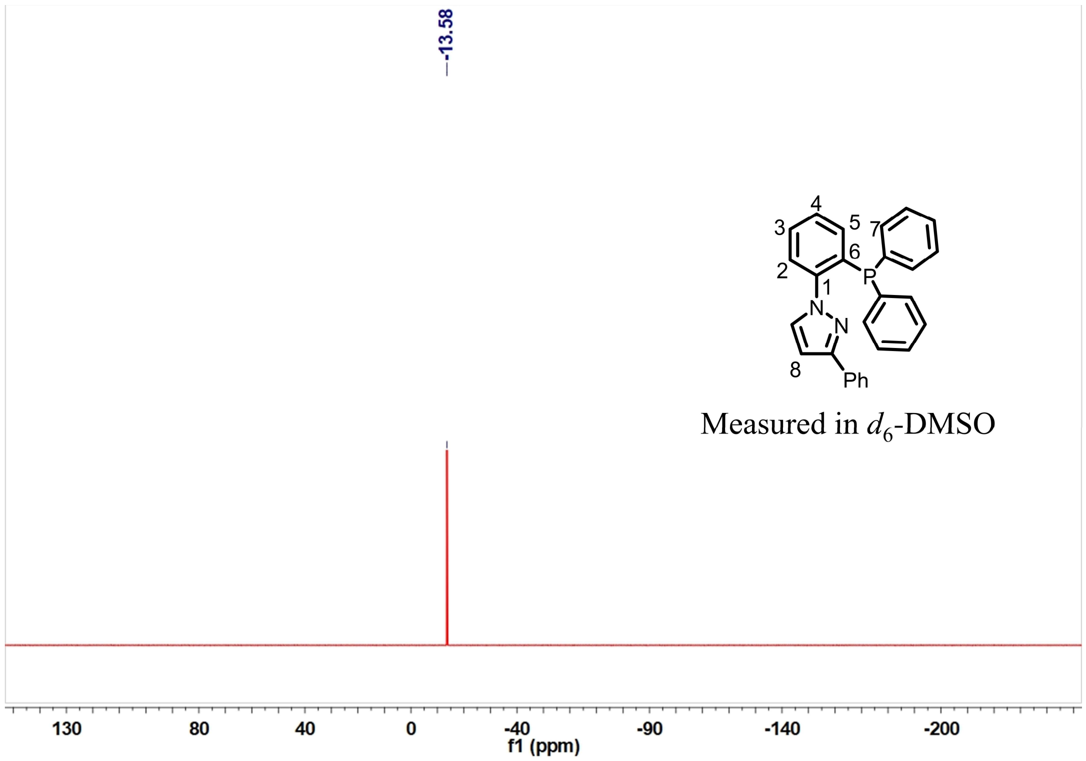
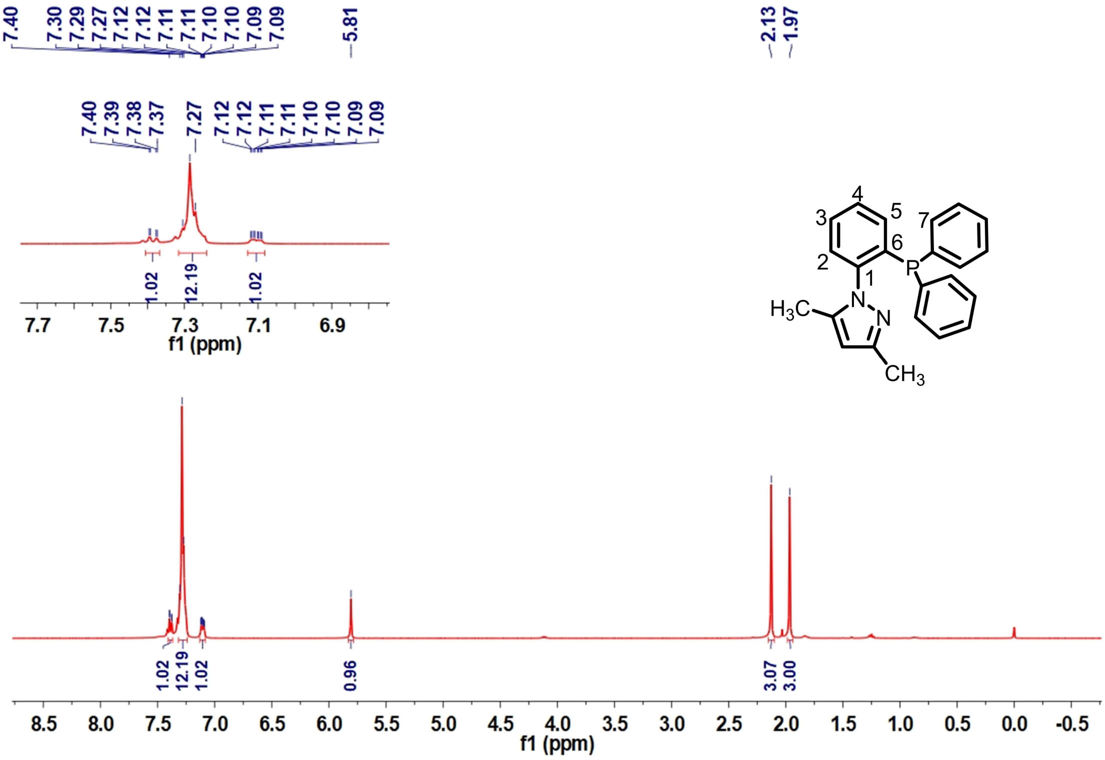
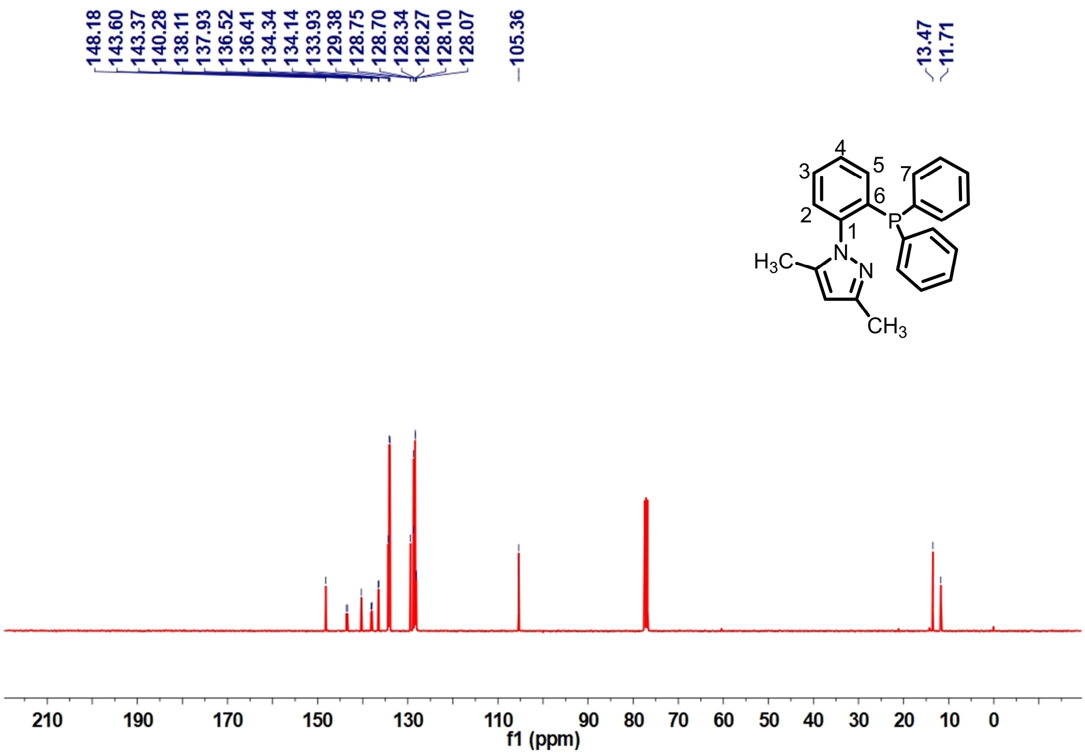
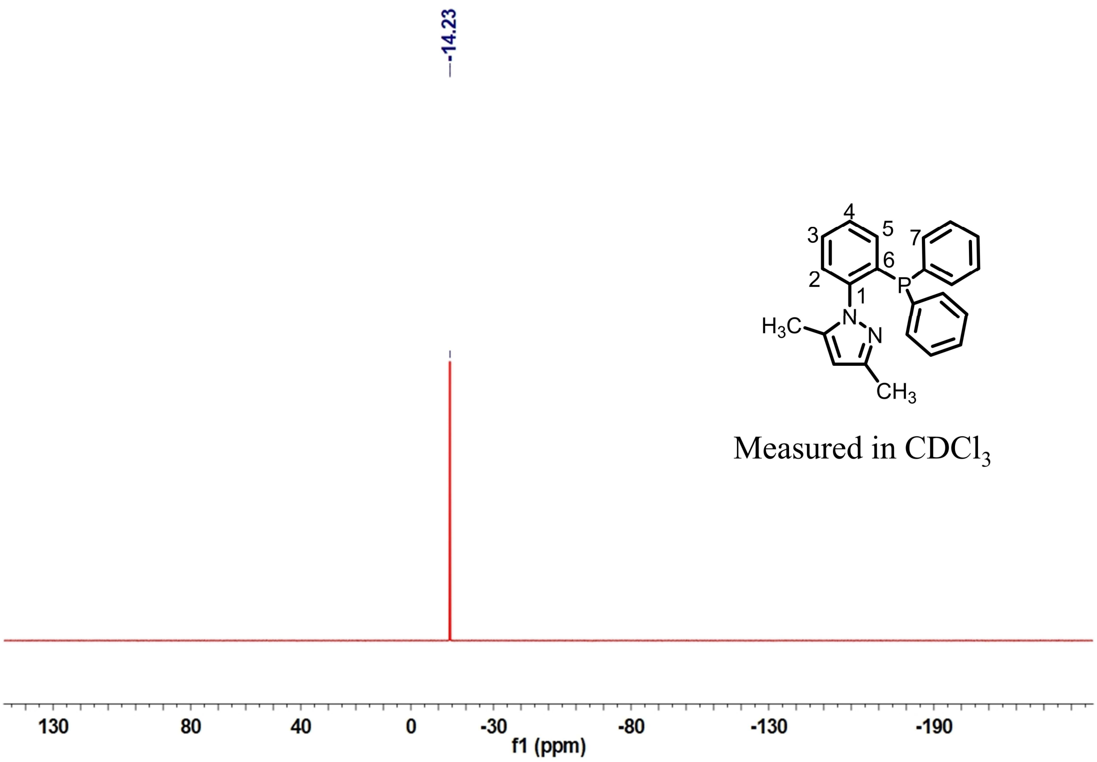

--13.58
Measured in d_6-DMSO
130
80
40
0
-40
-90
-140
-200
f1 (ppm)

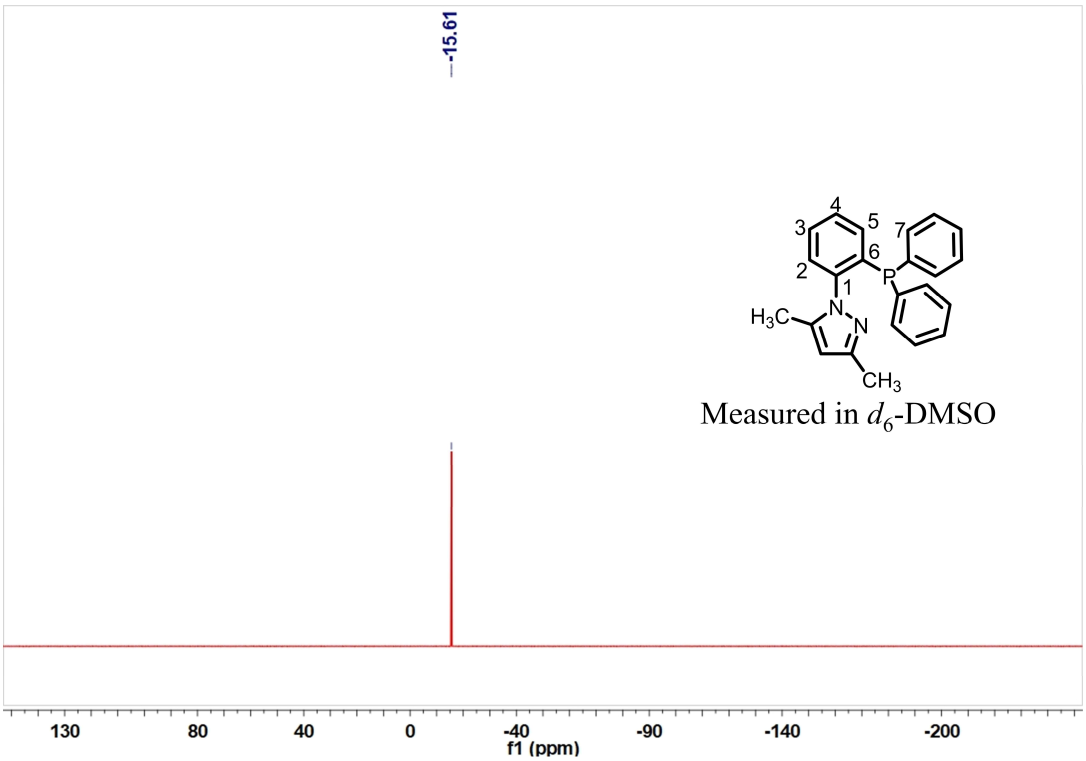
Fig. S17. The ^{1}H (400 MHz), $^{13}C\{^{1}H\}$ (101 MHz) and ^{31}P (162 MHz) NMR spectra for 1-(2-(diphenylphosphanyl)phenyl)-3,5-dimethyl-1H-pyrazole (**1d**) in $CDCl_3$ and ^{31}P (162 MHz) NMR spectra in d_6-DMSO.





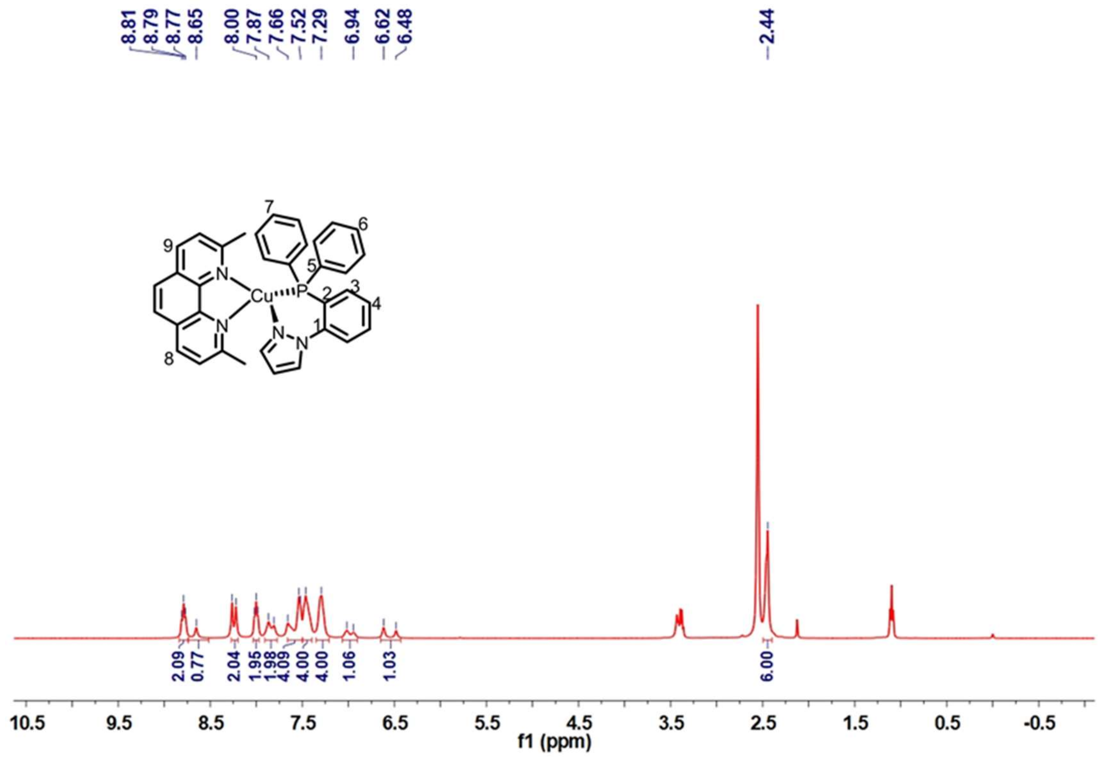


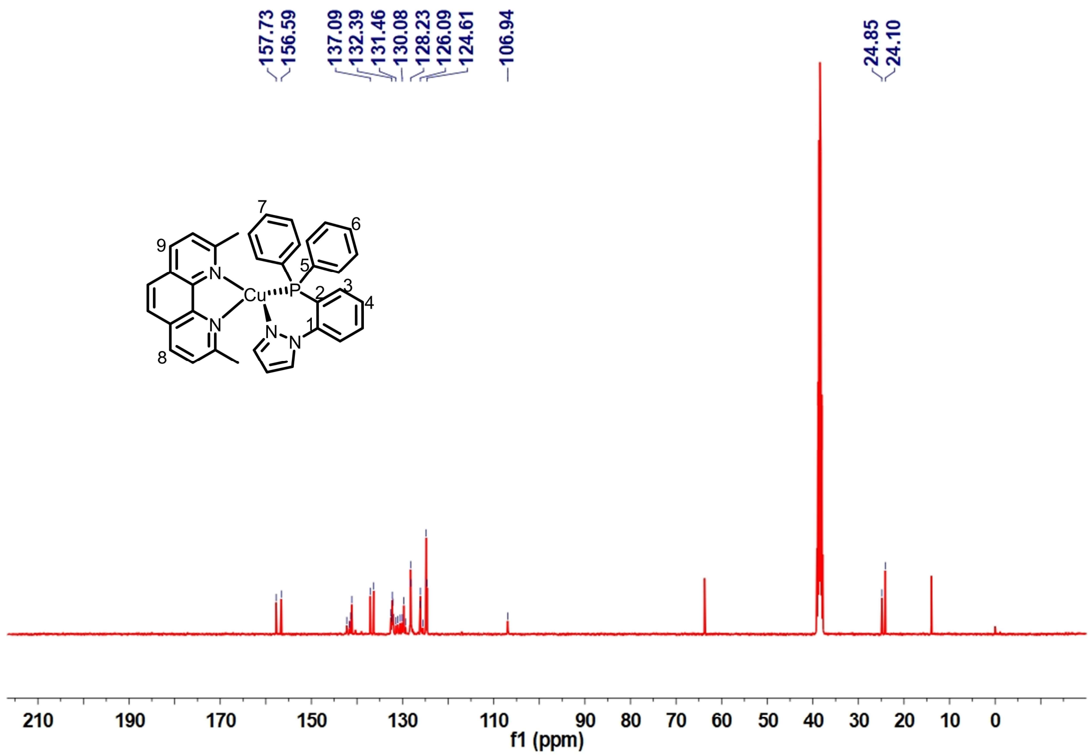
-14.23
Measured in CDCl$_3$
130
80
40
0
-30
-80
-130
-190
f1 (ppm)



-15.61
Measured in d_6-DMSO
130
80
40
0
-40
-90
-140
-200
f1 (ppm)

Fig. S18. The ^{1}H (400 MHz), $^{13}C\{^{1}H\}$ (101 MHz) and ^{31}P (162 MHz) NMR spectra for **2a** in *d_6*-DMSO.





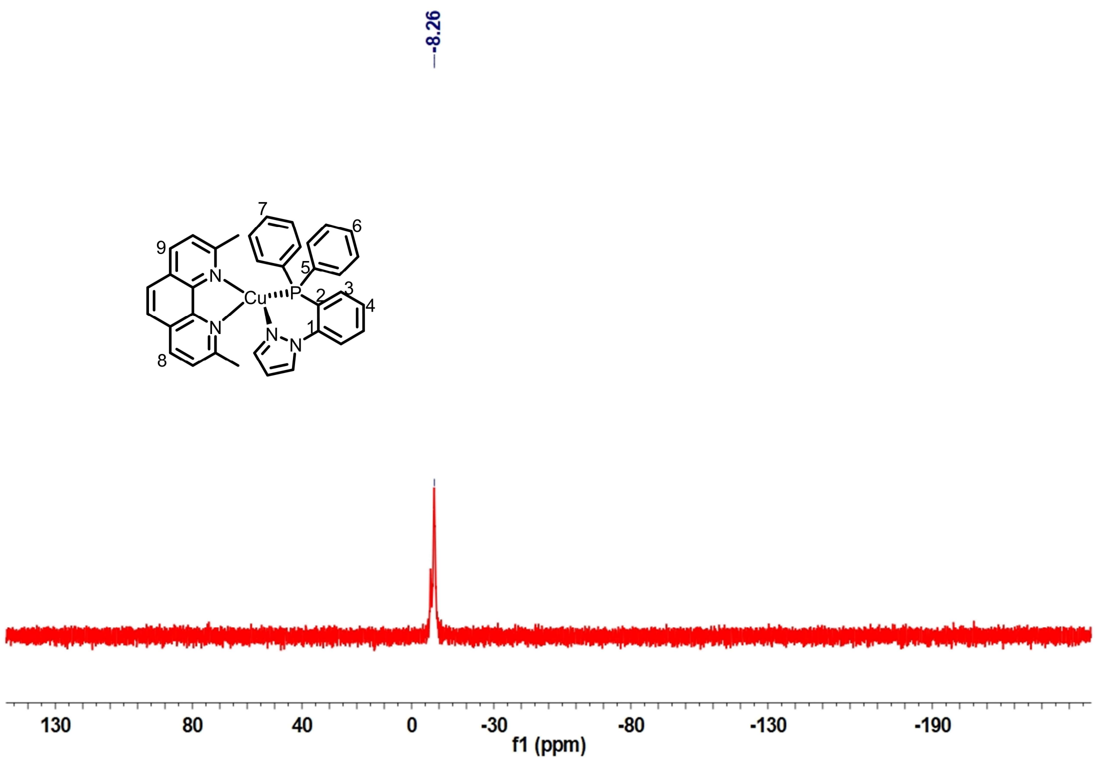
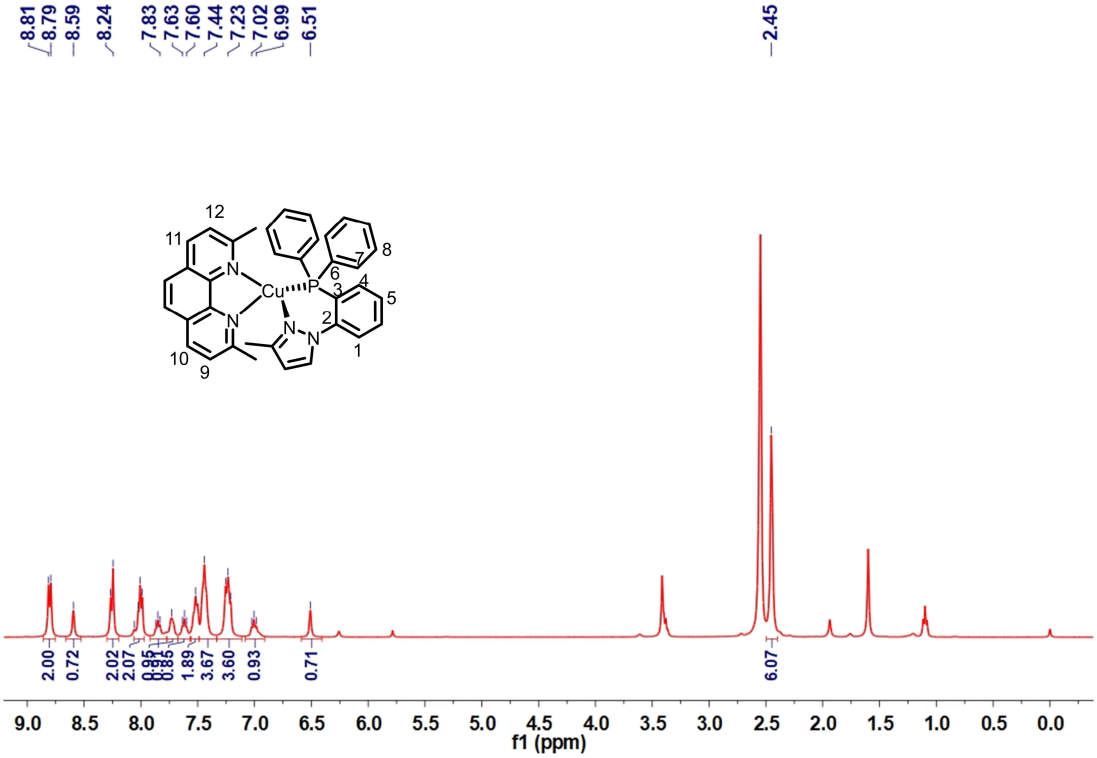
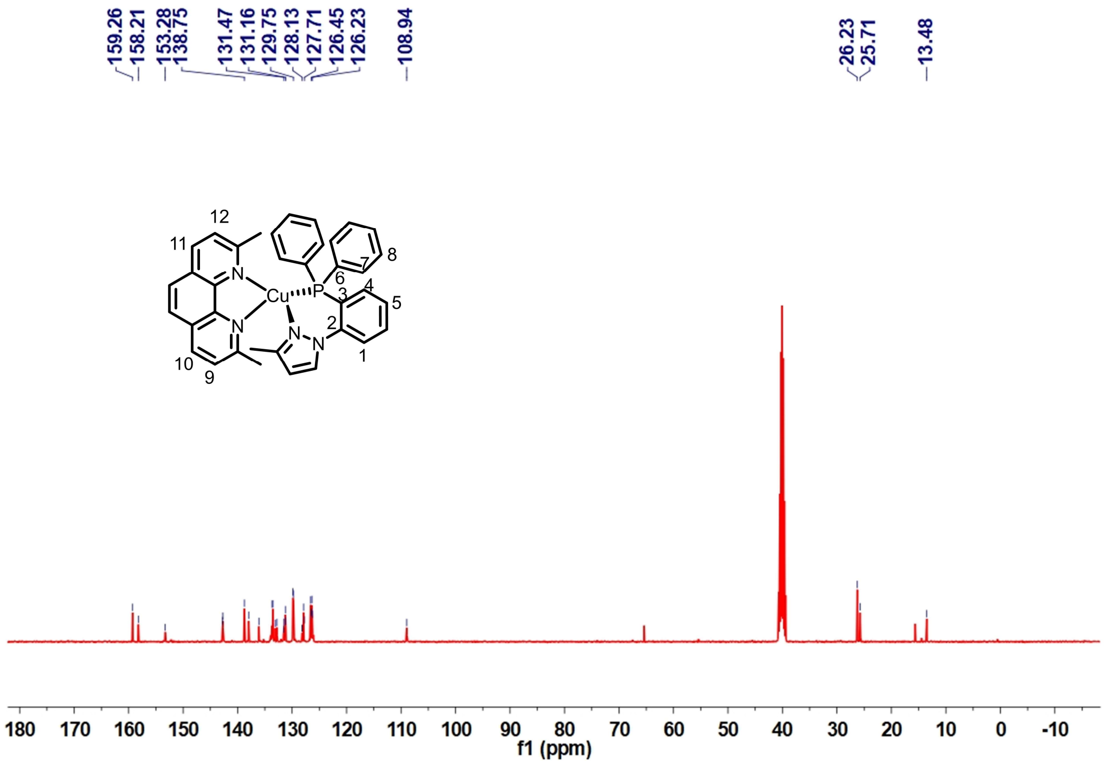
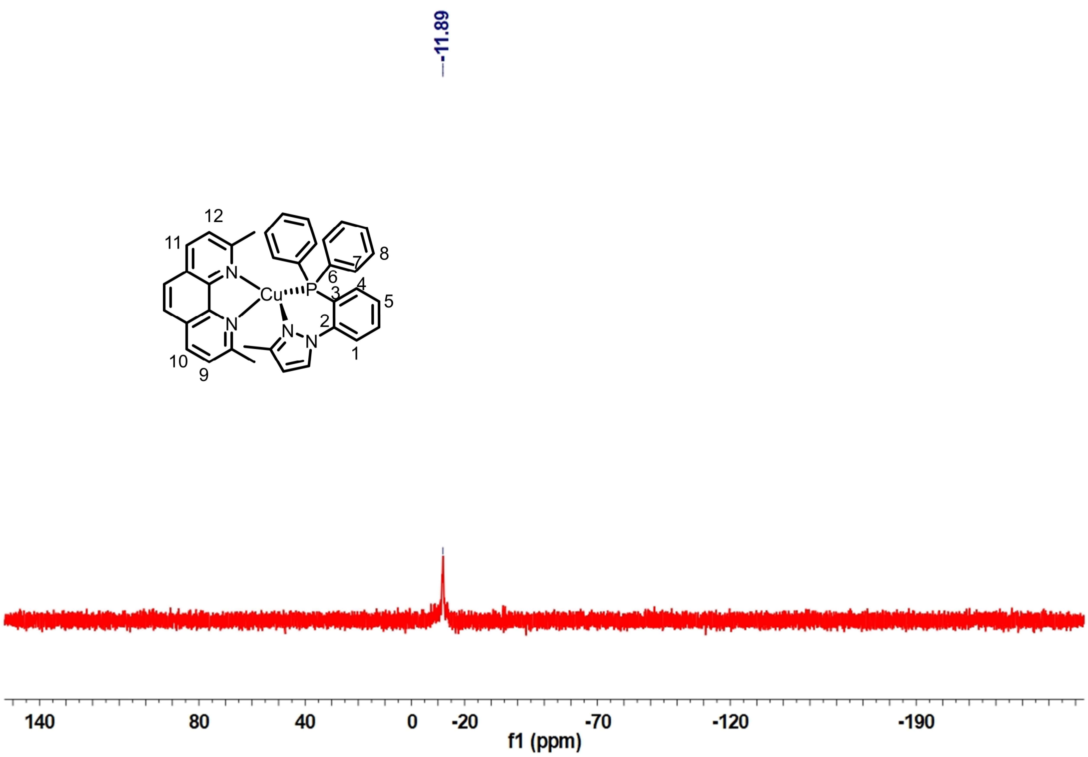

-8.26
7
6
9
5
3
2
4
1
8
Cu
P
N
130
80
40
0
-30
-80
-130
-190
f1 (ppm)

Fig. S19. The ^{1}H (400 MHz), $^{13}C\{^{1}H\}$ (101 MHz) and ^{31}P (162 MHz) NMR spectra for **2b** in *d_6*-DMSO.

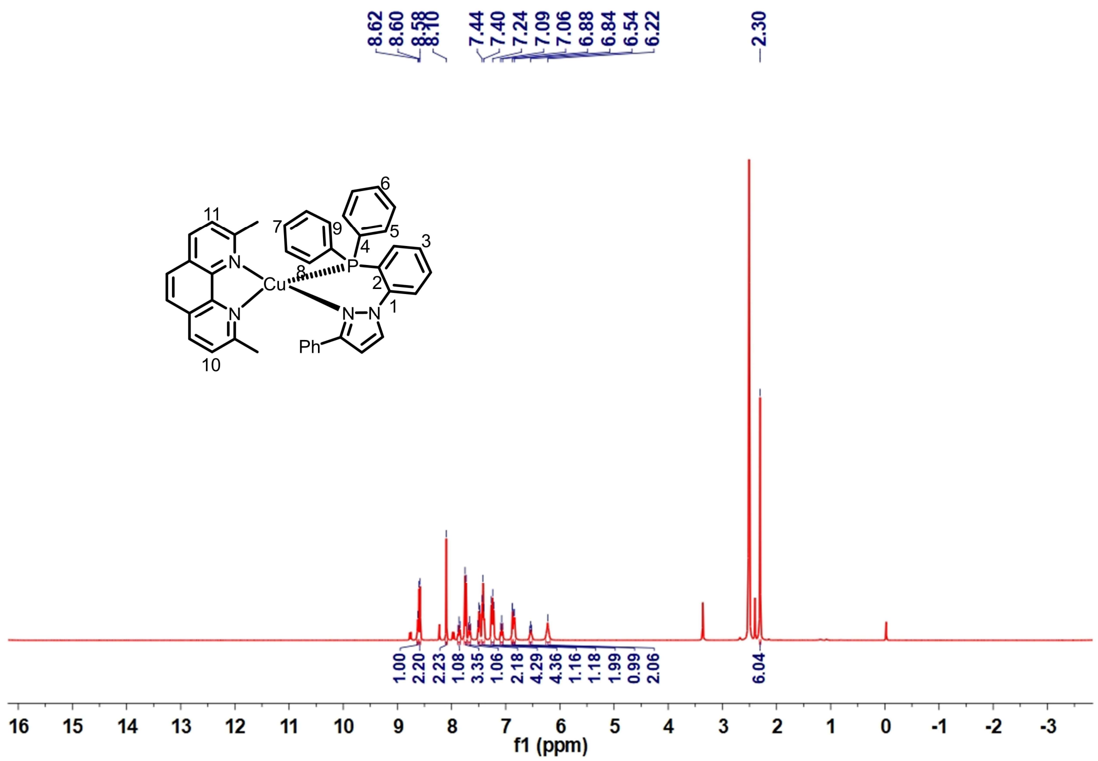


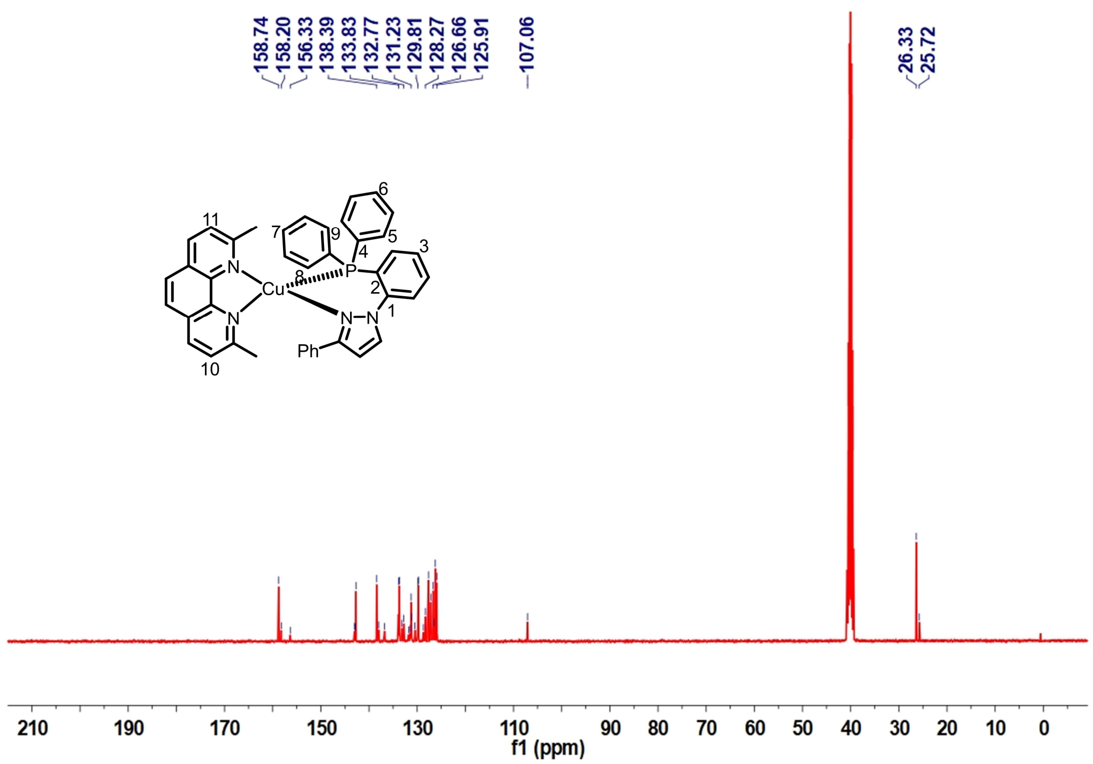


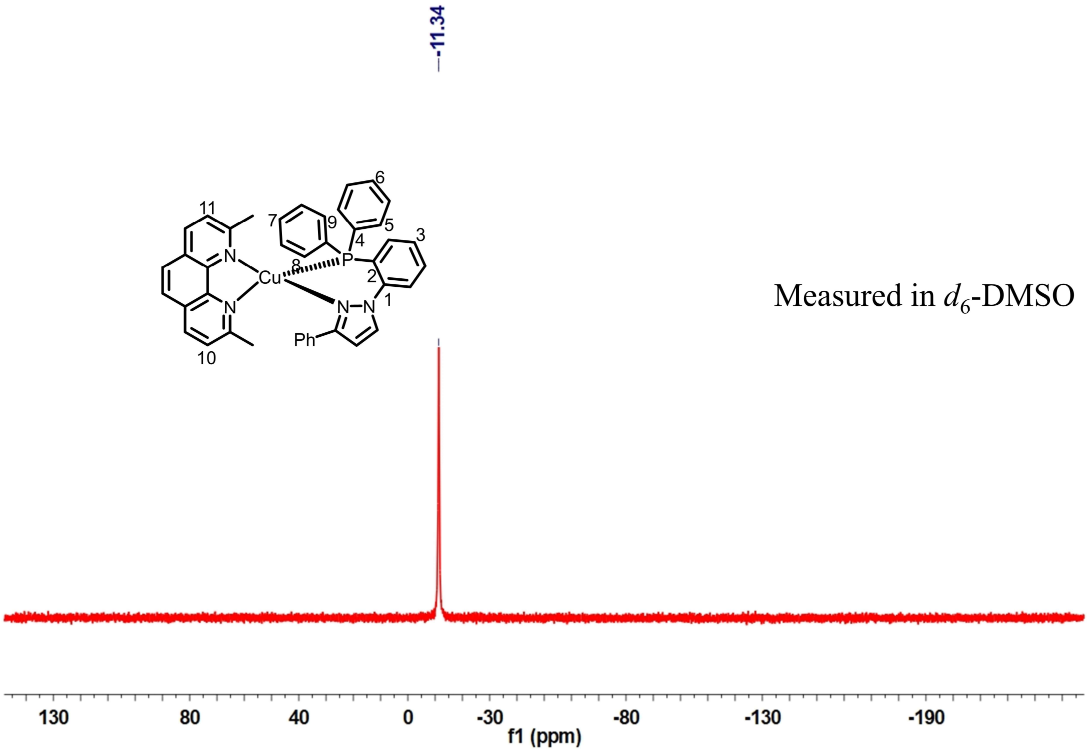


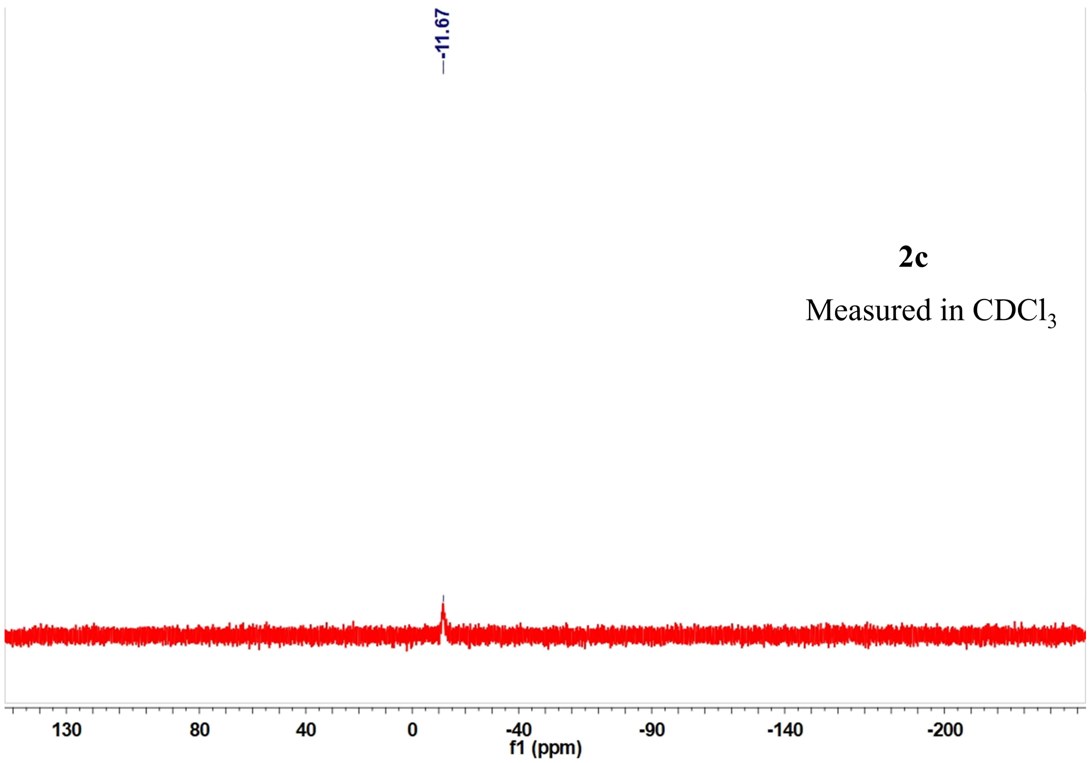
-11.89
12
11
10
9
N
N
Cu
P
N
N
1
2
3
4
5
6
7
8
140
80
40
0
-20
-70
-120
-190
f1 (ppm)

Fig. S20. The ^{1}H (400 MHz), $^{13}C\{^{1}H\}$ (101 MHz) and ^{31}P (162 MHz) NMR spectra for **2c** in d_6-DMSO and ^{31}P (162 MHz) NMR spectra inCDCl$_3$.





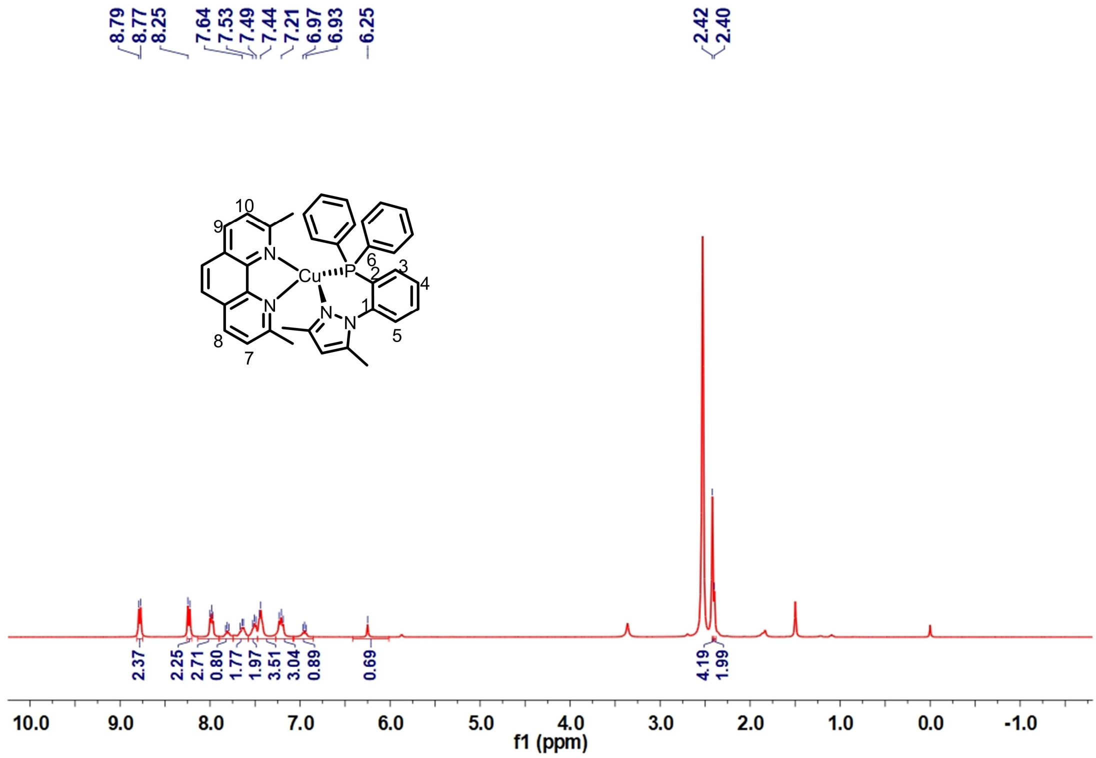


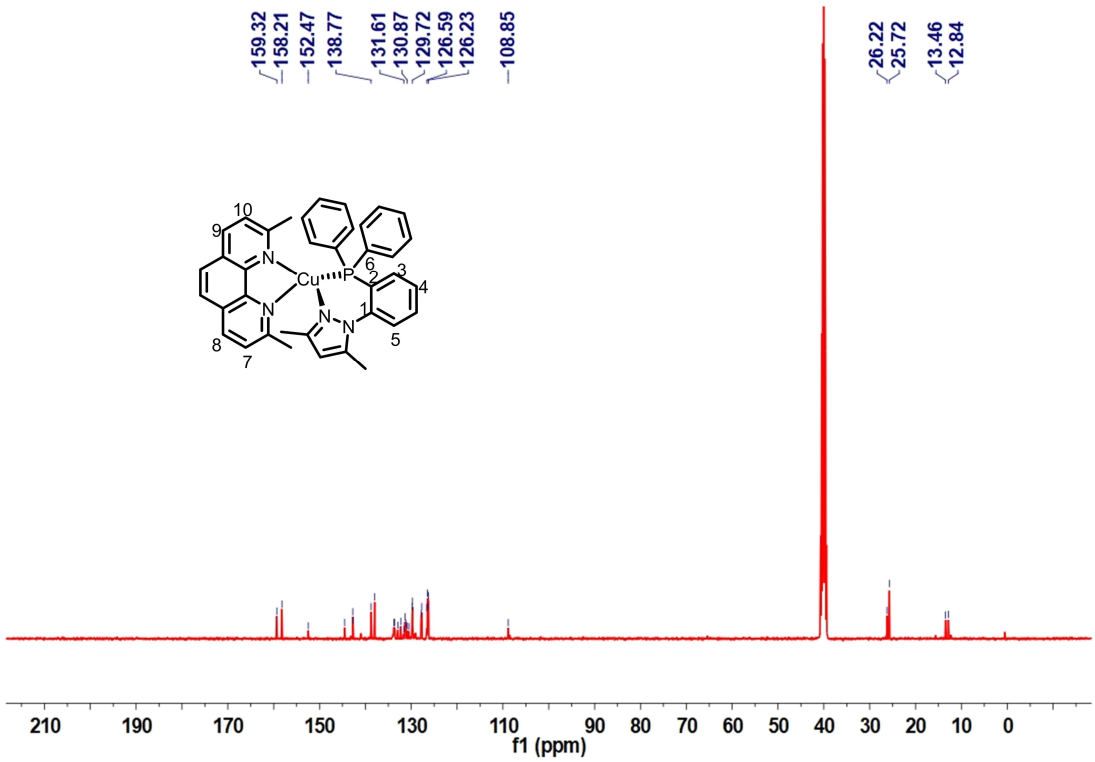


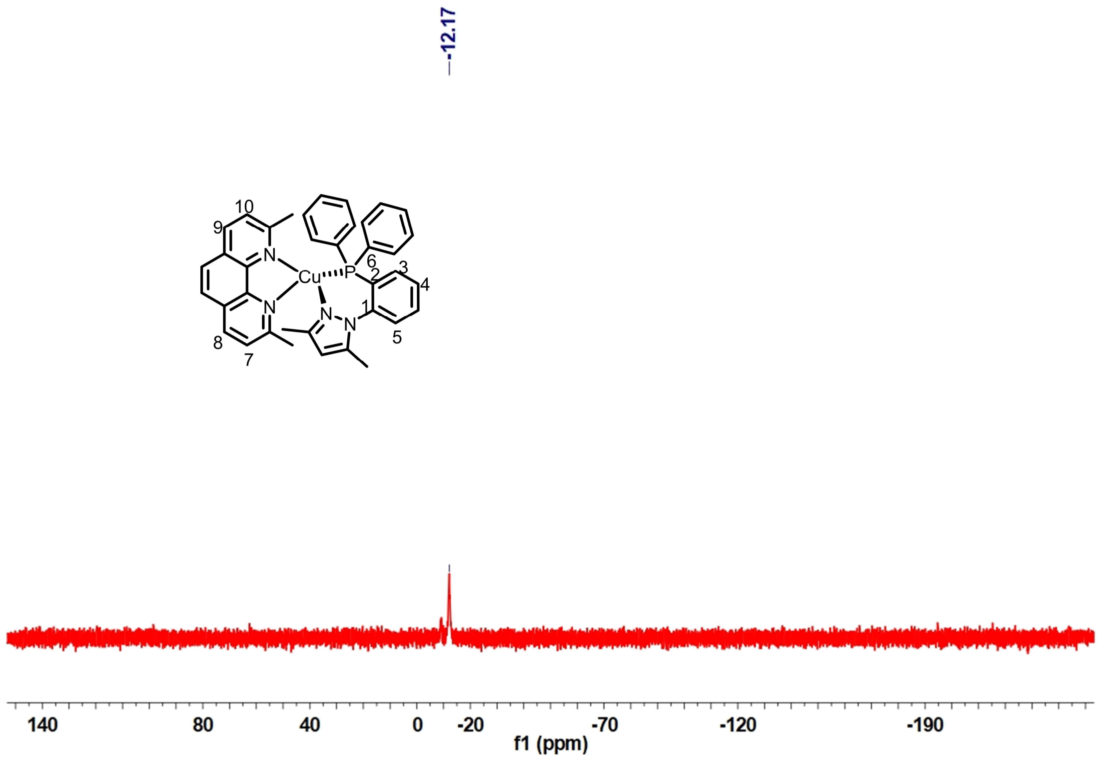
2c

Measured in $CDCl_3$

Fig. S21. The ^{1}H (400 MHz), ^{13}C{^{1}H} (101 MHz) and ^{31}P (162 MHz) NMR spectra for **2d** in *d*$_6$-DMSO.

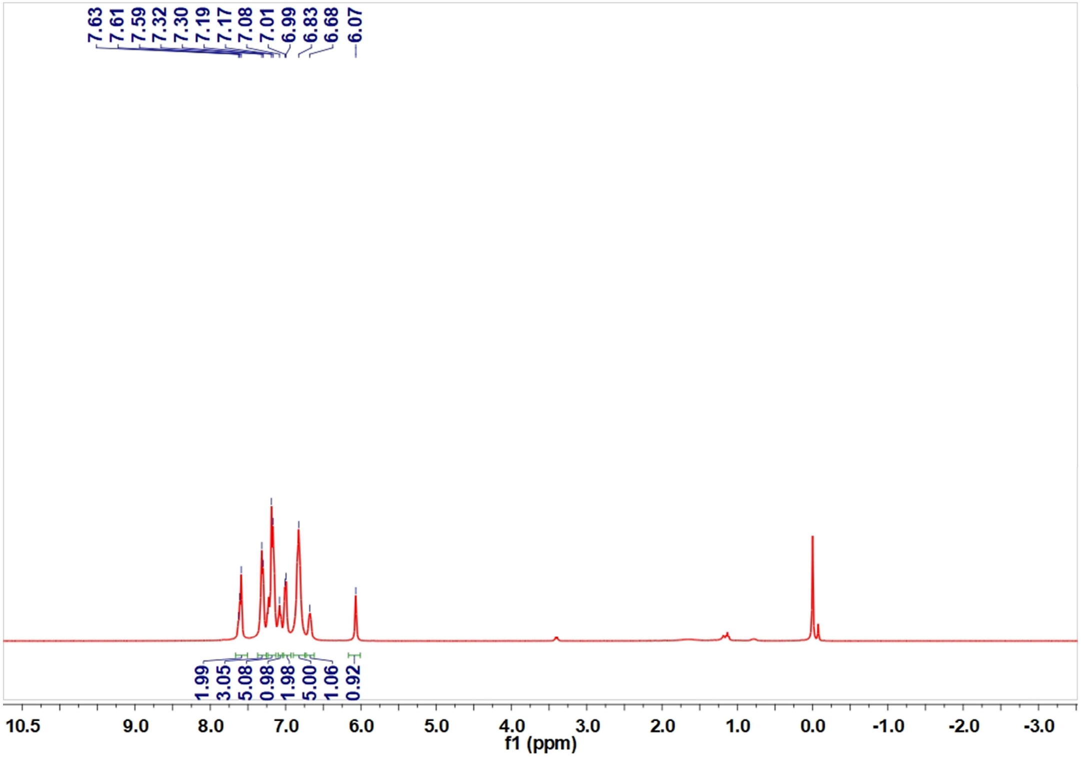






-12.17
10
9
N
Cu
P
6
2
3
4
1
N
N
N
5
8
7
140
80
40
0
-20
-70
-120
-190
f1 (ppm)

Fig. S22. The [1]H (400 MHz) and [31]P (162 MHz) NMR spectra for [Cu(**1c**)]BF_4 in $CDCl_3$.



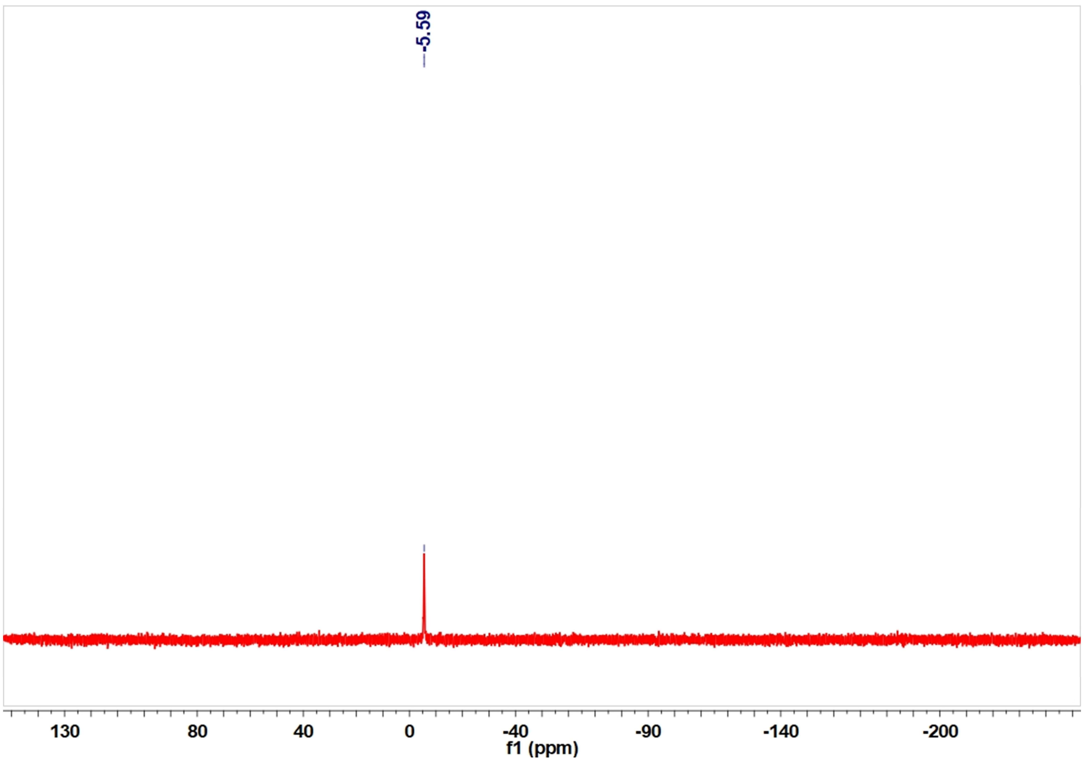
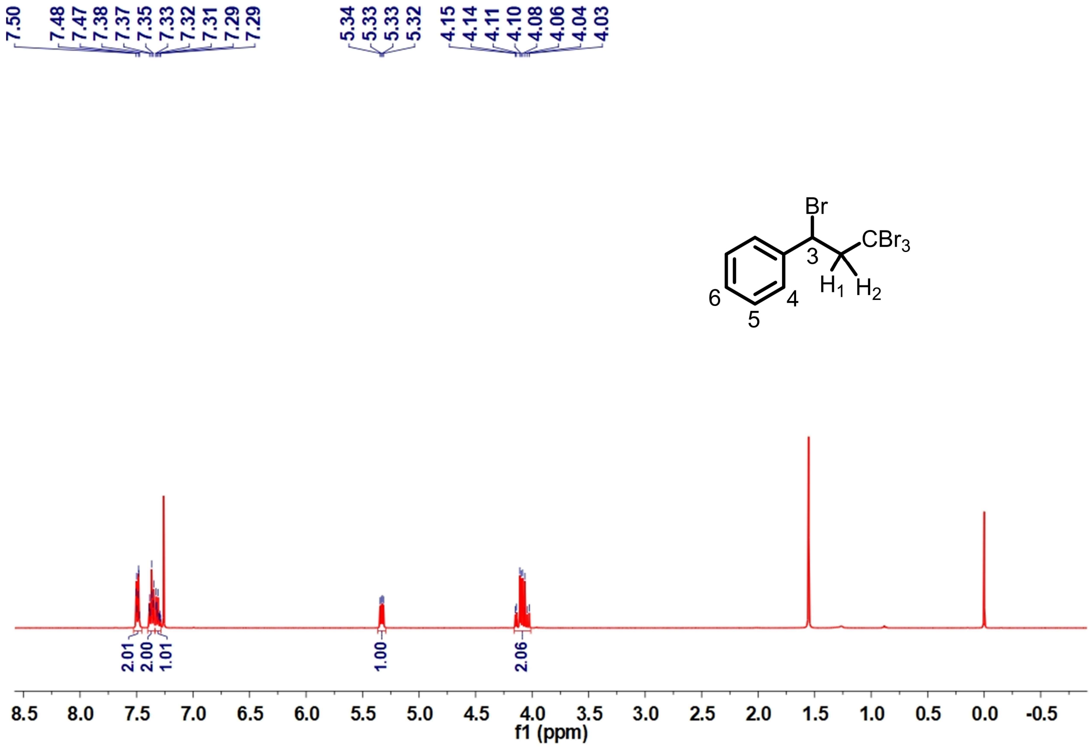


Fig. S23. The ^{1}H (400 MHz) and $^{13}C\{^{1}H\}$ (101 MHz) NMR spectra for (1,3,3,3-tetrabromopropyl)benzene **(5a)** in $CDCl_3$.



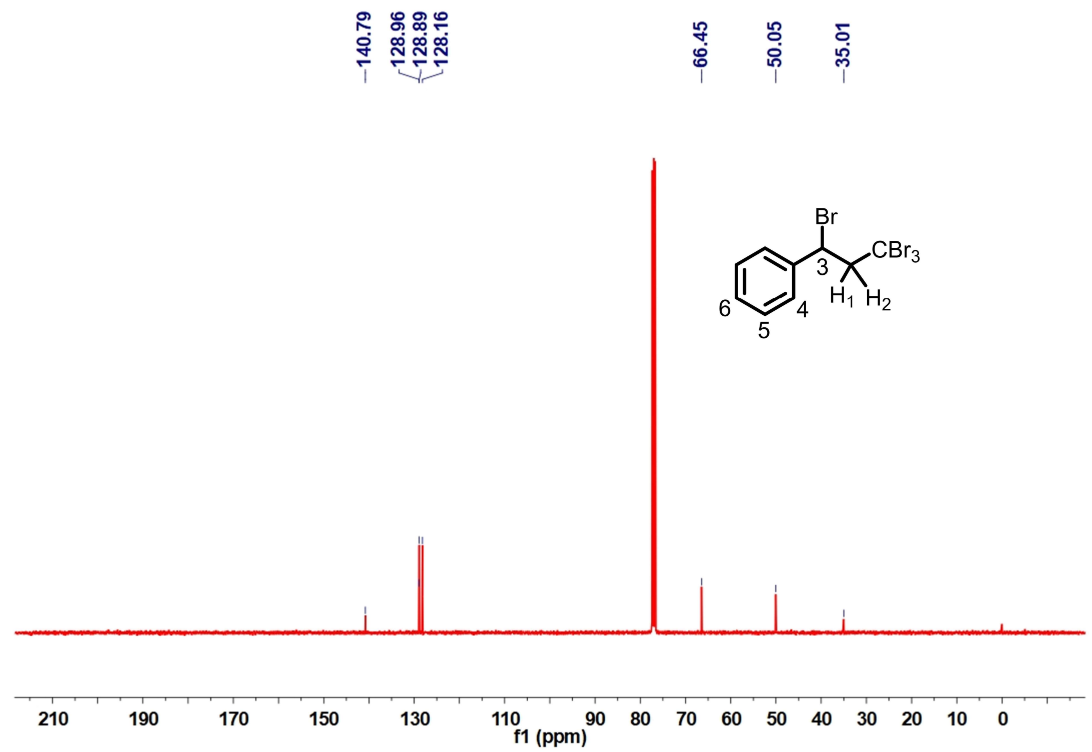
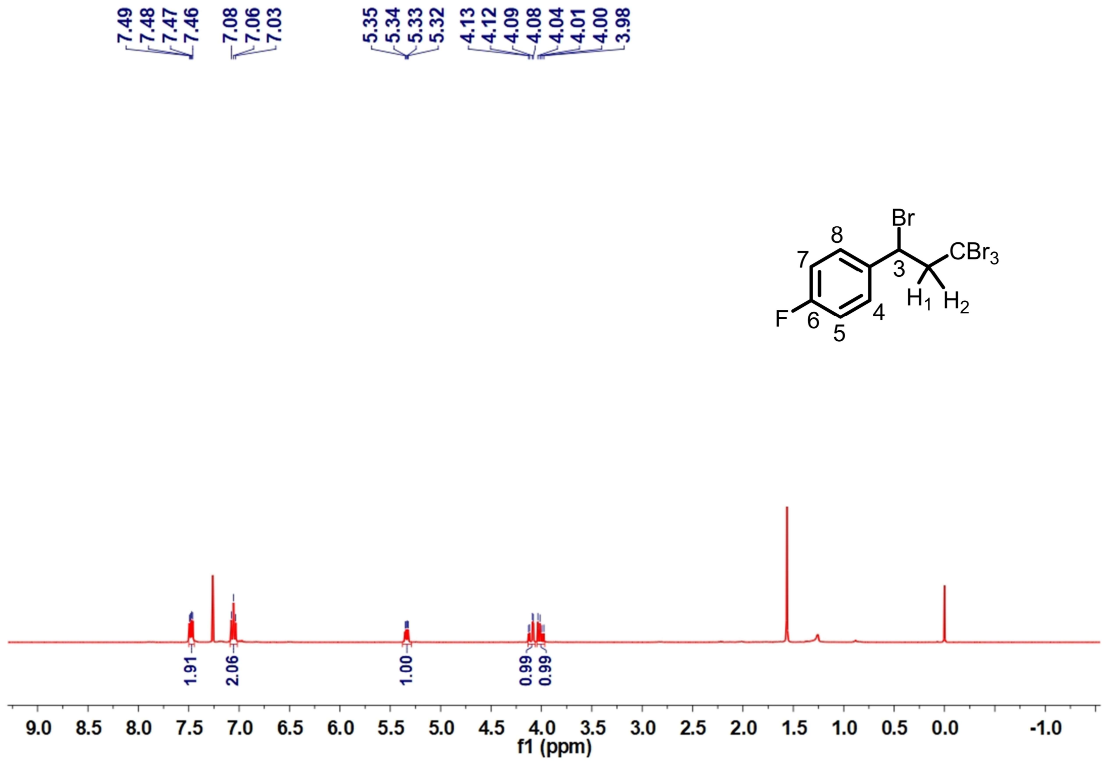
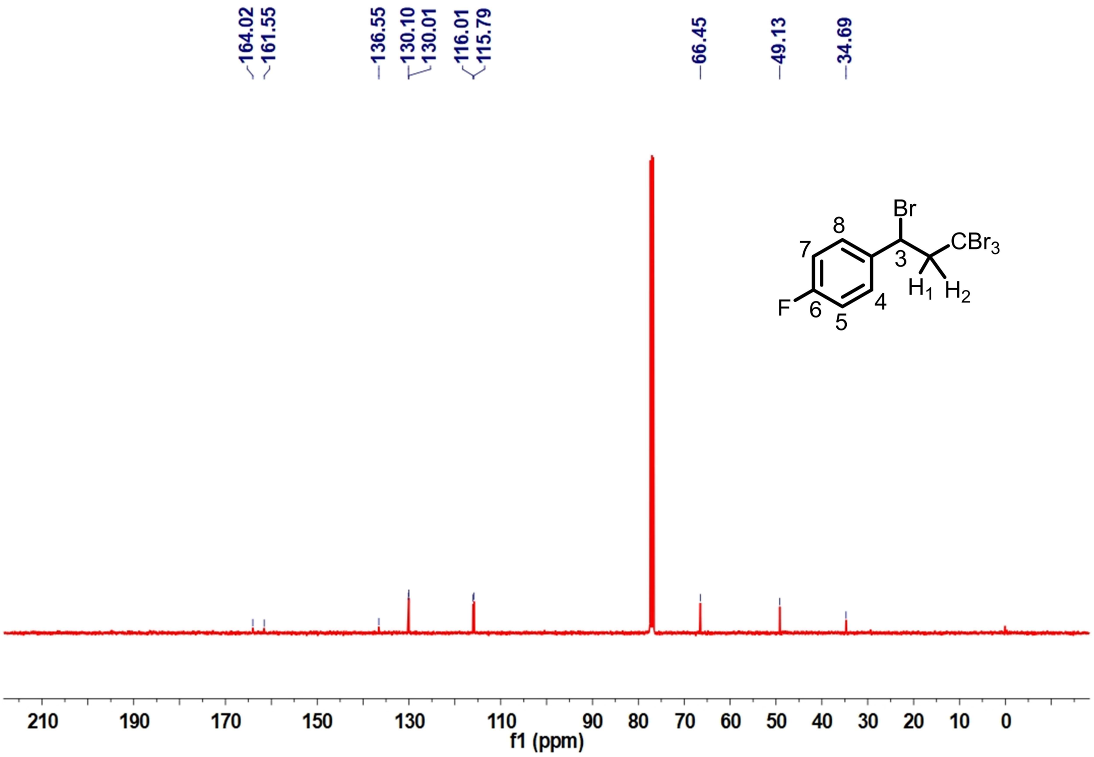


Fig. S24. The [1]H (400 MHz), [13]C{[1]H} (101 MHz) and [19]F (377 MHz) NMR spectra for 1-fluoro-4-(1,3,3,3-tetrabromopropyl)benzene **(5b)** in $CDCl_3$.





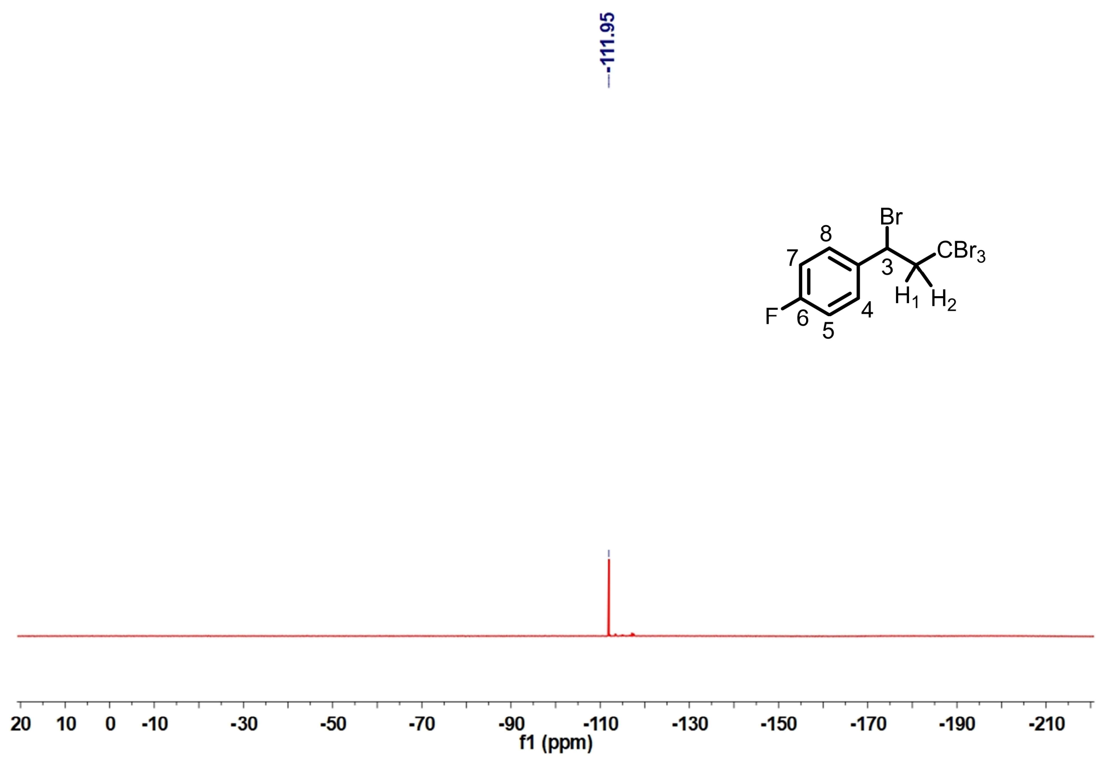
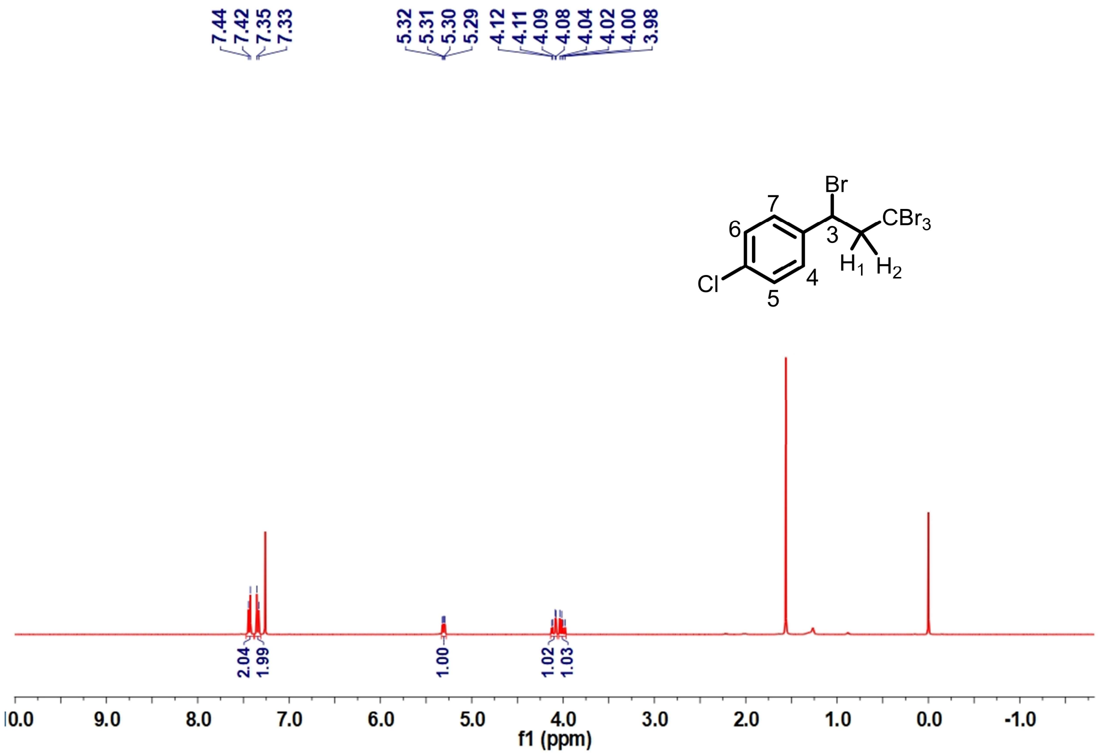

-111.95
Br
CBr3
8
7
3
H1
H2
F
6
4
5
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

Fig. S25. The ^{1}H (400 MHz) and $^{13}C\{^{1}H\}$ (101 MHz) NMR spectra for 1-chloro-4-(1,3,3,3-tetrabromopropyl)benzene **(5c)** in $CDCl_3$.



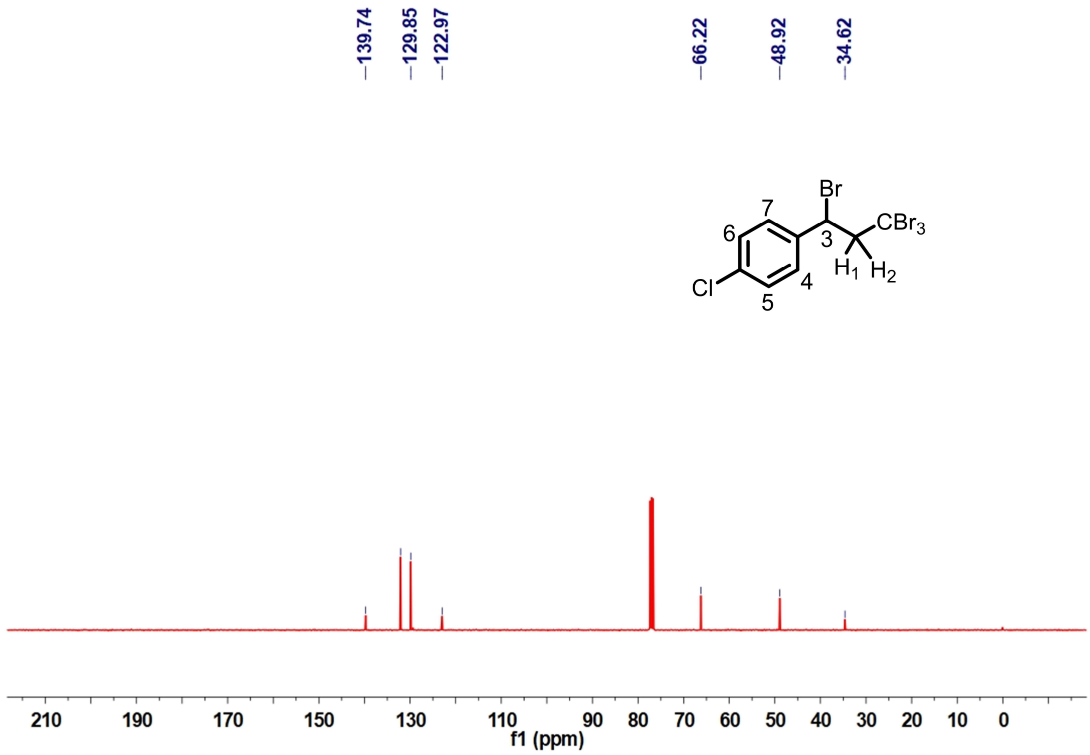
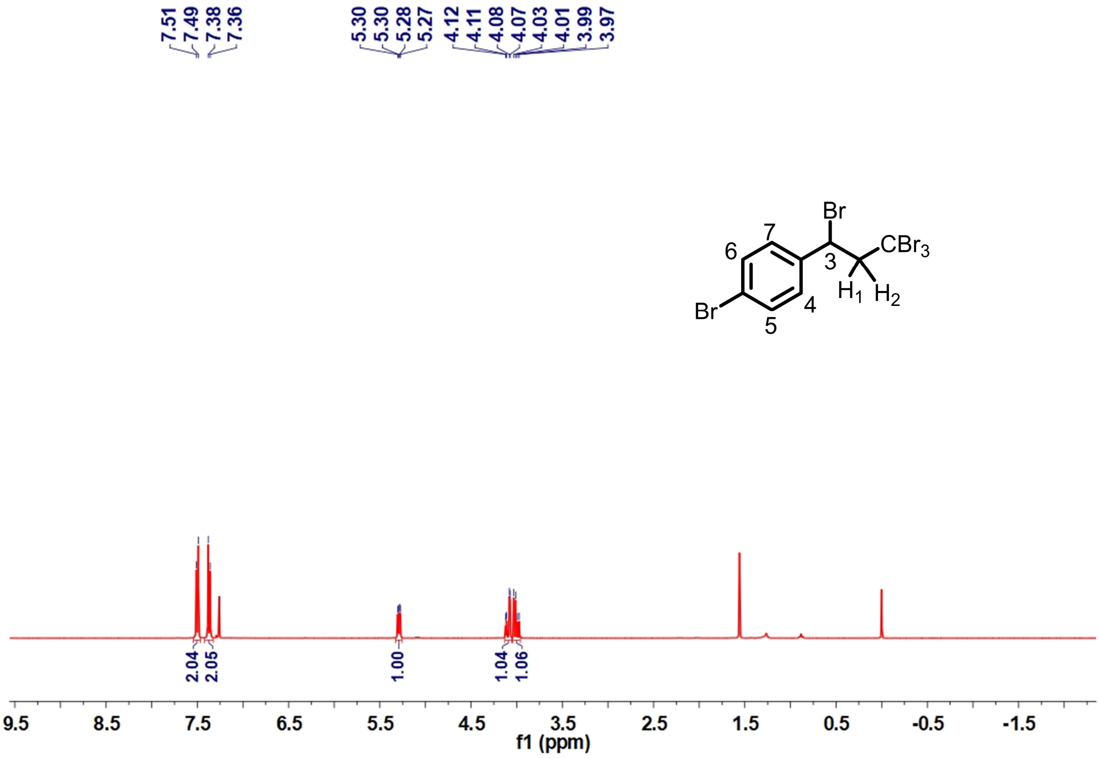


Fig. S26. The ^{1}H (400 MHz) and ^{13}C{^{1}H} (101 MHz) NMR spectra for 1-bromo-4-(1,3,3,3-tetrabromopropyl)benzene **(5d)** in $CDCl_3$.



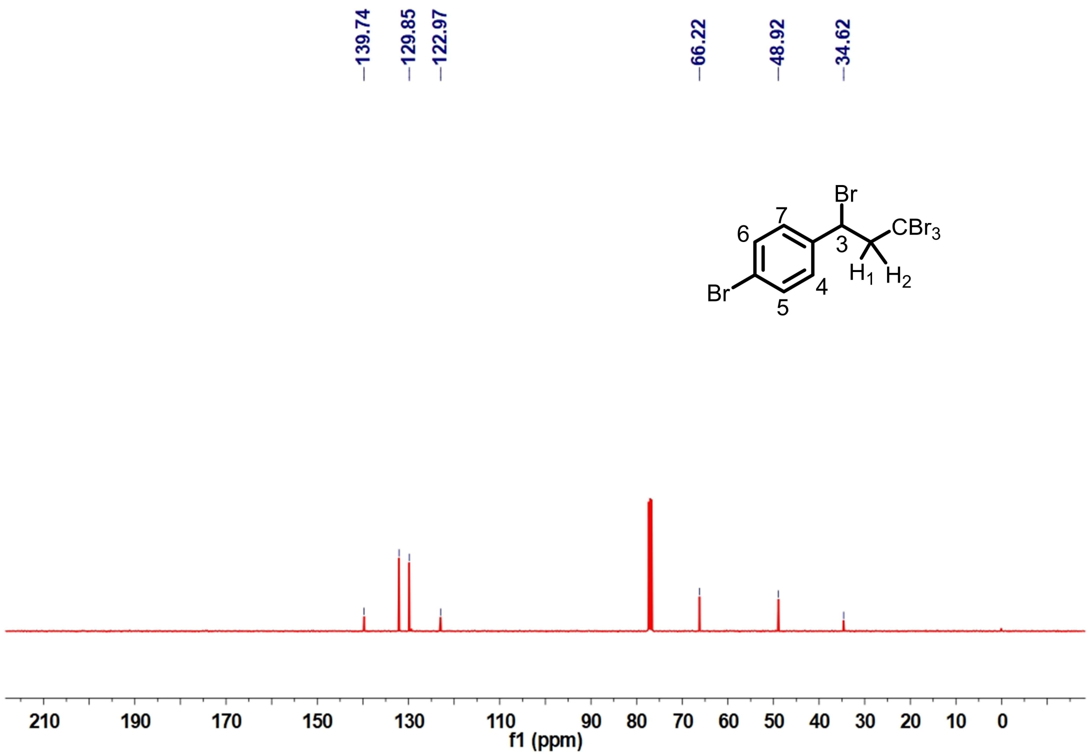
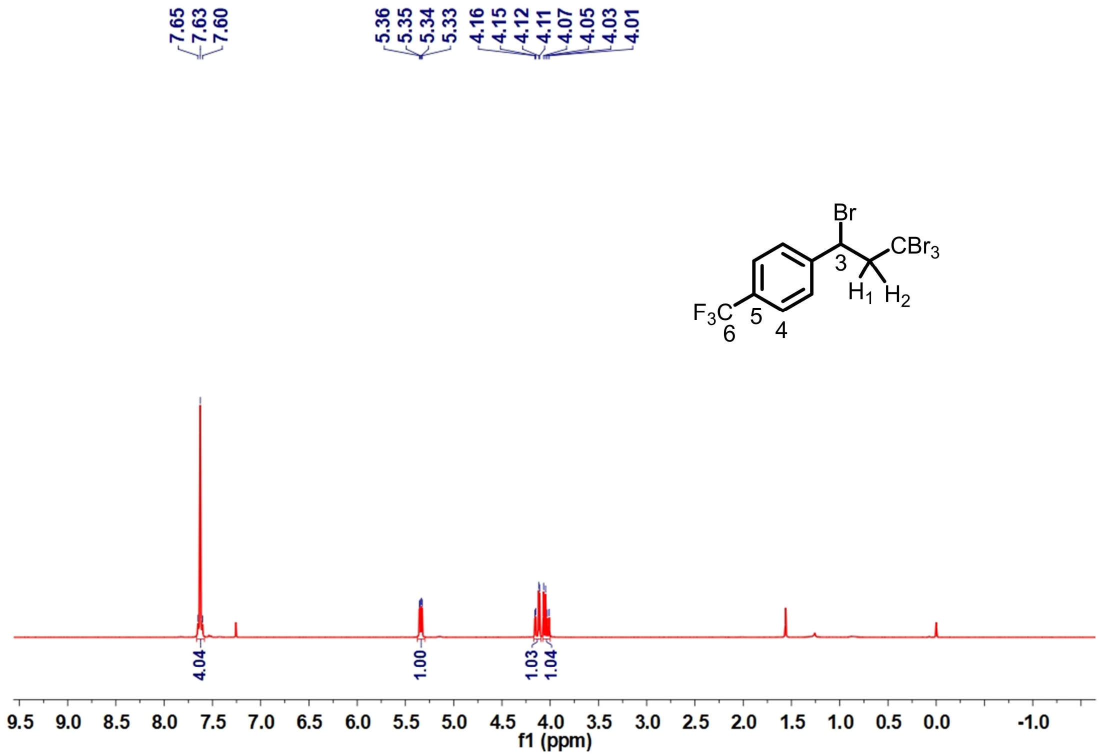
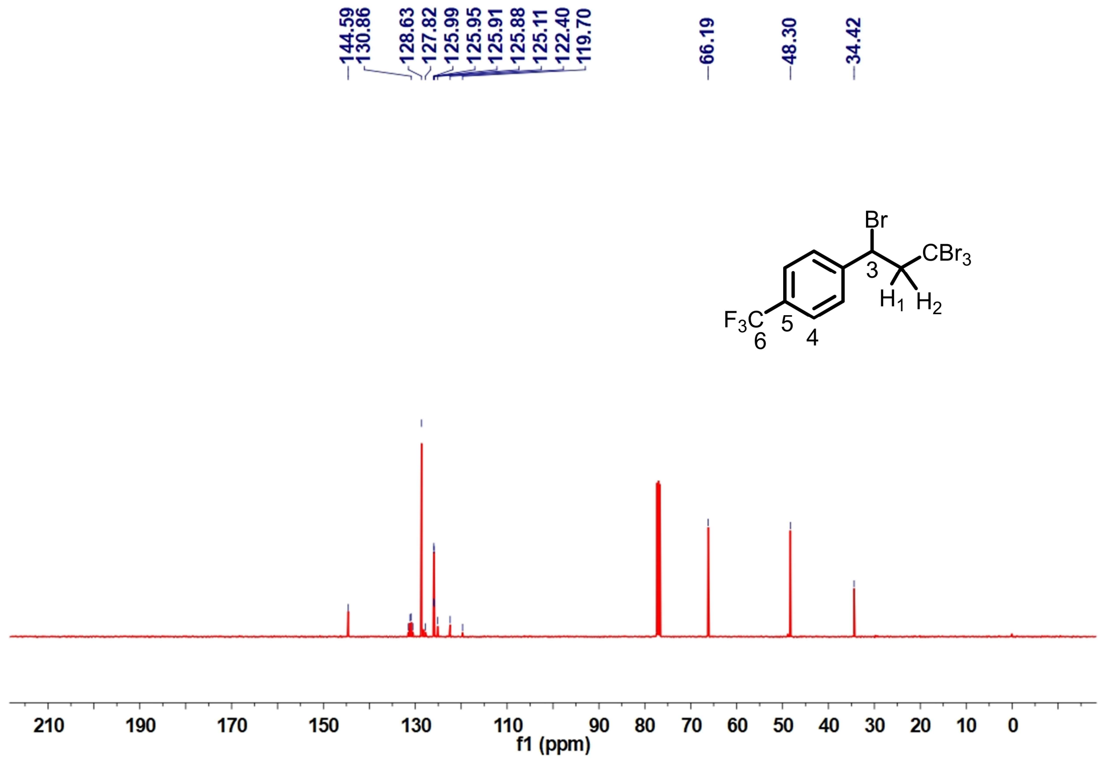


Fig. S27. The [1]H (400 MHz), [13]C{[1]H} (101 MHz) and [19]F (377 MHz) NMR spectra for 1-(1,3,3,3-tetrabromopropyl)-4-(trifluoromethyl)benzene **(5e)** in $CDCl_3$.





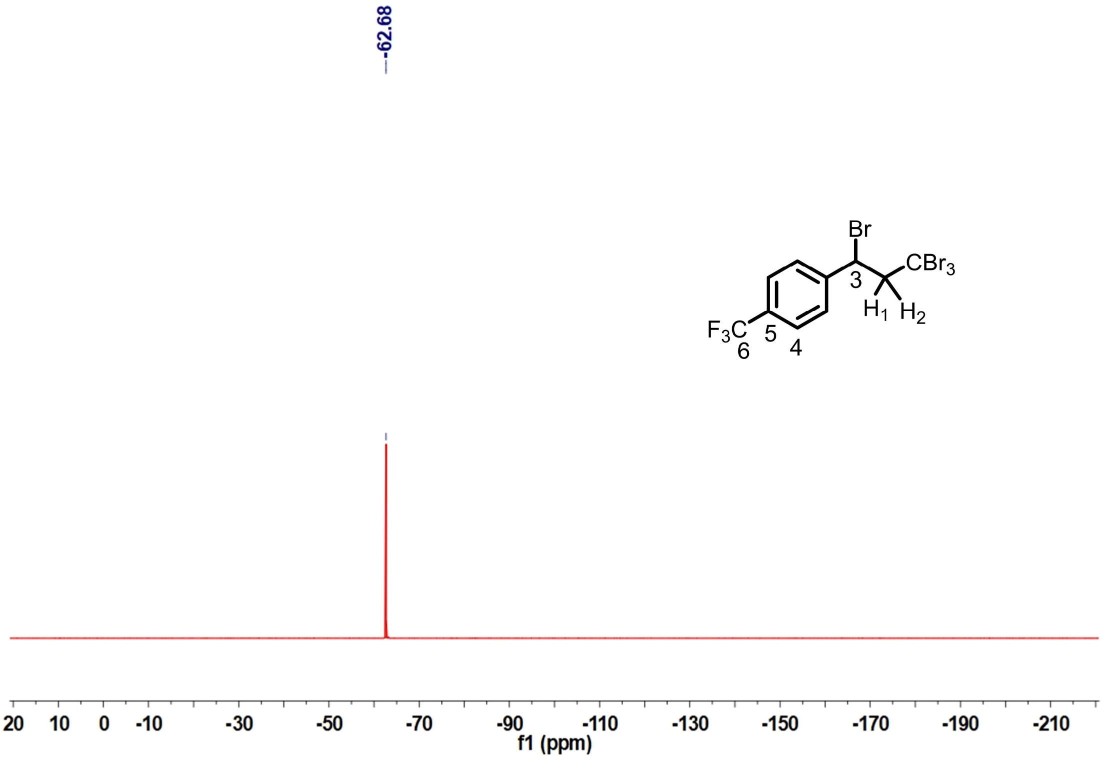
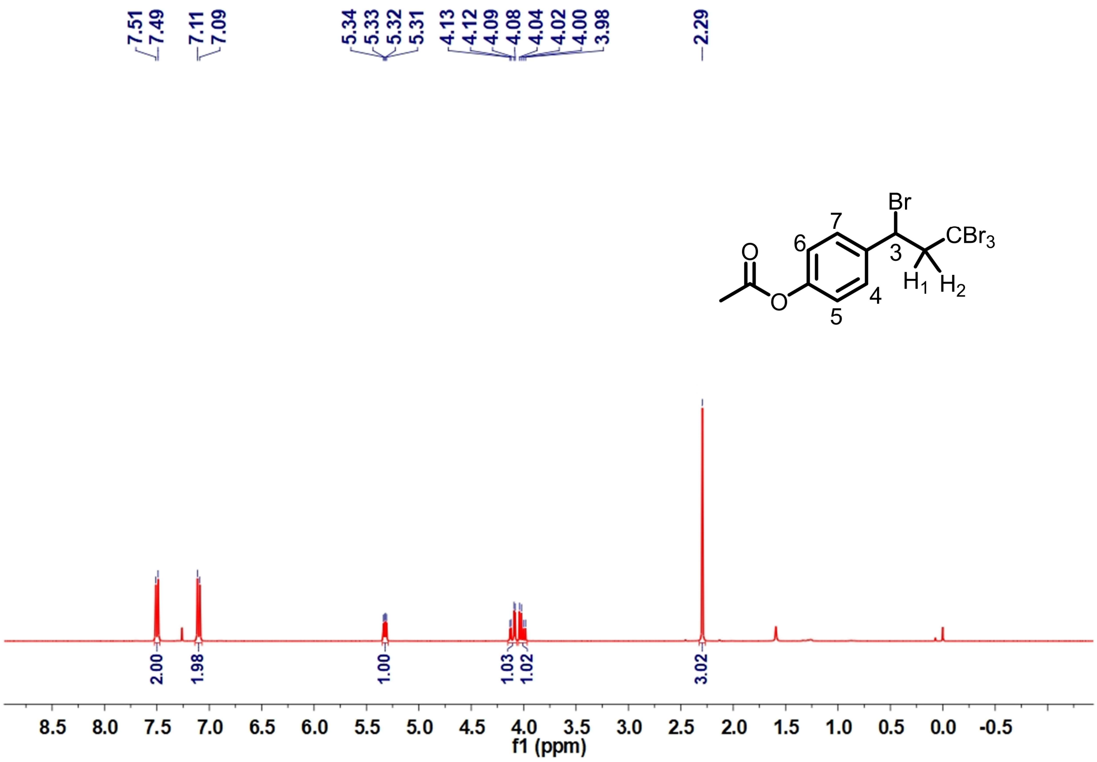

-62.68
Br
CBr3
3
H1 H2
F3C
5
6
4
20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

Fig. S28. The ^{1}H (400 MHz) and $^{13}C\{^{1}H\}$ (101 MHz) NMR spectra for 4-(1,3,3,3-tetrabromopropyl)phenyl acetate **(5f)** in $CDCl_3$.



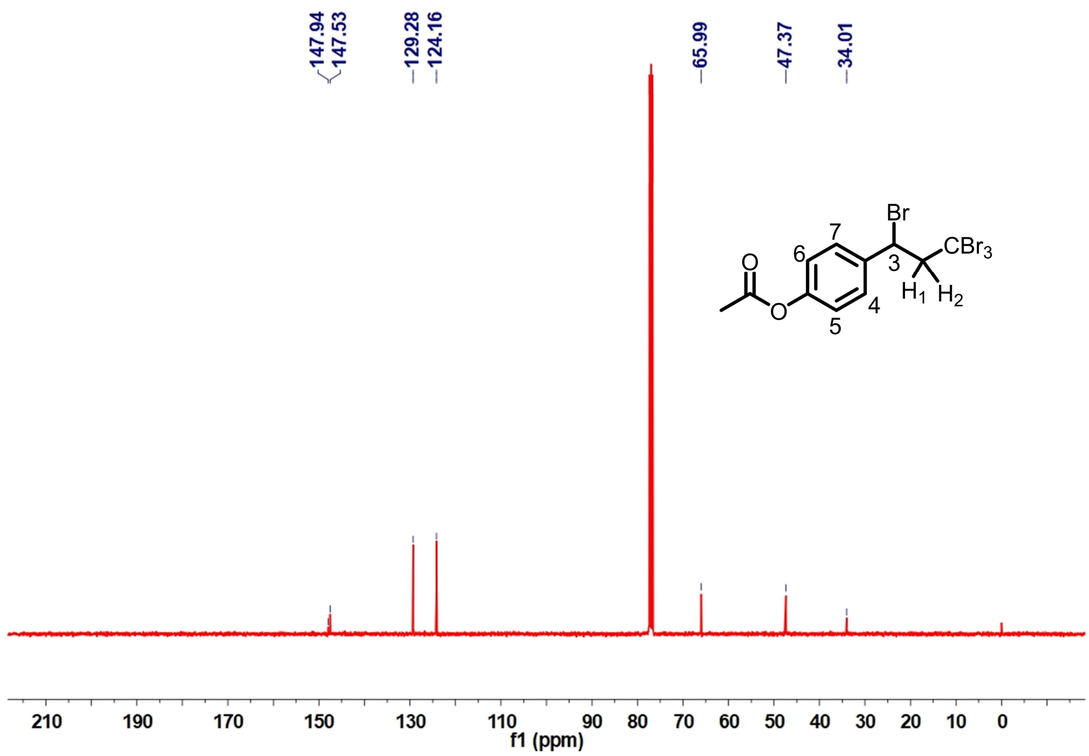
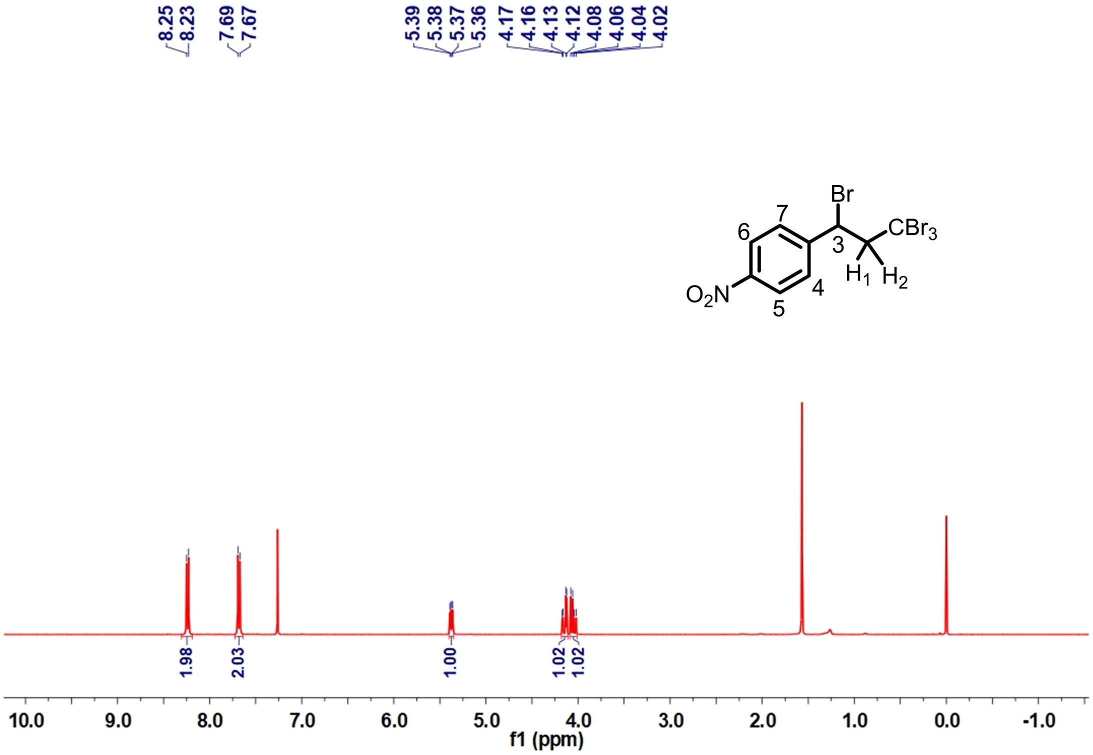


Fig. S29. The [1]H (400 MHz) and [13]C{[1]H} (101 MHz) NMR spectra for 1-nitro-4-(1,3,3,3-tetrabromopropyl)benzene **(5g)** in $CDCl_3$.



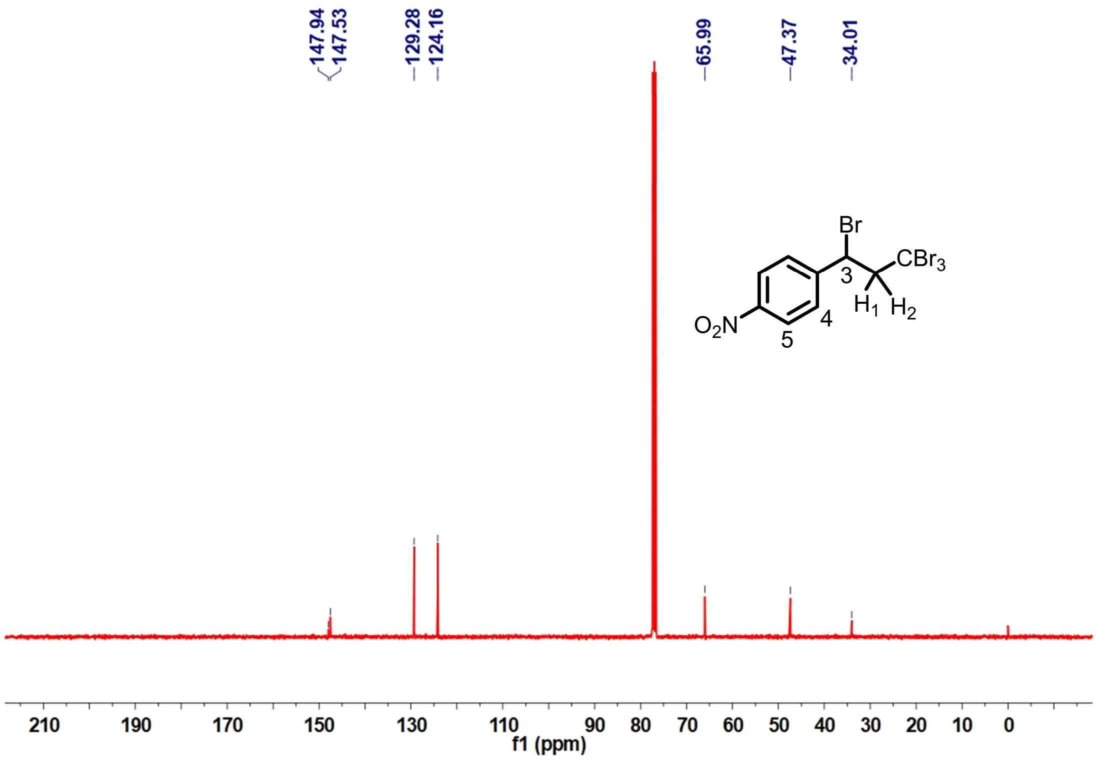
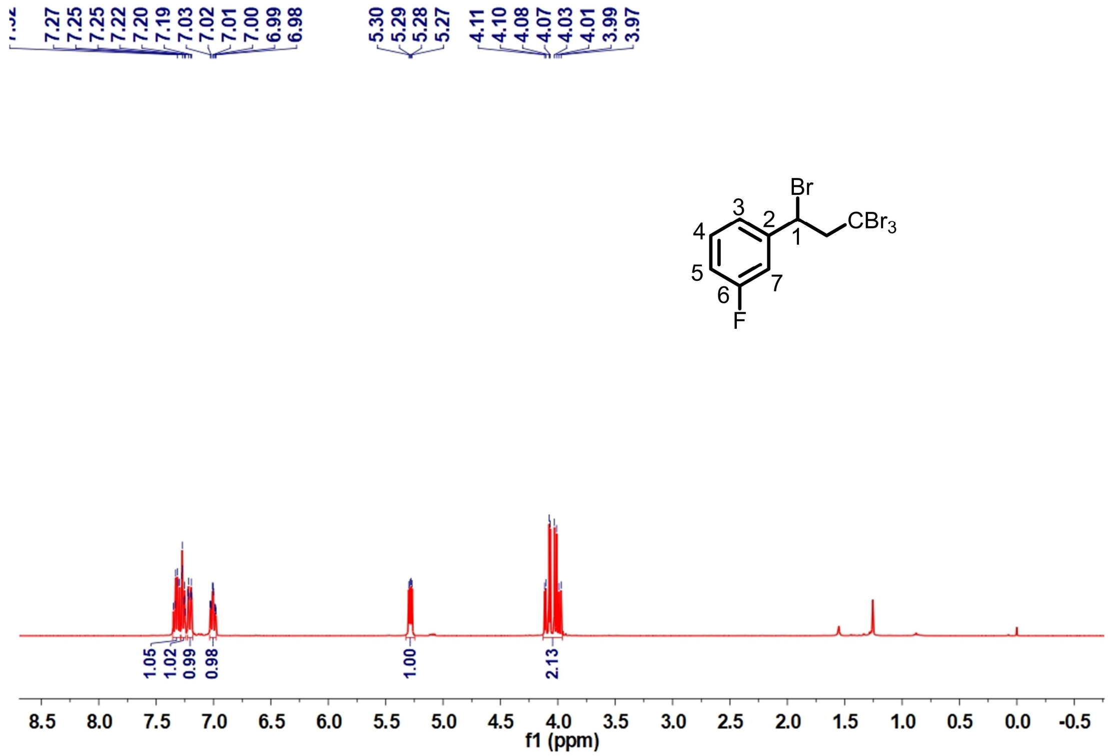
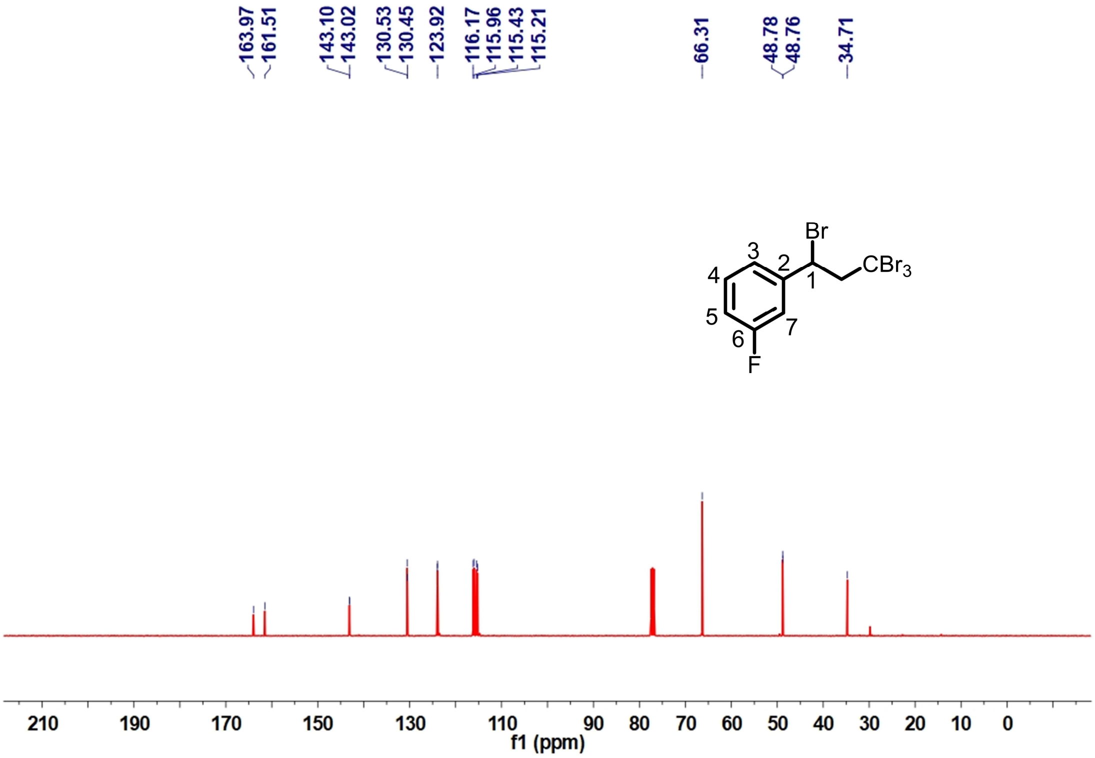
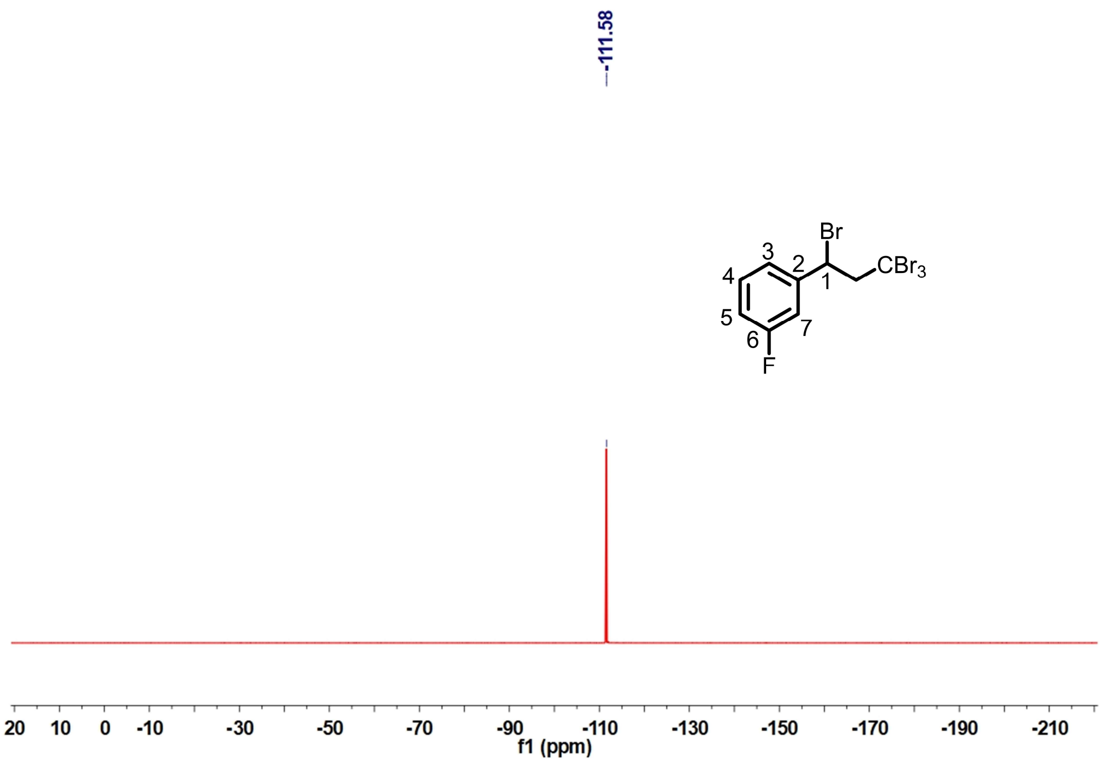


Fig. S30. The ^{1}H (400 MHz), ^{13}C{^{1}H} (101 MHz) and ^{19}F (377 MHz) NMR spectra for 1-fluoro-3-(1,3,3,3-tetrabromopropyl)benzene **(5h)** in $CDCl_3$.

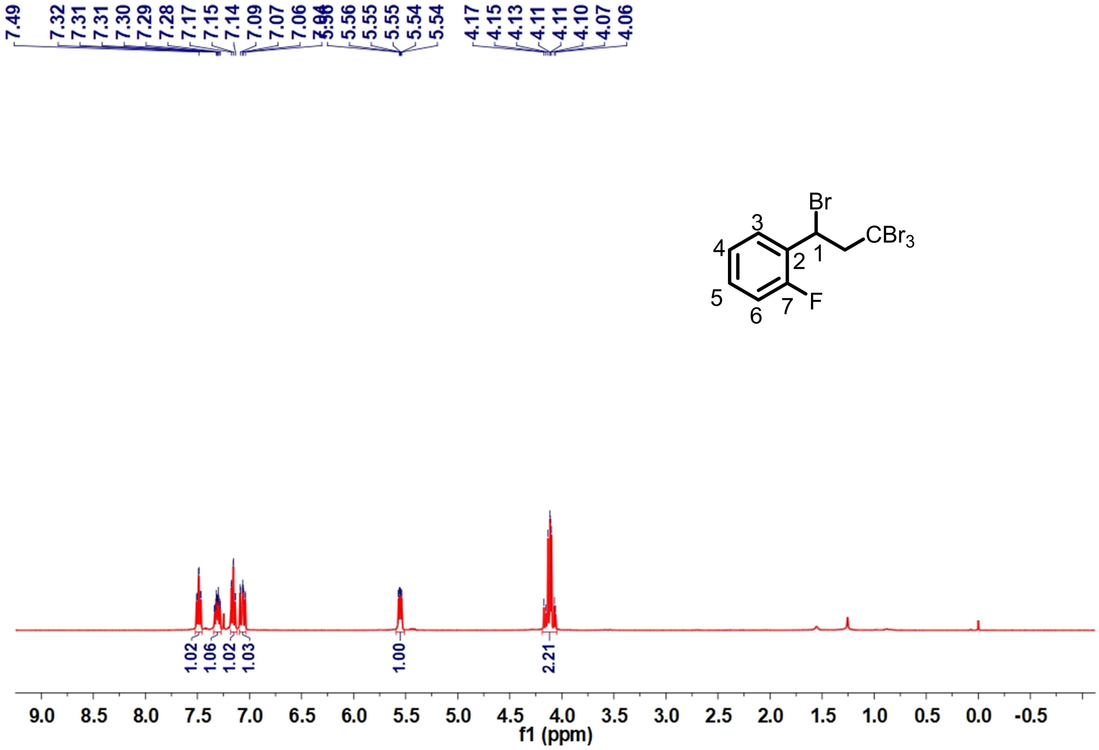


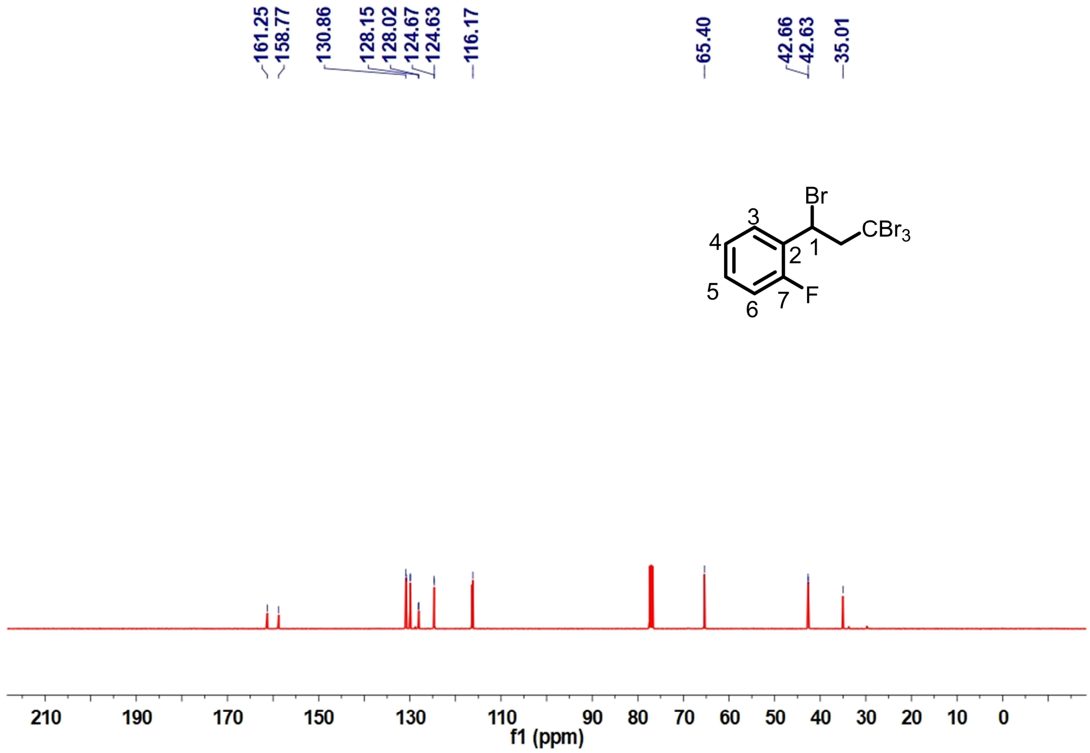


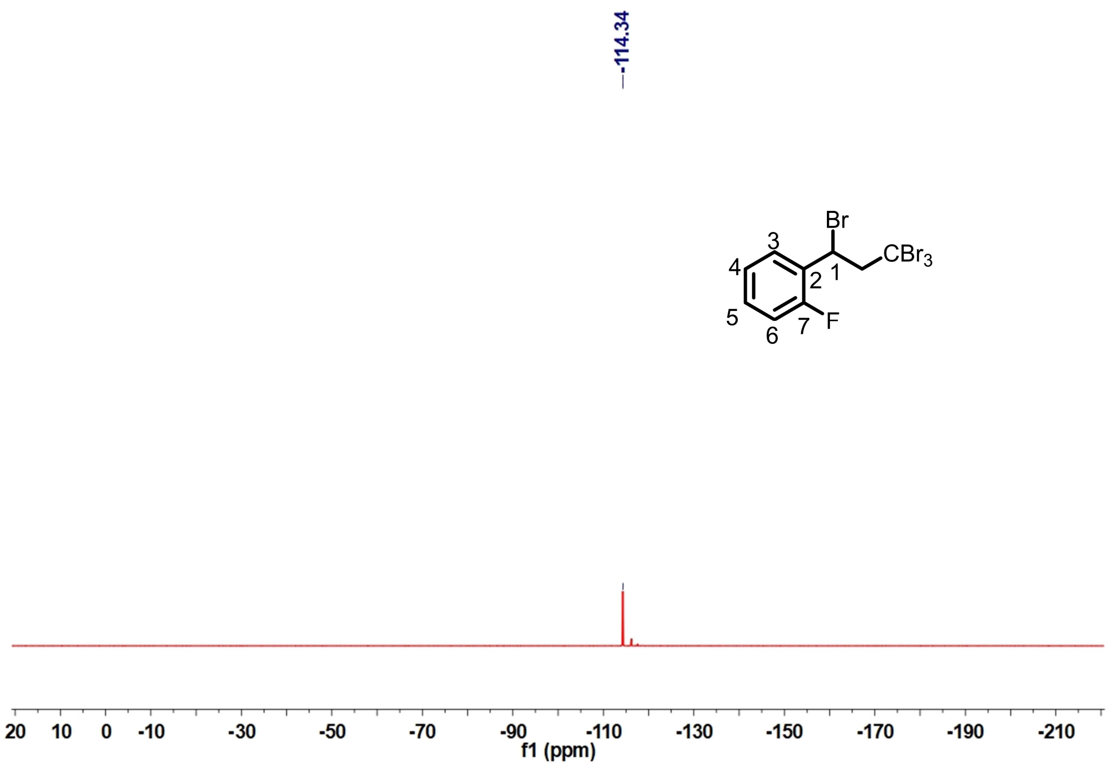


--111.58
Br
CBr3
1
2
3
4
5
6
7
F
20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

Fig. S31. The ^{1}H (400 MHz), $^{13}C\{^{1}H\}$ (101 MHz) and ^{19}F (377 MHz) NMR spectra for 1-fluoro-2-(1,3,3,3-tetrabromopropyl)benzene **(5i)** in $CDCl_3$.

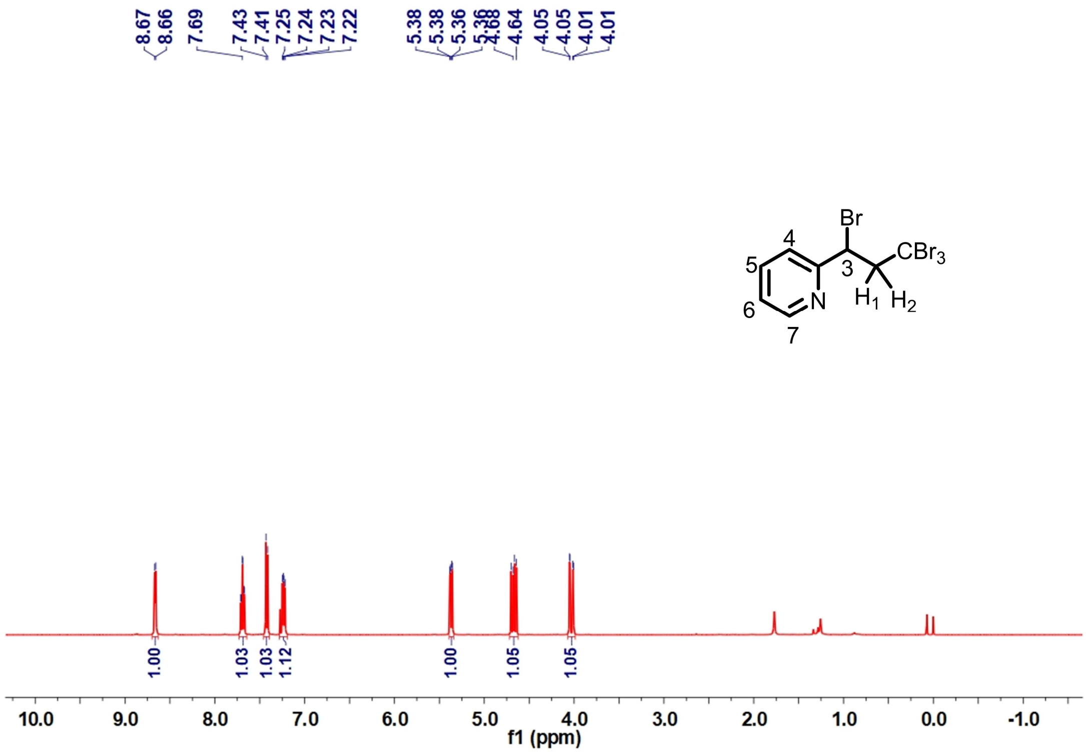






-114.34
Br
CBr3
3
4
2
1
5
6
7
F
20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

Fig. S32. The ^{1}H (400 MHz) and $^{13}C\{^{1}H\}$ (101 MHz) NMR spectra for 2-(1,3,3,3-tetrabromopropyl)pyridine **(6j)** in $CDCl_3$.



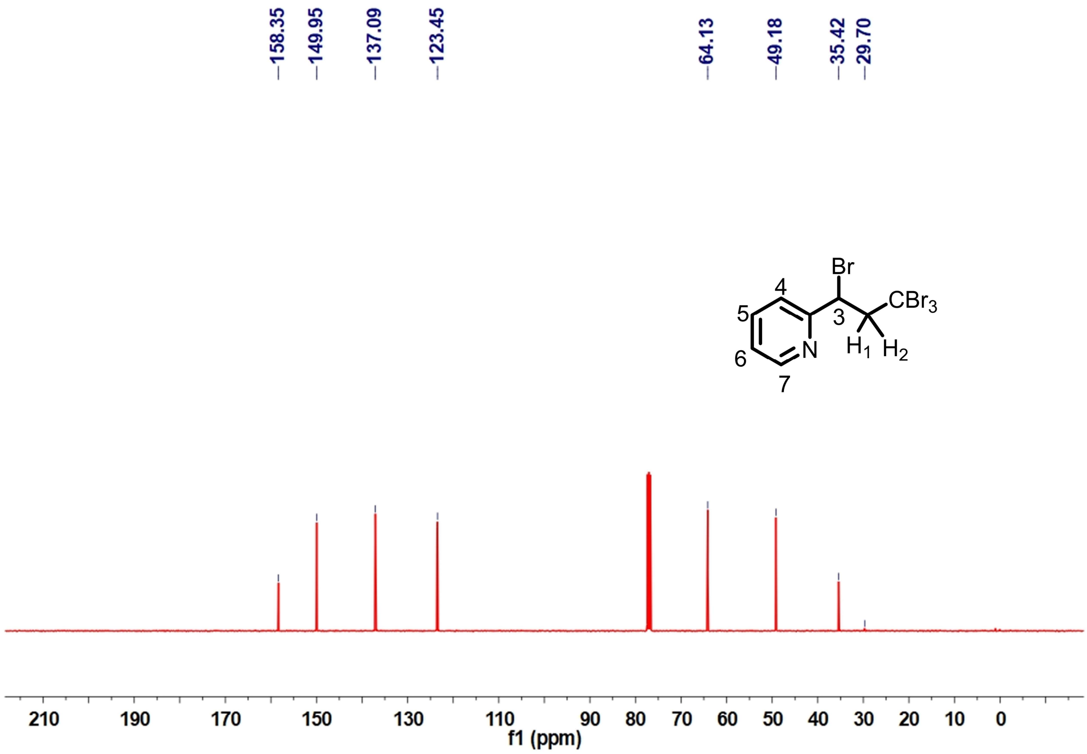
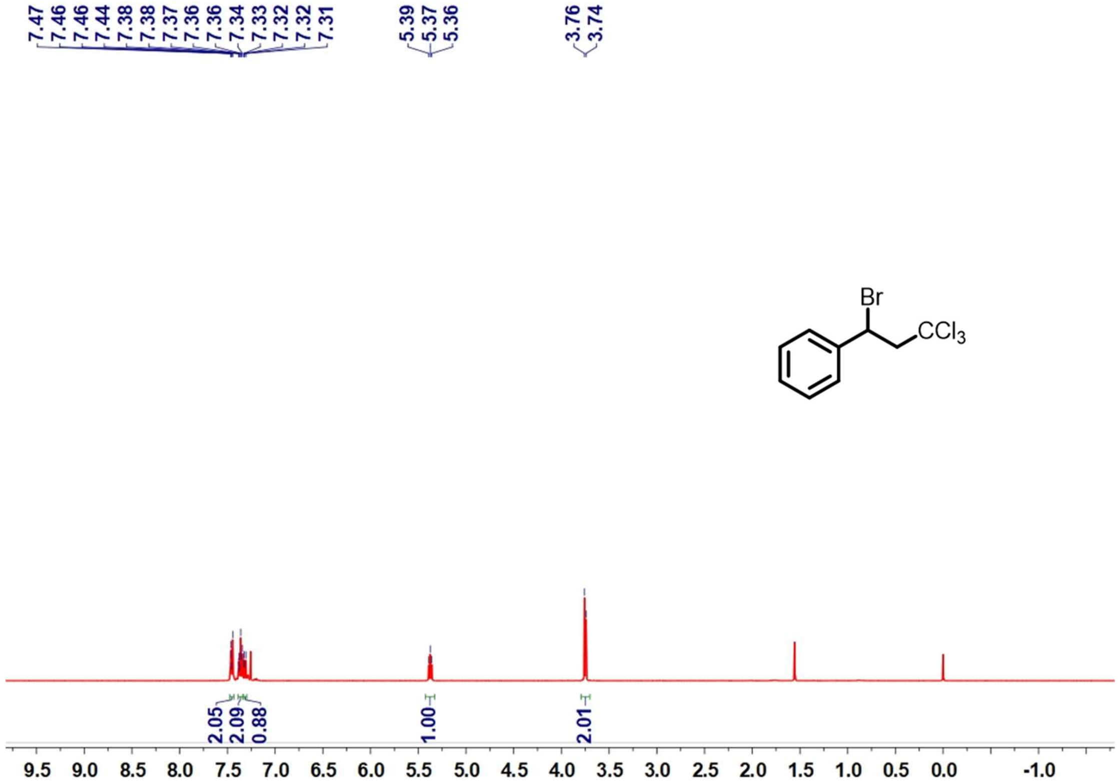


Fig. S33. The ^{1}H (400 MHz) and $^{13}C\{^{1}H\}$ (101 MHz) NMR spectra for (1-bromo-3,3,3-trichloropropyl)benzene (**5k**) in $CDCl_3$.



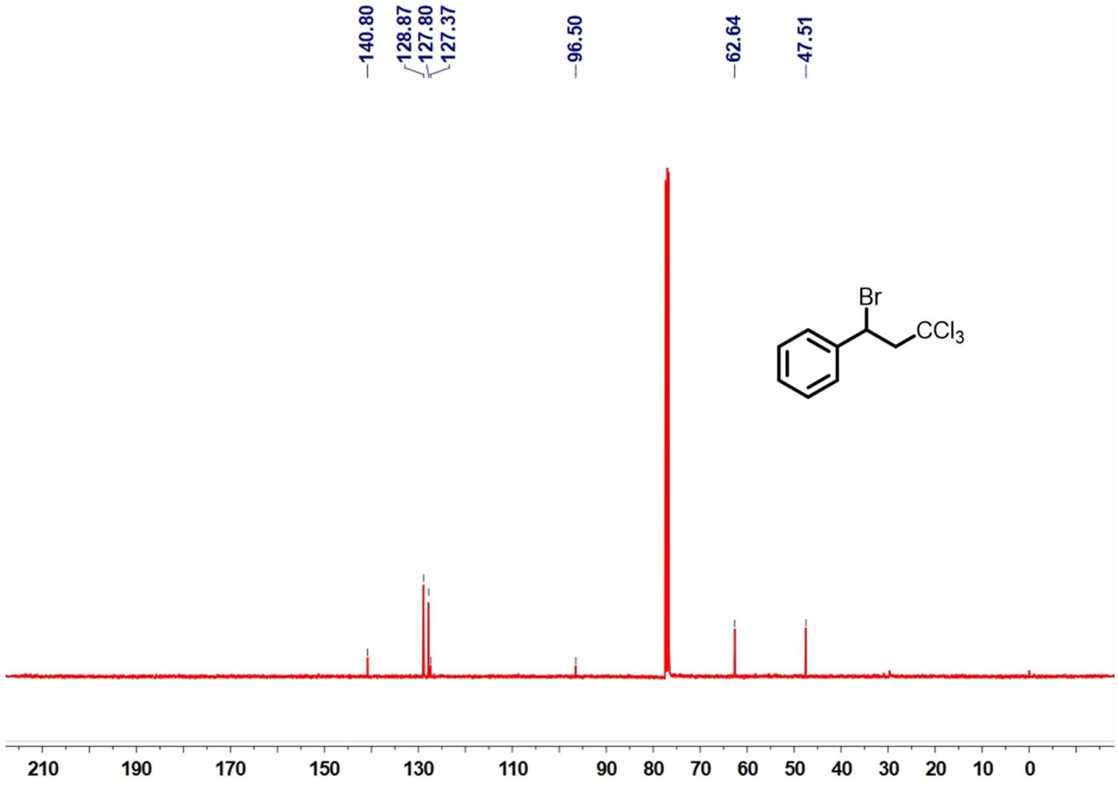
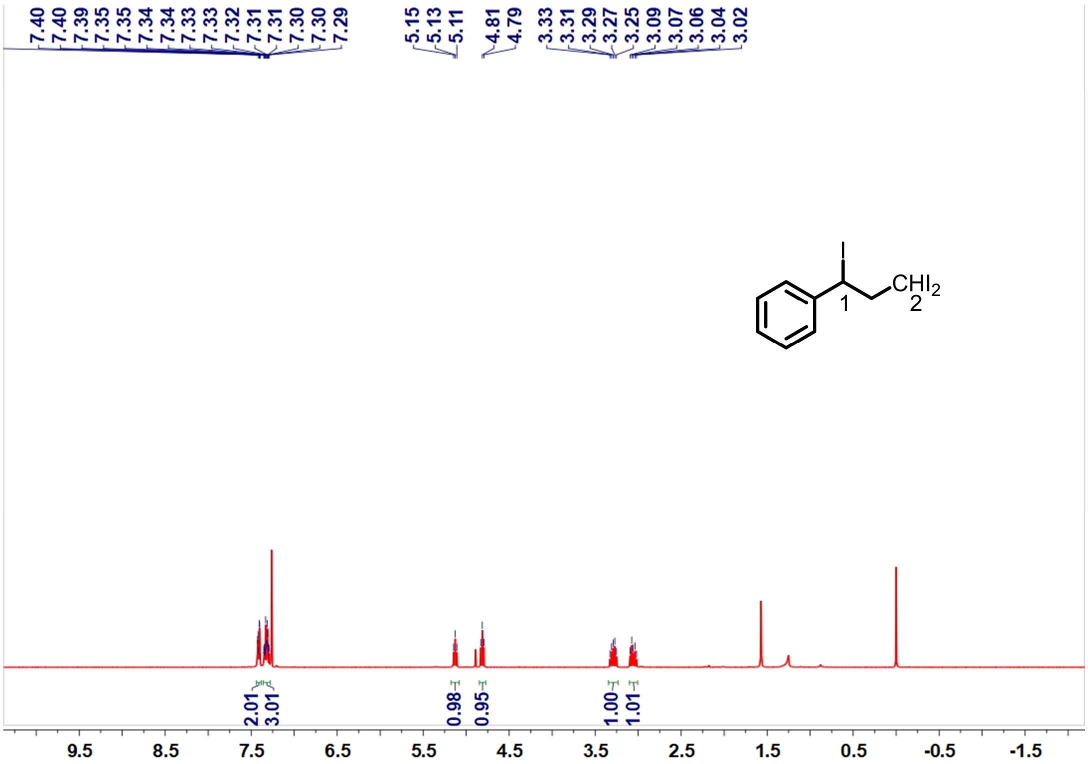


Fig. S34. The ^{1}H (400 MHz) and $^{13}C\{^{1}H\}$ (101 MHz) NMR spectra for (1,3,3-triiodopropyl)benzene (**5l**) in $CDCl_3$.



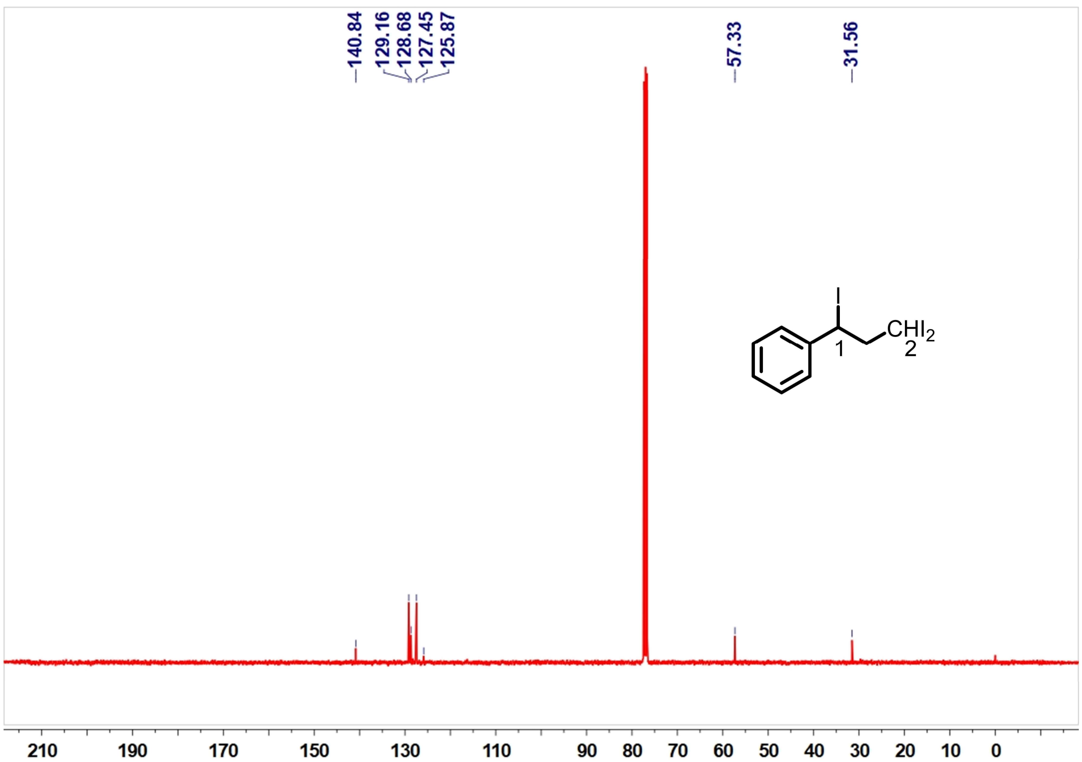
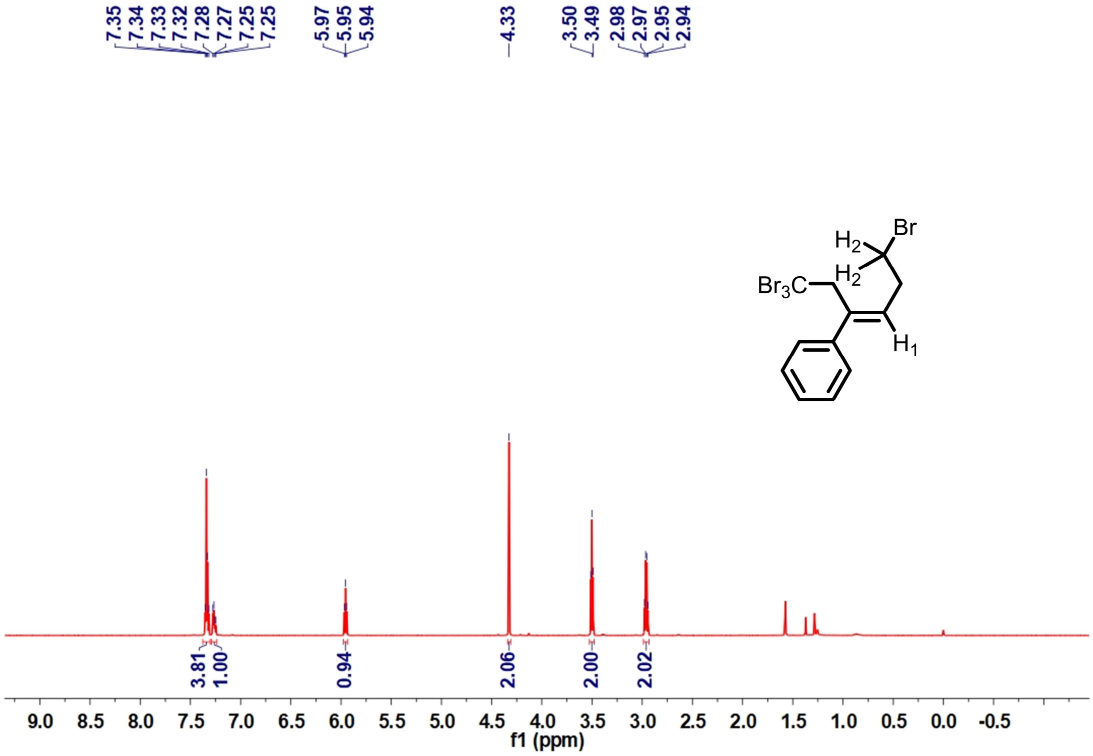


Fig. S35. The ^{1}H (600 MHz) and $^{13}C\{^{1}H\}$ (151 MHz) NMR spectra for (*E*)-(1,1,1,6-tetrabromohex-3-en-3-yl)benzene (**6a**) in $CDCl_3$.



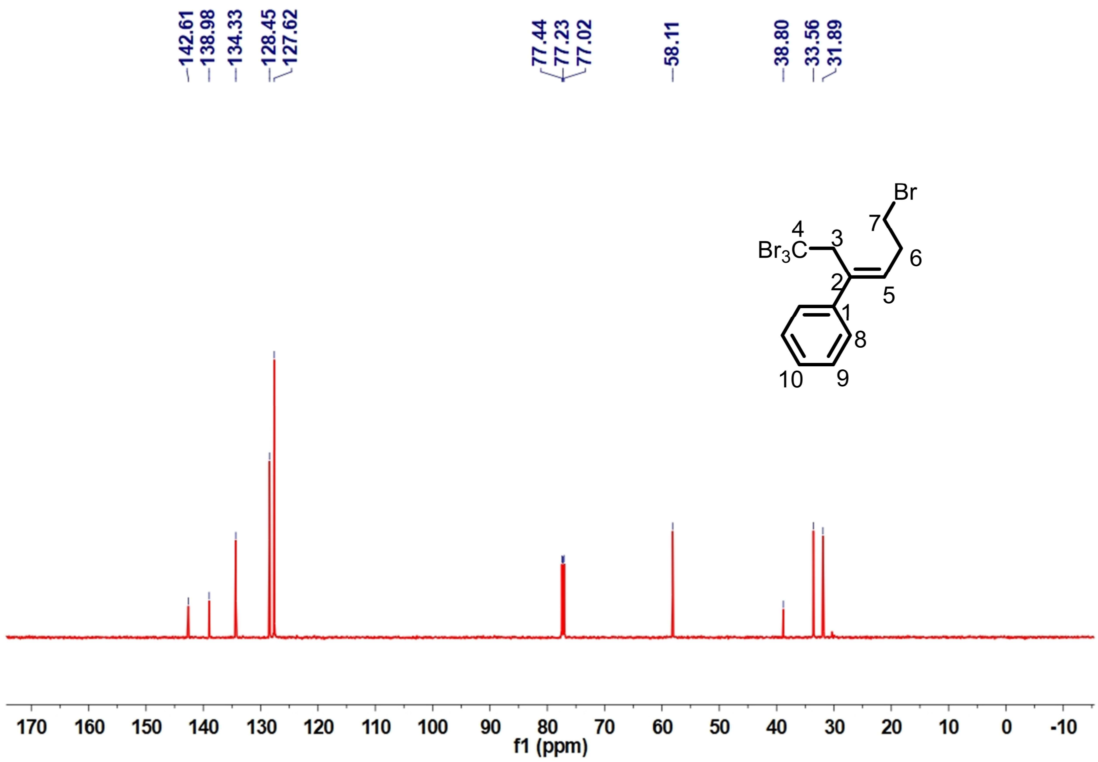


Fig. S36. The $^{13}C\{^{1}H\}$-NNE NMR spectra for (*E*)-(1,1,1,6-tetrabromohex-3-en-3-yl)benzene (**6a**) in $CDCl_3$.

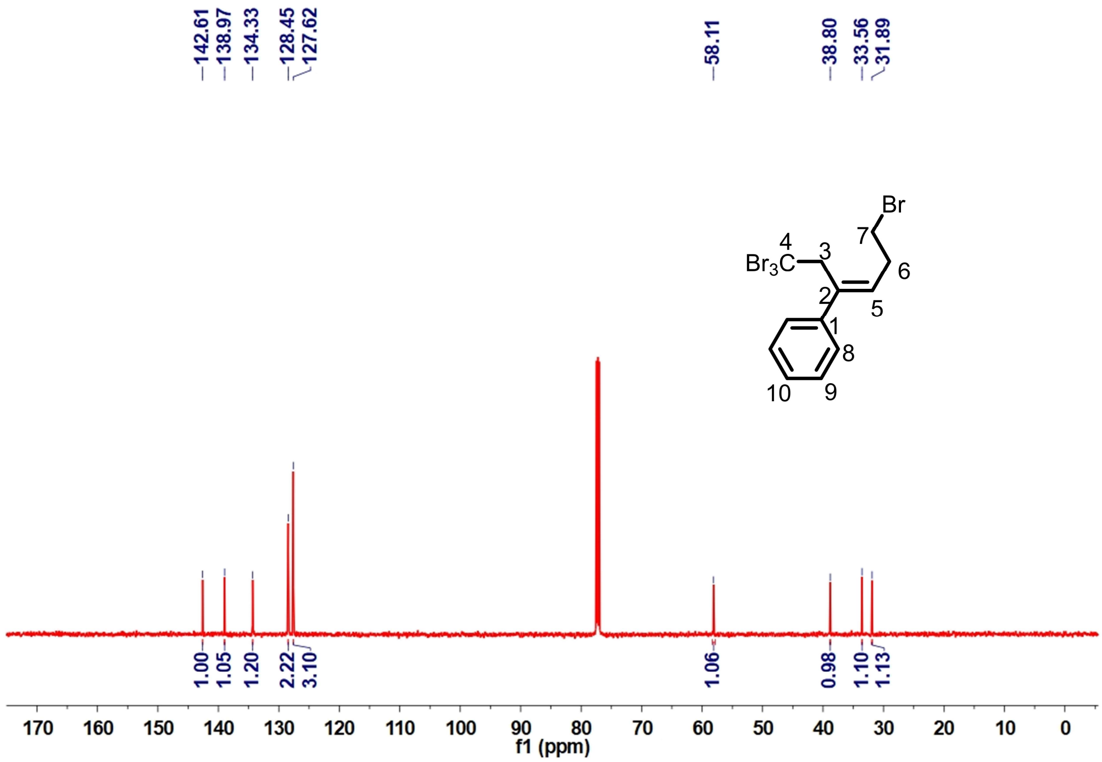


Fig. S37. The $^{13}C\{^{1}H\}$-DEPT NMR spectra for (*E*)-(1,1,1,6-tetrabromohex-3-en-3-yl)benzene (**6a**) in $CDCl_3$.

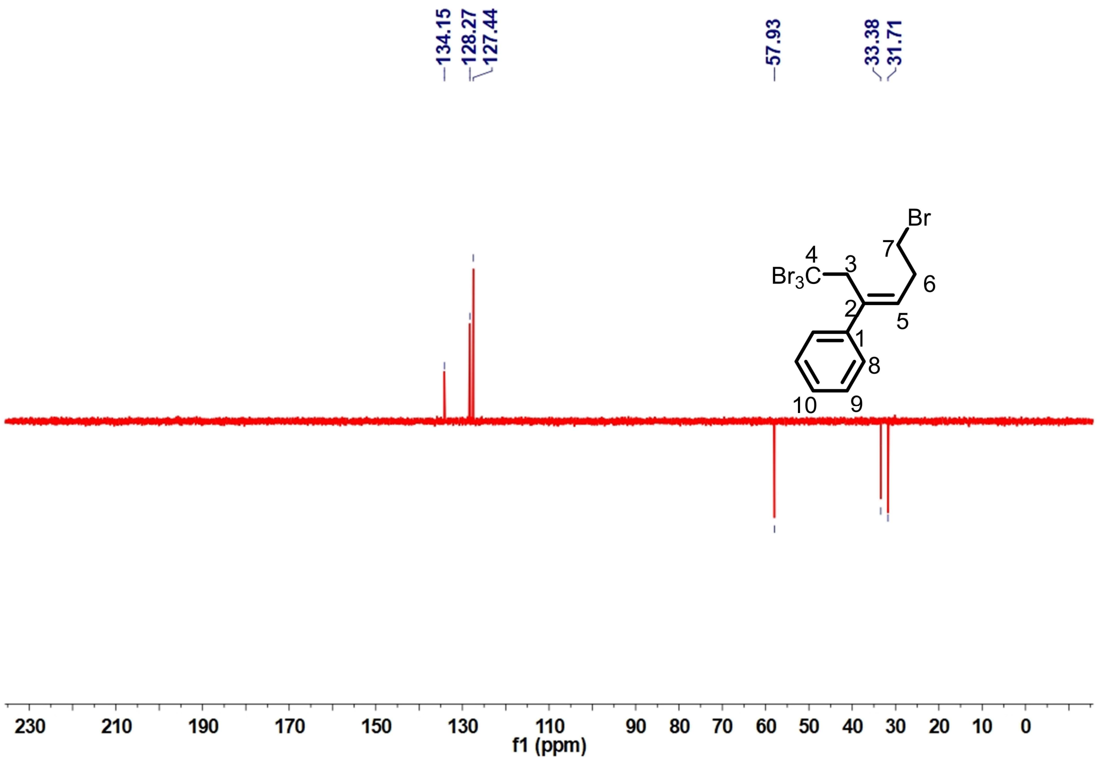
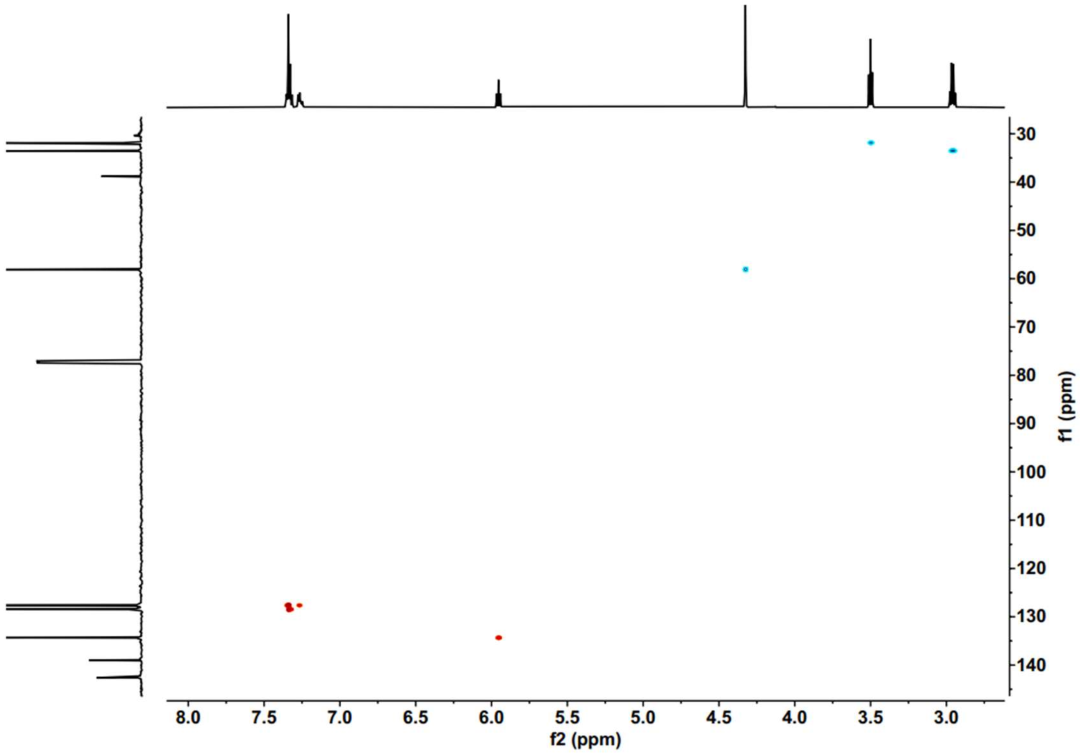


Fig. S38. The ^{13}C-^{1}H COSY NMR spectra for (*E*)-(1,1,1,6-tetrabromohex-3-en-3-yl)benzene (**6a**) in $CDCl_3$.



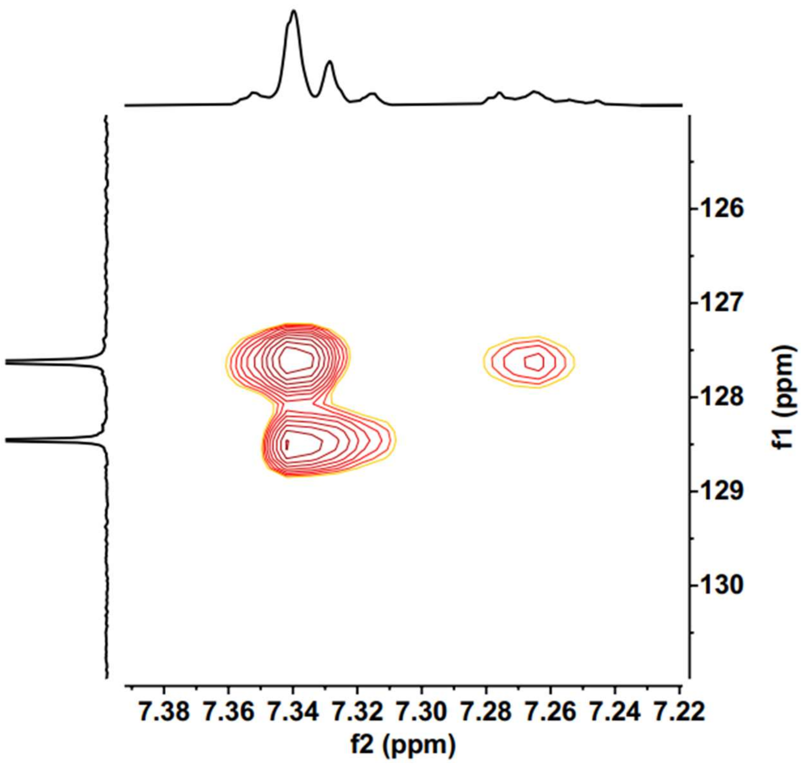
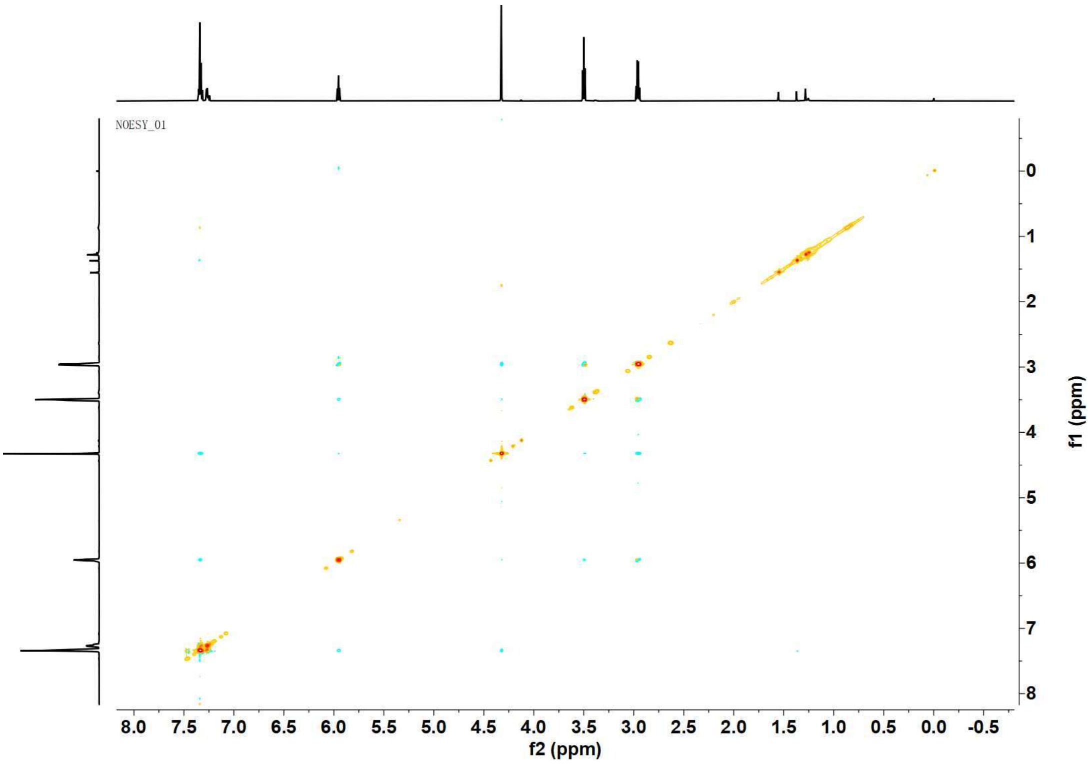


Fig. S39. The [1]H-[1]H NOSEY NMR spectra for (*E*)-(1,1,1,6-tetrabromohex-3-en-3-yl)benzene (**6a**) in $CDCl_3$.



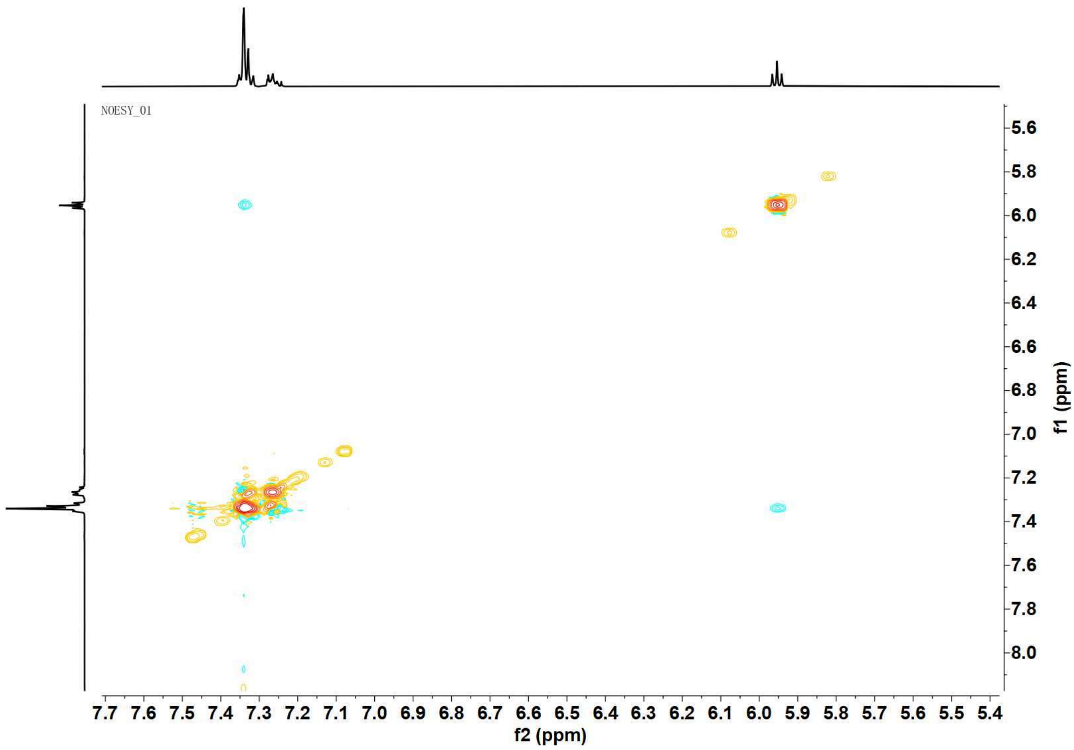
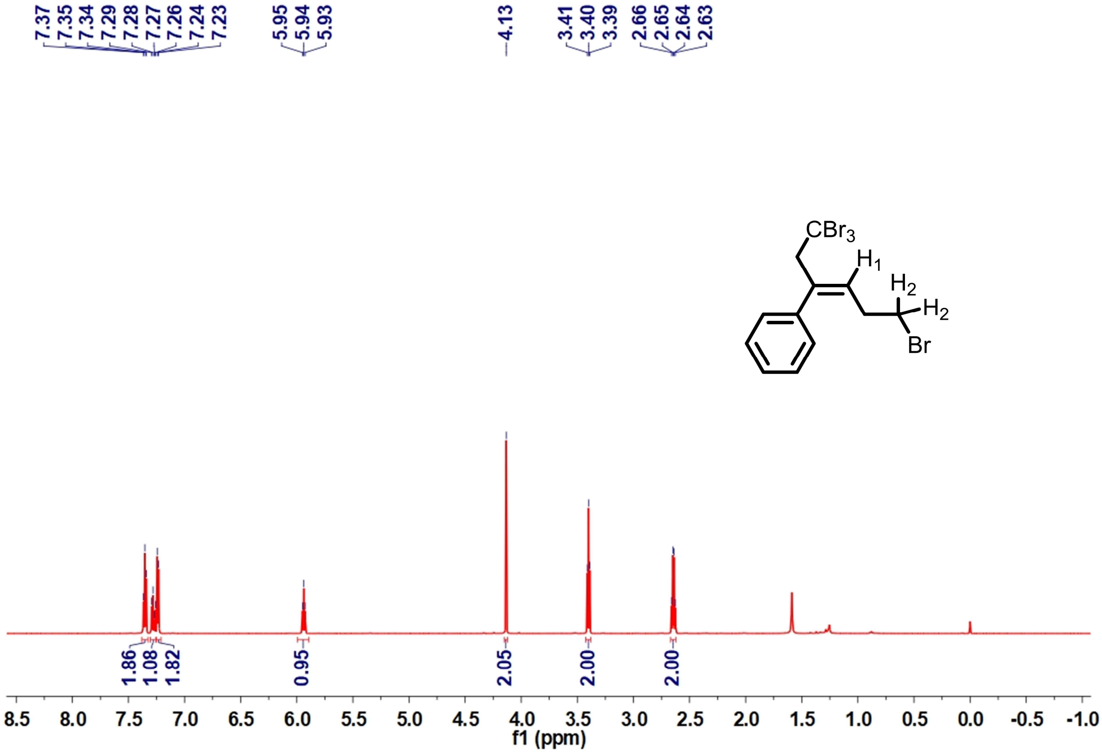


Fig. S40. The ^{1}H (600 MHz) and $^{13}C\{^{1}H\}$ (151 MHz) NMR spectra for (*Z*)-(1,1,1,6-tetrabromohex-3-en-3-yl)benzene (**6b**) in $CDCl_3$.



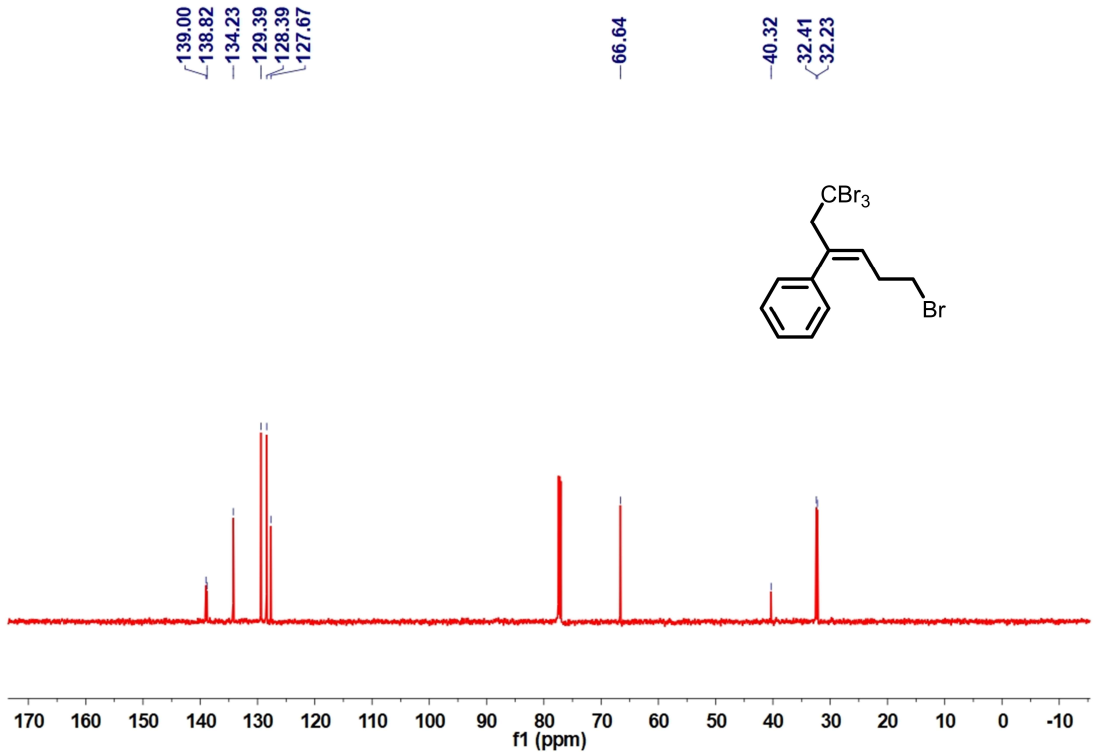


Fig. S41. The ^{1}H-^{1}H NOSEY NMR spectra for (*Z*)-(1,1,1,6-tetrabromohex-3-en-3-yl)benzene (**6b**) in $CDCl_3$.