Supporting Information

Synthesis of a Polar Phosphinoferrocene Amidosulfonate Ligand and Its Application in Pd-Catalyzed Cross-Coupling Reaction of Aromatic Boronic Acids and Acyl Chlorides in an Aqueous Medium

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Table S1. Summary of crystallographic data and structure refinement parameters for **3** and **10**·2MeOH·Et$_2$O.[a]

Compound	**3**	**10**·2MeOH·Et$_2$O
Formula	$C_{31}H_{28}FeNO_4P$	$C_{84}H_{92}Fe_2N_4O_{11}P_2Pd_2S_2$
M/g mol^{-1}	565.36	1784.18
Crystal system	triclinic	monoclinic
Space group	P –1 (no. 2)	$P2_1/c$ (no. 14)
a/Å	9.9841(2)	11.5169(2)
b/Å	11.0287(2)	13.5786(2)
c/Å	13.6068(3)	25.1951(4)
α/°	81.4675(7)	
β/°	75.3722(7)	97.0534(6)
γ/°	64.0570(7)	
V/Å^3	1302.38(5)	3910.3(1)
Z	2	2
μ(Mo Kα)/mm^{-1}	0.679	0.974
Diffrns collected	19589	36482
Independent/observed[b] diffrns	5972/5405	8974/8085
R_{int}[c]/%	1.67	2.04
No. of parameters	343	463
R[c] observed diffrns/%	2.74	2.36
R, wR[c] all data/%	3.09, 7.28	2.70, 6.04
Δρ/e Å^{-3}	0.38, –0.26	0.46, –0.44
CCDC entry	1492767	1492768

[a] Common details: T = 150(2) K. [b] Diffractions with $I > 2\sigma(I)$. [c] Definitions: $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma F_o^2$, where F_o^2(mean) is the average intensity of symmetry-equivalent diffractions. $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\, w(F_o^2)^2]^{1/2}$.

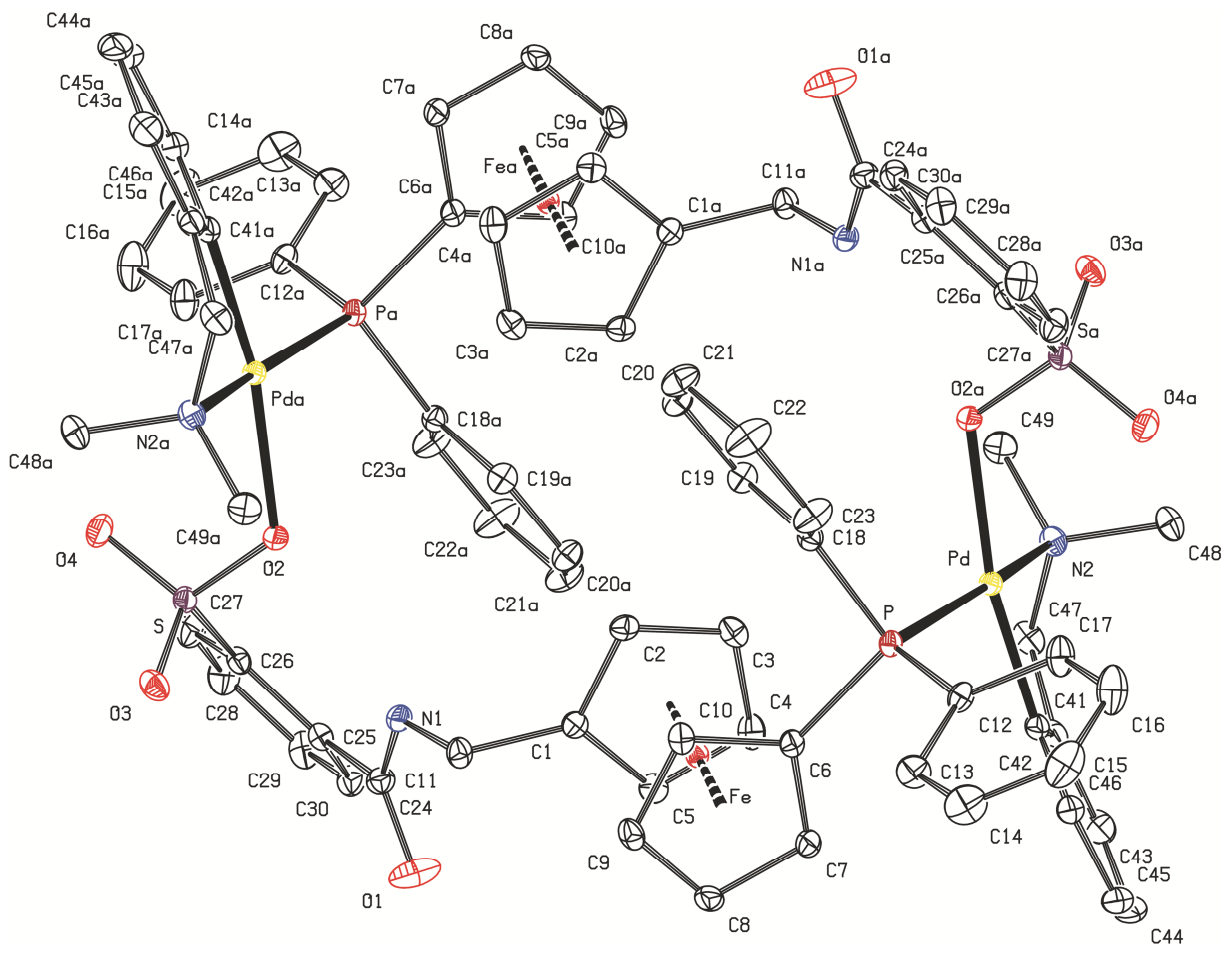
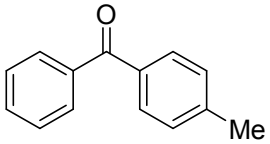


Figure S1. PLATON plot of the complex molecule in the structure of **10**·$2CH_3OH$·Et_2O showing displacement ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity.

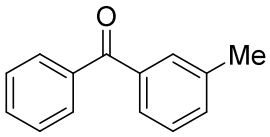
Analytical data for the coupling products **13**.

(Note: Analytical data for the coupling products are in agreement with the literature.[1])



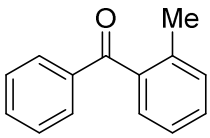
4-methylbenzophenone (13a)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.47 (s, 3 H, CH_3), 7.31 (dm, $J \approx 8$ Hz, 2 H aromatic CH), 7.50 (tm, $J \approx 7$ Hz, 2 H, aromatic CH), 7.60 (tm, $J \approx 7$ Hz, 1 H, aromatic CH), 7.75 (dm, $J \approx 8$ Hz, 2 H, aromatic CH), 7.81 (dm, $J \approx 7$ Hz, 2 H, aromatic CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 21.67 (CH_3), 128.21 (aromatic CH), 128.98 (aromatic CH), 129.93 (aromatic CH), 130.31 (aromatic CH), 132.16 (aromatic CH), 134.89 (aromatic C^{ipso}), 137.96 (aromatic C^{ipso}), 143.24 (aromatic C^{ipso}), 196.51 (CO).



3-methylbenzophenone (13b)

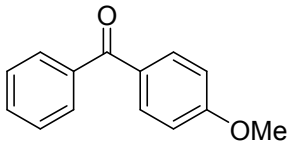
^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.45 (s, 3 H, CH_3), 7.45-7.35 (m, 2 H, aromatic CH), 7.50 (tm, $J \approx 7$ Hz, 2 H, aromatic CH), 7.60 (dm, $J \approx 7$ Hz, 2 H, aromatic CH), 7.65 (m, 1 H, aromatic CH), 7.83 (dm, $J \approx 7$ Hz, 2 H, aromatic CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 21.37 (CH_3), 127.37, 128.09, 128.24, 130.05, 130.46, 132.33, 133.19 (all aromatic CH), 137.64, 137.77, 138.16 (all aromatic C^{ipso}), 196.97 (CO).



2-methylbenzophenone (13c)

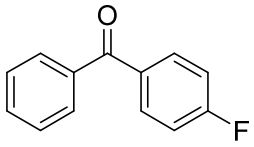
^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.36 (s, 3 H, CH_3), 7.28 (tm, $J \approx 8$ Hz, 1 H, aromatic CH), 7.33 (tm, $J \approx 8$ Hz, 2 H, aromatic CH), 7.42 ($J \approx 7$ Hz, 1 H, aromatic CH), 7.48 (tm, $J \approx 8$ Hz, 2 H, aromatic CH), 7.60 (tm, $J \approx 8$ Hz, 1 H, aromatic CH), 7.83 (dm, $J \approx 8$ Hz, 2 H, aromatic CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 19.99 (CH_3), 125.20, 128.64, 128.52, 130.13, 130.24, 131.00, 133.13 (all aromatic CH), 136.75, 137.75, 138.63 (all aromatic C^{ipso}), 198.64 (CO).

4-methoxybenzophenone (13d)



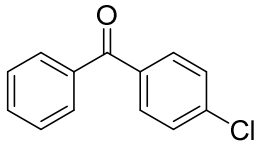
^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.88 (s, 3 H, OMe), 6.96 (dm, *J* ≈ 9 Hz, 2 H, aromatic CH), 7.47 (tm, *J* ≈ 8 Hz, 2 H, aromatic CH), 7.56 (tm, *J* ≈ 8 Hz, 1 H, aromatic CH), 7.76 (dm, *J* ≈ 8 Hz, 2 H, aromatic CH), 7.83 (dm, *J* ≈ 9 Hz, 2 H, aromatic CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 55.50 (OMe), 113.56 (aromatic CH), 128.19 (aromatic CH), 129.73 (aromatic CH), 130.16 (aromatic C^{ipso}), 131.89 (aromatic CH), 132.56 (aromatic CH), 138.30 (aromatic C^{ipso}), 163.23 (aromatic C^{ipso}OMe), 195.55 (CO).

4-fluorobenzophenone (13e)



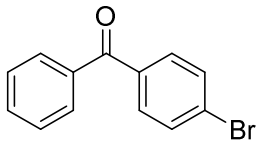
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.16 (tm, *J* ≈ 9 Hz, 2 H, aromatic CH), 7.49 (tm, *J* ≈ 7 Hz, 2 H, aromatic CH), 7.59 (tm, *J* ≈ 8 Hz, 1 H, aromatic CH), 7.77 (dm, *J* ≈ 7 Hz, 2 H, aromatic CH), 7.85 (m, 2 H, aromatic CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): 115.46 (d, $^{2}J_{FC}$ = 22 Hz, aromatic CH), 128.36, 129.88, 132.47 (all aromatic CH), 132.67 (d, $^{3}J_{FC}$ = 9 Hz, aromatic CH), 133.80 (d, $^{4}J_{FC}$ = 3 Hz, aromatic C^{ipso}), 137.50 (aromatic C^{ipso}), 165.39 (d, $^{1}J_{FC}$ =254 Hz, C^{ipso}-F), 195.26 (CO). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −105.98 (m).

4-chlorobenzophenone (13f)



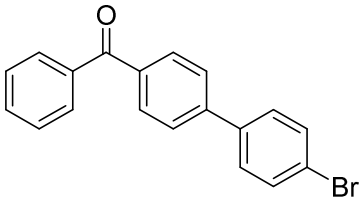
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46-7.53 (m, 4 H, aromatic CH), 7.62 (tm, *J* ≈ 8 Hz, 1 H, aromatic CH), 7.76-7.81 (m, 4 H, aromatic CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 128.41, 128.64, 129.93, 131.46, 132.64 (all aromatic CH), 135.87, 137.24, 138.89 (all aromatic C^{ipso}), 195.48 (CO).

4-bromobenzophenone (13g)



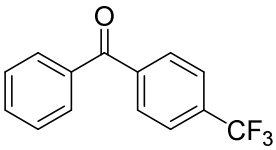
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51 (tm, J ≈ 8 Hz, 2 H, aromatic CH), 7.60-7.67 (m, 3 H, aromatic CH), 7.70 (dm, J ≈ 8 Hz, 2 H, aromatic CH), 7.80 (dm, J ≈ 8 Hz, 2 H, aromatic CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 127.51 (aromatic C^{ipso}), 128.42, 129.94, 131.57, 131.62, 132.69 (all aromatic CH), 136.31 (aromatic C^{ipso}), 137.16 (aromatic C^{ipso}), 195.57 (CO).

4-(4-bromophenyl)benzophenone (14)



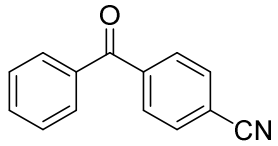
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48-7.54 (m, 4 H, aromatic CH), 7.59-7.64 (m, 3 H, aromatic CH), 7.67 (dm, J ≈ 8 Hz, 2 H, aromatic CH), 7.84 (dm, J ≈ 8 Hz, 2 H, aromatic CH), 7.90 (dm, J ≈ 8 Hz, 2 H, aromatic CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 122.62 (aromatic C^{ipso}), 126.78, 128.35, 128.86, 130.01, 130.81, 132.13, 132.48 (aromatic C^{ipso}), 136.60, 137.62, 138.99, 143.92 (aromatic C^{ipso}), 196.20 (CO).

4-trifluormethylbenzophenone (13h)



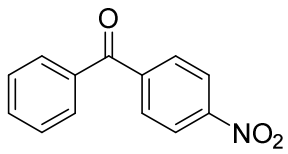
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51 (tm, J ≈ 7 Hz, 2 H, aromatic CH), 7.63 (tm, J ≈ 7 Hz, 1 H, aromatic CH), 7.76 (dm, J ≈ 8 Hz, 2 H, aromatic CH), 7.81 (dm, J ≈ 8 Hz, 2 H, aromatic CH), 7.90 (dm, J ≈ 7 Hz, 2 H, aromatic CH).^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 123.67 (q, $^{1}J_{FC}$ = 273 Hz, CF_3), 125.35 (q, $^{3}J_{FC}$ = 4 Hz, aromatic CH), 128.53, 130.10, 130.14, 133.09 (all aromatic CH), 133.72 (q, $^{2}J_{FC}$ = 33 Hz, aromatic C^{ipso}-CF_3), 136.73 (aromatic C^{ipso}), 140.74 (aromatic C^{ipso}), 195.53 (CO). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −63.01 (s).

4-cyanobenzophenone (13i)



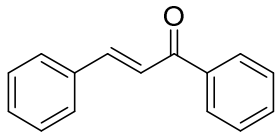
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 (tm, $J \approx 8$ Hz, 2 H, aromatic CH), 7.64 (tm, $J \approx 7$ Hz, 1 H, aromatic CH), 7.76-7.82 (m, 4 H, aromatic CH), 7.88 (dm, $J \approx 8$ Hz, 2 H, aromatic CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 115.67 (aromatic C^{ipso}), 118.02 (CN), 128.64, 130.07, 130.24, 132.17, 133.33 (all aromatic CH), 136.33 (aromatic C^{ipso}), 141.23 (aromatic C^{ipso}), 195.02 (CO).

4-nitrobenzophenone (13j)

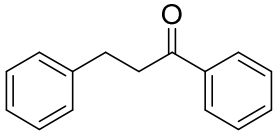


^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53 (tm, $J \approx 8$ Hz, 2 H, aromatic CH), 7.66 (tm, $J \approx 7$ Hz, 1 H, aromatic CH), 7.81 (dm, $J \approx 8$ Hz, 2 H, aromatic CH), 7.94 (dm, $J \approx 8$ Hz, 2 H, aromatic CH), 8.35 (dm, $J \approx 8$ Hz, 2 H, aromatic CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 125.55, 128.69, 130.10, 130.70, 133.48 (all aromatic CH), 136.29, 142.89, 149.83 (all aromatic C^{ipso}), 194.79 (CO).

***trans*-Chalcone (13k)**



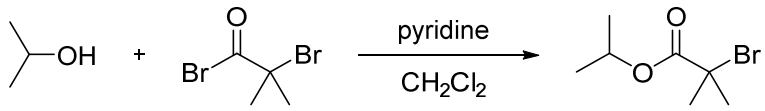
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40-7.45 (m, 3 H, aromatic CH), 7.52 (tm, $J \approx 8$ Hz, 2 H, aromatic CH), 7.56 (d, $^{3}J_{HH}$ = 15.7 Hz, 1 H, double bond CH), 7.57-7.61 (m, 1 H, aromatic CH), 7.64-7.68 (m, 2 H, aromatic CH), 7.85 (d, $^{3}J_{HH}$ = 15.7 Hz, 1 H, double bond CH), 8.06 (dm, $J \approx 8$ Hz, 2 H, aromatic CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 121.99 (CH=), 128.41(aromatic CH), 128.46 (aromatic CH), 128.57 (aromatic CH), 128.90 (aromatic CH), 130.50 (aromatic CH), 132.74 (aromatic CH), 134.81 (aromatic C^{ipso}), 138.13 (aromatic C^{ipso}), 144.73 (CH=), 190.37 (CO).



1,3-difenyl-1-propanone (13l)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.06 (t, $^{3}J_{HH}$ = 7.3 Hz, 2 H, CH_2), 3.29 (t, $^{3}J_{HH}$ = 7.3 Hz, 2 H, CH_2), 7.17-7.32 (m, 5 H, aromatic CH), 7.43 (tm, $J \approx 8$ Hz, 2 H, aromatic CH), 7.53 (tm, $J \approx 8$ Hz, 1 H, aromatic CH), 7.95 (dm, $J \approx 8$ Hz, 2 H aromatic CH). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz): δ 30.17 (CH_2), 40.48 (CH_2), 126.17 (aromatic CH), 128.07 (aromatic CH), 128.46 (aromatic CH), 128.56 (aromatic CH), 128.63 (aromatic CH), 133.09 (aromatic CH), 136.88 (aromatic C^{ipso}), 141.33 (aromatic C^{ipso}), 199.22 (CO).

Synthesis of isopropyl 2-bromo-2-methylpropanoate (**16**).



16

The method was adapted from ref.[2] A dry reaction flask was charged with 2-propanol (4.6 mL, 60 mmol), dry pyridine (4.8 mL, 60 mmol) and dry tetrahydrofurane (30 mL), and cooled in an ice bath. Neat 2-bromo-2-methylpropionyl bromide (5.0 mL, 50 mmol) was added dropwise to the stirred reaction mixture over 30 min, whereupon a white precipitate (pyridine·HBr) was deposited. After the addition was completed, the stirring was continued at 0 ºC for 30 min and then at room temperature for the same time. The precipitated solid was filtered off and the solid residue washed with THF (*ca*. 40 mL). The filtrate was evaporated and the residue was diluted with diethyl ether (10 mL) and filtered again to remove residual pyridinium salt. The filtrate was carefully evaporated under reduced pressure to afford ester **16** as a colorless oil (8.81 g, 84%).

^{1}H NMR ($CDCl_3$): δ 1.28 (d, $^{3}J_{HH}$ = 6.3 Hz, 6 H, CH*Me*$_2$), 1.92 (s, 6 H, CBr*Me*$_2$), 5.05 (sept, $^{3}J_{HH}$ = 6.3 Hz, 1 H, C*H*Me$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 21.25 (CH*Me*$_2$), 30.68 (CBr*Me*$_2$), 56.33 (*C*BrMe$_2$), 69.55 (C*H*Me$_2$), 171.12 (CO). The data are in agreement with those of an authentic sample.

Copies of the NMR spectra

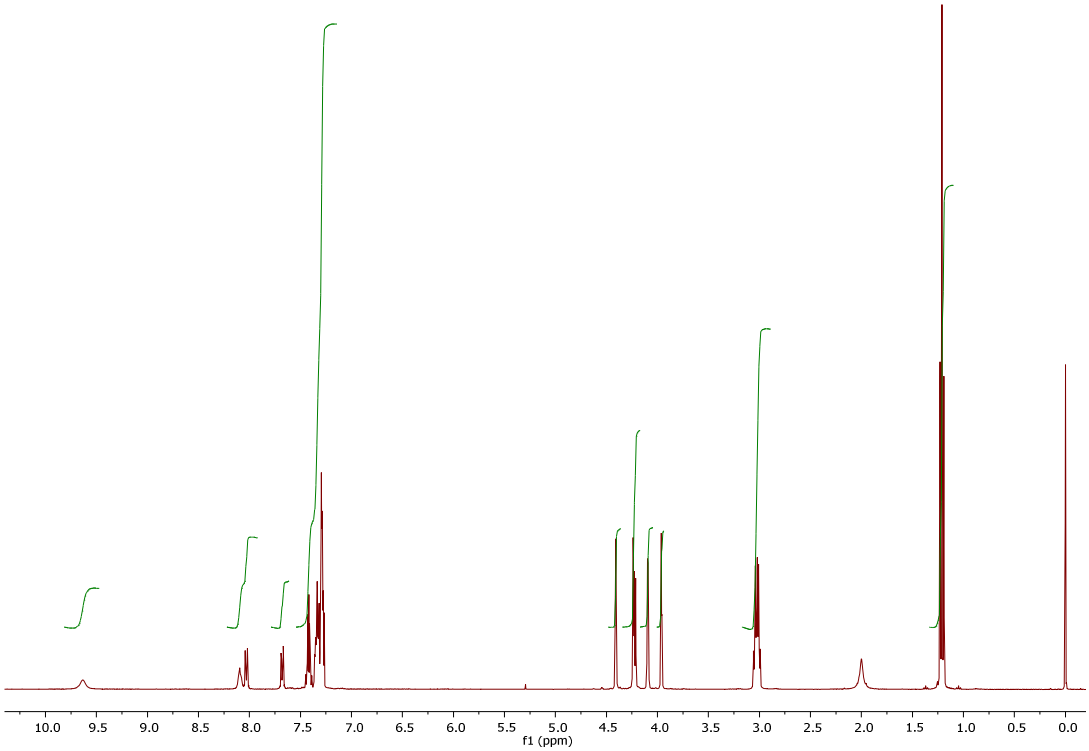


Figure S2. ^{1}H NMR spectrum of **2.**

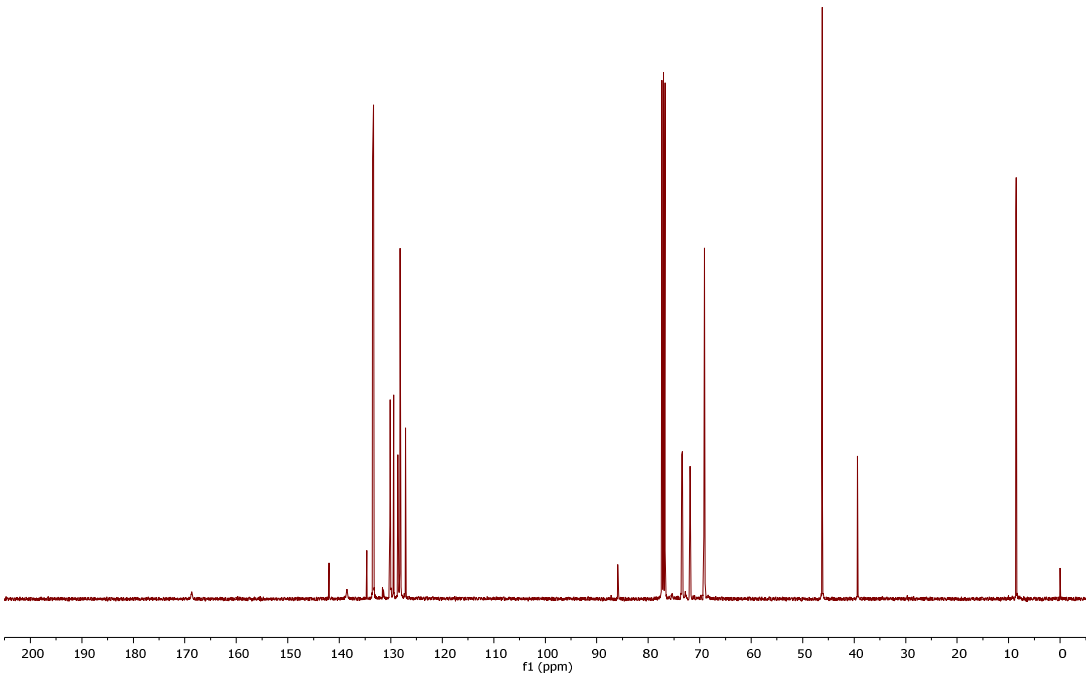


Figure S3. ^{13}C{^{1}H} NMR spectrum of **2.**

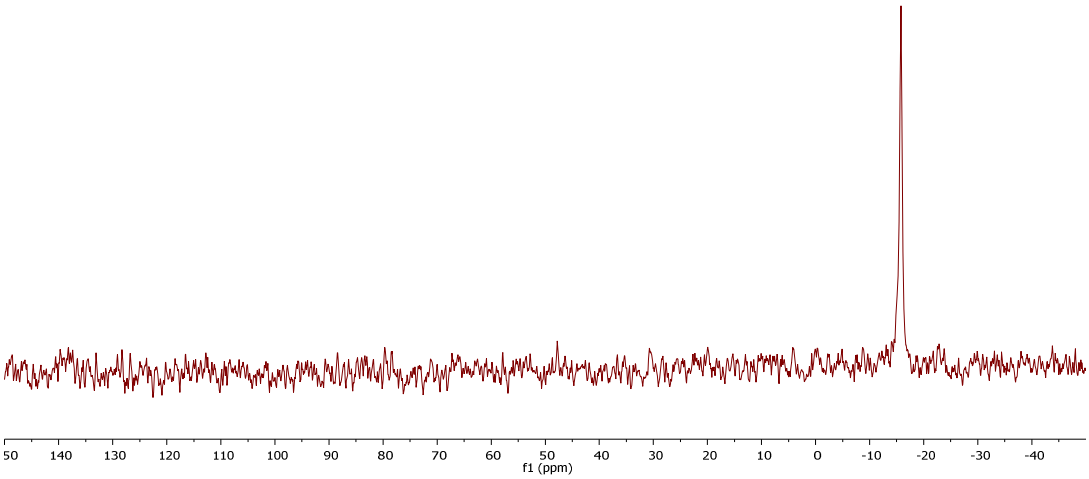


Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum of **2.**

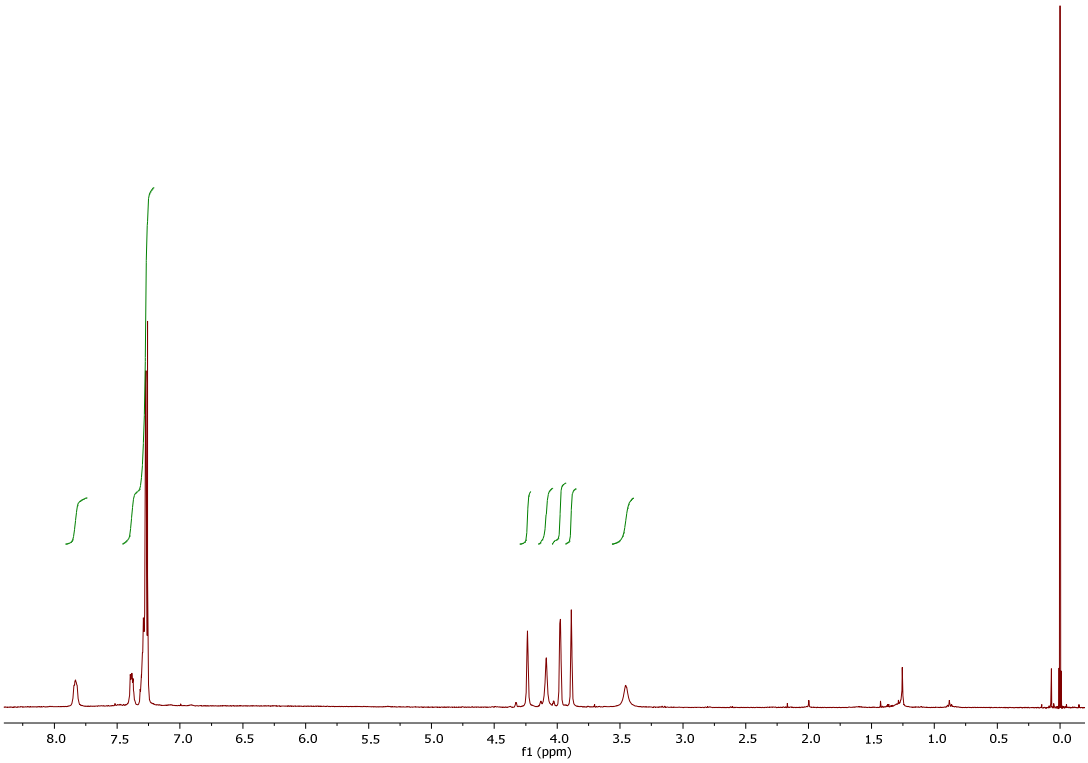


Figure S5. ^{1}H NMR spectrum of **3.**

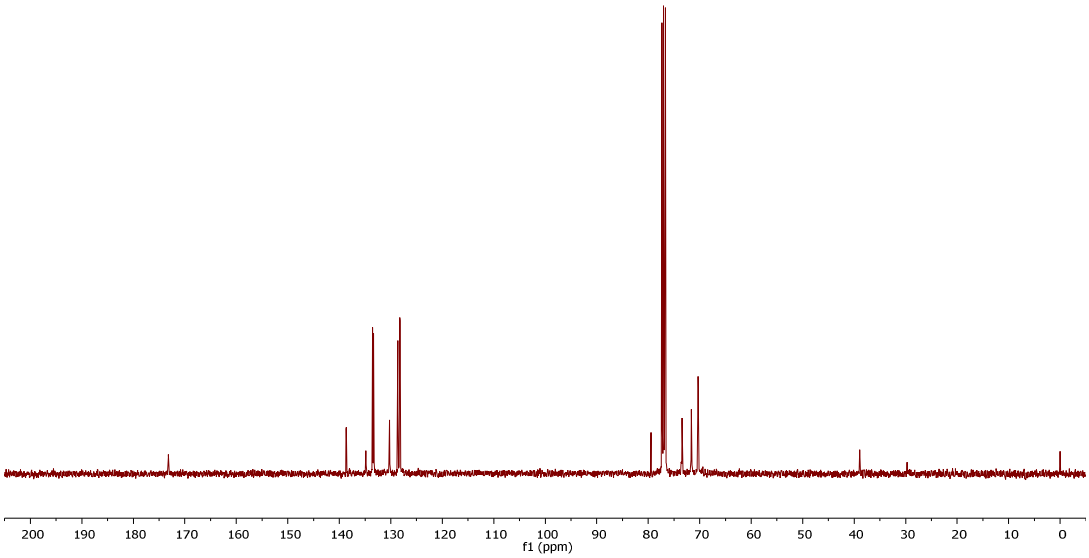


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **3.**

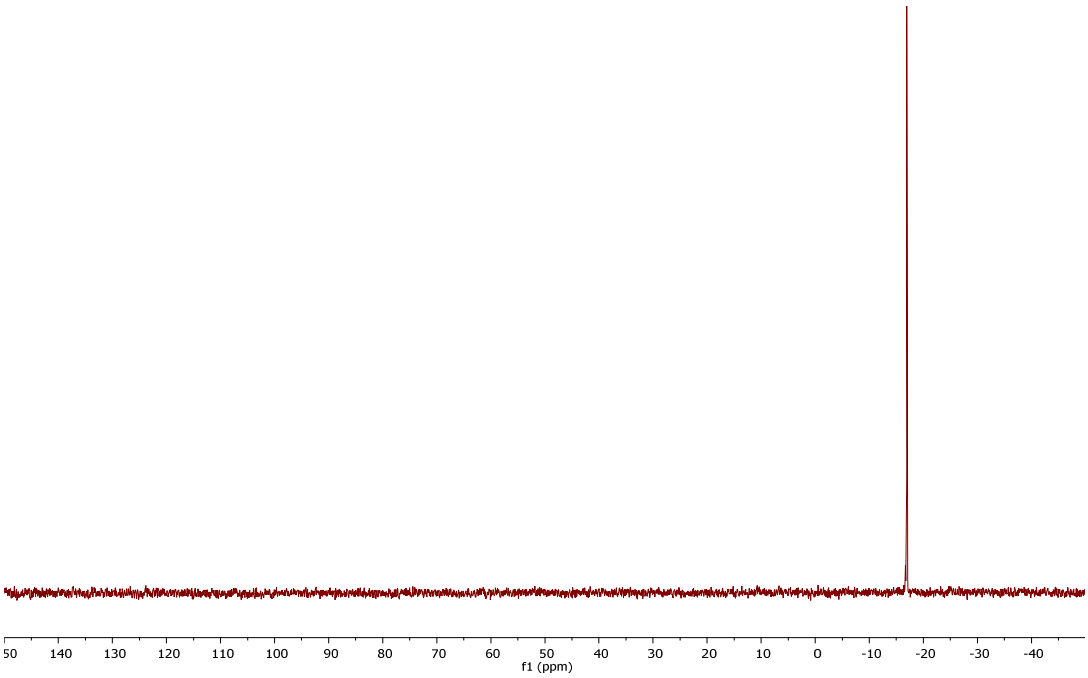


Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum of **3.**

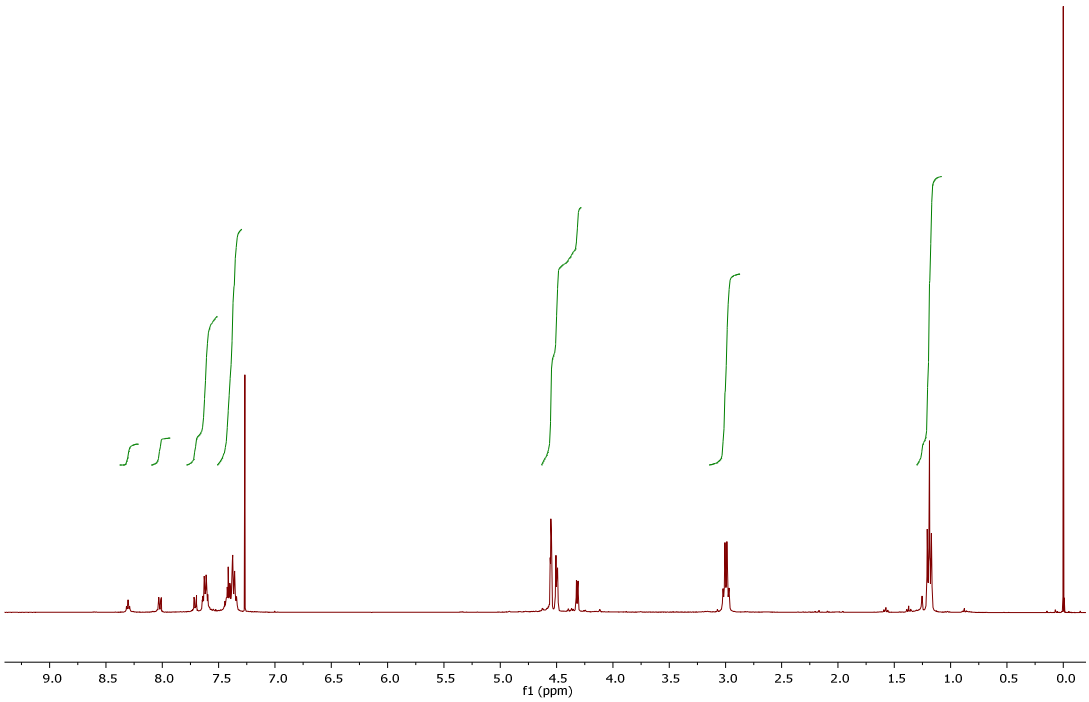


Figure S8. ^{1}H NMR spectrum of **4.**

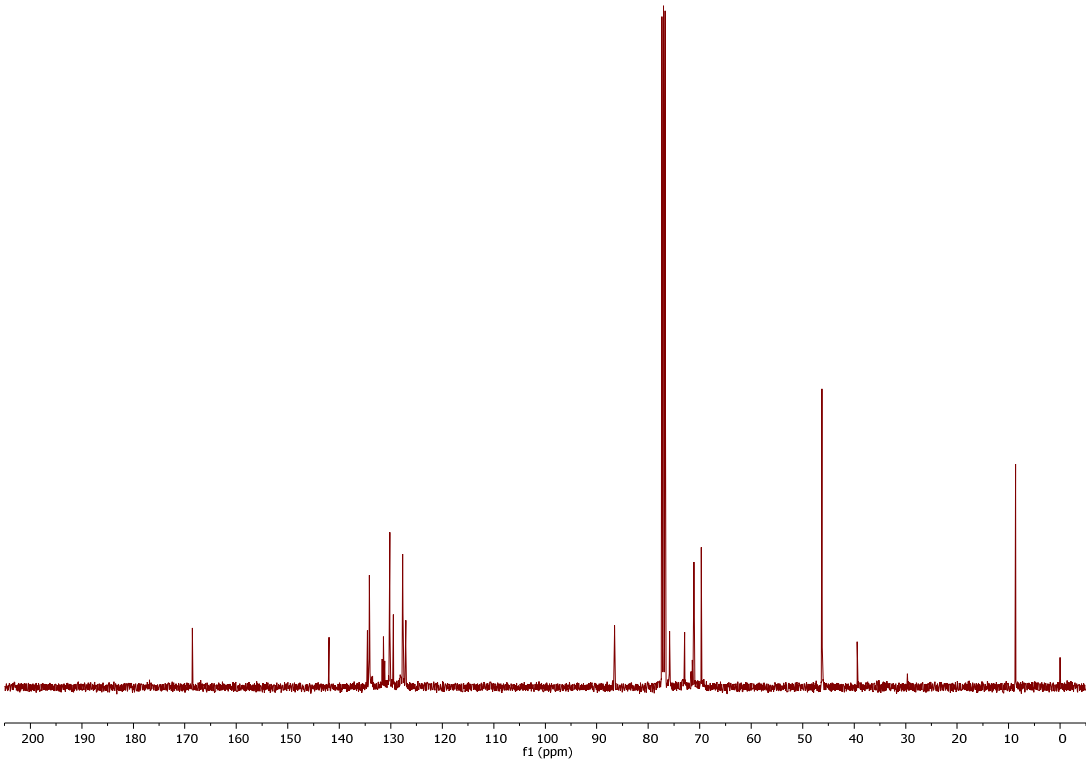


Figure S9. ^{13}C{^{1}H} NMR spectrum of **4.**

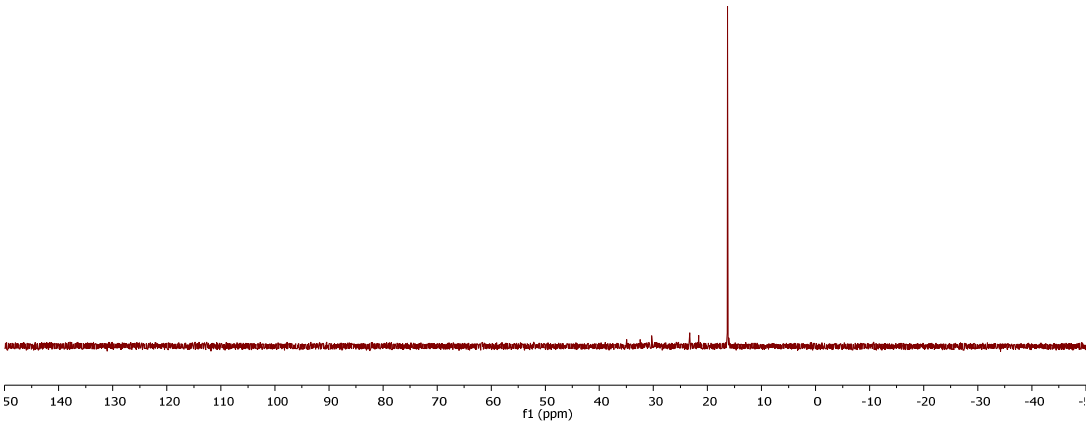


Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum of **4.**

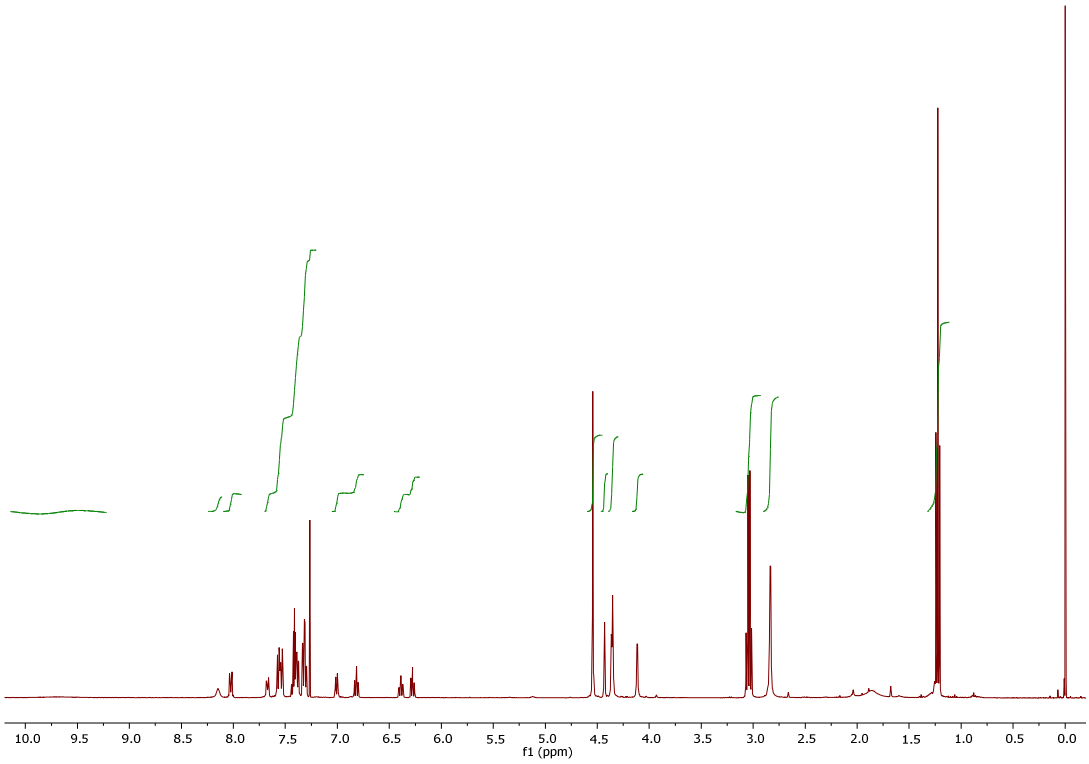


Figure S11. ^{1}H NMR spectrum of **7.**

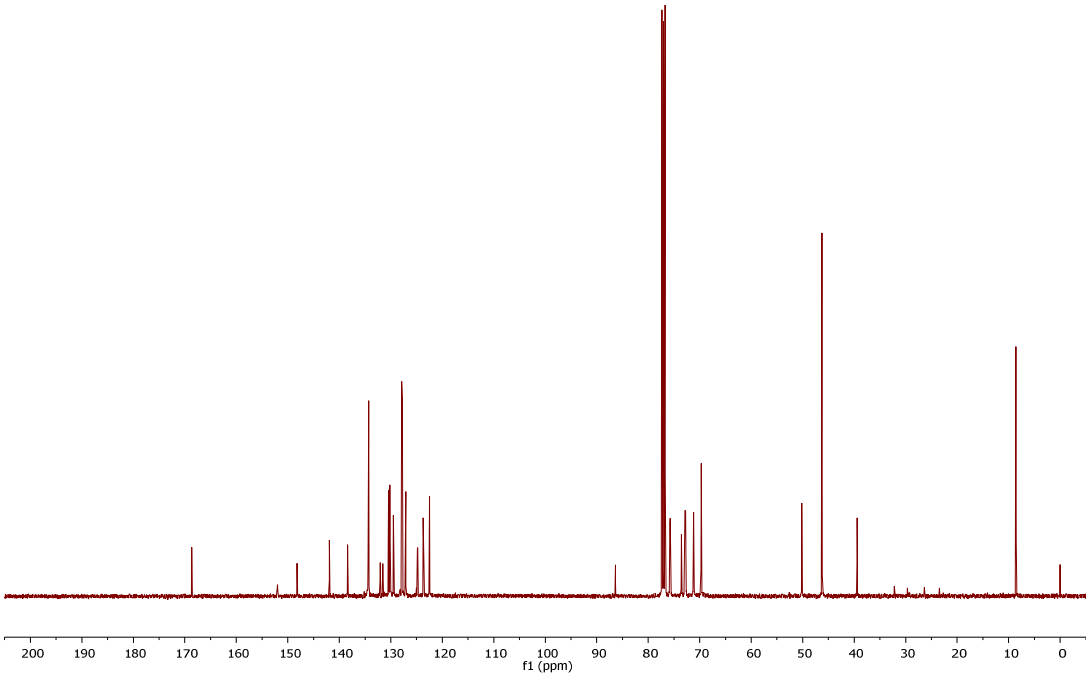


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of **7.**

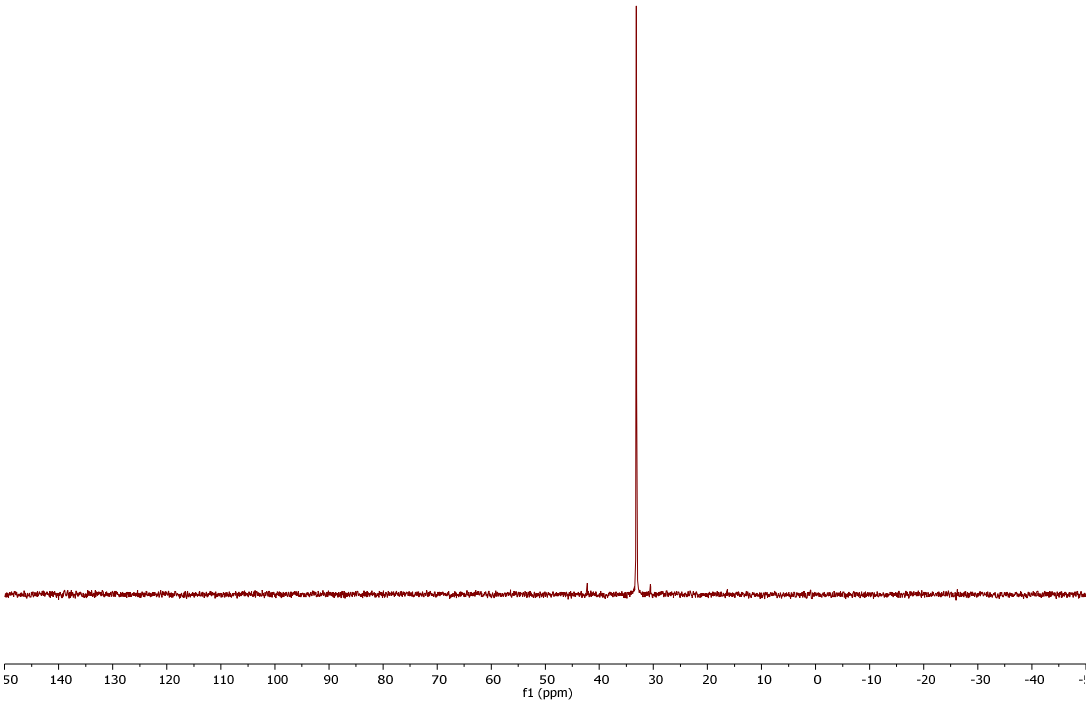


Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum of **7.**

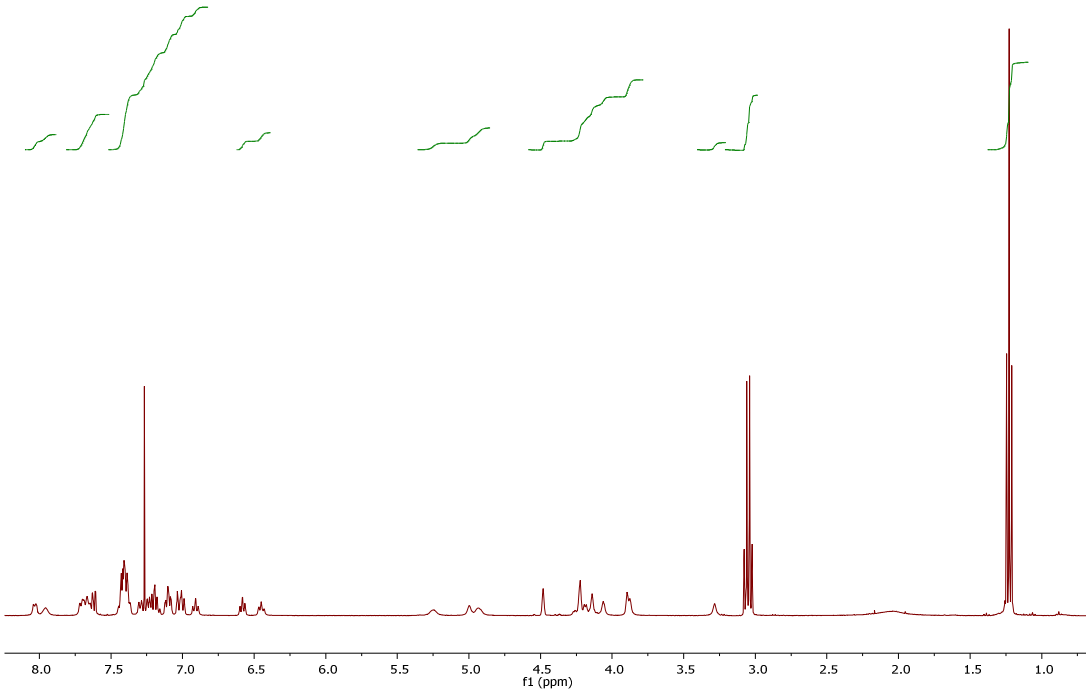


Figure S14. ^{1}H NMR spectrum of **8.**|

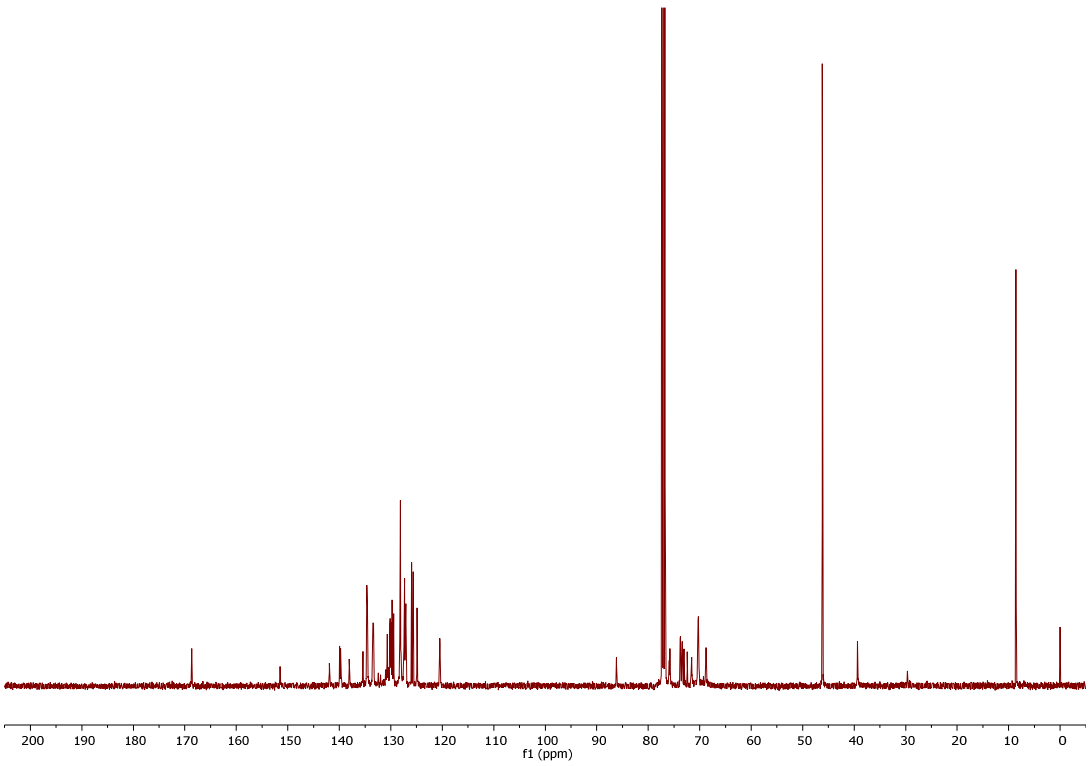


Figure S15. ^{13}C{^{1}H} NMR spectrum of **8.**

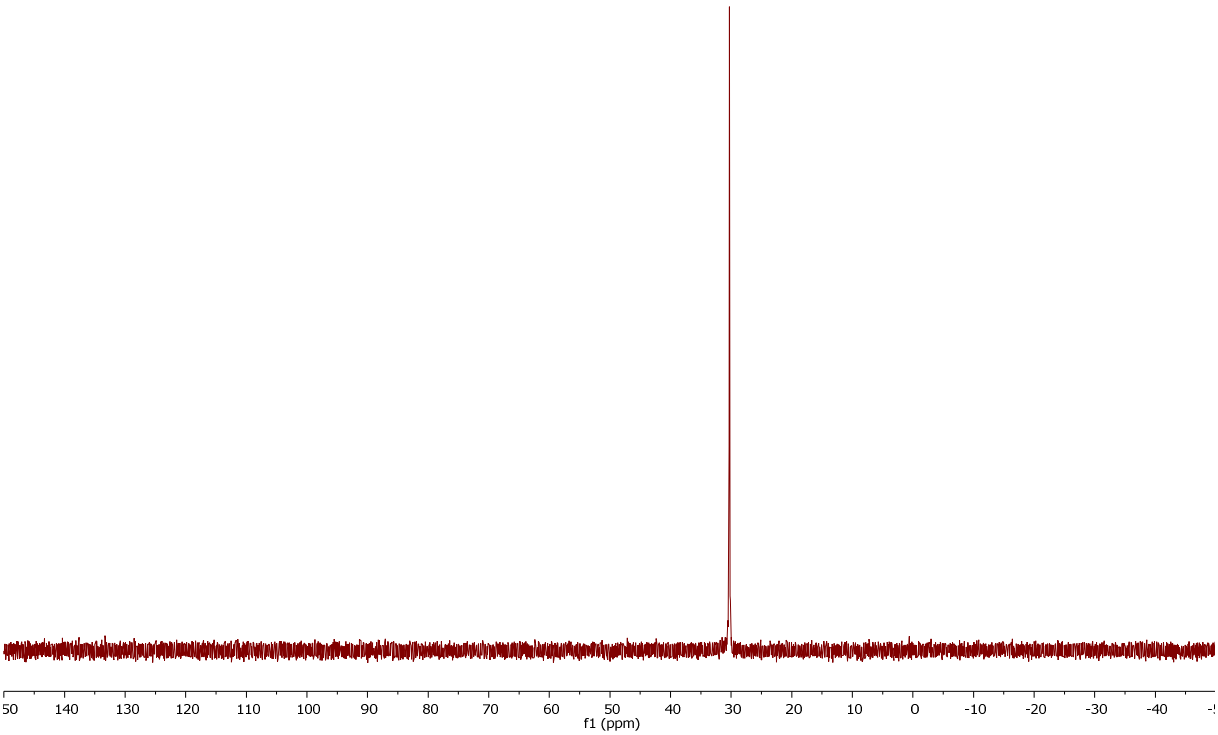


Figure S16. $^{31}P\{^{1}H\}$ NMR spectrum of **8.**

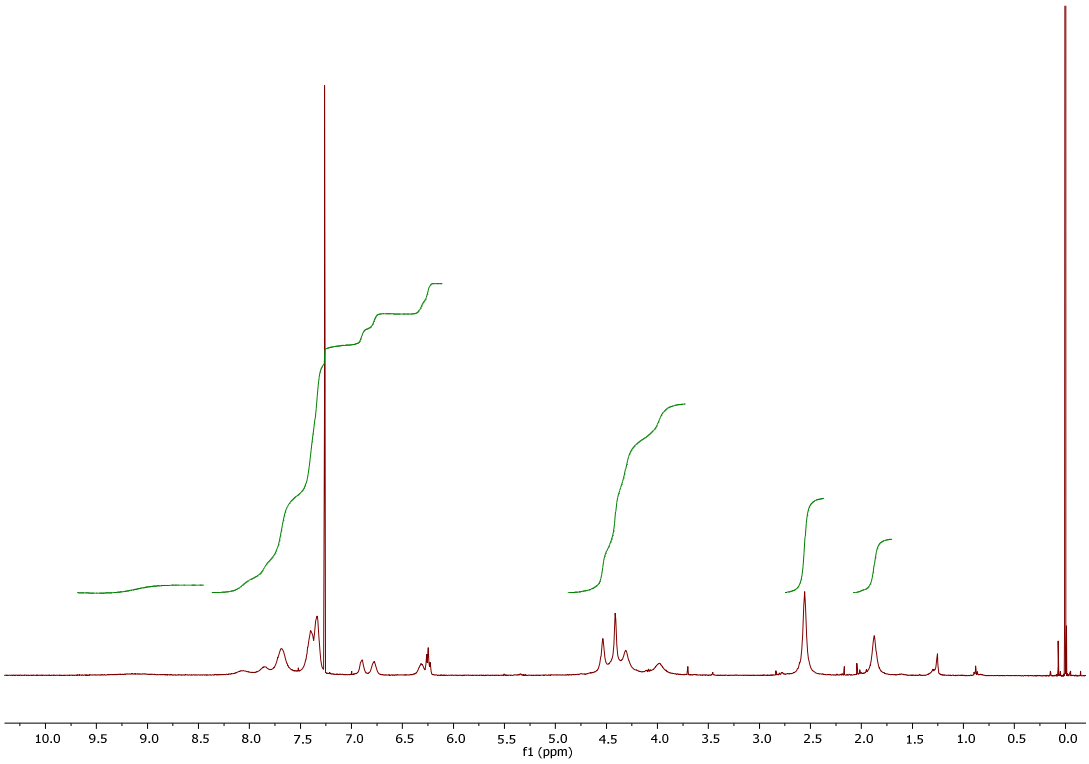


Figure S17. ^{1}H NMR spectrum of **10.**

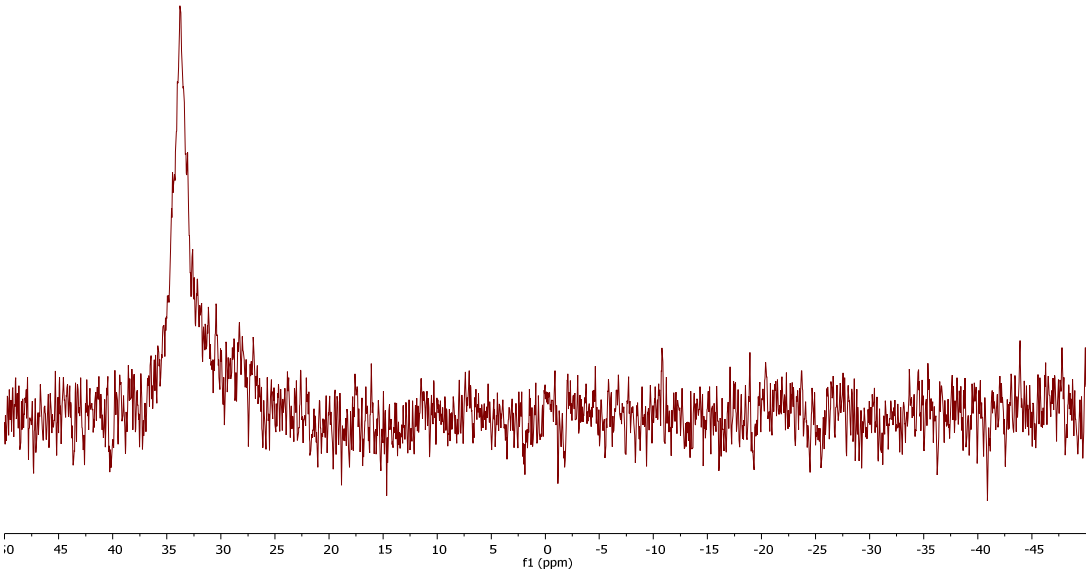


Figure S18. $^{31}P\{^{1}H\}$ NMR spectrum of **10.**

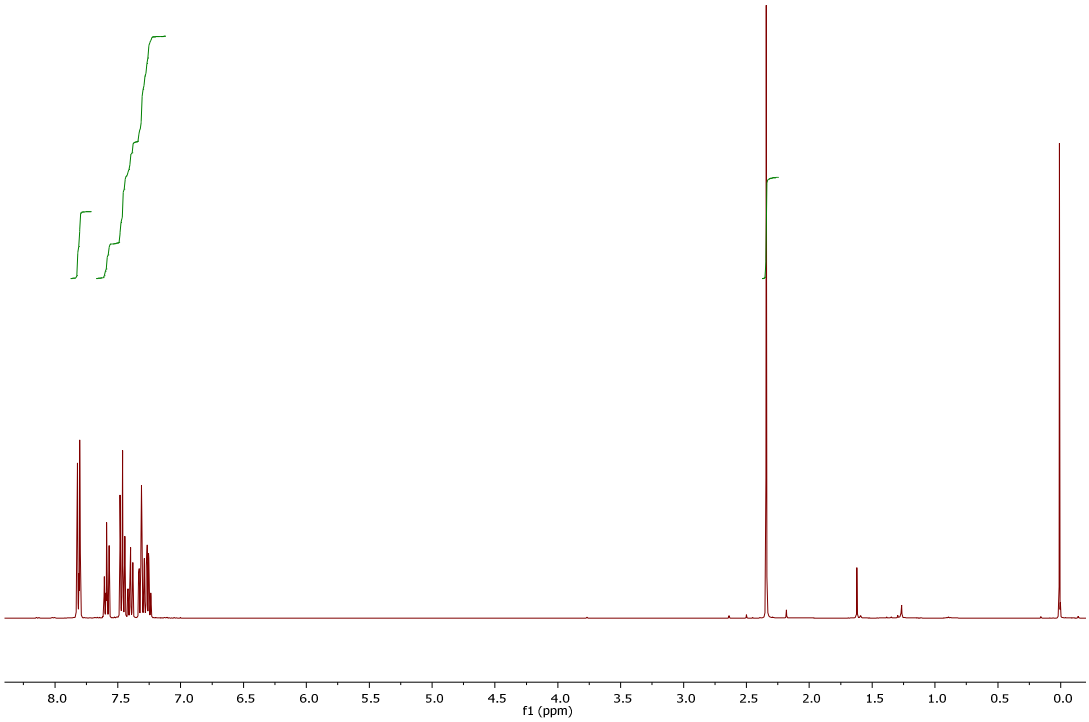


Figure S19. ^{1}H NMR spectrum of 2-methylbenzophenone (**13a**).

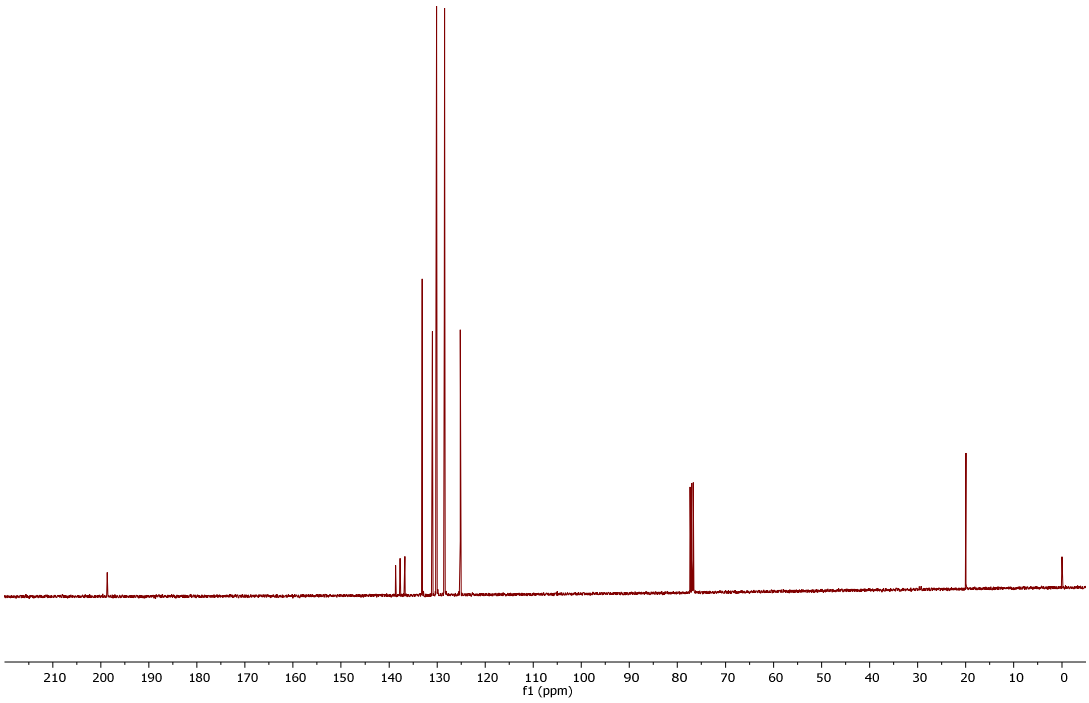


Figure S20. ^{13}C{^{1}H} NMR spectrum of 2-methylbenzophenone (**13a**).

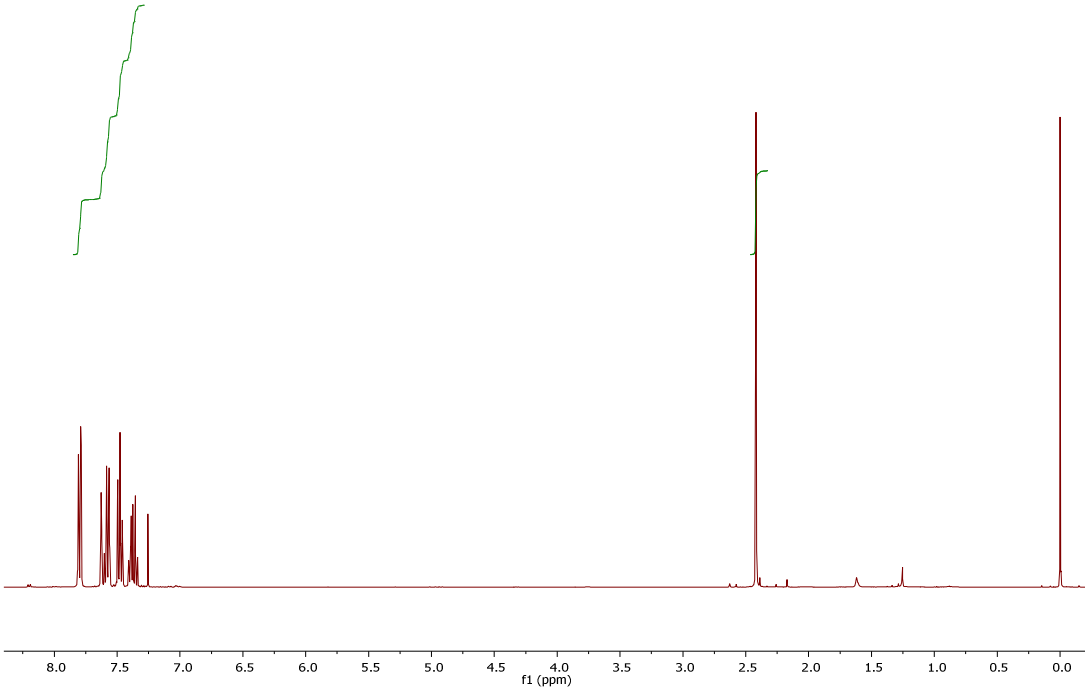


Figure S21. ^{1}H NMR spectrum of 3-methylbenzophenone (**13b**).

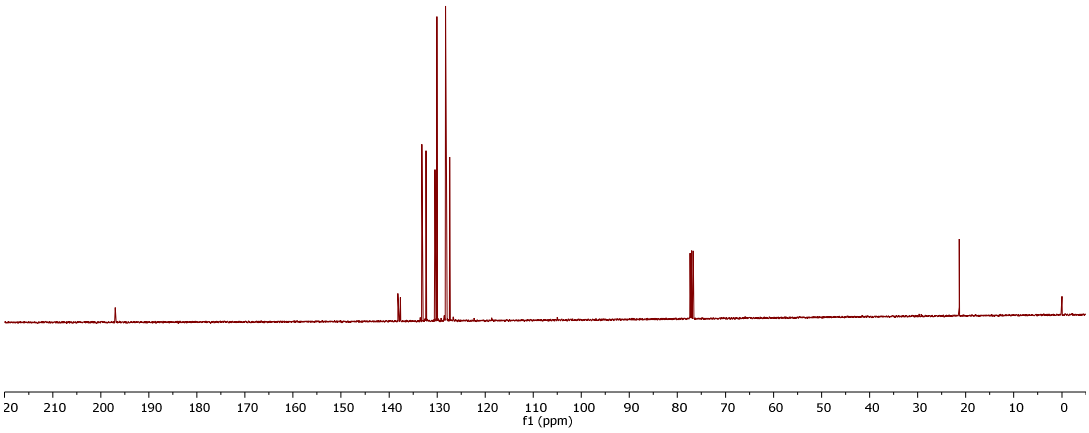


Figure S22. ^{13}C{^{1}H} NMR spectrum of 3-methylbenzophenone (**13b**).

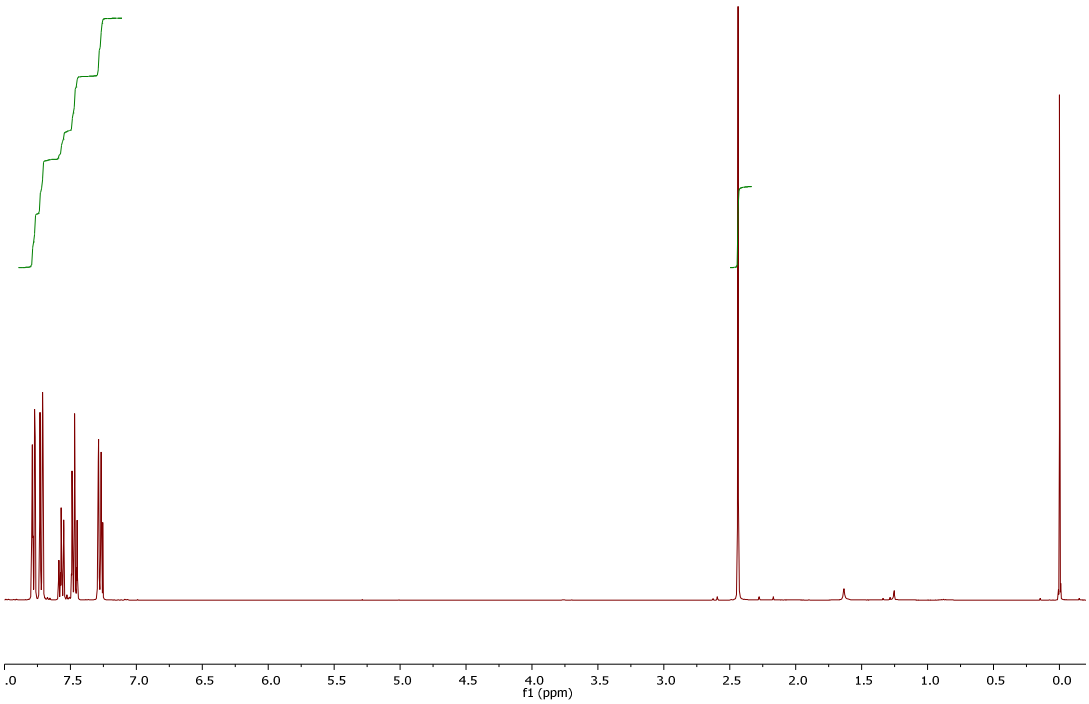


Figure S23. ^{1}H NMR spectrum of 4-methylbenzophenone (**13c**).

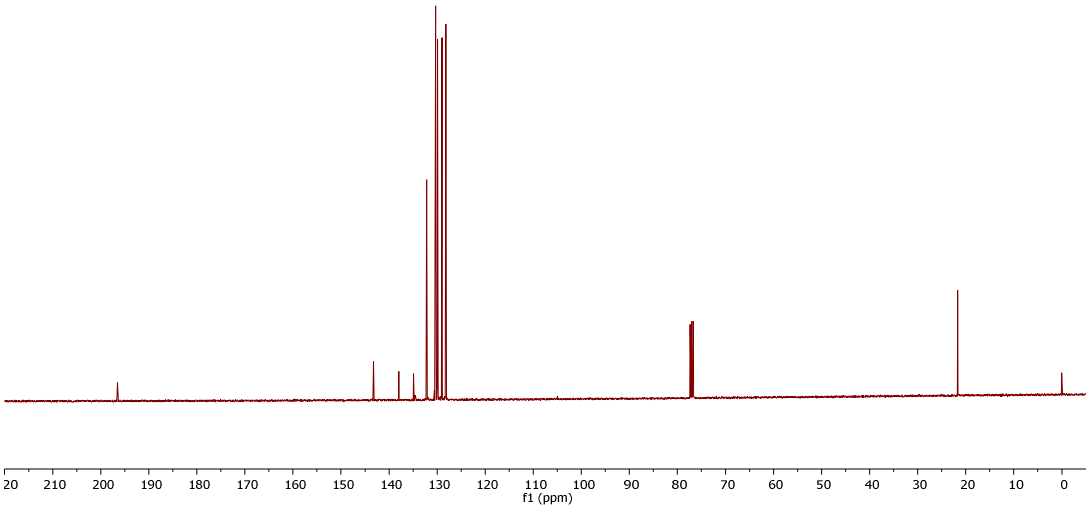


Figure S24. ^{13}C{^{1}H} NMR spectrum of 4-methylbenzophenone (**13c**).

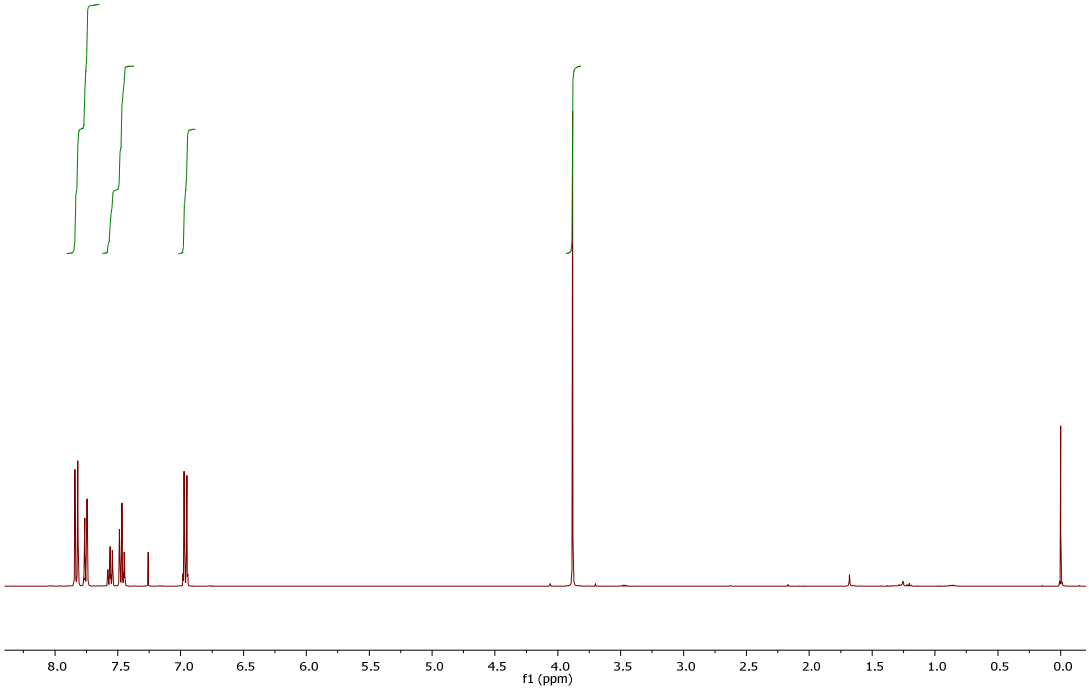


Figure S25. ^{1}H NMR spectrum of 4-methoxylbenzophenone (**13d**).

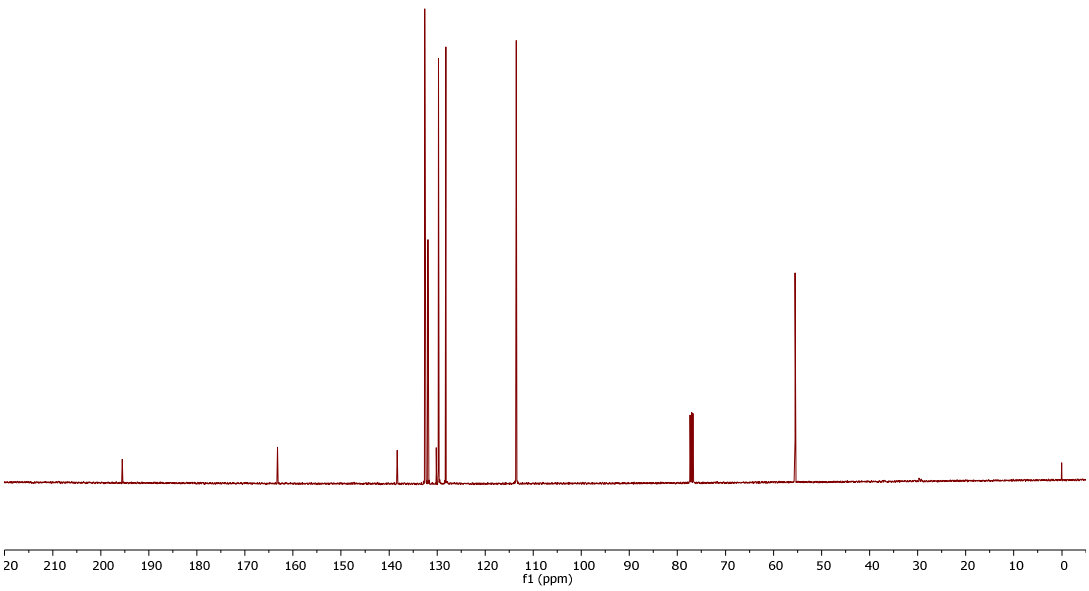


Figure S26. ^{13}C{^{1}H} NMR spectrum of 4-methoxylbenzophenone (**13d**).

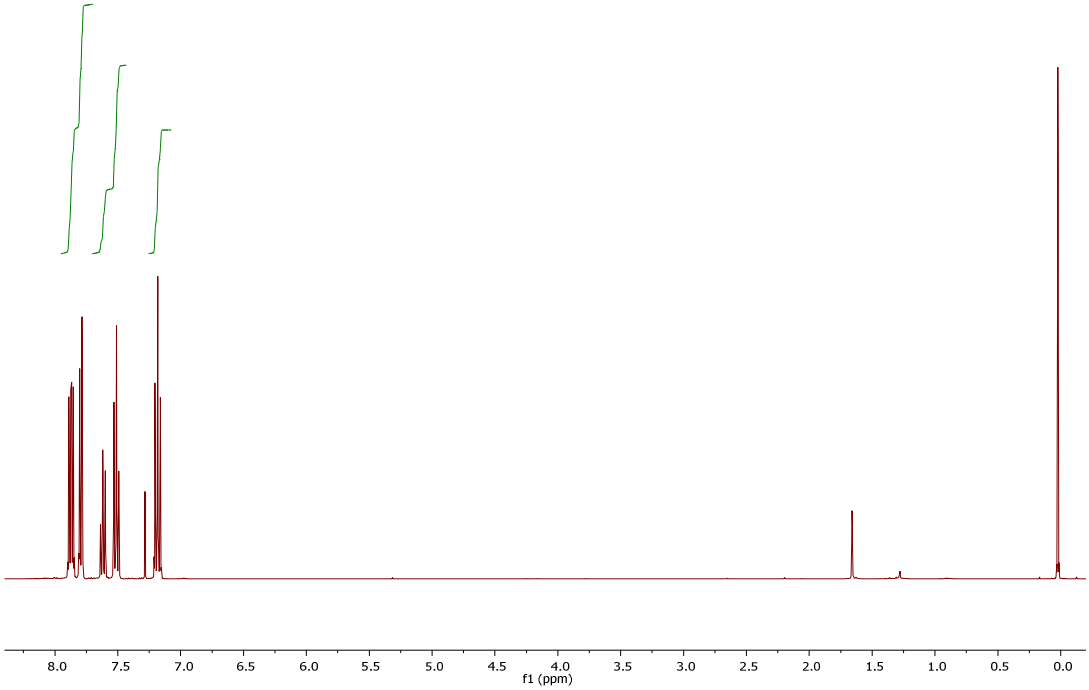


Figure S27. ^{1}H NMR spectrum of 4-fluorobenzophenone (**13e**).

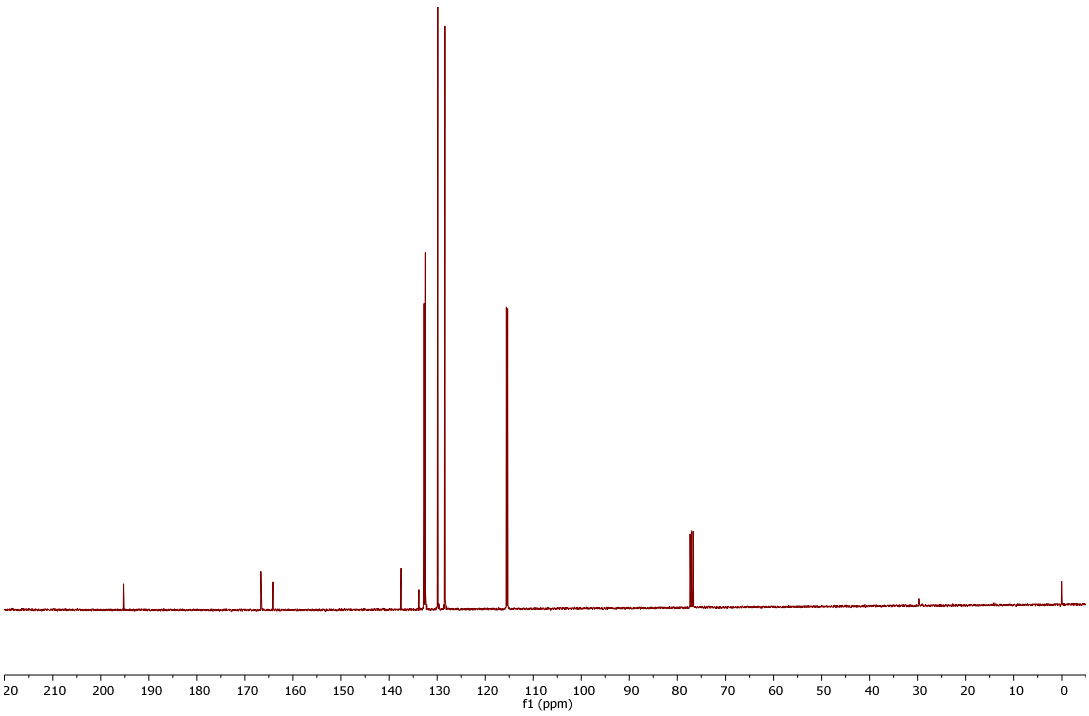


Figure S28. ^{13}C{^{1}H} NMR spectrum of 4-fluorobenzophenone (**13e**).

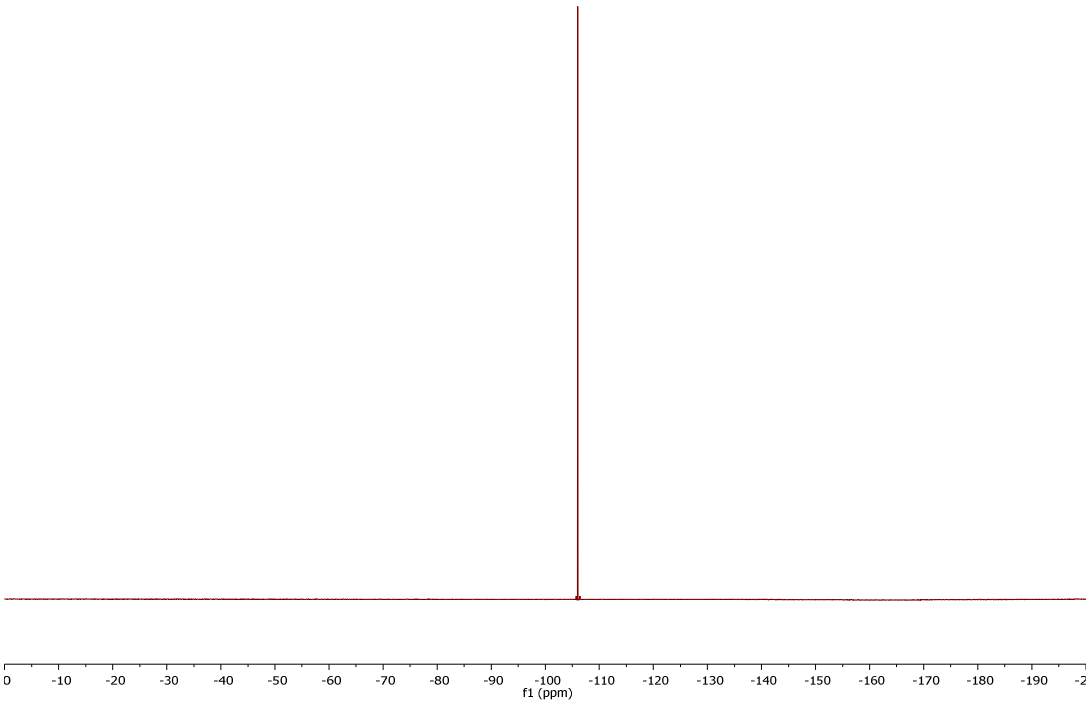


Figure S29. ^{19}F NMR spectrum of 4-fluorobenzophenone (**13e**).

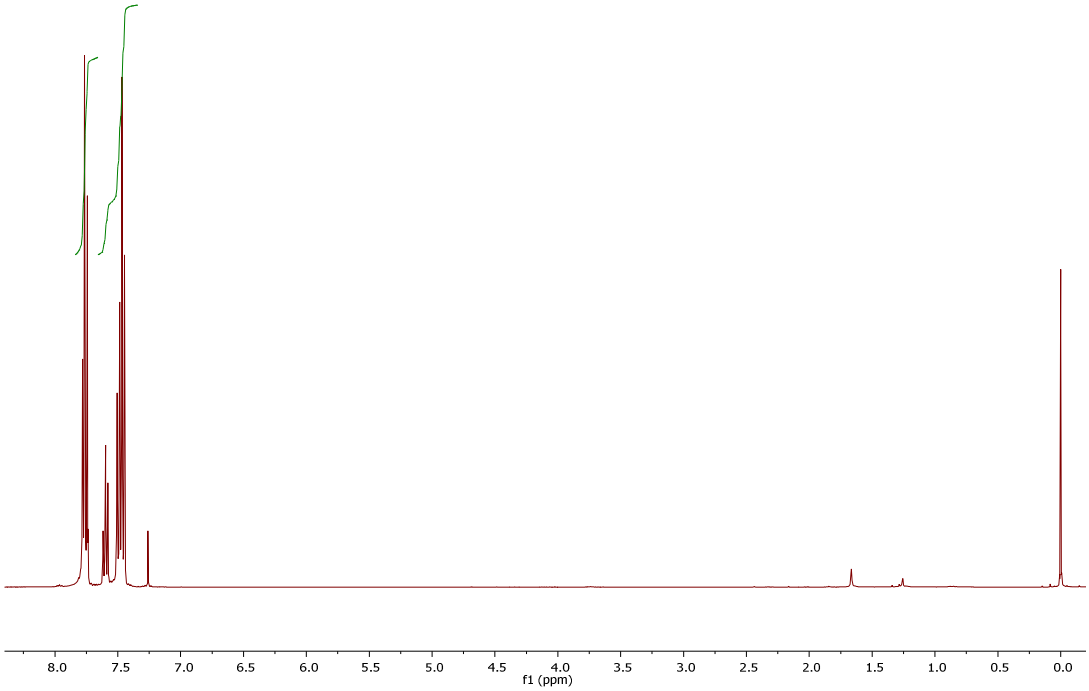


Figure S30. ^{1}H NMR spectrum of 4-chlorobenzophenone (**13f**).

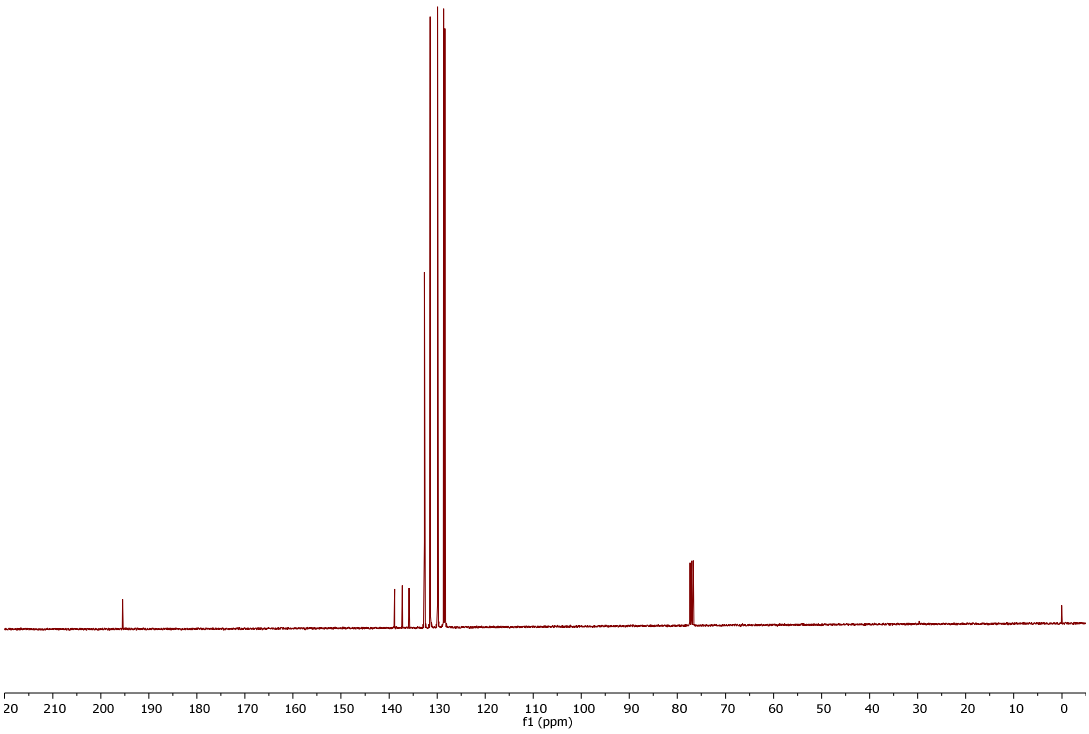


Figure S31. ^{13}C{^{1}H} NMR spectrum of 4-chlorobenzophenone (**13f**).

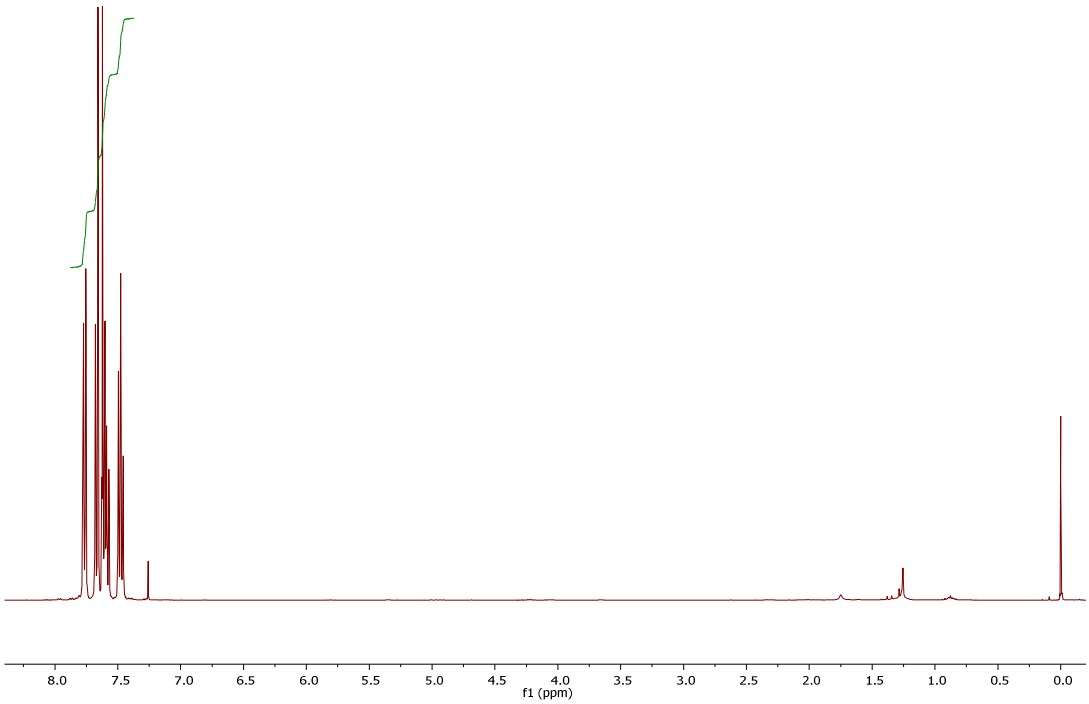


Figure S32. ^{1}H NMR spectrum of 4-bromobenzophenone (**13g**).

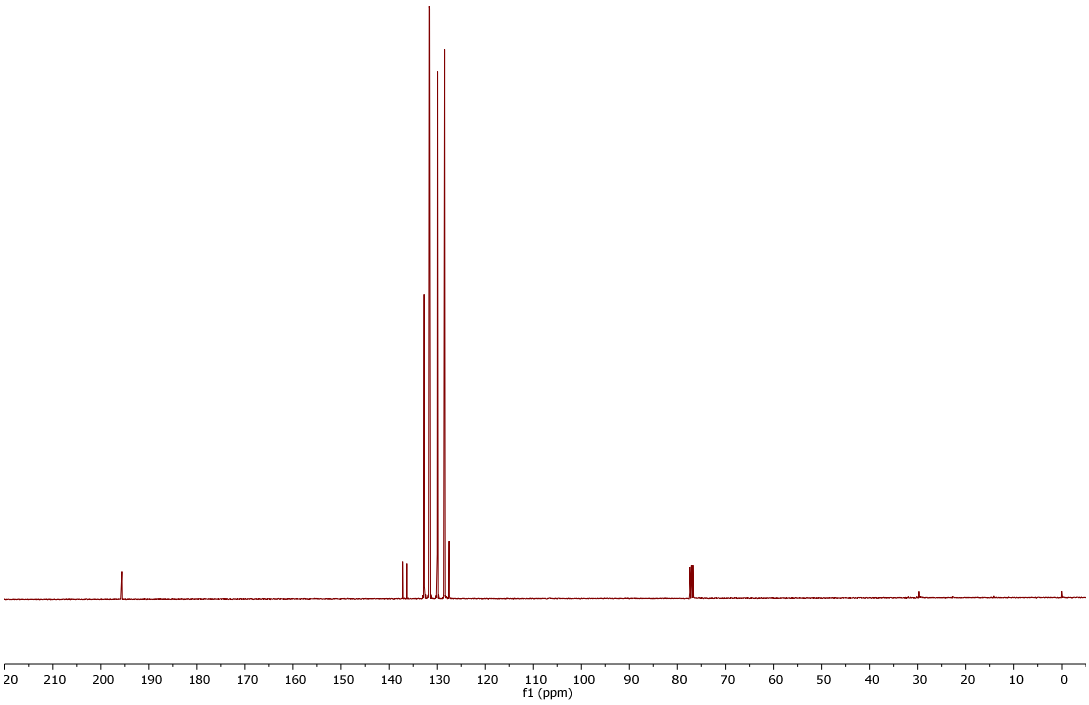


Figure S33. ^{13}C{^{1}H} NMR spectrum of 4-bromobenzophenone (**13g**).

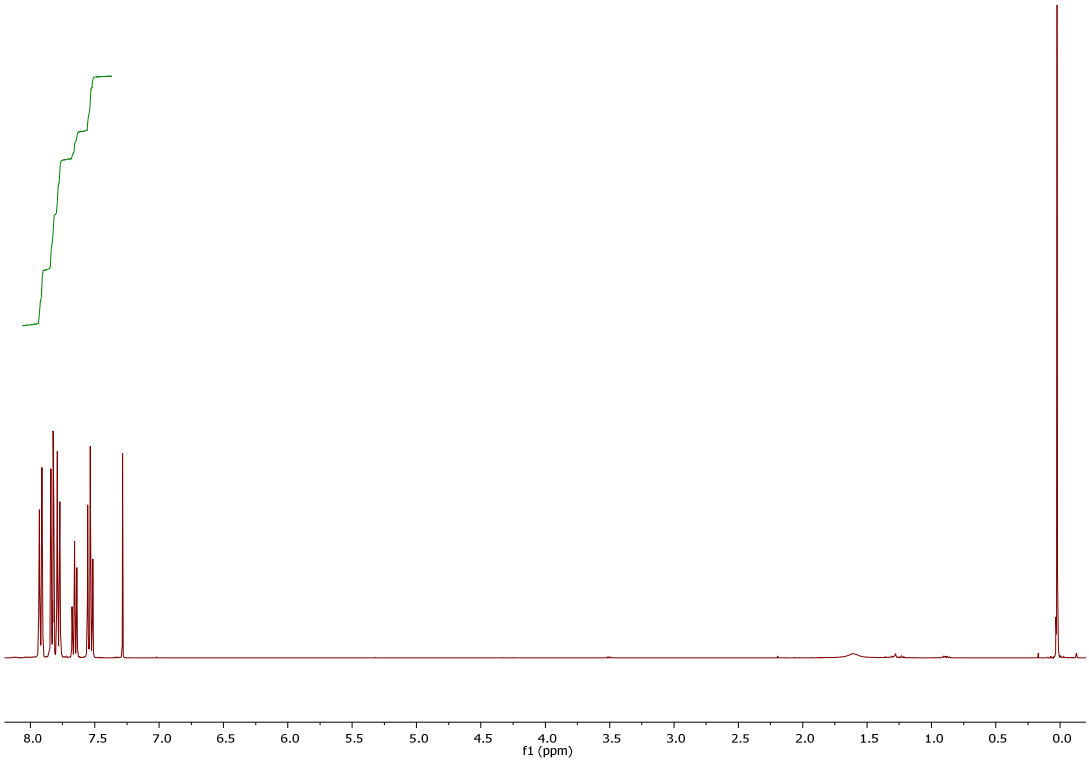


Figure S34. ^{1}H NMR spectrum of 4-(trifluoromethyl)benzophenone (**13h**).

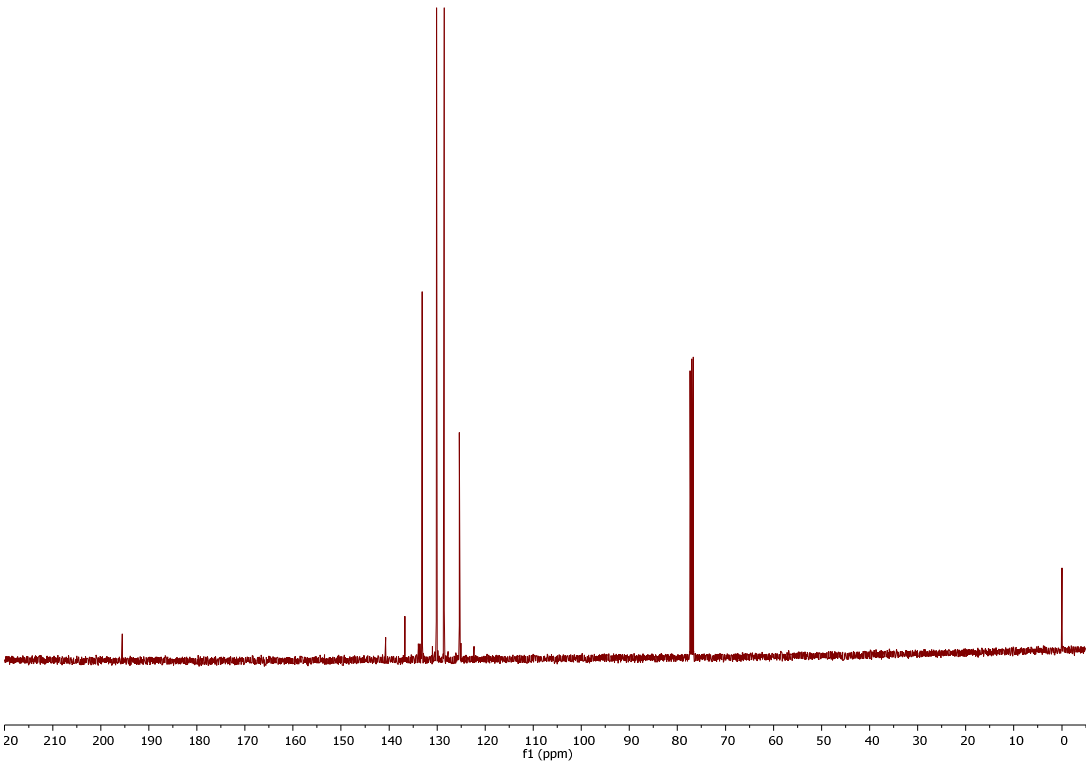


Figure S35. ^{13}C{^{1}H} NMR spectrum of 4-(trifluoromethyl)benzophenone (**13h**).

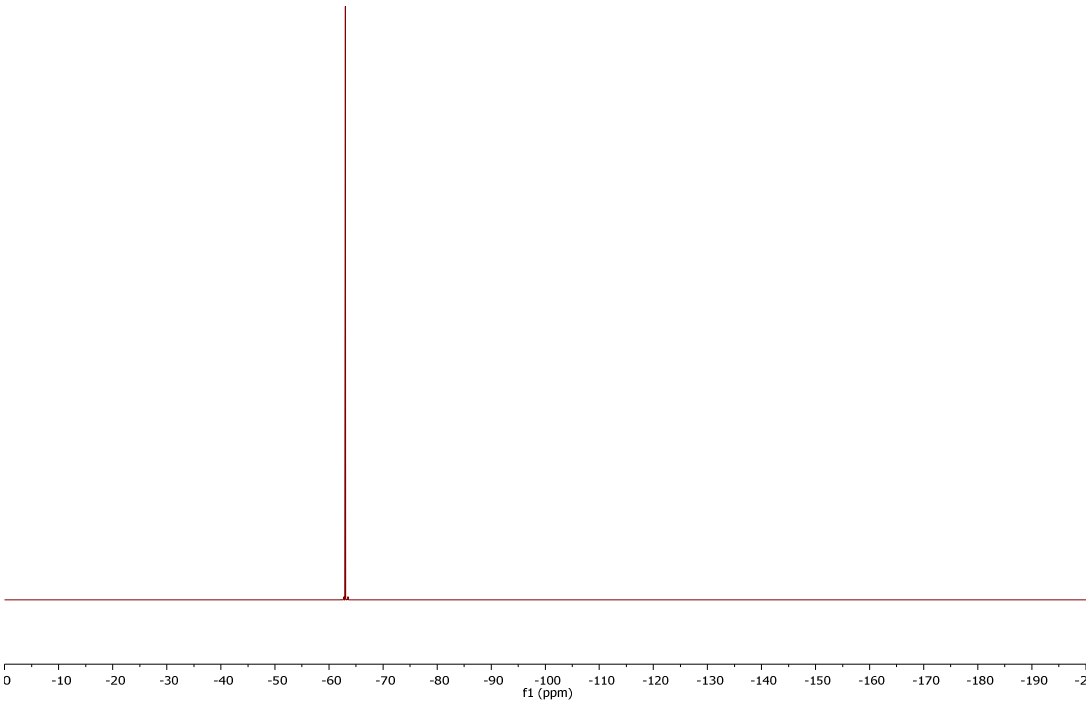


Figure S36. ^{19}F NMR spectrum of 4-(trifluoromethyl)benzophenone (**13h**).

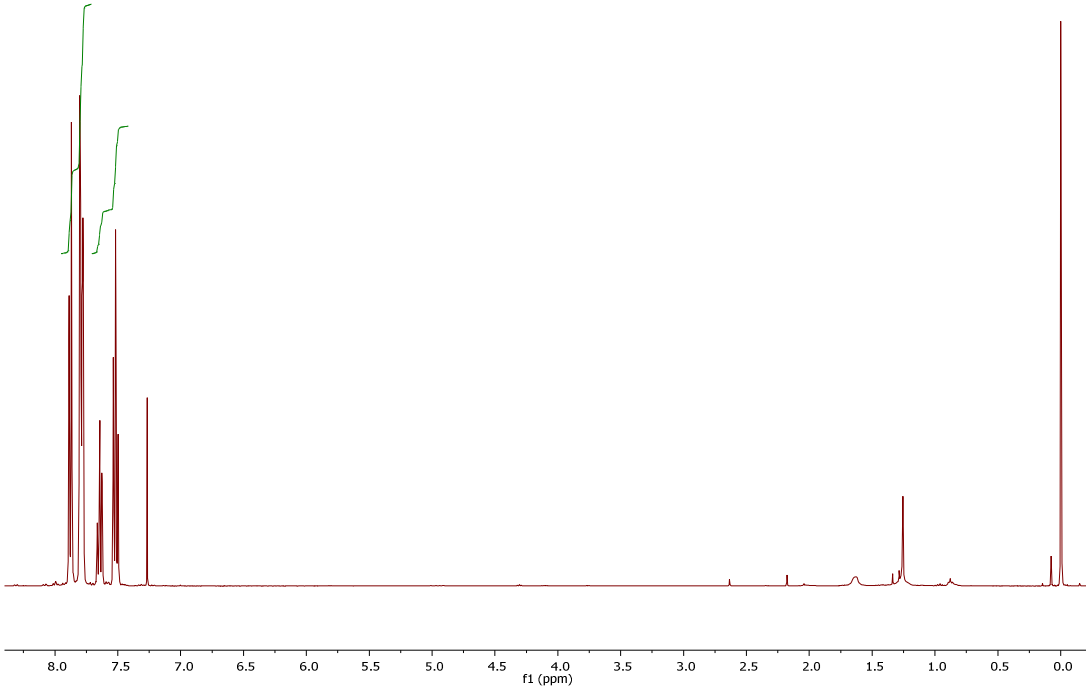


Figure S37. ^{1}H NMR spectrum of 4-cyanobenzophenone (**13i**).

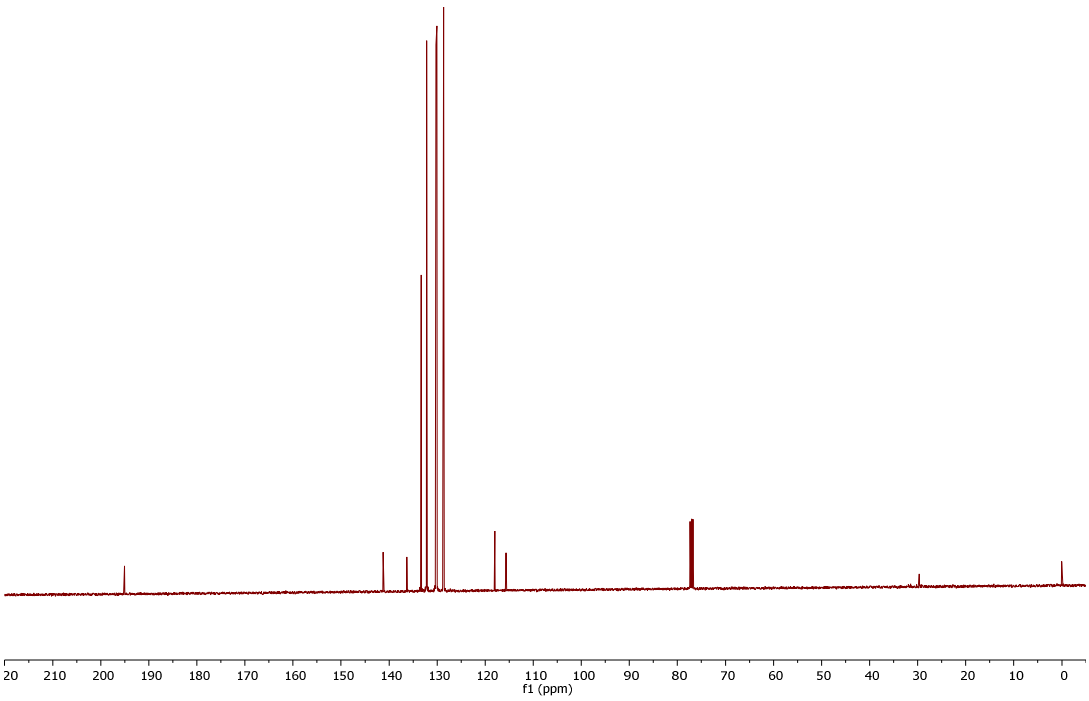


Figure S38. ^{13}C{^{1}H} NMR spectrum of 4-cyanobenzophenone (**13i**).

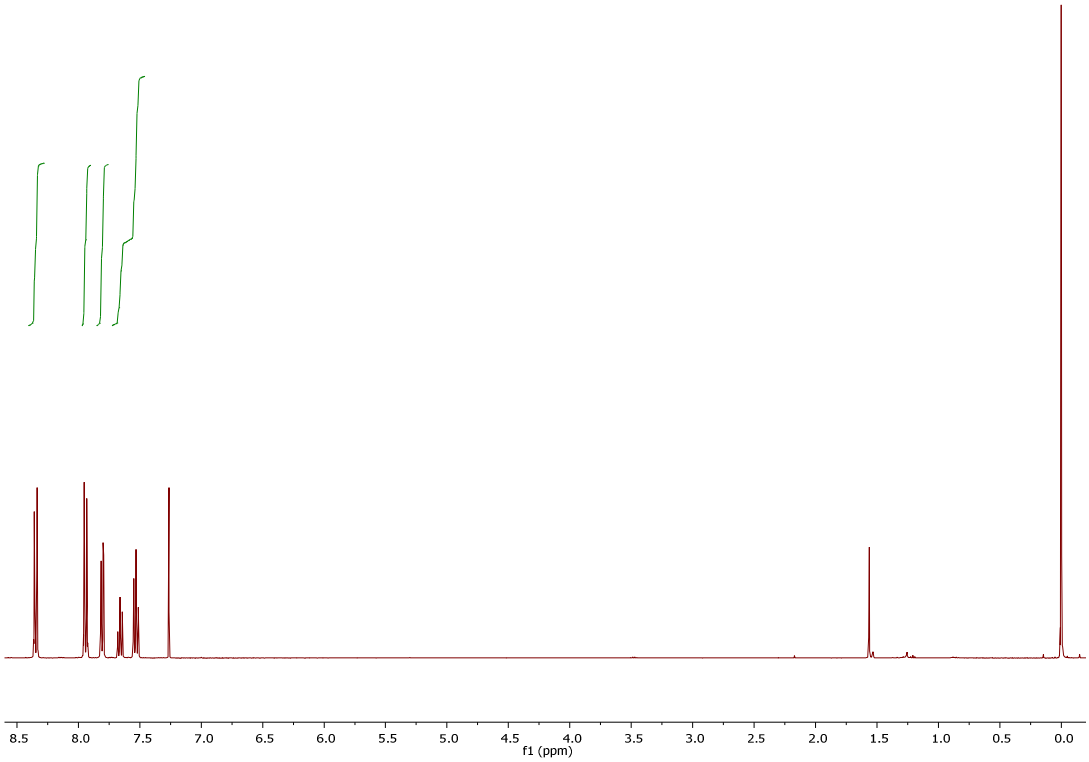


Figure S39. ^{1}H NMR spectrum of 4-nitrobenzophenone (**13j**).

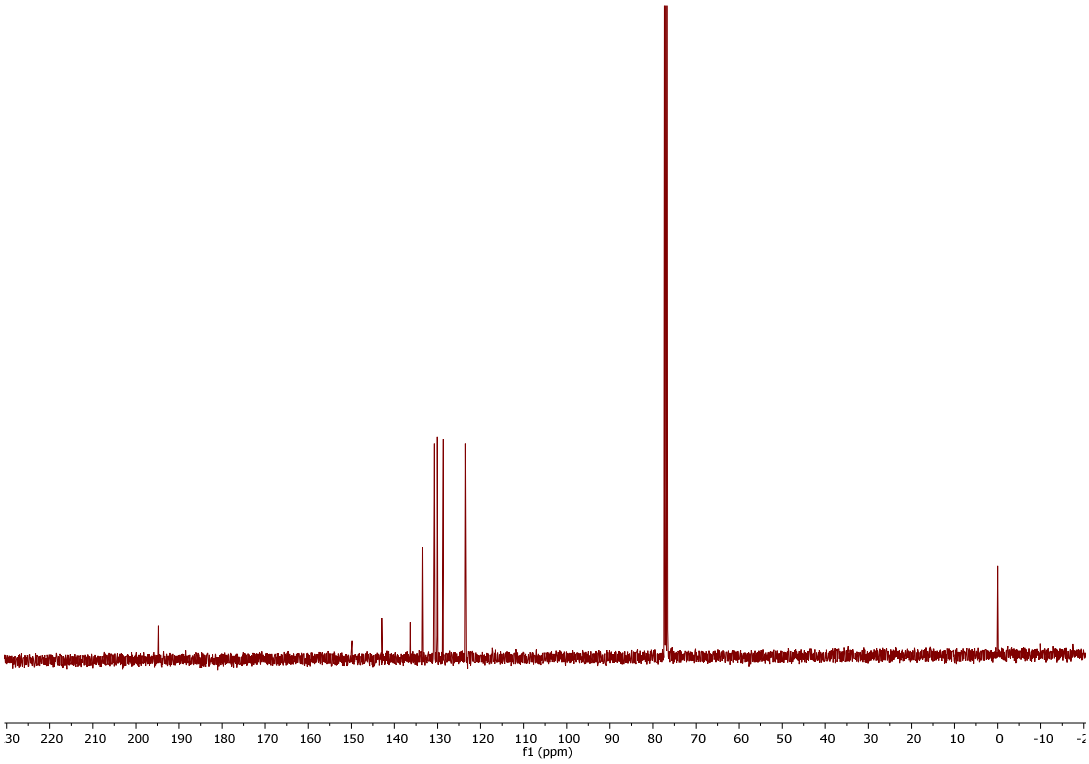


Figure S40. ^{13}C{^{1}H} NMR spectrum of 4-nitrobenzophenone (**13j**).

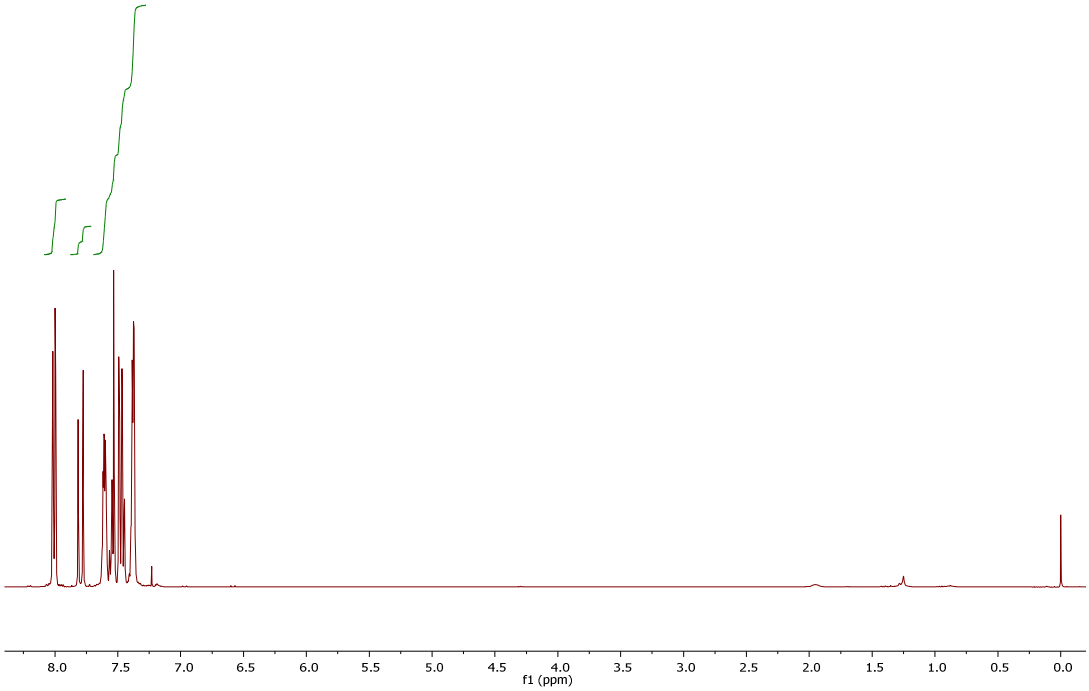


Figure S41. ^{1}H NMR spectrum of *trans*-chalcone (**13k**).

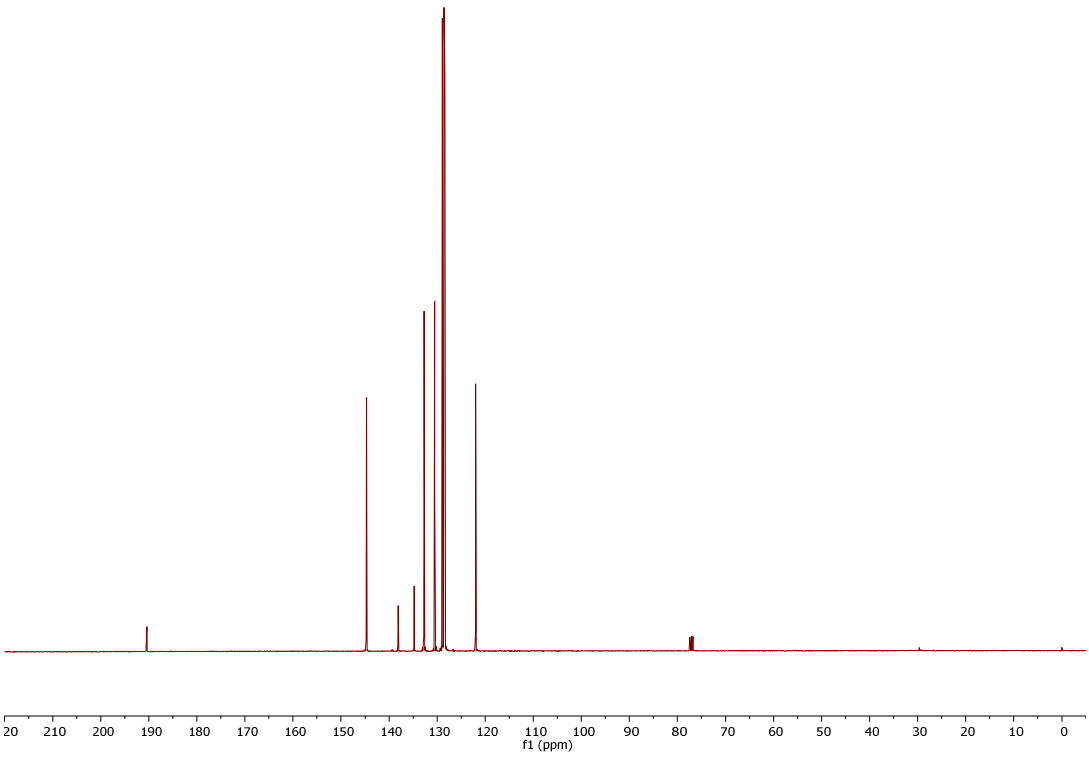


Figure S42. ^{13}C{^{1}H} NMR spectrum of *trans*-chalcone (**13k**).

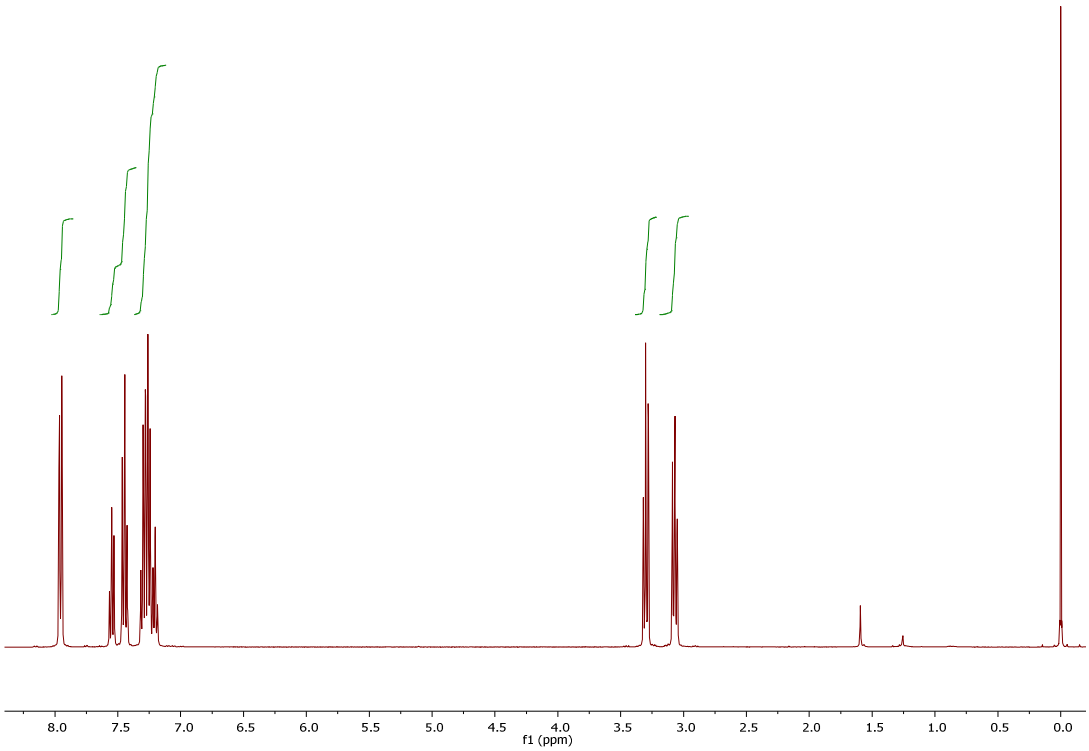


Figure S43. ^{1}H NMR spectrum of 1,3-diphenyl-1-propanone (**13l**).

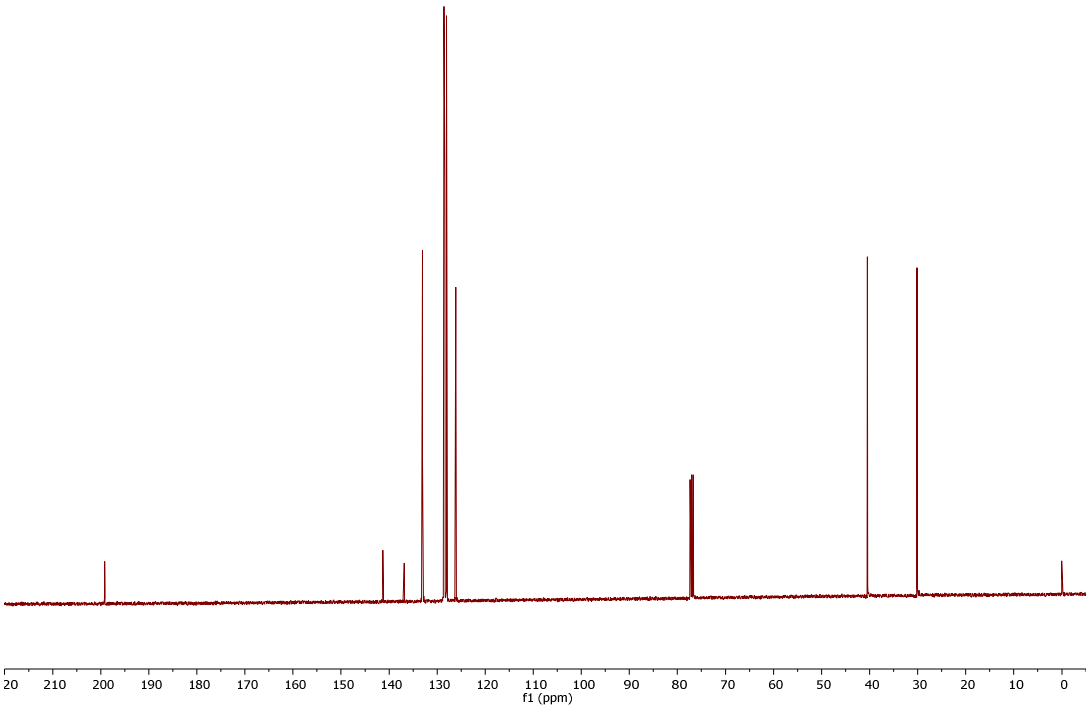


Figure S44. ^{13}C{^{1}H} NMR spectrum 1,3-diphenyl-1-propanone (**13l**).

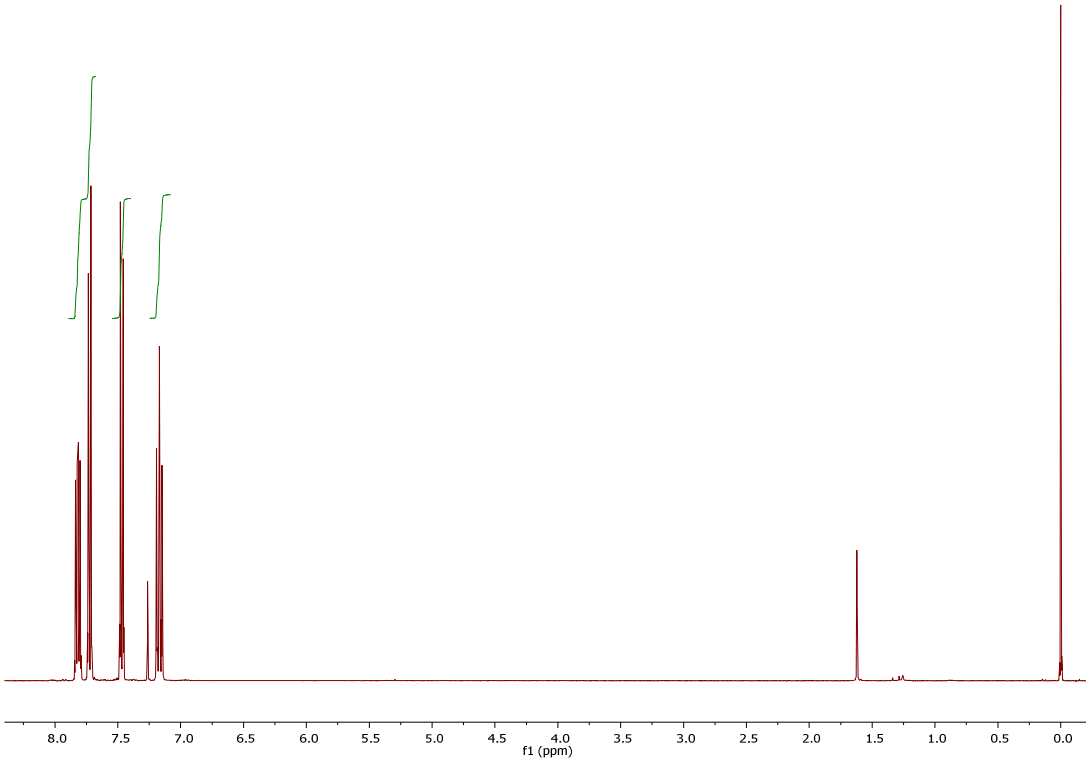


Figure S45. ^{1}H NMR spectrum of 4-chloro-4'-fluorobenzophenone (**13ef**).

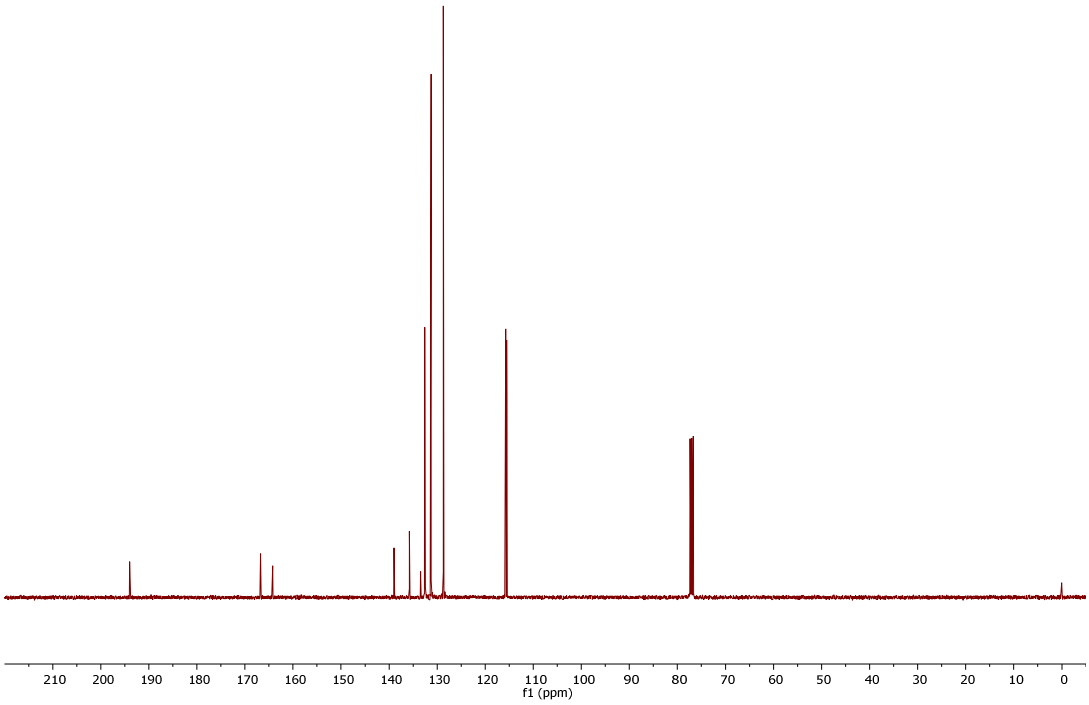


Figure S46. ^{13}C{^{1}H} NMR spectrum of 4-chloro-4'-fluorobenzophenone (**13ef**).

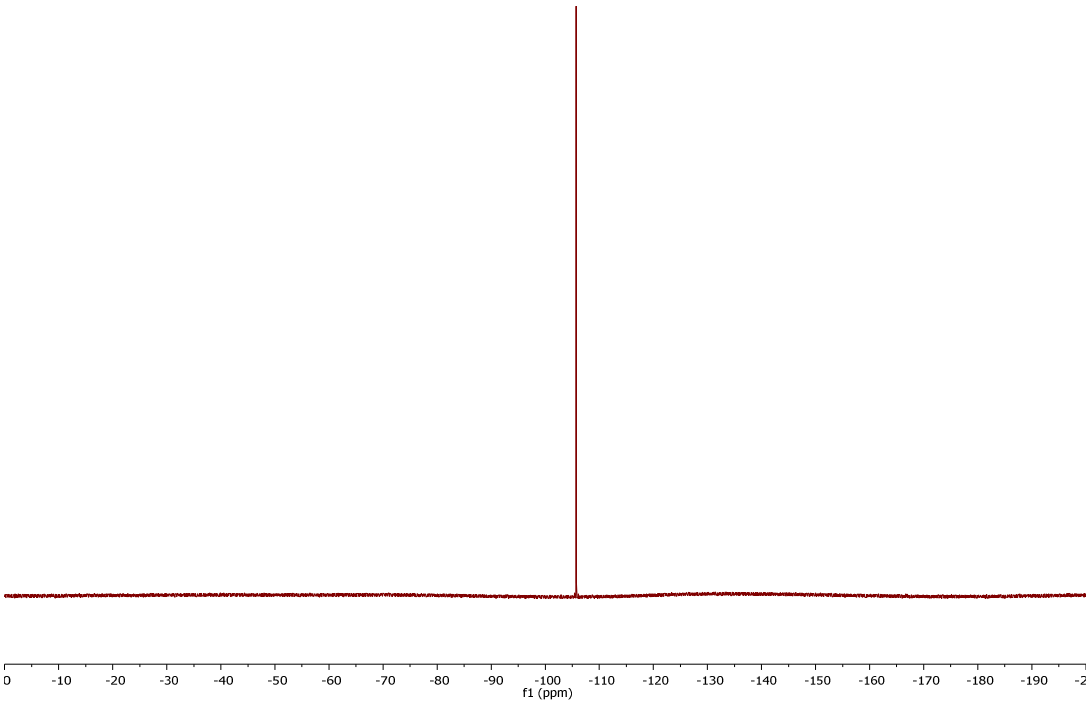


Figure S47. ^{19}F NMR spectrum of 4-chloro-4'-fluorobenzophenone (**13ef**).

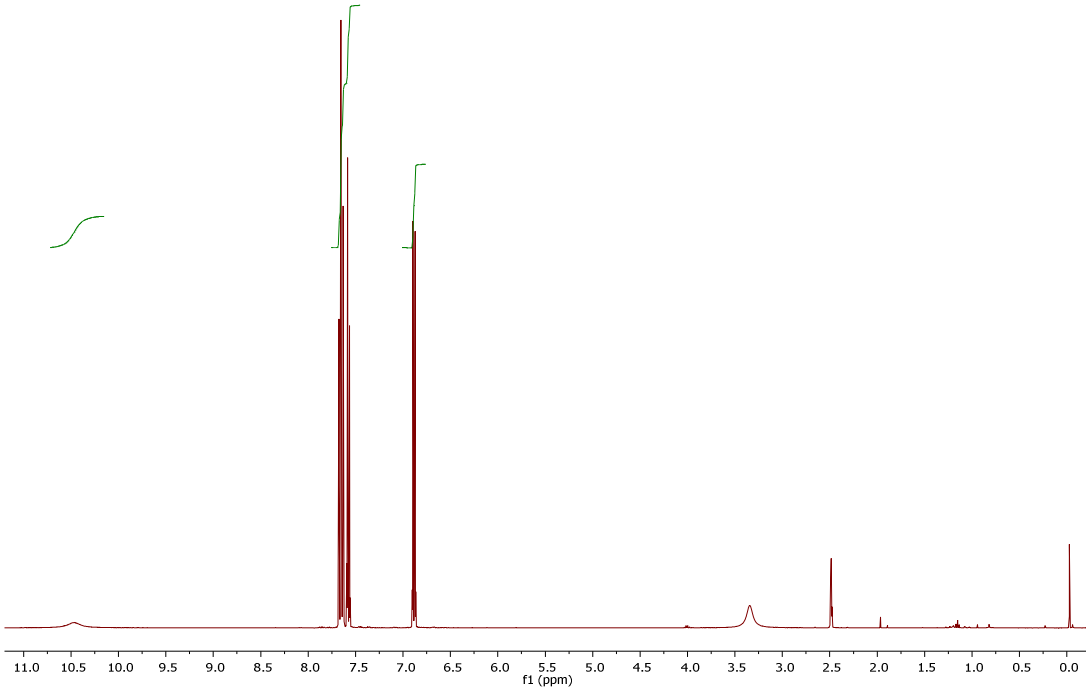


Figure S48. ^{1}H NMR spectrum of 4-chloro-4'-hydroxybenzophenone (**13fm**).

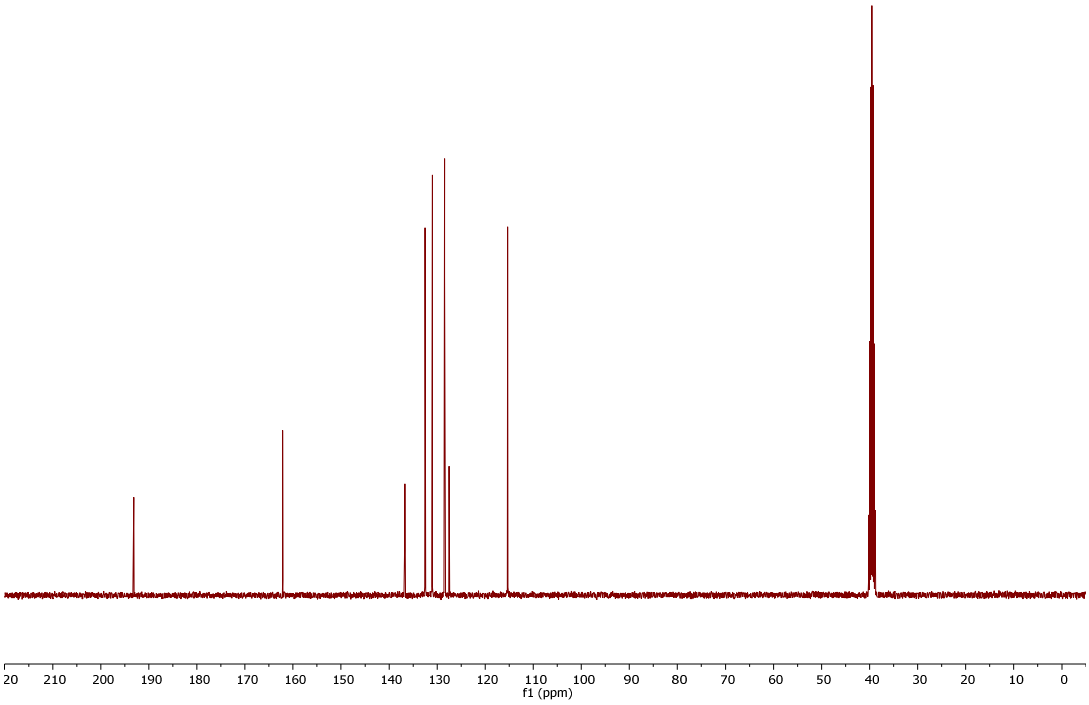


Figure S49. ^{13}C{^{1}H} NMR spectrum of 4-chloro-4'-hydroxybenzophenone (**13fm**).

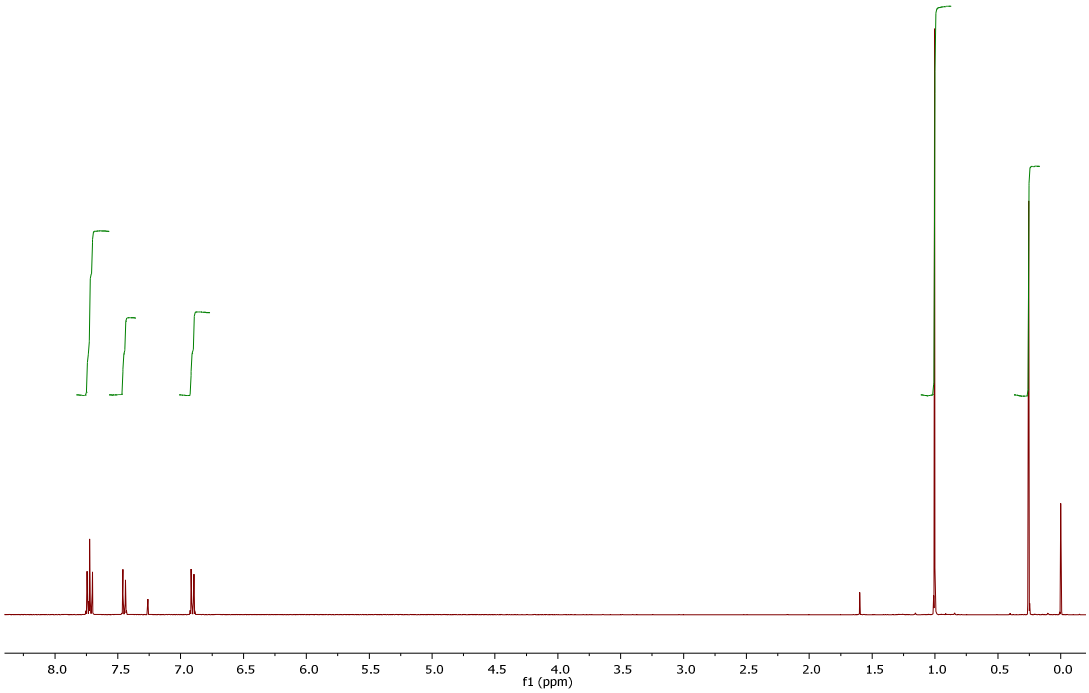


Figure S50. ^{1}H NMR spectrum of **13fn.**

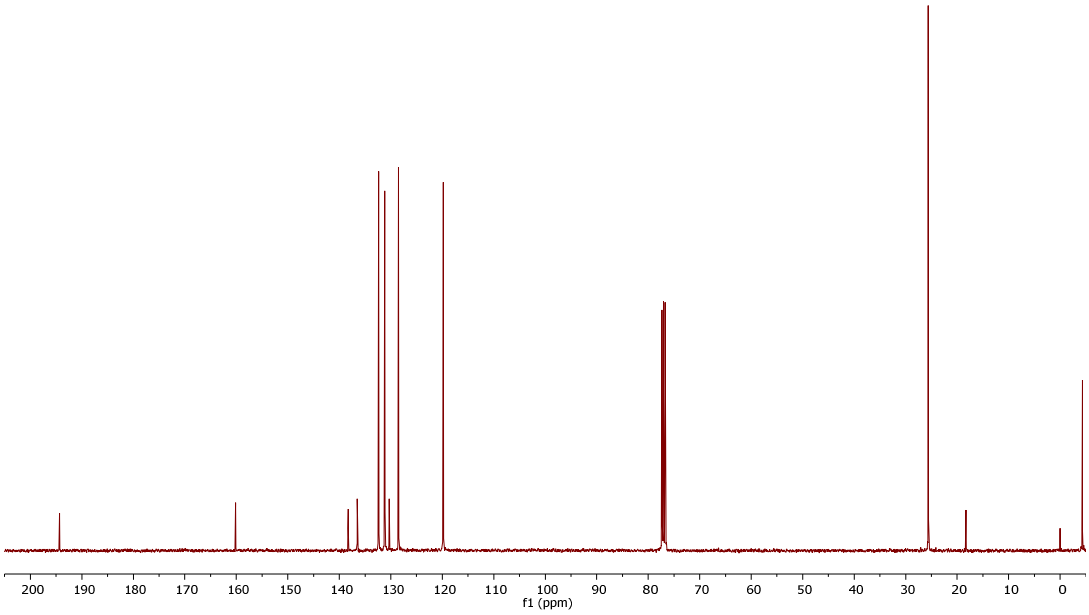


Figure S51. ^{13}C{^{1}H} NMR spectrum of **13fn.**

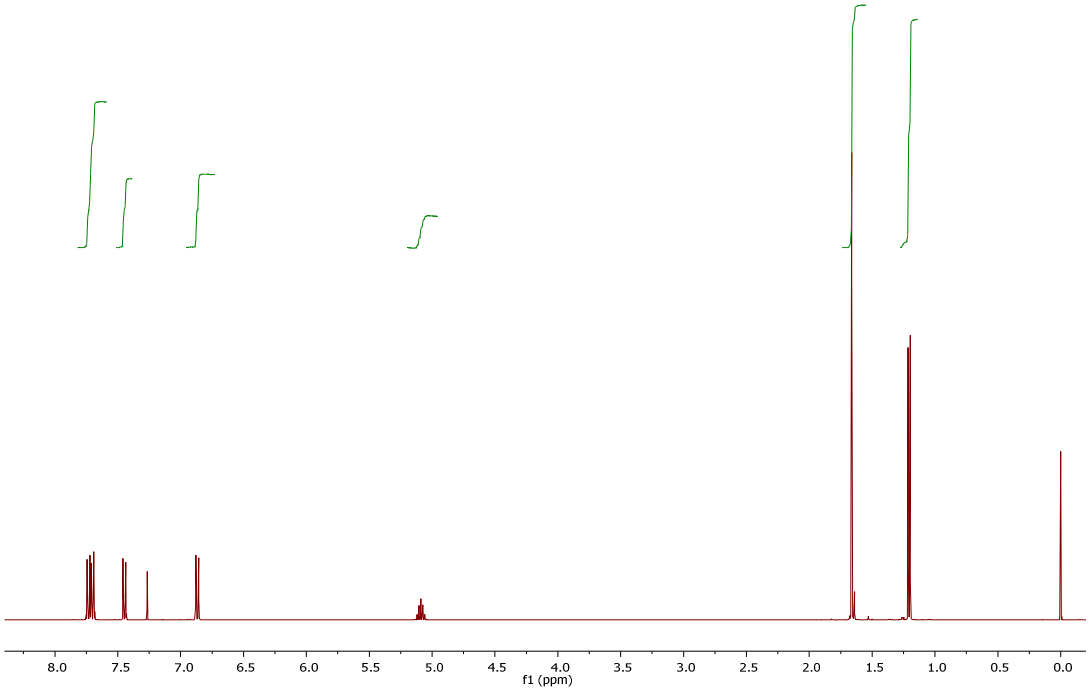


Figure S52. ^{1}H NMR spectrum of fenofibrate (**15**).

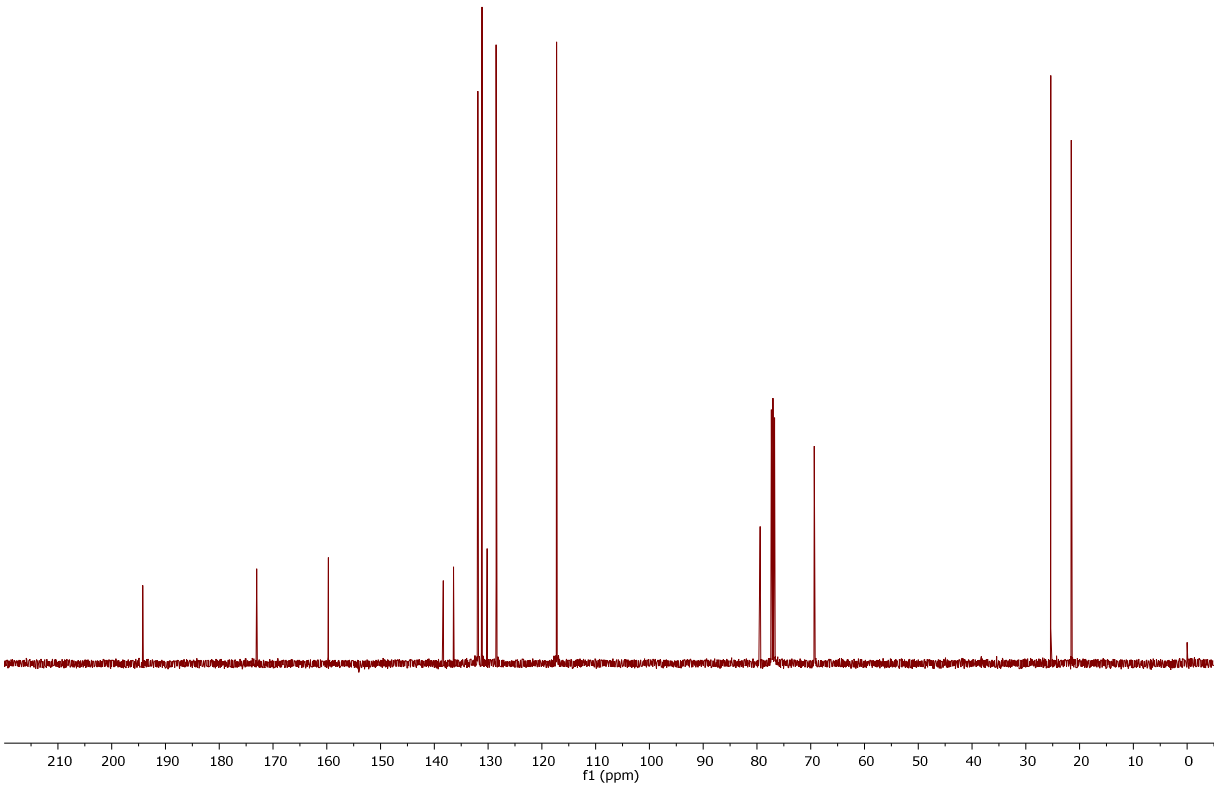


Figure S53. ^{13}C{^{1}H} NMR spectrum of fenofibrate (**15**).

References

1. For analytical data, see: Solařová, H.; Císařová, I.; Štěpnička, P. *Organometallics* **2014**, *33*, 4131-4147 and references cites therein.

2. Stolze, K.; Udilova. N.; Rosenau, T.; Hofinger, A.; Nohl, H. *Biochem. Pharmacol.* **2003**, *66*, 1717-1726.