Electronic Supplementary Information

Nickel-Palladium Alloy Nanoparticles Supported on the Reduced Graphene Oxide Decorated with Metallic Aluminum Nanoparticles (Al-rGO/NiPd): a multifunctional catalyst for the transfer hydrogenation of nitroarenes and olefines using water as hydrogen source

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Content

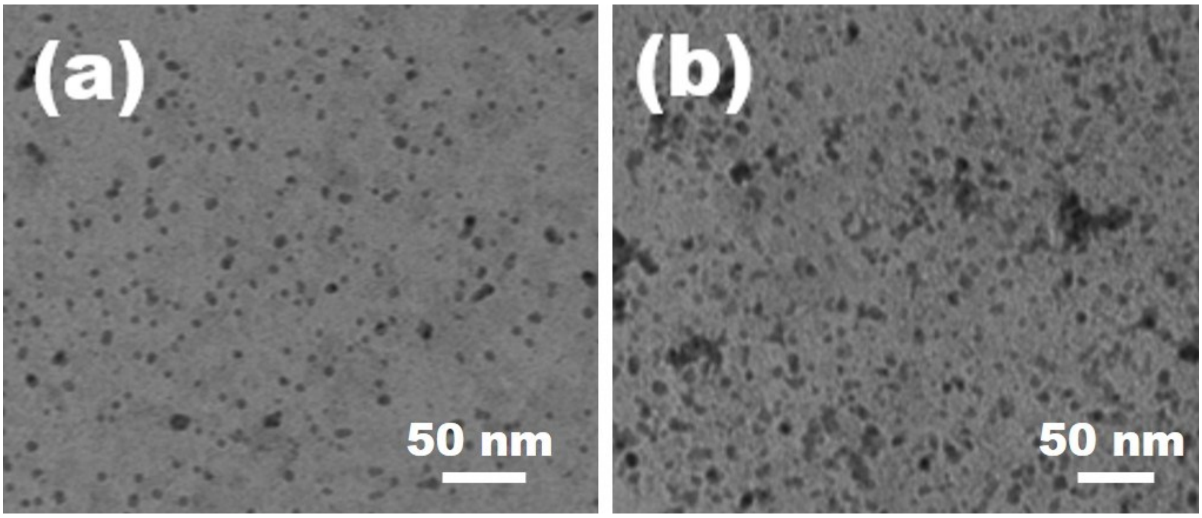


Figure S1. The representative TEM images of a) Al-rGO/$Ni_{20}Pd_{80}$ and b) Al-rGO/$Ni_{60}Pd_{40}$ nanocatalysts.

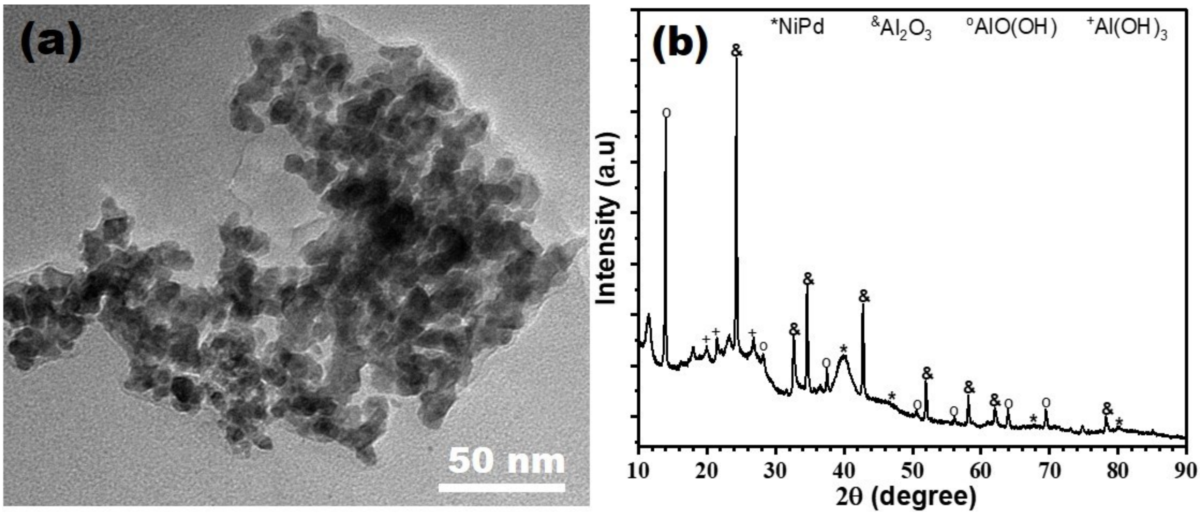


Figure S2. (a) TEM and (b) XRD pattern of Al-rGO/$Ni_{40}Pd_{60}$ nanocatalysts after the 10^{th} run of the recyclability test.

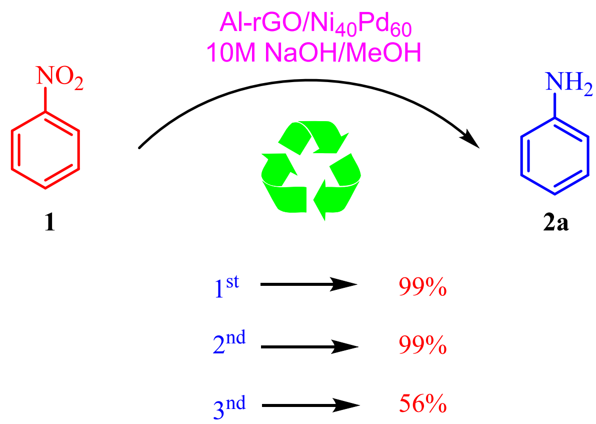
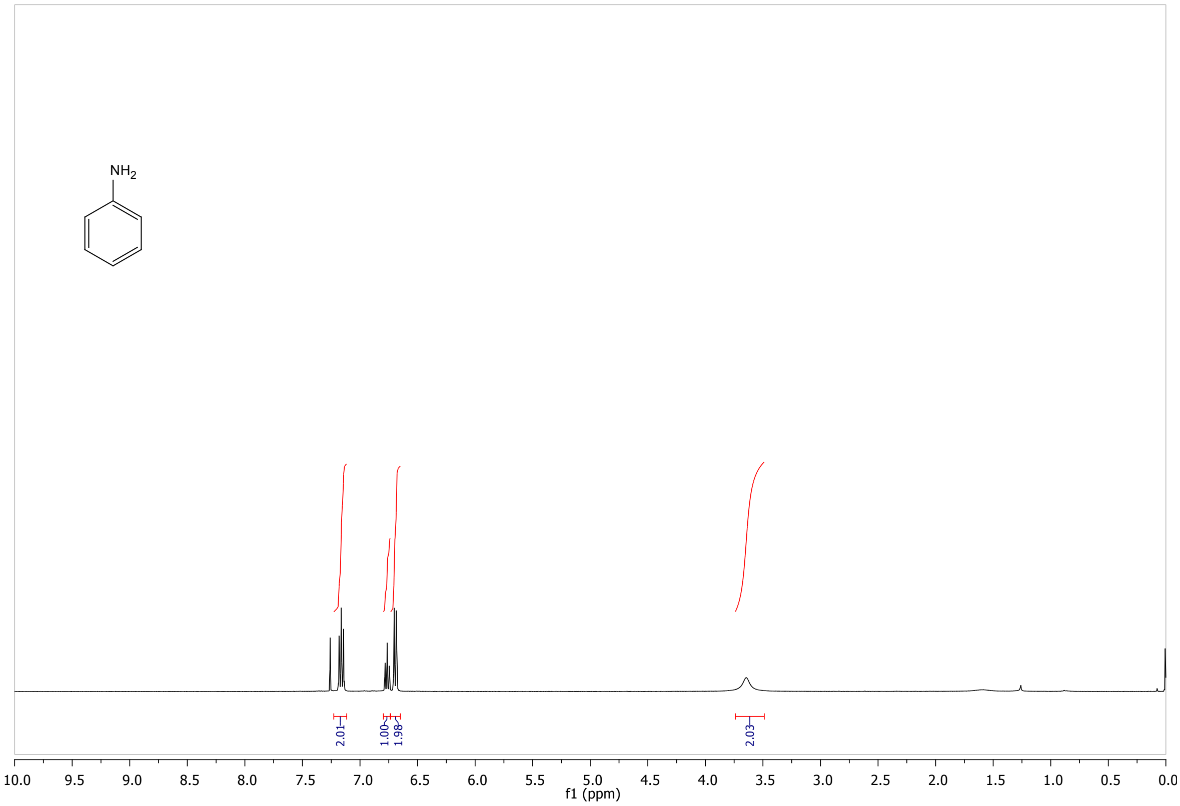


Figure S3. The reusability of Al-rGO/$Ni_{40}Pd_{60}$ nanocatalysts in the TH of nitrobenzene as a model substrate.



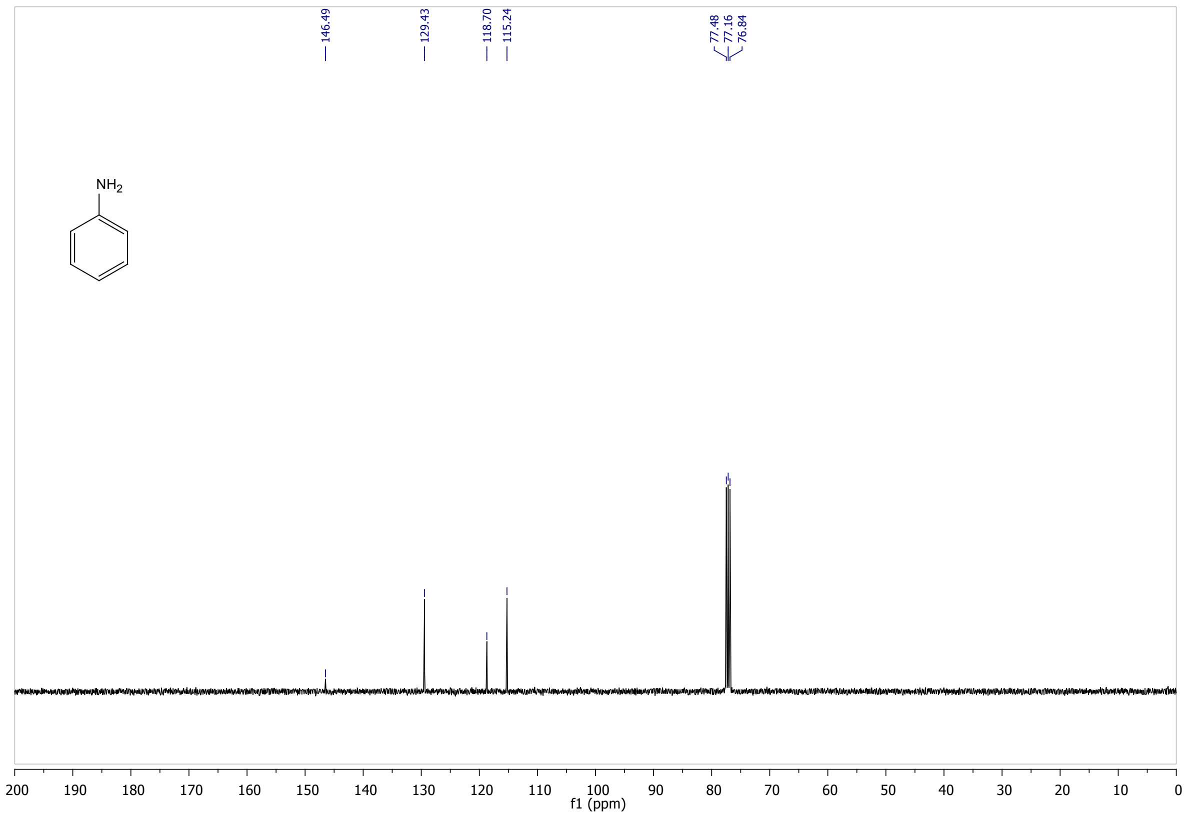
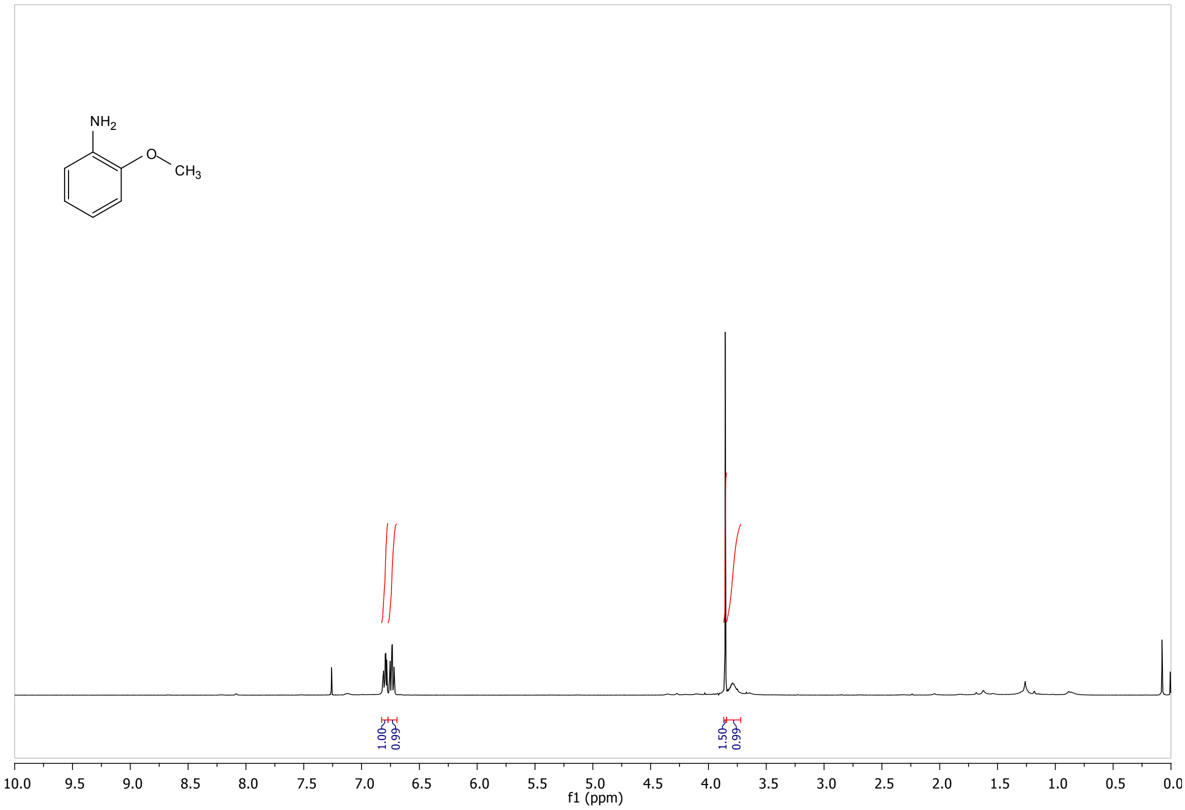


Figure S4. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectrum of 2a (CDCl3).



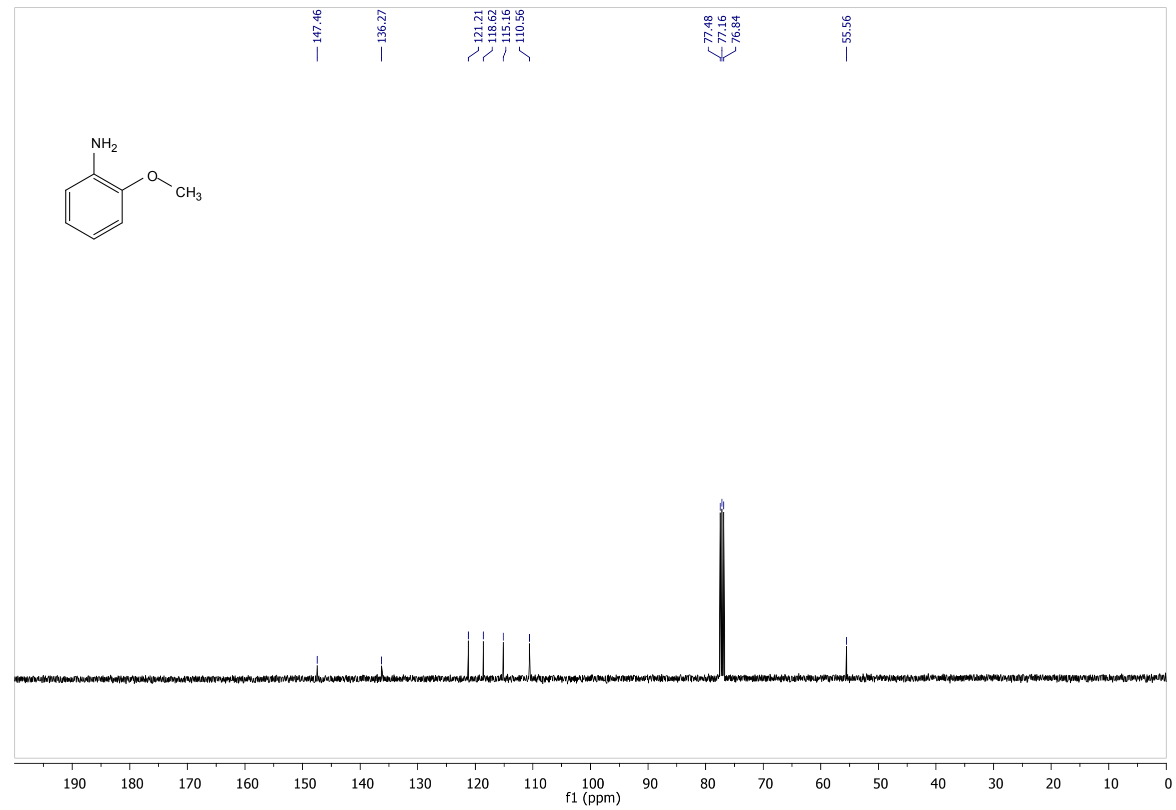
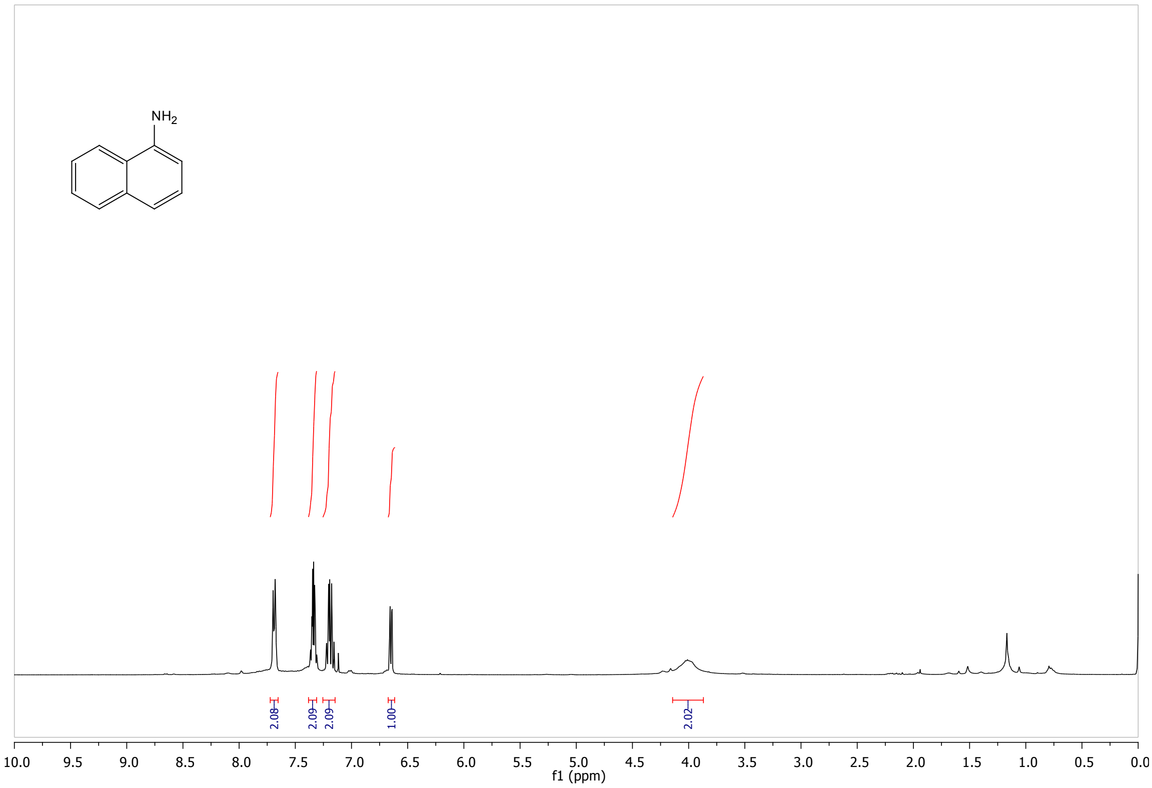


Figure S5. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectrum of 2f (CDCl3).



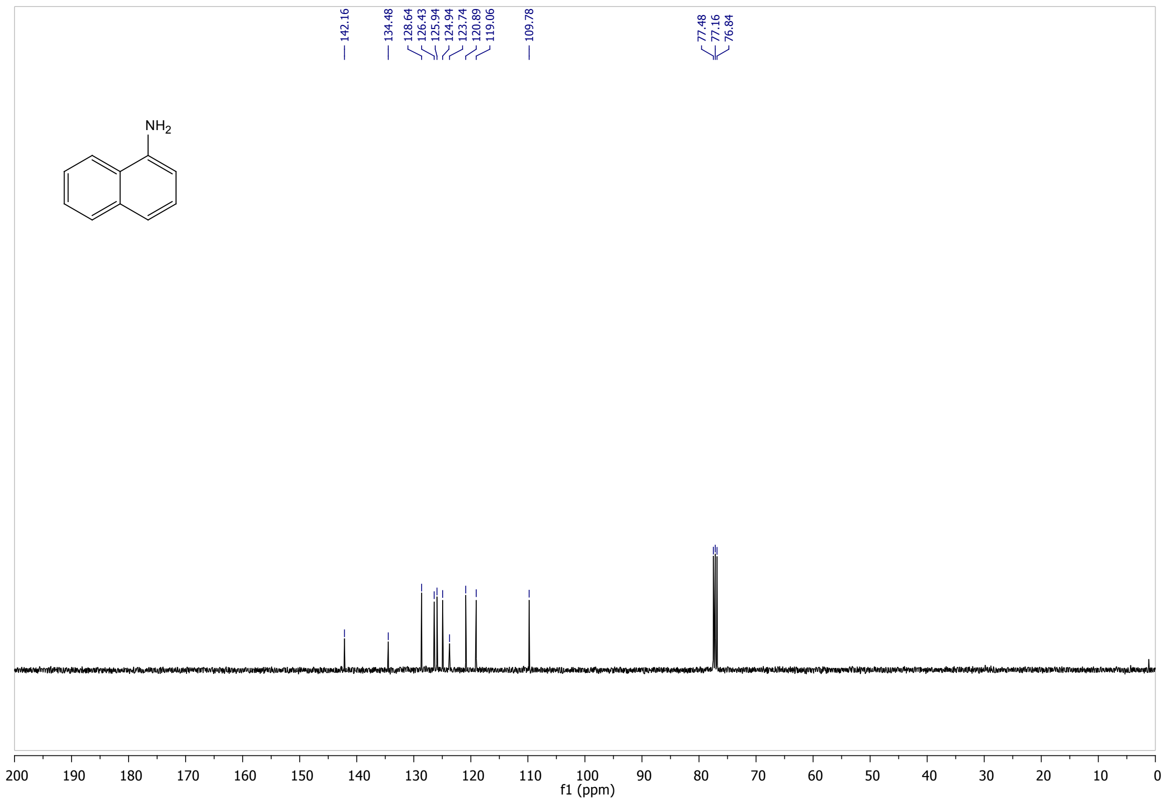
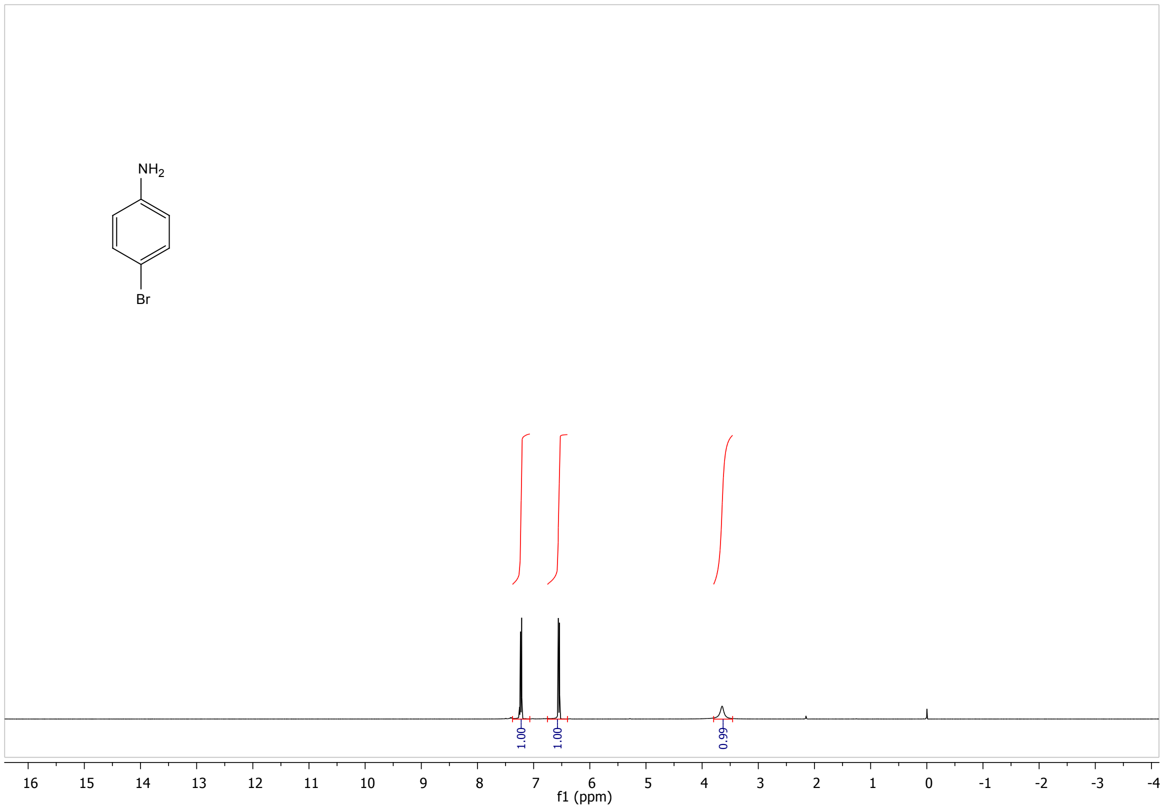


Figure S6. [1]H-NMR (400 MHz) and [13]C-NMR (100 MHz) spectrum of 2g (CDCl3).



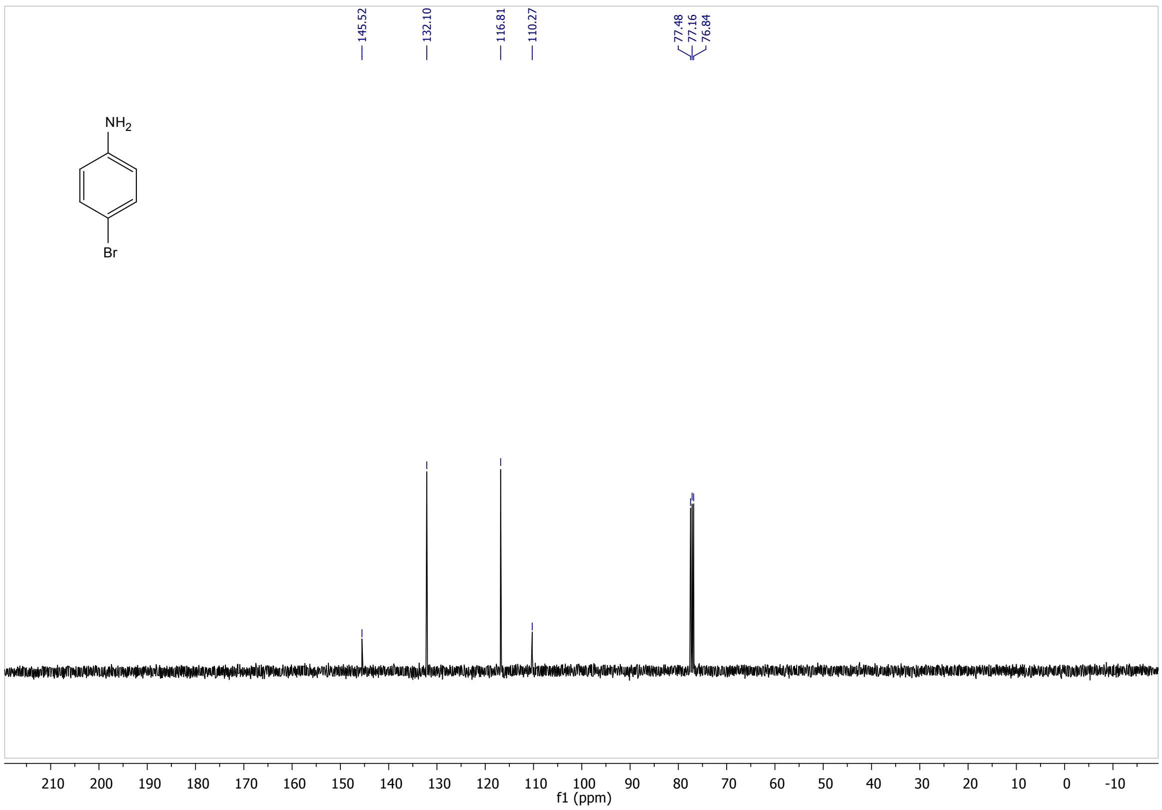
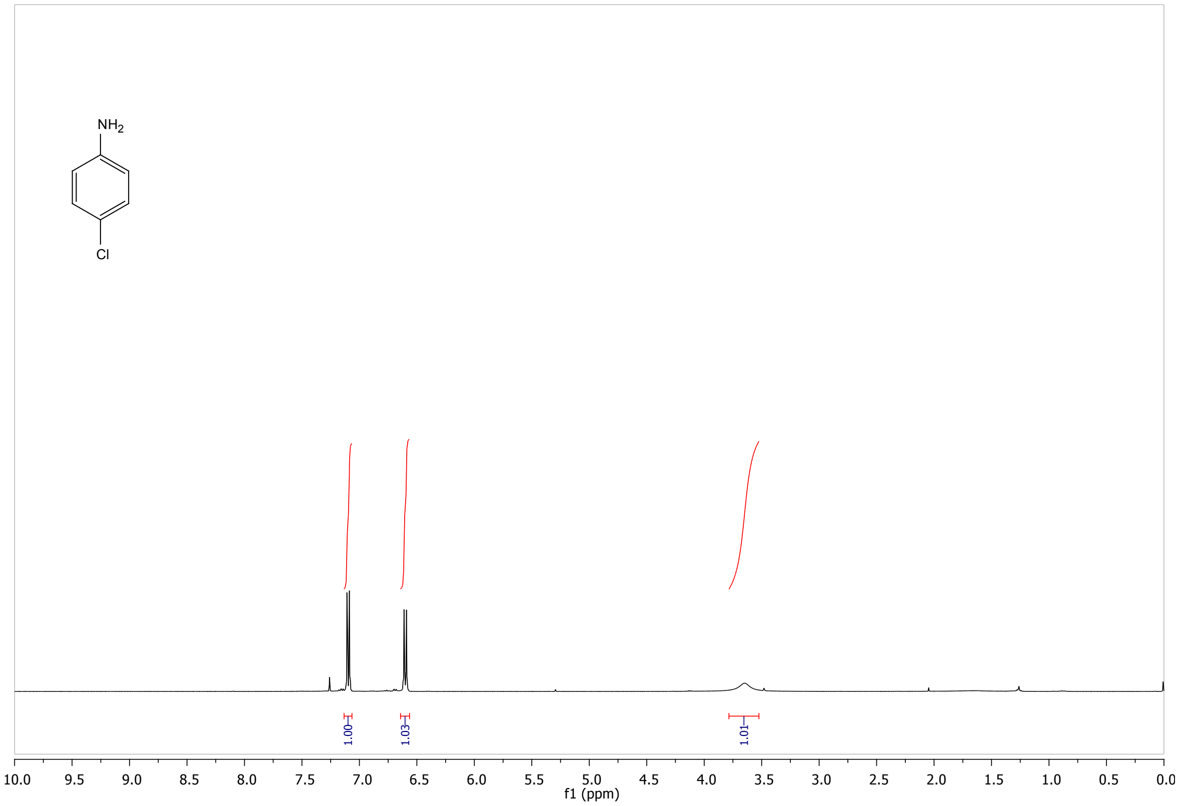


Figure S7. **^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectrum of 2h (CDCl3).**



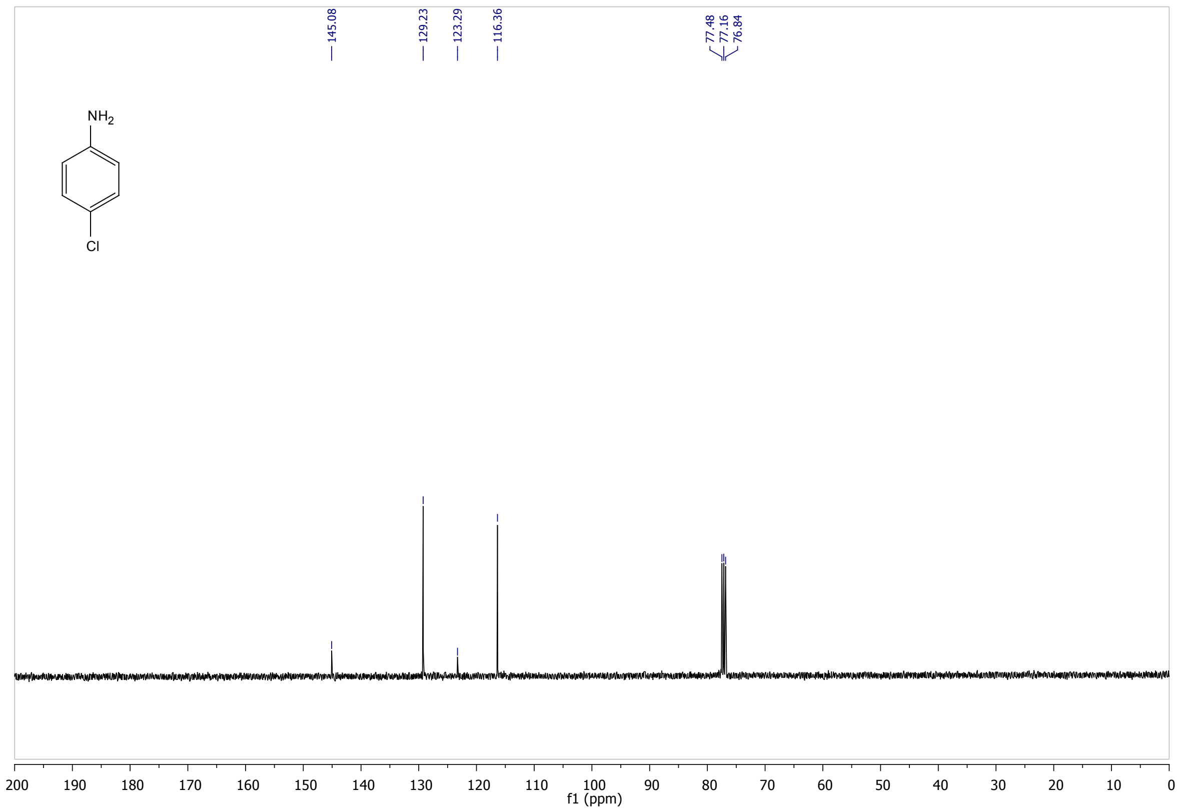
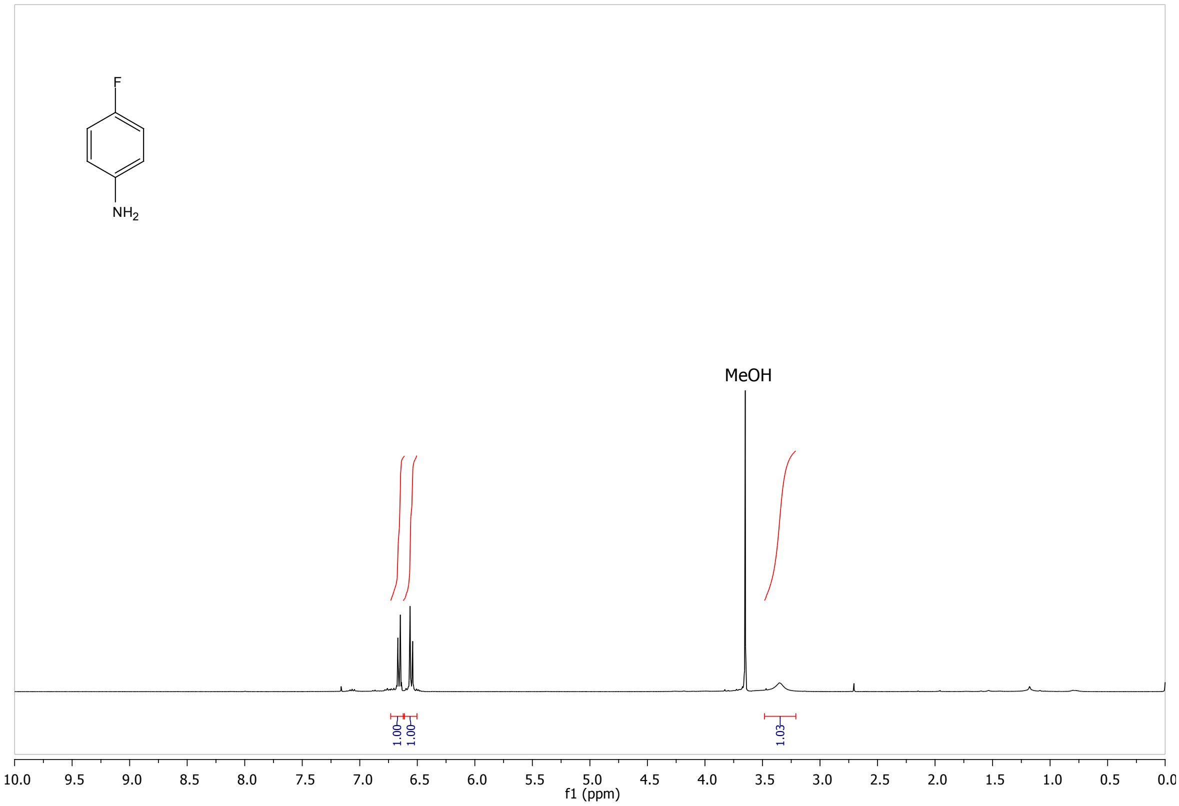


Figure S8. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectrum of 2i (CDCl3).



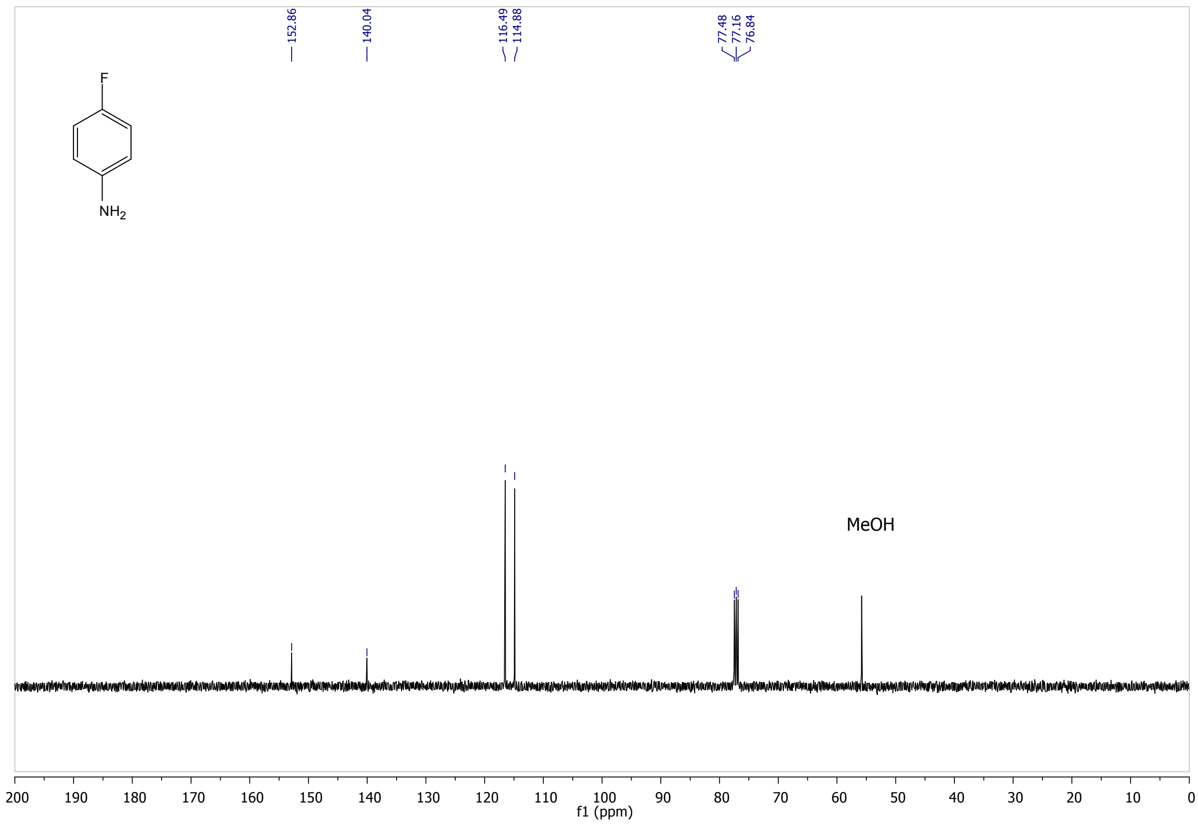
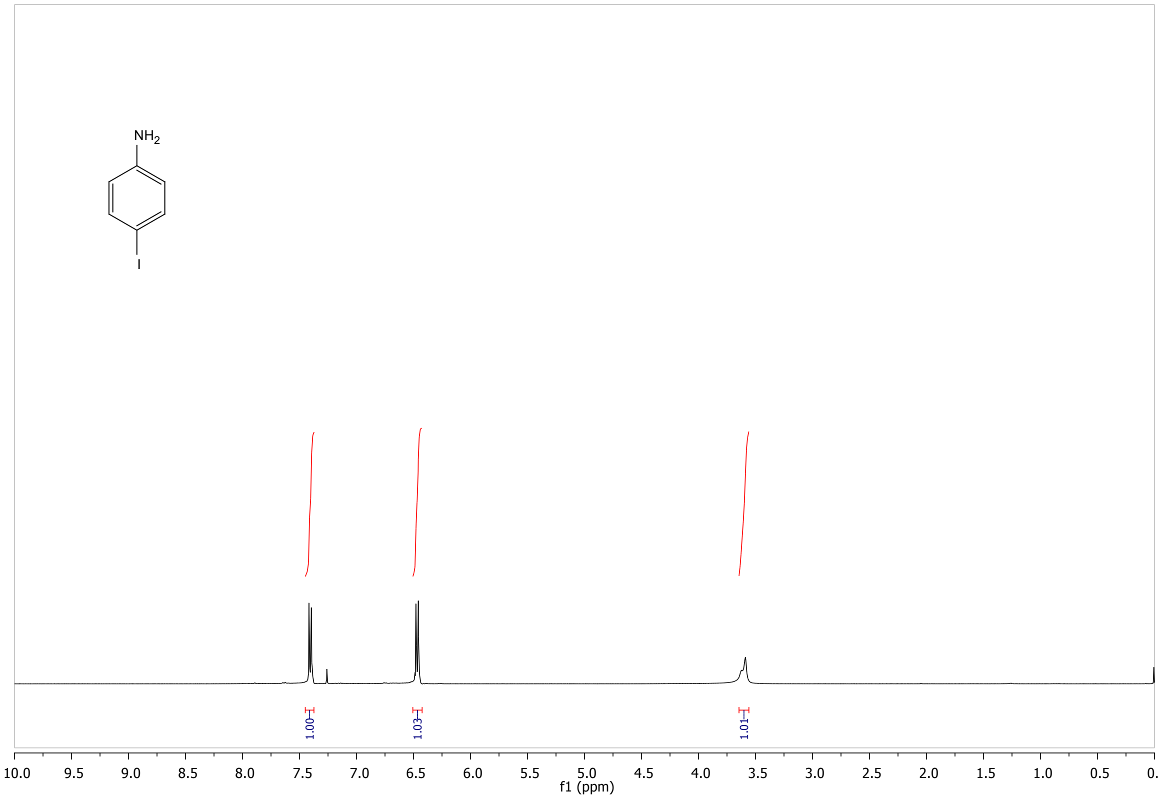


Figure S9. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectrum of 2j (CDCl3).



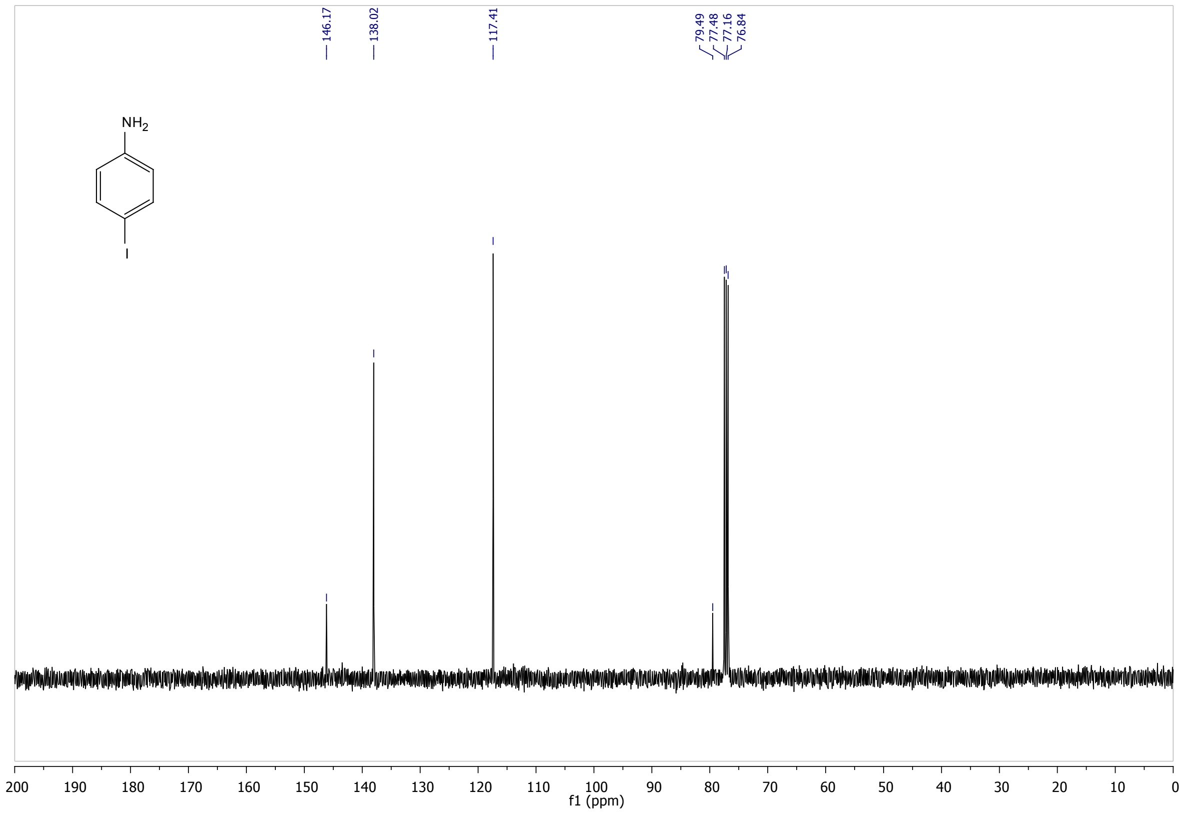
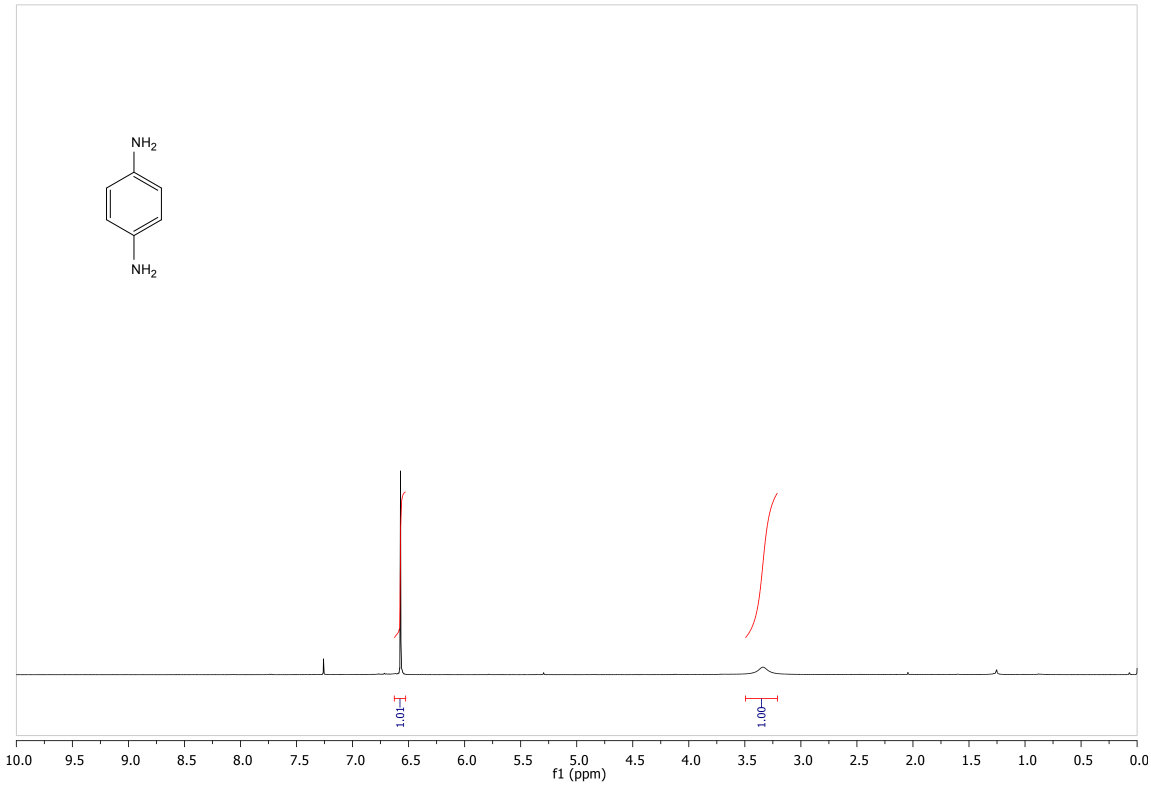


Figure S10. [1]H-NMR (400 MHz) and [13]C-NMR (100 MHz) spectrum of 2k (CDCl3).



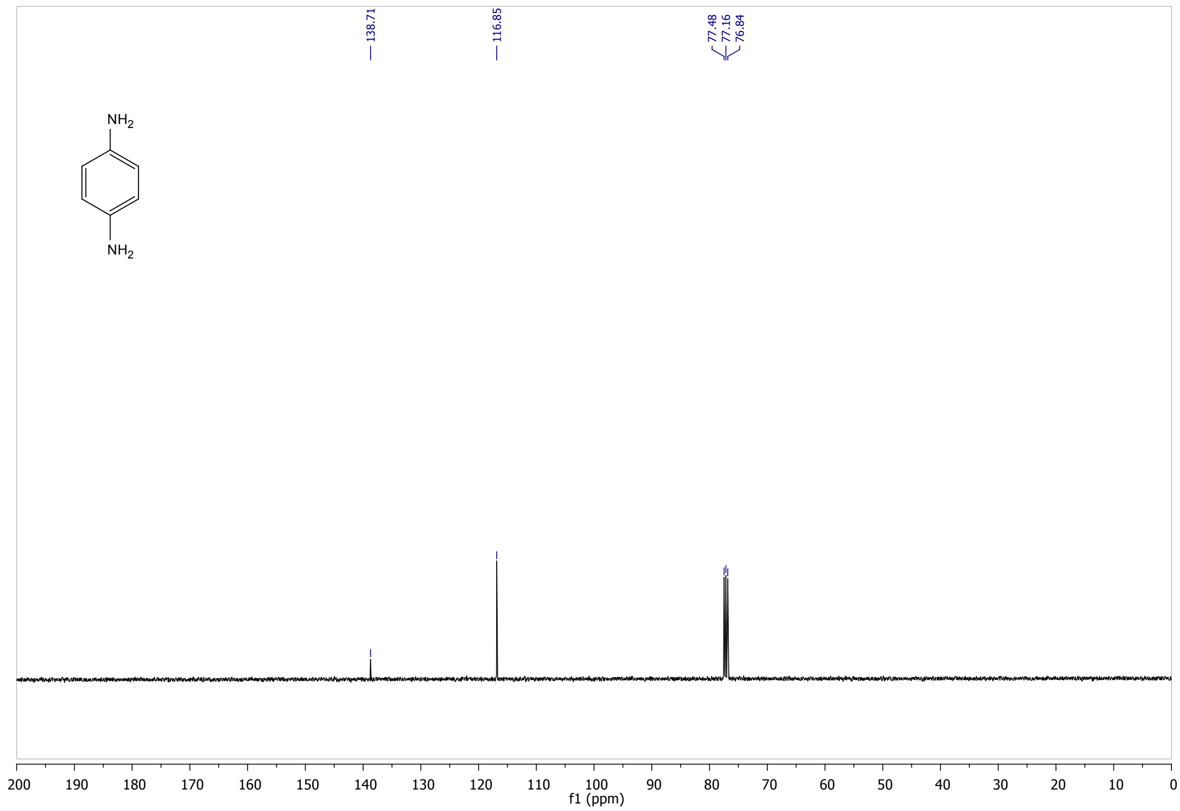
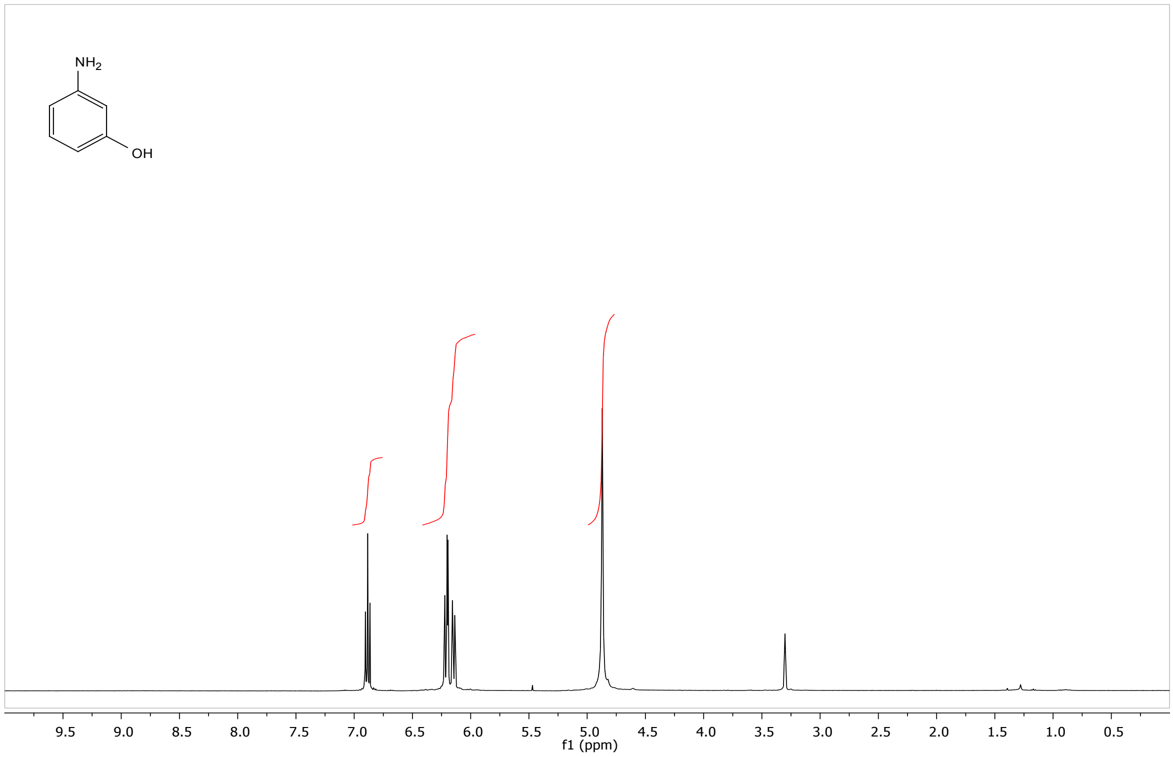


Figure S11. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectrum of 2l (CDCl3).



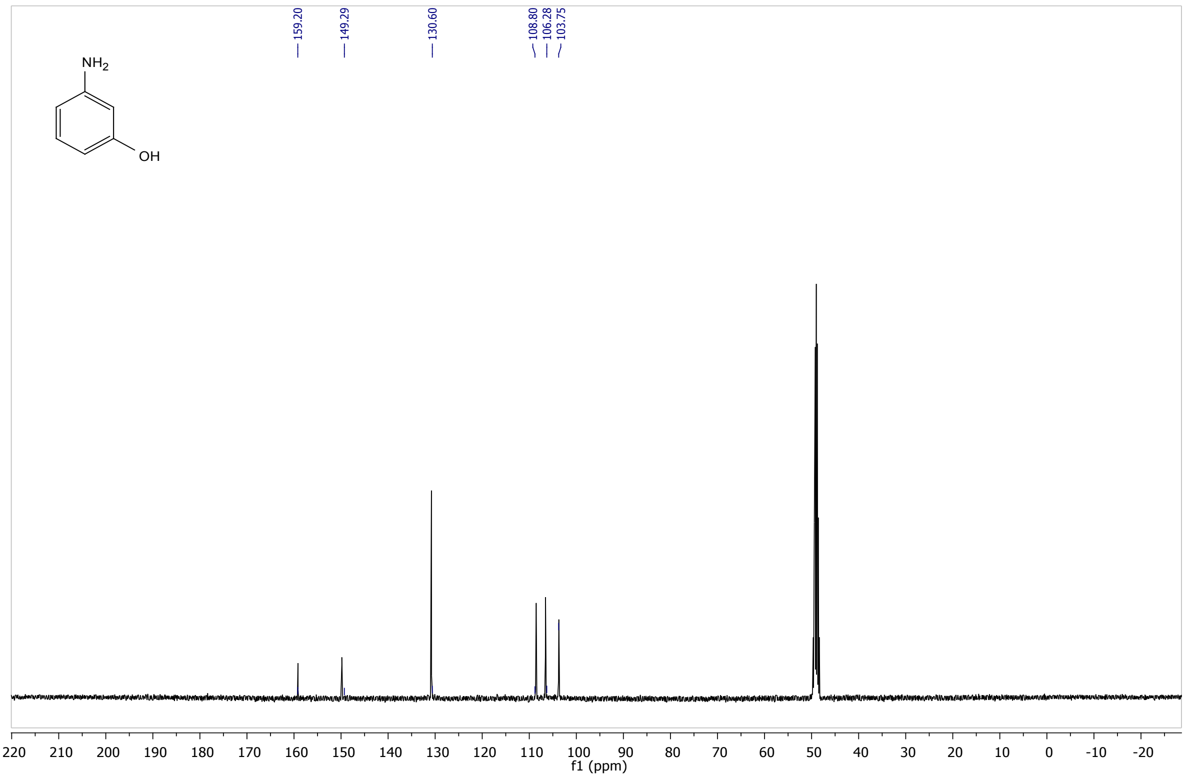
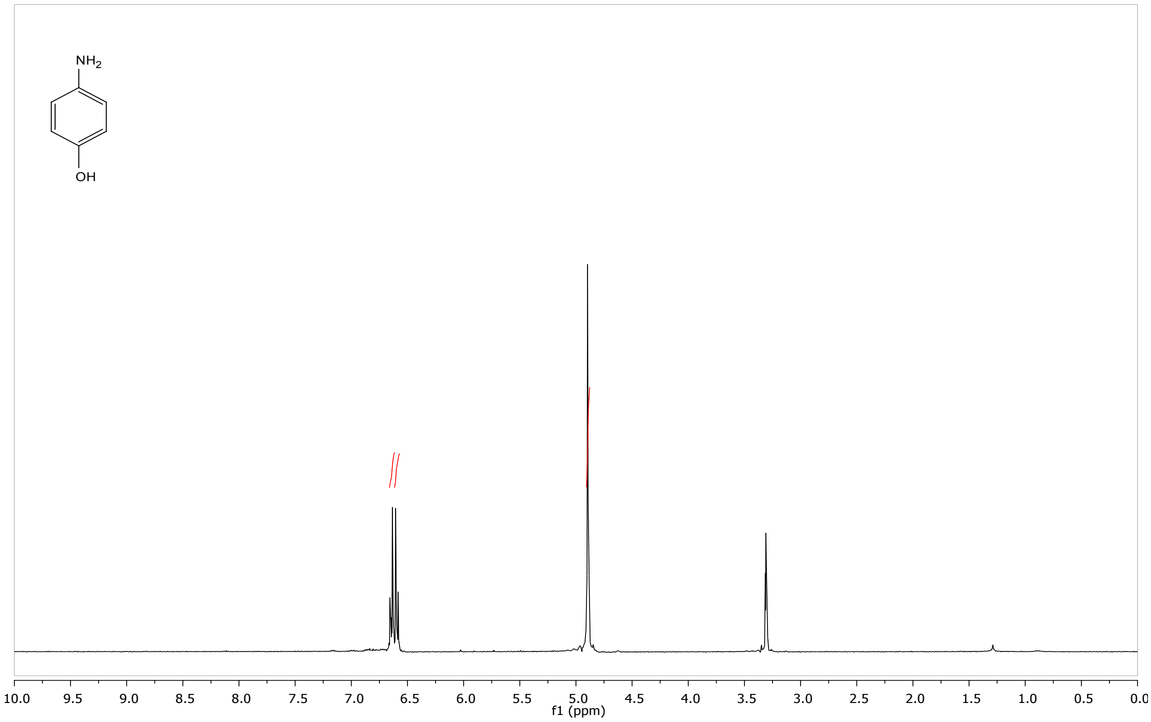


Figure S12. **^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectrum of 2m (CD_3OD).**



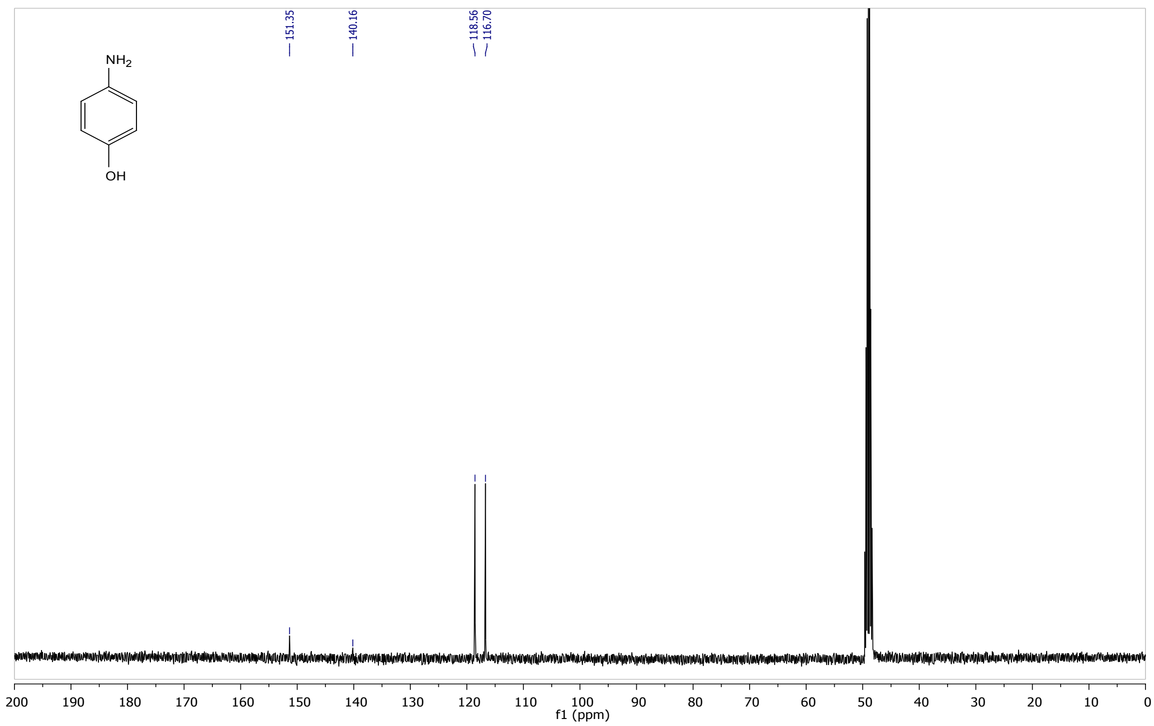
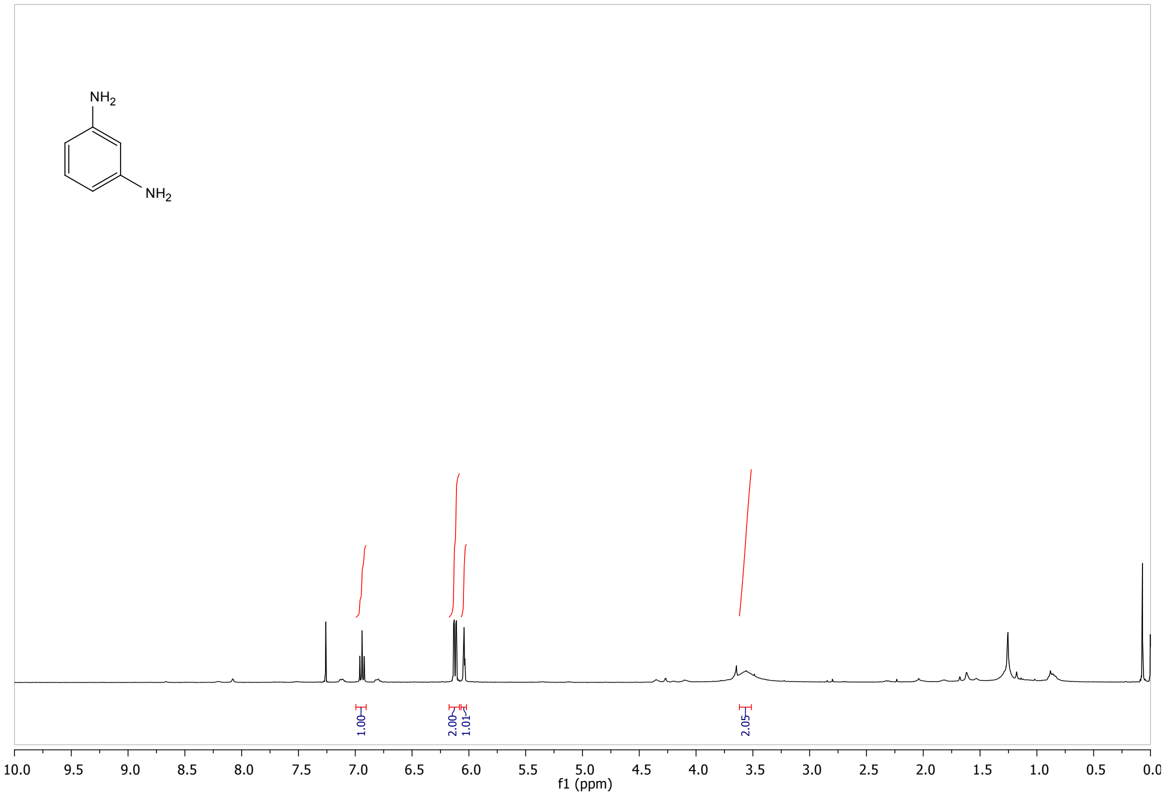


Figure S13. ^{1}**H-NMR (400 MHz) and** ^{13}**C-NMR (100 MHz) spectrum of 2n (**CD_3OD**).**



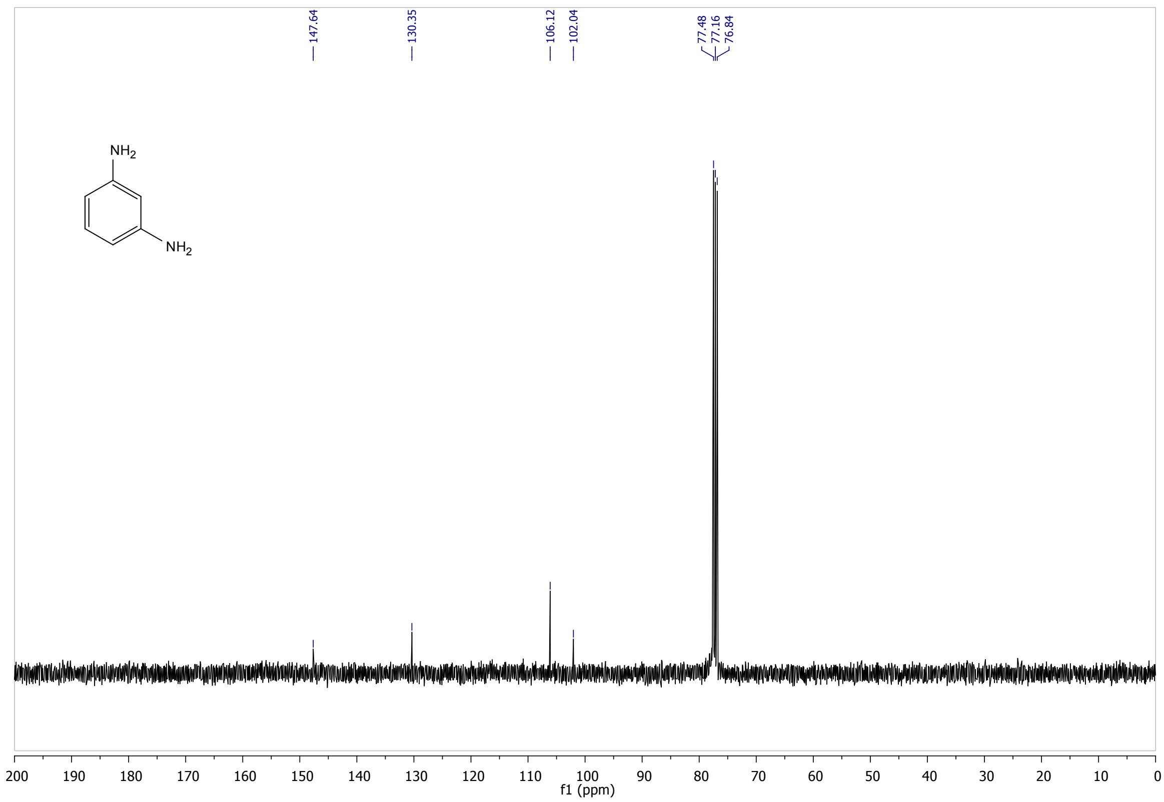
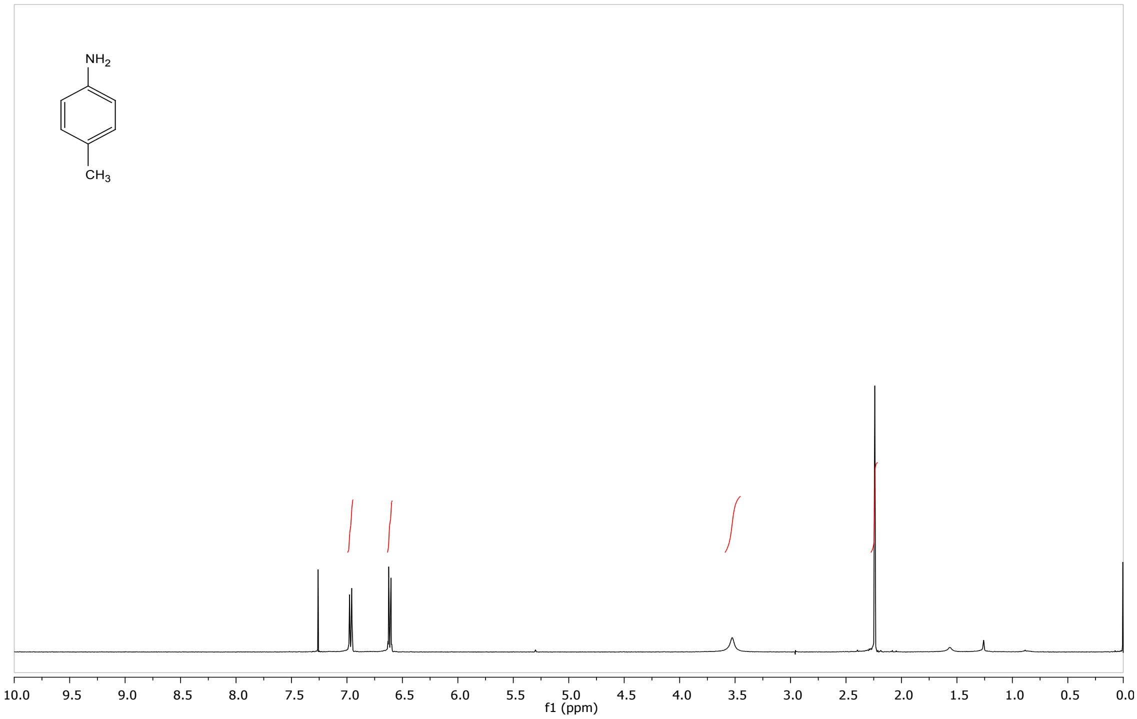


Figure S14. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectrum of 2o (CDCl3).



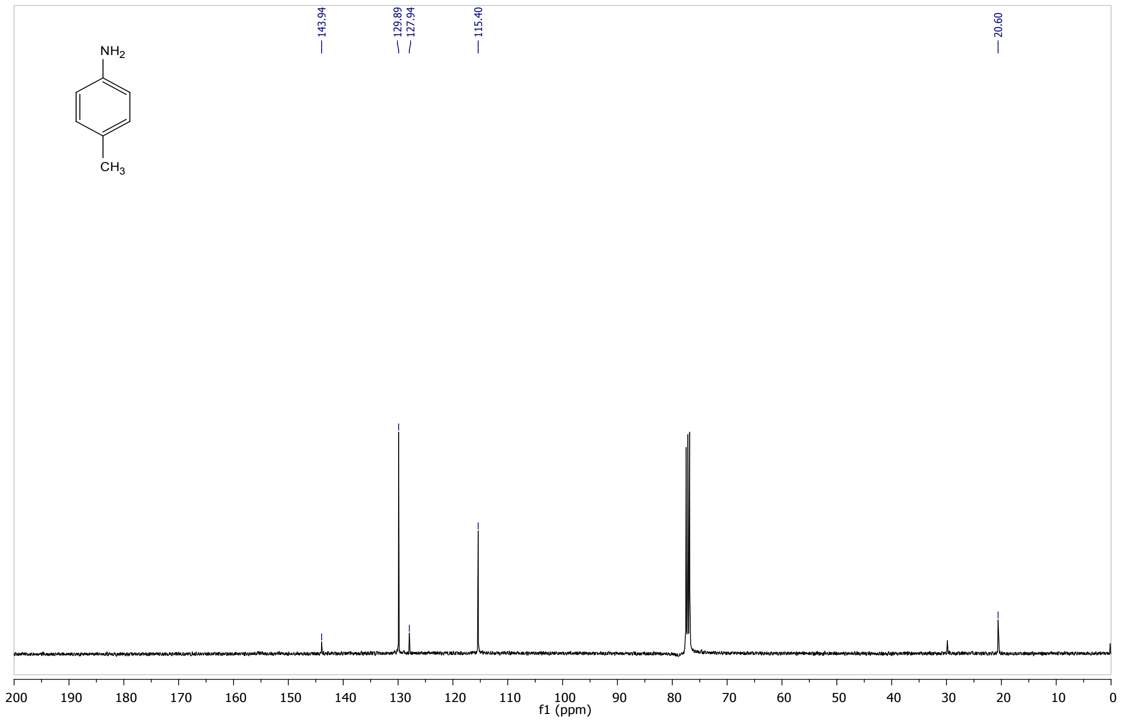
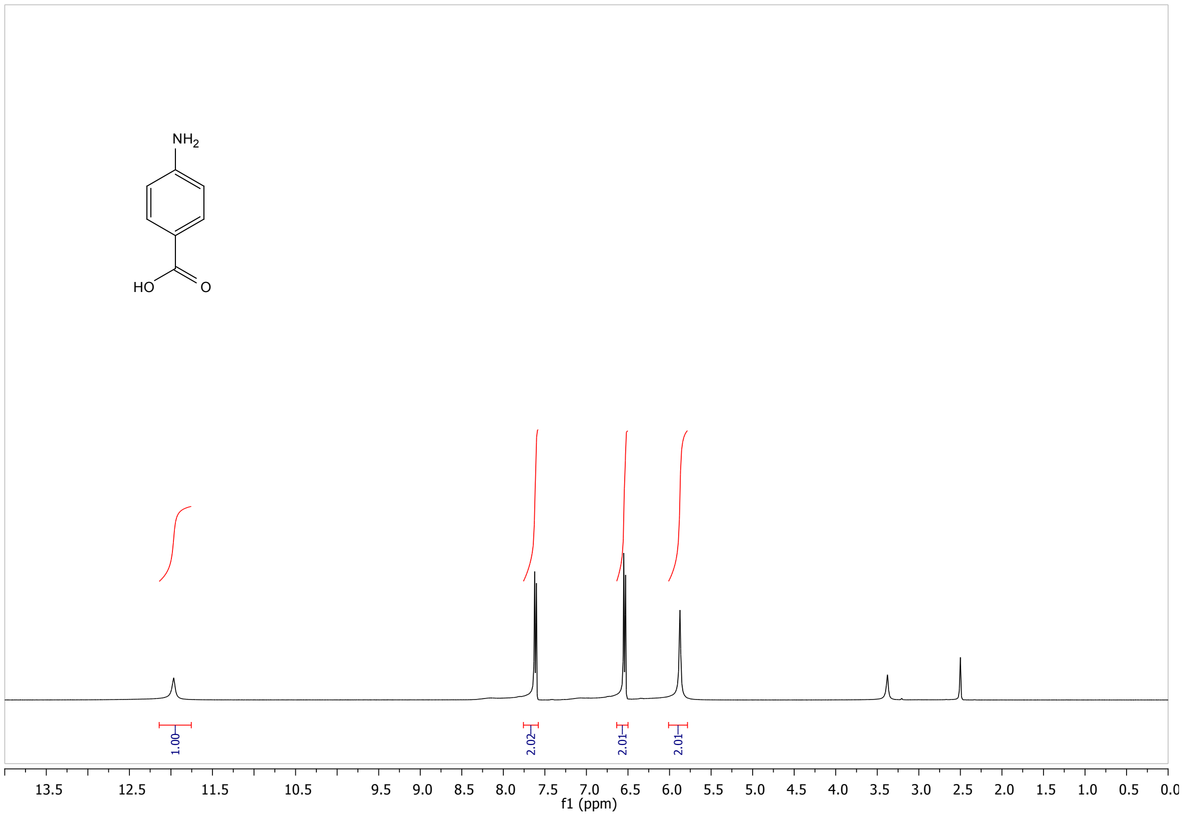


Figure S15. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectrum of 2p (CDCl3).



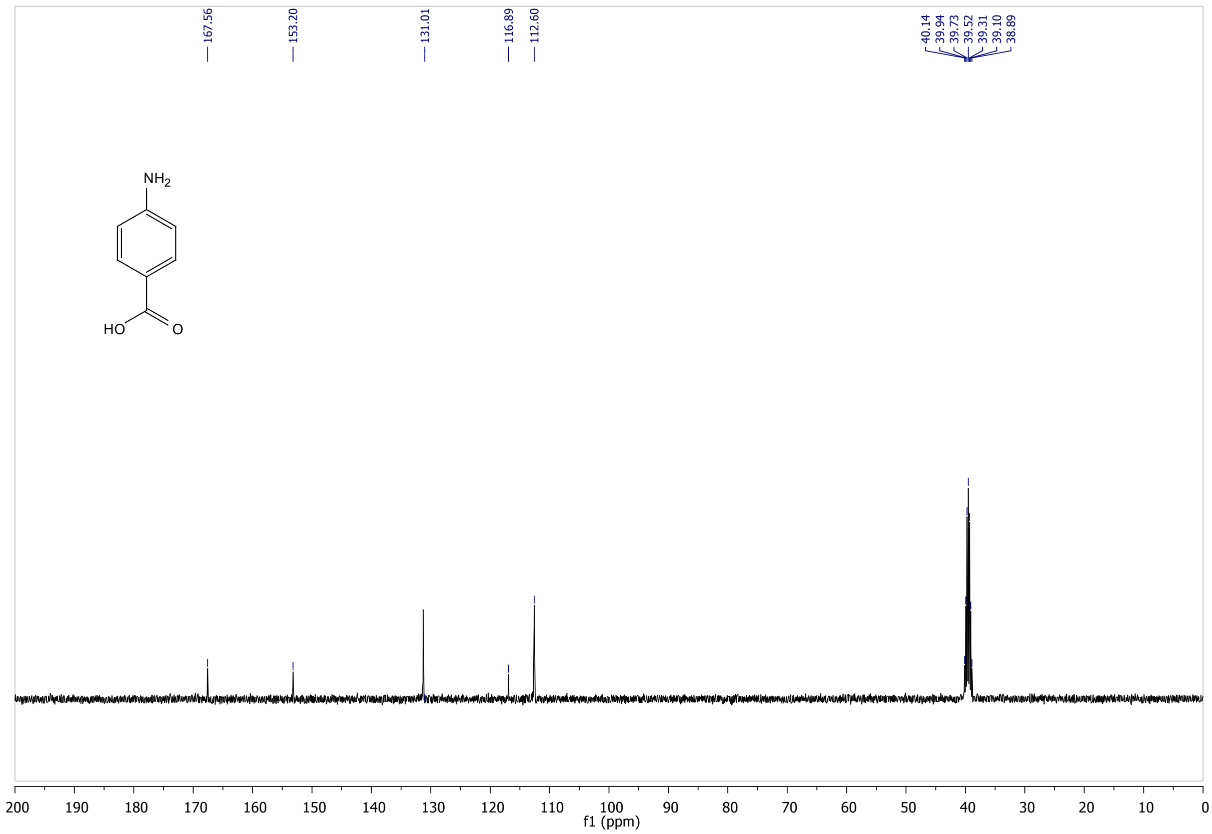
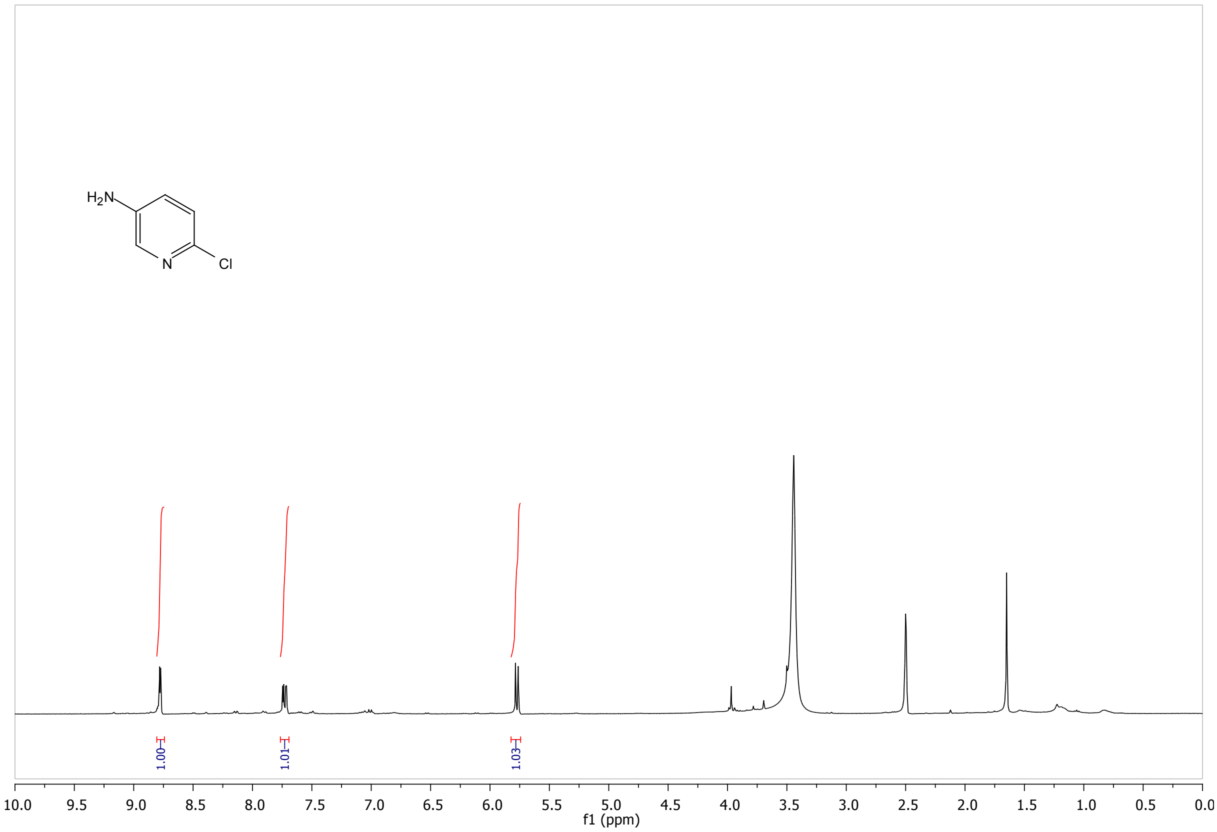


Figure S16. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectrum of 2r (DMSO).



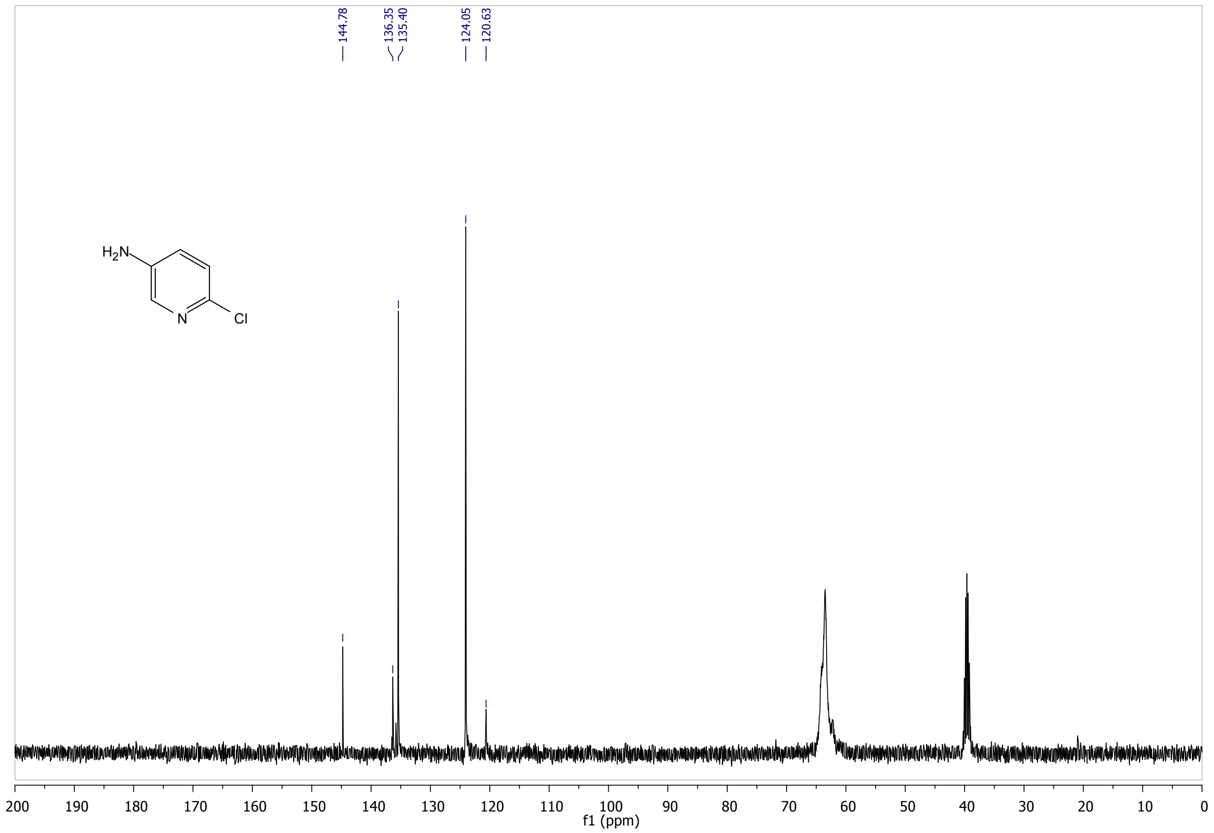
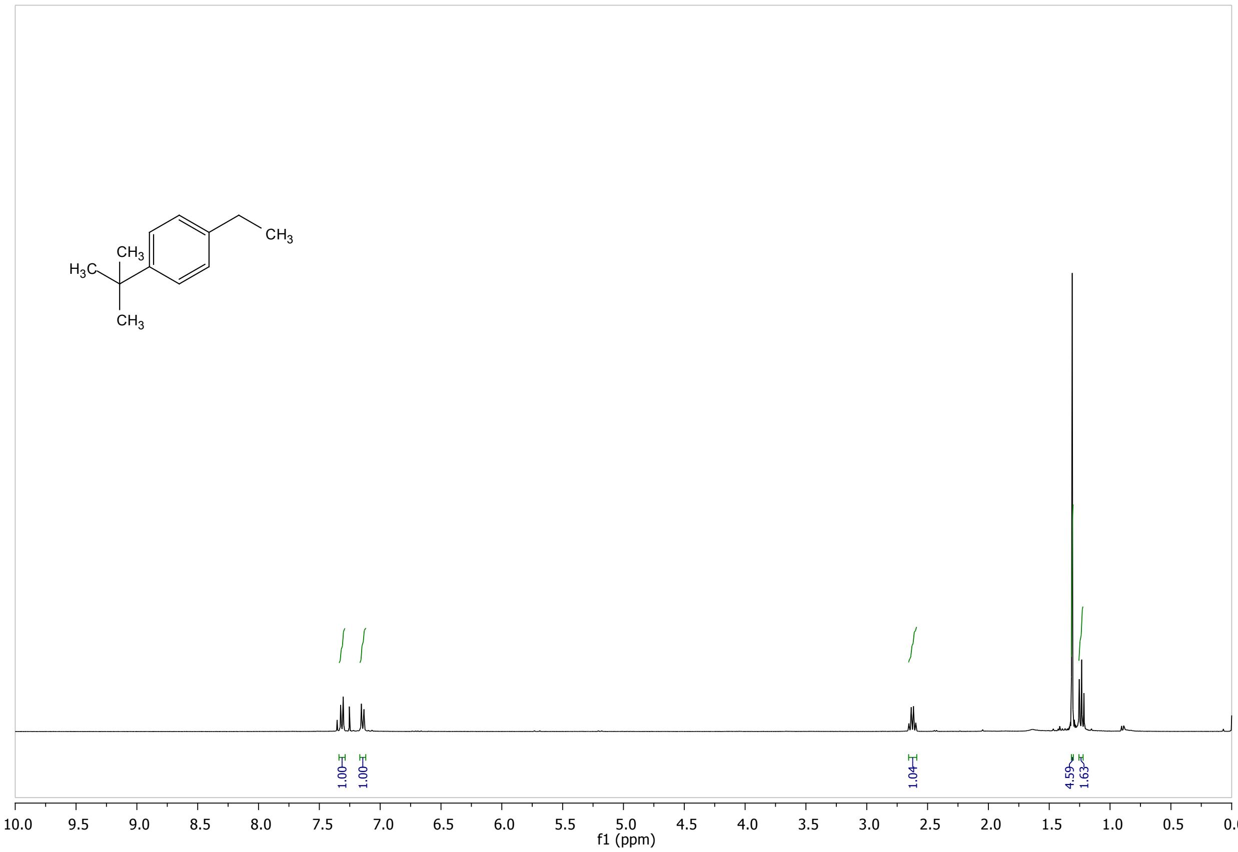


Figure S17. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectrum of 2s (DMSO).



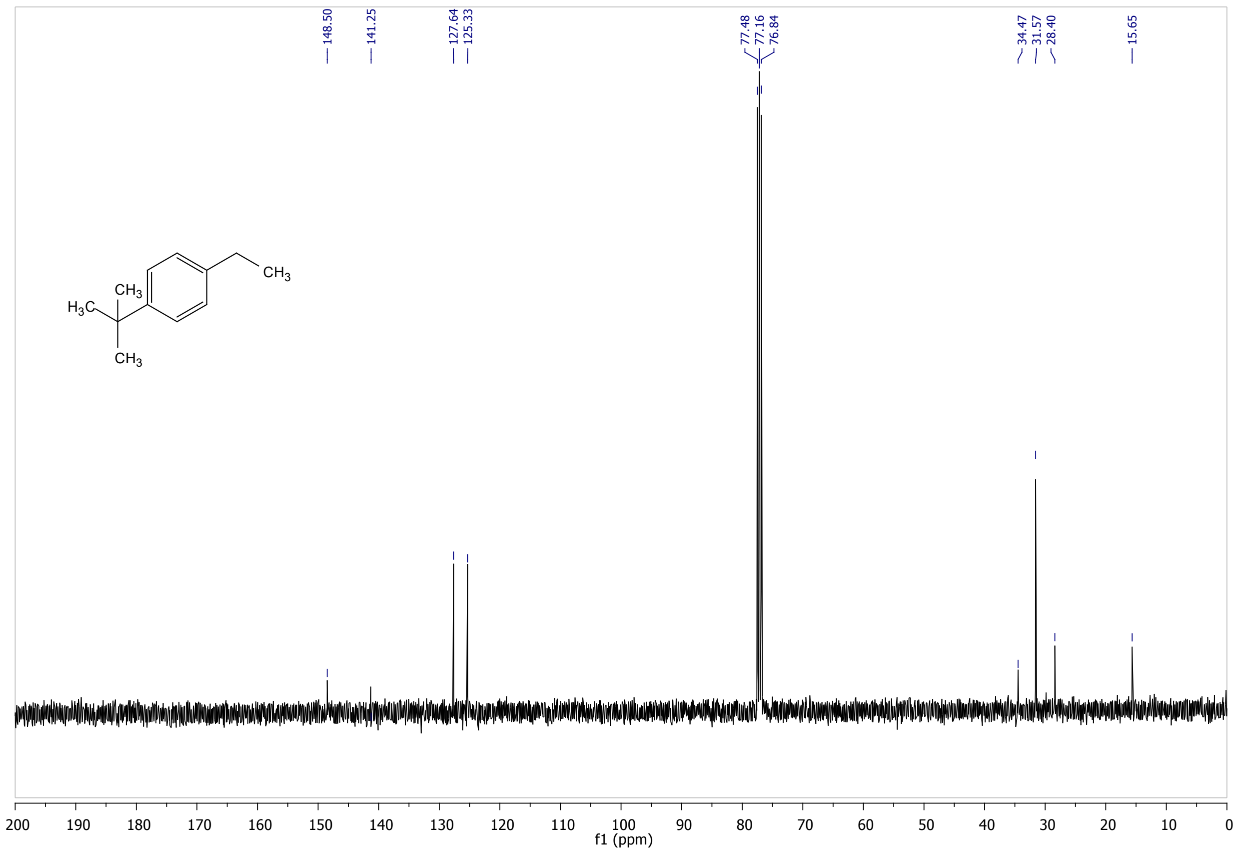
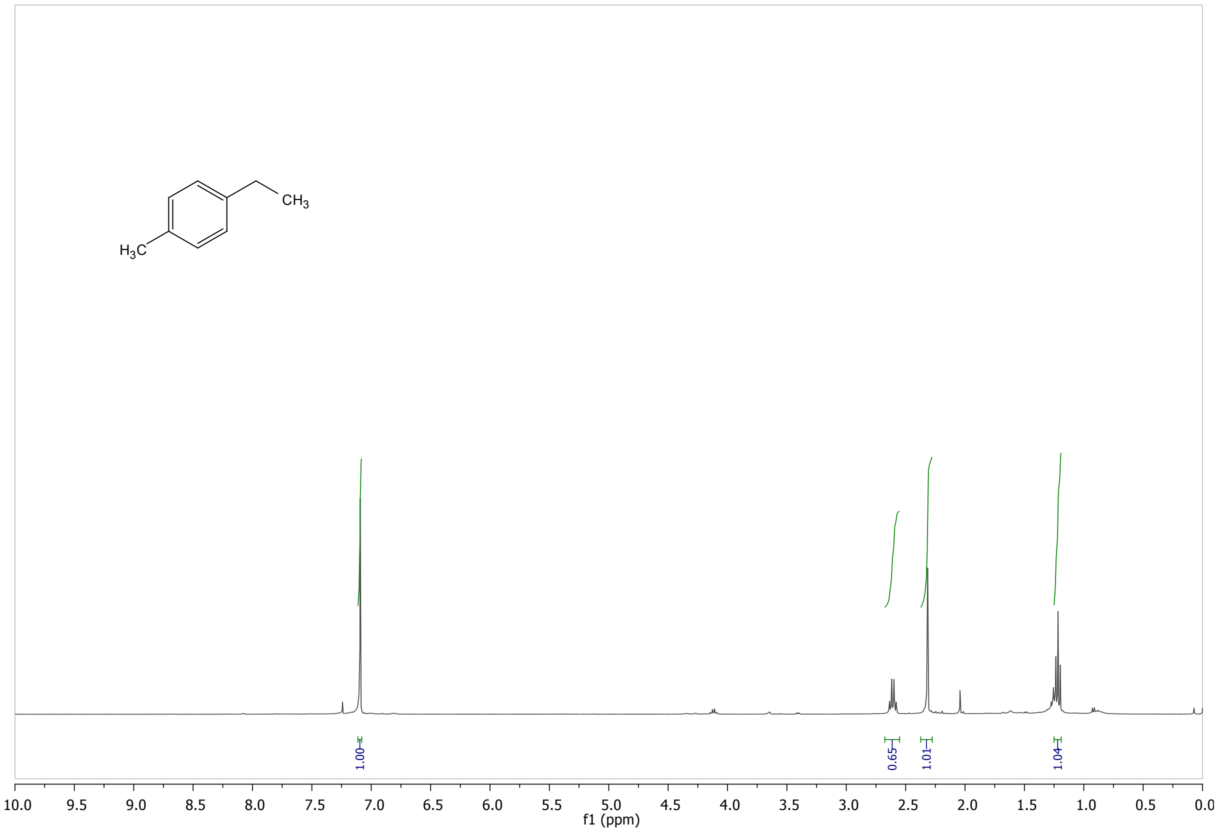


Figure S18. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectrum of 4a (CDCl3).



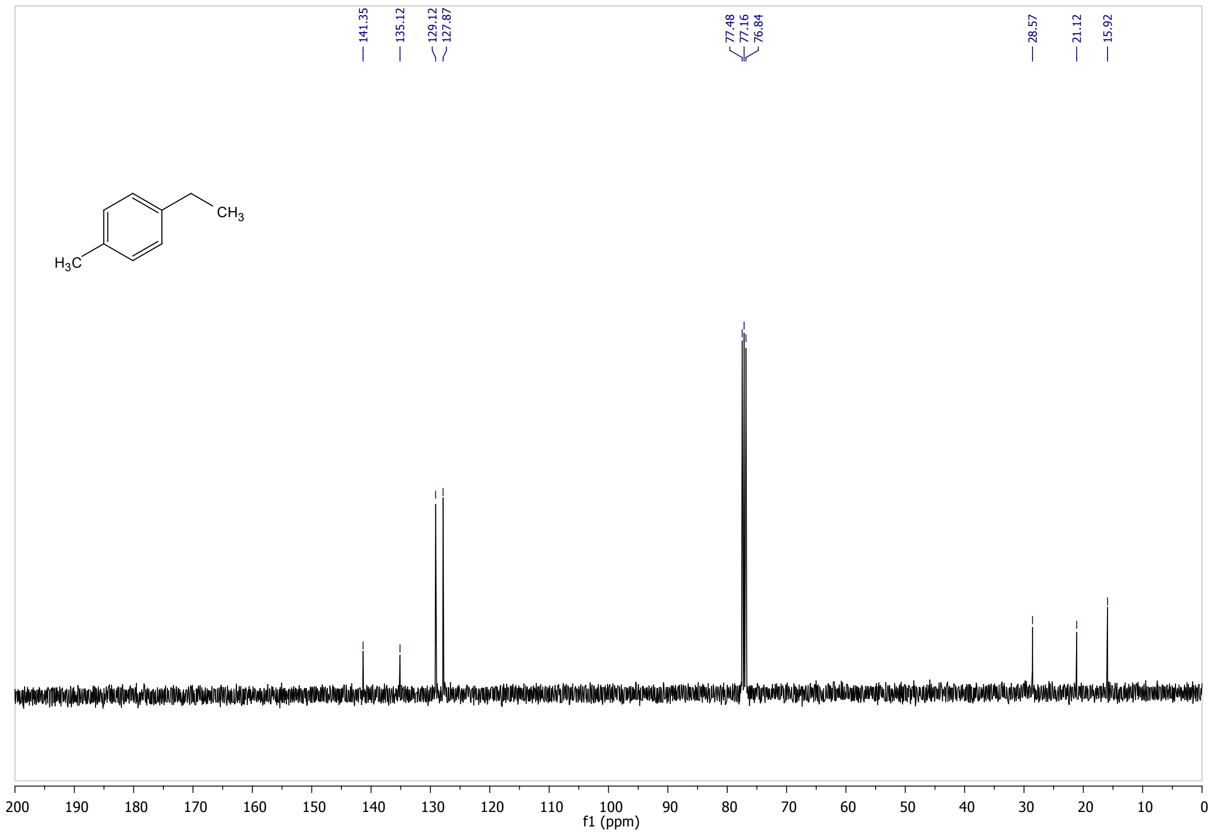
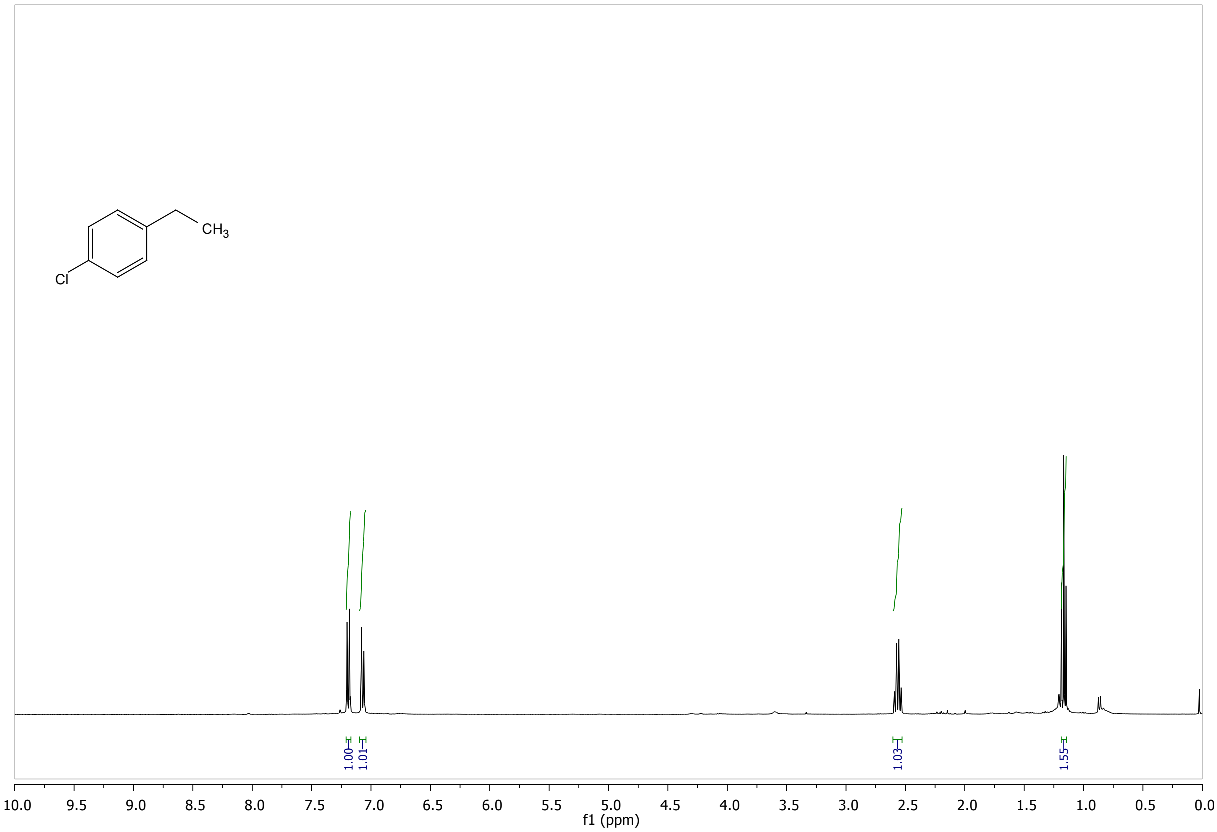


Figure S19. 1H-NMR (400 MHz) and 13C-NMR (100 MHz) spectrum of 4b (CDCl3).



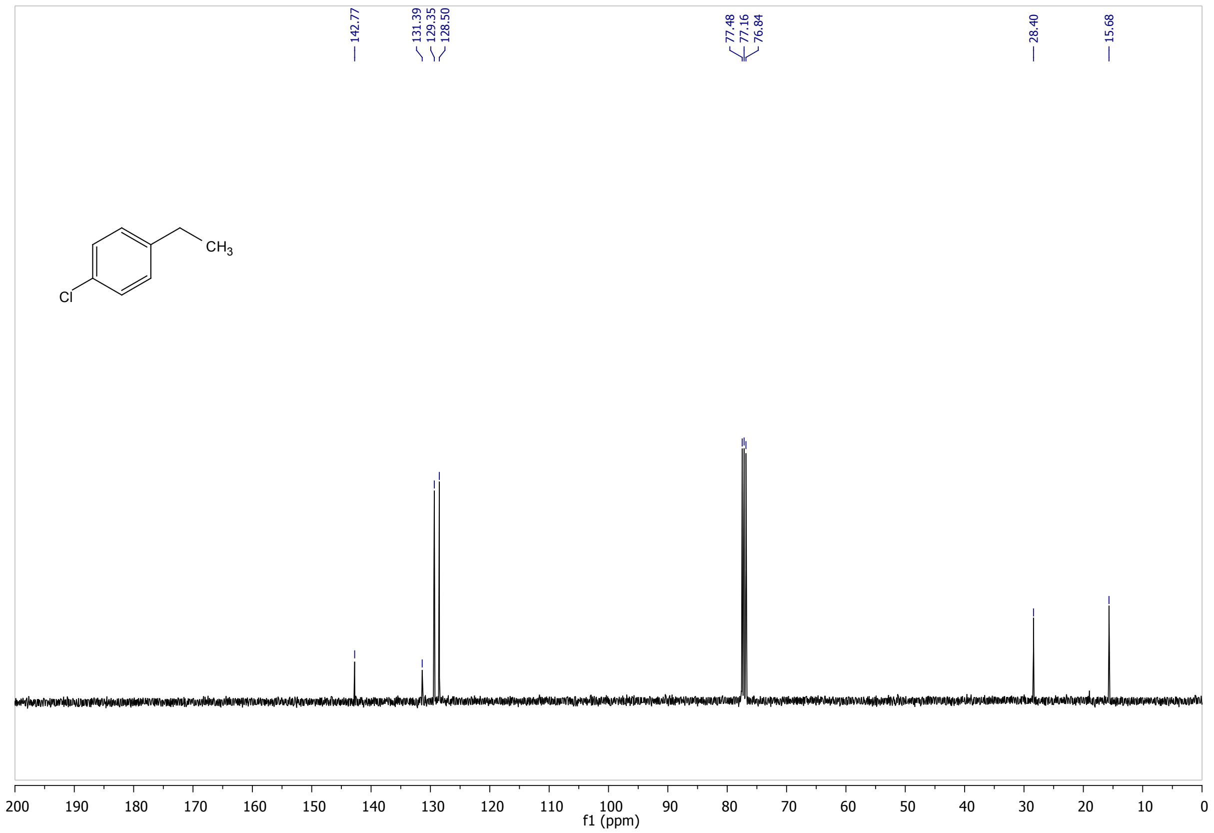
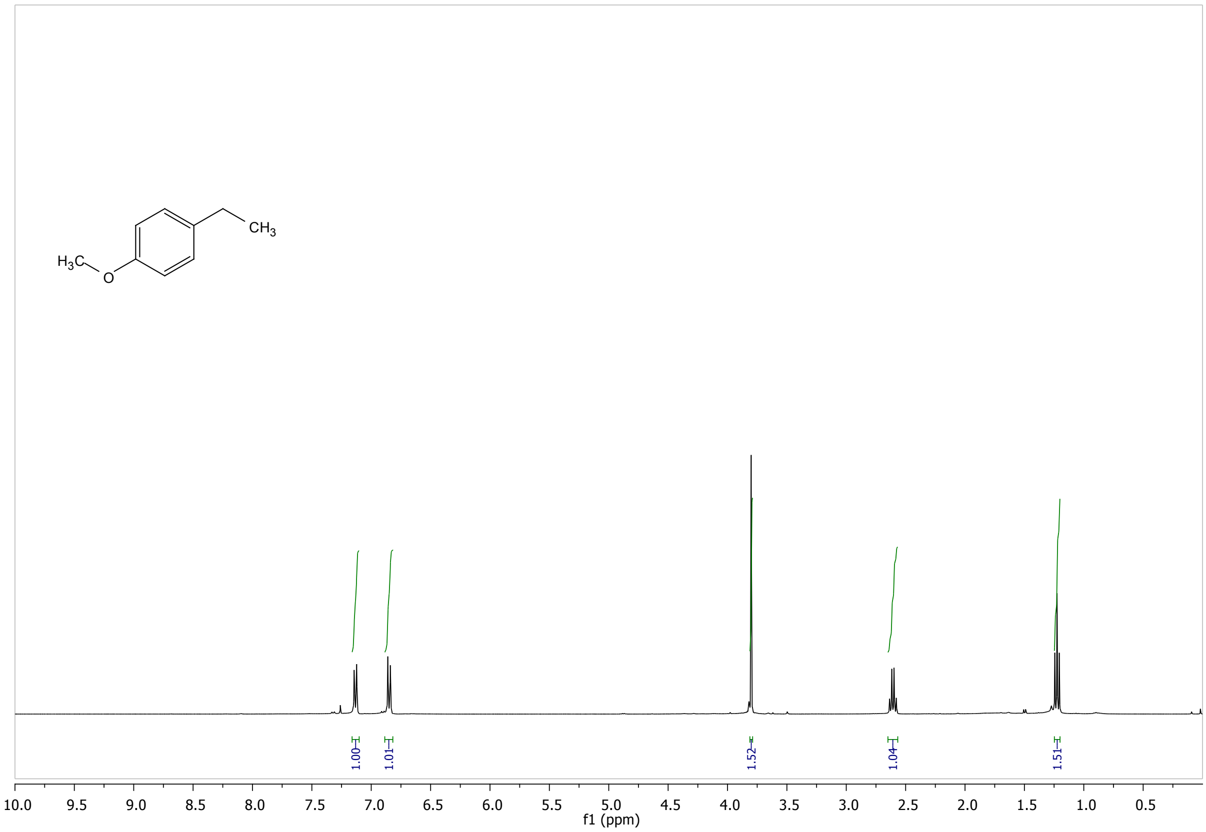


Figure S20. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectrum of 4c (CDCl3).



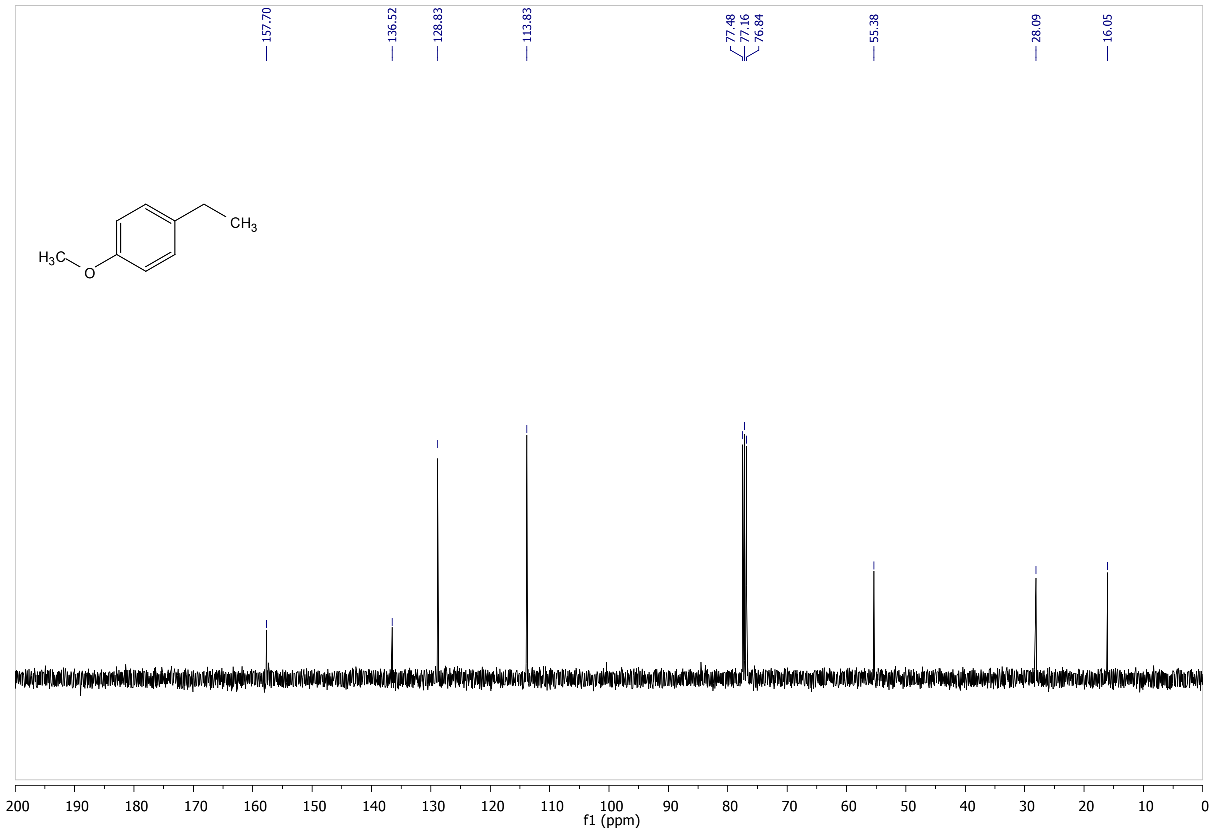
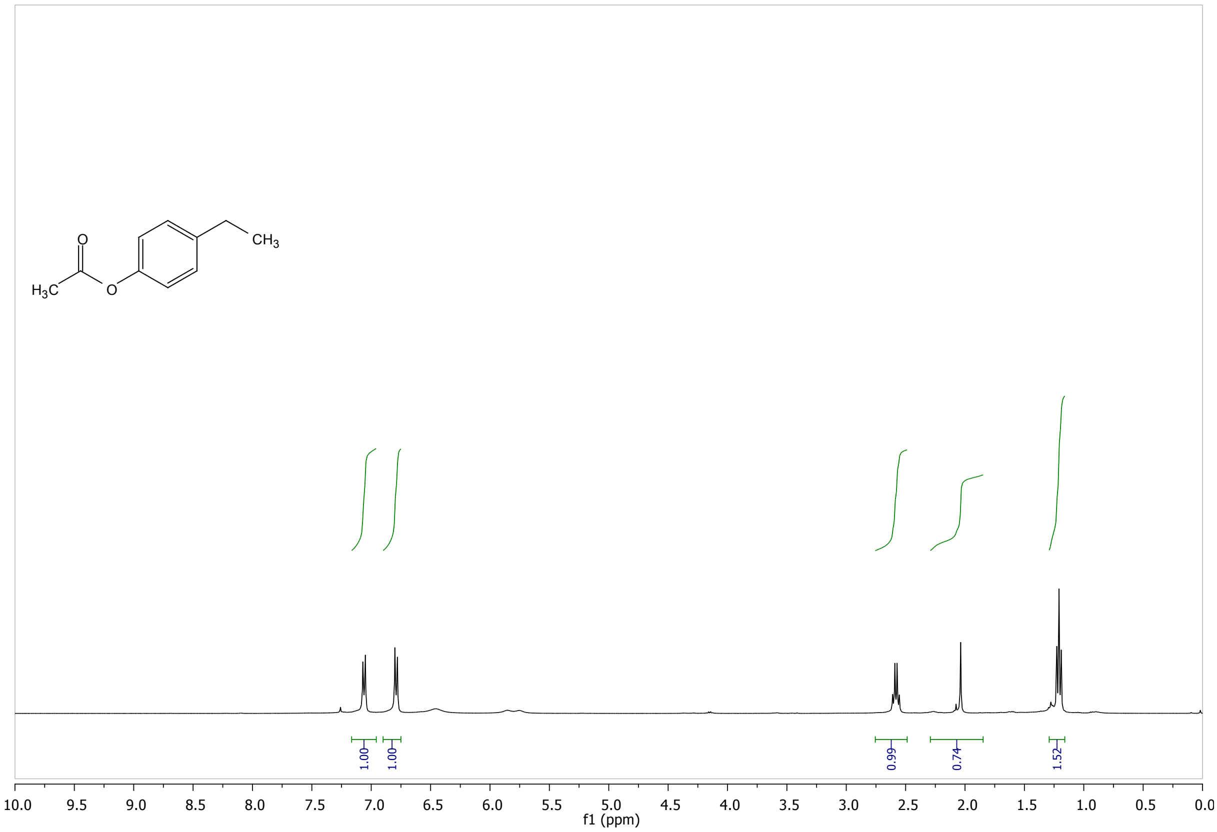


Figure S21. ¹H-NMR (400 MHz) and ¹³C-NMR (100 MHz) spectrum of 4d (CDCl3).



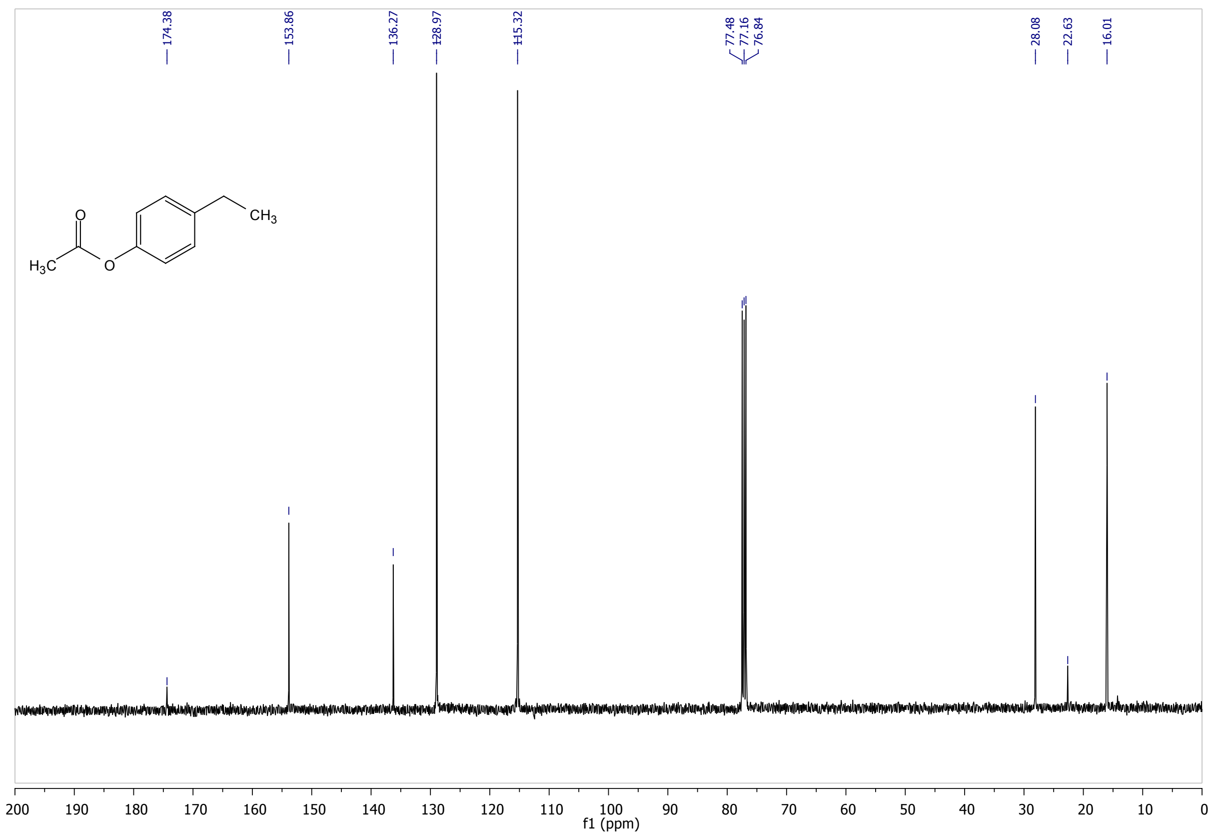
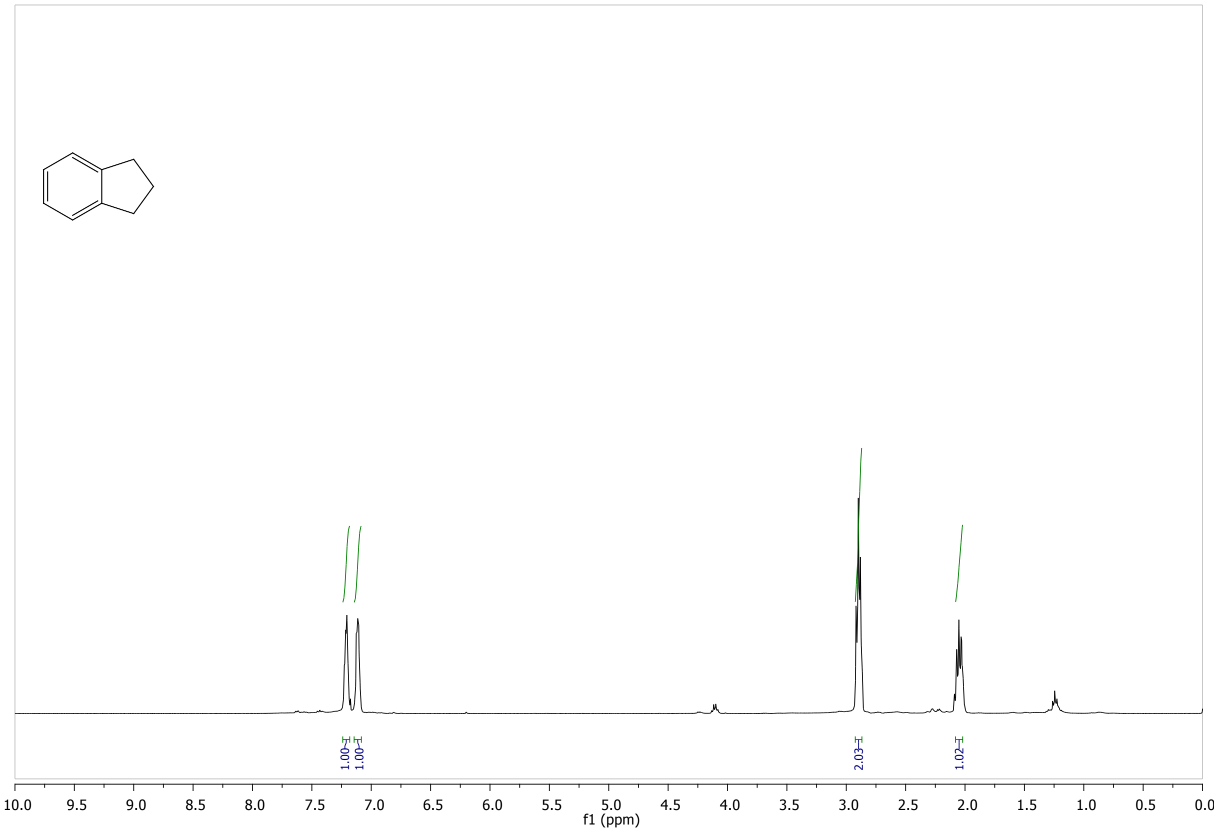


Figure S22. [1]H-NMR (400 MHz) and [13]C-NMR (100 MHz) spectrum of 4e (CDCl3).



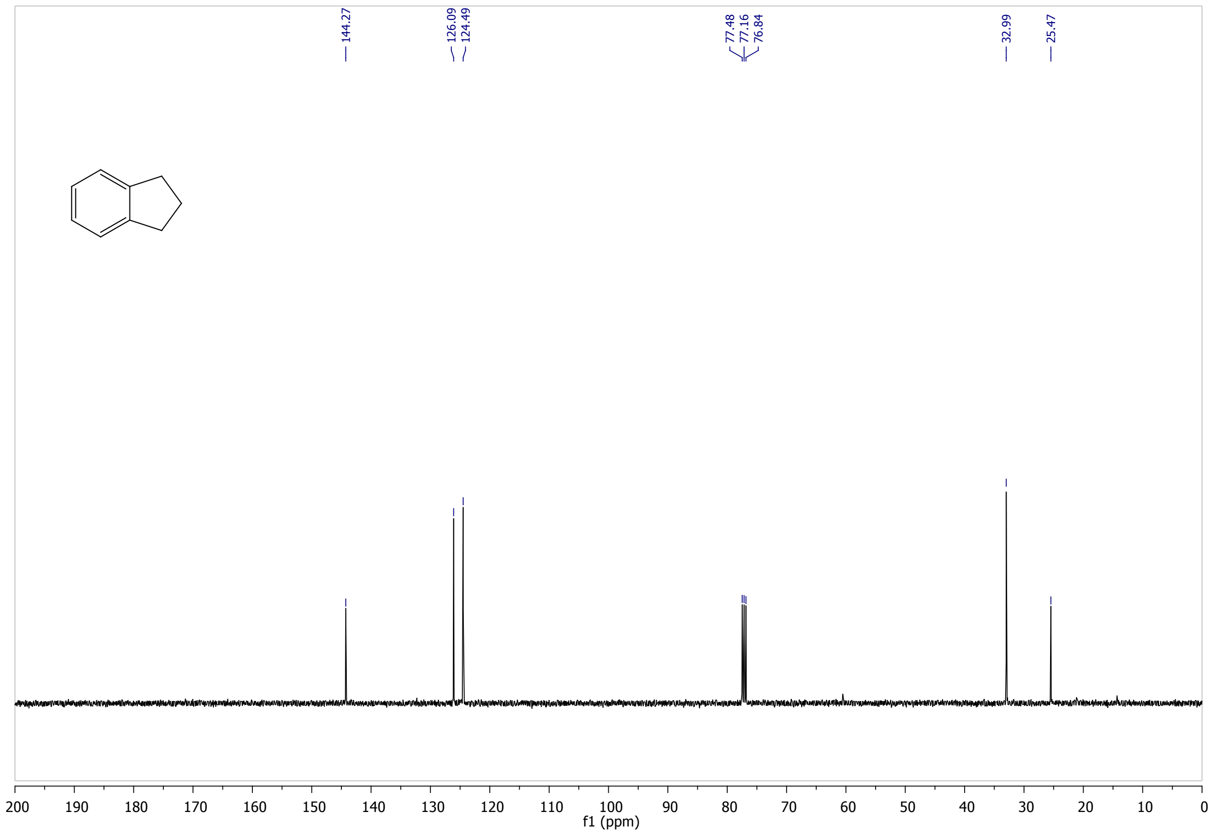
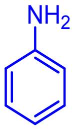
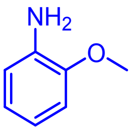


Figure S23. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectrum of 4f ($CDCl_3$).

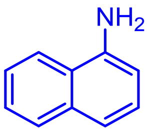
^{1}H-NMR and ^{13}C-NMR chemical shifts of the yielded products



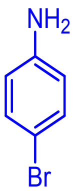
^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 7.17 (t, 2H, J= 8.0 Hz), 6.76 (t, 1H, J= 8.0 Hz), 6.68 (d, 2H, J= 8.0 Hz), 3.64 (s, 2H). **^{13}C-NMR($CDCl_3$, 100 MHz):** δ 146.49, 129.43, 118.70, 115.24.



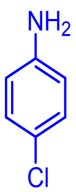
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.82-6.71 (m, 4H), 3.85 (s, 3H), 3.80 (s br, 2H). **^{13}C NMR (100 MHz)**: δ 147.46, 136.27, 121.21, 118.62, 115.16, 110.56, 55,56.



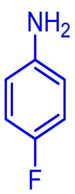
^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 7.70-7.67 (m, 2H), 7.37-7.31 (m, 2H), 7.22-7.16 (m, 2H), 6.66-6.64 (m, 1H), 4.00 (s, 2H). **^{13}C-NMR($CDCl_3$, 100 MHz):** δ 142.16, 134.48, 128.64, 126.43, 125.94, 124.94, 123.74, 120.89, 119.06, 109.78.



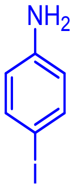
^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 7.22(d, 2H, J= 8 Hz), 6.55 (d, 2H, J= 8 Hz), 3.64 (s, 2H**). ^{13}C-NMR($CDCl_3$, 100 MHz):** δ 145.52, 132.10, 116.81, 110.27.



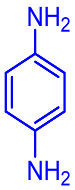
^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 7.27 (d, 2H, J= 8 Hz), 6.65 (d, 2H, J= 8 Hz), 3.58 (s, 2H). **^{13}C-NMR($CDCl_3$, 100 MHz):** δ 145.08, 129.23, 123.29, 116.36.



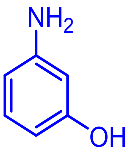
^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 6.67-6.65 (m, 2H), 6.56-6.54 (m, 2H), 3.36 (s, 2H). **^{13}C-NMR($CDCl_3$, 100 MHz):** δ 152.86,140.04, 116,49, 114.88.



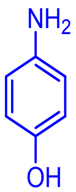
^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 7.40 (d, J= 8 Hz 2H), 6.46(d, J= 8 Hz 2H), 3.58 (s, 2H). **^{13}C-NMR($CDCl_3$, 100 MHz):** δ, 146.17, 138.02, 117.41, 79.49.



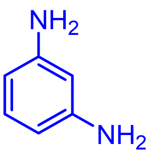
^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 6.57 (s, 4H), 3.34 (s, 4H) .**^{13}C-NMR($CDCl_3$, 100 MHz):** δ 138.71, 116.85.



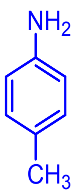
^{1}H NMR: (400 MHz, CD_3OD) δ (ppm): 4.44 (s, 2H), 6.39 (d, 1H, J=7.43 Hz), 6.52-6.64 (3H, m). **^{13}C NMR (CD_3OD 100 MHz)** δ 159.20, 149.29, 130.60, 108.80, 106.28, 103.75.



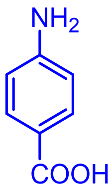
^{1}H NMR (400 MHz, CD_3OD): δ(ppm): 6.65 – 6.53 (m, 4H). **^{13}C-NMR(CD_3OD, 100 MHz):** δ 151.35, 140.16, 118.56, 116.70.



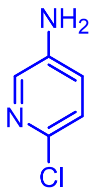
^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.94 (t, *J* = 7.8 Hz, 1 H), 6.12 (dd, *J* = 7.8, 2.2 Hz, 1 H), 6.04 (t, *J* = 7,8 Hz, 1 H), 3.56 (s, 4 H); **^{13}C NMR (100 MHz)** δ 147.64, 130.35, 106.12, 102.04



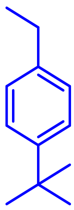
^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 7.0 (d, 2H, J= 8 Hz), 6.64 (d, 2H, J= 8 Hz), 3.52 (s, 2H), 2.26 (s, 3H). **^{13}C-NMR($CDCl_3$, 100 MHz):** δ 143.94, 129.89, 127.94, 115.40, 20.60.



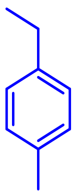
^{1}H NMR (400 MHz, DMSO) δ 11.97(bs, 1H), 7.61 (d, *J* = 8.5 Hz, 2H), 6.54 (d, *J* = 8.5 Hz, 2H), 3.38 (bs, 2H). **^{13}C NMR (100 MHz, DMSO):** δ 167.56, 153.20, 131.01, 116.89, 112.60.



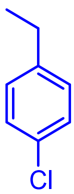
^{1}H NMR (400 MHz, DMSO) δ 8.78 (d, *J* = 3.4 Hz, 1H), 7.73 (dd, *J* = 9.5, 3.4 Hz, 1H), 5.77 (d, *J* = 9.5 Hz, 1H). **^{13}C NMR (100 MHz, DMSO):** δ 144,78, 136,35 135.40, 124.05, 120.63.



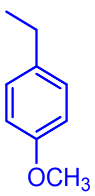
^{1}H NMR (400 MHz, CDCl3) *δ* 7.31 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.31 (s, 9H), 1.25 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR(100 MHz, CDCl3) *δ*** 148.5, 141.2, 127.6, 125.3, 34.4, 31.5, 28.4, 15.6;



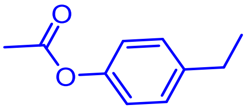
^{1}H NMR (400 MHz, CDCl3,) *δ* 7.13 (s, 4H), 2.61 (q, *J* =7.6 Hz, 2H), 2.26 (s, 3H), 1.28 (t, *J* = 7.6 Hz, 3H).**^{13}C-NMR ($CDCl_3$, 100 MHz)** δ 141.3, 135.1, 129.1, 127.8,28,5,21.1.,15.9;

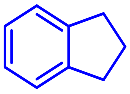


^{1}HNMR (400 MHz, CDCl3) *δ* 7.20 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 2.56 (q, *J* = 7.6 Hz, 2H), 1.17 (t, *J* = 7.6 Hz, 3H); **13C NMR (100 MHz, CDCl3) *δ*** 142.7, 131.4, 129.3, 128.5, 28.4, 15.7;

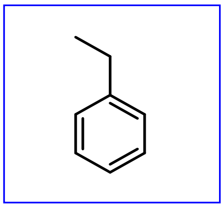


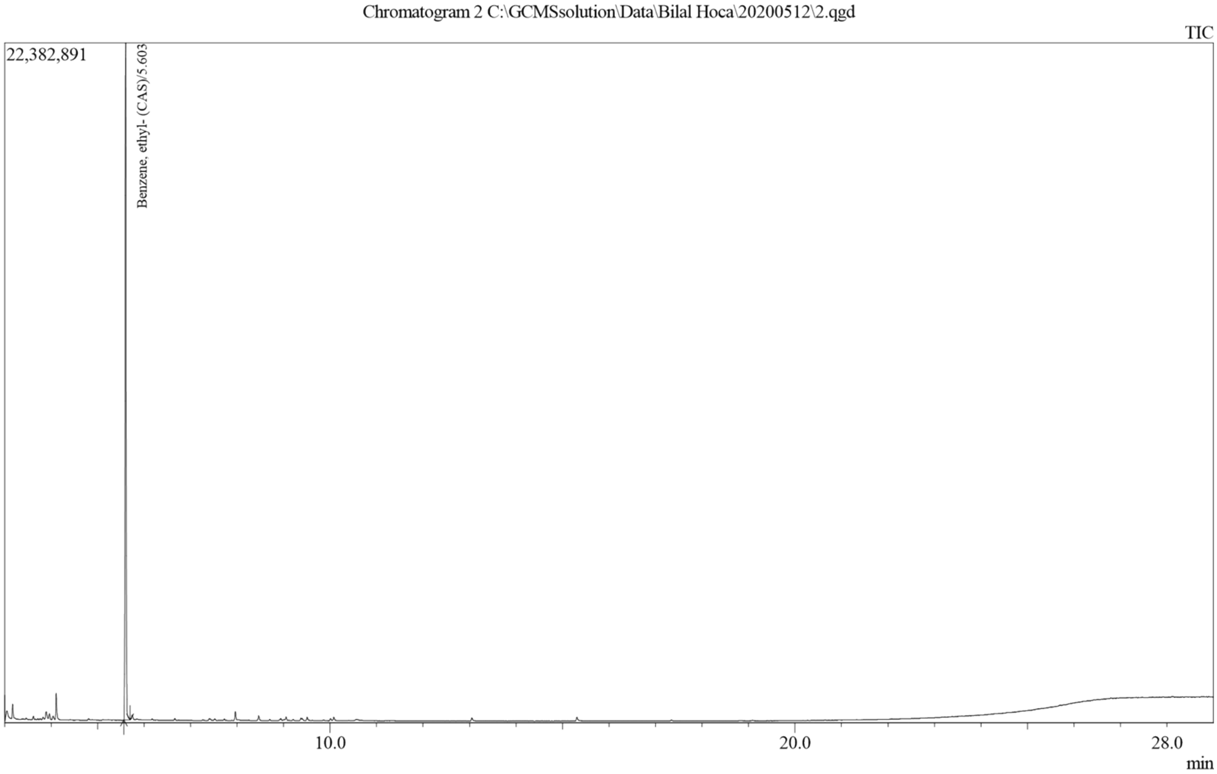
^{1}H NMR (400 MHz, CDCl3) *δ* 7.13 (d, *J* = 8.6 Hz, 2H),6.87(d, *J* = 8.6 Hz, 2H), 3.81 (s, 3H), 2.61 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR(100 MHz, CDCl3) *δ*** 157.7, 136.5, 128.8, 113.8, 55.4, 28.1, 16.0

 **[1]H NMR (400 MHz, CDCl3) δ** 7.04 (d, J = 8.4 Hz, 2 H), 6.79 (d, J = 8.4 Hz, 2 H), 2.58 (q, J = 7.6 Hz, 2 H), 2.04 (s, 3 H), 1.23 (t, J = 7.6 Hz, 3 H). **[13]C NMR (100 MHz, CDCl3) δ** 174.4, 153.8, 136,3 129.0, 115.3, 28.1, 22.6, 16.0

 **[1]H NMR (400 MHz, CDCl3,) *δ*** 7.24-7.21 (m, 2H), 7.13-7.11 (m, 2H), 2.91(t, *J* = 7.5 Hz, 4H), 2.10-2.02 (m, 2H); **[13]C NMR (100 MHz, CDCl3) *δ*** 144.2, 126.1, 124.5, 32.9,25.6;

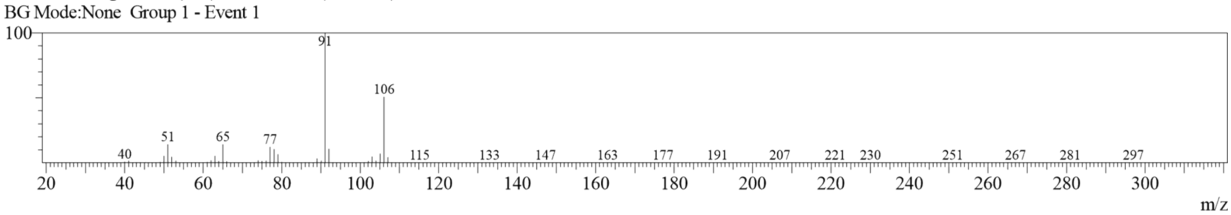
Mass spectra of the products





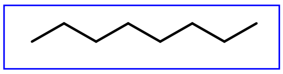
Peak# R.Time Area Area% Height Name
1 5.603 35333450 100.00 22282726 Benzene, ethyl- (CAS)
35333450 100.00 22282726

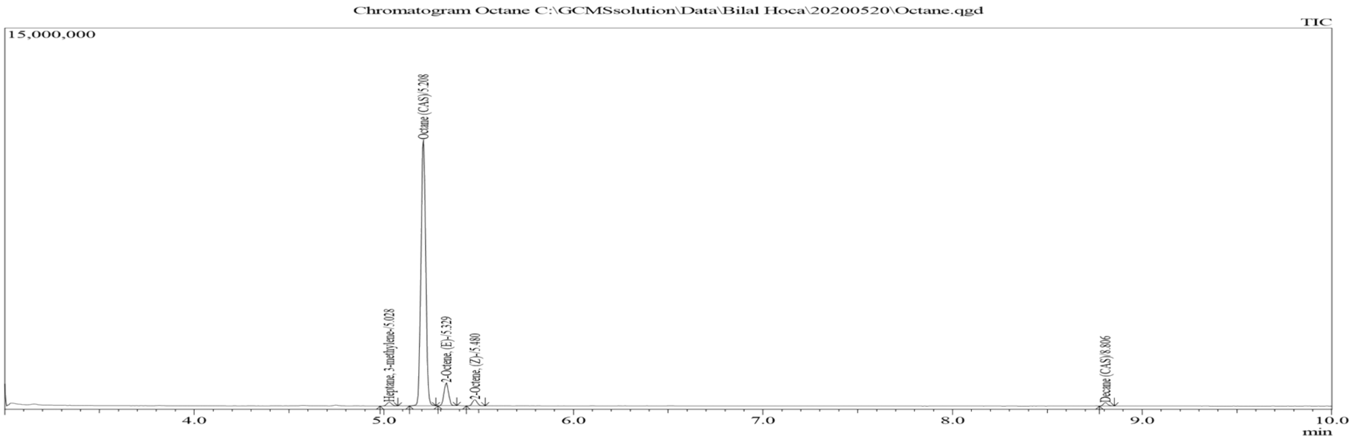
RawMode:Single 5.605(522) BasePeak:91(8195006)
BG Mode:None Group 1 - Event 1



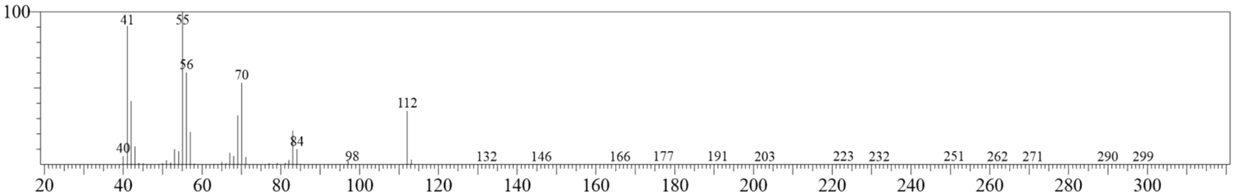
MS-C_8H_{10} (106) m/z (%): 106 (M^+, 52), 91 (100), 77 (9), 65 (17), 51 (15).

Figure S24. GC-MS spectrum of 4g



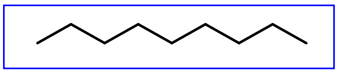


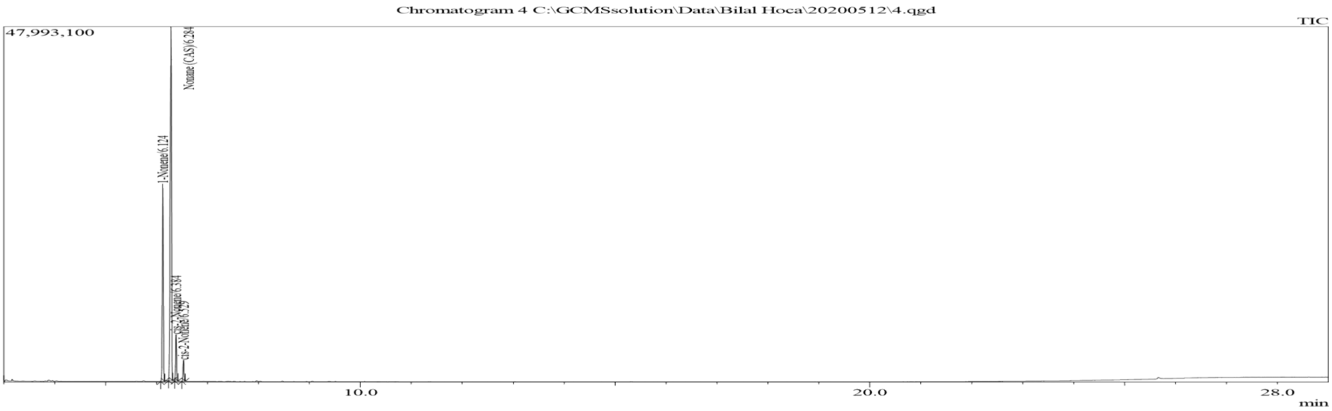
Peak#	R.Time	Area	Area%	Height	Name
1	5.028	275792	1.33	147415	Heptane, 3-methylene-
2	5.208	18262631	88.20	10542756	Octane (CAS)
3	5.329	1530337	7.39	904485	2-Octene, (E)-
4	5.480	426902	2.06	246527	2-Octene, (Z)-
5	8.806	210113	1.01	125932	Decane (CAS)
		20705775	100.00	11967115	



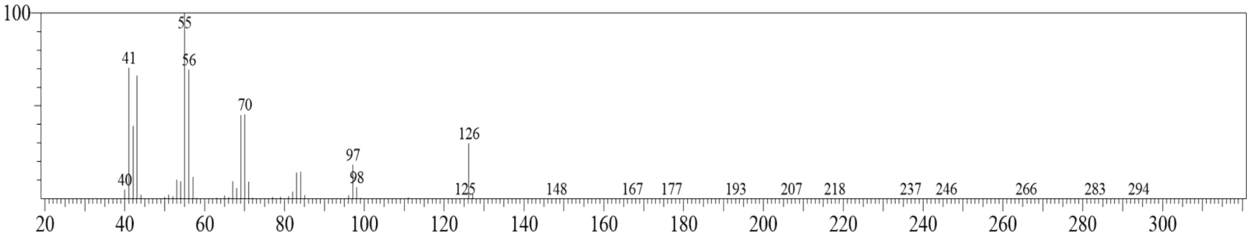
MS-C_8H_{18} (112) m/z (%): 112 (M^+, 55), 70 (50), 56 (52), 55 (100), 41 (80).

Figure S25. GC-MS spectrum of 4h



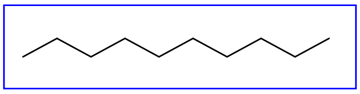


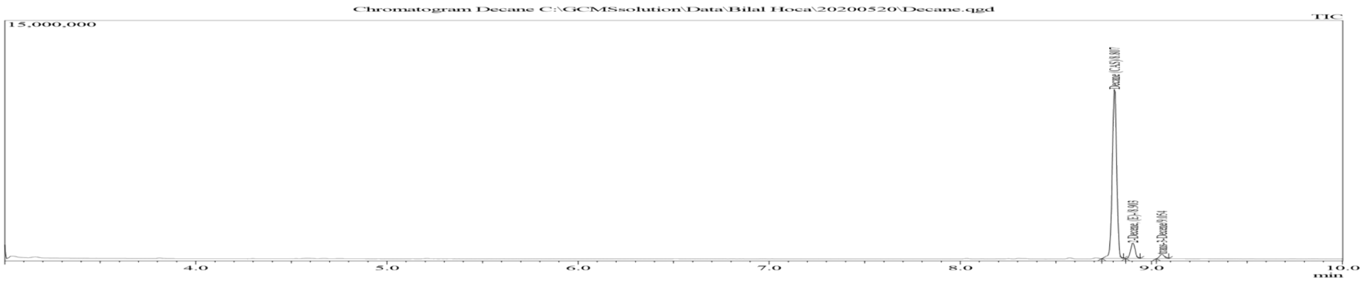
Peak# R.Time Area Area% Height Name
1 6.124 39384838 28.22 26685254 1-Nonene
2 6.284 87493229 62.70 47774231 Nonane (CAS)
3 6.384 8649882 6.20 6304185 cis-2-Nonene
4 6.529 4020147 2.88 2855657 cis-2-Nonene
139548096 100.00 83619327



MS-C_9H_{20} (126) m/z (%): 126 (M^+, 40), 70 (50), 56 (70), 55 (100), 41 (70).

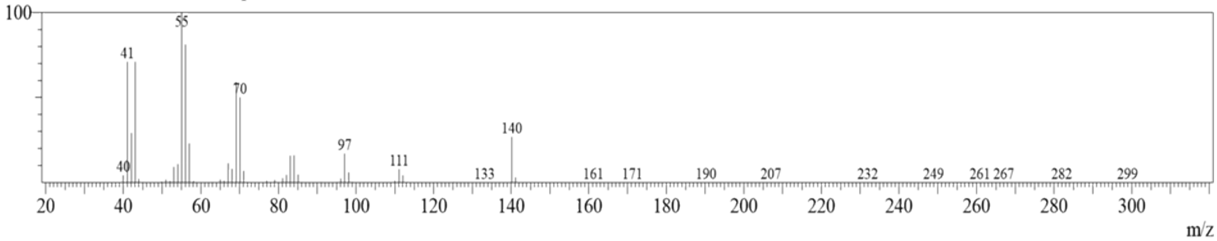
Figure S26. GC-MS spectrum of 4ı





Peak# R.Time Area Area% Height Name
1 8.807 17430187 89.52 10615332 Decane (CAS)
2 8.903 1600718 8.22 973738 2-Decene, (E)-
3 9.054 440188 2.26 270790 trans-3-Decene
19471093 100.00 11859860

RawMode:Averaged 8.900-8.910(1181-1183) BasePeak:55(137218)
BG Mode:Calc. from Peak Group 1 - Event 1

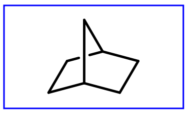


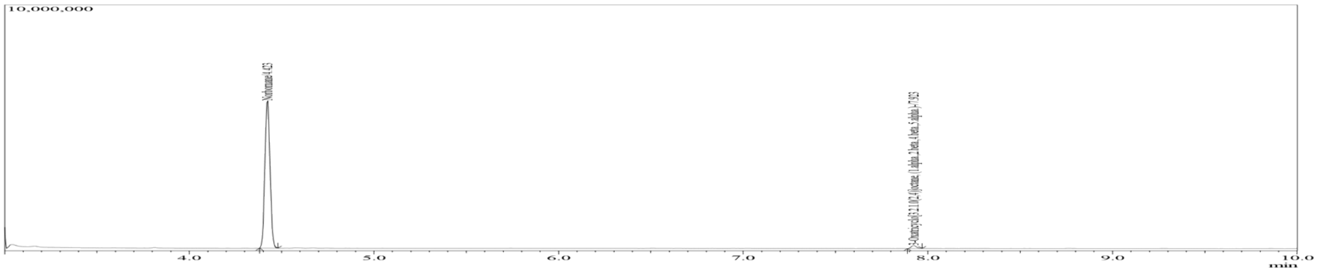
Line#:3 R.Time:9.055(Scan#:1212)

MS-$C_{10}H_{22}$ (140) m/z (%): 140 (M^+, 40), 97 (20), 70 (50), 55 (100), 41 (70).

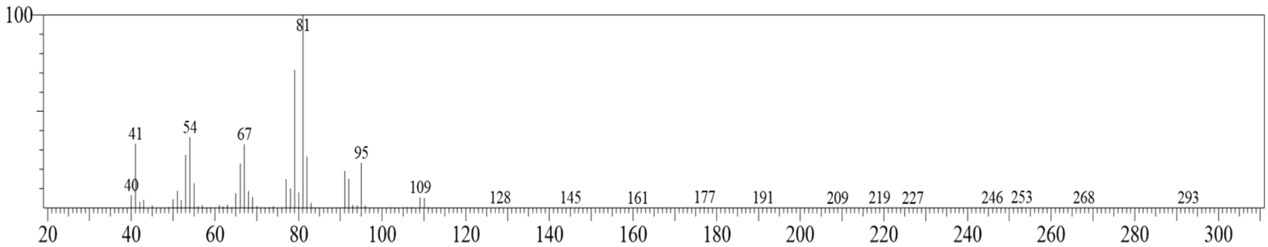
Figure S27. GC-MS spectrum of 4i

.





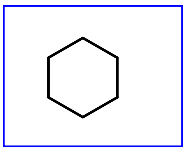
Peak# R.Time Area Area% Height Name
1 4.423 11689971 97.97 6031987 Norbornane
2 7.923 242752 2.03 122037 3-Oxatricyclo[3.2.1.0(2,4)]octane, (1.alpha.,2.beta.,4.beta.,5.alpha.)-
11932723 100.00 6154024

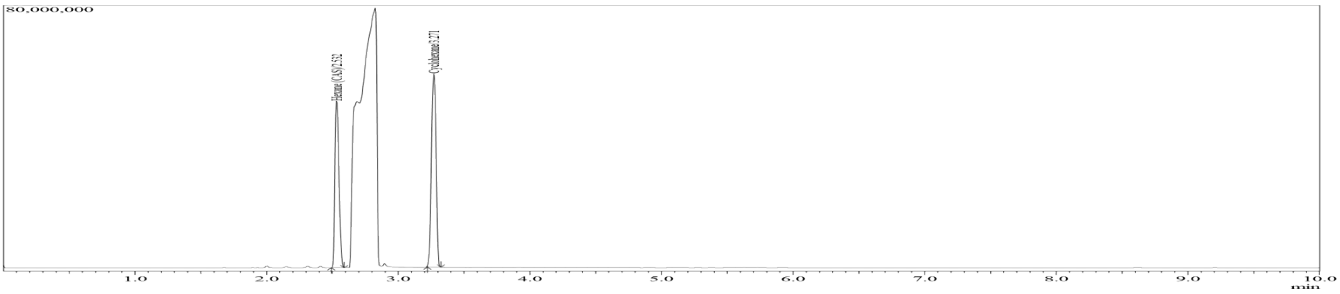


MS-C_7H_{12} (95) m/z (%): 95 (M^+, 20), 81 (100), 67 (40), 54(40), 41 (30).

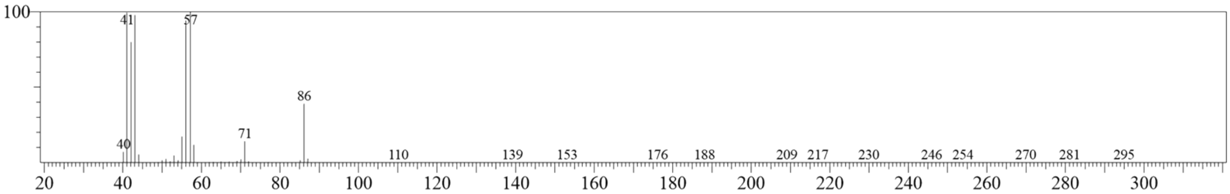
Figure S28. GC-MS spectrum of 4k

.



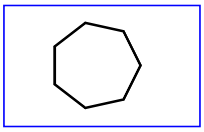


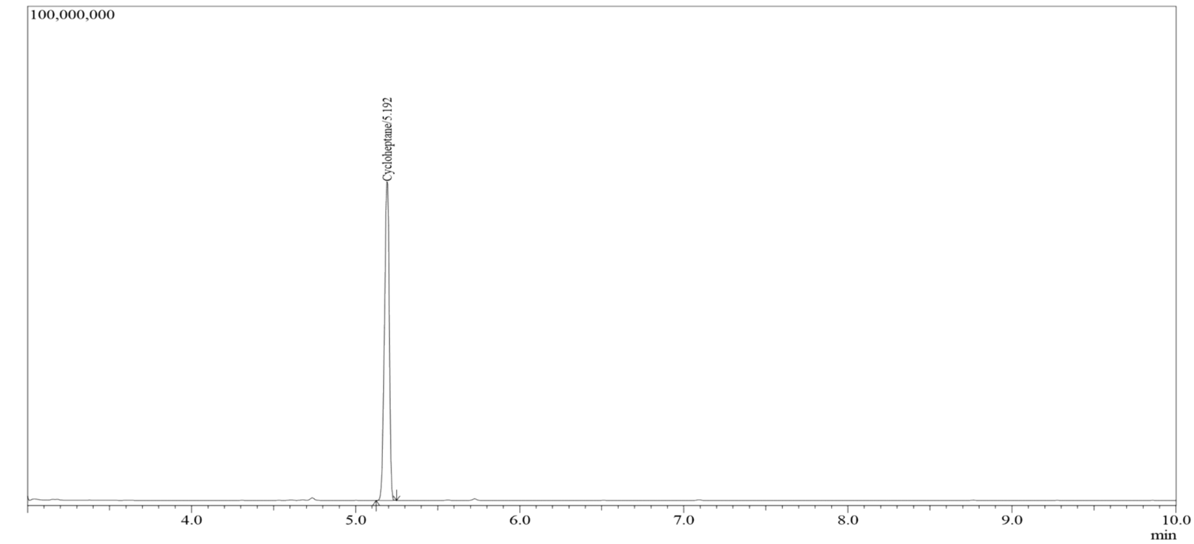
Peak#	R.Time	Area	Area%	Height	Name
1	2.532	106756336	43.06	50821337	Hexane (CAS)
2	3.271	141186798	56.94	58923378	Cyclohexane
		247943134	100.00	109744715	



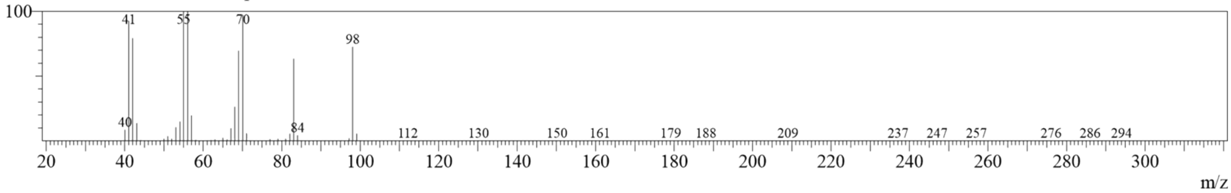
MS-C_6H_{12} (86) m/z (%): 86 (M^+, 42), 71 (10), 57 (100), 41 (100), 40(5).

Figure S29. GC-MS spectrum of 4l



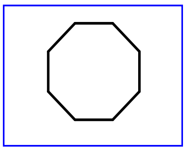


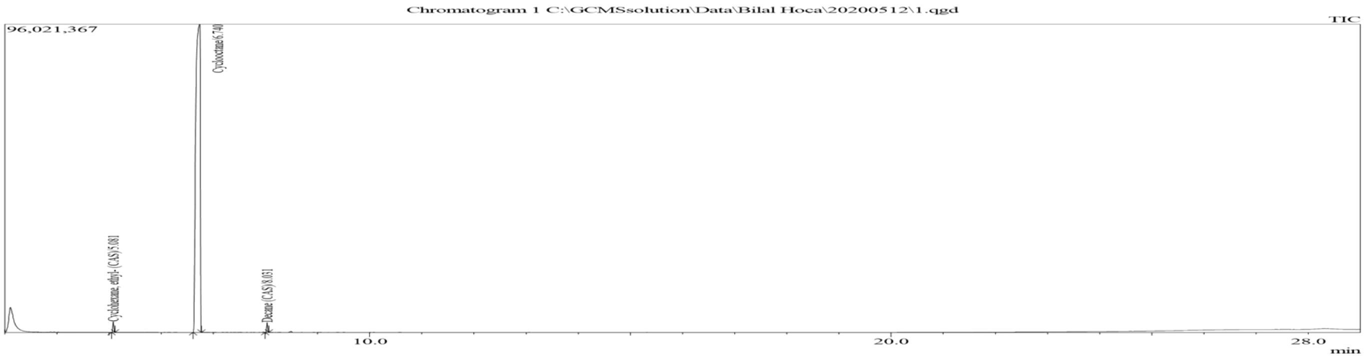
Peak# R.Time Area Area% Height Name
1 5.192 132753785 100.00 64480842 Cycloheptane
132753785 100.00 64480842
RawMode:Averaged 5.185-5.195(438-440) BasePeak:56(7625323)
BG Mode:Calc. from Peak Group 1 - Event 1



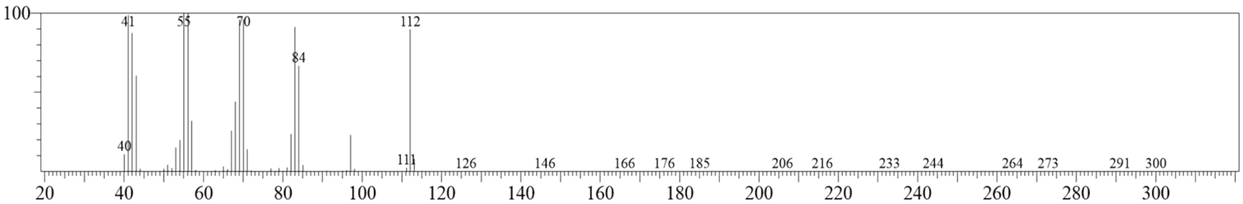
MS-C_7H_{14} (98) m/z (%): 98 (M^+, 70), 84(60), 70(90), 55 (100), 41 (80).

Figure S30. GC-MS spectrum of 4m





Peak# R.Time Area Area% Height Name
1 5.081 4714142 0.82 3278780 Cyclohexane, ethyl- (CAS)
2 6.740 566732063 98.45 95935958 Cyclooctane
3 8.031 4207400 0.73 3006170 Decane (CAS)
575653605 100.00 102220908



MS-C_8H_{16} (112) m/z (%): 112 (M^+, 85), 84(60), 70 (88), 55 (100), 41(98).

Figure S31. GC-MS spectrum of 4n