

Supplementary Material

(2-(Phenylseleninyl)ethene-1,1-diyl)dibenzene derivatives synthesis via a copper-catalyzed tandem reaction of C–Se bond coupling/selenoxidation

Zhuoran Chen,^a Qi Hu,^b Jiahao Hu,^b and Runsheng Xu^{*a,b}

a College of Food and Health, Zhejiang A&F University, Hangzhou, 311300, China

b College of Life and Health (Department of Physical Education), Huzhou College,
Huzhou 313000, China

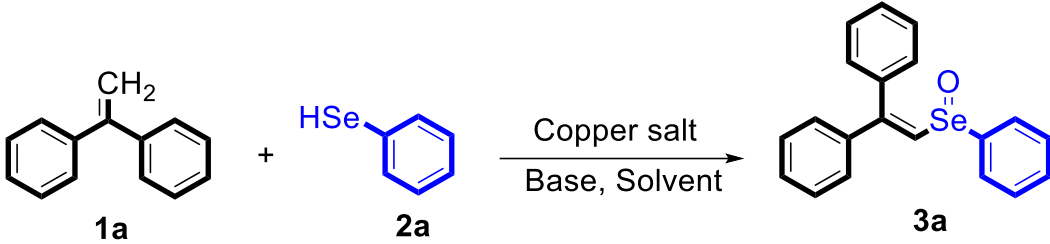
Email: xurunsheng2044@sina.com

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Optimization of the Reaction Conditions

The model reaction of ethene-1,1-diyldibenzene **1a** and benzeneselenol **2a** to study the reaction conditions, including the optimization of catalysts, bases, and solvents. As shown in Table 1, at the outset, copper salts were used as the catalyst (entries 1–6), and no desired product was gained when the reaction was conducted in the presence of CuO as the catalyst in DMF (entry 1). These results show that using the proper solvent is critical for this reaction as, when the reactions were conducted in an apolar solvent, the DMSO product was detected in a moderate yield. CuBr₂ was proven to be the most efficient catalyst species in this reaction (entry 5). Gratifyingly, the yield of product **3a** was obtained at 62% when the catalyst was changed to Cu(OAc)₂ (entry 6). By screening different bases for the reaction, Cs₂CO₃ was demonstrated to be a more suitable base than others such as NaOH, Na₂CO₃, Na₂SO₄, NaOEt, K₂CO₃, and K₂PO₃ (entries 6–12). A reduced yield was obtained in the reactions operated at 100 °C (62% yield, entry 15) and 120 °C (67% yield, entry 16). We also found that the yields of the product decreased when the amount of copper catalyst used was higher or lower than 10 mol% equivalent (entries 17 and 18). Finally, we determined that the optimal reaction conditions were as follows: Cu(OAc)₂ used as the catalyst, Cs₂CO₃ used as the base, a ratio of **1a:2a** of 1:1.5, N₂ atmosphere, 110 °C, and preparation for 24 h.

Table 1. Optimization of the reaction conditions ^a


Entry	Copper Salt	Base	Solvent	1a:2a	Yield (%) ^b
1	CuO	Na ₂ CO ₃	DMF	1:1	0
2	CuSO ₄	Na ₂ CO ₃	DMSO	1:1	21
3	CuI	Na ₂ CO ₃	DMSO	1:1	28
4	CuCl ₂	Na ₂ CO ₃	DMSO	1:1	37
5	CuBr ₂	Na ₂ CO ₃	DMSO	1:1	49
6	Cu(OAc) ₂	Na ₂ CO ₃	DMSO	1:1	62
7	Cu(OAc) ₂	Cs ₂ CO ₃	DMSO	1:1	64
8	Cu(OAc) ₂	NaOH	DMSO	1:1	45
9	Cu(OAc) ₂	Na ₂ SO ₄	DMSO	1:1	39
10	Cu(OAc) ₂	NaOEt	DMSO	1:1	67
11	Cu(OAc) ₂	K ₂ CO ₃	DMSO	1:1	54
12	Cu(OAc) ₂	K ₂ PO ₃	DMSO	1:1	57
13	Cu(OAc) ₂	Cs ₂ CO ₃	DMSO	1:1	5
14	Cu(OAc) ₂	Cs ₂ CO ₃	DMSO	1:1.5	73
15	Cu(OAc) ₂	Cs ₂ CO ₃	DMSO	1:1.5	62 ^c
16	Cu(OAc) ₂	Cs ₂ CO ₃	DMSO	1:1.5	67 ^d
17	Cu(OAc) ₂	Cs ₂ CO ₃	DMSO	1:1.5	73 ^e
18	Cu(OAc) ₂	Cs ₂ CO ₃	DMSO	1:1.5	59 ^f

^a Unless otherwise noted, reactions conditions were **1a** (10 mmol), **2a** (10 mmol), copper catalyst (10 mol%), base (2 equivalent, under N₂ atmosphere), solvent (10 mL), and 110 °C for 24 h.

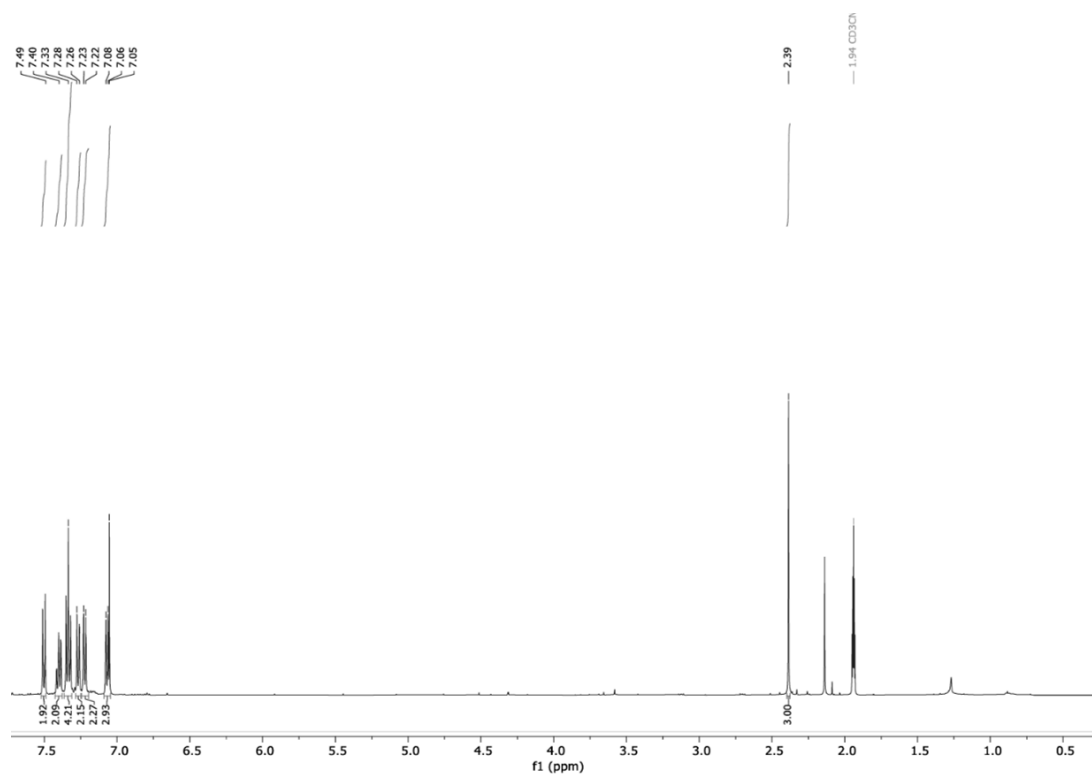
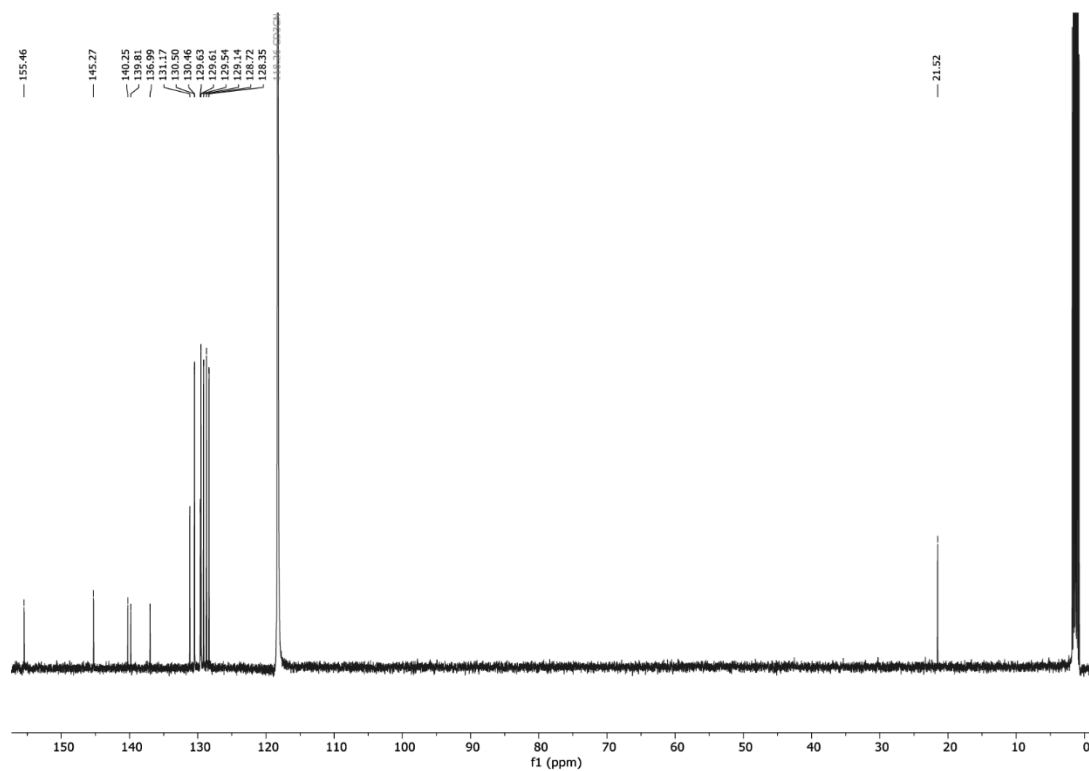
^b Isolated yield.

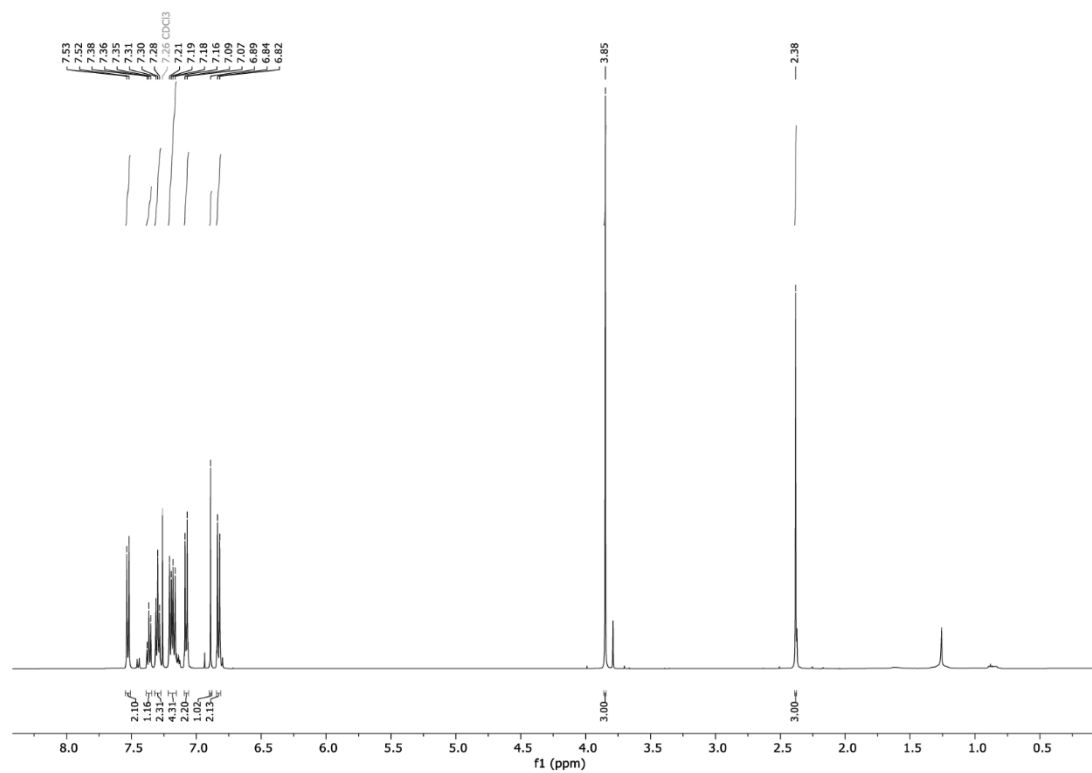
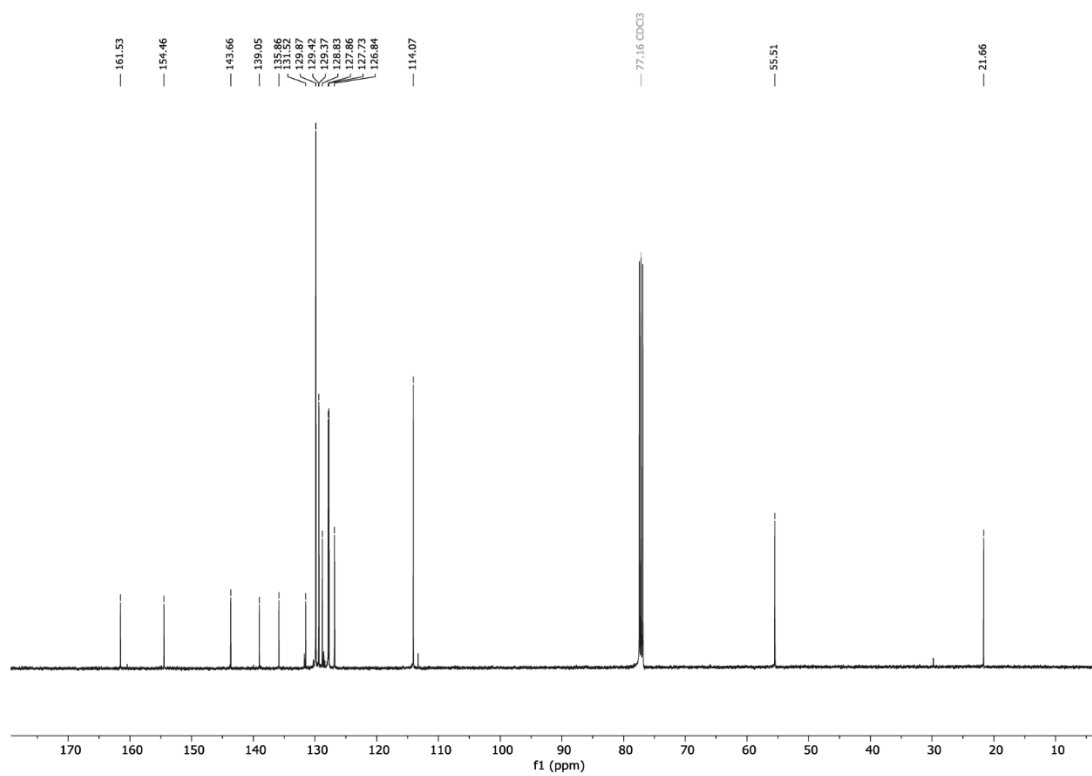
^c 100 °C.

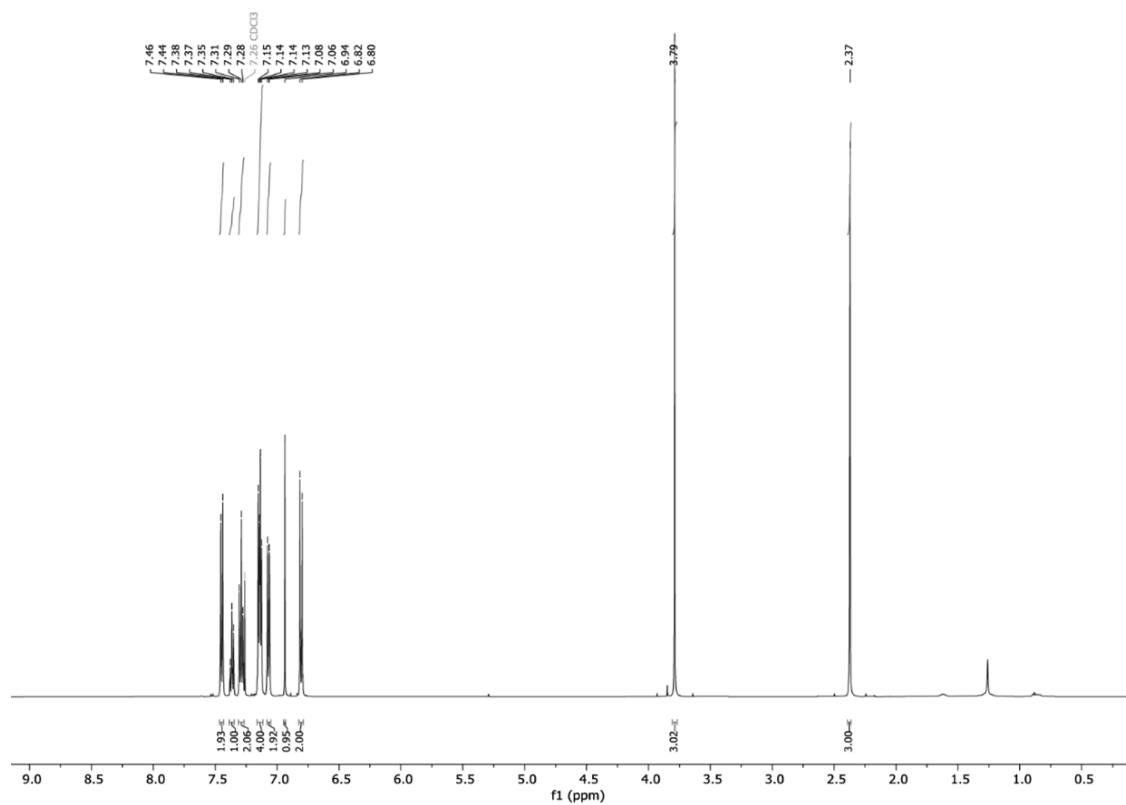
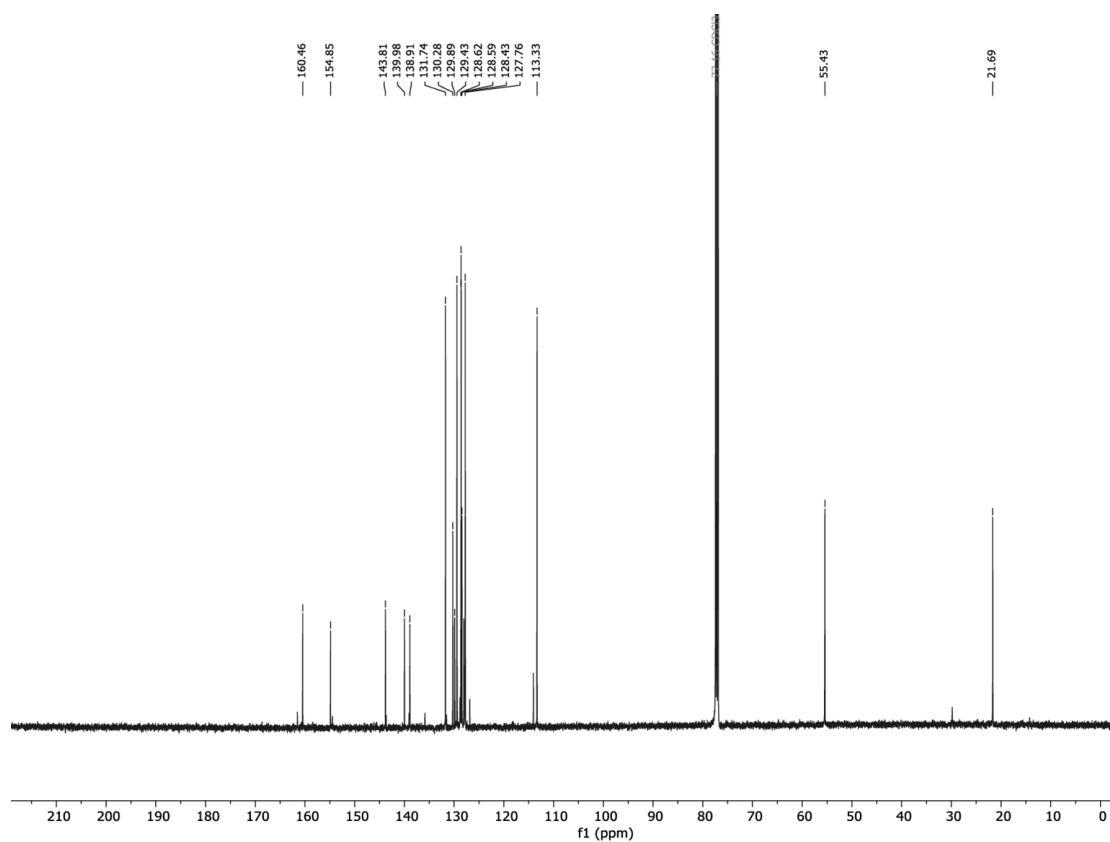
^d 120 °C.

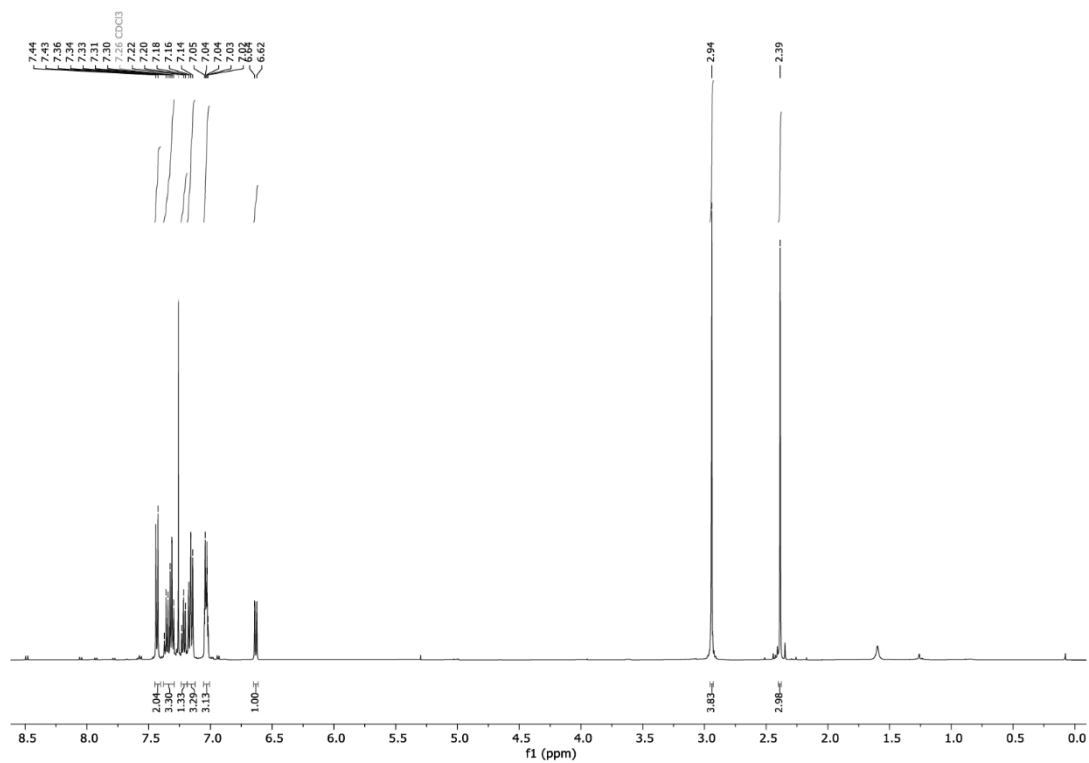
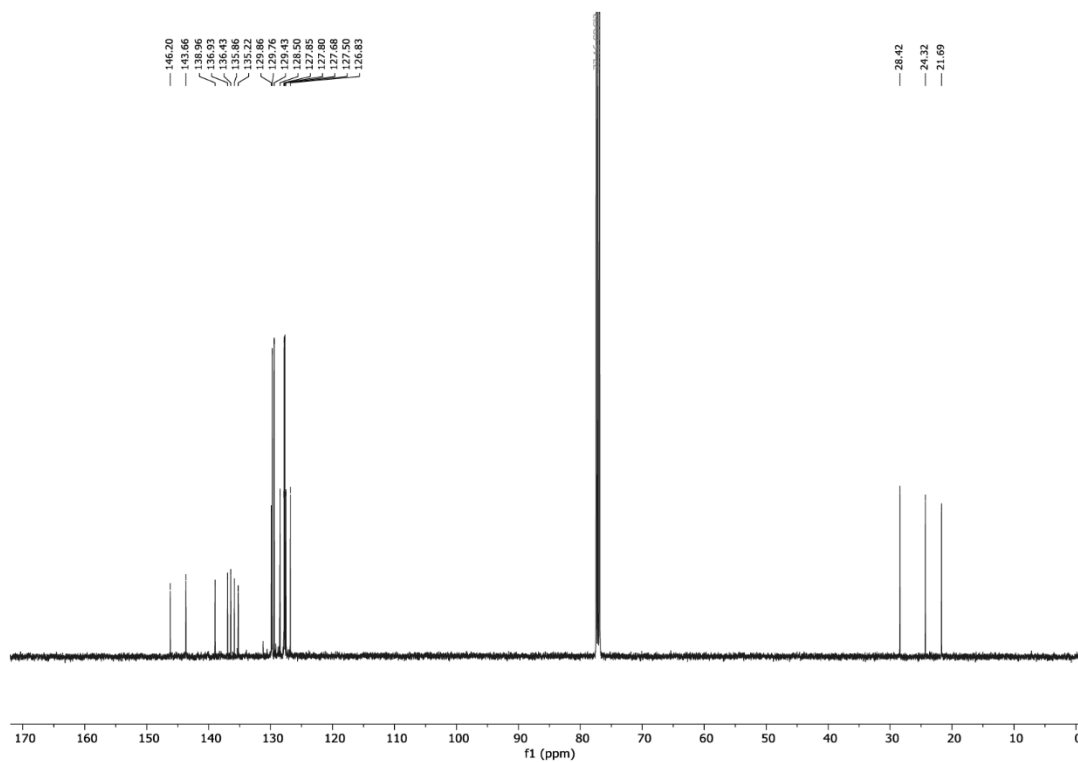
^e Cu(OAc)₂ (15 mol%).

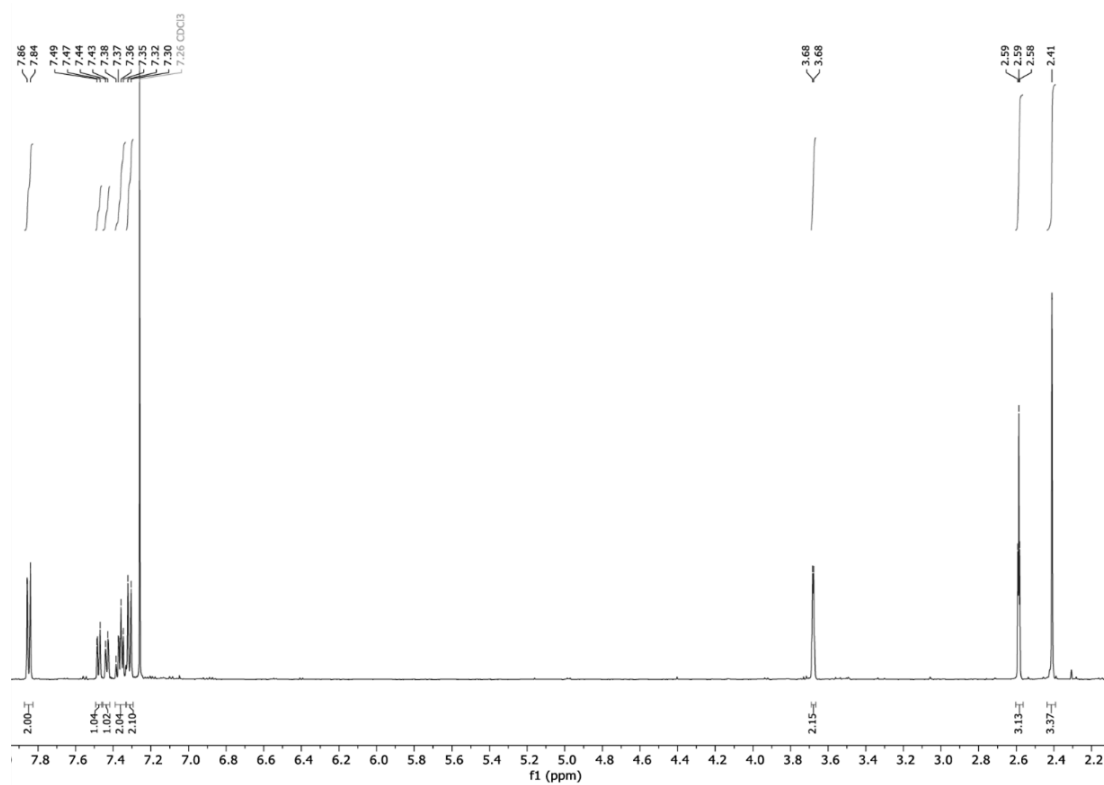
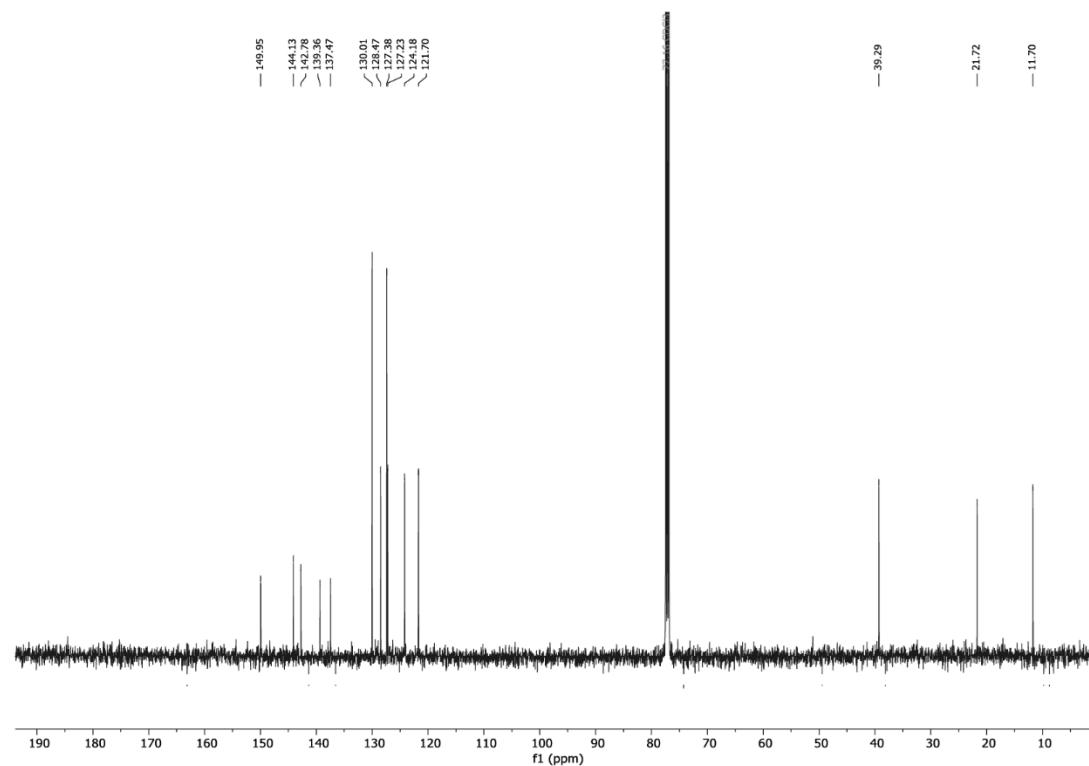
^f Cu(OAc)₂ (5 mol%).

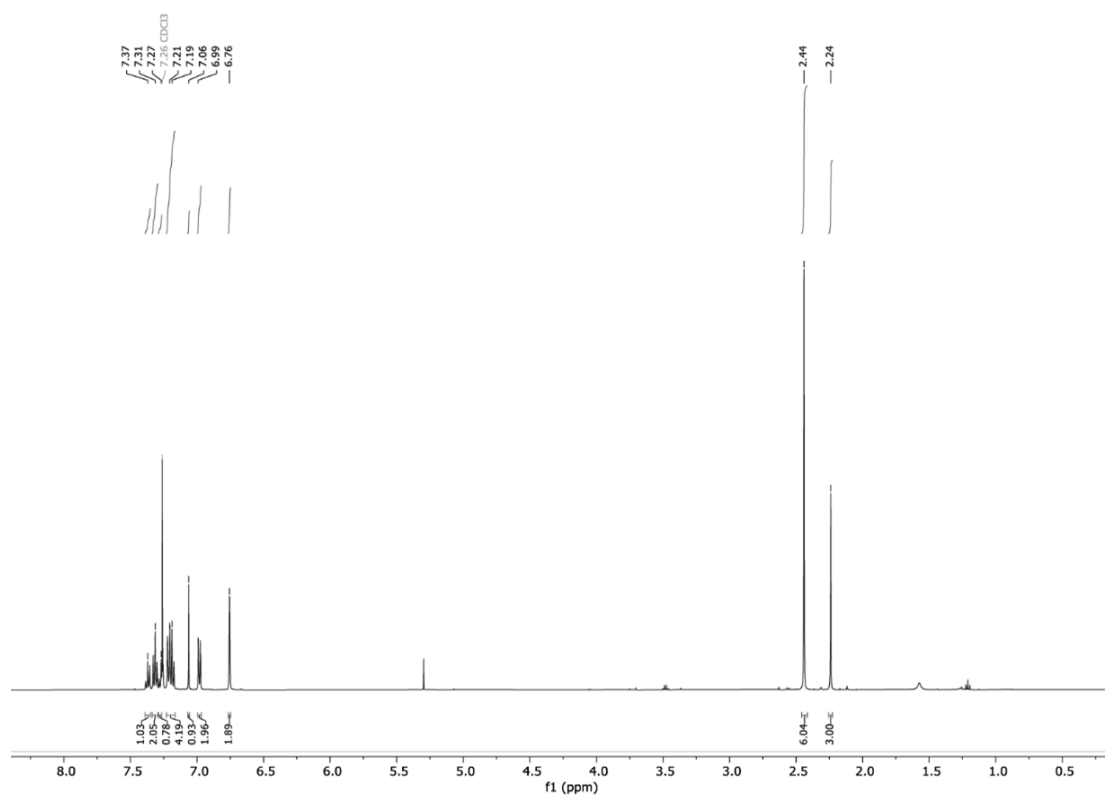
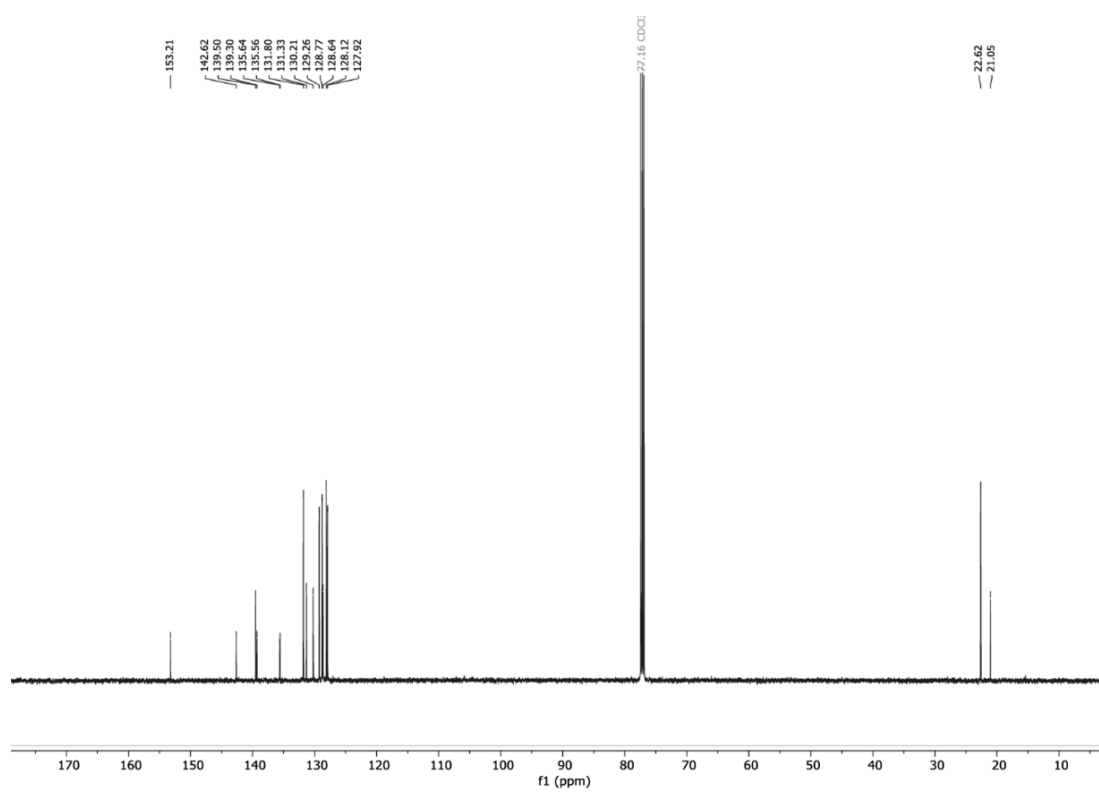
Figure 3. 3b ¹H NMR.Figure 4. 3b ¹³C NMR.

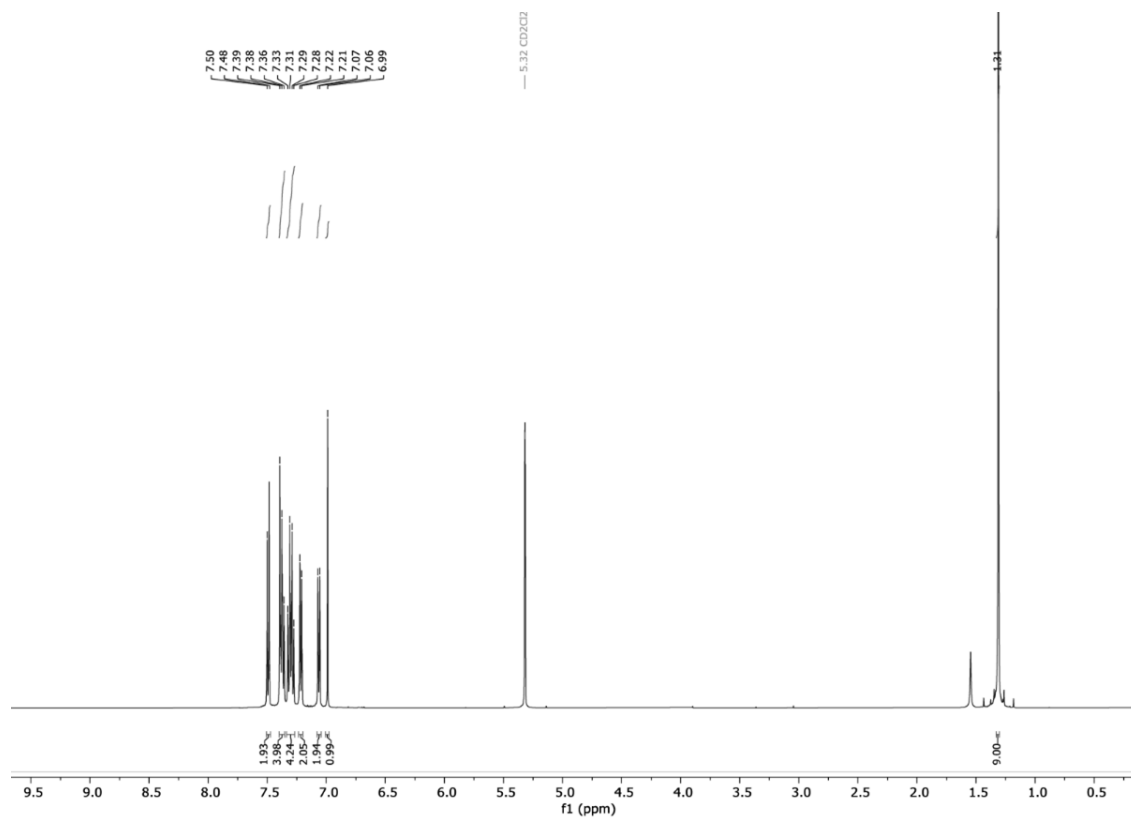
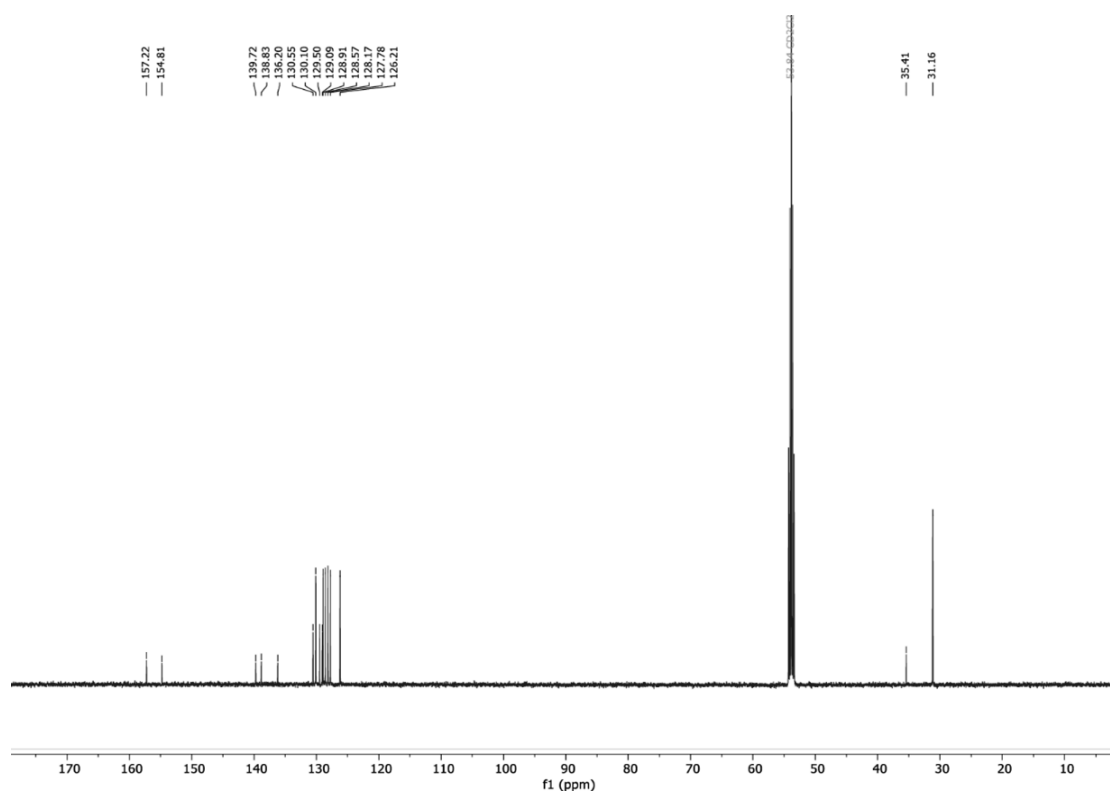
Figure 5. ^1H NMR.Figure 6. ^{13}C NMR.

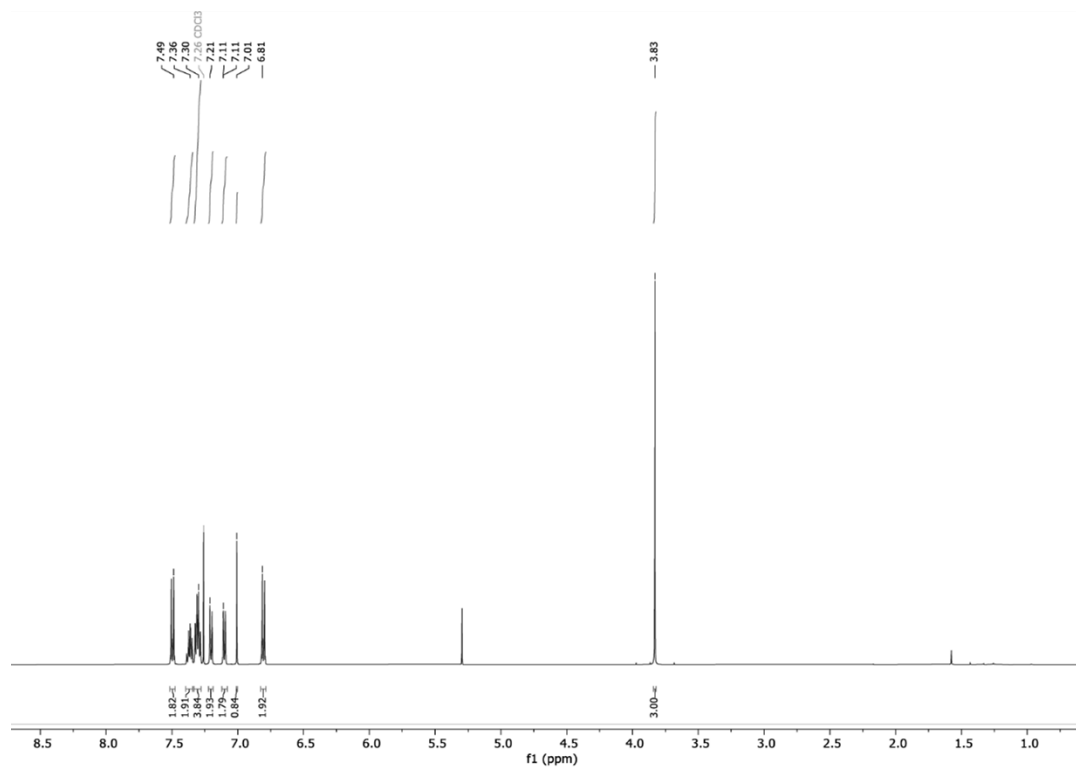
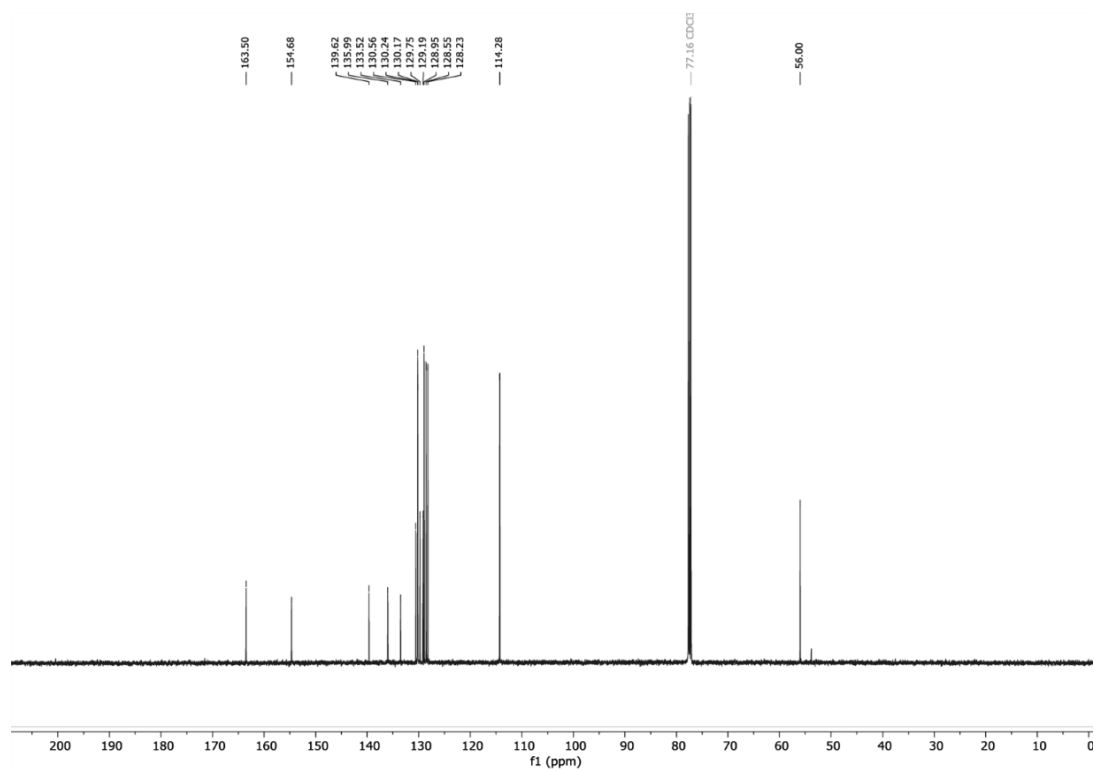
Figure 7. 3d ¹H NMR.Figure 8. 3d ¹³C NMR.

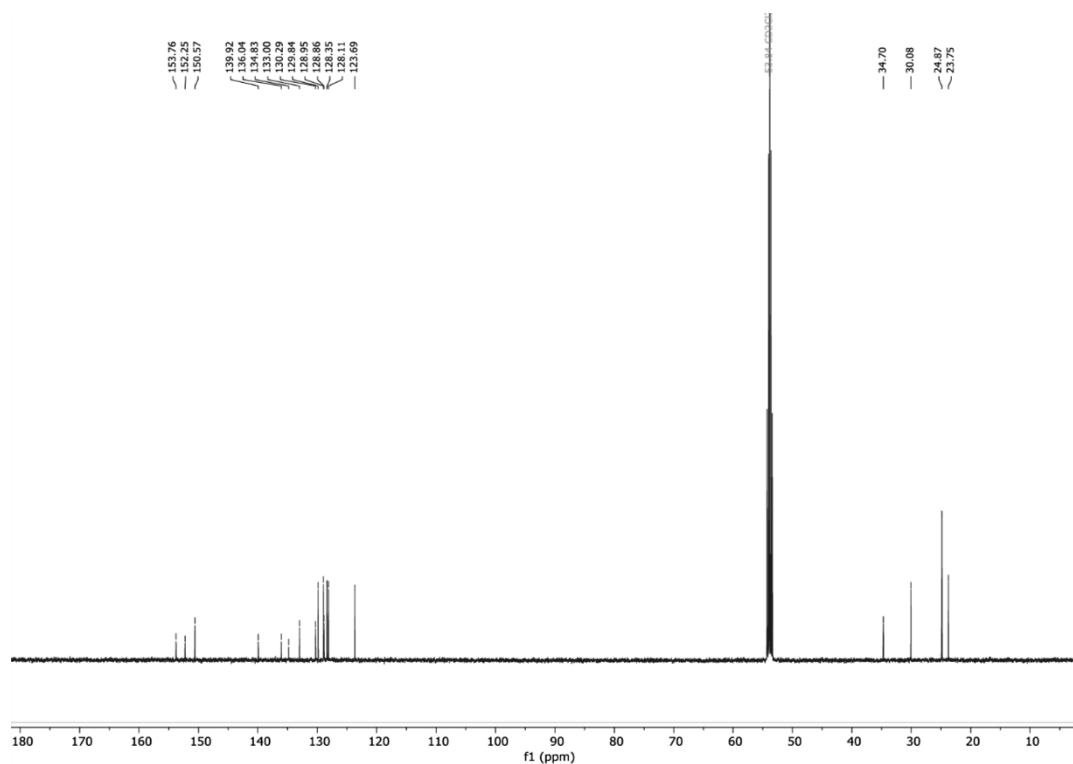
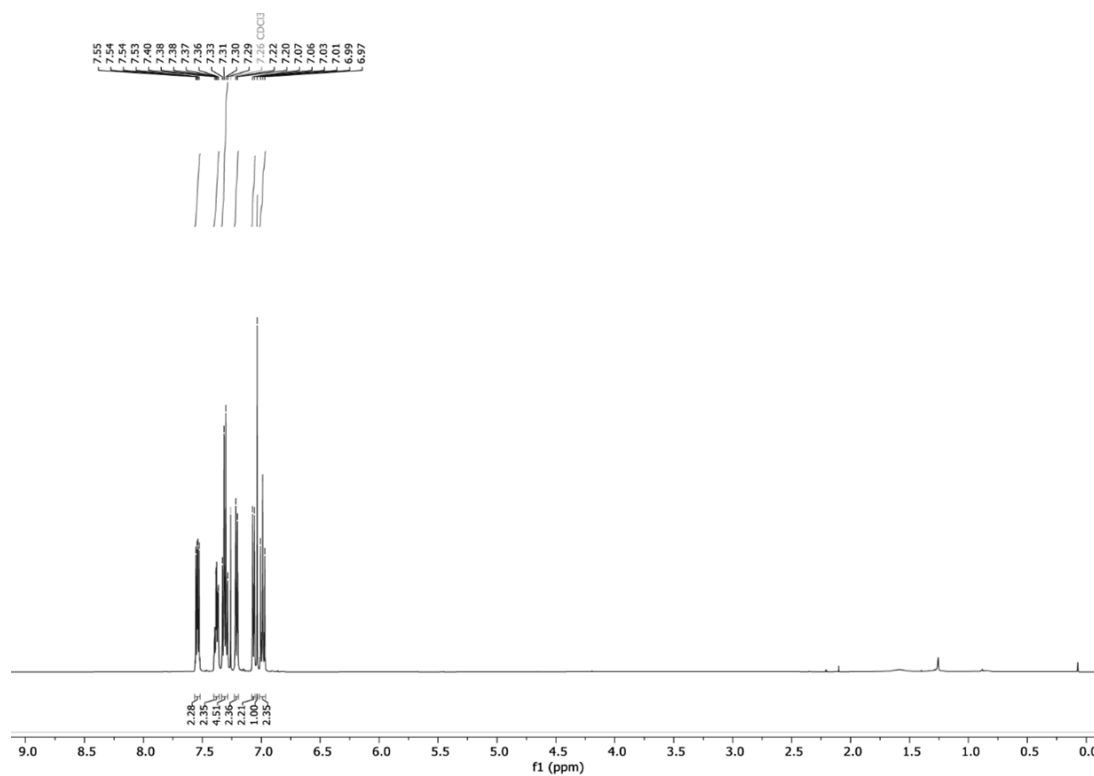
Figure 9. 3e ¹H NMR.Figure 10. 3e ¹³C NMR.

Figure 11. 3f ¹H NMR.Figure 12. 3f ¹³C NMR.

Figure 13. $3g$ ^1H NMR.Figure 14. $3g$ ^{13}C NMR.

Figure 15. **3h** ¹H NMR.Figure 16. **3h** ¹³C NMR.

Figure 17. 3i ^1H NMR.Figure 18. 3i ^{13}C NMR.

Figure 21. 3j ¹³C NMR.Figure 22. 3k ¹H NMR.

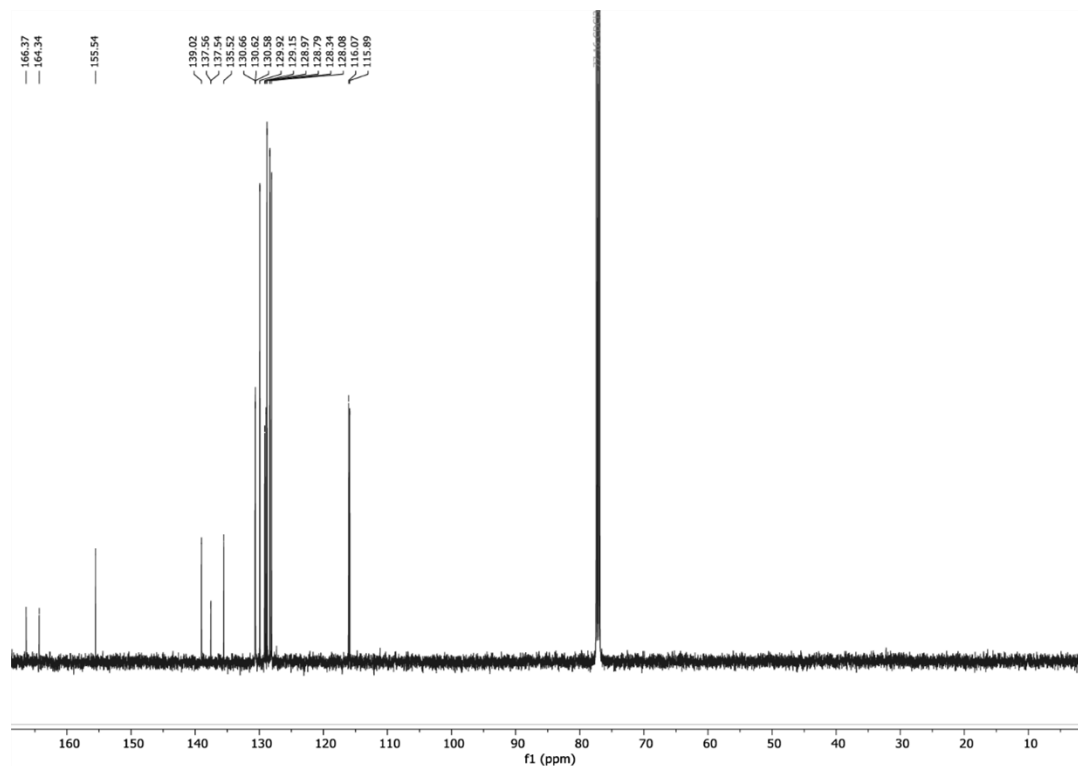


Figure 23. **3k** ^{13}C NMR.

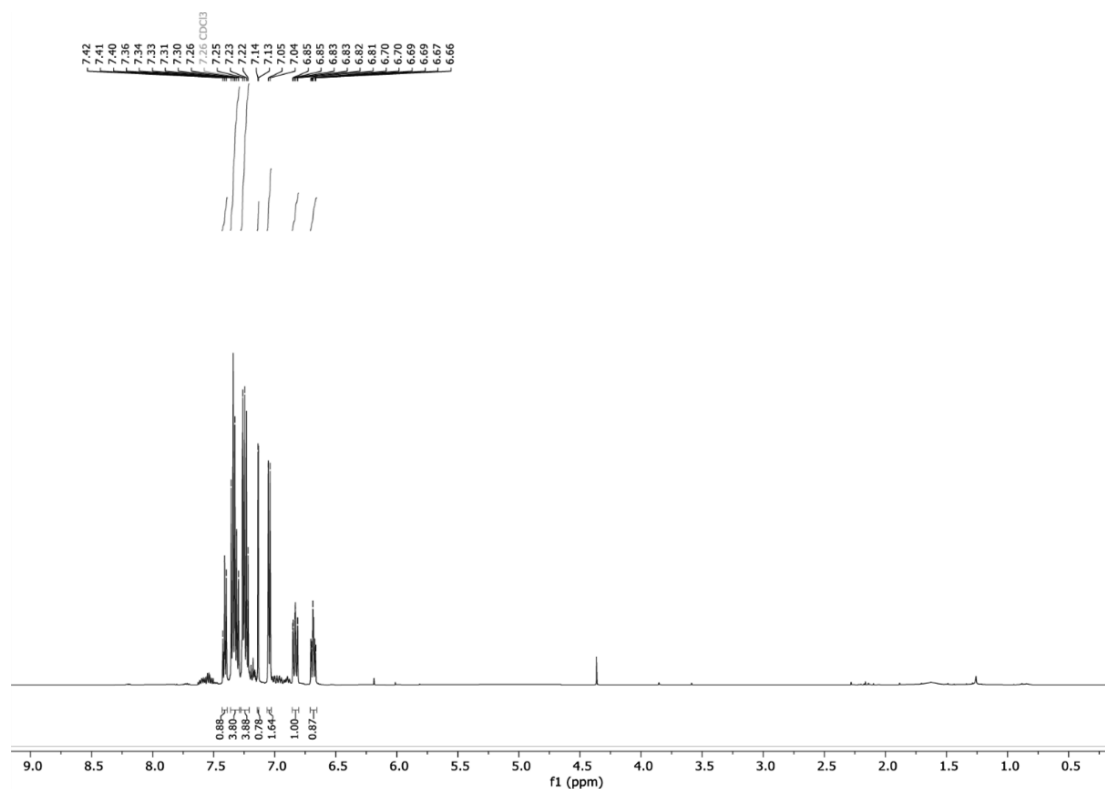
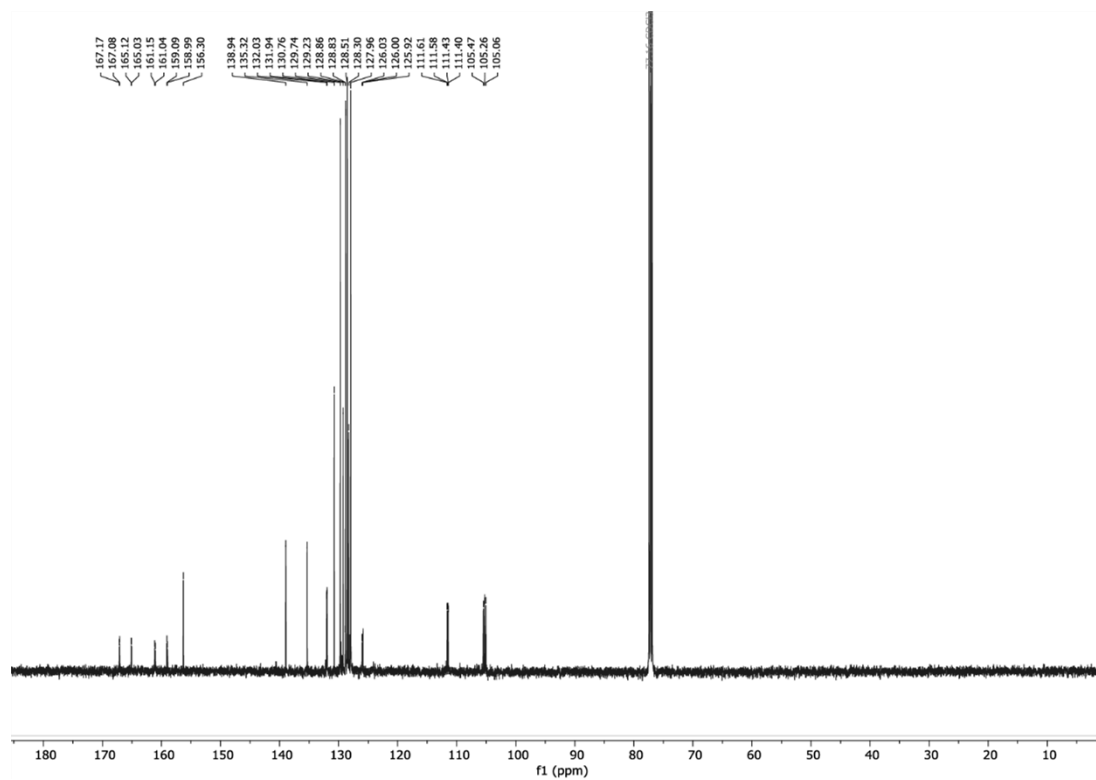
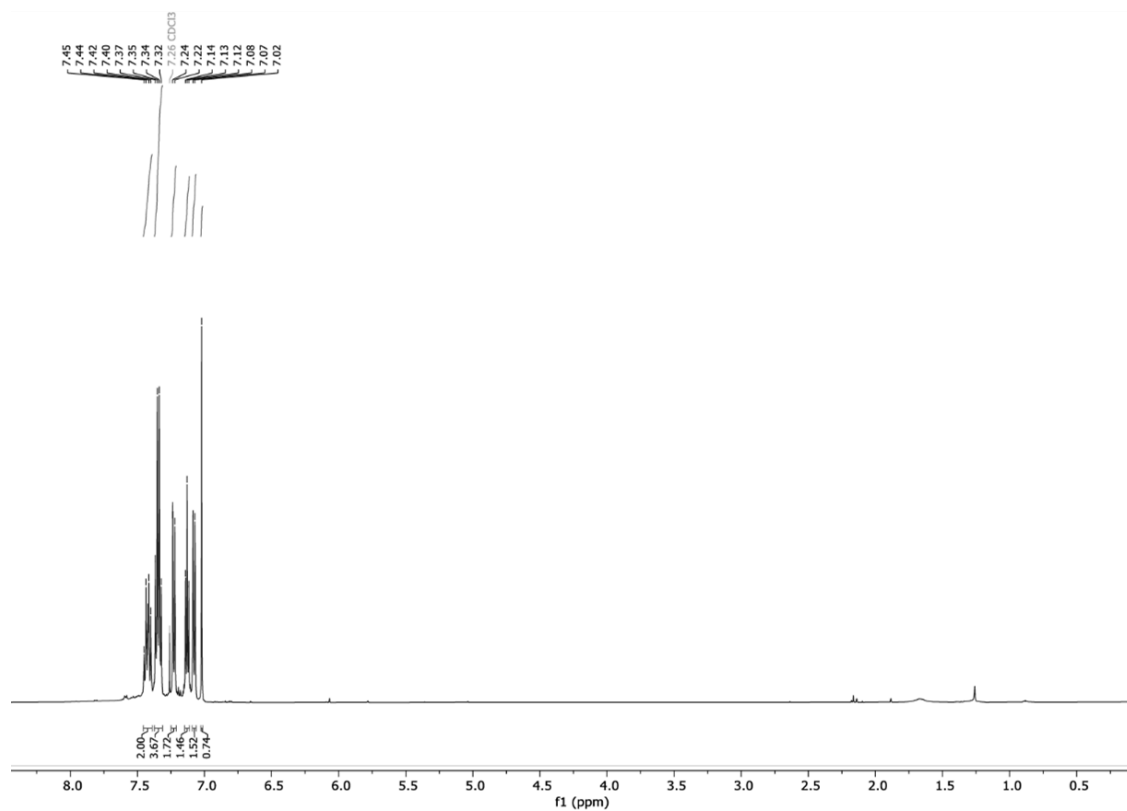
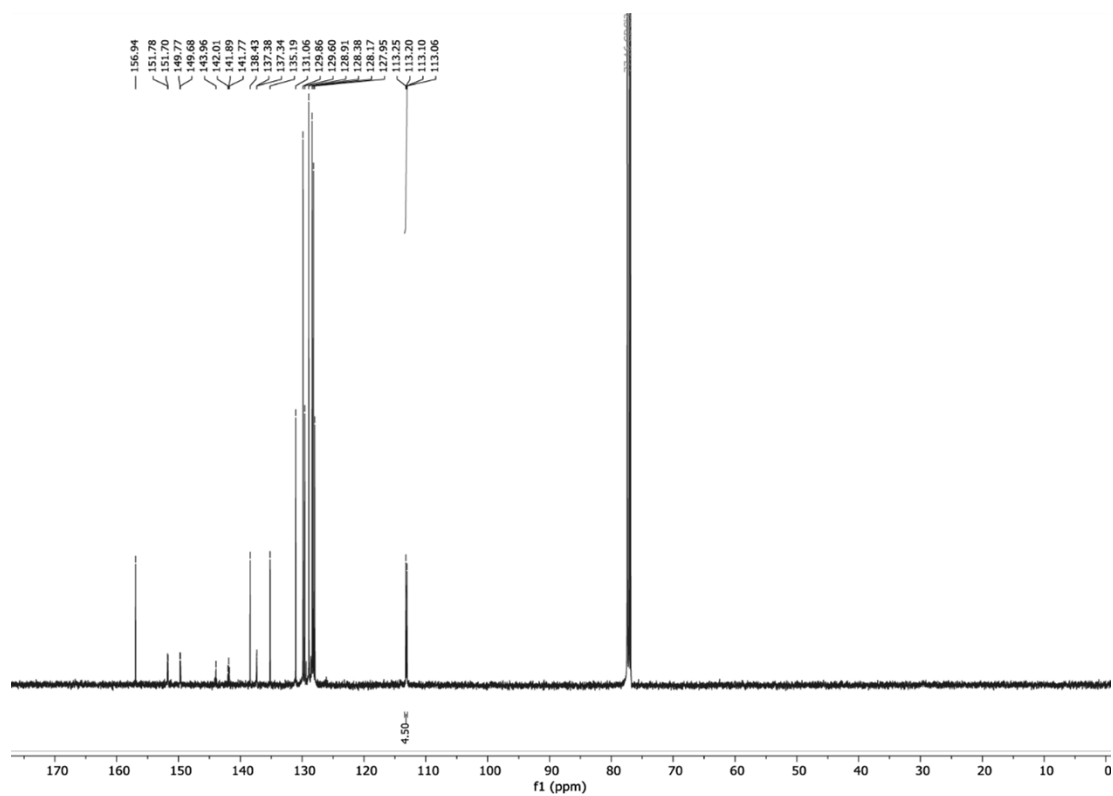
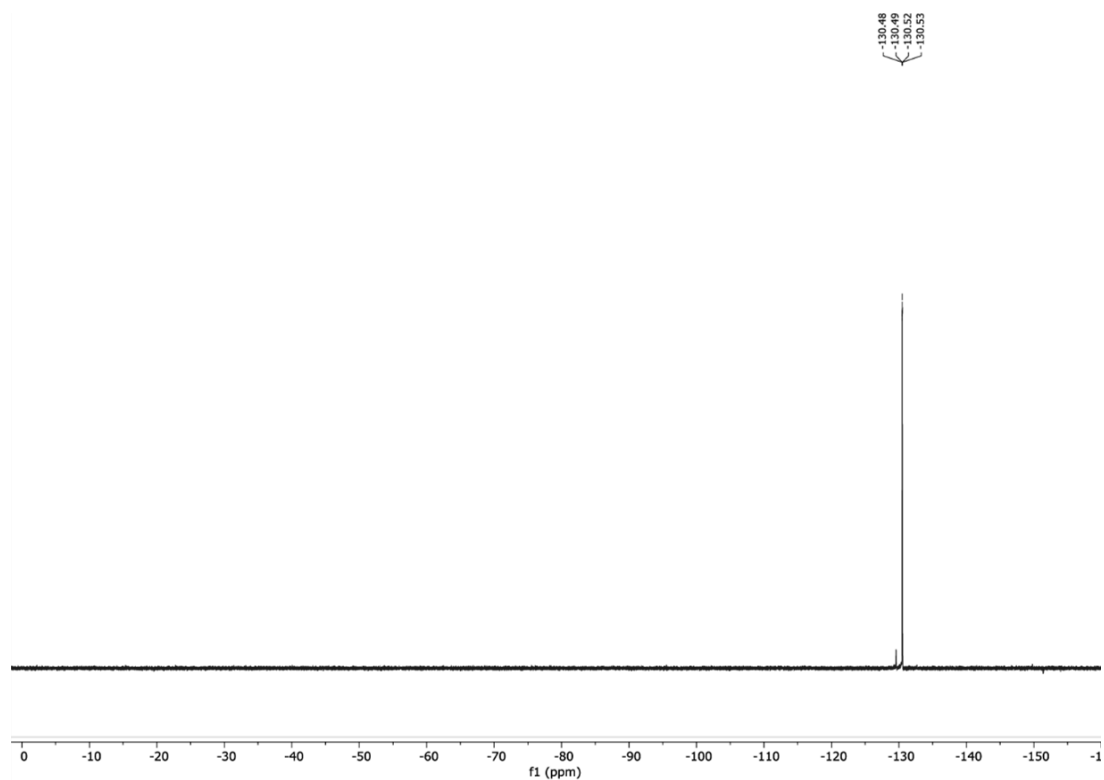
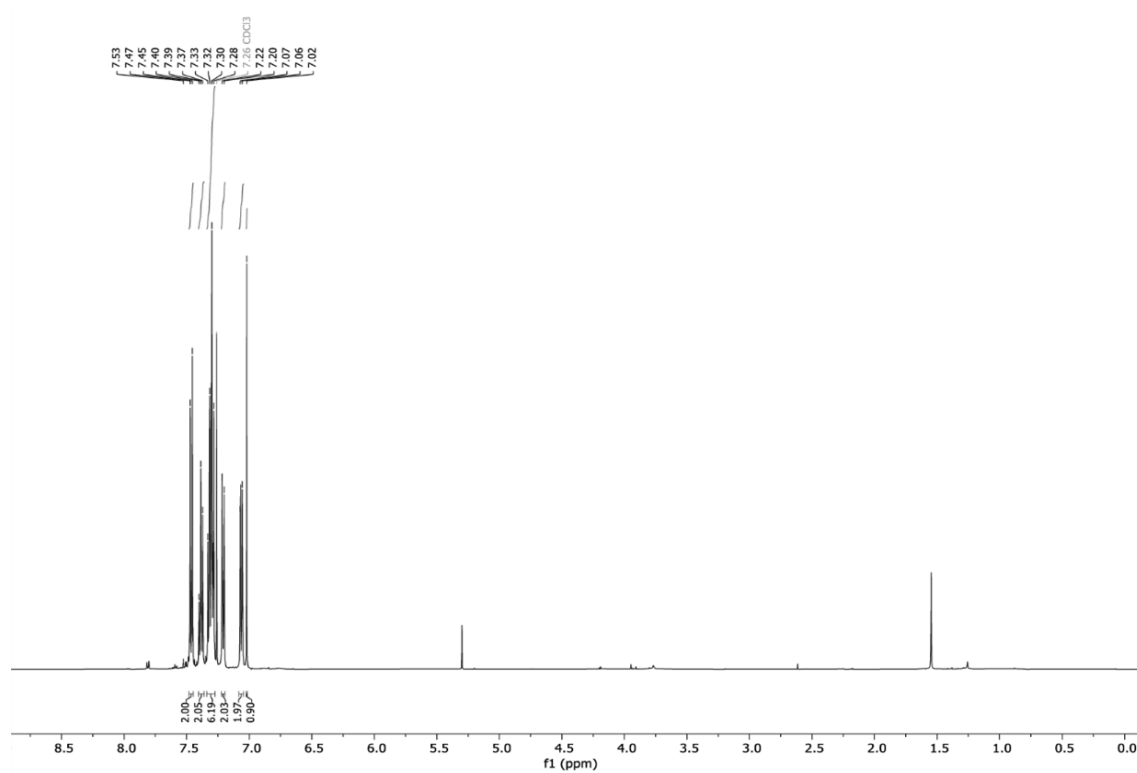
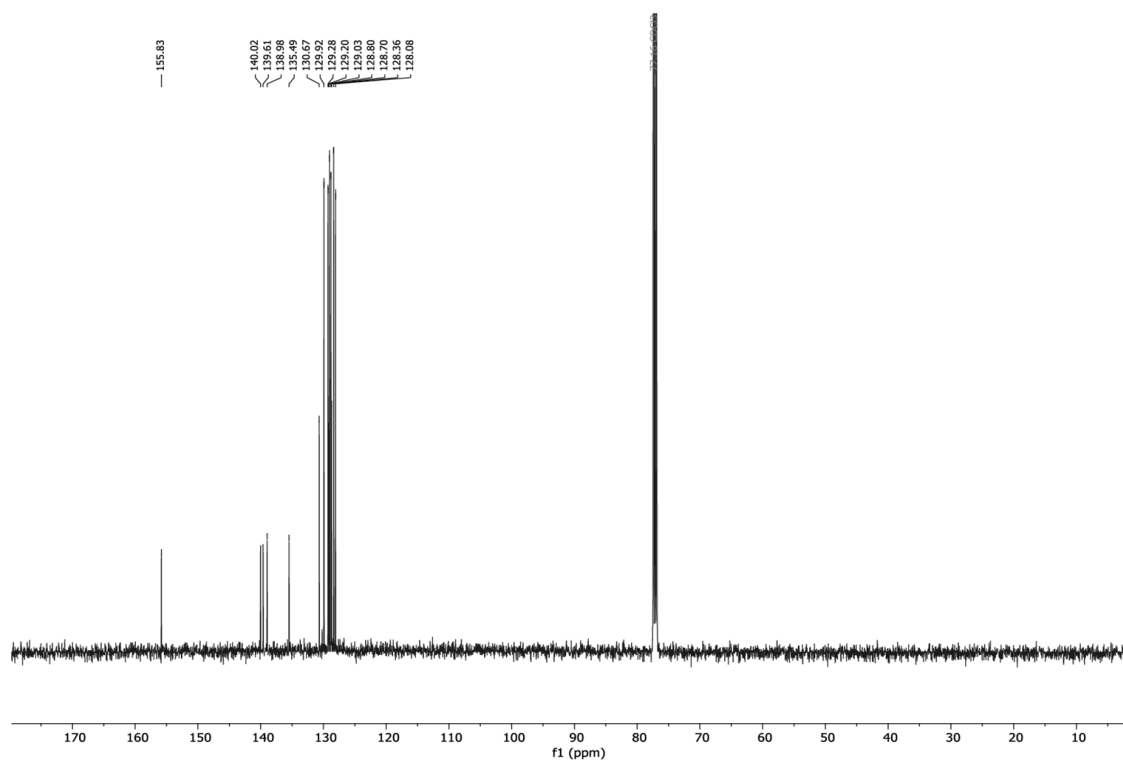
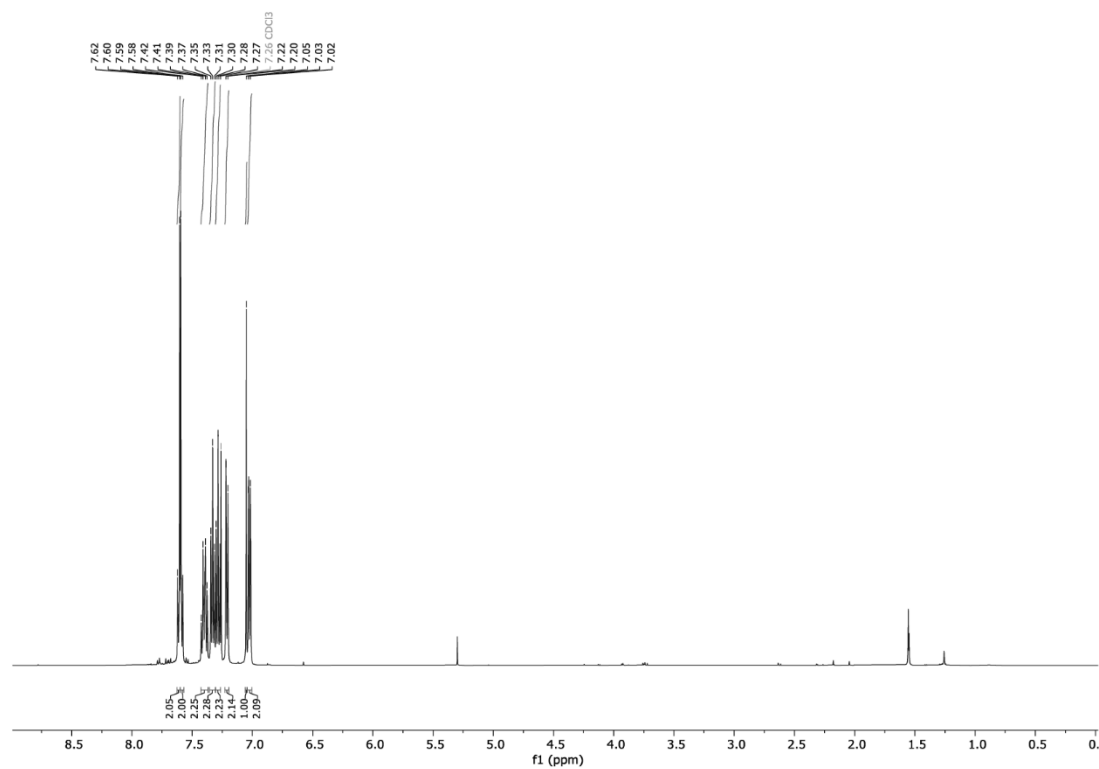
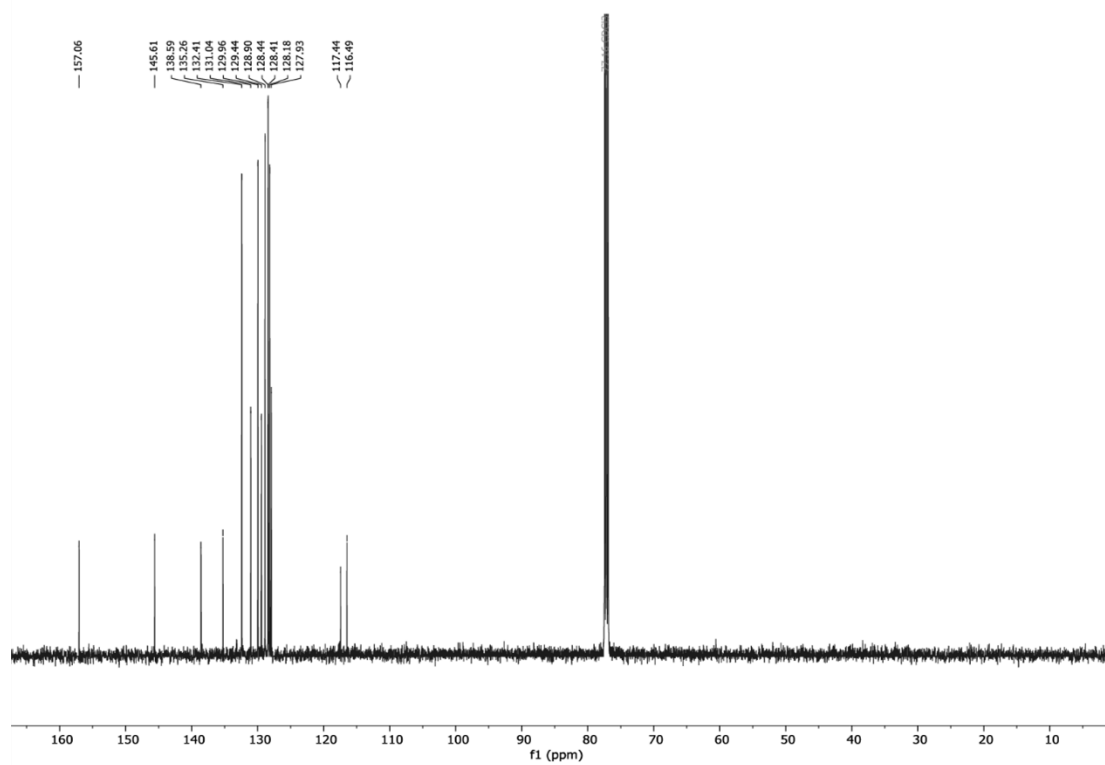


Figure 24. **3l** ^1H NMR.

Figure 25. 3I ^{13}C NMR.Figure 26. 3m ^1H NMR.

Figure 27. 3m ¹³C NMR.Figure 28. 3m ¹⁹F NMR.

Figure 29. 3n ¹H NMR.Figure 30. 3n ¹³C NMR.

Figure 31. 3o ¹H NMR.Figure 32. 3o ¹³C NMR.

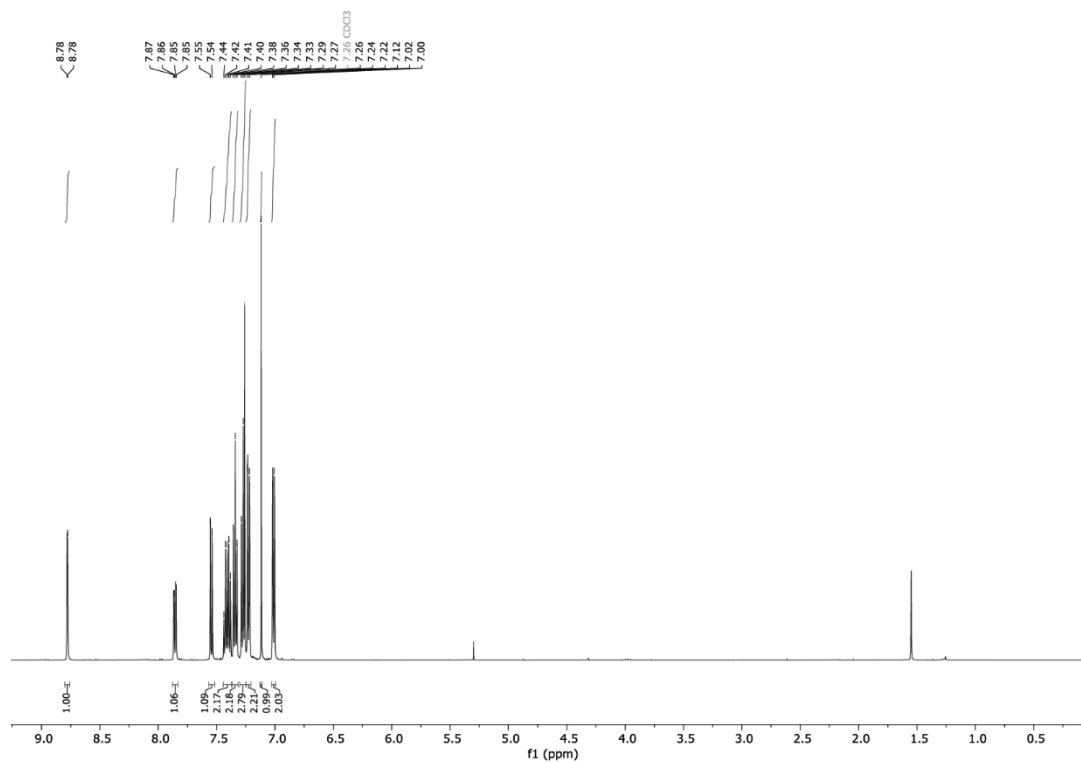


Figure 33. 3p ¹H NMR.

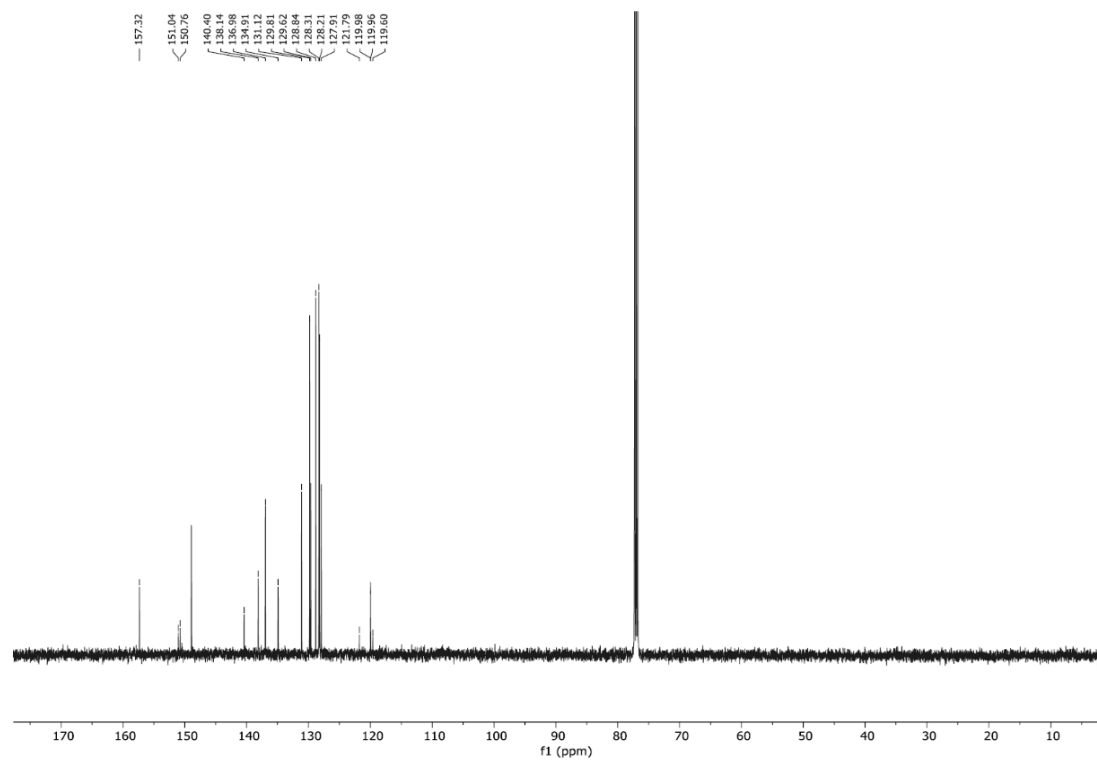
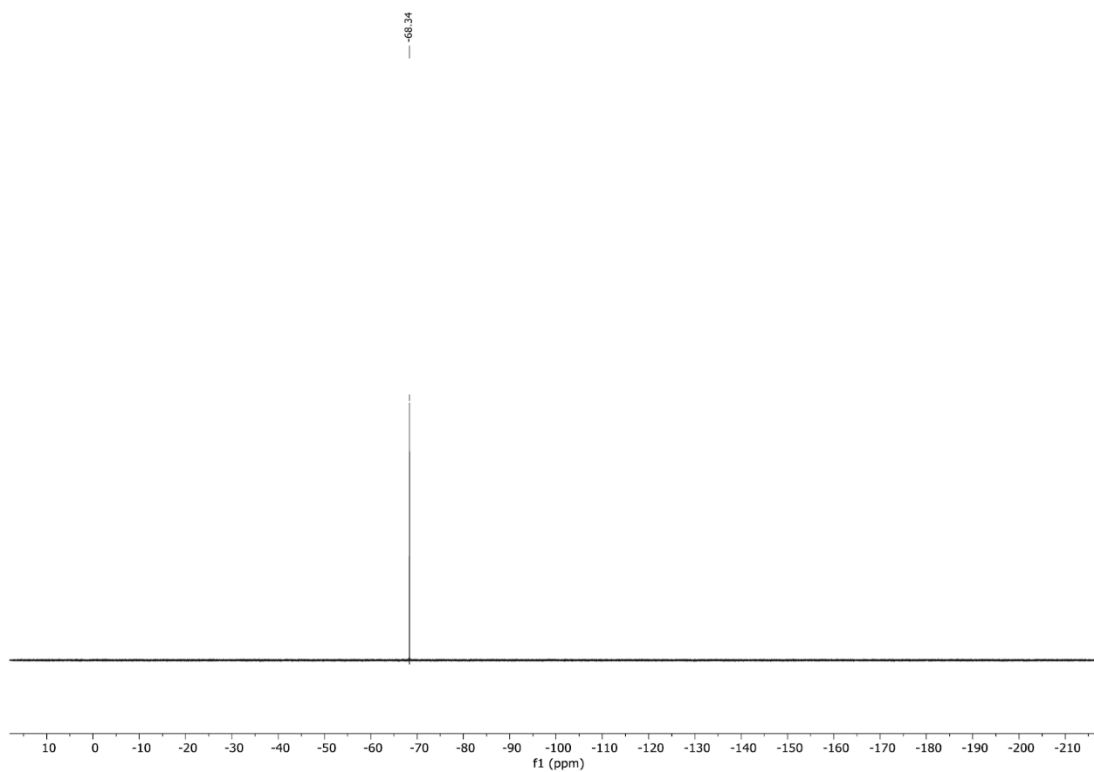
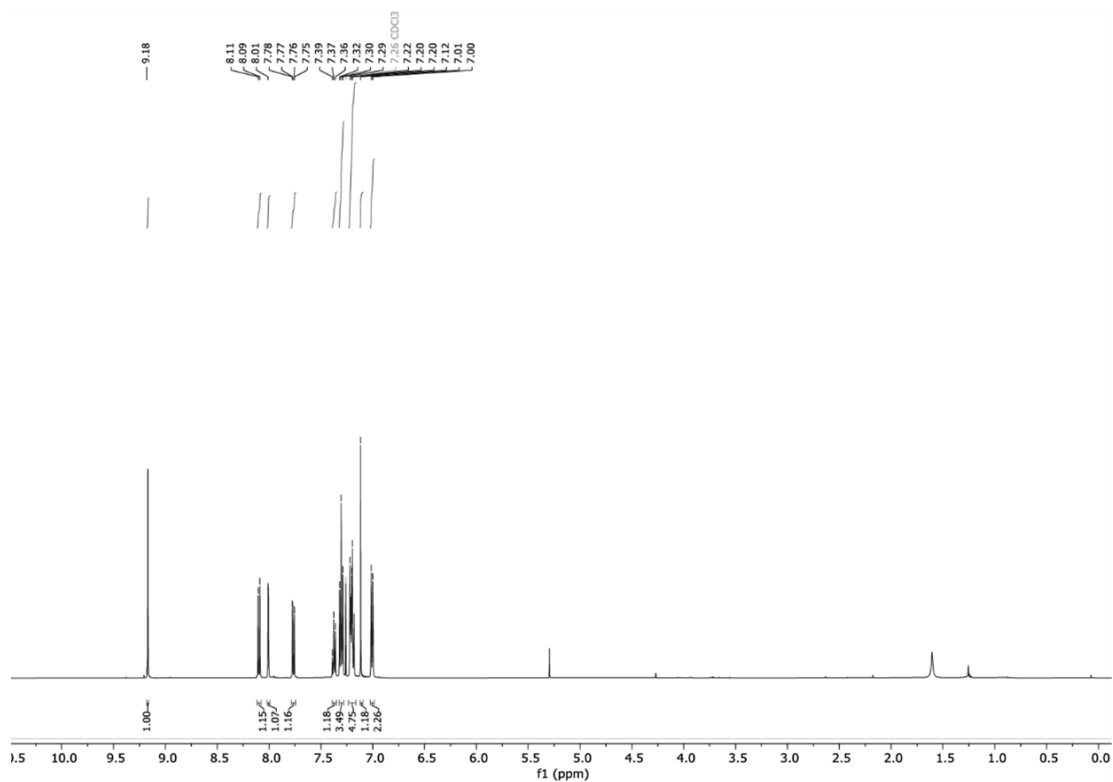


Figure 34. 3p ¹³C NMR.

Figure 35. 3p ^{19}F NMR.Figure 36. 3q ^1H NMR.

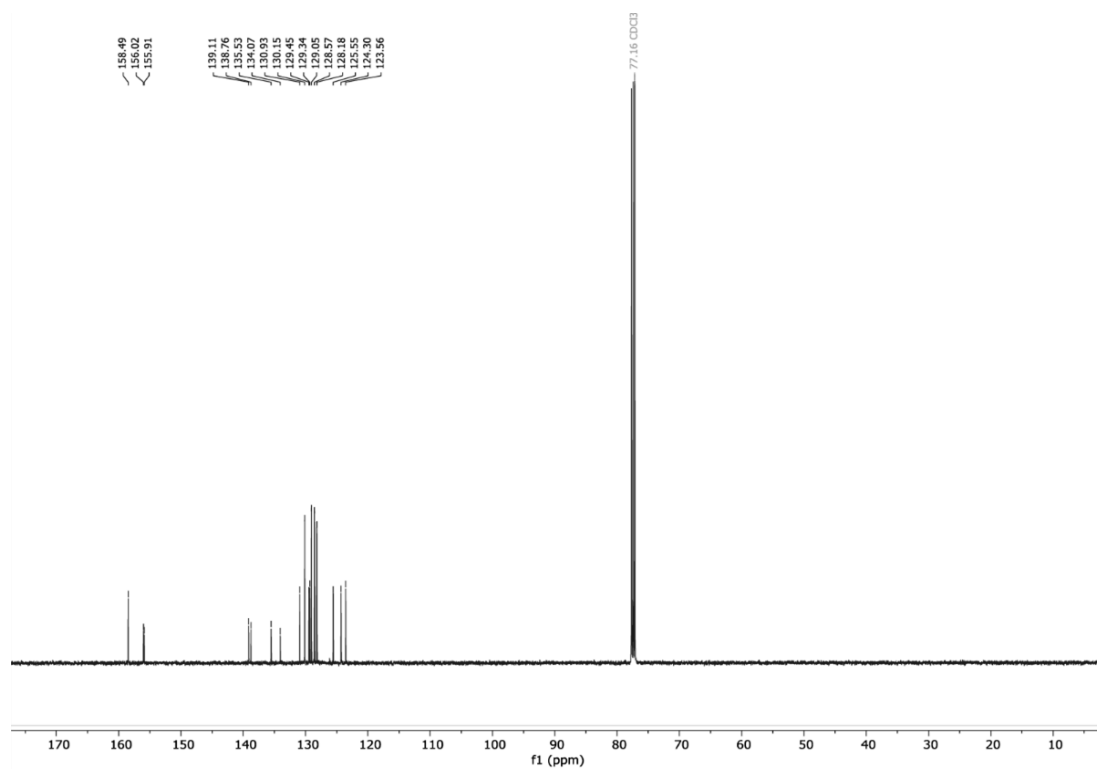


Figure 37. 3q ¹³C NMR.

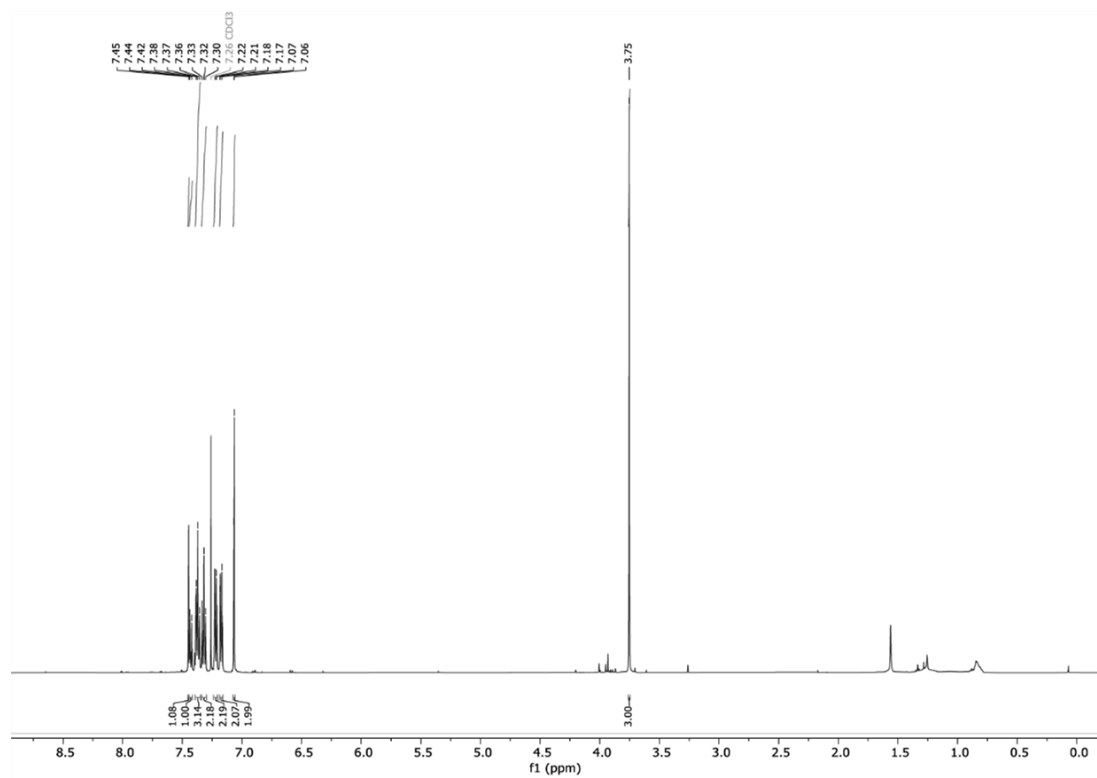
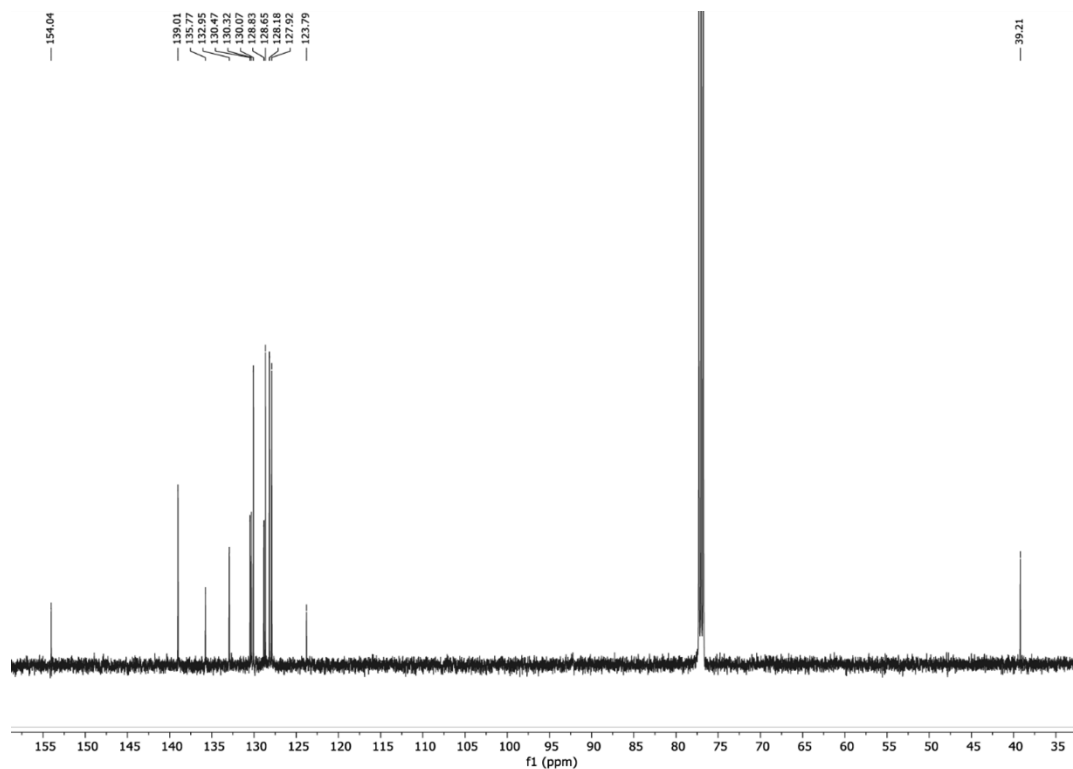
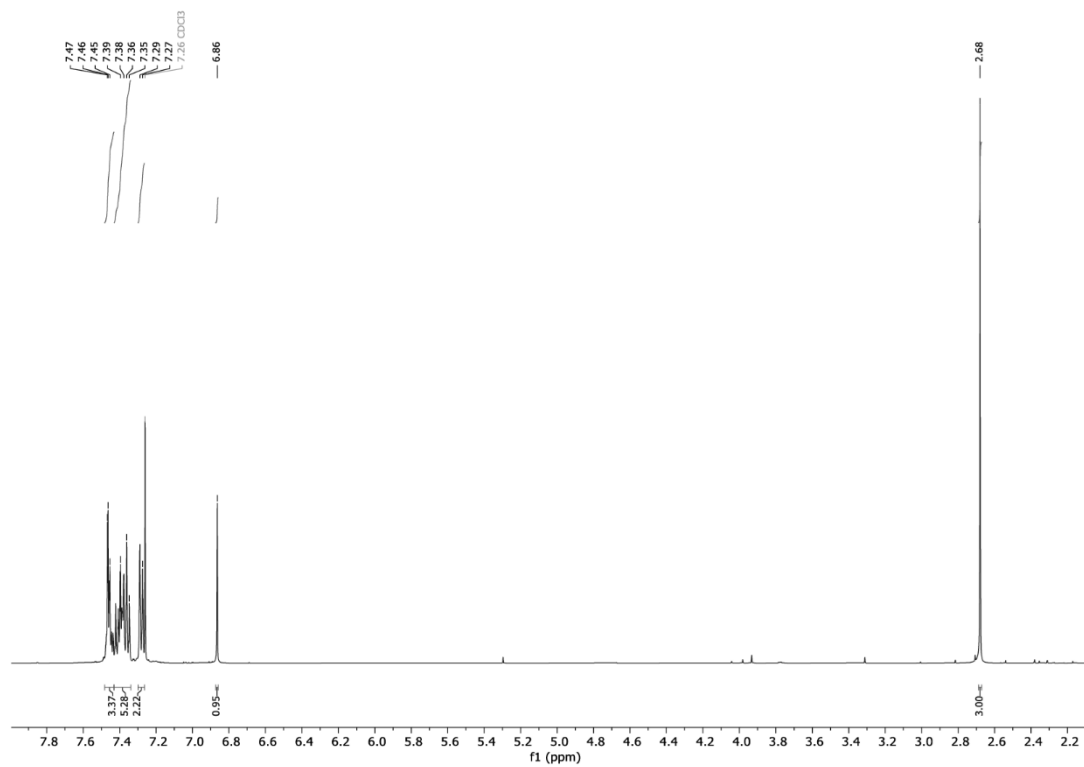
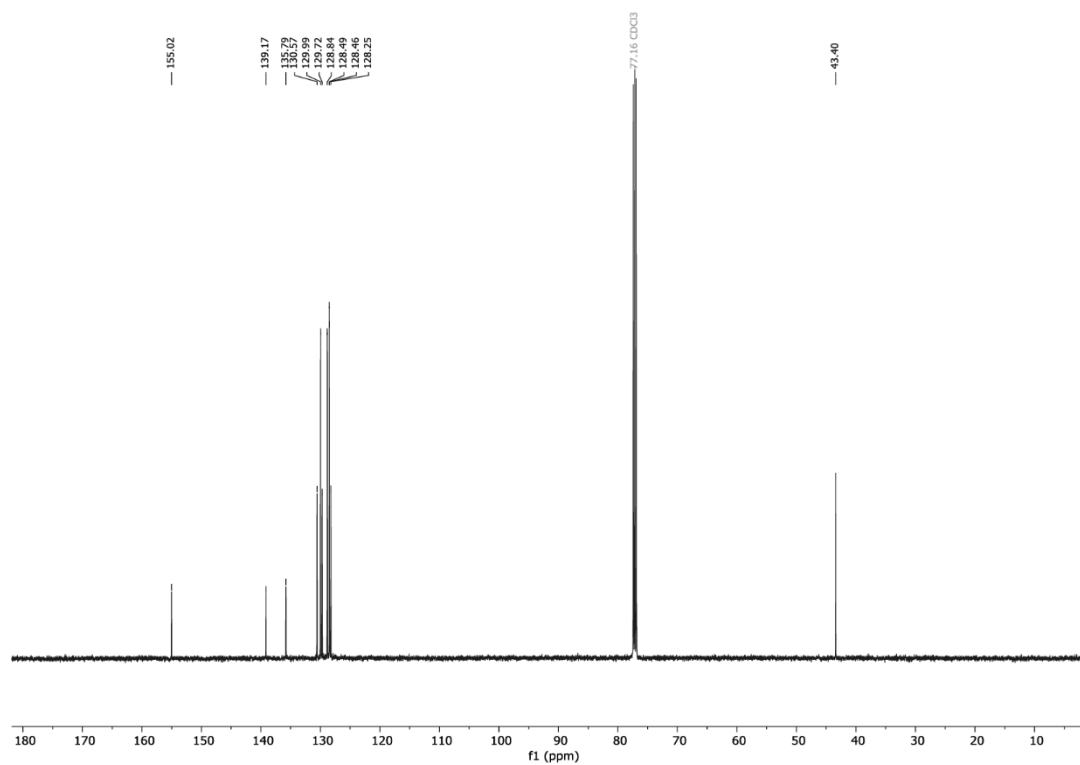
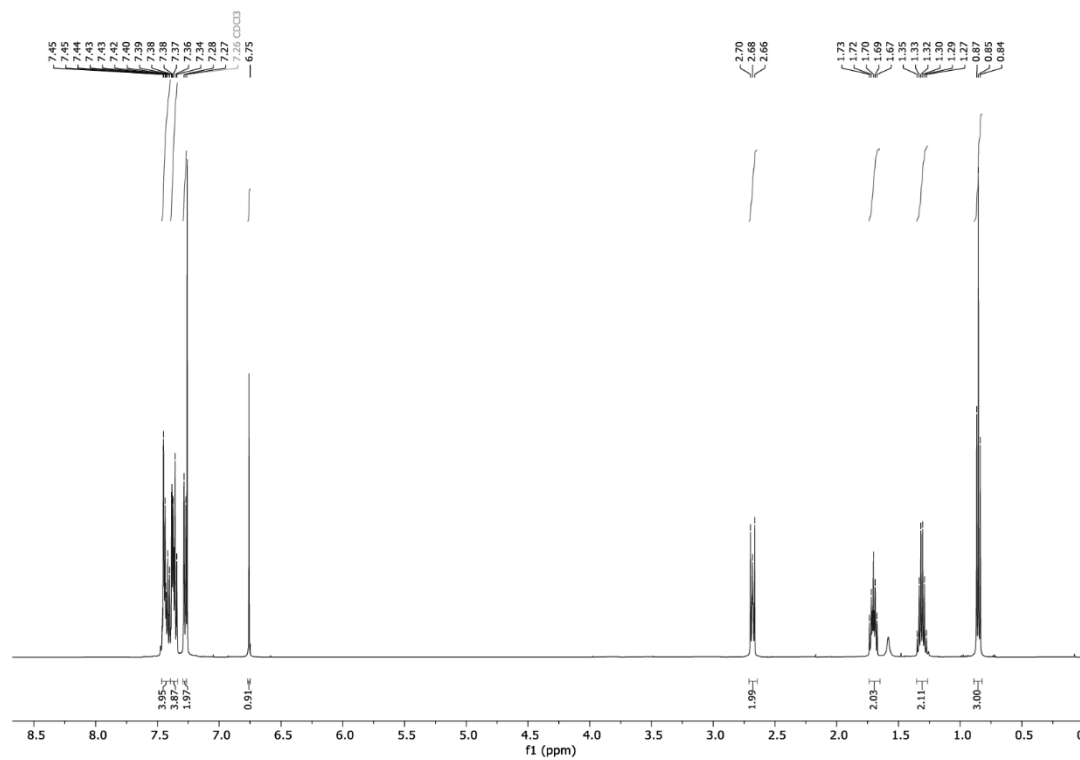
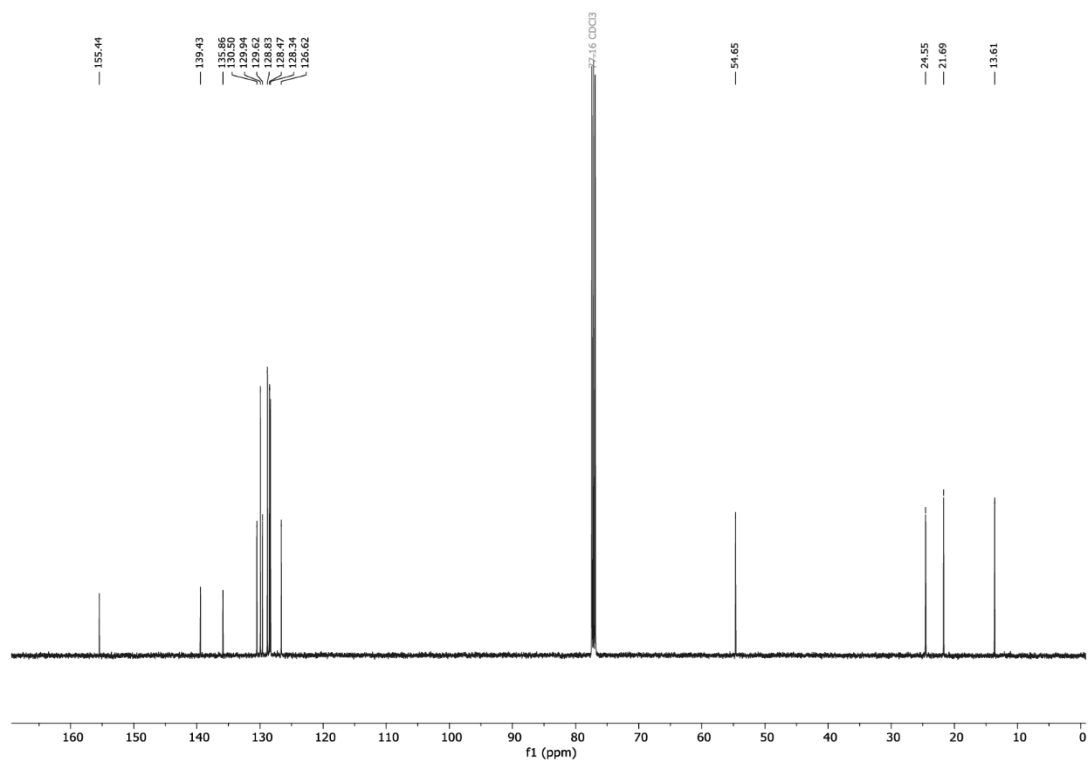
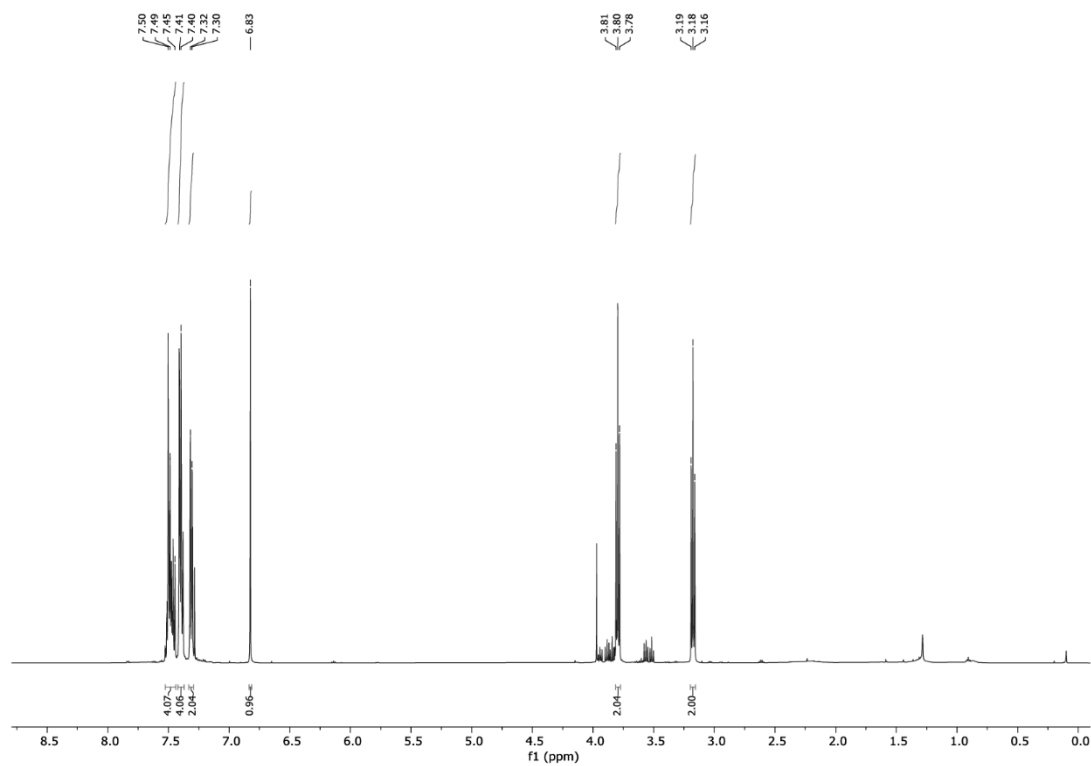


Figure 38. 3r ¹H NMR.

Figure 39. 3r ^{13}C NMR.Figure 40. 5a ^1H NMR.

Figure 41. 5a ^{13}C NMR.Figure 42. 5b ^1H NMR.

Figure 43. 5b ^{13}C NMR.Figure 44. 5c ^1H NMR.

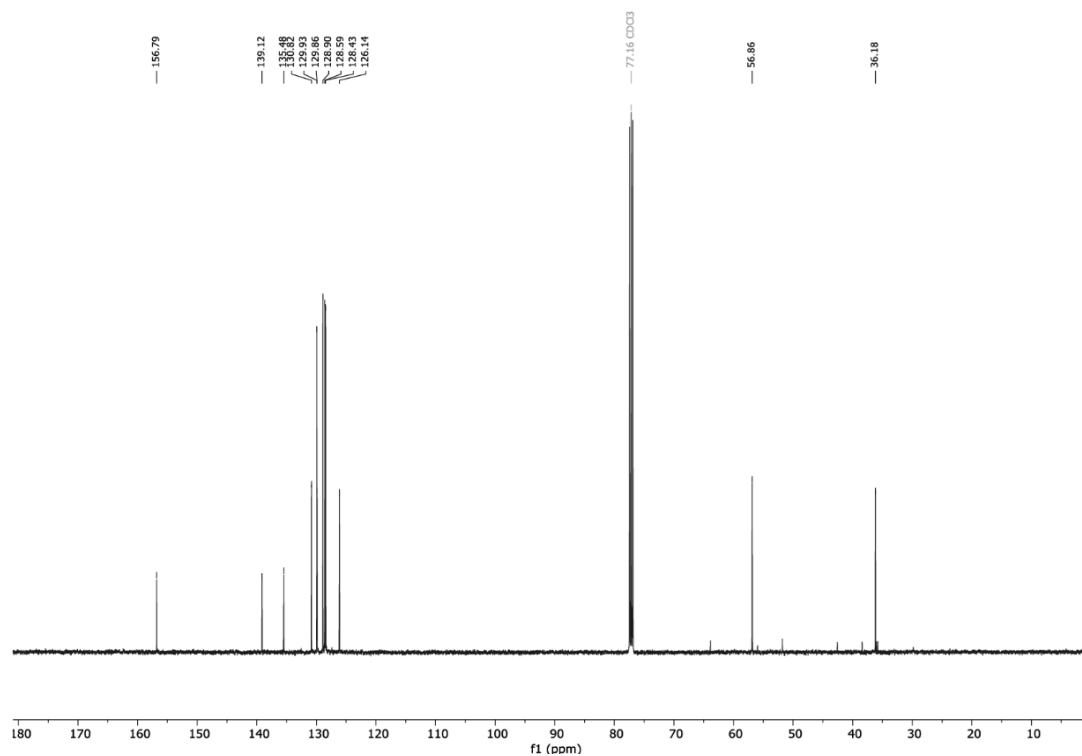


Figure 45. 5c ¹³C NMR.

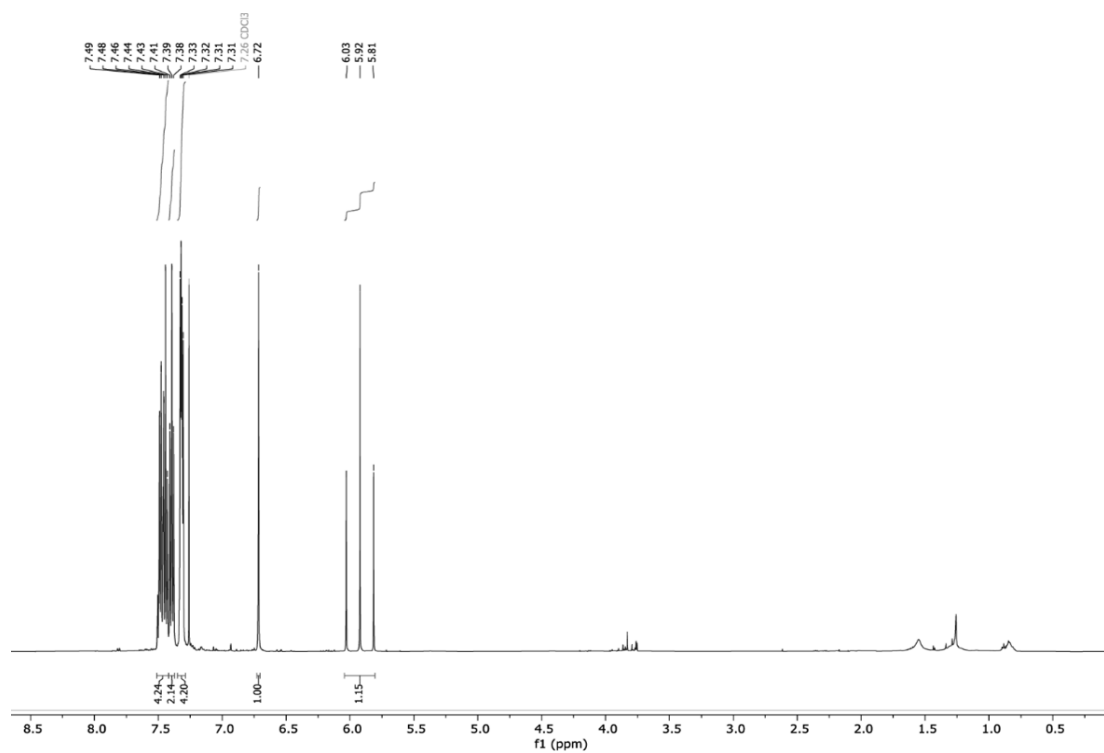


Figure 46. 5d ¹H NMR.

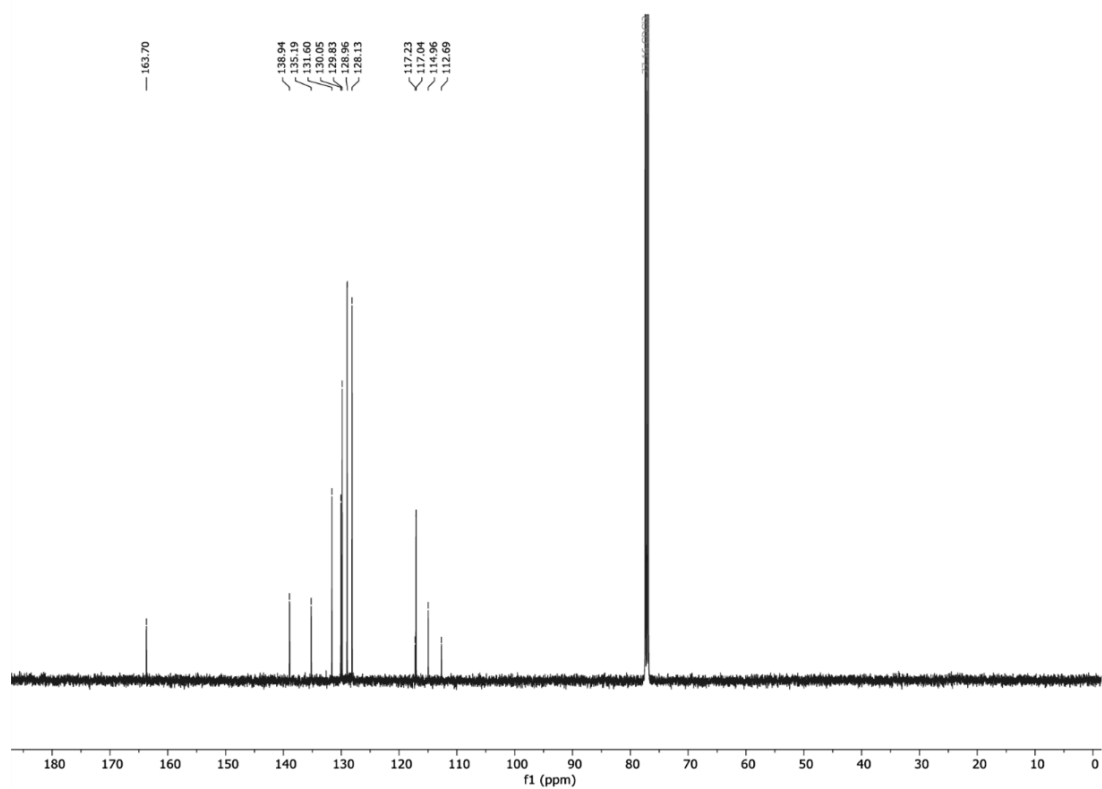


Figure 47. 5d ¹³C NMR.

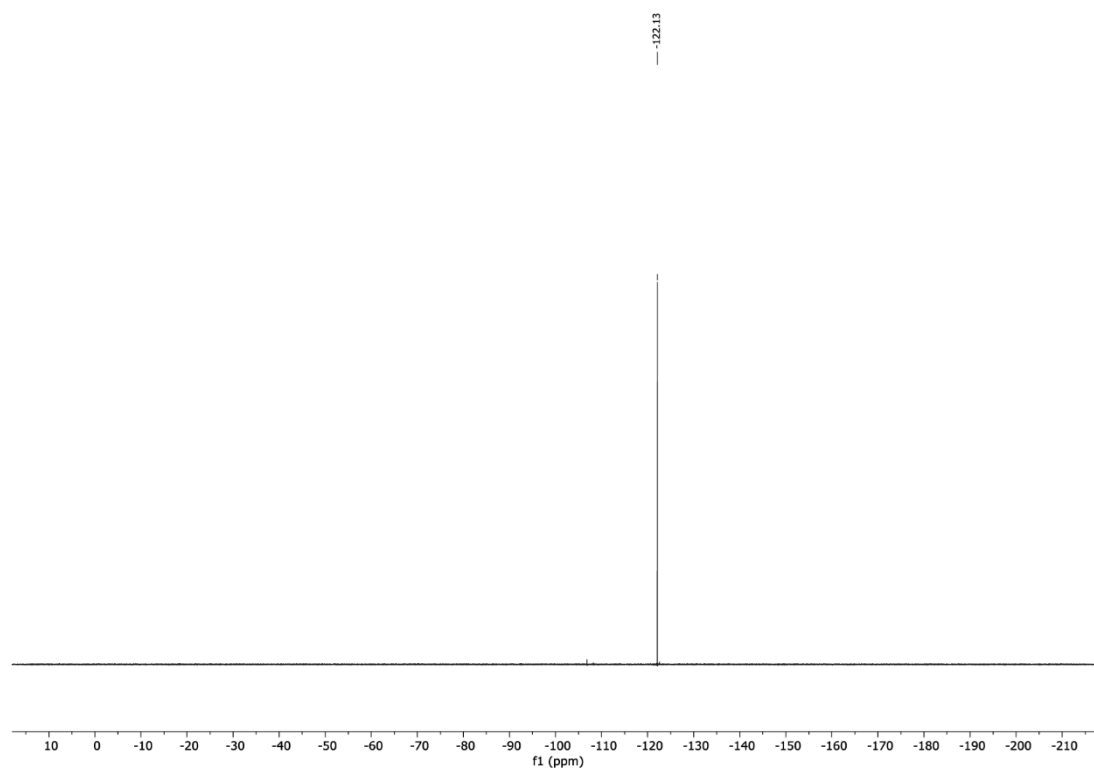
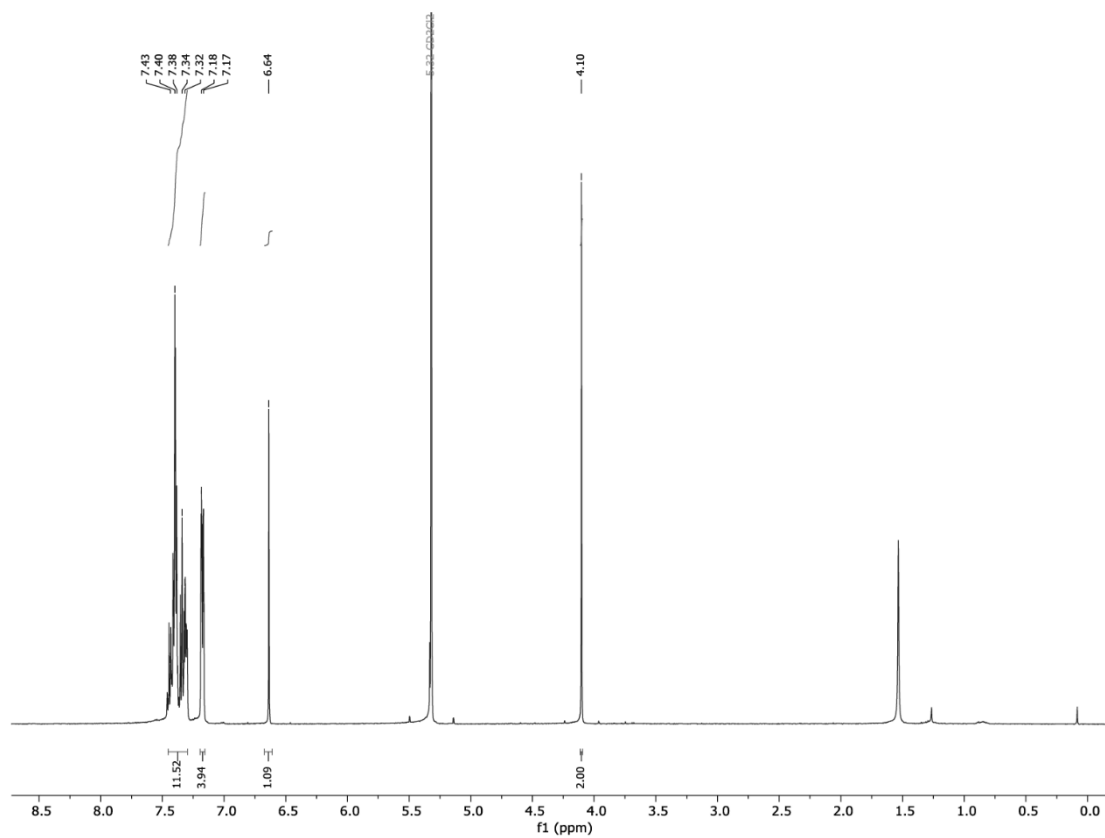
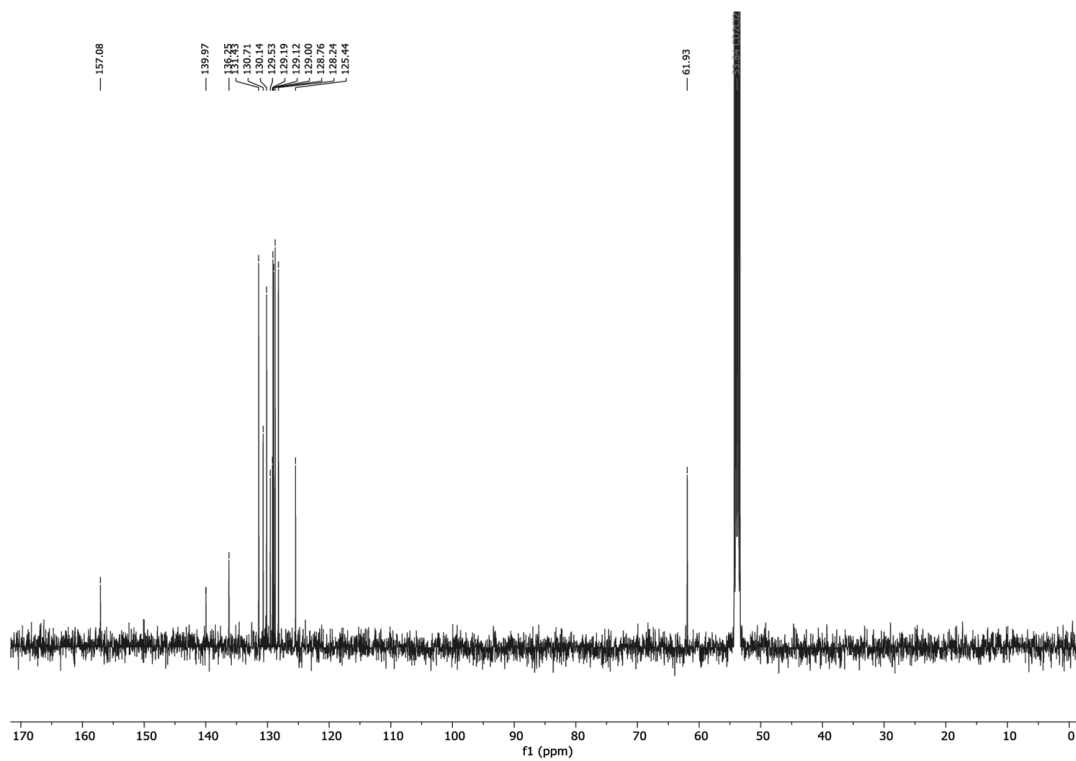
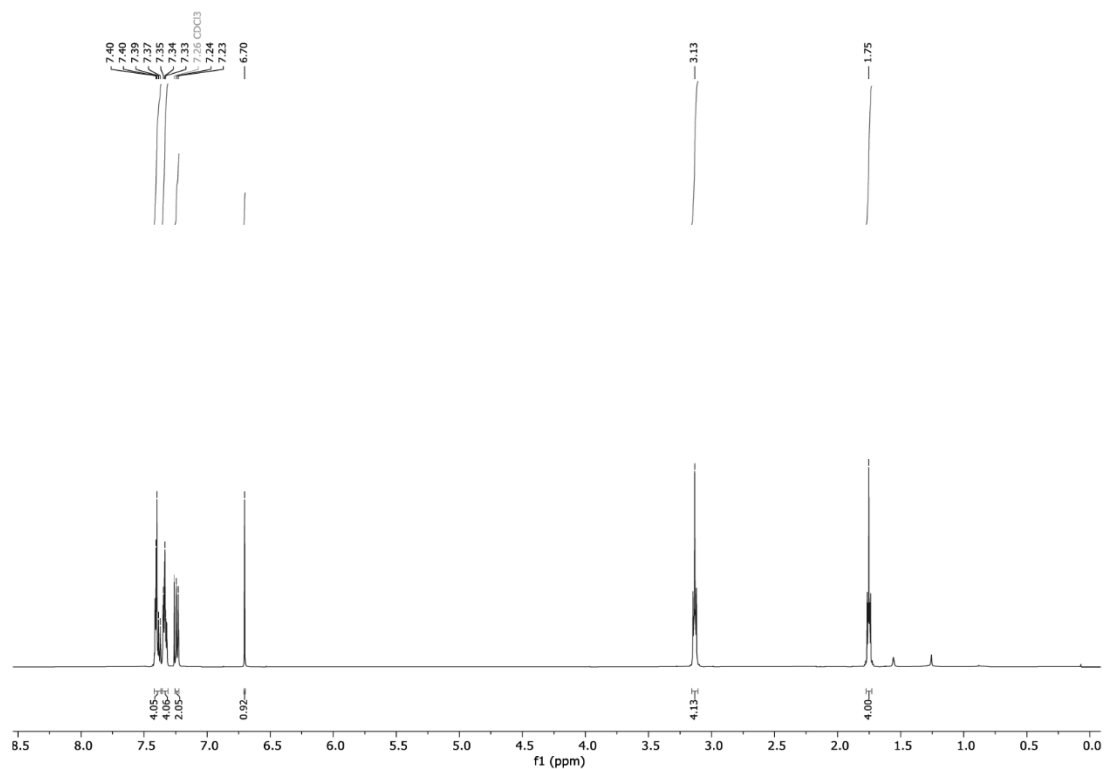
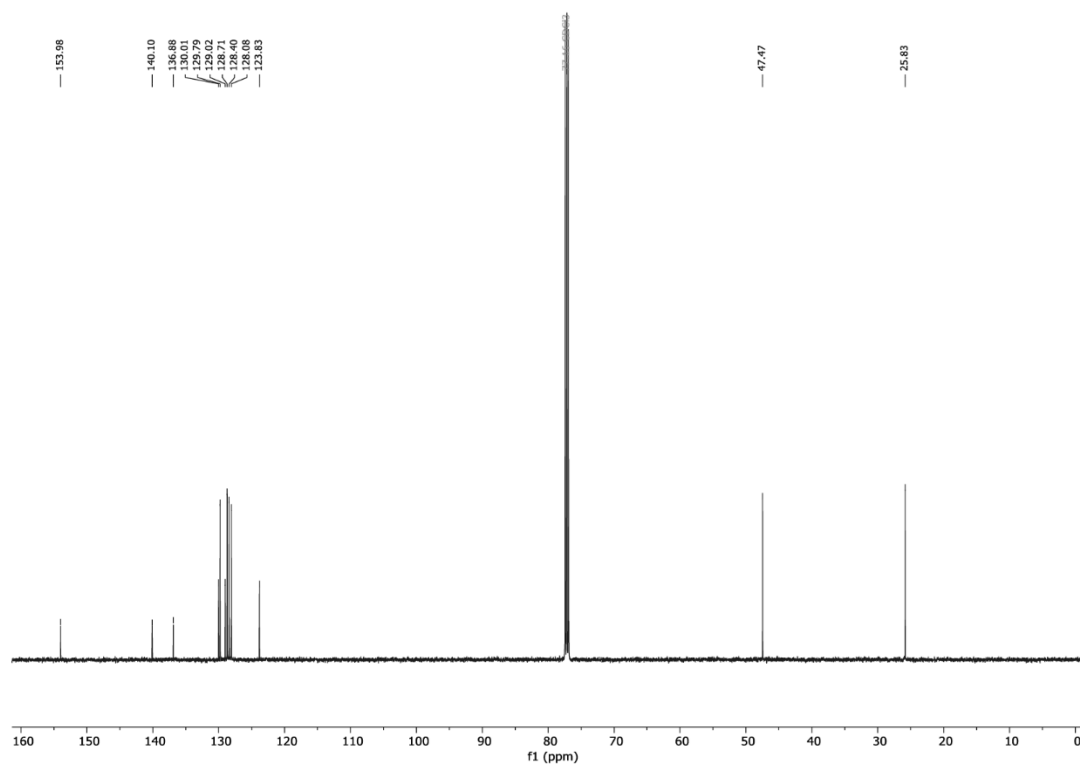
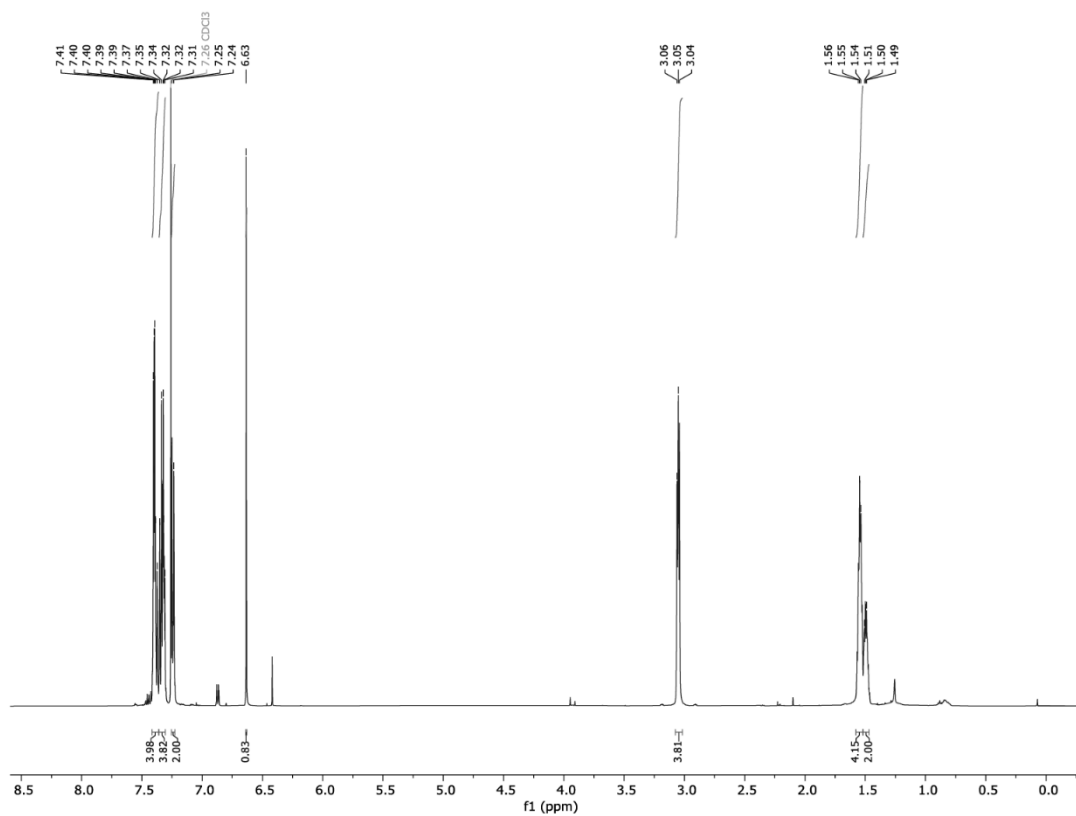
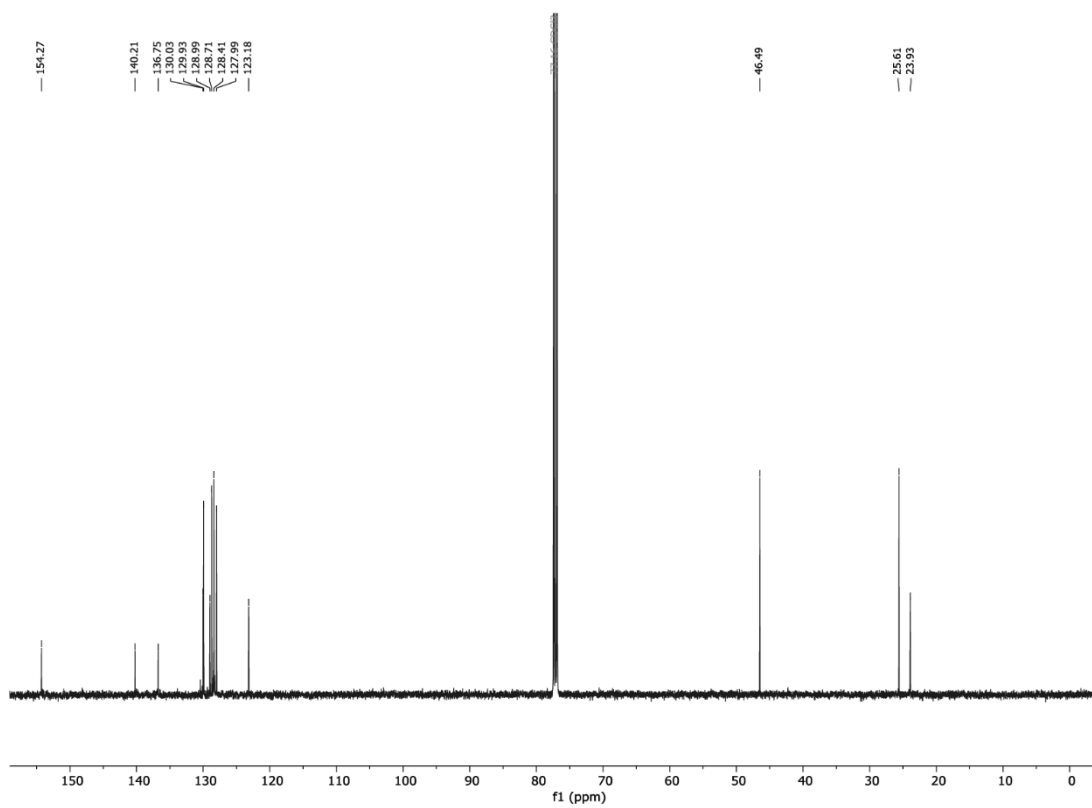
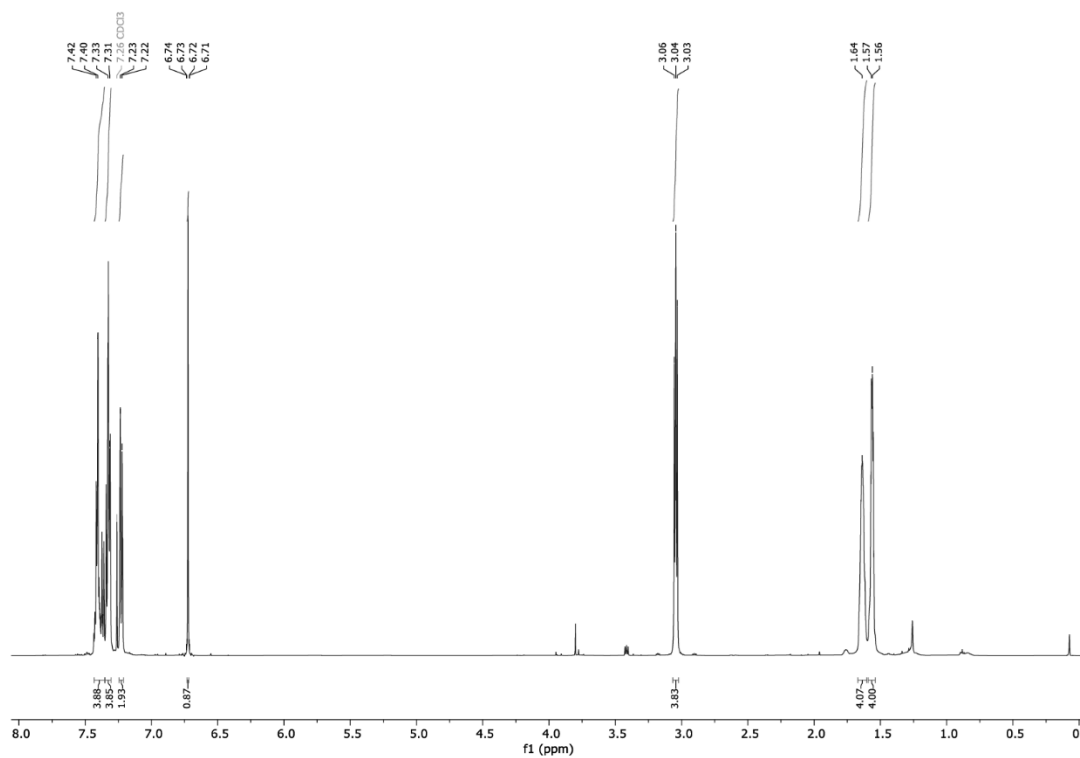
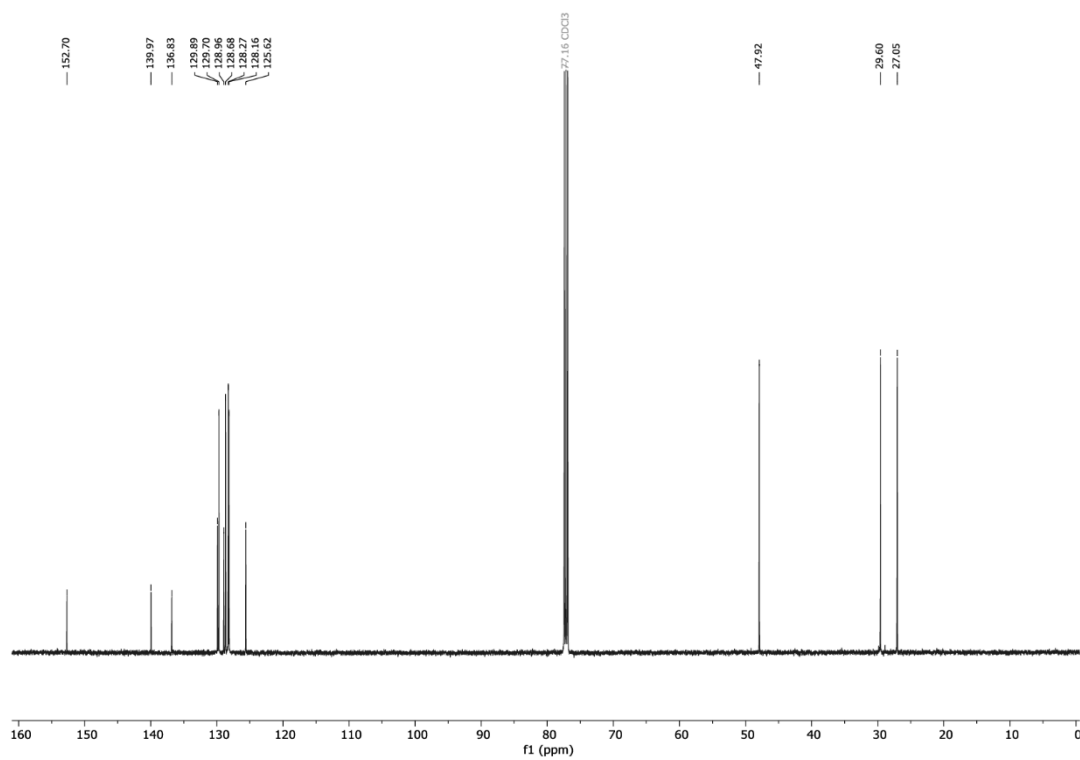


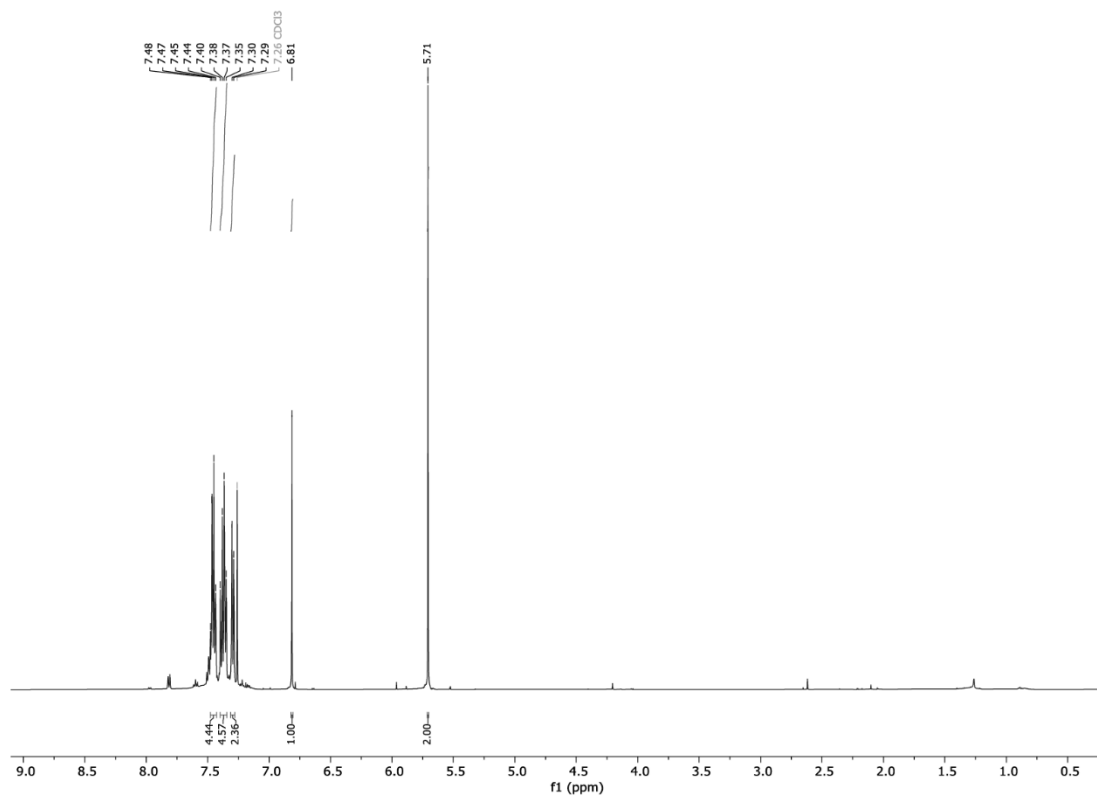
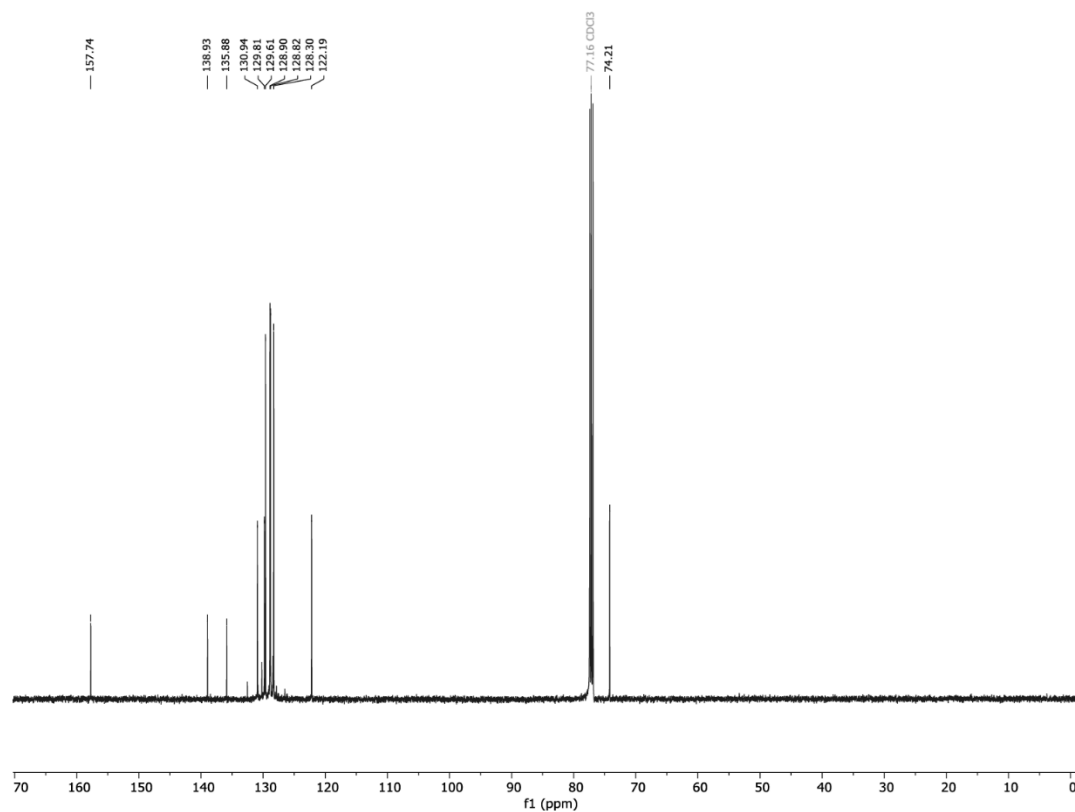
Figure 48. 5d ¹⁹F NMR.

Figure 49. 5e ¹H NMR.Figure 50. 5e ¹³C NMR.

Figure 51. 7a ^1H NMR.Figure 52. 7a ^{13}C NMR.

Figure 53. 7b ¹H NMR.Figure 54. 7b ¹³C NMR.

Figure 55. 7c ¹H NMR.Figure 56. 7c ¹³C NMR.

Figure 57. 7d ¹H NMR.Figure 58. 7d ¹³C NMR.