Supporting Information

Magnetic palladium nickel carbon nano-composite as a heterogeneous catalyst for the synthesis of distyrylbenzene and biphenyl derivatives

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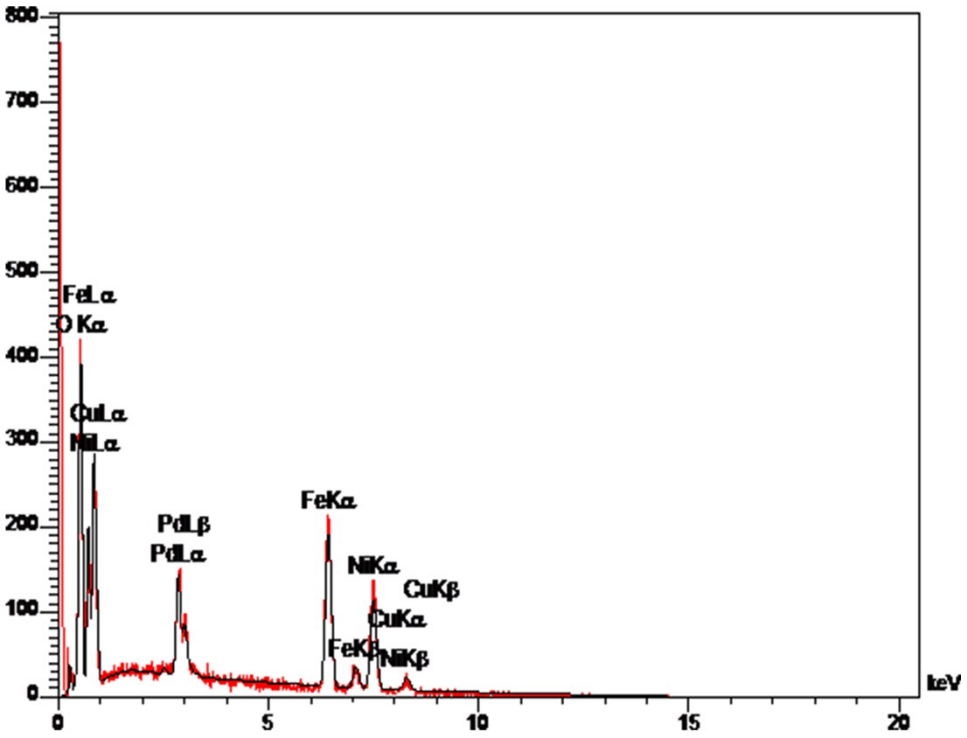
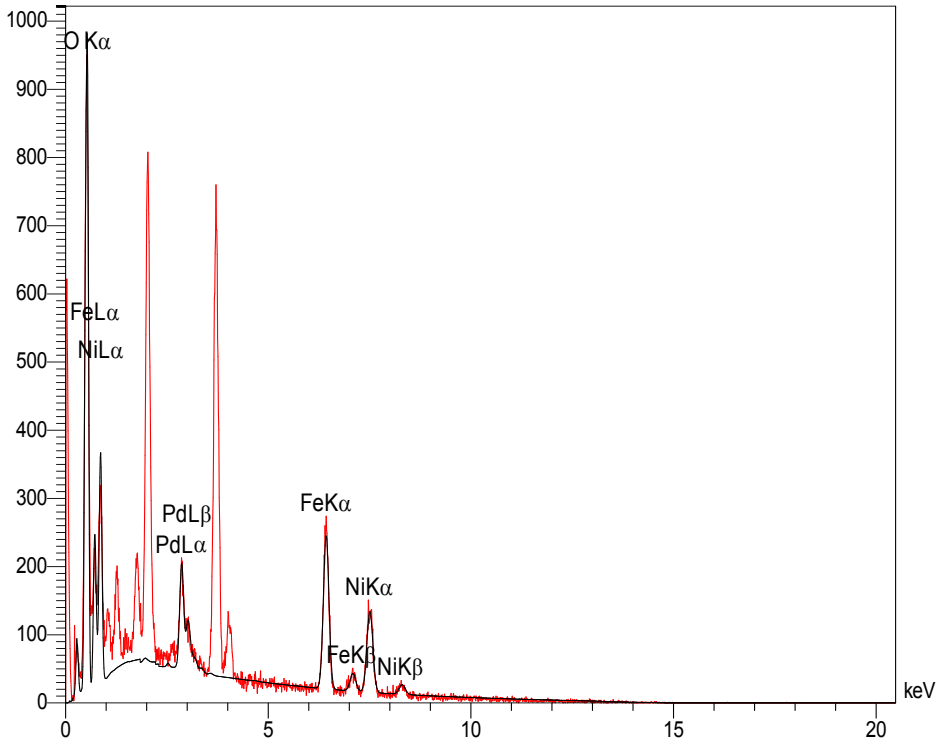
Experimental Section

General: Chemicals were purchased from Fluka, Merck and Aldrich Chemical Companies. The products were characterized by comparison of their spectral and physical data with those reported in literature. For recorded ^{1}H-NMR spectra we were using Bruker Avance (300 MHz or DRX 500 MHz) or Bruker Ultrashield (400 MHz) in pure deuterated $CDCl_3$ solvent with tetramethylsilane (TMS) as internal standards. X-ray diffraction (XRD, D8, Advance, Bruker, axs), FT-IR spectroscopy (Shimadzu FT-IR 8000 spectrophotometer), and SEM instrumentation (SEM, XL-30 FEG SEM, Philips, at 20 kV) were employed for characterization of catalysts. Surface spectroscopy analyses of the catalysts were performed in an ESCA/AES system. This system is equipped with a concentric hemispherical (CHA) electron energy analyzer (Specs model EA10 plus) suitable for X-ray photoelectron spectroscopy (XPS). Melting points determined in open capillary tubes in a Barnstead Electrothermal 9100 BZ circulating oil melting point apparatus. The reaction monitoring was accomplished by TLC on silica gel PolyGram SILG/UV254 plates. Column chromatography was carried out on columns of silica gel 60 (70–230 mesh). All the products were characterized with IR, NMR and the known compounds compared with those reported in literature.



Elt	Line	Int	Error	K	Kr	W%	A%	ZAF	Formula	Ox%	Pk
C	Ka	6.9	3.9693	0.0302	0.0234	8.02	22.12	0.2917		0.00	5.2
N	Ka	3.5	3.9693	0.0207	0.0160	5.17	12.22	0.3098		0.00	5.2
O	Ka	27.8	3.9693	0.0603	0.0467	12.60	26.07	0.3706		0.00	29.
Fe	Ka	103.2	0.7498	0.3887	0.3012	30.69	18.20	0.9813		0.00	17.
Ni	Ka	62.1	0.7498	0.3653	0.2830	30.66	17.29	0.9231		0.00	13.
Cu	Ka	0.7	0.7498	0.0054	0.0042	0.47	0.25	0.8822		0.00	2.2
Pd	La	50.7	0.6874	0.1295	0.1003	12.38	3.85	0.8104		0.00	6.4
Ag	La	0.0	0.0000	0.0000	0.0000	0.00	0.00	0.8260		0.00	4.5
				1.0000	0.7748	100.00	100.00			0.00	

Figure 1. EDX spectrum of fresh nano-composite (Fe_3O_4@Pd@Ni/C).



Elt	Line	Int	Error	K	Kr	W%	A%	ZAF	Formula	Ox%	Pk
C	Ka	15.3	20.1608	0.0476	0.0330	10.55	23.60	0.3127		0.00	4.0
O	Ka	121.6	20.1608	0.1887	0.1307	30.24	50.79	0.4322		0.00	26.
Fe	Ka	127.0	0.6682	0.3425	0.2373	25.28	12.16	0.9385		0.00	12.
Ni	Ka	72.4	0.6682	0.3049	0.2112	23.79	10.89	0.8880		0.00	9.7
Pd	La	63.7	51.8192	0.1164	0.0806	10.14	2.56	0.7951		0.00	5.1
				1.0000	0.6928	100.00	100.00			0.00	

Figure 2. EDX spectrum of nano-composite (Fe_3O_4@Pd@Ni/C) after 8 times recovery.

General procedure for the synthesis of distyrylbenzenes

To a mixture of aryl halide (1 mmol), alkene (1.2 mmol), and Na_2CO_3 (2.5 mmol) in DMF (3 mL), catalyst Fe_3O_4@Pd@Ni/C (0.075 g, with respect to Pd content 3.29 mol%) was added and heated on oil bath at 120 ˚C. The reaction was continuously followed by TLC to completion. After completion, the catalyst was removed by external magnet and was washed with dichloromethane (3 × 5 mL). Having extracted the reaction mixture from dichloromethane and water, the organic phase was dried

over Na_2SO_4. Evaporation of the solvent gave products. For further purification, the products passed through a short column of silica gel using *n*-hexane as eluent.
[It worth mentioning, in the case of 1,4-dihalobenzene or 9,10-dibromonanthracene (1 mmol), alkene (2.4 mmol), and Na_2CO_3 (2.5 mmol) in DMF (3 mL), catalyst Fe_3O_4@Pd@Ni/C (0.15 g, with respect to Pd content 6.58 mol%) was added and heated on oil bath at 120 ˚C].

Diethyl-3,3-(1,4-phenylene)-diacrylate (Scheme 4, **6a**): ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 1.18 (t, J = 7.1 Hz, 6H), 4.11 (q, J = 7.1 Hz, 4H), 6.31 (d, J = 15.9 Hz, 2H), 7.38 (s, 4H), 7.51 (d, J = 15.9 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 14.4, 60.7, 119.4, 128.5, 136.2, 143.5, 166.8.
Dimethyl-3,3-(1,4-phenylene)-diacrylate (Scheme 4, **6b**): ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 3.83 (s, 6H), 6.50 (d, J = 16.0 Hz, 2H), 7.56 (s, 4H), 7.70 (d, J = 16.0 Hz, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm): 52.2, 119.4, 126.6, 129.0, 136.6, 144.1, 167.6.
Diethyl-3,3-(1,4-phenylene)-diacrylate (Scheme 4, **6c**): ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 1.27 (t, J = 7.1 Hz, 6H), 2.34 (s, 6H), 4.20 (q, J = 7.1 Hz, 4H), 6.31 (d, J = 15.9 Hz, 2H), 7.32 (s, 2H), 7.83 (d, J = 15.9 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 14.4, 19.4, 60.2, 119.9, 128.7, 134.9, 135.6, 141.4, 167.0.
1,4-Bis-(4-methylstyryl)-benzene (Scheme 4, **7a**): ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 2.39 (s, 6H), 7.26-7.55 (m, 12H), 7.70 (d, J = 16.0 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 28.9, 123.6, 124.3, 126.1, 126.7, 127.1, 128.3, 128.6, 128.8.
1,4-Bis-(4-bromostyryl)-benzene (Scheme 4, **7b**): ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 6.91-7.05 (m, 3H), 7.16-7.31 (m, 8H), 7.40-7.46 (m, 3H), 7.59-7.61 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 126.6, 127.5, 128.0, 128.2, 128.8, 129.6, 136.9, 137.8.
2,5-Dimethoxy-1,4phenylene)-bis-(ethane-2,1-diyl)-dibenzene (Scheme 4, **7c**): ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 3.86 (s, 6H), 7.03-7.07 (m, 4H), 7.16-7.20 (m, 4H), 7.27-7.31 (m, 4H), 7.40-7.49 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 56.4, 109.2, 123.3, 126.6, 127.5, 128.7, 129.0, 137.9, 138.2, 152.0.

Diethyl-3,3-(anthracene-9,10-diyl)-diacrylate (Scheme 5, **9**): ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 1.45 (t, J = 7.1 Hz, 6H), 4.42 (q, J = 7.1 Hz, 4H), 6.42 (d, J = 16.3 Hz, 2H), 7.52-7.60 (m, 4H), 8.27 (dt, J_1 = 6.2 Hz, J_2 = 3.1 Hz, 4H), 8.63 (d, J = 16.3 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 14.4, 60.9, 125.9, 126.2, 127.9, 128.9, 131.0, 142.0, 166.3.
9,10-Di-(E)-styrylanthracene (DSA) (Scheme 5, **10a**): ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 6.98 (d, J = 16.5 Hz, 2H), 7.36-7.43 (m, 2H), 7.47-7.53 (m, 8H), 7.71-7.75 (m, 4H), 7.79 (d, J = 16.5 Hz, 2H), 8.40-8.46 (m**,** 4H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 125.2, 125.3, 126.5, 126.6, 128.1, 128.9, 129.6, 132.7, 137.3, 137.5.
9,10-Bis(E)-4-methylstyrylanthracene) (BMSA) (Scheme 5, **10b**): ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 2.46 (s, 6H), 6.94 (d, J = 16.5 Hz, 2H), 7.31 (d, J = 7.8 Hz, 4H), 7.47-7.52 (m, 4H), 7.62 (d, J = 7.9 Hz, 4H), 7.91 (d, J = 16.5 Hz, 2H), 8.40-8.45

(m**,** 4H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 21.6, 124.2, 125.2, 126.5, 129.5, 129.6, 132.8, 134.6, 137.3, 138.0.

9,10-Bis(E)-4-chlorostyrylanthracene) (BCSA) (Scheme 5, **10c**): ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 6.82 (d, J = 16.0 Hz, 2H), 7.35-7.37 (m, 4H), 7.41-7.44 (m, 4H), 7.54-7.56 (m, 4H), 7.84 (d, J = 16.0 Hz, 2H), 8.28-8.31 (m**,** 4H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 125.4, 125.8, 126.4, 127.8, 128.2, 129.0, 129.5, 132.3, 135.7, 136.3.

General procedure for the synthesis of biphenyls

To a round bottom flask (10 mL), aryl halide (1 mmol), phenylboronic acid derivatives (1.2 mmol), and sodium carbonate (2.5 mmol) in water (3 mL), catalyst Fe_3O_4@Pd@Ni/C (0.05 g, with respect to Pd content 2.19 mol%) was added and heated on oil bath at 80 ˚C. The reaction was continuously followed by TLC to completion. After completion, the catalyst was removed by external magnet and was washed with dichloromethane (3 × 5 mL). Having extracted the reaction mixture from dichloromethane and water, the organic phase was dried over Na_2SO_4. Evaporation of the solvent gave products. For further purification, the products passed through a short column of silica gel using *n*-hexane as eluent.

[It worth mentioning, in the case of 1,4-dihalobenzene (1 mmol), phenylboronic acid derivatives (2.4 mmol), and Na_2CO_3 (2.5 mmol) in water (3 mL), catalyst Fe_3O_4@Pd@Ni/C (0.1 g, with respect to Pd content 4.38 mol%) was added and heated on oil bath at 80 ˚C].

3,3"-Dimethyl-1,1';4',1"-terphenyl (Scheme 7, **14b**): ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 2.48 (s, 6H), 7.22 (d, J = 7.5 Hz, 2H), 7.39 (t, J = 7.5 Hz, 2H), 7.46-7.53 (m, 4H), 7.70 (s, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 21.6, 124.2, 127.5, 127.9, 128.1, 129.0, 138.4, 140.2, 140.8.

2,2"-Dimethyl-1,1';4',1"-terphenyl (Scheme 7, **14c**): ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 2.31 (s, 6H), 7.20-7.28 (m, 8H), 7.33 (s, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 20.5, 125.7, 127.2, 128.8, 129.8, 130.3, 135.4, 140.3, 141.6.

4,4"-Difluoro-1,1';4',1"-terphenyl (Scheme 7, **14d**): ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.14-7.23 (m, 4H), 7.59-7.63 (m, 4H), 7.64 (s, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 115.7 ($J_{C\text{-}F}$ = 22 Hz), 127.4, 128.6 ($J_{C\text{-}F}$ = 8 Hz), 136.7 ($J_{C\text{-}F}$ = 3 Hz), 139.2, 162.6 ($J_{C\text{-}F}$ = 245 Hz).

2,4-Di(naphthalene-1-yl)benzene (Scheme 7, **14e**): ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.39-7.52 (m, 8H), 7.55 (s, 4H), 7.80-7.89 (m, 4H), 7.98-8.02 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 125.5, 125.9, 126.1, 126.2, 127.1, 127.8, 128.4, 130.0, 131.7, 133.9, 139.7, 140.0.

4-Iodo-4'-methoxy-1,1'-biphenyl (Scheme 7, **15**): ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 3.78 (s, 6H), 6.87-6.94 (m, 2H), 7.19-7.24 (m, 2H), 7.38-7.44 (m, 2H), 7.62-7.71 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 55.4, 92.2, 114.4, 127.9, 128.6, 132.5, 137.8, 140.3, 159.5.

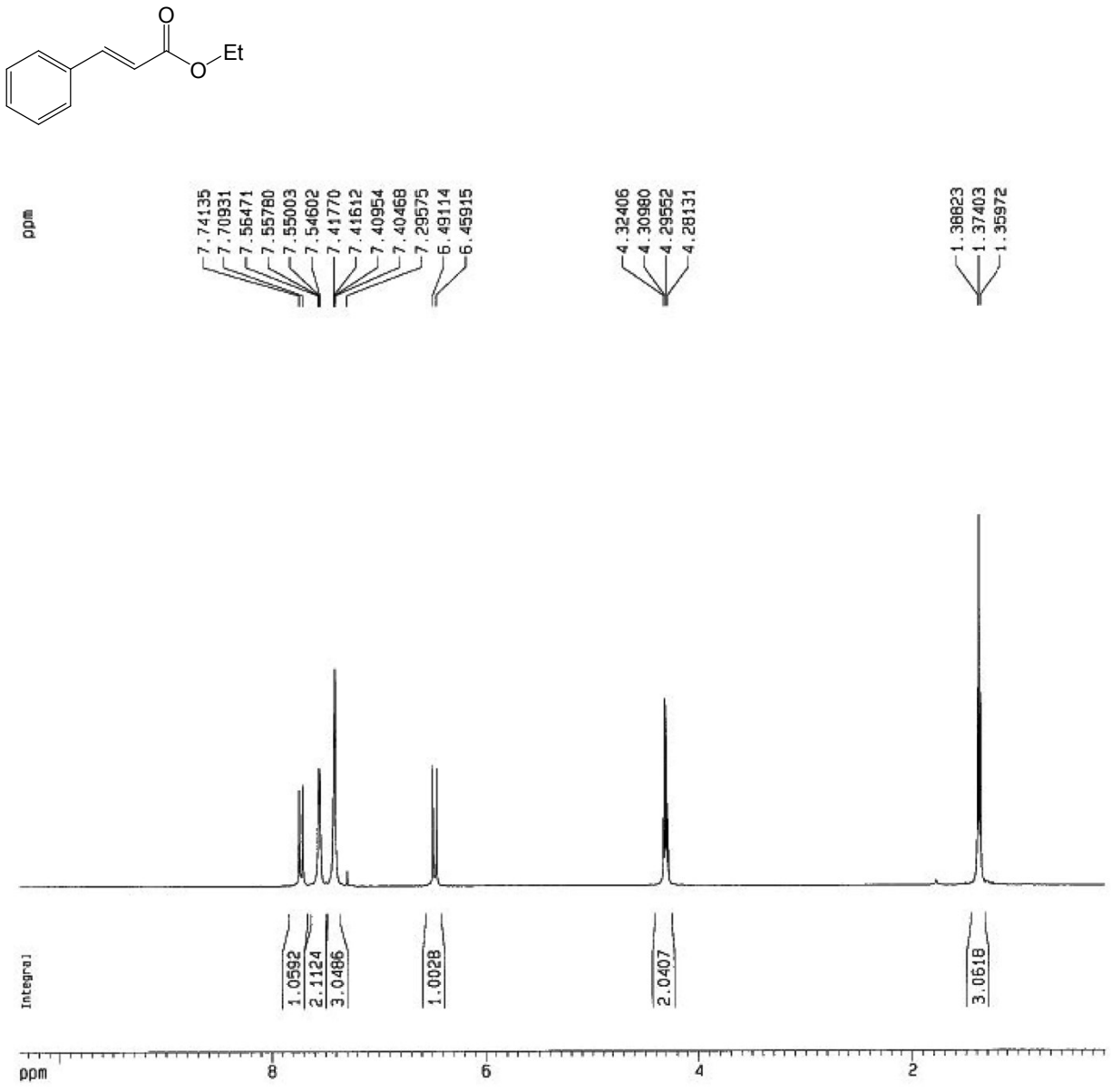


Figure 3. ^{1}H-NMR for compound **3a**

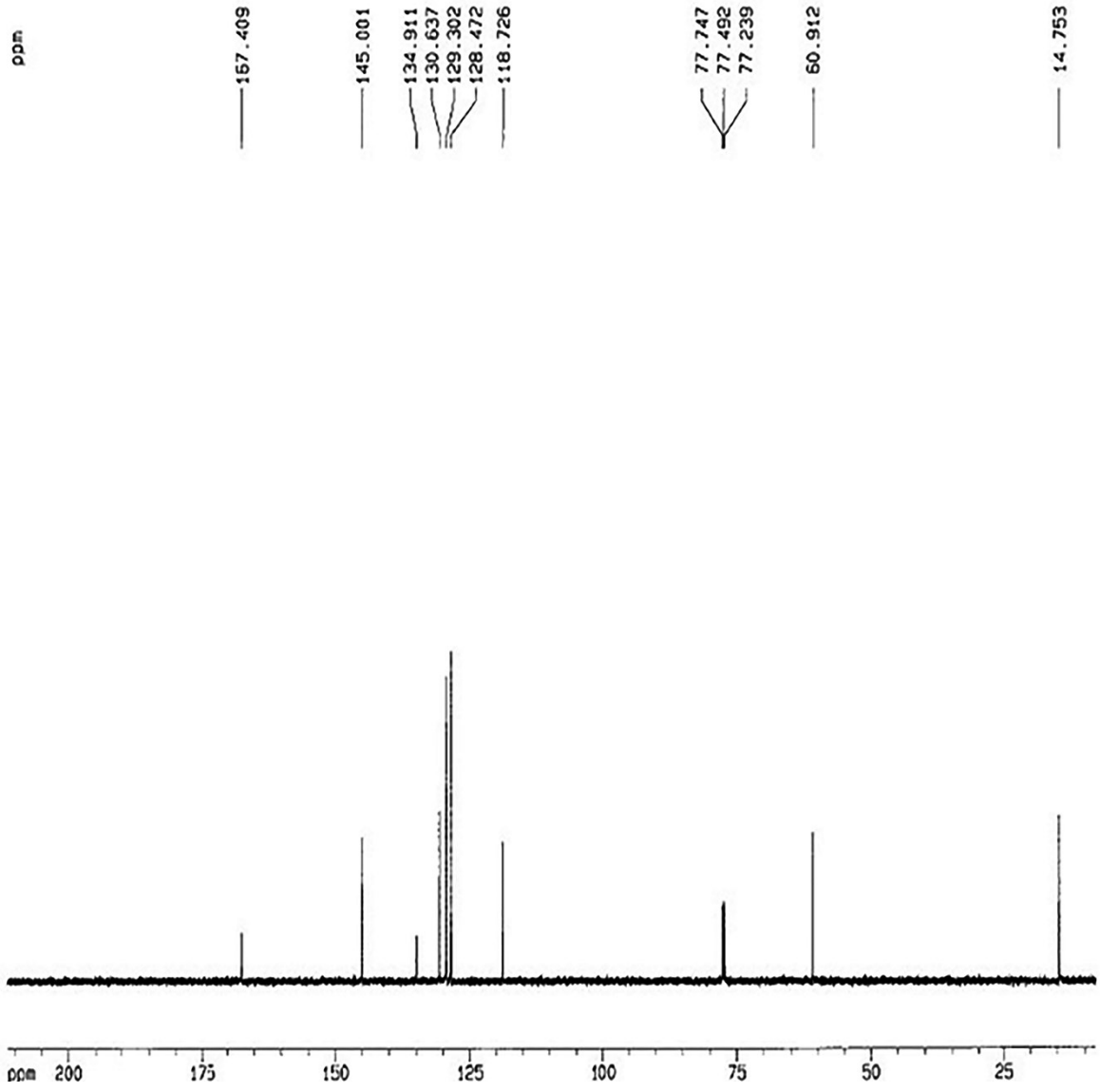


Figure 4. ^{13}C-NMR for compound **3a**

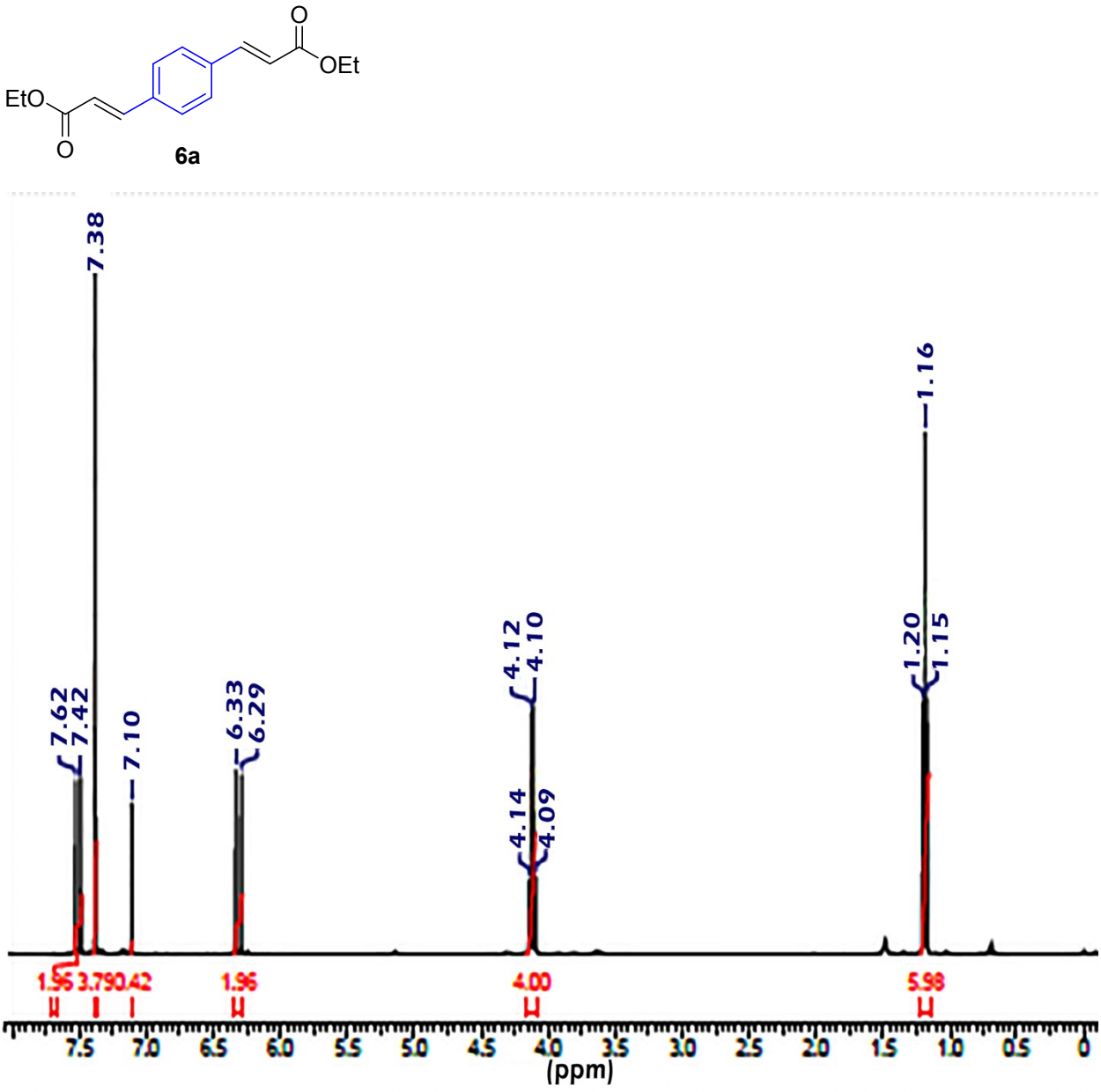


Figure 5. ^{1}H-NMR for compound **6a**

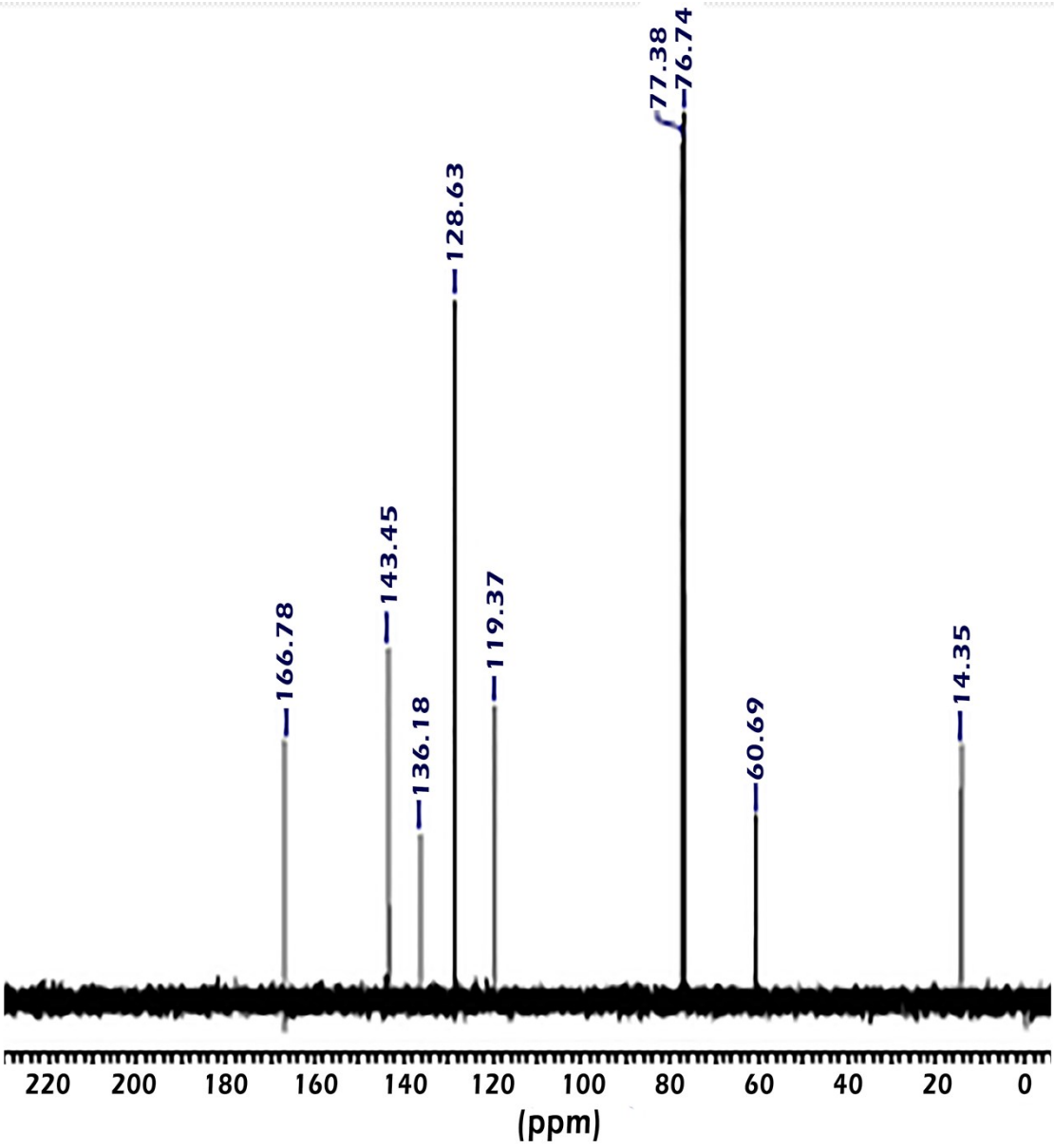


Figure 6. ^{13}C-NMR for compound **6a**

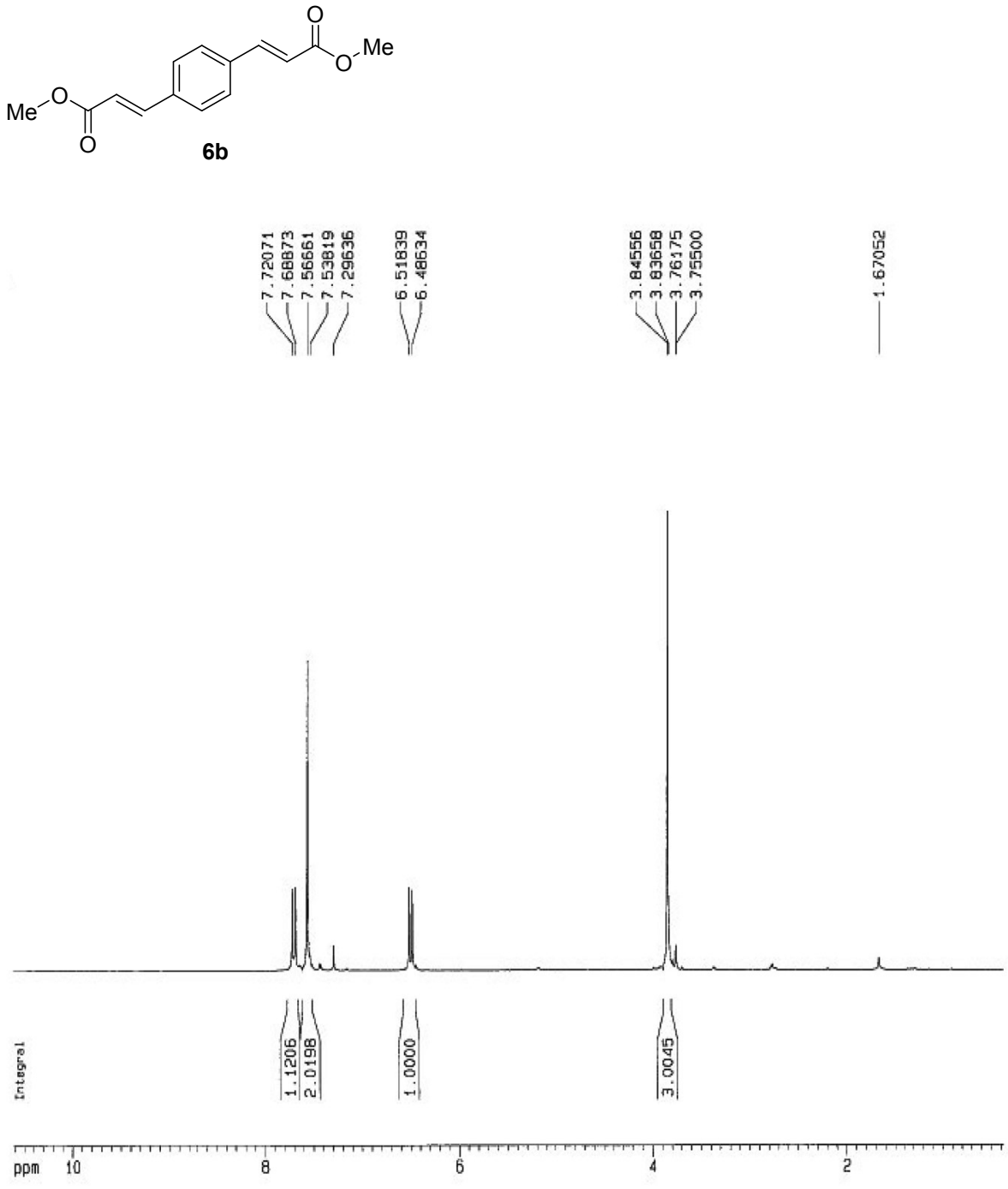


Figure 7. ^{1}H-NMR for compound **6b**

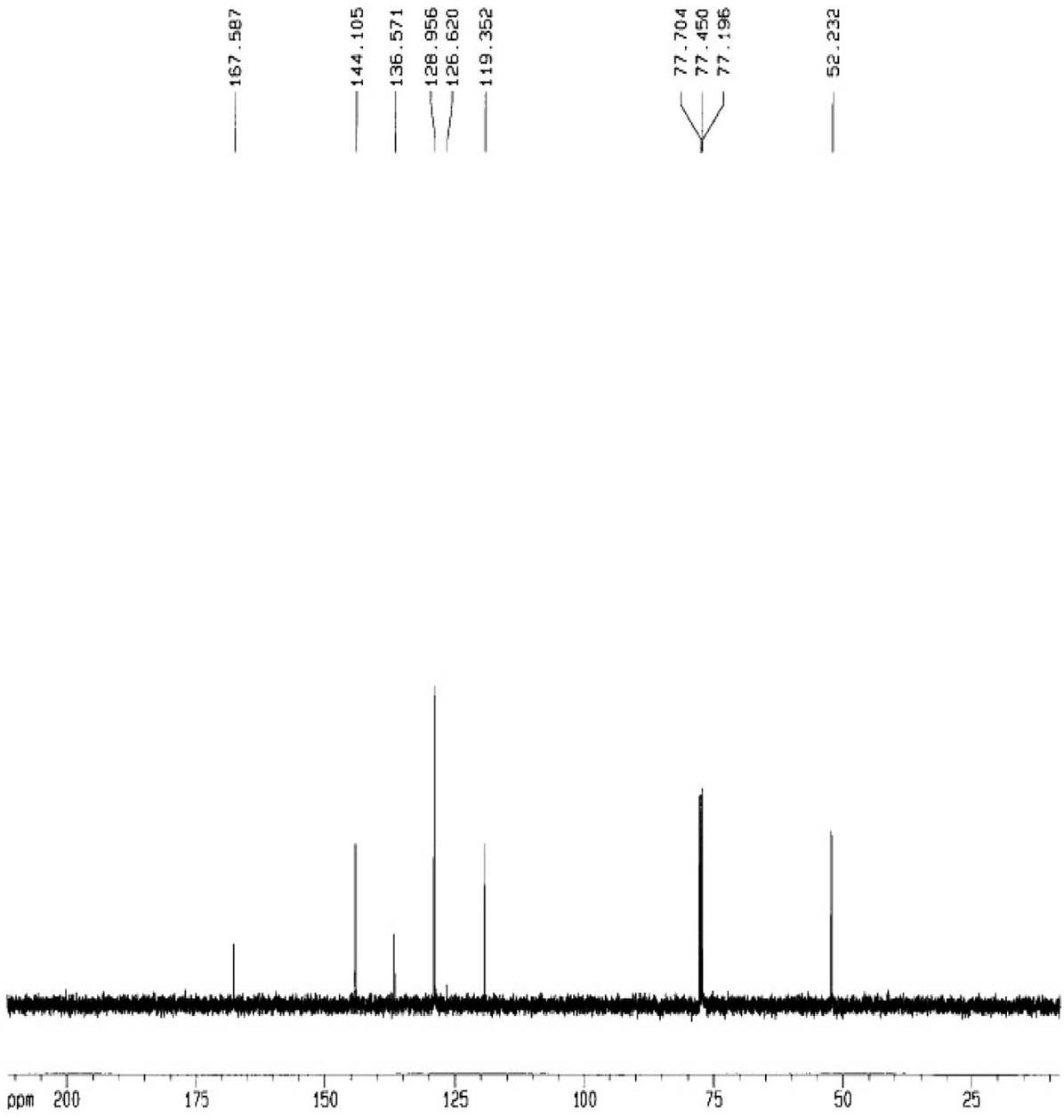
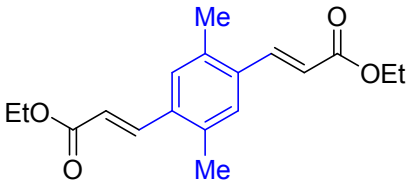


Figure 8. ^{13}C-NMR for compound **6b**



6c

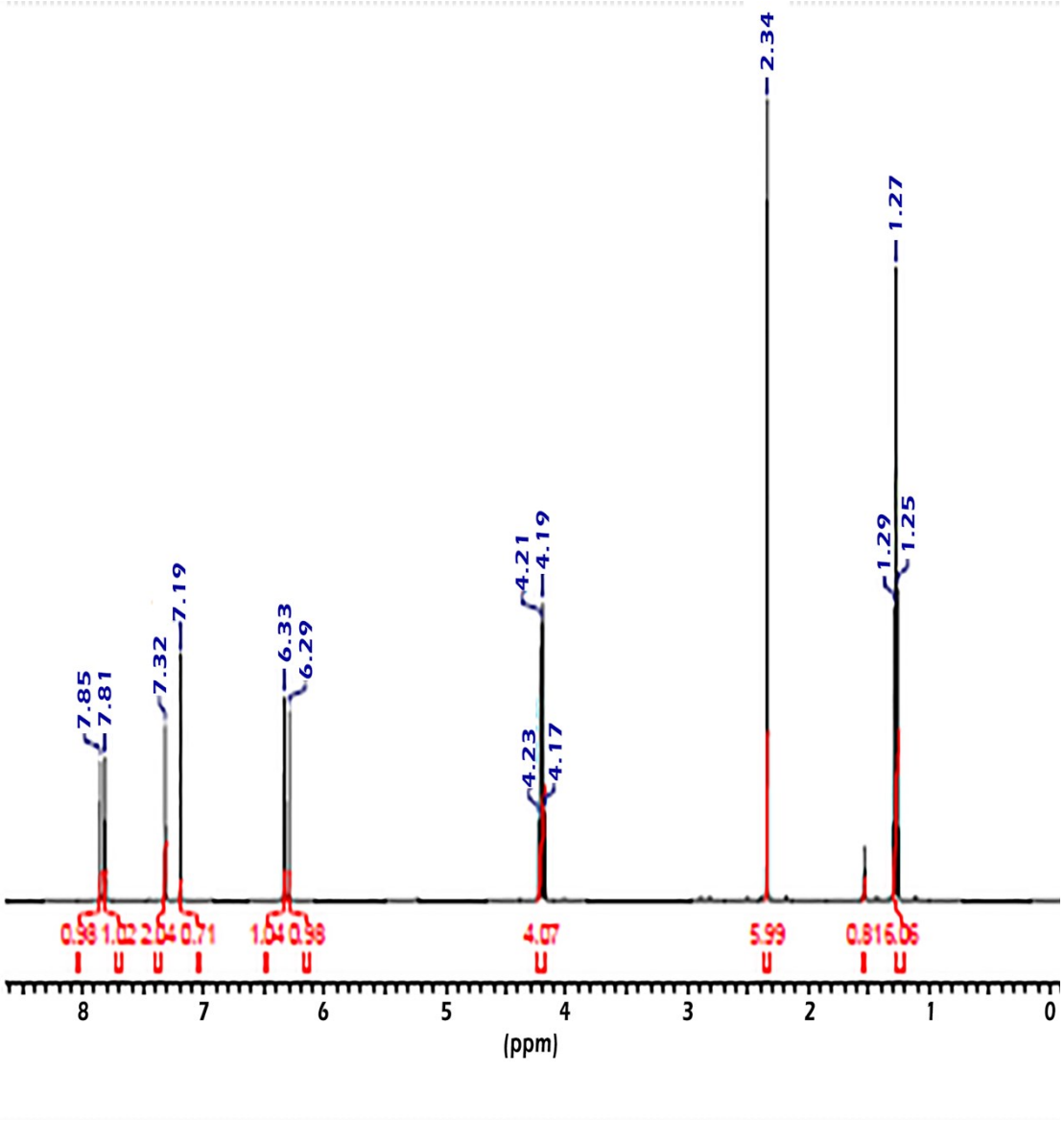


Figure 9. ^{1}H-NMR for compound **6c**.

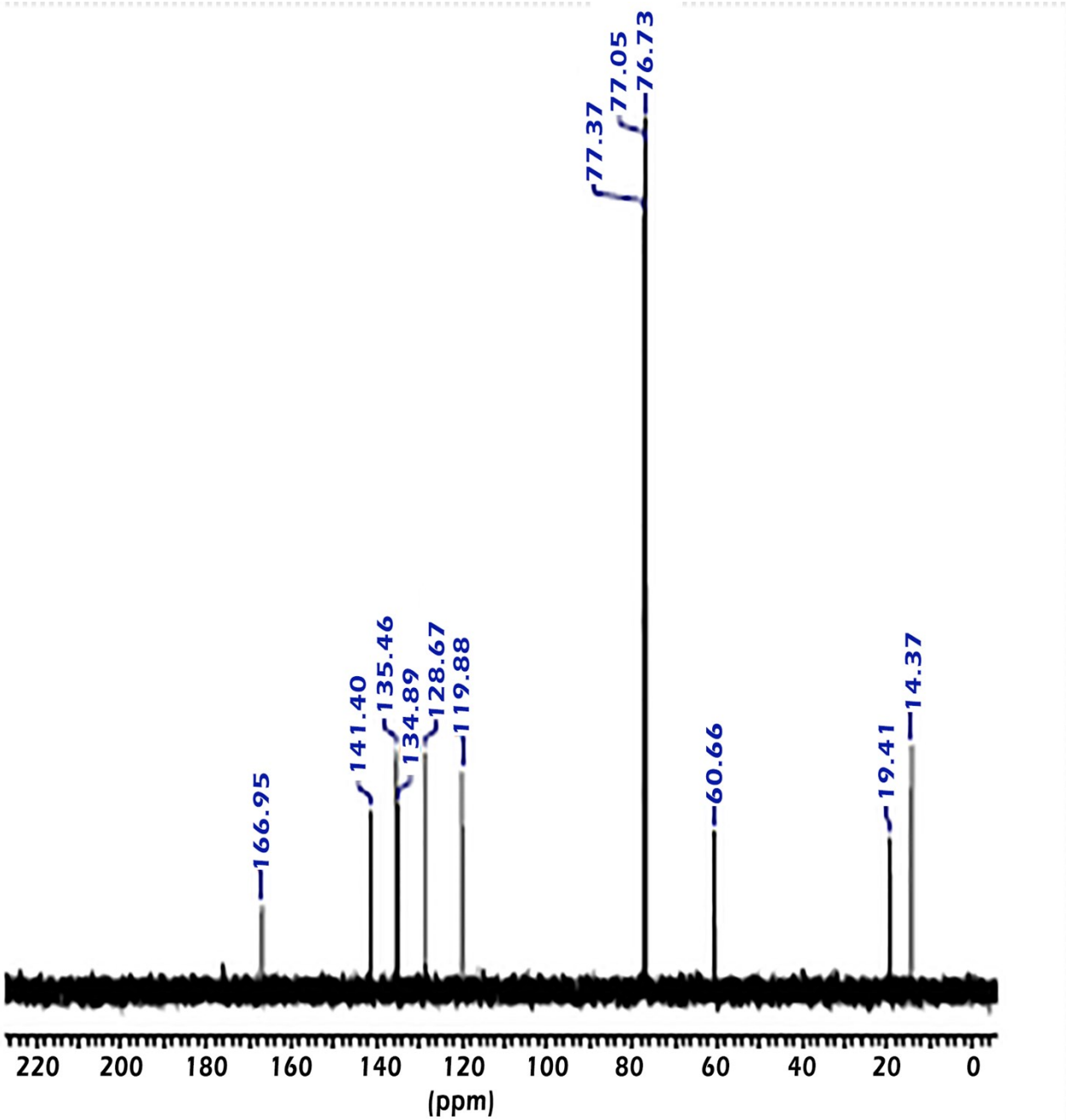
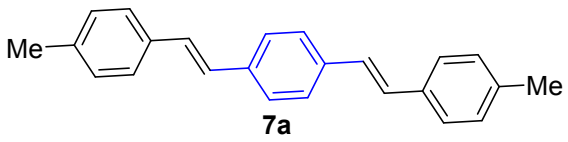


Figure 10. ^{13}C-NMR for compound **6c**.



7a

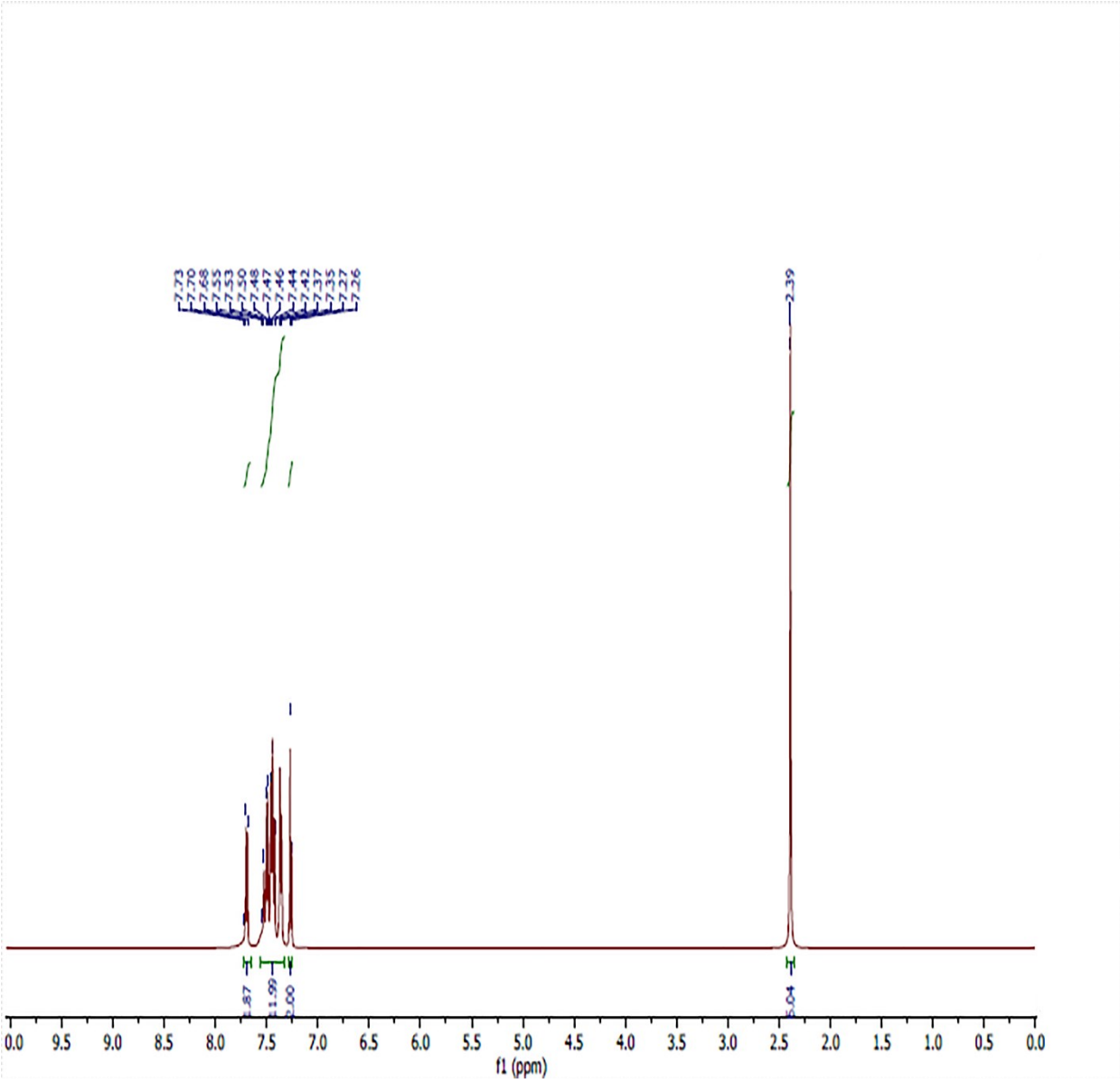


Figure 11. ^{1}H-NMR for compound **7a**.

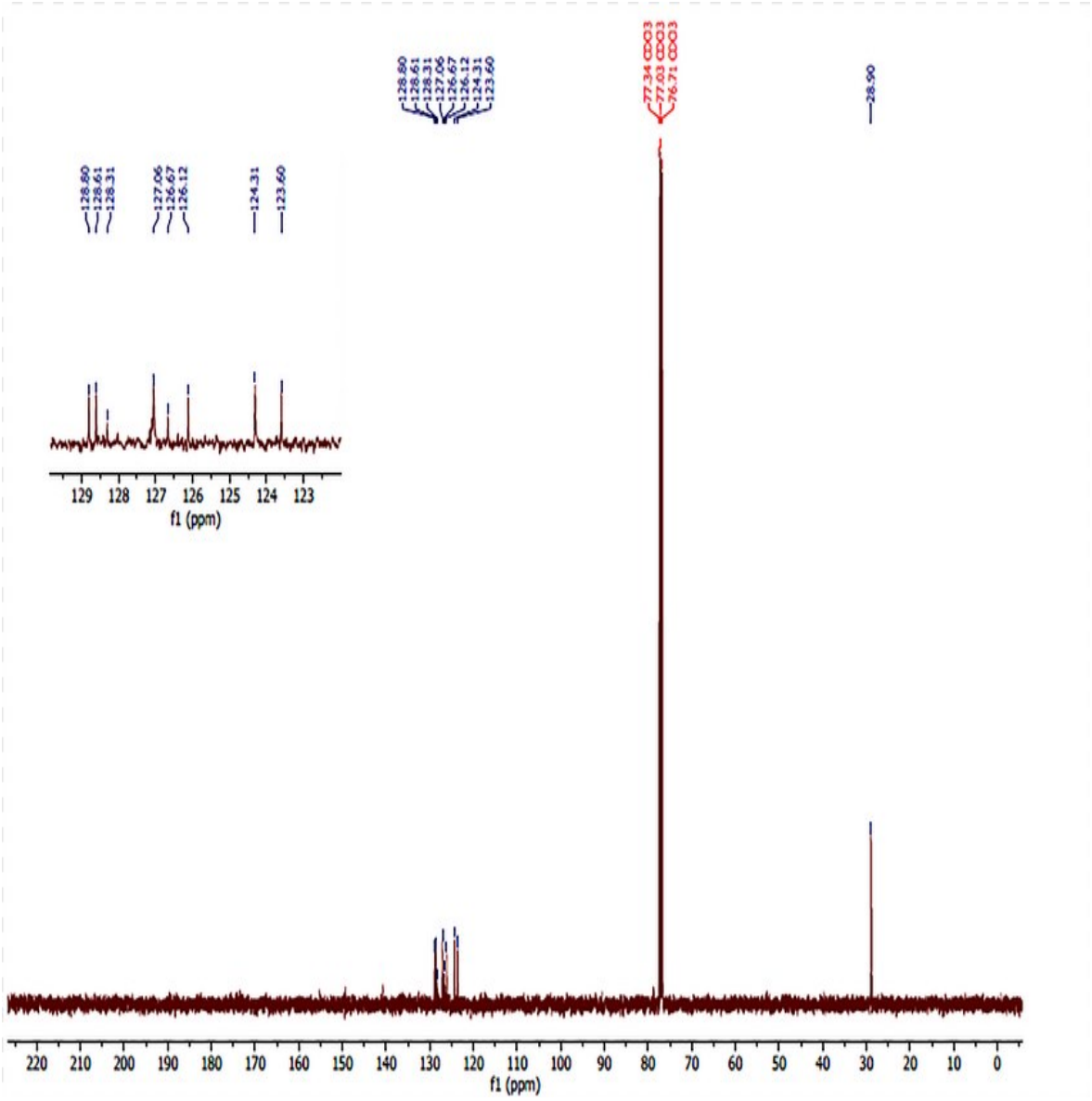
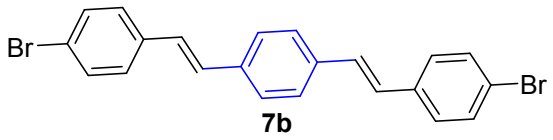


Figure 12. ^{13}C-NMR for compound **7a**.



7b

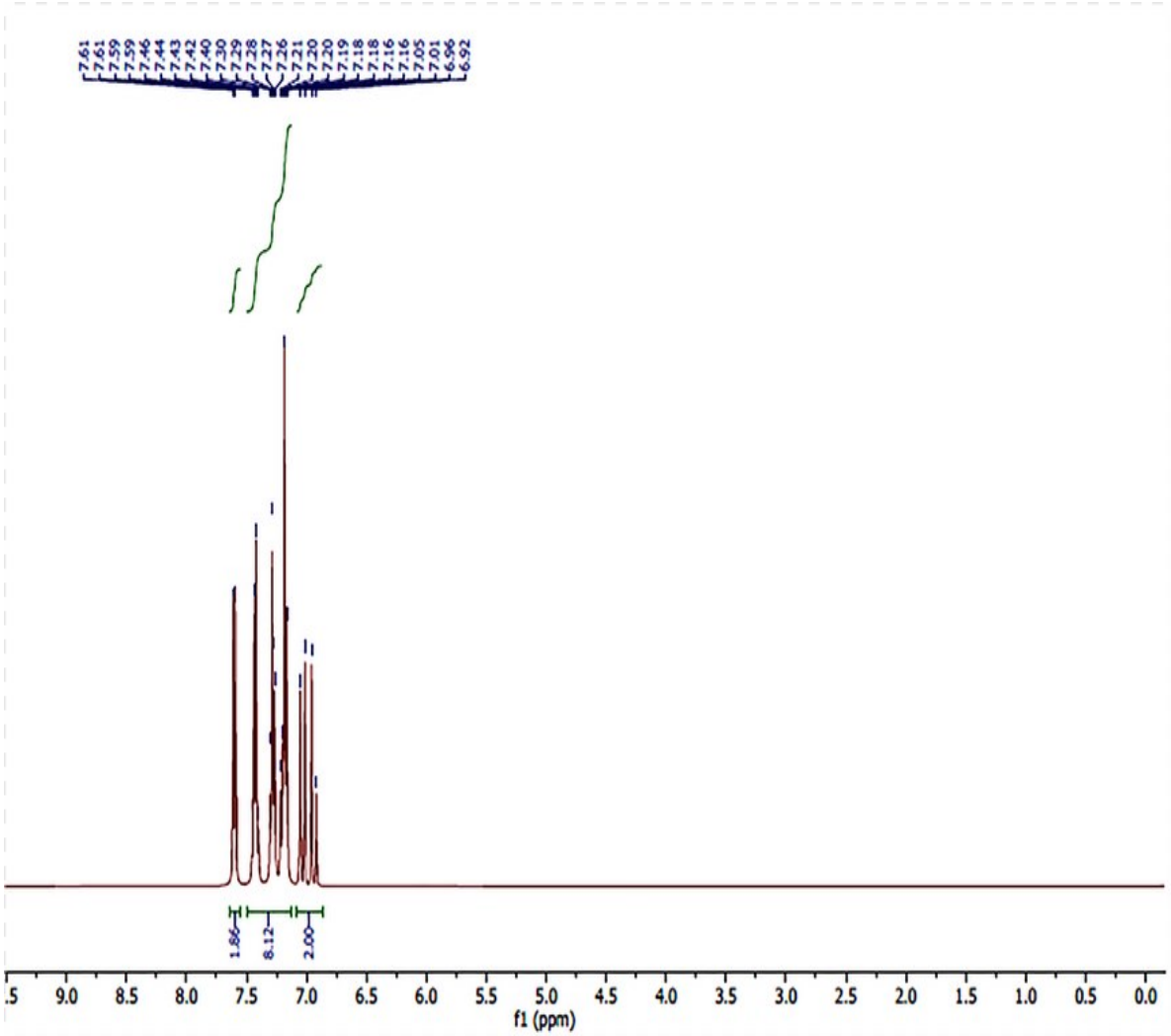


Figure 13. ^{1}H-NMR for compound **7b**.

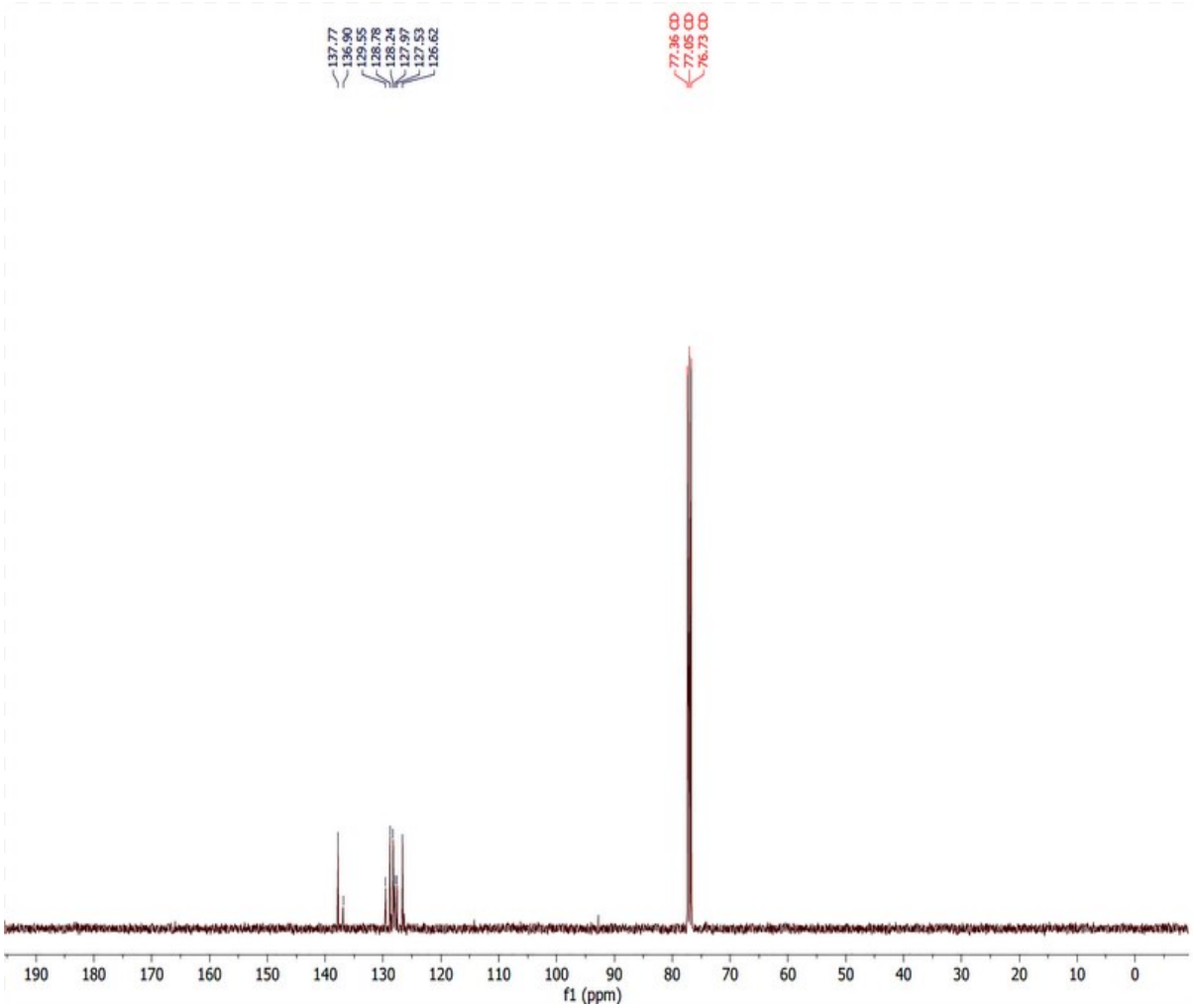
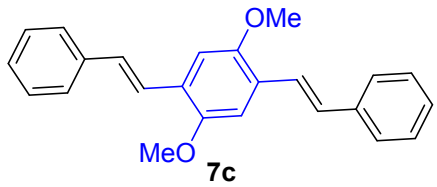


Figure 14. ^{13}C-NMR for compound **7b**.



7c

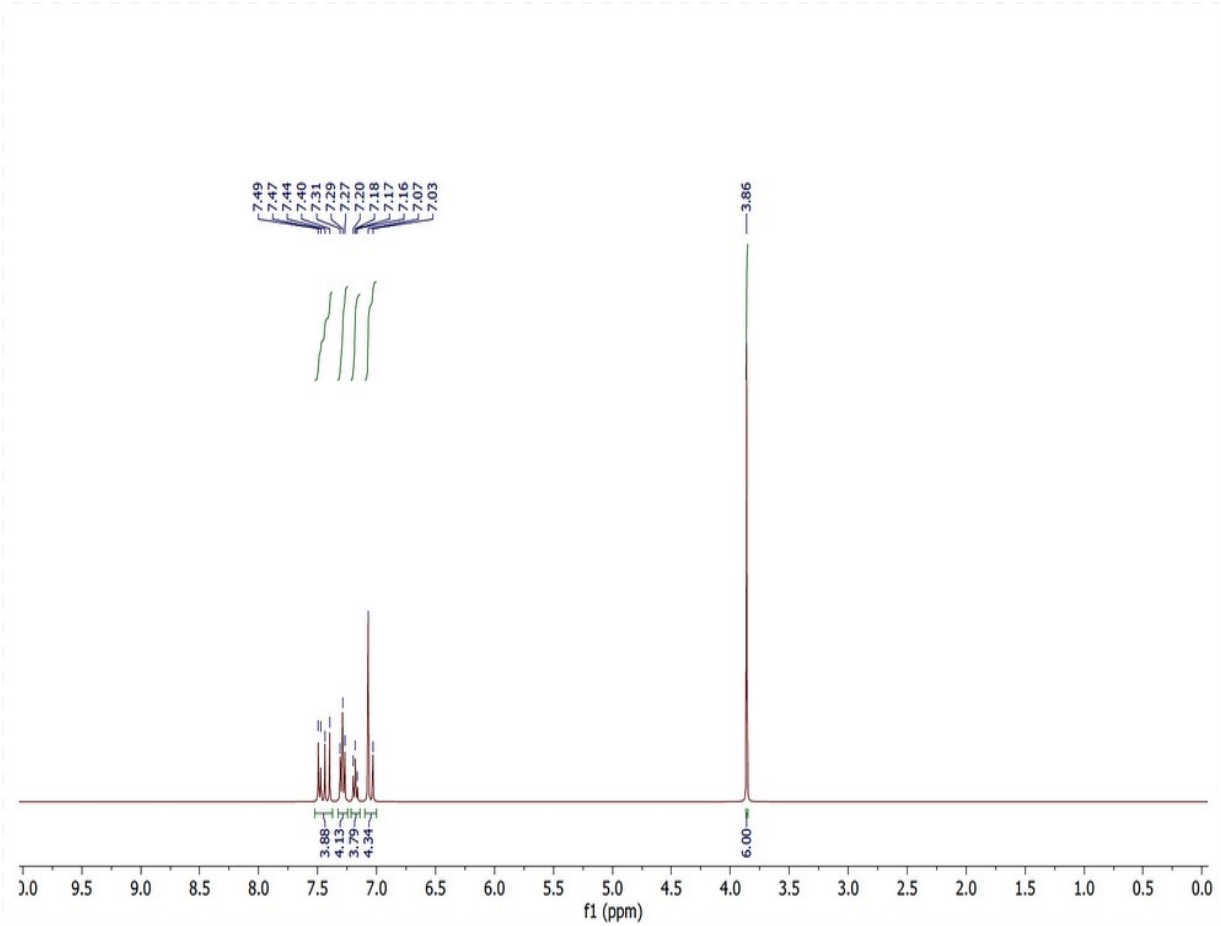


Figure 15. ^{1}H-NMR for compound **7c**.

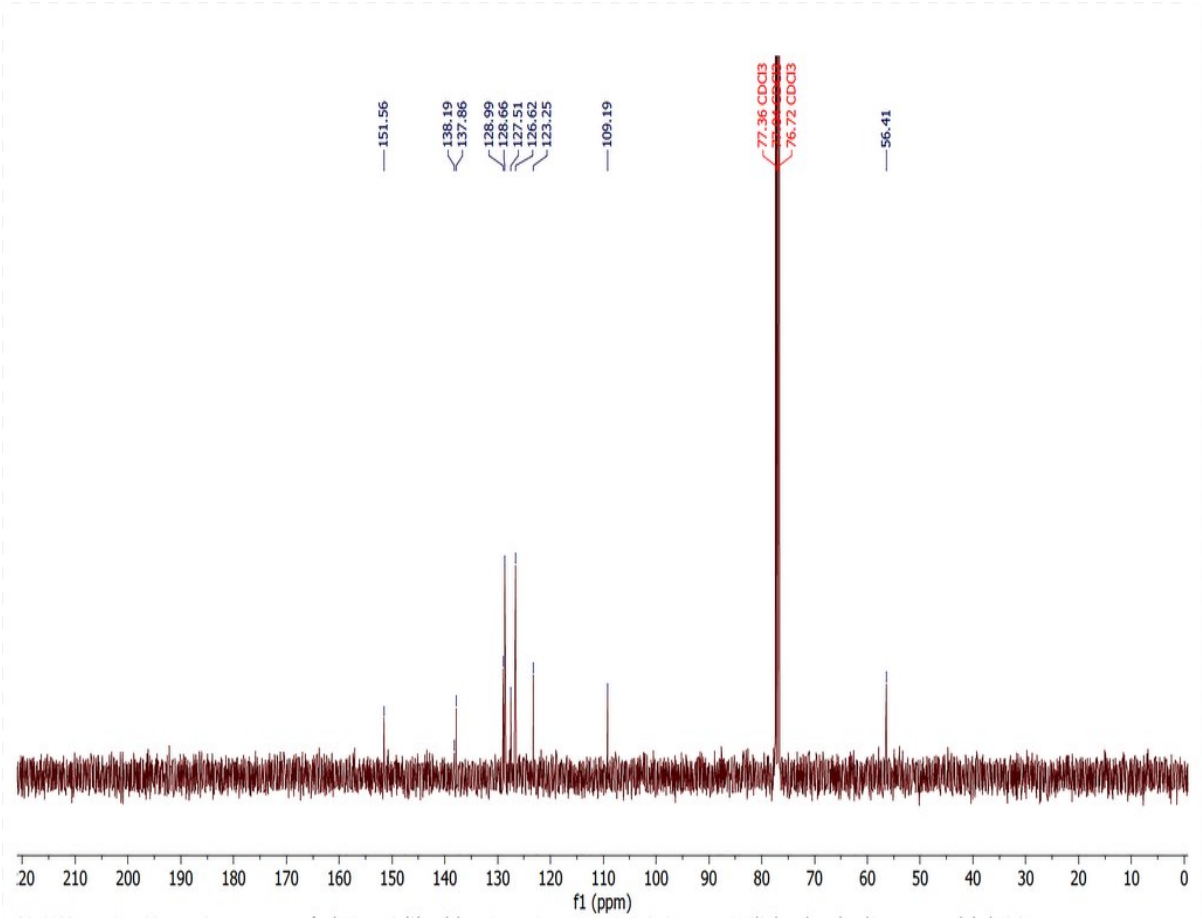
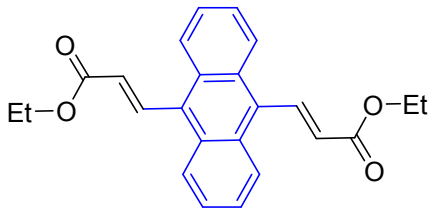


Figure 16. ^{13}C-NMR for compound **7c**.



9

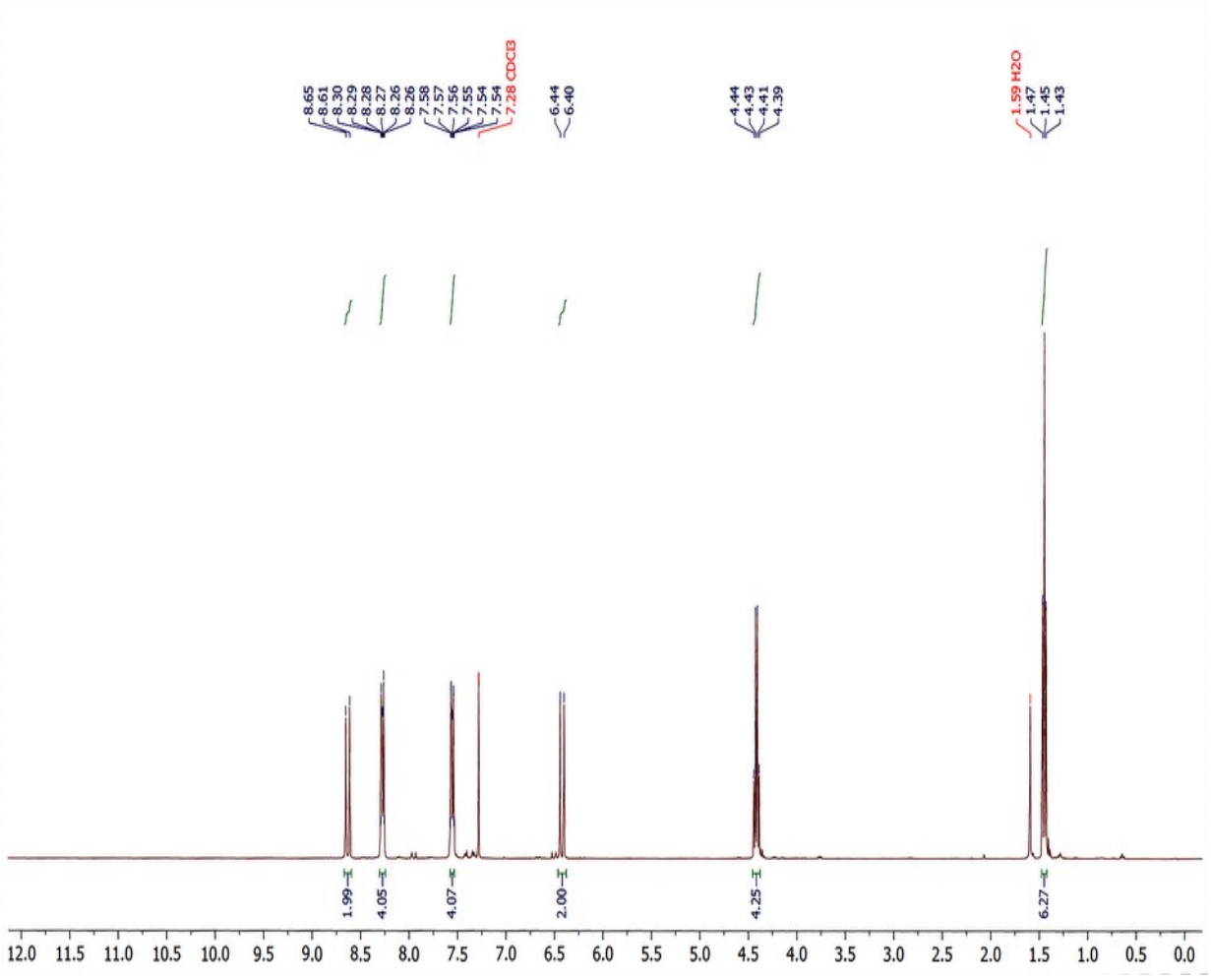


Figure 17. ^{1}H-NMR for compound **9**

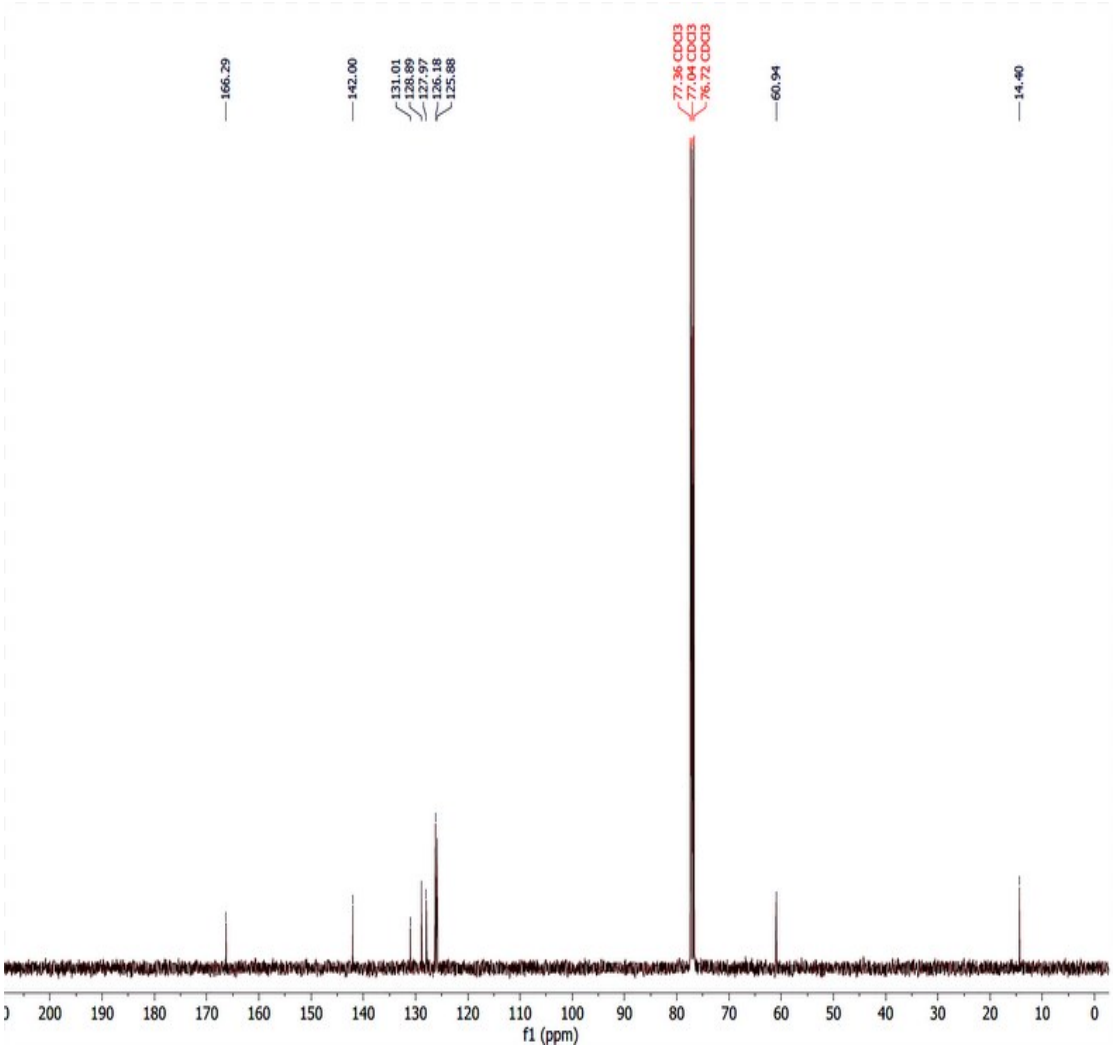
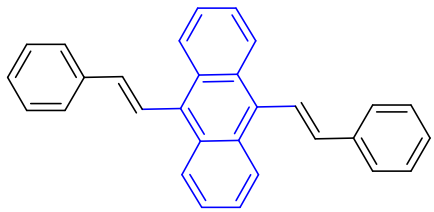


Figure 18. ^{13}C-NMR for compound **9**



10a

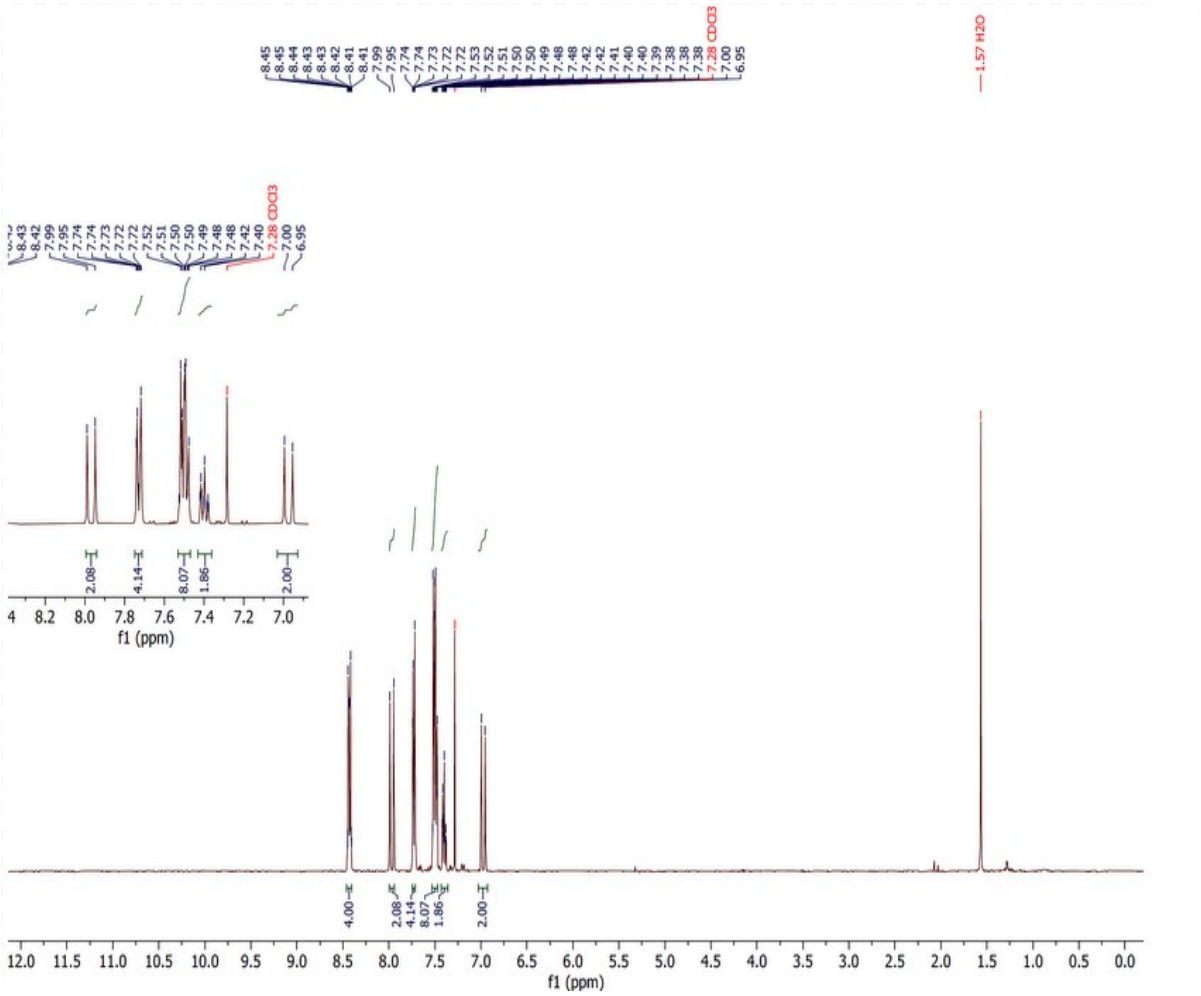


Figure 19. ^{1}H-NMR for compound **10a**

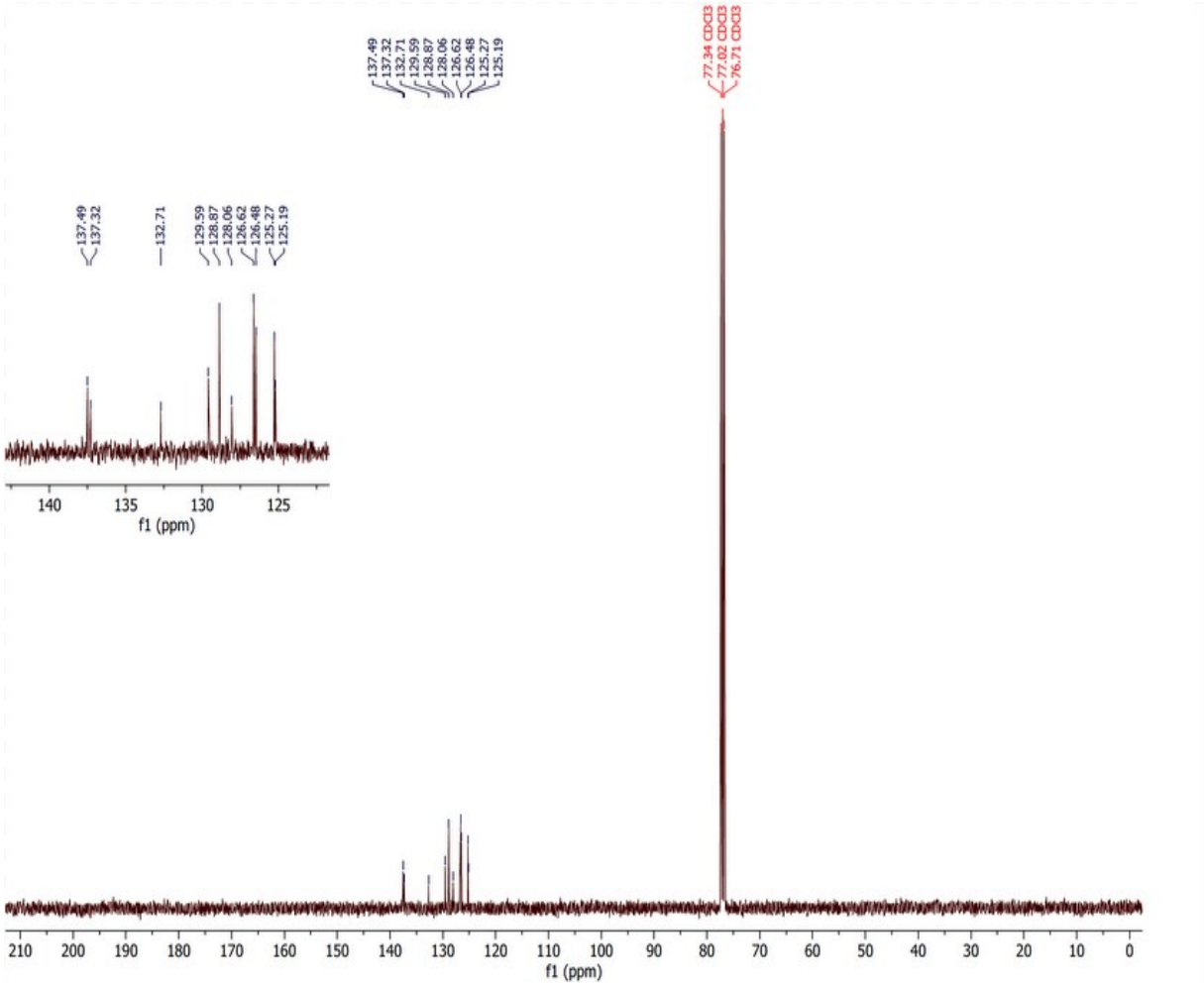
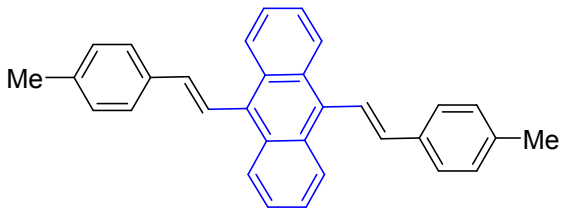


Figure 20. ^{13}C-NMR for compound **10a**



10b

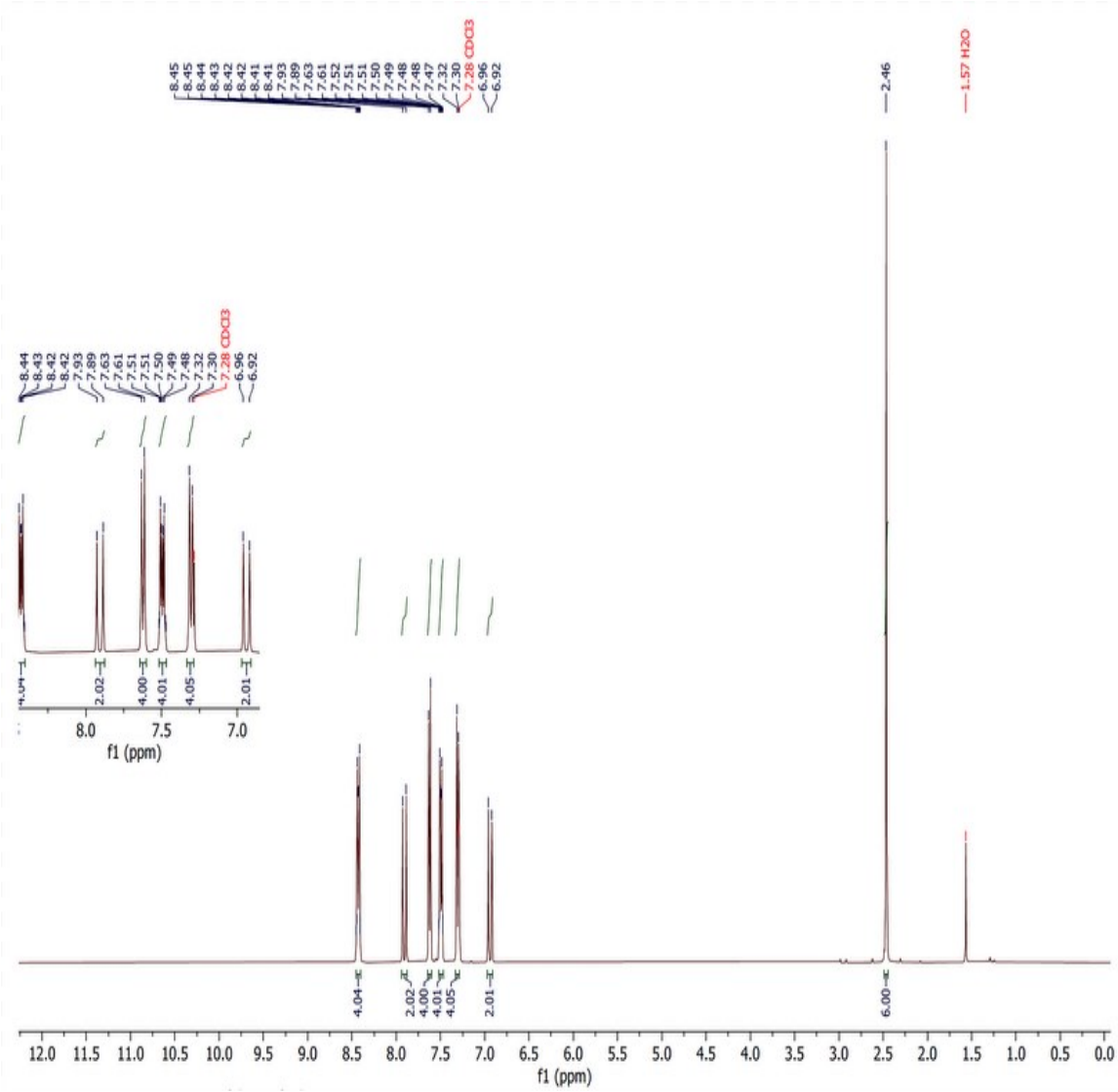


Figure 21. ^{1}H-NMR for compound **10b**

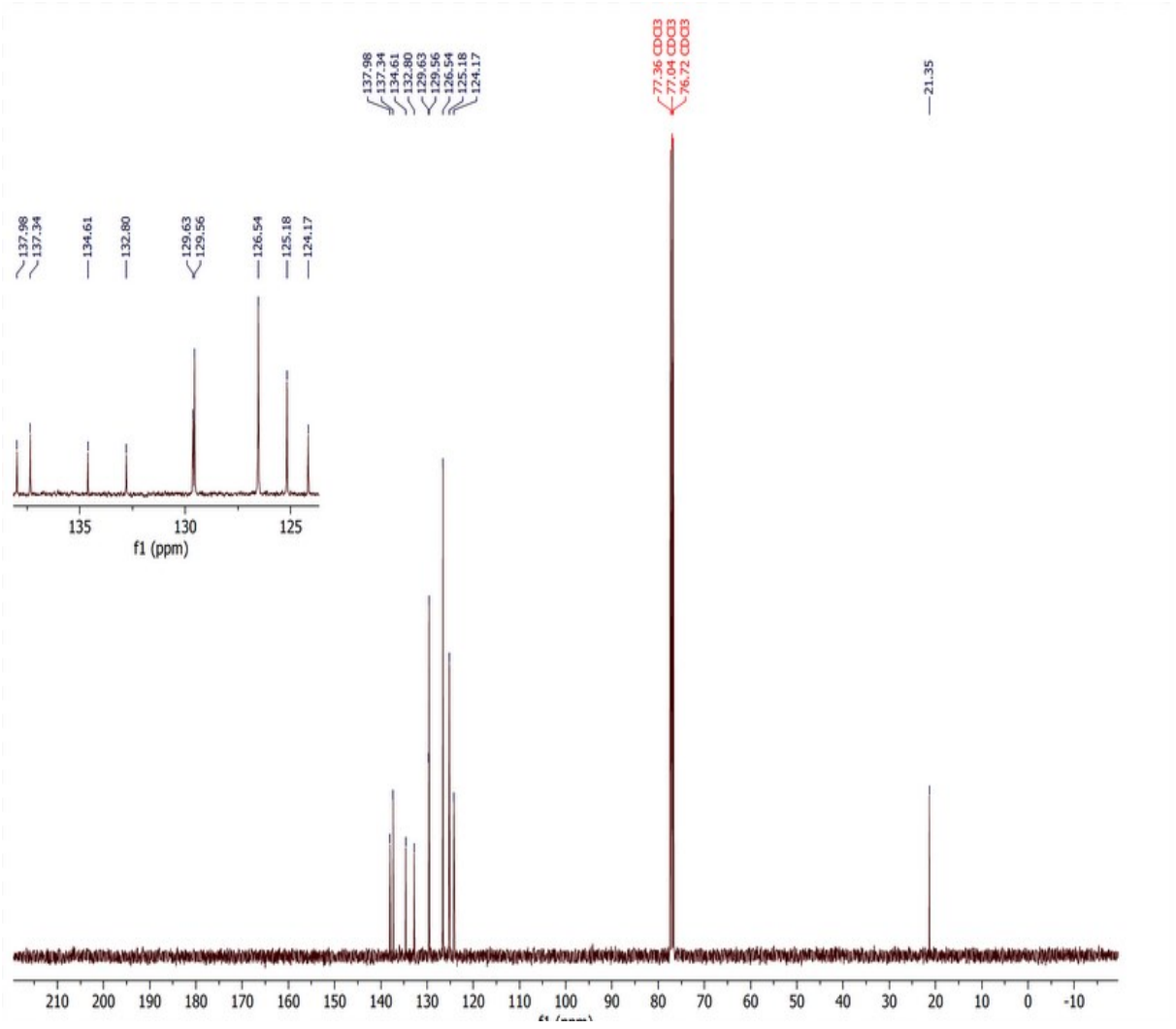


Figure 22. ^{13}C-NMR for compound **10b**

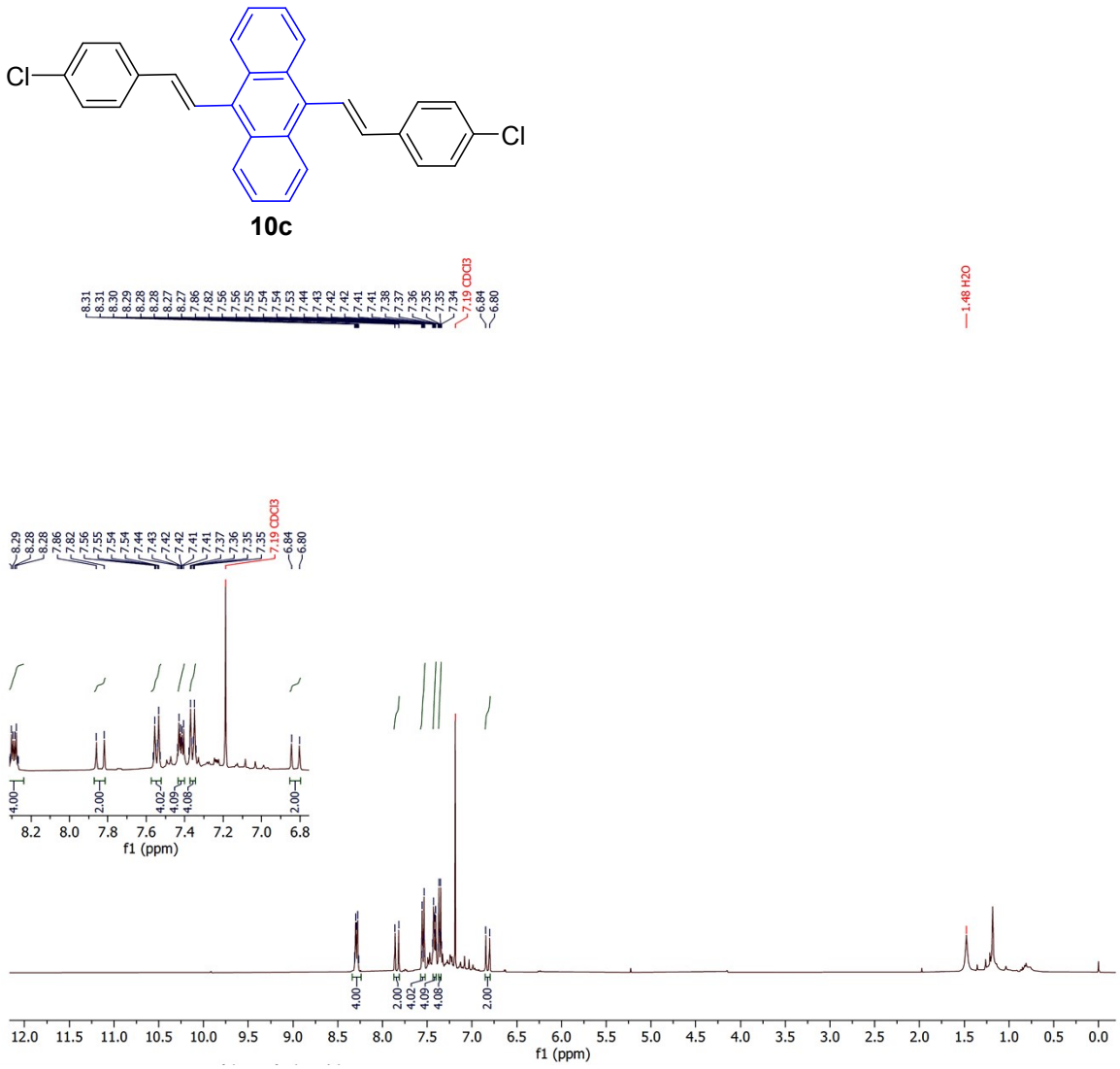


Figure 23. ^{1}H-NMR for compound **10c**

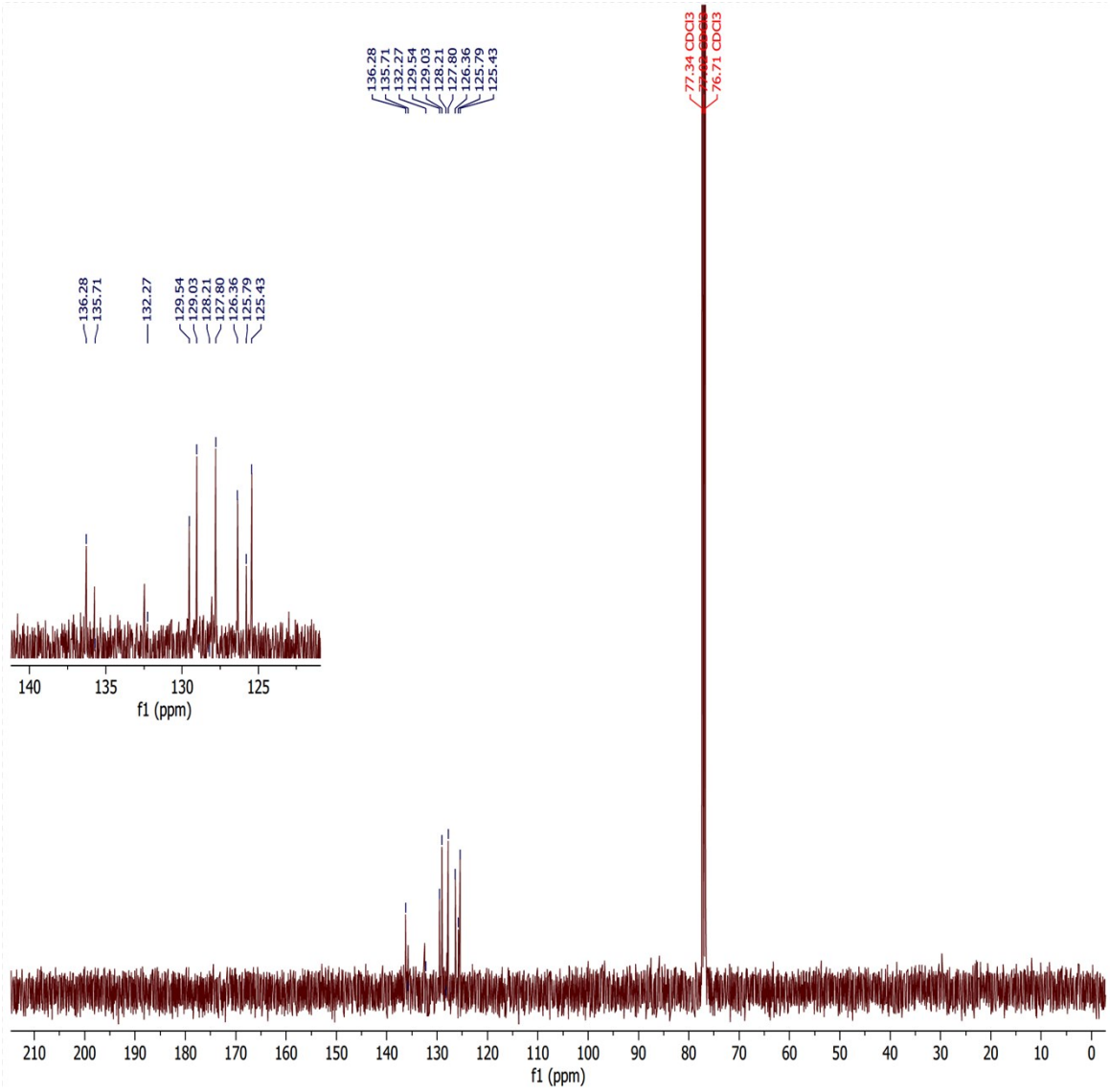


Figure 24. ^{13}C-NMR for compound **10c**

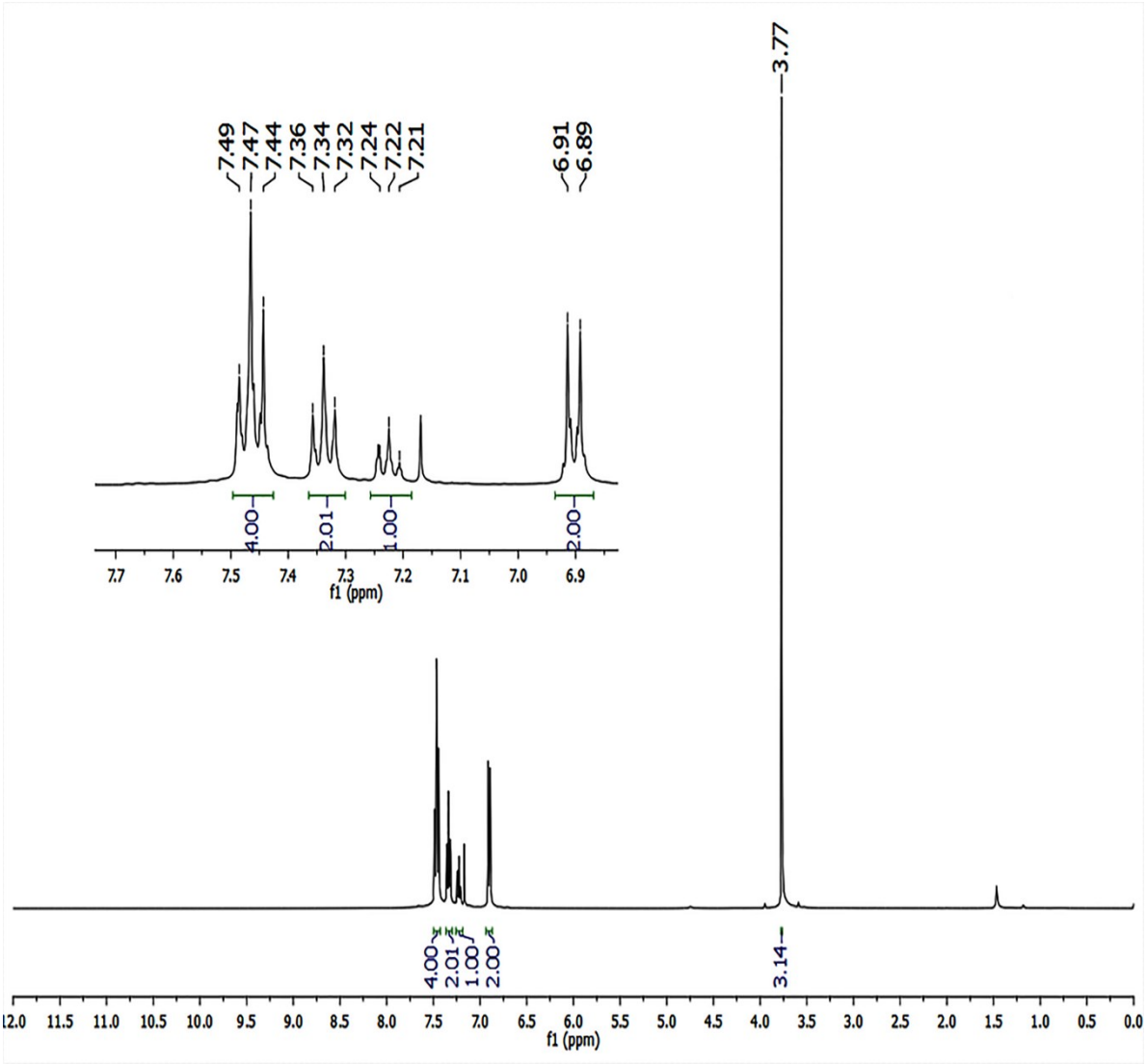


Figure 25. ^{1}H-NMR for compound **13**

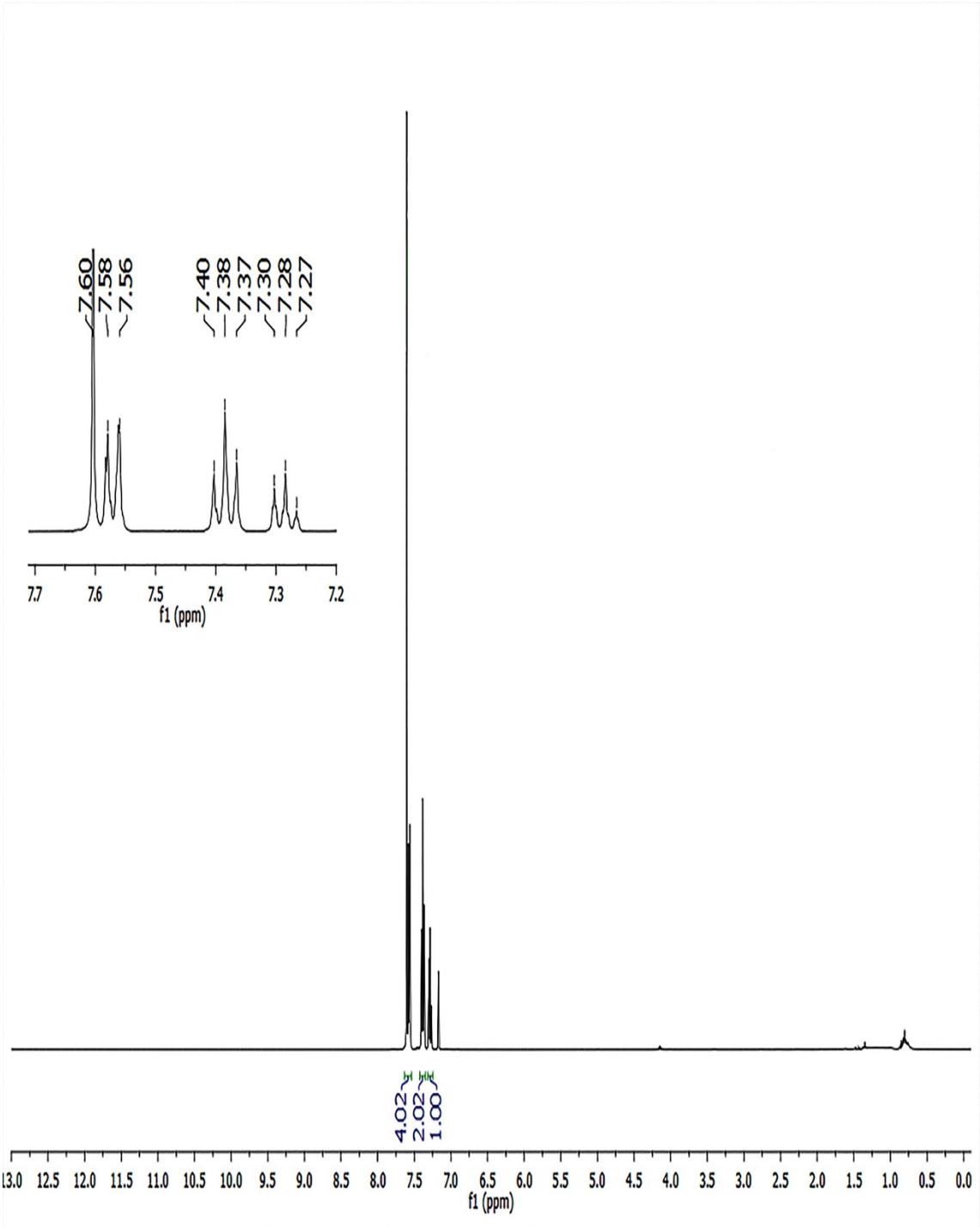


Figure 26. ^{1}H-NMR for compound **14a**

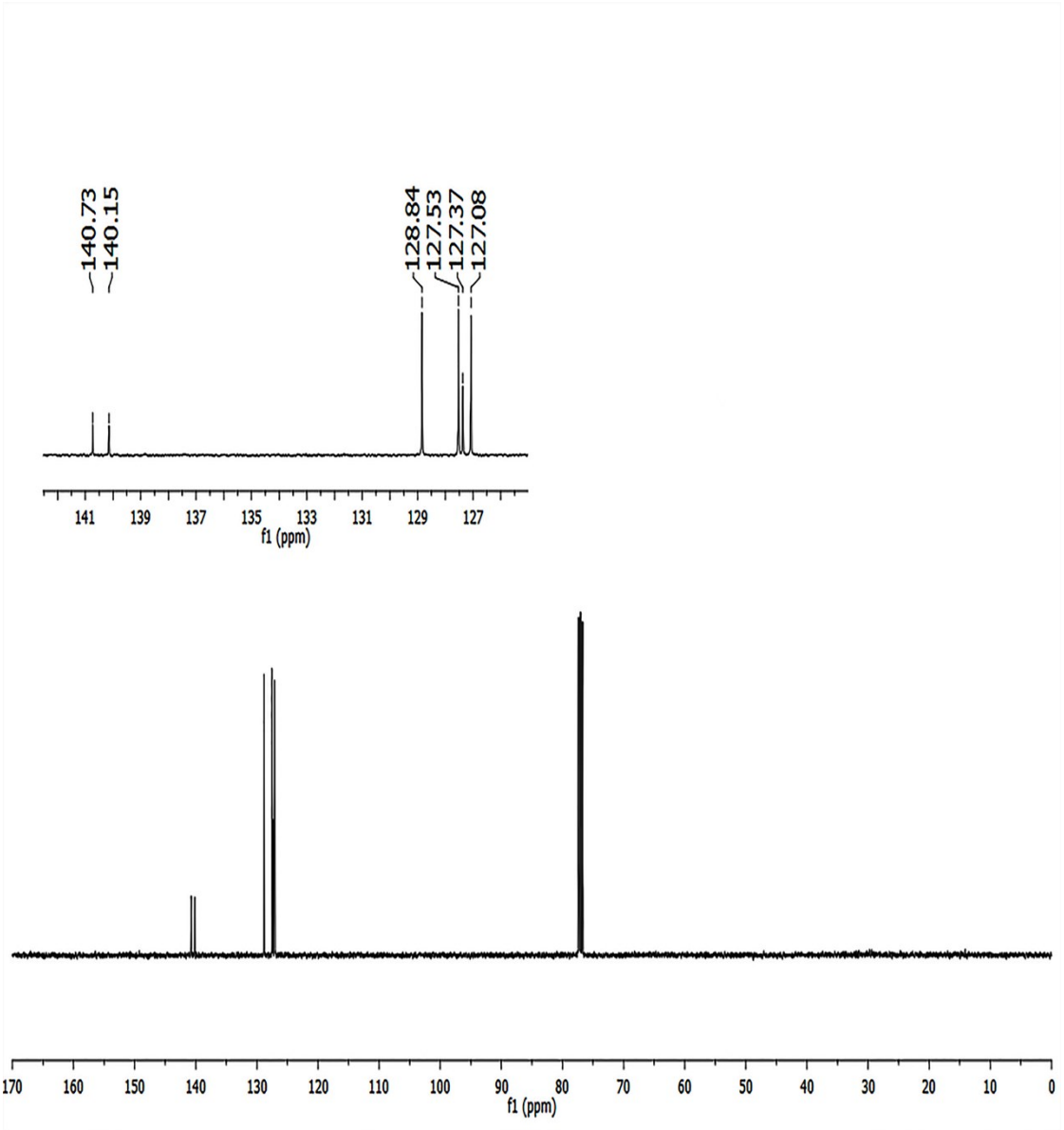


Figure 27. ^{13}C-NMR for compound **14a**

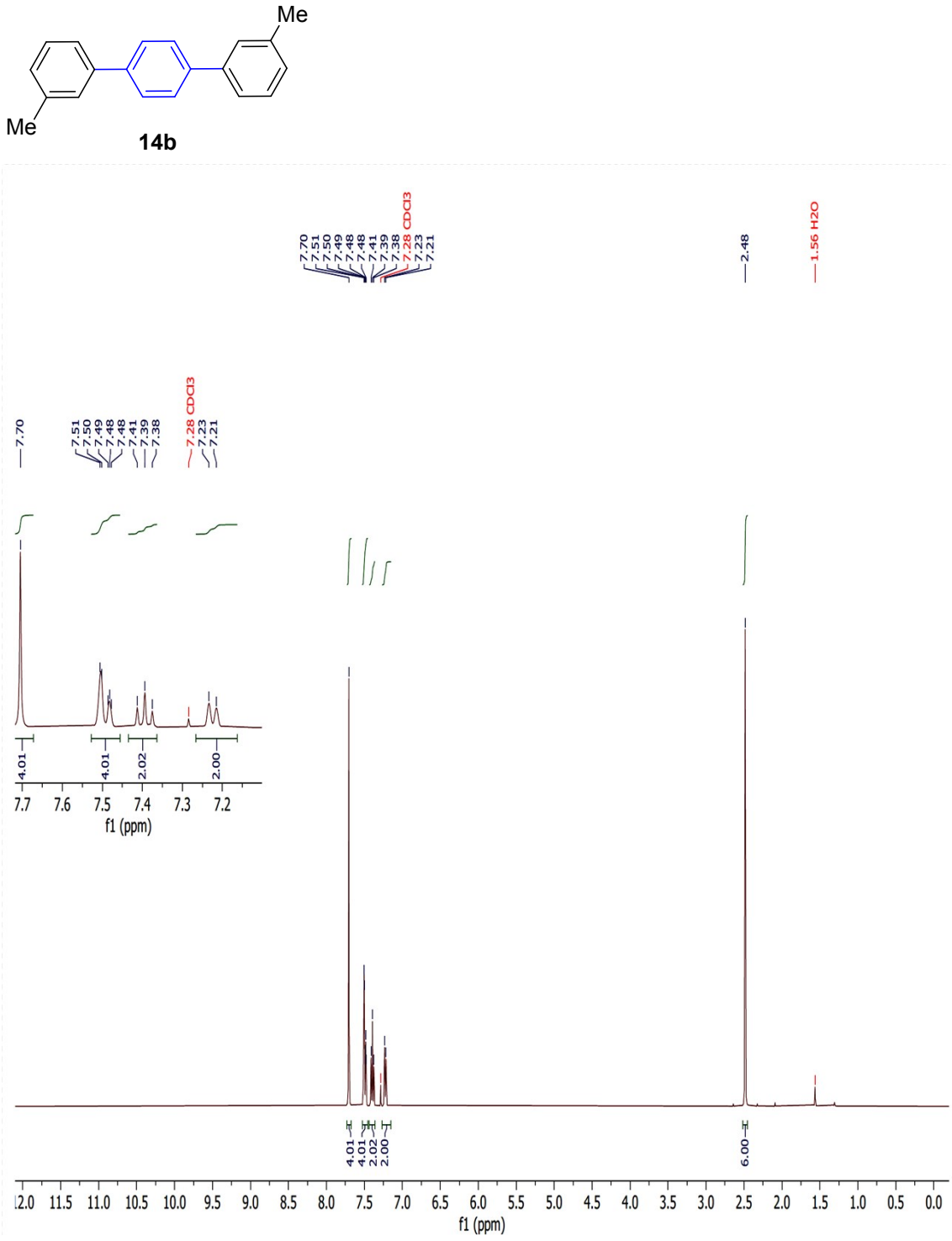


Figure 28. ^{1}H-NMR for compound **14b**

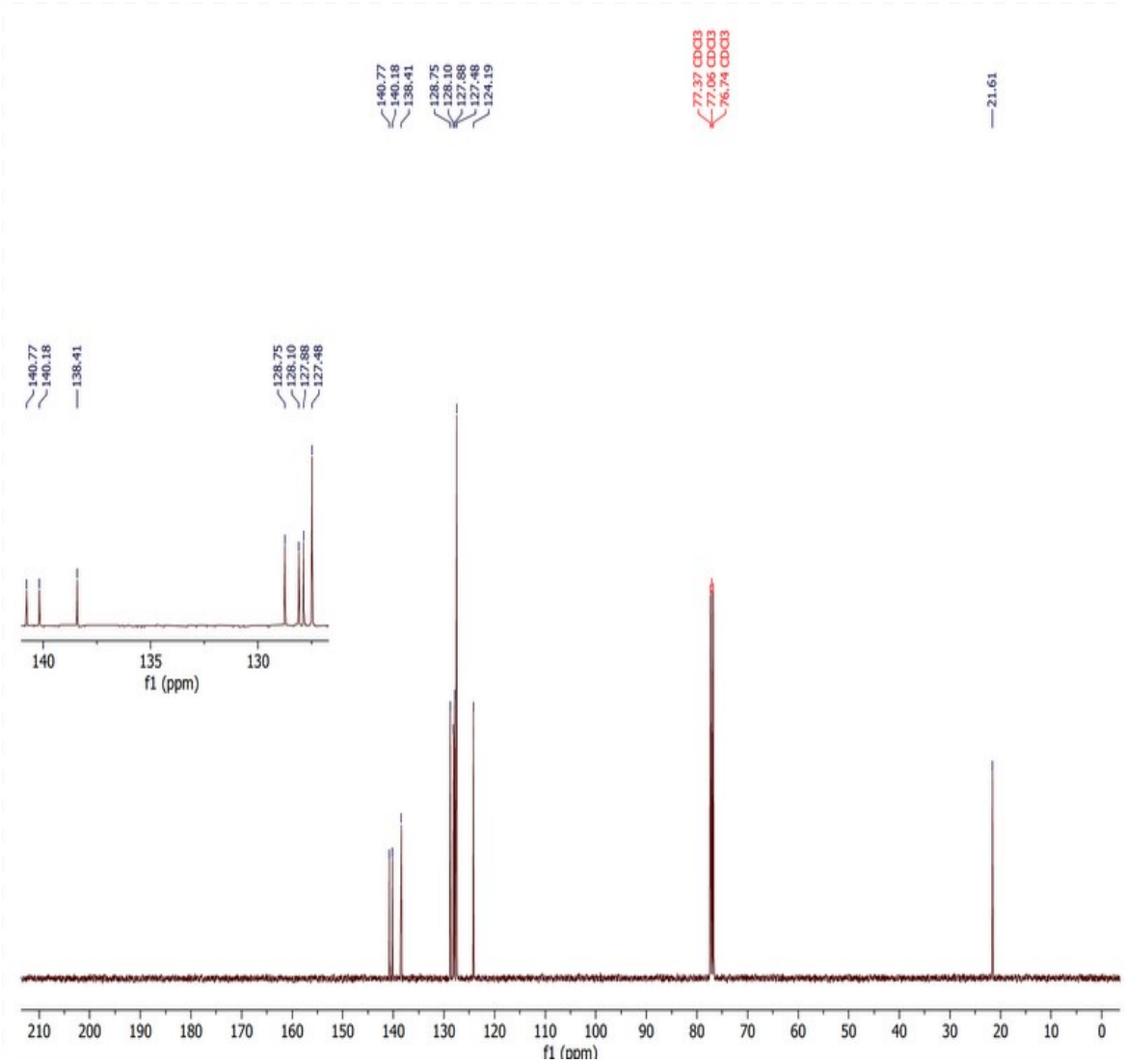
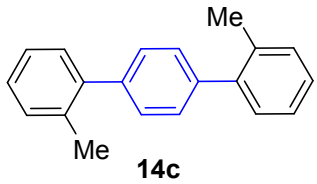


Figure 29. ^{13}C-NMR for compound **14b**



14c

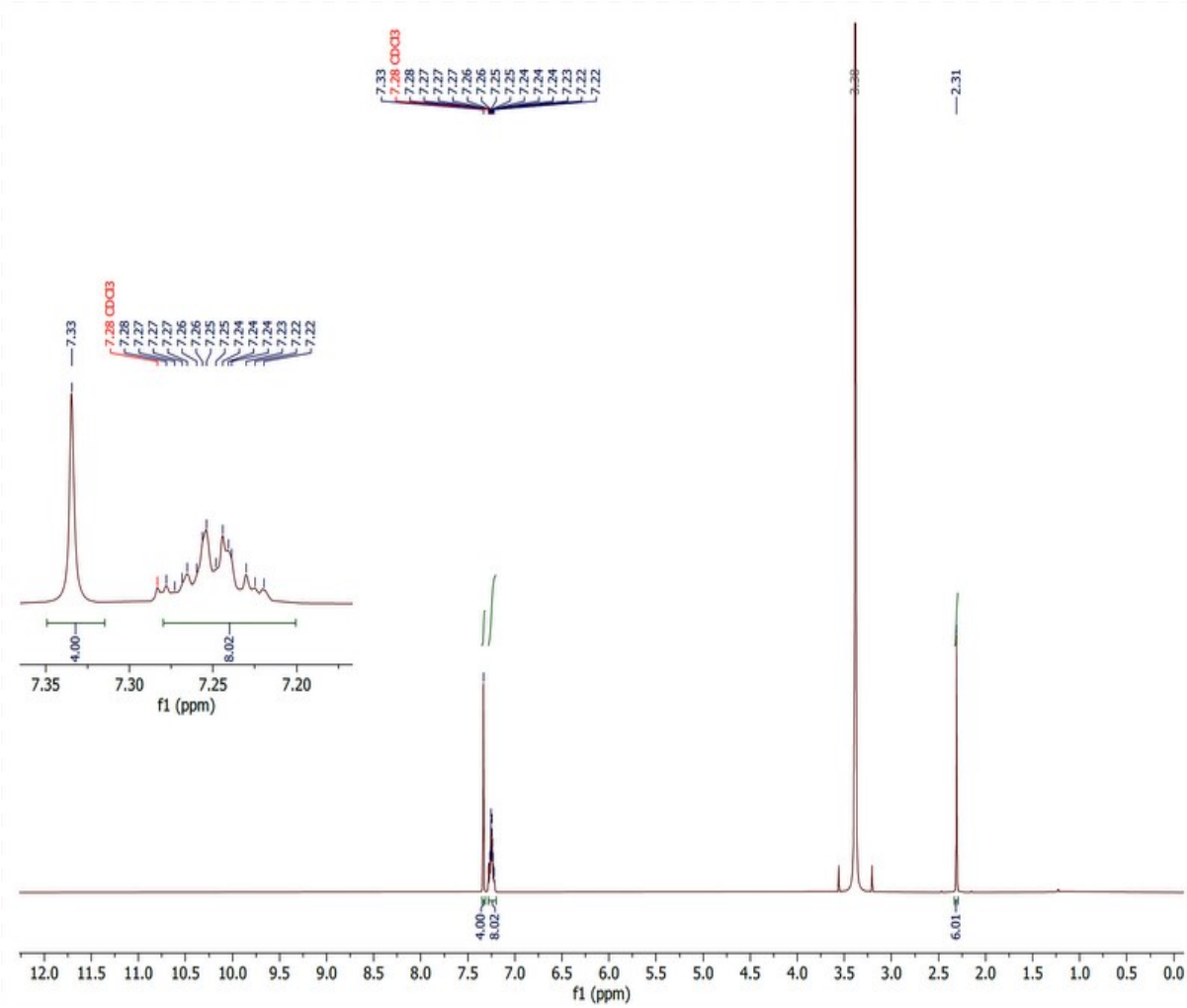


Figure 30. ^{1}H-NMR for compound **14c**

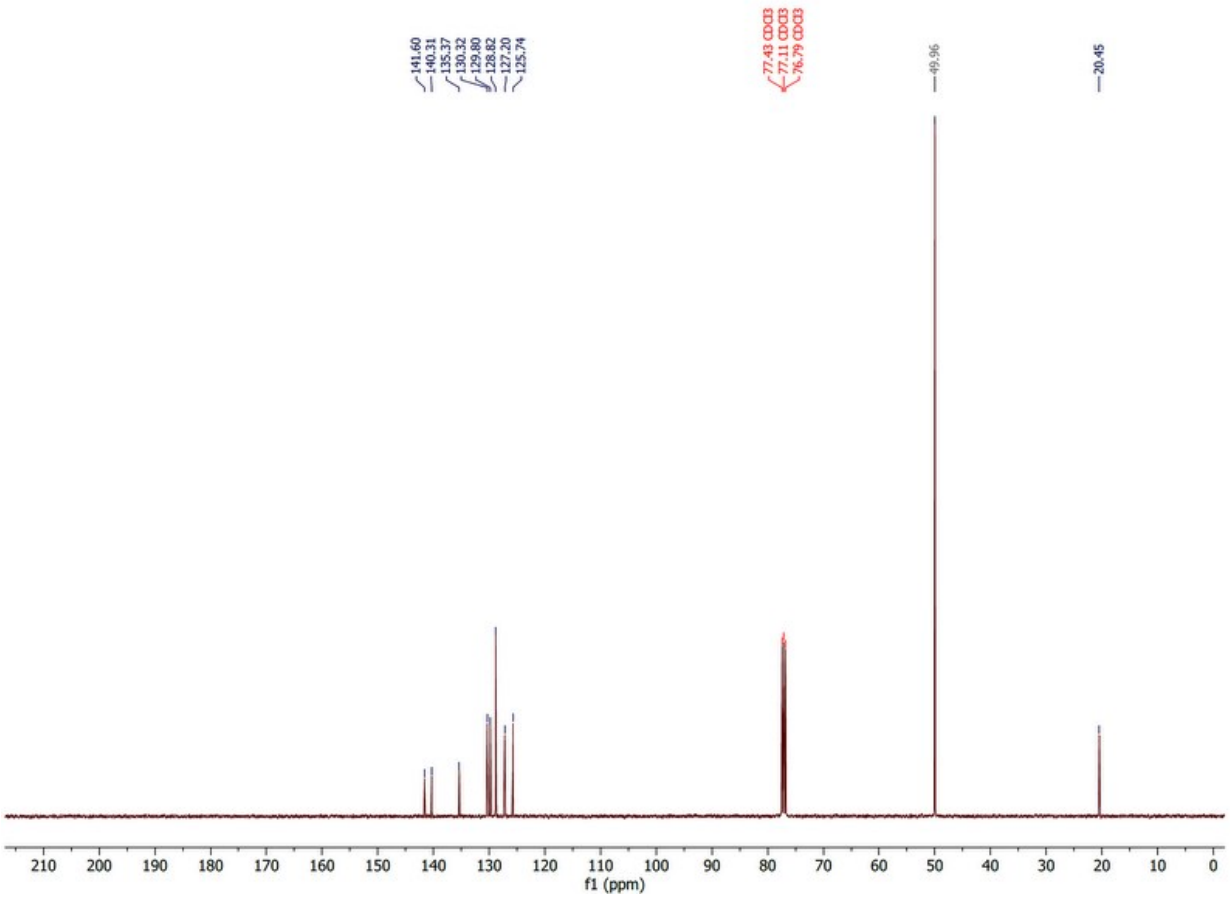


Figure 31. ^{13}C-NMR for compound **14c**

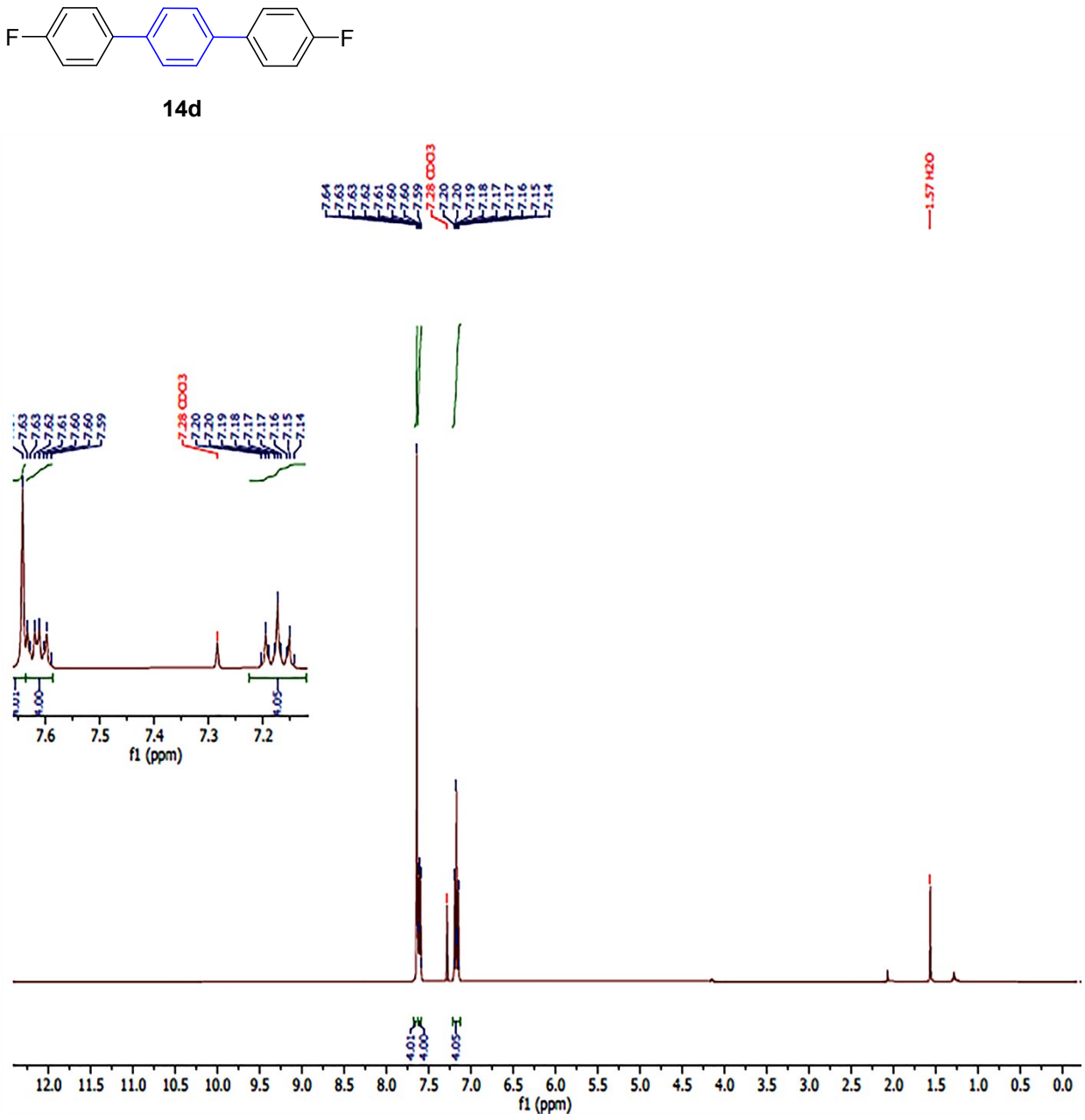


Figure 32. ^{1}H-NMR for compound **14d**

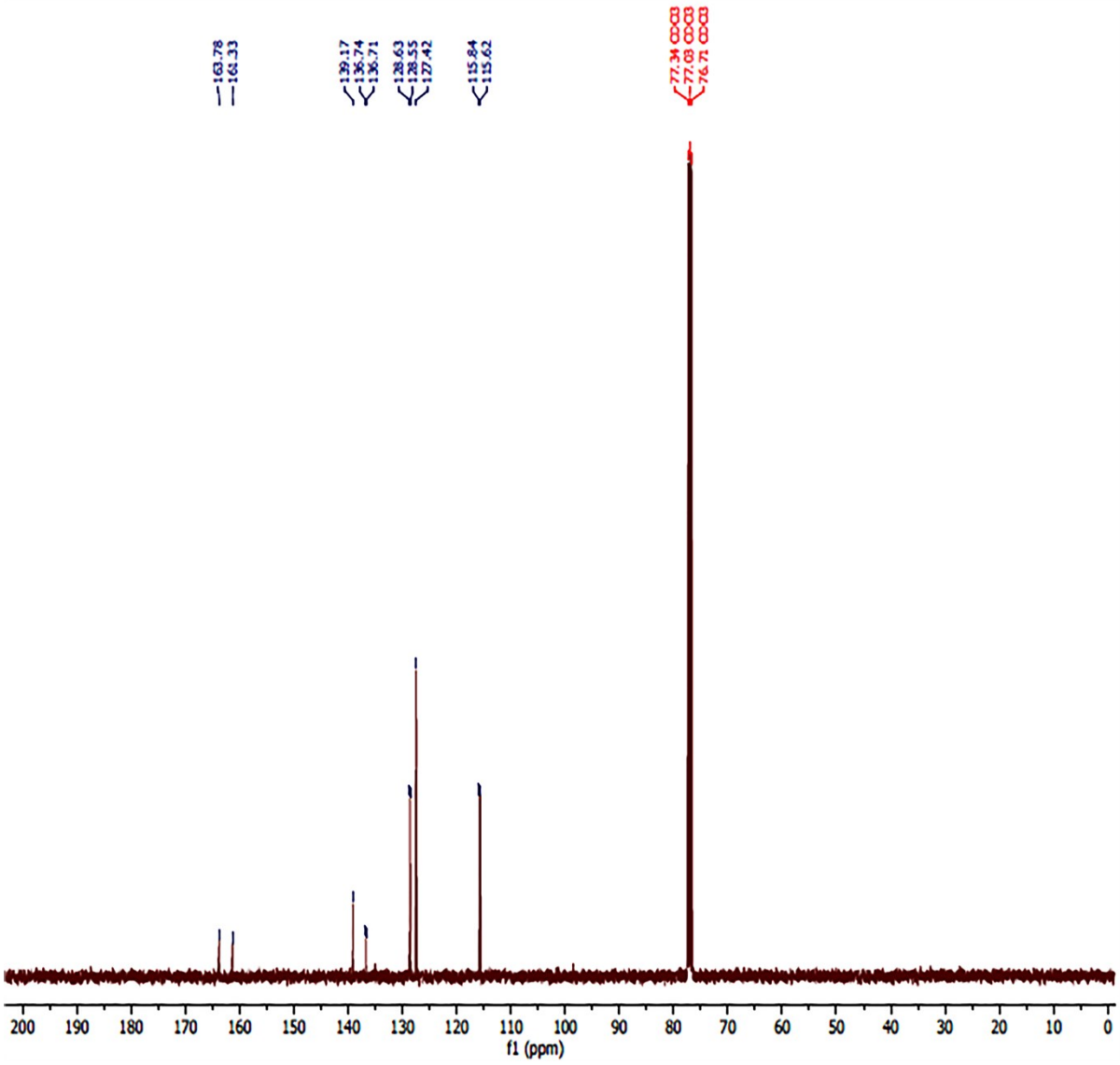


Figure 33. ^{13}C-NMR for compound **14d**

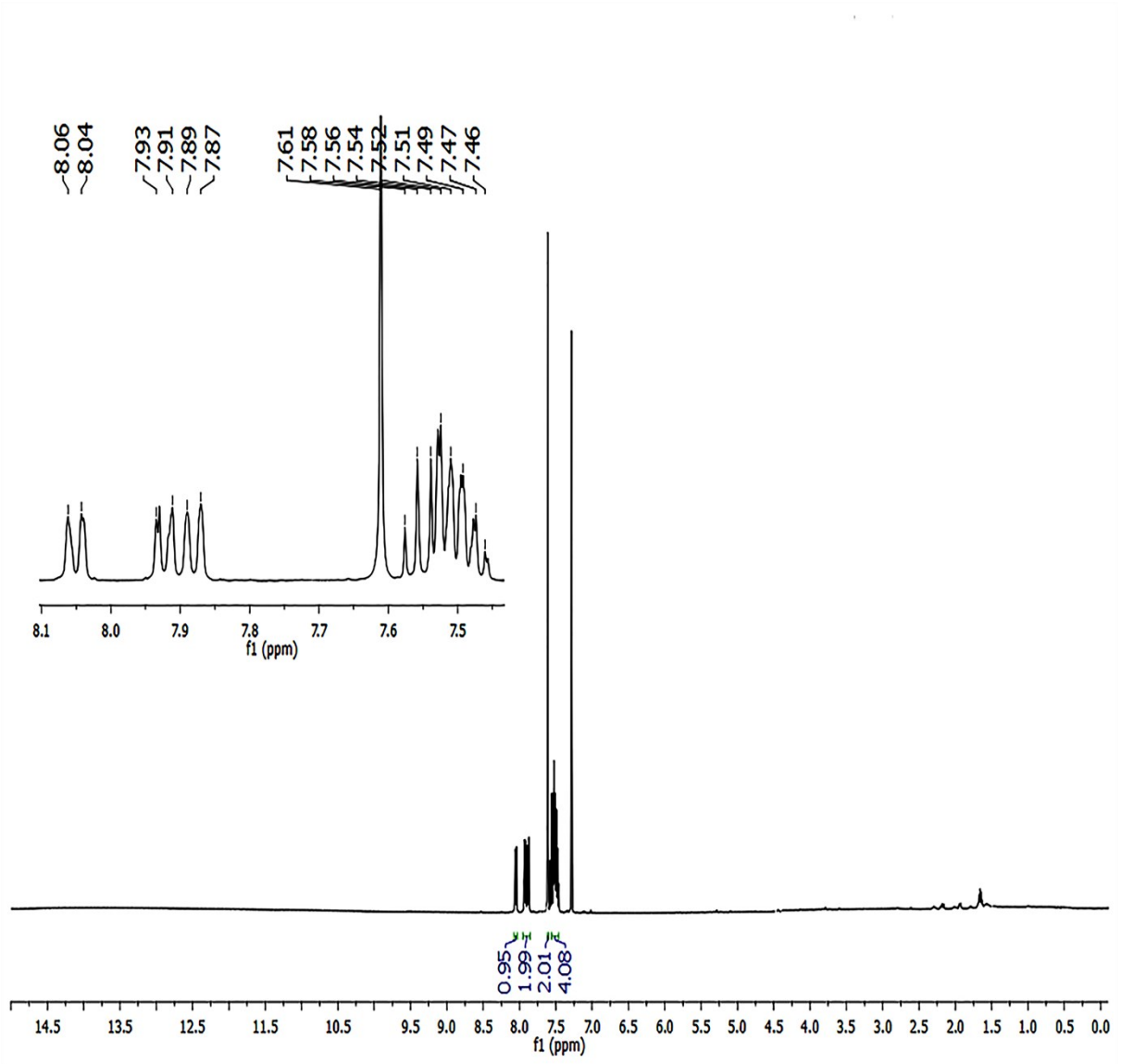


Figure 34. ^{1}H-NMR for compound **14e**

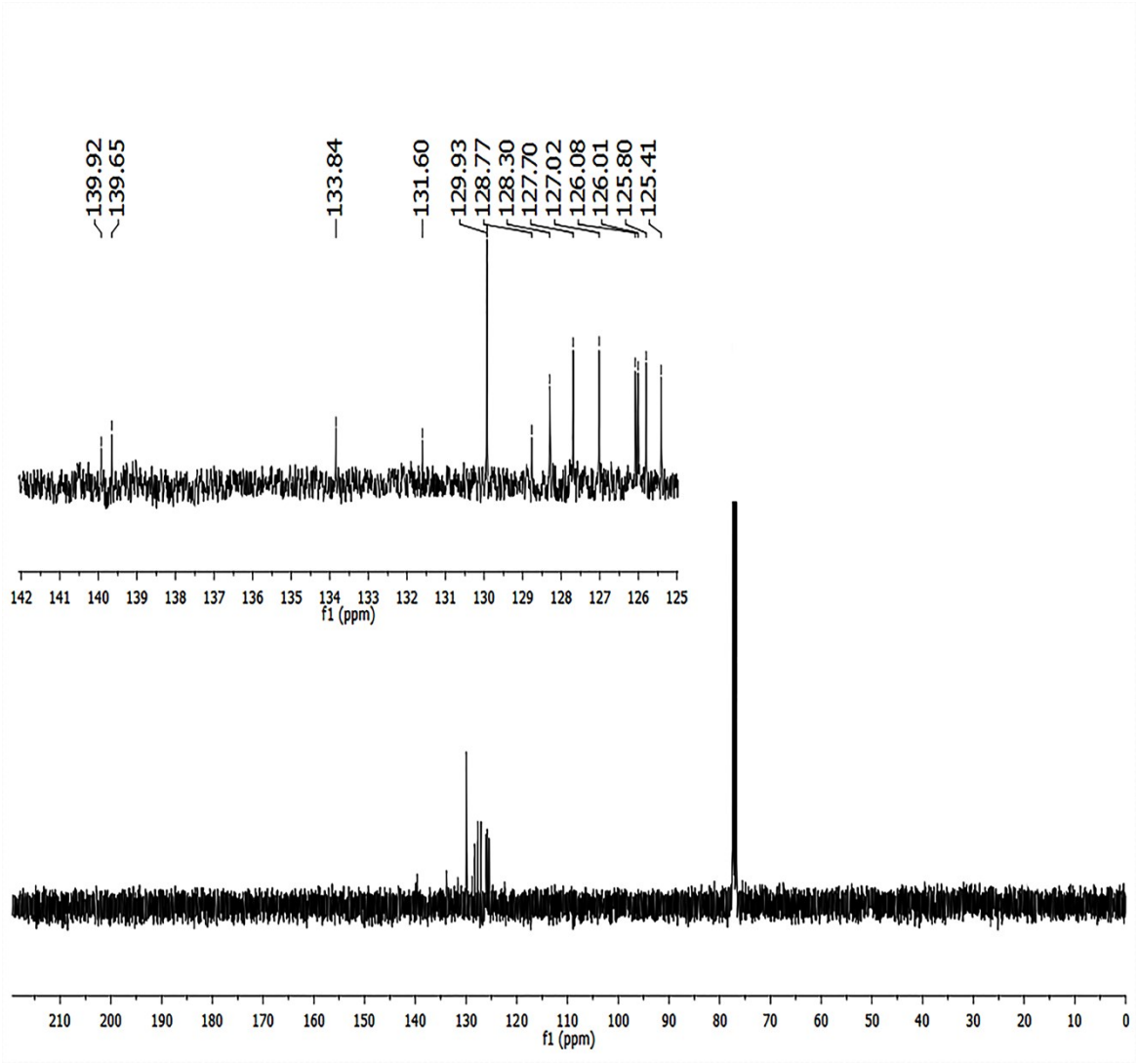
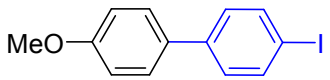


Figure 35. ^{13}C-NMR for compound **14e**



15

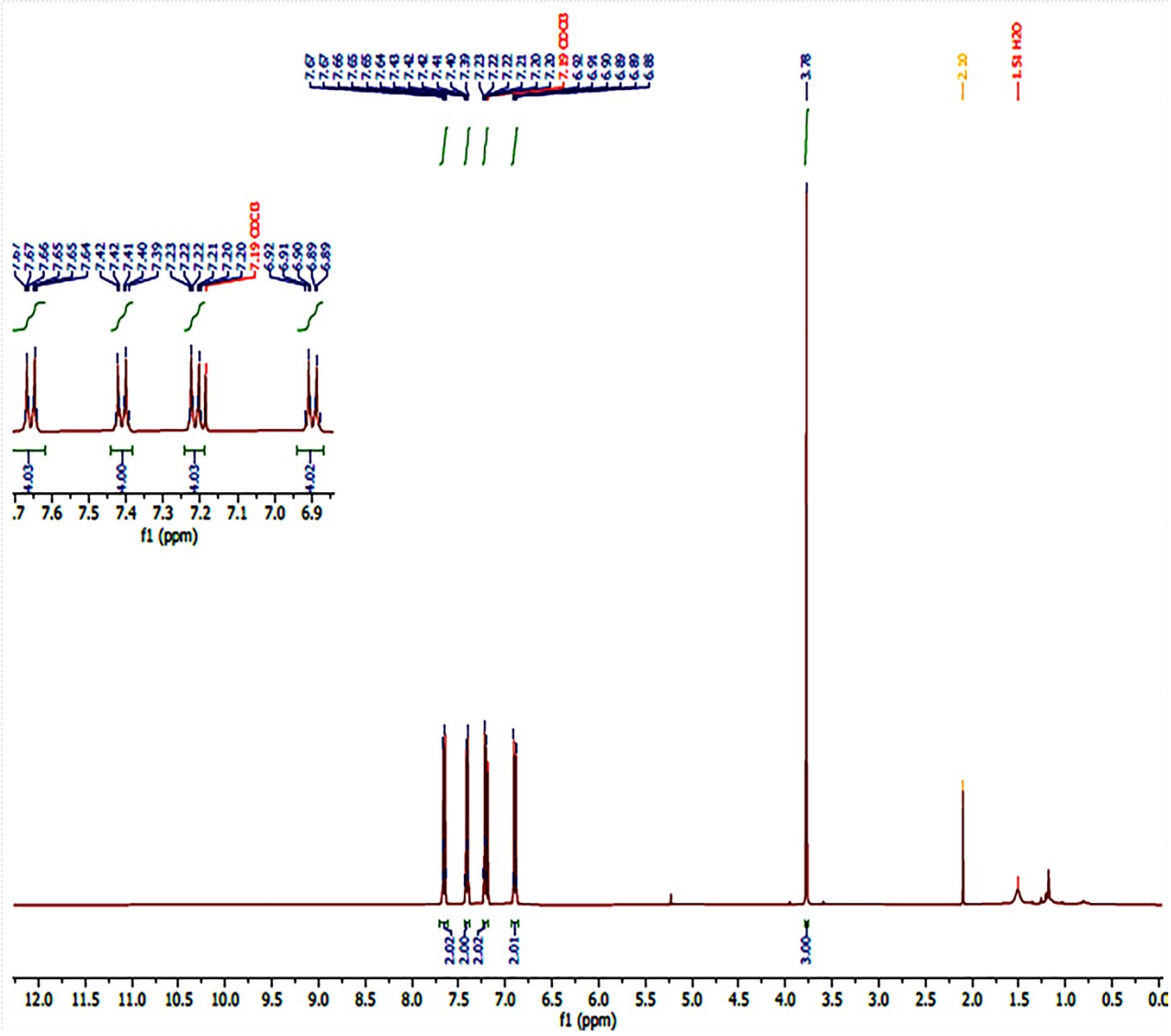


Figure 36. ^{1}H-NMR for compound **15**

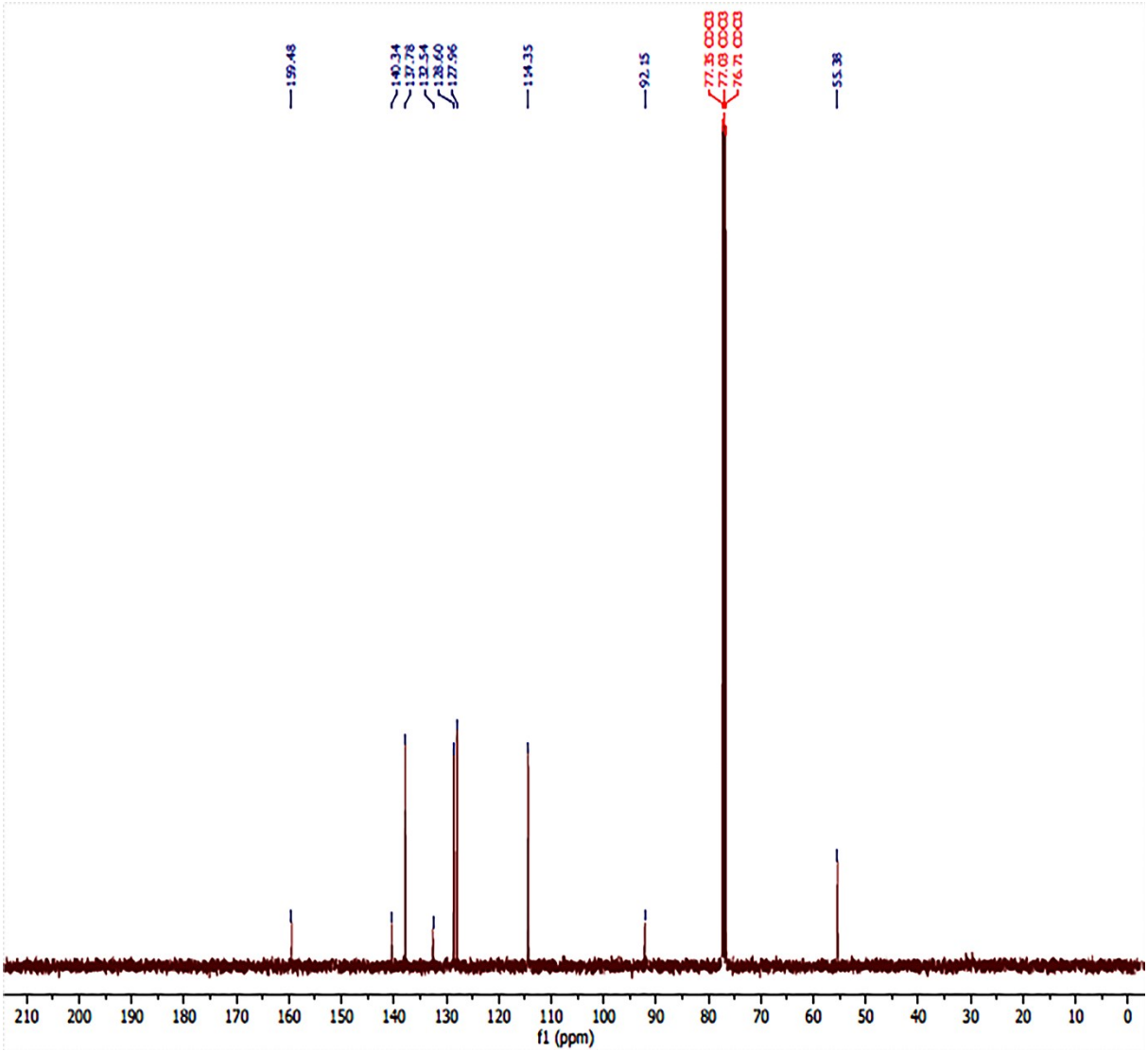


Figure 37. ^{13}C-NMR for compound **15**