Electronic Supplementary Information

Aldehyde/Ketone-Catalyzed Highly Selective Synthesis of 9-Monoalkylated Fluorenes by Dehydrative C-Alkylation with Primary and Secondary Alcohols

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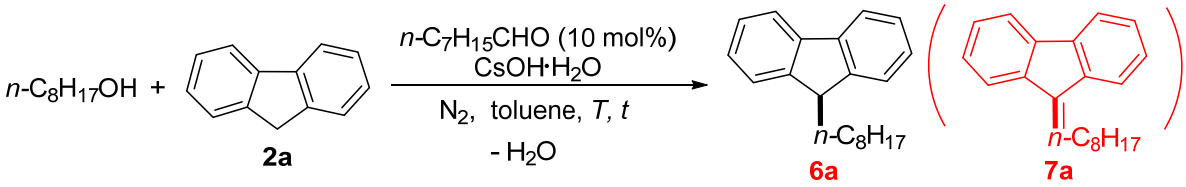
Table S1. Condition Optimization for Aliphatic Aldehyde-Catalyzed 9-C-Monoalkylation of Fluorene with Primary Aliphatic Alcohols.[a]



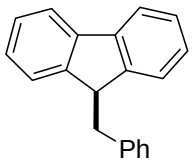
run	base (mol%)	T, t	**6a**%[b]	**6a**/**7a**[c]
1	$CsOH·H_2O$ (20)	130 °C, 24 h	52	-
2	$CsOH·H_2O$ (20)	150 °C, 24 h	92	-
3	$CsOH·H_2O$ (50)	130 °C, 24 h	90	-
4	$CsOH·H_2O$ (50)	150 °C, 24 h	99	***>99/1***
5	***$CsOH·H_2O$ (75)***	***130 °C, 24 h***	***99 (97)***	***>99/1***
6	KOH (75)	130 °C, 24 h	47	87/13

[a] The mixture of **2a** (3 mmol), 1-octanol (4 mmol, 1.33 equiv.), octaldehyde (10 mol%), toluene (0.5 mL), and $CsOH·H_2O$ was sealed under N_2 in a 20 mL Schlenk tube, heated for 24 h, and monitored by GC-MS and/or TLC. [b] GC yields (isolated yields in parenthesis) based on **2a**. [c] Ratios obtained by GC-MS analysis.

Experimental

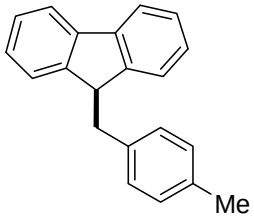
General. Except liquid aldehydes, which were purified by re-distillation of the commercial sample and stored under N_2 in a Schlenk flask (without any contaminants as confirmed by GC-Ms analysis), all other chemicals and bases are purchased and directly used without further purification. Unless otherwise noted, the reactions were all carried out in sealed Schlenk tubes under nitrogen and monitored by GC-MS or TLC. Products were purified by column chromatography on silica gel using petroleum ether and ethyl acetate as the eluent. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance instrument (300/500 MHz for ^{1}H and 125.4/75 MHz for ^{13}C NMR spectroscopy). Unless otherwise noted, $CDCl_3$ was used as the solvent. Chemical shift values for ^{1}H and ^{13}C were referred to internal Me_4Si (0 ppm). GC-MS and MS were measured on Shimadzu GCMS-QP2010 Plus and GCMS-QP2010 Ultra spectrometers (EI). GC-MS and MS were measured on Shimadzu GCMS-QP2010 Plus and GCMS-QP2010 Ultra spectrometers (EI). The parameters for GC-MS are as follows: Sample size: 1 μL, split ratio:15.2; Program Column Oven Temperature: 60 ^{o}C (stay 1 min), 40 ^{o}C/min to 200 ^{o}C (stay 1 min), 35 ^{o}C/min to 280 ^{o}C, stay till the end; Other parameters: carrier gas: He, sample temperature: 250 ^{o}C, pressure: 100.0 kPa, total flow: 32 mL/min, column flow: 1.61 mL/min, linear velocity: 46.3 cm/sec; Column: rxi-lms 30 m * 0.25 mm * 0.25 μm; MS parameter: ion source temperature: 200 ^{o}C, interface temperature: 250 ^{o}C, solvent cut: 3 min. HRMS analysis was measured on a Bruker micrOTOF-Q II instrument (ESI) at Wenzhou University or a Waters GCT Premier instrument (EI-TOF) at Zhejiang University.

Typical Procedure for (Hetero)Aryl Aldehyde-Catalyzed 9-C-Alkylation of Fluorenes with (Hetero)Aryl Methanols. The mixture of benzyl alcohol **1a** (0.433 g, 4.0 mmol, 1.33 equiv.), fluorene **2a** (0.499 g, 3.0 mmol), $CsOH·H_2O$ (0.101 g, 0.6 mmol, 20 mol%), benzaldehyde (31 μL, 0.3 mmol, 10 mol%), and toluene (0.5 mL) in a 20 mL schlenk tube was sealed under nitrogen, heated at 130 °C for 12 h, and monitored by GC-MS and/or TLC. After completion of the reaction, the reaction mixture was concentrated under vacuum. The residue was then purified through column chromatography on silica gel using ethyl acetate and petroleum ether (60-90 ^{o}C) (v/v 1/50) as the eluent, giving **3a** in 95% isolated yield (0.730 g).

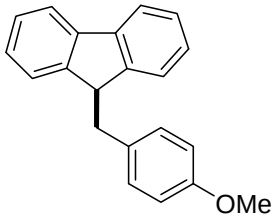


9-Benzyl-9H-fluorene (3a). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, J = 7.5 Hz, 2H), 7.35-7.14 (m, 11 H), 4.22 (t, J = 7.5 Hz, 1H), 3.10 (d, J = 7.5 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 146.8,

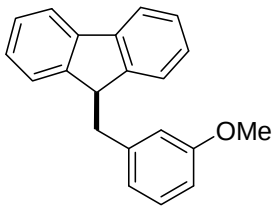
140.8, 139.8, 129.5, 128.3, 127.1, 126.6, 126.3, 124.8, 119.8, 48.7, 40.1. MS (EI): *m/z* (%) 91 (11), 164 (8), 165 (100), 166 (15), 256 (34), 257 (8). This compound was known: Fleckenstein, C. A.; Plenio, H. *Chem. Eur. J.* **2007**, *13*, 2701.



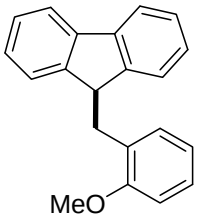
9-(4-Methylbenzyl)-9H-fluorene (3b). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, J = 7.5 Hz, 2H), 7.34 (t, J = 7.5 Hz, 2H), 7.23-7.20 (m, 2H), 7.18 (d, J = 7.5 Hz, 2H), 7.14-7.10 (m, 4H), 4.21 (t, J = 7.5 Hz, 1H), 3.06 (d, J = 7.5 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 146.9, 140.8, 136.7, 135.8, 129.4, 129.0, 127.0, 126.6, 124.8, 119.8, 48.8, 39.6, 21.1. MS (EI): *m/z* (%) 105 (100), 106 (10), 164 (7), 165 (63), 166 (9), 270 (35), 271 (8). This compound was known: Sieglitz, A.; Jassoy, H. *Ber. dtsch. Chem. Ges. A/B*. **1921**, *54*, 2133.



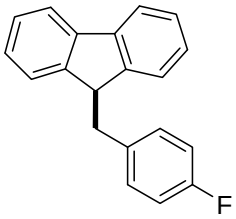
9-(4-Methoxybenzyl)-9H-fluorene (3c). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, J = 7.5 Hz, 2H), 7.35-7.32 (m, 2H), 7.23-7.20 (m, 2H), 7.17 (d, J = 7.5 Hz, 2H), 7.12 (d, J = 8.5 Hz, 2H), 6.83 (d, J = 9.0 Hz, 2H), 4.17 (t, J = 7.5 Hz, 1H), 3.80 (s, 3H), 3.04 (d, J = 8.0 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 158.1, 146.9, 140.8, 131.8, 130.4, 127.0, 126.6, 124.8, 119.8, 113.6, 55.2, 48.9, 39.1. MS (EI): *m/z* (%) 77 (5), 78 (3), 121 (100), 122 (9), 165 (10), 286 (7), 287 (2). This compound was known: Rabinovitz, M.; Salemnik, G.; Bergmann, E. D. *Tetrahedron Lett.* **1967**, *8*, 3271



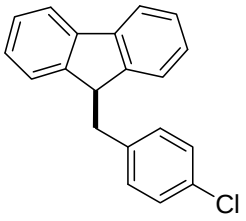
9-(3-Methoxybenzyl)-9H-fluorene (3d). ^{1}H NMR (300 MHz, $CDCl_3$): ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, J = 7.0 Hz, 2H), 7.32-7.30 (m, 2H), 7.21-7.17 (m, 5H), 6.82-6.74 (m, 3H), 4.21 (t, J = 7.5 Hz, 1H), 3.73 (s, 3H), 3.07 (d, J = 7.5 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 159.5, 146.7, 141.3, 140.8, 129.2, 127.1, 126.6, 124.8, 121.9, 119.8, 114.9, 112.0, 55.1, 48.5, 40.0. MS (EI): *m/z* (%) 121 (17), 164 (6), 165 (100), 166 (14), 286 (24), 287 (6). HRMS Calcd for $[C_{15}H_{15}NO_2 + H]^+$: 287.1430; found: 287.1448.



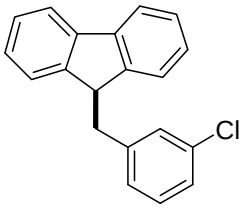
9-(2-Methoxybenzyl)-9H-fluorene (3e). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 (d, J = 7.5 Hz, 2H), 7.34-7.31 (m, 2H), 7.29-7.26 (m, 1H), 7.21-7.15 (m, 4H), 7.04 (d, J = 7.5 Hz, 1H), 6.93-6.88 (m, 2H), 4.35 (t, J = 7.5 Hz, 1H), 3.85 (s, 3H), 3.05 (d, J = 7.5 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 158.0, 147.7, 140.7, 131.5, 128.6, 127.8, 126.8, 126.5, 125.0, 120.1, 119.6, 110.3, 55.2, 46.7, 35.5. MS (EI): *m/z* (%) 65 (6), 91 (37), 93 (9), 121 (100), 122 (8), 165 (24), 286 (18), 287 (4). HRMS Calcd for $[C_{21}H_{18}O + H]^+$: 287.1430; found: 287.1445.



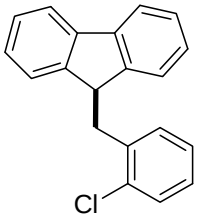
9-(4-Fluorobenzyl)-9H-fluorene (3f). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, J = 7.5 Hz, 2H), 7.35-7.32 (m, 2H), 7.23-7.20 (m, 2H), 7.17 (d, J = 7.5 Hz, 2H), 7.11-7.08 (m, 2H), 6.95-6.92 (m, 2H), 4.17 (t, J = 7.5 Hz, 1H), 3.09 (d, J = 7.5 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 161.6 (d, $J_{C\text{-}F}$ = 243.5 Hz), 146.5, 140.9, 135.2 (d, $J_{C\text{-}F}$ = 3.0 Hz), 130.8 (d, $J_{C\text{-}F}$ = 8.0 Hz), 127.2, 126.7, 124.7, 119.8, 114.9 (d, $J_{C\text{-}F}$ = 20.9 Hz), 48.7, 39.1. MS (EI): *m/z* (%) 109 (12), 139 (4), 163 (6), 164 (8), 165 (100), 166 (15), 273 (24), 274 (5). HRMS Calcd for $[C_{20}H_{15}F + Na]^+$: 298.1050; found: 298.1045.



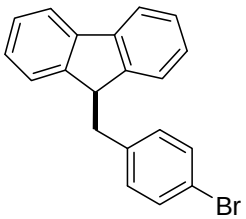
9-(4-Chlorobenzyl)-9H-fluorene (3g). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, J = 7.5 Hz, 2H), 7.36-7.33 (m, 2H), 7.25-7.12 (m, 4H), 7.19 (d, J = 7.5 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 4.19 (t, J = 7.5 Hz, 1H), 3.10 (d, J = 7.0 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 146.3, 140.9, 138.0, 132.1, 130.8, 128.3, 127.2, 126.7, 124.7, 119.9, 48.5, 39.2. MS (EI): *m/z* (%) 125 (8), 164 (7), 165 (100), 166 (15), 290 (16), 292 (6). This compound was known: Sieglitz, A.; Jassoy, H. *Ber. dtsch. Chem. Ges. A/B*. **1921**, *54*, 2133.



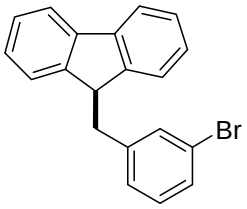
9-(3-Chlorobenzyl)-9H-fluorene (3h). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72 (d, J = 7.5 Hz, 2H), 7.36-7.33 (m, 2H), 7.24-7.20 (m, 5H), 7.17 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 6.5 Hz, 1H), 4.19 (t, J = 7.5 Hz, 1H), 3.07 (d, J = 7.5 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 146.3, 141.7, 140.8, 134.0, 129.5, 129.4, 127.7, 127.3, 126.7, 126.6, 124.7, 119.9, 48.3, 39.7. MS (EI): *m/z* (%) 81 (29), 164 (9), 165 (100), 166 (14), 246 (21), 165 (100), 166 (14), 290 (14), 291 (5). This compound was known: Sieglitz, A.; Jassoy, H. *Ber. dtsch. Chem. Ges. A/B*. **1921**, *54*, 2133.



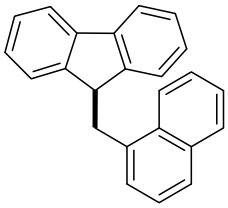
9-(2-Chlorobenzyl)-9H-fluorene (3i). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, J = 7.5 Hz, 2H), 7.43 (d, J = 7.5 Hz, 1H), 7.34-7.31 (m, 2H), 7.23-7.17 (m, 4H), 7.15-7.12 (m, 2H), 7.09 (d, J = 7.5 Hz, 1H), 4.35 (t, J = 7.5 Hz, 1H), 3.13 (d, J = 7.5 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 146.8, 140.7, 137.7, 134.6, 132.2, 129.7, 128.1, 127.1, 126.7, 126.5, 124.9, 119.8, 46.4, 38.5. MS (EI): *m/z* (%) 73 (5), 83 (16), 85 (11), 164 (6), 165 (100), 166 (14), 290 (17), 292 (5). This compound was known: Sieglitz, A.; Jassoy, H. *Ber. dtsch. Chem. Ges. A/B*. **1921**, *54*, 2133.



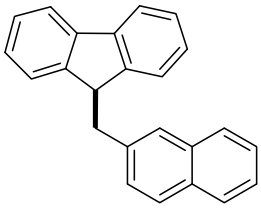
9-(4-Bromobenzyl)-9H-fluorene (3j). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, J = 7.5 Hz, 2H), 7.38-7.32 (m, 4H), 7.24-7.21 (m, 2H), 7.19 (d, J = 7.0 Hz, 2H), 7.02 (d, J = 8.5 Hz, 2H), 4.18 (t, J = 7.5 Hz, 1H), 3.08 (d, J = 7.5 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 146.3, 140.8, 138.5, 131.23, 131.21, 127.2, 126.7, 124.7, 120.1, 119.9, 48.4, 39.3. MS (EI): *m/z* (%) 90 (4), 139 (3), 165 (100), 166 (14), 334 (7), 336 (7). This compound was known: Rabinovitz, M.; Salemnik, G.; Bergmann, E. D. *Tetrahedron Lett.* **1967**, *8*, 3271



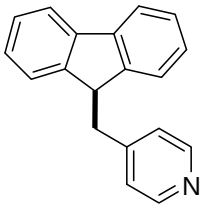
9-(3-Bromobenzyl)-9H-fluorene (3k). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 (d, J = 8.0 Hz, 2H), 7.38-7.33 (m, 4H), 7.24 (d, J = 7.5 Hz, 2H), 7.18-7.09 (m, 4H), 4.20 (t, J = 7.5 Hz, 1H), 3.07 (d, J = 7.5 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 146.3, 142.0, 140.8, 132.5, 129.7, 129.5, 128.2, 127.3, 126.7, 124.7, 122.3, 119.9, 48.4, 39.7. MS (EI): *m/z* (%) 90 (6), 139 (4), 165 (100), 166 (15), 334 (6), 336 (7). This compound was known: Sieglitz, A.; Jassoy, H. *Ber. dtsch. Chem. Ges. A/B*. **1921**, *54*, 2133.



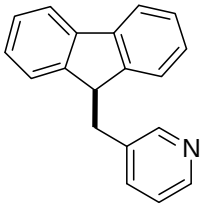
9-(Naphthalen-1-ylmethyl)-9H-fluorene (3l). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.30 (d, J = 8.5 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.5 Hz, 1H), 7.78 (d, J = 7.5 Hz, 2H), 7.59-7.52 (m, 2H), 7.47-7.44 (m, 1H), 7.37-7.34 (m, 2H), 7.28 (d, J = 7.0 Hz, 1H), 7.20-7.17 (m, 2H), 7.08 (d, J = 7.5 Hz, 2H), 4.41 (t, J = 8.0 Hz, 1H), 3.48 (d, J = 8.0 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 147.0, 140.7, 136.0, 134.1, 132.0, 129.1, 128.2, 127.5, 127.1, 126.6, 126.0, 125.7, 125.3, 125.1, 123.7, 119.8, 47.6, 38.0. MS (EI): *m/z* (%) 115 (18), 141 (100), 142 (12), 165 (33), 306 (14), 307 (4). This compound was known: Sieglitz, A.; Jassoy, H. *Ber. dtsch. Chem. Ges. A/B*. **1921**, *54*, 2133.



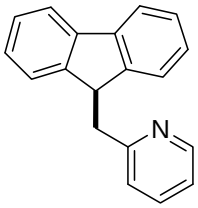
9-(Naphthalen-2-ylmethyl)-9H-fluorene (3m). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85-7.80 (m, 2H), 7.75-7.73 (m, 3H), 7.63 (s, 1H), 7.46-7.43 (m, 3H), 7.35-7.32 (m, 2H), 7.20-7.15 (m, 4H), 4.34 (t, J = 7.5 Hz, 1H), 3.26 (d, J = 7.5 Hz, 2H).^{13}C NMR (125.4 MHz, $CDCl_3$): δ 146.8, 140.8, 137.4, 133.5, 132.3, 128.0, 127.9, 127.8, 127.66, 127.64, 127.1, 126.7, 125.9, 125.4, 124.8, 119.8, 48.5, 40.3. MS (EI): *m/z* (%) 115 (17), 141 (100), 142 (12), 165 (41), 306 (24), 307 (6). This compound was known: Sieglitz, A.; Jassoy, H. *Ber. dtsch. Chem. Ges. A/B*. **1921**, *54*, 2133.



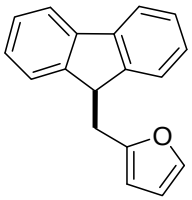
4-(9H-Fluoren-9-yl)methylpyridine (3n). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.44 (d, J = 6.0 Hz, 2H), 7.71 (d, J = 7.5 Hz, 2H), 7.37-7.32 (m, 2H), 7.24 (d, J = 4.0 Hz, 4H), 7.03 (d, J = 6.0 Hz, 2H), 4.26 (t, J = 7.0 Hz, 1H), 3.16 (d, J = 7.0 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 149.5, 148.3, 145.8, 140.9, 127.4, 126.8, 124.8, 124.5, 120.0, 47.5, 39.1. MS (EI): *m/z* (%) 115 (3), 139 (4), 164 (10), 165 (100), 166 (15), 257 (21), 258 (4). This compound was known: Kolyadina, N. M.; Soldatenkov, A. T.; Ryashentseva, M. A.; Prostakov, N. S. *Izv. Akad. Nauk Gruz. SSR, Ser. Khim.* **1996**, *1*, 180.



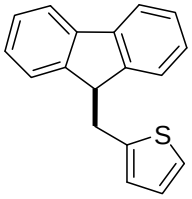
3-(9H-Fluoren-9-yl)methylpyridine (3o). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.37 (d, J = 40.0 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H), 7.34-7.31 (m, 3H), 7.26-7.22 (m, 4H), 7.10-7.08 (m, 1H), 4.22 (t, J = 7.0 Hz, 1H), 3.18 (d, J = 7.0 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 150.7, 147.7, 145.8, 140.9, 136.7, 134.4, 127.3, 126.8, 124.6, 122.9, 119.9, 48.1, 36.7. MS (EI): *m/z* (%) 65 (4), 139 (5), 163 (8), 164 (10), 165 (100), 166 (14), 257 (20). HRMS Calcd for $[C_{19}H_{15}N + H]^{+}$: 258.1277; found: 258.1303.



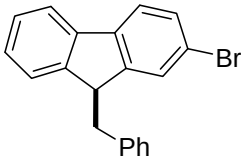
2-(9H-Fluoren-9-yl)methylpyridine (3p). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.64 (dd, J = 1.0 Hz, J = 5.0 Hz, 1H), 7.70 (d, J = 7.5 Hz, 2H), 7.51-7.48 (m, 1H), 7.31-7.28 (m, 2H), 7.17-7.14 (m, 2H), 7.13-7.11 (m, 1H), 7.05 (d, J = 7.5 Hz, 2H), 6.93 (d, J = 7.5 Hz, 1H), 4.62 (t, J = 7.5 Hz, 1H), 3.18 (d, J = 7.5 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 159.7, 149.3, 146.9, 140.6, 136.0, 126.9, 126.6, 124.5, 124.1, 121.5, 119.7, 47.0, 42.3. MS (EI): *m/z* (%) 69 (20), 79 (20), 165 (100), 207 (19), 218 (17), 256 (76), 257 (73). This compound was known: Pan, Y.; Rong, W. Jian, Z.; Cui, D. *J. Am. Chem. Soc.* **2012**, *45*, 1248 .



2-(9H-Fluoren-9-yl)methylfuran (3q). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (d, J = 7.5 Hz, 2H), 7.37 (s, 1H), 7.33-7.30 (m, 2H), 7.22-7.19 (m, 2H), 7.14 (d, J = 7.5 Hz, 2H), 6.29 (d, J = 1.5 Hz, 1H), 5.92 (d, J = 2.5 Hz, 1H), 4.28 (t, J = 7.5 Hz, 1H), 3.05 (d, J = 7.5 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 153.7, 146.4, 141.0, 140.8, 127.2, 126.8, 124.5, 119.8, 110.3, 107.0, 46.2, 32.2. MS (EI): *m/z* (%) 81 (30), 163 (7), 164 (9), 165 (100), 166 (14), 246 (20). HRMS Calcd for $[C_{18}H_{14}O + Na]^+$: 269.0937; found: 269.0952.



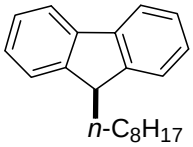
2-(9H-Fluoren-9-yl)methylthiophene (3r). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (d, J = 7.5 Hz, 2H), 7.34-7.31 (m, 2H), 7.26-7.23 (m, 3H), 7.21 (d, J = 7.5 Hz, 1H), 7.08 (d, J = 5.0 Hz, 1H), 6.85-6.83 (m, 1H), 6.67 (d, J = 3.0 Hz, 1H), 4.19 (t, J = 7.0 Hz, 1H), 3.35 (d, J = 7.0 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 146.1, 142.0, 141.0, 127.3, 126.8, 126.5, 125.9, 124.6, 123.7, 119.8, 48.9, 33.9. MS (EI): *m/z* (%) 97 (92), 98 (6), 163 (10), 164 (11), 165 (100), 166 (14), 262 (26). HRMS Calcd for $[C_{18}H_{14}S + H]^+$: 263.0889; found: 263.0901.



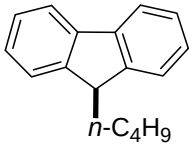
9-Benzyl-2-Bromo-9H-fluorene (3s). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (d, J = 7.5 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.46 (dd, J = 1.5 Hz, J = 8.0 Hz, 1H), 7.36-7.19 (m, 8H), 7.14 (d, J = 7.5 Hz, 1H), 4.20 (t, J = 7.5 Hz, 1H), 3.13-3.05 (m, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 148.8, 146.5, 139.84, 139.82, 139.2, 130.2, 129.5, 128.4, 128.2, 127.3, 127.1, 126.6, 124.9, 121.1, 120.4, 119.9, 48.7, 39.9. MS (EI): *m/z* (%) 91 (99), 163 (66), 164 (76), 243 (100), 245 (98), 246 (14), 255 (67), 256 (16), 334 (39), 336 (41). This compound was known: Rabinovitz, M.; Salemnik, G.; Bergmann, E. D. *Tetrahedron Lett.* **1967**, *8*, 3271

Typical Procedure for Aliphatic Aldehyde-Catalyzed 9-C-Alkylation of Fluorenes with Aliphatic Alcohols. The mixture of fluorene **2a** (0.499 g, 3.0 mmol), octan-1-ol (0.521 g, 4.0 mmol,

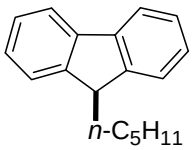
1.33 equiv.), $CsOH \cdot H_2O$ (0.378 g, 2.25 mmol, 75 mol%), octaldehyde (47 μL, 0.3 mmol, 10 mol%), and toluene (0.5 mL) in a 20 mL schlenk tube was sealed under nitrogen, heated at 130 °C for 24 h, and monitored by GC-MS and/or TLC. After completion of the reaction, the mixture was concentrated under vacuum. The residue was then purified through column chromatography on silica gel using ethyl acetate and petroleum ether (60-90 ^{o}C) (v/v 1/50) as the elunet, giving **6a** in 97% isolated yield (0.810 g).



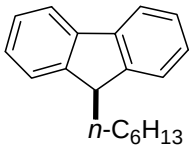
9-Octyl-9H-fluorene (6a). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, J = 7.5 Hz, 2H), 7.51 (d, J = 7.5 Hz, 2H), 7.37-7.34 (m, 2H), 7.31-7.28 (m, 2H), 3.96 (t, J = 6.0 Hz, 1H), 2.01-1.96 (m, 2H), 1.25-1.20 (m, 12H), 0.85 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 147.6, 141.1, 126.8, 126.7, 124.3, 119.7, 47.5, 33.1, 31.8, 30.0, 29.4, 29.3, 25.7, 22.6, 14.1. MS (EI): *m/z* (%) 57 (5), 165 (100), 166 (33), 178 (17), 179 (20), 180 (12), 278 (67), 279 (16). This compound was known: Cho, S. Y.; Grimsdale, A. C.; Jones, D. J.; Watkins, S. E.; Holmes, A. B. *J. Am. Chem. Soc.* **2007**, *129*, 11910.



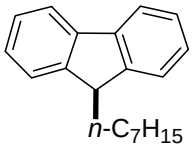
9-Butyl-9H-fluorene (6b). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, J = 7.5 Hz, 2H), 7.48 (d, J = 7.5 Hz, 2H), 7.34-7.31 (m, 2H), 7.29-7.26 (m, 2H), 3.94 (t, J = 6.0 Hz, 1H), 2.00-1.96 (m, 2H), 1.30-1.22 (m, 2H), 1.18-1.12 (m, 2H), 0.81 (t, J = 7.5 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 147.6, 141.1, 126.8, 126.7, 124.3, 119.7, 47.4, 32.8, 27.8, 23.0, 13.9. MS (EI): *m/z* (%) 115 (3), 164 (8), 165 (100), 166 (21), 178 (10), 179 (13), 180 (7), 222 (30). This compound was known: Sun, Y.; Yang, N.; Liu, J.; Cao, J.; Gong, H. *Polymer*. **2010**, *51*, 5712.



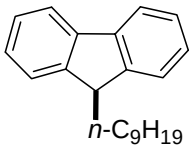
9-Pentyl-9H-fluorene (6c). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, J = 7.5 Hz, 2H), 7.50 (d, J = 7.5 Hz, 2H), 7.36-7.33 (m, 2H), 7.31-7.28 (m, 2H), 3.96 (t, J = 6.0 Hz, 1H), 2.00-1.96 (m, 2H), 1.24-1.20 (m, 6H), 0.82 (t, J = 6.5 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 147.6, 141.1, 126.8, 126.7, 124.3, 119.7, 47.5, 33.1, 32.1, 25.4, 22.4, 14.0. MS (EI): *m/z* (%) 165 (100), 166 (27), 178 (12), 179 (17), 180 (9), 236 (45), 237 (9). This compound was known: Albert, G. J.; Marcel, M.; Henri, M. *Bull. Soc. Chim. Fr.* **1965**, *6*, 1740.



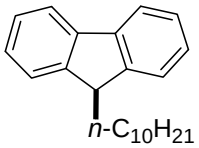
9-Hexyl-9H-fluorene (6d). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, J = 7.5 Hz, 2H), 7.51 (d, J = 7.5 Hz, 2H), 7.36-7.33 (m, 2H), 7.31-7.28 (m, 2H), 3.96 (t, J = 6.0 Hz, 1H), 2.01-1.96 (m, 2H), 1.25-1.18 (m, 8H), 0.83 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 147.6, 141.1, 126.8, 126.7, 124.3, 119.7, 47.5, 33.1, 31.6, 29.6, 25.7, 22.6, 14.0. MS (EI): *m/z* (%) 165 (100), 166 (30), 178 (14), 179 (17), 250 (42), 251 (8). This compound was known: Albert, G. J.; Marcel, M.; Henri, M. *Bull. Soc. Chim. Fr.* **1965**, *6*, 1740.



9-Heptyl-9H-fluorene (6e). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, J = 7.5 Hz, 2H), 7.50 (d, J = 7.5 Hz, 2H), 7.36-7.33 (m, 2H), 7.31-7.28 (m, 2H), 3.96 (t, J = 6.0 Hz, 1H), 2.00-1.96 (m, 2H), 1.26-1.19 (m, 10H), 0.84 (t, J = 7.5 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 147.6, 141.1, 126.8, 126.7, 124.3, 119.7, 47.5, 33.1, 31.8, 29.9, 29.1, 25.7, 22.6, 14.0. MS (EI): *m/z* (%) 57 (7), 165 (100), 166 (30), 178 (15), 179 (17), 264 (47), 265 (10). This compound was known: Bachman, G. B.; Polansky, S. *J. Org. Chem.* **1951**, *16*, 1690.

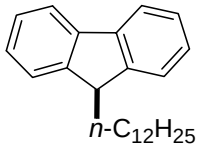


9-Nonyl-9H-fluorene (6f). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, J = 7.5 Hz, 2H), 7.50 (d, J = 7.5 Hz, 2H), 7.36-7.33 (m, 2H), 7.31-7.28 (m, 2H), 3.96 (t, J = 6.0 Hz, 1H), 2.00-1.96 (m, 2H), 1.28-1.20 (m, 14H), 0.86 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 147.6, 141.1, 126.8, 126.7, 124.3, 119.7, 47.5, 33.1, 31.8, 29.9, 29.6, 29.4, 29.3, 25.7, 22.6, 14.1. MS (EI): *m/z* (%) 165 (100), 166 (34), 178 (17), 179 (20), 292 (69), 293 (17). This compound was known: Soloducho, J.; Idzik, K.; Cabaj, J.; Doskocz, J.; Lapkowski, M.; Plewa, S. *ARKIVOC (Gainesville, FL, U. S.)*. **2007,** *6***,** 75**.**

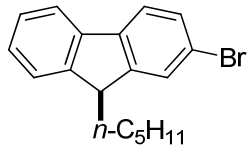


9-Decyl-9H-fluorene (6g). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, J = 7.5 Hz, 2H), 7.50 (d, J = 7.0 Hz, 2H), 7.36-7.33 (m, 2H), 7.31-7.28 (m, 2H), 3.96 (t, J = 5.0 Hz, 1H), 2.00-1.97 (m, 2H), 1.26-1.20 (m, 16H), 0.89-0.85 (m, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 147.6, 141.1, 126.8, 126.7,

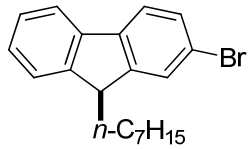
124.3, 119.7, 47.5, 33.1, 31.9, 29.9, 29.60, 29.56, 29.4, 29.3, 25.7, 22.7, 14.1. MS (EI): *m/z* (%) 57 (7), 165 (100), 166 (31), 178 (18), 179 (19), 306 (66), 307 (17). HRMS Calcd for $[C_{23}H_{30} + H]^+$: 307.2420; found: 307.2341.



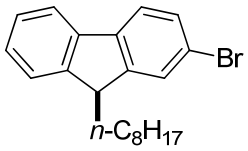
9-Dodecyl-9H-fluorene (6h). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 (d, J = 7.5 Hz, 2H), 7.49 (d, J = 7.5 Hz, 2H), 7.35-7.32 (m, 2H), 7.30-7.27 (m, 2H), 3.95 (t, J = 6.0 Hz, 1H), 1.99-1.95 (m, 2H), 1.29-1.19 (m, 20H), 0.87 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 147.6, 141.1, 126.8, 126.7, 124.3, 119.7, 47.5, 33.1, 31.9, 30.0, 29.64, 29.62, 29.4, 29.3, 25.7, 22.7, 14.1. MS (EI): *m/z* (%) 57 (12), 165 (100), 166 (33), 178 (20), 179 (21), 180 (12), 334 (60), 335 (12). This compound was known: McCluskey, G. E.; Watkins, S. E.; Holmes, A. B.; Ober, C. K.; Lee, J.-K.; Wong, W. W. H. *Polym. Chem.* **2013**, *4*, 5291.



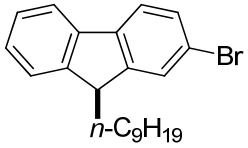
2-Bromo-9-Pentyl-9H-fluorene (6i). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, J = 7.0 Hz, 1H), 7.63 (s, 1H), 7.59 (d, J = 9.0 Hz, 1H), 7.48 (t, J = 8.0 Hz, 2H), 7.37-7.31 (m, 2H), 3.95 (t, J = 6.0 Hz, 1H), 2.03-1.92 (m, 2H), 1.25-1.16 (m, 6H), 0.82 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 149.7, 147.3, 140.2, 140.1, 130.0, 127.6, 127.2, 127.1, 124.4, 121.1, 120.6, 119.8, 47.5, 32.8, 32.1, 25.2, 22.4, 14.0. MS (EI): m/z (%) 316 (43), 314 (44), 245 (38), 243 (40), 235 (16), 179 (100), 178 (24), 165 (74), 164 (35), 163 (28), 57 (2). HRMS Calcd for $[C_{18}H_{19}Br]^+$: 314.0670; found: 314.0677.



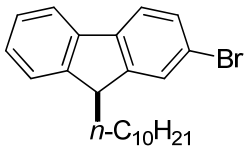
2-Bromo-9-Heptyl-9H-fluorene (6j). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (d, J = 7.5 Hz, 1H), 7.62 (s, 1H), 7.59 (d, J = 9.0 Hz, 1H), 7.48 (t, J = 8.0 Hz, 2H), 7.37-7.30 (m, 2H), 3.95 (t, J = 6.0 Hz, 1H), 2.02-1.91 (m, 2H), 1.26-1.12 (m, 10H), 0.85 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 149.8, 147.3, 140.2, 140.1, 130.0, 127.6, 127.2, 127.1, 124.4, 121.1, 120.7, 119.9, 47.6, 32.9, 31.8, 29.9, 29.1, 25.6, 22.6, 14.1. MS (EI): m/z (%) 344 (8), 342 (8), 306 (7), 304 (20), 245 (9), 243 (9), 179 (20), 166 (20), 165 (100), 164 (15), 163 (11), 139 (18), 103 (7), 57 (9). HRMS Calcd for $[C_{20}H_{23}Br]^+$: 342.0983; found: 342.0989.



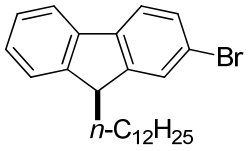
2-Bromo-9-Octyl-9H-fluorene (6k). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (d, *J* = 10.0 Hz, 1H), 7.63 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.37-7.30 (m, 2H), 3.95 (t, *J* = 6.0 Hz, 1H), 2.02-1.91 (m, 2H), 1.28-1.12 (m, 12H), 0.86 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 149.8, 147.3, 140.2, 140.1, 130.0, 127.6, 127.1, 124.4, 121.1, 120.7, 119.8, 47.6, 32.9, 31.8, 29.9, 29.3, 29.2, 25.6, 22.6, 14.1. MS (EI): m/z (%) 358 (62), 356 (66), 277 (11), 245 (42), 243 (44), 179 (80), 178 (29), 166 (16), 165 (100), 164 (30), 163 (21), 71 (7), 57(71). HRMS Calcd for $[C_{21}H_{25}Br]^{+}$: 356.1140; found: 356.1136.



2-Bromo-9-Nonyl-9H-fluorene (6l). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, *J* = 7.5 Hz, 2H), 7.63 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.37-7.31 (m, 2H), 3.95 (t, *J* = 6.0 Hz, 1H), 2.03-1.92 (m, 2H), 1.27-1.15 (m, 14H), 0.86 (t, *J* = 6.0 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 149.7, 147.3, 140.13, 140.10, 130.0, 127.6, 127.2, 127.0, 124.4, 121.1, 120.6, 119.8, 47.5, 32.9, 29.9, 29.6, 29.4, 29.3, 25.6, 22.7, 14.1. MS (EI): m/z (%) 372 (53), 370 (53), 291 (9), 245 (40), 243 (39), 179 (69), 178 (28), 166 (16), 165 (100), 164 (28), 163 (18), 71 (35), 57 (44). HRMS Calcd for $[C_{22}H_{27}Br]^{+}$: 370.1296; found: 356.1292.

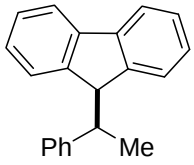


2-Bromo-9-Decyl-9H-fluorene (6m). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, *J* = 7.0 Hz, 2H), 7.63 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.37-7.30 (m, 2H), 3.95 (t, *J* = 6.0 Hz, 1H), 2.03-1.92 (m, 2H), 1.29-1.12 (m, 16H), 0.87 (t, *J* = 6.0 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 149.8, 147.3, 140.14, 140.11, 130.0, 127.6, 127.2, 127.0, 124.4, 121.1, 120.6, 119.8, 47.5, 31.9, 29.9, 29.60, 29.57, 29.4, 29.3, 25.6, 22.7, 14.1. MS (EI): m/z (%) 386 (54), 384 (57), 305 (8), 245 (38), 243 (39), 179 (67), 178 (28), 166 (16), 165 (100), 164 (25), 163 (16), 85 (22), 71 (31), 57 (36). HRMS Calcd for $[C_{23}H_{29}Br]^{+}$: 384.1453; found: 384.1453.

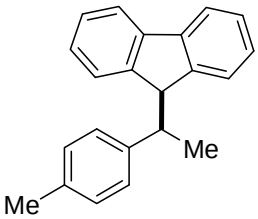


2-Bromo-9-Dodecyl-9H-fluorene (6n). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, J = 7.0 Hz, 2H), 7.63 (s, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.48 (t, J = 8.0 Hz, 2H), 7.37-7.31 (m, 2H), 3.95 (t, J = 6.0 Hz, 1H), 2.03-1.92 (m, 2H), 1.30-1.12 (m, 20H), 0.87 (t, J = 6.0 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 149.8, 147.3, 140.13, 140.10, 130.0, 127.6, 127.2, 127.0, 124.4, 121.1, 120.6, 119.8, 47.5, 31.9, 29.9, 29.64, 29.63, 29.60, 29.38, 29.35, 22.7, 14.1. MS (EI): m/z (%) 415 (16), 414 (61), 413 (17), 412 (62), 333 (6), 245 (39), 243 (37), 179 (58), 178 (25), 166 (16), 165 (100), 164 (21), 163 (12), 85 (21), 71 (28), 57 (44). HRMS Calcd for $[C_{25}H_{33}Br]^+$: 412.1766; found: 412.1768.

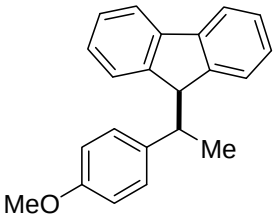
Typical Procedure for Ketone-Catalyzed 9-C-Alkylation of Fluorenes with Secondary Alcohols. The mixture of fluorene **2a** (0.166 g, 1.0 mmol), 1-phenylethanol **8a** (0.147 g, 1.2 mmol, 1.2 equiv.), $CsOH·H_2O$ (0.168 g, 1.0 mmol, 100 mol%), acetophenone (12 μL, 0.1 mmol, 10 mol%), and toluene (1.0 mL) in a 20 mL schlenk tube was sealed under nitrogen, heated at 160 °C for 24 h, and monitored by GC-MS and/or TLC. After completion of the reaction, the reaction mixture was concentrated under vacuum. The residue was then purified through column chromatography on silica gel using ethyl acetate and petroleum ether (60-90 ^{o}C) (v/v 1/50) as the eluent, giving **9a** in 88% isolated yield (0.238 g).



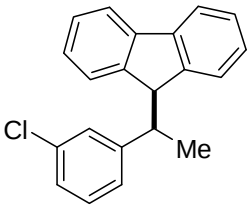
9-(1-Phenylethyl)-9H-fluorene (9a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82-7.77 (m, 2H), 7.56 (d, J = 7.2 Hz, 1H), 7.47-7.32 (m, 8H), 7.22-7.17 (m, 1H), 6.92 (d, J = 7.8 Hz, 1H), 4.38 (d, J = 4.5 Hz, 1H), 3.79-3.71 (m, 1H), 1.02 (d, J = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.5, 144.56, 144.55, 141.8, 141.3, 128.1, 128.0, 127.04, 126.99, 126.8, 126.3, 126.2, 125.6, 124.3, 119.65, 119.58, 54.2, 41.9, 13.9. This compound was known: Murphy, W. S.; Hauser, C. R. *J. Org. Chem.* **1965**, *31*, 85.



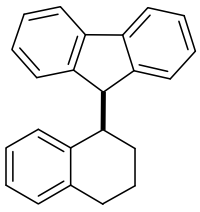
9-(1-(*p*-Tolyl)ethyl)-9H-fluorene (9b). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91-7.87 (m, 2H), 7.66 (d, J = 7.2 Hz, 1H), 7.57-7.46 (m, 3H), 7.41-7.28 (m, 5H), 7.06 (d, J = 7.5 Hz, 1H), 4.46 (d, J = 4.5 Hz, 1H), 3.87-3.78 (m, 1H), 2.56 (s, 3H), 1.10 (d, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.6, 144.6, 141.7, 141.5, 141.3, 135.6, 128.8, 127.9, 127.0, 126.9, 126.7, 126.1, 125.6, 124.2, 119.6, 119.5, 54.2, 41.4, 21.0, 13.9. HRMS Calcd for $[C_{22}H_{20} + Na]^+$: 307.1457; found: 307.1445.



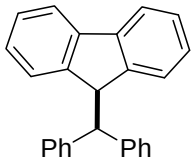
9-(1-(4-Methoxyphenyl)ethyl)-9H-fluorene (9c). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80-7.76 (m, 2H), 7.56 (d, J = 7.2 Hz, 1H), 7.46-7.35 (m, 3H), 7.28 (d, J = 8.7 Hz, 2H), 7.22-7.17 (m, 1H), 6.96-6.92 (m, 3H), 4.32 (d, J = 4.5 Hz, 1H), 3.88 (s, 3H), 3.74-3.66 (m, 1H), 0.99 (d, J = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.0, 146.5, 144.7, 141.7, 141.3, 136.6, 128.9, 127.0, 126.9, 126.7, 126.2, 125.6, 124.3, 119.63, 119.55, 113.5, 55.2, 54.3, 41.1, 14.2. HRMS Calcd for $[C_{22}H_{20}O + H]^+$: 301.1587; found: 301.1597.



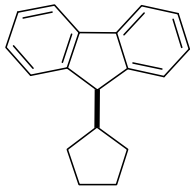
9-(1-(3-Chlorophenyl)ethyl)-9H-fluorene (9d). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (dd, J = 7.5 Hz, J = 11.5 Hz, 2H), 7.48 (d, J = 7.5 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.33-7.29 (m, 2H), 7.26-7.22 (m, 3H), 7.15-7.12 (m, 2H), 4.25 (d, J = 4.5 Hz, 1H), 3.66-3.60 (m, 1H), 0.93 (d, J = 7.0 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 146.7, 146.0, 144.2, 141.8, 141.4, 134.0, 129.3, 128.3, 127.3, 127.2, 126.5, 126.4, 126.3, 125.4, 124.3, 119.8, 119.7, 53.9, 41.9, 14.1. MS (EI): m/z (%) 306 (4), 304 (18), 166 (9), 165 (100), 164 (7), 141 (7), 139 (26), 103 (10). HRMS Calcd for $[C_{21}H_{17}Cl]^+$: 304.1019; found: 304.1015.



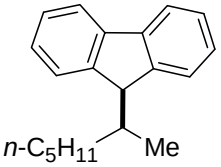
9-(1,2,3,4-Tetrahydronaphthalen-1-yl)-9H-fluorene (9e). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01-7.93 (m, 3H), 7.80 (d, J = 6.9 Hz, 1H), 7.62-7.47 (m, 5H), 7.38 (d, J = 6.9 Hz, 1H), 7.24-7.22 (m, 1H), 6.66 (d, J = 7.8 Hz, 1H), 4.88 (d, J = 3.9 Hz, 1H), 4.13-4.07 (m, 1H), 2.87-2.65 (m, 2H), 1.65-1.54 (m, 3H), 1.06-0.93 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.4, 145.2, 141.8, 141.4, 139.1, 138.6, 129.2, 128.2, 126.91, 126.87, 126.85, 126.5, 126.0, 125.8, 125.2, 123.6, 119.7, 119.4, 52.4, 40.5, 30.2, 23.2, 21.8. HRMS Calcd for $[C_{23}H_{20} + H]^+$: 297.1638; found: 297.1647.



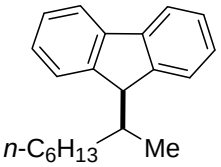
9-Benzhydryl-9H-fluorene (9f). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (d, J = 7.5 Hz, 2H), 7.31-7.25 (m, 10H), 7.24-7.22 (m, 2H), 7.01-6.98 (m, 2H), 6.60 (d, J = 8.0 Hz, 2H), 4.83 (d, J = 9.0 Hz, 1H), 4.17 (d, J = 9.0 Hz, 1H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 145.6, 143.1, 141.2, 128.9, 128.4, 127.1, 126.6, 126.3, 125.7, 119.5, 55.8, 51.7. This compound was known: Murphy, W. S.; Hauser, C. R. *J. Org. Chem.* **1966**, *31*, 85.



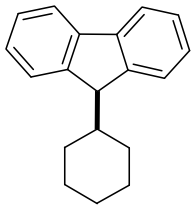
9-Cyclopentyl-9H-fluorene (9g). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 7.5 Hz, 2H), 7.38-7.35 (m, 2H), 7.30-7.27 (m, 2H), 4.03 (d, J = 5.5 Hz, 1H), 2.44-2.35 (m, 1H), 1.80-1.74 (m, 2H), 1.62-1.57 (m, 2H), 1.52-1.44 (m, 2H), 1.41-1.33 (m, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 147.1, 141.3, 126.8, 126.5, 125.1, 119.6, 51.2, 44.4, 30.0, 25.2. Praefcke, K. and Weichsel, C. *Liebigs Annalen der Chemie.* **1980**, *10*, 1604.



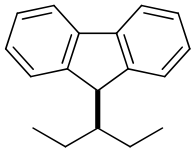
9-(Heptan-2-yl)-9H-fluorene (9g). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82-7.78 (m, 2H), 7.58-7.55 (m, 2H), 7.44-7.31 (m, 4H), 4.05 (d, J = 3.0 Hz, 1H), 2.48-2.39 (m, 1H), 1.51-1.33 (m, 8H), 0.95 (t, J = 6.3 Hz, 3H), 0.67 (d, J = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.1, 145.8, 141.9, 141.5, 126.8, 126.73, 126.71, 126.5, 125.1, 124.4, 119.6, 119.5, 52.5, 37.2, 34.5, 32.0, 27.6, 22.7, 15.7, 14.1. HRMS Calcd for $[C_{20}H_{24} + Na]^+$: 287.1770; found: 287.1809.



9-(Octan-2-yl)-9H-fluorene (9i). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82-7.78 (m, 2H), 7.59-7.55 (m, 2H), 7.44-7.31 (m, 4H), 4.05 (d, J = 3.3 Hz, 1H), 2.49-2.37 (m, 1H), 1.48-1.33 (m, 10H), 0.95 (t, J = 6.8 Hz, 3H), 0.67 (d, J = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.1, 145.8, 141.9, 141.5, 126.8, 126.72, 126.71, 126.5, 125.1, 124.4, 119.6, 119.5, 52.5, 37.2, 34.5, 31.9, 29.4, 27.9, 22.7, 15.7, 14.1. HRMS Calcd for $[C_{21}H_{26} + Na]^+$: 301.1927; found: 301.1994.

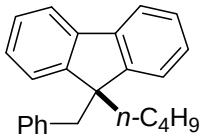


9-Cyclohexyl-9H-fluorene (9j). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, J = 6.9 Hz, 2H), 7.72 (d, J = 6.9 Hz, 2H), 7.55-7.44 (m, 4H), 4.09-4.04 (m, 1H), 2.39-2.32 (m, 1H), 1.86-1.79 (m, 3H), 1.66 (d, J = 11.1 Hz, 2H), 1.48-1.22 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.4, 141.6, 126.7, 126.6, 124.8, 119.5, 53.5, 43.1, 29.6, 26.9, 26.4. This compound was known: Patsidis, K.; Alt, H. G. *J. Organomet. Chem*. **1995**, *501*, 31.



9-(Pentan-3-yl)-9H-fluorene (9k). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, J = 7.5 Hz, 2H), 7.50 (d, J = 7.5 Hz, 2H), 7.35 (t, J = 7.5 Hz, 2H), 7.27 (t, J = 7.5 Hz, 2H), 4.12 (d, J = 2.5 Hz, 1H), 2.06-2.00 (m, 1H), 1.32-1.14 (m, 4H), 0.89 (t, J = 7.5 Hz, 6H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 146.9, 141.7, 126.7, 126.6, 124.7, 119.6, 49.4, 46.2, 24.1, 12.7. MS (EI): m/z (%) 237 (6), 236 (29), 207 (3), 193 (5), 178 (5), 167 (11), 166 (85), 165 (100), 164 (10), 163 (10), 139 (5), 115 (3), 82 (6), 71 (4). HRMS Calcd for $[C_{18}H_{20}]^{+}$: 236.1565; found: 236.1570.

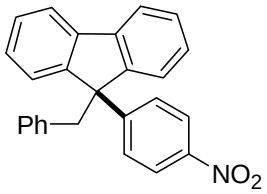
Procedure for Base-Mediated 9-C-Butylation of 9-Benzyl-9H-fluorene with Butyl Bromide. The mixture of 9-benzyl-9H-fluorene **3a** (0.256 g, 1.0 mmol), 1-bromobutane (0.550 g, 4.0 mmol, 4.0 equiv.), TBAI (0.074 g, 0.2 mmol, 20 mol%), NaOH (0.5 g) and water (0.50 mL) in a 20 mL schlenk tube was sealed under N_2, heated at 80 °C for 24 h, and then monitored by GC-MS and/or TLC. After completion of the reaction, the mixture was successively washed with dil. HCl, water and brine, and then extracted with ethyl acetate. The combined organic layer was concentrated under vacuum, which as then purified through column chromatography on silica gel using ethyl acetate and petroleum ether (60-90 ^{o}C) (v/v 1/50), giving gave **12** in 85% isolated yield (0.265g).



9-Benzyl-9-Butyl-fluorene (12). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74-7.71 (m, 2H), 7.47-7.43 (m, 6H), 7.16-7.12 (m, 3H), 6.85 (d, J = 6.3 Hz, 2H), 3.33 (s, 2H), 2.35-2.30 (m, 2H), 1.35-1.23 (m, 2H), 0.87-0.73 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.4, 140.9, 137.3, 130.3, 127.0, 126.8, 126.6,

125.8, 123.6, 119.6, 55.8, 46.8, 38.6, 25.9, 23.0, 13.8. MS (EI): *m/z* (%) 149.4, 140.9, 137.3, 130.3, 127.0, 126.8, 126.6, 125.8, 123.6, 119.6, 55.8, 46.8, 38.6, 25.9, 23.0, 13.8. HRMS Calcd for $[C_{24}H_{24} + H]^+$: 313.1951; found: 313.1958.

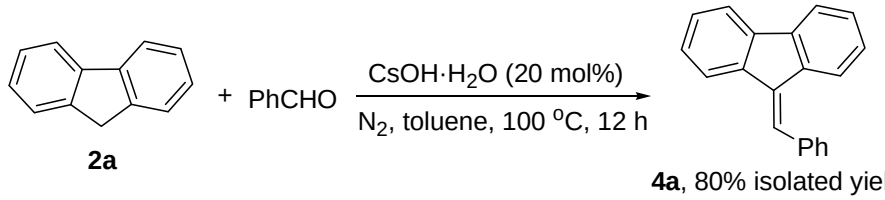
Procedure for 9-C-Arylation of 9-Benzyl-9H-fluorene with *p*-Chloronitrobenzene. The mixture of 9-benzyl-9H-fluorene **3a** (0.256 g, 1.0 mmol), *p*-chloronitrobenzene (0.246 g, 1.5 mmol, 1.5 equiv.), $CsOH \cdot H_2O$ (0.252 g, 1.5 mmol, 150 mol%), and acetonitrile (1.0 mL) in a 20 mL Schlenk tube was sealed under nitrogen, heated at 80 °C for 12 h, and then monitored by GC-MS and/or TLC. After completion of the reaction, the mixture was successively washed with dil. HCl, water and brine, and then extracted with ethyl acetate. The combined organic layer was concentrated under vacuum and then purified through column chromatography on silica gel using ethyl acetate and petroleum ether (60-90 ^oC) (v/v 1/50) as the eluent, giving **13** in 75% isolated yield (0.283 g).



9-Benzyl-9-(4-Nitrophenyl) fluorene (13). ^1H NMR (500 MHz, $CDCl_3$): δ 8.10 (d, J = 8.5 Hz, 2H), 7.51-7.49 (m, 2H), 7.43 (d, J = 9.0 Hz, 2H), 7.30-7.25 (m, 6H), 6.90-6.87 (m, 1H), 6.80-6.77 (m, 2H), 6.42 (d, J = 7.5 Hz, 2H), 3.80 (s, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 152.6, 149.4, 146.6, 140.9, 135.5, 129.9, 127.83, 127.80, 127.4, 126.9, 126.0, 124.8, 123.6, 120.1, 59.9, 43.5. HRMS Calcd for $[C_{26}H_{19}NO_2 + H]^+$: 378.1489; found: 378.1482.

Mechanistic Studies

1. The Initial Condensation Step

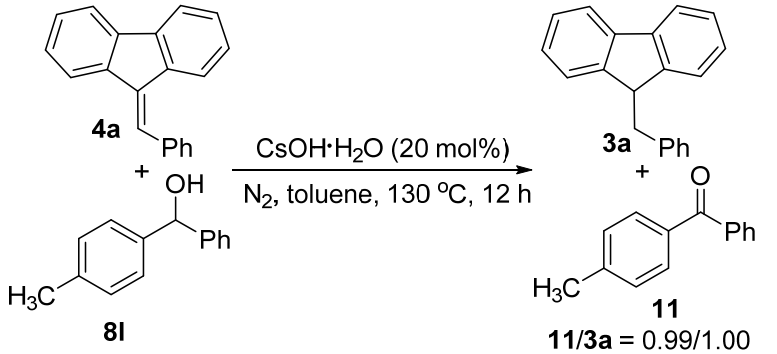


2a

4a, 80% isolated yield

The mixture of **2a** (0.499 g, 3 mmol), PhCHO (0.425 g, 4 mmol, 1.33 equiv.), and $CsOH·H_2O$ (0.101 g, 0.6 mmol, 20 mol%) in toluene (1 mL) was sealed under N_2 in a 20 mL Schlenk tube, heated at 100 °C for 12 h, and then monitored by TLC/GC-MS. The mixture was then concentrated under vacuum and purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluent, giving **4a** in 80% isolated yield.

2. The Transfer Hydrogenation Step

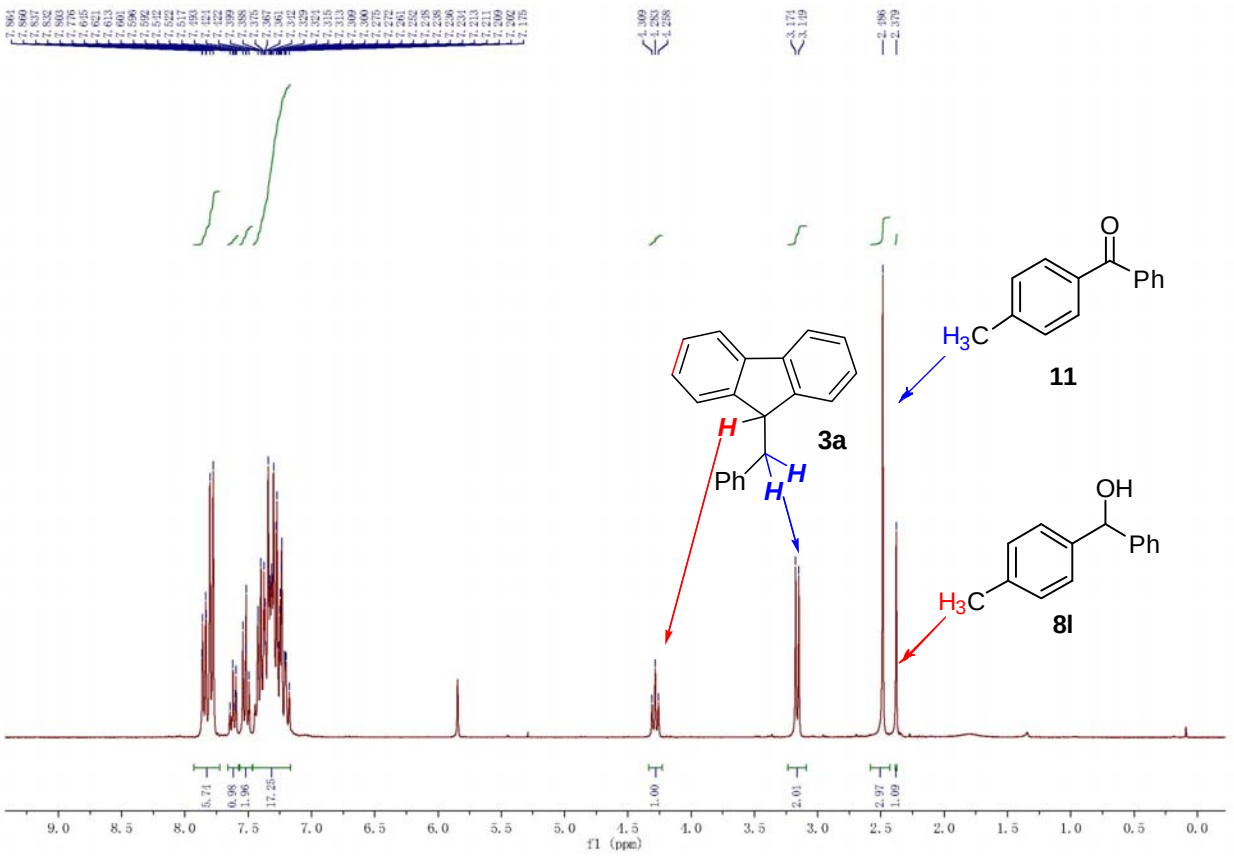


8l

11

11/3a = 0.99/1.00
(mol/mol by ^{1}H NMR)

The mixture of **4a** (0.763 g, 3 mmol), **8l** (0.793 g, 4 mmol, 1.33 equiv.), $CsOH·H_2O$ (0.101 g, 20 mol%), and toluene (0.5 mL) was sealed under N_2 in a 20 mL Schlenk tube, heated at 130 °C for 12 h, and then monitored by ^{1}H NMR. ^{1}H NMR spectra of the reaction mixture (see next page) showed that conversion of **4a** to **3a** is complete. The molar ratio of ketone **11** and product **3a** is ca. 0.99/1.00. That is to say, with the generation of the target product **3a**, an equivalent amount of the byproduct ketone **11** could also be produced. This clearly means that, in the reaction mechanism, the added carbonyl catalyst can be regenerated quantitatively during the transfer hydrogenation step, which will then be recycled to participate in next reaction cycle as the intermediate/catalyst.

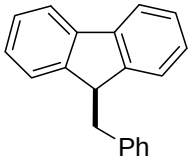


Product **3a**: (1.00 + 2.01/2)/2 = 1.0025

Byproduct ketone **11**: 2.97/3 = 0.99

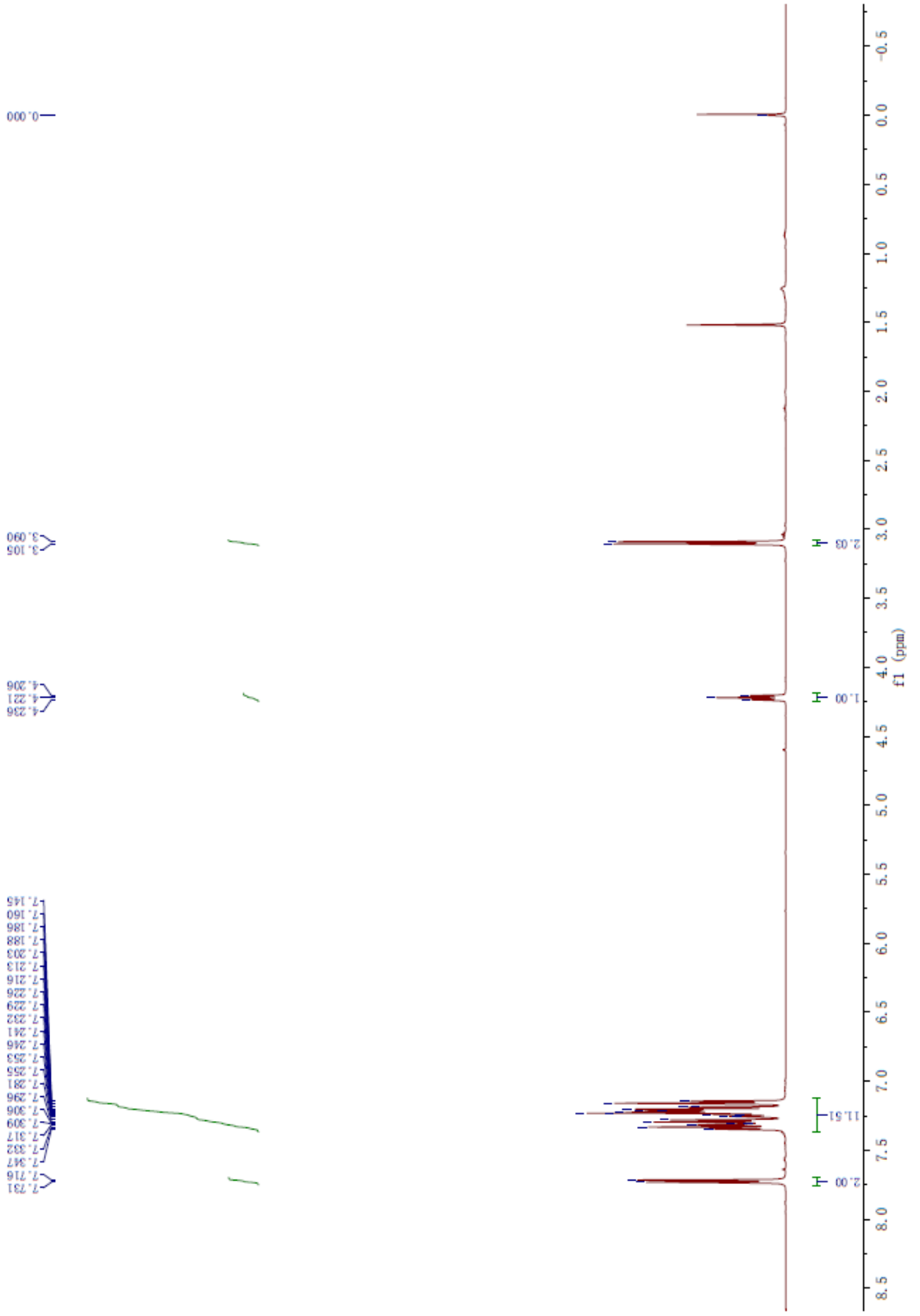
Mol(ketone **11**)/ Mol(product **3a**): 0.99/1.0025 = 0.99/1.00

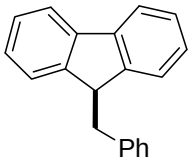
^{1}H and ^{13}C NMR Spectra of the Products



3a

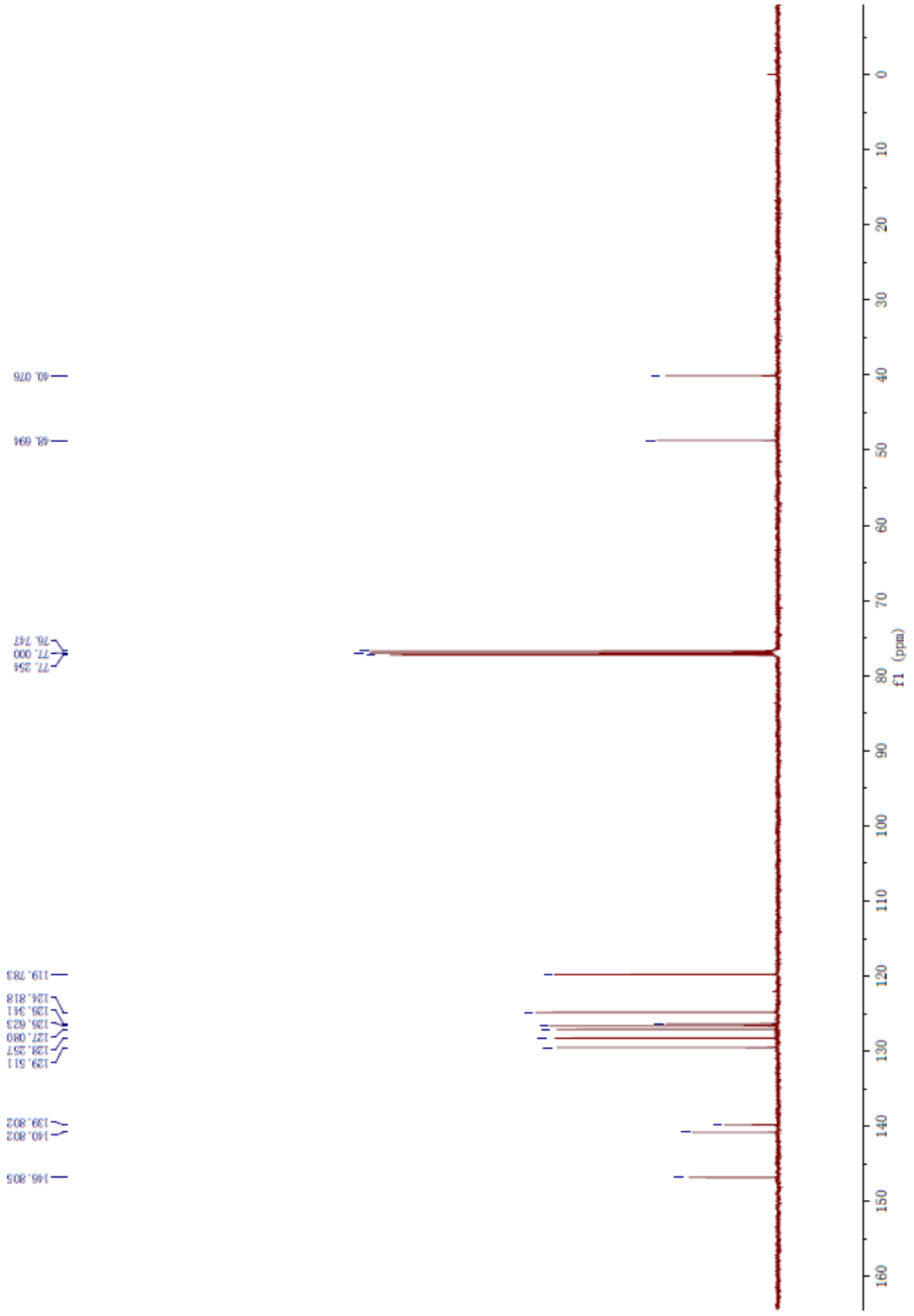
^{1}H NMR

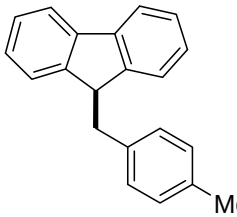



Ph

3a

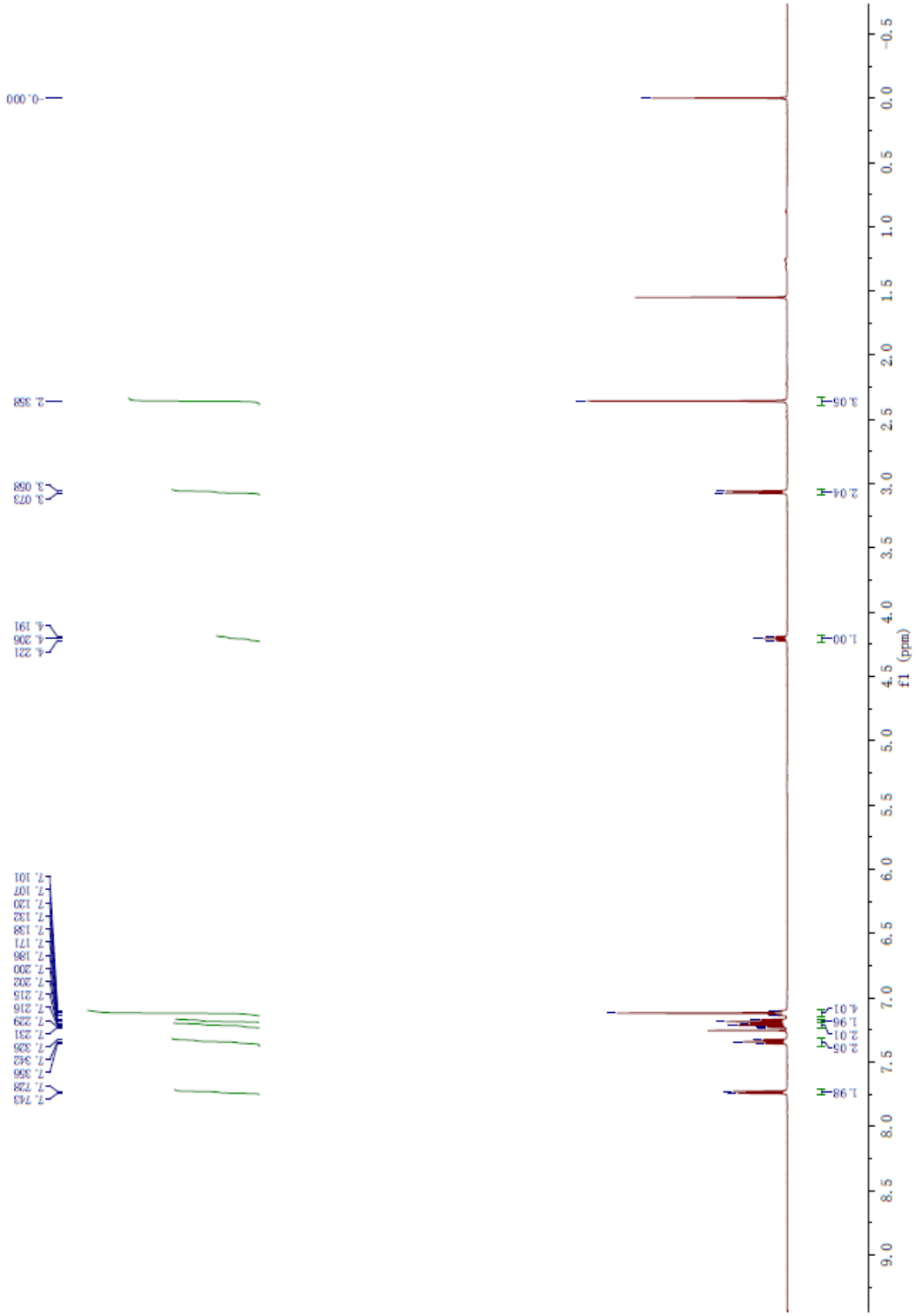
^{13}C NMR

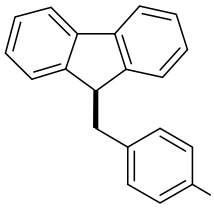

40.076
48.694
76.747
77.000
77.254
119.783
124.818
126.341
126.623
127.080
128.257
129.511
139.802
140.802
146.805
f1 (ppm)



3b

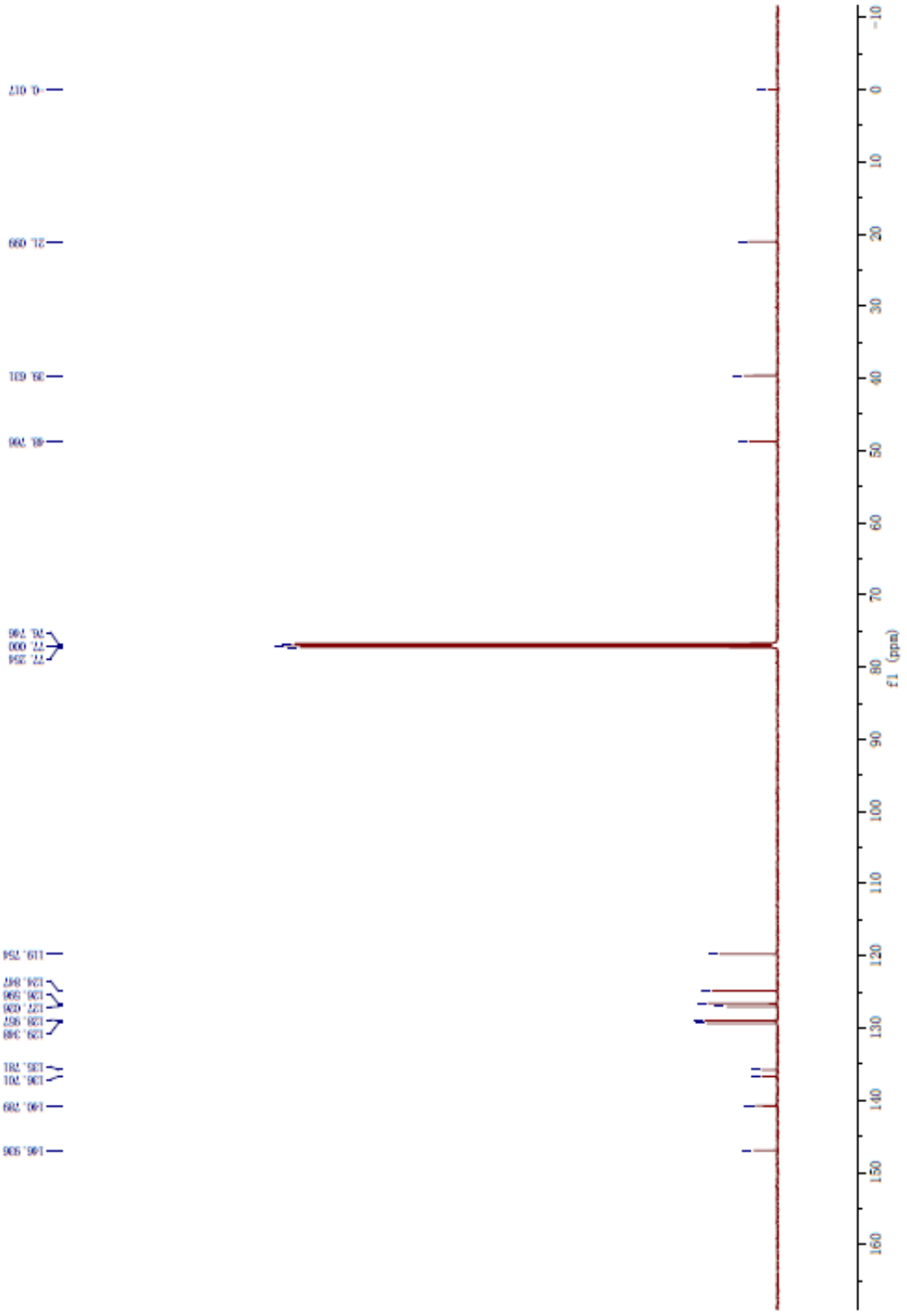
^{1}H NMR

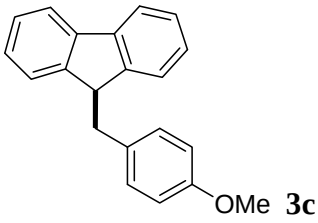




3b

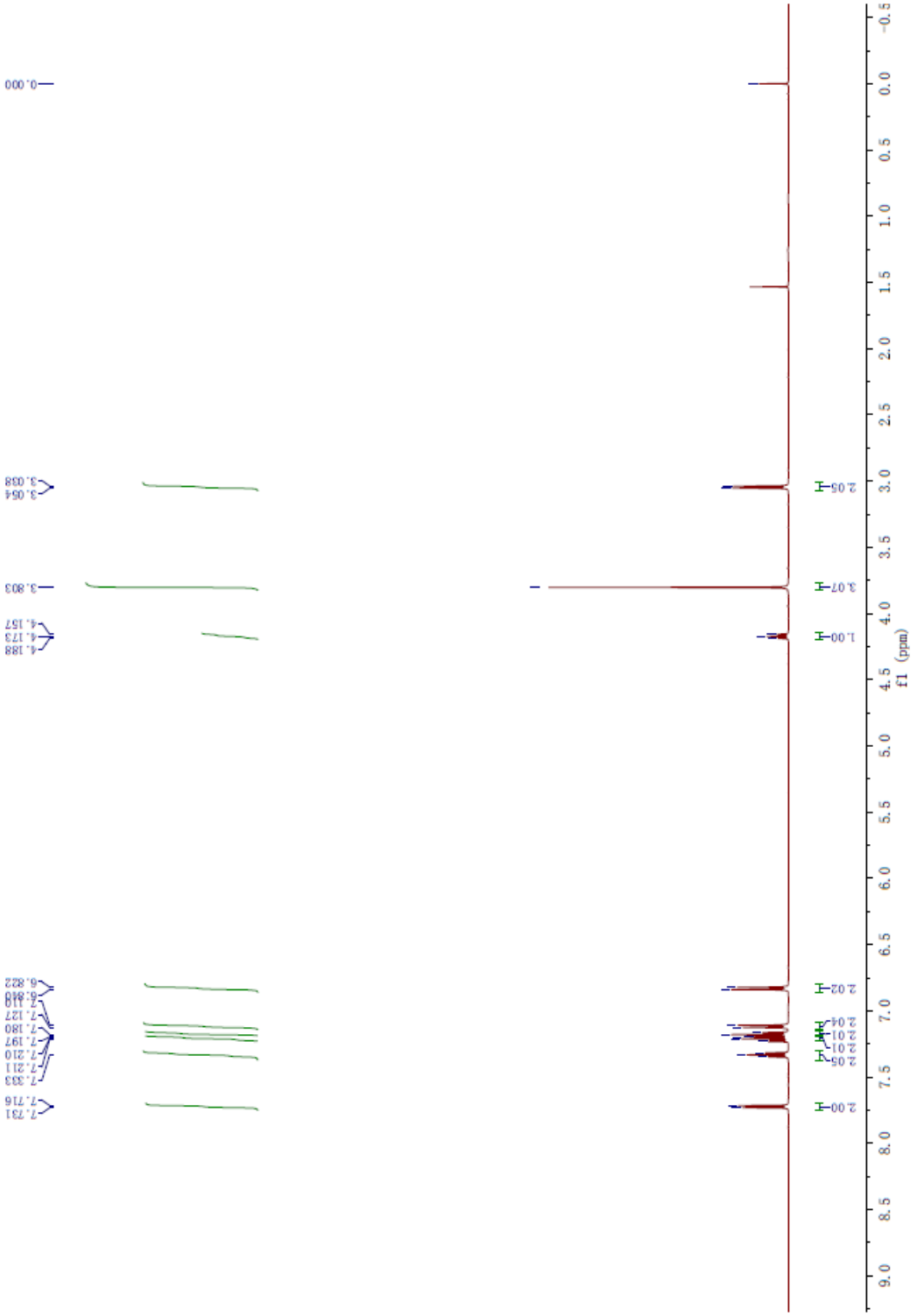
^{13}C NMR

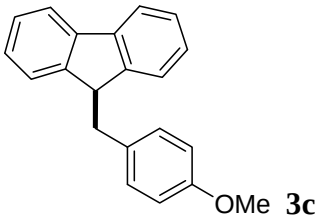




3c

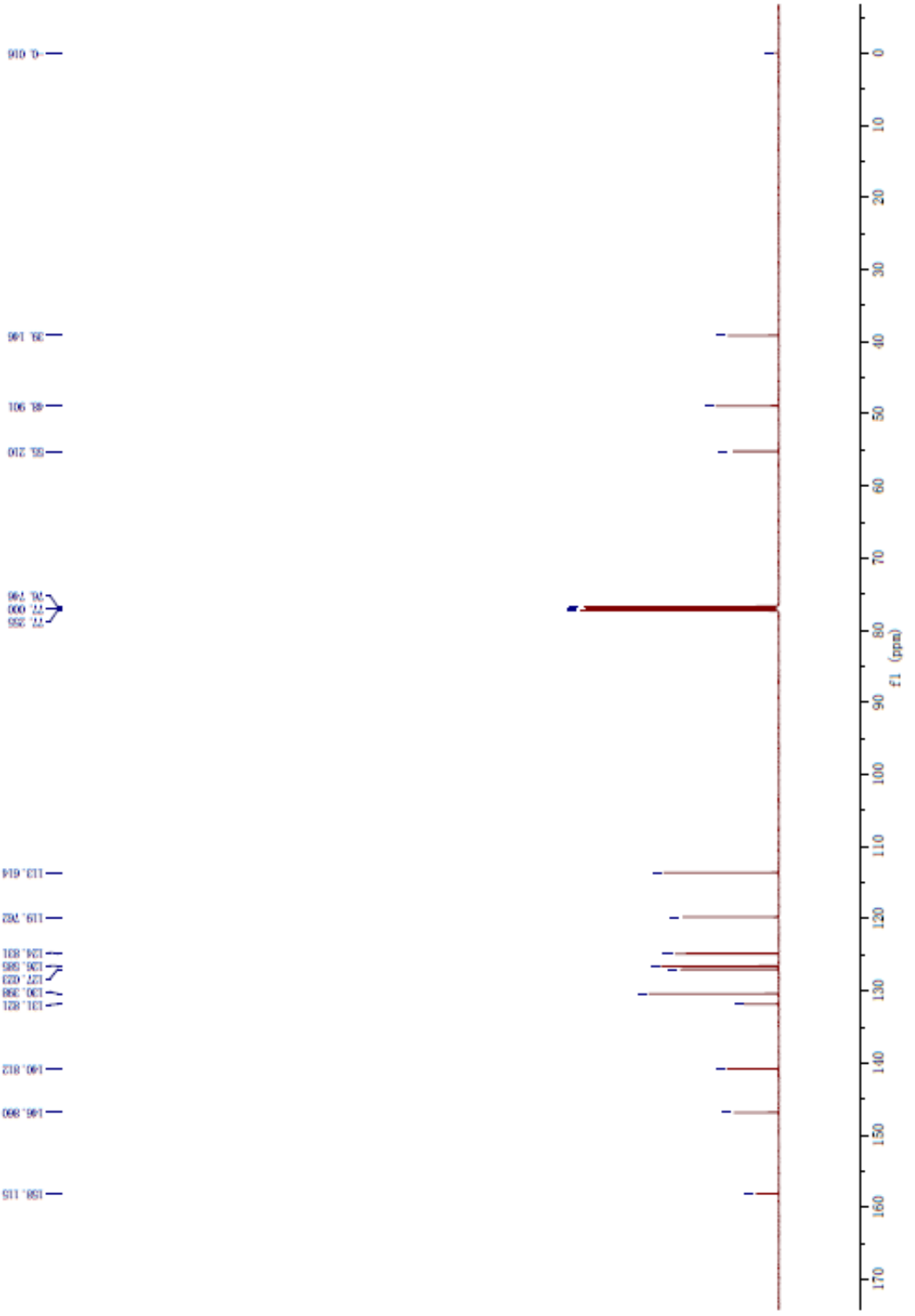
^{1}H NMR

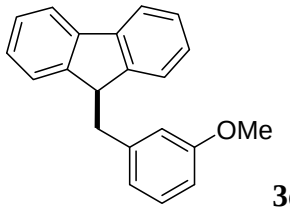




3c

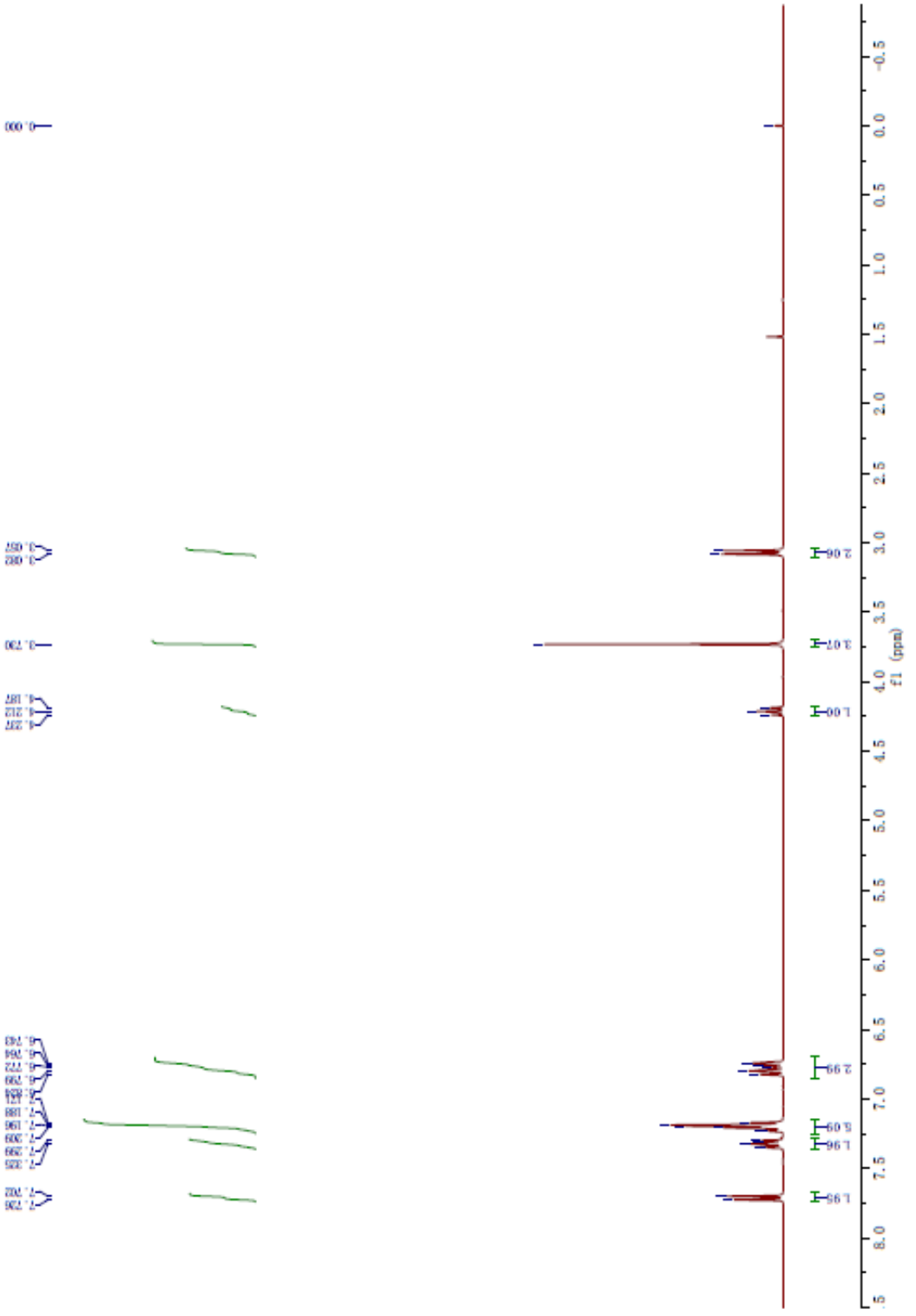
^{13}C NMR

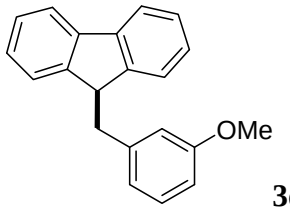




3d

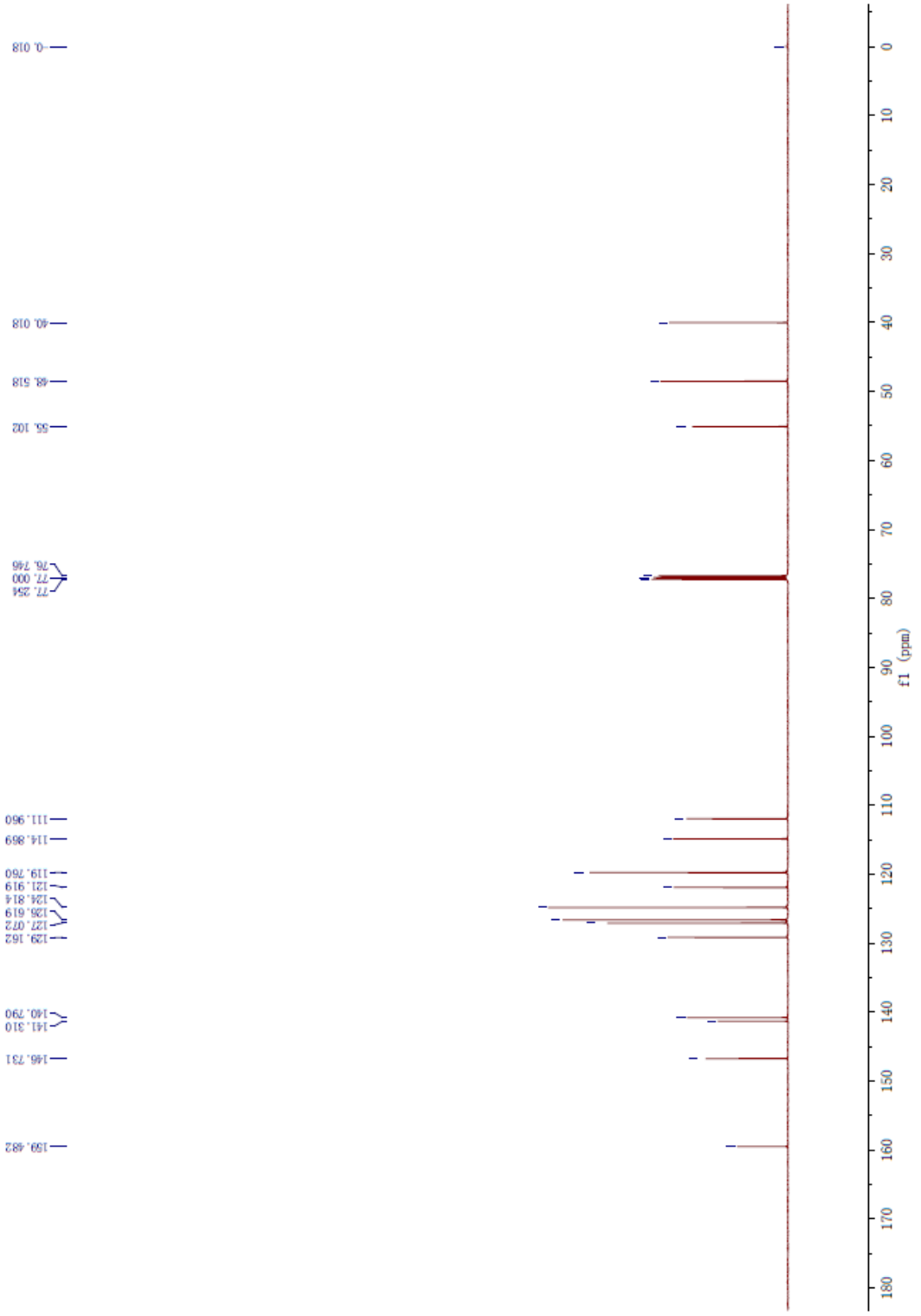
^{1}H NMR

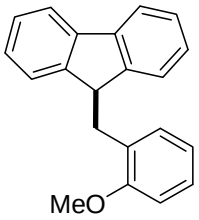



OMe

3d

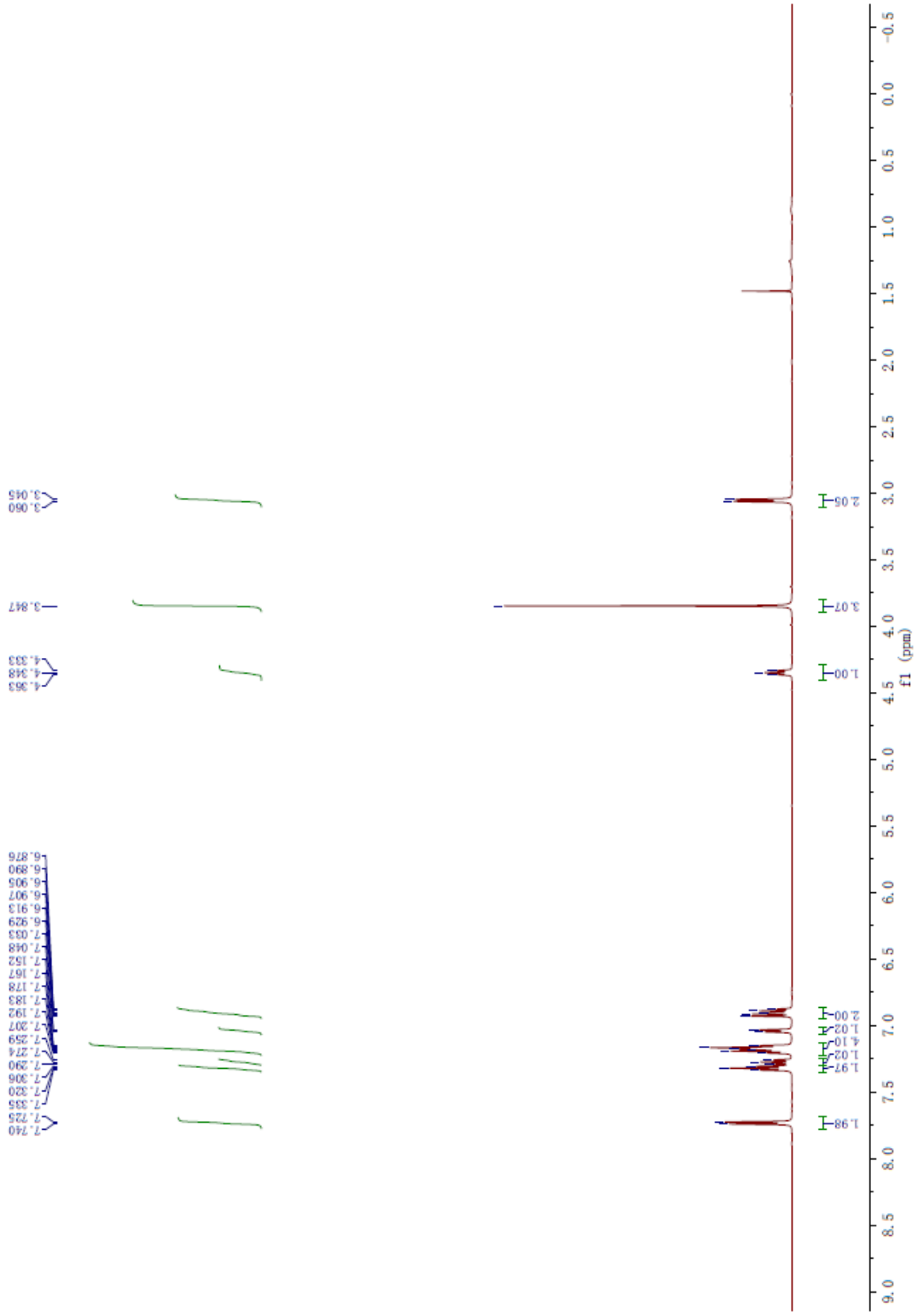
^{13}C NMR

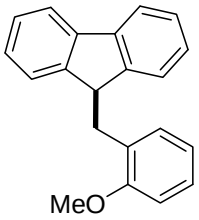

0.018
40.018
48.518
55.102
76.746
77.000
77.254
111.960
114.869
119.760
121.919
124.814
126.619
127.072
129.162
140.790
141.310
146.731
159.482
f1 (ppm)



3e

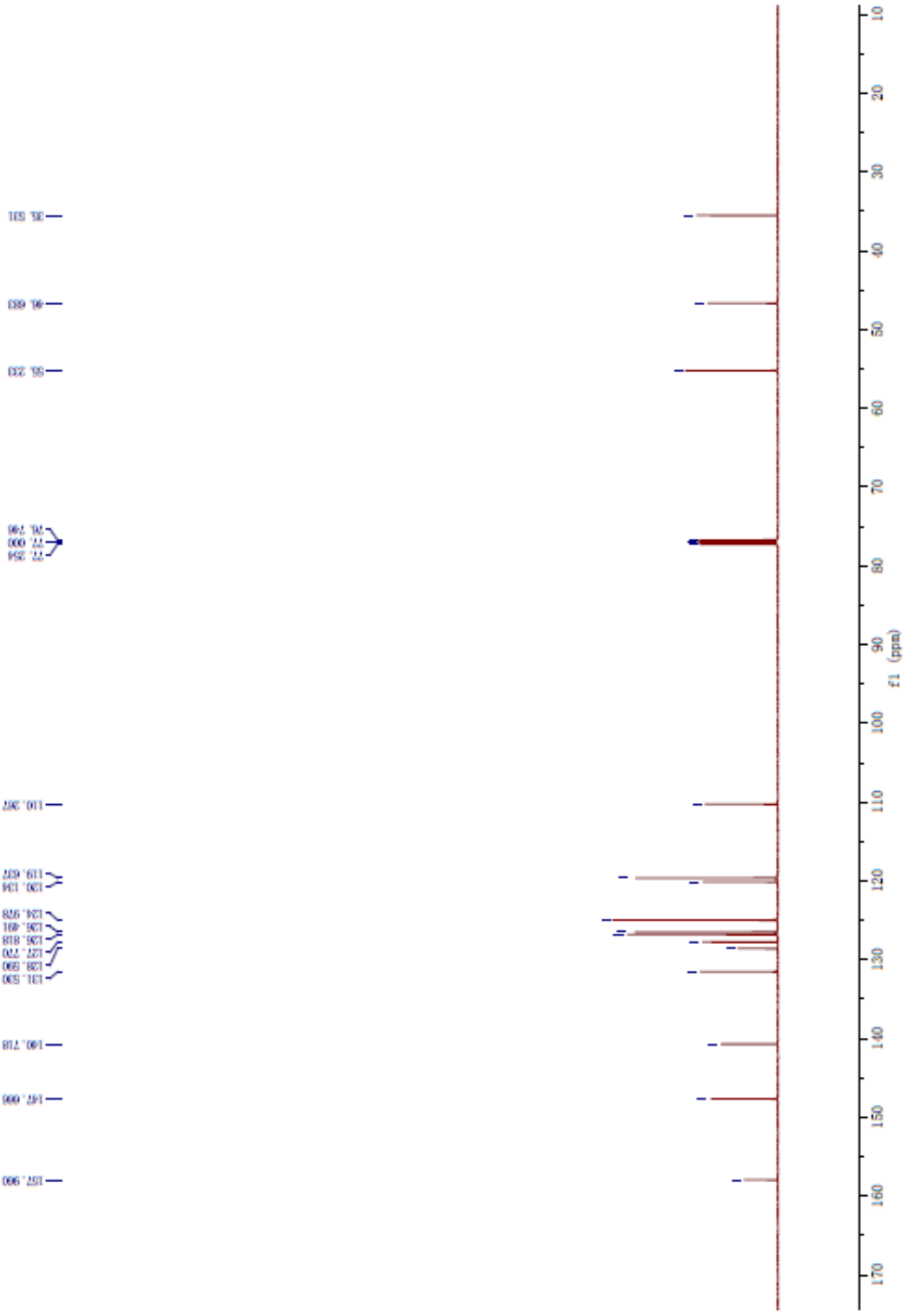
^{1}H NMR

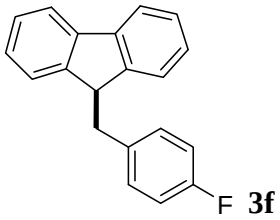




3e

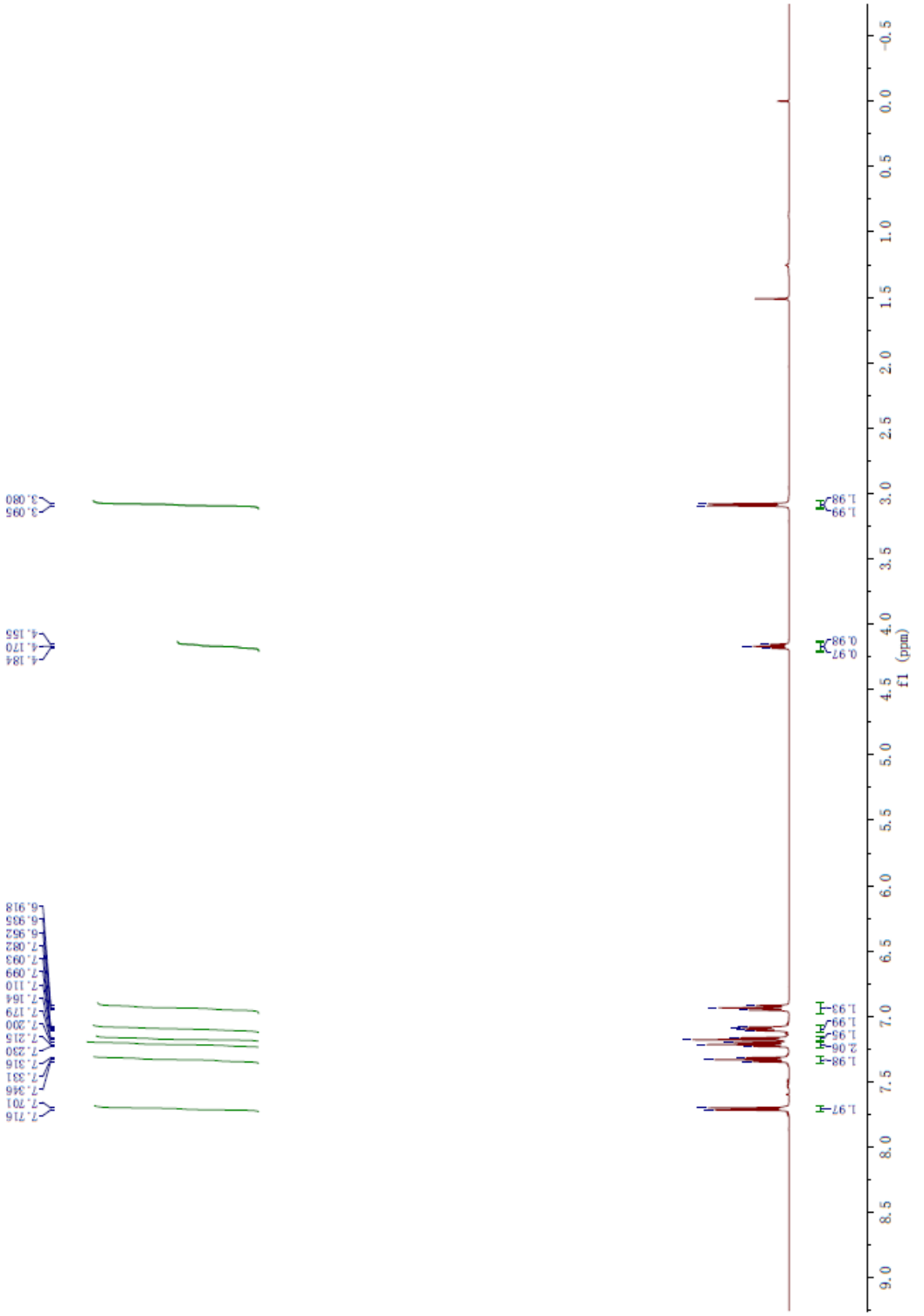
^{13}C NMR

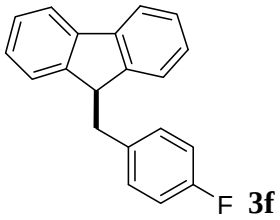




3f

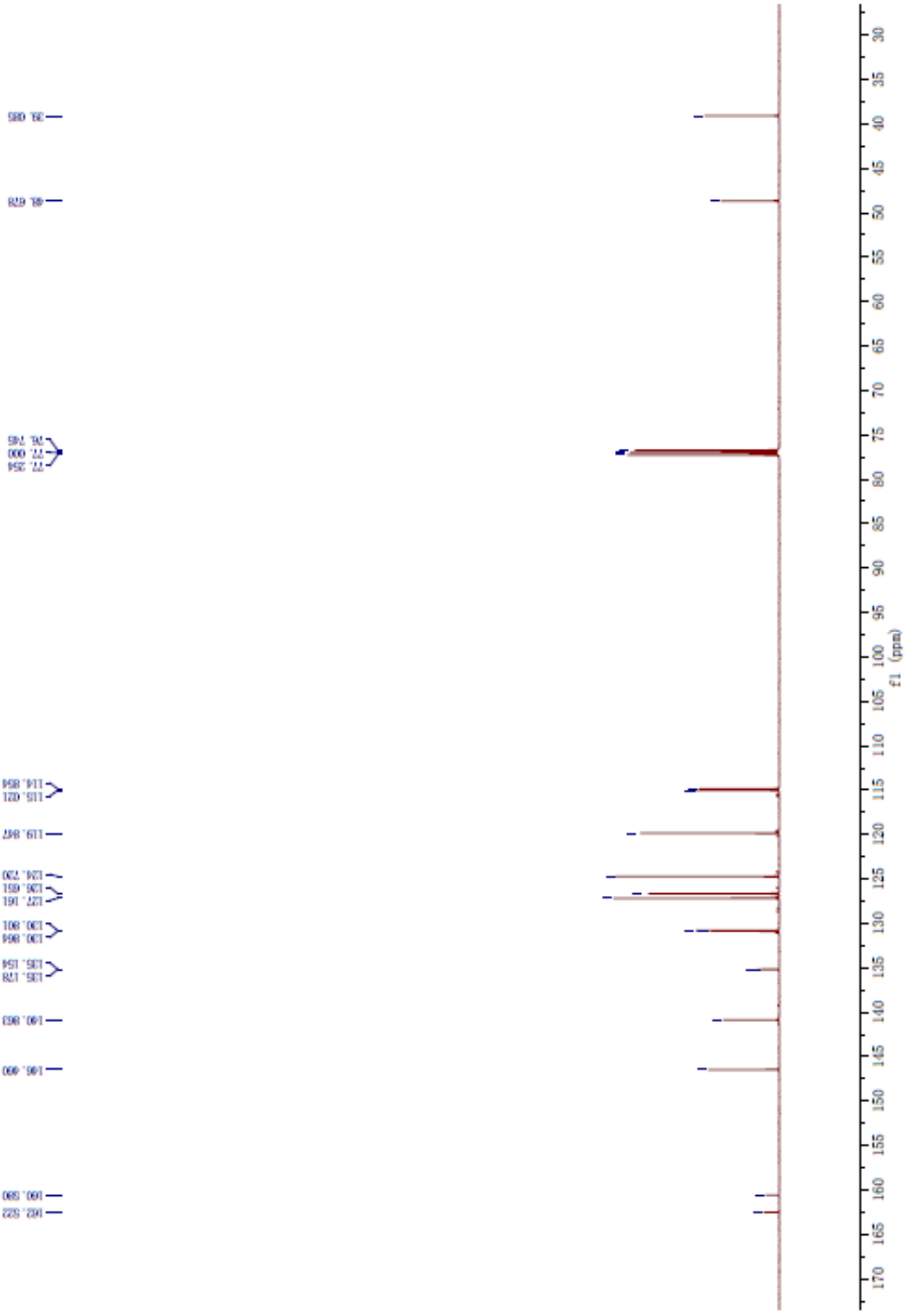
^{1}H NMR

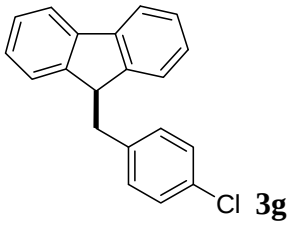




3f

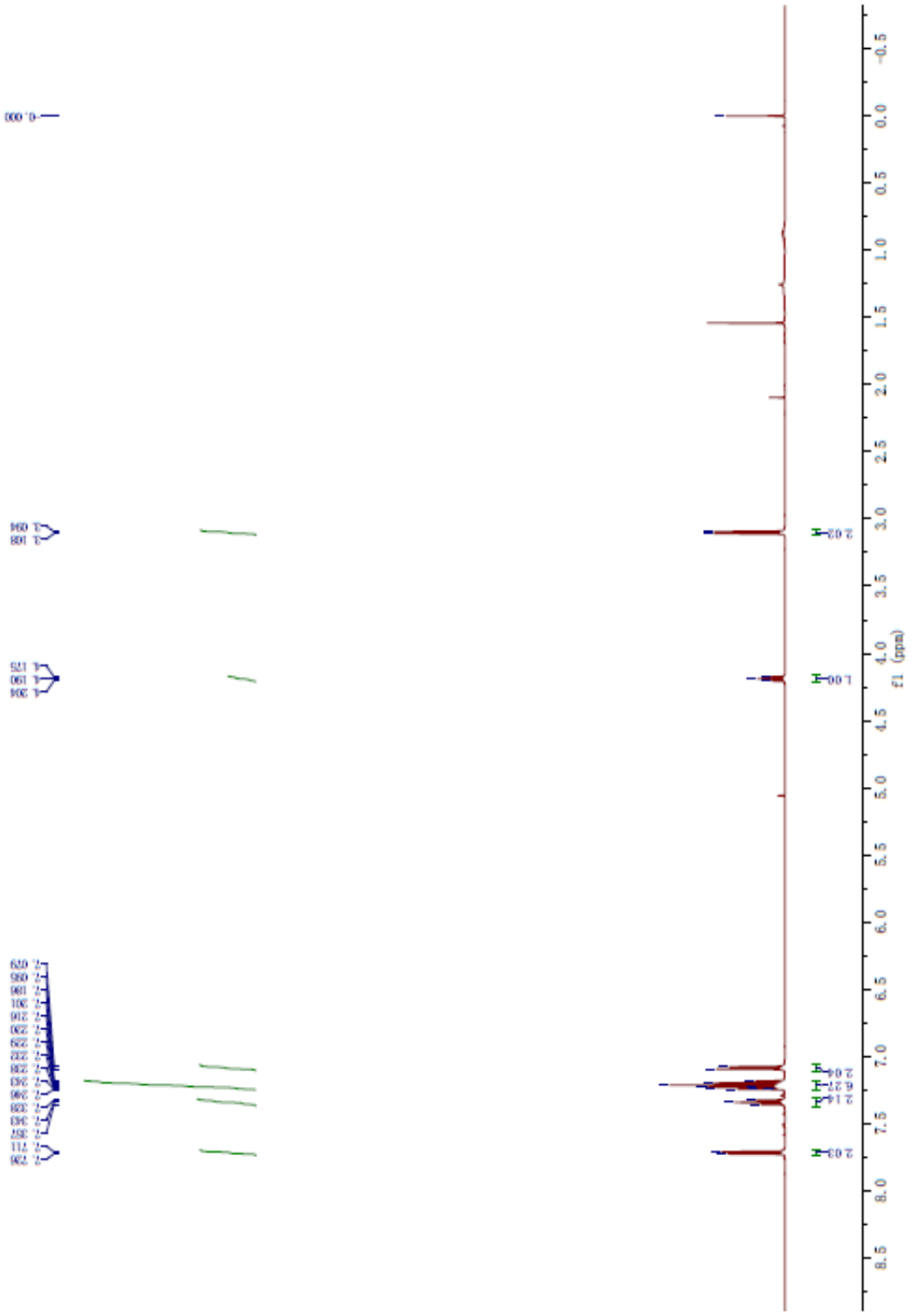
^{13}C NMR

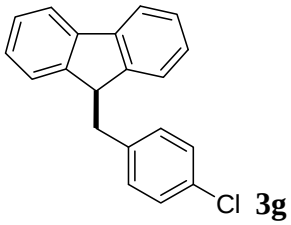




3g

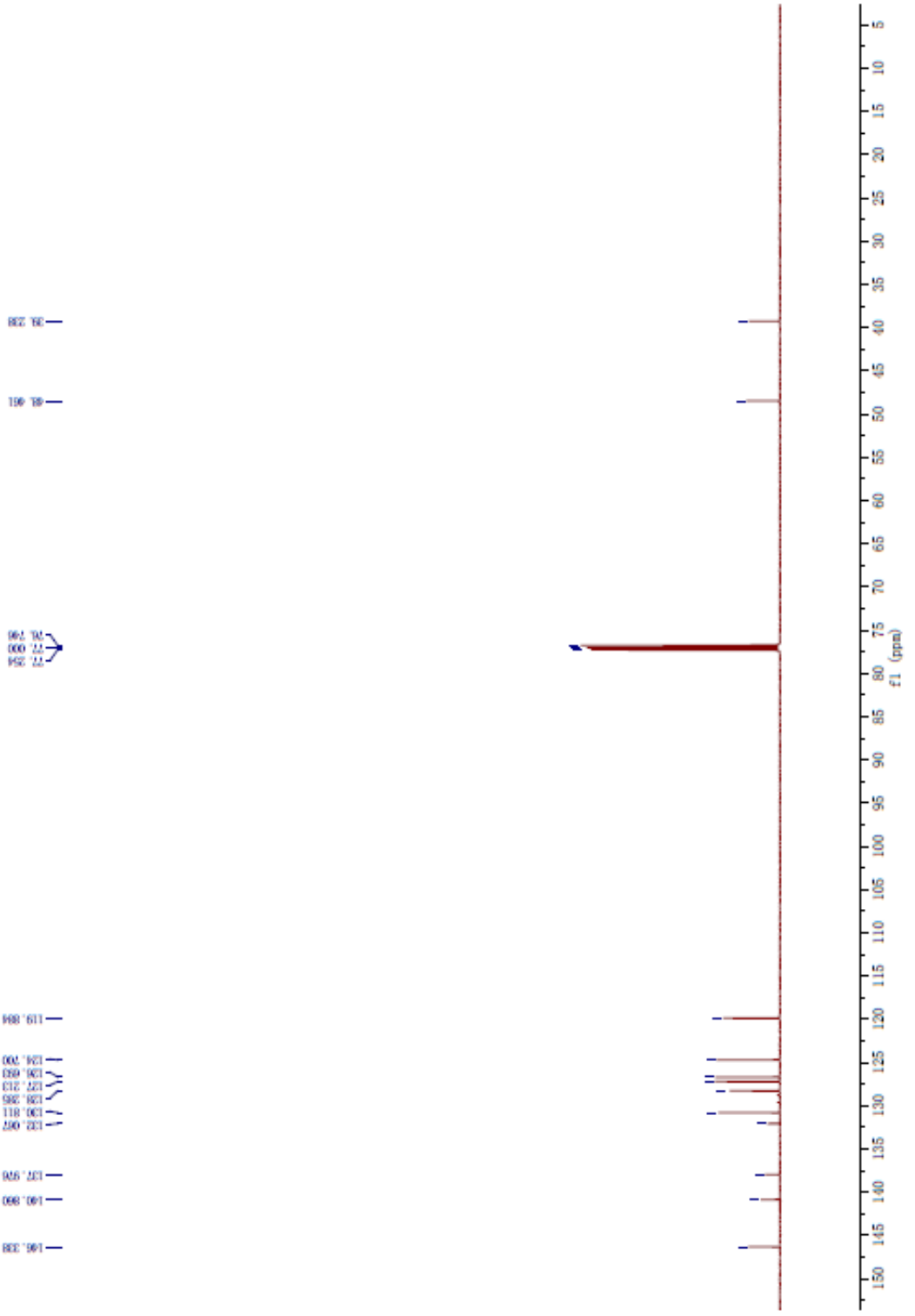
^{1}H NMR

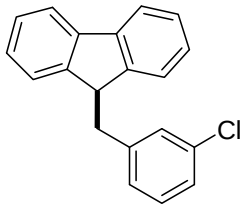




3g

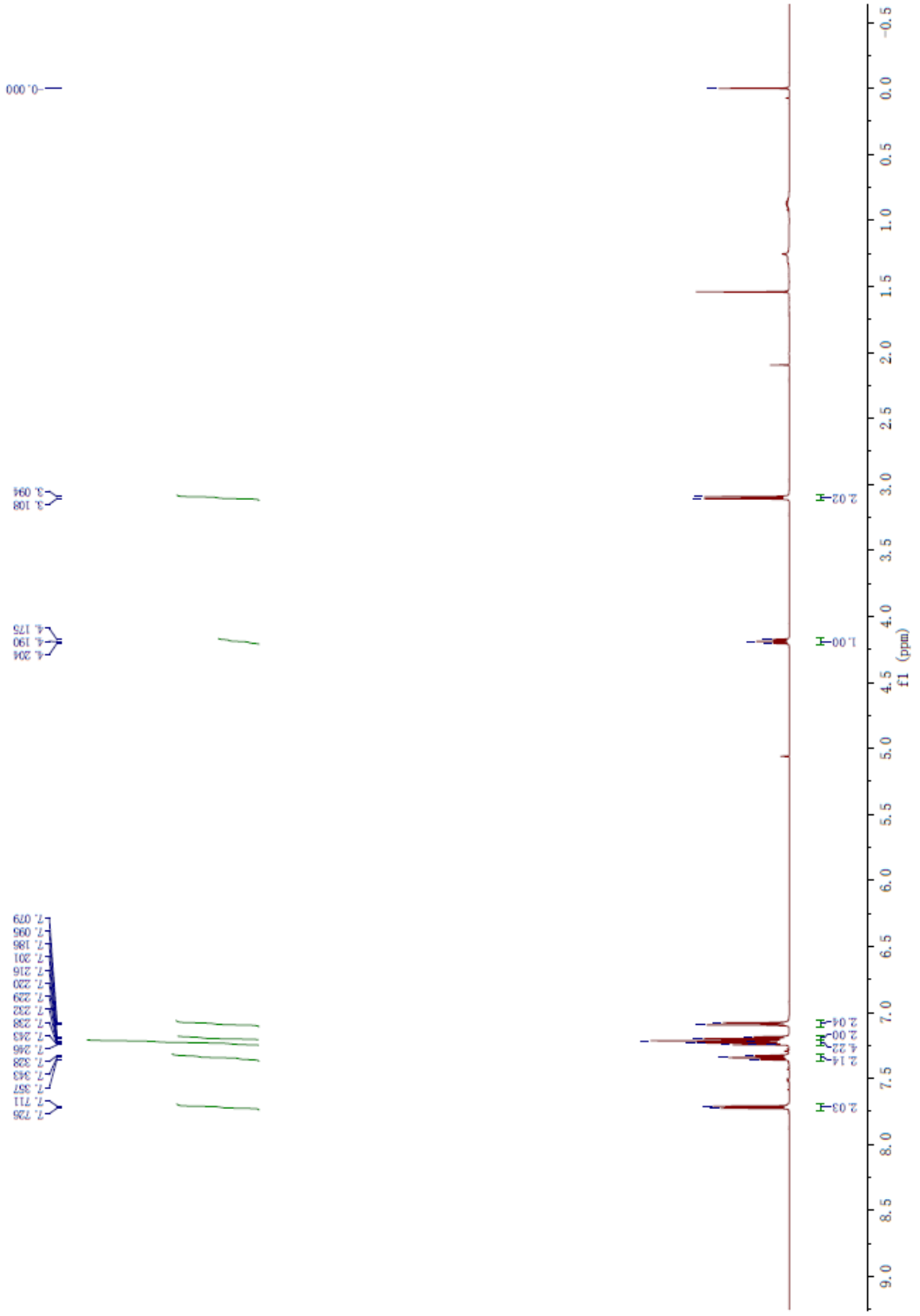
^{13}C NMR

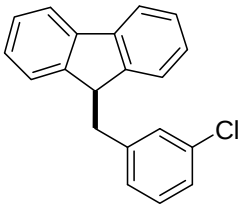




3h

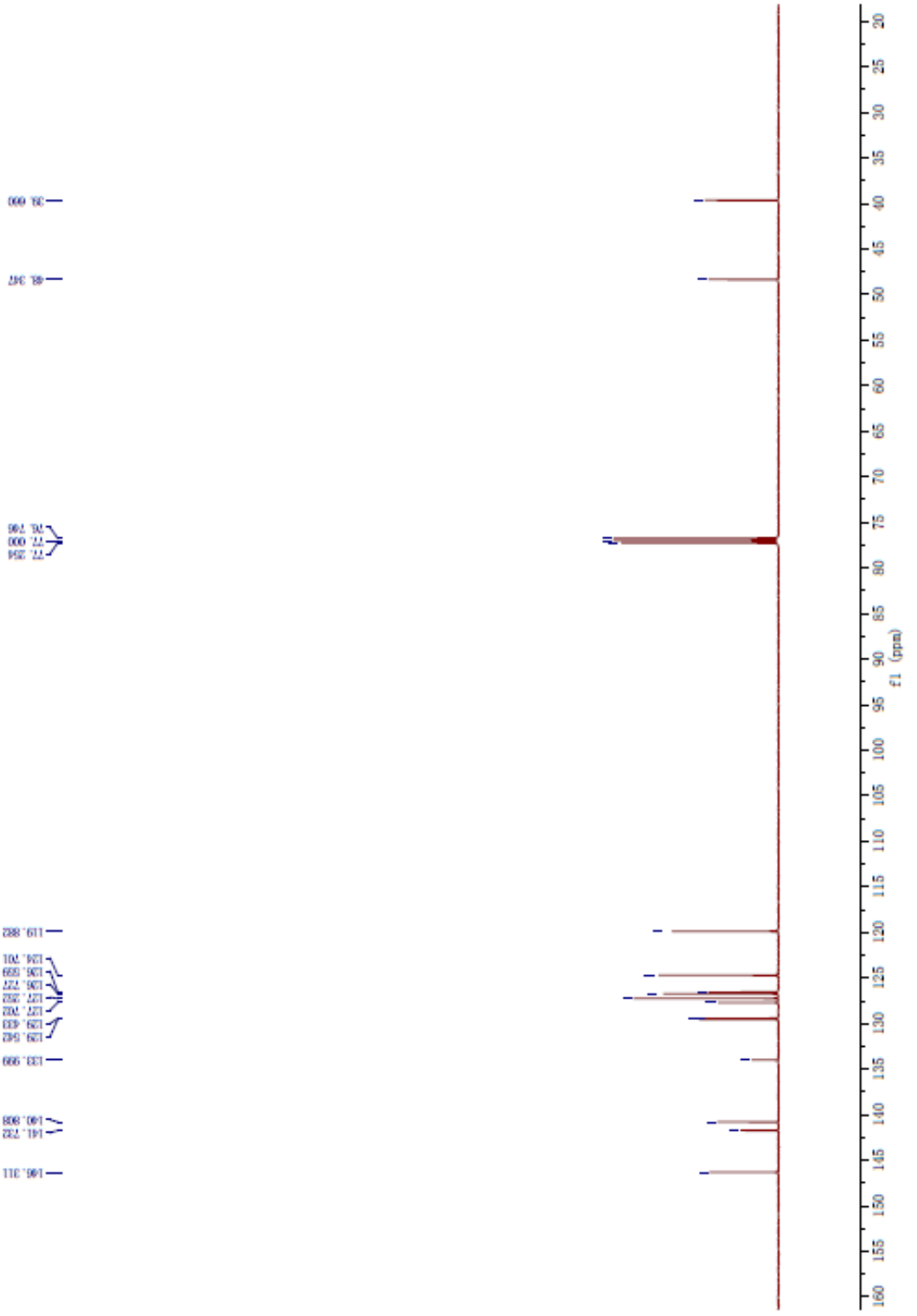
^{1}H NMR

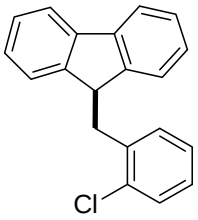




3h

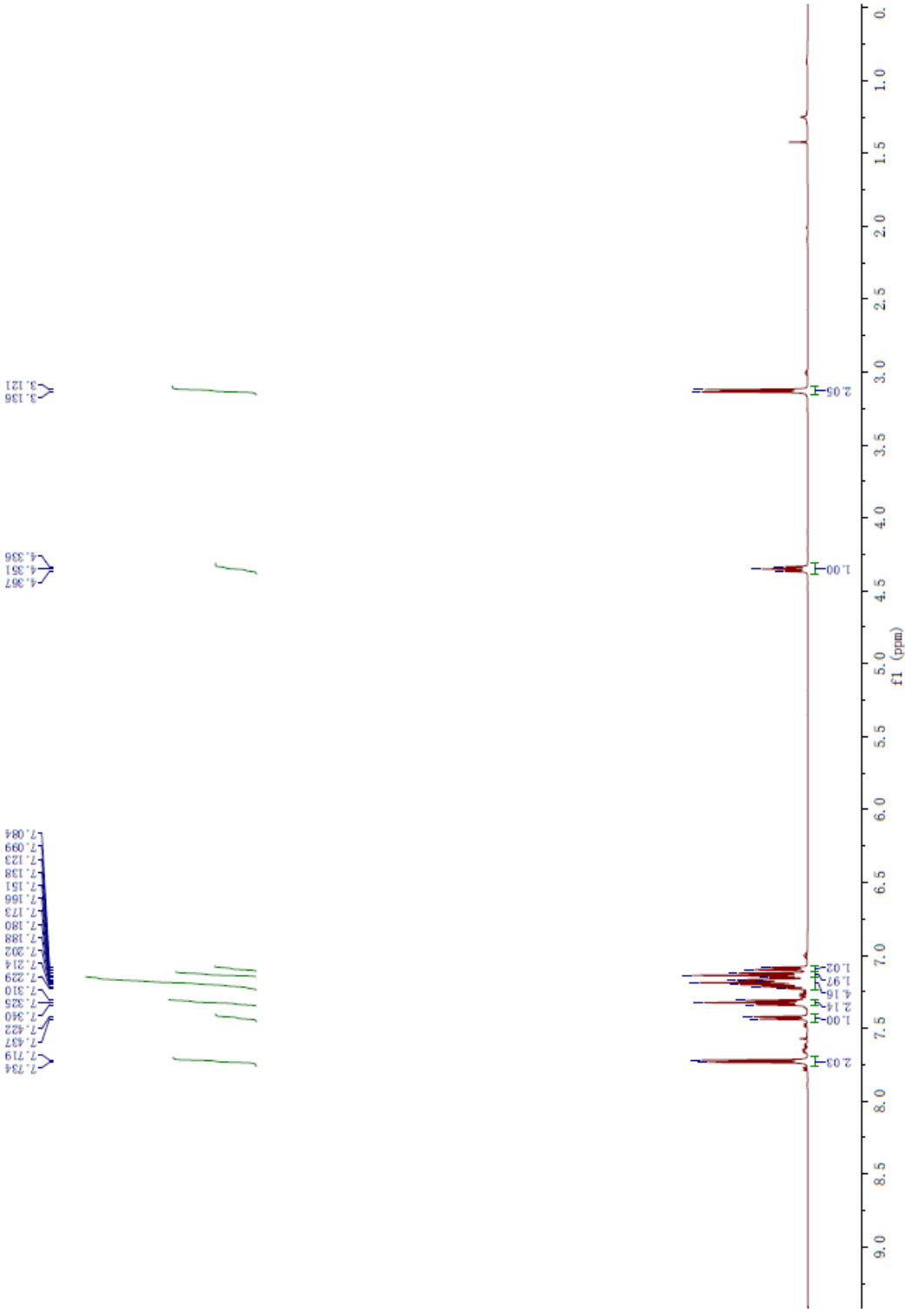
^{13}C NMR

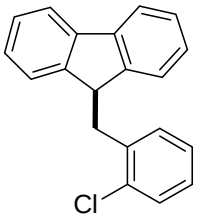




3i

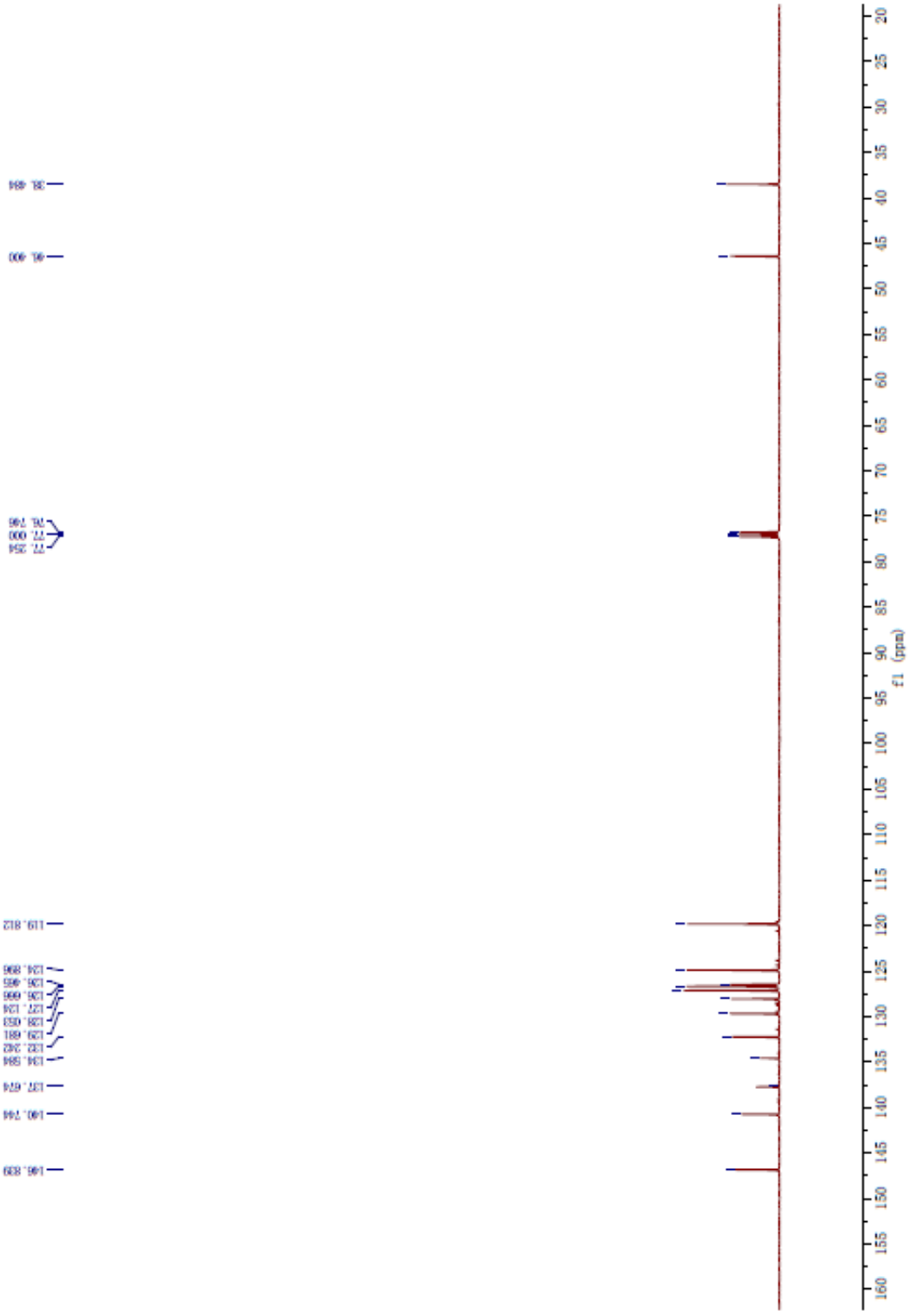
^{1}H NMR

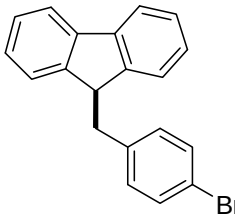




3i

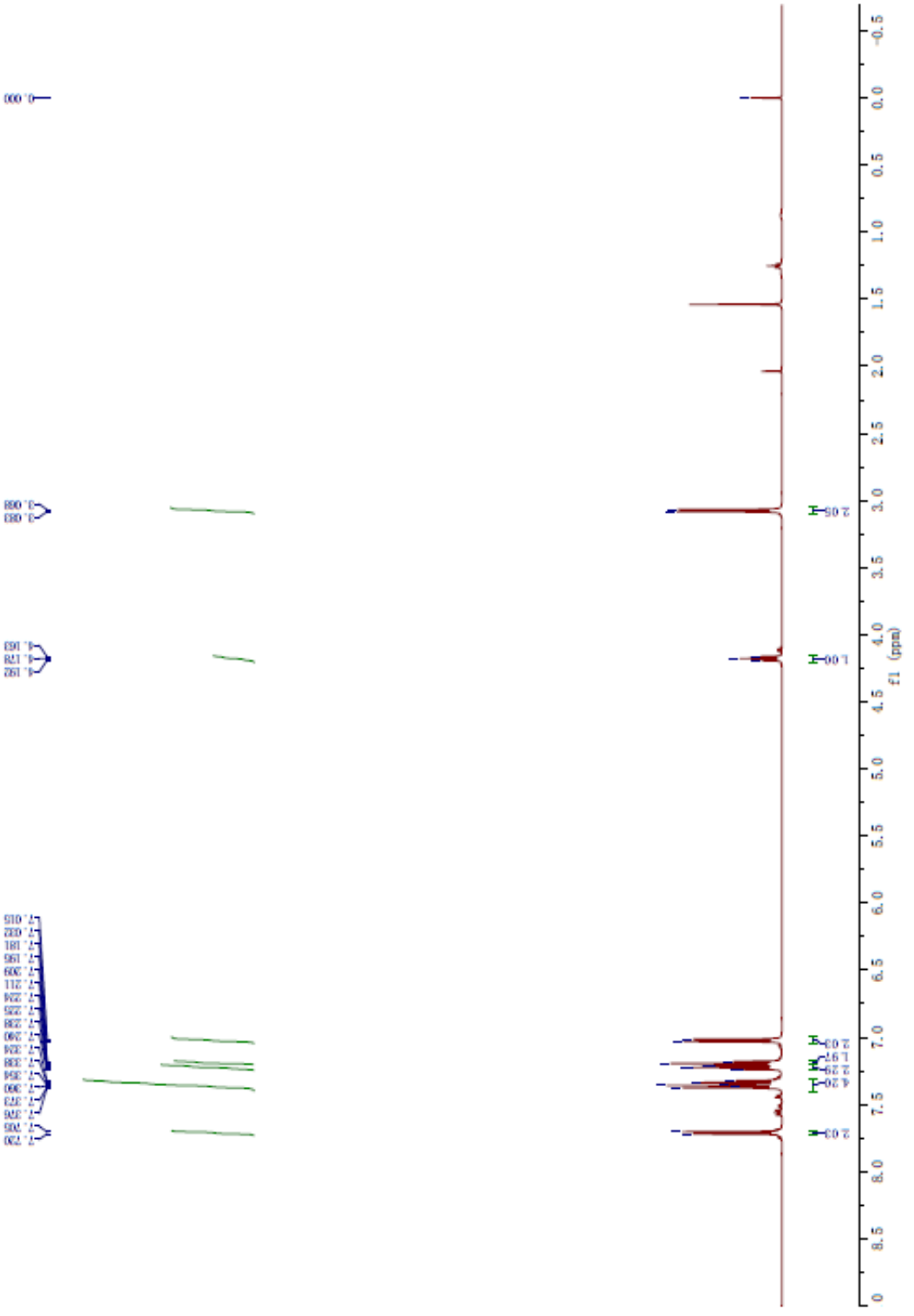
^{13}C NMR

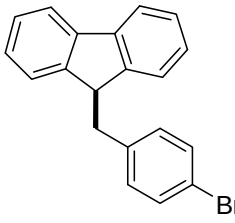




3j

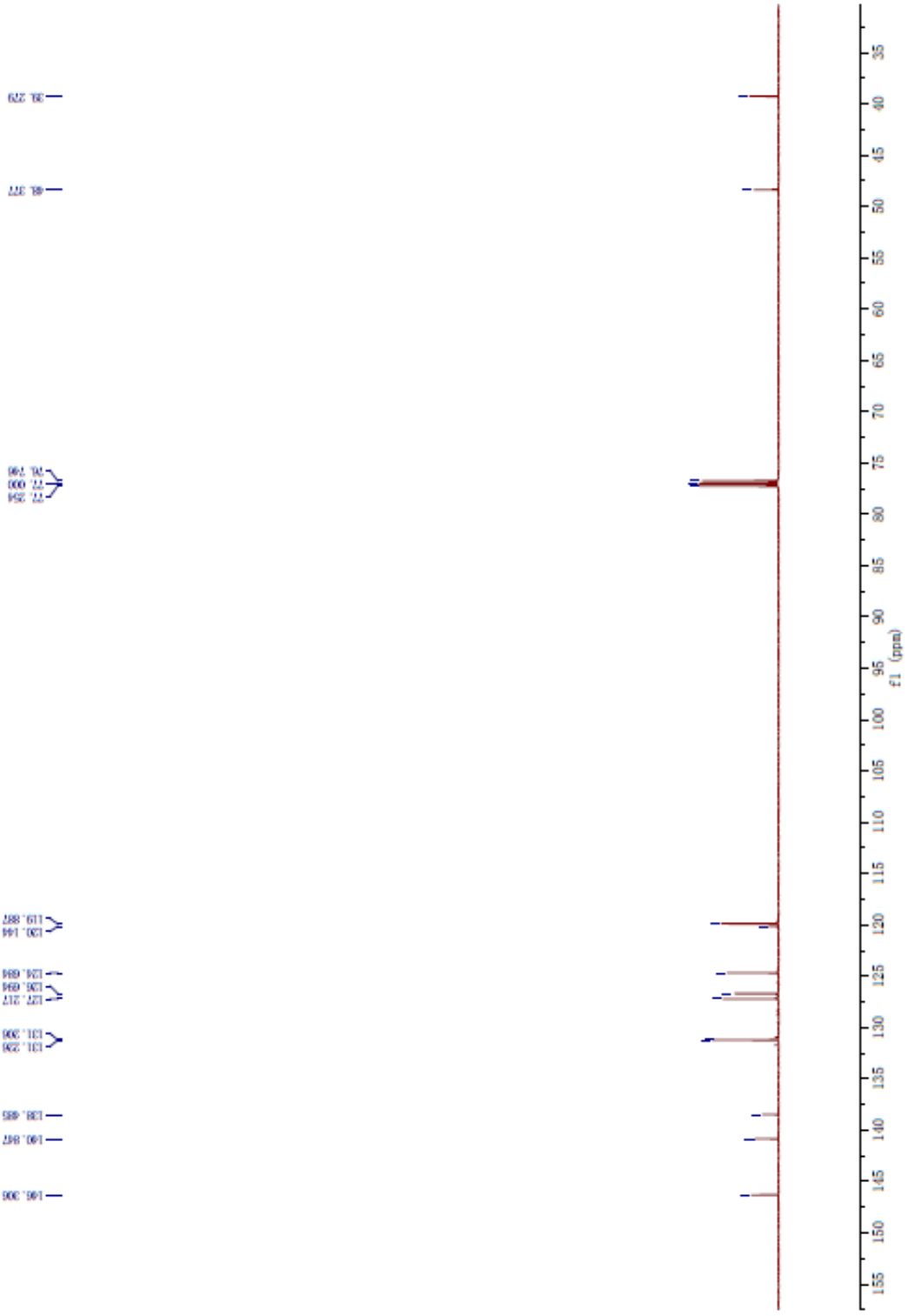
^{1}HNMR

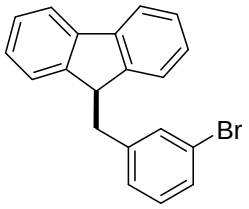




3j

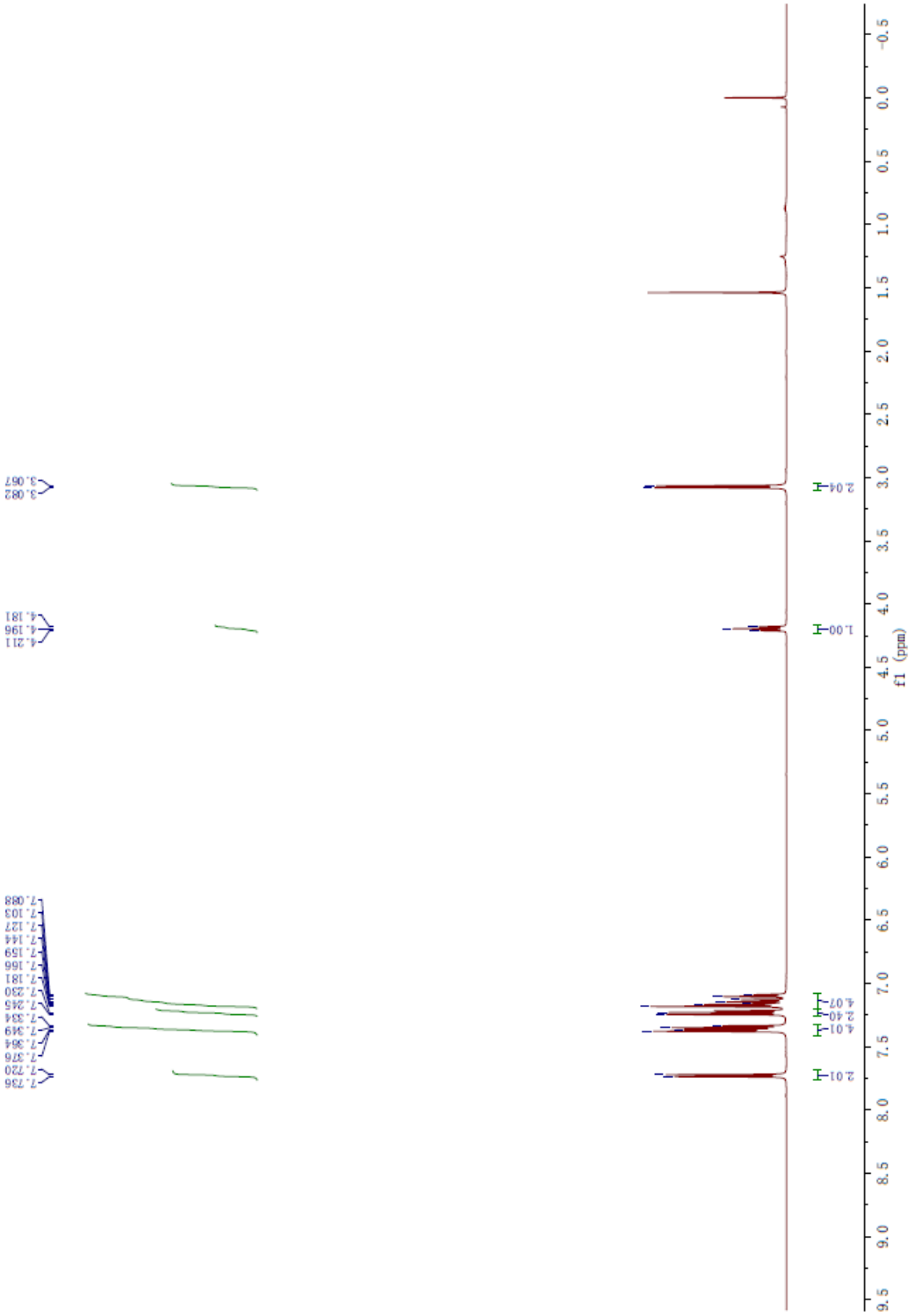
^{13}C NMR




Br

3k

^{1}H NMR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4.181
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7.376
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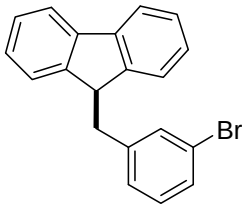
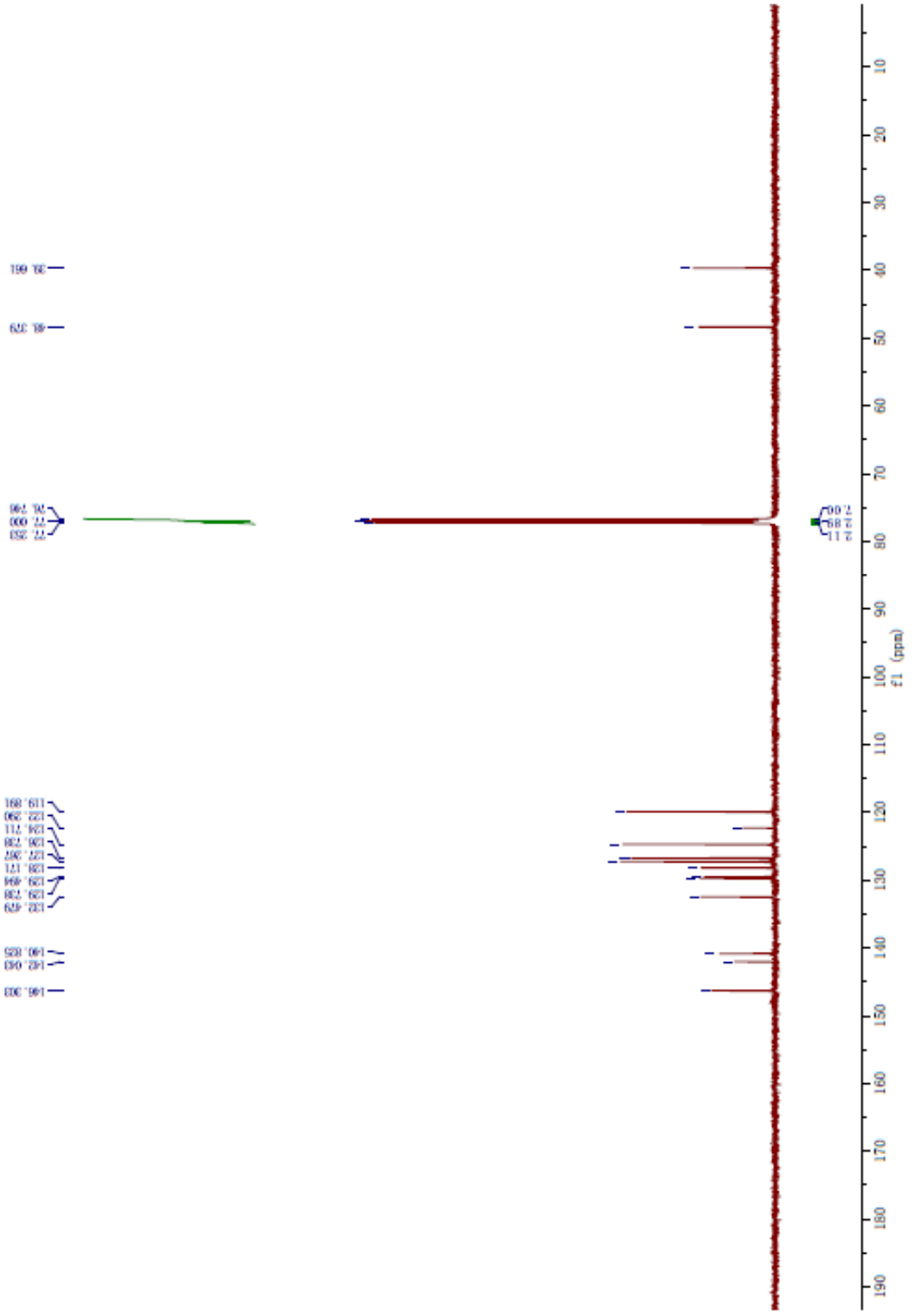
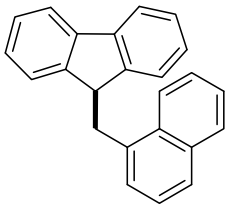
7.265
7.230
7.181
7.166
7.159
7.144
7.127
7.103
7.088
2.04
1.00
4.07
2.40
4.01
2.01
f1 (ppm)



3k

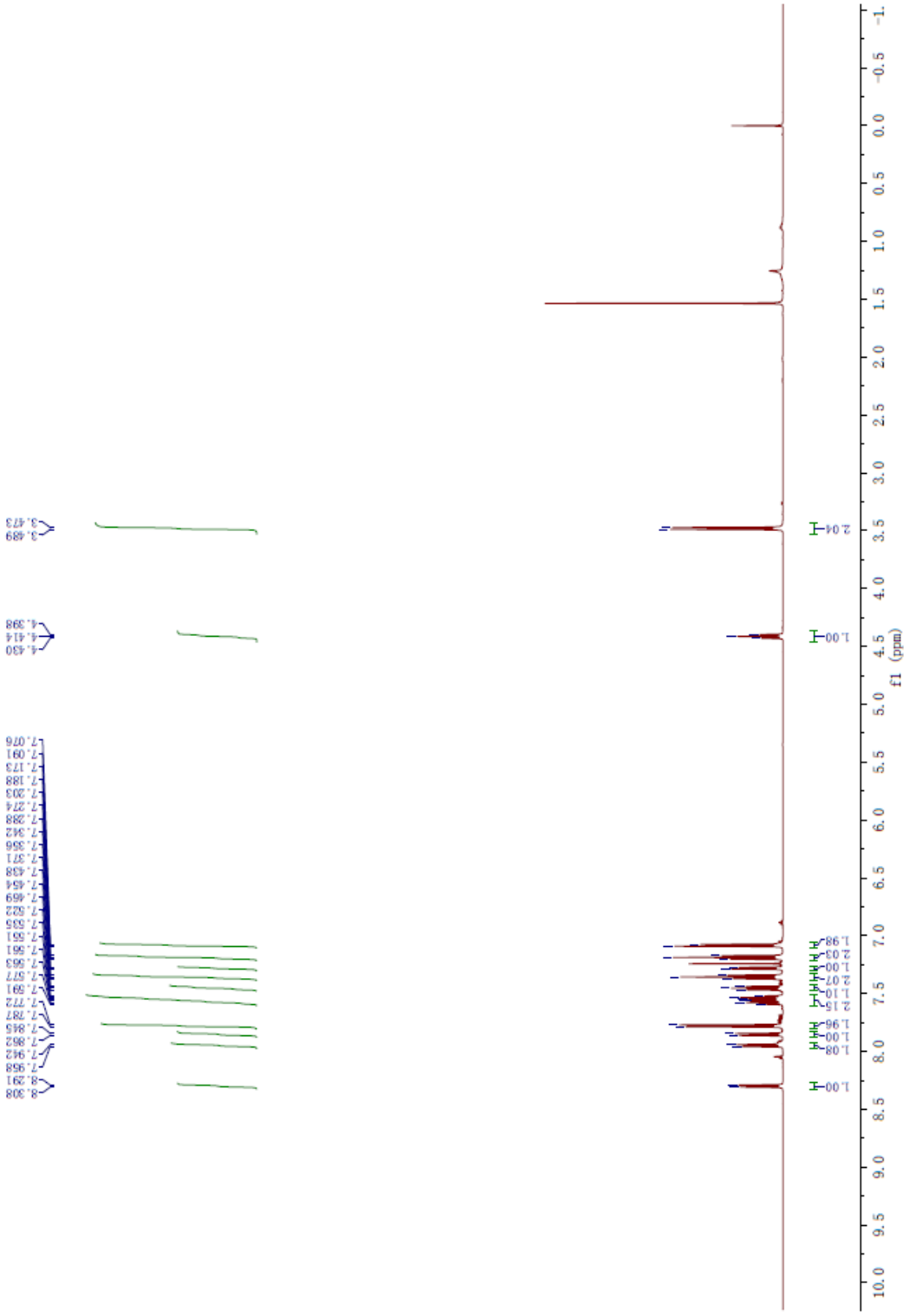
^{13}C NMR

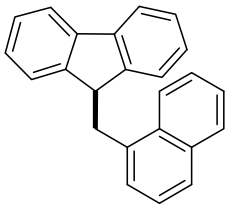




3l

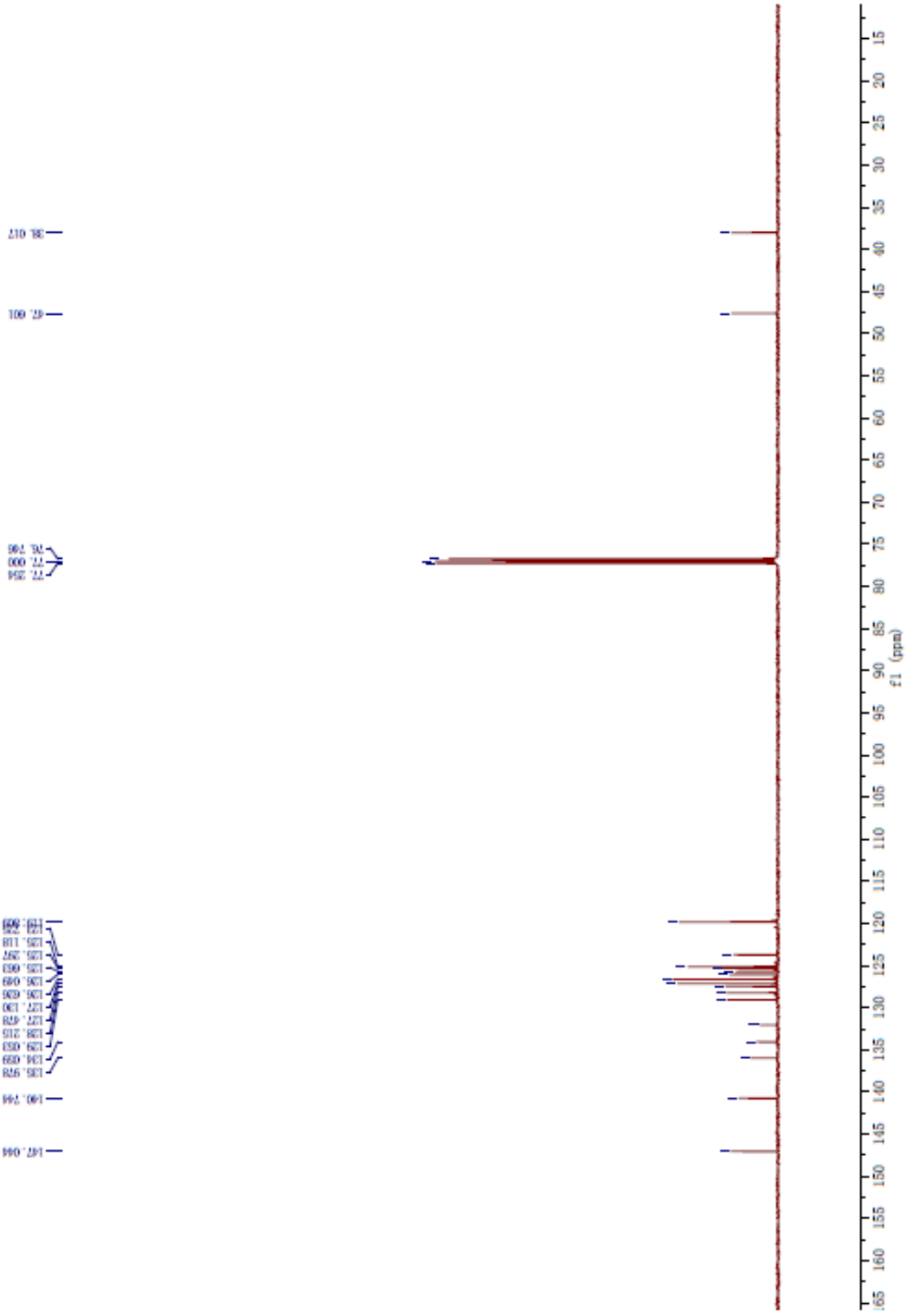
^{1}H NMR

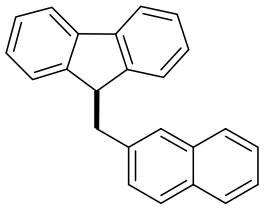




3l

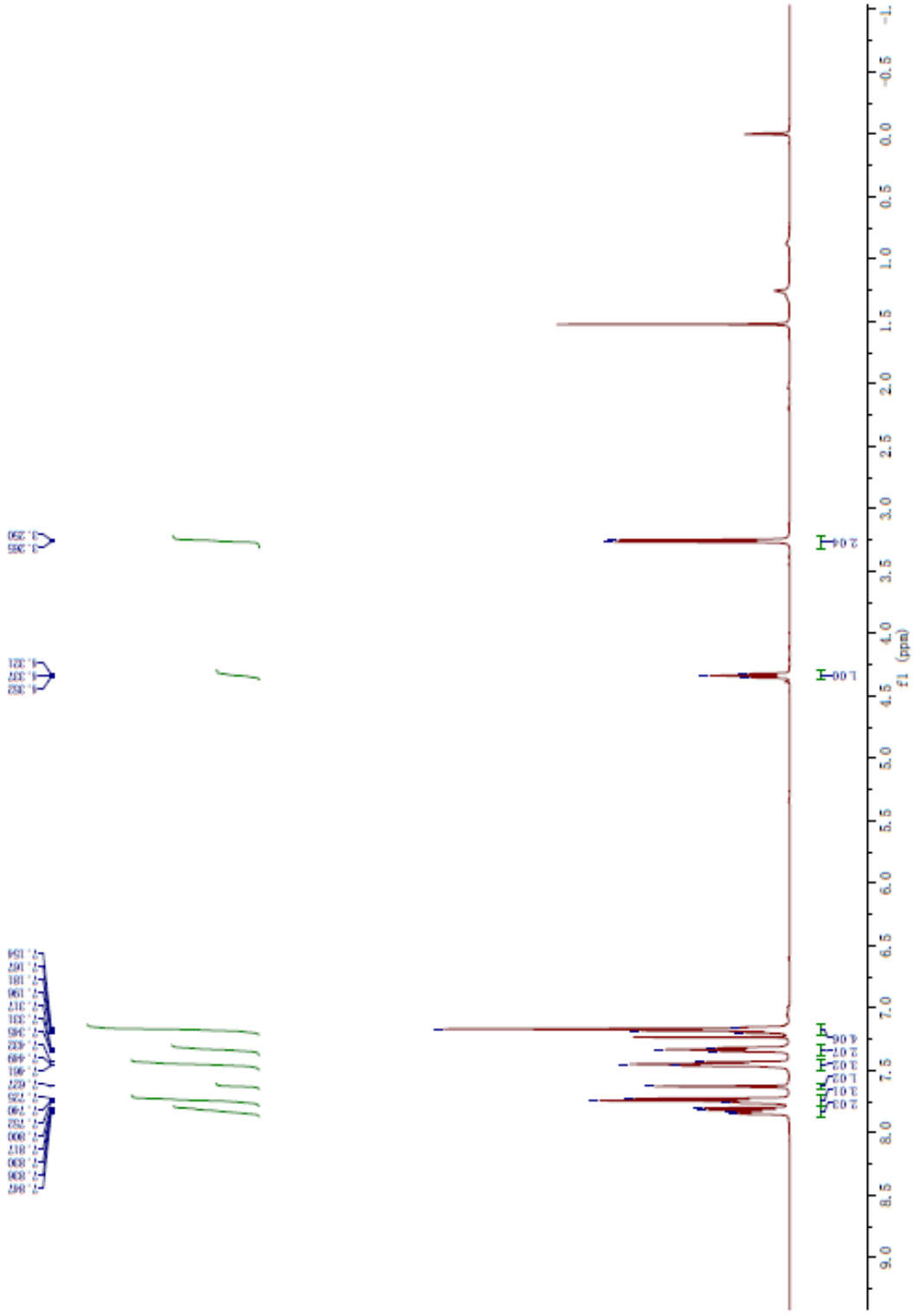
^{13}C NMR

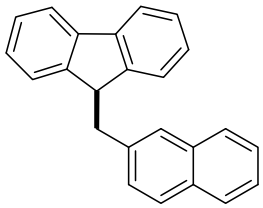




3m

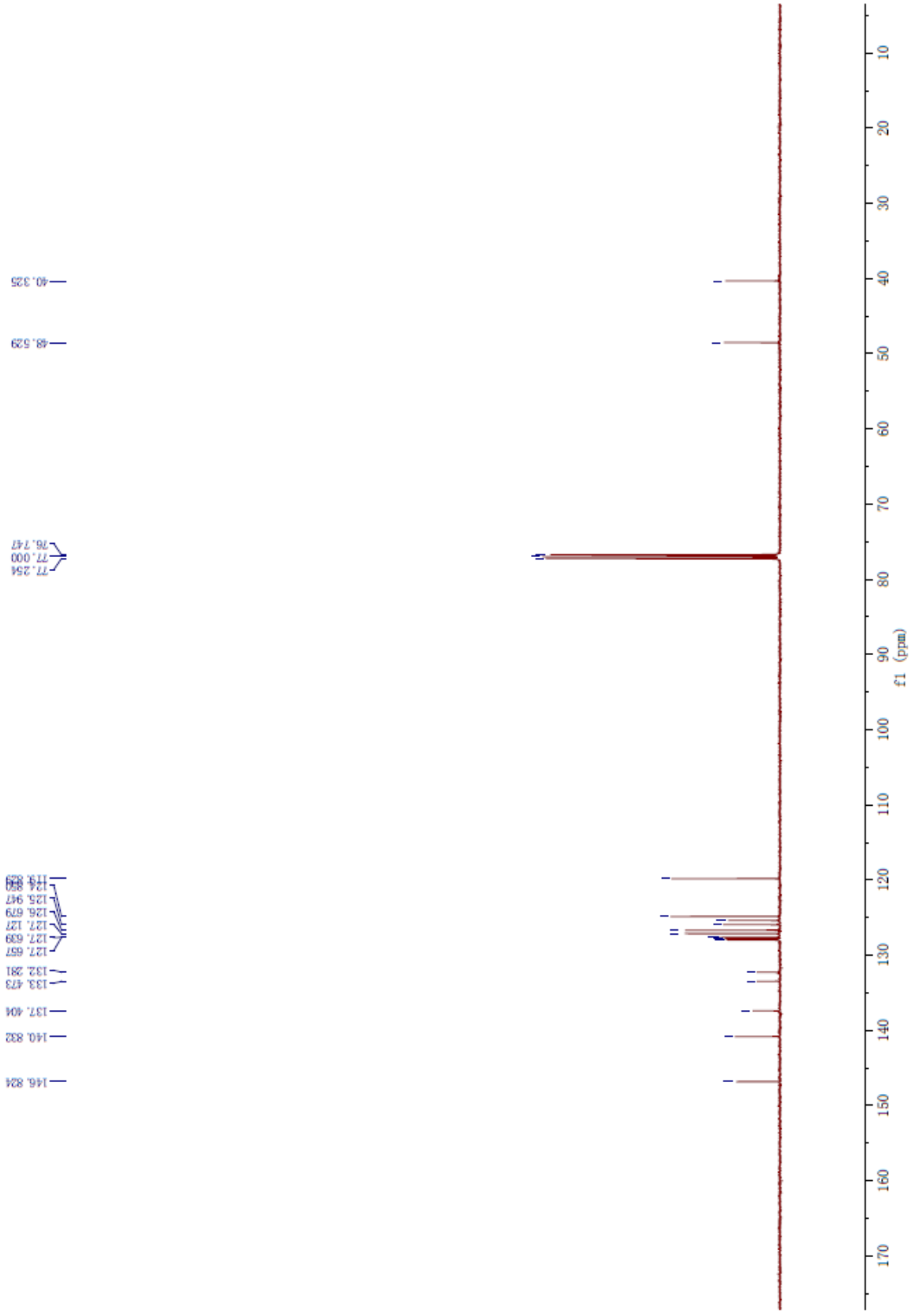
^{1}H NMR





3m

^{13}C NMR


40.325
48.529
76.747
77.000
77.254
119.829
124.850
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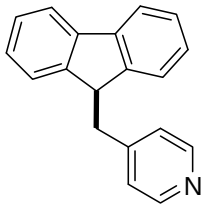
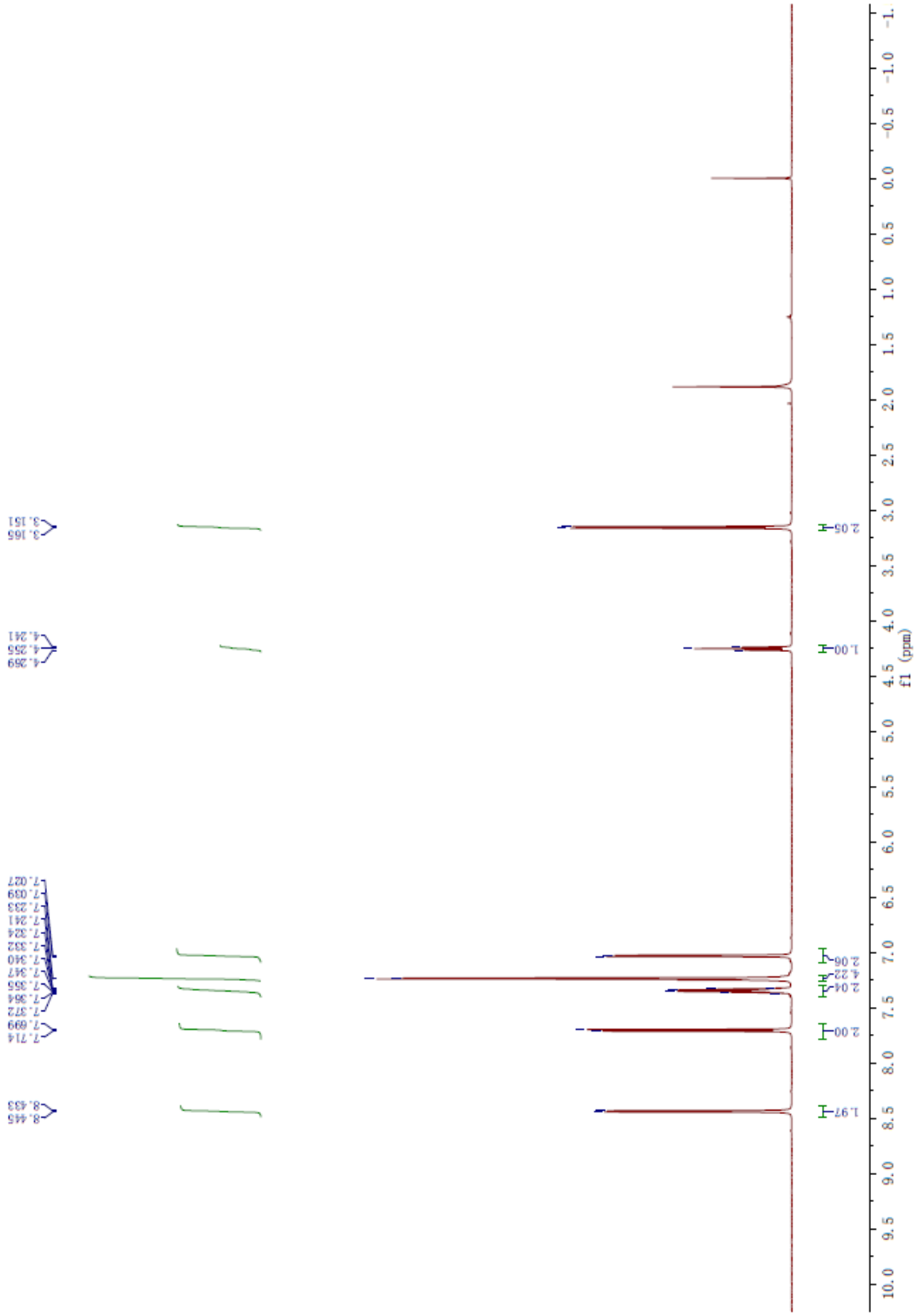
127.127
127.639
127.657
132.281
133.473
137.404
140.832
146.824
f1 (ppm)


N

3n

^{1}H NMR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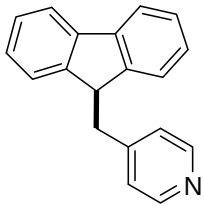
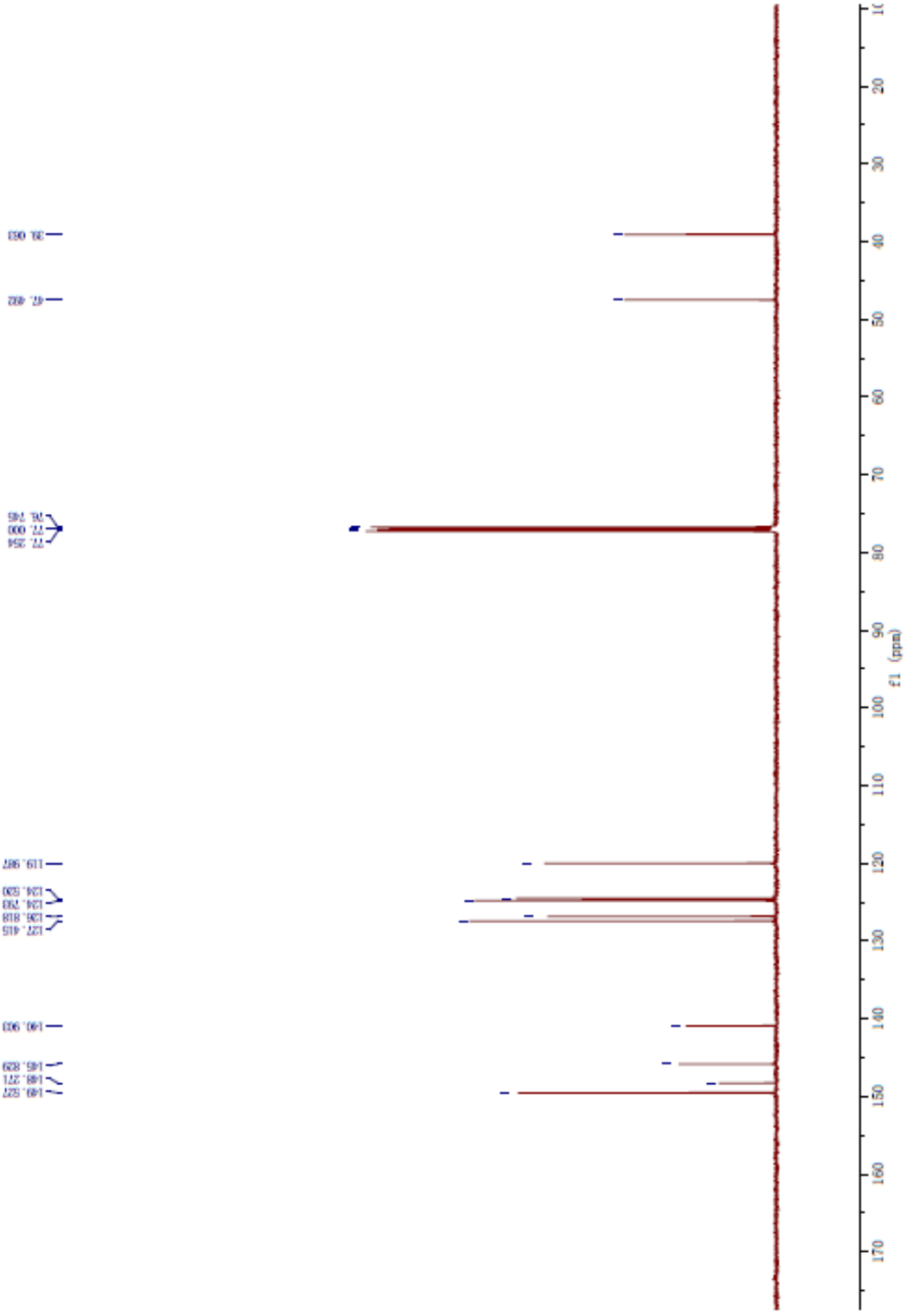
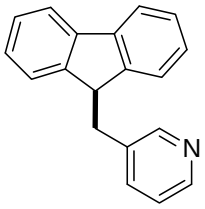
3.151
4.269
4.255
4.241
7.714
7.699
8.465
8.433
2.05
1.00
2.06
4.22
2.04
2.00
1.97
f1 (ppm)



3n

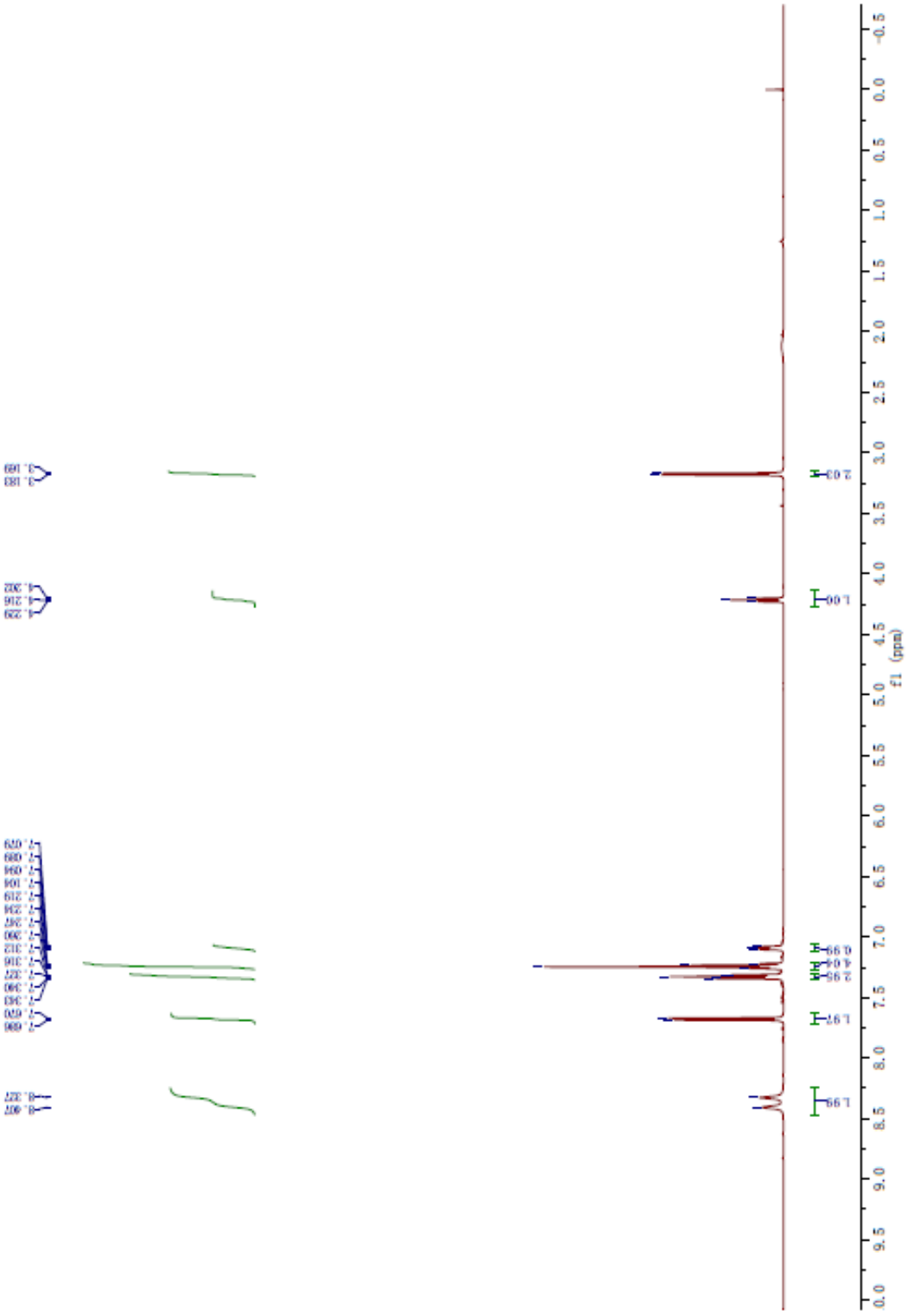
^{13}C NMR

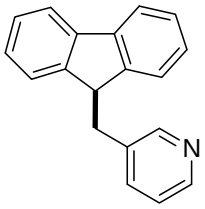




3o

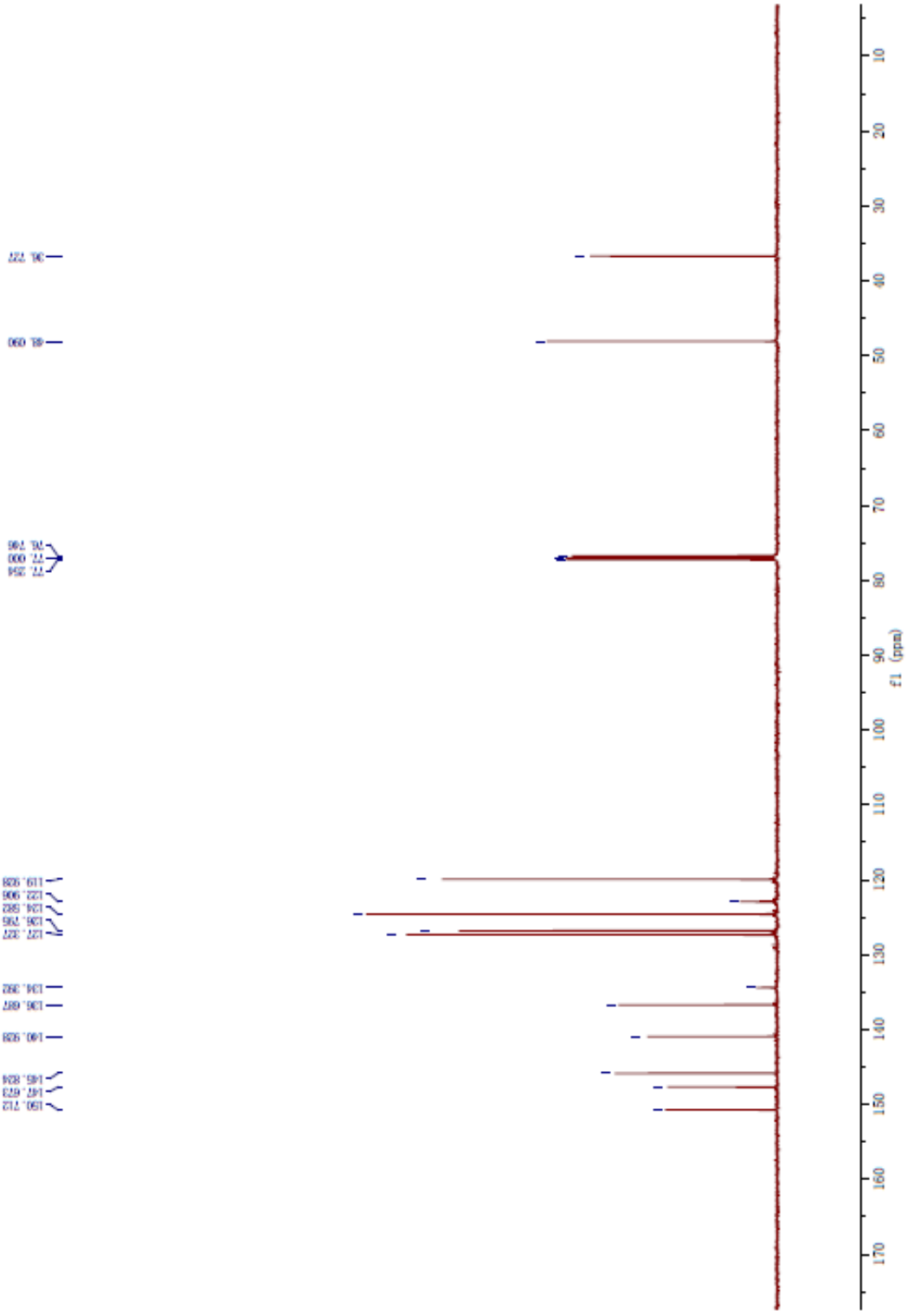
^{1}H NMR

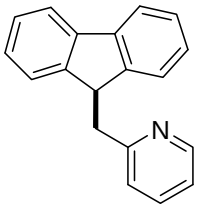




3o

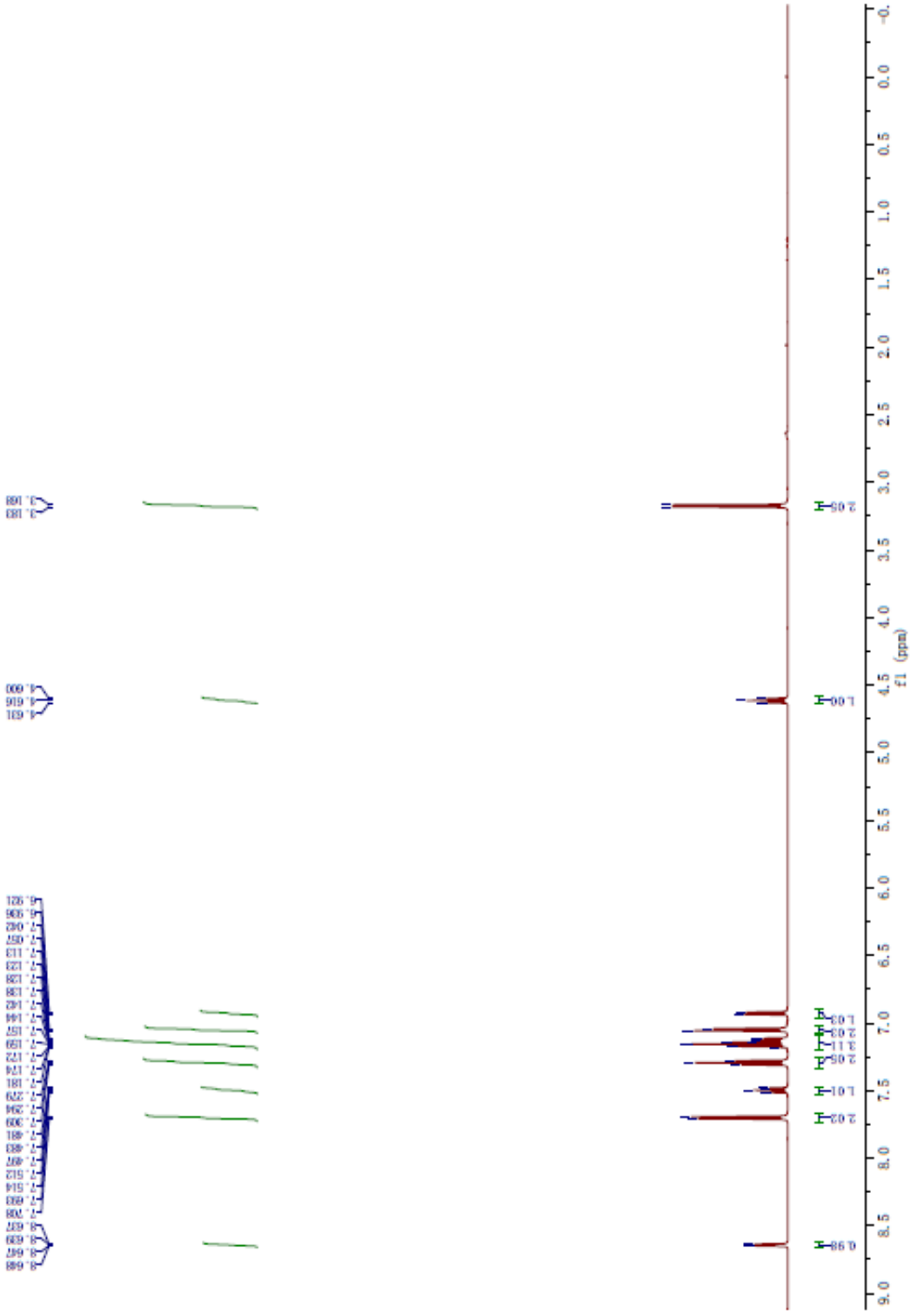
^{13}C NMR

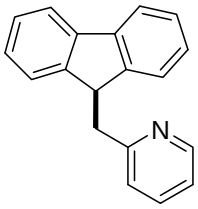




3p

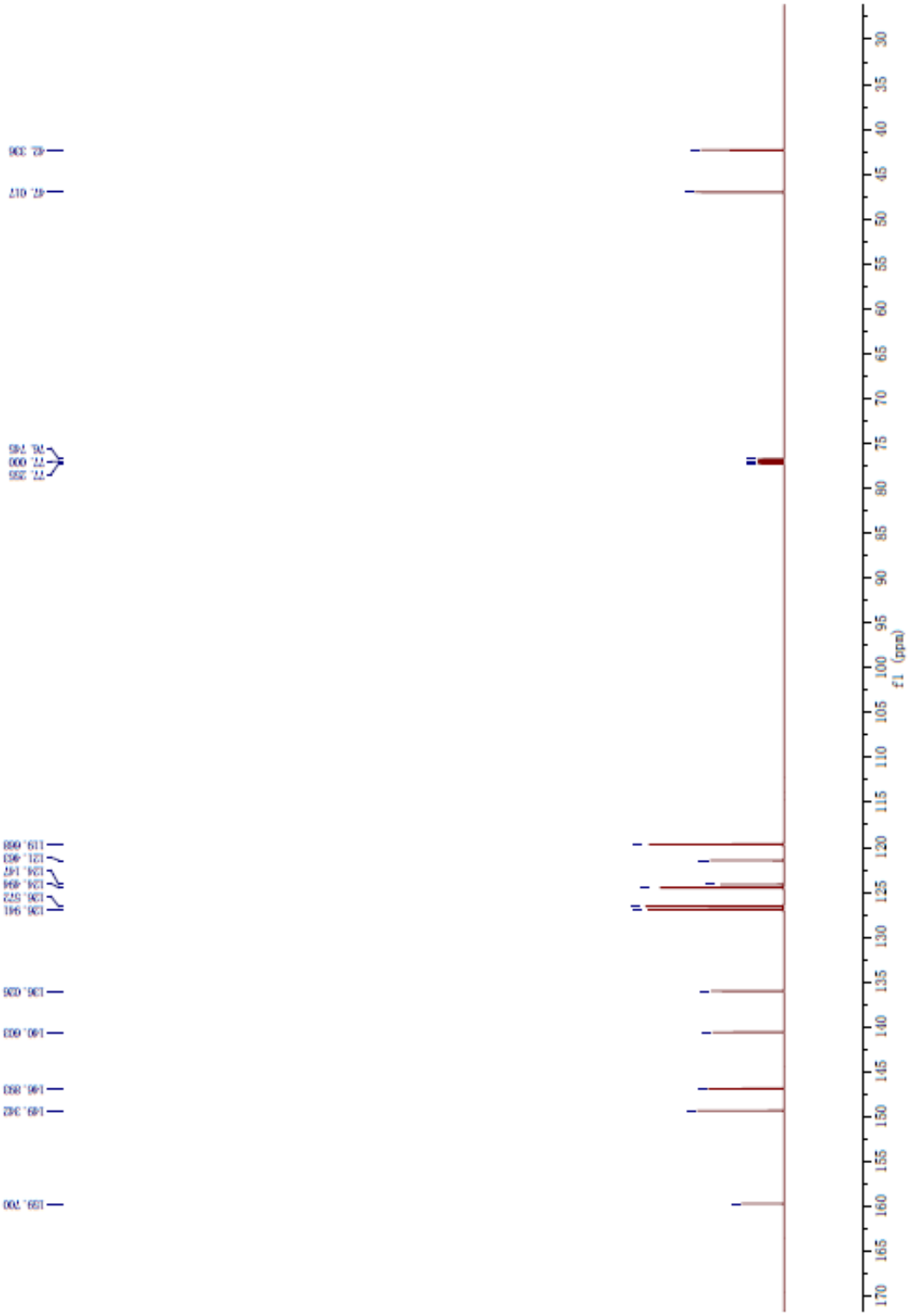
^{1}H NMR

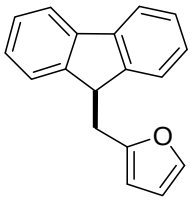




3p

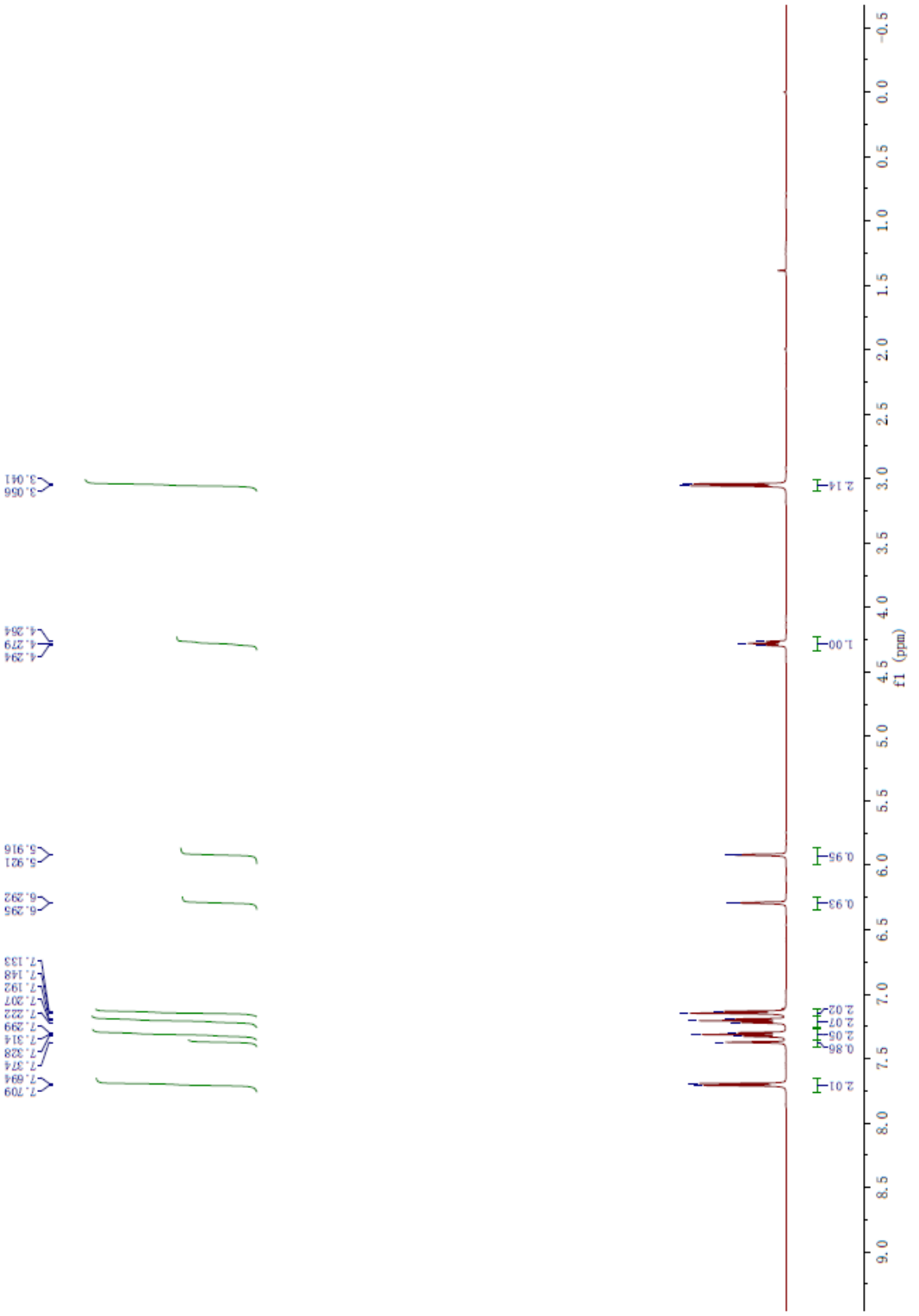
^{13}C NMR





3q

^{1}H NMR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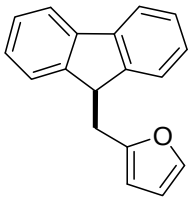
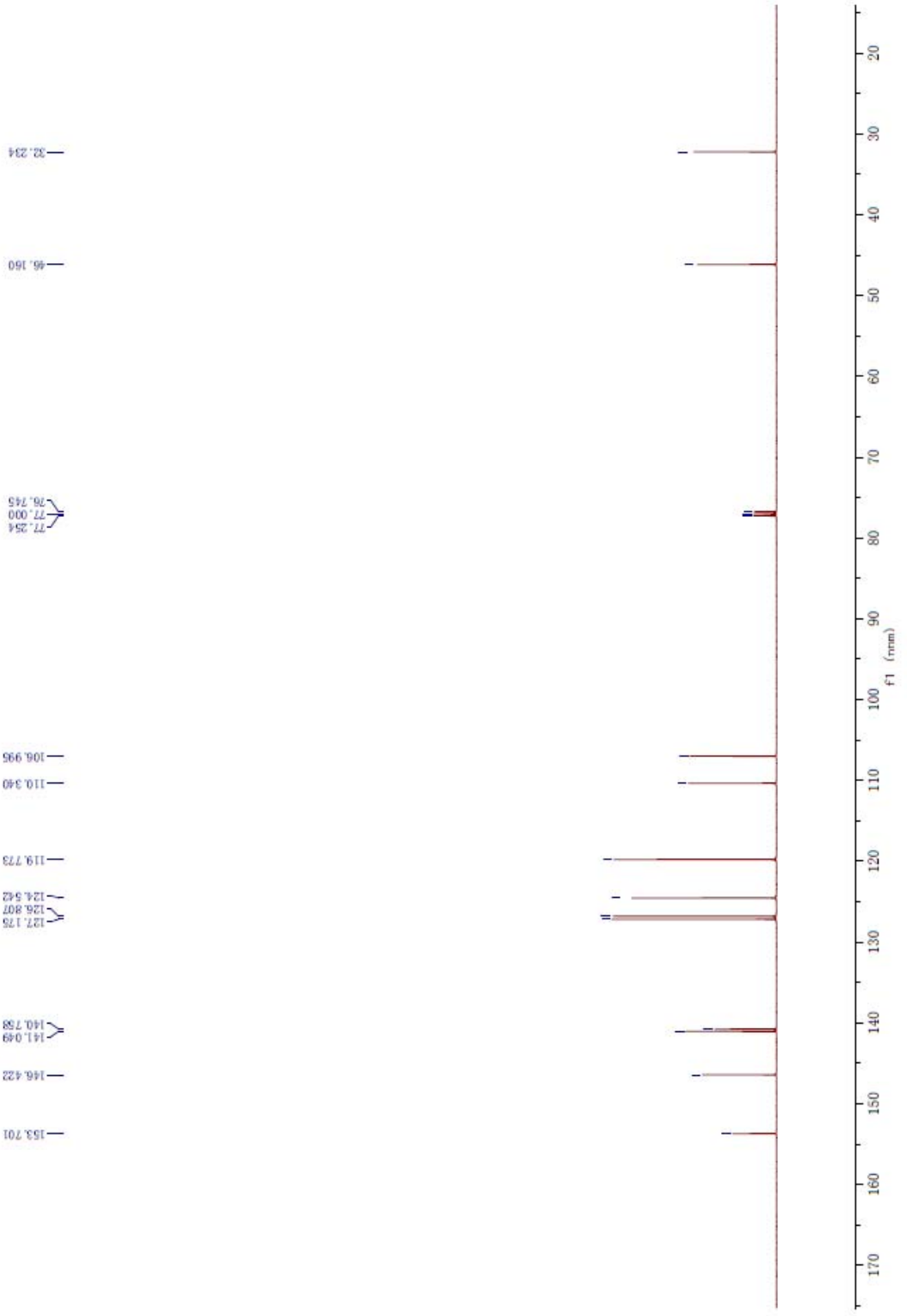
4.279
4.264
5.921
5.916
6.295
6.292
7.709
7.694
7.374
7.328
7.314
7.299
7.222
7.207
7.192
7.148
7.133
2.14
1.00
0.95
0.93
2.02
2.07
2.05
0.86
2.01
f1 (ppm)



3q

^{13}C NMR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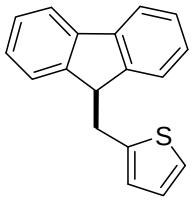
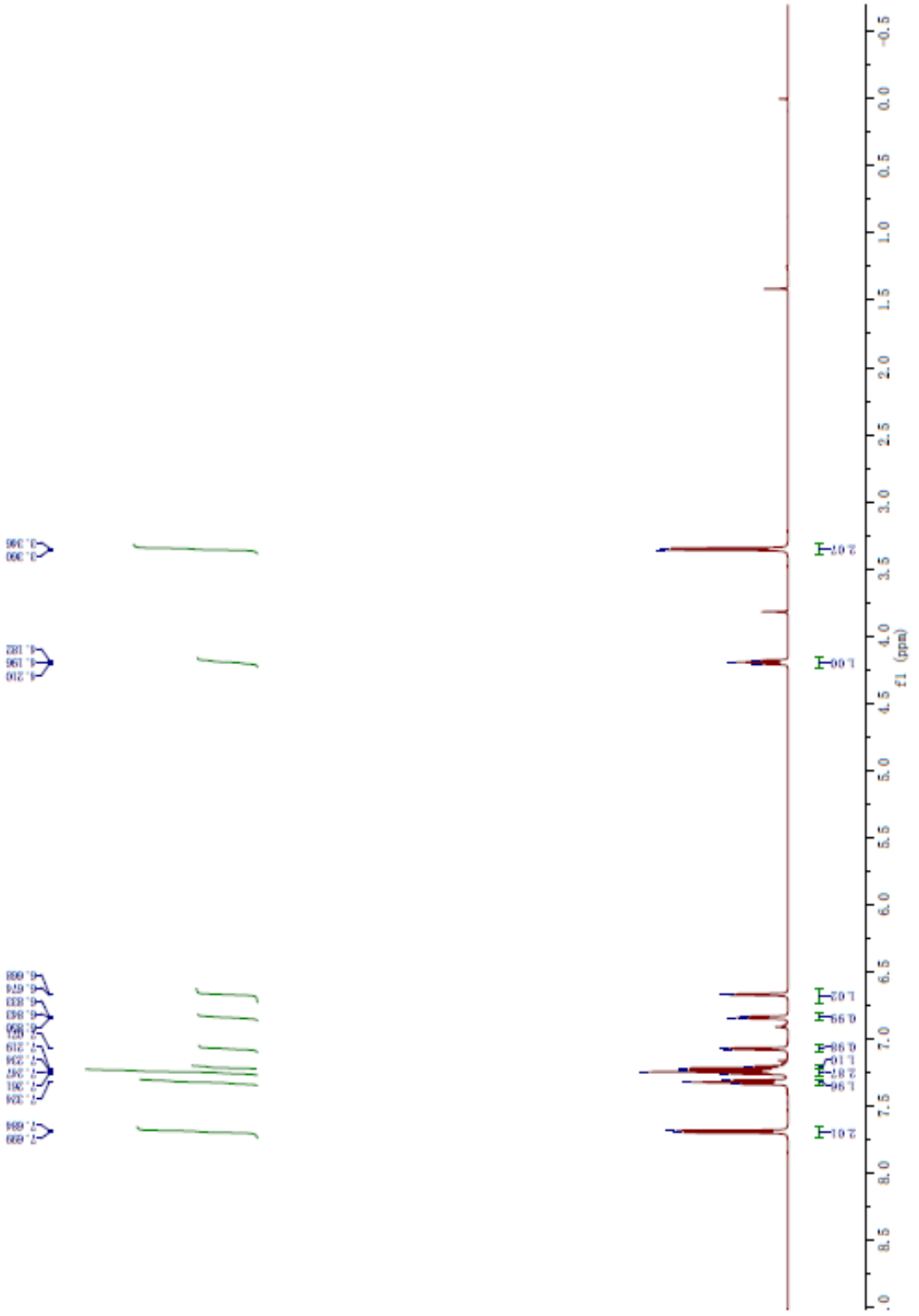
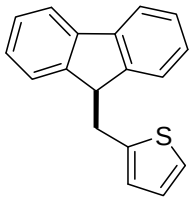
77.000
77.254
106.995
110.340
119.773
124.562
126.807
127.125
140.758
141.049
146.422
153.701
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
f1 (ppm)



3r

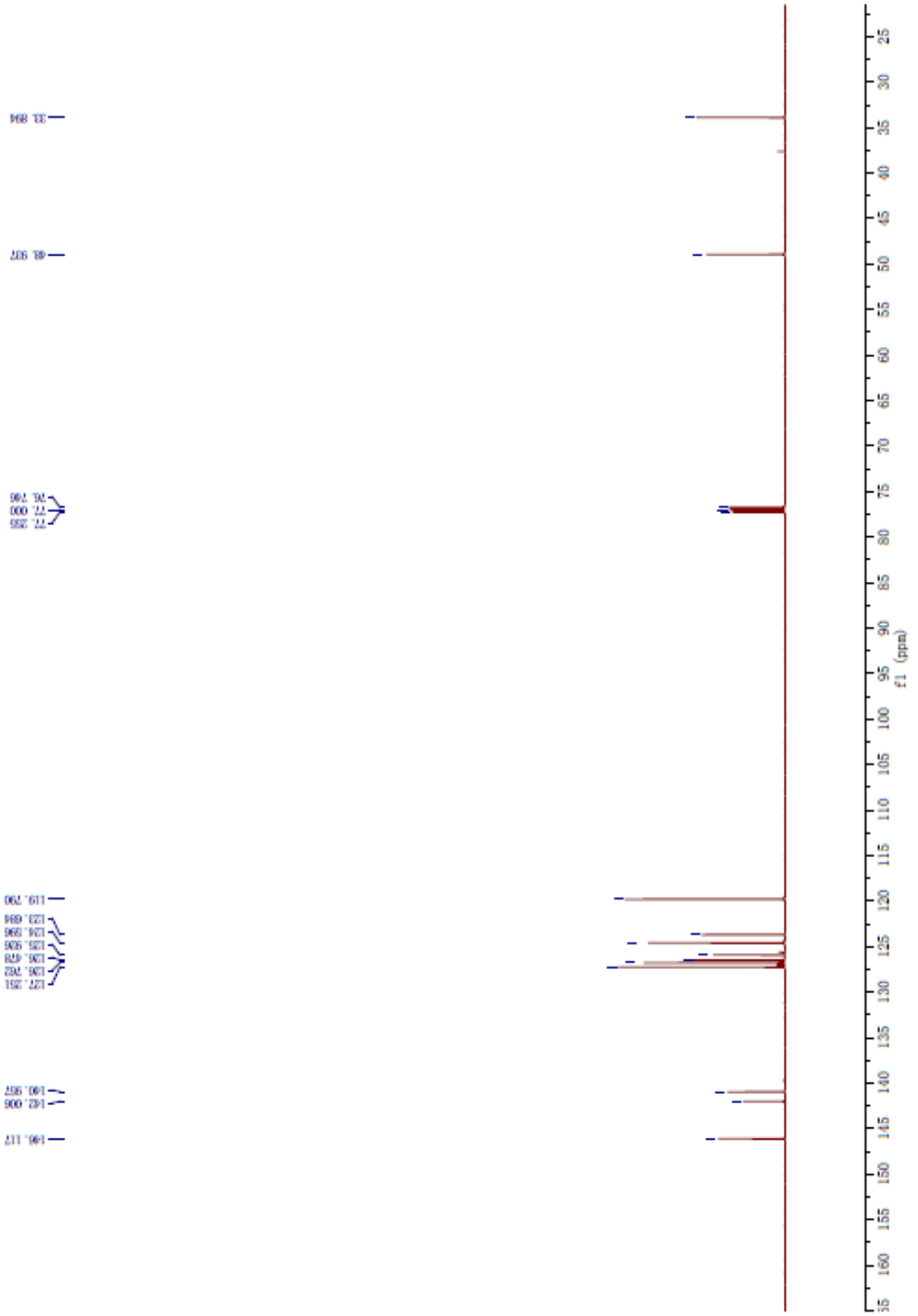
^{1}H NMR

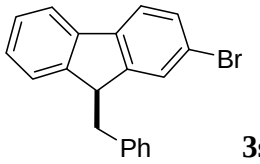




3r

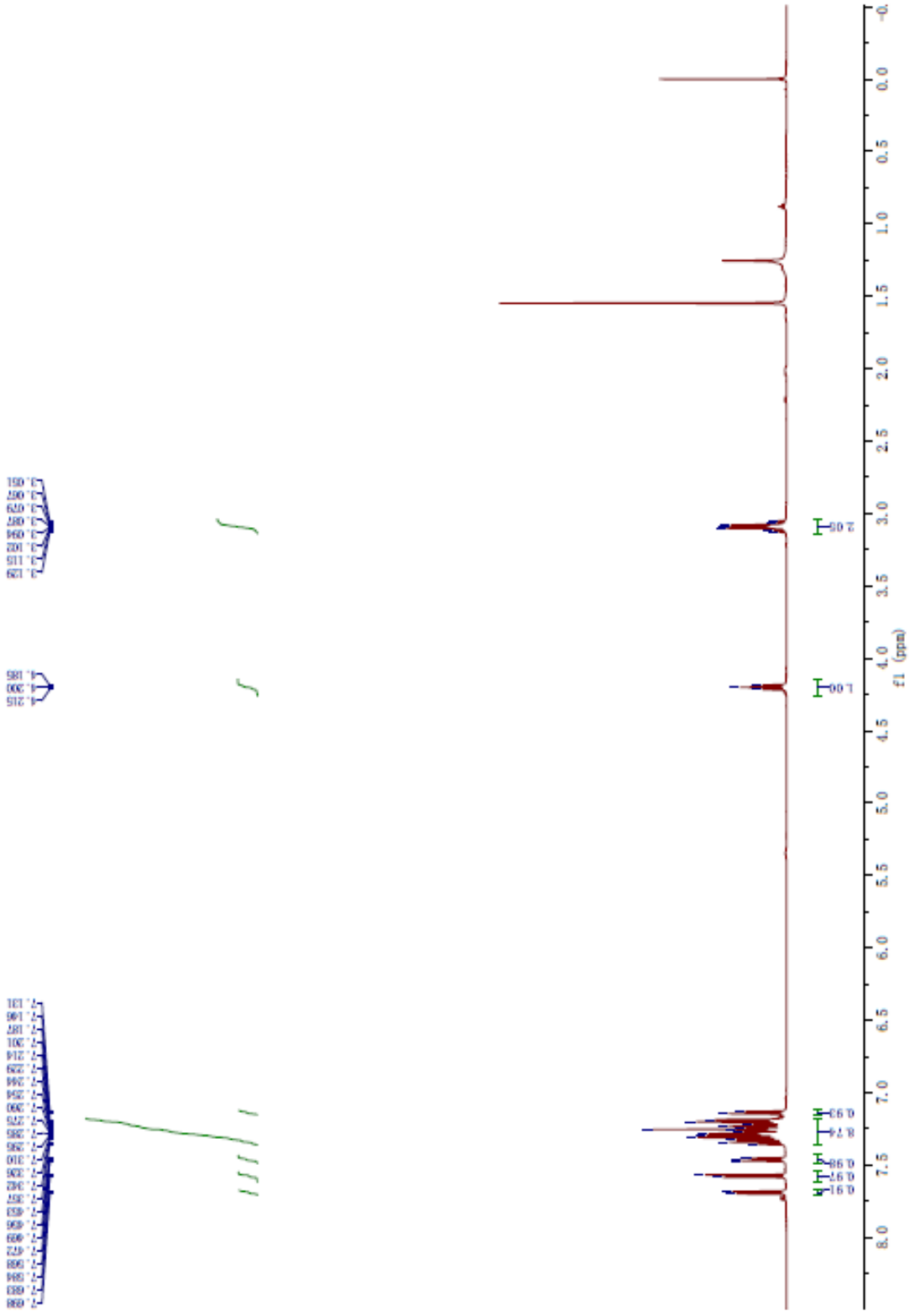
^{13}C NMR

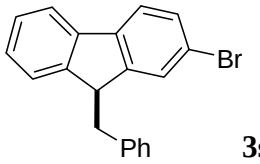




3s

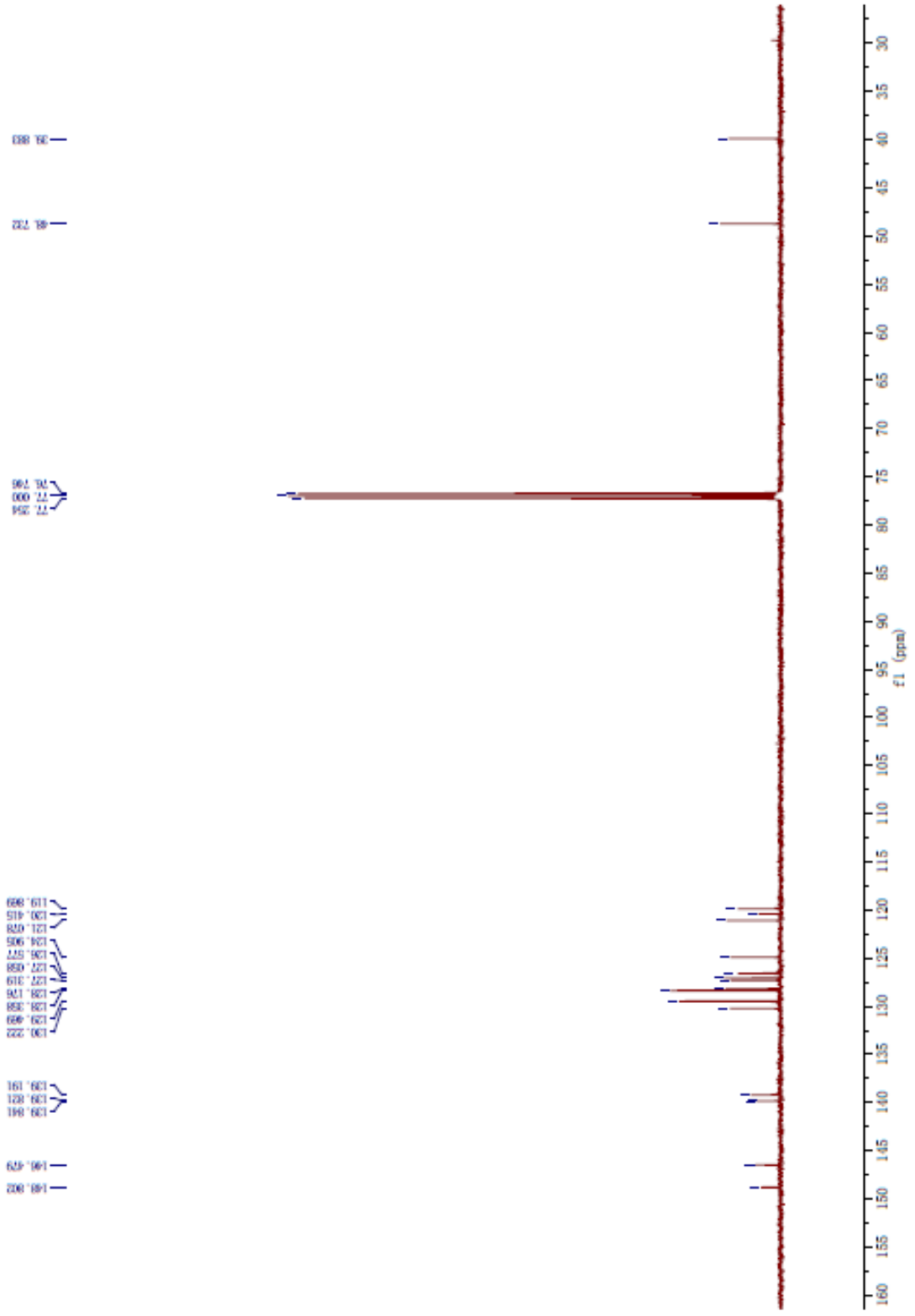
^{1}H NMR

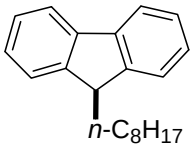




3s

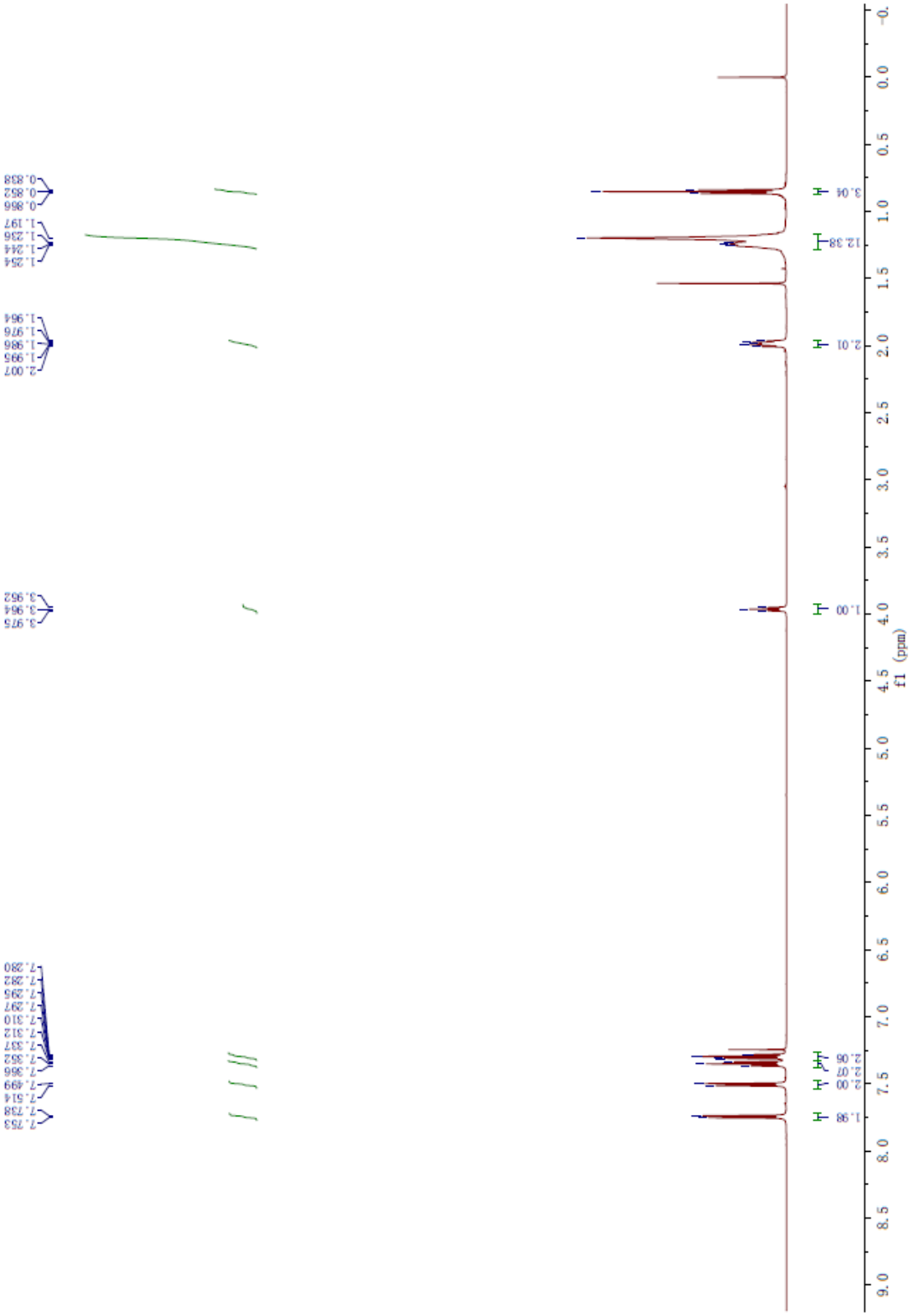
^{13}C NMR

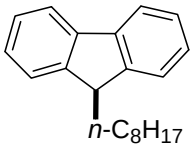




n-C_8H_{17} **6a**

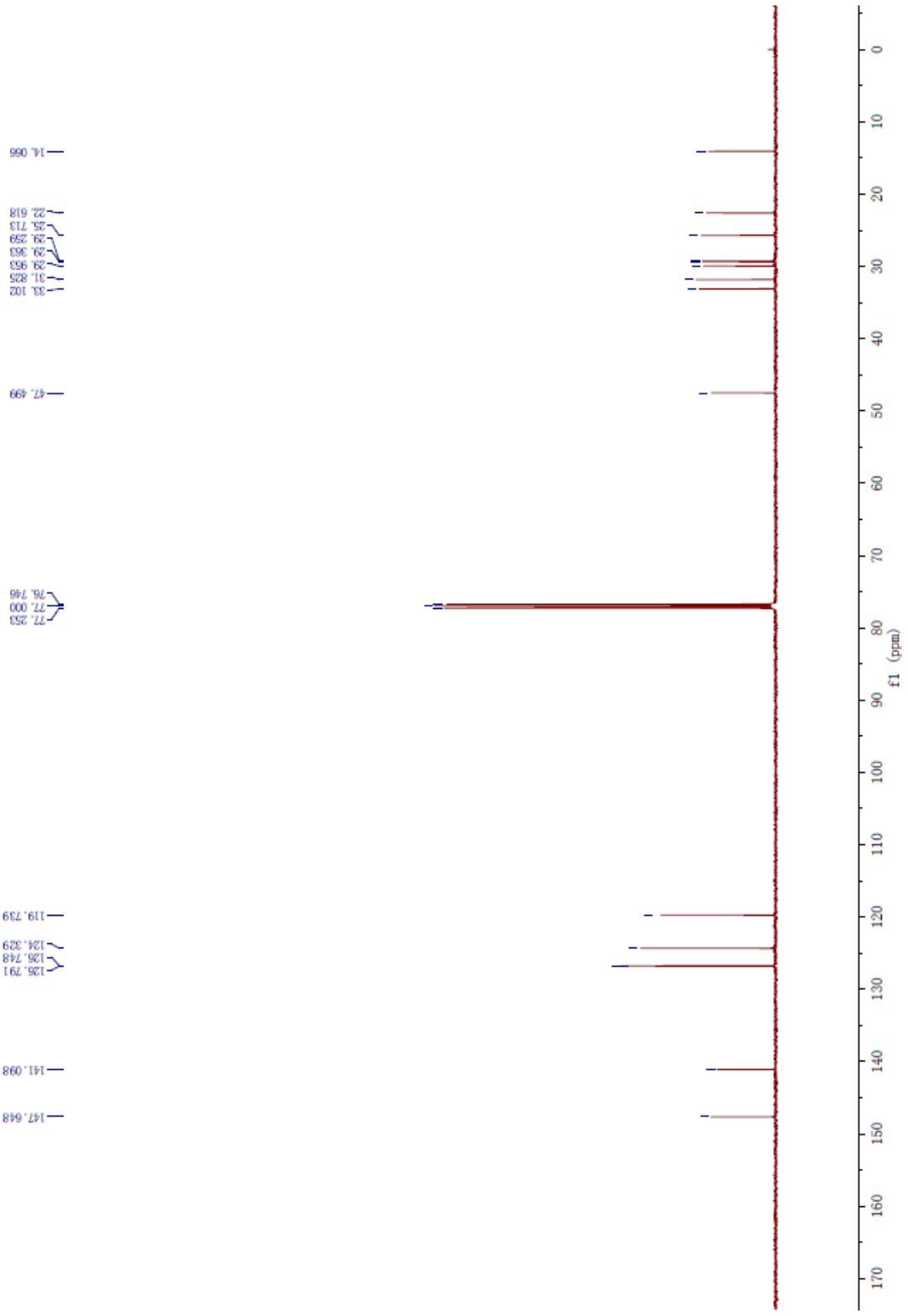
^{1}H NMR

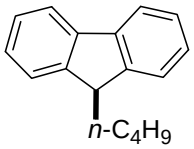




n-C_8H_{17} **6a**

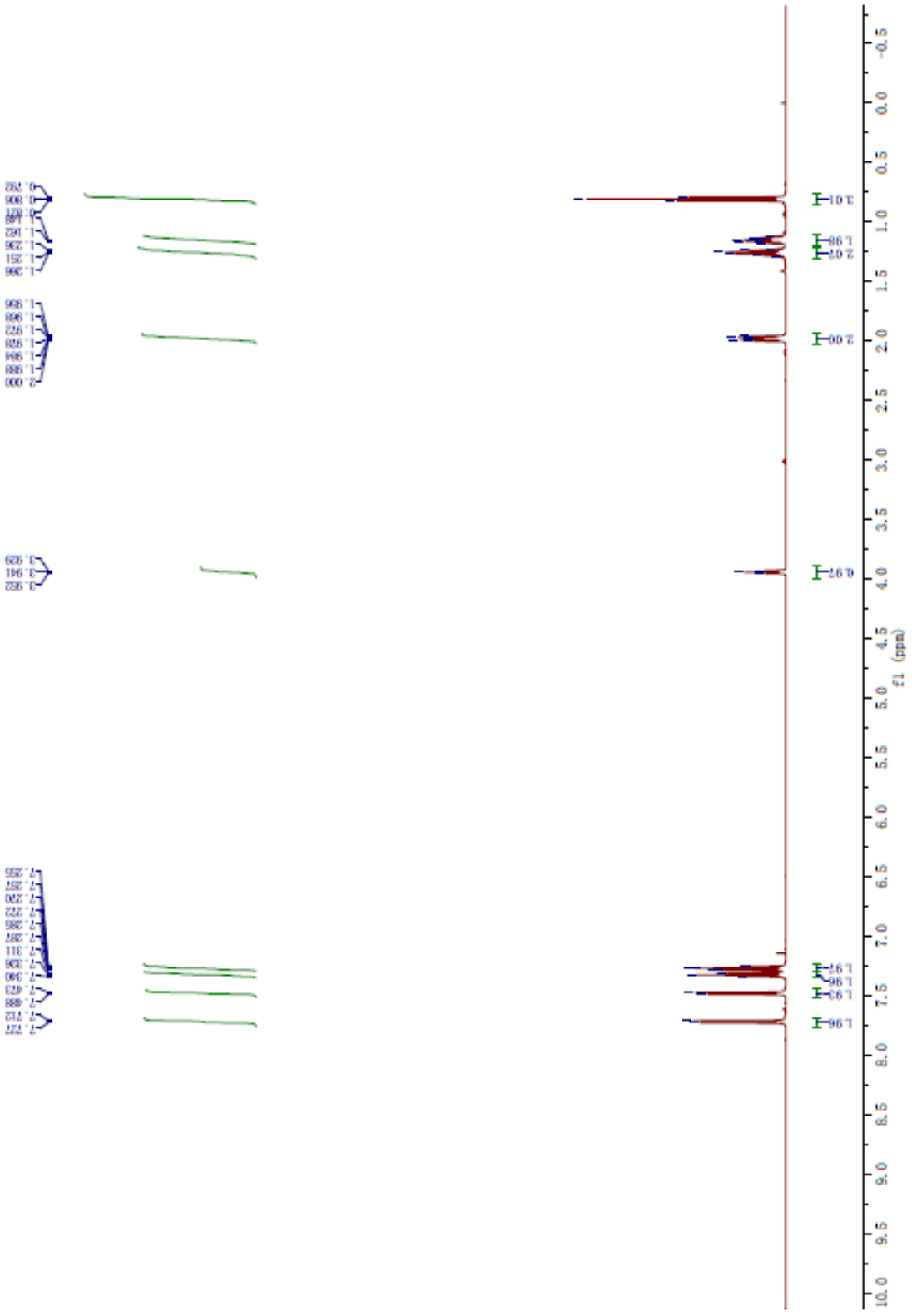
^{13}C NMR

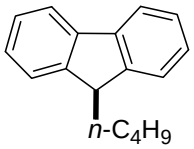




6b

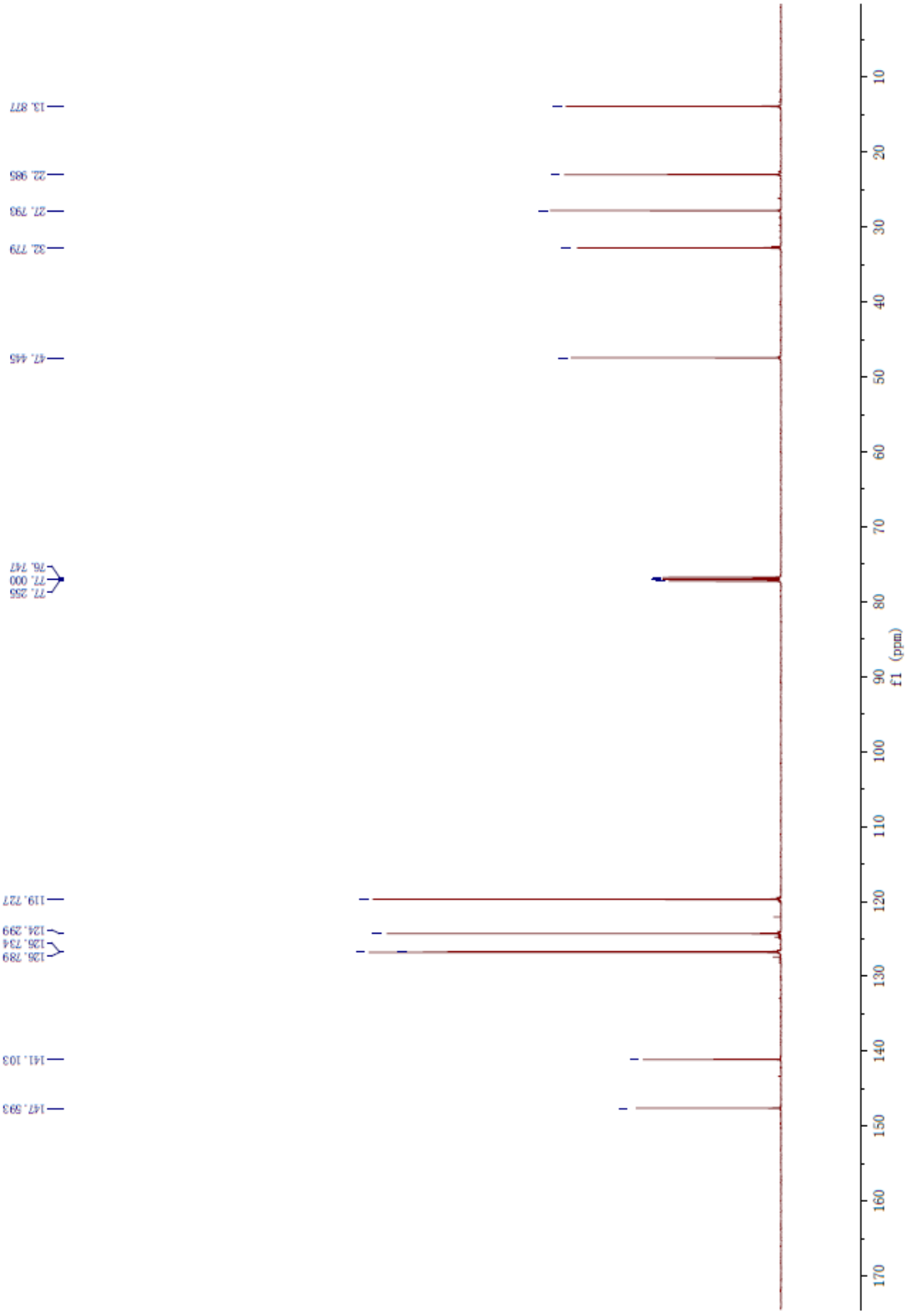
^{1}H NMR

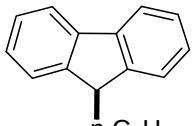



n-C4H9

6b

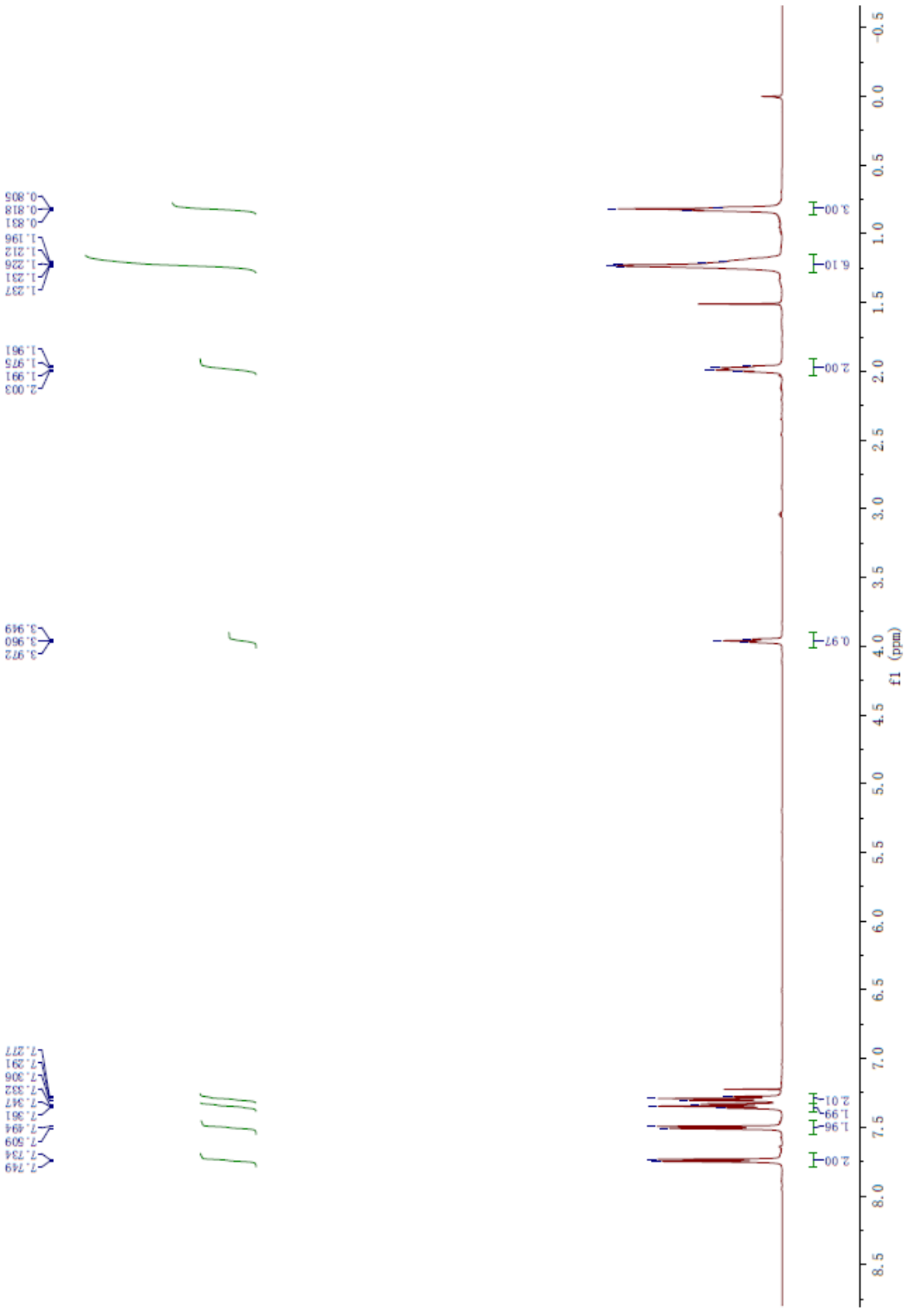
^{13}C NMR

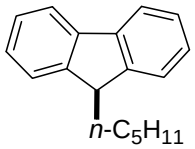

13.877
22.985
27.793
32.779
47.445
76.747
77.000
77.255
119.727
124.299
126.734
126.789
141.103
147.593
f1 (ppm)



n-C_5H_{11} **6c**

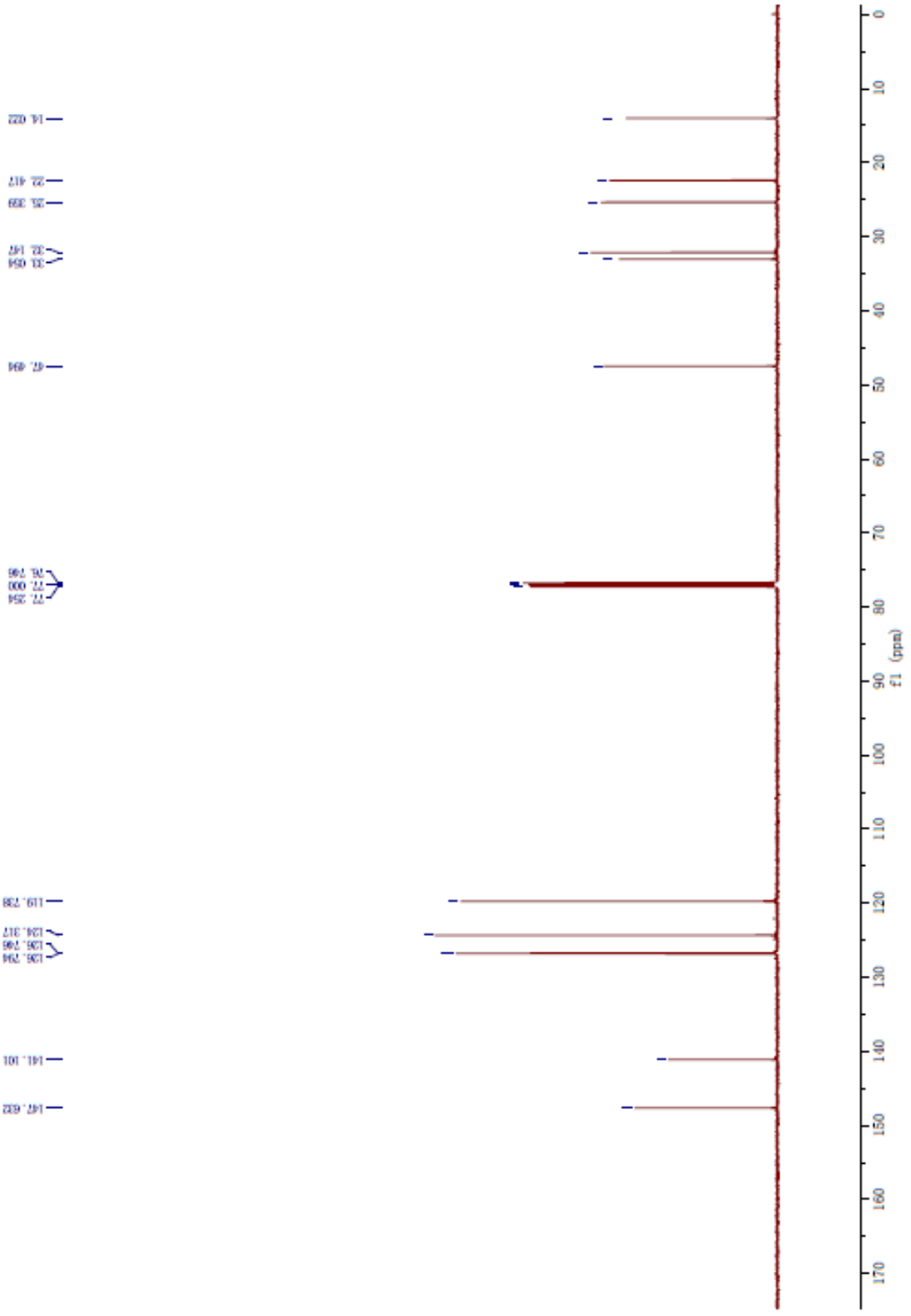
^{1}H NMR

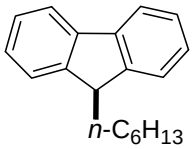




n-C_5H_{11} **6c**

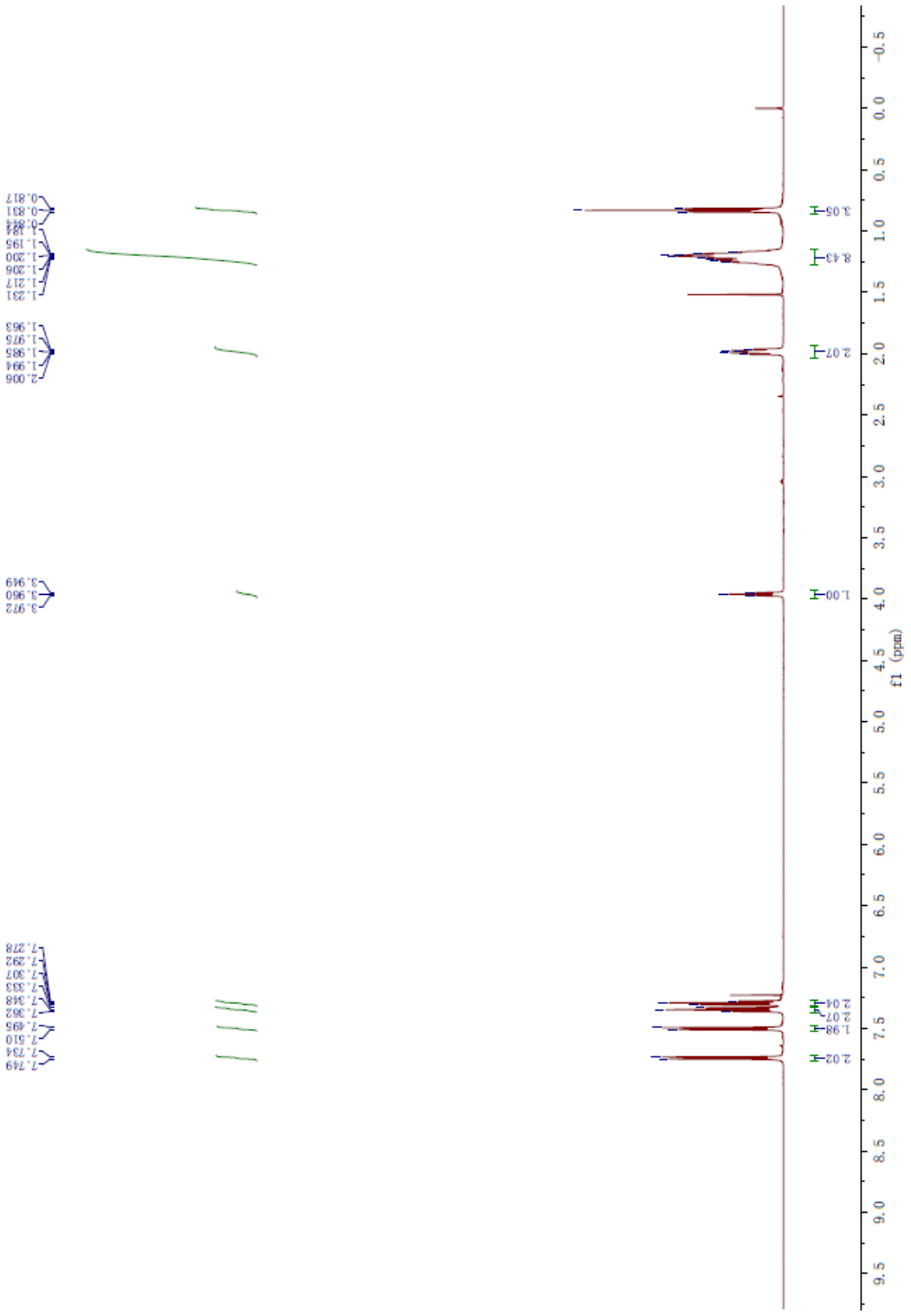
^{13}C NMR

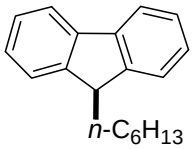




n-C_6H_{13} **6d**

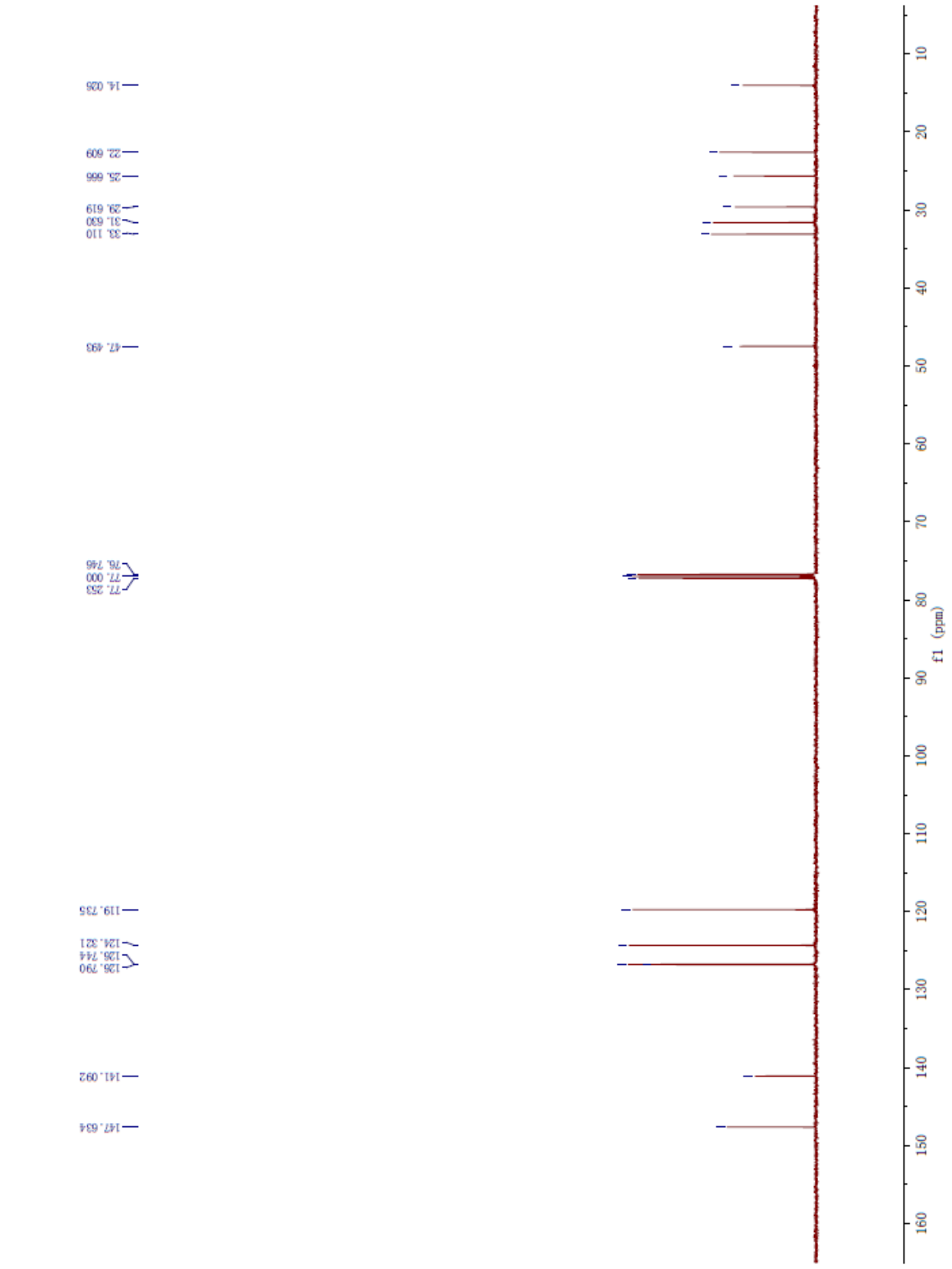
^{1}H NMR

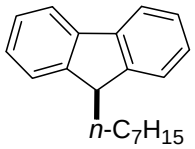




n-C_6H_{13} **6d**

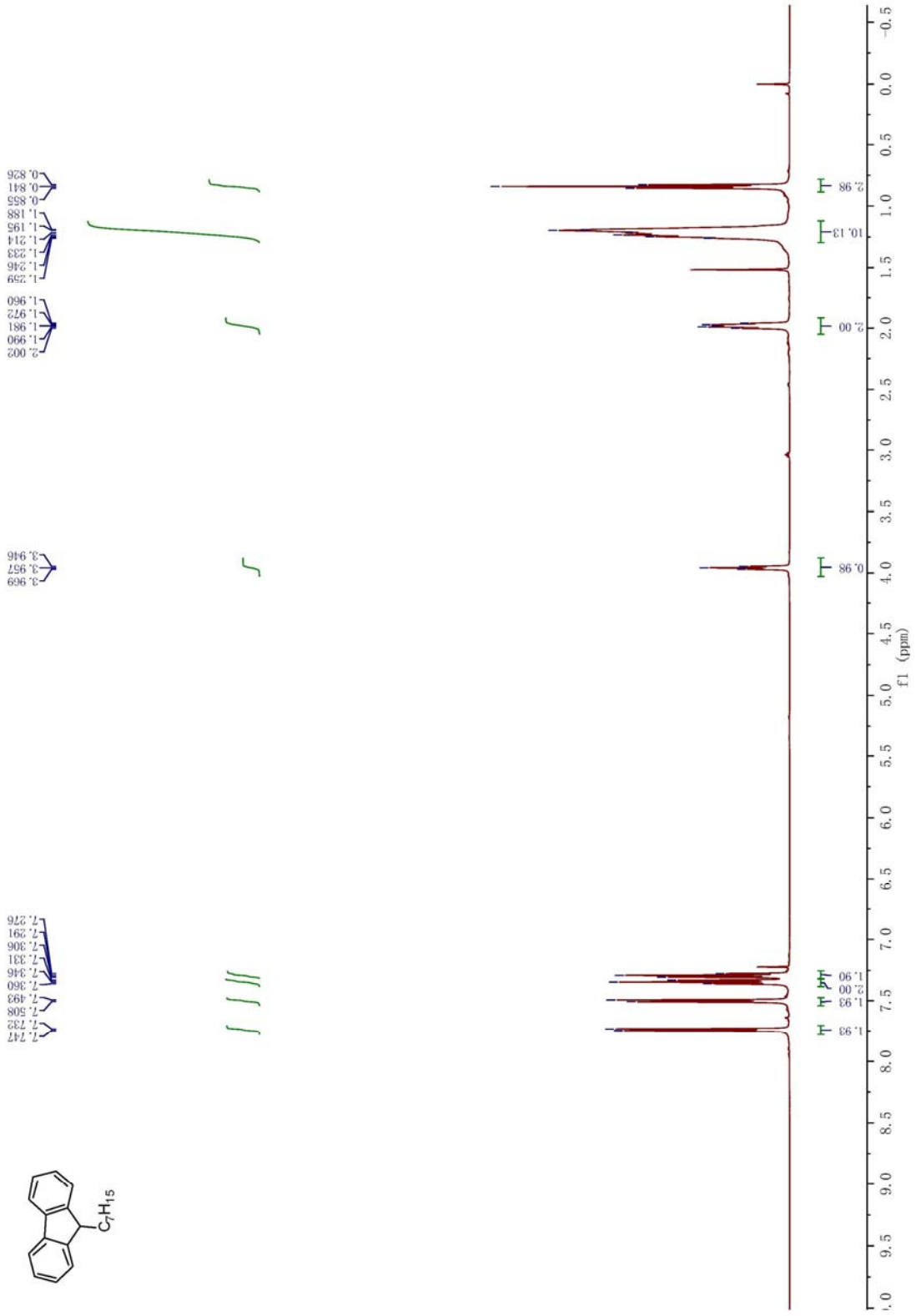
^{13}C NMR

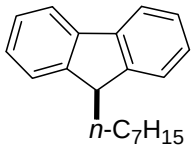




n-C_7H_{15} **6e**

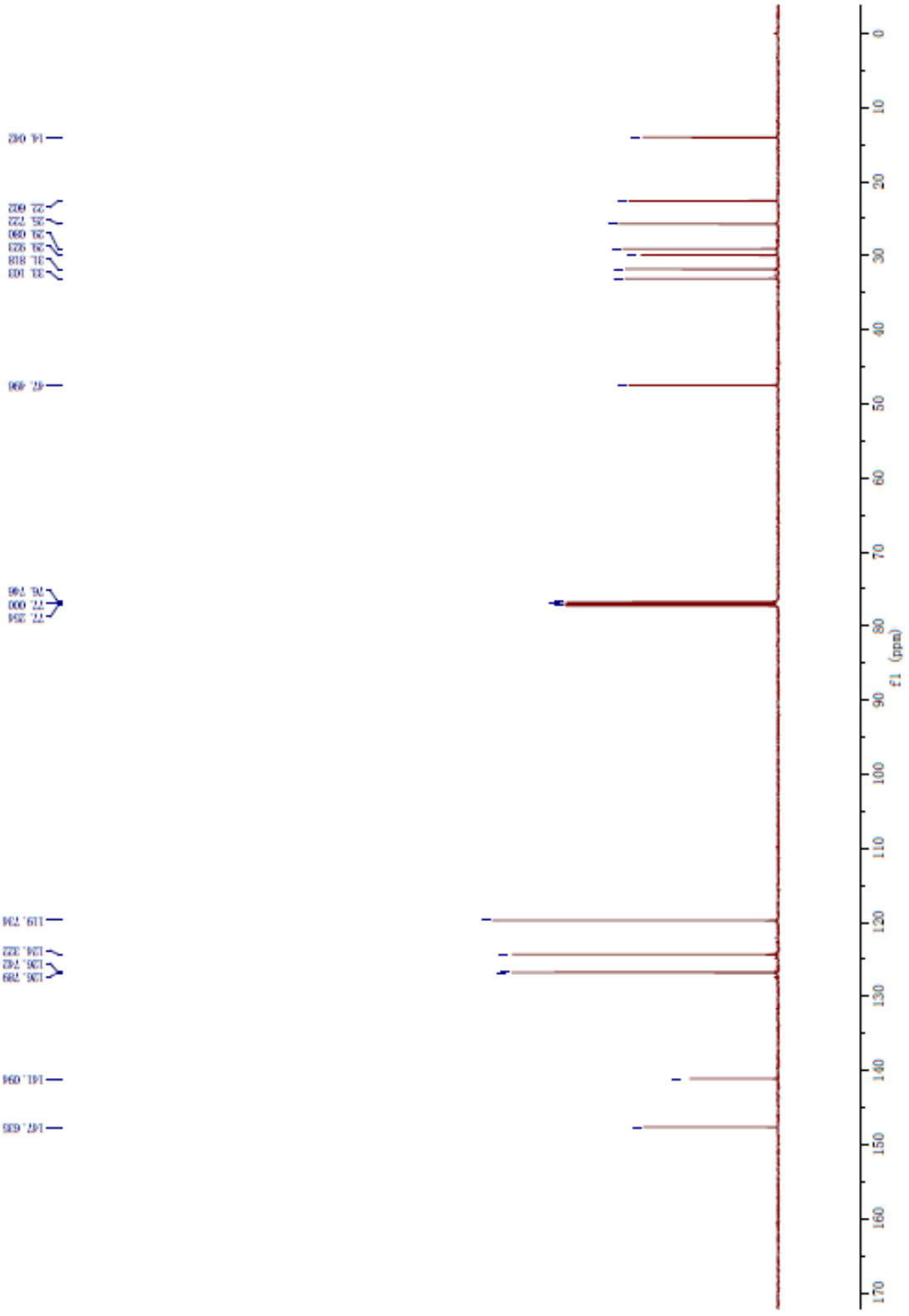
^{1}H NMR

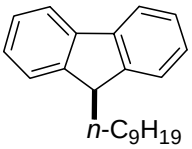




n-C_7H_{15} **6e**

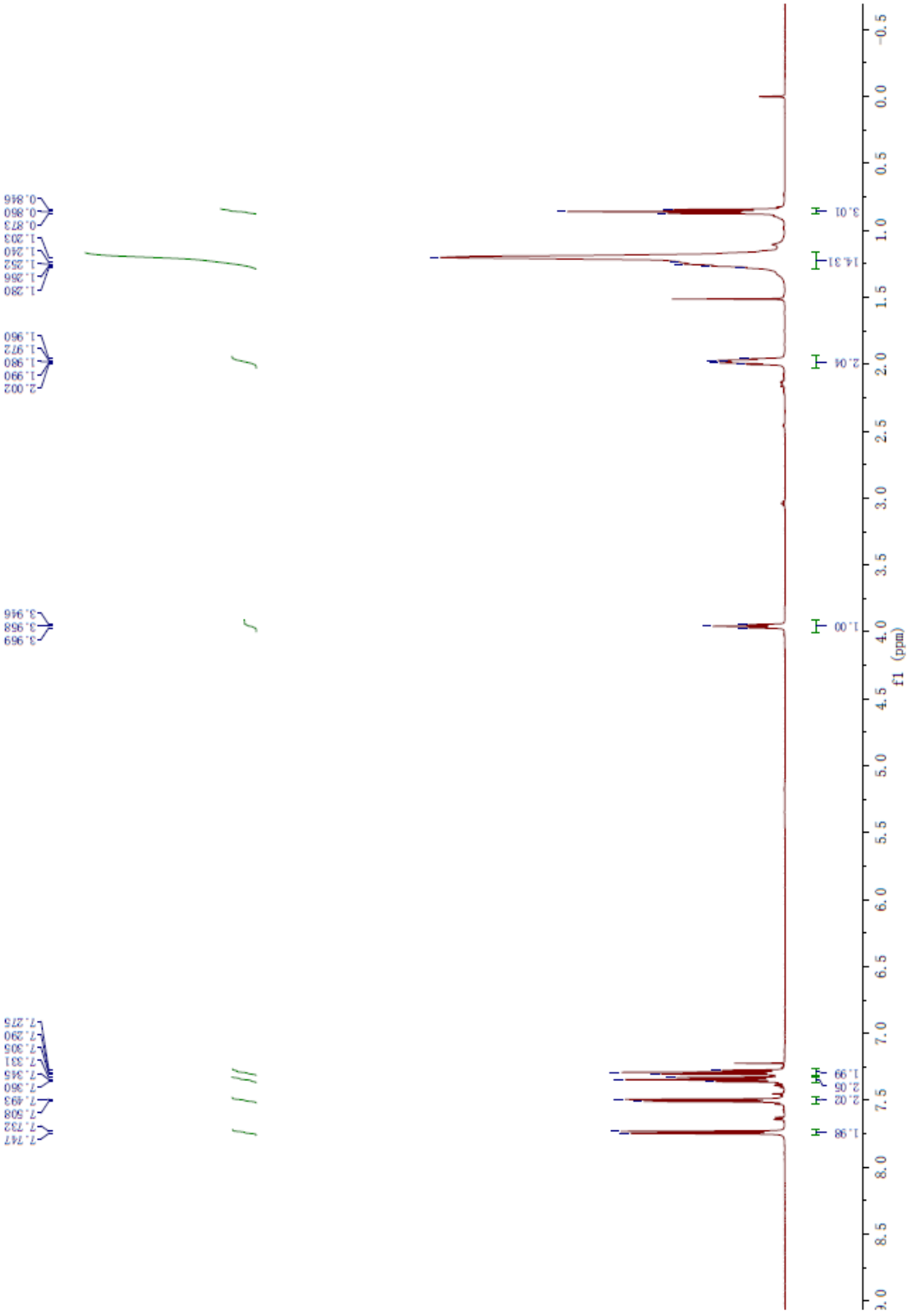
^{13}C NMR

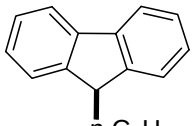




n-C_9H_{19} **6f**

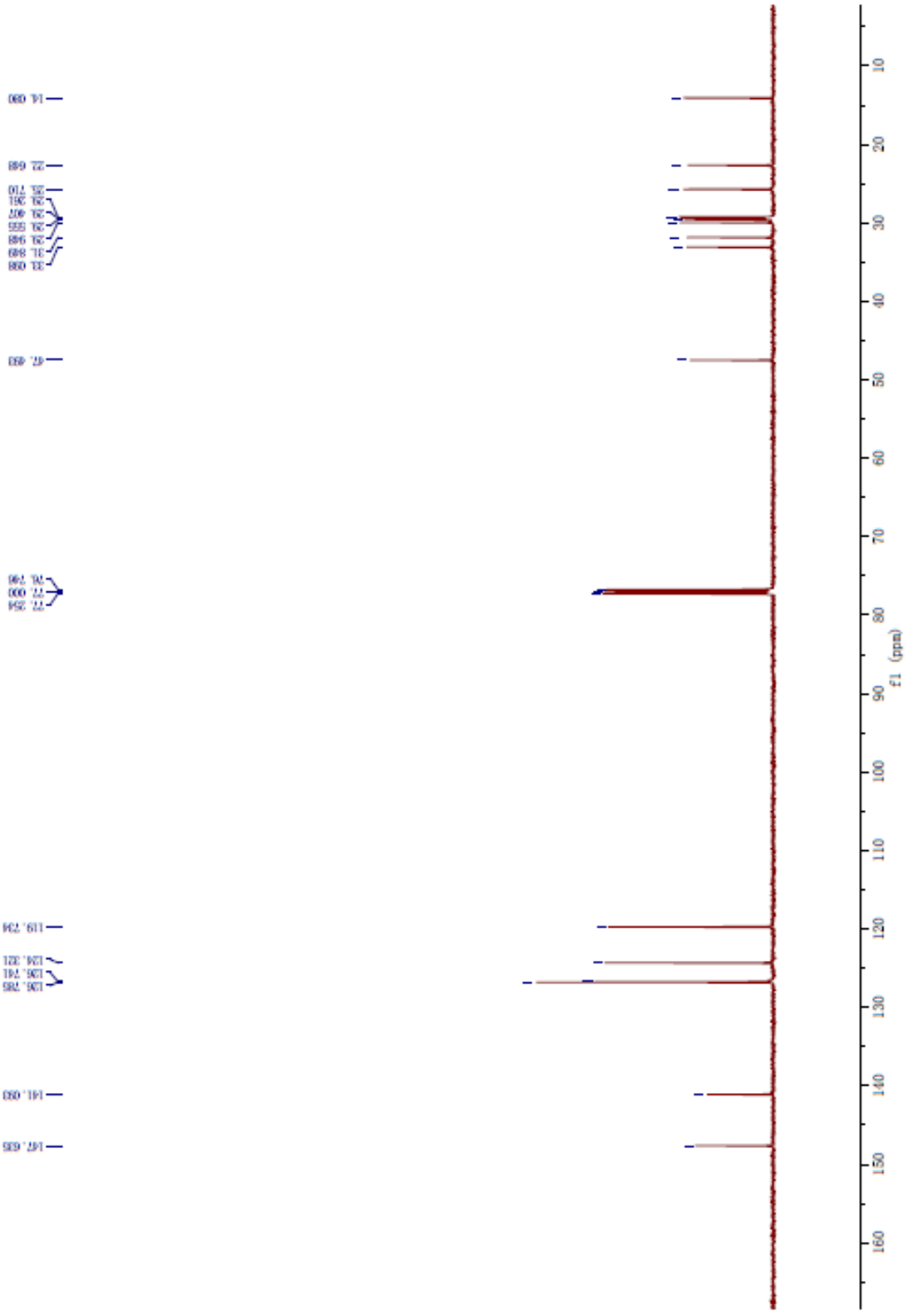
^{1}H NMR

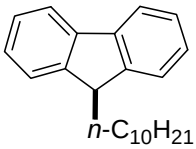




n-C_9H_{19} **6f**

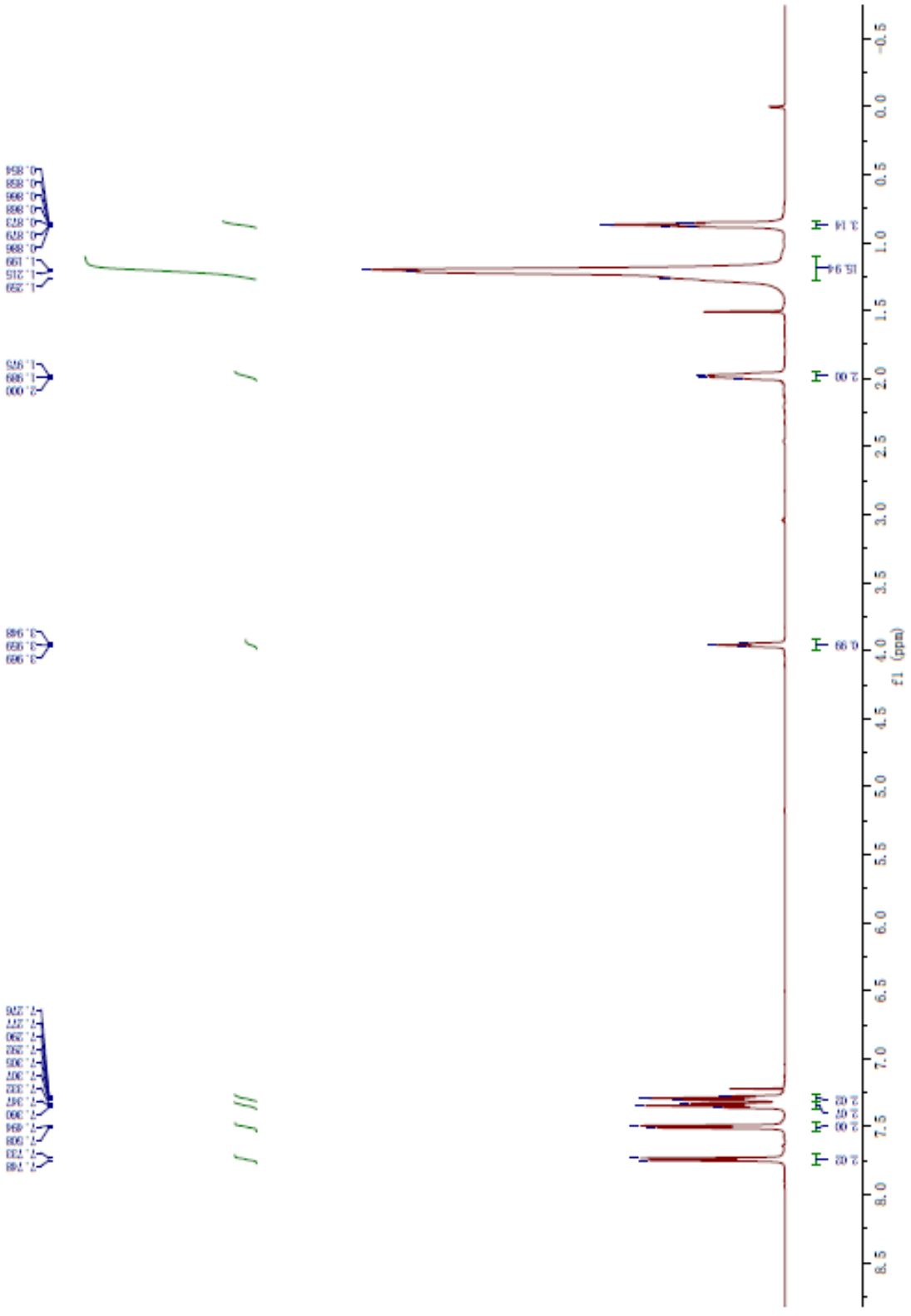
^{13}C NMR

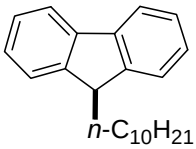




n-$C_{10}H_{21}$ **6g**

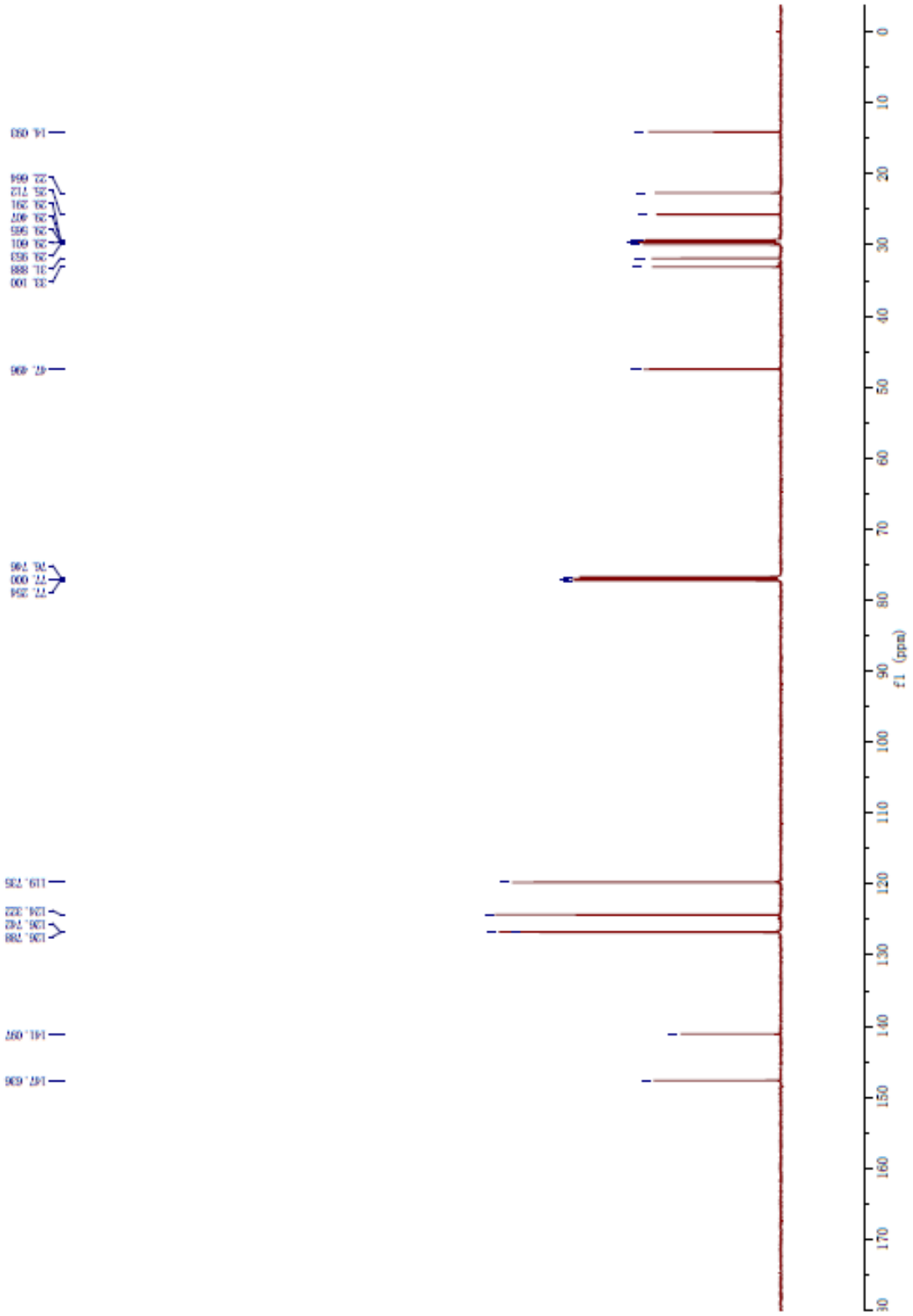
^{1}H NMR

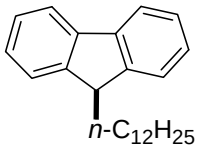




n-$C_{10}H_{21}$ **6g**

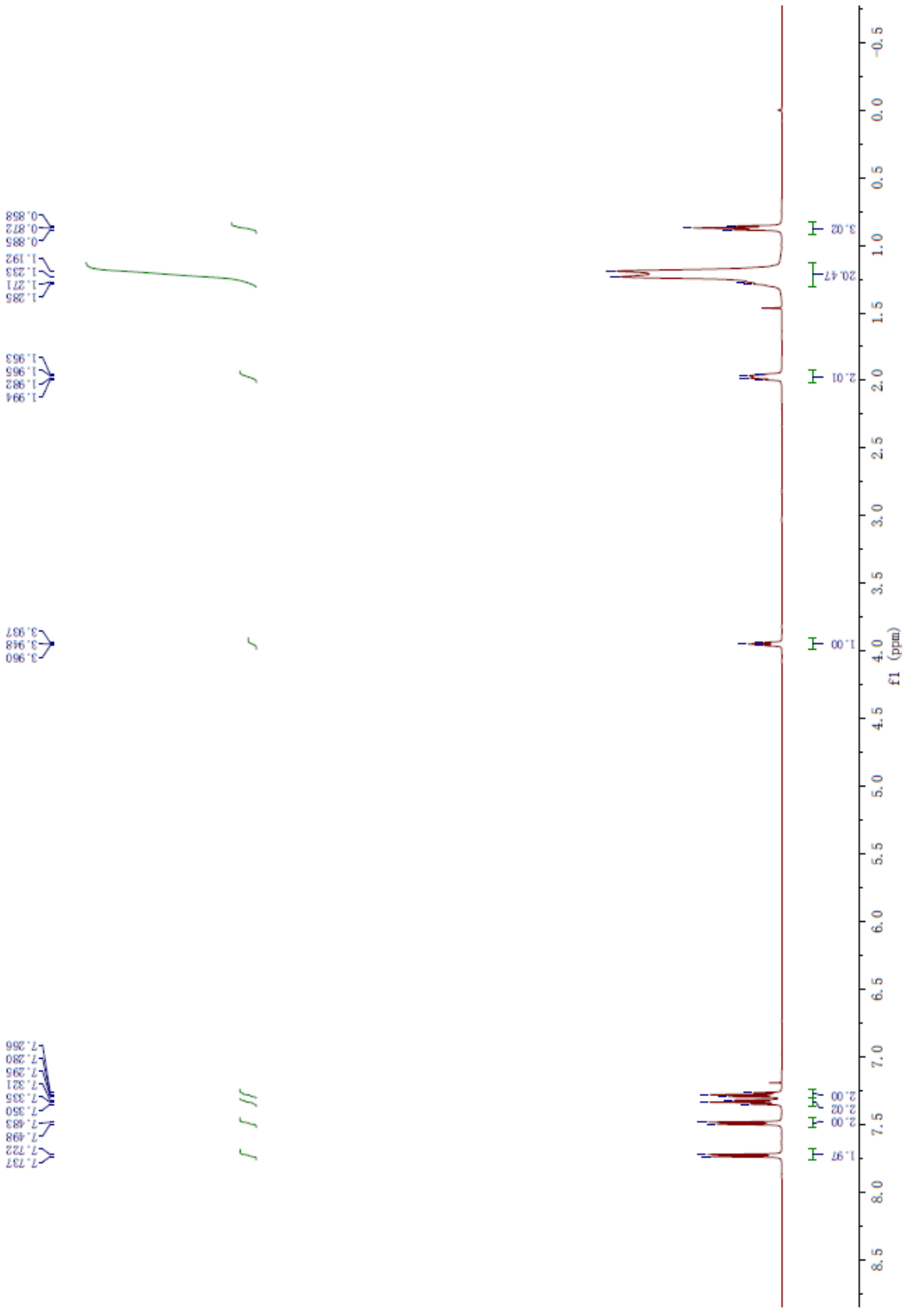
^{13}C NMR

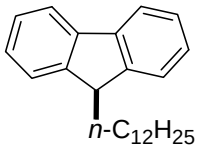




n-$C_{12}H_{25}$ **6h**

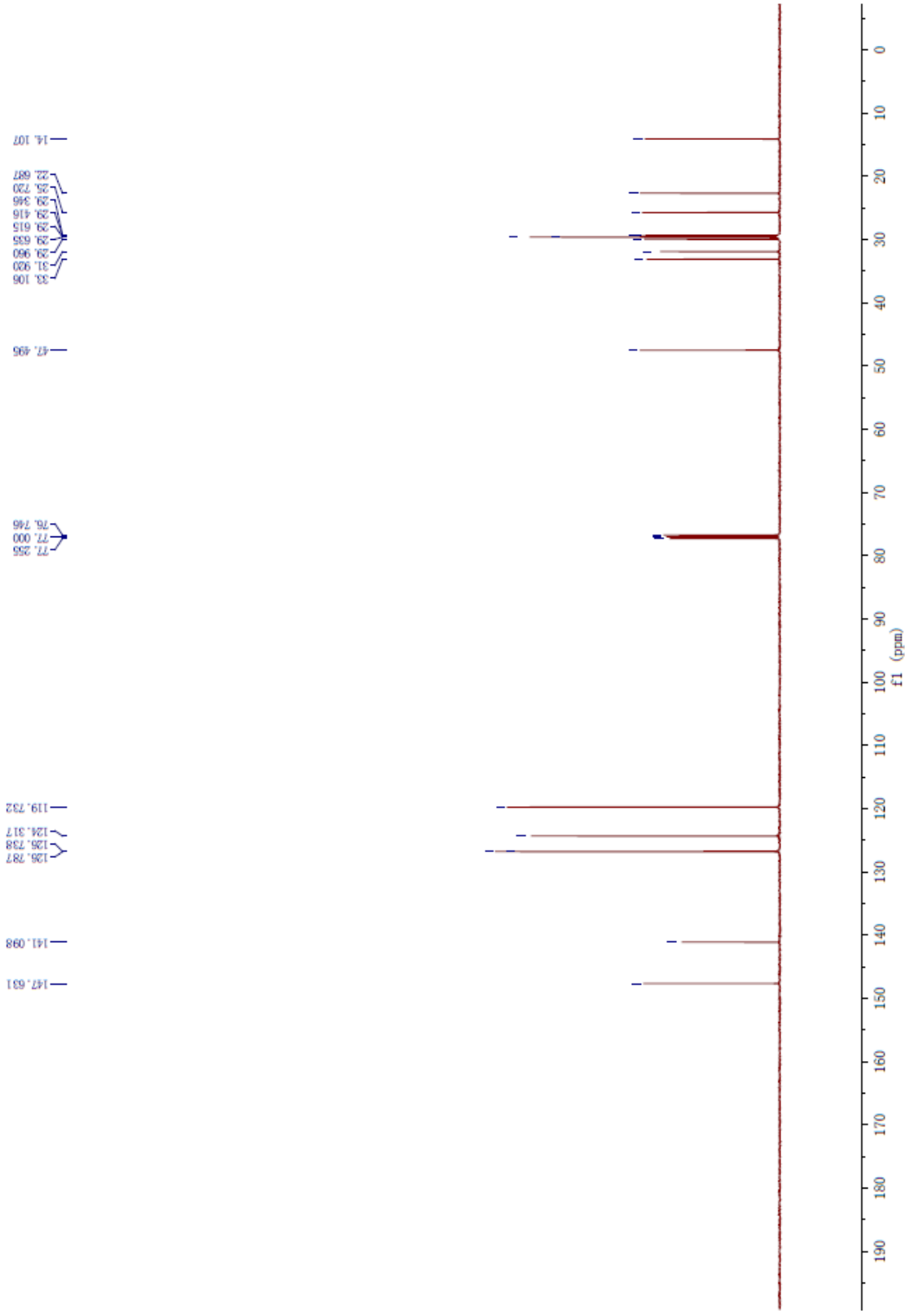
^{1}H NMR

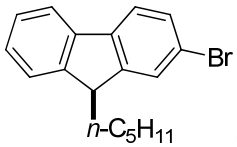




n-$C_{12}H_{25}$ **6h**

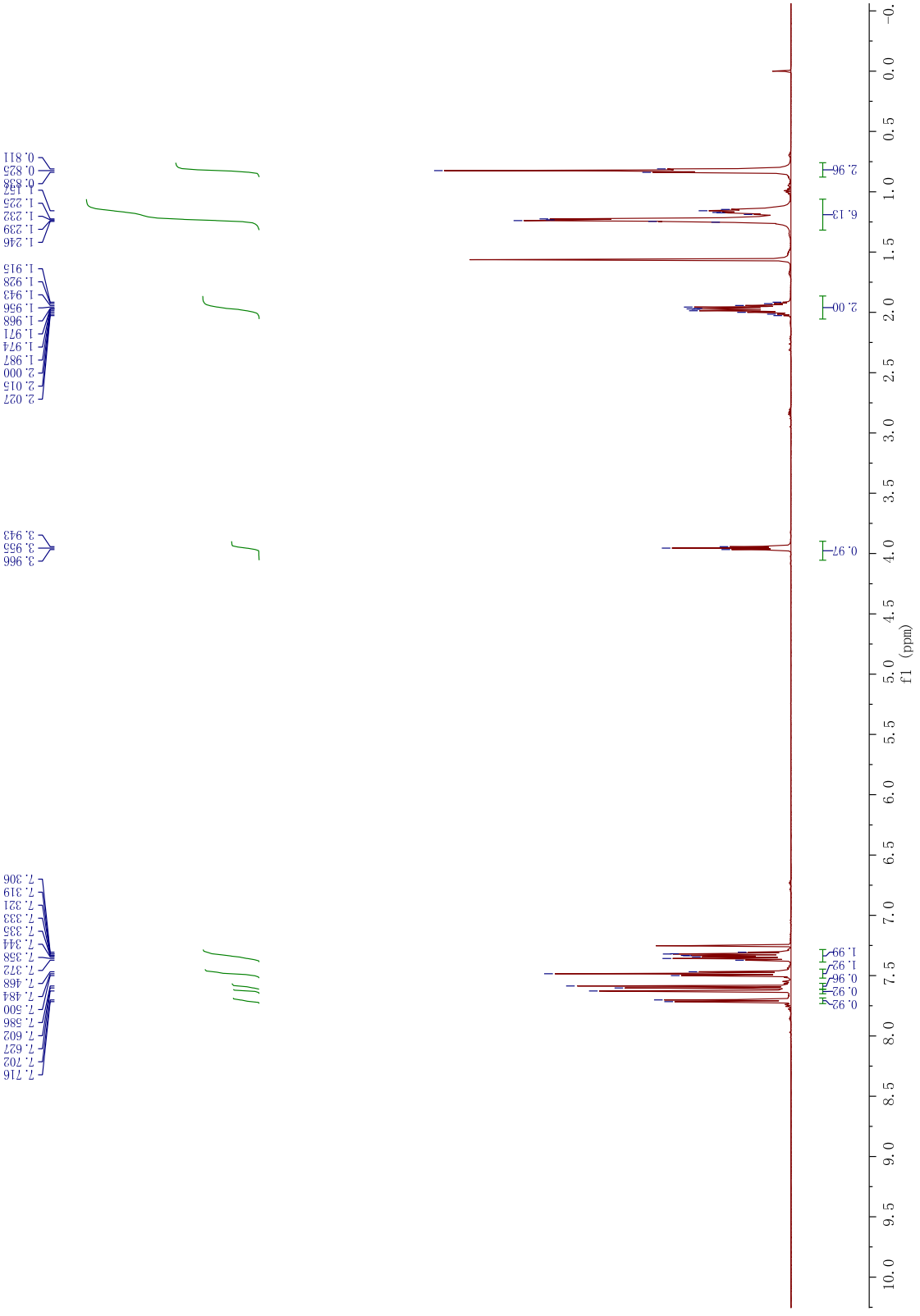
^{13}C NMR

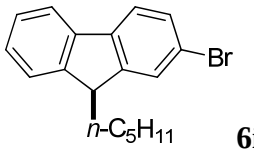




6i

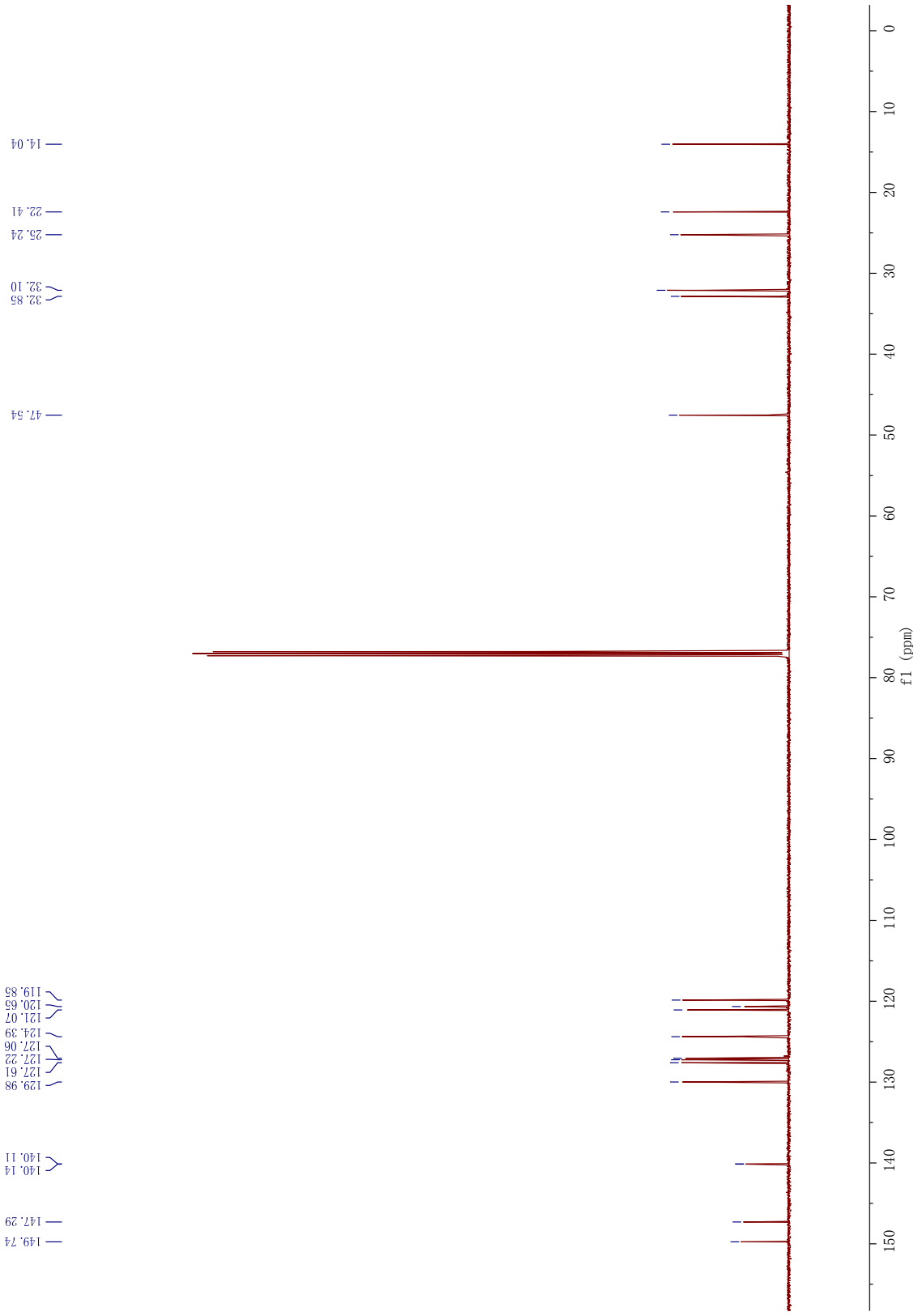
^{1}H NMR

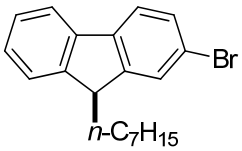



Br
n-C5H11

6i

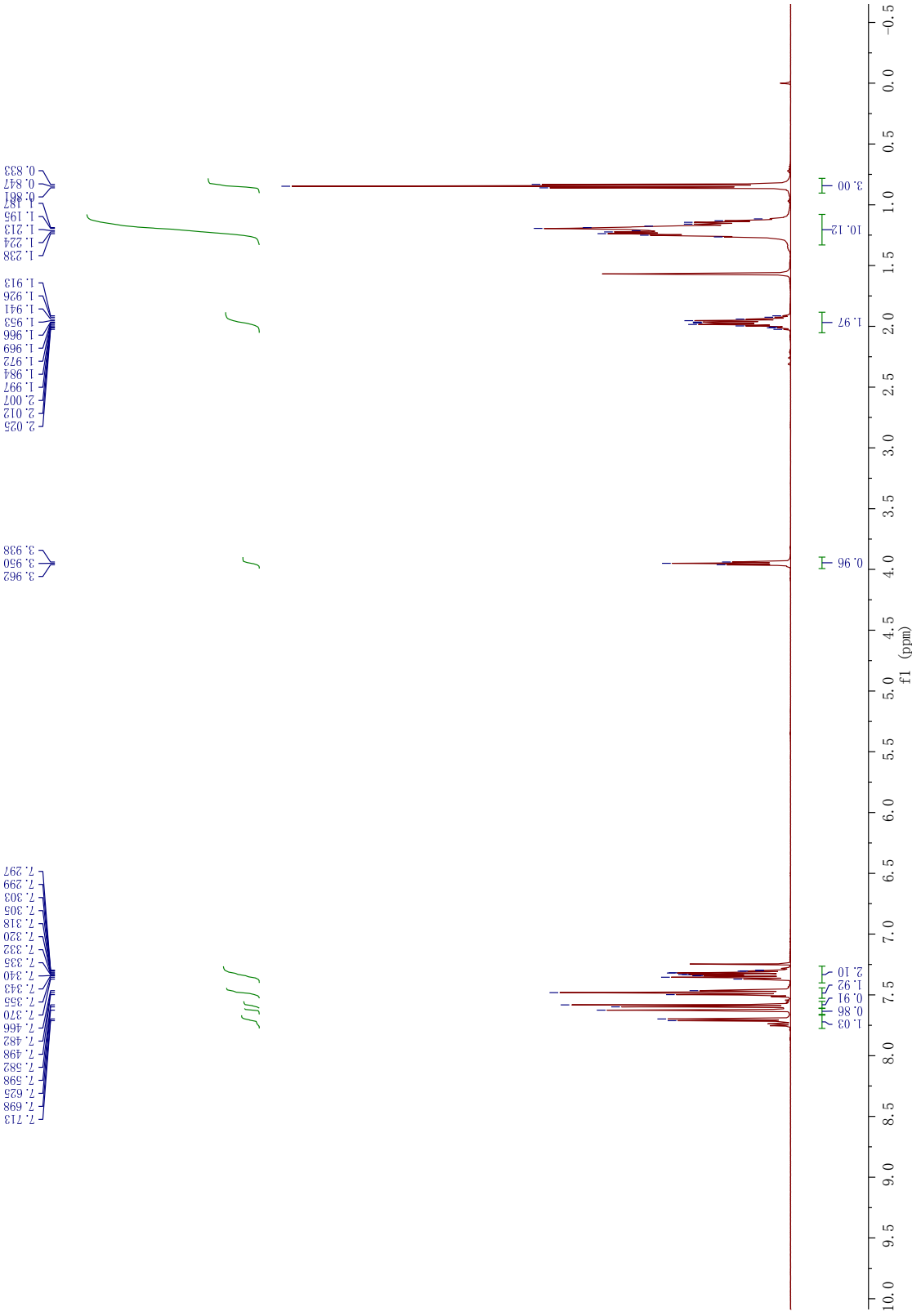
^{13}C NMR

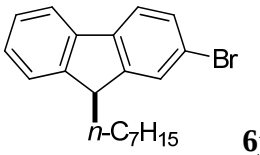

14.04
22.41
25.24
32.10
32.85
47.54
119.85
120.65
121.07
124.39
127.06
127.22
127.61
129.98
140.11
140.14
147.29
149.74
f1 (ppm)


Br
n-C7H15

6j

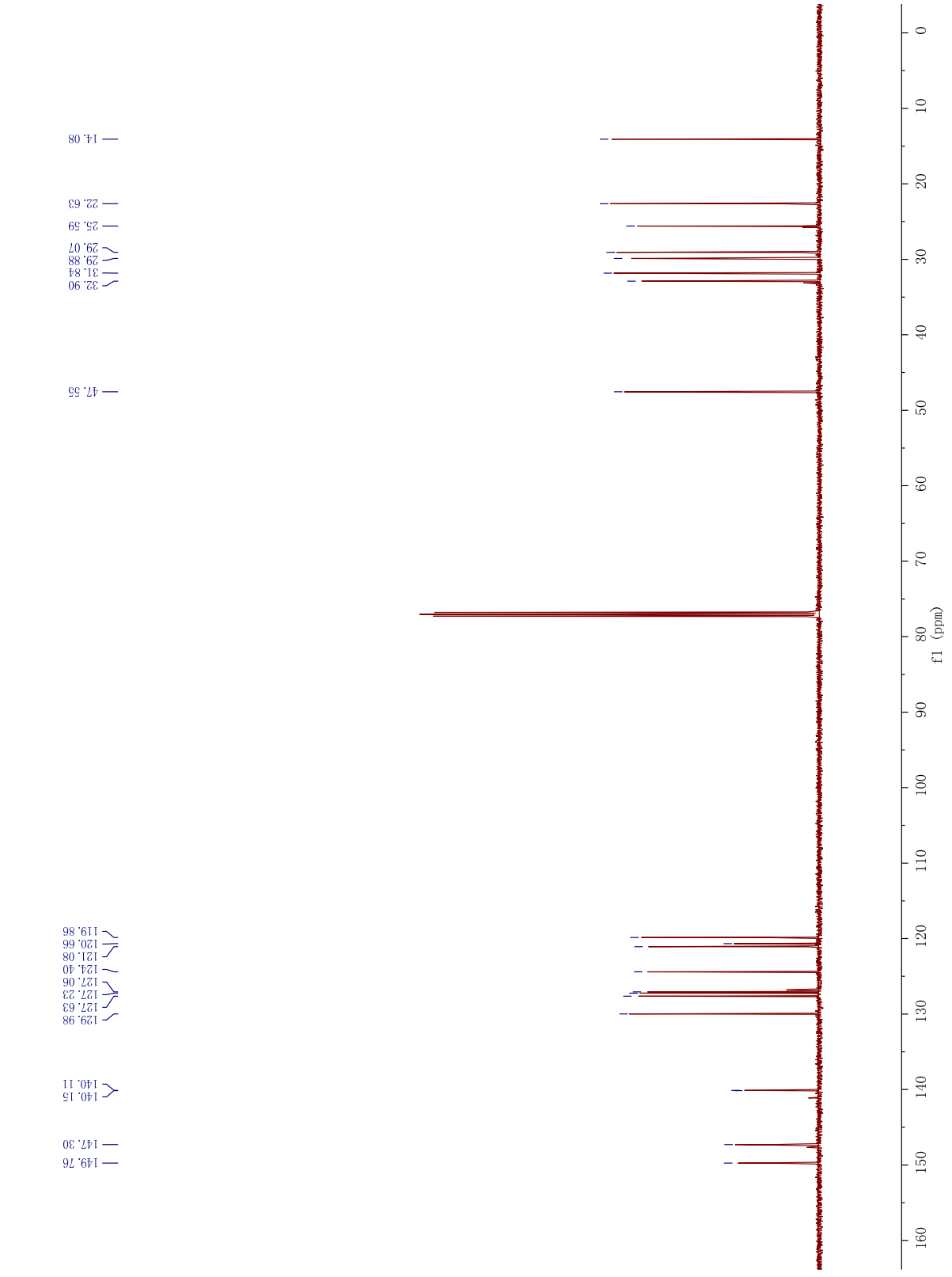
^{1}H NMR

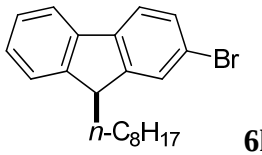

7.713
7.698
7.625
7.598
7.582
7.498
7.482
7.466
7.370
7.355
7.343
7.340
7.335
7.332
7.320
7.318
7.305
7.303
7.299
7.297
3.962
3.950
3.938
2.025
2.012
2.007
1.997
1.984
1.972
1.969
1.966
1.953
1.941
1.926
1.913
1.238
1.224
1.213
1.195
1.182
0.861
0.847
0.833
3.00
10.12
1.97
0.96
2.10
1.92
0.91
0.86
1.03
f1 (ppm)


Br
n-C7H15

6j

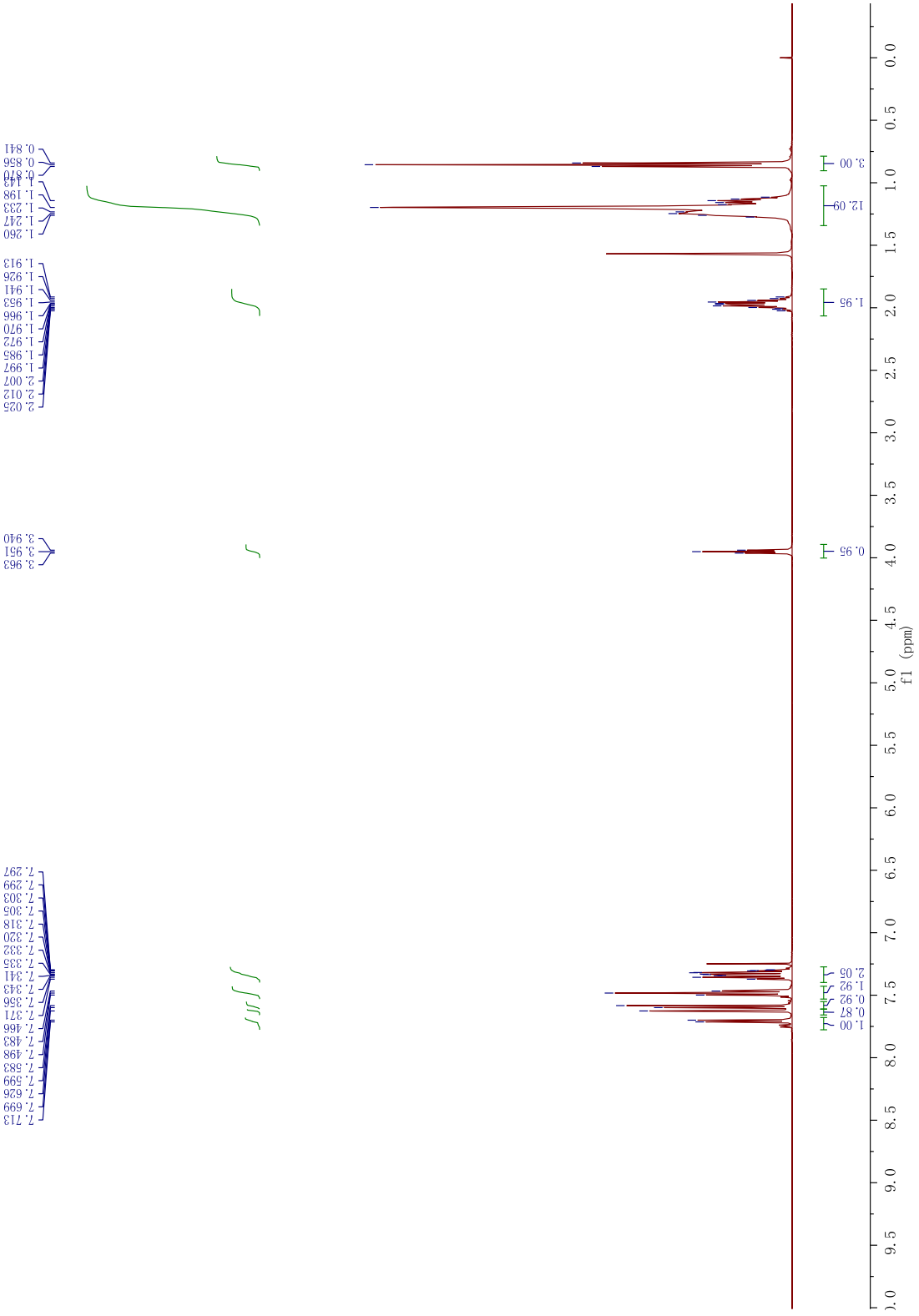
^{13}C NMR

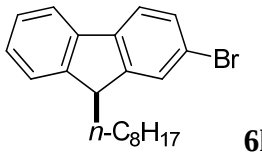

14.08
22.63
25.59
29.07
29.88
31.84
32.90
47.55
119.86
120.66
121.08
124.40
127.06
127.23
127.63
129.98
140.11
140.15
147.30
149.76
f1 (ppm)



6k

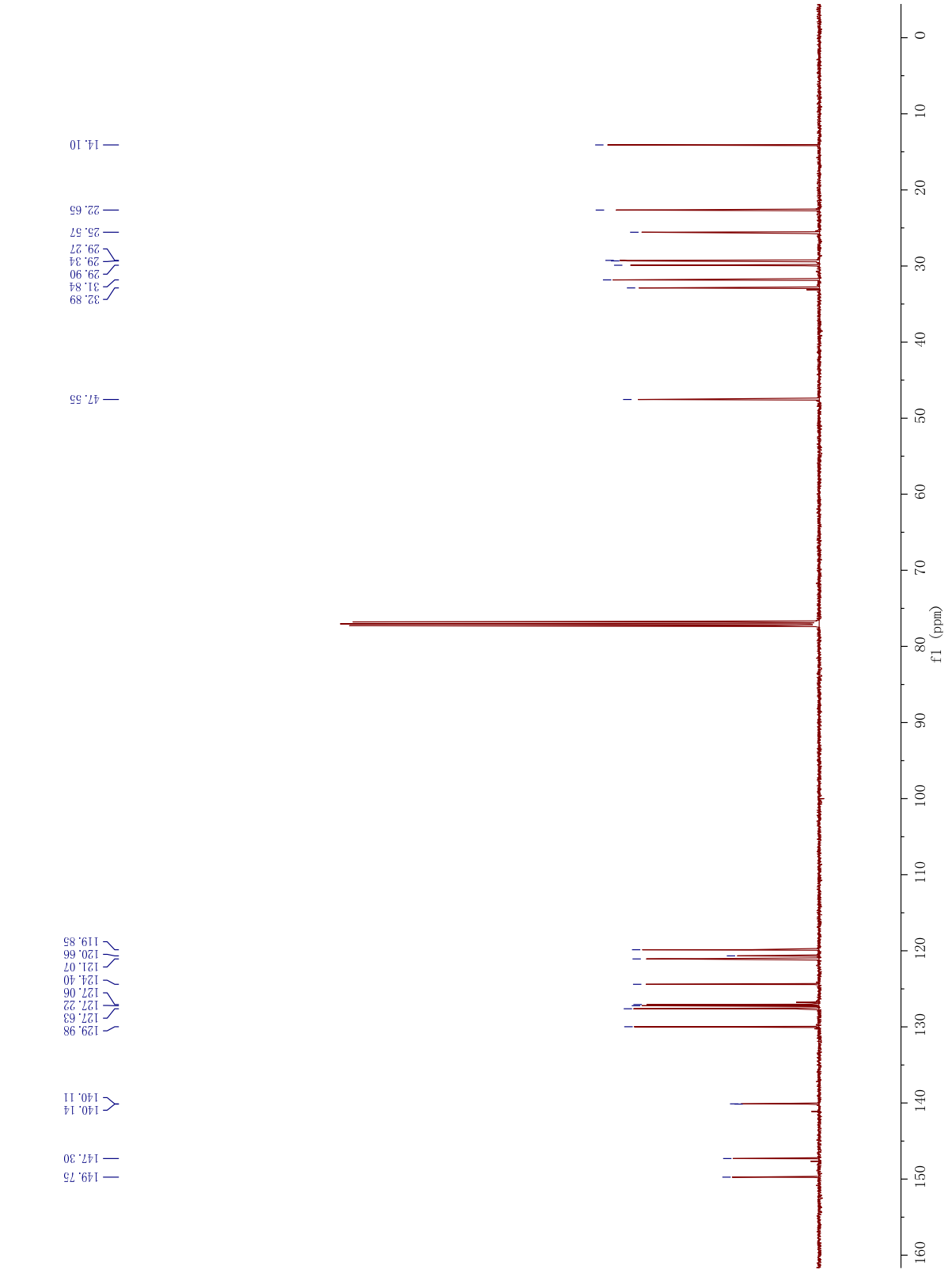
^{1}H NMR

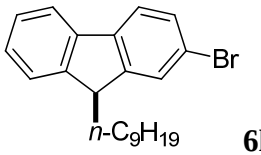



Br
n-C8H17

6k

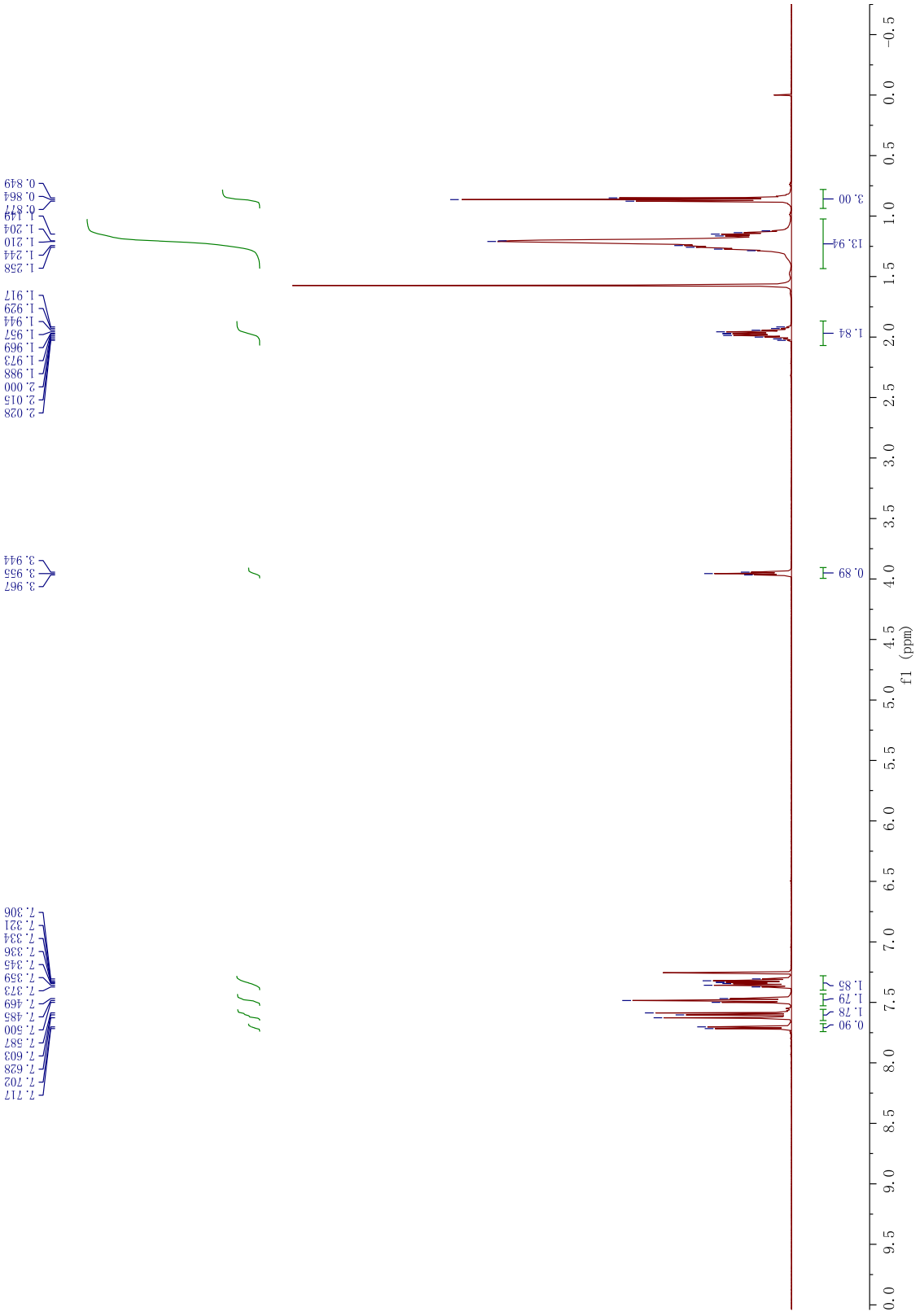
^{13}C NMR

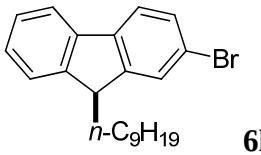

14.10
22.65
25.57
29.27
29.34
29.90
31.84
32.89
47.55
119.85
120.66
121.07
124.40
127.06
127.22
127.63
129.98
140.14
140.11
147.30
149.75
f1 (ppm)


Br
n-C9H19

6l

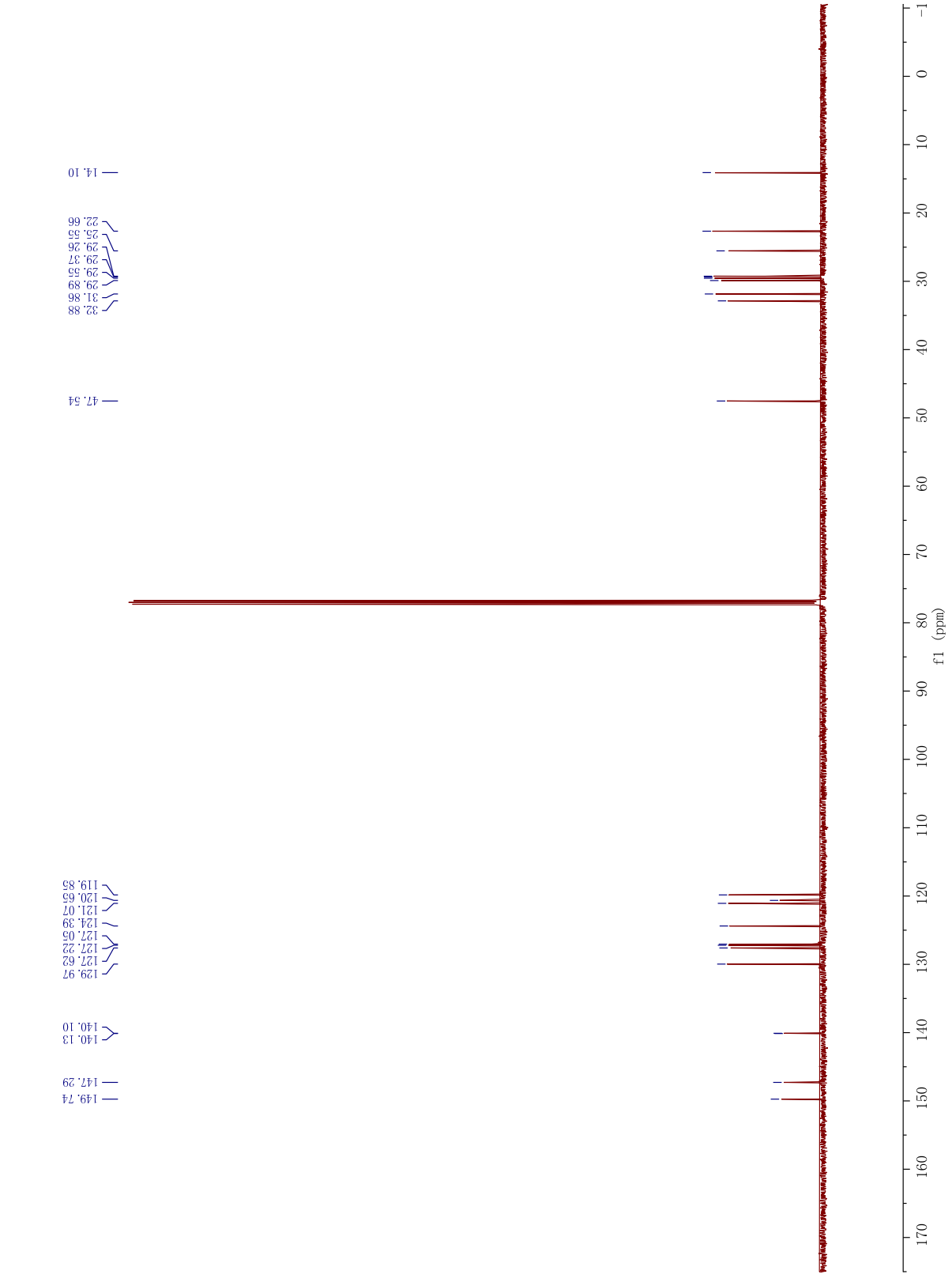
^{1}H NMR

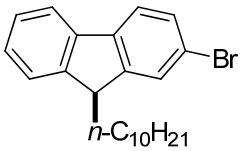

0.849
0.864
0.877
1.149
1.204
1.210
1.244
1.258
1.917
1.929
1.944
1.957
1.969
1.973
1.988
2.000
2.015
2.028
3.944
3.955
3.967
7.306
7.321
7.334
7.336
7.345
7.359
7.373
7.469
7.485
7.500
7.587
7.603
7.628
7.702
7.717
3.00
13.94
1.84
0.89
1.85
1.79
1.78
0.90
f1 (ppm)


Br
n-C9H19

6l

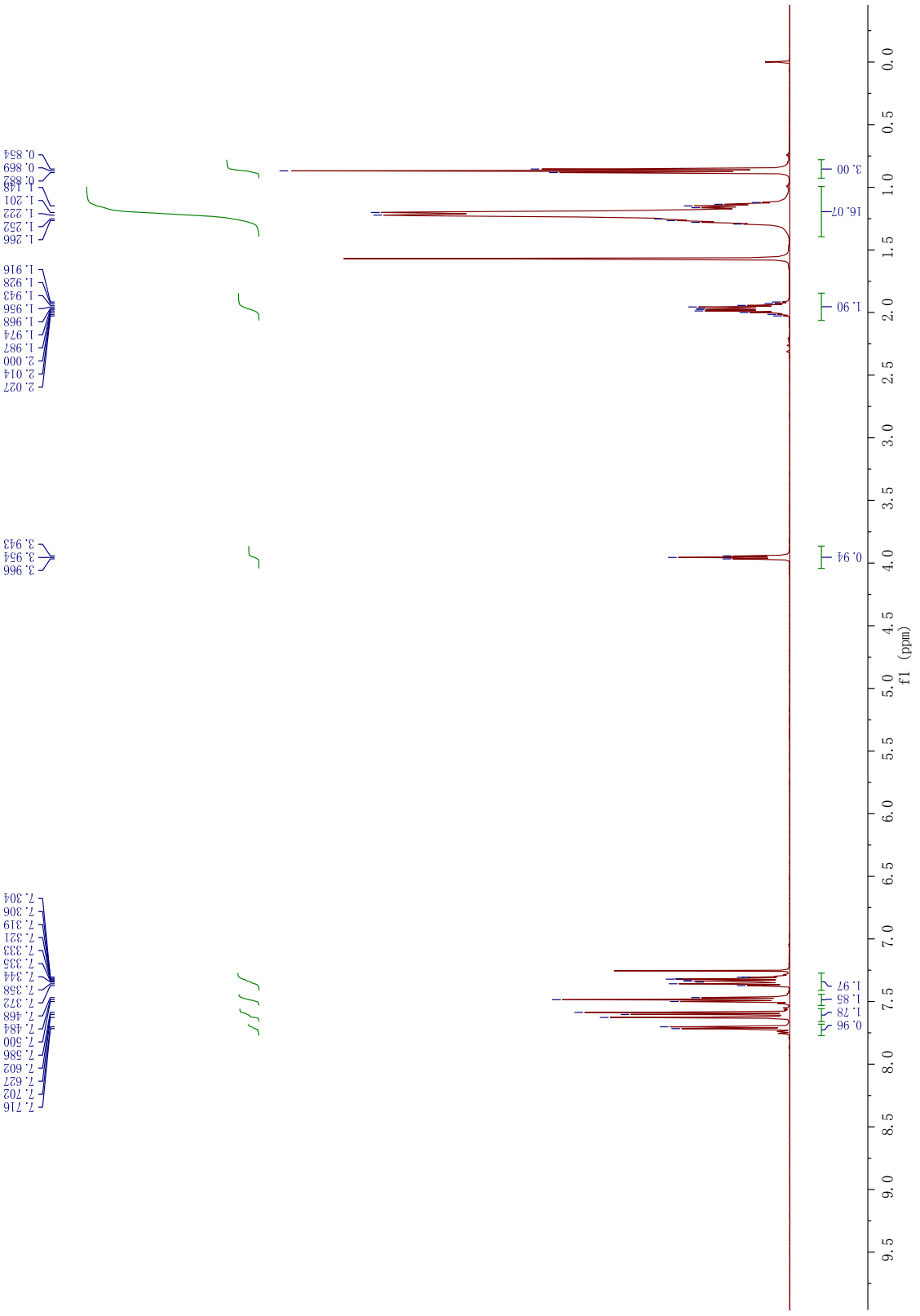
^{13}C NMR

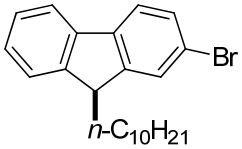

14.10
22.66
25.55
29.26
29.37
29.55
29.89
31.86
32.88
47.54
119.85
120.65
121.07
124.39
127.05
127.22
127.62
129.97
140.10
140.13
147.29
149.74
f1 (ppm)


Br
n-C10H21

6m

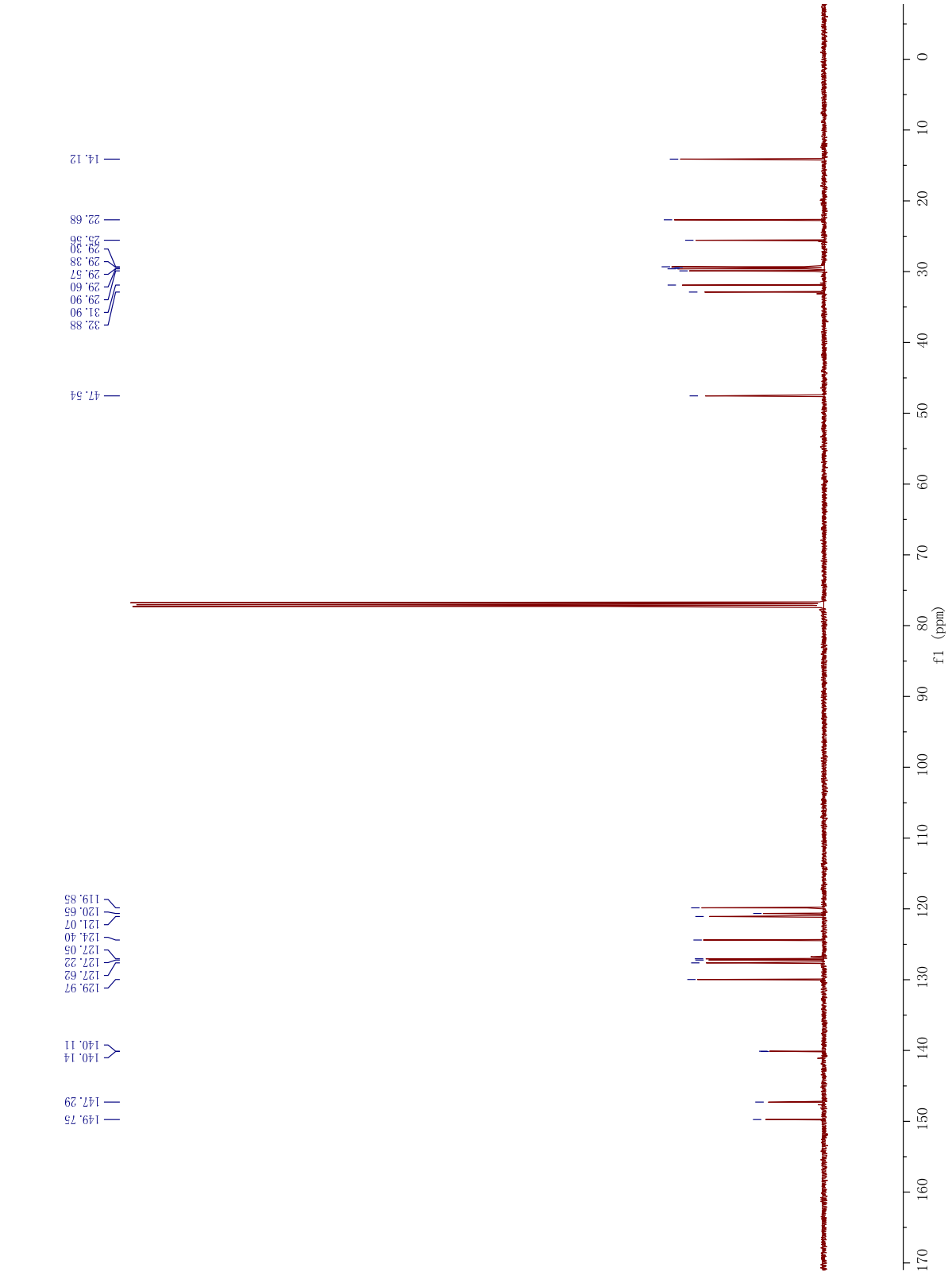
^{1}H NMR

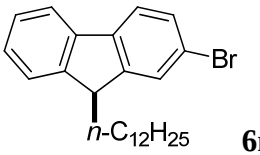

0.854
0.869
0.882
1.148
1.201
1.222
1.252
1.266
1.916
1.928
1.943
1.956
1.968
1.974
1.987
2.000
2.014
2.027
3.943
3.954
3.966
7.304
7.306
7.319
7.321
7.333
7.335
7.344
7.358
7.372
7.468
7.484
7.500
7.586
7.602
7.627
7.702
7.716
3.00
16.07
1.90
0.94
1.97
1.85
1.78
0.96
f1 (ppm)


Br
n-C10H21

6m

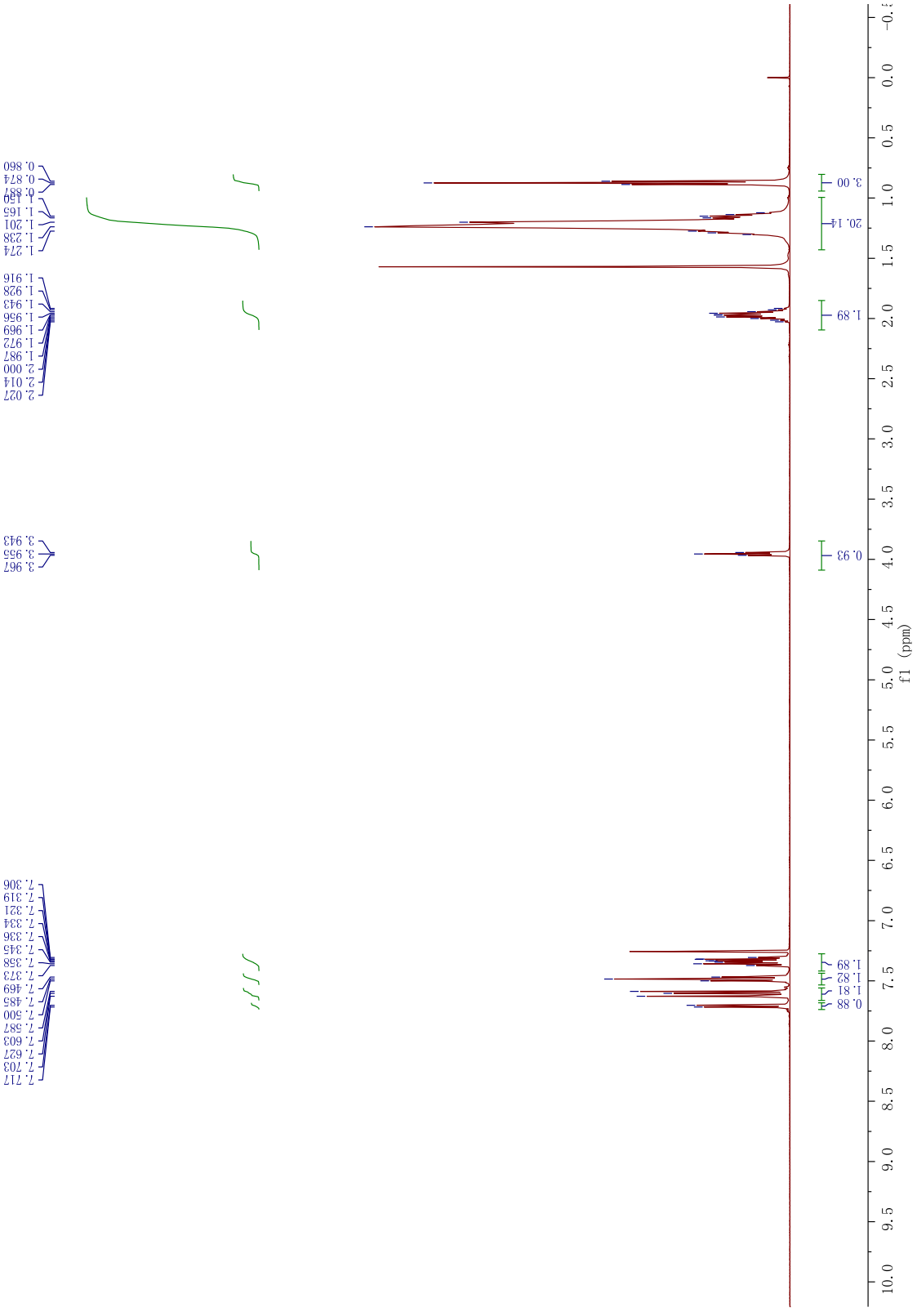
^{13}C NMR

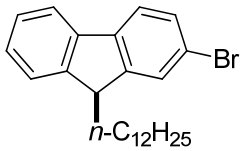

14.12
22.68
25.36
29.30
29.38
29.57
29.60
29.90
31.90
32.88
47.54
119.85
120.65
121.07
124.40
127.05
127.22
127.62
129.97
140.11
140.14
147.29
149.75
f1 (ppm)



6n

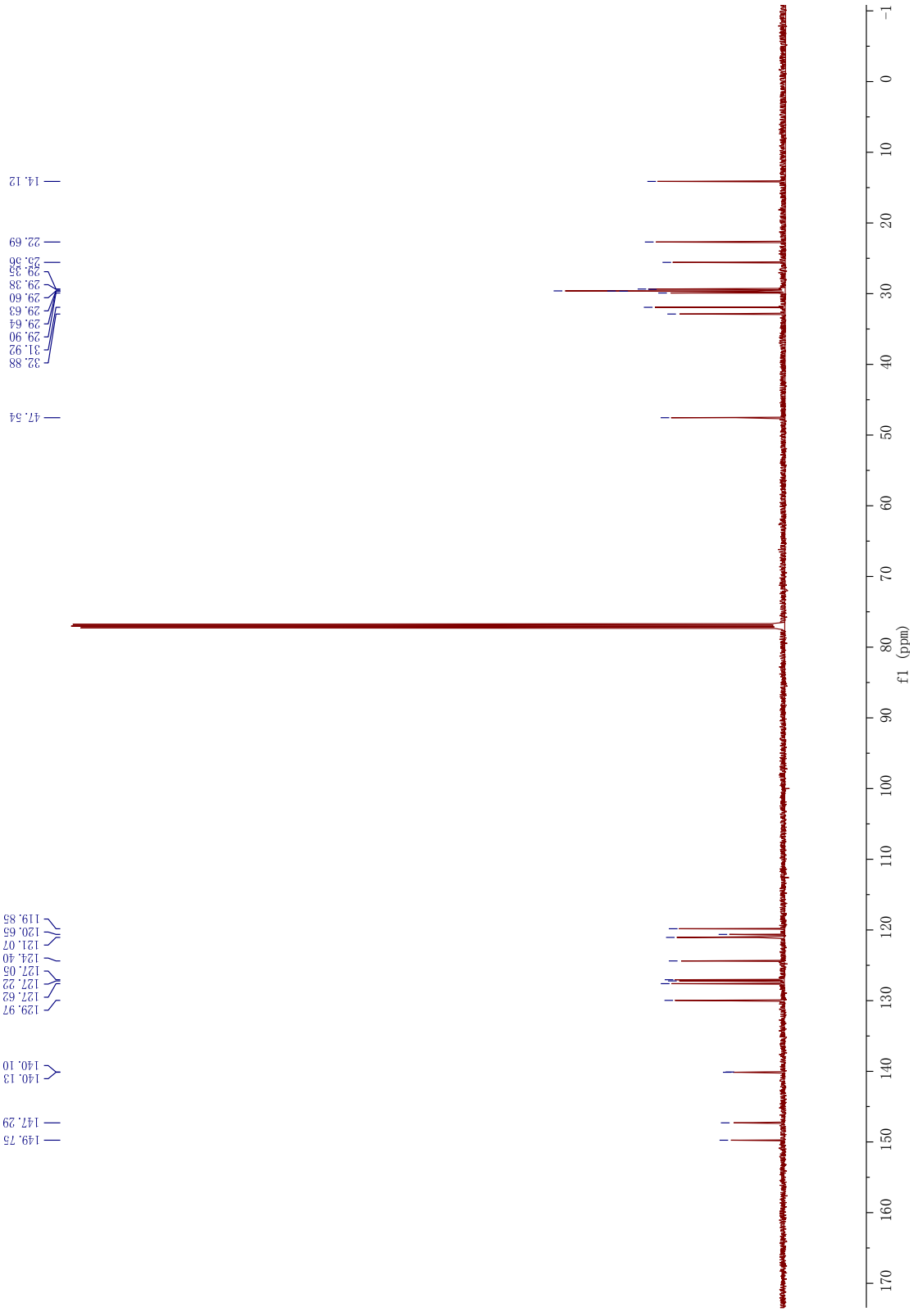
^{1}H NMR

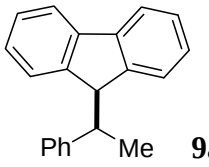



Br
n-C12H25

6n

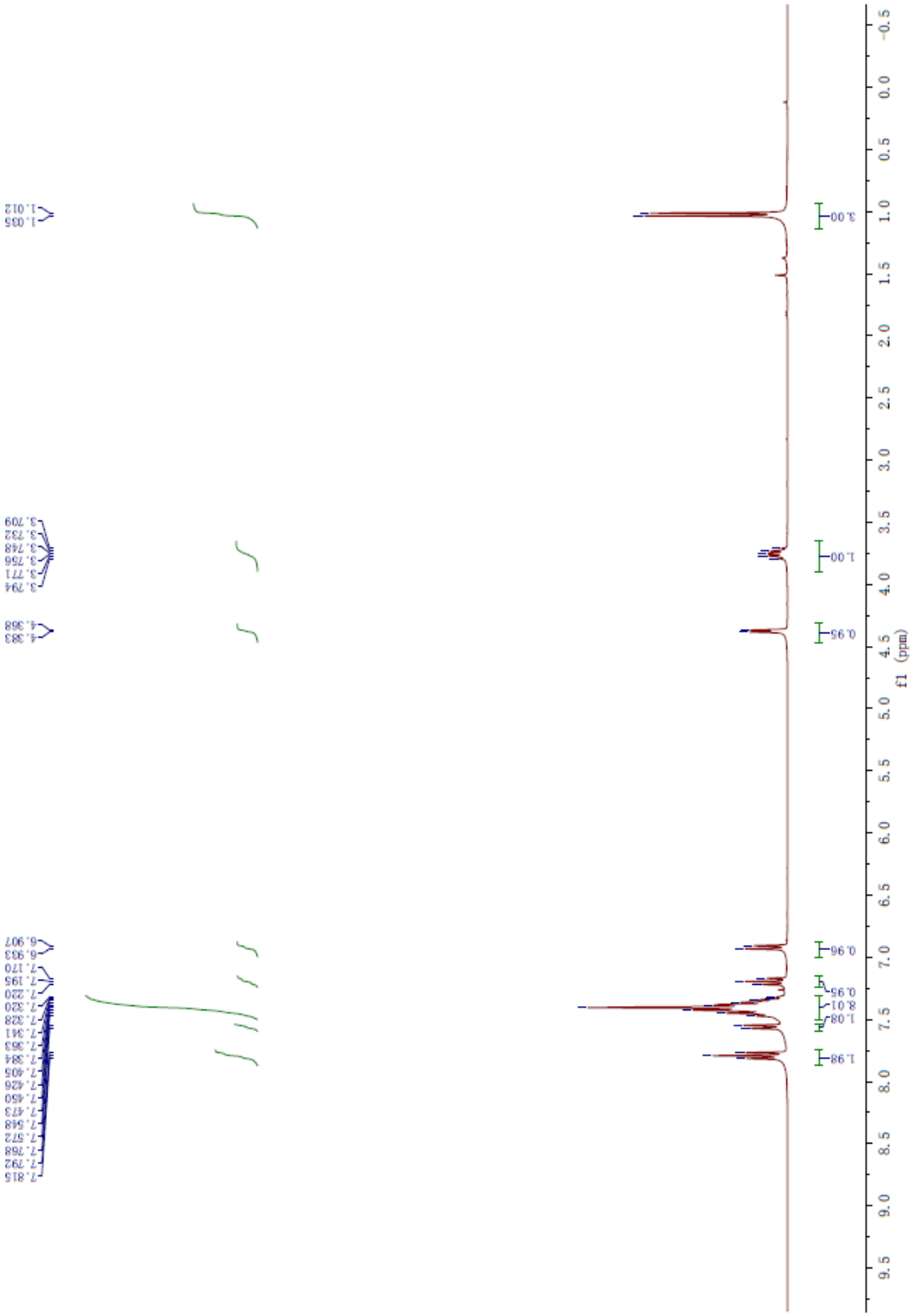
^{13}C NMR

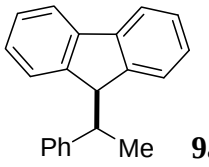

14.12
22.69
25.56
29.35
29.38
29.60
29.63
29.64
29.90
31.92
32.88
47.54
119.85
120.65
121.07
124.40
127.05
127.22
127.62
129.97
140.10
140.13
147.29
149.75
f1 (ppm)



9a

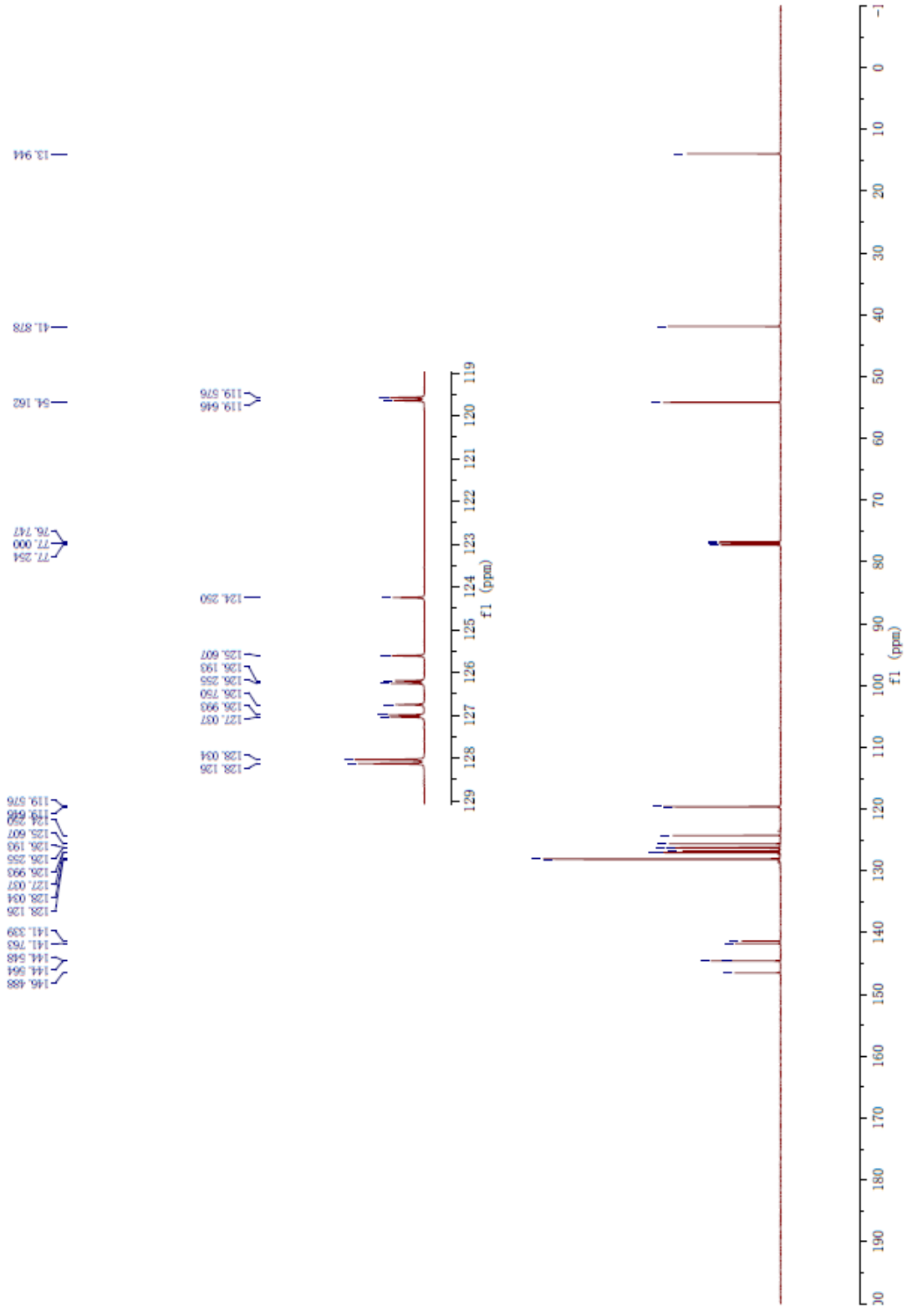
^{1}H NMR

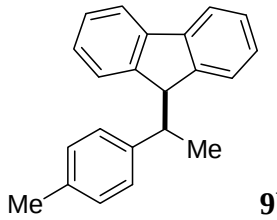



Ph
Me

9a

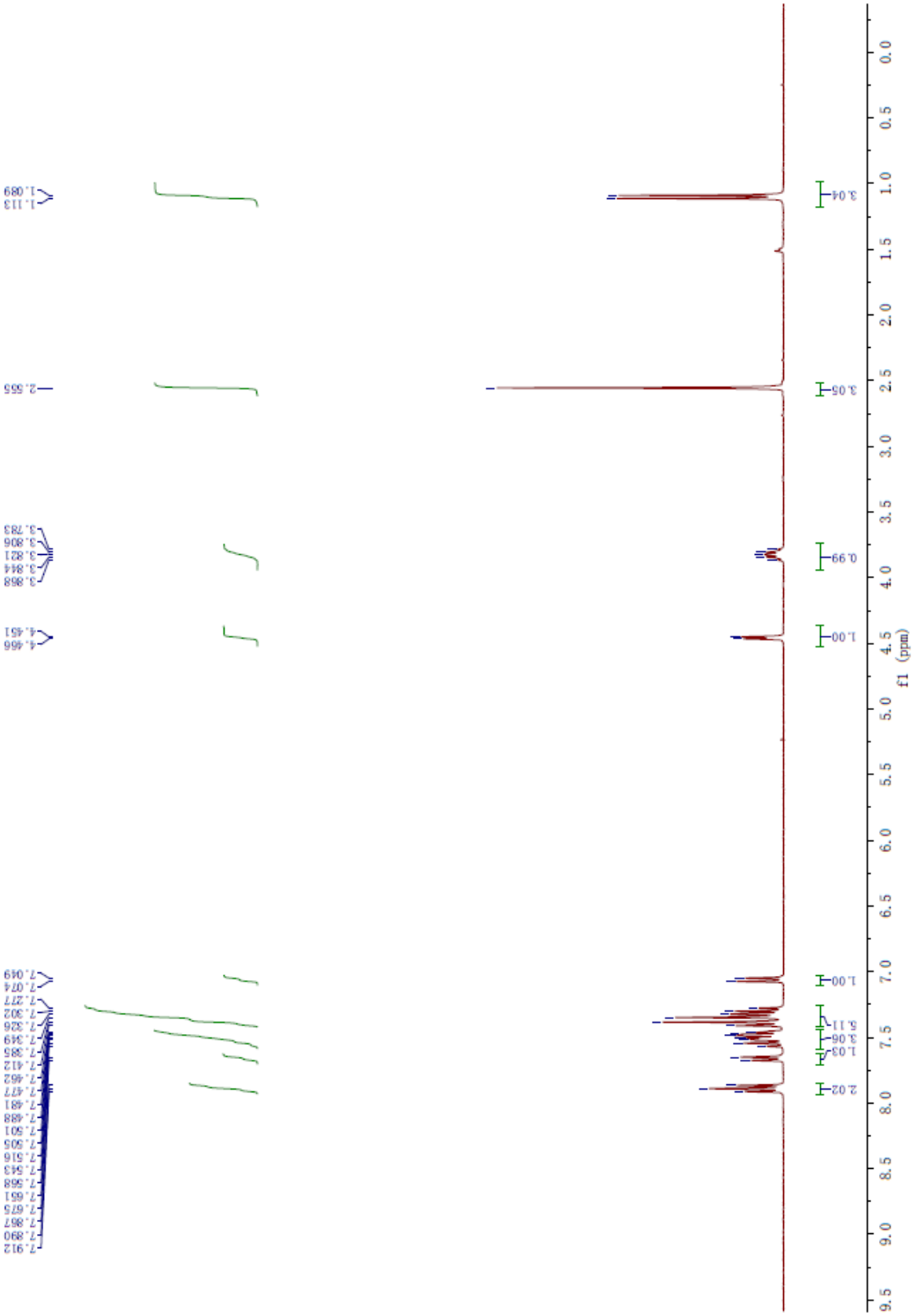
^{13}C NMR

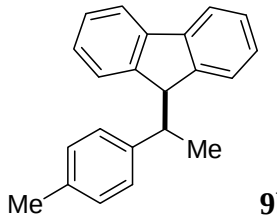

13.944
41.878
54.162
76.147
77.000
77.254
119.576
119.666
124.290
125.607
126.193
126.255
126.750
126.993
127.057
128.034
128.126
141.339
141.763
144.548
144.564
146.488
f1 (ppm)



9b

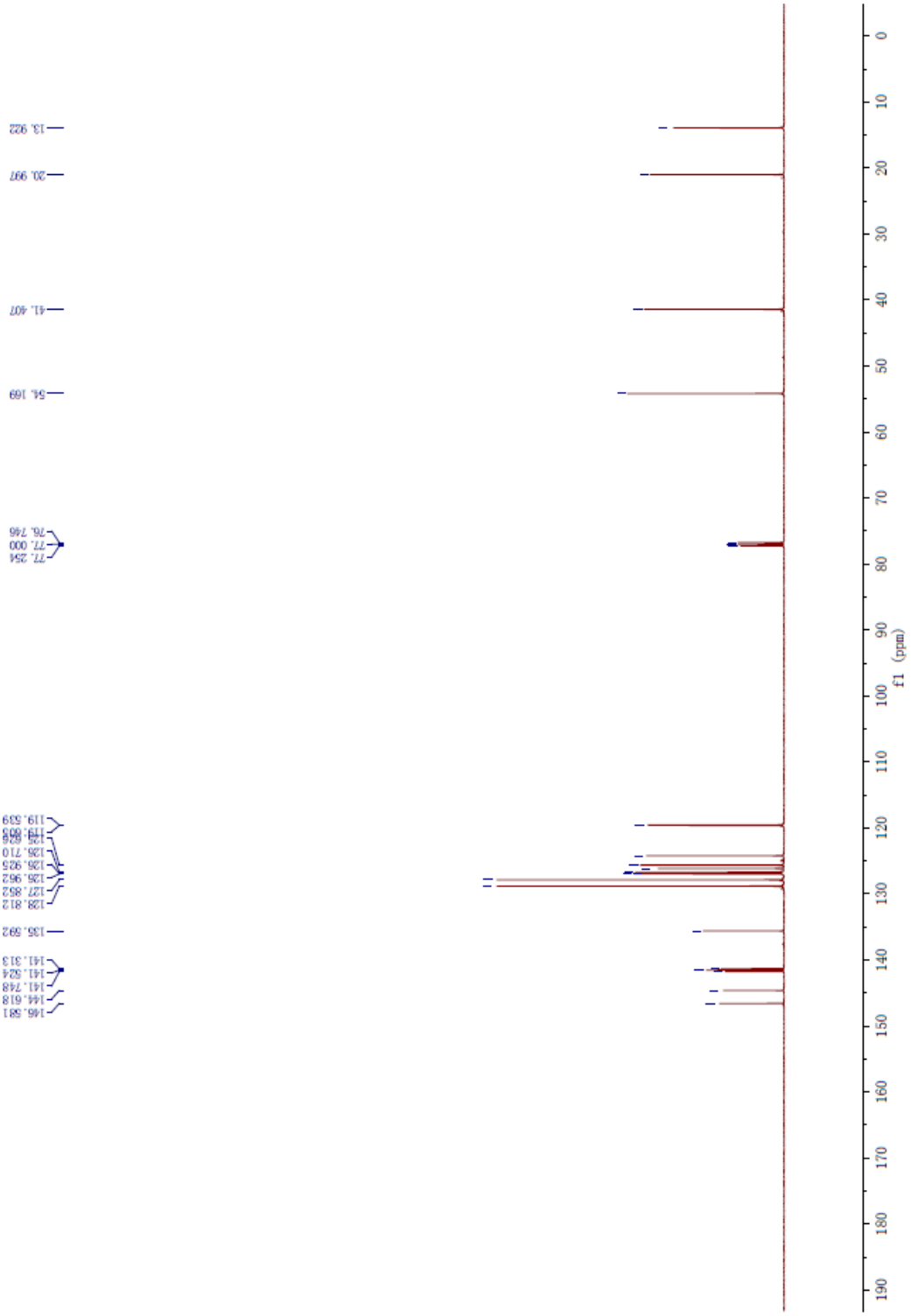
^{1}H NMR




Me
Me

9b

^{13}C NMR


13.922
20.997
41.407
54.169
76.746
77.000
77.254
119.539
119.693
125.656
126.710
126.925
126.962
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128.812
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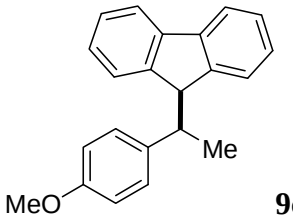
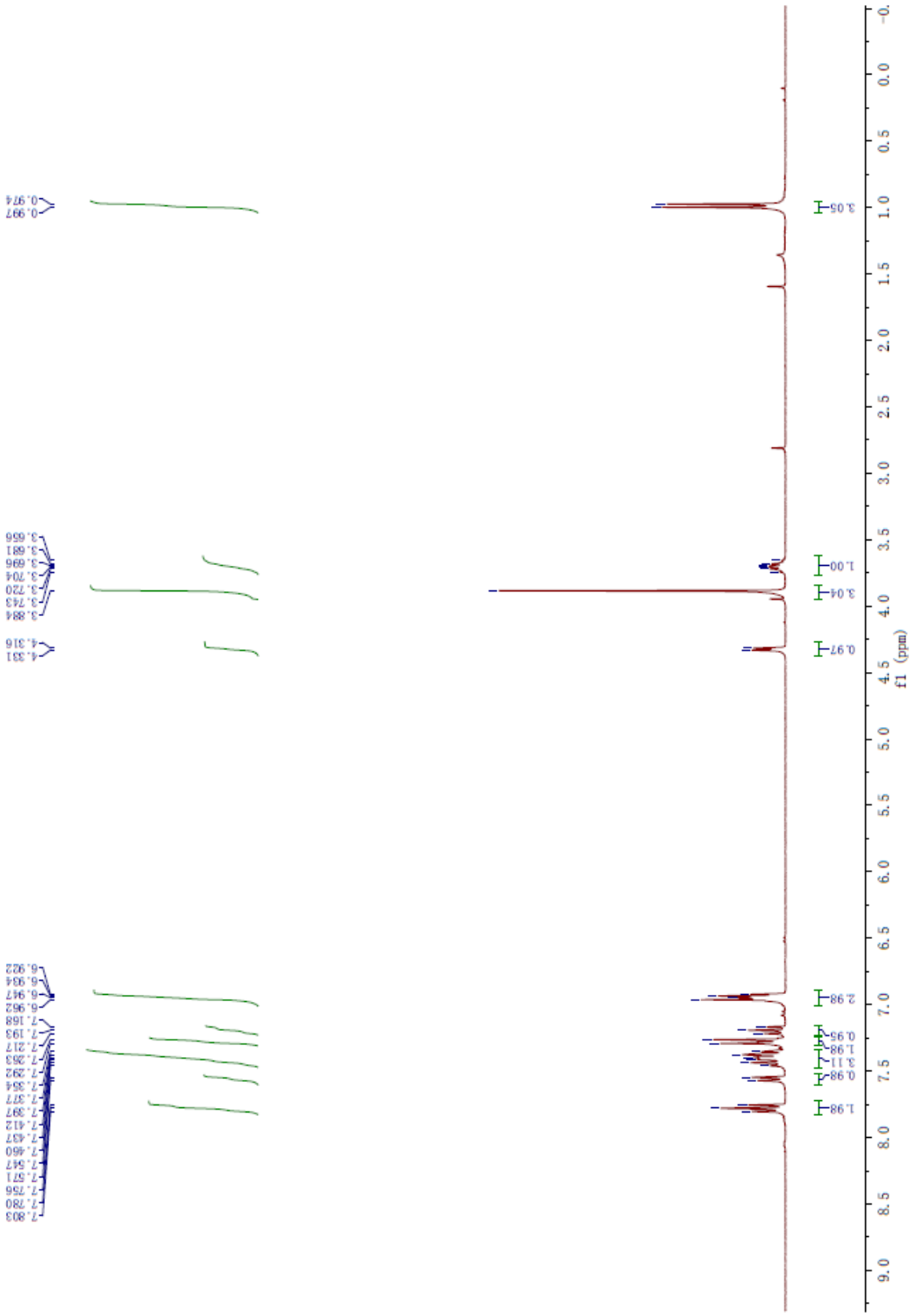
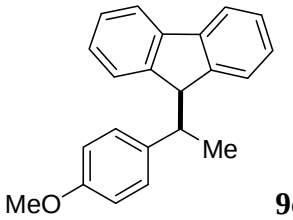
141.524
141.748
144.618
146.581
f1 (ppm)



9c

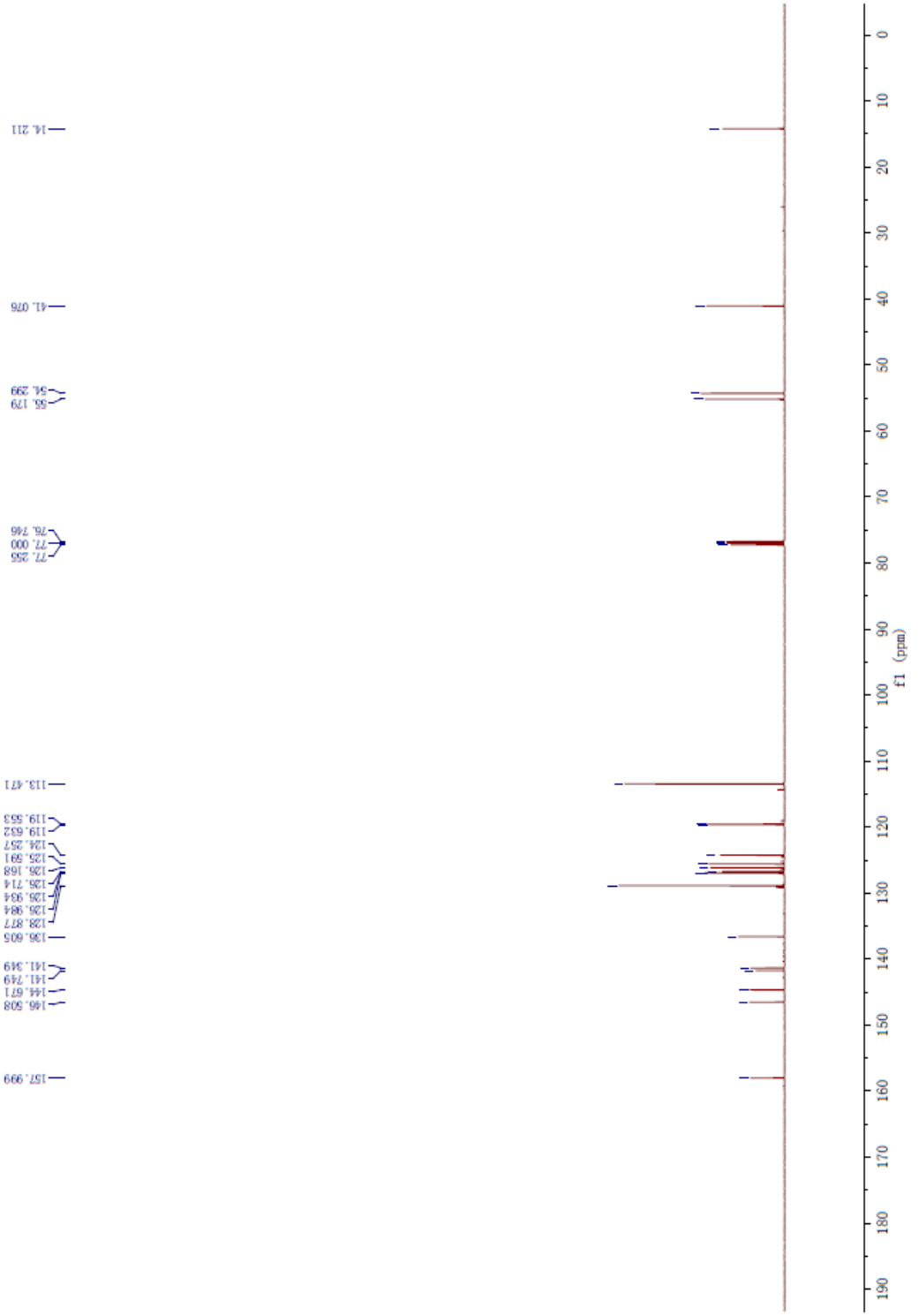
^{1}H NMR




Me
MeO

9c

^{13}C NMR


14.211
41.076
54.299
55.179
76.766
77.000
77.255
113.471
119.553
119.652
124.257
125.591
126.168
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136.605
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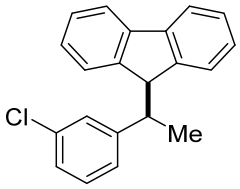
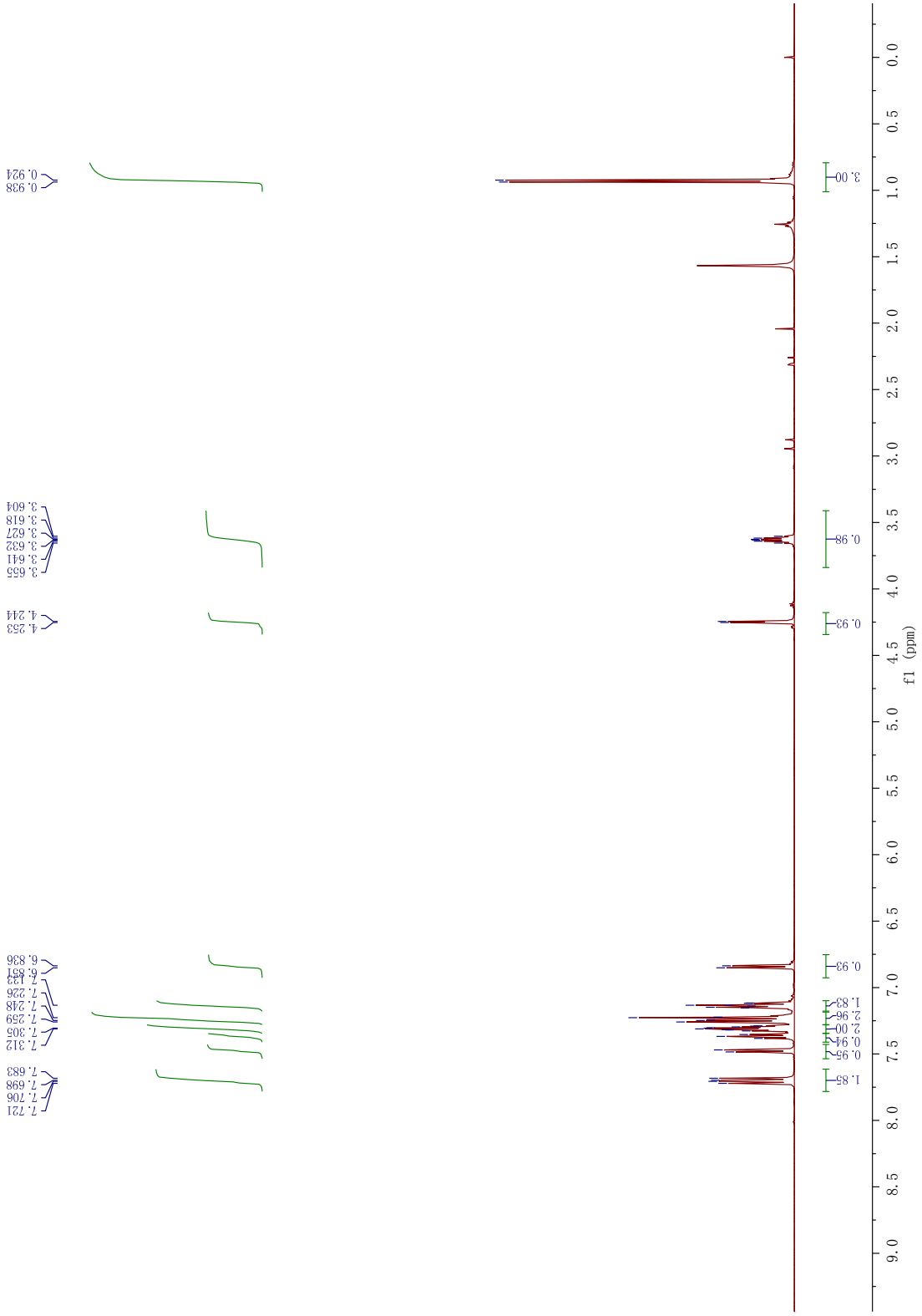
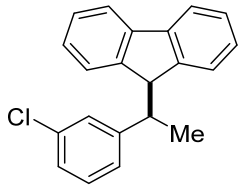
141.749
144.671
146.508
157.999
f1 (ppm)


Cl
Me

9d

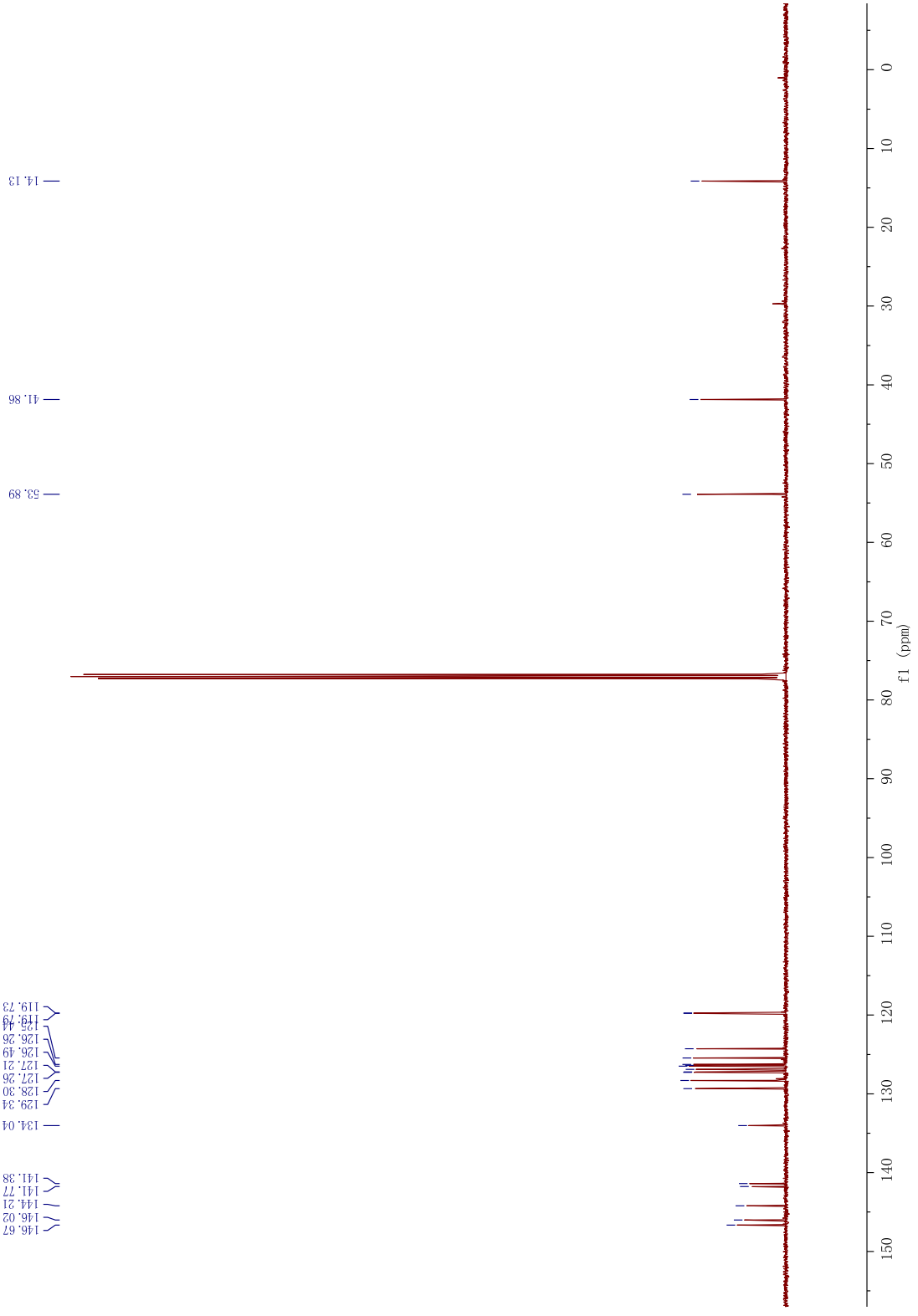
^{1}H NMR

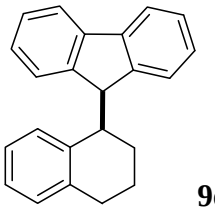

0.924
0.938
3.604
3.618
3.627
3.632
3.641
3.655
4.244
4.253
6.836
6.851
7.133
7.226
7.248
7.259
7.305
7.312
7.683
7.698
7.706
7.721
3.00
0.98
0.93
0.93
1.83
2.96
2.00
0.94
0.95
1.85
f1 (ppm)


Cl
Me

9d

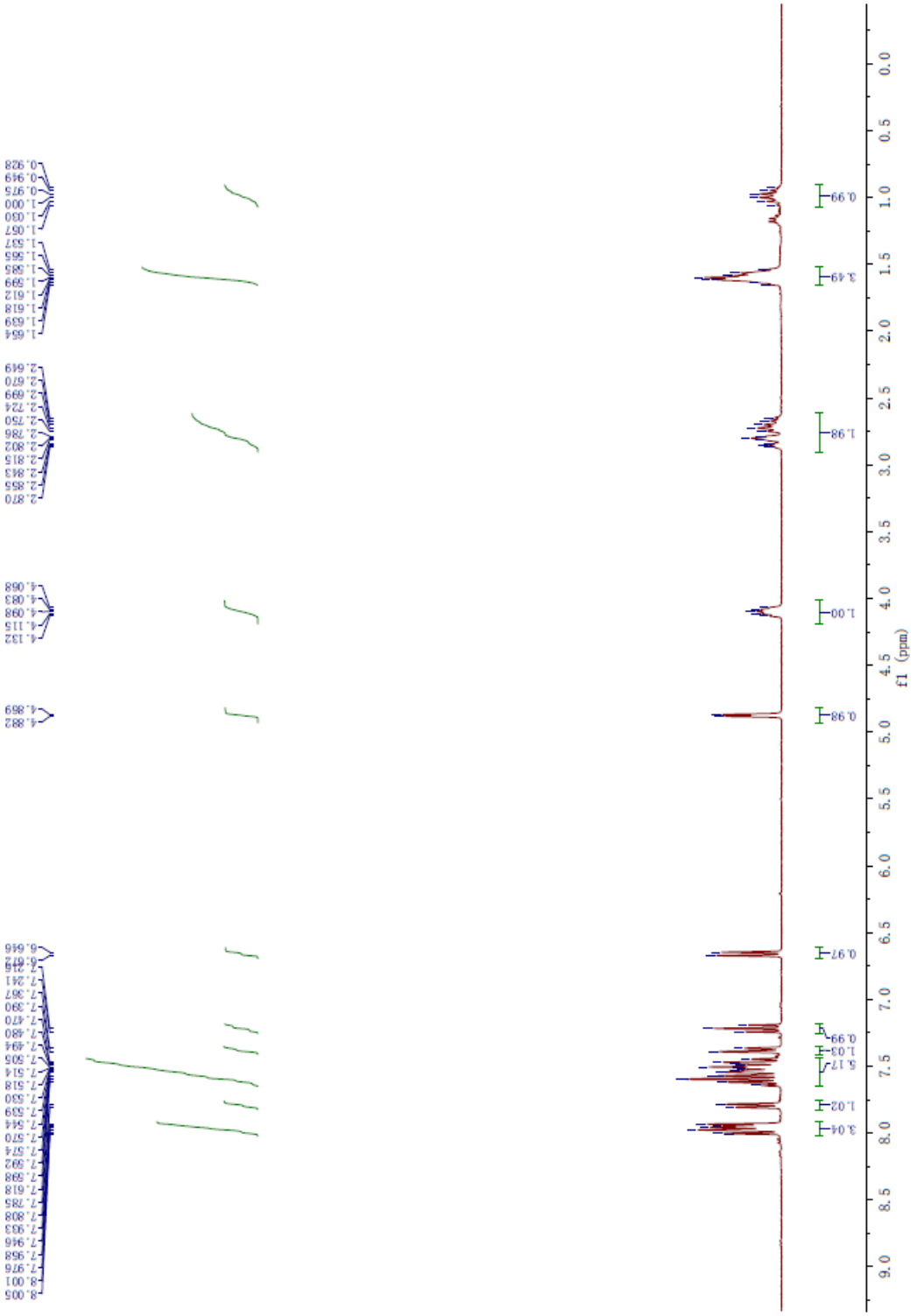
^{13}C NMR

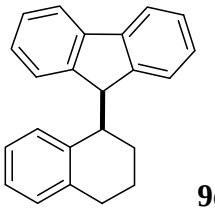

14.13
41.86
53.89
119.73
119.79
125.44
126.26
126.49
127.21
127.26
128.30
129.34
134.04
141.38
141.77
144.21
146.02
146.67
f1 (ppm)



9e

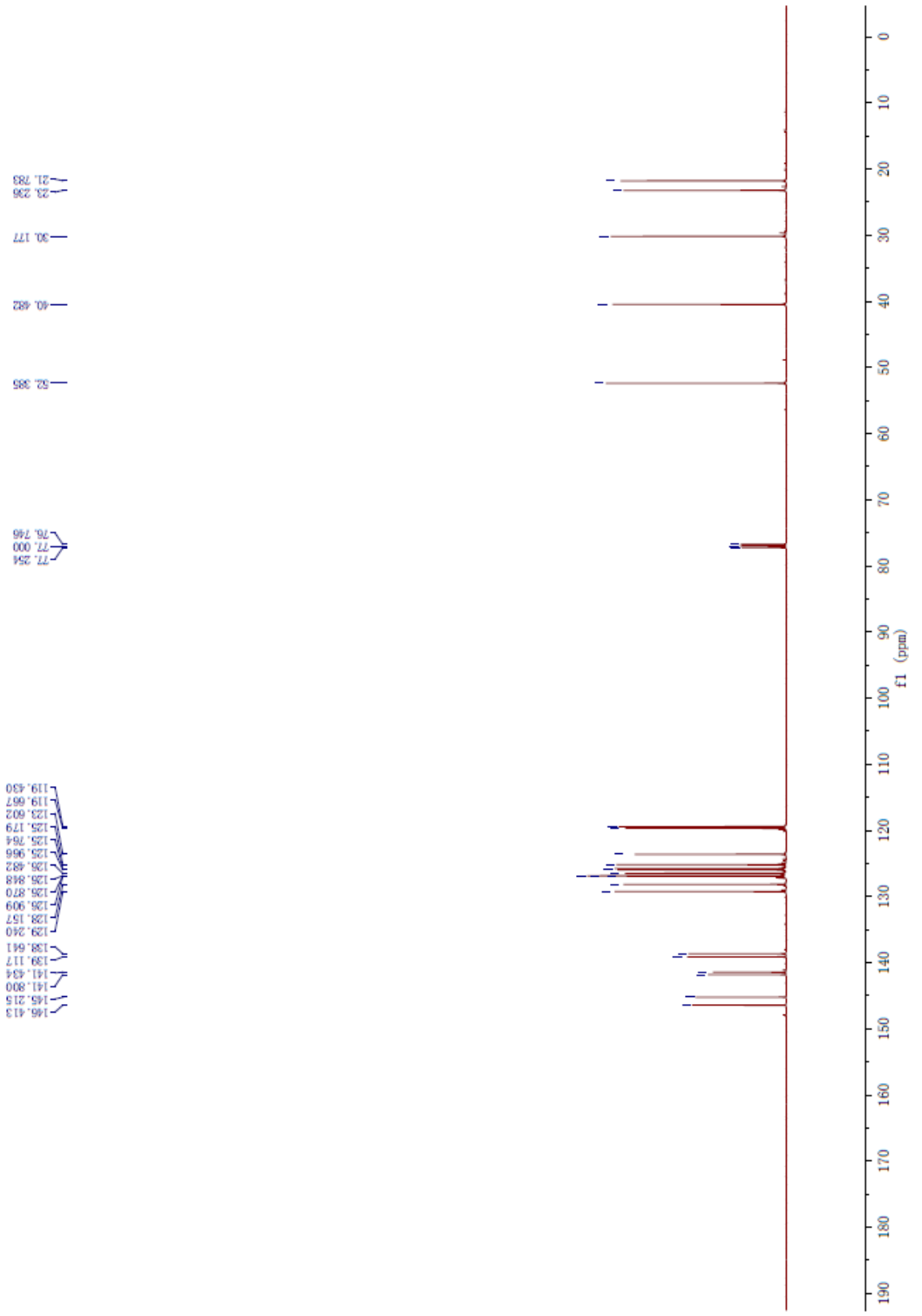
^{1}H NMR

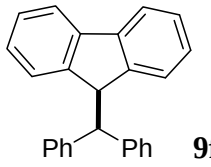




9e

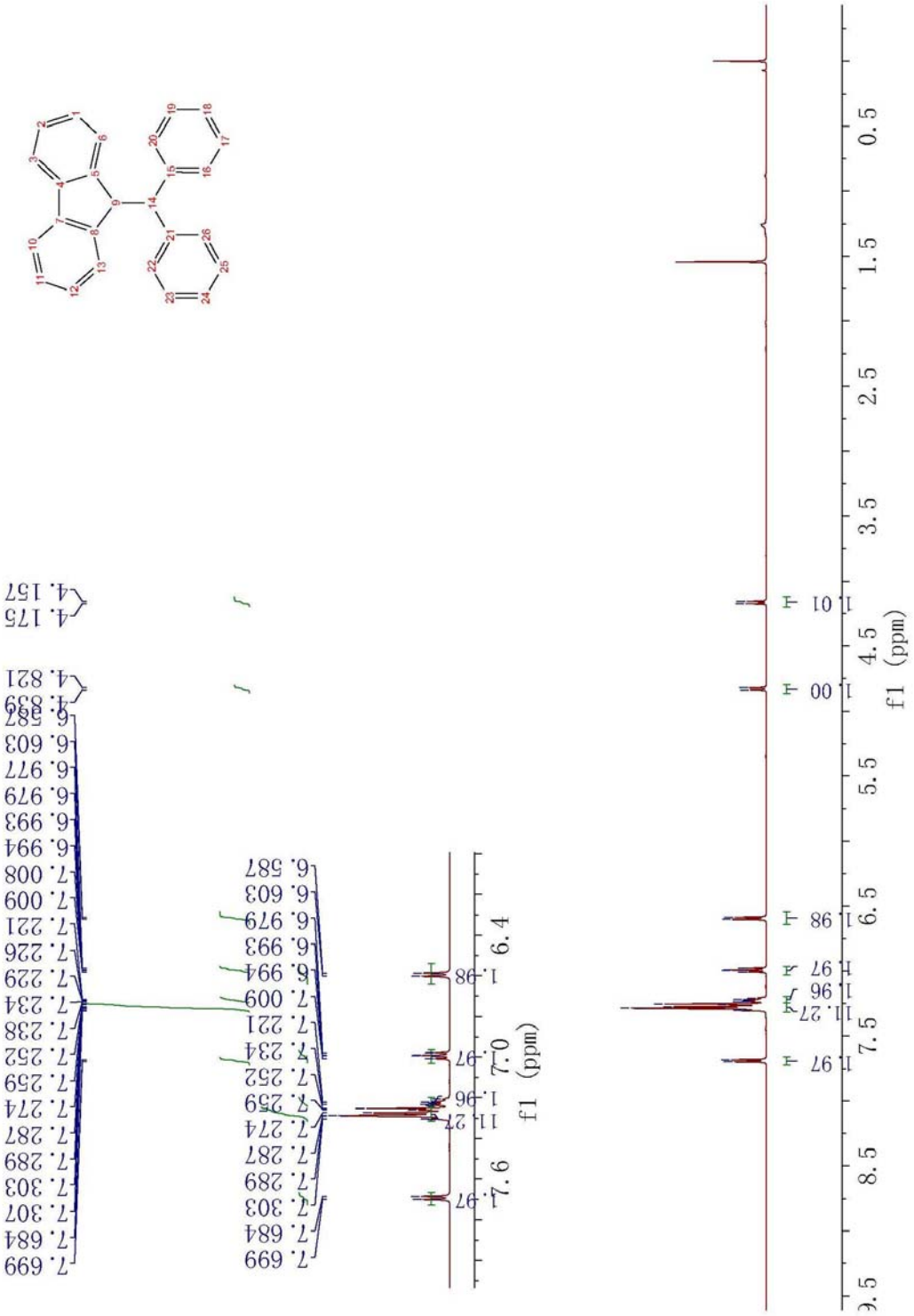
^{13}C NMR

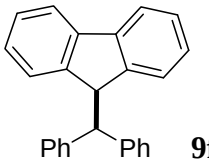

21.783
23.236
30.177
40.482
52.385
76.746
77.000
77.254
119.430
119.667
125.602
125.179
125.764
125.966
126.482
126.848
126.870
126.909
128.157
129.240
138.661
139.117
141.434
141.800
145.215
146.413
f1 (ppm)



9f

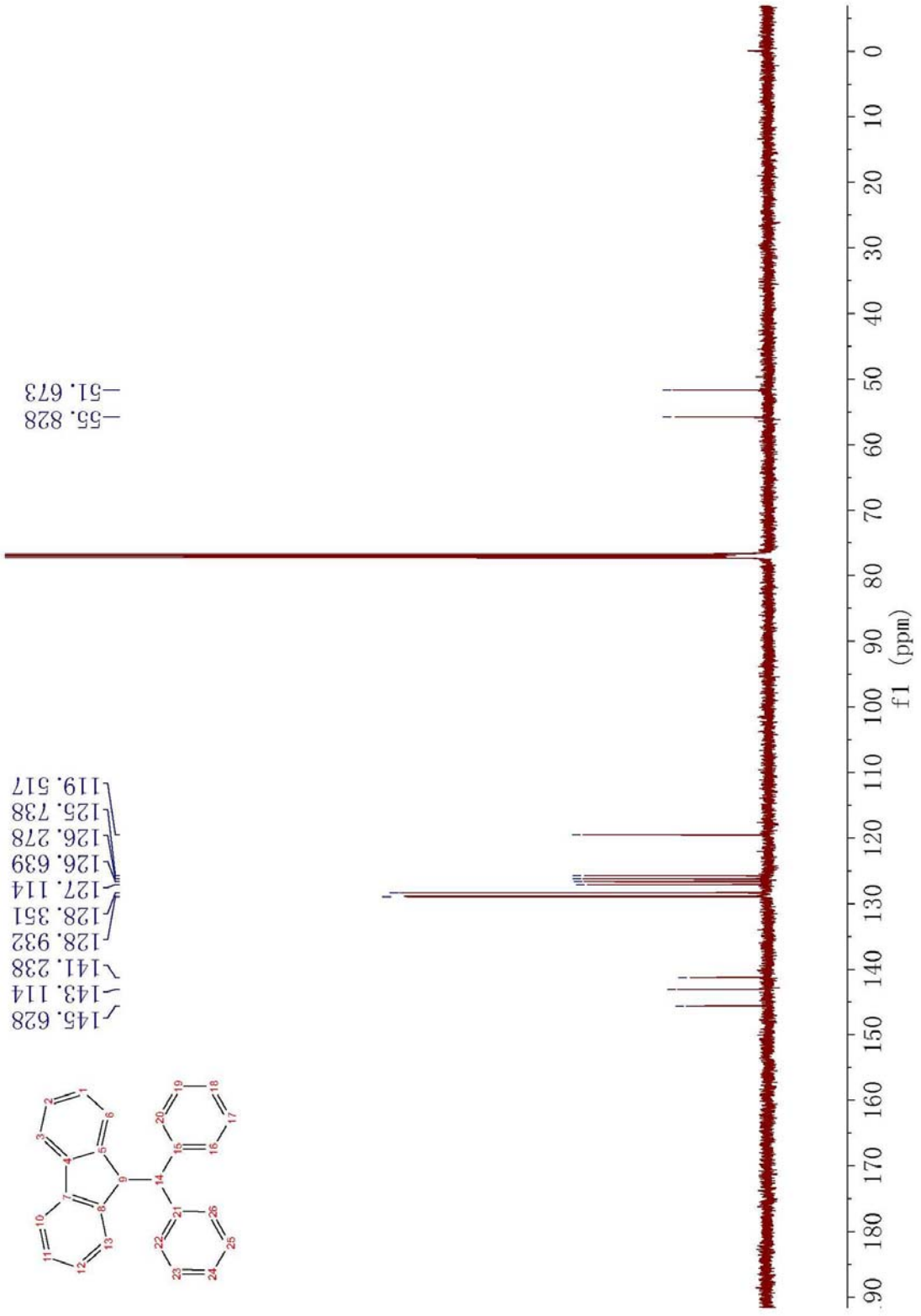
^{1}H NMR

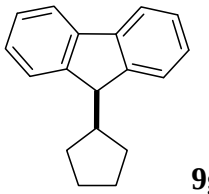



Ph
Ph

9f

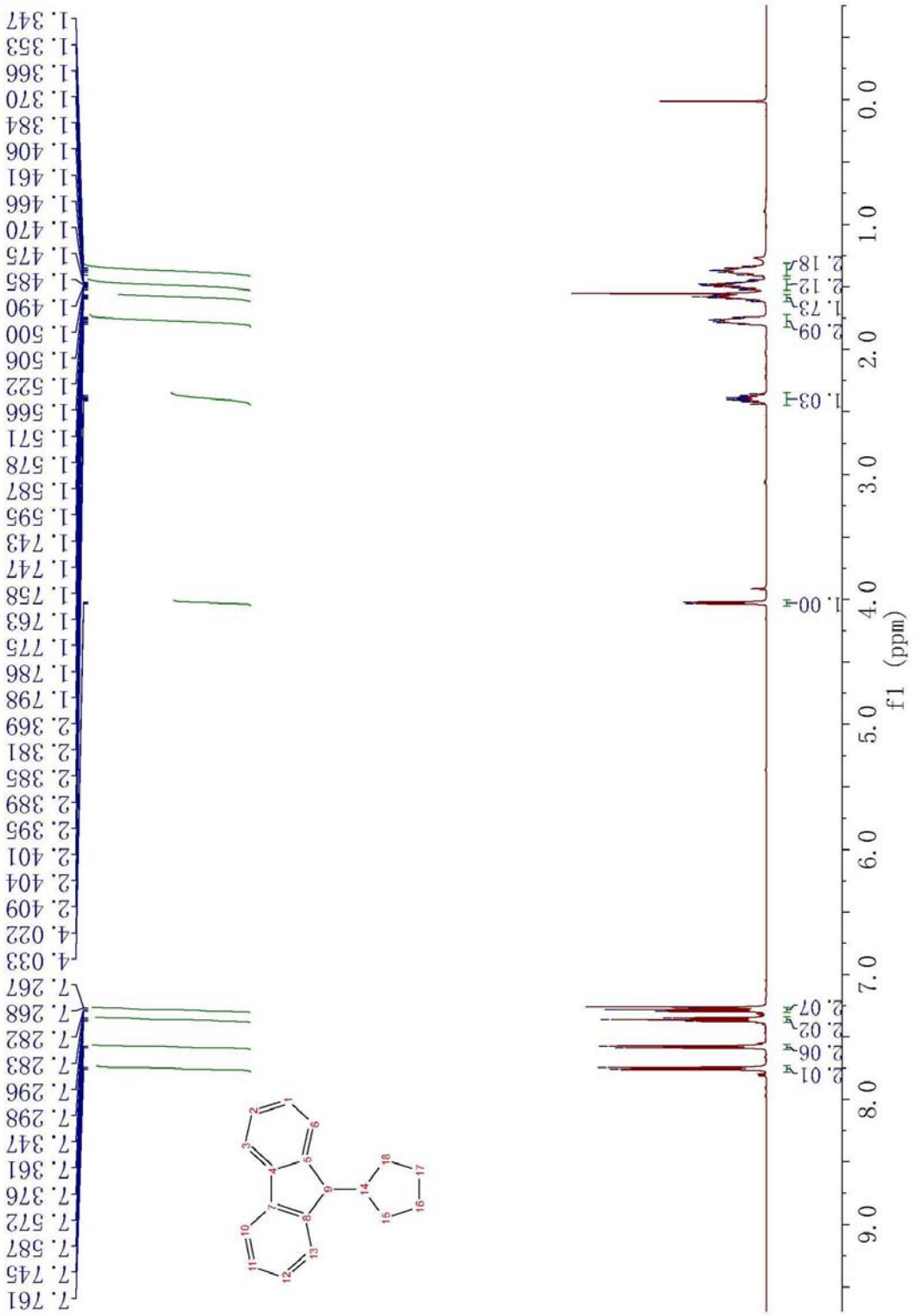
^{13}C NMR

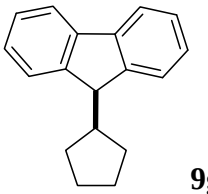

145.628
143.114
141.238
128.932
128.351
127.114
126.639
126.278
125.738
119.517
55.828
51.673
f1 (ppm)



9g

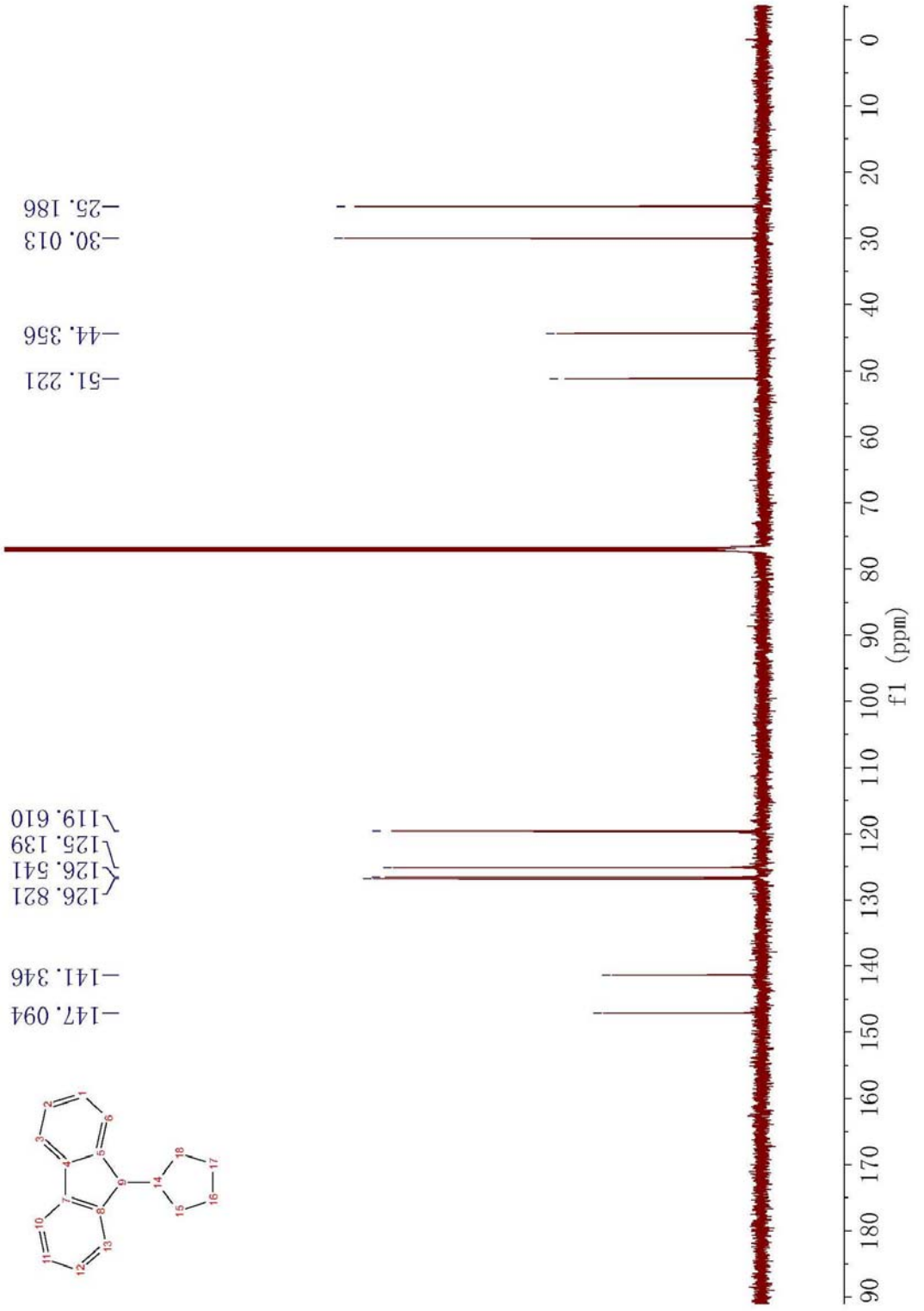
^{1}H NMR

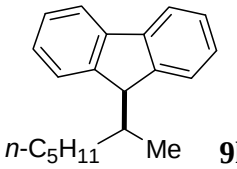




9g

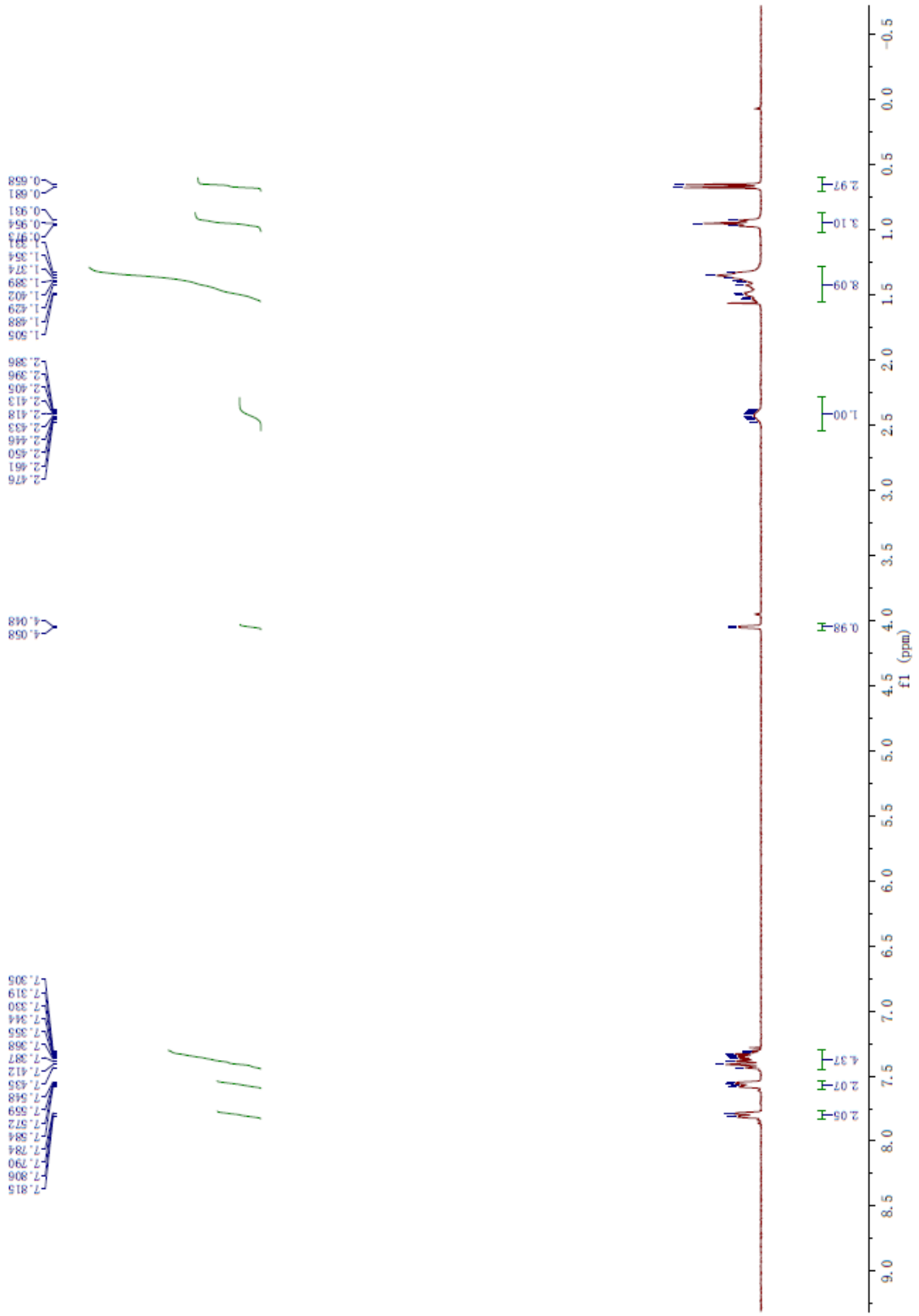
^{13}C NMR

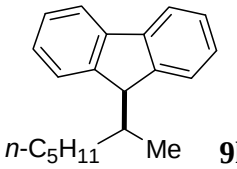

25.186
30.013
44.356
51.221
126.821
126.541
125.139
119.610
141.346
147.094
f1 (ppm)



9h

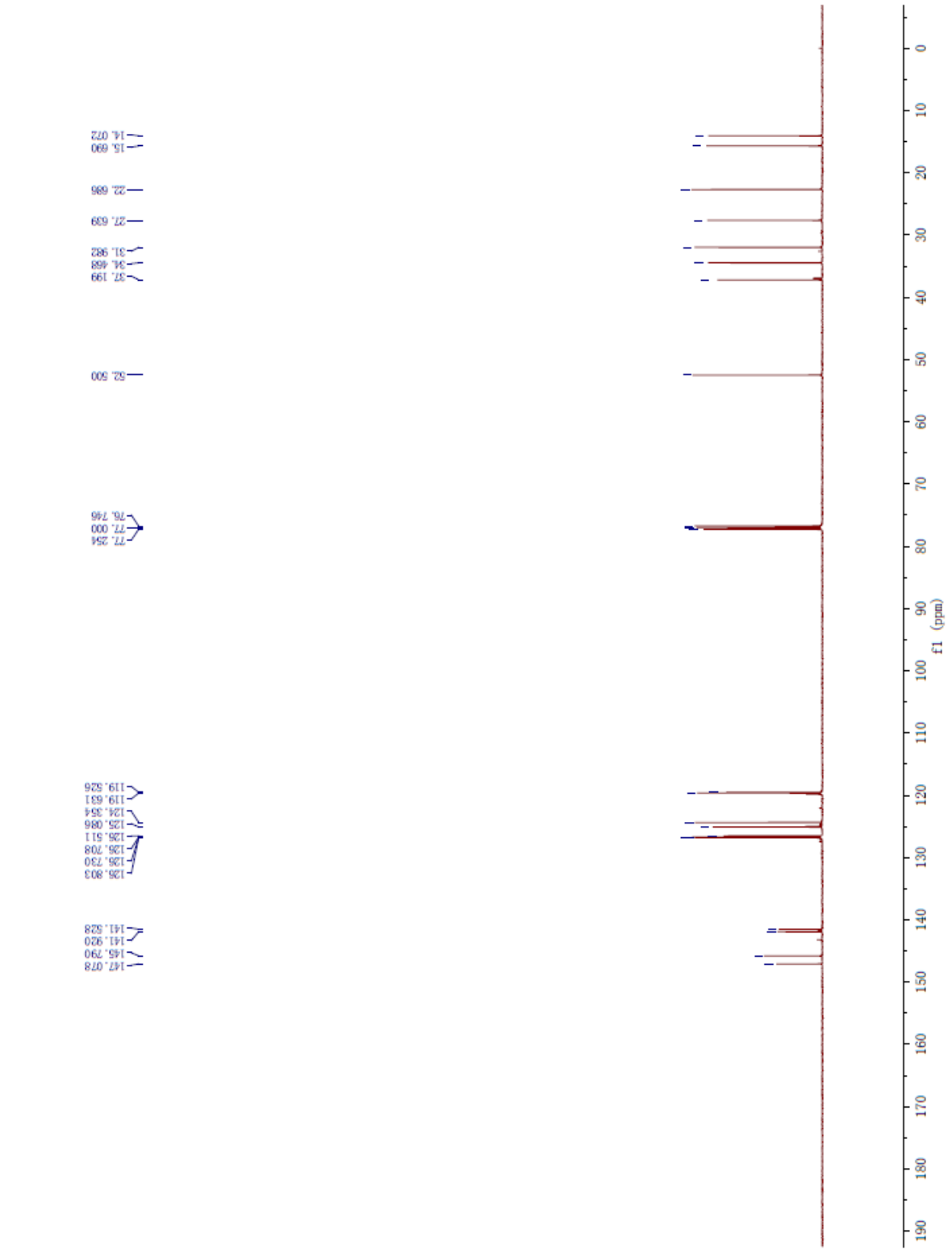
^{1}H NMR

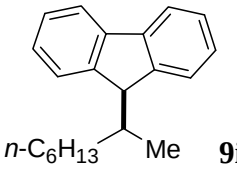



n-C5H11
Me

9h

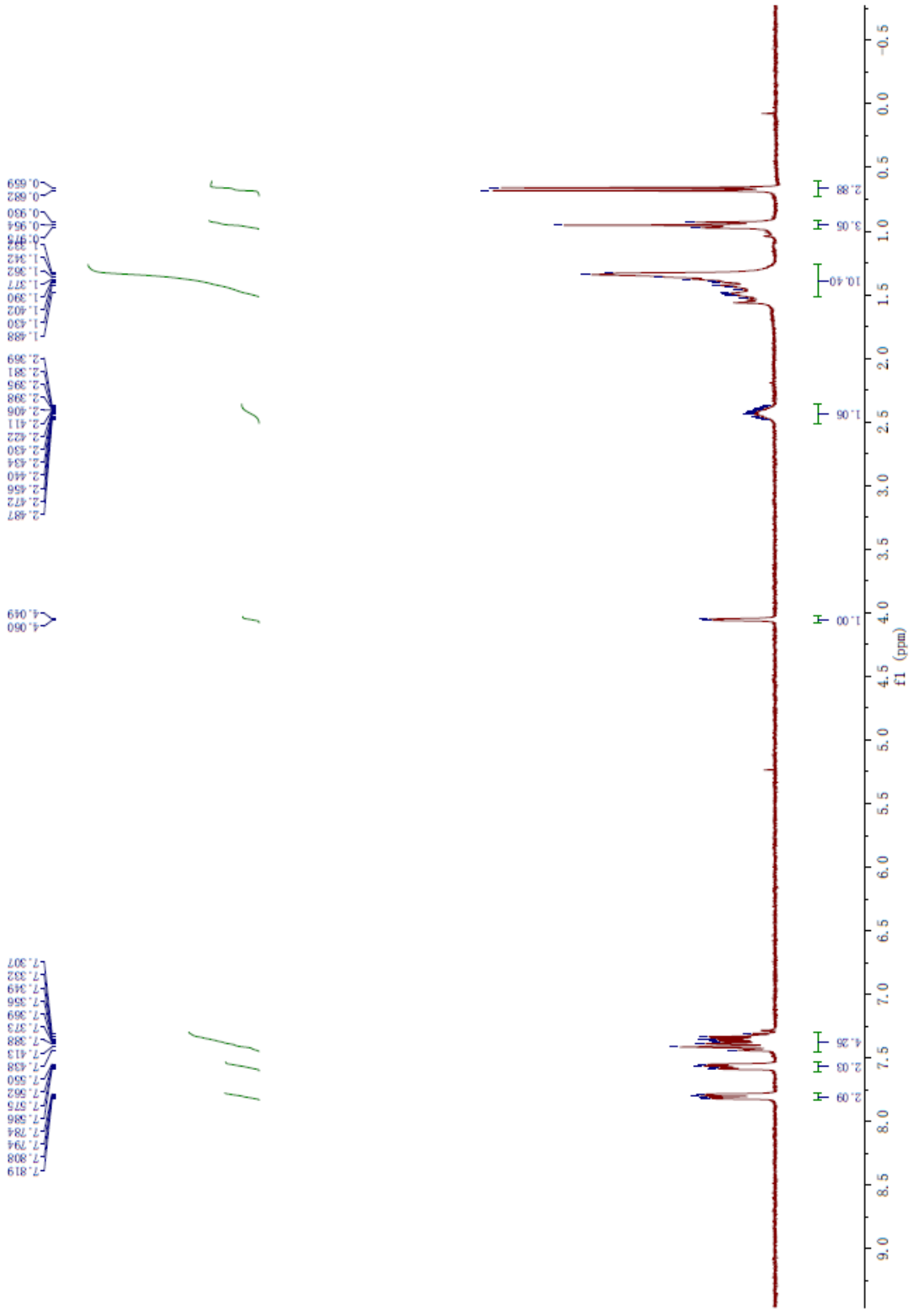
^{13}C NMR

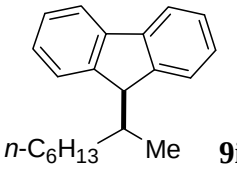

14.072
15.690
22.686
27.639
31.982
34.468
37.199
52.500
76.746
77.000
77.254
119.526
119.631
124.364
125.086
126.511
126.708
126.730
126.803
141.528
141.920
145.790
147.078
f1 (ppm)



9i

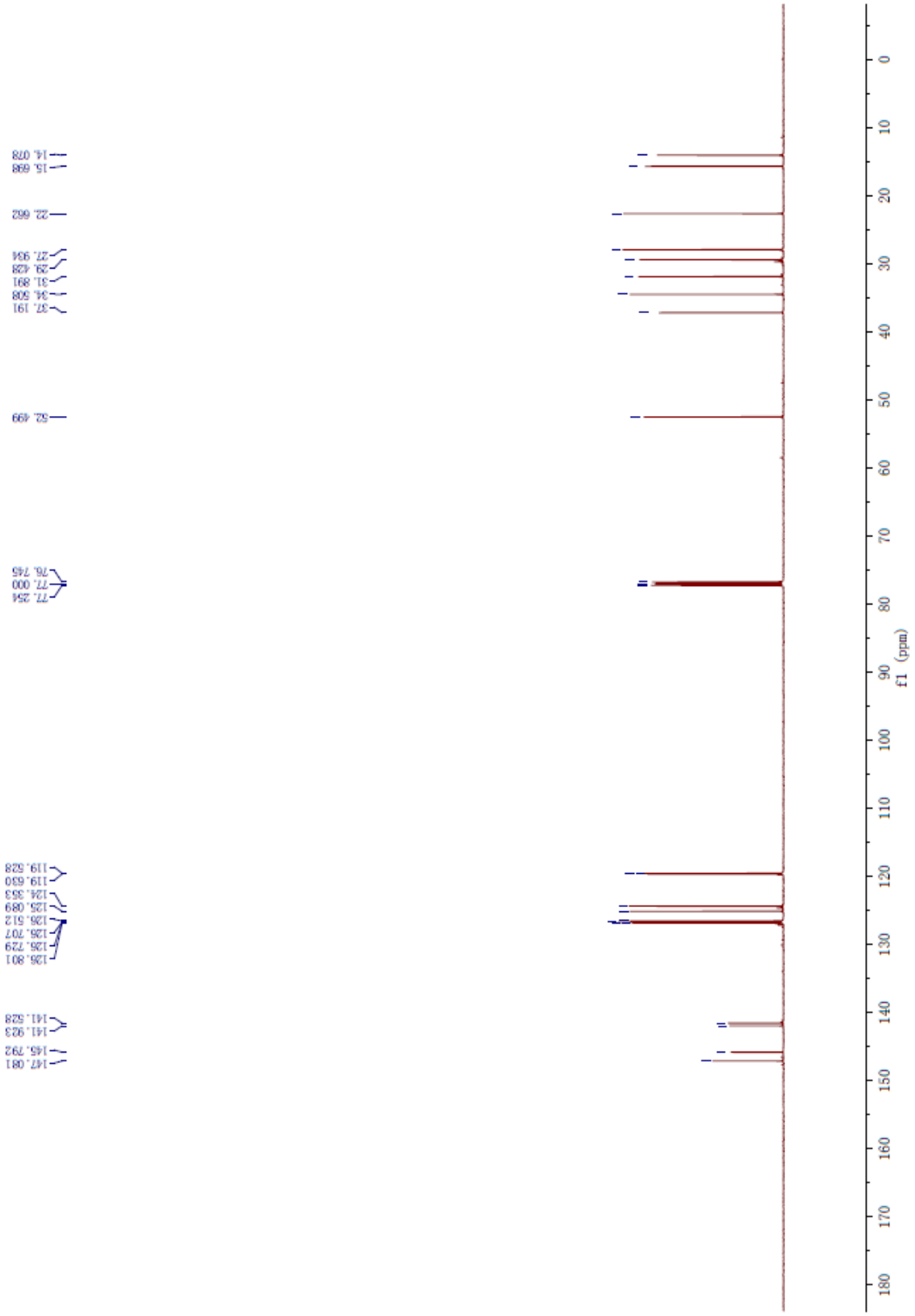
^{1}H NMR

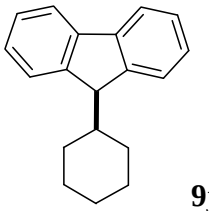



n-C6H13
Me

9i

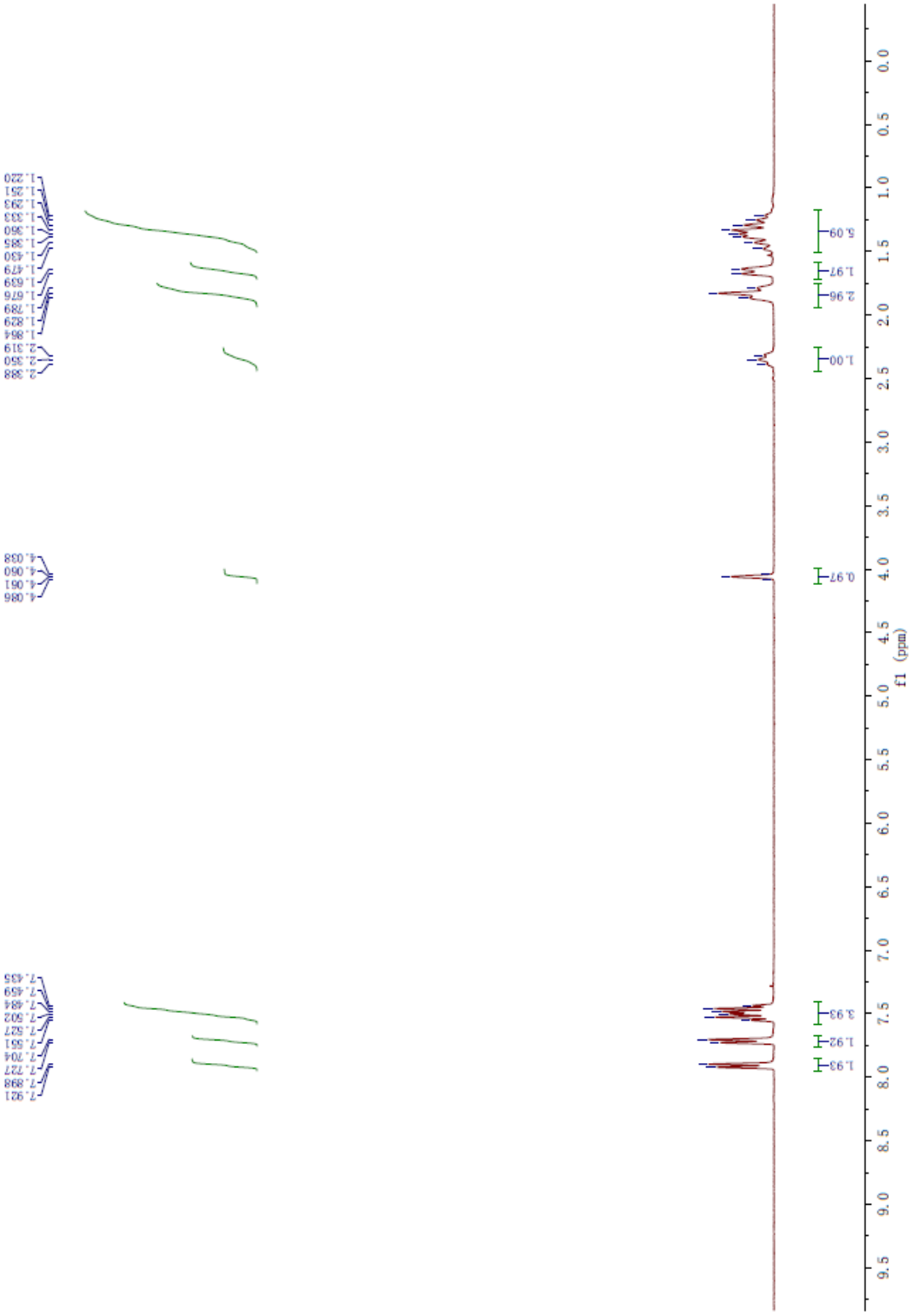
^{13}C NMR

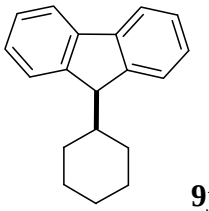

14.078
15.698
22.662
27.934
29.428
31.891
34.508
37.191
52.499
76.745
77.000
77.254
119.528
119.650
124.353
125.089
126.512
126.707
126.729
126.801
141.528
141.923
145.792
147.081
f1 (ppm)



9j

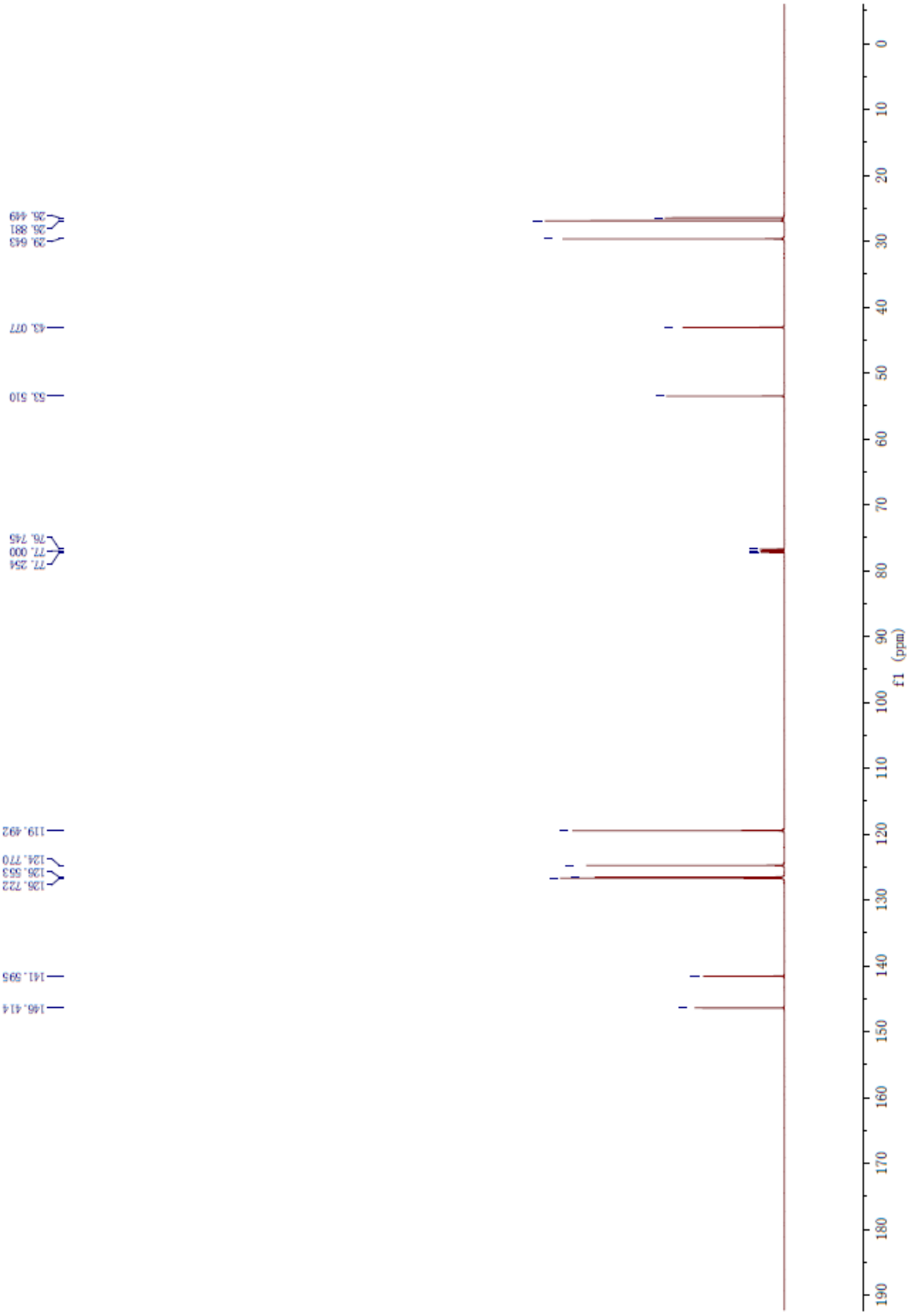
^{1}H NMR

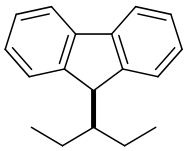

7.921
7.898
7.727
7.704
7.651
7.627
7.502
7.484
7.459
7.435
4.086
4.061
4.060
4.038
2.388
2.350
2.319
1.864
1.829
1.789
1.676
1.639
1.479
1.430
1.385
1.360
1.333
1.293
1.251
1.220
5.09
1.97
2.96
1.00
0.97
3.93
1.92
1.93
f1 (ppm)



9j

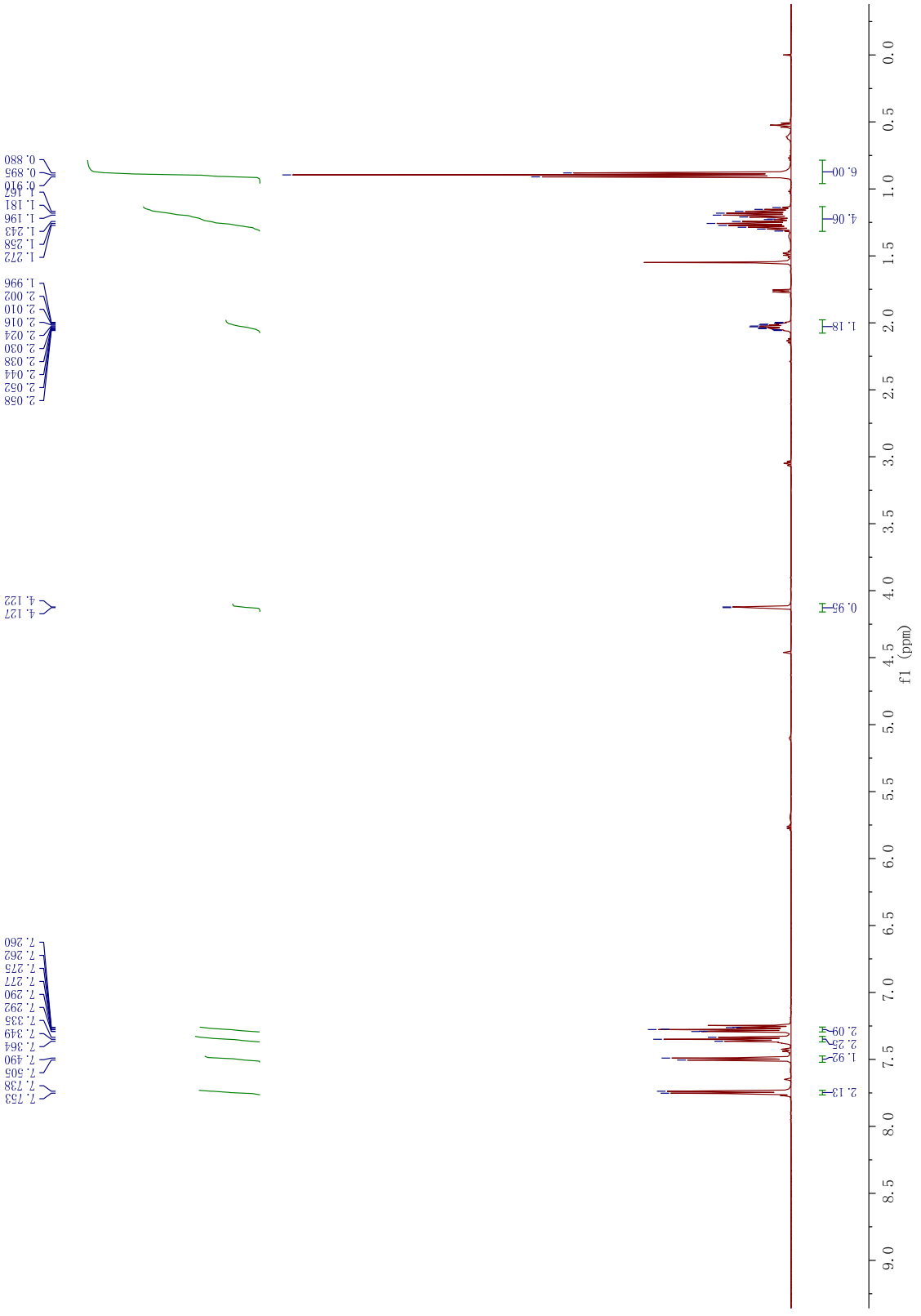
^{13}CNMR

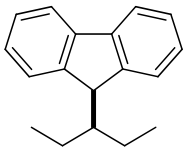

29.649
36.881
36.499
43.077
53.510
76.745
77.000
77.254
119.492
124.770
126.363
126.722
141.895
146.414
f1 (ppm)



9k

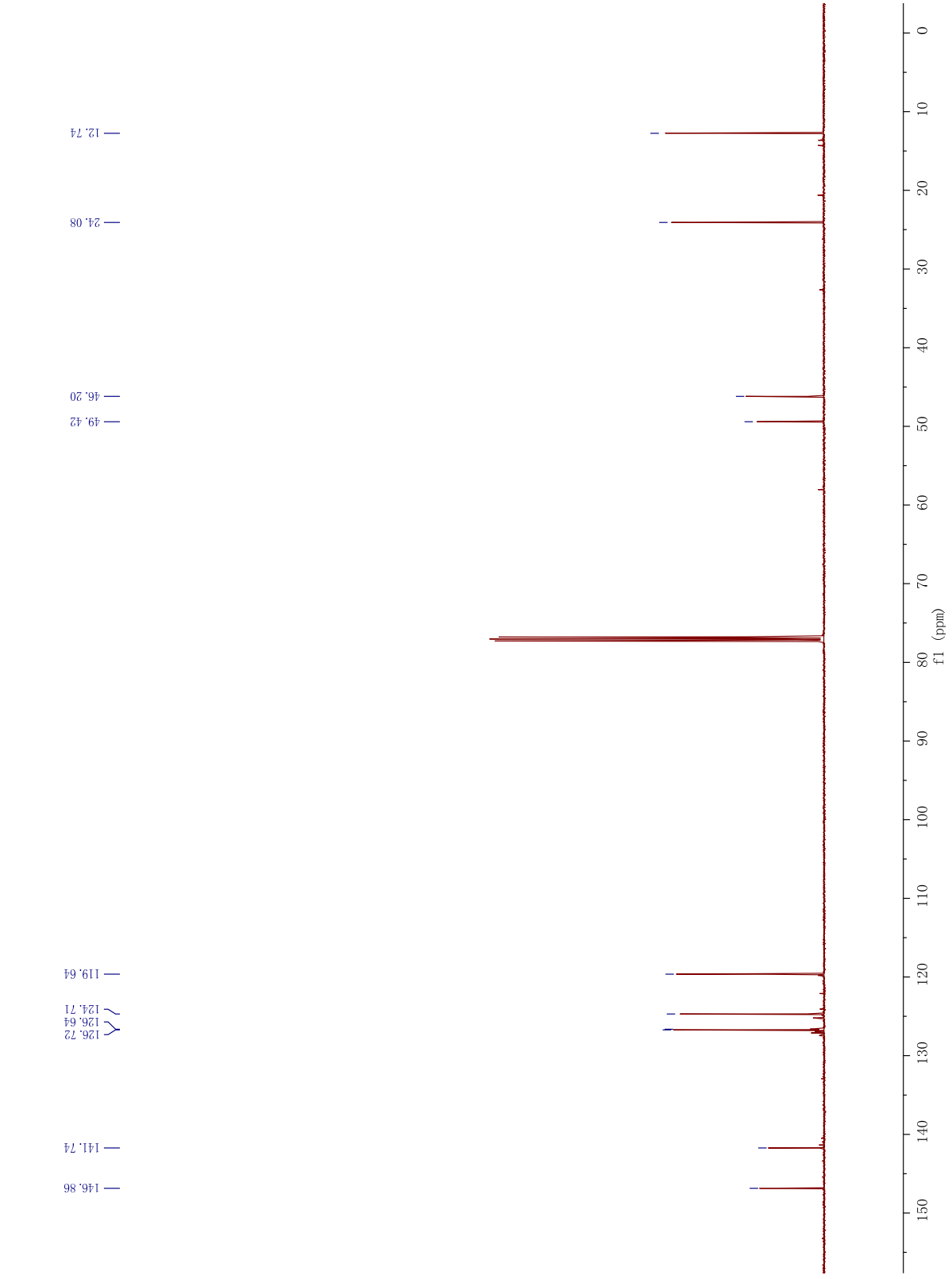
^{1}H NMR

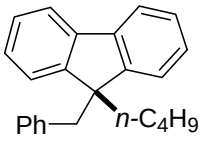

0.880
0.895
0.910
1.157
1.181
1.196
1.243
1.258
1.272
1.996
2.002
2.010
2.016
2.024
2.030
2.038
2.044
2.052
2.058
4.122
4.127
7.260
7.262
7.275
7.277
7.290
7.292
7.335
7.339
7.364
7.490
7.505
7.738
7.753
6.00
4.06
1.18
0.95
2.09
2.25
1.92
2.13
f1 (ppm)



9k

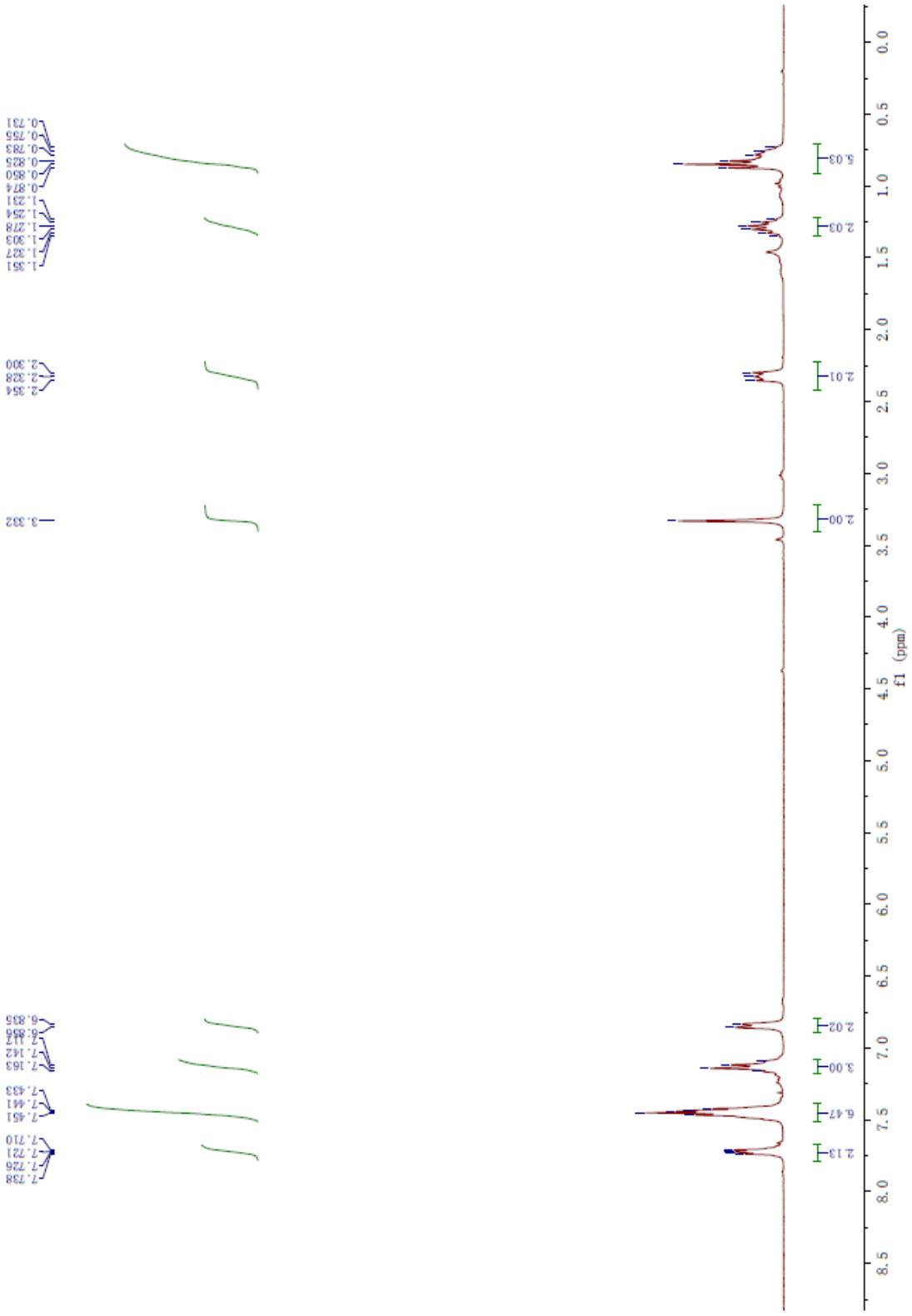
^{13}C NMR

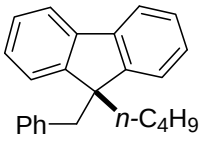

12.74
24.08
46.20
49.42
119.64
124.71
126.64
126.72
141.74
146.86
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)



12

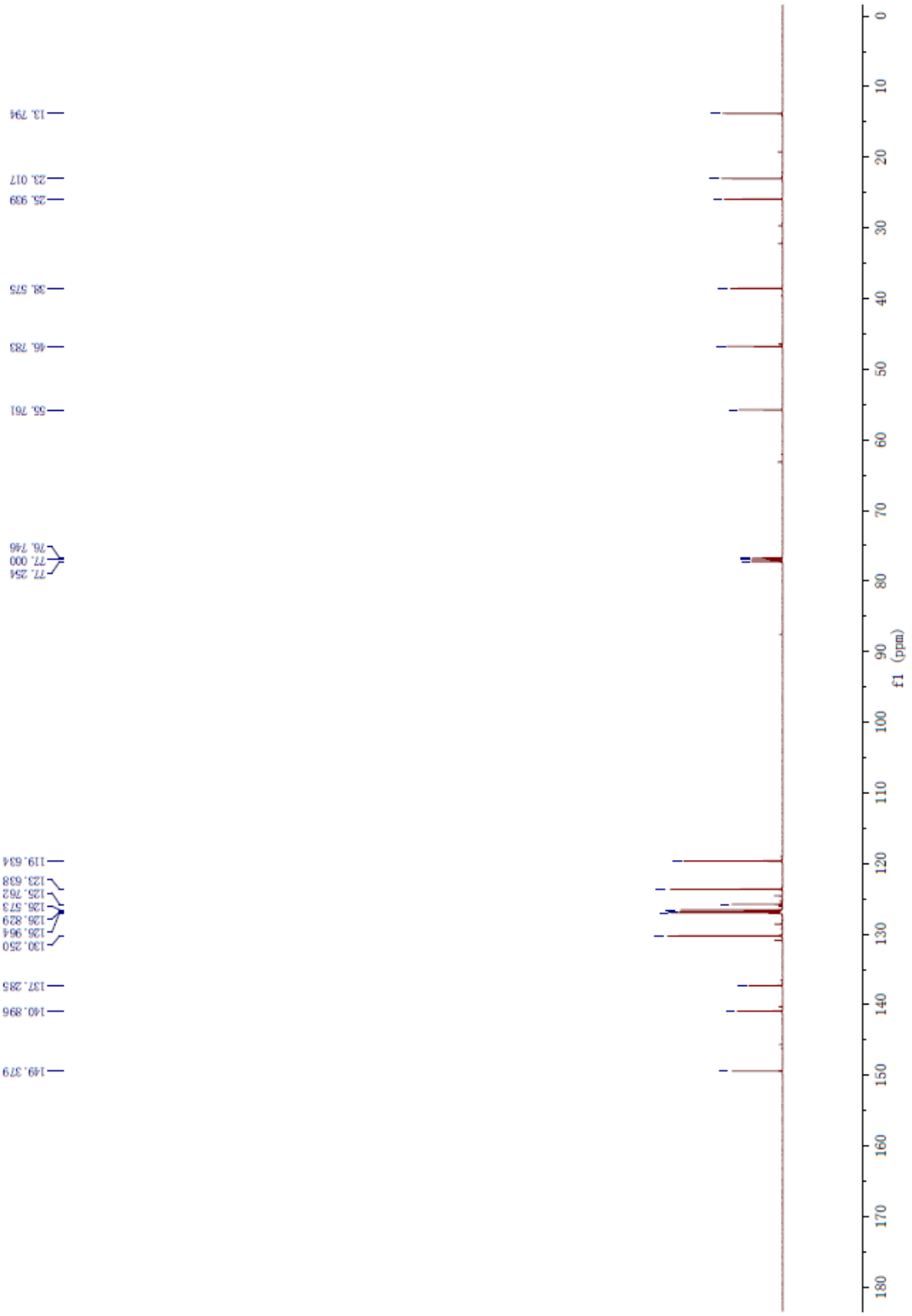
^{1}H NMR

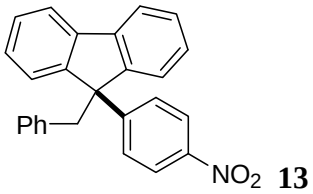



Ph
n-C4H9

12

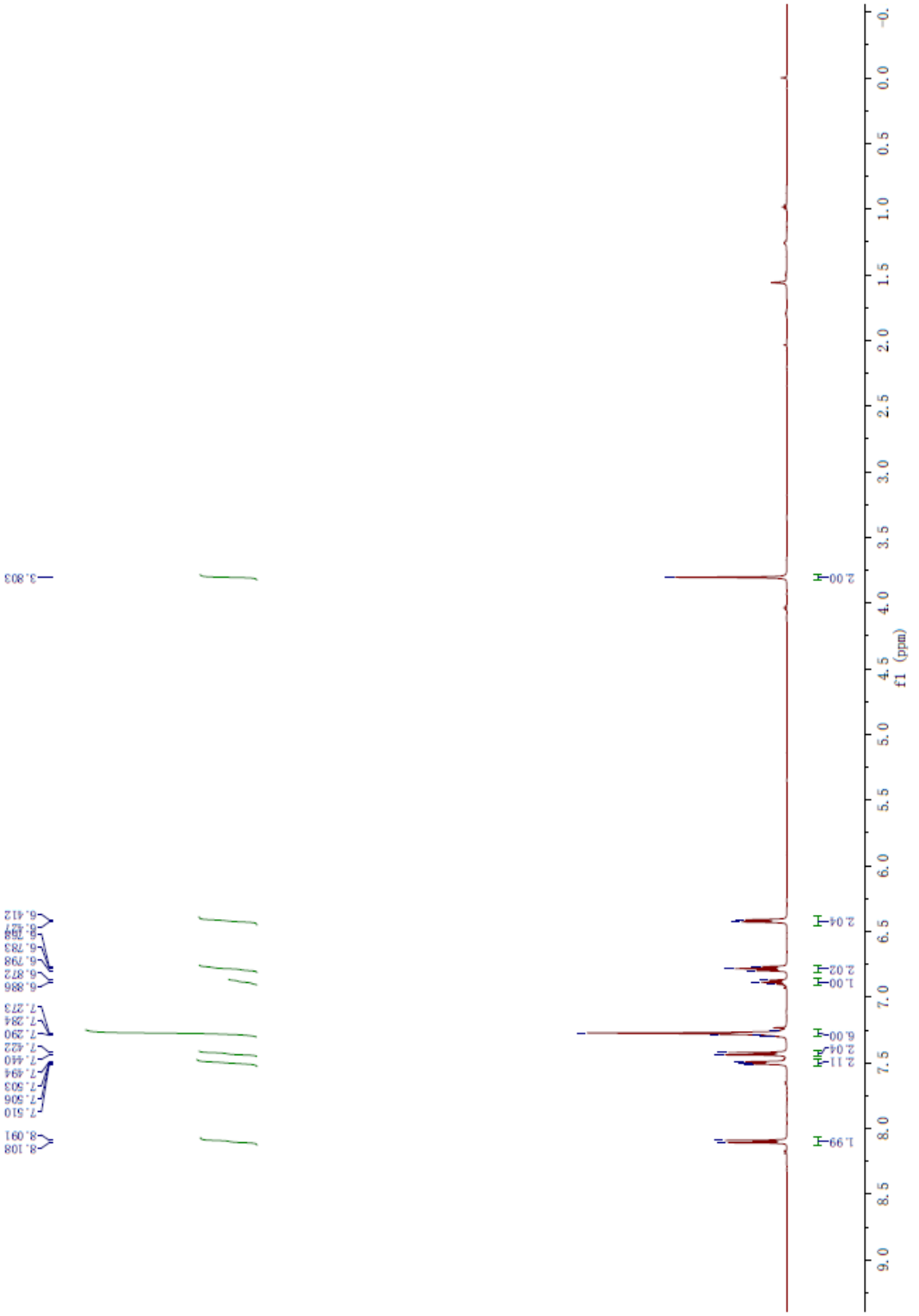
^{13}C NMR

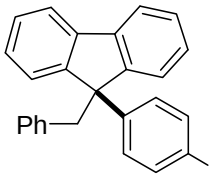

13.794
23.017
25.939
38.575
46.783
55.761
76.746
77.000
77.254
119.634
123.638
125.762
126.573
126.829
126.964
130.250
137.285
140.896
149.379
f1 (ppm)



13

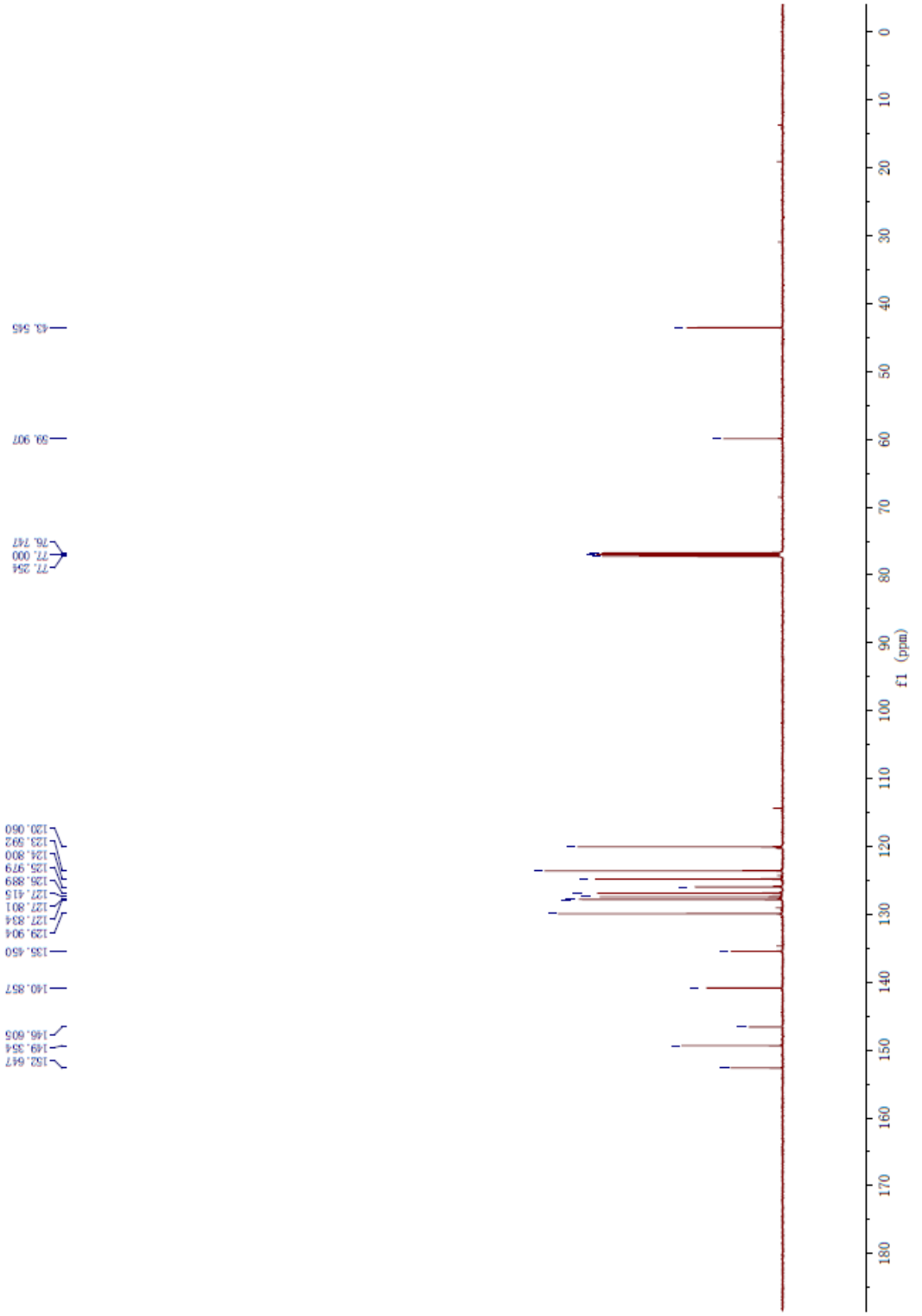
^{1}H NMR




Ph
NO2

13

^{13}C NMR


43.545
59.907
76.747
77.000
77.254
120.060
123.592
124.800
125.979
126.889
127.415
127.801
127.854
129.904
135.450
140.857
146.605
149.354
152.647
f1 (ppm)