

Supplementary Information

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General Methods: Acetonitrile and dichloromethane were distilled from P₂O₅, then CaH₂, and dried over Molecular Sieves 4A. VO(OEt)Cl₂ was prepared according to the literature procedures.ⁱ Other chemicals were of commercial quality. ¹H and ¹³C NMR chemical shifts were reported in parts per million relative to residual non-deuterated solvent as an internal standard. ¹¹B NMR chemical shifts were reported in parts per million relative to BF₃·OEt₂ in CDCl₃ as an external standard.

Preparation of Sodium Tetraarylborate 1. The borate **1** was prepared according to the reported method.ⁱⁱ

Sodium tetraphenylborate (1a) [143-66-8]

Sodium tetrakis(4-chlorophenyl)borate (1b) [14644-80-5]

Sodium tetrakis(4-methylphenyl)borate (1c) [15738-23-5]

Sodium tetrakis(3-methylphenyl)borate (1d) [123026-51-7]

Sodium tetrakis(2-methylphenyl)borate (1e) ¹H NMR (300 MHz, acetone-*d*₆) δ 7.45 (d, 4H, *J* = 6.3 Hz), 6.92-6.86 (m, 12H), 2.37 (s, 12H). ¹³C NMR (75 MHz, acetone-*d*₆) 142.1, 133.0, 132.9, 129.3, 126.4, 124.4, 22.3 ppm. ¹¹B NMR (127 MHz, acetone-*d*₆)

-6.73 ppm. IR (KBr) 3634, 3055, 3003, 1616, 1437, 1213, 931, 756 cm^{-1} . HRMS (FAB-TOF: $[\text{M}-\text{Na}]^-$) calcd. for $\text{C}_{28}\text{H}_{28}\text{B}^-$ 375.2284, found 375.2288.

Sodium tetrakis(4-methoxyphenyl)borate (1f) [26546-24-7]

Biphenyl (2a) [92-52-4]: ^1H NMR (300 MHz, CDCl_3) δ 7.58 (d, 2H, $J = 8.1$ Hz), 7.43 (t, 4H, $J = 7.8$ Hz), 7.34 (d, 2H, $J = 7.5$ Hz). ^{13}C NMR (75 MHz, CDCl_3) 140.8, 128.7, 127.2, 127.1 ppm. IR (KBr) 3086, 3057, 3033, 1942, 1875 cm^{-1} .

4,4'-Dichlorobiphenyl (2b) [2050-68-2]: ^1H NMR (300 MHz, CDCl_3) δ 7.46 (d, 2H, $J = 8.4$ Hz), 7.39 (d, 2H, $J = 8.4$ Hz). ^{13}C NMR (75 MHz, CDCl_3) 138.4, 133.7, 129.0, 128.2 ppm. IR (KBr) 2924, 2853, 1903, 1503, 1472, 1089, 815 cm^{-1} .

4,4'-Dimethylbiphenyl (2c) [613-33-2]: ^1H NMR (300 MHz, CDCl_3) δ 7.46 (d, 2H, $J = 8.1$ Hz), 7.22 (d, 2H, $J = 8.7$ Hz), 2.37 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3) 138.3, 136.7, 129.4, 126.8, 21.1 ppm. IR (KBr) 3022, 2915, 2851, 1902, 1501, 802 cm^{-1} .

3,3'-Dimethylbiphenyl (2d) [612-75-9]: ^1H NMR (300 MHz, CDCl_3) δ 7.38 (d, 4H, $J = 7.8$ Hz), 7.31 (t, 2H, $J = 7.5$ Hz), 7.14 (d, 2H, $J = 7.8$ Hz), 2.41 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3) 141.3, 138.2, 128.6, 128.0, 127.9, 124.3, 21.5 ppm. IR (liquid film) 3027, 2919, 1604, 1474, 1091, 878, 772, 697 cm^{-1} .

2,2'-Dimethylbiphenyl (2e) [605-39-0]: ^1H NMR (300 MHz, CDCl_3) δ 7.25-7.18 (m, 6H), 7.08 (d, 2H, $J = 6.0$ Hz). ^{13}C NMR (75 MHz, CDCl_3) 141.6, 135.8, 129.8, 129.3,

127.1, 125.5, 19.8 ppm. IR (liquid film) 3059, 3016, 2921, 1914, 1600, 1452, 757, 730 cm^{-1} .

4,4'-Dimethoxybiphenyl (2f) [2132-80-1]: ^1H NMR (300 MHz, CDCl_3) δ , 7.46 (d, 2H, $J = 8.7$ Hz), 6.94 (d, 4H, $J = 9.0$ Hz), 3.83 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3) 158.7, 133.5, 127.7, 114.1, 55.4 ppm. IR (KBr) 2957, 2839, 1606, 1500, 1276, 1250, 1041, 824 cm^{-1} .

4-Chlorobiphenyl (6b) [2051-62-9]: ^1H NMR (300 MHz, CDCl_3) δ 7.32-7.55 (m, 9H). ^{13}C NMR (75 MHz, CDCl_3) 140.0, 139.7, 133.4, 128.9, 128.4, 127.5, 127.0 ppm. IR (KBr) 3058, 3032, 1904, 1478, 1098, 757 cm^{-1} .

4-Methylbiphenyl (6c) [644-08-6]: ^1H NMR (300 MHz, CDCl_3) δ 7.58 (d, 2H, $J = 6.9$ Hz), 7.49 (d, 2H, $J = 8.1$ Hz), 7.42 (t, 2H, $J = 7.2$ Hz) 7.32 (m, 1H), 7.25 (d, 2H, $J = 7.5$ Hz), 2.39 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) 141.1, 138.3, 137.0, 129.5, 128.7, 127.0, 126.9, 21.1 ppm. IR (KBr) 3031, 2915, 1908, 1487, 1444, 1402, 1128, 1006, 822, 754 cm^{-1} .

3-Methylbiphenyl (6d) [643-93-6]: ^1H NMR (300 MHz, CDCl_3) δ 7.60-7.56 (m, 2H), 7.45-7.30 (m, 6H), 7.18-7.14 (m, 1H) 2.41 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) 141.6, 141.5, 138.6, 128.9, 128.2, 127.4, 124.5, 21.8 ppm. IR (liquid film) 3031, 2919, 1944, 1600, 1481, 1455 cm^{-1} .

2-Methylbiphenyl (6e) [643-58-3]: ^1H NMR (300 MHz, CDCl_3) δ 7.21-7.40 (m, 9H), 2.26 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) 141.9, 135.3, 130.3, 129.8, 129.2, 128.0, 127.2, 126.7, 125.7, 20.5 ppm. IR (liquid film) 3059, 1950, 1807, 1599, 1479, 1439, 1010 cm^{-1} .

4-Methoxybiphenyl (6f) [613-37-6]: ^1H NMR (300 MHz, CDCl_3) δ 7.53 (m, 4H), 7.40 (t, 2H, $J = 7.2$ Hz), 7.28 (t, 1H, $J = 7.5$ Hz), 6.96 (d, 2H, $J = 8.7$ Hz), 3.84 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) 128.7, 128.1, 126.7, 126.6, 114.2, 55.3 ppm. IR (KBr) 3066, 3002, 2836, 1890, 1606, 1521, 1482, 1286 cm^{-1} .

4-*N,N*-Dimethylaminobiphenyl (6g) [1137-79-7]: ^1H NMR (300 MHz, CDCl_3) δ 7.56-7.48 (m, 4H), 7.38 (t, 2H, $J = 7.5$ Hz), 7.24 (t, 1H, $J = 9.0$ Hz) 6.80 (d, 2H, $J = 9.0$ Hz), 2.98 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) 150.0, 141.2, 128.6, 127.7, 126.3, 126.0, 112.7, 40.6 ppm. IR (KBr) 3030, 2879, 2800, 1880, 1610, 1491, 1354, 1230, 1062, 819, 758 cm^{-1} .

1-Phenylnaphtalene (6h) [605-02-7]: ^1H NMR (300 MHz, CDCl_3) δ 7.92-7.84 (m, 3H), 7.55-7.41 (m, 9H). ^{13}C NMR (75 MHz, CDCl_3) 140.7, 140.2, 133.8, 131.6, 130.0, 128.2, 127.6, 127.2, 126.9, 126.0, 125.7, 125.4 ppm. IR (liquid film) 3055, 1814, 1591, 1493, 1395, 961, 802, 702 cm^{-1} .

2-Phenylthiophene (6i) [825-55-8]: ^1H NMR (300 MHz, CDCl_3) δ 7.60 (d, 2H, $J = 7.2$ Hz), 7.36 (t, 2H, $J = 7.2$ Hz), 7.31-7.25 (m, 3H), 7.07 (dd, 1H). ^{13}C NMR (75 MHz, CDCl_3) 144.4, 134.4, 128.9, 128.0, 127.4, 125.9, 124.8, 123.0 ppm. IR (KBr) 3067, 2927, 1945, 1594, 1488, 1446, 1074, 850, 754, 689 cm^{-1} .

Preparation of Potassium Diphenyldifluoroborate (7a). The synthesis of **7a** was based on the method reported by Ito et al¹⁰ to give **7a** as a white powder in 63% yield.

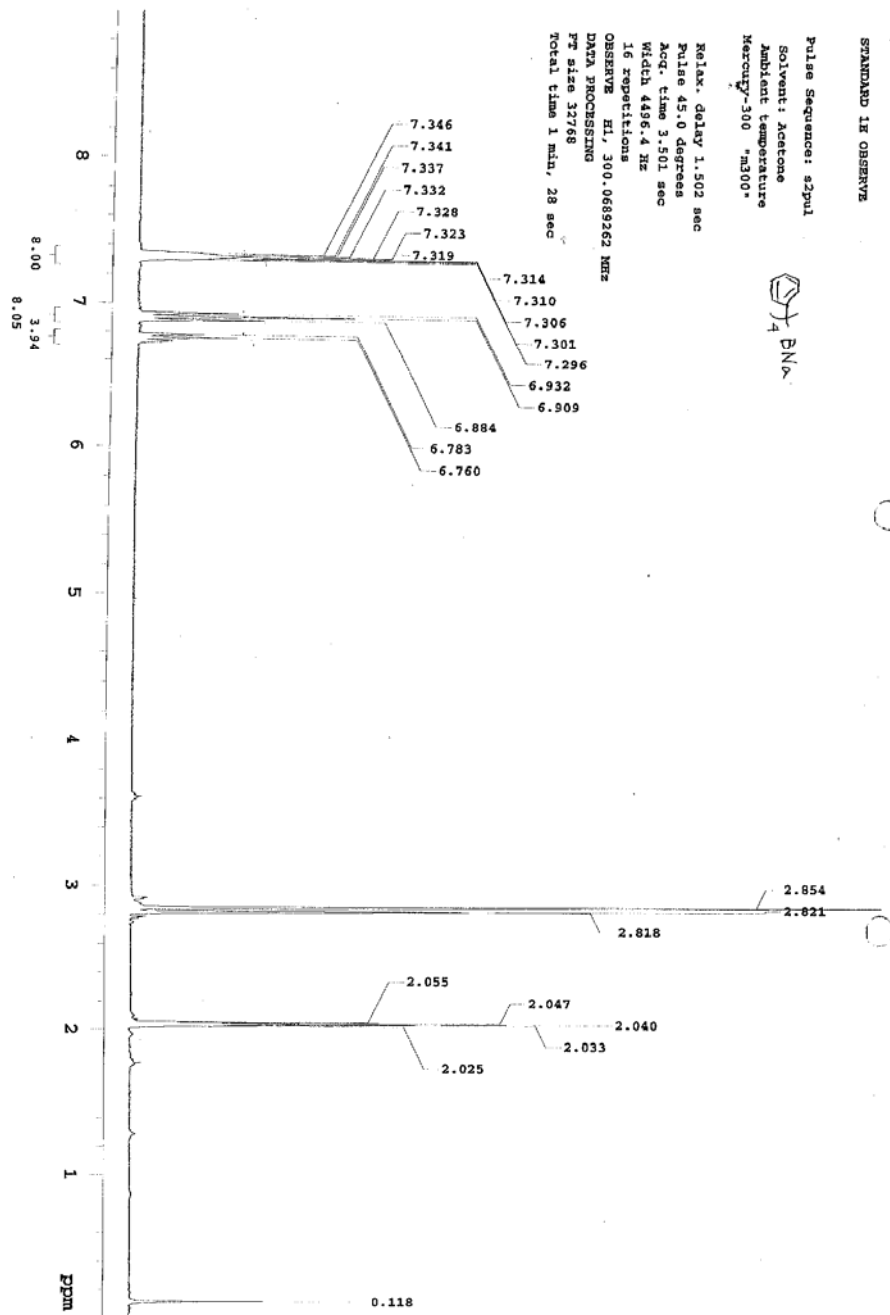
Potassium diphenyldifluoroborate (7a) [18114-68-6]

Procedure for the Oxidative Ligand Coupling of Potassium Diphenyldifluoroborate (7a). Potassium diphenyldifluoroborate (**7a**, 48.4 mg, 0.20 mmol) and a stirring bar were placed in a 20 mL 2-necked round bottom flask, and dried. 2 mL of acetonitrile and 0.87 mL of dichloromethane were added into the flask, followed by the addition VO(OEt)Cl₂ (0.80 M solution in dichloromethane, 0.13 mL, 0.10 mmol) under an oxygen atmosphere. The reaction mixture was allowed to reflux smoothly and stirred for 10 h. Then, 1M aqueous HCl (3 mL) was added so as to quench the reaction. After extraction with Et₂O (3 × 10 mL), the combined organic layer was washed with brine, dried over MgSO₄, and evaporated. The purification of the crude product with preparative TLC (hexane) gave biphenyl (**2a**, 78% yield, Scheme 2).

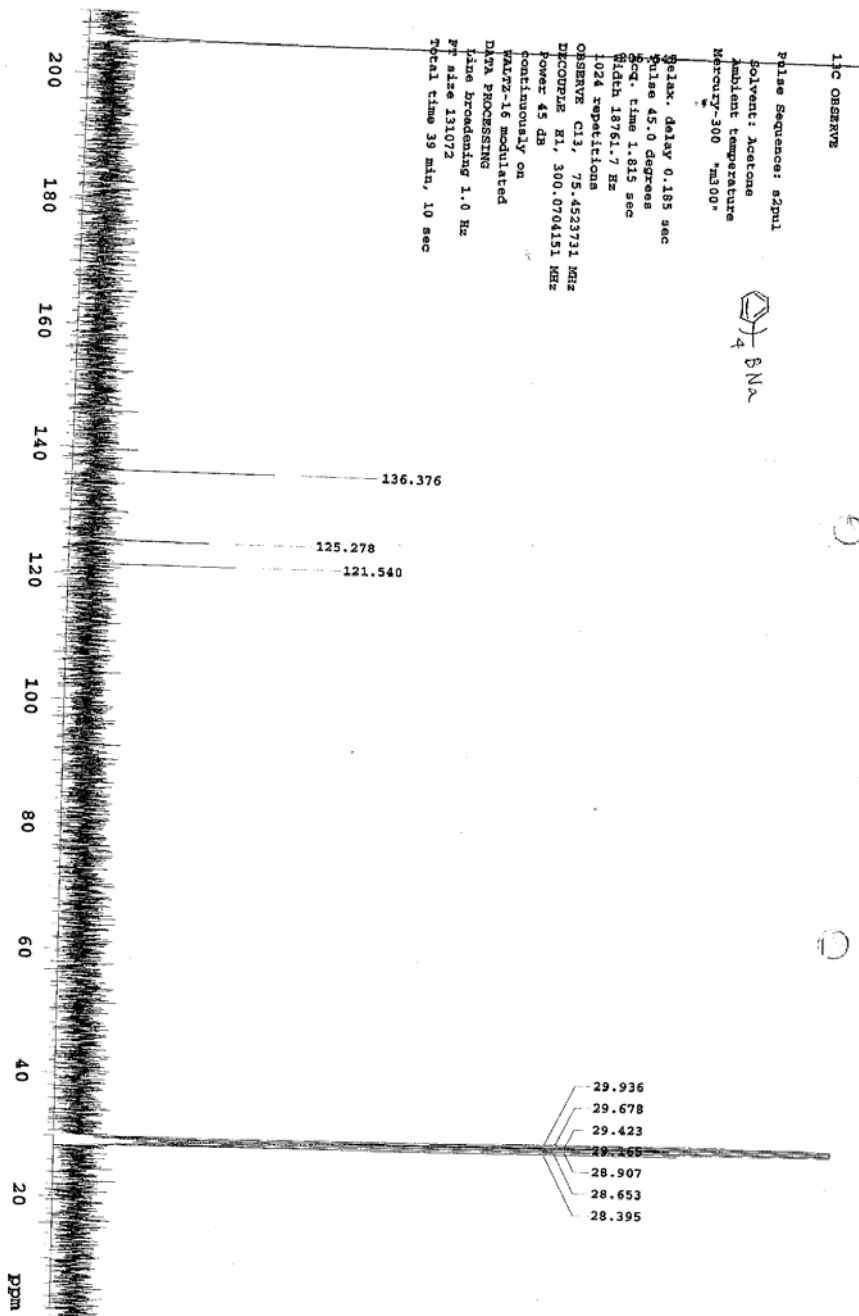
References

- (i) (a) Funk, H.; Weiss, W.; Zeising, M. *Anorg. Allg. Chem.* **1958**, *36*, 296. (b) Hirao, T.; Mori, M.; Ohshiro, Y. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2399.
- (ii) Ohashi, K.; Banno, T.; Umeno, M.; Honma, S.; Abe, F. Jpn. Kohkai Tokkyo Koho JP8169892.

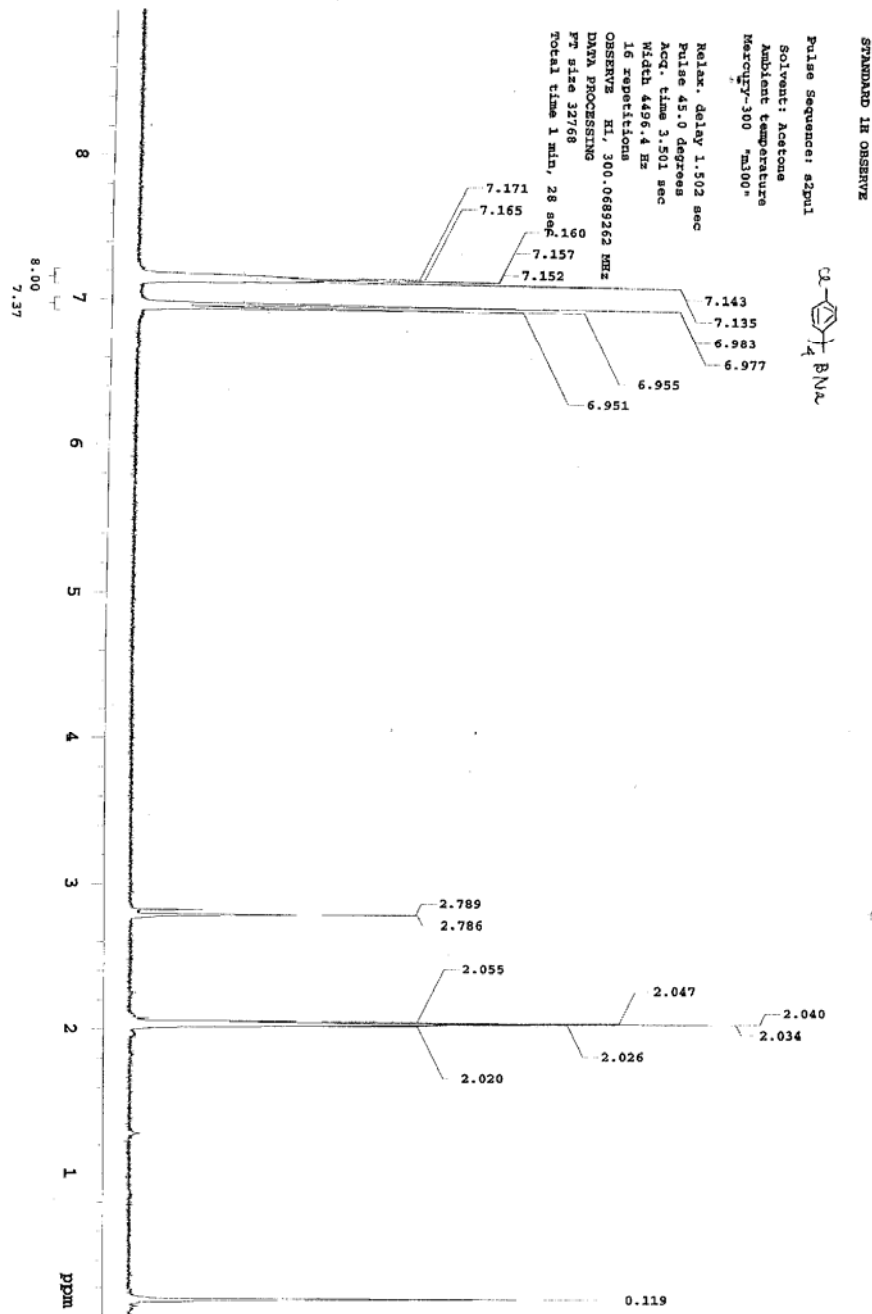
¹H NMR spectrum of **1a**



¹³C NMR spectrum of **1a**

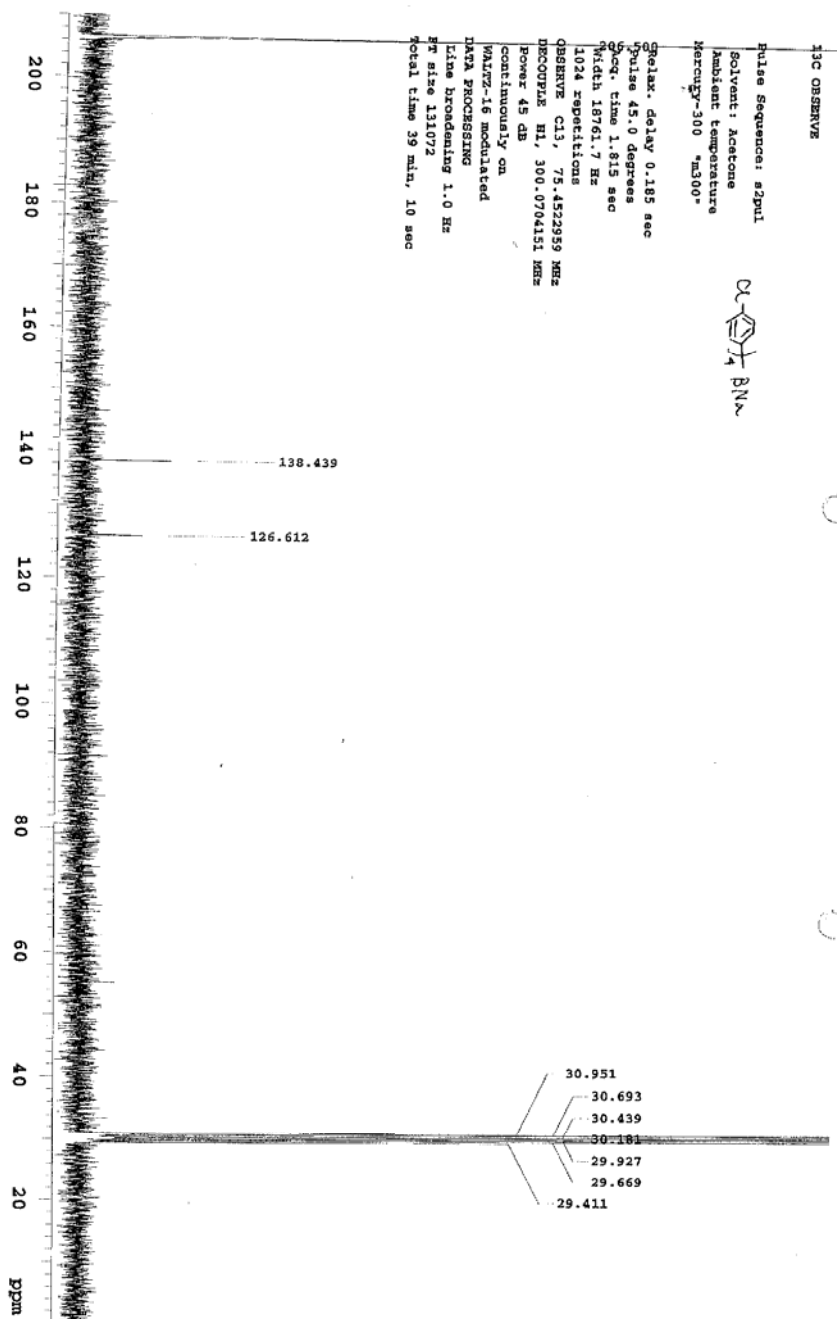


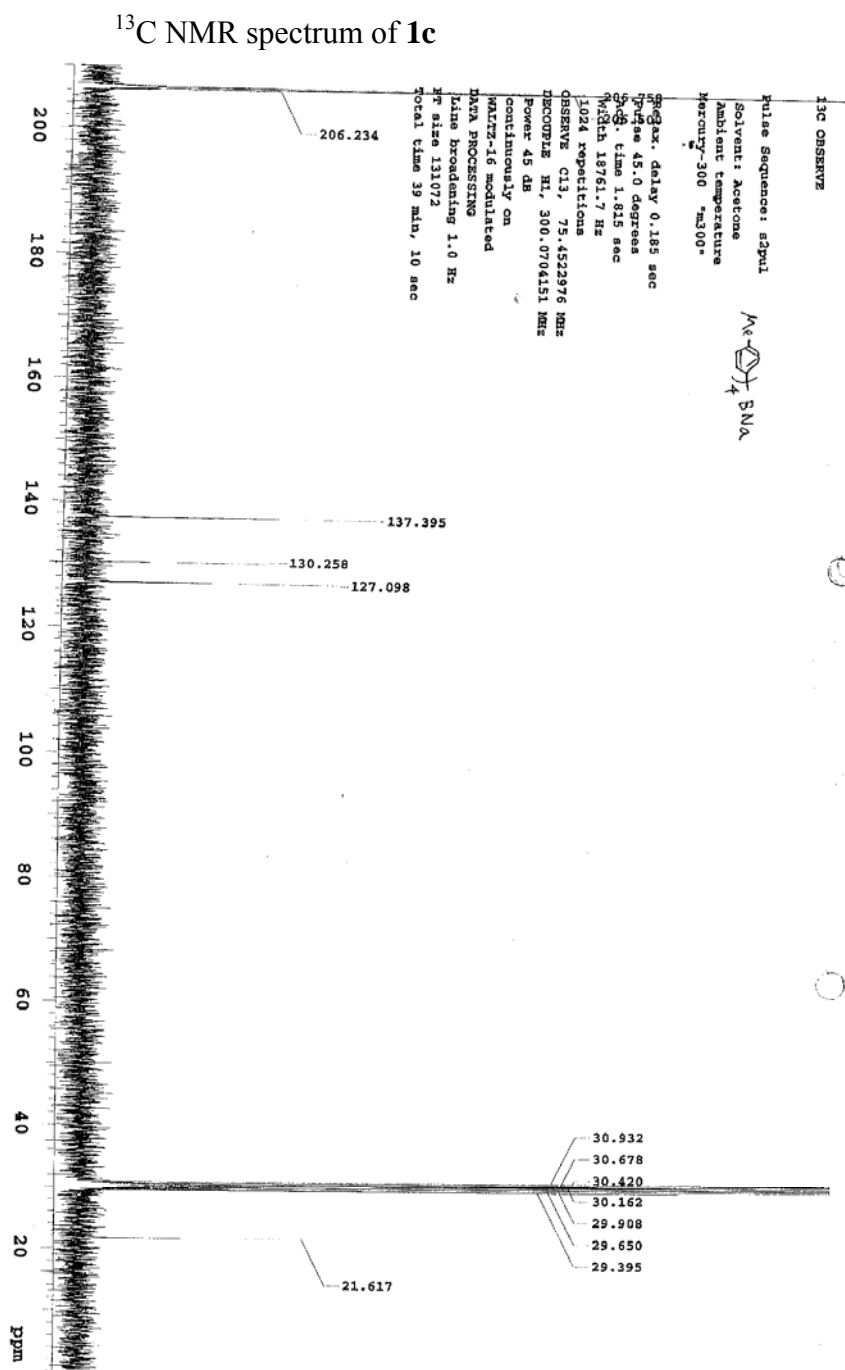
^1H NMR spectrum of **1b**



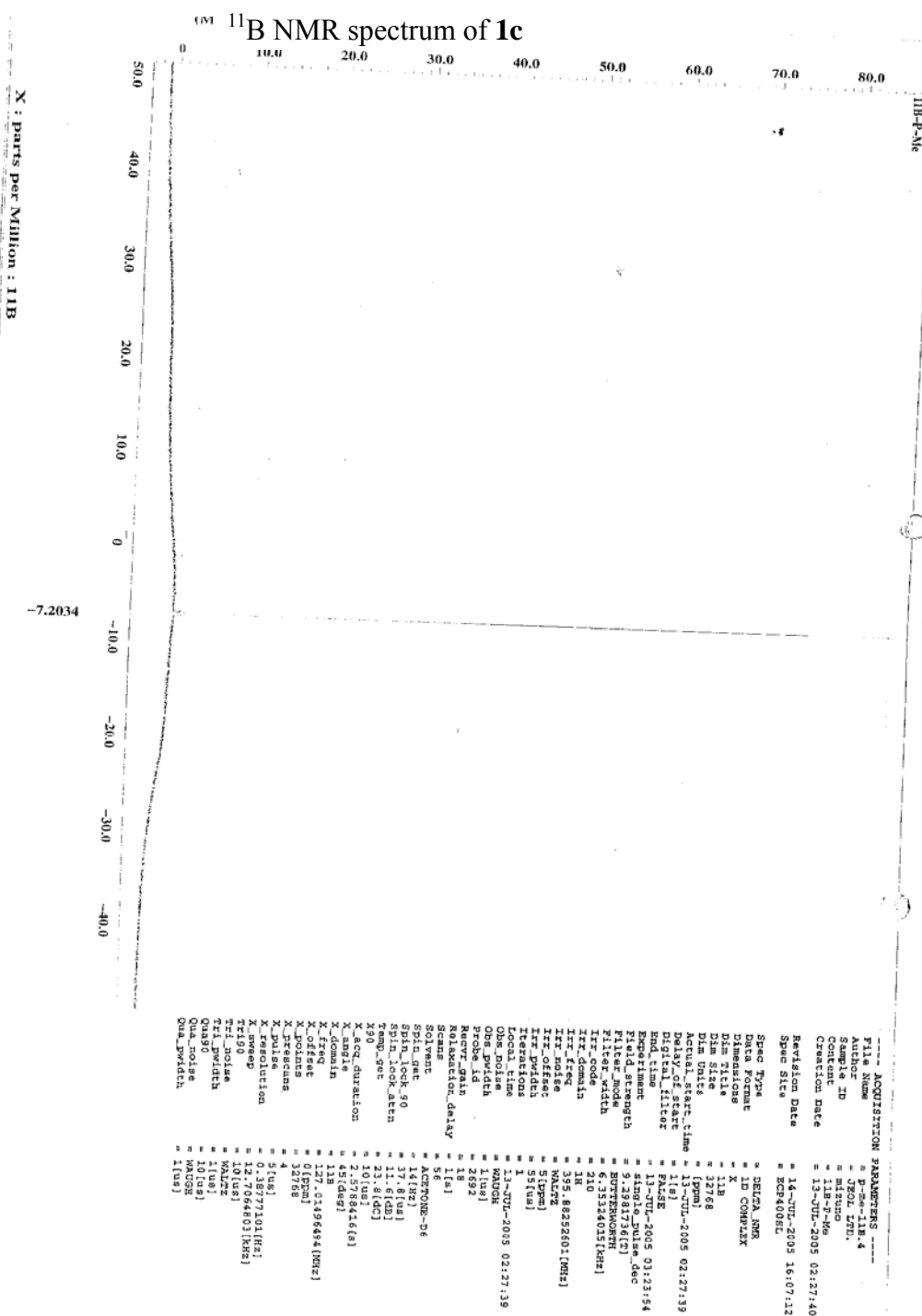
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¹³C NMR spectrum of **1b**



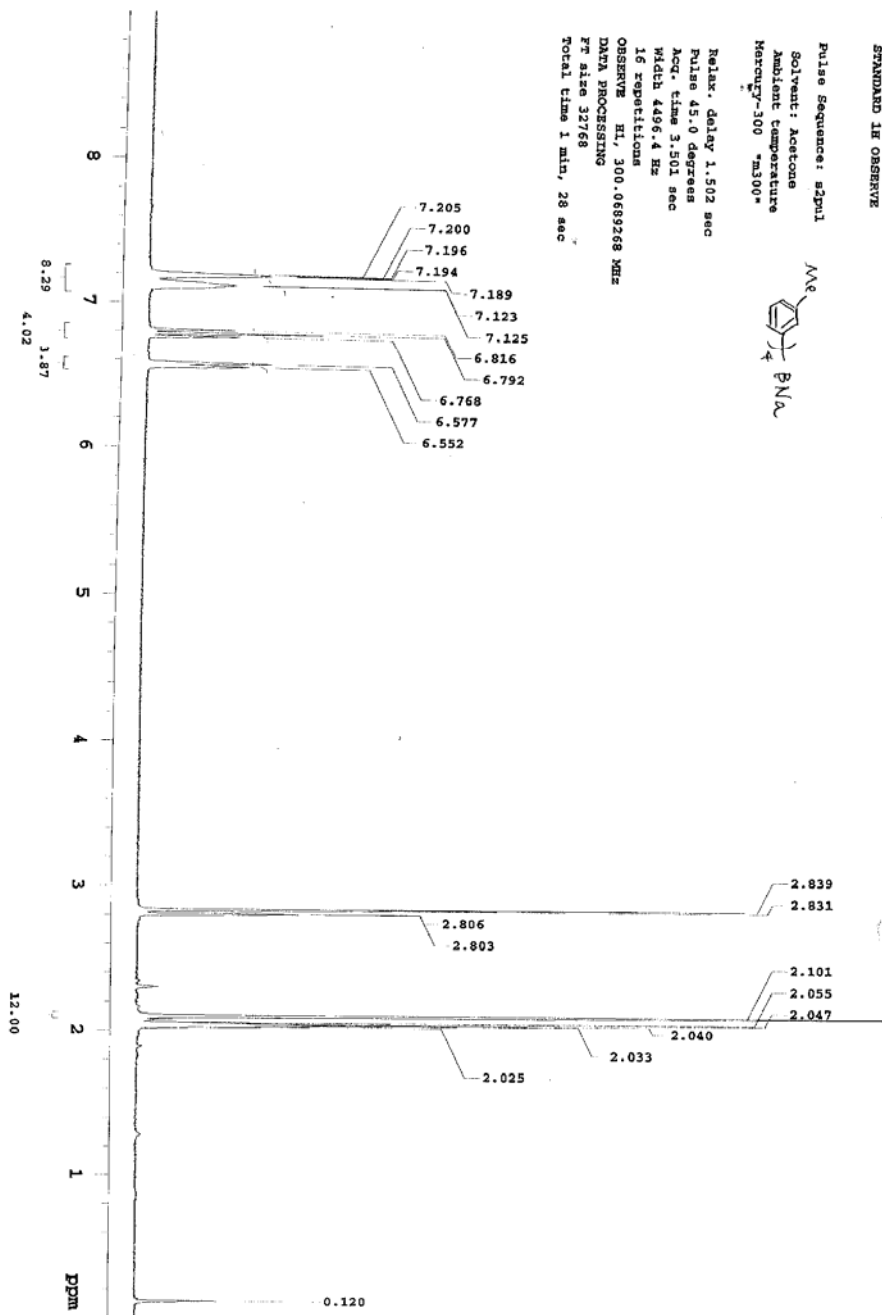


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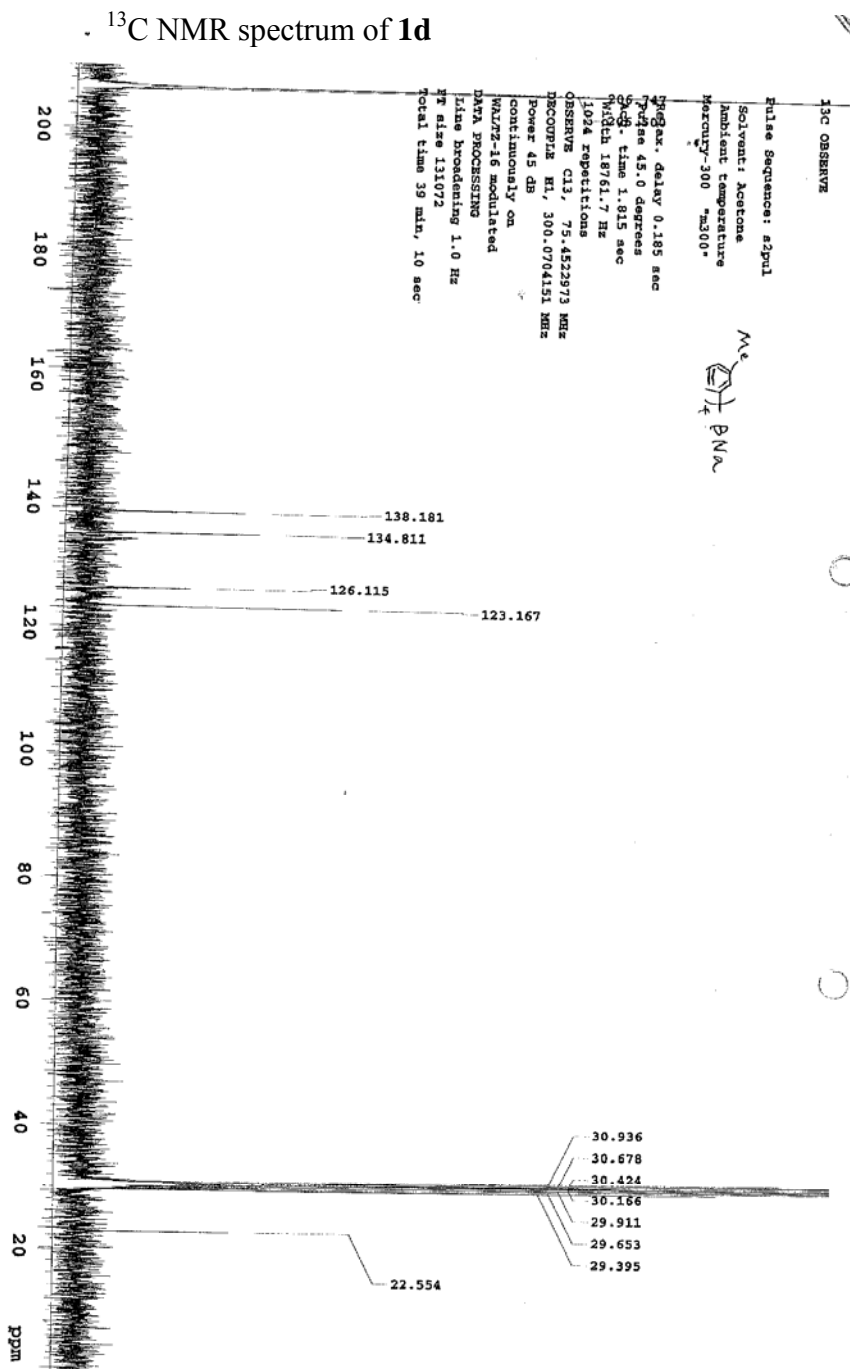


S 12

¹H NMR spectrum of **1d**

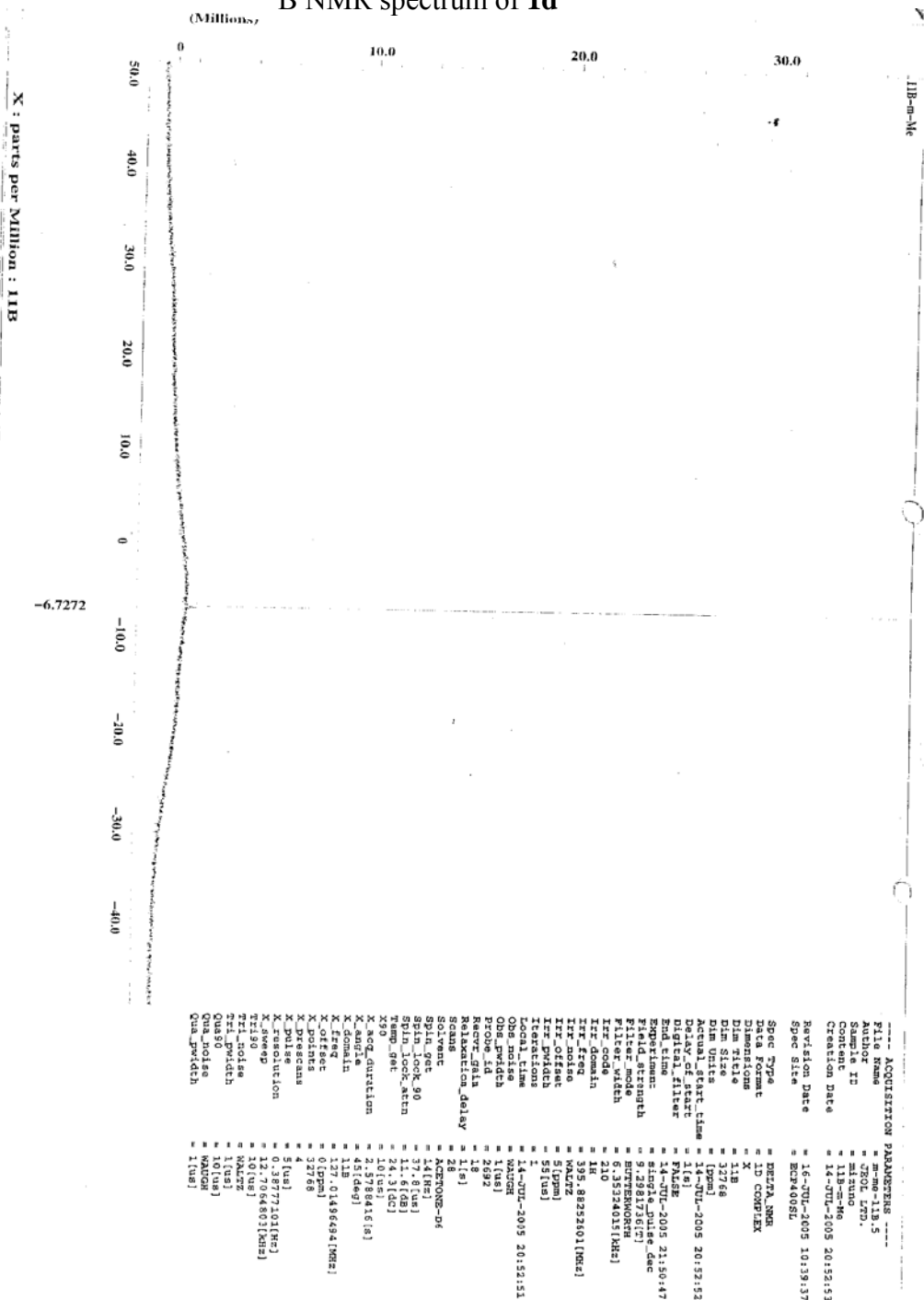


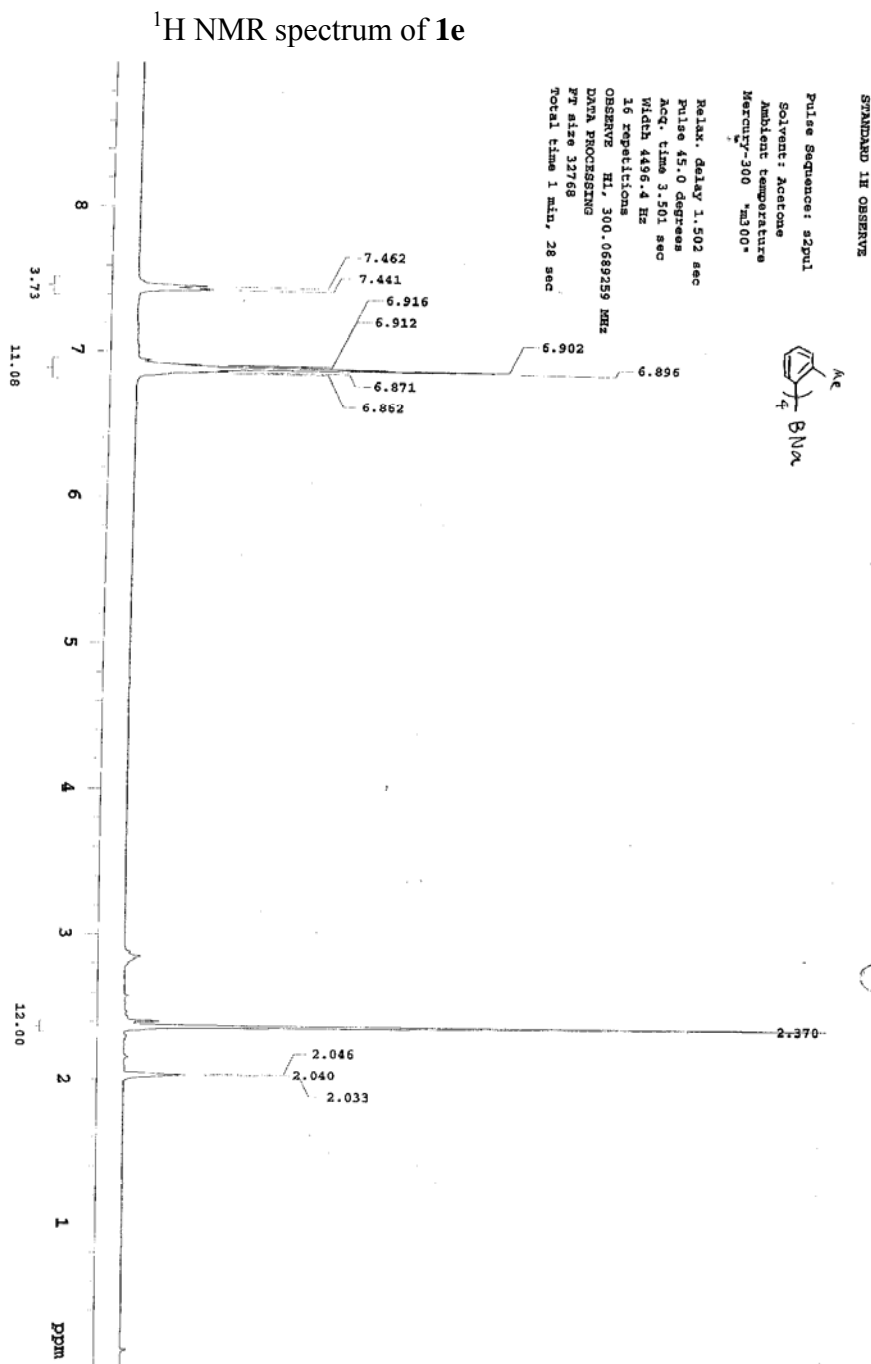
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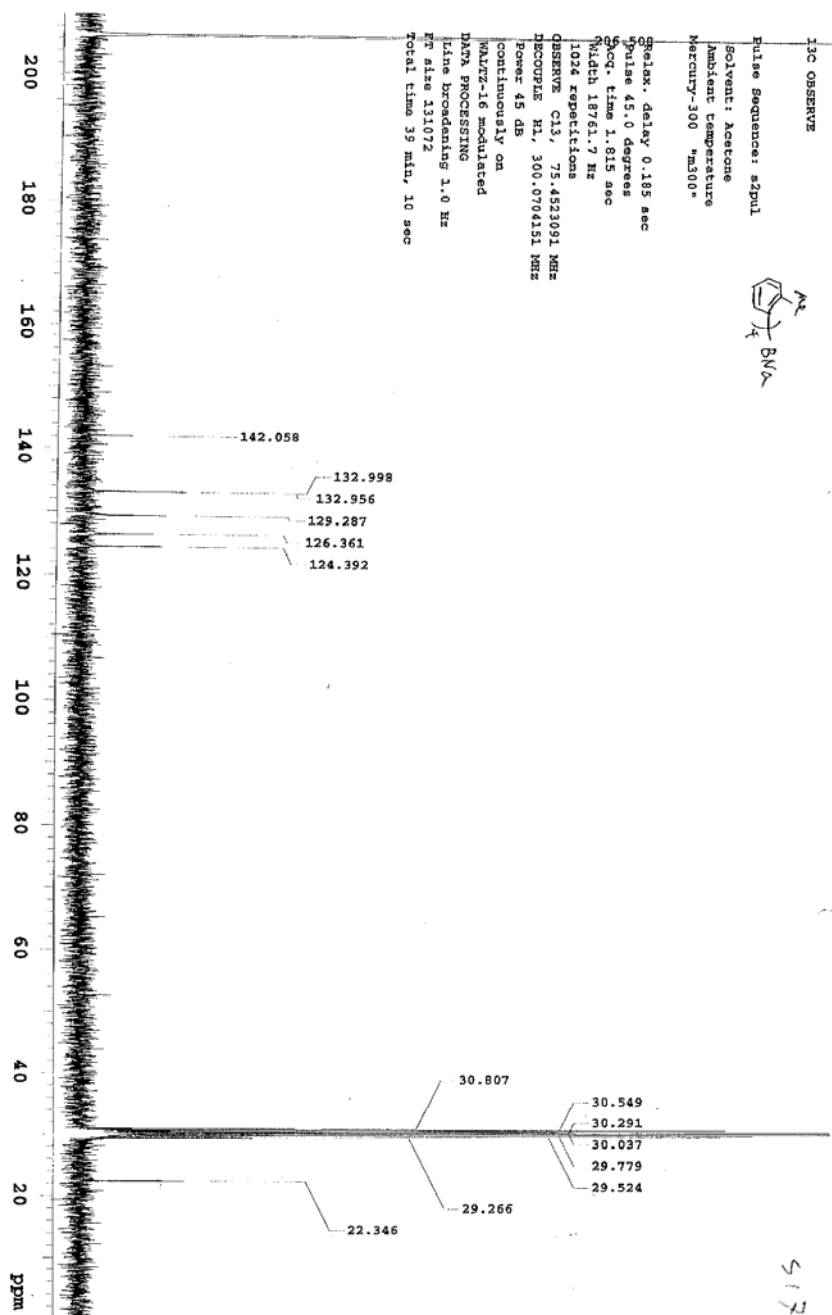
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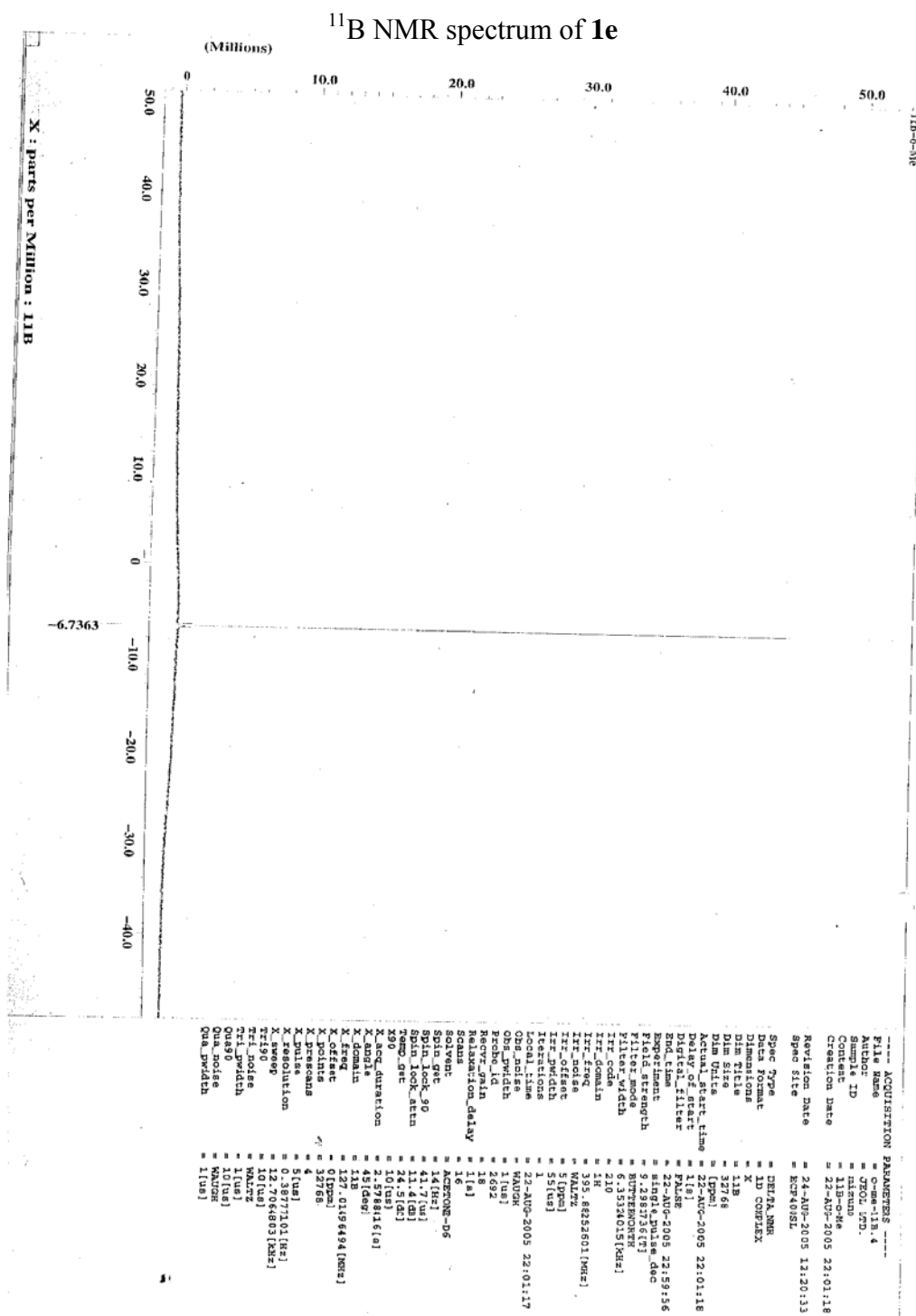
¹¹B NMR spectrum of **1d**





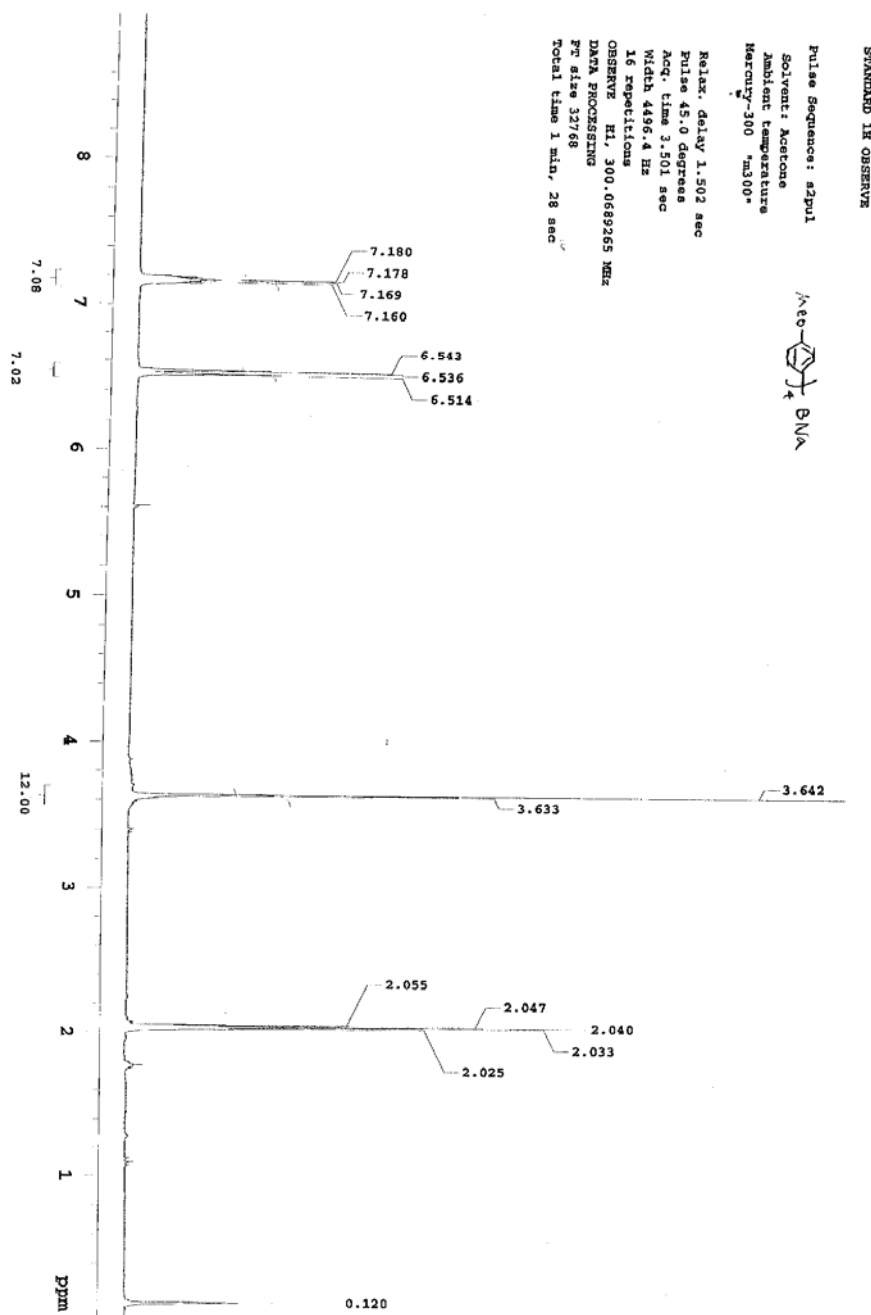
¹³C NMR spectrum of **1e**



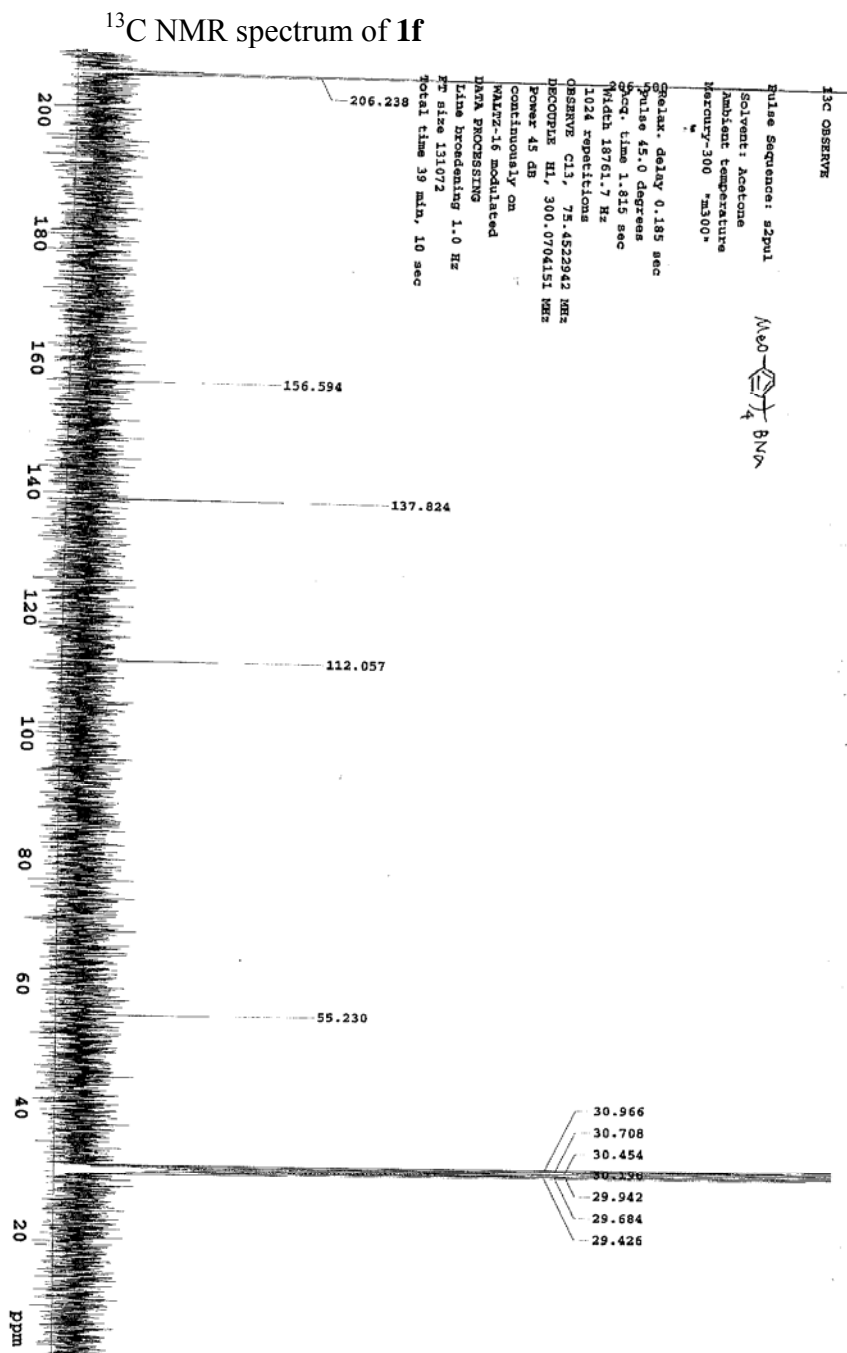


518

¹H NMR spectrum of **1f**

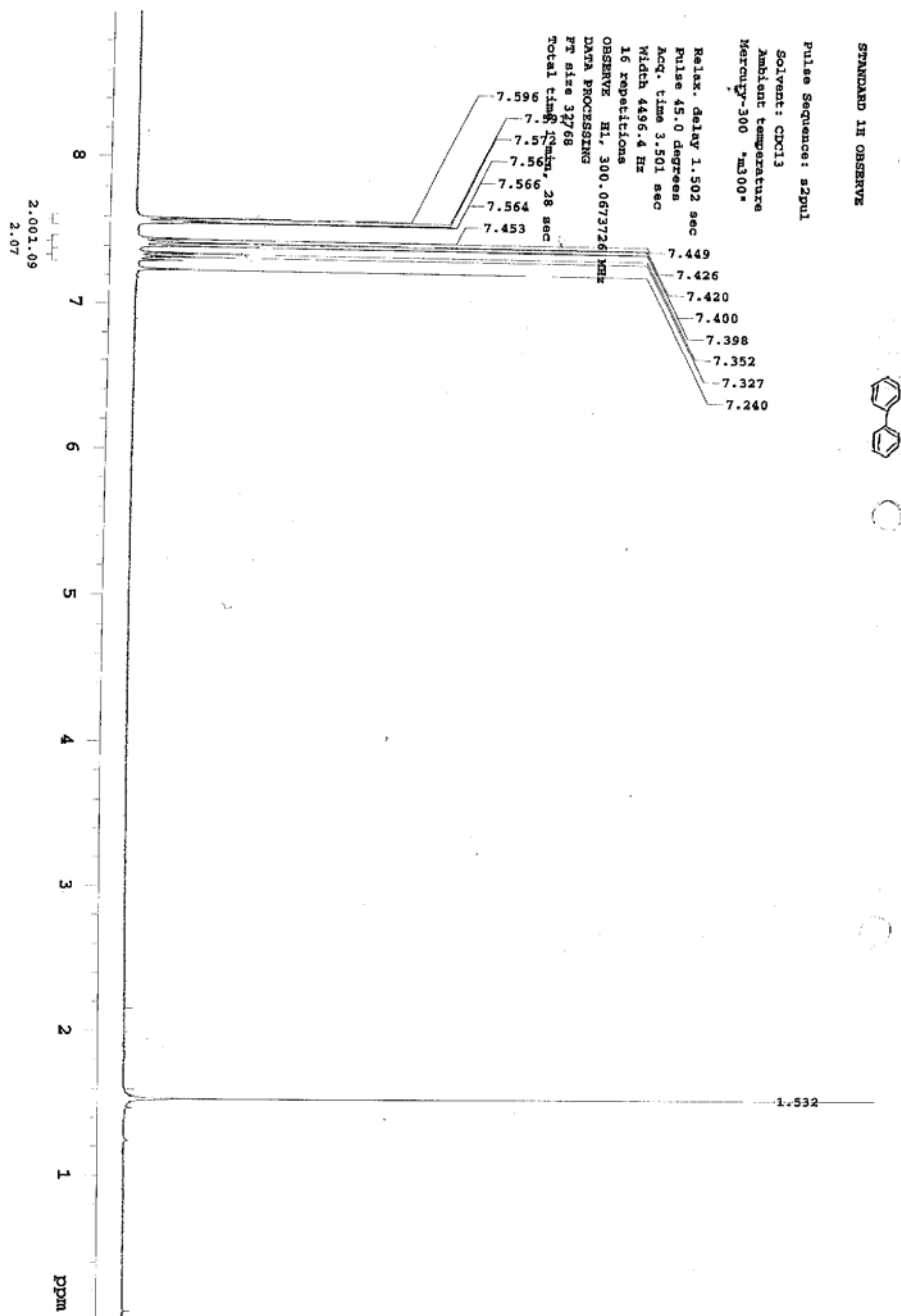


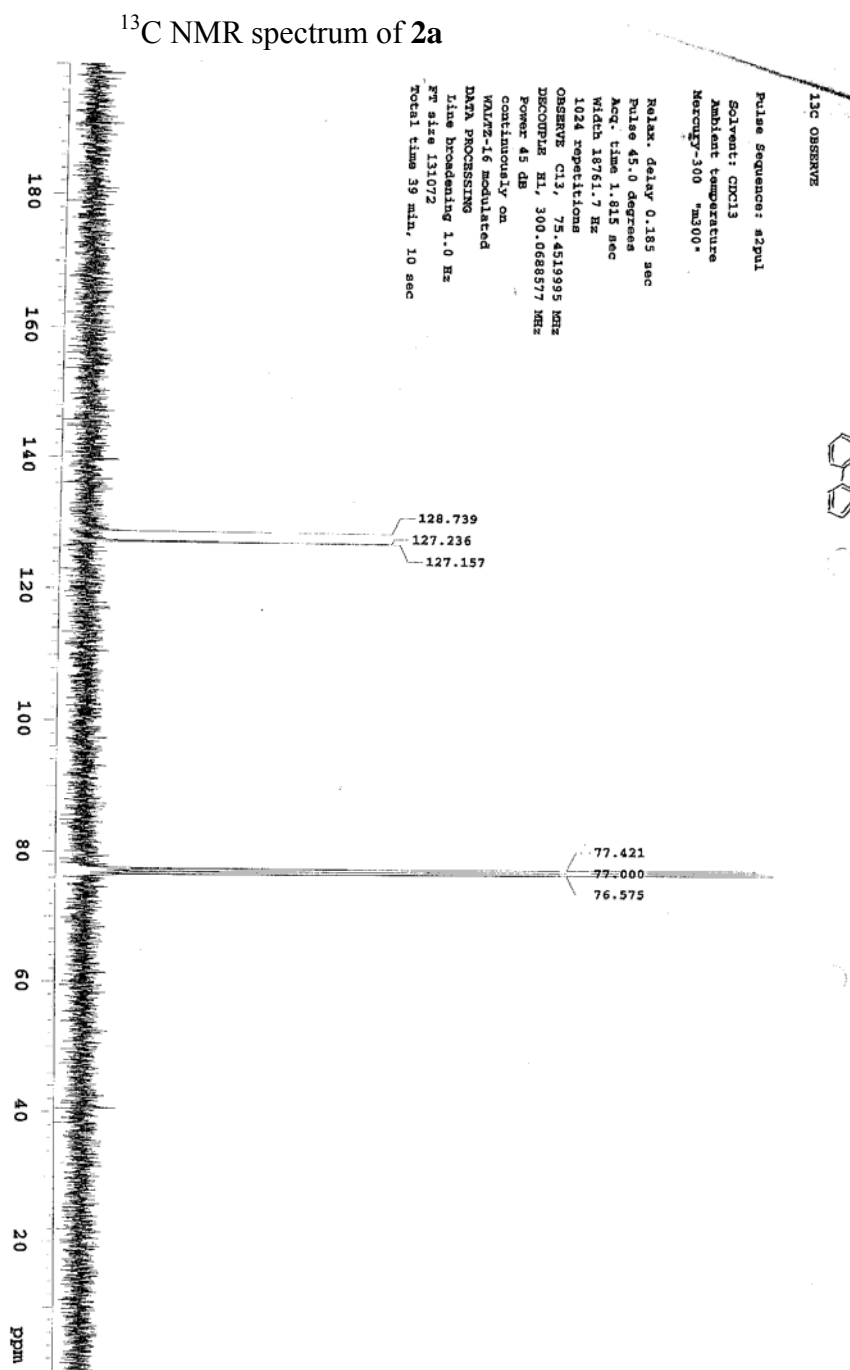
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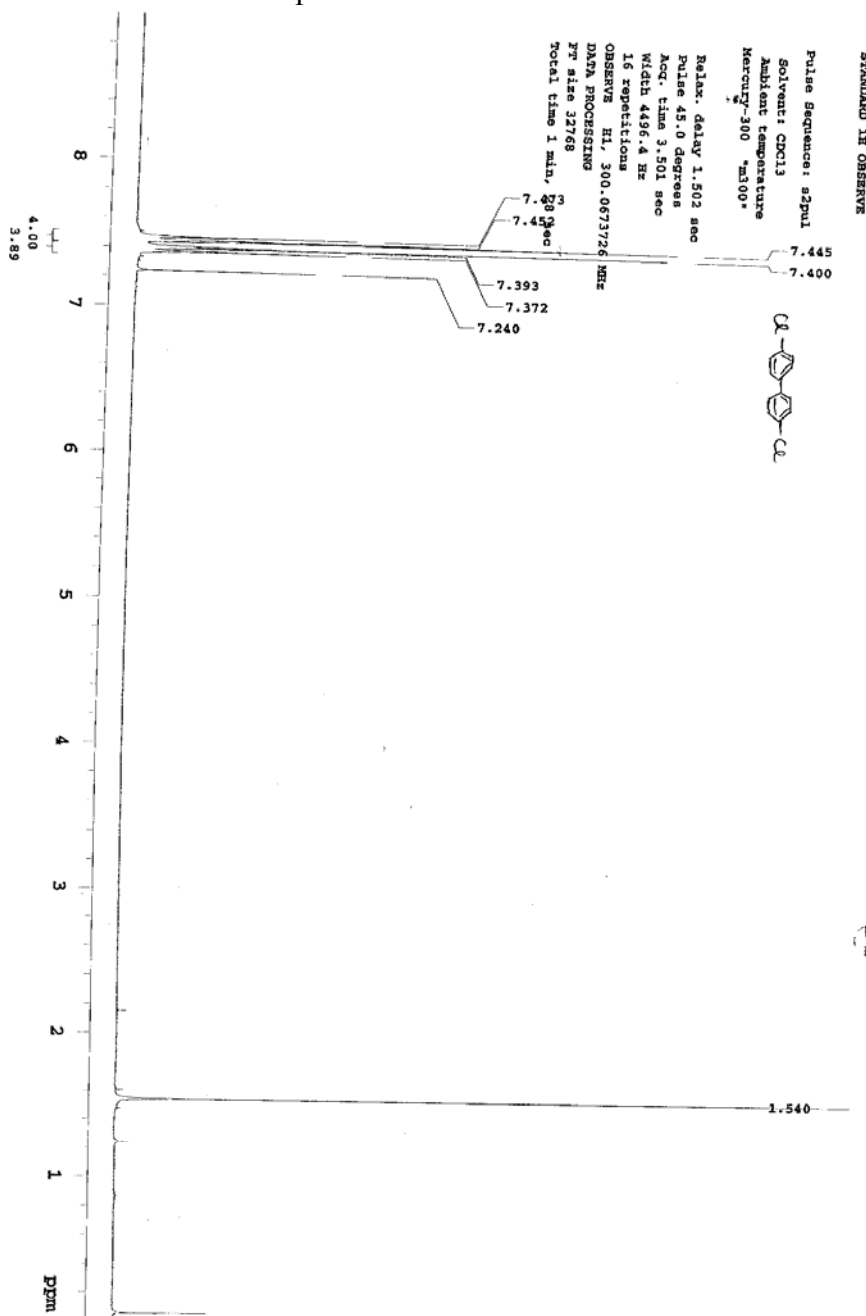
S 10

^1H NMR spectrum of **2a**

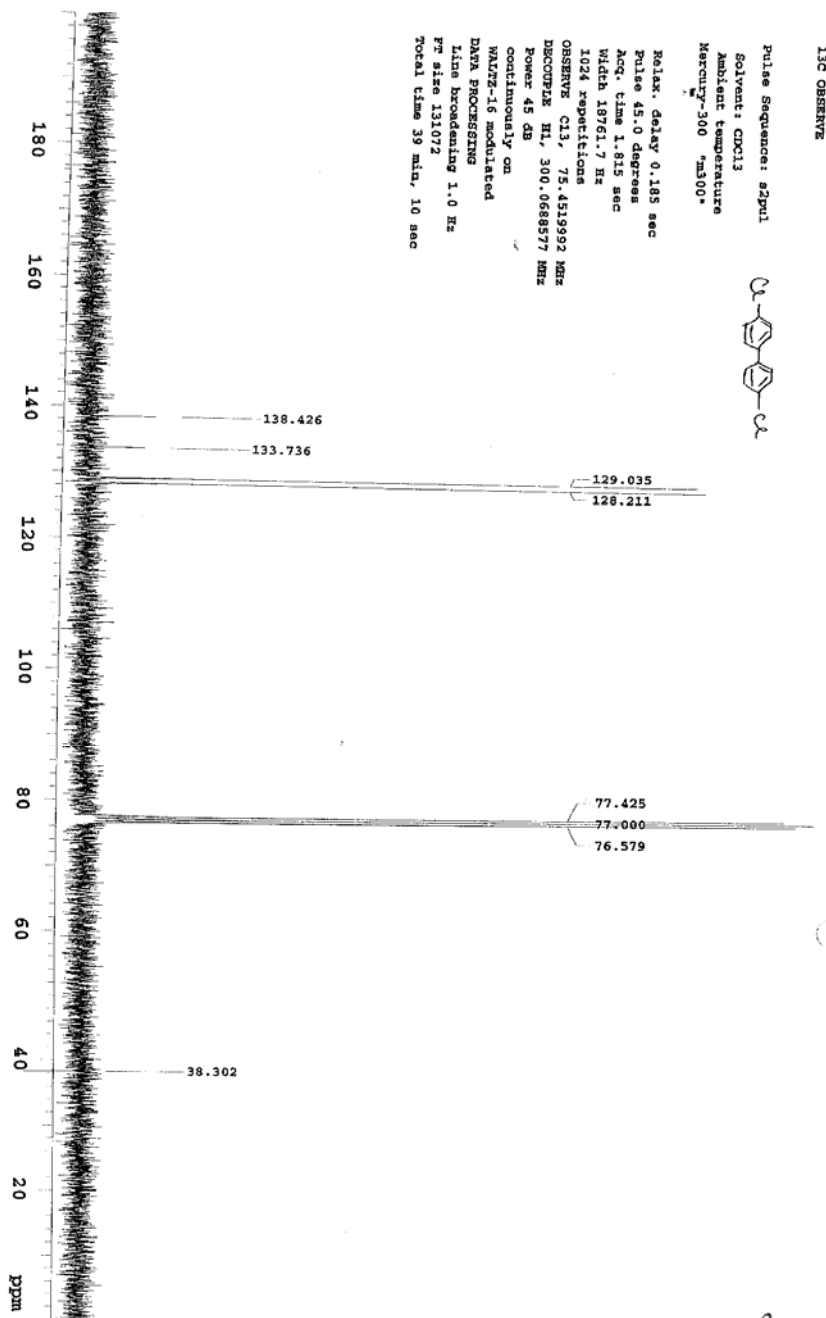




¹H NMR spectrum of **2b**

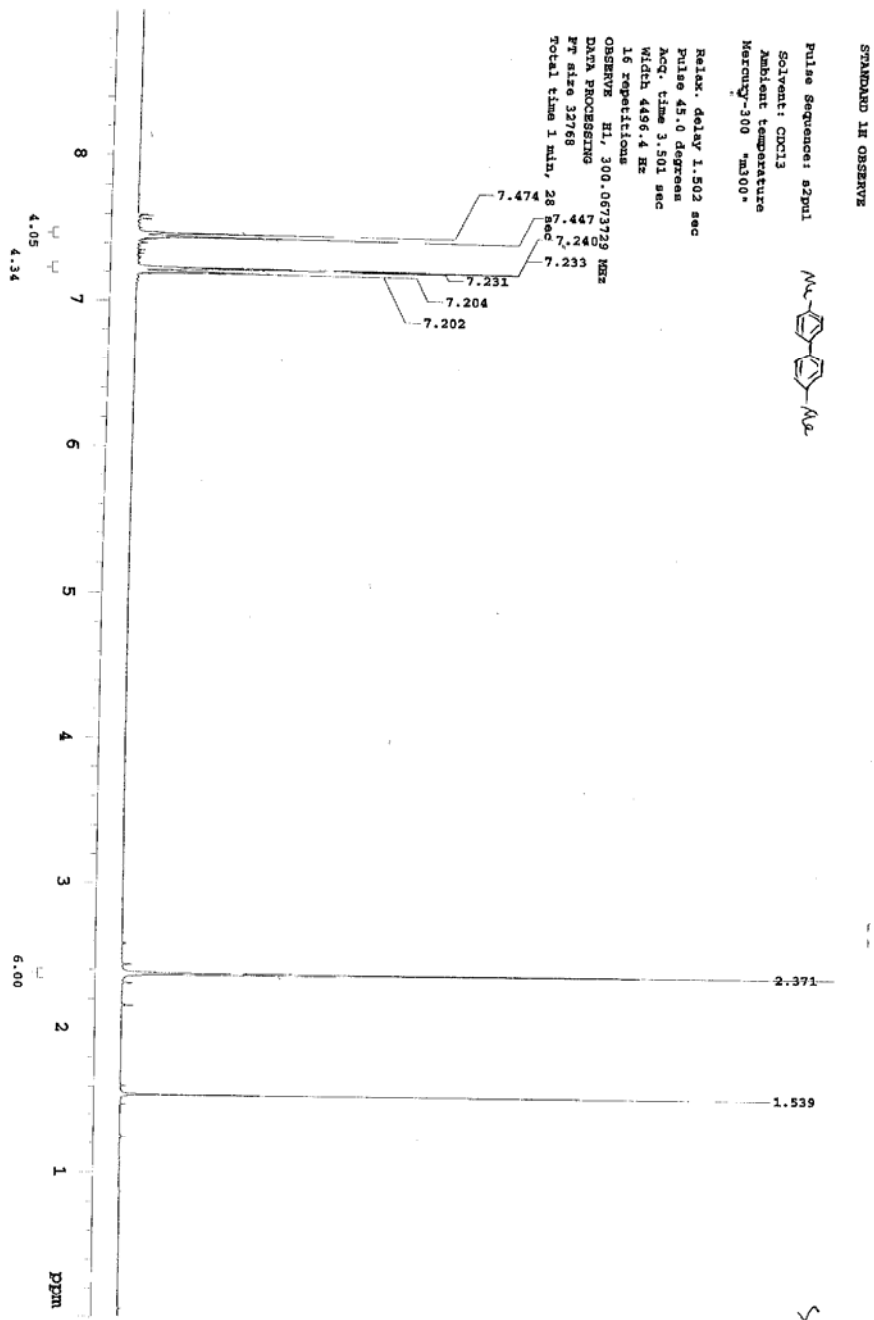


¹³C NMR spectrum of **2b**

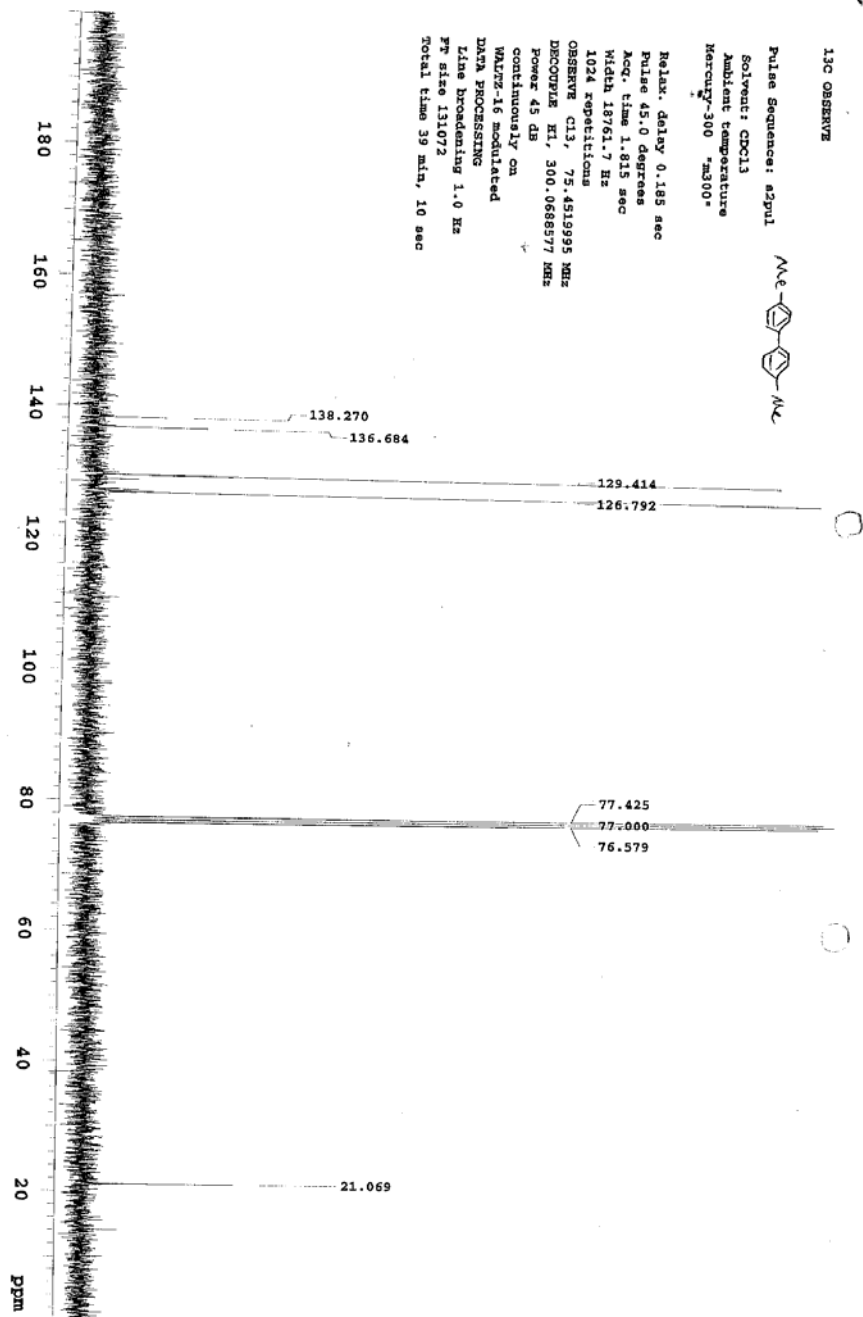


S 25

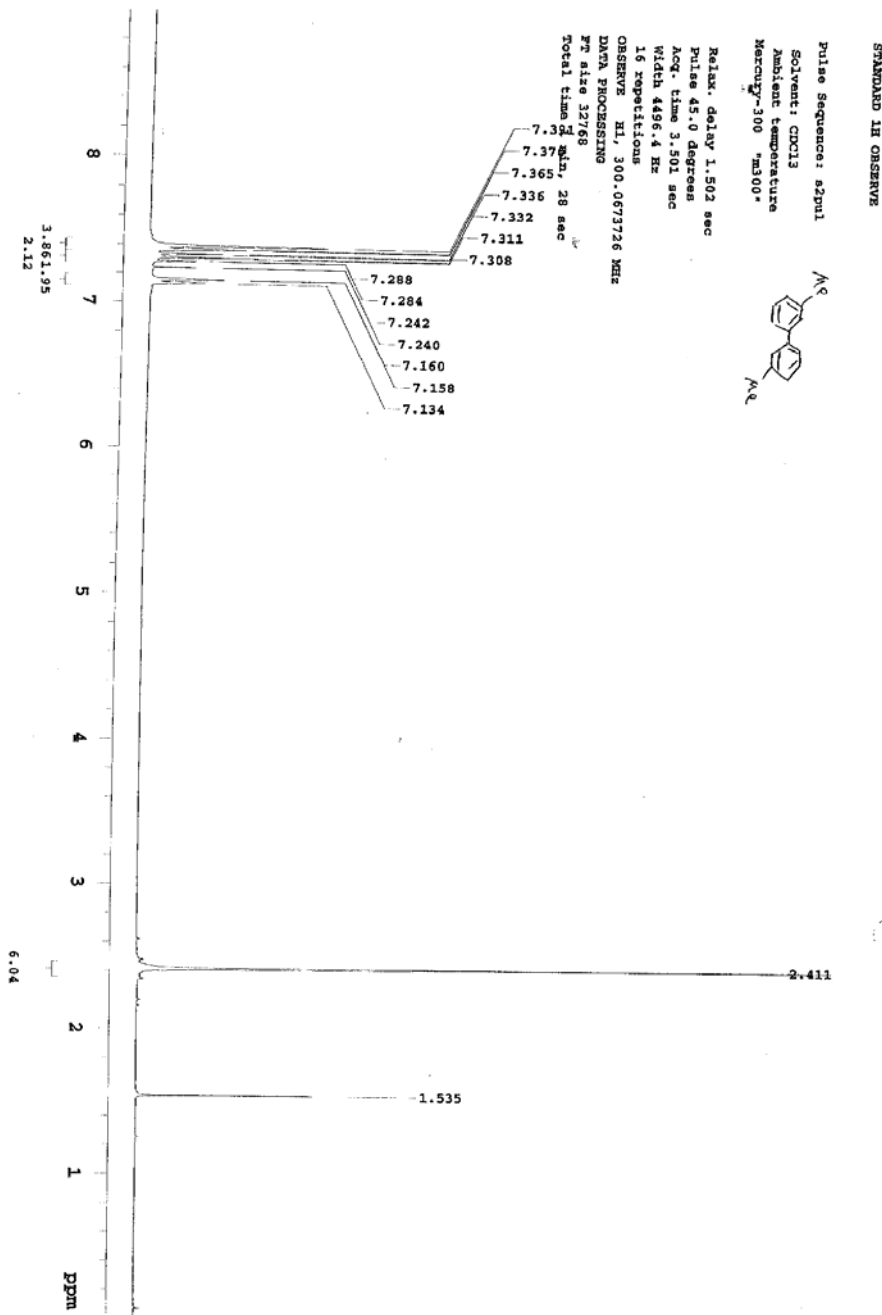
¹H NMR spectrum of 2c



¹³C NMR spectrum of **2c**

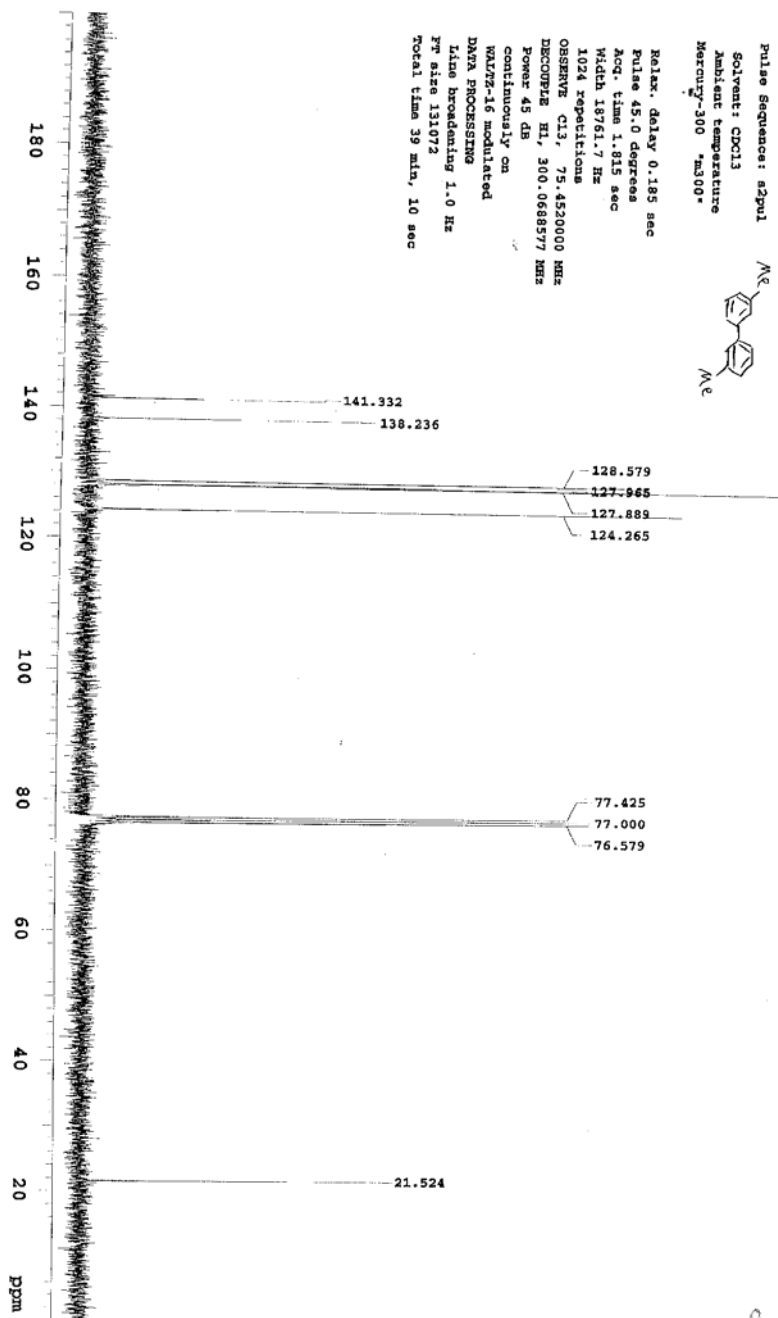


¹H NMR spectrum of 2d

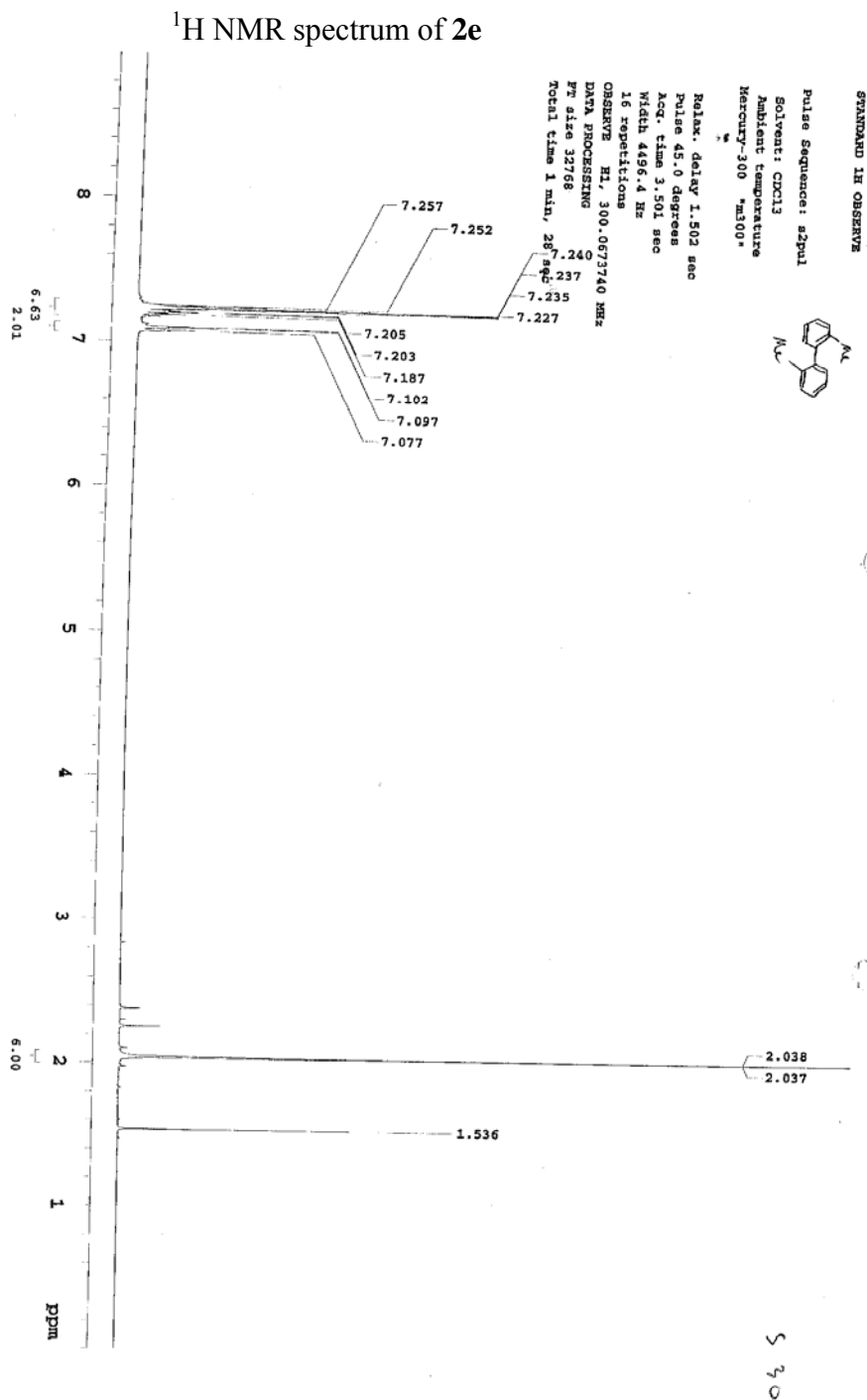


S28

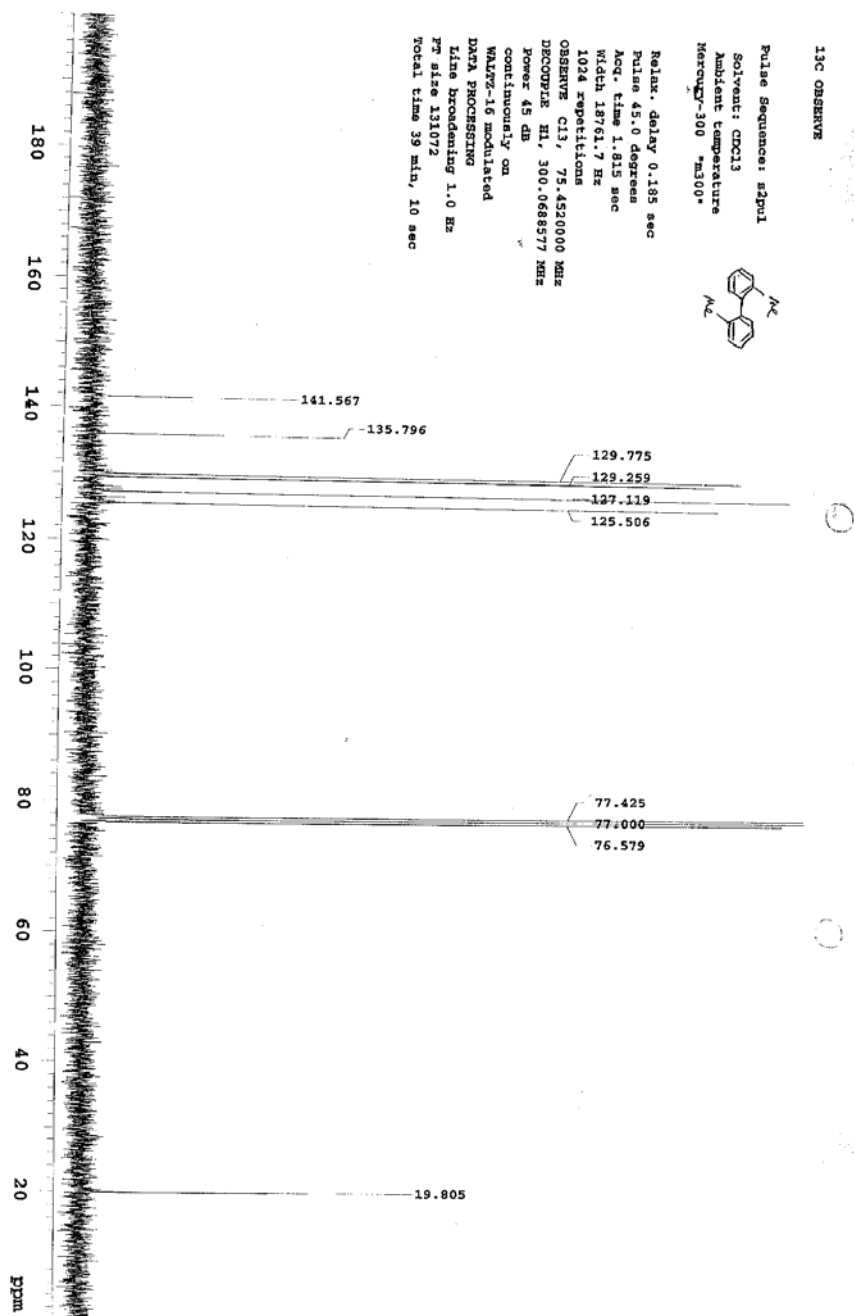
¹³C NMR spectrum of **2d**



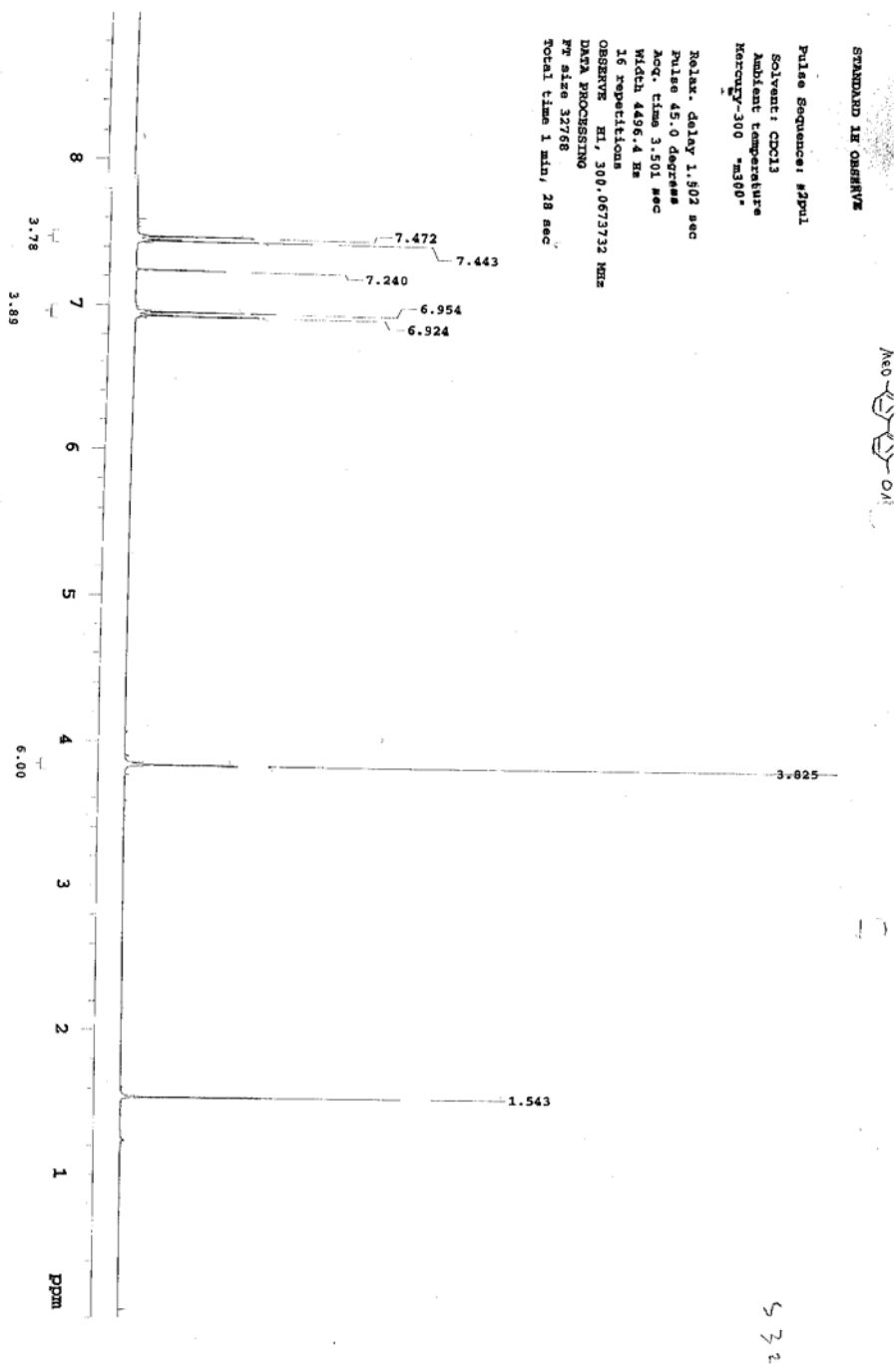
S 19



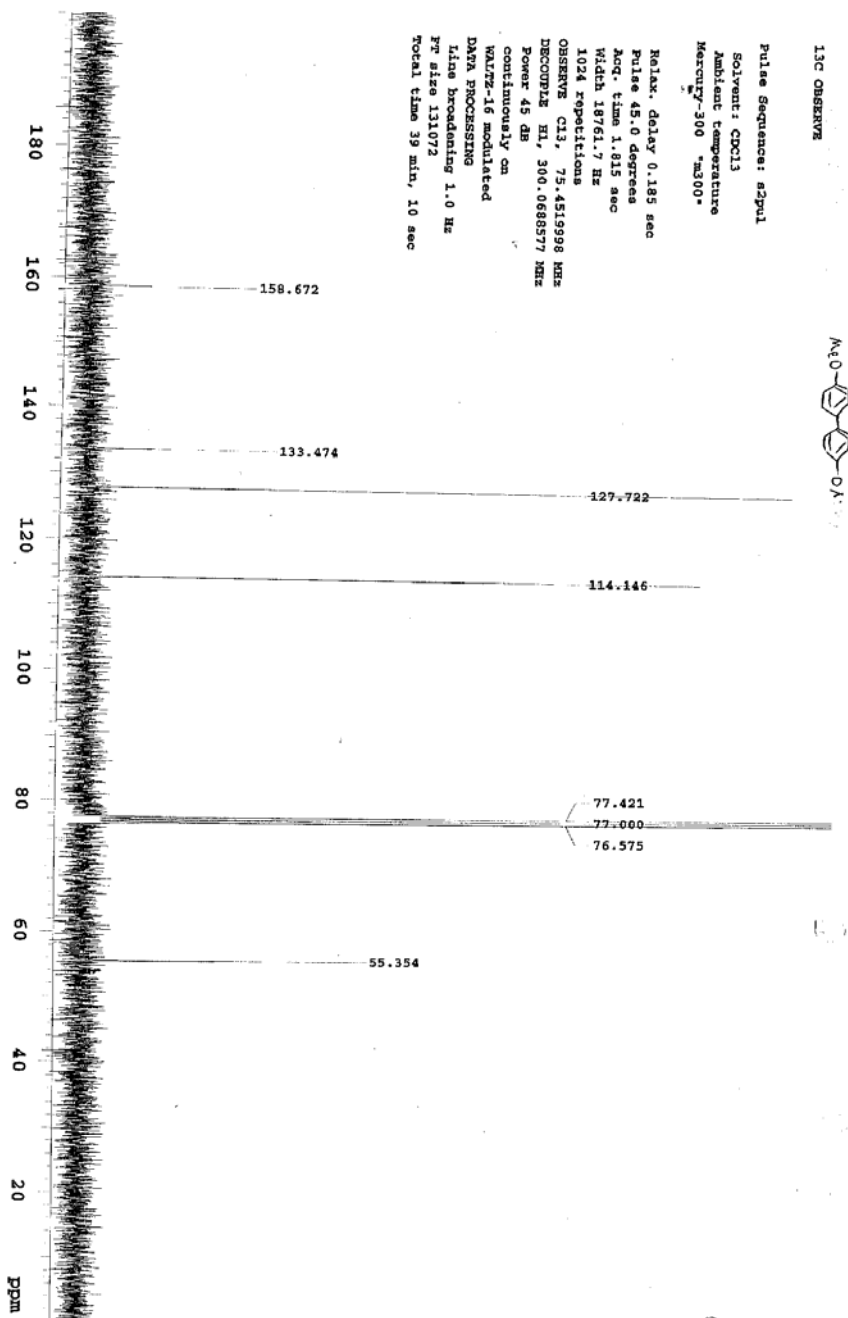
^{13}C NMR spectrum of **2e**



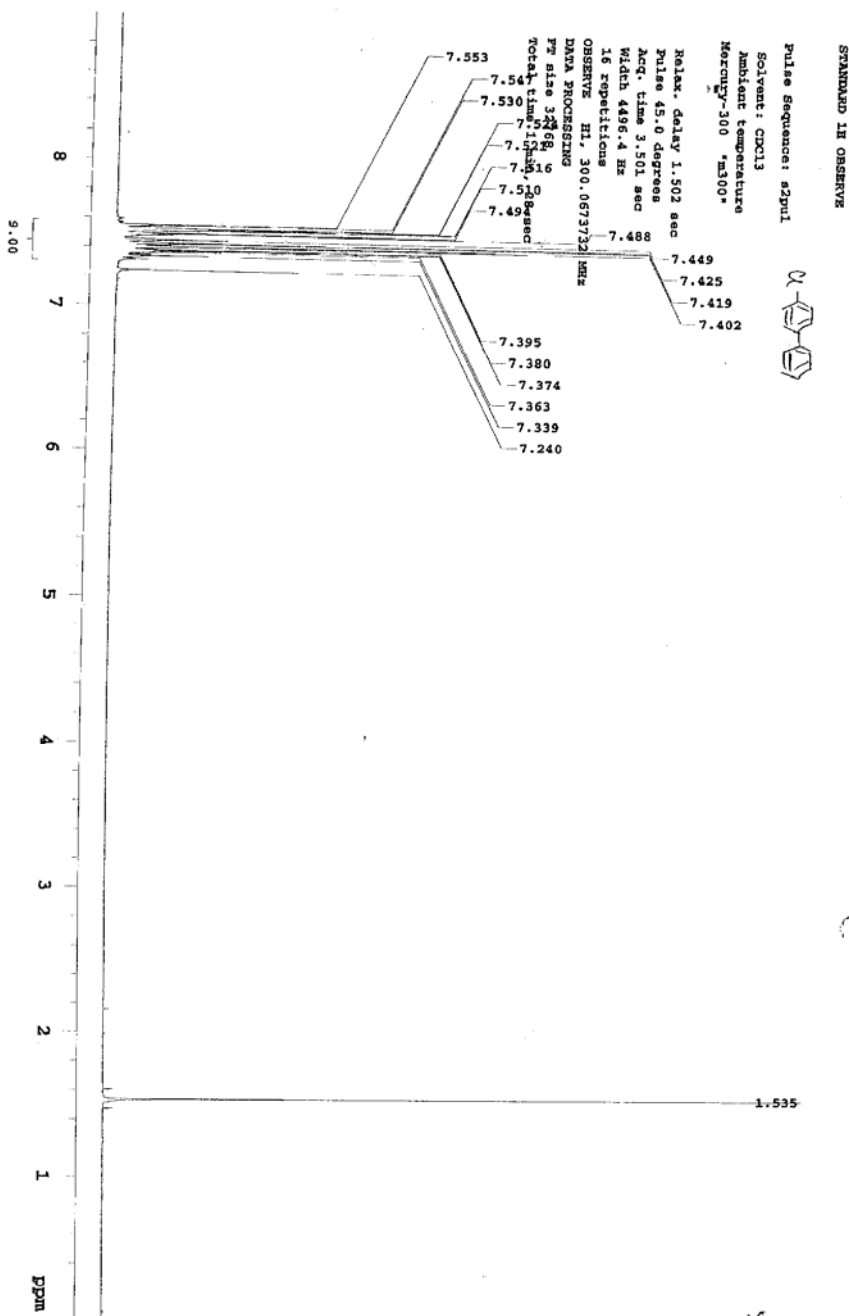
¹H NMR spectrum of 2f



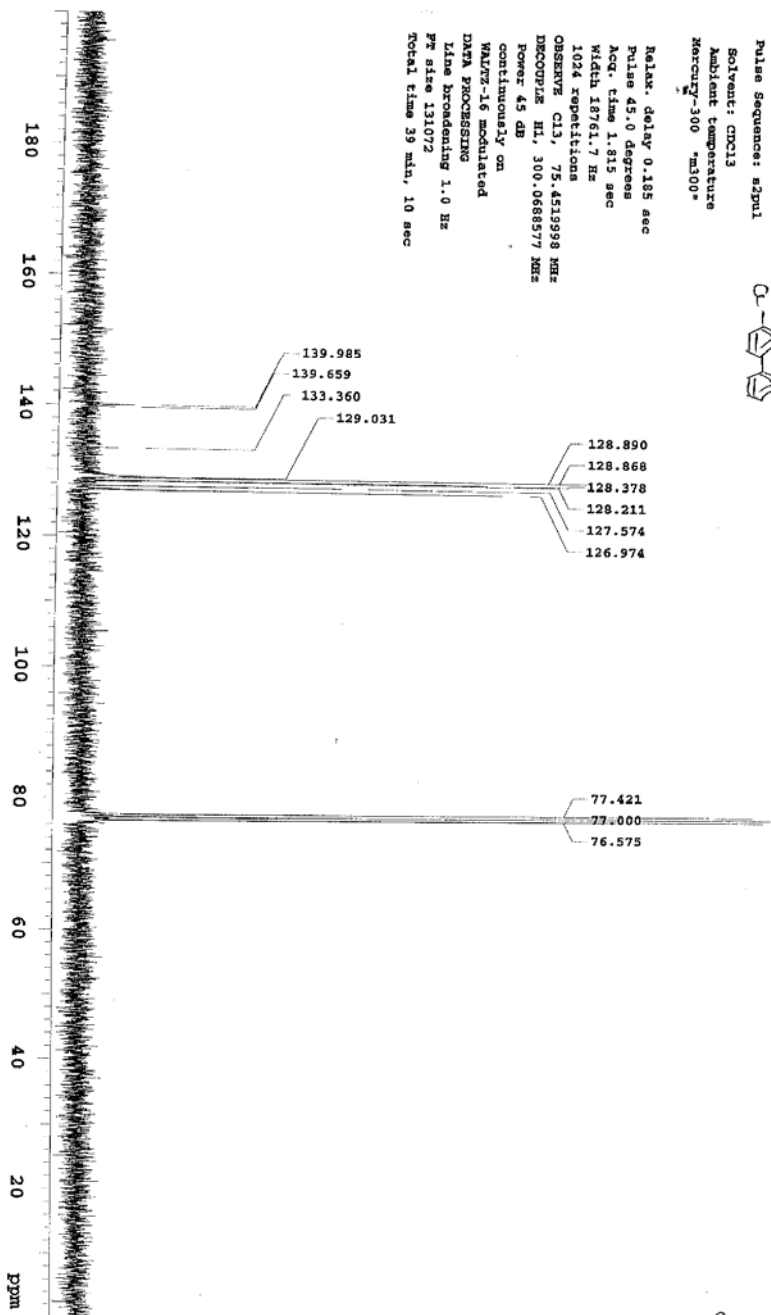
^{13}C NMR spectrum of **2f**



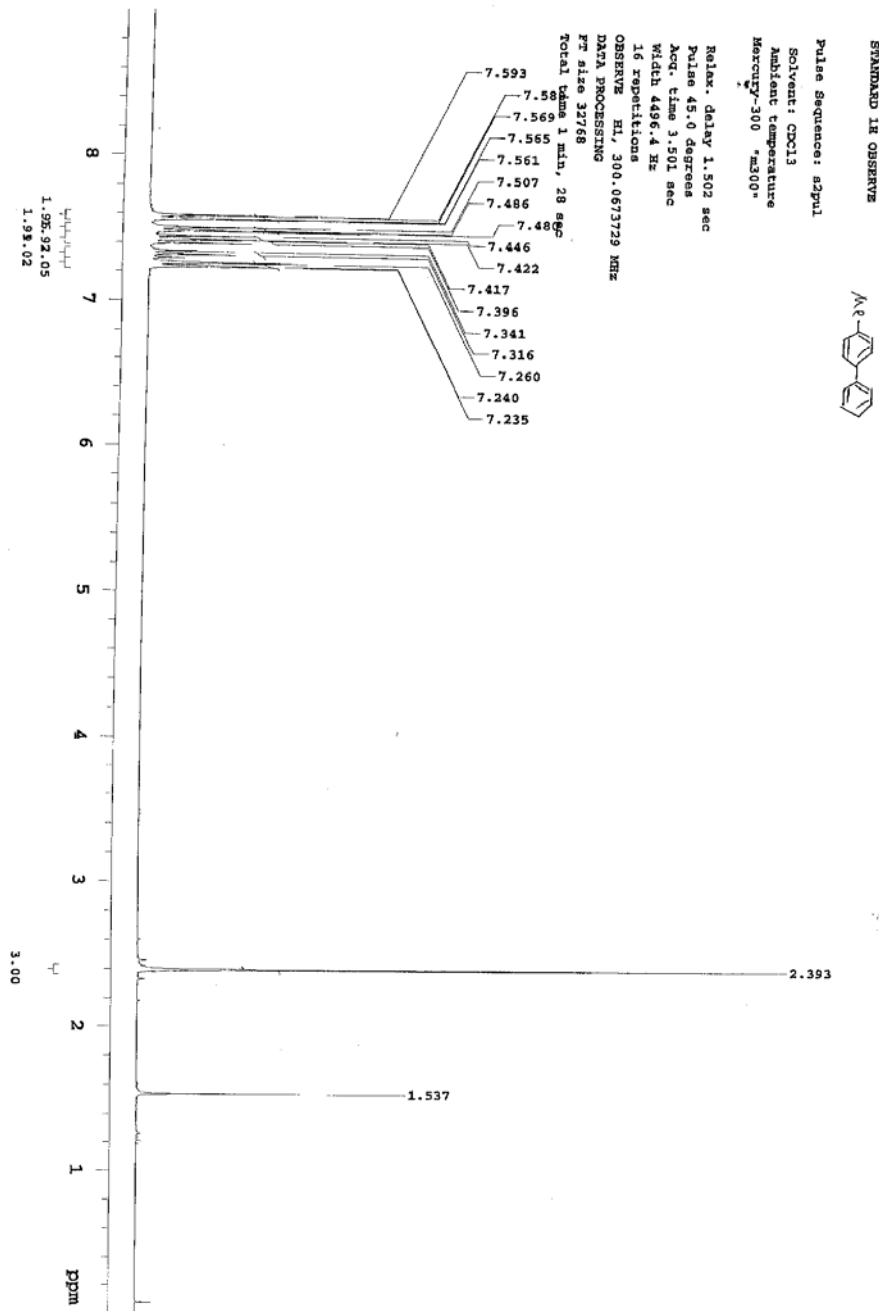
¹H NMR spectrum of **6b**



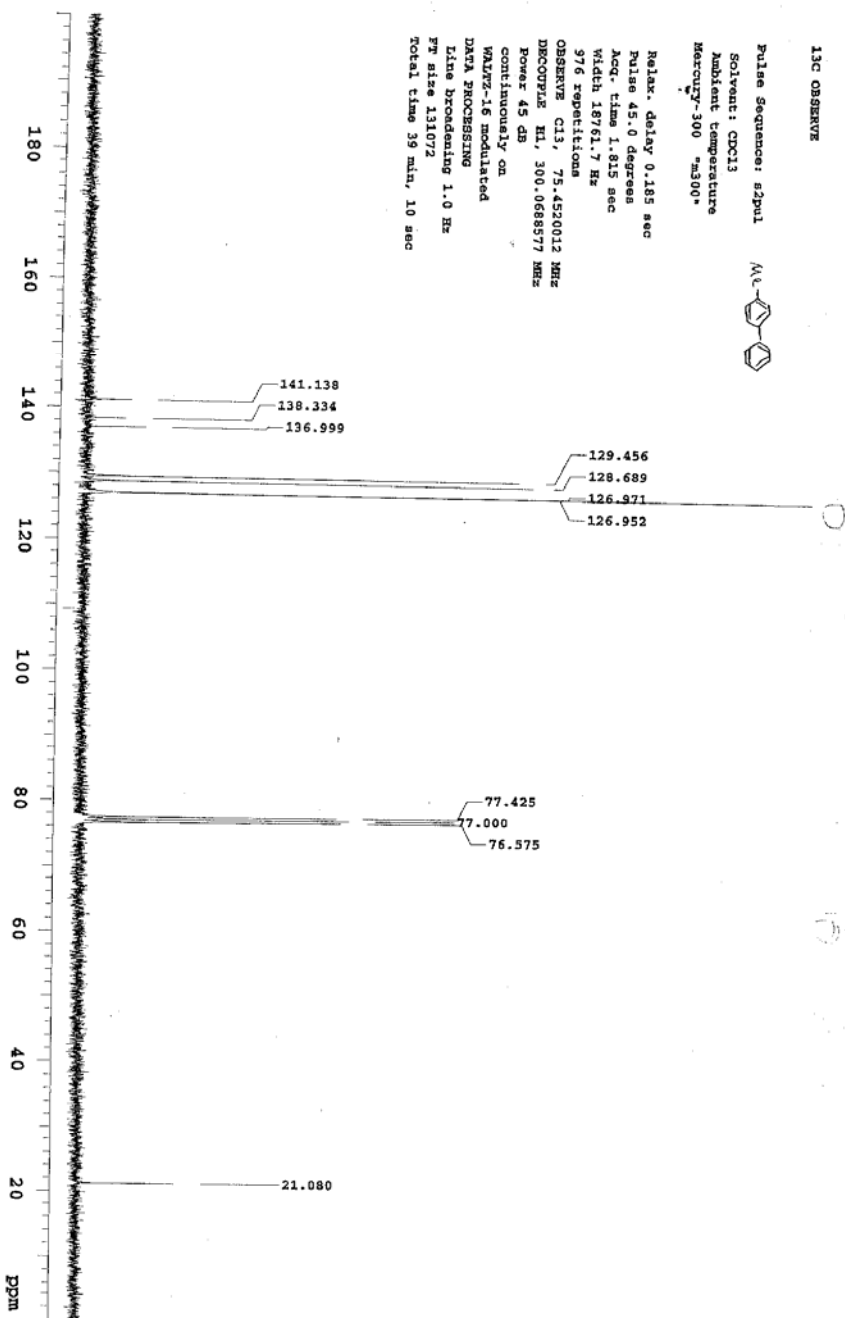
¹³C NMR spectrum of **6b**



¹H NMR spectrum of **6c**



¹³C NMR spectrum of **6c**



¹³C OBSERVE



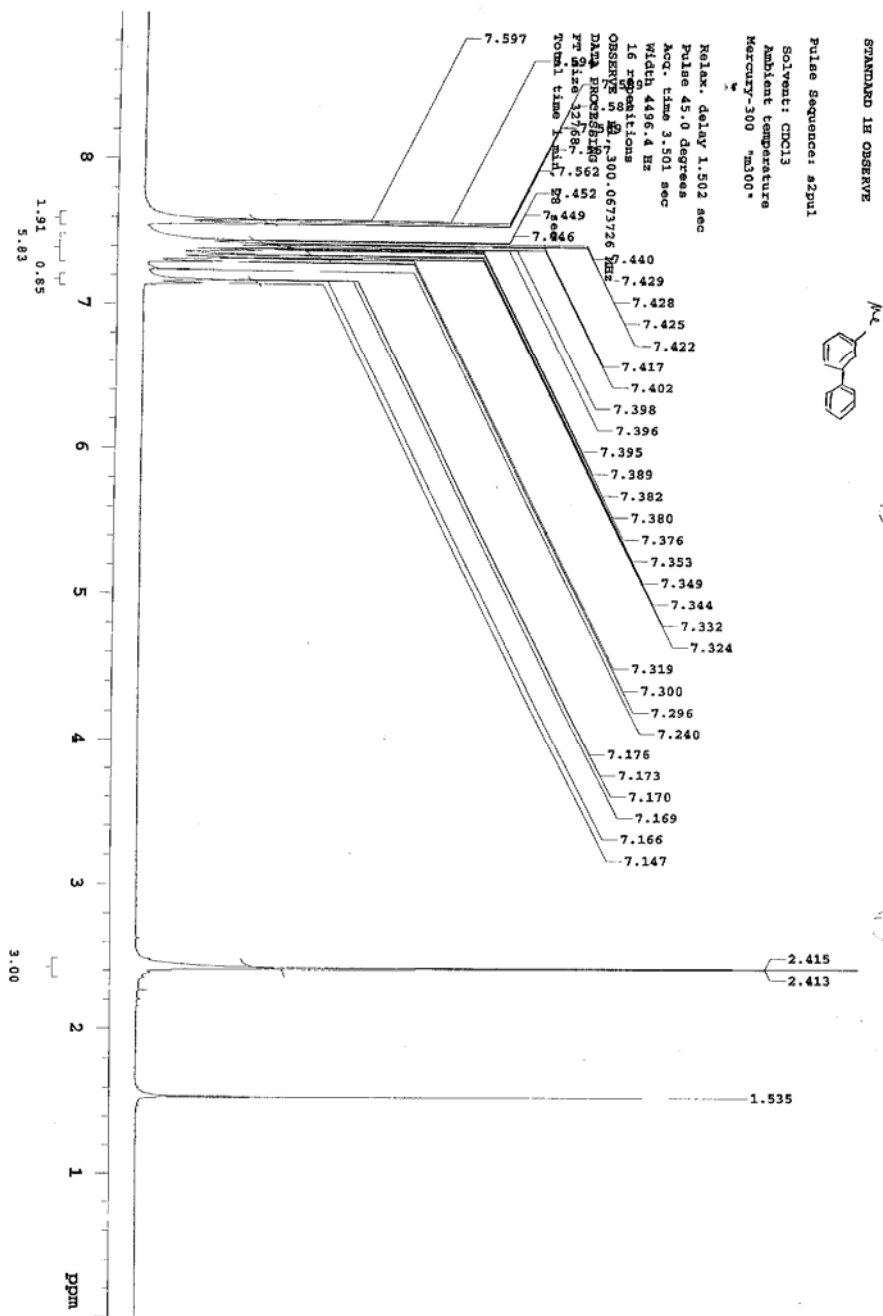
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Pulse 45.0 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
976 repetitions

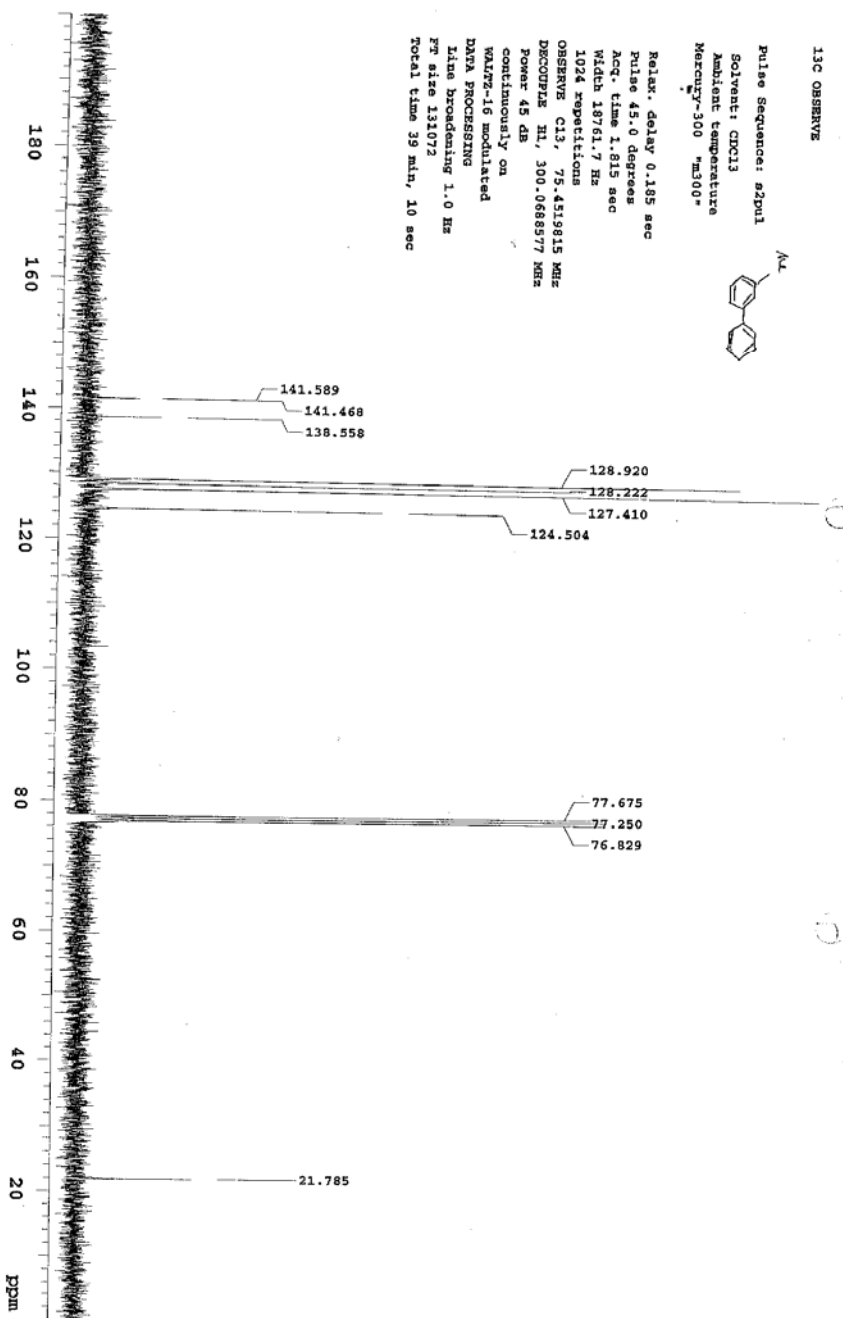
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DATA PROCESSING
Line broadening 1.0 Hz
FM size 131072
Total time 39 min, 10 sec

537

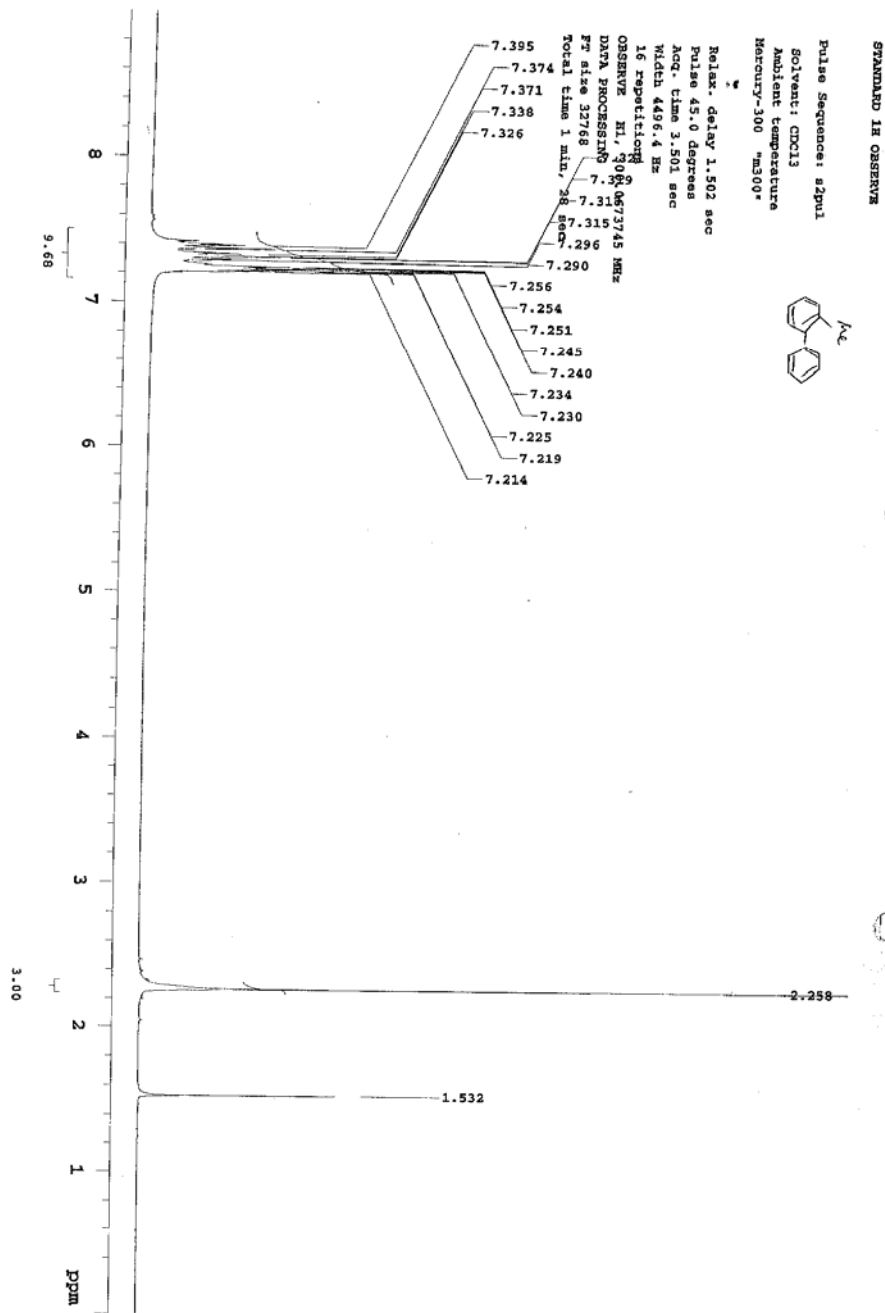
¹H NMR spectrum of **6d**



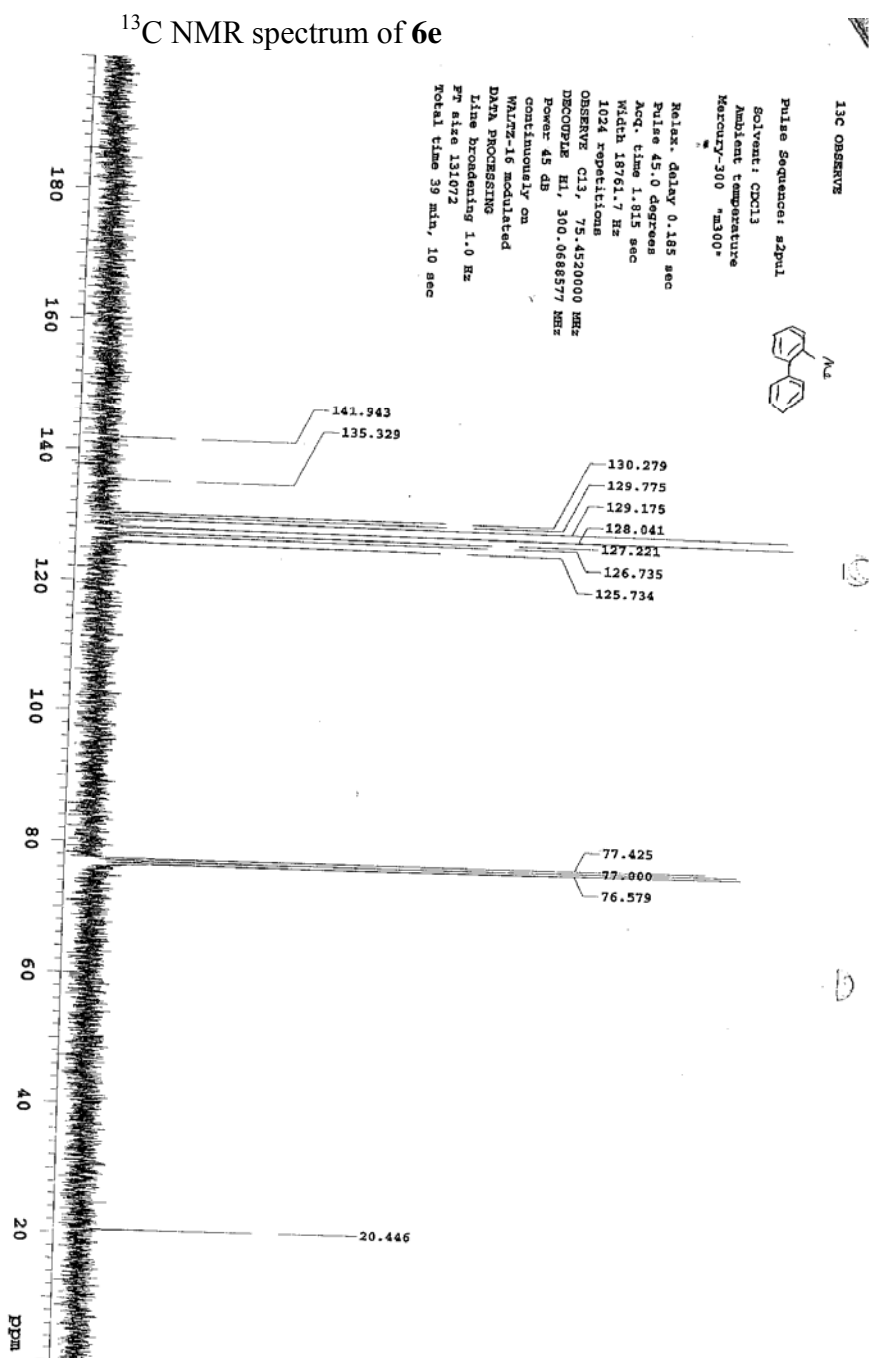
¹³C NMR spectrum of **6d**

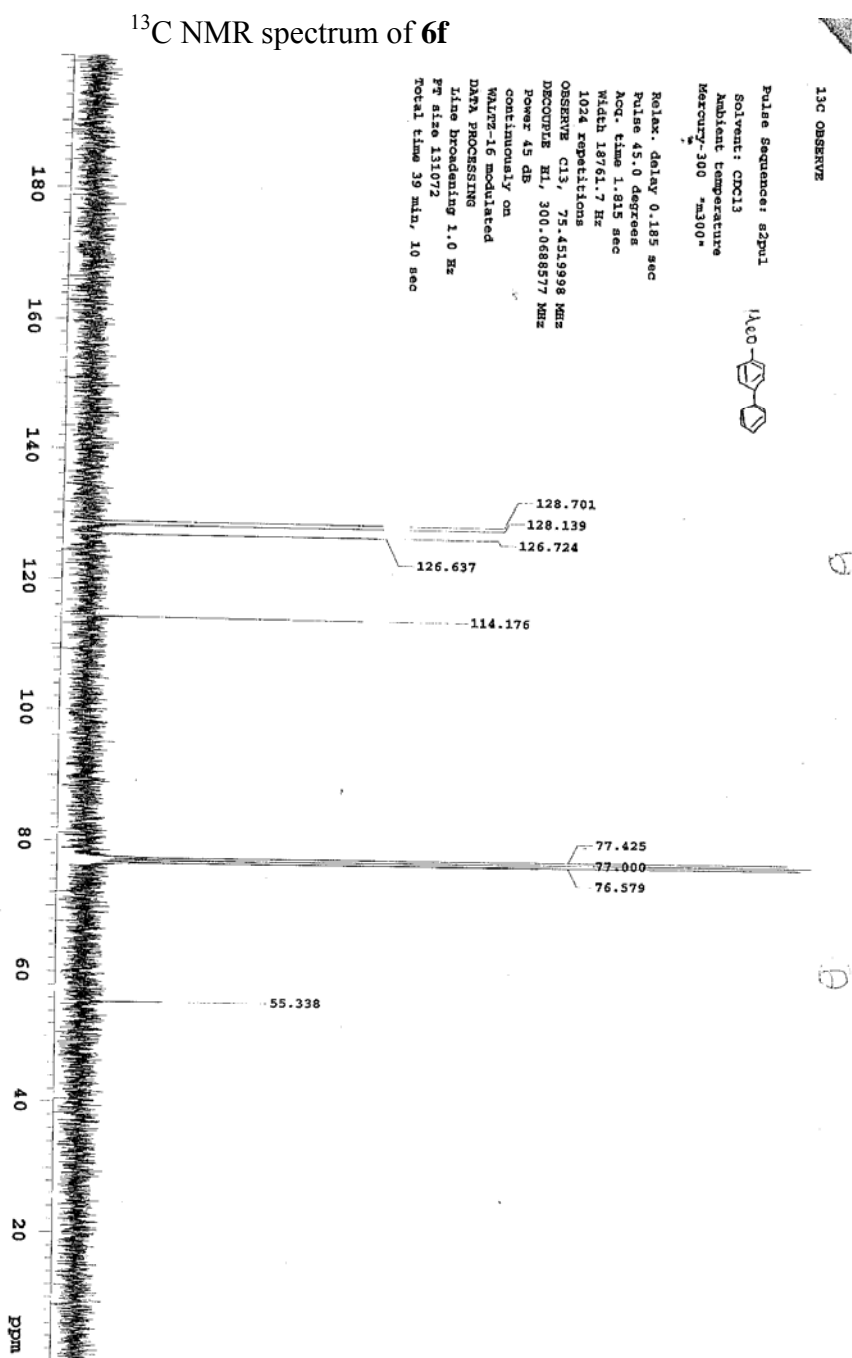


^1H NMR spectrum of **6e**

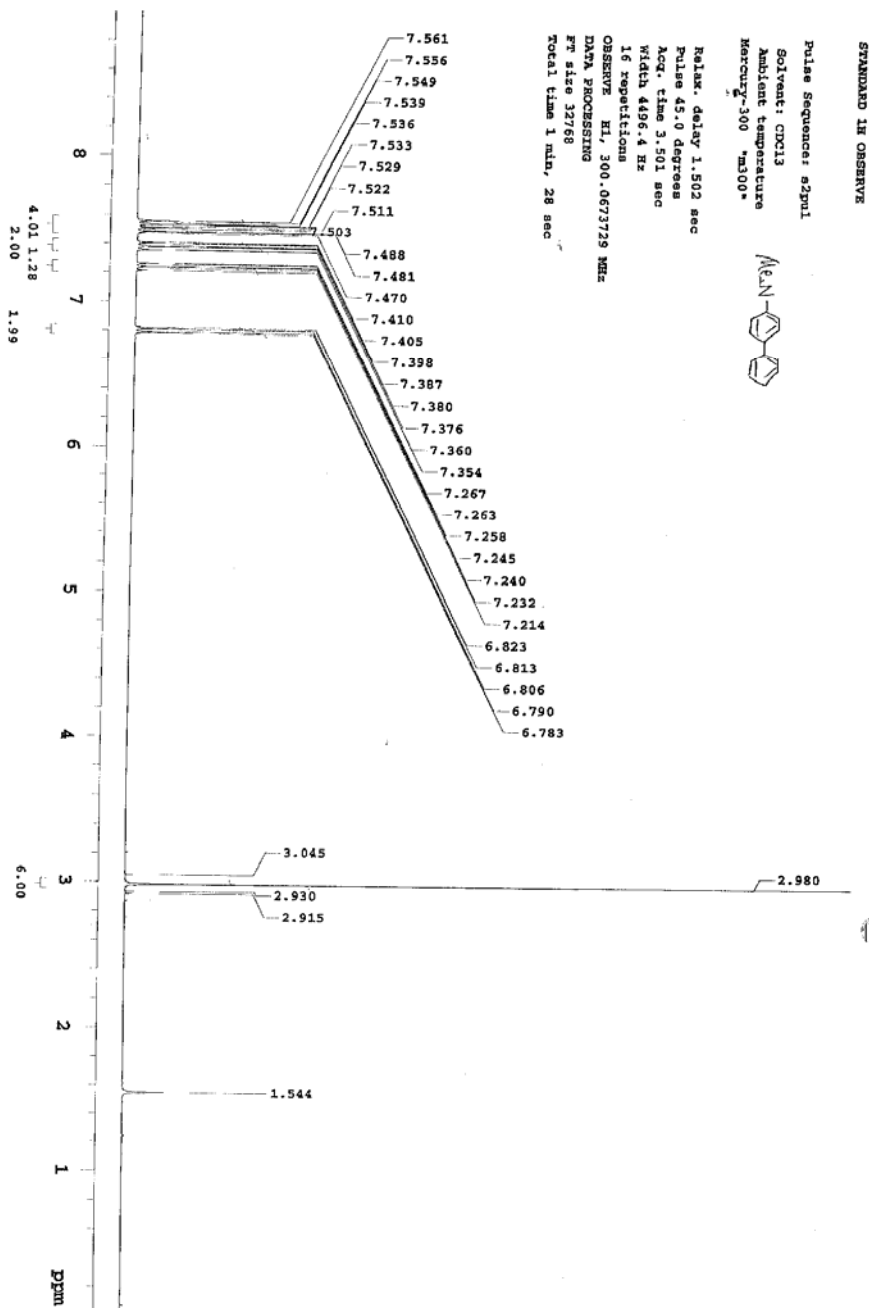


S 40

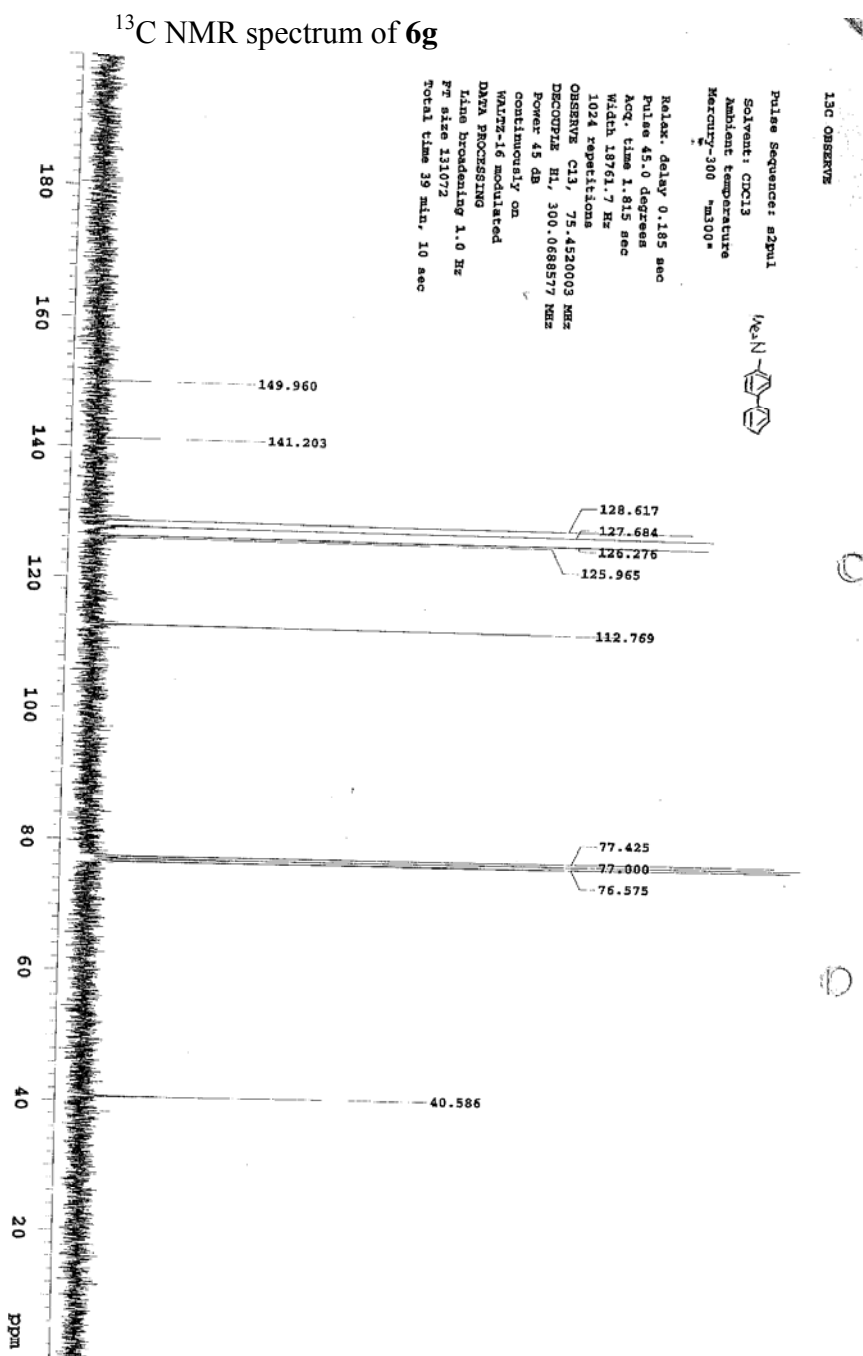


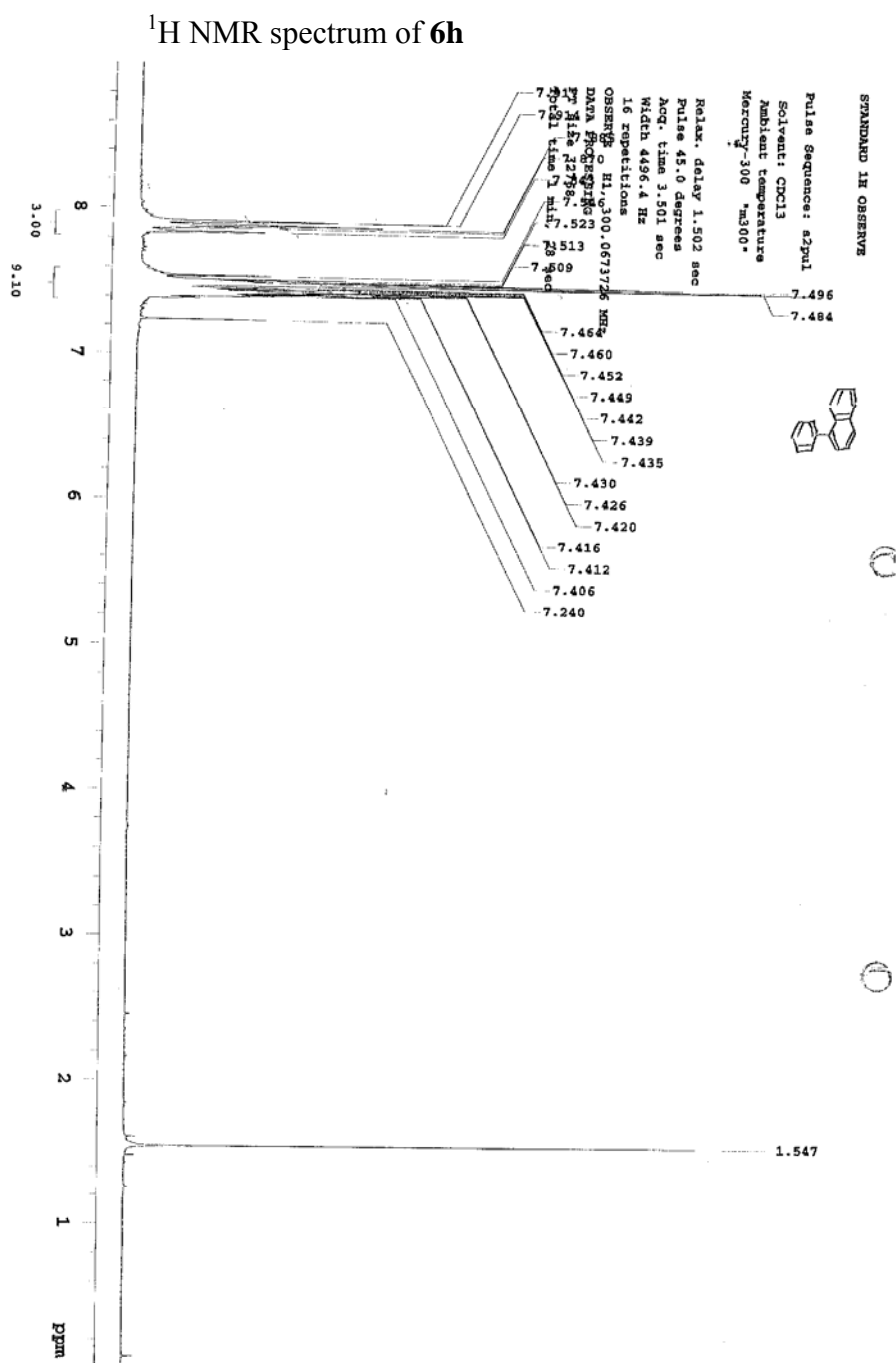


¹H NMR spectrum of 6g



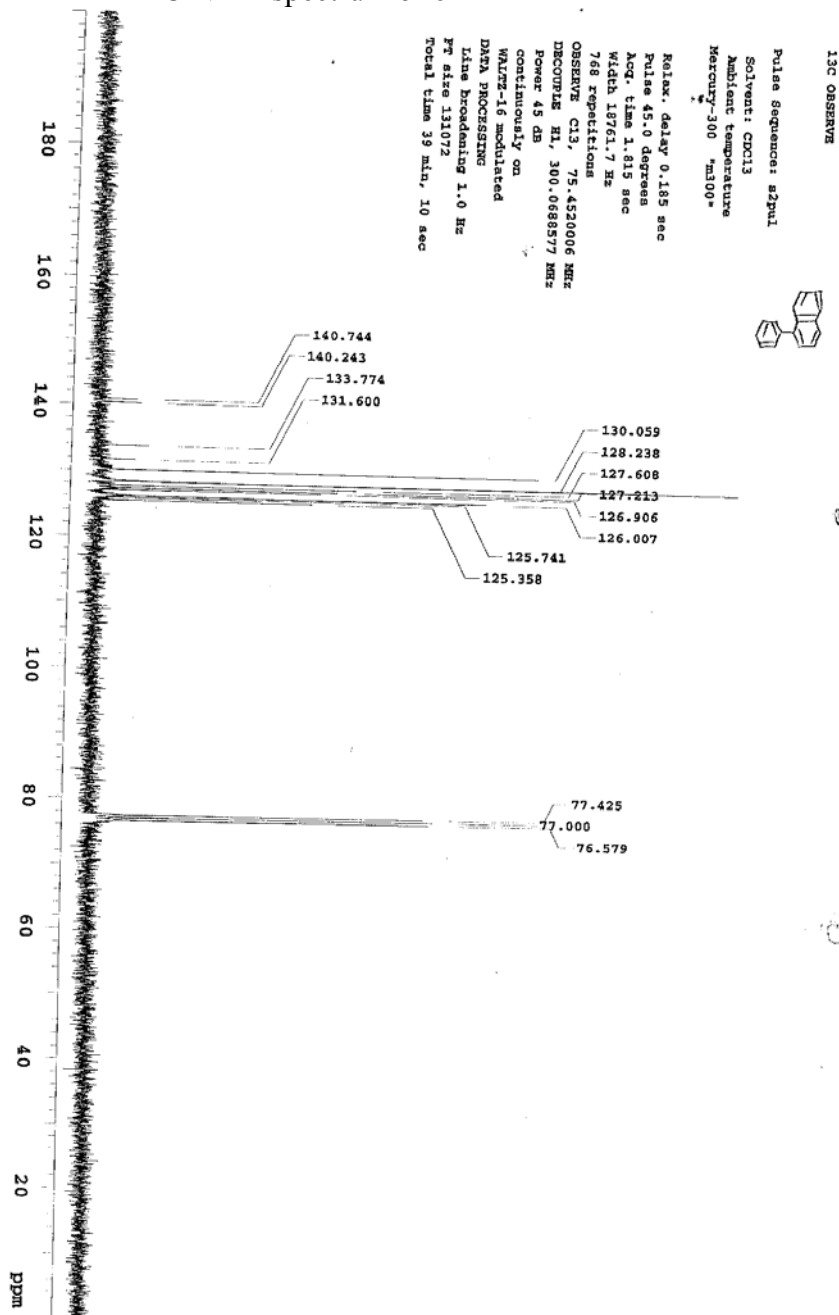
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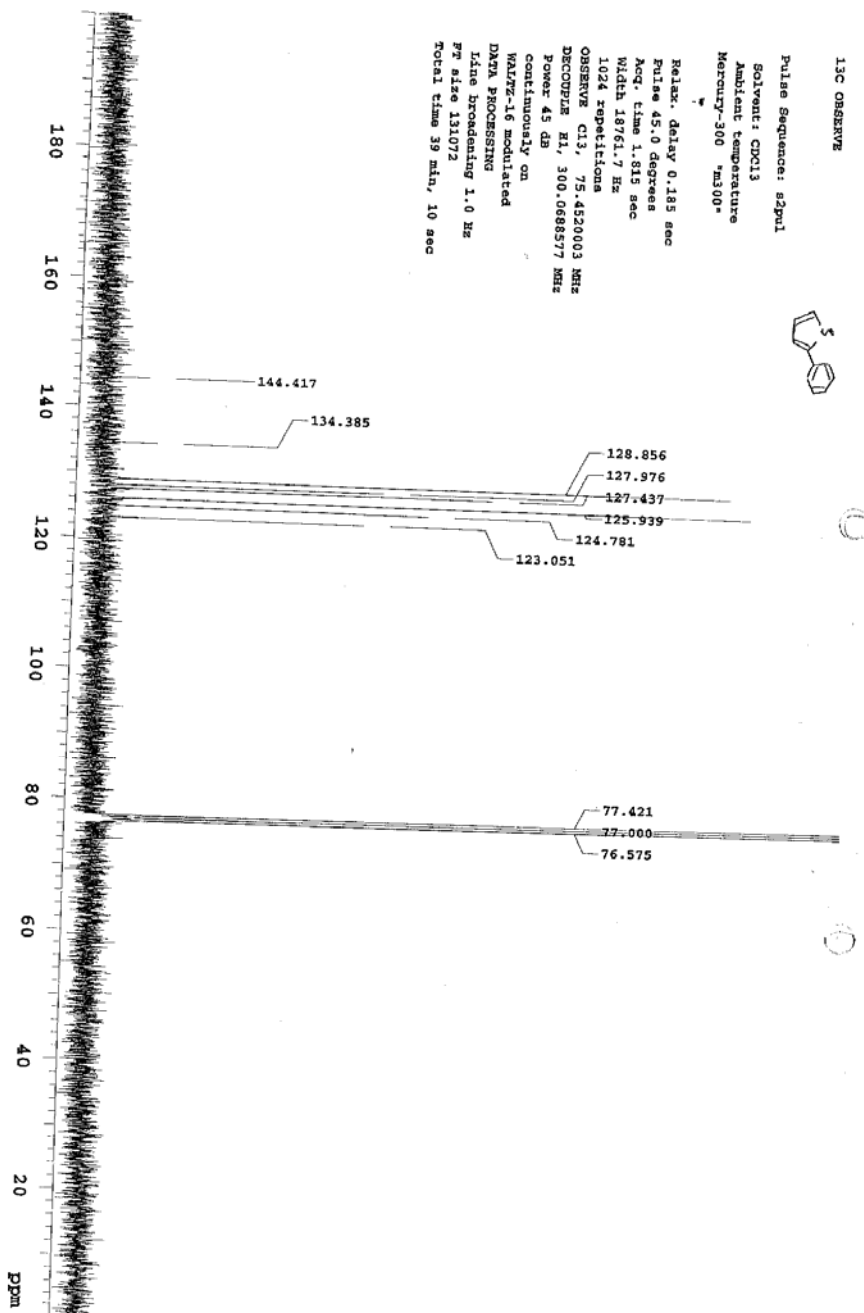


S-16

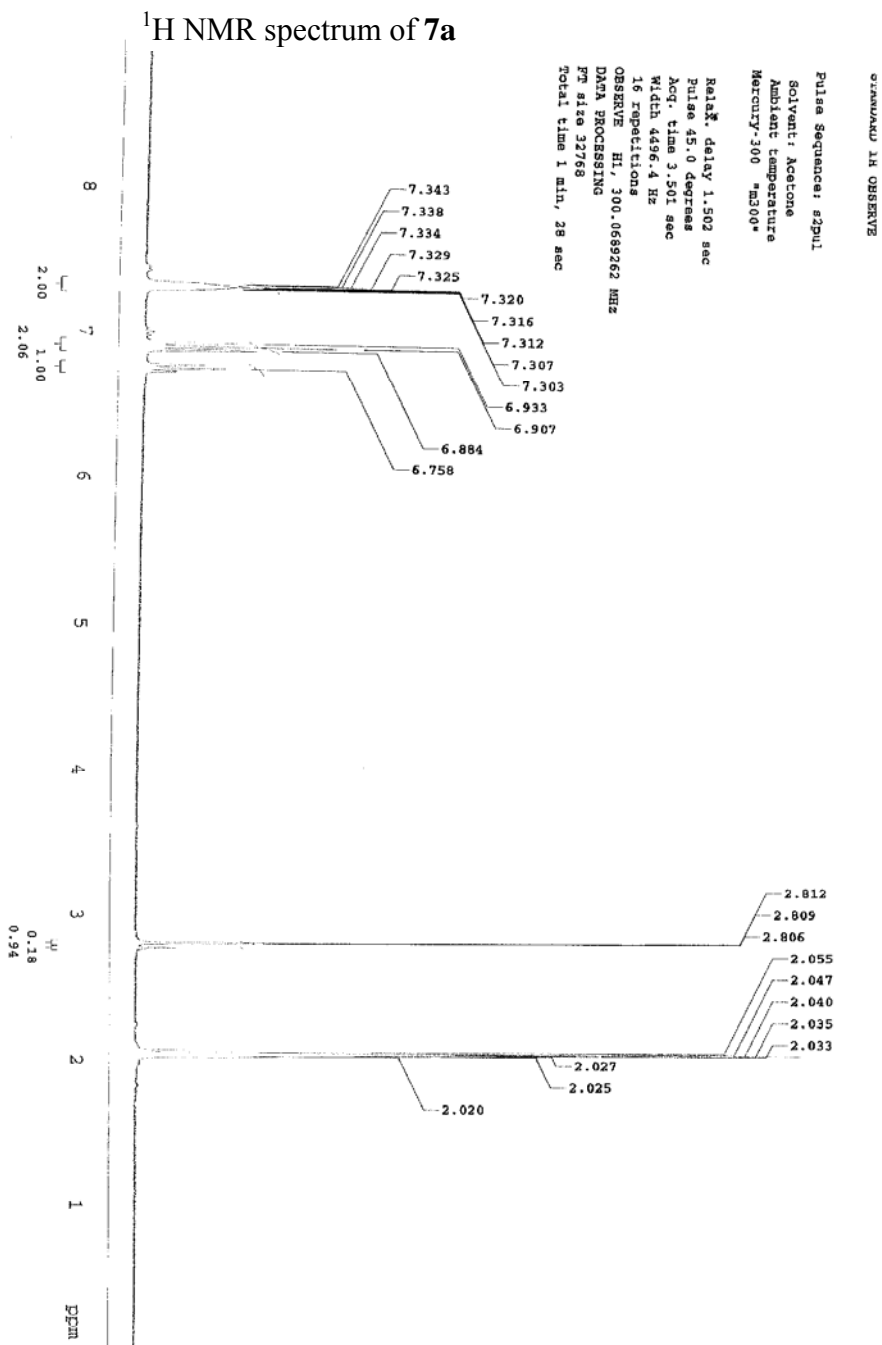
¹³C NMR spectrum of **6h**



^{13}C NMR spectrum of **6i**



529



550

ESR spectrum of vanadium(IV) species

