Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Connecting a carbonyl and a π-conjugated group through a *p*-phenylene linker by (5 + 1) benzene ring formation

Tatsuya Morofuji*, Hanae Kinoshita, Naokazu Kano*

† Department of Chemistry, Faculty of Science, Gakushuin University, 1-5-1 Mejiro, Toshima-ku, Tokyo 171-8588, Japan

*tatsuya.morofuji@gakushuin.ac.jp
*naokazu.kano@gakushuin.ac.jp

1. General

Pyridine (**7a**), 4-phenylpyridine (**7b**), and 4-*tert*-butylpyridine (**7i**) were commercially available. 4-(2-Naphthyl)pyridine (**7d**), [1] 4-(1-pyrenyl)pyridine (**7f**), [2] 4-(diphenylamino)pyridine (**7g**), [3] *N*-(2,4-dinitrophenyl)pyridinium chloride (**8a**),[4] *N*-(2,4-dinitrophenyl)-4-phenylpyridinium chloride (**8b**),[5] and *N*-(2,4-dinitrophenyl)-4-*tert*-butylpyridinium chloride (**8i**)[5] were synthesized according to the reported literature. 1-Methyl-3-acetylindole[6] and 4,4',4"-triacetyltriphenylamine[7] were synthesized according to the literature. Other methyl ketones were purchased and used. THF was purified by an MBraun solvent purification system (MB-SPS-compact). Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Flash chromatography was carried out on a silica gel (Kanto Chem. Co., Silica Gel N, spherical, neutral, 40-100 μm). (5 + 1) Annulation was carried out in a pressure tube with a Teflon screw cap (40 mL) (Figure S1). Gram scale (5 + 1) annulation was carried out in a pressure tube with a Teflon screw cap (400 mL) (Figure S2). All NMR spectra were measured on Unity Inova-400 instrument (Varian Inc., 400 MHz for ^{1}H, 100 MHz for ^{13}C) or AVANCE III HD Nano Bay (Bruker Co., 400 MHz for ^{1}H, 100 MHz for ^{13}C) at 22 ºC using $CDCl_3$ as a solvent unless otherwise noted. Tetramethylsilane (TMS) ($\delta = 0$) or $CHCl_3$ ($\delta = 7.26$) served as an internal standard for ^{1}H NMR spectra, and $CDCl_3$ was used as an internal standard ($\delta = 77.0$) for ^{13}C NMR spectra.

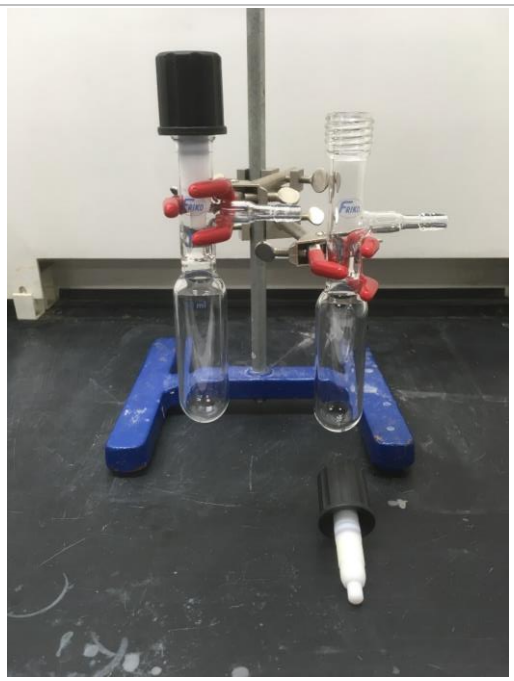


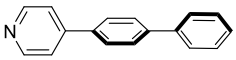
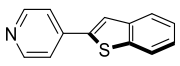
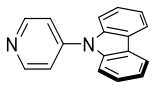
Figure S1. Pressure tube (40 mL), closed (left), open (right).

Figure S2. Pressure tube (400 mL).

[1] A. Asai, J. Sawada, K. Matsumoro, N. Ogo, J. Nishigaki, M. Kojima, JP2008120699 (A)
[2] J. Creus, R. Matheu, I. Peñafiel, D. Moonshiram, P. Blondeau, J. Benet-Buchholz, J. García-Antón, X. Sala, *Angew. Chem. Int. Ed*., 2016, **55**, 15382–15386.
[3] A. Morandeira, I. Lopez-Duarte, B. O'Regan, M. V. Martinez-Diaz, A. Forneli, E. Palomares, T. Torres, J. R. Durranta. *J. Mater. Chem.*, 2009, **19**, 5016–5026.
[4] A. Y. Hong, C. D. Vanderwal, *J. Am. Chem. Soc.*, 2015, **137**, 7306–7309.
[5] K. K. Redda, K. N. Rao, A. S. Heiman, F. Y. Onayemi, J. B. Clark, *Chem. Pharm. Bull*., **1991**, *39*, 786–791.
[6] F. Zhang, Y. Zhao, L. Sun, L. Ding, Y. Gu, P. Gong, *Eur. J. Med. Chem*., 2011, **46**, 3149–3157.
[7] B. Adlilzzi, I. A. W. Filot, A. R. A. Palmans, E. W. Meijer, *Chem. Eur. J*., 2017, **23**, 6103–6110.

Synthesis of streptocyanines

2-1. Synthesis of 4-substituted pyridines

 **7c**	**4-(4-biphenylyl)pyridine (7c).**[8] To a 100 mL flask equipped with a magnetic stirring bar and a reflux condenser, 4-biphenylboronic acid (2.28 g, 12 mmol), 4-bromopyridine hydrochloride (1.92 g, 9.9 mmol), Cs_2CO_3 (6.45 g, 20 mmol), $Pd(PPh_3)_4$ (0.91 g, 8 mol%), and DME/H_2O (60 mL/15 mL) were added. The mixture was refluxed for overnight, and extracted with EtOAc (50 mL × 3). Combined extracts were washed with brine (50 mL), and was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the crude product was purified with flash chromatography to obtain the title compound (1.33 g, 58%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, 2H, J = 6.0 Hz), 7.73 (s, 4H), 7.65 (d, 2H, J = 8.4 Hz), 7.56 (d, 2H, J = 6.0 Hz), 7.48 (t, 2H, J = 7.6 Hz), 7.39 (t, 1H, J = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3, 147.8, 142.0, 140.2, 136.9, 128.9, 127.8, 127.7, 127.4, 127.1, 121.4.
 **7e**	**4-(2-benzothiophenyl)pyridine (7e).**[9] To a 100 mL flask equipped with a magnetic stirring bar and a reflux condenser, benzo[*b*]thiophene-2-boronic acid (1.96 g, 11 mmol), 4-bromopyridine hydrochloride (1.94 g, 10 mmol), K_2CO_3 (4.21 g, 30 mmol), $Bu_4N^+Br^-$ (3.23 g, 10 mmol), $Pd(OAc)_2$ (0.25 g, 10 mol%), and toluene/H_2O (45 mL/10 mL) were added. The mixture was refluxed for overnight. The organic layer was washed with H_2O (50 mL × 3) and was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the crude product was purified with flash chromatography to obtain the title compound (0.96 g, 46%) as pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (d, 2H, J = 4.8 Hz), 7.82-7.87 (m, 2H), 7.73 (s, 1H), 7.58 (m, 2H), 7.38-7.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 141.4, 140.9, 140.1, 139.9, 125.5, 124.9, 124.3, 122.5, 122.1, 120.5.
 **7h**	**4-(1-carbazolyl)pyridine (7h).**[10] To a 100 mL flask equipped with a magnetic stirring bar and a reflux condenser, carbazole (1.68 g, 10 mmol), 4-bromopyridine hydrochloride (2.93 g, 15 mmol), NaO^{t}Bu (3.91 g, 41 mmol), ^{t}Bu$_3$PH$^+$ · BF$_4^-$ (0.29 g, 10 mol%), $Pd(dba)_2$ (0.51 g, 10 mol%), and *o*-xylene/H_2O (60 mL/15 mL) were added. The mixture was stirred at 160 ºC for 2 days, and extracted with EtOAc (50 mL × 3). Combined extracts were washed with brine (50 mL), and was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the crude product

[8] O. Kobayashi, D. Uraguchi, T. Yamakawa, *Org. Lett.*, 2009, **11**, 2679–2682.
[9] D. Ghosh, H. M. Lee, *Org. Lett.*, 2012, **14**, 5534–5537.
[10] W-J. Yoo, T. Tsukamoto, S. Kobayashi, *Org. Lett.*, 2015, **17**, 3640–3642.

	was purified with flash chromatography to obtain the title compound (2.08 g, 85%) as pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.83 (d, 2H, *J* = 6.0 Hz), 8.13 (d, 2H, *J* = 7.6 Hz), 7.54-7.58 (m, 4H), 7.43 (t, 2H, *J* = 7.6 Hz), 7.33 (t, 2H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 145.5, 139.5, 126.4, 124.2, 121.1, 120.6, 109.8. (one peak is missing)

2-2. General synthesis of streptocyanines

Synthetic procedure of streptocyanines **2** was described as follows (Figure S3).

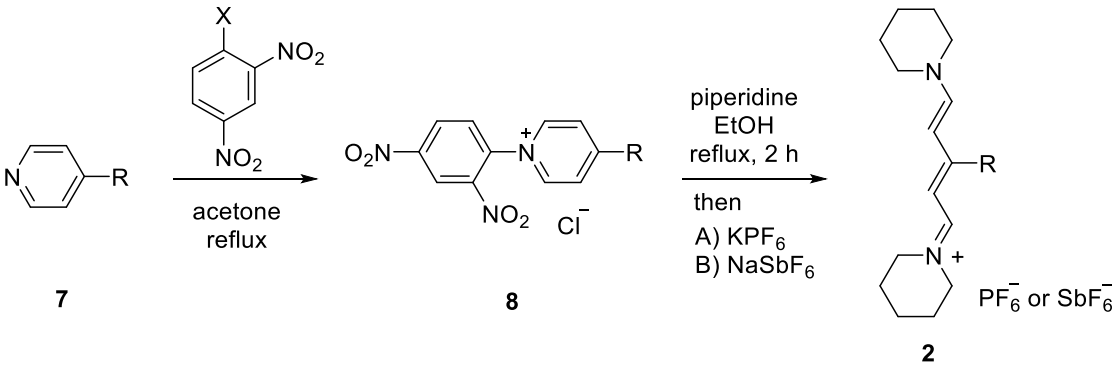
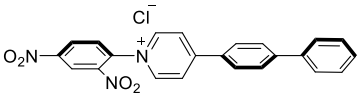
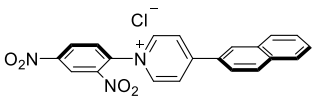
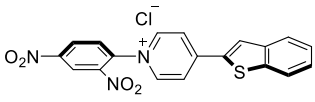
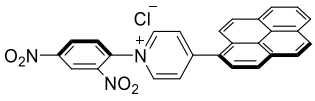


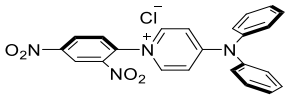
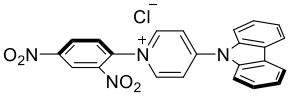
Figure S3. Synthetic procedure of streptocyanines **2**.

Synthetic procedure of *N*-(2,4-dinitrophenyl)pyridinium chlorides 8.

To a 100 mL flask equipped with a magnetic stirring bar and a reflux condenser, 4-substituted pyridine (**7**), 2,5-dinitrochlorobenzene, and acetone were added. The mixture was refluxed for hours under argon atmosphere. The mixture was cooled to room temperature, and precipitate was collected by filtration and washed with hexane. The resulting solid was dried under vacuum to give the corresponding pyridinium salt **8**.

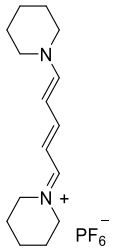
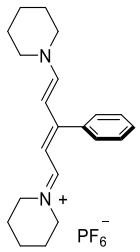
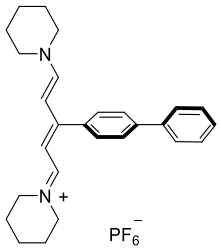
 **8c**	***N*-(2,4-dinitrophenyl)-4-(4-biphenylyl)pyridinium chloride (8c)** Reaction of 4-(4-biphenylyl)pyridine (**7c**) (1.27 g, 5.5 mmol) and 2,5-dinitrochlorobenzene (3.40 g, 16.8 mmol) in acetone (30 mL) with refluxing for 24 h gave the title compound (1.26 g, 53%, pale yellow solid). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.43 (d, 2H, *J* = 5.6 Hz), 9.11 (d, 1H, *J* = 2.0 Hz), 8.97 (dd, 1H, *J* = 2.0, 6.8 Hz), 8.90 (d, 2H, *J* = 5.6 Hz), 8.47 (d, 1H, *J* = 8.8 Hz), 8.37 (d, 2H, *J* = 8.0 Hz), 8.01 (d, 2H, *J* = 8.4 Hz), 7.83 (d, 2H, *J* = 7.6 Hz), 7.42-7.54 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 157.1, 149.5, 146.3, 145.0, 143.7, 139.0, 138.8, 132.6, 132.2, 130.7, 129.9, 129.6, 129.2, 128.4, 127.5, 124.2, 121.9; IR (KBr): 3426, 2926, 1631, 1599, 1543, 1479, 1457, 1342, 1223, 836, 774, 702 cm^{-1}; HRMS (ESI): calcd. for $[M-Cl]^+$ $C_{23}H_{16}N_3O_4$, 398.11353, found: 398.1135; m.p. (decomp.) 230-231 ºC.

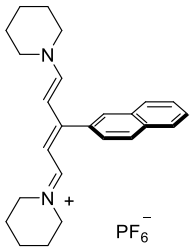
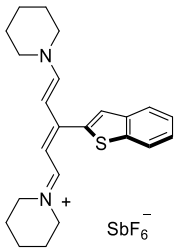
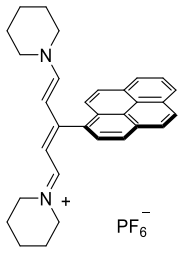
 **8d**	***N*-(2,4-dinitrophenyl)-4-(2-napthyl)pyridinium chloride (8d)** Reaction of 4-(2-naphthyl)pyridine (**7d**) (0.64 g, 3.1 mmol) and 2,5-dinitrochlorobenzene (0.67 g, 3.1 mmol) in acetone (5 mL) with refluxing for 6 h gave the title compound (0.82 g, 71%, yellow solid). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.54 (s, 2H), 9.16 (d, 1H, J = 2.4 Hz), 9.01-9.06 (m, 4H), 8.54 (dd, 1H, J = 3.6, 8.8 Hz), 8.34 (d, 1H, J = 8.8 Hz), 8.24 (d, 1H, J = 8.8 Hz), 8.18 (d, 1H, J = 7.6 Hz), 8.10 (d, 1H, J = 8.0 Hz), 7.75 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 157.7, 149.5, 146.4, 143.7, 139.1, 135.2, 133.3, 132.7, 130.8, 130.7, 130.1, 130.0, 129.6, 128.3, 128.0, 124.7, 124.6, 121.9 (one peak was missing); IR (KBr): 2920, 1637, 1612, 1544, 1465, 1344, 1229, 835, 819, 474 cm^{-1}; HRMS (ESI): calcd. for $[M-Cl]^+$ $C_{21}H_{14}N_3O_4$, 372.09788, found: 372.0982; m.p. (decomp.) 226-228 ºC.
 **8e**	***N*-(2,4-Dinitrophenyl)-4-(2-benzothiophenyl)pyridinium chloride (8e)** Reaction of 4-(2-benzothiophenyl)pyridine (**7e**) (0.90 g, 4.3 mmol) and 2,5-dinitrochlorobenzene (0.89 g, 4.3 mmol) in acetone (10 mL) with refluxing for 16 h gave the title compound (0.85 g, 48%, yellow solid). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.41 (d, 2H, J = 6.4 Hz), 9.14 (d, 1H, J = 2.0 Hz), 9.00 (dd, 1H, J = 2.0, 8.4 Hz), 8.93 (s, 1H), 8.80 (d, 2H, J = 6.8 Hz), 8.49 (d, 1H, J = 8.8 Hz), 8.23 (d, 1H, J = 8.0 Hz), 8.10 (d, 1H, J = 7.6 Hz), 7.55-7.64 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 151.3, 149.5, 146.5, 143.7, 142.4, 140.2, 139.0, 136.9, 132.6, 131.8, 130.7, 128.7, 126.6, 126.5, 123.8, 123.4, 121.9; IR (KBr): 1629, 1545, 1518, 1461, 1421, 1341, 1222, 835, 851, 723 cm^{-1}; HRMS (ESI): calcd. for $[M-Cl]^+$ $C_{19}H_{12}N_3O_4S_1$, 378.05430, found: 378.0548; m.p. (decomp.) 207-211 ºC.
 **8f**	***N*-(2,4-dinitrophenyl)-4-(1-pyrenyl)pyridinium chloride (8f)** Reaction of 4-(1-pyrenyl)pyridine (**7f**) (1.43 g, 5.1 mmol) and 2,5-dinitrochlorobenzene (1.11 g, 5.1 mmol) in acetone (10 mL) with refluxing for 16 h gave the title compound (2.29 g, 99%, red solid). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.62 (d, 2H, J = 6.4 Hz), 9.21 (d, 1H, J = 2.4 Hz), 9.09 (dd, 1H, J = 2.4, 8.6 Hz), 8.82 (d, 2H, J = 6.8 Hz), 8.56-8.62 (m, 2H), 8.31-8.50 (m, 7H), 8.22 (t, 1H, J = 7.6 Hz); ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.8, 149.6, 146.2, 143.7, 139.3, 133.3, 132.6, 131.3, 130.8, 130.7, 130.3, 130.1, 129.3, 128.5, 128.4, 127.7, 127.6, 127.3, 126.8, 125.9, 124.5, 124.0, 123.4, 122.0 (one peak is missing); IR (KBr): 2997, 1633, 1608, 1538, 1456, 1334, 1276, 1212, 901, 854, 844, 724 cm^{-1}; HRMS (ESI): calcd. for $[M-Cl]^+$ $C_{27}H_{16}N_3O_4$, 446.11353, found: 446.1135; m.p. (decomp,) 210-214 ºC.

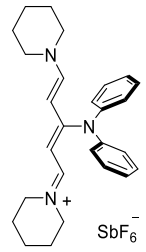
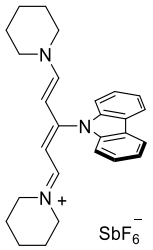
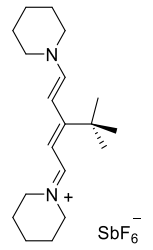
 **8g**	***N*-(2,4-dinitrophenyl)-4-(diphenylamino)pyridinium chloride (8g)** Reaction of 4-(diphenylamino)pyridine (**7g**) (2.41 g, 9.8 mmol) and 2,5-dinitrochlorobenzene (2.05 g, 10 mmol) in acetone (10 mL) with refluxing for 4.5 h gave the title compound (3.75 g, 86%, pale yellow solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.05 (d, 1H, *J* = 2.4 Hz), 8.88 (dd, 1H, *J* = 2.4, 8.8 Hz), 8.64 (d, 2H, *J* = 7.2 Hz), 8.28 (d, 1H, *J* = 8.8 Hz), 7.62-7.68 (m, 8H), 7.52-7.55 (m, 2H), 6.92 (d, 2H, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2, 148.8, 144.5, 144.2, 142.1, 139.2, 132.5, 131.4, 130.5, 129.7, 127.7, 122.0, 110.2; IR (KBr): 3400, 1644, 1607, 1512, 1485, 1386, 1348, 1214, 1078, 833, 766, 701 cm^{-1}; HRMS (ESI): calcd. for $[M-Cl]^+$ $C_{23}H_{17}N_4O_4$, 413.12443, found: 413.1247; m.p. (decomp.) 227-234 ºC.
 **8h**	***N*-(2,4-dinitrophenyl)-4-(*N*-carbazolyl)pyridinium chloride (8h)** Reaction of 4-(*N*-carbazolyl)pyridine (**7h**) (2.03 g, 8.3 mmol) and 2,5-dinitrochlorobenzene (1.70 g, 8.3 mmol) in acetone (15 mL) with refluxing for 14 h gave the title compound (2.32 g, 63%, yellow solid). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.46 (d, 2H, *J* = 6.8 Hz), 9.17 (d, 1H, *J* = 2.0 Hz), 9.03 (dd, 1H, *J* = 2.4, 8.8 Hz), 8.81 (d, 2H, *J* = 7.6 Hz), 8.50 (d, 1H, *J* = 8.8 Hz), 8.37 (d, 2H, *J* = 7.6 Hz), 8.03 (d, 2H, *J* = 8.4 Hz), 7.64 (t, 2H, *J* = 7.4 Hz), 7.54 (t, 2H, *J* = 7.4 Hz); ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.3, 149.5, 147.7, 143.9, 139.1, 138.3, 132.7, 130.7, 128.0, 126.0, 124.5, 122.0, 121.8, 121.7, 112.1; IR (KBr): 1636, 1604, 1510, 1446, 1380, 1334, 1219, 843, 751 cm^{-1}; HRMS (ESI): calcd. for $[M-Cl]^+$ $C_{23}H_{15}N_4O_4$, 411.10878, found: 411.1087; m.p. (decomp.) 222-226 ºC.

Conversion of pyridinium salt 8 to streptocyanines 2.

To a 50 mL or 100 mL flask equipped with a magnetic stirring bar and a reflux condenser, pyridinium salt **8**, EtOH, and piperidine were added. The resulting mixture was stirred at 80 ºC for 2 hours under argon atmosphere. After the heating, the mixture was cooled to room temperature. Aqueous solution of NH_4PF_6, KPF_6, or $NaSbF_6$ (0.3 M) was added to the mixture, and yellow or orange solid was precipitated. The precipitate was collected by filtration and washed with H_2O and Et_2O. The resulting solid was dried under vacuum to give streptocyanine **2**. Streptocyanines **2** were used for (5 + 1) annulation without further purification.

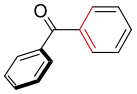
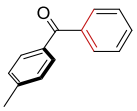
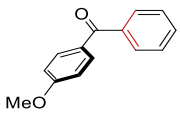
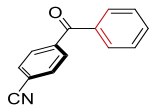
 **2a**	**1-[5-(1-piperidinyl)-2,4-pentadienylidene]piperidinium hexafluorophosphate (2a)** Reaction of pyridinium **8a** (5.66 g, 20 mmol) and piperidine (5.95 mL, 60 mmol) in EtOH (35 mL) and following salt exchange with NH_4PF_6 (3.56 g, 20 mmol) gave the title compound (6.89 g, 91%, orange solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (t, 1H, *J* = 12.4 Hz), 7.39 (d, 2H, *J* = 11.6 Hz), 5.78 (t, 2H, *J* = 12.2 Hz), 3.55 (br, 4H), 3.48 (br, 4H), 1.72 (br, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 159.6, 102.4, 56.5, 47.5, 26.7, 25.4, 23.5; IR (KBr): 1652, 1558, 1452, 1176, 1022, 993, 839, 556 cm^{-1}; HRMS (ESI): calcd. for $[M-PF_6]^+$ $C_{15}H_{25}N_2^+$, 233.2012, found: 233.2021; m.p. (decomp.) 154-155 ºC.
 **2b**	**1-[3-phenyl-5-(1-piperidinyl)-2,4-pentadienylidene]piperidinium hexafluorophosphate (2b)** Reaction of pyridinium **8b** (2.83 g, 7.9 mmol) and piperidine (2.37 mL, 24 mmol) in EtOH (20 mL) and following salt exchange with KPF_6 (2.91 g, 16 mmol) gave the title compound (3.21 g, 89%, yellow solid). ^{1}H NMR (400 MHz, DMSO-d_6, 100 ºC): δ 7.52-7.50 (m, 3H), 7.32-7.31 (m, 2H), 7.20 (br, 2H), 6.12 (d, 2H, *J* = 12.0 Hz), 3.55 (br, 8H), 1.66 (br, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.5, 156.6, 134.6, 129.6, 129.5, 128.7, 105.2, 57.0, 47.7, 26.8, 25.4, 23.7, 23.6; IR (KBr): 1558, 1517, 1446, 1399, 1210, 1126, 1103, 1000, 837, 773, 557 cm^{-1}; HRMS (ESI): calcd. for $[M-PF_6]^+$ $C_{21}H_{29}N_2^+$, 309.2325, found: 309.2325; m.p. (decomp.) 216-221 ºC.
 **2c**	**1-[3-(4-biphenylyl)-5-(1-piperidinyl)-2,4-pentadienylidene]piperidinium hexafluorophosphate (2c)** Reaction of pyridinium **8c** (1.01 g, 2.3 mmol) and piperidine (0.59 mL, 6.0 mmol) in EtOH (5 mL) and following salt exchange with KPF_6 (0.76 g, 4.1 mmol) gave the title compound (1.04 g, 85%, yellow solid). ^{1}H NMR (400 MHz, DMSO-d_6, 100 ºC): δ 7.81 (d, 2H, *J* = 8.4 Hz), 7.76 (d, 2H, *J* = 7.6 Hz), 7.53 (t, 2H, *J* = 7.8 Hz), 7.43 (d, 3H *J* = 7.6 Hz), 7.33 (br, 2H), 6.16 (d, 2H, *J* = 12.0 Hz), 3.60 (br, 8H), 1.70 (br, 12H); ^{13}C NMR (100 MHz, DMSO-d_6, 100 ºC): δ169.9, 155.5, 140.7, 138.7, 129.2, 128.3, 127.2, 126.1, 126.0, 101.4, 78.4, 25.2, 25.1, 22.3; ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.1, 156.5, 142.3, 139.8, 133.6, 130.1, 129.3, 129.0, 128.0, 127.3, 127.1,

	105.3, 57.0, 47.7, 26.8, 25.4, 23.6; IR (KBr): 1568, 1517, 1448, 1405, 1242, 1213, 1127, 1022, 838, 557 cm^{-1}; HRMS (ESI): calcd. for $[M-PF_6]^+$ $C_{27}H_{33}N_2$, 385.2638, found: 385.2643; m.p. (decomp.) 212-214 ºC.
 **2d**	**1-[3-(3-naphthyl)-5-(1-piperidinyl)-2,4-pentadienylidene]piperidinium hexafluorophosphate (2d)** Reaction of pyridinium **8d** (0.75 g, 1.8 mmol) and piperidine (0.59 mL, 6.0 mmol) in EtOH (5 mL) and following salt exchange with KPF_6 (0.69 g, 3.75 mmol) gave the title compound (0.78 g, 84%, yellow solid). ^{1}H NMR (400 MHz, DMSO-d_6, 100 ºC): δ 8.04 (br, 3H), 7.91 (br, 1H), 7.64 (br, 2H), 7.46 (br, 1H), 7.29 (br, 2H), 6.25 (br, 2H), 3.59 (br, 8H), 1.70 (br, 12H); ^{13}C NMR (100 MHz, CD_3CN): δ 173.1, 157.9, 134.3, 133.7, 133.3, 129.9, 129.2, 128.9, 128.6, 128.2, 127.9, 127.7, 105.0, 57.1, 48.1, 27.2, 26.1, 24.1; IR (KBr): 1627, 1565, 1518, 1447, 1402, 1237, 1128, 1000, 840, 557 cm^{-1}; HRMS (ESI): calcd. for $[M-PF_6]^+$ $C_{25}H_{31}N_2$, 359.2482, found: 359.2499; m.p. (decomp.) 120-124 ºC.
 **2e**	**1-[3-(2-benzothiophenyl)-5-(1-piperidinyl)-2,4-pentadienylidene]piperidinium hexafluoroantimonate (2e)** Reaction of pyridinium **8e** (0.75 g, 1.8 mmol) and piperidine (0.53 mL, 5.4 mmol) in EtOH (8 mL) and following salt exchange with $NaSbF_6$ (0.92 g, 3.8 mmol) gave the title compound (0.87 g, 80%, orange solid). ^{1}H NMR (400 MHz, DMSO-d_6, 100 ºC): δ 7.94-8.02 (m, 2H), 7.68-7.74 (m, 3H), 7.46-7.50 (m, 2H), 6.15-6.22 (m, 2H), 3.64 (br, 8H), 1.70 (br, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, r.t.): δ 163.3, 161.6, 156.2, 155.0, 140.5, 139.2, 134.2, 127.5, 126.2, 125.7, 125.2, 124.7, 122.1, 105.2, 98.7, 57.2, 47.9, 26.8, 25.5, 23.5; ^{13}C NMR (100 MHz, DMSO-d_6, 160 ºC): δ160.9, 155.3, 139.7, 138.6, 138.1, 126.3, 124.8, 124.0, 123.7, 121.3 100.9, 50.9, 24.6, 21.9; IR (KBr): 1626, 1562, 1516, 1445, 1405, 1234, 943, 796, 657 cm^{-1}; HRMS (ESI): calcd. for $[M-SbF_6]^+$ $C_{23}H_{29}N_2S_1$, 365.2046, found: 365.2047; m.p. (decomp.) 168-172 ºC.
 **2f**	**1-[3-(1-pyrenyl)-5-(1-piperidinyl)-2,4-pentadienylidene]piperidinium hexafluorophosphate (2f)** Reaction of pyridinium **8f** (1.40 g, 2.9 mmol) and piperidine (0.89 mL, 9.0 mmol) in EtOH (8 mL) and following salt exchange with KPF_6 (0.98 g, 5.3 mmol) gave the title compound (1.24 g, 74%, yellow solid). ^{1}H NMR (400 MHz, DMSO-d_6, 100 ºC): δ 8.33-8.41 (m, 5H), 8.27-8.29 (m, 1H), 8.22-8.23 (m, 1H), 8.13 (br, 1H), 7.92-7.93 (m, 1H), 6.96 (br, 2H), 6.52 (br, 2H), 3.49 (br, 8H), 1.64 (br, 12H) ; ^{13}C NMR (100 MHz, CD_3CN): δ 172.2, 158.1, 132.9, 132.3, 131.9, 130.9, 130.6, 129.5, 129.2, 128.6, 128.4, 127.7, 126.9, 126.7, 125.8, 125.7, 125.6, 125.3, 106.6, 57.1, 48.5, 27.4, 26.4, 24.2; IR (KBr): 1561, 1515, 1446, 1401, 1209, 1129, 1021, 998, 839, 557 cm^{-1}; HRMS (ESI): calcd. for $[M-PF_6]^+$ $C_{31}H_{33}N_2$, 433.2638, found: 433.2657; m.p.

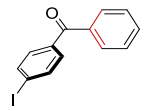
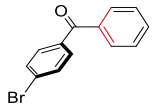
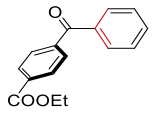
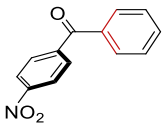
	(decomp.) 149-155 ºC.
 **2g**	**1-[3-diphenylamino-5-(1-piperidinyl)-2,4-pentadienylidene]piperidinium hexafluoroantimonate (2g)** Reaction of pyridinium **8g** (1.25 g, 2.78 mmol) and piperidine (0.89 mL, 9.0 mmol) in EtOH (8 mL) and following salt exchange with $NaSbF_6$ (1.33 g, 5.1 mmol) gave the title compound (1.15 g, 65%, yellow solid). ^{1}H NMR (400 MHz, DMSO-d_6, 100 ºC): δ 7.40-7.43 (m, 6H), 7.25-7.31 (m, 2H), 7.19-7.25 (m, 4H), 5.01 (d, 2H, J = 11.6 Hz), 3.33 (br, 8H), 1.54-1.61 (br, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4, 155.0, 145.4, 129.6, 127.3, 126.8, 93.5, 55.6, 46.7, 26.5, 25.1, 23.7; IR (KBr): 2943, 1626, 1584, 1489, 1454, 1402, 1243, 993, 763, 699, 654 cm^{-1}; HRMS (ESI): calcd. for $[M-SbF_6]^+$ $C_{27}H_{34}N_3$, 400.2747, found: 400.2766; m.p. (decomp.) 171-174 ºC.
 **2h**	**1-[3-(*N*-carbarolyl)-5-(1-piperidinyl)-2,4-pentadienylidene]piperidinium hexafluoroantimonate (2h)** Reaction of pyridinium **8h** (1.34 g, 3 mmol) and piperidine (0.89 mL, 9.0 mmol) in EtOH (10 mL) and following salt exchange with $NaSbF_6$ (1.53 g, 5.9 mmol) gave the title compound (1.58 g, 83%, yellow solid). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.19 (d, 2H, J = 8.0 Hz), 7.45-7.46 (m, 5H), 7.29-7.33 (m, 3H), 6.17 (br, 2H), 3.54 (br,8H), 1.65 (br, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.7, 153.8, 141.4, 140.6, 127.1, 126.7, 124.7, 123.4, 121.7, 121.2, 120.6, 120.4, 112.2, 110.5, 57.3, 57.1, 48.4, 27.0, 25.7, 25.6, 23.5, 23.4; ^{13}C NMR (100 MHz, DMSO-d_6, 100 ºC): δ 160.3, 154.6, 140.4, 125.8, 123.4, 120.4, 119.8, 110.7, 96.4, 25.3, 25.2, 22.3; IR (KBr): 1575, 1447, 1410, 1240, 998, 853, 760, 658 cm^{-1}; HRMS (ESI): calcd. for $[M-SbF_6]^+$ $C_{27}H_{32}N_3$, 398.2591, found: 398.2590; m.p. (decomp.) 197-199 ºC.
 **2i**	**1-[3-*tert*-butyl-5-(1-piperidinyl)-2,4-pentadienylidene]piperidinium hexafluoroantimonate (2i)** Reaction of pyridinium **8i** (1.66 g, 4.9 mmol) and piperidine (1.48 mL, 15 mmol) in EtOH (10 mL) and following salt exchange with $NaSbF_6$ (3.13 g, 12 mmol) gave the title compound (1.97 g, 76%, yellow solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.03 (d, 2H, J = 10.8 Hz), 5.59 (d, 2H, J = 10.4 Hz), 3.64 (br, 4H), 3.57 (br, 4H), 1.74 (br, 12H), 1.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.9, 156.1, 100.4, 56.1, 48.2, 38.0, 30.3, 26.4, 25.1, 23.5; IR (KBr): 2946, 1625, 1561, 1488, 1447, 1414, 1235, 963, 854, 821, 659 cm^{-1}; HRMS (ESI): calcd. for $[M-SbF_6]^+$ $C_{19}H_{33}N_2$, 289.2638, found: 289.2652; m.p. (decomp.) 116-119 ºC.

2. Procedure of (5 + 1) annulation

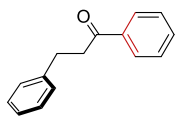
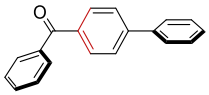
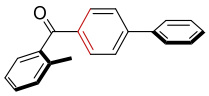
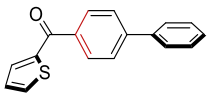
To a 40 mL pressure tube equipped with a magnetic stirring bar and a septum, NaO^{t}Bu was added. The tube was dried under vacuum with heating. After the tube was cooled to room temperature, argon was purged into the tube. THF (4 mL), streptocyanine **2**, and methyl ketone **1** were added to the tube, and it was sealed by Teflon cap and heated at 120 ºC with magnetic stirring for 10 hours. The reaction mixture was cooled to room temperature and the tube was opened to air. After removal of the solvent under vacuum, the crude product was purified with flash chromatography to obtain the desired product **6**.

 **6a**	**benzophenone (6a)**[11] Reaction of acetophenone (**2a**) (57 μL, 0.49 mmol) and streptocyanine **2a** (286 mg, 0.76 mmol) in the presence of NaO^{t}Bu (81 mg, 0.84 mmol) gave the title compound (84 mg, 94%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (dd, 4H, J = 1.2, 8.0 Hz), 7.60 (t, 2H, J =7.4 Hz), 7.49 (t, 4H, J = 8.4 Hz); ^{13}C NMR (100 MHz, CDCl3): δ 196.7, 137.6, 132.4, 130.0, 128.3.
 **6b**	**4-methylbenzophenone (6b)**[12] Reaction of 4-methylacetophenone (67 mg, 0.50 mmol) and streptocyanine **2a** (282 mg, 0.75 mmol) in the presence of NaO^{t}Bu (79 mg, 0.75 mmol) gave the title compound (91 mg, 93%, yellow solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, 2H, J = 8.0 Hz), 7.73 (d, 2H, J = 6.8 Hz), 7.58 (t, 1H, J = 6.8 Hz), 7.48 (t, 2H, J = 7.4 Hz), 7.26-7.30 (m, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.3, 143.1, 137.8, 134.7, 132.0, 130.1, 129.7, 128.8, 128.0, 21.5.
 **6c**	**4-methoxybenzophenone (6c)**[12] Reaction of 4-methoxyacetophenone (73 mg, 0.50 mmol) and streptocyanine **2a** (284 mg, 0.75 mmol) in the presence of NaO^{t}Bu (81 mg, 0.75 mmol) gave the title compound (98 mg, 95%, yellow solid) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, 2H, J = 8.8 Hz), 7.76 (d, 2H, J = 8.0 Hz), 7.57 (t, 1H, J = 7.2 Hz), 7.48 (dt, 2H, J = 2.0, 7.4 Hz), 6.97 (d, 2H, J = 8.8 Hz), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.1, 162.8, 137.9, 132.2, 131.5, 129.6, 129.3, 127.8, 113.2, 55.1.
 **6d**	**4-cyanobenzophenone (6d)**[12] Reaction of 4-cyanoacetophenone (72 mg, 0.50 mmol) and streptocyanine **2a** (284 mg, 0.75 mmol) in the presence of NaO^{t}Bu (76 mg, 0.75 mmol) gave the title compound (89 mg, 86%, yellow solid).

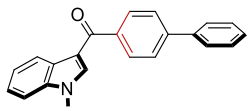
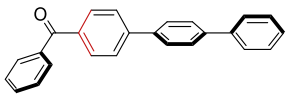
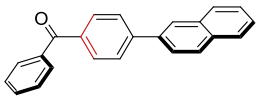
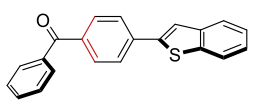
[11] P. Lei, G. Meng, S. Shi, Y. Ling, J. An, R. Szostak, M. Szostak, *Chem. Sci*., 2017, **8**, 6525–6530.
[12] J. Karthikeyan, K. Parthasarathy, C.-H. Cheng, *Chem. Commun.*, 2011, **47**, 10461–10463.

	^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, 2H, J = 8.4 Hz), 7.78-7.81 (m, 4H), 7.65 (t, 1H, J = 6.8 Hz), 7.52 (t, 2H, J = 7.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.0, 141.2, 136.3, 133.3, 132.2, 130.2, 130.1, 128.6, 118.0, 115.6.
 **6e**	**4-iodobenzophenone (6e)**[13] Reaction of 4-iodoacetophenone (123 mg, 0.50 mmol) and streptocyanine **2a** (284 mg, 0.75 mmol) in the presence of NaO^{t}Bu (81 mg, 0.84 mmol) gave the title compound (140 mg, 91%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, 2H, J = 8.0 Hz,), 7.76 (d, 2H, J = 8.0 Hz,), 7.58 (t, 1H, J = 7.4 Hz,), 7.45-7.52 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.8, 137.6, 137.1, 136.9, 132.7, 131.5, 130.0, 128.5, 100.2.
 **6f**	**4-bromobenzophenone (6f)**[12] Reaction of 4-bromoacetophenone (99 mg, 0.49 mmol) and streptocyanine **2a** (284 mg, 0.75 mmol) in the presence of NaO^{t}Bu (78 mg, 0.81 mmol) gave the title compound (111 mg, 86%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (dd, 2H, J = 1.2, 8.4 Hz), 7.68 (d, 2H, J = 8.8 Hz), 7.59-7.65 (m, 3H), 7.50 (t, 2H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.6, 137.1, 136.3, 132.7, 131.60, 131.56, 129.9, 128.4, 127.5.
 **6g**	**ethyl 4-benzoylbenzoate (6g)**[14] Reaction of ethyl 4-acetylbenzoate (94 mg, 0.49 mmol) and streptocyanine **2a** (283 mg, 0.75 mmol) in the presence of NaO^{t}Bu (80 mg, 0.83 mmol) gave the title compound (59 mg, 47%, yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, 2H, J = 8.0 Hz), 7.79-7.84 (m, 4H), 7.61 (t, 1H, J = 7.2 Hz), 7.49 (t, 2H, J = 7.4 Hz), 4.42 (q, 2H, J = 7.2 Hz), 1.42 (t, 3H, J = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.0, 165.8, 141.2, 137.0, 133.6, 132.9, 130.1, 129.7, 129.5, 128.5, 61.4, 14.3.
 **6h**	**4-nitrobenzophenone (6h)**[12] Reaction of 4-nitroacetophenone (84 mg, 0.51 mmol) and streptocyanine **2a** (284 mg, 0.75 mmol) in the presence of NaO^{t}Bu (81 mg, 0.85 mmol) gave the title compound (66 mg, 57%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (d, 2H, J = 8.8 Hz), 7.94 (d, 2H, J = 8.8 Hz), 7.81 (d, 2H, J = 8.4 Hz), 7.63 (t, 1H, J = 7.6 Hz), 7.53 (t, 2H, J = 7.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.8, 149.8, 142.8, 136.2, 133.5, 130.7, 130.1, 128.7, 123.5.

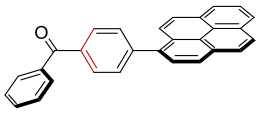
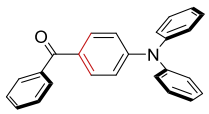
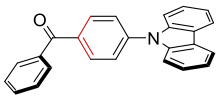
[13] H. Kim, A. Nagaki, J. Yoshida, *Nat. Commun.*, 2011, **2**, 264.
[14] R. Shang, Y. Fu, J.-B. Li, S.-L. Zhang, Q.-X. Guo, L. Liu, *J. Am. Chem. Soc.*, 2009, **131**, 5738–5739.

 6i	**1,3-diphenyl-1-propanone (6i)**[15] Reaction of 4-phenyl-2-butanone (29 mg, 0.20 mmol) and streptocyanine **2b** (114 mg, 0.30 mmol) in the presence of NaO^{t}Bu (35 mg, 0.36 mmol) gave the title compound (22 mg, 52%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, 2H, *J* = 7.2 Hz), 7.58 (t, 1H, *J* = 7.6 Hz), 7.47 (t, 2H, *J* = 7.6 Hz), 7.35-7.20 (m, 5H), 3.33 (t, 2H, *J* = 7.6 Hz), 3.09 (t, 2H, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.2, 141.3, 136.8, 133.0, 128.6, 128.5, 128.4, 128.0, 126.1, 40.4, 30.1.
 6j	**4-henylbenzophenone (6j)**[16] Reaction of acetophenone (**1a**) (57 μL, 0.49 mmol) and streptocyanine **2b** (342 mg, 0.75 mmol) in the presence of NaO^{t}Bu (89 mg, 0.92 mmol) gave the title compound (119 mg, 94%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, 2H, *J* = 8.4 Hz), 7.84 (d, 2H, *J* = 8.4 Hz), 7.71 (d, 2H, *J* = 8.4 Hz), 7.66 (d, 2H, *J* = 7.2 Hz), 7.61 (t, 1H, *J* = 7.6 Hz), 7.47-7.53 (m, 4H), 7.41 (t, 1H, *J* = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.3, 145.2, 139.9, 137.8, 136.2, 132.4, 130.8, 130.0, 129.0, 128.4, 128.2, 127.3, 127.0.
 6k	**4'-phenyl-2-methylbenzophenone (6k)**[17] Reaction of 2-methylacetophenone (26 μL, 0.20 mmol) and streptocyanine **2b** (133 mg, 0.29 mmol) in the presence of NaO^{t}Bu (37 mg, 0.38 mmol) gave the title compound (45.8 mg, 86%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, 2H, *J* = 8.4 Hz), 7.68 (d, 2H, *J* = 8.8 Hz), 7.64 (dd, 2H, *J* = 1.2, 8.4 Hz), 7.48 (t, 2H, *J* = 7.4 Hz), 7.41 (dt, 2H, *J* = 1.6, 7.2 Hz), 7.27-7.35 (m, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.4, 146.1, 140.1, 138.9, 136.9, 136.6, 131.2, 131.0, 130.4, 129.2, 128.6, 128.5, 127.5, 127.3, 125.4, 20.2.
 6l	**4-biphenylyl 2-thienyl ketone (6l)**[18] Reaction of 2-acetylthiphene (22 μL, 0.20 mmol) and streptocyanine **2b** (139 mg, 0.30 mmol) in the presence of NaO^{t}Bu (41 mg, 0.36 mmol) gave the title compound (35 mg, 66%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, 2H, *J* = 8.4 Hz), 7.72 (d, 4H, *J* = 8.0 Hz), 7.65 (d, 2H, *J* = 7.2 Hz), 7.48 (t, 2H, *J* = 7.4 Hz), 7.41 (t, 1H, *J* = 7.2 Hz), 7.18 (dd, 1H, *J* = 3.6, 4.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.8, 145.1, 143.7, 140.0, 136.8, 134.7, 134.2, 129.9, 129.0, 128.2, 128.0, 127.3, 127.1.

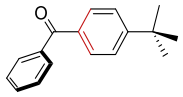
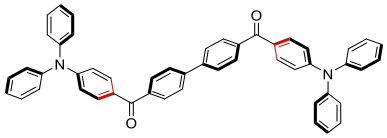
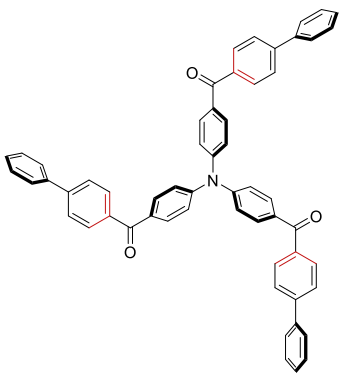
[15] D. J. Fox, D. S. Pedersen, S. Warren, *Org. Biomol. Chem.*, 2006, **4**, 3102–3107.
[16] D. Paul, S. Rudra, P. Rahman, S. Khatua, M. Pradhan, P. N. Chatterjee, *J. Organomet. Chem.*, 2018, **871**, 96–102.
[17] S. Gobbi, A. Cavalli, M. Negri, K. E. Schewe, F. Belluti, L. Piazzi, R. W. Hartmann, M. Recanatini, A. Bisi, *J. Med. Chem.*, 2007, **50**, 3420–3422.
[18] H. Wu, B. Xu, Y. Li, F. Hong, D. Zhu, J. Jian, X. Pu, Z. Zeng, *J. Org. Chem.*, 2016, **81**, 2987–2992.

 6m	**4-biphenyl 3-(1-methylindolyl) ketone (6m)** Reaction of 1-methyl-3-acetylindole (33 mg, 0.19 mmol) and streptocyanine **2b** (139 mg, 0.31 mmol) in the presence of NaO^{t}Bu (41 mg, 0.43 mmol) gave the title compound (44 mg, 74%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, 1H, *J* = 4.4 Hz), 7.85 (d, 2H, *J* = 8.0 Hz), 7.64 (d, 2H, *J* = 8.4 Hz), 7.61 (d, 2H, *J* = 7.2 Hz), 7.51 (s, 1H), 7.44 (t, 2H , *J* = 7.6 Hz), 7.37 (d, 1H, *J* = 7.6 Hz), 7.31-7.35 (m, 3H), 3.76 (s, 1H); ^{13}C NMR (100 MHz, CD_3CN): δ190.5, 144.2, 140.7, 140.6, 139.8, 138.5, 130.0, 129.8, 128.8, 127.93, 127.89, 127.6, 124.2, 123.1, 122.8, 115.3, 111.1, 33.8; IR (KBr): 1617, 1523, 1460, 1367, 1266, 1234, 1124, 1074, 880, 855, 746, 700 cm^{-1}; HRMS (ESI): calcd. for $[M+Na]^+$ $C_{22}H_{17}N_1Na_1O_1$, 334.1208, found: 334.1204; Anal. Calcd for $C_{22}H_7N_1O_1$: C, 84.86; H, 5.50, N, 4.50. Found: C, 84.77; H, 5.52; N, 4.38%.; m.p. 136-138 ºC.
 6n	**4-(4-biphenylyl)benzophenone (6n)**[19] Reaction of acetophenone (**2a**) (22 μL, 0.19 mmol) and streptocyanine **2c** (159 mg, 0.30 mmol) in the presence of NaO^{t}Bu (34 mg, 0.35 mmol) gave the title compound (60 mg, 93%, pale yellow solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, 2H, *J* = 8.4 Hz), 7.85 (d, 2H, *J* = 8.4 Hz), 7.71-7.78 (m, 6H), 7.60-7.67 (m, 3H), 7.43-7.53 (m, 4H), 7.37 (t, 1H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.4, 144.7, 141.1, 140.4, 138.8, 137.8, 136.3, 132.4, 130.8, 130.0, 128.9, 128.3, 127.72, 127.70, 127.6, 127.1, 126.8.
 6o	**4-(2-naphtyl)benzophenone (6o)**[20] Reaction of acetophenone (**1a**) (57 μL, 0.49 mmol) and streptocyanine **2d** (376 mg, 0.74 mmol) in the presence of NaO^{t}Bu (83 mg, 0.86 mmol) gave the title compound (103 mg, 68%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.72-7.93 (m, 10H), 7.58 (t, 1H, *J* = 7.0 Hz), 7.46-7.52 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.4, 145.1, 137.8, 137.3, 136.3, 133.6, 133.1, 132.5, 130.9, 130.1, 128.8. 128.43, 128.39, 127.8, 127.2, 126.6, 126.5, 126.4, 125.3.
 6p	**4-(2-benzothiophenyl)benzophenone (6p)** Reaction of acetophenone (**1a**) (23 μL, 0.20 mmol) and streptocyanine **2e** (171 mg, 0.29 mmol) in the presence of NaO^{t}Bu (42 mg, 0.44 mmol) gave the title compound (32 mg, 50%, yellow solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79-7.91 (m, 8H), 7.68 (s, 1H), 7.61 (t, 1H, *J* = 7.4 Hz), 7.51 (t, 2H, *J* = 7.6 Hz), 7.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ

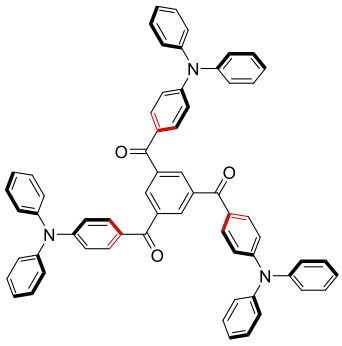
[19] Z. Zhao, B. He, H. Nie, B. Chen, P. Lu, A. Qina, B. Z. Tang, *Chem. Commun.*, 2014, **50**, 1131–1133.
[20] W. K. Chow, C. M. So, C. P. Lau, F. Y. Kwong, *J. Org. Chem.*, 2010, **75**, 5109–5112.

	195.9, 142.8, 140.5, 139.9, 138.2, 137.6, 136.9, 132.5, 130.9, 130.0, 128.4, 126.1, 125.0, 124.8, 124.0, 122.4, 121.1; IR (KBr): 1644, 1576, 1404, 1290, 938, 827, 793, 723, 692 cm^{-1}; HRMS (ESI): calcd. for $[M+Na]^+$ $C_{21}H_{14}Na_1O_1S_1$, 337.06631, found: 337.0666; Anal. Calcd for $C_{21}H_{14}O_1S_1$: C, 80.23; H, 4.49, N, 0.00. Found: C, 79.95; H,4.57; N, 0.00%.; m.p. (decomp.) 202-207 ºC.
 6q	**4-(1-pyrenyl)benzophenone (6q)**[21] Reaction of acetophenone (**1a**) (23 μL, 0.19 mmol) and streptocyanine **2f** (176 mg, 0.3 mmol) in the presence of NaO^{t}Bu (43 mg, 0.45 mmol) gave the title compound (64 mg, 87%, yellow solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11-8.20 (m, 4H), 8.05 (s, 2H), 7.88-8.03 (m, 7H), 7.69 (d, 2H, *J* = 7.6 Hz), 7.60 (t, 1H, *J* = 7.4 Hz), 7.51 (t, 2H, *J* = 7.4 Hz); ^{13}C NMR (100 MHz, CDCl3): δ 196.5, 145.6, 137.8, 136.37, 136.36, 132.6, 131.5, 131.1, 130.9, 130.6, 130.3, 130.2, 128.44, 128.41, 128.0, 127.9, 127.4, 126.2, 125.5, 125.1, 125.0, 124.84, 124.81, 124.77. (one peak is missing)
 6r	**4-(diphenylamino)benzophenone (6r)**[22] Reaction of acetophenone (**1a**) (58 μL, 0.50 mmol) and streptocyanine **2g** (476 mg, 0.75 mmol) in the presence of NaO^{t}Bu (585 mg, 6.1 mmol) gave the title compound (117 mg, 67%, yellow solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, 2H, *J* = 7.6 Hz), 7.70 (d, 2H, *J* = 8.0 Hz), 7.52 (t, 1H, *J* = 7.4 Hz), 7.44 (t, 2H, *J* = 7.6 Hz), 7.31 (t, 4H, *J* = 7.6 Hz), 7.12-7.178 (m, 6H), 7.01 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.1, 151.8, 146.4, 138.4, 131.9, 131.6, 129.6, 129.5, 129.4, 128.1, 125.9, 124.6, 119.4.
 6s	**4-(*N*-carbazolyl)benzophenone (6s)**[23] Reaction of acetophenone (**2a**) (23 μL, 0.20 mmol) and streptocyanine **2h** (619 mg, 1 mmol) in the presence of NaO^{t}Bu (282 mg, 2.9 mmol) gave the title compound (41 mg, 61%, yellow solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (dd, 2H, *J* = 0.8, 6.8 Hz), 8.08 (d, 2H, *J* = 8.4 Hz), 7.91 (dd, 2H, *J* = 1.6, 8.4 Hz), 7.74 (d, 2H, *J* = 8.4 Hz), 7.65 (t, 1H, *J* = 7.6 Hz), 7.52-7.58 (m, 4H), 7.45 (dt, 2H, *J* = 1.2 7.2 Hz), 7.33 (dt, 2H, *J* = 0.8, 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.6, 141.6, 140.2, 137.4, 136.0, 132.7, 131.9, 130.1, 128.5, 126.3, 126.2, 123.8, 120.6, 120.5, 109.8.

[21] M.-A. Tehfe, F. Dumur, B. Graff, F. Morlet-Savary. D. Gigmes, J.-P. Fouassier, J. Lalevée, *Polym. Chem*., 2013, **4**, 2313–2324.
[22] A. T. Jensen, X. Liang, D. Tanner, N. Skjaerbaek, *J. Org. Chem*., 2004, **69**, 4936–4947.
[23] Z. Yang, Z. Mao, X. Zhang, D. Ou, Y. Mu, Y. Zhang, C. Zhao, S. Liu, Z. Chi, J. Xu, Y.-C. Wu, P.-Y. Lu, A. Lien, M. R. Bryce, *Angew. Chem. Int. Ed*., 2016, **55,** 2181–2185.

 6t	**4-*tert*-butylbenzophenone (6t)**[24] Reaction of acetophenone (**1a**) (58 μL, 0.50 mmol) and streptocyanine **2i** (396 mg, 0.75 mmol) in the presence of NaO^{t}Bu (199 mg, 2.1 mmol) gave the title compound (91 mg, 77%, orange oil). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, 2H, *J* = 7.2 Hz), 7.77 (d, 2H, *J* = 8.8 Hz), 7.58 (t, 1H, *J* = 7.6 Hz), 7.46-7.51 (m, 4H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, CDCl3): δ 196.4, 156.1, 137.9, 134.8, 132.2, 130.1, 130.0, 128.2, 125.2, 35.1, 31.2.
 6u	**4, 4'-di{[4-(diphenylamino)phenyl)]carbonyl}biphenyl (6u)** Reaction of 4,4'-diacetylbiphenyl (46 mg, 0.19 mmol) and streptocyanine **2g** (499 mg, 0.78 mmol) in the presence of NaO^{t}Bu (295 mg, 3.1 mmol) gave the title compound (70 mg, 52%, yellow solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, 4H, *J* = 6.8 Hz), 7.72-7.75 (m, 8H), 7.33 (t, 8H, *J* = 6.6 Hz), 7.13-7.20 (m, 12H), 7.03 (d, 4H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.6, 152.0, 146.4, 143.3, 137.8, 131.9, 130.4, 129.6, 129.4, 127.0, 126.0, 124.7, 119.5; IR (KBr): 1648, 1583, 1488, 1274, 1175, 927, 849, 754, 696 cm^{-1}; HRMS (ESI): calcd. for $[M+Na]^+$ $C_{50}H_{36}N_2Na_1O_2$, 719.26745, found: 719.2659; Anal. Calcd for $C_{50}H_{36}N_2O_2$: C, 86.18; H, 5.21, N, 4.02. Found: C, 85.96; H, 5.24; N, 3.96%.; m.p. (decomp.) 202-207 ºC.
 6v	**4, 4', 4"-tris(4-biphenylylcarbonylphenyl)amine (6v)** Reaction of 4,4',4"-triacetyltriphenylamine (71 mg, 0.19 mmol) and streptocyanine **2b** (404 mg, 0.89 mmol) in the presence of NaO^{t}Bu (98 mg, 1.0 mmol) gave the title compound (130 mg, 87%, yellow solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, 6H, *J* = 8.4 Hz), 7.84 (d, 6H, *J* = 8.4 Hz), 7.69 (d, 6H, *J* = 8.4 Hz), 7.63 (d, 6H, *J* = 7.2 Hz), 7.46 (t, 6H, *J* = 7.4 Hz), 7.38 (t, 3H, *J* = 7.6 Hz), 7.26 (d, 6H, *J* = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.8, 150.0, 145.1, 139.9, 136.4, 133.2, 132.0, 130.5, 129.0, 128.2, 127.3, 127.0, 123.9; IR (KBr): 1652, 1587, 1504, 1312, 1268, 1176, 930, 856, 751, 696 cm^{-1}; HRMS (ESI): calcd. for $[M+Na]^+$ $C_{57}H_{39}N_1Na_1O_3$, 808.2828 found: 808.2822; Anal. Calcd for $C_{57}H_{39}N_1O_3$: C, 87.11; H, 5.00, N, 1.78. Found: C, 86.80; H, 5.13; N, 1.79%.; m.p. (decomp.)186-187 ºC.

[24] A. T. Biju, F. Glorius, *Angew. Chem. Int. Ed.*, 2010, **49**, 9761–9764.

 6w	**1,3,5-tris[4-(diphenylamino)phenylcarbonyl]benzene (6w)**[25] Reaction of 1,3,5-triacetylbenzene (43 mg, 0.21 mmol) and streptocyanine **2g** (776, 1.2 mmol) in the presence of NaO^{t}Bu (359 mg, 3.7 mmol) gave the title compound (132 mg, 70%, yellow solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 3H), 7.71 (d, 6H, J = 8.8 Hz), 7.33 (t, 12H, J = 7.8 Hz), 7.11-7.20 (m, 18H), 7.00 (d, 6H, J = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.6, 152.4, 146.2, 138.8, 132.8, 132.1, 129.7, 128.4, 126.2, 125.0, 119.2.

4. Procedure of gram scale (5 + 1) annulation

To a 400 mL sealed tube equipped with a magnetic stirring bar and a septum, NaO^{t}Bu (1.19 g, 12.3 mmol) was added. The tube was dried under vacuum with heating. After the tube was cooled to room temperature, argon was purged into the tube. THF (50 mL), streptocyanine **2b** (5.28 g, 10.2 mmol), and acetophenone (**1a**) (0.90 mL, 7.74 mmol) were added to the tube, and it was sealed by Teflon cap and heated at 120 ºC with magnetic stirring for 10 hours. The reaction mixture was cooled to room temperature and transferred to a 200 mL round-bottom flask. After removal of the solvent under vacuum, the crude product was purified with flash chromatography to obtain the desired product **6j** (1.73 g, 87 %).

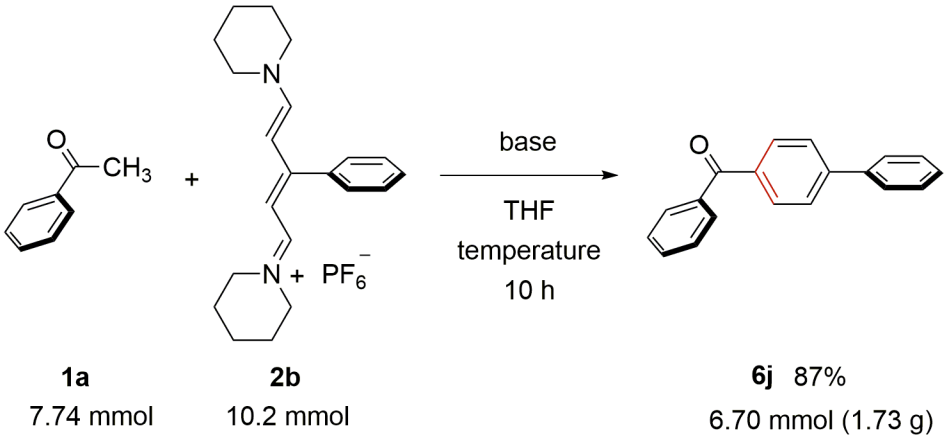
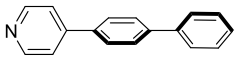


Figure S4. Gram scale synthesis of **6j**.

[25] A. Qin, J. W. Y. Lam, H. Lu, W. Dong, C. K. W. Jim, Y. Dong, M. Ha1ussler, H. Y. H. Sung, I. D. Williams, G. K. L. Wong, B. Z. Tang, *Macromolecules,* 2007, **40**, 4879–4886.

5. NMR spectra



7c

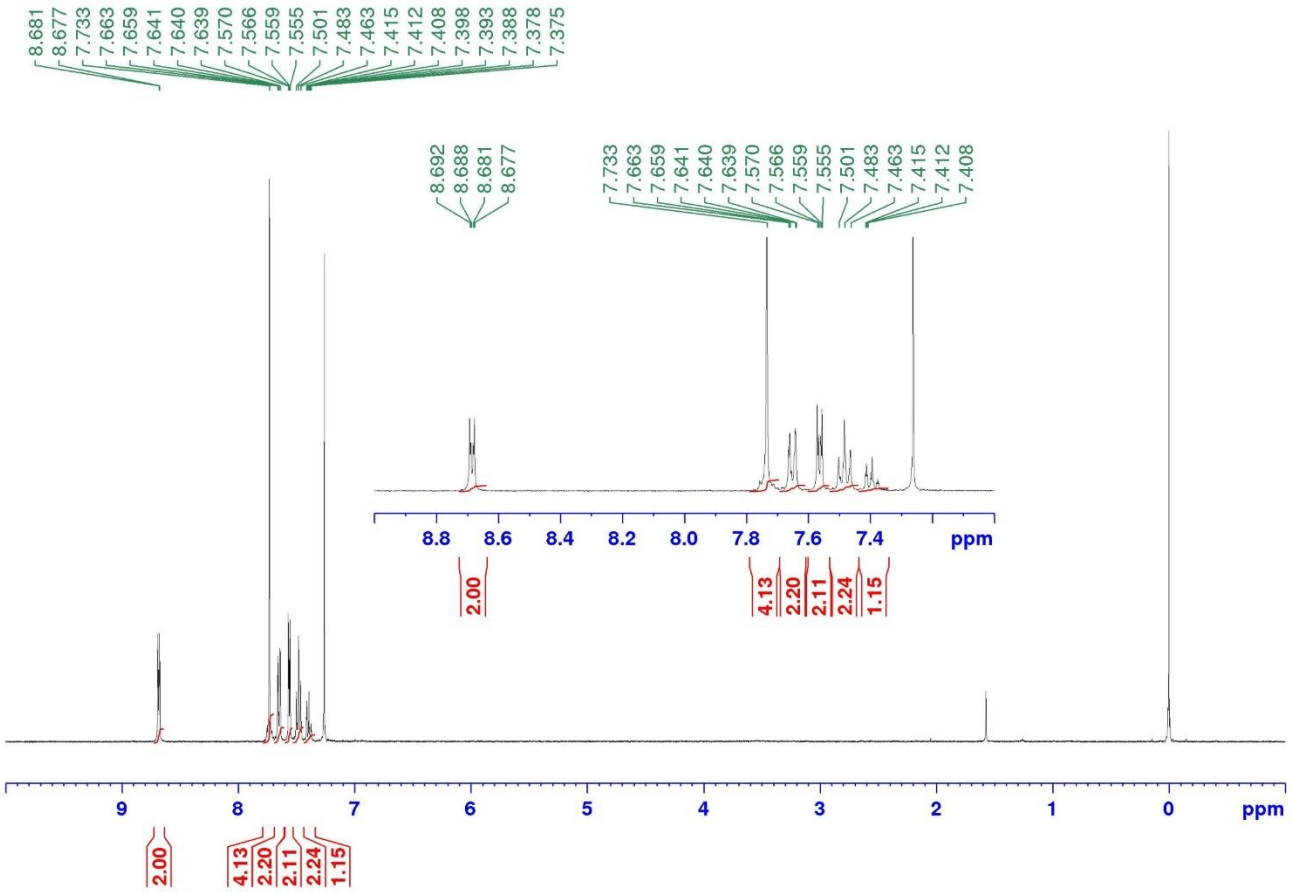


Figure S5. ^{1}H NMR spectrum of **7c** in $CDCl_3$.

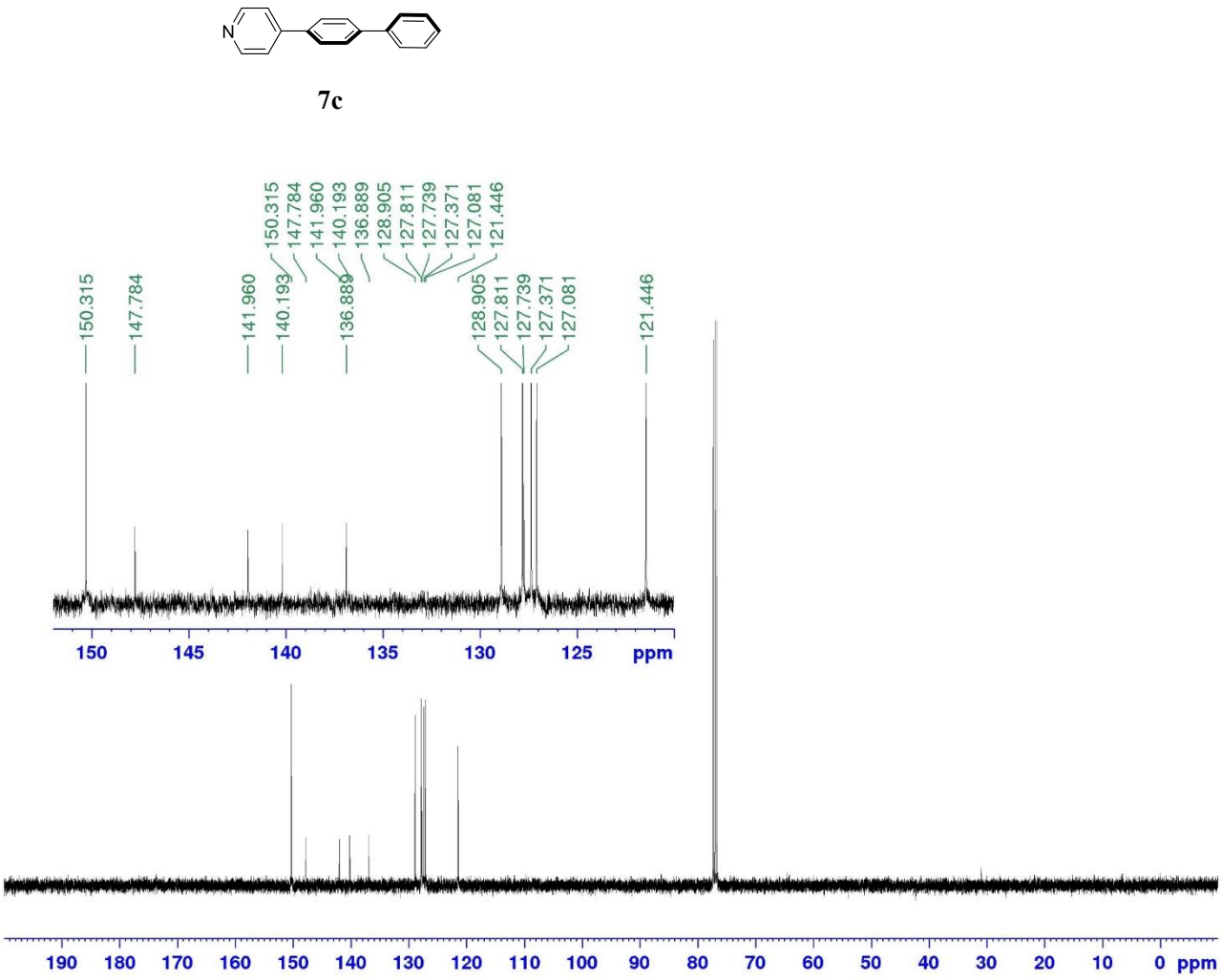


Figure S6. ^{13}C NMR spectrum of **7c** in $CDCl_3$.

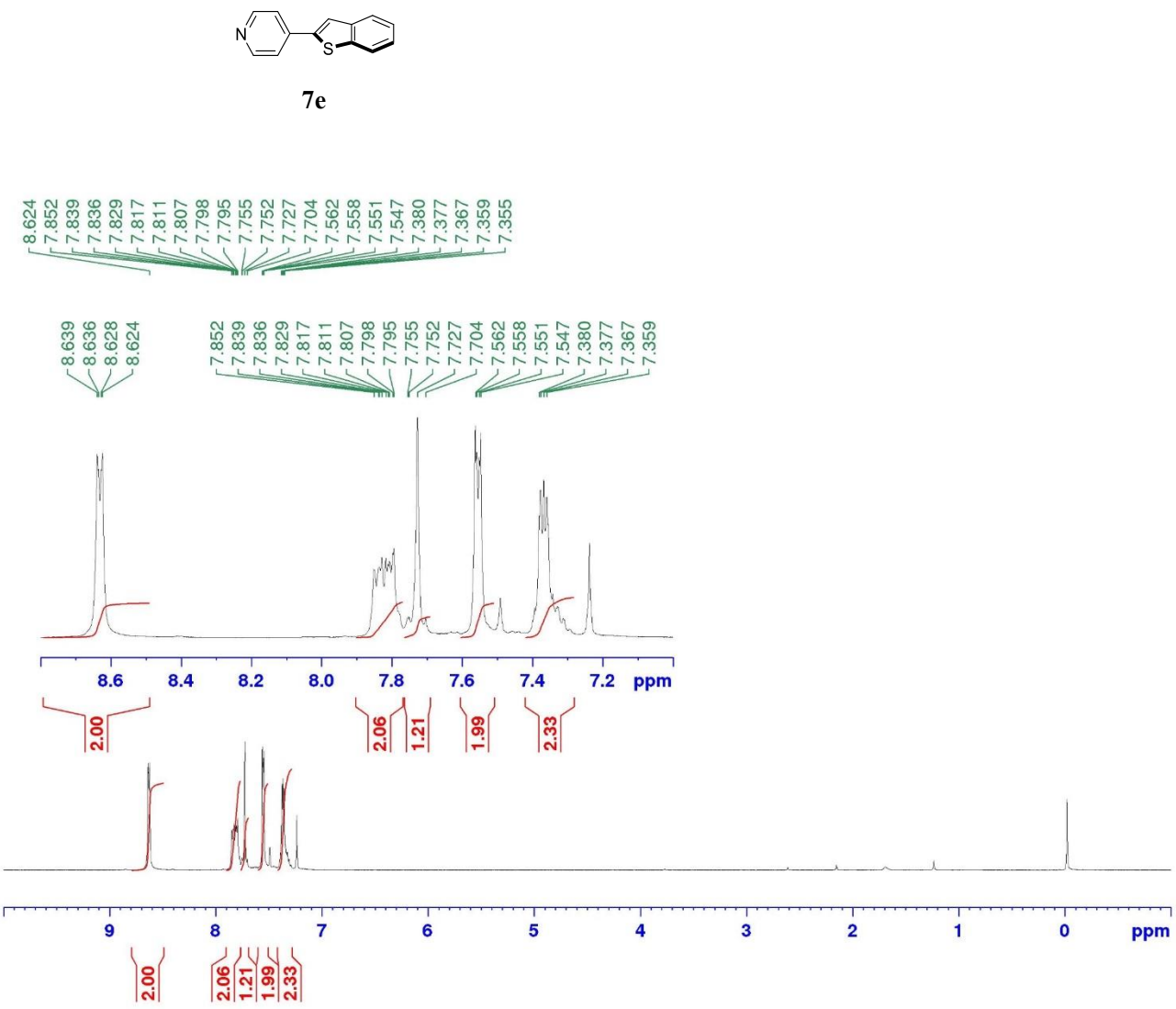


Figure S7. ^{1}H NMR spectrum of **7e** in $CDCl_3$.

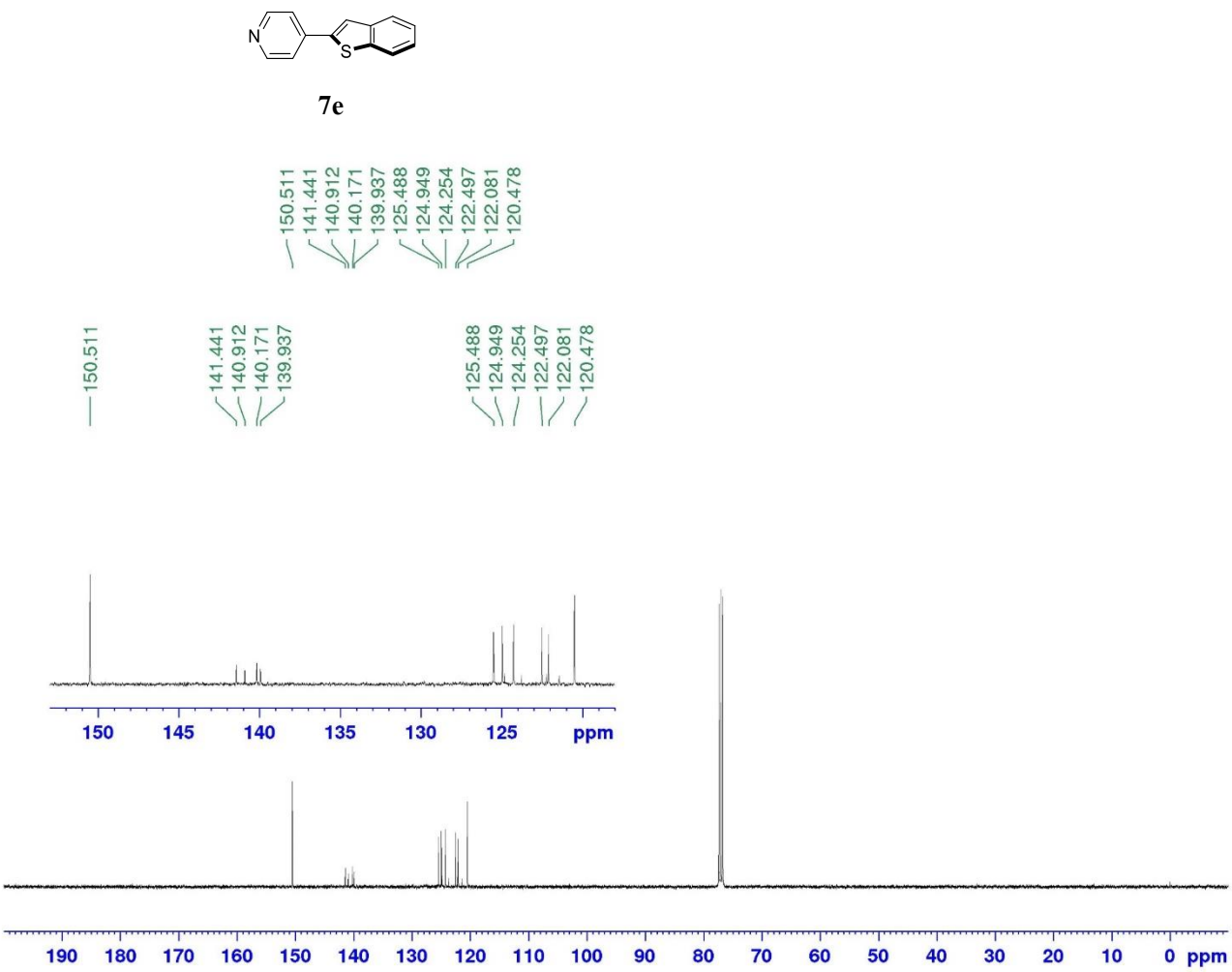


Figure S8. ^{13}C NMR spectrum of **7e** in $CDCl_3$.

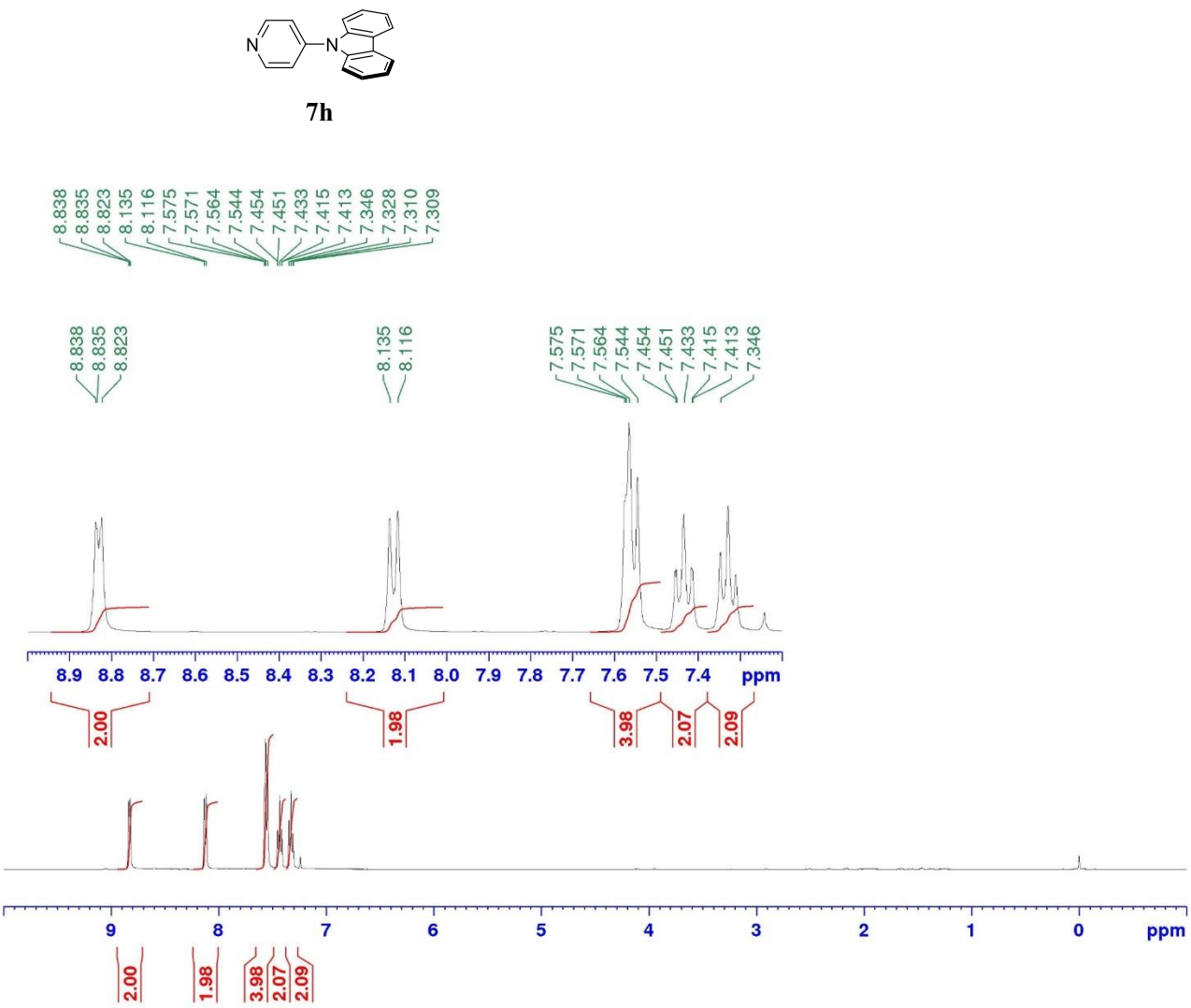


Figure S9. ^{1}H NMR spectrum of **7h** in $CDCl_3$.

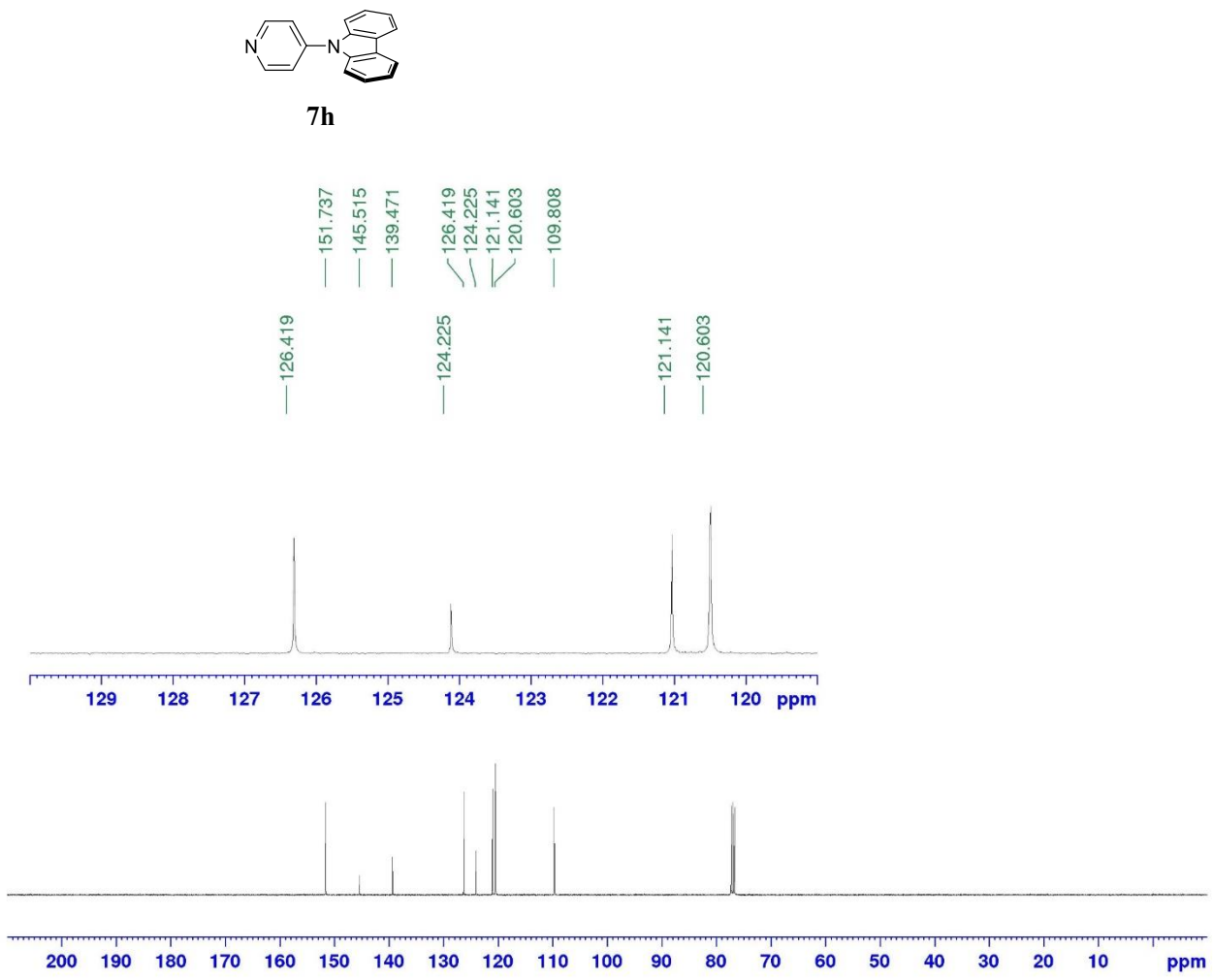
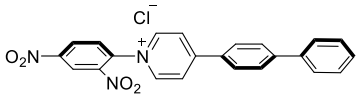


Figure S10. ^{13}C NMR spectrum of **7h** in $CDCl_3$.



8c

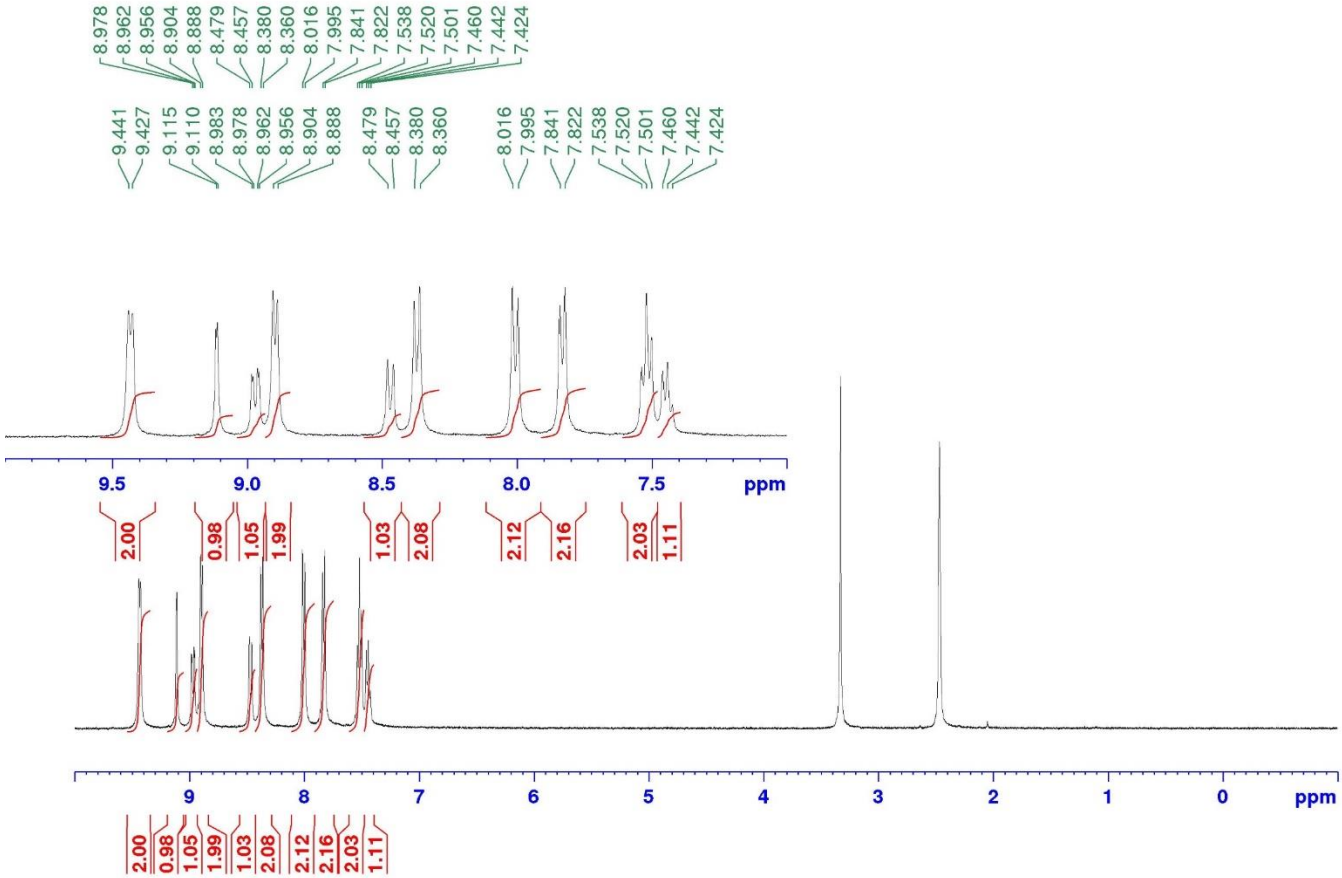
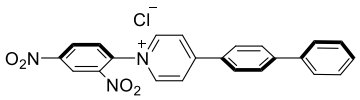


Figure S11. ^{1}H NMR spectrum of **8c** in DMSO-d_6.



8c

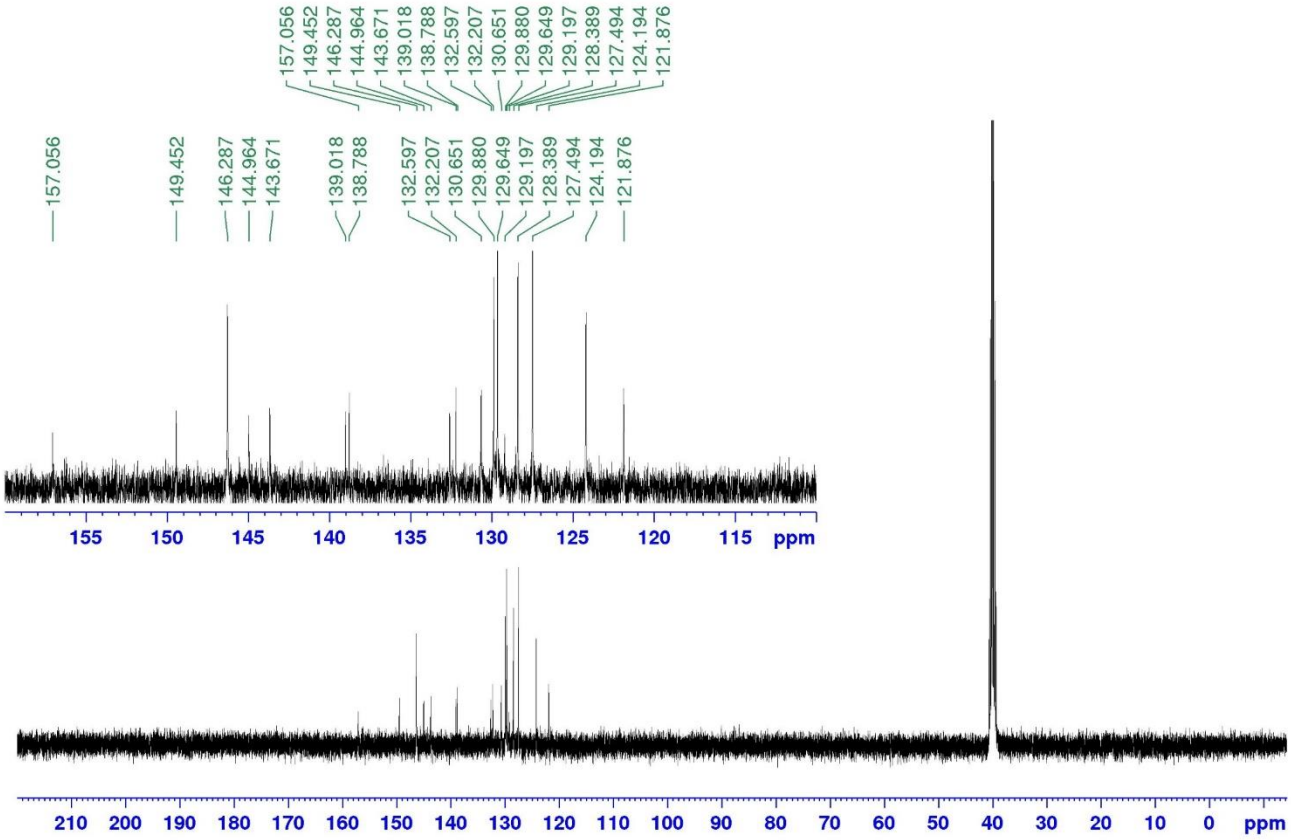
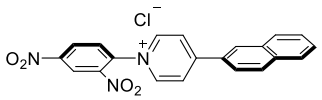


Figure S12. ^{13}C NMR spectrum of **8c** in DMSO-d_6.



8d

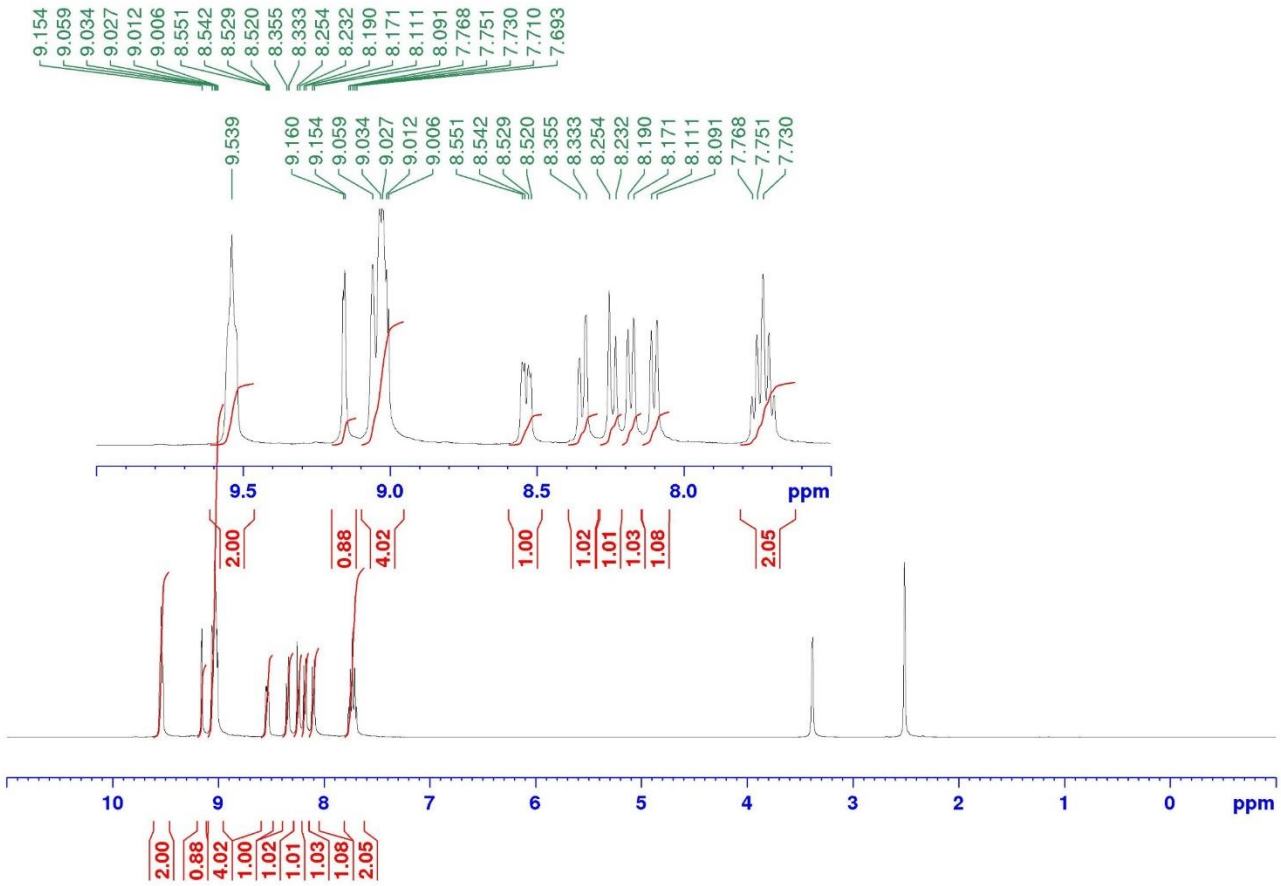
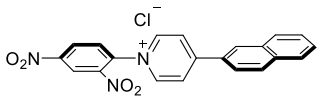


Figure S13. ^{1}H NMR spectrum of **8d** in DMSO-d_6.



8d

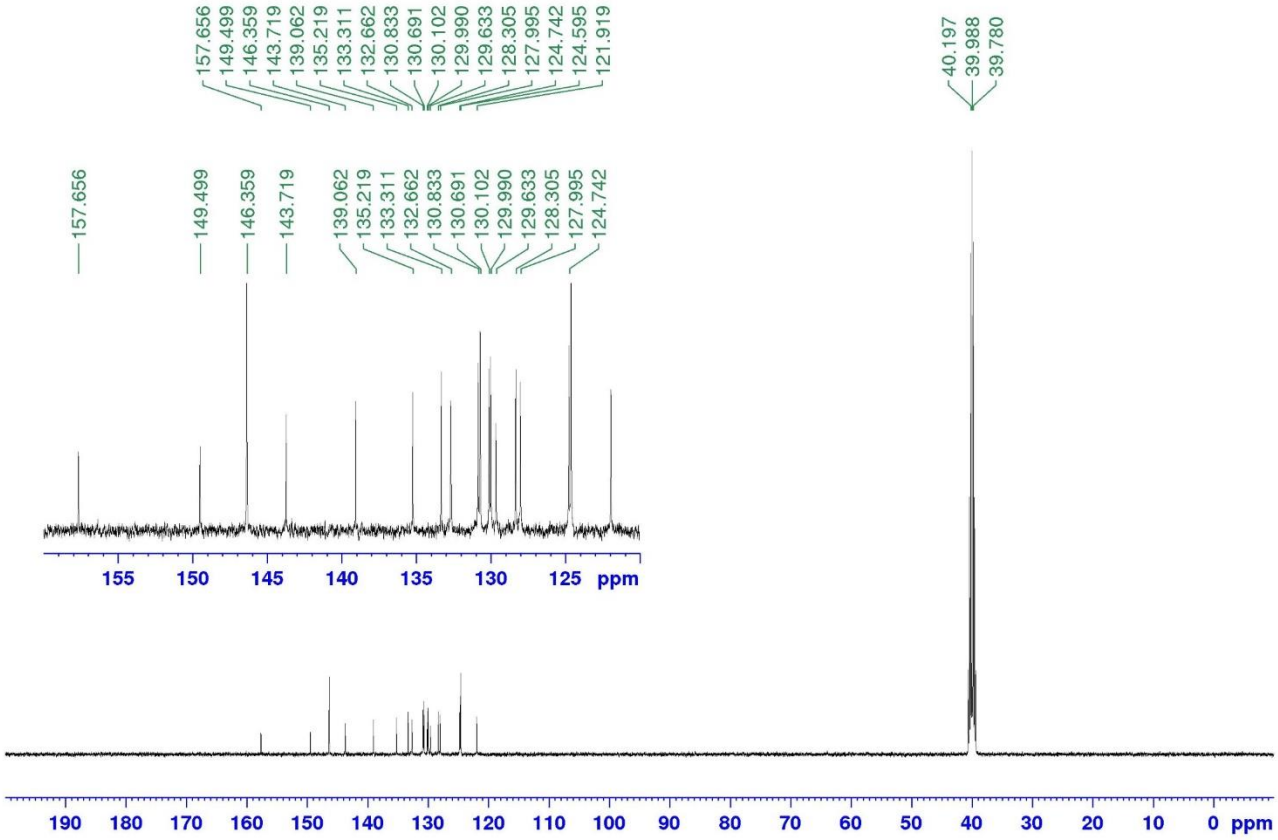


Figure S14. ^{13}C NMR spectrum of **8d** in DMSO-d_6.

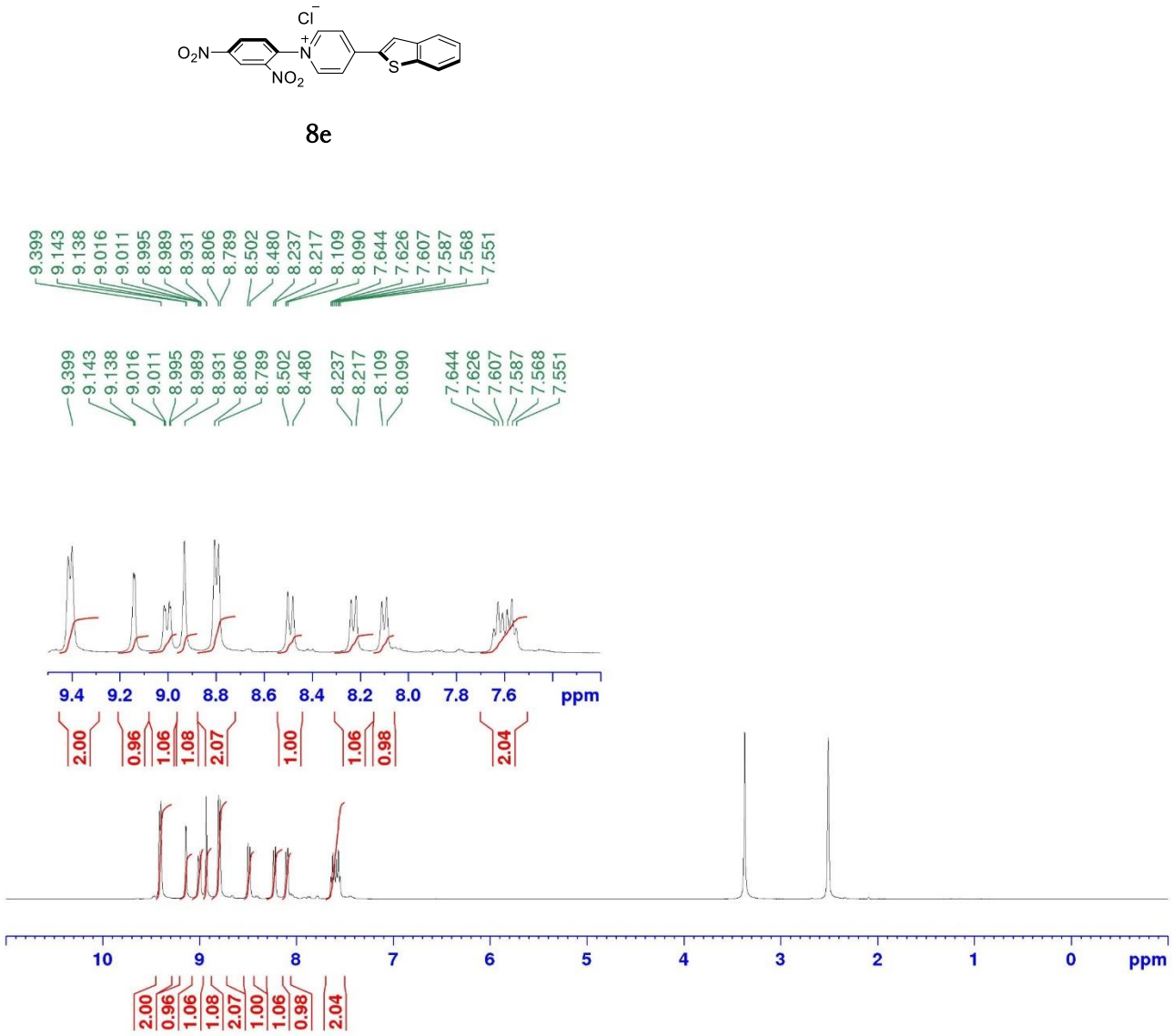


Figure S15. ^{1}H NMR spectrum of **8e** in DMSO-d_6.

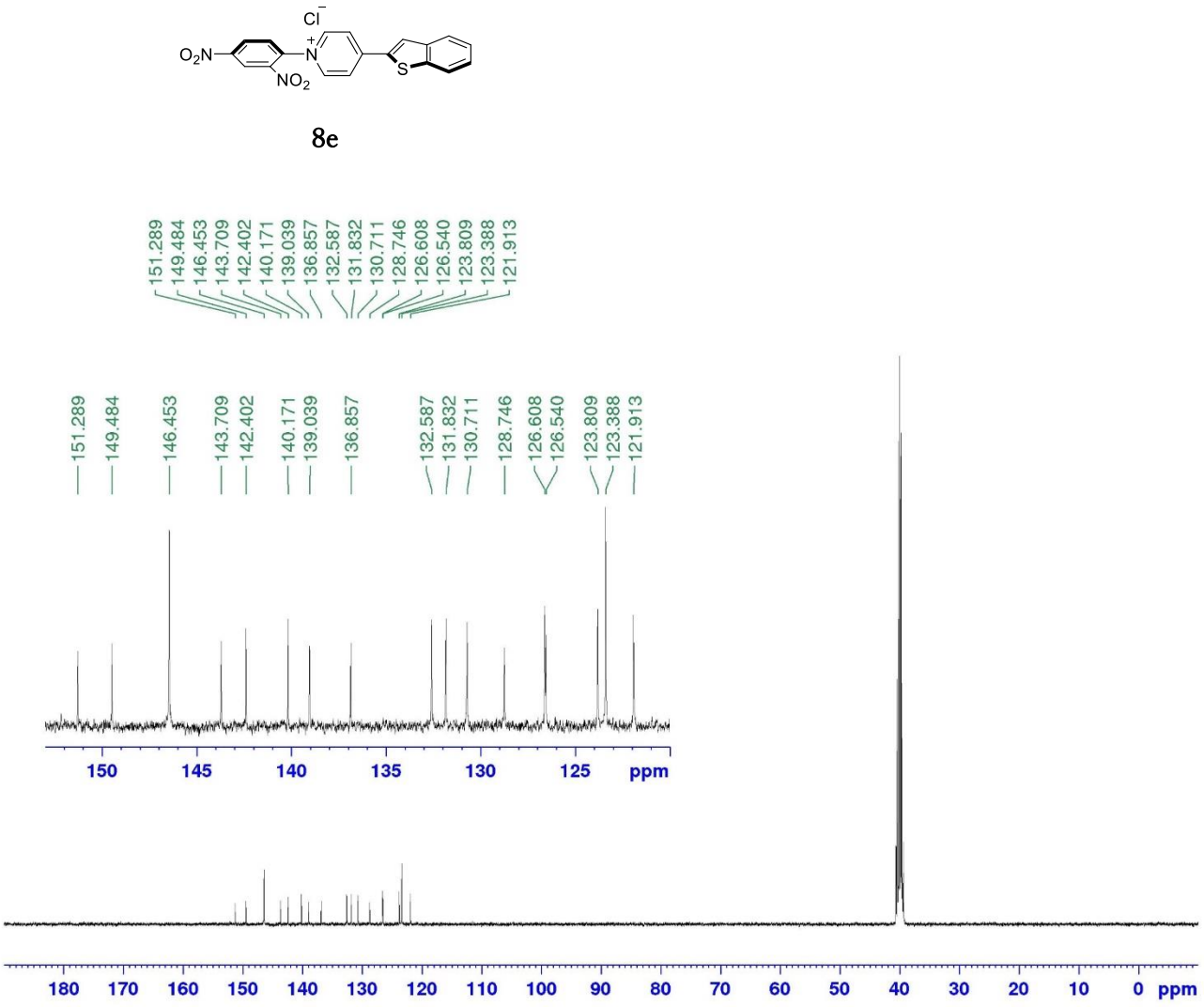


Figure S16. ^{13}C NMR spectrum of **8e** in DMSO-d_6.

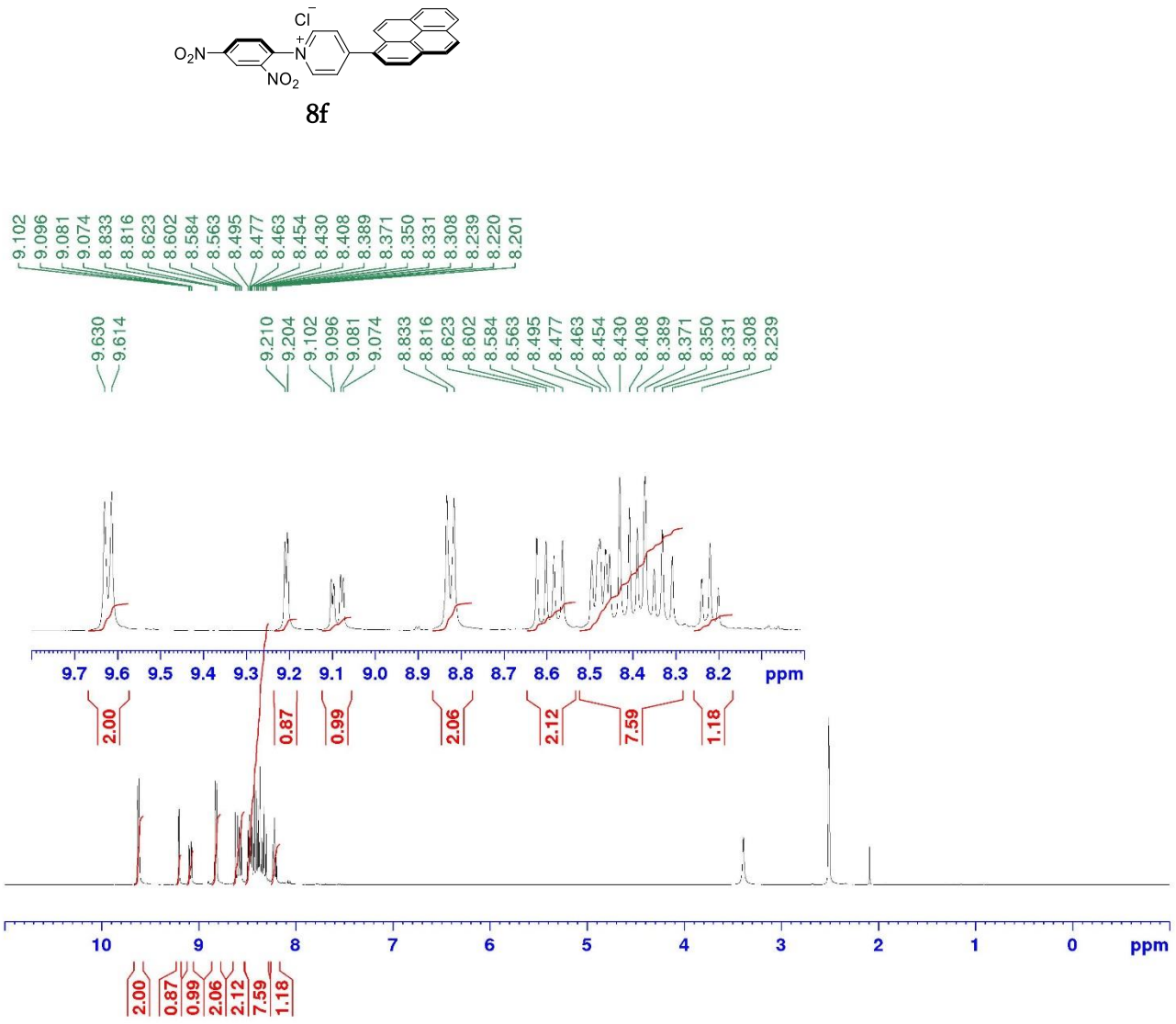


Figure S17. ^{1}H NMR spectrum of **8f** in DMSO-d_6.

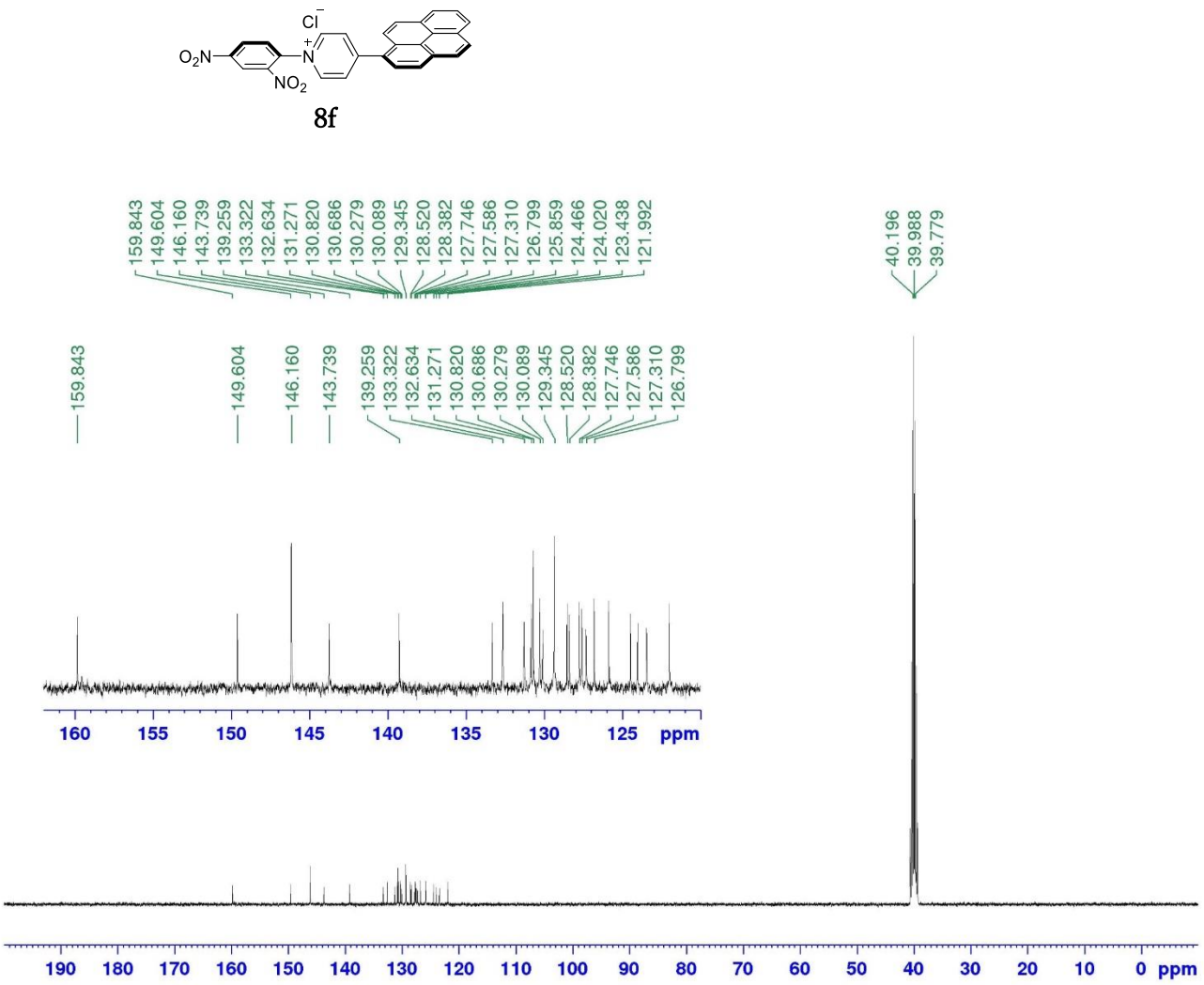


Figure S18. ^{13}C NMR spectrum of **8f** in DMSO-d_6.

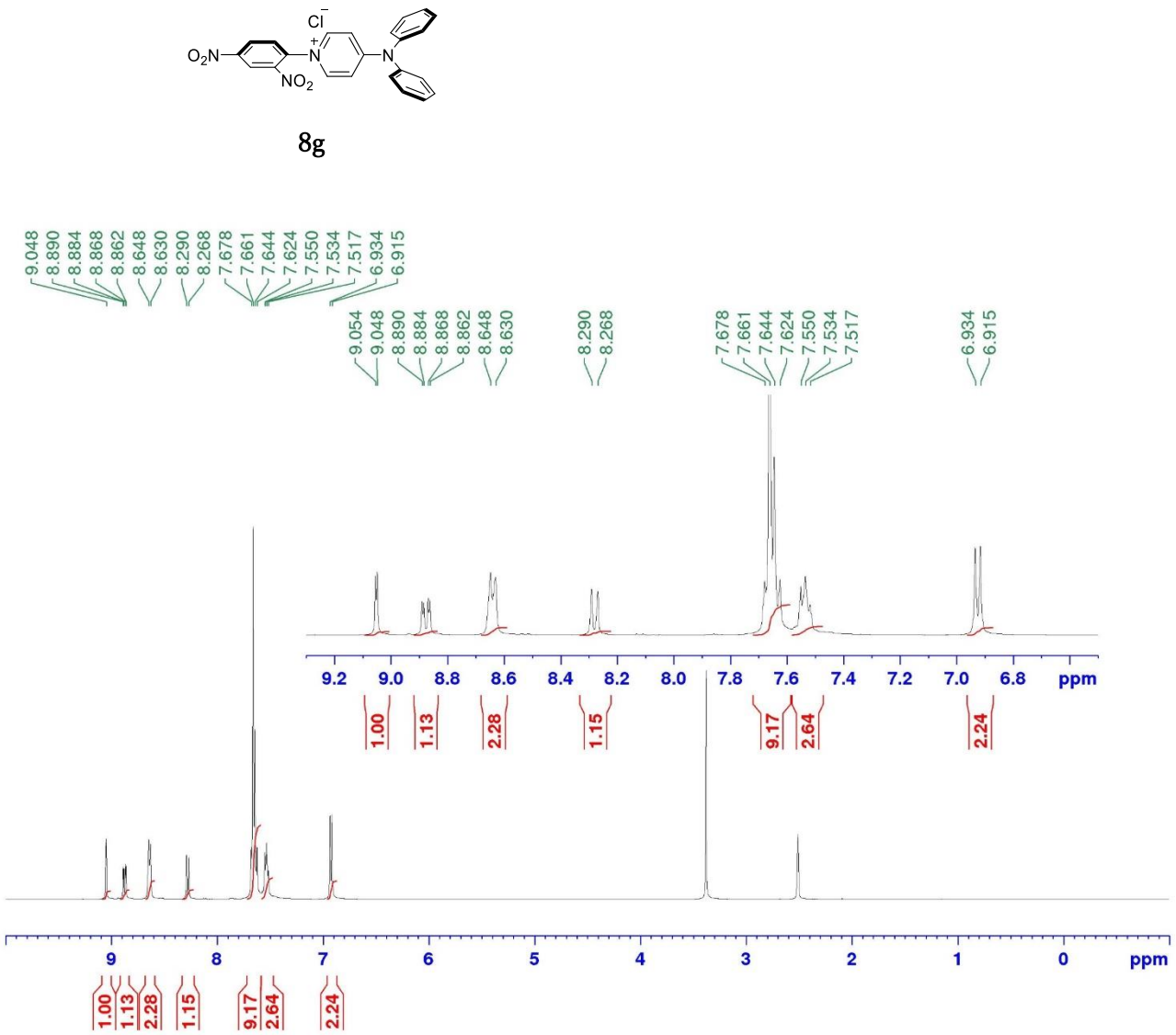
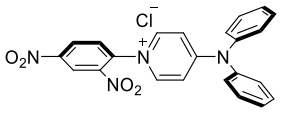


Figure S19. ^{1}H NMR spectrum of **8g** in DMSO-d_6.



8g

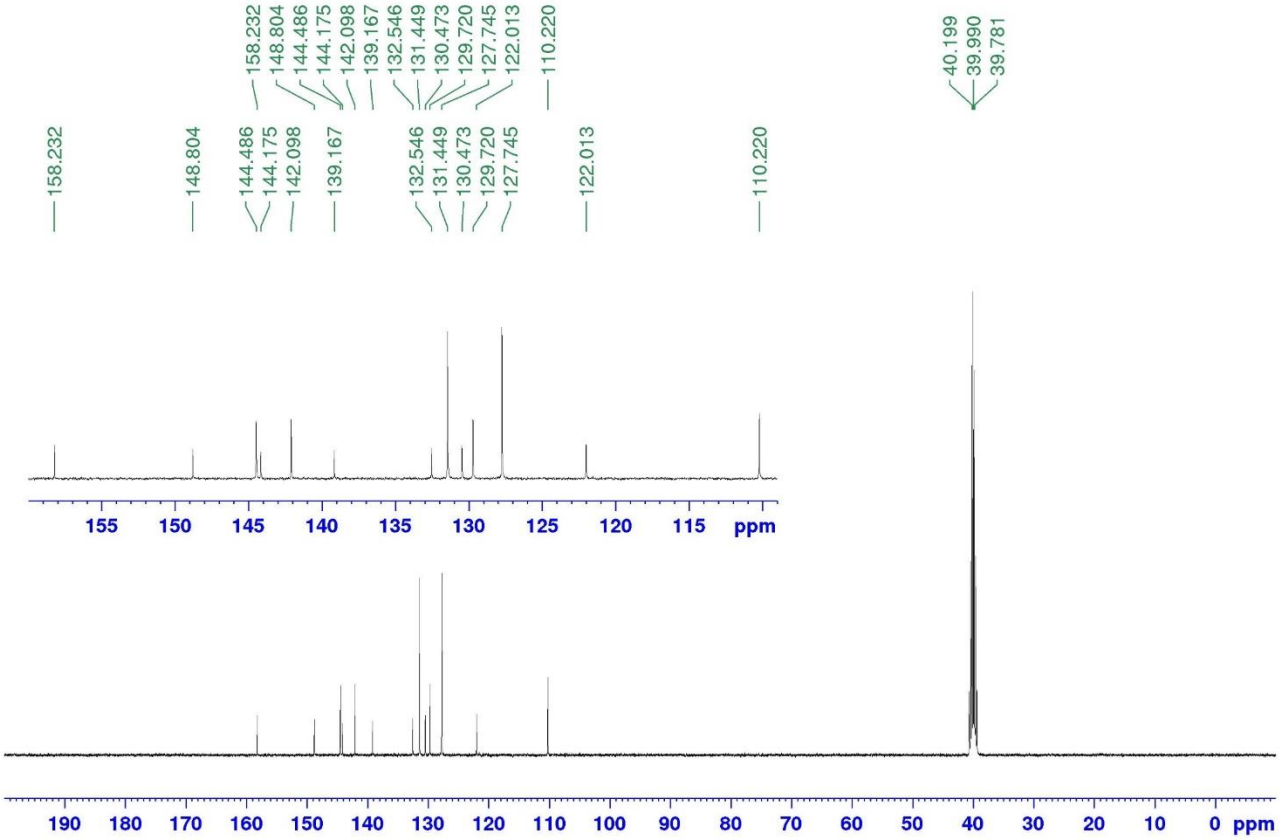


Figure S20. ^{13}C NMR spectrum of **8g** in DMSO-d_6.

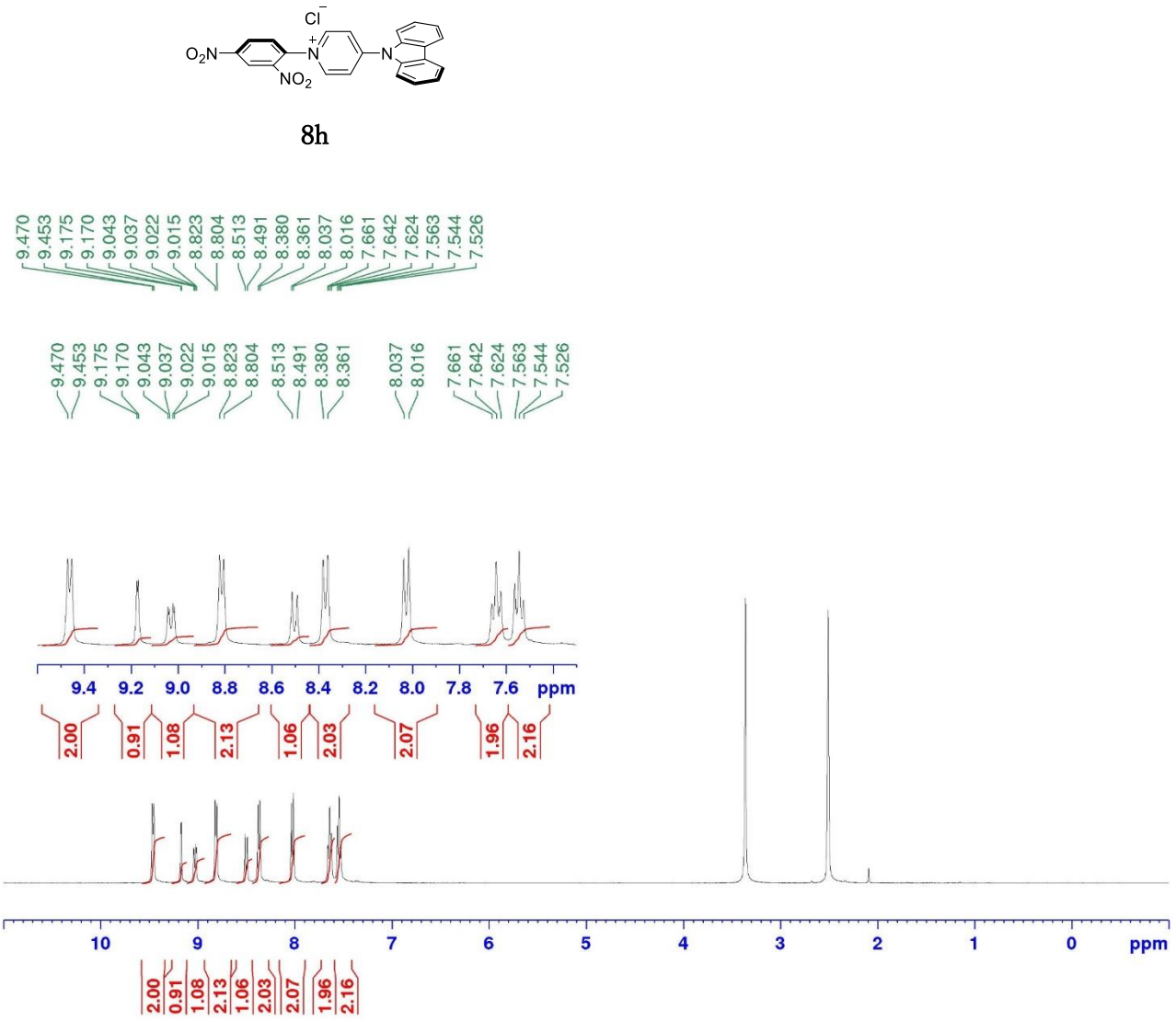
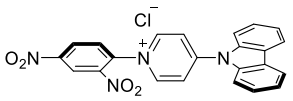


Figure S21. ^{1}H NMR spectrum of **8h** in DMSO-d_6.



8h

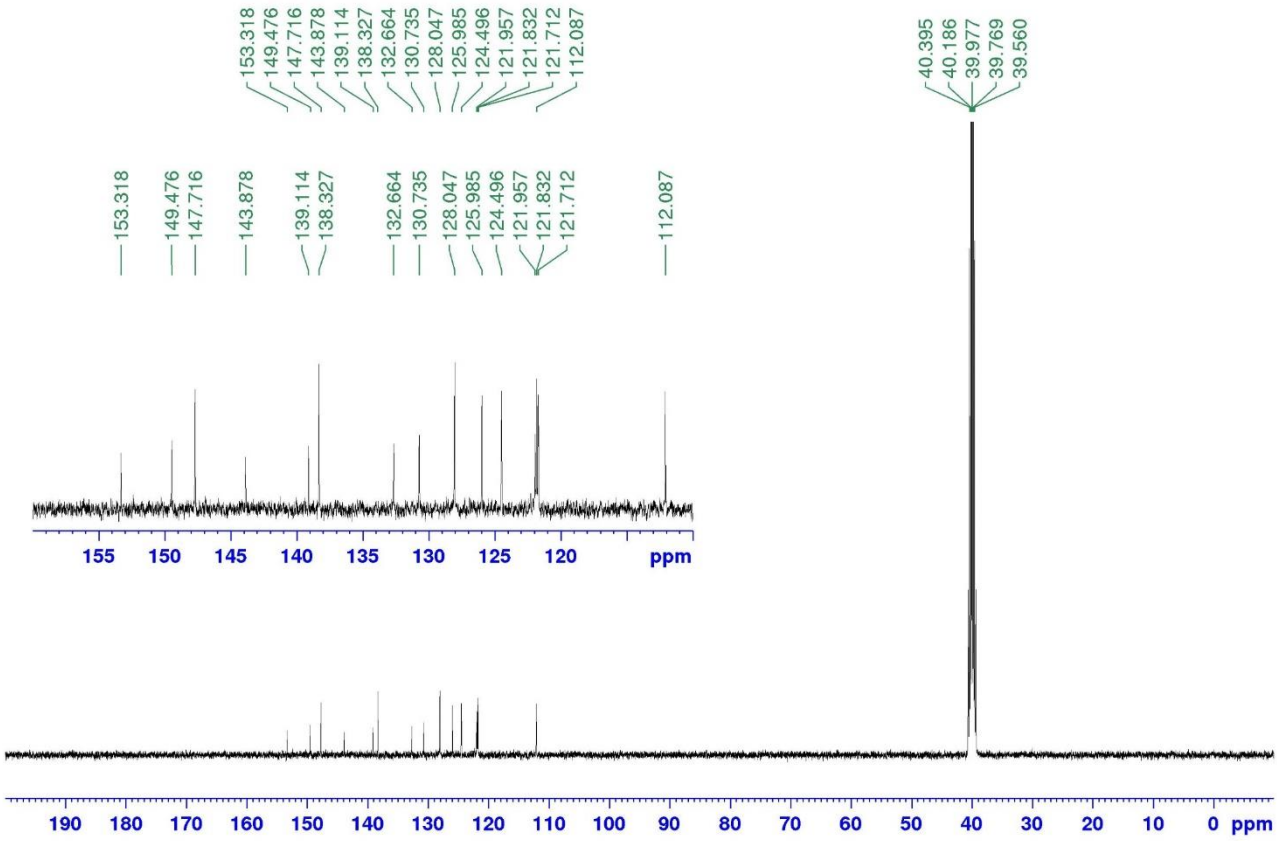


Figure S22. ^{13}C NMR spectrum of **8h** in DMSO-d_6.

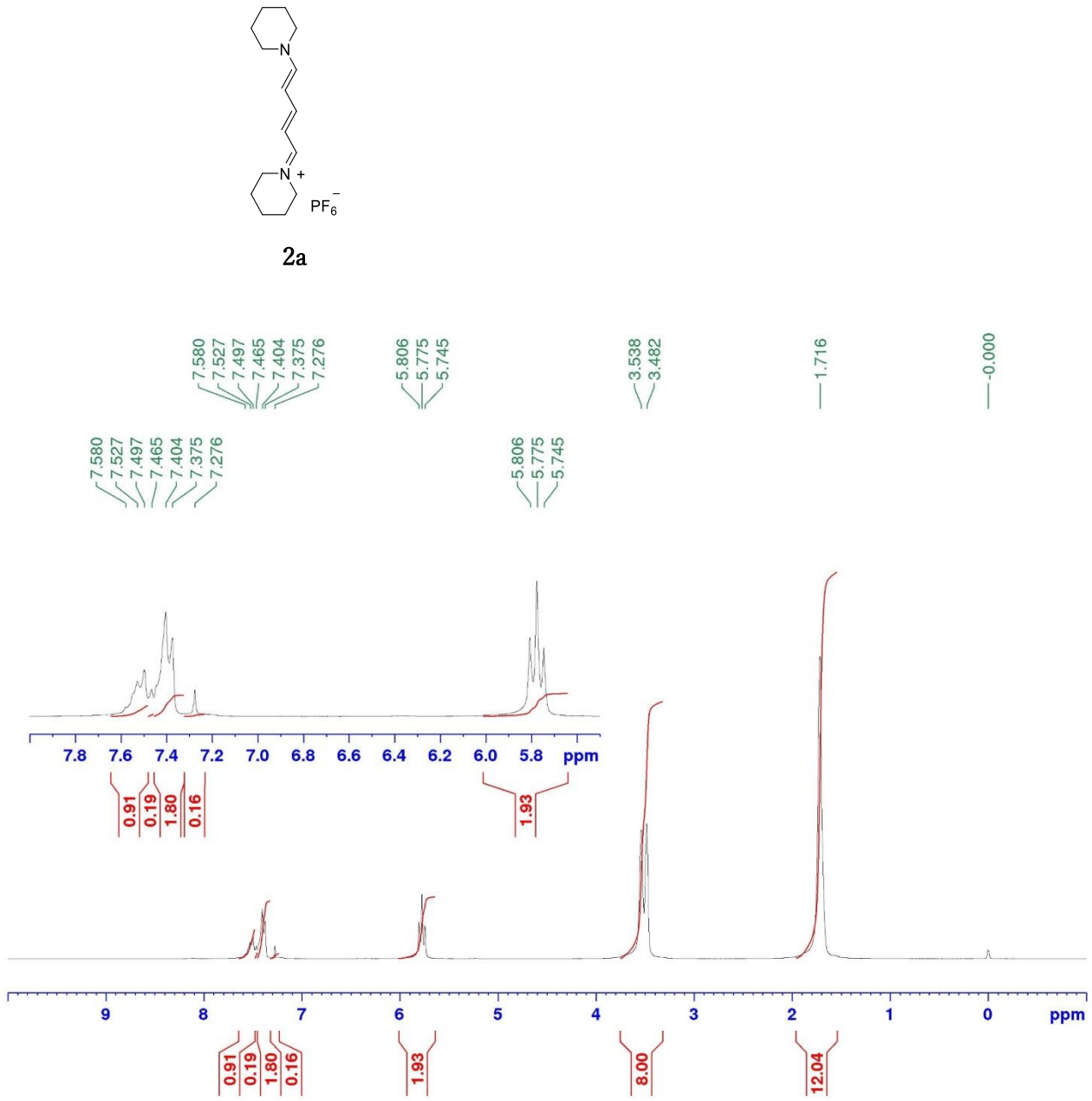


Figure S23. ^{1}H NMR spectrum of **2a** in $CDCl_3$.

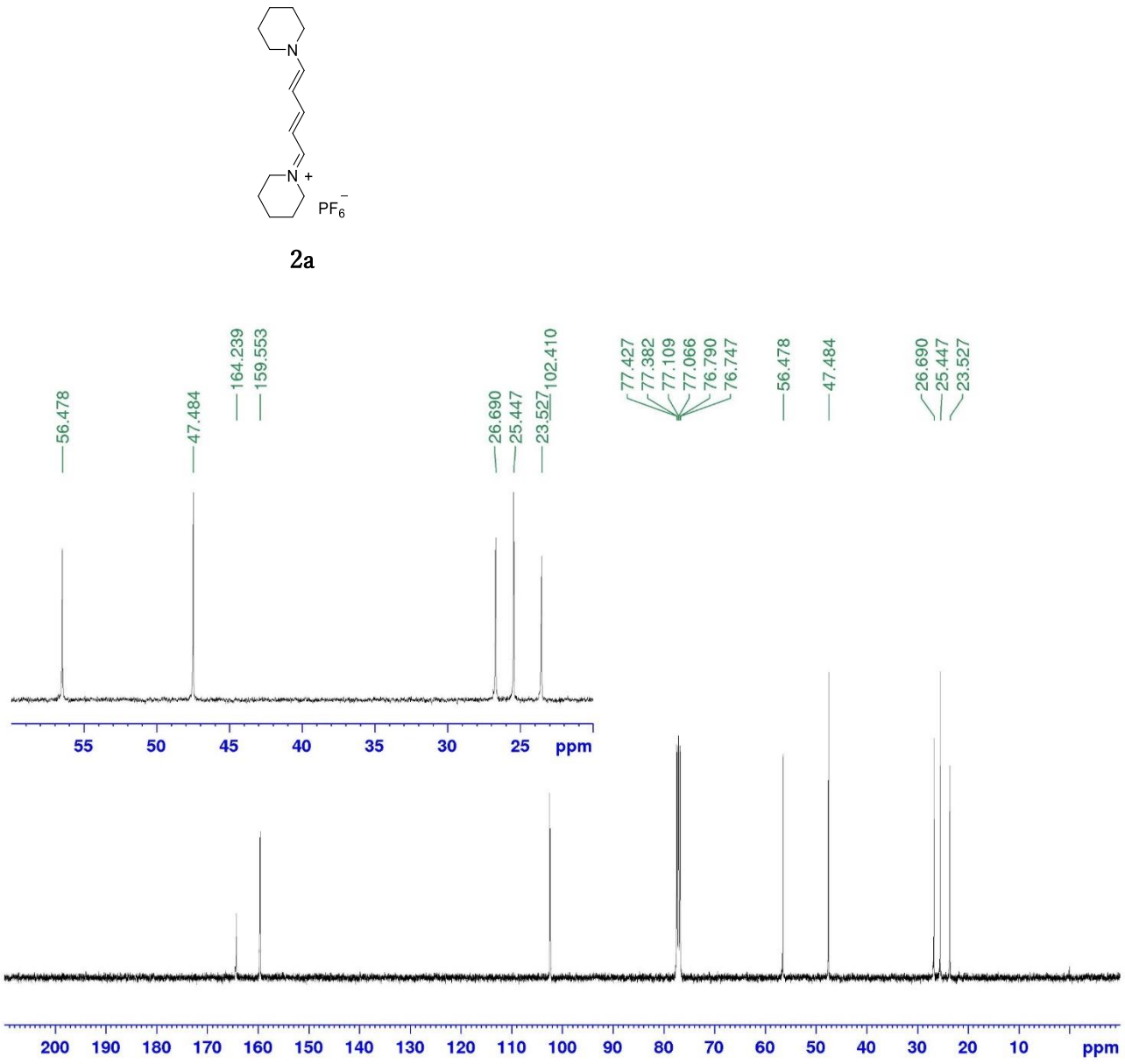


Figure S24. ^{13}C NMR spectrum of **2a** in $CDCl_3$.

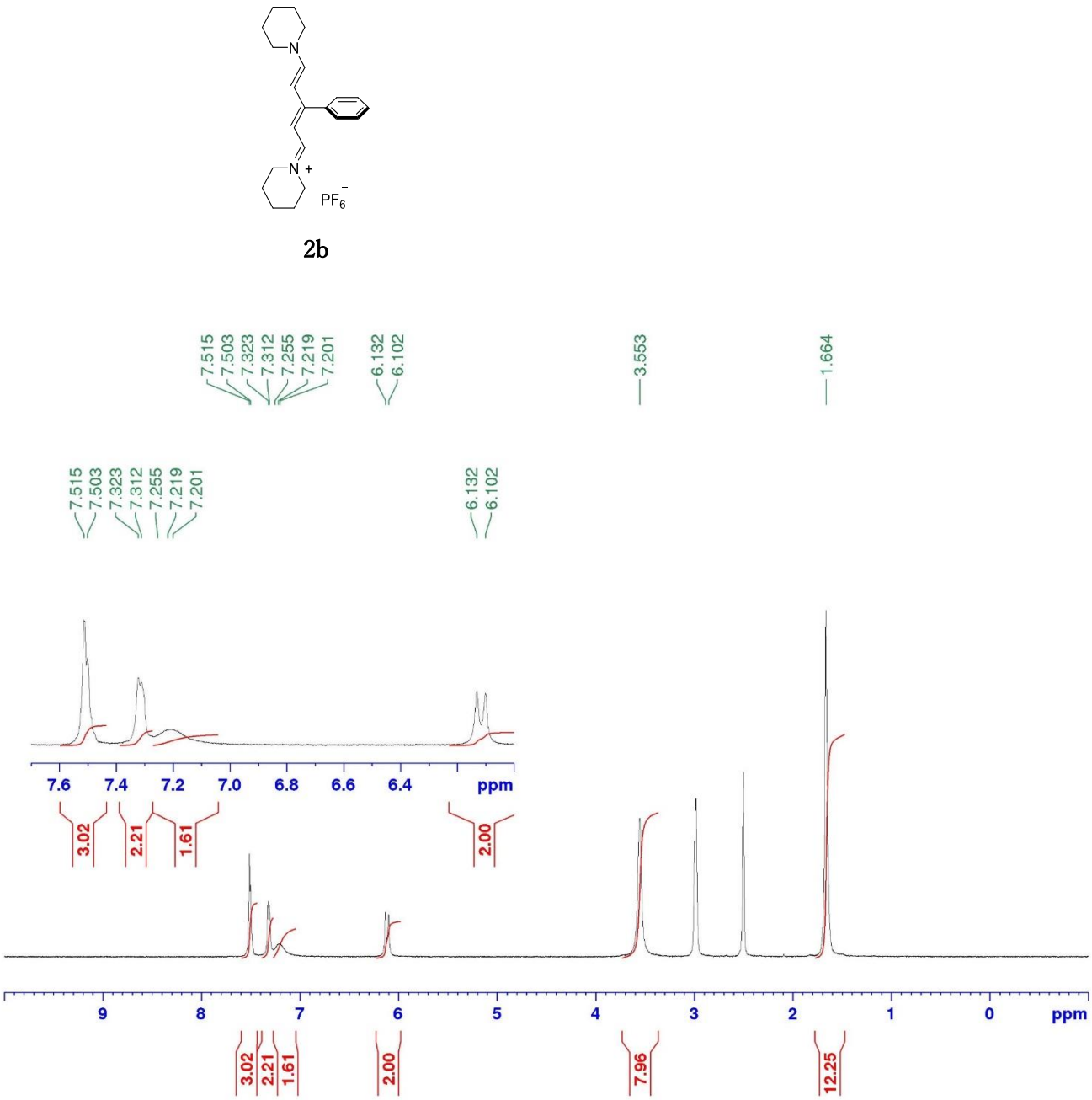


Figure S25. ^{1}H NMR spectrum of **2b** in DMSO-d_6.

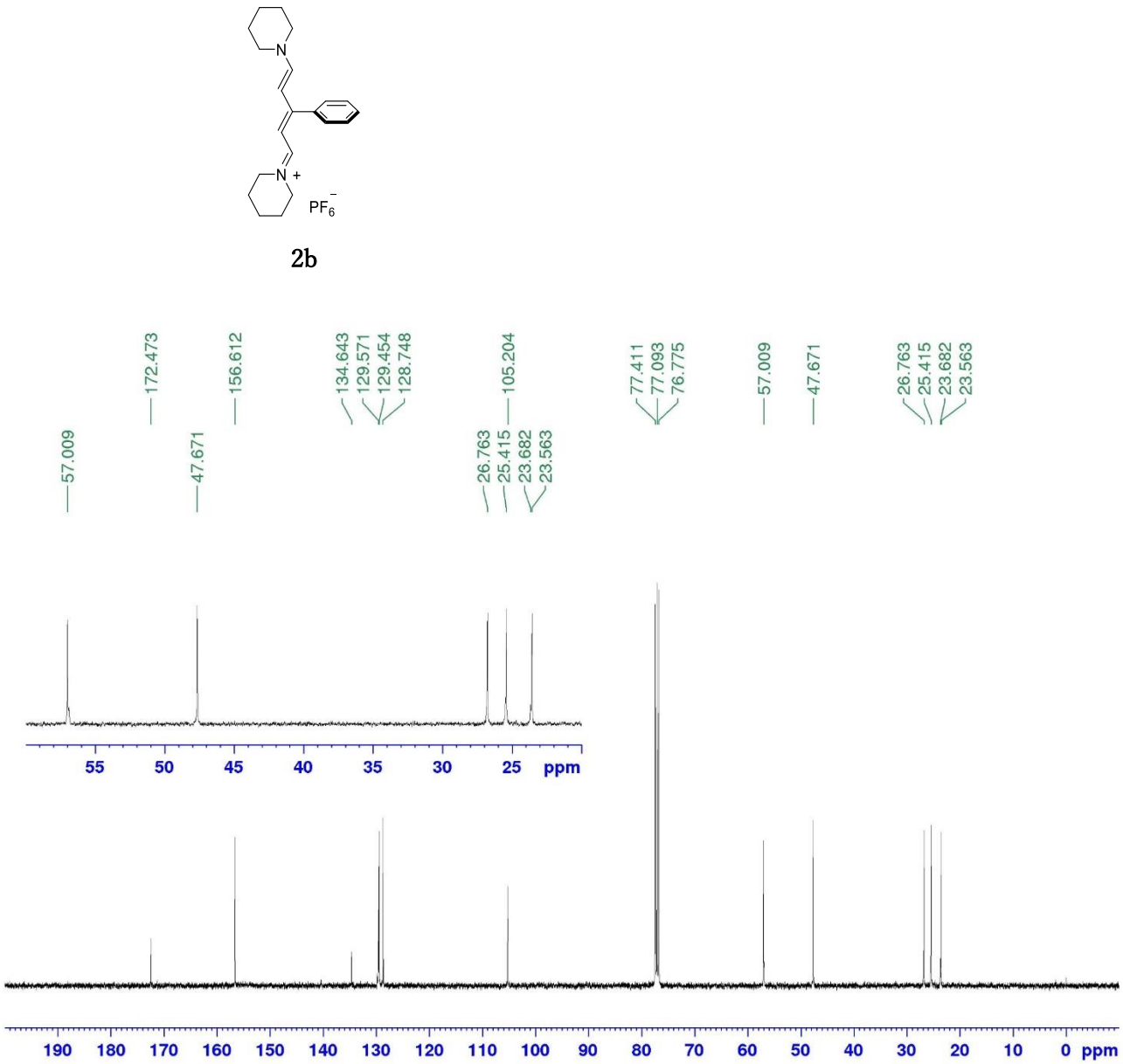


Figure S26. ^{13}C NMR spectrum of **2b** in $CDCl_3$.

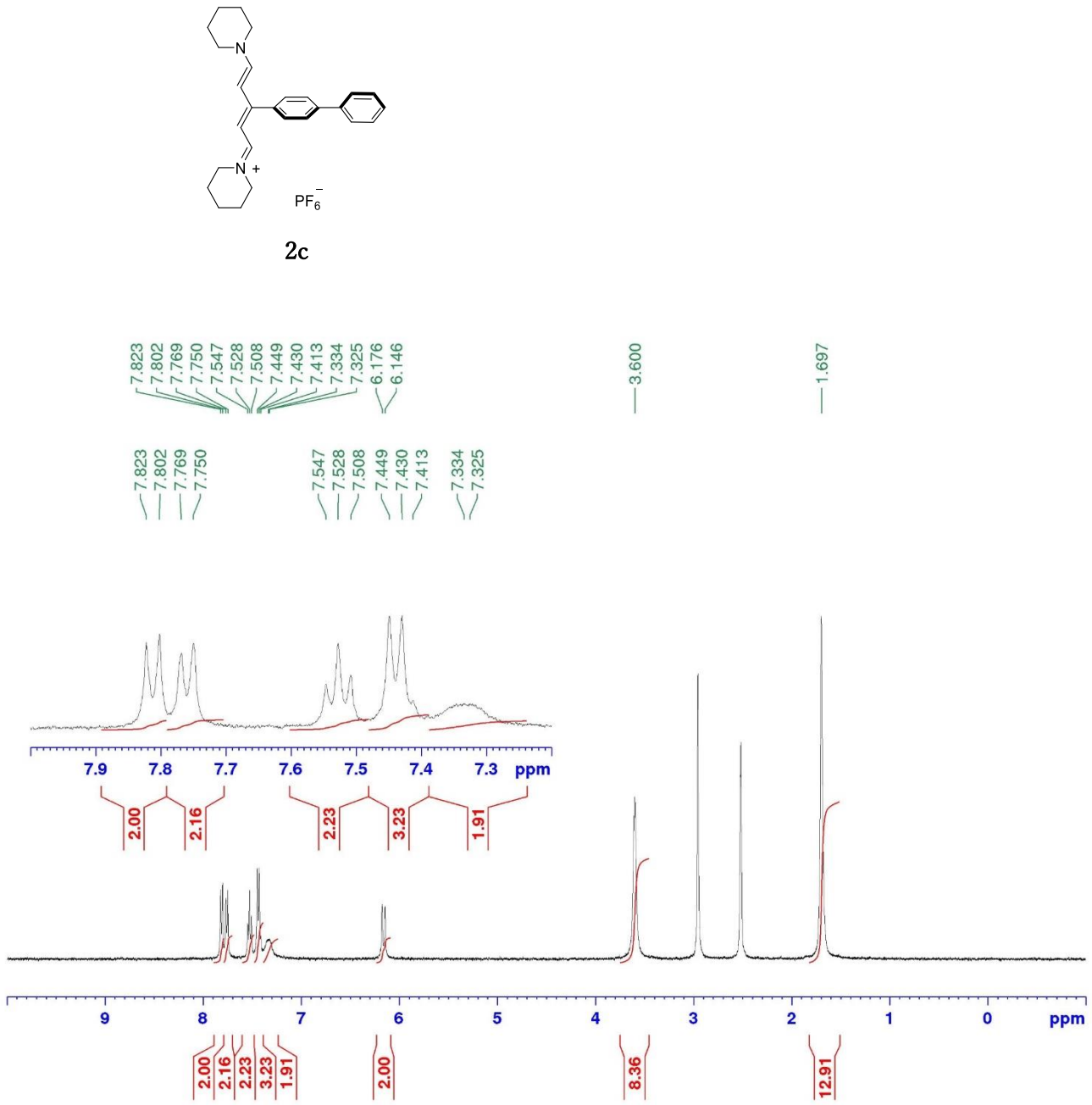


Figure S27. ^{1}H NMR spectrum of **2c** in DMSO-d_6.

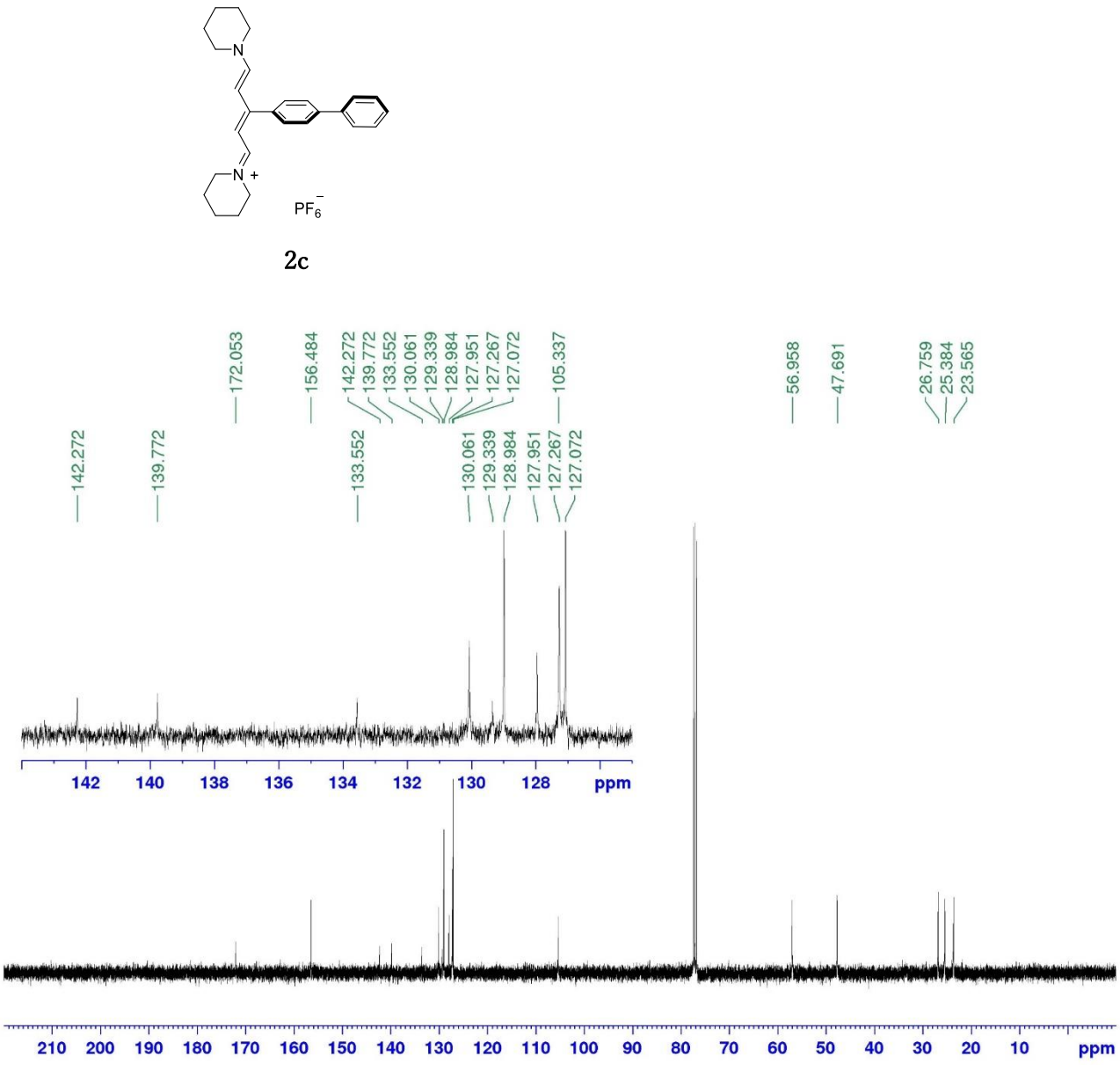


Figure S28. ^{13}C NMR spectrum of **2c** in $CDCl_3$.

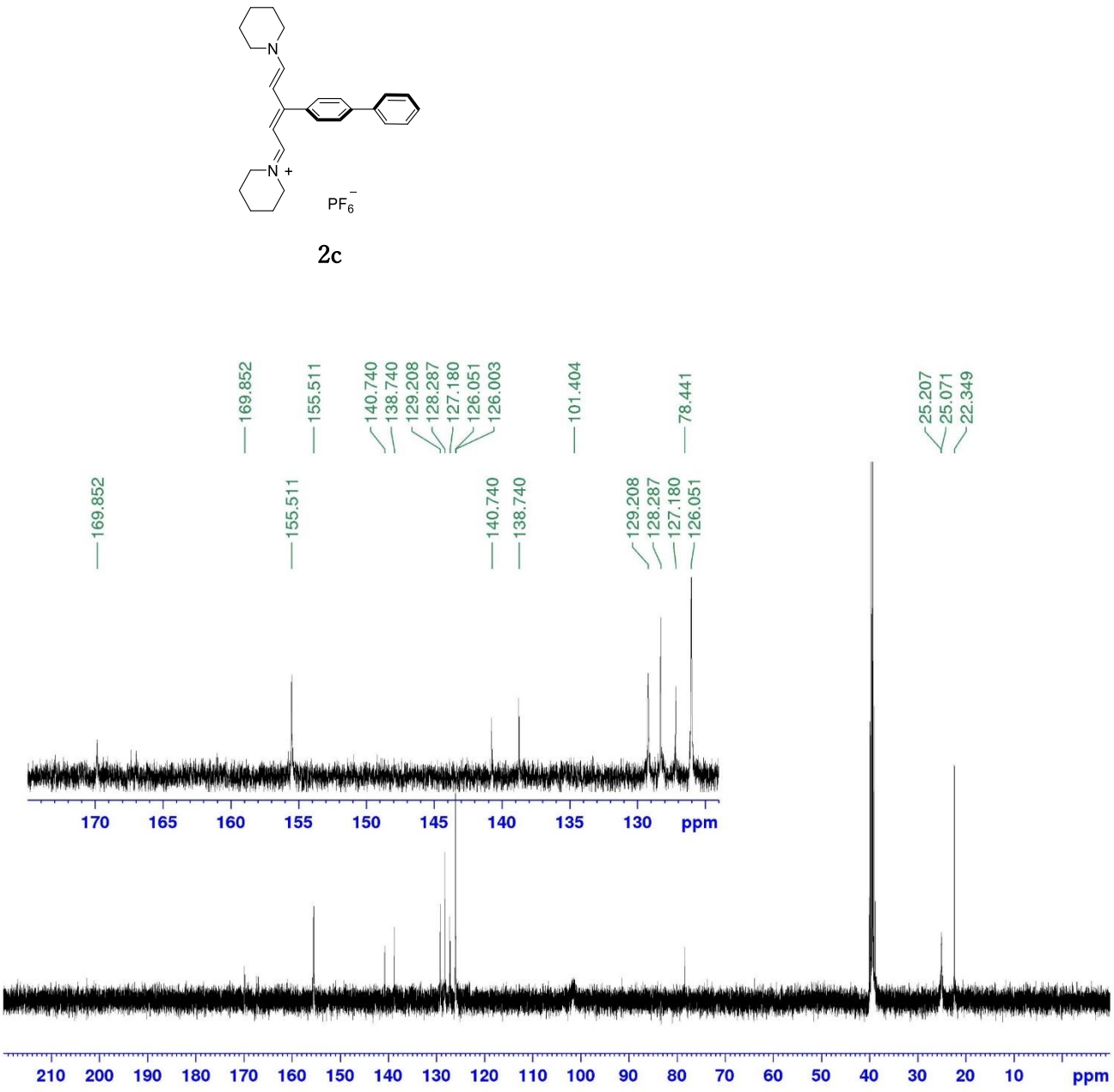


Figure S29. ^{13}C NMR spectrum of **2c** in DMSO-d_6 at 100 ºC.

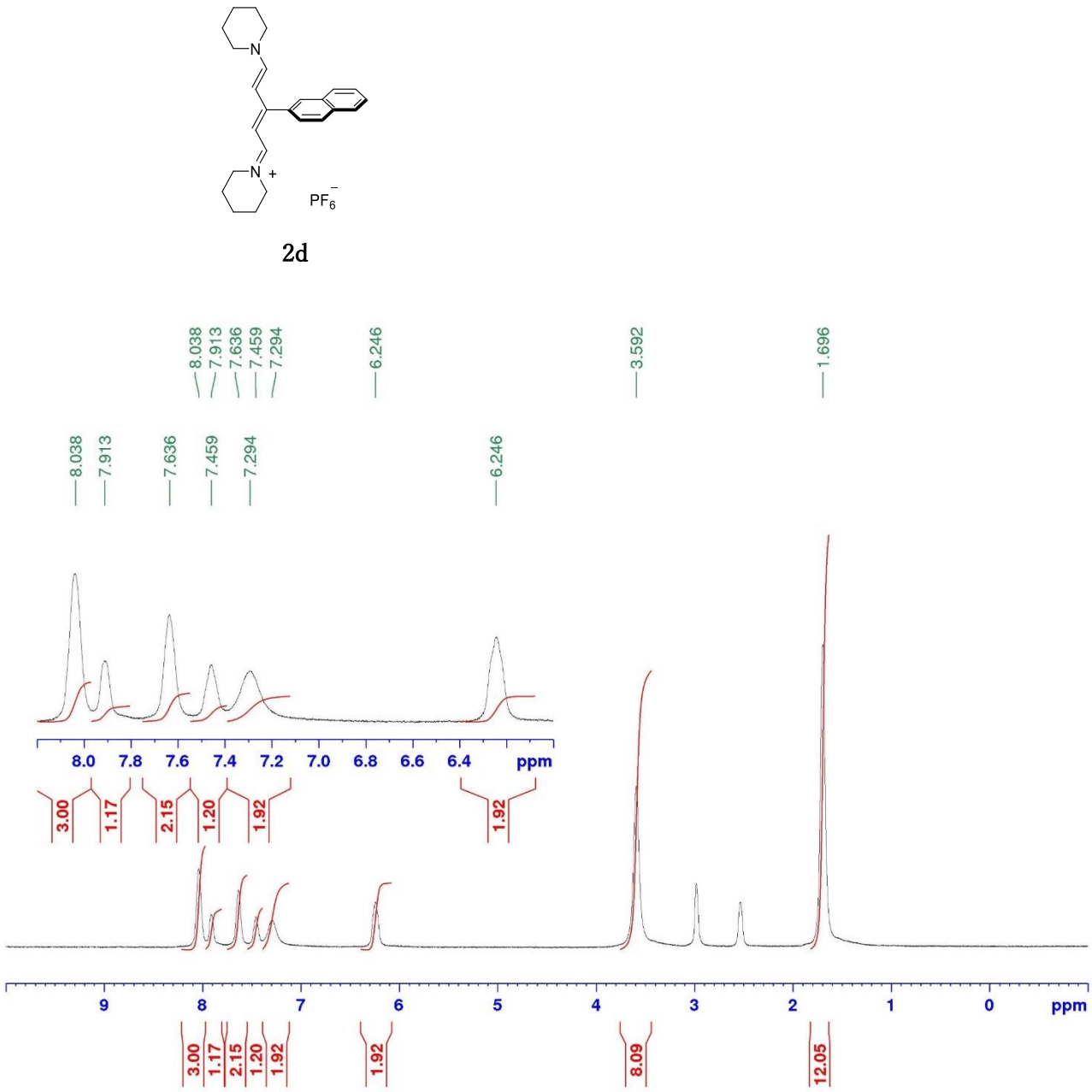


Figure S30. ^{1}H NMR spectrum of **2d** in DMSO-d_6.

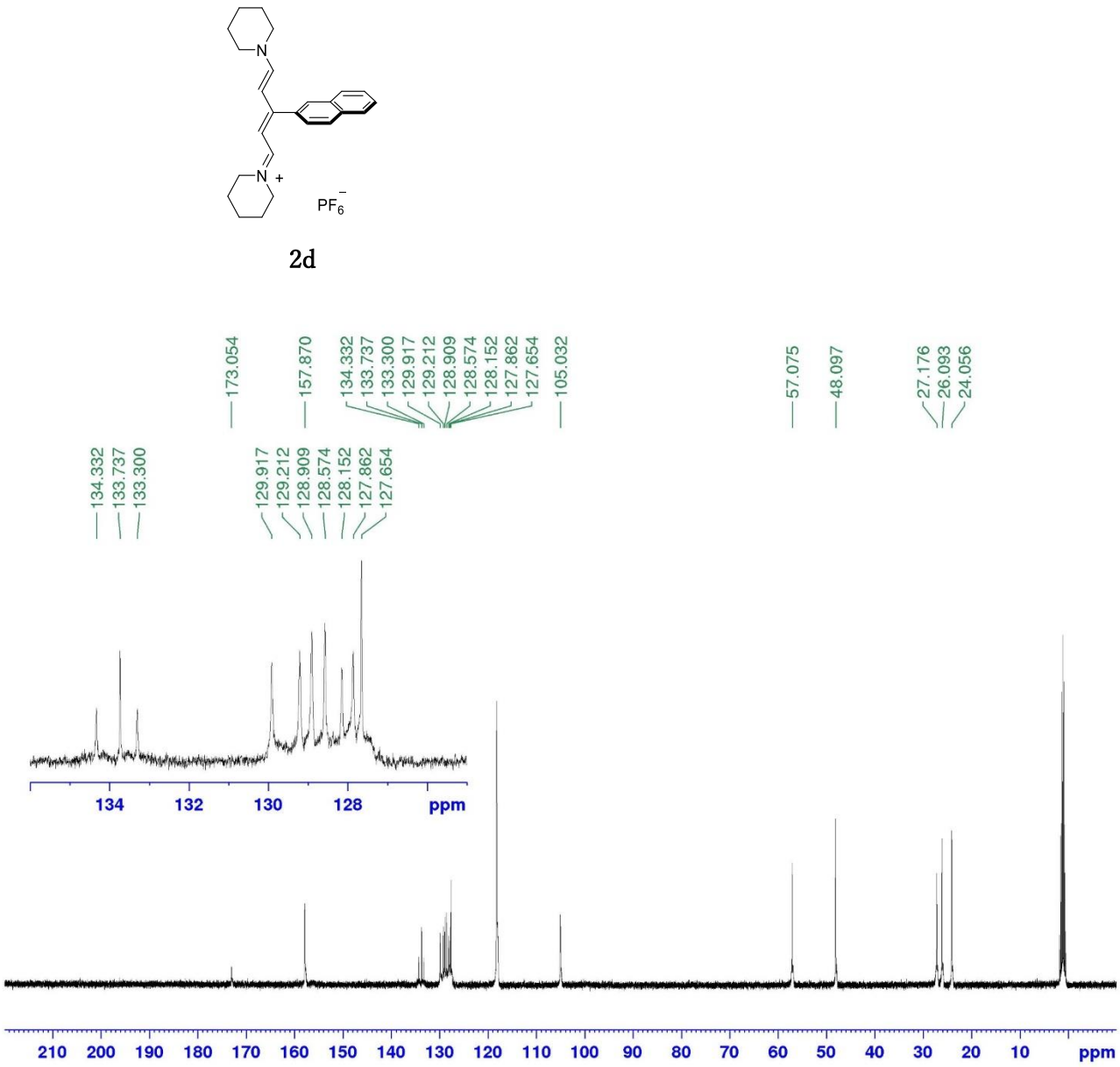


Figure S31. ^{13}C NMR spectrum of **2d** in CD_3CN.

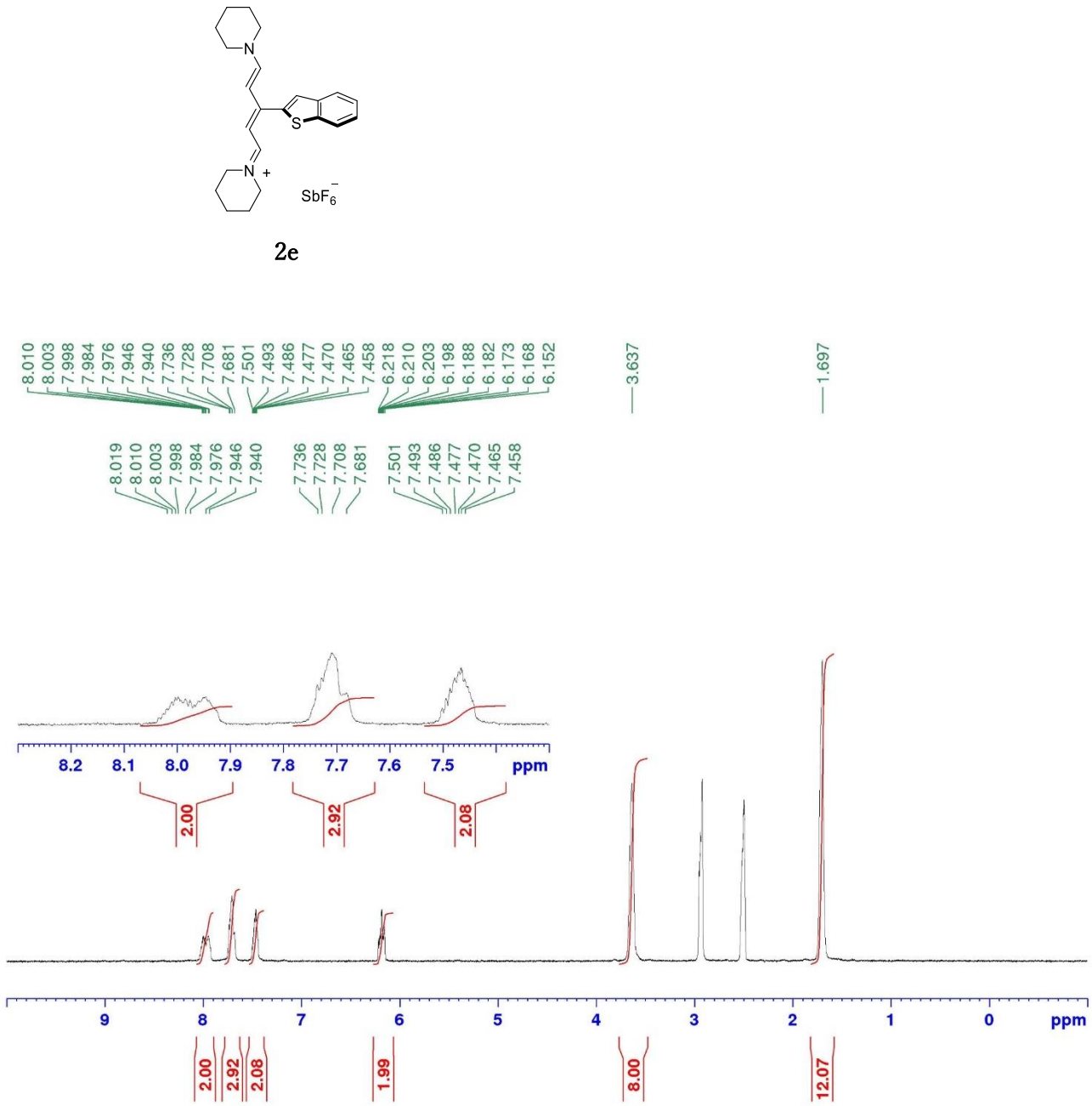


Figure S32. ^{1}H NMR spectrum of **2e** in DMSO-d_6.

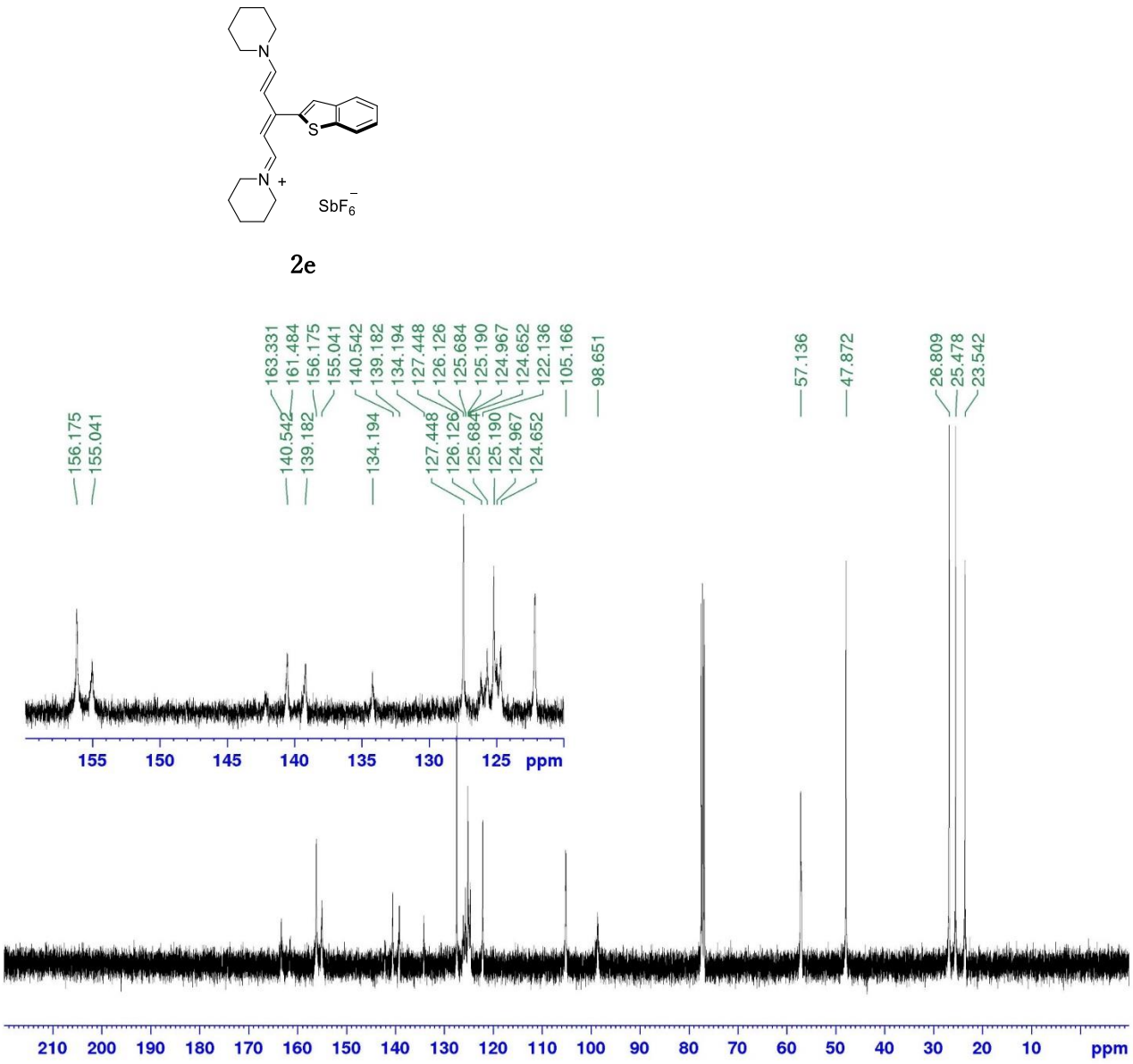


Figure S33. ^{13}C NMR spectrum of **2e** in $CDCl_3$.

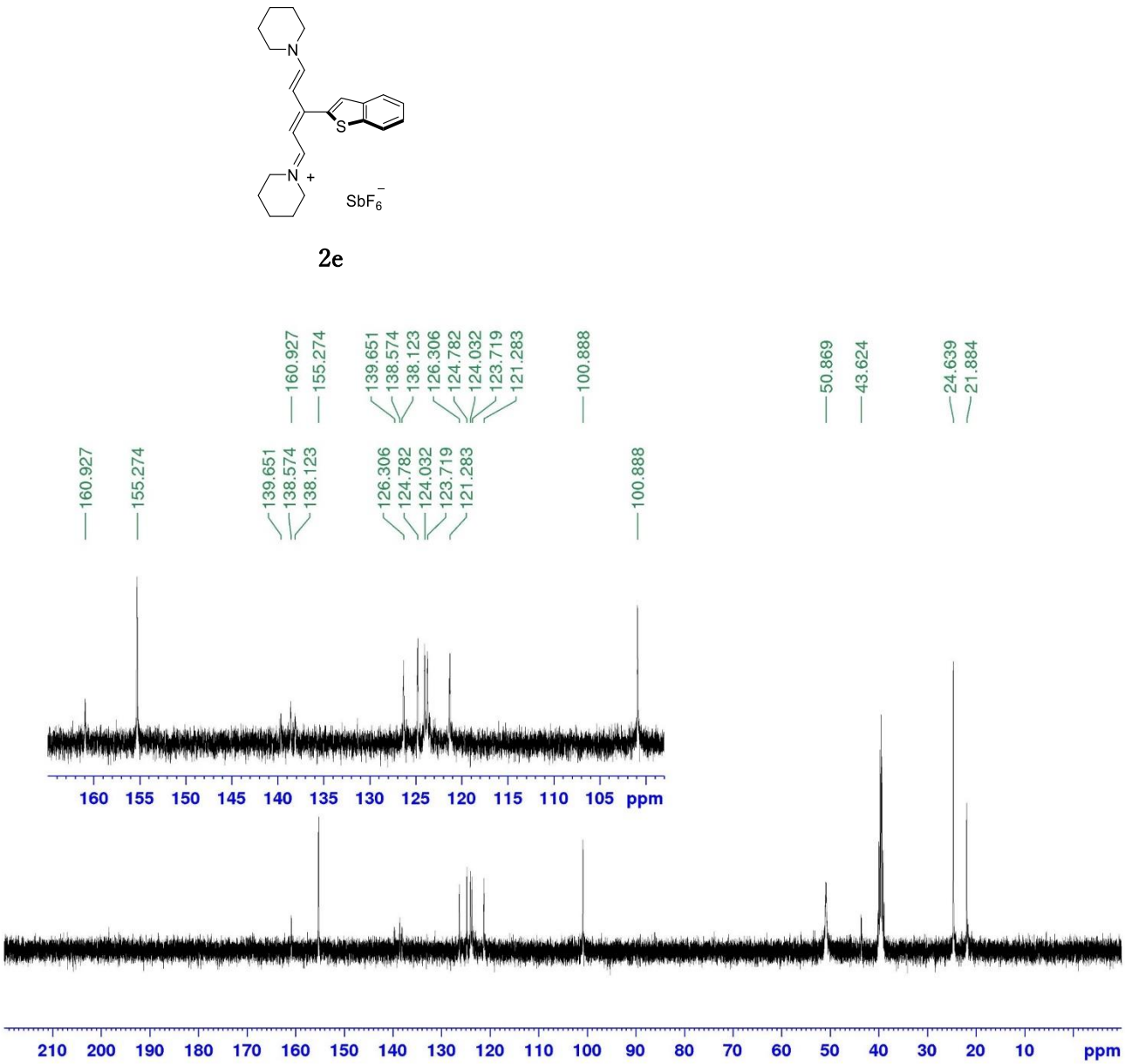
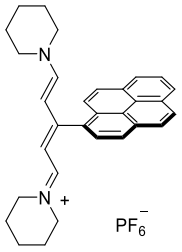


Figure S34. ^{13}C NMR spectrum of **2e** in DMSO-d_6 at 160 ºC.



2f

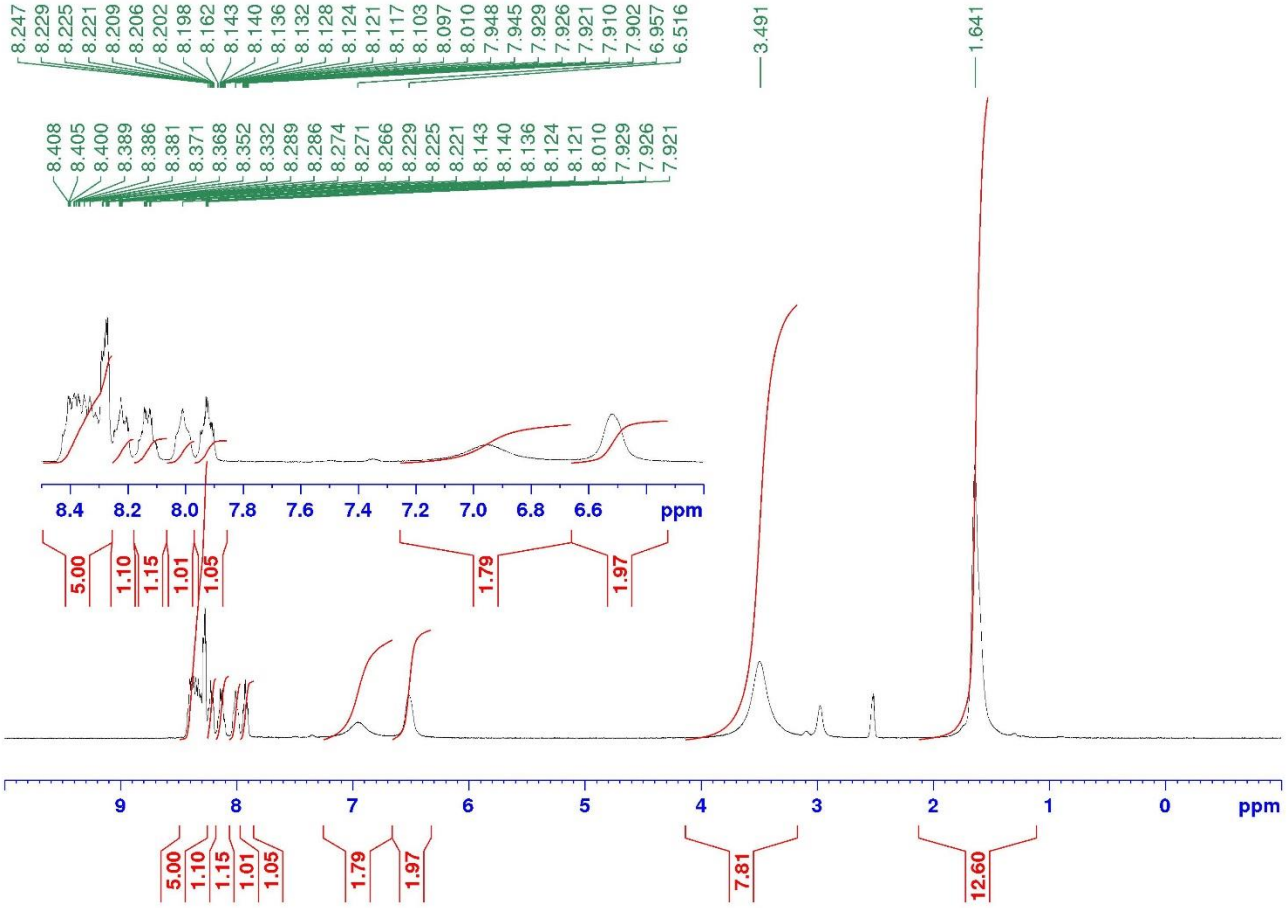
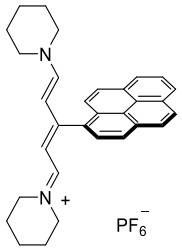


Figure S35. ^{1}H NMR spectrum of **2f** in DMSO-d_6.



2f

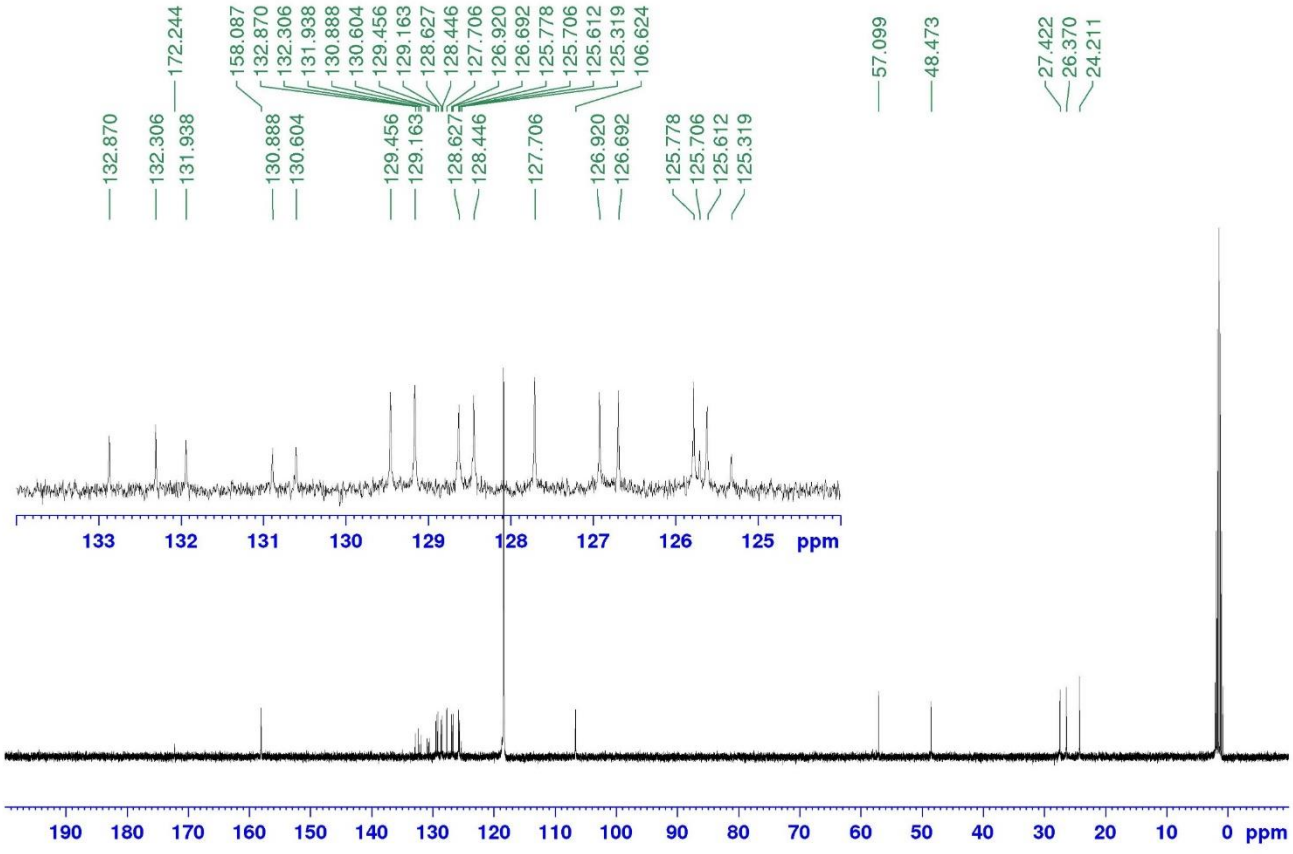


Figure S36. ^{13}C NMR spectrum of **2f** in CD_3CN.

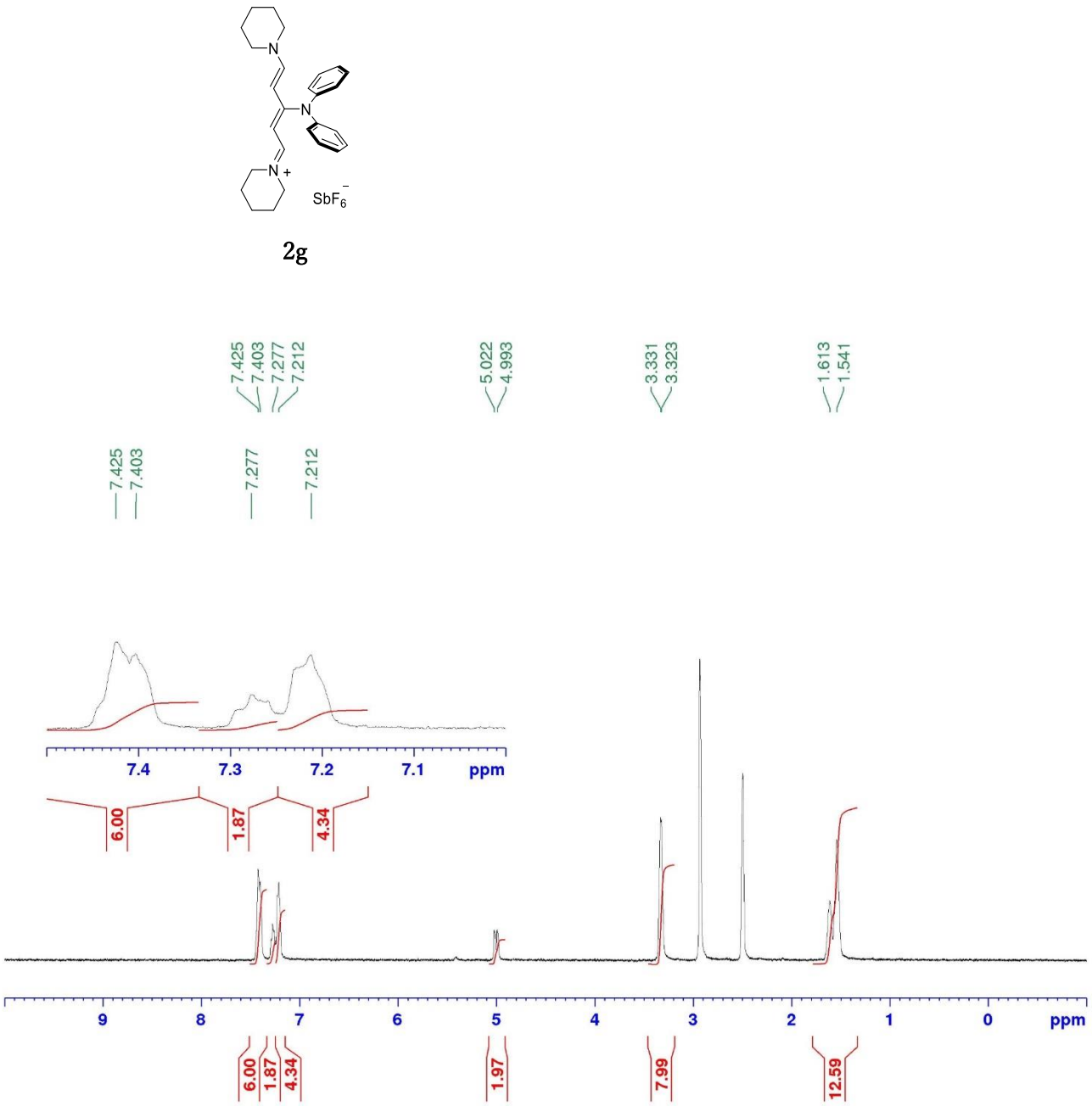


Figure S37. ^{1}H NMR spectrum of **2g** in DMSO-d_6.

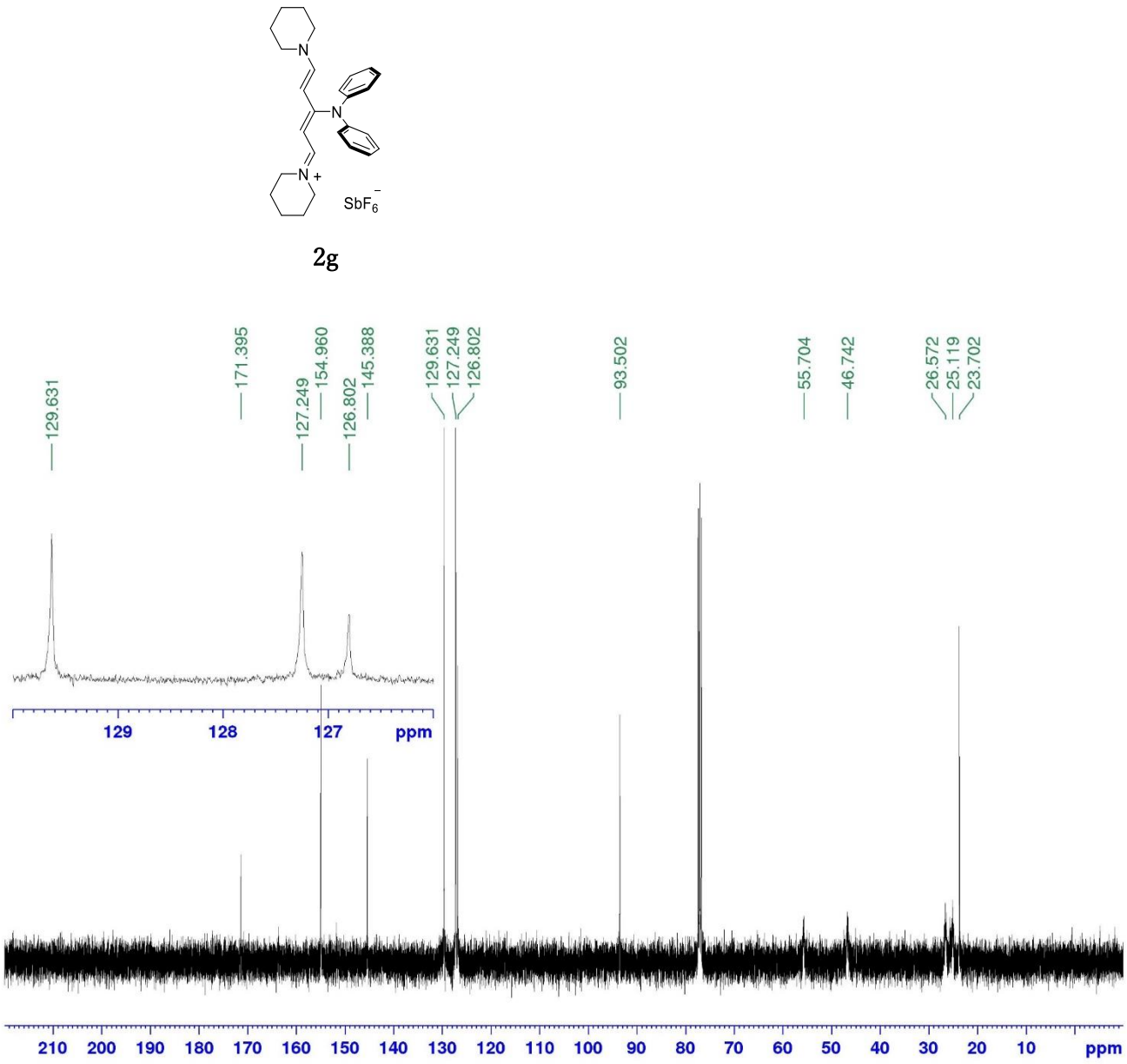
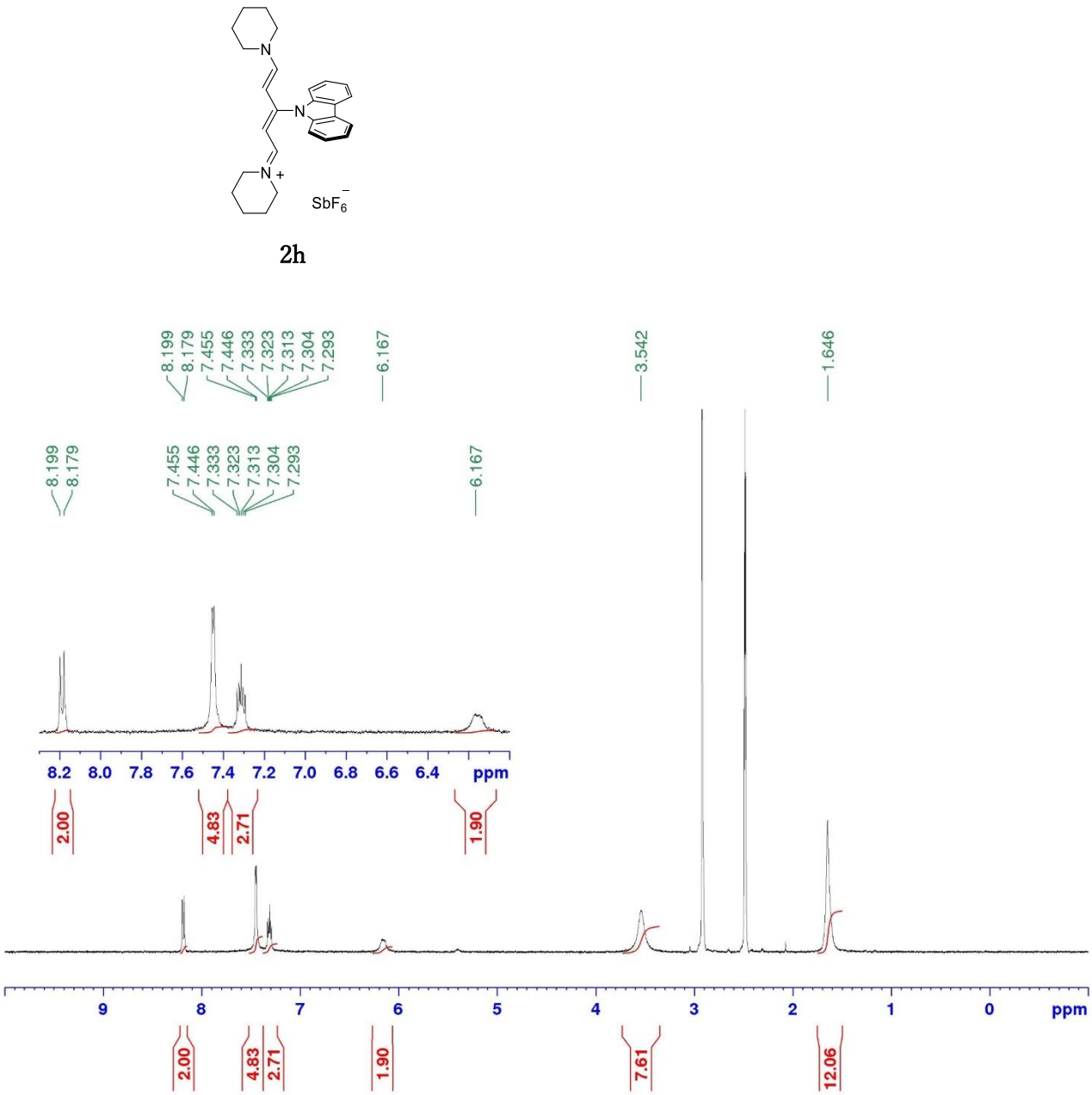
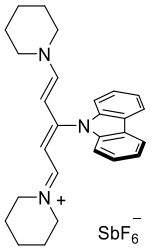


Figure S38. ^{13}C NMR spectrum of **2g** in $CDCl_3$.



2h

Figure S39. ^{1}H NMR spectrum of **2h** in DMSO-d_6.



2h

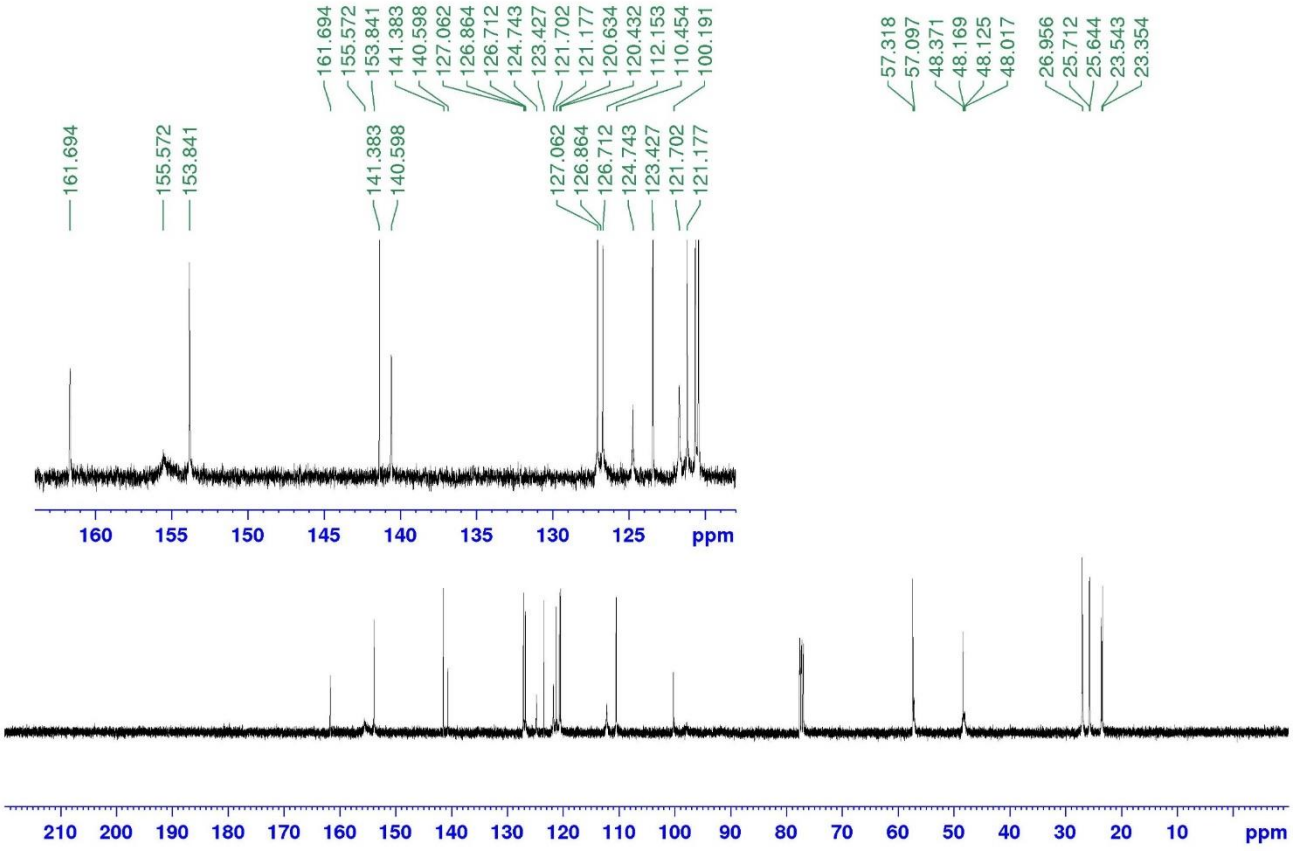


Figure S40. ^{13}C NMR spectrum of **2h** in $CDCl_3$.

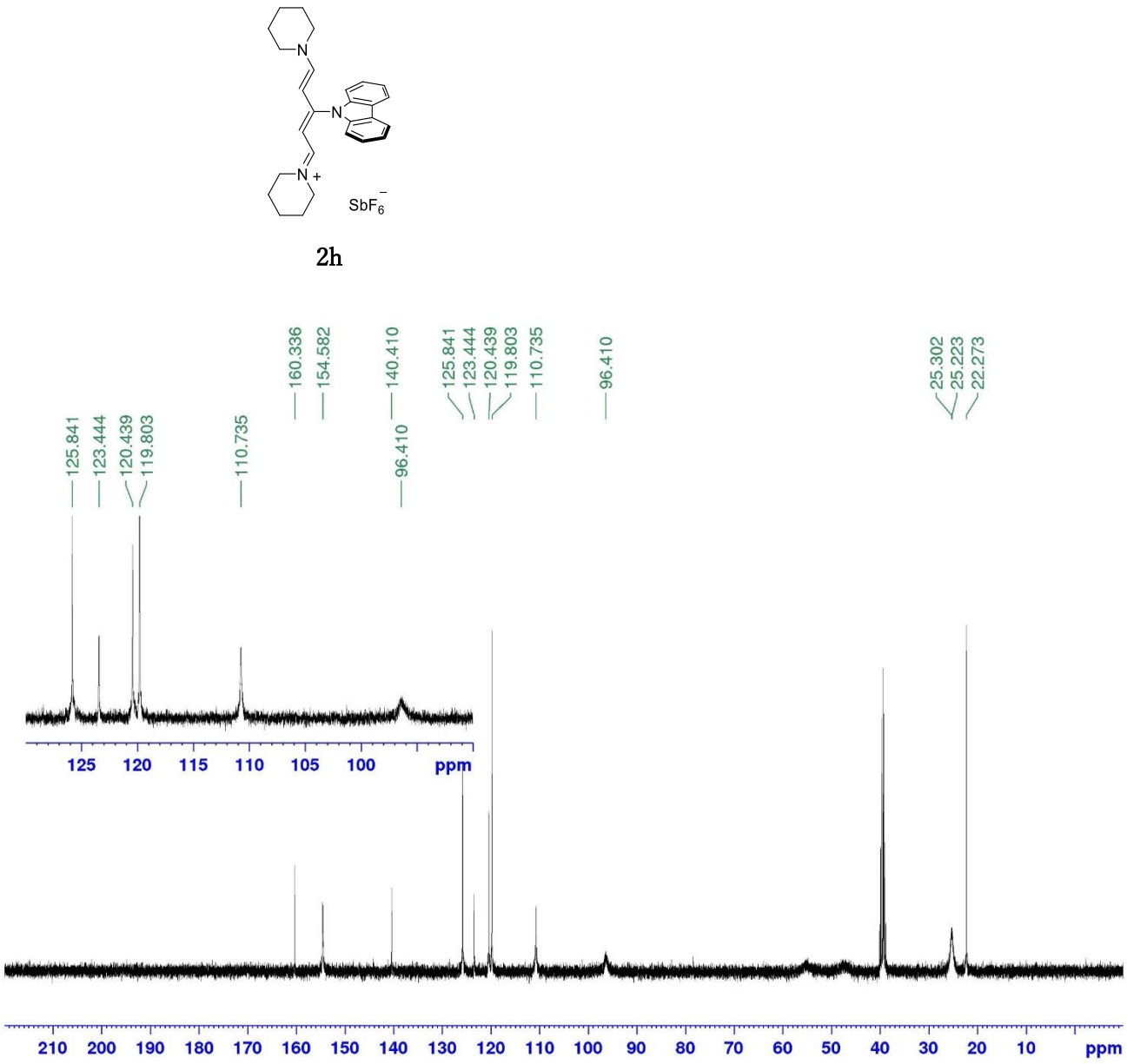
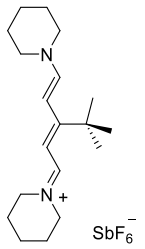


Figure S41. ^{13}C NMR spectrum of **2h** in DMSO-d_6 at 100 ºC



2i

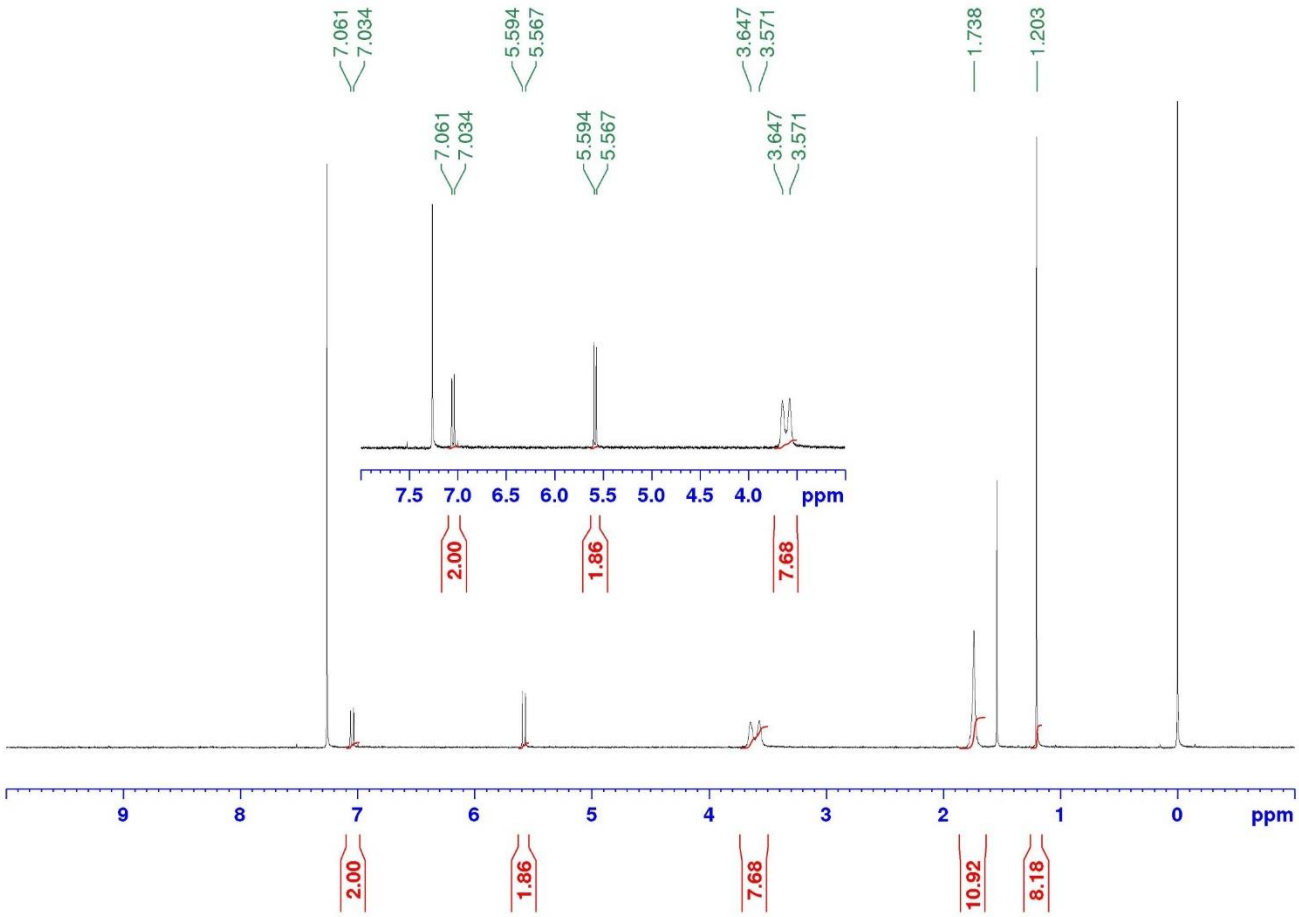


Figure S42. ^{1}H NMR spectrum of **2i** in $CDCl_3$.

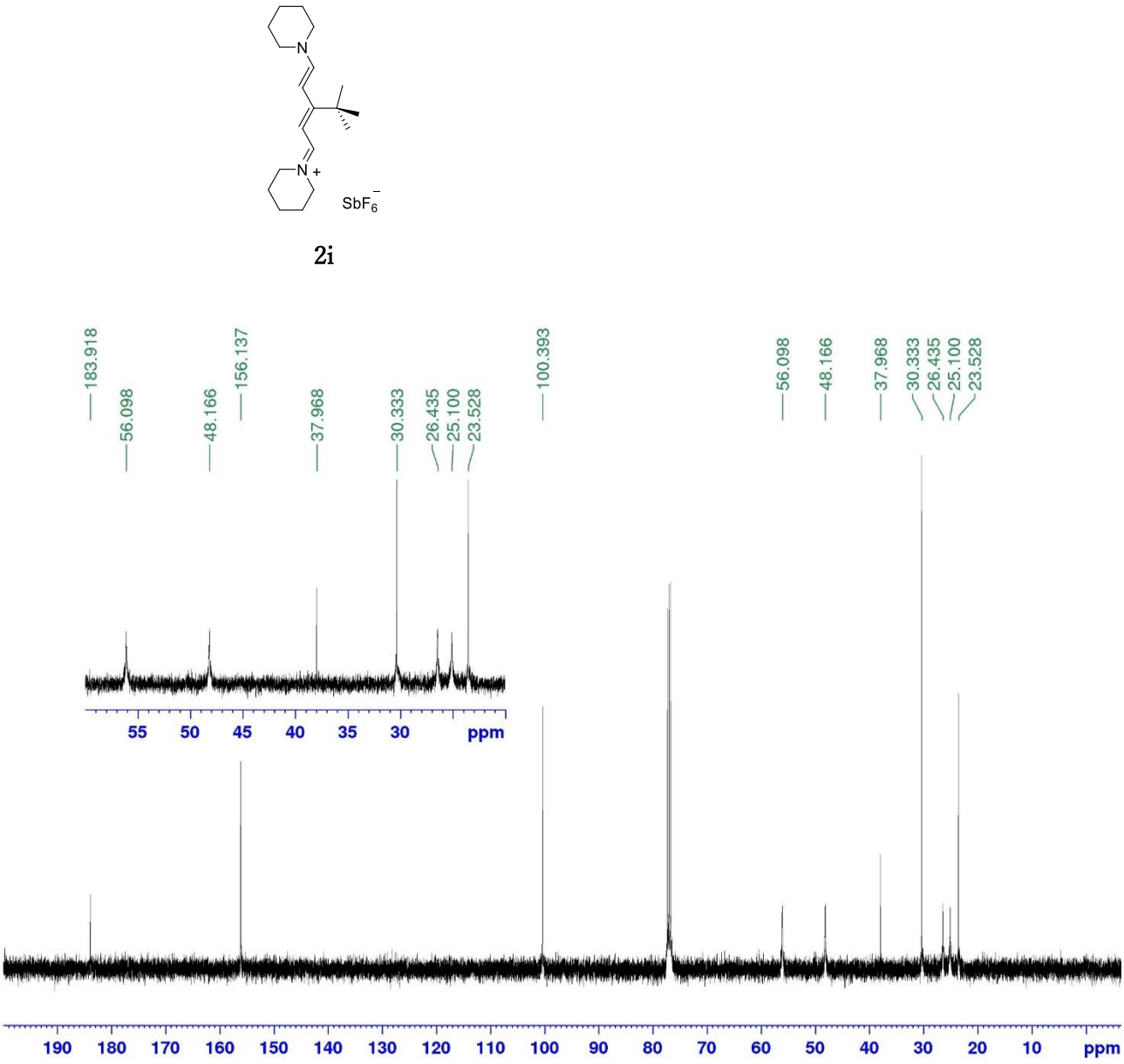


Figure S43. ^{13}C NMR spectrum of **2i** in $CDCl_3$.

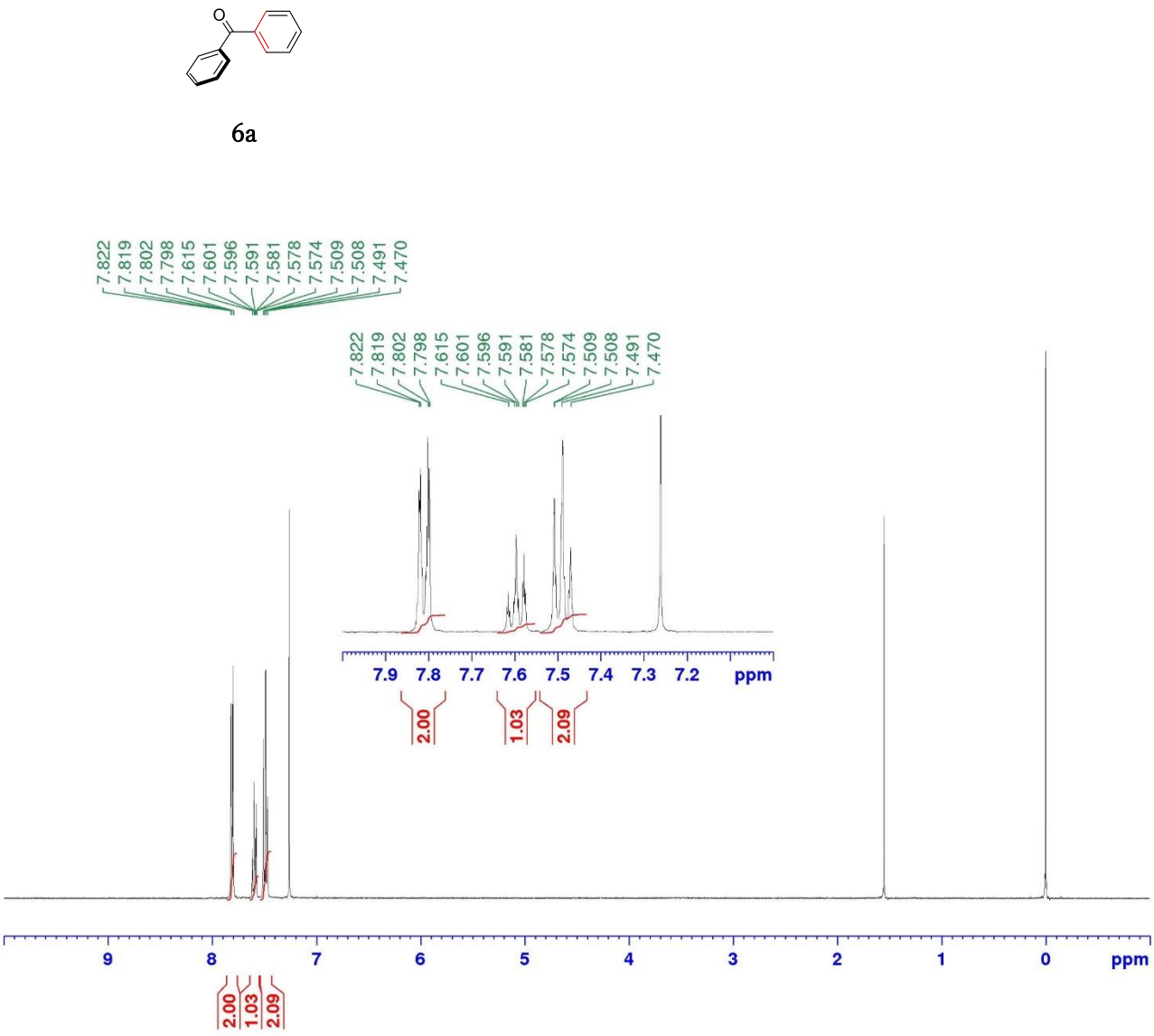


Figure S44. ^{1}H NMR spectrum of **6a** in $CDCl_3$.

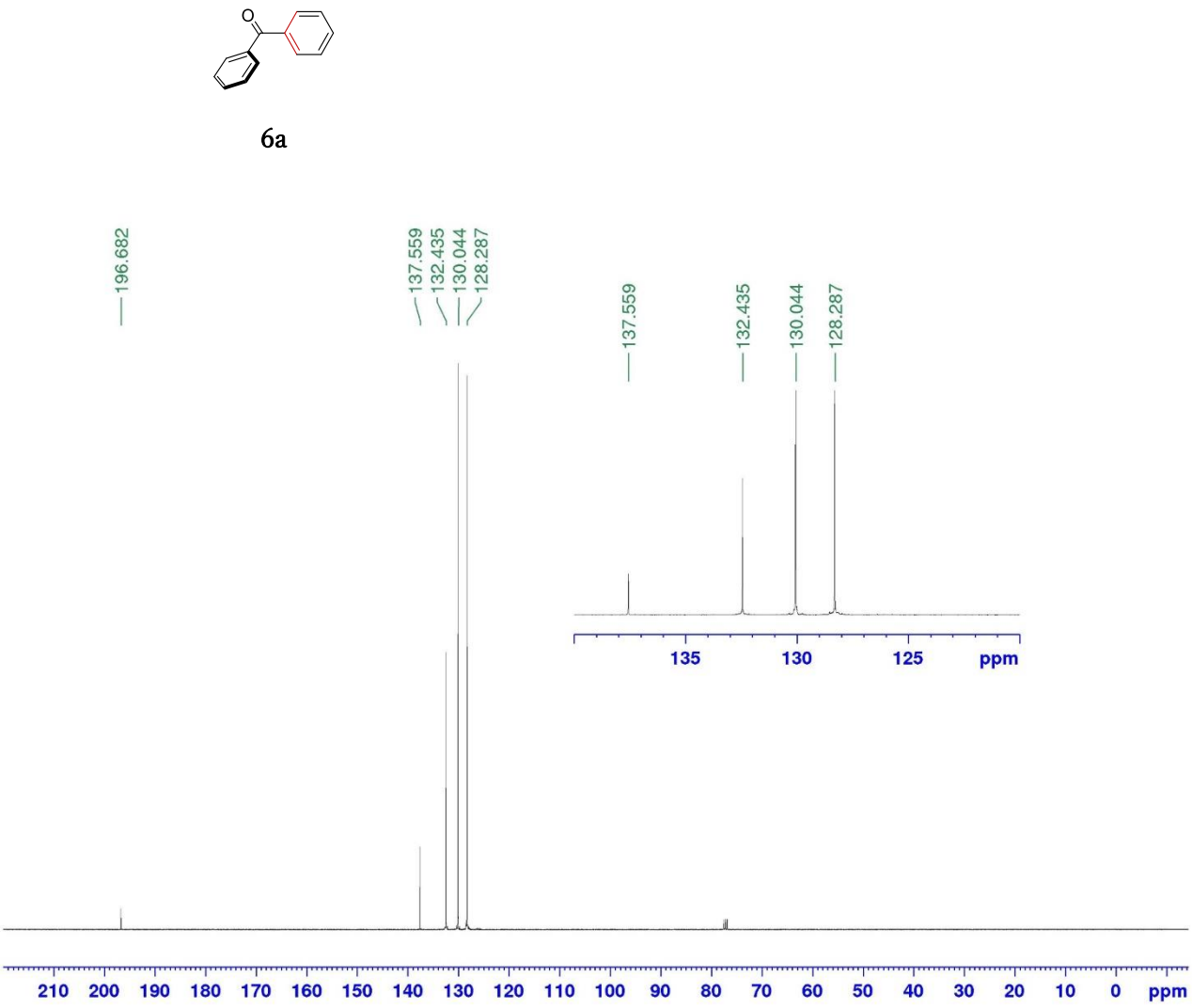
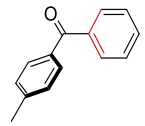


Figure S45. ^{13}C NMR spectrum of **6a** in $CDCl_3$.



6b

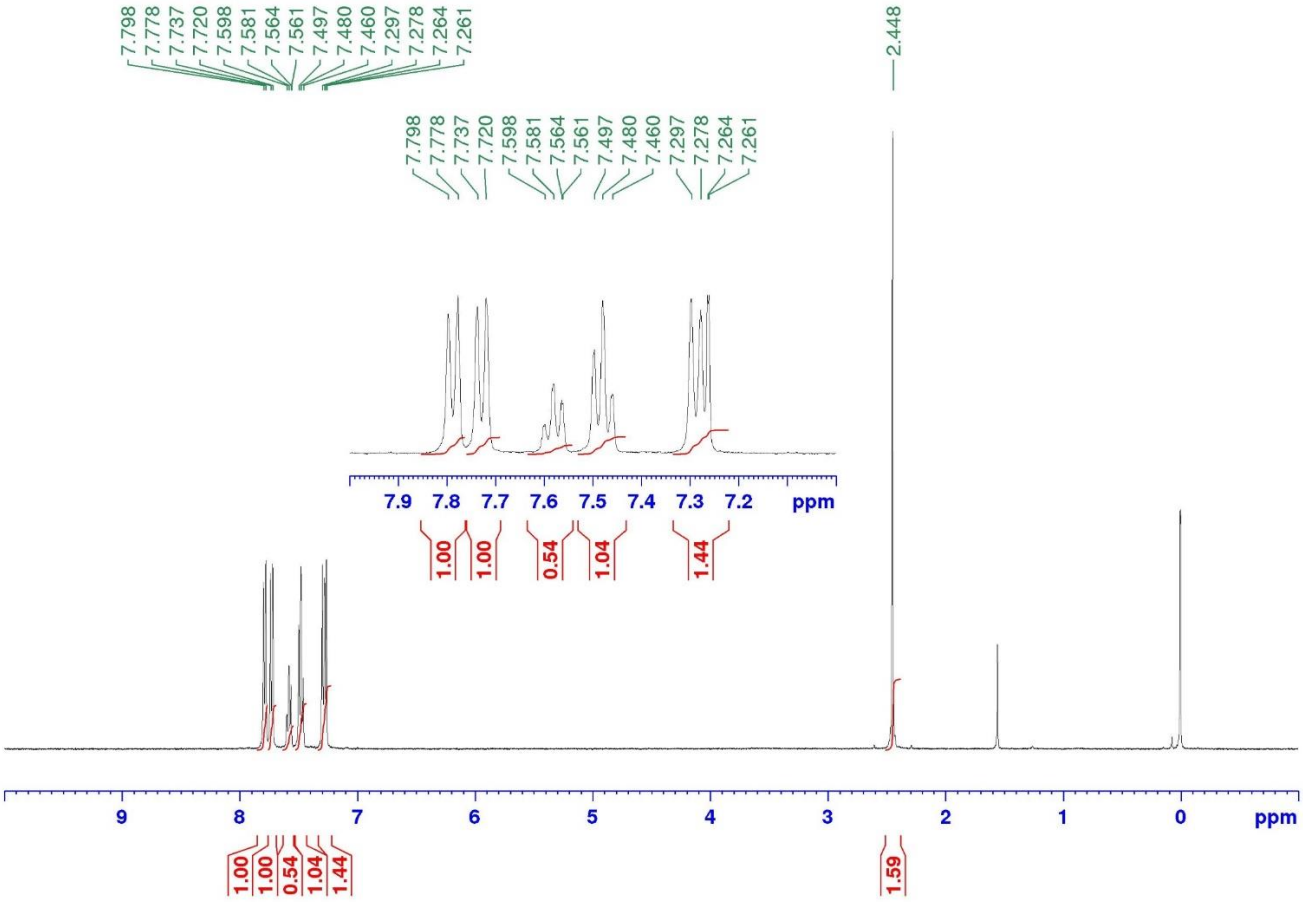


Figure S46. ^{1}H NMR spectrum of **6b** in $CDCl_3$.

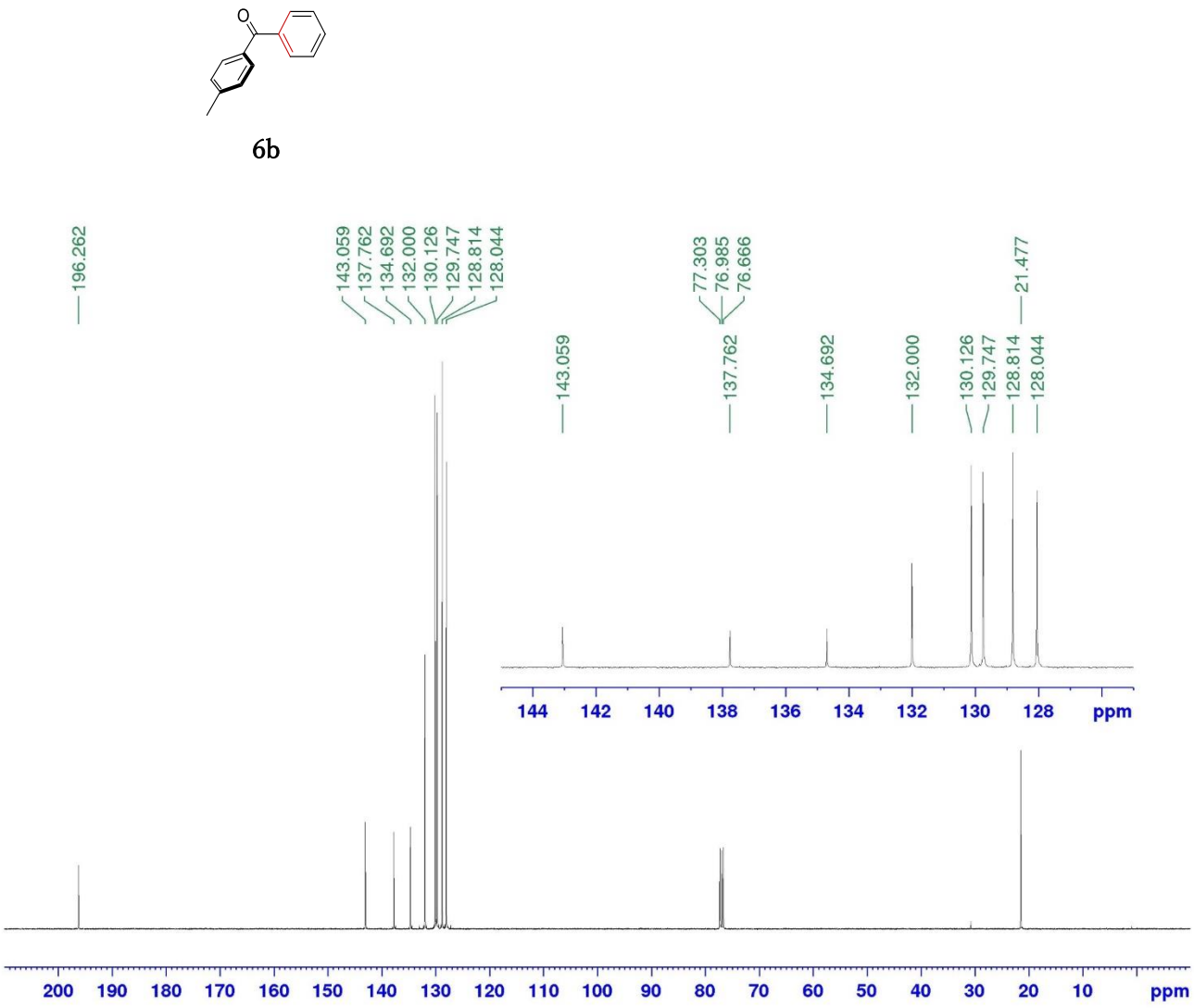
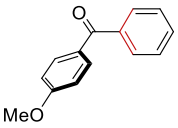


Figure S47. ^{13}C NMR spectrum of **6b** in $CDCl_3$.



6c

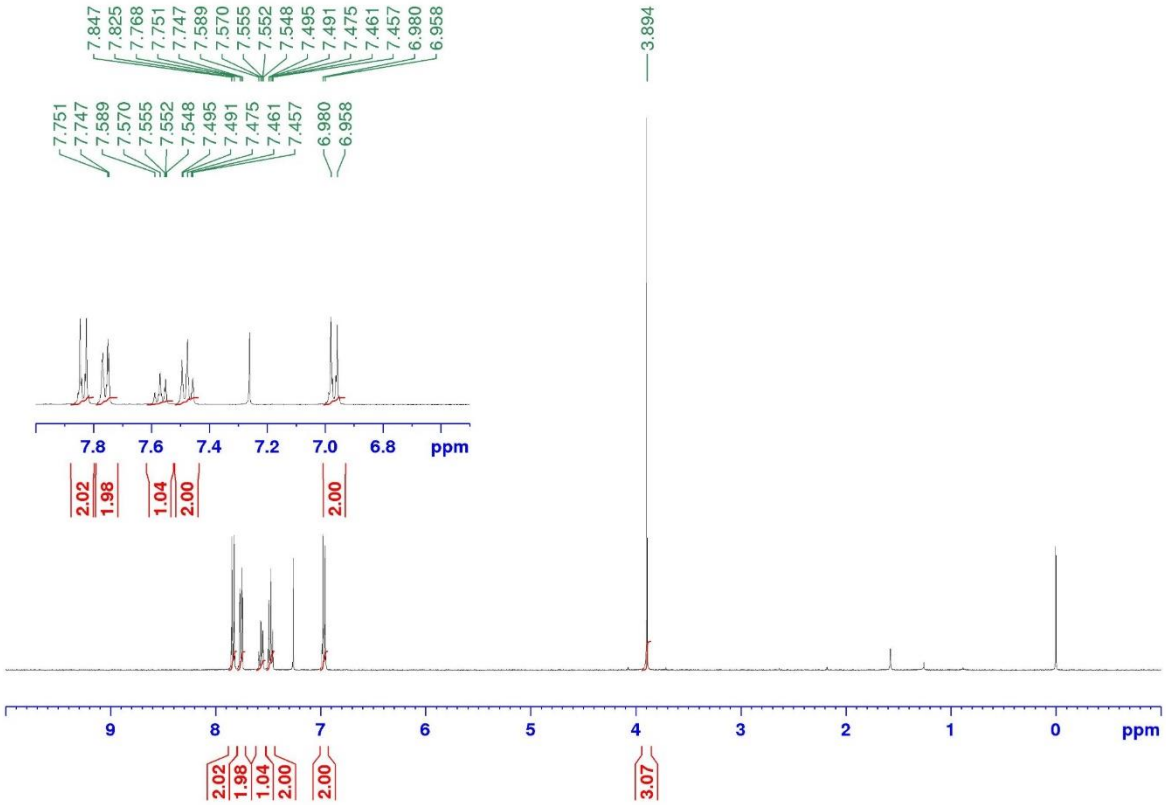


Figure S48. ^{1}H NMR spectrum of **6c** in $CDCl_3$.

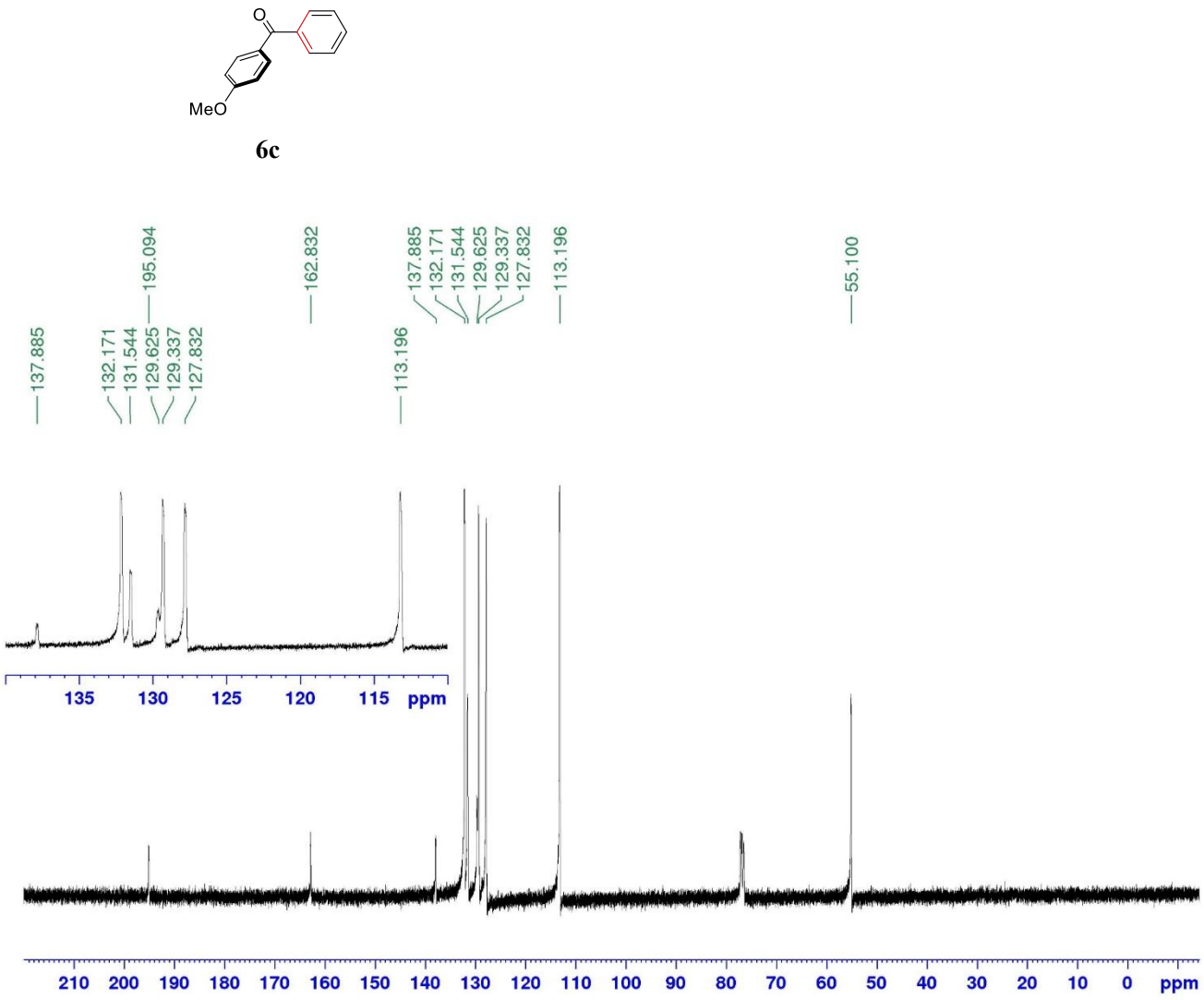
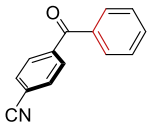


Figure S49. ^{13}C NMR spectrum of **6c** in $CDCl_3$.



6d

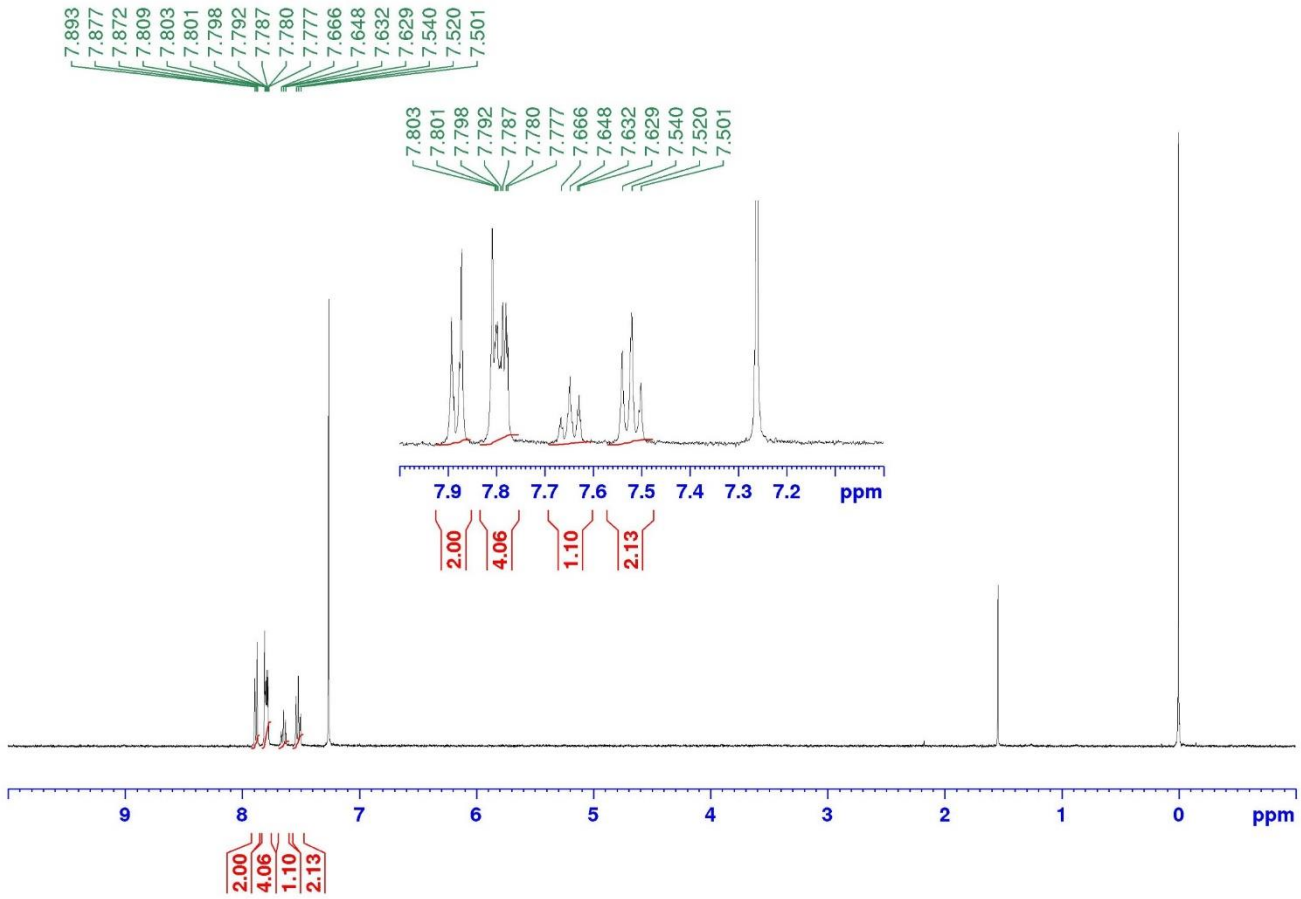


Figure S50. ^{1}H NMR spectrum of **6d** in $CDCl_3$.

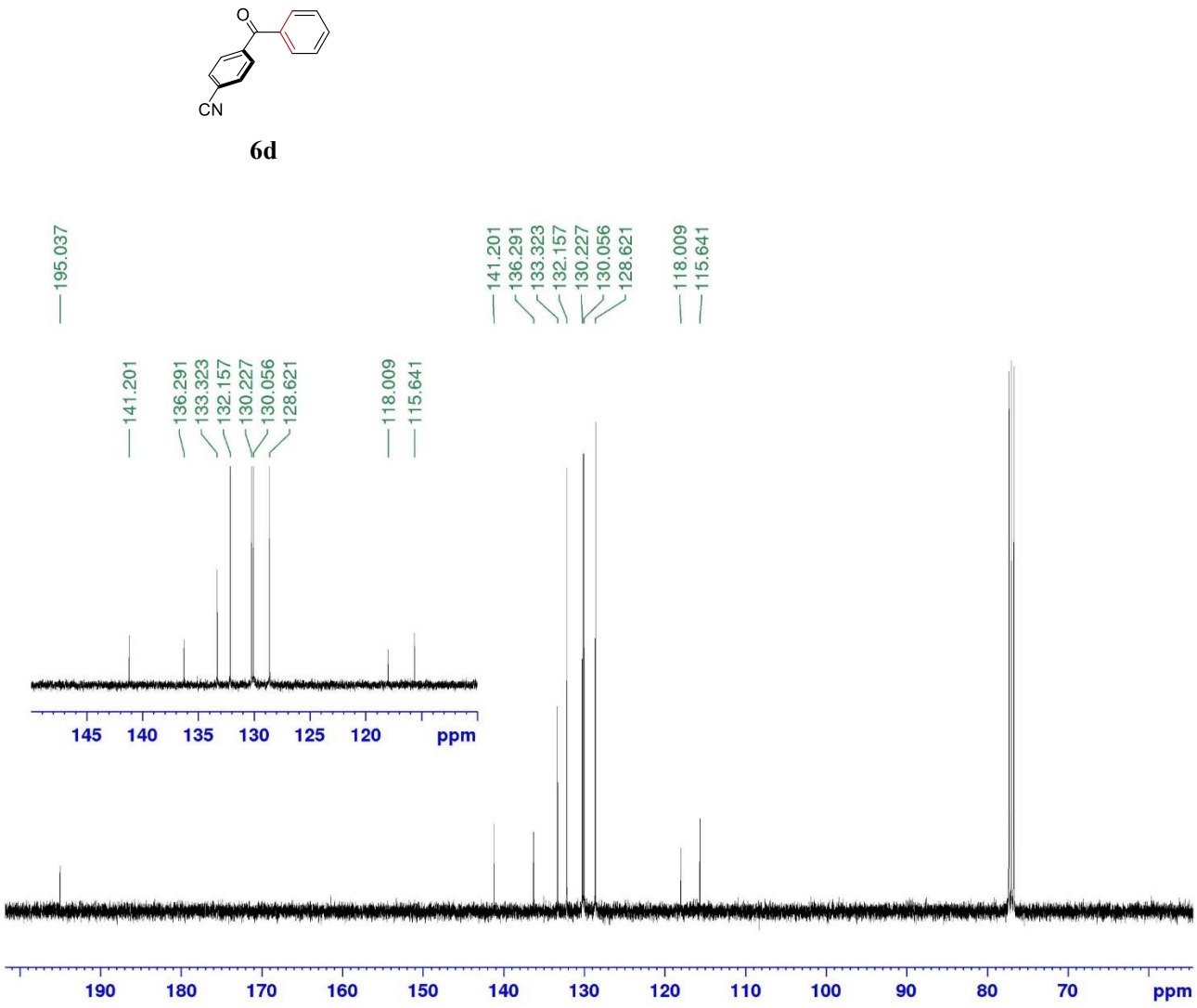


Figure S51. ^{13}C NMR spectrum of **6d** in $CDCl_3$.

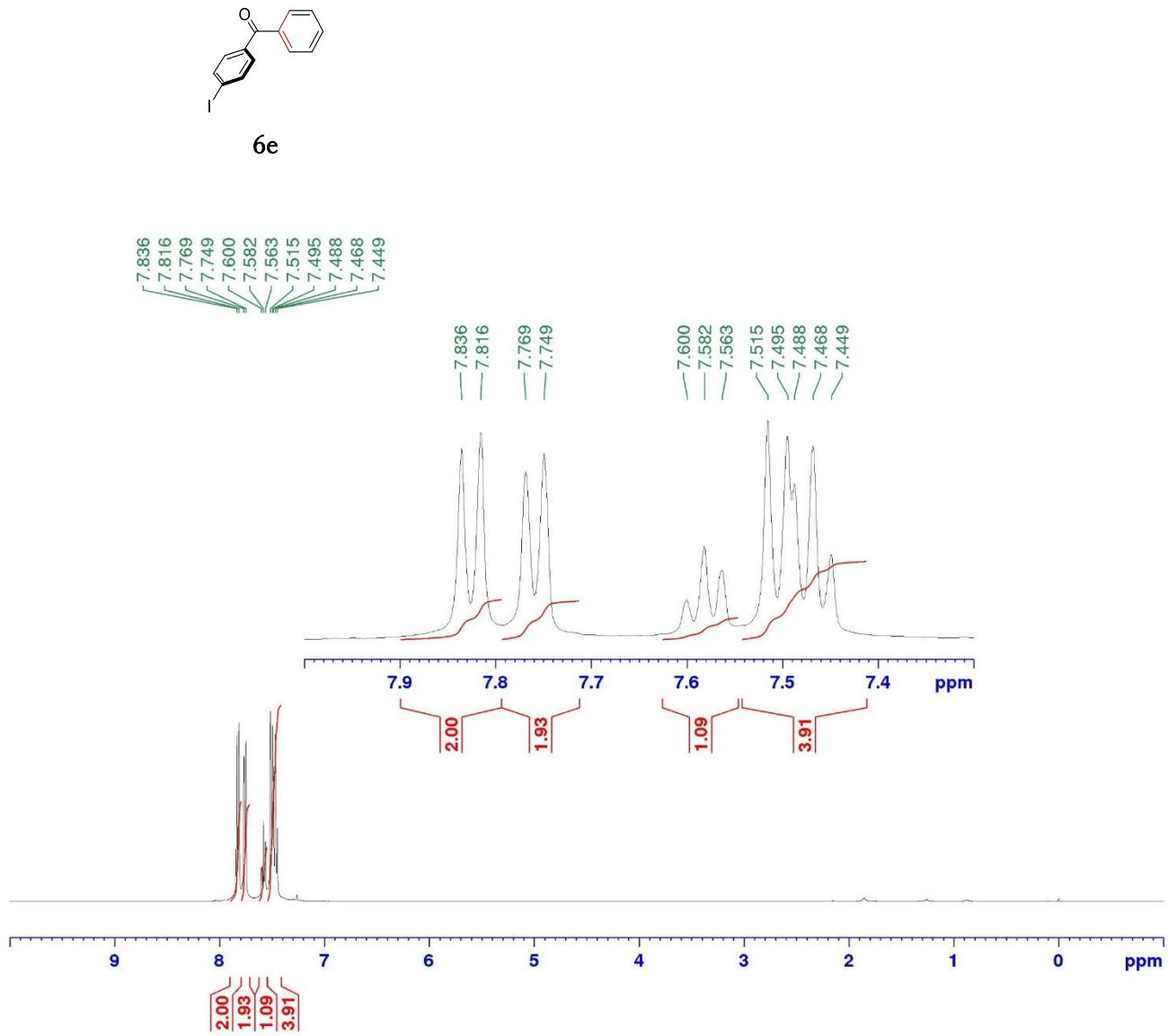


Figure S52. ^{1}H NMR spectrum of **6e** in $CDCl_3$.

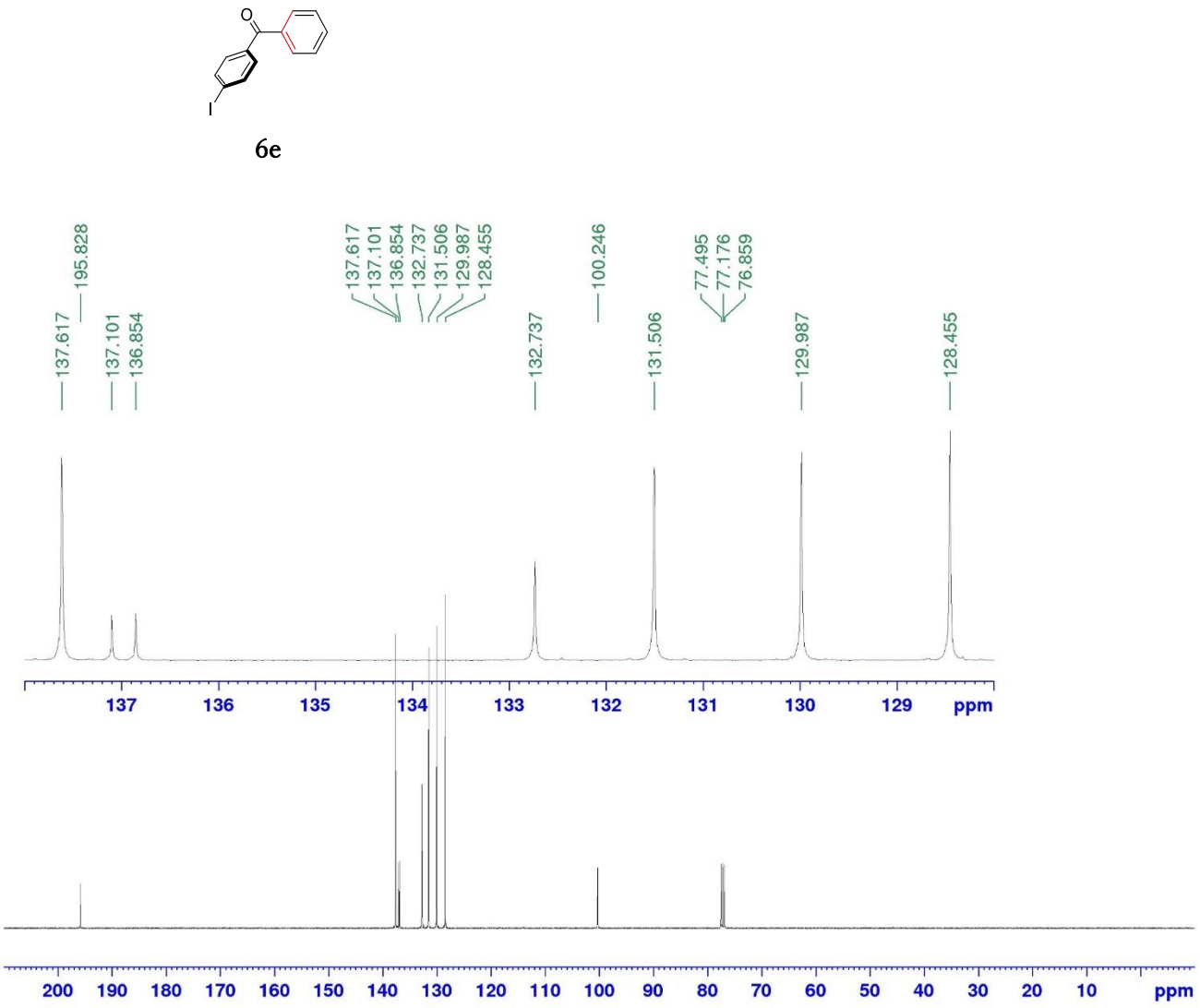
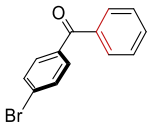


Figure S53. ^{13}C NMR spectrum of **6e** in $CDCl_3$.



6f

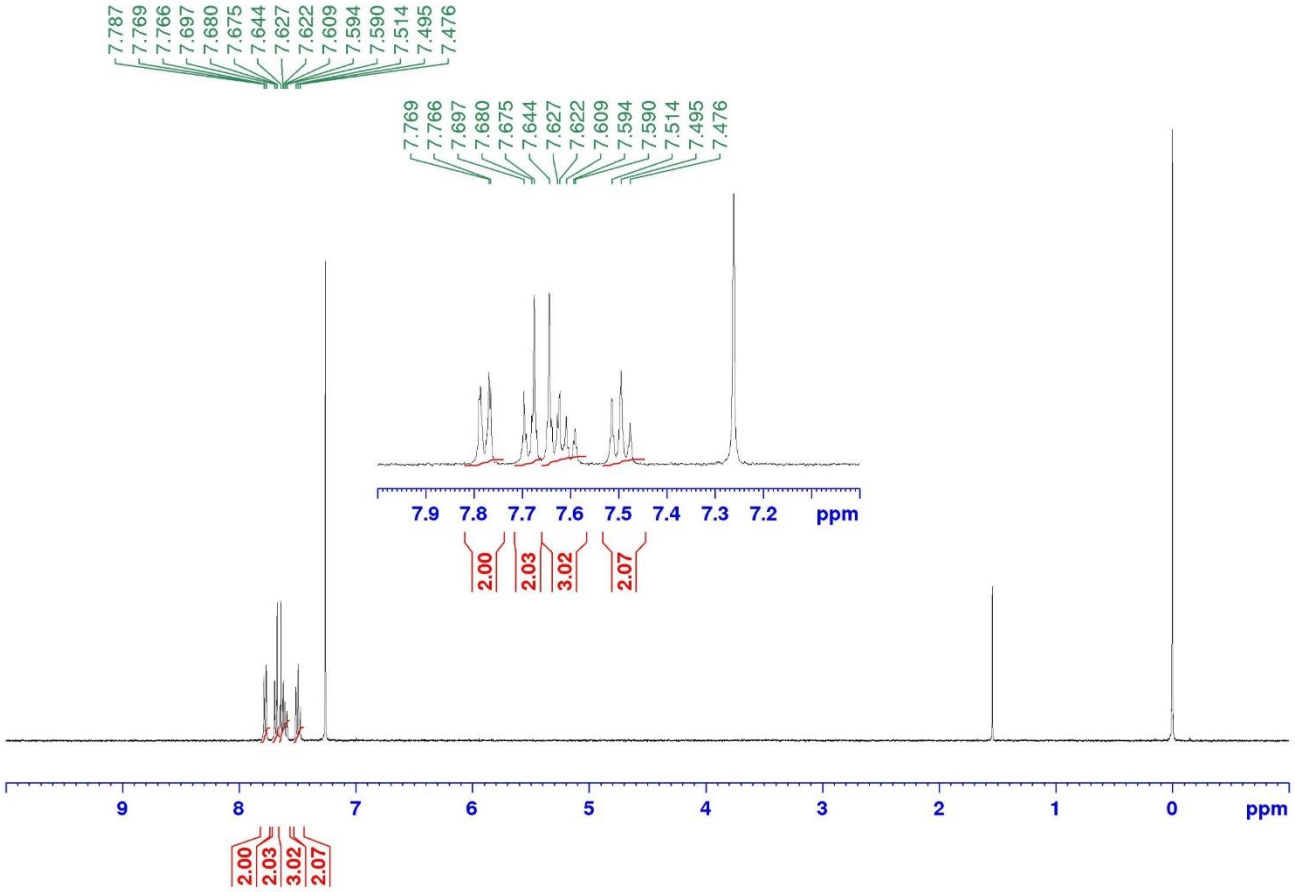


Figure S54. ^{1}H NMR spectrum of **6f** in $CDCl_3$.

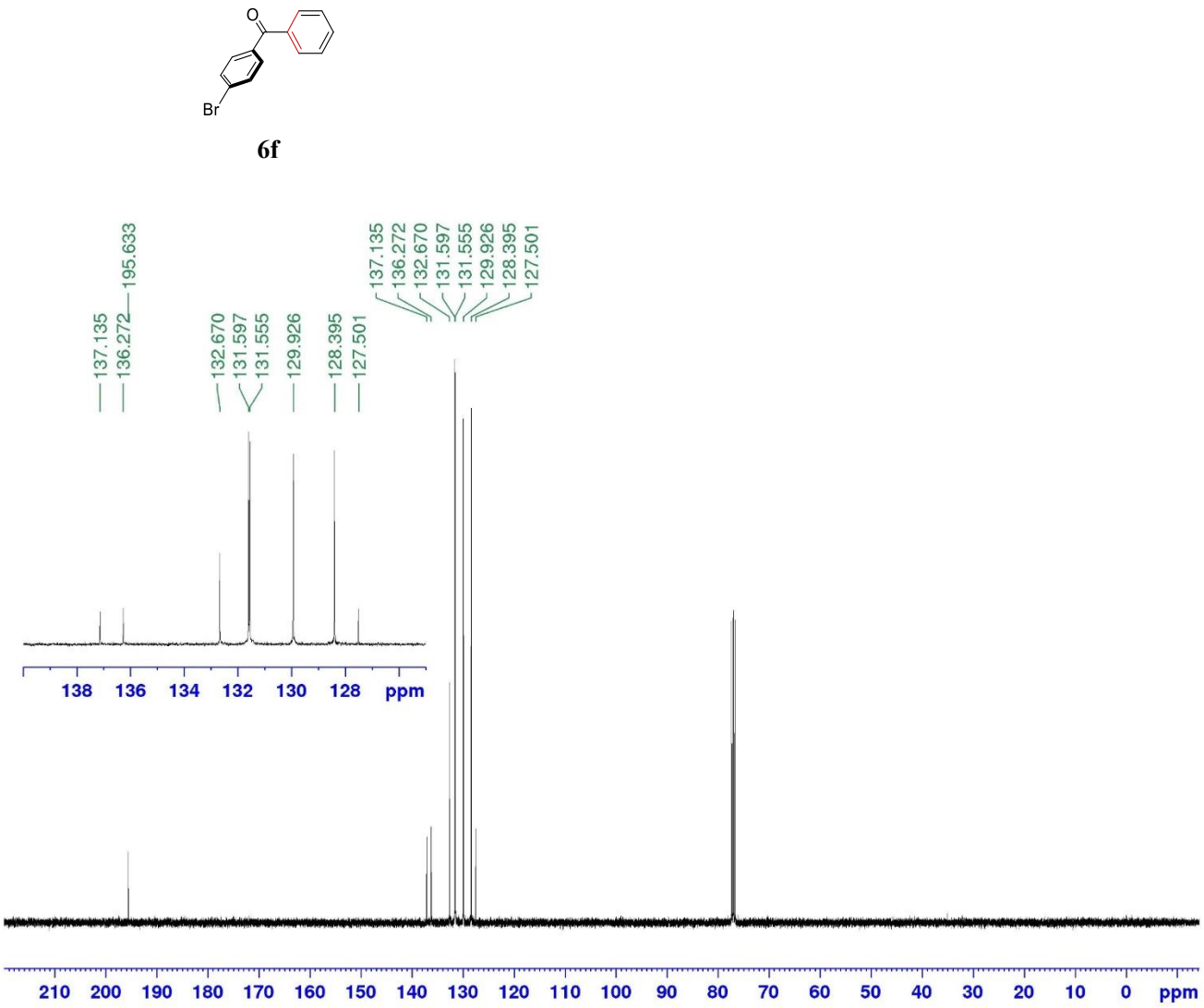
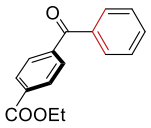


Figure S55. ^{13}C NMR spectrum of **6f** in $CDCl_3$.



6g

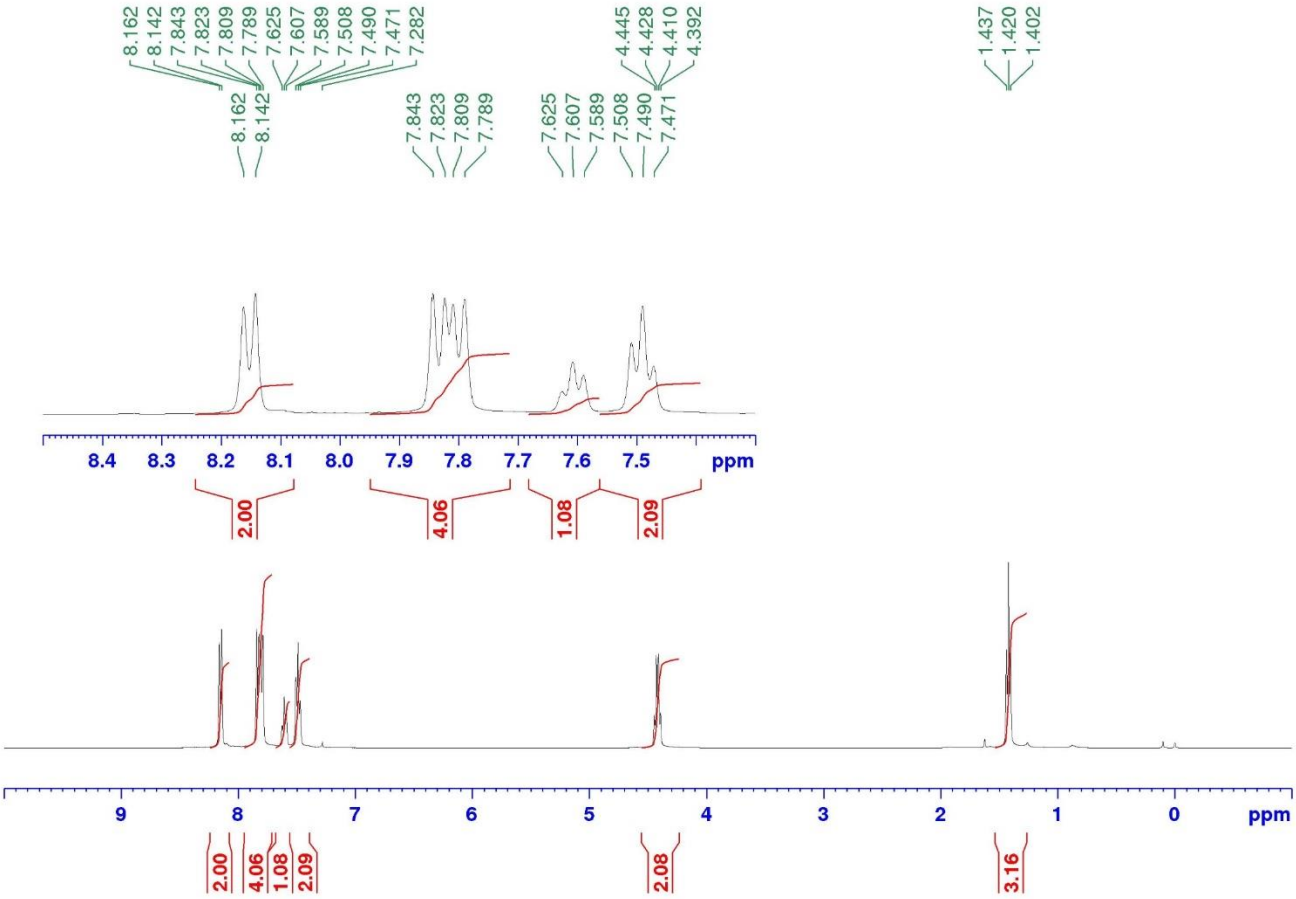
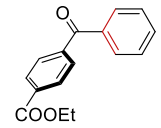


Figure S56. ^{1}H NMR spectrum of **6g** in $CDCl_3$.



6g

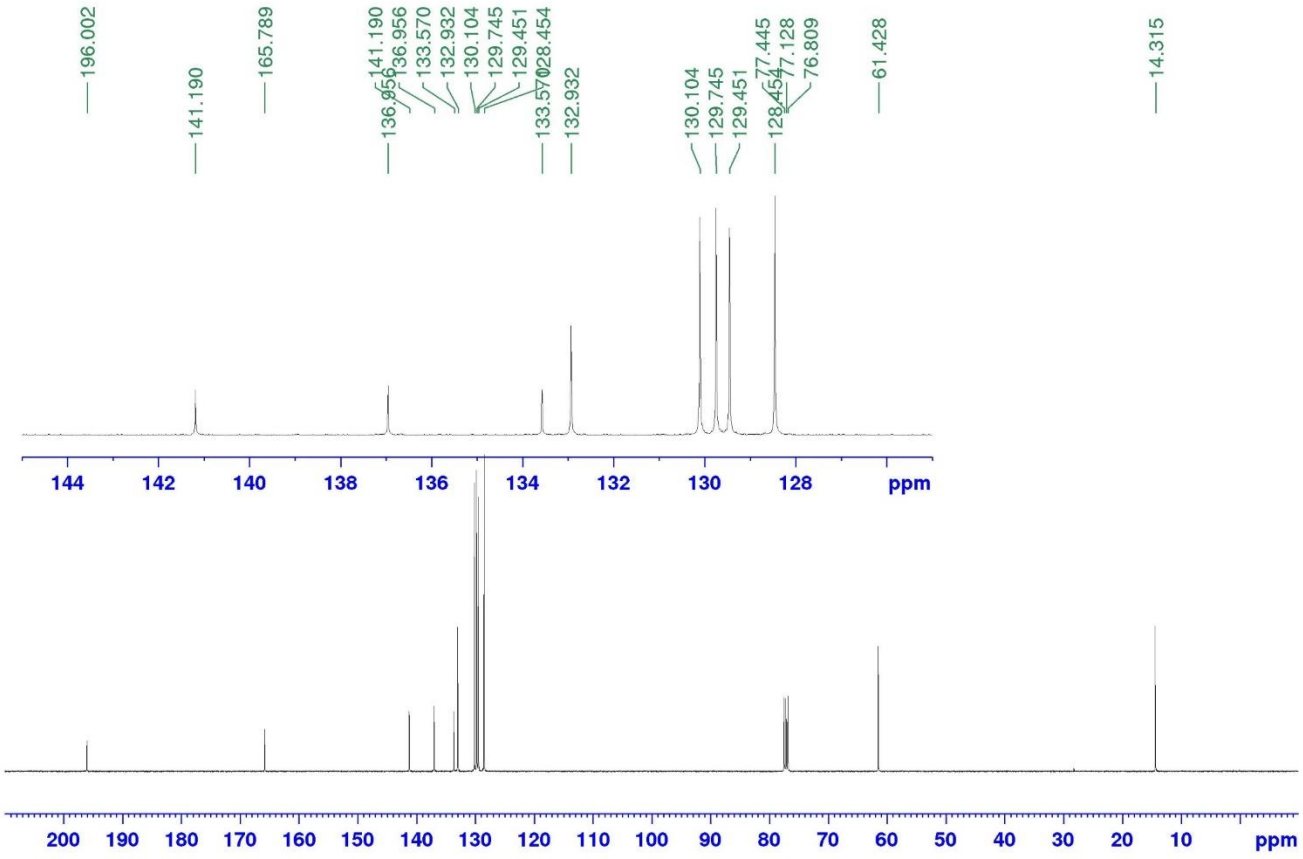
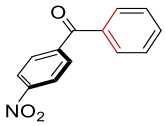


Figure S57. ^{13}C NMR spectrum of **6g** in $CDCl_3$.



6h

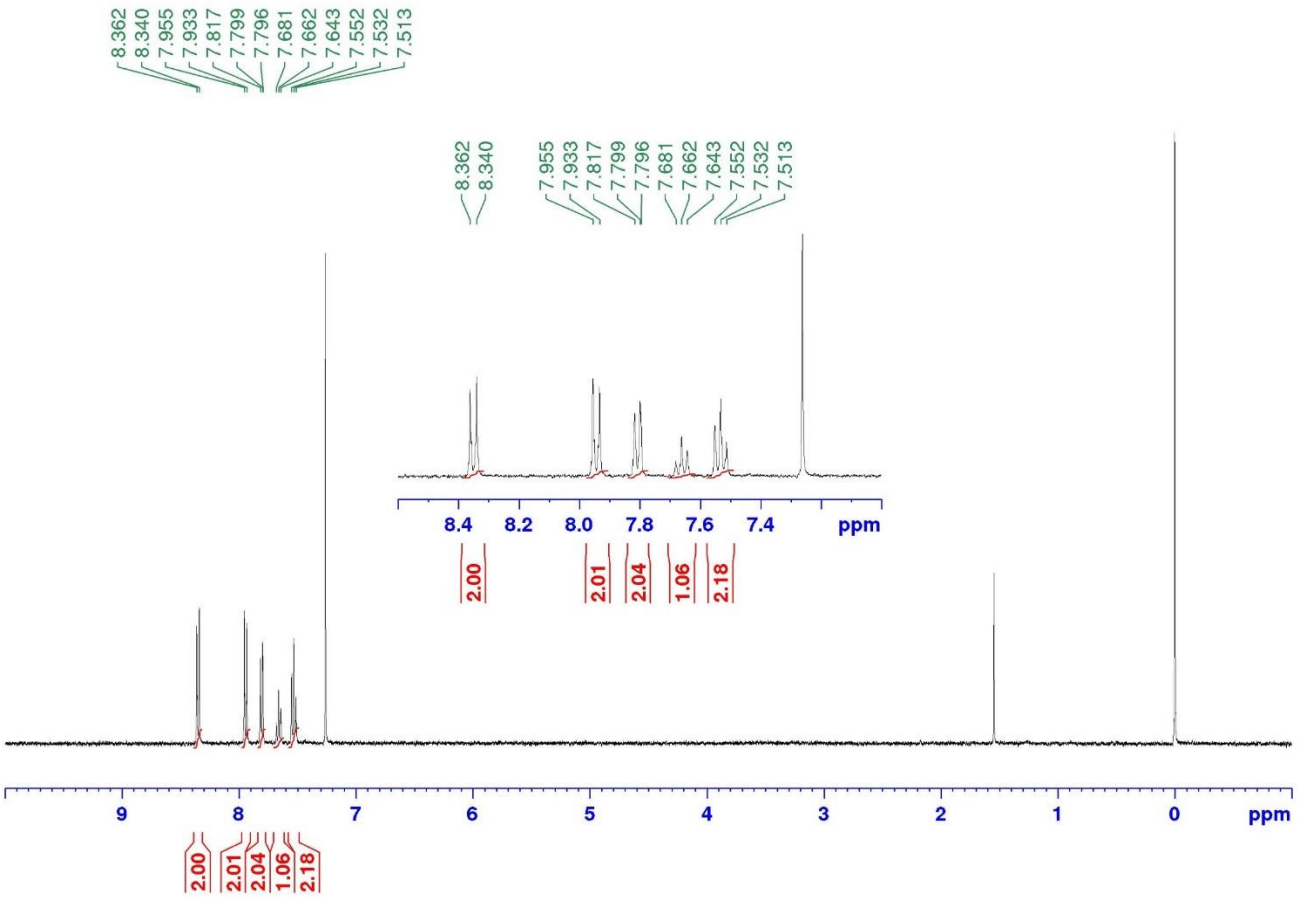
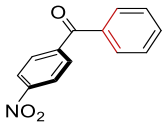


Figure S58. ^{1}H NMR spectrum of **6h** in $CDCl_3$.



6h

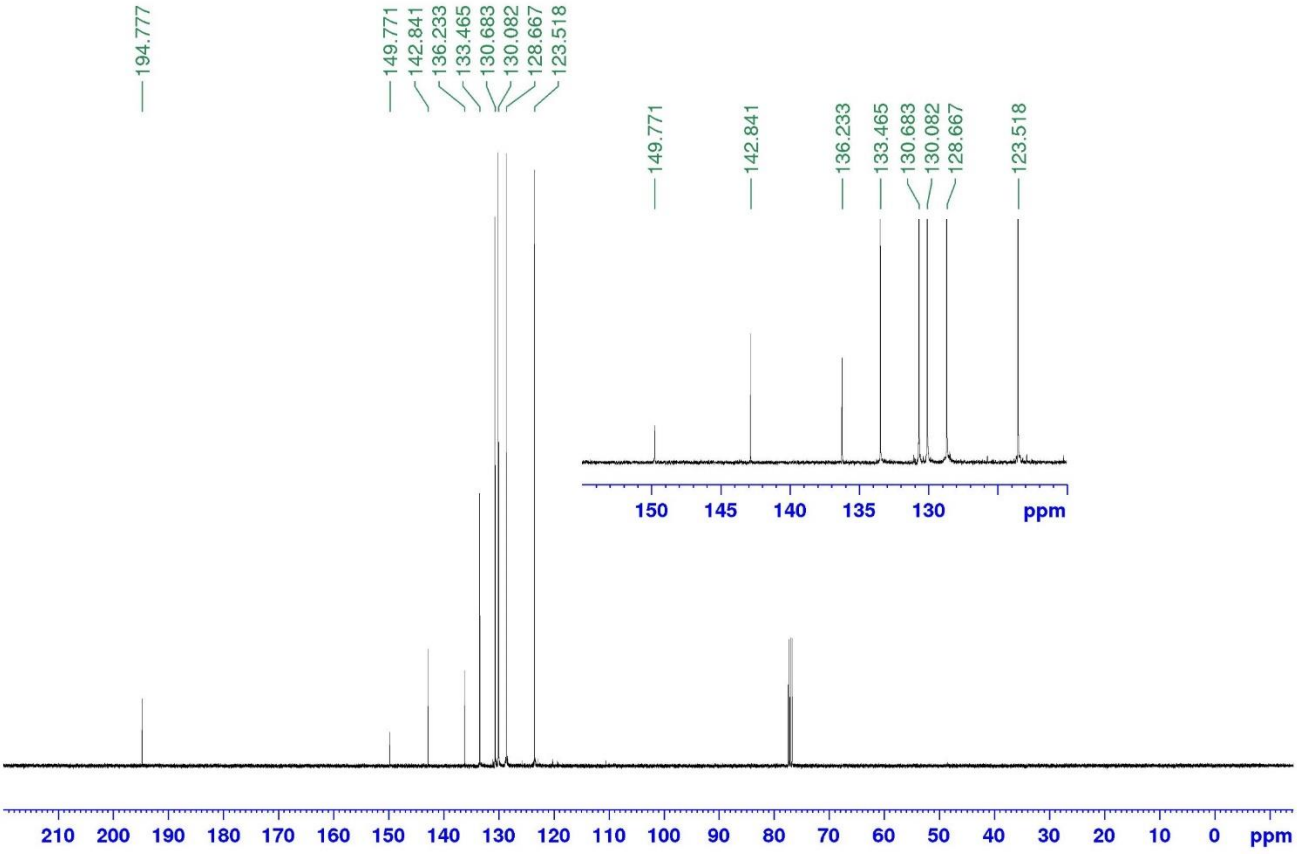
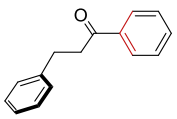


Figure S59. ^{13}C NMR spectrum of **6h** in $CDCl_3$.



6i

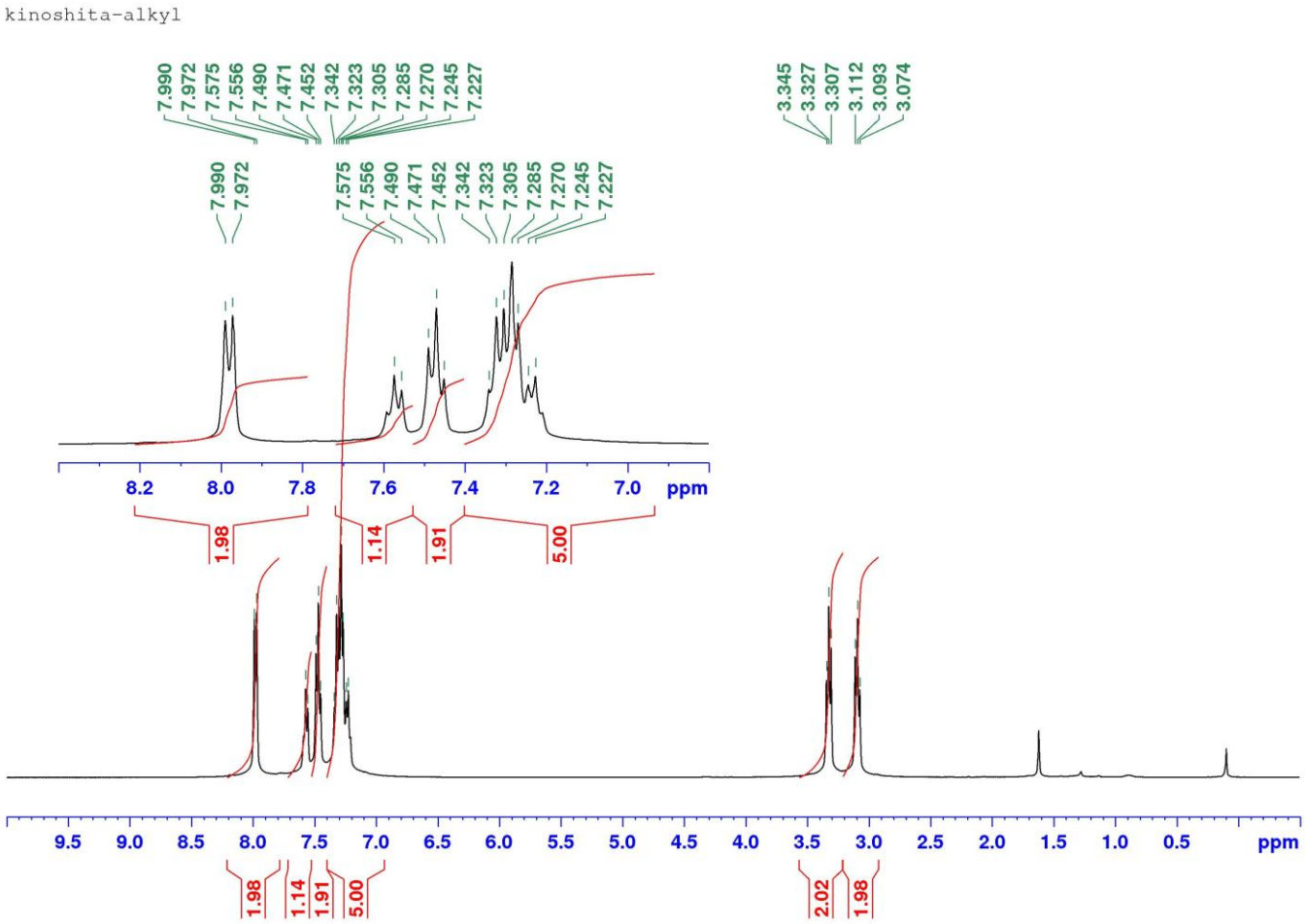
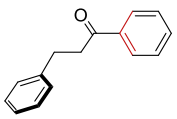


Figure S60. ^{1}H NMR spectrum of **6i** in $CDCl_3$.



6i

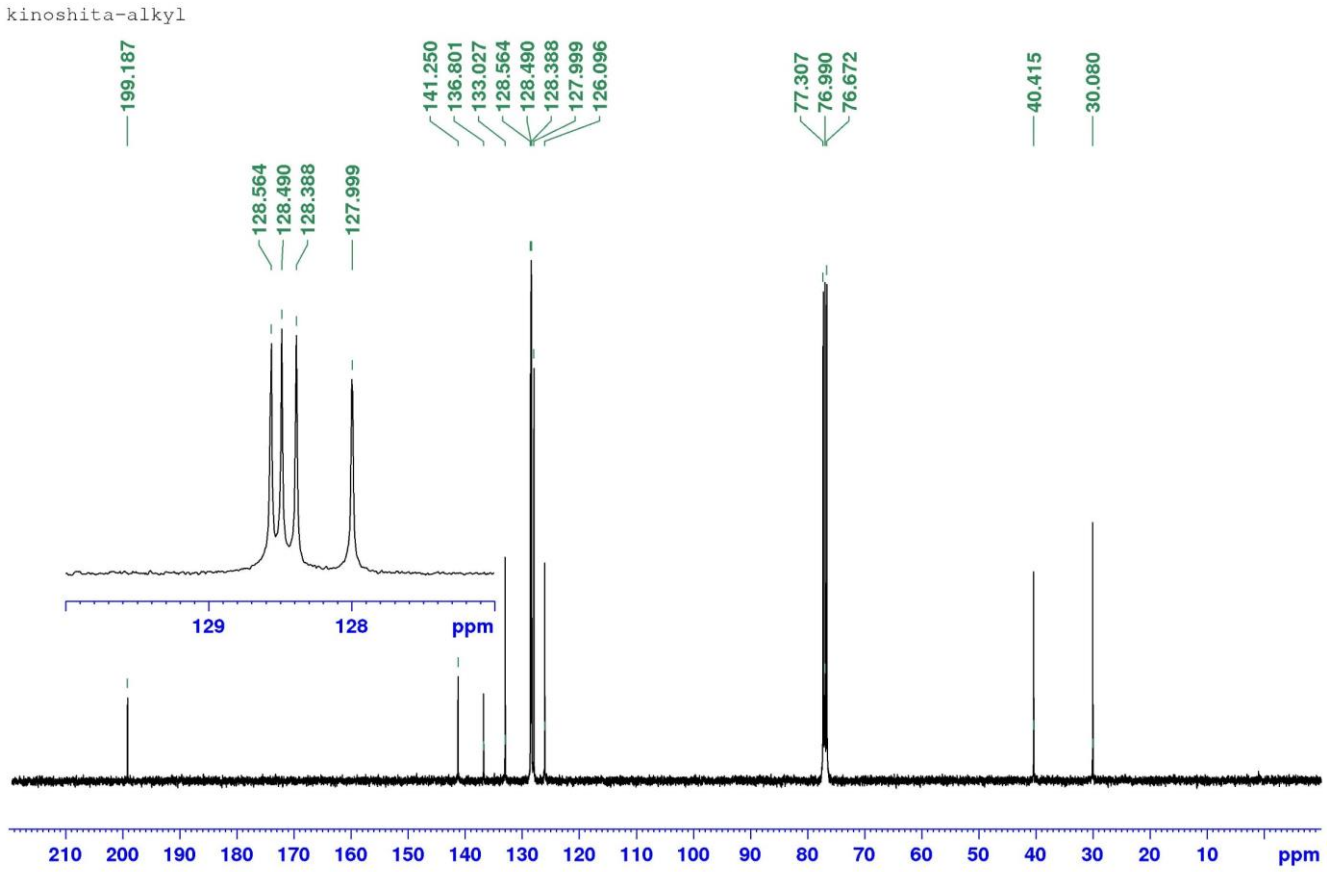


Figure S61. ^{13}C NMR spectrum of **6i** in $CDCl_3$.

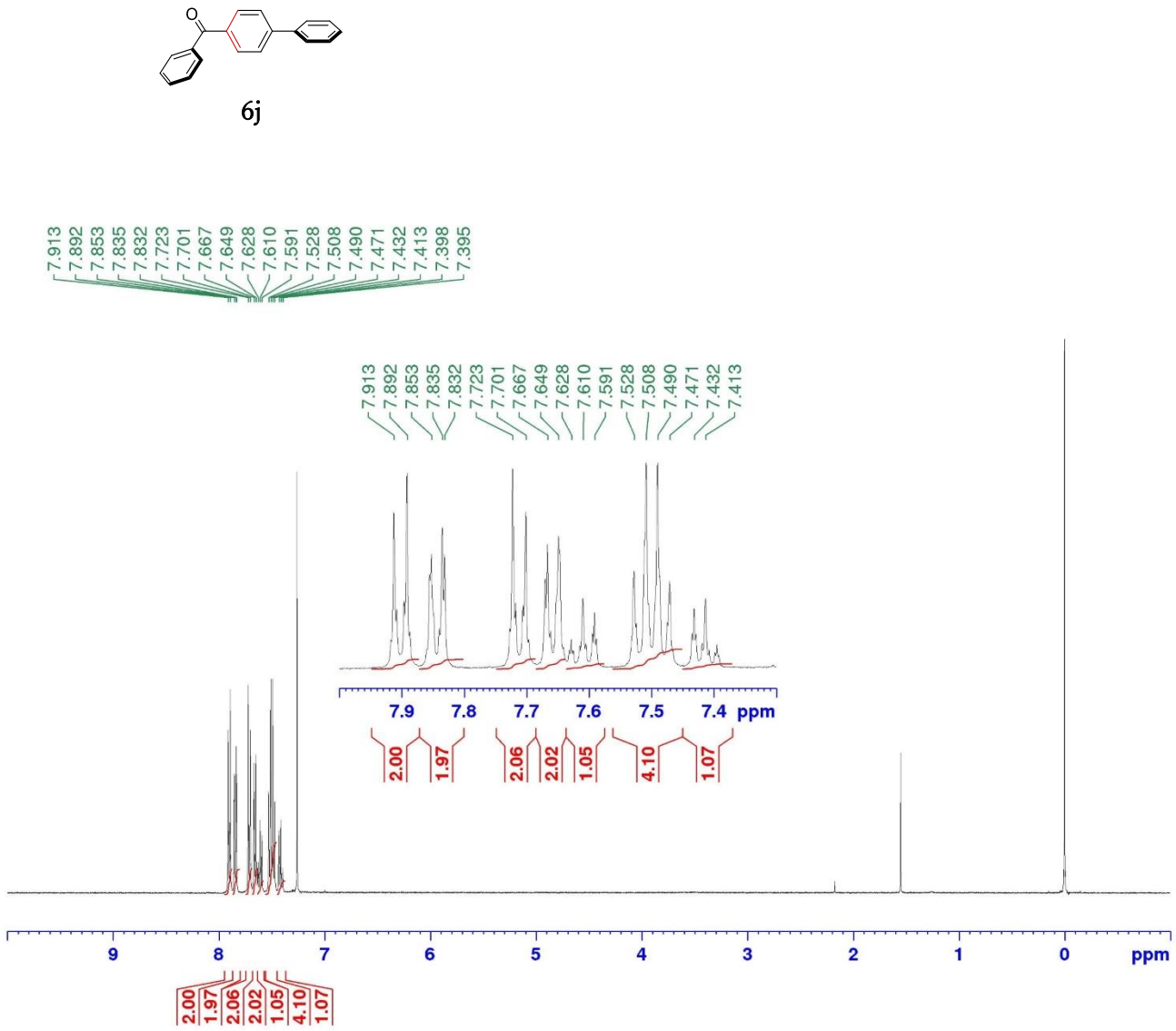


Figure S62. ^{1}H NMR spectrum of **6j** in $CDCl_3$.

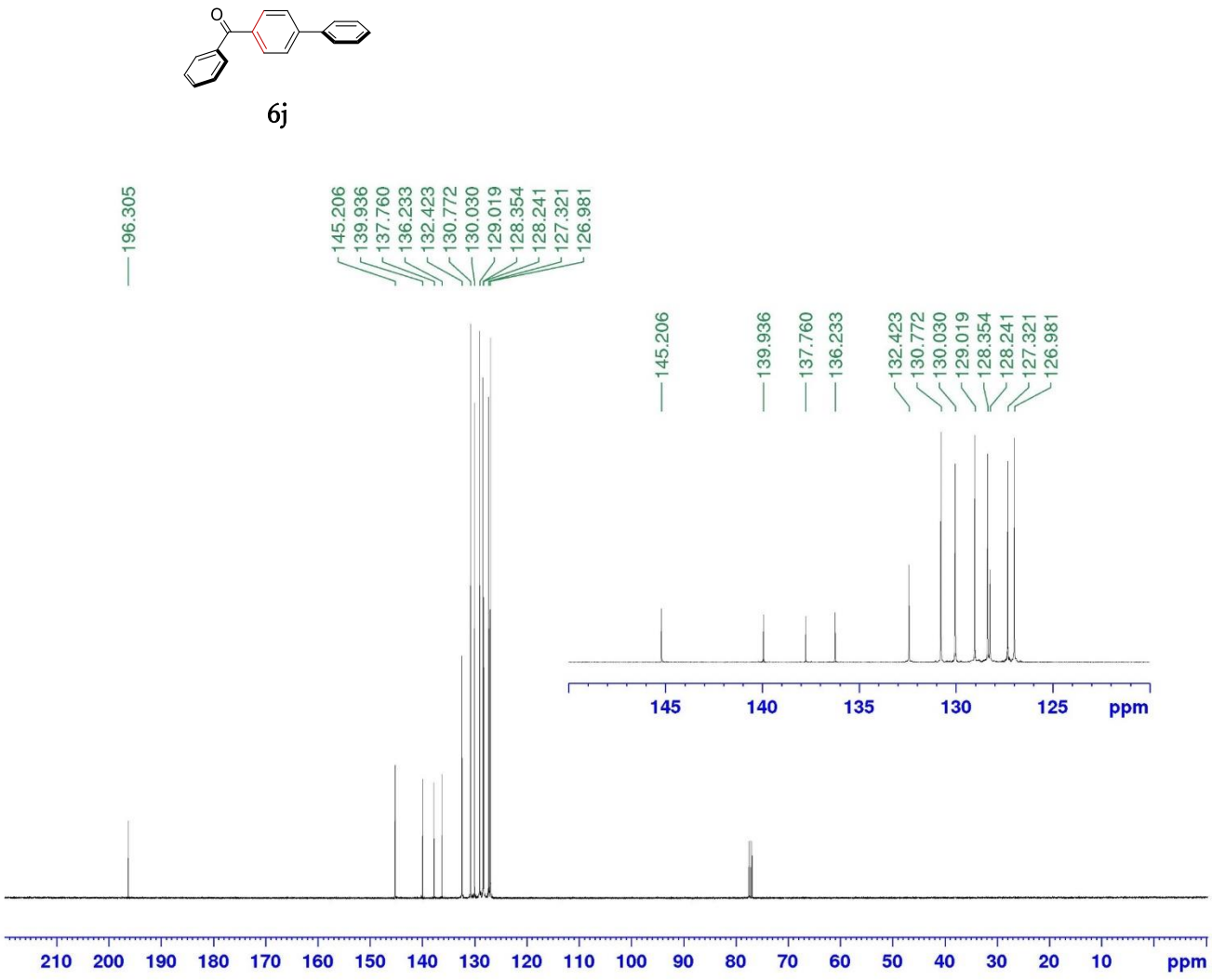


Figure S63. ^{13}C NMR spectrum of **6j** in $CDCl_3$.

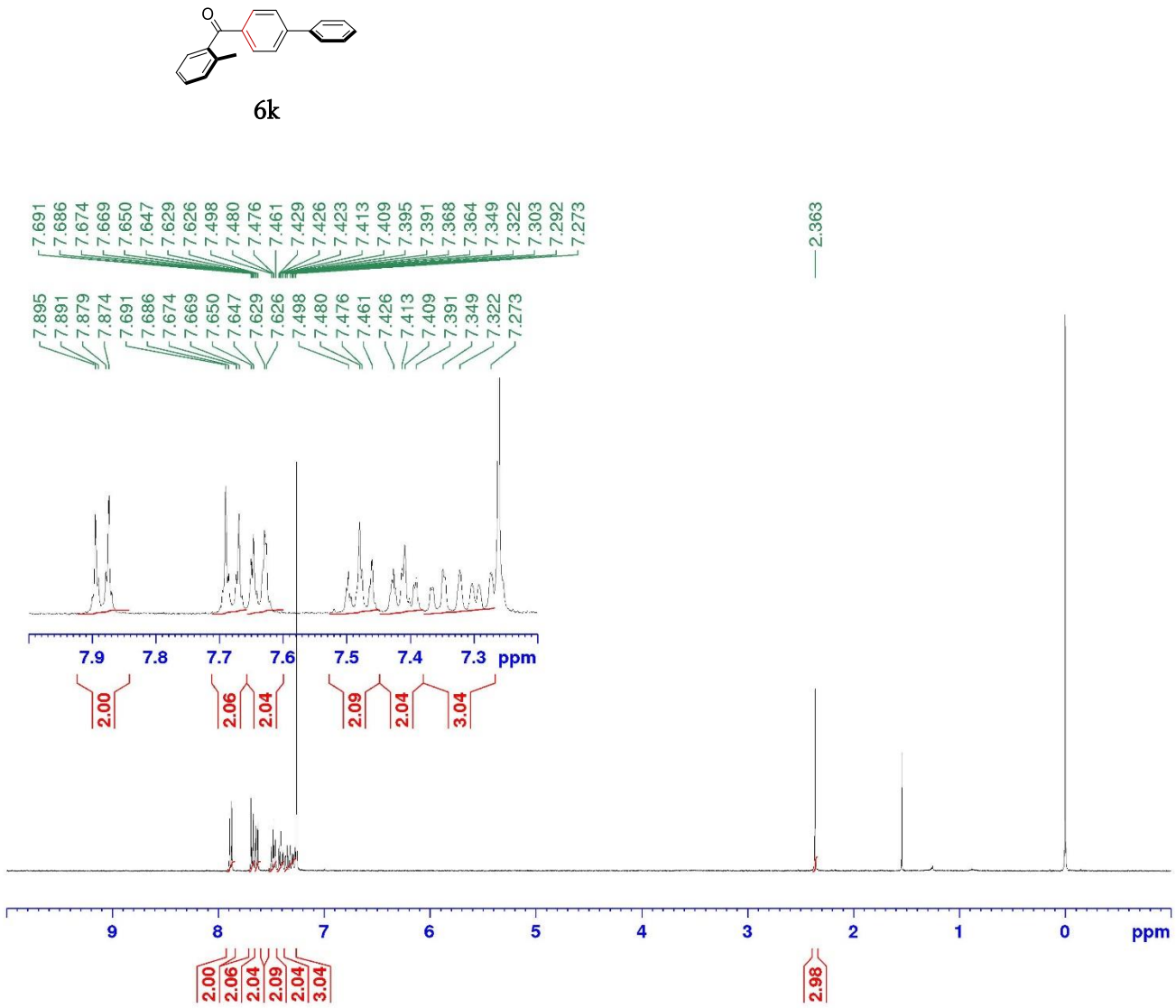


Figure S64. ^{1}H NMR spectrum of **6k** in $CDCl_3$.

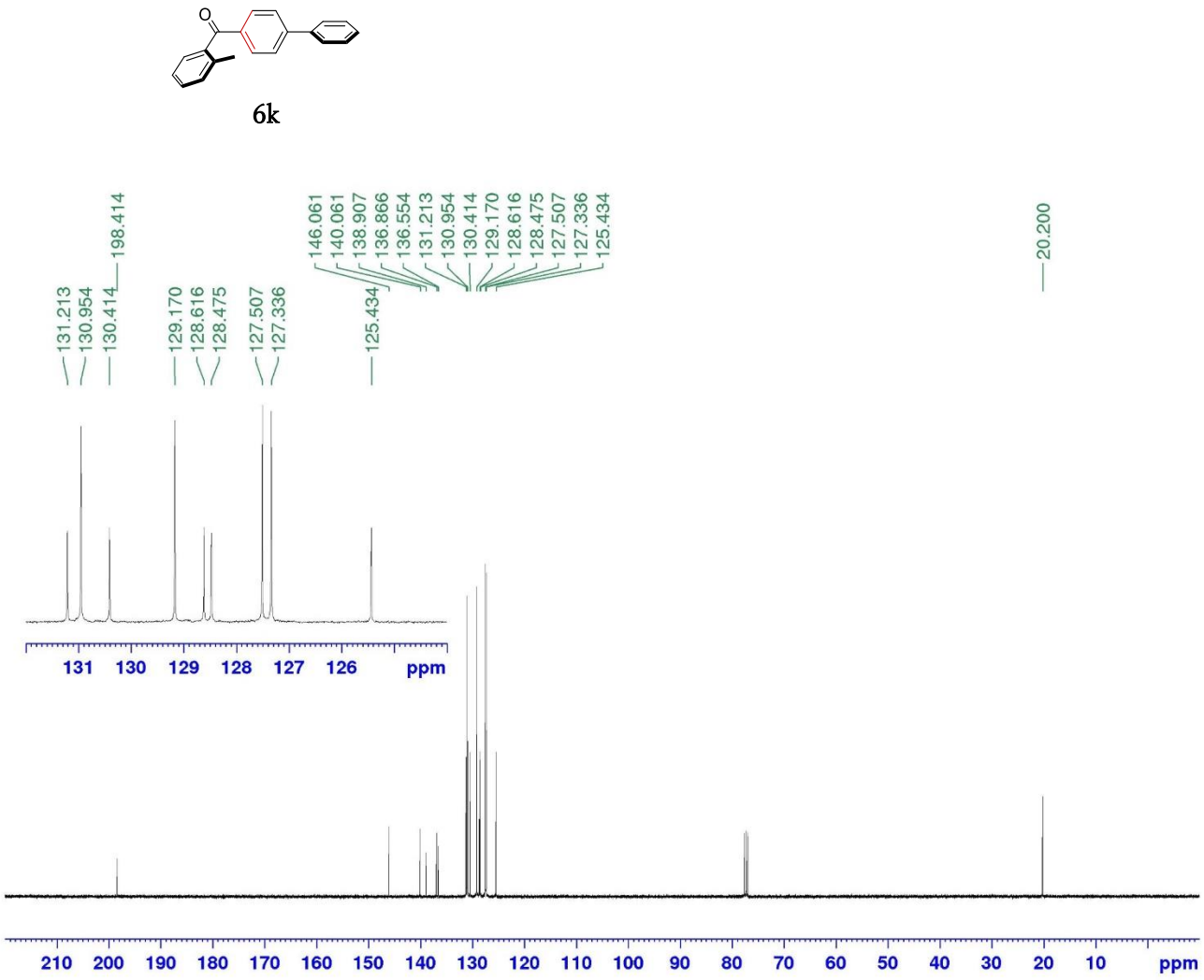
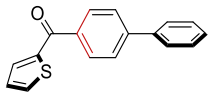


Figure S65. ^{13}C NMR spectrum of **6k** in $CDCl_3$.



6l

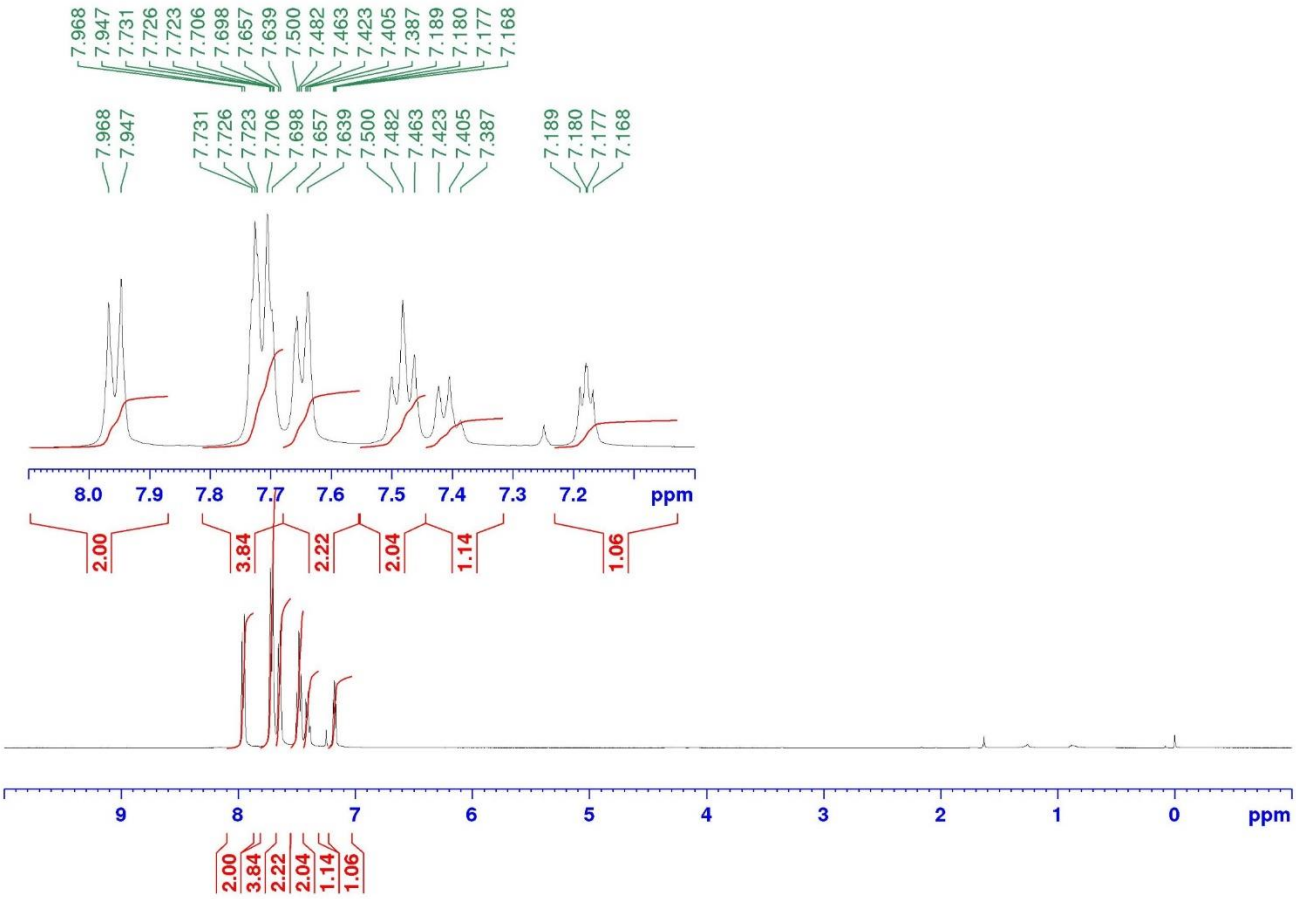


Figure S66. ^{1}H NMR spectrum of **6l** in $CDCl_3$.

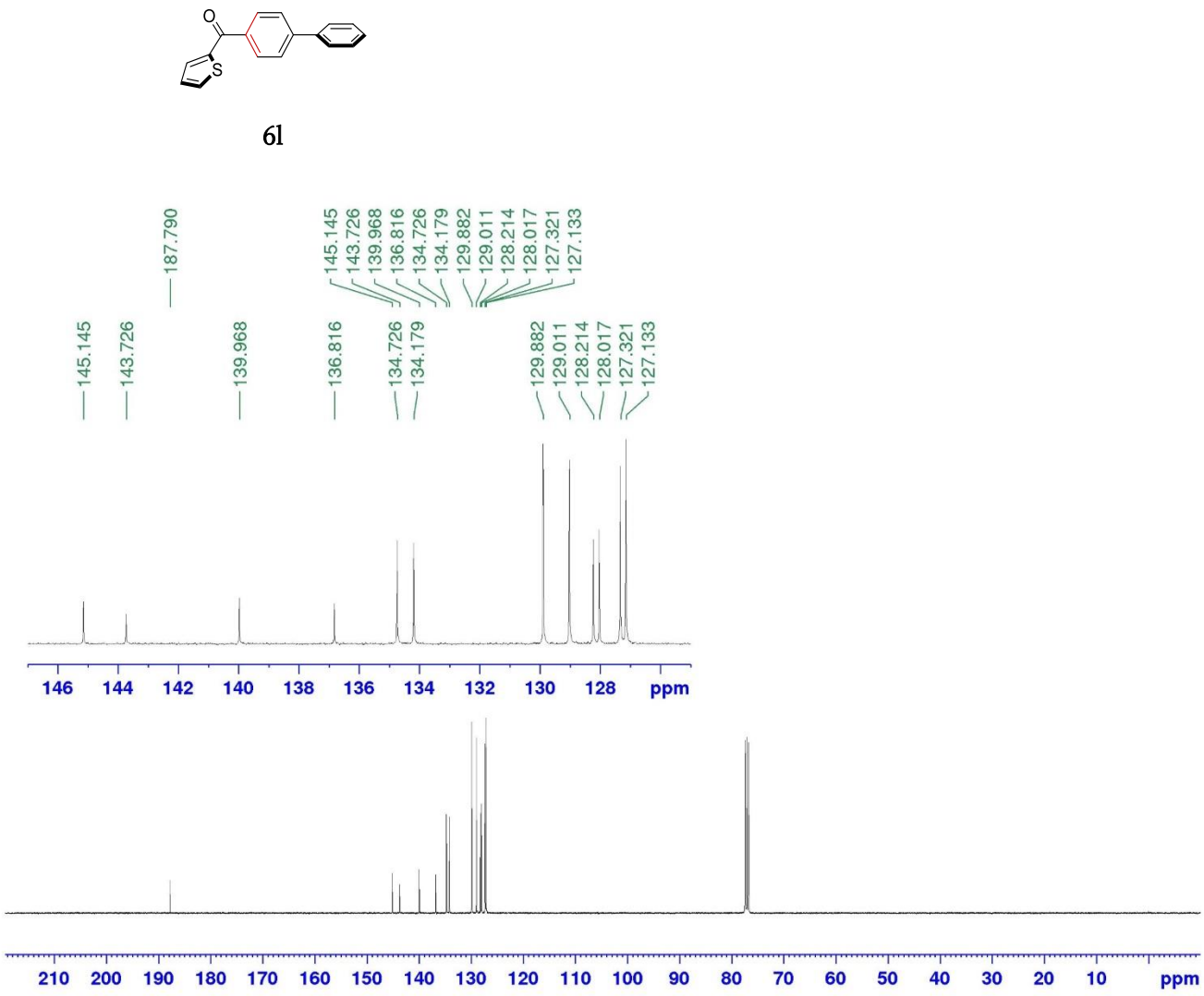


Figure S67. ^{13}C NMR spectrum of **6l** in $CDCl_3$.

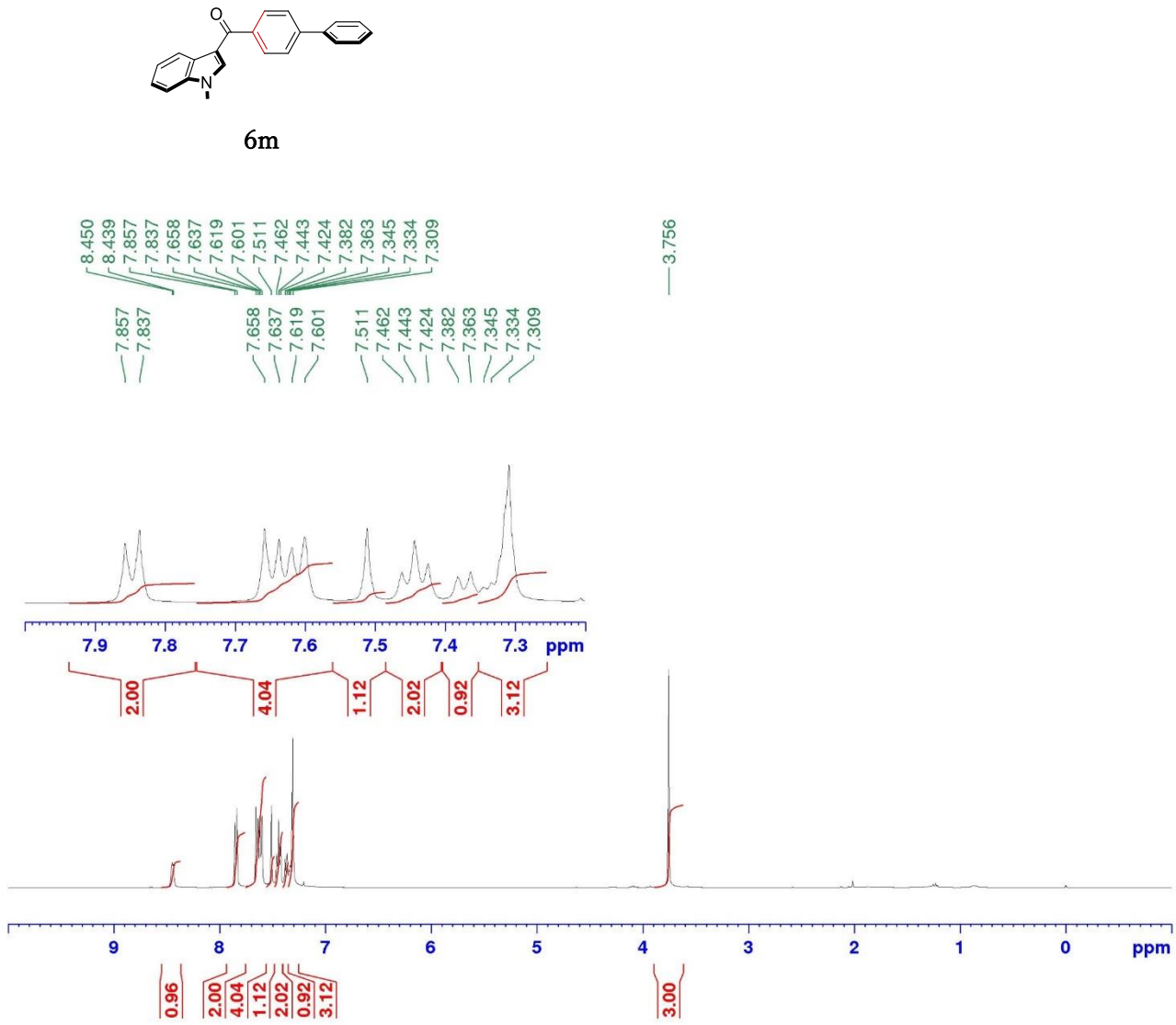


Figure S68. ^{1}H NMR spectrum of **6m** in $CDCl_3$.

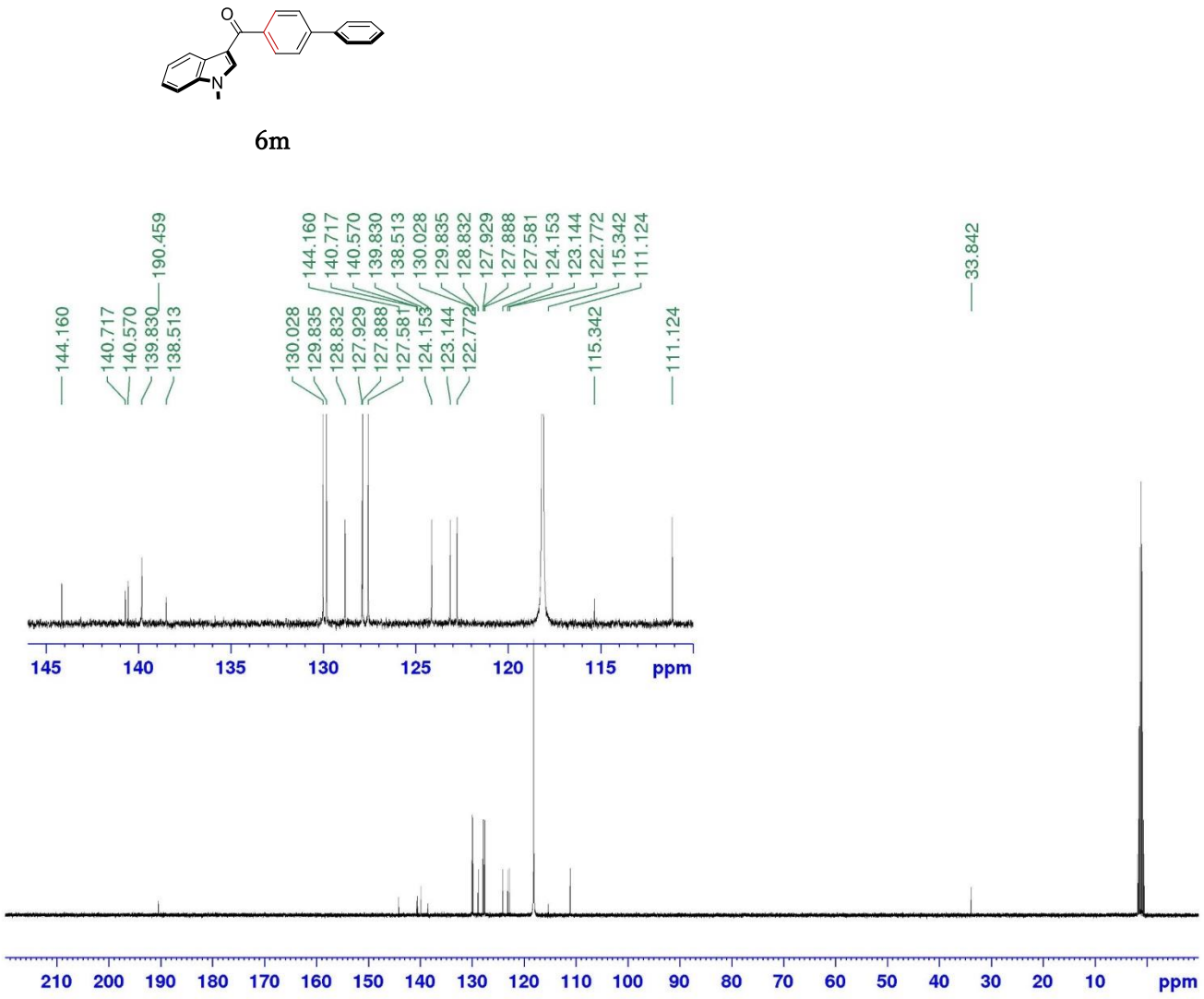


Figure S69. ^{13}C NMR spectrum of **6m** in $CDCl_3$.

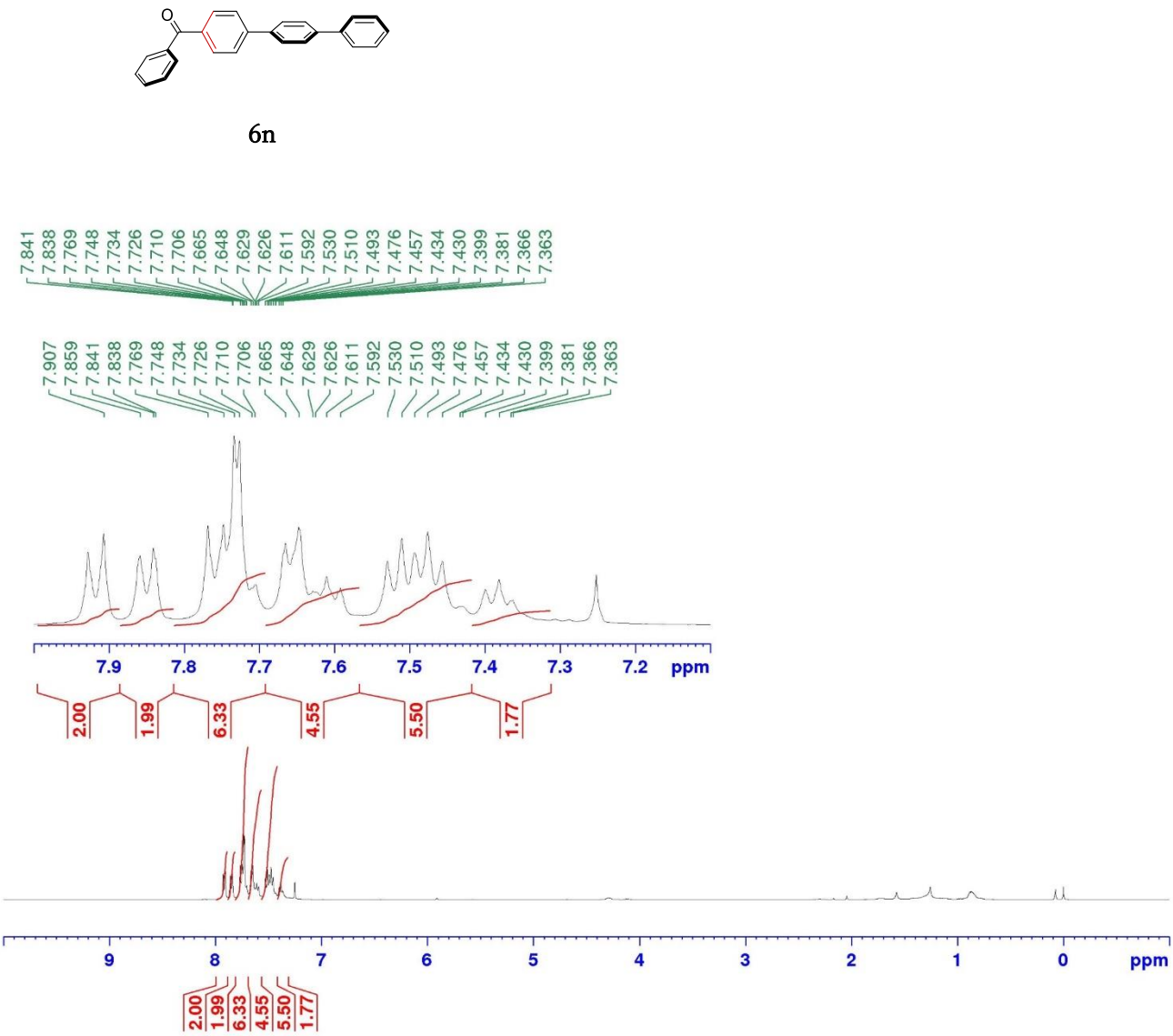


Figure S70. ^{1}H NMR spectrum of **6n** in $CDCl_3$.

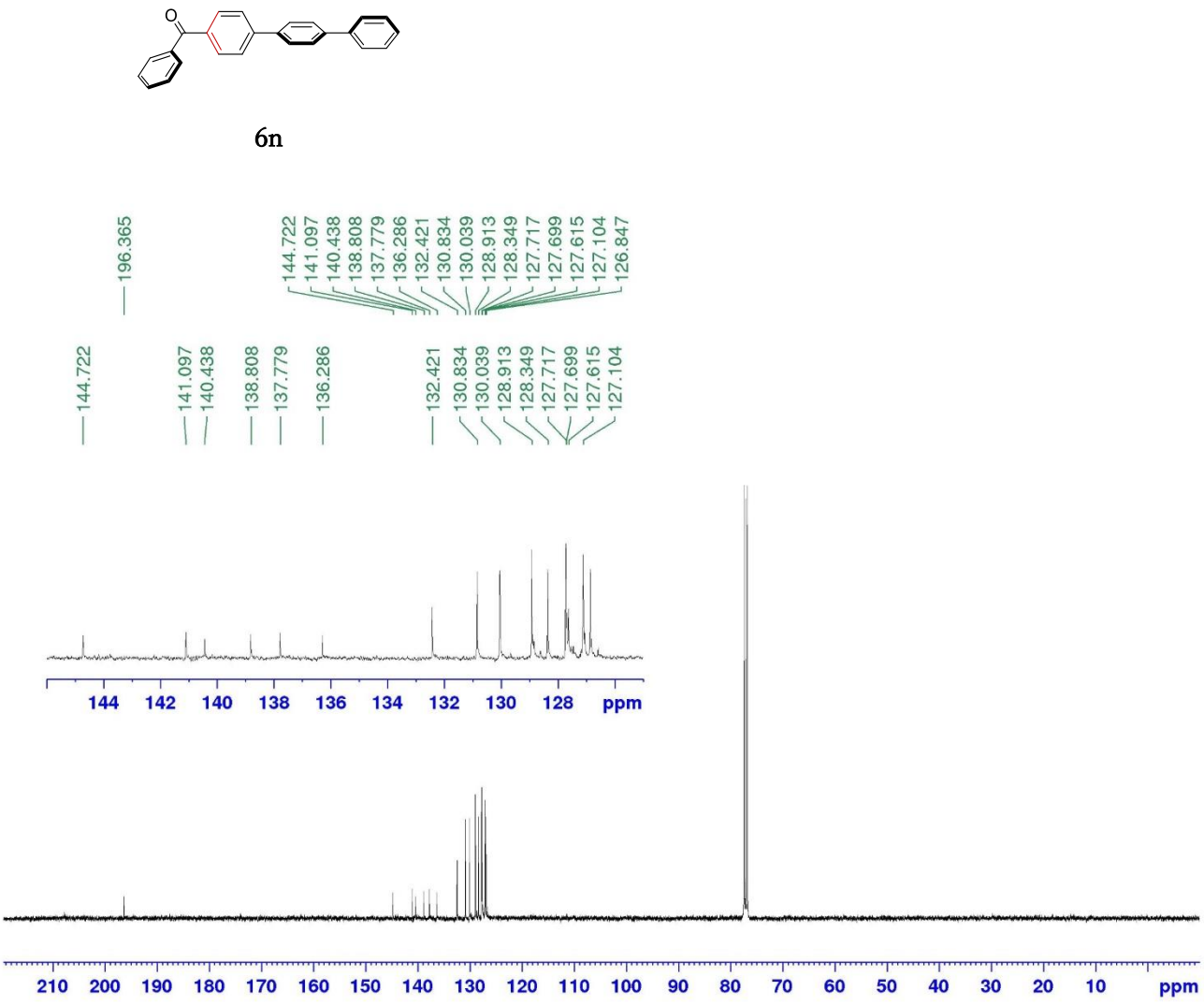


Figure S71. ^{13}C NMR spectrum of **6n** in $CDCl_3$.

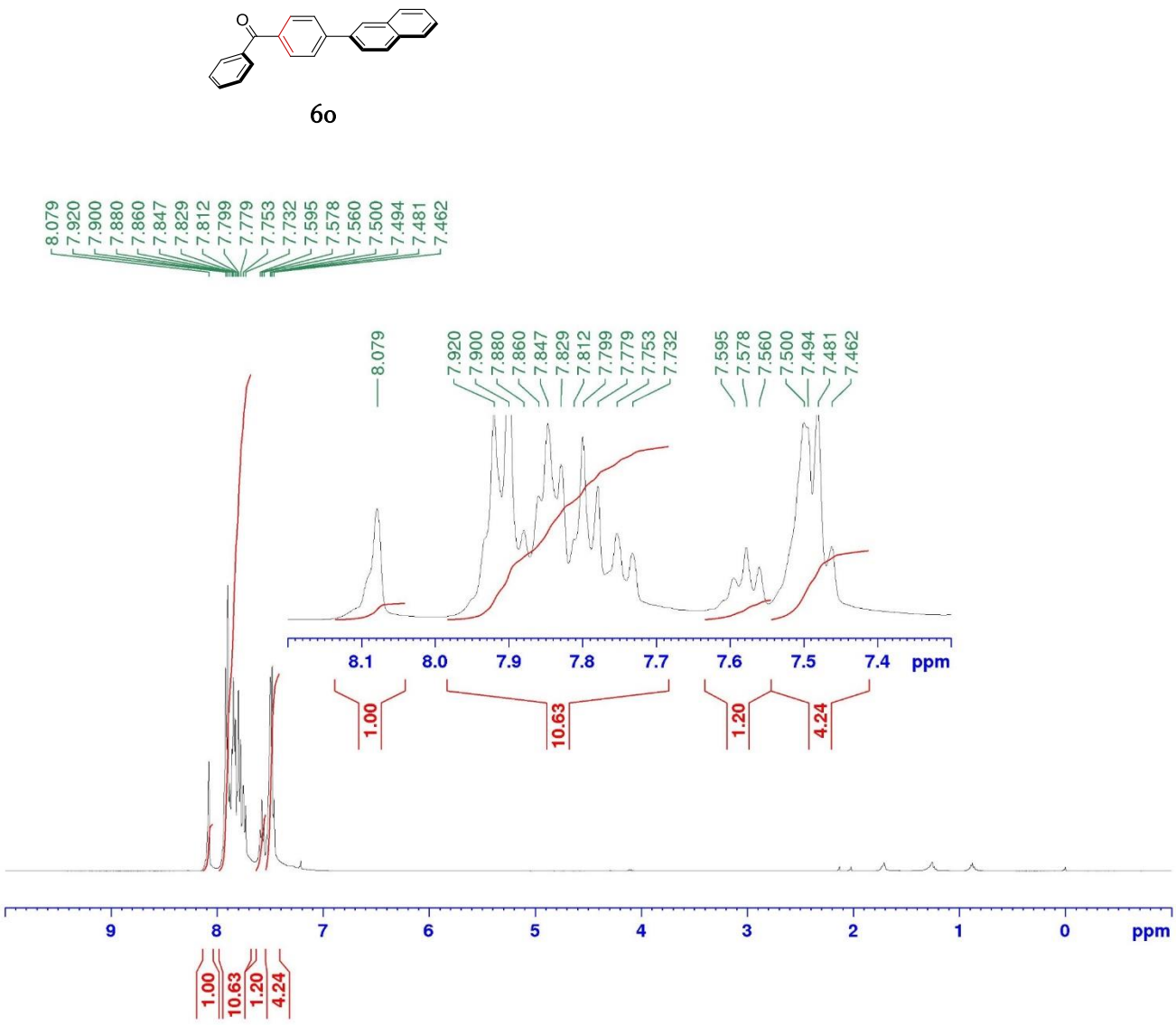


Figure S72. ^{1}H NMR spectrum of **6o** in $CDCl_3$.

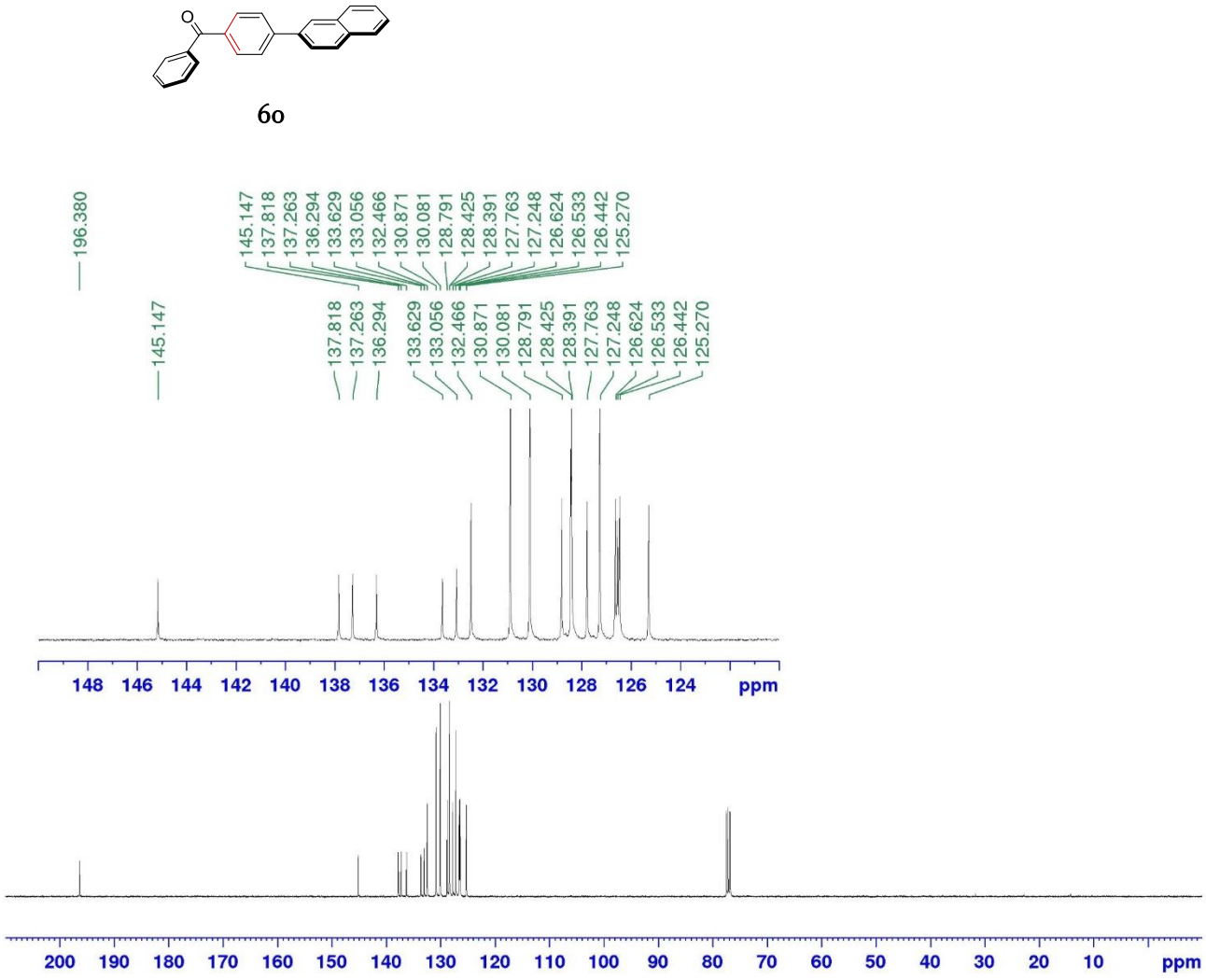
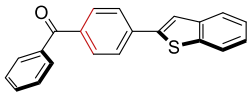


Figure S73. ^{13}C NMR spectrum of **6o** in $CDCl_3$.



6p

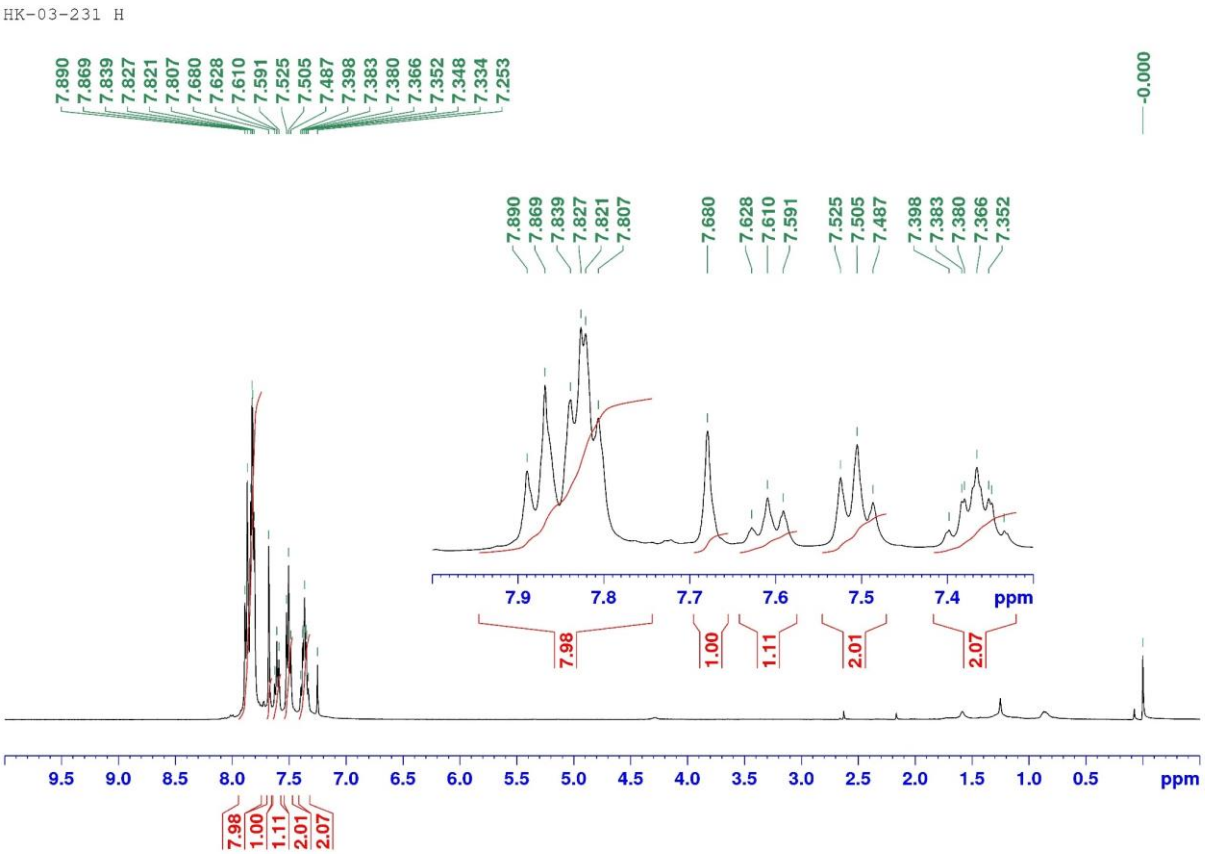
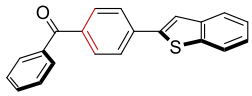


Figure S74. ^{1}H NMR spectrum of **6p** in $CDCl_3$.



6p

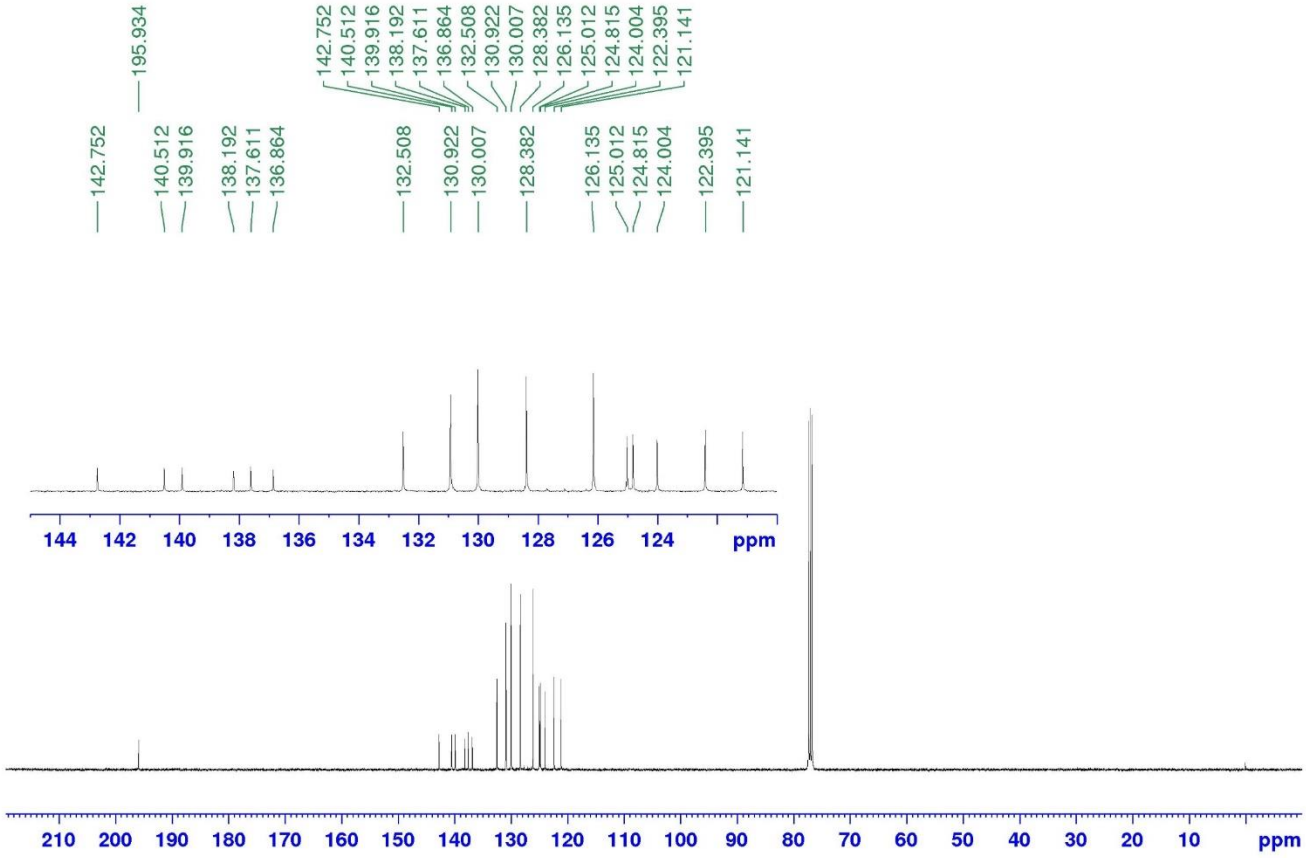


Figure S75. ^{13}C NMR spectrum of **6p** in $CDCl_3$.

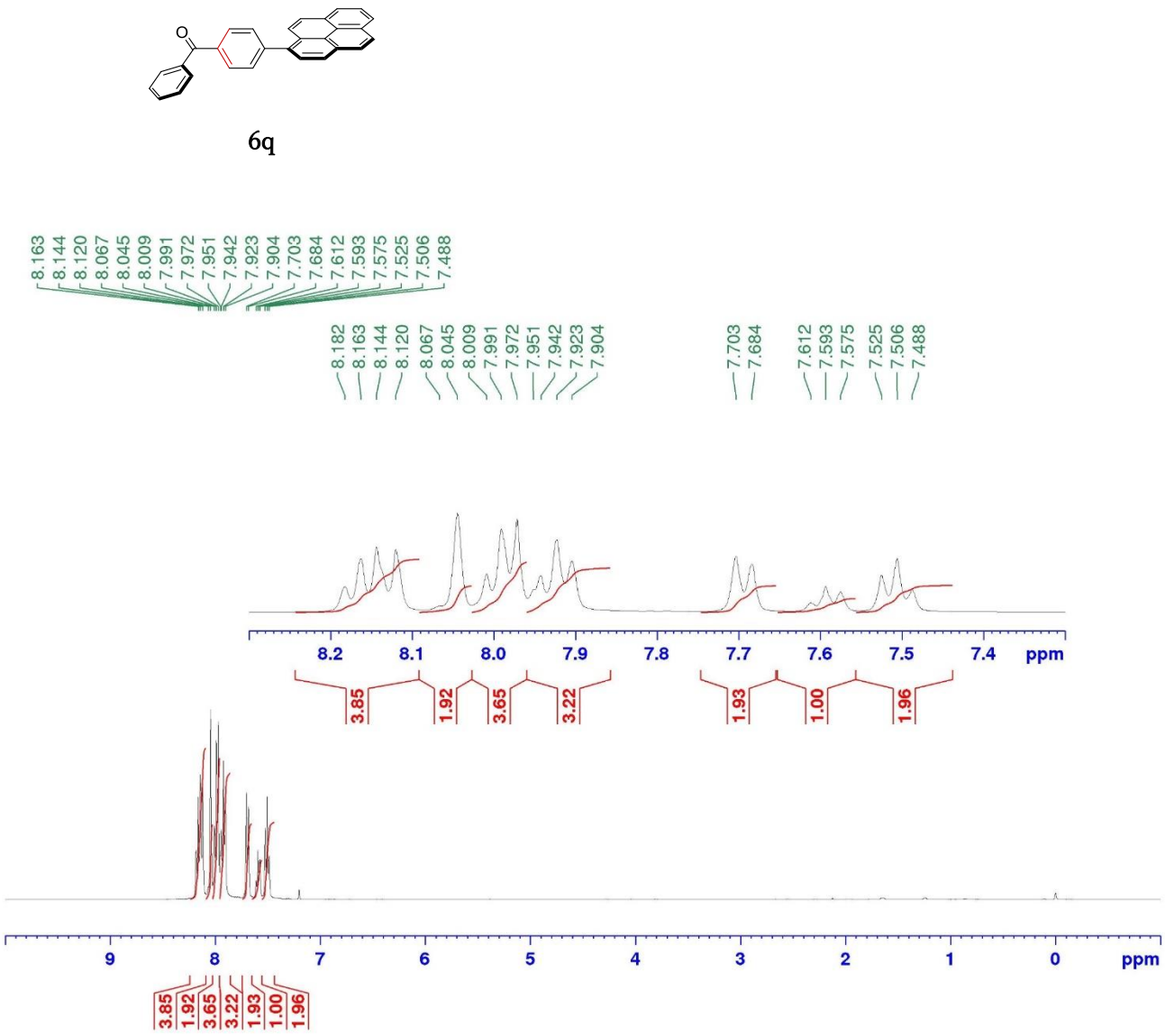


Figure S76. ^{1}H NMR spectrum of **6q** in $CDCl_3$.

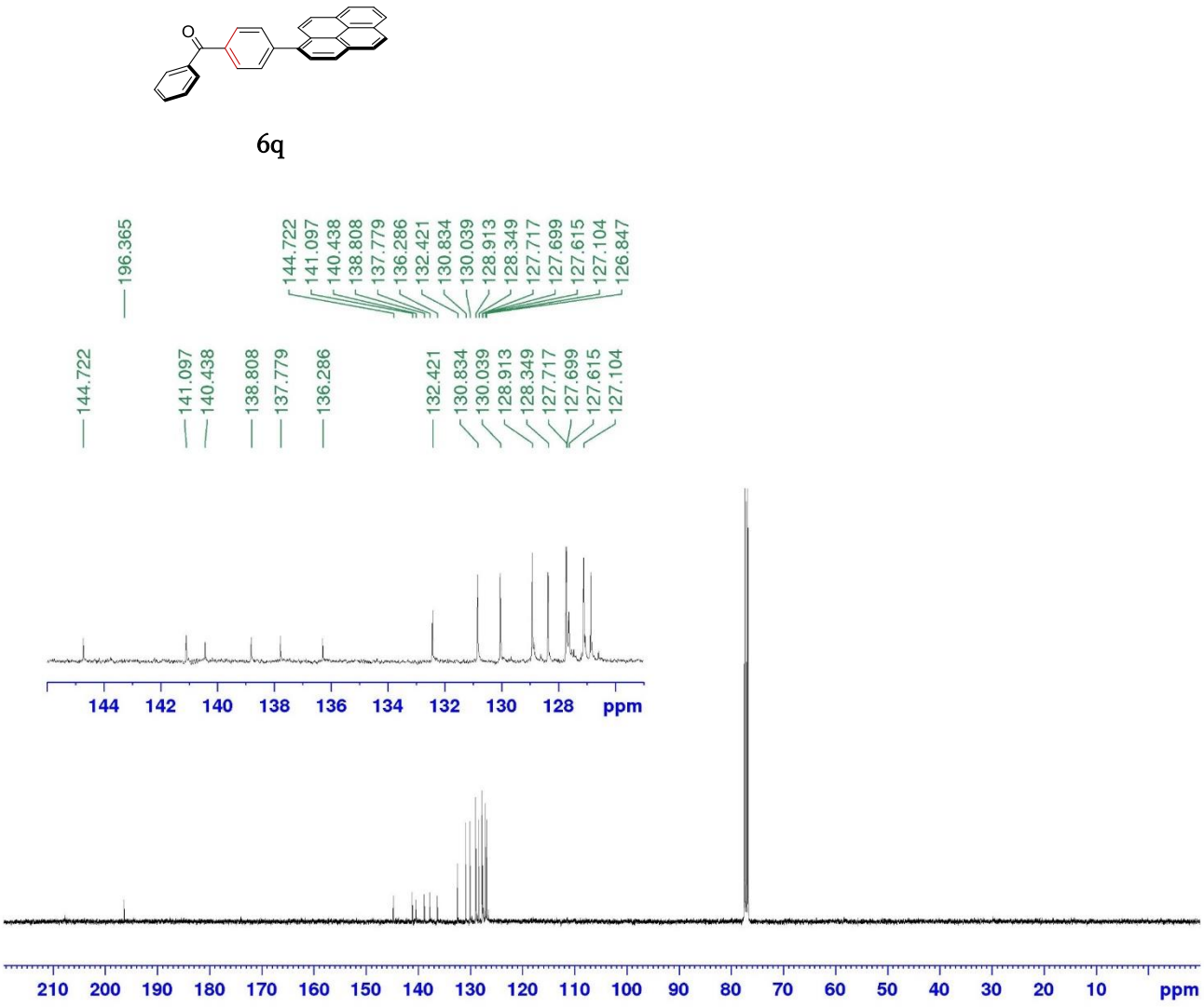


Figure S77. ^{13}C NMR spectrum of **6q** in $CDCl_3$.

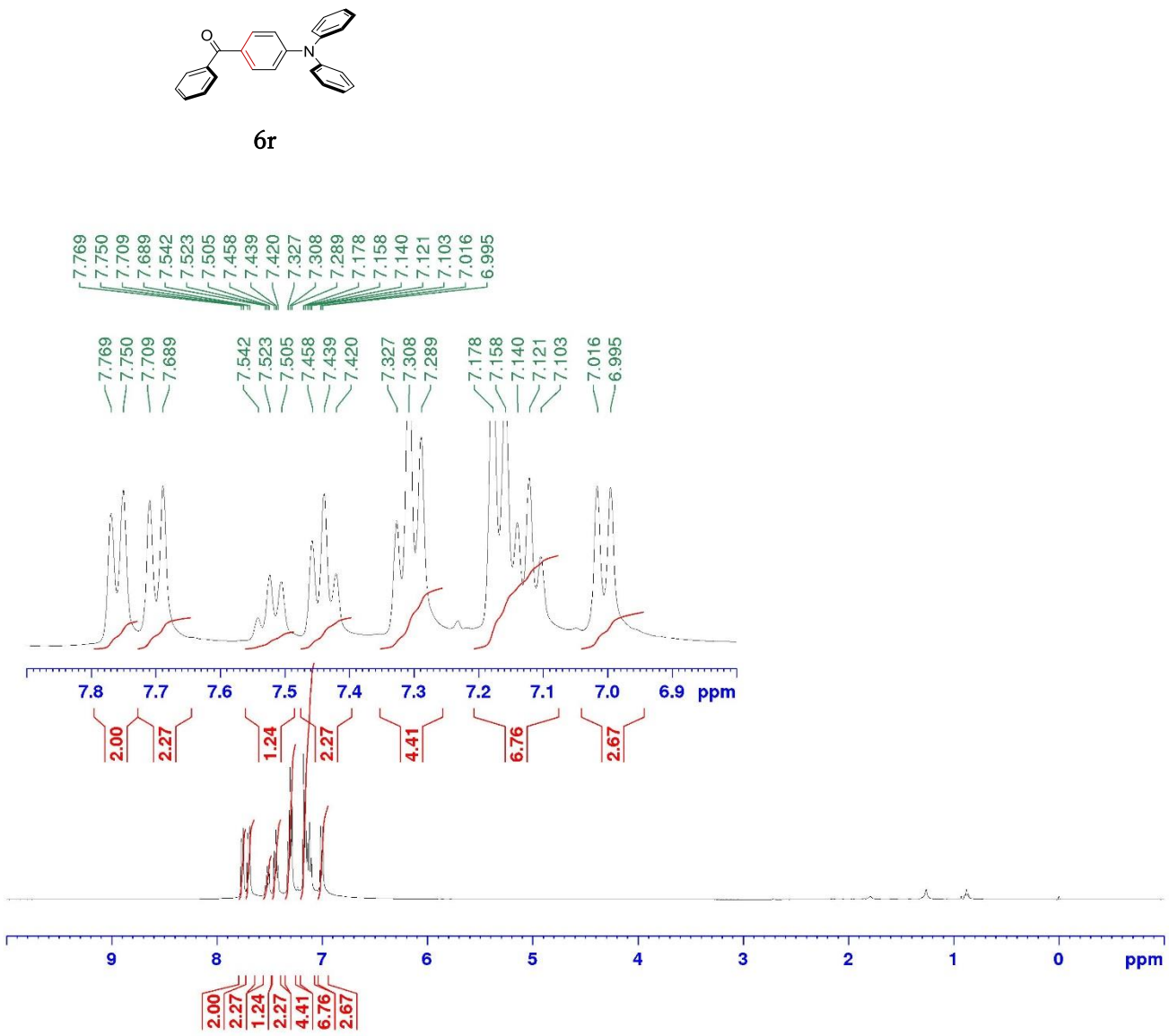


Figure S78. ^{1}H NMR spectrum of **6r** in $CDCl_3$.

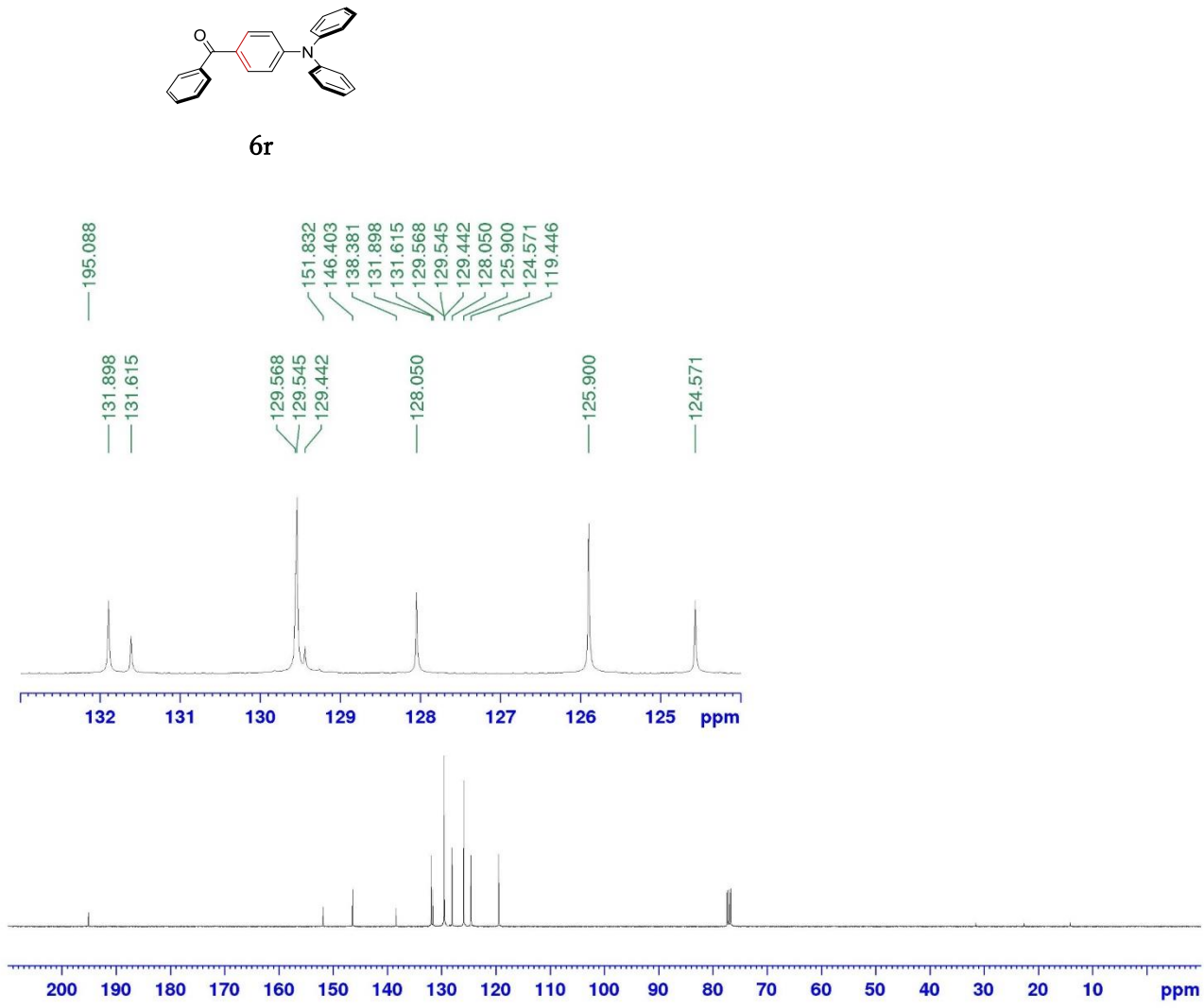


Figure S79. ^{13}C NMR spectrum of **6r** in $CDCl_3$.

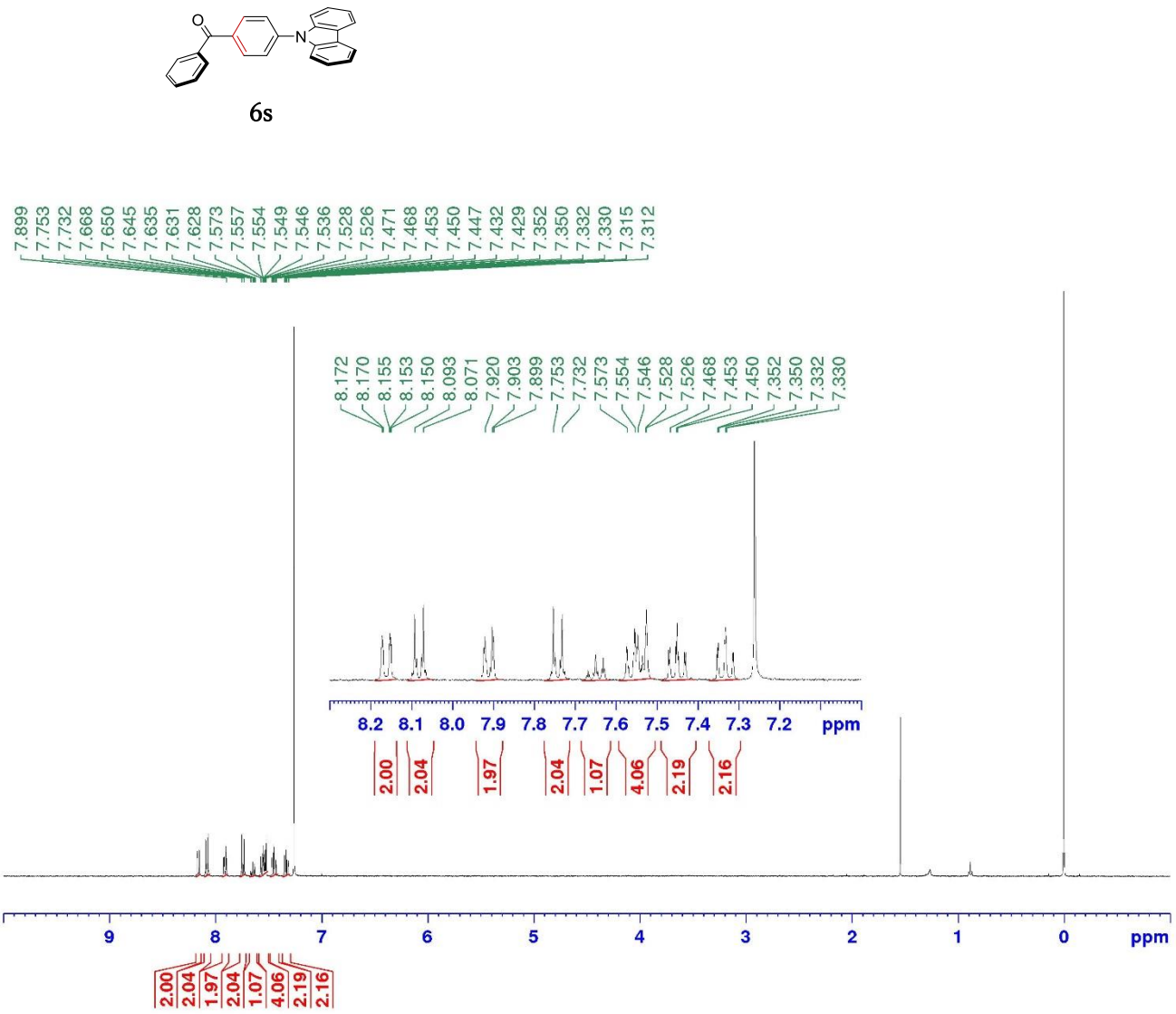


Figure S80. ^{1}H NMR spectrum of **6s** in $CDCl_3$.

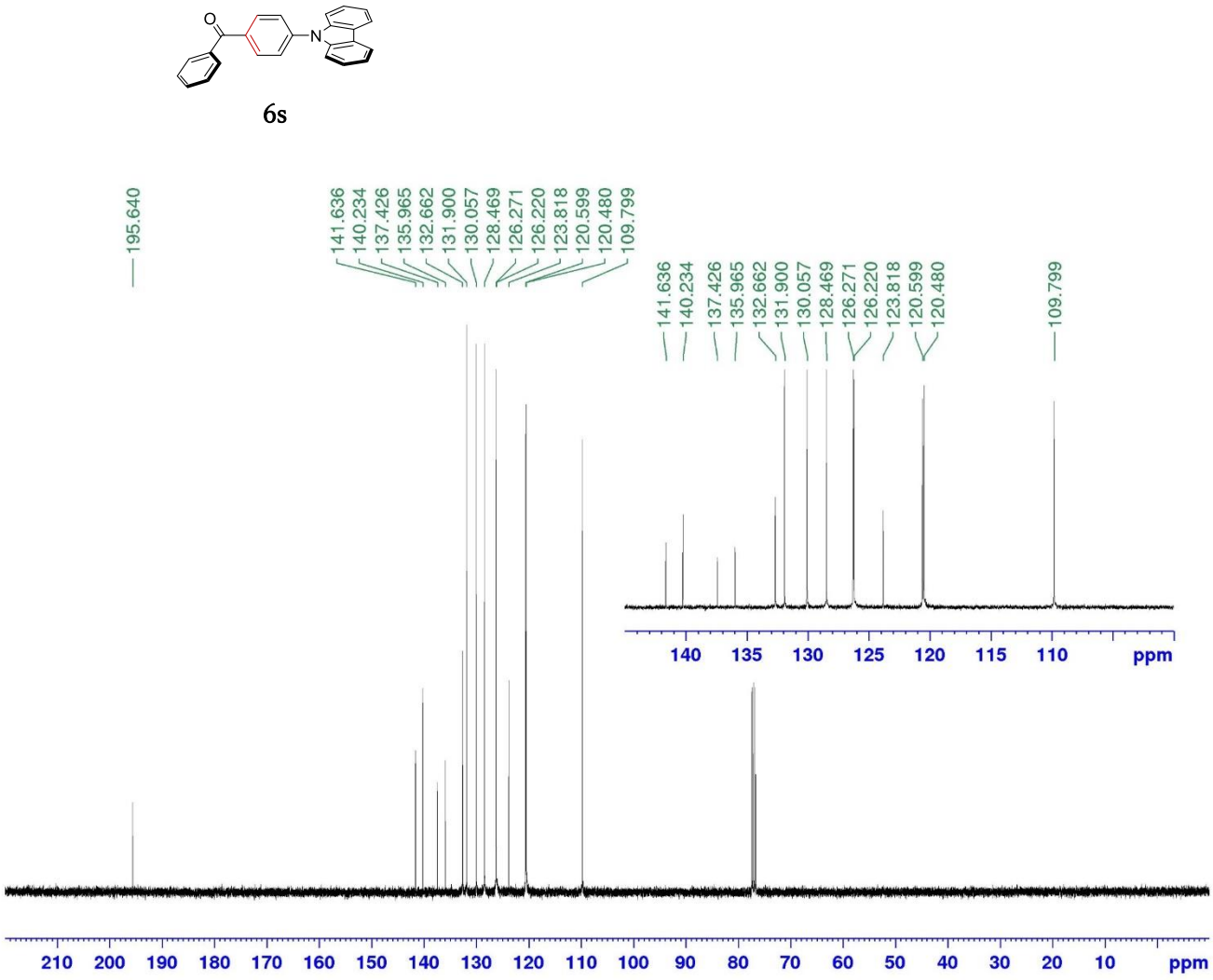
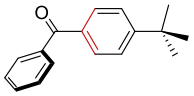


Figure S81. ^{13}C NMR spectrum of **6s** in $CDCl_3$.



6t

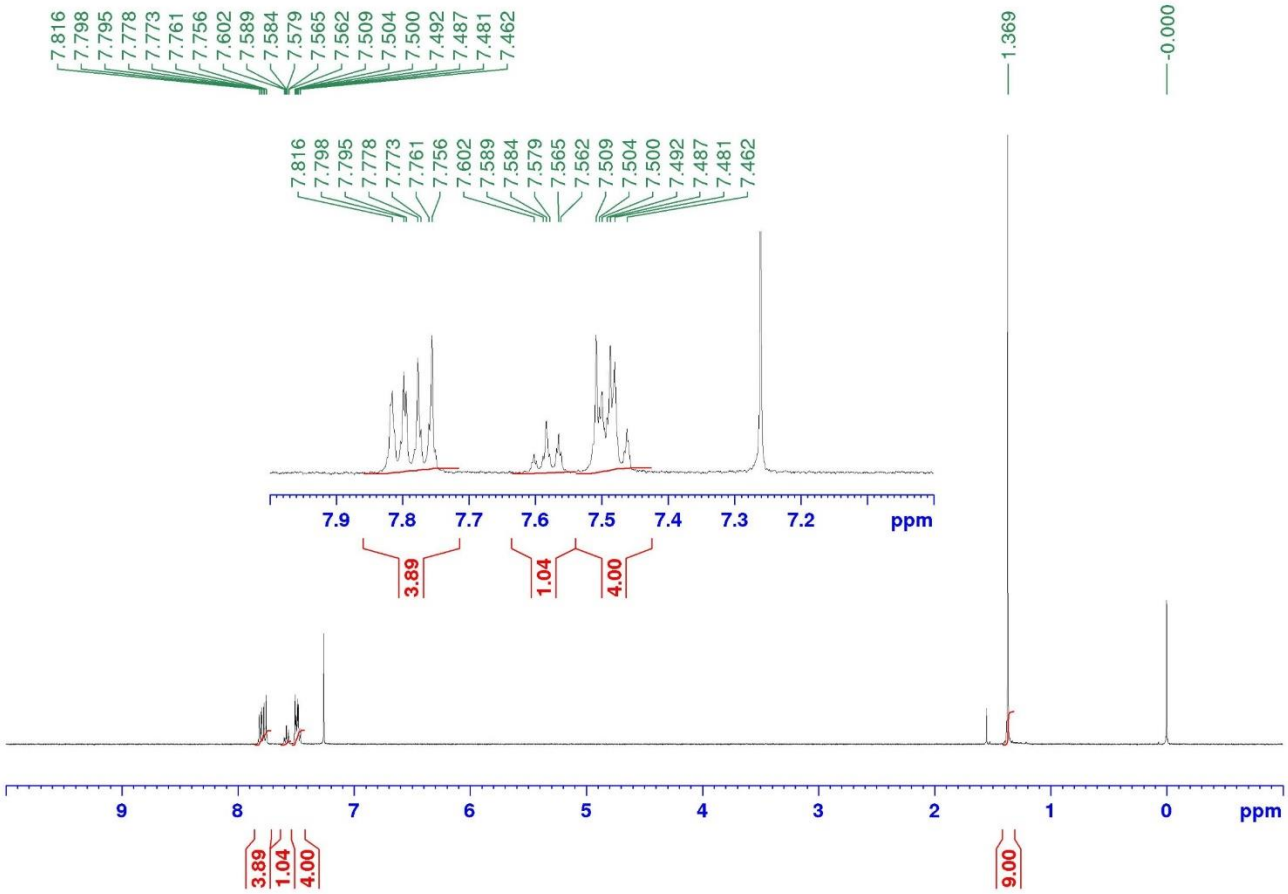


Figure S82. ^{1}H NMR spectrum of **6t** in $CDCl_3$.

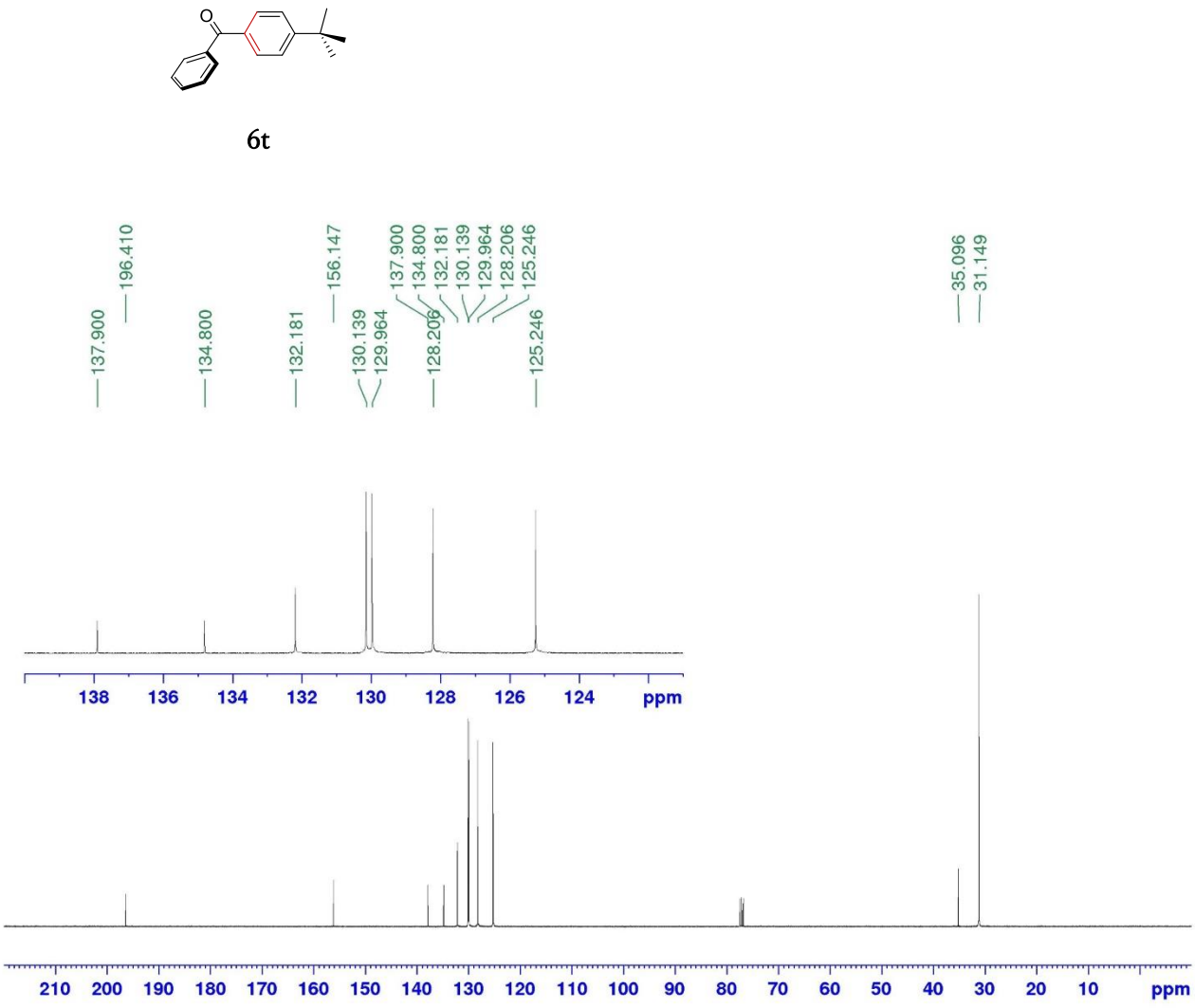
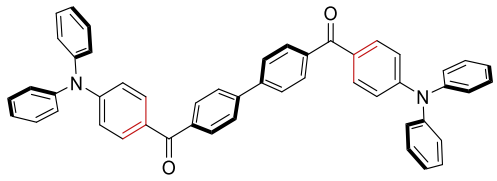


Figure S83. ^{13}C NMR spectrum of **6t** in $CDCl_3$.



6u

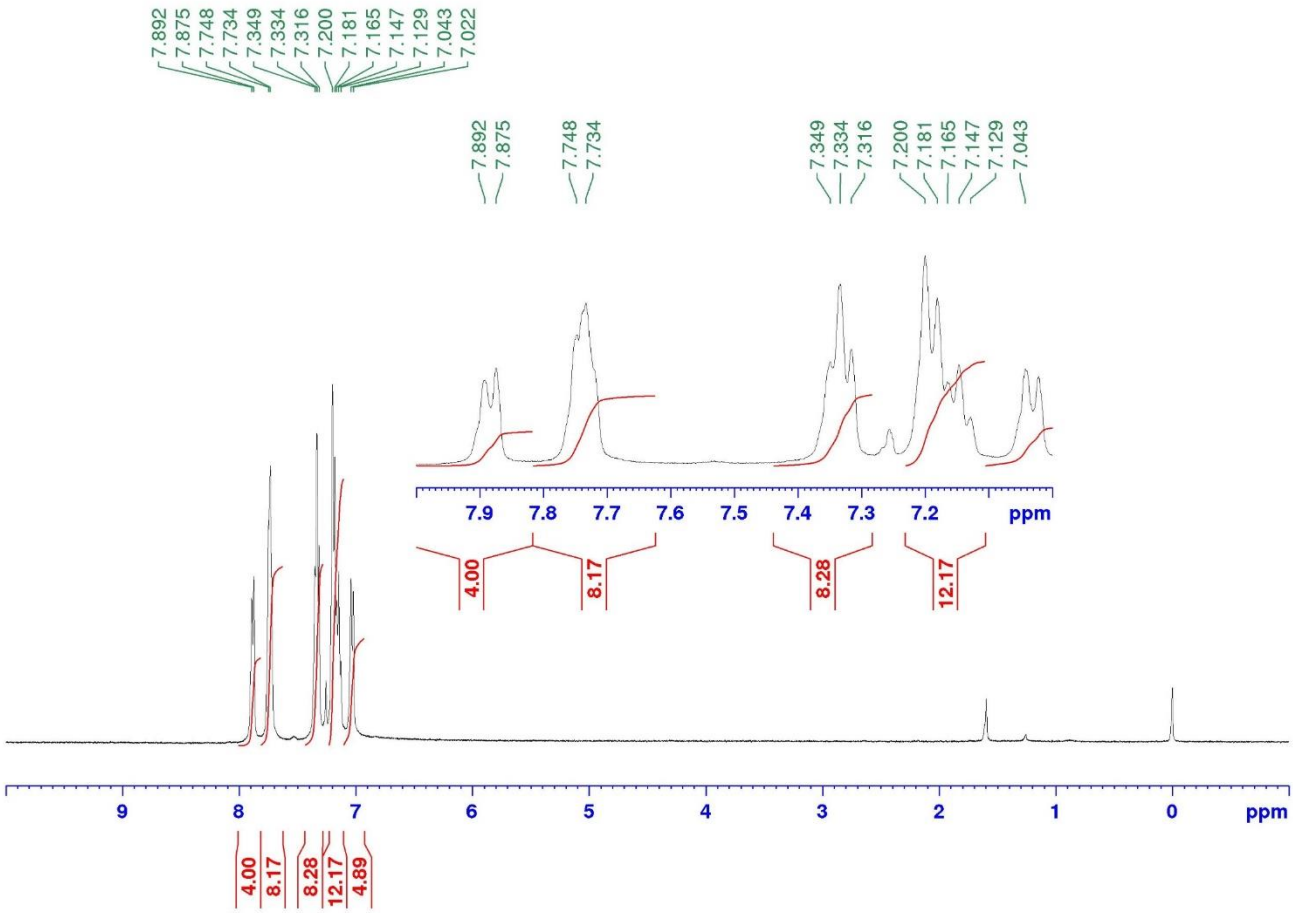
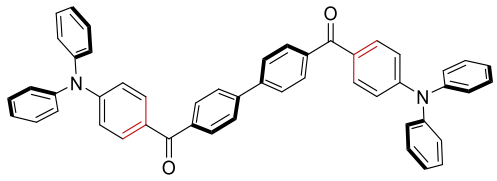


Figure S84. ^{1}H NMR spectrum of **6u** in $CDCl_3$.



6u

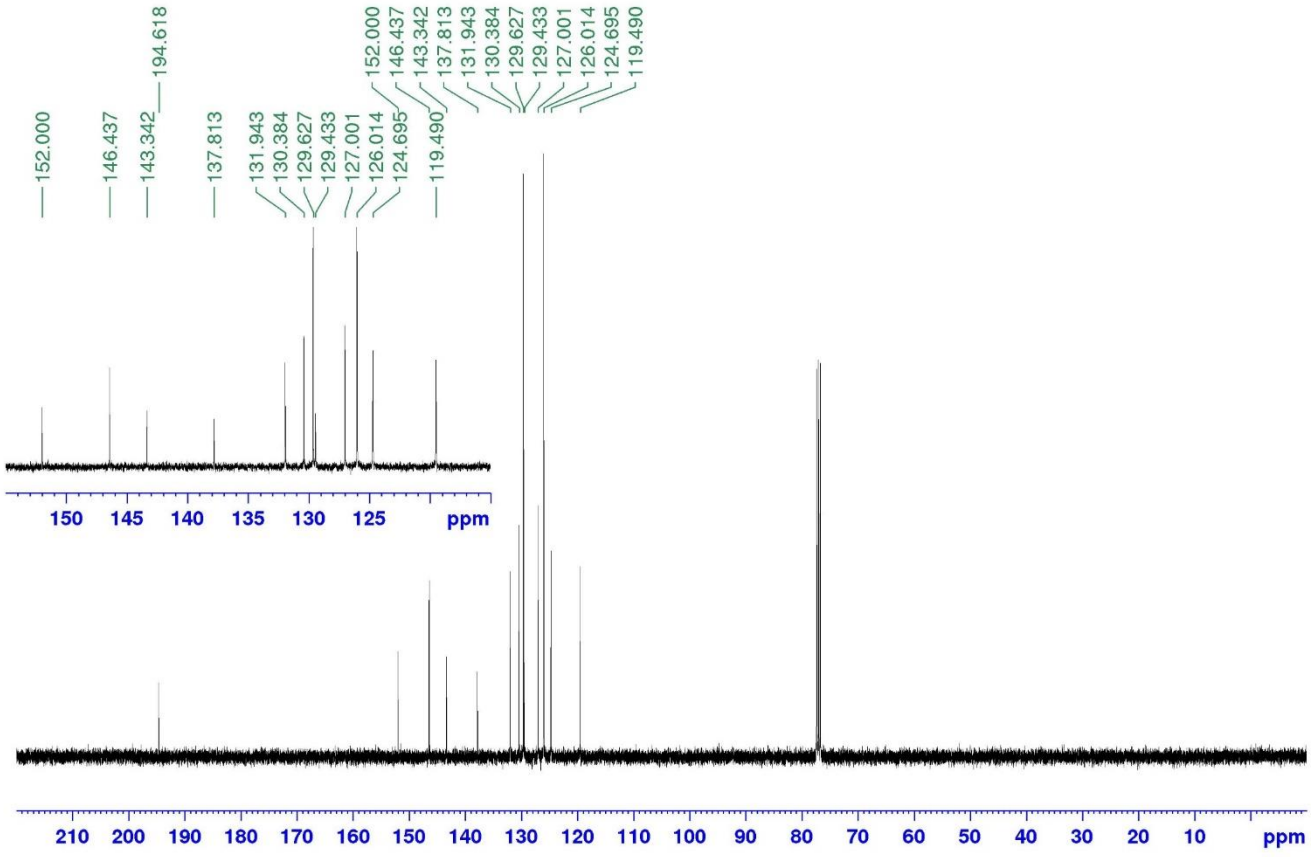
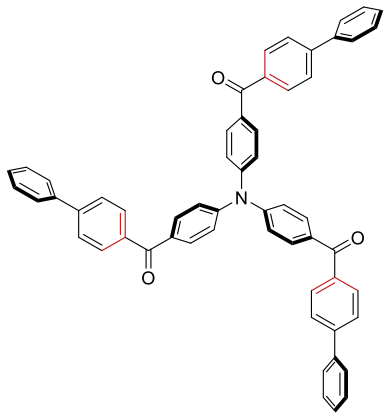


Figure S85. ^{13}C NMR spectrum of **6u** in $CDCl_3$.



6v

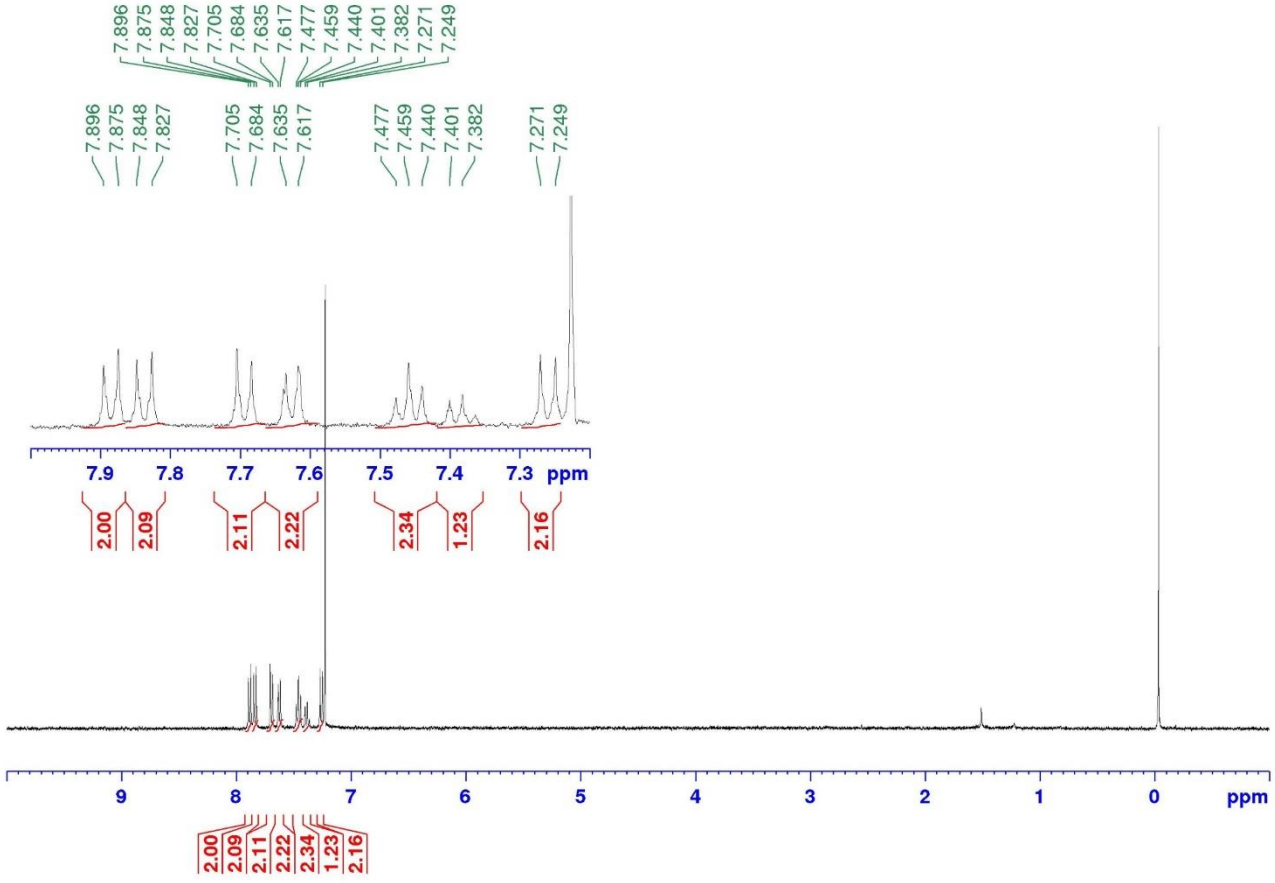


Figure S86. ^{1}H NMR spectrum of **6v** in $CDCl_3$.

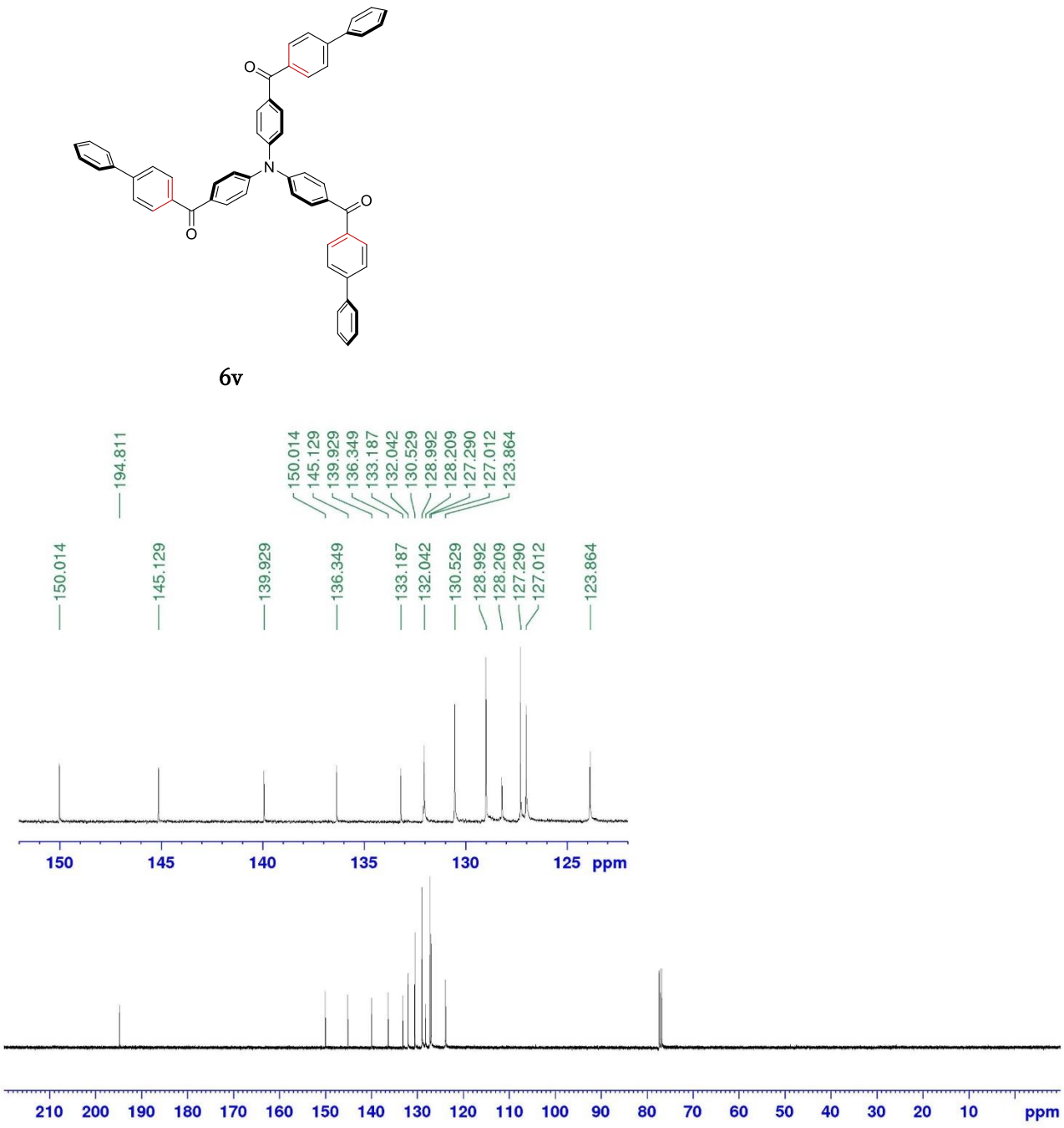


Figure S87. ^{13}C NMR spectrum of **6v** in $CDCl_3$.

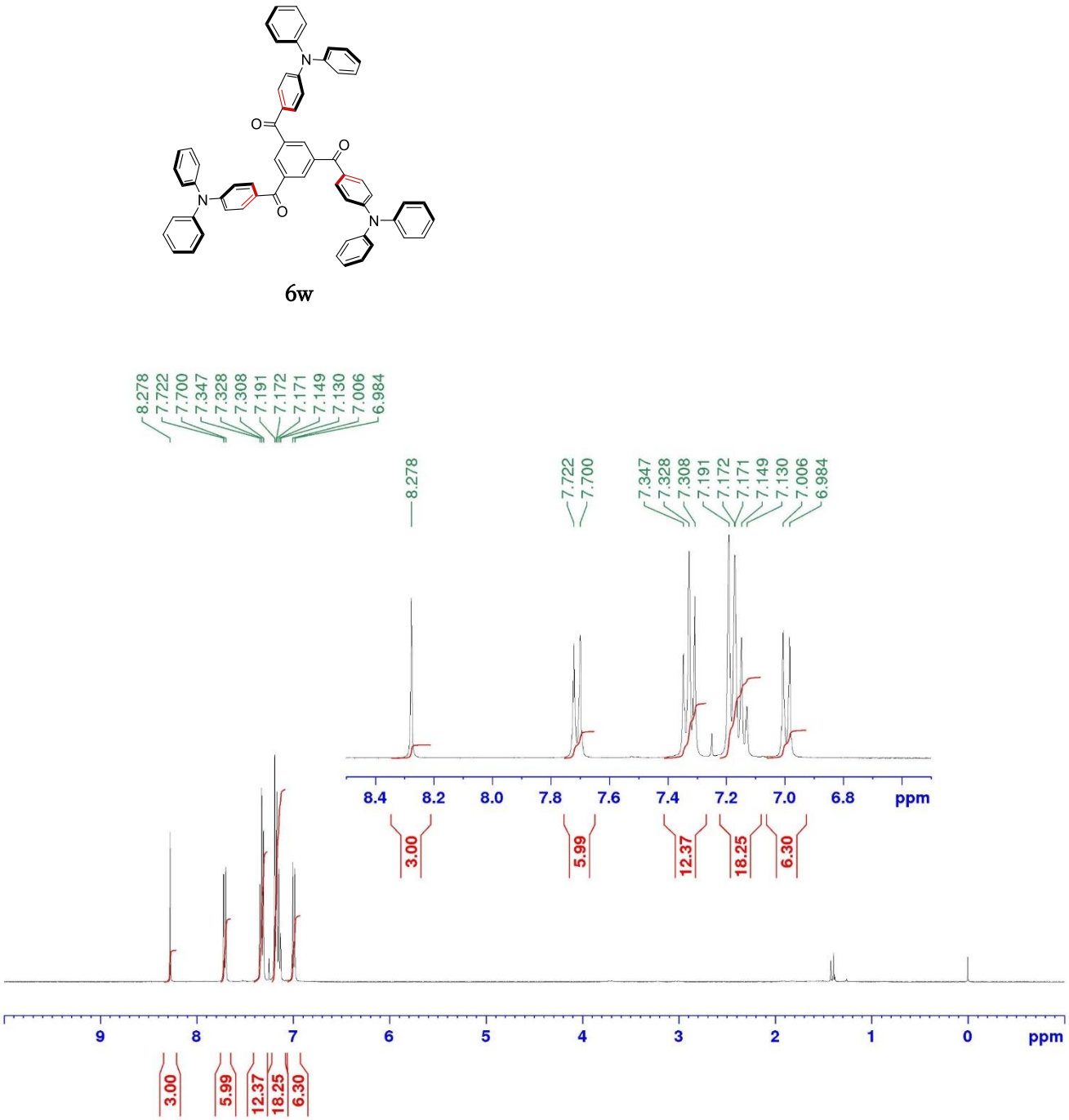


Figure S88. ^{1}H NMR spectrum of **6w** in $CDCl_3$.

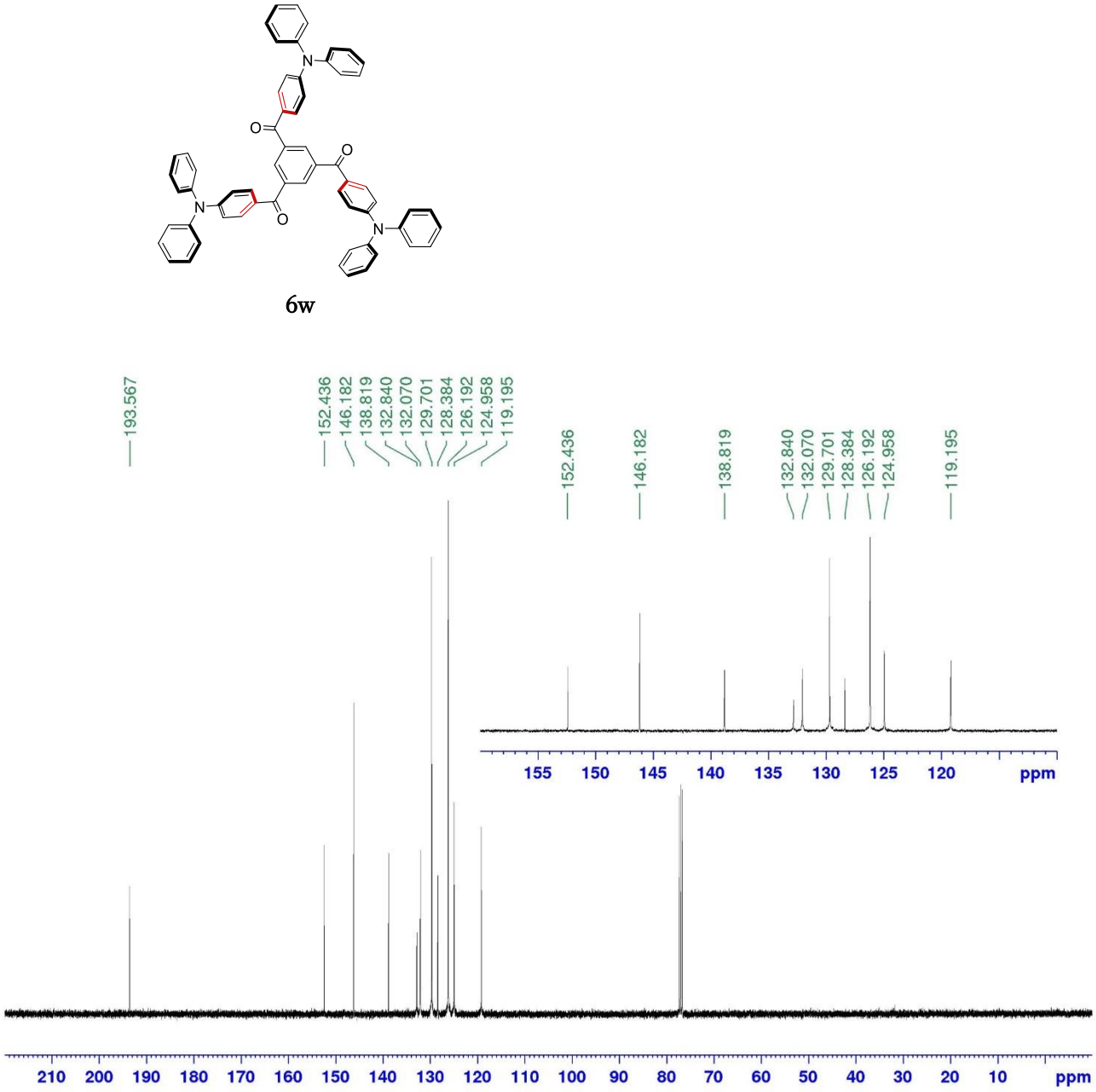


Figure S89. ^{13}C NMR spectrum of **6w** in $CDCl_3$.