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Electronic Supplementary Information

Cationic iron-catalyzed intramolecular alkyne-hydroarylation with electron-deficient arenes

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General

Nuclear magnetic resonance spectra were taken on JEOL EX-270 (^{1}H NMR, 270.05 MHz; 67.8 MHz; ^{13}C NMR) spectrometer or JEOL Lambda-400 (^{1}H NMR, 395.75 MHz; 99.5 MHz; ^{13}C NMR) spectrometer using residual chloroform (for ^{1}H NMR, 7.26 ppm) and $CDCl_3$ (for ^{13}C NMR, 77.0 ppm) as an internal standard. Low-resolution mass spectra (EI) were obtained at 70 eV on a Shimazu QP-5050. High-resolution mass experiments (EI) for novel products were performed on JEOL-SX102A at the Natural Science Center for Basic Research and Development (N-BARD) of Hiroshima University. Melting points were recorded on YANAKO micro melting point apparatus, and uncorrected. Column chromatography was performed with silica gel Merck 60 (Merck, type 60, 230-400 mesh). TLC monitoring was performed with silica gel aluminium sheets (Merck, type 60 F_{254}). 1,4-Dioxane and toluene were distilled from Na/benzophenone ketyl. Acetonitrile and nitromethane were distilled from P_2O_5 and stored over molecular sieves. 1,2-Dichloroethane were distilled from CaH_2. $Fe(OTf)_3$[1] and substrates **1b–1w**[2], **3a–3g**[3] were prepared by according to literature method. Unless otherwise noted, commercially available reagents were used without further purification.

Data of products

4-Phenyl-1-tosyl-1,2-dihydroquinoline (2b).[4] 72% isolated as a white solid (Mp. 157.0-158.0 ºC); R*f* (SiO_2, Hexane:EtOAc = 7:1) = 0.28; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 2.27 (3H, s), 4.54 (2H, d, *J* = 4.4 Hz), 5.58 (1H, t, *J* = 4.4 Hz), 6.69-6.63 (2H, m), 6.87 (1H, dd, *J* = 7.7, 1.5 Hz), 7.01-7.04 (2H, m), 7.14 (1H, ddd, *J* = 7.7, 7.7, 1.3 Hz), 7.20-7.28 (3H, m), 7.30-7.36 (3H, m), 7.80 (1H, dd, *J* = 7.9, 1.0 Hz); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 21.3, 45.5, 121.6, 126.0, 126.9, 127.5, 127.6, 128.0, 128.2, 128.5, 129.0, 130.9, 135.5, 136.1, 138.4, 138.6, 143.4, one peak was obscured due to overlap with other peaks.

6-Bromo-4-phenyl-1-tosyl-1,2-dihydroquinoline (2c). 81% isolated as a white solid (Mp. 168.0-169.0 ºC); R*f* (SiO_2, Hexane:EtOAc = 10:1) = 0.23; ^{1}H NMR ($CDCl_3$, 395.75 MHz) δ 2.29 (3H, s), 4.53 (2H, d, *J* = 4.4 Hz), 5.61 (1H, t, *J* = 4.4 Hz), 6.68-6.70 (2H, m), 6.99 (1H, d, *J* = 2.2 Hz), 7.07 (2H, d, *J* = 8.2 Hz), 7.23-7.36 (5H, m), 7.45 (1H, dd, *J* = 8.1, 2.2 Hz), 7.67 (1H, d, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 21.3, 45.3, 120.3, 122.9, 127.5, 127.9, 128.2, 128.4, 128.7, 129.21, 129.24, 131.1, 132.7, 134.5, 135.8, 137.2, 137.8, 143.7; HRMS *m/z* (EI): M^+ calcd for $C_{22}H_{18}BrNO_2S$, 439.0242; found 439.0239.

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8-Bromo-1-tosyl-4-p-tolyl-1,2-dihydroquinoline (2d). 67% isolated as a yellow oil; R*f* (SiO_2, Hexane:EtOAc = 7:1) = 0.21; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 2.24 (3H, s), 2.34 (3H, s), 4.07 (1H, dd, *J* = 18.5, 2.5 Hz), 4.84 (1H, dd, *J* = 18.5, 5.8 Hz), 5.51 (1H, dd, *J* = 5.8, 2.5 Hz), 6.70 (2H, d, *J* = 7.9 Hz), 6.91 (1H, d, *J* = 7.6 Hz), 7.01-7.10 (5H, m), 7.47 (2H, d, *J* = 7.9 Hz), 7.60-7.63 (1H, m); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 21.1, 21.3, 46.0, 123.5, 125.0, 128.1, 128.2, 128.3, 128.6, 128.9, 129.4, 133.6, 134.21, 134.25, 134.5, 136.4, 137.6, 138.6, 144.7; HRMS *m/z* (EI): M^+ calcd for $C_{23}H_{20}BrNO_2S$, 453.0398; found 453.0399.

6-Fluoro-4-phenyl-1-tosyl-1,2-dihydroquinoline (2e). 76% isolated as a white solid (Mp. 140.0-141.0 ºC); R*f* (SiO_2, Hexane:EtOAc = 7:1) = 0.34; ^{1}H NMR ($CDCl_3$, 395.75 MHz) δ 2.28 (3H, s), 4.54 (2H, d, *J* = 4.2 Hz), 5.63 (1H, t, *J* = 4.2 Hz), 6.57 (1H, dd, *J* = 9.6, 2.9 Hz), 6.68 (2H, dd, *J* = 7.7, 1.9 Hz), 7.00-7.06 (3H, m), 7.22-7.33 (5H, m), 7.75-7.78 (1H, m); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 21.3, 45.5, 112.6 (d, *J* = 24.6 Hz), 114.9 (d, *J* = 22.8 Hz), 122.8, 127.6, 127.9, 128.1, 128.4, 129.1, 129.4 (d, *J* = 8.4 Hz), 131.3 (d, *J* = 2.8 Hz), 132.8 (d, *J* = 8.4 Hz), 135.8, 137.3, 138.1 (d, *J* = 2.2 Hz), 143.6, 160.9 (d, *J* = 246.2 Hz); HRMS *m/z* (EI): M^+ calcd for $C_{22}H_{18}FNO_2S$, 379.1042; found 379.1039.

4-Phenyl-1-tosyl-1,2-dihydroquinoline-6-carboxylic acid methyl ester (2f). 79% isolated as a yellow oil; R*f* (SiO_2, Hexane:EtOAc = 5:1) = 0.21; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 2.27 (3H, s), 3.84 (3H, s), 4.56 (2H, d, *J* = 4.5 Hz), 5.64 (1H, t, *J* = 4.5 Hz), 6.72-6.75 (2H, m), 7.04 (2H, d, *J* = 8.4 Hz), 7.24-7.29 (3H, m), 7.35 (2H, d, *J* = 8.6 Hz), 7.57 (1H, d, *J* = 2.0 Hz), 7.87 (1H, d, *J* = 8.6 Hz), 7.99 (1H, dd, *J* = 8.2, 2.0 Hz); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 21.3, 45.4, 52.2, 122.3, 127.2, 127.3, 127.4, 127.9, 128.1, 128.2, 128.3, 129.2, 129.3, 130.8, 135.9, 137.5, 138.3, 139.8, 143.8, one carbon was obscured; HRMS *m/z* (EI): M^+ calcd for $C_{24}H_{21}NO_4S$, 419.1191; found 419.1190.

6-Nitro-1-tosyl-4-p-tolyl-1,2-dihydroquinoline (2g). 71% isolated as a yellow solid (Mp. 200.0-201.0 ºC); R*f* (SiO_2, Hexane:EtOAc = 5:1) = 0.40; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 2.31 (3H, s), 2.37 (3H, s), 4.59 (2H, d, *J* = 4.5 Hz), 5.71 (1H, t, *J* = 4.5 Hz), 6.64 (2H, d, *J* = 8.2 Hz), 7.08-7.12 (4H, m), 7.38 (2H, d, *J* = 8.2 Hz), 7.77 (1H, d, *J* = 2.6 Hz), 7.95 (1H, d, *J* = 8.9 Hz), 8.16 (1H, dd, *J* = 8.9, 2.6 Hz); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 21.2, 21.4, 45.4, 121.2, 122.9, 123.2, 127.3, 127.7, 128.2, 129.2, 129.5, 131.2, 133.7, 135.8, 137.5, 138.3, 141.3, 144.2, 145.6; HRMS *m/z* (EI): M^+ calcd for $C_{23}H_{20}N_2O_4S$, 420.1144; found 420.1145.

5,7-Difluoro-4-phenyl-1-tosyl-1,2-dihydroquinoline (2h). 76% isolated as a yellow solid (Mp. 119.0-120.0 ºC); R*f* (SiO_2, Hexane:EtOAc = 5:1) = 0.38; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 2.18 (3H, s), 4.41 (2H, d, *J* = 4.8 Hz), 5.53 (1H, t, *J* = 4.8 Hz), 6.54-6.62 (3H, m), 6.97 (2H, d, *J* = 8.3 Hz), 7.11-7.19 (3H, m), 7.33 (2H, d, *J* = 8.2 Hz), 7.37-7.42 (1H, m), ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 21.3, 45.3, 103.3 (t, *J* = 26.0 Hz), 110.8 (d, *J* = 24.5 Hz), 111.0 (d, *J* = 24.5 Hz), 123.0 (d, *J* = 2.5 Hz), 126.70, 126.73, 127.4, 127.6, 129.4, 134.88, 135.9, 138.73, 138.69, 144.0, 155.4 (d, *J* = 245.0 Hz), 158.0 (d, *J* = 250.0 Hz); HRMS *m/z* (EI): M^+ calcd for $C_{23}H_{17}F_2NO_2S$, 397.0948; found 397.0942.

6-Methyl-4-phenyl-1-tosyl-1,2-dihydroquinoline (2i). 57% isolated as a white solid (Mp. 172.0-173.0 ºC); R*f* (SiO_2, Hexane:EtOAc = 7:1) = 0.36; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 2.30 (3H, s), 2.35 (3H, s), 4.43 (2H, d, *J* = 4.3 Hz), 5.47 (1H, d, *J* = 4.3 Hz), 6.59-6.64 (3H, m), 6.96 (2H, d, *J* = 8.2 Hz), 7.07 (1H, d, *J* = 8.2 Hz), 7.15-7.18 (3H, m), 7.26 (2H, d, *J* = 8.2 Hz), 7.60 (1H, d, *J* = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 21.2, 21.3, 45.5, 121.6, 126.4, 127.4, 127.49, 127.54, 127.9, 128.5, 128.95, 129.01, 130.6, 132.9, 136.1, 136.4, 138.2, 138.7, 143.3; HRMS *m/z* (EI): M^+ calcd for $C_{23}H_{21}BNO_2S$, 375.1293; found 375.1290.

6-Methoxy-4-phenyl-1-tosyl-1,2-dihydroquinoline (2j). 19% isolated as a white solid (Mp.

196.0-197.0 ºC); R*f* (SiO_2, Hexane:EtOAc = 10:1) = 0.15; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 2.20 (3H, s), 3.63 (3H, s), 4.44 (2H, d, *J* = 4.5 Hz), 5.51 (1H, t, *J* = 4.5 Hz), 6.32 (1H, d, *J* = 2.6 Hz), 6.61-6.65 (2H, m), 6.81 (1H, dd, *J* = 8.9 Hz), 6.96 (2H, d, *J* = 7.9 Hz), 7.12-7.19 (3H, m), 7.25 (2H, d, *J* = 8.2 Hz), 7.65 (1H, d, *J* = 8.9 Hz); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 21.3, 45.6, 55.4, 111.7, 112.9, 122.2, 127.61, 127.64, 128.0, 128.4, 128.5, 128.8, 129.0, 132.1, 136.0, 137.9, 138.6, 143.3, 157.9; HRMS *m/z* (EI): M^+ calcd for $C_{23}H_{21}NO_3S$, 391.1242; found 391.1245.

8-Methoxy-4-phenyl-1-tosyl-1,2-dihydroquinoline (2k). 13% isolated as a yellow oil; R*f* (SiO_2, Hexane:EtOAc = 7:1) = 0.15; ^{1}H NMR ($CDCl_3$, 395.75 MHz) δ 2.26 (3H, s), 3.95 (3H, s), 4.43 (2H, brs), 5.60 (1H, t, *J* = 4.3 Hz), 6.56 (1H, d, *J* = 8.0 Hz), 6.87-6.89 (2H, m, aromatic-*H*), 6.98 (1H, d, *J* = 7.7 Hz, aromatic-*H*), 7.09 (2H, d, *J* = 8.6 Hz, aromatic-*H*), 7.14 (1H, t, *J* = 8.2 Hz), 7.24-7.27 (3H, m), 7.51 (2H, d, *J* = 7.7 Hz); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 21.3, 45.9, 56.3, 112.6, 118.4, 123.5, 126.2, 127.6, 127.86, 127.90, 128.6, 128.7, 129.2, 129.4, 133.0, 137.9, 139.0, 143.3, 156.0; HRMS *m/z* (EI): M^+ calcd for $C_{23}H_{21}NO_3S$, 391.1242; found 391.1237.

8-Isopropyl-4-phenyl-1-tosyl-1,2-dihydroquinoline (2l). 46% isolated as a yellow oil; R*f* (SiO_2, Hexane:EtOAc =5:1) = 0.54; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 1.13 (3H, d, ***J* =** 6.8 Hz), 1.47 (3H, d, ***J* =** 6.8 Hz), 2.24 (3H, s), 3.95-4.09 (2H, m), 4.95 (1H, dd, *J* = 18.2, 6.0 Hz), 5.57 (1H, dd, *J* = 6.0, 2.6 Hz), 6.70-6.75 (3H, m), 7.02 (2H, d, *J* = 8.3 Hz), 7.14-7.25 (4H, m), 7.33-7.40 (3H, m); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 21.3, 21.9, 25.9, 28.5, 46.4, 122.6, 123.5, 126.8, 127.4, 127.5, 127.8, 128.3, 128.6, 129.1, 132.1, 132.5, 136.3, 137.9, 139.9, 143.3, 148.8; HRMS *m/z* (EI): M^+ calcd for $C_{25}H_{25}NO_2S$, 403.1606; found 403.1612.

1-Tosyl-4-p-tolyl-1,2-dihydroquinoline (2s). 83% isolated as a white solid (Mp. 158.5-159.5 ºC); R*f* (SiO_2, Hexane:EtOAc = 7:1) = 0.37; ^{1}H NMR ($CDCl_3$, 395.75 MHz) δ 2.28 (3H, s), 2.34 (3H, s), 4.53 (2H, d, *J* = 4.4 Hz), 5.55 (1H, t, *J* = 4.4 Hz), 6.60 (2H, d, *J* = 7.7 Hz), 6.89 (1H, d, *J* = 7.7 Hz), 7.02-7.06 (4H, m), 7.13 (1H, tm, *J* = 7.6 Hz), 7.31-7.35 (3H, m), 7.79 (1H, d, *J* = 8.1 Hz); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 21.1, 21.3, 45.5, 121.2, 126.0, 126.5, 127.51, 127.53, 128.1, 128.4, 128.6, 129.0, 131.1, 135.1, 135.5, 136.0, 137.3, 138.5, 143.3; HRMS *m/z* (EI): calcd for $C_{23}H_{21}NO_2S$, 375.1293; found 375.1292.

4-(4-Methoxymethylphenyl)-1-tosyl-1,2-dihydroquinoline (2t). 65% isolated as a colorless oil; R*f* (SiO_2, Hexane:EtOAc = 5:1) = 0.26; ^{1}H NMR ($CDCl_3$, 395.75 MHz) δ 2.27 (3H, s), 3.42 (3H, s), 4.44 (2H, s), 4.53 (2H, d, *J* = 4.5 Hz), 5.57 (1H, t, *J* = 4.5 Hz), 6.70 (2H, d, *J* = 7.7 Hz), 6.85-6.87 (1H, m), 7.02 (2H, d, *J* = 8.7 Hz), 7.13 (1H, t, *J* = 7.3 Hz), 7.21 (2H, t, *J* = 7.7 Hz), 7.31-7.35 (3H, m), 7.79 (1H, d, *J* = 8.7 Hz); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 21.4, 45.4, 58.3, 74.4, 121.6, 126.0, 126.6, 127.4, 127.5, 127.6, 128.2, 128.6, 129.0, 130.9, 135.5, 136.1, 137.5, 137.6, 138.4, 143.4; HRMS *m/z* (EI): calcd for $C_{23}H_{21}NO_3S$, 405.1399; found 405.1399.

4-(4-anisyl)-1-tosyl-1,2-dihydroquinoline (2u). 75% isolated as a white solid (Mp. 66.0-67.5 ºC); R*f* (SiO_2, Hexane:EtOAc = 5:1) = 0.37; ^{1}H NMR ($CDCl_3$, 395.75 MHz) δ 2.27 (3H, s), 3.81 (3H, s), 4.51 (2H, d, *J* = 4.3 Hz), 5.53 (1H, t, *J* = 4.3 Hz), 6.64 (2H, d, *J* = 8.9 Hz), 6.77 (2H, d, *J* = 8.6 Hz), 6.89 (1H, dd, *J* = 7.8, 1.6 Hz), 7.02 (2H, d, *J* = 8.6 Hz), 7.12-7.16 (1H, m), 7.31-7.35 (3H, m), 7.79 (1H, d, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 99.45 MHz) δ 21.4, 45.5, 55.2, 113.3, 120.8, 126.0, 126.5, 127.4, 127.6, 128.1, 129.0, 129.6, 130.5, 131.2, 135.6, 136.1, 138.2, 143.3, 159.1; HRMS *m/z* (EI): M^+ calcd for $C_{23}H_{21}NO_3S$, 391.1242; found 391.1228.

4-(2-Anisyl)-1-tosyl-1,2-dihydroquinoline (2v). 72% isolated as a yellow solid (Mp. 170.0-171.0 ºC); R*f* (SiO_2, Hexane:EtOAc = 5:1) = 0.31; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 2.27 (3H, s), 3.55

(3H, s), 4.53 (2H, brs), 5.54 (1H, t, *J* = 4.3 Hz), 6.14 (1H, dd, *J* = 7.4, 1.8 Hz), 6.60 (1H, dd, *J* = 7.7, 1.5 Hz), 6.72 (1H, ddd, *J* = 7.4, 7.4, 1.3 Hz), 6.77-6.80 (1H, m), 6.97-7.04 (3H, m), 7.15-7.22 (2H, m), 7.33 (2H, d, *J* = 8.2 Hz), 7.70 (1H, dd, *J* = 8.2, 1.3 Hz); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 21.4, 45.4, 55.3, 110.8, 120.1, 123.1, 125.8, 126.2, 126.8, 126.9, 127.6, 127.7, 129.0, 129.1, 130.6, 130.7, 134.9, 135.0, 136.7, 143.2, 157.0; HRMS *m/z* (EI): M^+ calcd for $C_{23}H_{21}NO_3S$, 391.1242; found 391.1236.

4-(2,3,4-Trimethoxyphenyl)-1-tosyl-1,2-dihydroquinoline (2w). 77% isolated as a colorless oil; R*f* (SiO_2, Hexane:EtOAc = 3:1) = 0.21; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 2.36 (3H, s), 3.53 (3H, s), 3.85 (3H, s), 3.86 (3H, s), 4.58 (2H, brs), 5.62 (1H, t, *J* = 4.3 Hz), 5.94 (1H, d, *J* = 8.7 Hz), 6.49 (1H, d, *J* = 8.6 Hz), 6.74 (1H, d, *J* = 7.2 Hz), 7.07-7.13 (3H, m), 7.28-7.31 (1H, m), 7.42 (2H, d, *J* = 8.0 Hz), 7.79 (1H, d, *J* = 7.9 Hz); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 21.4, 45.5, 56.6, 60.8, 60.9, 106.5, 123.0, 124.5, 124.8, 125.8, 126.2, 126.7, 127.5, 127.9, 129.2, 130.9, 134.6, 135.0, 136.7, 142.0, 143.2, 151.9, 153.4; HRMS *m/z* (EI): M^+ calcd for $C_{25}H_{25}NO_5S$, 451.1453; found 451.1455.

2-Cyano-10-phenylphenanthrene (4a). Isolated in 86% yield as a yellow solid (Mp. 118.0-119.0 ºC); R*f* (SiO_2, Hexane:EtOAc=20:1) = 0.38; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 7.48-7.57 (5H, m), 7.72-7.95 (4H, m), 7.92-7.95 (1H, m), 8.26 (1H, d, *J* = 8.6 Hz), 8.68-8.71 (1H, m), 8.82 (1H, d, *J* = 8.6 Hz); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 109.8, 119.3, 123.0, 124.0, 127.4, 127.7, 128.0, 128.5, 128.7, 128.88, 128.91, 129.2, 129.9, 130.8, 132.3, 132.5, 133.1, 138.0, 139.2; LRMS *m/z*: 279 (M^+, 100), 250 (15), 139 (15), 125 (94); HRMS *m/z* (EI): M^+ calcd for $C_{21}H_{13}N$, 279.1048; found 279.1039.

2-Methoxycarbonyl-10-phenylphenanthrene (4b). Isolated in 85% yield as a yellow solid (Mp. 138.0-139.0 ºC); R*f* (SiO_2, Hexane:EtOAc=20:1) = 0.24; ^{1}H NMR ($CDCl_3$, 395.75 MHz) δ 3.93 (3H, s), 7.50-7.57 (5H, m), 7.66-7.75 (3H, m), 7.92 (1H, d, *J* = 7.7 Hz), 8.28 (1H, d, *J* = 8.6 Hz), 8.68 (1H, s), 8.73 (1H, d, *J* = 7.7 Hz), 8.82 (1H, d, *J* = 9.1 Hz); ^{13}C NMR ($CDCl_3$, 99.45 MHz) δ 52.2, 123.1, 123.2, 126.3, 126.9, 127.6, 127.9, 128.4, 128.5, 128.7, 129.1, 129.3, 130.0, 130.5, 132.4, 133.7, 139.1, 140.0, 167.2, one carbon was obscured due to overlap with other peaks; LRMS *m/z* (EI): 312 (M^+, 30), 281 (40), 140 (20), 126 (100); HRMS *m/z* (EI): M^+ calcd for $C_{22}H_{16}O_2$, 312.1150; found 312.1158.

2-Nitro-10-phenylphenanthrene (4c). Isolated in 79% yield as a yellow solid (Mp. 178.0-179.0 ºC); R*f* (SiO_2, Hexane:EtOAc=10:1) = 0.39; ^{1}H NMR ($CDCl_3$, 395.75 MHz) δ 7.52-7.57 (5H, m), 7.74-7.76 (2H, m), 7.83 (1H, s), 7.94-7.97 (1H, m), 8.43 (1H, d, *J* = 9.7 Hz), 8.72-8.74 (1H, m), 8.34-8.88 (2H, m); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 120.1, 122.9, 123.4, 124.4, 127.5, 128.1, 128.78, 128.83, 129.0, 129.6, 129.9, 130.8, 132.8, 134.6, 139.0, 139.2, 145.9, one carbon was obscured; LRMS *m/z* (EI): 299 (M^+, 48), 282 (8), 252 (91), 125 (100); HRMS *m/z* (EI): M^+ calcd for $C_{20}H_{13}NO_2$, 299.0946; found 299.0939.

2-Trifluoromethyl-10-phenylphenanthrene (4d). Isolated in 95% yield as a white solid (Mp. 105.0-106.0 ºC); R*f* (SiO_2, Hexane) = 0.30; ^{1}H NMR ($CDCl_3$, 395.75 MHz) δ 7.49-7.62 (5H, m), 7.67-7.76 (2H, m), 7.79 (1H, s), 7.87 (1H, dm, *J* = 8.8 Hz), 7.92-7.96 (1H, m), 8.25 (1H, s), 8.71-8.75 (1H, m), 8.86 (1H, d, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 122.3 (q, *J* = 3.6 Hz), 122.9, 123.8, 124.2, (q, *J* = 4.4 Hz), 124.4 (q, *J* = 272.2 Hz), 127.1, 127.8, 127.9, 128.2, (q, *J* = 32.2 Hz), 128.6, 128.8, 128.9, 129.2, 129.9, 130.5, 132.2, 132.68-132.69 (m), 138.6, 139.7; LRMS *m/z* (EI): 322 (M^+, 100), 252 (42), 151 (48), 126 (85); HRMS *m/z* (EI): M^+ calcd for $C_{21}H_{13}F_3$, 322.0969; found 322.0956

1,3-Difluoro-10-phenylphenanthrene (4e). Isolated in 91% yield as a white solid (Mp. 172.0-173.0 ºC); R*f* (SiO_2, Hexane) = 0.38; ^{1}H NMR ($CDCl_3$, 395.75 MHz) δ 6.99-7.05 (1H, m), 7.42-7.47 (5H, m), 7.57 (1H, s), 7.65-7.71 (2H, m), 7.86-7.89 (1H, m), 8.22 (1H, dm, *J* = 10.6 Hz),

8.53-8.55 (1H, m); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 103.1 (t, *J* = 26.9 Hz), 104.3 (dd, *J* = 21.8, 4.5 Hz), 117.4 (dd, *J* = 9.8, 2.5 Hz), 123.0, 126.9, 127.1, 127.5, 128.1, 128.6, 128.66, 128.71, 129.3 (d, *J* = 2.2 Hz), 131.71 (d, *J* = 1.1 Hz), 133.8 (dd, *J* = 9.8, 4.8 Hz), 134.8, 142.8 (d, *J* = 3.9 Hz), 160.3 (dd, *J* = 258.1, 12.7 Hz), 160.7 (dd, *J* = 246.9, 13.6 Hz); LRMS *m/z* (EI): 290 (M^+, 100), 270 (26), 143 (48), 135 (73), 122 (24); HRMS *m/z* (EI): M^+ calcd for $C_{20}H_{12}F_2$, 290.0907; found 290.0897.

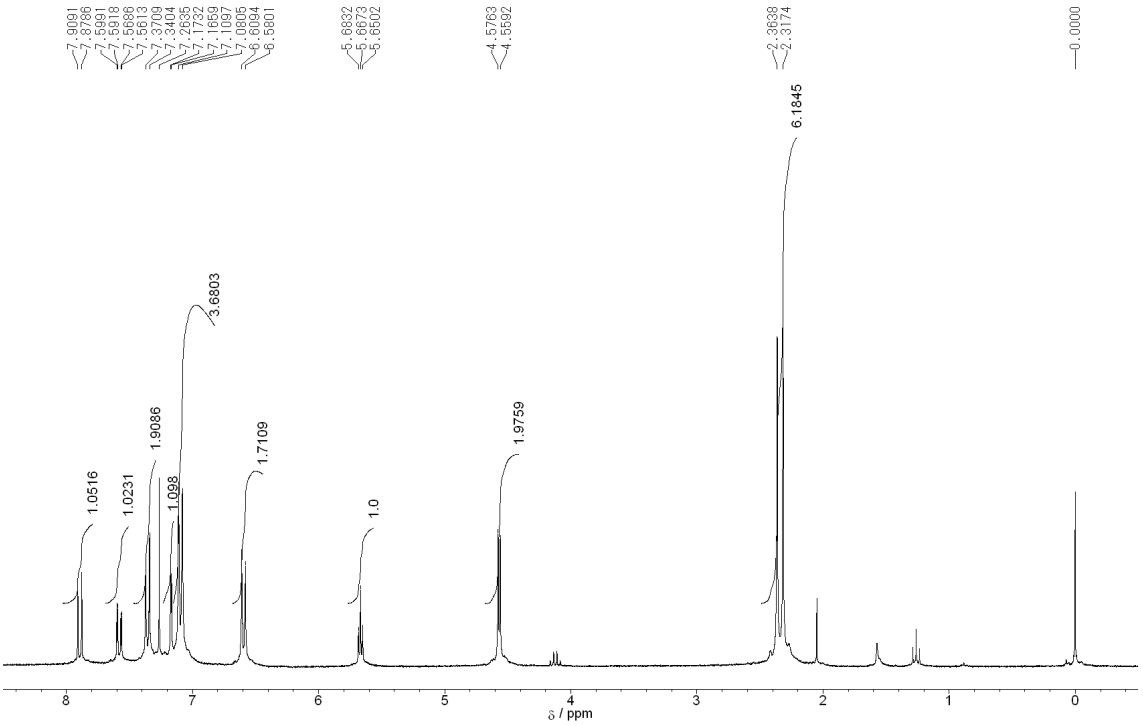
9-Phenylphenanthrene (4f).[5] Isolated in 86% yield as a white solid (Mp. 84.0-85.0 ºC); R*f* (SiO_2, Hexane) = 0.41; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 7.48-7.71 (10H, m), 7.90-7.97 (2H, m), 8.75 (1H, d, *J* = 8.0 Hz), 8.80 (1H, d, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 122.5, 122.9, 126.4, 126.5, 126.6, 126.8, 126.9, 127.3, 127.5, 128.3, 128.6, 129.9, 130.1, 130.6, 131.1, 131.5, 138.7, 140.7; LRMS *m/z* (EI): 254 (M^+, 59), 126 (100), 113 (42), 100 (6).

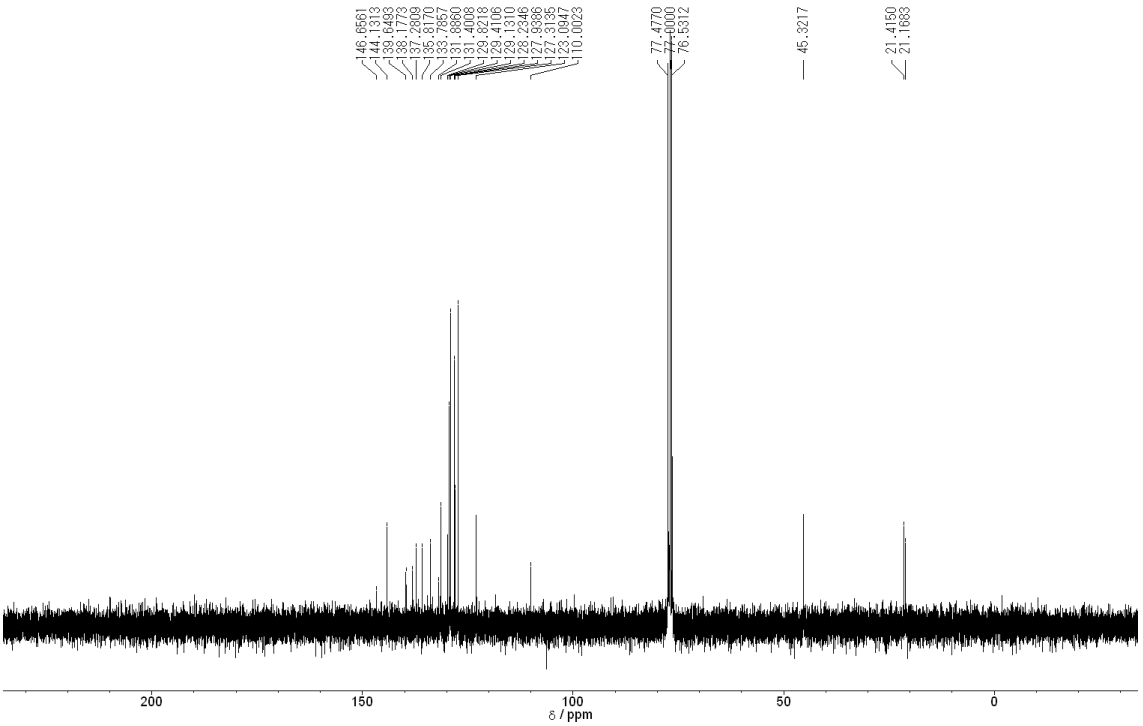
2-Methoxy-10-phenylphenanthrene (4g)[6] **and 9-benzylidene-2-methoxy-9*H*-fluorene (4g').** Isolated as a mixture of **4g** and **4g'** (yellow oil); R*f* (SiO_2, Hexane:EtOAc=20:1) = 0.26; ^{1}H NMR ($CDCl_3$, 270.05 MHz) for **4g**: δ 3.81 (3H, s), 7.19 (1H, dd, *J* = 9.1, 2.6 Hz), 7.30 (1H, d, *J* = 2.7 Hz), 7.34 (1H, s), 7.46-7.65 (6H, m), 7.69 (1H, s), 7.84-7.91 (1H, m), 8.63 (1H, d, *J* = 8.2 Hz), 8.69 (1H, d, *J* = 8.7 Hz); for **4g'** (assignable peaks only): δ 4.04 (3H, s), 8.16 (1H, d, *J* = 2.6 Hz); ^{13}C NMR ($CDCl_3$, 67.8 MHz) for **4g**: δ 55.3, 107.80, 116.3, 122.0, 124.5, 124.9, 125.8, 126.7, 127.4, 128.1, 128.4, 128.6, 129.9, 130.0, 130.5, 132.5, 138.2, 140.9, 158.2, for **4g'**: δ 55.4, 104.2, 122.5, 125.2, 125.7, 126.1, 126.9, 127.3, 128.3, 128.5, 128.7, 129.98, 132.0, 132.1, 140.9, 158.22, three peaks were obscured due to overlap with other peaks.

5 K. Kanno, Y. Liu, A. Iesato, K. Nakajima and T. Takahashi, *Org. Lett.*, 2005, **7**, 5453.

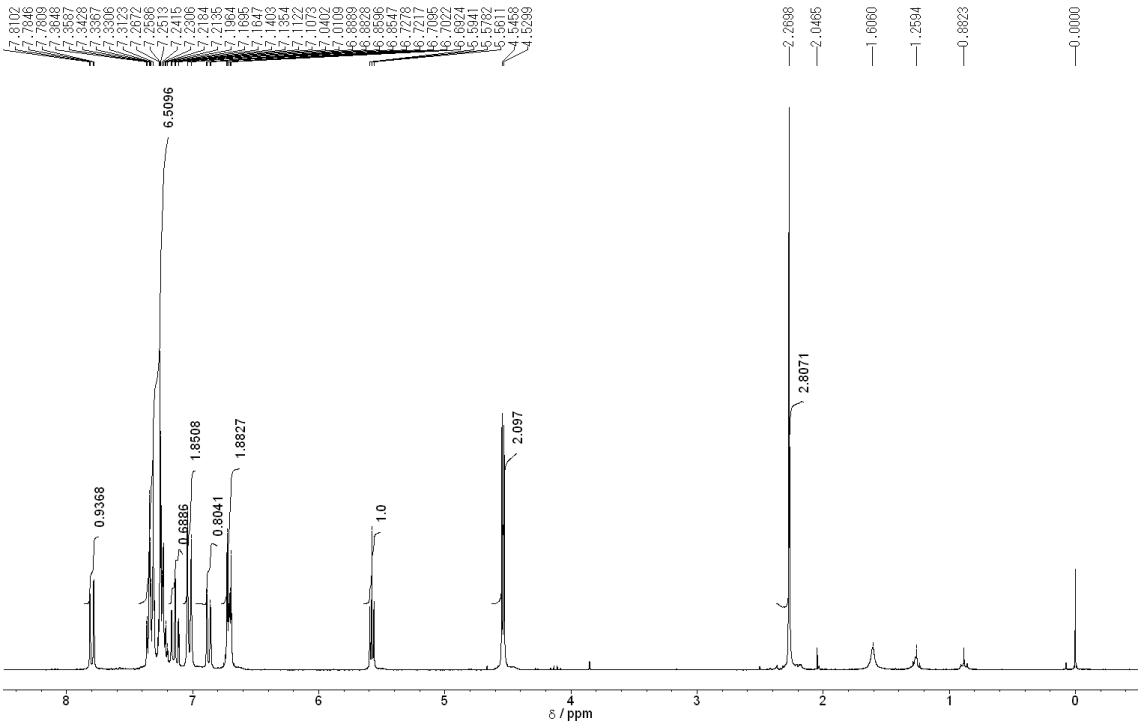
6 D. García-Cuadrado, P. de Mendoza, A. A. C. Braga, F. Maseras, A. M. Echavarren, *J. Am. Chem. Soc.* 2007, **129**, 6880.

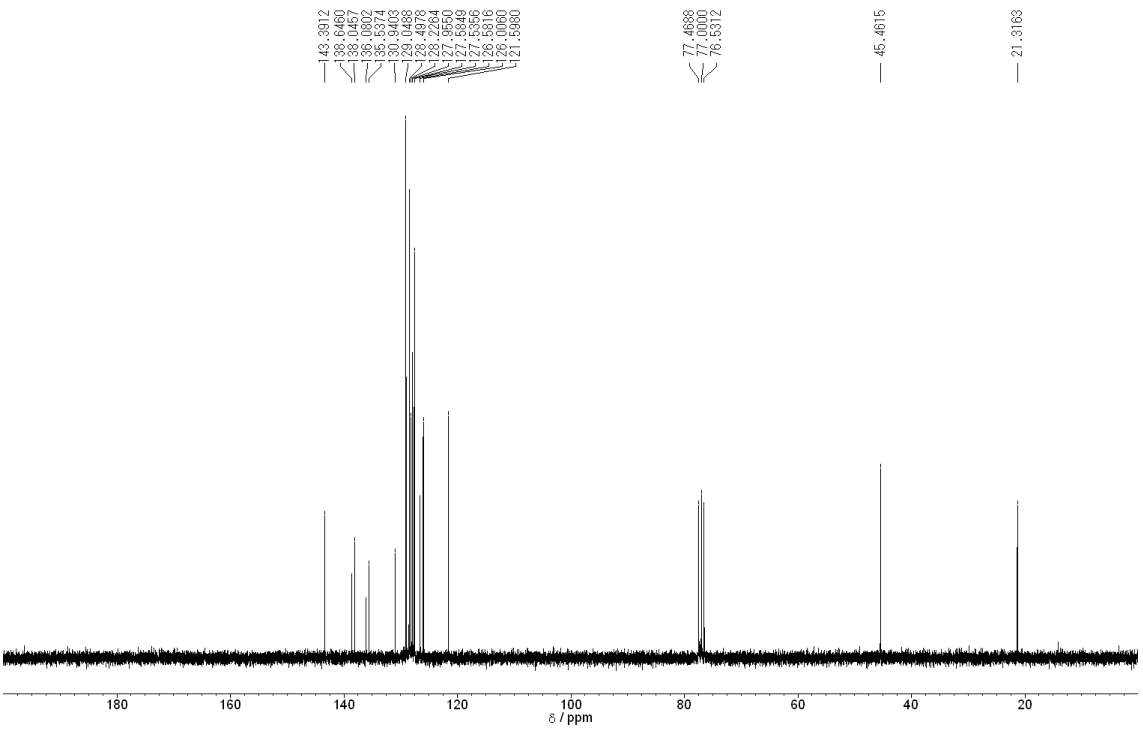
6-Cyano-4-(4-Tol)-1-tosyl-1,2-dihydroquinoline (2a).



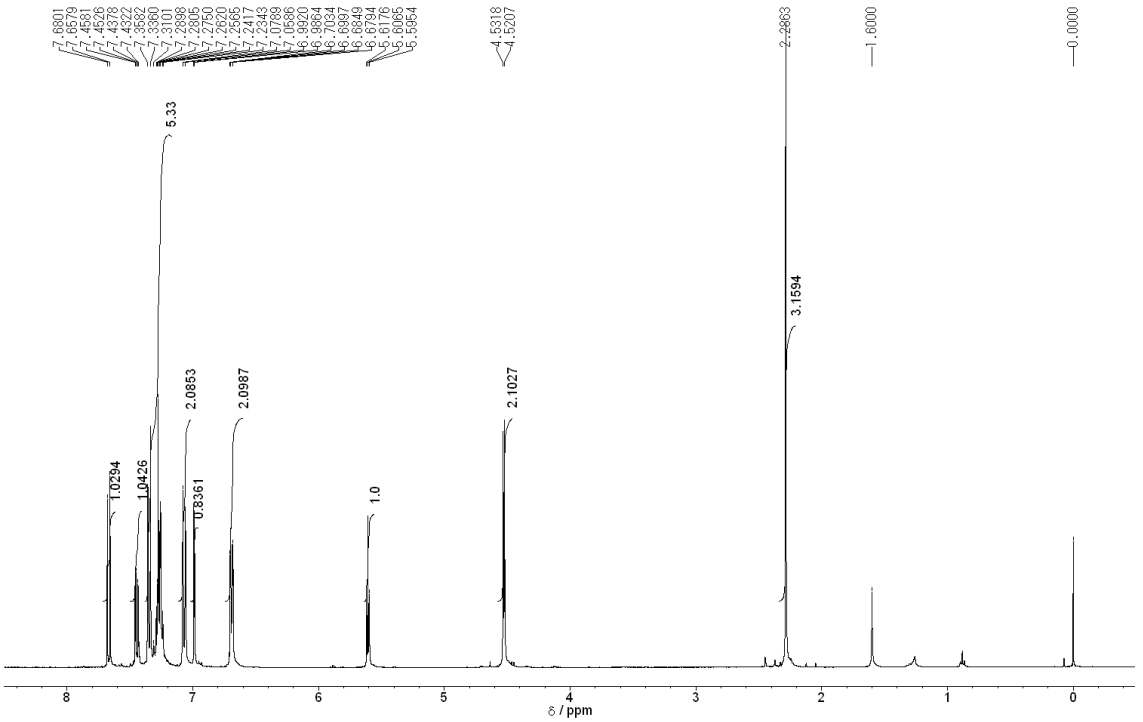


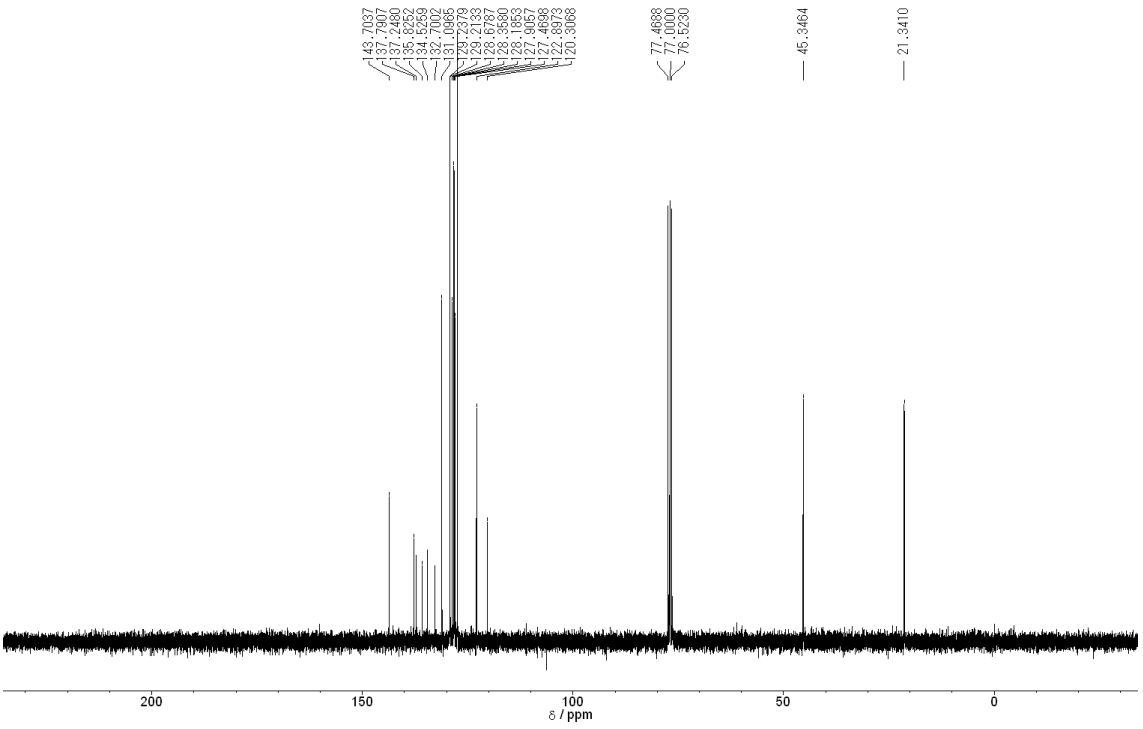
4-Phenyl-1-tosyl-1,2-dihydroquinoline (2b).



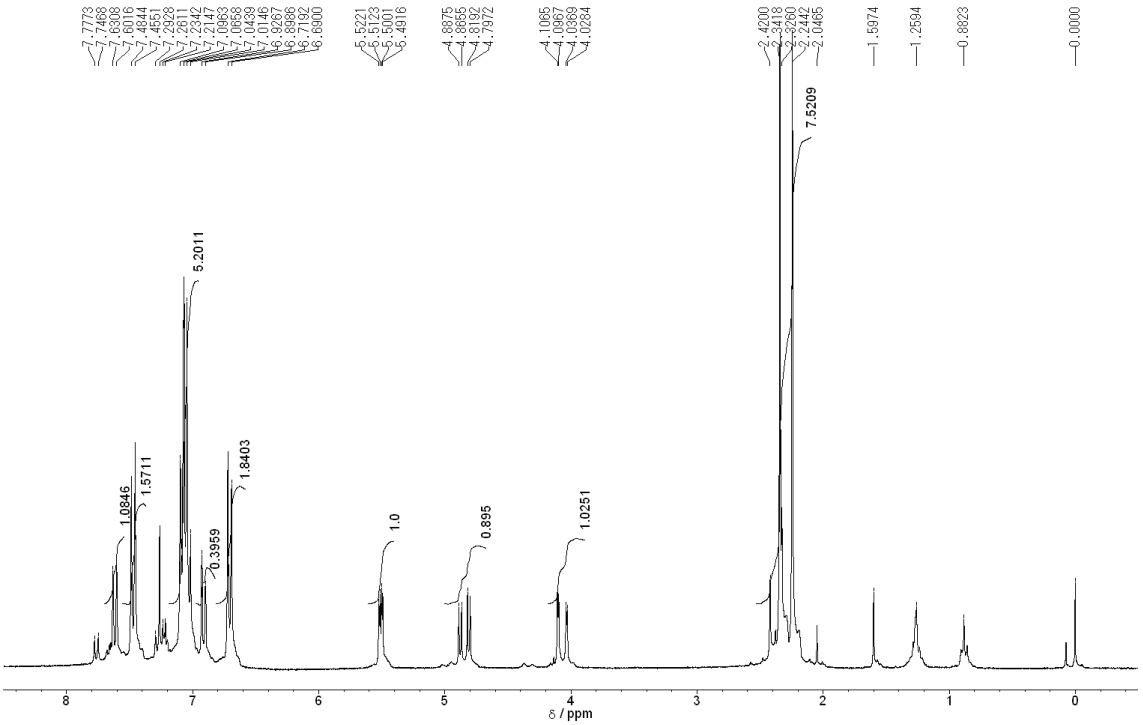


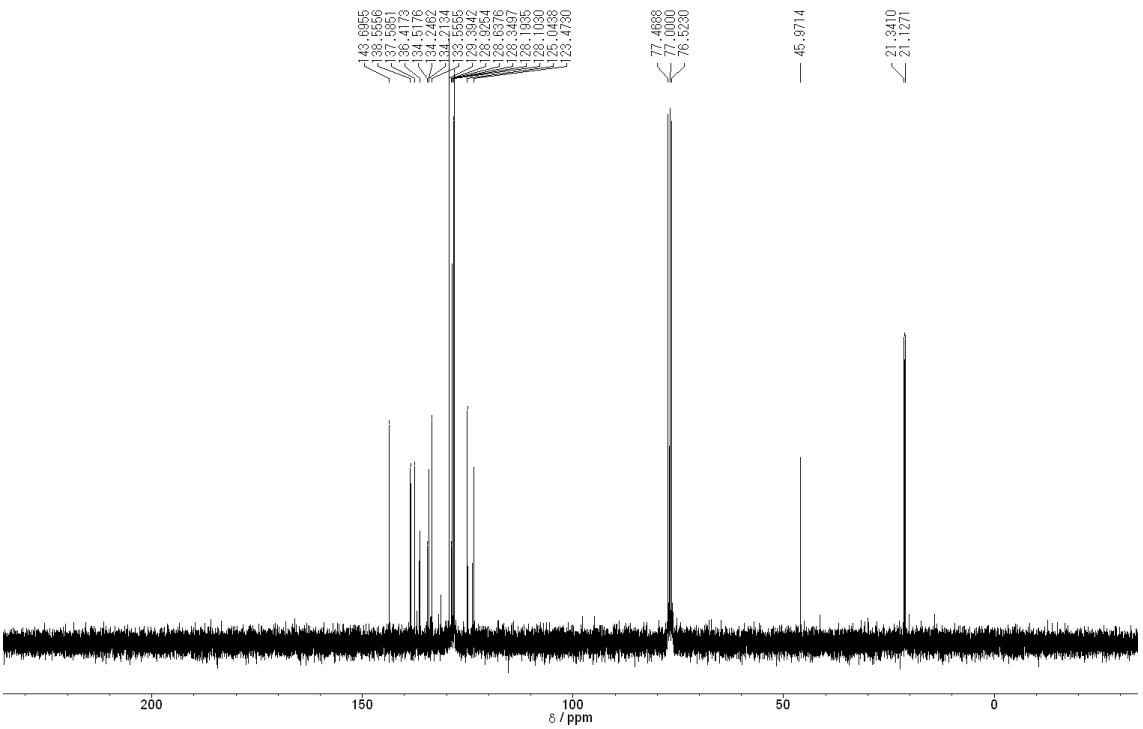
6-Bromo-4-phenyl-1-tosyl-1,2-dihydroquinoline (2c).



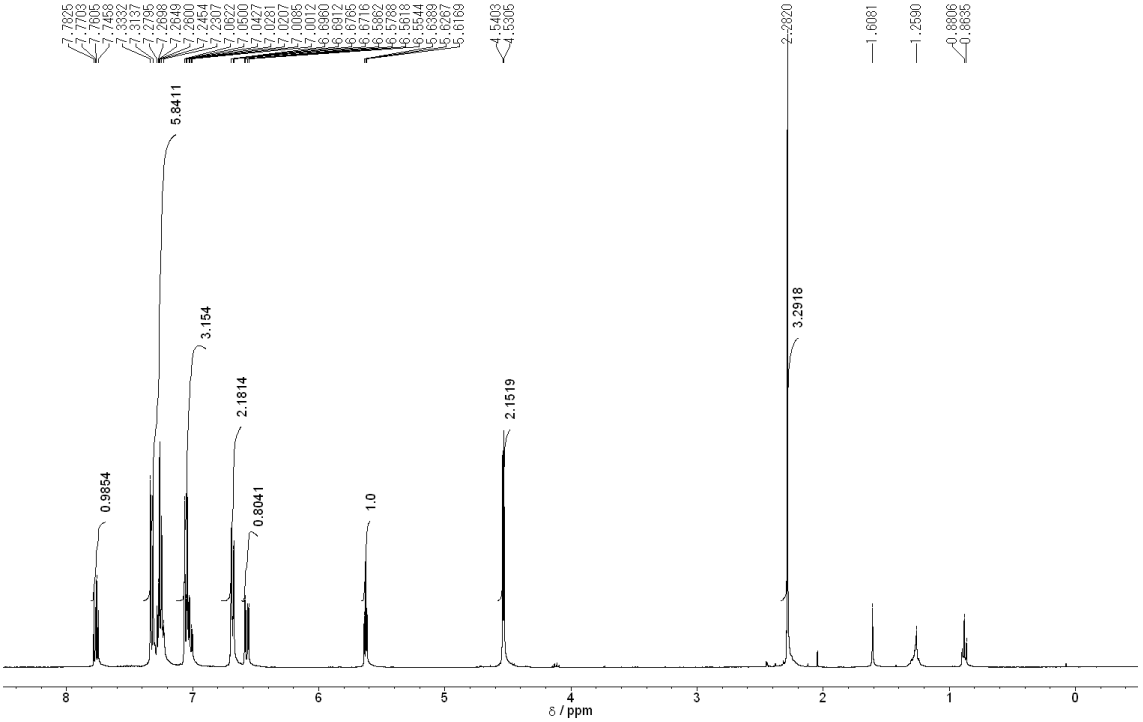


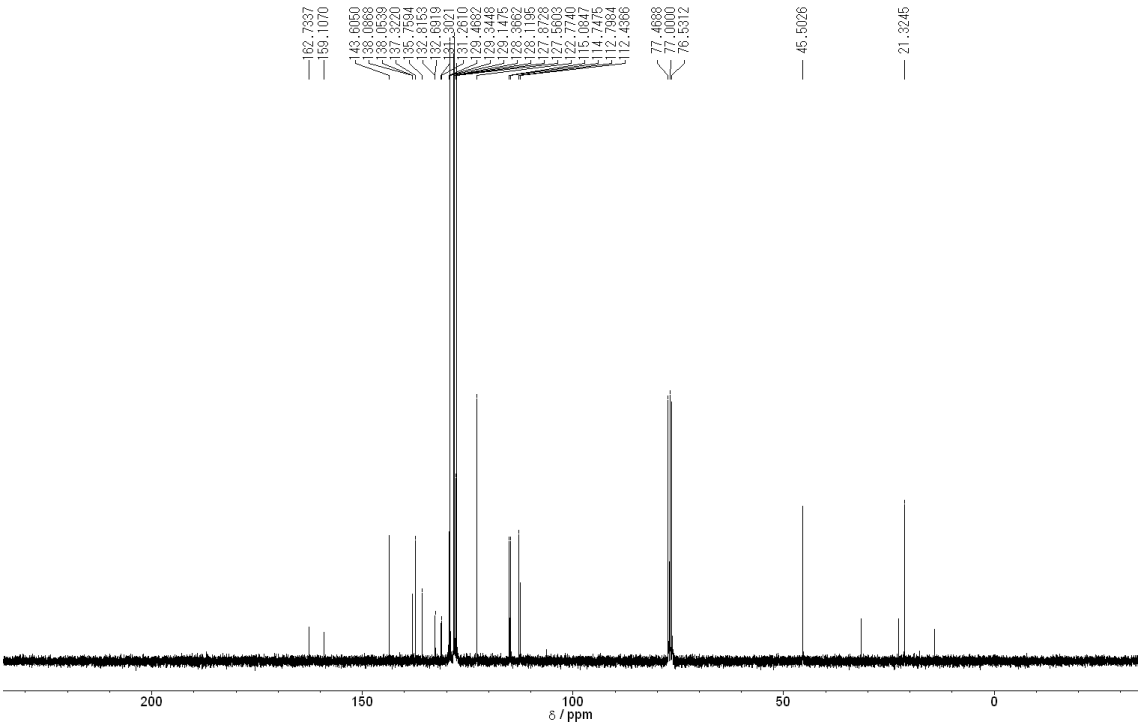
8-Bromo-1-tosyl-4-p-tolyl-1,2-dihydroquinoline (2d).



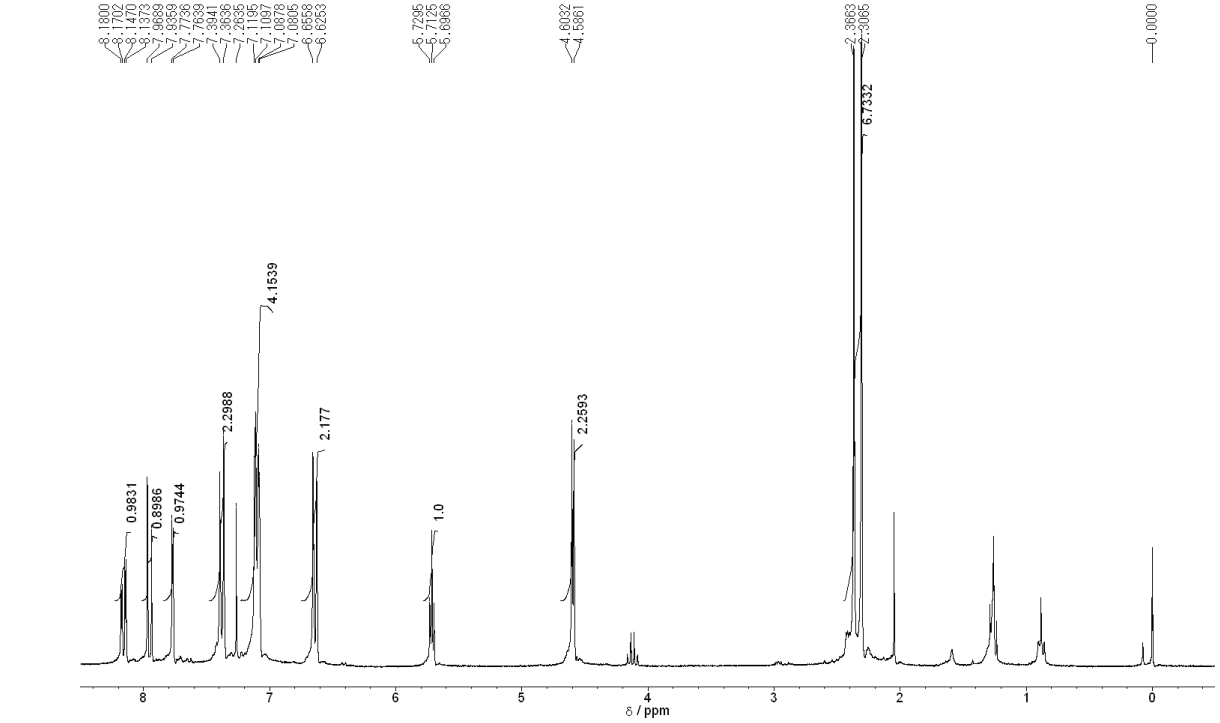


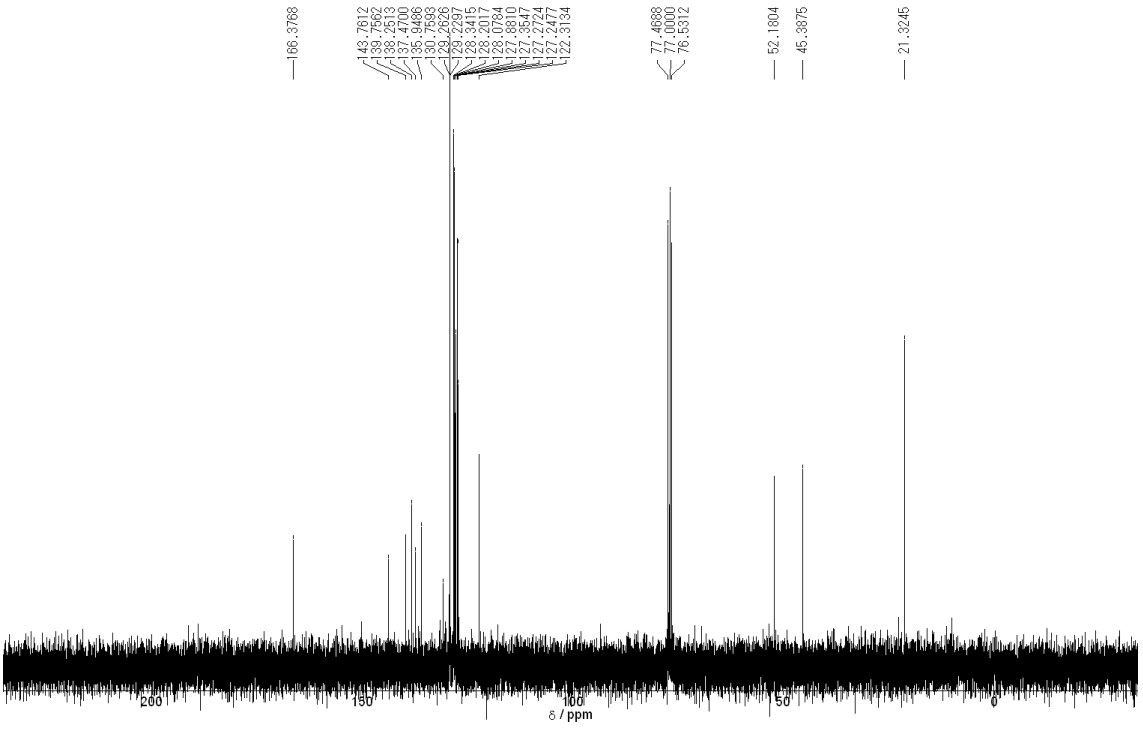
6-Fluoro-4-phenyl-1-tosyl-1,2-dihydroquinoline (2e).



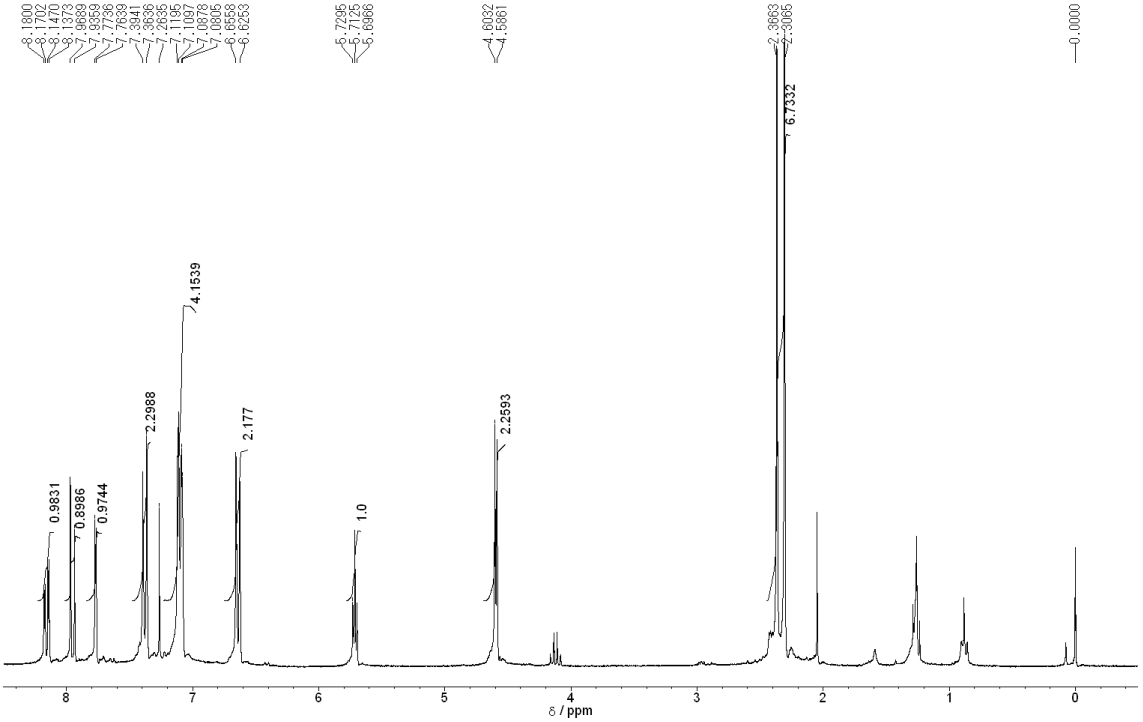


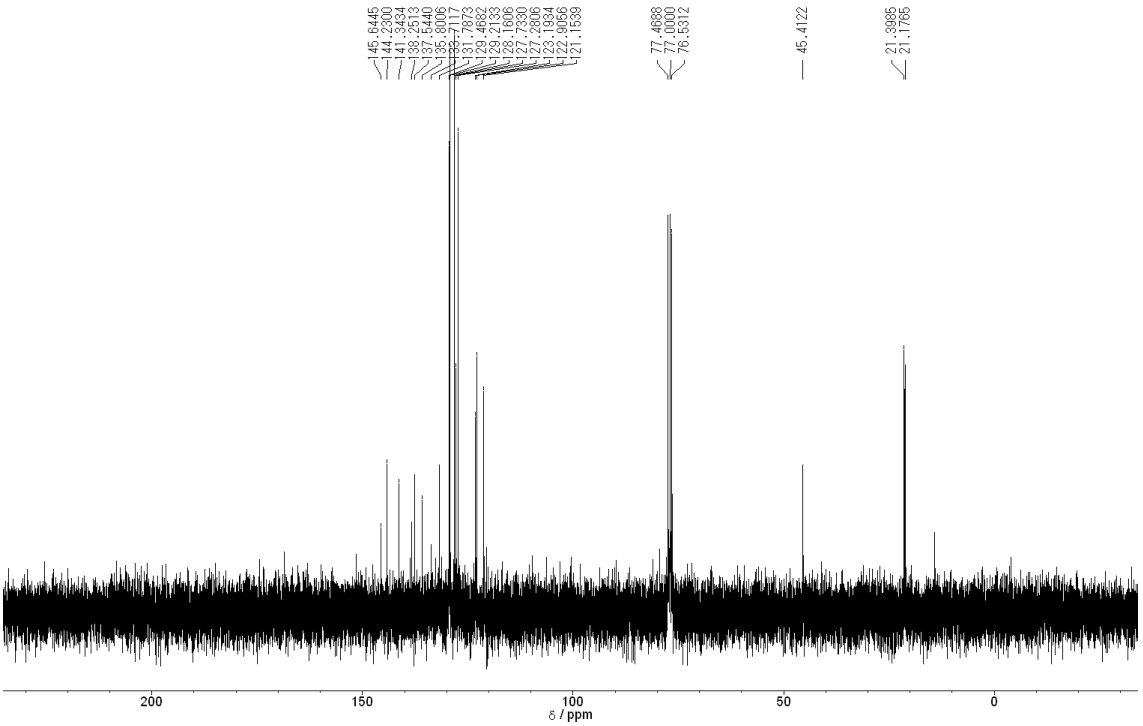
4-Phenyl-1-tosyl-1,2-dihydroquinoline-6-carboxylic acid methyl ester (2f).



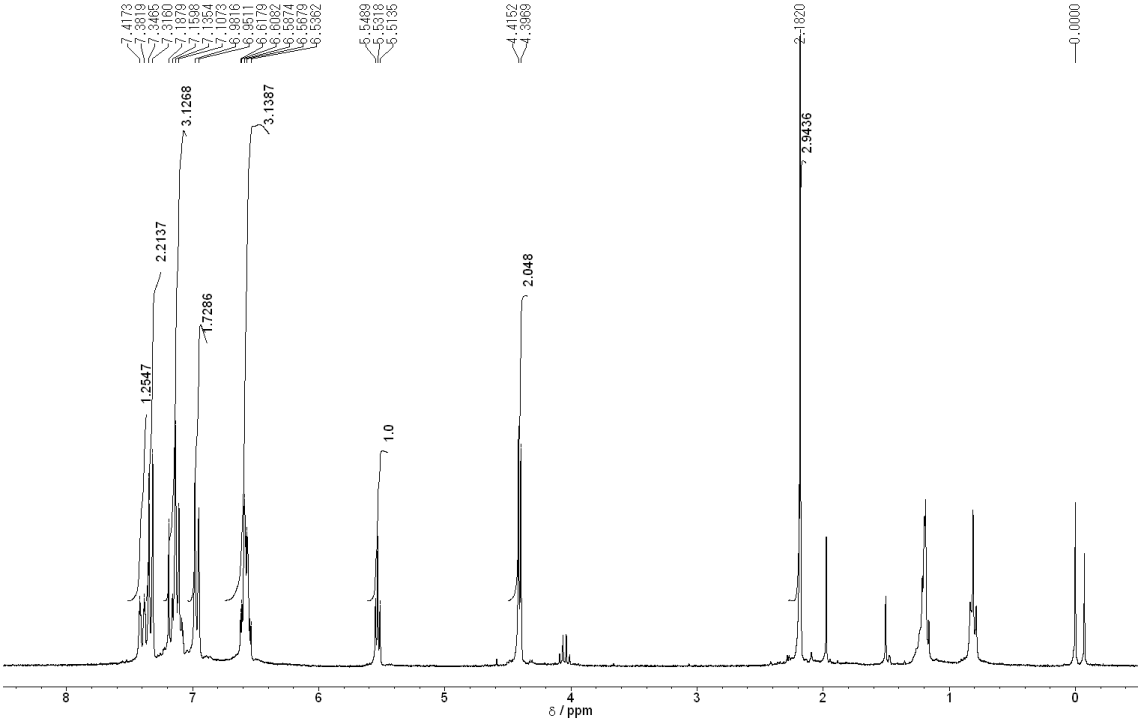


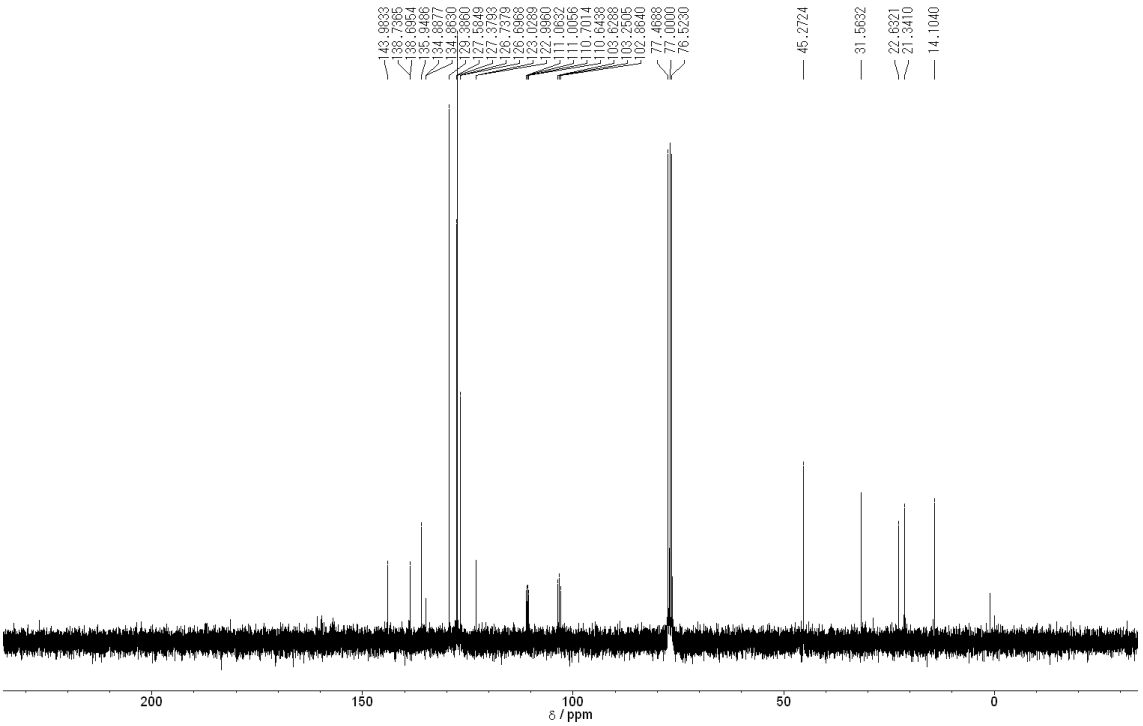
6-Nitro-1-tosyl-4-p-tolyl-1,2-dihydroquinoline (2g).



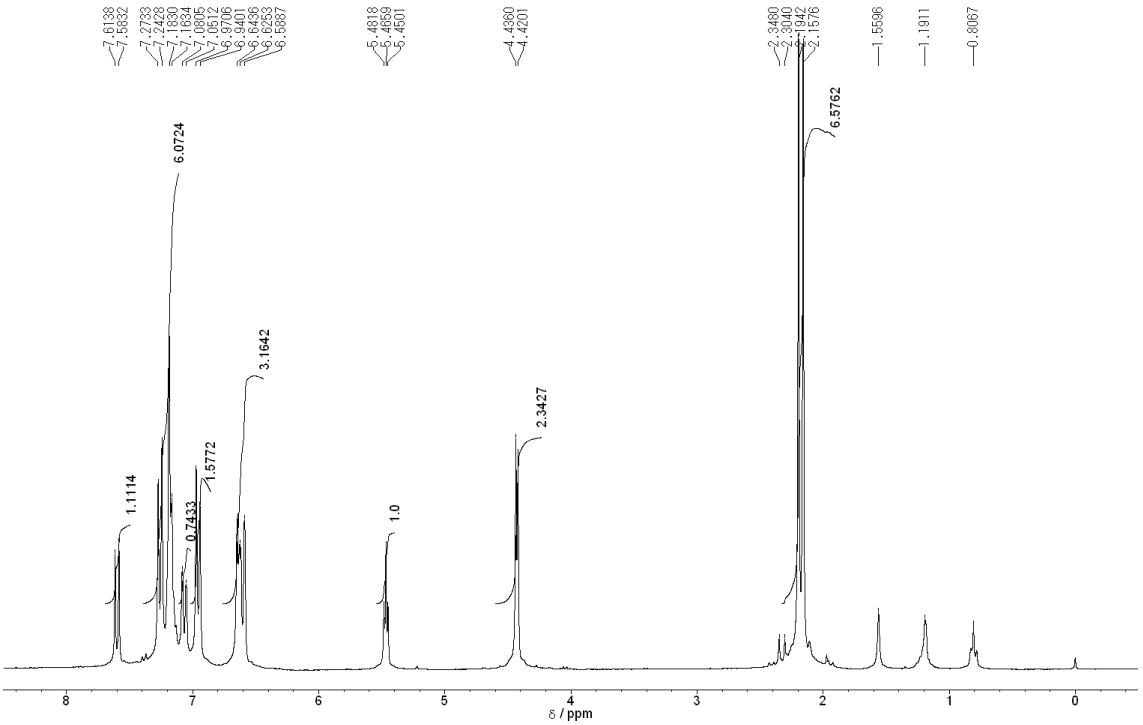


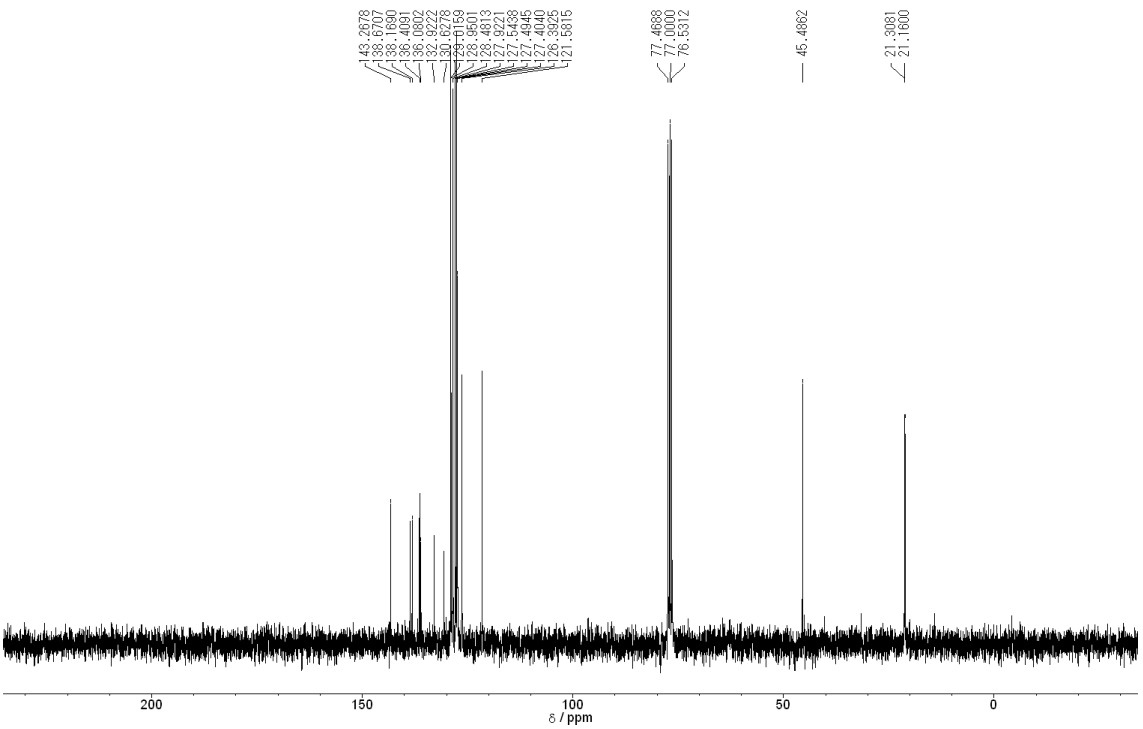
5,7-Difluoro-4-phenyl-1-tosyl-1,2-dihydroquinoline (2h).



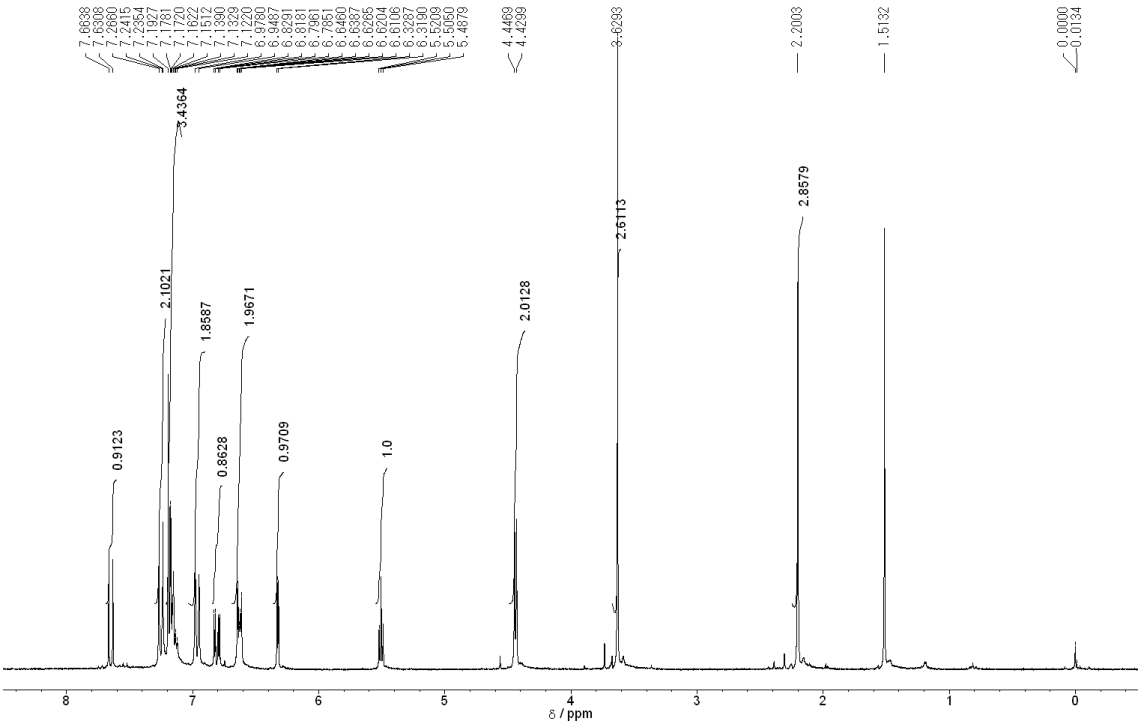


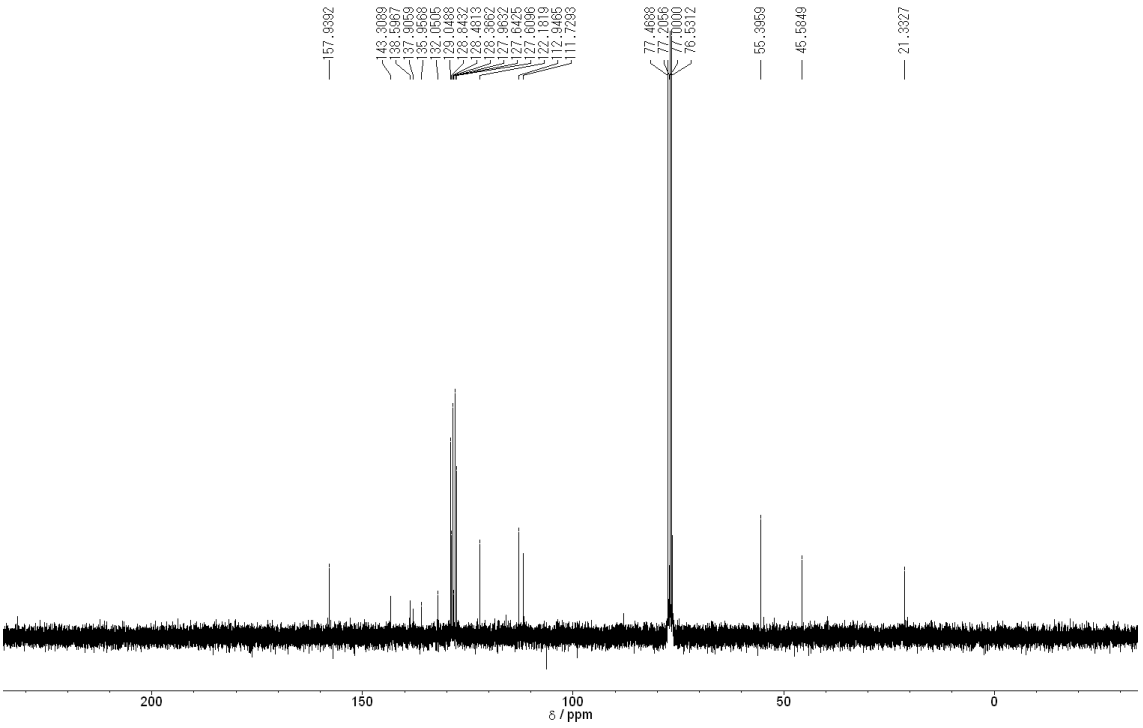
6-Methyl-4-phenyl-1-tosyl-1,2-dihydroquinoline (2i).



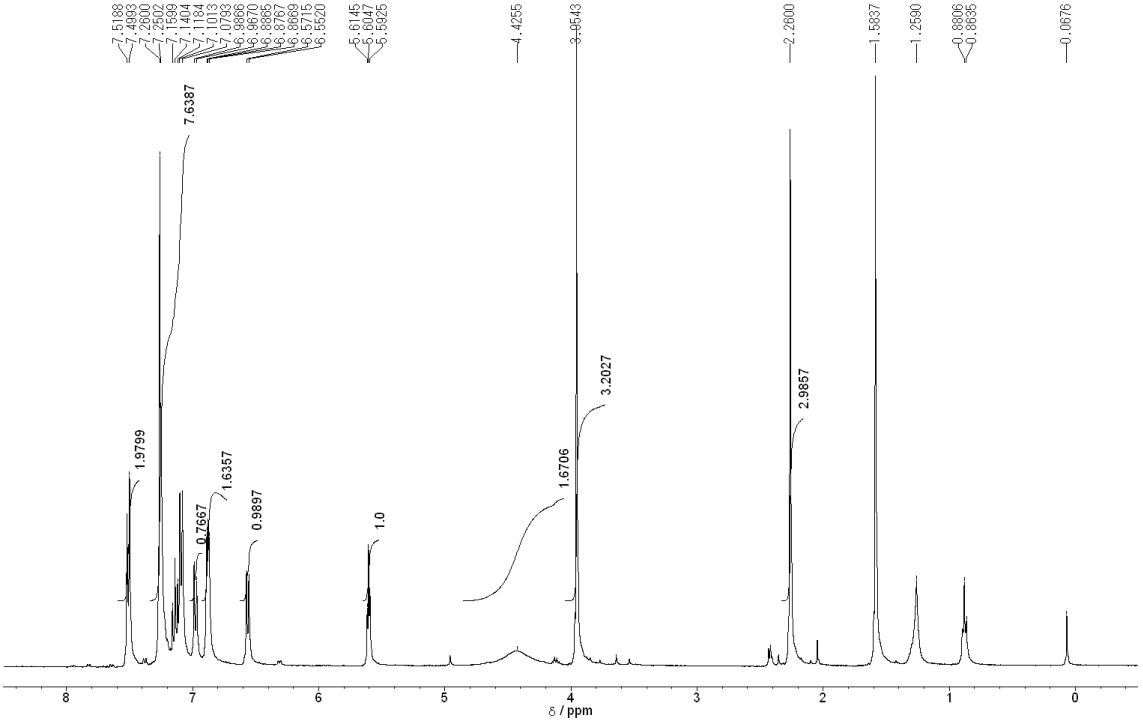


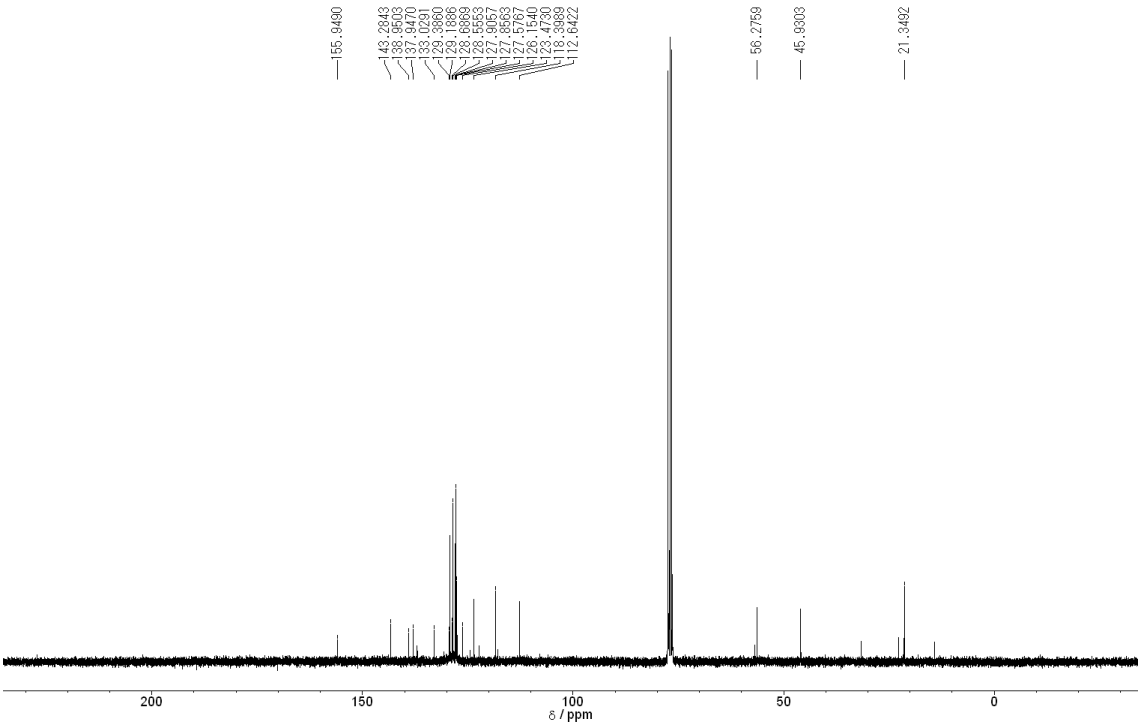
6-Methoxy-4-phenyl-1-tosyl-1,2-dihydroquinoline (2j).



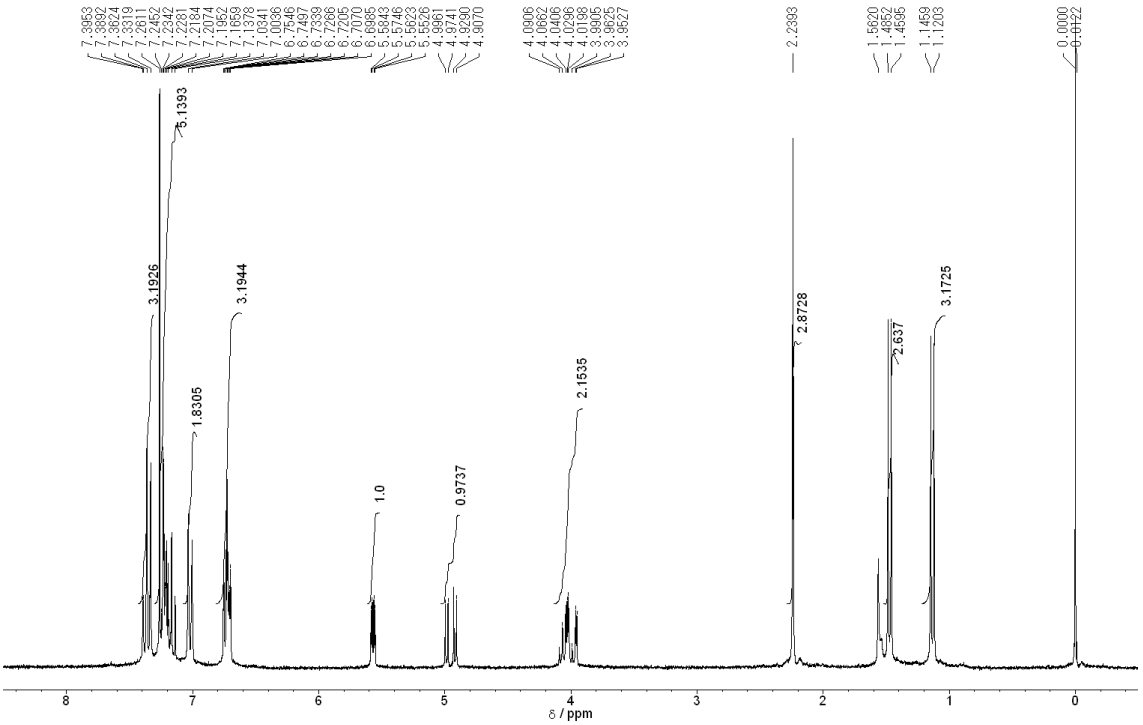


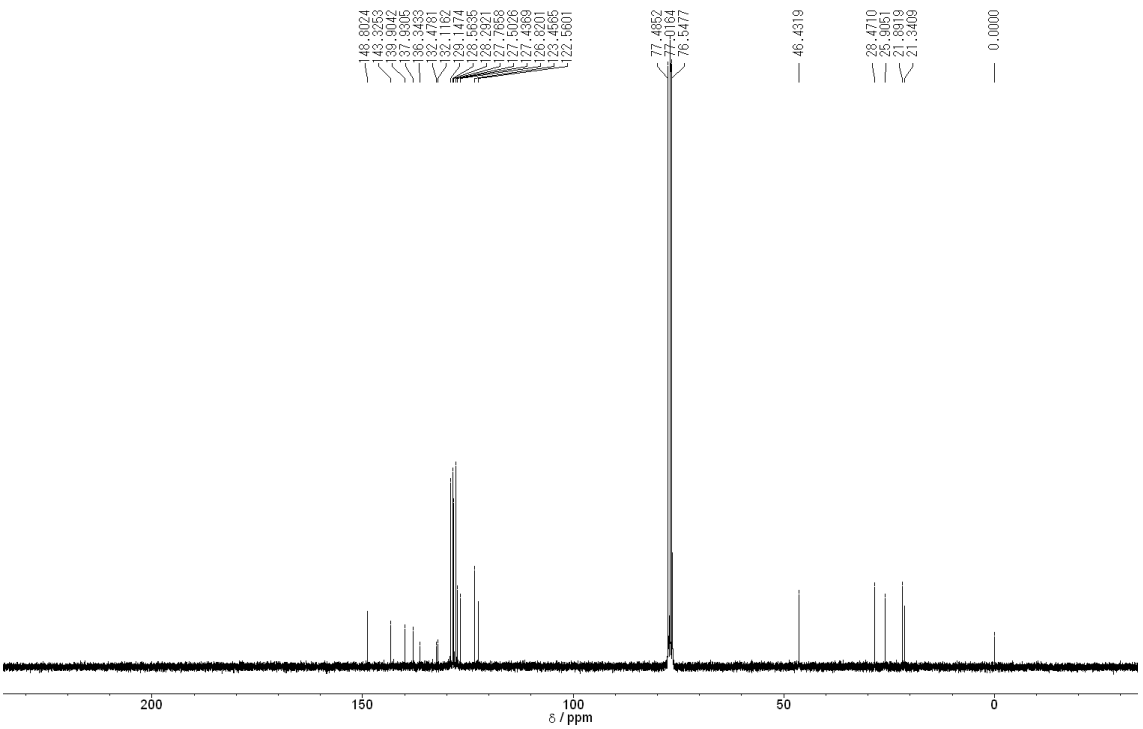
8-Methoxy-4-phenyl-1-tosyl-1,2-dihydroquinoline (2k).



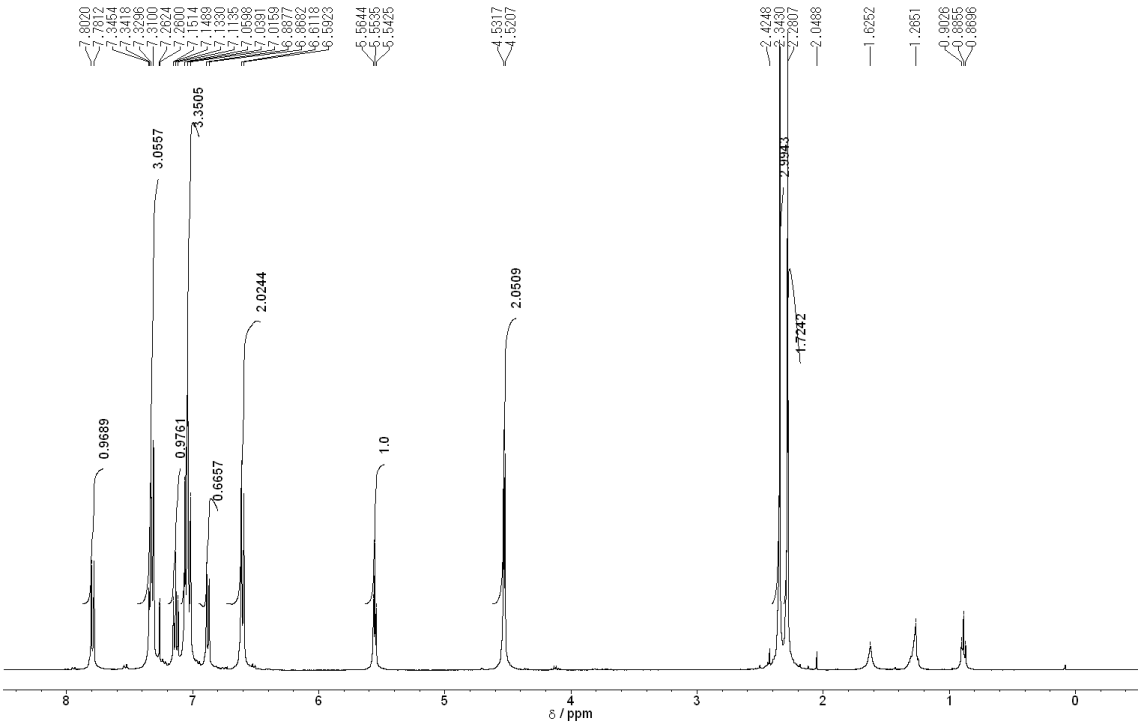


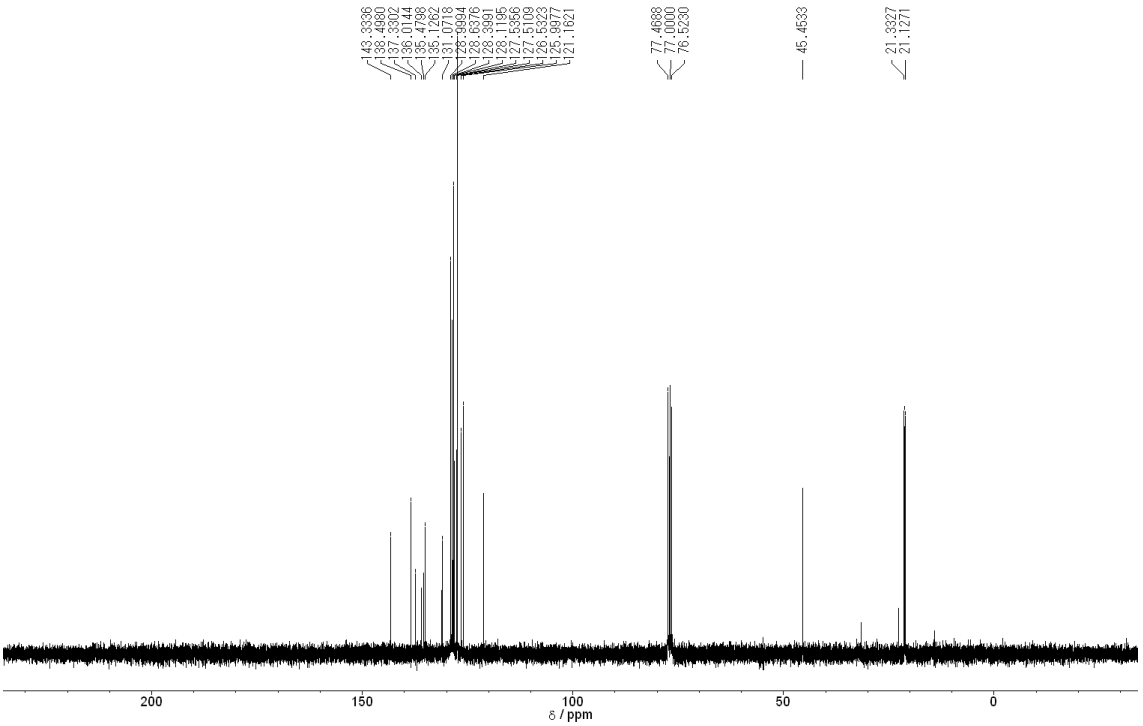
8-Isopropyl-4-phenyl-1-tosyl-1,2-dihydroquinoline (2l).



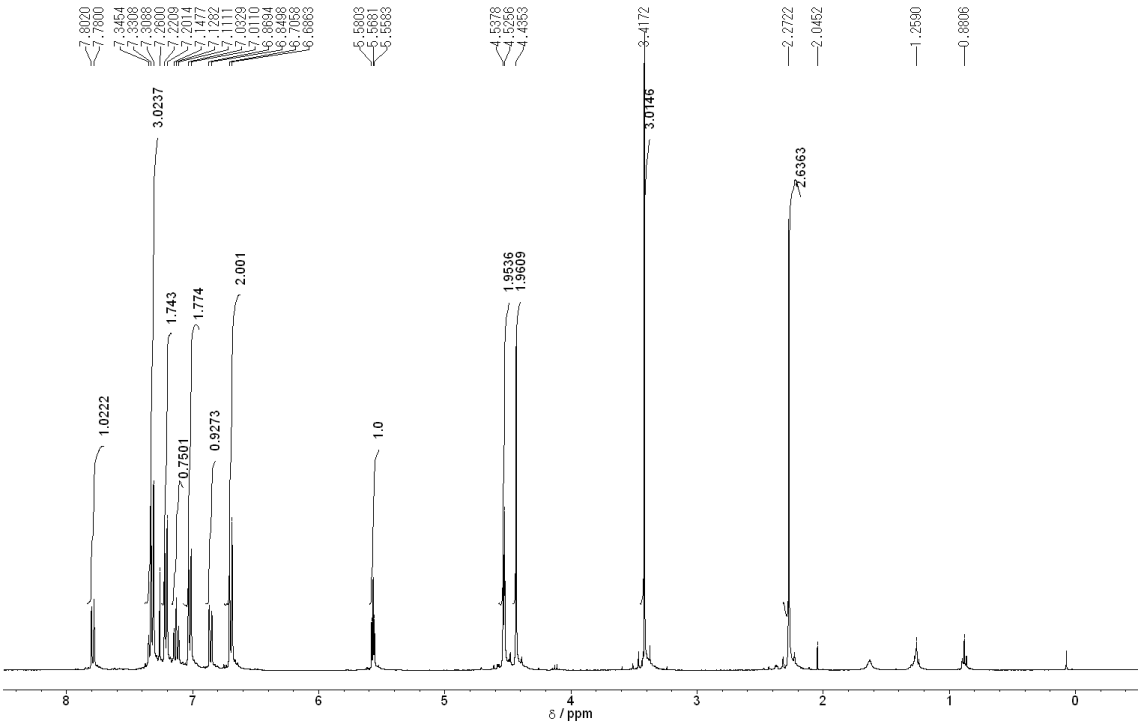


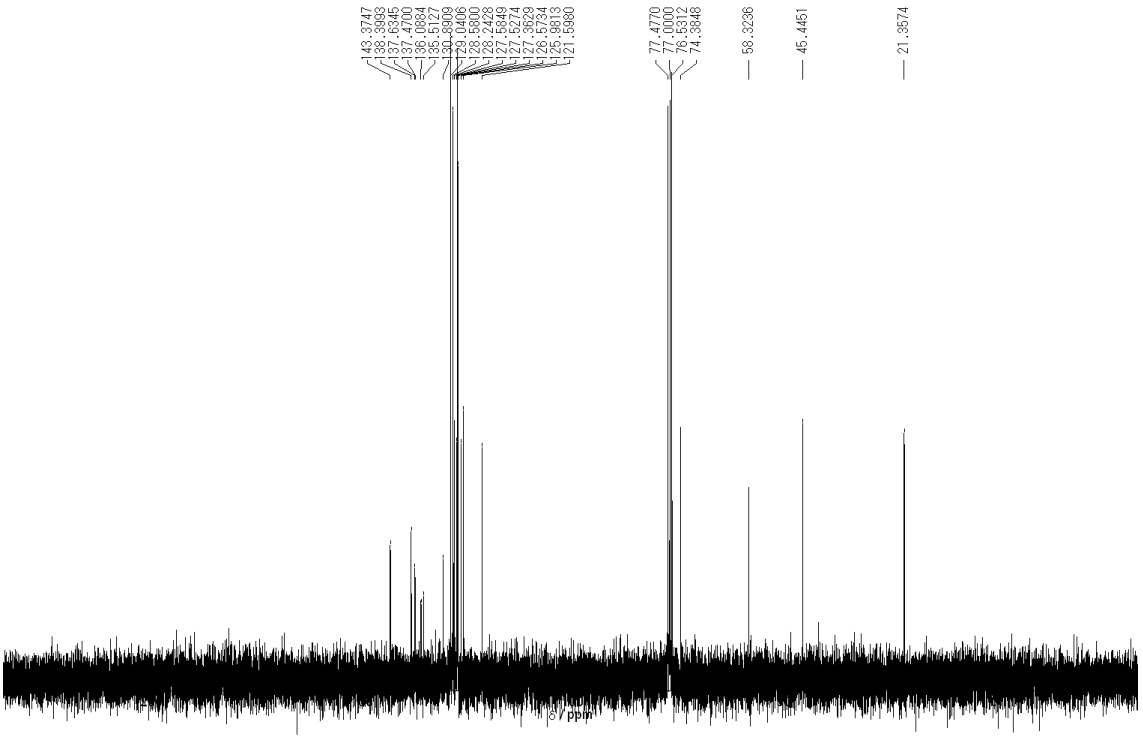
1-Tosyl-4-p-tolyl-1,2-dihydroquinoline (2s).



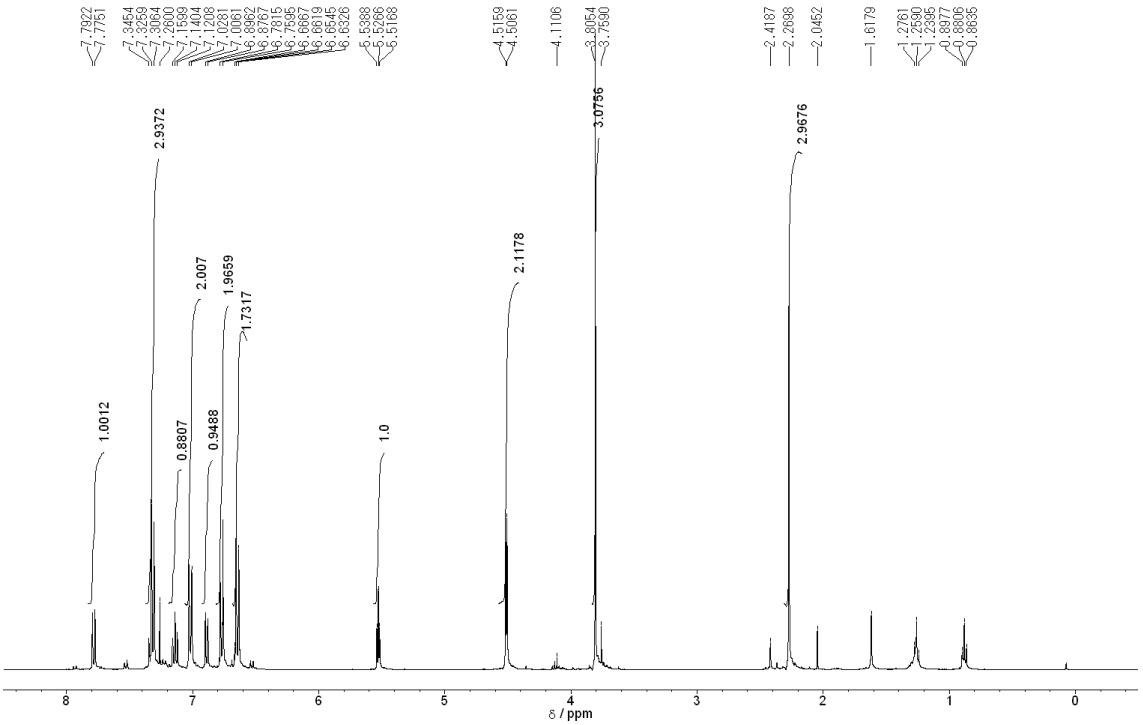


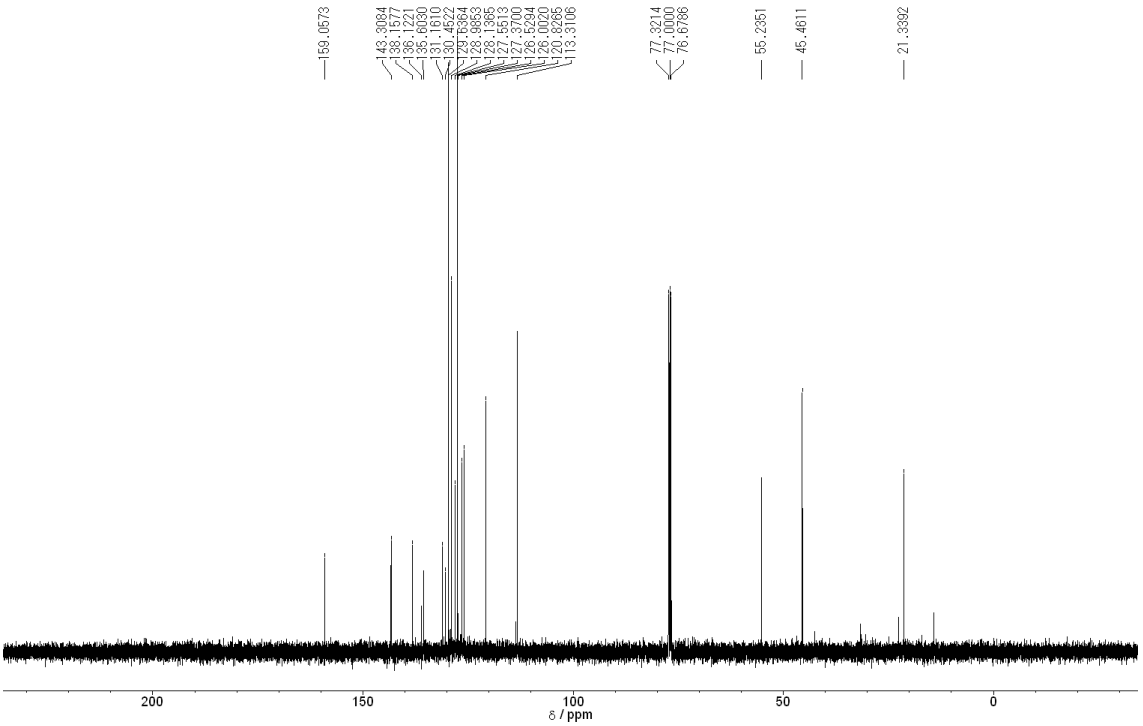
4-(4-Methoxymethylphenyl)-1-tosyl-1,2-dihydroquinoline (2t).



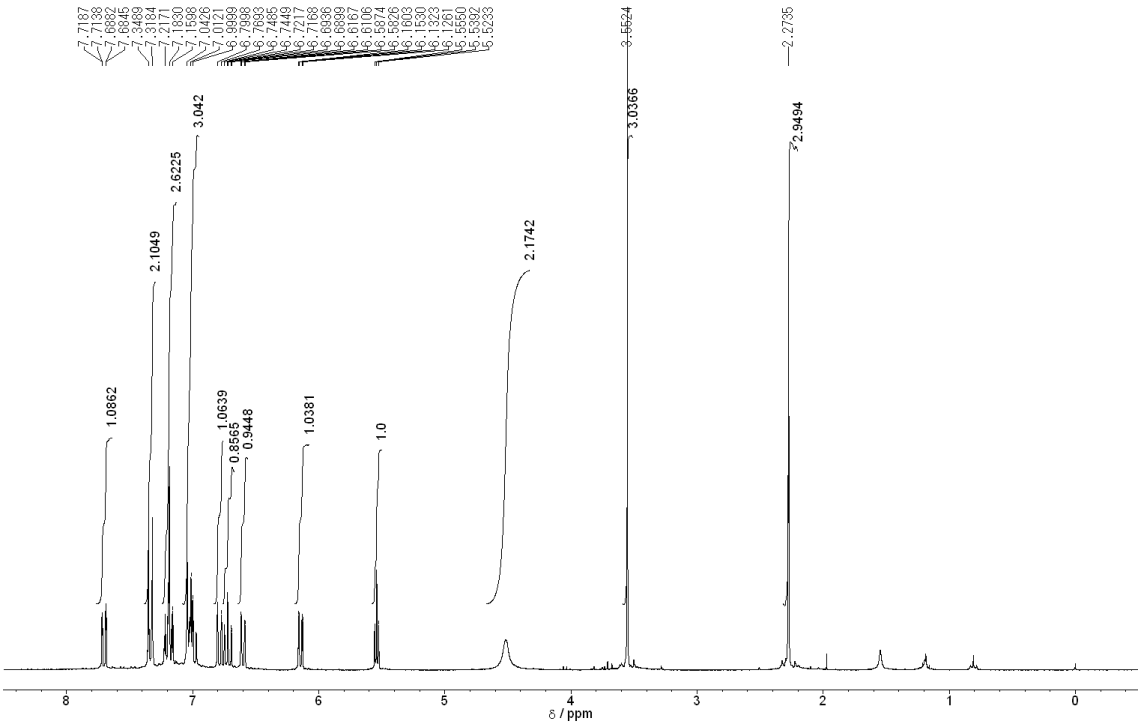


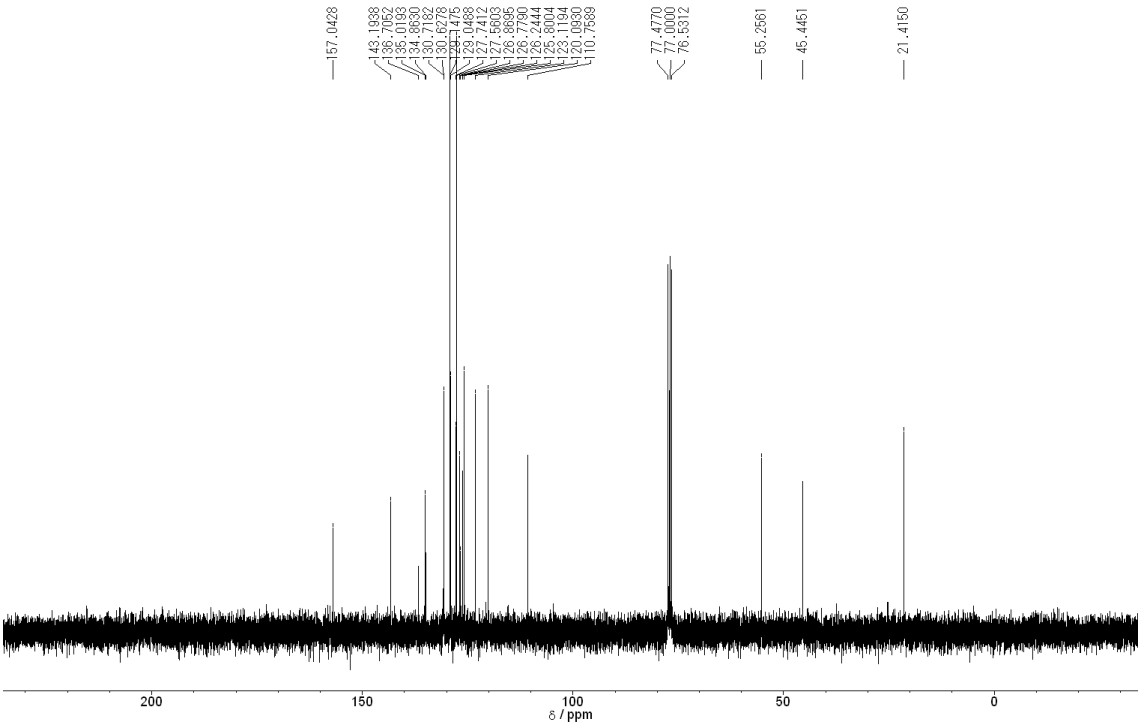
4-(4-anisyl)-1-tosyl-1,2-dihydroquinoline (2u).



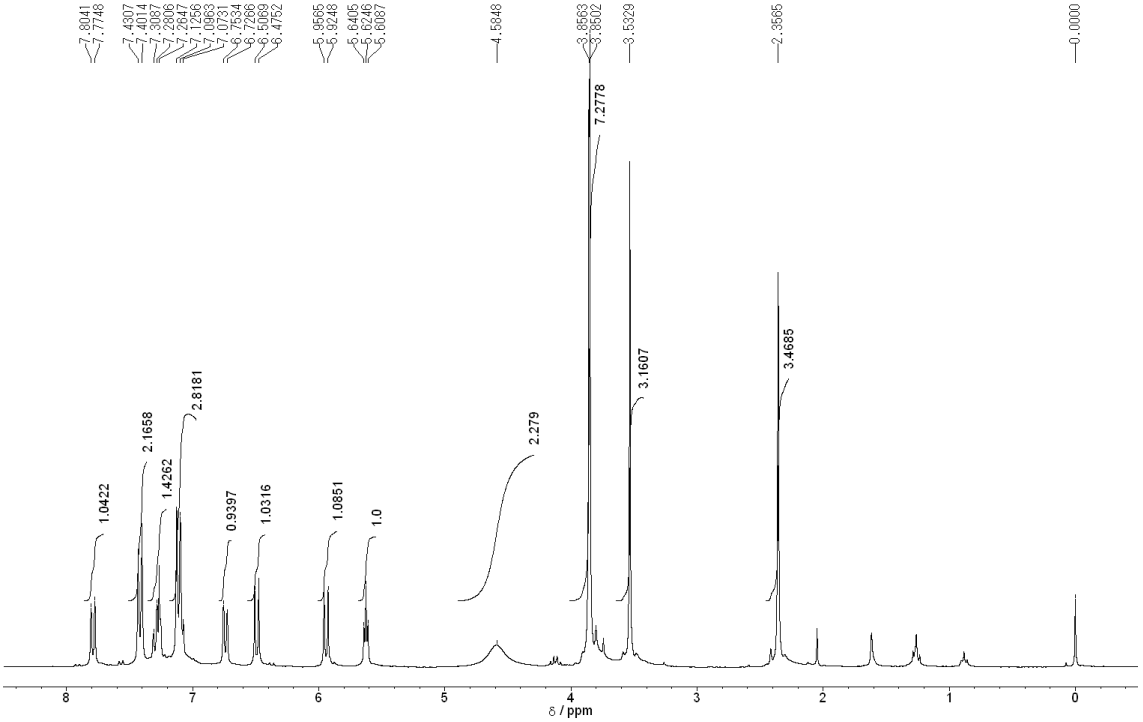


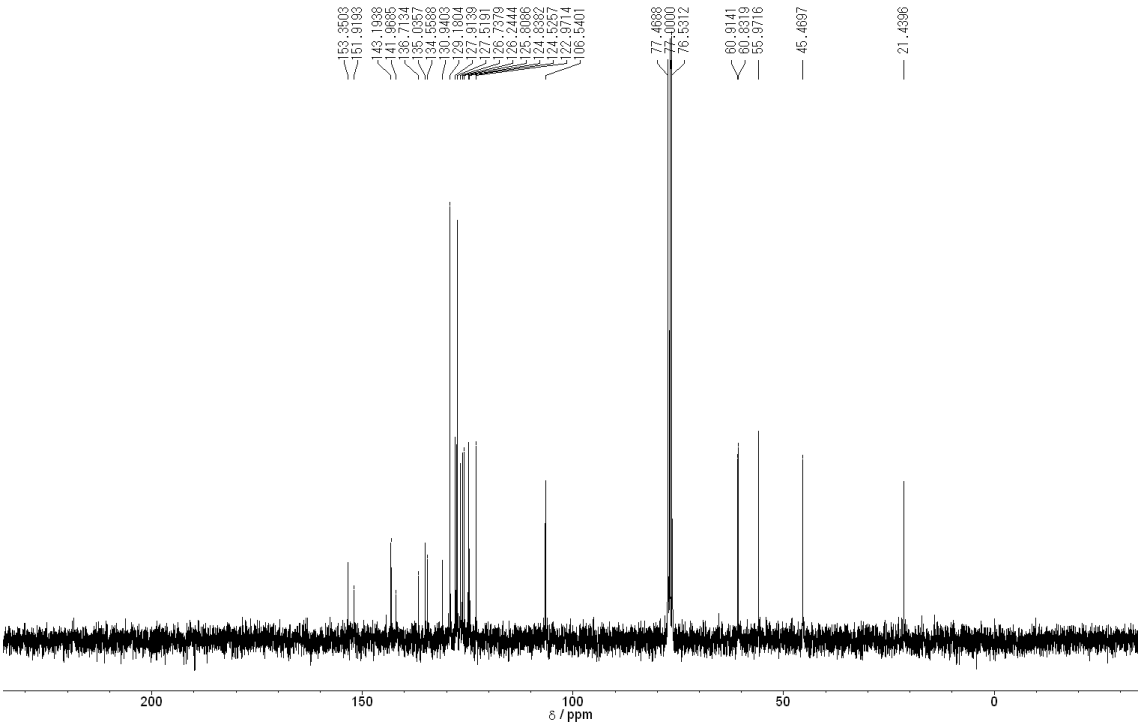
4-(2-Anisyl)-1-tosyl-1,2-dihydroquinoline (2v).



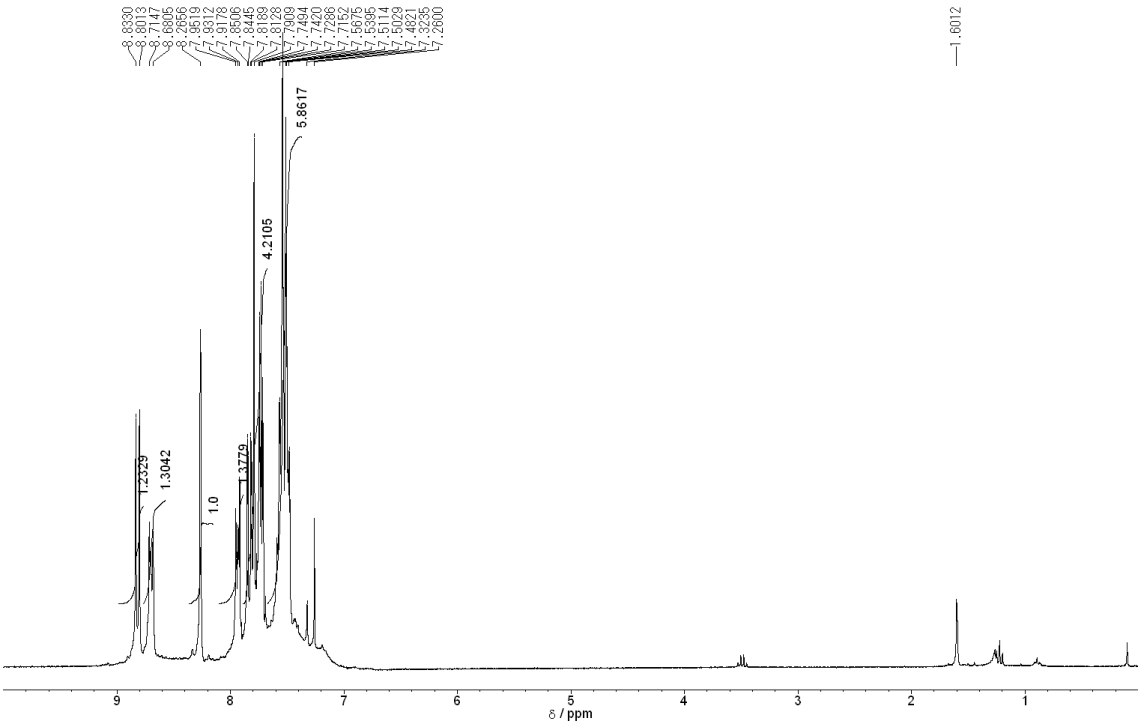


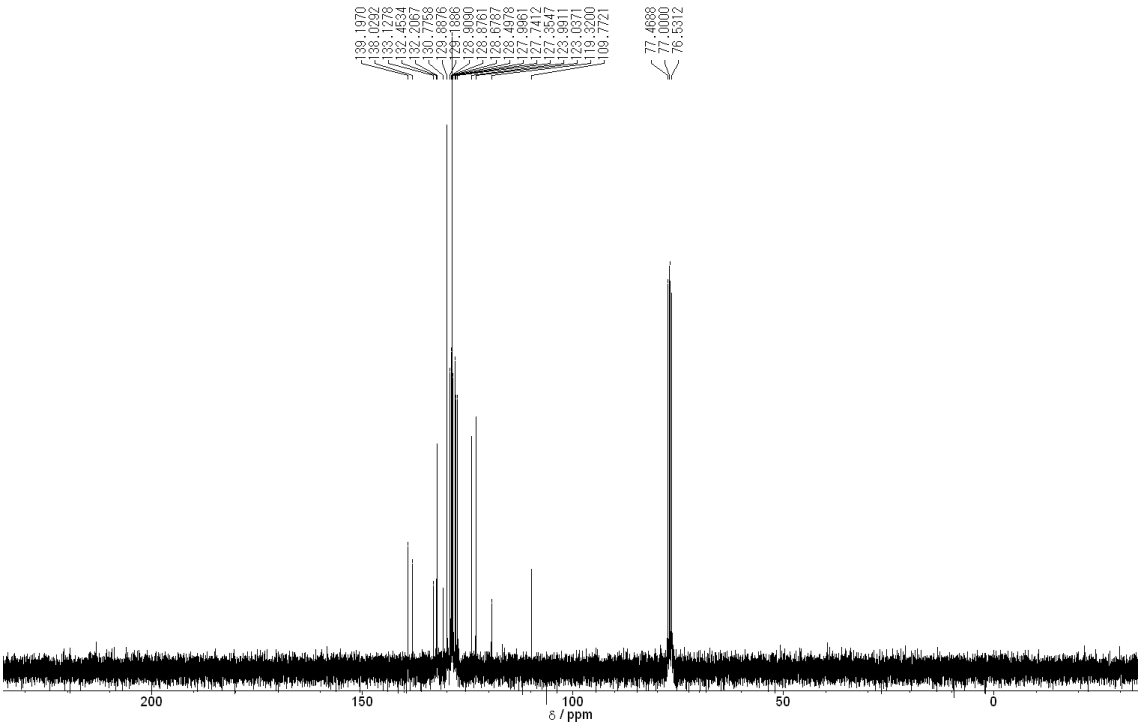
4-(2,3,4-Trimethoxyphenyl)-1-tosyl-1,2-dihydroquinoline (2w).



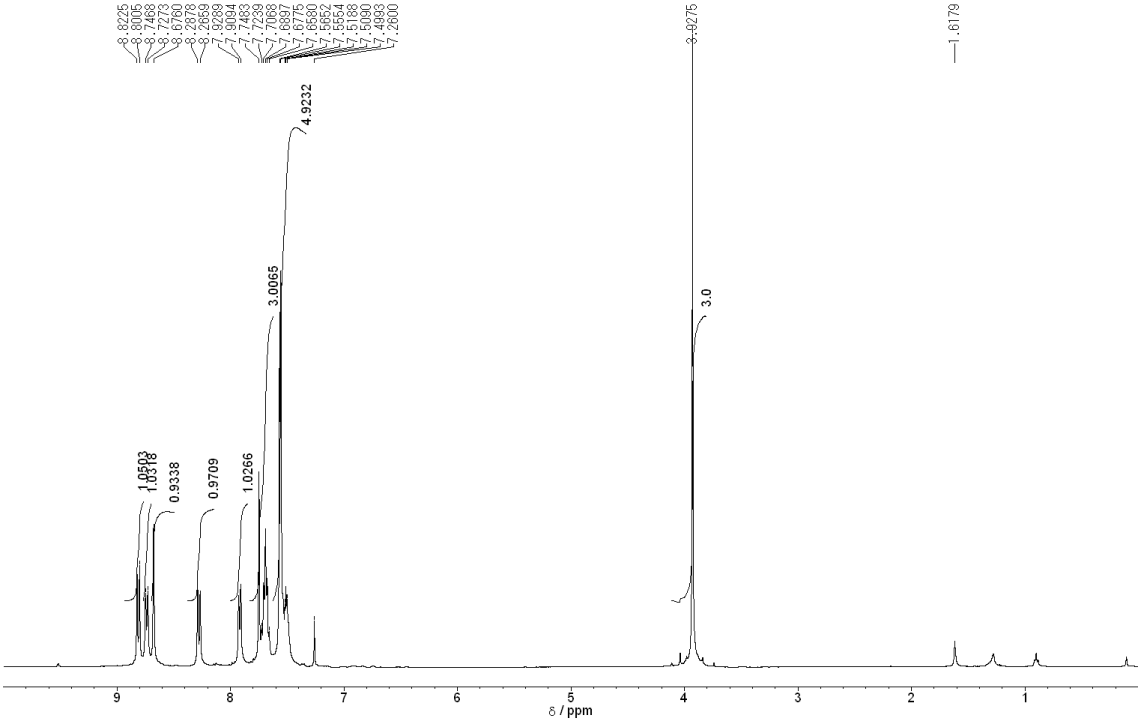


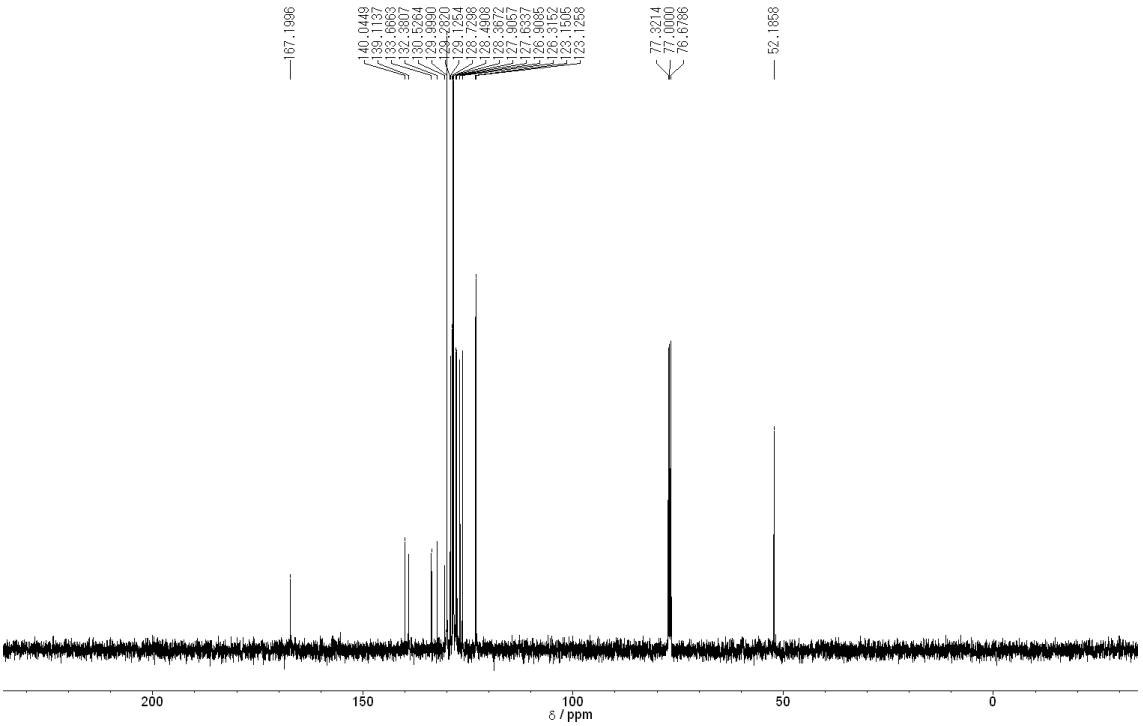
2-Cyano-10-phenylphenanthrene (4a).



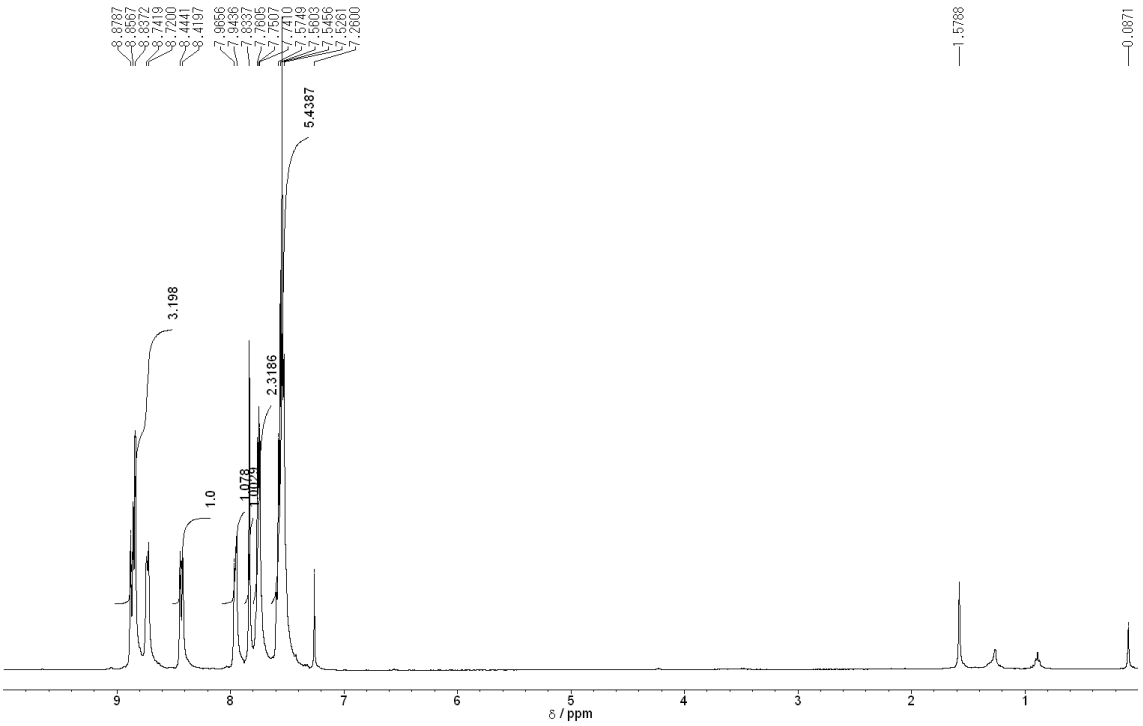


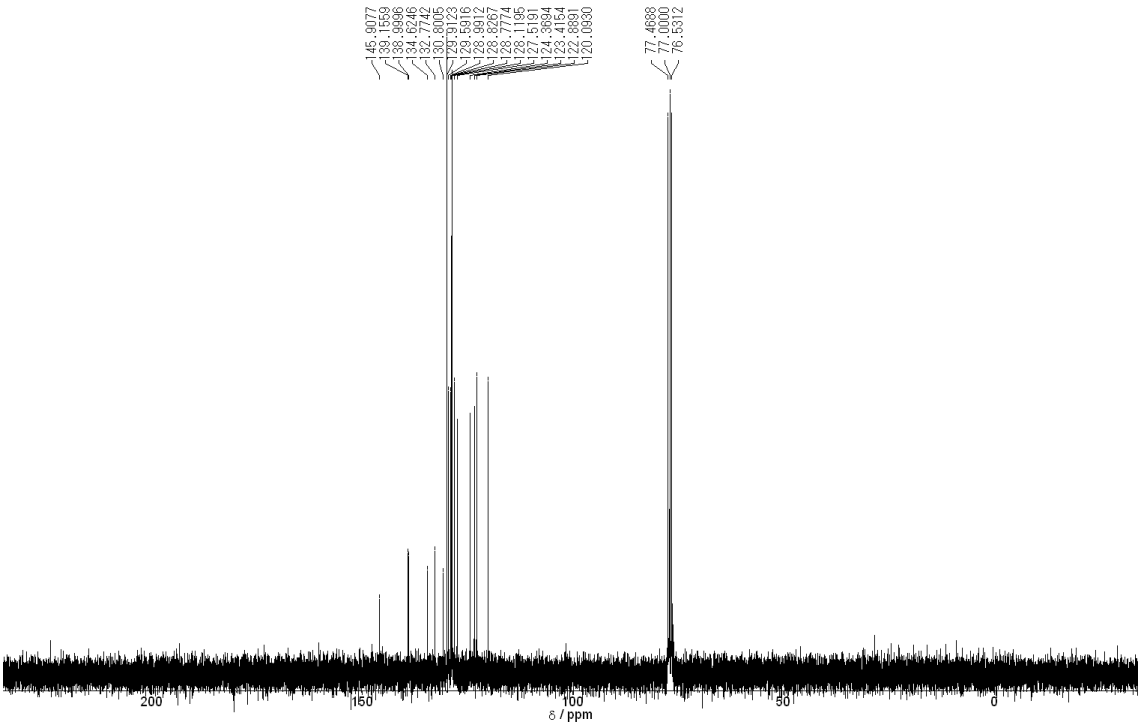
2-Methoxycarbonyl-10-phenylphenanthrene (4b).



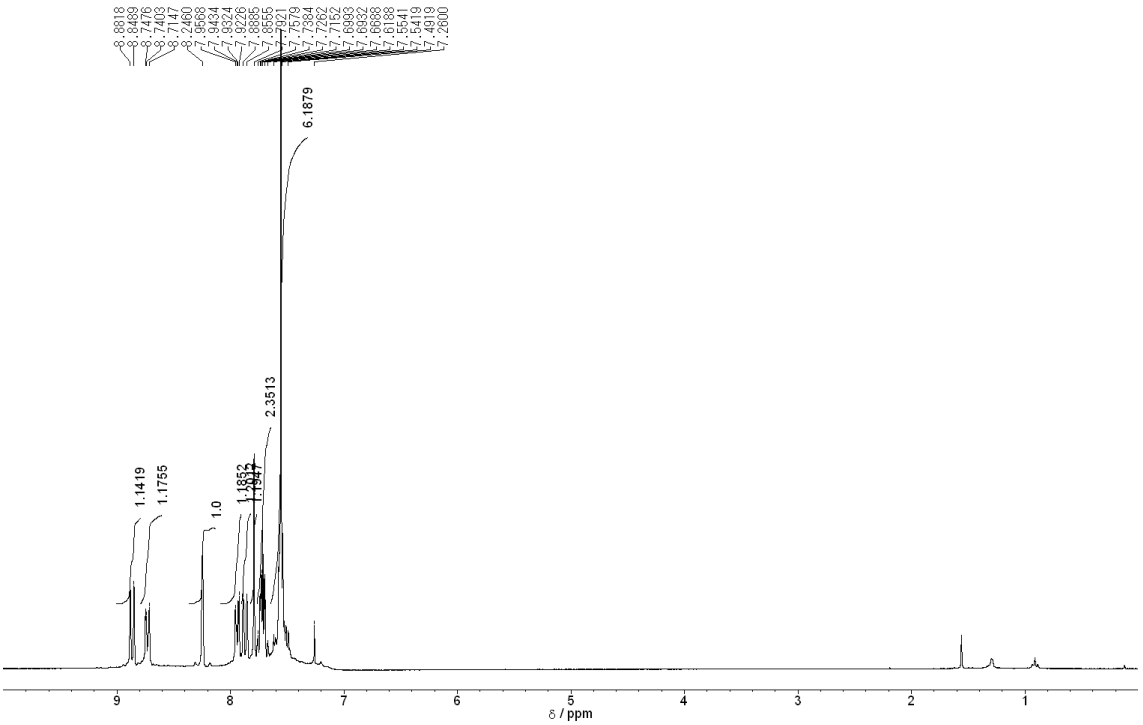


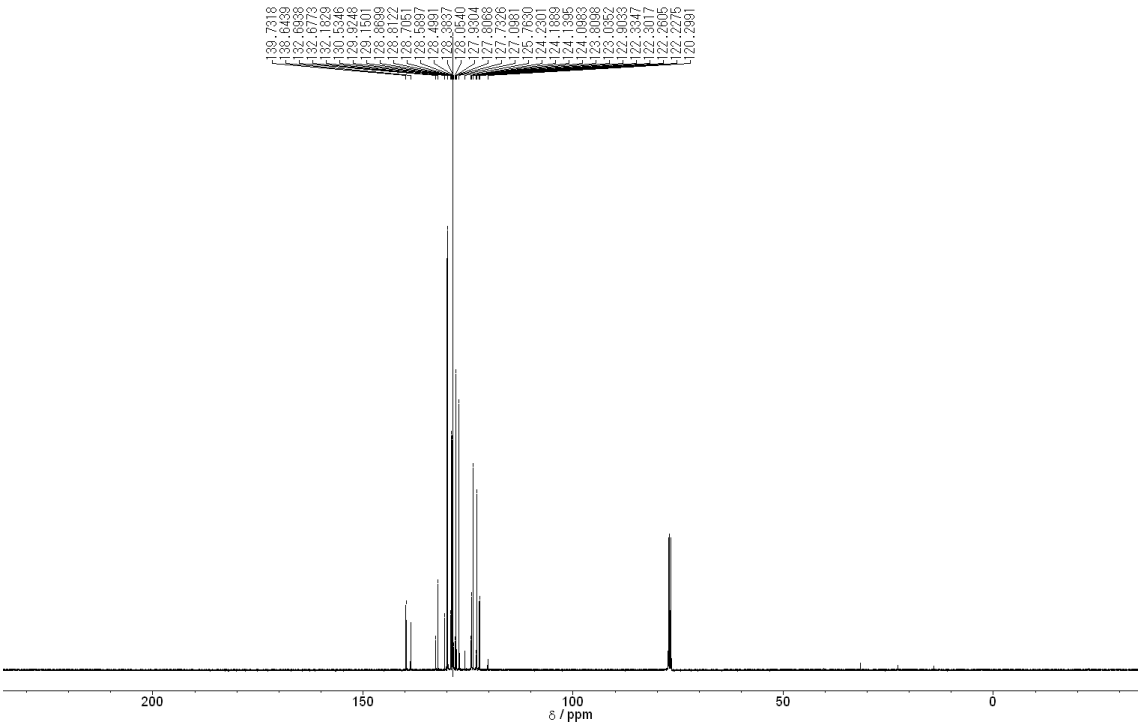
2-Nitro-10-phenylphenanthrene (4c).



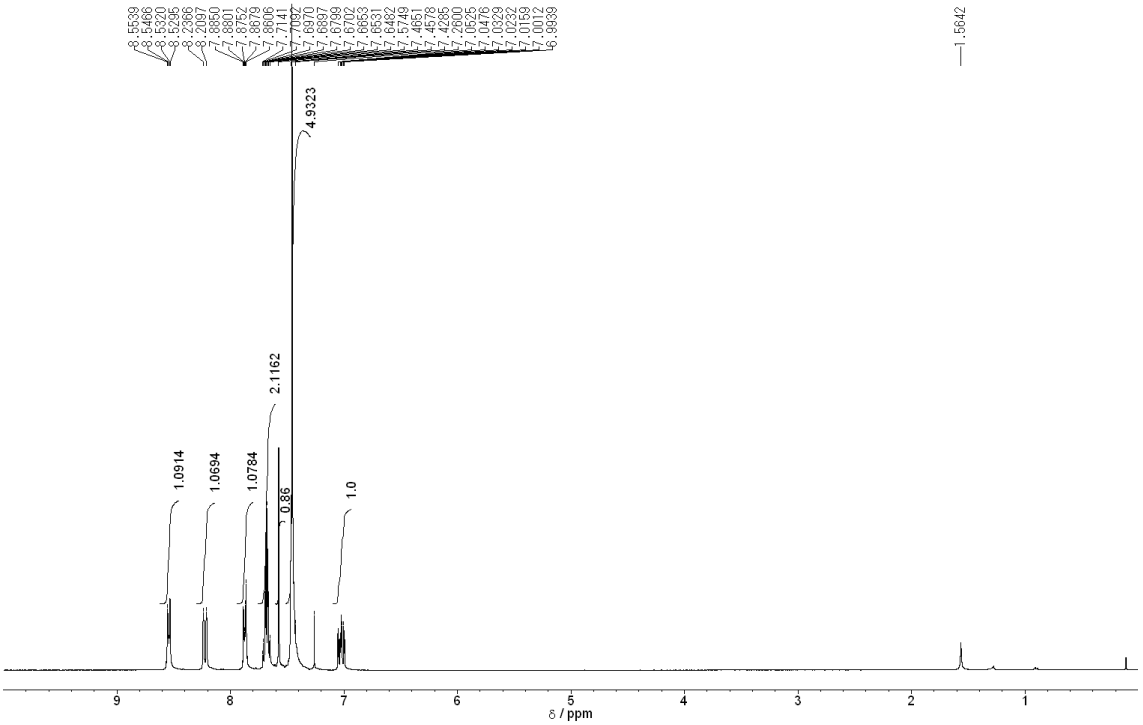


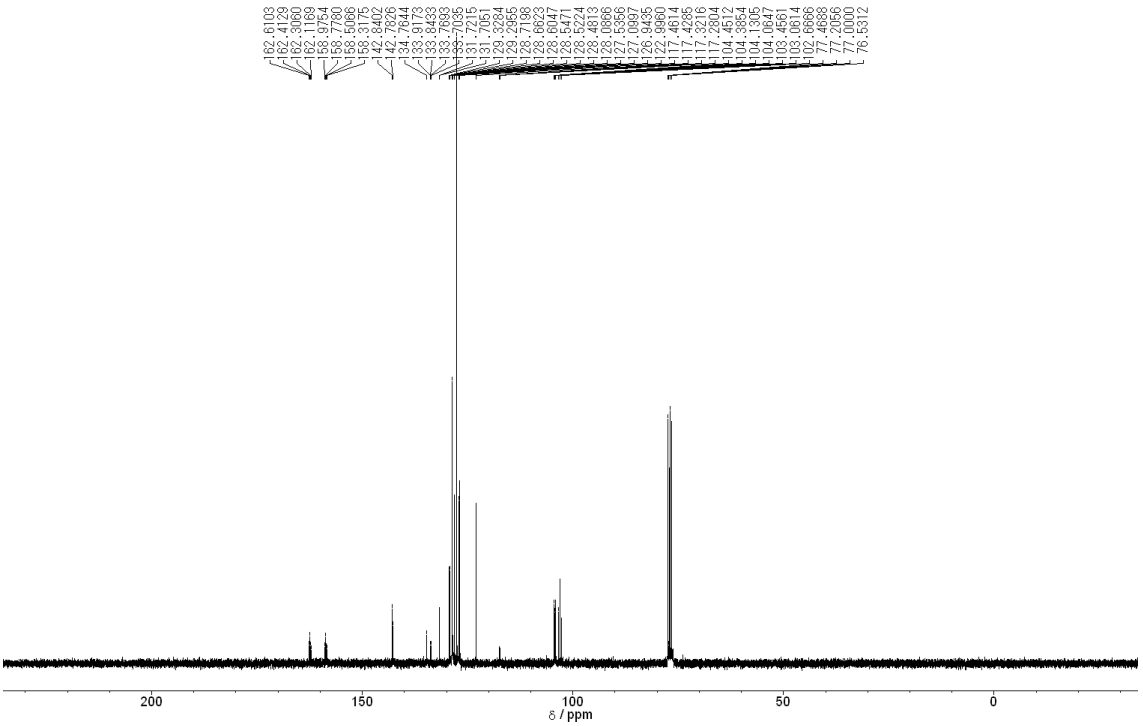
2-Trifluoromethyl-10-phenylphenanthrene (4d).





1,3-Difluoro-10-phenylphenanthrene (4e).





9-Phenylphenanthrene (4f).