Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

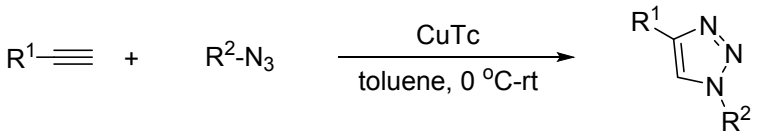
Supporting Information

Synthesis of α-cyano sulfone via thermal rearrangement of 1,4-disubstituted triazole mediated by carbene and radical species

1. General information

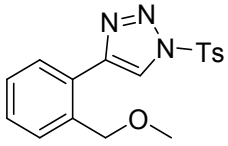
All reactions were carried out under nitrogen atmosphere with anhydrous solvents in oven-dried glassware, unless otherwise noted. Analytical thin layer chromatography (TLC) was performed using Silica Gel HSGF254 pre-coated plates. Flash column chromatography was performed using 200 - 300 Mesh Silica Gel. IR spectra were recorded using Nicolet Avatar 370 infrared spectrometer and wave number was reported in cm^{-1}. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded using Brucker Avance II DMX 400MHz spectrometer. Chemical shift (δ) is reported in parts per million (ppm) downfield relative to tetramethylsilane (TMS, 0.00 ppm) or $CDCl_3$ (7.26 ppm). Coupling constants (J) are reported in Hz. Multiplicities are reported using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; Carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra were recorded using a Brucker Avance II DMX 400 spectrometer at 100 MHz. Chemical shift is reported in ppm relative to the carbon resonance of $CDCl_3$ (77.00 ppm). High resolution mass spectra (HRMS) were obtained by Center for Instrumental Analysis of Zhejiang Sci-Tech University and a Waters TOFMS GCT Premier instrument for HRMS. The results are reported as m/e (relative ratio). Accurate masses are reported for the molecular ion (M^+) or a suitable fragment ion.

2. Synthesis of 1-sulfonyl-1,2,3-triazole



General Procedure: Dry toluene (4 mL) was added to a flask charged with copper (I) thiophene-2-carboxylate (CuTc, 38 mg, 0.2 mmol, 0.1 equiv) and the alkyne (2 mmol, 1 equiv). The reaction mixture was cooled in an ice-water bath. Subsequently, the sulfonyl azide (2.4 mmol, 1.2 equiv) was added slowly as the limiting reagent to avoid a run-away exotherm, and the reaction mixture was allowed to warm to room temperature and stirred until TLC analysis showed that alkyne was completely consumed. The reaction mixture filtered through a short plug of silica gel. The filtrate was concentrated and then purified by flash chromatography to give the corresponding product.

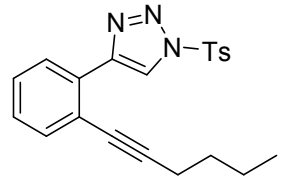
1b, **1e**, **1f**, **1h**, **1i**, **1u**, **1w**, **1j**, **1s**, **1z**, **1ac**, **1ae** and **1ad** were reported in ref. 1; **1c**, **1r**, **1z** and **1aa** were reported in ref. 2; **1a**, **1d**, **1g**, **1j**, **1v** and **1w** were reported in ref 3; **1l**, **1m**, **1n**, **1p**, **1q** **1x** and **1y** were reported in ref. 4.



1k

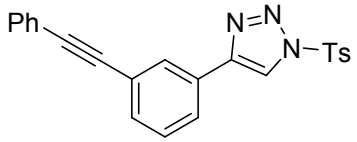
4-(2-(methoxymethyl)phenyl)-1-tosyl-1H-1,2,3-triazole: white solid, m.p: 190.7 ℃, 515.1 mg, yield: 75%; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.51 (s, 1H), 8.11 – 8.07 (m, 2H), 7.94 – 7.89 (m, 1H), 7.51 (s, 1H), 7.45 (m, 4H), 4.49 (s, 2H), 3.46 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ

147.31, 145.54, 135.02, 133.24, 130.50, 130.47, 129.41, 128.89, 128.73, 128.58, 122.01, 73.15, 57.71, 21.85. HRMS (ESI) m/z calcd for $C_{17}H_{18}N_3O_3S$ $[M + H]^+$ 344.1063, found 344.1071.



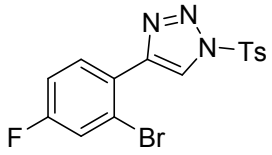
1p

4-(2-(hex-1-yn-1-yl)phenyl)-1-tosyl-1H-1,2,3-triazole: white solid, m.p: 191.7 ℃, 622.4 mg, yield: 82%; ^{1}H NMR (400 MHz, Chloroform-d) δ 9.02 (s, 1H), 8.24 (d, *J* = 7.9 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.42 (m, *J* = 11.5, 7.5 Hz, 3H), 7.34 (d, *J* = 7.5 Hz, 1H), 2.58 (t, *J* = 7.2 Hz, 2H), 2.49 (s, 3H), 1.74 (p, *J* = 7.2 Hz, 2H), 1.57 (m, *J* = 15.0, 7.4 Hz, 2H), 1.05 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 147.23, 145.34, 133.51, 130.43, 129.92, 128.66, 128.36, 128.14, 127.56, 121.65, 121.05, 96.29, 80.29, 30.58, 22.26, 21.84, 19.46, 13.65. HRMS (ESI) m/z calcd for $C_{21}H_{22}N_3O_2S$ $[M + H]^+$ 380.1427, found 380.1432.



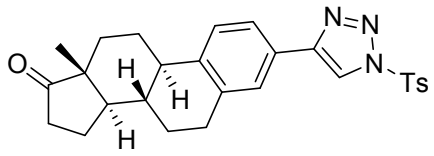
1t

4-(3-(phenylethynyl)phenyl)-1-tosyl-1H-1,2,3-triazole: white solid, m.p: 179.7 ℃, 559.3 mg, yield: 70%; 1H NMR (400 MHz, Chloroform-d) δ 8.39 (s, 1H), 8.10 (d, 2H), 8.04 (s, 1H), 7.88 (d, 1H), 7.59 (m, 3H), 7.46 (m, 2H), 7.44 (s, 1H), 7.40 (m, 2H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 147.45, 146.65, 133.06, 132.06, 131.67, 130.52, 129.19, 129.15, 129.10, 128.74, 128.51, 128.41, 125.81, 124.19, 122.97, 119.25, 90.22, 88.65, 21.85. HRMS (ESI) m/z calcd for $C_{23}H_{18}N_3O_2S$ $[M + H]^+$ 400.1114, found 400.1127.



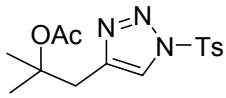
1ab

4-(2-bromo-4-fluorophenyl)-1-tosyl-1H-1,2,3-triazole: white solid, m.p: 154.5 ℃, 158.5 mg, yield: 20%; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.79 (s, 1H), 8.14 – 8.10 (m, 1H), 8.09 (d, *J* = 8.3 Hz, 2H), 7.45 (m, *J* = 8.2 Hz, 3H), 7.21 – 7.15 (m, 1H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 162.26 (d, *J* = 254.0 Hz), 147.50, 144.11, 133.02, 132.02 (d, *J* = 8.6 Hz), 130.53, 128.79, 126.15, 122.01, 121.58 (d, *J* = 9.6 Hz), 120.91 (d, *J* = 24.4 Hz), 115.29 (d, *J* = 21.2 Hz), 21.86. HRMS (ESI) m/z calcd for $C_{15}H_{12}BrFN_3O_2S$ $[M + H]^+$ 395.9812, found 395.9817.



1af

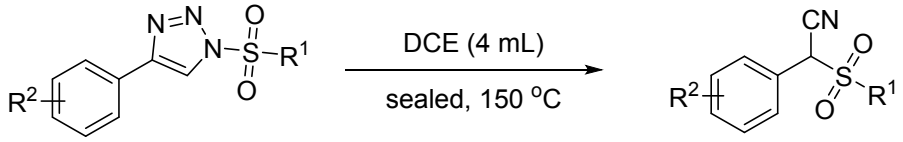
(8R,9S,13S,14S)-13-methyl-3-(1-tosyl-1H-1,2,3-triazol-4-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one: white solid, m.p: 181.6 °C, 675.4 mg, yield: 71%; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.31 (s, 1H), 8.08 – 8.03 (m, 2H), 7.65 – 7.58 (m, 2H), 7.41 (dd, *J* = 16.1, 8.2 Hz, 3H), 3.03 – 2.95 (m, 2H), 2.55 (dd, *J* = 18.7, 8.6 Hz, 1H), 2.49 (s, 3H), 2.37 (ddd, *J* = 15.7, 8.0, 3.9 Hz, 1H), 2.21 (s, 3H), 2.20 – 1.97 (m, 4H), 1.67 (s, 2H), 1.66 – 1.59 (m, 2H), 1.58 – 1.47 (m, 3H), 0.96 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 220.67, 147.36, 147.29, 140.97, 137.30, 133.19, 130.45, 128.69, 126.60, 126.35, 126.01, 123.47, 118.65, 50.54, 47.96, 44.46, 38.04, 35.84, 31.59, 29.34, 26.39, 25.68, 21.84, 21.60, 13.86. HRMS (ESI) m/z calcd for $C_{27}H_{30}N_3O_3S$ $[M + H]^+$ 476.2002 found 476.2000.



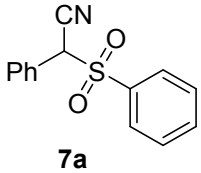
1ah

2-methyl-1-(1-tosyl-1H-1,2,3-triazol-4-yl)propan-2-yl acetate: white solid, m.p: 131.4 °C, 337.4 mg, yield: 68%; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.94 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 3.26 (s, 2H), 2.50 (s, 3H), 2.00 (s, 3H), 1.50 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 170.46, 147.19, 143.48, 133.27, 130.39, 128.58, 122.07, 80.72, 36.21, 26.08, 22.34, 21.78. HRMS (ESI) m/z calcd for $C_{15}H_{20}N_3O_4S$ $[M + H]^+$ 338.1169 found 338.1163.

3. Procedure for synthesis of α-cyano sulfone



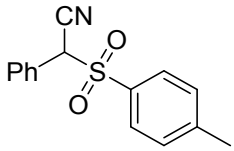
General Procedure: Dry DCE (4 mL) was added to sealed tube charged with stirring bar and 1-sulfonyl-1,2,3-triazole **1** (0.2 mmol) at room temperature and the tube was sealed by a screwed stopper tightly. Then the reaction mixture was stirred at 150 °C for 3 h (**7f**, **7m**, **7p** and **7ae** for 2 h; **7z** and **7aa** for 6 h). The reaction mixture was cooled to room temperature and filtered through a short plug of silica gel. The filtrate was concentrated and the residue was purified by flash chromatography with PE/EtOAc (3:1) as eluent to give the corresponding product **7**.



7a

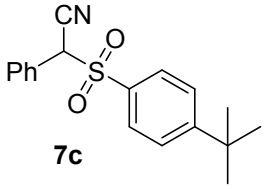
2-phenyl-2-(phenylsulfonyl)acetonitrile: white solid, m.p: 166.8 ℃，29.3 mg, yield: 57%; FT-IR (KBr) *v* 3064, 2960, 2923, 2850, 2252, 1456, 1332, 1154, 1083, 796, 758, 726, 685, 585, 550, 530, 498.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.79 – 7.74 (m, 3H), 7.57 (t, *J* = 7.9 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.33 (s, 1H), 7.31 (d, *J* = 3.8 Hz, 1H), 5.18 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 135.28, 134.44, 130.58, 130.17, 129.78, 129.17 (d, *J* = 14.0 Hz), 125.46, 113.41, 63.20. HRMS (ESI) m/z calcd for $C_{14}H_{11}NNaO_2S$ $[M + Na]^+$ 280.0403, found 280.0417.



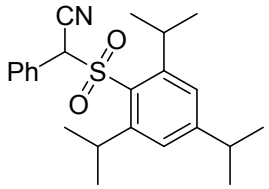
7b

2-phenyl-2-tosylacetonitrile: white solid, m.p: 171.0 ℃, 38.5 mg, yield: 71%; FT-IR (KBr) *v* 3088, 3061, 3031, 2961, 2931, 2850, 2255, 1593, 1456, 1334, 1293, 1260, 1152, 1083, 1016, 816, 779, 696, 672, 624, 583, 534, 474. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.50 (t, *J* = 7.3 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 8.7 Hz, 4H), 5.15 (s, 1H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 146.68, 131.41, 130.45, 130.15, 129.80 (d, *J* = 7.3 Hz), 129.02, 125.57, 113.52, 63.15, 21.81. HRMS (ESI) m/z calcd for $C_{15}H_{13}NNaO_2S$ $[M + Na]^+$ 294.0559, found 294.0565.



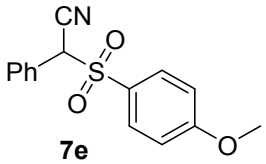
7c

2-((4-(tert-butyl)phenyl)sulfonyl)-2-phenylacetonitrile: white solid, m.p: 151.0 ℃, 37.0 mg, yield: 59%; FT-IR (KBr) *v* 3066, 2965, 2930, 2871, 2251, 1592, 1494, 1457, 1336, 1158, 1109, 1083, 841, 796, 654, 606, 586, 542, 517. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.70 (d, *J* = 8.6 Hz, 2H), 7.59 – 7.54 (m, 2H), 7.53 – 7.46 (m, 1H), 7.41 (dd, *J* = 8.5, 6.8 Hz, 2H), 7.36 – 7.32 (m, 1H), 5.15 (s, 1H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 159.61, 131.47, 130.44, 129.79, 129.79, 128.98, 126.23, 125.57, 113.58, 63.11, 35.47, 30.99. HRMS (ESI) m/z calcd for $C_{18}H_{19}NNaO_2S$ $[M + Na]^+$ 336.1029, found 336.1039.



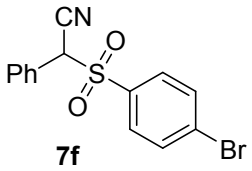
7d

2-phenyl-2-((2,4,6-triisopropylphenyl)sulfonyl)acetonitrile: white solid, m.p: 161.9 ℃, 16.9 mg, yield: 22%; FT-IR (KBr) *v* 3066, 3036, 2960, 2925, 2870, 2251, 1597, 1457, 1425, 1365, 1328, 1152, 1085, 886, 779, 695, 670, 583, 517. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.51 – 7.46 (m, 5H), 7.26 (s, 2H), 5.19 (s, 1H), 3.98 (p, *J* = 6.7 Hz, 2H), 3.02 – 2.92 (m, 1H), 1.32 (t, *J* = 6.5 Hz, 12H), 1.25 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 155.45, 152.83, 130.51, 130.22, 129.37, 129.17, 125.34, 124.55, 113.39, 63.64, 34.31, 30.39, 25.15, 25.00, 23.44. HRMS (ESI) m/z calcd for $C_{23}H_{29}NNaO_2S$ $[M + Na]^+$ 406.1811, found 406.1821.



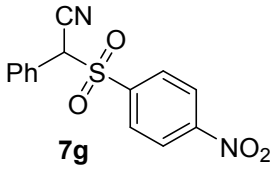
7e

2-((4-methoxyphenyl)sulfonyl)-2-phenylacetonitrile: white solid, m.p: 197.1 ℃, 35.6 mg, yield: 62%; FT-IR (KBr) *v* 3098, 3064, 2927, 2847, 2251, 1594, 1497, 1457, 1334, 1267, 1149, 1085, 1022, 835, 810, 782, 696, 675, 584, 545. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.74 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 7.1 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 7.6 Hz, 2H), 7.08 (d, *J* = 8.8 Hz, 2H), 5.23 (s, 1H), 4.02 (s,3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 165.12, 132.55, 130.49, 129.82, 129.08, 125.93, 125.69, 114.48, 113.75, 63.37, 55.90. HRMS (ESI) m/z calcd for $C_{15}H_{13}NNaO_3S$ $[M + Na]^+$ 310.0508, found 310.0520.



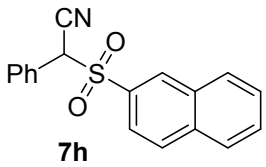
7f

2-((4-bromophenyl)sulfonyl)-2-phenylacetonitrile: white solid, m.p: 149.7 ℃, 42.2 mg, yield: 63%; FT-IR (KBr) *v* 3090, 3066, 2927, 2851, 2252, 1690, 1573, 1471, 1456, 1390, 1338, 1279, 1157, 1083, 1068, 1010, 824, 795, 779, 746, 698, 592, 545. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.71 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 7.5 Hz, 2H), 5.20 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 133.18, 132.55, 131.48, 131.10, 130.69, 129.69, 129.16, 125.08, 113.19, 63.12. HRMS (ESI) m/z calcd for $C_{14}H_{10}BrNNaO2S$ $[M + Na]^+$. 357.9508, found 357.9512



7g

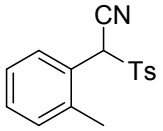
2-((4-nitrophenyl)sulfonyl)-2-phenylacetonitrile: yellow solid, m.p: 148.3 ℃, 31.4 mg, yield: 52%; FT-IR (KBr) *v* 3066, 3034, 2924, 2853, 2256, 1660, 1534, 1456, 1348, 1314, 1157, 1081, 856, 749, 737, 695, 592, 574. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.40 (d, *J* = 8.7 Hz, 2H), 7.95 (d, *J* = 8.7 Hz, 2H), 7.55 (d, *J* = 14.8 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.35 (d, *J* = 7.6 Hz, 2H), 5.28 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 151.68, 139.67, 131.71, 131.09, 129.71, 129.41, 124.46, 124.22, 112.82, 63.27. HRMS (ESI) m/z calcd for $C_{14}H_{11}N_2O_4S$ $[M + H]^+$ 303.0434, found 303.0450.



7h

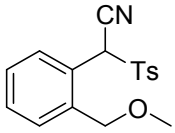
2-(naphthalen-2-ylsulfonyl)-2-phenylacetonitrile: yellow solid, m.p: 158.1 ℃, 38.7 mg, yield: 63%; FT-IR (KBr) *v* 3061, 3029, 2959, 2922, 2851, 2248, 1587, 1495, 1446, 1331, 1260, 1152, 1129, 1070, 1019, 800, 695, 668, 637, 606, 573, 474. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.35 (s, 1H), 7.99 (d, *J* = 8.5 Hz, 3H), 7.81 – 7.75 (m, 1H), 7.70 (t, *J* = 7.7 Hz, 2H), 7.53 – 7.47 (m, 1H), 7.39 (t, *J* = 7.7 Hz, 2H),

7.34 (d, J = 7.5 Hz, 2H), 5.24 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 135.93, 132.74, 131.82, 131.27, 130.55, 130.16, 129.82, 129.76, 129.35, 129.06, 128.05, 128.03, 125.50, 123.92, 113.44, 63.28. HRMS (ESI) m/z calcd for $C_{18}H_{13}NNaO_2S$ $[M + Na]^+$ 330.0559, found 330.0569.



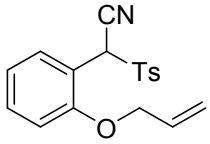
7j

2-(o-tolyl)-2-tosylacetonitrile: white solid, m.p: 171.1 ℃, 33.1 mg, yield: 58%; FT-IR (KBr) v 3067, 3022, 2925, 2249, 1596, 1492, 1464, 1335, 1155, 1154, 1084, 815, 777, 734, 713, 667, 584, 510, 455. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.73 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 7.9 Hz, 2H), 7.39 – 7.36 (m, 1H), 7.31 (s, 1H), 7.23 – 7.20 (m, 2H), 5.43 (s, 1H), 2.54 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 146.72, 138.22, 131.91, 131.28, 130.55, 130.22, 130.04, 129.92, 126.61, 124.36, 114.19, 59.70, 21.83, 19.59. HRMS (ESI) m/z calcd for $C_{16}H_{15}NNaO_2S$ $[M + Na]^+$ 308.0716, found 308.0715.



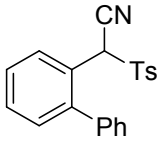
7k

2-(2-(methoxymethyl)phenyl)-2-tosylacetonitrile: white solid, m.p: 172.0 ℃, 32.1 mg, yield: 51%; FT-IR (KBr) v 3085, 3026, 2925, 2827, 2245, 1595, 1453, 1336, 1155, 1102, 1083, 945, 908, 816, 779, 744, 669, 584, 513. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.76 (d, J = 8.3 Hz, 2H), 7.48 – 7.43 (m, 1H), 7.42 (d, J = 8.0 Hz, 2H), 7.37 (s, 2H), 7.35 (s, 1H), 6.19 (s, 1H), 5.02 (d, J = 12.3 Hz, 1H), 4.33 (d, J = 12.3 Hz, 1H), 3.40 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 146.65, 137.74, 132.25, 130.81, 130.51, 130.44, 130.05, 129.97, 128.71, 125.18, 114.35, 73.67, 58.71, 58.23, 21.84. HRMS (ESI) m/z calcd for $C_{17}H_{17}NNaO_3S$ $[M + Na]^+$ 338.0821, found 338.0829.



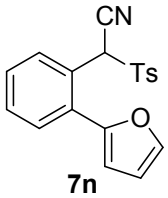
7l

2-(2-(allyloxy)phenyl)-2-tosylacetonitrile: white solid, m.p: 122.5 ℃, 45.1 mg, yield: 69%; FT-IR (KBr) v 3084, 2942, 2920, 2866, 2251, 1598, 1493, 1455, 1336, 1292, 1256, 1154, 1084, 1017, 996, 934, 815, 767, 753, 571, 584, 526. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.69 (d, J = 8.1 Hz, 2H), 7.46 – 7.39 (m, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.04 (t, J = 7.5 Hz, 1H), 6.89 (d, J = 8.3 Hz, 1H), 6.05 – 5.93 (m, 1H), 5.87 (s,1H), 5.38 (dd, J = 22.7, 13.9 Hz, 2H), 4.51 (dd, J = 12.6, 5.2 Hz, 1H), 4.42 (dd, J = 12.6, 4.9 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 156.13, 146.23, 132.65, 132.37, 132.02, 130.63, 130.02, 129.70, 121.24, 118.15, 114.76, 113.90, 112.32, 69.50, 56.15, 21.77. HRMS (ESI) m/z calcd for $C_{18}H_{17}NNaO_3S$ $[M + Na]^+$ 350.0821, found 350.0827.



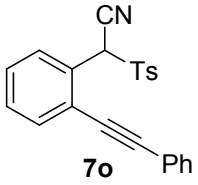
7m

2-([1,1'-biphenyl]-2-yl)-2-tosylacetonitrile: white solid, m.p: 167.8 °C, 30.5 mg, yield: 44%; FT-IR (KBr) *v* 3062, 3029, 2924, 2852, 2247, 1596, 1480, 1451, 1338, 1155, 1085, 920, 814, 776, 747, 704, 669, 584, 541, 498. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.74 (d, *J* = 7.5 Hz, 1H), 7.59 – 7.54 (m, 3H), 7.52 (d, *J* = 1.9 Hz, 1H), 7.46 (m, 3H), 7.34 (d, *J* = 6.7 Hz, 3H), 7.25 (m, 2H), 5.40 (s, 1H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 146.52, 143.91, 138.77, 132.94, 130.74, 130.46, 130.05, 129.77, 129.65, 129.32, 128.67, 128.32, 128.14, 123.67, 114.18, 58.77, 21.80. HRMS (ESI) m/z calcd for $C_{21}H_{17}NNaO_2S$ [M + Na]$^+$ 370.0872, found 370.0882.



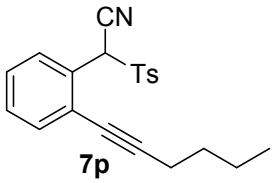
7n

2-(2-(furan-2-yl)phenyl)-2-tosylacetonitrile: white solid, m.p: 182.1 °C, 25.0 mg, yield: 37%; FT-IR (KBr) *v* 3152, 3123, 3063, 2965, 2924, 2853, 2246, 1661, 1596, 1509, 1466, 1409, 1335, 1155, 1088, 887, 813, 738, 668, 584, 566. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.59 (dd, *J* = 11.9, 6.6 Hz, 3H), 7.53 (t, *J* = 7.6 Hz,1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.65 (d, *J* = 3.3 Hz, 1H), 6.57 – 6.53 (m,1H), 6.37 (s, 1H), 2.51 (s,3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 151.98, 146.47, 142.95, 132.47, 131.64, 130.97, 130.59, 129.87, 129.83, 128.99, 128.50, 122.44, 114.17, 111.83, 109.73, 59.35, 21.79. HRMS (ESI) m/z calcd for $C_{19}H_{15}NNaO_3S$ [M + Na]+ 360.0665, found 360.0673.



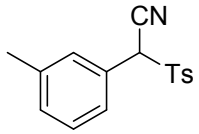
7o

2-(2-(phenylethynyl)phenyl)-2-tosylacetonitrile: white solid, m.p: 190.0 °C, 44.5 mg, yield: 60%; FT-IR (KBr) *v* 3063, 2923, 2900, 2253, 2218, 1596, 1496, 1444, 1339, 1155, 1084, 814, 775, 757, 691, 666, 584, 532, 474. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.62 – 7.57 (m, 2H), 7.54 (d, *J* = 4.1 Hz, 2H), 7.52 – 7.47 (m, 2H), 7.45 (m, *J* = 4.9, 2.0 Hz, 3H), 7.31 (d, *J* = 3.3 Hz, 2H), 5.96 (s, 1H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 146.65, 132.59, 132.40, 131.67, 131.52, 130.44, 129.96, 129.65, 129.19, 129.06, 128.57, 127.34, 124.90, 122.07, 113.68, 95.49, 85.44, 60.66, 21.84. HRMS (ESI) m/z calcd for $C_{23}H_{17}NNaO_2S$ [M + Na]$^+$ 394.0872, found 394.0880.



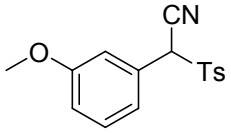
7p

2-(2-(hex-1-yn-1-yl)phenyl)-2-tosylacetonitrile: white solid, m.p: 168.9 ˚C, 24.3 mg, yield: 36%; FT-IR (KBr) *v* 3064, 3031, 2957, 2929, 2872, 2253, 2230, 1596, 1487, 1339, 1156, 1085, 814, 776, 754, 717, 666, 584, 528, 474. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.46 (dd, *J* = 6.1, 3.4 Hz, 2H), 7.41 (d, *J* = 1.5 Hz, 1H), 7.39 – 7.35 (m, 3H), 5.91 (s, 1H), 2.51 (s, 3H), 2.46 (t, *J* = 7.1 Hz, 2H), 1.64 (t, *J* = 7.5 Hz, 2H), 1.57 – 1.48 (m, 2H), 1.01 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 146.53, 132.51, 132.48, 130.24, 130.01, 129.93, 129.28, 128.17, 127.20, 125.79, 113.84, 97.23, 60.38, 30.91, 22.14, 21.82, 19.24, 13.62. HRMS (ESI) m/z calcd for $C_{21}H_{21}NNaO_2S$ [M + Na]+ 374.1185, found 374.1197.



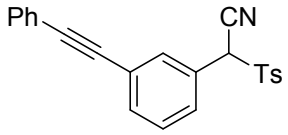
7r

2-(m-tolyl)-2-tosylacetonitrile: white solid, m.p.: 176.2 ˚C, 40.5 mg, yield: 71%; FT-IR (KBr) *v* 3071, 3034, 2918, 2851, 2246, 1595, 1491, 1452, 1336, 1155, 1084, 796, 704, 671, 587, 516, 444. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.28 (m, 2H), 7.13 (m, *J* = 8.4 Hz, 2H), 5.11 (s, 1H), 2.52 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 146.61, 138.99, 131.53, 131.22, 130.38, 130.17, 129.78, 128.85, 126.90, 125.37, 113.65, 63.13, 21.79, 21.25. HRMS (ESI) m/z calcd for $C_{16}H_{15}NNaO_2S$ $[M + Na]^+$ 308.0716, found 308.0728.



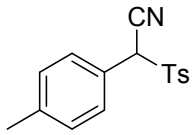
7s

2-(3-methoxyphenyl)-2-tosylacetonitrile: white solid, m.p: 179.0 ˚C, 44.6 mg, yield: 74%; FT-IR (KBr) *v* 3096, 3050, 2919, 2849, 2253, 1646, 1601, 1492, 1469, 1335, 1293, 1155, 1084, 1048, 800, 691, 671, 598, 573, 526. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 9.6 Hz, 1H), 7.02 (d, *J* = 10.6 Hz, 1H), 6.88 (s, 1H), 6.84 (s, 1H), 5.12 (s, 1H), 3.80 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 159.87, 146.67, 131.50, 130.18, 130.01, 129.83, 126.78, 122.07, 116.58, 114.89, 113.52, 63.17, 55.39, 21.81. HRMS (ESI) m/z calcd for $C_{16}H_{15}NNaO_3S$ $[M + Na]^+$ 324.0665, found 324.0678.



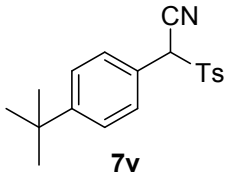
7t

2-(3-(phenylethynyl)phenyl)-2-tosylacetonitrile: white solid, m.p: 182.2 °C, 32.7 mg, yield: 44%; FT-IR (KBr) *v* 3061, 3031, 2926, 2848, 2248, 2216, 1596, 1494, 1443, 1337, 1155, 1084, 893, 803, 757, 690, 670, 595, 572, 527. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.59 – 7.56 (m, 2H), 7.49 (s, 1H), 7.43 – 7.40 (m, 6H), 7.39 (s, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 5.14 (s, 1H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 146.91, 133.41, 132.74, 131.69, 131.27, 130.18, 129.94, 129.22, 129.03, 128.73, 128.44, 126.01, 124.56, 122.65, 113.29, 91.01, 87.79, 62.85, 21.81. HRMS (ESI) m/z calcd for $C_{23}H_{17}NNaO_2S$ $[M + Na]^+$ 394.0872, found 394.0877.



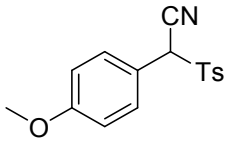
7u

2-(p-tolyl)-2-tosylacetonitrile: white solid, m.p: 172.4 °C, 32.5 mg, yield: 57%; FT-IR (KBr) *v* 3061, 3033, 2960, 2924, 2850, 2248, 1595, 1514, 1453, 1335, 1295, 1264, 1155, 1085, 1019, 815, 737, 709, 661, 592, 573, 534, 504, 480. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.66 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.22 (m, 4H), 5.12 (s, 1H), 2.51 (s, 3H), 2.42 (s, 3H). 13C NMR (101 MHz, Chloroform-d) δ 146.59, 140.81, 131.56, 130.15, 129.83, 129.72, 129.66, 122.44, 113.69, 62.88, 21.81, 21.30. HRMS (ESI) m/z calcd for $C_{16}H_{15}NNaO_2S$ $[M + Na]^+$ 308.0716, found 308.0728.



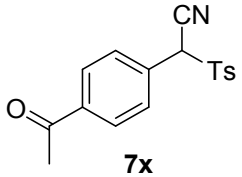
7v

2-(4-(tert-butyl)phenyl)-2-tosylacetonitrile: white solid, m.p: 150.0 °C, 40.6 mg, yield: 62%; FT-IR (KBr) *v* 3068, 3036, 2993, 2928, 2870, 2251, 1595, 1462, 1415, 1337, 1155, 1085, 1019, 842, 814, 725, 700, 654, 589, 527. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 5.13 (s, 1H), 2.53 (s, 3H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 153.99, 146.57, 131.72, 130.11, 129.81, 129.53, 126.05, 122.28, 113.65, 62.81, 34.84, 31.18, 21.82. HRMS (ESI) m/z calcd for $C_{19}H_{21}NNaO_2S$ $[M + Na]^+$ 350.1185, found 350.1195.



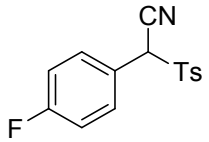
7w

2-(4-methoxyphenyl)-2-tosylacetonitrile: white solid, m.p: 175.8 ℃, 40.3 mg, yield: 67%; FT-IR (KBr) *v* 3066, 3041, 2960, 2925, 2853, 2250, 1610, 1513, 1462, 1334, 1259, 1179, 1154, 1085, 1030, 837, 814, 737, 712, 662, 593, 580, 520, 483. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.65 (d, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 6.92 (d, *J* = 8.2 Hz, 2H), 5.10 (s, 1H), 3.87 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 154.03, 139.30, 124.24, 123.88, 122.87, 122.58, 109.92, 107.21, 106.47, 55.28, 48.17, 14.54. HRMS (ESI) m/z calcd for $C_{16}H_{15}NNaO_3S$ $[M + Na]^+$ 324.0665, found 324.0674.



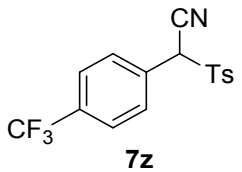
7x

2-(4-acetylphenyl)-2-tosylacetonitrile: white solid, m.p: 159.0 ℃, 35.1 mg, yield: 56%; FT-IR (KBr) *v* 3055, 2986, 2927, 2853, 2305, 1733, 1422, 1374, 1266, 1046, 896, 739, 705, 589. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.01 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 5.21 (s, 1H), 2.68 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 197.01, 147.10, 138.48, 131.27, 130.18, 130.12, 130.03, 128.77, 113.10, 62.82, 26.74, 21.86. HRMS (ESI) m/z calcd for $C_{17}H_{15}NNaO_3S$ $[M + Na]^+$ 336.0665, found 336.0671.



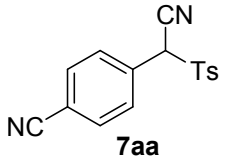
7y

2-(4-fluorophenyl)-2-tosylacetonitrile: white solid, m.p: 167.7 ℃, 31.2 mg, yield: 54%; FT-IR (KBr) *v* 3070, 2927, 2856, 2256, 1560, 1509, 1452, 1421, 1403, 1336, 1238, 1155, 1084, 1017, 844, 815, 787, 738, 709, 661, 592, 572, 535, 514, 482. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.65 (d, *J* = 7.0 Hz, 2H), 7.38 (d, J = 7.5 Hz, 2H), 7.33 (dt, J = 6.9, 3.6 Hz, 2H), 7.11 (t, J = 8.4 Hz, 2H), 5.15 (s, 1H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 163.98 (d, *J* = 251.8 Hz), 146.90, 131.78 (d, *J* = 8.8 Hz), 131.25, 130.12, 129.97, 121.48 (d, *J* = 3.4 Hz), 116.30 (d, *J* = 22.2 Hz), 113.41, 62.28, 21.84. HRMS (ESI) m/z calcd for $C_{15}H_{12}FNNaO_2S$[M + Na]$^+$ 312.0465, found 312.0464.



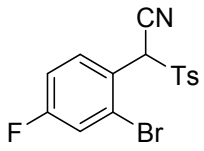
7z

2-tosyl-2-(4-(trifluoromethyl)phenyl)acetonitrile: white solid, m.p: 163.4 ℃, 17.6 mg, yield: 26%; FT-IR (KBr) *v* 3067, 2982, 2928, 2850, 2255, 1595, 1510, 1422, 1326, 1155, 1131, 1085, 1069, 1020, 852, 815, 739, 721, 680, 602, 582, 534, 514, 481. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.69 (t, *J* = 8.6 Hz, 4H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 5.22 (s, 1H), 2.53 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 147.21, 132.68 (q, *J* = 33.2 Hz), 131.50, 131.22, 130.29, 130.11, 130.08, 126.00 (q, *J* = 3.7 Hz), 123.48 (q, *J* = 272.6 Hz), 113.04, 62.58, 21.85. HRMS (ESI) m/z calcd for $C_{16}H_{12}F_3NNaO_2S$[M + Na]$^+$ 362.0433, found 362.0442.



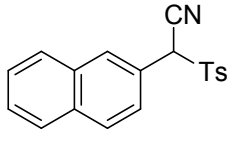
7aa

4-(cyano(tosyl)methyl)benzonitrile: white solid, m.p: 162.8 ℃, 12.4 mg, yield: 21%; FT-IR (KBr) *v* 3096 3065, 2924, 2851, 2232, 1595, 1504, 1452, 1416, 1338, 1294, 1156, 1085, 1019, 850, 815, 736, 710, 658, 587, 561, 525, 464. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 5.22 (s, 1H), 2.55 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 147.41, 132.65, 131.10, 130.53, 130.17, 130.08, 117.59, 114.64, 112.75, 62.64, 21.88. HRMS (ESI) m/z calcd for $C_{16}H_{13}N_2O_2S$ [M + H]$^+$ 297.0692, found 297.0701.



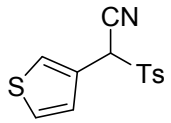
7ab

2-(2-bromo-4-fluorophenyl)-2-tosylacetonitrile: white solid, m.p: 156.7 ℃, 36.7 mg, yield: 50%; FT-IR (KBr) *v* 3093, 3069, 2921, 2850, 2258, 1647, 1597, 1488, 1397, 1340, 1230, 1158, 1085, 1038, 885, 864, 815, 736, 706, 662, 582, 566, 550, 528, 460. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.62 (dd, *J* = 8.8, 5.6 Hz, 1H), 7.47 – 7.40 (m, 3H), 7.19 (td, *J* = 8.7, 8.2, 2.6 Hz, 1H), 5.78 (s, 1H), 2.54 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 163.38 (d, *J* = 256.9 Hz), 147.13, 132.56 (d, *J* = 9.2 Hz), 132.26, 130.25, 129.97, 126.23 (d, *J* = 9.8 Hz), 122.21 (d, *J* = 3.6 Hz), 121.01 (d, *J* = 24.9 Hz), 115.82 (d, *J* = 21.7 Hz), 113.36, 60.62, 21.88. HRMS (ESI) m/z calcd for $C_{15}H_{12}BrFNO_2S$ [M + H]$^+$ 367.9751, found 367.9752.



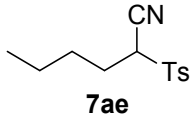
7ac

2-(naphthalen-2-yl)-2-tosylacetonitrile: white solid, m.p: 175.2 ℃, 41.1 mg, yield: 64%; FT-IR (KBr) *v* 3059, 2924, 2852, 2246, 1596, 1509, 1452, 1335, 1306, 1294, 1265, 1155, 1084, 1018, 964, 896, 862, 816, 754, 736, 702, 667, 587, 536, 510, 477. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.90 (t, *J* = 7.9 Hz, 2H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.81 (s, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.63 – 7.56 (m, 2H), 7.41 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 5.32 (s, 1H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 146.72, 133.76, 132.78, 131.42, 130.18, 130.14, 129.86, 128.97, 128.32, 127.79, 127.73, 127.08, 125.96, 122.82, 113.67, 63.35, 21.81. HRMS (ESI) m/z calcd for $C_{19}H_{15}NNaO_2S$ $[M + Na]^+$ 344.0716, found 344.0728.



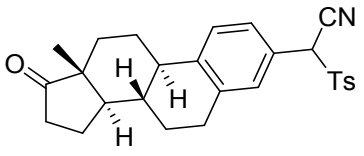
7ad

2-(thiophen-3-yl)-2-tosylacetonitrile: white solid, m.p: 158.0 ℃, 36.0 mg, yield: 65%; FT-IR (KBr) *v* 3106, 2925, 2848, 2246, 1595, 1334, 1154, 1084, 1018, 940, 866, 797, 735, 702, 661, 637, 578, 528, 513, 483, 466, 445. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.41 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 3H), 7.13 (d, *J* = 5.0 Hz, 1H), 5.27 (s, 1H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 146.71, 131.23, 130.01, 129.85, 127.96, 127.69, 127.27, 125.33, 113.45, 58.58, 21.82. HRMS (ESI) m/z calcd for $C_{13}H_{12}NO_2S_2$ $[M + H]^+$ 278.0304, found 278.0309.



7ae

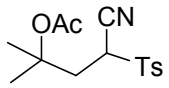
2-tosylhexanenitrile: white oil, 28.1 mg, yield: 56%; FT-IR (KBr) *v* 3067, 3029, 2961, 2930, 2873, 2246, 1597, 1467, 1402, 1382, 1334, 1217, 1185, 1155, 1086, 1043, 1018, 957, 816, 771, 716, 704, 665, 636, 588, 529, 514, 486. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 3.92 (dd, *J* = 11.1, 4.4 Hz, 1H), 2.53 (s, 3H), 2.28 – 2.17 (m, 1H), 1.99 – 1.86 (m, 1H), 1.65 (d, *J* = 8.3 Hz, 1H), 1.53 – 1.36 (m, 3H), 0.97 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 146.63, 132.68, 130.23, 129.63, 114.18, 57.68, 28.68, 26.48, 21.91, 21.80, 13.57. HRMS (ESI) m/z calcd for $C_{13}H_{18}NO_2S$ $[M + H]^+$ 252.1053, found 252.1053.



7af

2-((8S,9R,13R,14R)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)-2-tosylacetonitrile: white solid, m.p: 190.2 ℃, 53.7 mg, yield: 60%; FT-IR (KBr) *v* 3064, 3029, 2929, 2866, 2246, 1735, 1596, 1497, 1455, 1405, 1375, 1335, 1306, 1294, 1263, 1154, 1085, 1054, 1009, 900, 816, 736, 709, 677, 588, 528, 480, 442. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.74 (dd, *J* = 8.3, 1.6 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.34 (dd, *J* = 8.1, 4.8 Hz, 1H),

7.10 (q, *J* = 6.6, 5.0 Hz, 2H), 5.06 (s, 1H), 2.93 (dd, *J* = 19.9, 7.4 Hz, 2H), 2.61 – 2.54 (m, 1H), 2.53 (s, 3H), 2.44 (d, *J* = 3.7 Hz, 1H), 2.37 (s, 1H), 2.23 – 2.00 (m, 3H), 1.72 – 1.63 (m, 3H), 1.60 (d, *J* = 5.5 Hz, 1H), 1.55 (dd, *J* = 10.9, 4.0 Hz, 2H), 1.50 (s, 1H), 0.97 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 220.43, 146.61, 142.57, 137.65, 131.86, 130.27, 129.86, 127.17 , 126.08, 122.54, 113.72, 62.78, 50.53, 47.90, 44.37, 37.85, 35.81, 31.55, 29.19, 26.21, 25.59, 21.83, 21.59, 13.85. HRMS (ESI) m/z calcd for $C_{27}H_{29}NNaO_3S$ $[M + Na]^+$ 470.1760, found 470.1766.

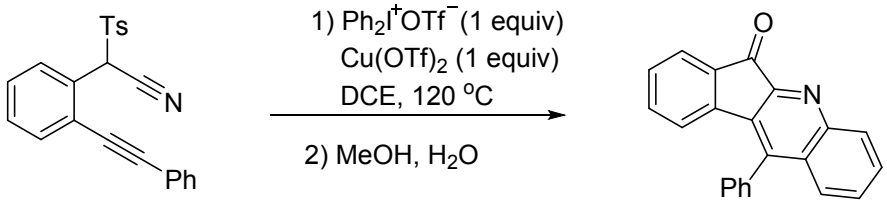


7ah

4-cyano-2-methyl-4-tosylbutan-2-yl acetate: clear oil, 13.2 mg, yield: 22%, FT-IR (KBr) *v* 3096, 3066, 3044, 2982, 2924, 2846, 2246, 1738, 1596, 1540, 1456, 1392, 1370, 1334, 1252, 1219, 1155, 1086, 1019, 950, 816, 759, 704, 669, 638, 589, 534, 515. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 4.07 (dd, *J* = 10.8, 2.8 Hz, 1H), 2.54 (s, 3H), 2.52 – 2.40 (m, 2H), 2.03 (s, 2H), 1.63 (s, 3H), 1.55 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ170.14, 146.85, 132.21, 130.28, 129.79, 114.67, 79.13, 53.67 (s, 3H), 37.65 (s, 0H), 26.15 (s, 4H), 25.74 (s, 4H), 22.06, 21.82. HRMS (ESI) m/z calcd for $C_{15}H_{19}NNaO_4S$ $[M + Na]^+$ 332.0927 found 332.0922.

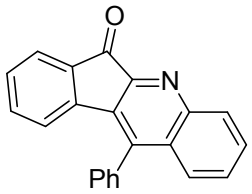
4. Procedures for derivations of 7o

4.1 synthesis of 11-phenyl-6H-indeno[2,1-b]quinolin-6-one



7o **10**, 50% yield

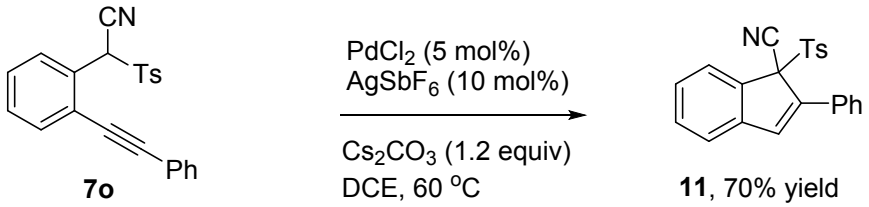
Procedure: Under a nitrogen atmosphere, 2-(2-(phenylethynyl)phenyl)-2-tosylacetonitrile (**7o**) (0.12 mmol, 44.5 mg), diphenyliodonium trifluoromethanesulfonate (0.12 mmol, 51.5 mg) and $Cu(OTf)_2$ (0.12 mmol, 43.3 mg) were added to a sealed tube charged with stirring bar, then dry DCE (0.2 mL) was added. The tube was sealed tightly by a screwed stopper. The reaction mixture was stirred at 120 °C for 11 h. After the reaction mixture was cooled to room temperature, DCE was removed by evaporation and MeOH (2 mL) and silica gel (20 mg) was added. After stirred for 4 h under air, the mixture was filtered through a short plug of silica gel. The filtrate was concentrated and the residue was purified by flash chromatography with PE/EtOAc (10:1) as eluent to give the corresponding product.



10

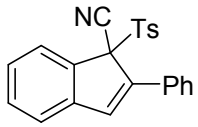
11-phenyl-6H-indeno[2,1-b]quinolin-6-one: yellow solid, m.p: 209 ℃, 30.0 mg, yield: 50%; FT-IR (KBr) *v* 2954, 2924, 2854, 1725, 1578, 1459, 1377, 1260, 1042, 955, 804, 760, 730, 703, 469.^{1}H NMR (400 MHz, Chloroform-d) δ 8.41 – 8.32 (m, 1H), 7.88 – 7.85 (m, 1H), 7.74 (dt, *J* = 8.5, 3.7 Hz, 1H), 7.69 (dd, *J* = 5.1, 1.5 Hz, 2H), 7.56 (d, *J* = 3.8 Hz, 2H), 7.48 (d, *J* = 9.2 Hz, 2H), 7.37 – 7.31 (m, 2H), 6.57 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 192.46, 154.01, 148.43, 143.11, 141.75, 135.79, 135.02, 134.61, 131.80, 130.91, 129.93, 129.51, 129.45, 129.42, 129.17, 129.06, 128.89, 126.59, 124.79, 123.92. HRMS (ESI) m/z calcd for $C_{22}H_{14}NO$ $[M + H]^+$ 308.1070, found 308.1078.

4.2 synthesis of 2-phenyl-1-tosyl-1*H*-indene-1-carbonitrile



7o **11**, 70% yield

Procedure: 2-(2-(phenylethynyl)phenyl)-2-tosylacetonitrile **7o** (0.1 mmol, 37.1 mg), Cs_2CO_3 (0.12 mmol, 39.1 mg), $AgSbF_6$ (10 mol %, 3.4 mg) and $PdCl_2$ (5 mol %, 0.9 mg) were added to a round bottle charged with stirring bar, then DCE (0.5 mL) was added. The reaction mixture was stirred at 60 °C for 2 h and then filtered through a short plug of silica gel. The filtrate was concentrated and the residue was purified by flash chromatography with PE/EtOAc (8:1) as eluent to give the corresponding product **11**.



11

2-phenyl-1-tosyl-1*H*-indene-1-carbonitrile: white solid, m.p: 154.9 ℃, 26.0 mg, yield: 70%; FT-IR (KBr) *v* 3065, 2960, 2923, 2853, 2238, 1595, 1458, 1335, 1152, 762, 577. ^{1}H NMR (400 MHz, DMSO-d6) δ 7.84 (d, *J* = 7.3 Hz, 1H), 7.79 (m, *J* = 7.8, 1.7 Hz, 2H), 7.59 – 7.51 (m, 3H), 7.47 (m, *J* = 7.2 Hz, 3H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d6) δ 147.32 , 143.31 , 138.29 , 136.76 , 135.65 , 132.42 , 131.99 , 130.30 , 129.65 , 129.48 – 129.02 (m), 128.23 , 127.39 , 125.85 , 123.22 , 114.91 , 72.43 , 21.64. HRMS (ESI) m/z calcd for $C_{23}H_{17}NNaO_2S$ $[M + Na]^+$ 394.0872, found 394.0873.

References:

(1) W. Cheng, Y. Tang, Z.-F. Xu and C.-Y. Li, Synthesis of multifunctionalized 2-carbonylpyrrole by rhodium-catalyzed transannulation of 1-sulfonyl-1,2,3-triazole with β-diketone, *Org. Lett.,* 2016, **18**, 6168.

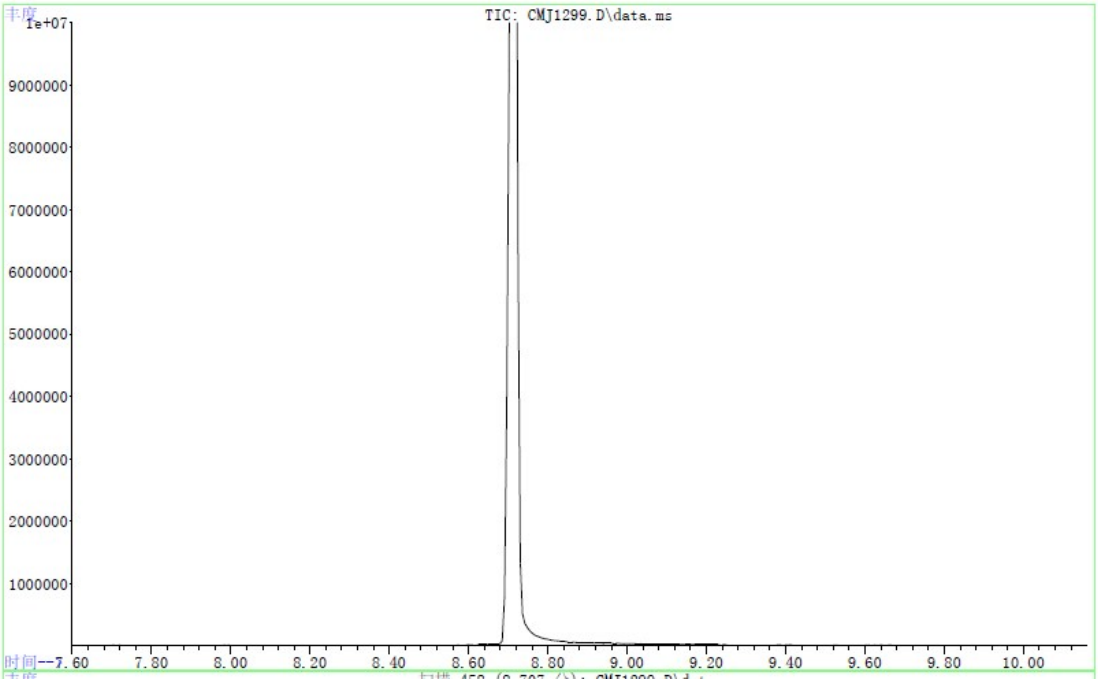
(2) Y. Shi, X. Yu and C.-Y. Li, Rhodium-catalyzed synthesis of 2,5-epoxybenzo[f][1,4] oxazepines by tandem reaction of 1-sulfonyl-1,2,3-triazoles and salicylaldehydes, *Eur. J. Org. Chem*., 2015, 6429.

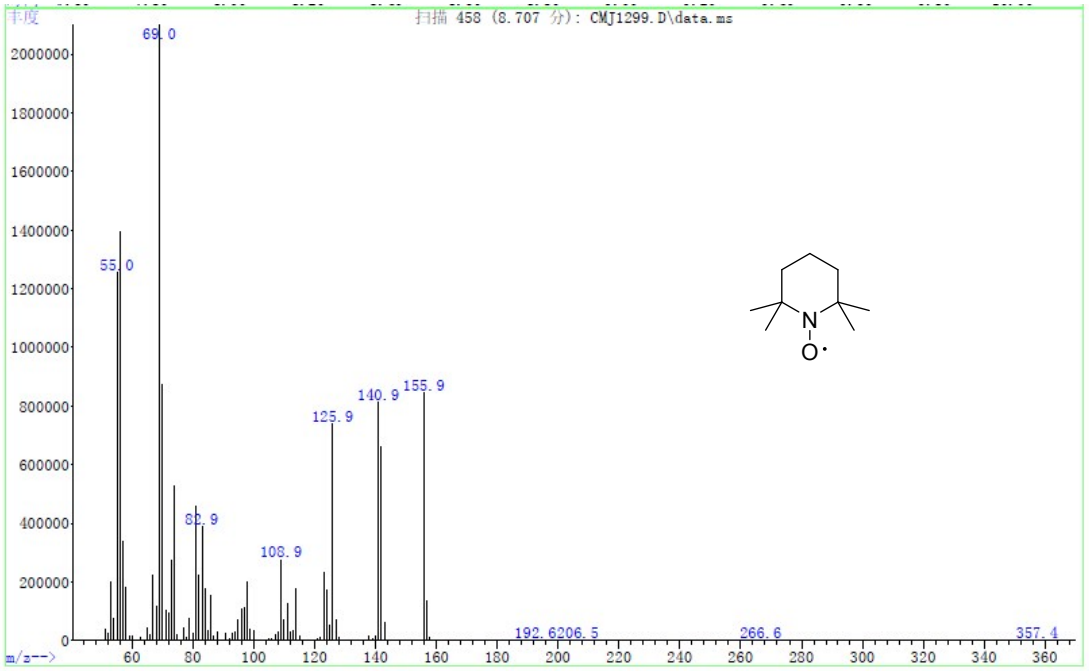
(3) Z.-F. Xu, L. Shan, W. Zhang, M. Cen and C.-Y. Li, Metal-free synthesis of imidazole by $BF_3 \cdot Et_2O$ promoted denitrogenative transannulation of N-sulfonyl-1,2,3-triazole, *Org. Chem. Front.,* 2019, **6**, 1391.

(4) B. Seo, W. H. Jeon, J. Kim, S. Kim and P. H. Lee, Synthesis of fluorenes via tandem copper-catalyzed [3 + 2] cycloaddition and rhodium-catalyzed denitrogenative cyclization in a 5-exo mode from 2-ethynylbiaryls and N-sulfonyl azides in one pot, *J. Org. Chem.*, 2015, **80**, 722.

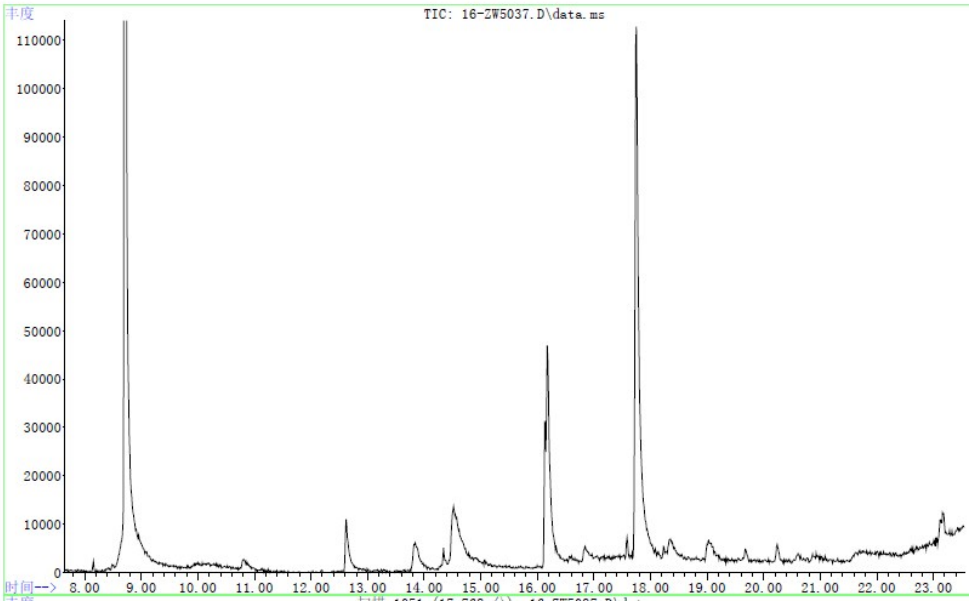
LC-MS and NMR spectra

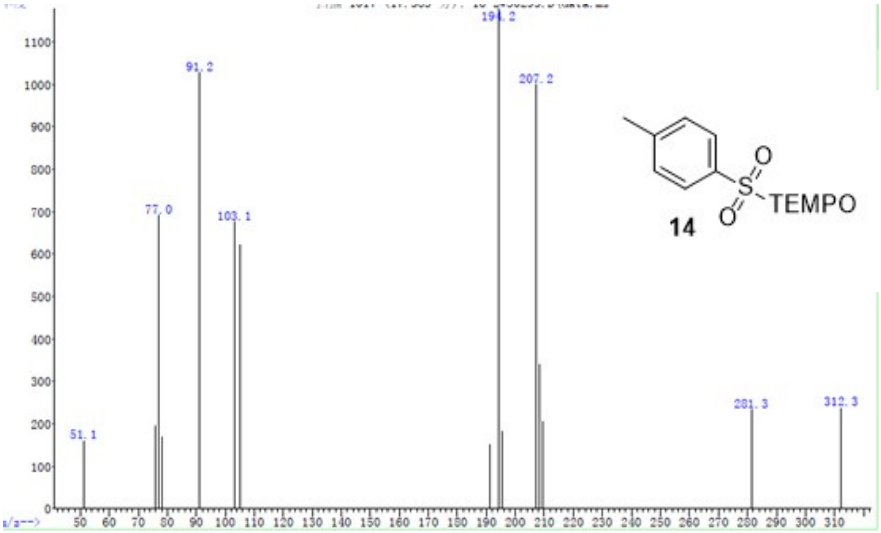
TEMPO heated in DCE at 150 °C for 3 h

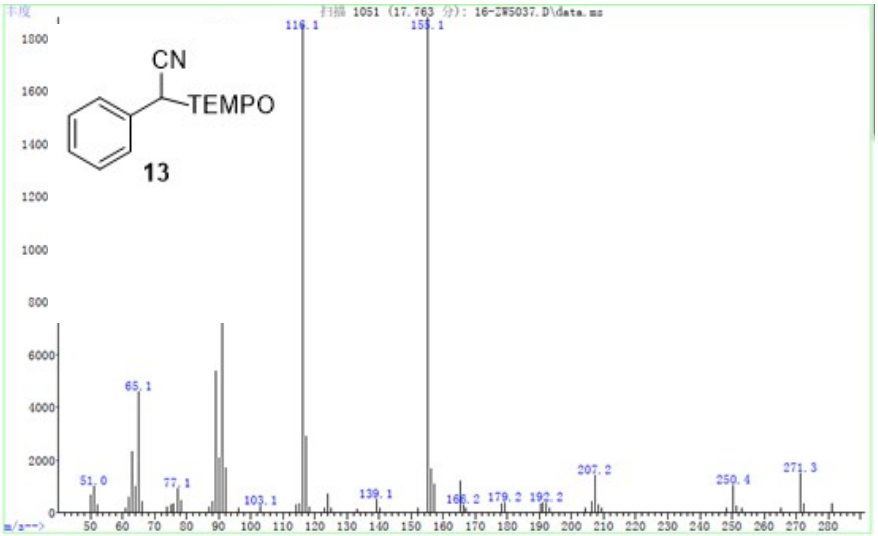




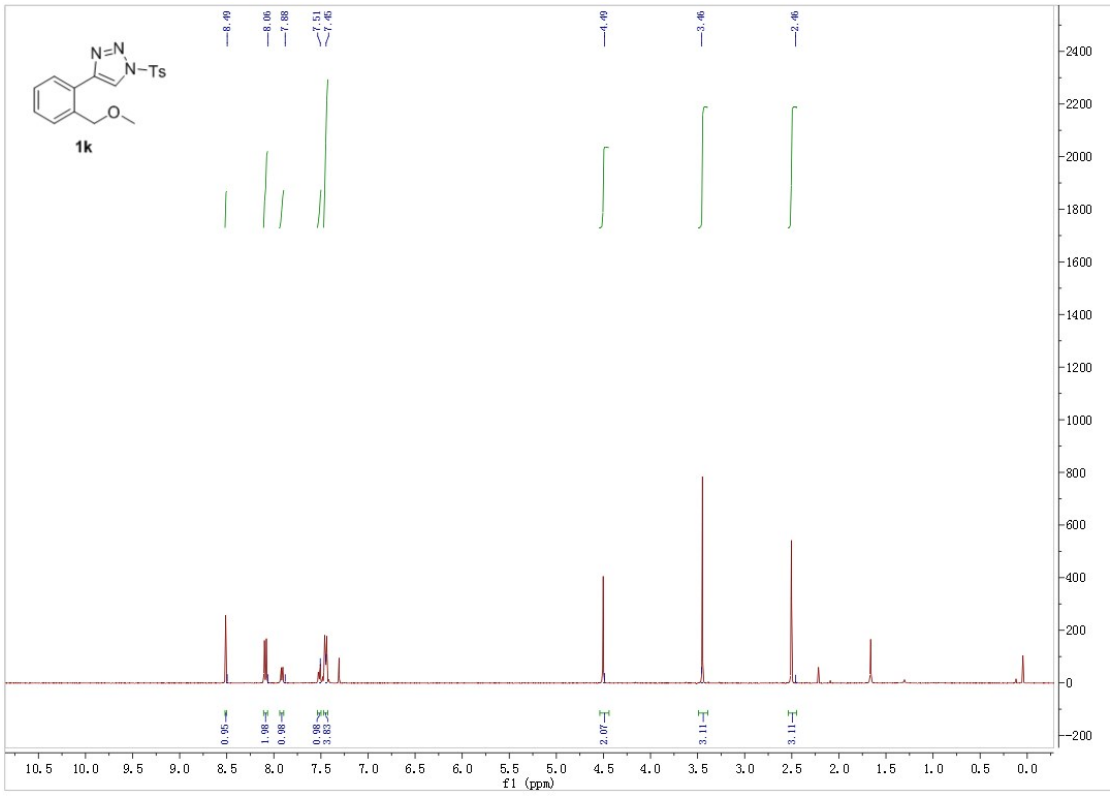
Capture of radical

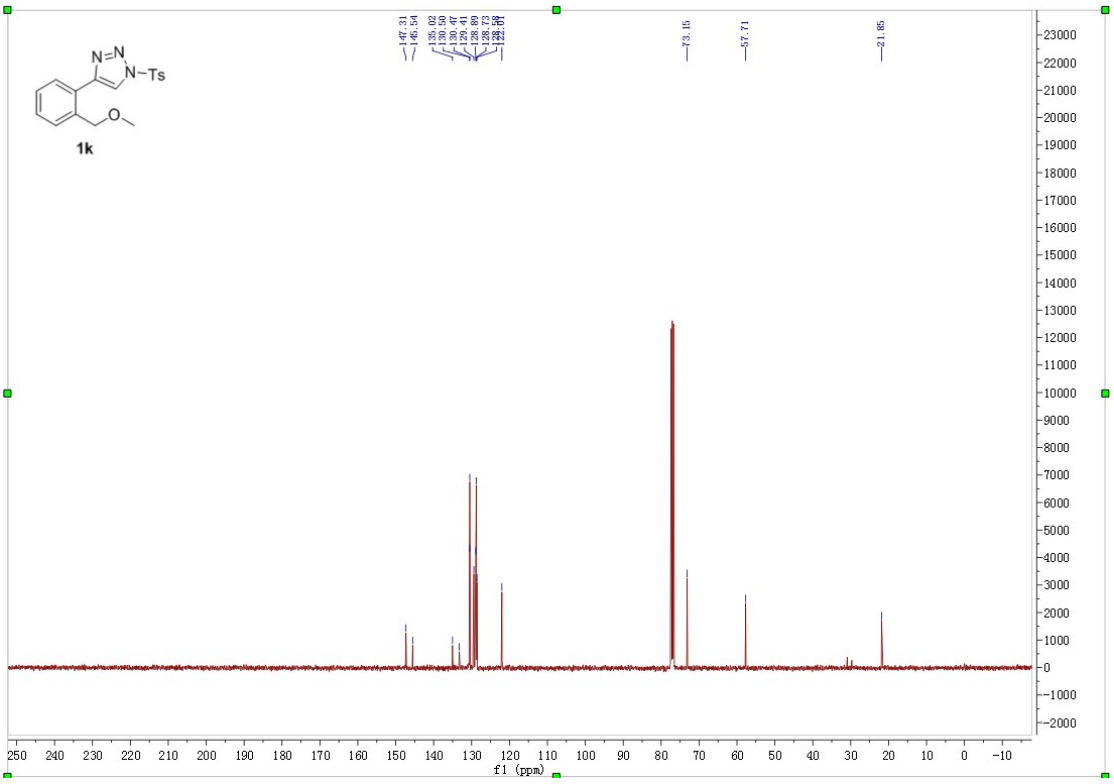


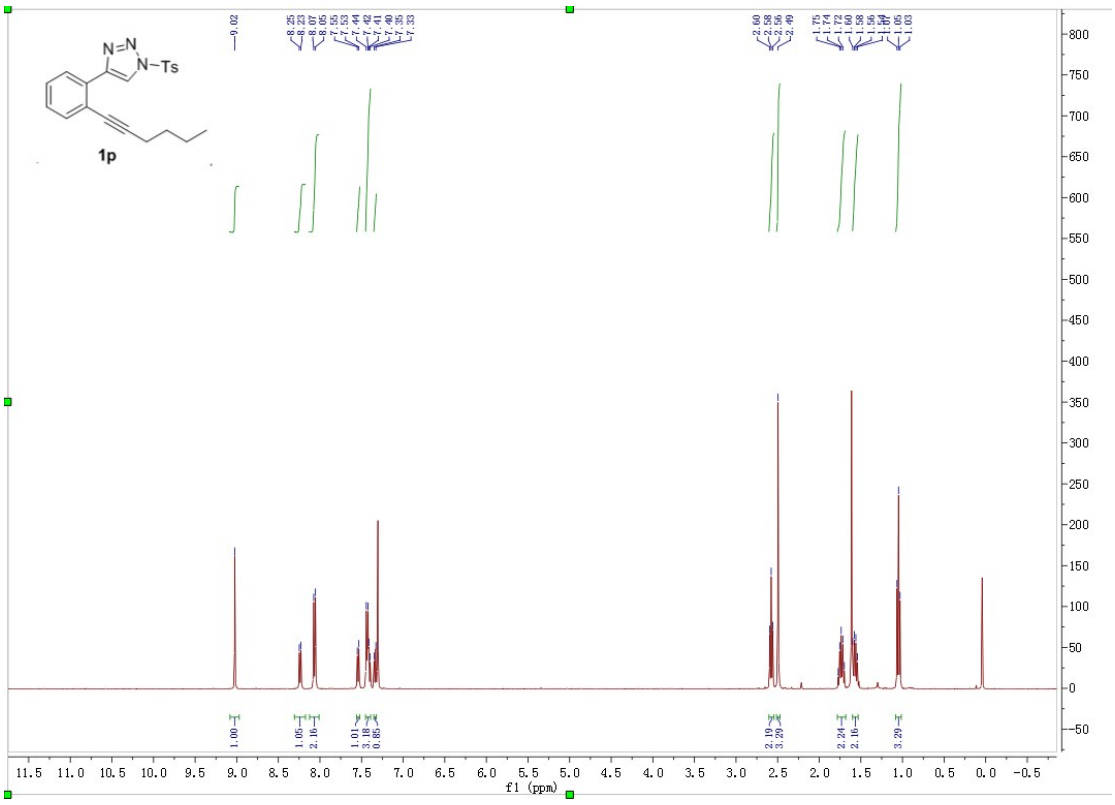




NMR spectra



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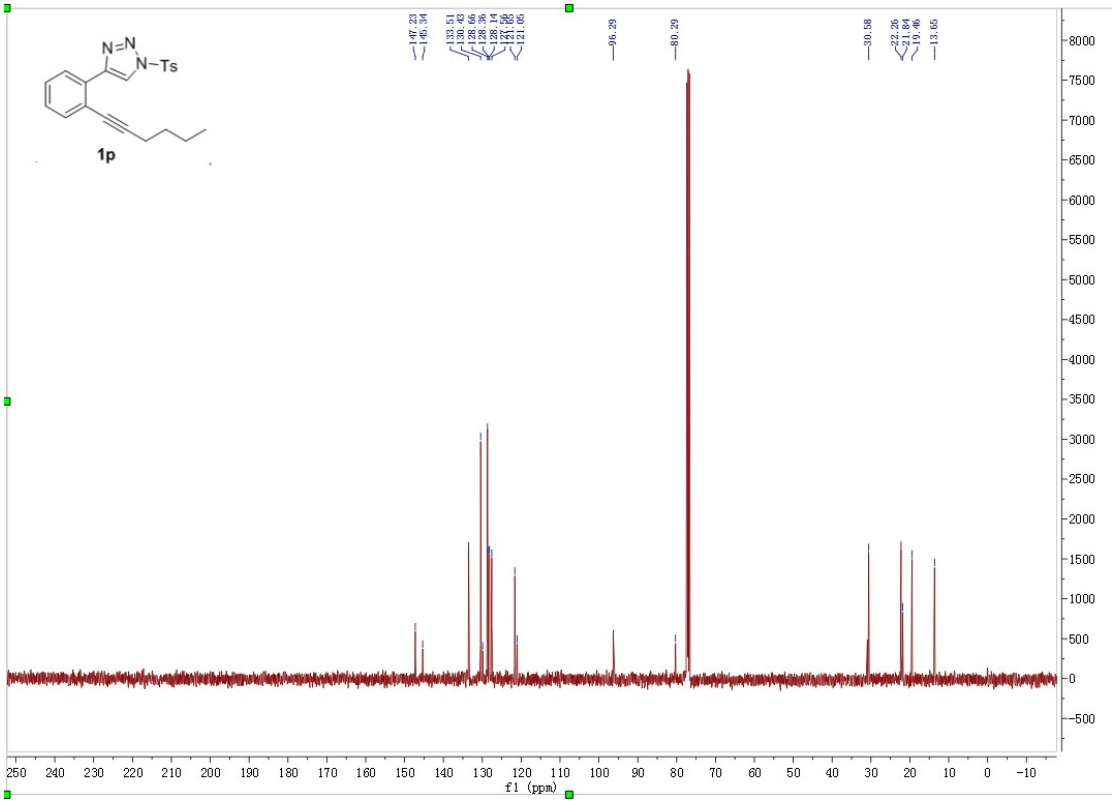
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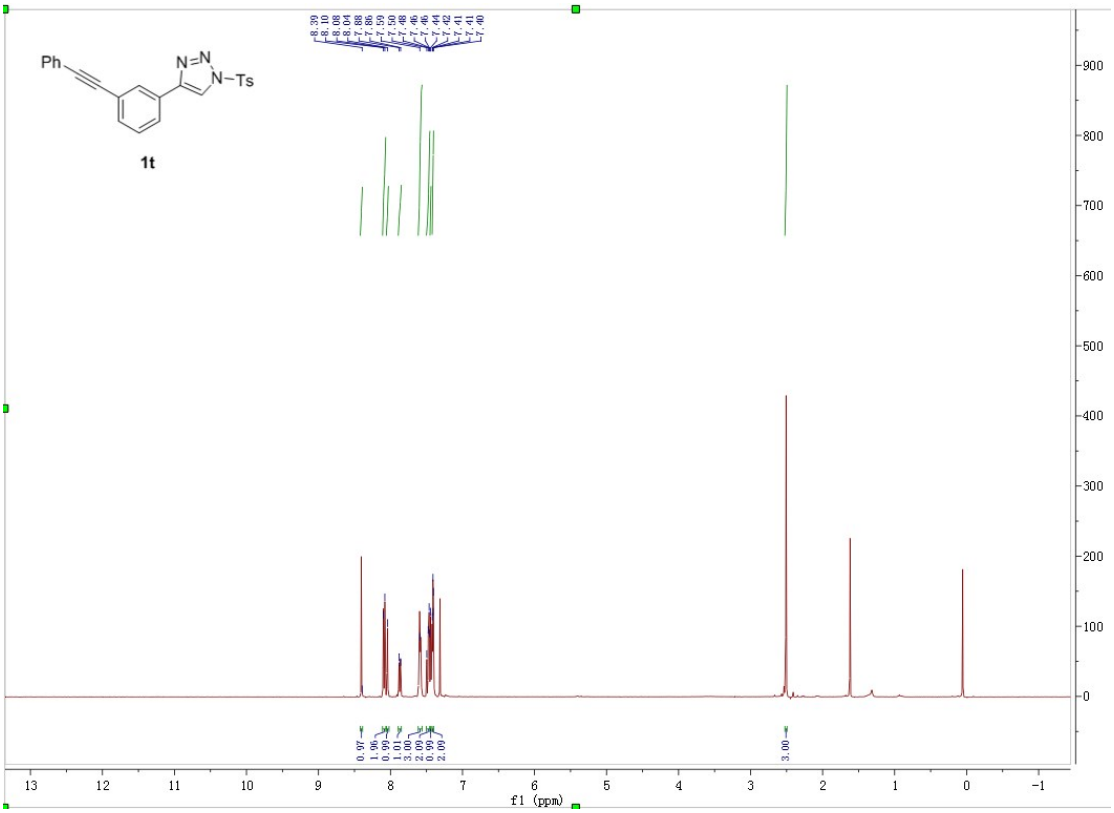
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N–Ts
1t
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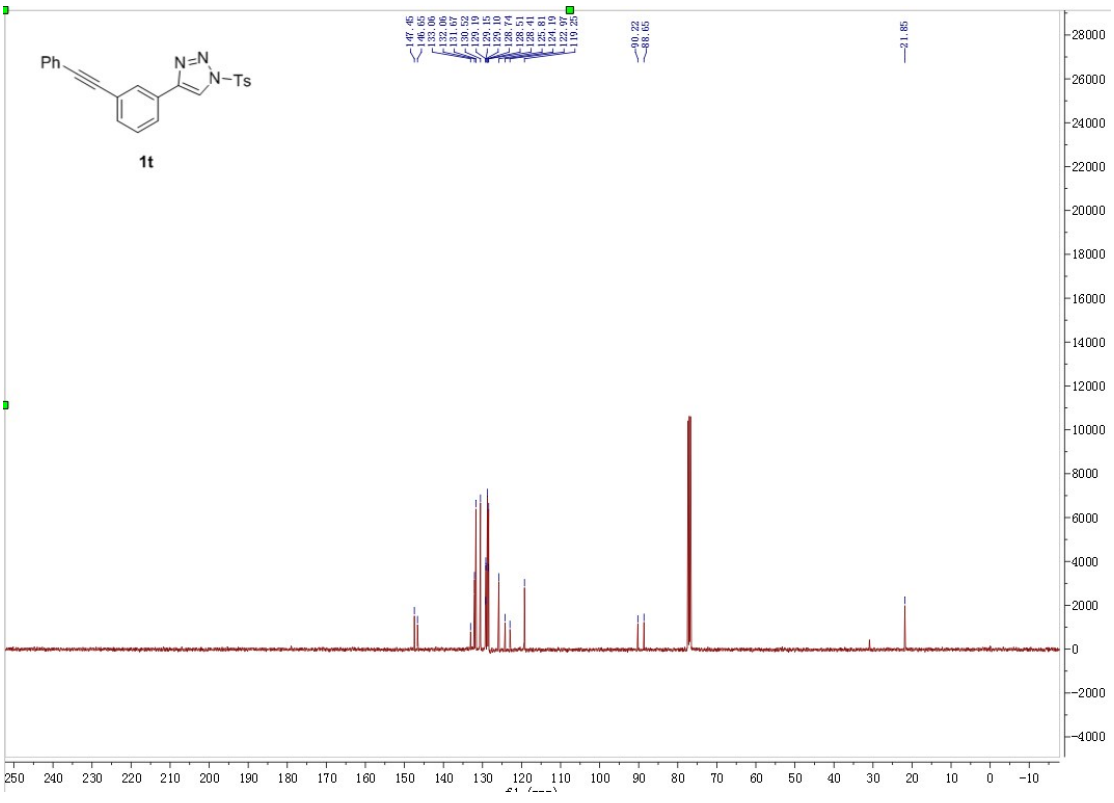
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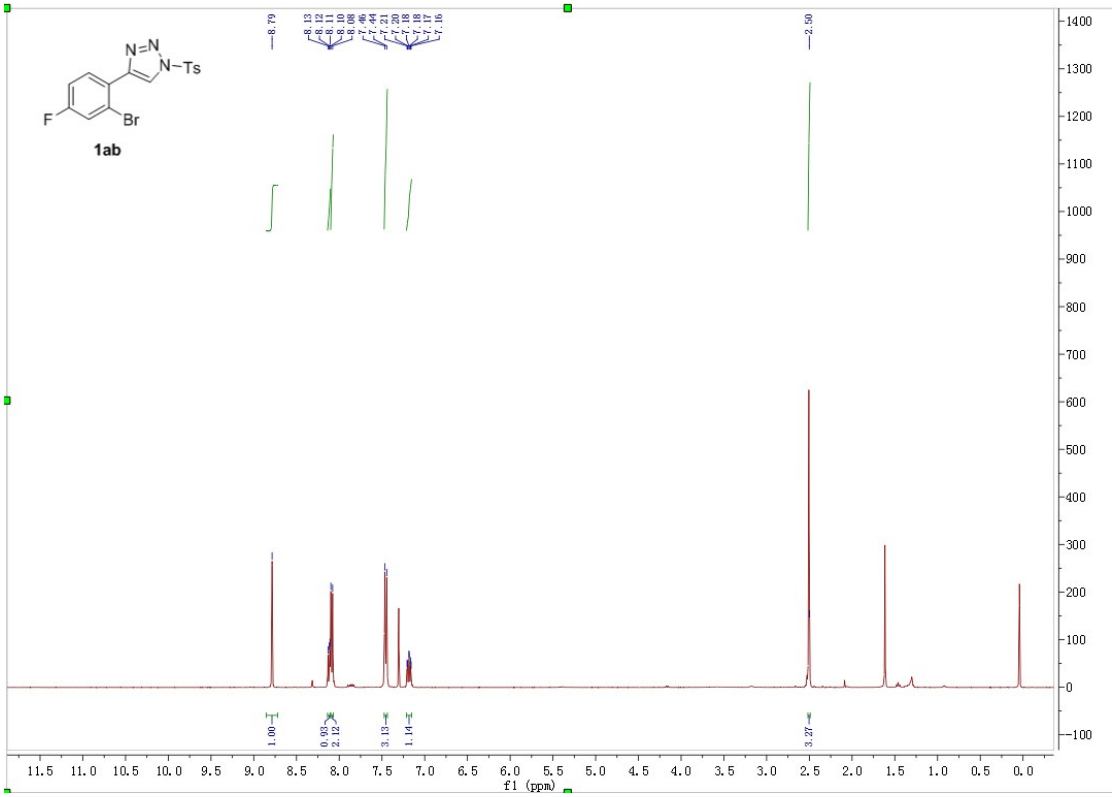
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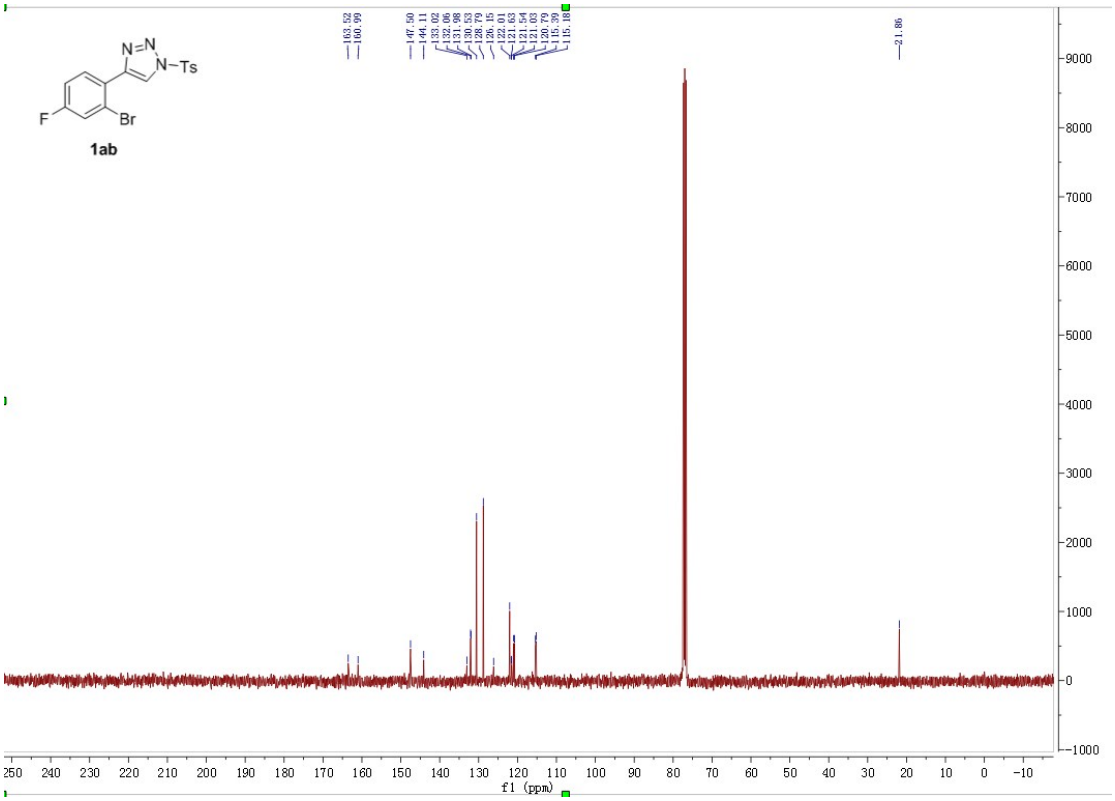
3.27
f1 (ppm)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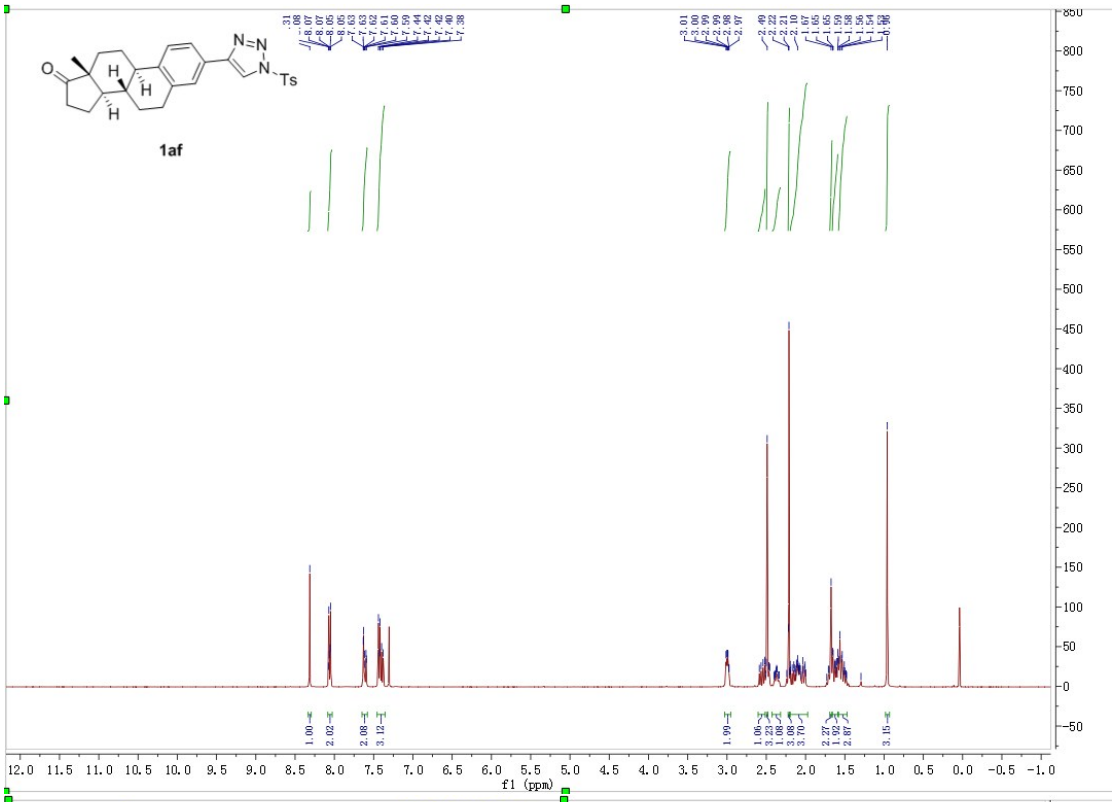
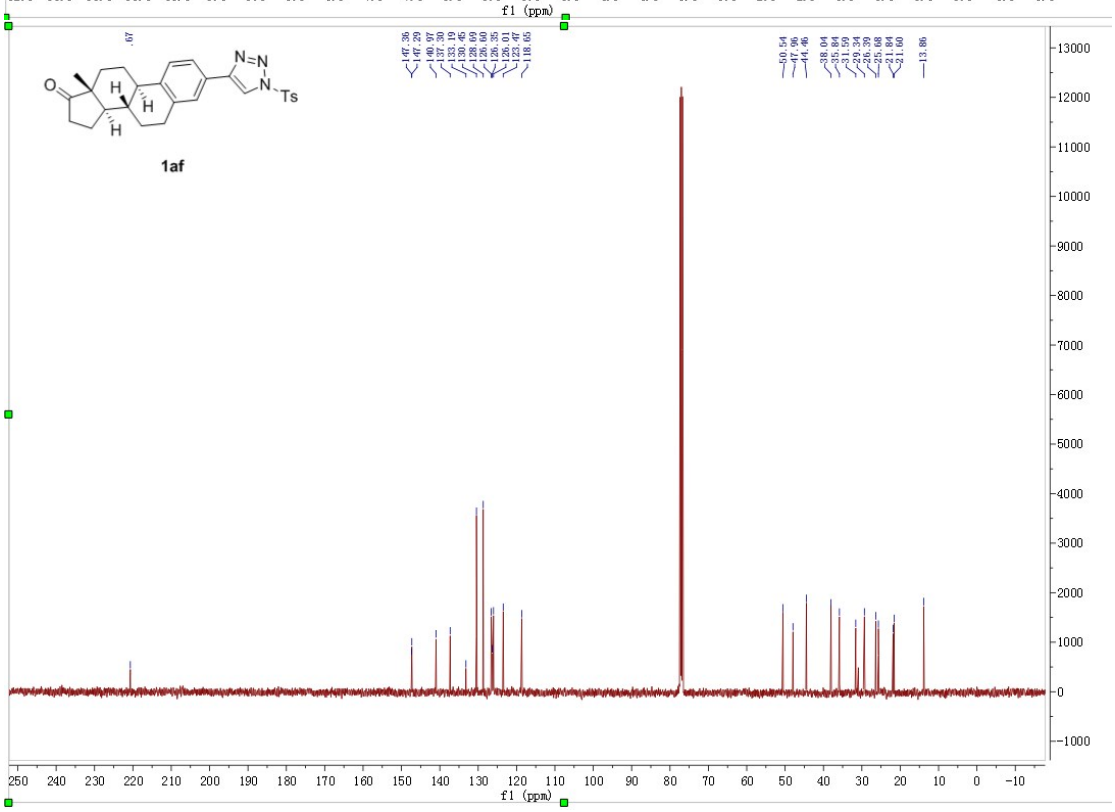
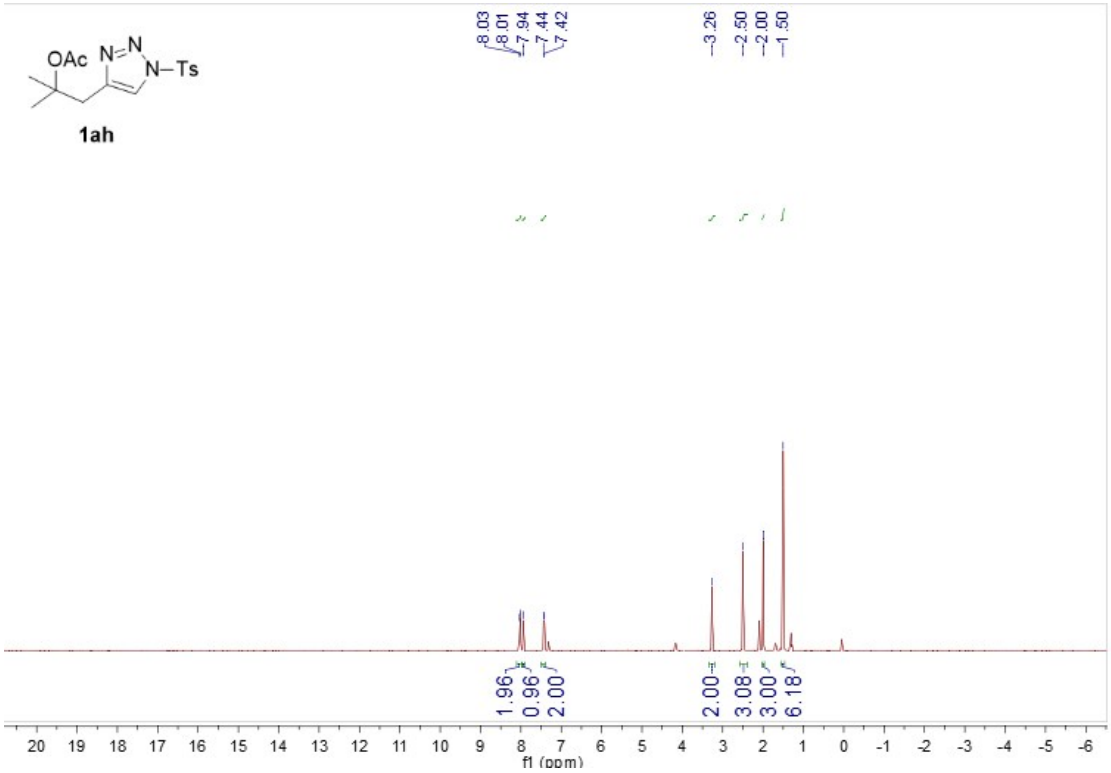
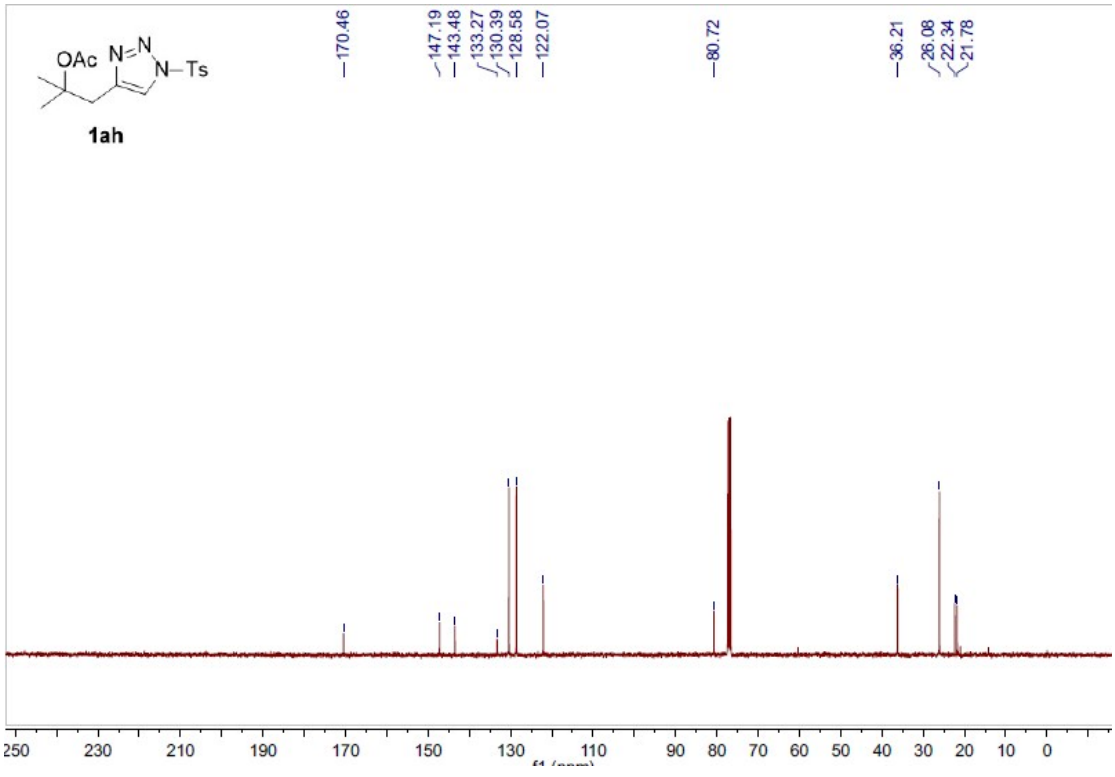
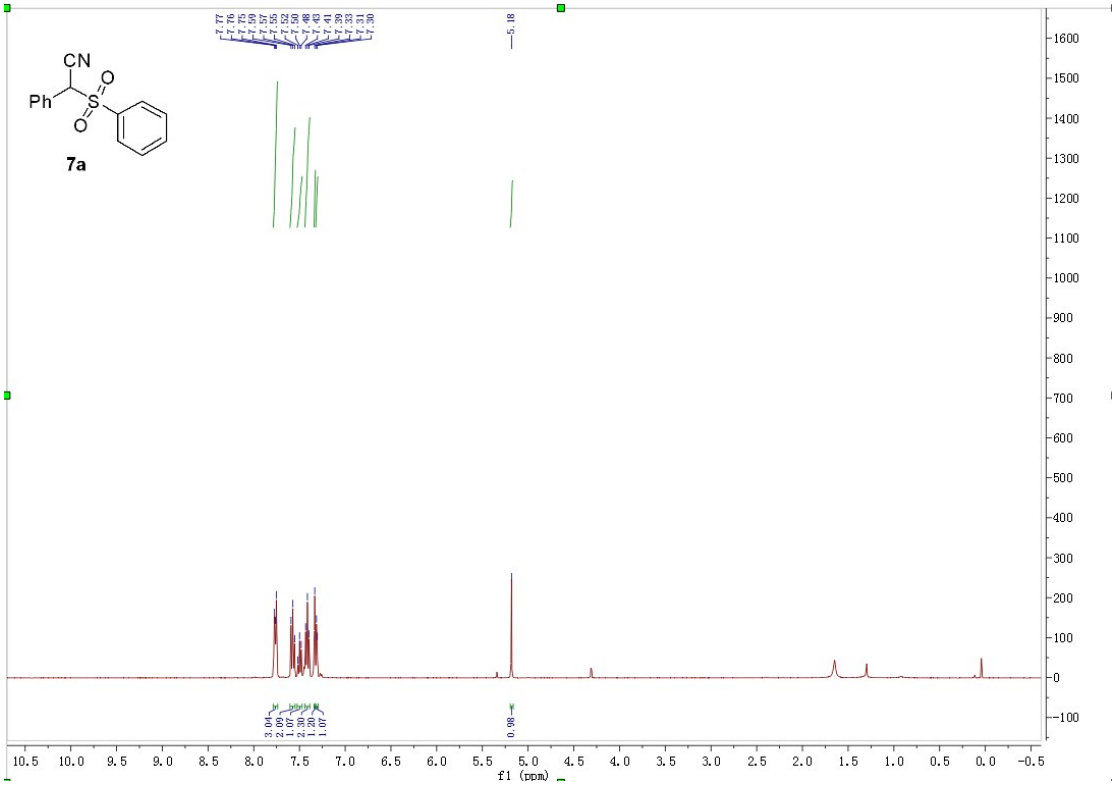
f1 (ppm)

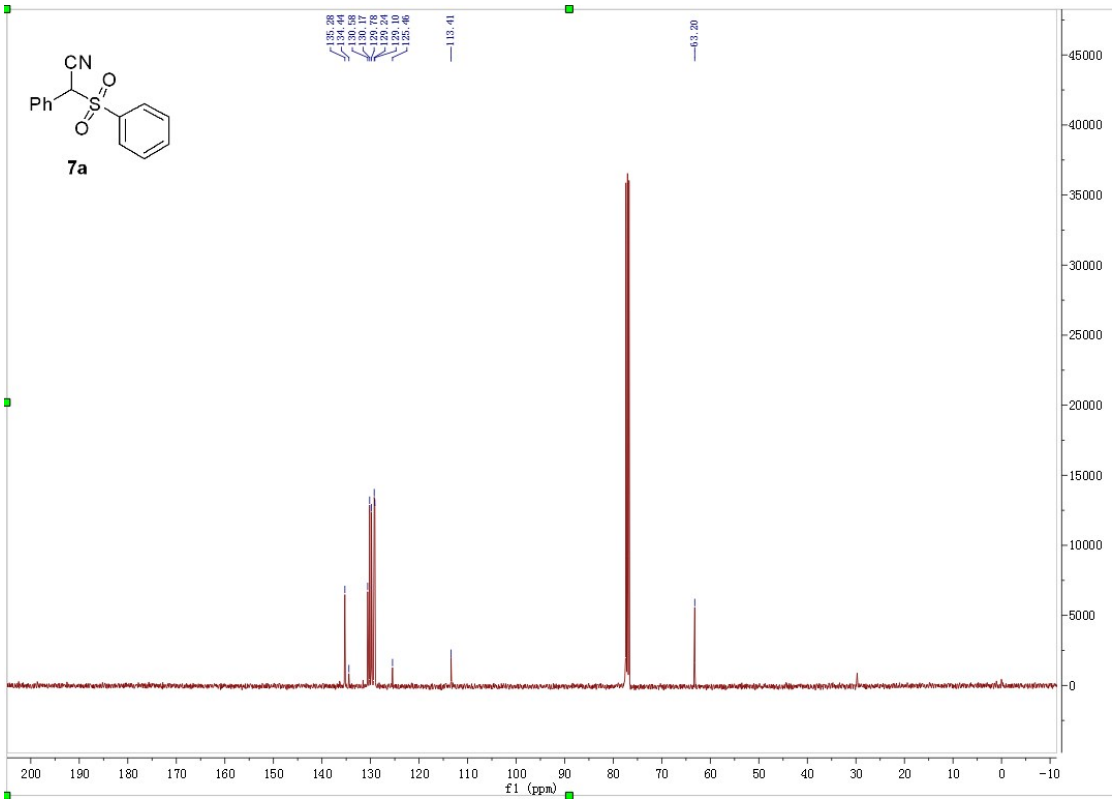

1af
f1 (ppm)

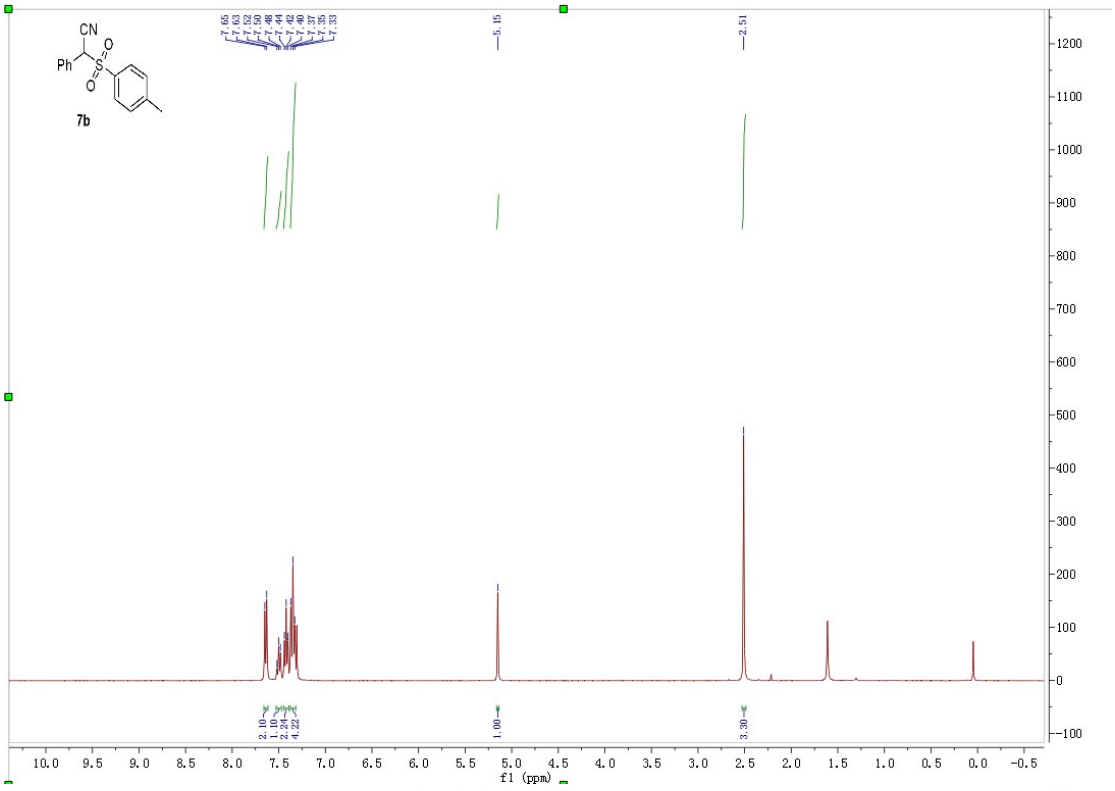

1af
f1 (ppm)

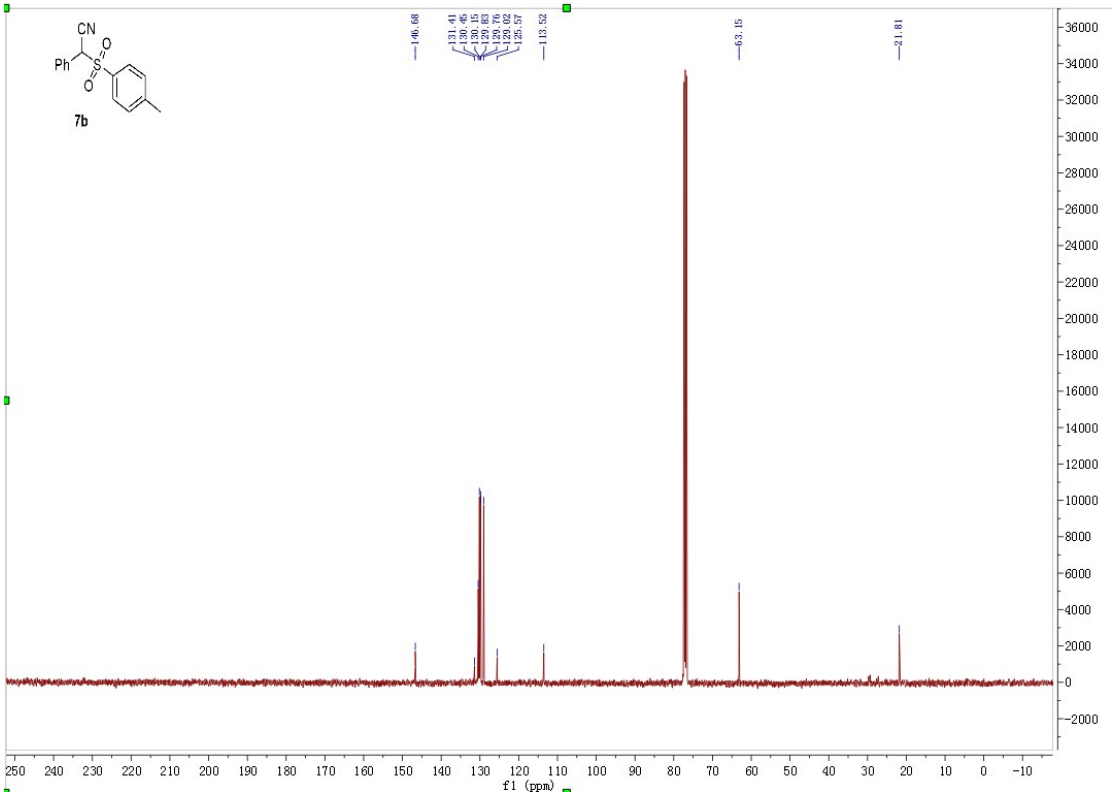

OAc
N=N
N–Ts
1ah
8.03
8.01
7.94
7.44
7.42
3.26
2.50
2.00
1.50
1.96
0.96
2.00
2.00
3.08
3.00
6.18
f1 (ppm)

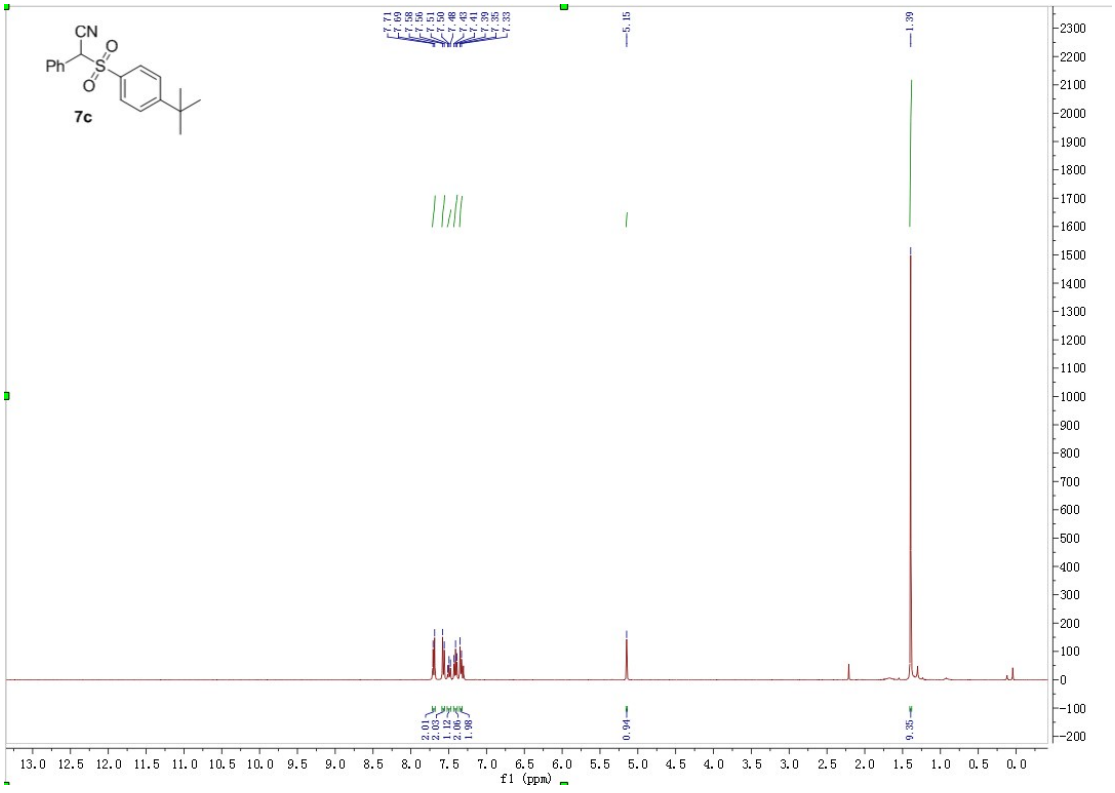

OAc
N=N
N–Ts
1ah
170.46
147.19
143.48
133.27
130.39
128.58
122.07
80.72
36.21
26.08
22.34
21.78
f1 (ppm)

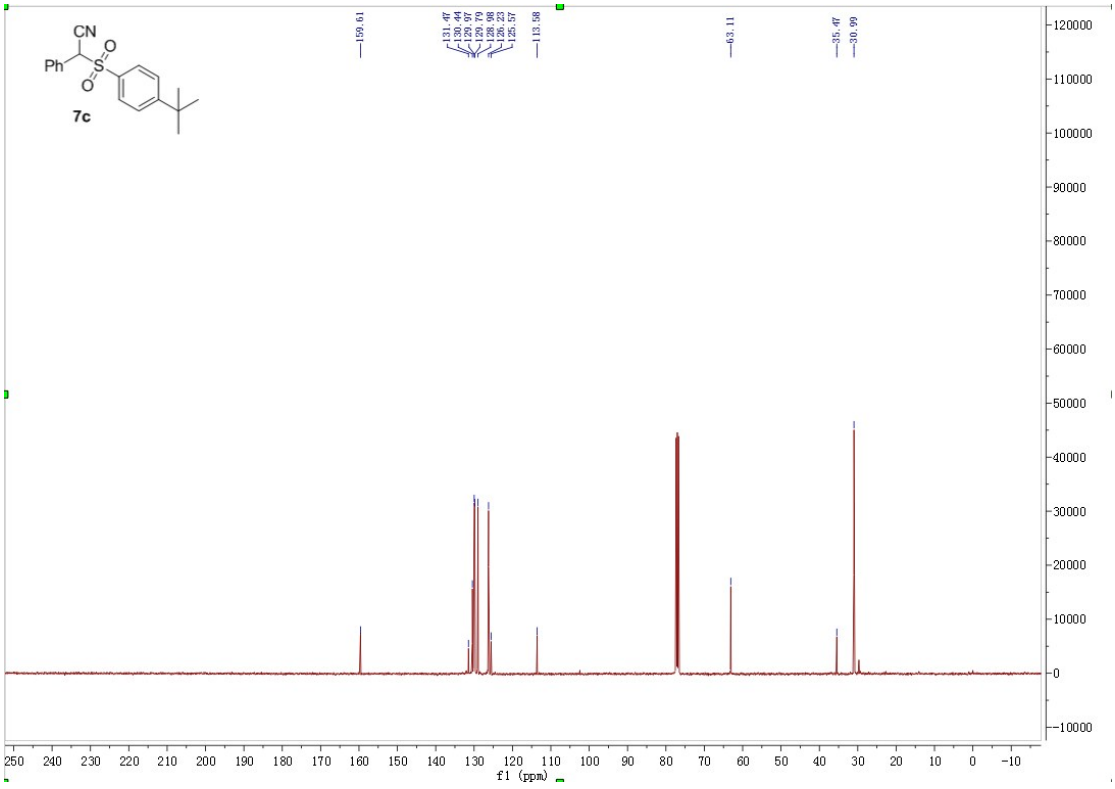

CN
Ph
O
S
O
7a
7.77
7.76
7.75
7.59
7.57
7.55
7.52
7.50
7.48
7.43
7.41
7.39
7.33
7.31
7.30
5.18
3.04
2.09
1.07
2.30
1.20
1.07
0.98
f1 (ppm)

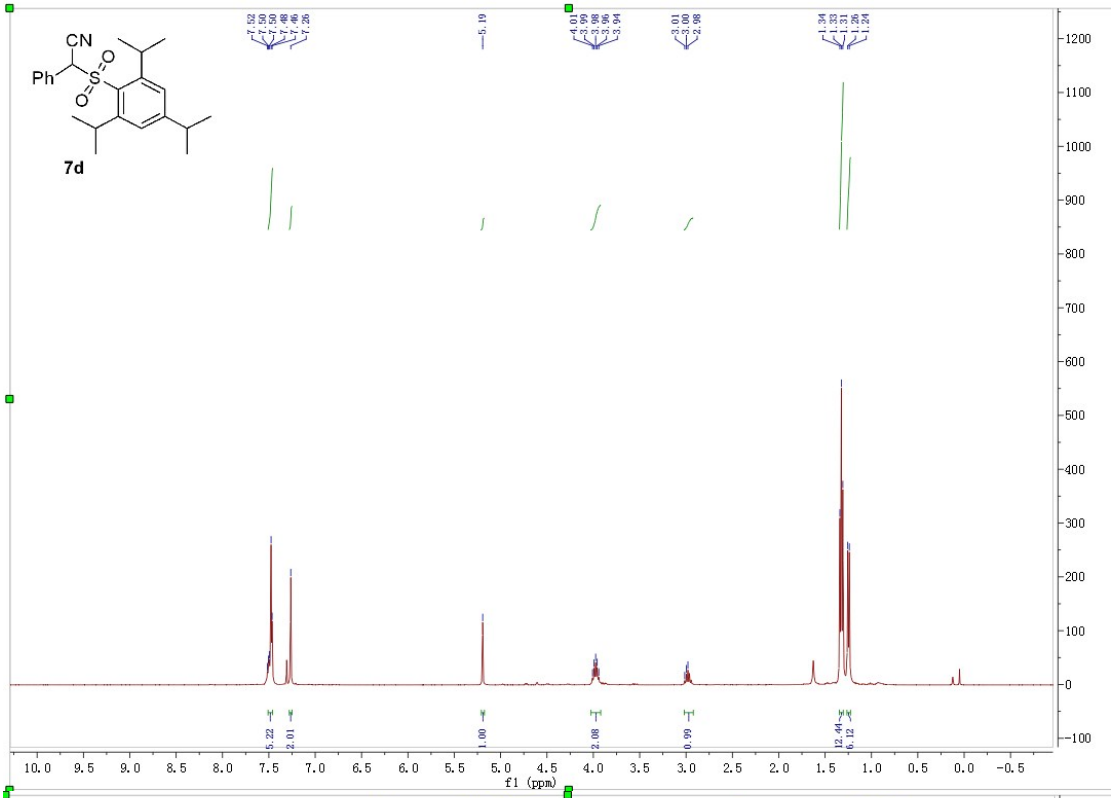

CN
Ph
O
S
O
7a
135.28
134.44
130.68
130.17
129.78
129.24
129.10
125.46
113.41
63.20
f1 (ppm)

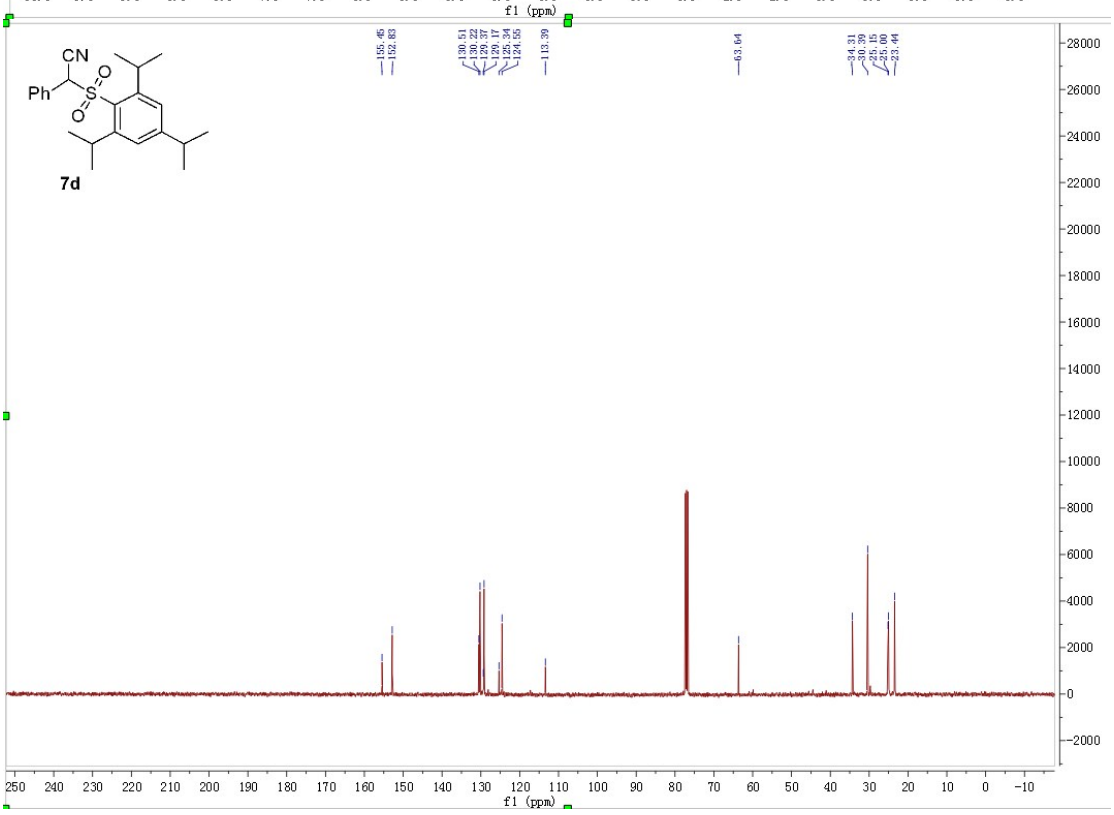

CN
Ph
O
O
S
O
7b
7.65
7.63
7.52
7.50
7.48
7.44
7.42
7.40
7.37
7.35
7.33
5.15
2.51
2.10
1.10
2.24
4.22
1.00
3.30
f1 (ppm)

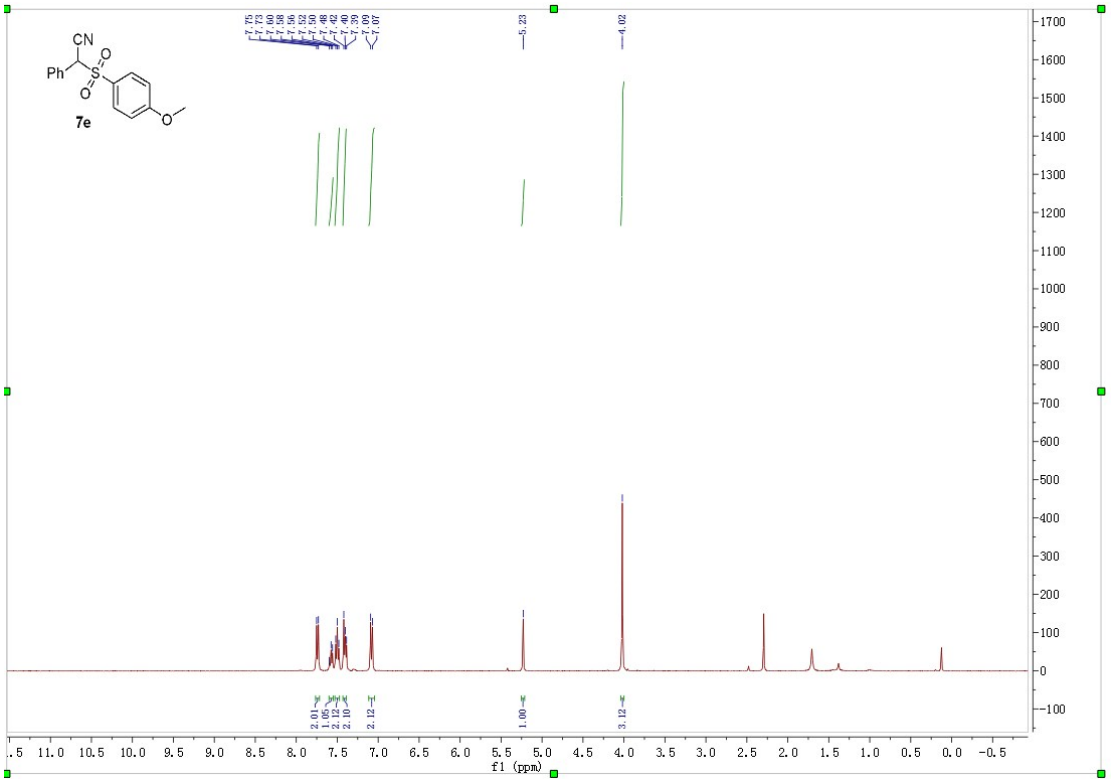

CN
Ph
O
O
S
O
7b
146.68
131.41
130.46
130.15
129.83
129.76
129.02
125.57
113.52
63.15
21.81
f1 (ppm)

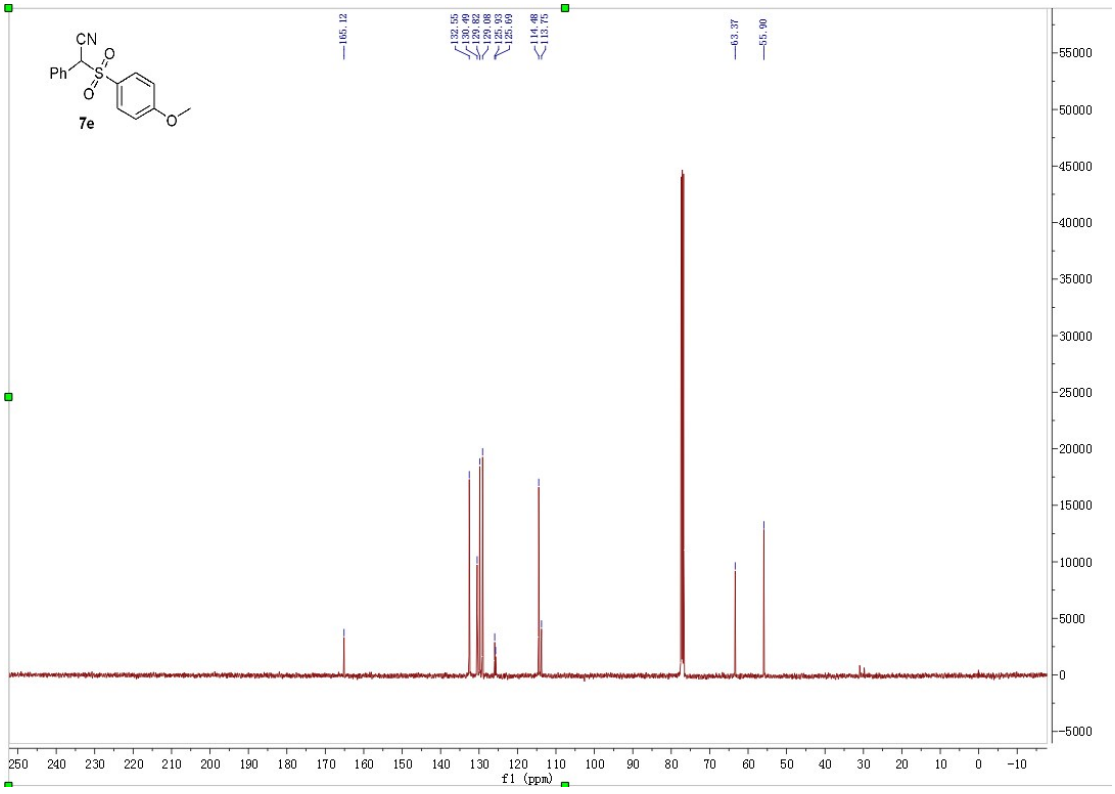

CN
Ph
O
S
O
7c
7.71
7.69
7.58
7.56
7.51
7.50
7.48
7.47
7.41
7.39
7.35
7.33
5.15
1.39
2.01
2.02
2.12
2.06
1.98
0.94
9.35
f1 (ppm)

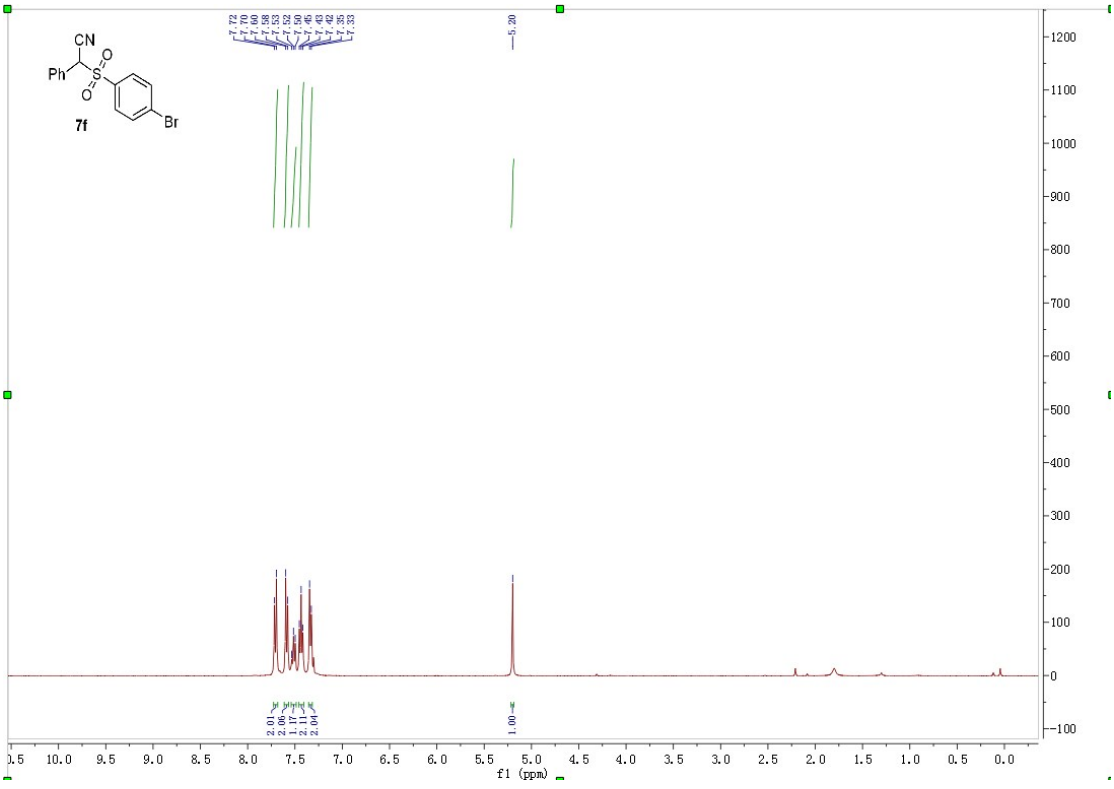

CN
Ph
O
S
O
7c
159.61
131.47
130.44
129.97
129.79
128.98
126.23
125.57
113.58
63.11
35.47
30.99
f1 (ppm)

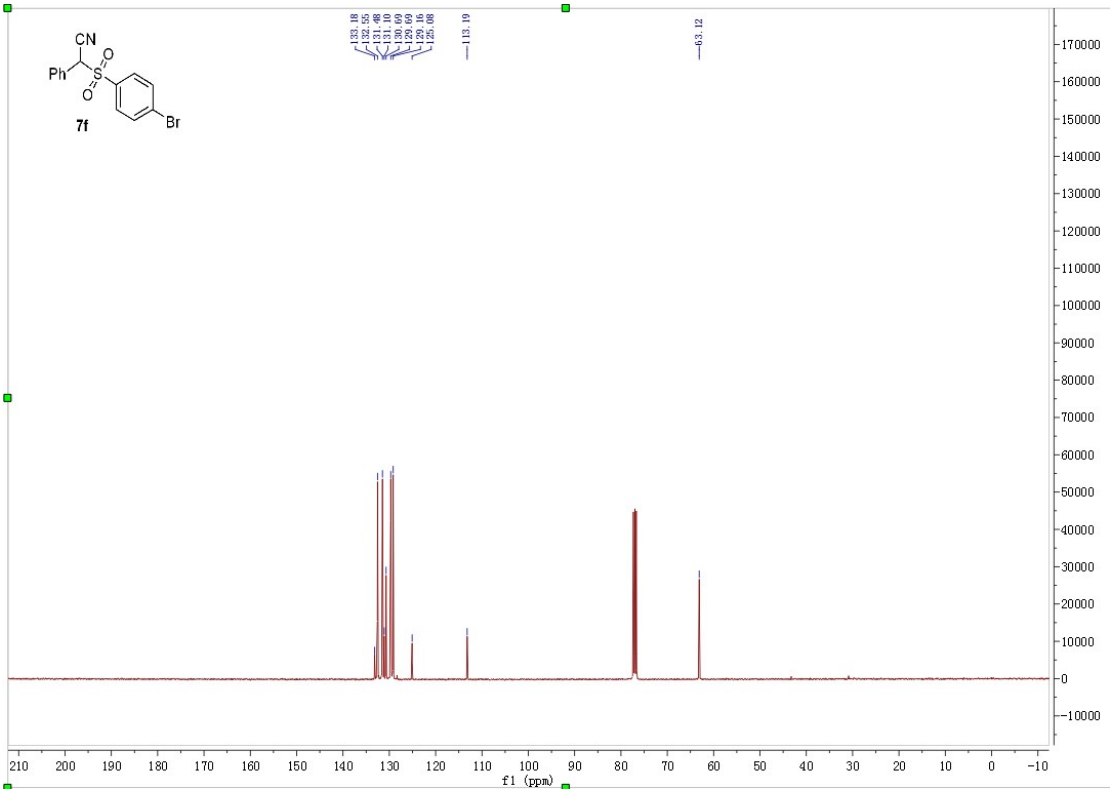

CN
Ph
O
O
S
7d
7.52
7.50
7.48
7.46
7.26
5.19
4.01
3.99
3.98
3.96
3.94
3.01
3.00
2.98
1.34
1.33
1.31
1.26
1.24
5.22
2.01
1.00
2.08
0.99
12.44
6.12
f1 (ppm)

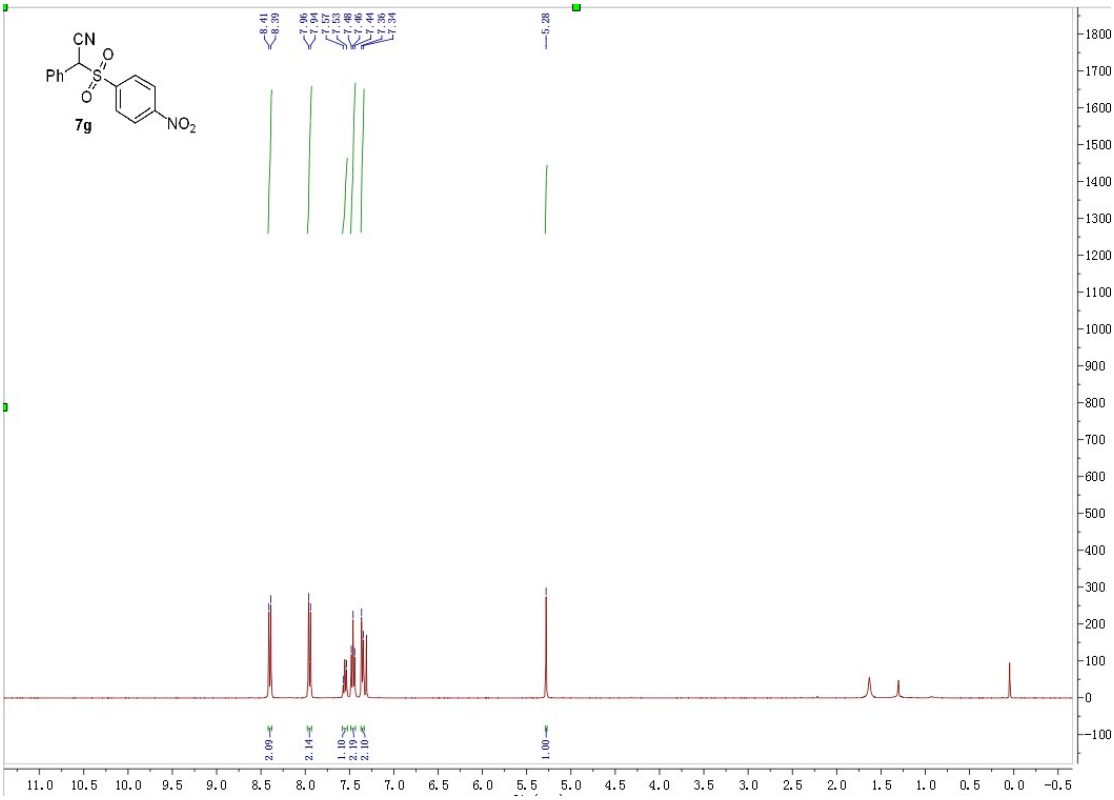

CN
Ph
O
O
S
7d
155.45
132.83
130.51
130.22
129.37
129.17
125.54
124.58
113.39
63.64
34.31
30.39
25.15
23.90
23.44
f1 (ppm)

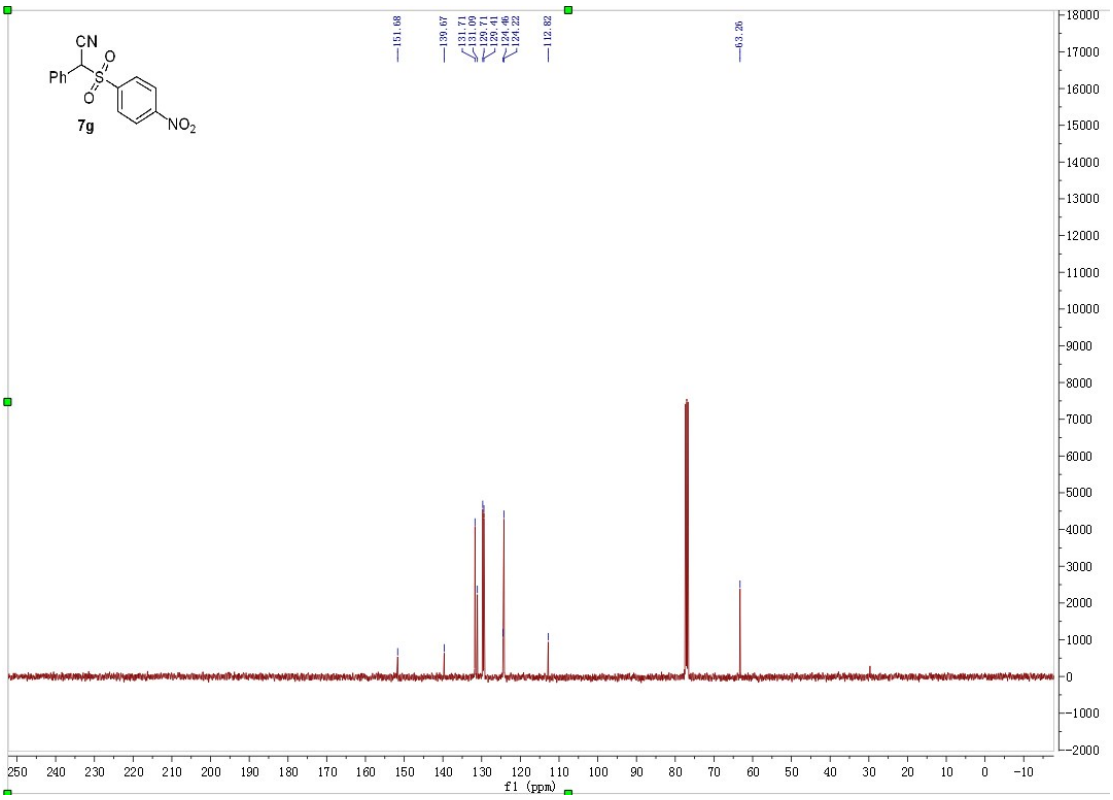

7e
7.75
7.73
7.60
7.58
7.56
7.52
7.50
7.46
7.42
7.40
7.39
7.09
7.07
5.23
4.02
2.01
1.05
2.15
2.10
2.12
1.00
3.12
f1 (ppm)

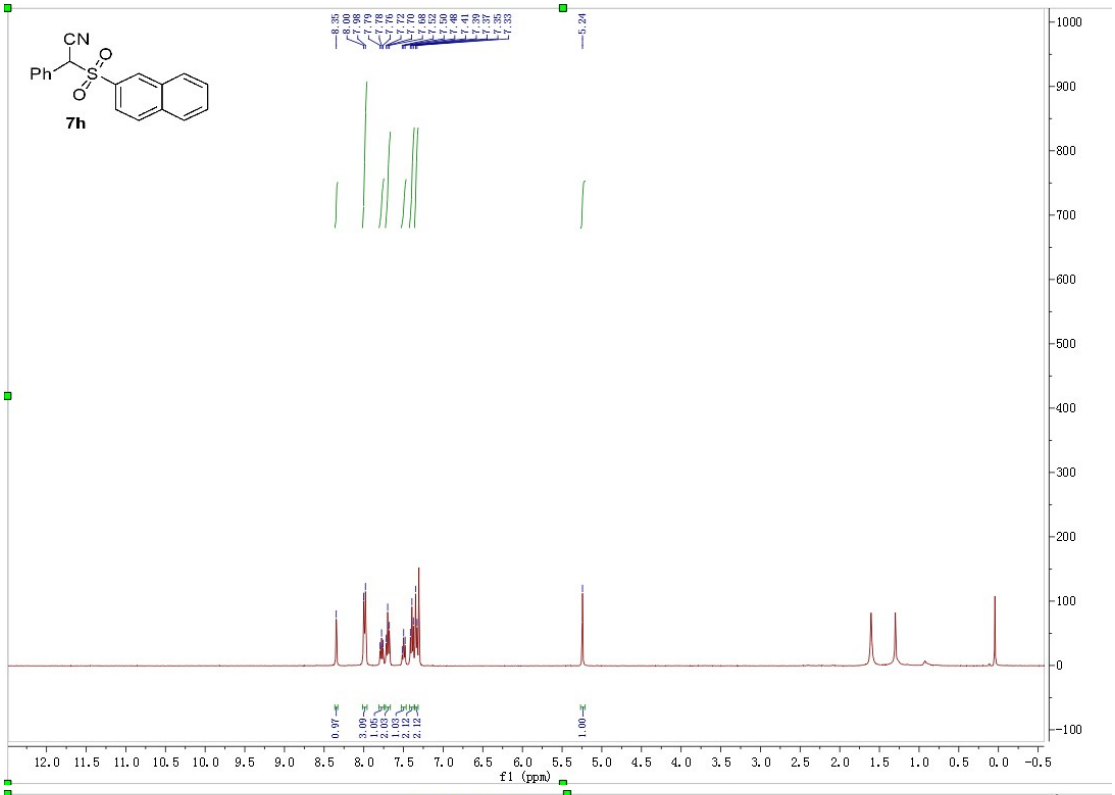

7e
165.12
132.55
130.49
130.42
129.08
125.93
125.69
114.48
113.75
63.37
55.90
f1 (ppm)

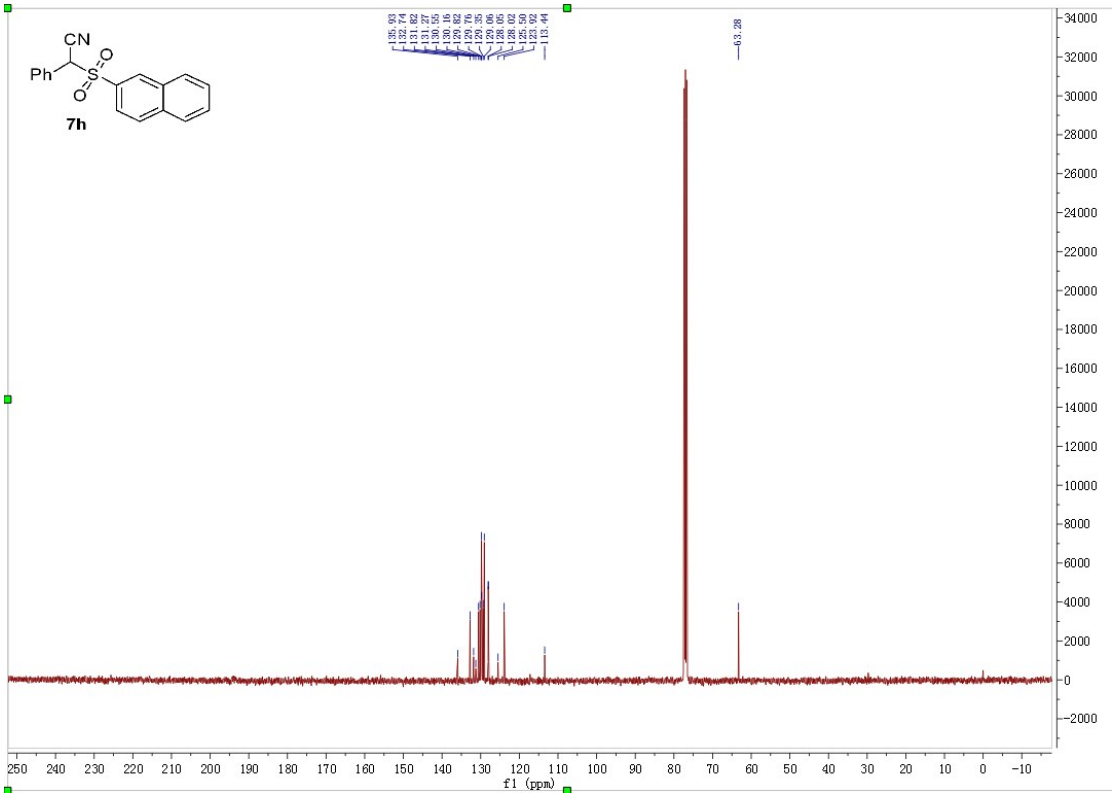

7f
7.72
7.70
7.69
7.68
7.53
7.52
7.50
7.46
7.43
7.42
7.35
7.33
5.20
2.01
2.09
2.17
2.11
2.04
1.00
f1 (ppm)

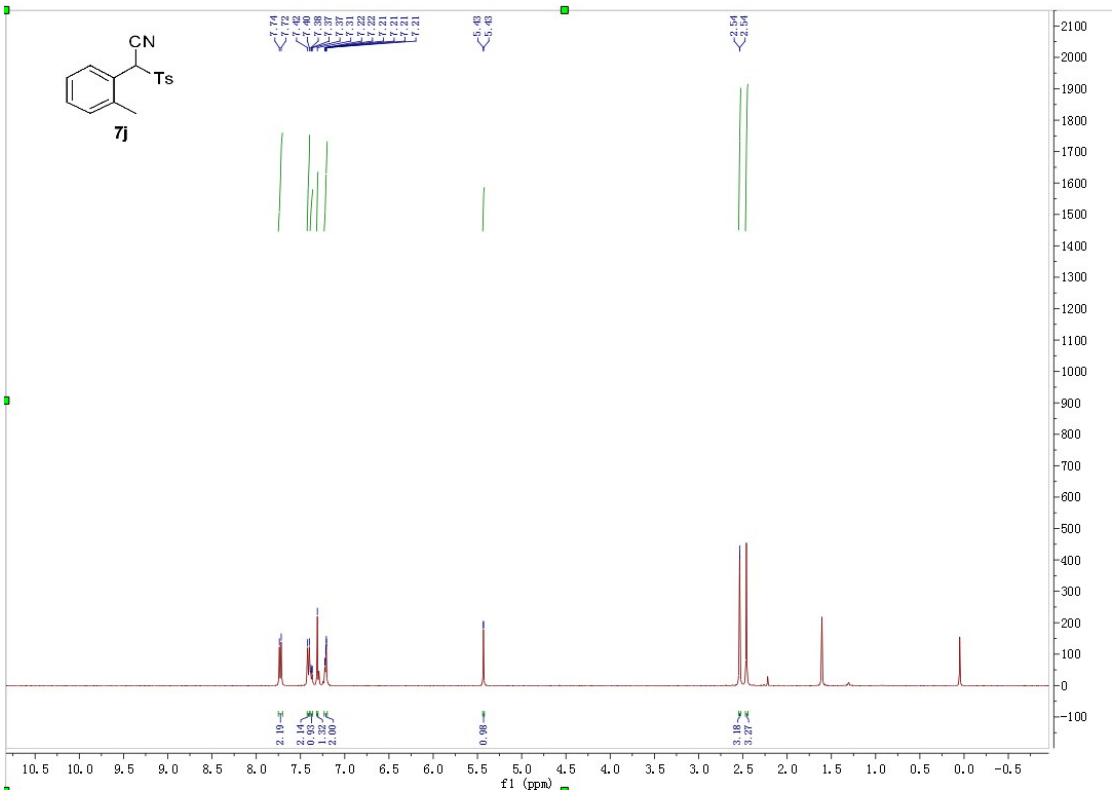

7f
133.18
132.55
131.46
131.10
130.69
129.69
129.16
125.08
113.19
63.12
f1 (ppm)

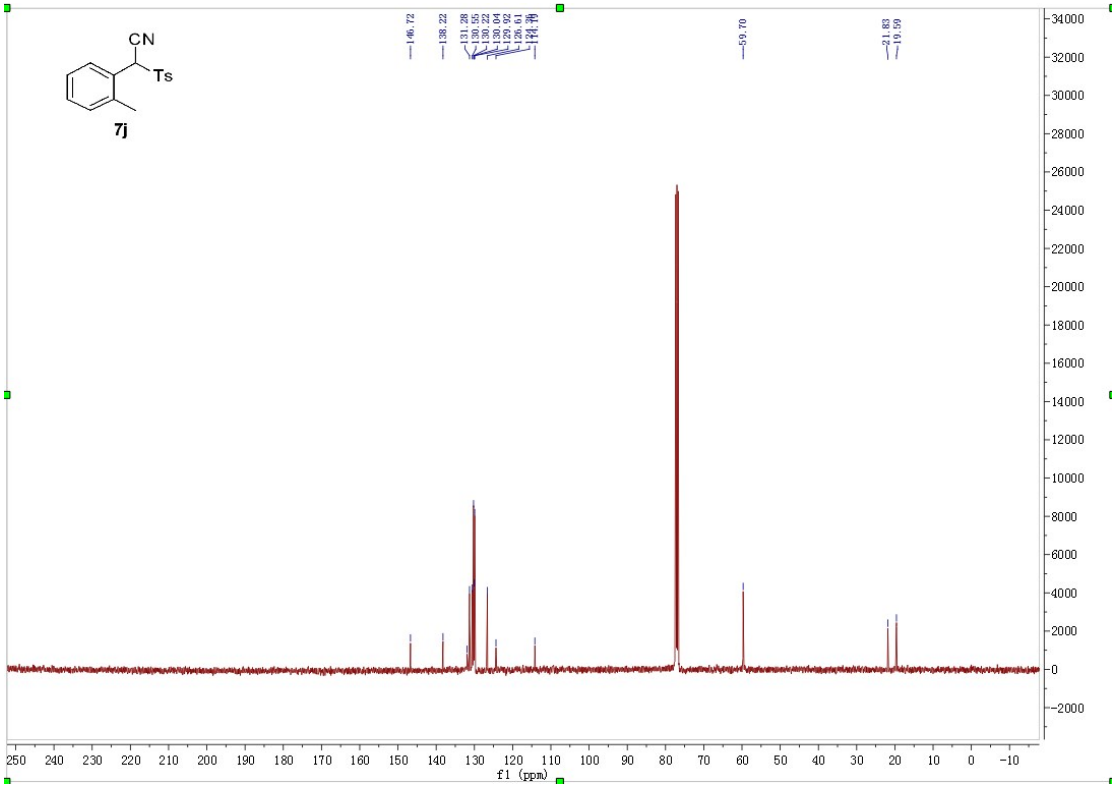

CN
Ph
O
O
S
O
NO2
7g
8.41
8.39
7.96
7.94
7.57
7.53
7.48
7.46
7.44
7.36
7.34
5.28
2.09
2.14
1.10
2.19
2.10
1.00

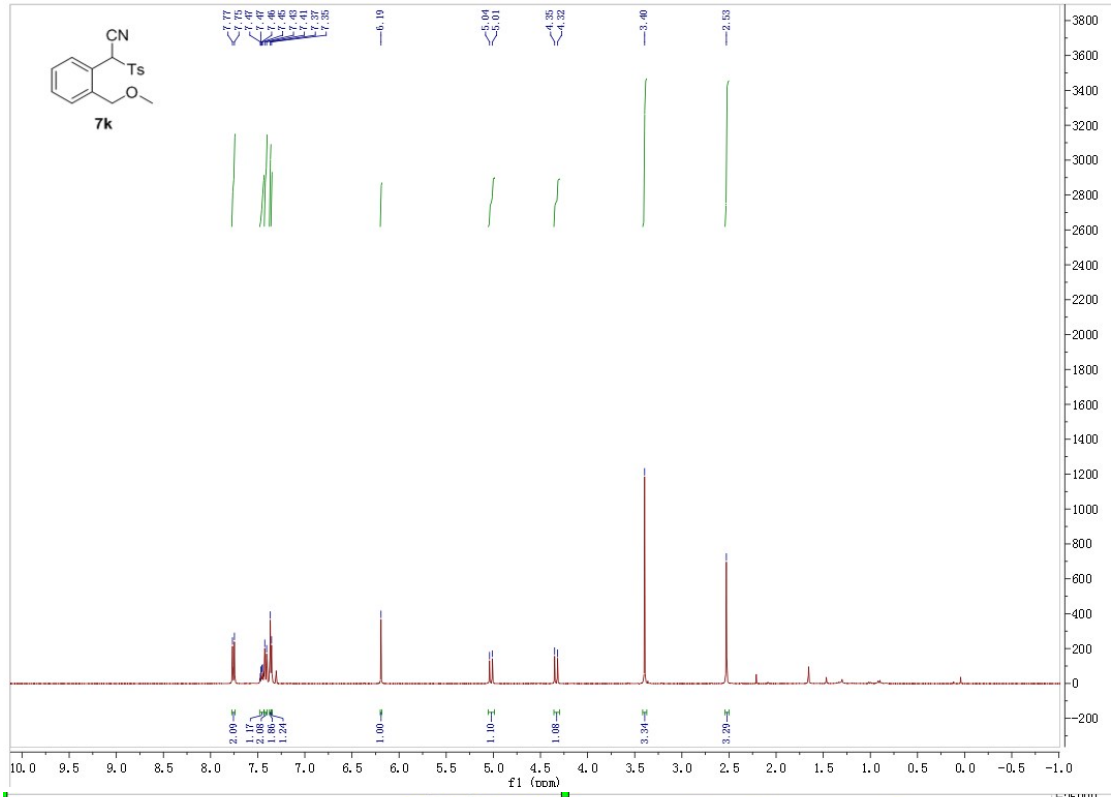

CN
Ph
O
O
S
O
NO2
7g
151.68
139.67
131.71
131.09
129.71
129.41
124.46
124.22
112.82
63.26
f1 (ppm)

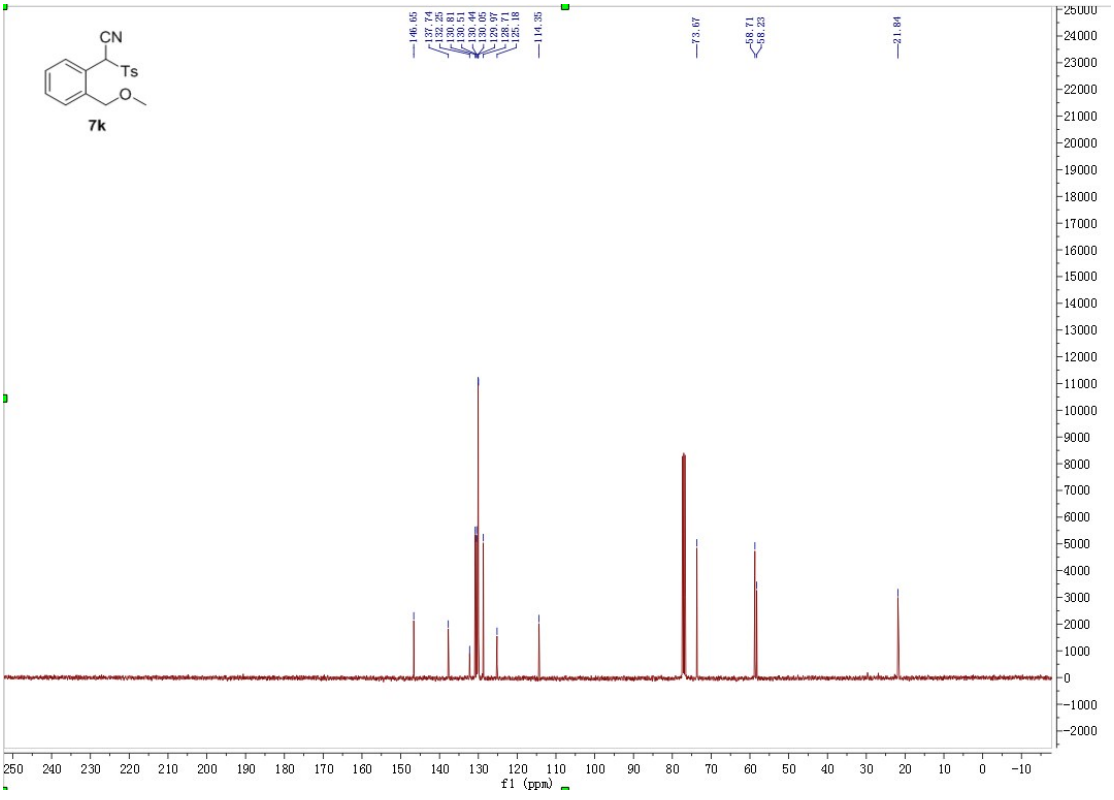

CN
Ph
O
S
O
7h
8.35
8.00
7.98
7.79
7.78
7.76
7.72
7.70
7.68
7.52
7.50
7.48
7.41
7.39
7.37
7.35
7.33
5.24
0.97
3.09
1.05
2.03
1.03
2.12
1.00
f1 (ppm)

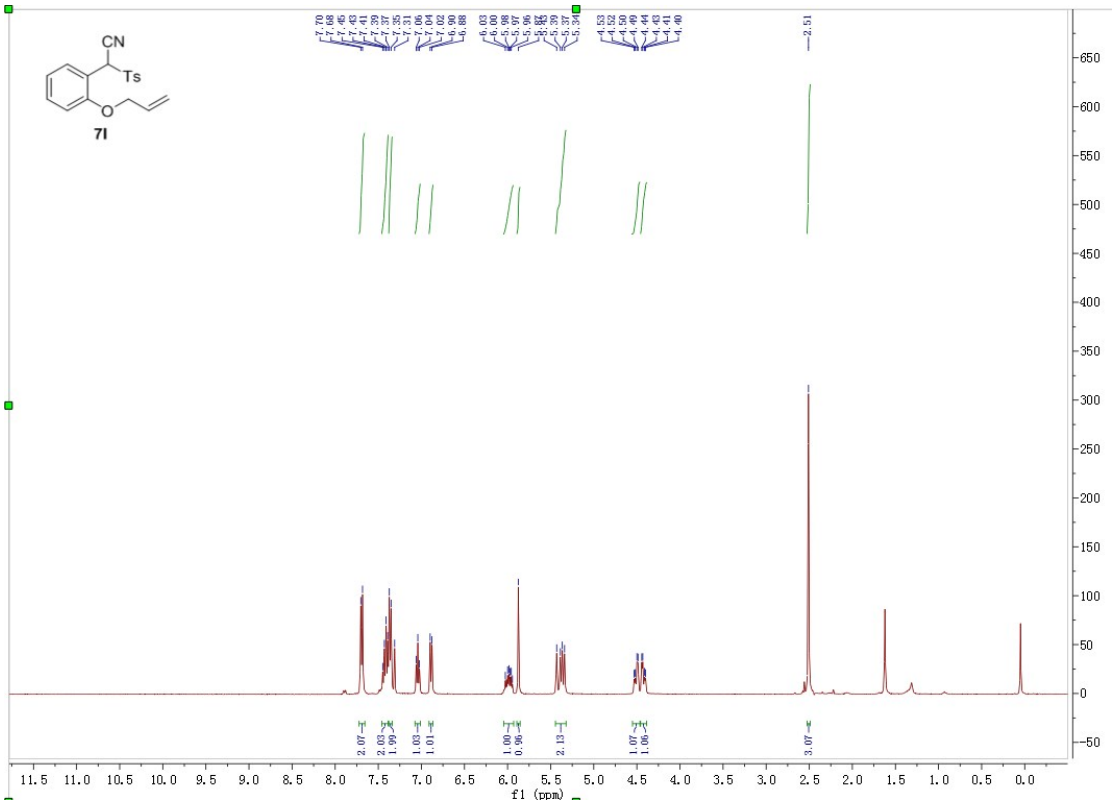

CN
Ph
O
S
O
7h
135.93
132.74
131.82
131.27
130.55
130.16
129.82
129.76
129.35
129.06
128.05
128.02
125.50
123.92
113.44
63.28
f1 (ppm)

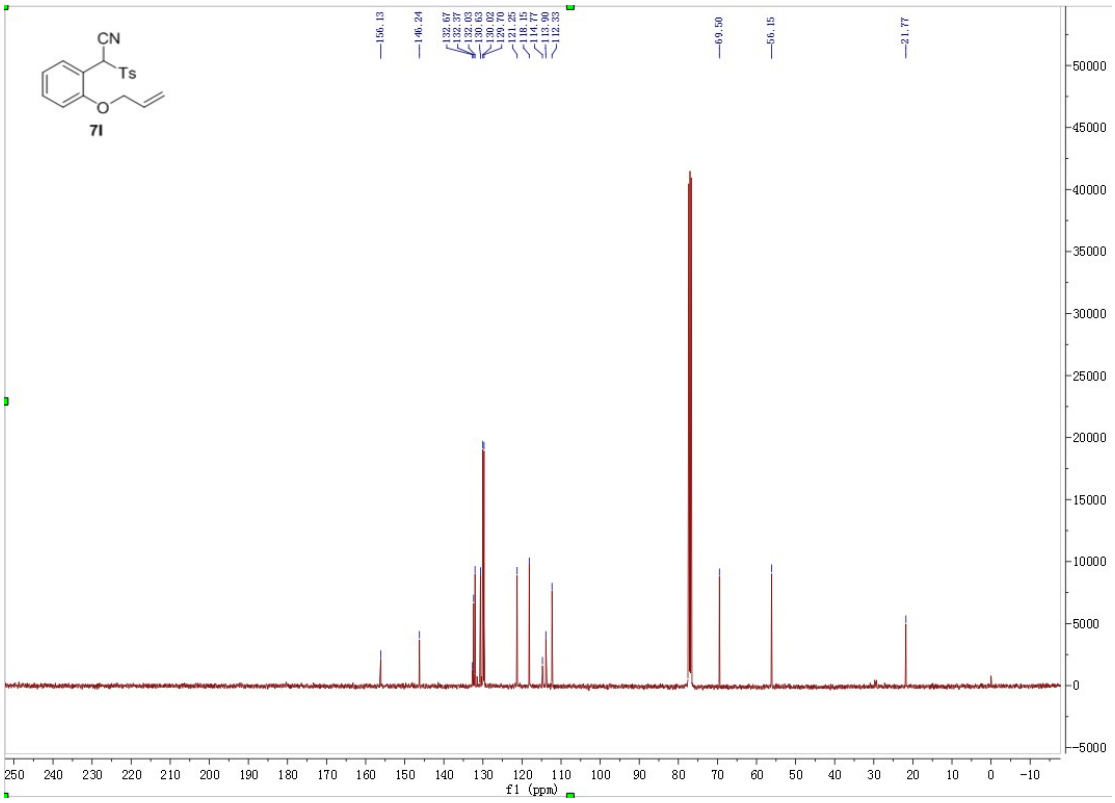

CN
Ts
7j
7.74
7.72
7.46
7.38
7.37
7.31
7.22
7.21
7.21
7.21
5.43
5.43
2.54
2.54
2.19
2.14
0.93
0.32
2.00
0.98
3.18
3.27
f1 (ppm)

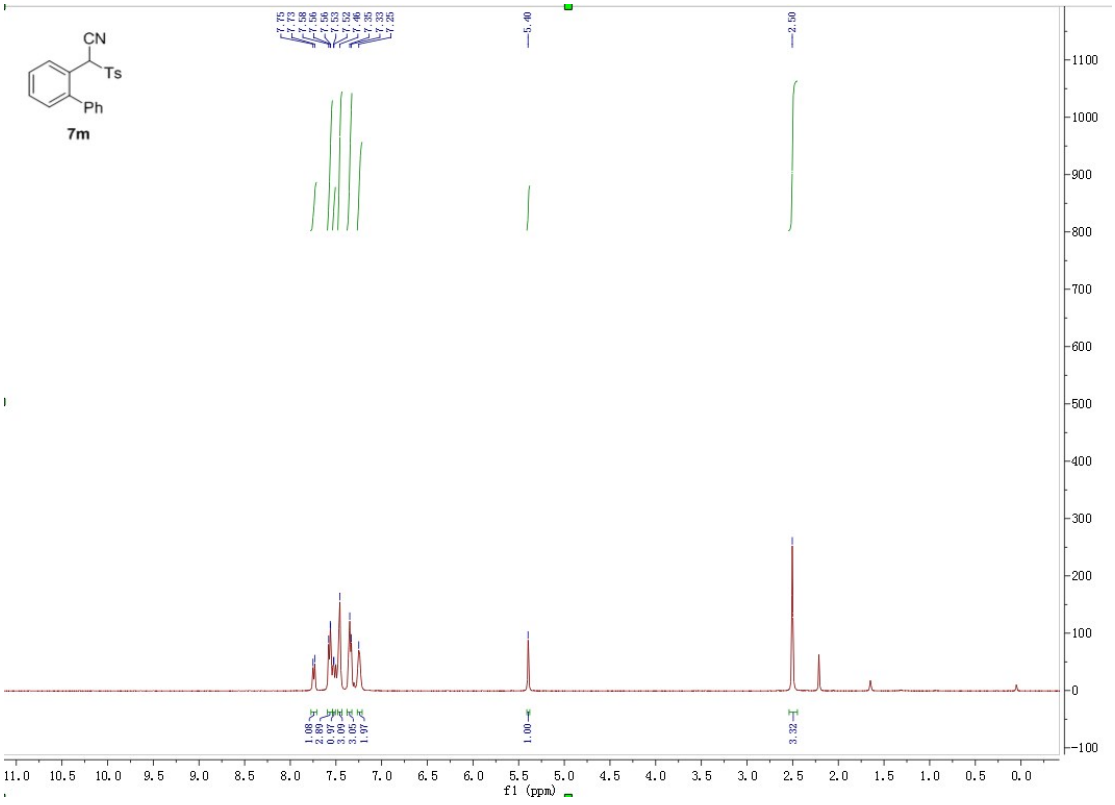

CN
Ts
7j
146.72
138.22
131.28
130.55
130.22
130.04
129.92
129.61
59.70
21.83
19.59
f1 (ppm)

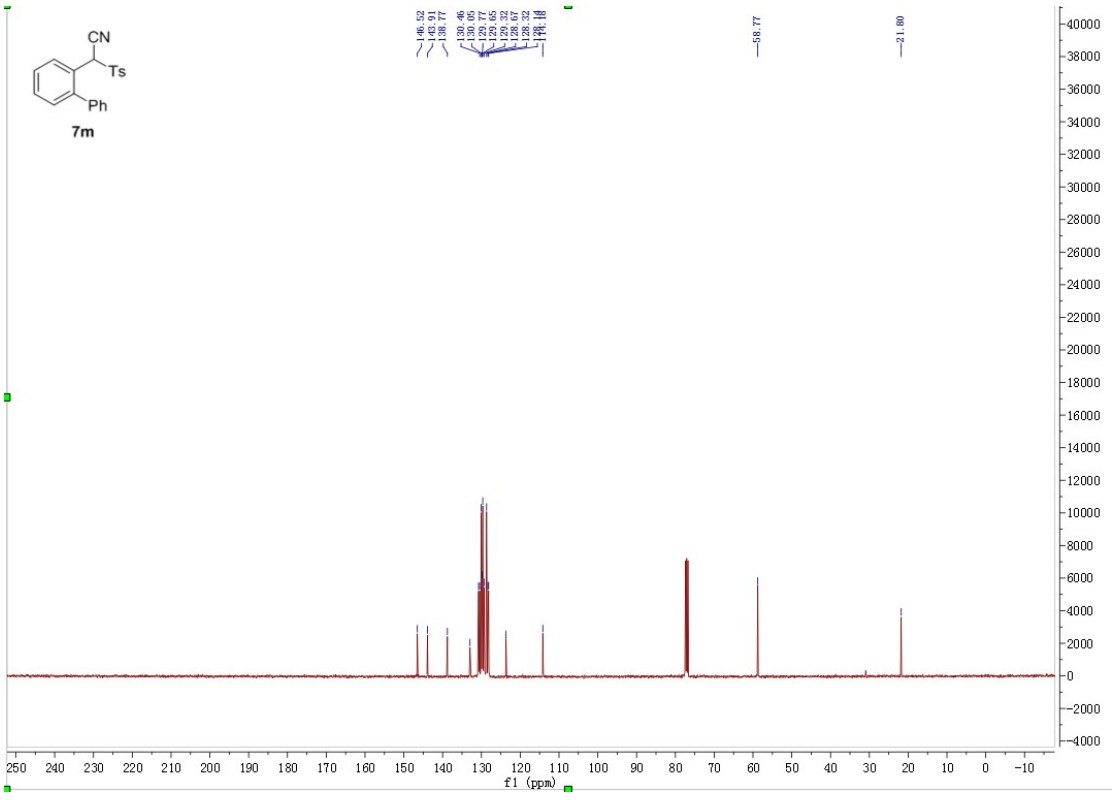

CN
Ts
O
7k
7.77
7.75
7.47
7.47
7.46
7.45
7.45
7.41
7.37
7.35
6.19
5.04
5.01
4.35
4.32
3.40
2.53
2.09
1.17
2.08
1.86
1.24
1.00
1.10
1.08
3.34
3.29
f1 (ppm)

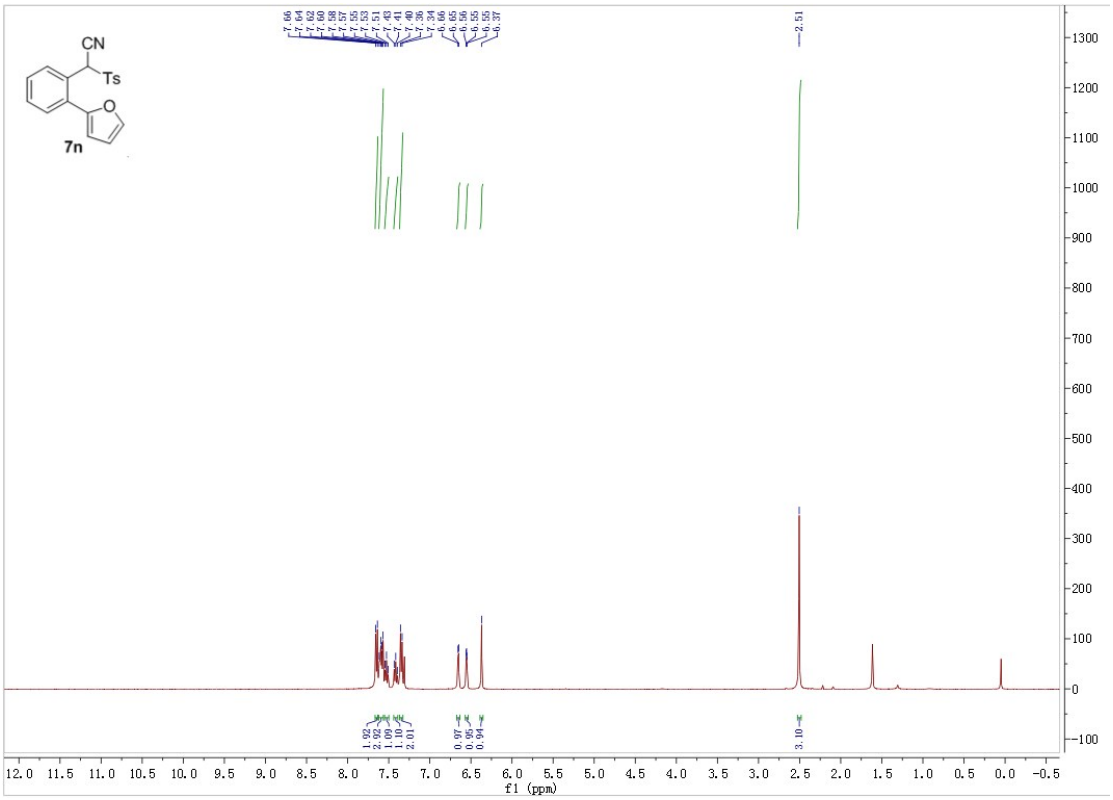

CN
Ts
O
7k
146.65
137.74
132.25
130.81
130.53
130.44
130.05
129.97
128.71
125.18
114.35
73.67
68.71
68.23
21.84
f1 (ppm)

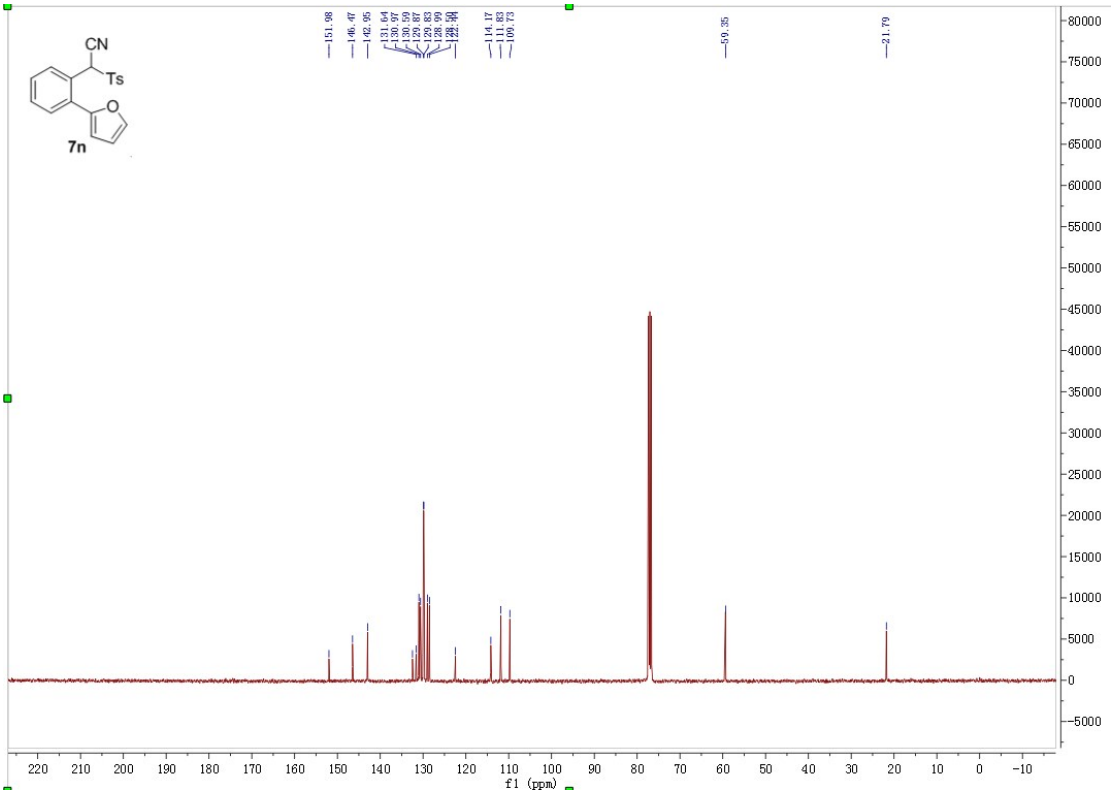

CN
Ts
O
7l
7.70
7.68
7.45
7.43
7.41
7.39
7.37
7.35
7.31
7.06
7.04
7.02
6.98
6.96
6.00
5.98
5.97
5.96
5.39
5.34
4.53
4.52
4.50
4.49
4.43
4.41
4.40
2.51
2.07
2.03
1.99
1.03
1.01
1.00
0.96
2.13
1.07
1.06
3.07
f1 (ppm)

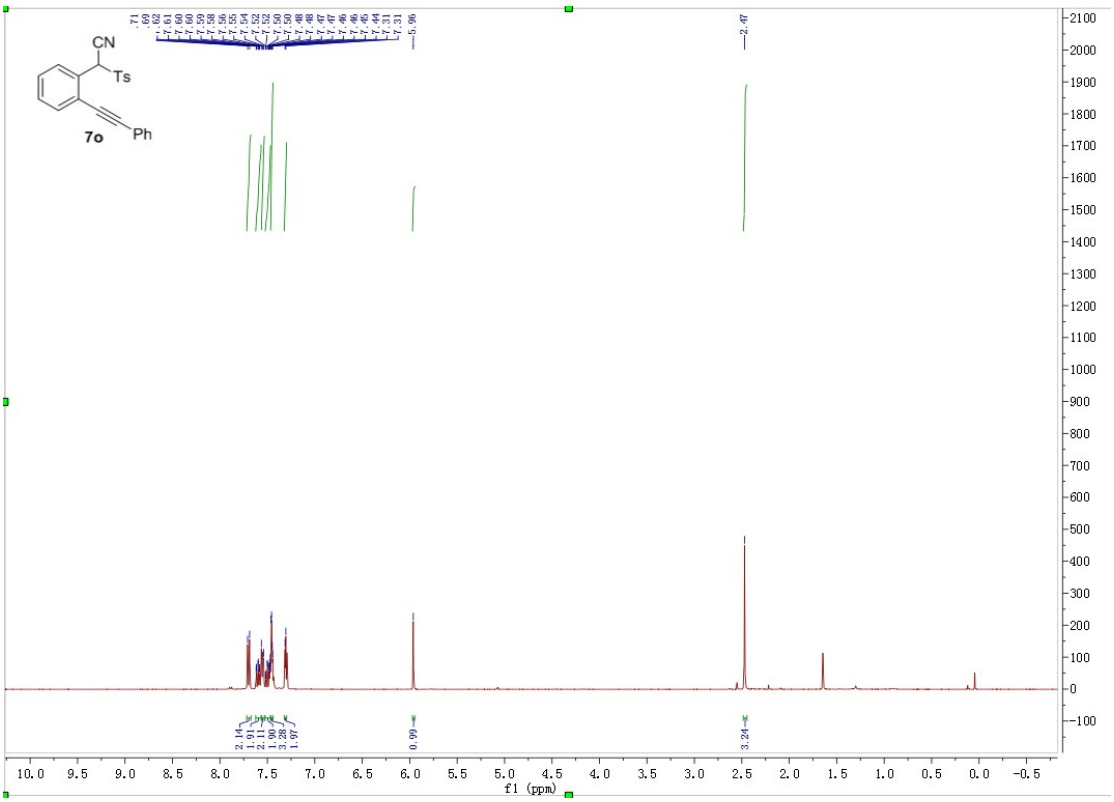

CN
Ts
O
7l
156.13
146.24
132.67
132.37
132.03
130.63
130.02
129.70
121.25
118.15
114.77
113.90
112.33
69.50
56.15
21.77
f1 (ppm)

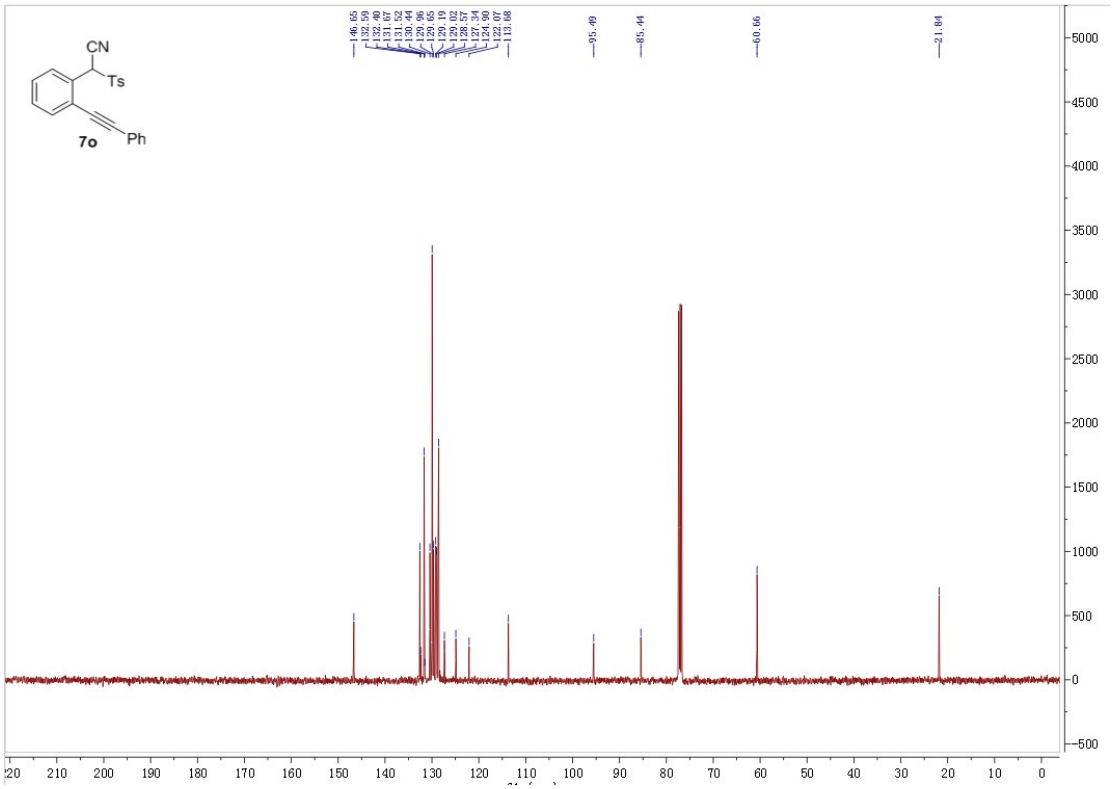

CN
Ts
Ph
7m
f1 (ppm)

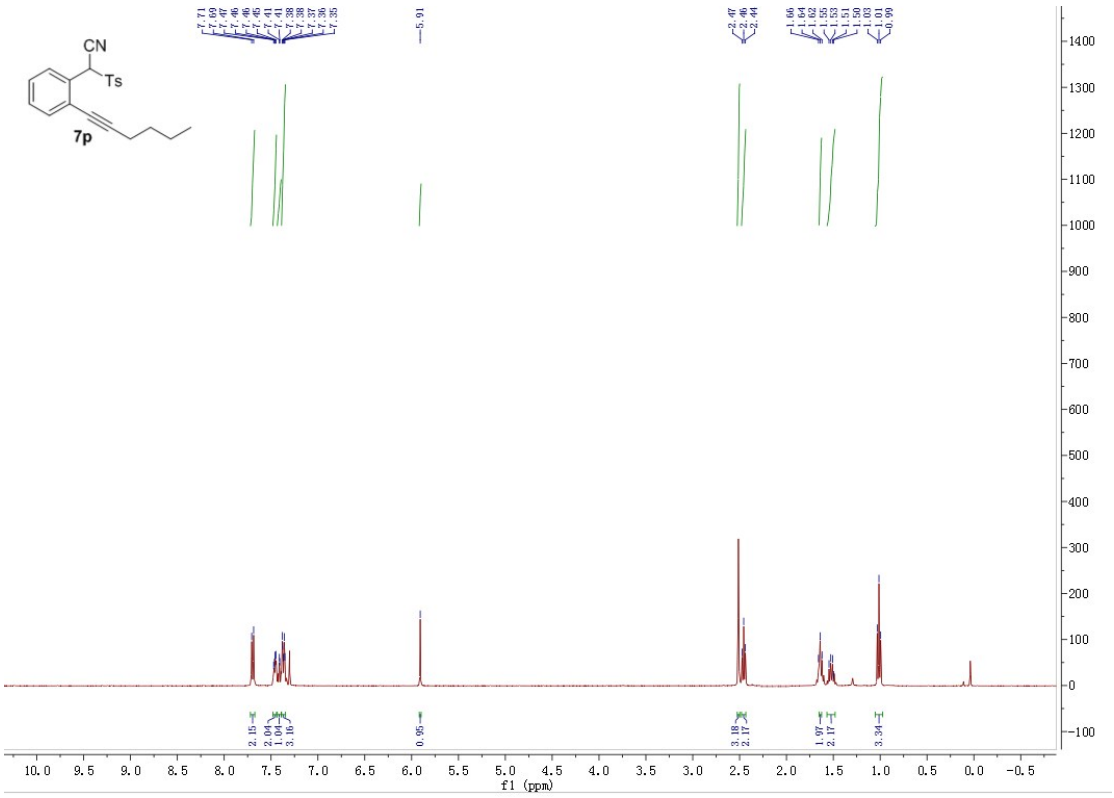

CN
Ts
Ph
7m
f1 (ppm)

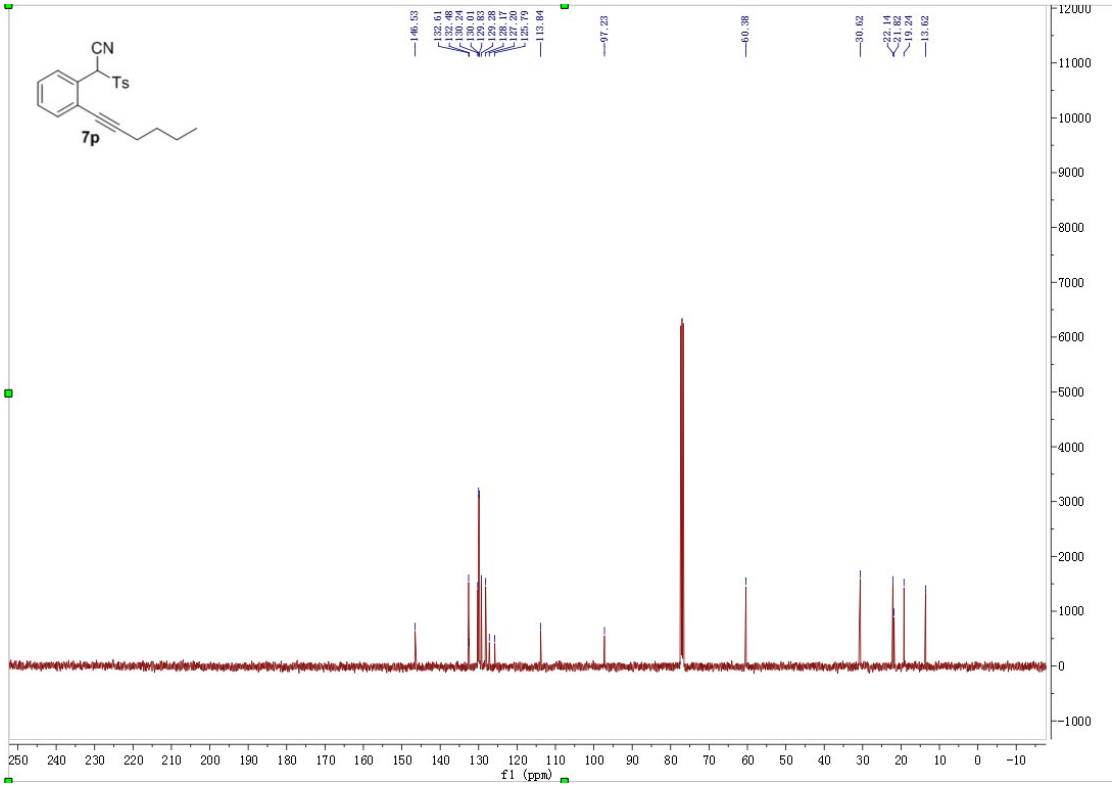

CN
Ts
O
7n
7.66
7.64
7.62
7.60
7.58
7.57
7.55
7.53
7.51
7.43
7.41
7.40
7.38
7.36
6.66
6.65
5.56
5.55
5.55
5.37
2.51
1.92
1.92
1.09
1.10
2.01
0.97
0.95
0.94
3.10
f1 (ppm)

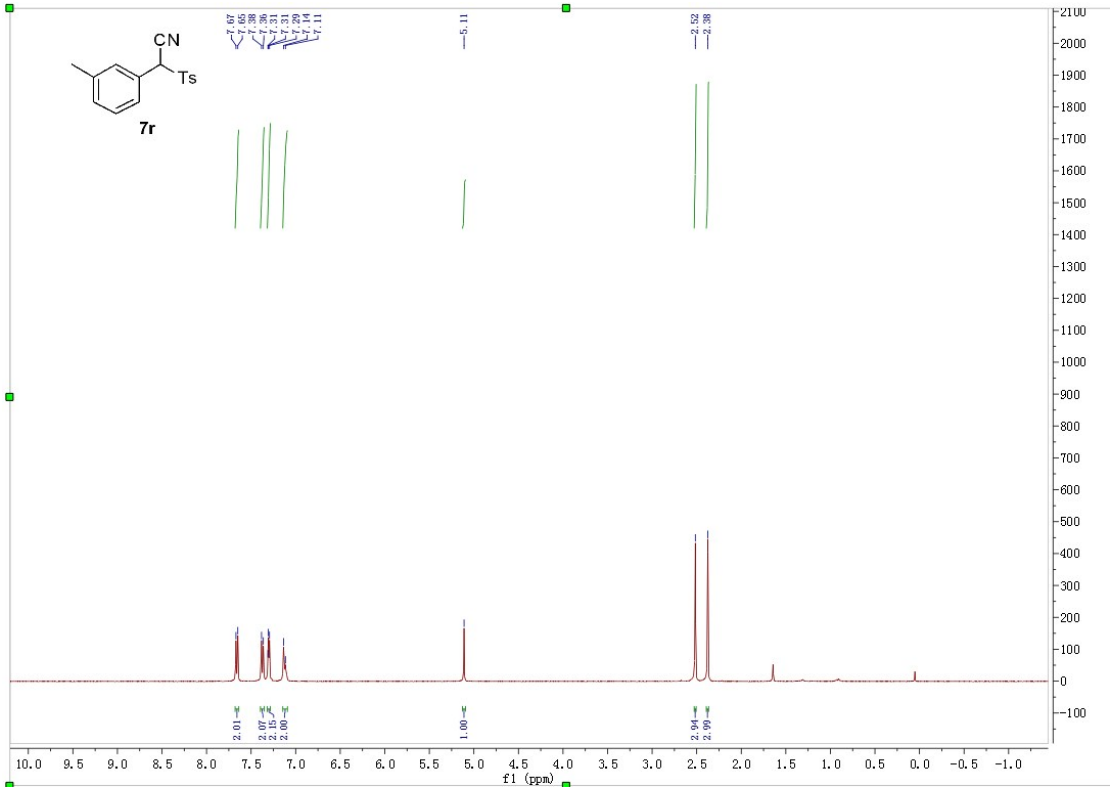

CN
Ts
O
7n
151.98
146.47
142.95
131.64
130.97
130.59
129.87
129.83
128.99
114.17
111.83
109.73
59.35
21.79
f1 (ppm)

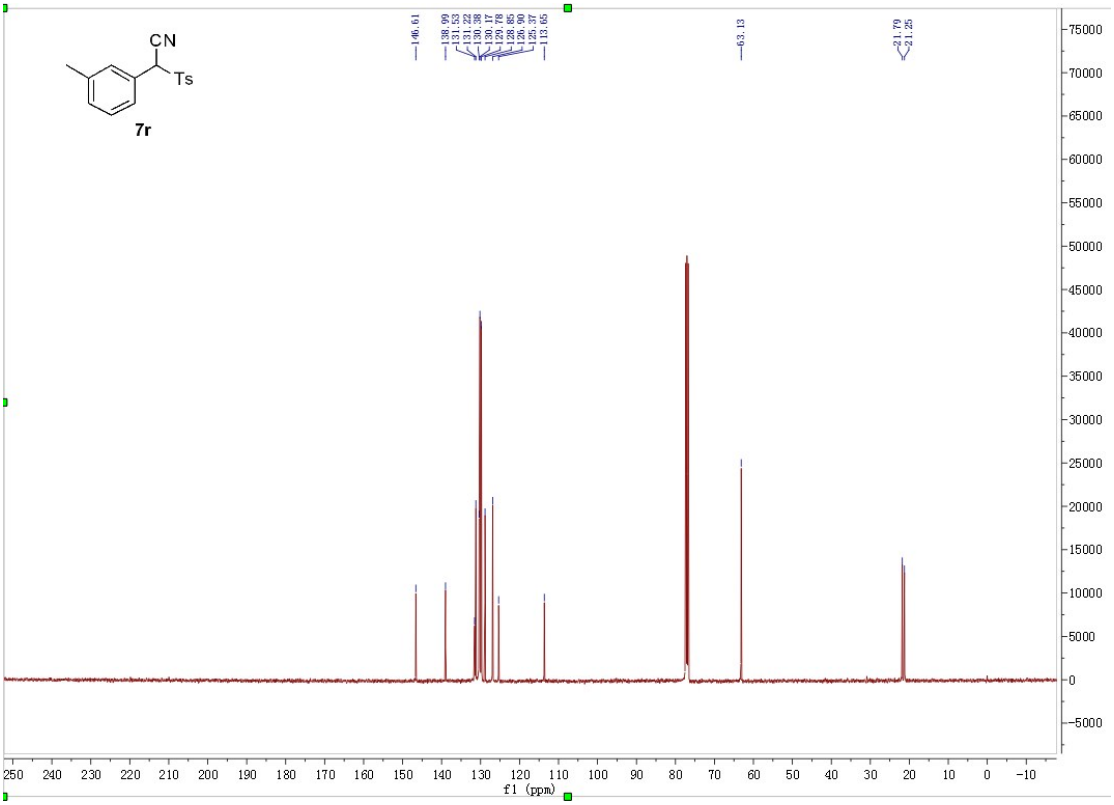

CN
Ts
Ph
7o
f1 (ppm)

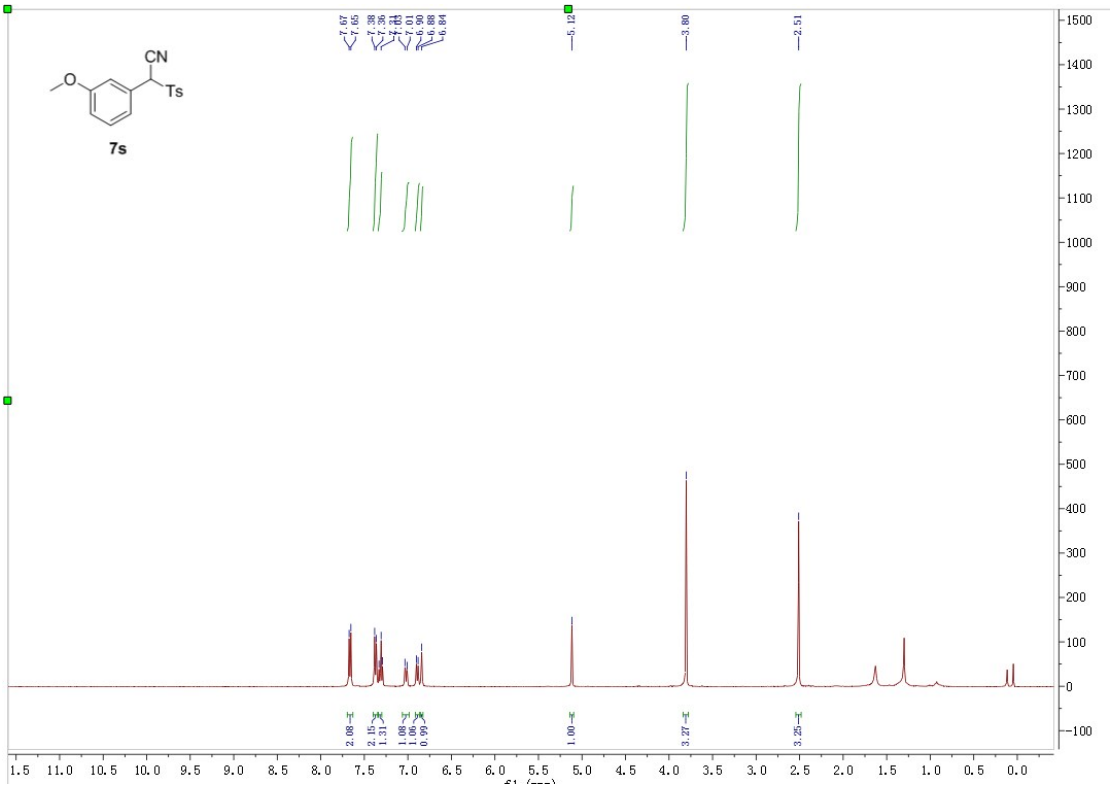

CN
Ts
Ph
7o

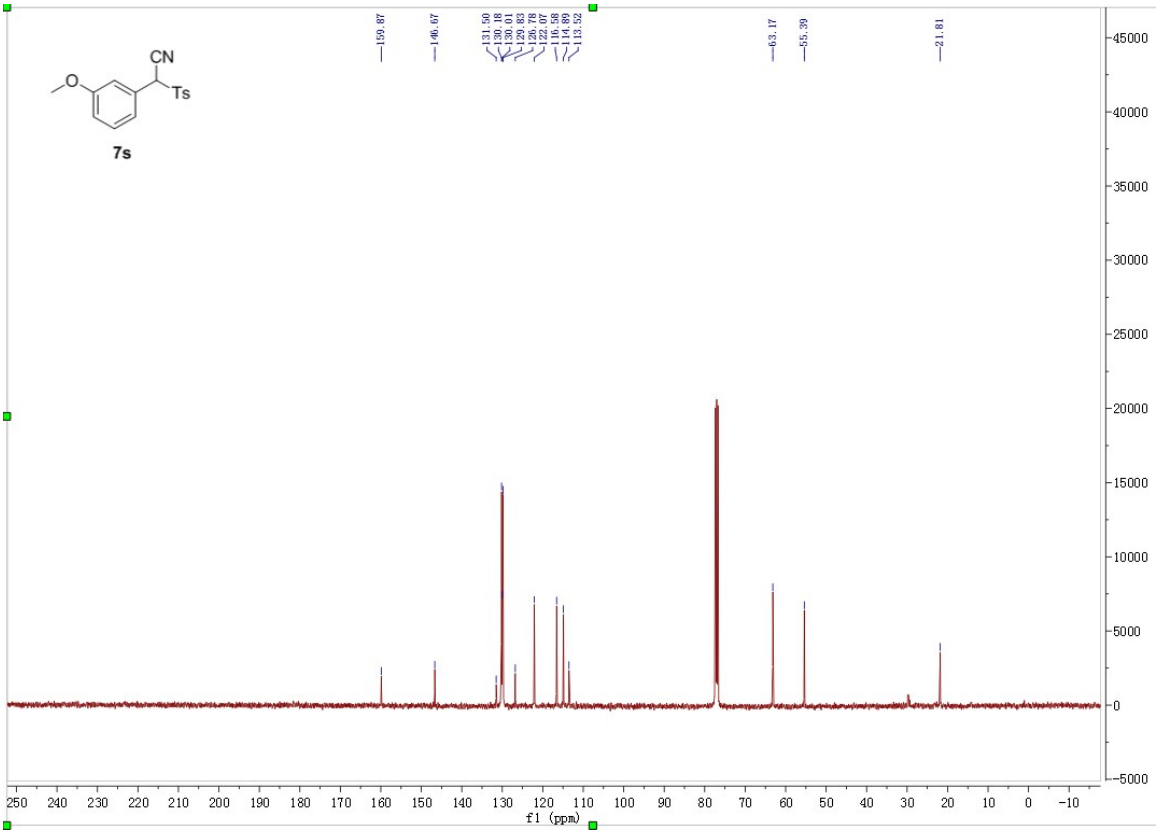

CN
Ts
7p
f1 (ppm)

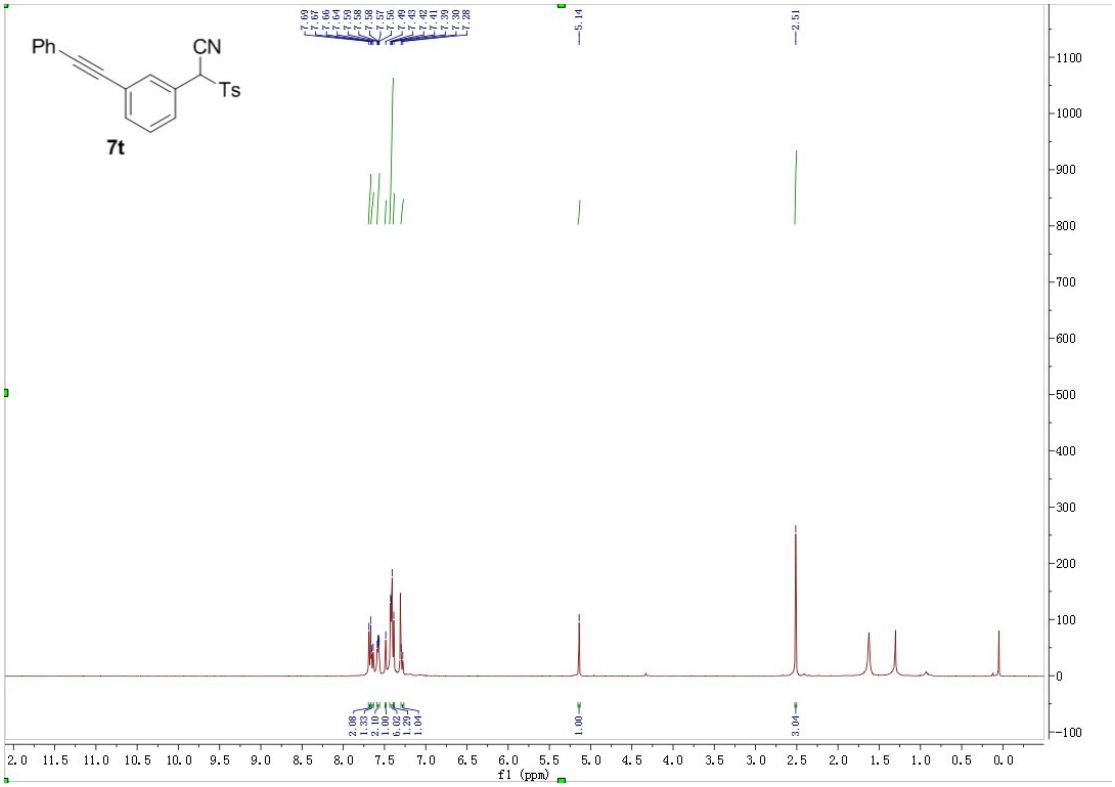

CN
Ts
7p
f1 (ppm)

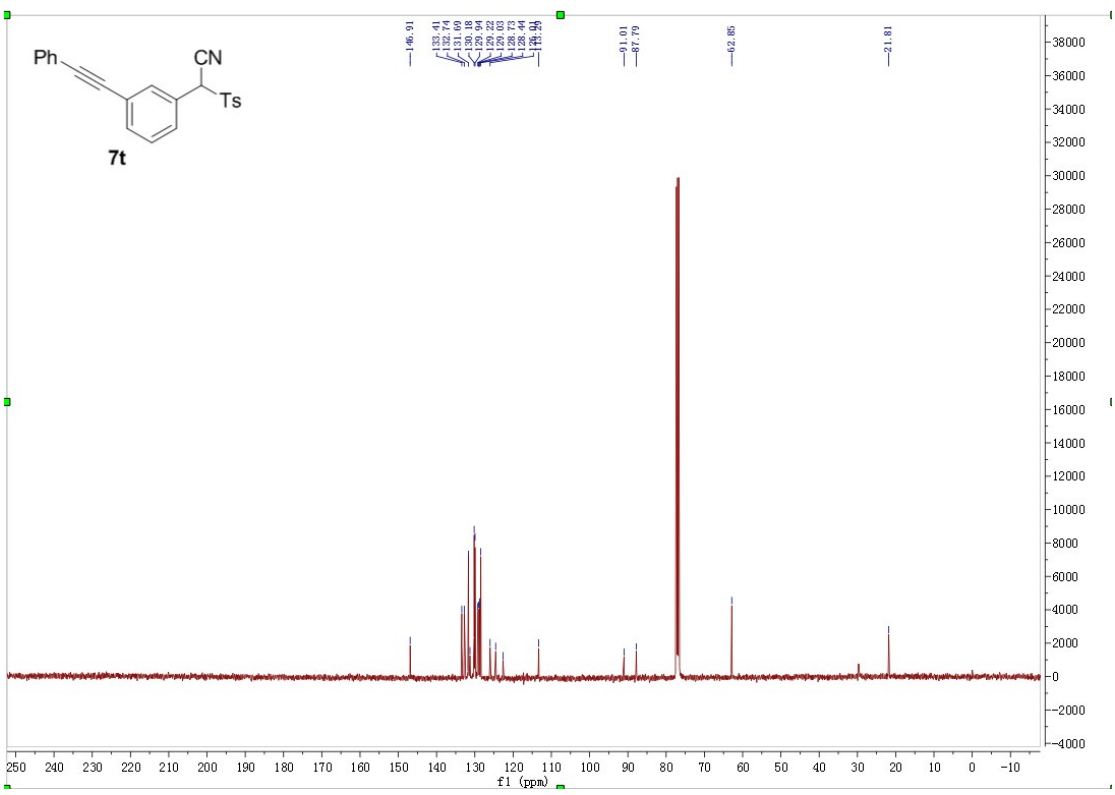

CN
Ts
7r
7.67
7.65
7.38
7.36
7.31
7.29
7.14
7.11
5.11
2.52
2.38
2.01
2.07
2.15
2.00
1.00
2.94
2.99
f1 (ppm)

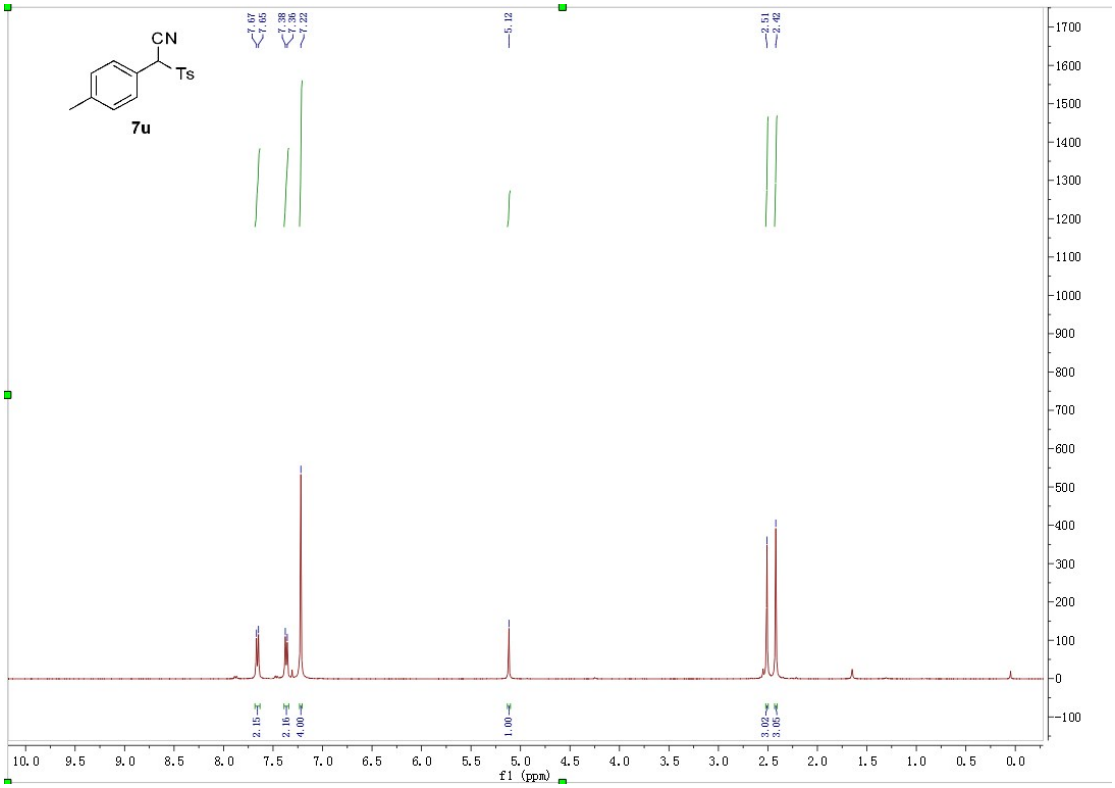

CN
Ts
7r
146.61
138.99
131.53
131.22
130.38
130.17
129.78
128.85
126.90
126.37
113.65
63.13
21.79
21.25
f1 (ppm)

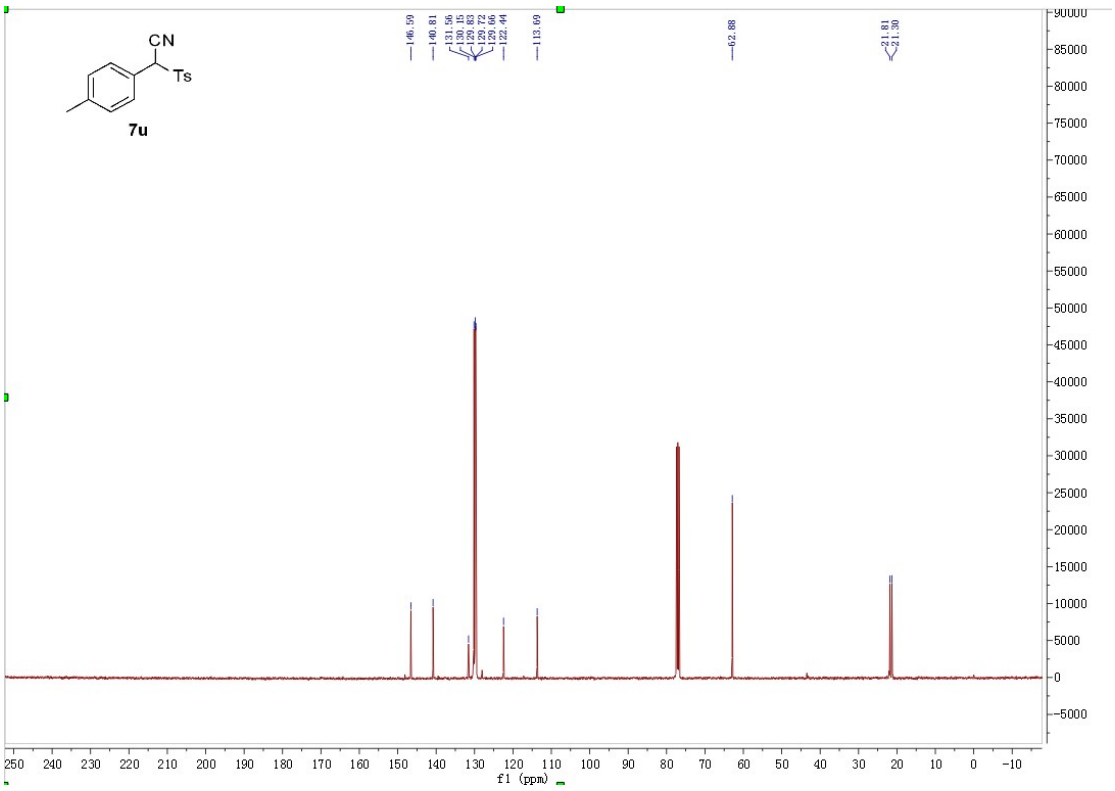

CN
Ts
O
7s
7.67
7.65
7.38
7.36
7.04
7.01
6.89
6.88
6.84
5.12
3.80
2.51
2.08
2.15
1.31
1.08
1.06
0.99
1.00
3.27
3.25

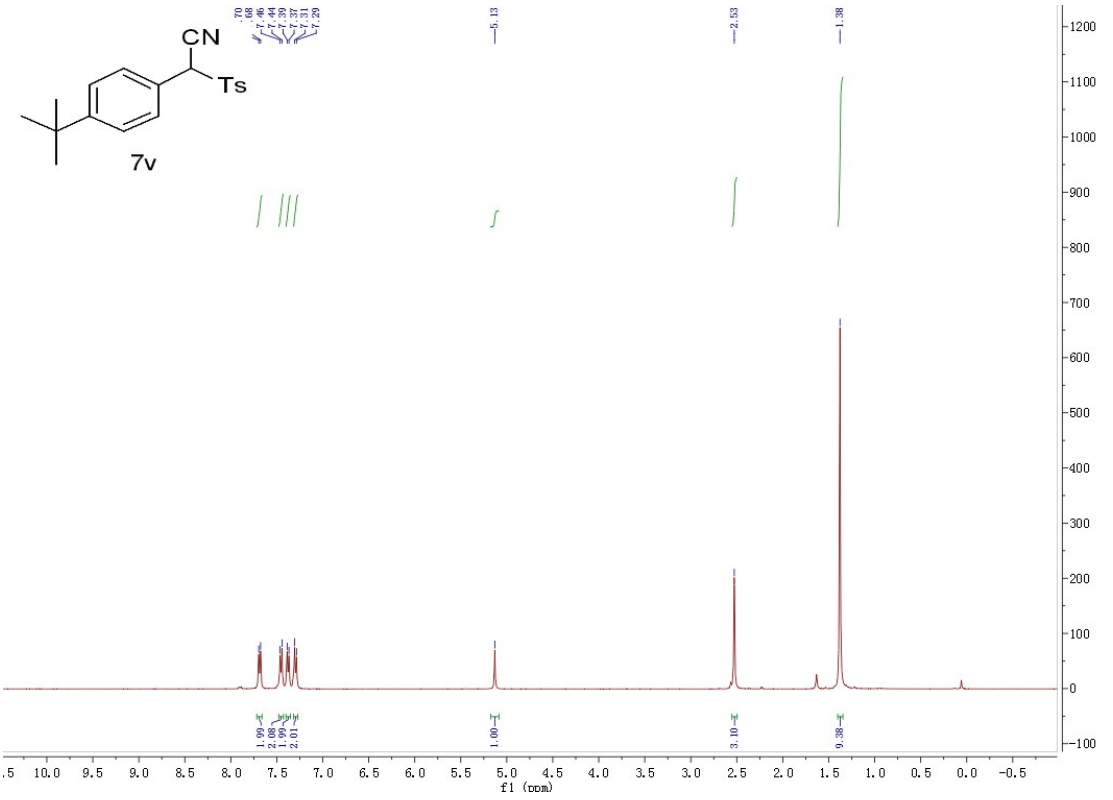

CN
Ts
O
7s
159.87
146.67
131.50
130.18
130.01
129.83
126.79
122.07
116.58
114.89
113.52
63.17
55.39
21.81
f1 (ppm)

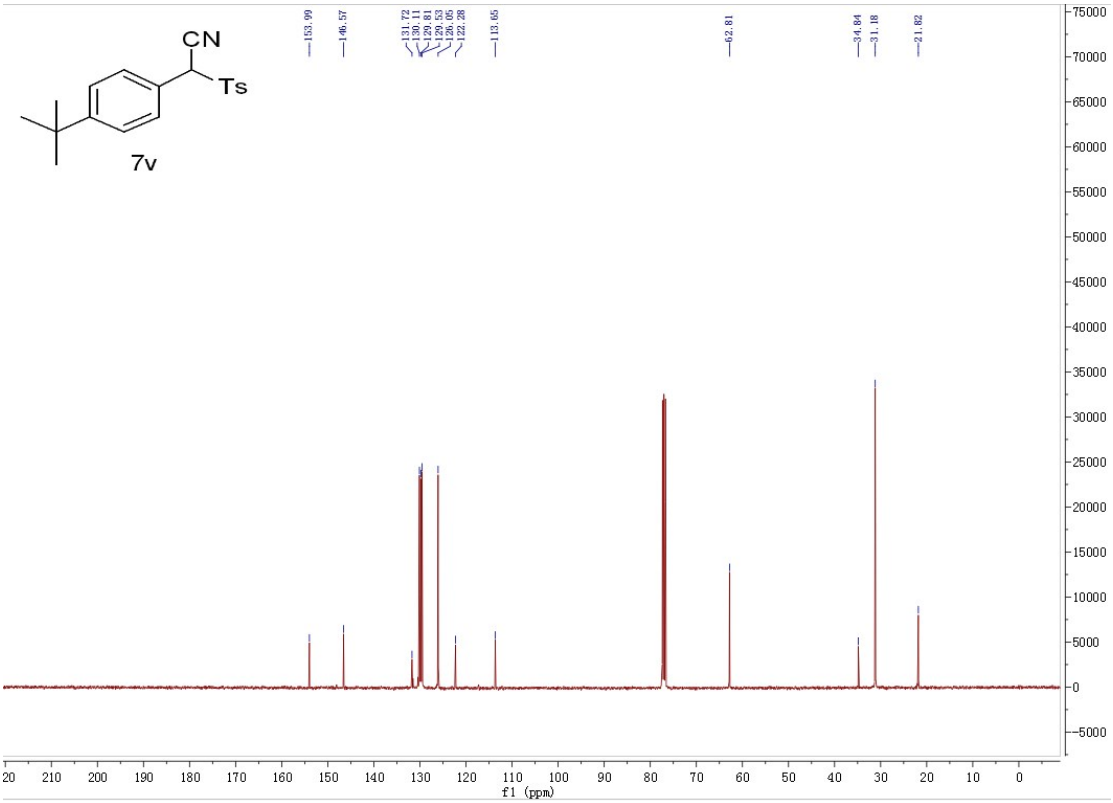

Ph
CN
Ts
7t
7.69
7.67
7.66
7.65
7.59
7.58
7.57
7.56
7.49
7.43
7.42
7.41
7.39
7.30
7.28
5.14
2.51
2.08
2.33
2.10
1.00
6.02
2.01
1.04
1.00
3.04
f1 (ppm)

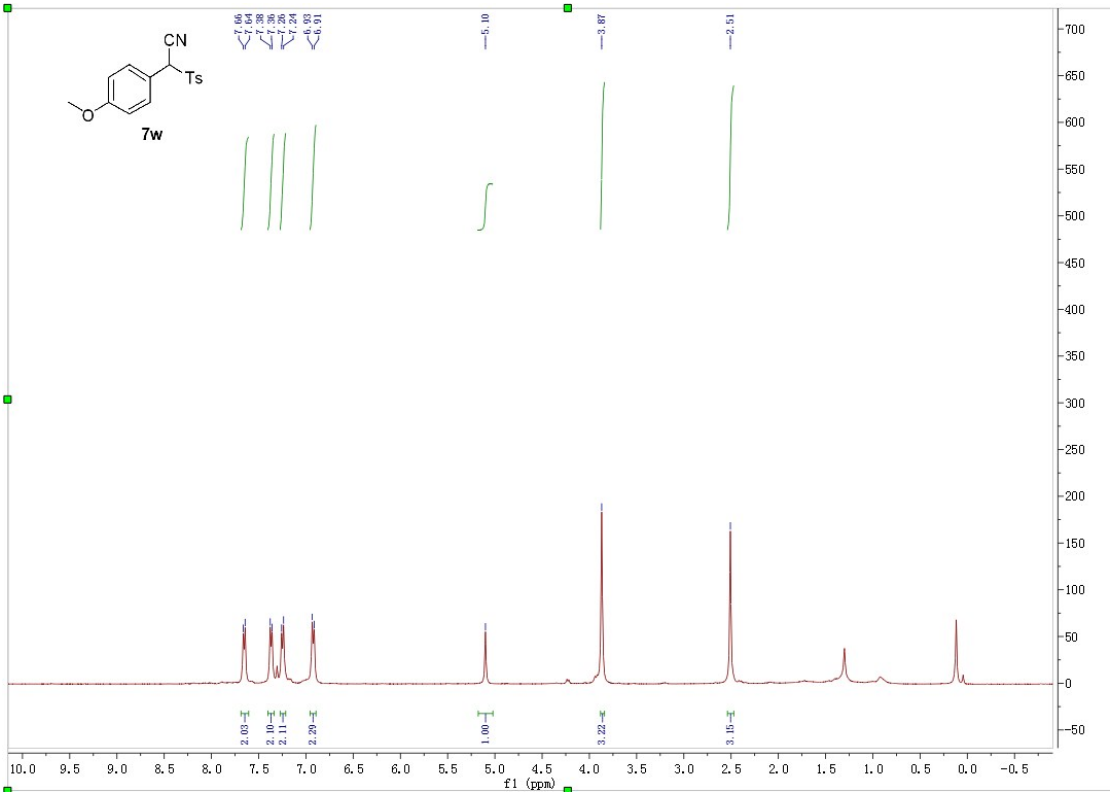

Ph
CN
Ts
7t
146.91
133.41
132.74
131.69
130.18
129.94
129.22
129.03
128.73
128.44
91.01
87.79
62.85
21.81
f1 (ppm)

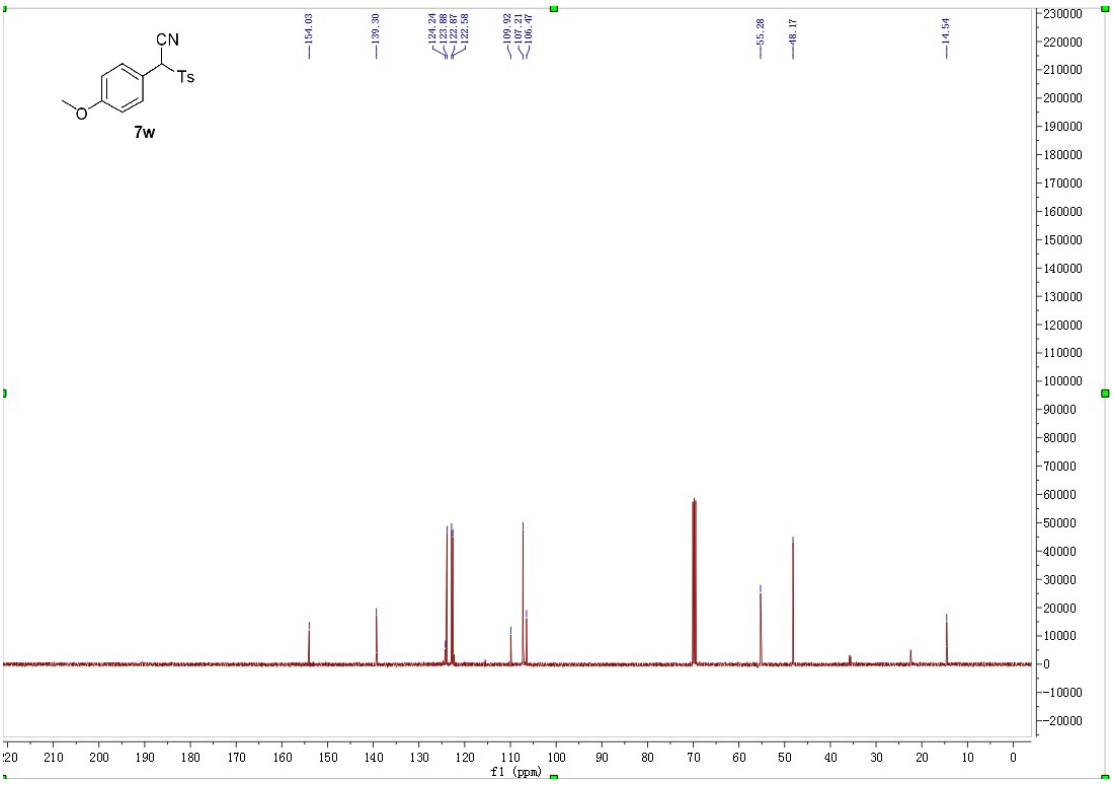

CN
Ts
7u
7.67
7.65
7.38
7.36
7.22
5.12
2.51
2.42
2.15
2.16
4.00
1.00
3.02
3.05
f1 (ppm)

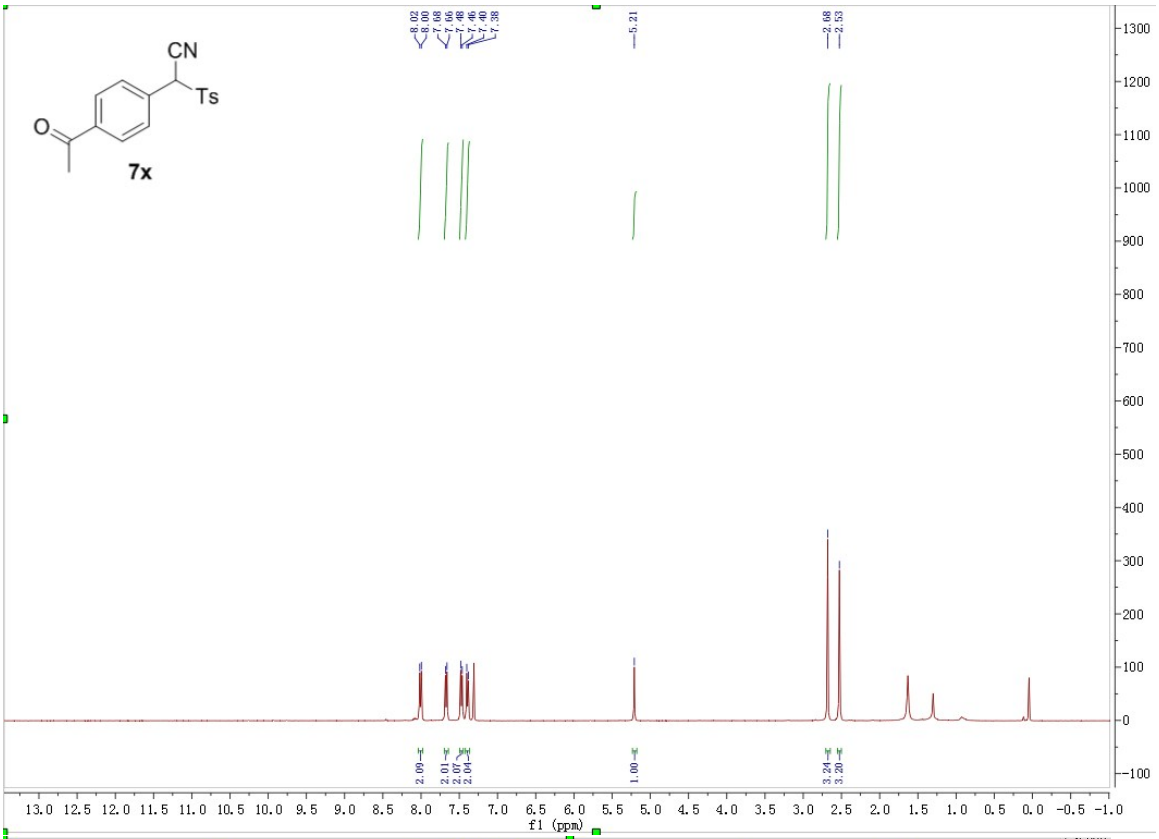

CN
Ts
7u
146.59
140.81
131.56
130.15
129.83
129.72
129.66
122.44
113.69
62.88
21.81
21.30
f1 (ppm)

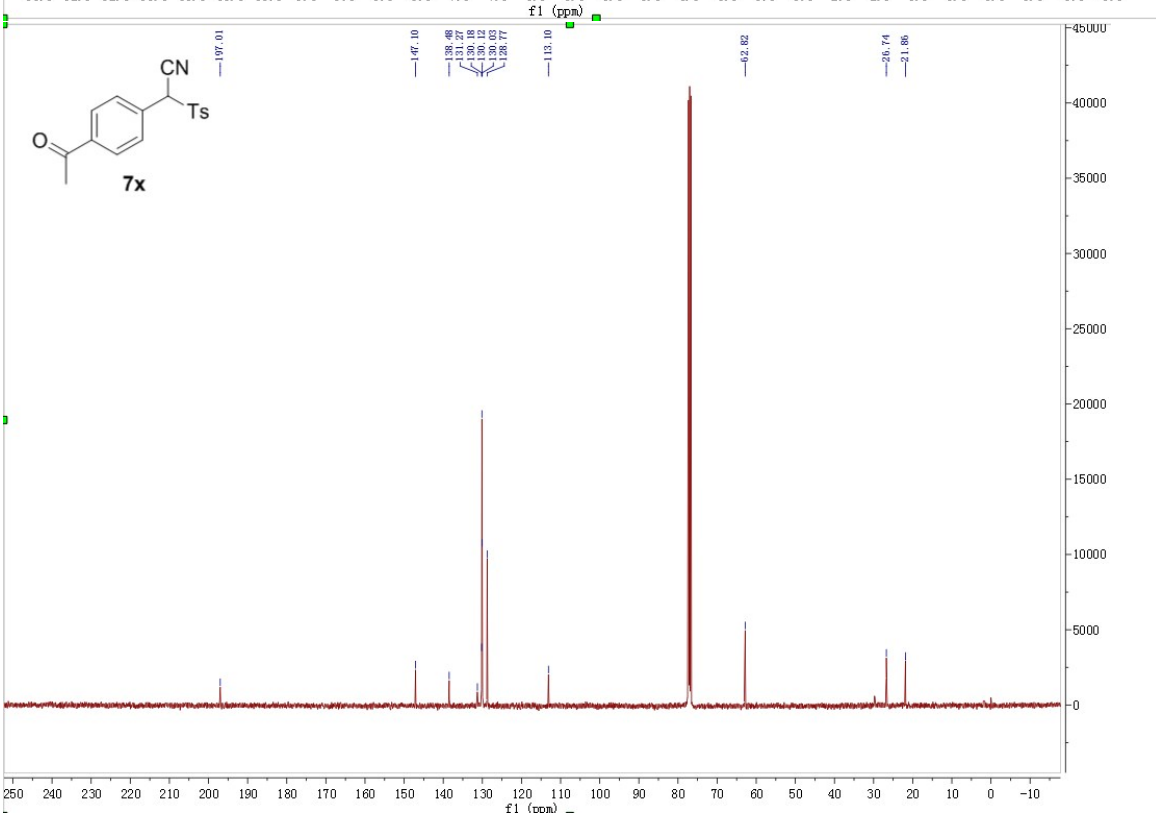

CN
Ts
7v
7.70
7.68
7.46
7.44
7.39
7.37
7.31
7.29
5.13
2.53
1.38
1.99
2.08
1.89
2.01
1.00
3.10
9.38
f1 (ppm)

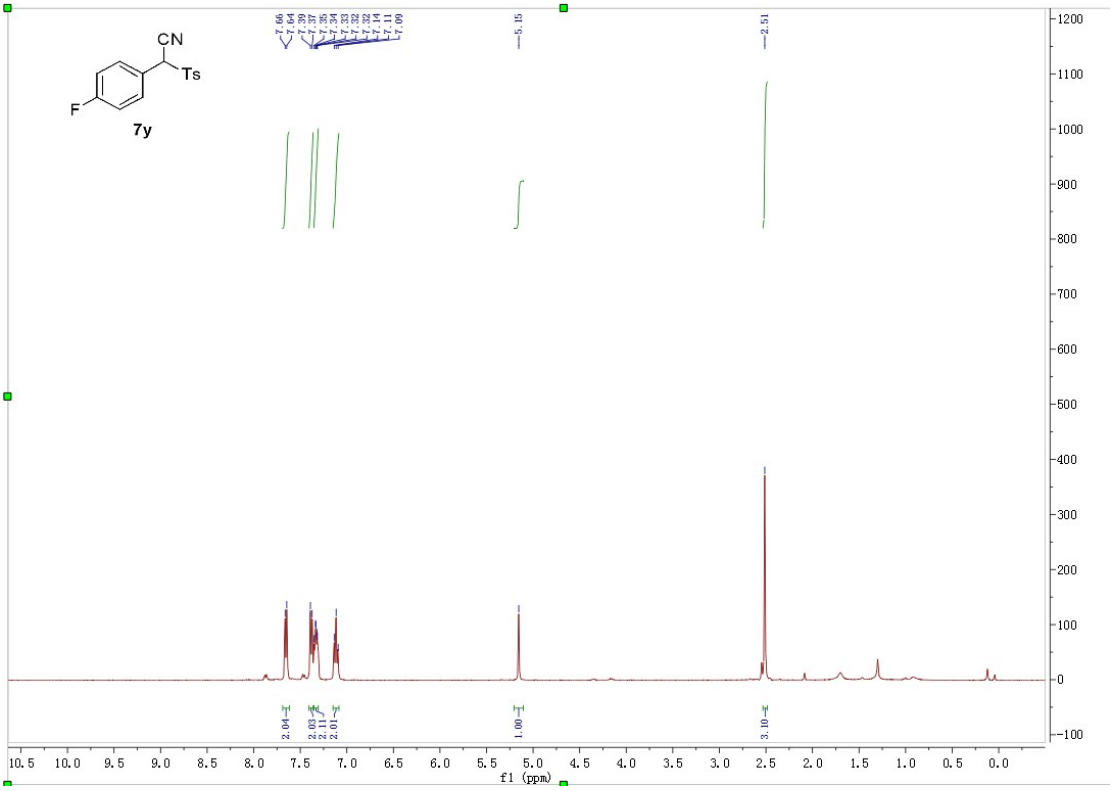

CN
Ts
7v
153.99
146.57
131.72
130.11
129.81
120.53
120.05
122.28
113.65
62.81
34.84
31.18
21.82
f1 (ppm)

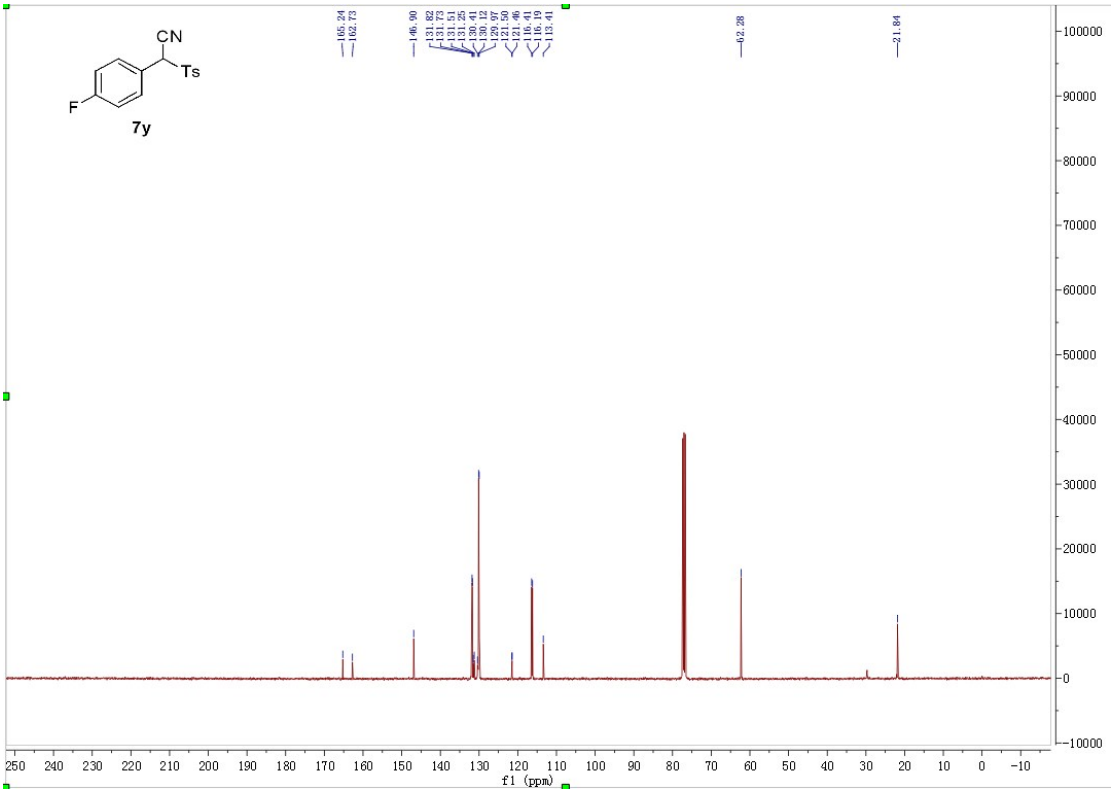

CN
Ts
O
7w
7.66
7.64
7.38
7.36
7.26
7.24
6.93
6.91
5.10
3.87
2.51
2.03
2.10
2.11
2.29
1.00
3.22
3.15
f1 (ppm)

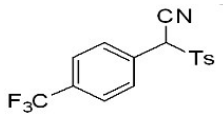

CN
Ts
O
7w
154.03
139.30
124.24
123.88
122.87
122.58
109.92
107.21
106.47
55.28
48.17
14.54
f1 (ppm)


CN
Ts
O
7x
8.02
8.00
7.68
7.66
7.48
7.46
7.40
7.38
5.21
2.68
2.53
2.09
2.01
2.07
2.04
1.00
3.24
3.20
f1 (ppm)


CN
Ts
O
7x
197.01
147.10
138.48
131.27
130.18
130.12
130.03
128.77
113.10
62.82
26.74
21.86
f1 (ppm)

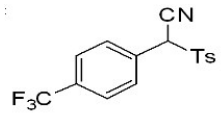

CN
Ts
F
7y
7.66
7.64
7.39
7.37
7.35
7.34
7.33
7.32
7.32
7.14
7.11
7.09
5.15
2.51
2.04
2.03
2.11
2.01
1.00
3.10
f1 (ppm)


CN
Ts
F
7y
165.24
162.73
146.90
131.82
131.73
131.51
131.25
130.41
130.12
129.97
129.50
121.46
116.41
116.19
113.41
62.28
21.84
f1 (ppm)


CN
Ts
F3C

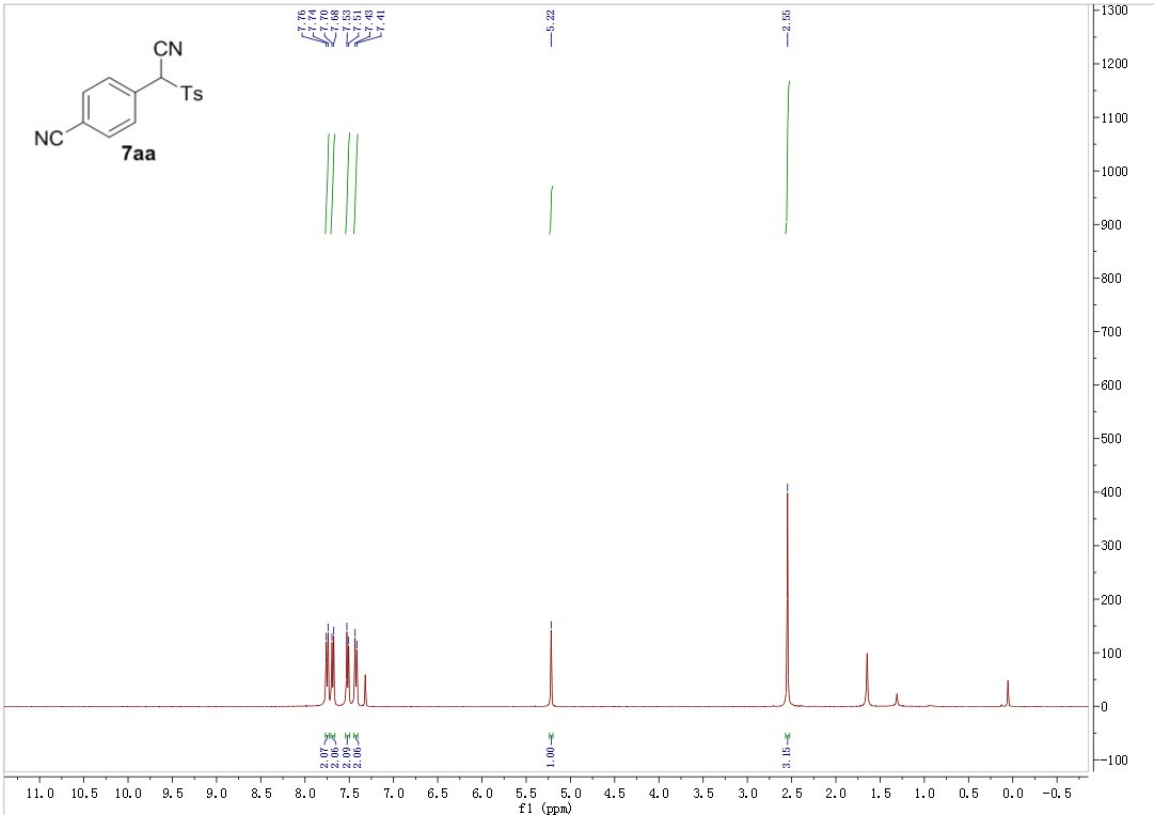
7Z

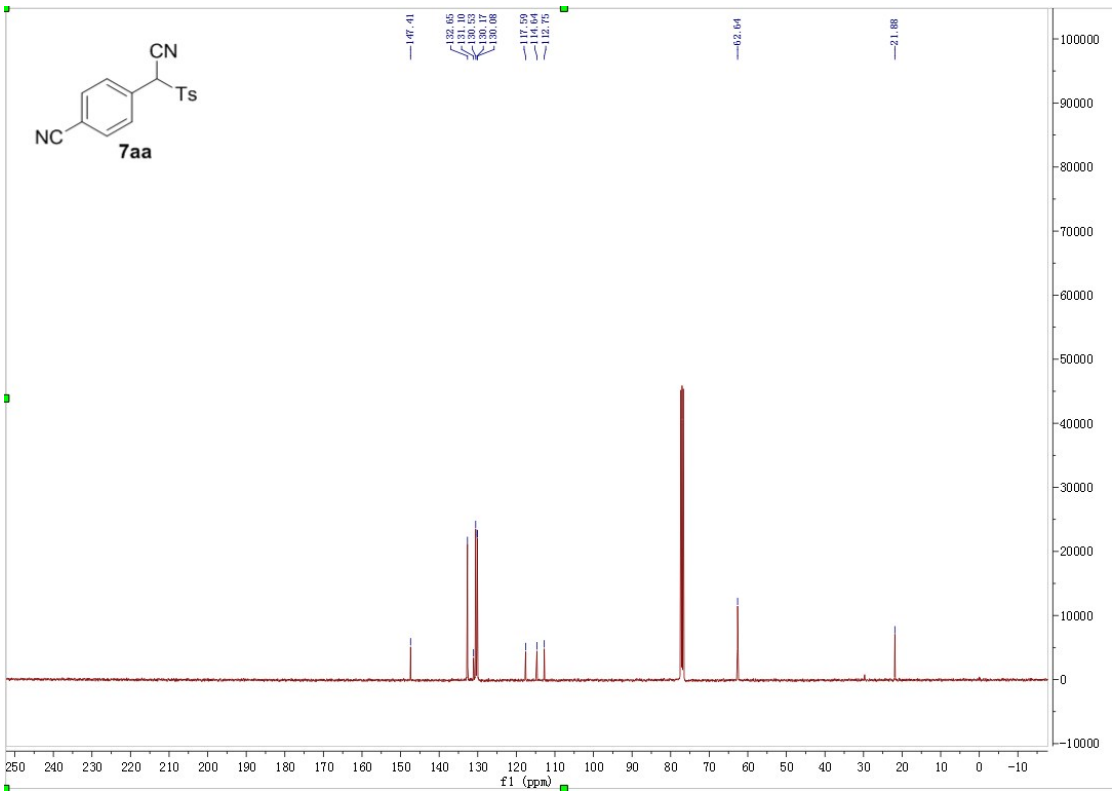
7.72
7.69
7.67
7.53
7.50
7.42
7.39
5.22
2.53
4.25
2.12
2.06
0.96
3.00

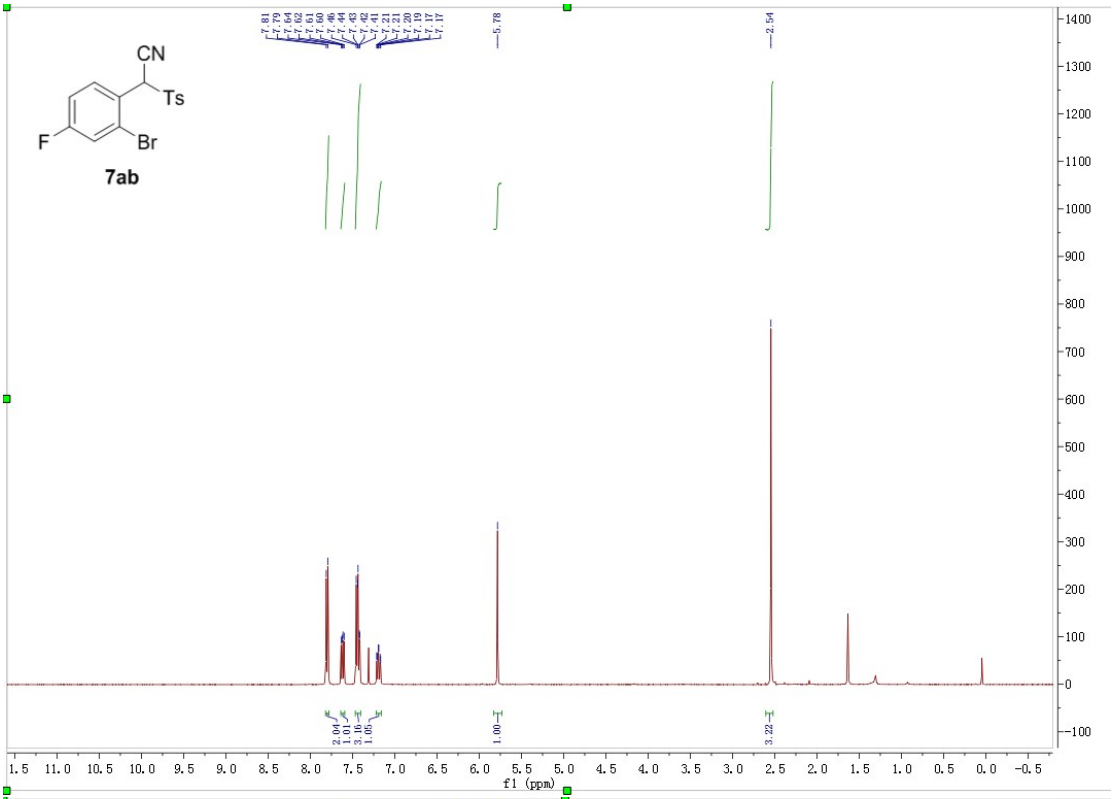

CN
Ts
F3C

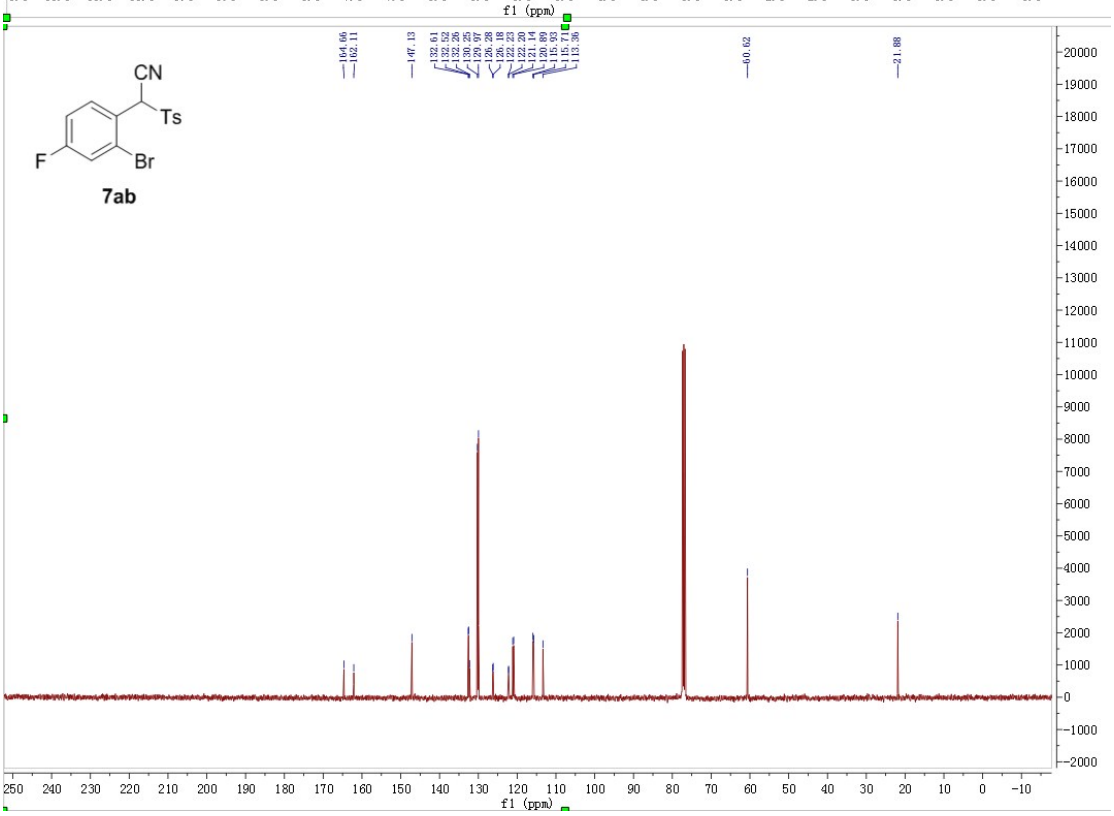
7Z

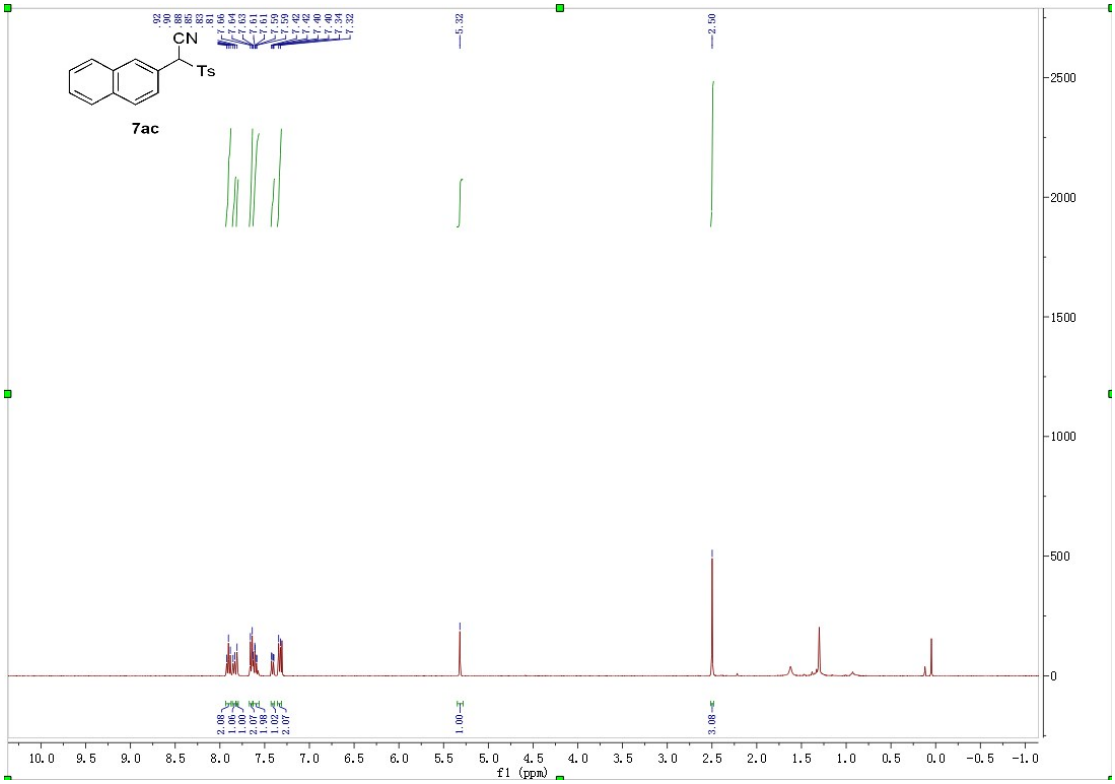
147.21
131.50
131.22
130.40
130.29
130.11
130.08
129.46
126.06
126.02
125.99
125.94
62.58
21.85

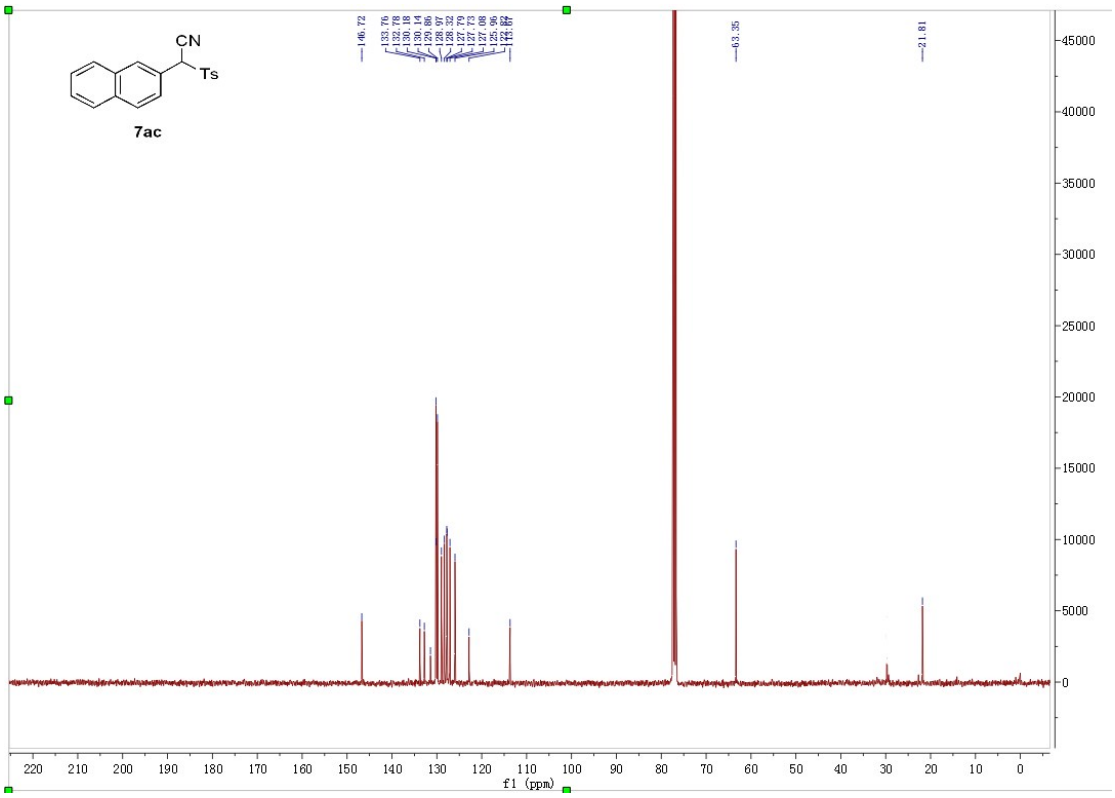

CN
Ts
NC
7aa
7.76
7.74
7.70
7.68
7.53
7.51
7.43
7.41
5.22
2.55
2.07
2.00
2.00
2.06
1.00
3.15
f1 (ppm)

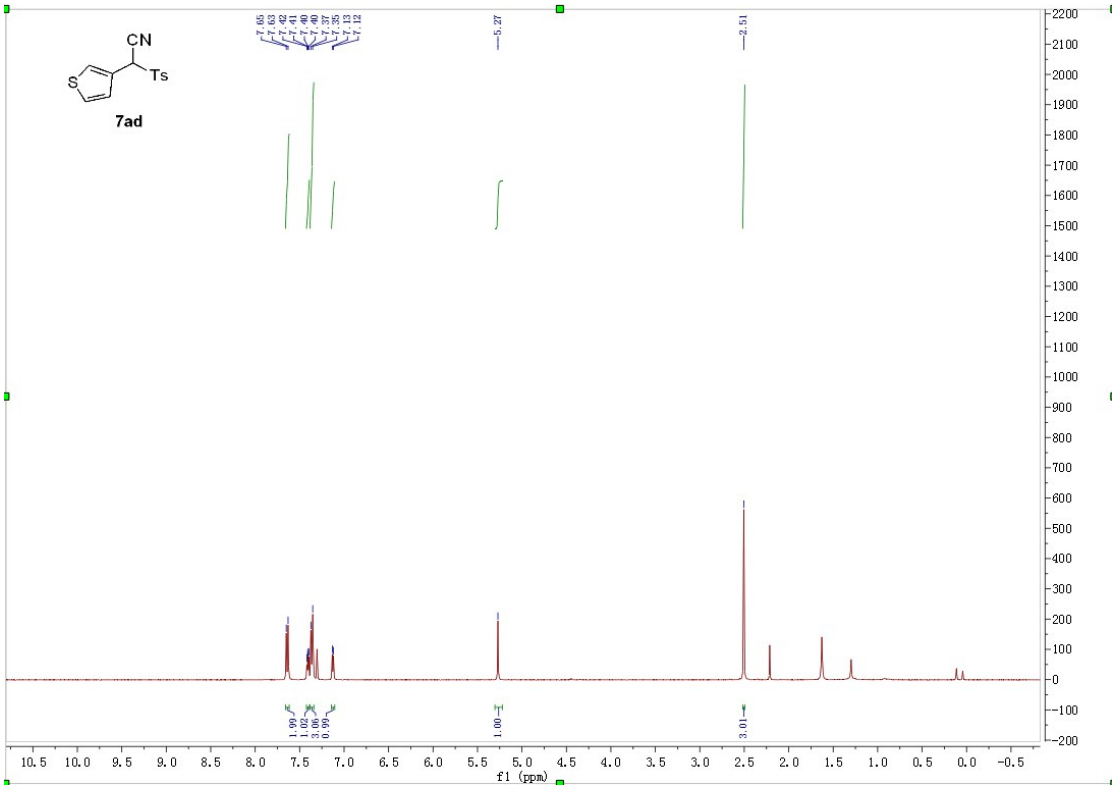

CN
Ts
NC
7aa
147.41
132.65
131.10
130.53
130.17
130.08
117.59
114.64
112.75
62.64
21.88
f1 (ppm)

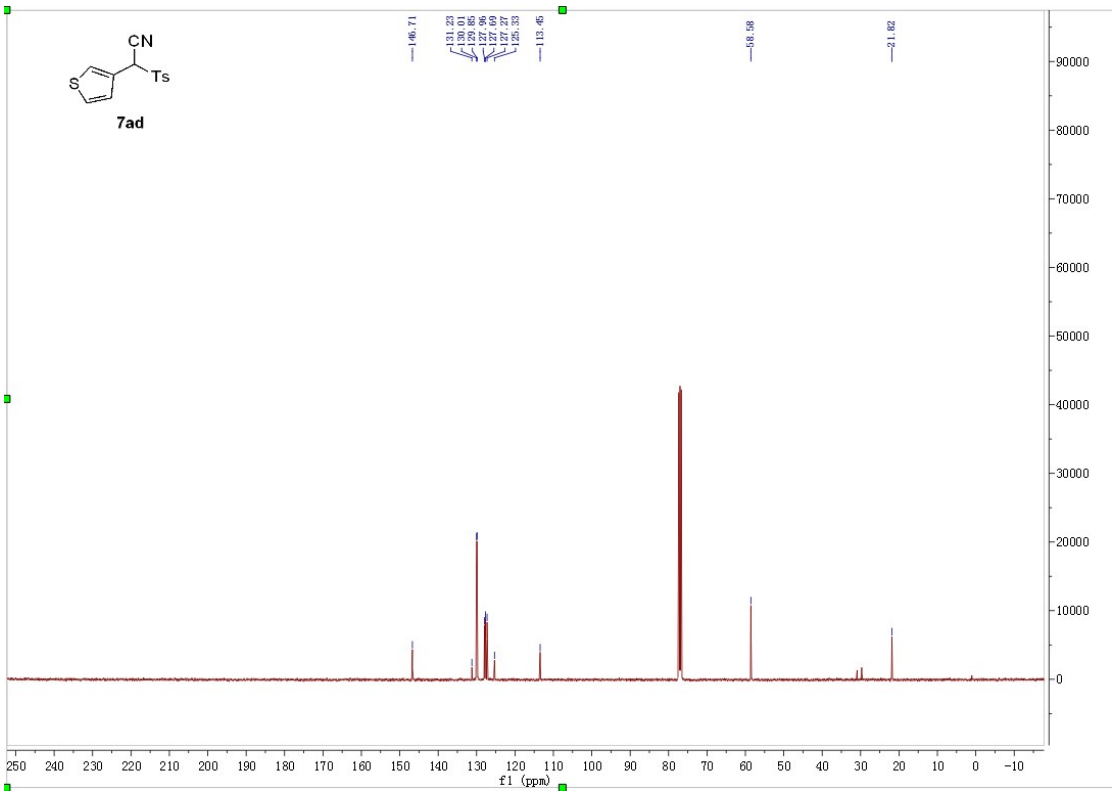

CN
Ts
F
Br
7ab
7.81
7.79
7.64
7.62
7.61
7.60
7.46
7.44
7.43
7.42
7.41
7.21
7.20
7.19
7.17
7.17
5.78
2.54
2.04
1.01
3.16
1.05
1.00
3.22
f1 (ppm)

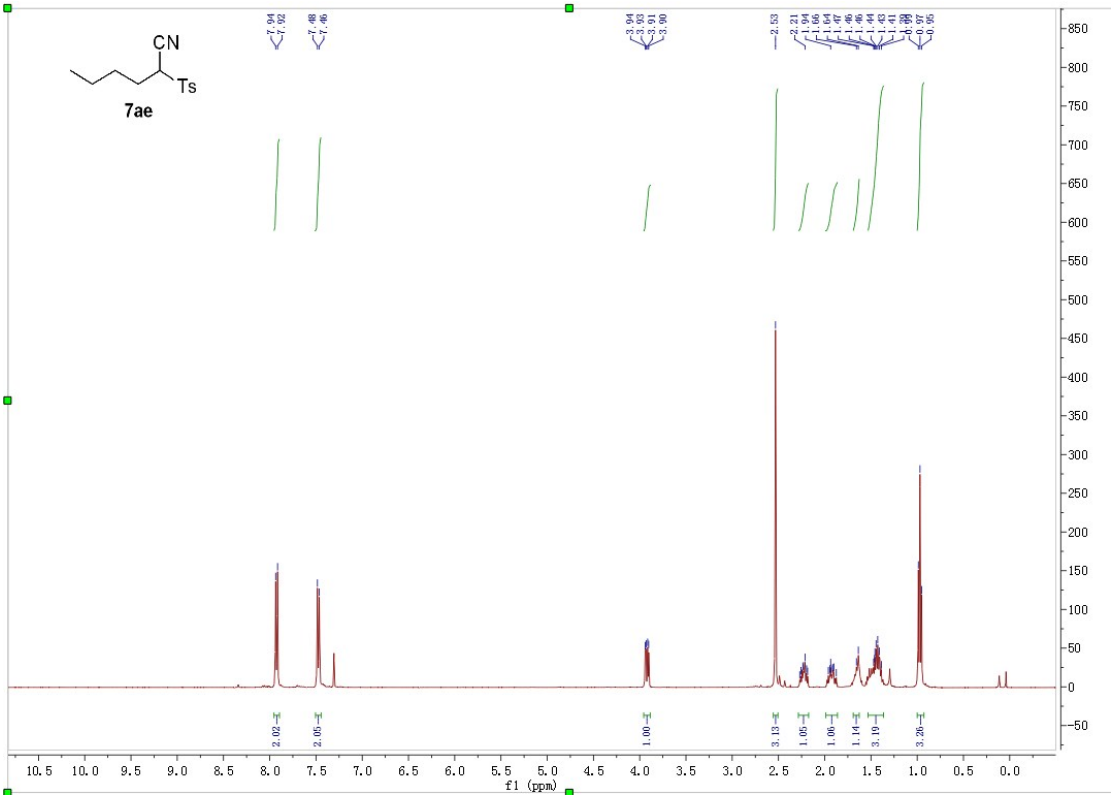

CN
Ts
F
Br
7ab
164.66
162.11
147.13
132.61
132.52
132.26
130.25
129.97
129.28
126.18
122.23
122.20
121.14
120.89
115.93
115.71
113.36
60.62
21.88
f1 (ppm)

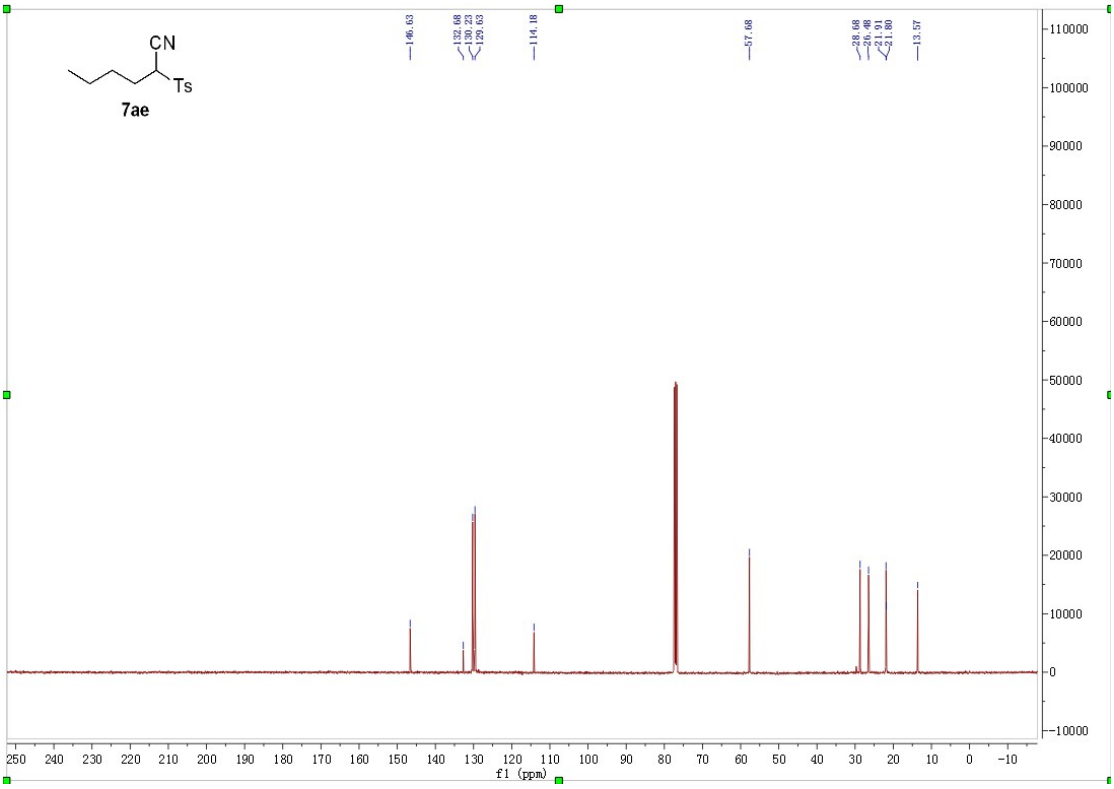

CN
Ts
7ac
5.32
2.50
2.08
1.06
1.00
1.07
1.98
1.02
2.07
1.00
3.08
f1 (ppm)

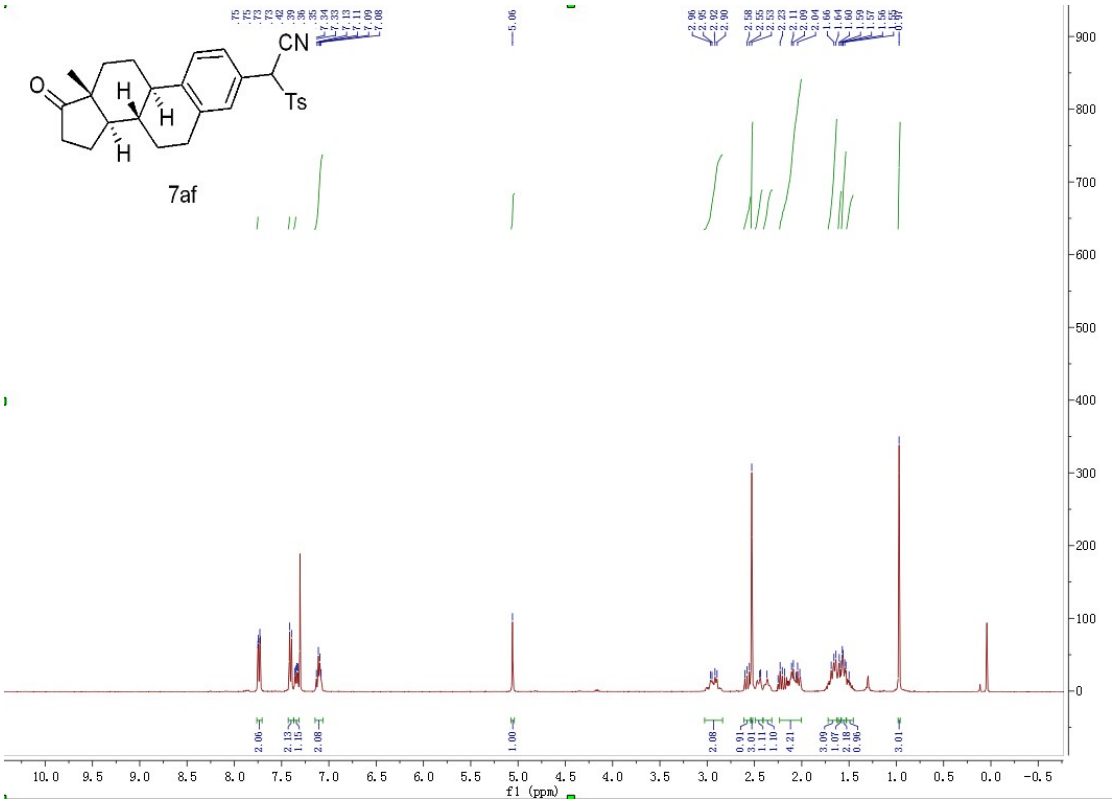

CN
Ts
7ac
146.72
133.76
132.78
130.18
130.14
129.86
128.97
128.32
127.79
127.73
127.08
125.96
63.35
21.81
f1 (ppm)

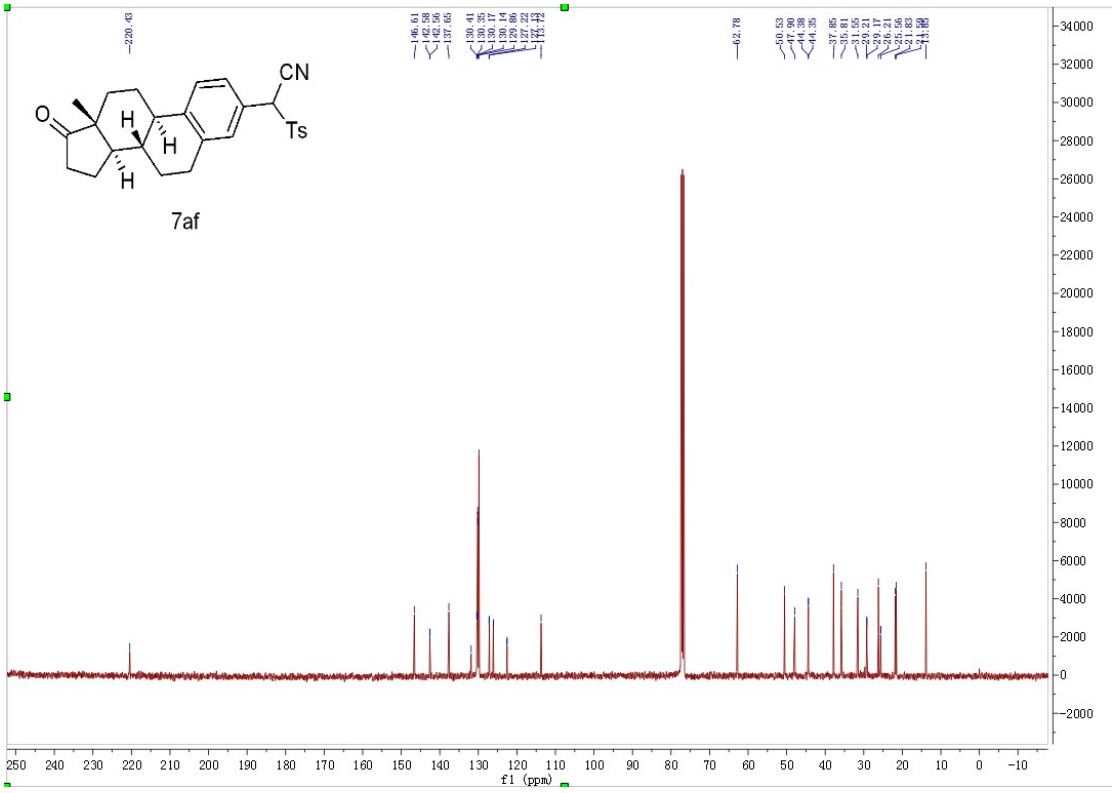

CN
Ts
S
7ad
7.65
7.63
7.62
7.41
7.40
7.40
7.37
7.35
7.13
7.12
5.27
2.51
1.99
1.02
3.06
0.99
1.00
3.01
f1 (ppm)

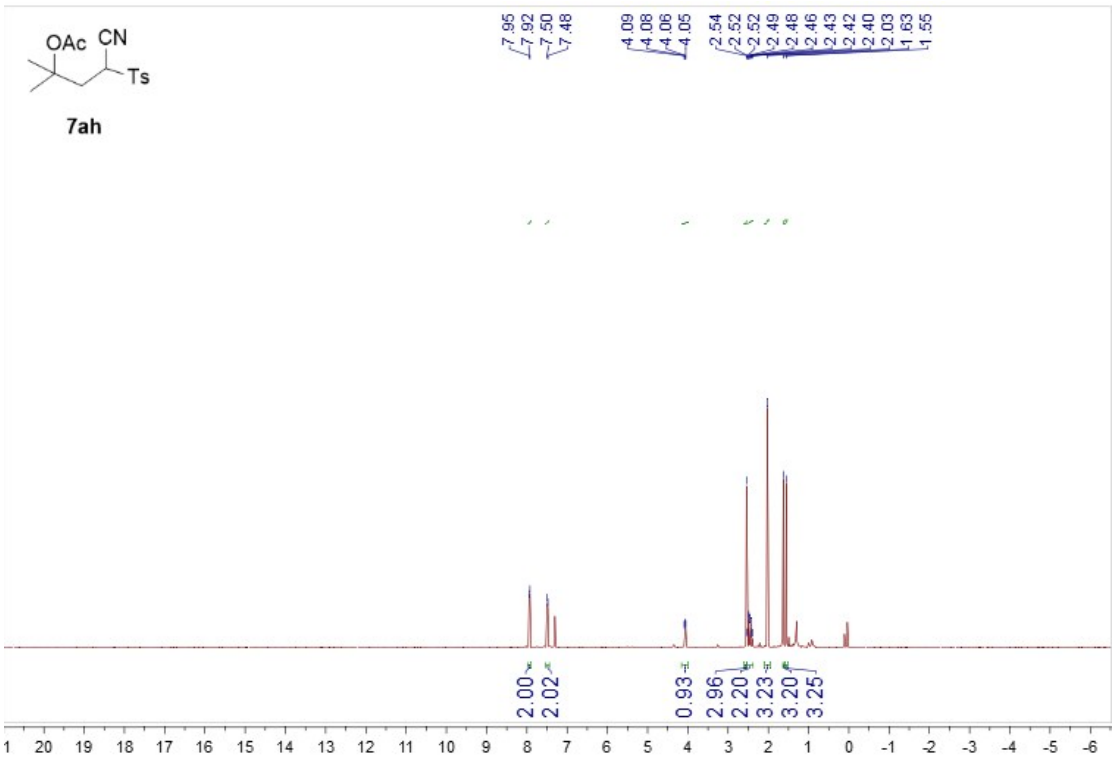

CN
Ts
S
7ad
146.71
131.23
130.01
129.85
127.96
127.69
127.37
125.33
113.45
58.58
21.82
f1 (ppm)

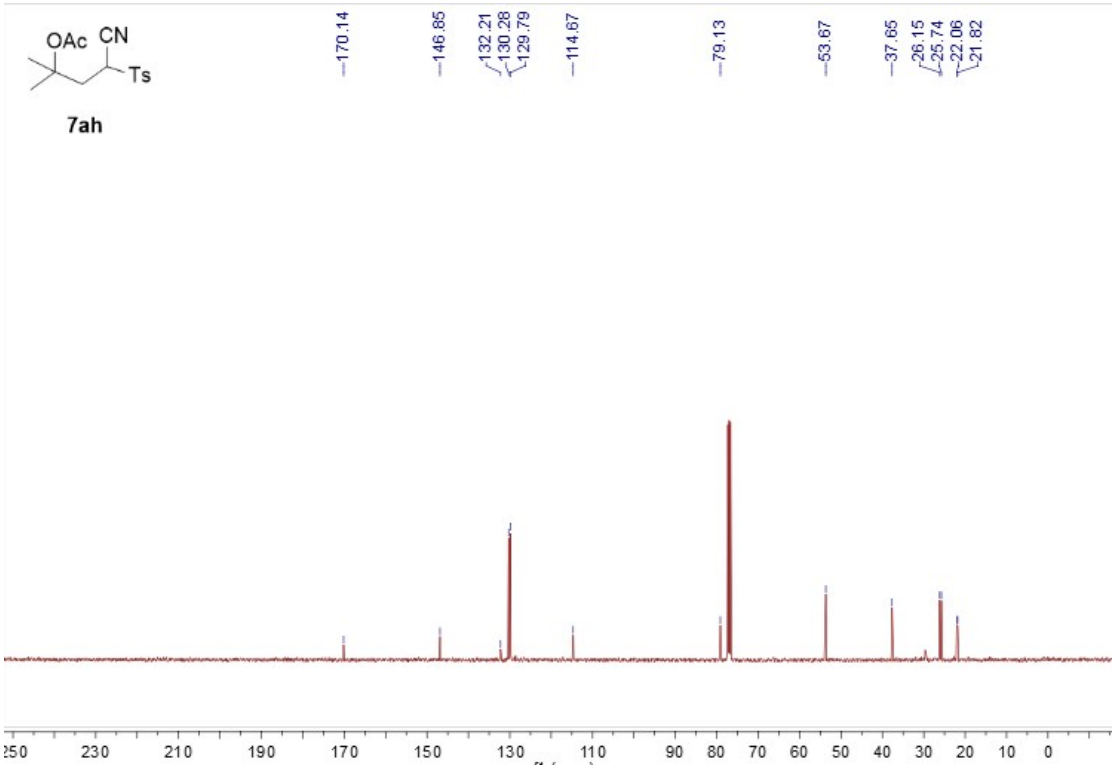

CN
Ts
7ae
f1 (ppm)

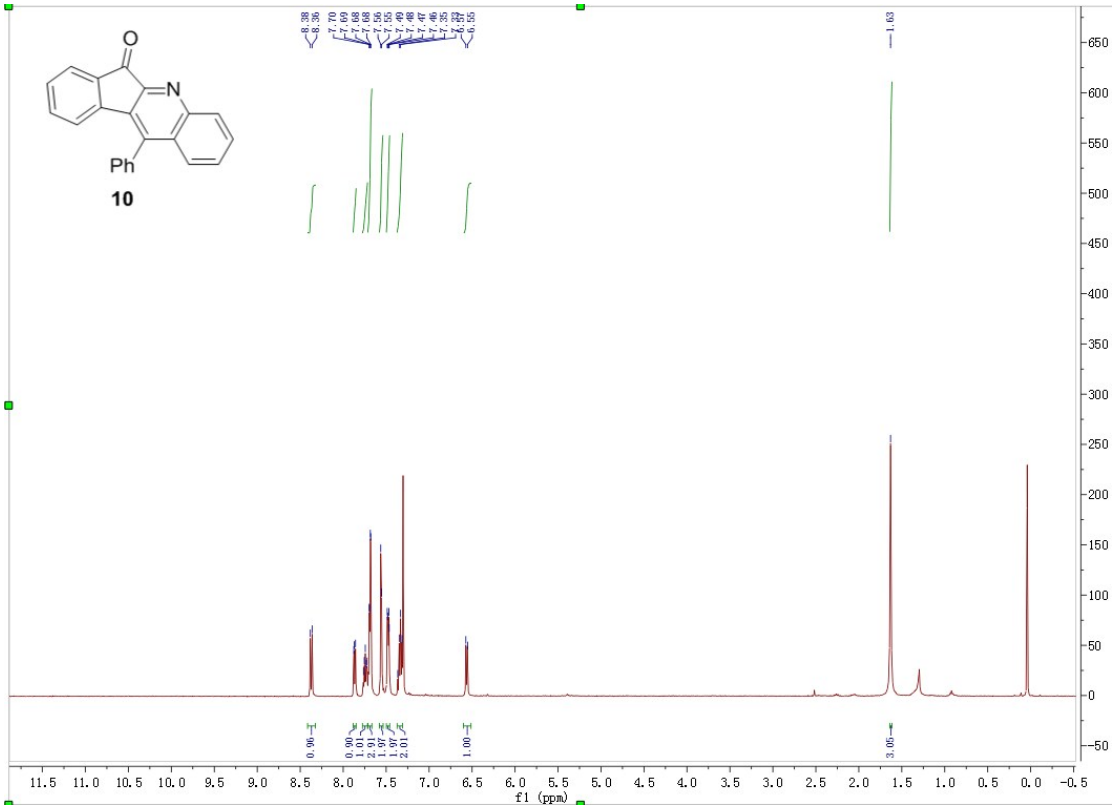

CN
Ts
7ae
f1 (ppm)

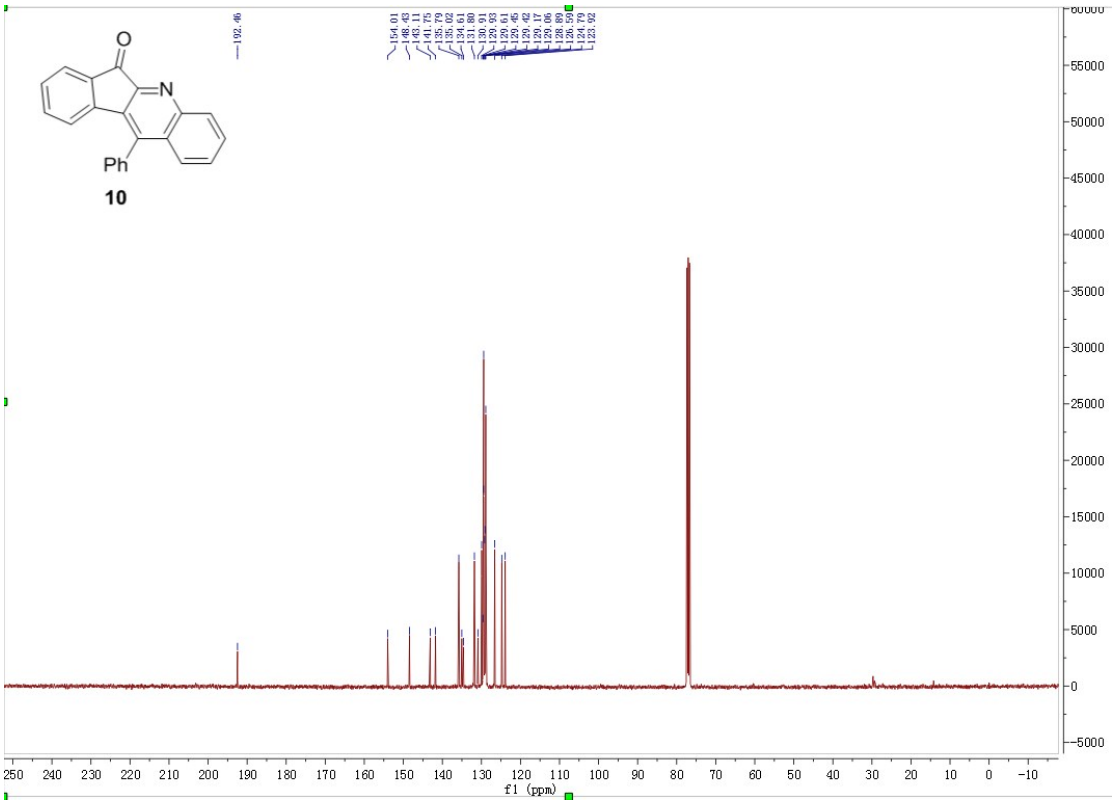

CN
Ts
O
H
H
H
7af
f1 (ppm)


CN
Ts
O
H
H
H
7af
f1 (ppm)

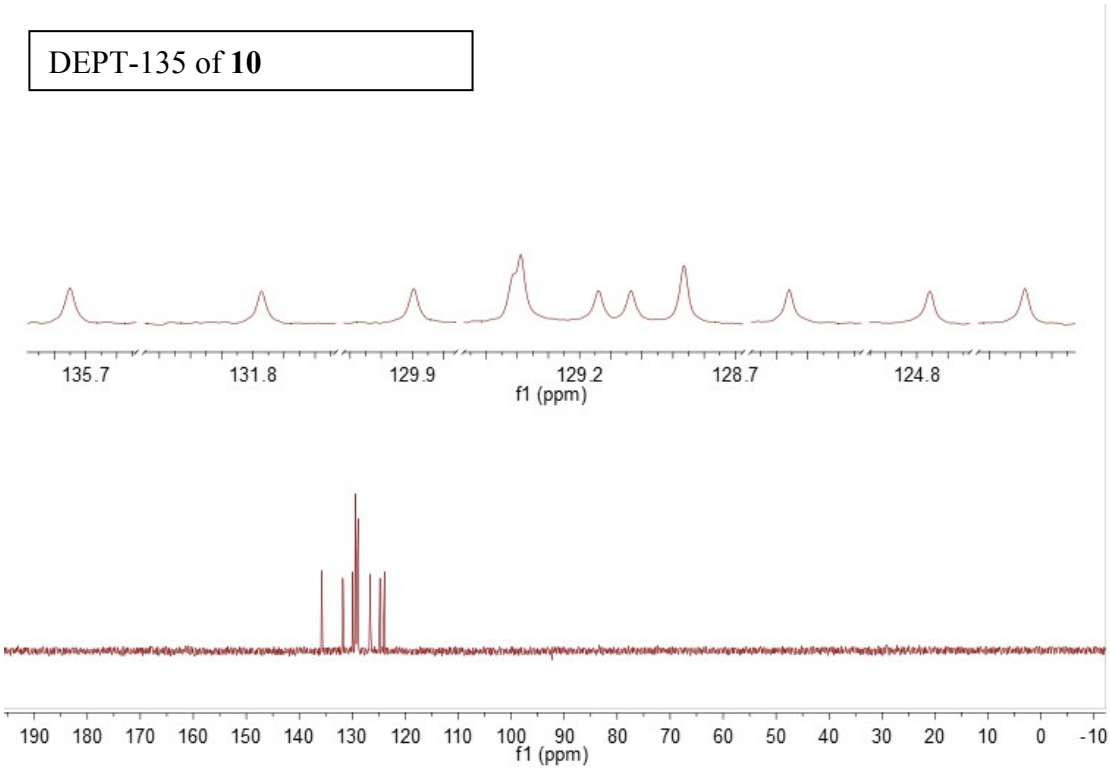

OAc CN
Ts
7ah
7.95
7.92
7.50
7.48
4.09
4.08
4.06
4.05
2.54
2.52
2.52
2.49
2.48
2.46
2.43
2.42
2.40
2.03
1.63
1.55
2.00
2.02
0.93
2.96
2.20
3.23
3.20
3.25


OAc CN
Ts
7ah
170.14
146.85
132.21
130.28
129.79
114.67
79.13
53.67
37.65
26.15
25.74
22.06
21.82

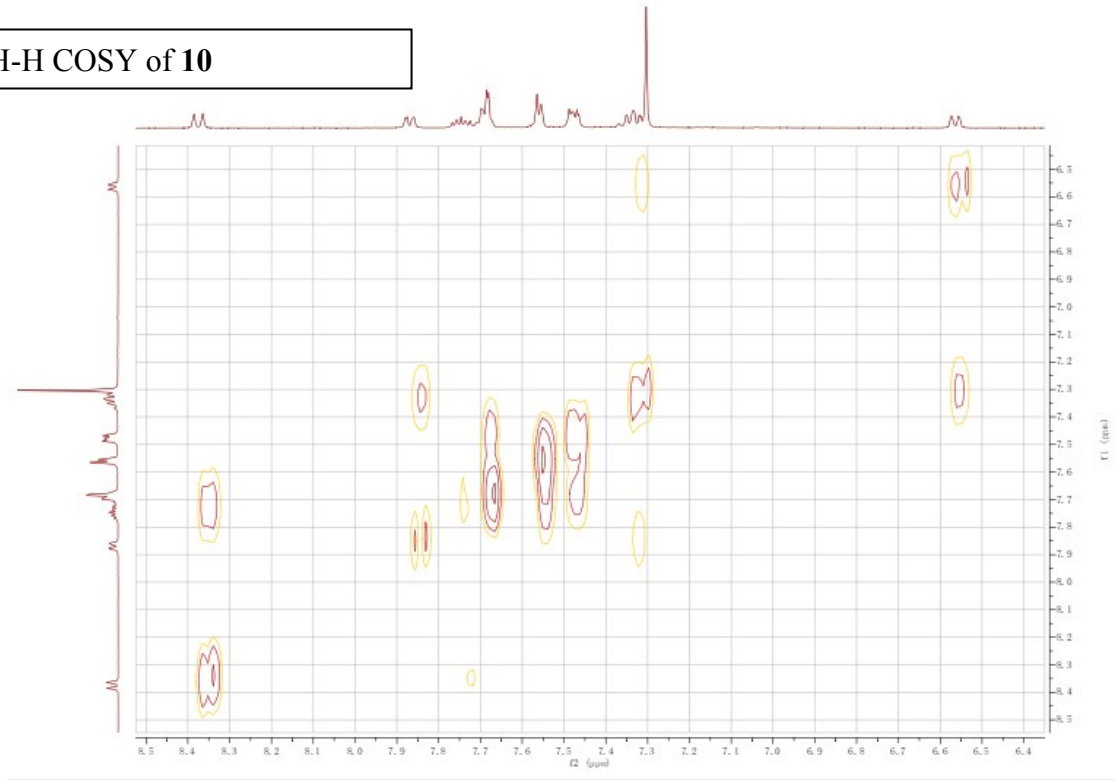

O
N
Ph
10
f1 (ppm)


O
N
Ph
10
f1 (ppm)

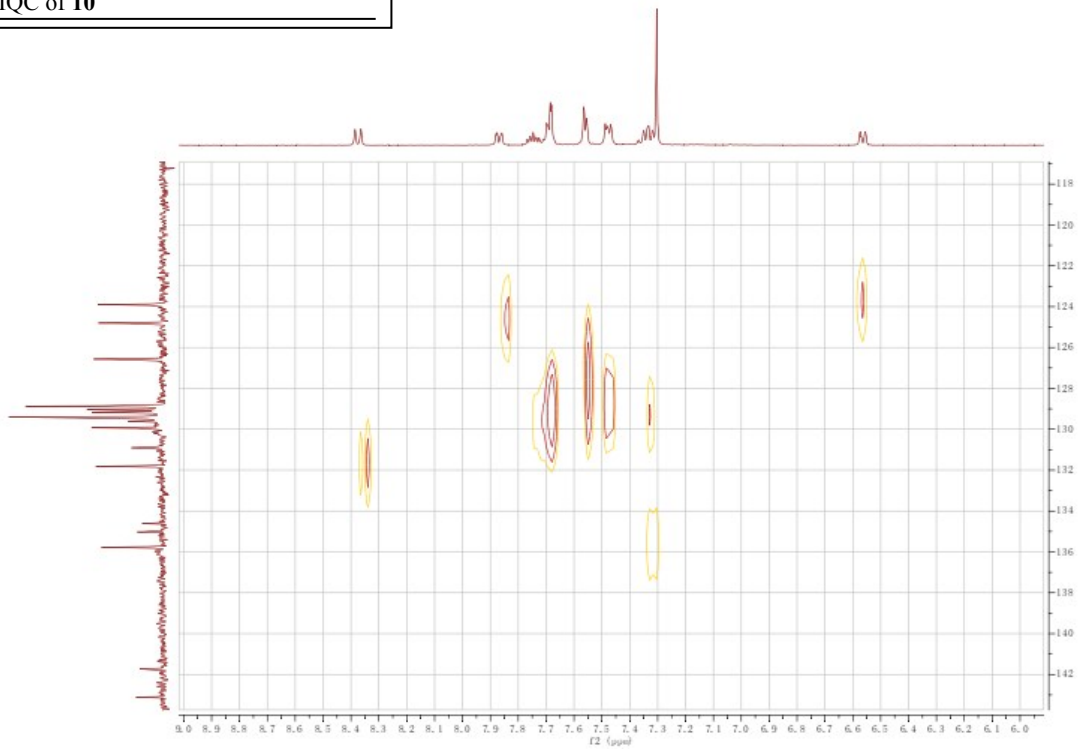
DEPT-135 of **10**



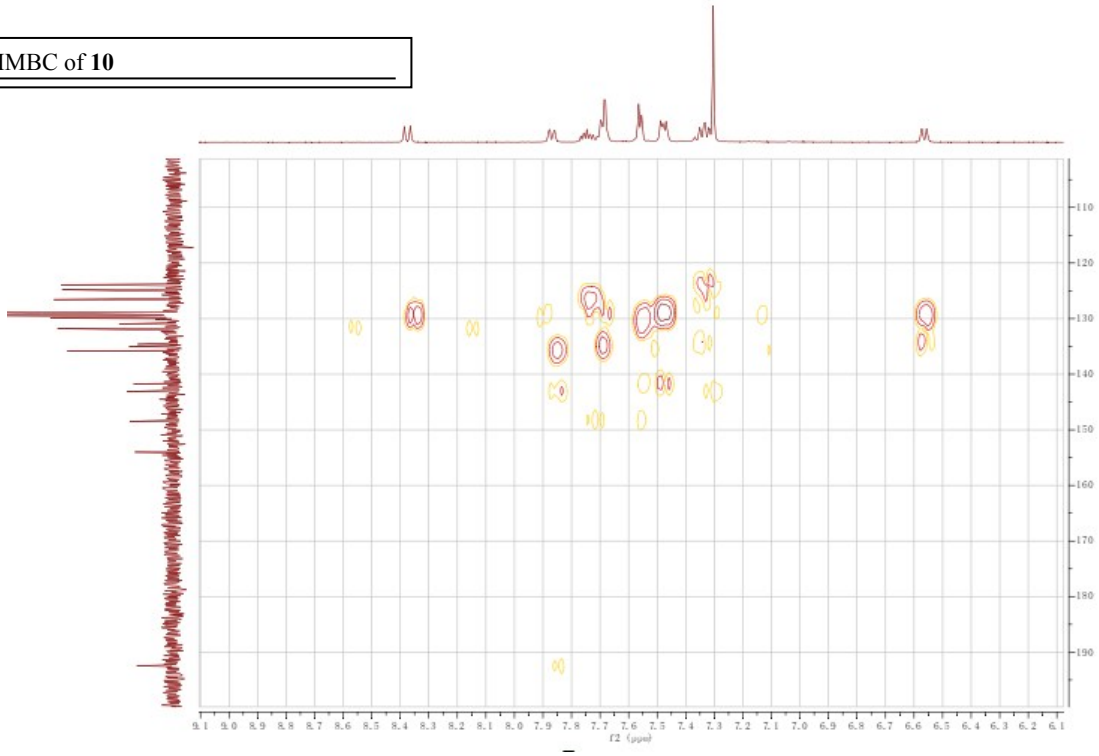
H-H COSY of **10**

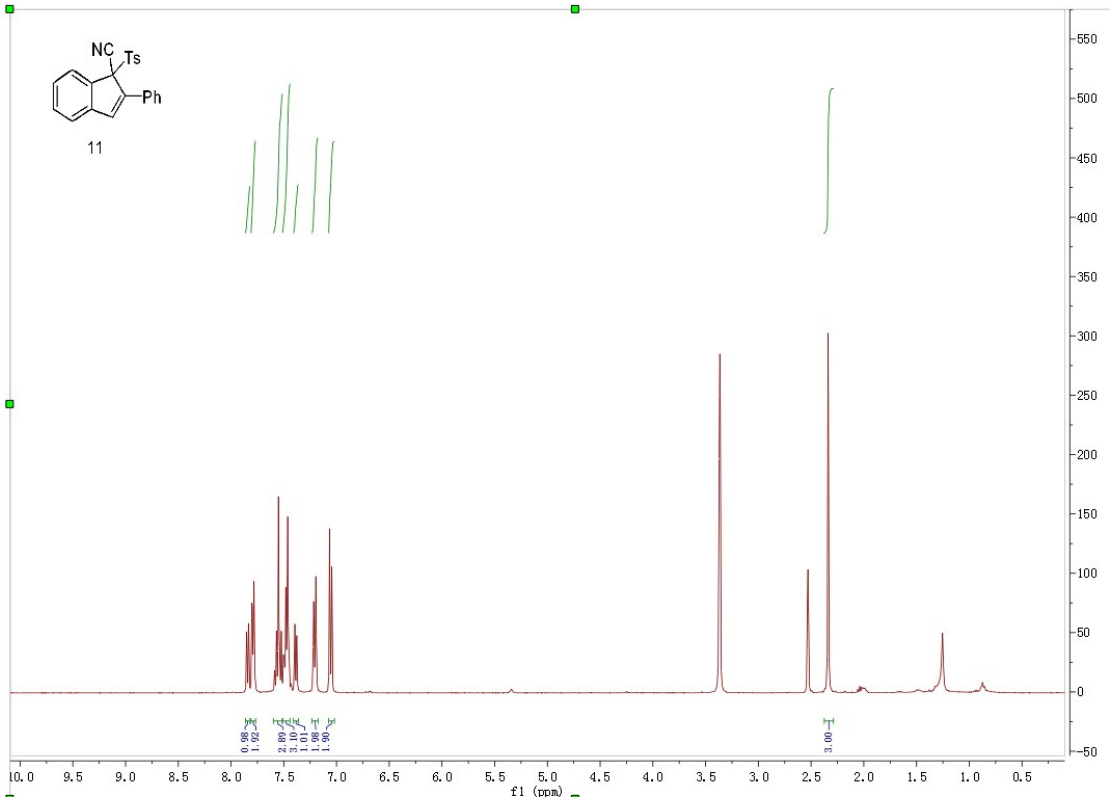


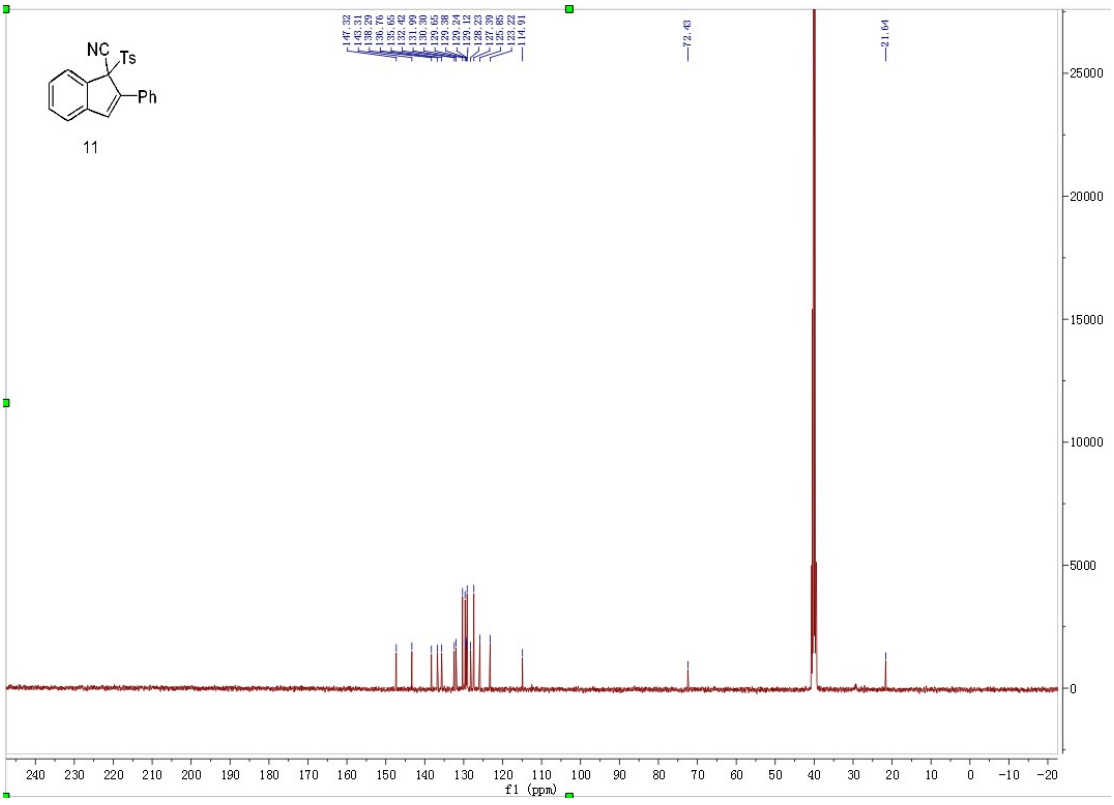
HMQC of **10**



HMBC of **10**




NC
Ts
Ph
11
f1 (ppm)


NC
Ts
Ph
11
72.43
21.64
f1 (ppm)