Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

One-Pot Synthesis of Tetrasubstituted 2-Aminofurans via Au(I)-Catalyzed Cascade Reaction of Ynamides with Propargylic Alcohols

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Contents

General Information

All manipulations were performed under N_2 atmosphere unless stated otherwise. Solvents were purified under N_2 using The Ultimate Solvent System (Glass Counter Inc.) (THF, Toluene, DMF, CH_3CN) or were distilled under an N_2 atmosphere from CaH_2 ($ClCH_2CH_2Cl$). All other solvents and reagents were purified when necessary by standard procedures. Column chromatography was performed on silica gel (Wakogel® FC-40). TLC and PTLC were performed on Wako Silicagel 70 F254. IR spectra were obtained on a JASCO FT/IR 460Plus spectrometer. ^{1}H NMR spectroscopy was recorded on JEOL ECX400P (400 MHz), JEOL ECS400 (400 MHz), JEOL ECP400 (400 MHz), and JEOL ECA500 (500 MHz) NMR spectrometer. Chemical shifts are reported in ppm from the solvent as the internal standard ($CDCl_3$: δ = 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, br = broad, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectroscopy was recorded on JEOL ECX400P (100 MHz), JEOL ECS400 (100 MHz), JEOL ECP400 (100 MHz), and JEOL ECA500 (125 MHz) NMR spectrometer. Chemical shifts are reported in ppm from the solvent as the internal standard ($CDCl_3$: δ = 77.00 ppm). Mass spectra were obtained on JEOL JMS-T100LP and JMS-T100GCV and JEOL JMS-FAB mate mass spectrometer, and Thermo Scientific Exactive mass spectrometer.

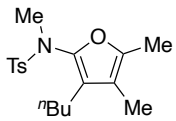
Synthesis of Furan 4aa from 3,4-Dienamide 3aa (Table 1, entry 6)

In a test tube under a nitrogen atmosphere, **3aa** (99.5 mg, 0.30 mmol) was dissolved in toluene (0.6 mL). To the solution was added Au(IPr)NTf_2 (2.6 mg, 0.003 mmol, 1 mol% to a substrate) and PPTS (3.9 mg, 0.015 mmol, 5 mol% to a substrate). The mixture was stirred at 80 °C for 3 h. Yield of **4aa** was determined to be 76% by ^{1}H-NMR using 1,1,2,2-tetrachloroethane as an internal standard.

General Procedure for the Polysubstituted Furans

In a test tube under a nitrogen atmosphere, ynamide (0.3 mmol) and alcohol (0.3 mmol) in toluene (0.6 mL) was dissolved in Toluene (0.6 mL). To the solution was added Au(IPr)NTf_2 (0.003 mmol, 1 mol% to a substrate) and PPTS (0.015 mmol, 5 mol% to a substrate). The mixture was stirred at rt until the substrate disappeared on TLC. After removal of the solvent, the residue was purified by column chromatography on silica gel to give product.

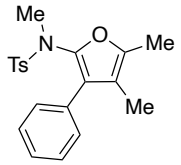
Spectral Data of Polysubstituted Furans



Furan 4aa (1 mmol scale reaction)

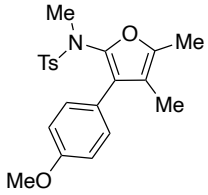
According to the general procedure, a crude product was obtained from **1a**[1] (266.3 mg, 1.0 mmol), **2a**[2] (1.0 mL of 1.0 M solution in toluene, 1.0 mmol), Au(IPr)NTf_2 (8.7 mg, 0.01 mmol) and PPTS (12.6 mg, 0.05 mmol) in Toluene (2.0 mL) at rt for 24 h. Purification of the crude product by silica-gel column chromatography (*n*-hexane/EtOAc = 5/1) to give **4aa** (305.2 mg, 91% yield) as a colorless liquid. Spectral data of **4aa**: IR (CH_2Cl_2) 3065, 2929, 1766, 1597 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 7.26 (s, 2H), 3.05 (s,

3H), 2.44 (s, 3H), 2.33 (t, J = 7.7 Hz, 2H), 2.06 (d, J = 3.6 Hz, 3H), 1.86 (s, 3H), 1.51-1.43 (m, 2H), 1.38-1.31 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 143.6, 140.0, 135.4, 129.4, 128.1, 122.0, 115.4, 37.8, 31.3, 23.2, 22.7, 21.5, 13.9, 11.4, 8.6; HRMS (EI) calcd for $C_{18}H_{25}NO_3S$ [M^+] 335.1555, found 335.1557.



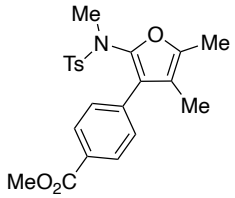
Furan 4ba

According to the general procedure, a crude product was obtained from **1b**[10] (85.6 mg, 0.30 mmol), **2a** (0.30 mL of 1.0 M solution in toluene, 0.3 mmol), Au(IPr)NTf_2 (2.6 mg, 0.003 mmol) and PPTS (3.8 mg, 0.015 mmol) in Toluene (0.6 mL) at 60 °C for 24 h. Purification of the crude product by silica-gel column chromatography (*n*-hexane/EtOAc = 15/1) to give **4ba** (73.6 mg, 69% yield) as a colorless liquid. Spectral data of **4ba**: IR (CH_2Cl_2) 3064, 2925, 1704, 1645, 1606, 1496 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.2 Hz, 2H), 7.26-7.22 (m, 4H), 7.20-7.16 (m, 1H), 7.13 (t, J = 6.6 Hz, 2H), 2.91 (s, 3H), 2.31 (s, 3H), 2.07 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 143.7, 140.4, 135.6, 132.1, 129.4, 129.1, 128.4, 128.3, 127.2, 123.1, 115.1, 38.1, 21.7, 11.7, 9.4; HRMS (EI) calcd for $C_{20}H_{21}NO_3S$ [M^+] 355.1242, found 355.1240.



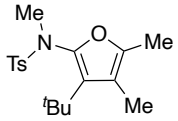
Furan 4ca

According to the general procedure, a crude product was obtained from **1c**[10] (94.2 mg, 0.30 mmol), **2a** (0.30 mL of 1.0 M solution in toluene, 0.3 mmol), Au(IPr)NTf_2 (2.6 mg, 0.003 mmol) and PPTS (3.8 mg, 0.015 mmol) in Toluene (0.6 mL) at 60 °C for 24 h. Purification of the crude product by silica-gel column chromatography (*n*-hexane/EtOAc = 10/1) to give **4ca** (51.1 mg, 44% yield) as a yellow liquid. Spectral data of **4ca**: IR (CH_2Cl_2) 3064, 2925, 1764, 1590, 1513 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 3.79 (s, 3H), 2.98 (s, 3H), 2.39 (s, 3H), 2.13 (s, 3H), 1.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 145.2, 143.7, 140.1, 135.6, 130.2, 129.4, 128.2, 124.3, 122.7, 115.2, 113.9, 55.3, 38.1, 21.7, 11.7, 9.5; HRMS (EI) calcd for $C_{21}H_{23}NO_4S$ [M^+] 385.1348, found 385.1342.



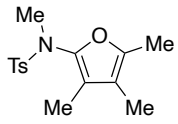
Furan 4da

According to the general procedure, a crude product was obtained from **1d**[1] (102.5 mg, 0.30 mmol), **2a** (0.30 mL of 1.0 M solution in toluene, 0.3 mmol), Au(IPr)NTf_2 (2.6 mg, 0.003 mmol) and PPTS (3.8 mg, 0.015 mmol) in Toluene (0.6 mL) at 60 °C for 24 h. Purification of the crude product by silica-gel column chromatography (*n*-hexane/EtOAc = 20/1 to 10/1) to give **4da** (63.1 mg, 51% yield) as a colorless liquid. Spectral data of **4da**: IR (CH_2Cl_2) 3062, 2953, 1718, 1613, 1436 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 3.93 (s, 3H), 3.04 (s, 3H), 2.41 (s, 3H), 2.18 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 145.9, 143.9, 140.9, 137.0, 135.4, 129.7, 129.5, 128.9, 128.8, 128.2, 122.2, 114.9, 52.2, 38.1, 21.7, 11.7, 9.5; HRMS (EI) calcd for $C_{22}H_{23}NO_5S$ [M^+] 413.1297, found 413.1290.



Furan 4ea

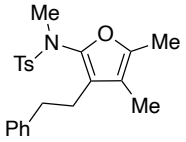
According to the general procedure, a crude product was obtained from **1e**[3] (53.0 mg, 0.20 mmol), **2a** (0.20 mL of 1.0 M solution in toluene, 0.2 mmol), Au(IPr)NTf_2 (8.6 mg, 0.010 mmol) and PPTS (2.8 mg, 0.011 mmol) in Toluene (0.4 mL) at 60 °C for 24 h. Purification of the crude product by silica-gel column chromatography (*n*-hexane/EtOAc = 10/1) to give **4ea** (20.6 mg, 31% yield) as a colorless liquid. Spectral data of **4ea**: IR (CH_2Cl_2) 2961, 1578, 1347, 1159 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 3.02 (s, 3H), 2.45 (s, 3H), 2.03 (s, 6H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 143.6, 138.9, 135.6, 129.4, 128.7, 128.6, 115.2, 38.5, 31.8, 30.2, 21.7, 11.9, 11.3; HRMS (EI) calcd for $C_{18}H_{25}NO_3S$ [M^+] 335.1555, found 335.1549.



Furan 4fa

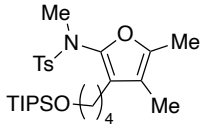
According to the general procedure, a crude product was obtained from **1f**[4] (53.0 mg, 0.20 mmol), **2a** (0.20 mL of 1.0 M solution in toluene, 0.2 mmol), Au(IPr)NTf_2 (8.6 mg, 0.010 mmol) and PPTS (2.8 mg, 0.011 mmol) in Toluene (0.4 mL) at rt for 24 h. Purification of the crude product by silica-gel column chromatography (*n*-hexane/EtOAc = 10/1) to give **4fa** (32.2 mg, 55% yield) as a colorless liquid. Spectral data of **4fa**: IR (CH_2Cl_2) 3064, 2924, 1732, 1597 1349 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H),

3.06 (s, 3H), 2.44 (s, 3H), 2.06 (s, 3H), 1.84 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 143.7, 140.1, 135.3, 129.5, 128.1, 117.5, 116.0, 37.5, 21.7, 11.5, 8.6, 8.4; HRMS (EI) calcd for $C_{15}H_{19}NO_3S$ [M^+] 293.1086, found 293.1082.



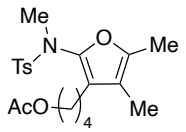
Furan 4ga

According to the general procedure, a crude product was obtained from **1g**[5] (94.0 mg, 0.30 mmol), **2a** (0.30 mL of 1.0 M solution in toluene, 0.3 mmol), Au(IPr)NTf_2 (2.6 mg, 0.003 mmol) and PPTS (3.8 mg, 0.015 mmol) in Toluene (0.6 mL) at rt for 24 h. Purification of the crude product by silica-gel column chromatography (*n*-hexane/EtOAc = 15/1) to give **4ga** (102.8 mg, 89% yield) as a colorless liquid. Spectral data of **4ga**: IR (CH_2Cl_2) 3064, 2924, 1651, 1596, 1453 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.6 Hz, 2H), 7.31-7.25 (m, 5H), 7.19 (d, *J* = 7.7 Hz, 2H), 2.86-2.81 (m, 5H), 2.69-2.67 (m, 2H), 2.44 (s, 3H), 2.06 (t, *J* = 2.3 Hz, 3H), 1.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 143.7, 142.0, 140.4, 135.4, 129.5, 128.7, 128.4, 128.2, 126.0, 121.1, 115.5, 37.6, 35.4, 25.7, 21.7, 11.5, 8.7; HRMS (EI) calcd for $C_{22}H_{25}NO_3S$ [M^+] 383.1555, found 383.1551.



Furan 4ha

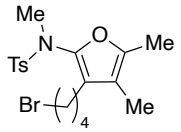
According to the general procedure, a crude product was obtained from **1h** (85.9 mg, 0.20 mmol), **2a** (0.20 mL of 1.0 M solution in toluene, 0.2 mmol), Au(IPr)NTf_2 (8.6 mg, 0.010 mmol) and PPTS (2.5 mg, 0.010 mmol) in Toluene (0.4 mL) at 60 °C for 24 h. Purification of the crude product by silica-gel column chromatography (*n*-hexane/EtOAc = 10/1) to give **4ha** (60.9 mg, 60% yield) as a colorless liquid. Spectral data of **4ha**: IR (neat) 3584, 2941, 2865, 1596, 1462 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.6 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 3.70 (d, *J* = 5.9 Hz, 2H), 3.05 (s, 3H), 2.44 (s, 3H), 2.42-2.32 (m, 2H), 2.04 (s, 3H), 1.86 (s, 3H), 1.58-1.54 (m, 4H), 1.11-1.02 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 143.7, 140.1, 135.5, 129.5, 128.3, 122.1, 115.6, 63.2, 38.0, 33.2, 25.5, 23.5, 21.7, 18.2, 18.1, 11.5, 8.8; HRMS (EI) calcd for $C_{27}H_{45}NO_4SSi$ [M^+] 507.2839, found 507.2834.



Furan 4ia

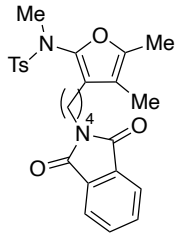
According to the general procedure, a crude product was obtained from **1i**[5] (63.9 mg, 0.20 mmol), **2a** (0.20 mL of 1.0 M solution in toluene, 0.2 mmol), Au(IPr)NTf_2 (8.7 mg, 0.010 mmol) and PPTS (2.6 mg, 0.010 mmol) in

Toluene (0.4 mL) at 60 °C for 24 h. Purification of the crude product by silica-gel column chromatography (*n*-hexane/EtOAc = 10/1) to give **4ia** (55.0 mg, 70% yield) as a colorless liquid. Spectral data of **4ia**: IR (neat) 2943, 2256, 1735, 1596 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 4.08 (t, *J* = 6.3 Hz, 2H), 3.04 (s, 3H), 2.43 (s, 3H), 2.38 (t, *J* = 7.6 Hz, 2H), 2.04 (s, 6H), 1.86 (s, 3H), 1.65-1.58 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 144.8, 143.8, 140.3, 135.2, 129.5, 128.2, 121.5, 115.4, 64.4, 37.9, 28.6, 25.5, 23.2, 21.7, 21.1, 11.5, 8.8; HRMS (EI) calcd for $C_{20}H_{27}NO_5S$ [M^+] 393.1610, found 393.1609.



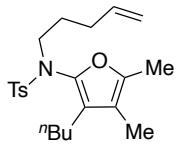
Furan 4ja

According to the general procedure, a crude product was obtained from **4j** (68.6 mg, 0.20 mmol), **2a** (0.20 mL of 1.0 M solution in toluene, 0.2 mmol), Au(IPr)NTf_2 (8.8 mg, 0.010 mmol) and PPTS (2.6 mg, 0.010 mmol) in Toluene (0.4 mL) at rt for 24 h. Purification of the crude product by silica-gel column chromatography (*n*-hexane/EtOAc = 10/1) to give **4ja** (62 mg, 75% yield) as a colorless liquid. Spectral data of **4ja**: IR (neat) 2923, 1596, 1351 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 3.43 (t, *J* = 7.0 Hz, 2H), 3.05 (s, 3H), 2.44 (s, 3H), 2.39 (t, *J* = 7.9 Hz, 2H), 2.04 (s, 3H), 1.91-1.87 (m, 5H), 1.67-1.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 143.8, 140.3, 135.2, 129.5, 128.2, 121.3, 115.4, 37.9, 33.8, 32.6, 27.6, 22.7, 21.7, 11.5, 8.8; HRMS (EI) calcd for $C_{18}H_{24}BrNO_3S$ [M^+] 413.0660, found 413.0658.



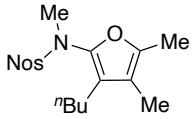
Furan 4ka

According to the general procedure, a crude product was obtained from **1k** (82.6 mg, 0.20 mmol), **2a** (0.20 mL of 1.0 M solution in toluene, 0.2 mmol), Au(IPr)NTf_2 (8.7 mg, 0.010 mmol) and PPTS (2.6 mg, 0.010 mmol) in Toluene (0.4 mL) at rt for 24 h. Purification of the crude product by silica-gel column chromatography (*n*-hexane/EtOAc = 10/1) to give **4ka** (72.7 mg, 75% yield) as a colorless liquid. Spectral data of **4ka**: IR (neat) 2941, 1771, 1713, 1596cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83-7.82 (m, 2H), 7.70-7.69 (m, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 3.69 (t, *J* = 7.2 Hz, 2H), 3.05 (s, 3H), 2.42-2.37 (m, 5H), 2.02 (s, 3H), 1.83 (s, 3H), 1.74-1.66 (m, 2H), 1.59-1.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 144.7, 143.7, 140.3, 135.3, 134.0, 132.2, 129.5, 128.2, 123.3, 121.4, 115.5, 38.0, 37.9, 28.6, 26.4, 23.2, 21.7, 11.5, 8.8; HRMS (ESI) calcd for $C_{26}H_{28}N_2NaO_5S$ [$(M+Na)^+$] 503.1611, found 503.1600.



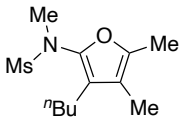
Furan 4la

According to the general procedure, a crude product was obtained from **1l** (62.3 mg, 0.20 mmol), **2a** (0.20 mL of 1.0 M solution in toluene, 0.2 mmol), Au(IPr)NTf_2 (8.7 mg, 0.010 mmol) and PPTS (2.6 mg, 0.010 mmol) in Toluene (0.4 mL) at 60 °C for 24 h. Purification of the crude product by silica-gel column chromatography (*n*-hexane/EtOAc = 15/1) to give **4la** (62.0 mg, 82% yield) as a colorless liquid. Spectral data of **4la**: IR (CH_2Cl_2) 2961, 2873, 1687, 1655, 1611 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 5.8 Hz, 4H), 5.75-5.70 (m, 1H), 4.98-4.94 (m, 2H), 3.35-3.33 (m, 2H), 2.43 (s, 3H), 2.29 (t, *J* = 8.1 Hz, 2H), 2.06-2.01 (m, 5H), 1.88 (s, 3H), 1.53-1.33 (m, 6H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 143.5, 137.8, 137.7, 136.5, 129.5, 128.1, 124.2, 115.6, 115.2, 49.7, 31.6, 30.7, 27.5, 23.7, 23.2, 21.7, 14.1, 11.6, 9.0; HRMS (EI) calcd for $C_{22}H_{31}NO_3S$ [M^+] 389.2025, found 389.2026.



Furan 4ma

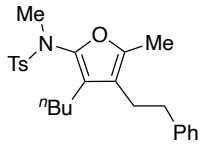
According to the general procedure, a crude product was obtained from **1m**[5] (58.8 mg, 0.20 mmol), **2a** (0.20 mL of 1.0 M solution in toluene, 0.2 mmol), Au(IPr)NTf_2 (8.6 mg, 0.010 mmol) and PPTS (2.6 mg, 0.010 mmol) in Toluene (0.4 mL) at 60 °C for 24 h. Purification of the crude product by silica-gel column chromatography (*n*-hexane/EtOAc = 8/1) to give **4ma** (65.2 mg, 89% yield) as a pale yellow liquid. Spectral data of **4ma**: IR (CH_2Cl_2) 3104, 2930, 2254, 1732cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.37-8.34 (m, 2H), 7.99-7.96 (m, 2H), 3.11 (s, 3H), 2.36 (t, *J* = 7.7 Hz, 2H), 2.03 (s, 3H), 1.87 (s, 3H), 1.53-1.45 (m, 2H), 1.37-1.33 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 145.2, 144.3, 139.0, 129.5, 124.1, 123.0, 116.0, 100.1, 38.6, 31.4, 23.3, 22.8, 14.0, 11.5, 8.7, 6.6; HRMS (EI) calcd for $C_{17}H_{22}N_2O_5S$ [M^+] 366.1249, found 366.1253.



Furan 4na

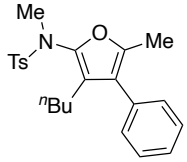
According to the general procedure, a crude product was obtained from **1n**[6] (57.4 mg, 0.30 mmol), **2a** (0.30 mL of 1.0 M solution in toluene, 0.3 mmol), Au(IPr)NTf_2 (2.6 mg, 0.003 mmol) and PPTS (4.0 mg, 0.015 mmol) in Toluene (0.6 mL) at 60 °C for 24 h. Purification of the crude product by silica-gel column chromatography (*n*-hexane/EtOAc = 10/1) to give **4na** (69.6 mg, 90% yield) as a colorless liquid. Spectral data of **4na**: IR (neat) 2930, 1654, 1596 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.20 (s, 3H), 2.99 (s, 3H), 2.33 (t, *J* = 7.9 Hz, 2H), 2.13 (s, 3H),

1.85 (s, 3H), 1.50-1.29 (m, 4H), 0.91 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 139.8, 122.3, 115.8, 38.4, 37.5, 31.4, 23.2, 22.8, 14.0, 11.6, 8.7; HRMS (EI) calcd for $C_{12}H_{21}NO_3S$ [M^+] 259.1241, found 259.1246.



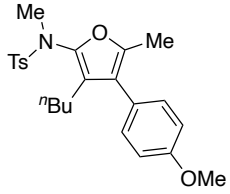
Furan 4ab

According to the general procedure, a crude product was obtained from **1a** (80.1 mg, 0.30 mmol), **2b**[7] (0.30 mL of 1.0 M solution in toluene, 0.3 mmol), Au(IPr)NTf_2 (2.7 mg, 0.003 mmol) and PPTS (3.8 mg, 0.015 mmol) in Toluene (0.6 mL) at rt for 24 h. Purification of the crude product by silica-gel column chromatography (*n*-hexane/EtOAc = 15/1) to give **4ab** (117.3 mg, 92% yield) as a colorless liquid. Spectral data of **4ab**: IR (CH_2Cl_2) 3064, 2932, 1596, 1495, 1454 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.1 Hz, 2H), 7.31-20 (m, 5H), 7.15 (d, J = Hz, 2H), 3.08 (s, 3H), 2.77 (t, J = 7.6 Hz, 2H), 2.60 (t, J = 7.6 Hz, 2H), 2.45 (s, 3H), 2.38 (t, J = 7.9 Hz, 2H), 1.82 (s, 3H), 1.56-1.52 (m, 2H), 1.41-1.33 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 143.7, 141.7, 140.3, 135.3, 129.4, 128.8, 128.4, 128.2, 126.0, 121.7, 119.1, 37.9, 36.7, 31.8, 26.2, 23.3, 22.9, 21.7, 14.0, 11.3; HRMS (EI) calcd for $C_{25}H_{31}NO_3S$ [M^+] 425.2025, found 425.2024.



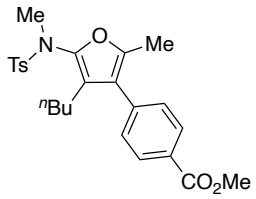
Furan 4ac

According to the general procedure, a crude product was obtained from **1a** (79.0 mg, 0.30 mmol), **2c**[8] (0.30 mL of 1.0 M solution in toluene, 0.3 mmol), Au(IPr)NTf_2 (2.6 mg, 0.003 mmol) and PPTS (3.8 mg, 0.015 mmol) in Toluene (0.6 mL) at 60 °C for 24 h. Purification of the crude product by silica-gel column chromatography (*n*-hexane/EtOAc = 50/1) to give **4ac** (106.4 mg, 89% yield) as a colorless liquid. Spectral data of **4ac**: IR (CH_2Cl_2) 3019, 2958, 2253, 1732, 1607 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.1 Hz, 2H), 7.40-7.39 (m, 2H), 7.33-7.31 (m, 3H), 7.27-7.26 (m, 2H), 3.13 (s, 3H), 2.44-2.41 (m, 5H), 2.14 (s, 3H), 1.30-1.13 (m, 4H), 0.76 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 143.8, 140.9, 135.4, 133.7, 129.5, 129.3, 128.4, 128.2, 126.9, 122.9, 121.6, 38.0, 31.0, 23.1, 22.6, 21.7, 13.8, 12.2; HRMS (EI) calcd for $C_{23}H_{27}NO_3S$ [M^+] 397.1712, found 397.1715.



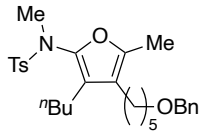
Furan 4ad

According to the general procedure, a crude product was obtained from **1a** (53.0 mg, 0.20 mmol), **2d**[8] (0.20 mL of 1.0 M solution in toluene, 0.2 mmol), Au(IPr)NTf_2 (8.8 mg, 0.010 mmol) and PPTS (2.5 mg, 0.010 mmol) in Toluene (0.4 mL) at 60 °C for 24 h. Purification of the crude product by silica-gel column chromatography (*n*-hexane/EtOAc = 10/1) to give **4ad** (67.6 mg, 74% yield) as a pale yellow liquid. Spectral data of **4ad**: IR (neat) 2956, 1735, 1587, 1511 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 8.1 Hz, 2H), 3.84 (s, 3H), 3.11 (s, 3H), 2.45 (s, 3H), 2.39 (t, *J* = 7.6 Hz, 2H), 2.11 (s, 3H), 1.30-1.13 (m, 4H), 0.77 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 145.4, 143.8, 140.7, 135.5, 130.5, 129.5, 128.3, 125.9, 122.5, 121.8, 113.9, 55.3, 38.0, 31.1, 23.2, 22.6, 21.7, 13.9, 12.2; HRMS (EI) calcd for $C_{24}H_{29}NO_4S$ [M^+] 427.1817, found 427.1815.



Furan 4ae

According to the general procedure, a crude product was obtained from **1a** (52.6 mg, 0.20 mmol), **2e**[8] (0.20 mL of 1.0 M solution in toluene, 0.2 mmol), Au(IPr)NTf_2 (8.9 mg, 0.010 mmol) and PPTS (2.5 mg, 0.010 mmol) in Toluene (0.4 mL) at 60 °C for 24 h. Purification of the crude product by silica-gel column chromatography (*n*-hexane/EtOAc = 10/1) to give **4ae** (69.1 mg, 76% yield) as a colorless liquid. Spectral data of **4ae**: IR (neat) 2954, 1722, 1612, 1436 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.6 Hz, 2H), 7.73 (d, *J* = 8.6 Hz, 2H), 7.35-7.31 (m, 4H), 3.93 (s, 3H), 3.12 (s, 3H), 2.44-2.41 (m, 5H), 2.14 (s, 3H), 1.24-1.16 (m, 4H), 0.75 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 146. 2, 144.0, 141.4, 138.7, 135.3, 129.8, 129.6, 129.2, 128.6, 128.2, 122.2, 121.4, 52.2, 38.0, 31.1, 23.2, 22.6, 21.7, 13.8, 12.4; HRMS (ESI) calcd for $C_{25}H_{29}NNaO_5S$ [$(M+Na)^+$] 478.1659, found 478.1655.



Furan 4af

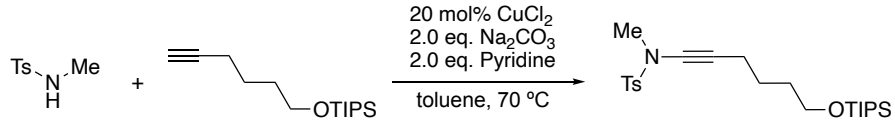
According to the general procedure, a crude product was obtained from **1a** (52.6 mg, 0.20 mmol), **2f**[9] (0.20 mL of 1.0 M solution in toluene, 0.2 mmol), Au(IPr)NTf_2 (8.9 mg, 0.010 mmol) and PPTS (2.5 mg, 0.010 mmol) in Toluene (0.4 mL) at rt for 24 h. Purification of the crude product by silica-gel column chromatography (*n*-hexane/EtOAc = 10/1) to give **4af** (55.5 mg, 56% yield) as a colorless liquid. Spectral data of **4af**: IR (neat) 2933, 1455, 1353, 1161 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.5 Hz, 2H), 7.35-7.27 (m, 7H), 4.51 (s, 2H), 3.48 (t, *J* = 6.5 Hz, 2H), 3.05 (s, 3H), 2.44 (s, 3H), 2.32-2.27 (m, 4H), 2.05 (s, 3H), 1.69-1.62 (m, 2H), 1.52-1.24

(m, 8H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 143.7, 140.2, 138.8, 135.5, 129.4, 128.5, 128.3, 127.7, 127.6, 121.8, 120.3, 73.1, 70.5, 37.9, 31.7, 30.4, 29.8, 26.3, 24.0, 23.3, 22.9, 21.7, 14.0, 11.8; HRMS (ESI) calcd for $C_{29}H_{39}NNaO_4S$ [$(M+Na)^+$] 520.2492, found 520.2487.

Preparation of Ynamides.

Ynamide **1h** were prepared following the reported procedure.[10] Ynamides **1j**, **1k** were synthesized via following procedure. Ynamides **1l** were synthesized by copper-catalyzed amidation of bromoalkynes according to established procedure.[11]

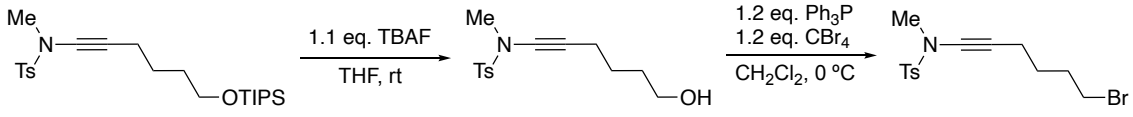
Ynamide 1h



S1 (5.0 eq.) **S2** **1h**

In a 250 ml three-neck round-bottom flask equipped with a stir-bar, $CuCl_2$ (168.9 mg, 1.3 mmol), *N*-Methyl-*p*-toluenesulfonamide (**S1**) (5.82 g, 31.4 mmol) and Na_2CO_3 (1.33 g, 12.6 mmol) were combined. The reaction flask was purged with oxygen gas for 15 minutes. A solution of pyridine (1.01 mL, 12.6 mmol) in toluene (30 mL) was added to the reaction flask via a syringe. A balloon filled with oxygen gas was connected to the reaction flask via a needle. The flask was placed in an oil-bath and heated to 70 °C. A solution of **S2**[12] (1.60 g, 6.3 mmol) in toluene (30 mL) was added to the flask over 4 h by using a syringe pump. After the addition of **S2**/toluene solution, the reaction mixture was allowed to stir at 70 ºC for another 4 h and then cooled to room temperature. After the crude mixture was concentrated under vacuum, the reaction mixture was purified by silica-gel column chromatography (*n*-hexane/EtOAc = 10/1) to give **1h** (2.13 g, 78% yield) as a colorless liquid. Spectral data of **1h**: IR (neat) 2941, 2254, 1597, 1463, 1367 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 3.69-3.67 (m, 2H), 3.01 (s, 3H), 2.45 (s, 3H), 2.28-2.26 (m, 2H), 1.59-1.56 (m, 4H), 1.08-1.05 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 133.3, 129.7, 127.9, 75.1, 68.6, 63.0, 39.5, 32.2, 32.1, 25.5, 25.0, 21.8, 18.3, 18.2, 17.8, 12.4, 12.1 (^{13}C NMR spectra indicate rotamers are present.); HRMS (ESI) calcd for $C_{23}H_{39}NNaO_3SSi$ [$(M+Na)^+$] 460.2312, found 460.2311.

Ynamide 1j

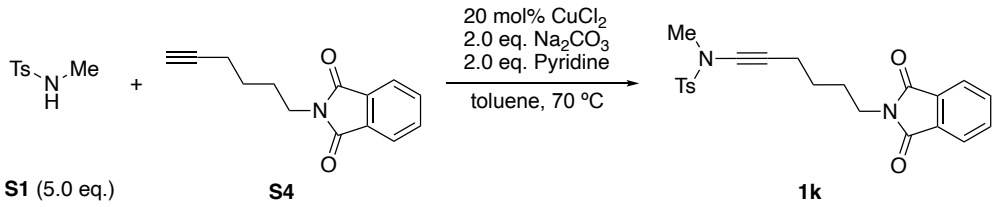


1h **S3** **1j**

To a solution of **1h** (1.73 g, 3.95 mmol) in THF (2.5 mL) was added a solution of TBAF in THF (1.0 M, 4.34 mL, 4.34 mmol) at 0 °C, and the mixture was stirred at room temperature for 4 h. To the mixture was added water at 0 °C, and the aqueous layer was extracted with AcOEt. The organic layer was washed with saturated aqueous

solution of NaCl, dried over Na_2SO_4, and concentrated. The crude product was roughly purified by column chromatography on silica gel (*n*-hexane/EtOAc = 5/1) to give a crude alcohol (1.15 g). To a solution of crude alcohol (983.0 mg, 3.50 mmol) in CH_2Cl (60 mL) was added CBr_4 (1.39 g, 4.20 mmol) at 0 °C, and the mixture was stirred for 3 h. To the mixture was added PPh_3 (1.10 g, 4.20 mmol) at 0 ºC, and stirred at room temperature for 4 h. After removal of the solvent, the residue was purified by column chromatography (*n*-hexane/EtOAc = 10/1) to give **1j** (777.5 mg, 65% yield) as a colorless liquid. Spectral data of **1j**: IR (neat) 2936, 2254, 1700, 1597, 1452 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 3.38 (t, *J* = 6.7 Hz, 2H), 2.98 (s, 3H), 2.43 (s, 3H), 2.26 (t, *J* = 7.0 Hz, 2H), 1.93-1.84 (m, 2H), 1.63-1.55 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 133.0, 129.6, 127.7, 75.5, 67.7, 39.3, 33.3, 31.6, 27.3, 21.7, 17.6; HRMS (ESI) calcd for $C_{14}H_{18}BrNNaO_2S$ [$(M+Na)^+$] 366.0134, found 366.0136.

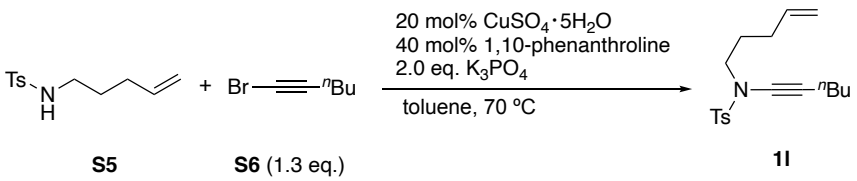
Ynamide 1k



S1 (5.0 eq.) **S4** **1k**

In a 300 ml three-neck round-bottom flask equipped with a stir-bar, $CuCl_2$ (135 mg, 1.0 mmol), *N*-Methyl-*p*-toluenesulfonamide (**S1**) (4.60 g, 25.0 mmol) and Na_2CO_3 (1.06 g, 10.0 mmol) were combined. The reaction flask was purged with oxygen gas for 15 min. A solution of pyridine (0.8 mL, 10.0 mmol) in toluene (25 mL) was added to the reaction flask via a syringe. A balloon filled with oxygen gas was connected to the reaction flask via a needle. The flask was placed in an oil-bath and heated to 70 °C. A solution of **S4**[13] (1.14 g, 5.0 mmol) in toluene (25 mL) was added to the flask over 4 h by using a syringe pump. After the addition of acetylene/toluene solution, the reaction mixture was allowed to stir at 70 ºC for another 4 h and then cooled to room temperature. After the crude mixture was concentrated under vacuum, the reaction mixture was purified by silica-gel column chromatography (CH_2Cl/MeOH = 20/1) to give **1k** (1.46 g, 71% yield) as a colorless liquid. Spectral data of **1k**: IR (neat) 3028, 2941, 2254, 1771, 1713 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84-7.80 (m, 2H), 7.76-7.69 (m, 4H), 7.34 (d, *J* = 8.1 Hz, 2H), 3.67 (t, J = 7.0 Hz, 2H), 2.99 (s, 3H), 2.42 (s, 3H), 2.29 (t, *J* = 7.0 Hz, 2H), 1.77-1.69 (m, 2H), 1.55-1.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 144.6, 134.0, 133.2, 132.2, 129.8, 127.9, 123.3, 75.5, 67.9, 39.4, 37.5, 27.8, 26.2, 21.7, 18.1; HRMS (EI) calcd for $C_{22}H_{22}N_2O_4S$ [M^+] 410.1300, found 410.1291.

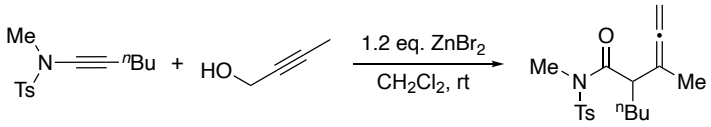
Ynamide 1l



S5 **S6** (1.3 eq.) **1l**

To a solution of **S5**[14] (2.40 g, 10.1 mmol) and **S6**[15] (2.20 g, 13.7 mmol) in toluene (20 mL) were added K_3PO_4 (4.30 g, 20.2 mmol), $CuSO_4 \cdot 5H_2O$ (510 mg, 2.0 mmol), and 1,10- phenanthroline (720 mg, 4.0 mmol), and the mixture was stirred at 60 °C for 24 h. The mixture was filtered through Celite® pad, and the filtrate was concentrated in vacuo. After the crude mixture was concentrated under vacuum, the reaction mixture was purified by silica-gel column chromatography (*n*-hexane/EtOAc = 20/1) to give **1l** (2.50 g, 78% yield) as a colorless liquid. Spectral data of **1l**: IR (neat) 2932, 2254, 1642, 1598, 1447 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 5.80-5.70 (m, 1H), 5.01-4.97 (m, 2H), 3.25 (t, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 2.24 (t, *J* = 7.0 Hz, 2H), 2.07 (q, *J* = 7.2 Hz, 2H), 1.74-1.67 (m, 2H), 1.48-1.30 (m, 4H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 137.3, 134.6, 129.7, 127.7, 115.5, 73.1, 70.2, 50.9, 31.1, 30.4, 27.0, 21.9, 21.7, 18.2, 13.6; HRMS (EI) calcd for $C_{17}H_{22}NO_2S$ [$(M–Me)^+$] 304.1371, found 304.1367.

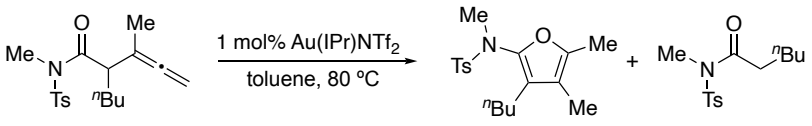
Synthesis and Spectral Data of 3,4-dienamide 3aa



1a **2a** (1.5 eq.) **3aa**

To a solution of **1a** (4.50 g, 17.0 mmol) and **2a** (1.9 mL, 25.5 mmol) in DCM (30 mL) was added $ZnBr_2$ (4.50 g, 20.0 mmol) under a nitrogen atmosphere. After stirring at room temperature for 16 h, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The reaction mixture was purified by silica-gel column chromatography (*n*-hexane/EtOAc = 20/1) to give **3aa** (3.60 g, 63% yield) as a colorless liquid. Spectral data of **3aa**: IR (neat) 2957, 1958, 1698, 1597, 1457 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 4.59-4.50 (m, 2H), 3.46 (t, *J* = 7.2 Hz, 1H), 3.34 (s, 3H), 2.40 (s, 3H), 1.72-1.63 (m, 1H), 1.57-1.49 (m, 4H), 1.24-1.09 (m, 4H), 0.81 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.1, 173.2, 144.7, 136.5, 129.6, 127.9, 96.5, 75.3, 49.2, 33.2, 30.0, 29.6, 22.6, 21.6, 15.9, 14.0; HRMS (ESI) calcd for $C_{18}H_{25}NNaO_3S$ [$(M+Na)^+$] 358.1447, found 358.1444.

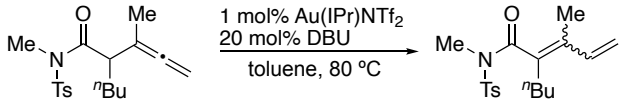
Reaction of 3aa and Spectral Data of amide 8 and 1,3-dienamide S7.



3aa **4aa** **8**

In a test tube under a nitrogen atmosphere, **3aa** (99.7 mg, 0.30 mmol) was dissolved in Toluene (0.6 mL). To the solution was added $Au(IPr)NTf_2$ (2.7 mg, 0.003 mmol). The mixture was stirred at 80 °C for 24 h. After removal of the solvent, yields of **4aa** and **8** were determined to be 42% and 42% by 1H NMR using 1,1,2,2-tetrachloroethane as an internal standard. Purification of the crude product by silica-gel column chromatography (*n*-hexane/EtOAc = 20/1) to give **4aa** (41.2 mg, 42% yield) and **8** (35.2 mg, 42% yield) as a colorless liquid. Spectral data of **8**: IR (neat) 2956, 1703, 1596, 1358 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 3.30

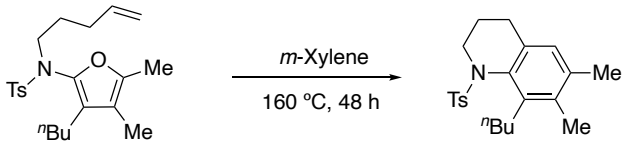
(s, 3H), 2.63 (t, J = 7.4 Hz, 2H), 2.44 (s, 3H), 1.61-1.53 (m, 2H), 1.27-1.21 (m, 4H), 0.85 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 144.9, 136.6, 130.0, 127.5, 36.6, 33.2, 31.3, 24.5, 22.5, 21.8, 14.0; HRMS (ESI) calcd for $C_{14}H_{21}NNaO_3S$ [(M+Na)$^+$] 306.1134, found 306.1130.



3aa **S7**

In a test tube under a nitrogen atmosphere, **3aa** (99.5 mg, 0.30 mmol) was dissolved in Toluene (0.6 mL). To the solution was added Au(IPr)NTf_2 (2.7 mg, 0.003 mmol) and DBU (6.6 mg, 0.015 mmol). The mixture was stirred at 80 °C for 24 h. After removal of the solvent, yield of **S7** was determined to be 90% by 1H NMR using 1,1,2,2-tetrachloroethane as an internal standard. Purification of the crude product by silica-gel column chromatography (*n*-hexane/EtOAc = 20/1) to give **S7** (90.5 mg, 91% yield) as a colorless liquid. Spectral data of **S7** (a mixture of stereoisomer): IR (neat) 2956, 1703, 1596, 1358 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.5 Hz, 2H), 7.29 (d, J = 8.5 Hz, 2H), 6.67-6.63 (m, 1H, major), 5.93-5.88 (m, 1H, minor), 5.20-4.98 (m, 2H), 3.31 (s, 3H, major), 3.27 (s, 3H, minor), 2.41 (s, 3H), 2.28-2.26 (m, 2H), 1.76 (s, 3H, minor), 1.41 (s, 3H, major), 1.29-1.24 (m, 4H), 0.82 (t, J = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 171.9, 144.9, 144.9, 135.9, 135.8, 134.8, 133.0, 132.7, 131.5, 129.5, 129.4, 128.4, 128.4, 116.9, 115.7, 33.6, 33.4, 30.9, 30.7, 30.2, 29.4, 22.8, 21.7, 15.3, 13.8, 12.5 (There are some overlapped signals in ^{13}C NMR spectra.); HRMS (EI) calcd for $C_{18}H_{25}NO_3S$ [M$^+$] 335.1555, found 335.1554.

Intramolecular Diels-Alder Reaction of Furan 4la



4la **9**

To an oven-dried shield tube was placed **4la** (35.0 mg, 0.090 mmol) in *m*-Xylene (0.2 mL). The mixture was heated at 160 ºC for 48 h. After the mixture was concentrated in vacuo, the residue was purified by silica-gel column chromatography (*n*-hexane/EtOAc = 10/1) to give **9** (26.3 mg, 79%) as a colorless solid. Spectral data of **9**: IR (CH_2Cl_2) 2956, 1498, 1467, 1341 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 6.65 (s, 1H), 4.07-4.04 (m, 1H), 3.40-3.38 (m, 1H), 3.28-3.25 (m, 1H), 2.71-2.68 (m, 1H), 2.41 (s, 3H), 2.24 (s, 6H), 2.16-2.13 (m, 1H), 1.97-1.96 (m, 1H), 1.46-1.29 (m, 6H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 141.2, 137.5, 136.3, 135.2, 134.1, 134.0, 129.6, 127.8, 127.0, 46.0, 32.5, 29.0, 25.5, 23.8, 22.9, 21.7, 20.9, 16.1, 14.2; HRMS (EI) calcd for $C_{22}H_{29}NO_2S$ [M$^+$] 371.1919, found 371.1920.

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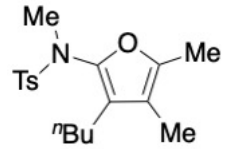
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4aa

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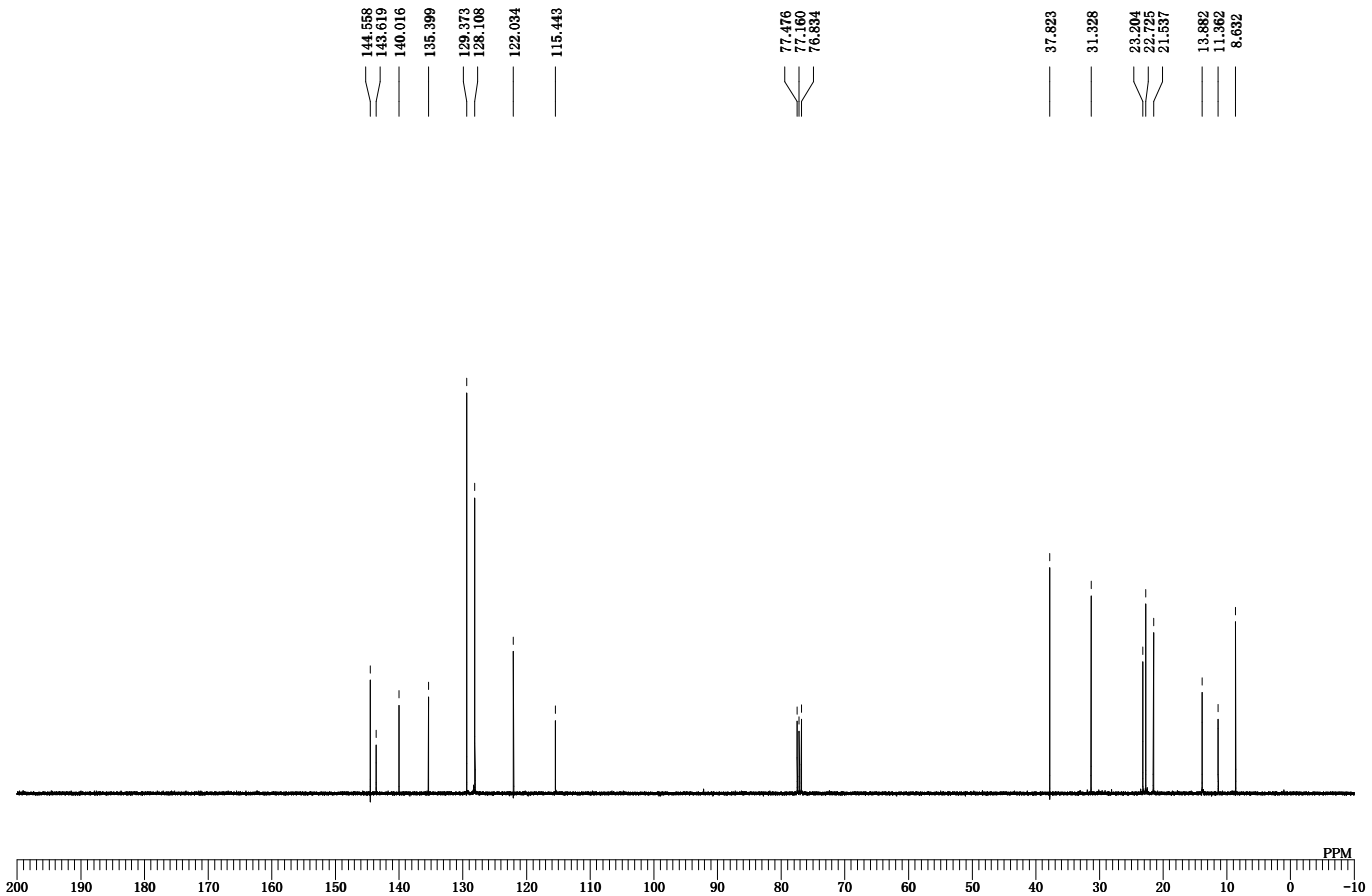
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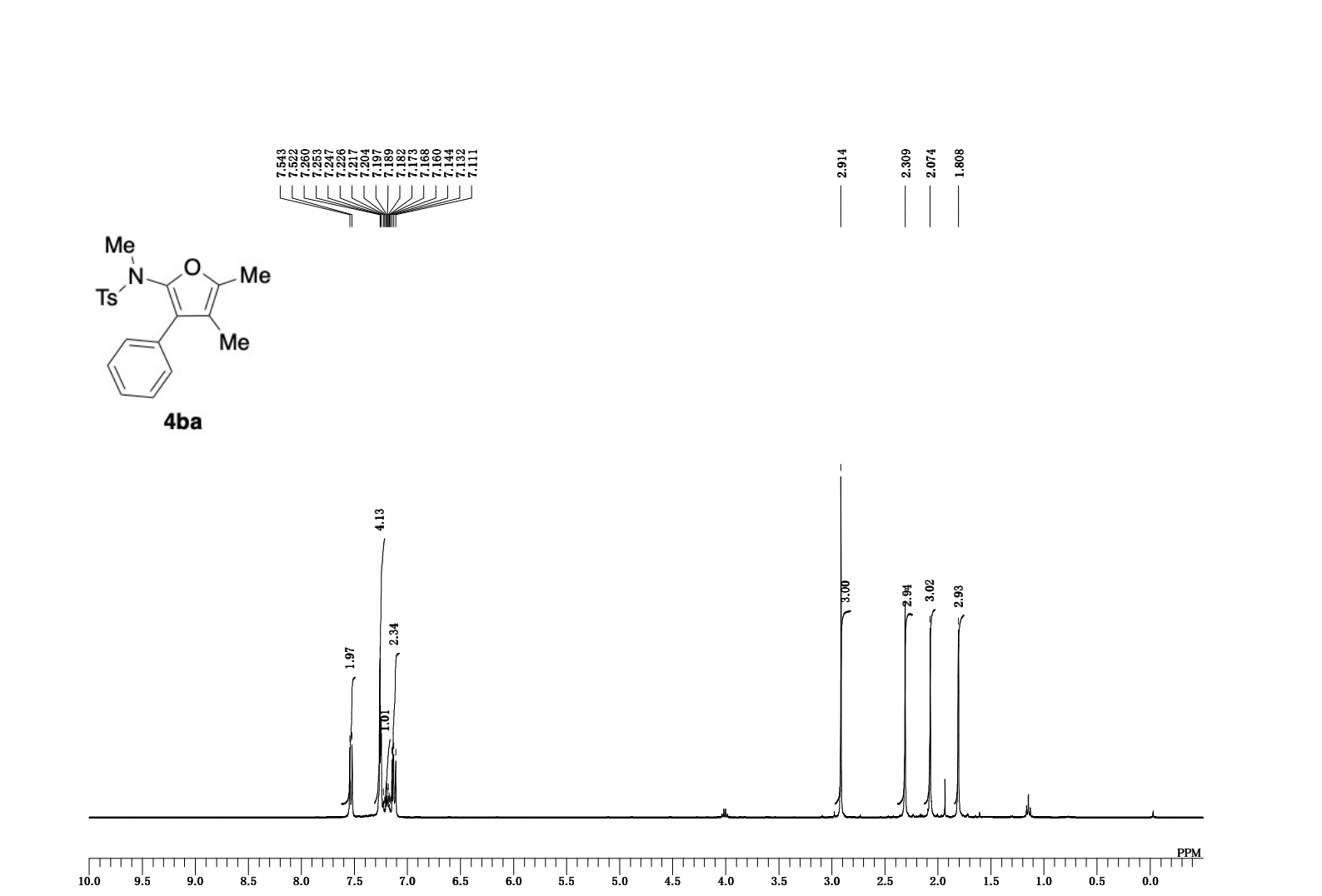
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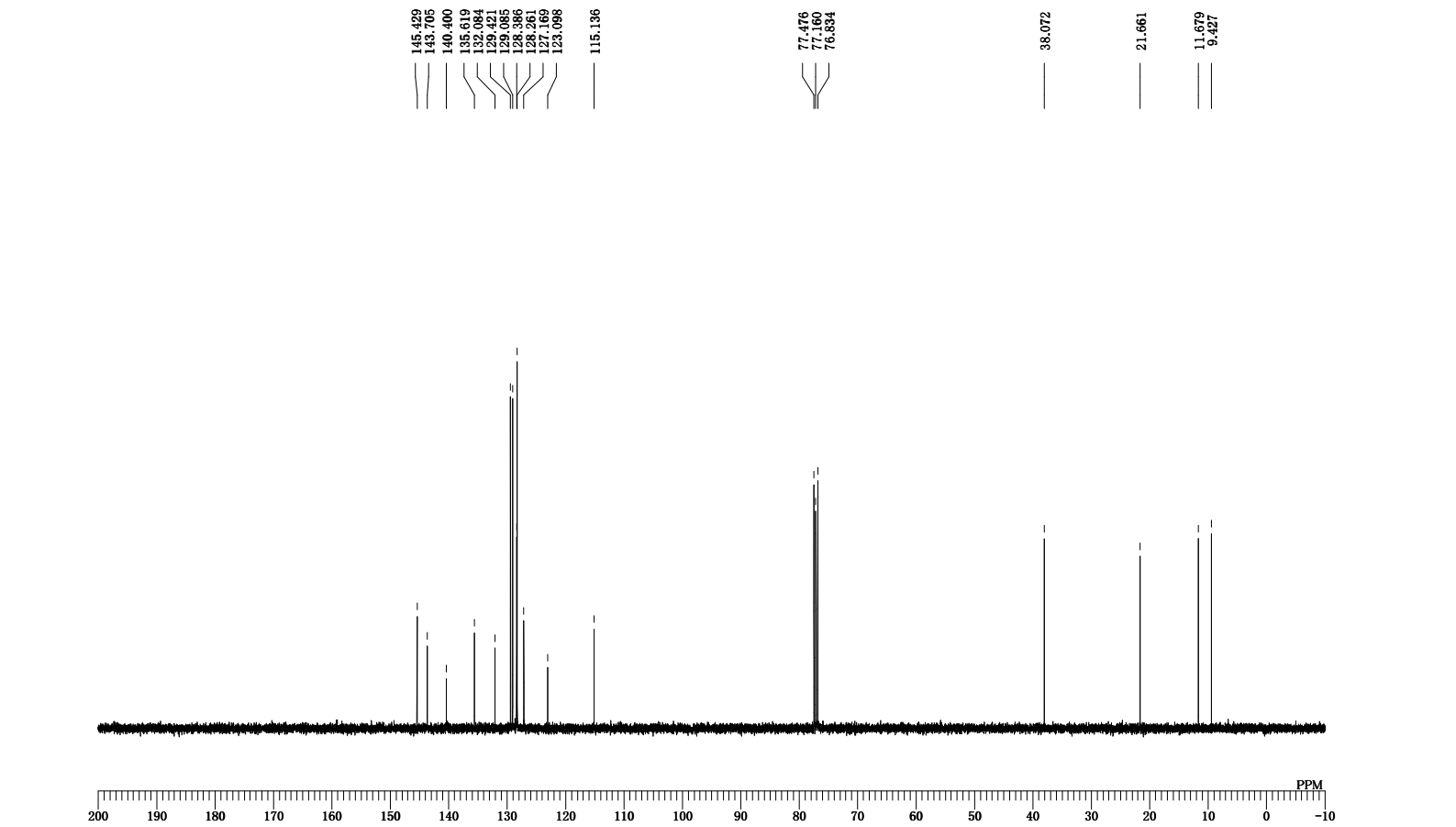
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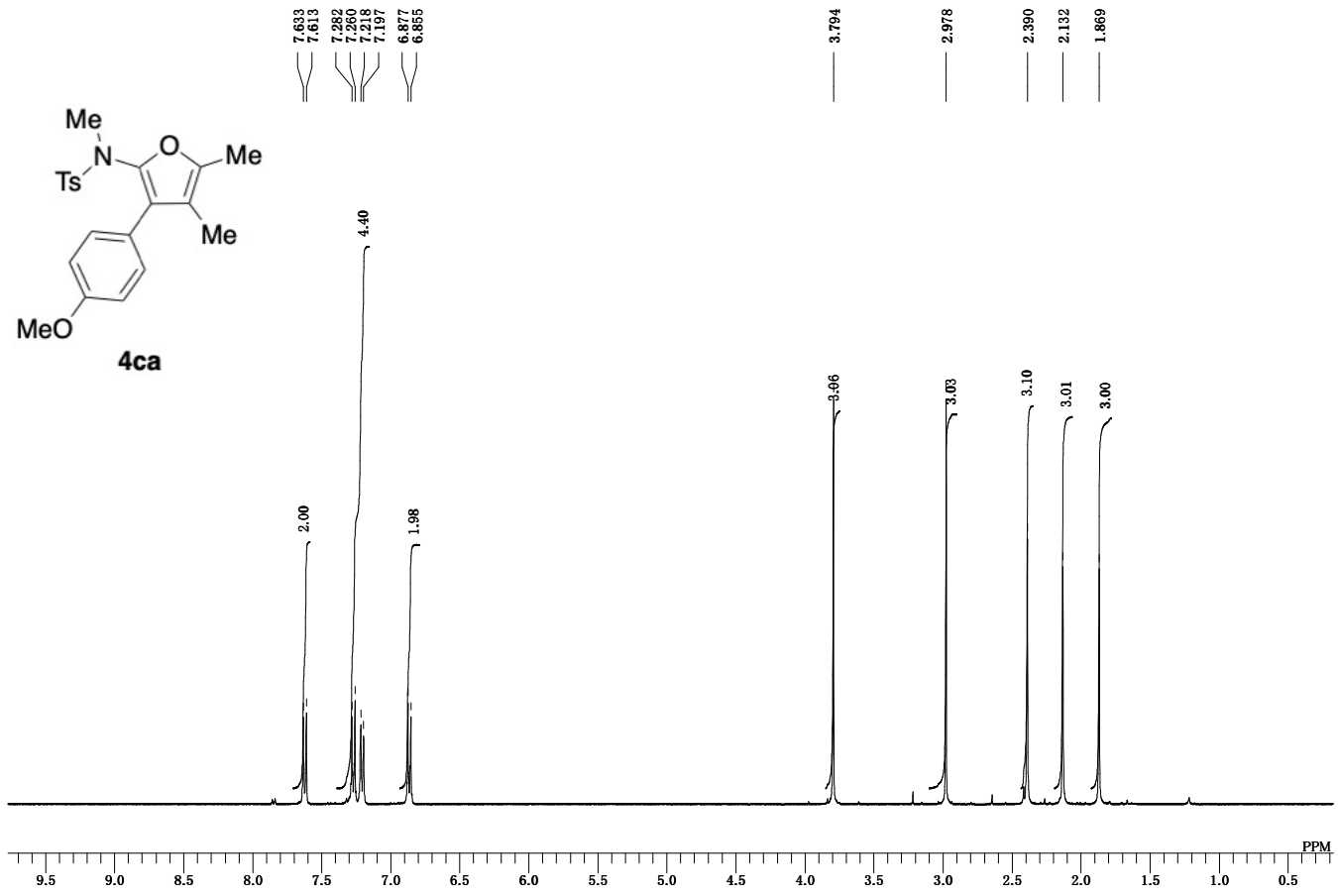
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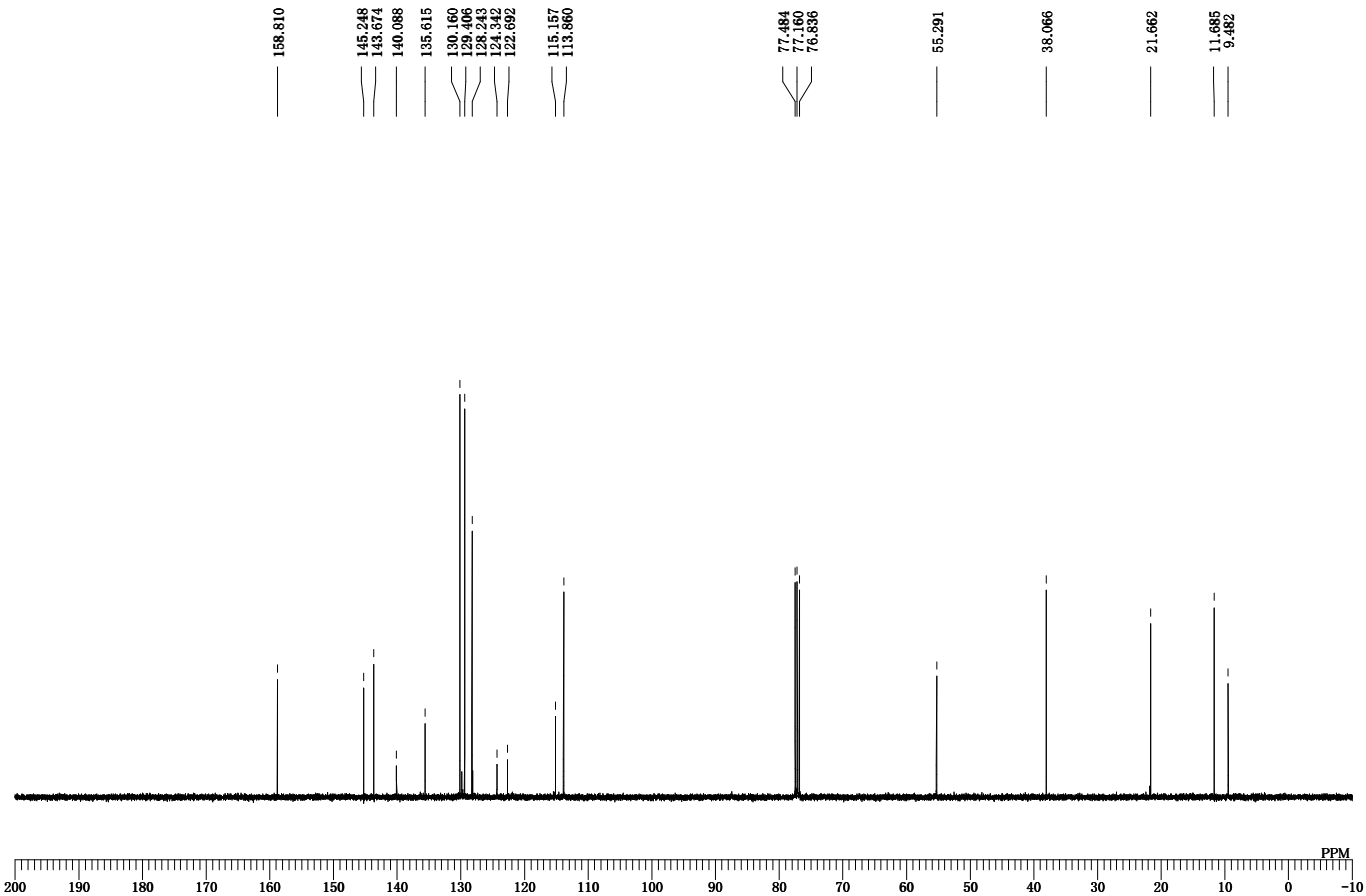
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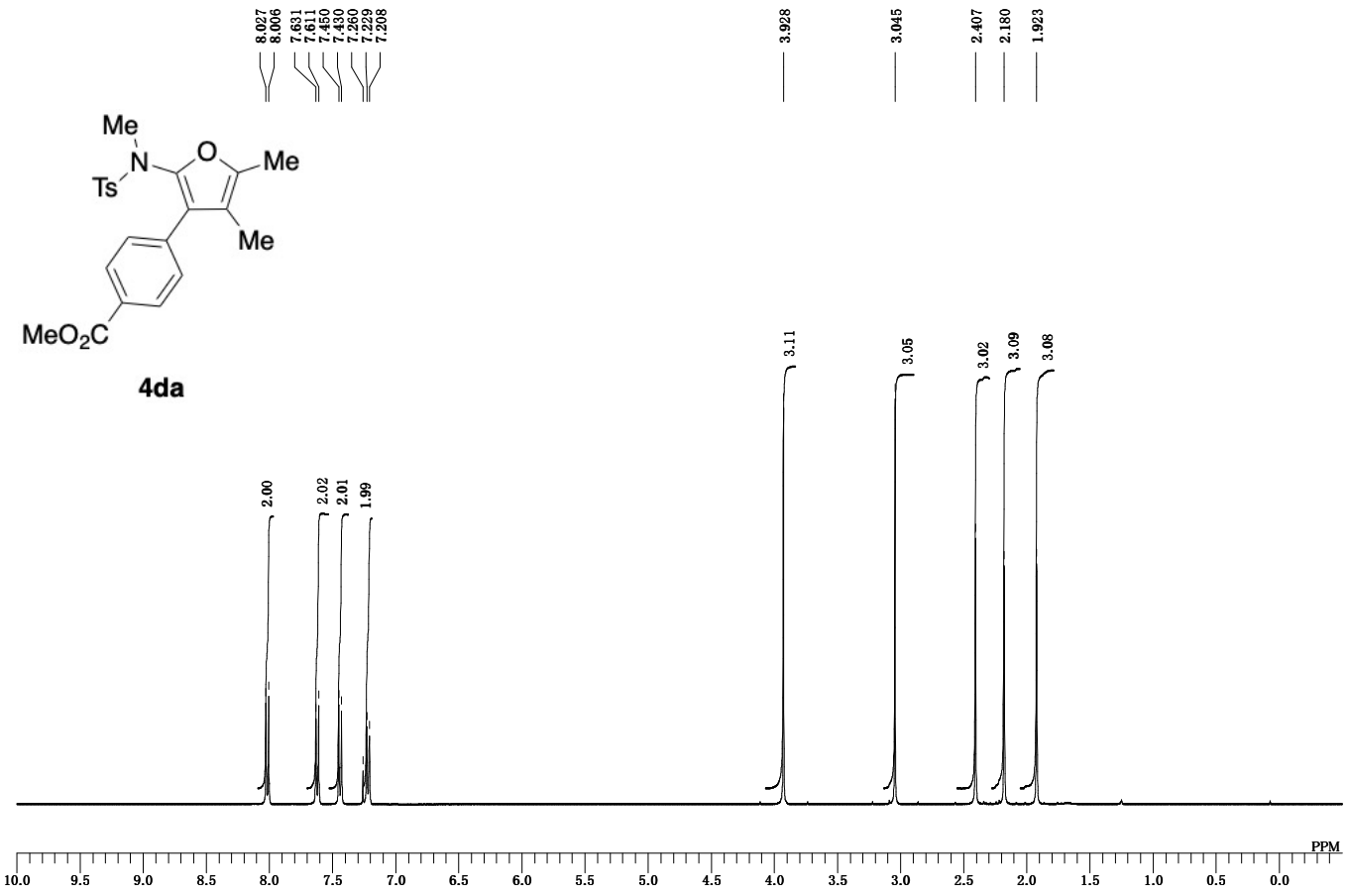
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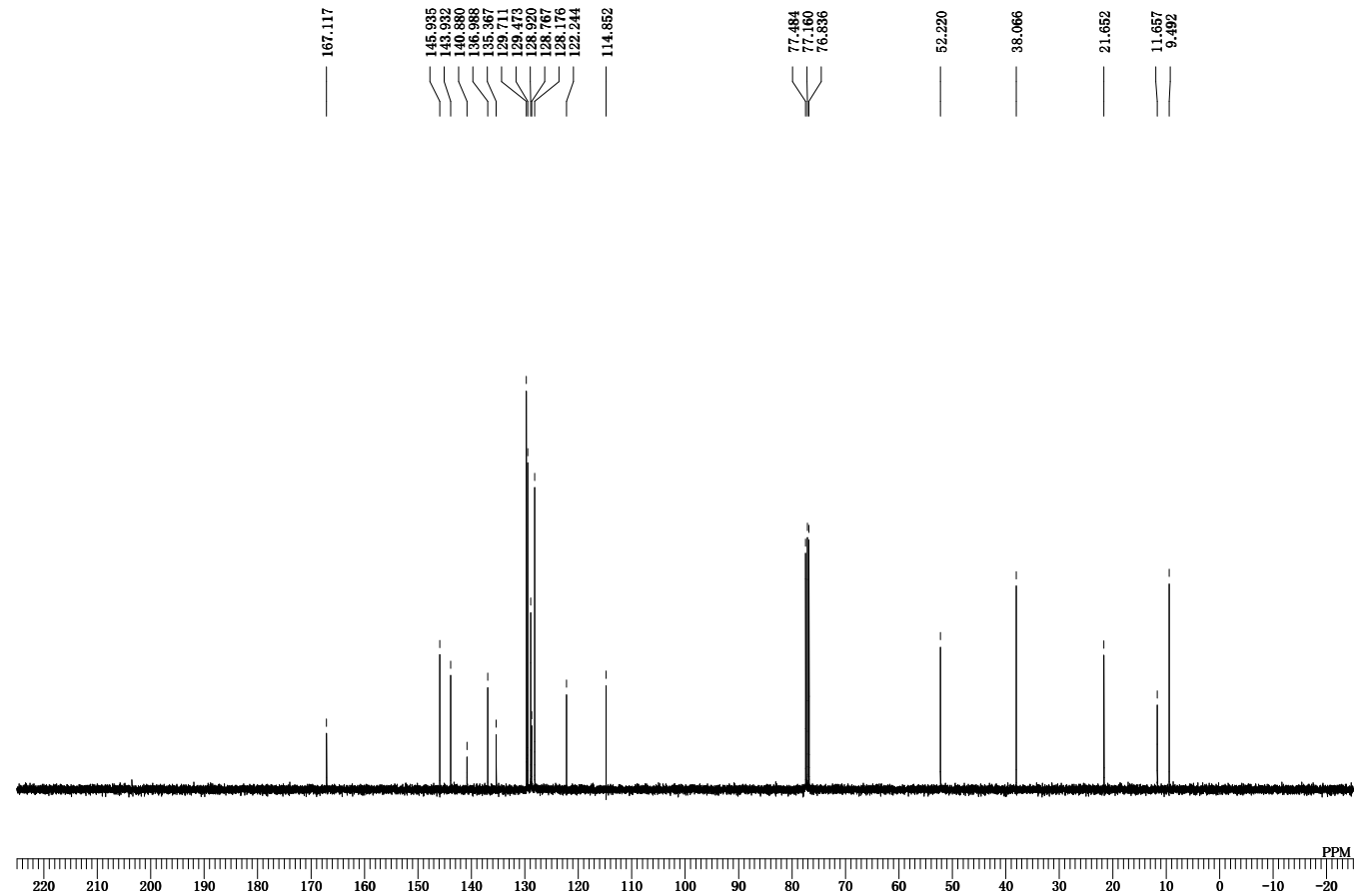
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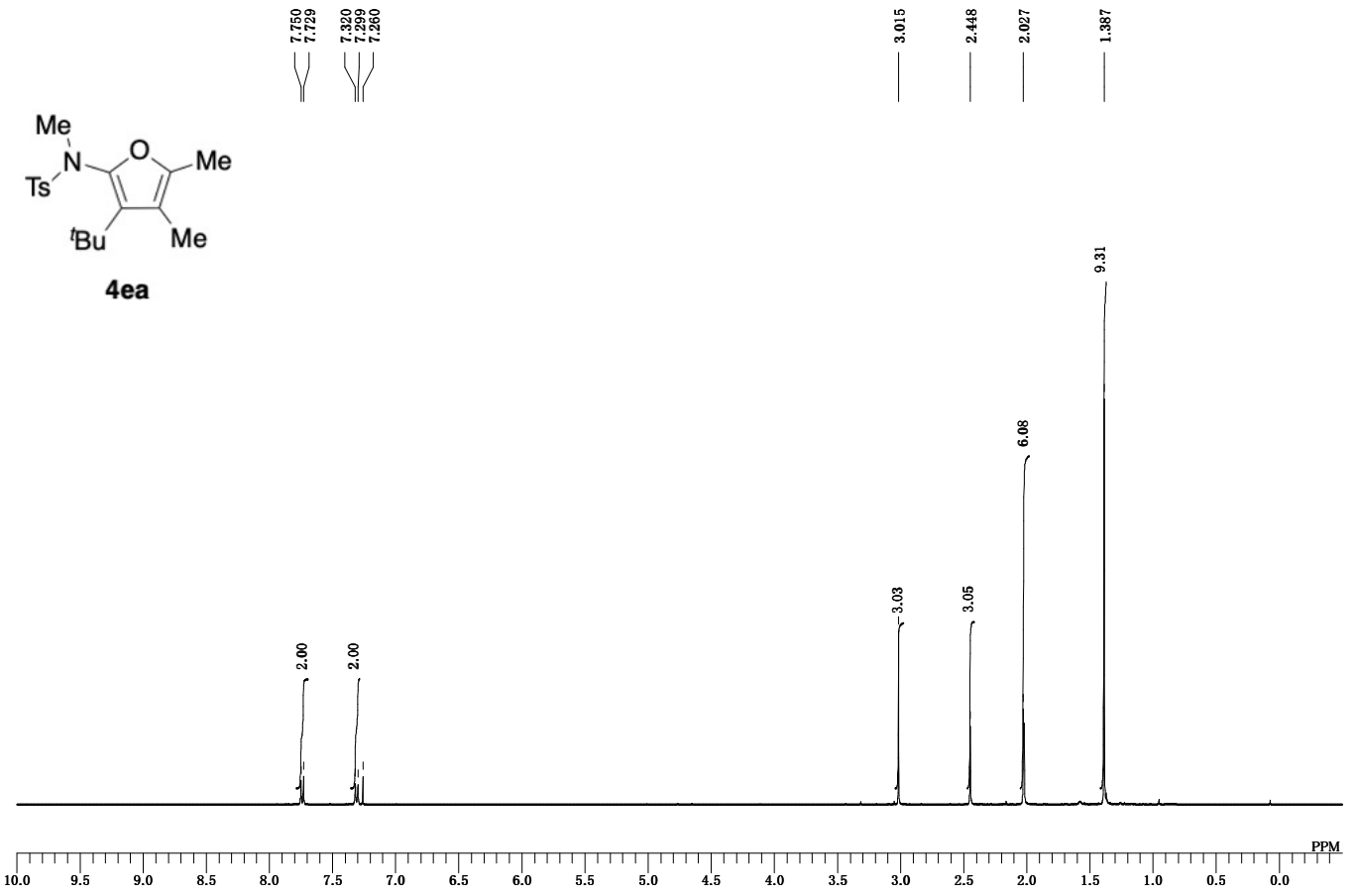
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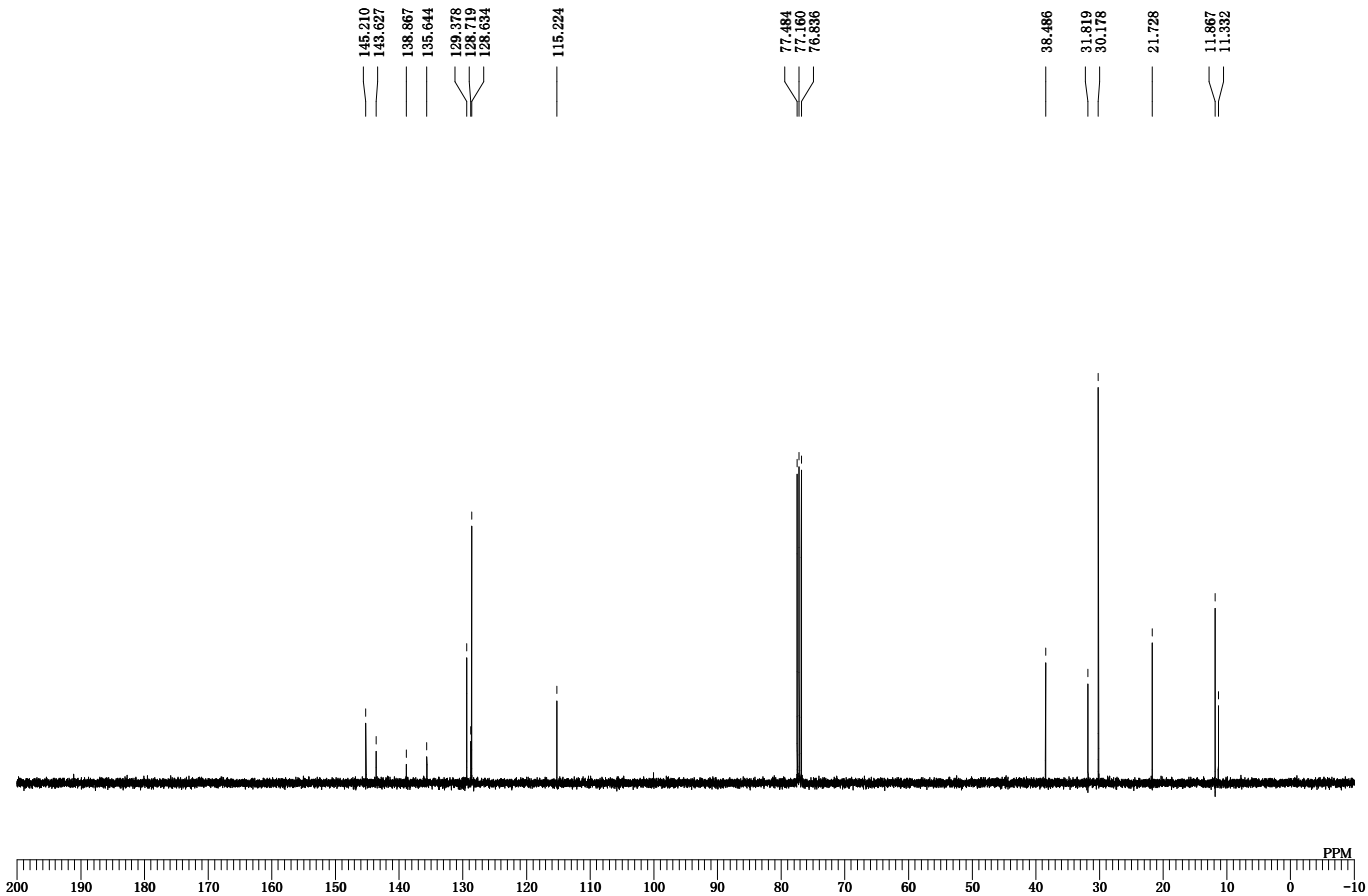
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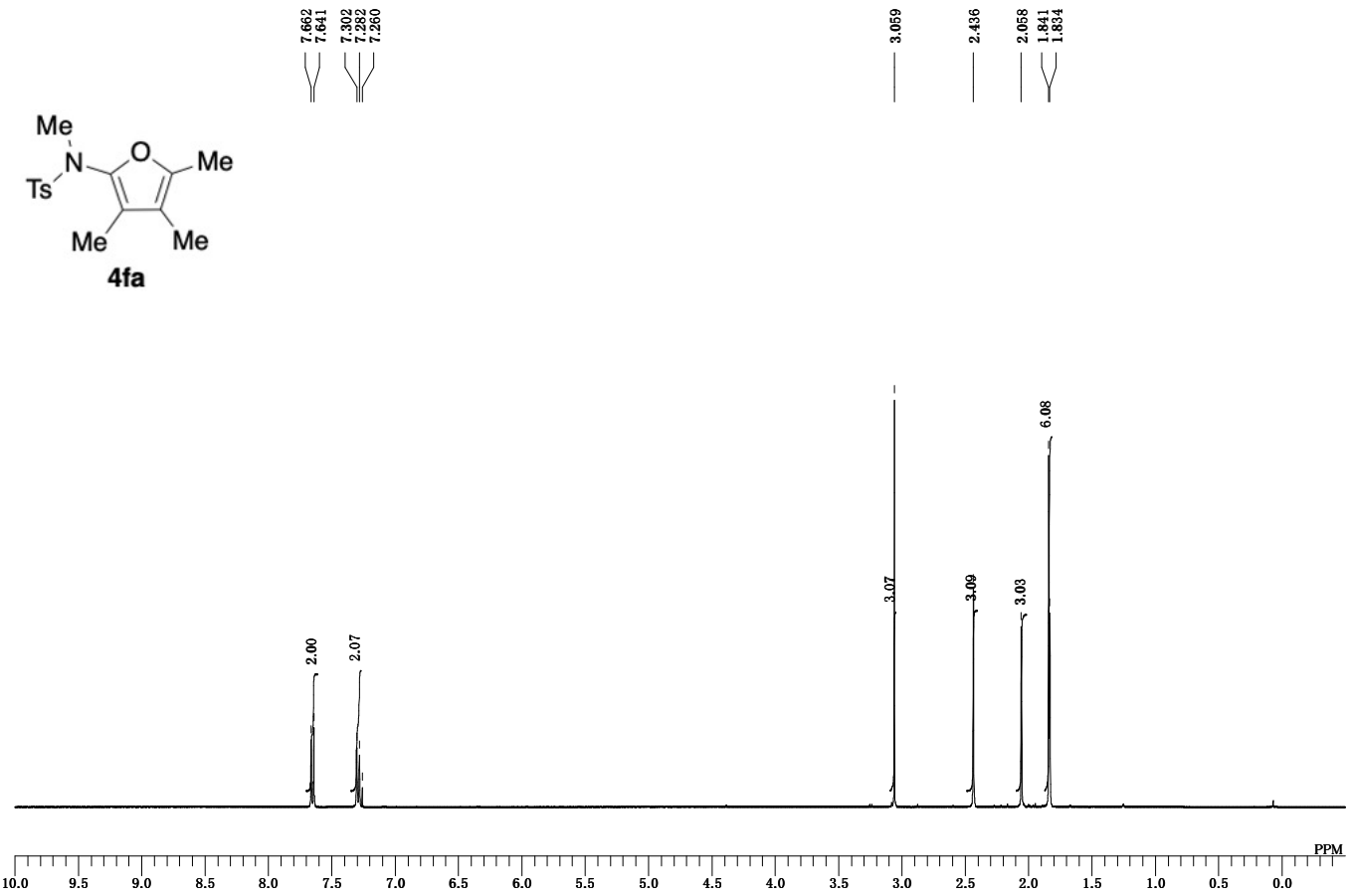
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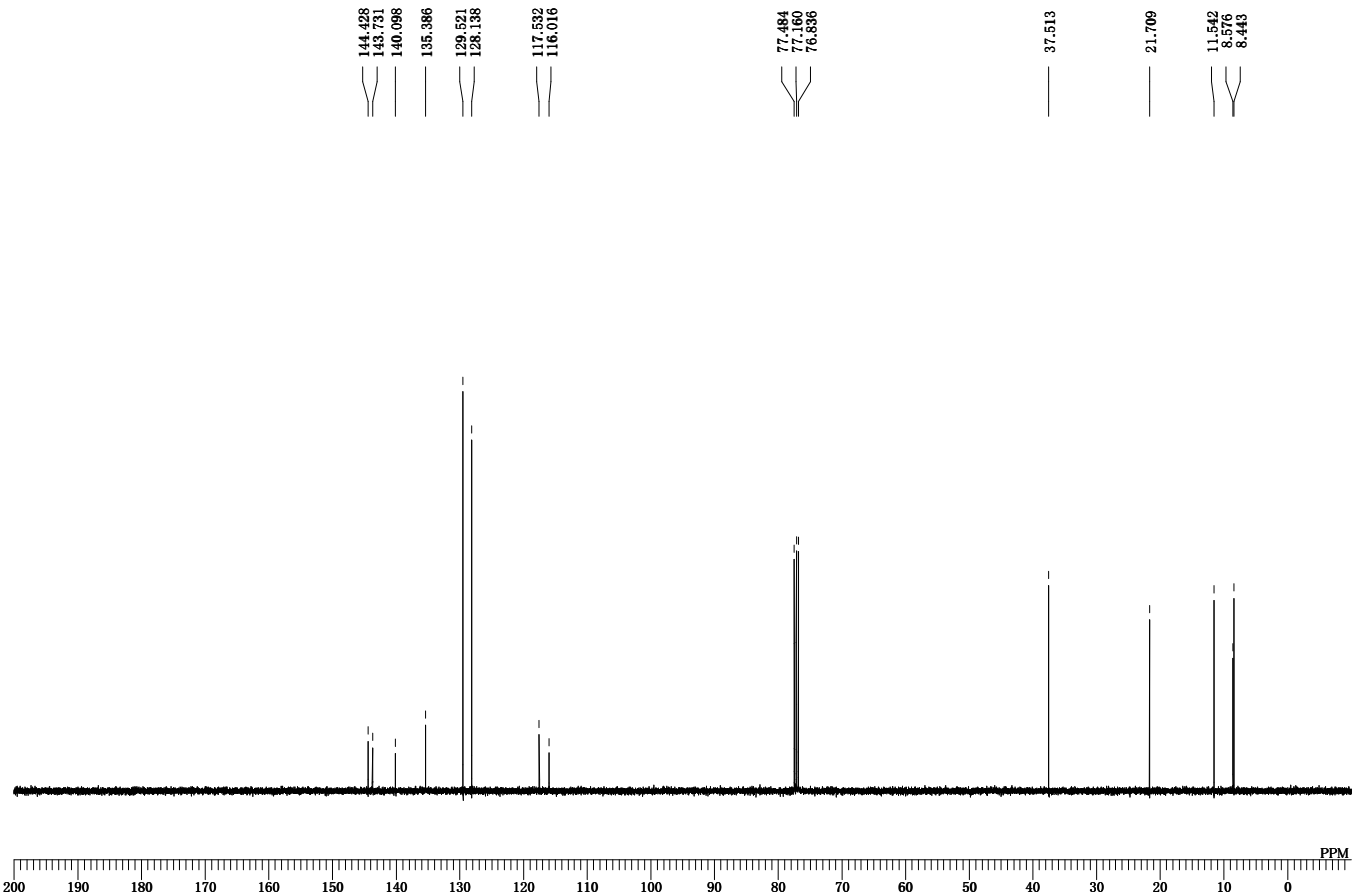
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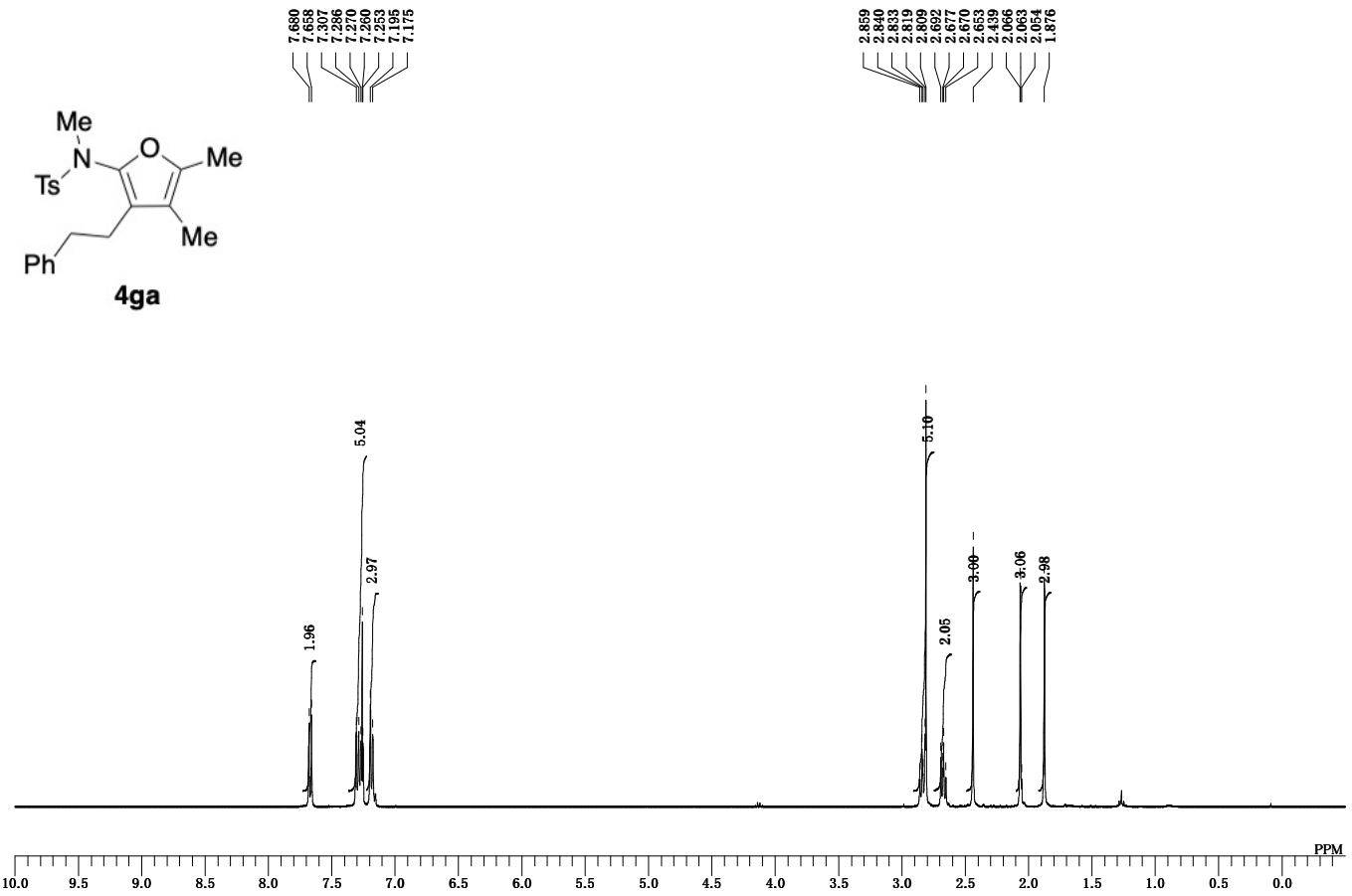
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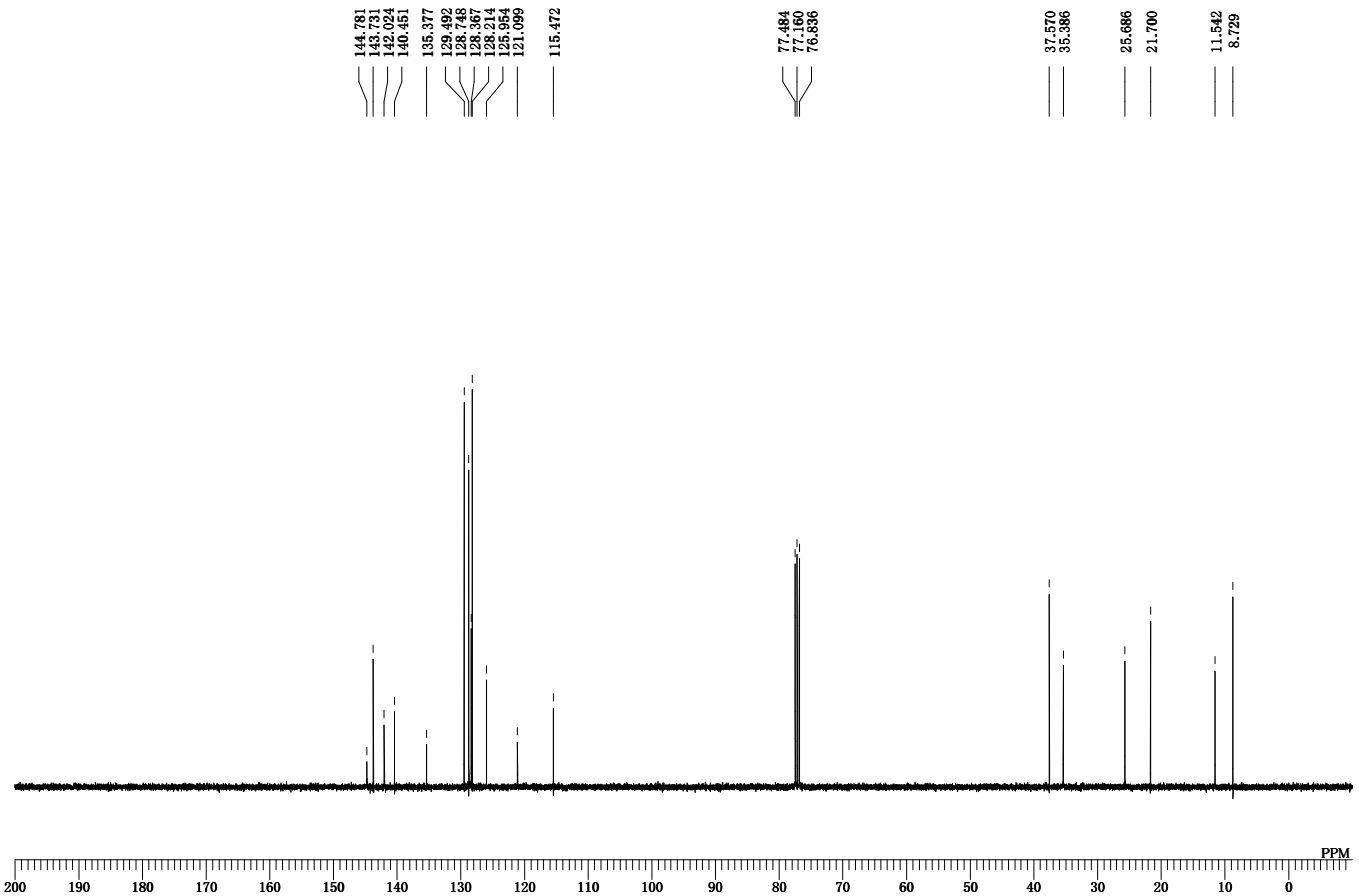
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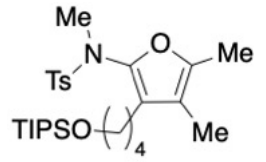
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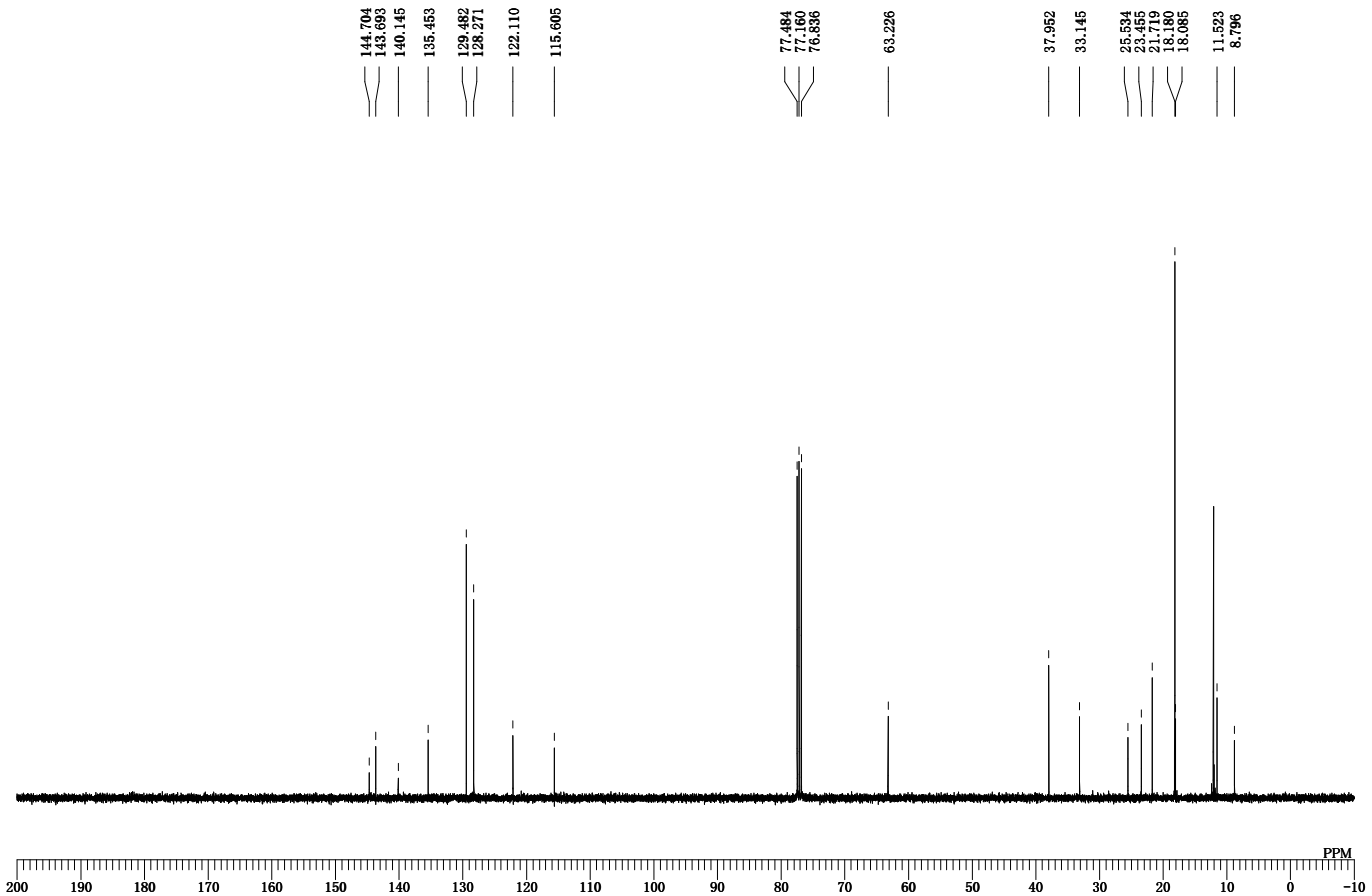
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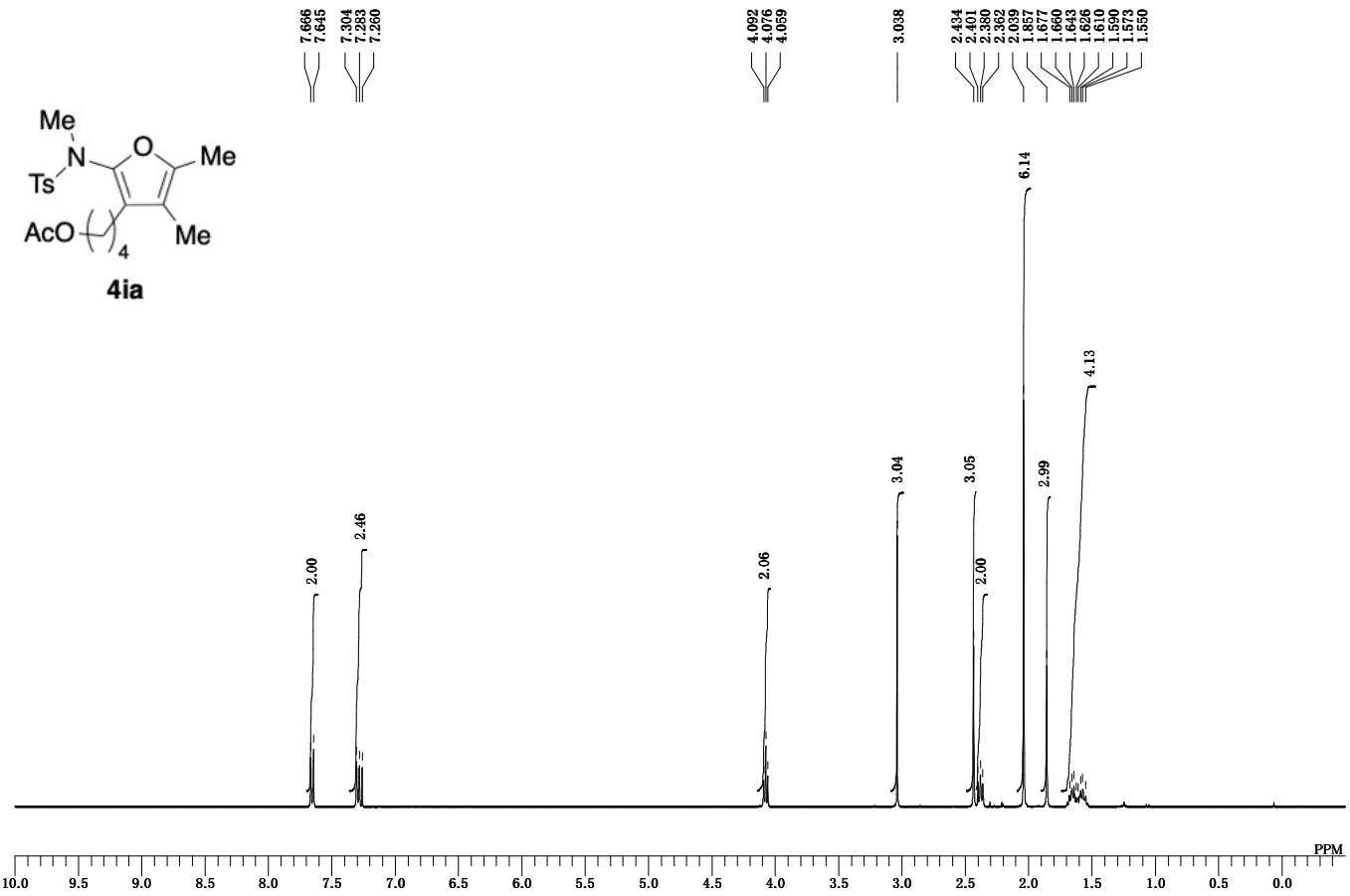
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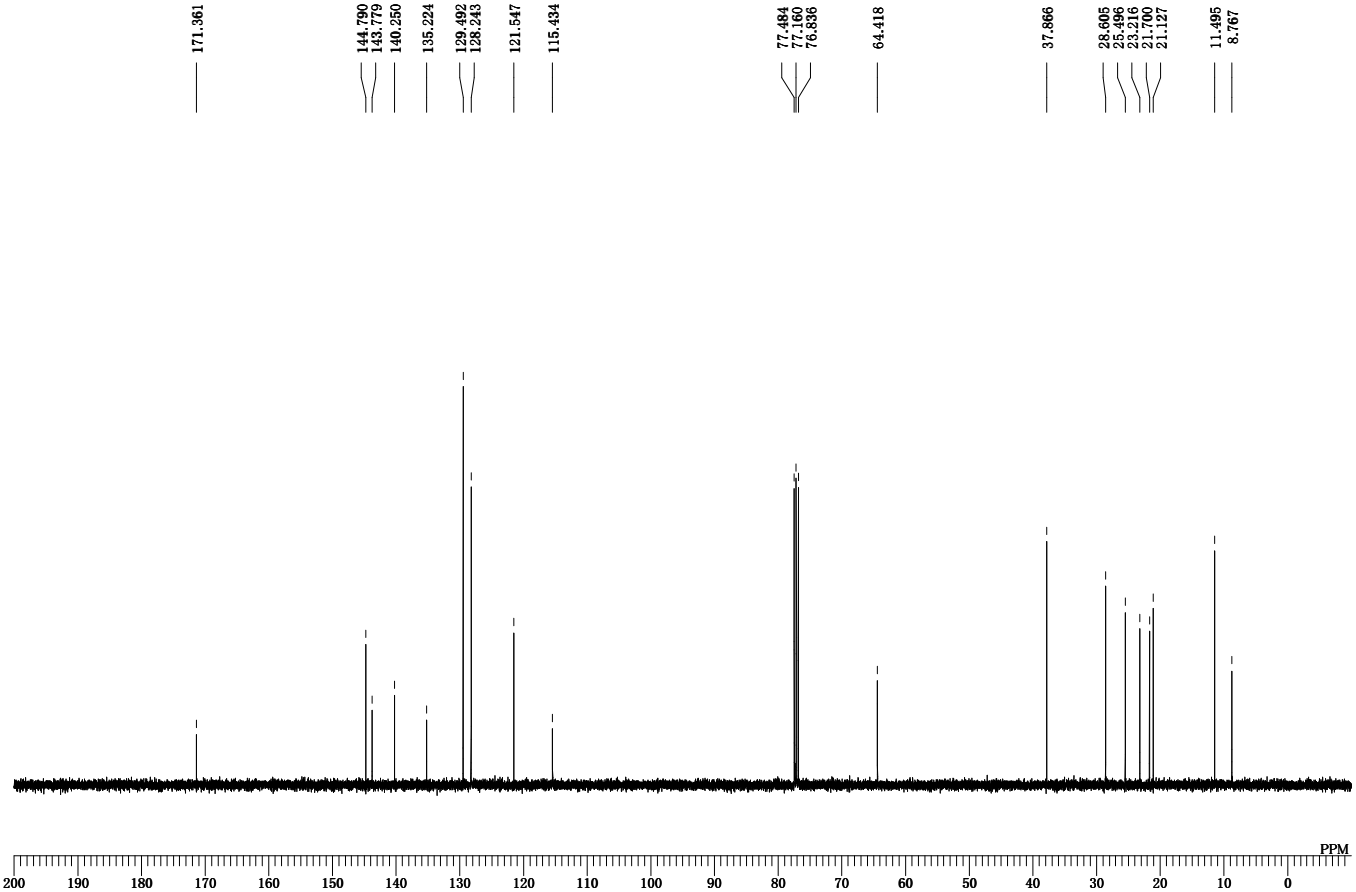
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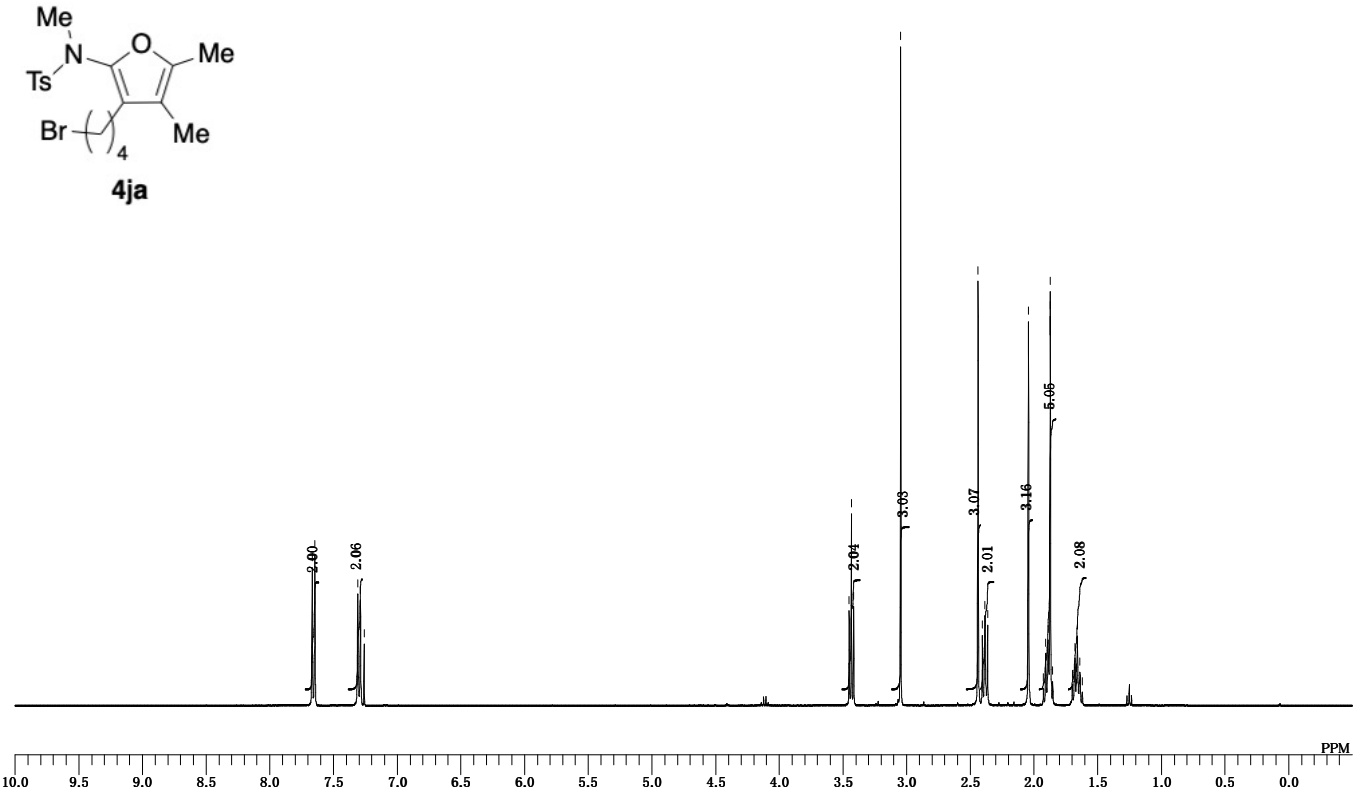
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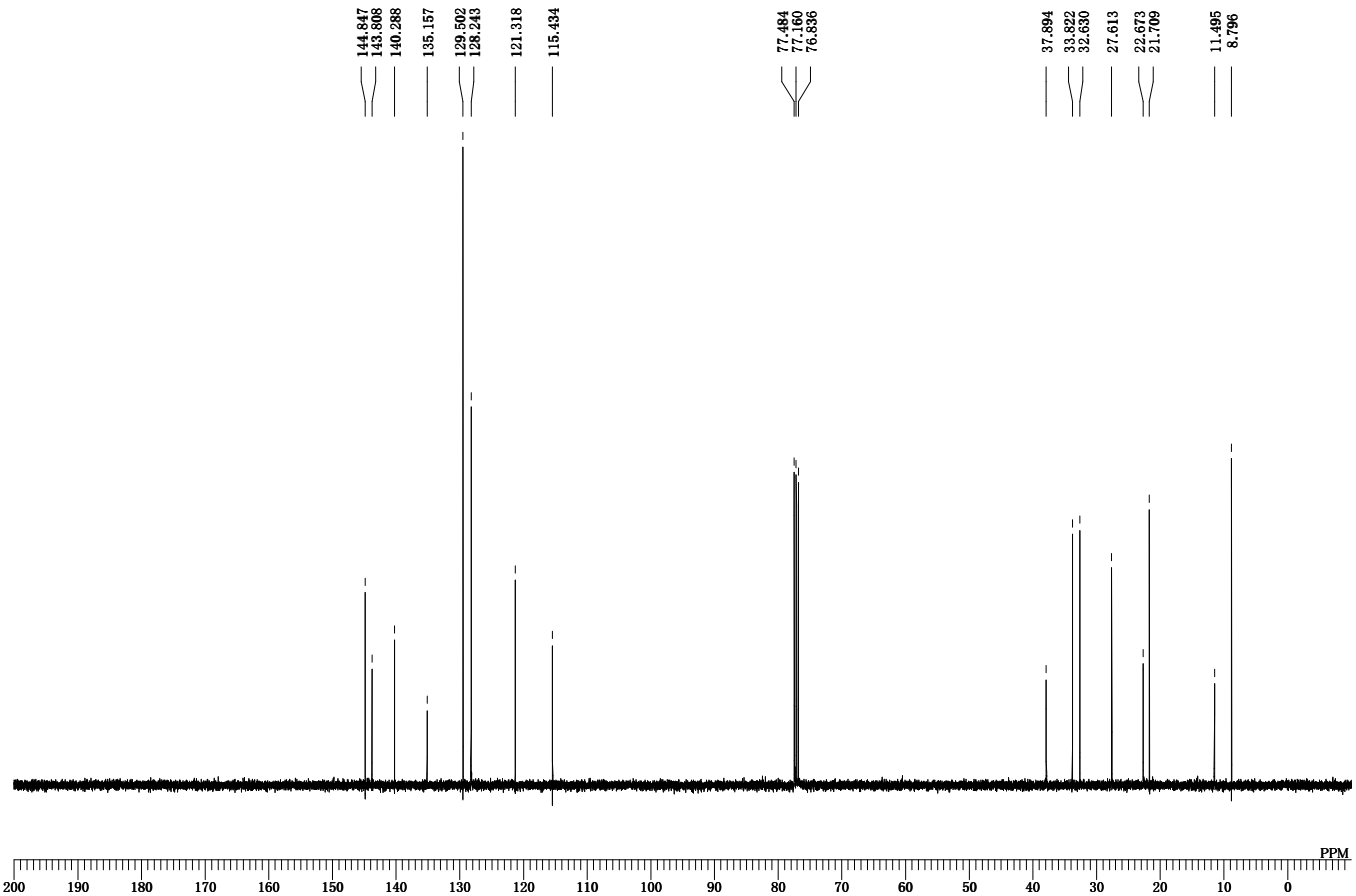
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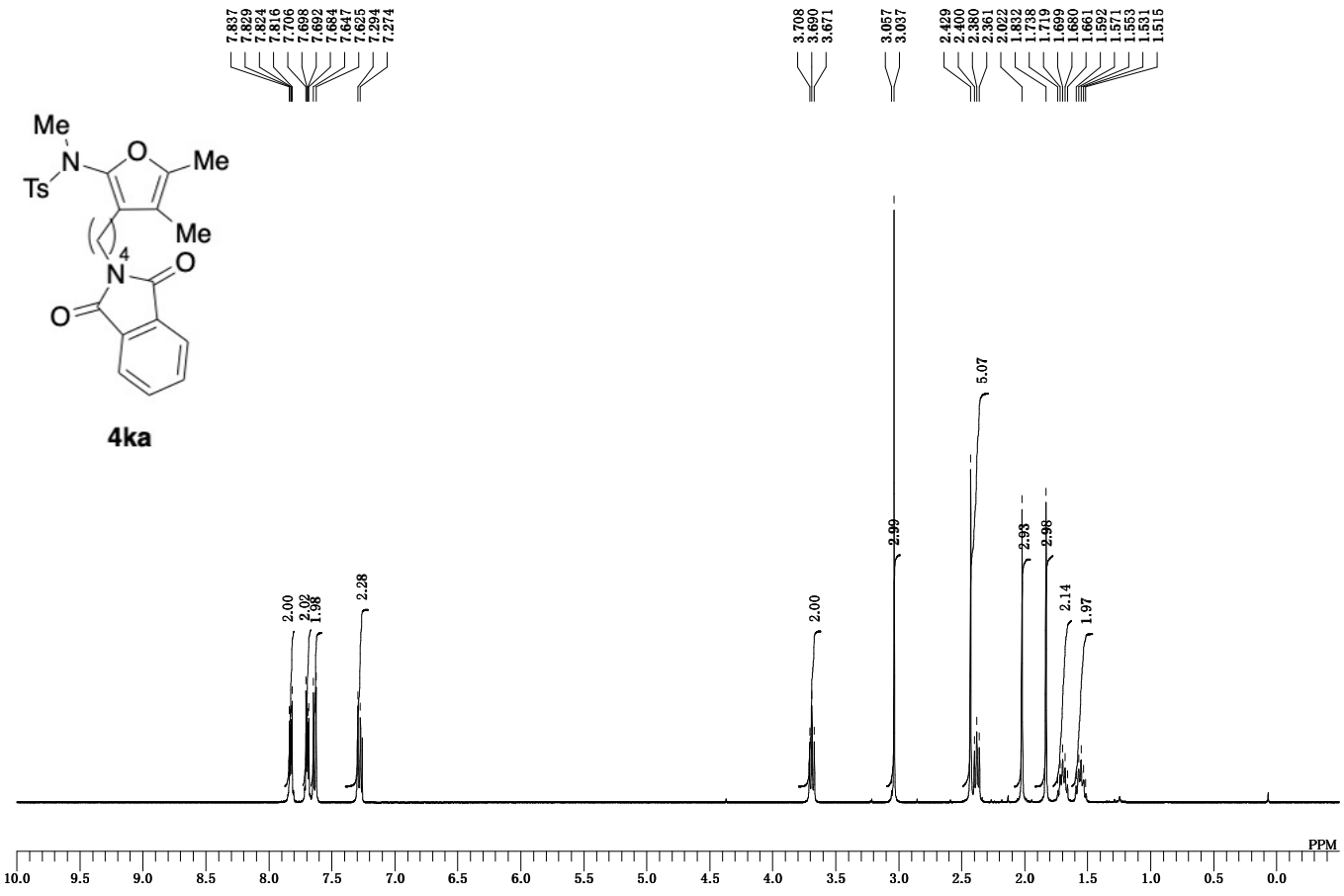
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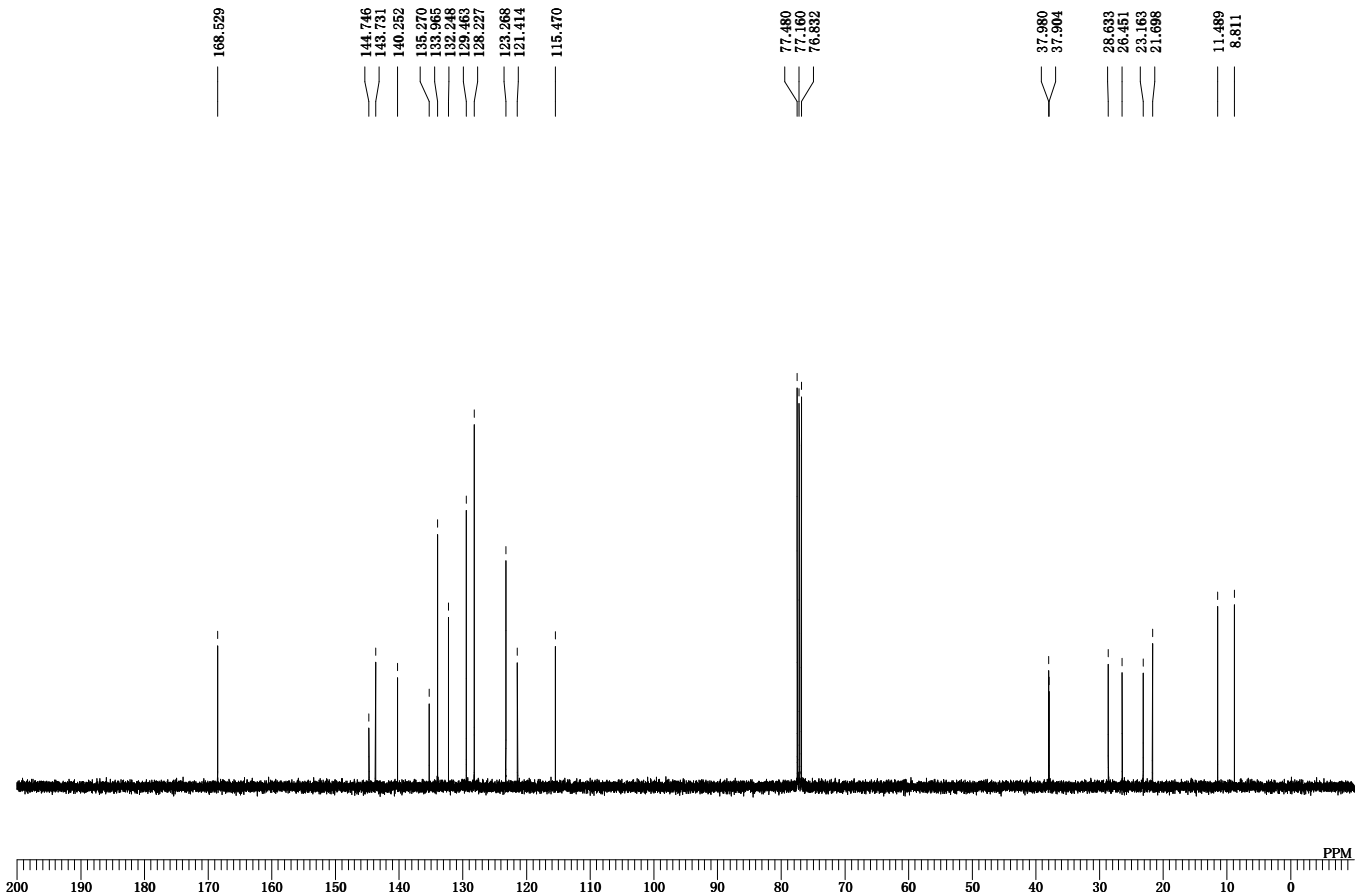
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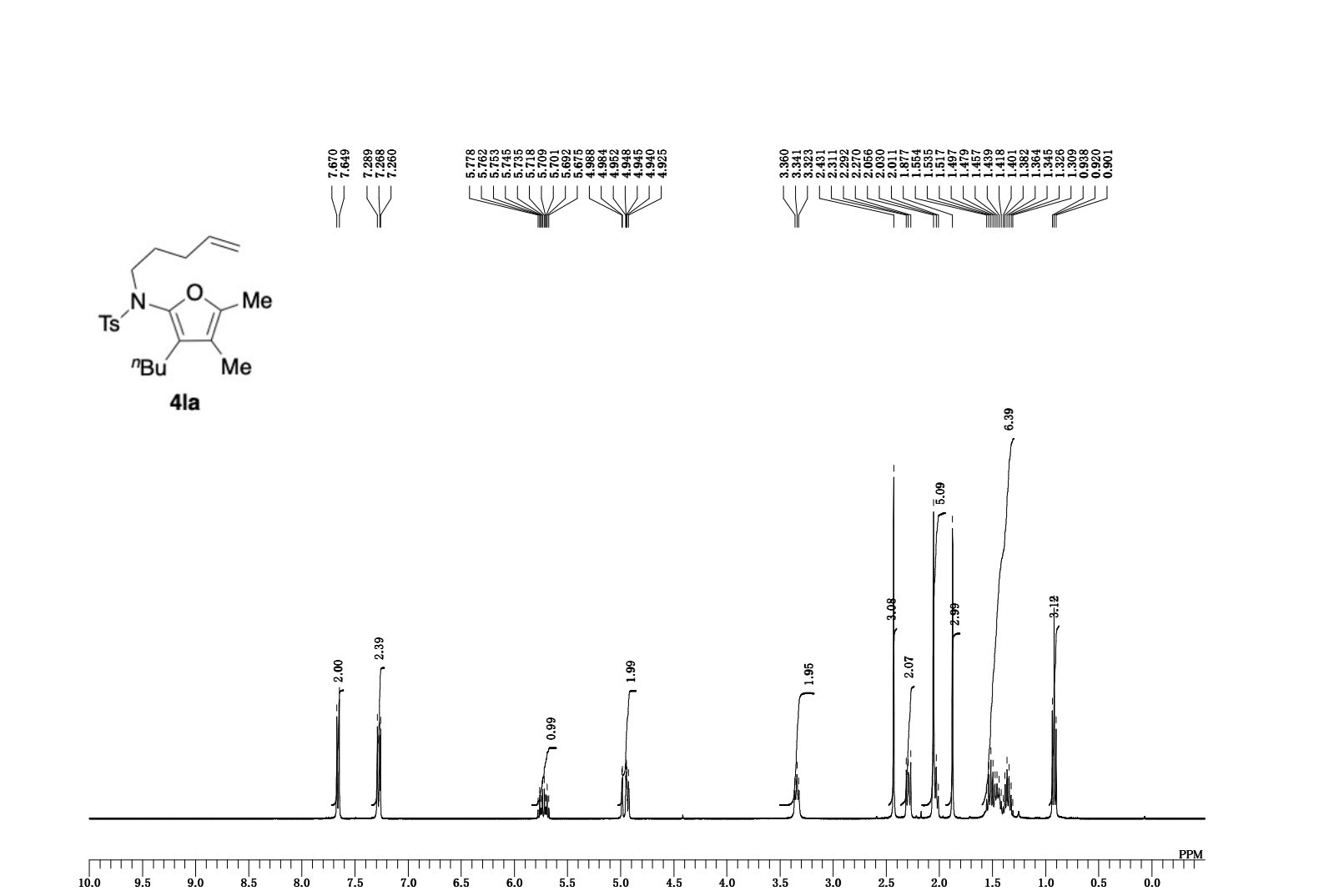
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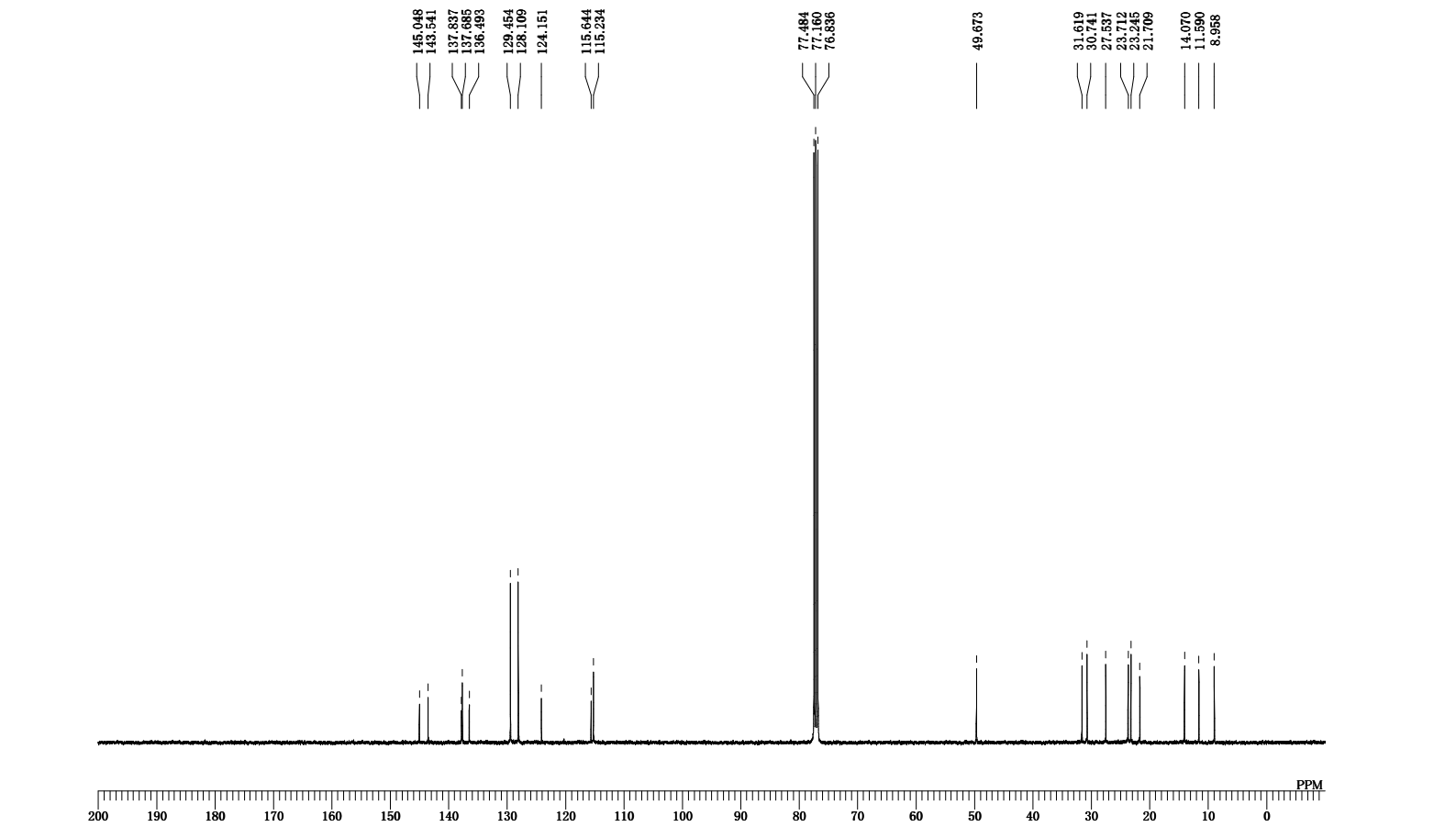
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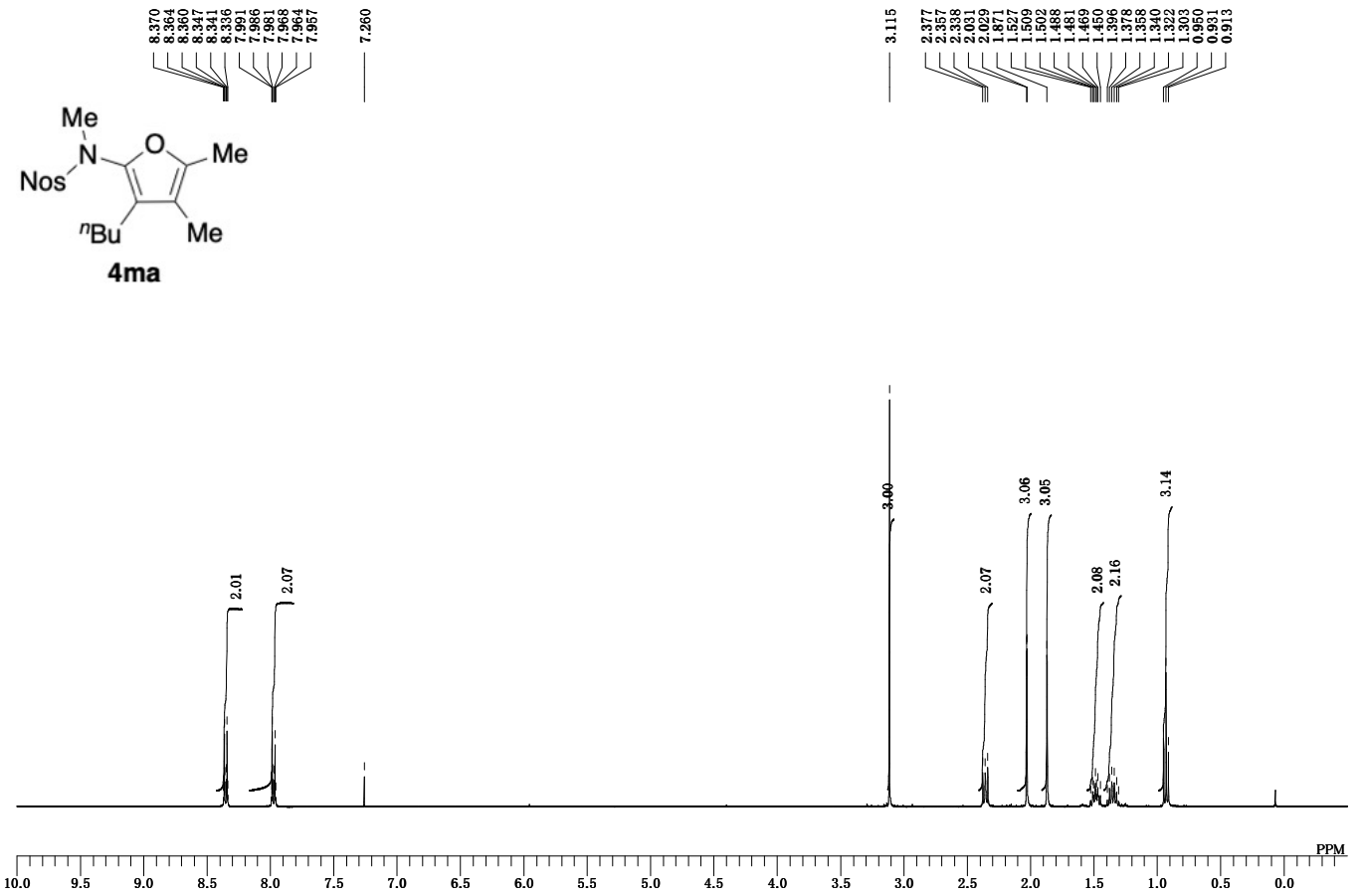
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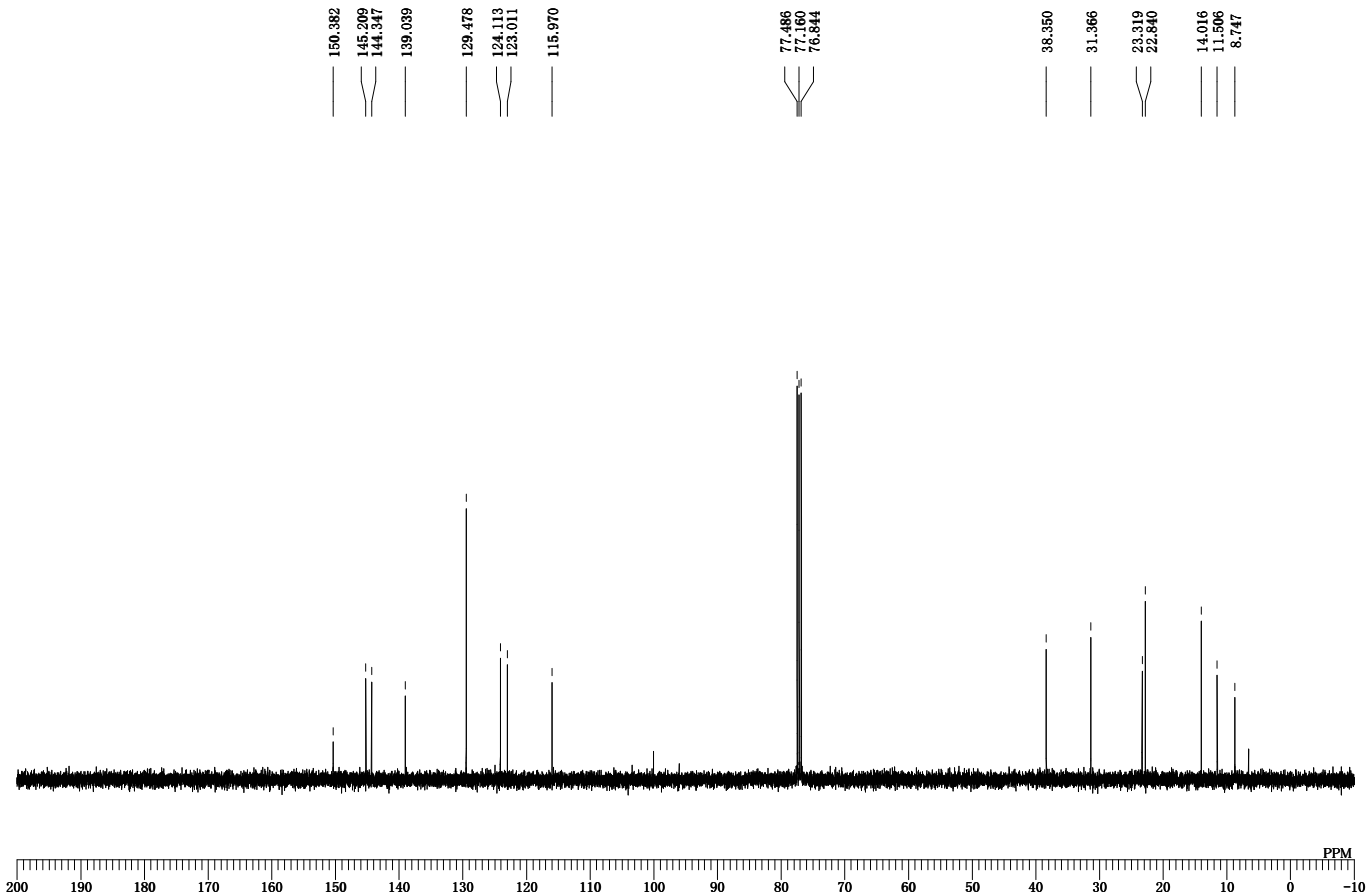
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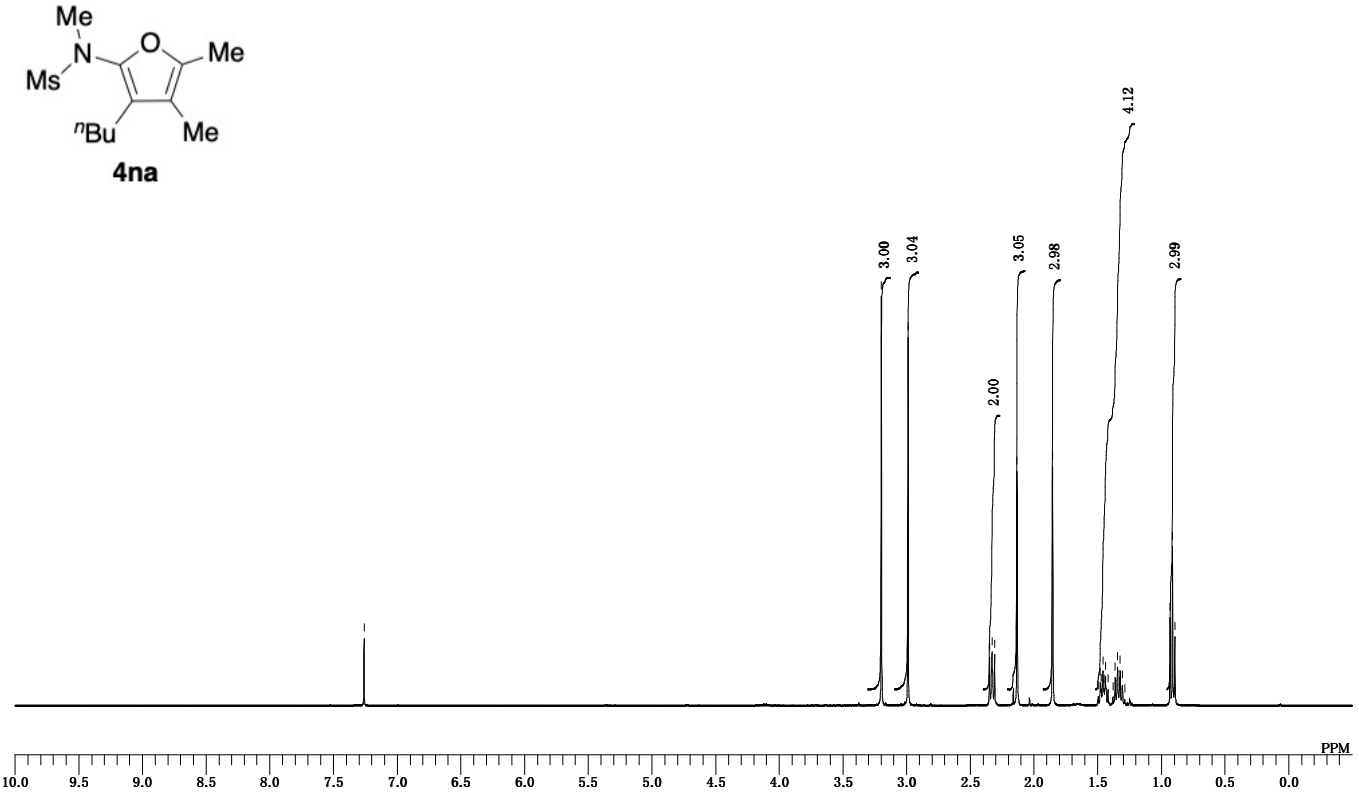
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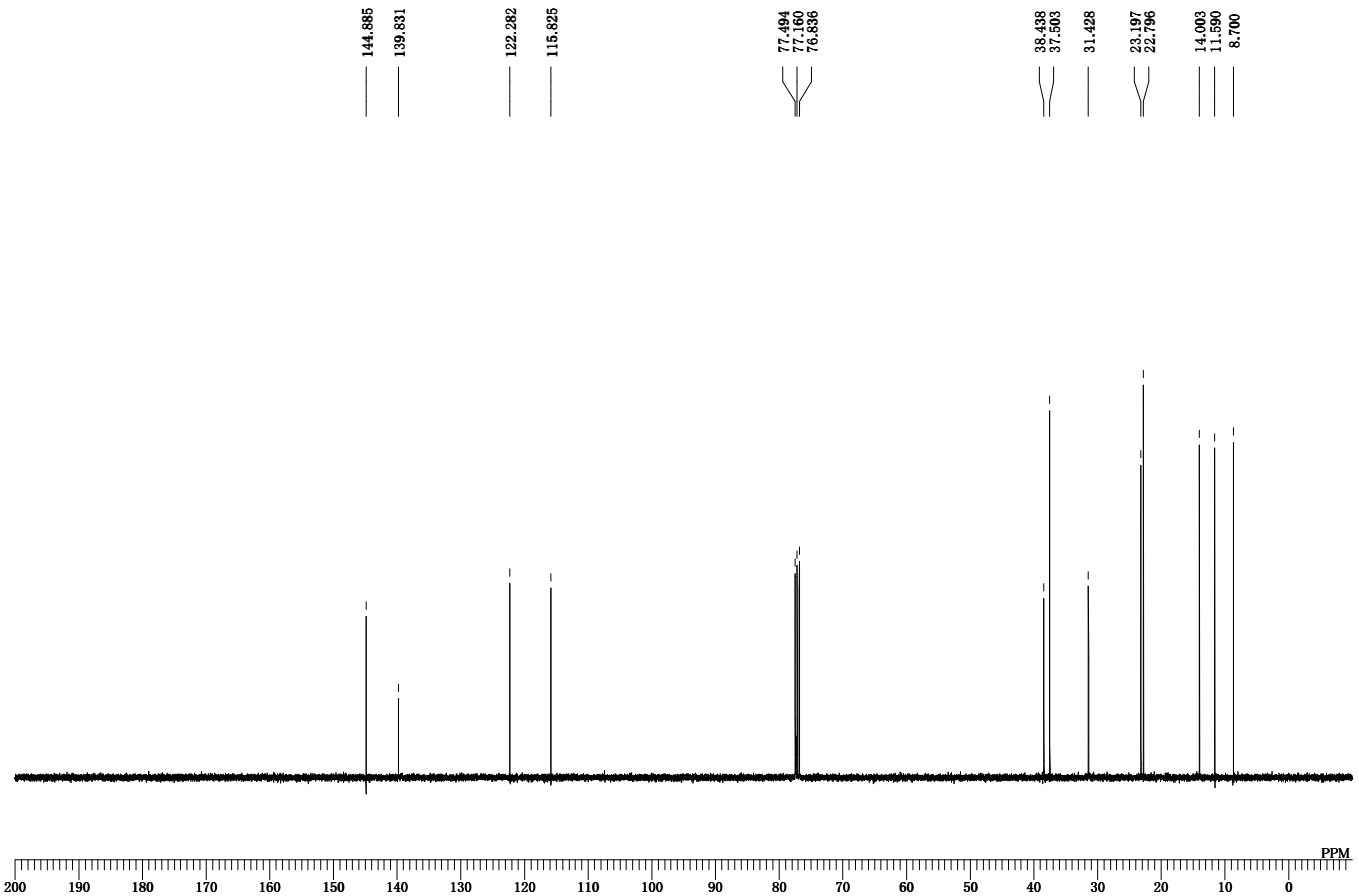
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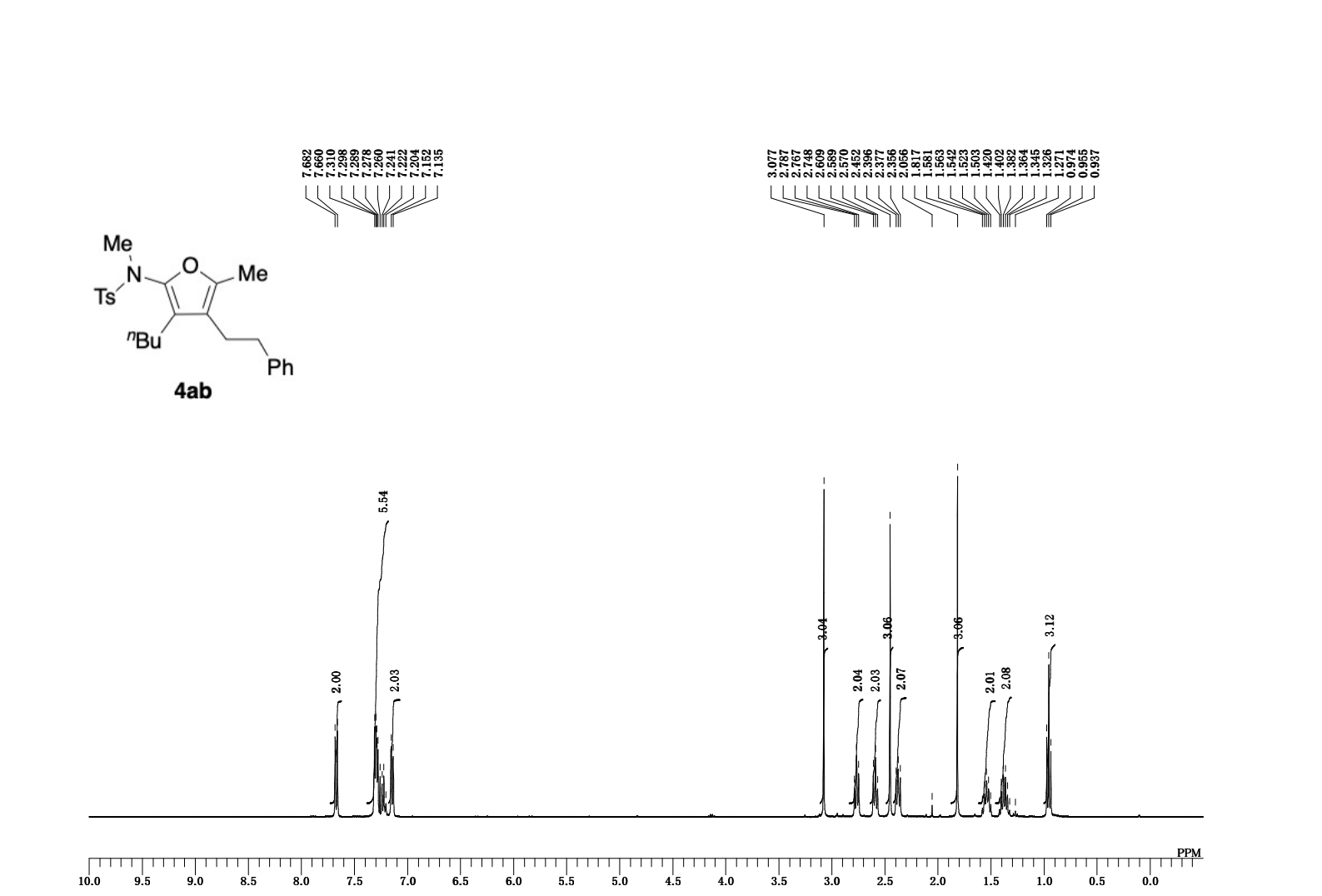
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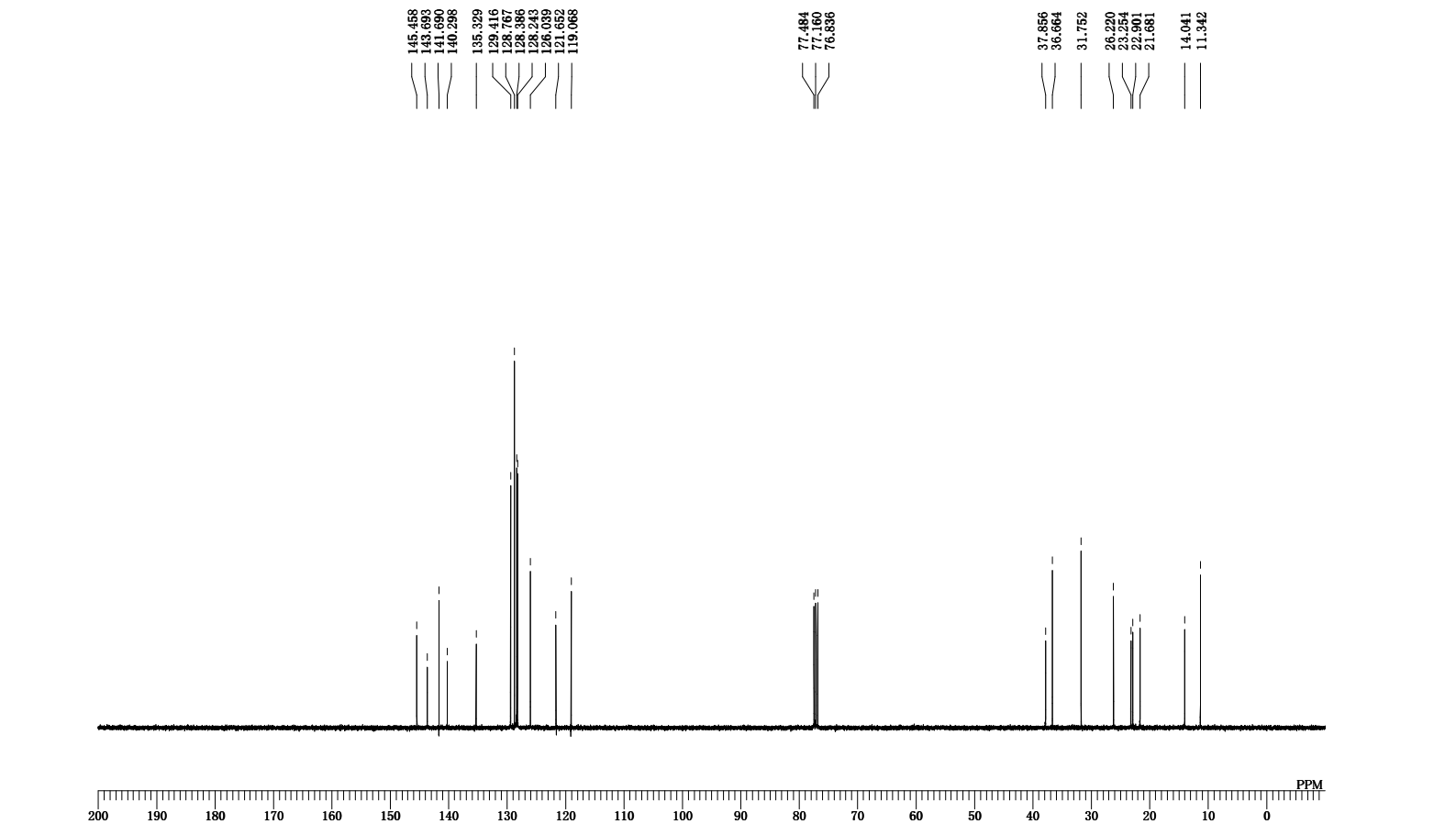
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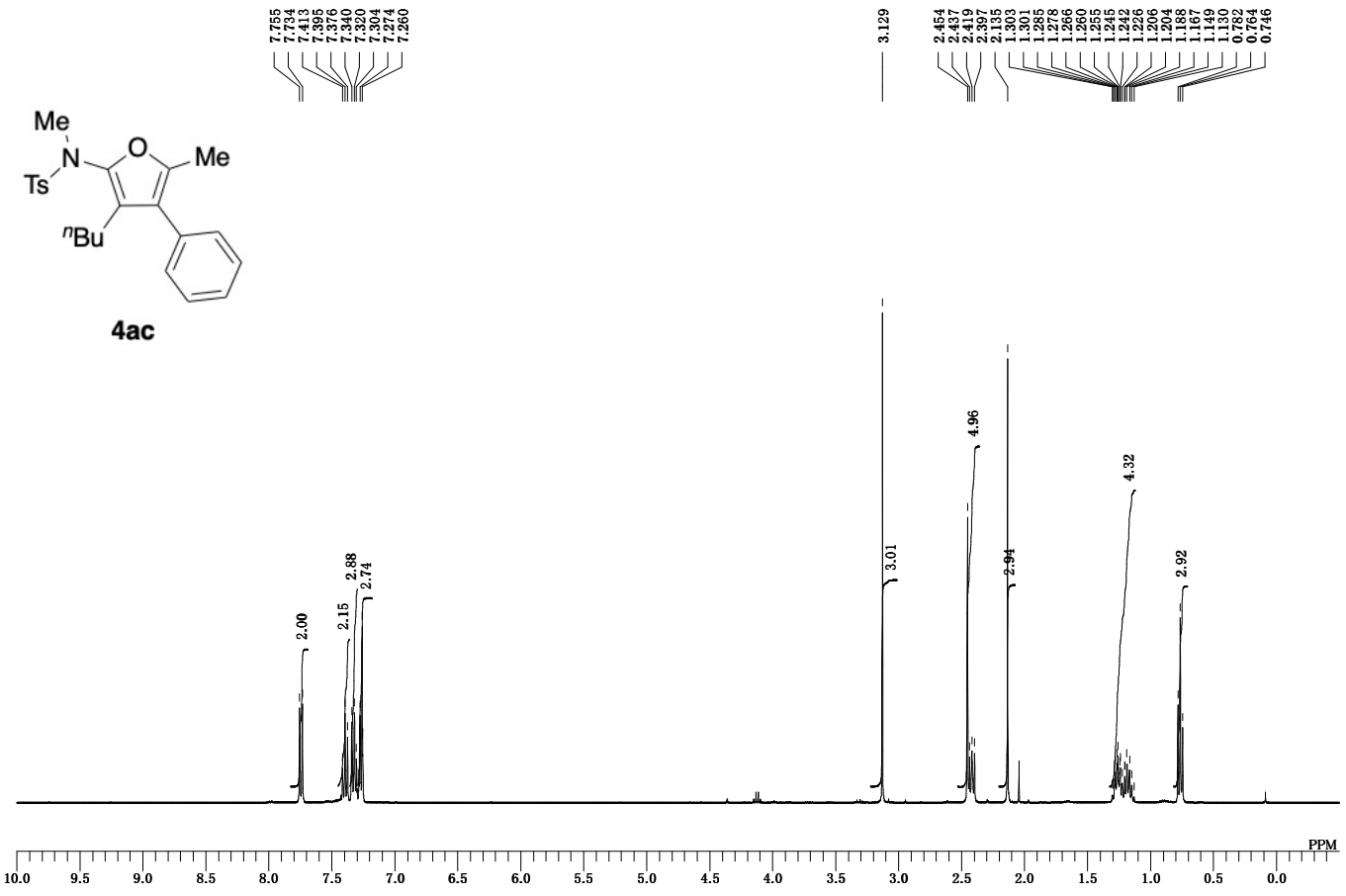
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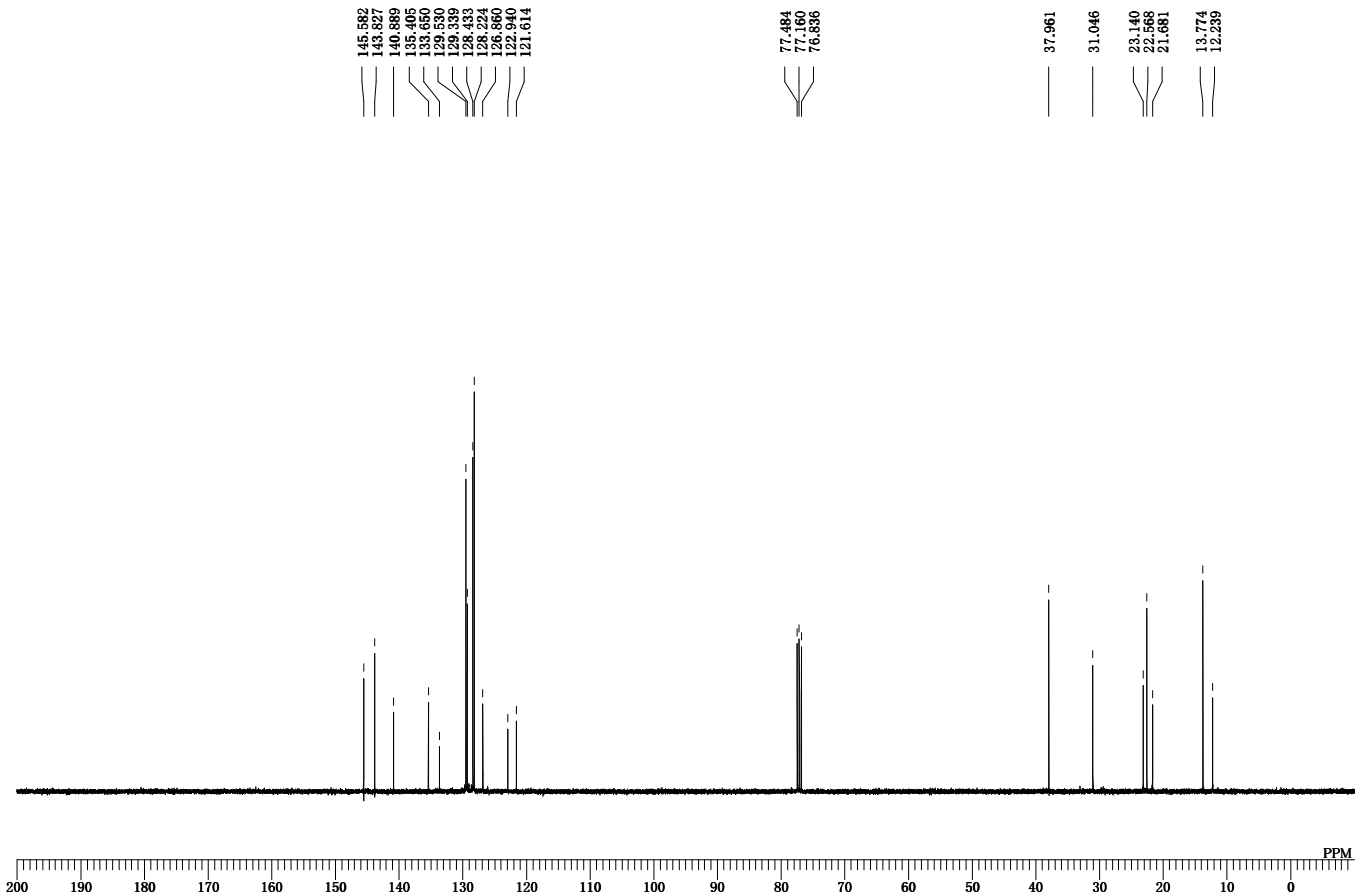
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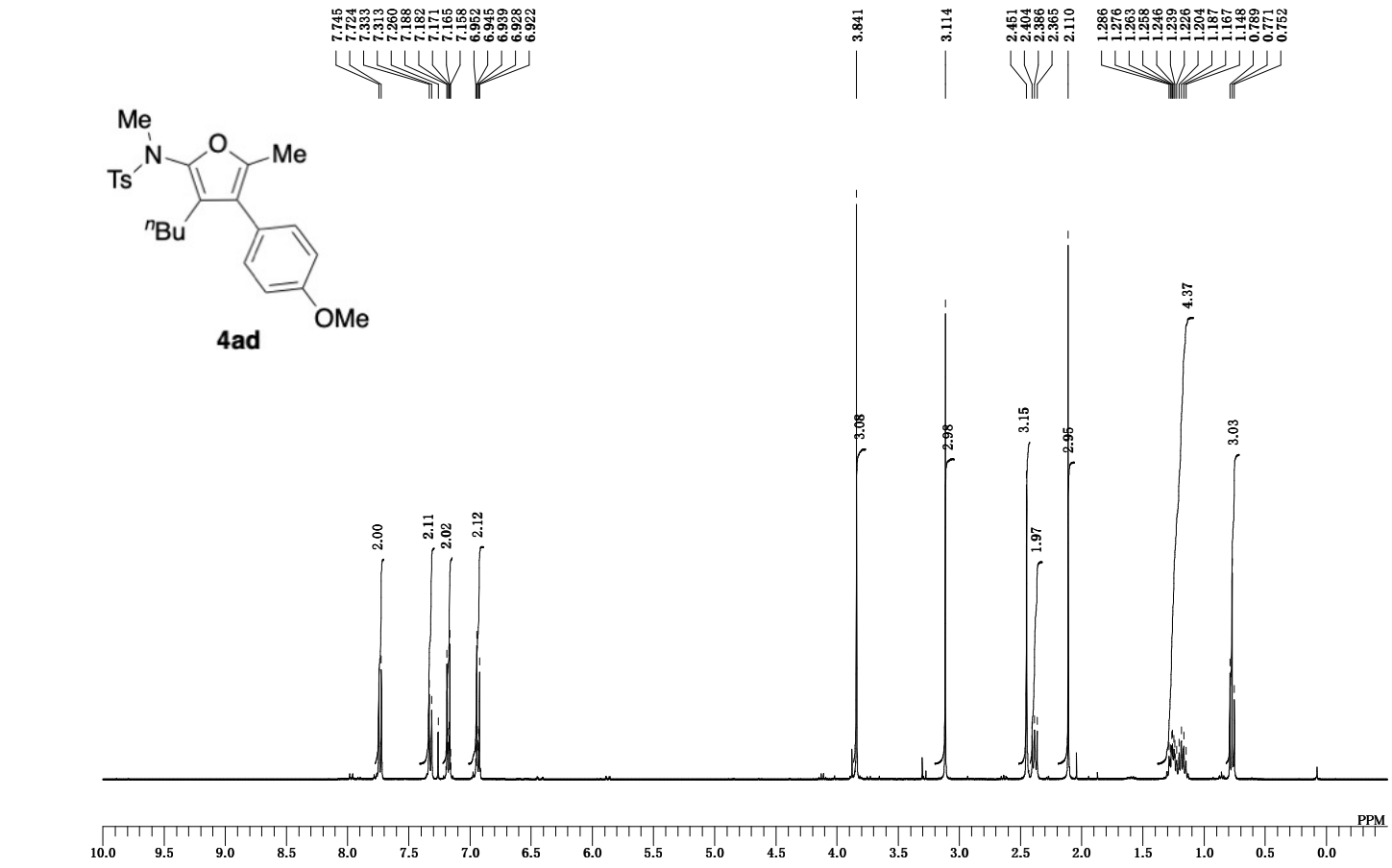
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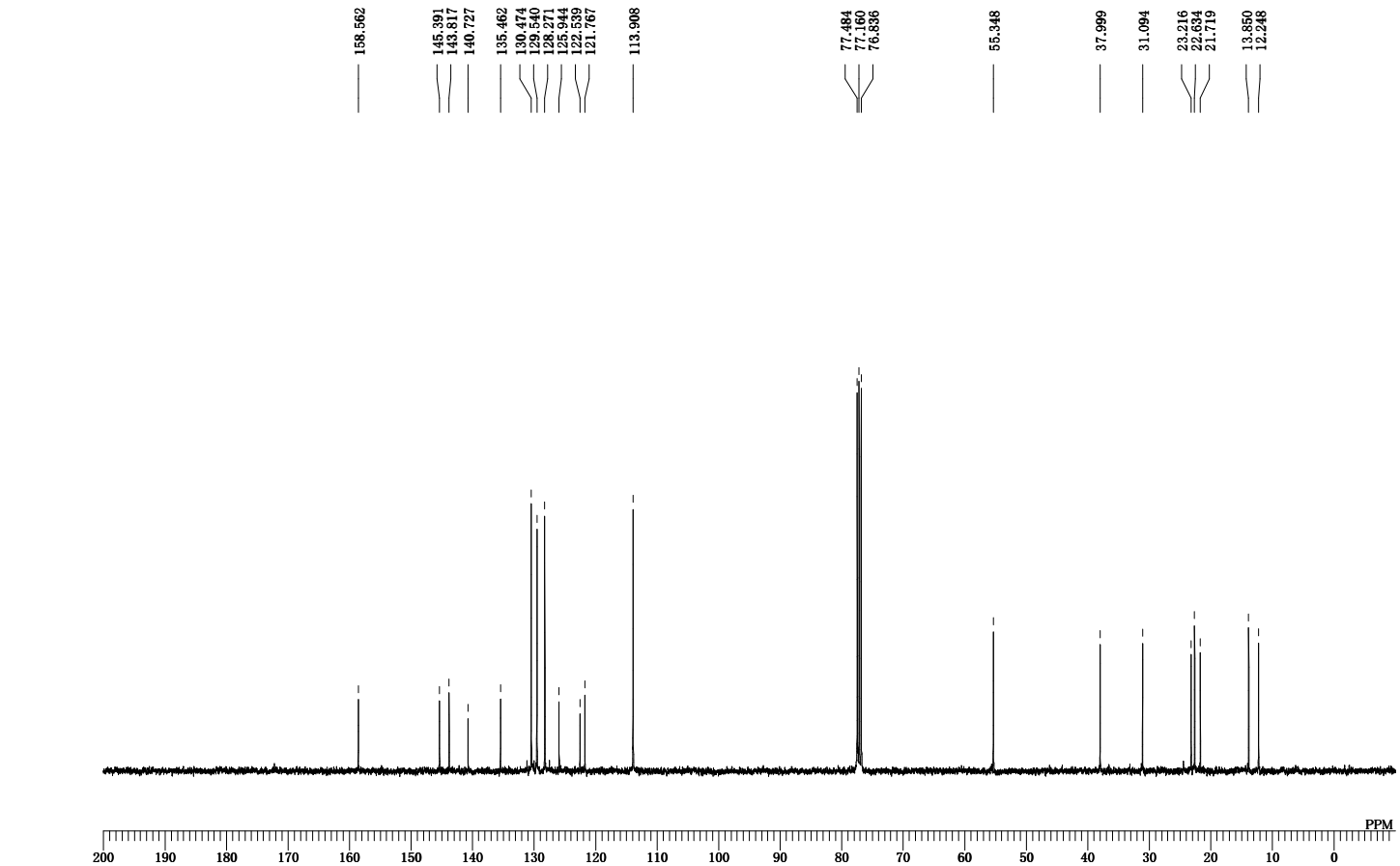
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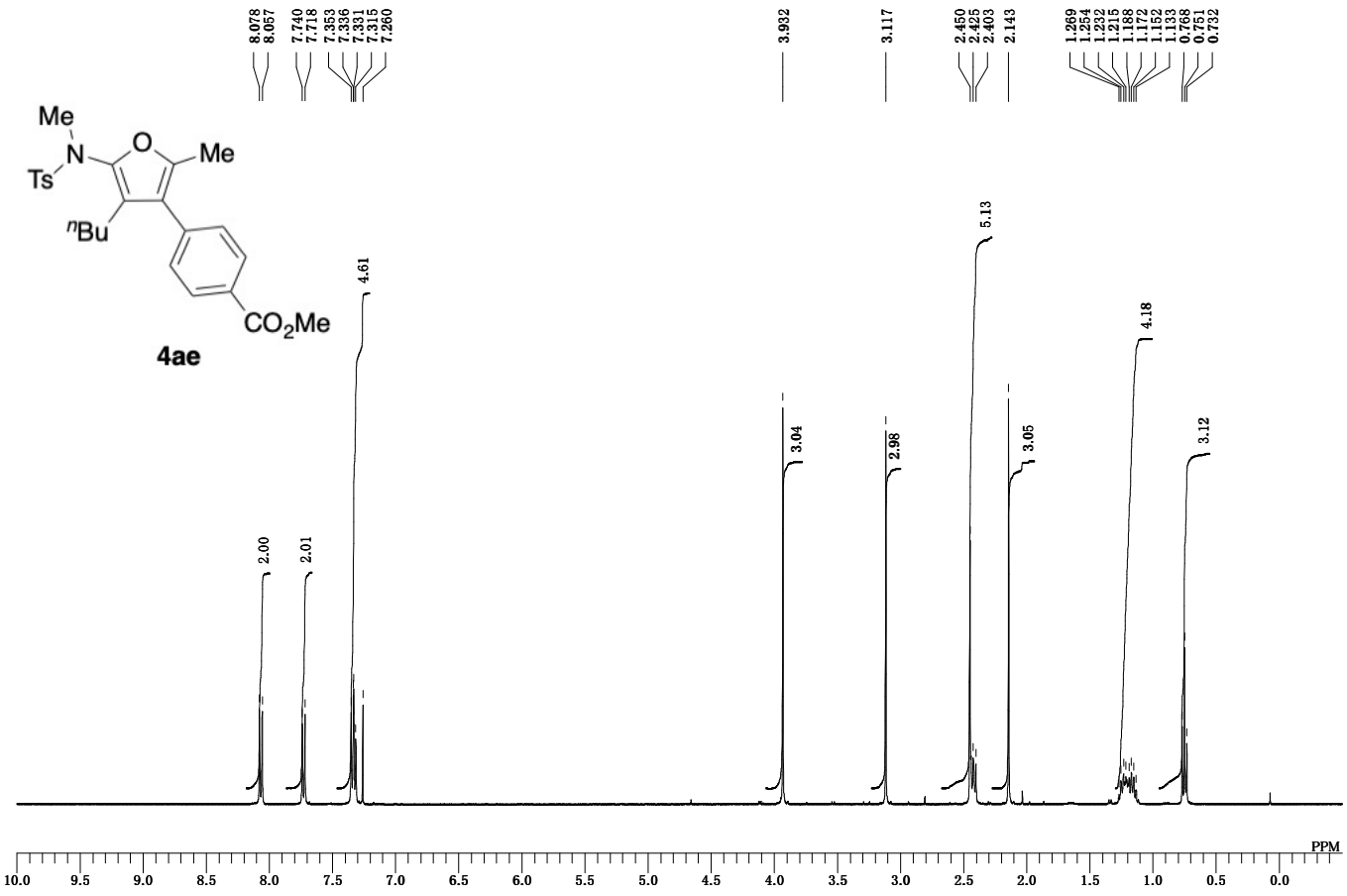
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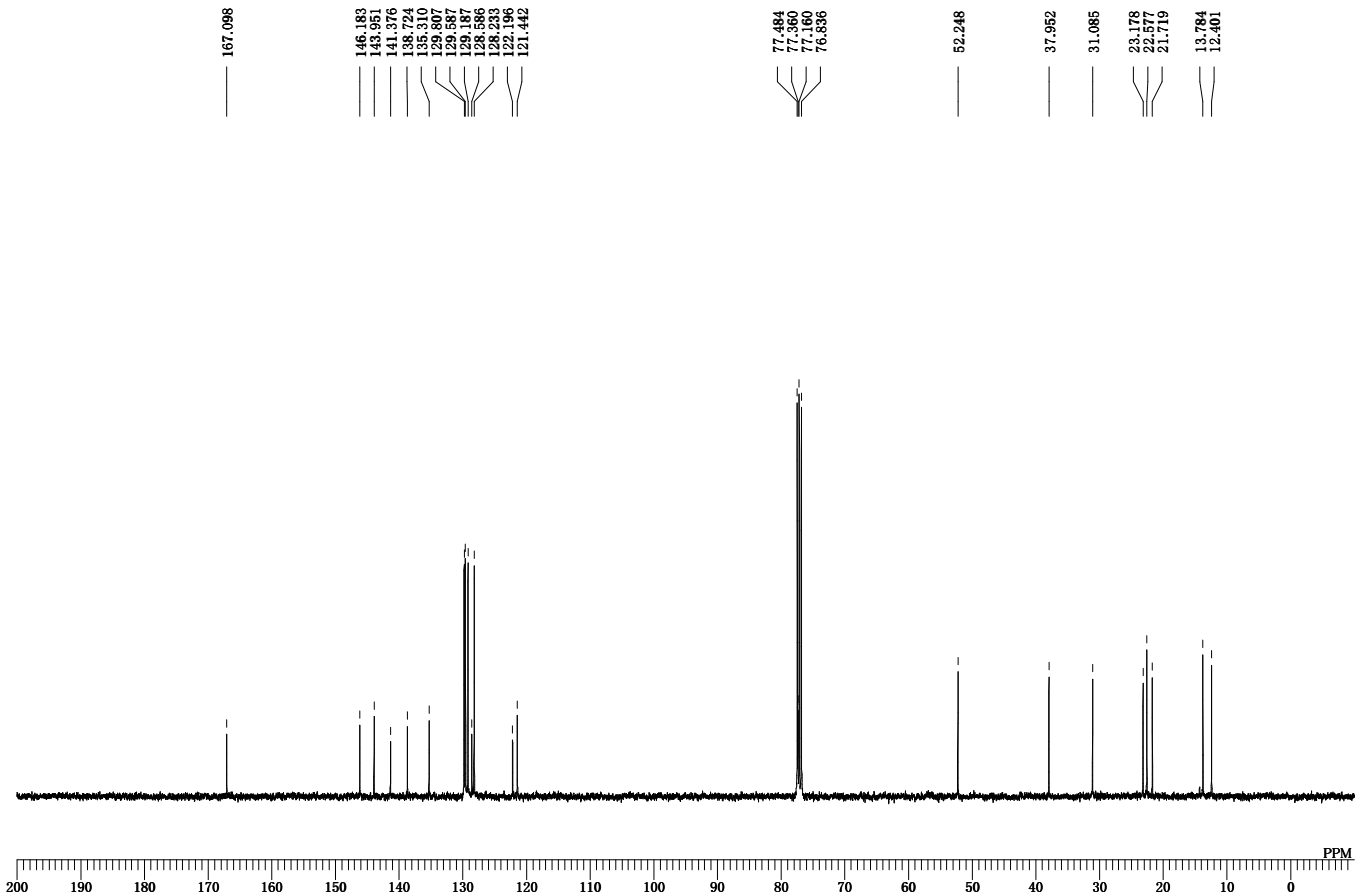
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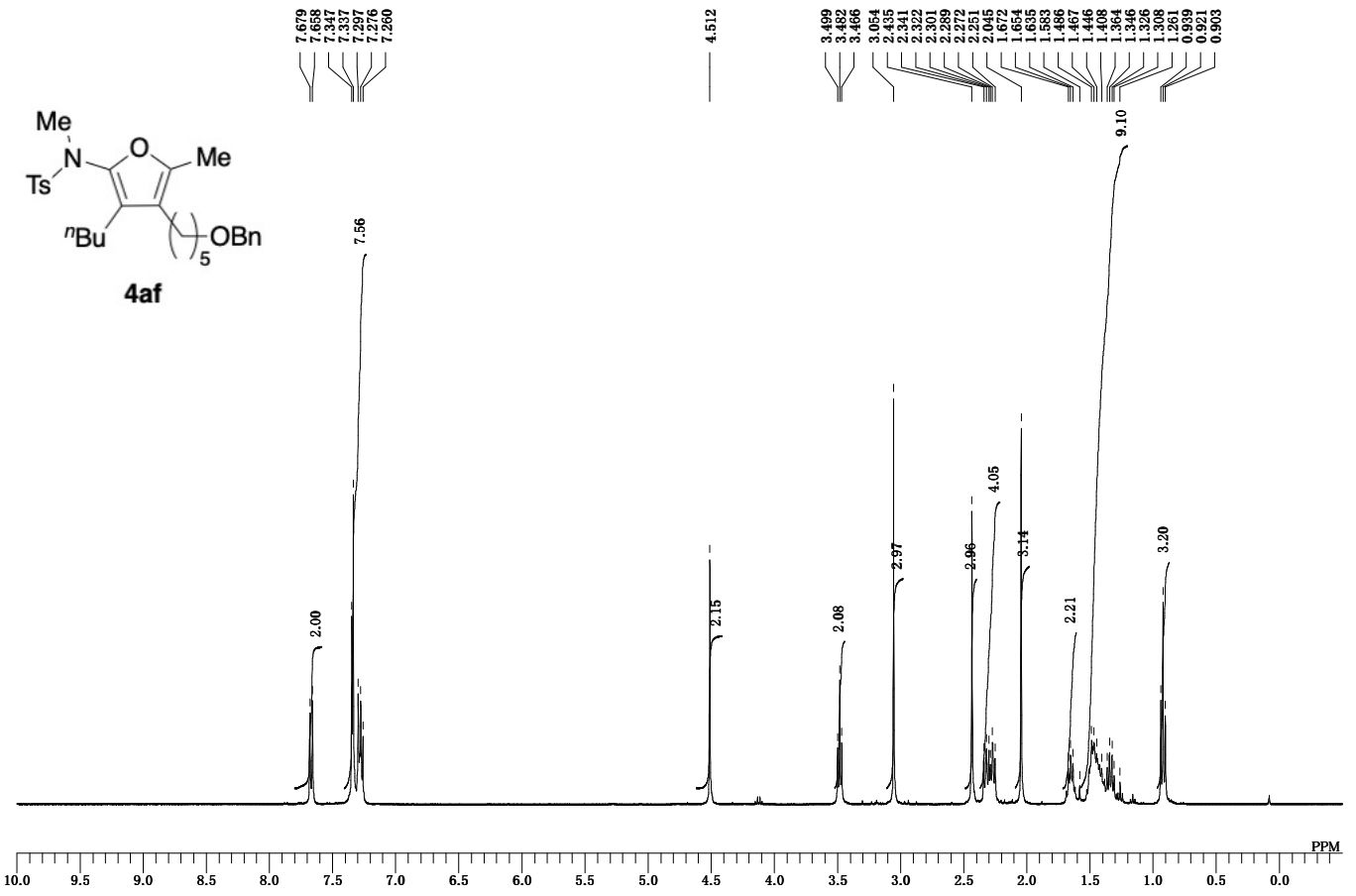
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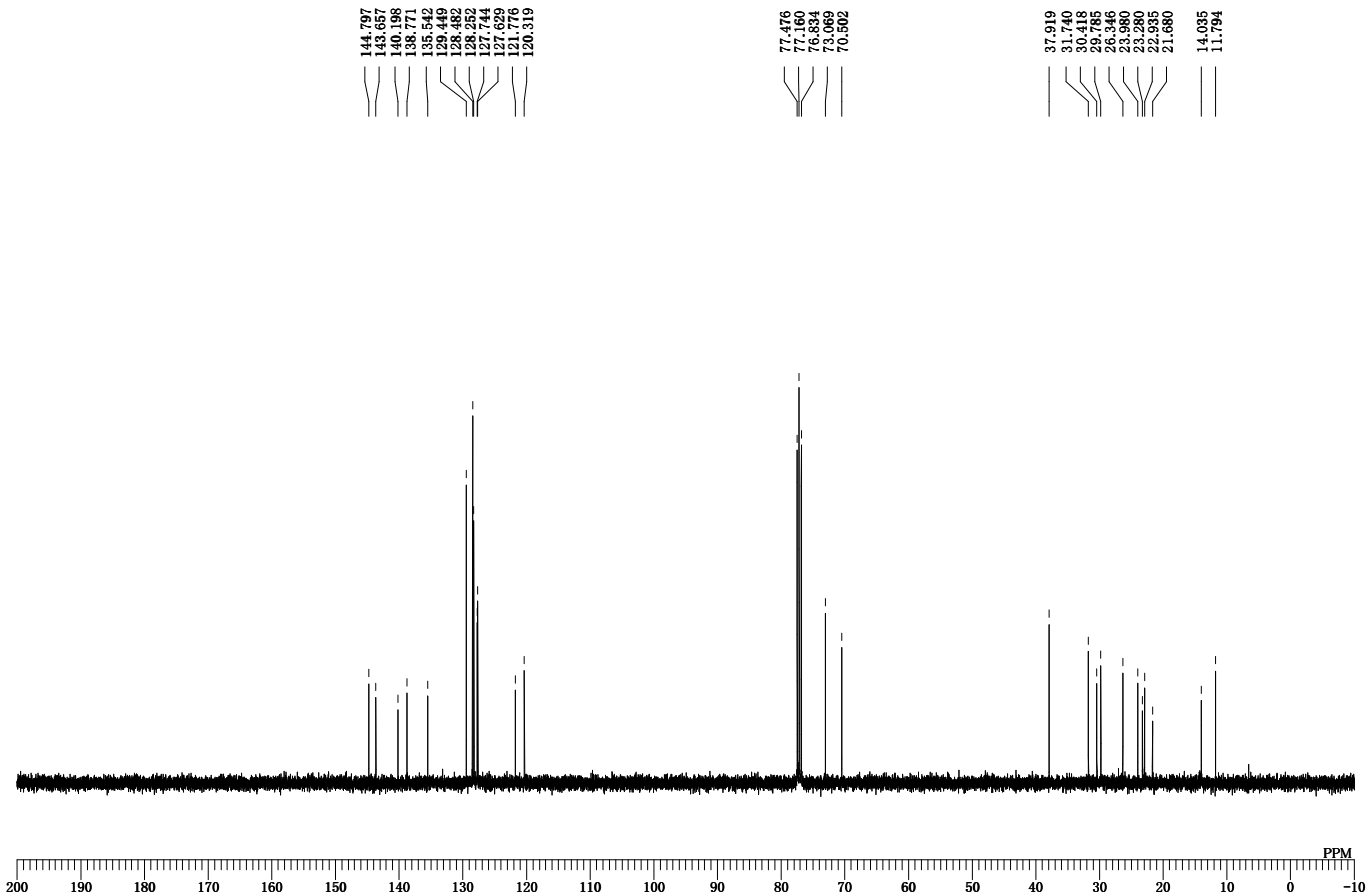
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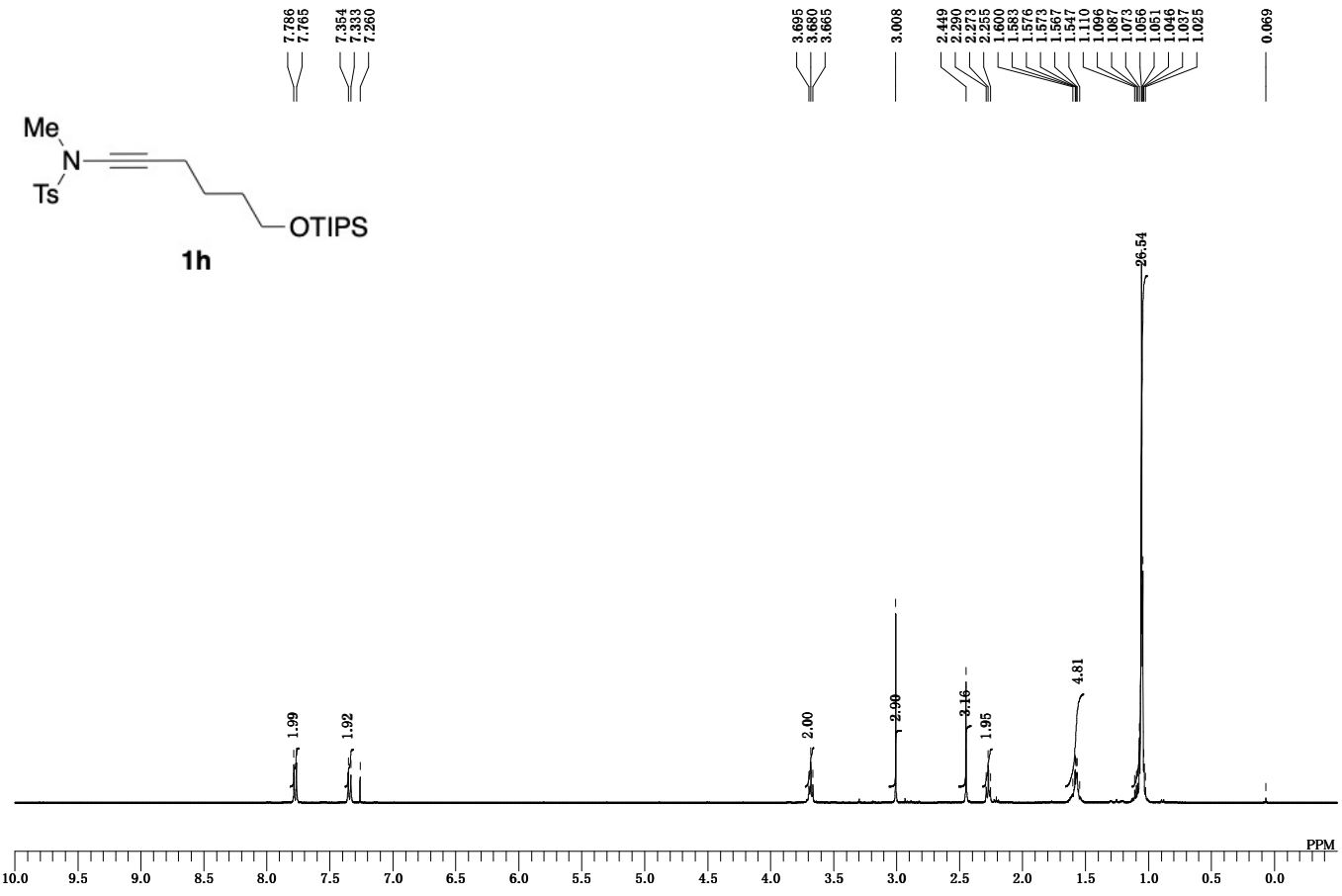
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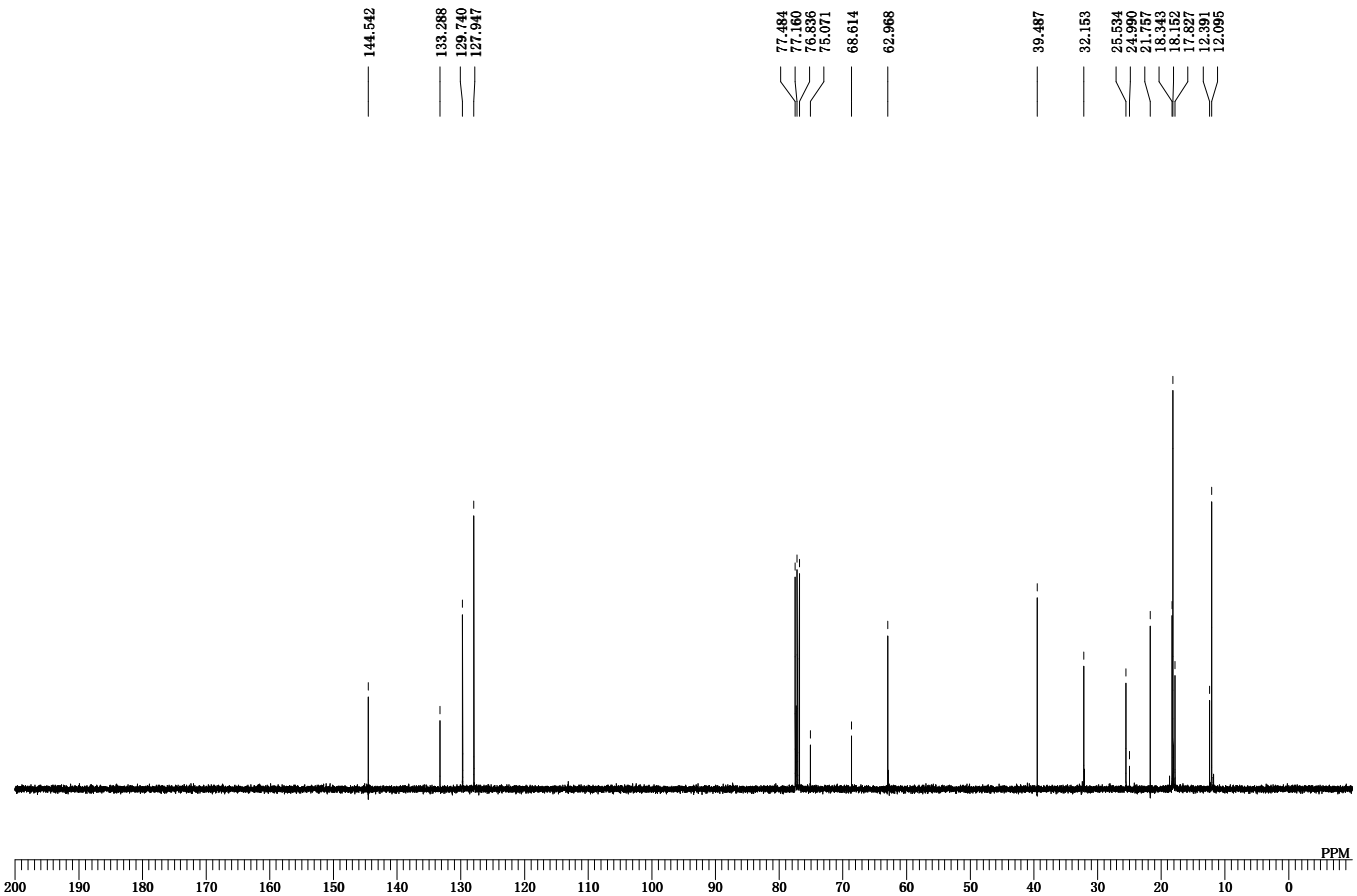
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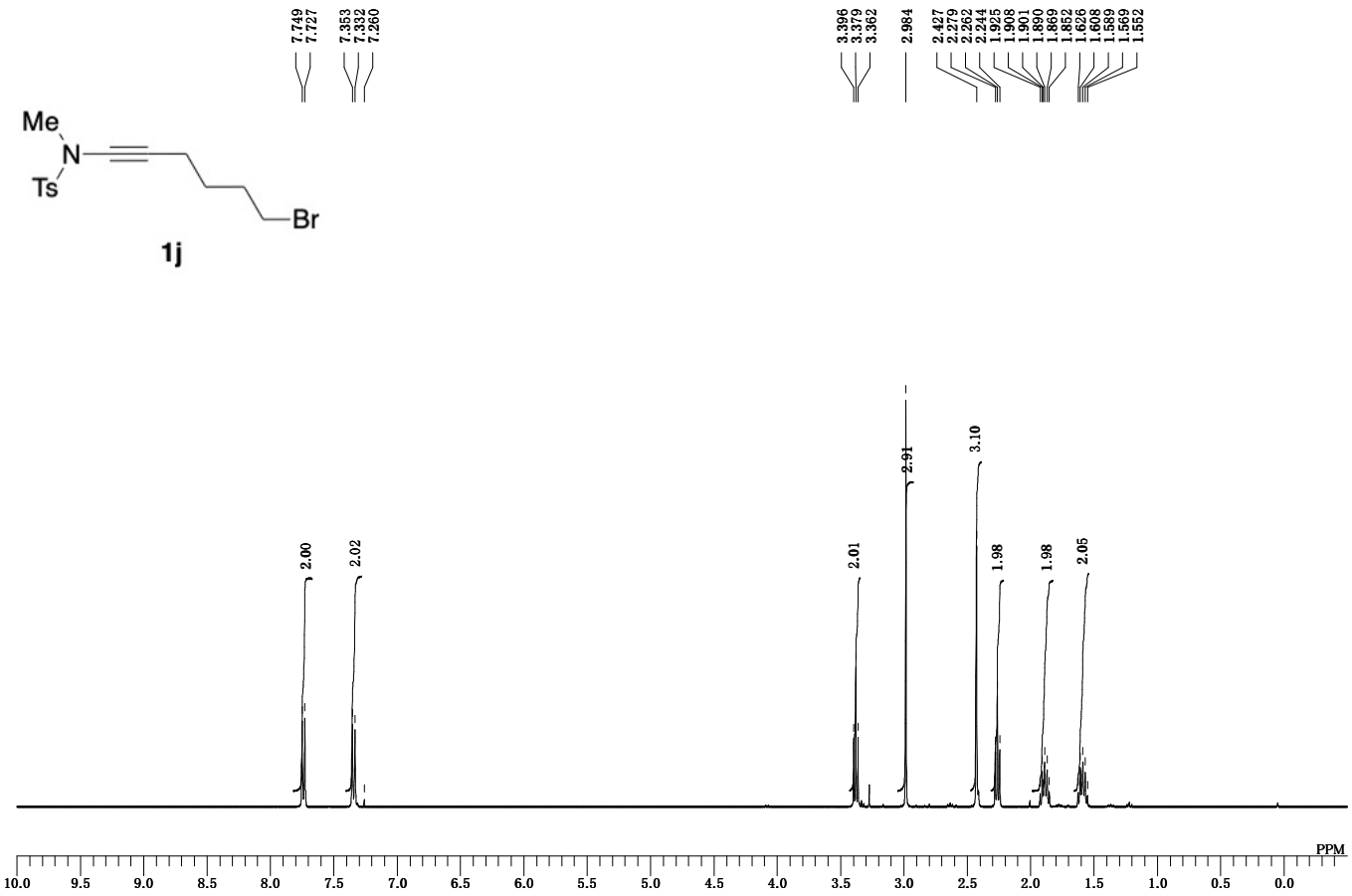
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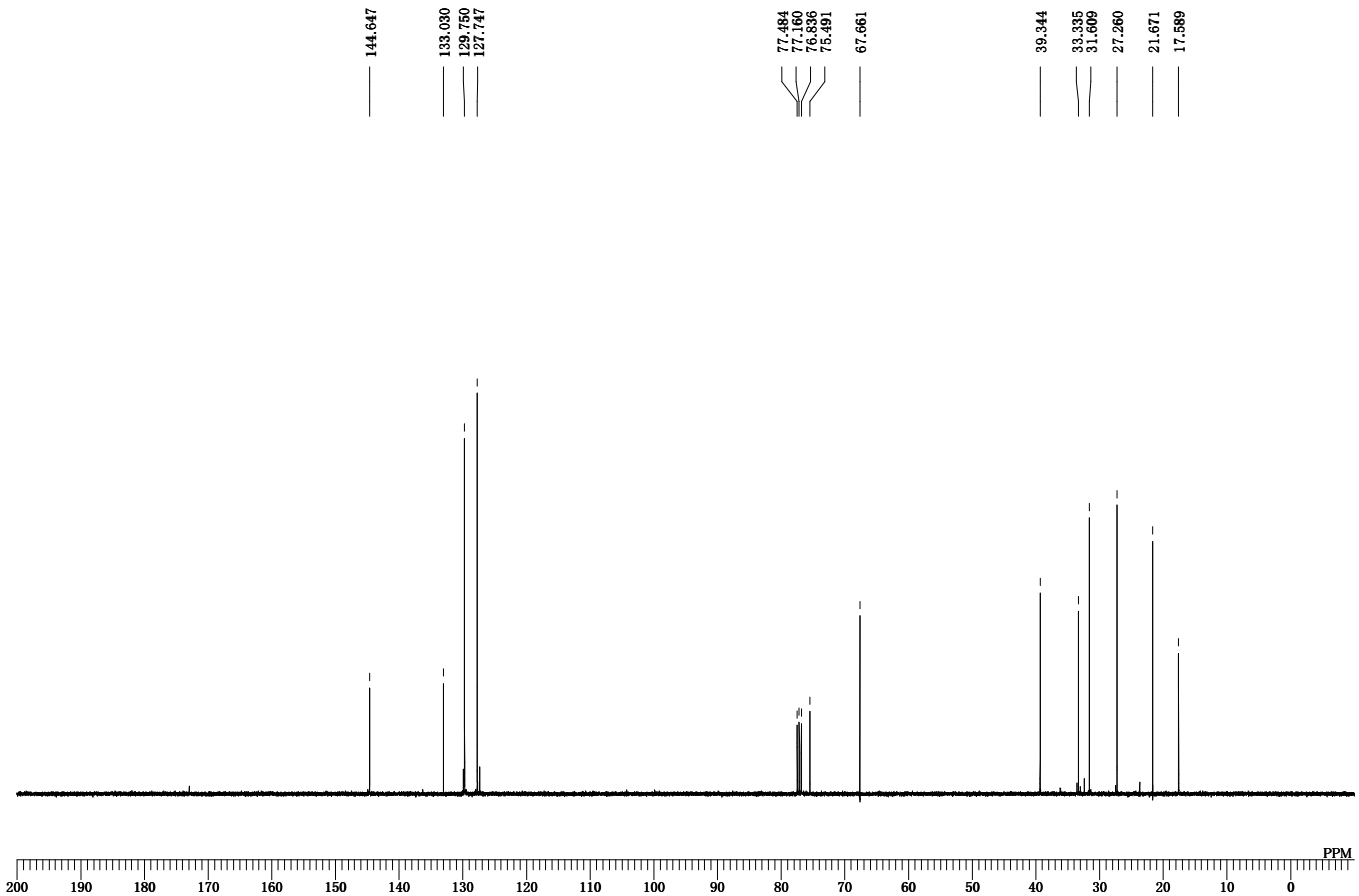
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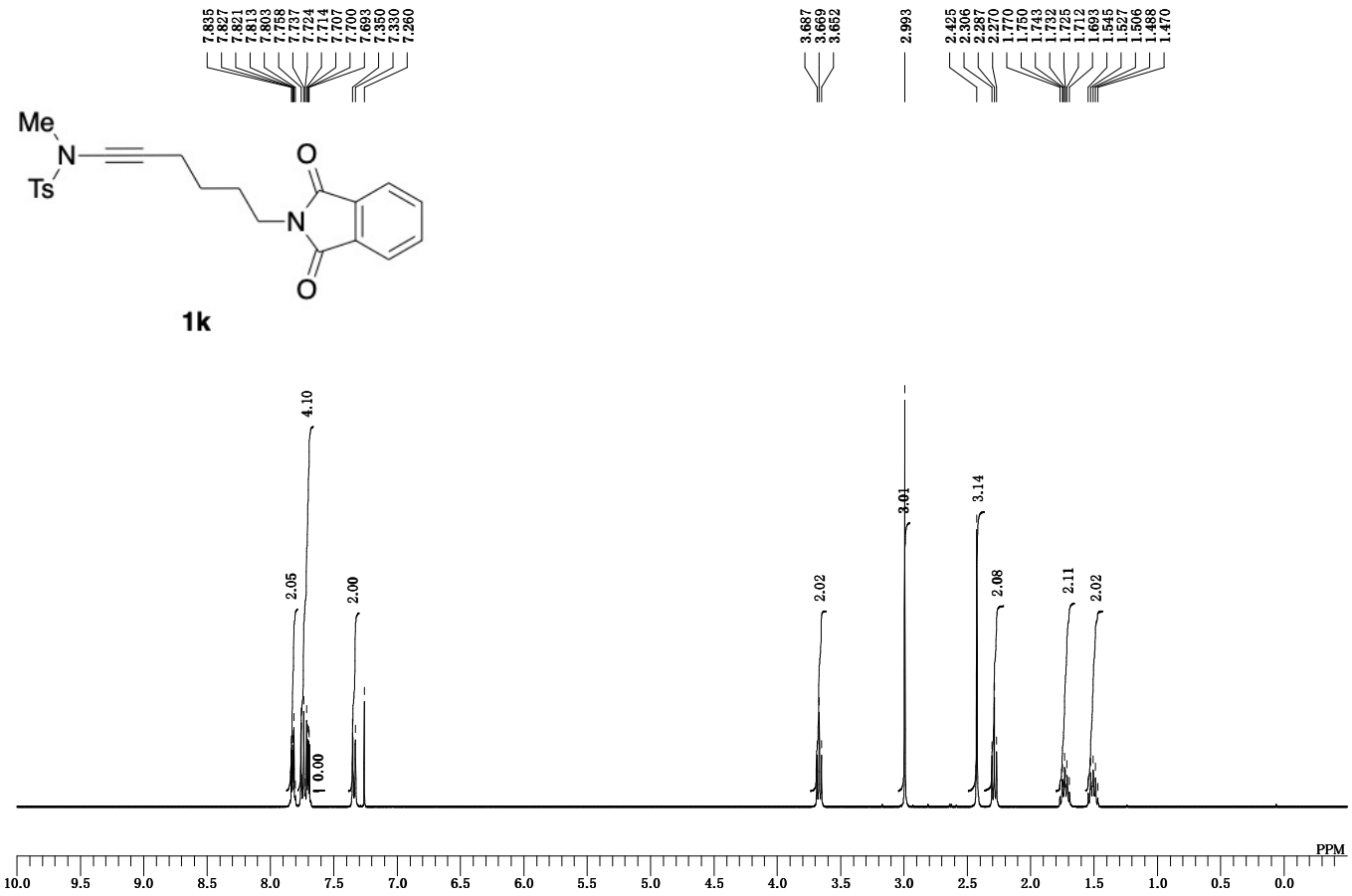
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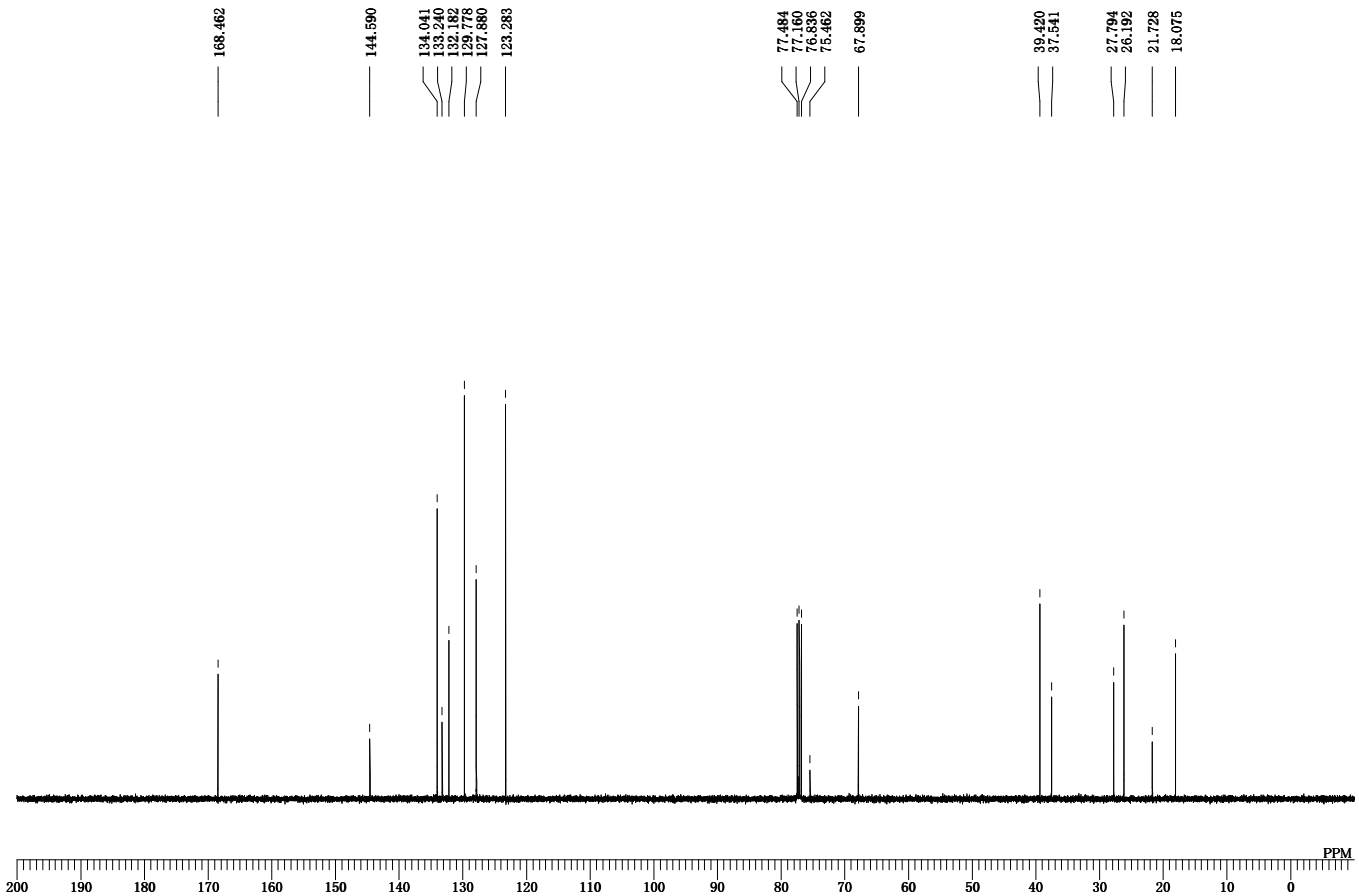
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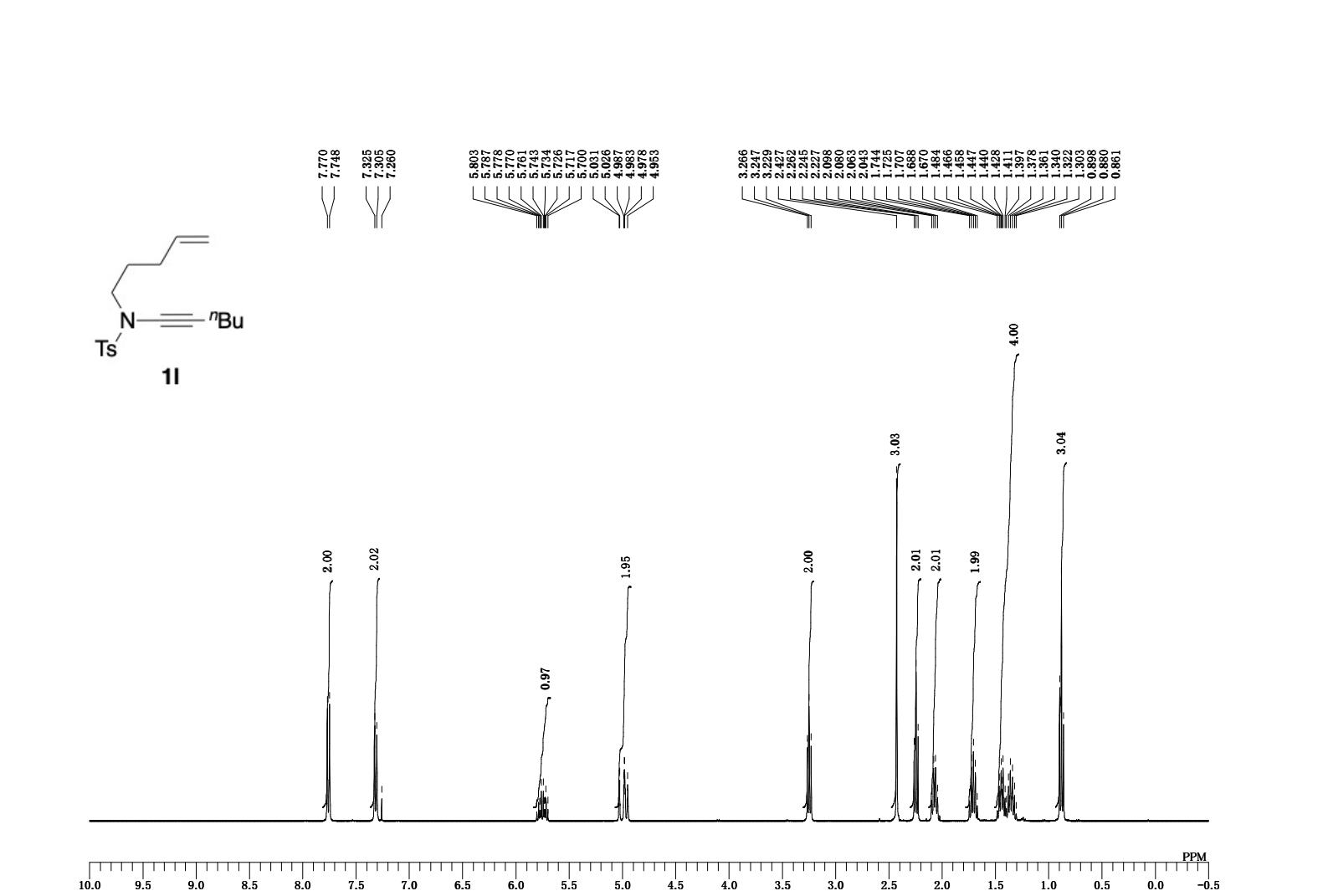
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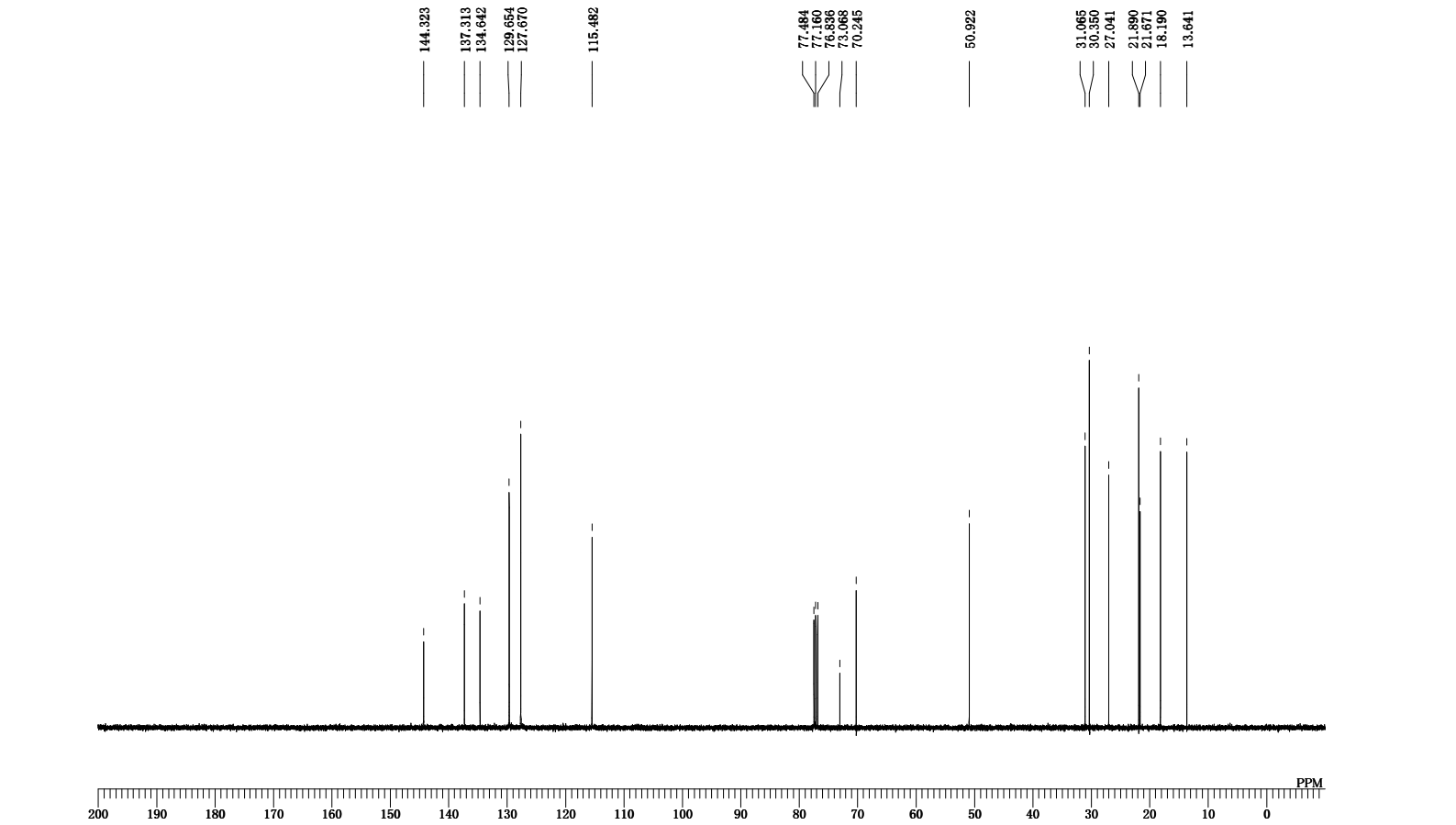
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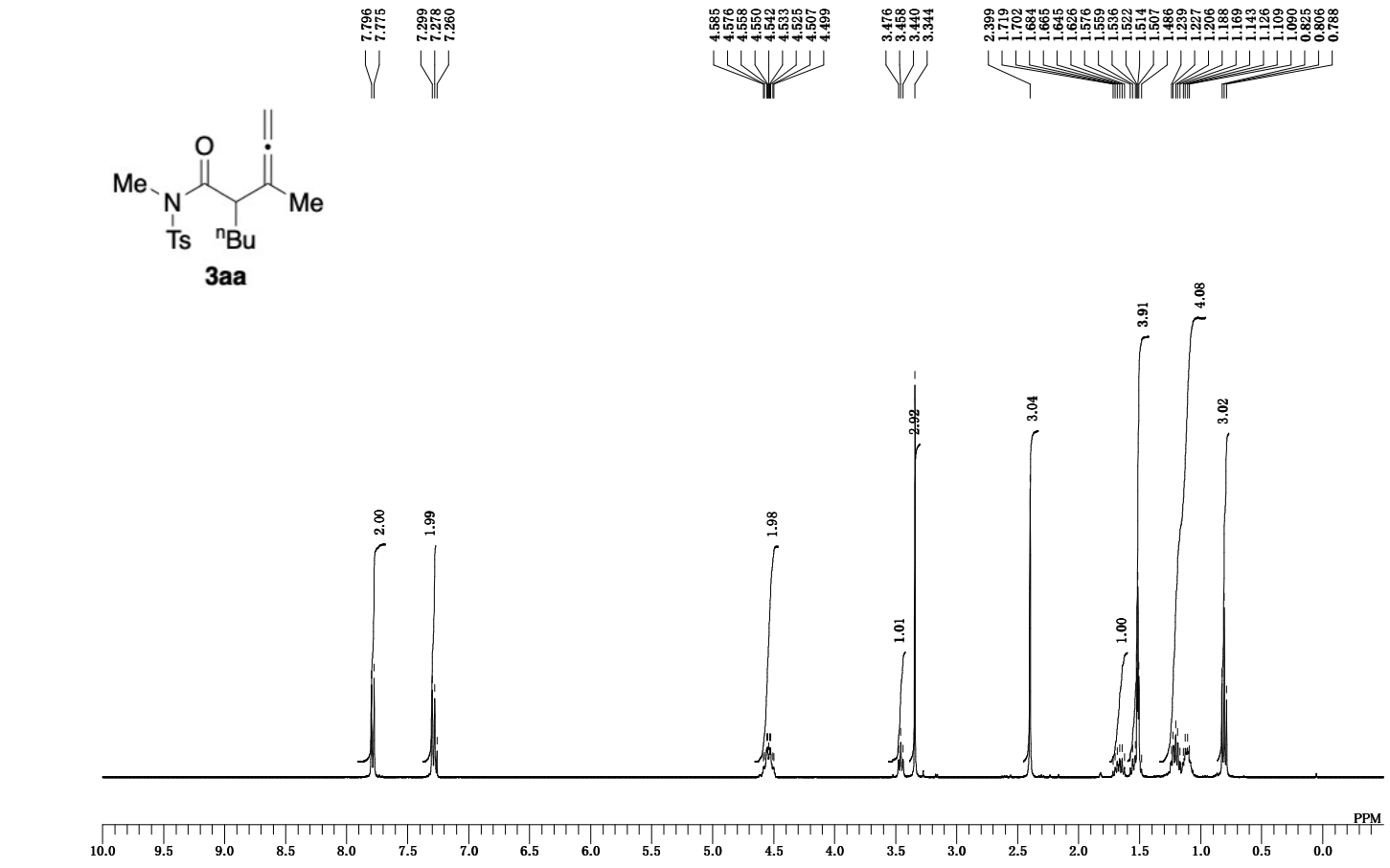
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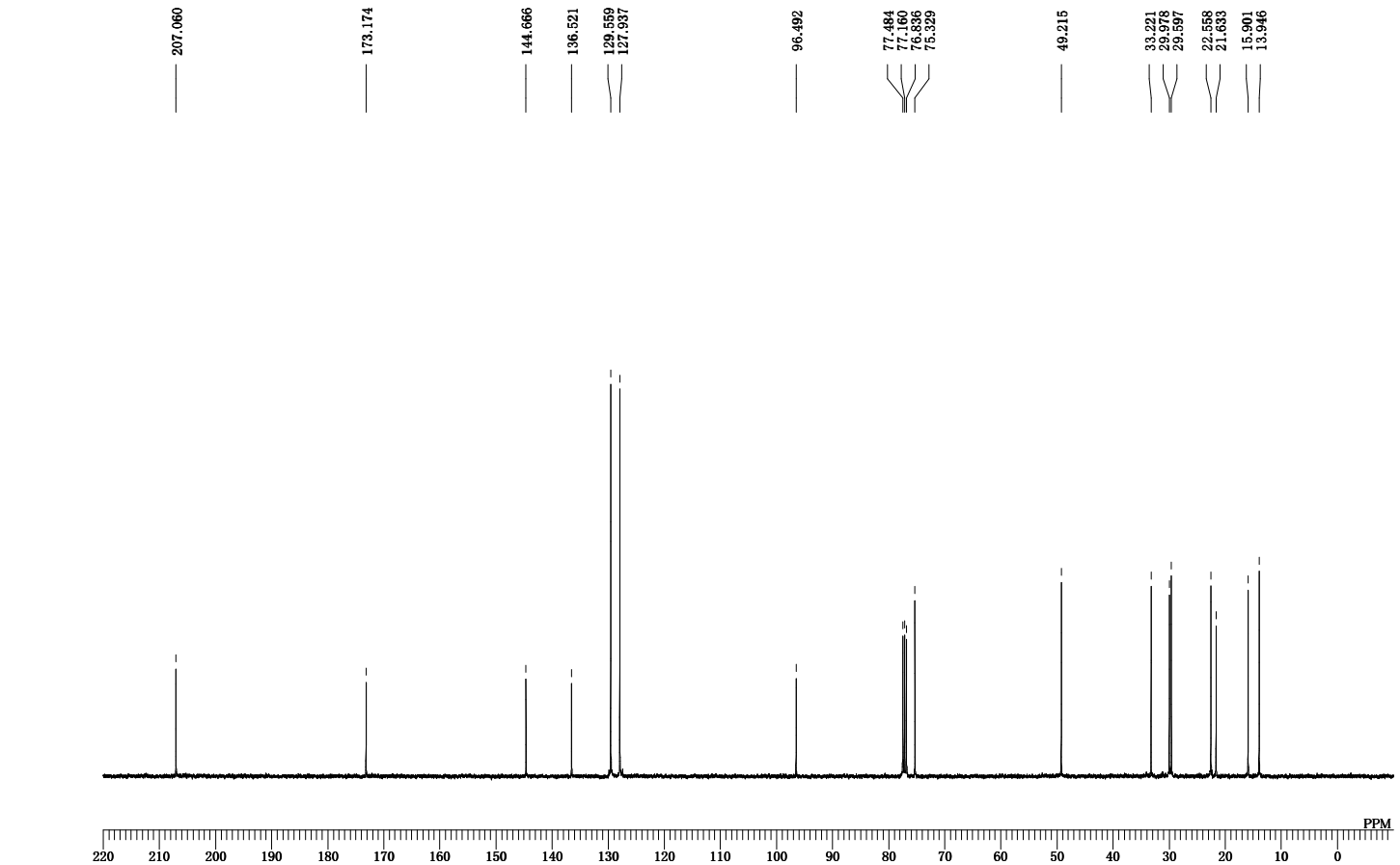
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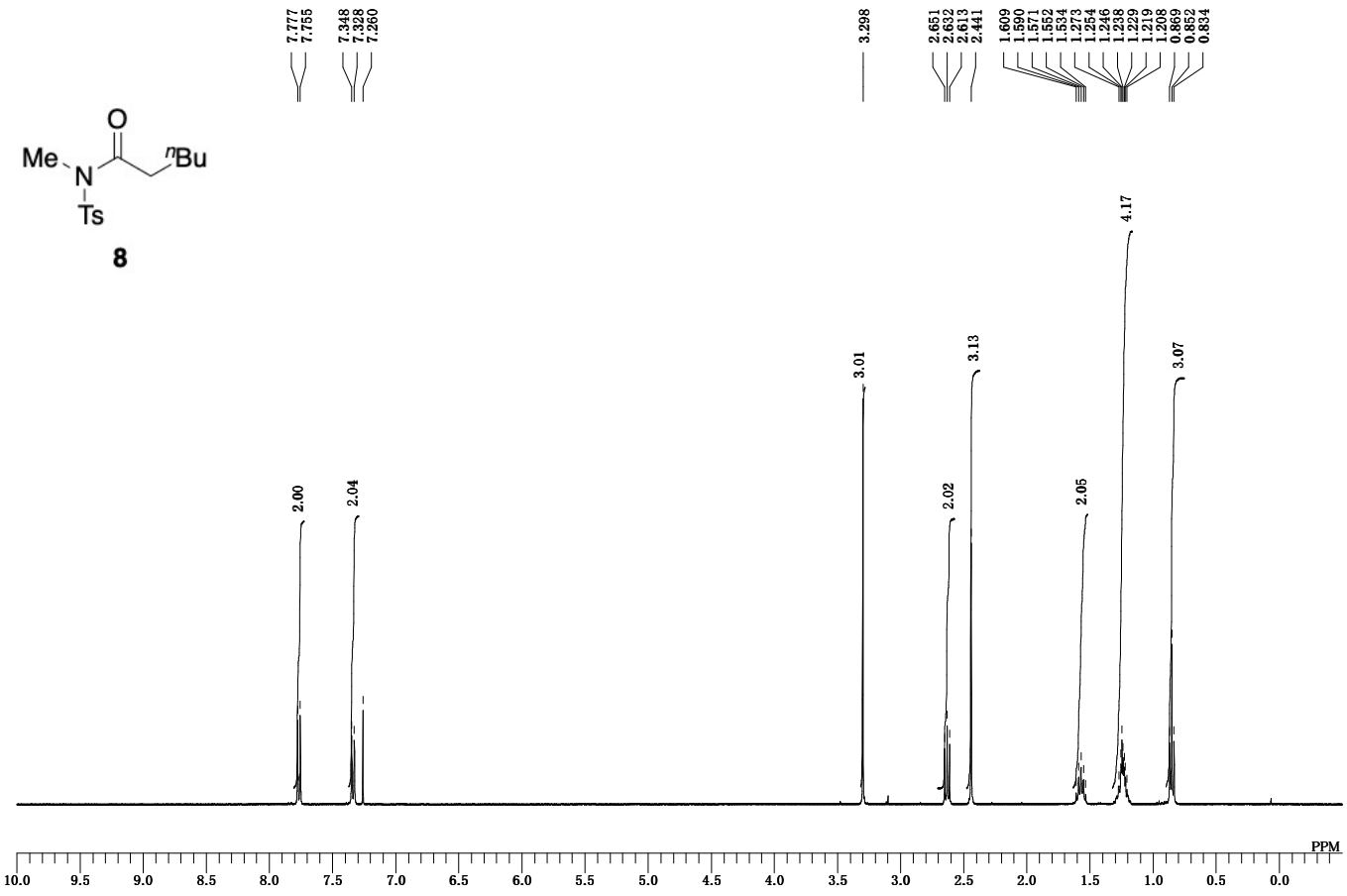
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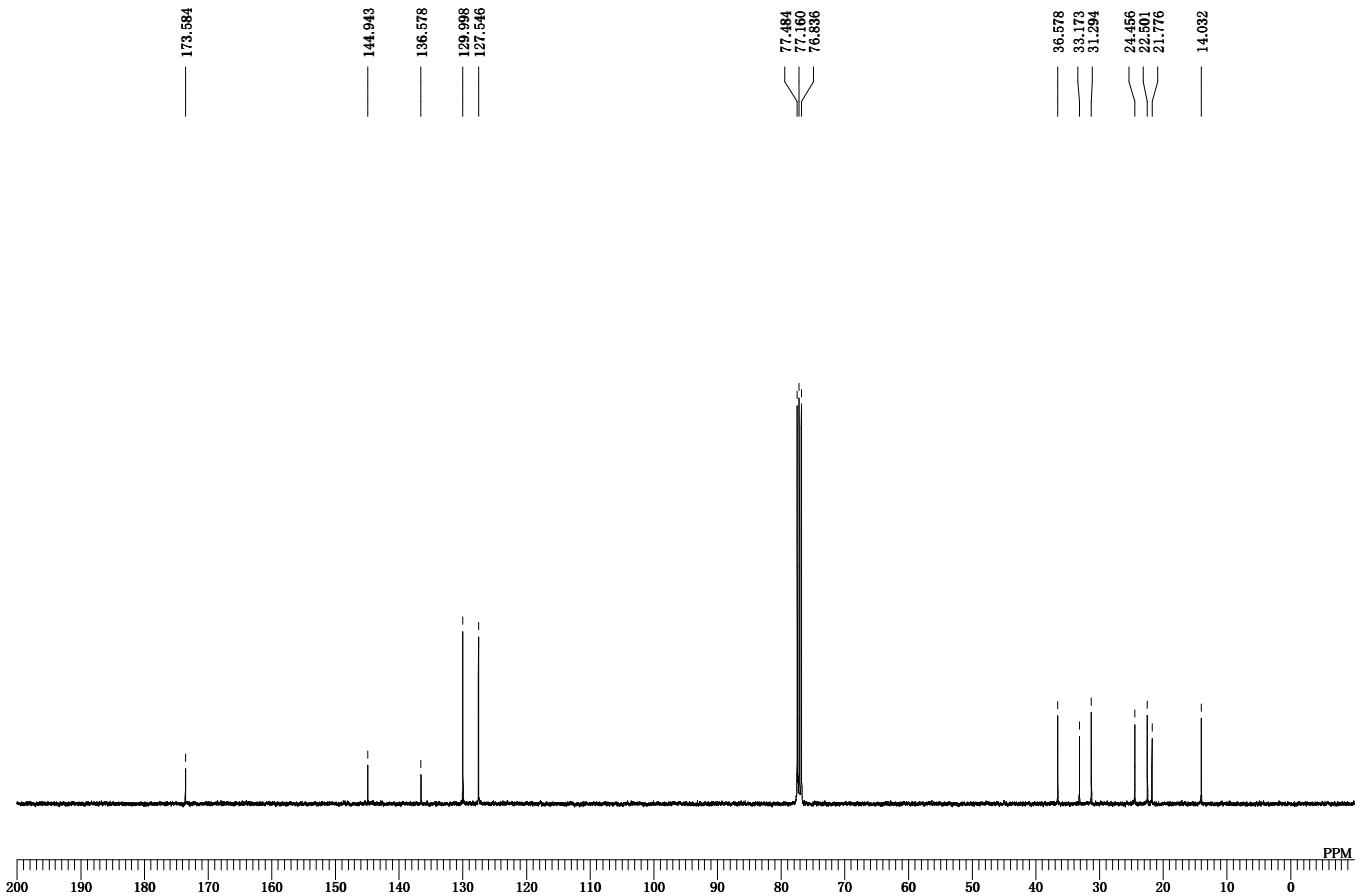
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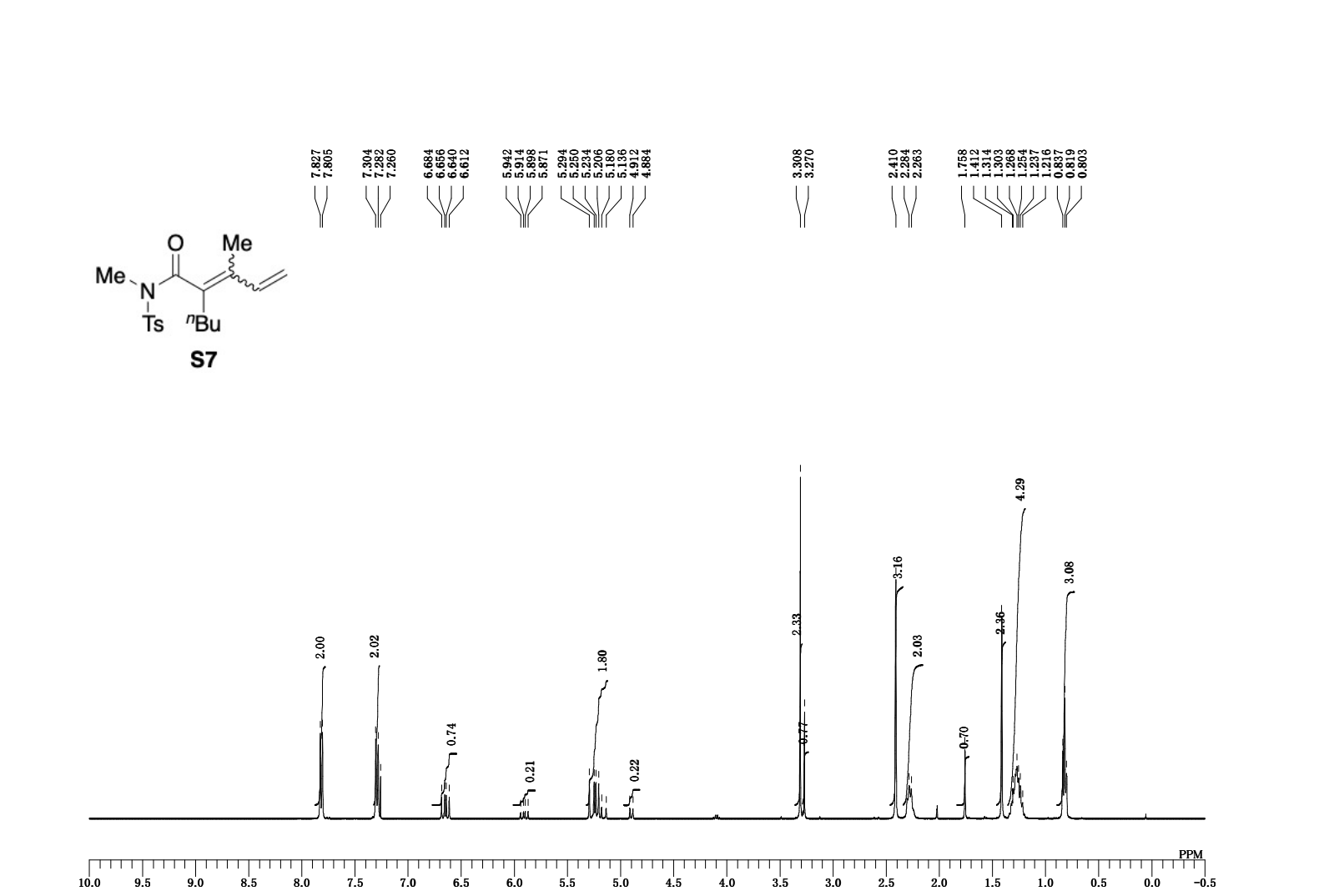
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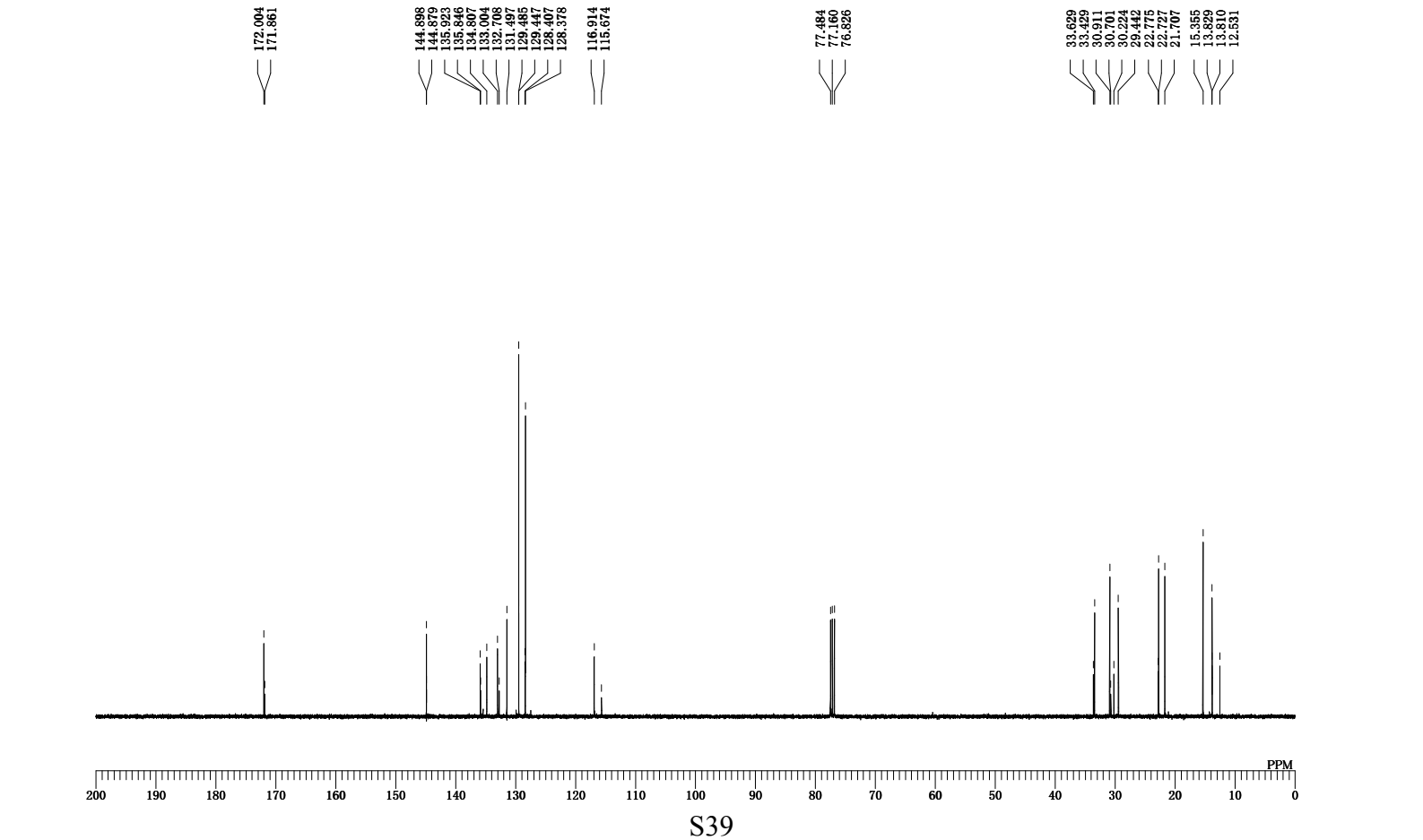
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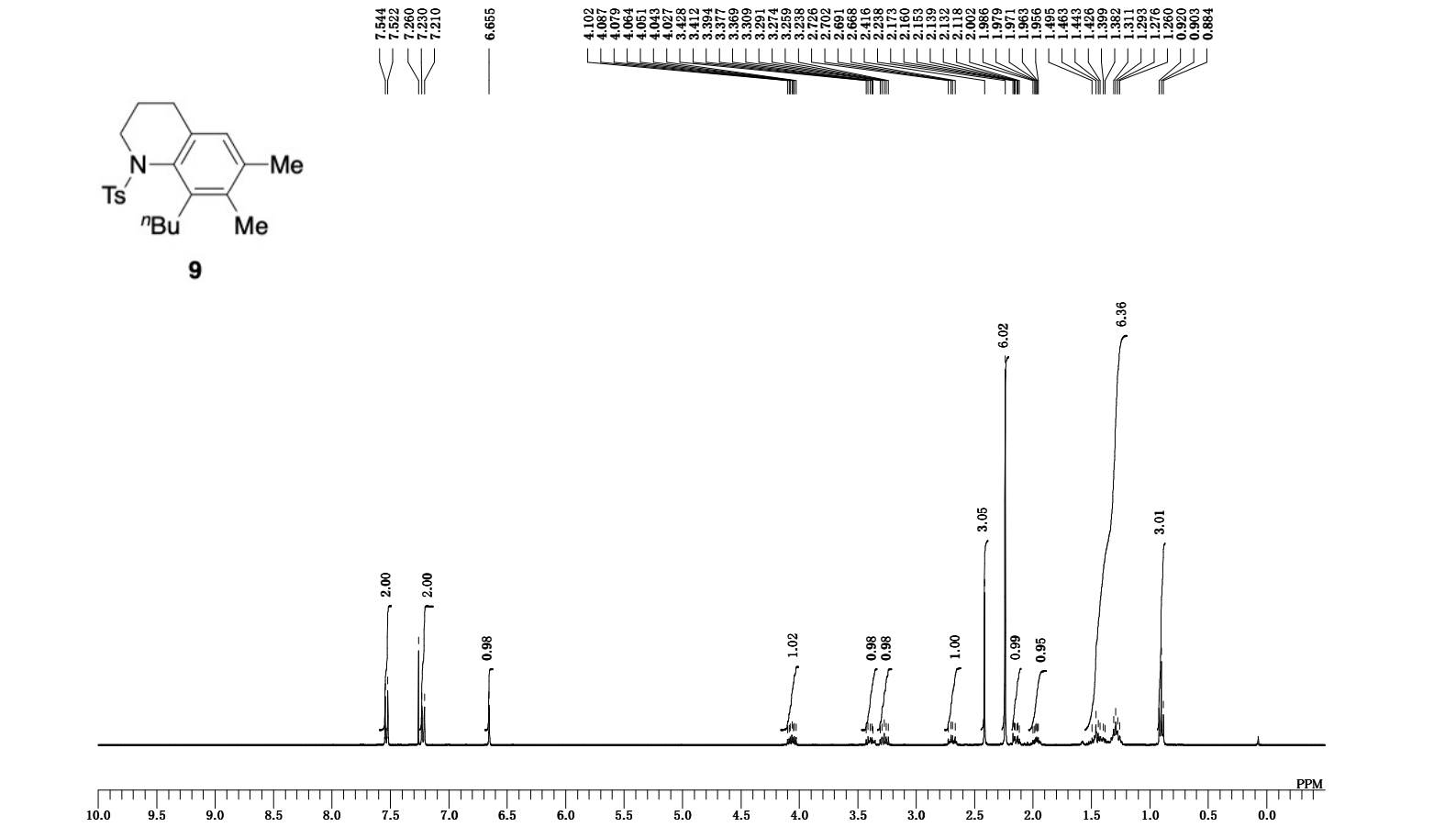
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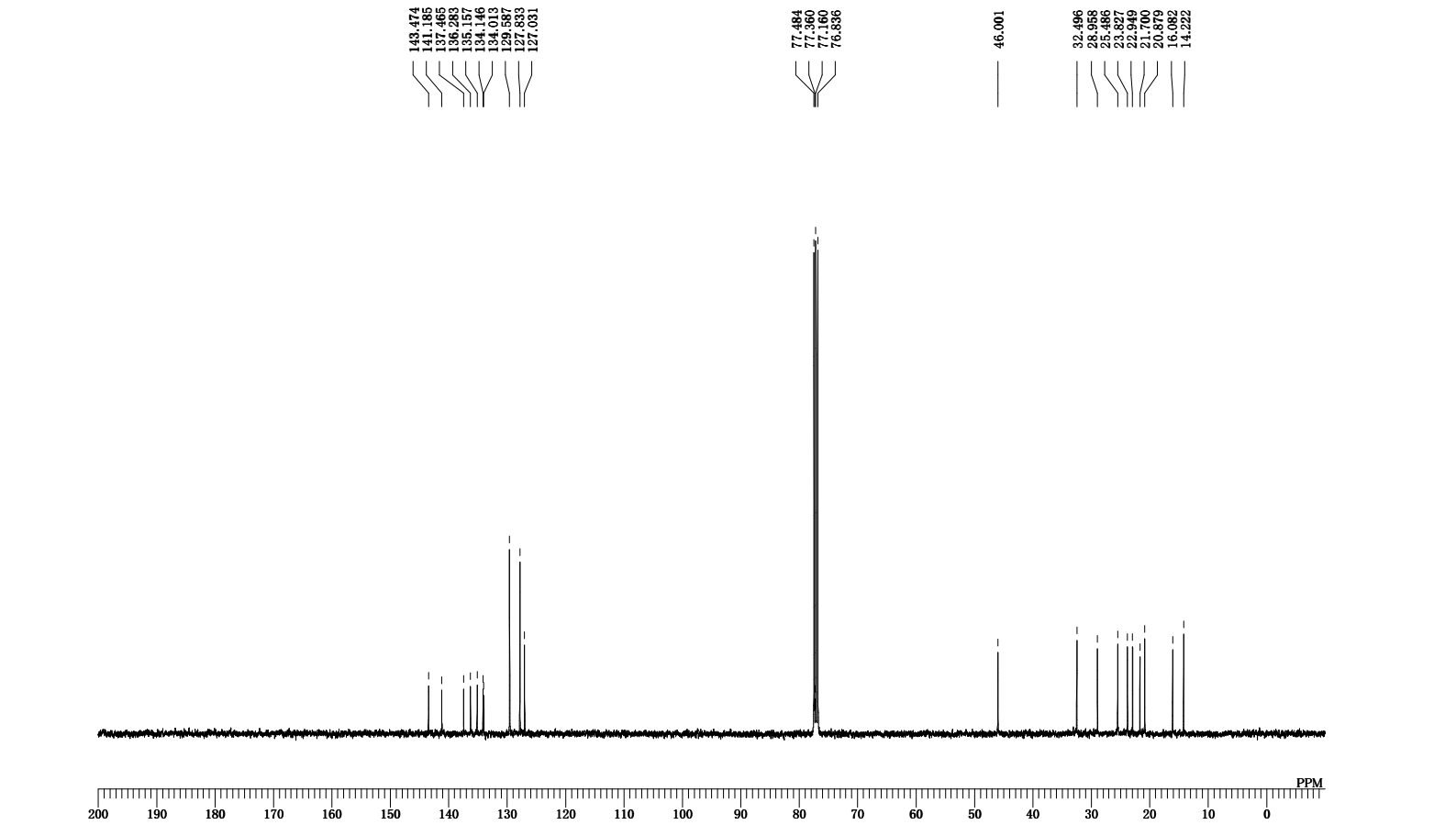
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