Electronic Supplementary Information

Intramolecular Azavinyl Carbene-Triggered Rearrangement of Furans

*Anton S. Makarov,[a] Maxim G. Uchuskin,[*a] and A. Stephen K. Hashmi[*b,c]*

[a]Department of Chemistry, Perm State University, Bukireva 15, 614990 Perm (Russia);
E-mail: mu@psu.ru
[b] Institut für Organische Chemie, Heidelberg University, Im Neuenheimer Feld 270, 69120 Heidelberg (Germany);
[c] Chemistry Department, King Abdulaziz University, Jeddah 21589, (Saudi Arabia);
E-mail: hashmi@hashmi.de

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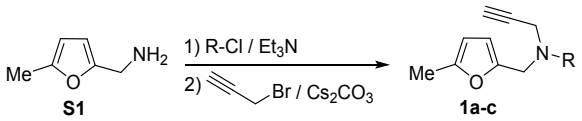
1. General Information

Chemicals reagents, building block and solvents were purchased from commercial suppliers, such as Sigma-Aldrich, Strem, Carbolution, Alfa Aesar, Acros, ABCR, TCI, and used as delivered. Rhodium octanoate was purchased from TCI, CuTC was purchased from Sigma-Aldrich. Dry solvents were dispensed from the solvent purification system MB SPS-800 or from solvent stills. Deuterated solvents were bought from Euriso-Top, Cambridge Isotope Laboratories Inc., or Deutero. Reactions requiring inert conditions were carried out in flame-dried glassware under an atmosphere of nitrogen using standard Schlenk-techniques or in a glovebox. NMR spectra were recorded at room temperature on the following spectrometers: Bruker Avance-III-300, Bruker Avance III HD 400, Bruker Avance DRX-300, Bruker-Avance DRX-500 and Bruker Avance-III-500. Chemical shifts were given in ppm and coupling constants in Hz. ^{1}H and ^{13}C spectra were calibrated in relation to deuterated solvents, namely $CDCl_3$ (7.26 ppm; 77.16 ppm), DMSO-d_6 (2.50 ppm; 39.52 ppm). Splitting patterns of an apparent multiplets associated with an averaged coupling constants were designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broadened) as well as combinations of them. Mass spectra (MS and HRMS) were obtained at the chemistry department of the University of Heidelberg under the direction of Dr. J. Gross. EI+ -spectra were measured on a JOEL JMS-700 spectrometer. For ESI+-spectra a Bruker ApexQu FT-ICR-MS spectrometer was applied. Melting Points were measured in open glass capillaries in a Büchi melting point apparatus. Flash Column Chromatography was accomplished using Silica gel 60 (0.063-0.200 mm/ 230 mesh ASTM) purchased from Sigma-Aldrich or Macherey-Nagel. Analytical Thin Layer Chromatography (TLC) was carried out on precoated Macherey-Nagel POLYGRAM® SIL G/UV254 or POLYGRAM® ALOX N/UV254 plastic sheets. Detection was accomplished using UV-light (254 nm), $KMnO_4$ [in 1.5M Na_2CO_3 (aq.)] and $Ce(SO_4)_2$ (in 15% H_2SO_4).

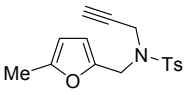
2. Synthesis of Starting Materials

Synthesis of acetylenes 1a-c



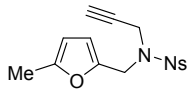
Commercially available 5-methylfurfurylamine **S1** (555 mg, 5 mmol) was dissolved in DCM (50 ml) followed by the addition of Et_3N (700 µL, 5 mmol). To the resulting mixture was added a corresponding sulfonyl chloride (5 mmol) portionwise at room temperature upon stirring. The reaction mixture was stirred at the same temperature until full conversion of starting amine **S1** (TLC-control) at which point in was poured into water (100 ml). Aqueous phase was discarded while the organic phase was washed with additional 100 ml of water, 50 ml of brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was dissolved in acetone (30 mL) followed by the addition of Cs_2CO_3 (2443 mg, 7.5 mmol, 1.5 equiv) and propargyl bromide (80 % w/w in toluene, 724 µL, 6.5 mmol, 1.3 equiv) at room temperature. The reaction mixture was stirred at the same temperature until the full conversion of intermediate sulfonamide (TLC-control); then the mixture was concentrated *in vacuo*, dry loaded on silica gel and subjected to column chromatography (silica gel, eluent: hexanes/ethyl acetate, gradient elution from 99:1 to 50:1) to afford a target acetylene.

4-Methyl-*N*-[(5-methylfuran-2-yl)methyl]-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1a).[1]



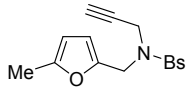
Transparent prisms (1.50 g, 99% yield), mp 66-67 °C (hex/EtOAc). R_f = 0.29 (9:1 hex:EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.67 – 7.63 (m, 2H), 7.23 – 7.18 (m, 2H), 6.07 (d, ^3J = 3.0 Hz, 1H), 5.77 (d, ^3J = 3.0 Hz, 1H), 4.29 (s, 2H), 3.93 (d, ^4J = 2.5 Hz, 2H), 2.33 (s, 3H), 2.11 (s, 3H), 1.99 (t, ^4J = 2.5 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ = 152.8, 146.5, 143.6, 136.1, 129.5 (2C), 127.8 (2C), 111.1, 106.3, 76.6, 73.9, 42.9, 36.1, 21.6, 13.6 ppm.

***N*-[(5-Methylfuran-2-yl)methyl]-4-nitro-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1b).**



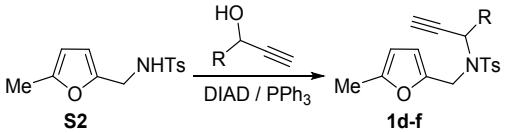
Pale yellow solid (1.65 g, 99% yield), mp 109-110 °C (hex/EtOAc). R_f = 0.25 (8:1 hex:EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.37 – 8.29 (m, 2H), 8.07 – 8.00 (m, 2H), 6.17 (d, ^3J = 3.0 Hz, 1H), 5.84 (d, ^3J = 3.0 Hz, 1H), 4.41 (s, 2H), 4.05 (d, ^4J = 2.4 Hz, 2H), 2.14 (s, 3H), 2.11 (t, ^4J = 2.4 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ = 153.1, 150.1, 145.7, 145.0, 129.0 (2C), 124.1 (2C), 111.7, 106.5, 76.0, 74.5, 43.2, 36.3, 13.5 ppm; ESI-HRMS: $[M+Na]^+$ (*m/z*) calcd. for $C_{15}H_{14}N_2NaO_5S^+$ 357.0516, found 357.0512.

4-Bromo-*N*-[(5-methylfuran-2-yl)methyl]-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1c).



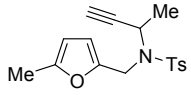
Pale yellow solid (1.82 g, 99% yield), mp 79-80 °C (hex/EtOAc). R_f = 0.36 (8:1 hex:EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.79 – 7.69 (m, 2H), 7.63 – 7.51 (m, 2H), 6.16 (d, ^3J = 3.0 Hz, 1H), 5.85 (d, ^3J = 3.0 Hz, 1H), 4.38 (s, 2H), 4.01 (d, ^4J = 2.4 Hz, 2H), 2.18 (s, 3H), 2.10 (t, ^4J = 2.4 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 153.0, 146.1, 138.3, 132.1 (2C), 129.4 (2C), 127.8, 111.4, 106.4, 76.4, 74.2, 43.1, 36.2, 13.6 ppm; ESI-HRMS: $[M+Na]^+$ (*m/z*) calcd. for $C_{15}H_{14}BrNNaO_3S^+$ 389.9770, found 389.9765.

Synthesis of acetylenes 1d-f



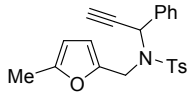
To a solution of sulfonamide **S2** [1] (1325 mg, 5 mmol), a corresponding propargyl alcohol (5 mmol) and PPh_3 (1311 mg, 5 mmol) in THF (40 mL) was added DIAD (1010 µL, 4 mmol) slowly at 0 °C upon stirring. The mixture was allowed to warm to room temperature and stirred further until full conversion of starting sulfonamide **S2** (TLC-control) at which point the mixture was concentrated *in vacuo*, dry loaded on silica gel and subjected to to column chromatography (silica gel, eluent: hexanes/ethyl acetate, gradient elution from 50:1 to 20:1) to afford a target acetylene.

***N*-(But-3-yn-2-yl)-4-methyl-*N*-[(5-methylfuran-2-yl)methyl]benzenesulfonamide (1d).**



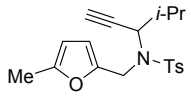
Yellow solid (0.71 g, 45% yield), mp 90-91 °C (hex/EtOAc). R_f = 0.36 (8:1 hex:EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.72 – 7.68 (m, 2H), 7.30 – 7.24 (m, 2H), 6.14 (d, ^3J = 3.0 Hz, 1H), 5.85 (d, ^3J = 3.0, 1H), 4.90 (qd, ^3J = 7.1 Hz, ^4J = 2.3 Hz, 1H), 4.51 (d, ^2J = 16.1 Hz, 1H), 4.25 (d, ^2J = 16.1 Hz, 1H), 2.41 (s, 3H), 2.20 (s, 3H), 2.17 (d, ^4J = 2.3 Hz, 1H), 1.30 (d, ^3J = 7.1 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ = 151.8, 148.8, 143.4, 136.7, 129.5 (2C), 127.6 (2C), 110.3, 106.5, 81.1, 73.5, 45.8, 41.2, 22.1, 21.6, 13.6 ppm; ESI-HRMS: $[M+Na]^+$ (*m/z*) calcd. for $C_{17}H_{19}NNaO_3S^+$ 340.0978, found 340.0973.

4-Methyl-*N*-[(5-methylfuran-2-yl)methyl]-*N*-(1-phenylprop-2-yn-1-yl)benzenesulfonamide (1e).



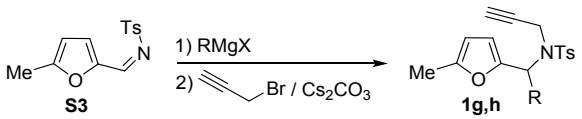
Pale yellow solid (0.96 g, 51% yield), mp 74-75 °C (hex/EtOAc). R_f = 0.39 (8:1 hex:EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.73 – 7.70 (m, 2H), 7.44 – 7.39 (m, 2H), 7.26 – 7.10 (m, 5H), 6.07 (d, ^4J = 2.4 Hz, 1H), 5.66 (d, ^3J = 3.0 Hz, 1H), 5.49 (d, ^3J = 3.0 Hz, 1H), 4.24 (d, ^2J = 15.6 Hz, 1H), 4.11 (d, ^2J = 15.6 Hz, 1H), 2.37 (s, 3H), 2.31 (d, ^4J = 2.4 Hz, 1H), 1.86 (s, 3H) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ = 151.5, 147.2, 143.5, 136.7, 135.6, 129.5 (2C), 128.1 (2C), 127.9 (2C), 127.8 (2C), 127.7, 111.0, 106.0, 78.0, 76.6, 52.8, 41.4, 21.7, 13.3 ppm; ESI-HRMS: $[M+Na]^+$ (*m/z*) calcd. for $C_{22}H_{21}NNaO_3S^+$ 402.1134, found 402.1128.

4-Methyl-*N*-[(5-methylfuran-2-yl)methyl]-*N*-(4-methylpent-1-yn-3-yl)benzenesulfonamide (1f).



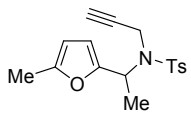
Transparent oil (0.83 g, 48% yield). R_f = 0.39 (8:1 hex:EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.79 – 7.70 (m, 2H), 7.34 – 7.30 (m, 2H), 6.17 (d, ^3J = 3.0 Hz, 1H), 5.88 (d, ^{3}J = 3.0 Hz, 1H), 4.49 (d, ^2J = 15.9 Hz, 1H), 4.30 (dd, ^3J = 10.6 Hz, ^{4}J = 2.4 Hz, 1H), 4.18 (d, ^2J = 15.9 Hz, 1H), 2.44 (s, 3H), 2.23 (s, 3H), 2.19 (d, ^4J = 2.4 Hz, 1H), 1.72 – 1.65 (m, 1H), 1.02 (d, ^3J = 6.6 Hz, 3H), 0.92 (d, ^3J = 6.6 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ = 151.8, 148.5, 143.4, 136.5, 129.4 (2C), 127.8 (2C), 110.6, 106.4, 79.7, 74.8, 57.6, 41.6, 32.3, 21.6, 20.2, 19.3, 13.6 ppm; ESI-HRMS: $[M+Na]^+$ (*m/z*) calcd. for $C_{19}H_{23}NNaO_3S^+$ 368.1291, found 368.1285.

Synthesis of acetylenes 1g,h



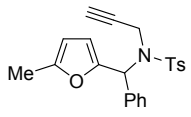
To a solution of imine **S3**[2] (1316 mg, 5 mmol) in THF (40 mL) was added a solution of a corresponding Gringard reagent (*i*-PrMgBr 1.0 M in THF/Sigma-Aldrich or PhMgBr 3.0 M in Et_2O/Sigma-Aldrich, 10 mmol, 2 equiv) dropwise at 0 °C upon stirring. The mixture was allowed to warm to room temperature and stirred further until full conversion of starting imine **S3** (TLC-control). Upon completion, the reaction mixture was cooled to 0 °C, quenched with sat. NH_4Cl (5 ml), diluted with water (50 mL) and extracted with ethyl acetate (2 × 50 mL). The organic phase was washed with water (50 mL) and brine (50 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was dissolved in acetone (30 mL) followed by the addition of Cs_2CO_3 (2443 mg, 7.5 mmol, 1.5 equiv) and propargyl bromide (80 % w/w in toluene, 724 µL, 6.5 mmol, 1.3 equiv) at room temperature. The reaction mixture was stirred at the same temperature until the full conversion of intermediate sulfonamide (TLC-control); then the mixture was concentrated *in vacuo*, dry loaded on silica gel and subjected to column chromatography (silica gel, eluent: hexanes/ethyl acetate, gradient elution from 99:1 to 50:1) to afford a target acetylene.

4-Methyl-*N*-[1-(5-methylfuran-2-yl)ethyl]-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1g).



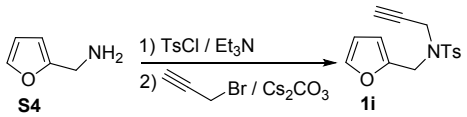
Pale yellow oil (1.41 g, 89% yield). R_f = 0.40 (8:1 hex:EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.77 – 7.72 (m, 2H), 7.24 – 7.18 (m, 2H), 5.97 (d, ^3J = 3.0 Hz, 1H), 5.73 (d, ^3J = 3.0 Hz, 1H), 5.06 (q, ^3J = 7.1 Hz, 1H), 3.96 (dd, ^2J = 18.5 Hz, ^4J = 2.5 Hz, 1H), 3.67 (dd, ^2J = 18.5 Hz, ^4J = 2.5 Hz, 1H), 2.34 (s, 3H), 2.00 (s, 3H), 1.96 (t, ^4J = 2.5 Hz, 1H), 1.46 (d, ^3J = 7.1 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ = 152.0, 150.7, 143.2, 137.7, 129.3 (2C), 127.8 (2C), 109.4, 106.0, 79.8, 71.7, 50.9, 32.6, 21.6, 17.4, 13.4 ppm; ESI-HRMS: $[M+Na]^+$ (*m/z*) calcd. for $C_{17}H_{19}NNaO_3S^+$ 340.0978, found 340.0973.

4-Methyl-*N*-[(5-methylfuran-2-yl)(phenyl)methyl]-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1h).



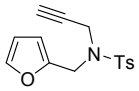
Pale yellow oil (1.76 g, 93% yield). R_f = 0.39 (8:1 hex:EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.72 – 7.67 (m, 2H), 7.24 – 7.21 (m, 5H), 7.15 – 7.14 (m, 2H), 6.20 (s, 1H), 5.88 (d, ^3J = 3.1 Hz, 1H), 5.74 (d, ^3J = 3.1 Hz, 1H), 4.10 (dd, ^2J = 18.4 Hz, ^4J = 2.4 Hz, 1H), 3.87 (dd, ^2J = 18.4 Hz, ^4J = 2.4 Hz, 1H), 2.32 (s, 3H), 2.02 (s, 3H), 1.80 (t, ^4J = 2.4 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ = 152.4, 149.1, 143.3, 137.3, 136.8, 129.2 (2C), 128.5 (2C), 128.1 (2C), 128.0 (3C), 111.8, 106.2, 78.8, 71.7, 58.8, 34.6, 21.6, 13.5 ppm; ESI-HRMS: $[M+Na]^+$ (*m/z*) calcd. for $C_{22}H_{21}NNaO_3S^+$ 402.1134, found 402.1129.

Synthesis of acetylene 1i



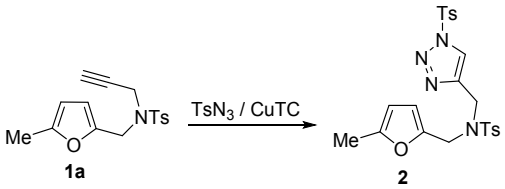
Commercially available 5-methylfurfurylamine **S4** (485 mg, 5 mmol) was dissolved in DCM (50 ml) followed by the addition of Et_3N (700 µL, 5 mmol). To the resulting mixture was added tosyl chloride (953 mg, 5 mmol) portionwise at room temperature upon stirring. The reaction mixture was stirred at the same temperature until full conversion of starting amine **S4** (TLC-control) at which point in was poured into water (100 ml). Aqueous phase was discarded while the organic phase was washed with additional 100 ml of water, 50 ml of brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was dissolved in acetone (30 mL) followed by the addition of Cs_2CO_3 (2443 mg, 7.5 mmol, 1.5 equiv) and propargyl bromide (80 % w/w in toluene, 724 µL, 6.5 mmol, 1.3 equiv) at room temperature. The reaction mixture was stirred at the same temperature until the full conversion of intermediate sulfonamide (TLC-control); then the mixture was concentrated *in vacuo*, dry loaded on silica gel and subjected to column chromatography (silica gel, eluent: hexanes/ethyl acetate, gradient elution from 99:1 to 50:1) to afford a target acetylene.

***N*-(Furan-2-ylmethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1i).**[3]



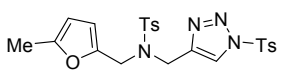
Transparent prisms (1.43 g, 99% yield), mp 64-65 °C (hex/EtOAc). R_f = 0.71 (3:1 hex:EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.75 – 7.72 (m, 2H), 7.35 (dd, ^3J = 1.6 Hz, ^3J = 1.1 Hz, 1H), 7.32 – 7.28 (m, 2H), 6.32 – 6.28 (m, 2H), 4.43 (s, 2H), 4.02 (d, ^4J = 2.4 Hz, 2H), 2.43 (s, 3H), 2.07 (t, ^4J = 2.4 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ = 148.8, 143.8, 143.1, 136.1, 129.6 (2C), 127.9 (2C), 110.6, 110.1, 76.6, 74.1, 42.8, 36.3, 21.7 ppm.

Synthesis of triazole 2



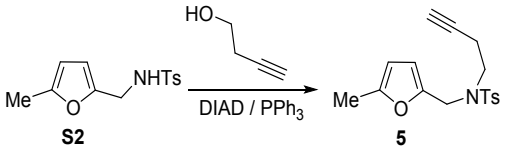
To a solution of acetylene **1a** (910 mg, 3 mmol) and TsN_3 (591 mg, 3 mmol) in toluene (30 mL) was added CuTC (28 mg, 5 mol%) at 0 °C. The resulting mixture was stirred at the same temperature for 3 h (TLC-control). Upon completion, the reaction mixture was concentrated *in vacuo*, dry loaded on silica gel and subjected to column chromatography (silica gel, eluent: hexanes/ethyl acetate, gradient elution from 20:1 to 5:1) to afford compound **2**.

4-Methyl-*N*-[(5-methylfuran-2-yl)methyl]-*N*-[(1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl]benzenesulfonamide (2).



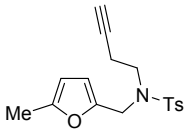
White solid (1.48 g, 99% yield), mp 94-95 °C (hex/EtOAc). R_f = 0.36 (3:1 hex:EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.00 – 7.95 (m, 2H), 7.90 (s, 1H), 7.68 – 7.64 (m, 2H), 7.41 – 7.36 (m, 2H), 7.29 – 7.23 (m, 2H), 6.04 (d, ^3J = 3.0 Hz, 1H), 5.74 (d, ^3J = 3.0 Hz, 1H), 4.42 (s, 2H), 4.35 (s, 2H), 2.45 (s, 3H), 2.42 (s, 3H), 2.09 (s, 3H) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ = 152.8, 147.5, 146.7, 144.2, 143.8, 136.7, 133.1, 130.6 (2C), 129.7 (2C), 128.9 (2C), 127.4 (2C), 122.8, 111.4, 106.4, 44.5, 42.2, 22.0, 21.6, 13.5 ppm; DART-HRMS: $[M+H]^+$ (*m/z*) calcd. for $C_{23}H_{25}N_4O_5S_2^+$ 501.1261, found 501.1261.

Synthesis of acetylene 5



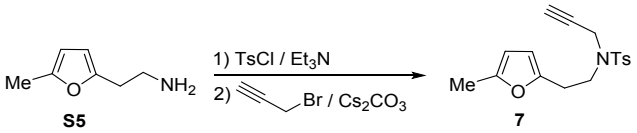
To a solution of sulfonamide **S2**, [1] commercially available 3-butyn-1-ol (350 mg, 5 mmol) and PPh_3 (1311 mg, 5 mmol) in THF (40 mL) was added DIAD (1010 µL, 4 mmol) slowly at 0 °C upon stirring. The mixture was allowed to warm to room temperature and stirred further until full conversion of starting sulfonamide **S2** (TLC-control) at which point the mixture was concentrated *in vacuo*, dry loaded on silica gel and subjected to to column chromatography (silica gel, eluent: hexanes/ethyl acetate, gradient elution from 50:1 to 20:1) to afford compound **5**.

***N*-(But-3-yn-1-yl)-4-methyl-*N*-[(5-methylfuran-2-yl)methyl]benzenesulfonamide (5).**



Pale yellow solid (1.16 g, 73% yield), mp 89-90 °C (hex/EtOAc). R_f = 0.42 (8:1 hex:EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.69 – 7.65 (m, 2H), 7.28 – 7.22 (m, 2H), 6.05 (d, ^3J = 3.0 Hz, 1H), 5.82 (d, ^3J = 3.0 Hz, 1H), 4.39 (s, 2H), 3.29 (t, ^3J = 7.4 Hz, 2H), 2.41 (s, 3H), 2.37 (dd, ^3J = 7.7 Hz, ^4J = 2.7 Hz, 2H), 2.13 (s, 3H), 1.96 (t, ^4J = 2.7 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ = 152.5, 147.4, 143.3, 137.0, 129.6 (2C), 127.4 (2C), 110.7, 106.4, 81.2, 70.2, 46.1, 44.7, 21.6, 19.3, 13.5 ppm; ESI-HRMS: $[M+Na]^+$ (*m/z*) calcd. for $C_{17}H_{19}NNaO_3S^+$ 340.0978, found 340.0973.

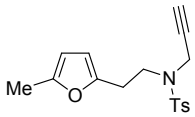
Synthesis of acetylene 7



S5 **7**

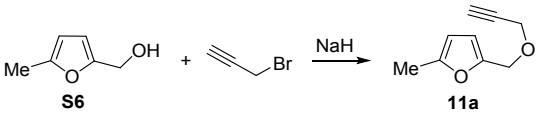
5-Methylhomofurfurylamine **S5**[4] (625 mg, 5 mmol) was dissolved in DCM (50 ml) followed by the addition of Et_3N (700 µL, 5 mmol). To the resulting mixture was added tosyl chloride (953 mg, 5 mmol) portionwise at room temperature upon stirring. The reaction mixture was stirred at the same temperature until full conversion of starting amine **S5** (TLC-control) at which point in was poured into water (100 ml). Aqueous phase was discarded while the organic phase was washed with additional 100 ml of water, 50 ml of brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was dissolved in acetone (30 mL) followed by the addition of Cs_2CO_3 (2443 mg, 7.5 mmol, 1.5 equiv) and propargyl bromide (80 % w/w in toluene, 724 µL, 6.5 mmol, 1.3 equiv) at room temperature. The reaction mixture was stirred at the same temperature until the full conversion of intermediate sulfonamide (TLC-control); then the mixture was concentrated *in vacuo*, dry loaded on silica gel and subjected to column chromatography (silica gel, eluent: hexanes/ethyl acetate, gradient elution from 99:1 to 50:1) to afford a target acetylene.

4-Methyl-*N*-[2-(5-methylfuran-2-yl)ethyl]-*N*-(prop-2-yn-1-yl)benzenesulfonamide (7).



Colorless oil (1.54 g, 97% yield). R_f = 0.46 (3:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.74 – 7.68 (m, 2H), 7.30 – 7.24 (m, 2H), 5.94 (d, ^3J = 3.0 Hz, 1H), 5.84 (d, ^3J = 3.0 Hz, 1H), 4.07 (d, ^4J = 2.4 Hz, 2H), 3.46 (t, ^3J = 7.4 Hz, 2H), 2.88 (t, ^3J = 7.4 Hz, 2H), 2.40 (s, 3H), 2.22 (s, 3H), 2.06 (t, ^4J = 2.4 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 151.0, 150.2, 143.6, 136.1, 129.6 (2C), 127.7 (2C), 107.3, 106.2, 76.8, 73.8, 45.4, 36.9, 27.5, 21.5, 13.5 ppm; ESI-HRMS: $[M+H]^+$ (*m/z*) calcd. for $C_{17}H_{20}NO_3S^+$ 318.1158, found 318.1159.

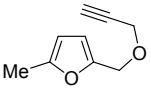
Synthesis of acetylene 11a



S6 **11a**

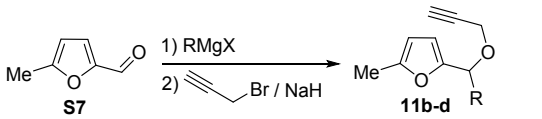
To a solution of commercially available (5-methyl-2-furyl)methanol **S6** (897 mg, 8 mmol) in THF (40 mL) was added NaH (60% w/w in mineral oil, 384 mg, 9.6 mmol, 1.2 equiv) portionwise at 0 °C. The resulting suspension was stirred at the same temperature for 10 min, then warmed to room temperature and stirred for additional 30 min. A solution of propargyl bromide in toluene (80% w/w, 1158 µL, 12 mmol, 1.5 equiv) was added portionwise to the reaction mixture upon stirring. The mixture was stirred up to the full conversion of the starting alcohol **S6**. Upon completion, the reaction mixture was cooled to 0 °C, quenched with sat. NH_4Cl (5 ml), diluted with water (50 mL) and extracted with ethyl acetate (2×75 mL). The organic phase was washed with water (50 mL) and brine (50 mL), dried over anhydrous Na_2SO_4, concentrated *in vacuo*, dry loaded on silica gel and subjected to column chromatography (silica gel, eluent: hexanes/ethyl acetate, gradient elution from 99:1 to 50:1) to afford compound **11a**.

2-Methyl-5-[(prop-2-yn-1-yloxy)methyl]furan (11a).[5]



Pale yellow oil (1.17 g, 97% yield). R_f = 0.64 (8:1 hex:EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.22 (d, ^3J = 3.0 Hz, 1H), 5.90 (d, ^3J = 3.0 Hz, 1H), 4.47 (s, 2H), 4.12 (d, ^3J = 2.4 Hz, 2H), 2.44 (t, ^3J = 2.4 Hz, 1H), 2.26 (s, 3H) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ = 152.9, 148.9, 111.1, 106.2, 79.4, 74.7, 63.1, 56.5, 13.5 ppm.

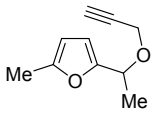
Synthesis of acetylenes 11b-d



R = Me, Ph, $MeOC_6H_5$

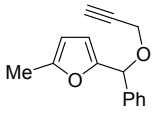
To a solution of commercially available 5-methylfurfural **S7** (881 mg, 8 mmol) in THF (50 mL) was added a solution of a corresponding Gringard reagent (MeMgBr 3.0 M in Et_2O/Sigma-Aldrich, or PhMgBr 3.0 M in Et_2O/Sigma-Aldrich, or *p*-$OMeC_6H_4MgBr$ 0.5 M in THF/Sigma-Aldrich, 16 mmol, 2 equiv) dropwise at 0 °C upon stirring. The mixture was allowed to warm to room temperature and stirred further until full conversion of starting 5-methylfurfural **S7** (TLC-control). Upon completion, the reaction mixture was cooled to 0 °C, quenched with sat. NH_4Cl (5 ml), diluted with water (50 mL) and extracted with ethyl acetate (2 × 50 mL). The organic phase was washed with water (50 mL) and brine (50 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was dissolved in THF (40 mL) followed by portionwise addition of NaH (60% w/w in mineral oil, 384 mg, 9.6 mmol, 1.2 equiv) at 0 °C. The resulting suspension was stirred at the same temperature for 10 min, then warmed to room temperature and stirred for additional 30 min. A solution of propargyl bromide in toluene (80% w/w, 1158 µL, 12 mmol, 1.5 equiv) was added portionwise to the reaction mixture upon stirring. The mixture was stirred up to the full conversion of the intermediate alcohol. Upon completion, the reaction mixture was cooled to 0 °C, quenched with sat. NH_4Cl (5 ml), diluted with water (50 mL) and extracted with ethyl acetate (2 × 75 mL). The organic phase was washed with water (50 mL) and brine (50 mL), dried over anhydrous Na_2SO_4, concentrated *in vacuo*, dry loaded on silica gel and subjected to column chromatography (silica gel, eluent: hexanes/ethyl acetate, gradient elution from 99:1 to 50:1) to afford a target acetylene.

2-Methyl-5-(1-(prop-2-yn-1-yloxy)ethyl)furan (11b).[3]



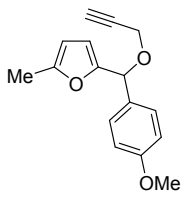
Pale yellow oil (1.20 g, 91% yield). R_f = 0.64 (8:1 hex:EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.16 (d, ^3J = 3.0 Hz, 1H), 5.89 (d, ^3J = 3.0 Hz, 1H), 4.63 (q, ^3J = 6.6 Hz, 1H), 4.12 (dd, ^2J = 15.8 Hz, ^3J = 2.4 Hz, 1H), 3.97 (dd, ^2J = 15.8 Hz, ^3J = 2.4 Hz, 1H), 2.39 (t, ^4J = 2.4 Hz, 1H), 2.27 (s, 3H), 1.51 (d, ^3J = 6.6 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ = 152.3, 152.2, 109.0, 106.0, 80.1, 74.1, 69.3, 55.3, 19.6, 13.6 ppm; ESI-HRMS: $[M]^{+\cdot}$ (*m/z*) calcd. for $C_{10}H_{12}O_2^{+\cdot}$ 164.0832, found 164.0838.

2-Methyl-5-[phenyl(prop-2-yn-1-yloxy)methyl]furan (11c).[6]



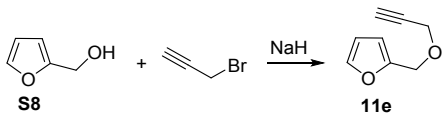
Pale yellow oil (1.67 g, 92% yield). R_f = 0.68 (8:1 hex:EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.53 – 7.49 (m, 2H), 7.41 – 7.36 (m, 3H), 6.11 (d, ^3J = 3.0 Hz, 1H), 5.94 (d, ^3J = 3.0 Hz, 1H), 5.68 (s, 1H), 4.25 (dd, ^2J = 15.8 Hz, ^4J = 2.4 Hz, 1H), 4.19 (dd, ^2J = 15.8 Hz, ^4J = 2.4 Hz, 1H), 2.50 (t, ^4J = 2.4 Hz, 1H), 2.32 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ = 152.9, 151.6, 138.6, 128.5 (2C), 128.1, 127.5 (2C), 110.5, 106.2, 79.6, 75.5, 74.9, 55.7, 13.7 ppm; ESI-HRMS: $[M+Na]^+$ (*m/z*) calcd. for $C_{15}H_{14}NaO_2^+$ 249.0886, found 249.0886.

2-[(4-Methoxyphenyl)(prop-2-yn-1-yloxy)methyl]-5-methylfuran (11d).[6]



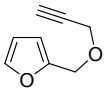
Pale yellow oil (1.52 g, 74% yield). R_f = 0.60 (8:1 hex:EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.41 – 7.38 (m, 2H), 6.93 – 6.90 (m, 2H), 6.06 (d, ^3J = 3.0 Hz, 1H), 5.90 (d, ^3J = 3.0 Hz, 1H), 5.60 (s, 1H), 4.19 (dd, ^2J = 15.8 Hz, ^4J = 2.4 Hz, 1H), 4.12 (dd, ^2J = 15.8 Hz, ^4J = 2.4 Hz, 1H), 3.81 (s, 3H), 2.47 (t, ^4J = 2.4 Hz, 1H), 2.29 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ = 159.5, 152.7, 151.9, 130.6, 128.9 (2C), 113.9 (2C), 110.1, 106.2, 79.7, 75.1, 74.8, 55.5, 55.3, 13.7 ppm; ESI-HRMS: $[M]^{+\cdot}$ (*m/z*) calcd. for $C_{16}H_{16}NaO_3^{+\cdot}$ 279.0992, found 279.0991.

Synthesis of acetylene 11e



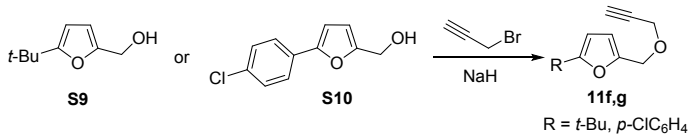
To a solution of commercially available furfuryl alcohol **S8** (785 mg, 8 mmol) in THF (40 mL) was added NaH (60% w/w in mineral oil, 384 mg, 9.6 mmol, 1.2 equiv) portionwise at 0 °C. The resulting suspension was stirred at the same temperature for 10 min, then warmed to room temperature and stirred for additional 30 min. A solution of propargyl bromide in toluene (80% w/w, 1158 µL, 12 mmol, 1.5 equiv) was added portionwise to the reaction mixture upon stirring. The mixture was stirred up to the full conversion of the starting alcohol **S8**. Upon completion, the reaction mixture was cooled to 0 °C, quenched with sat. NH_4Cl (5 ml), diluted with water (50 mL) and extracted with ethyl acetate (2 × 75 mL). The organic phase was washed with water (50 mL) and brine (50 mL), dried over anhydrous Na_2SO_4, concentrated *in vacuo*, dry loaded on silica gel and subjected to column chromatography (silica gel, eluent: hexanes/ethyl acetate, gradient elution from 99:1 to 50:1) to afford compound **11e.**

2-[(Prop-2-yn-1-yloxy)methyl]furan (11e).[7]



Colorless liquid (1.08 g, 99% yield). R_f = 0.60 (8:1 hex:EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.39 (dd, ^3J = 1.8 Hz, ^4J = 0.9 Hz, 1H), 6.35 (br d, ^3J = 3.2 Hz, 1H), 6.32 (dd, ^3J = 3.2 Hz, ^3J = 1.8 Hz, 1H), 4.53 (s, 2H), 4.12 (d, ^4J = 2.4 Hz, 2H), 2.46 (t, ^4J = 2.4 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ = 150.8, 143.0, 110.3, 110.0, 79.3, 74.8, 62.9, 56.6 ppm.

Synthesis of acetylenes 11f,g

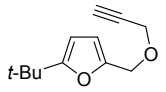


S9 **S10** **11f,g**

R = *t*-Bu, *p*-ClC_6H_4

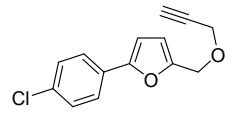
To a solution of alcohol **S9** [8] or **S10** [9] (8 mmol) in THF (40 mL) was added NaH (60% w/w in mineral oil, 384 mg, 9.6 mmol, 1.2 equiv) portionwise at 0 °C. The resulting suspension was stirred at the same temperature for 10 min, then warmed to room temperature and stirred for additional 30 min. A solution of propargyl bromide in toluene (80% w/w, 1158 µL, 12 mmol, 1.5 equiv) was added portionwise to the reaction mixture upon stirring. The mixture was stirred up to the full conversion of the starting alcohol **S8**. Upon completion, the reaction mixture was cooled to 0 °C, quenched with sat. NH_4Cl (5 ml), diluted with water (50 mL) and extracted with ethyl acetate (2 × 75 mL). The organic phase was washed with water (50 mL) and brine (50 mL), dried over anhydrous Na_2SO_4, concentrated *in vacuo*, dry loaded on silica gel and subjected to column chromatography (silica gel, eluent: hexanes/ethyl acetate, gradient elution from 99:1 to 50:1) to afford compound **11e.**

2-*tert*-Butyl-5-[(prop-2-yn-1-yloxy)methyl]furan (11f).



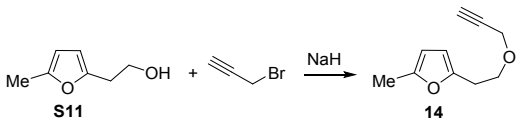
Pale yellow oil (1.45 g, 94% yield). R_f = 0.53 (5:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.23 (d, ^3J = 3.0 Hz, 1H), 5.91 (d, ^3J = 3.0 Hz, 1H), 4.51 (s, 2H), 4.14 (d, ^4J = 2.3 Hz, 2H), 2.44 (t, ^4J = 2.3 Hz, 1H), 1.28 (s, 9H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 165.1, 148.9, 110.7, 102.7, 79.7, 74.6, 63.4, 56.5, 32.7, 29.1 (3C) ppm; ESI-HRMS: $[M+H]^+$ (*m/z*) calcd. for $C_{12}H_{17}O_2^+$ 193.1223, found 193.1226.

2-(4-chlorophenyl)-5-((prop-2-yn-1-yloxy)methyl)furan (11g).



Pale yellow oil (1.93 g, 98% yield). R_f = 0.54 (5:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62 – 7.58 (m, 2H), 7.36 – 7.32 (m, 2H), 6.59 (d, ^3J = 3.3, 1H), 6.45 (d, ^3J = 3.3 Hz, 1H), 4.61 (s, 2H), 4.21 (d, ^4J = 2.3 Hz, 2H), 2.48 (t, ^4J = 2.3 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 153.6, 151.0, 133.4, 129.3, 129.0 (2C), 125.3 (2C), 112.4, 106.3, 79.5, 75.0, 63.4, 57.0 ppm; ESI-HRMS: $[M+H]^+$ (*m/z*) calcd. for $C_{14}H_{12}ClO_2^+$ 247.0520, found 247.0522.

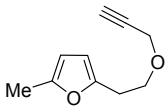
Synthesis of acetylene 14



S11 **14**

To a solution of alcohol **S11**[10] (1009 mg, 8 mmol) in THF (40 mL) was added NaH (60% w/w in mineral oil, 384 mg, 9.6 mmol, 1.2 equiv) portionwise at 0 °C. The resulting suspension was stirred at the same temperature for 10 min, then warmed to room temperature and stirred for additional 30 min. A solution of propargyl bromide in toluene (80% w/w, 1158 µL, 12 mmol, 1.5 equiv) was added portionwise to the reaction mixture upon stirring. The mixture was stirred up to the full conversion of the starting alcohol **S11**. Upon completion, the reaction mixture was cooled to 0 °C, quenched with sat. NH_4Cl (5 ml), diluted with water (50 mL) and extracted with ethyl acetate (2 × 75 mL). The organic phase was washed with water (50 mL) and brine (50 mL), dried over anhydrous Na_2SO_4, concentrated *in vacuo*, dry loaded on silica gel and subjected to column chromatography (silica gel, eluent: hexanes/ethyl acetate, gradient elution from 99:1 to 50:1) to afford compound **15**.

2-Methyl-5-[2-(prop-2-yn-1-yloxy)ethyl]furan (14).[10]



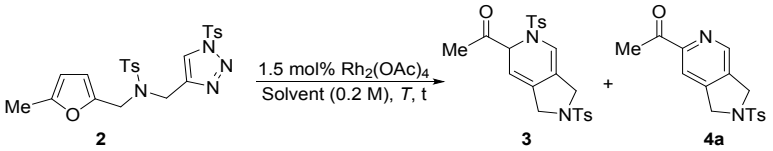
Pale yellow oil (1.17 g, 86% yield). R_f = 0.68 (8:1 hex:EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 5.95 (d, ^3J = 2.9 Hz, 1H), 5.86 (d, ^3J = 2.9 Hz, 1H), 4.16 (d, ^4J = 2.4 Hz, 2H), 3.77 (t, ^3J = 7.0 Hz, 2H), 2.89 (t, ^3J = 7.0 Hz, 2H), 2.43 (t, ^4J = 2.4 Hz, 1H), 2.25 (s, 3H) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ = 150.9, 150.7, 106.7, 106.1, 79.8, 74.5, 68.3, 58.2, 28.8, 13.6 ppm.

3. Optimization of reaction conditions for the synthesis of pyridines 4

General considerations

Unless otherwise stated, all reactions were performed at 0.05 mmol scale of triazole **2** under inert atmosphere (argon or nitrogen); dried solvents and Et_3N (freshly distilled over a proper drying agent or dispensed from a solvent purification system) were additionally degassed by "freeze-pump-thaw" method, stored in glovebox and used within 24 h.

Table S1. Screening of solvents

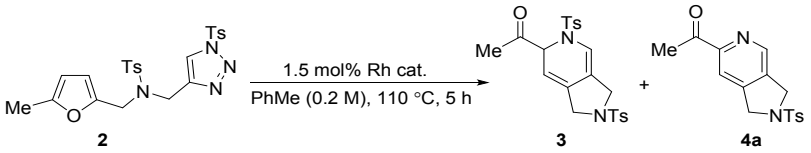


2 **3** **4a**

Entry	Solvent	*T*, °C	t, h	Yield of **3**, %[a]	Yield of **4a**, %[a]
1	DCM	35	5	13	trace
2	$CHCl_3$	50	5	23	trace
3	$CHCl_3$	50	10	31	trace
4	$CHCl_3$	60	5	36	trace
5	THF	65	5	trace	trace
6	ethyl acetate	75	5	trace	trace
7	DCE	80	5	39	trace
8	PhH	80	5	43	15
9	MeCN	80	5	0	trace
10	1,4-dioxane	100	5	trace	trace
11	PhMe	110	5	51	19

[a] NMR yields with CH_2Br_2 as internal standard

Table S2. Screening of rhodium sources

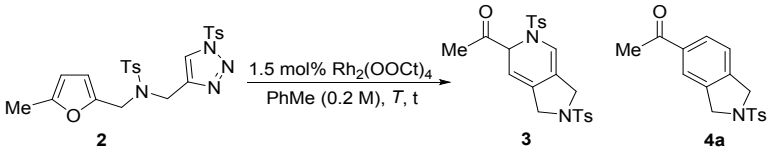


2 **3** **4a**

Entry	Rh cat.	Yield of **3**, %[a]	Yield of **4a**, %[a]
1	$Rh_2(OAc)_4$	51	19
2	$Rh_2(OCOTr)_4$	53	12
3	$Rh_2(OPiv)_4$	59	9
4	$Rh_2(OHex)_4$	58	12
5	$Rh_2(OOct)_4$	65	13

[a] NMR yields with CH_2Br_2 as internal standard

Table S3. Screening of reaction parameters

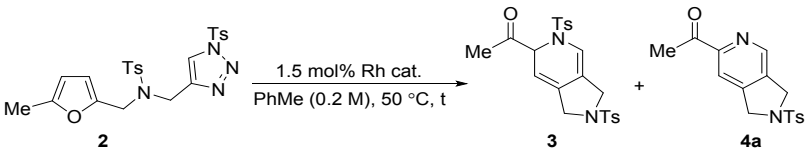


2 **3** **4a**

Entry	*T*, °C	t, h	Yield of **3**, %[a]	Yield of **4a**, %[a]
1	110	5	65	13
2	100	5	64	12
3	90	5	66	9
4	80	5	80	trace
5	70	5	81	trace
6	60	5	80	trace
7	50	5	79	trace
8	40	5	69	trace
9	50	10	90	trace
10	50	15	90	trace

[a] NMR yields with CH_2Br_2 as internal standard

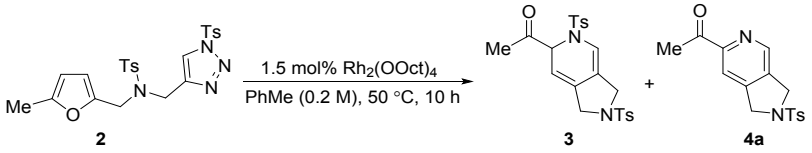
Table S4. Additional screening of rhodium sources



Entry	Rh cat.	t, h	Yield of **3**, %[a]	Yield of **4a**, %[a]
1	$Rh_2(OAc)_4$	5	48	11
2	$Rh_2(OCOTr)_4$	5	51	10
3	$Rh_2(OPiv)_4$	5	53	trace
4	$Rh_2(OHex)_4$	5	59	trace
5	$Rh_2(OOct)_4$	5	79	trace
6	$Rh_2(OAc)_4$	10	52	12
7	$Rh_2(OCOTr)_4$	10	58	11
8	$Rh_2(OPiv)_4$	10	55	trace
9	$Rh_2(OHex)_4$	10	62	trace
10	$Rh_2(OOct)_4$	10	90	trace
11	$Rh_2(OOct)_4$[b]	10	75	trace

[a] NMR yields with CH_2Br_2 as internal standard. [b] 1 mol% of $Rh_2(OOct)_4$.

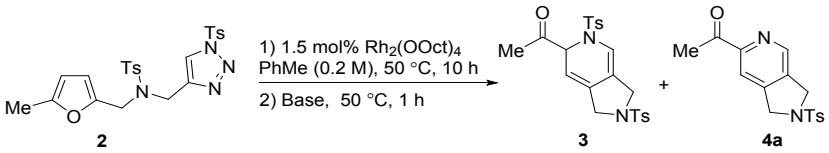
Table S5. Control experiments.



Entry	Yield of **3**, %[a]	Yield of **4a**, %[a]
1	90	trace
2[b]	77	trace
3[c]	69	trace
4[d]	NR[e]	NR

[a] NMR yields with CH_2Br_2 as internal standard.
[b] One equivalent of water was added.
[c] Open flask. [d] no $Rh_2(OOct)_4$ was added.
[d] No Rh cat. was added.
[e] No conversion of triazole **2** was detected.

Table S6. Screening of bases.



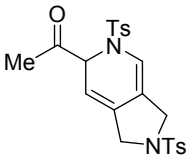
Entry	Base (equiv.)	Yield of **3**, %[a]	Yield of **4a**, %[a]
1	DIPEA, (0.1)	88	9
2	DIPEA, (0.5)	40	31
3	DIPEA, (1)	trace	80
4	DIPEA, (2)	trace	82
5	DIPEA, (3)	trace	81
6	DMAP, (2)	trace	78
7	imidazole, (2)	15	65
8	DBU, (2)	trace	77
9	DABCO, (2)	trace	76
10	K_2CO_3, (2)	18	48
11	Cs_2CO_3, (2)	10	61
12	Et_3N, (2)	trace	83 (82)[b]
13	Et_3N, (3)	trace	83

[a] NMR yields with CH_2Br_2 as an internal standard.
[b] Yield of isolated product in parentheses, 0.5 mmol of **2**.

Example of the procedure for the optimization of reaction conditions for the synthesis of intermediate dihydropyridine 3 (Table S3, entry 9)

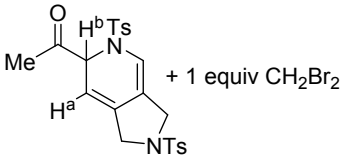
In a glovebox, 1 mL Weaton microreactor was charged with triazole **2** (25 mg, 0.05 mmol), $Rh_2(OOct)_4$ (0.58 mg, 0.75 μmol, 1.5 mol%) and toluene (0.25 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated (50 °C) aluminum block. The reaction mixture was stirred for 10 h at this temperature. After completion, the reaction mixture was filtered through a pad of silica, concentrated *in vacuo*, dissolved in $CDCl_3$ (0.6 mL). CH_2Br_2 (3.5 μL, 0.05 mmol, 1 equiv) was added to the solution, and the resulting mixture was analyzed by ^1H NMR. *NOTE: compound **3** is acid- and base-sensitive. All attempts to purify dihydropyridine **3** by silica gel or aluminum oxide column chromatography resulted in transformation of compound **3** into pyridine **4a** with partial decomposition.*

1-(2,5-ditosyl-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridin-6-yl)ethan-1-one (3)

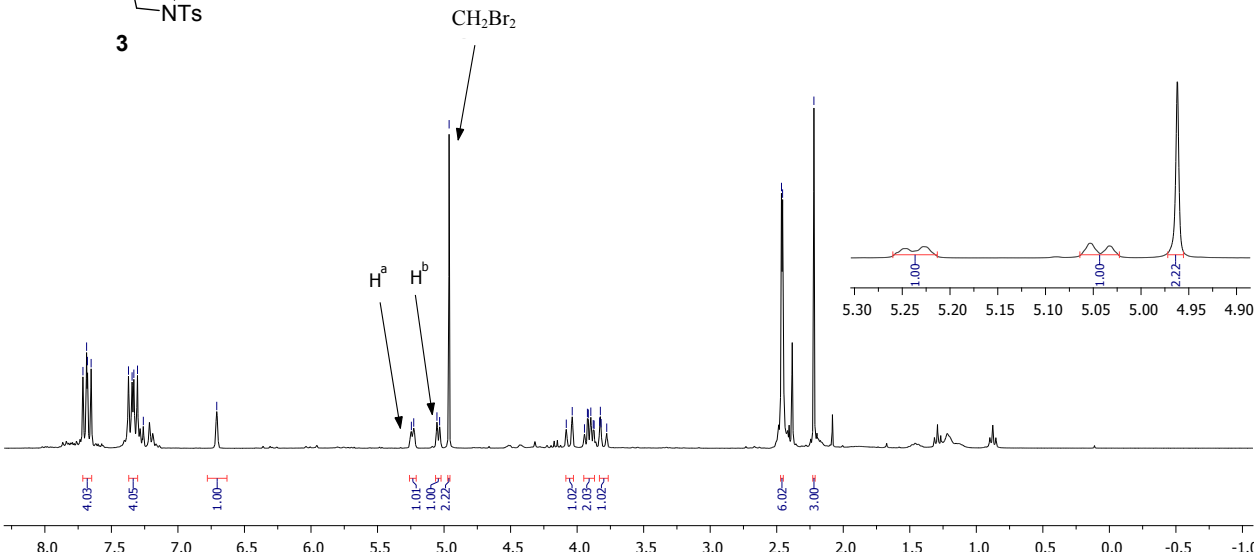


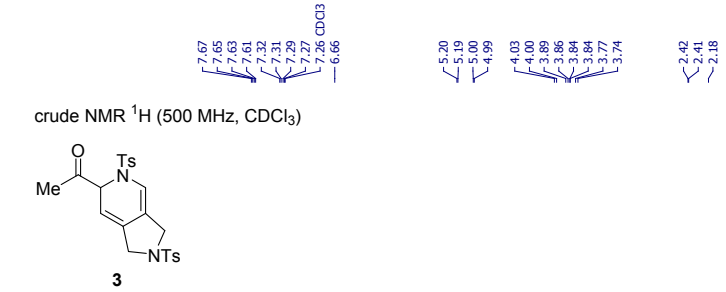
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.65 – 7.67 (m, 2H), 7.61 – 7.63 (m 2H), 7.31 – 7.32 (m, 2H), 7.27 – 7.29 (m, 2H), 6.66 (s, 1H), 5.19 (d, ^{2}J = 6.0 Hz, 1H), 5.00 (d, ^{2}J = 6.0 Hz, 1H), 4.00 – 4.03 (m, 1H), 3.84 – 3.89 (m, 2H), 3.74 – 3.77 (m, 1H), 2.42 (s, 3H), 2.41 (s, 3H), 2.18 (s, 3H) ppm; ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ = 203.9; 144.8; 144.3; 135.4; 134.5; 132.6; 130.1 (2C); 130.0 (2C); 129.1; 127.8; 127.0; 119.0; 117.5; 106.7; 62.8; 50.5; 49.3; 26.0; 21.7; 26.6 ppm; ESI-HRMS: $[M+H]^+$ (*m/z*) calcd. for $C_{23}H_{25}N_2O_5S_2^+$ 473.1199, found 473.1190.

crude NMR ^{1}H (300 MHz, $CDCl_3$)



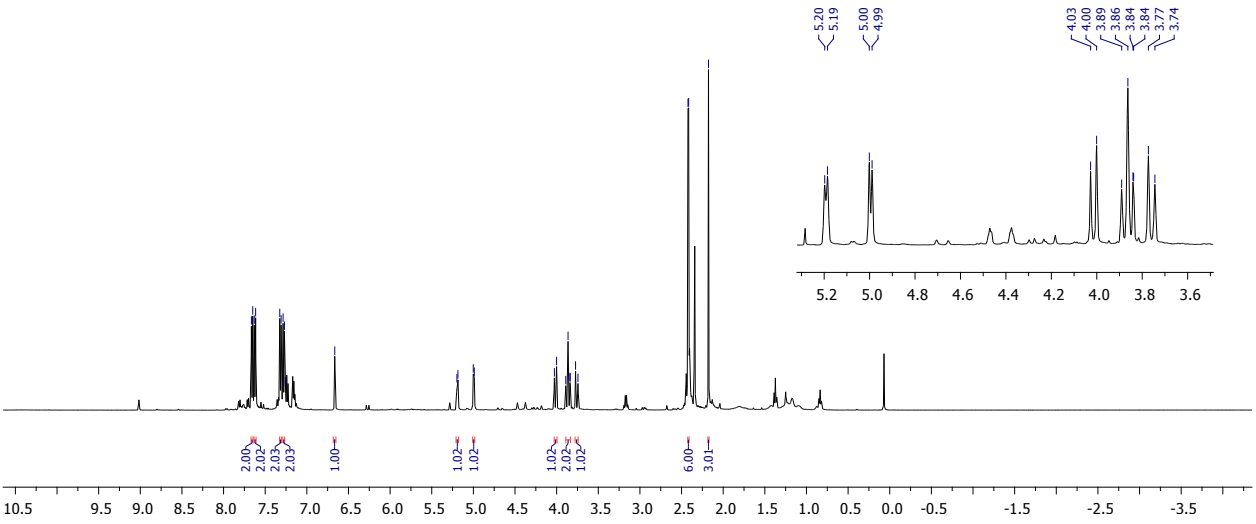
3



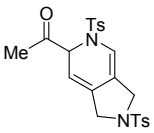


crude NMR ^{1}H (500 MHz, $CDCl_3$)

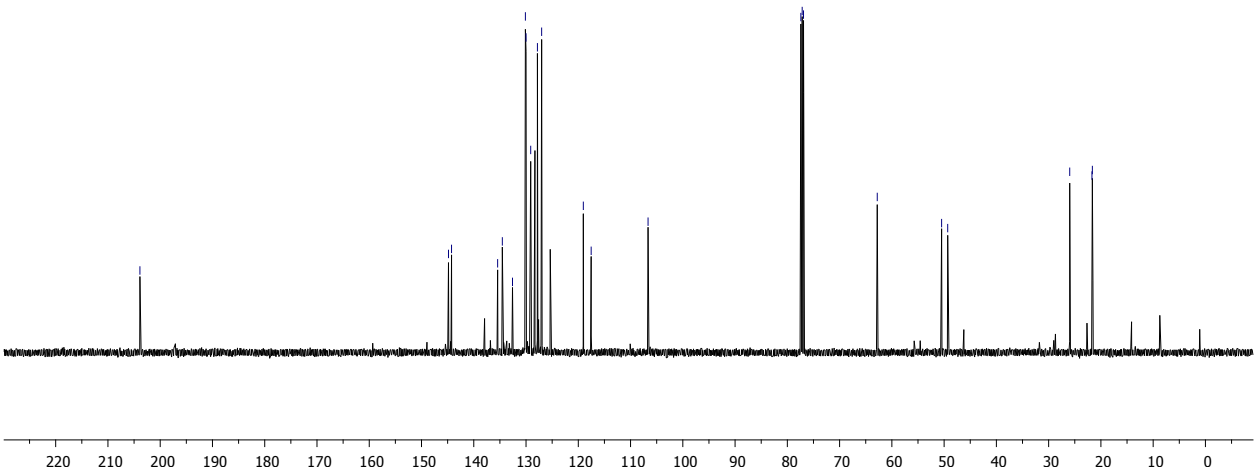
3

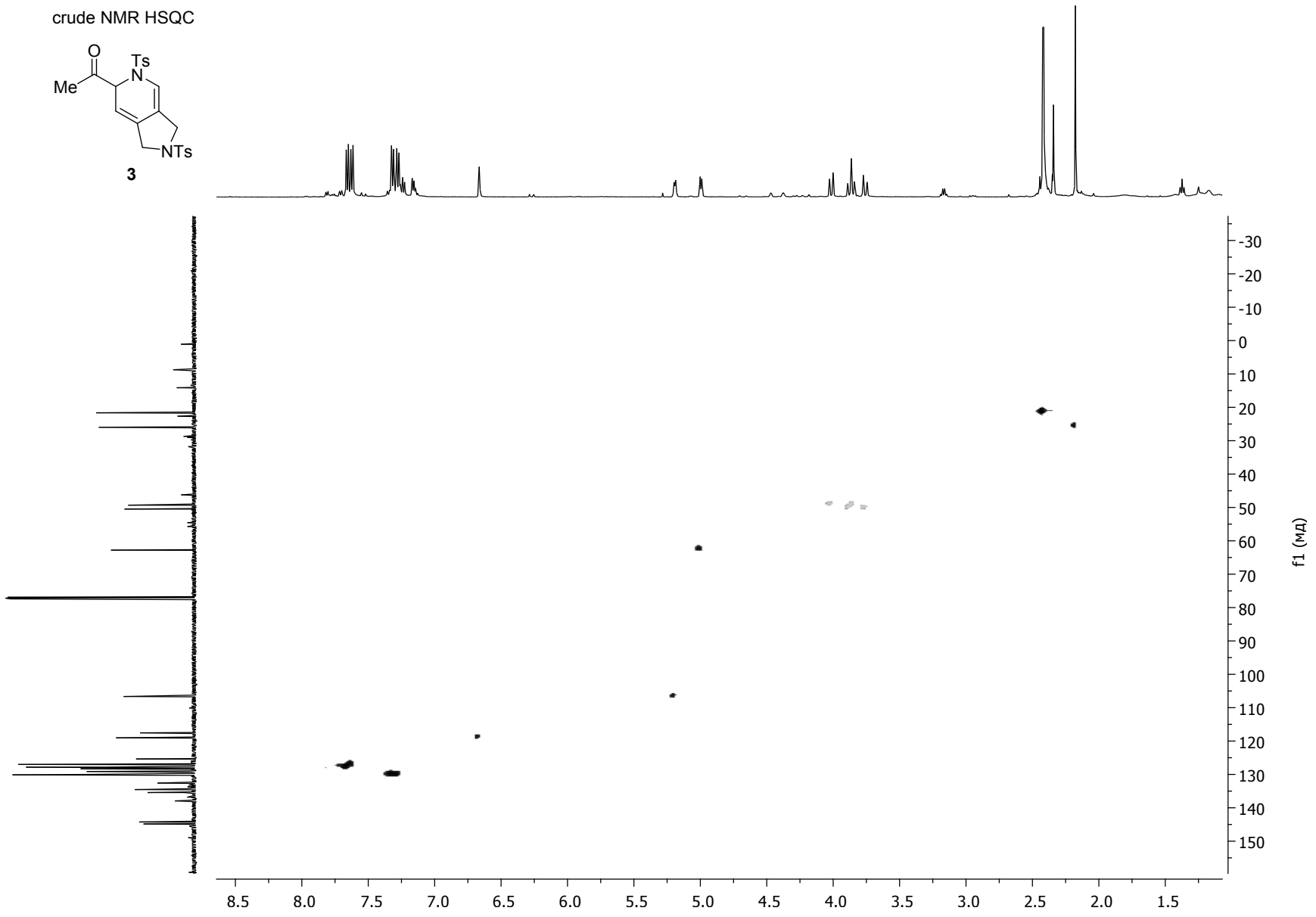


crude NMR ^{13}C (125 MHz, $CDCl_3$)

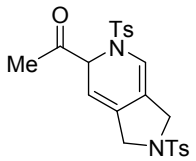


3




crude NMR HSQC
O
Ts
N
Me
NTs
3
-30
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5

crude NMR HMBC

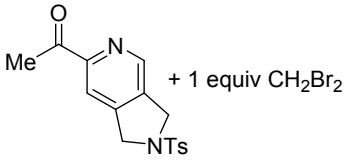


3

Example of the procedure for the optimization of reaction conditions for the synthesis of pyridine 4a (Table S6, entry 12)

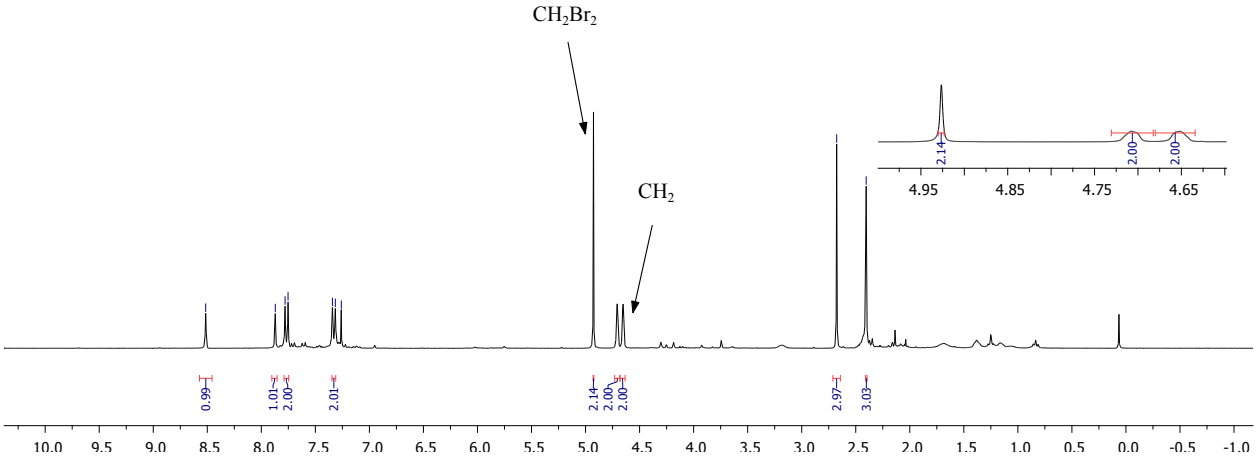
In a glovebox, 1 mL Weaton microreactor was charged with triazole **2** (25 mg, 0.05 mmol), $Rh_2(OOct)_4$ (0.58 mg, 0.75 μmol, 1.5 mol%) and PhMe (0.25 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated (50 °C) aluminum block. The reaction mixture was stirred for 10 h at this temperature. In 10 h, Et_3N (14 μL, 0.1 mmol, 2 equiv) was added, and the reaction mixture was stirred at the same temperature for 1 h. After completion, the reaction mixture was filtered through a pad of silica, concentrated *in vacuo*, dissolved in $CDCl_3$ (0.6 mL). CH_2Br_2 (3.5 μL, 0.05 mmol, 1 equiv) was added to the solution, and the resulting mixture was analyzed by ^1H NMR.

crude ^1H NMR (300 MHz, $CDCl_3$)



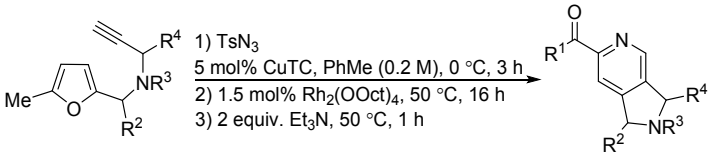
+ 1 equiv CH_2Br_2

4a



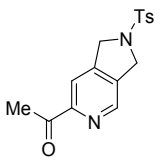
4. Synthesis of the Products

General procedure for the synthesis of pyridines 4a-e, g



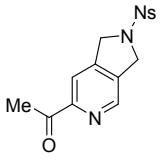
Flame-dried 10 mL Schlenk tube was charged with an acetylene **1** (0.5 mmol) and TsN_3 (98 mg, 0.5 mmol); the air was removed by high vacuum pump, and the flask was backfilled with nitrogen. The flask content was dissolved in toluene (2.5 mL) by addition of the solvent by a syringe and cooled to 0 °C. CuTC (4.7 mg, 5 mol%) was added to the resulting solution at the same temperature upon stirring (counterflow addition). The mixture was stirred at 0 °C for 3 h at which point $Rh_2(OOct)_4$ (5.8 mg, 1.5 mol%) was added (counterflow addition). The flask was then placed into the preheated oil bath (50 °C), and the reaction mixture was stirred at 50 °C for 16 h. After 16 h, Et_3N (140 µL, 1 mmol, 2 equiv) was added by a syringe, and the resulting mixture was additionally stirred for 1 h at the same temperature. Upon completion, the reaction mixture was concentrated *in vacuo*, dry loaded on silica gel and subjected to column chromatography (silica gel, eluent: hexanes/ethyl acetate, gradient elution from 30:1 to 5:1) to afford a target compound.

4-Methyl-*N*-[(5-methylfuran-2-yl)methyl]-*N*-[(1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl]benzenesulfonamide (4a).



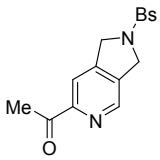
White solid (139 mg, 88% yield), mp 224-225 °C (hex/EtOAc). R_f = 0.43 (2:1 hex:EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.50 (s, 1H), 7.87 (s, 1H), 7.78 – 7.76 (m, 2H), 7.34 – 7.22 (m, 2H), 4.71 (s, 2H), 4.65 (s, 2H), 2.67 (s, 3H), 2.40 (s, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 199.4, 153.3, 147.0, 144.4, 143.5, 136.4, 133.5, 130.2 (2C), 127.7 (2C), 116.1, 53.3, 51.9, 26.1, 21.7 ppm; EI-HRMS: $[M+Na]^+$ (*m/z*) calcd. for $C_{16}H_{16}N_2NaO_3S^+$ 339.0774, found 339.0775.

1-{2-[(4-Nitrophenyl)sulfonyl]-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]pyridin-6-yl}ethanone (4b).



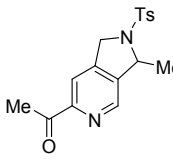
Pale yellow solid (142 mg, 82% yield), mp 230-231 °C (hex/EtOAc). R_f = 0.36 (2:1 hex:EtOAc). ^{1}H NMR (400 MHz, DMSO) δ = 8.60 (s, 1H), 8.40 – 8.37 (m, 2H), 8.15 – 8.13 (m, 2H), 7.87 (s, 1H), 4.78 (s, 2H), 4.75 (s, 2H), 2.58 (s, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, DMSO) δ = 198.9, 152.3, 150.2, 146.9, 143.9, 141.5, 136.4, 129.1 (2C), 124.9 (2C), 115.9, 53.3, 51.9, 25.9 ppm; ESI-HRMS: $[M+H]^+$ (*m/z*) calcd. for $C_{15}H_{14}N_3O_5S^+$ 348.0649, found 348.0649.

1-{2-[(4-Bromophenyl)sulfonyl]-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]pyridin-6-yl}ethanone (4c).



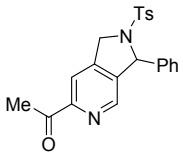
White solid (158 mg, 83% yield), mp 201-202 °C (hex/EtOAc). R_f = 0.46 (2:1 hex:EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.52 (s, 1H), 7.89 (s, 1H), 7.77 – 7.74 (m, 2H), 7.70 – 7.67 (m, 2H), 4.72 (br s, 2H), 4.66 (br s, 2H), 2.68 (s, 3H) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ = 199.4, 153.4, 146.6, 143.6, 136.0, 135.7, 132.9 (2C), 129.0 (2C), 128.6, 116.1, 53.3, 52.0, 26.1 ppm; ESI-HRMS: $[M+Na]^+$ (*m/z*) calcd. for $C_{15}H_{13}BrN_2NaO_3S^+$ 402.9722, found 402.9717.

1-(3-Methyl-2-tosyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]pyridin-6-yl)ethanone (4d).



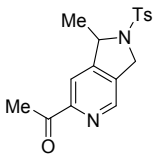
Pale yellow oil (110 mg, 67% yield). R_f = 0.29 (4:1 hex:EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.37 (s, 1H), 7.77 (s, 1H), 7.69 – 7.66 (m, 2H), 7.24 – 7.21 (m, 2H), 4.99 (q, ^3J = 6.6 Hz, 1H), 4.67 (d, ^2J = 15.5 Hz, 1H), 4.54 (d, ^2J = 15.5 Hz, 1H), 2.60 (s, 3H), 2.31 (s, 3H), 1.64 (d, J = 6.6 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ = 199.4, 153.3, 145.8, 144.2, 143.5, 141.5, 134.3, 130.1 (2C), 127.6 (2C), 116.0, 60.5, 53.2, 26.0, 23.8, 21.6 ppm; ESI-HRMS: $[M+H]^+$ (*m/z*) calcd. for $C_{17}H_{19}N_2O_3S^+$ 331.1111, found 331.1109.

1-(3-Phenyl-2-tosyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]pyridin-6-yl)ethanone (4e).



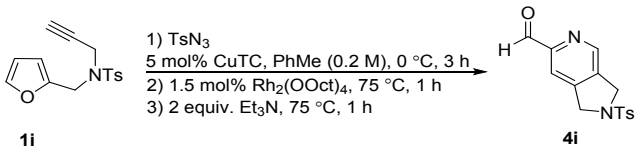
Pale yellow oil (96 mg, 49% yield). R_f = 0.23 (4:1 hex:EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.16 (s, 1H), 7.87 (s, 1H), 7.44 – 7.42 (m, 2H), 7.22 – 7.19 (m, 3H), 7.13 – 7.08 (m, 4H), 6.00 (s, 1H), 4.84 (d, ^2J = 15.1 Hz, 1H), 4.75 (d, ^2J = 15.1 Hz, 1H), 2.58 (s, 3H), 2.28 (s, 3H) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ = 199.5, 153.2, 145.8, 144.8, 143.9, 140.8, 140.3, 135.2, 129.8 (2C), 128.9 (2C), 128.6, 127.6 (2C), 127.4 (2C), 116.0, 67.8, 53.5, 26.1, 21.6 ppm; ESI-HRMS: $[M+H]^+$ (*m/z*) calcd. for $C_{22}H_{21}N_2O_3S^+$ 393.1267, found 393.1268.

1-(1-Methyl-2-tosyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]pyridin-6-yl)ethanone (4g).



Pale yellow oil (112 mg, 68% yield). R_f = 0.38 (2:1 hex:EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.42 (s, 1H), 7.74 (s, 1H), 7.68 – 7.66 (m, 2H), 7.23 – 7.21 (m, 2H), 4.88 (q, ^3J = 6.5 Hz, 1H), 4.73 (d, ^2J = 15.1 Hz, 1H), 4.60 (d, ^2J = 15.1 Hz, 1H), 2.59 (s, 3H), 2.31 (s, 3H), 1.60 (d, ^3J = 6.5 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ = 199.5, 153.4, 152.1, 144.2, 143.5, 135.2, 134.2, 130.1 (2C), 127.5 (2C), 115.7, 61.6, 52.0, 26.0, 23.1, 21.6 ppm; ESI-HRMS: $[M+H]^+$ (*m/z*) calcd. for $C_{17}H_{19}N_2O_3S^+$ 331.1111, found 331.1110.

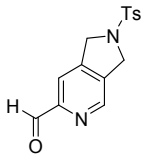
Synthesis of pyridine 4i



1i **4i**

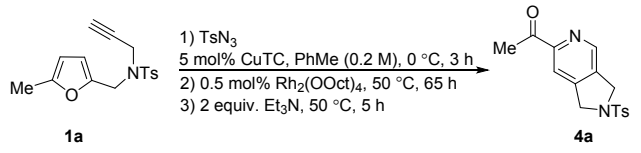
Flame-dried 10 mL Schlenk tube was charged with an acetylene **1i** (114 mg, 0.5 mmol) and TsN_3 (98 mg, 0.5 mmol); the air was removed by high vacuum pump, and the flask was backfilled with nitrogen. The flask content was dissolved in toluene (2.5 mL) by addition of the solvent by a syringe and cooled to 0 °C. CuTC (4.7 mg, 5 mol%) was added to the resulting solution at the same temperature upon stirring (counterflow addition). The mixture was stirred at 0 °C for 3 h at which point $Rh_2(OOct)_4$ (5.8 mg, 1.5 mol%) was added (counterflow addition). The flask was then placed into the preheated oil bath (75 °C), and the reaction mixture was stirred at 75 °C for 1 h. After 1 h, Et_3N (140 μL, 1 mmol, 2 equiv) was added by a syringe, and the resulting mixture was additionally stirred for 1 h at the same temperature. Upon completion, the reaction mixture was concentrated *in vacuo*, dry loaded on silica gel and subjected to column chromatography (silica gel, eluent: hexanes/ethyl acetate, gradient elution from 30:1 to 5:1) to afford pyridine **5i**.

2-Tosyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]pyridine-6-carbaldehyde (4i).



Pale yellow oil (95 mg, 63% yield). R_f = 0.36 (2:1 hex:EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 10.03 (s, 1H), 8.62 (s, 1H), 7.80 – 7.76 (m, 3H), 7.35 – 7.32 (m, 2H), 4.72 (s, 2H), 4.67 (s, 2H), 2.41 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 192.6, 152.6, 147.3, 144.8, 144.5, 137.5, 133.4, 130.2 (2C), 127.7 (2C), 116.0, 53.2, 51.9, 21.7 ppm; ESI-HRMS: $[M+Na]^+$ (*m/z*) calcd. for $C_{15}H_{14}N_2NaO_3S^+$ 325.0617, found 325.0619.

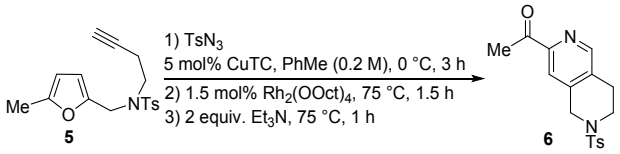
Gram-scale synthesis of pyridine 4a



1a **4a**

Flame-dried 50 mL Schlenk tube was charged with acetylene **1a** (1213 mg, 4 mmol) and TsN_3 (784 mg, 8 mmol); the air was removed by high vacuum pump, and the flask was backfilled with nitrogen. The flask content was dissolved in toluene (20 mL) by addition of the solvent by a syringe and cooled to 0 °C. CuTC (37.6 mg, 5 mol%) was added to the resulting solution at the same temperature upon stirring (counterflow addition). The mixture was stirred at 0 °C for 3 h at which point $Rh_2(OOct)_4$ (15.5 mg, 0.5 mol%) was added (counterflow addition). The flask was then placed into the preheated oil bath (50 °C), and the reaction mixture was stirred at 50 °C for 65 h. After 65 h, Et_3N (1120 μL, 16 mmol, 2 equiv) was added by a syringe, and the resulting mixture was additionally stirred for 5 h at the same temperature. Upon completion, the reaction mixture was concentrated *in vacuo*, dry loaded on silica gel and subjected to column chromatography (silica gel, eluent: hexanes/ethyl acetate, gradient elution from 30:1 to 5:1) to afford pyridine **4a** with 84% yield (1063 mg).

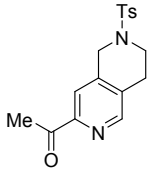
Synthesis of pyridine 6



5 **6**

Flame-dried 10 mL Schlenk tube was charged with an acetylene **5** (159 mg, 0.5 mmol) and TsN_3 (98 mg, 0.5 mmol); the air was removed by high vacuum pump, and the flask was backfilled with nitrogen. The flask content was dissolved in toluene (2.5 mL) by addition of the solvent by a syringe and cooled to 0 °C. CuTC (4.7 mg, 5 mol%) was added to the resulting solution at the same temperature upon stirring (counterflow addition). The mixture was stirred at 0 °C for 3 h at which point $Rh_2(OOct)_4$ (5.8 mg, 1.5 mol%) was added (counterflow addition). The flask was then placed into the preheated oil bath (75 °C), and the reaction mixture was stirred at 75 °C for 1.5 h. After 1.5 h, Et_3N (140 μL, 1 mmol, 2 equiv) was added by a syringe, and the resulting mixture was additionally stirred for 1 h at the same temperature. Upon completion, the reaction mixture was concentrated *in vacuo*, dry loaded on silica gel and subjected to column chromatography (silica gel, eluent: hexanes/ethyl acetate, gradient elution from 30:1 to 5:1) to afford pyridine **6**.

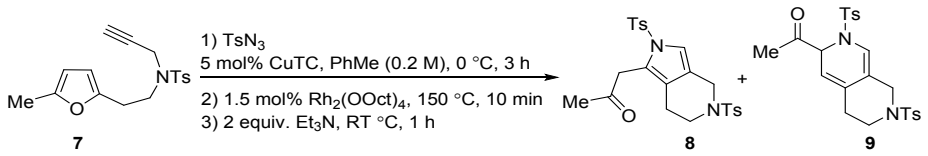
1-(6-Tosyl-5,6,7,8-tetrahydro-2,6-naphthyridin-3-yl)ethanone (6).



Pale yellow oil (129 mg, 78% yield). R_f = 0.25 (2:1 hex:EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.48 (s, 1H), 7.75 – 7.71 (m, 3H), 7.36 – 7.33 (m, 2H), 4.29 (s, 2H), 3.42 (t, ^3J = 5.8 Hz, 2H), 3.01 (t, ^3J = 5.7 Hz, 2H), 2.67 (s, 3H), 2.43 (s, 3H) ppm;

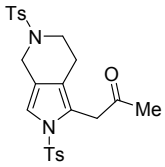
$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 199.8, 151.8, 149.6, 144.3, 141.8, 133.4, 133.1, 130.1 (2C), 127.8 (2C), 119.3, 47.0, 43.1, 26.5, 25.9, 21.7 ppm; ESI-HRMS: $[M+Na]^+$ (*m/z*) calcd. for $C_{17}H_{18}N_2NaO_3S^+$ 353.0930, found 353.0928.

Synthesis of pyrrole 8 and dihydropyridine 9



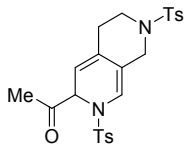
Flame-dried 10 mL Schlenk tube was charged with an acetylene **7** (159 mg, 0.5 mmol) and TsN_3 (98 mg, 0.5 mmol); the air was removed by high vacuum pump, and the flask was backfilled with nitrogen. The flask content was dissolved in toluene (2.5 mL) by addition of the solvent by a syringe and cooled to 0 °C. CuTC (4.7 mg, 5 mol%) was added to the resulting solution at the same temperature upon stirring (counterflow addition). The mixture was stirred at 0 °C for 3 h at which point $Rh_2(OOct)_4$ (5.8 mg, 1.5 mol%) was added (counterflow addition). The flask was then placed into the preheated oil bath (150 °C), and the reaction mixture was stirred at 150 °C for 10 min. After this time, Et_3N (140 μL, 1 mmol, 2 equiv) was added by a syringe, and the resulting mixture was additionally stirred for 1 h at room temperature. Upon completion, the reaction mixture was concentrated *in vacuo*, dry loaded on silica gel and subjected to column chromatography (silica gel, eluent: hexanes/ethyl acetate, gradient elution from 10:1 to 3:1) to afford pyrrole **8** and dihydropyridine **9**.

1-(2,5-Ditosyl-4,5,6,7-tetrahydro-2*H*-pyrrolo[3,4-*c*]pyridin-1-yl)propan-2-one (8).



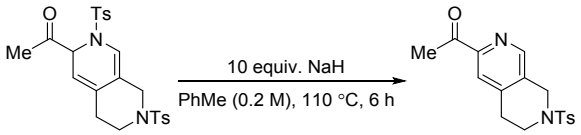
Pale yellow oil (102 mg, 42% yield). R_f = 0.42 (1:1 hex:EtOAc). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.68 – 7.66 (m, 2H), 7.61 – 7.59 (m, 2H), 7.29 – 7.27 (m, 4H), 7.00 (s, 1H), 4.13 (s, 2H), 3.68 (s, 2H), 3.30 (t, ^3J = 6.0 Hz, 2H), 2.46 (t, ^3J = 6.0 Hz, 2H), 2.41 (s, 6H), 2.07 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 203.7, 145.3, 143.8, 136.4, 134.2, 130.2 (2C), 129.9 (2C), 127.7 (2C), 126.9 (2C), 122.9, 121.9, 119.3, 116.6, 44.1, 43.3, 40.1, 29.2, 21.8, 21.7, 21.6 ppm; ESI-HRMS: $[M+H]^+$ (*m/z*) calcd. for $C_{24}H_{27}N_2O_5S_2^+$ 487.1356, found 487.1361.

1-(2,7-Ditosyl-2,3,5,6,7,8-hexahydro-2,7-naphthyridin-3-yl)ethanone (9).



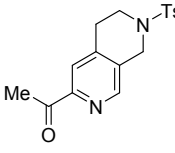
Pale yellow oil (131 mg, 54% yield). R_f = 0.52 (1:1 hex:EtOAc). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.68 – 7.66 (m, 2H), 7.62 – 7.60 (m, 2H), 7.34 – 7.32 (m, 2H), 7.26 – 7.24 (m, 2H), 6.66 (s, 1H), 5.30 (br s, 1H), 4.38 (d, ^3J = 4.3 Hz, 1H), 3.82 (d, ^2J = 14.0 Hz, 1H), 3.71 (d, ^2J = 14.0 Hz, 1H), 3.66 (br s, 2H), 2.71 – 2.68 (m, 1H), 2.44 (s, 3H), 2.40 (s, 3H), 2.17 (s, 3H), 1.80 – 1.75 (m, 1H) ppm; $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ = 206.5, 144.7, 143.9, 135.8, 133.7, 130.3 (2C), 129.8 (2C), 127.8 (2C), 127.1 (2C), 125.0, 119.7, 119.4, 114.8, 61.5, 45.8, 45.3, 28.2, 26.7, 21.7, 21.6 ppm; ESI-HRMS: $[M+H]^+$ (*m/z*) calcd. for $C_{24}H_{27}N_2O_5S_2^+$ 487.1356, found 487.1356.

Synthesis of pyridine 10



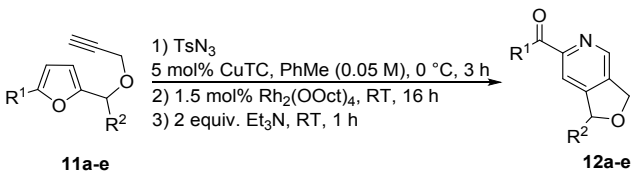
In a 1 mL Wheaton microreactor vial equipped with a Teflon pressure cap, a mixture of dihydropyridine **9** (48.6 mg, 0.1 mmol) and NaH (24 mg, 1 mmol) in toluene (0.5 mL) was stirred at 110 °C for 6 h. Upon completion, the reaction mixture was quenched with water (100 μL), concentrated *in vacuo*, dry loaded on silica gel and subjected to column chromatography (silica gel, eluent: hexanes/ethyl acetate, gradient elution from 10:1 to 3:1) to afford pyridine **10**.

1-(7-Tosyl-5,6,7,8-tetrahydro-2,7-naphthyridin-3-yl)ethanone (10).



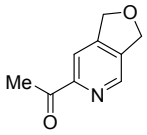
Pale yellow oil (32 mg, 99% yield). R_f = 0.48 (1:1 hex:EtOAc). ^1H NMR (400 MHz, $CDCl_3$) δ = 8.37 (s, 1H), 7.77 (s, 1H), 7.74 – 7.72 (m, 2H), 7.35 – 7.33 (m, 2H), 4.34 (s, 2H), 3.40 (t, ^3J = 5.9 Hz, 2H), 2.98 (t, ^3J = 5.9 Hz, 2H), 2.68 (s, 3H), 2.43 (s, 3H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ = 199.8, 152.1, 147.3, 144.3, 143.6, 133.5, 132.2, 130.1 (2C), 127.9 (2C), 121.7, 45.7, 43.0, 28.6, 25.9, 21.7 ppm; ESI-HRMS: $[M+H]^+$ (*m/z*) calcd. for $C_{17}H_{19}N_2O_3S^+$ 331.1111, found 331.1113.

General procedure for the synthesis of pyridines 12a-e



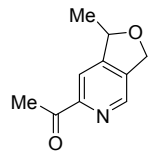
Flame-dried 25 mL Schlenk tube was charged with an acetylene **11** (0.5 mmol) and TsN_3 (98 mg, 0.5 mmol); the air was removed by high vacuum pump, and the flask was backfilled with nitrogen. The flask content was dissolved in toluene (10 mL) by addition of the solvent by a syringe and cooled to 0 °C. CuTC (4.7 mg, 5 mol%) was added to the resulting solution at the same temperature upon stirring (counterflow addition). The mixture was stirred at 0 °C for 3 h at which point $Rh_2(OOct)_4$ (5.8 mg, 1.5 mol%) was added (counterflow addition). The flask was warmed to room temperature and stirred for 16 h. After 16 h, Et_3N (140 μL, 1 mmol, 2 equiv) was added by a syringe, and the resulting mixture was additionally stirred for 1 h at the same temperature. Upon completion, the reaction mixture was concentrated *in vacuo*, dry loaded on silica gel and subjected to column chromatography (silica gel, eluent: hexanes/ethyl acetate, gradient elution from 40:1 to 15:1) to afford a target compound.

1-(1,3-Dihydrofuro[3,4-*c*]pyridin-6-yl)ethanone (12a).



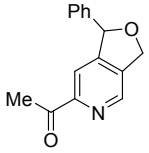
Pale yellow oil (74 mg, 91% yield). R_f = 0.32 (4:1 hex:EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.56 (s, 1H), 7.94 (s, 1H), 5.18 (br s, 2H), 5.12 (br s, 2H), 2.71 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ = 199.7, 153.1, 150.1, 142.0, 139.2, 114.7, 72.9, 71.8, 26.2 ppm; ESI-HRMS: $[M]^{+\bullet}$ (*m/z*) calcd. for $C_9H_9NO_2^{+\bullet}$ 163.0628, found 163.0632.

1-(1-Methyl-1,3-dihydrofuro[3,4-*c*]pyridin-6-yl)ethanone (12b).



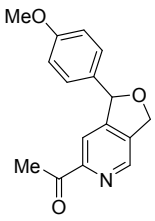
Pale yellow oil (76 mg, 86% yield). R_f = 0.37 (4:1 hex:EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.56 (s, 1H), 7.89 (s, 1H), 5.36 – 5.30 (m, 1H), 5.25 – 5.09 (m, 2H), 2.73 (s, 3H), 1.53 (d, ^3J = 6.5 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ = 199.8, 154.0, 153.3, 142.0, 139.3, 114.6, 79.7, 70.6, 26.2, 21.0 ppm; ESI-HRMS: $[M]^{+\bullet}$ (*m/z*) calcd. for $C_{10}H_{11}NO_2^{+\bullet}$ 177.0784, found 177.0777.

1-(1-Phenyl-1,3-dihydrofuro[3,4-*c*]pyridin-6-yl)ethanone (12c).



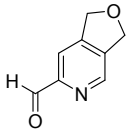
Pale yellow oil (90 mg, 75% yield). R_f = 0.36 (4:1 hex:EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.64 (s, 1H), 7.77 (s, 1H), 7.39 – 7.30 (m, 5H), 6.18 (br s, 1H), 5.45 (dd, ^2J = 13.5 Hz, ^4J = 2.5 Hz, 1H), 5.31 (dd, ^2J=13.5 Hz, ^4J = 1.4 Hz, 1H), 2.70 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 199.6, 153.5, 152.8, 142.2, 140.1, 138.9, 129.0 (2C), 128.9, 126.8 (2C), 115.8, 85.7, 71.7, 26.2 ppm; ESI-HRMS: $[M+Na]^+$ (*m/z*) calcd. for $C_{15}H_{13}NNaO_2^+$ 262.0838, found 262.0840.

1-{1-(4-Methoxyphenyl)-1,3-dihydrofuro[3,4-*c*]pyridin-6-yl}ethanone (12d).



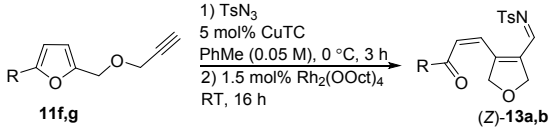
Pale yellow oil (98 mg, 73% yield). R_f = 0.25 (4:1 hex:EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.64 (s, 1H), 7.74 (s, 1H), 7.22 – 7.19 (m, 2H), 6.90 – 6.87 (m, 2H), 6.13 (br s, 1H), 5.41 (dd, ^2J = 13.4 Hz, ^4J = 2.5 Hz, 1H), 5.27 (dd, ^2J = 13.5 Hz, ^4J = 1.6 Hz, 1H), 3.80 (s, 3H), 2.71 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 199.7, 160.1, 153.5, 153.0, 142.2, 139.1, 132.2, 128.4 (2C), 115.9, 114.4 (2C), 85.5, 71.4, 55.5, 26.2 ppm; ESI-HRMS: $[M+Na]^+$ (*m/z*) calcd. for $C_{16}H_{15}NNaO_3^+$ 292.0944, found 292.0943.

1,3-Dihydrofuro[3,4-*c*]pyridine-6-carbaldehyde (12e).



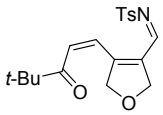
Colorless oil (44 mg, 59% yield). R_f = 0.30 (2:1 hex:EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 10.11 (s, 1H), 8.69 (s, 1H), 7.88 (s, 1H), 5.22 (br s, 2H), 5.16 (br s, 2H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 192.9, 152.5, 150.4, 143.3, 140.3, 114.7, 72.9, 71.7 ppm; ESI-HRMS: $[M+Na]^+$ (*m/z*) calcd. for $C_8H_7NNaO_2^+$ 172.0369, found 172.0367.

Synthesisi of (*Z*)-azatrienes 13



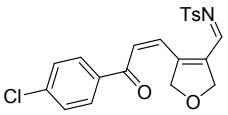
Flame-dried 25 mL Schlenk tube was charged with an acetylene **11f** or **11g** (0.5 mmol) and TsN_3 (98 mg, 0.5 mmol); the air was removed by high vacuum pump, and the flask was backfilled with nitrogen. The flask content was dissolved in toluene (10 mL) by addition of the solvent by a syringe and cooled to 0 °C. CuTC (4.7 mg, 5 mol%) was added to the resulting solution at the same temperature upon stirring (counterflow addition). The mixture was stirred at 0 °C for 3 h at which point $Rh_2(OOct)_4$ (5.8 mg, 1.5 mol%) was added (counterflow addition). The flask was warmed to room temperature and stirred for 16 h. Upon completion, the reaction mixture was concentrated *in vacuo*, dry loaded on silica gel and subjected to column chromatography (silica gel, eluent: hexanes/ethyl acetate, gradient elution from 20:1 to 5:1) to afford a target compound. *NOTE: the column chromatography should be performed as quickly as possible in order to prevent partial isomerization of a target compound.*

***N*-({4-[(*Z*)-4,4-Dimethyl-3-oxopent-1-en-1-yl]-2,5-dihydrofuran-3-yl}methylene)-4-methylbenzenesulfonamide [(*Z*)-13a].**



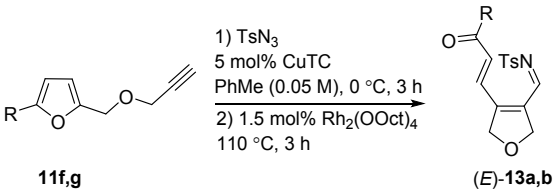
Pale yellow oil (170 mg, 94% yield). R_f = 0.58 (2:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.00 (s, 1H), 7.83 – 7.79 (m, 2H), 7.35 – 7.31 (m, 2H), 6.80 (d, ^3J = 12.6 Hz, 1H), 6.71 (d, ^3J = 12.6 Hz, 1H), 4.84 (s, 4H), 2.44 (s, 3H), 1.18 (s, 9H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 207.0, 160.1, 153.5, 145.0, 136.9, 135.1, 131.4, 130.0 (2C), 128.3 (2C), 126.2, 77.6, 74.3, 44.2, 26.5 (3C), 21.8 ppm; ESI-HRMS: $[M+H]^+$ (*m/z*) calcd. for $C_{19}H_{24}NO_4S^+$ 362.1421, found 362.1424.

***N*-({4-[(*Z*)-3-(4-Chlorophenyl)-3-oxoprop-1-en-1-yl]-2,5-dihydrofuran-3-yl}methylene)-4-methylbenzenesulfonamide [(*Z*)-13b].**



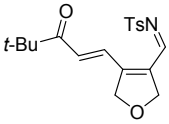
Pale yellow oil (200 mg, 96% yield). R_f = 0.35 (2:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.07 (s, 1H), 7.89 – 7.85 (m, 2H), 7.82 – 7.78 (m, 2H), 7.50 – 7.46 (m, 2H), 7.35 – 7.31 (m, 2H), 7.05 (d, ^3J = 12.6 Hz, 1H), 6.96 (d, ^3J = 12.6 Hz, 1H), 4.85 – 4.79 (m, 4H), 2.44 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 191.1, 159.8, 152.6, 145.1, 140.9, 137.5, 135.0, 134.9, 132.6, 130.4 (2C), 130.0 (2C), 129.5 (2C), 128.3 (2C), 126.5, 77.5, 74.3, 21.8 ppm; ESI-HRMS: $[M+H]^+$ (*m/z*)calcd. for $C_{21}H_{19}ClNO_4S^+$ 416.0718, found 416.0719.

Synthesisi of (*E*)-azatrienes 13



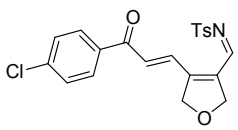
Flame-dried 25 mL Schlenk tube was charged with an acetylene **11f** or **11g** (0.5 mmol) and TsN_3 (98 mg, 0.5 mmol); the air was removed by high vacuum pump, and the flask was backfilled with nitrogen. The flask content was dissolved in toluene (10 mL) by addition of the solvent via a syringe and cooled to 0 °C. CuTC (4.7 mg, 5 mol%) was added to the resulting solution at the same temperature upon stirring (counterflow addition). The mixture was stirred at 0 °C for 3 h at which point $Rh_2(OOct)_4$ (5.8 mg, 1.5 mol%) was added (counterflow addition). The flask was then placed into the preheated oil bath (110 °C), and the reaction mixture was stirred at 110 °C for 3 h. Upon completion, the reaction mixture was concentrated *in vacuo*, dry loaded on silica gel and subjected to column chromatography (silica gel, eluent: hexanes/ethyl acetate, gradient elution from 20:1 to 5:1) to afford a target compound.

***N*-({4-[(*E*)-4,4-Dimethyl-3-oxopent-1-en-1-yl]-2,5-dihydrofuran-3-yl}methylene)-4-methylbenzenesulfonamide [(*E*)-13a].**



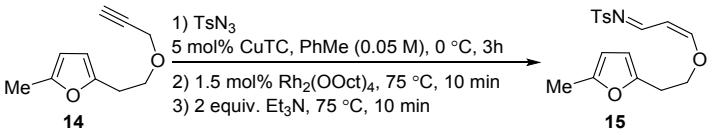
Pale yellow oil (179 mg, 99% yield). R_f = 0.44 (3:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.12 (s, 1H), 7.85 – 7.81 (m, 2H), 7.74 (d, ^3J = 15.5 Hz, 1H), 7.36 – 7.32 (m, 2H), 6.60 (d, ^3J = 15.5 Hz, 1H), 5.03 – 4.99 (m, 2H), 4.96 – 4.92 (m, 2H), 2.44 (s, 3H), 1.20 (s, 9H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 203.3, 159.6, 151.6, 145.1, 138.4, 134.9, 130.1 (2C), 128.6, 128.4 (2C), 128.3, 76.3, 75.7, 43.6, 26.2 (3C), 21.8 ppm; ESI-HRMS: $[M+H]^+$ (*m/z*) calcd. for $C_{19}H_{24}NO_4S^+$ 362.1421, found 362.1423.

***N*-({4-[(*E*)-3-(4-Chlorophenyl)-3-oxoprop-1-en-1-yl]-2,5-dihydrofuran-3-yl}methylene)-4-methylbenzenesulfonamide [(*E*)-13b].**



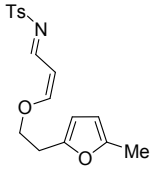
Pale yellow oil (206 mg, 99% yield). R_f = 0.58 (1:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.15 (s, 1H), 7.93 – 7.82 (m, 5H), 7.53 – 7.47 (m, 2H), 7.38 – 7.32 (m, 2H), 6.97 (d, ^3J = 15.5 Hz, 1H), 5.13 – 5.08 (m, 2H), 5.01 – 4.96 (m, 2H), 2.45 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 187.9, 159.4, 151.2, 145.2, 140.5, 139.3, 135.6, 134.8, 130.3, 130.1 (2C), 130.0 (2C), 129.4 (2C), 128.8, 128.5 (2C), 76.3, 75.8, 21.8 ppm; ESI-HRMS: $[M+H]^+$ (*m/z*) calcd. for $C_{21}H_{19}ClNO_4S^+$ 416.0718, found 416.0722.

Synthesis of enol ether 15



Flame-dried 25 mL Schlenk tube was charged with an acetylene **14** (82 mg, 0.5 mmol) and TsN_3 (98 mg, 0.5 mmol); the air was removed by high vacuum pump, and the flask was backfilled with nitrogen. The flask content was dissolved in toluene (10 mL) by addition of the solvent by a syringe and cooled to 0 °C. CuTC (4.7 mg, 5 mol%) was added to the resulting solution at the same temperature upon stirring (counterflow addition). The mixture was stirred at 0 °C for 3 h at which point $Rh_2(OOct)_4$ (5.8 mg, 1.5 mol%) was added (counterflow addition). The flask was then placed into the preheated oil bath (75 °C), and the reaction mixture was stirred at 75 °C for 10 min. After that time, Et_3N (140 µL, 1 mmol, 2 equiv) was added by a syringe, and the resulting mixture was additionally stirred for 10 min at the same temperature. Upon completion, the reaction mixture was quickly passed through a Pasteur pipette with a thin layer of silica gel and concentrated *in vacuo* to afford a compound **15** with high NMR purity. *NOTE: compound **15** is extremely acid-sensitive, we have not been able to use a conventional silica gel chromatography as well as column chromatography with neutral or basic aluminum oxide: in all attempts we observed complete decomposition. However, furan **15** in a crude form has acceptable purity; it could be handled as dry oil or as a solution in toluene of chloroform at room temperature for ca. 1 h without detectable decomposition.*

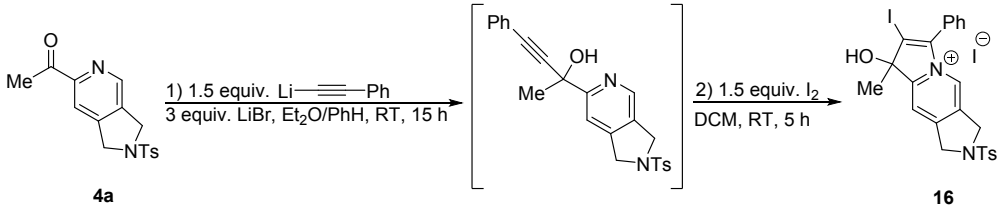
***Z*)-4-Methyl-*N*-{(Z)-3-[2-(5-methylfuran-2-yl)ethoxy]allylidene}benzenesulfonamide (15).**



Pale yellow oil (157 mg, 94% yield). R_f = 0.62 (2:1 hex:EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.53 (d, ^3J = 10.0 Hz, 1H), 7.80 – 7.76 (m, 2H), 7.34 (d, ^3J = 12.4 Hz, 1H), 7.31 – 7.27 (m, 2H), 5.96 (d, ^3J = 2.9 Hz, 1H), 5.85 (d, ^3J = 2.9 Hz, 1H), 5.82 (dd, ^3J = 12.4 Hz, ^3J = 10.0 Hz, 1H), 4.20 (t, ^3J = 6.6 Hz, 2H), 3.00 (t, ^3J = 6.6 Hz, 2H), 2.40 (s, 3H), 2.23 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ = 170.2, 170.0, 151.5, 148.5, 144.0, 136.3, 129.7 (2C), 127.6 (2C), 108.0, 106.3, 105.7, 70.7, 28.1, 21.6, 13.5 ppm; ESI-HRMS: $[M+Na]^+$ (*m/z*) calcd. for $C_{17}H_{19}NNaO_4S^+$ 356.0927, found 356.0931.

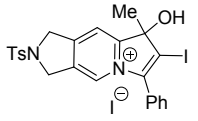
5. Further Transformations of Pyridine 4a

Synthesis of indolizinium salt 16



Solution of *n*-butyllithium in hexanes (2.5 M, 900 µL, 2.25 mmol, 1.5 equiv) was added dropwise to phenylacetylene (250 µL, 2.25 mmol, 1.5 equiv) in Et_2O (10 mL) at 0 °C, and the resulting mixture was stirred for 30 min at this temperature. The lithium acetylide solution was added dropwise to a vigorously stirred mixture of pyridine **4a** (474 mg, 1.5 mmol, 1 equiv) and lithium bromide (390 mg, 4.5 mmol, 3 equiv) in a 1:1 mixture of Et_2O and benzene (total volume = 40 mL). The reaction mixture was stirred at ambient temperature for 15 h at which point sat. NH_4Cl (10 mL) was added to quench the reaction. The aqueous layer was extracted with EtOAc (3 x 30 mL). The organic layers were combined, washed with water (2 x 20 mL) and brine (40 mL), dried over Na_2SO_4, concentrated and dried *in vacuo*. The crude propargyl alcohol was dissolved in DCM (20 mL) followed by the addition of I_2 (571 mg, 2.25 mmol, 1.5 equiv). The resulting suspension was vigorously stirred at room temperature for 5 h. Indolizinium salt **16**, which was formed in the course of the reaction as a brown solid, was filtered through paper, washed with DCM (20 mL) and dried under reduced pressure.

8-Hydroxy-7-iodo-8-methyl-6-phenyl-2-tosyl-1,2,3,8-tetrahydropyrrolo[3,4-*f*]indolizin-5-ium iodide (16).

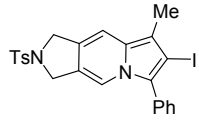


Pale yellow solid (938 mg, 93% yield), mp 229 °C (decomp.) (DCM). R_f = 0.11 (3:2 hex:acetone). ^{1}H NMR (500 MHz, DMSO) δ = 8.57 (s, 1H), 8.35 (s, 1H), 7.78 – 7.74 (m, 2H), 7.72 – 7.66 (m, 3H), 7.62 – 7.55 (m, 2H), 7.46 – 7.44 (m, 2H), 6.75 (br s, 1H), 4.95 (d, ^2J = 18.0 Hz, 1H), 4.85 (d, ^2J = 18.0 Hz, 1H), 4.72 (d, ^2J = 15.5 Hz, 1H), 4.66 (d, ^2J = 15.5 Hz, 1H), 2.38 (s, 3H), 1.58 (s, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, DMSO) δ = 158.9, 155.0, 144.2, 141.9, 136.7, 132.3, 131.4, 131.3, 130.5, 130.2 (2C), 129.5 (2C), 127.5 (2C), 125.4, 117.8, 112.3, 81.3, 53.8, 51.7, 30.7, 24.3, 21.1 ppm; ESI-HRMS: $[M\text{-}I]^+$ (*m/z*) calcd. for $C_{24}H_{22}IN_2O_3S^+$ 545.0390, found 545.0384.

Synthesis of indolizine 17

Indolizinium salt **16** (545 mg, 1 mmol) was suspended in MeOH (20 mL). $NaBH_4$ (76 mg, 2 mmol, 2 equiv) was added portionwise upon stirring at room temperature. The reaction mixture was stirred for 30 min at the same temperature at which point sat. NH_4Cl (5 mL) was added to quench the reaction. The aqueous layer was extracted with EtOAc (2 x 30 mL). The organic layers were combined, washed with water (2 x 20 mL) and brine (40 mL), dried over Na_2SO_4, and concentrated to dryness. Indolizine **17** was further recrystallized from MeOH/ethyl acetate.

7-Iodo-8-methyl-6-phenyl-2-tosyl-2,3-dihydro-1*H*-pyrrolo[3,4-*f*]indolizine (17).



Pale yellow solid (523 mg, 99% yield), mp 196-197 °C (MeOH/EtOAc). R_f = 0.33 (8:1 hex:EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.77 – 7.72 (m, 2H), 7.71 (s, 1H), 7.54 – 7.47 (m, 2H), 7.46 – 7.38 (m, 3H), 7.34 – 7.28 (m, 2H), 7.10 (s, 1H), 4.50 (s, 2H), 4.41 (s, 2H), 2.40 (s, 3H), 2.30 (s, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 144.1, 133.3, 131.4, 130.6 (2C), 130.0 (2C), 129.7, 129.1 (2C), 128.6, 127.8 (2C), 126.9, 125.1, 121.3, 115.7, 112.2, 110.0, 79.4, 52.2, 50.6, 21.7, 12.8 ppm; ESI-HRMS: $[M]^{+\bullet}$ (*m/z*) calcd. for $C_{24}H_{21}IN_2O_2S^{+\bullet}$ 528.0363, found 528.0363.

6. References

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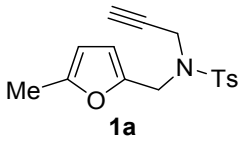
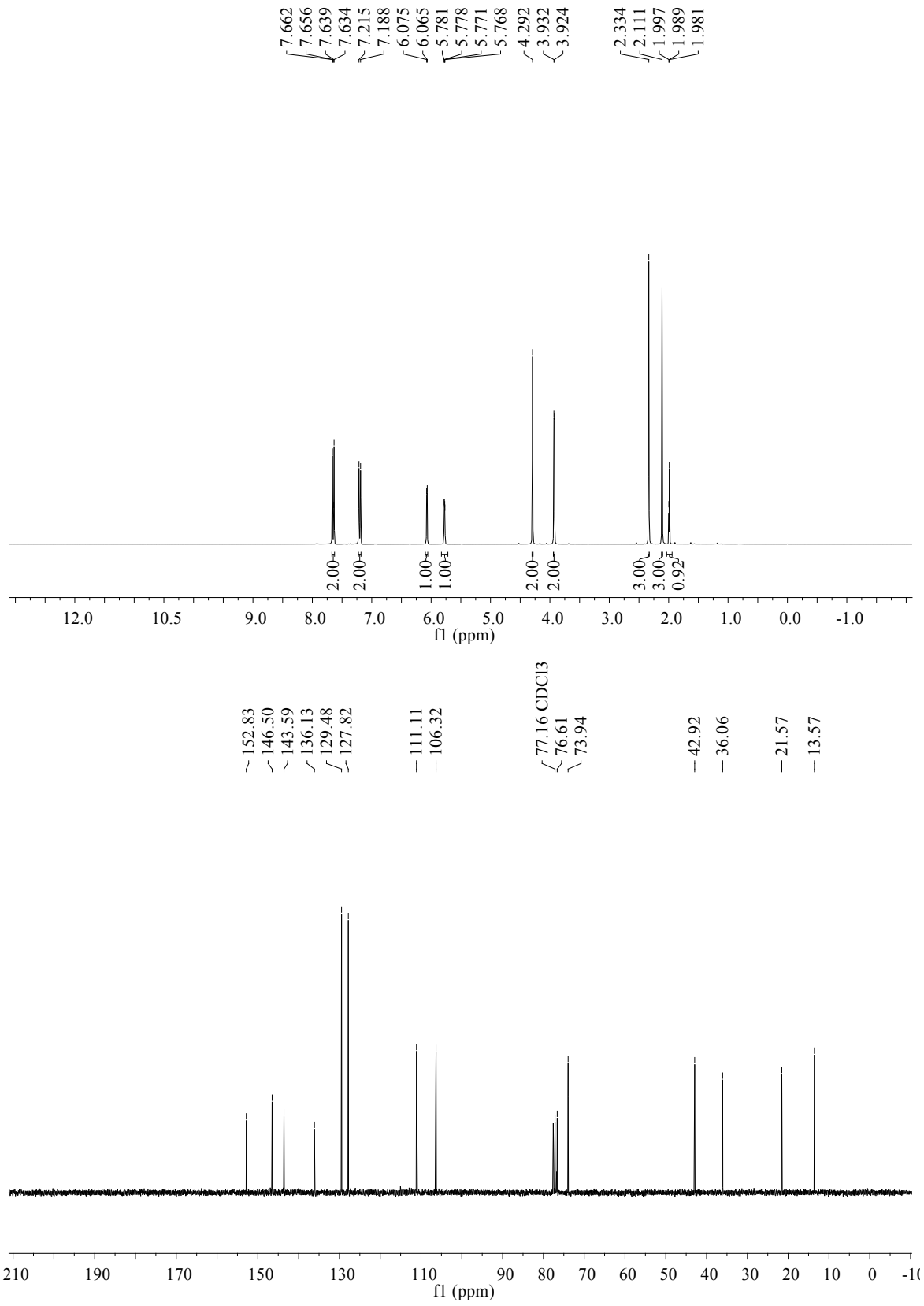
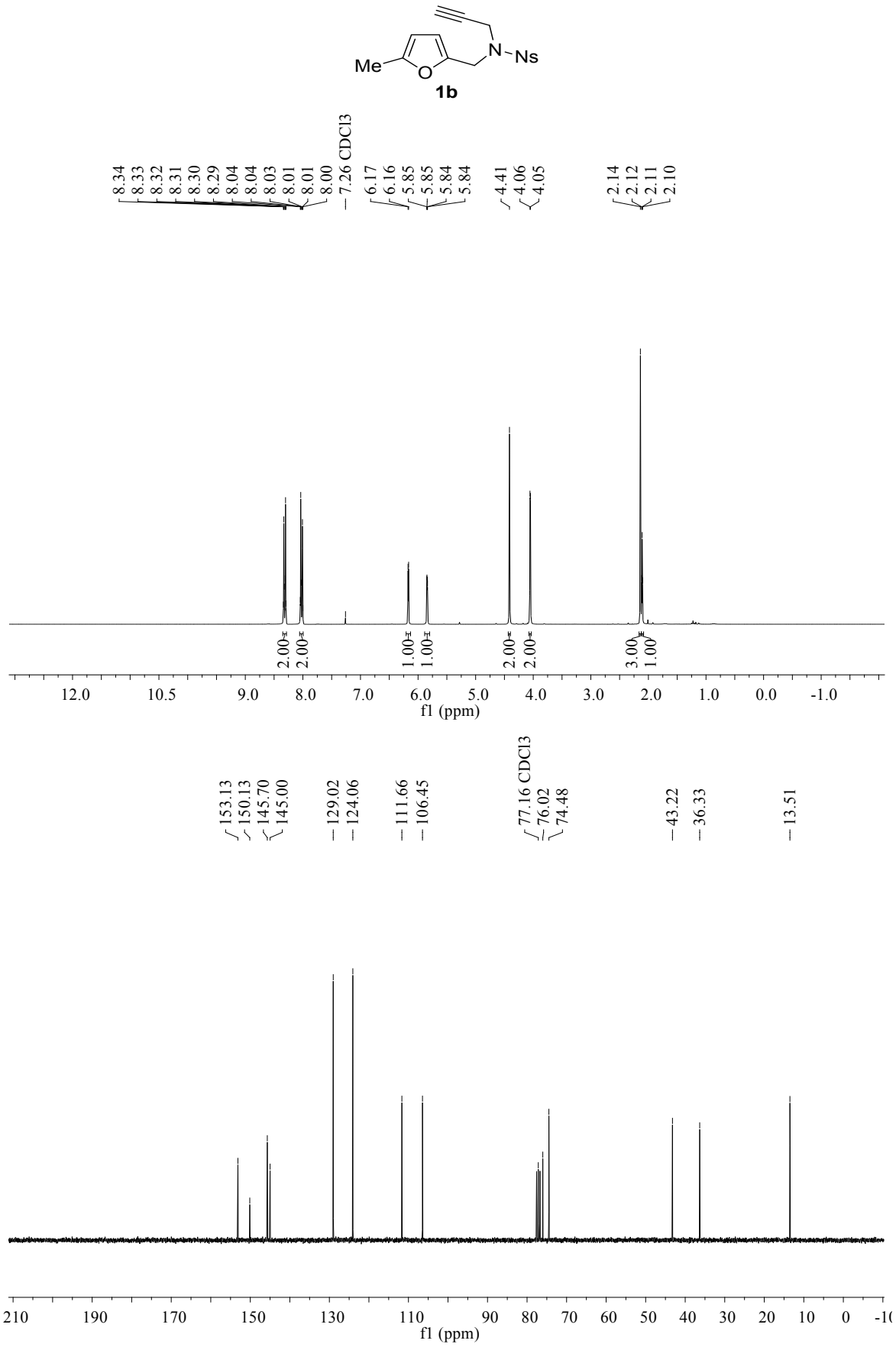
7. NMR Spectra



1a

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N
Ns
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8.32
8.31
8.30
8.29
8.04
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8.01
8.00
7.26 CDCl3
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6.16
5.85
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4.41
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12.0
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7.0
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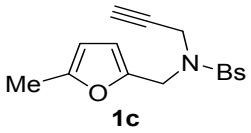
f1 (ppm)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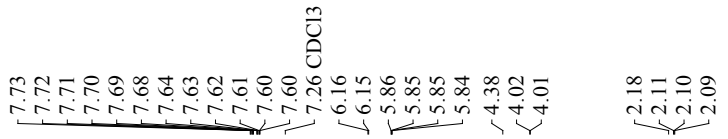
N
Bs

1c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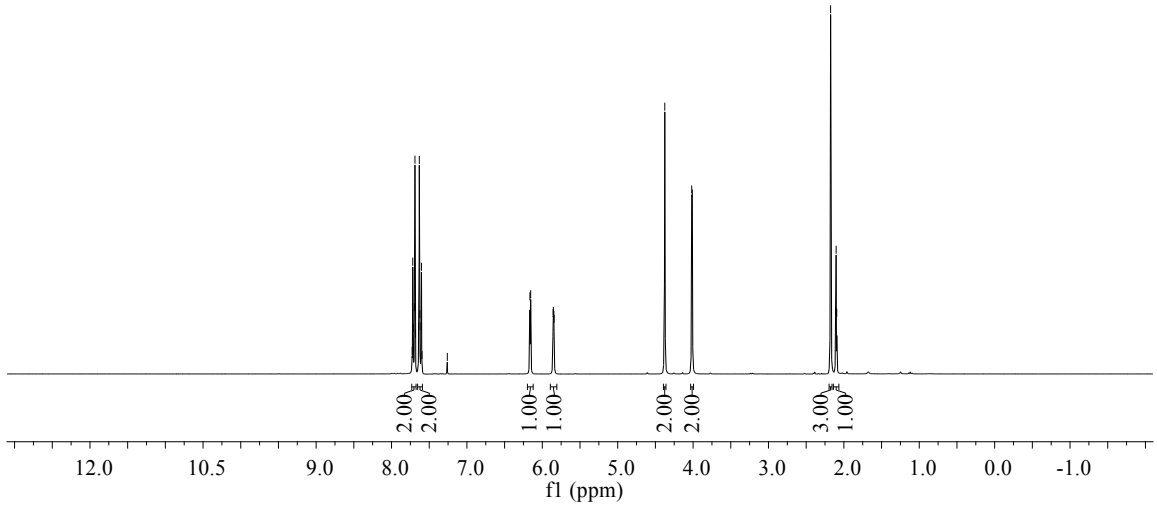
2.09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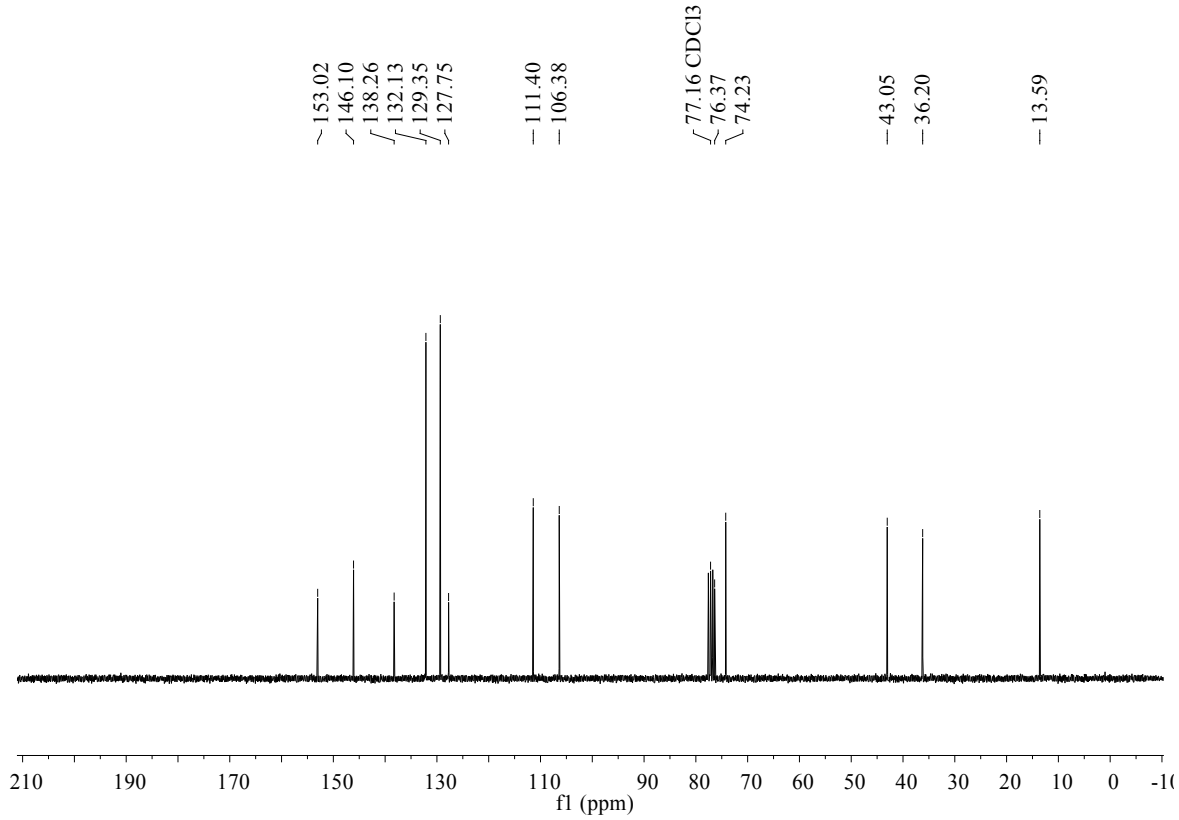
f1 (ppm)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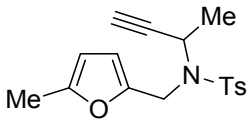
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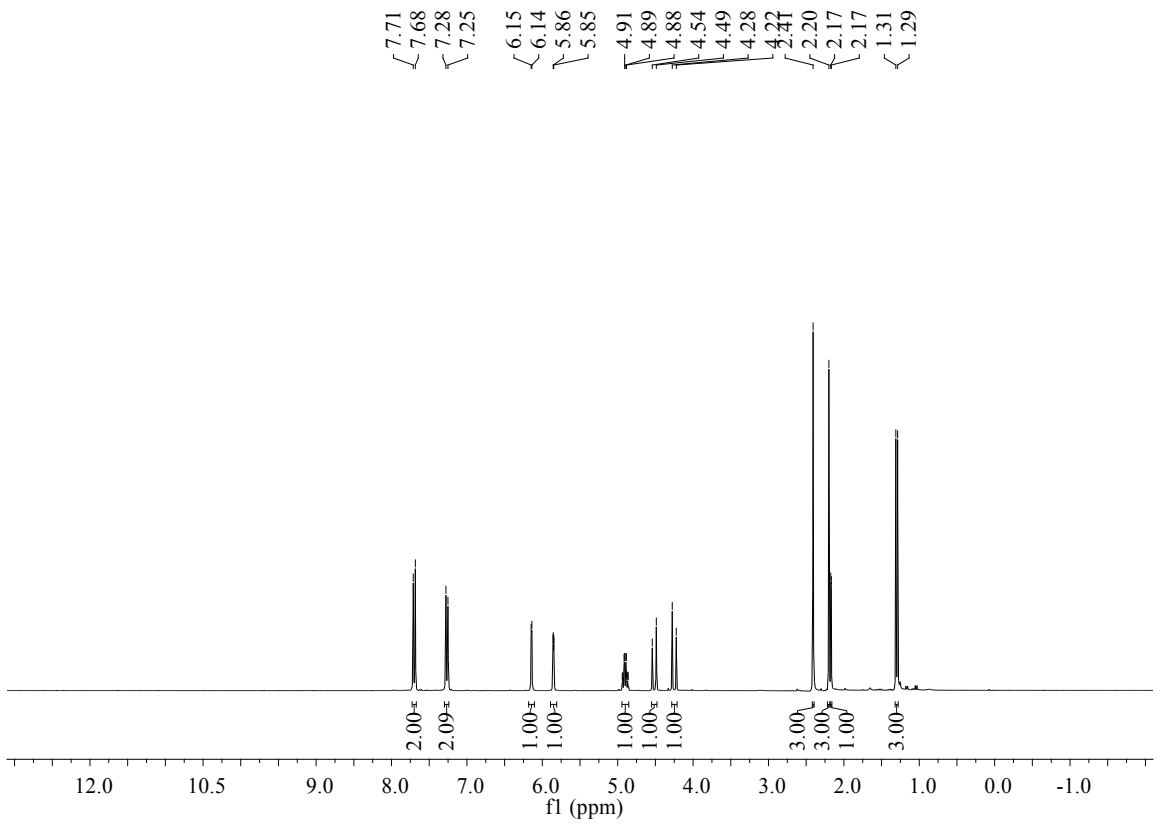
O

1d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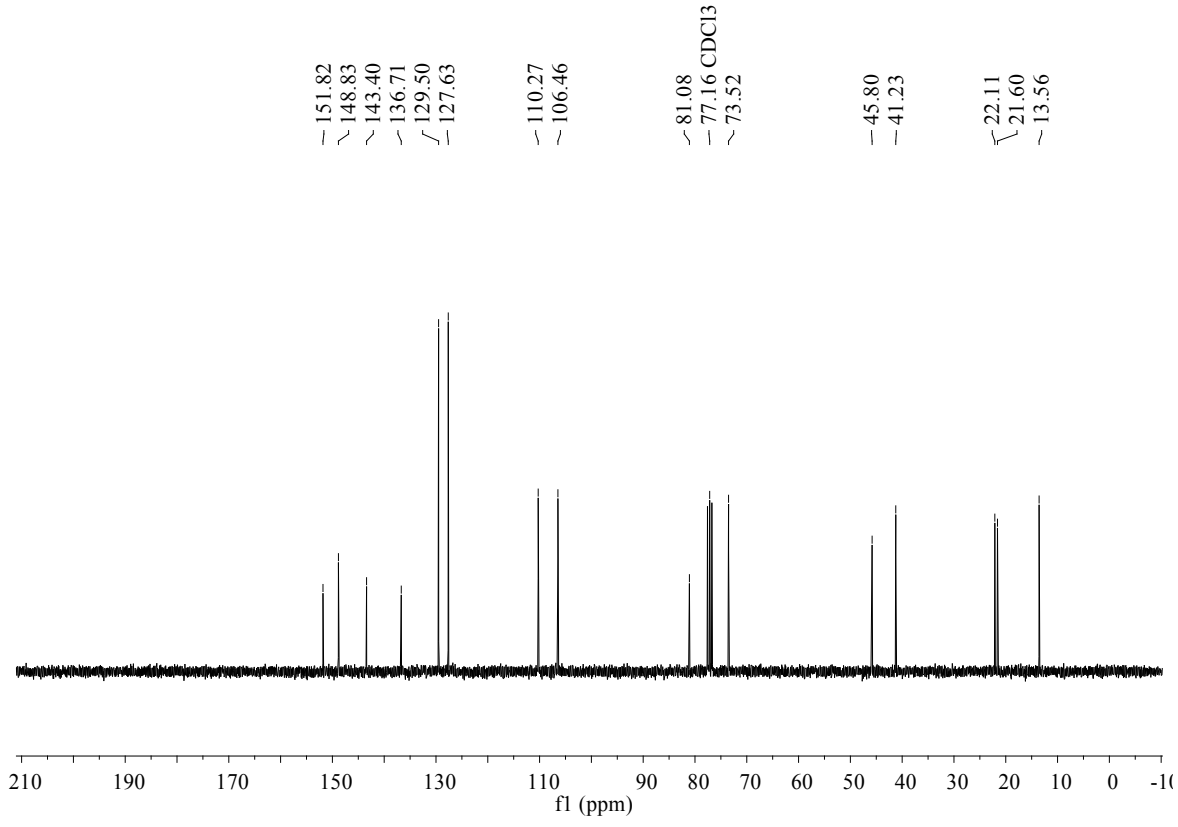
f1 (ppm)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22.11
21.60
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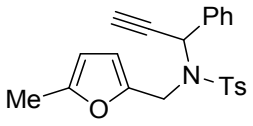
f1 (ppm)


Ph
N
Ts
Me
O

1e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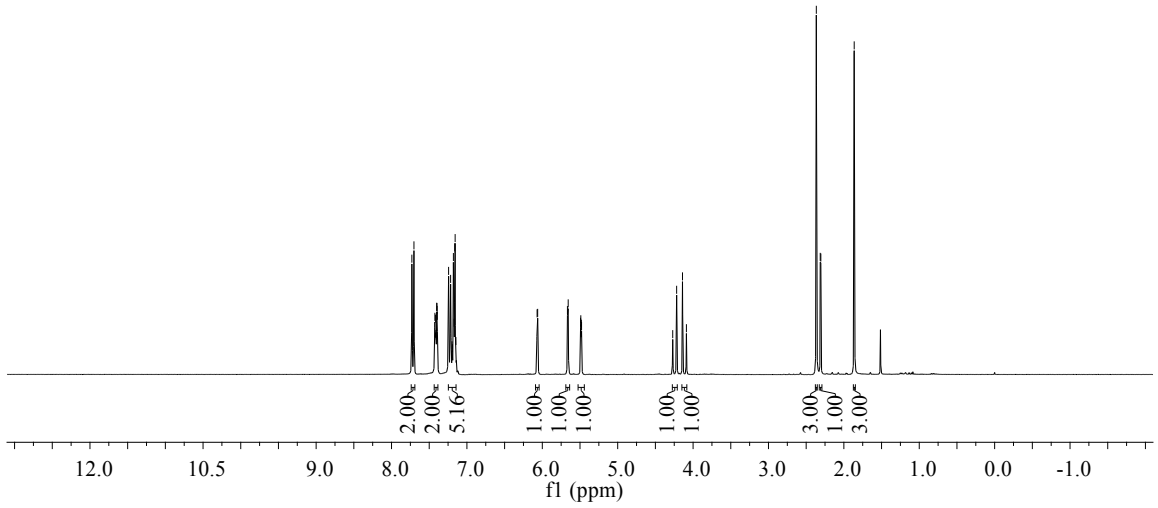
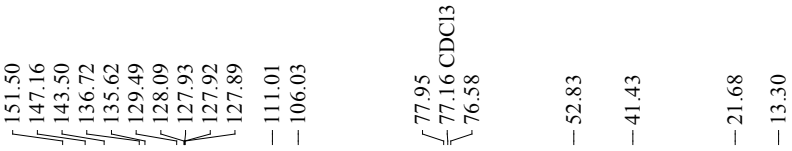
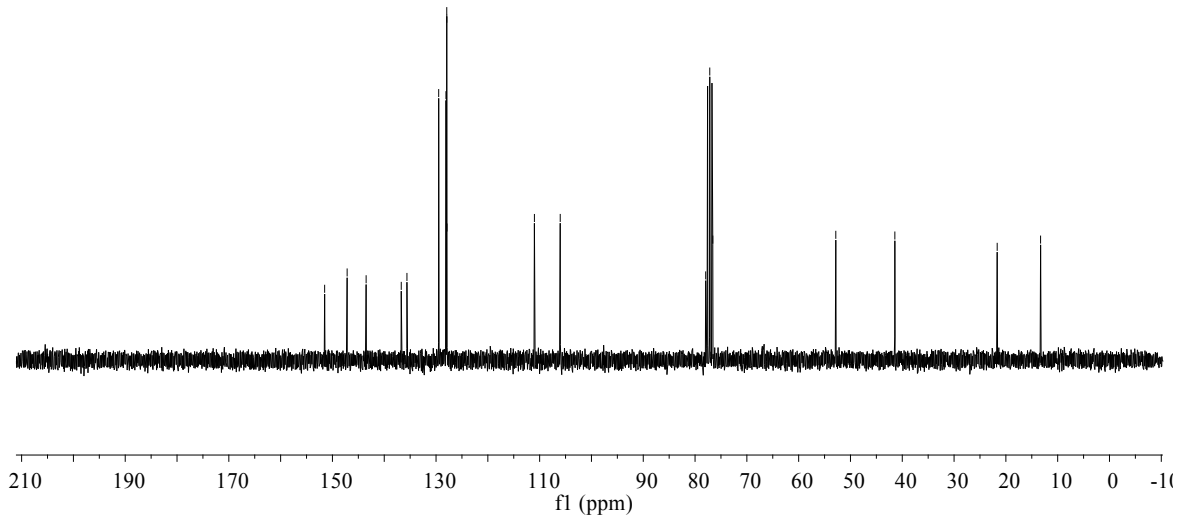
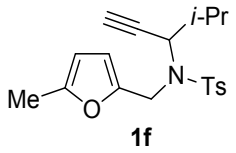
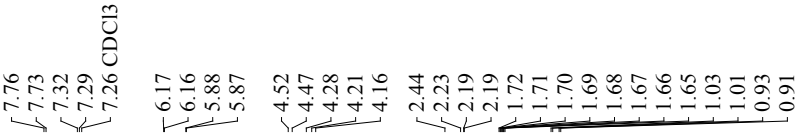

2.00
2.00
5.16
1.00
1.00
1.00
1.00
1.00
3.00
1.00
3.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

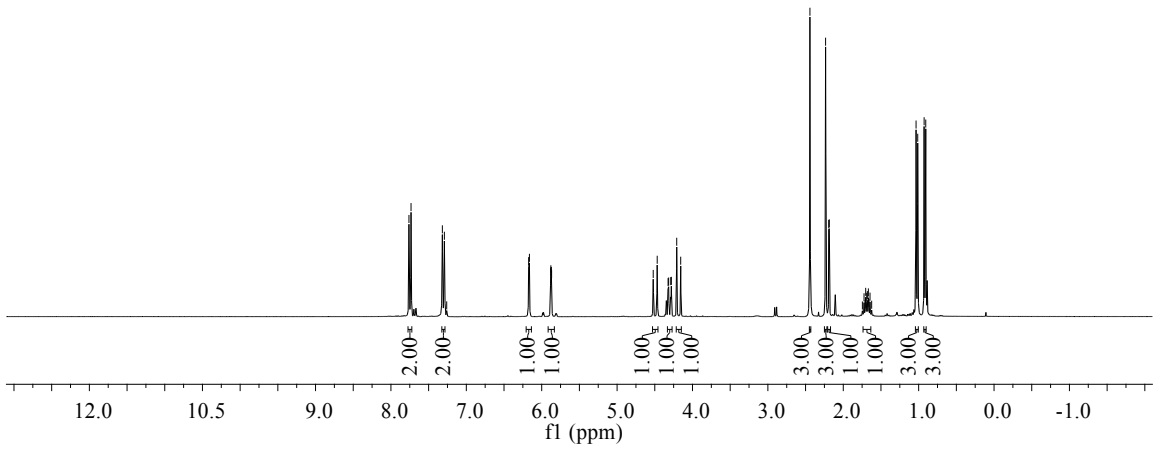

151.50
147.16
143.50
136.72
135.62
129.49
128.09
127.93
127.92
127.89
111.01
106.03
77.95
77.16 CDCl3
76.58
52.83
41.43
21.68
13.30


210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

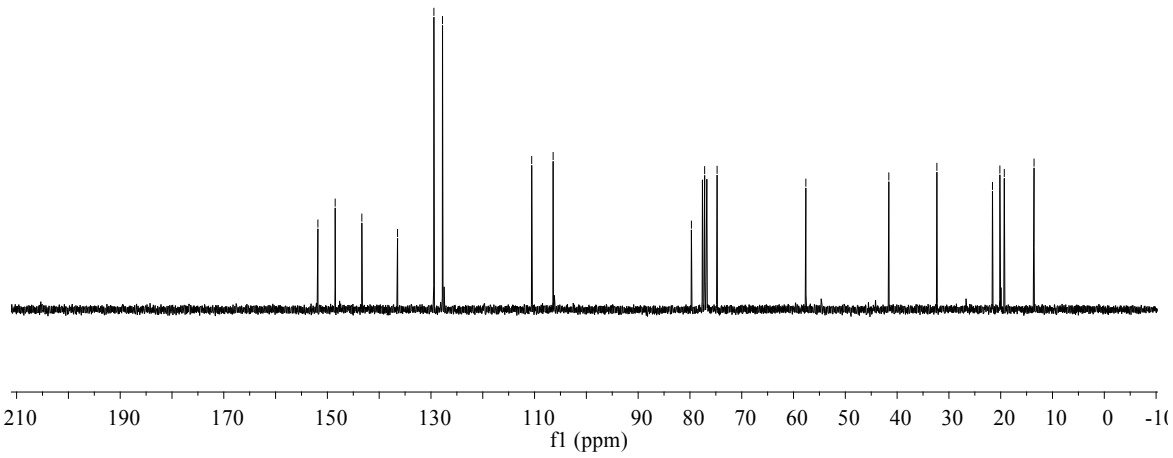

i-Pr
N
Ts
Me
O

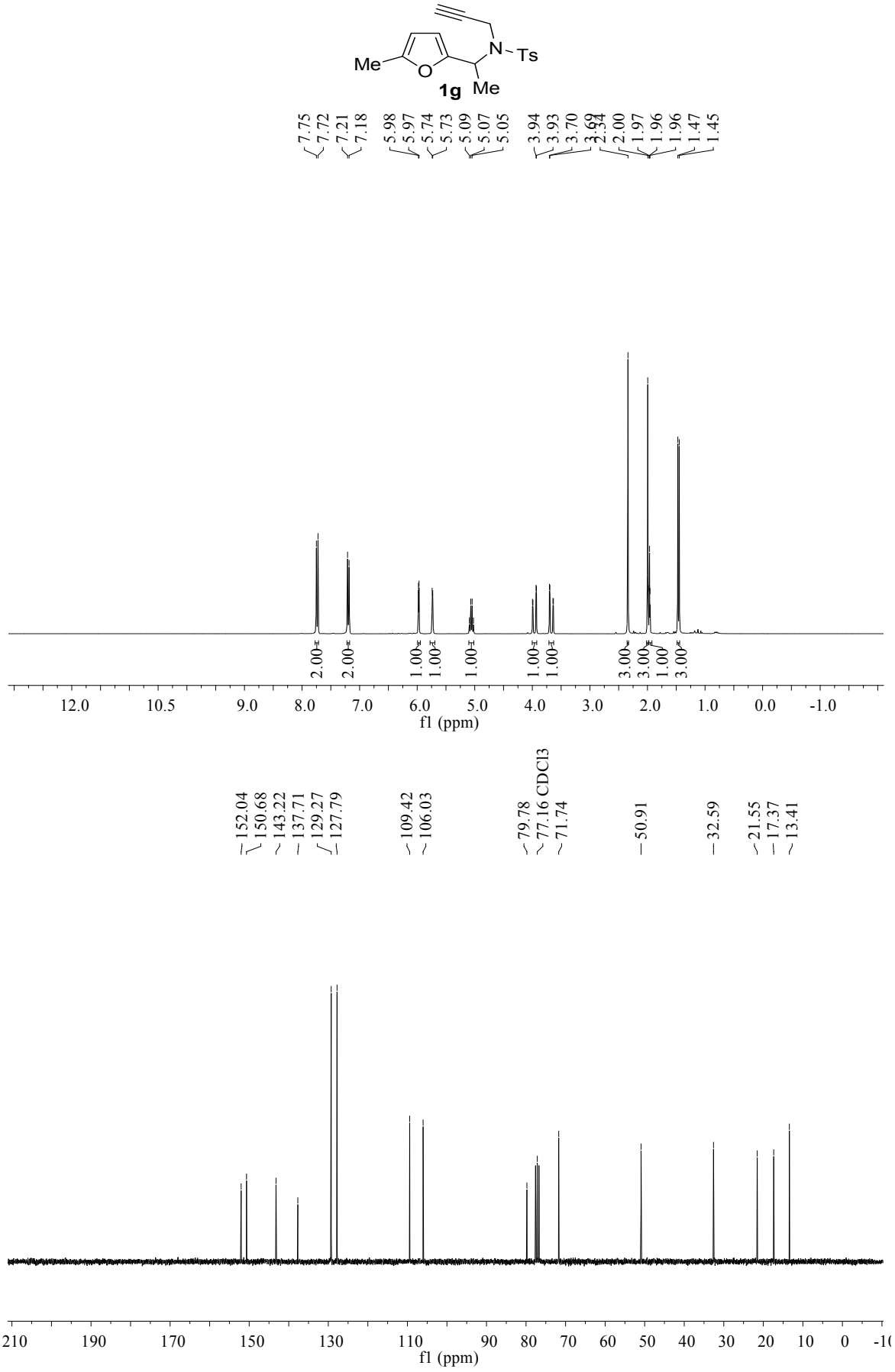
1f

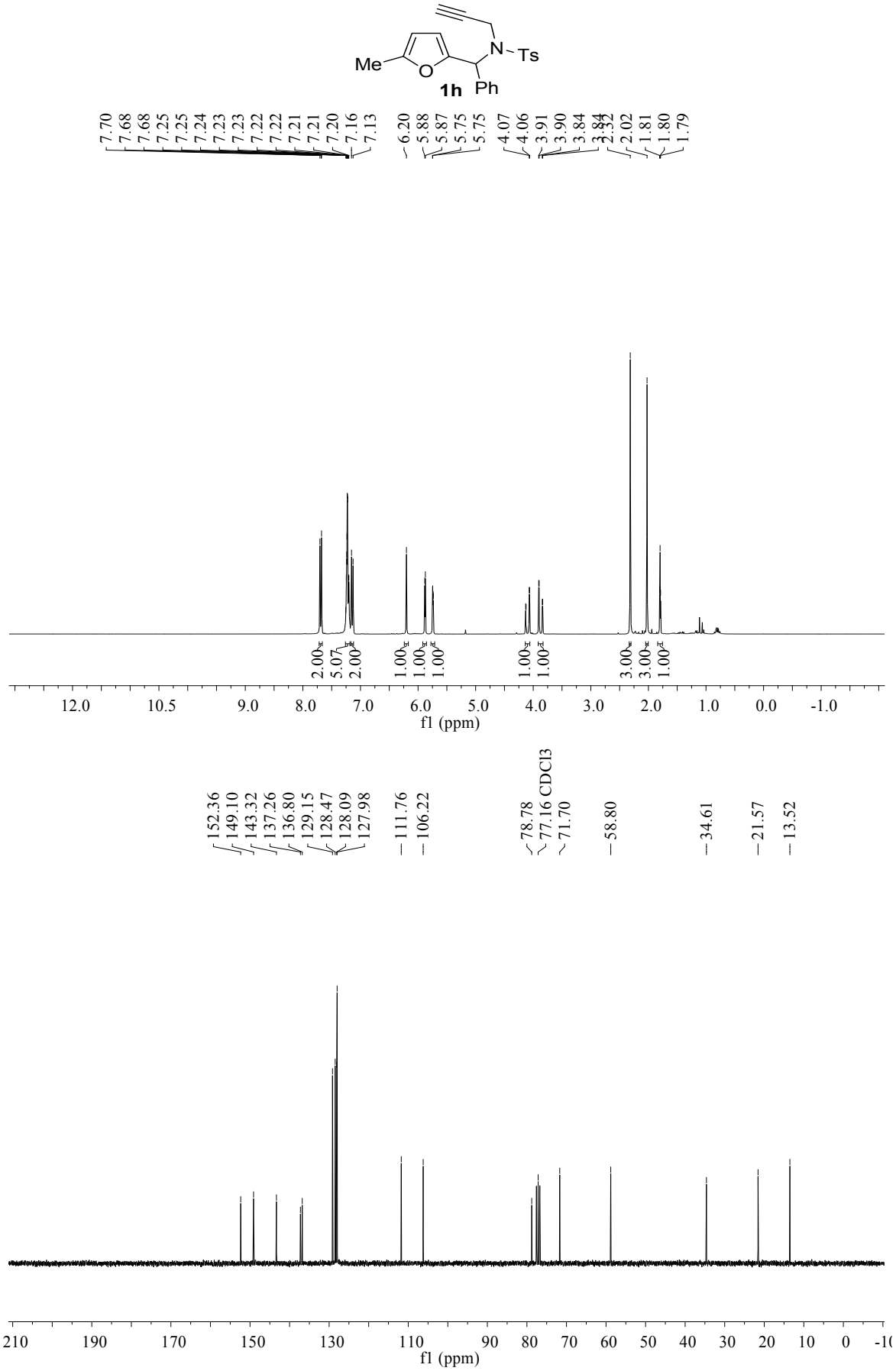

7.76
7.73
7.32
7.29
7.26 CDCl3
6.17
6.16
5.88
5.87
4.52
4.47
4.28
4.21
4.16
2.44
2.23
2.19
2.19
1.72
1.71
1.70
1.69
1.68
1.67
1.66
1.65
1.03
1.01
0.93
0.91

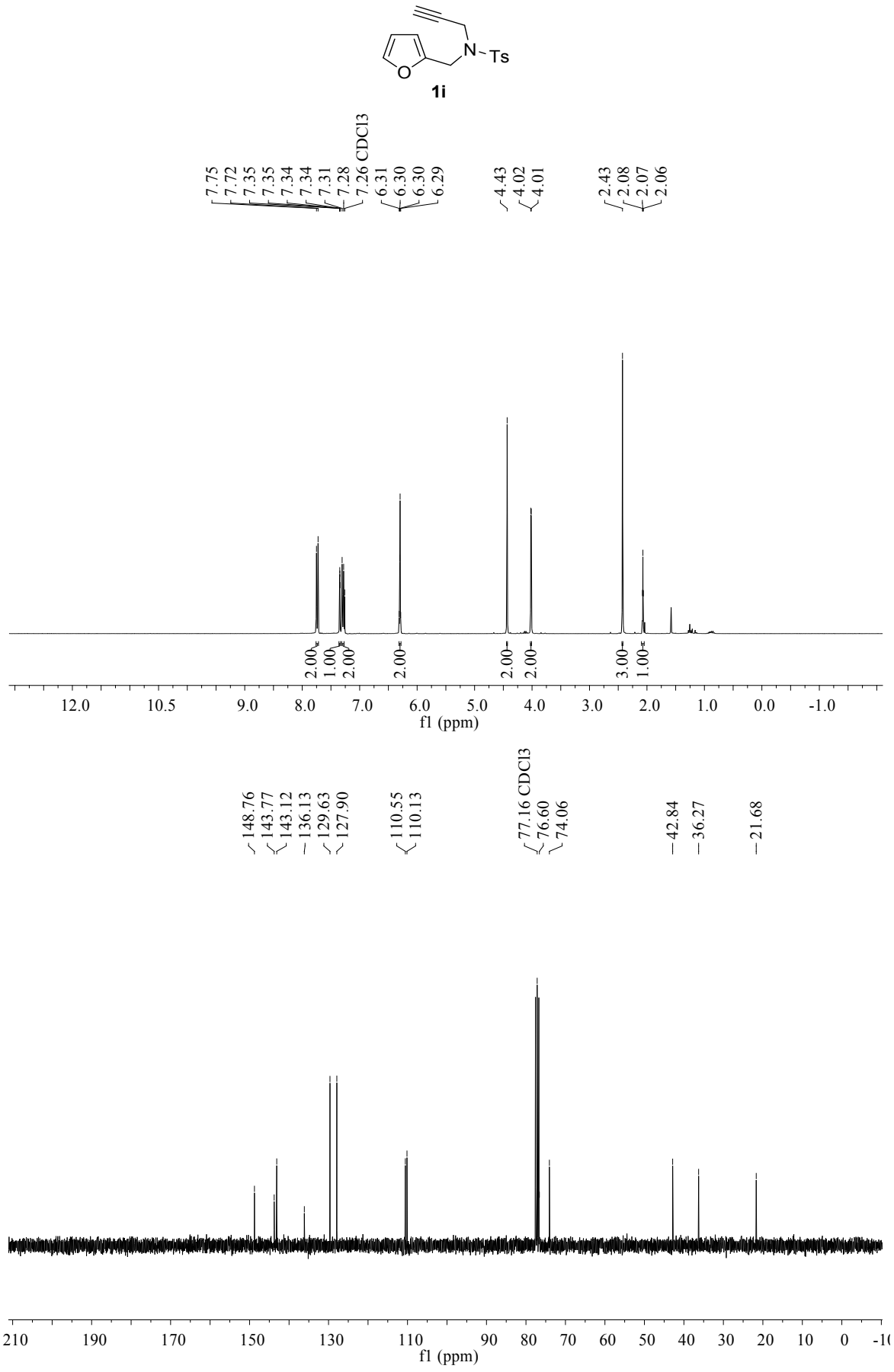

2.00
2.00
1.00
1.00
1.00
1.00
1.00
3.00
3.00
1.00
1.00
3.00
3.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

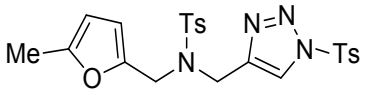

151.83
148.49
143.35
136.45
129.44
127.77
110.55
106.41
79.72
77.16 CDCl3
74.76
57.62
41.60
32.32
21.59
20.16
19.31
13.56


210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

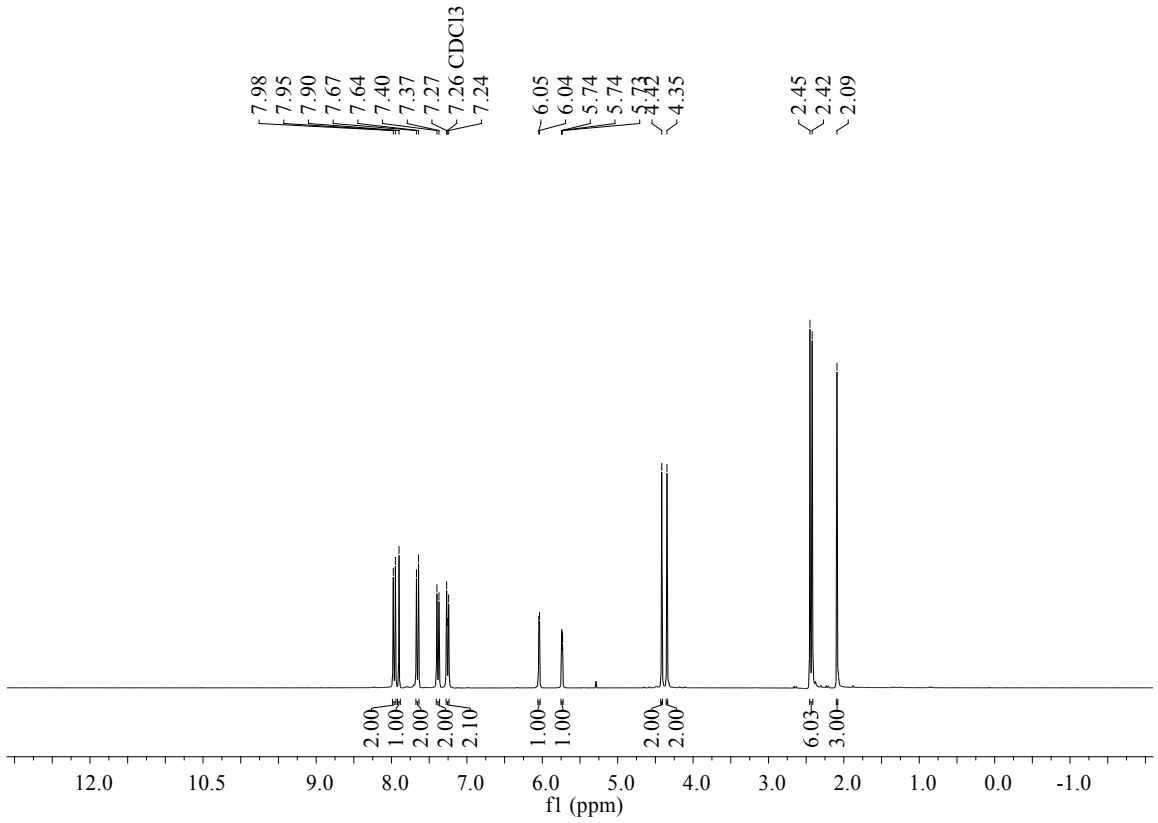

Me
O
N
Ts
Me
1g
7.75
7.72
7.21
7.18
5.98
5.97
5.74
5.73
5.09
5.07
5.05
3.94
3.93
3.70
3.69
2.34
2.00
1.97
1.96
1.96
1.47
1.45
2.00
2.00
1.00
1.00
1.00
1.00
1.00
3.00
3.00
1.00
3.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)
152.04
150.68
143.22
137.71
129.27
127.79
109.42
106.03
79.78
77.16 CDCl3
71.74
50.91
32.59
21.55
17.37
13.41
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

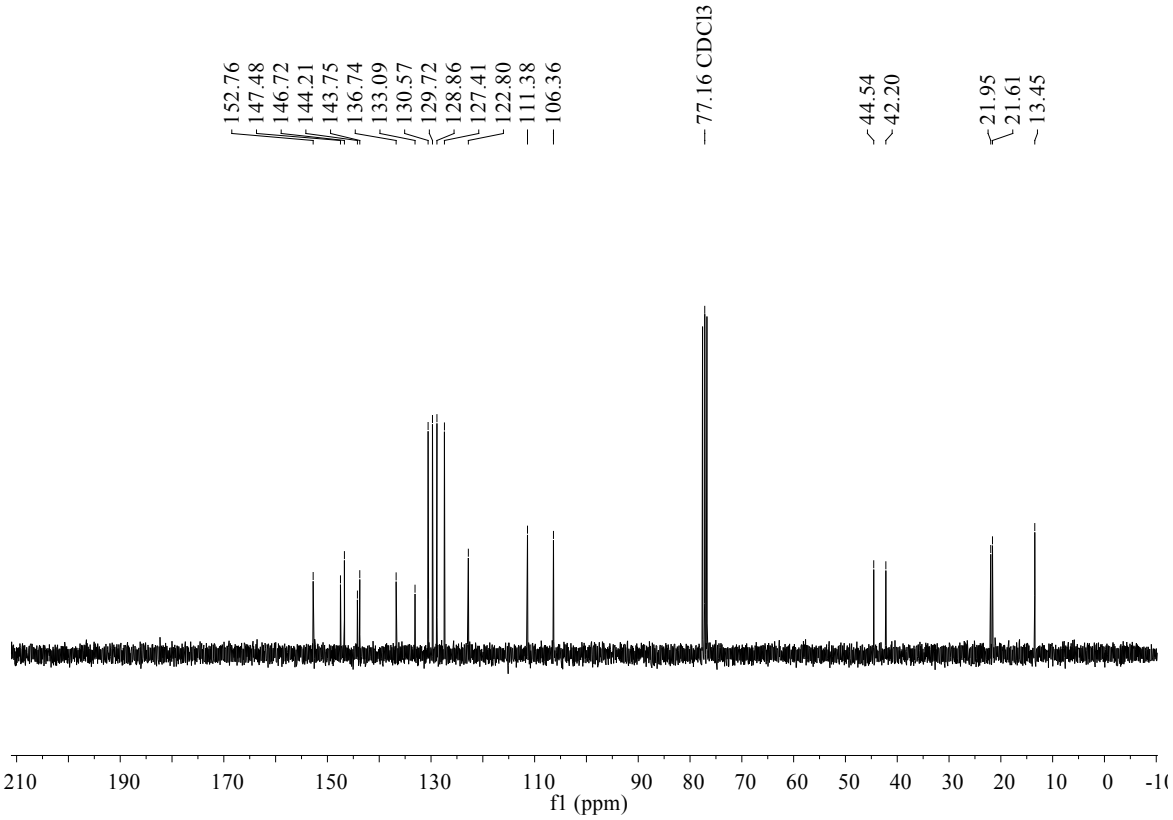

Me
O
N
Ts
Ph
1h
7.70
7.68
7.25
7.25
7.24
7.23
7.23
7.22
7.22
7.21
7.21
7.20
7.16
7.13
6.20
5.88
5.87
5.75
5.75
4.07
4.06
3.91
3.90
3.84
2.32
2.02
1.81
1.80
1.79
2.00
5.07
2.00
1.00
1.00
1.00
1.00
1.00
3.00
3.00
1.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)
152.36
149.10
143.32
137.26
136.80
129.15
128.47
128.09
127.98
111.76
106.22
78.78
77.16 CDCl3
71.70
58.80
34.61
21.57
13.52
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

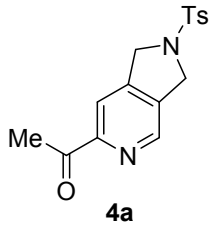

N
Ts
O
1i
7.75
7.72
7.35
7.35
7.34
7.34
7.31
7.28
7.26 CDCl3
6.31
6.30
6.30
6.29
4.43
4.02
4.01
2.43
2.08
2.07
2.06
2.00
1.00
2.00
2.00
2.00
2.00
3.00
1.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)
148.76
143.77
143.12
136.13
129.63
127.90
110.55
110.13
77.16 CDCl3
76.60
74.06
42.84
36.27
21.68
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
O
N
Ts
N=N
N
Ts

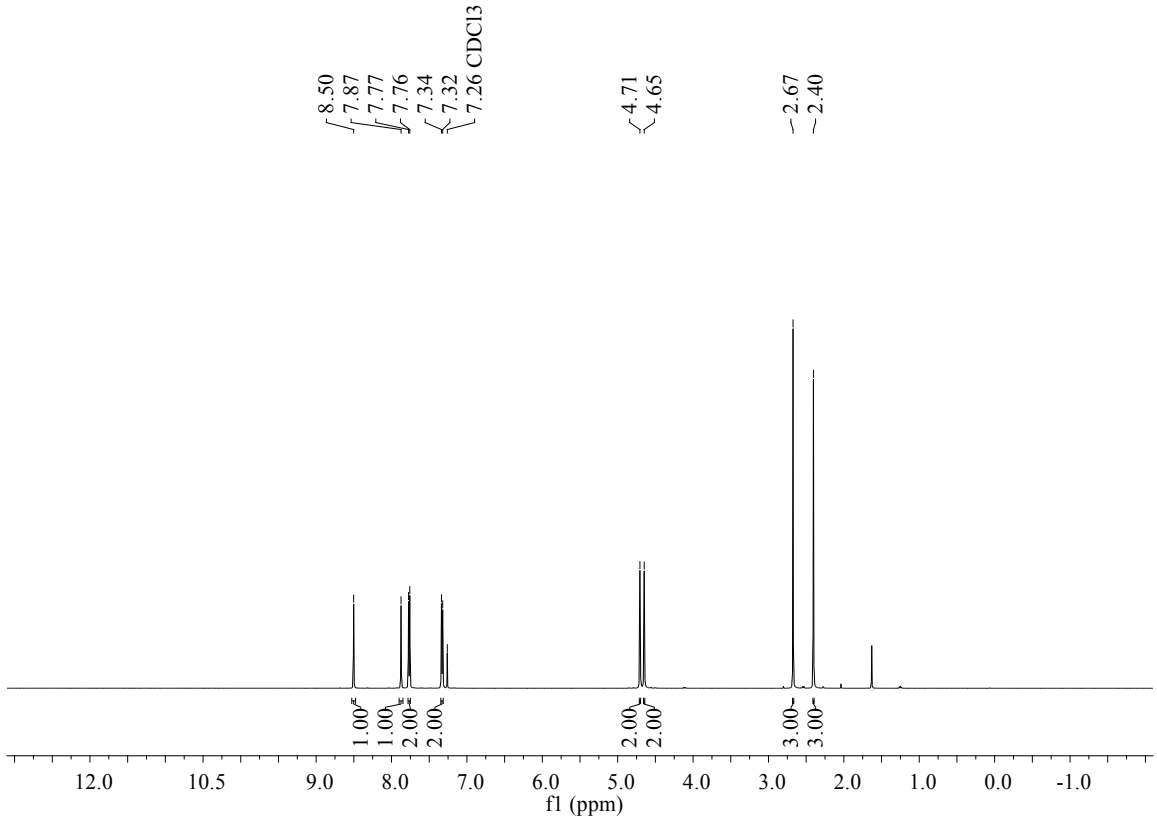
2a

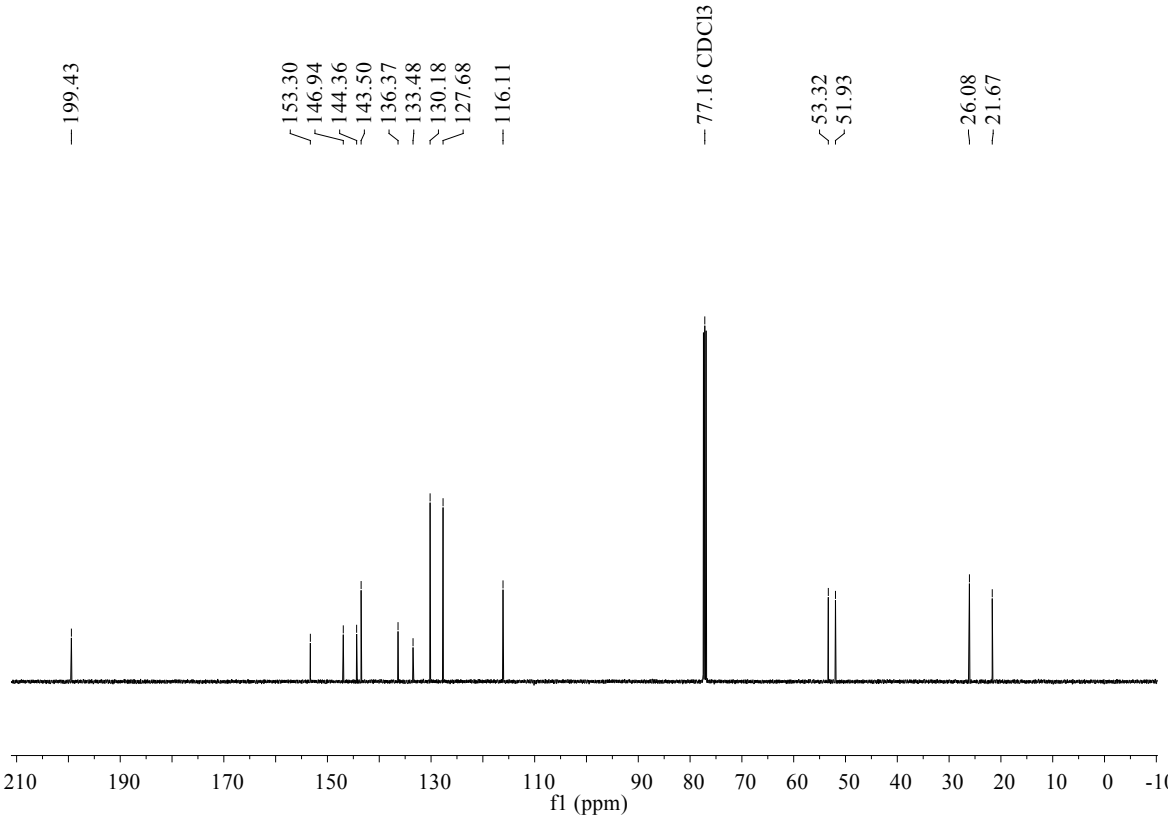

7.98
7.95
7.90
7.67
7.64
7.40
7.37
7.27
7.26 CDCl3
7.24
6.05
6.04
5.74
5.74
4.42
4.35
2.45
2.42
2.09
2.00
1.00
2.00
2.00
2.10
1.00
1.00
2.00
2.00
6.03
3.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

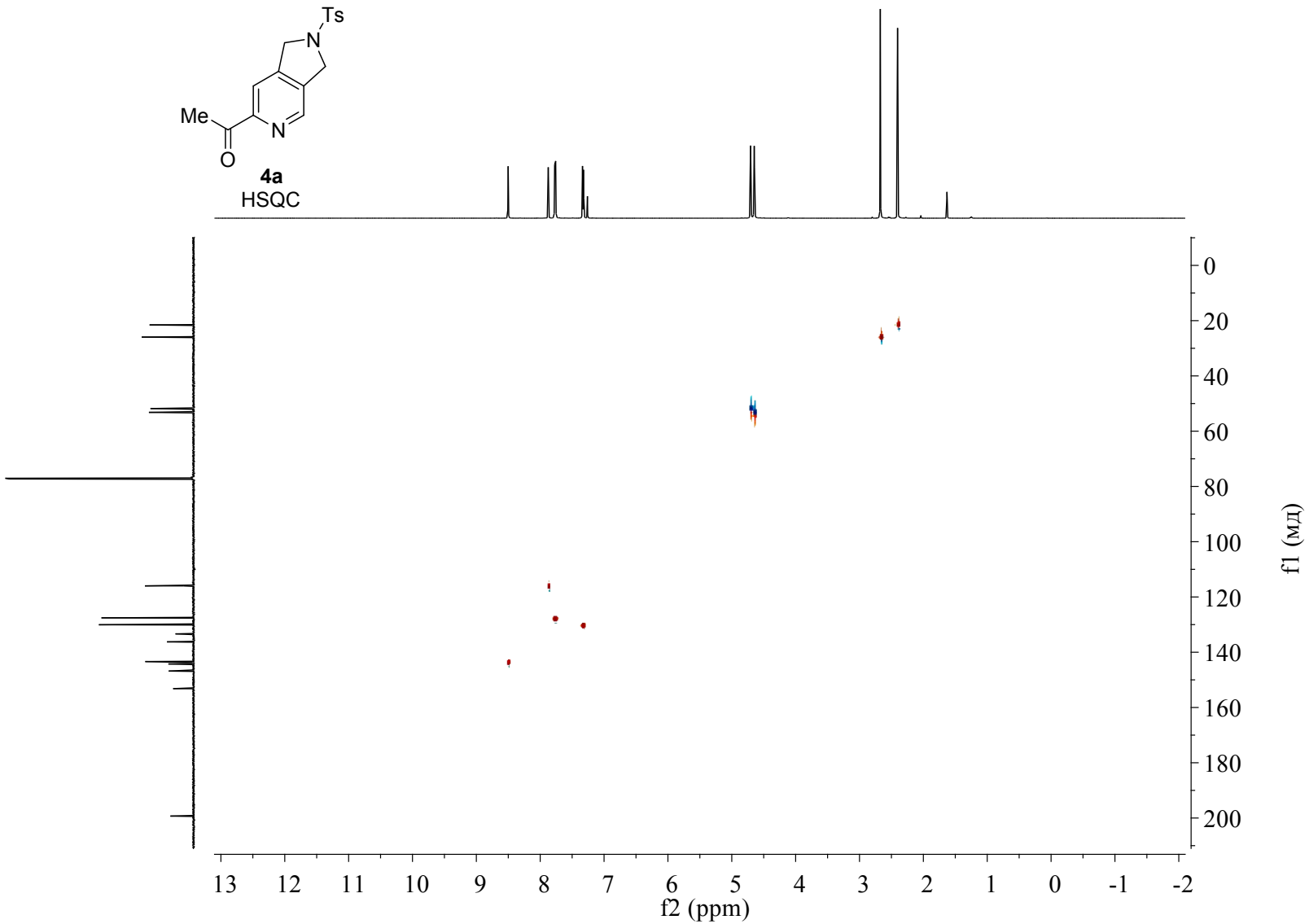

152.76
147.48
146.72
144.21
143.75
136.74
133.09
130.57
129.72
128.86
127.41
122.80
111.38
106.36
77.16 CDCl3
44.54
42.20
21.95
21.61
13.45
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

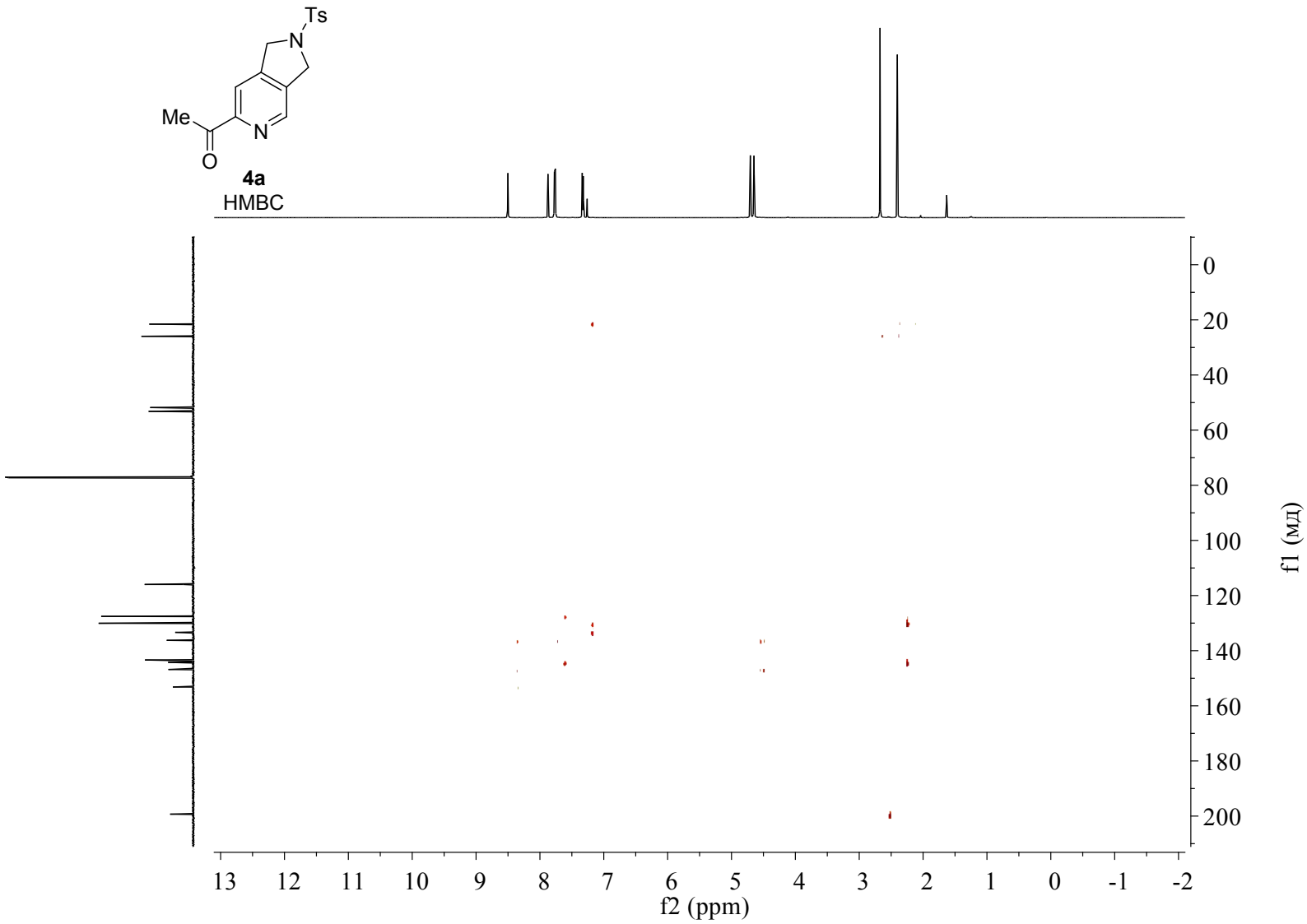

Ts
N
Me
N
O

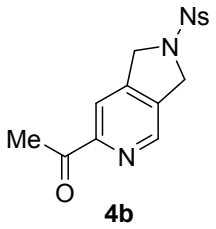
4a


8.50
7.87
7.77
7.76
7.34
7.32
7.26 CDCl3
4.71
4.65
2.67
2.40
1.00
1.00
2.00
2.00
2.00
2.00
3.00
3.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

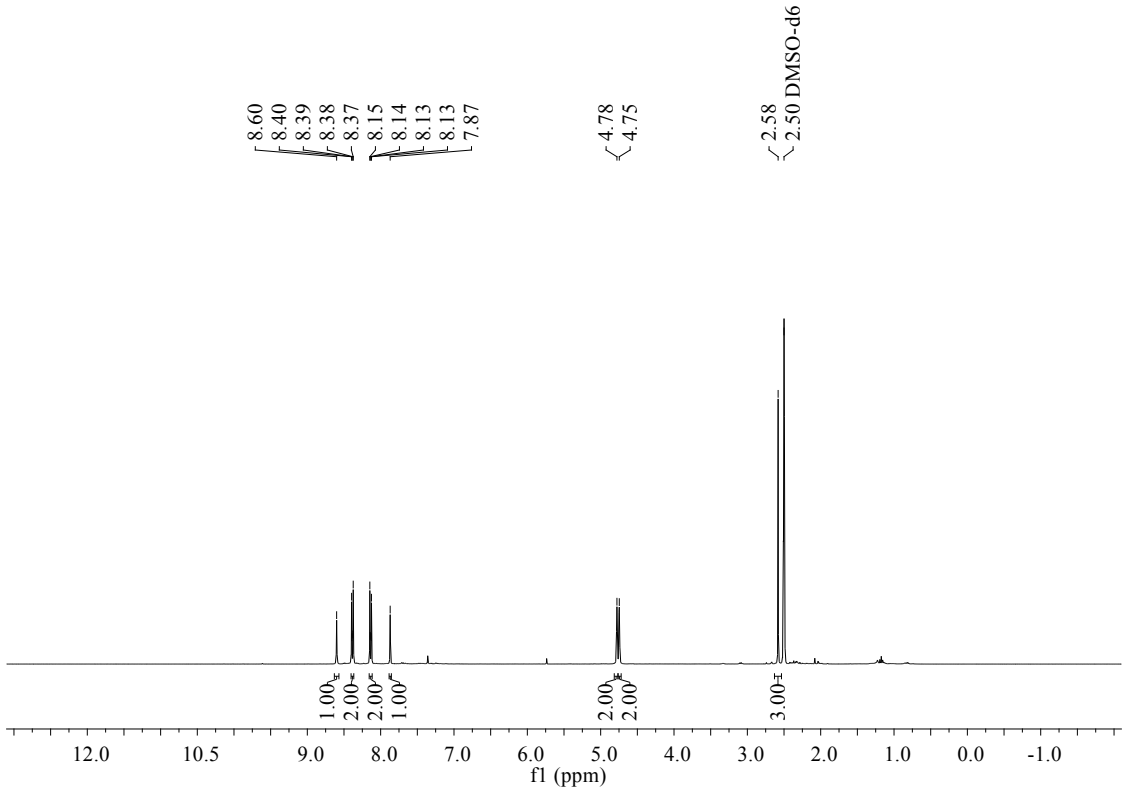

199.43
153.30
146.94
144.36
143.50
136.37
133.48
130.18
127.68
116.11
77.16 CDCl3
53.32
51.93
26.08
21.67
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

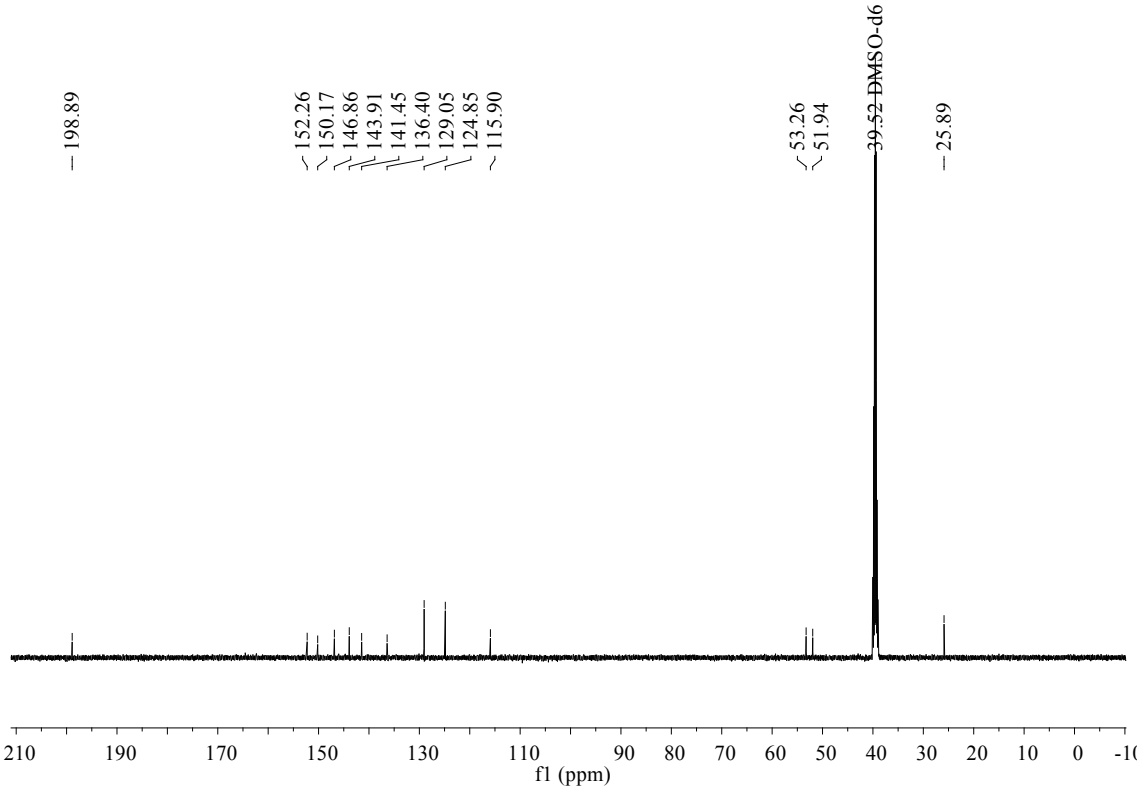

Ts
N
Me
N
O
4a
HSQC
0
20
40
60
80
100
120
140
160
180
200
f1 (мд)
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f2 (ppm)

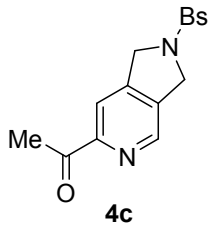

Ts
N
Me
N
O
4a
HMBC
0
20
40
60
80
100
120
140
160
180
200
f1 (мд)
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f2 (ppm)


Ns
N
Me
N
O

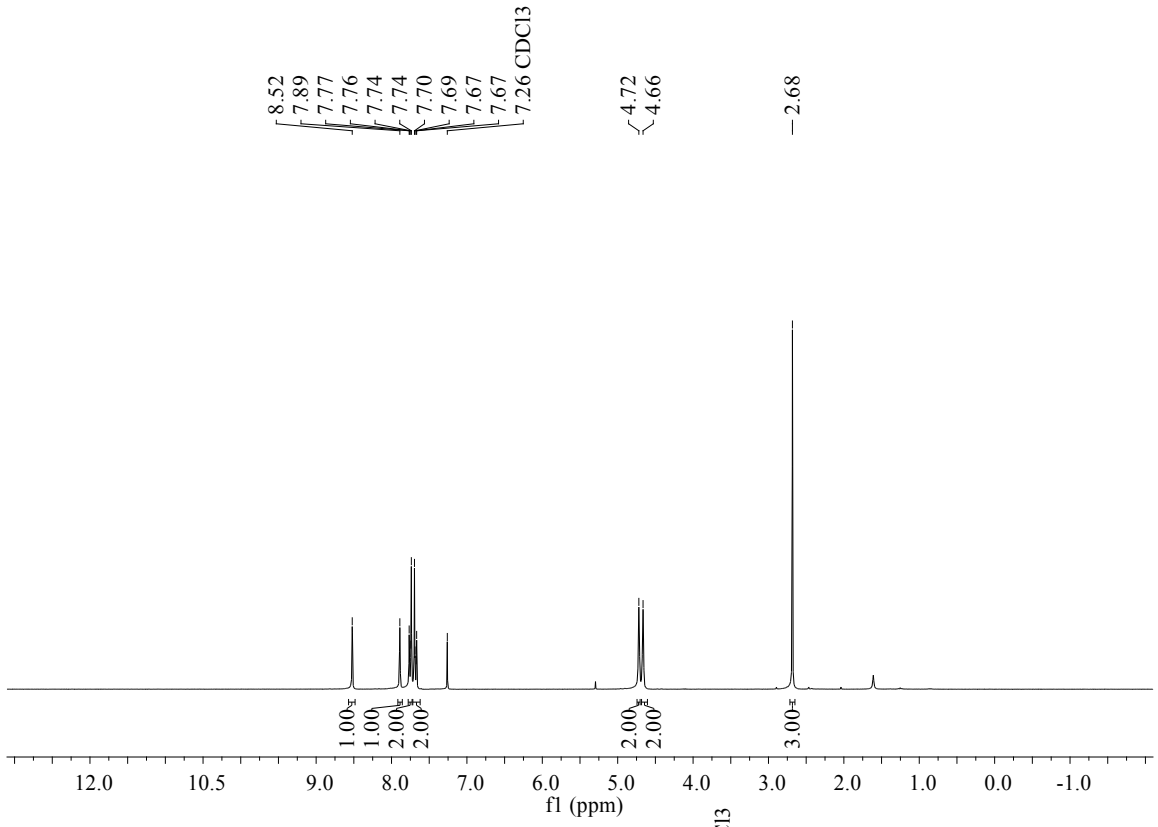
4b

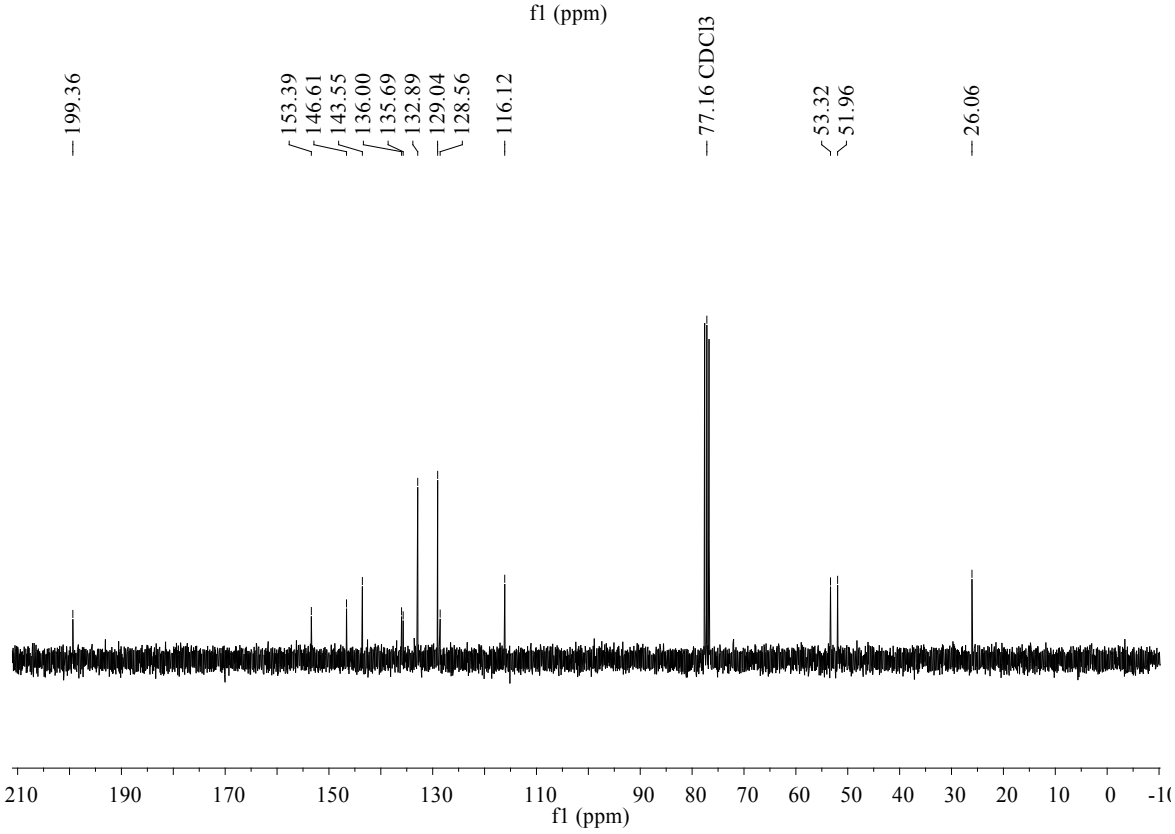

8.60
8.40
8.39
8.38
8.37
8.15
8.14
8.13
8.13
7.87
4.78
4.75
2.58
2.50 DMSO-d6
1.00
2.00
2.00
1.00
2.00
2.00
3.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

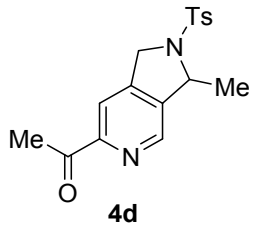

198.89
152.26
150.17
146.86
143.91
141.45
136.40
129.05
124.85
115.90
53.26
51.94
39.52 DMSO-d6
25.89
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Bs
N
Me
N
O

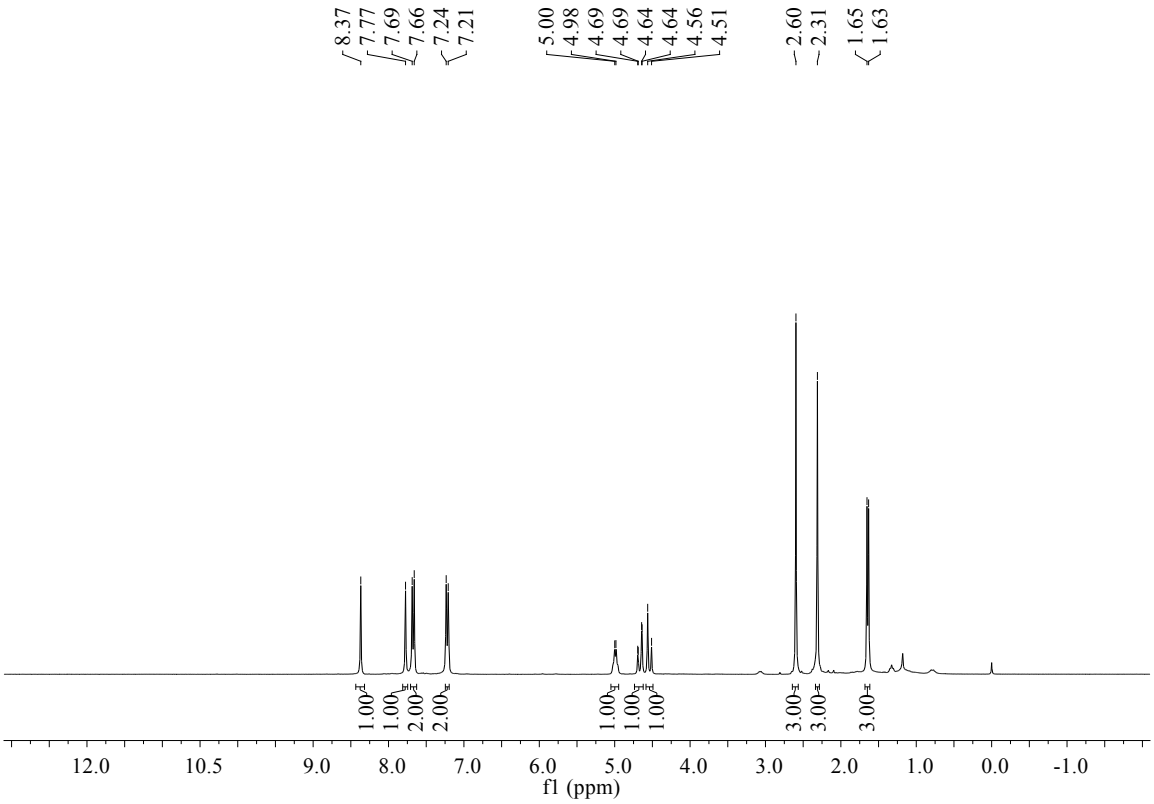
4c

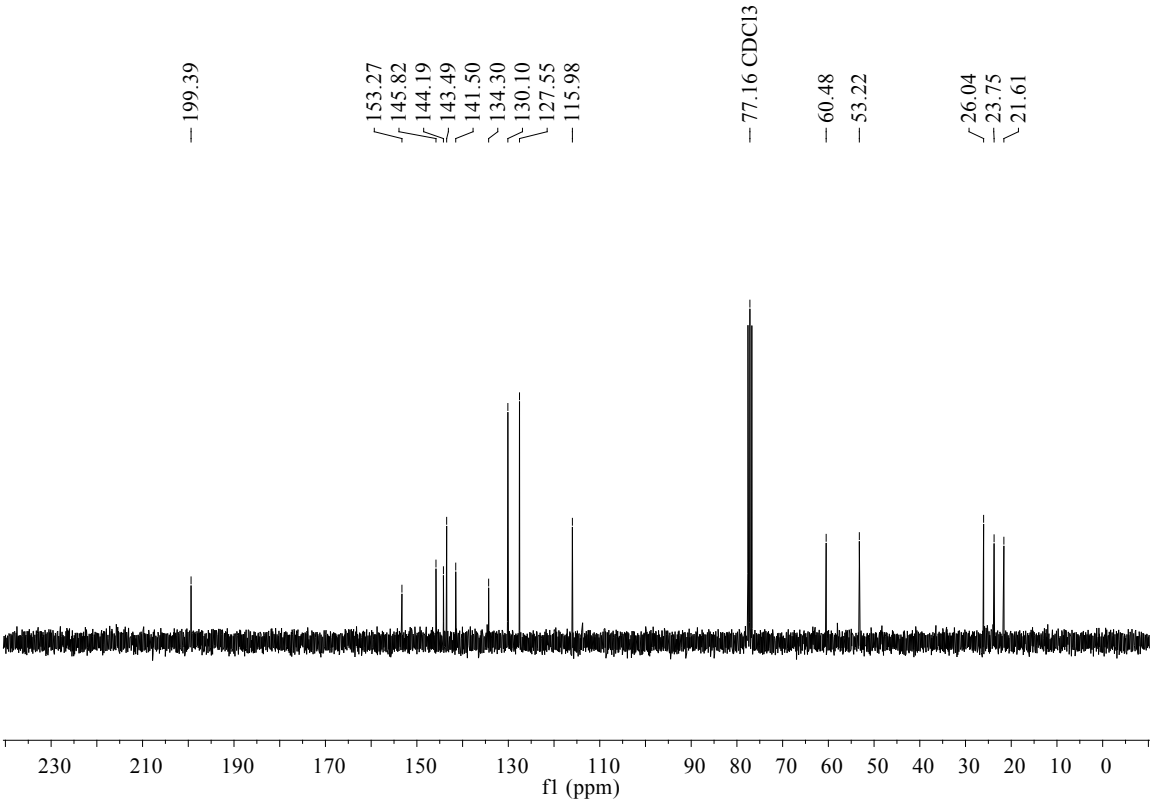

8.52
7.89
7.77
7.76
7.74
7.74
7.70
7.69
7.67
7.67
7.26 CDCl3
4.72
4.66
2.68
1.00
1.00
2.00
2.00
2.00
2.00
3.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

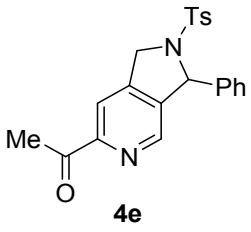

199.36
153.39
146.61
143.55
136.00
135.69
132.89
129.04
128.56
116.12
77.16 CDCl3
53.32
51.96
26.06
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ts
N
Me
Me
N
O

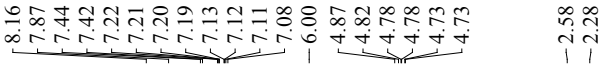
4d

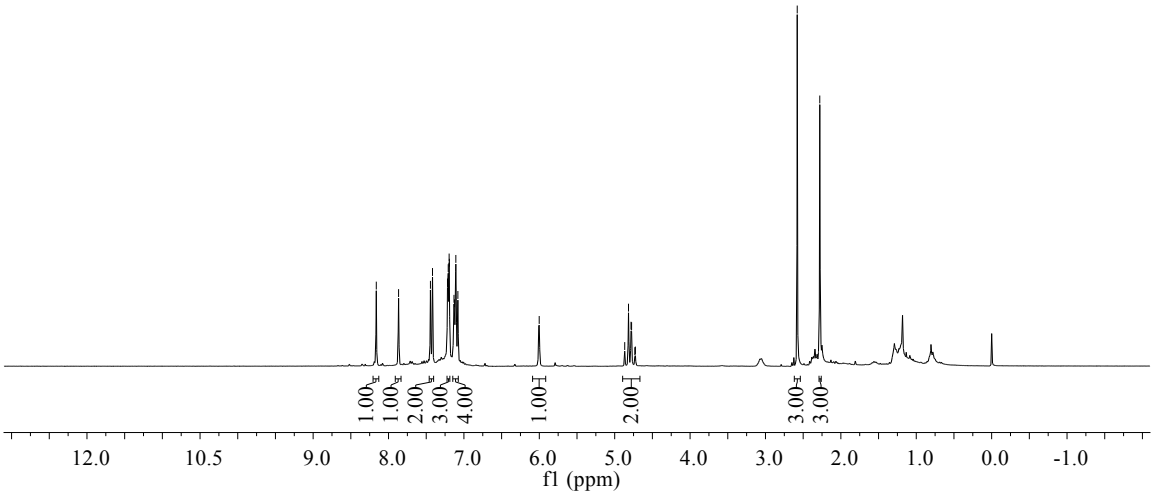

8.37
7.77
7.69
7.66
7.24
7.21
5.00
4.98
4.69
4.69
4.64
4.64
4.56
4.51
2.60
2.31
1.65
1.63
1.00
1.00
2.00
2.00
1.00
1.00
1.00
3.00
3.00
3.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

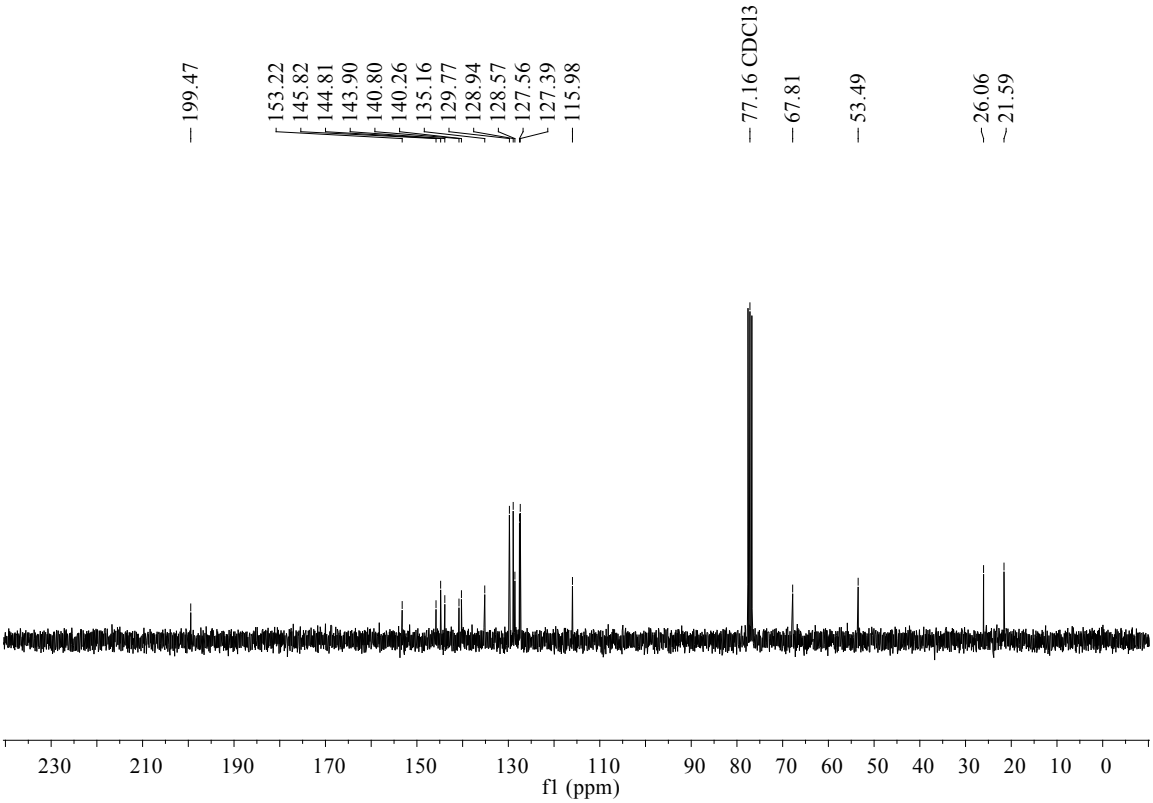

199.39
153.27
145.82
144.19
143.49
141.50
134.30
130.10
127.55
115.98
77.16 CDCl3
60.48
53.22
26.04
23.75
21.61
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

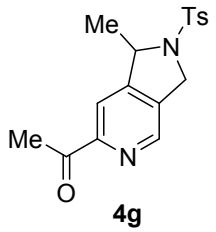

Ts
N
Ph
Me
N
O

4e

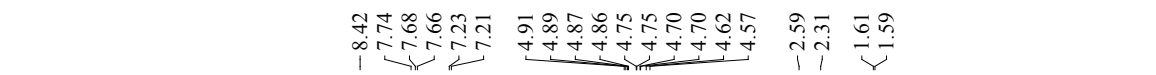

8.16
7.87
7.44
7.42
7.22
7.21
7.20
7.19
7.13
7.12
7.11
7.08
6.00
4.87
4.82
4.78
4.78
4.73
4.73
2.58
2.28

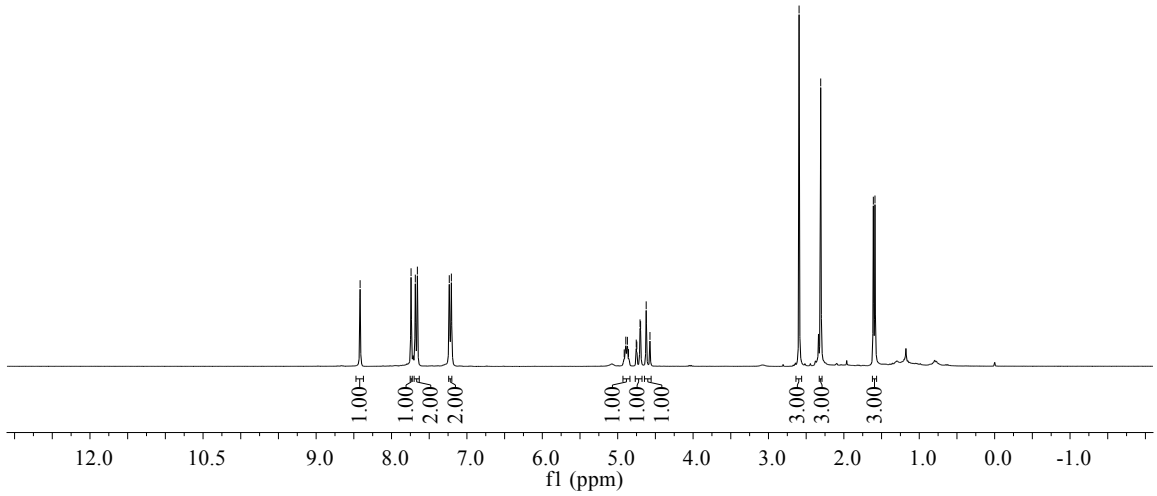

1.00
1.00
2.00
3.00
4.00
1.00
2.00
3.00
3.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

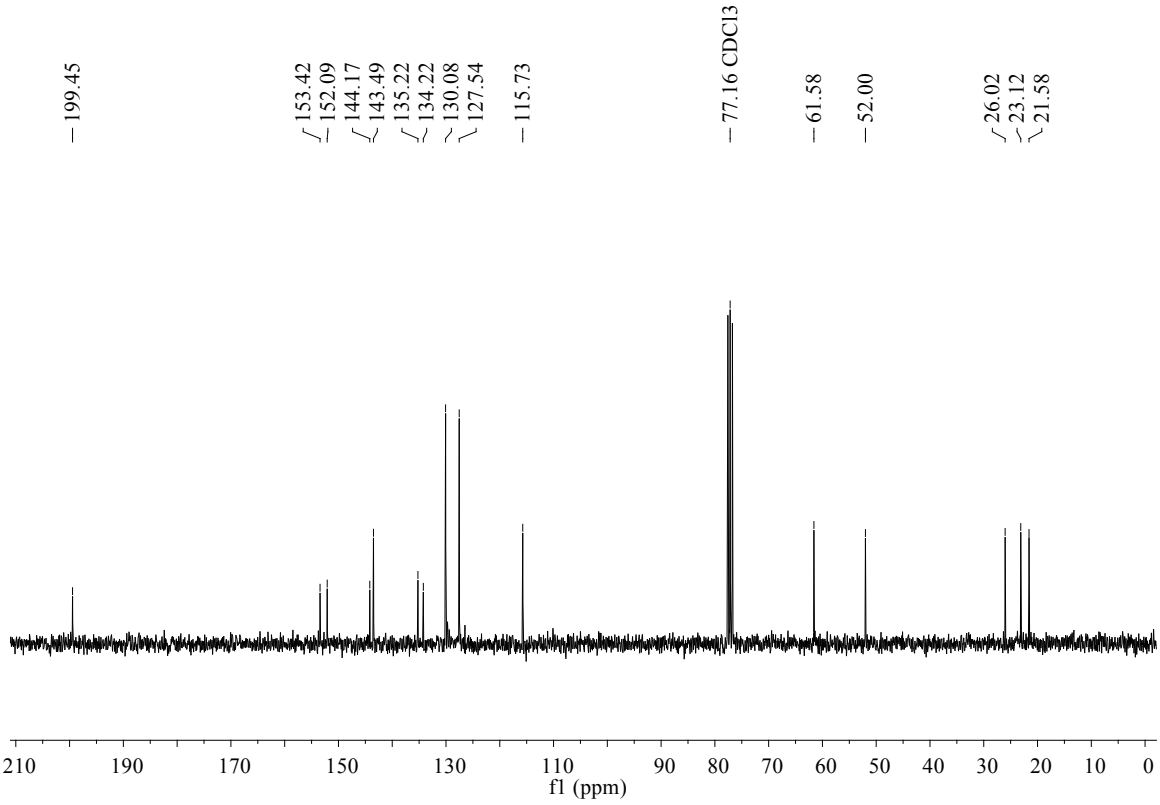

199.47
153.22
145.82
144.81
143.90
140.80
140.26
135.16
129.77
128.94
128.57
127.56
127.39
115.98
77.16 CDCl3
67.81
53.49
26.06
21.59
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

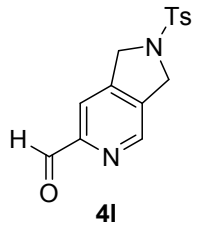

Me
Ts
N
Me
N
O

4g

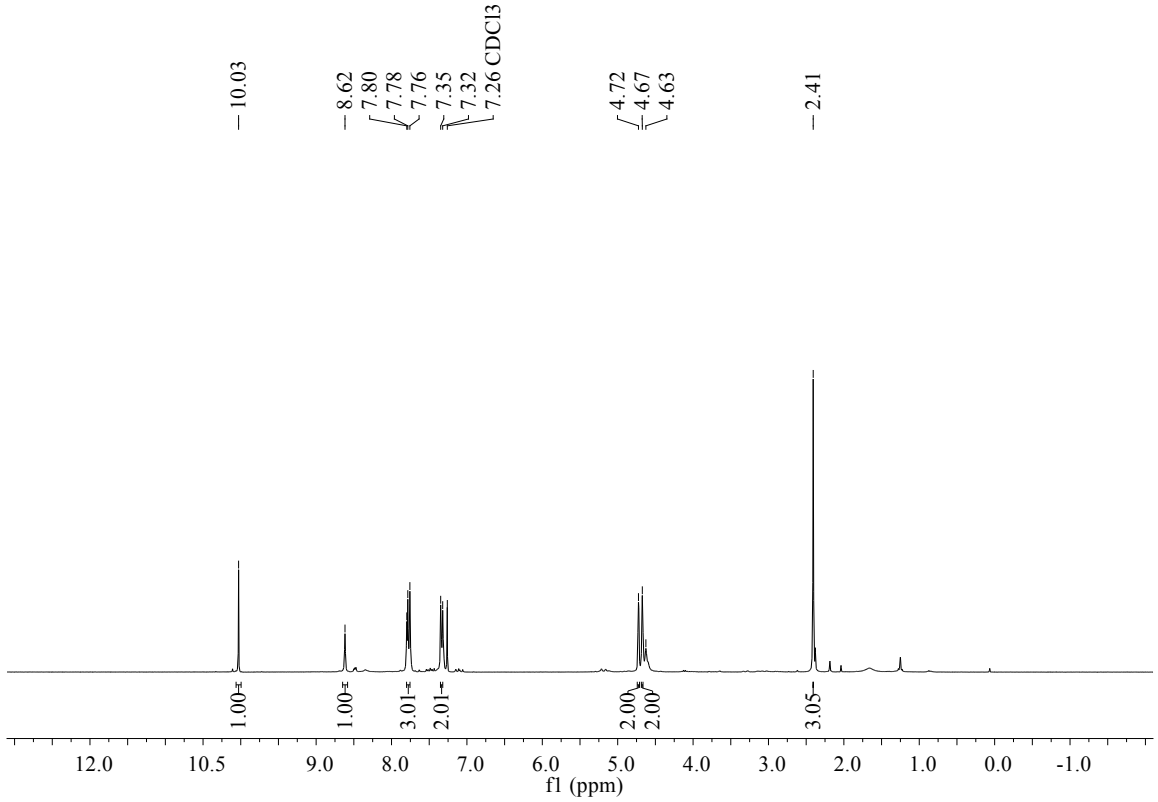

8.42
7.74
7.68
7.66
7.23
7.21
4.91
4.89
4.87
4.86
4.75
4.75
4.70
4.70
4.62
4.57
2.59
2.31
1.61
1.59

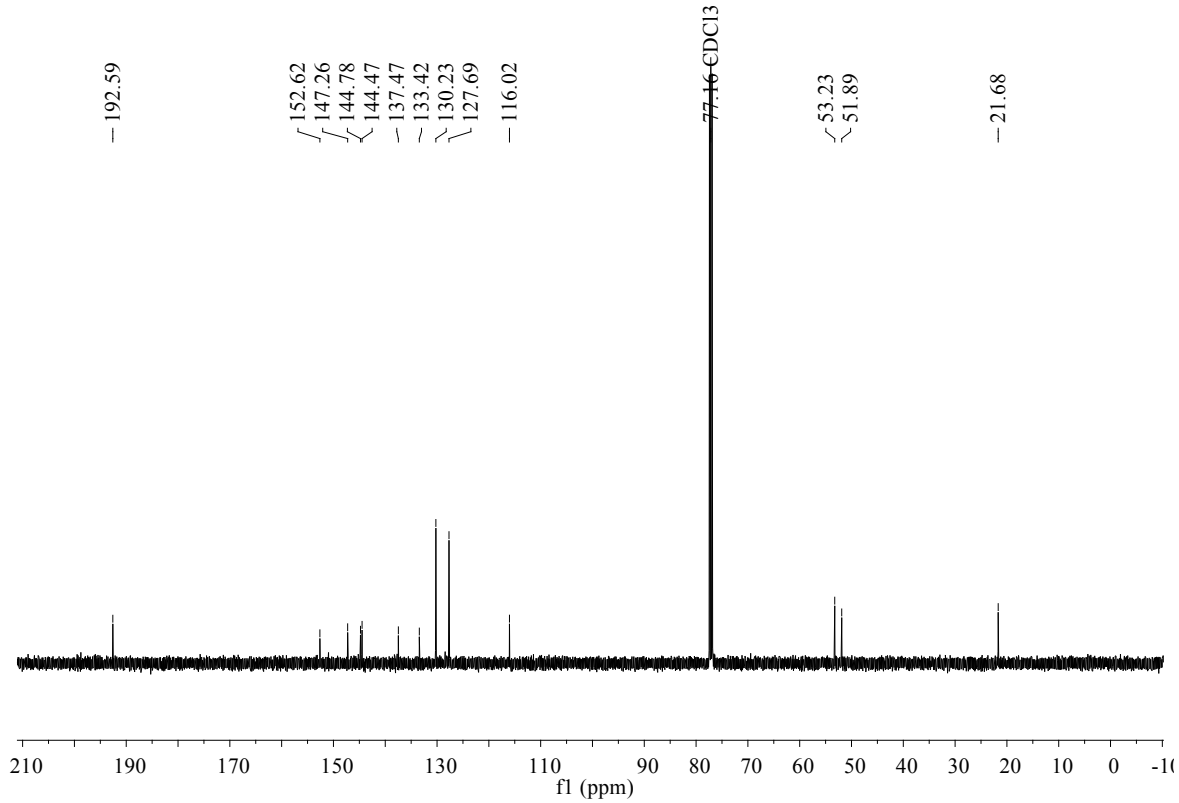

1.00
1.00
2.00
2.00
1.00
1.00
1.00
3.00
3.00
3.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

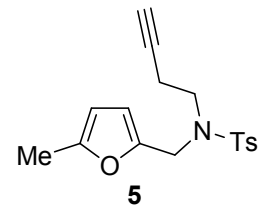

199.45
153.42
152.09
144.17
143.49
135.22
134.22
130.08
127.54
115.73
77.16 CDCl3
61.58
52.00
26.02
23.12
21.58
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ts
N
H
N
O

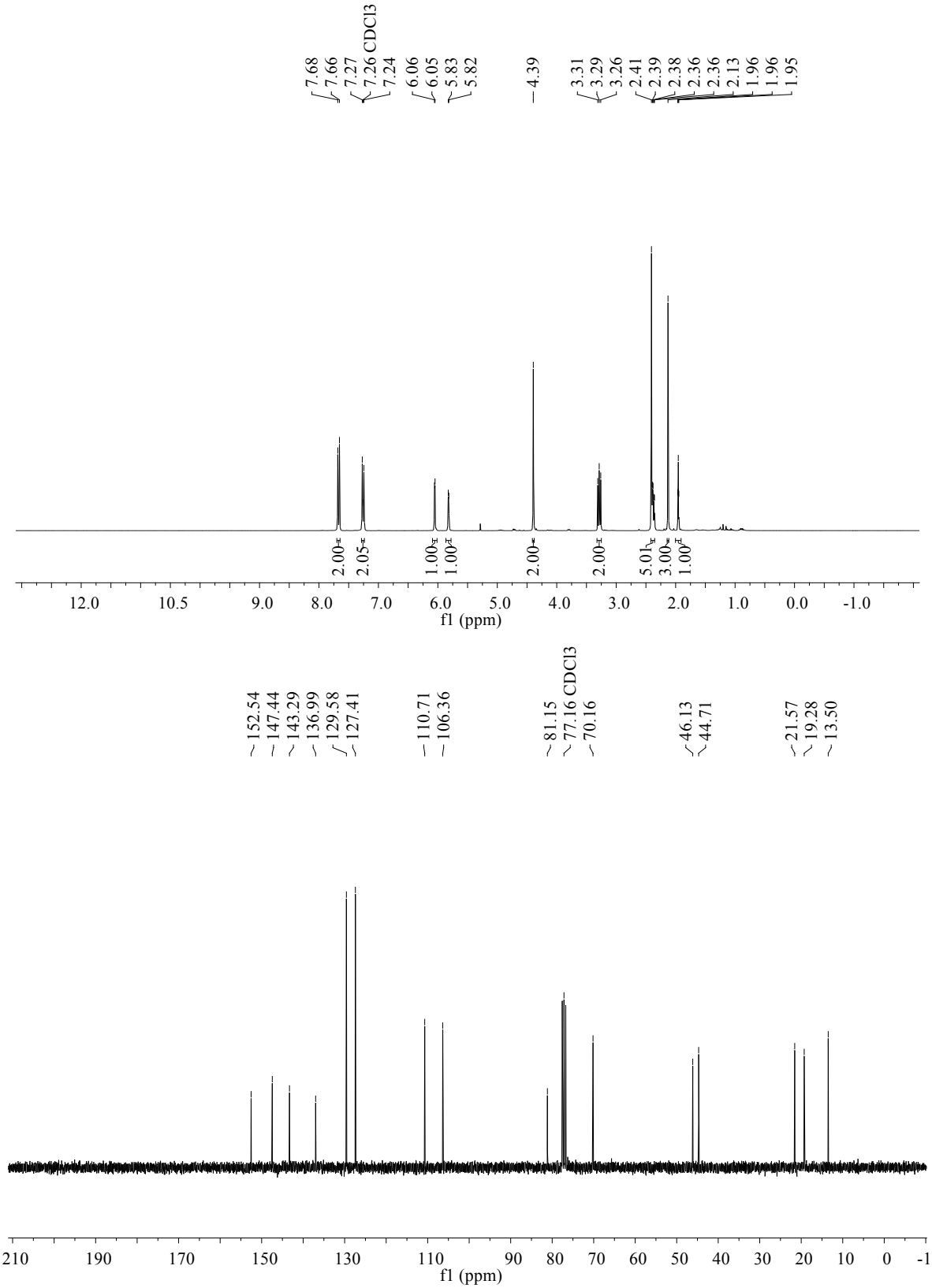
4l

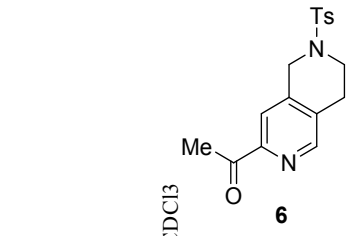

10.03
8.62
7.80
7.78
7.76
7.35
7.32
7.26 CDCl3
4.72
4.67
4.63
2.41
1.00
1.00
3.01
2.01
2.00
2.00
3.05
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


192.59
152.62
147.26
144.78
144.47
137.47
133.42
130.23
127.69
116.02
77.16 CDCl3
53.23
51.89
21.68
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

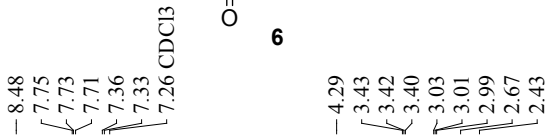

Me
O
N
Ts

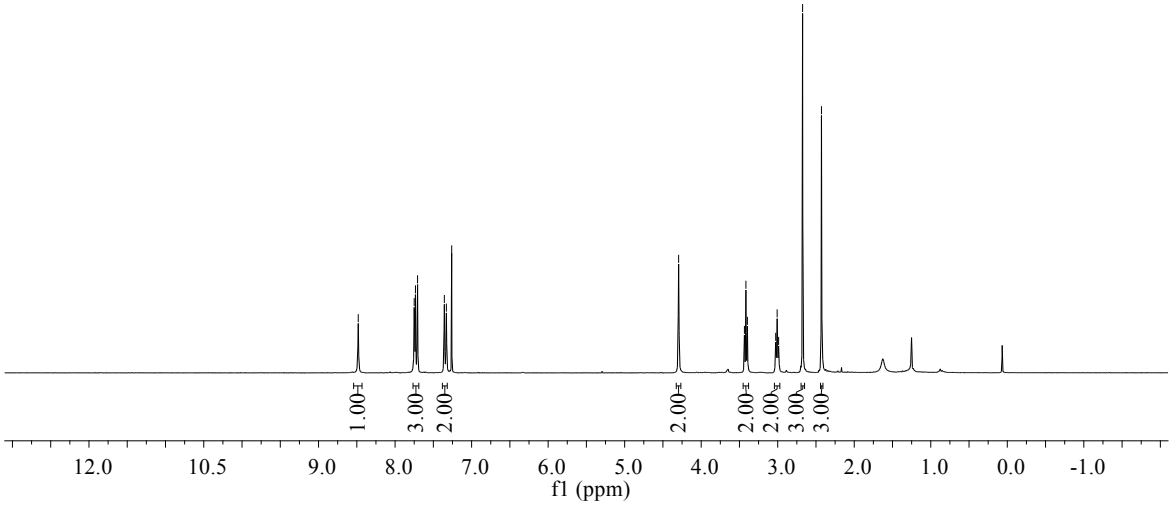
5

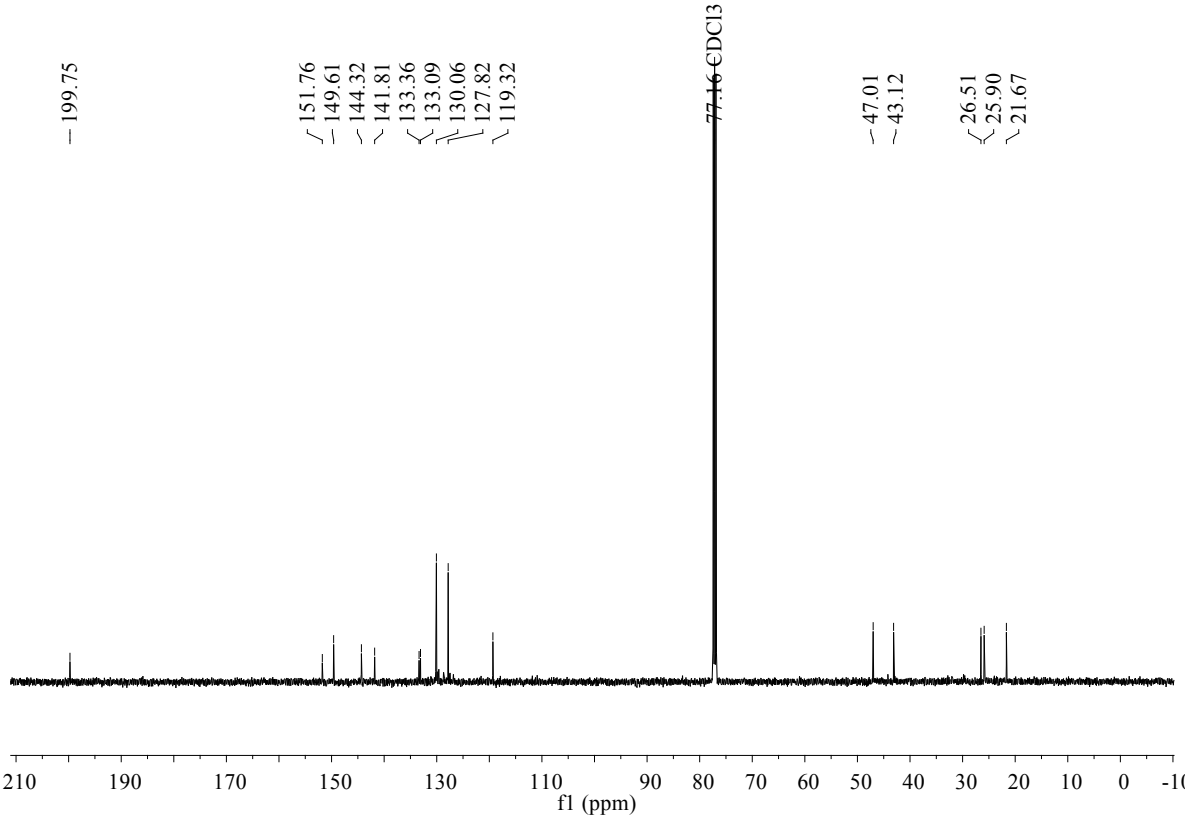

7.68
7.66
7.27
7.26 CDCl3
7.24
6.06
6.05
5.83
5.82
4.39
3.31
3.29
3.26
2.41
2.39
2.38
2.36
2.36
2.13
1.96
1.96
1.95
2.00
2.05
1.00
1.00
2.00
2.00
5.01
3.00
1.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)
152.54
147.44
143.29
136.99
129.58
127.41
110.71
106.36
81.15
77.16 CDCl3
70.16
46.13
44.71
21.57
19.28
13.50
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

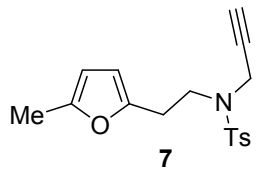

Ts
N
Me
N
O

6

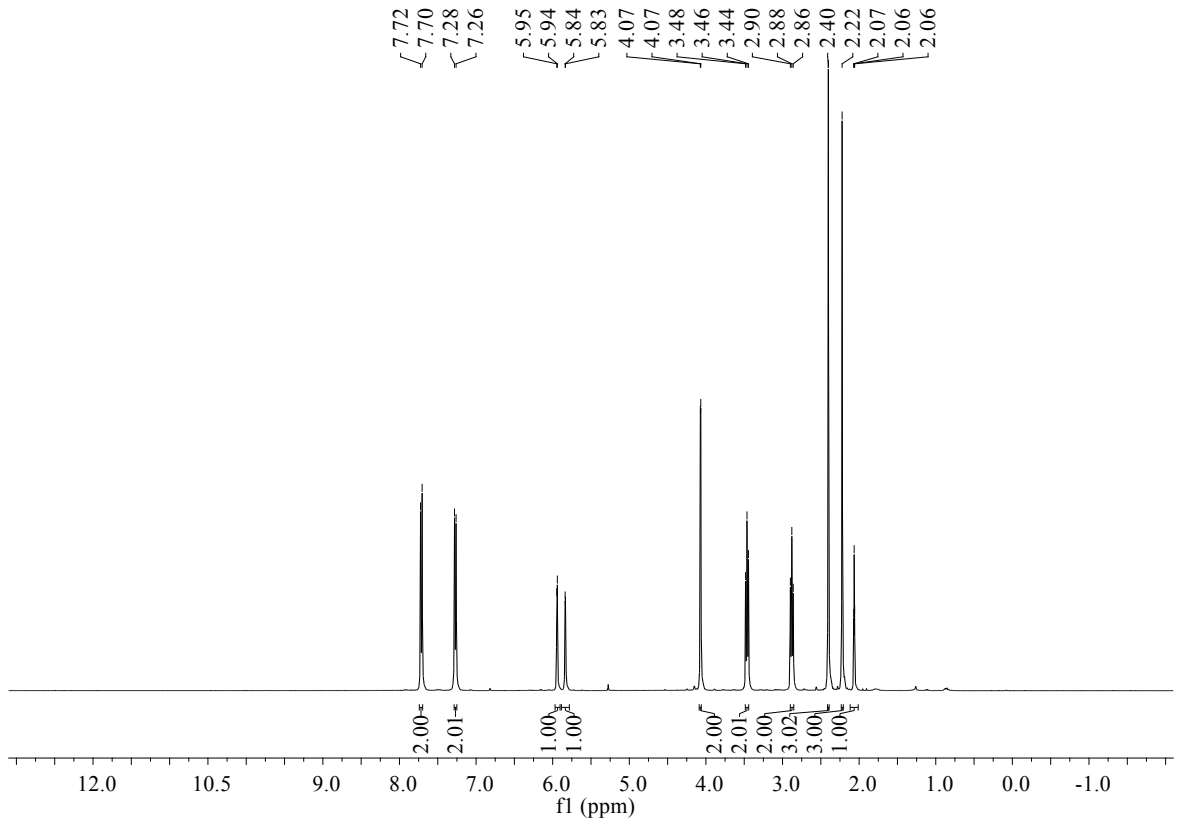

8.48
7.75
7.73
7.71
7.36
7.33
7.26 CDCl3
4.29
3.43
3.42
3.40
3.03
3.01
2.99
2.67
2.43

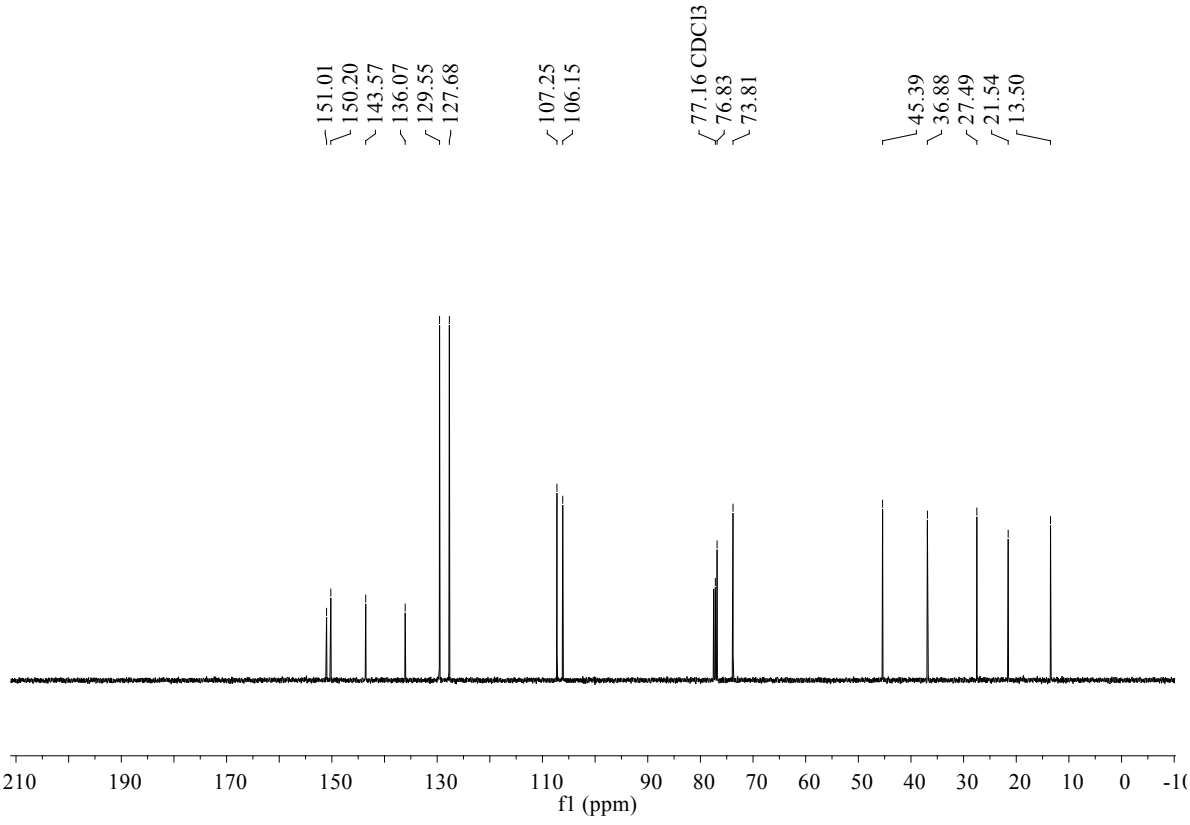

1.00
3.00
2.00
2.00
2.00
2.00
3.00
3.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

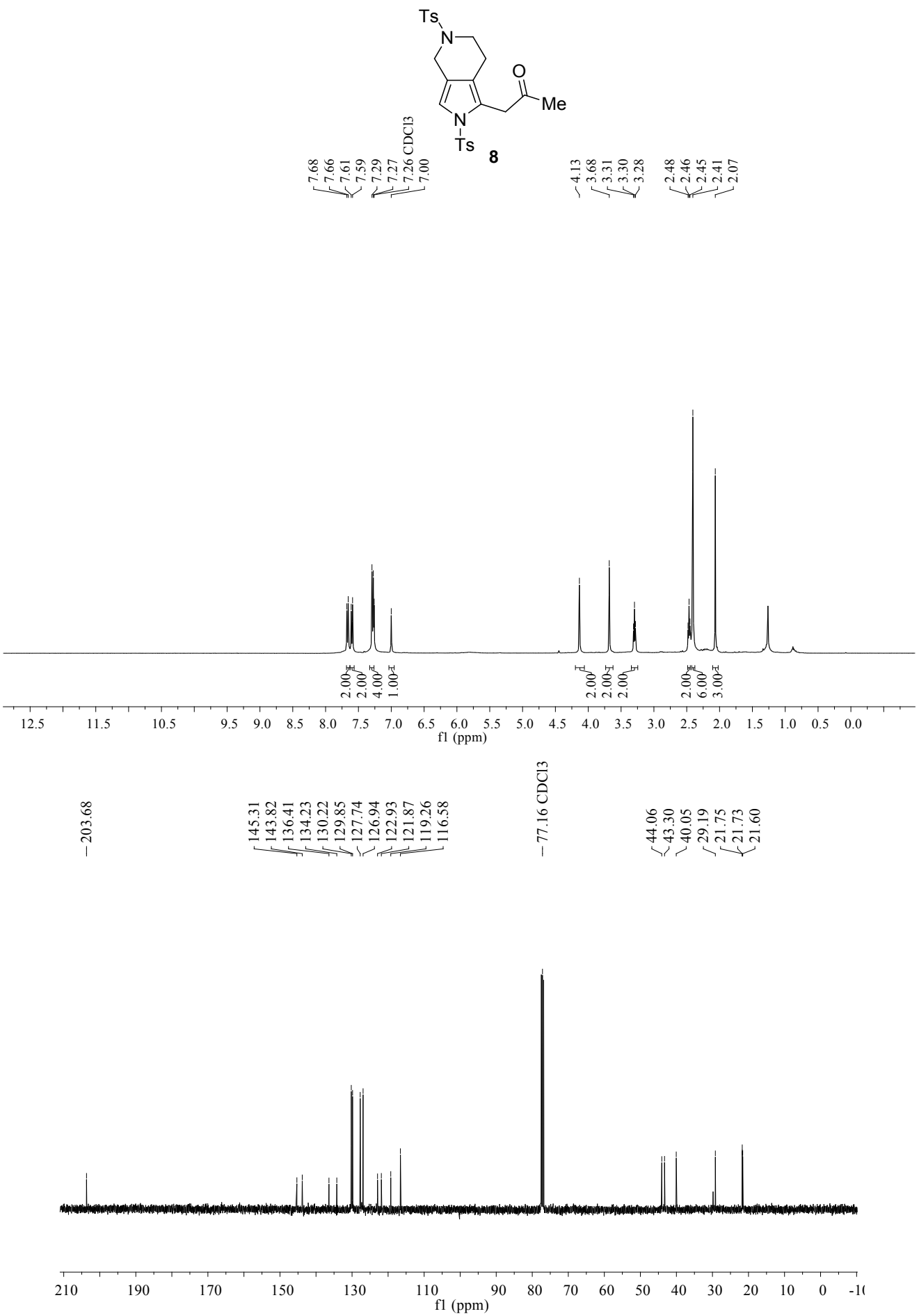

199.75
151.76
149.61
144.32
141.81
133.36
133.09
130.06
127.82
119.32
77.16 CDCl3
47.01
43.12
26.51
25.90
21.67
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

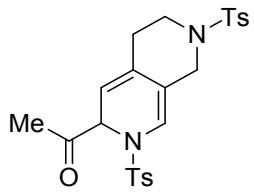

Me
O
N
Ts

7

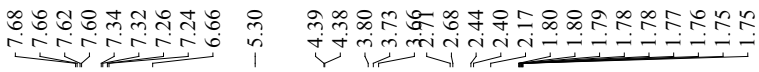

7.72
7.70
7.28
7.26
5.95
5.94
5.84
5.83
4.07
4.07
3.48
3.46
3.44
2.90
2.88
2.86
2.40
2.22
2.07
2.06
2.06
2.00
2.01
1.00
1.00
2.00
2.01
2.00
3.02
3.00
1.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

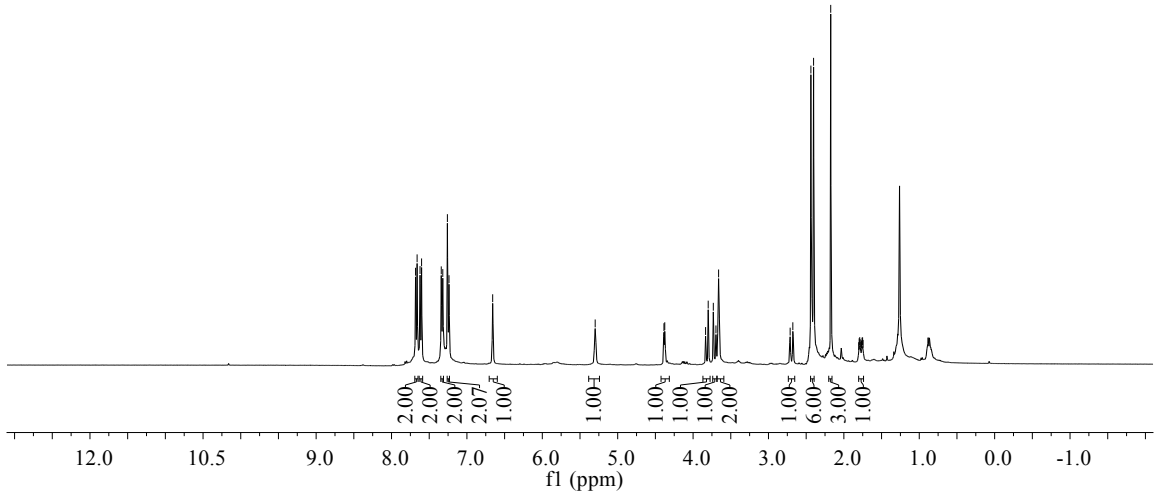

151.01
150.20
143.57
136.07
129.55
127.68
107.25
106.15
77.16 CDCl3
76.83
73.81
45.39
36.88
27.49
21.54
13.50
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

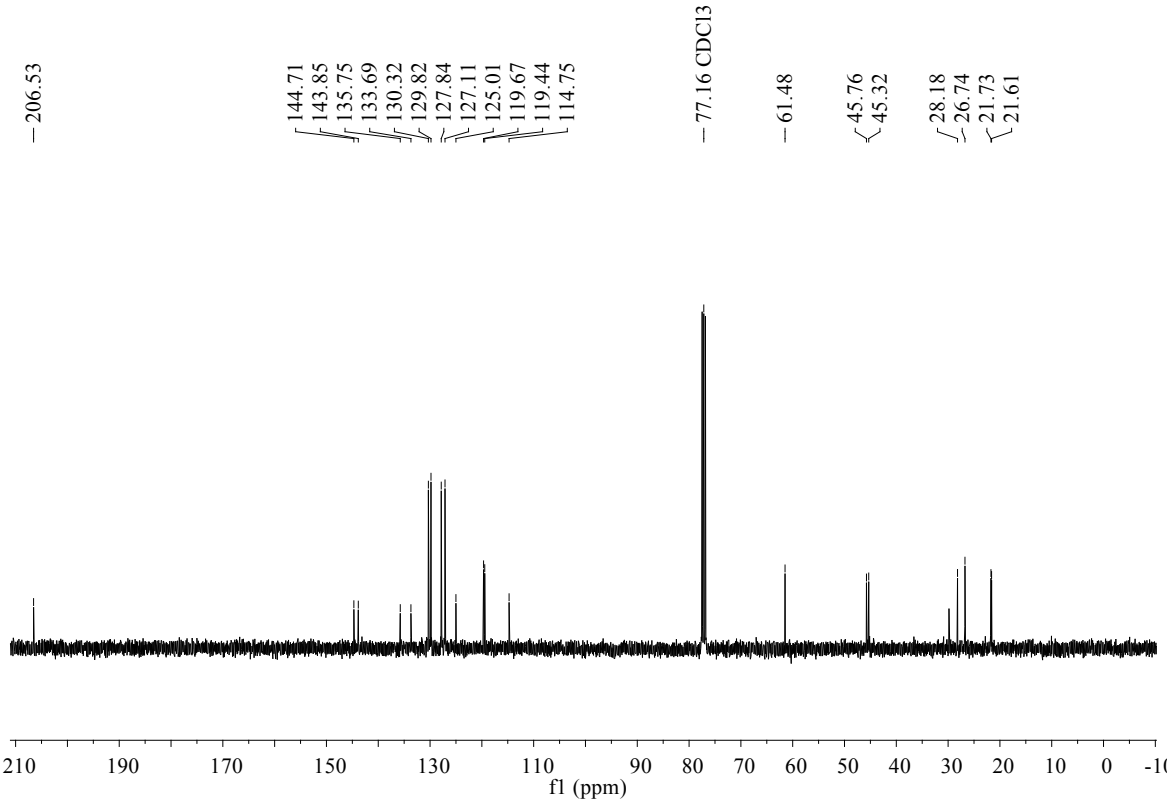

Ts
N
O
Me
N
Ts
8
7.68
7.66
7.61
7.59
7.29
7.27
7.26 CDCl3
7.00
4.13
3.68
3.31
3.30
3.28
2.48
2.46
2.45
2.41
2.07
2.00
2.00
4.00
1.00
2.00
2.00
2.00
2.00
6.00
3.00
f1 (ppm)
203.68
145.31
143.82
136.41
134.23
130.22
129.85
127.74
126.94
122.93
121.87
119.26
116.58
77.16 CDCl3
44.06
43.30
40.05
29.19
21.75
21.73
21.60
f1 (ppm)

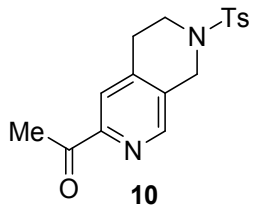

Me
O
N
Ts
N
Ts

9

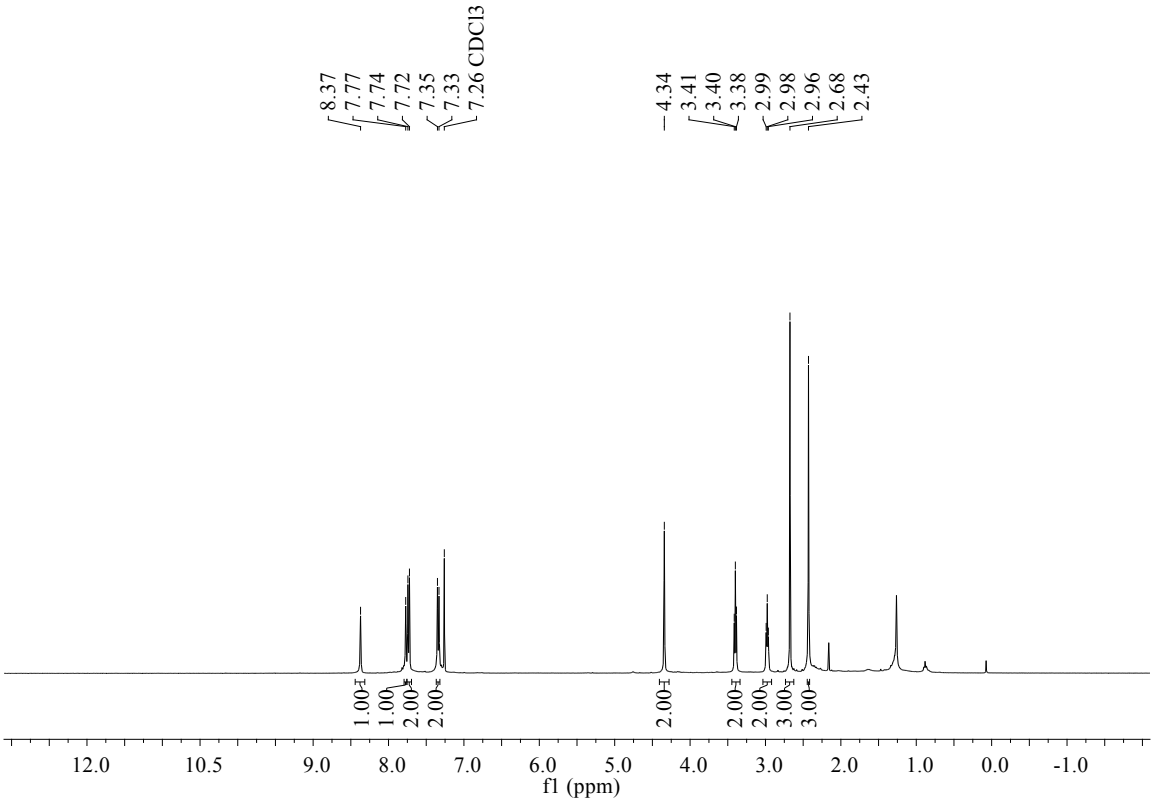

7.68
7.66
7.62
7.60
7.34
7.32
7.26
7.24
6.66
5.30
4.39
4.38
3.80
3.73
2.68
2.44
2.40
2.17
1.80
1.80
1.79
1.78
1.78
1.77
1.76
1.75
1.75

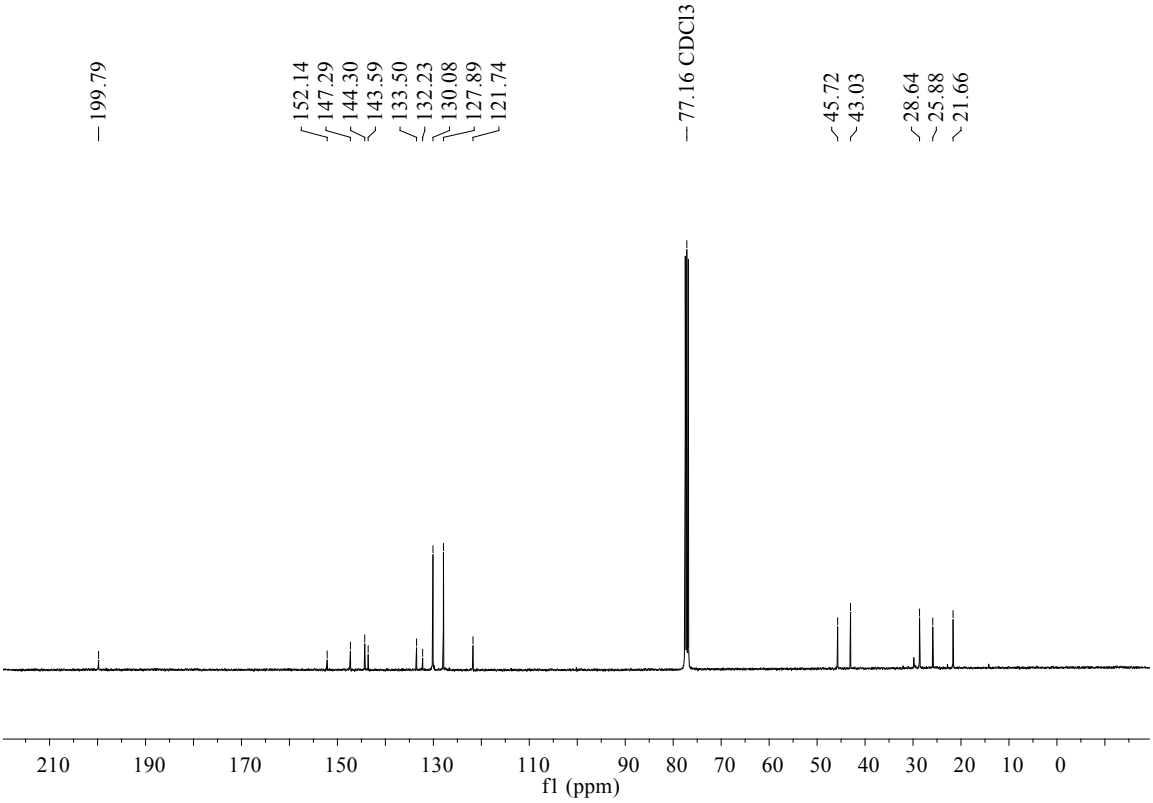

2.00
2.00
2.00
2.07
1.00
1.00
1.00
1.00
1.00
2.00
1.00
6.00
3.00
1.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

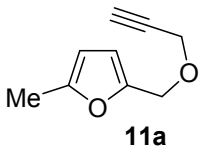

206.53
144.71
143.85
135.75
133.69
130.32
129.82
127.84
127.11
125.01
119.67
119.44
114.75
77.16 CDCl3
61.48
45.76
45.32
28.18
26.74
21.73
21.61
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ts
N
Me
N
O

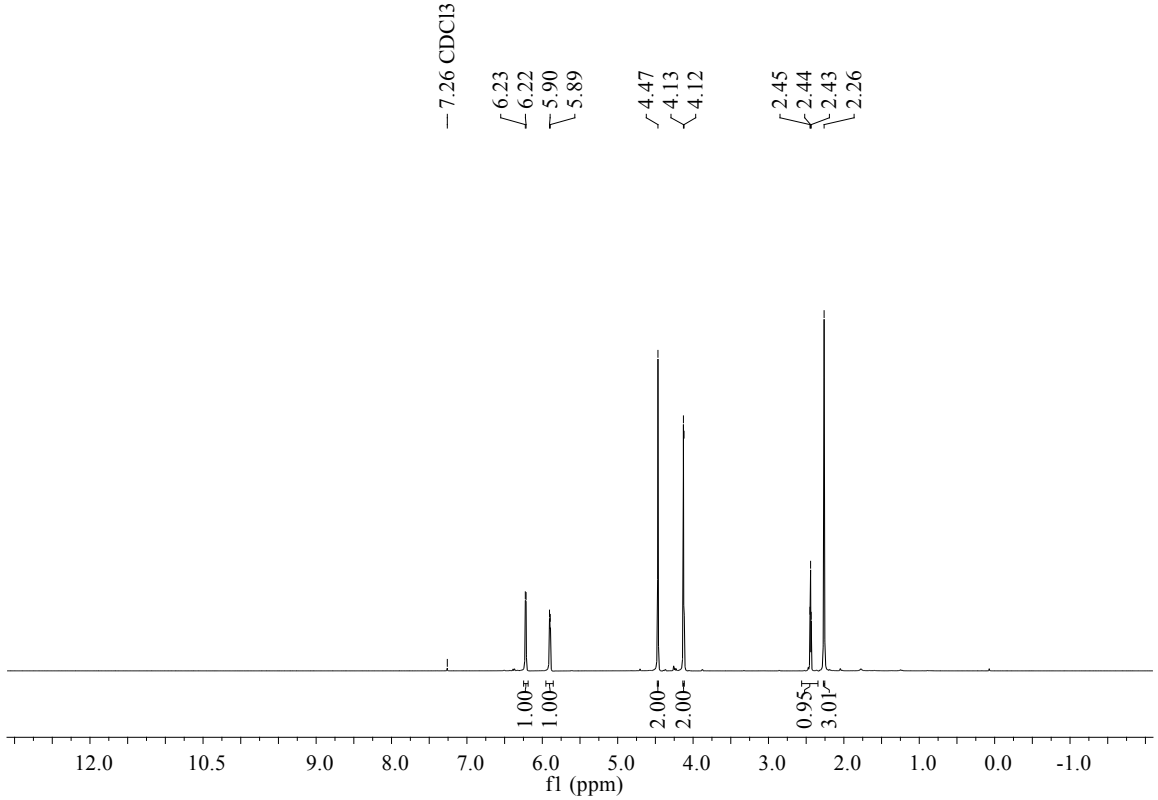
10

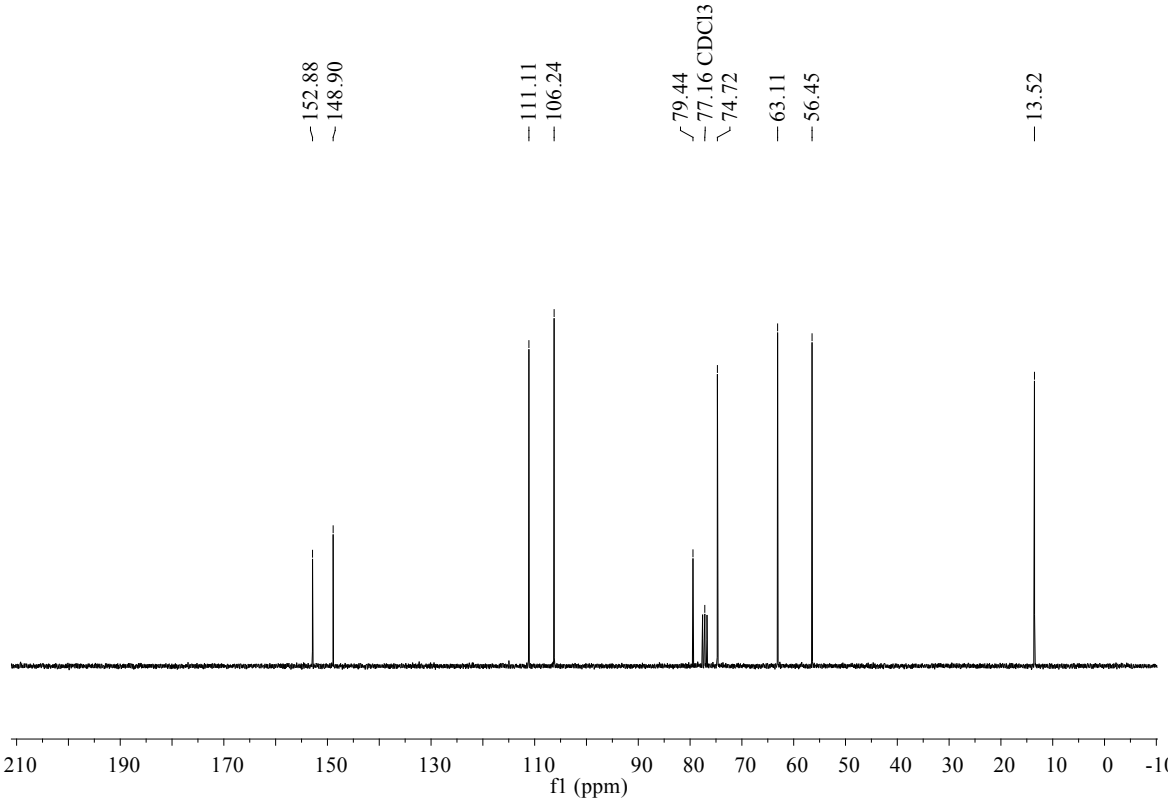

8.37
7.77
7.74
7.72
7.35
7.33
7.26 CDCl3
4.34
3.41
3.40
3.38
2.99
2.98
2.96
2.68
2.43
1.00
1.00
2.00
2.00
2.00
2.00
3.00
3.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

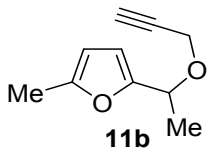

199.79
152.14
147.29
144.30
143.59
133.50
132.23
130.08
127.89
121.74
77.16 CDCl3
45.72
43.03
28.64
25.88
21.66
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
O
O

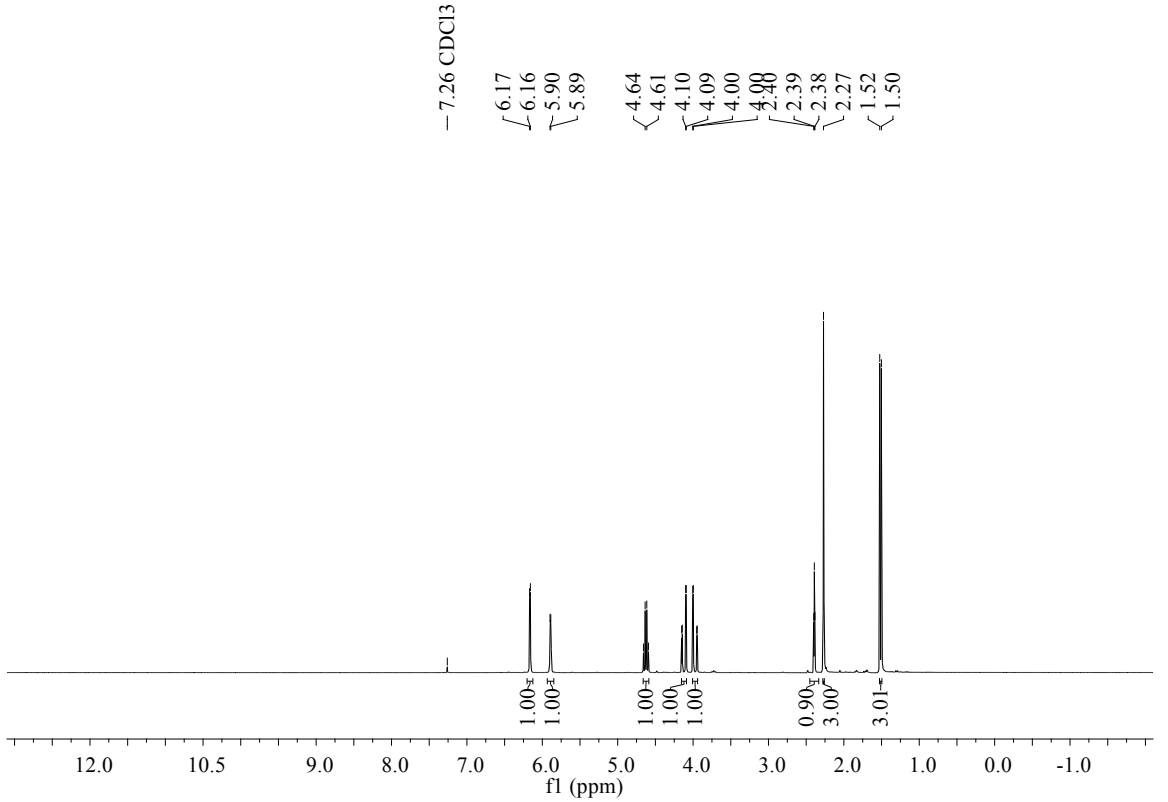
11a

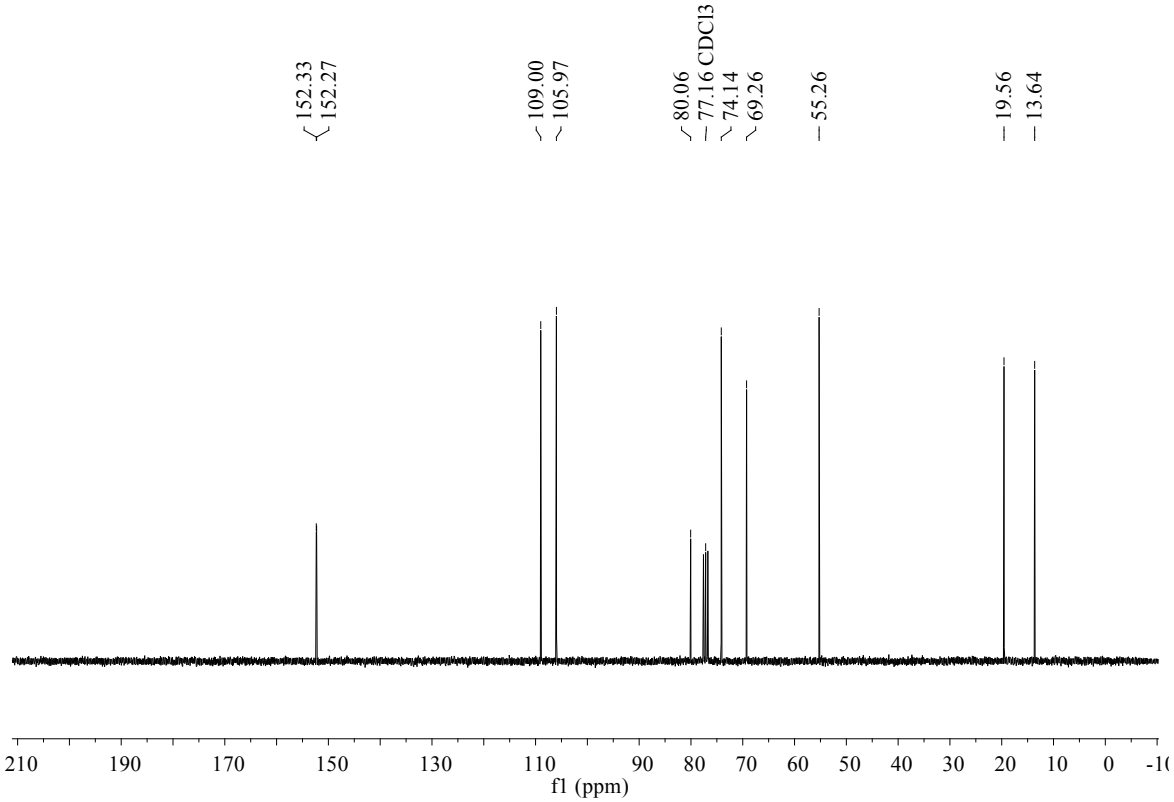

7.26 CDCl3
6.23
6.22
5.90
5.89
4.47
4.13
4.12
2.45
2.44
2.43
2.26
1.00
1.00
2.00
2.00
0.95
3.01
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

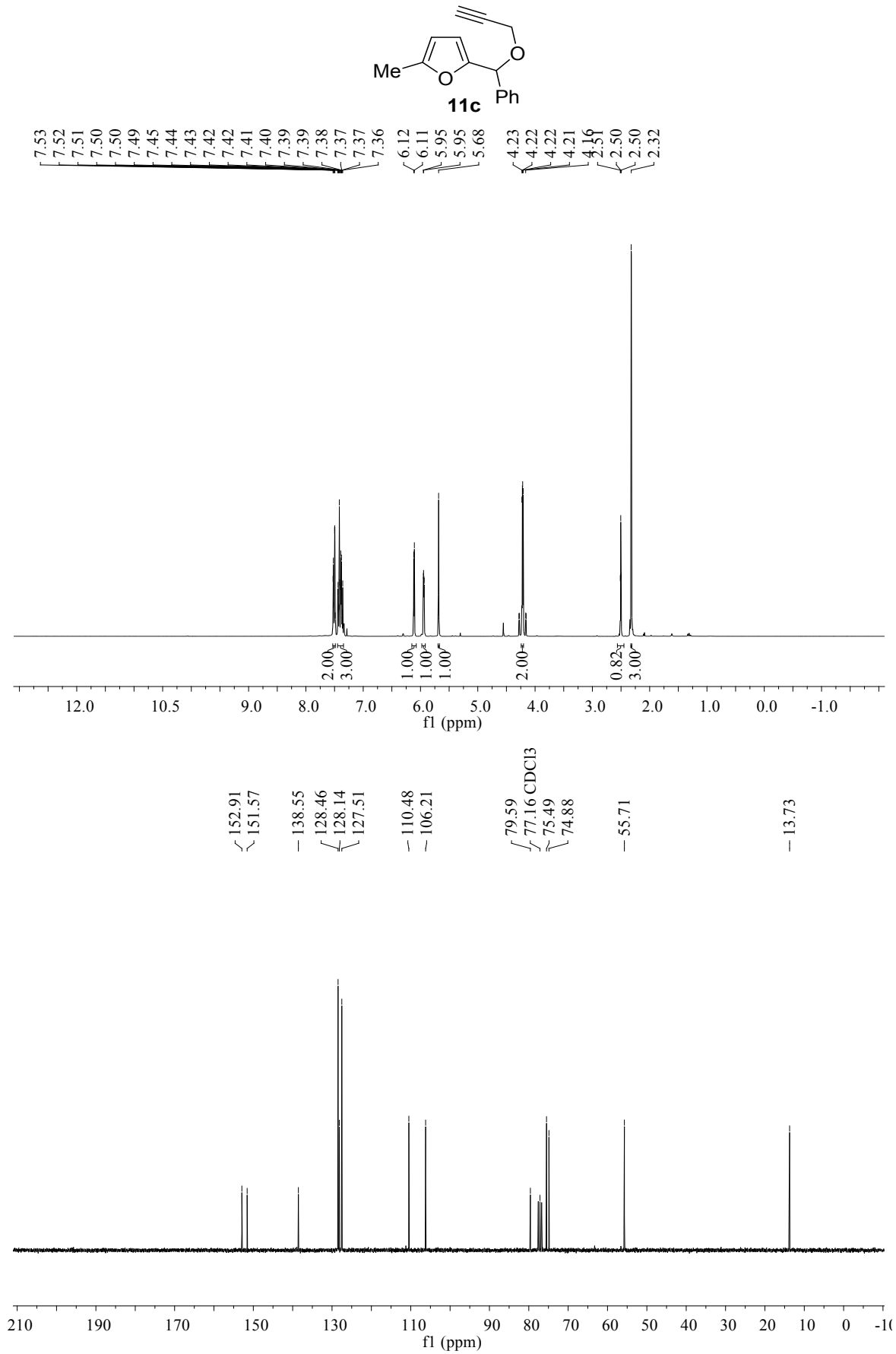

152.88
148.90
111.11
106.24
79.44
77.16 CDCl3
74.72
63.11
56.45
13.52
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

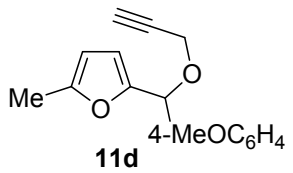

Me
O
O
Me

11b

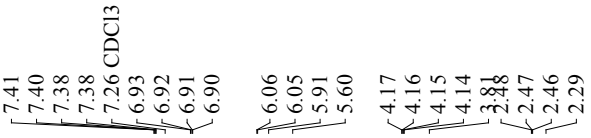

7.26 CDCl3
6.17
6.16
5.90
5.89
4.64
4.61
4.10
4.09
4.00
2.39
2.38
2.27
1.52
1.50
1.00
1.00
1.00
1.00
1.00
0.90
3.00
3.01
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

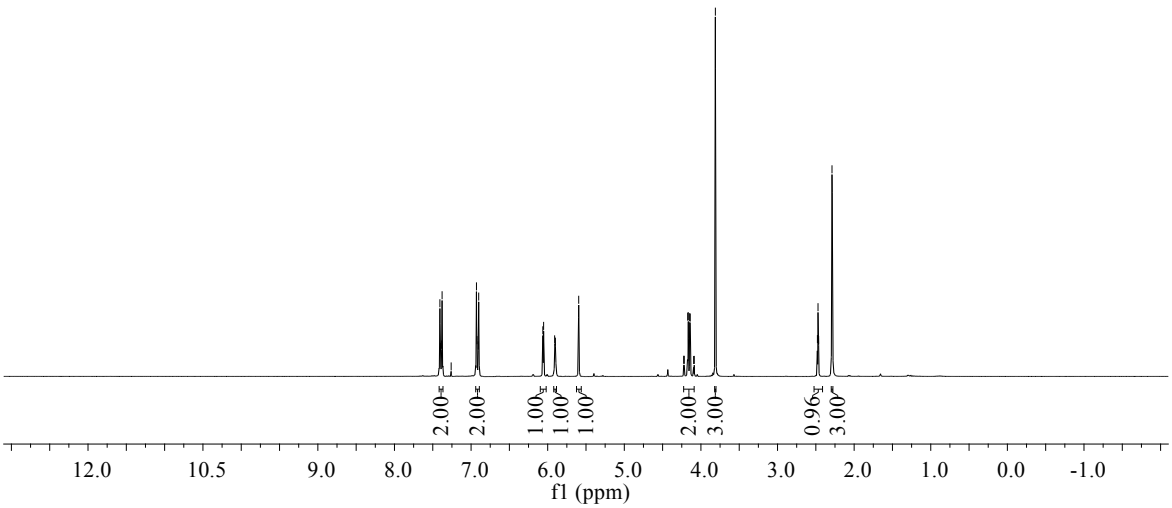

152.33
152.27
109.00
105.97
80.06
77.16 CDCl3
74.14
69.26
55.26
19.56
13.64
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

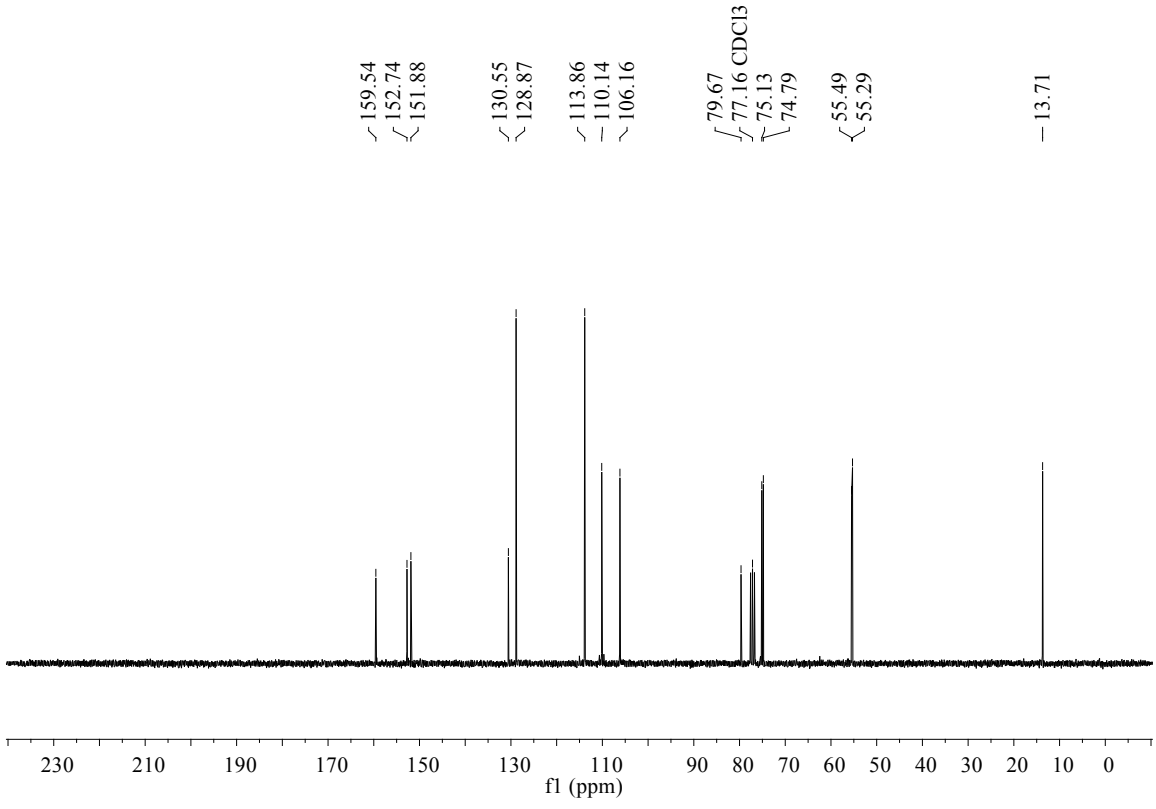

Me
O
O
Ph
11c
7.53
7.52
7.51
7.50
7.50
7.49
7.45
7.44
7.43
7.42
7.42
7.41
7.40
7.39
7.39
7.38
7.37
7.37
7.36
6.12
6.11
5.95
5.95
5.68
4.23
4.22
4.22
4.21
4.16
2.51
2.50
2.50
2.32
2.00
3.00
1.00
1.00
1.00
2.00
0.82
3.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)
152.91
151.57
138.55
128.46
128.14
127.51
110.48
106.21
79.59
77.16 CDCl3
75.49
74.88
55.71
13.73
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

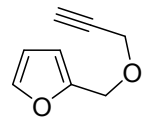

Me
O
O
4-MeOC6H4

11d

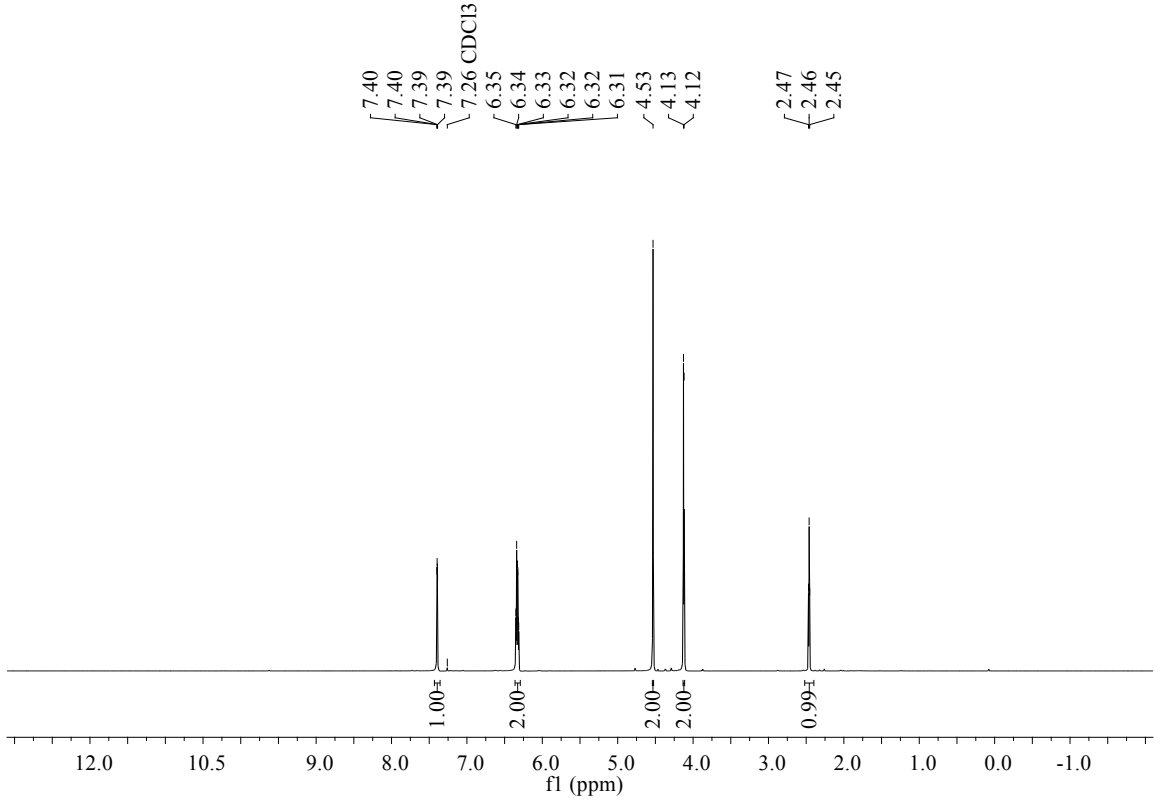

7.41
7.40
7.38
7.38
7.26 CDCl3
6.93
6.92
6.91
6.90
6.06
6.05
5.91
5.60
4.17
4.16
4.15
4.14
3.81
2.48
2.47
2.46
2.29

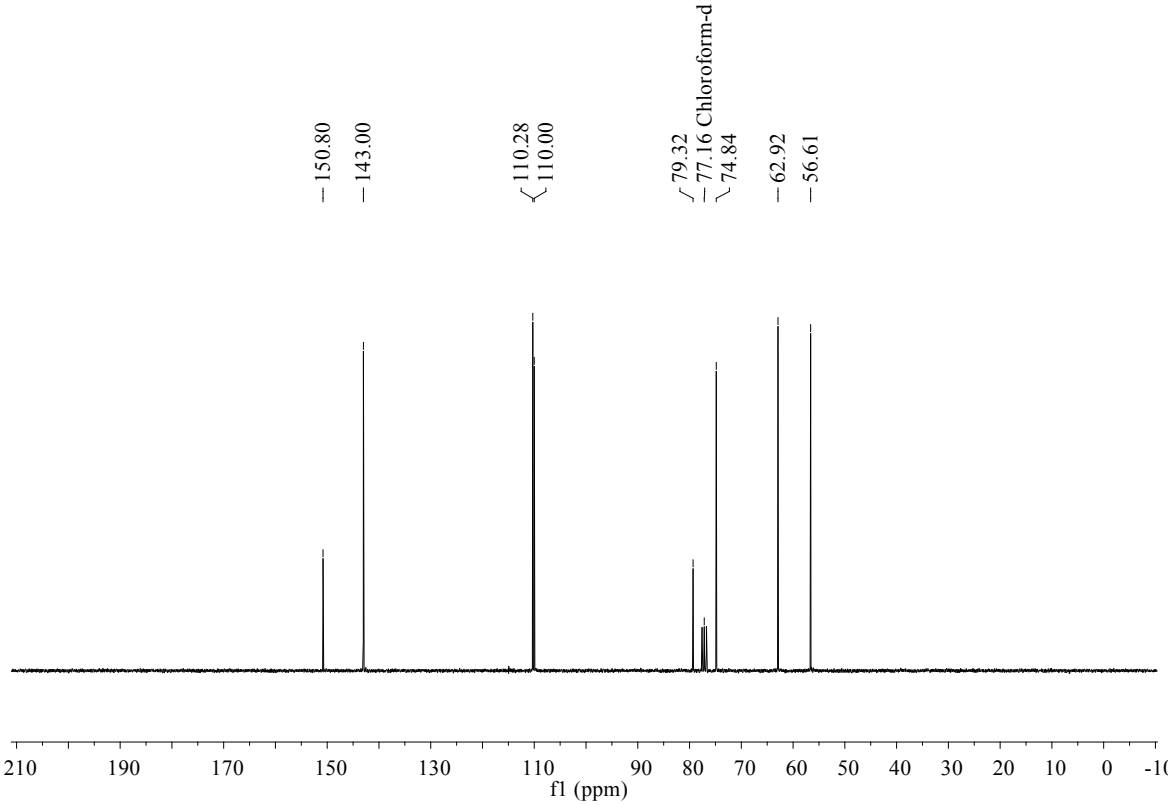

2.00
2.00
1.00
1.00
1.00
2.00
3.00
0.96
3.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

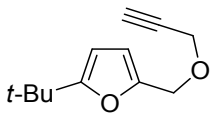

159.54
152.74
151.88
130.55
128.87
113.86
110.14
106.16
79.67
77.16 CDCl3
75.13
74.79
55.49
55.29
13.71
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



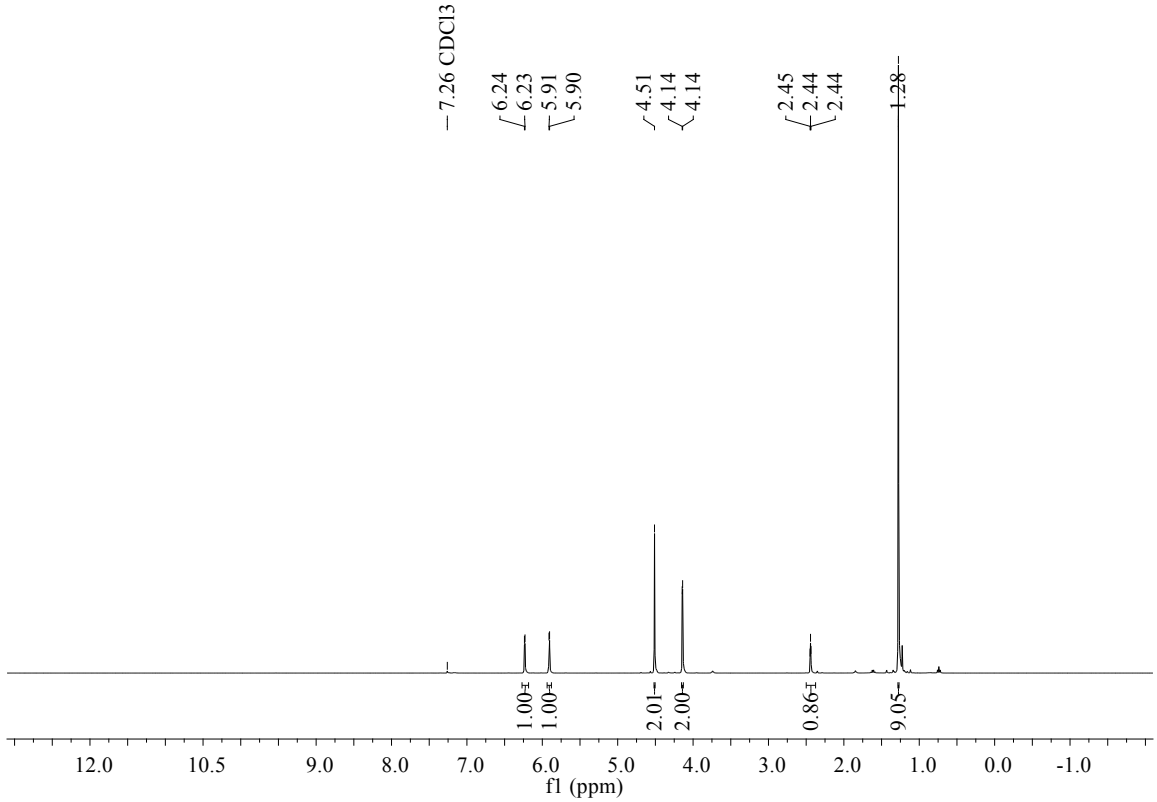
11e

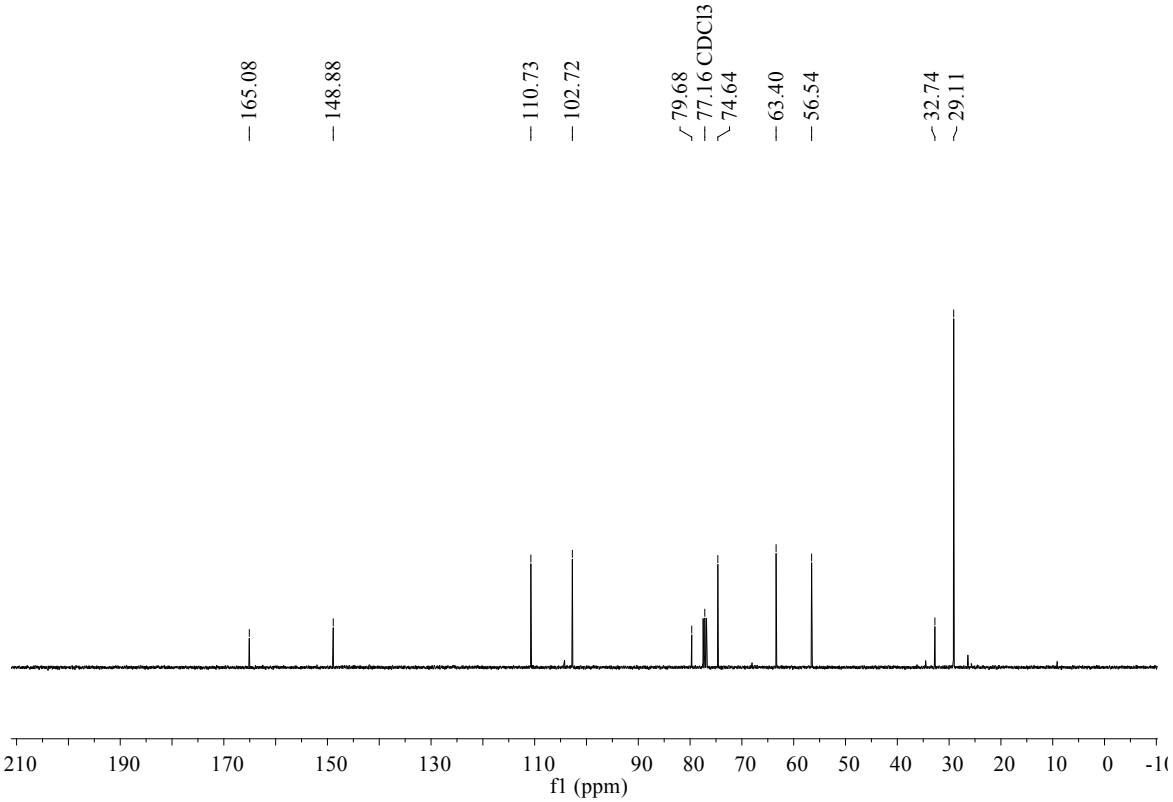

7.40
7.40
7.39
7.39
7.26 CDCl3
6.35
6.34
6.33
6.32
6.32
6.31
4.53
4.13
4.12
2.47
2.46
2.45
1.00
2.00
2.00
2.00
0.99
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

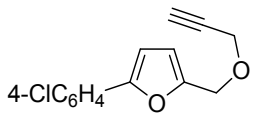

150.80
143.00
110.28
110.00
79.32
77.16 Chloroform-d
74.84
62.92
56.61
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


t-Bu
O
O

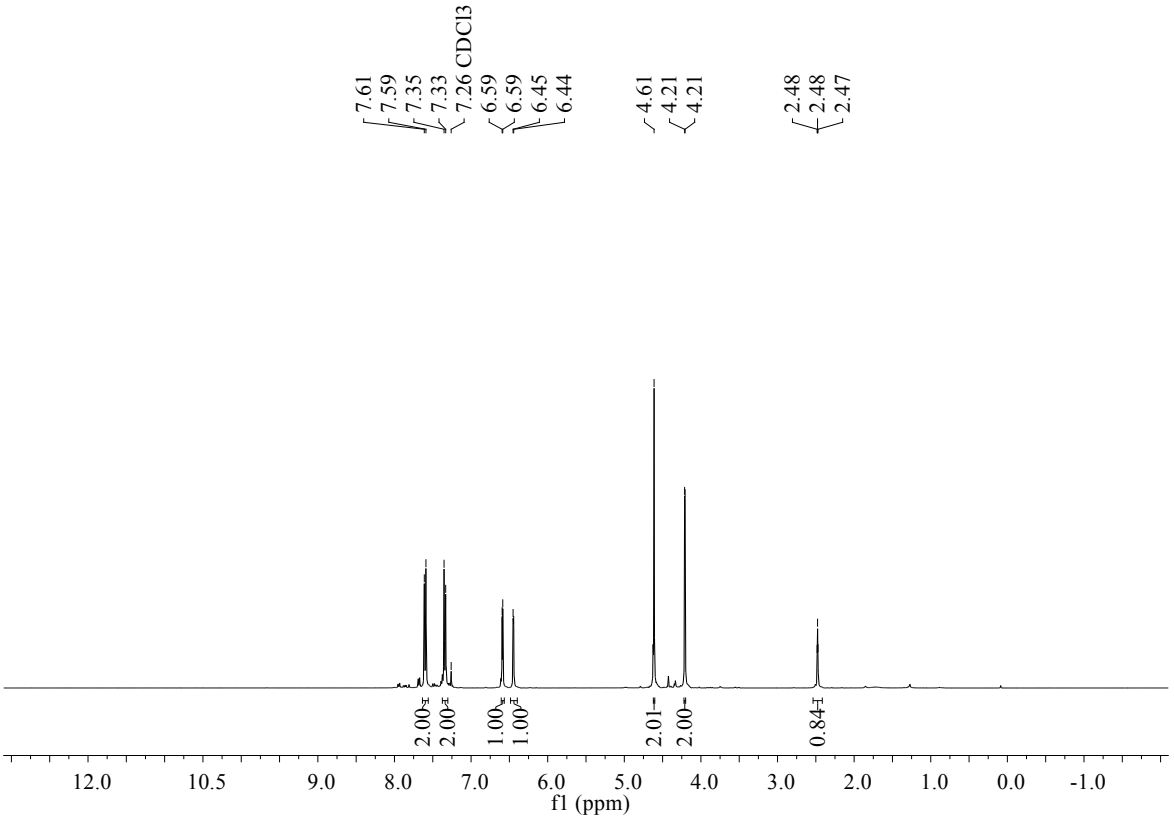
11f

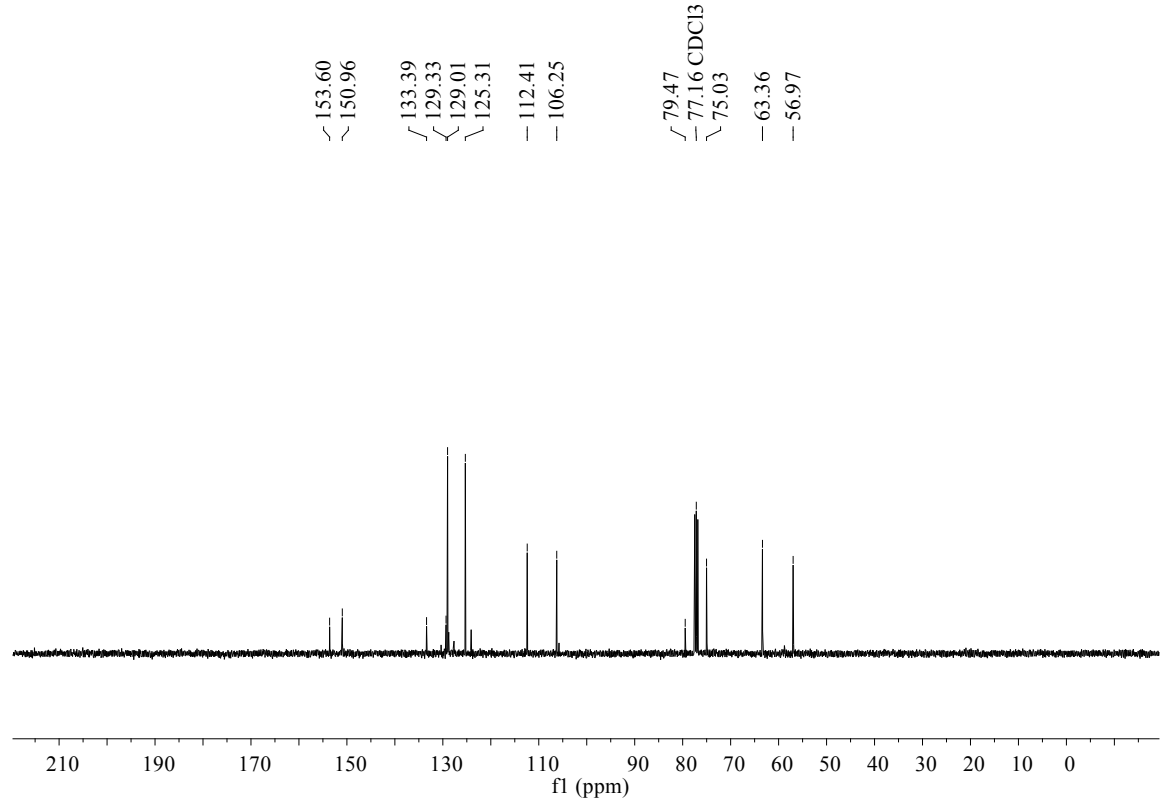

7.26 CDCl3
6.24
6.23
5.91
5.90
4.51
4.14
4.14
2.45
2.44
2.44
1.28
1.00
1.00
2.01
2.00
0.86
9.05
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

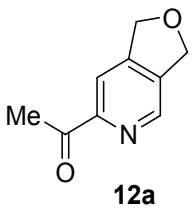

165.08
148.88
110.73
102.72
79.68
77.16 CDCl3
74.64
63.40
56.54
32.74
29.11
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


4-ClC6H4
O
O

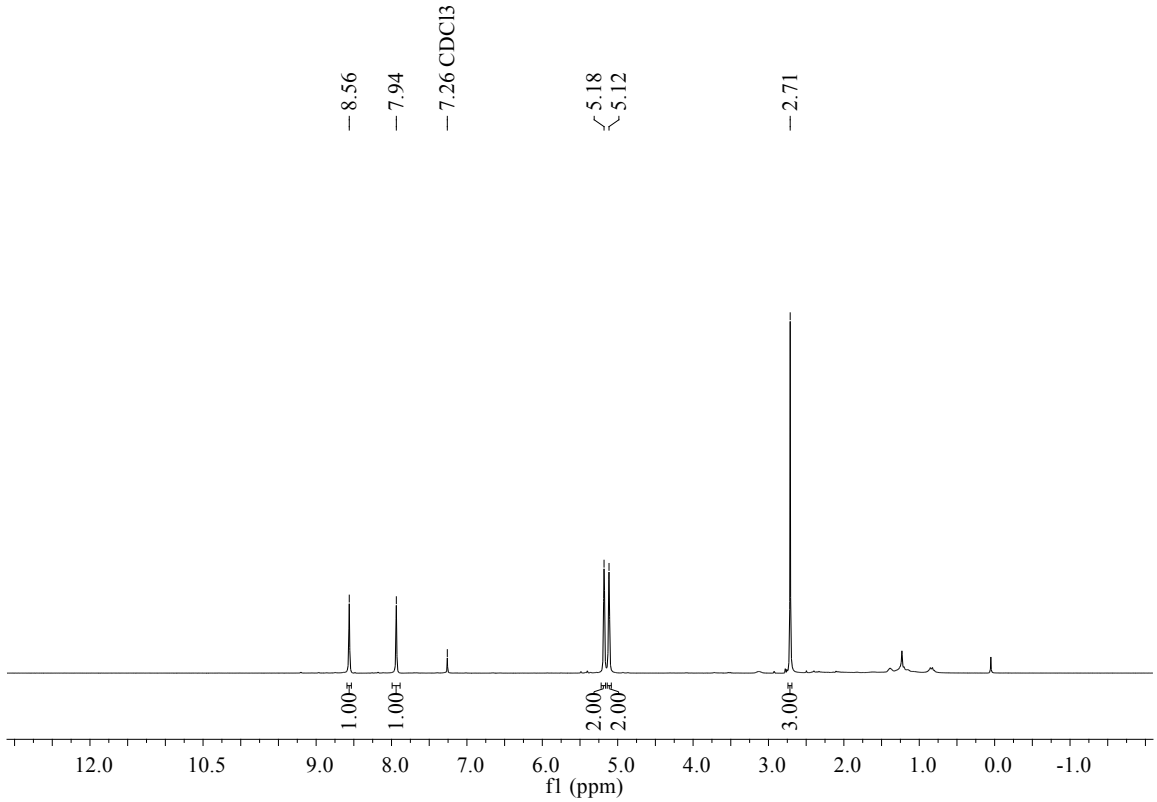
11g

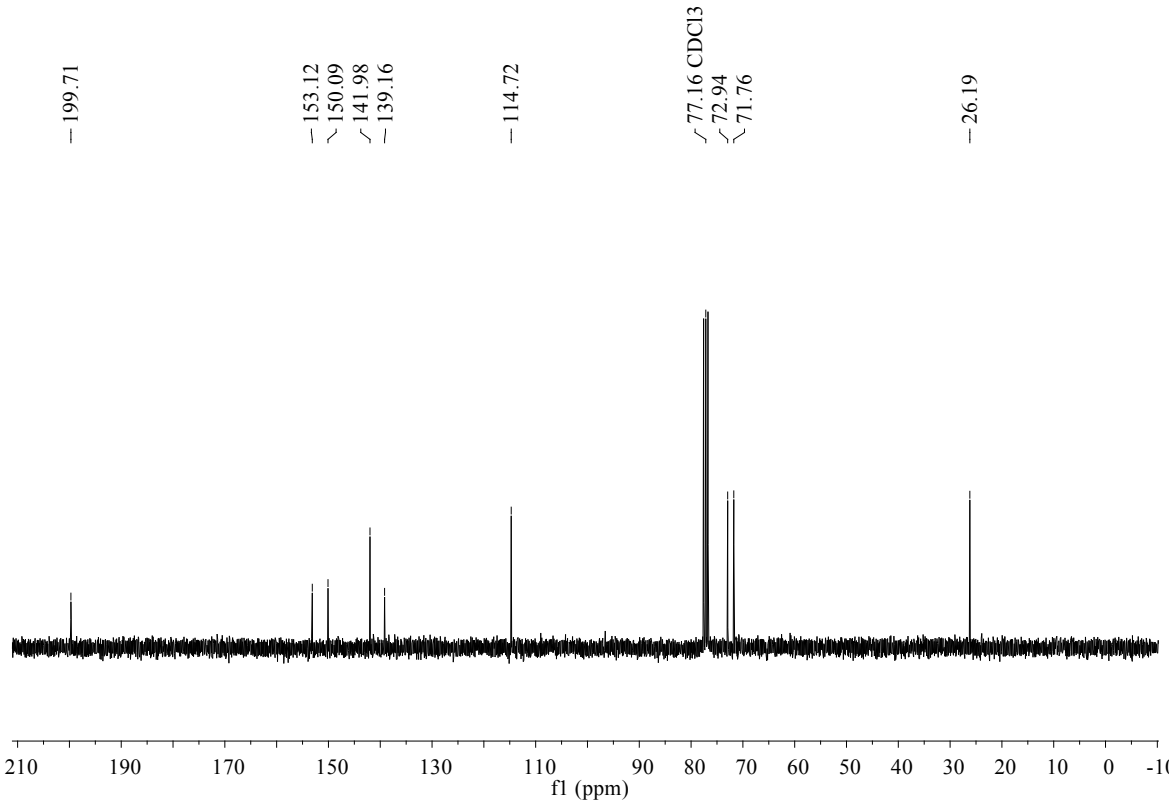

7.61
7.59
7.35
7.33
7.26 CDCl3
6.59
6.59
6.45
6.44
4.61
4.21
4.21
2.48
2.48
2.47
2.00
2.00
1.00
1.00
2.01
2.00
0.84
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

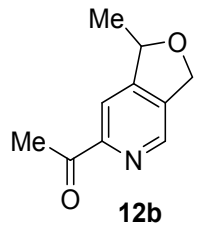

153.60
150.96
133.39
129.33
129.01
125.31
112.41
106.25
79.47
77.16 CDCl3
75.03
63.36
56.97
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
O
N
O

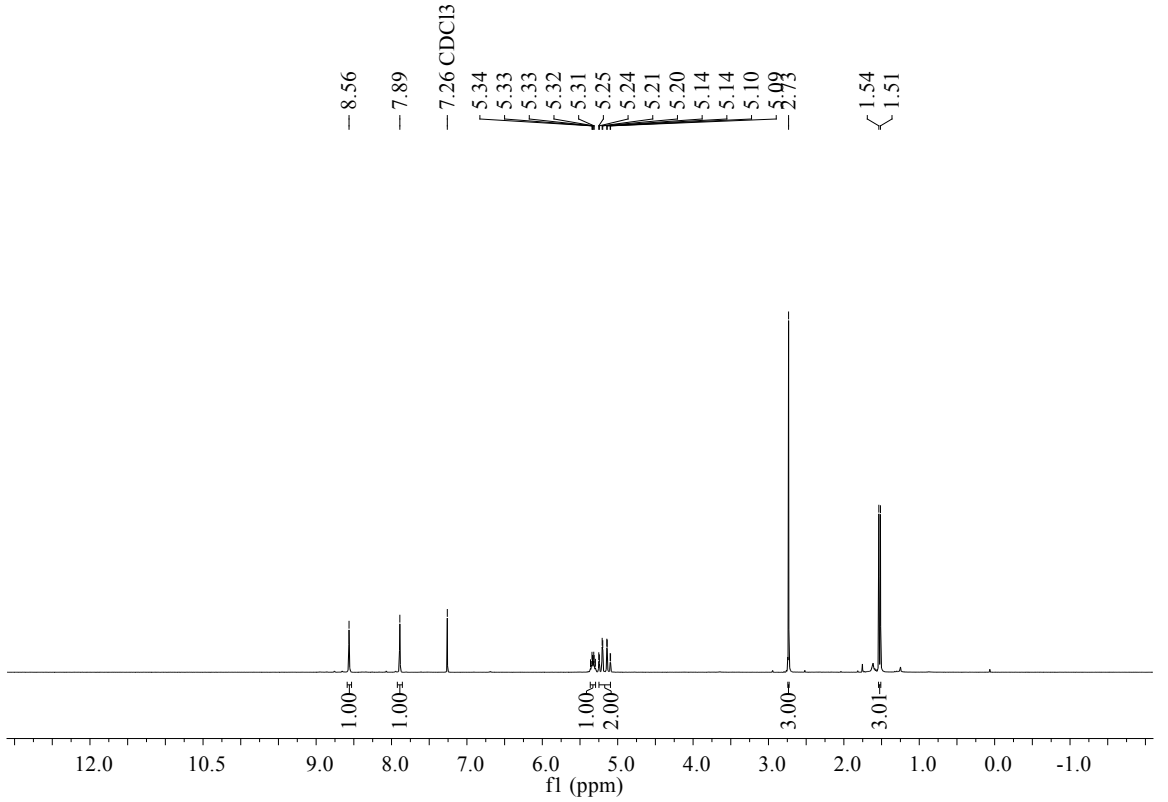
12a

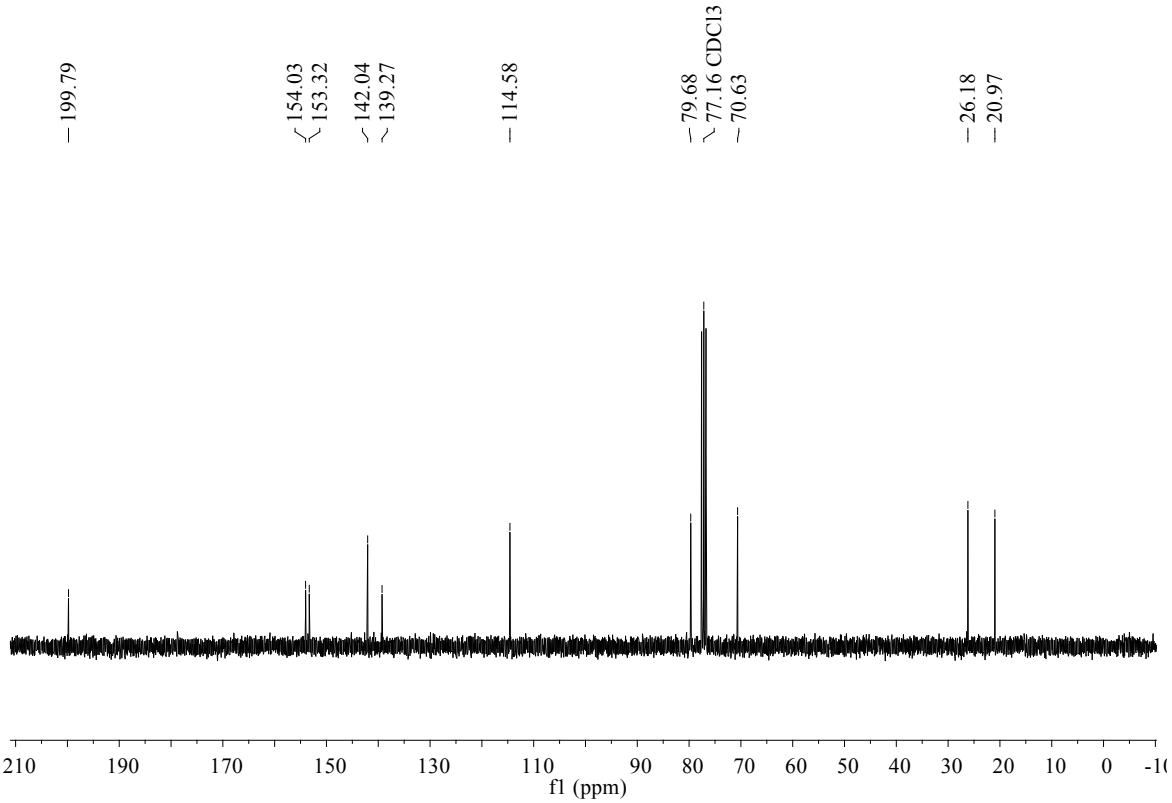

8.56
7.94
7.26 CDCl3
5.18
5.12
2.71
1.00
1.00
2.00
2.00
3.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

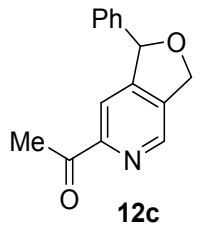

199.71
153.12
150.09
141.98
139.16
114.72
77.16 CDCl3
72.94
71.76
26.19
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
O
Me
N
O

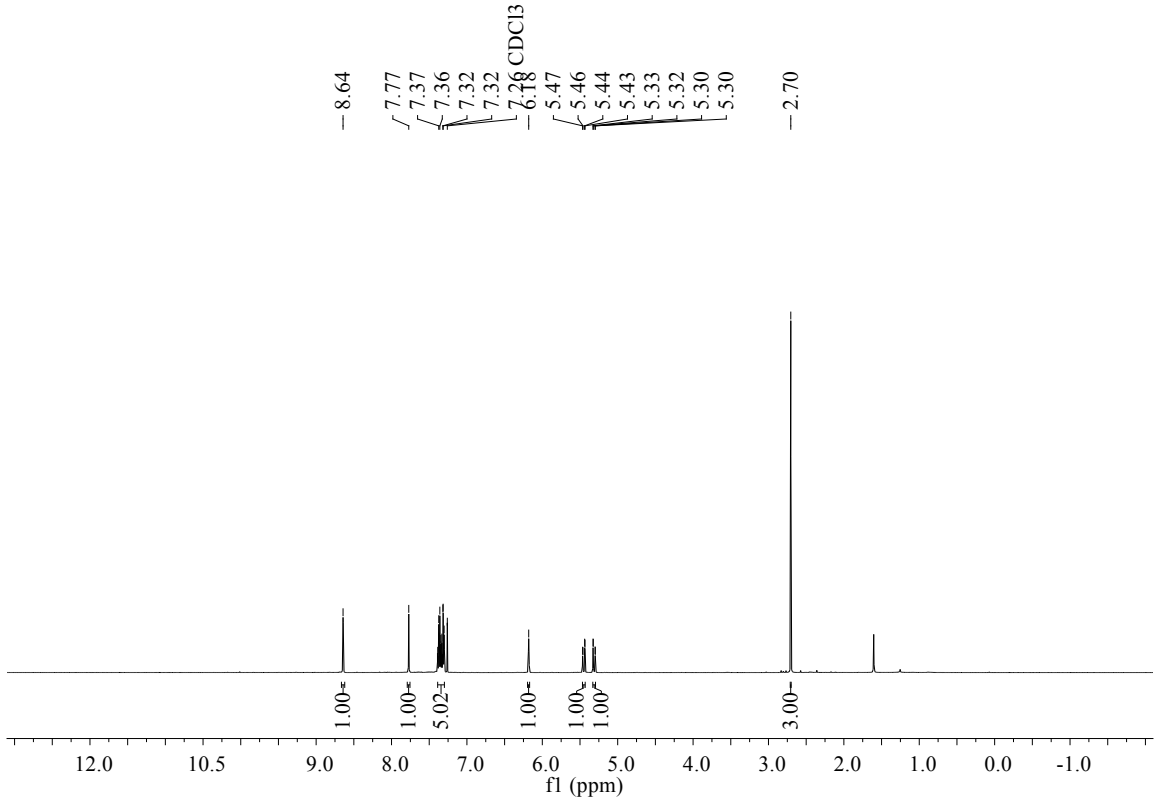
12b

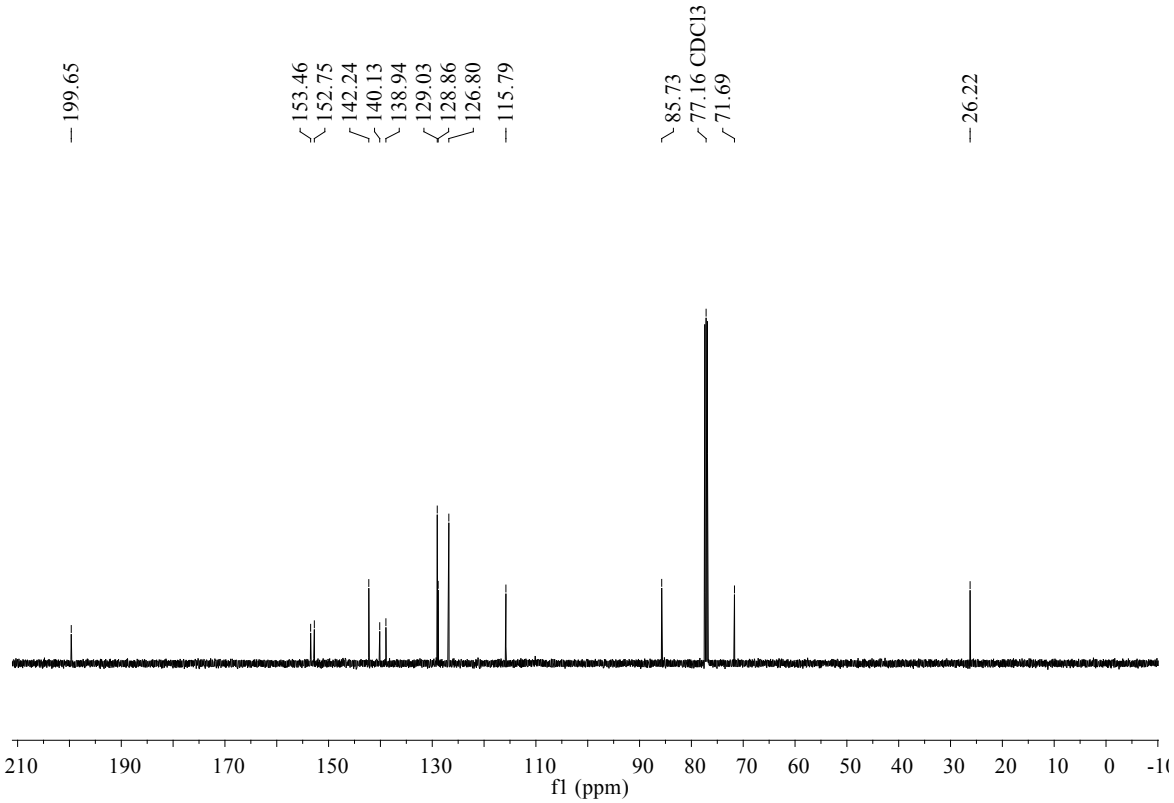

8.56
7.89
7.26 CDCl3
5.34
5.33
5.33
5.32
5.31
5.25
5.24
5.21
5.20
5.14
5.14
5.10
5.09
2.73
1.54
1.51
1.00
1.00
1.00
2.00
3.00
3.01
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

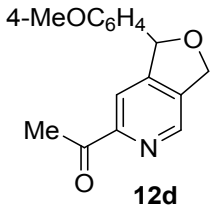

199.79
154.03
153.32
142.04
139.27
114.58
79.68
77.16 CDCl3
70.63
26.18
20.97
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ph
O
Me
N
O

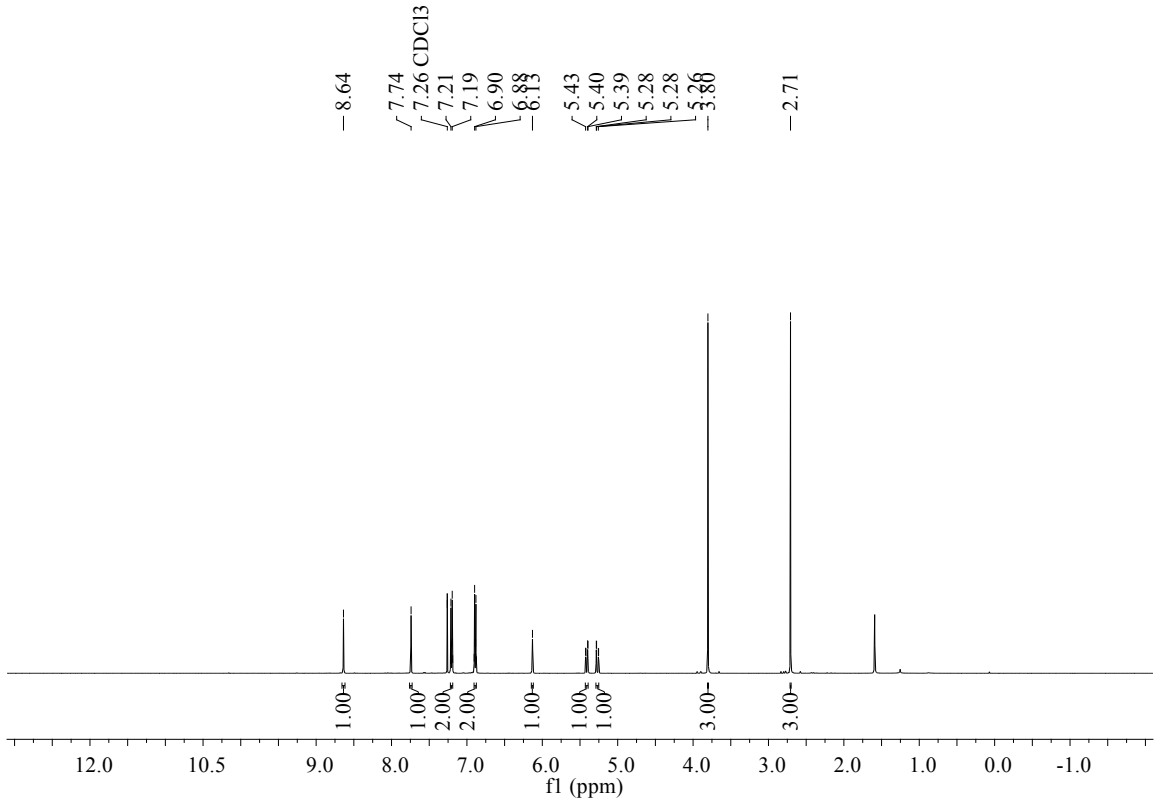
12c

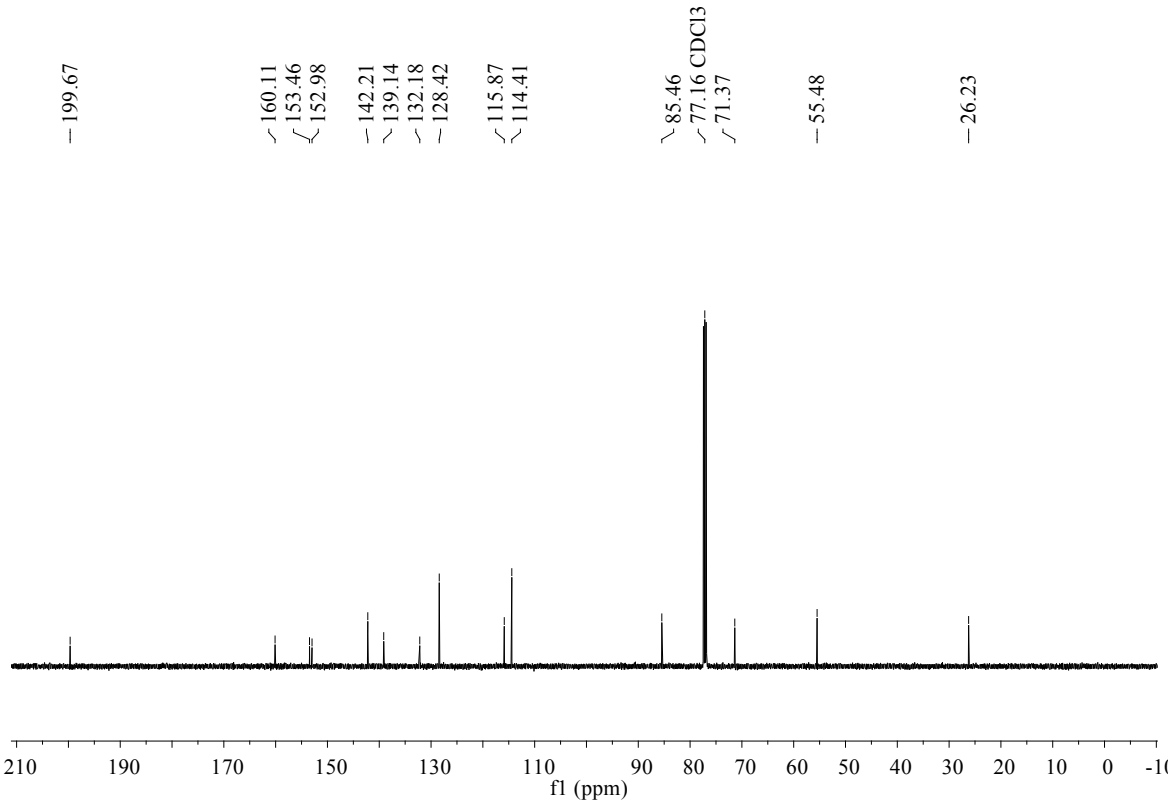

8.64
7.77
7.37
7.36
7.32
7.32
7.26 CDCl3
6.18
5.47
5.46
5.44
5.43
5.33
5.32
5.30
5.30
2.70
1.00
1.00
5.02
1.00
1.00
1.00
3.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

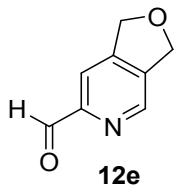

199.65
153.46
152.75
142.24
140.13
138.94
129.03
128.86
126.80
115.79
85.73
77.16 CDCl3
71.69
26.22
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


4-MeOC6H4
O
Me
N
O

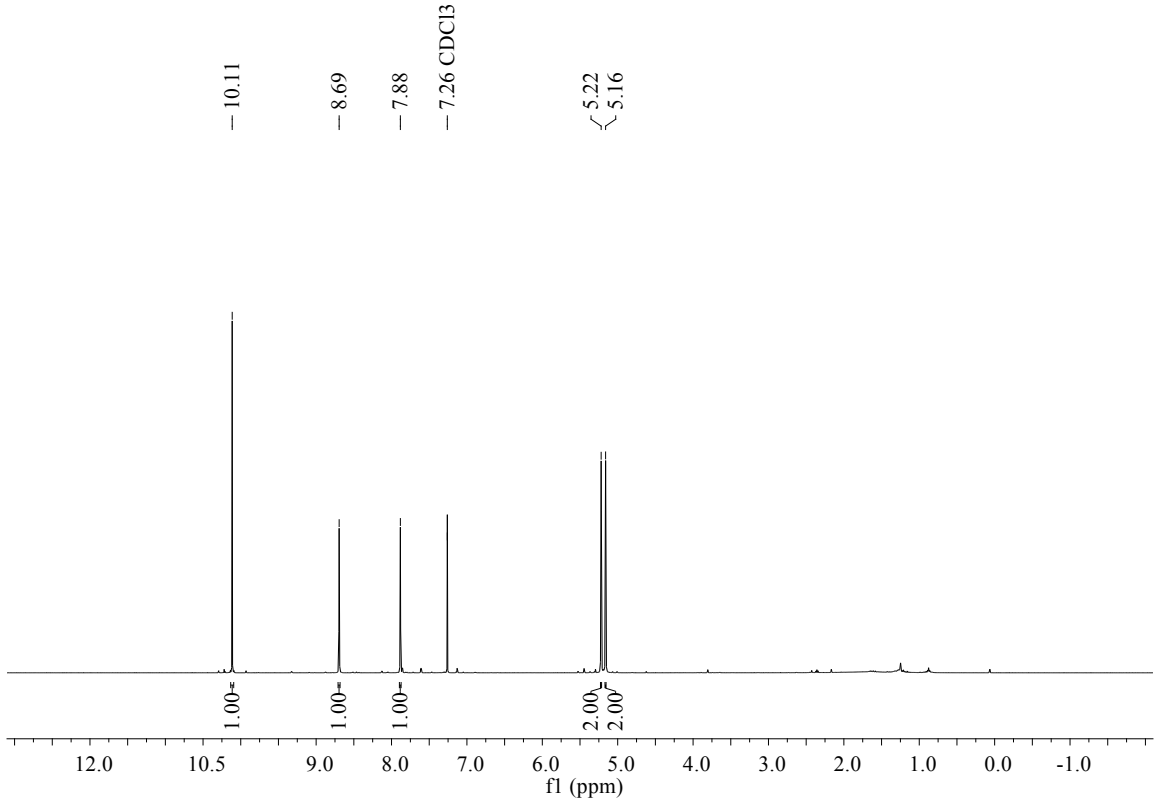
12d

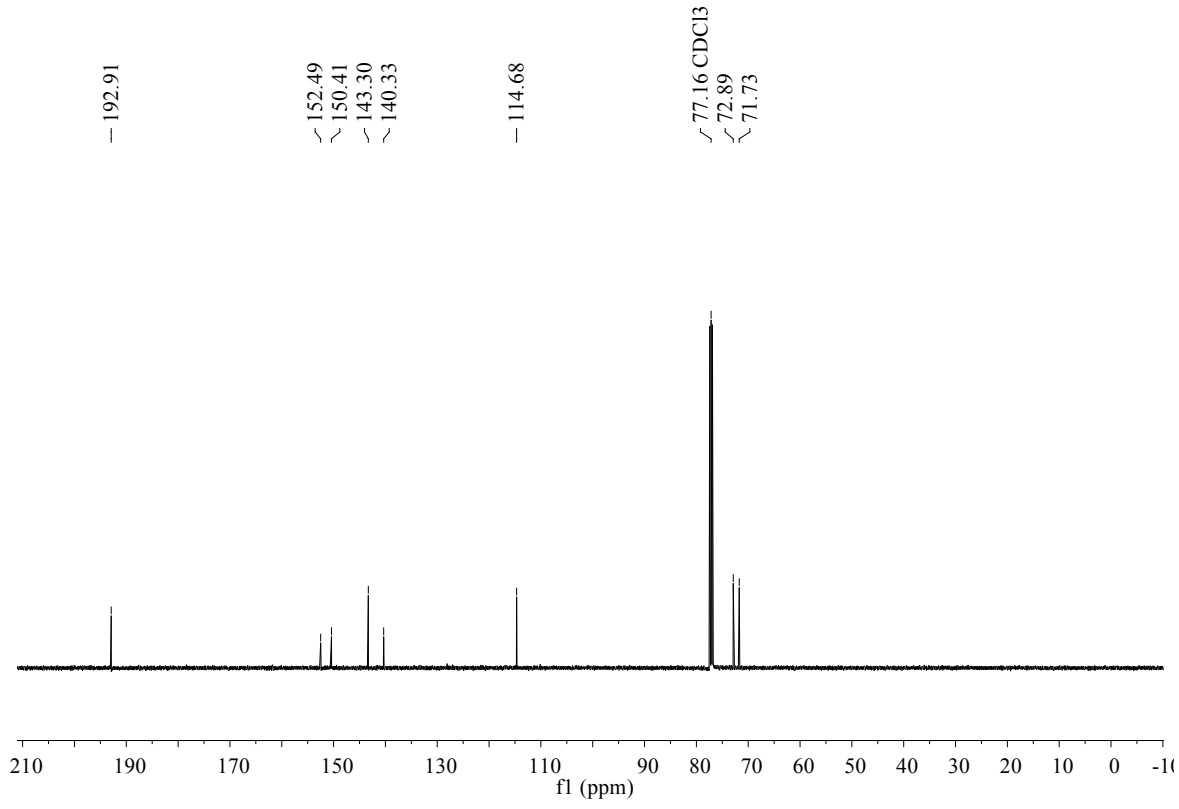

8.64
7.74
7.26 CDCl3
7.21
7.19
6.90
6.88
6.13
5.43
5.40
5.39
5.28
5.28
5.26
3.80
2.71
1.00
1.00
2.00
2.00
1.00
1.00
1.00
3.00
3.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

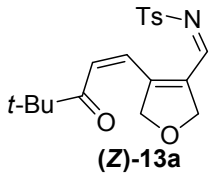

199.67
160.11
153.46
152.98
142.21
139.14
132.18
128.42
115.87
114.41
85.46
77.16 CDCl3
71.37
55.48
26.23
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
H
N
O

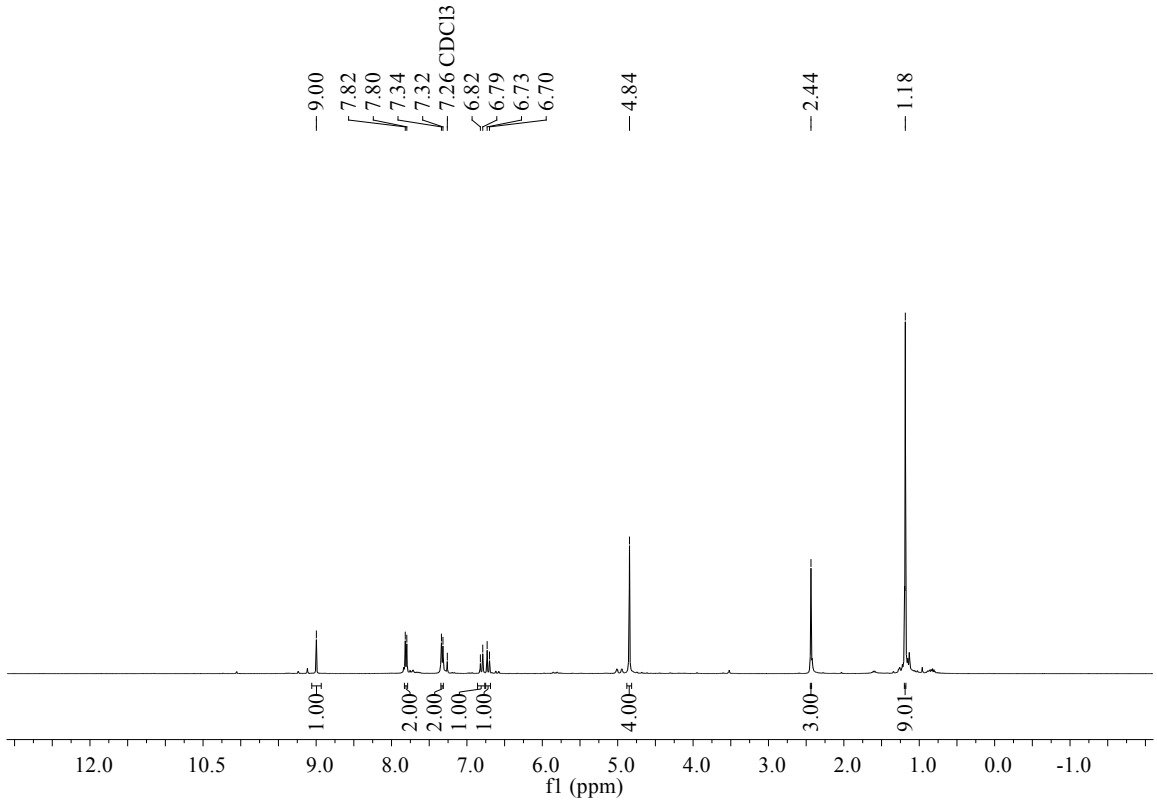
12e

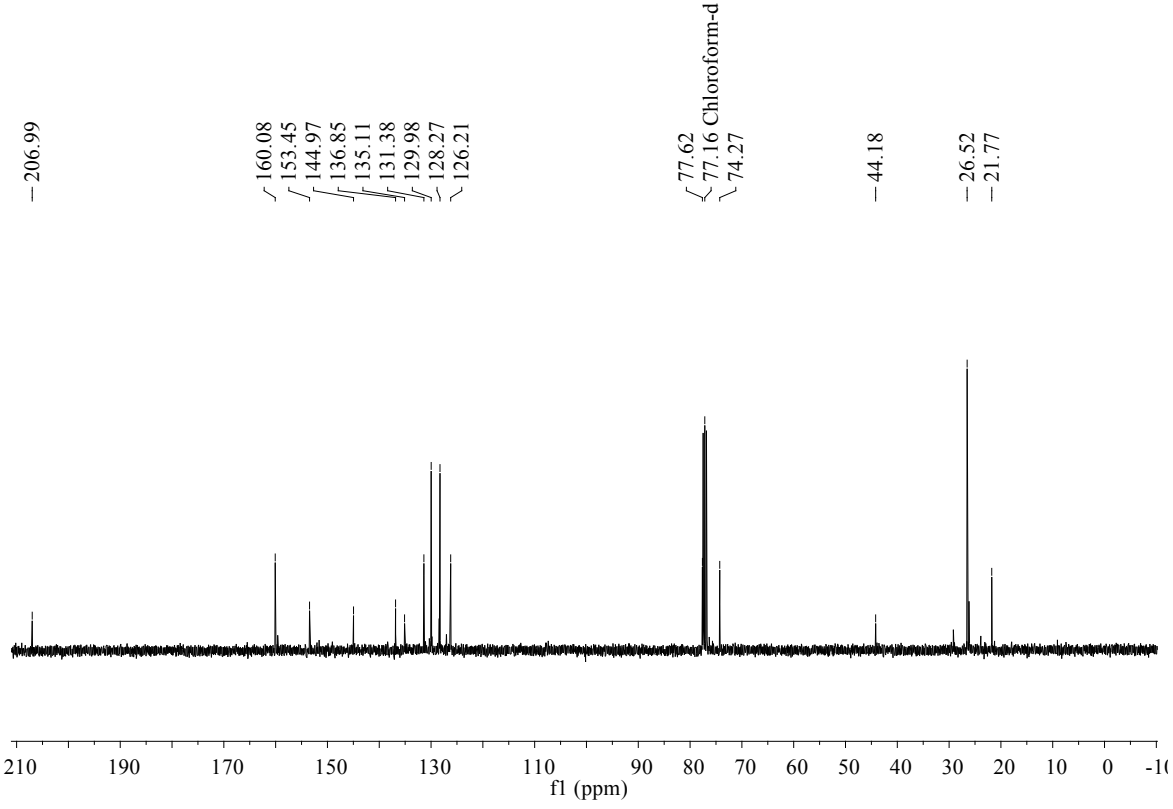

10.11
8.69
7.88
7.26 CDCl3
5.22
5.16
1.00
1.00
1.00
2.00
2.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

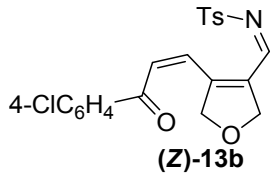

192.91
152.49
150.41
143.30
140.33
114.68
77.16 CDCl3
72.89
71.73
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ts
N
t-Bu
O
O

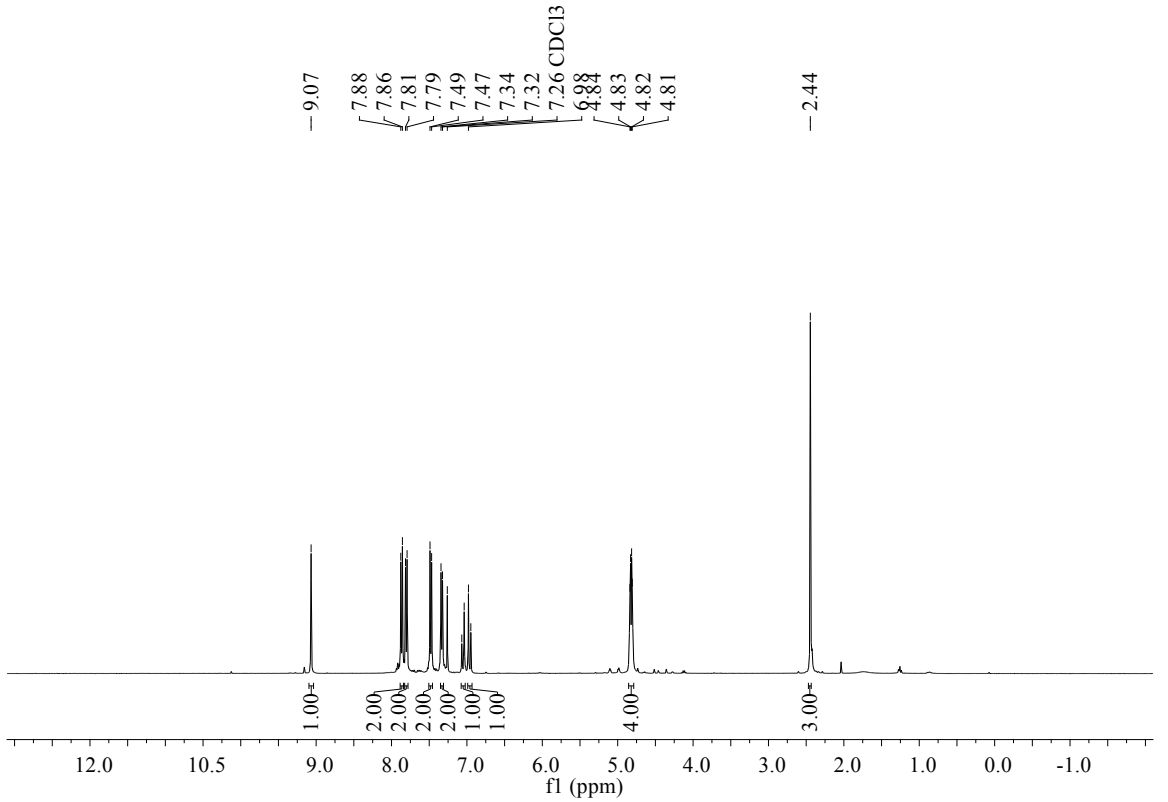
(*Z*)-13a

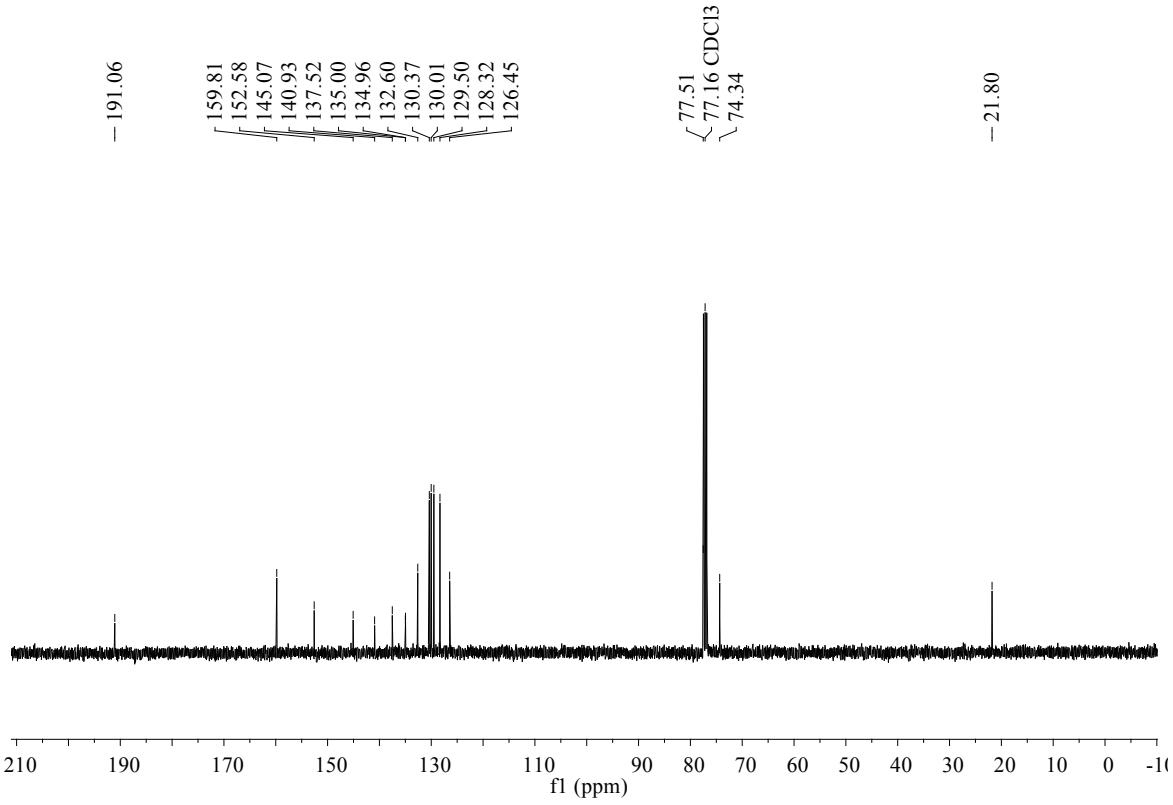

9.00
7.82
7.80
7.34
7.32
7.26 CDCl3
6.82
6.79
6.73
6.70
4.84
2.44
1.18
1.00
2.00
2.00
1.00
1.00
4.00
3.00
9.01
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

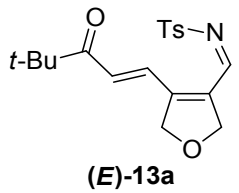

206.99
160.08
153.45
144.97
136.85
135.11
131.38
129.98
128.27
126.21
77.62
77.16 Chloroform-d
74.27
44.18
26.52
21.77
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ts
N
4-ClC6H4
O
O

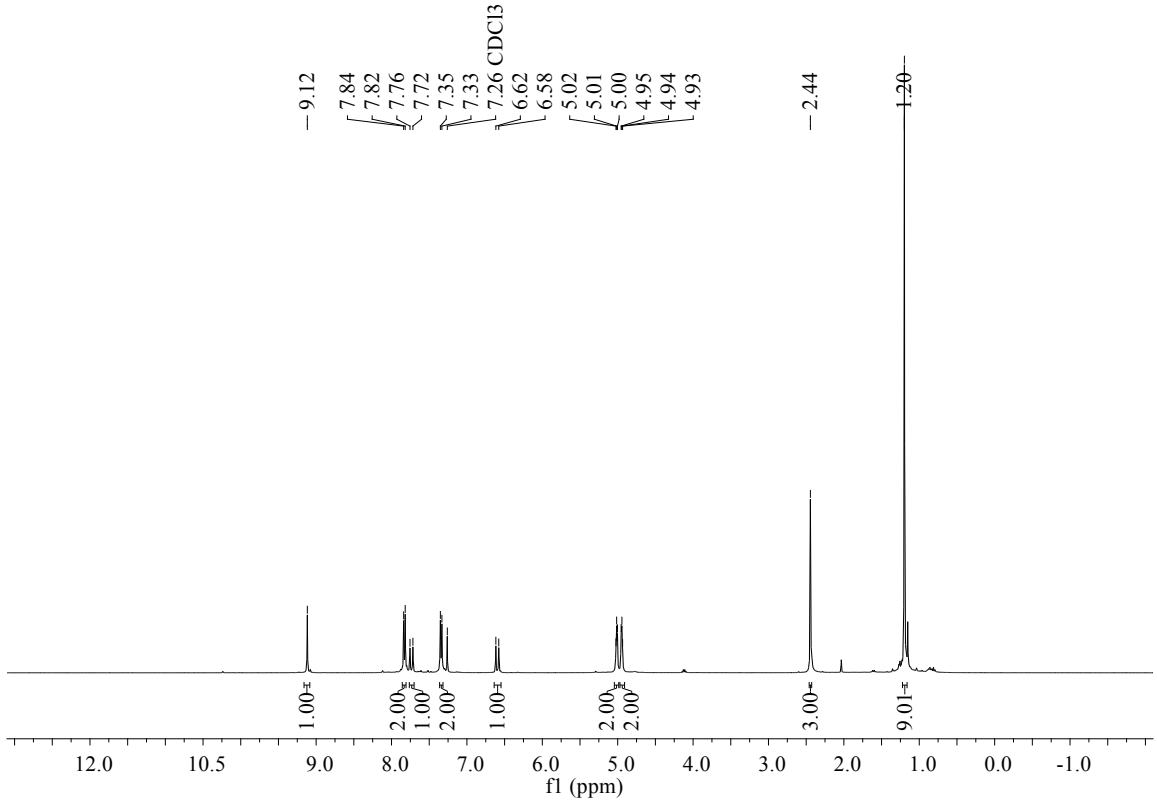
(*Z*)-13b

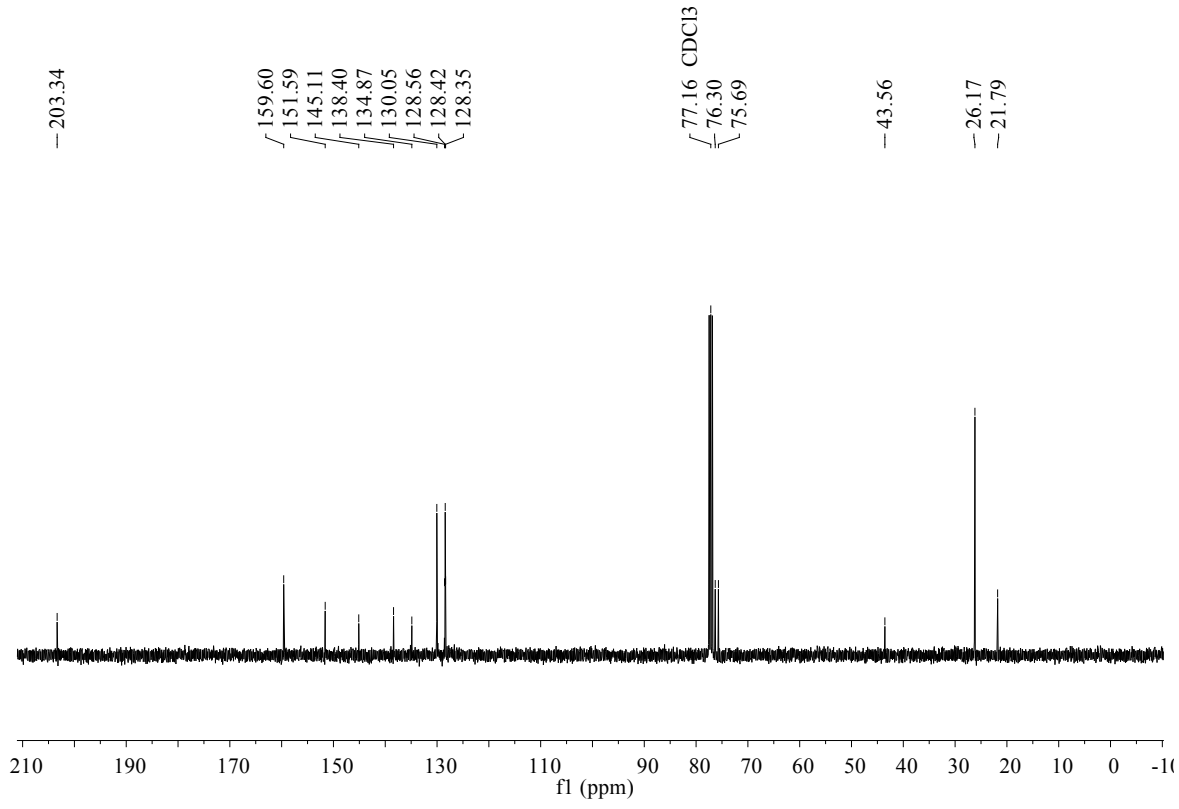

9.07
7.88
7.86
7.81
7.79
7.49
7.47
7.34
7.32
7.26 CDCl3
6.98
4.84
4.83
4.82
4.81
2.44
1.00
2.00
2.00
2.00
2.00
1.00
1.00
4.00
3.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

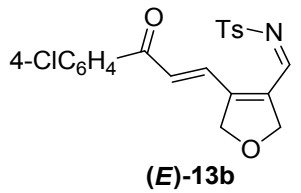

191.06
159.81
152.58
145.07
140.93
137.52
135.00
134.96
132.60
130.37
130.01
129.50
128.32
126.45
77.51
77.16 CDCl3
74.34
21.80
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
Ts–N
t-Bu
O

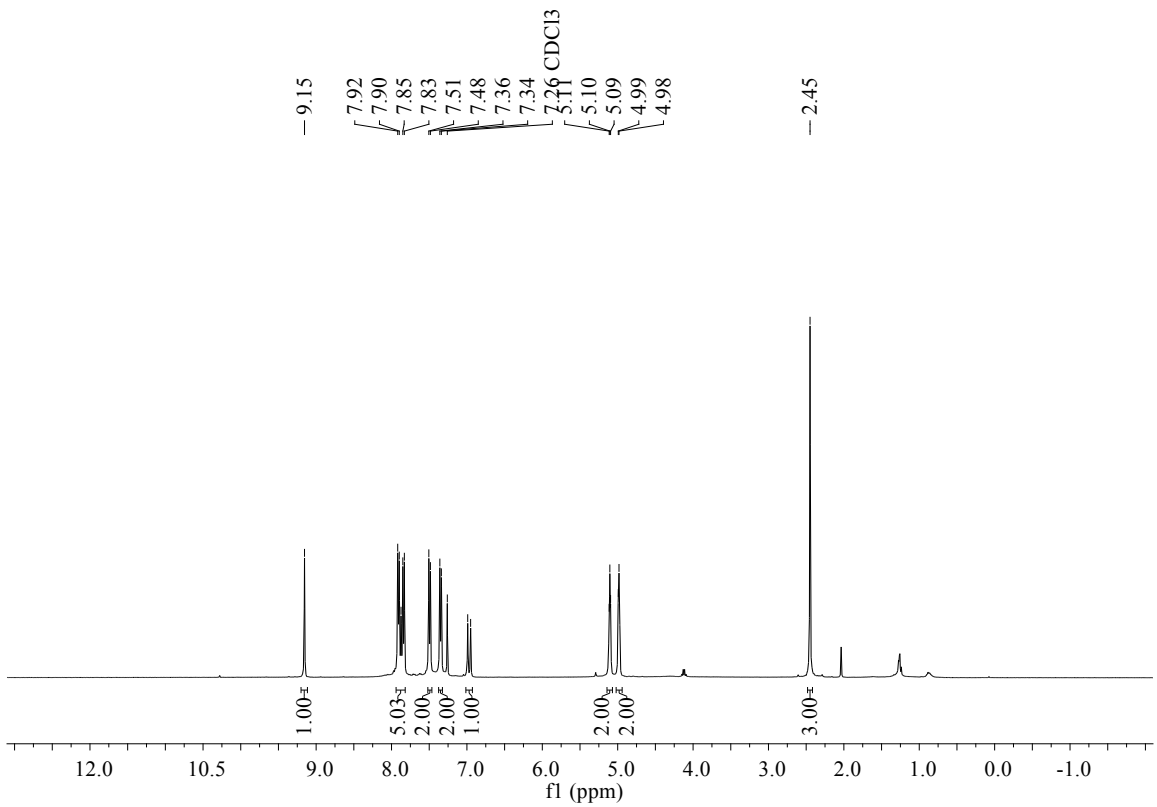
(*E*)-13a

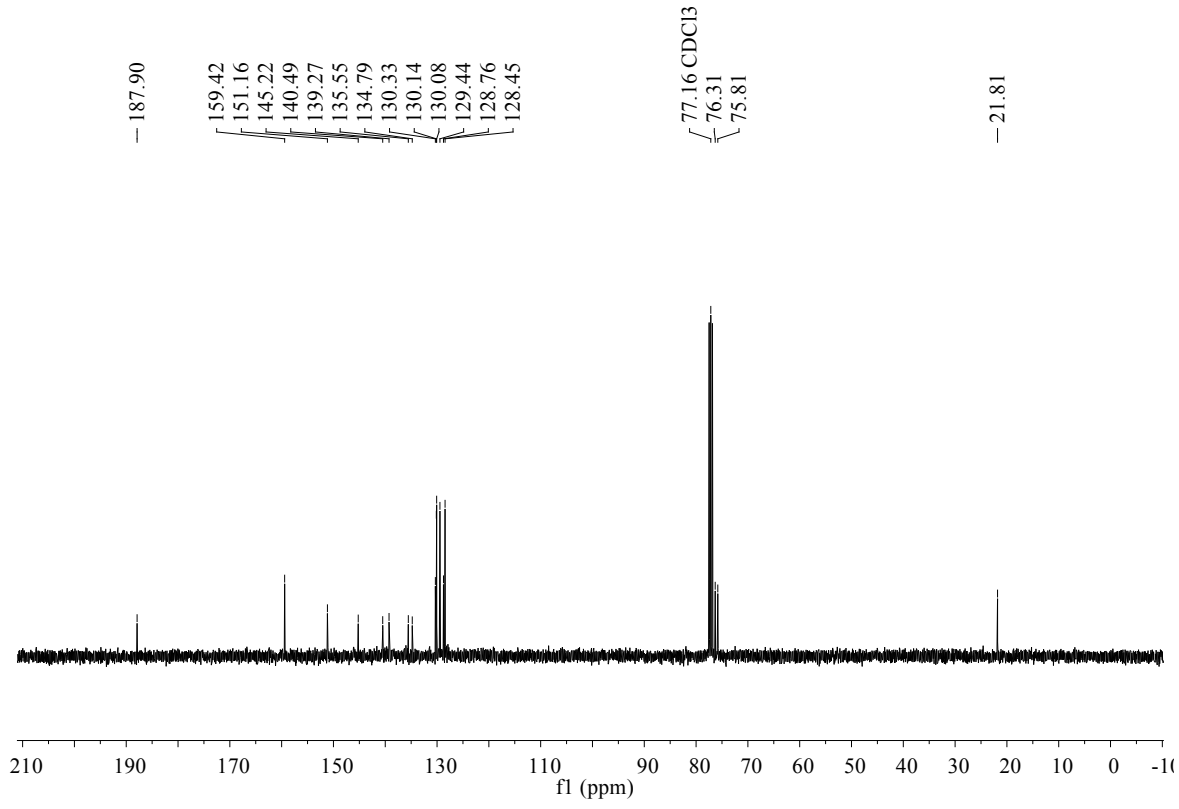

9.12
7.84
7.82
7.76
7.72
7.35
7.33
7.26 CDCl3
6.62
6.58
5.02
5.01
5.00
4.95
4.94
4.93
2.44
1.20
1.00
2.00
1.00
2.00
1.00
2.00
2.00
3.00
9.01
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

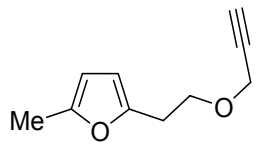

203.34
159.60
151.59
145.11
138.40
134.87
130.05
128.56
128.42
128.35
77.16 CDCl3
76.30
75.69
43.56
26.17
21.79
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
Ts–N
4-ClC6H4
O

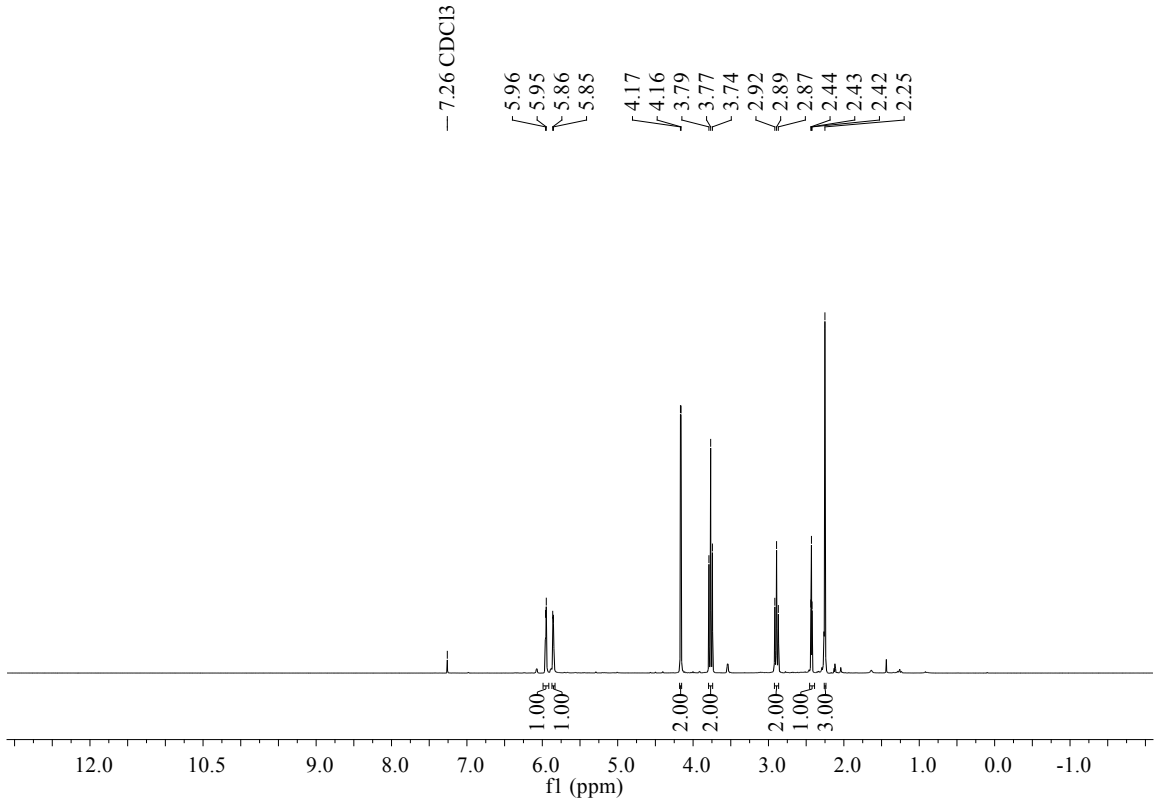
(*E*)-13b

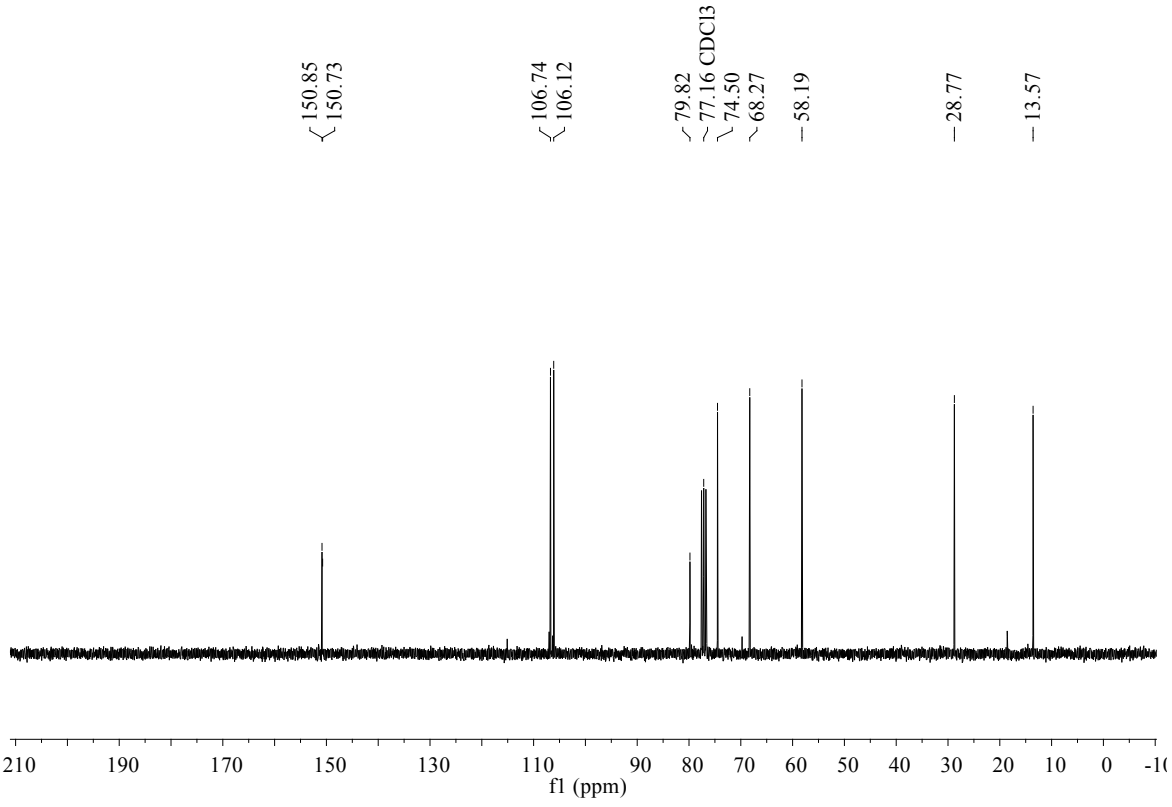

9.15
7.92
7.90
7.85
7.83
7.51
7.48
7.36
7.34
7.26 CDCl3
5.11
5.10
5.09
4.99
4.98
2.45
1.00
5.03
2.00
2.00
1.00
2.00
2.00
3.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

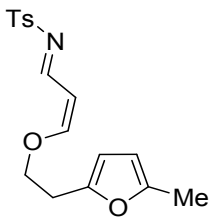

187.90
159.42
151.16
145.22
140.49
139.27
135.55
134.79
130.33
130.14
130.08
129.44
128.76
128.45
77.16 CDCl3
76.31
75.81
21.81
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
O
O

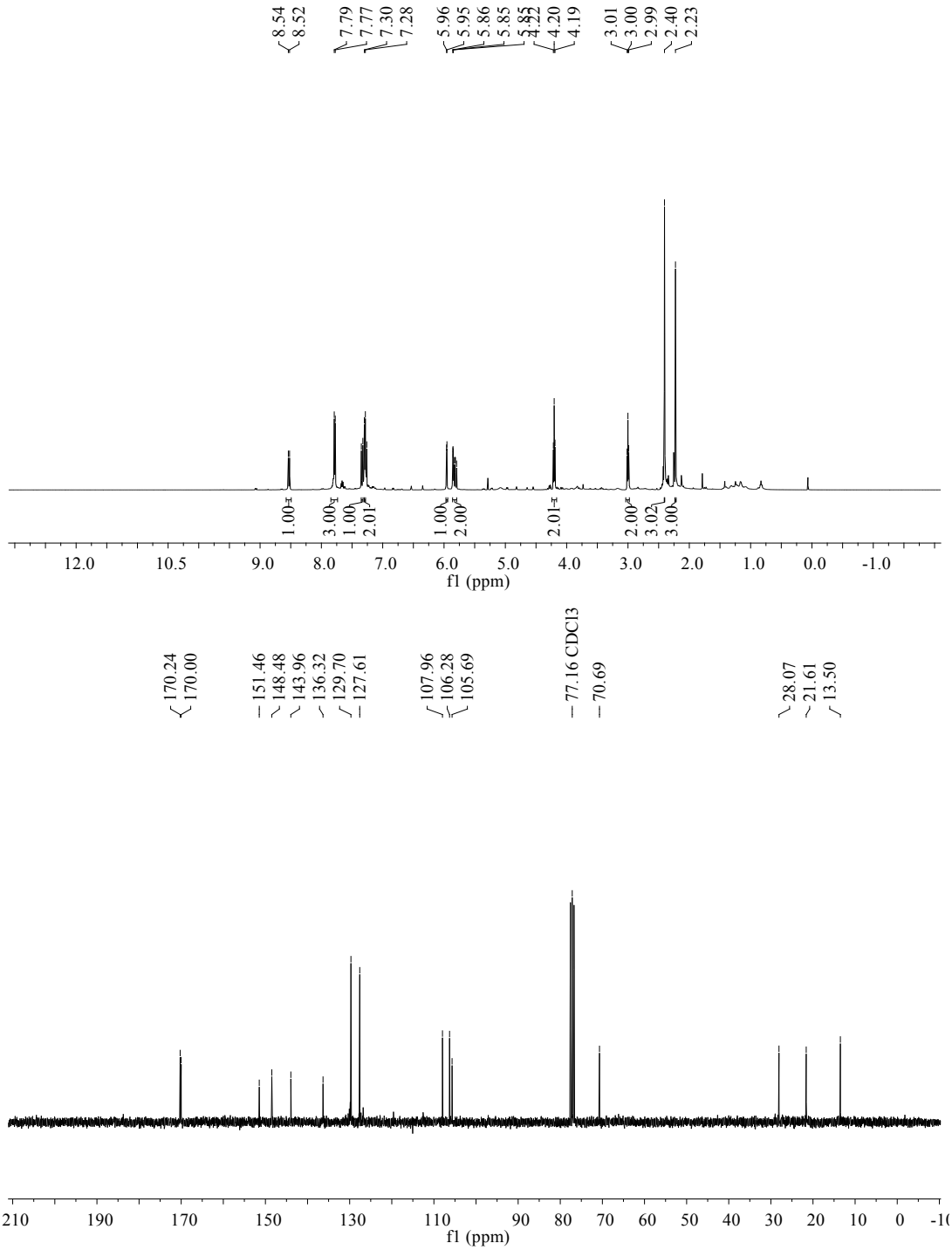
14

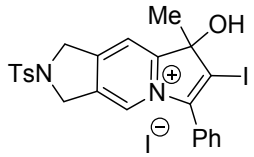

7.26 CDCl3
5.96
5.95
5.86
5.85
4.17
4.16
3.79
3.77
3.74
2.92
2.89
2.87
2.44
2.43
2.42
2.25
1.00
1.00
2.00
2.00
2.00
1.00
3.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


150.85
150.73
106.74
106.12
79.82
77.16 CDCl3
74.50
68.27
58.19
28.77
13.57
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

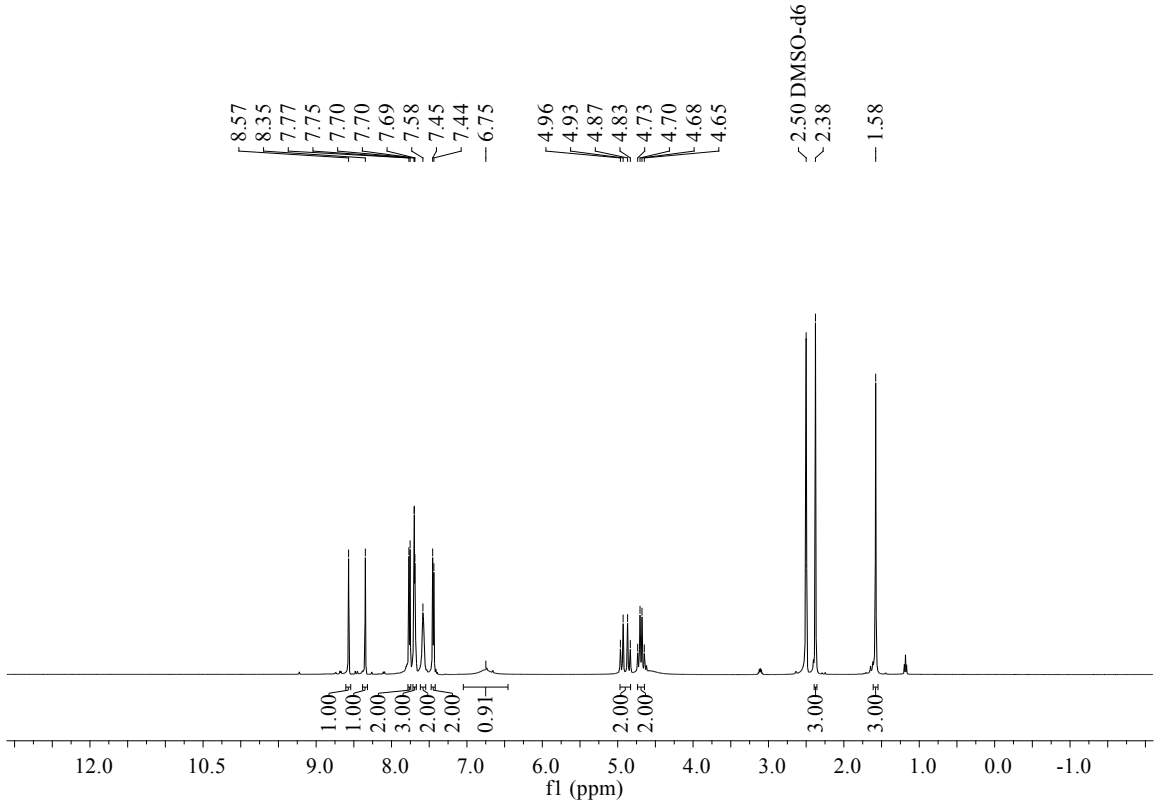

Ts
N
O
O
Me

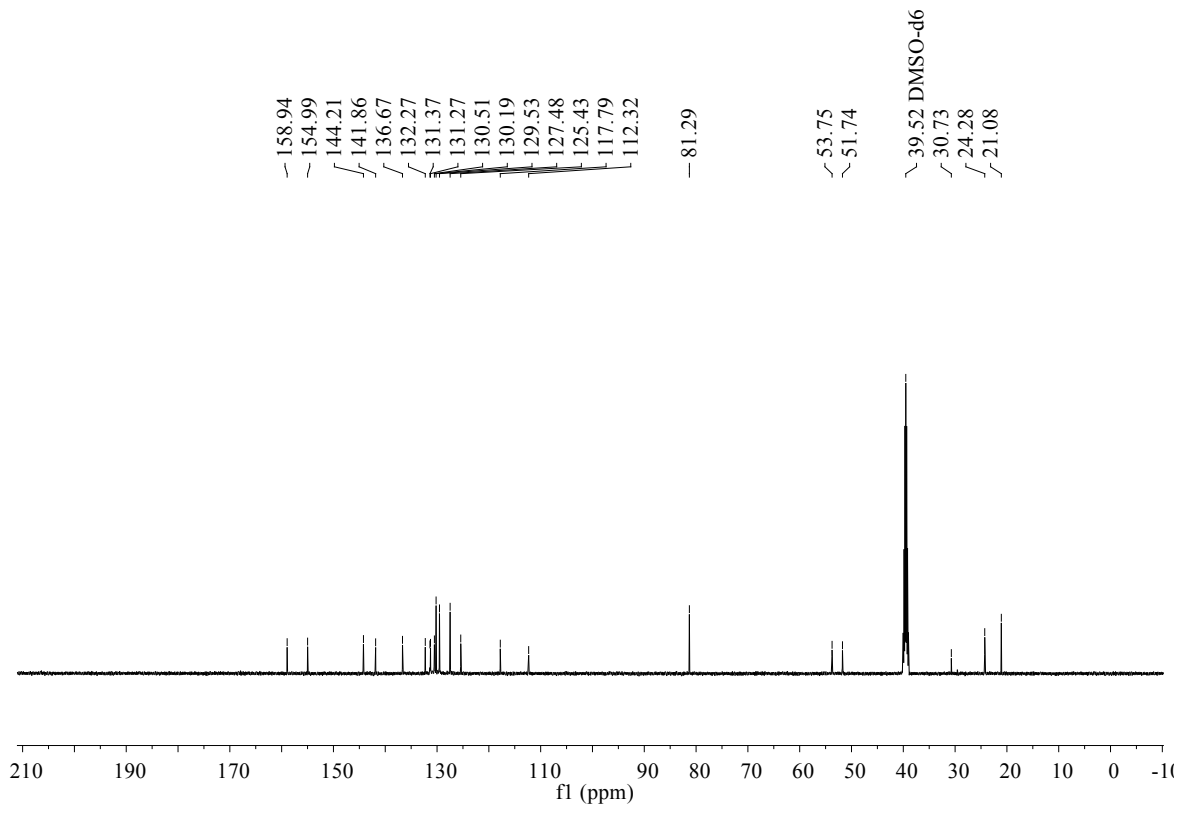
15, crude

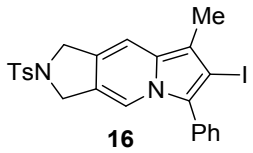

8.54
8.52
7.79
7.77
7.30
7.28
5.96
5.95
5.86
5.85
4.20
4.19
3.01
3.00
2.99
2.40
2.23
1.00
3.00
1.00
2.01
1.00
2.00
2.01
2.00
3.02
3.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)
170.24
170.00
151.46
148.48
143.96
136.32
129.70
127.61
107.96
106.28
105.69
77.16 CDCl3
70.69
28.07
21.61
13.50
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
OH
TsN
N
I
I
Ph

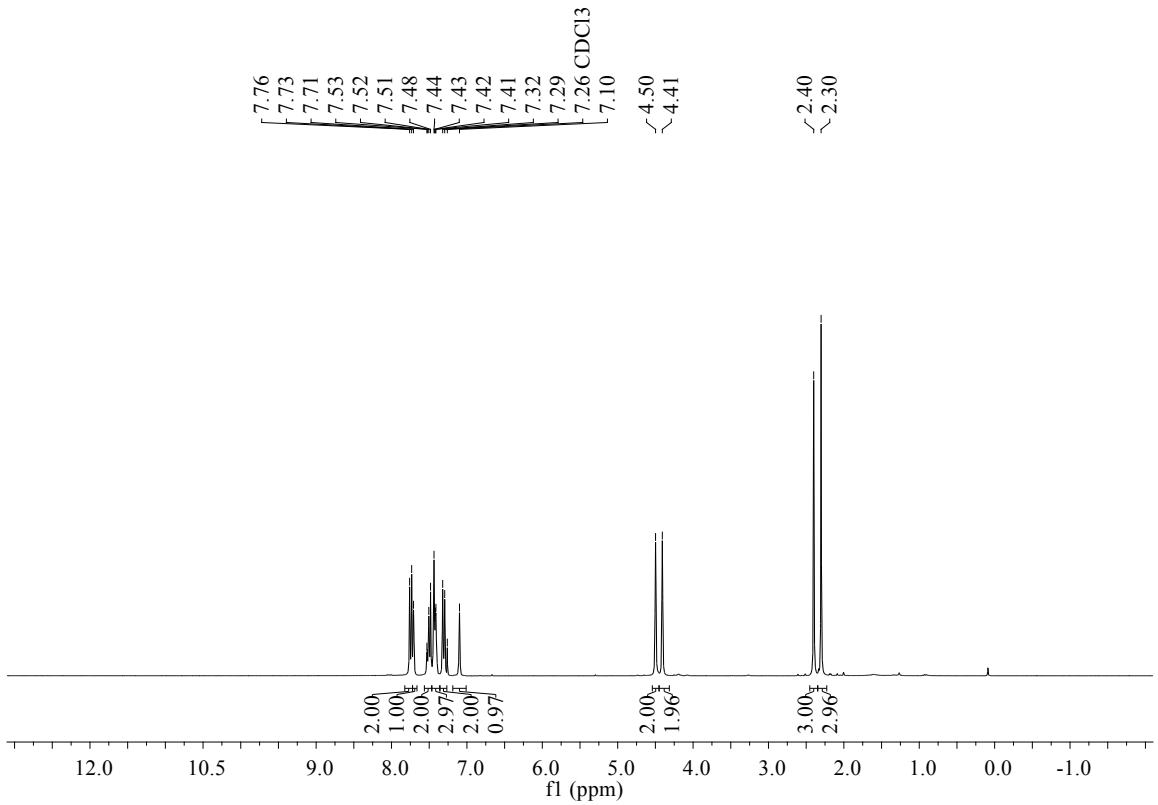
16

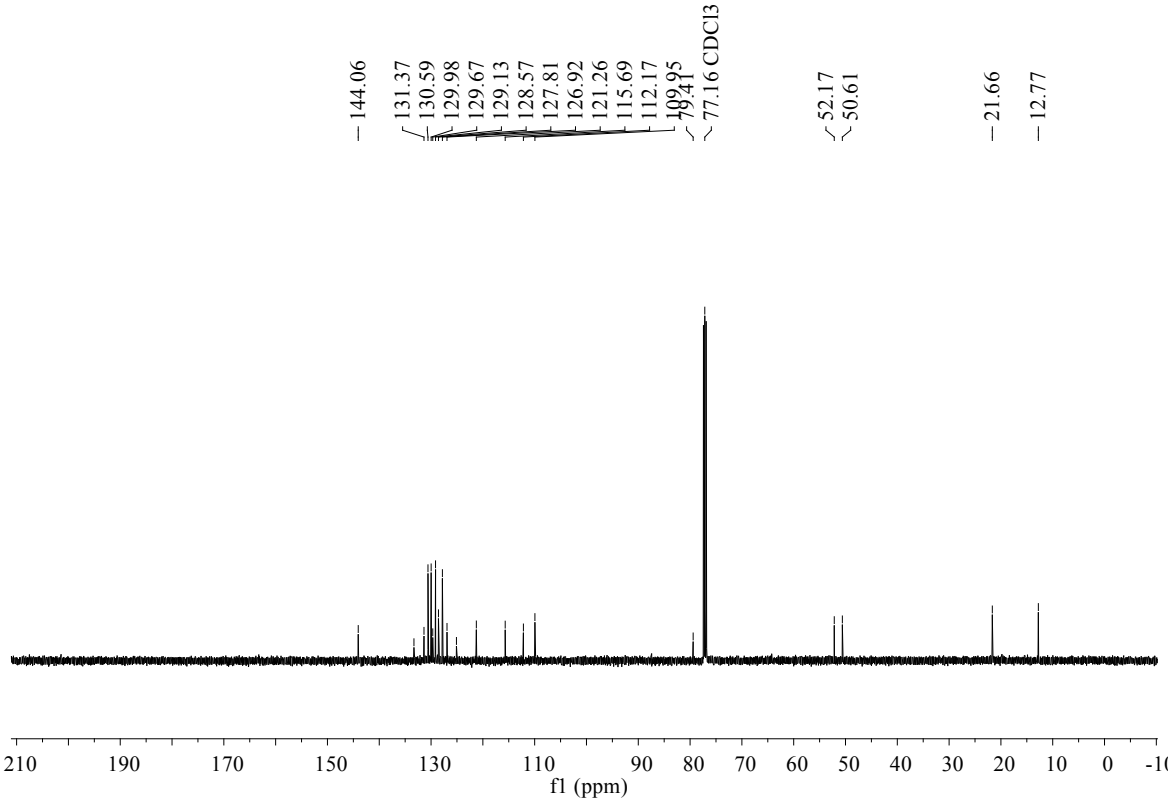

8.57
8.35
7.77
7.75
7.70
7.70
7.69
7.58
7.45
7.44
6.75
4.96
4.93
4.87
4.83
4.73
4.70
4.68
4.65
2.50 DMSO-d6
2.38
1.58
1.00
1.00
2.00
3.00
2.00
2.00
0.91
2.00
2.00
3.00
3.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


158.94
154.99
144.21
141.86
136.67
132.27
131.37
131.27
130.51
130.19
129.53
127.48
125.43
117.79
112.32
81.29
53.75
51.74
39.52 DMSO-d6
30.73
24.28
21.08
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
TsN
I
N
Ph

16


7.76
7.73
7.71
7.53
7.52
7.51
7.48
7.44
7.43
7.42
7.41
7.32
7.29
7.26 CDCl3
7.10
4.50
4.41
2.40
2.30
2.00
1.00
2.00
2.97
2.00
0.97
2.00
1.96
3.00
2.96
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


144.06
131.37
130.59
129.98
129.67
129.13
128.57
127.81
126.92
121.26
115.69
112.17
109.95
79.41
77.16 CDCl3
52.17
50.61
21.66
12.77
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)