

Supporting Information

Synthesis and Characterization of Organogold Complexes Containing Acid Stable Au-C Bond through Triazole-yne 5-Endo-Dig Cyclization

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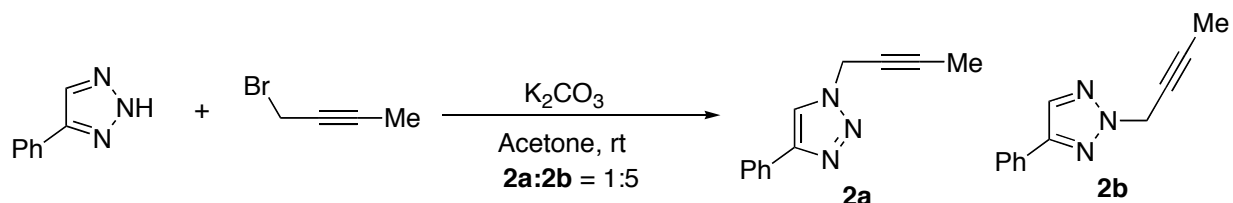
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I. General Methods and Materials:

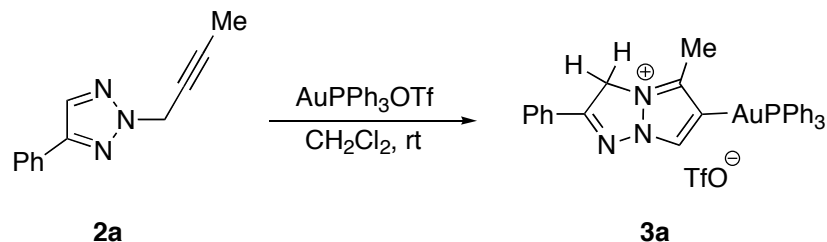
Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. ^1H NMR and ^{13}C NMR spectra and ^{31}P NMR were recorded on Varian 600 MHz spectrometers. Chemical shifts were reported relative to internal CDCl_3 (δ 7.26 ppm) or CD_3CN (δ 1.94 ppm) for ^1H and CDCl_3 (δ 77.0 ppm) or CD_3CN (δ 1.39 ppm) for ^{13}C . The H_3PO_4 (85% in MeOH) in a sealed capillary tube was applied as the internal standard (all the 0 ppm signals) for the ^{31}P NMR spectra. Flash column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with precoated glass baked plates (250 μ) and visualized by fluorescence and by charring after treatment with potassium permanganate stain. HRMS were recorded on LTQ-FTUHRA spectrometer.

Representative procedure for synthesis of substrate 2a



To a mixture of 4-phenyl-2H-1,2,3-triazole (500 mg, 3.45 mmol) and K_2CO_3 (715 mg, 5.18 mmol) in acetone (20 mL) was added 1-bromobut-2-yne (550 mg, 4.14 mmol). The resulting reaction mixture was stirring at room temperature and monitored by TLC. After the reaction completed, the mixture was diluted with acetone followed by filtration. The filtrate was condensed under reduced pressure and the product was purified by flash silica gel chromatography give the N-2 substituted triazole compound **2a** as colorless oil. At the same time, there is also N-1 substituted triazole compound formation as white solid.

Representative procedure for synthesis of triazole-Au compounds

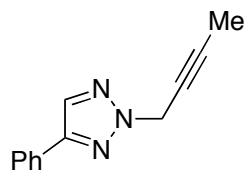


To a solution of AuPPh_3Cl (120 mg, 0.24 mmol, 0.8 equiv) in dry CH_2Cl_2 (5 mL) was added the AgOTf (62 mg, 0.24 mmol, 0.8 equiv). The mixture was stirring at room temperature for 3 minutes, and the mixture was filtrated through a short celite column to remove the insoluble salt to give a clear solution. Then this clear solution was transferred into the solution of **2a** (60 mg, 0.30 mmol, 1.0 equiv) in CH_2Cl_2 (5 mL). The mixture was stirring at room temperature for 1~2 h. The solution was condensed under reduced pressure, and hexane was added to give white

solid, the white solid was filtrated and can be further purified by crystallization from CH_2Cl_2 /Hexane (2 : 1, V/V) to get **3a** as white crystals.

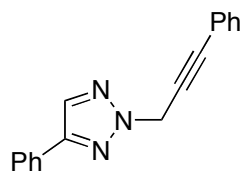
3b and **3e** were obtained from the filtration of reaction mixture in CH_2Cl_2 .

II. Compounds Characterization



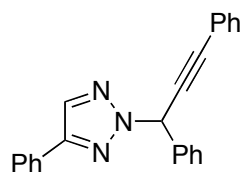
2a

2-(but-2-ynyl)-4-phenyl-2H-1,2,3-triazole (2a). Colorless oil. ^1H NMR (600 MHz, CDCl_3): δ 7.97 (s, 1H), 7.78-7.80 (m, 2H), 7.40-7.44 (m, 2H), 7.33-7.36 (m, 1H), 5.20 (q, $J = 2.4$ Hz, 2H), 1.87 (t, $J = 2.4$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 148.2, 131.5, 130.2, 128.8, 128.5, 125.9, 82.8, 71.3, 45.0, 3.6; HRMS Calculated for $[\text{C}_{12}\text{H}_{11}\text{N}_3+\text{H}]^+$: 198.10257, Found: 198.10256.



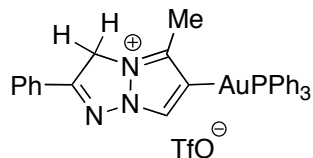
2b

4-phenyl-2-(3-phenylprop-2-ynyl)-2H-1,2,3-triazole (2b). Light-yellow oil. ^1H NMR (600 MHz, CDCl_3): δ 7.93 (s, 1H), 7.83-7.86 (m, 2H), 7.49-7.52 (m, 2H), 7.43-7.47 (m, 2H), 7.34-7.39 (m, 1H), 7.28-7.33 (m, 3H), 5.50 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ 148.2, 131.8, 131.6, 130.0, 128.7, 128.6, 128.4, 128.1, 125.8, 121.9, 86.0, 81.2, 45.2; HRMS Calculated for $[\text{C}_{17}\text{H}_{13}\text{N}_3]^+$: 260.11822, Found: 260.11825.



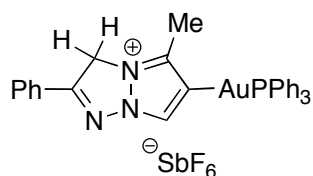
2c

4-phenyl-2-(1,3-diphenylprop-2-ynyl)-2H-1,2,3-triazole (2c). White solid. ^1H NMR (600 MHz, CDCl_3): δ 7.94 (s, 1H), 7.83-7.85 (m, 2H), 7.68-7.71 (m, 2H), 7.56-7.59 (m, 2H), 7.41-7.46 (m, 4H), 7.33-7.40 (m, 5H), 6.94 (s, 1H); ^{13}C NMR (150 MHz, CDCl_3): δ 148.2, 136.4, 132.0, 131.9, 130.2, 128.9, 128.8, 128.7, 128.5, 128.2, 127.6, 126.0, 122.0, 88.1, 83.7, 61.0; HRMS Calculated for $[\text{C}_{23}\text{H}_{17}\text{N}_3]^+$: 336.14952, Found: 336.14966.



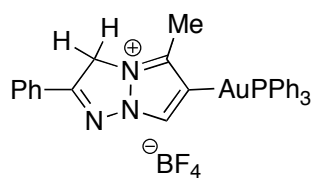
3a

3a: White solid. ¹H NMR (600 MHz, CDCl₃): δ 7.99 (d, *J* = 7.2 Hz, 2H), 7.77 (s, 1H), 7.50-7.58 (m, 18H), 5.98 (s, 2H), 2.74 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 168.0, 148.9, 134.2, 134.1, 133.7, 131.8, 130.5, 129.7, 129.5, 129.4, 128.2, 126.7, 121.8, 53.8, 15.6; ³¹P NMR (242.7 MHz, CDCl₃): δ 41.7.



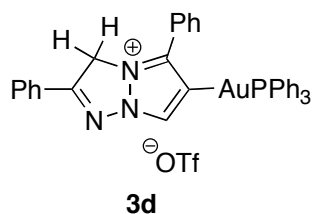
3b

3b: White solid. ¹H NMR (600 MHz, CD₃CN): δ 8.00 (s, 1H), 7.92 (d, *J* = 7.2 Hz, 2H), 7.67-7.71 (m, 1H), 7.55-7.65 (m, 18H), 5.60 (s, 2H), 2.59 (s, 3H); ¹³C NMR (150 MHz, CD₃CN): δ 168.9, 149.0, 135.3, 135.2, 134.8, 133.0, 131.8, 130.7, 130.6, 130.5, 128.8, 128.2, 54.4, 15.6; ³¹P NMR (242.7 MHz, CD₃CN): δ 41.1.

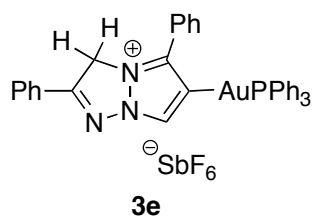


3c

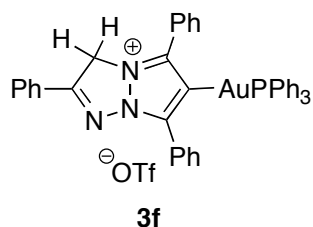
3c: White solid. ¹H NMR (600 MHz, CDCl₃): δ 7.97-7.99 (m, 2H), 7.75 (s, 1H), 7.50-7.59 (m, 18H), 5.88 (s, 2H), 2.75 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 168.1, 149.2, 134.24, 134.15, 133.8, 131.8, 130.5, 129.8, 129.6, 129.4, 128.2, 126.7, 53.5, 15.4; ³¹P NMR (242.7 MHz, CDCl₃): δ 41.7.



3d: White solid. ^1H NMR (600 MHz, CDCl_3): δ 8.32 (d, $J = 8.4$ Hz, 2H), 8.05 (d, $J = 8.4$ Hz, 2H), 7.95 (s, 1H), 7.48-7.58 (m, 21H), 6.16 (s, 2H), ^{13}C NMR (150 MHz, CDCl_3): δ 167.9, 150.2, 134.2, 134.1, 133.9, 131.9, 131.5, 131.1, 129.5, 129.43, 129.41, 129.3, 128.5, 128.4, 127.9, 126.5, 55.6; ^{31}P NMR (242.7 MHz, CDCl_3): δ 40.5.



3e: White solid. ^1H NMR (600 MHz, CD_3CN): δ 8.19-8.21 (m, 3H), 7.97 (d, $J = 7.2$ Hz, 2H), 7.70-7.74 (m, 1H), 7.54-7.65 (m, 20H), 5.85 (s, 2H); ^{13}C NMR (150 MHz, CD_3CN): δ 168.9, 150.3, 135.25, 135.16, 135.08, 133.1, 132.2, 130.9, 130.8, 130.6, 130.5, 130.4, 130.1, 129.0, 128.7, 128.0, 56.5; ^{31}P NMR (242.7 MHz, CD_3CN): δ 41.9.



3f: White solid. ^1H NMR (600 MHz, CDCl_3): δ 8.33-8.37 (m, 4H), 8.09 (d, $J = 7.8$ Hz, 2H), 7.47-7.57 (m, 24H), 6.21 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ 167.4, 150.0, 145.2, 134.15, 134.06, 133.8, 131.8, 131.1, 130.6, 129.7, 129.44, 129.42, 129.38, 129.31, 129.25, 128.8, 128.6, 128.1, 126.7, 121.9, 55.3; ^{31}P NMR (242.7 MHz, CDCl_3): δ 41.2.

III. ORTEP Drawing of the Crystal Structures

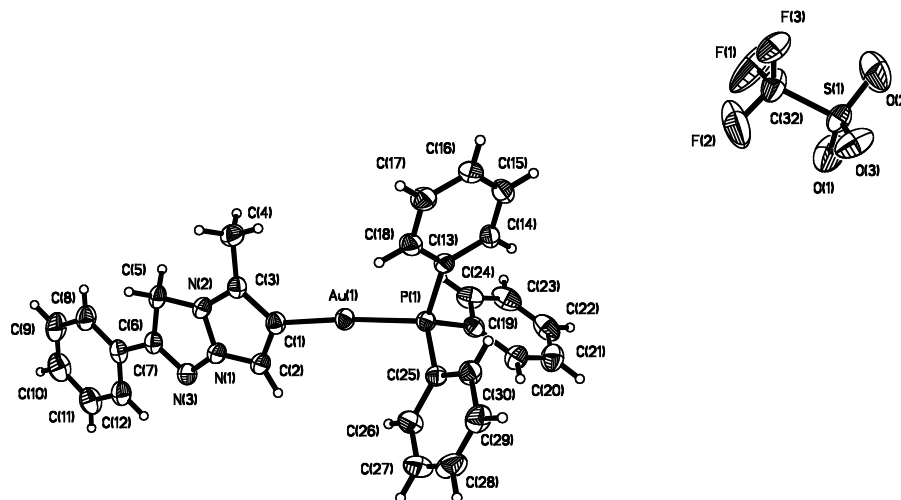


Figure 1. Perspective view of the molecular structure of **3a** with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability. CCDC number: 756836.

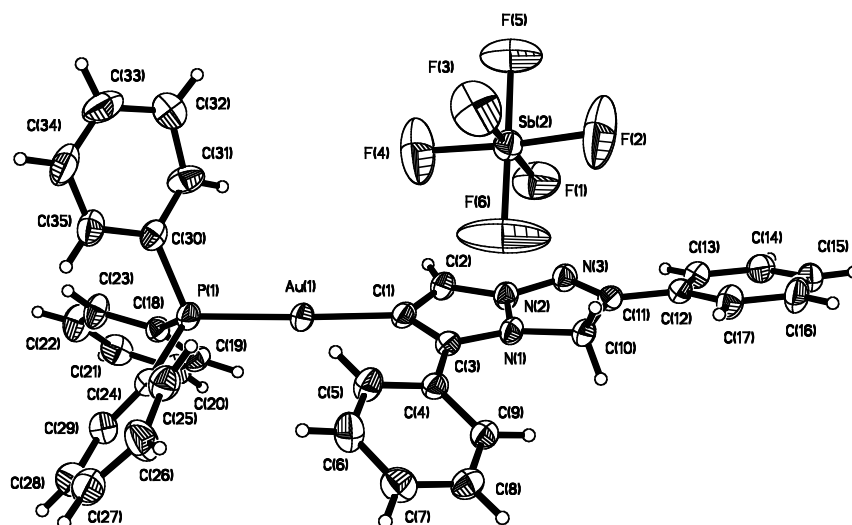
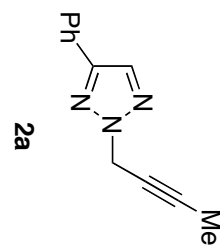
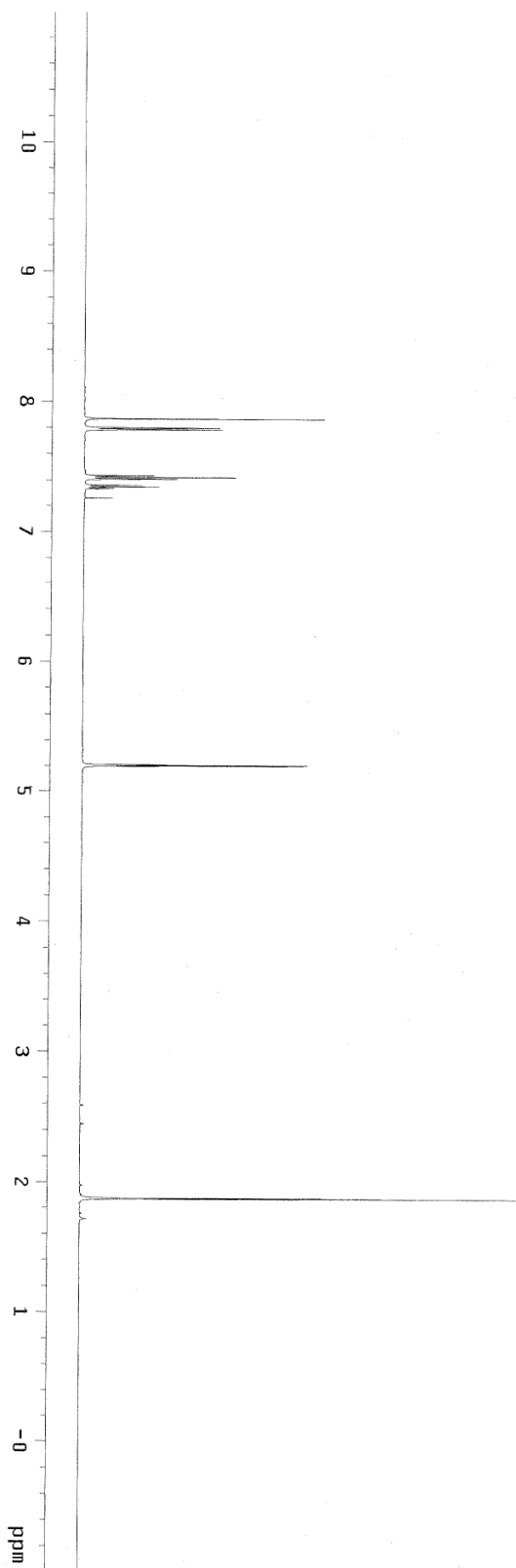
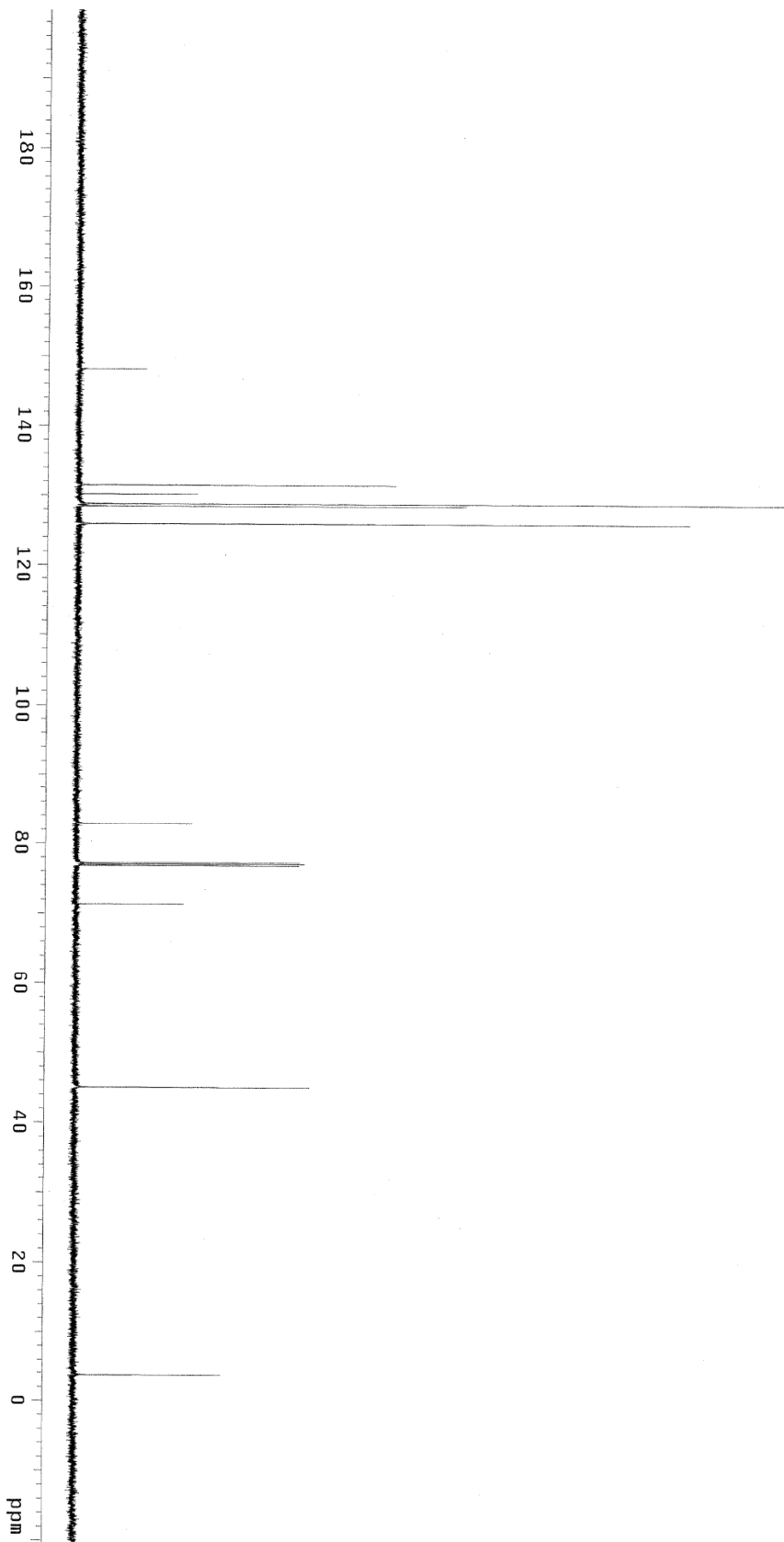
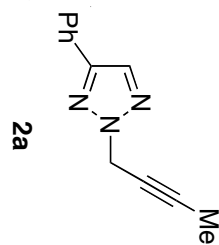
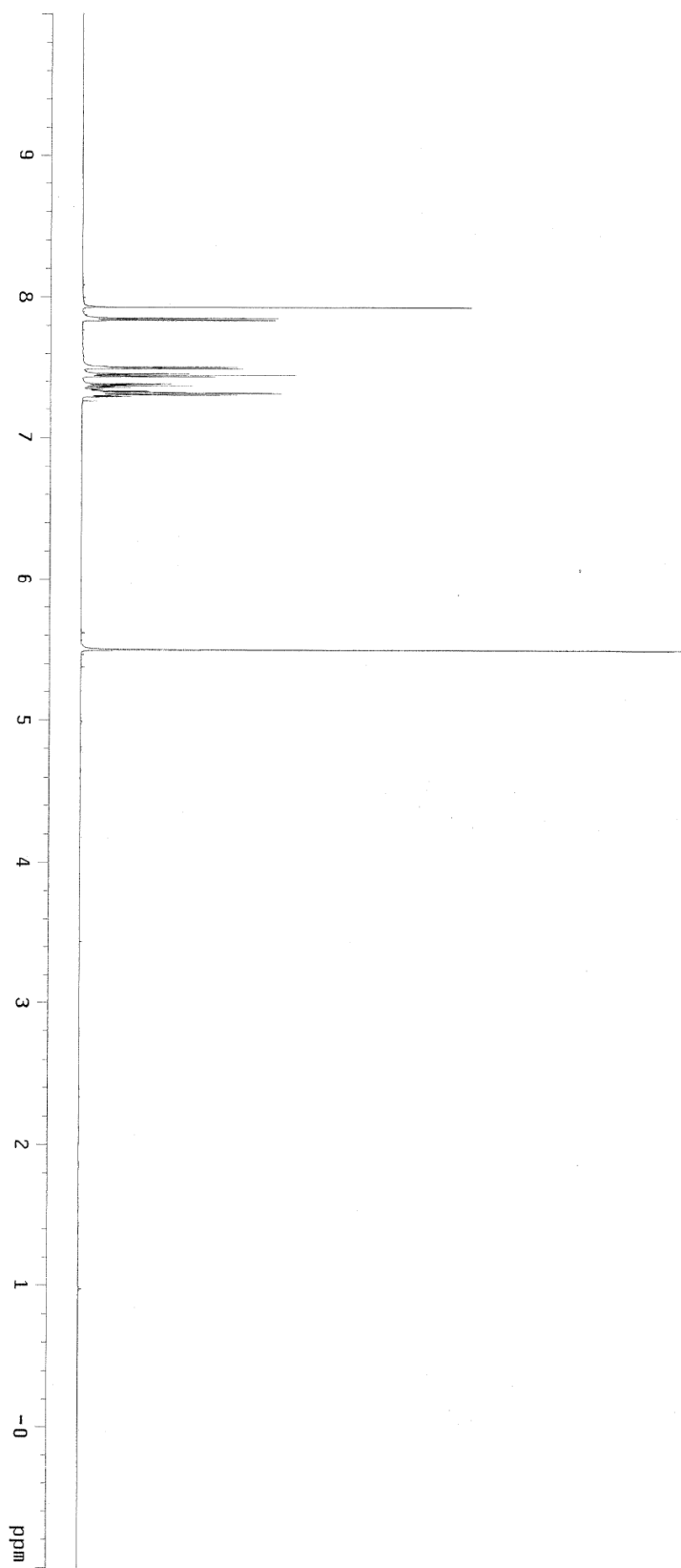
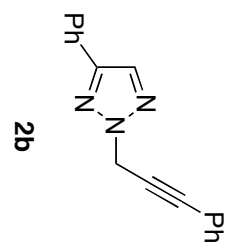


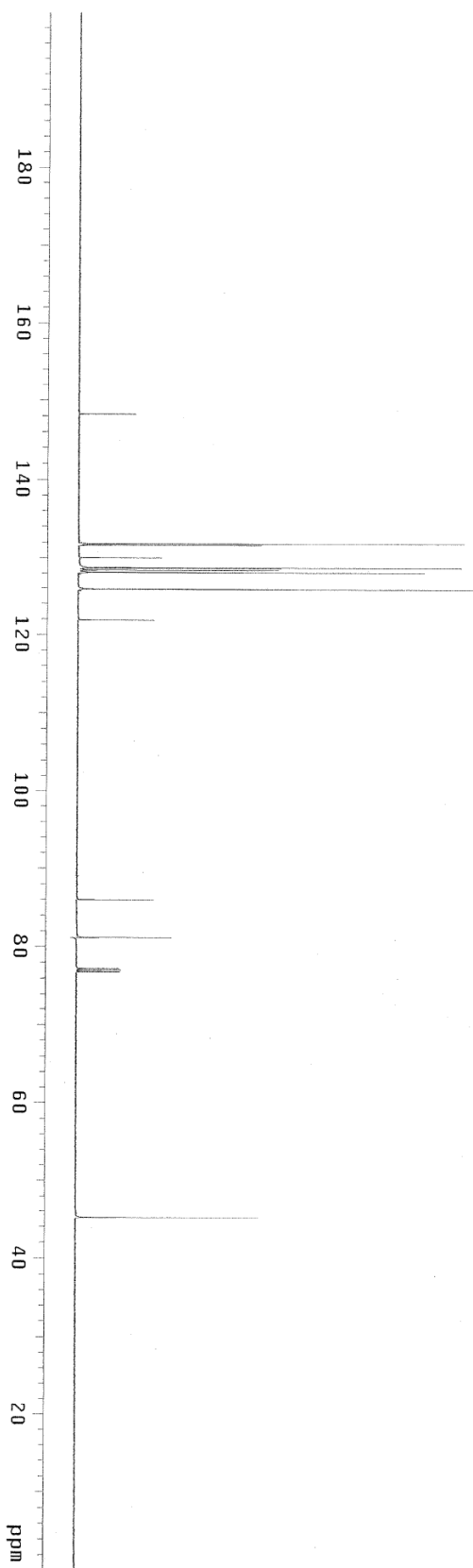
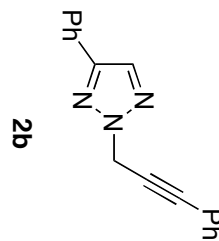
Figure 2. Perspective view of the molecular structure of **3e** with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability. CCDC number: 756837.

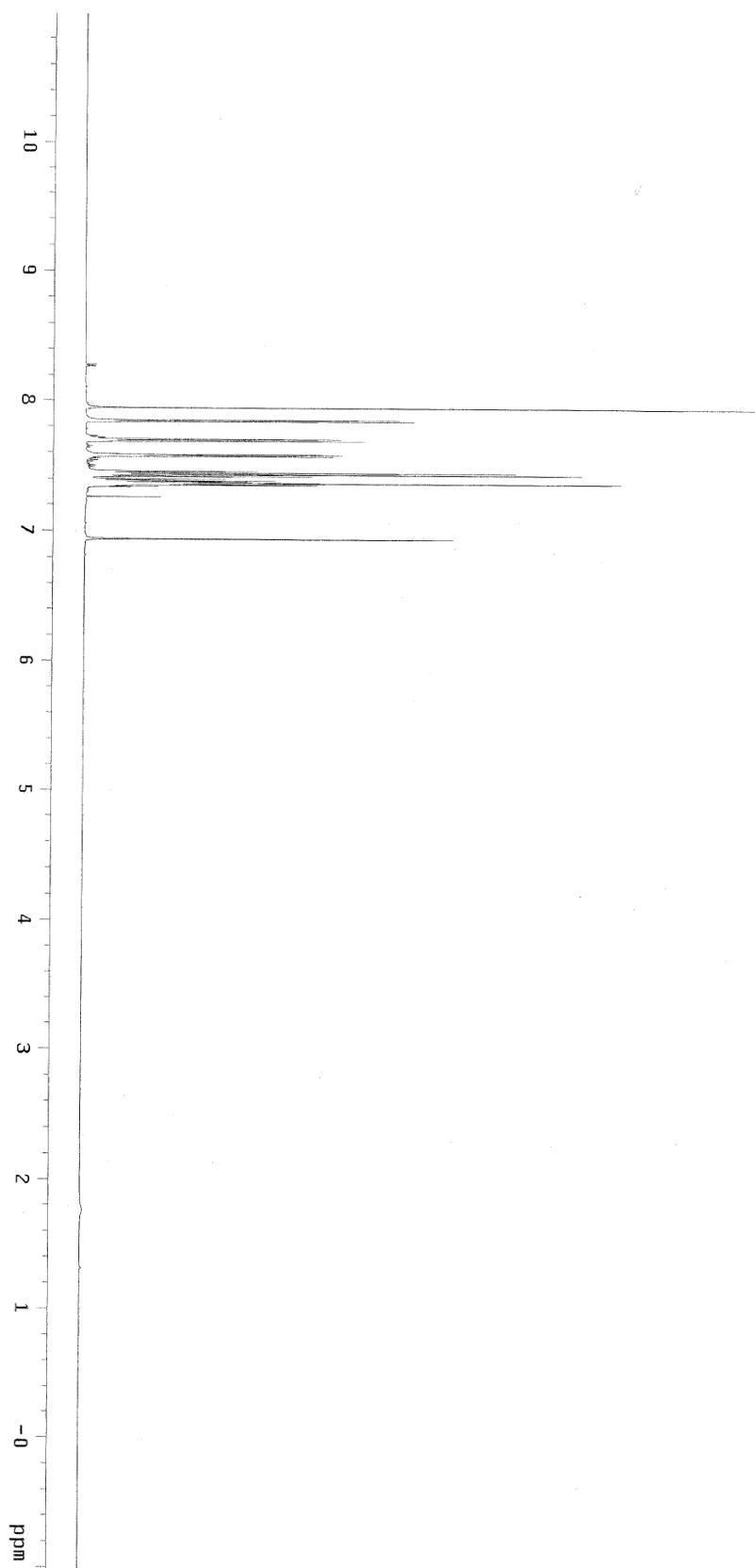
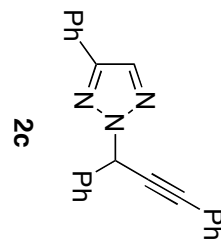
IV. NMR Spectra Data

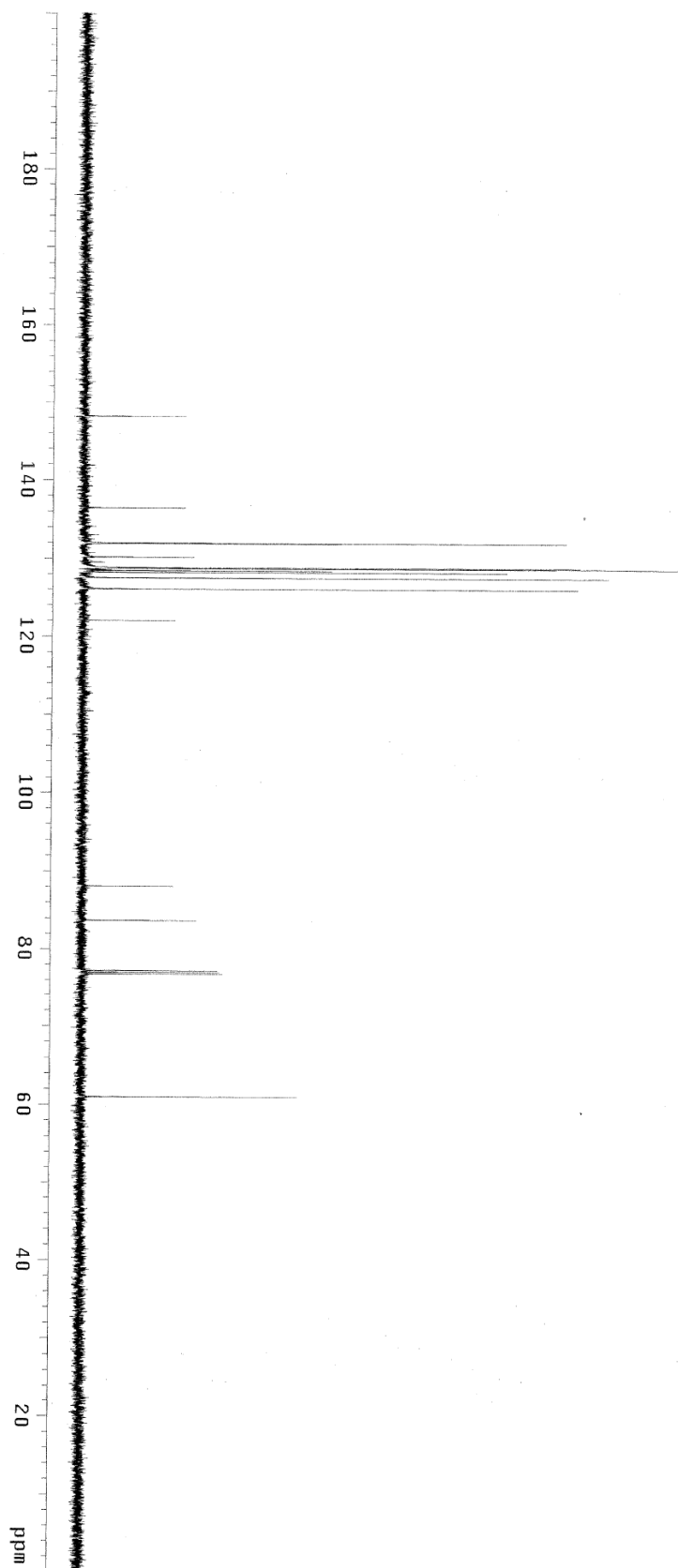
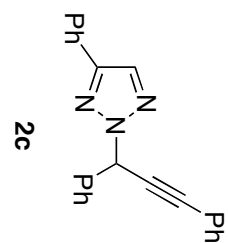


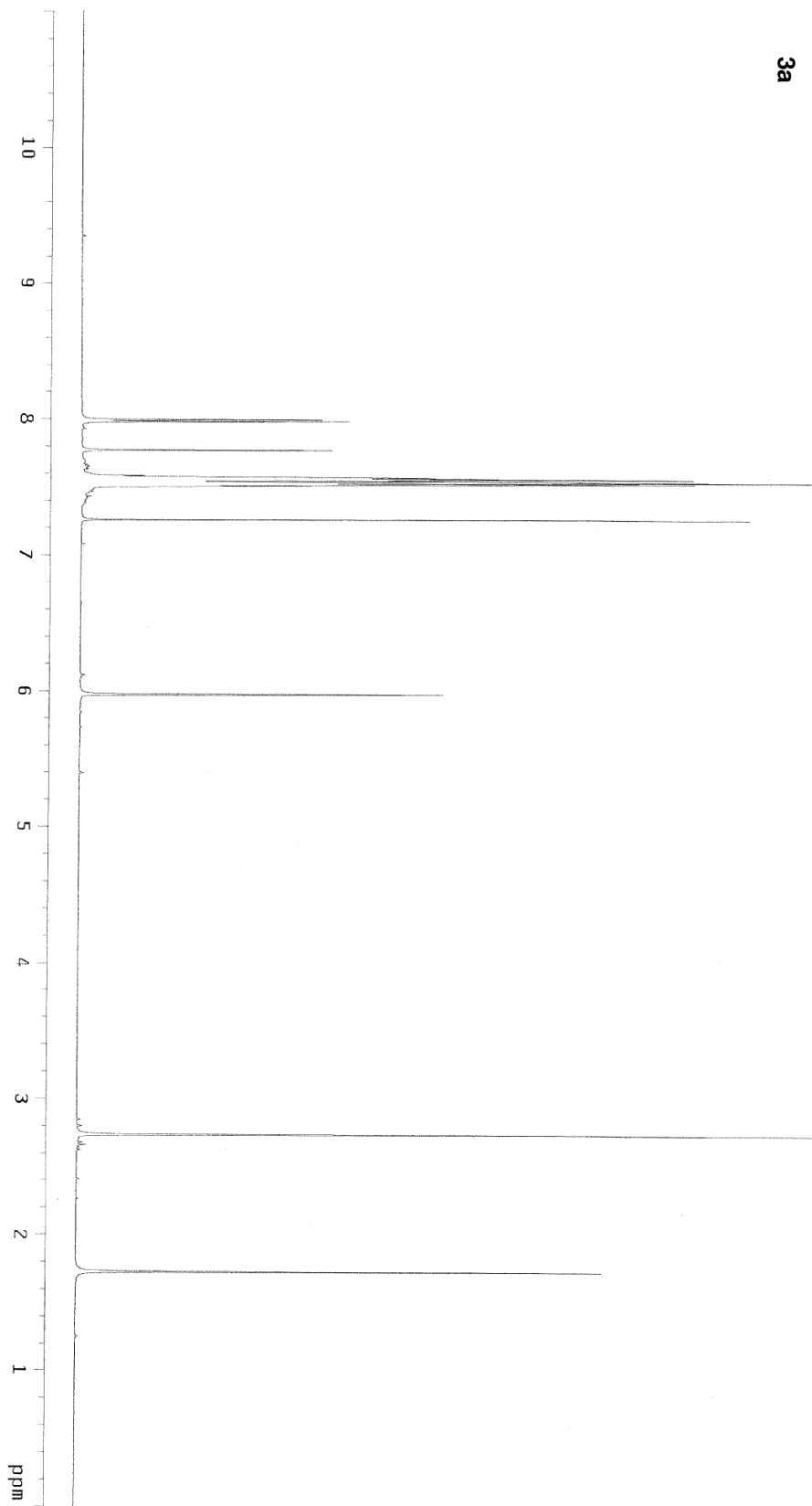
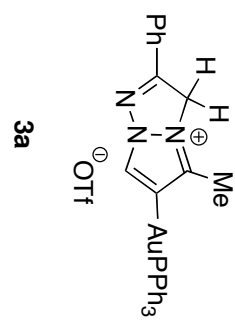


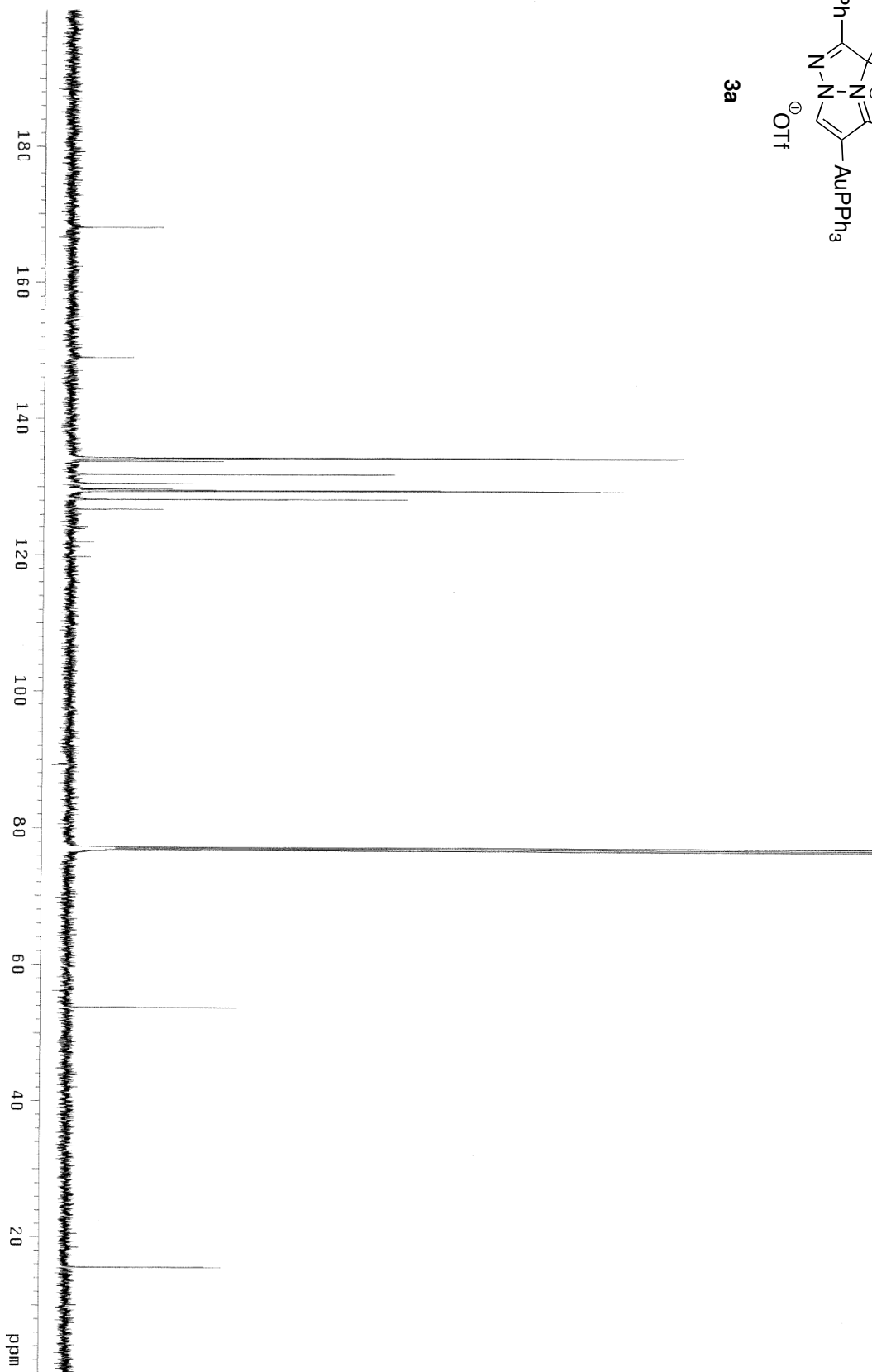
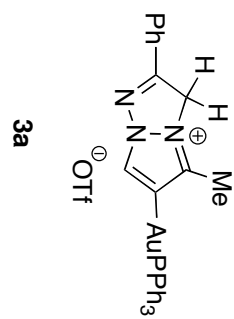


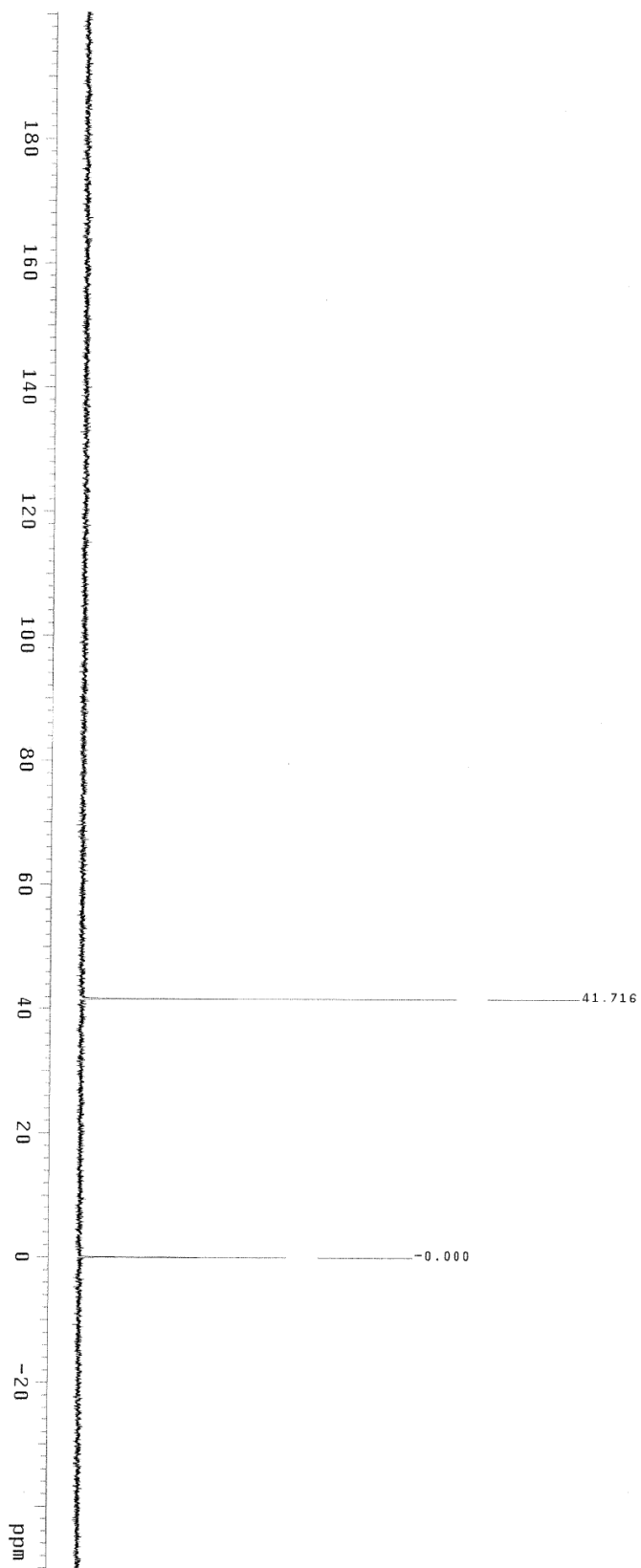
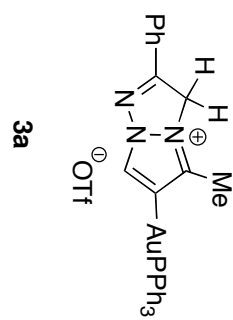


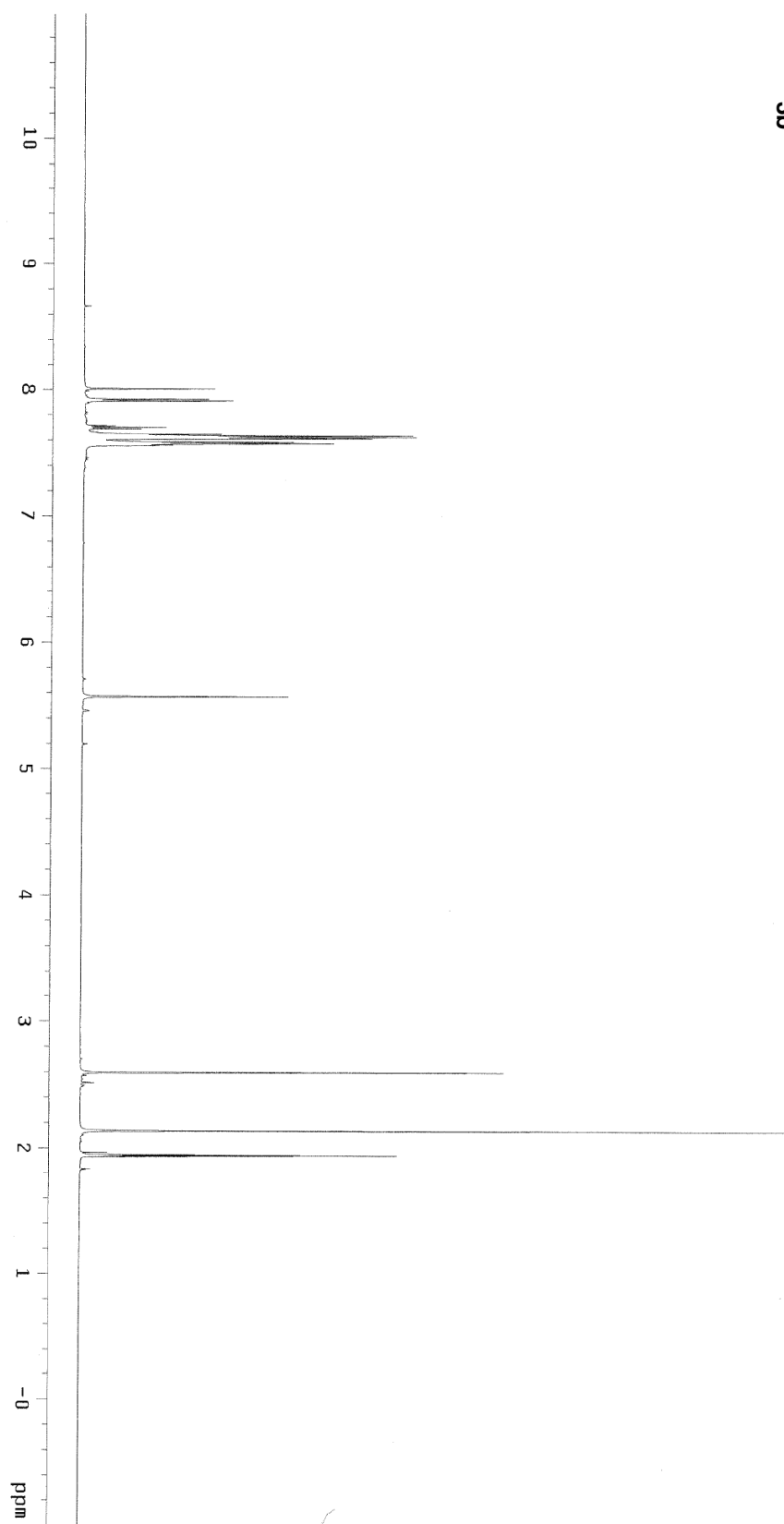
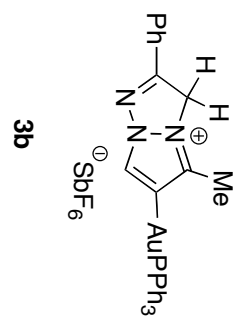


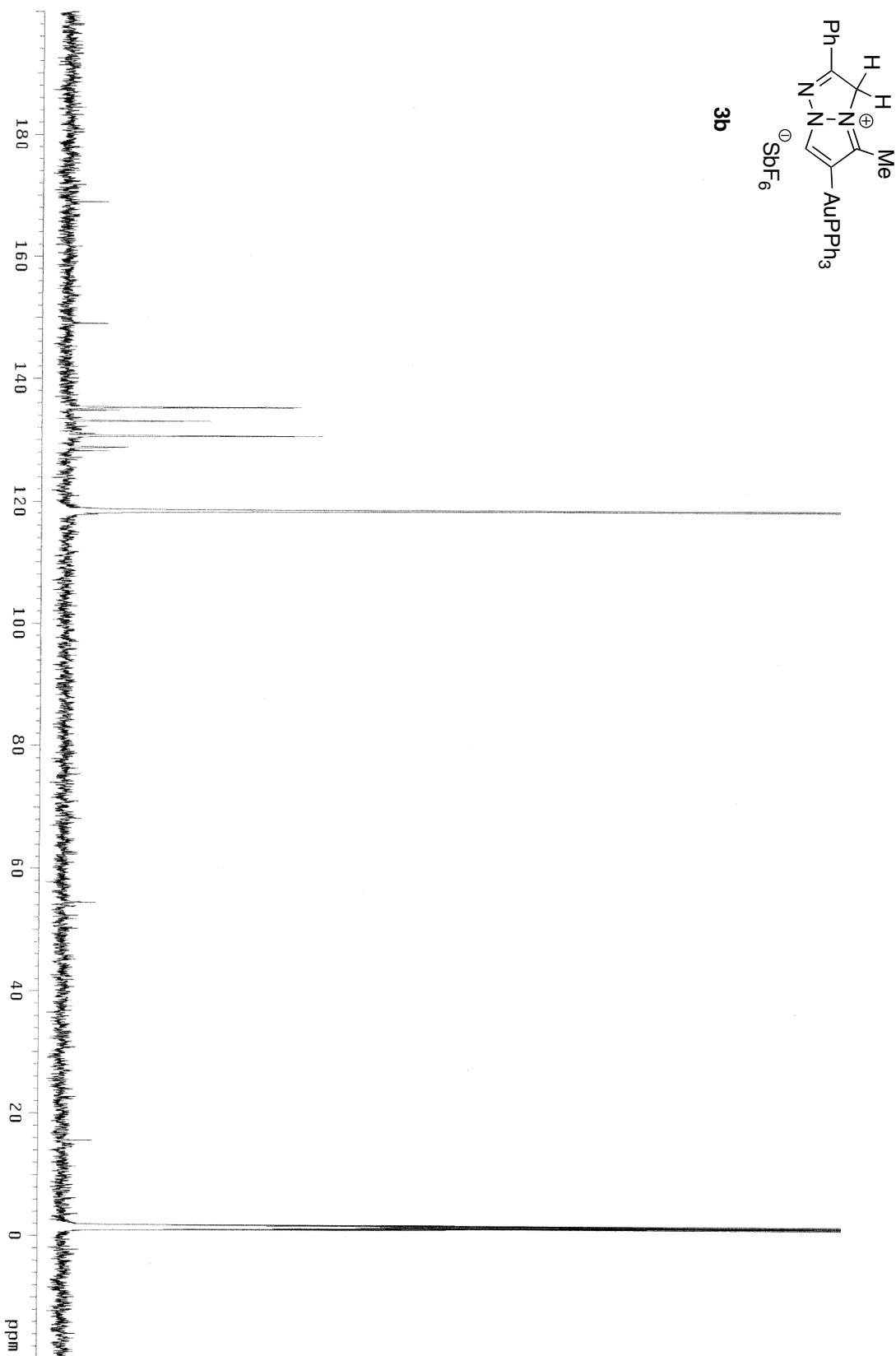


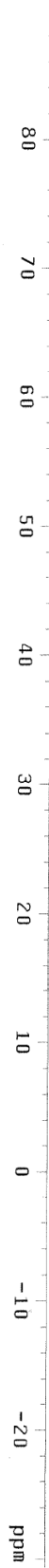
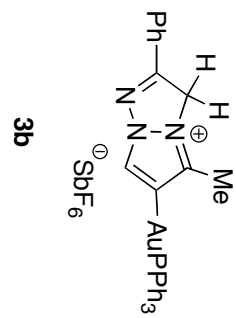


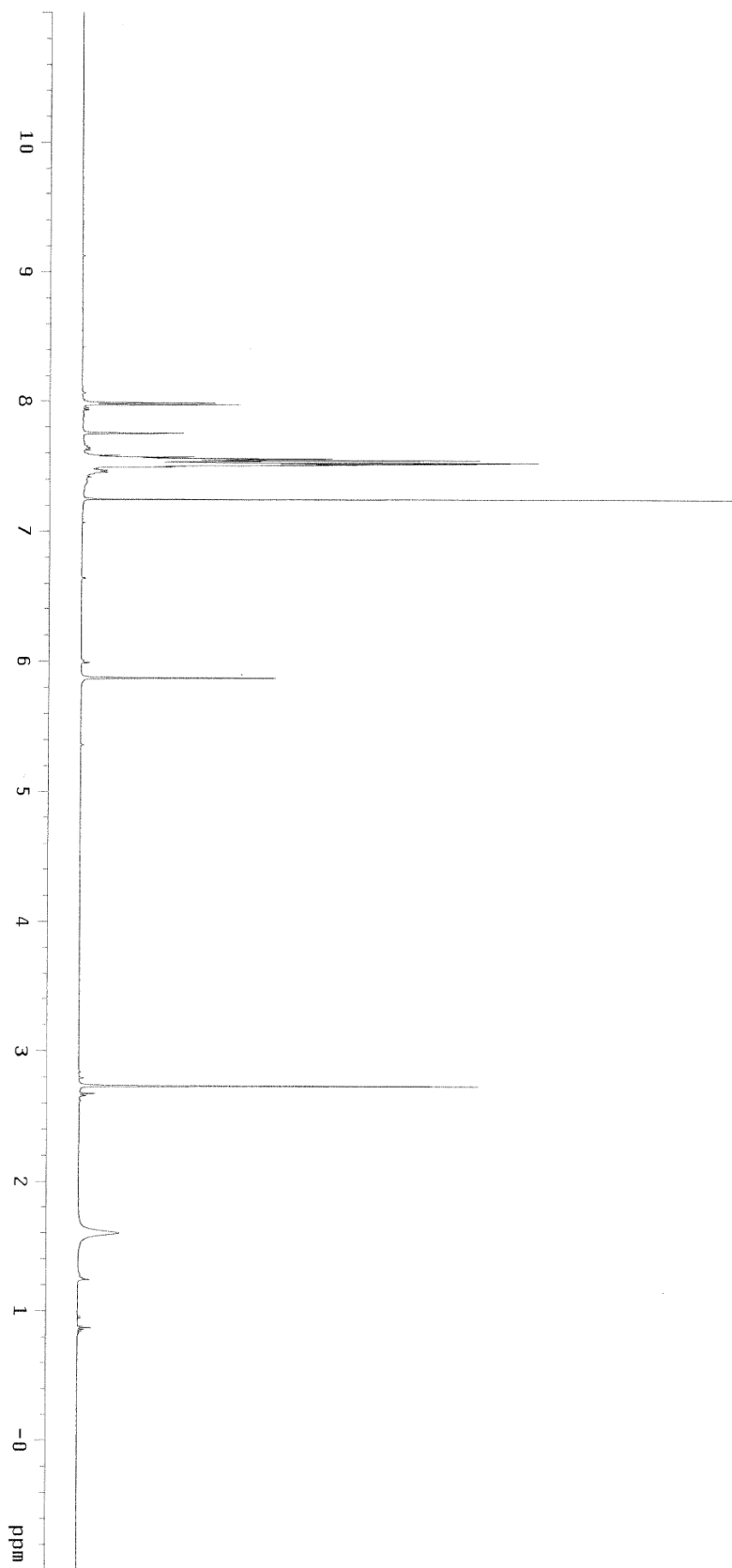
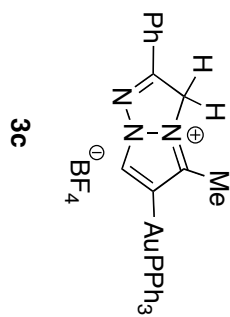


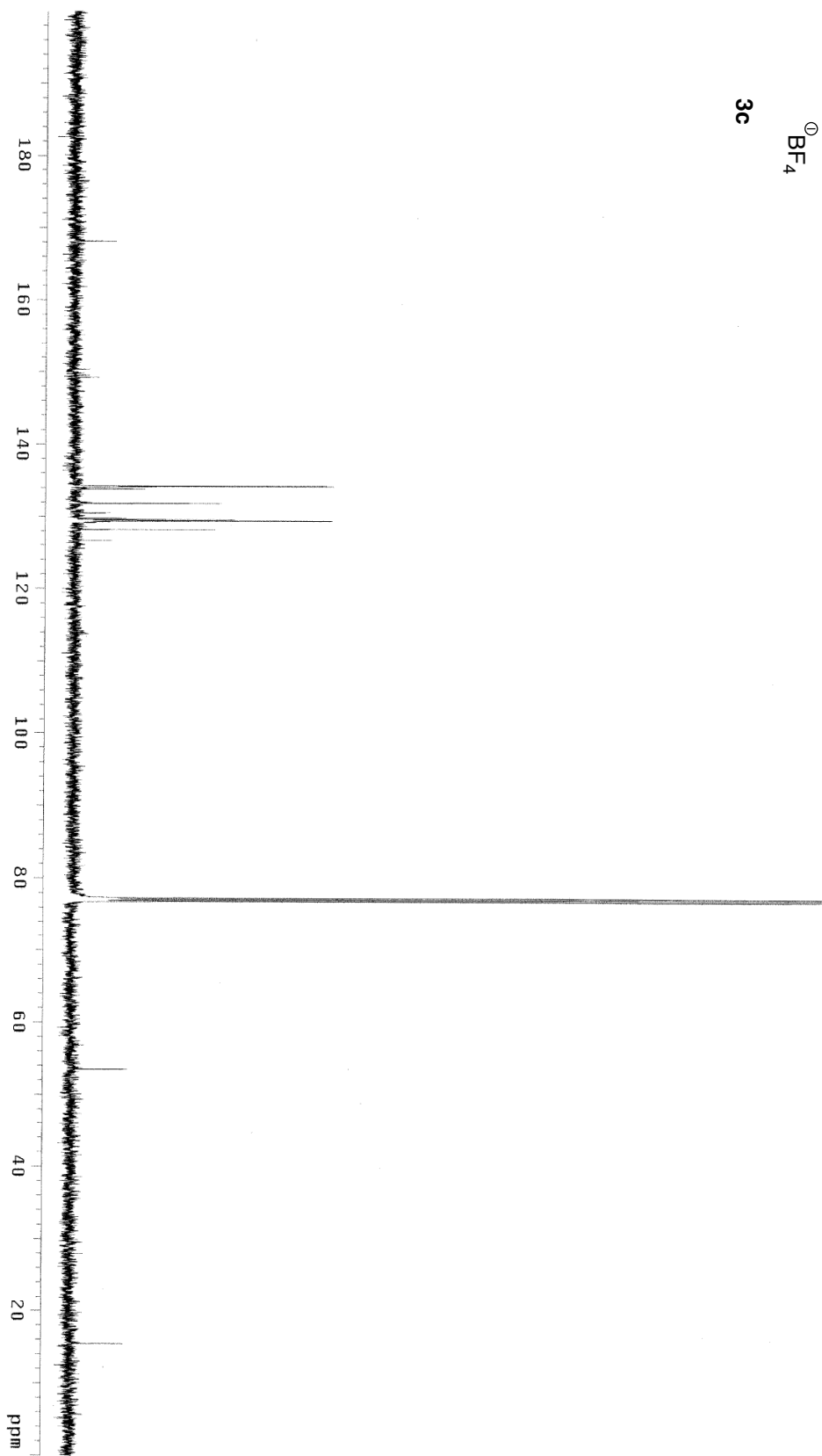
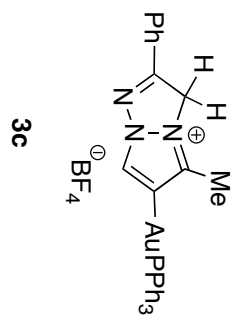


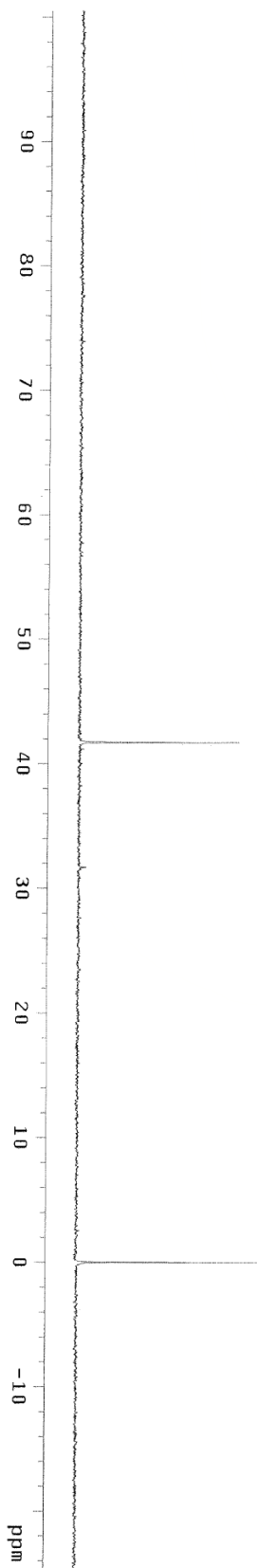
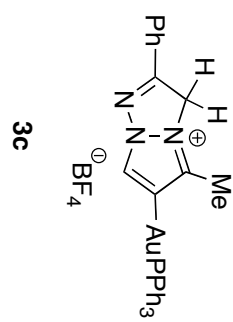


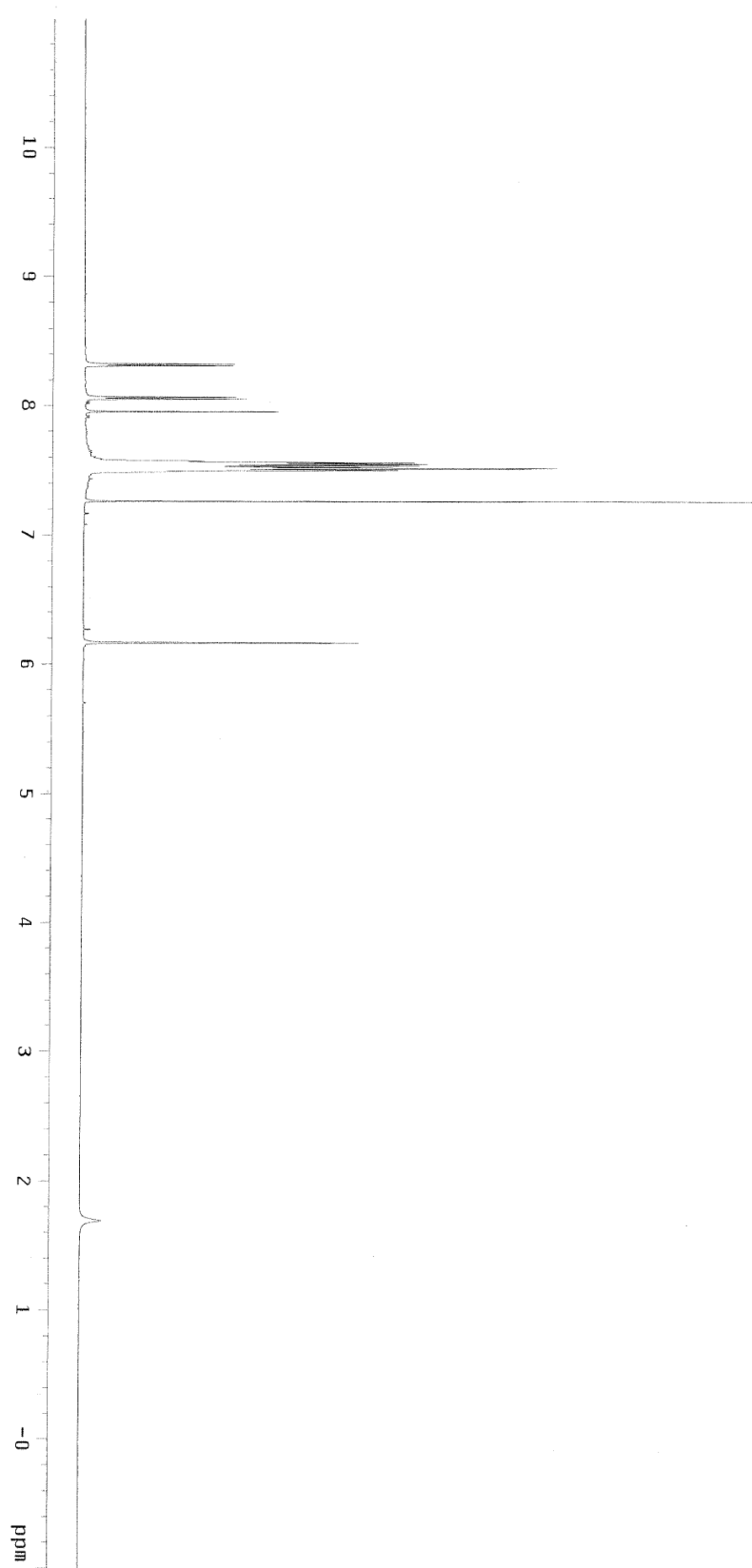
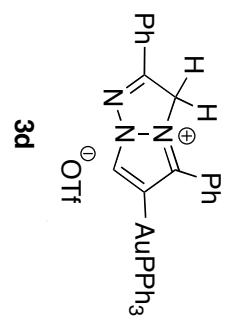


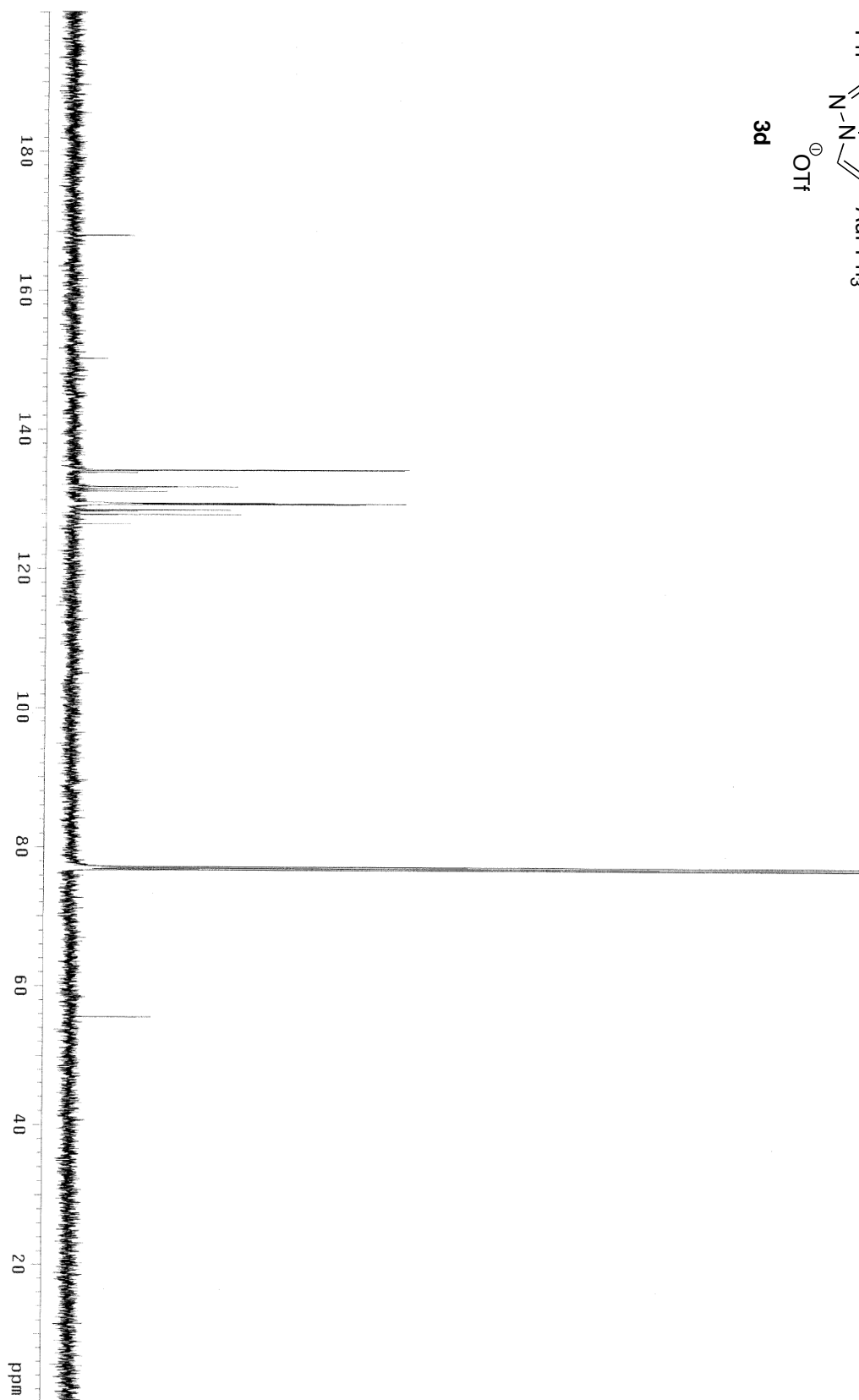
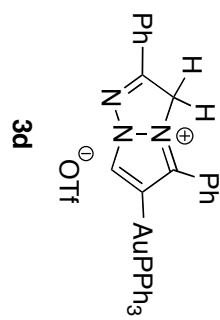


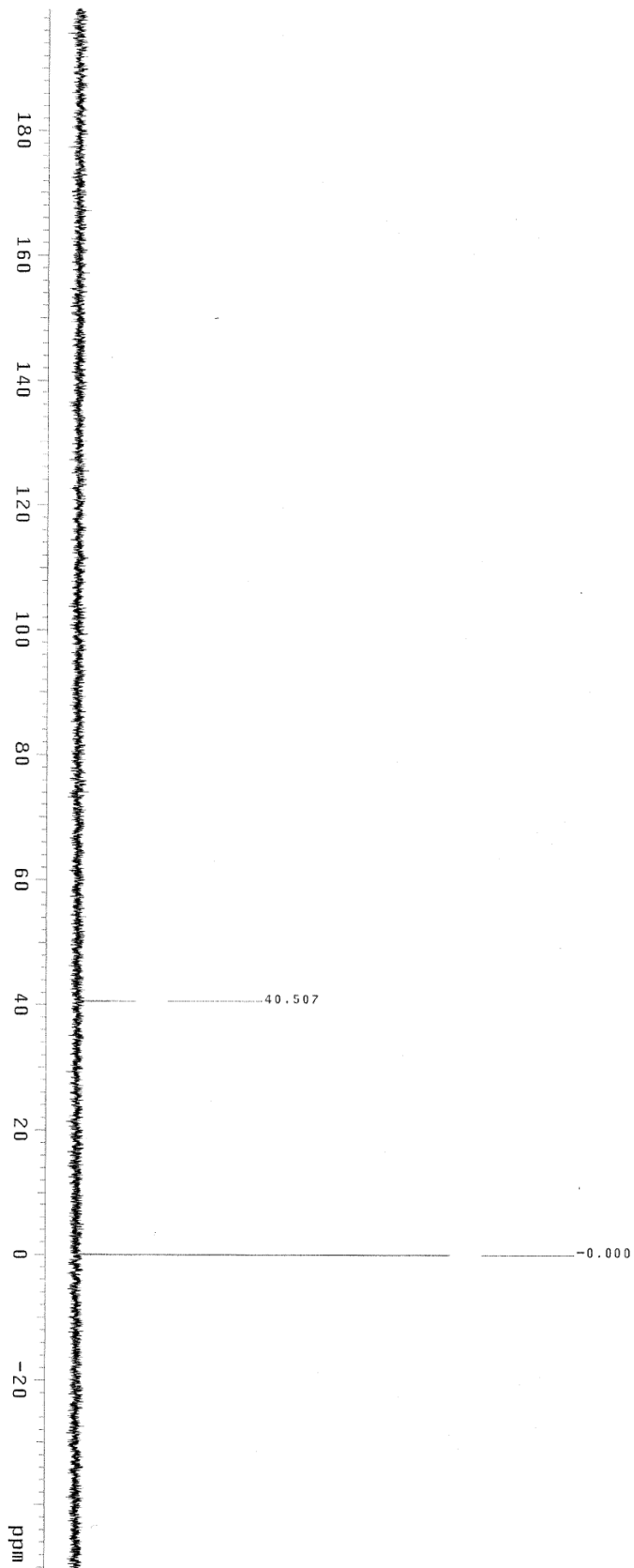
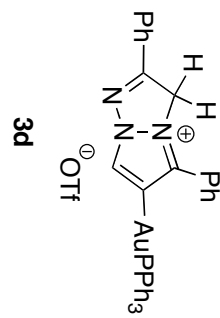


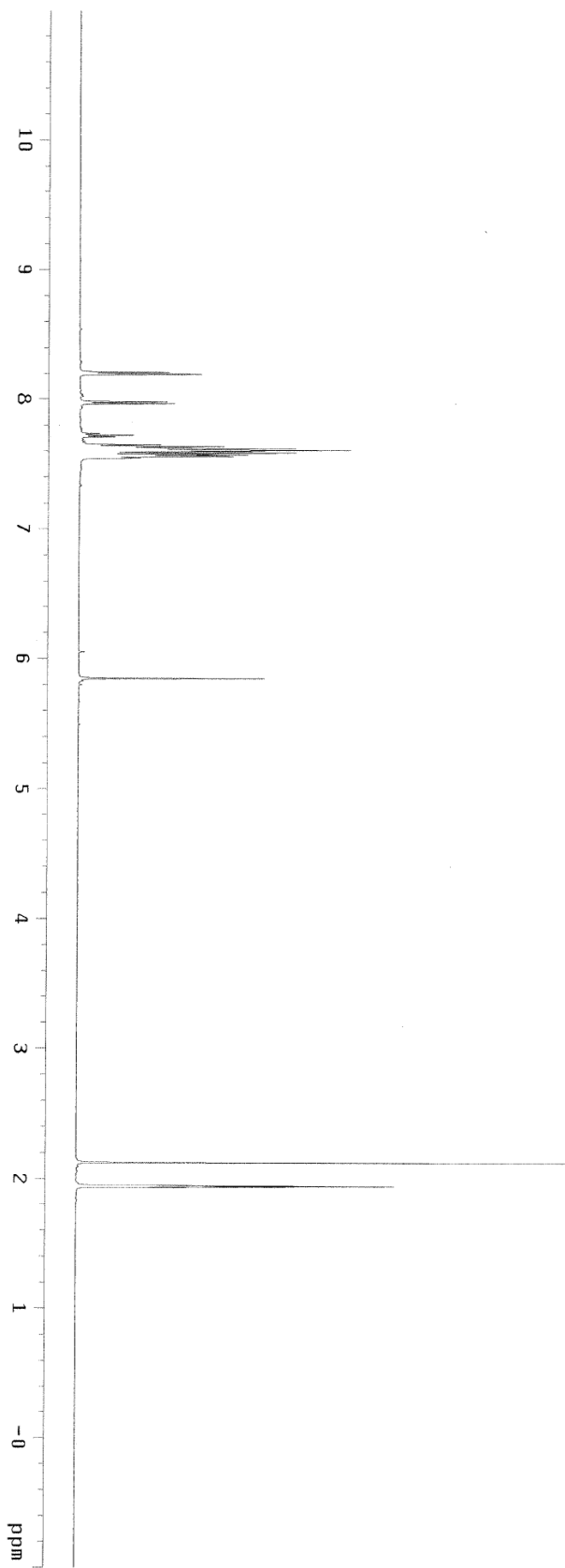
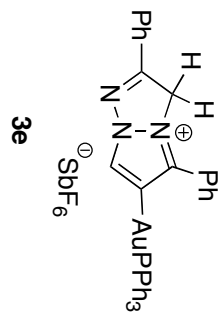


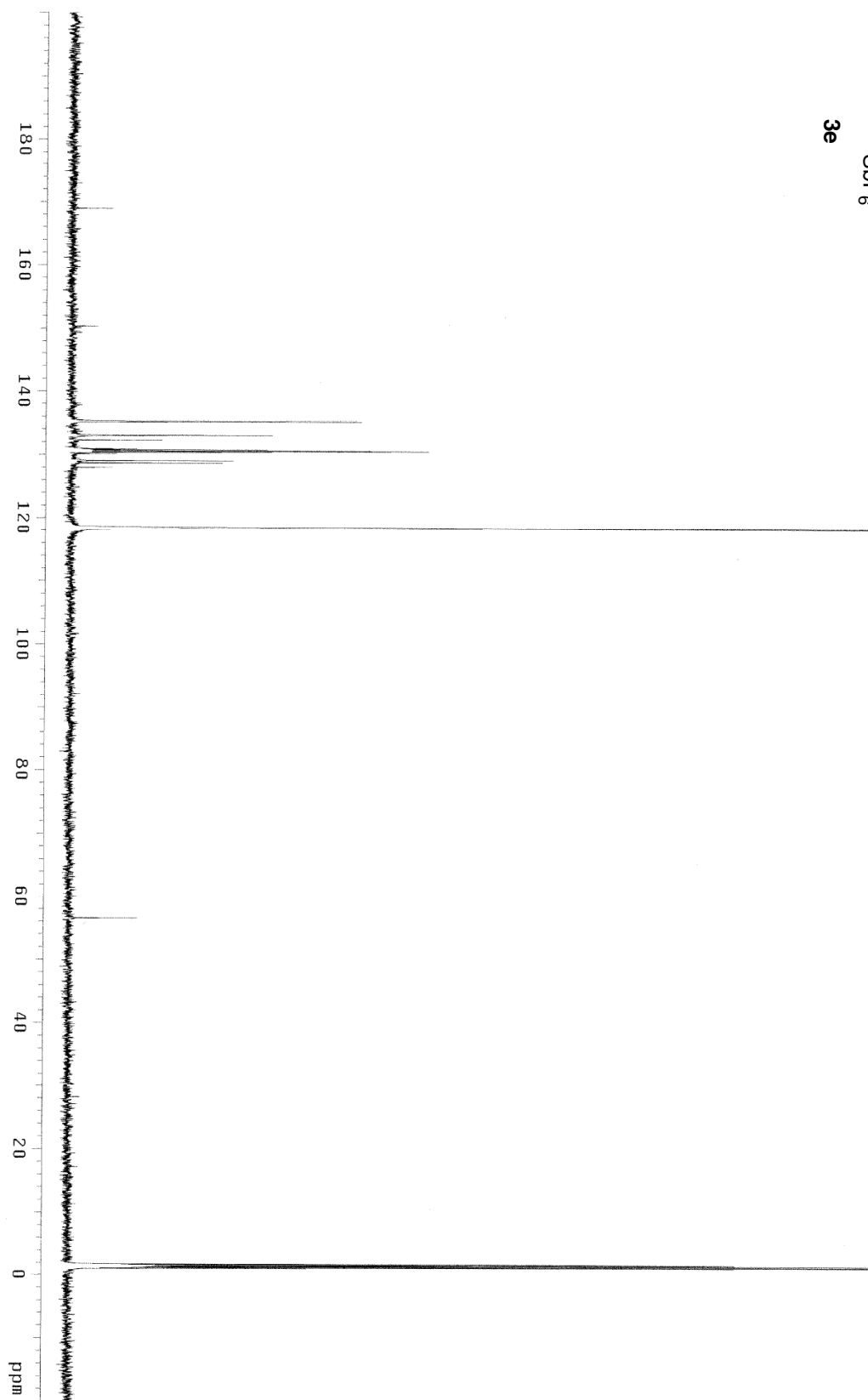
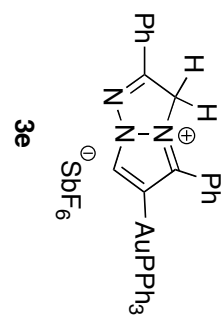


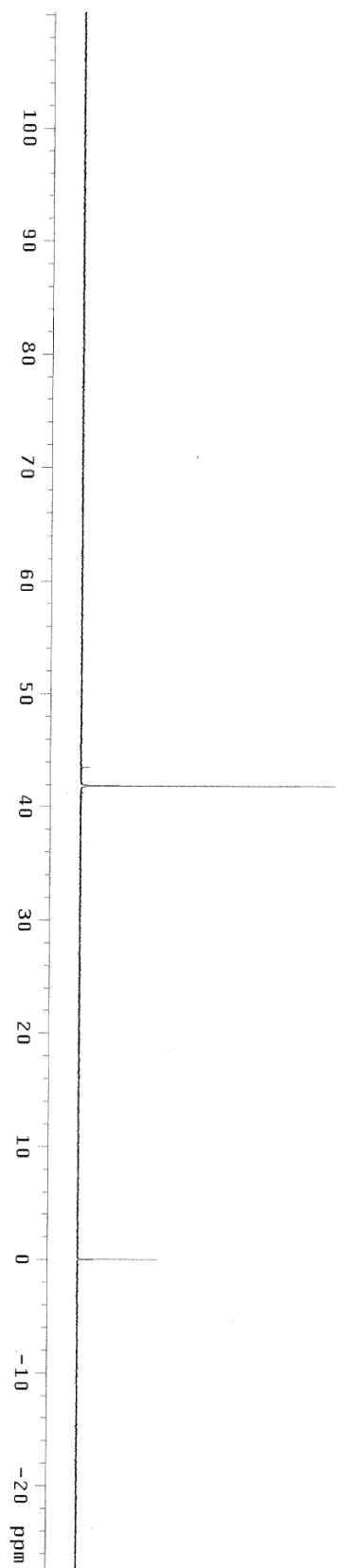
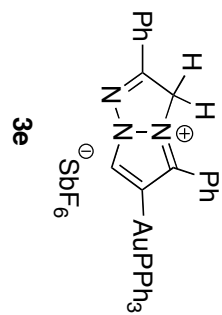


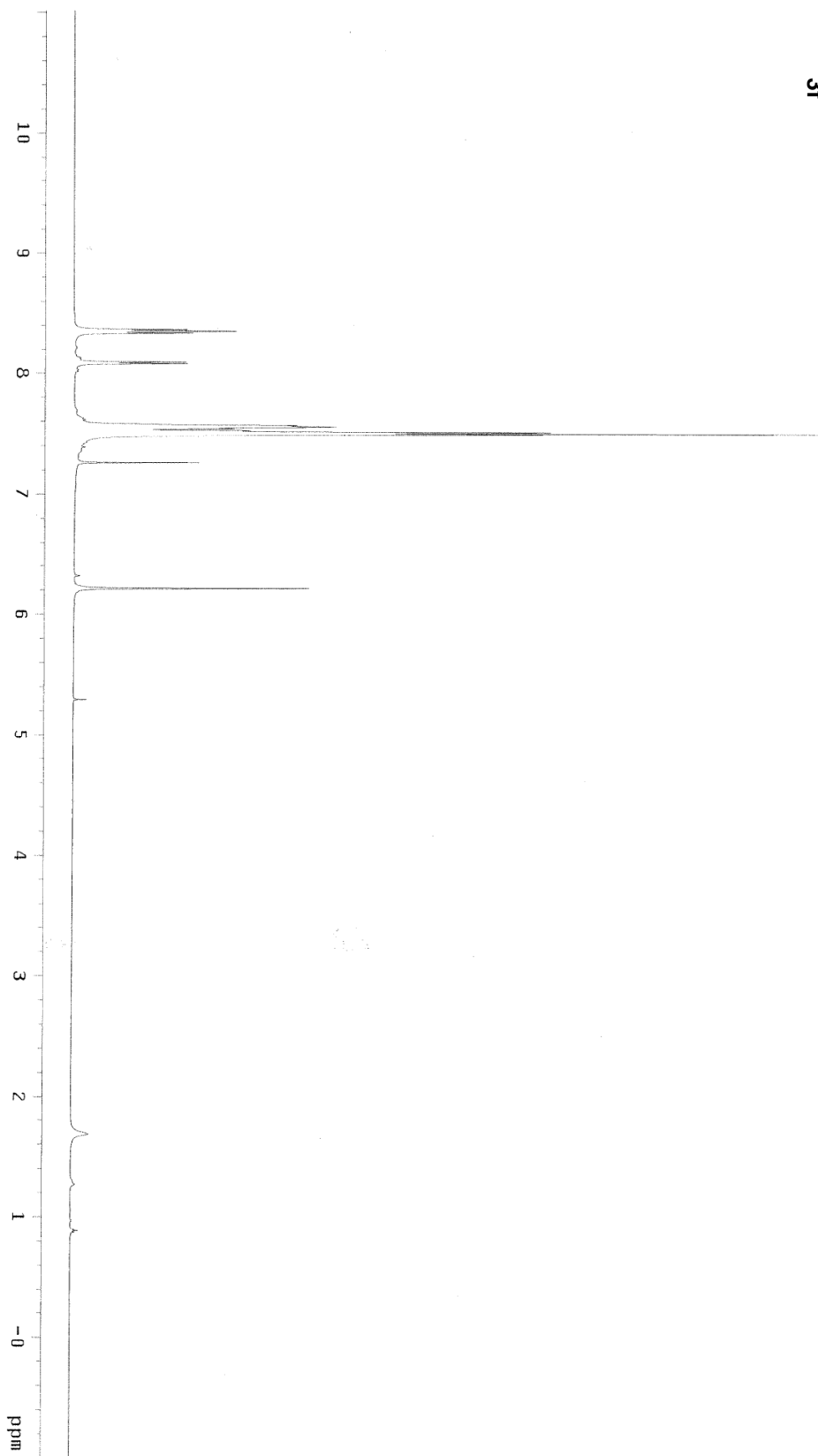
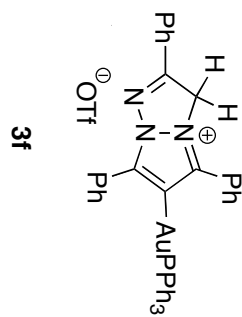


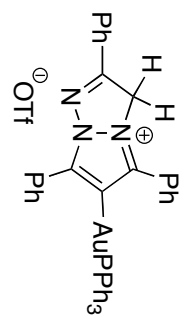












3f

