

Supporting Information

Preparation, Structure, and Versatile Reactivity of Pseudocyclic Benziodoxole Triflate, New Hypervalent Iodine Reagent

Akira Yoshimura,* Khiem C. Nguyen, Scott C. Klasen, Akio Saito, Victor N. Nemykin,
and Viktor V. Zhdankin*

^a Department of Chemistry and Biochemistry, University of Minnesota Duluth,
Duluth, Minnesota 55812, USA

^b Division of Applied Chemistry, Institute of Engineering, Tokyo University of
Agriculture and Technology, 2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan

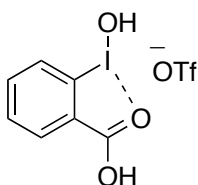
| Table of Contents | pp |
|--|----|
| 1. General experimental remarks | 2 |
| 2. Preparation of of IBA-OTf 4 | 2 |
| 3. ESI-Mass Spectrum of IBA-OTf 4 in MeOH | 3 |
| 4. Reactions of IBA-OTf with Nucleophiles | 3 |
| 5. IBA-OTf-Mediated Catalytic Cyclization of 10 | 10 |
| 6. Control Experiments for Catalytic Preparation of 1,2,4-oxadiazole 10 | 13 |
| 7. References | 14 |
| 8. Spectra of products | 15 |

1. General experimental remarks

All reactions were performed under dry argon atmosphere with flame-dried glassware. All commercial reagents were ACS reagent grade and used without further purification. Dichloromethane was distilled from CaH₂ immediately prior to use. Diethyl ether was distilled from Na/benzophenone. Melting points were determined in an open capillary tube with a Mel-temp II melting point apparatus. Infrared spectra were recorded as a KBr pellet on a Perkin-Elmer 1600 series FT-IR spectrophotometer. ¹H NMR spectra were recorded on a Varian Inova 500 MHz NMR spectrometer; ¹³C NMR spectra were recorded on Varian Inova 500 and Varian 300 MHz NMR spectrometers at 125 and 75 MHz, respectively. Chemical shifts are reported in parts per million (ppm). ¹H and ¹³C chemical shifts are referenced relative to tetramethylsilane.

2. Preparation and characterization of IBA-OTf 4

1,3-Dihydroxy-1*H*-1λ³-benzo[*d*][1,2]iodoxol-1-yl trifluoromethanesulfonate (4)



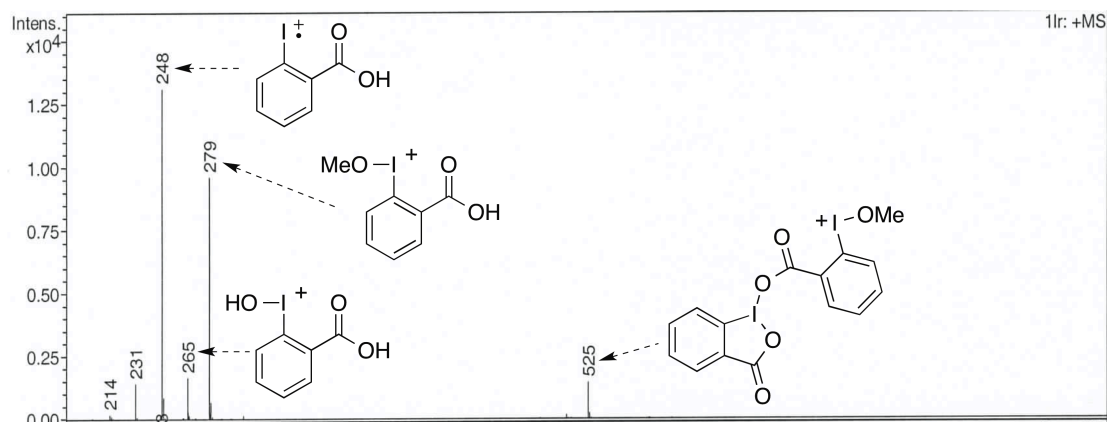
Trifluoromethanesulfonic acid (158 mg, 1.05 mmol) was added dropwise at 0 °C to a stirred mixture of 2-iodosylbenzoic acid (264 mg, 1.00 mmol) with CH₂Cl₂ (2 mL). The reaction was stirred at 0 °C for 2 h. After completion of the reaction, the solvent was removed under reduced pressure and the solid product was washed with hexane and diethyl ether several times then dried in vacuum to give 384 mg (93%) of compound **4** as a white solid. Recrystallization of product **4** from acetonitrile at 0 °C afforded colorless prisms; mp 154.6-155.1 °C; IR (KBr) cm⁻¹ 3568, 3218, 3077, 3008, 2908, 2411, 1710, 1592, 1534, 1404, 1281, 1243, 1181, 740, 633; ¹H NMR (500 MHz, CD₃CN): δ 8.38 (d, *J*

= 7.8 Hz 1H), 8.25-8.19 (m, 1H), 8.02 (d, $J = 8.5$ Hz, 1H), 7.94-7.89 (m, 1H); ^{13}C NMR (125 MHz, CD_3CN): δ 174.8, 138.5, 133.2, 131.9, 126.5, 125.7, 121.7, 120.4 (q, $^1J_{\text{CF}} = 317.7$ Hz); ^{19}F NMR (470 MHz, CD_3CN): δ -79.3; Anal. Calcd for $\text{C}_8\text{H}_6\text{F}_3\text{IO}_6\text{S}$: C, 23.20; H, 1.46; I, 30.65; S, 7.74. Found: C, 23.28; H, 1.59; I, 30.40; S, 7.48; HRMS (ESI): calcd for $\text{C}_7\text{H}_6\text{IO}_3$ ($[\text{M}-\text{OTf}]^+$): 264.9362, found: 264.9360.

In solid state IBA-OTf is a stable compound at room temperature, and it melts at 154.6-155.1 °C without any observed decomposition. IBA-OTf solution in CD_3CN does not show any decomposition after one week in a refrigerator.

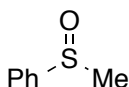
Single crystals of product **4** suitable for X-ray crystallographic analysis were obtained by slow crystallization from the acetonitrile solution. X-ray diffraction data for **4** were collected on Rigaku RAPID II Image Plate system using graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å) at 123 K. The structure was solved by the Patterson method (SHELXS 86) and refined by full-matrix least-squares refinement on F^2 using Crystals for Windows program. Crystal data for **4** $\text{C}_8\text{H}_6\text{F}_3\text{IO}_6\text{S}$: M 414.09, triclinic, space group P-1, $a = 5.4618(6)$, $b = 9.7781(11)$, $c = 11.8765(13)$ Å, $\alpha = 98.200(7)$, $\beta = 93.463(7)$, $\gamma = 91.657(7)$ °, $V = 626.19(12)$ Å³, $Z = 2$, $\mu = 2.781$ mm⁻¹, 4879 reflections measured, 2283 unique; final $R_1 = 0.0834$, $R_w = 0.2099$. CCDC-1047273.

3. ESI-Mass Spectrum of IBA-OTf **4** in MeOH



4. Reactions of IBA-OTf with Nucleophiles

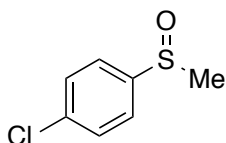
Methyl phenyl sulfoxide (**5**)¹



Thioanisole (16 mg, 0.125 mmol) was added to a solution of **4** (62 mg, 0.15 mmol) in acetonitrile (1 mL). The reaction was stirred at room temperature for 10 minutes. After completion of the reaction, 5% aqueous Na₂S₂O₃ (5 mL) and saturated NaHCO₃ (5 mL) were added, and the mixture was extracted with dichloromethane. The organic phase was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. Purification by preparative TLC (hexane-ethyl acetate = 3 : 1) afforded 15 mg (83%) of analytically pure **5**, yellow oil; IR (CH₂Cl₂) cm⁻¹ 3054, 2916, 2849, 1443, 1048, 749, 692; ¹H NMR (500 MHz, CDCl₃): δ 7.68-7.63 (m, 2H), 7.57-7.48 (m, 3H), 2.73 (s, 3H).

Recovery of 2-iodobenzoic acid: The aqueous layer was acidified with 12M HCl to pH about 1-2 and then extracted with dichloromethane. The organic phase was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure to give of 36 mg (97%) the 2-iodobenzoic acid.

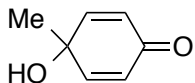
p-Chlorophenyl methyl sulfoxide (**6**)¹



p-Chlorophenyl methyl sulfide (20 mg, 0.125 mmol) was added to a solution of **4** (62 mg, 0.15 mmol) in acetonitrile (1 mL). The reaction was stirred at room temperature for 10 minutes. After completion of the reaction, 5% aqueous Na₂S₂O₃ (5 mL) and saturated NaHCO₃ (5 mL) were added, and the mixture was extracted with dichloromethane. The organic phase was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. Purification by preparative TLC (hexane-ethyl acetate = 3 : 1) afforded 20 mg (91%) of analytically pure **6**, yellow oil; IR (CH₂Cl₂) cm⁻¹ 3050, 2915, 2849, 1476, 1090, 1053, 741; ¹H NMR (500 MHz, CDCl₃): δ 7.60 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H),

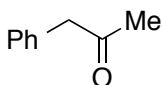
2.72 (s, 3H).

4-Hydroxy-4-methylcyclohexa-2,5-dienone (**7**)²



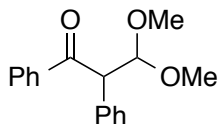
p-Cresol (14 mg, 0.125 mmol) was added to a solution of **4** (62 mg, 0.15 mmol) in methylene chloride (1.5 mL) and water (75 μ L). The reaction was stirred at 0 °C to room temperature for 24 hour. After completion of the reaction, 5% aqueous Na₂S₂O₃ (5 mL) and saturated NaHCO₃ (5 mL) were added, and the mixture was extracted with dichloromethane. The organic phase was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. Purification by preparative TLC (hexane-ethyl acetate = 3 : 1) afforded 8 mg (50 %) of analytically pure **7**, colorless oil; IR (CH₂Cl₂) cm⁻¹ 3374, 2925, 2857, 1662, 1054; ¹H NMR (500 MHz, CDCl₃): δ 6.88 (d, *J* = 10.3 Hz, 2H), 6.15 (d, *J* = 10.3 Hz, 2H), 1.49 (s, 3H).

1-Phenyl-2-propanone (**8**)³



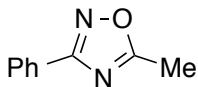
α -Methyl styrene (15 mg, 0.125 mmol) was added to a solution of **4** (62 mg, 0.15 mmol) in methylene chloride (1.5 mL) and water (75 μ L). The reaction was stirred at room temperature for 24 hour. After completion of the reaction, 5% aqueous Na₂S₂O₃ (5 mL) and saturated NaHCO₃ (5 mL) were added, and the mixture was extracted with dichloromethane. The organic phase was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. Purification by preparative TLC (hexane-ethyl acetate = 5 : 1) afforded 10 mg (59 %) of analytically pure **8**, colorless oil; IR (CH₂Cl₂) cm⁻¹ 2921, 2851, 1726, 1712, 1452, 1245, 747, 699; ¹H NMR (500 MHz, CDCl₃): δ 7.38-7.31 (m, 2H), 7.27 (t, *J* = 7.0 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 3.70 (s, 2H), 2.15 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 206.4, 134.3, 129.4, 128.8, 127.1, 51.1, 29.3.

3,3-Dimethoxy-1,2-diphenylpropan-1-one (**9**)⁴



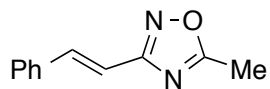
Chalcone (26 mg, 0.125 mmol) was added to a solution of **4** (62 mg, 0.15 mmol) in methanol (1.5 mL). The reaction was stirred at room temperature for 24 hour. After completion of the reaction, 5% aqueous Na₂S₂O₃ (5 mL) and saturated NaHCO₃ (5 mL) were added, and the mixture was extracted with dichloromethane. The organic phase was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. Purification by preparative TLC (hexane-ethyl acetate = 5 : 1) afforded 21 mg (62 %) of analytically pure **9**, white solid: mp 92.7-93.1 °C (lit.⁵, mp 94 °C); IR (CH₂Cl₂) cm⁻¹ 2932, 2832, 1681, 1068, 699; ¹H NMR (500 MHz, CDCl₃): δ 7.98 (d, *J* = 8.5 Hz, 2H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.46-7.38 (m, 4H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.25-7.22 (m, 1H), 5.13 (d, *J* = 8.5 Hz, 1H), 4.90 (d, *J* = 8.5 Hz, 1H), 3.45, (s, 3H), 3.21 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 197.8, 136.9, 134.8, 133.1, 129.0, 128.8, 128.7, 128.6, 127.6, 106.9, 57.0, 56.2, 54.5.

5-Methyl-3-phenyl-1,2,4-oxadiazole (**10**)⁶



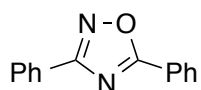
Benzaldoxime (15 mg, 0.125 mmol) was added to a solution of **4** (62 mg, 0.15 mmol) in acetonitrile (1 mL). The reaction was stirred at room temperature for 1 hour. After completion of the reaction, 5% aqueous Na₂S₂O₃ (5 mL) and saturated NaHCO₃ (5 mL) were added, and the mixture was extracted with dichloromethane. The organic phase was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. Purification by preparative TLC (hexane-ethyl acetate = 3 : 1) afforded 18 mg (90%) of analytically pure **10**, white solid: mp 38.7-38.9 °C (lit.⁶, mp 36.2-38.1 °C); IR (CH₂Cl₂) cm⁻¹ 3068, 3036, 2930, 2854, 1597, 1574, 1446, 1388, 721, 693; ¹H NMR (500 MHz, CDCl₃): δ 8.09-8.05 (m, 2H), 7.53-7.45 (m, 3H), 2.66 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 176.8, 168.6, 131.3, 129.1, 127.6, 127.1, 12.6.

(*E*)-5-Methyl-3-styryl-1,2,4-oxadiazole (**11**)⁷



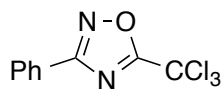
(1*E*,2*E*)-Cinnamaldehyde oxime (18 mg, 0.125 mmol) was added to a solution of **4** (62 mg, 0.15 mmol) in acetonitrile (1 mL). The reaction was stirred at room temperature for 1 hour. After completion of the reaction, 5% aqueous Na₂S₂O₃ (5 mL) and saturated NaHCO₃ (5 mL) were added, and the mixture was extracted with dichloromethane. The organic phase was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. Purification by preparative TLC (hexane-ethyl acetate = 5 : 1) afforded 16 mg (70%) of analytically pure **11**, white solid: mp 79.3-79.6 °C (lit.⁷, mp 80-81 °C); IR (CH₂Cl₂) cm⁻¹ 3058, 3025, 2929, 1645, 1592, 1446, 1387, 1366, 971, 761, 689; ¹H NMR (500 MHz, CDCl₃): δ 7.67 (d, *J* = 16.3 Hz, 1H), 7.59-7.54 (m, 2H), 7.43-7.33 (m, 3H), 7.04 (d, *J* = 16.3 Hz, 1H) 2.62 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 175.8, 167.9, 138.9, 135.3, 129.4, 128.9, 127.4, 112.8, 12.3.

3,5-Diphenyl-1,2,4-oxadiazole (**12**)⁶



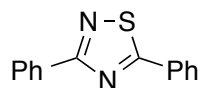
Benzaldoxime (15 mg, 0.125 mmol) was added to a solution of **4** (62 mg, 0.15 mmol) in benzonitrile (1 mL). The reaction was stirred at room temperature for 1 hour. After completion of the reaction, 5% aqueous Na₂S₂O₃ (5 mL) and saturated NaHCO₃ (5 mL) were added, and the mixture was extracted with dichloromethane. The organic phase was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. Purification by preparative TLC (hexane-ethyl acetate = 3 : 1) afforded 24 mg (86%) of analytically pure **12**, white solid: mp 107.3-107.6 °C (lit.⁶, mp 104.9-106.1 °C); IR (CH₂Cl₂) cm⁻¹ 3060, 2952, 1609, 1562, 1445, 1365, 726, 708, 688; ¹H NMR (500 MHz, CDCl₃): δ 8.23 (d, *J* = 7.0 Hz, 2H), 8.21-8.16 (m, 2H), 7.63-7.59 (m, 1H), 7.58-7.46 (m, 5H); ¹³C NMR (75 MHz, CDCl₃): δ 175.9, 169.2, 133.0, 131.4, 129.3, 129.1, 128.4, 127.8, 127.2, 124.6.

3-Phenyl-5-(trichloromethyl)-1,2,4-oxadiazole (**13**)⁸



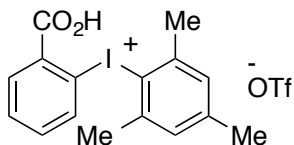
Benzaldoxime (15 mg, 0.125 mmol) was added to a solution of **4** (62 mg, 0.15 mmol) in 2,2,2-trichloroacetonitrile (1 mL). The reaction was stirred at room temperature for 1 hour. After completion of the reaction, 5% aqueous Na₂S₂O₃ (5 mL) and saturated NaHCO₃ (5 mL) were added, and the mixture was extracted with dichloromethane. The organic phase was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. Purification by preparative TLC (hexane-ethyl acetate = 5 : 1) afforded 22 mg (67%) of analytically pure **13**, colorless oil; IR (CH₂Cl₂) cm⁻¹ 3132, 3071, 3031, 2926, 1593, 1568, 1446, 1354, 847, 825, 724, 690; ¹H NMR (500 MHz, CDCl₃): δ 8.15-8.08 (m, 2H), 7.59-7.47 (m, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 174.4, 169.1, 132.0, 129.0, 127.7, 125.4, 83.5.

3,5-Diphenyl-1,2,4-thiadiazole (**14**)⁹



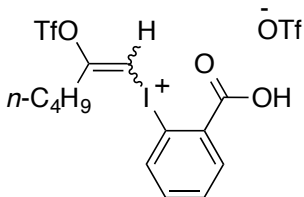
Benzaldoxime (15 mg, 0.125 mmol) was added to a solution of **4** (83 mg, 0.20 mmol) in acetonitrile (1 mL). The reaction was stirred at room temperature for 1 hour. After completion of the reaction, 5% aqueous Na₂S₂O₃ (5 mL) and saturated NaHCO₃ (5 mL) were added, and the mixture was extracted with dichloromethane. The organic phase was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. Purification by preparative TLC (hexane-ethyl acetate = 3 : 1) afforded 12 mg (80%) of analytically pure **14**, white solid: mp 88.3-88.9 °C (lit.⁹, mp 89.8-90.2 °C); IR (CH₂Cl₂) cm⁻¹ 3046, 3025, 2924, 1509, 1476, 1439, 1417, 1329, 1275, 1241; ¹H NMR (500 MHz, Acetone-d₆): δ 8.43-8.38 (m, 2H), 8.18-8.14 (m, 2H), 7.68-7.54 (m, 6H); ¹³C NMR (75 MHz, Acetone-d₆): δ 189.3, 174.4, 133.8, 133.1, 131.4, 130.4, 129.7, 129.0, 128.3.

2-(Mesityl-λ³-iodanyl)benzoic acid triflate salt (**15**)



Mesitylene (24 mg, 0.20 mmol) was added to a solution of **4** (83 mg, 0.20 mmol) in 2,2,2-trifluoroethanol (1 mL). The reaction was stirred at room temperature for 24 hour. After completion of reaction, the mixture was evaporated under reduced pressure and the solid product was washed with diethyl ether several times and then dried in vacuum to give **15**; 92 mg (89%) as a light pink solid. Recrystallization of **15** from dichloromethane-diethyl ether gave colorless needles: mp 185.3-186.6 °C (dec); IR (KBr) cm^{-1} 3087, 3031, 2980, 2930, 1682, 1585, 1407, 1288, 1259, 1155, 749, 635; ^1H NMR (500 MHz, CD_3OD): δ 8.44 (d, $J = 7.5$ Hz, 1H), 7.78 (t, $J = 7.5$ Hz, 1H), 7.71-7.64 (m, 1H), 7.38 (s, 2H), 6.94 (d, $J = 8.0$ Hz, 1H), 2.56 (s, 6H), 2.47 (s, 3H); ^{13}C NMR (125 MHz, CD_3OD): δ 171.1, 147.1, 145.4, 138.4, 134.9, 132.9, 131.7, 129.6, 122.0 (d, $^1J_{\text{CF}} = 316.8$ Hz), 118.1, 113.8, 26.8, 21.5; ^{19}F NMR (470 MHz, CD_3CN): δ -80.1.

2-((2-(((Trifluoromethyl)sulfonyl)oxy)hex-1-en-1-yl)- λ^3 -iodanyl)benzoic acid triflate salt (16**)¹⁰**



Hexynyl trimethylsilane (31 mg, 0.20 mmol) and trifluoromethanesulfonic acid (30 mg, 0.20 mmol) was added to a solution of **4** (83 mg, 0.20 mmol) in 2,2,2-trifluoroethanol (1 mL). The reaction was stirred at room temperature for 24 hour. After completion of reaction, the mixture was evaporated under reduced pressure and the solid product was washed with diethyl ether several times and then dried in vacuum to give **16**; 78 mg (62%) as a white solid. Recrystallization of **16** from methanol-diethyl ether gave colorless blocks: mp 148.7-149.2 °C (lit.¹⁰, mp 149 °C); IR (KBr) cm^{-1} 3099, 2974, 2947, 2885, 2508, 1670, 1590, 1411, 1310, 1224, 1197, 795, 632; ^1H NMR (500 MHz, CD_3CN): δ

8.38 (d, $J = 7.5$ Hz, 1H), 7.98-7.82 (m, 2H), 7.79 (d, $J = 8.5$ Hz, 1H), 7.17 (s, 1H), 2.85 (t, $J = 8.0$ Hz, 2H), 1.68-1.50 (m, 2H), 1.40-1.25 (m, 2H), 0.85 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (125 MHz, CD_3CN): δ 170.1, 165.5, 137.9, 133.7, 132.3, 129.7, 126.4, 118.6 (d, $^1J_{\text{CF}} = 317.6$ Hz), 114.0, 91.3, 34.6, 28.3, 21.7, 13.0; ^{19}F NMR (470 MHz, CD_3CN): δ -74.4, -79.3.

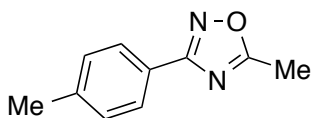
5. IBA-OTf Mediated *Typical Procedure of Catalytic Cyclization of Aldoximes*

2-Iodobenzoic acid (3.1 mg, 0.0125 mmol), *m*CPBA (52 mg, 0.300 mmol), and trifluoromethanesulfonic acid (45 mg, 0.300 mmol) were added to a solution of aldoxime **17** (0.250 mmol) in 2.0 mL of the appropriate nitrile solvent. The reaction mixture was stirred at room temperature for 24 hour. After completion of the reaction, 5% aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (5 mL) and then saturated NaHCO_3 (5 mL) were added, and the mixture was extracted with dichloromethane. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification by preparative TLC (hexane-ethyl acetate = 3 : 1 or 5 : 1) afforded analytically pure oxadiazoles **19**.

5-Methyl-3-phenyl-1,2,4-oxadiazole (10)⁶

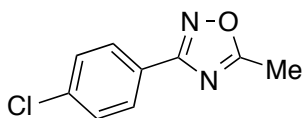
Reaction of benzaldehyde oxime (30 mg, 0.25 mmol) according to the general procedure afforded 33 mg (83%) of product **10**, isolated as a white solid.

5-Methyl-3-(*p*-tolyl)-1,2,4-oxadiazole (20)¹¹



Reaction of 4-methylbenzaldehyde oxime (34 mg, 0.25 mmol) according to the general procedure afforded 37 mg (84%) of product **20**, isolated as a white solid: mp 77.6-78.2 °C (lit.¹¹, mp 77-79 °C); IR (CH₂Cl₂) cm⁻¹ 3029, 2972, 2921, 2857, 1593, 1568, 1484, 1411, 1382, 744, 707; ¹H NMR (500 MHz, CDCl₃): δ 7.50 (d, *J* = 6.8 Hz, 2H), 7.28 (d, *J* = 6.8 Hz, 2H), 2.64 (s, 3H), 2.41 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 176.3, 168.4, 141.4, 129.5, 127.3, 124.0, 21.5, 12.4.

3-(4-Chlorophenyl)-5-methyl-1,2,4-oxadiazole (**21**)¹²



Reaction of 4-chlorobenzaldehyde oxime (39 mg, 0.25 mmol) according to the general procedure afforded 38 mg (78%) of product **21**, isolated as a white solid: mp 92.5-93.0 °C (lit.¹², mp 90-92 °C); IR (CH₂Cl₂) cm⁻¹ 3098, 3076, 2930, 2852, 1595, 1570, 1411, 1372, 1088, 834, 744; ¹H NMR (500 MHz, CDCl₃): δ 8.01 (d, *J* = 6.8 Hz, 2H), 7.46 (d, *J* = 6.8 Hz, 2H), 2.66 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 176.7, 167.6, 137.3, 129.2, 128.7, 125.3, 12.4.

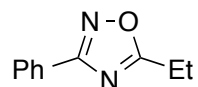
(*E*)-5-Methyl-3-styryl-1,2,4-oxadiazole (**11**)⁷

Reaction of (*1E,2E*)-cinnamaldehyde oxime (37 mg, 0.25 mmol) according to the general procedure afforded 29 mg (62%) of product **12**, isolated as white solid.

3,5-Diphenyl-1,2,4-oxadiazole (**12**)⁶

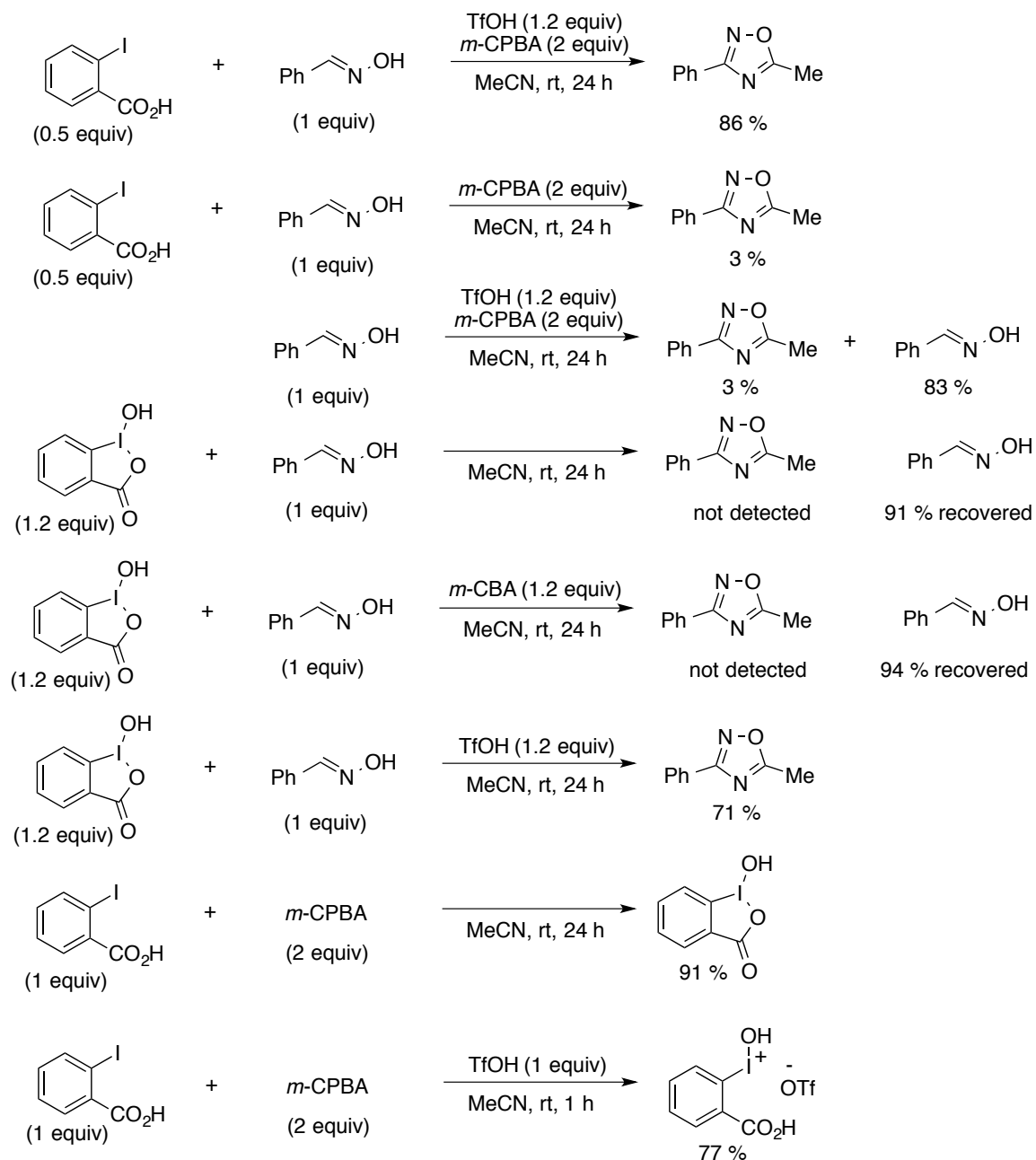
Reaction of benzaldehyde oxime (30 mg, 0.25 mmol) in benzonitrile according to the general procedure afforded 35 mg (63%) of product **12**, isolated as a white solid.

5-Ethyl-3-phenyl-1,2,4-oxadiazole (**22**)¹¹



Reaction of benzaldehyde oxime (30 mg, 0.25 mmol) in propionitrile according to the general procedure afforded 31 mg (70%) of product **22**, isolated as a colorless oil; IR (CH₂Cl₂) cm⁻¹ 3068, 3036, 2985, 2942, 2881, 1594, 1477, 1446, 1364, 715, 683; ¹H NMR (500 MHz, CDCl₃): δ 8.12-8.06 (m, 2H), 7.54-7.44 (m, 3H), 2.98 (q, *J* = 7.5 Hz, 2H), 1.46 (t, *J* = 7.5 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 180.7, 168.3, 131.0, 128.8, 127.4, 127.0, 20.3, 10.8.

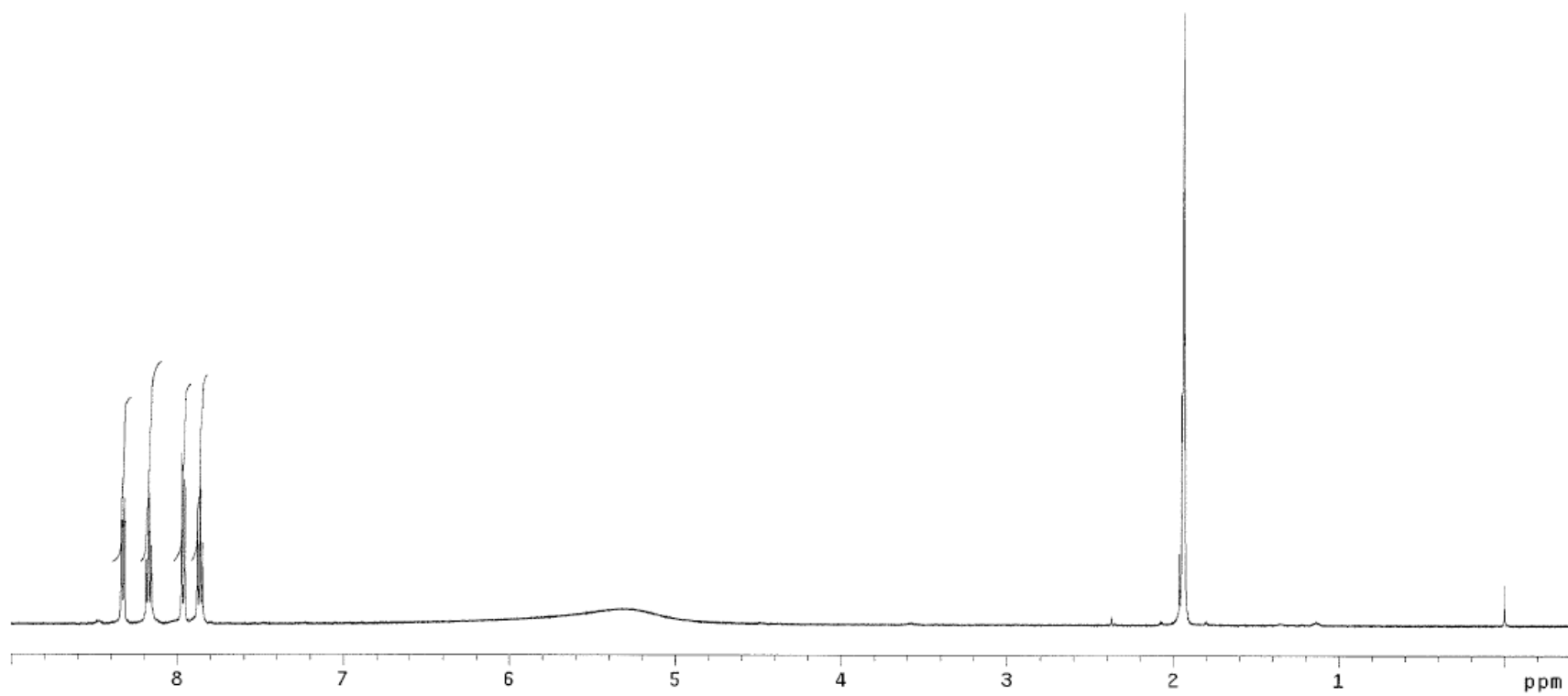
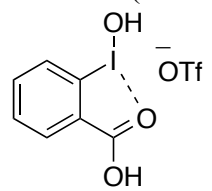
6. Control Experiments for Catalytic Preparation of 1,2,4-oxadiazole 10



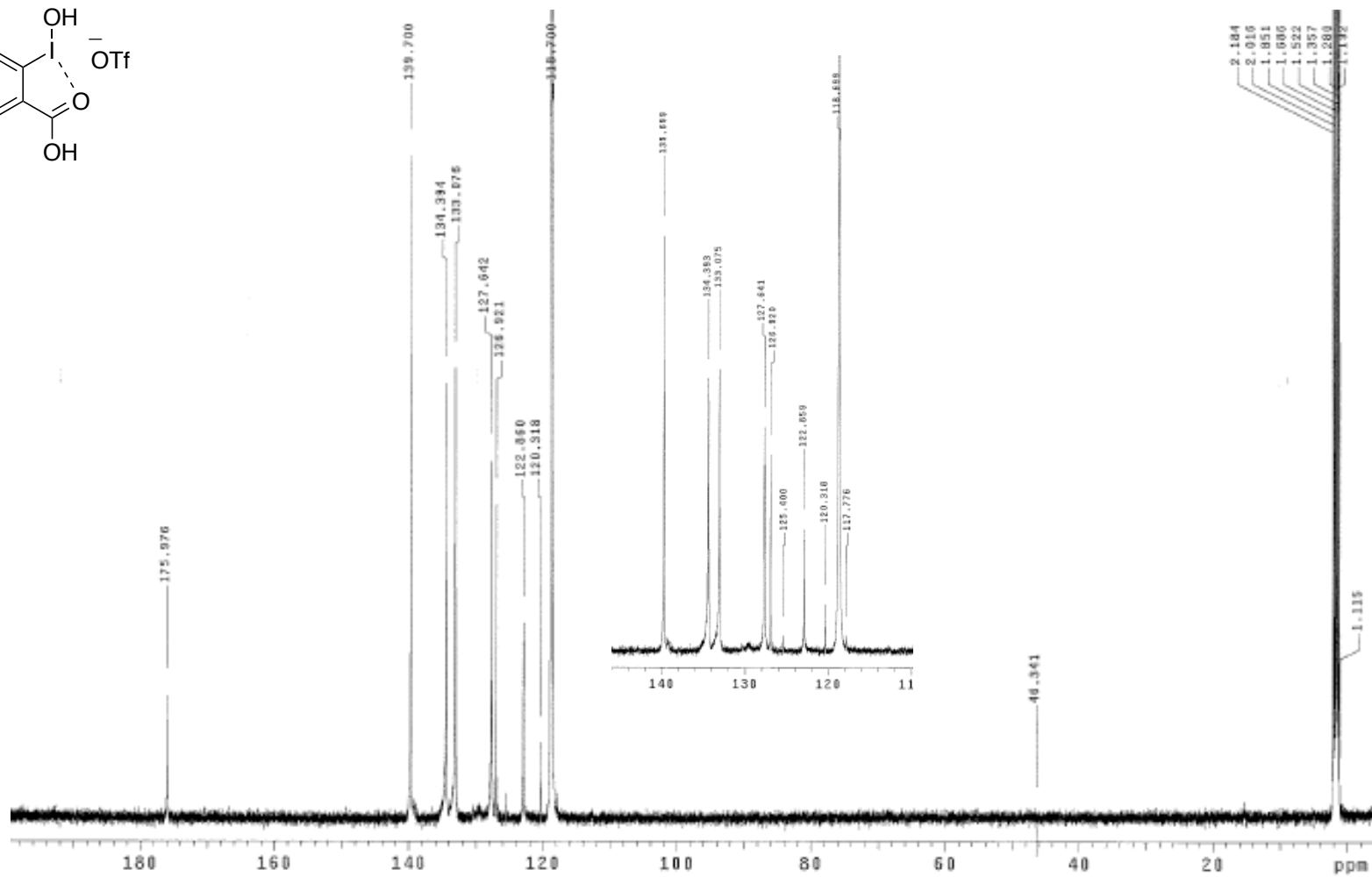
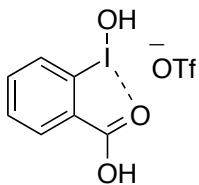
References:

1. A. Yoshimura, C. T. Banek, M. S. Yusubov, V. N. Nemykin, V. V. Zhdankin, *J. Org. Chem.* **2011**, *76*, 3812-3819.
2. T. Yakura, M. Omoto, Y. Yamauchi, Y. Tian, A. Ozono, *Tetrahedron* **2010**, *66*, 5833-5840.
3. L. Li, P. Cai, Q. Guo, S. Xue, *J. Org. Chem.* **2008**, *73*, 3516-3522.
4. M. Ochiai, K. Miyamoto, M. Shiro, T. Ozawa, K. Yamaguchi, *J. Am. Chem. Soc.* **2003**, *125*, 13006-13007.
5. R. M. Moriarty, J. S. Khosrowshahi, O. Prakash, *Tetrahedron Lett.* **1985**, *26*, 2961-2964.
6. J. K. Augustine, V. Akabote, S. G. Hegde, P. Alagarsamy, *J. Org. Chem.* **2009**, *74*, 5640-5643.
7. A. K. M. M. Hoque, W. K. Lee, H. J. Shine, D. C. Zhao, *J. Org. Chem.* **1991**, *56*, 1332-1334.
8. M. E. Layton, M. J. Kelly, K. J. Rodzinak, P. E. Sanderson, S. D. Young, R. A. Bednar, A. G. DiLella, T. P. McDonald, H. Wang, S. D. Mosser, J. F. Fay, M. E. Cunningham, D. R. Reiss, C. Fandozzi, N. Trainor, A. Liang, E. V. Lis, G. R. Seabrook, M. O. Urban, J. Yergey, K. S. Koblan, *ACS Chem. Neurosci.* **2011**, *2*, 352-362.
9. A. Yoshimura, A. D. Todora, B. J. Kastern, S. R. Koski, V. V. Zhdankin, *Eur. J. Org. Chem.* **2014**, 5149-5152.
10. V. V. Zhdankin, C. J. Kuehl, A. P. Krasutsky, J. T. Bolz, A. J. Simonsen, *J. Org. Chem.* **1996**, *61*, 6547-6551.
11. M. Adib, M. Mahdavi, N. Mahmoodi, H. Pirelahi, H. R. Bijanzadeh, *Synlett* **2006**, 1765-1767.
12. A. H. Moustafa, *Synthesis* **2003**, 837-840.

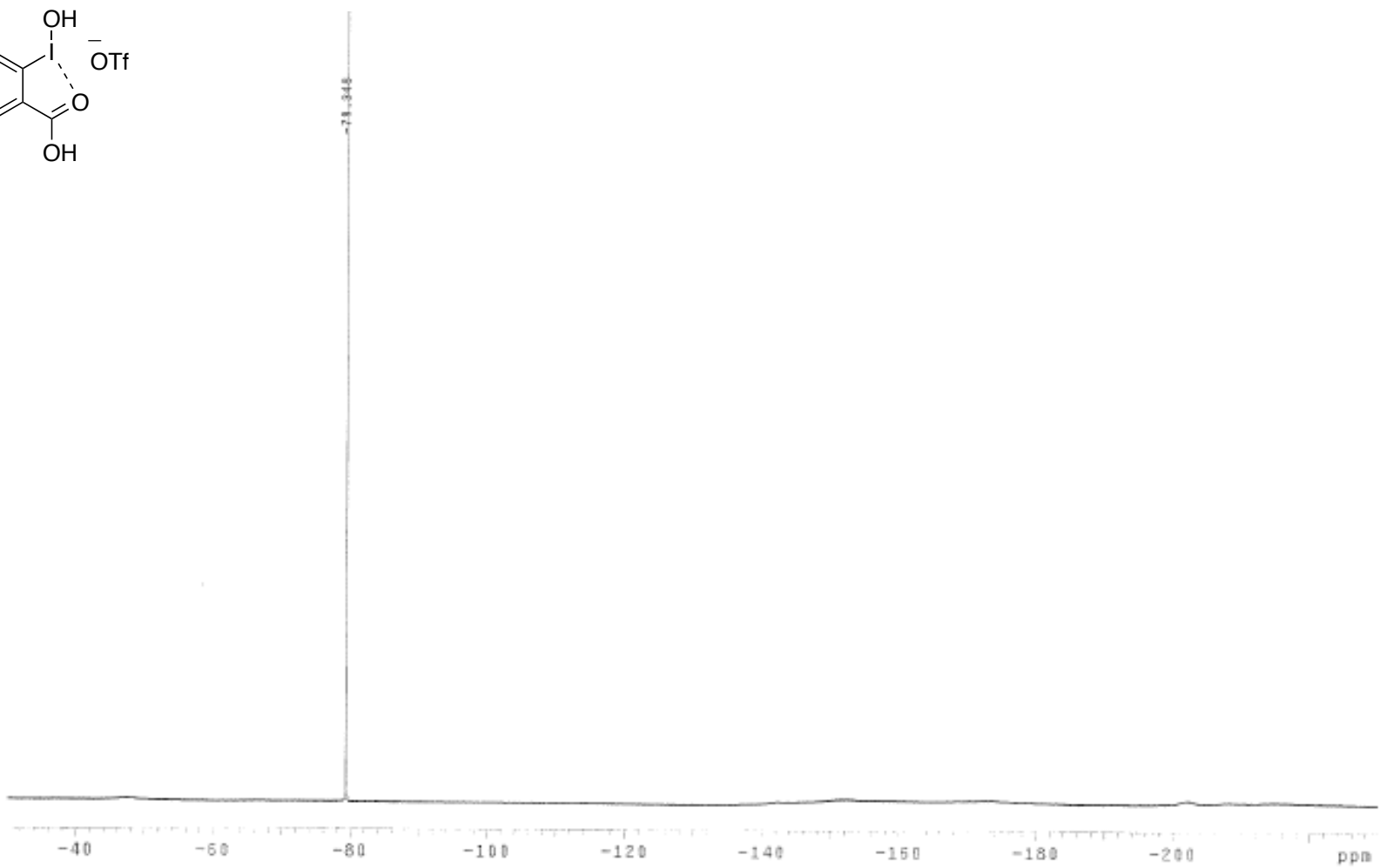
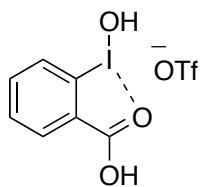
^1H NMR (500 MHz, CD_3CN)



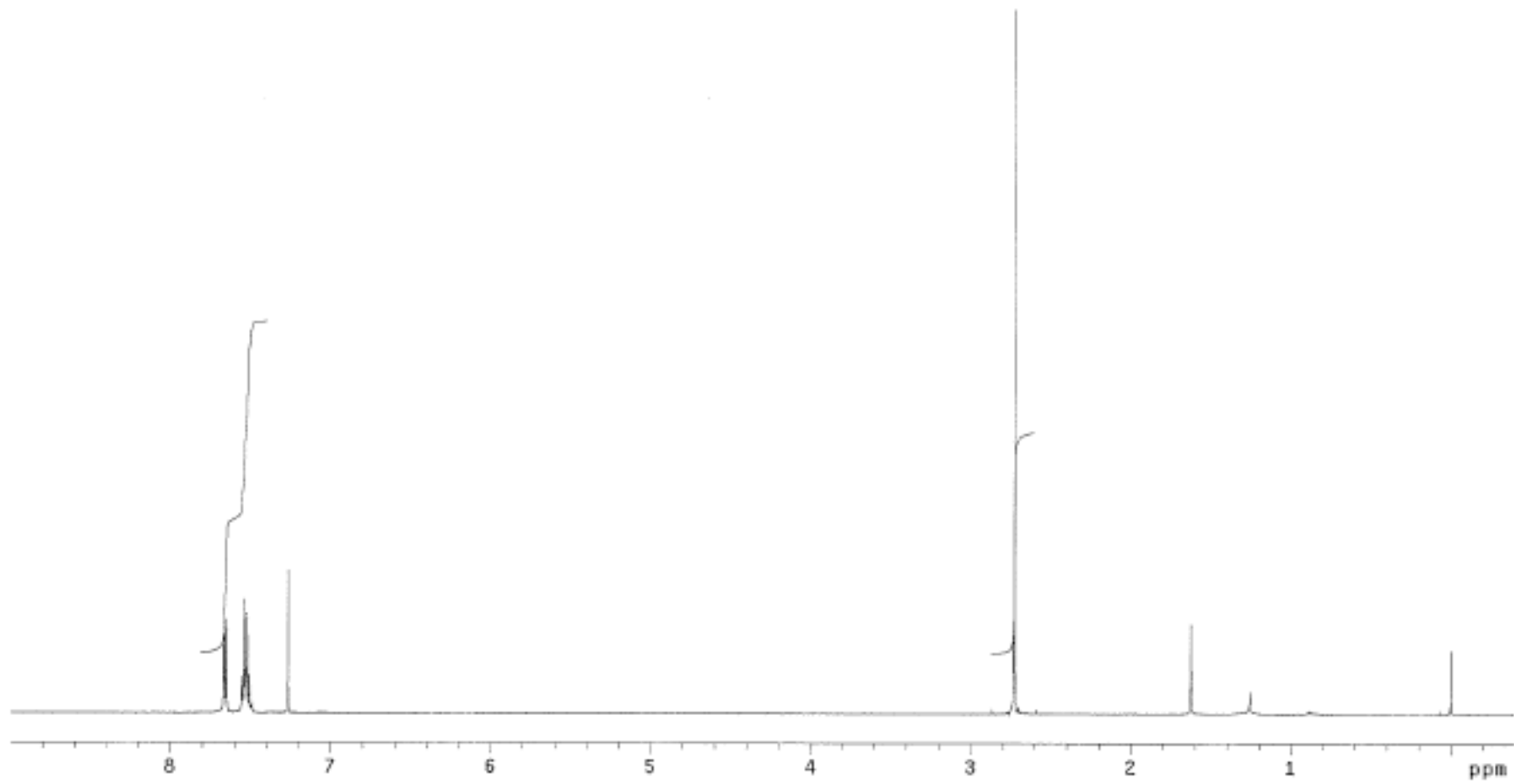
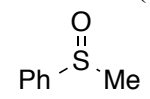
^{13}C NMR (125 MHz, CD_3CN)



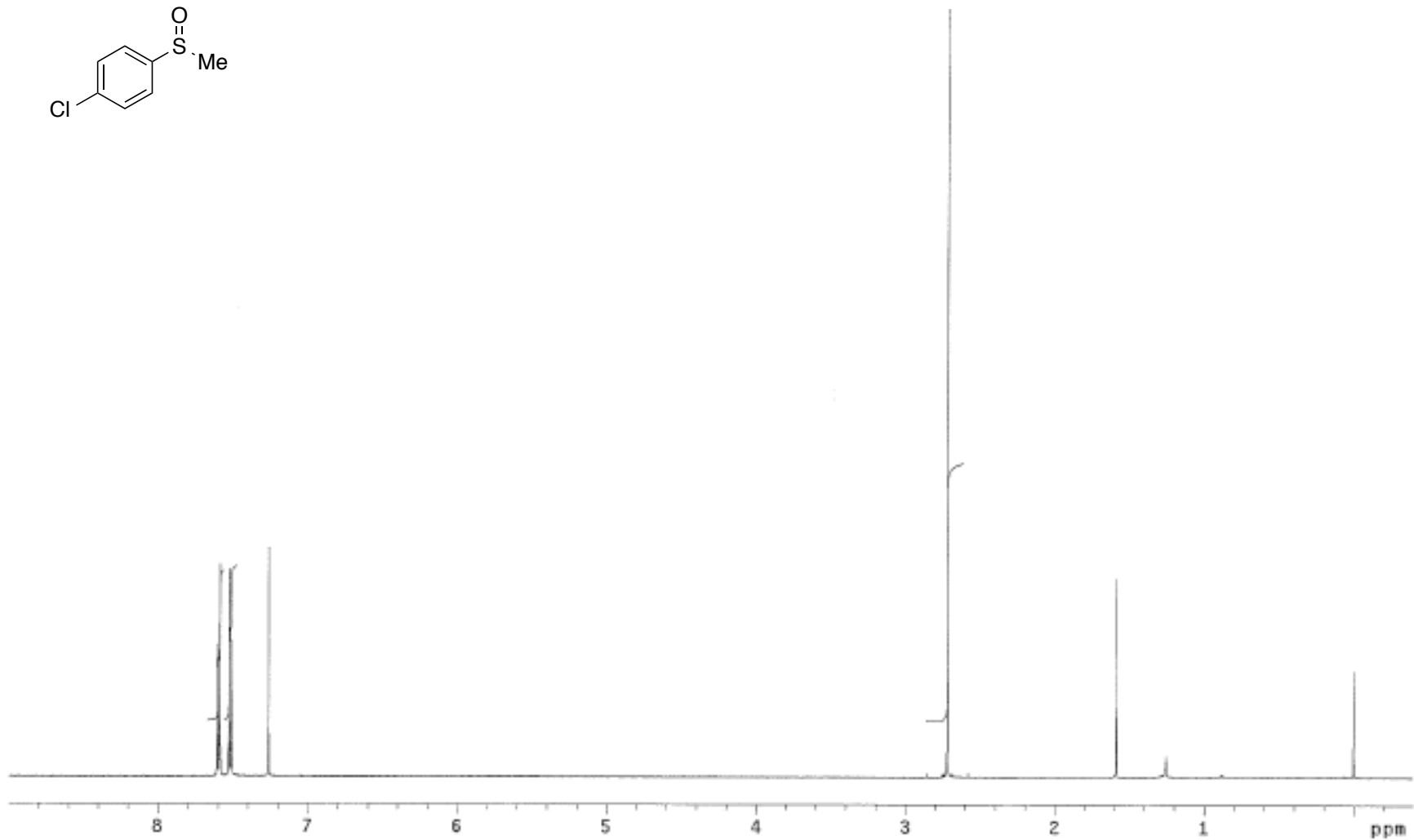
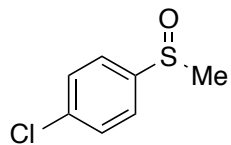
^{19}F NMR (470 MHz, CD_3CN)



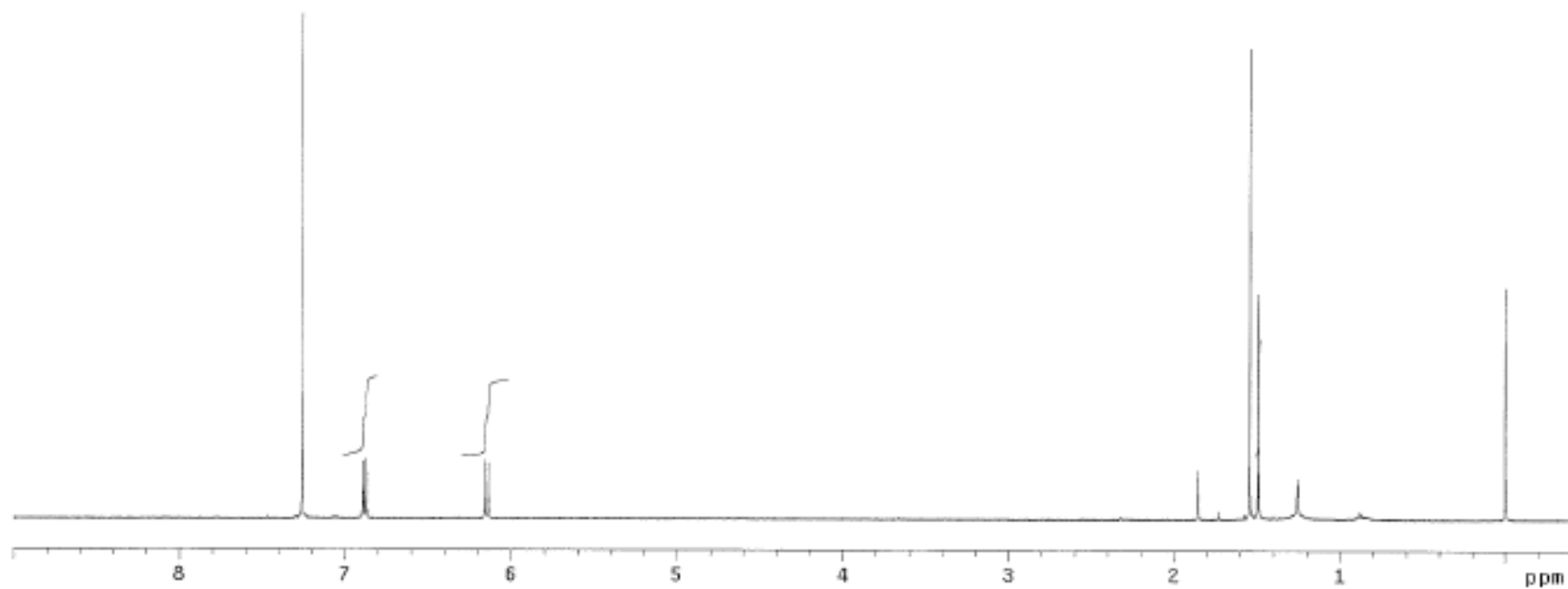
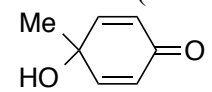
^1H NMR (500 MHz, CDCl_3)



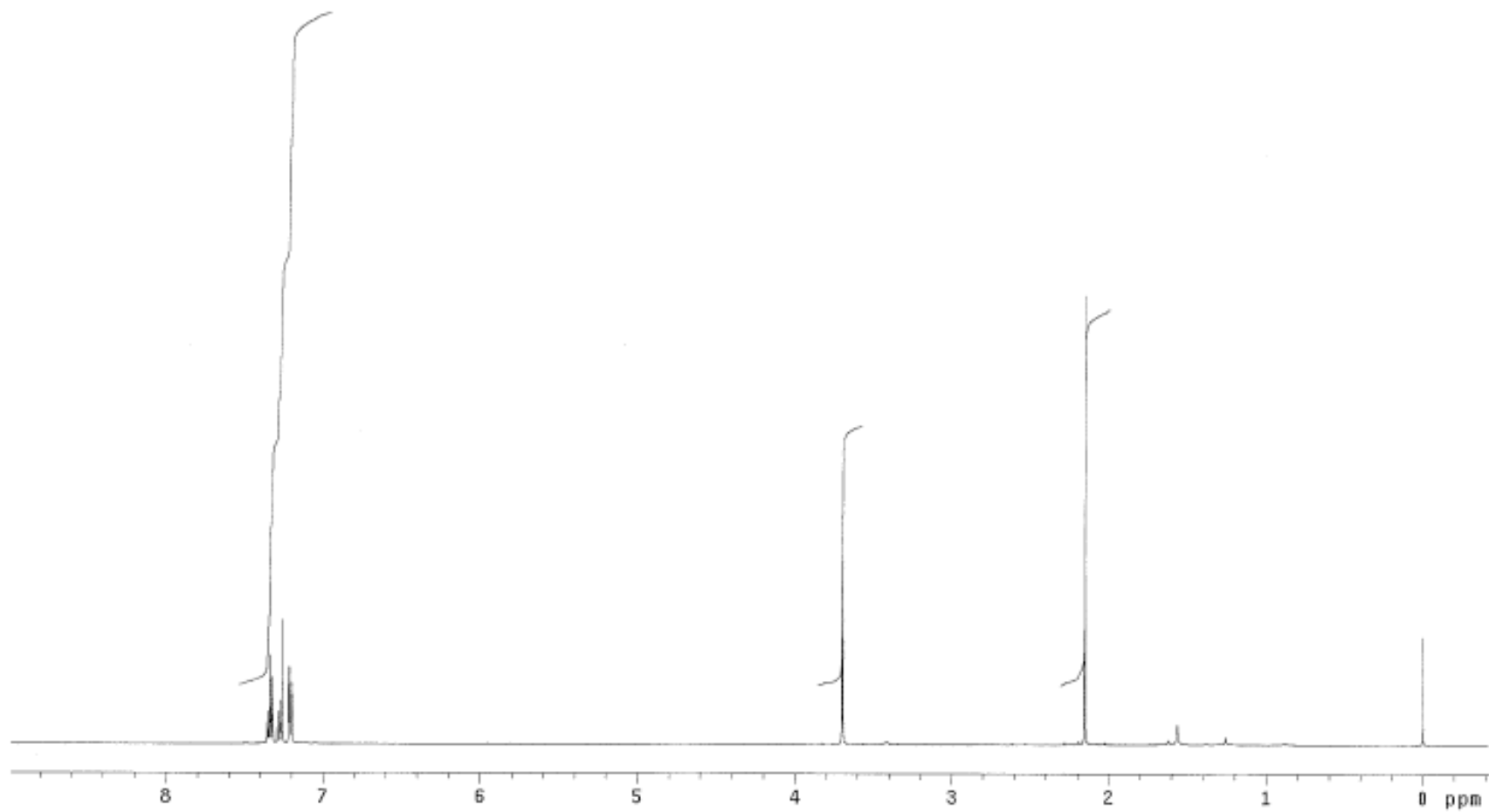
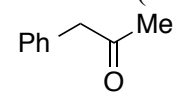
^1H NMR (500 MHz, CDCl_3)



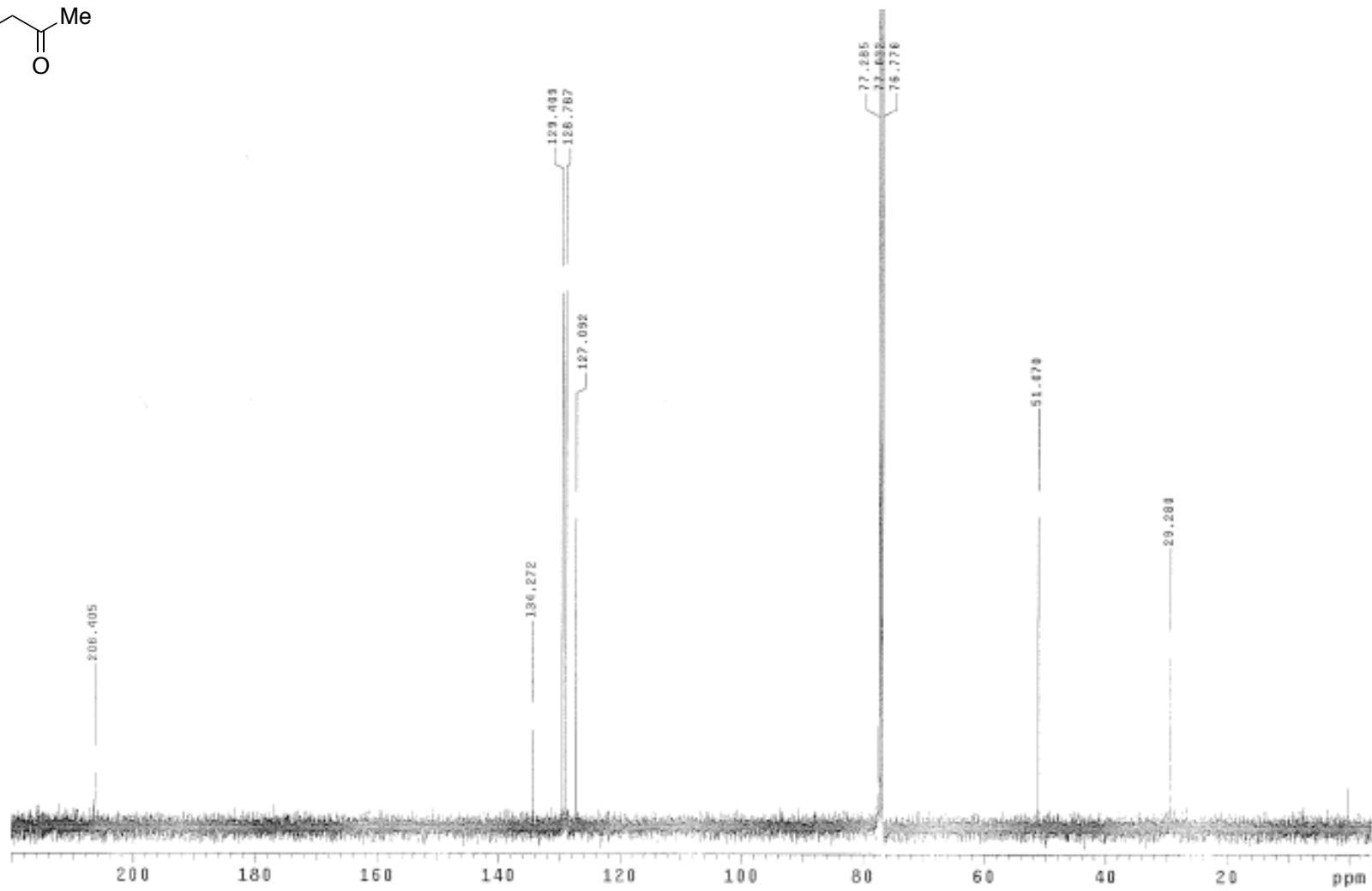
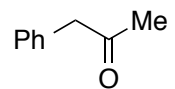
^1H NMR (500 MHz, CDCl_3)



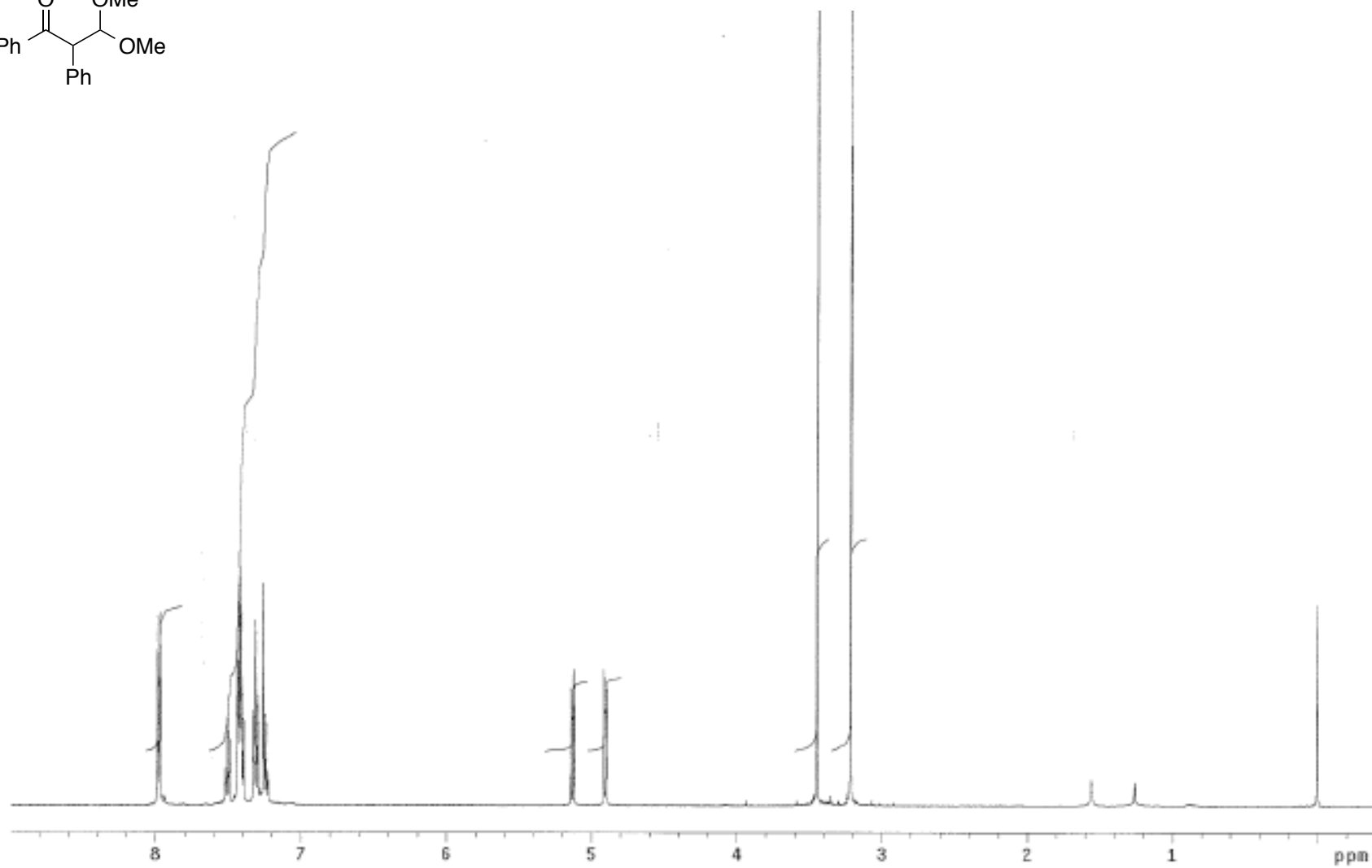
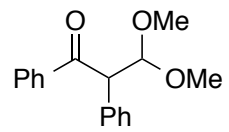
^1H NMR (500 MHz, CDCl_3)



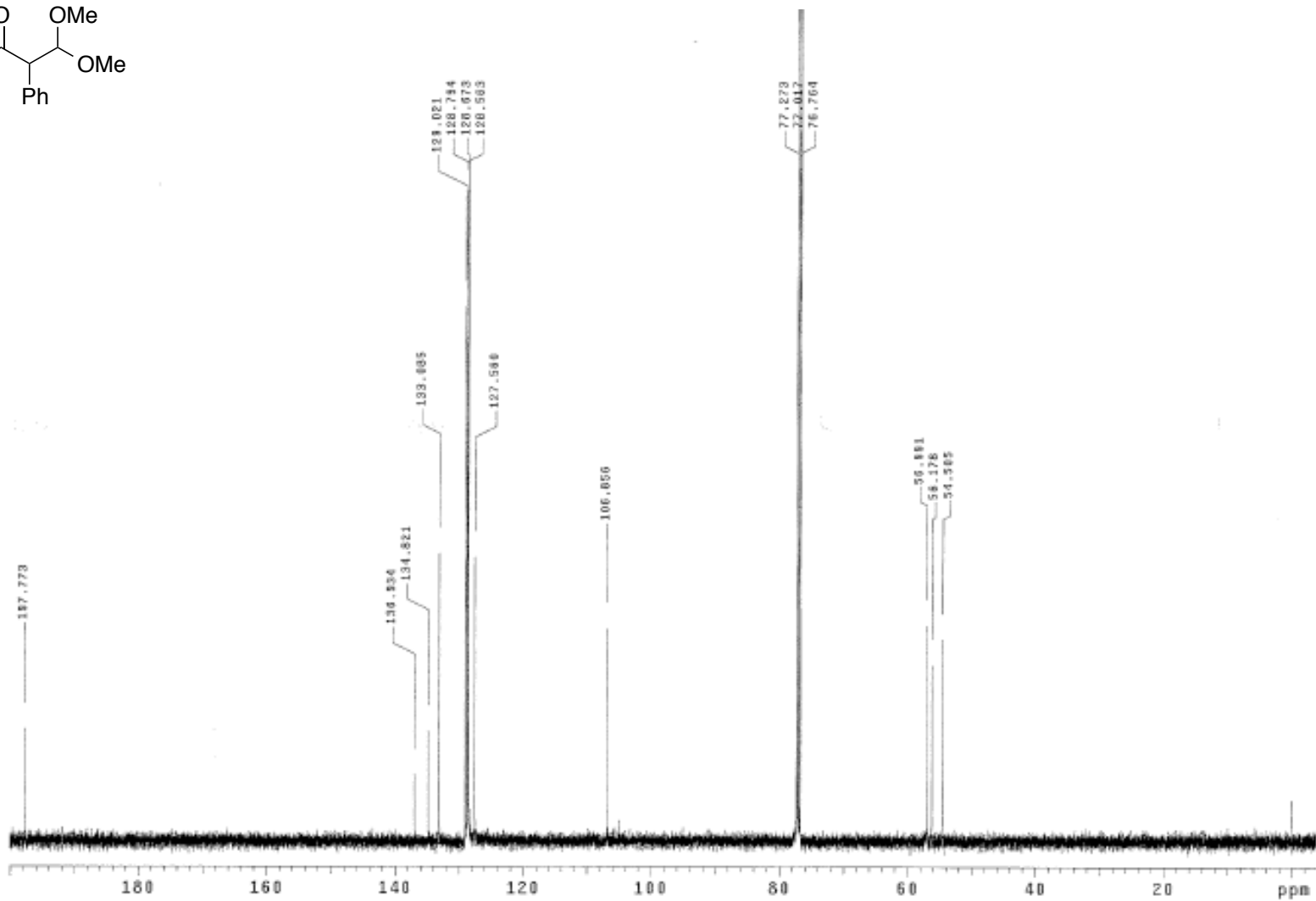
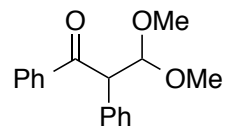
^{13}C NMR (125 MHz, CDCl_3)



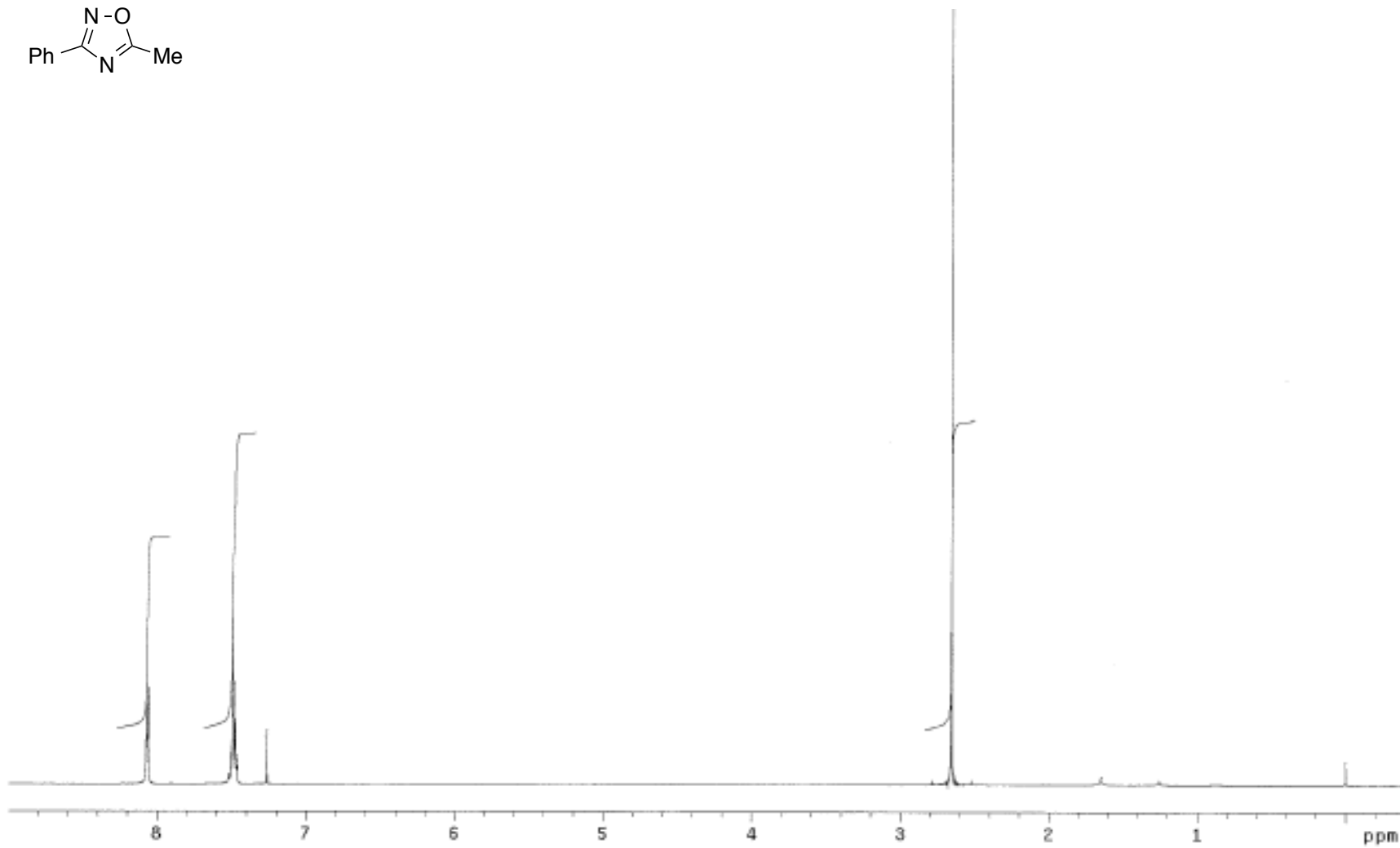
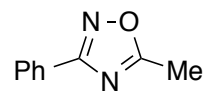
^1H NMR (500 MHz, CDCl_3)



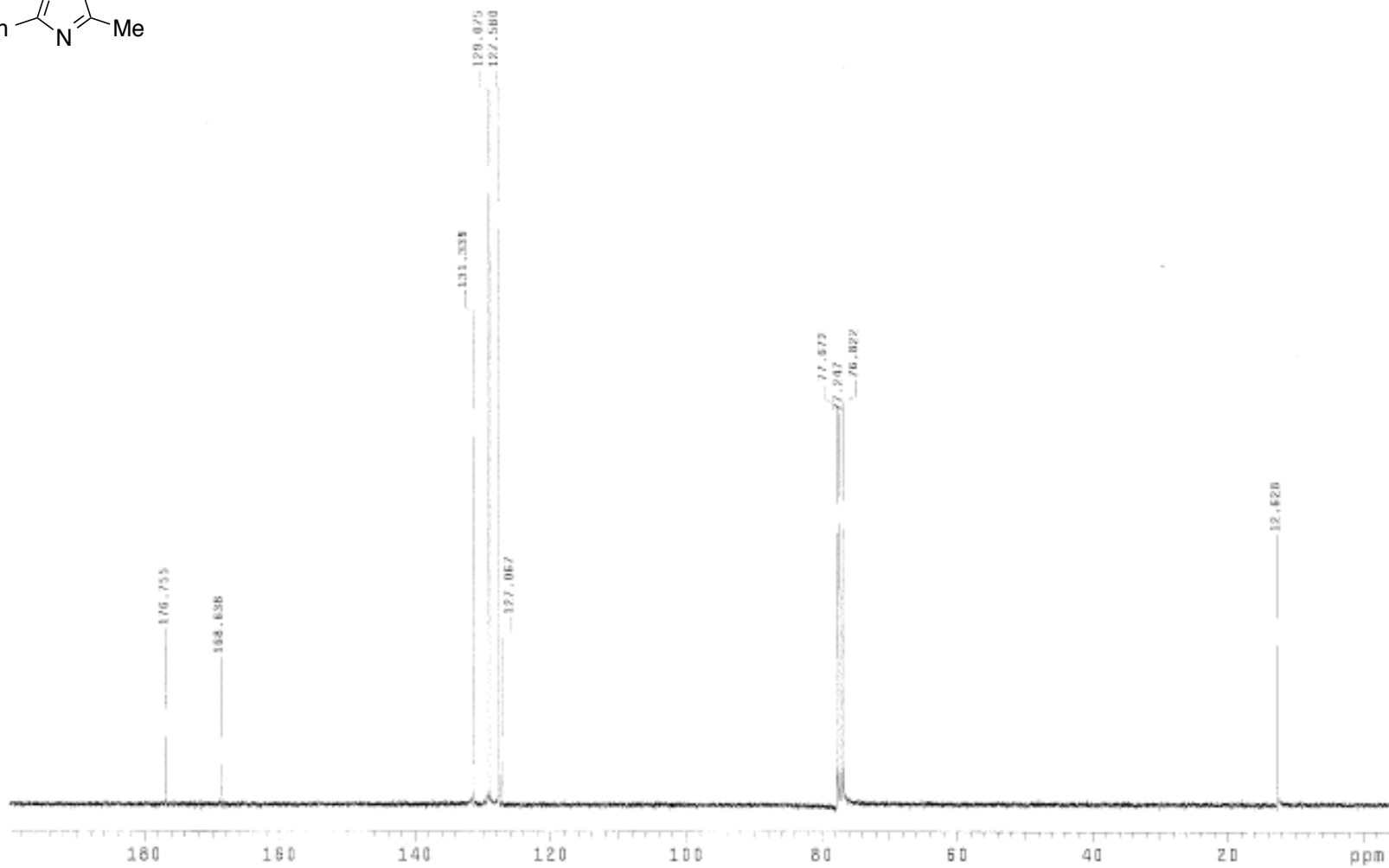
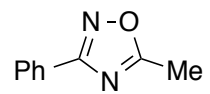
^{13}C NMR (125 MHz, CDCl_3)



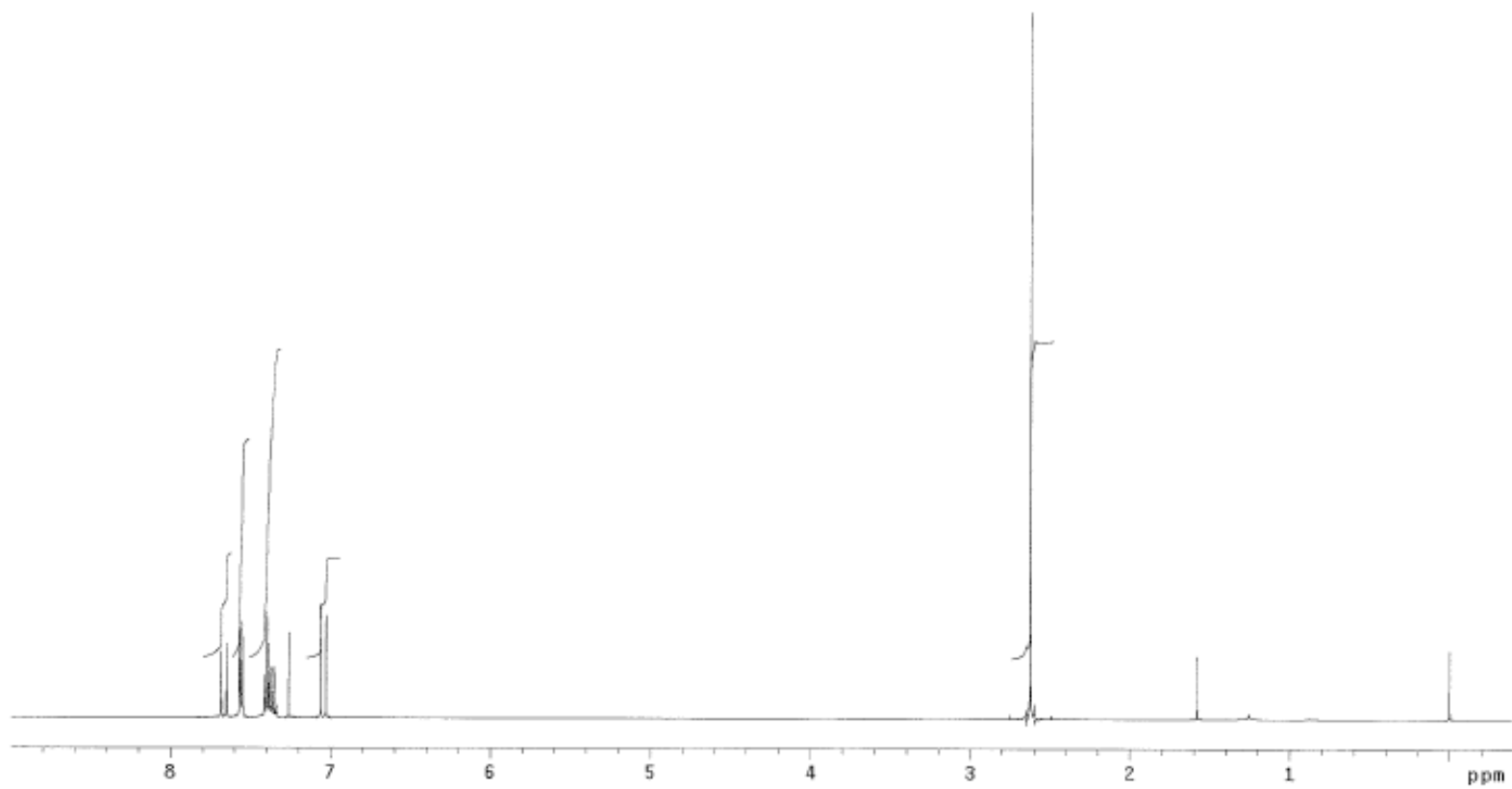
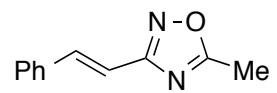
^1H NMR (500 MHz, CDCl_3)



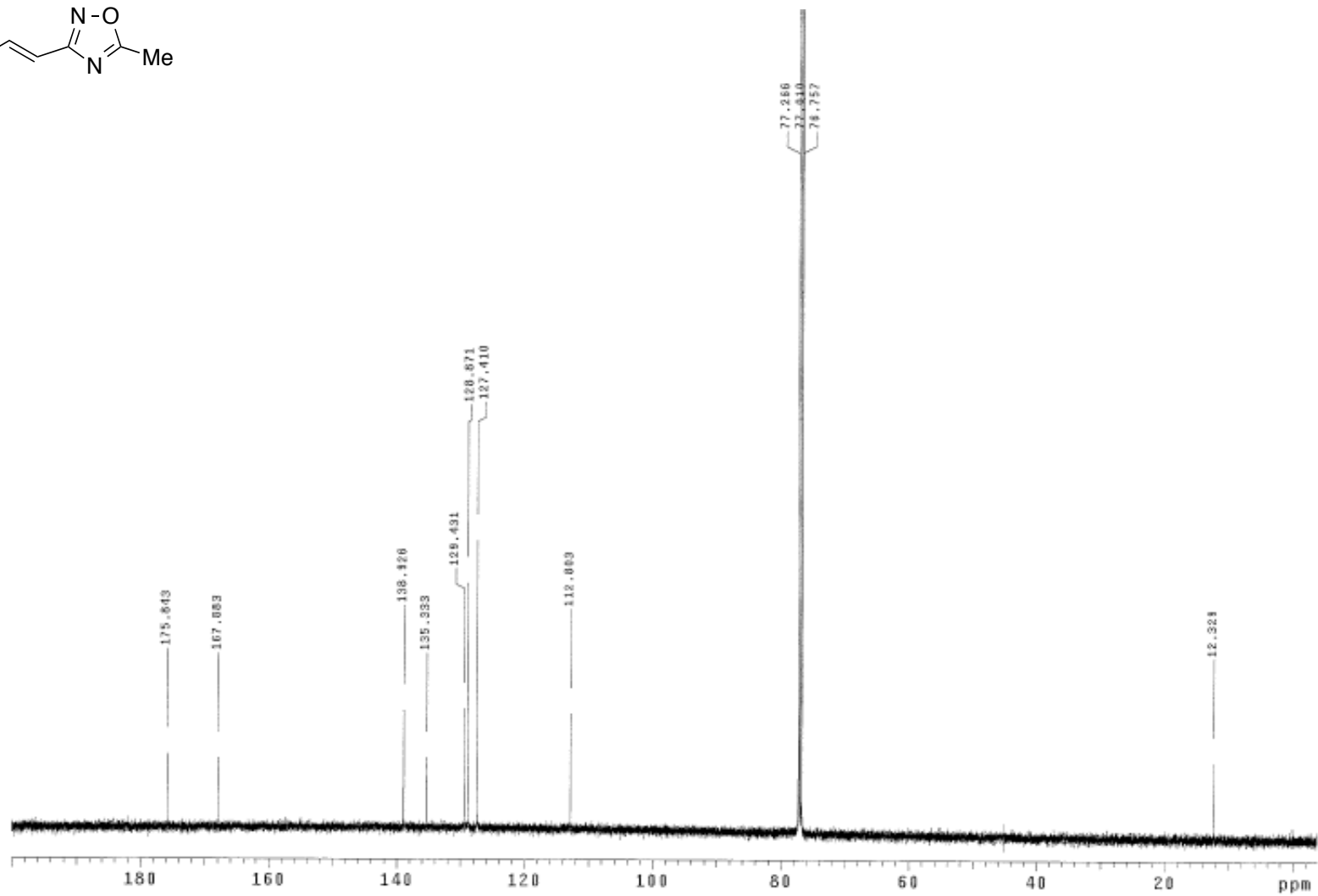
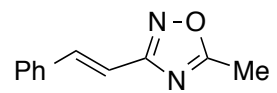
^{13}C NMR (75 MHz, CDCl_3)



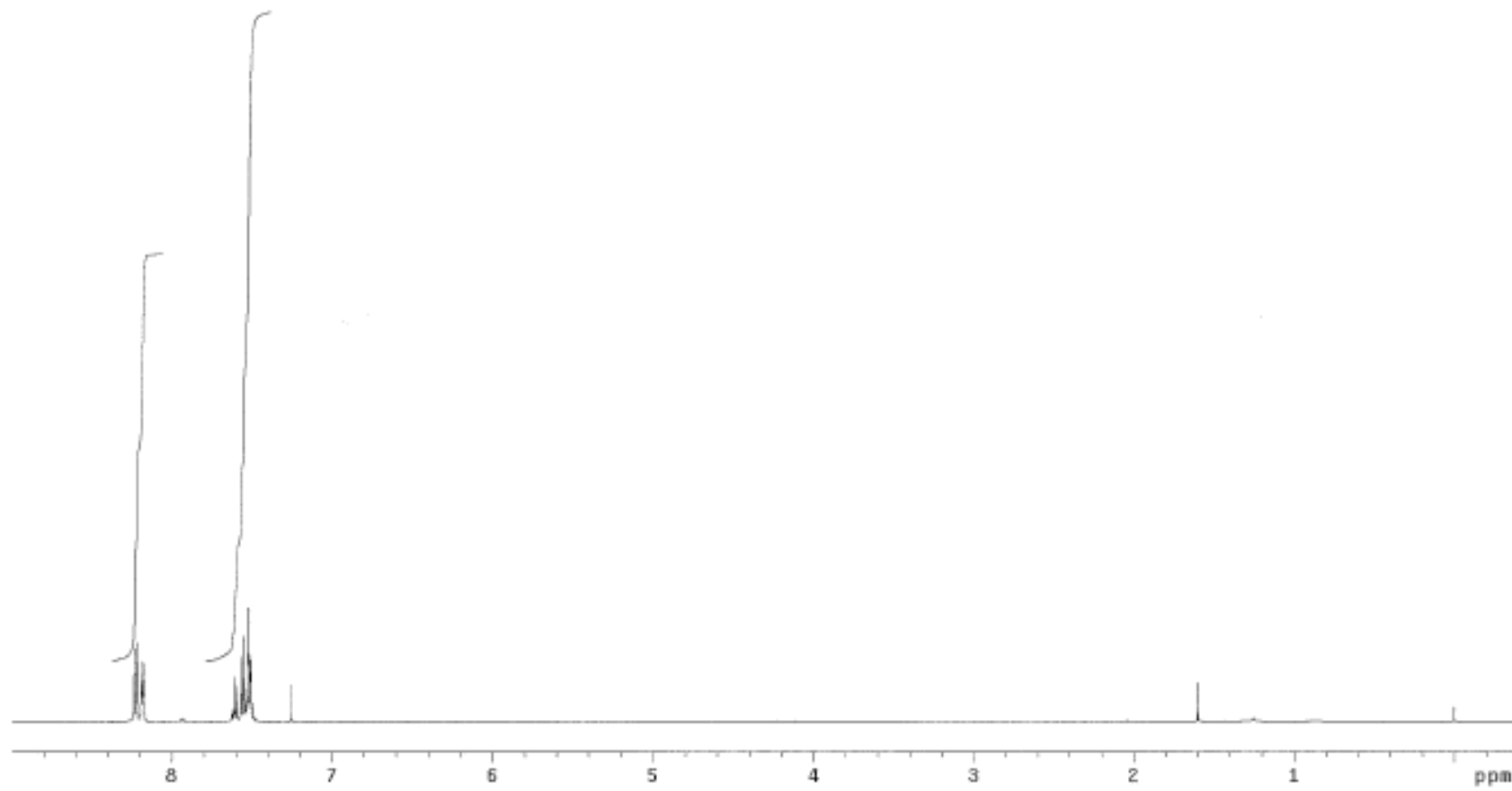
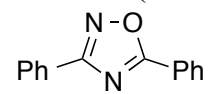
^1H NMR (500 MHz, CDCl_3)



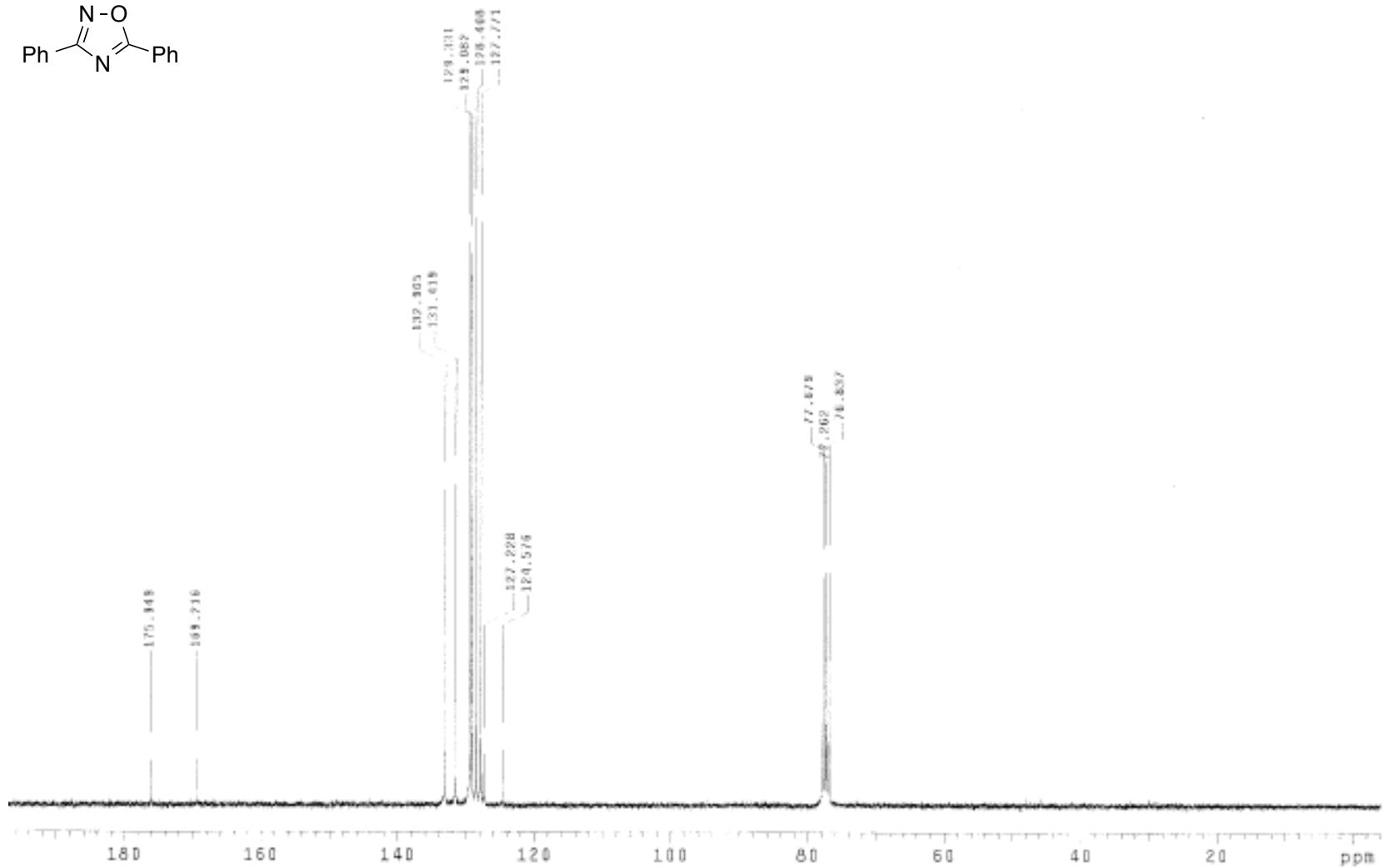
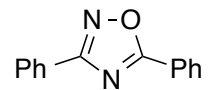
^{13}C NMR (125 MHz, CDCl_3)



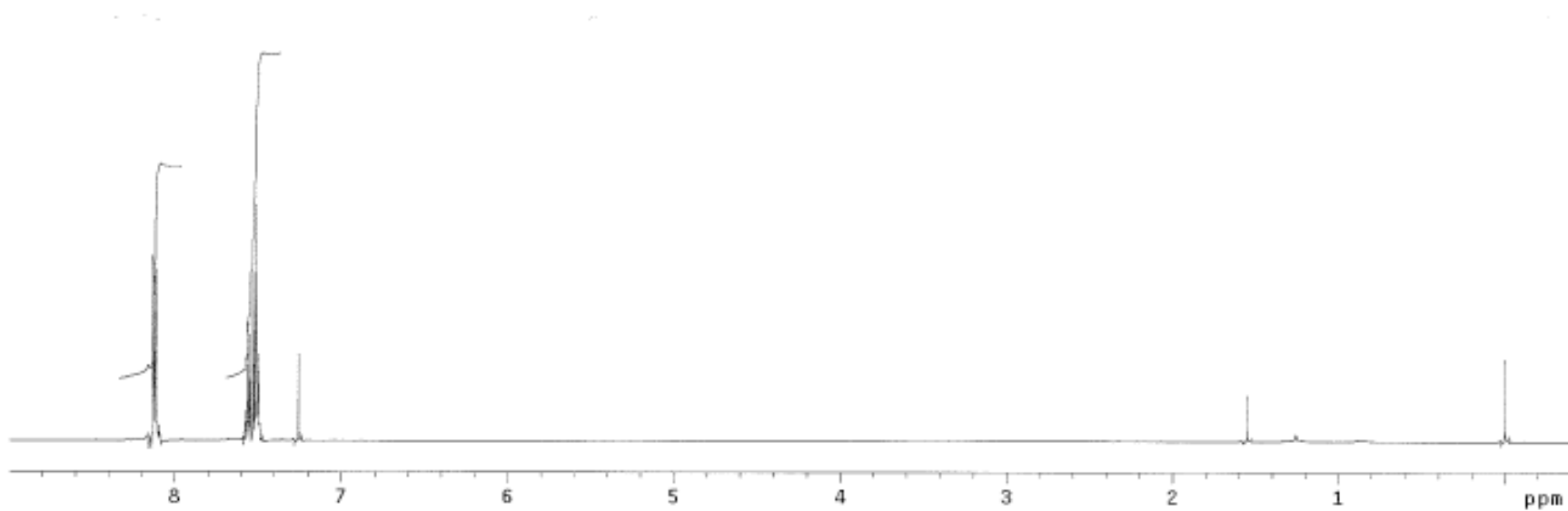
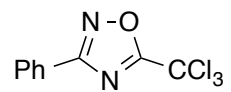
^1H NMR (500 MHz, CDCl_3)



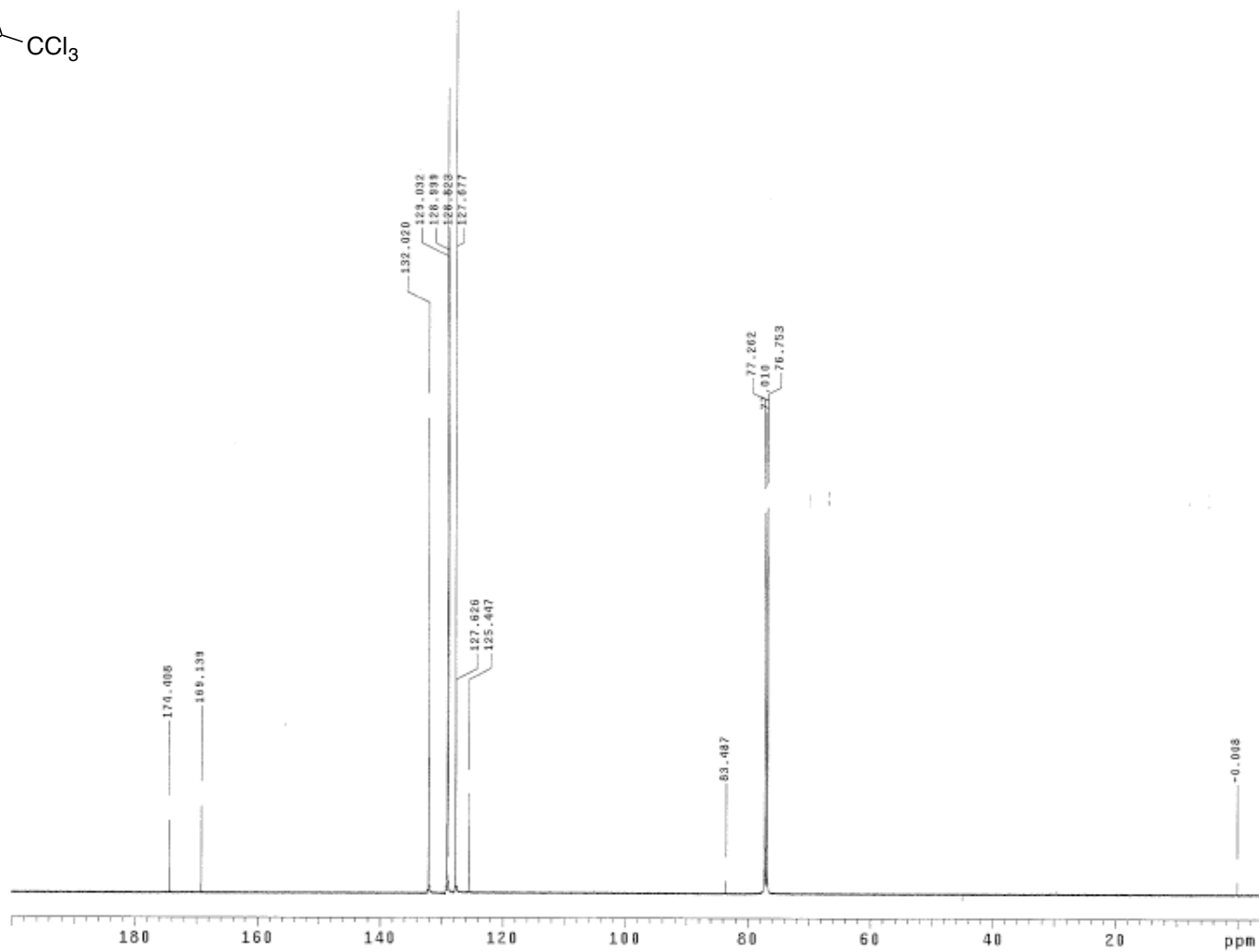
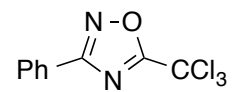
^{13}C NMR (75 MHz, CDCl_3)



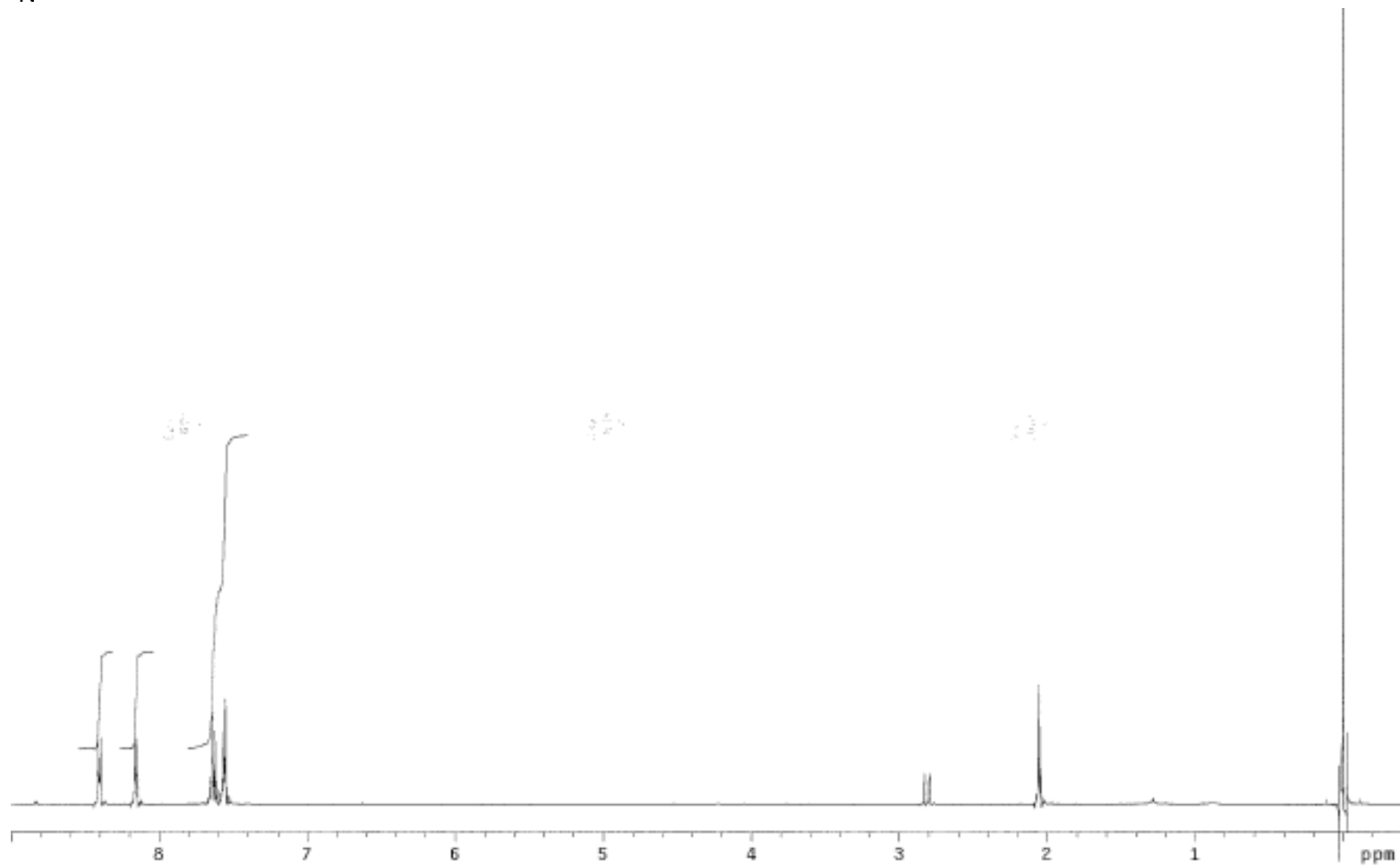
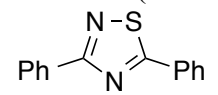
^1H NMR (500 MHz, CDCl_3)



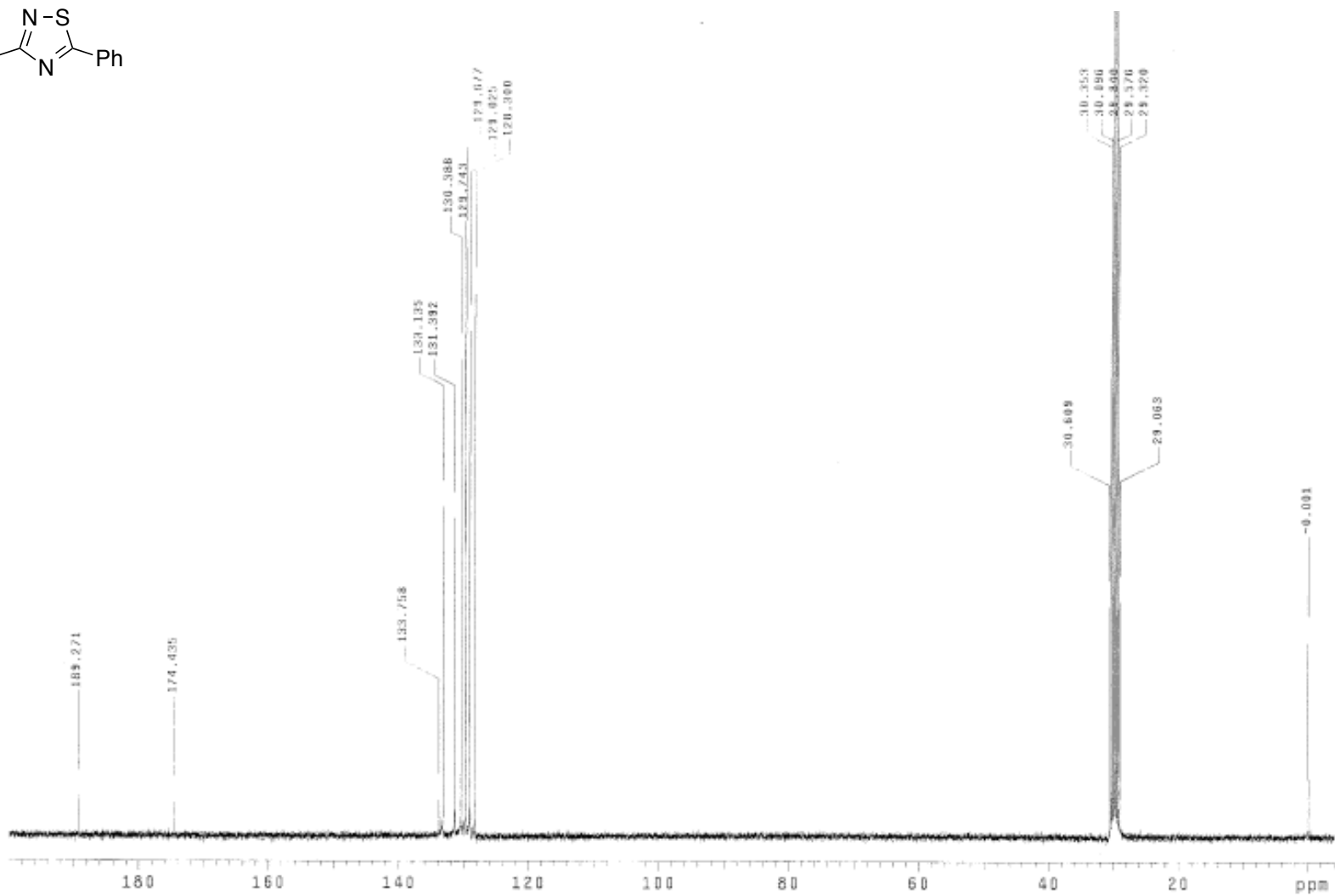
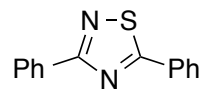
^{13}C NMR (125 MHz, CDCl_3)



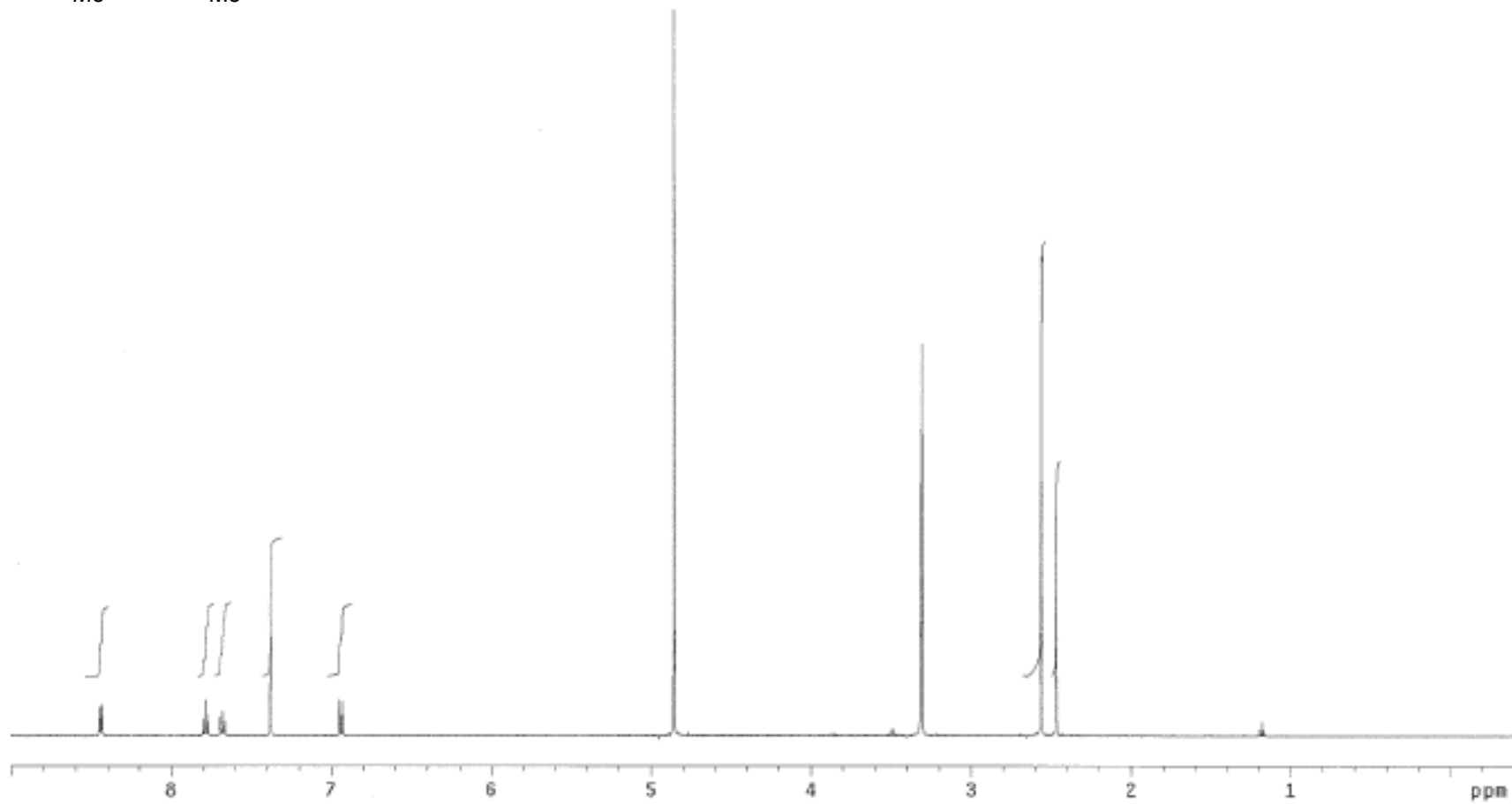
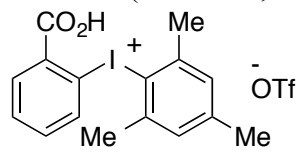
^1H NMR (500 MHz, Acetone- d_6)



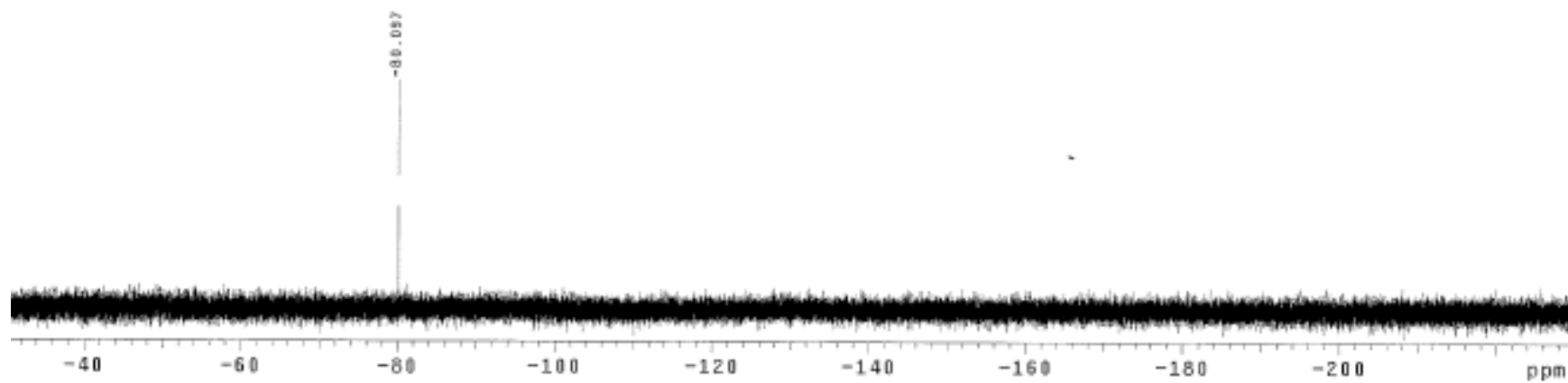
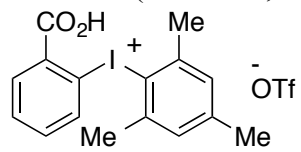
^{13}C NMR (125 MHz, Acetone- d_6)



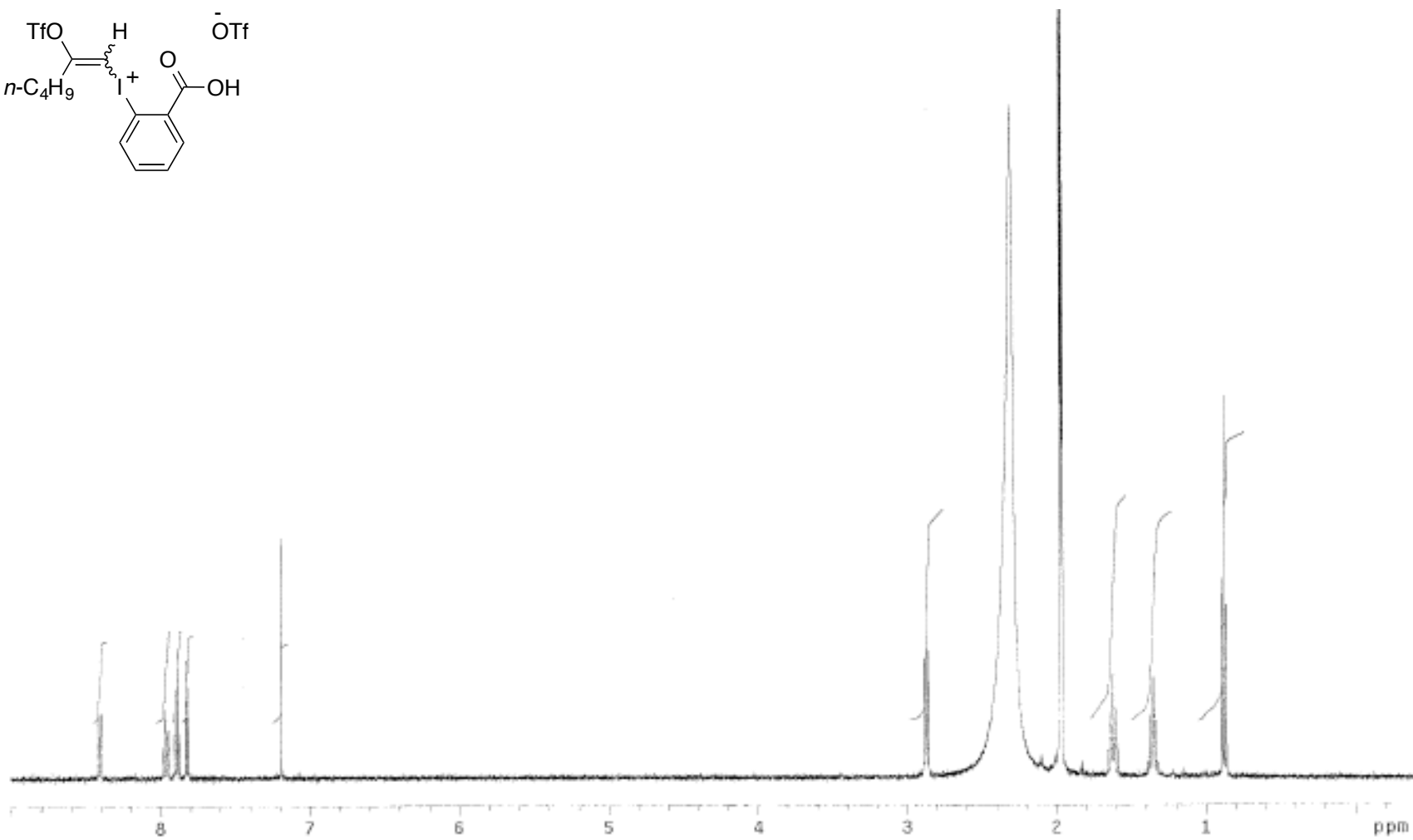
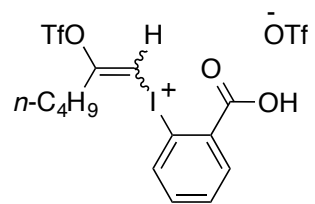
^1H NMR (500 MHz, CD_3OD)



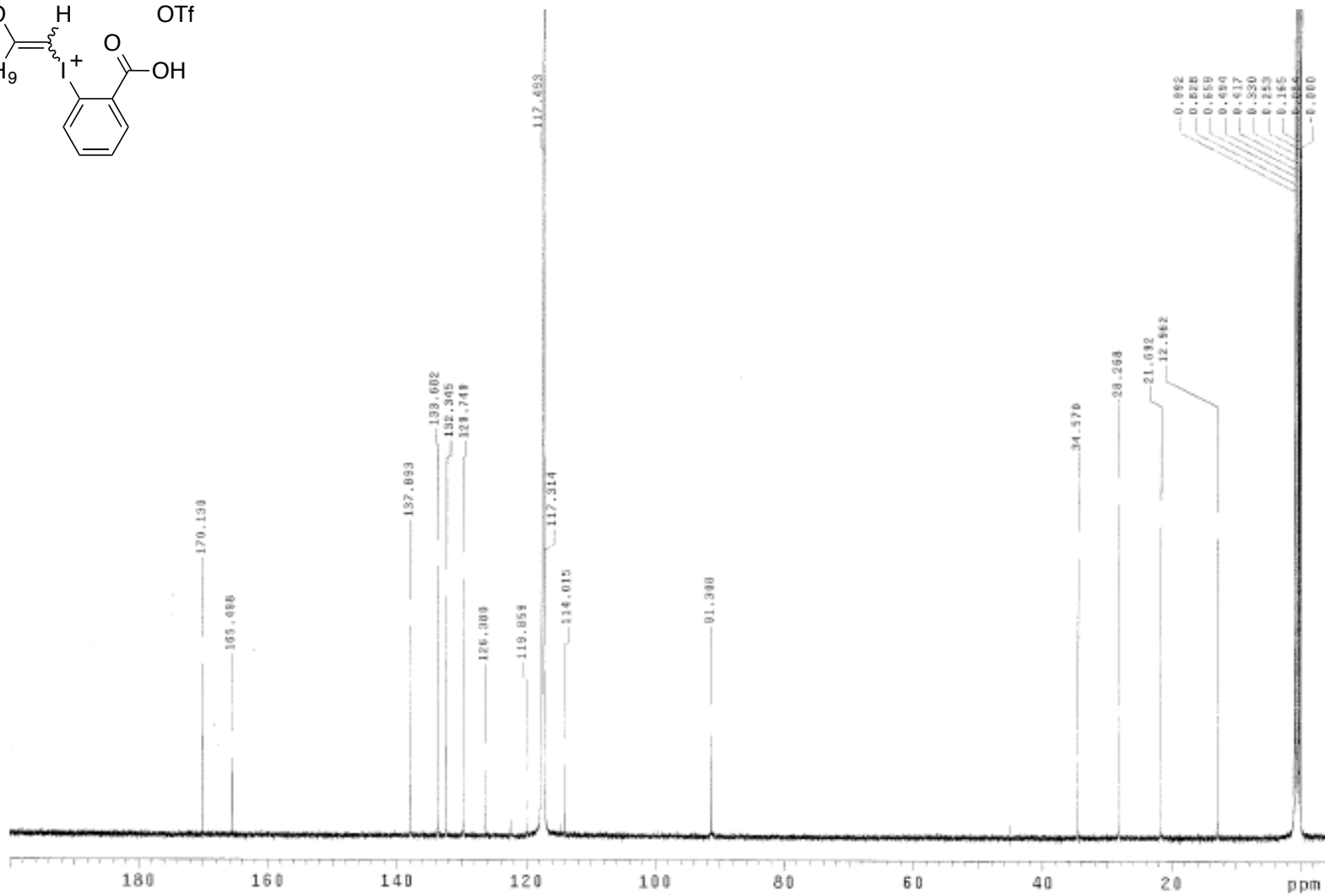
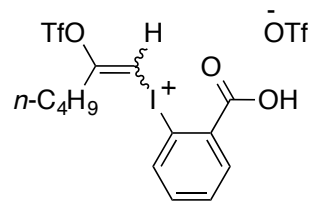
^{19}F NMR (470 MHz, CD_3OD)



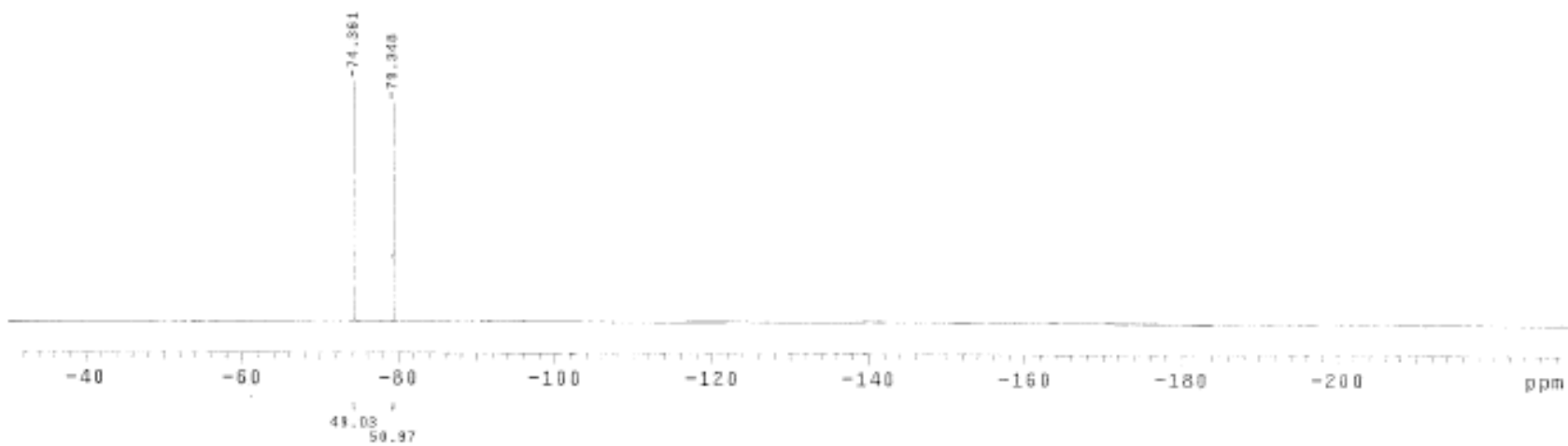
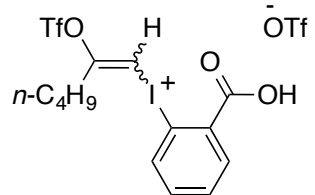
^1H NMR (500 MHz, CD_3CN)



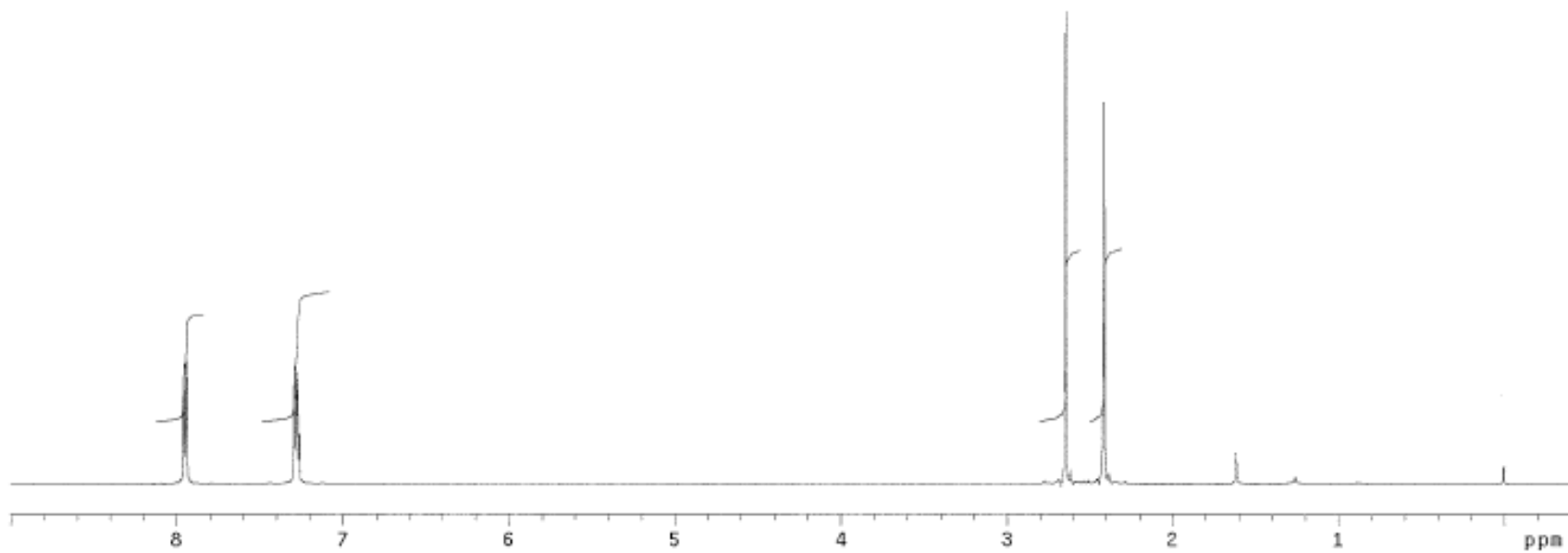
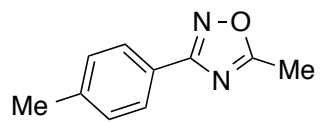
^{13}C NMR (125 MHz, CD_3CN)



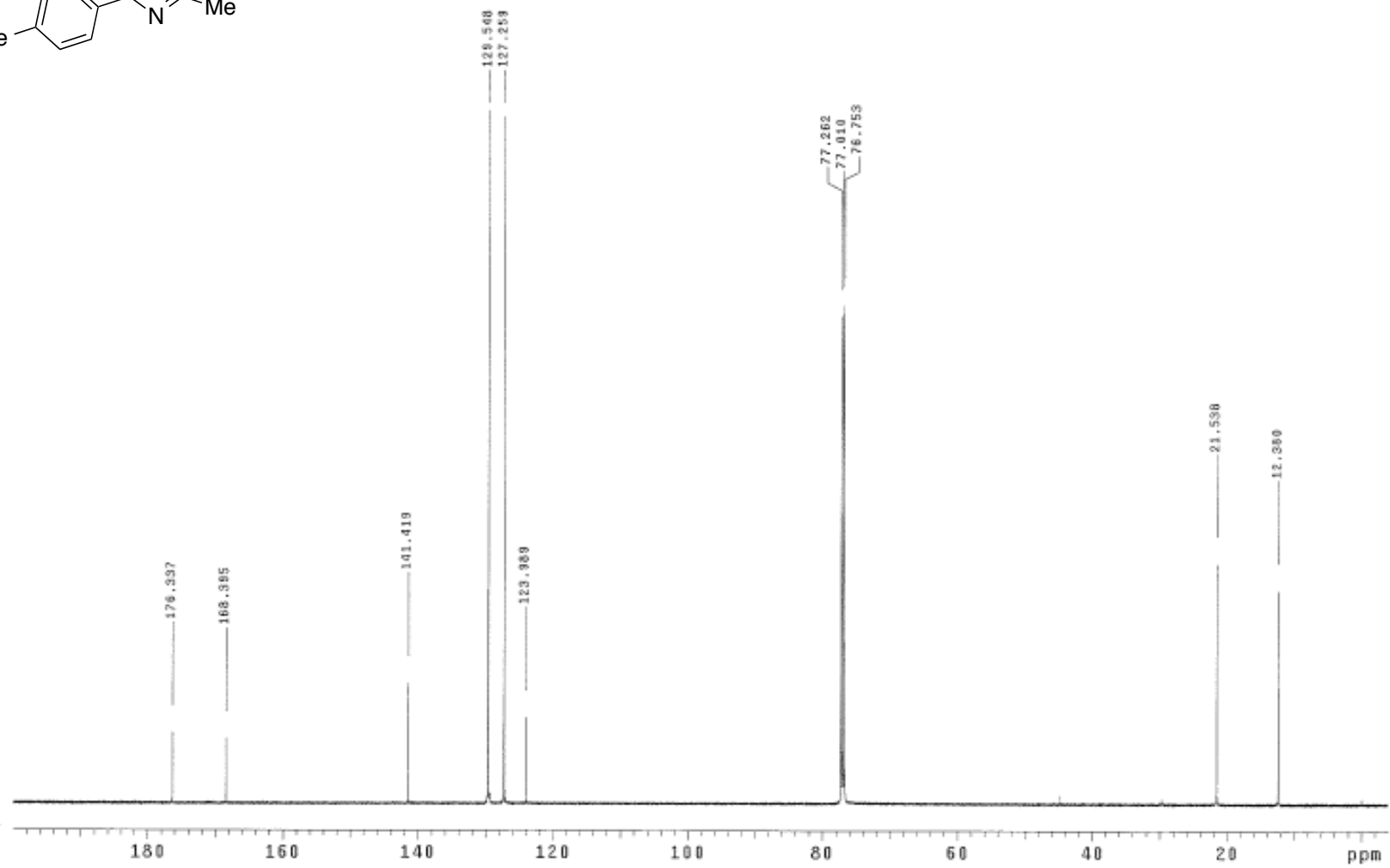
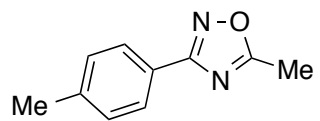
^{19}F NMR (470 MHz, CD_3CN)



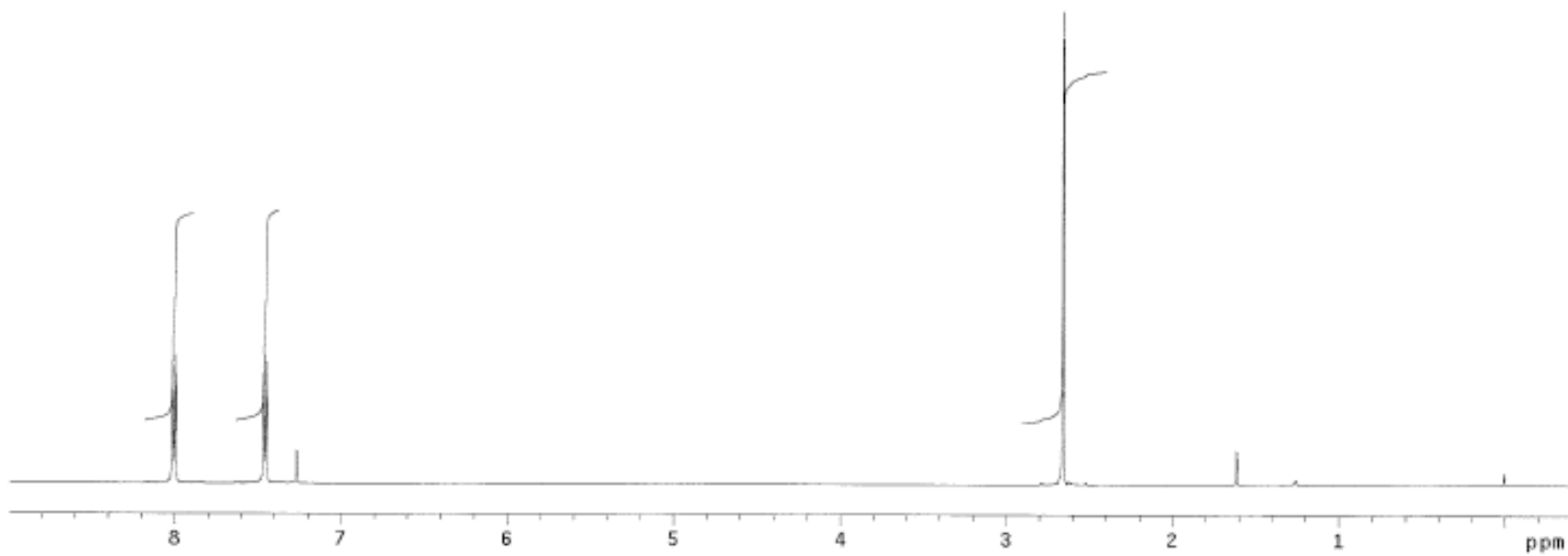
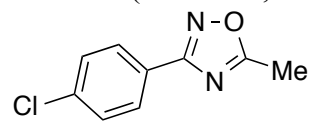
^1H NMR (500 MHz, CDCl_3)



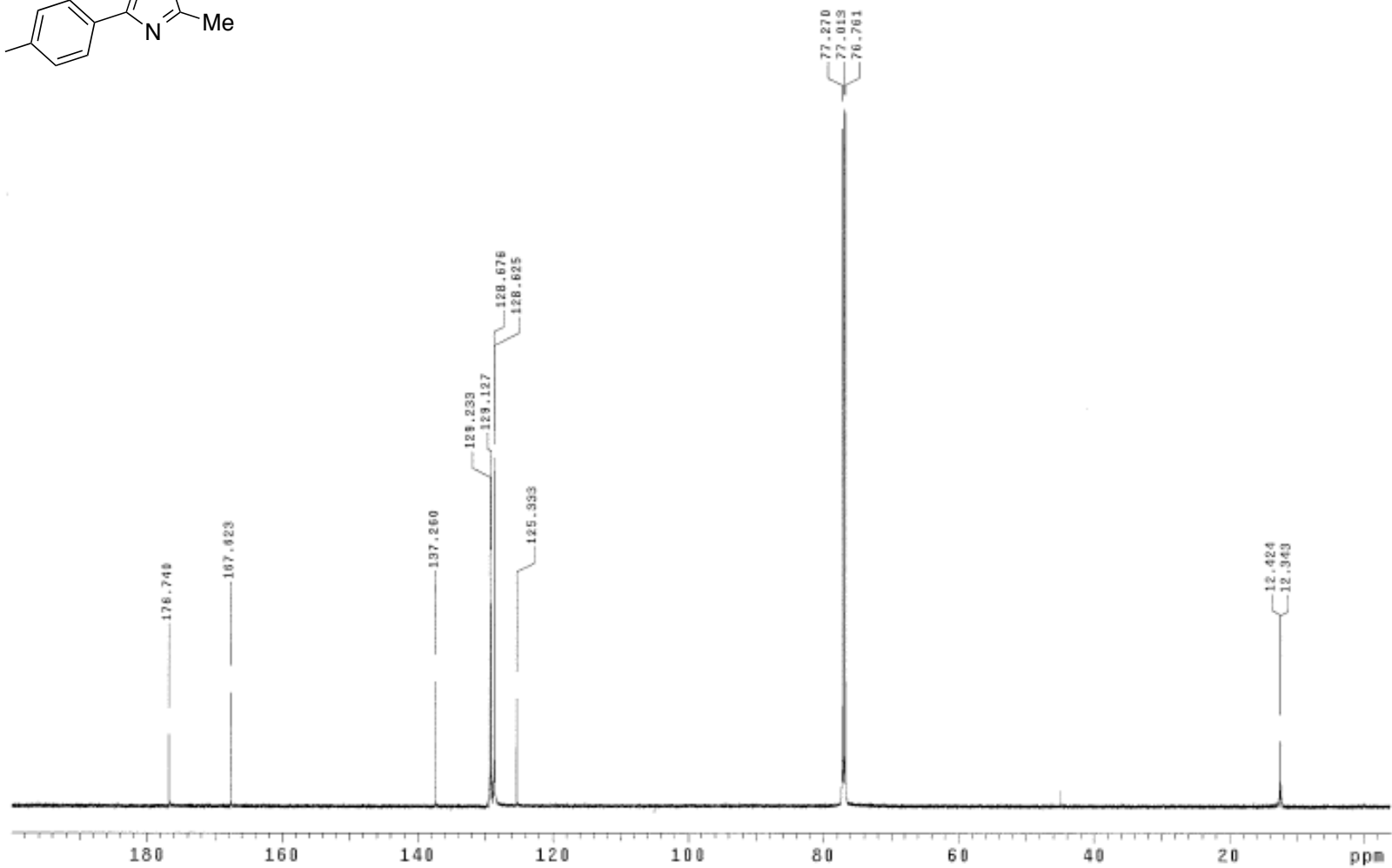
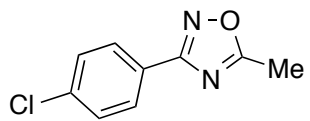
^{13}C NMR (125 MHz, CDCl_3)



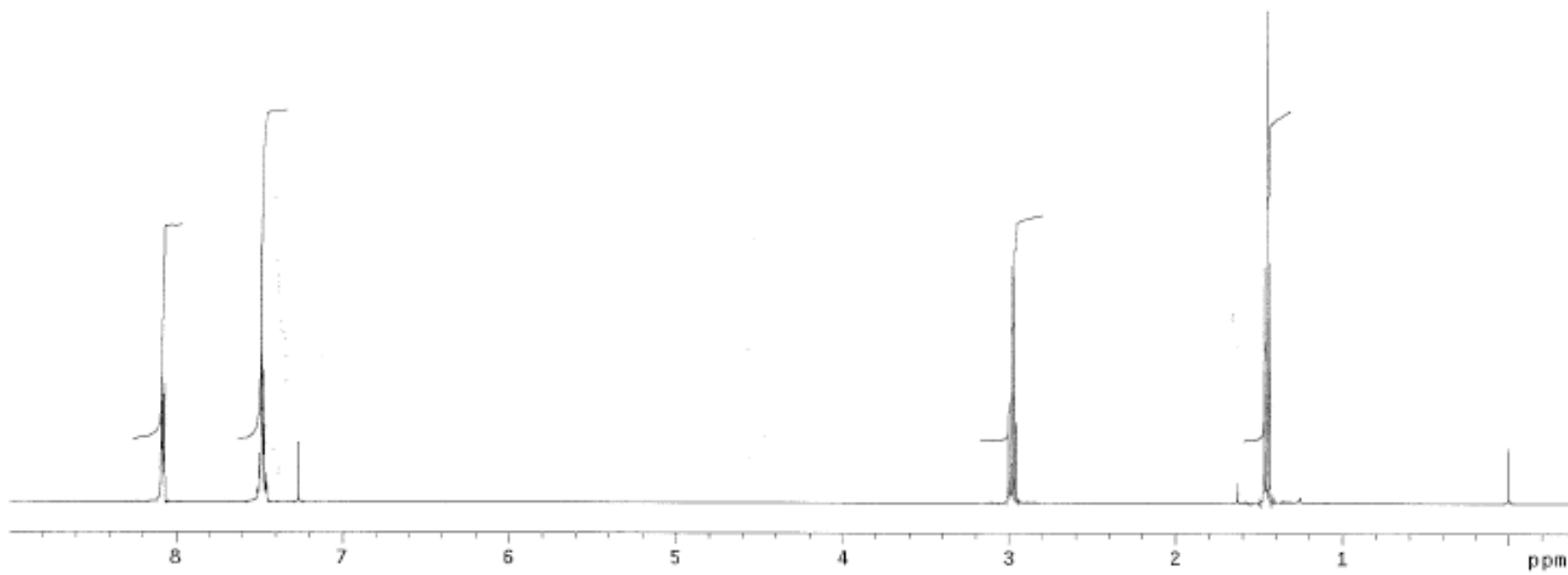
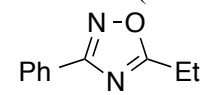
^1H NMR (500 MHz, CDCl_3)



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



^1H NMR (500 MHz, CDCl_3)



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

