

Synthesis of Diaziridines and Diazirines *via* Resin-bound Sulfonyl Oximes

Irina Protasova^a, Bekir Bulat^{a,§}, Nicole Jung^{a,b*}, and Stefan Bräse^{a,b*}

^a Irina Protasova, Dr. Nicole Jung, Prof. Dr. Stefan Bräse
ITG-ComPlat, KIT-Campus North
Herrmann von Helmholtz Platz 1
76344 Eggenstein-Leopoldshafen (Germany)
E-mail: stefan.braese@kit.edu Fax: (+49) 0721-608-8581
Homepage: <http://www.ioc.kit.edu/braese/>

^b Institute of Organic Chemistry
KIT – Karlsruhe Institute of Technology
Fritz-Haber-Weg 6,
76131 Karlsruhe (Germany)

[§]Bekir Bulat
Lehrstuhl für Molekulare Physikalische Chemie
Heinrich-Heine-Universität Düsseldorf
Universitätsstr. 14
0225 Düsseldorf

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1. General Procedures GP0 to GP8

GP0 General washing procedure for solid phases.

Using CH_2Cl_2 the resins were transferred into a filter and subsequently washed according to the following procedure: 3 \times successive treatment with MeOH, DMF, MeOH, 2 \times successive treatment with THF, MeOH, DMF and MeOH, 2 \times washing with CH_2Cl_2 .

GP1 Synthesis of Oximes (7)

1.00 equiv. of trifluoromethylketone was dissolved in ethanol at room temperature and 5.00 equiv. of hydroxylamine hydrochloride and 2.50 equiv. of pyridine were added. After stirring overnight under reflux conditions, water was added and the aqueous phase was extracted three times with ethyl acetate. The combined organic layers were dried over MgSO_4 , the solvent was removed under reduced pressure and the crude product was purified by column chromatography.

GP2 Anchoring of oximes (7a-j) to solid-supported sulfonyloximes (8a-j)

1.00 equiv. of the commercially available sulfonylchloride containing resin (loading = 125 mmol/g) was suspended in DMF and was shaken for 5 min. Then, 1.50 equiv. of the oxime, 10.0 equiv. of trimethylamine and 0.50 equiv. of DMAP were added. The vial was sealed and the mixture was shaken at 80 °C for 48 h. After cooling to room temperature the resin was washed according to the general washing procedure **GP0** and dried in vacuo to give the target resin.

GP3 Cleavage of diaziridines (5a-z) from sulfonyl oxime resins (8a-z)

Resins **8a-z** were swollen in 3 mL a saturated solution of NH_3^1 in dioxane. The cleavage mixture was shaken for 12 h at room temperature. The resin was separated *via* filtration and the product-containing filtrate was evaporated under reduced pressure. The target substance was obtained after flash chromatography of the crude mixture.

GP4 Oxidation of diaziridines (5) to diazirines (3) with iodine

The diaziridine **5** (0.03 mmol) was dissolved in 2 mL dichloromethane and iodine (25.4 mg, 0.10 mmol, 3.3 equiv.) was added in one portion at room temperature. The reaction was monitored by TLC. After complete conversion of the starting material, the crude reaction was purified *via* flash column chromatography without further workup.

GP5 Oxidation of diaziridines (5f and 5j) to diazirines (3j and 3k) with MnO_2

The diaziridine (0.03 mmol) was dissolved in dichloromethane and freshly prepared MnO_2 (8.69 mg, 0.10 mmol, 3.3 equiv.) was added in one portion at room temperature. The reaction was monitored by TLC. After complete conversion of the starting material, the crude reaction was purified by flash column chromatography without further workup.

Preparation of MnO_2

2.00 mmol of manganese sulfate (302 mg, 1.00 equiv.) and 2.00 mmol of potassium permanganate (316 mg, 1.00 equiv.) were dissolved in 200 mL of H_2O and stirred for 4 h at room temperature. The precipitate was filtered off, washed three times with water and diethyl ether and dried in vacuo to give MnO_2 in quantitative yield.

GP6 Click-reaction on solid phases

The immobilized alkyne was treated in a CrimpTop vial with freshly prepared azide containing solution. Reaction monitoring was conducted *via* Raman spectroscopy. After complete conversion of the starting material (10–60 min), the resin was washed thoroughly with 10 mL

of methanol–water–DMF–Cupral*, DMF–methanol–CH₂Cl₂–Cupral* and DMF–CH₂Cl₂–methanol–acetone–methanol–CH₂Cl₂.

*Cupral = saturated solution of diethyl dithiocarbamic acid sodium salt in DMF

Preparation of azide-containing solution:

A. 2.00 mmol of alkyl bromide were dissolved in 4.00 mL of anhydrous DMF, then 1.80 mmol of sodium azide (0.9 equiv.) were added and the mixture was shaken overnight at room temperature. The mixture, 20 mL of water and 40 mL of ethyl acetate were transferred into a separating funnel. The organic layer was washed three times with water and dried over MgSO₄. The solvent was removed carefully under reduced pressure and the crude azide was used without further purification.

B. The crude material obtained from **A** was dissolved in THF/water (10:1) and 47.5 mg (0.25 mmol, 0.14 equiv.) of CuI and 0.10 mL of DIPEA (76.0 µg, 0.59 mmol) were added.

GP7 Preparation of azides 9 (alternative to GP6)

2.00 mmol of the alkyl bromide (1.00 equiv.) were dissolved in 4.00 mL of anhydrous DMF and 5.00 mmol of sodium azide were added. After stirring for 12 h at room temperature, 50 mL of H₂O were added, the aqueous layer was extracted with ethyl acetate three times, the organic layer was dried over MgSO₄ and the crude product was purified *via* column chromatography.

GP8 Amidation on solid phases

Acetic chloride (0.05 mmol, 1.50 equiv.) and triethylamine (10 µL, 0.01 mmol, 0.200 equiv.) were dissolved in DMF and stirred for 15 min at 0 °C. The immobilized amine (1.00 equiv.) was suspended in DMF, added to the reaction mixture and shaken for 10 min at 0 °C. The reaction mixture was shaken overnight at room temperature. The resin was washed according the general washing procedure **GP0** and was dried *in vacuo* to give the target resin.

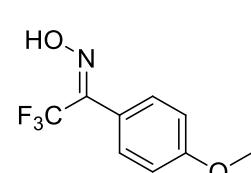
2. Synthesis of Oxime Precursors 7a-7k

2,2,2-Trifluoro-1-phenylethanone oxime (7a)

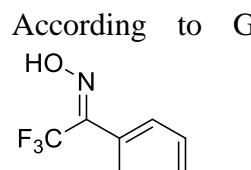
According to GP1, 3.00 g (17.2 mmol, 1.00 equiv.) of 2,2,2-trifluoro-1-phenylethanone were reacted with 5.97 g (86.2 mmol, 5.00 equiv.) of hydroxylamine hydrochloride and 3.44 mL (3.41 g, 43.1 mmol, 2.50 equiv.) of pyridine in ethanol at 80 °C. The solvent was removed under reduced pressure and the residue was purified *via* column chromatography (cyclohexane/ethyl acetate; 20:1). The target compound was isolated in 95% yield (3.10 g, 16.4 mmol). – R_f = 0.57 (cyclohexane/ethyl acetate; 20:1). – ¹H NMR (400 MHz, CDCl₃, ppm), δ = 7.46–7.57 (m, 5 H), 9.23 (s, 1 H). – ¹³C NMR (100 MHz, CDCl₃, ppm), δ = 120.6 (q, ¹J = 275 Hz), 125.9 (2 C), 128.6 (2 C), 130.7, 132.4, 147.8 (q, ²J = 32.5 Hz). – ¹⁹F NMR (376 Hz, CDCl₃), δ = -75.35 (s, 3 F). – IR (ATR), ν: 3263, 2914, 1705, 1578, 1459, 1438, 1335, 1279, 1204, 1181, 1129, 1038, 1012, 959, 923, 844, 771, 745, 705, 691, 610, 537, 518, 481, 459 cm⁻¹. – EI-MS (m/z, 70 eV,

30 °C): 189 (89) [M⁺], 170 (4), 127 (14), 120 (24), 103 (33), 77 (100), 51 (23). – HRMS (C₈H₆F₃NO): calc. 189.0401, found. 189.0401. – Mp.: 80.5–83.5 °C.

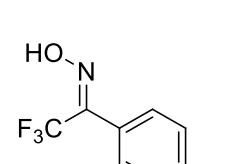
1-(4-Methoxyphenyl)-2,2,2-trifluoroethanone oxime (7b)

 According to GP1, 682 mg (3.34 mmol, 1.00 equiv.) of 1-(4-bromophenyl)-2,2,2-trifluoroethanone were reacted with 1.16 g (16.7 mmol, 5.00 equiv.) of hydroxylamine hydrochloride and 653 µL (661 µg, 8.35 mmol, 2.50 equiv.) of pyridine in ethanol at 80 °C. The solvent was removed under reduced pressure and the residue was purified *via* column chromatography (cyclohexane/ethyl acetate; 20:1). The target compound was isolated in 80% yield (586 mg, 2.67 mmol). – ¹H NMR (250 MHz, CDCl₃, ppm), δ = 3.95 (s, 3 H), 7.06–7.13 (m, 2 H), 7.68–7.72 (m, 2 H), 9.92 (s, 1 H). – ¹⁹F NMR (376 Hz, CDCl₃, ppm), δ = -70.97 (s, 3 F). The analytical data correspond to the literature.^[3]

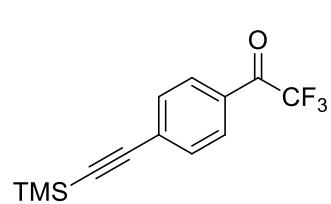
1-(4-Chlorophenyl)-2,2,2-trifluoroethanone oxime (7c)

 According to GP1, 1.00 g (4.81 mmol, 1.00 equiv.) of 1-(4-chlorophenyl)-2,2,2-trifluoroethanone were reacted with 1.02 mL (948 mg, 11.2 mmol, 2.50 equiv.) of pyridine and 1.67 mg (24.0 mmol, 5.00 equiv.) of hydroxylamine hydrochloride in ethanol at 80 °C. The solvent was removed under reduced pressure and the residue was purified *via* column chromatography (cyclohexane/ethyl acetate; 20:1). The target compound was isolated in 91% yield (980 mg, 4.38 mmol). – ¹H NMR (250 MHz, CDCl₃, ppm), δ = 7.41–7.55 (m, 4 H), 8.39 (br s, 1 H). – ¹³C NMR (63 MHz, CDCl₃, ppm), δ = 120.5 (q, ¹J = 275 Hz), 128.6, 128.9 (2 C), 130.1 (2 C), 136.8, 146.5 (q, ²J = 32.3 Hz). The analytical data correspond to the literature.^[1]

1-(4-Bromophenyl)-2,2,2-trifluoroethanone oxime (7d)

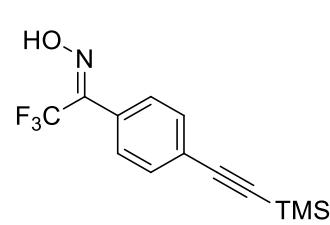
 According to GP1, 130 mg (514 µmol, 1.00 equiv.) of 1-(4-bromophenyl)-2,2,2-trifluoroethanone were reacted with 179 mg (2.57 mmol, 5.00 equiv.) of hydroxylamine hydrochloride and 104 µL (102 mg, 1.29 mmol, 2.50 equiv.) of pyridine in ethanol at 80 °C. The solvent was removed under reduced pressure and the residue was purified *via* column chromatography (cyclohexane/ethyl acetate; 20:1). The target compound was isolated in 93% yield (128 mg, 478 µmol). – ¹H NMR (250 MHz, CDCl₃, ppm), δ = 7.36–7.52 (m, 2 H), 7.55–7.71 (m, 2 H), 9.26 (br s, 1 H). – ¹³C NMR (63 MHz, CDCl₃, ppm), δ = 120.3 (q, ¹J = 275 Hz), 125.4, 129.8, 130.3 (2 C), 131.9 (2 C), 146.8 (q, ²J = 32.3 Hz). The analytical data correspond to the literature.^[2]

2,2,2-Trifluoro-4-(trimethylsilylethynyl)acetophenone (SM-7e)*

 Mg-turnings (428 mg, 17.7 mmol, 1.00 equiv.), 4.45 g ((4-bromophenyl)ethynyl)trimethylsilane (17.7 mmol, 1.00 equiv.), and dry THF (10 mL) were placed in a 100 mL round bottom flask. The mixture was heated cautiously until a vigorous reaction took place. The exothermic reaction was allowed to proceed until almost

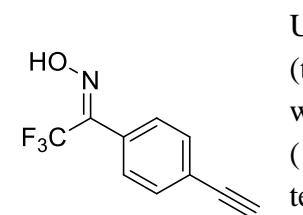
all of the Mg turnings had dissolved. The reaction mixture was then cooled to room temperature. A solution of 7.46 mL TFAA (11.2 g, 52.8 mmol, 3.00 equiv.) in 20 mL of dry THF was treated dropwise with the Grignard reagent under constant stirring over a period of 1 h at 0 °C. After stirring the mixture for 2 h, the reaction was quenched with saturated aqueous NH₄Cl-solution (50 mL) and extracted three times with ethyl acetate. The organic layer was dried over MgSO₄ and the crude product was purified *via* column chromatography (cyclohexane/ethyl acetate; 10:1). The target compound was isolated in 33% yield (1.57 g, 5.81 mmol). – R_f = 0.27 (cyclohexane/ethyl acetate; 10:1). – ¹H NMR (250 MHz, CDCl₃, ppm), δ = 0.25 (s, 9 H, CH₃), 7.54–7.58 (m, 2 H, CH), 7.91–8.10 (m, 2 H, CH). – ¹³C NMR (62.5 MHz, CDCl₃, ppm), δ = 0.1 (3 C), 100.8, 103.4, 120.5 (q, ¹J = 238 Hz), 129.2, 130.3 (2 C), 130.8, 132.5 (2 C), 179.9 (q, ²J = 35.4 Hz). – ¹⁹F NMR (376 Hz, CDCl₃, ppm), δ = -71.39 (s, 3 F). – IR (ATR, ̅): 3424, 2962, 2161, 1788, 1720, 1601, 1556, 1412, 1335, 1315, 1286, 1252, 1206, 1173, 1149, 940, 864, 766, 744, 701, 664, 599, 541 cm⁻¹. – EI-MS (m/z, 70 eV, 100 °C): 270 (21) [M]⁺, 256 (17), 255 (100), 219, (1), 201 (5), 158 (15), 149 (5), 129 (1), 77 (2), 58 (2), 43 (5). – HRMS (C₁₃H₁₃F₃OSi): calc. 270.0687, found. 270.0686. – Mp.: 74.5–77.5 °C.

2,2,2-Trifluoromethyl-1-(4-(trimethylsilylethynyl)phenyl)ketoxime (7e)



According to GP1, 1.65 g of 2,2,2-trifluoro-1-(4-((trimethylsilyl)ethynyl)phenyl)ethanone (**SM-7e**) (6.10 mmol, 1.00 equiv.) were reacted with 2.13 g of hydroxylamine hydrochloride (30.5 mmol, 5.00 equiv.) and 1.23 mL (15.3 mmol, 2.50 equiv.) of pyridine in ethanol at 80 °C. The solvent was removed under reduced pressure and the residue was purified *via* column chromatography (cyclohexane/ethyl acetate; 10:1). The target compound was isolated in 81% yield (1.40 g, 4.91 mmol). – R_f = 0.45 (cyclohexane/ethyl acetate; 10:1). – ¹H NMR (300 MHz, CDCl₃, ppm), δ = 0.26 (s, 9 H), 7.47–7.57 (m, 4 H), 9.57 (s, 1 H). – ¹³C NMR (75 MHz, CDCl₃, ppm), δ = 0.1 (3 C), 97.1, 104.3, 120.8 (q, ¹J = 275 Hz), 126.0, 128.3, 128.9 (2 C), 132.2 (2 C), 147.2 (q, ²J = 32.4 Hz). – ¹⁹F NMR (376 Hz, CDCl₃, ppm), δ = -66.34 (s, 3 F). – IR (ATR, ̅): 3311, 2959, 2162, 1605, 1505, 1436, 1331, 1251, 1203, 1179, 1140, 1112, 1031, 1009, 964, 857, 835, 758, 744, 733, 702, 682, 634, 545, 520, 440 cm⁻¹. – EI-MS (m/z, 70 eV, 100 °C): 285 (5) [M]⁺, 271 (8), 270 (25), 184 (100), 156 (4), 130 (6), 75 (5), 43 (10). – HRMS (C₁₃H₁₄F₃NOSi): calc. 285.0791, found. 285.0792. – Mp.: 80.5 °C.

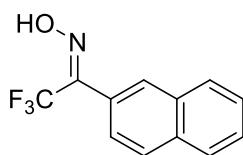
1-(4-Ethynphenyl)-2,2,2-trifluoromethylketoxime (7f)



Under a nitrogen atmosphere, 550 mg of 2,2,2-trifluoromethyl-1-(4-(trimethylsilylethynyl)phenyl)ketoxime (**7e**) (1.93 mmol, 1.00 equiv.) were dissolved in dry THF and 1.93 mL of 1 M TBAF-solution (1.93 mmol, 1.00 equiv.) were added. After stirring for 12 h at room temperature, 50 mL of H₂O were added, the aqueous layer was extracted three times with ethyl acetate, the organic layer was dried over MgSO₄ and the crude product was purified *via* column chromatography (cyclohexane/ethyl acetate; 10:1). The target compound was isolated in 97% yield (399 mg, 1.87 mmol). – R_f = 0.44 (cyclohexane/ethyl acetate; 10:1). – ¹H NMR (300 MHz, CDCl₃, ppm), δ = 3.10 (s, 1 H), 7.40–7.47 (m, 2 H), 7.48–7.56 (m, 2 H), 9.01 (s, 1 H). – ¹³C NMR (75 MHz, CDCl₃, ppm), δ = 79.2,

89.7, 120.5 (q, $^1J = 275$ Hz), 126.3, 128.7, 132.2 (2 C), 133.2 (2 C), 147.2 (q, $^2J = 33.1$ Hz). – ^{19}F NMR (376 Hz, $CDCl_3$, ppm), $\delta = -66.43$ (s, 3 F). – IR (ATR, $\tilde{\nu}$): 3291, 2923, 2111, 1662, 1606, 1442, 1401, 1329, 1312, 1270, 1207, 1187, 1171, 1135, 1028, 1010, 963, 847, 836, 803, 742, 727, 6685, 652, 633, 547, 526, 508, 465, 419 cm^{-1} . – EI-MS (m/z, 70 eV, 20 °C): 213 (100) [M] $^+$, 162 (3), 144 (8), 127 (43), 102 (33), 75 (10), 63 (5), 51 (5). – HRMS ($C_{10}H_6F_3NO$): calc. 213.0401, found. 213.0401. – Mp.: 85.5 °C.

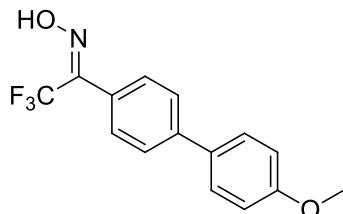
2,2,2-Trifluoro-1-(naphthalen-2-yl)ethanone oxime (7g)



According to GP1, 790 mg of 2,2,2-1-(4'-bromo-[1,1'-biphenyl]-4-yl)-2,2,2-trifluoroethanone (3.52 mmol, 1.00 equiv.) were reacted with 1.22 g of hydroxylamine hydrochloride (17.6 mmol, 5.00 equiv.) and 711 μ L (697 mg, 8.81 mmol, 2.50 equiv.) of pyridine in ethanol at 80 °C.

The solvent was removed under reduced pressure and the residue was purified *via* column chromatography (cyclohexane/ethyl acetate; 10:1). The target compound was isolated in quantitative yield (893 mg, 3.52 mmol). – $R_f = 0.42$ (cyclohexane/ethyl acetate; 4:1). 1H NMR (300 MHz, $CDCl_3$, ppm), $\delta = 7.52$ –7.69 (m, 3 H), 7.95–8.07 (m, 3 H), 8.18 (s, 1 H), 9.03 (s, 1 H). The analytical data correspond to the literature.^[4]

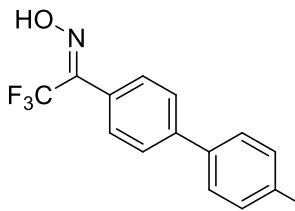
2,2,2-Trifluoro-1-(4'-methoxy-[1,1'-biphenyl]-4-yl)ethanone-oxime (7h)



According to GP1, 1.37 g of 2,2,2-trifluoro-1-(4'-methoxy-[1,1'-biphenyl]-4-yl)ethanone (4.90 mmol, 1.00 equiv.) were reacted with 1.70 g of hydroxylamine hydrochloride (24.5 mmol, 5.00 equiv.) and 1.00 mL (12.3 mmol, 2.50 equiv.) of pyridine in ethanol at 80 °C. The solvent was removed under reduced pressure and the residue was purified *via* column chromatography

(cyclohexane/ethyl acetate; 20:1). The target compound was isolated in 78% yield (1.13 g, 3.83 mmol). – 1H NMR (300 MHz, $CDCl_3$, ppm), $\delta = 3.88$ (s, 3 H), 7.01 (d, $^3J = 8.9$ Hz, 2 H), 7.50–7.70 (m, 6 H), 8.40 (s, 1 H). – ^{13}C NMR (63 MHz, $CDCl_3$, ppm), $\delta = 55.9$, 115.5 (2 C), 128.0 (q, $^1J = 275$ Hz), 127.4 (2 C), 129.3 (2 C), 129.3, 130.5 (2 C), 133.9, 143.6 (q, $^2J = 33.5$ Hz), 143.8 (s, 1 C), 161.4 (s, 1 C). – IR (ATR, $\tilde{\nu}$): 3248, 1604, 1530, 1498, 1445, 1420, 1401, 1338, 1320, 1292, 1261, 1211, 1178, 1137, 1031, 1007, 954, 822, 748, 726, 587, 528, 496, 406 cm^{-1} . – EI-MS (m/z, 70 eV, 100 °C): 295 (100) [M] $^+$, 279 (4), 247 (3), 209 (4), 184 (2). – HRMS ($C_{15}H_{12}F_3NO_2$): calc. 295.0815, found. 295.0816.

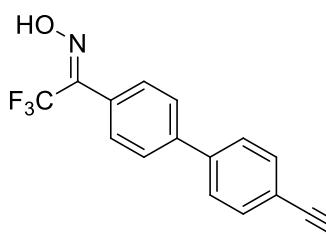
1-(4'-Bromo-[1,1'-biphenyl]-4-yl)-2,2,2-trifluoroethanone-oxime (7i)



According to GP1, 897 mg of 2,2,2-1-(4'-bromo-[1,1'-biphenyl]-4-yl)-2,2,2-trifluoroethanone (2.73 mmol, 1.00 equiv.) were reacted with 947 mg of hydroxylamine hydrochloride (13.6 mmol, 5.00 equiv.) and 0.55 mL (539 mg, 6.83 mmol, 2.50 equiv.) of pyridine in ethanol at 80 °C. The solvent was removed under reduced pressure and the residue was purified *via* column chromatography (cyclohexane/ethyl acetate; 10:1). The target compound was isolated in 95% yield (893 mg, 2.60 mmol). – $R_f = 0.42$ (cyclohexane/ethyl acetate; 4:1). – 1H NMR (250 MHz,

*CDCl*₃, ppm), δ = 7.43–7.53 (m, 2 H), 7.55–7.69 (m, 6 H), 9.07 (s, 1 H). – ¹³C NMR (67 MHz, *CDCl*₃, ppm), δ = 118.4 (q, 1J = 275.3 Hz), 122.5, 125.0, 127.0 (2 C), 128.8 (2 C), 129.3 (2 C), 132.1 (2 C), 138.8, 142.3, 147.4 (q, 3J = 32.3 Hz). – IR (ATR, $\tilde{\nu}$): 3256, 1906, 1719, 1607, 1587, 1482, 1445, 1411, 1390, 1341, 1319, 1189, 1139, 1080, 1037, 1009, 966, 949, 853, 814, 775, 742, 708, 672, 626, 610, 553, 519, 492 cm⁻¹. – EI-MS (m/z, 70 eV, 30 °C): 343/345 [M]⁺ (1/1), 222 (12), 176 (13), 149 (100), 132 (2), 121 (4), 105 (6), 93 (4), 77 (2), 58 (3). – HRMS (C₁₄H₉F₃NOBr): calc. 342.9820, found. 342.9816.

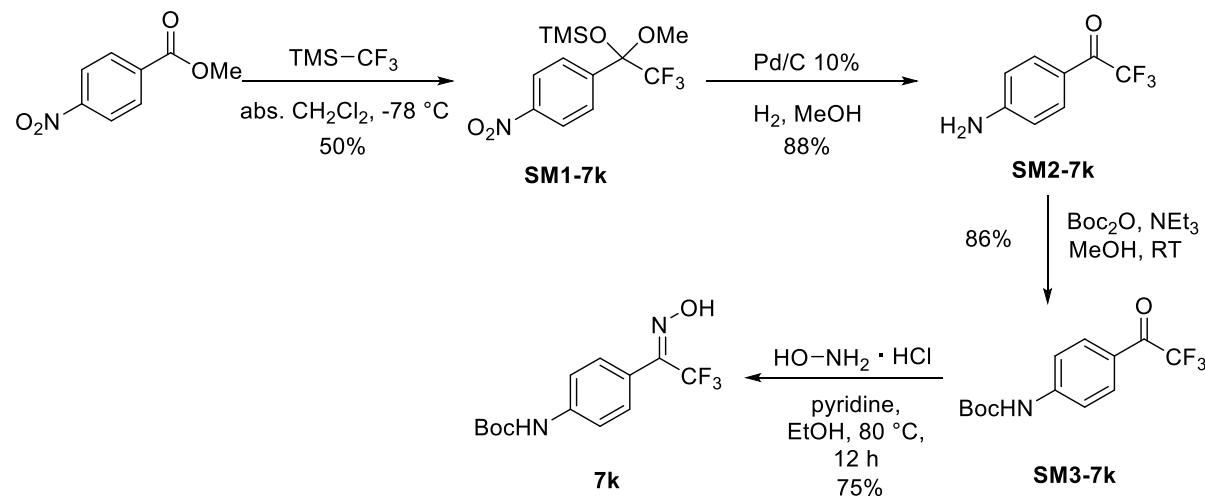
1-(4'-Ethynyl-[1,1'-biphenyl]-4-yl)-2,2,2-trifluoromethylketoxime (7j)



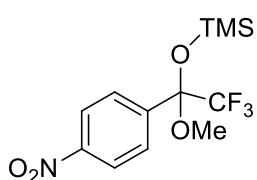
Under a nitrogen atmosphere, 900 mg of 2,2,2-trifluoro-1-(4'-((trimethylsilyl)ethynyl)-[1,1'-biphenyl]-4-yl)ethanone oxime (2.49 mmol, 1.00 equiv.) were dissolved in dry THF and 2.49 mL of 1 M TBAF-solution in THF (2.49 mmol, 1.00 equiv.) were added. After stirring for 12 h at room temperature, 50 mL of H₂O were added, the aqueous layer was extracted three times

with ethyl acetate, the organic layer was dried over MgSO₄ and the crude product was purified *via* column chromatography (cyclohexane/ethyl acetate; 10:1). The target compound was isolated in 55% yield (396 g, 1.37 mmol). – R_f = 0.39 (cyclohexane/ethyl acetate; 10:1). – ¹H NMR (300 MHz, *CDCl*₃, ppm), δ = 3.12 (s, 1 H), 7.55–7.68 (m, 8 H), 8.51 (s, 1 H). – ¹³C NMR (75 MHz, *CDCl*₃, ppm), δ = 78.3, 83.3, 118.8, 121.9, 125.2, 127.1 (q, 1J = 234 Hz), 127.2 (2 C), 129.3 (2 C), 132.7 (2 C), 140.3 (2 C), 142.5, 147.4 (q, 2J = 32.5 Hz) – ¹⁹F NMR (376 Hz, *CDCl*₃, ppm), δ = -62.27 (s, 3 F). – IR (ATR, $\tilde{\nu}$): 3287, 2919, 1715, 1604, 1491, 1448, 1399, 1336, 1251, 1207, 1176, 1139, 1035, 1010, 963, 822, 746, 725, 645, 621, 558, 537, 518, 430 cm⁻¹. – EI-MS (m/z, 70 eV, 60 °C): 289 (100) [M]⁺, 265 (27), 203 (22), 178 (12), 154 (8), 120 (4), 89 (4), 77 (29), 58 (9), 43 (48). – HRMS (C₁₆H₁₀F₃NO): calc. 289.0714, found. 289.0711. – Mp.: 181.5–184 °C.

Scheme SM-1: Schematic overview for the synthesis of precursor building block **7k**

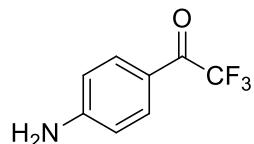


Trimethyl(2,2,2-trifluoro-1-methoxy-1-(4-nitrophenyl)ethoxy)silane (SM1-7k)



Under nitrogen atmosphere, 3.00 g of methyl 4-nitrobenzoate (13.8 mmol, 1.00 equiv.) were dissolved in 20 mL dry CH_2Cl_2 and treated with 2.55 mL of trimethyl(trifluoromethyl)silane (17.3 mmol, 1.25 equiv.). The mixture was cooled to -78°C and 430 μL of TBAF-solution (1 M in THF, 430 μmol , 2.50 mol%) was added dropwise. After stirring for 12 h at room temperature, 20 mL of 1 M HCl were added, the aqueous layer was extracted three times with CH_2Cl_2 , the organic layer was dried over MgSO_4 and the crude product was purified *via* column chromatography (cyclohexane/ethyl acetate; 10:1). The target compound was isolated in 50% yield (2.25 g, 6.96 mmol). $- R_f = 0.52$ (cyclohexane/ethyl acetate; 4:1). $- ^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm), $\delta = 0.29$ (s, 9 H, CH_3), 3.23 (s, 3 H, OCH_3), 7.78–7.92 (m, 2 H, CH), 8.24–8.27 (m, 2 H, CH). $- ^{13}\text{C NMR}$ (75 MHz, CDCl_3 , ppm), $\delta = 0.0$ (3 C), 49.7 (1 C), 96.9 (q, $^2J = 31.5$ Hz, 1 C), 121.0 (q, $^1J = 289$ Hz, 1 C), 122.2 (2 C), 128.5 (2 C), 135.6, 147.7. $- ^{19}\text{F NMR}$ (400 MHz, CDCl_3 , ppm): $\delta = -80.42$ (s, 3 F). $- \text{IR (ATR, } \tilde{\nu} \text{):}$ 2962, 2846, 1610, 1529, 1445, 1410, 1352, 1313, 1257, 1236, 1184, 1136, 1111, 1092, 996, 977, 959, 885, 854, 814, 759, 731, 709, 692, 640, 564, 477 cm^{-1} . $- \text{FAB-MS (m/z, 70 eV, } 190^\circ\text{C):}$ 324 [$\text{M} + \text{H}]^+$, 308, 307, 292, 258, 254, 234, 226, 212, 201, 184, 166, 120, 107. $- \text{HRMS (C}_{12}\text{H}_{17}\text{F}_3\text{NO}_4\text{Si) } [\text{M} + \text{H}]^+$: calc. 324.0873, found. 324.0874. $- \text{EA: C}_{12}\text{H}_{16}\text{F}_3\text{NO}_4\text{Si (323.1): calc. C 44.57, H 4.99, N 4.33, found. C 44.98, H 5.05, N 4.23.}$

1-(4-Aminophenyl)-2,2,2-trifluoroethanone (SM2-7k)



A solution of 439 mg of trimethyl(2,2,2-trifluoro-1-methoxy-1-(4-nitrophenyl)ethoxy)silane (2.00 mmol, 1.00 equiv.) in 10 mL ethanol was added to 1.37 g of SnCl_2 (7.21 mmol, 3.60 equiv.) in 2.0 mL of a aqueous HCl-solution (1:1). After stirring for 12 h at room temperature, 20 mL of 2 M NaOH were added (pH = 10), the aqueous layer was extracted three times with ethyl acetate, and the organic layer was dried over MgSO_4 . The crude product was purified *via* column chromatography (cyclohexane/ethyl acetate; 20:1) and the target compound was isolated in 88% yield (331 mg, 1.75 mmol). $- R_f = 0.52$ (cyclohexane/ethyl acetate; 4:1). $- ^1\text{H NMR}$ (250 MHz, CDCl_3 , ppm), $\delta = 4.45$ (br s, 2 H), 6.44–6.82 (m, 2 H), 7.75–8.02 (m, 2 H). $- ^{13}\text{C NMR}$ (63 MHz, CDCl_3 , ppm), $\delta = 117.2$ (q, $^1J = 291.8$ Hz), 113.8 (2 C), 119.7, 133.0 (d, $^3J = 2.4$ Hz, 2 C), 153.3, 178.2 (q, $^2J = 34.2$ Hz). $- ^{19}\text{F NMR}$ (400 MHz, CDCl_3 , ppm), $\delta = -70.5$. $- \text{IR (ATR, } \tilde{\nu} \text{):}$ 3451, 3358, 3233, 1676, 1632, 1576, 1555, 1451, 1351, 1210, 1182, 1131, 934, 840, 768, 743, 703, 642, 618, 522 cm^{-1} . $- \text{EA: C}_8\text{H}_6\text{F}_3\text{NO (189.0): calc. C 50.80, H 3.20, N 7.41; found. C 50.64, H 3.19, N 7.29. - EI-MS (m/z, 70 eV, } 20^\circ\text{C):}$ 189 (22) [$\text{M}]^+$, 120 (100), 92 (44), 90 (2), 65 (39), 63 (6), 60 (3), 52 (3). $- \text{HRMS (C}_8\text{H}_6\text{F}_3\text{NO) } [\text{M}]^+$: calc. 189.0396, found. 189.0395.

1-(tert-Butyloxycarbonylaminophenyl)-2,2,2-trifluoroacetyl (SM3-7k)

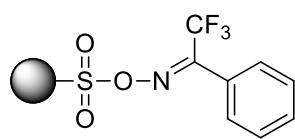
840 mg (4.44 mmol, 1.00 equiv.) of amine were dissolved in 20 mL methanol and treated with 1.23 mL (899 mg, 8.88 mmol, 2.00 equiv.) triethyl amine and 1.90 mL Boc₂O (1.94 g, 8.88 mmol, 2.00 equiv.). After stirring for 12 h at room temperature, 20 mL of brine were added, the aqueous layer was extracted with ethyl acetate three times, the organic layer was dried over MgSO₄ and the crude product was purified *via* column chromatography (cyclohexane/ethyl acetate; 20:1). The target compound was isolated in 86% yield (1.15 g, 3.81 mmol). – R_f = 0.55 (cyclohexane/ethyl acetate; 4:1). – ¹H NMR (250 MHz, CDCl₃, ppm), δ = 1.50 (s, 9 H, CH₃), 6.81 (s, 1 H, NH), 7.50–7.61 (m, 2 H, CH), 7.94–8.08 (m, 2 H, CH) – ¹³C NMR (62.5 MHz, CDCl₃, ppm), δ = 27.2 (3 C), 80.9 (1 C), 116.9 (q, ¹J = 291 Hz, 1 C), 116.6 (2 C), 124.2 (1 C), 130.9 (1 C), 144.2 (1 C), 150.8 (2 C), 179.0 (q, ²J = 34.7 Hz, 1 C). – ¹⁹F NMR (376 Hz, CDCl₃, ppm), δ = –70.69 (s, 3 F). – IR (ATR, ˜): 3367, 2970, 1734, 1688, 1583, 1523, 1459, 1421, 1393, 1368, 1345, 1318, 1277, 1226, 1174, 1135, 1049, 1025, 939, 895, 855, 829, 763, 736, 702, 644, 600, 529, 502, 460, 433 cm^{–1}. – EI-MS (m/z, 70 eV, 30 °C): 289 (5) [M]⁺, 233 (18), 216 (15), 189 (9), 164 (12), 146 (3), 120 (9), 59 (15), 57 (100). – HRMS (C₁₃H₁₄F₃NO₃): calc. 289.0926, found. 289.0926.

1-(4-tert-Butyloxycarbonylaminophenyl)-2,2,2-trifluoromethylketoxim (7k)

According to GP1, 1.15 g of *tert*-butyl (4-(2,2,2-trifluoroacetyl)phenyl)carbamate (4.00 mmol, 1.00 equiv.) were reacted with 1.39 g of hydroxylamine hydrochloride (20.0 mmol, 5.00 equiv.) and 800 μL (10.0 mmol, 2.50 equiv.) of pyridine in 20 mL ethanol at 80 °C. The solvent was removed under reduced pressure and the residue was purified *via* column chromatography (cyclohexane/ethyl acetate; 20:1). The target compound was isolated in 75% yield (907 mg, 2.98 mmol). – R_f = 0.76 (cyclohexane/ethyl acetate; 10:1). – ¹H NMR (250 MHz, CDCl₃, ppm), δ = 1.53 (s, 9 H, CH₃), 6.70 (s, 1 H, NH), 7.53–7.44 (m, 4 H, CH), 8.55 (s, 1 H, OH). – ¹³C NMR (62.5 MHz, CDCl₃, ppm), δ = 28.3 (3 C), 82.1 (1 C), 117.7 (2 C), 120.4 (q, ¹J = 278, 1 C), 125.7 (1 C), 132.1 (2 C), 133.5 (1 C), 145.1 (1 C), 151.8 (1 C). – ¹⁹F NMR (376 Hz, CDCl₃, ppm), δ = –66.24 (s, 3 F). – IR (ATR, ˜): 3369, 2989, 1735, 1690, 1585, 1524, 1458, 1421, 1394, 1319, 1278, 1229, 1210, 1177, 1137, 1050, 1027, 998, 976, 942, 897, 856, 829, 795, 764, 703, 646, 630, 602, 530, 461 cm^{–1}. – EI (m/z, 70 eV, 30 °C): 289 (5) [M]⁺, 233 (18), 216 (15), 189 (9), 164 (12), 146 (3), 120 (9), 59 (15), 57 (100). – HRMS (C₁₂H₁₂F₃N₂O₃) [M–CH₃]⁺: calc. 289.0800, found. 289.0802.

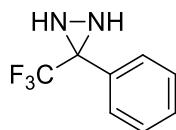
3. Synthesis of immobilized sulfonyl oximes 8 and cleavage to diaziridines 5

Phenyl-2,2,2-trifluoromethyl-(*O*-sulfonylpolystyryl)ketoxime (8a)



According to GP2, 2,2,2-trifluoro-1-phenylethanone oxime was immobilized on 453 mg of commercially available sulfonylchloride resin **6** (566 μ mol, *loading*: 1.25 mmol/g). After drying under high vacuum, 529 mg of the resin were obtained in 88% yield (*loading* = 0.94 g/mol). – Raman (1064, 500 mW, $\tilde{\nu}$): 3061, 2982, 2905, 2855, 1637, 1601, 1450, 1328, 1200, 1183, 1157, 1094, 1033, 1003, 798, 754, 622 cm^{-1} .

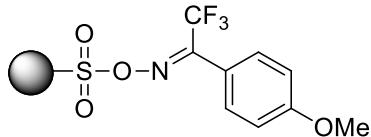
3-Phenyl-3-(trifluoromethyl)diaziridine (5a)



Resin **8a** (121 mg, 127 μ mol; *loading*: 0.94 mmol/g) was treated with NH_3 /dioxane solution according to GP3 to give 19.6 mg (104 μ mol) of the target substance in 82% yield. – R_f = 0.44 (cyclohexane/ethyl acetate; 4:1). Column chromatography: cyclohexane/ethyl acetate (10:1 → 4:1). – R_f = 0.36 (cyclohexane/ethyl acetate; 4:1). – ^1H NMR (250 MHz, CDCl_3 , ppm), δ = 2.25 (d, 3J = 8.6 Hz, 1 H), 2.80 (d, 3J = 8.6 Hz, 1 H), 7.40–7.49 (m, 2 H), 7.60–7.64 (m, 3 H). – ^{13}C NMR (75 MHz, CDCl_3 , ppm), δ = 58.0 (q, 2J = 36.9 Hz), 123.5 (q, 1J = 278.2 Hz), 128.1 (d, 4J = 1.1 Hz, 2 C), 128.7 (2 C), 131.7, 130.1. – ^{19}F NMR (376 Hz, CDCl_3 , ppm), δ = -66.69 (s, 3 F). – IR (ATR, $\tilde{\nu}$): 3194, 1501, 1450, 1391, 1336, 1314, 1252, 1138, 1077, 1027, 1001, 946, 878, 786, 761, 712, 695, 644, 629, 569, 518, 495. – EI-MS (m/z, 70 eV, 60 °C): 187 (57) [$\text{M}-1$]⁺, 167 (24), 159 (18), 149 (100), 119 (23), 107 (12), 69 (25). – HRMS [$\text{M}-1$]⁺ ($\text{C}_8\text{H}_7\text{F}_3\text{N}_2$): calc. 187.0483, found. 187.0481.

Combined yield starting with sulfonyloxime resin and finishing with the isolation of compound **5** via chromatography: 72%

1-(4-Methoxyphen-1-yl)-2,2,2-trifluoroethanone *O*-polystyrene methylsulfonyl oxime (8b)



Commercially available sulfonylchloride resin **6** (500 mg, 625 μ mol, *loading*: 1.25 mmol/g) was converted with 2,2,2-trifluoro-1-(4-methoxyphenyl)ethanone oxime according to GP2 to give 733 mg of resin-bound 1-(4-methoxyphen-1-yl)-2,2,2-trifluoroethanone *O*-sulfonyl oxime in quantitative yield (*loading*: 0.853 mmol/g). – ^{13}C Gel-NMR (75 MHz, CDCl_3 , ppm), δ = 55.4, 114.4, 116.0, 130.9, 153.1. – IR (ATR, $\tilde{\nu}$): 2921, 2093, 1603, 1512, 1493, 1452, 1384, 1342, 1296, 1262, 1198, 1175, 1144, 1030, 1007, 889, 830, 768, 736, 696, 670, 665, 570 cm^{-1} .

3-(4-Methoxyphenyl)-3-(trifluoromethyl)diaziridine (5b)

Resin **8b** (113 mg, batch **1.1**, 96.4 μ mol; *loading*: 0.853 mmol/g) was treated with NH_3 /dioxane solution according to GP3 to give 16.8 mg (77 μ mol) of the target substance in 80% yield. – R_f = 0.64 (cyclohexane/ethyl acetate; 1:1). Column chromatography: cyclohexane/ethyl acetate (4:1 → 1:1). – ^1H NMR (250 MHz, CDCl_3 , ppm), δ = 2.15 (d, 3J = 8.8 Hz, 1 H), 2.73 (d, 3J = 8.8 Hz, 1 H), 3.80 (s, 3 H), 6.88–6.94 (m, 2 H), 7.50–7.53 (m, 2 H). – ^{13}C NMR (62.5 MHz, CDCl_3 , ppm), δ = 55.3, 57.6 (q, 2J = 35.9 Hz), 114.1 (2 C), 123.6 (q, 1J = 278.2 Hz), 123.7, 129.5 (d, 4J = 1.0 Hz, 2 C), 160.8. – ^{19}F NMR (376 Hz, CDCl_3 , ppm), δ = -75.76 (s, 3 F). – IR (ATR, $\tilde{\nu}$): 3259, 2940, 2843, 1708, 1614, 1585, 1519, 1465, 1397, 1304, 1254, 1219, 1155, 1032, 948, 878, 835, 734, 701, 592, 531 cm^{-1} . – EI-MS (m/z, 20 °C): 218 (27) [M] $^+$, 217 (100), 197 (38), 183 (6), 149 (12). – HRMS ($\text{C}_9\text{H}_9\text{ON}_2\text{F}_3$): calc. 218.0667, found. 218.0670.

Combined yield starting with sulfonyloxime resin and finishing with the isolation of compound **5** *via* chromatography: 80%

1-(4-Chlorophen-1-yl)-2,2,2-trifluoroethanone *O*-polystyrene methylsulfonyl oxime (8c)

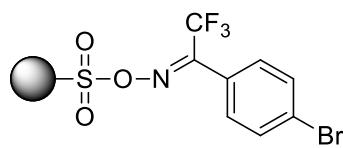
According to GP2, 1-(4-chlorophenyl)-2,2,2-trifluoroethanone oxime was immobilized on 3.13 g of commercially available sulfonylchloride resin (3.91 mmol, loading: 1.25 mmol/g). After drying in *vacuo*, 4.10 g (*loading*: 0.954 mmol/g) of the resin were obtained in quantitative yield. – Raman (1064 nm, 500 mW, $\tilde{\nu}$): 3060, 3002, 2980, 2904, 2855, 2835, 2821, 1598, 1453, 1373, 1334, 1200, 1183, 1157, 1127, 1096, 1032, 1002, 841, 797, 633, 622 cm^{-1} .

3-(4-Chlorophenyl)-3-(trifluoromethyl)diaziridine (5c)

Resin **8c** (242 mg, 231 μ mol; *loading*: 0.954 mmol/g) was treated with NH_3 /dioxane solution according to GP3 to give 32.2 mg (145 μ mol) of the target substance in 63% yield. – R_f = 0.82 (cyclohexane/ethyl acetate; 1:1). Column chromatography: cyclohexane/ethyl acetate (4:1 → 1:1). – ^1H NMR (250 MHz, CDCl_3 , ppm), δ = 2.20 (d, 3J = 8.8 Hz, 1 H), 2.81 (d, 3J = 8.8 Hz, 1 H), 7.38–7.43 (m, 2 H), 7.54–7.58 (m, 2 H). – ^{13}C NMR (62.5 MHz, CDCl_3 , ppm), δ = 57.6 (q, 2J = 36.3 Hz), 123.3 (q, 1J = 278.3 Hz), 129.1 (2 C), 129.5 (d, 4J = 1.1 Hz, 2 C), 130.2, 136.4. – IR (DRIFT, $\tilde{\nu}$): 2228, 2925, 1912, 1711, 1679, 1602, 1498, 1397, 1316, 1299, 1219, 1154, 1095, 1017, 952, 879, 831, 784, 735, 717, 686, 570, 572, 478 cm^{-1} . – EI-MS (m/z, 70 eV, 80 °C): 222/224 (22/7) [M] $^+$, 221/223 (100/35), 201/203 (37/10), 190/192 (45/16), 153 (77). – HRMS ($\text{C}_8\text{H}_5\text{ClN}_2\text{F}_3$) [M–1] $^+$: calc. 221.0093, found. 221.0090.

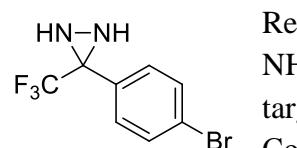
Combined yield starting with sulfonyloxime resin and finishing with the isolation of compound **5** *via* chromatography: 63%

1-(4-Bromophenyl)-2,2,2-trifluoromethyl-(*O*-sulfonylstyryl)ketoxime (8d)



According to GP2, 1-(4-bromophenyl)-2,2,2-trifluoroethanone oxime was immobilized on 1.19 g of commercially available sulfonylchloride resin (1.49 mmol, *loading*: 1.25 mmol/g). After drying under high vacuum, 1.61 g (*loading*: 0.924 mmol/g) of the resin were obtained in quantitative yield. – Raman (1064 nm, 500 mW, $\tilde{\nu}$): 3058, 3001, 2976, 2918, 2905, 2851, 1630, 1600, 1447, 1326, 1200, 1183, 1156, 1125, 1074, 1032, 1002, 799, 754, 740, 622 cm^{-1} .

3-(4-Bromophenyl)-3-(trifluoromethyl)diaziridine (5d)



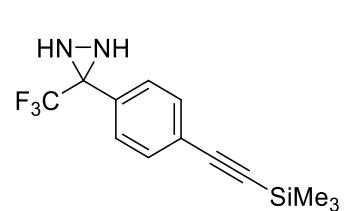
Resin **8d** (200 mg, 185 μmol ; *loading*: 0.924 mmol/g) was treated with NH_3 /dioxane solution according to GP3 to give 34.5 mg (129 μmol) of the target substance in 70% yield. – $R_f = 0.15$ (cyclohexane/ethyl acetate; 4:1). Column chromatography: cyclohexane/ethyl acetate (10:1 → 4:1). – ^1H NMR (250 MHz, CDCl_3 , ppm), $\delta = 2.19$ (d, $^3J = 8.7$ Hz, 1 H, NH), 2.79 (d, $^3J = 8.7$ Hz, 1 H, NH), 7.43–7.54 (m, 4 H, CH). – ^{13}C NMR (62.5 MHz, CDCl_3 , ppm), $\delta = 57.8$ (q, $^2J = 36.3$ Hz), 123.1 (q, $^1J = 278$ Hz), 124.8, 129.9 (d, $^4J = 1.1$ Hz, 2 C), 130.8, 132.2 (2 C). – IR (ATR, $\tilde{\nu}$): 3259, 2924, 2854, 1597, 1493, 1396, 1299, 1218, 1152, 1097, 1071, 1013, 951, 878, 826, 783, 730, 710, 674, 570, 518, 438. – EI-MS (m/z, 70 eV, 20 °C): 267/269 (100/41) [M + H] $^+$, 266/268 (13/16) [M] $^+$, 245/247 (16/17), 199/201 (24/14), 157 (17), 118 (28). – HRMS ($\text{C}_8\text{H}_6\text{BrN}_2\text{F}_3$): calc. 265.9667, found. 265.9666.

Combined yield starting with sulfonyloxime resin and finishing with the isolation of compound **5** *via* chromatography: 70%

1-(4-Trimethylsilylethynylphen-1-yl)-2,2,2-trifluoroethanone *O*-polystyrene methylsulfonyl oxime (8e)

According to GP2, 255 mg 2,2,2-trifluoro-1-(4-((trimethylsilyl)ethynyl)phenyl)ethanone oxime (810 μmol , 1.50 equiv.) were immobilized on 400 mg of commercially available sulfonylchloride resin (540 μmol , *loading*: 1.25 mmol/g). After drying under high vacuum, 526 mg (*loading*: 0.951 mmol/g) of the resin were obtained in quantitative yield. – Raman (1064 nm, 500 mW, $\tilde{\nu}$): 3058, 2962, 2901, 2854, 2162, 1605, 1504, 1452, 1412, 1397, 1334, 1223, 1199, 1182, 1156, 1095, 1032, 1002, 832, 796, 742, 704, 667, 634, 621, 607, 536, 433, 399, 347, 220 cm^{-1} .

3-(Trifluoromethyl)-3-(4-((trimethylsilyl)ethynyl)phenyl)-3H-diaziridine (5e)



Resin **8e** (105 mg, 99.8 μmol ; *loading*: 0.951 mmol/g) was treated with NH_3 /dioxane solution according to GP3 to give 19.6 mg (69.0 μmol) of the target substance in 69% yield. – $R_f = 0.37$ (cyclohexane/ethyl acetate; 4:1). Column chromatography: cyclohexane/ethyl acetate (10:1 → 4:1). – ^1H NMR (400 MHz, CDCl_3 , ppm), $\delta = 0.25$ (s, 9 H), 2.21 (d, $^3J = 8.7$ Hz, 1 H), 2.81 (d,

$^3J = 8.7$ Hz, 1 H), 7.49–7.56 (m, 4 H). – ^{13}C NMR (100 MHz, CDCl_3 , ppm), $\delta = -0.15$ (3 C), 57.8 (q, $^2J = 36.1$ Hz), 96.3, 103.8, 123.4 (q, $^1J = 278.2$ Hz), 125.2, 127.9 (2 C), 131.6, 132.2 (2 C). – IR (ATR, $\tilde{\nu}$): 3254, 2961, 2161, 1721, 1611, 1511, 1396, 1301, 1252, 1218, 1153, 1097, 1020, 944, 865, 843, 761, 739, 705, 652, 609, 575 cm^{-1} . – EI-MS (m/z): 284 (25) [M] $^+$, 283 (100), 263 (19), 215 (51), 184 (21). – HRMS ($\text{C}_{13}\text{H}_{15}\text{SiN}_2\text{F}_3$): calc. 284.0957, found. 284.0959.

Combined yield starting with sulfonyloxime resin and finishing with the isolation of compound **5** via chromatography: 69%

1-(4-Ethynylphenyl)-2,2,2- trifluoromethyl-(O-sulfonylpolystyryl)ketoxim (8f)

According to GP2, 579 mg of 1-(4-ethynylphenyl)-2,2,2-trifluoroethanone oxime (2.72 mmol, 1.60 equiv.) were immobilized on 1.22 g of commercially available sulfonylchloride resin (1.53 mmol, *loading*: 1.25 mmol/g). After drying under high vacuum, 1.58 g (*loading*: 0.965 mmol/g) of the resin were obtained in quantitative yield (example batch **1.1** see table of loading). – ^{13}C Gel-NMR (75 MHz, CDCl_3 , ppm), $\delta = 40.5$, 46.5, 127.9, 132.4, 144.8. – ^{19}F Gel-NMR (400 MHz, CDCl_3 , ppm), $\delta = -66.17$. – Raman (1064 nm, 500 mW, $\tilde{\nu}$): 3058, 2908, 2112, 1605, 1452, 1179, 1002 cm^{-1} . – IR (ATR, ν): 3288, 3024, 2924, 2107, 1596, 1492, 1571, 1386, 1337, 1197, 1177, 1150, 1121, 1032, 1005, 893, 819, 763, 720, 696, 664, 616, 571, 499, 411 cm^{-1} .

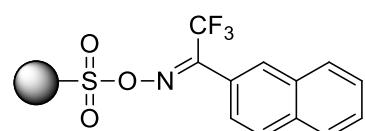
Table of batch-loading:

No	Start. amount [g]	mmol	yield[g]	conversion	loading [mmol/g]
1.1	1.22	1.53	1.58	quant	0.965
1.2	0.470	0.588	0.596	quant	0.986
1.3	0.844	1.06	1.05	quant	1.00
1.4	0.877	1.10	1.03	79%	0.841
1.5	0.833	1.04	0.952	65%	0.707

3-(4-Ethynylphenyl)-3-(trifluoromethyl)diaziridine (5f)

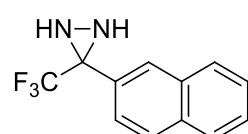
Resin **8f batch 1.2** (121 mg, 133 μmol ; *loading*: 1.10 mmol/g) was treated with NH_3 /dioxane solution according to GP3 to give 21.8 mg (103 μmol) of the target substance in 77% yield. – $R_f = 0.44$ (cyclohexane/ethyl acetate; 4:1). Column chromatography: cyclohexane/ethyl acetate (10:1 → 4:1). – ^1H NMR (400 MHz, CDCl_3 , ppm), $\delta = 2.20$ (d, $^3J = 8.4$ Hz, 1 H, NH), 2.79 (d, $^3J = 8.4$ Hz, 1 H, NH), 3.11 (s, 1 H, CH), 7.47–7.62 (m, 4 H, CH). – ^{13}C NMR (100 MHz, CDCl_3 , ppm), $\delta = 57.8$ (q, $^2J = 36.1$ Hz), 78.9, 82.6, 123.3 (q, $^1J = 278$ Hz), 124.2, 126.3, 128.0, 132.4 (2 C), 132.0. – ^{19}F NMR (376 Hz, CDCl_3 , ppm), $\delta = -75.28$ (s, 3 F). – IR (DRIFT, $\tilde{\nu}$): 3291, 3194, 2923, 1932, 1610, 1509, 1396, 1340, 1254, 1178, 1147, 1017, 953, 887, 838, 795, 739, 701, 670, 634, 573, 554, 533, 447 cm^{-1} . – EI-MS (m/z): 212 (83) [M] $^+$, 211 (100), 191 (81), 143 (81), 116 (20). – HRMS ($\text{C}_{10}\text{H}_7\text{N}_2\text{F}_3$): calc. 212.0561, found. 212.0562.

1-Naphtha-2-yl-2,2,2-trifluoroethanone O-polystyrene methylsulfonyl oxime (8g)



According to GP2, 339 mg of 2,2,2-trifluoro-1-(naphthalen-2-yl)ethanone oxime (1.42 mmol, 1.79 equiv.) was immobilized on 636 mg of commercially available sulfonylchloride resin (795 μ mol, *loading*: 1.25 mmol/g). After drying under high vacuum, 808 mg (*loading*: 0.984 mmol/g) of the resin were obtained in quantitative yield.

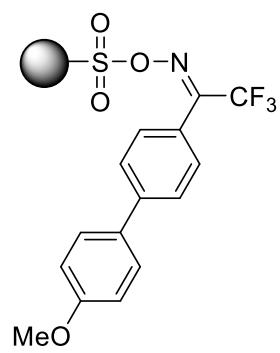
3-(Naphthalin-2-yl)-3-(trifluoromethyl)diaziridine (5g)



Resin **8g** (100 mg, 98.4 μ mol; *loading*: 0.984 mmol/g) was treated with NH₃/dioxane solution according to GP3 to give 22.6 mg (95.0 μ mol) of the target substance in 96% yield. – R_f = 0.42 (cyclohexane/ethyl acetate; 4:1). Column chromatography: cyclohexane/ethyl acetate (10:1 → 4:1). – ¹H NMR (400 MHz, CDCl₃, ppm), δ = 2.36 (d, ³J = 8.5 Hz, 1 H), 2.91 (d, ³J = 8.5 Hz, 1 H), 7.52–7.58 (m, 2 H), 7.67–7.69 (m, 1 H), 7.86–7.91 (m, 3 H), 8.13 (br s, 1 H). – ¹³C NMR (100 MHz, CDCl₃, ppm), δ = 58.2 (q, ²J = 35.9 Hz), 123.6 (q, ¹J = 278.8 Hz), 124.5, 126.8, 127.3, 127.7, 128.3, 128.3, 128.7, 129.0, 132.7, 133.8. – IR (ATR, $\tilde{\nu}$): 3208, 3059, 2928, 1688, 1600, 1508, 1386, 1357, 1327, 1248, 1207, 1134, 970, 948, 898, 868, 831, 817, 775, 749, 734, 710, 652, 627, 576, 560, 486, 476, 417 cm⁻¹. – EI-MS (m/z, 70 eV, 30 °C): 238 (68) [M]⁺, 237 (100) [M – 1]⁺, 217 (45), 188 (5), 169 (17). – HRMS [M – 1]⁺ (C₁₂H₈F₃N₂): calc. 237.0640, found. 237.0643.

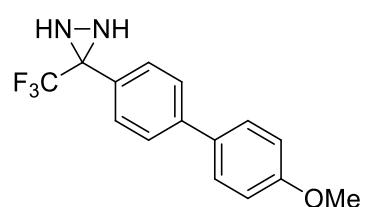
Combined yield starting with sulfonyloxime resin and finishing with the isolation of compound **5** via chromatography: 96%

3-(1'-Methoxy-4,4'-biphen-1-yl)-2,2,2-trifluoromethyl-(O-sulfonylpolystyryl)ketoxim (8h)



According to GP2, 1-(4-methoxybiphenyl)-2,2,2-trifluoroethanone oxime was immobilized on 136 mg of commercially available sulfonylchloride resin (170 μ mol, *loading*: 1.25 mmol/g). After drying under high vacuum, 161 mg (*loading*: 0.600 mmol/g) of the resin were obtained in 57% yield (loading according to 100% conversion: 1.06 mmol/g). ¹³C-Gel-NMR (75 MHz, CDCl₃ ppm), δ = 55.4, 114.6. – Raman (1064 nm, 100 mW, $\tilde{\nu}$): 3054, 2908, 2870, 2446, 1605, 1451, 1291, 1182, 1159, 1125, 1115, 1091, 1077, 1033, 1002, 805, 783, 622 cm⁻¹.

3-(4'-Methoxybiphenyl)-3-(trifluoromethyl)diaziridine (5h)

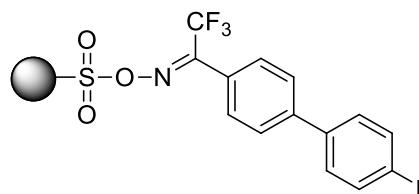


Resin **8h** (97.2 mg, 102 μ mol; *loading*: 0.600 mmol/g) was treated with NH₃/dioxane solution according to GP3 to give 19.0 mg (64.6 μ mol) of the target substance in quantitative yield. – R_f = 0.28 (cyclohexane/ethyl acetate; 4:1). Column chromatography: cyclohexane/ethyl acetate (10:1 → 4:1). – ¹H NMR (300 MHz, CDCl₃, ppm), δ = 2.26 (d, ³J = 8.2 Hz, 1 H),

2.83 (d, $^3J = 8.2$ Hz, 1 H), 3.86 (s, 3 H), 7.00 (d, $^3J = 8.4$ Hz, 2 H), 7.53 (d, $^3J = 8.4$ Hz, 2 H), 7.59 (d, $^3J = 8.1$ Hz, 2 H), 7.66 (d, $^3J = 8.1$ Hz, 2 H). – ^{13}C NMR (75 MHz, CDCl_3 , ppm), $\delta = 55.3$, 57.9 (q, $^2J = 36.0$ Hz), 123.6 (q, $^1J = 278.7$ Hz), 126.9 (2 C), 128.2 (2 C), 128.5 (2 C), 129.9 (2 C), 132.5, 134.6, 142.7, 159.6. – IR (ATR, $\tilde{\nu}$): 3253, 3204, 2924, 1674, 1603, 1581, 1530, 1499, 1458, 1444, 1400, 1333, 1290, 1240, 1174, 1139, 1112, 1030, 1011, 999, 943, 883, 847, 816, 743, 712, 688, 632, 515, 491 cm^{-1} . – EI-MS (m/z, 70 eV, 60 °C): 294 (74) $[\text{M}]^+$, 293 $[\text{M}-1]^+$ (55), 280 (97), 279 (28), 225 (54), 211 (100), 153 (26). – HRMS ($\text{C}_{15}\text{H}_{13}\text{OF}_3\text{N}_2$): calc. 294.0980, found. 294.0981.

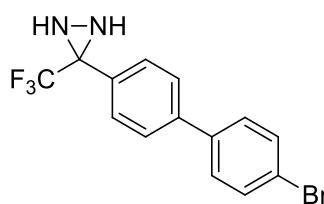
Comment: due to the nature of the resin and the difficulties in the yield calculation on bead, we obtained in this reaction (yielding compound **5h**) more material than the theoretical possible amount. Calculation of the yield without estimation of the loading of **8h** gave a combined yield starting with alkyne resin **8f** and finishing with the isolation of compound **5h** of 63%.

3-(4'-Bromo-1,1'-biphen-4-yl)-2,2,2-trifluoromethyl-(O-sulfonylpolystyryl)ketoxim (8i)



According to GP2, 1-(4-bromobiphenyl)-2,2,2-trifluoroethanone oxime was immobilized on 660 mg of commercially available sulfonylchloride resin (825 μmol , loading: 1.25 mmol/g). After drying under high vacuum, 908 mg (loading: 0.888 mmol/g) of the resin were obtained in 98% yield. Raman (1064 nm, 100 mW, $\tilde{\nu}$): 3064, 3051, 2913, 1608, 1521, 1455, 1288, 1184, 1161, 1078, 1032, 1002, 804, 623 cm^{-1} .

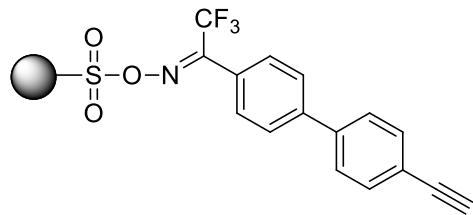
3-(4'-Bromobiphenyl)-3-(trifluoromethyl)diaziridine (5i)



Resin **8i** (131 mg, 78.6 μmol ; loading: 0.888 mmol/g) was treated with NH_3 /dioxane solution according to GP3 to give 32.3 mg (94.1 μmol) of the target substance in 81% yield. – $R_f = 0.50$ (cyclohexane/ethyl acetate; 2:1). Column chromatography: cyclohexane/ethyl acetate (10:1 → 2:1). – ^1H NMR (250 MHz, CDCl_3 , ppm), $\delta = 2.27$ (d, $^3J = 8.7$ Hz, 1 H), 2.85 (d, $^3J = 8.7$ Hz, 1 H), 7.43–7.49 (m, 2 H), 7.57–7.64 (m, 4 H), 7.68–7.74 (m, 2 H). – ^{13}C NMR (62.5 MHz, CDCl_3 , ppm), $\delta = 57.8$ (q, $^2J = 36.6$ Hz), 123.5 (q, $^1J = 278.1$ Hz), 122.3, 127.3 (2 C), 128.7 (2 C), 128.7 (2 C), 131.0, 132.0 (2 C), 138.9, 141.9. – IR (ATR, $\tilde{\nu}$): 3184, 1675, 1588, 1484, 1388, 1341, 1143, 1079, 1001, 946, 888, 849, 813, 770, 739, 706, 656, 628, 574, 546, 503 cm^{-1} . – EI-MS (m/z, 70 eV, 50 °C): 342/344 (49/71) $[\text{M}]^+$, 341/343 (92/100) $[\text{M}-1]^+$, 328/330 (48/48), 321/323 (22/22), 273/275 (41/40), 259/261 (58/57), 194 (46), 152 (70). – HRMS $[\text{M}+1]^+$ ($\text{C}_{14}\text{H}_{11}\text{BrF}_3\text{N}_2$): calc. 343.0058, found. 343.0056.

Combined yield starting with sulfonyloxime resin and finishing with the isolation of compound **5** via chromatography: 79%

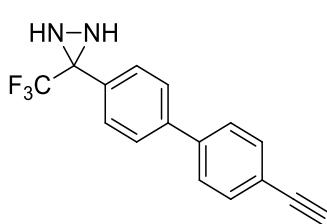
1-(4'-Ethynyl-[1,1'-biphenyl]-4-yl)-2,2,2-trifluoromethyl-(*O*-sulfonylpolystyryl)ketoxime (8j)



According to GP2, 180 mg of 1-(4'-ethynyl-[1,1'-biphenyl]-4-yl)-2,2,2-trifluoroethanone oxime (623 mmol, 1.51 equiv.) was immobilized on 277 mg of commercially available sulfonylchloride resin (346 μ mol, *loading*: 1.25 mmol/g). After drying under high vacuum, 377 mg (*loading*: 0.862 mmol/g) of the

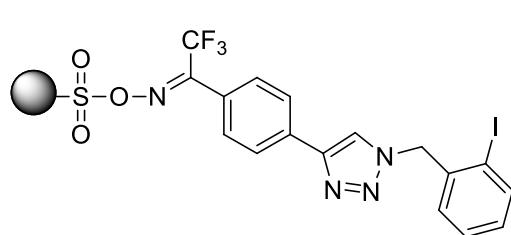
resin were obtained in quantitative yield. – Raman (1064 nm, 500 mW, ν): 3055, 2907, 2109, 1607, 1452, 1289, 1183, 1157, 1124, 1033, 1002, 798, 622 cm^{-1} .

3-(4'-Ethynyl-[1,1'-biphenyl]-4-yl)-3-(trifluoromethyl)diaziridine (5j)



Resin **8j** (50.0 mg, 43.1 μ mol; *loading*: 0.862 mmol/g) was treated with NH_3 /dioxane solution according to GP3 to give 12.0 mg (42.0 μ mol) of the target substance in 97% yield. – R_f = 0.76 (cyclohexane/ethyl acetate; 4:1). Column chromatography: cyclohexane/ethyl acetate (10:1 \rightarrow 4:1). – ^1H NMR (400 MHz, CDCl_3 , ppm), δ = 2.21 (d, 3J = 8.5 Hz, 1 H, NH), 2.81 (d, 3J = 8.5 Hz, 1 H, NH), 3.11 (s, 1 H, CH), 7.49–7.74 (m, 8 H, CH). – ^{13}C NMR (100 MHz, CDCl_3 , ppm), δ = 57.9 (q, 2J = 36.1 Hz), 78.2, 83.3, 121.7, 123.5 (q, 1J = 278 Hz), 127.1 (2 C), 127.4 (2 C), 128.7 (2 C), 131.1, 132.7 (2 C), 140.4, 142.2. – ^{19}F NMR (376 Hz, CDCl_3 , ppm), δ = –75.35 (s, 3 F). – IR (ATR, $\tilde{\nu}$): 3309, 3247, 2923, 1921, 1716, 1603, 1493, 1394, 1273, 1218, 1137, 1097, 1003, 979, 943, 914, 881, 857, 819, 768, 727, 700, 668, 645, 626, 577, 548, 537, 519 cm^{-1} . EI-MS (m/z, 70 eV, 50 °C): 287 (22) [M] $^+$, 274 (95), 263 (71), 243 (40), 234 (23), 205 (100), 176 (51), 151 (27), 115 (7), 107 (15), 102 (29), 84 (99), 73 (24), 58 (32), 43 (60). – HRMS ($\text{C}_{16}\text{H}_{11}\text{F}_3\text{N}_2$): calc. 288.0874, found. 288.0875.

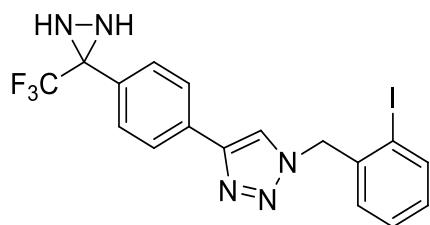
1-(4-(1-(2-Iodophenyl)-1*H*-1,2,3-triazol-4-yl)phenyl)-2,2,2-trifluoromethyl-(*O*-sulfonylpolystyryl)ketoxime (8l)



According to GP6, 144 mg of aryl alkyne resin (batch **1.3**, *loading*: 1.00 mmol/g, 144 μ mol) were reacted with 61.0 mg of 1-(azidomethyl)-2-iodobenzene (236 μ mol, 1.64 equiv.), CuI (5.00 mg/100 mg resin), H_2O (200 mg/50 mg resin) and DIPEA (100 mg/50 mg resin) in DMF. The resin

was washed according to the washing procedure for click reactions GP6 followed by the general washing procedure GP0 and was dried in high vacuum to give 158 mg of the product resin in 38% yield (*loading* = 0.342 mmol/g). – Raman (Gel in DMF) (1064 nm, 300 mW, $\tilde{\nu}$): 3058, 2910, 1615, 1444, 1363, 1185, 1032, 1002, 795, 622, 402, 82 cm^{-1} . – IR (ATR, $\tilde{\nu}$): 3430, 2921, 1598, 1492, 1451, 1385, 1177, 1126, 1038, 1008, 891, 806, 744, 674, 569 cm^{-1} .

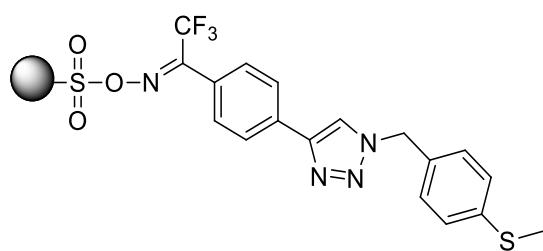
1-(2-Iodophenyl)-4-(4-(3-(trifluoromethyl)diaziridin-3-yl)phenyl)-1*H*-1,2,3-triazole (5l)



Resin **R-8l** (158 mg) was treated with NH_3 /dioxane solution according to GP3 to give 12.6 mg (27.0 μmol) of the target substance in 49% yield. – R_f = 0.63 (cyclohexane/ethyl acetate; 1:1). The crude product was purified by column chromatography: cyclohexane/ethyl acetate (4:1 → 1:1). – ^1H NMR (250 MHz, CDCl_3 , ppm), δ = 2.11 (d, 3J = 8.6 Hz, 1 H), 2.72 (d, 3J = 8.6 Hz, 1 H), 5.69 (s, 2 H), 7.06–7.12 (m, 1 H), 7.14–7.16 (m, 1 H), 7.34–7.45 (m, 2 H), 7.66–7.69 (m, 2 H), 7.80 (m, 1 H), 7.86–7.94 (m, 2 H). – ^{13}C NMR (62.5 MHz, CDCl_3 , ppm), δ = 57.9 (q, 2J = 35.8 Hz), 58.6, 98.7, 120.5, 123.6 (q, 1J = 278 Hz), 126.2 (2 C), 129.5 (2 C), 130.1, 130.8, 131.5, 132.6, 133.5, 137.4, 140.2, 147.2. – ^{19}F NMR (376 Hz, CDCl_3 , ppm), δ = -75.30 (s, 3 F). – IR (ATR, $\tilde{\nu}$): 3194, 3101, 2922, 2854, 1718, 1458, 1436, 1937, 1338, 1253, 1235, 1179, 1144, 1081, 1049, 1014, 981, 907, 887, 734, 685, 665, 648, 621, 584 cm^{-1} . – EI-MS (m/z, 70 eV, 100 °C): 471 (44) [M] $^+$, 441 (35), 316 (26), 301 (21), 231 (29), 226 (43), 217 (100), 211 (22), 166 (15), 151 (15), 149 (17), 125 (23), 111 (18), 109 (21), 97 (47), 90 (32), 85 (35), 83 (50), 71 (40), 57 (60), 55 (25). – HRMS ($\text{C}_{17}\text{H}_{13}\text{F}_3\text{N}_5\text{I}$): calc. 471.0167, found. 471.0169.

Combined yield starting with alkyne resin **8f** and finishing with the isolation of compound **5** via chromatography: 19%

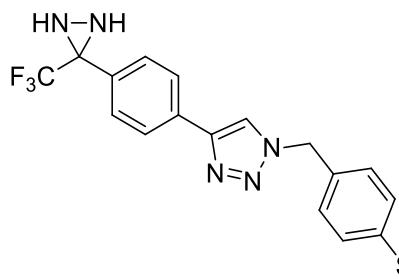
1-(4-(1-(4-(Methylthio)benzyl)-1*H*-1,2,3-triazol-4-yl)phenyl)-2,2,2-trifluoromethyl-(*O*-sulfonylpolystyryl)ketoxime (8m)



According to GP6, 144 mg of aryl alkyne resin (batch **1.3**, 1.00 mmol/g, 144 μmol) were reacted with 56.0 mg (4-(azidomethyl)phenyl)-(methyl)sulfane (315 μmol , 2.19 equiv.), CuI (5.00 mg/100 mg resin), H_2O (200 mg/50 mg resin) and DIPEA (100 mg/50 mg resin) in DMF. The resin was washed according to the washing

procedure for click reactions GP6 followed by the general washing procedure GP0 and was dried in high vacuum to give 159 mg of the product resin in 58% yield (loading = 0.526). – Raman (Gel in DMF) (1064 nm, 300 mW, $\tilde{\nu}$): 3057, 3002, 297, 2907, 2854, 1603, 1584, 1495, 1451, 1332, 1184, 1156, 1132, 1033, 1002, 975, 797, 622, 405, 223 cm^{-1} . – IR (ATR, $\tilde{\nu}$): 3447, 3024, 2915, 1639, 1599, 1492, 1449, 1410, 1170, 1123, 1034, 1006, 889, 871, 832, 753, 696, 670, 614, 575 cm^{-1} .

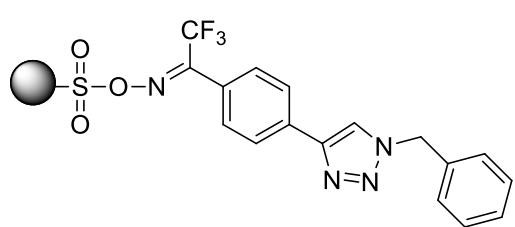
1-(4-(Methylthio)benzyl)-4-(4-(3-trifluoromethyl)diaziridin-3-yl)phenyl)-1*H*-1,2,3-triazole (5m)



Resin **8m** (134 mg, loading = 0.526, 70.5 μmol) was treated with NH_3 /dioxane solution according to GP3 to give 18.6 mg (48.0 μmol) of the target substance in 67% yield. – R_f = 0.42 (cyclohexane/ethyl acetate; 1:1). Column chromatography: cyclohexane/ethyl acetate (4:1 → 2:1). – ^1H NMR (400 MHz, CDCl_3 , ppm), δ = 2.26 (d, 3J = 8.7 Hz, 1 H), 2.83 (d, 3J = 8.7 Hz, 1 H), 2.49 (s, 3 H), 5.54 (s, 2 H), 7.26–7.27 (m, 4 H), 7.65–7.67 (m, 2 H), 7.69 (s, 1 H), 7.85–7.87 (m, 2 H). – ^{13}C NMR (100 MHz, CDCl_3 , ppm), δ = 15.5, 53.9, 57.8 (q, 2J = 36.2 Hz), 119.8, 123.5 (q, 1J = 278.4 Hz), 125.9 (2 C), 126.8 (2 C), 128.6 (bs, 2 C), 128.7 (2 C), 130.9, 131.3, 132.4, 139.9, 147.2. – ^{19}F NMR (376 Hz, CDCl_3 , ppm), δ = -73.29 (s, 3 F). – IR (ATR, $\tilde{\nu}$): 3231, 3191, 3091, 2926, 1601, 1495, 1455, 1433, 1407, 1334, 1245, 1224, 1144, 1117, 1050, 1017, 1050, 1017, 979, 953, 886, 833, 800, 765, 746, 723, 698, 683, 668, 629, 574, 539, 496, 468 cm^{-1} . – EI-MS (m/z, 70 eV, 100 °C): 391 (96) [M]⁺, 362 (17), 316 (20), 226 (26), 137 (100), 199 (2). – HRMS (C₁₈H₁₆F₃N₅S): calc. 391.1079, found. 391.1076.

Combined yield starting with alkyne resin **8f** and finishing with the isolation of compound **5** via chromatography: 39%

1-(4-(1-Phenyl-1*H*-1,2,3-triazol-4-yl)phenyl)-2,2,2-trifluoromethyl-(*O*-sulfonylpolystyryl)ketoxime (8n)

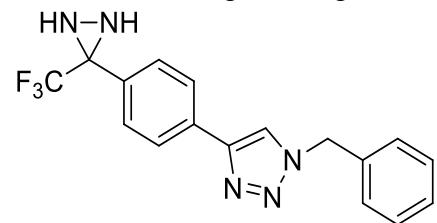


According to GP6, 55.0 mg of aryl alkyne resin **8e** (batch **1.3**, 1.00 mmol/g, 55.0 μmol) were reacted with 16.5 mg of benzyl azide (125 μmol , 2.27 equiv.), 8.16 mg of CuI (5.00 mg/100 mg resin), H_2O (200 mg/50 mg resin) and DIPEA (100 mg/50 mg resin) in DMF. The resin was washed

according to the washing procedure GP6 for click reactions followed by the general washing procedure GP0 and was dried in high vacuum to give the product resin (66.2 mg) in 73% yield (loading = 0.646 mmol/g). – Raman (Gel in DMF) (1064 nm, 300 mW, $\tilde{\nu}$): 3058, 2908, 1605, 1452, 1179, 1002 cm^{-1} .

1-Phenyl-4-(4-(3-(trifluoromethyl)diaziridin-3-yl)phenyl)-1*H*-1,2,3-triazol (5n)

Resin **8n** (66.2 mg, loading = 0.646 mmol/g, 42.8 μmol) was treated with NH_3 /dioxane solution

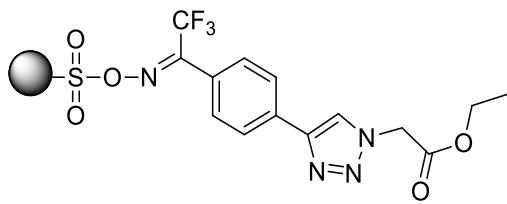


according to GP3 to give 16.0 mg (46.0 μmol) of the target substance in quantitative yield. – R_f = 0.33 (cyclohexane/ethyl acetate; 1:1). Column chromatography: cyclohexane/ethyl acetate (4:1 → 2:1). – ^1H NMR (400 MHz, CDCl_3 , ppm), δ = 2.25 (d, 3J = 9.2 Hz, 1 H), 2.81 (d, 3J = 9.2 Hz, 1 H), 5.59 (s, 2 H), 7.31–7.40 (m, 5 H), 7.64–7.66 (m, 2 H), 7.70 (s, 1 H), 7.84–7.86 (m, 2 H). – ^{13}C NMR (100 MHz, CDCl_3 , ppm), δ = 54.3,

57.8 (q, $^2J = 36.1$ Hz), 119.9, 123.5 (q, $^1J = 278$ Hz), 125.9 (2 C), 128.1 (2 C), 128.6 (2 C), 128.9, 129.2 (2 C), 132.4 (q, $^3J = 2.7$ Hz), 134.4, 136.4, 147.2. – ^{19}F NMR (376 Hz, CDCl_3 , ppm), $\delta = -75.38$ (s, 3 F). – IR (ATR, $\tilde{\nu}$): 2379, 1610, 1497, 1457, 1435, 1350, 1142, 1075, 1049, 1016, 977, 825, 727, 694, 673, 658, 635, 609, 581, 535, 477 cm^{-1} . – EI-MS (m/z, 70 eV, 100 °C): 345 (17) [M] $^+$, 330 (10), 316 (12), 302 (21), 301 (17), 226 (21), 212 (20), 206 (13), 179 (9), 104 (14), 91 (100). – HRMS ($\text{C}_{17}\text{H}_{14}\text{F}_3\text{N}_5$): calc. 345.1201, found. 345.1203.

Comment: due to the nature of the resin and the difficulties in the yield calculation on bead, we obtained in this reaction (yielding compound **5n**) more material than the theoretical possible amount. Calculation of the yield without estimation of the loading of **8n** gave a combined yield starting with alkyne resin **8f** and finishing with the isolation of compound **5** via chromatography of 84%.

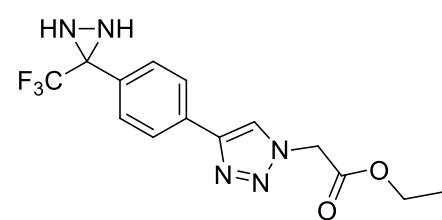
Ethyl 2-(4-(4-(2,2,2-trifluoro-1-(((methylsulfonyl)oxy)imino)ethyl)phenyl)-1*H*-1,2,3-triazol-1-yl)acetate (8o)



According to GP6, 73.2 mg of aryl alkyne resin (batch **1.4** 0.841 mmol/g, 61.5 μmol) were reacted with 22.0 mg of ethyl 2-azidoacetate (167 μmol , 2.72 equiv.), CuI (5.00 mg/100 mg resin), H_2O (200 mg/50 mg resin) and DIPEA (100 mg/50 mg resin) in DMF. The resin was washed according to

the washing procedure for click reactions GP6 followed by the general washing procedure GP0 and was dried in high vacuum to give 73.2 mg the product resin (yield is not available due to problems in isolating all of the resin, the yield is given in a combined yield with the next step, loading according to 100 % conversion = 0.840 mmol/g). – Raman (Gel in DMF) (1064 nm, 300 mW, $\tilde{\nu}$): 3057, 2933, 2220, 1614, 1558, 1495, 1410, 1262, 1184, 1097, 1023, 1002, 9752, 867, 796, 661, 406, 80 cm^{-1} . ^{13}C Gel-NMR (75 MHz, CDCl_3 , ppm), $\delta = 14.3$ (CH_3), 40.7 (CH_2), 51.0 (CH_2), 62.6, 128.1, 145.7. – IR (ATR, $\tilde{\nu}$): 3427, 2920, 1745, 1597, 1493, 1452, 1379, 1179, 1126, 1037, 1008, 891, 807, 754, 673, 568 cm^{-1} .

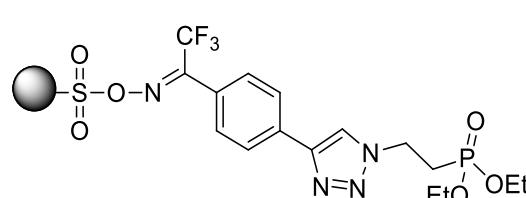
Ethyl-2-(4-(4-(3-(trifluoromethyl)diaziridin-3-yl)phenyl)-1*H*-1,2,3-triazol-1-yl)acetate (5o)



Resin **8o** (54.0 mg, loading = 0.840 mmol/g, 45.4 μmol) was treated with NH_3 /dioxane solution according to GP3 to give 6 mg (18 μmol) of the target substance in 40% yield. – $R_f = 0.34$ (cyclohexane/ethyl acetate; 1:1). The crude product was purified by column chromatography: cyclohexane/ethyl acetate (4:1 → 2:1). – ^1H NMR (300 MHz, CDCl_3 , ppm), $\delta = 1.33$ (t, $^3J = 7.2$ Hz, 3 H), 2.27 (d, $^3J = 8.8$ Hz, 1 H), 2.84 (d, $^3J = 8.8$ Hz, 1 H), 4.31 (q, $^3J = 7.2$ Hz, 2 H), 5.23 (s, 2 H), 7.64–7.78 (m, 2 H), 7.92–8.84 (m, 2 H), 7.97 (s, 1 H). – ^{13}C NMR (100 MHz, CDCl_3 , ppm), $\delta = 14.1$, 51.0, 57.8 (q, $^2J = 35.9$ Hz), 62.6, 124.0 (q, $^1J = 278.1$ Hz), 121.4 (1 C), 126.1 (2 C), 128.6 (2 C), 131.4, 132.2, 147.2, 166.2. – IR (ATR, $\tilde{\nu}$): 3194, 2989, 1620, 1464, 394, 1371, 1340, 1256, 1234, 1181, 1144, 1063, 1018, 966, 887, 835, 786, 767, 747, 712, 678, 640, 574, 535, 520, 412 cm^{-1} . – EI-MS (m/z, 70 eV,

120 °C): 341 (67) [M]⁺, 326 (5), 312 (76), 298 (5), 284 (11), 272 (6), 256 (15), 240 (37), 226 (100), 201 (27), 199 (35), 191 (14), 157 (17), 143 (18), 131 (17), 115 (9), 101 (8), 60 (8). – HRMS (C₁₄H₁₄F₃O₂N₅): calc. 341.1094, found. 341.1092.

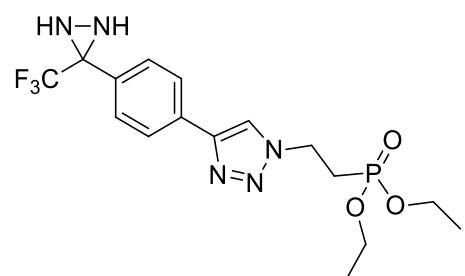
Diethyl (2-(4-(2,2,2-trifluoro-1-((methylsulfonyl)oxy)imino)ethyl)phenyl)-1*H*-1,2,3-triazol-1-yl)ethyl)phosphonate (8p)



According to GP6, 148 mg of aryl alkyne resin (batch **1.3**, 1.00 mmol/g, 148 µmol) were reacted with 67 mg of diethyl (2-azidoethyl)phosphonate (324 µmol, 2.19 equiv.), CuI (5.00 mg/100 mg resin), H₂O (200 mg/50 mg resin) and DIPEA (100 mg/50 mg resin) in DMF. The resin was washed according to the washing procedure for click reactions GP6 followed by the general washing procedure GP0 and was dried in high vacuum to give 157 mg of the product resin (yield is not available/realistic due to problems in isolating all of the resin, the yield is given in a combined yield with the next step, loading according to 100% conversion: 0.943). – Raman (1064 nm, 500 mW, $\tilde{\nu}$): 3058, 3000, 2976, 2912, 2241, 2203, 2185, 2158, 2139, 2076, 2061, 2044, 1616, 1559, 1450, 1184, 1157, 1033, 1003, 975, 799, 622, 231 cm⁻¹. – IR (ATR, $\tilde{\nu}$): 3431, 2922, 1598, 1493, 1452, 1386, 1179, 1127, 1037, 1008, 973, 892, 807, 756, 696, 570 cm⁻¹.

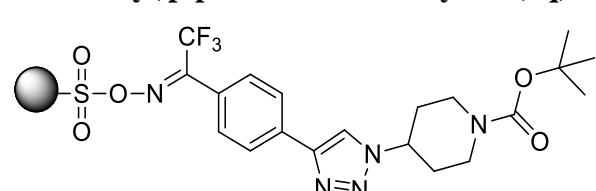
(100 mg/50 mg resin) in DMF. The resin was washed according to the washing procedure for click reactions GP6 followed by the general washing procedure GP0 and was dried in high vacuum to give 157 mg of the product resin (yield is not available/realistic due to problems in isolating all of the resin, the yield is given in a combined yield with the next step, loading according to 100% conversion: 0.943). – Raman (1064 nm, 500 mW, $\tilde{\nu}$): 3058, 3000, 2976, 2912, 2241, 2203, 2185, 2158, 2139, 2076, 2061, 2044, 1616, 1559, 1450, 1184, 1157, 1033, 1003, 975, 799, 622, 231 cm⁻¹. – IR (ATR, $\tilde{\nu}$): 3431, 2922, 1598, 1493, 1452, 1386, 1179, 1127, 1037, 1008, 973, 892, 807, 756, 696, 570 cm⁻¹.

Diethyl(2-(4-(4-(3-(trifluoromethyl)diaziridin-3-yl)phenyl)-1*H*-1,2,3-triazol-1-yl)ethyl)phosphonate (5p)



Resin **8p** (135 mg, loading = 0.943, 127 µmol) was treated with NH₃/dioxane solution according to GP3 to give 26.9 mg (64.0 µmol) of the target substance in 50% yield. – R_f = 0.36 (CH₂Cl₂/MeOH; 10:1). Column chromatography: CH₂Cl₂/MeOH; 50:1 → 10:1). – ¹H NMR (400 MHz, CDCl₃, ppm), δ = 1.30 (t, *J* = 7.1 Hz, 6 H), 2.29 (d, ³J = 8.6 Hz, 1 H), 2.47 (dt, ²J = 18.4 Hz, ³J = 7.5 Hz, 2 H), 2.84 (d, ³J = 8.6 Hz, 1 H), 4.03–4.16 (m, 4 H), 4.69 (dt, ²J = 13.2 Hz, ³J = 7.5 Hz, 2 H), 7.68 (d, ³J = 8.1 Hz, 2 H), 7.84–7.96 (m, 3 H). – ¹³C NMR (100 MHz, CDCl₃, ppm), δ = 16.3 (d, ²J = 6.6 Hz, 2 C), 27.2 (d, ¹J = 143.4 Hz), 44.7 (d, ³J = 2.2 Hz), 57.8 (q, ²J = 36.6 Hz), 62.2 (d, ²J = 6.6 Hz, 2 C), 123.9 (q, ¹J = 278.8 Hz), 120.7, 125.9 (2 C), 128.7 (2 C), 131.4, 132.3, 146.7. – EI-MS (m/z, 70 eV, 150 °C): 419 (28) [M]⁺, 405 (13), 389 (4), 363 (5), 349 (5), 293 (7), 253 (5), 226 (8), 199 (4), 165 (48), 137 (73), 109 (100), 91 (10), 81 (18). – HRMS (C₁₆H₂₁O₃F₃N₅P): calc. 419.1329, found. 419.1328.

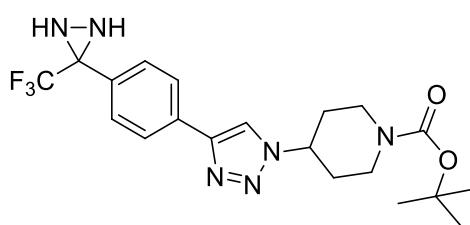
tert-Butyl 4-(4-(2,2,2-trifluoro-1-((methylsulfonyl)oxy)imino)ethyl)phenyl)-1*H*-1,2,3-triazol-1-yl)piperidine-1-carboxylate (8q)



According to GP6, 151 mg of aryl alkyne resin (batch **1.3** loading = 1.00 mmol/g, 151 µmol) were reacted with 76 mg of *tert*-butyl 4-azidopiperidine-1-carboxylate (342 µmol,

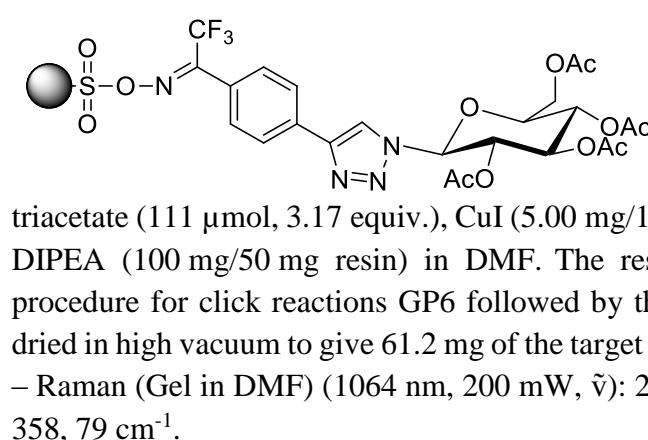
2.26 equiv.), CuI (5.00 mg/100 mg resin), H₂O (200 mg/50 mg resin) and DIPEA (100 mg/50 mg resin) in DMF. The resin was washed according to the washing procedure for click reactions GP6 followed by the general washing procedure GP0 and was dried in high vacuum to give 161 mg of the product resin (yield is not available/realistic due to problems in isolating all of the resin, the yield is given in a combined yield with the next step, loading according to 100% conversion: 0.938). – Raman (Gel in DMF) (1064 nm, 300 mW, $\tilde{\nu}$): 3057, 3002, 2977, 2906, 2852, 1603, 1584, 1558, 1495, 1451, 1332, 1184, 1156, 1132, 1033, 1002, 975, 797, 637, 622, 226 cm⁻¹. – IR (ATR, $\tilde{\nu}$): 3442, 2923, 1683, 1492, 1386, 1177, 1126, 1037, 1007, 891, 808, 754, 696, 566 cm⁻¹.

tert-Butyl-4-(4-(4-(3-(trifluoromethyl)diaziridin-3-yl)phenyl)-1*H*-1,2,3-triazol-1-yl)piperidine-1-carboxylate (5q)



Resin **8q** (161 mg, loading = 0.938, 151 μ mol) was treated with NH₃/dioxane solution according to GP3 to give 19.1 mg (44.0 μ mol) of the target substance in 29% yield. – R_f = 0.34 (cyclohexane/ethyl acetate; 1:1). The crude product was purified by column chromatography: (cyclohexane/ethyl acetate 10:1 → 1:1). – ¹H NMR (400 MHz, *CDCl*₃, ppm), δ = 1.42 (s, 9 H), 1.88–1.97 (m, 2 H), 2.16–2.23 (m, 3 H), 2.82 (d, ³J = 8.6 Hz, 1 H), 2.87–2.92 (m, 2 H), 4.16–4.24 (m, 2 H), 4.46–4.64 (m, 1 H), 7.60–7.62 (m, 2 H), 7.75 (s, 1 H), 7.80–7.92 (m, 2 H). – ¹³C NMR (100 MHz, *CDCl*₃, ppm), δ = 28.4 (3 C), 32.4 (bs, 2 C), 42.6 (bs, 2 C), 57.8 (q, ²J = 36.0 Hz), 58.3, 80.2, 123.5 (q, ¹J = 278.7 Hz), 117.8, 125.9 (2 C), 128.6 (2 C), 131.3, 132.4, 146.6, 154.4. – ¹⁹F NMR (376 Hz, *CDCl*₃, ppm), δ = -75.35 (s, 3 F). – IR (ATR, $\tilde{\nu}$): 3226, 3130, 2934, 2866, 1739, 1674, 1454, 1406, 1385, 1369, 1331, 1244, 1138, 1053, 1017, 992, 976, 947, 912, 888, 858, 844, 822, 779, 731, 6812, 575, 539, 478 cm⁻¹. – EI-MS (m/z): 438 (26) [M]⁺, 408 (9), 382 (30), 365 (17), 256 (35), 126 (85), 82 (79), 57 (100). – HRMS (C₂₀H₂₅F₃N₆O₂): calc. 438.1989, found. 438.1991.

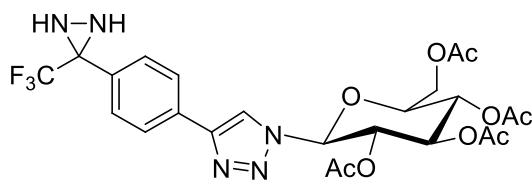
(2*S*,3*S*,4*R*,5*S*,6*S*)-2-(Acetoxymethyl)-6-(4-(4-(*Z*)-2,2,2-trifluoro-1-((methylsulfonyl)oxy)imino)ethyl)phenyl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (8r)



According to GP6, 50 mg of aryl alkyne resin (batch **1.5**, loading = 0.707 mmol/g, 35.4 μ mol) were reacted with 41 mg of (2*S*,3*S*,4*R*,5*S*,6*S*)-2-(acetoxymethyl)-6-

azidotetrahydro-2*H*-pyran-3,4,5-triyl triacetate (111 μ mol, 3.17 equiv.), CuI (5.00 mg/100 mg resin), H₂O (200 mg/50 mg resin) and DIPEA (100 mg/50 mg resin) in DMF. The resin was washed according to the washing procedure for click reactions GP6 followed by the general washing procedure GP0 and was dried in high vacuum to give 61.2 mg of the target resin in 85% yield (loading = 0.490 mmol/g). – Raman (Gel in DMF) (1064 nm, 200 mW, $\tilde{\nu}$): 2933, 1660, 1441, 1410, 1097, 867, 660, 407, 358, 79 cm⁻¹.

(2S,3S,4R,5S,6S)-2-(Acetoxymethyl)-6-(4-(4-(3-(trifluoromethyl)diaziridin-3-yl)phenyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (5r)

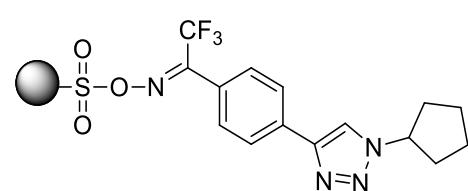


Resin **8r** (60.7 mg, loading = 0.490 mmol/g, 29.8 μ mol) was treated with NH₃/dioxane solution according to GP3 to give 18.7 mg (31.9 μ mol) of the target substance in quantitative yield. – R_f = 0.58 (cyclohexane/ethyl acetate; 4:1). Column

chromatography. – ¹H NMR (400 MHz, CDCl₃, ppm), δ = 1.96–2.08 (m, 12 H), 2.51 (d, ³J = 8.4 Hz, 1 H), 2.95 (d, ³J = 8.4 Hz, 1 H), 3.61–3.84 (m, 2 H), 3.98–4.15 (m, 2 H), 4.19–4.35 (m, 1 H), 4.96–5.58 (m, 2 H), 6.67–7.91 (m, 4 H), 8.03 (s, 1 H). – ¹³C NMR (100 MHz, CDCl₃, ppm), δ = 20.6, 20.6, 20.7, 22.9, 29.7 (2 C), 53.5, 57.9 (q, ²J = 35.8 Hz), 61.7, 67.7, 72.3, 75.2, 86.3, 119.4, 123.5 (q, ¹J = 278.5 Hz), 126.2, 128.7, 131.7, 131.9, 147.2, 169.3, 170.4, 170.6, 171.0. – IR (ATR, $\tilde{\nu}$): 2928, 1746, 1651, 1538, 1431, 1372, 1224, 1184, 1152, 1102, 1030, 927, 880, 833, 717, 680, 595, 574, 537, 494, 455, 423 cm⁻¹. – FAB-MS (m/z, 70 eV, 60 °C): 585 [M+H]⁺ 841, 437, 391, 330, 288, 256, 228, 210, 168, 154, 136. – HRMS (C₂₄H₂₆O₈F₃N₆): calc. 585.1915, found. 585.1917.

Comment: due to the nature of the resin and the difficulties in the yield calculation on bead, we obtained in this reaction to compound **5r** more material then the theoretical possible amount. Calculation of the yield without estimation of the loading of **8r** gave a combined yield starting with alkyne resin **8f** and finishing with the isolation of compound **5r** via chromatography of 90%.

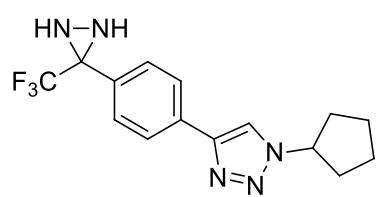
1-(4-(1-Cyclopentyl-1H-1,2,3-triazol-4-yl)phenyl)-2,2,2-trifluoromethyl-(O-sulfonylpolystyryl)ketoxime (8s)



According to GP6, 144 mg of aryl alkyne resin (batch **1.3**, loading: 1.00 mmol/g, 144 μ mol) were reacted with 35.0 mg of azidocyclopentane (315 μ mol, 2.19 equiv.), CuI (5.00 mg/100 mg resin), H₂O (200 mg/50 mg resin) and DIPEA (100 mg/50 mg resin) in DMF. The resin was

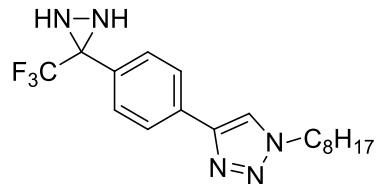
washed according to the washing procedure for click reactions GP6 followed by the general washing procedure GP0 and was dried in high vacuum to give 148 mg of the product resin (yield is not available/realistic due to problems in isolating all of the resin, the yield is given in a combined yield with the next step, loading according to 100% conversion: 0.973). – Raman (1064 nm, 300 mW, $\tilde{\nu}$): 3058, 3002, 2977, 2908, 2852, 1616, 1584, 1558, 1469, 1451, 1378, 1333, 1184, 1156, 1133, 1096, 1032, 1002, 975, 796, 622, 402, 226 cm⁻¹. – IR (ATR, $\tilde{\nu}$): 3446, 2921, 1598, 1493, 1451, 1385, 1176, 1126, 1037, 1008, 891, 807, 755, 671, 570 cm⁻¹.

1-Cyclopentyl-4-(4-(3-(trifluoromethyl)diaziridin-3-yl)phenyl)-1*H*-1,2,3-triazole (5s)



Resin **8s** (124 mg, loading = 0.973 mmol/g, 121 μ mol) was treated with NH₃/dioxane solution according to GP3 to give 12.0 mg (37.0 μ mol) of the target substance in 31% yield. – R_f = 0.40 (cyclohexane/ethyl acetate; 1:1). Column chromatography (cyclohexane/ethyl acetate 10:1 → 1:1). – ¹H NMR (250 MHz, CDCl₃, ppm), δ = 1.75–2.17 (m, 6 H), 2.22–2.38 (m, 3 H), 2.82 (d, ³J = 8.6 Hz, 1 H), 4.93–5.04 (m, 1 H), 7.65–7.68 (m, 2 H), 7.79 (s, 1 H), 7.87–7.91 (m, 2 H). – ¹³C NMR (62.5 MHz, CDCl₃, ppm), δ = 24.1 (2 C), 33.4 (2 C), 57.5 (q, ²J = 39.7 Hz), 62.0, 118.5, 123.5 (q, ¹J = 279.7 Hz), 125.8 (2 C), 128.6 (d, ⁴J = 1.0 Hz, 2 C), 131.1, 132.7, 146.5. – IR (ATR, $\tilde{\nu}$): 3193, 2963, 1440, 1394, 1339, 1252, 1181, 1146, 1046, 978, 949, 887, 837, 747, 711, 684, 641, 619, 575, 540 cm⁻¹. – EI-MS (m/z): 323 (72) [M]⁺, 294 (95), 267 (20), 254 (14), 226 (100), 199 (14). – HRMS (C₁₅H₁₆F₃N₅): calc. 323.1358, found. 323.1355.

1-Octyl-4-(4-(3-(trifluoromethyl)diaziridin-3-yl)phenyl)-1*H*-1,2,3-triazole (5t)

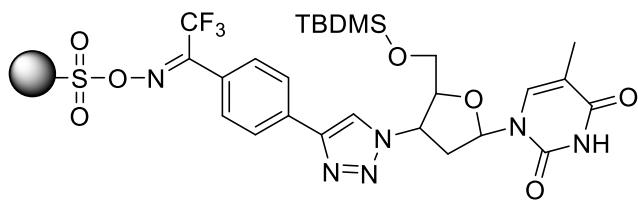


Step 1: According to GP2, 100 mg (batch **1.3**, loading 1.00 mmol/g, 100 μ mol) of aryl alkyne resin were reacted with 35.0 mg of 1-azidoctane (229 μ mol, 2.29 equiv.), 15.0 mg (80.0 μ mol, 0.700 equiv.) of CuI, 200 mL/50 mg resin H₂O, and DIPEA (100 mg/50 mg resin). The resin was washed according to the washing procedure for click reactions. Then, the resin was

treated according to the general washing procedure GP0 and was dried in high vacuum to give 101 mg of the target resin (yield is not available/realistic due to problems in isolating all of the resin, the yield is given in a combined yield with the next step, loading according to 100% conversion: 0.990).

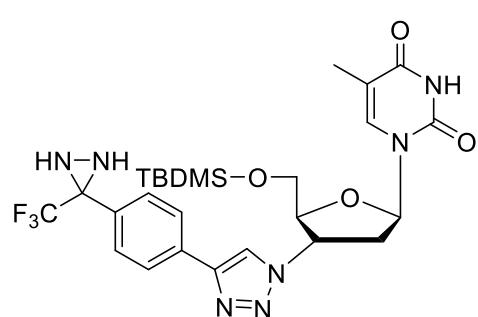
Step 2: Resin **R-8s** (101 mg, loading = 0.990 mmol/g, 100 μ mol) was treated with NH₃/dioxane solution according to GP3 to give 11.3 mg (30.8 μ mol) of the target substance in 31% yield. – R_f = 0.52 (cyclohexane/ethyl acetate; 2:1). Column chromatography (cyclohexane/ethyl acetate 10:1 → 2:1). – ¹H NMR (400 MHz, CDCl₃, ppm), δ = 0.87 (t, ³J = 6.8 Hz, 3 H), 1.26–1.34 (m, 9 H), 1.91–1.99 (m, 3 H), 2.27 (d, ³J = 8.9 Hz, 1 H), 2.83 (d, ³J = 8.9 Hz, 1 H), 4.40 (t, ³J = 7.2 Hz, 2 H), 7.79 (s, 1 H), 7.66–7.68 (m, 2 H), 7.88–7.90 (m, 2 H). – ¹³C NMR (100 MHz, CDCl₃, ppm), δ = 14.0, 22.6, 26.5, 28.9, 29.0, 30.3, 31.7, 50.5, 57.8 (q, ²J = 35.9 Hz), 119.8, 123.5 (q, ¹J = 278.4 Hz), 125.9 (2 C), 128.6 (2 C), 131.2, 132.6, 146.6. – ¹⁹F NMR (376 Hz, CDCl₃, ppm), δ = –75.37 (s, 3 F). – IR (ATR, $\tilde{\nu}$): 3092, 2925, 2856, 2379, 1620, 1462, 1351, 1227, 1192, 1157, 1144, 1084, 1041, 1017, 979, 887, 863, 836, 780, 746, 712, 686, 673, 649, 634, 610, 574, 357 cm⁻¹. – EI-MS (m/z): 368 (100) [M]⁺, 339 (48), 299 (38), 284 (22), 271 (17), 255 (18), 241 (12), 227 (48), 197 (27), 159 (15), 144 (13), 132 (10), 69 (14), 57 (21), 43 (35). HRMS (C₁₈H₂₄F₃N₅): calc. 367.1984, found. 367.1985.

(5'-O-TBDMS-(thymid-3'-yl-(1,2,3-triazol-4-yl)phen-1-yl)-2,2,2-trifluoromethyl)-O-(sulfonyl-polystyryl)ketoxime (8u)



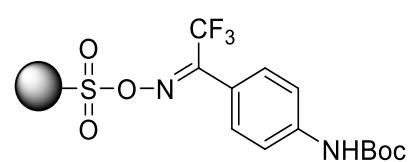
According to GP6, 50.1 mg of aryl alkyne resin (batch **1.5**, loading 0.707 mmol/g, 35.4 μ mol) were reacted with 43.1 mg of 1-(4-azido-5-((*tert*-butyldimethylsilyl)oxy)methyl)-tetrahydrofuran-2-yl)-5-methylpyrimidine-2,4(1*H*,3*H*)-dione (113 μ mol, 2.62 equiv.), CuI (5.00 mg/100 mg resin), H₂O (200 mg/50 mg resin) and DIPEA (100 mg/50 mg resin) in DMF. The resin was washed according to the washing procedure for click reactions GP6 followed by the general washing procedure GP0 and was dried in high vacuum to give 60.7 mg of the target resin in 66% yield (loading = 0.458 mmol/g, loading according to 100% yield = 0.694 mmol/g). – Raman (Gel in DMF) (1064 nm, 400 mW, $\tilde{\nu}$): 2936, 2812, 1659, 1441, 1412, 1099, 1002, 867, 662, 407, 362, 79 cm⁻¹.

1-(3-(5-O-*tert*-Butyldimethylsilyl-thymidin))-4-(4-(3-(trifluoromethyl)diaziridin-3-yl)phenyl)-1*H*-1,2,3-triazole (5u)



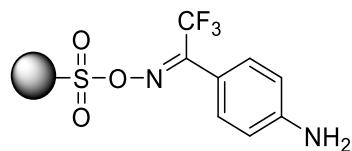
Resin **8u** (60.7 mg, loading = 0.694 mmol/g, 42.1 μ mol) was treated with NH₃/dioxane solution according to GP3 to give 18.7 mg (31.5 μ mol) of the target substance in 75% yield. – R_f = 0.58 (cyclohexane/ethyl acetate; 4:1). Column chromatography (cyclohexane/ethyl acetate; 10:1). – ¹H NMR (250 MHz, CDCl₃, ppm), δ = 0.25 (d, *J* = 2.5 Hz, 6 H), 1.02 (s, 9 H), 2.03 (s, 3 H), 2.39 (d, ³*J* = 8.6 Hz, 1 H), 2.63–2.89 (m, 1 H), 2.98 (d, *J* = 8.1 Hz, 1 H), 3.07–3.11 (m, 1 H), 3.96 (dd, ³*J* = 11.6 Hz, ⁴*J* = 2.5 Hz, 1 H), 4.13 (dd, ³*J* = 11.6, ⁴*J* = 2.5 Hz, 1 H), 4.56 (dt, ³*J* = 4.7, ⁴*J* = 2.5 Hz, 1 H), 5.46 (dt, ³*J* = 8.8 Hz, ⁴*J* = 4.6 Hz, 1 H), 6.56 (t, *J* = 6.6 Hz, 1 H), 7.52 (s, 1 H), 7.72 (d, *J* = 8.1 Hz, 2 H), 7.80–8.03 (m, 3 H), 8.46 (br s, 1 H). – ¹³C NMR (100 MHz, CDCl₃, ppm), δ = –5.2, 5.3, 12.6, 18.4, 25.9 (3 C), 38.6, 58.4 (q, ²*J* = 31.1 Hz), 59.9, 62.7, 84.8, 85.5, 111.3, 119.5, 123.5 (q, ¹*J* = 275 Hz), 126.0 (2 C), 128.8 (2 C), 131.5, 131.8, 135.2, 147.3, 150.1, 163.5. – ¹⁹F NMR (376 Hz, CDCl₃, ppm), δ = –75.35 (s, 3 F). – IR (ATR, $\tilde{\nu}$): 3211, 2927, 2855, 1683, 1464, 1364, 1259, 1149, 1121, 1077, 1006, 973, 927, 879, 833, 779, 671, 606, 551, 489, 412 cm⁻¹. – FAB-MS (m/z, 70 eV, 60 °C): 594 [M + H]⁺, 580, 548, 536, 486, 440, 410, 371, 339, 305, 281, 256, 213, 183, 154, 115, 89. – HRMS [M + H]⁺ (C₂₆H₃₅O₄F₃N₇Si): calc. 594.2472, found. 594.2474.

1-(4-aminophenyl)-2,2,2-trifluoroethanone O--(sulfonyl-polystyryl)ketoxime (8k)



Step 1: According to GP2, 807 mg *tert*-butyl (4-(2,2,2-trifluoro-1-(hydroxymino)ethyl)phenyl)carbamate (2.65 mmol, 1.50 equiv.) was immobilized on 1.31 g of commercially available sulfonylchloride resin (1.64 mmol, loading: 1.25 mmol/g). After drying under high vacuum,

1.61 g (*loading*: 1.02 mmol/g according to 100% conversion) of the resin were obtained. – ^{13}C Gel-NMR (75 MHz, CDCl_3 , ppm), δ = 8.8, 28.3, 40.4, 46.5, 127.91, 146.0. – Raman (Gel in DMF) (1064 nm, 500 mW, $\tilde{\nu}$): 3056, 2980, 2908, 1605, 1452, 1325, 1184, 1157, 1032, 1002, 903, 841, 796, 733, 622, 408, 80 cm^{-1} . – IR (ATR, $\tilde{\nu}$): 3024, 2923, 2121, 2086, 1738, 1666, 1600, 1499, 1482, 1392, 1286, 1261, 1188, 1113, 1076, 1031, 1006, 904, 805, 696, 670, 565, 532, 514, 416, 405 cm^{-1} .



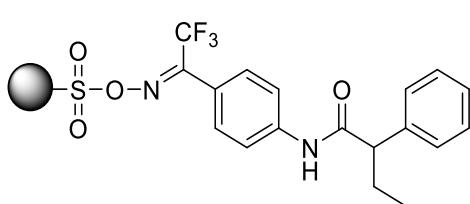
Step 2: Boc-protected amine resin of step 1 (613 mg, *loading*: 1.02 mmol/g, 624 μmol) was suspended in DCM and was shaken for 5 min. Then, 0.80 mL TFA (10.4 mmol, 16.7 equiv.) were added. The vial was sealed and the mixture was shaken at room temperature for 12 h. The resin was washed according the general washing procedure GP0 and was dried under high vacuum to give 568 mg of the target resin in 72% yield (*loading*: 0.791 mmol/g, loading according to 100% conversion = 1.10 mmol/g) in quantitative yield. Alternative procedure (instead of step1 and step2, batch **1.3**): 1-(4-Aminophenyl)-2,2,2-trifluoroethan-1-one oxime (575 mg, 2.82 mmol, 2.41 equiv.) was immobilized on 0.939 g of commercially available sulfonylchloride resin (1.17 mmol, *loading*: 1.25 mmol/g) via reaction with a mixture of NEt_3 (119 mg, 1.17 mmol, 1 equiv) and DMAP (14.3 mg, 0.117 mmol, 0.1 equiv.) in 10 mL of dry DMF. The reaction was heated to 80 °C over a period of 14 h and was washed according the general washing procedure GP0. After drying under high vacuum, 1.21 g (*loading*: 0.968 mmol/g according to 100% conversion) of the target resin were obtained. – ^{13}C Gel-NMR (75 MHz, CDCl_3 , ppm), δ = 40.4, 50.6, 53.4, 127.91, 132.0. – Raman (1064 nm, 500 mW, $\tilde{\nu}$): 3054, 2921, 2902, 2855, 1602, 1494, 1450, 1184, 1157, 1126, 1094, 1058, 1002, 906, 840, 800, 781, 622, 409 cm^{-1} . – IR (ATR, $\tilde{\nu}$): 3024, 2923, 2121, 2086, 1737, 1666, 1600, 1499, 1482, 1392, 1286, 1261, 1188, 1113, 1076, 1032, 1007, 904, 806, 697, 670, 565, 532, 513, 416, 404 cm^{-1} .

Table of loading*:

No	start. amount [g]	mmol	yield[g]	conversion	loading [mmol/g]	loading (100%) [mmol/g]
1.1	0.613	0.624	0.568	72%	0.791	1.10
1.2	0.932	0.815	0.829	quant	1.15	1.15
1.3	0.939	1.17	1.21	quant	0.968	0.968

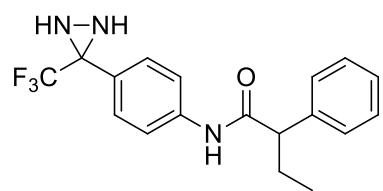
As the loading of solid phases is difficult to determine, especially if the target resin loses weight in comparison to the starting material, we report the calculated yield according to the difference in mass and the loading according to 100% conversion of the starting material.

2-Phenyl-N-(4-(3-(trifluoromethyl)diaziridin-3-yl)phenyl)butanamide (5v)



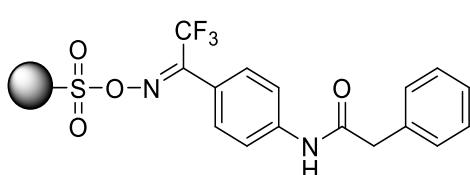
Step 3a: 84 μL 2-phenylbutanoyl chloride (91.3 mg, 0.5 mmol, 1.65 equiv.) and trimethylamine (65 μl /50 mg resin) were dissolved in DMF and stirred for 15 min at 0 °C. The aryl amine resin **8k** (batch **1.2**, 48.0 mg, loading = 1.15 mmol/g, 55.2 μmol) was suspended in DMF, added to the reaction mixture and shaken for 10 min first at 0 °C and then overnight at

room temperature. The resin was washed according the general washing procedure and was dried in high vacuum to give 56.2 mg of the intermediate product resin **8-v** (loading according to 100% conversion = 0.982 mmol/g).

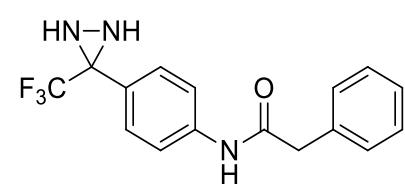


Step 4a: Resin **8v** (54.3, loading = 0.982 mmol/g, 53.3 μmol) was treated with NH_3 /dioxane solution according to GP3 to give 3.40 mg (9.73 μmol) of the target substance in 18% yield (calculated over 4 steps [1-4a] on solid phases). – R_f = 0.48 (cyclohexane/ethyl acetate; 10:1). Column chromatography cyclohexane/ethyl acetate; 10:1). – ^1H NMR (400 MHz, CDCl_3 , ppm), δ = 0.86 (t, 3J = 7.4 Hz, 3 H, CH_3), 1.75–1.86 (m, 1 H, CH_2), 2.08 (d, 3J = 8.8 Hz, 1 H, NH), 2.15–2.27 (m, 1 H, CH_2), 2.68 (d, 3J = 8.8 Hz, 1 H, NH), 3.31–3.35 (m, 1 H, CH), 7.13 (s, 1 H, NH), 7.29–7.43 (m, 5 H), 7.49–7.66 (m, 4 H, CH). – ^{13}C NMR (100 MHz, CDCl_3 , ppm), δ = 12.3 (1 C), 26.4 (1 C), 56.2 (1 C), 57.6 (q, 2J = 36.1 Hz, 1 C), 119.2 (2 C), 126.0 (q, 1J = 233 Hz, 1 C), 127.7 (2 C), 128.0 (1 C), 128.9 (2 C), 129.2 (2 C), 129.5 (1 C), 139.2 (1 C), 139.5 (1 C), 171.8 (1 C). – ^{19}F NMR (376 Hz, CDCl_3 , ppm), δ = -75.55 (s, 3 F). – IR (ATR, $\tilde{\nu}$): 3265, 3063, 2920, 2852, 1913, 1667, 1601, 1538, 1455, 1411, 1021, 945, 883, 842, 732, 700, 627, 572, 532, 507 cm^{-1} . – EI (m/z, 70 eV, 100 °C): 349 (20) [M] $^+$, 348 (33), 335 (3), 298 (100), 278 (34), 230 (28), 202 (8), 187 (13), 160 (6), 145 (6), 119 (9), 91 (26), 71 (10), 43 (13). – HRMS ($\text{C}_{18}\text{H}_{18}\text{F}_3\text{N}_3\text{O}$): calc. 349.1402, found. 349.1402.

2-Phenyl-N-(4-(3-(trifluoromethyl)diaziridin-3-yl)phenyl)acetamide (5w)

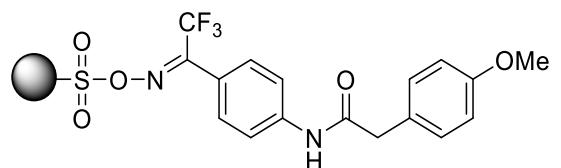


Step 3b: 66 μL 2-phenylacetyl chloride (77.0 mg, 0.5 mmol, 1.42 equiv.) and trimethylamine (65 μl /50 mg resin) were dissolved in DMF and stirred for 15 min at 0 °C. The aryl amine resin **8k** (87.7 mg, batch **1.2** loading = 1.15 mmol/g, 101 μmol) was suspended in DMF and added to the reaction mixture and shaken for 10 min first at 0 °C and then overnight at room temperature. The resin was washed according the general washing procedure and was dried in high vacuum to give 96.5 mg of the target resin (loading according to 100% conversion = 1.05 mmol/g).



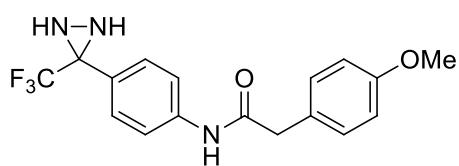
Step 4b: Resin **8w** (96.5 mg, loading = 1.05 mmol/g, 101 μmol) was treated with NH_3 /dioxane solution according to GP3 to give 13.0 mg (40.5 μmol) of the target substance in 40% yield (calculated over 4 steps [1-4b] on solid phases). – R_f = 0.57 (cyclohexane/ethyl acetate; 4:1). Column chromatography cyclohexane/ethyl acetate; 4:1). – ^1H NMR (400 MHz, CDCl_3 , ppm), δ = 2.12 (d, 3J = 8.2 Hz, 1 H), 2.71 (d, 3J = 8.2 Hz, 1 H), 3.71 (s, 2 H), 7.19 (s, 1 H), 7.31–7.56 (m, 9 H). – ^{13}C NMR (100 MHz, CDCl_3 , ppm), δ = 44.9, 57.7 (q, 2J = 36.0 Hz), 119.7 (2 C), 126.2 (q, 1J = 278 Hz), 127.8 (2 C), 128.9, 129.3 (2 C), 129.5 (2 C), 131.1, 134.0, 139.2, 169.2. – ^{19}F NMR (376 Hz, CDCl_3 , ppm), δ = -75.55 (s, 3 F). – IR (ATR, $\tilde{\nu}$): 3204, 2349, 2136, 1990, 1657, 1598, 1526, 1454, 1407, 1326, 1221, 1138, 941, 882, 725, 696, 670, 665, 657, 567 cm^{-1} . – EI (m/z, 70 eV, 120 °C): 320 (100) [M – H] $^+$, 252 (35), 202 (32), 182 (18), 134 (21), 118 (9), 91 (61), 65 (7). – HRMS ($\text{C}_{16}\text{H}_{14}\text{F}_3\text{N}_3\text{O}$): calc. 321.1089, found. 321.1089.

2-(4-Methoxyphenyl)-N-(4-(3-(trifluoromethyl)diaziridin-3-yl)phenyl)acetamide (5x)



Step 3c: 76.0 mg 2-(4-methoxyphenyl)acetic acid (0.5 mmol, 4.00 equiv.), 32.0 mg DIC (250 μ mol, 2.00 equiv.) and 100 mg HOBT (653 μ mol, 5.30 equiv.) were dissolved in DCM and stirred for 15 min at rt. The aryl amine resin **8k** (batch **1.3**, 110 mg, loading = 0.968 mmol/g, 106 μ mol) was suspended in DMF and added to the reaction mixture and shaken for 10 min first at 0 °C and then overnight at room temperature. The resin was washed according the general washing procedure and was dried in high vacuum to give 127 mg of the product resin (loading according to 100% conversion = 0.839 mmol/g).

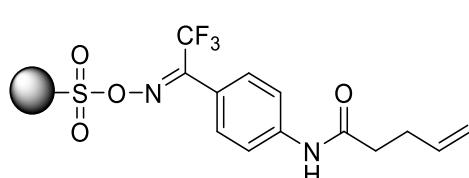
Step 4c: Resin **8x** (127 mg, loading = 0.839 mmol/g, 107 μ mol) was treated with NH_3 /dioxane



solution according GP3, to give 19.0 mg (54.0 μ mol) of the target substance in 50% yield (calculated over 3 steps [1/2-4c] on solid phases). $-R_f = 0.40$ (cyclohexane/ethyl acetate; 1:1). Column chromatography: cyclohexane/ethyl acetate (10:1 → 4:1 → 1:1) – ^1H NMR

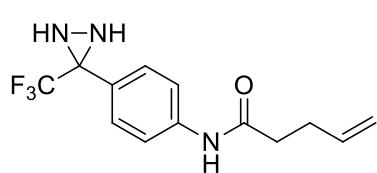
(250 MHz, CDCl_3 , ppm), $\delta = 2.15$ (d, $^3J = 8.6$ Hz, 1 H), 2.75 (d, $^3J = 8.6$ Hz, 1 H), 3.83 (s, 2 H), 3.69 (s, 3 H), 6.92–6.95 (m, 2 H), 7.15 (bs, 1 H), 7.22–7.26 (m, 2 H), 7.45–7.55 (m, 4 H). – ^{13}C NMR (62.5 MHz, CDCl_3 , ppm), $\delta = 43.9$, 55.3, 57.6 (q, $^2J = 36.2$ Hz), 114.8 (s, 2 C), 119.6 (s, 2 C), 123.4 (q, $^1J = 281.9$ Hz), 126.1, 127.5, 128.9 (q, $^5J = 1.2$ Hz, 2 C), 130.7, 131.3, 139.2, 159.2, 169.6. – IR (ATR, $\tilde{\nu}$): 3304, 3206, 2921, 2853, 1664, 1614, 1598, 1530, 1513, 1463, 1408, 1351, 1304, 1249, 1173, 1138, 1036, 969, 939, 886, 827, 774, 735, 705, 620, 570, 531, 513, 453 cm^{-1} . – EI-MS (m/z, 70 eV, 120 °C): 351 (47) [M] $^+$, 350 (49), 322 (6), 282 (21), 2002 (20), 121 (100). – HRMS ($\text{C}_{17}\text{H}_{16}\text{F}_3\text{N}_3\text{O}_2$): calc. 351.1195, found. 351.1193.

N-(4-(3-(Trifluoromethyl)diaziridin-3-yl)phenyl)pent-4-enamide (5y)



Step 3d: 33.0 mg of pent-4-enoyl chloride (280 mmol, 5.00 equiv.) and trimethylamine (65 μ l/50 mg resin) were dissolved in DMF and stirred for 15 min at 0 °C. The aryl amine resin **8k** (batch **1.3**, 50 mg, loading = 0.968 mmol/g, 48.4 μ mol) was suspended in

DMF and added to the reaction mixture and shaken for 10 min first at 0 °C and then overnight at room temperature. The resin was washed according the general washing procedure and was dried in high vacuum to give the intermediate product resin **8y**.

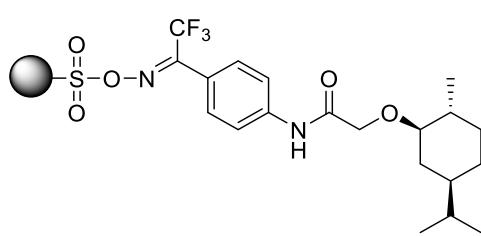


Step 4d: Resin **8y** was treated with NH_3 /dioxane solution according GP3, to give 6.5 mg (22.8 μ mol) of the target substance in 47% yield (calculated over 3 steps [1/2-4d] on solid phases). $-R_f = 0.65$ (cyclohexane/ethyl acetate; 1:1). Column chromatography: cyclohexane/ethyl acetate (10:1 → 4:1) – ^1H

NMR (400 MHz, CDCl_3 , ppm), $\delta = 2.18$ (d, $^3J = 8.9$ Hz, 1 H), 2.48–2.50 (m, 4 H), 2.77 (d, $^3J = 8.9$ Hz, 1 H), 5.06–5.16 (m, 2 H), 5.80–5.94 (m, 1 H), 7.26 (br s, 1 H), 7.57 (br s, 4 H). –

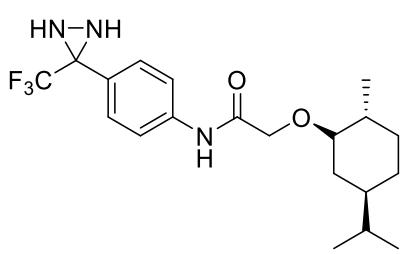
¹³C NMR (100 MHz, *CDCl*₃, ppm), δ = 28.3, 28.7, 54.5 (q, ²*J* = 33.3 Hz), 115.2, 115.6, 118.6 (2 C), 122.5 (q, ¹*J* = 277.1 Hz), 128.0 (2 C), 135.7, 138.4, 169.6. – IR (ATR, $\tilde{\nu}$): 3272, 2922, 2853, 1659, 1593, 1527, 1493, 1410, 1392, 1345, 1287, 1257, 1217, 1159, 1134, 1094, 1015, 965, 948, 917, 881, 821, 728, 718, 672, 596, 565, 537, 497, 413 cm⁻¹. – EI-MS (m/z, 70 eV, 80 °C): 285 (36)[M]⁺, 284 (99) [M-H]⁺, 216 (40), 202 (51), 149 (100). – HRMS (C₁₃H₁₄F₃N₃O): calc. 285.1089, found. 285.1086.

2-(((1*S*,2*S*,5*R*)-2,5-Diisopropylcyclohexyl)oxy)-*N*-(4-(3-(trifluoromethyl)diaziridin-3-yl)phenyl)acetamide (5z)



Step 3e: 113 μ L 2-(((1*S*,2*R*,5*R*)-5-isopropyl-2-methylcyclohexyl)oxy)acetyl chloride (52.0 mg, 0.5 mmol, 1.42 equiv.) and trimethylamine (65 μ L/50 mg resin) were dissolved in DMF and stirred for 15 min at 0 °C. The aryl amine resin **8k** (52.0 mg, batch **1.2**, 1.15 mmol/g) was suspended in DMF and

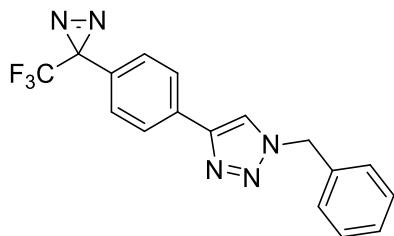
added to the reaction mixture and shaken for 10 min first at 0 °C and then overnight at room temperature. The resin was washed according the general washing procedure and was dried in high vacuum to give 61.0 mg of the target resin (loading according to 100% conversion = 0.980 mmol/g).



Step 4e: Resin **R-8z** (58.5 mg, conversion = 0.980 mmol/g, 57.3 μ mol) was treated with NH₃/dioxane solution according to GP3 to give 3.50 mg (8.77 μ mol) of the target substance in 15% yield (calculated over 4 steps [1-4e] on solid phases). – R_f = 0.53 (cyclohexane/ethyl acetate; 1:1). Column chromatography cyclohexane/ethyl acetate; 1:1). – ¹H NMR (400 MHz, *CDCl*₃, ppm), δ = 0.76 (d, ³*J* = 6.9 Hz, 6 H), 0.89 (m, 3 H), 1.27–1.37 (m, 4 H), 1.59–1.65 (m, 4 H), 2.0 (d, ³*J* = 10.0 Hz, 1 H), 2.09–2.15 (m, 1 H), 2.71 (d, ³*J* = 10.0 Hz, 1 H), 3.15–3.22 (m, 1 H), 4.03 (dd, ²*J* = 15.4 Hz, ³*J* = 8.23 Hz, 2 H), 7.51–7.58 (m, 4 H), 8.39 (s, 1 H). – ¹³C NMR (100 MHz, *CDCl*₃, ppm), δ = 20.9 (2 C), 16.4, 23.4, 26.5, 31.5, 34.3, 40.2, 48.1, 67.9, 81.0, 57.7 (q, ²*J* = 36.1 Hz), 119.6 (2 C), 123.5 (q, ¹*J* = 278 Hz), 127.4, 129.0 (2 C), 138.9, 168.7. – ¹⁹F NMR (376 Hz, *CDCl*₃, ppm), δ = -75.54 (s, 3 F). – IR (ATR, $\tilde{\nu}$): 3378, 2922, 2870, 1693, 1593, 18525, 1454, 1411, 1316, 1213, 1147, 1101, 1042, 1016, 940, 921, 881, 837, 768, 7385, 682, 568, 527, 405 cm⁻¹. – EI-MS (m/z, 70 eV, 180 °C): 399 (31) [M]⁺, 384 (9), 260 (23), 246 (35), 230 (44), 202 (9), 188 (11), 155 (5), 138 (22), 123 (11), 95 (29), 83 (100), 69 (39), 55 (40). – HRMS (C₂₀H₂₈F₃N₃O₂): calc. 399.2134, found. 399.2137.

4. Synthesis of Diazirines 3a-3j

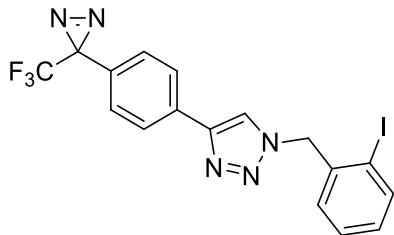
1-Benzyl-4-(4-(3-(trifluoromethyl)diazirin-3-yl)phenyl)-1*H*-1,2,3-triazole (3a)



According to GP4, 7.20 mg (21.0 μmol) of compound **5n** were oxidized to give 6.70 mg (20.0 μmol) of the target substance in 95% yield. $- R_f = 0.47$ (cyclohexane/ethyl acetate; 10:1). Column chromatography: cyclohexane/ethyl acetate (20:1 \rightarrow 10:1). $- ^1\text{H}$ NMR (300 MHz, CDCl_3 , ppm), $\delta = 5.63$ (s, 2 H), 7.16–7.52 (m, 7 H), 7.79 (s, 1 H), 7.81 (d, $^3J = 8.3$ Hz, 2 H). $- ^{13}\text{C}$ NMR (100 MHz, CDCl_3 , ppm), $\delta = 29.9$ (q, $^2J = 47.8$ Hz), 54.3, 119.9, 122.1 (q, $^1J = 274.6$ Hz), 126.9 (q, $^4J = 1.0$ Hz, 2 C), 125.9 (2 C), 128.1 (2 C), 128.7, 128.9, 129.2 (2 C), 131.9, 134.4, 146.9. $- ^{19}\text{F}$ NMR (376 Hz, CDCl_3 , ppm), $\delta = -70.69$ (s, 3 F). $- \text{IR}$ (ATR, $\tilde{\nu}$): 3138, 2922, 2851, 2088, 1720, 1611, 1497, 1454, 1344, 1228, 1183, 1146, 1077, 1048, 975, 938, 825, 773, 748, 726, 693, 665, 581, 547, 454, 409 cm^{-1} . $- \text{EI-MS}$ (m/z, 70 eV, 140 $^{\circ}\text{C}$): 343 (5) [M] $^+$, 315 (100), 286 (18), 240 (12), 218 (10), 196 (7), 149 (31), 91 (69). $- \text{HRMS}$ ($\text{C}_{17}\text{H}_{12}\text{F}_3\text{N}_5$): calc. 343.1045, found. 343.1042.

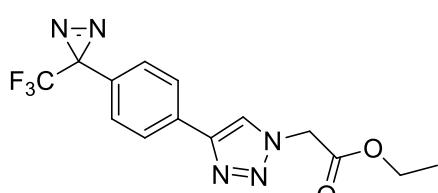
1-(2-Iodobenzyl)-4-(4-(3-(trifluoromethyl)diazirin-3-yl)phenyl)-1*H*-1,2,3-triazole (3b)

According to GP4, 3.0 mg (6.37 μmol) of compound **5l** were oxidized to give 2.00 mg



(6.18 μmol) of the target substance in 97% yield. $- R_f = 0.57$ (cyclohexane/ethyl acetate; 4:1). Column chromatography: cyclohexane/ethyl acetate (10:1 \rightarrow 4:1) $- ^1\text{H}$ NMR (400 MHz, CDCl_3 , ppm), $\delta = 5.69$ (s, 1 H), 6.99–7.44 (m, 5 H), 7.76–8.01 (m, 4 H). $- ^{13}\text{C}$ NMR (100 MHz, CDCl_3 , ppm), $\delta = 28.4$ (q, $^2J = 41.0$ Hz), 58.6, 98.8, 120.3, 122.1 (q, $^1J = 274$ Hz), 126.0 (2 C), 126.9 (2 C), 128.8, 129.2, 129.8, 130.6, 131.8, 137.1, 140.0, 146.8. $- ^{19}\text{F}$ NMR (376 Hz, CDCl_3 , ppm), $\delta = -71.3$ (s, 3 F). $- \text{IR}$ (ATR, $\tilde{\nu}$): 3194, 3101, 2921, 2852, 1718, 1620, 1459, 1438, 1394, 1338, 1253, 1234, 1179, 1145, 1081, 1049, 1014, 981, 945, 907, 887, 835, 807, 733, 684, 666, 648, 620, 585, 573, 536 cm^{-1} . $- \text{EI-MS}$ (m/z, 70 eV, 70 $^{\circ}\text{C}$): 469 (44) [M] $^+$, 441 (35), 322 (22), 316 (26), 301 (21), 231 (29), 226 (43), 217 (100). $- \text{HRMS}$ ($\text{C}_{17}\text{H}_{11}\text{F}_3\text{IN}_5$): calc. 469.2024, found. 469.2022.

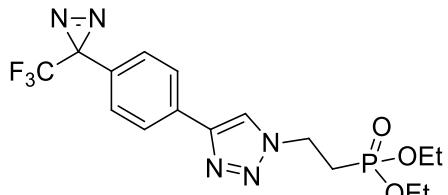
Ethyl 2-(4-(4-(3-(trifluoromethyl)-3*H*-diazirin-3-yl)phenyl)-1*H*-1,2,3-triazol-1-yl)acetate (3c)



According to GP4, 1.5 mg (3.21 μmol) of compound **5o** were oxidized to give 1.00 mg (2.57 μmol) of the target substance in 80% yield. $- R_f = 0.35$ (cyclohexane/ethyl acetate; 1:1). Column chromatography: cyclohexane/ethyl acetate (10:1 \rightarrow 1:1). $- ^1\text{H}$ NMR (300 MHz, CDCl_3 , ppm), $\delta = 1.33$ (t, $^3J = 7.2$ Hz, 3 H), 4.30 (q, $^3J = 7.2$ Hz, 2 H), 5.22 (s, 2 H), 7.22–7.26 (m, 2 H), 7.77–8.09 (m, 3 H). $- ^{13}\text{C}$ NMR (101 MHz, CDCl_3 , ppm), $\delta = 13.1$, 27.4 (q, $^2J = 40.3$ Hz), 50.0, 61.6, 121.1 (q, $^1J = 275$ Hz), 120.8, 125.0 (2 C), 125.9

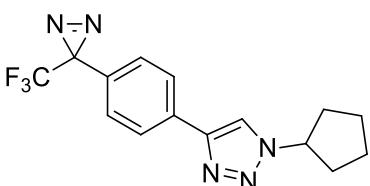
(2 C), 128.3, 130.7, 146.0, 165.1. – IR (ATR, $\tilde{\nu}$): 3112, 2927, 2088, 1722, 1611, 1501, 1448, 1372, 1343, 1262, 1179, 1138, 1076, 1043, 1019, 970, 937, 896, 859, 826, 749, 698, 662, 606, 549, 536, 490. – EI-MS (m/z): 338 (22) [M–CH₃]⁺, 326 (32), 297 (18), 254 (12), 197 (23), 101 (56). – HRMS (C₁₄H₁₁F₃N₅O₂) [M–H]⁺ calc. 338.0865, found. 338.0869.

Diethyl (2-(4-(4-(trifluoromethyl)-3H-diazirin-3-yl)phenyl)-1*H*-1,2,3-triazol-1-yl)ethyl)phosphonate (3d)



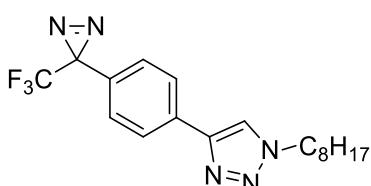
According to GP4, 2.12 mg (4.83 μ mol) of compound **5p** were oxidized to give 1.50 mg (3.43 μ mol) of the target substance in 71% yield. R_f = 0.52 (CH₂Cl₂/MeOH acetate; 10:1). Column chromatography: cyclohexane/ethyl acetate (20:1 → 10:1 → 4:1). – ¹H NMR (300 MHz, CDCl₃, ppm), δ = 1.23 (t, ³J = 7.0 Hz, 6 H), 2.29–2.52 (m, 2 H), 3.86–4.13 (m, 4 H), 4.54–4.74 (m, 2 H), 7.16 (s, 1 H), 7.79 (d, ³J = 8.7 Hz, 1 H), 7.85 (s, 1 H), 7.93–8.00 (m, 1 H), 8.03–8.11 (m, 1 H). – ¹³C NMR (101 MHz, CDCl₃, ppm), δ = 16.4 (d, *J* = 6.6 Hz, 2 C), 27.2 (dd, *J* = 142 Hz, *J* = 2.2 Hz), 28.4 (q, *J* = 40.3 Hz), 44.8 (dd, *J* = 13.2 Hz, *J* = 2.2 Hz), 62.3 (dd, *J* = 6.6 Hz, *J* = 4.4 Hz), 116.7 (q, *J* = 295 Hz), 121.2 (d, *J* = 112 Hz), 125.9 (2 C), 127.0, 129.0 (d, *J* = 37.3 Hz), 130.9 (d, *J* = 2.2 Hz), 131.8, 137.3, 146.2 (d, *J* = 53.4 Hz). – ¹⁹F NMR (376 Hz, CDCl₃, ppm), δ = -71.30 (s, 3 F). – IR (ATR, $\tilde{\nu}$): 3138, 2983, 1716, 1611, 1442, 1393, 1342, 1226, 1162, 1101, 1019, 963, 939, 822, 712, 644, 534, 490.

1-Cyclopentyl-4-(4-(trifluoromethyl)-3H-diazirin-3-yl)phenyl-1*H*-1,2,3-triazole (3e)



According to GP4, 2.30 mg (7.11 μ mol) of compound **5s** were oxidized to give 1.10 mg (3.42 μ mol) of the target substance in 48% yield. – R_f = 0.62 (cyclohexane/ethyl acetate; 10:1). Column chromatography: cyclohexane/ethyl acetate (20:1 → 10:1). – ¹H NMR (400 MHz, CDCl₃, ppm), δ = 1.76–1.84 (m, 2 H), 1.89–1.99 (m, 2 H), 2.06–2.14 (m, 2 H), 2.26–2.35 (m, 2 H), 4.95–5.01 (m, 1 H), 7.22–7.24 (m, 2 H), 7.78 (s, 1 H), 7.85–7.87 (m, 2 H). – ¹³C NMR (100 MHz, CDCl₃, ppm), δ = 24.1 (2 C), 33.5 (2 C), 28.4 (q, ²J = 40.4 Hz), 62.0, 118.5, 122.1 (q, ¹J = 274.6 Hz), 125.9 (2 C), 126.9 (q, ⁵J = 1.5 Hz, 2 C), 130.9 (q, ⁴J = 2.1 Hz), 132.2, 146.2. – ¹⁹F NMR (376 Hz, CDCl₃, ppm), δ = -73.32 (s, 3 F). – IR (DRIFT, $\tilde{\nu}$): 2924, 2854, 1713, 1610, 1452, 1417, 1367, 1264, 1170, 1131, 1047, 974, 393, 823, 771, 743, 714, 689, 635, 624, 535, 430 cm⁻¹. – EI-MS (m/z): 322 (2) [M⁺H], 320 (3), 293 (40), 264 (51), 236 (42), 197 (34), 169 (100). – HRMS [M⁺H] (C₁₅H₁₅F₃N₅): calc. 322.1276, found. 322.1277.

1-Octyl-4-(4-(trifluoromethyl)diazirin-3-yl)phenyl-1*H*-1,2,3-triazole (3f)



According to GP4, 2.90 mg (7.89 μ mol) of compound **5t** were oxidized to give 2.00 mg (5.47 μ mol) of the target substance in 69% yield. – R_f = 0.53 (cyclohexane/ethyl acetate; 4:1). Column chromatography: cyclohexane/ethyl acetate (10:1 → 4:1). – ¹H NMR (400 MHz, CDCl₃, ppm), δ = 0.86 (m, 3 H), 1.21–1.34 (m, 10 H), 1.91–1.96 (m, 2 H), 4.40 (t, ³J = 7.3 Hz, 2 H), 7.23–

7.25 (m, 2 H), 7.78 (s, 1 H), 7.85–7.88 (m, 2 H). – ^{13}C NMR (100 MHz, CDCl_3 , ppm), δ = 14.1, 22.6, 26.5, 29.0, 29.1, 30.0 (q, 2J = 47.9 Hz), 30.4, 31.7, 50.6, 119.9, 122.1 (q, 1J = 274.6 Hz), 125.9 (2 C), 127.0 (q, 4J = 1.2 Hz, 2 C), 128.7, 132.1, 146.4. – IR (ATR, $\tilde{\nu}$): 3135, 2925, 2853, 1720, 1614, 1561, 1500, 1464, 1347, 1230, 1187, 1155, 1076, 1050, 975, 940, 872, 809, 764, 723, 690, 607 cm^{-1} . – EI-MS (m/z, 70 eV, 70 °C): 365 (3) [M] $^+$, 337 (35), 280 (6), 254 (24), 223 (12), 197 (24), 149 (100). – HRMS ($\text{C}_{18}\text{H}_{22}\text{F}_3\text{N}_5$): calc. 365.1827, found. 365.1830.

3-(4-Ethynylphenyl)-3-(trifluoromethyl)-3*H*-diazirine (3g)

According to GP5, 1.82 mg (8.33 μmol) of compound **5f** were oxidized to give 1.75 mg (8.33 μmol) of the target substance in quantitative yield. – R_f = 0.47 (cyclohexane/ethyl acetate; 4:1). Column chromatography: cyclohexane/ethyl acetate (10:1 → 4:1). – ^1H NMR (400 MHz, CDCl_3 , ppm), δ = 3.11 (s, 1 H, CH), 7.47–7.62 (m, 4 H, CH). – ^{13}C NMR (100 MHz, CDCl_3 , ppm), δ = 28.4 (q, 2J = 40 Hz), 79.4, 82.4, 121.9 (q, 1J = 275 Hz), 123.7, 127.2 (2 C), 130.0, 132.5 (2 C).

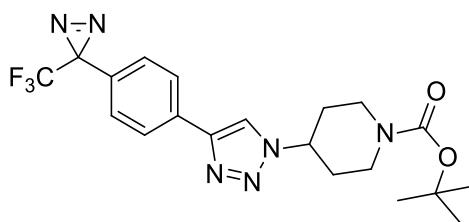
3-(4'-Ethynyl-[1,1'-biphenyl]-4-yl)-3-(trifluoromethyl)-3*H*-diazirine (3h)

According to GP5, 23.9 mg (83.3 μmol) of compound **5j** were oxidized to give 16.0 mg (56.0 μmol) of the target substance in 67% yield. – R_f = 0.39 (cyclohexane/ethyl acetate; 4:1). Column chromatography: cyclohexane/ethyl acetate (10:1 → 4:1). – ^1H NMR (400 MHz, CDCl_3 , ppm), δ = 3.07 (s, 1 H), 7.40–7.56 (m, 8 H). – ^{13}C NMR (100 MHz, CDCl_3 , ppm), δ = 28.4 (q, 2J = 40.3 Hz), 78.2, 83.2, 122.1 (q, 1J = 274.4 Hz), 121.8, 127.0 (3 C), 127.4 (2 C), 128.5 (2 C), 132.6 (2 C), 140.0, 141.6. – ^{19}F NMR (376 Hz, CDCl_3 , ppm), δ = -65.06 (s, 3 F). – IR (ATR, $\tilde{\nu}$): 3301, 1716, 1604, 1493, 1400, 1343, 1145, 1051, 1002, 970, 939, 851, 514, 744, 692, 660, 633, 534 cm^{-1} . – EI-MS (m/z, 70 eV, 100 °C): 286 (6) [M] $^+$, 258 (100), 256 (22), 238 (6), 207 (11) 189 (59), 176 (2), 163 (5), 139 (4), 129 (5), 119 (2), 69 (4). – HRMS ($\text{C}_{16}\text{H}_9\text{F}_3\text{N}_2$): calc. 286.0712, found. 286.0713.

3-(4'-Methoxy-[1,1'-biphenyl]-4-yl)-3-(trifluoromethyl)-3*H*-diazirine (3i)

According to GP4, 2.1 mg (7.14 μmol) of compound **5h** were oxidized to give 2.0 mg (6.84 μmol) of the target substance in 96% yield. – R_f = 0.52 (cyclohexane/ethyl acetate; 10:1). Column chromatography: cyclohexane/ethyl acetate (20:1 → 4:1). – ^1H NMR (400 MHz, CDCl_3 , ppm), δ = 3.78 (s, 3 H), 6.86–6.96 (m, 2 H), 7.12–7.18 (m, 2 H), 7.41–7.46 (m, 2 H), 7.50 (d, 3J = 8.3 Hz, 2 H). – ^{13}C NMR (101 MHz, CDCl_3 , ppm), δ = 28.4 (q, 2J = 42.4 Hz), 55.4, 114.4 (2 C), 122.2 (q, 1J = 276.6 Hz), 126.8 (2 C), 127.0 (2 C), 127.3, 128.2 (2 C), 132.2, 142.1, 159.7. – IR (ATR, $\tilde{\nu}$): 2959, 1711, 1598, 1527, 1498, 1462, 1442, 1404, 1345, 1249, 1170, 1124, 1036, 1000, 940, 811, 770, 744, 709, 683, 622, 590, 552, 522, 418 cm^{-1} . – EI-MS (m/z, 70 eV, 50 °C): 292 (8) [M] $^+$, 280 (95), 264 (73), 249 (17), 231 (10), 221 (174), 211 (100), 201 (12), 196 (3), 183 (11), 152 (40), 139 (30), 115 (6), 106 (11), 69 (11). – HRMS ($\text{C}_{15}\text{H}_{11}\text{ON}_2\text{F}_3$): calc. 292.0818, found. 292.0820.

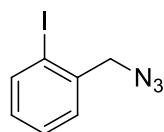
tert-Butyl 4-(4-(4-(3-(trifluoromethyl)diazirin-3-yl)phenyl)-1*H*-1,2,3-triazol-1-yl)piperidine-1-carboxylate (3j)



According to GP4, 14.9 mg (34.0 μ mol) of compound **5q** were oxidized to give 12.1 mg (28.0 μ mol) of the target substance in 82% yield. – R_f = 0.50 (cyclohexane/ethyl acetate; 1:1). Column chromatography: cyclohexane/ethyl acetate (4:1 → 1:1). – ¹H NMR (400 MHz, *CDCl*₃, ppm), δ = 1.49 (s, 9 H), 1.95–2.04 (m, 2 H), 2.23–2.26 (m, 2 H), 2.90–2.99 (m, 2 H), 4.22–4.38 (m, 2 H), 4.63–4.71 (m, 1 H), 7.23–7.66 (m, 2 H), 7.79 (s, 1 H), 7.84–7.87 (m, 2 H). – ¹³C NMR (100 MHz, *CDCl*₃, ppm), δ = 26.9, 28.4 (3 C), 29.9 (q, ²*J* = 47.8 Hz), 42.7 (bs, 2 C), 58.4 (2 C), 80.2, 117.8, 122.11 (q, ¹*J* = 274.6 Hz), 125.9 (2 C), 127.0 (2 C), 128.8, 131.9, 146.4, 154.5. – IR (ATR, $\tilde{\nu}$): 2923, 2853, 2089, 1676, 1611, 1429, 1366, 1247, 1156, 1123, 1079, 1050, 1007, 937, 877, 858, 821, 769, 716, 691, 549. – EI-MS (m/z, 70 eV, 140 °C): 436 (4) [M]⁺, 408 (37), 368 (7), 323 (3), 242 (5), 197 (5), 126 (33), 57 (100). – HRMS (C₂₀H₂₃F₃N₆O₂): calc. 436.1835, found. 436.1837.

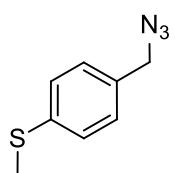
5. Synthesis of Azides 9

1-(Azidomethyl)-2-iodobenzene (9a)



According to GP7, 50.0 mg of 1-(bromomethyl)-2-iodobenzene (168 μ mol, 1.00 equiv.) were reacted with 27.0 mg of NaN₃ (421 μ mol, 2.50 equiv.) in 2 mL DMF. After stirring for 12 h at room temperature, 10 mL of H₂O were added, the aqueous layer was extracted three times with ethyl acetate, the organic layer was dried over MgSO₄ and the crude product was purified *via* column chromatography (cyclohexane/ethyl acetate; 10:1). The target compound was isolated in 87% yield (38.0 mg, 146 μ mol). – R_f = 0.84 (cyclohexane/ethyl acetate; 4:1). – ¹H NMR (250 MHz, *CDCl*₃, ppm), δ = 4.44 (s, 2 H), 6.99–7.05 (m, 1 H), 7.35–7.37 (m, 2 H), 7.86 (d, ³*J* = 7.8 Hz, 1 H). – ¹³C NMR (62.5 MHz, *CDCl*₃, ppm), δ = 59.0, 98.9, 128.6, 129.4, 129.9, 138.0, 139.7. – IR (ATR, $\tilde{\nu}$): 3442, 3060, 2927, 2099, 1676, 1584, 1566, 1466, 1438, 1385, 1342, 1256, 1200, 1090, 1015, 883, 752, 660, 440 cm⁻¹. – EI-MS (m/z, 70 eV, 30 °C): 259 (23) [M]⁺, 230 (38), 203 (6), 154 (1), 141 (1), 127 (100), 103 (16), 77 (30), 74 (10), 50 (12). – HRMS (C₇H₆IN₃): calc. 258.9606, found. 258.9605.

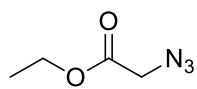
(4-(Azidomethyl)phenyl)(methyl)sulfane (9b)



According to GP7 300 mg of (4-(bromomethyl)phenyl)(methyl)sulfane (1.38 mmol, 1.00 equiv.) were reacted with 225 mg of NaN₃ (3.45 mmol, 2.50 equiv.) in 10 mL DMF. After stirring for 12 h at room temperature, 50 mL of H₂O were added, the aqueous layer was extracted three times with ethyl acetate, the organic layer was dried over MgSO₄ and the crude product was purified *via* column chromatography (cyclohexane/ethyl acetate; 10:1). The target compound was isolated in 74% yield (183 mg, 1.02 mmol). – R_f = 0.79 (cyclohexane/ethyl acetate; 4:1). – ¹H NMR (300 MHz, *CDCl*₃, ppm), δ = 2.48 (d, ³*J* = 0.6 Hz, 3 H), 4.29 (s, 2 H), 7.19–7.26 (m, 4 H). – ¹³C NMR (75 MHz, *CDCl*₃, ppm), δ = 15.6, 54.3, 126.6 (2 C), 128.7 (2 C), 131.9, 138.8.

– IR (ATR, $\tilde{\nu}$): 2919, 2089, 1598, 1492, 1436, 1404, 1342, 1244, 1203, 1091, 1015, 956, 733, 676, 557, 517, 429 cm^{-1} – EI (m/z, 70 eV, 25 °C): 179 [M]⁺ (79), 150 (12), 137 (100), 122 (31), 109 (21), 91 (5), 77 (7), 65 (6).

Ethyl 2-azidoacetate (9c)

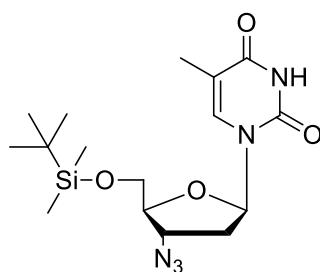


According to GP6, 50.0 mg of ethyl 2-bromoacetate (300 μmol , 1.20 equiv.)

were reacted with 16.0 mg of NaN_3 (250 μmol , 1.00 equiv.) in 2 mL DMF.

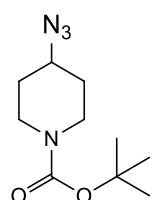
After stirring for 12 h at room temperature 50 mL of H_2O were added, the aqueous layer was extracted three times with ethyl acetate, and the organic layer was dried over MgSO_4 . After evaporation of the solvent the crude product was used without further purification. – ¹³C NMR (75 MHz, CDCl_3 , ppm), δ = 14.0, 50.2, 61.7, 168.2. The analytical data correspond to the literature. ^[5]

3-Aza-5-O-thymidine (9d)



A mixture of 3'-deoxy-3'-azidothymidine (400 mg, 1.49 mmol, 1.00 equiv.) and imidazole (336 mg, 2.23 mmol, 1.50 equiv.) was evaporated with dry acetonitrile (3×5 ml) and dissolved in 10 mL dry acetonitrile followed by the addition of 280 mg TBDMS-Cl (1.87 mmol, 1.25 equiv.) under stirring. The mixture was kept overnight at room temperature. After the addition of 10 mL water, the mixture was evaporated and divided between water (50 mL) and ethyl acetate (50 mL). The aqueous layer was extracted with ethyl acetate, the combined organic layers were washed with 10% aqueous KHSO_4 (2×20 ml), saturated aqueous NaHCO_3 (2×20 ml), water, and dried with anhydrous Na_2SO_4 and evaporated. The target compound was purified via column chromatography (cyclohexane/ethyl acetate; 4:1) and isolated in 80% yield (457 mg, 1.19 mmol). – R_f = 0.46 (cyclohexane/ethyl acetate; 1:1). – ¹H NMR (250 MHz, CDCl_3 , ppm), δ = 0.08 (s, 6 H, CH_3), 0.88 (s, 9 H, CH_3), 1.89 (d, 4J = 1.2 Hz, 3 H, CH_3), 2.21 (td, 3J = 7.0, 3J = 13.6 Hz, 1 H, CH), 2.39 (td, 3J = 6.1, 3J = 13.6 Hz, 1 H, CH), 3.75 (dd, 3J = 3.0, 3J = 12.1 Hz, 1 H, CH), 3.85–3.92 (m, 2 H, CH_2), 4.19 (m, 2 H, CH_2), 6.18 (t, 3J = 6.5 Hz, 1 H, CH), 7.39 (d, 4J = 1.2 Hz, 1 H, CH), 9.26 (s, 1 H, NH). – ¹³C NMR (62.5 MHz, CDCl_3 , ppm), δ = -5.5, -5.4, 12.5, 18.3, 25.9 (2 C), 37.9 (3 C), 60.4, 84.4, 84.5, 111.0, 134.9, 150.3, 163.8. – IR (ATR, $\tilde{\nu}$): 3195, 3066, 2928, 2856, 2099, 1707, 1678, 1462, 1402, 1361, 1321, 1289, 1252, 1198, 1120, 1070, 991, 958, 931, 887, 830, 778, 734, 670, 601, 550, 4879, 419 cm^{-1} . – FAB-MS (m/z, 70 eV, 60 °C): 382 [M + H]⁺, 324, 281, 213, 154, 145, 127, 97, 95, 89, 81. – HRMS ($\text{C}_{16}\text{H}_{28}\text{O}_4\text{N}_5\text{Si}$): calc. 382.1911, found. 382.1914. – Mp.: 98–100 °C. ^[6]

tert-Butyl 4-azidopiperidine-1-carboxylate (9e)



According to GP7, 200 mg (757 μmol , 1.00 equiv.) of 1-Boc-4-bromopiperidine were reacted with 98.0 mg of NaN_3 (1.52 mmol, 2.00 equiv.) and 113 mg (757 μmol , 1.00 equiv.) of NaI in DMF. After stirring for 12 h at room temperature, 20 mL of H_2O were added, the aqueous layer was extracted three times with 50 mL CH_2Cl_2 , and the organic layer was dried over MgSO_4 . After

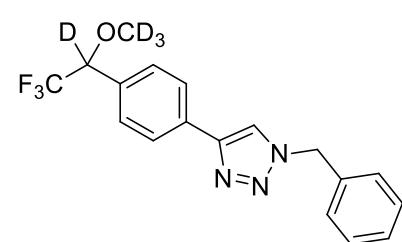
evaporation of the solvent, the crude product was used without further purification (171 mg, 755 mol). – ^1H NMR (250 MHz, CDCl_3 , ppm), δ = 1.44 (s, 9 H), 1.55 (ddd, 3J = 13.2 Hz, 3J = 9.3 Hz, 3J = 4.2 Hz, 2 H), 1.72–1.95 (m, 2 H), 3.07 (ddd, 3J = 13.5 Hz, 3J = 9.7 Hz, 3J = 3.3 Hz, 2 H), 3.56 (quin, 3J = 4.3 Hz, 1 H), 3.68–3.94 (m, 2 H). – ^{13}C NMR (75 MHz, CDCl_3 , ppm), δ = 28.3 (3 C), 30.5 (2 C), 41.3 (br. s., 2 C), 57.5, 79.7, 154.5. – EI-MS (m/z, 70 eV, 30 °C): 204, 176, 151, 126, 102, 88, 75, 51. The analytical data correspond to the literature.^[8]

Diethyl (2-azidoethyl)phosphonate (9f)

According to GP7, 200 mg (816 μmol , 1.00 equiv.) of diethyl (2-bromoethyl)phosphonate were reacted with 531 mg of NaN_3 (8.16 mmol, 10.0 equiv.) in DMF. After stirring for 12 h at 80 °C, 50 mL of H_2O were added, the aqueous layer was extracted three times with CH_2Cl_2 , and the organic layer was dried over MgSO_4 . After evaporation of the solvent, the crude product was used without further purification (169 mg, 816 μmol). – ^1H NMR (300 MHz, CDCl_3 , ppm), δ = 1.27 (t, 3J = 14.2 Hz, 6 H), 1.99 (dt, 3J = 18.5, 3J = 7.6 Hz, 2 H), 3.48 (dt, 3J = 12.2 Hz, 3J = 7.7 Hz, 2 H), 3.94–4.18 (m, 4 H). – ^{13}C NMR (75 MHz, CDCl_3 , ppm), δ = 16.3 (d, 2J = 6.0 Hz, 2 C), 25.9 (d, 1J = 141.1 Hz), 45.3 (d, 2J = 1.6 Hz, 1 C), 61.9 (d, 2J = 6.0 Hz, 2 C). – IR (ATR, $\tilde{\nu}$): 2982, 2098, 1445, 1392, 1366, 1243, 1163, 1017, 955, 789, 531 cm^{-1} . – EI-MS (m/z, 70 eV, 20 °C): 208 [M]⁺(3), 152 (43), 125 (100), 108 (28), 97 (83), 80 (33), 65 (14). – HRMS ($\text{C}_6\text{H}_{15}\text{O}_3\text{N}_3\text{P}$) [M+H]⁺: calc. 208.0846, found. 208.0848.

6. Application – Deuteration experiment

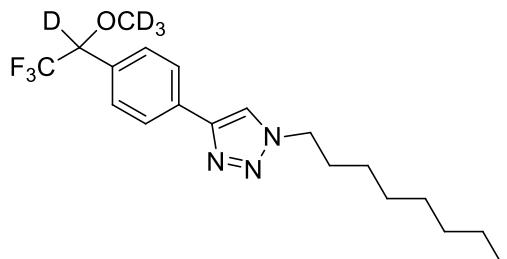
1-Benzyl-4-(4-(2,2,2-trifluoro-1- OCD₃-ethyl)phenyl)-1*H*-1,2,3-triazole (10a)



1.00 mg 1-benzyl-4-(4-(3-(trifluoromethyl)-3*H*-diazirin-3-yl)phenyl)-1*H*-1,2,3-triazole (**3a**) (2.91 μmol) was dissolved in 0.6 mL of methanol-d₄, placed in a reactor (RAYONET reactor model RPR-100) irradiated for 2 h (360 nm). The target compound has been identified in solution *via* ^1H , ^{13}C spectroscopy. GC-MS analysis showed complete conversion

of the starting material. – R_f = 0.31 (cyclohexane/ethyl acetate; 2:1). – ^1H NMR (400 MHz, CDCl_3 , ppm), δ = 5.60 (s, 2 H), 7.32–7.50 (m, 7 H), 7.70 (s, 1 H), 7.86–7.93 (m, 2 H). – ^{13}C NMR (101 MHz, CDCl_3 , ppm), δ = 54.3, 119.8 (2 C), 125.9 (2 C), 128.1 (2 C), 128.7 (2 C), 128.9, 129.2 (2 C), 131.8, 134.5, 149.8. – EI-MS (m/z, 70 eV): 351 [M]⁺, 322, 288, 269, 254, 232, 219, 206, 191, 179, 163, 145, 129, 117, 104, 91, 77, 65, 51.

1-Octyl-4-(4-(2,2,2-trifluoro-1-OCD₃-ethyl)phenyl)-1*H*-1,2,3-triazole (10b)

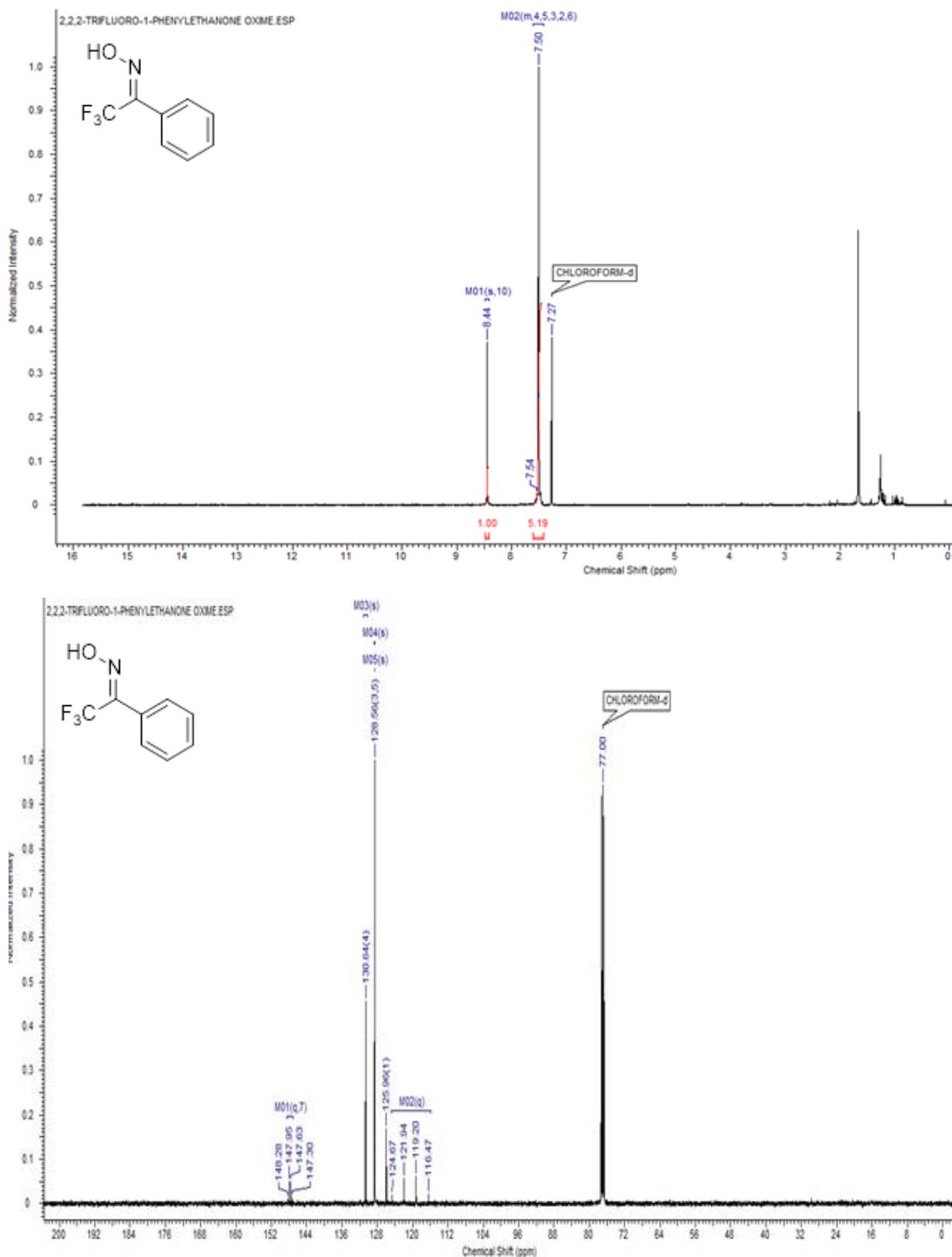


1.00 mg of 1-octyl-4-(4-(3-(trifluoromethyl)-3*H*-diazirin-3-yl)phenyl)-1*H*-1,2,3-triazole (**3f**) (3.11 μ mol) was dissolved in methanol-d₄, placed in the reactor (RAYONET reactor model RPR-100) and irradiated for 2 h (360 nm). The TLC analysis showed complete conversion of the starting material. After evaporation of the solvent the target compound was purified *via* column chromatography

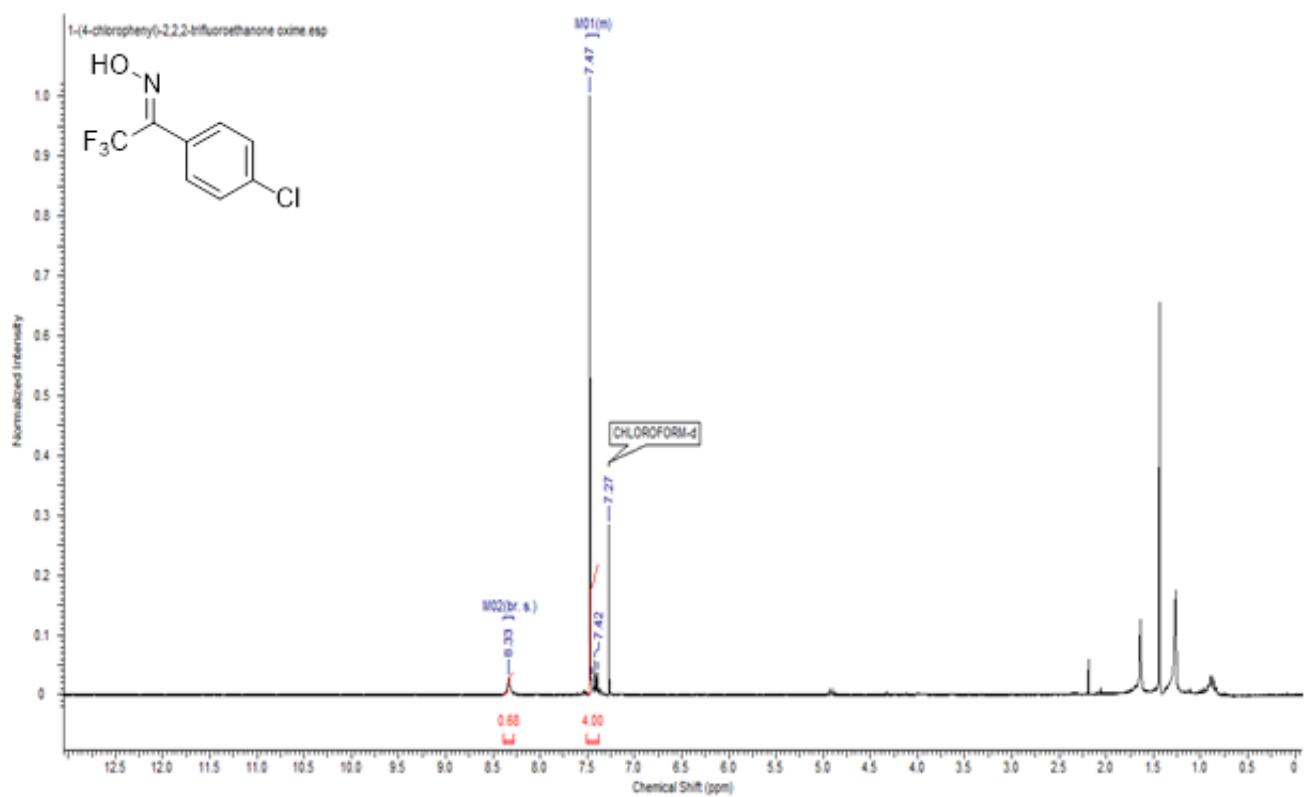
(cyclohexane/ethyl acetate; 20:1) to give the target compound with small impurities in quantitative yield (1.6 mg). ^1H NMR (500 MHz, *CDCl*₃, ppm), δ = 0.89 (t, 3J = 6.9 Hz, 3 H), 1.21–1.43 (m, 10 H), 1.92–2.05 (m, 2 H), 4.40–4.52 (m, 2 H), 7.50–7.71 (m, 2 H), 7.85–7.92 (m, 2 H), 8.37–8.41 (m, 1 H). ^{13}C NMR (126 MHz, *CDCl*₃, ppm), δ = 14.6, 23.8, 27.7, 30.2, 30.4, 31.4, 33.1, 52.4, 57.7 (q, 2J = 22.1 Hz), 125.6 (q, 1J = 280.4 Hz), 126.4, 126.9 (2 C), 130.2 (2 C), 133.2, 134.2, 148.3. – EI-MS (m/z, 70 eV, 140 °C): 373 [M]⁺ (100), 353 (35), 345 (45), 325 (14), 303 (16), 288 (42), 268 (28), 261 (52), 249 (40), 233 (33), 213 (15), 192 (22), 164 (31), 151 (17), 131 (7), 70 (14), 57 (19), 43 (22). HRMS (C₁₉H₂₂D₄F₃N₃O): calc. 373.4491, found. 373.4493.

7. Spectra

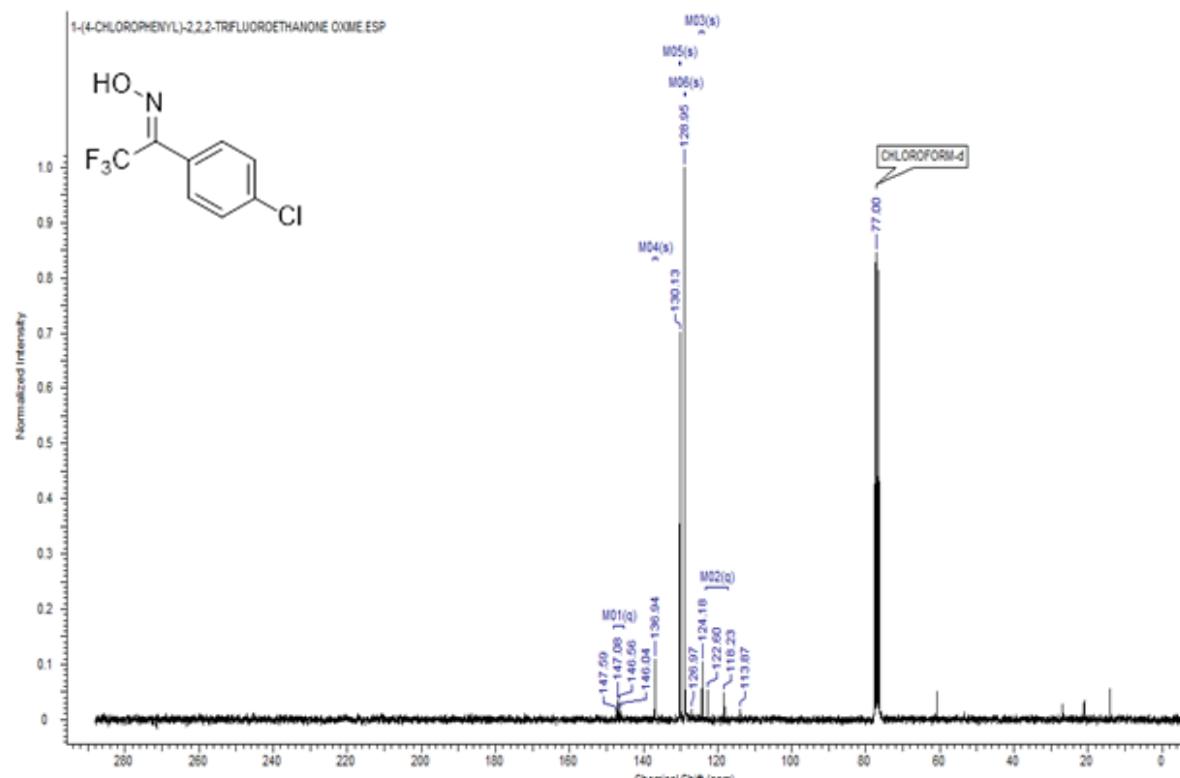
Compound 7a



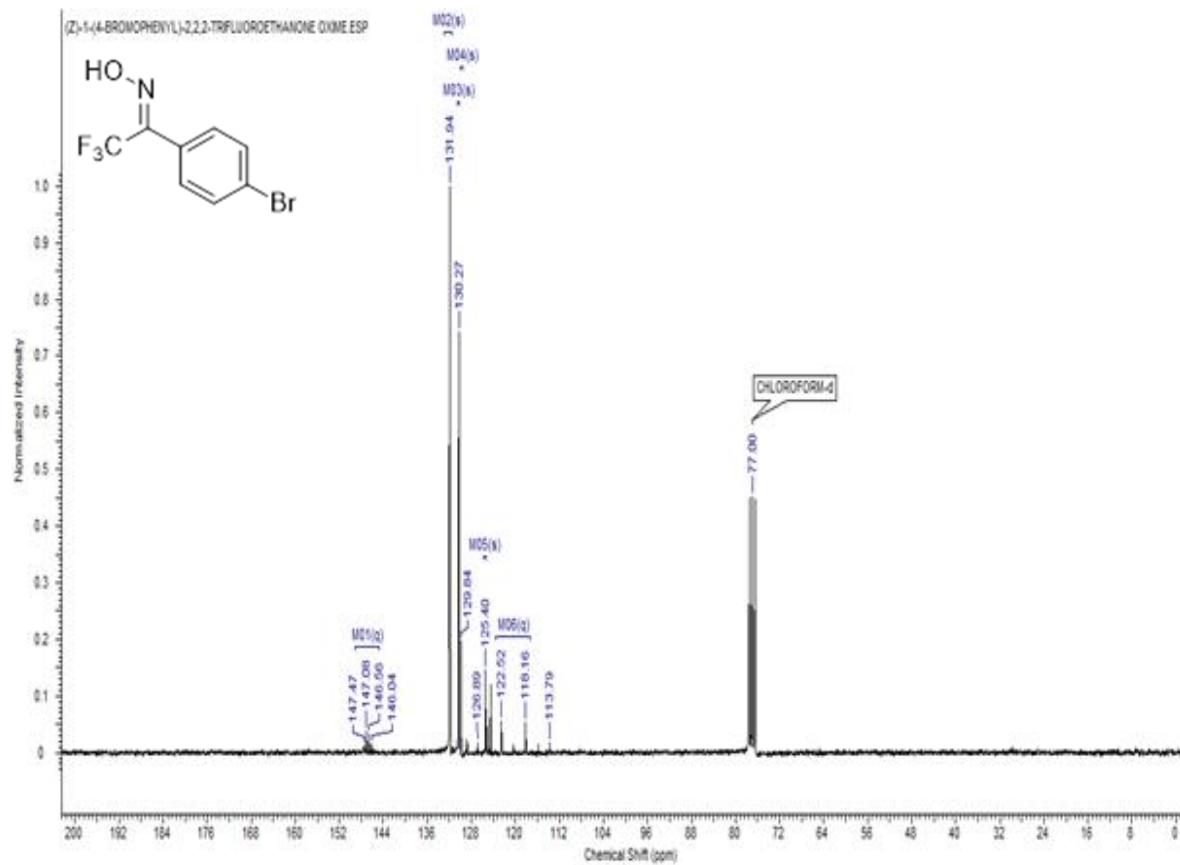
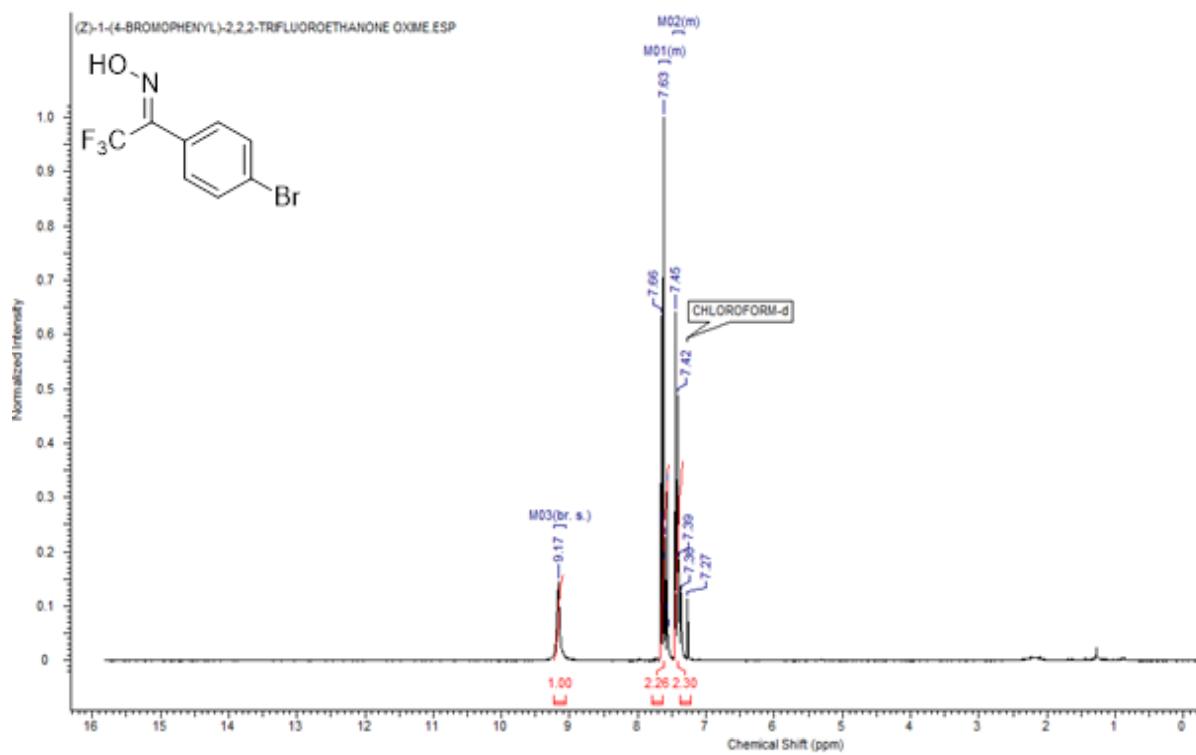
Compound 7c



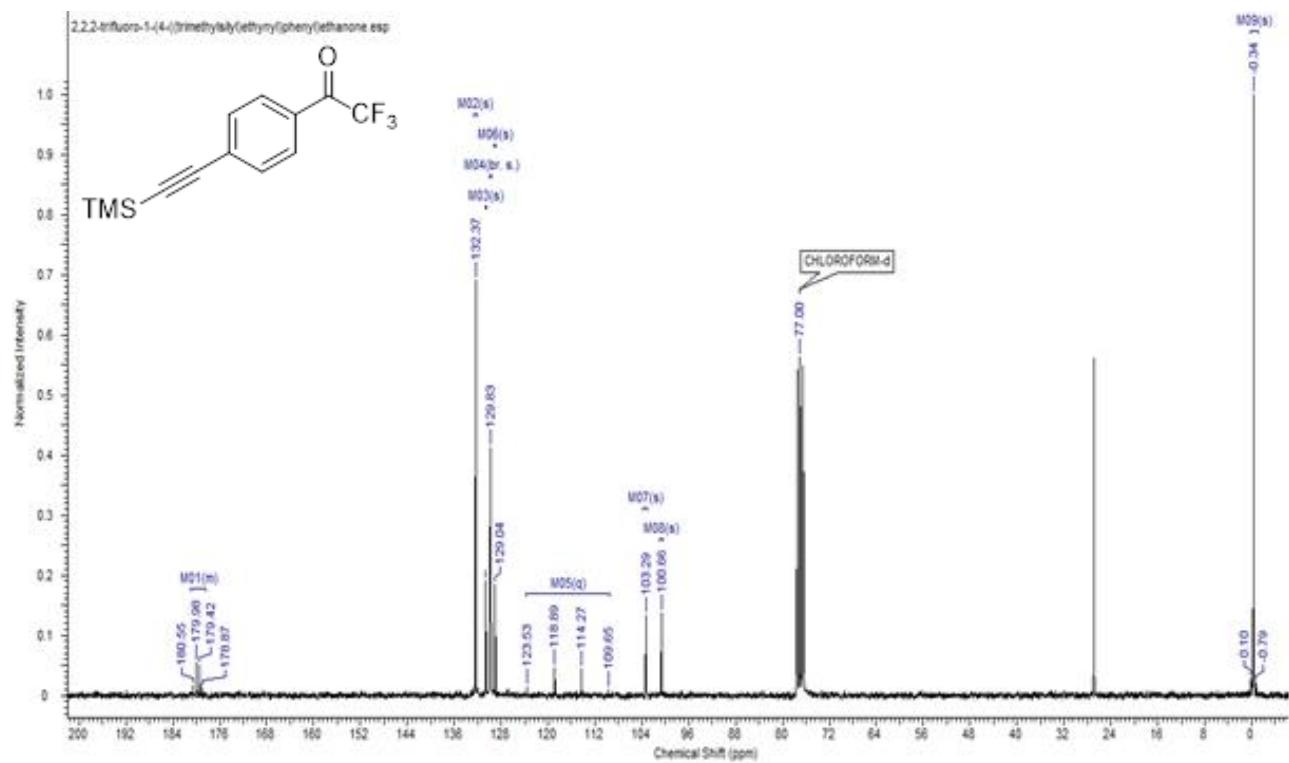
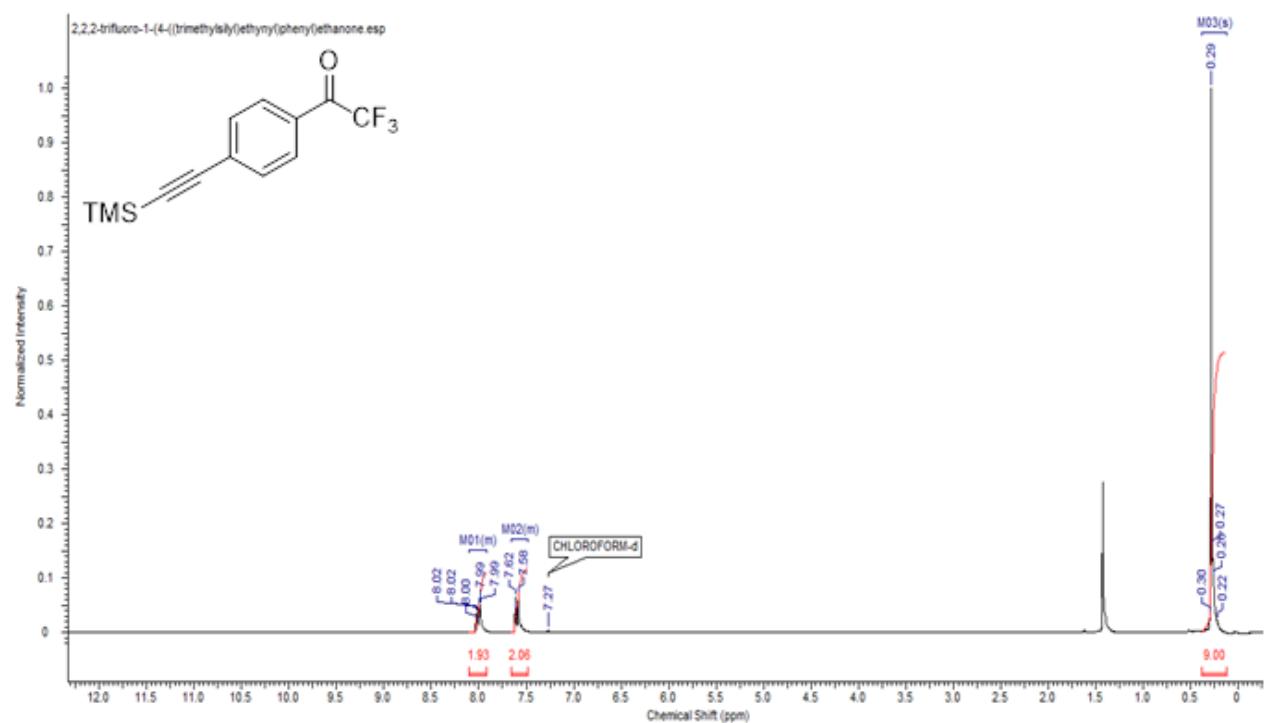
Compound 7c



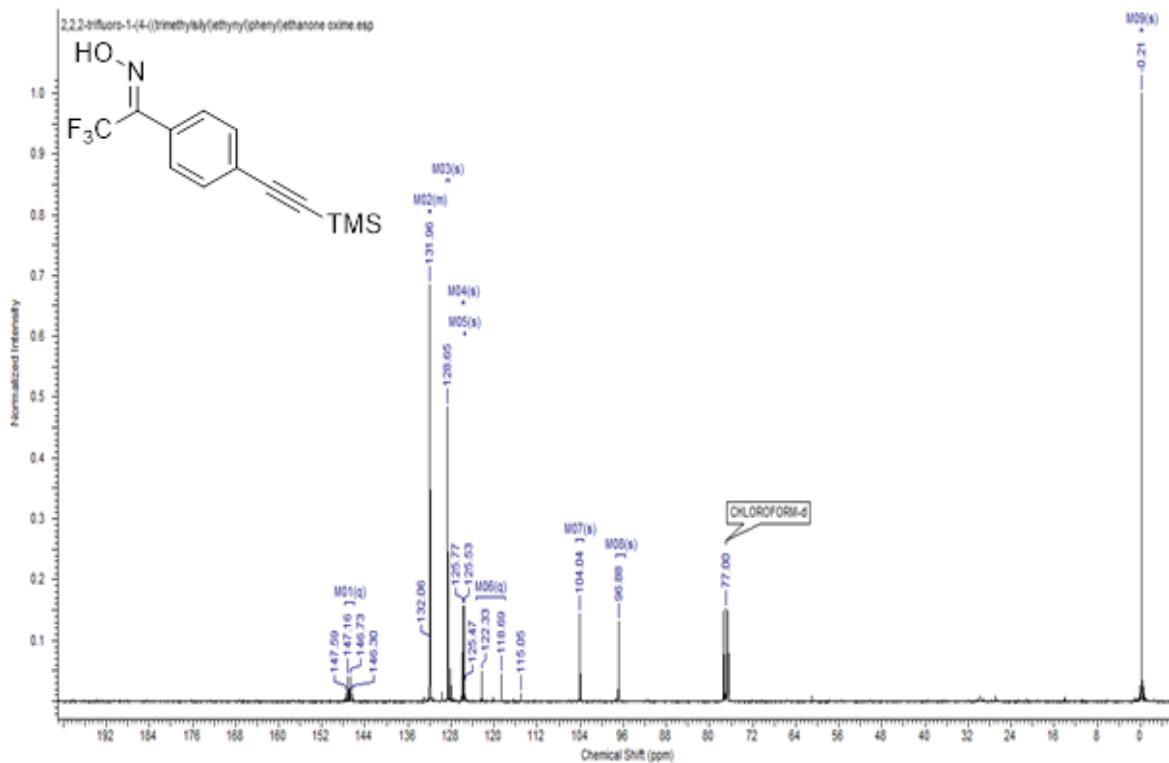
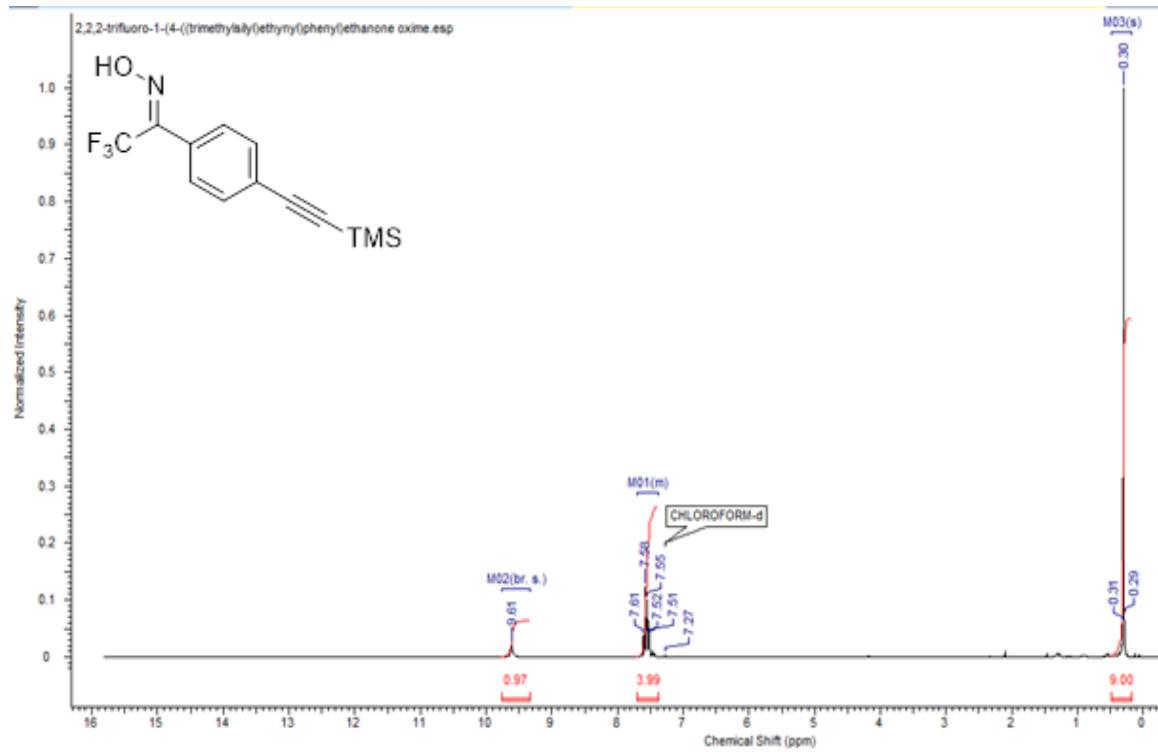
Compound 7d



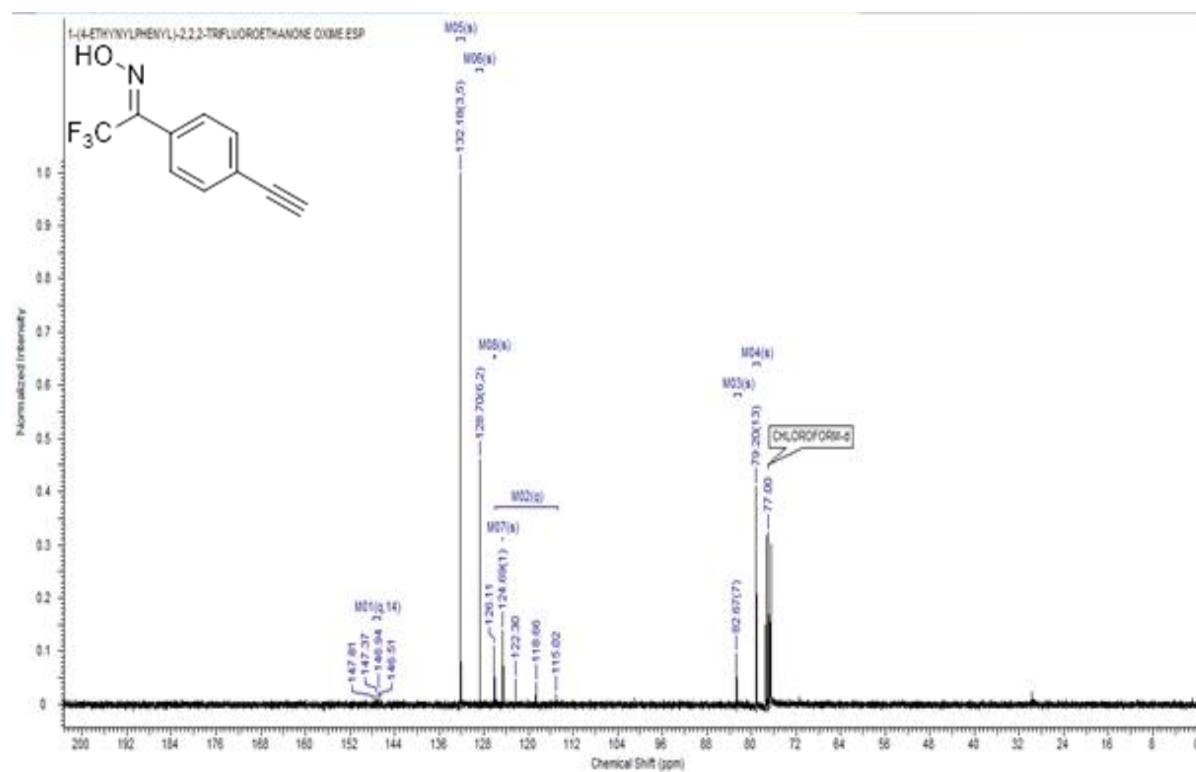
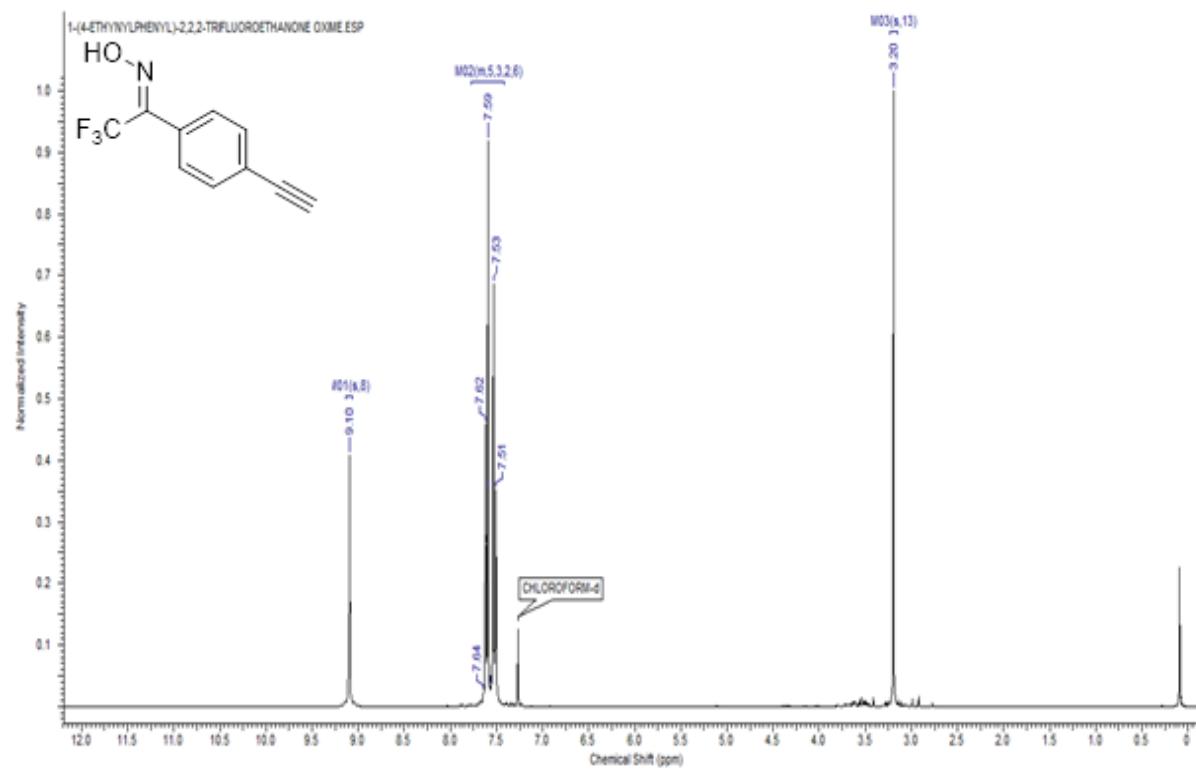
Compound 7e*



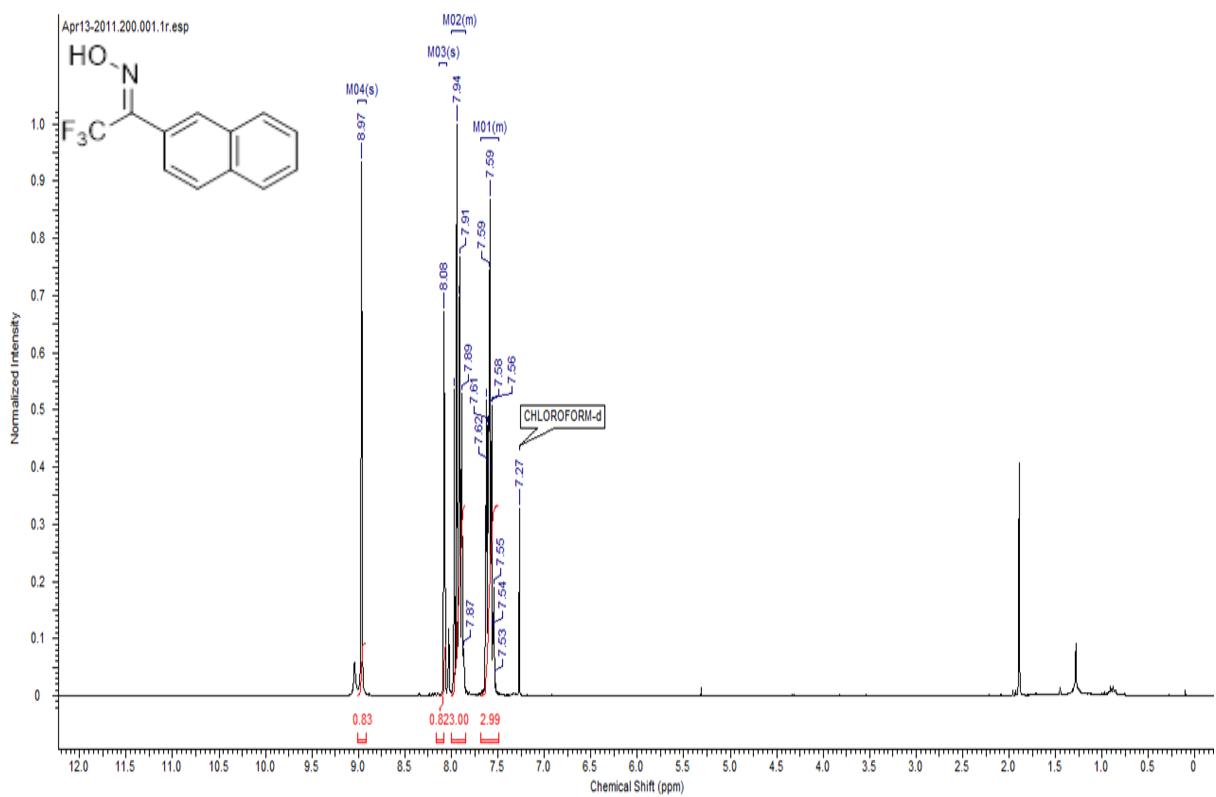
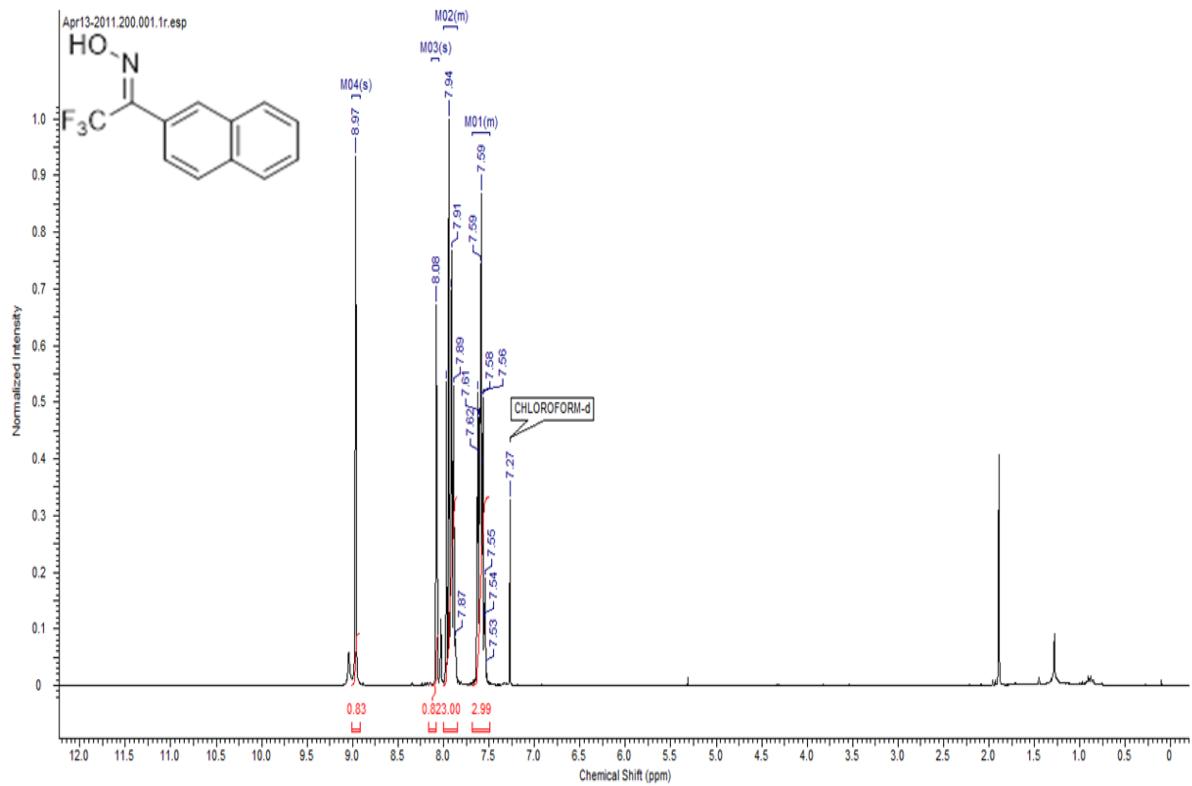
Compound 7e



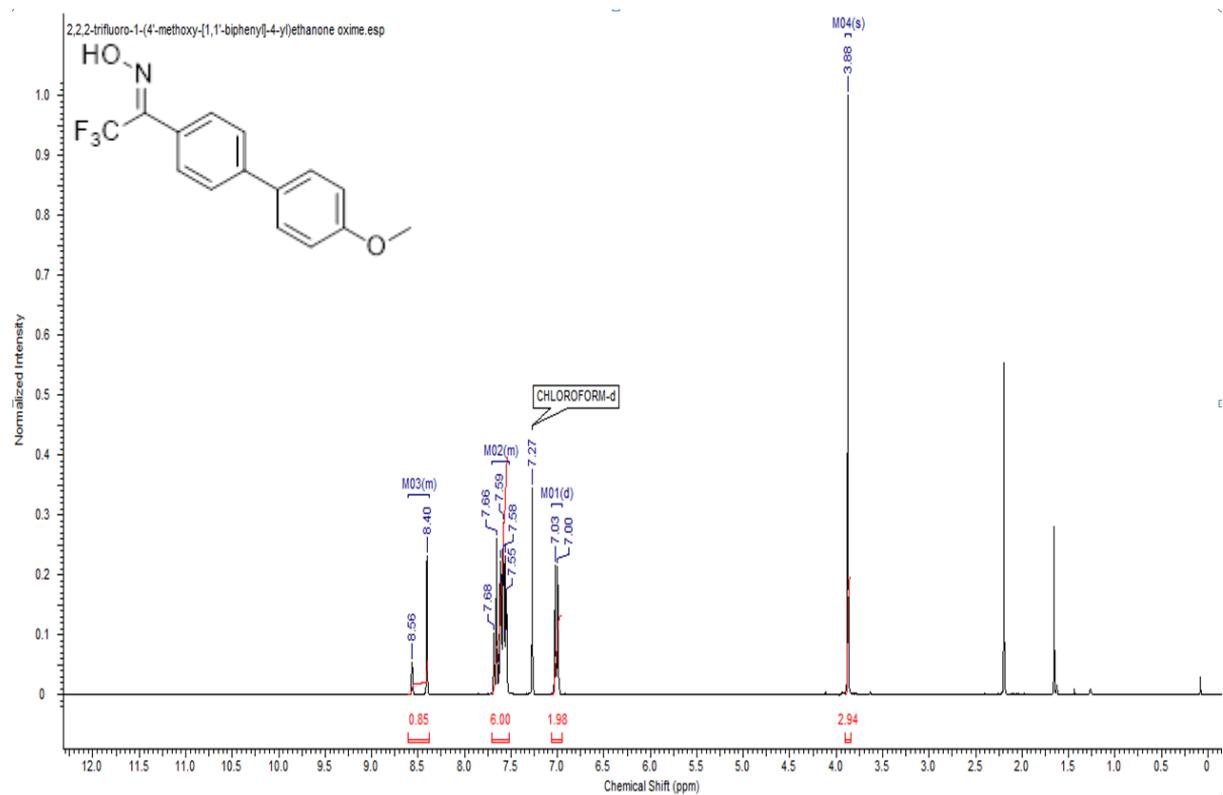
Compound 7f



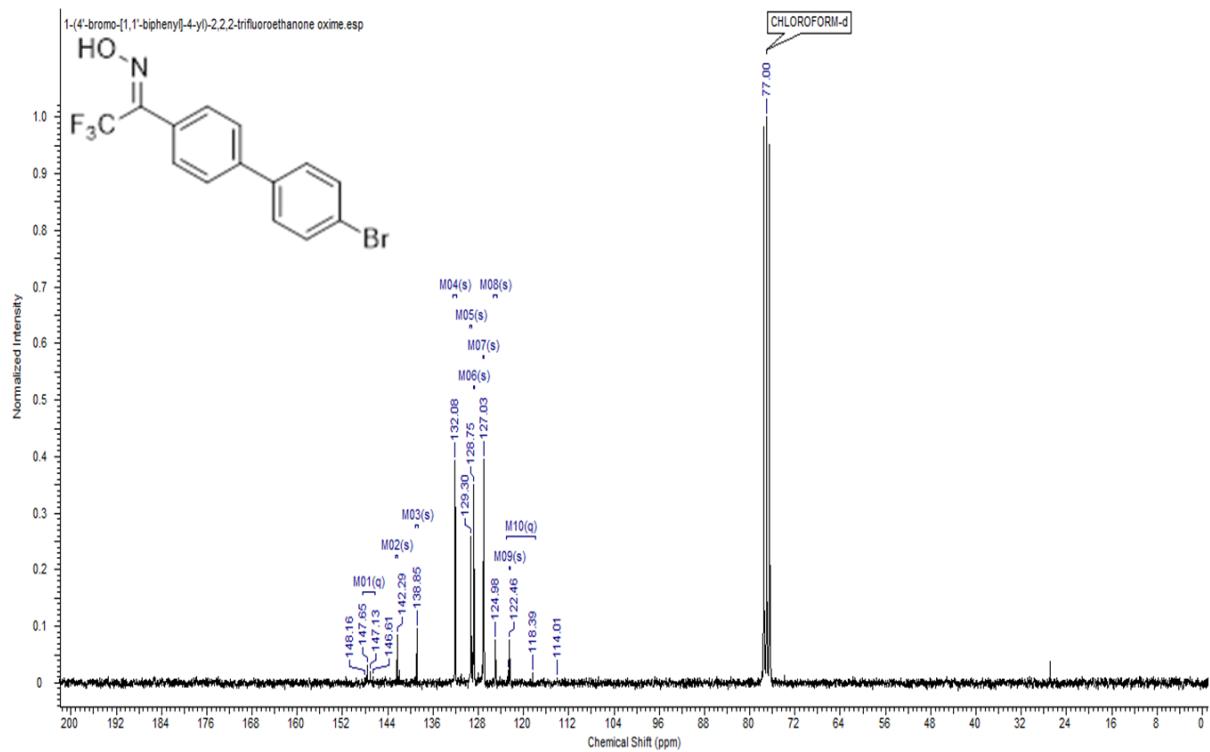
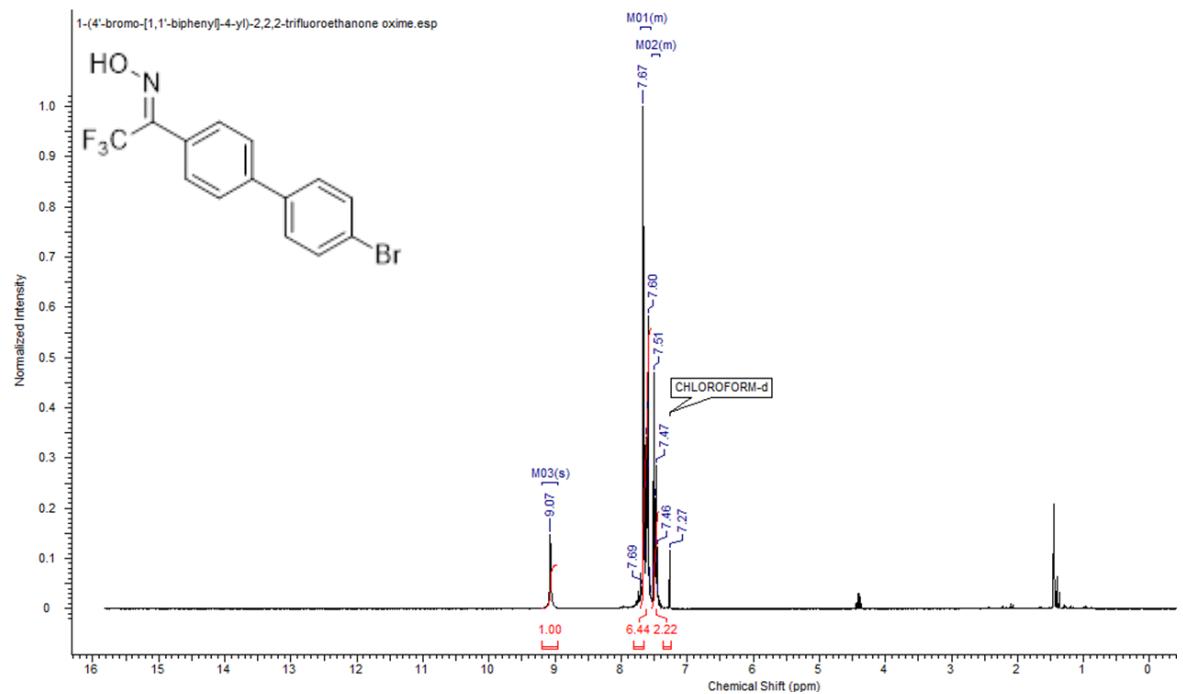
Compound 7g



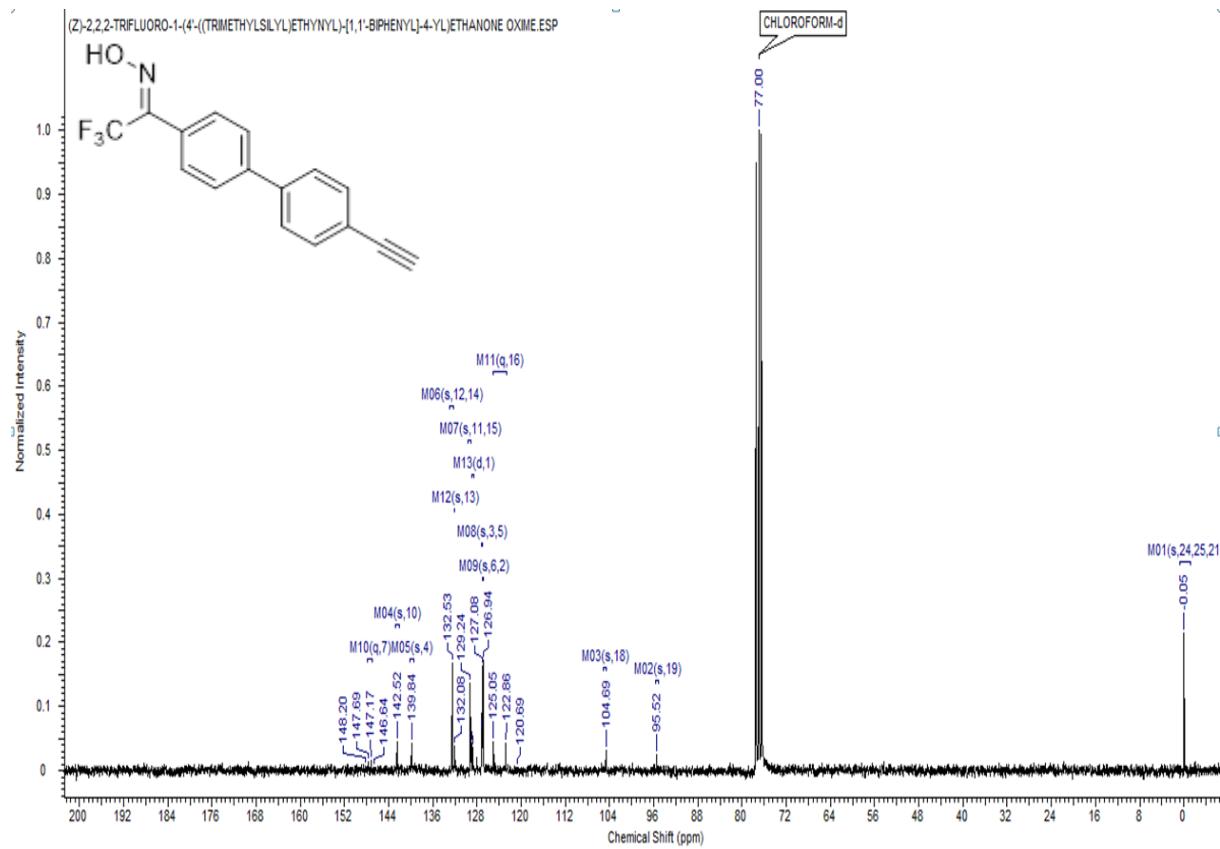
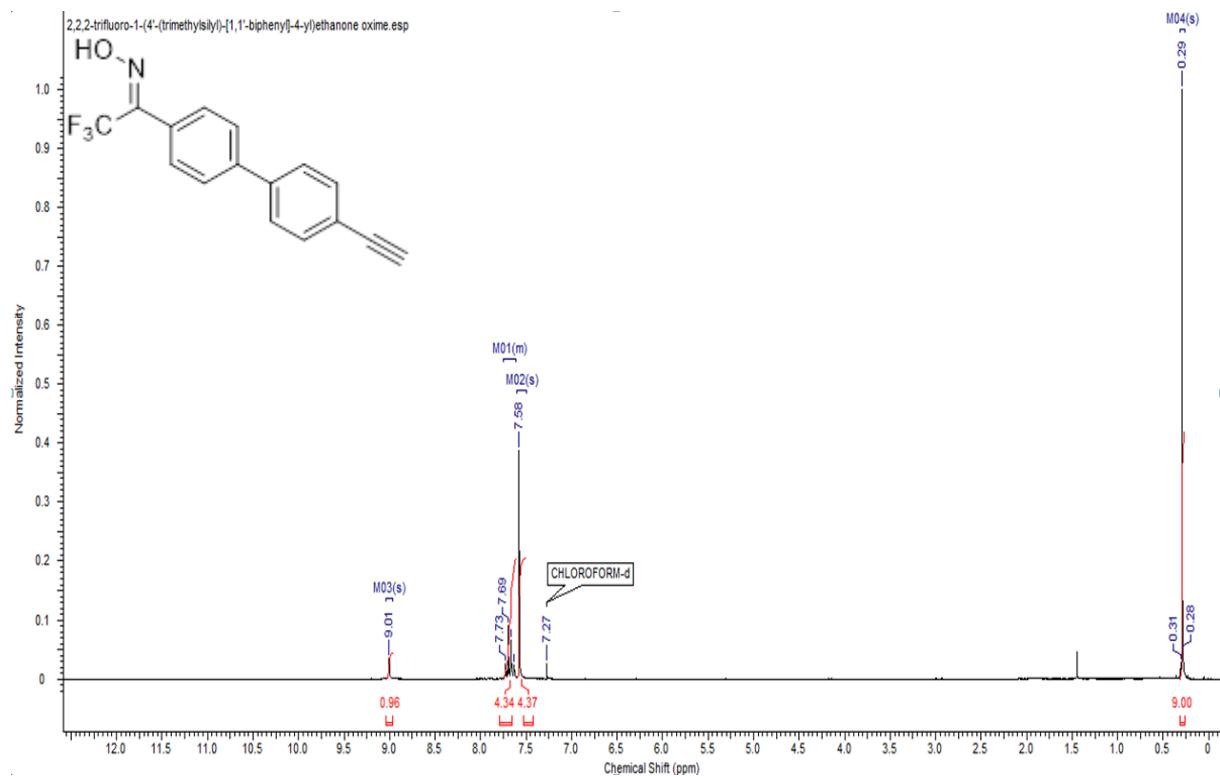
Compound 7h



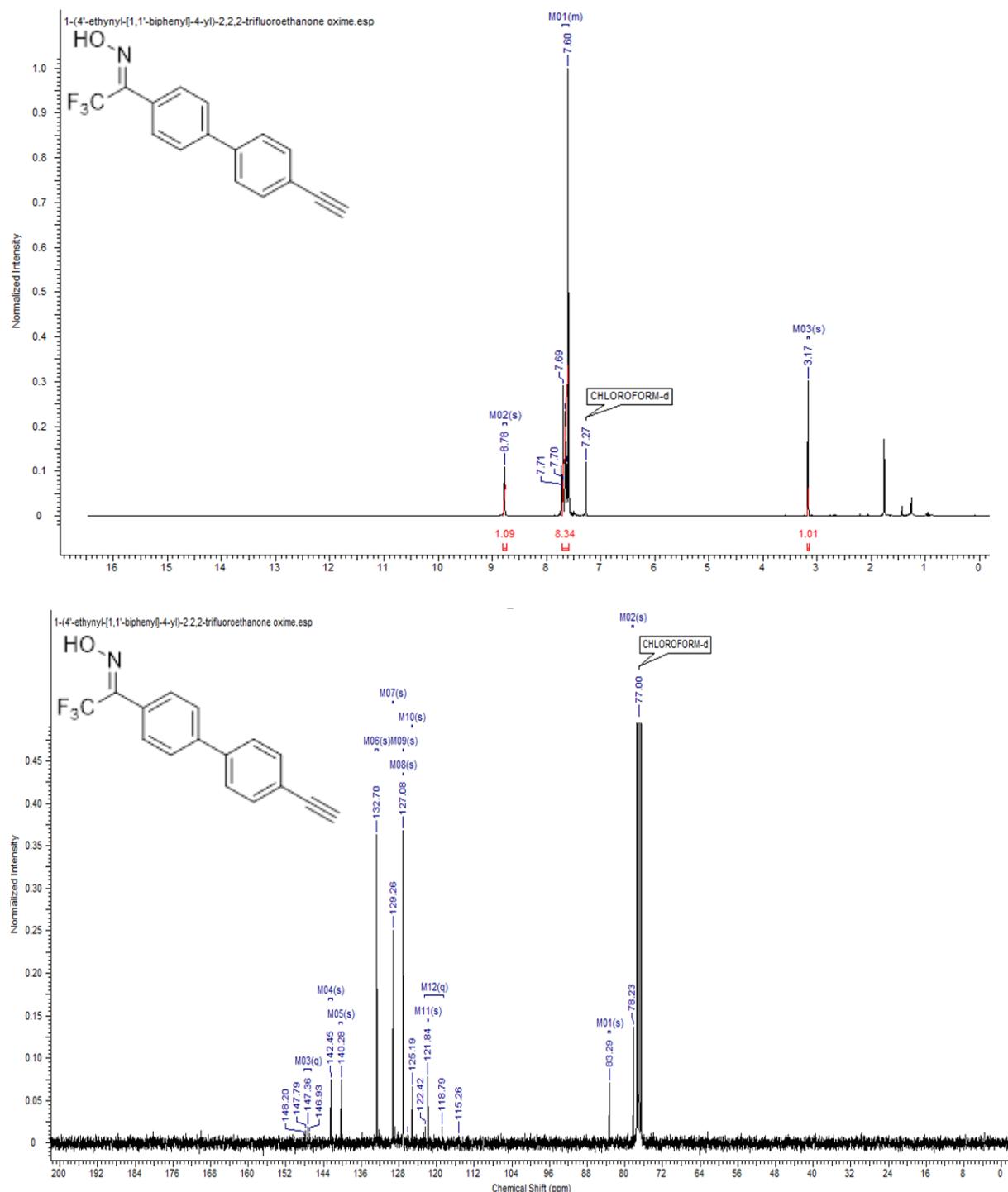
Compound 7i



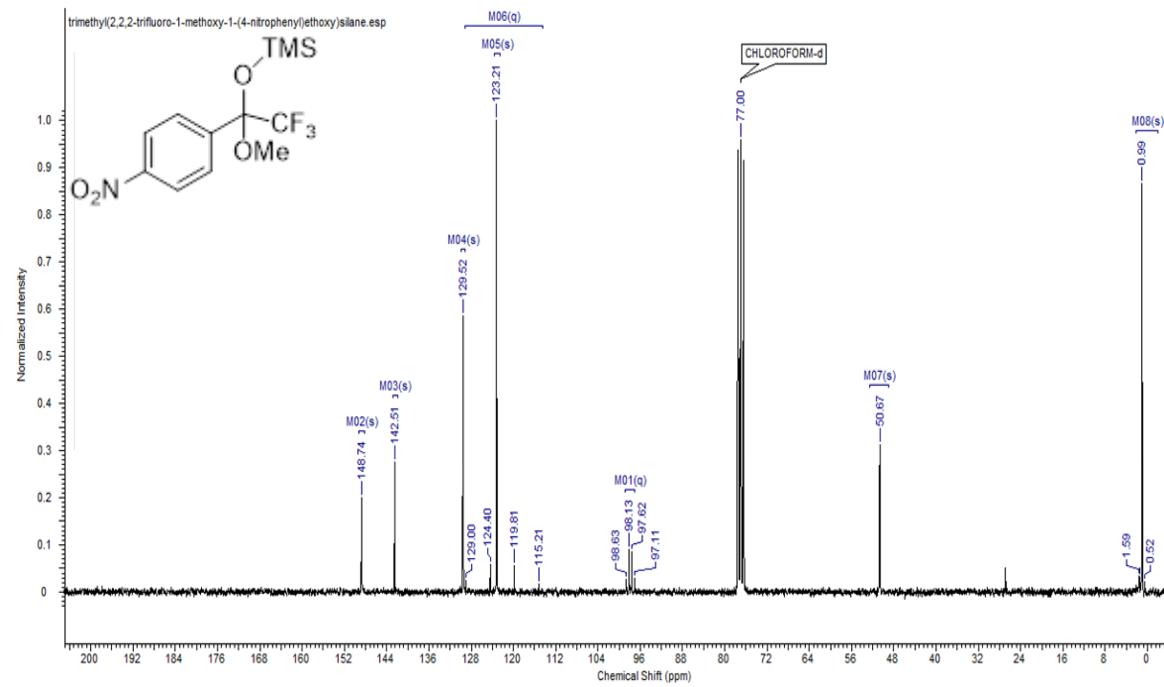
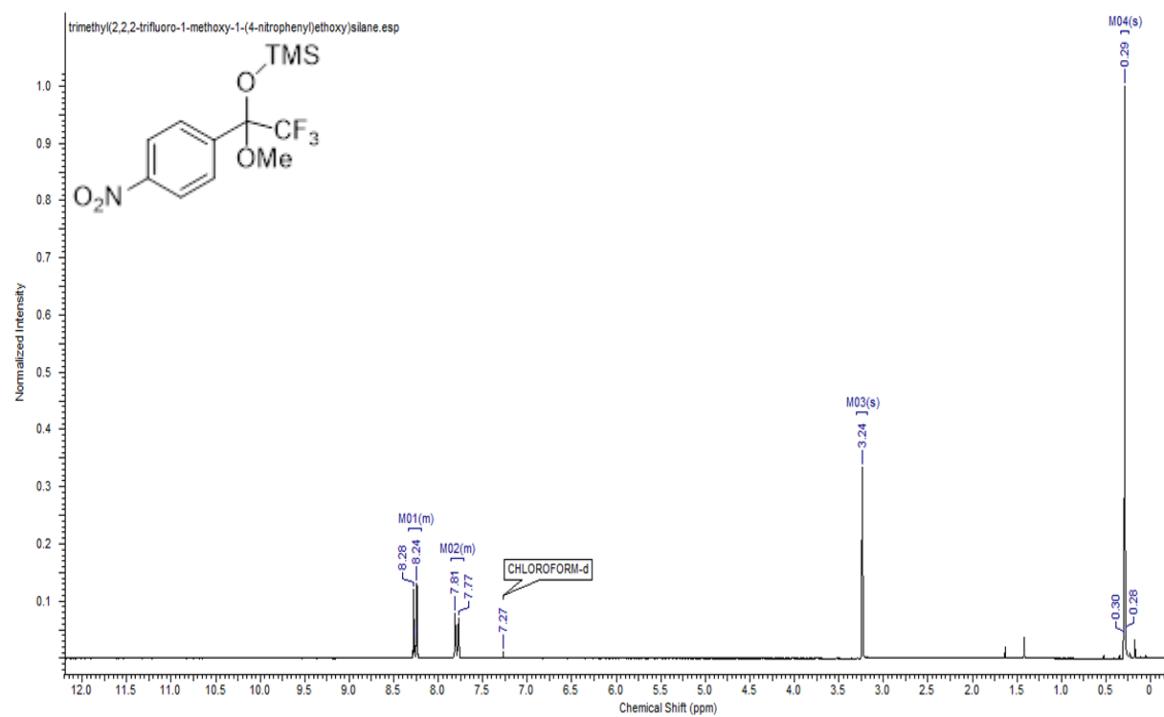
Compound 7j*



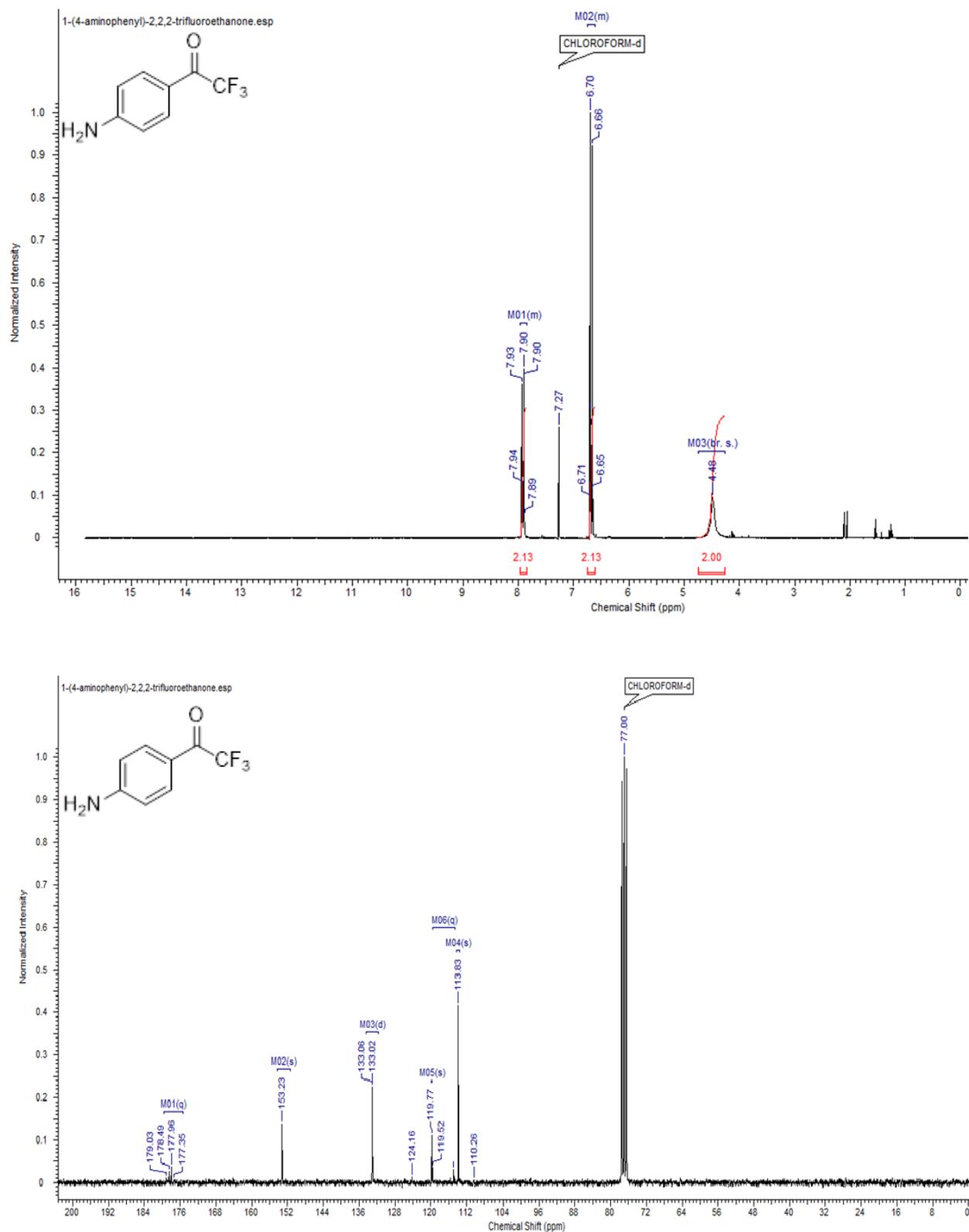
Compound 7j



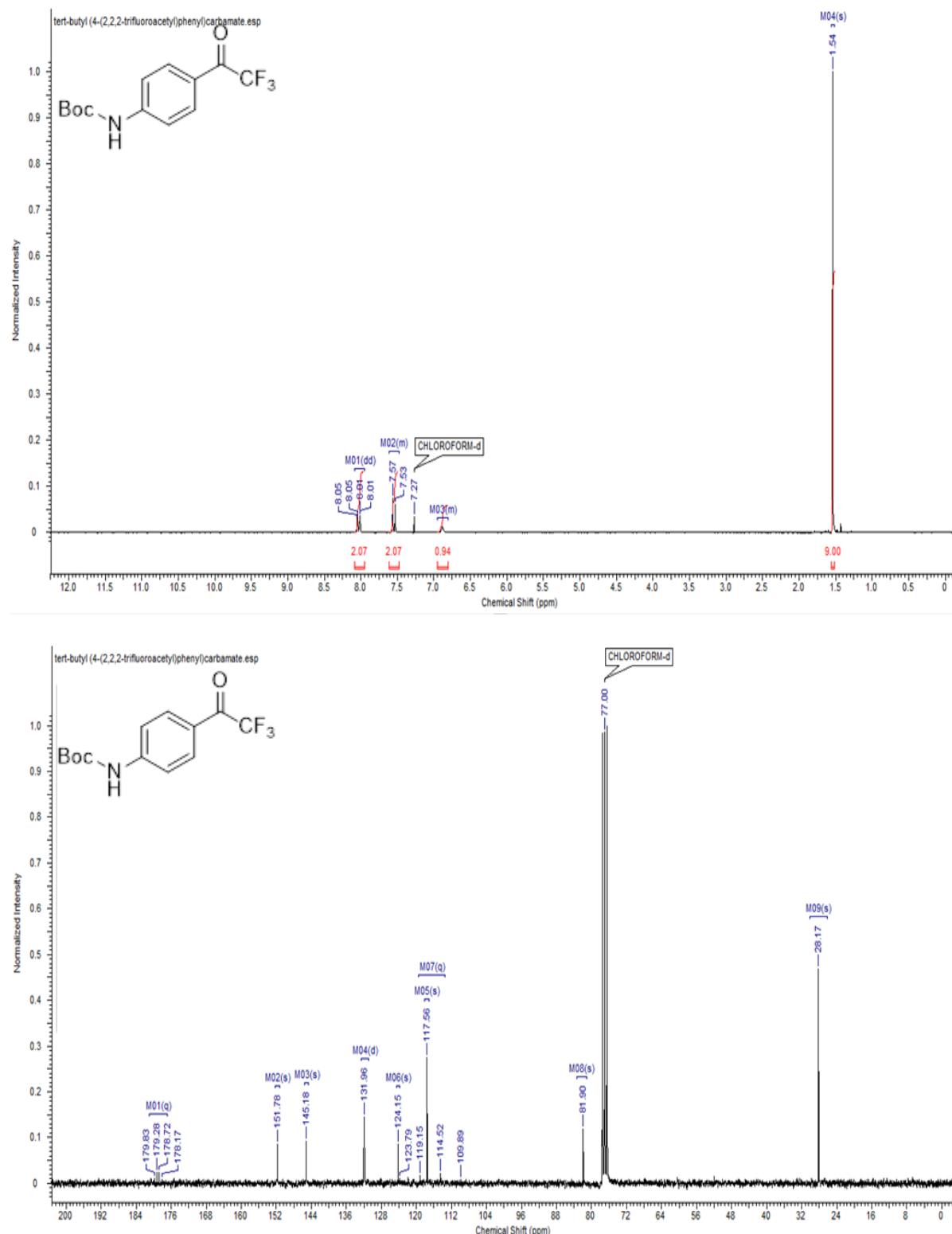
Compound SM1-7k



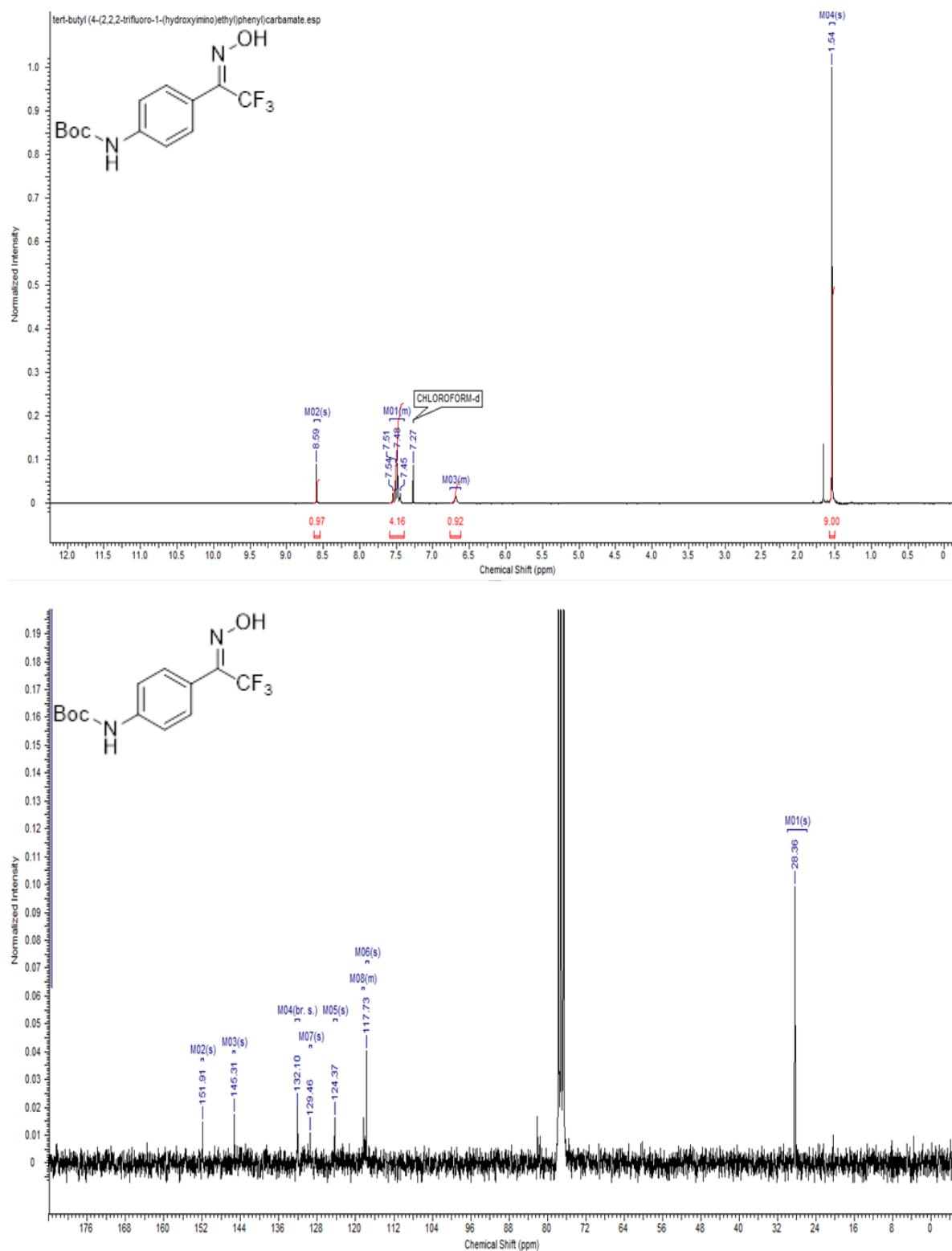
Compound SM2-7k



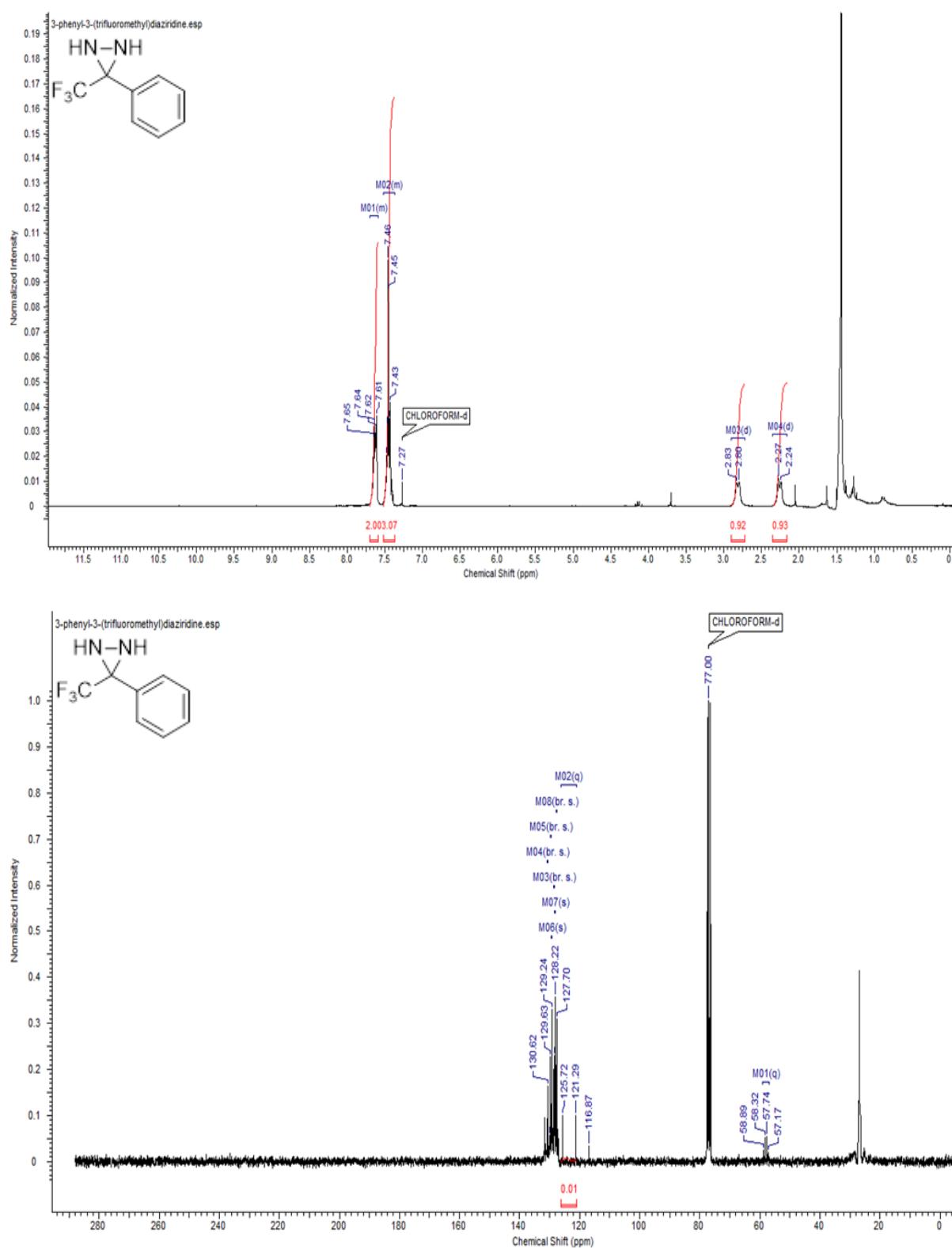
Compound SM3-7k



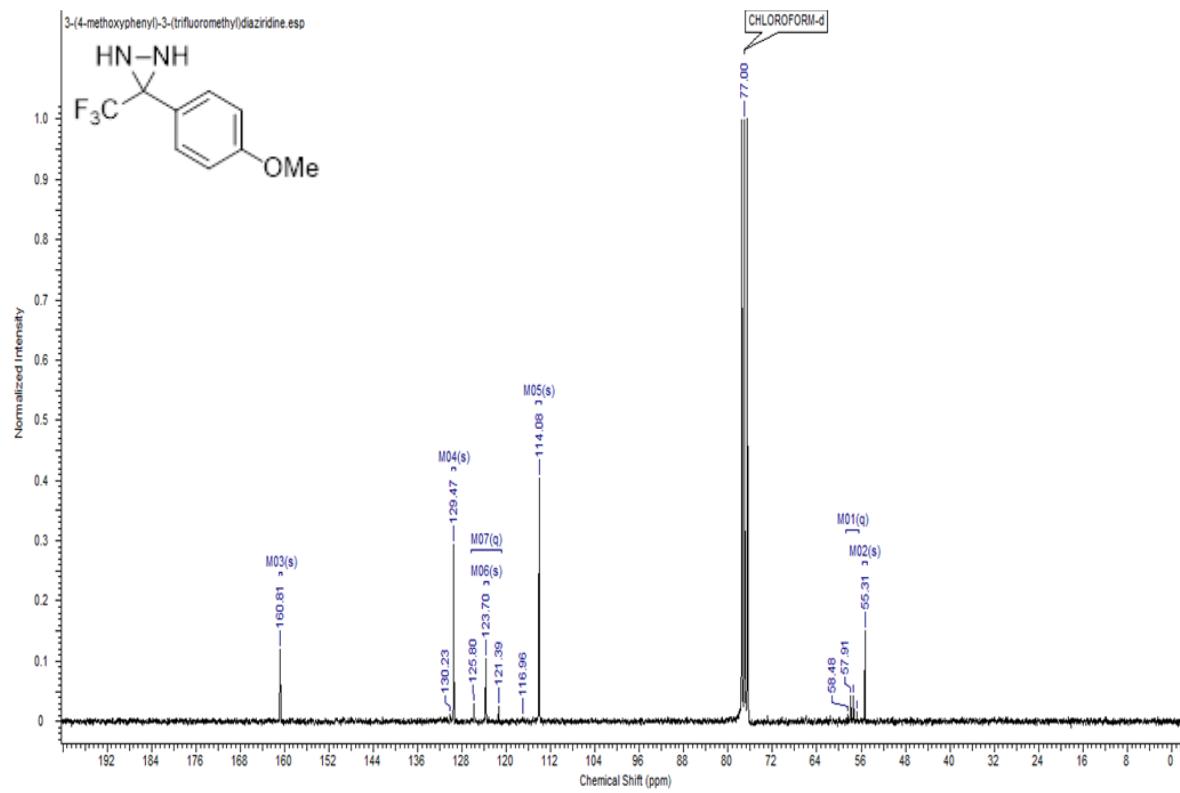
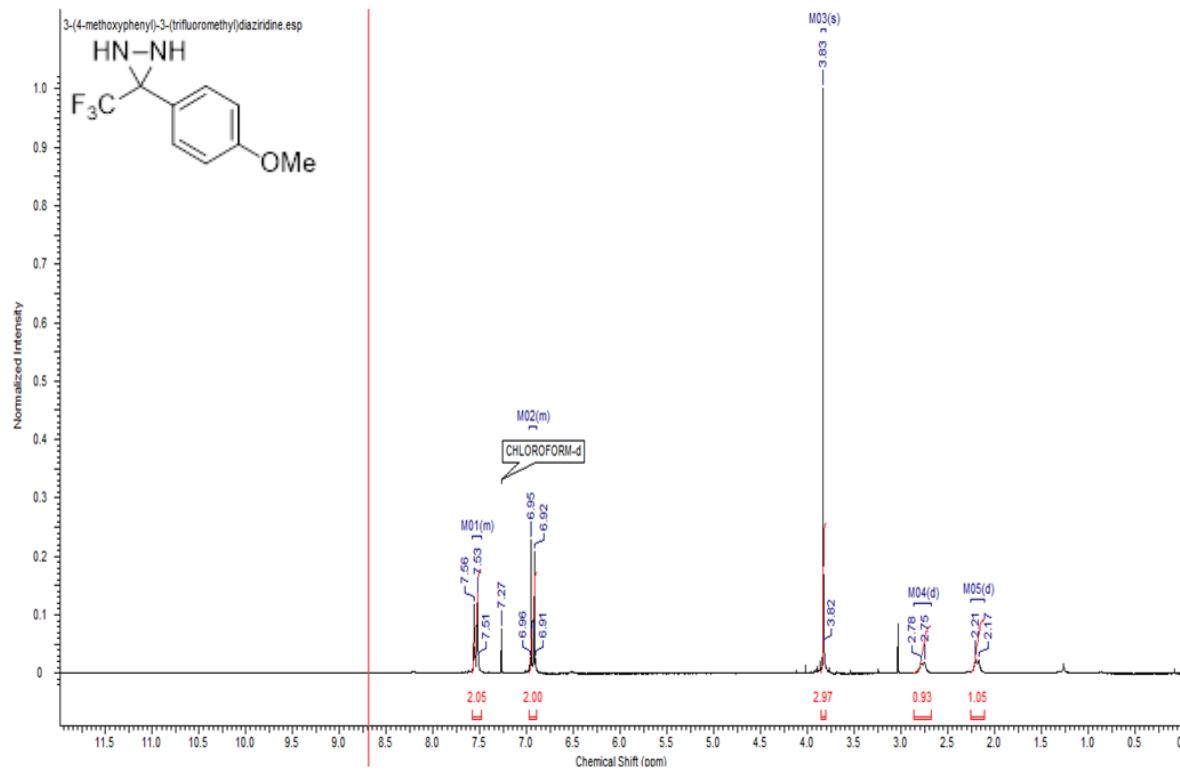
Compound SM4-7k



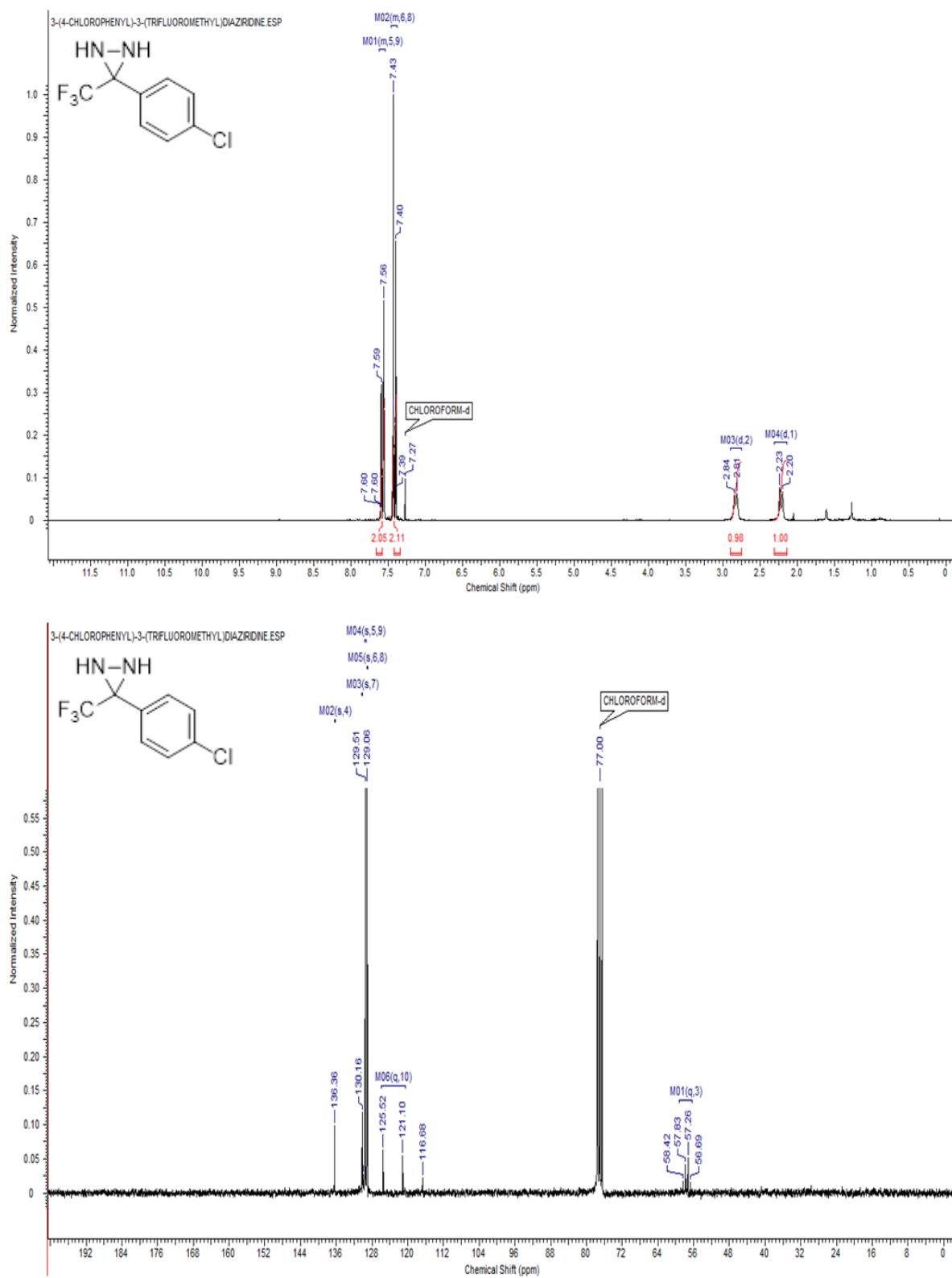
Compound 5a



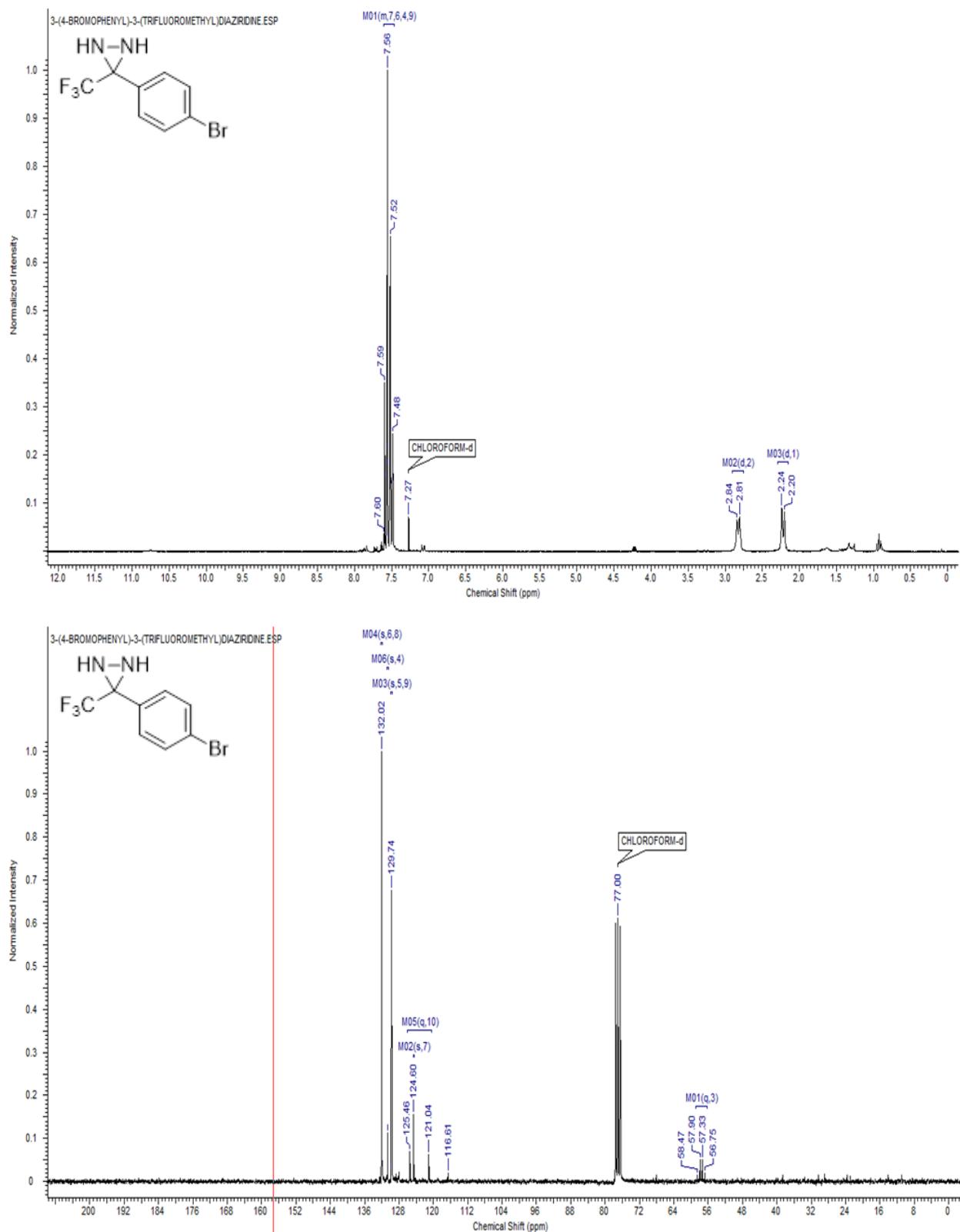
Compound 5b



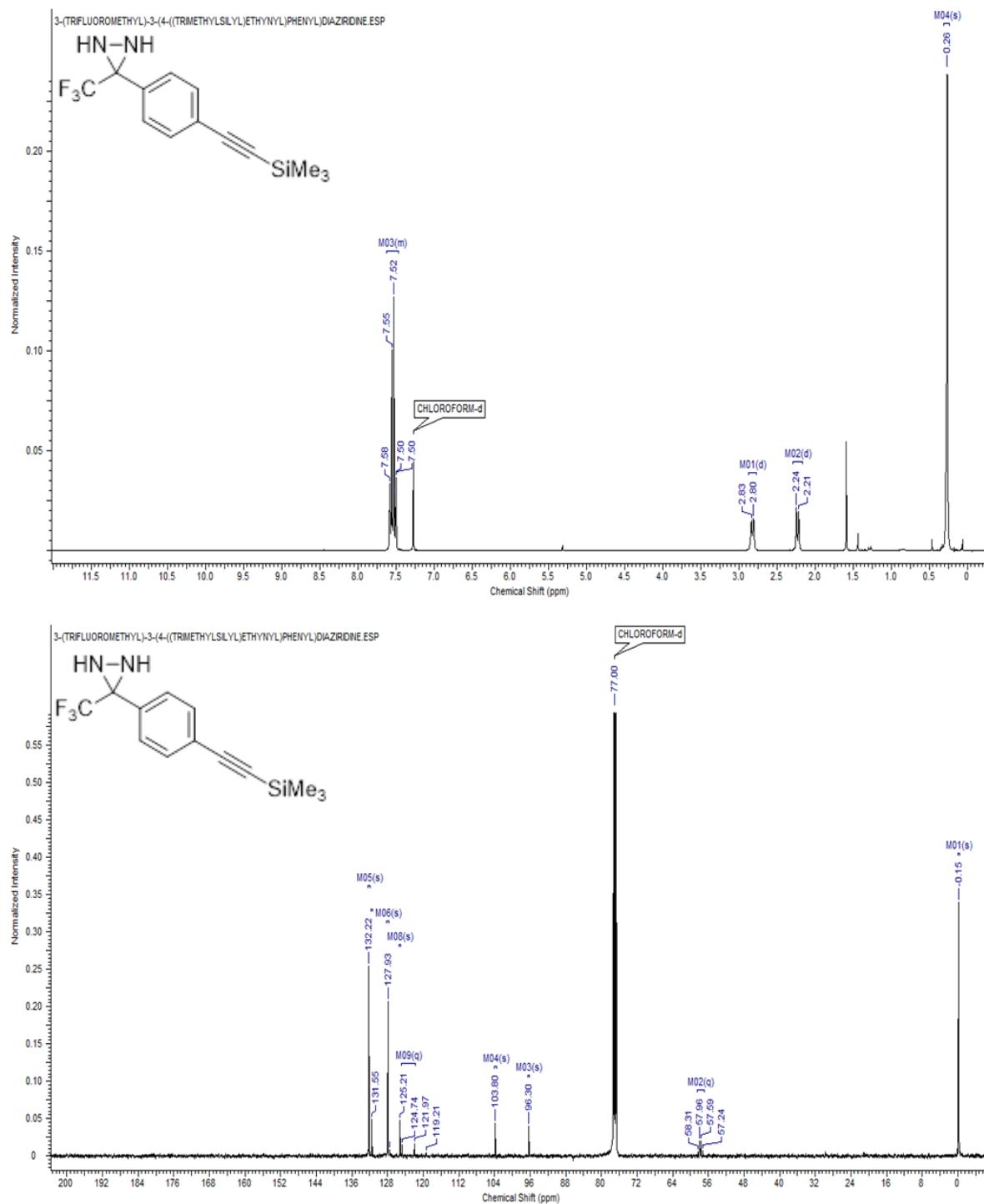
Compound 5c



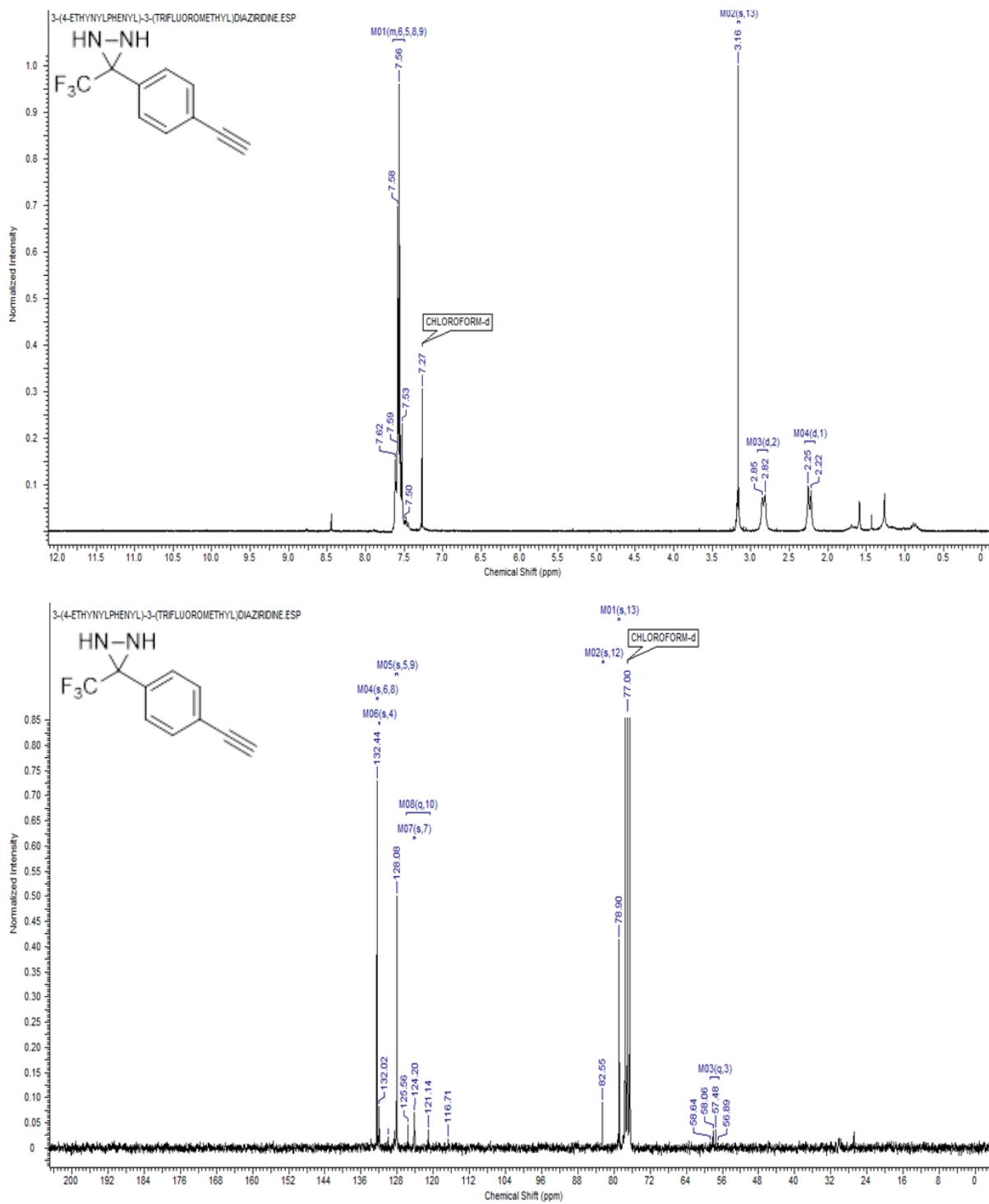
Compound 5d



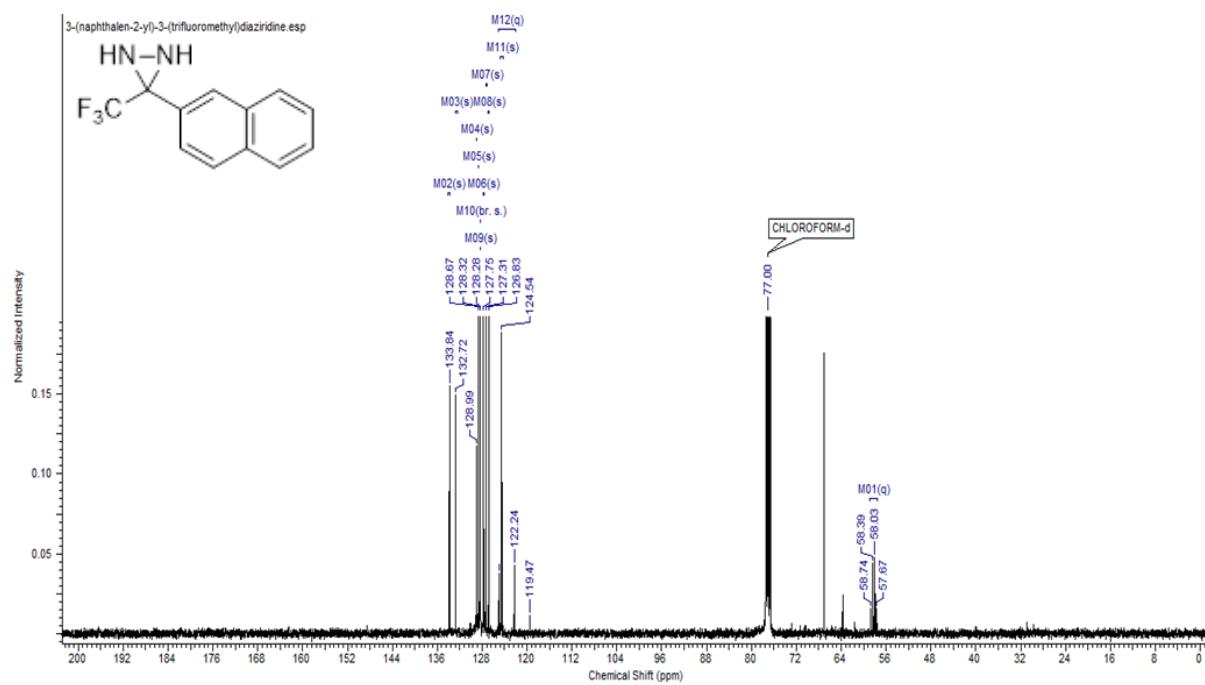
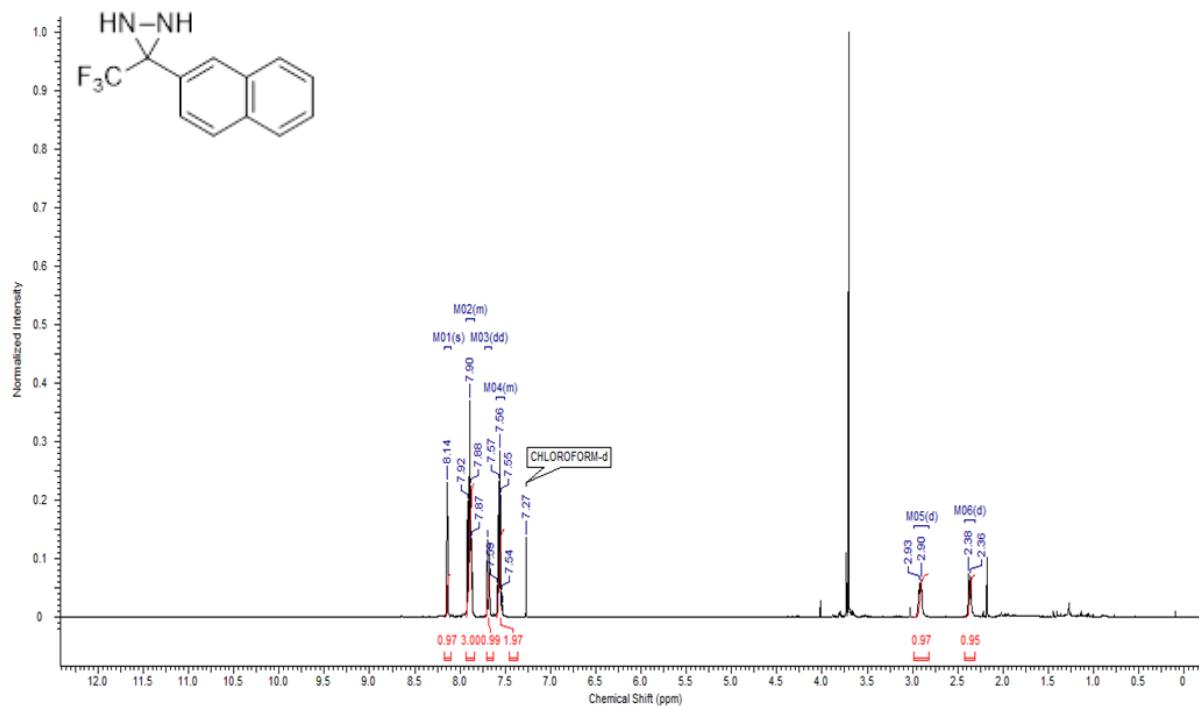
Compound 5e



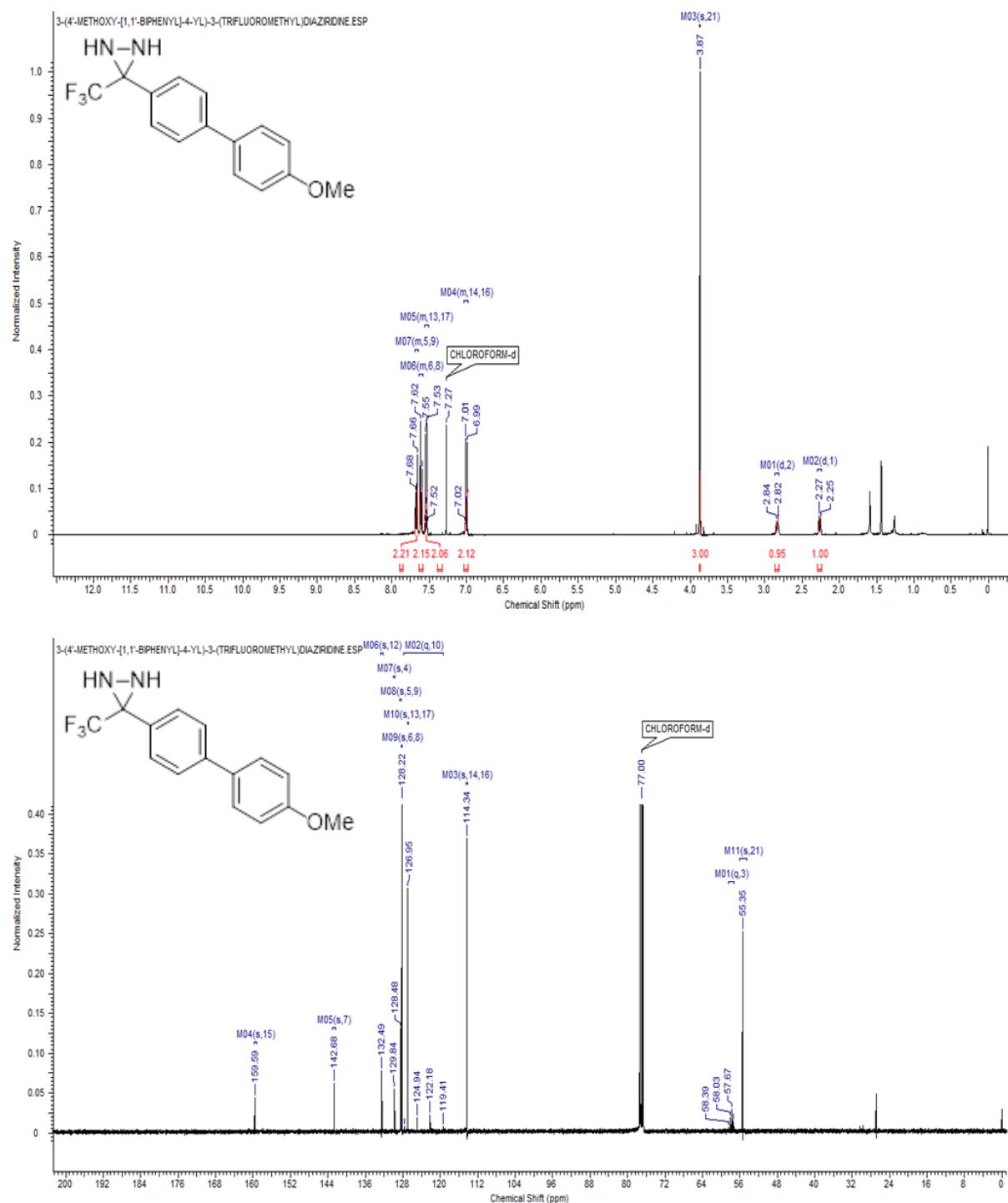
Compound 5f



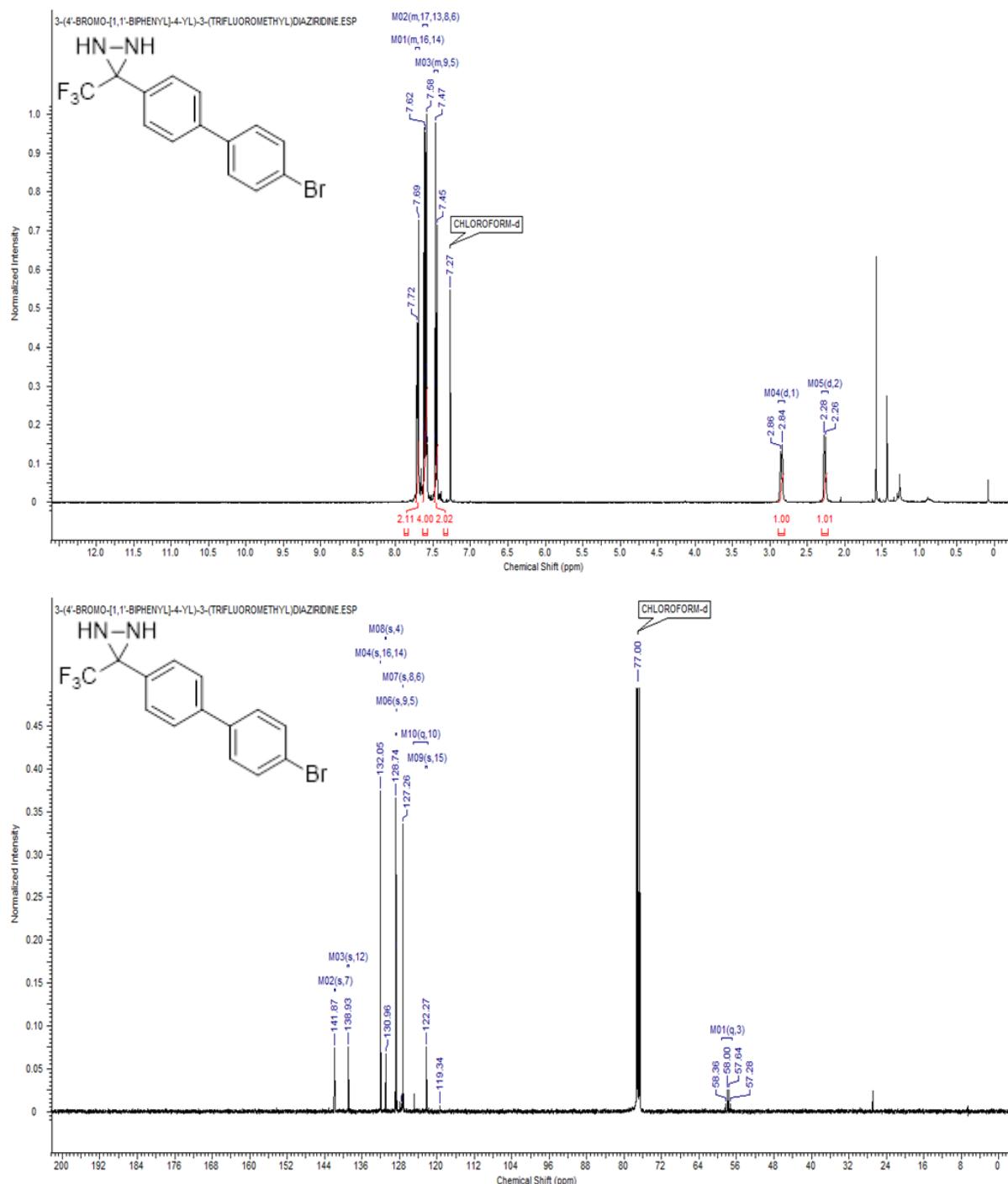
Compound 5g



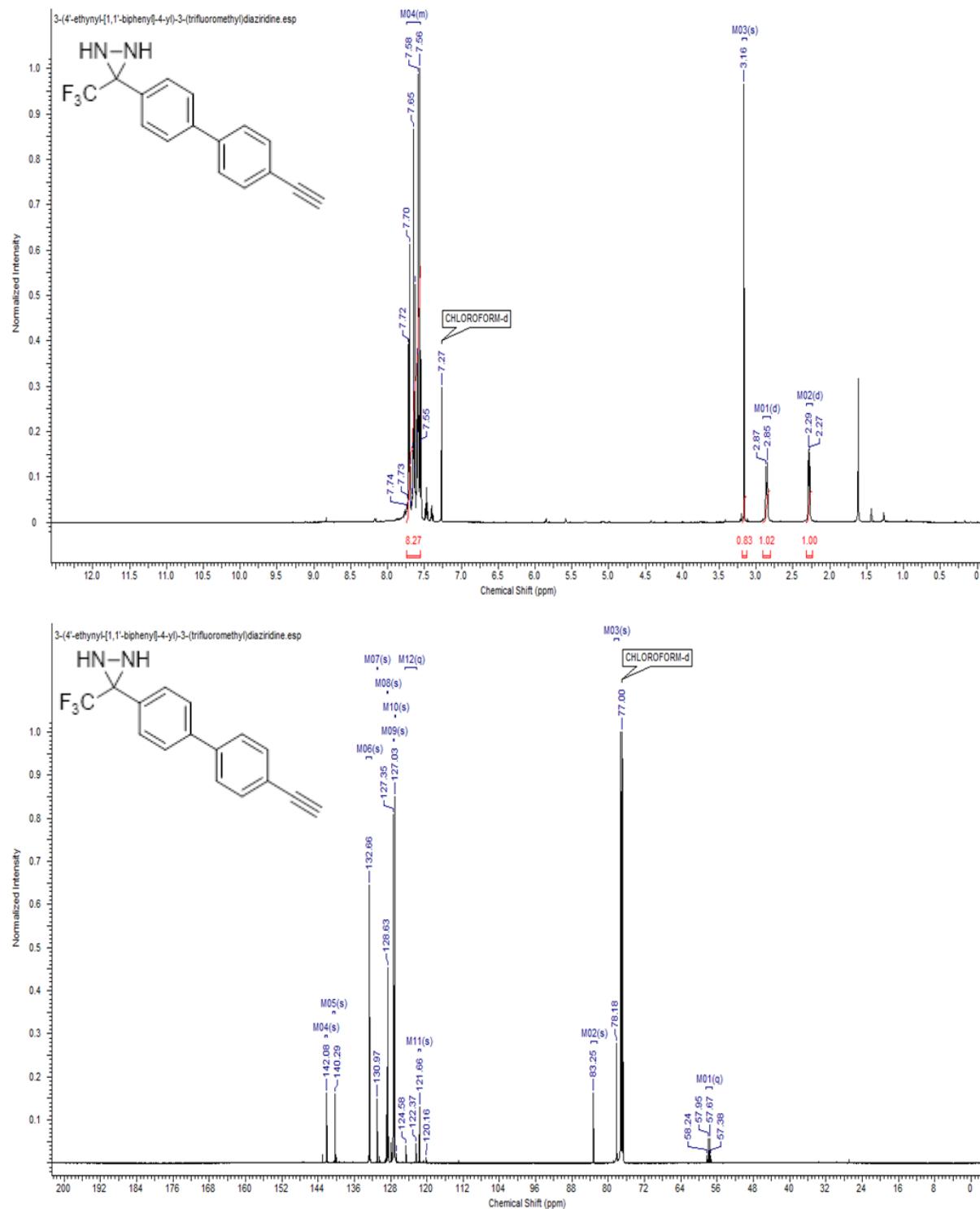
Compound 5h



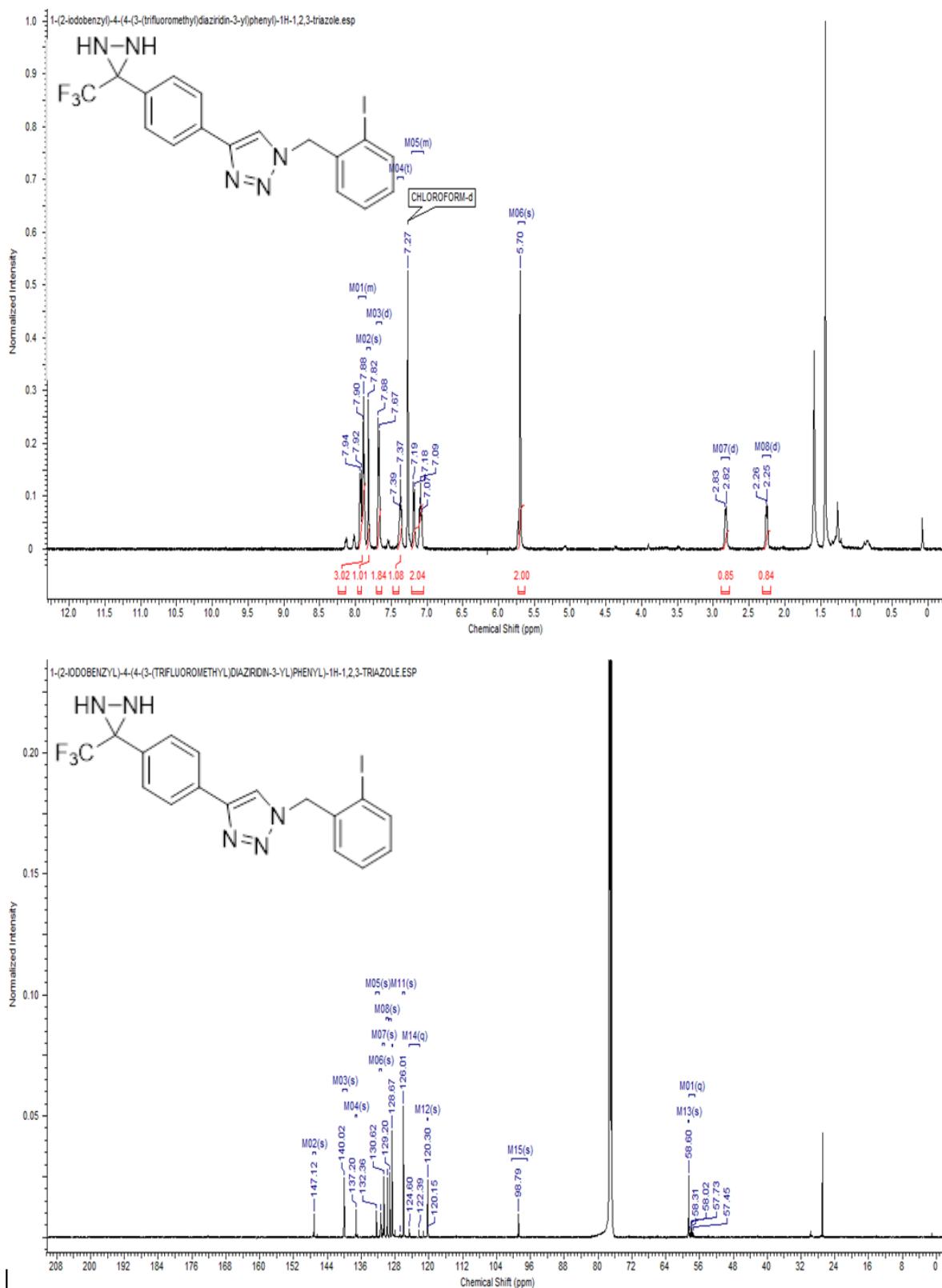
Compound 5i



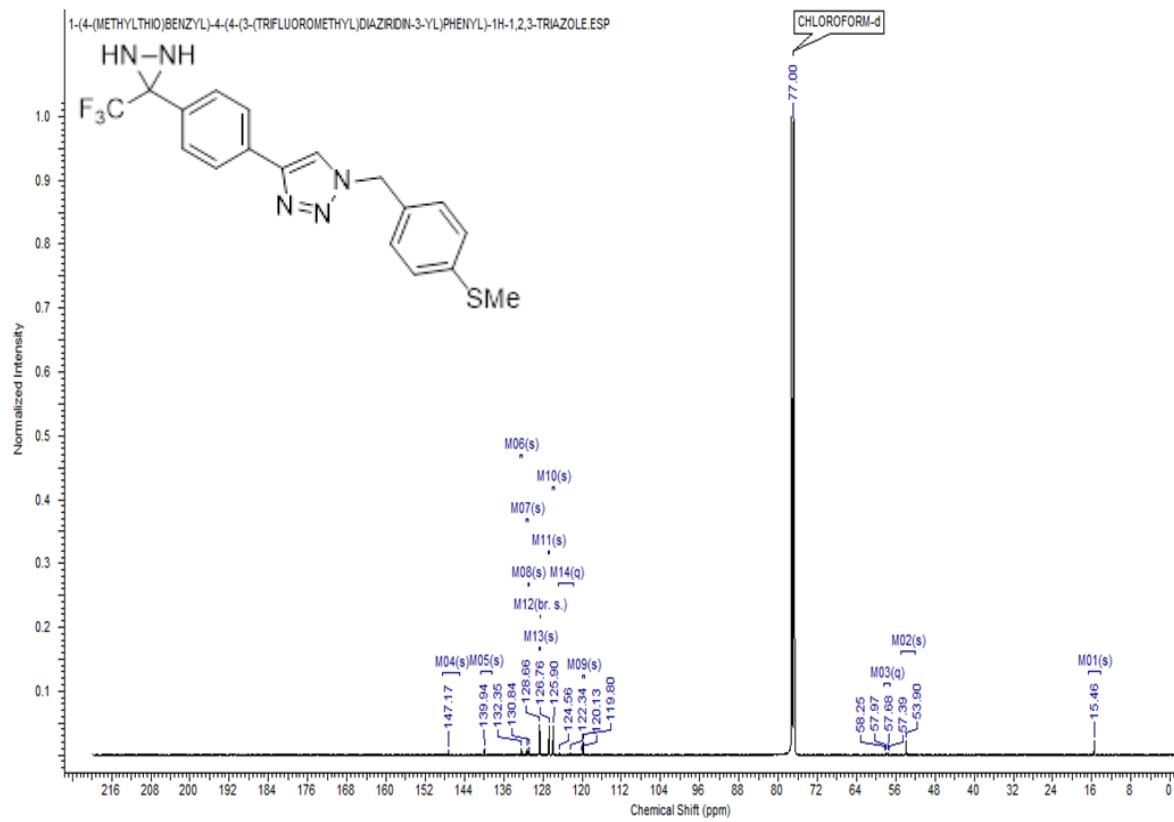
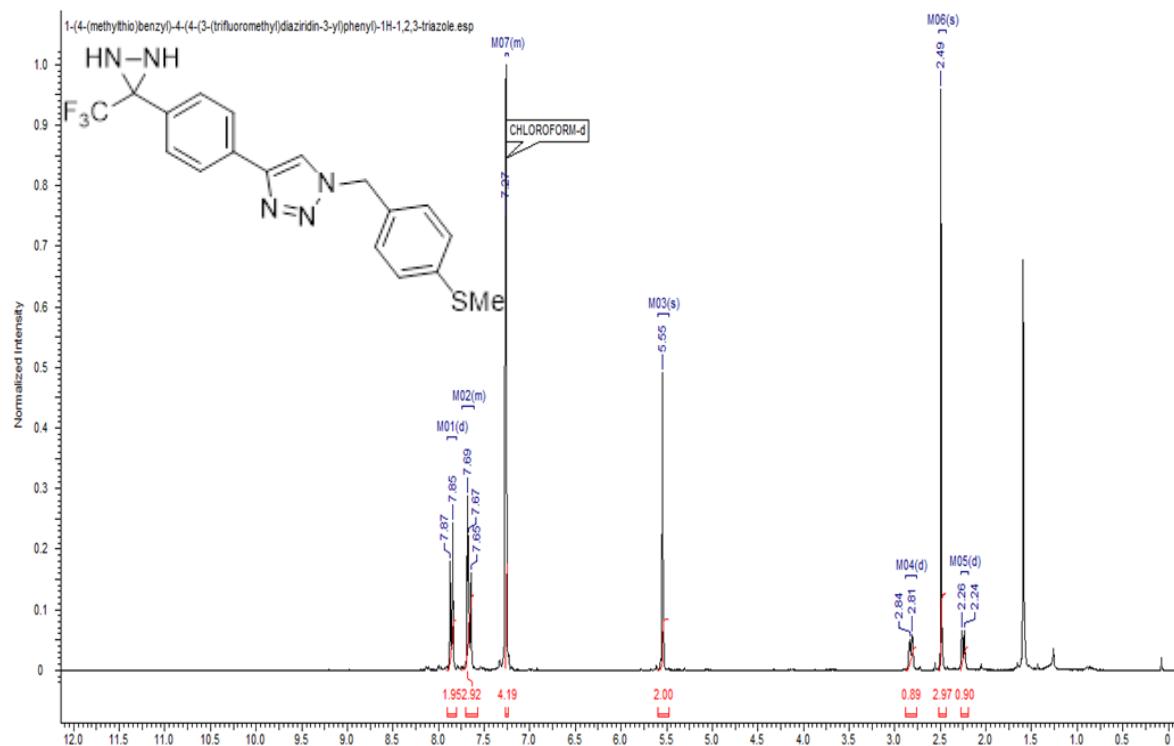
Compound 5j



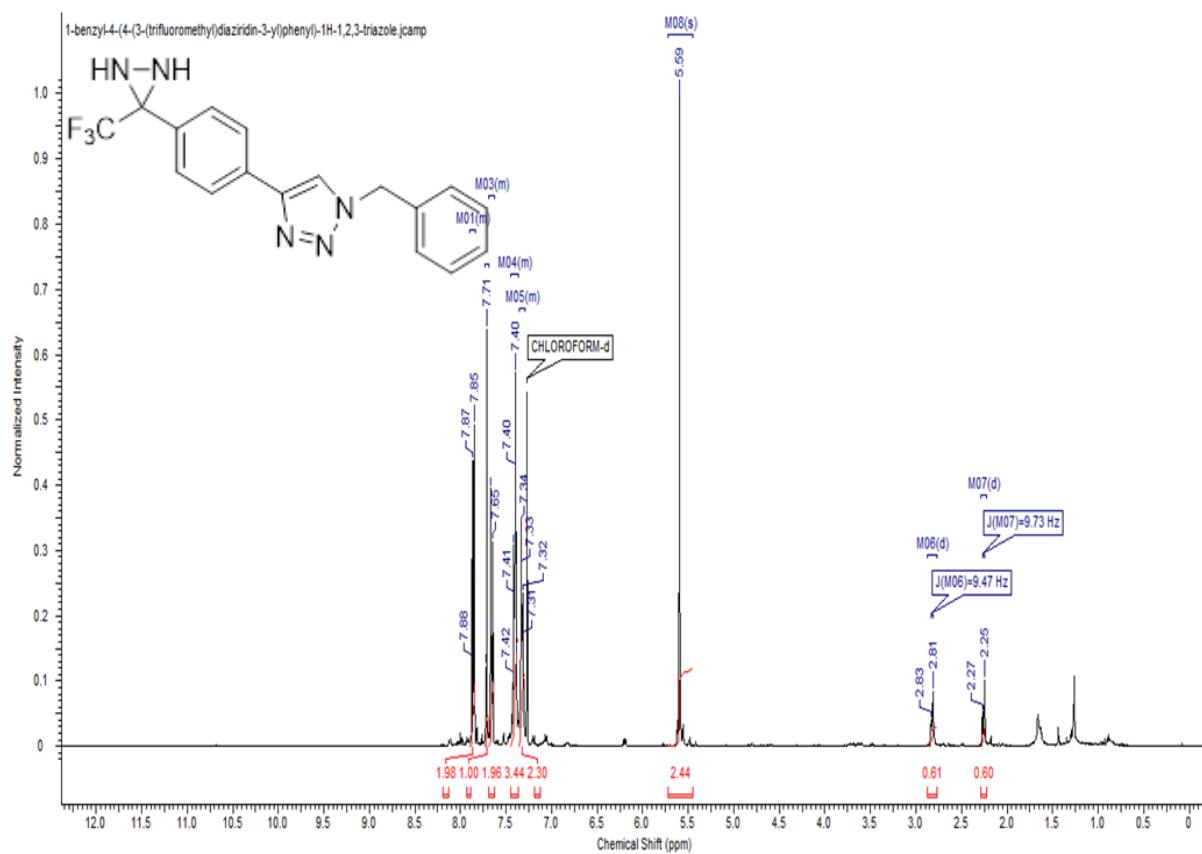
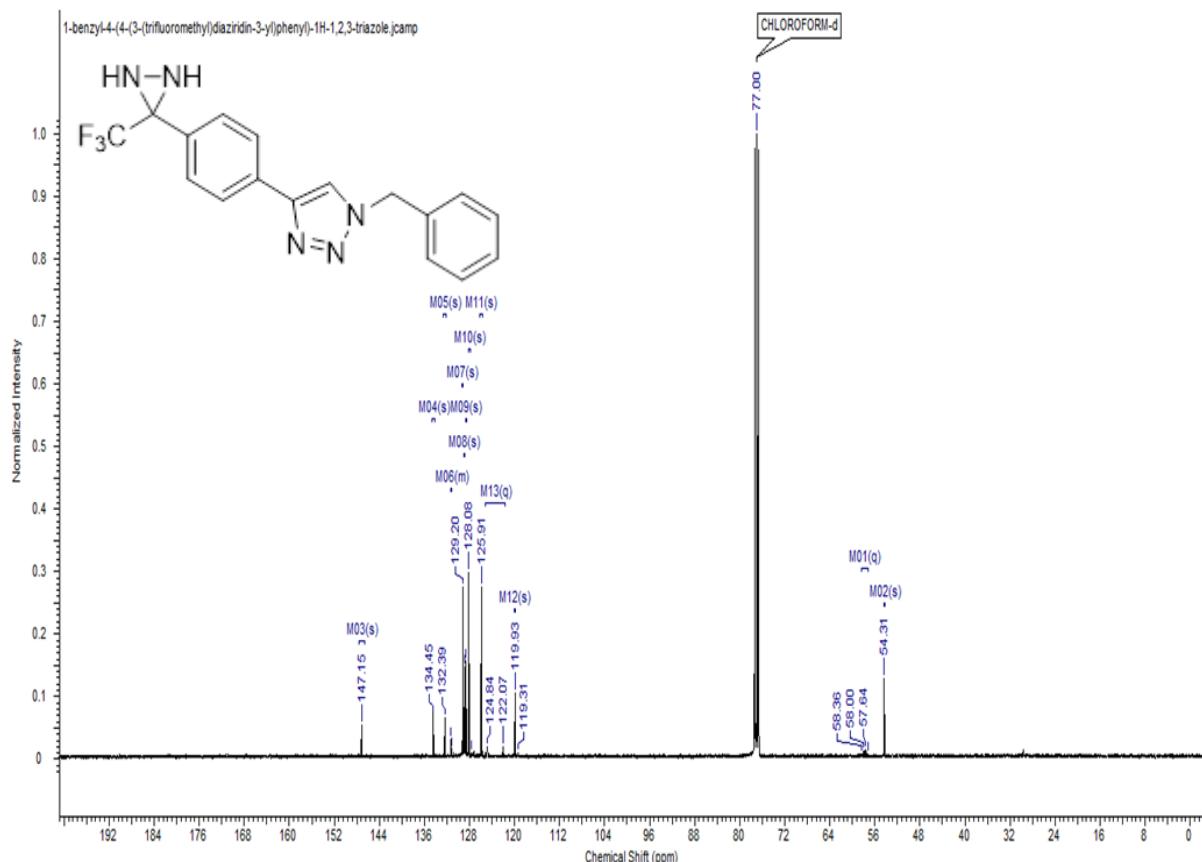
Compound 51



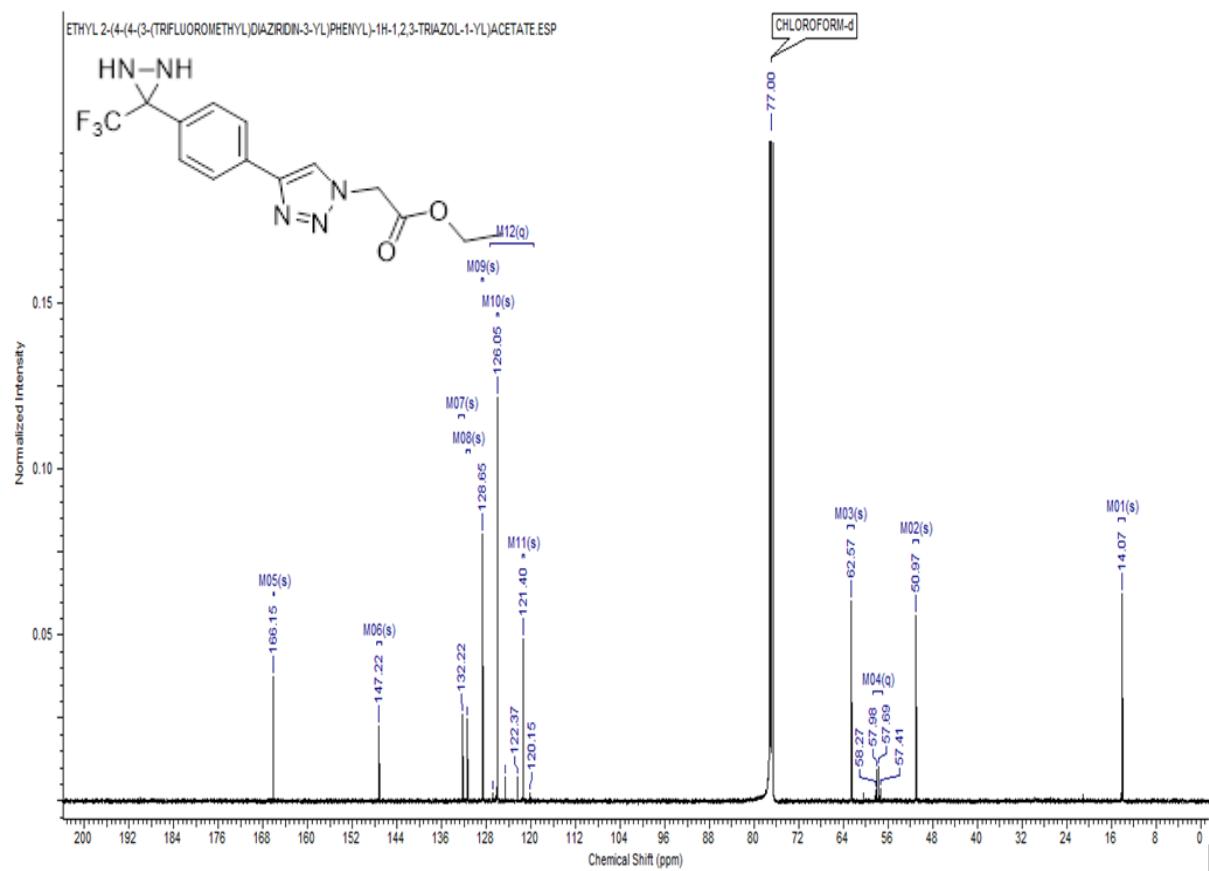
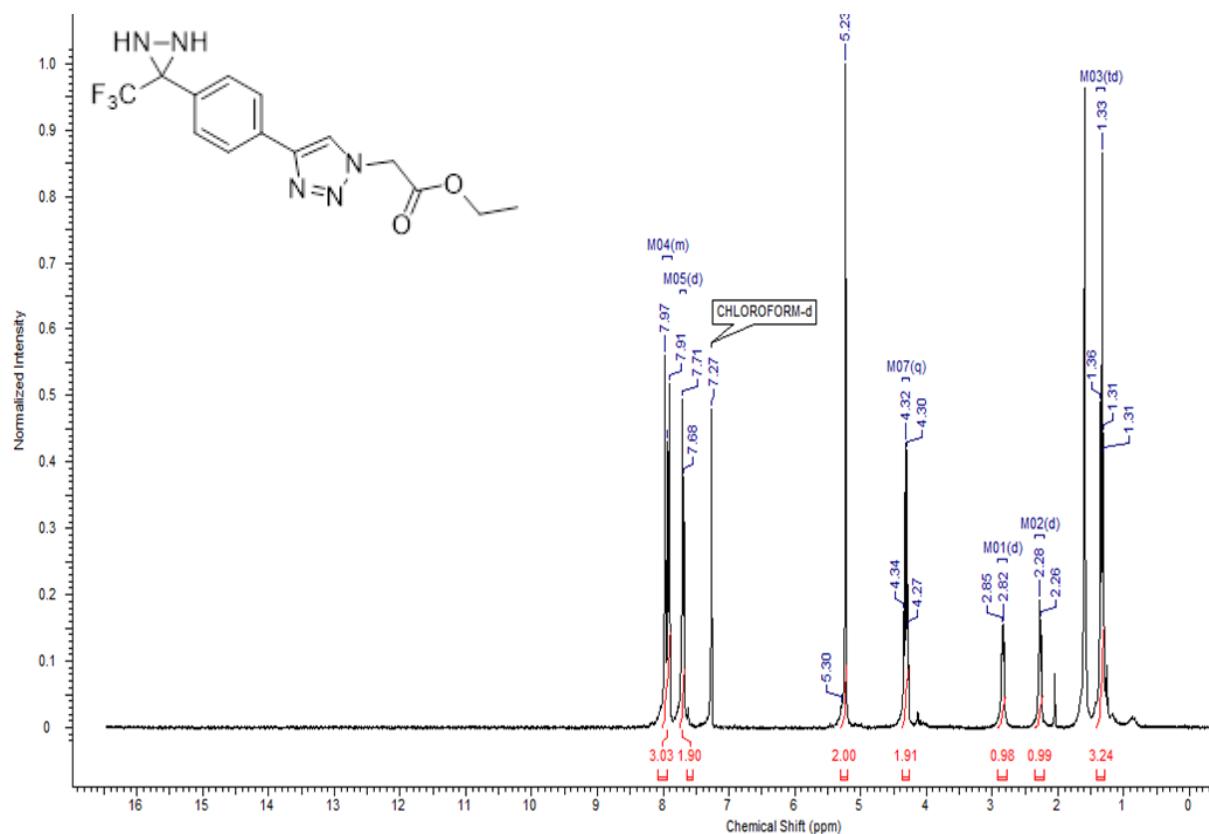
Compound 5m



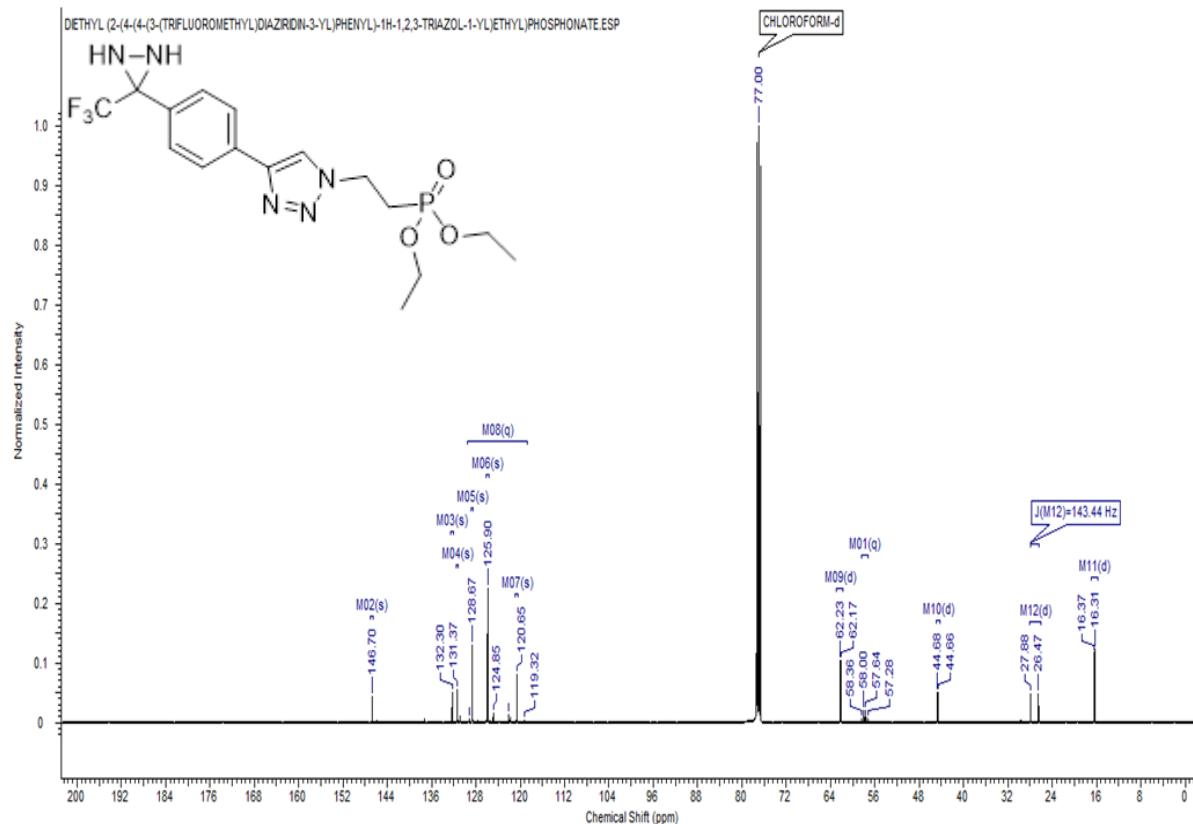
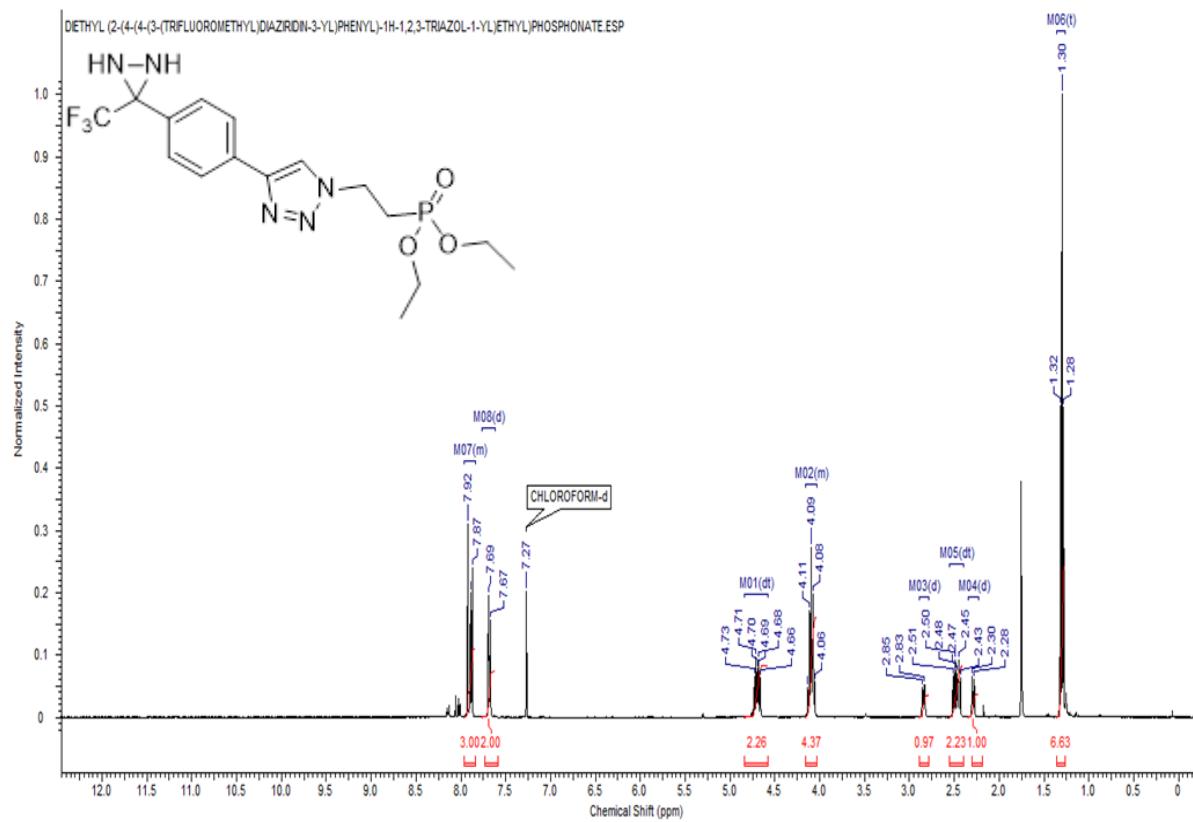
Compound 5n



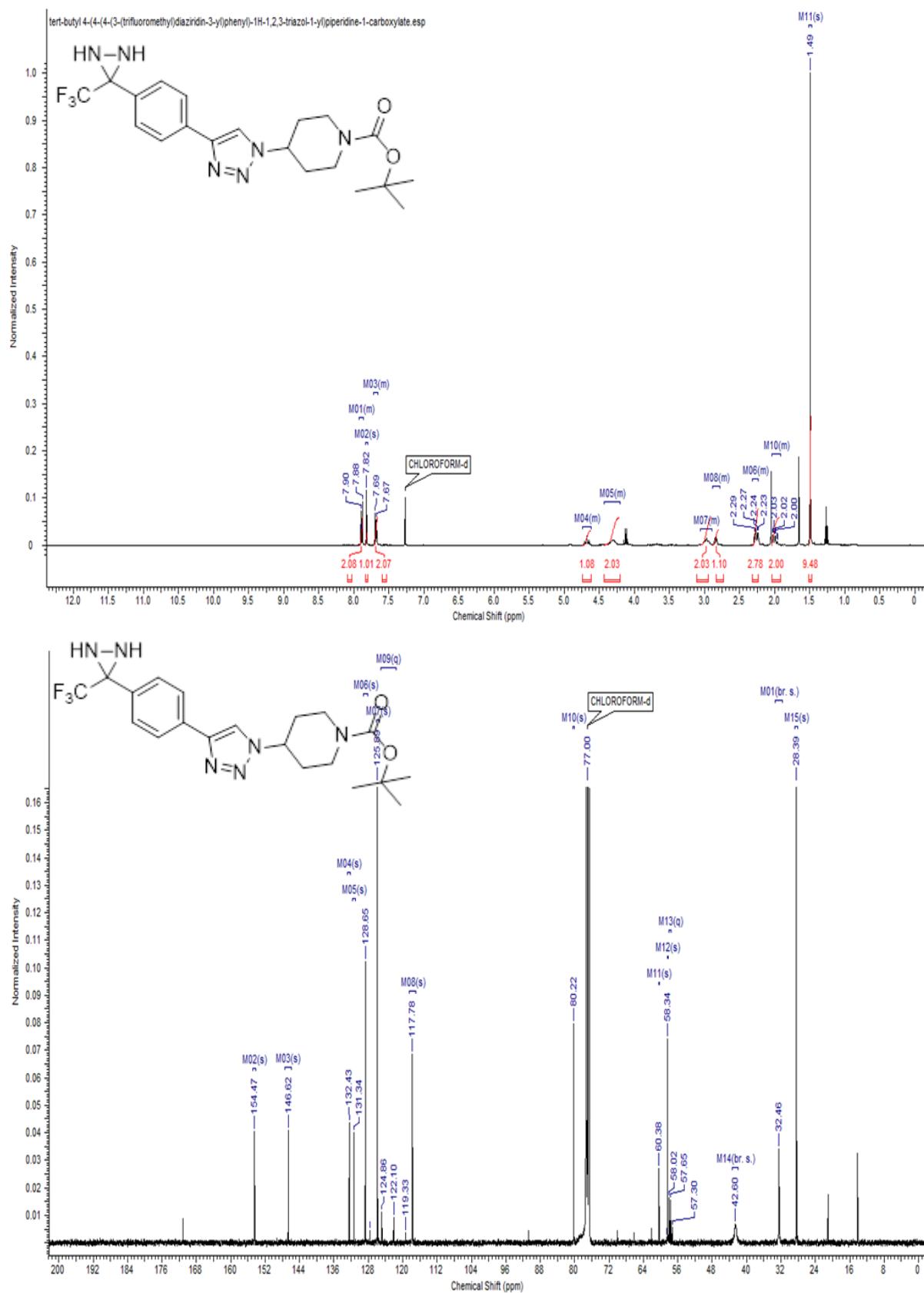
Compound 5o



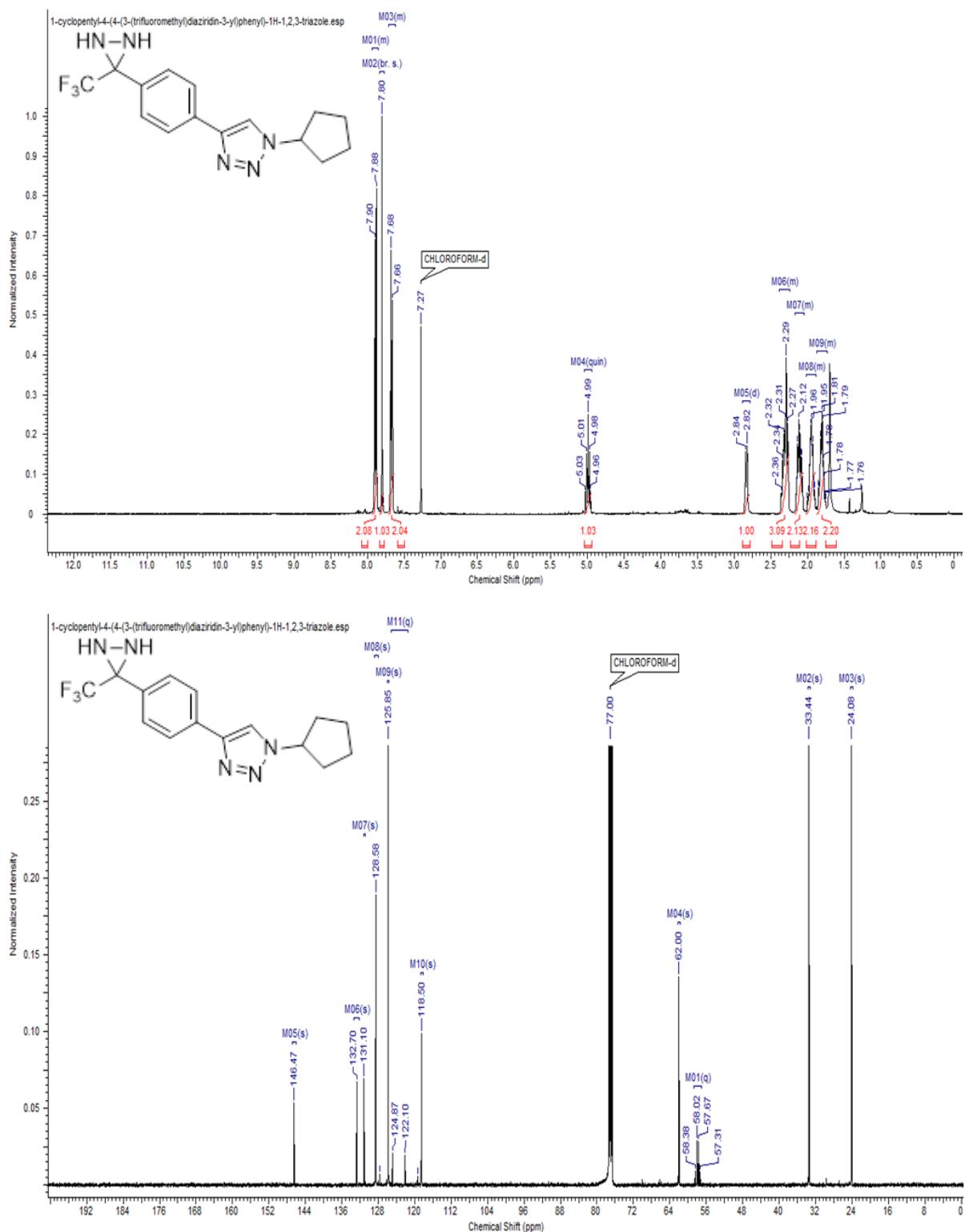
Compound 5p



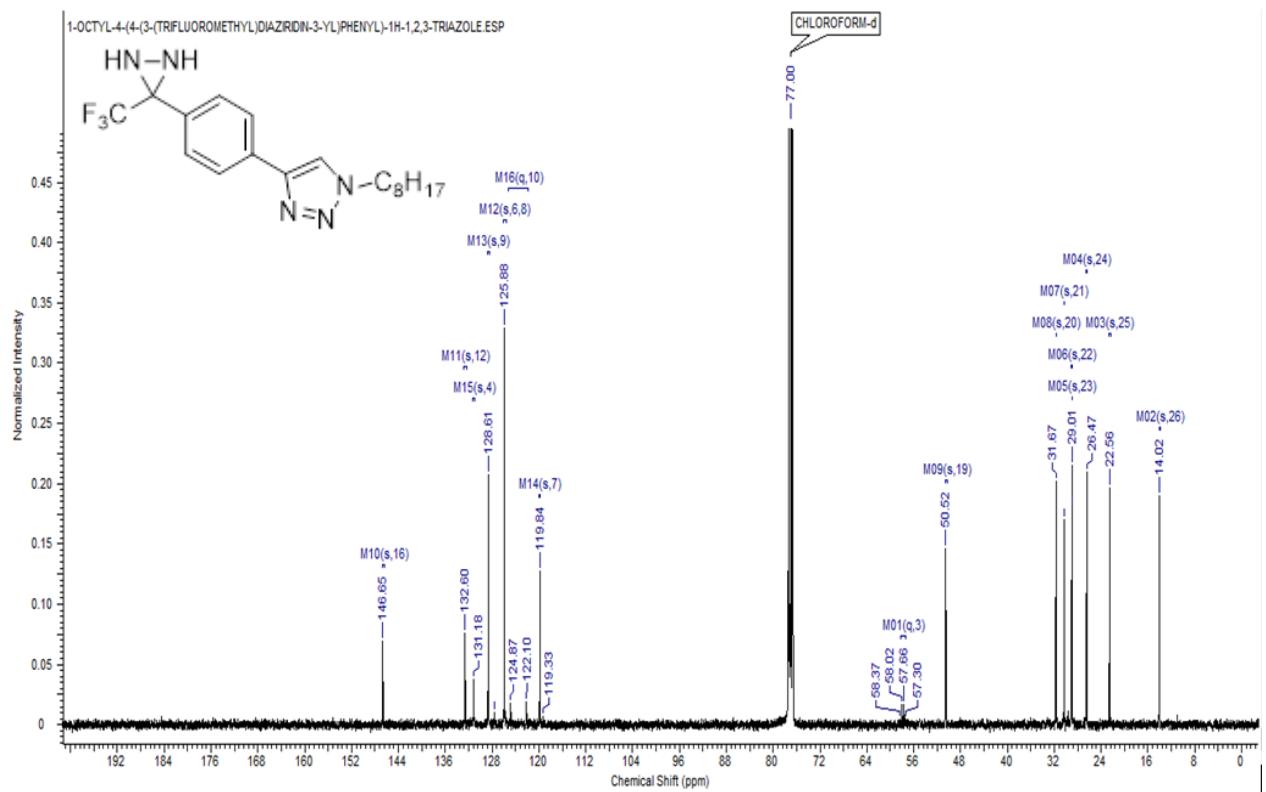
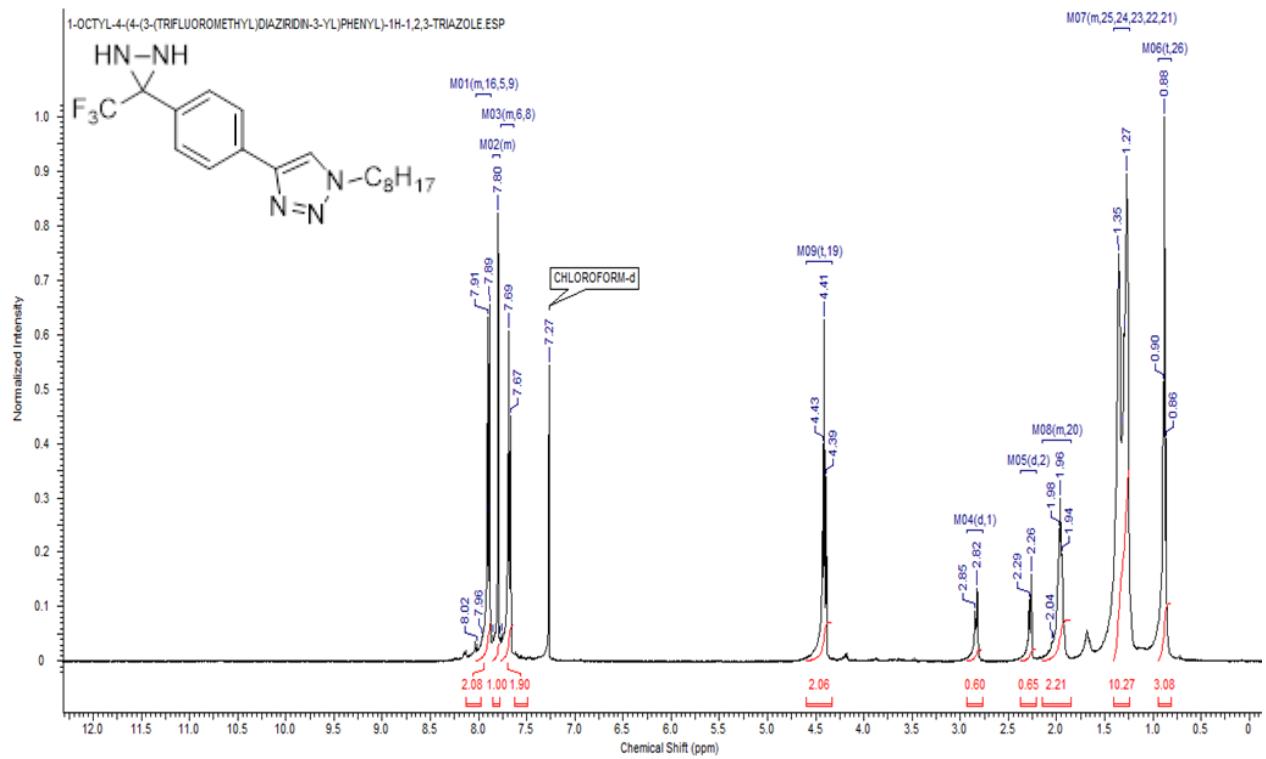
Compound 5q



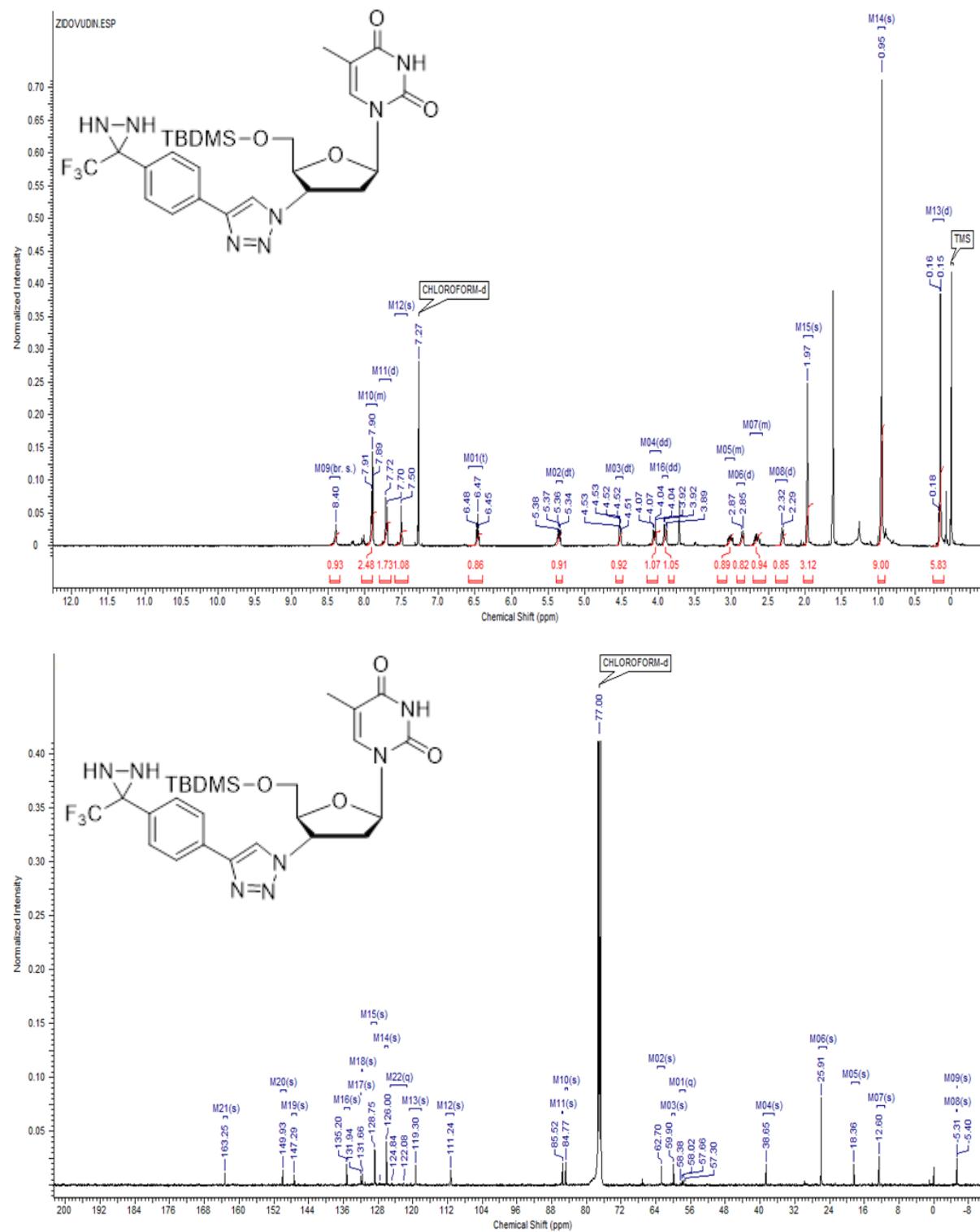
Compound 5s



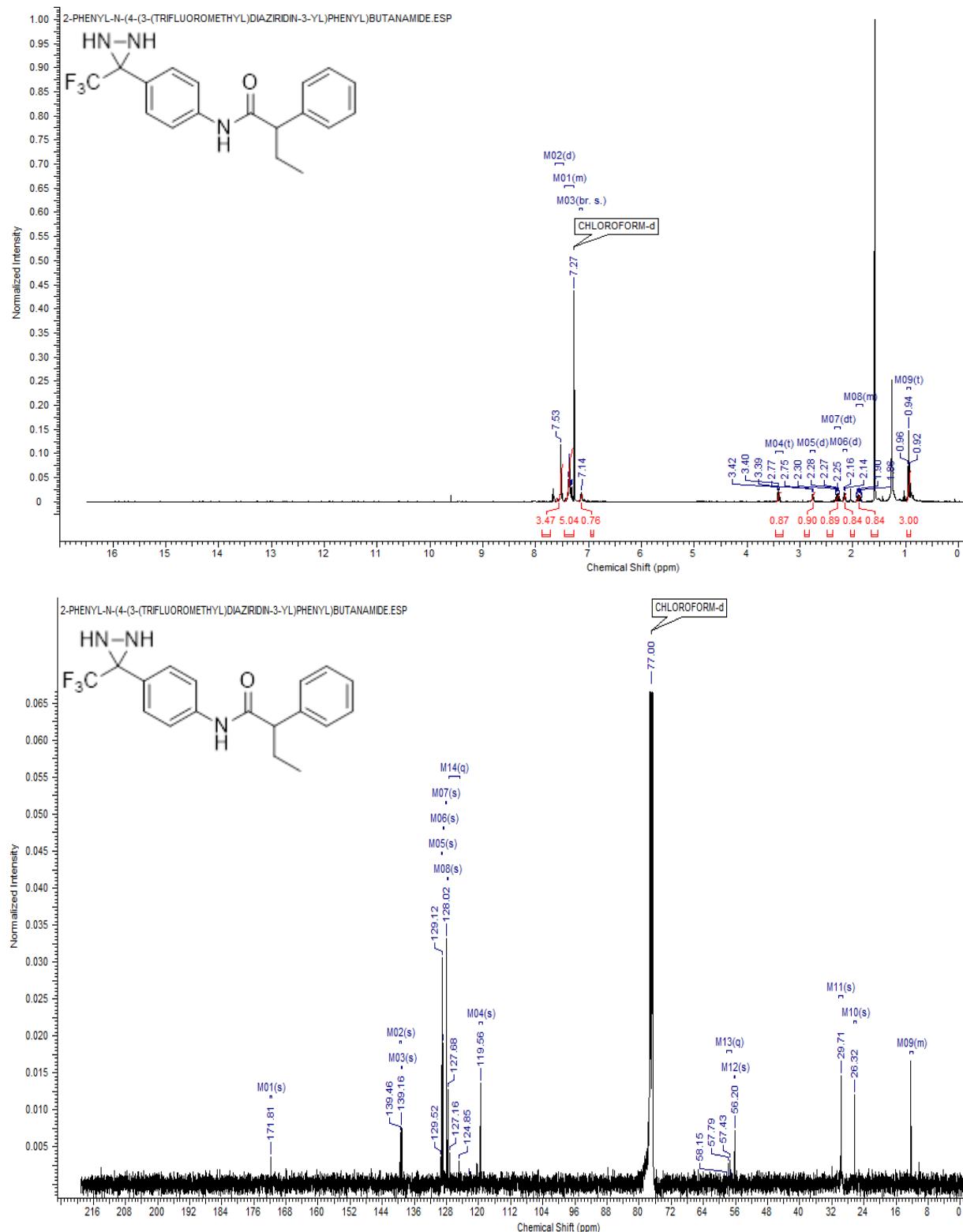
Compound 5t



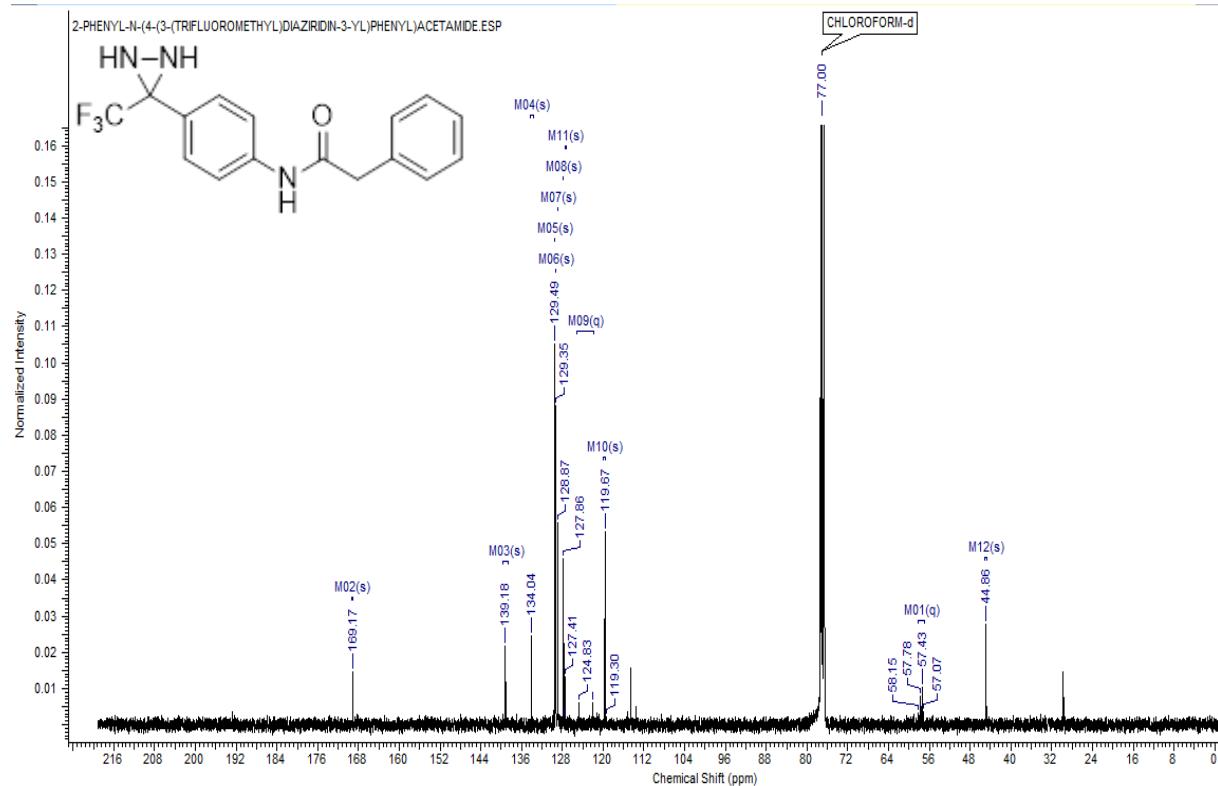
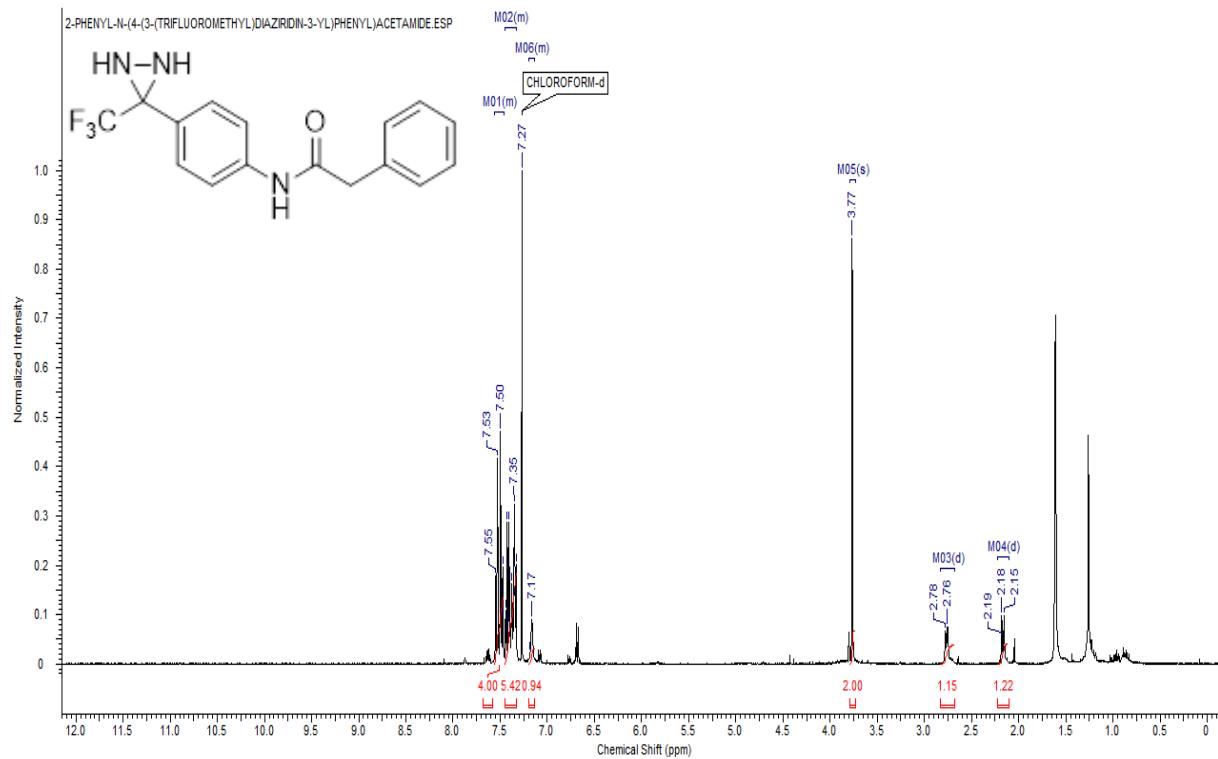
Compound 5u



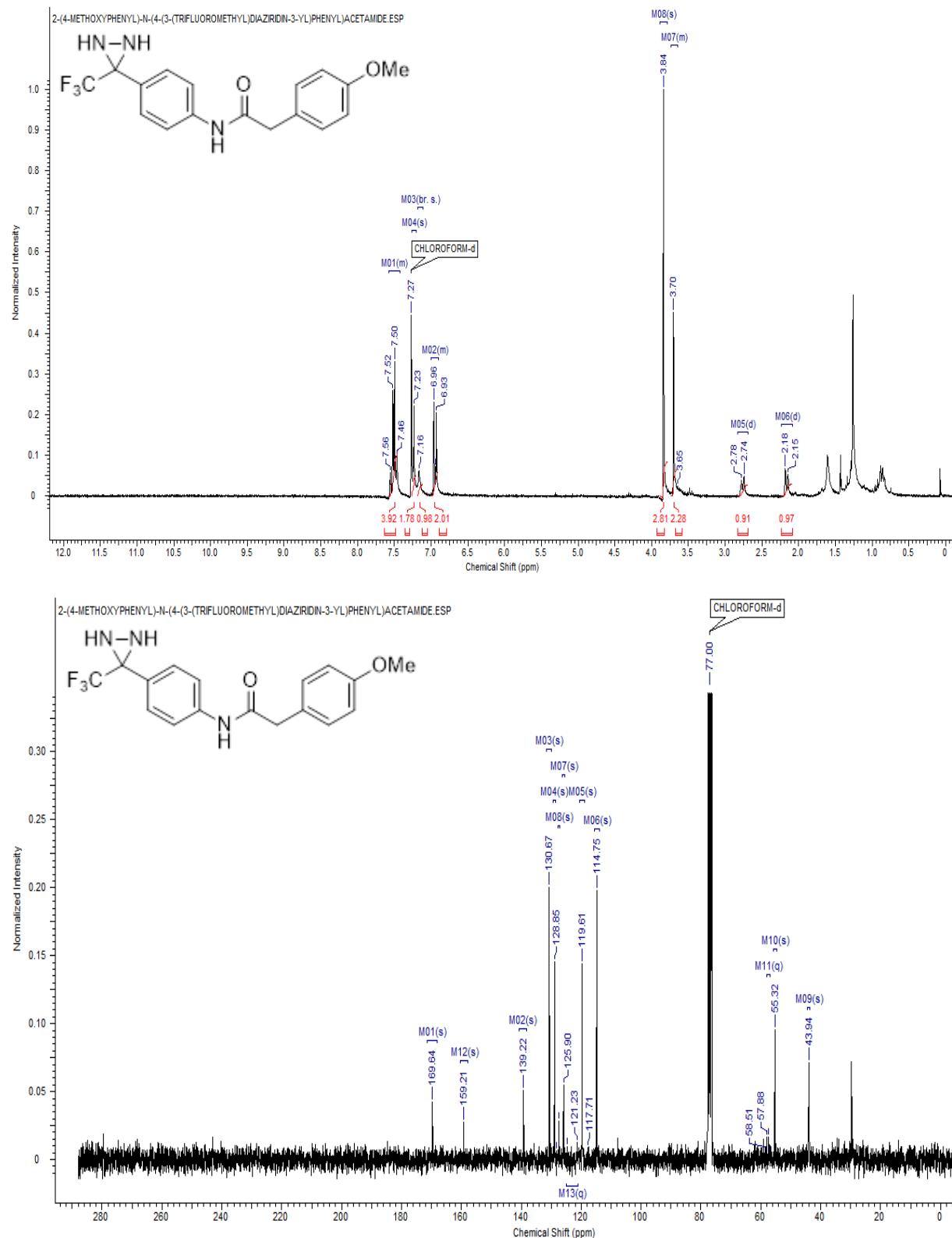
Compound 5v



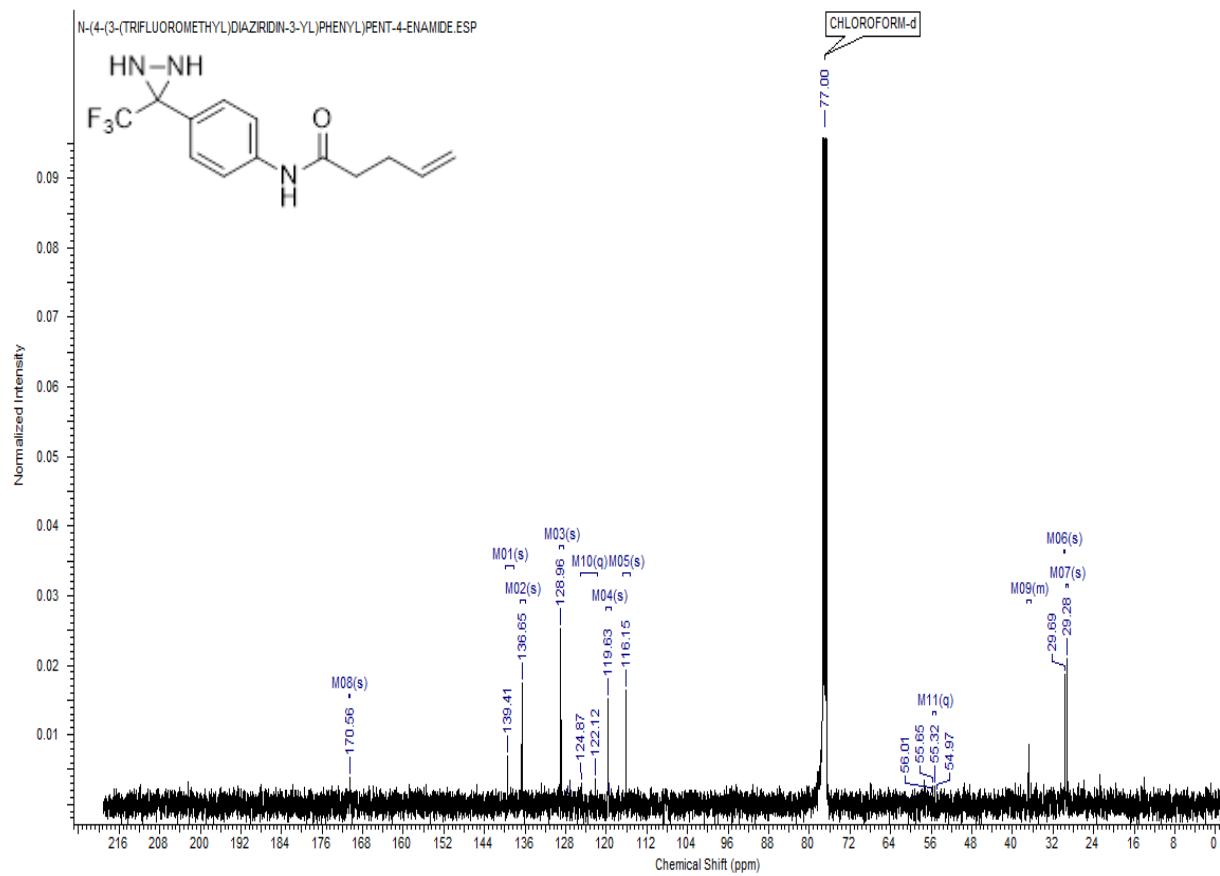
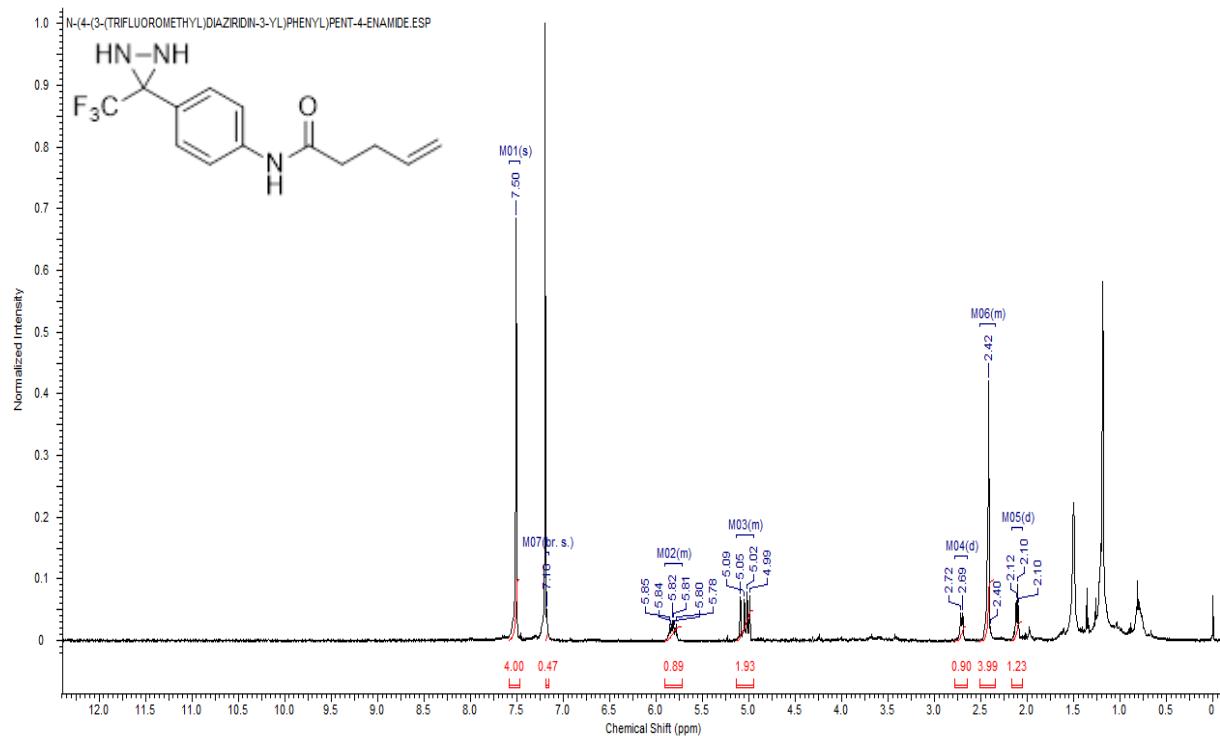
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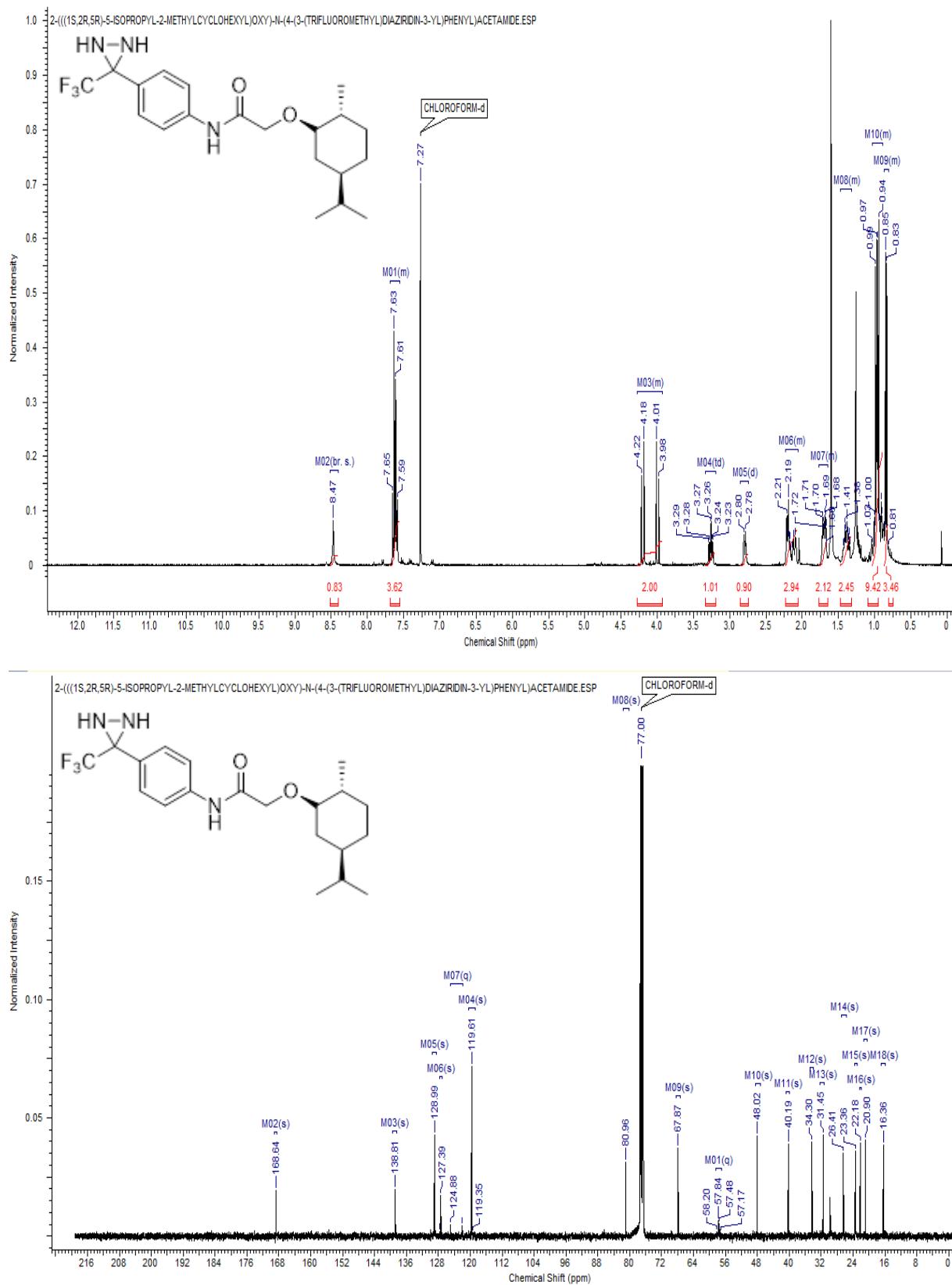
Compound 5x



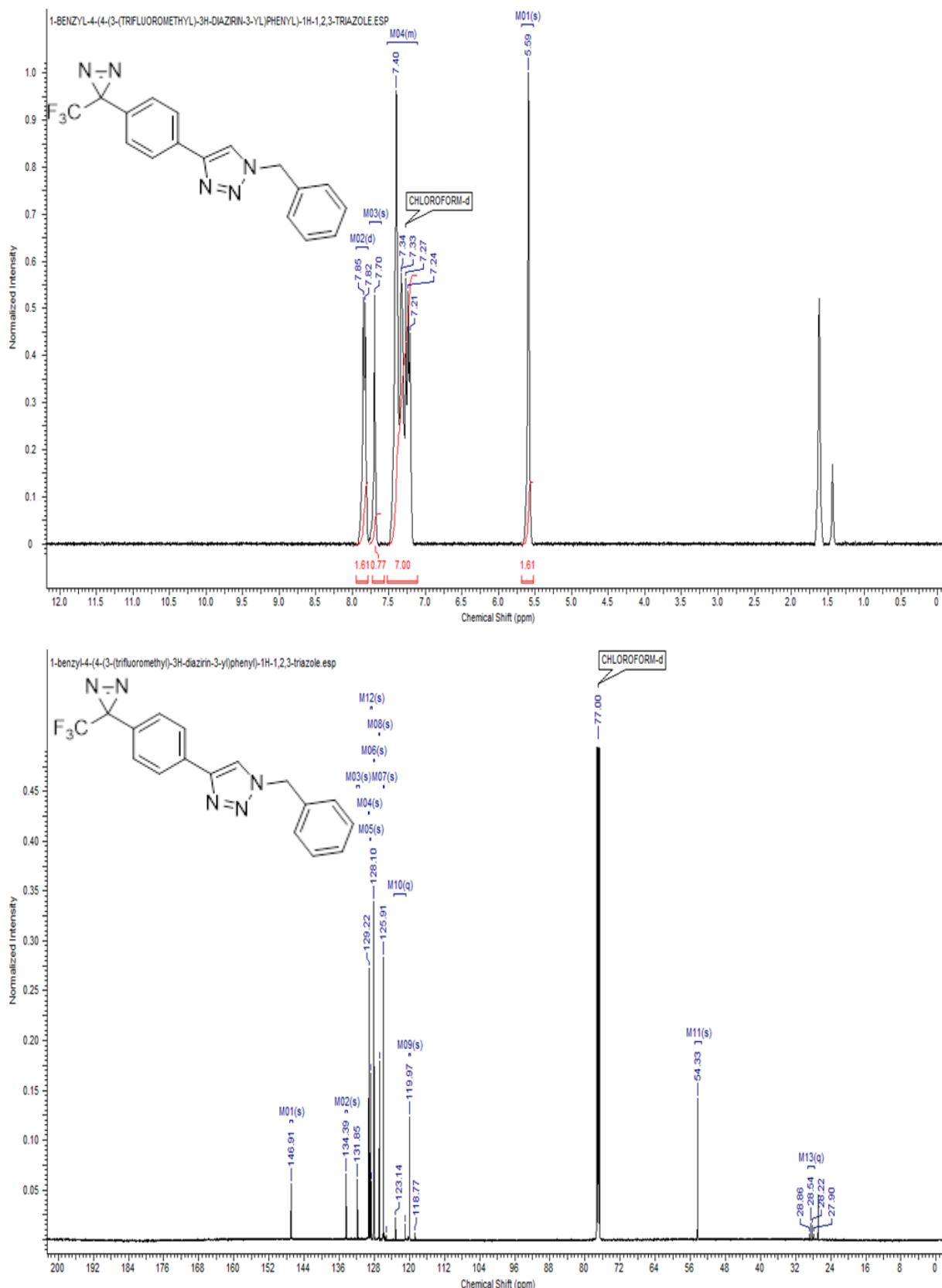
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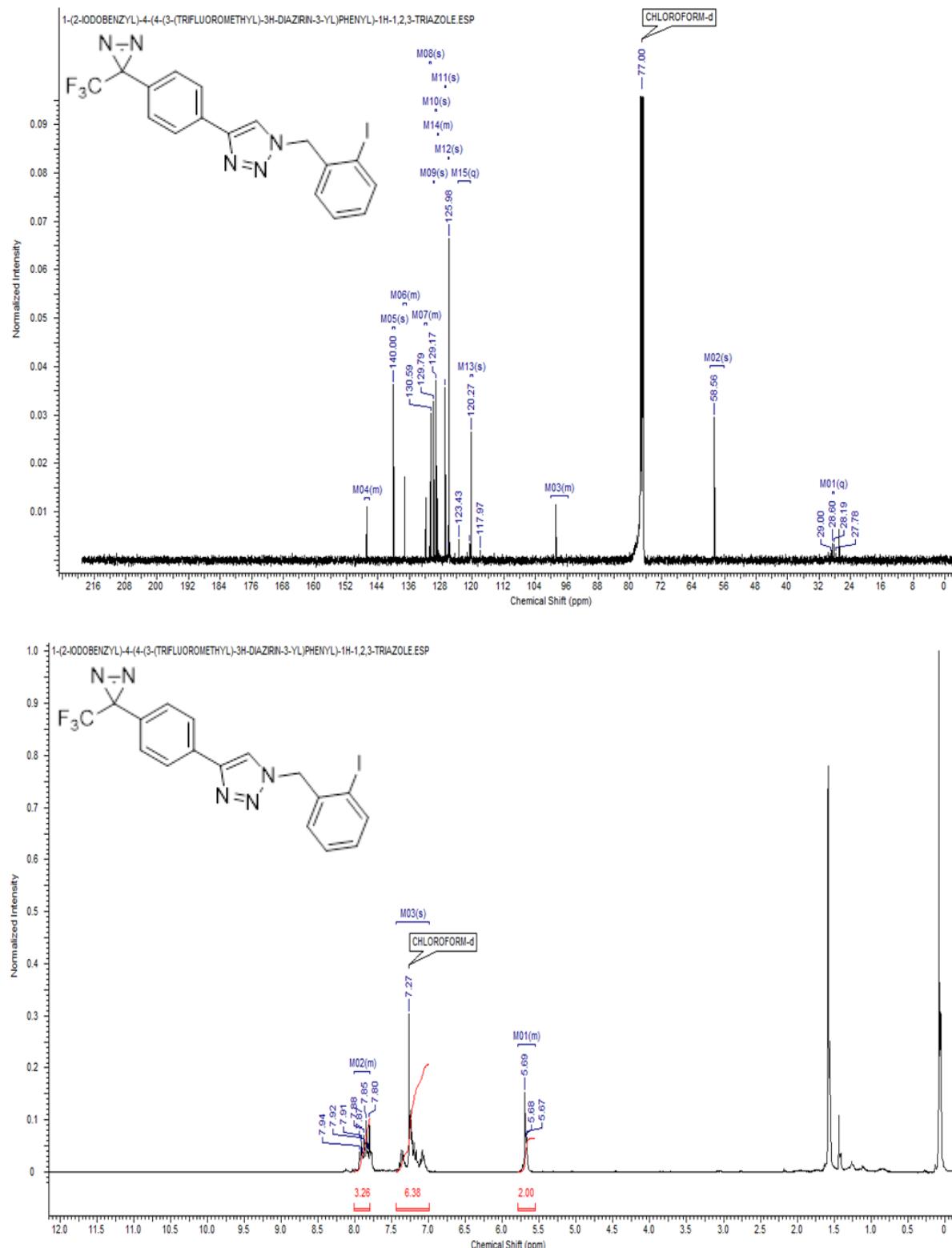
Compound 5z



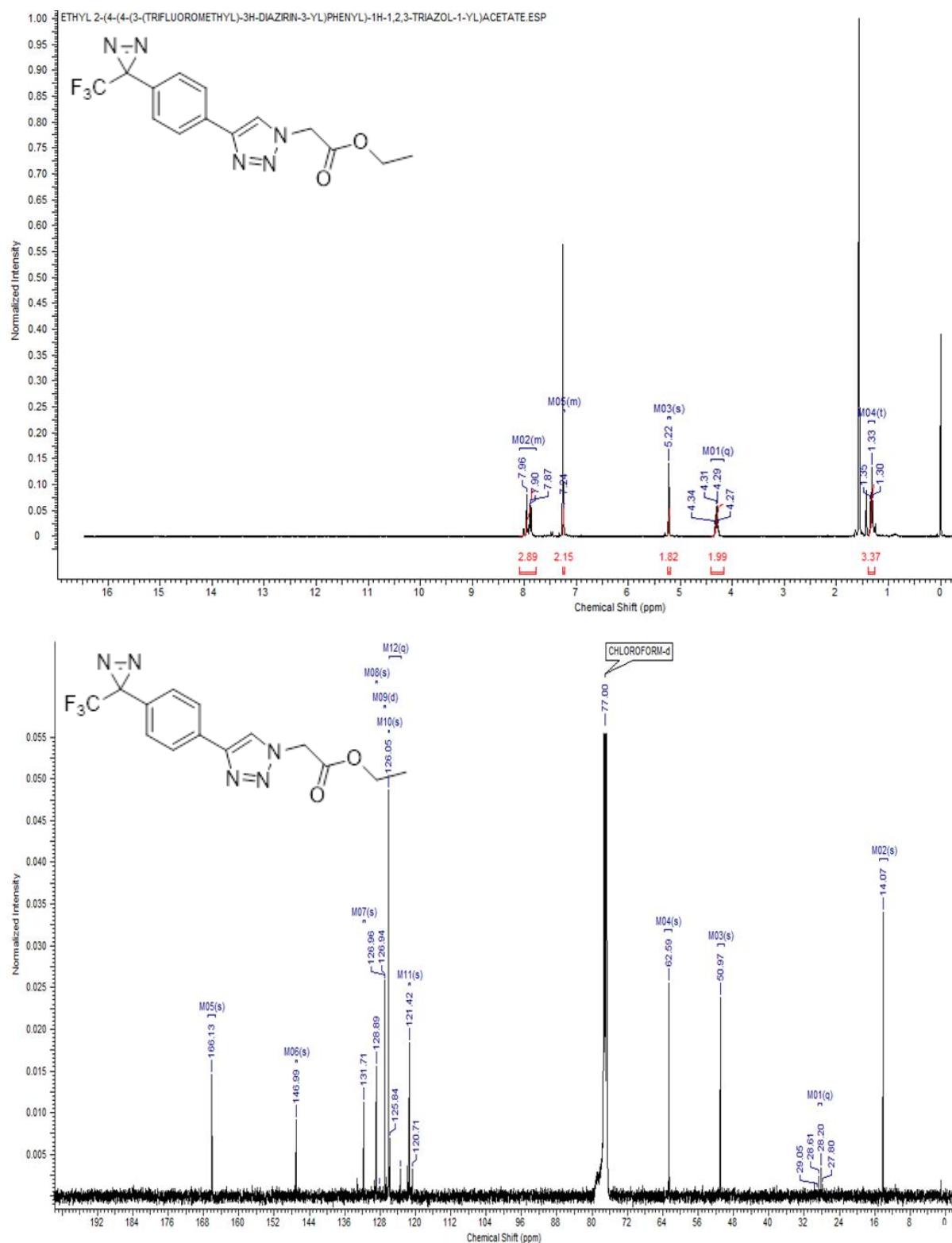
Compound 3a



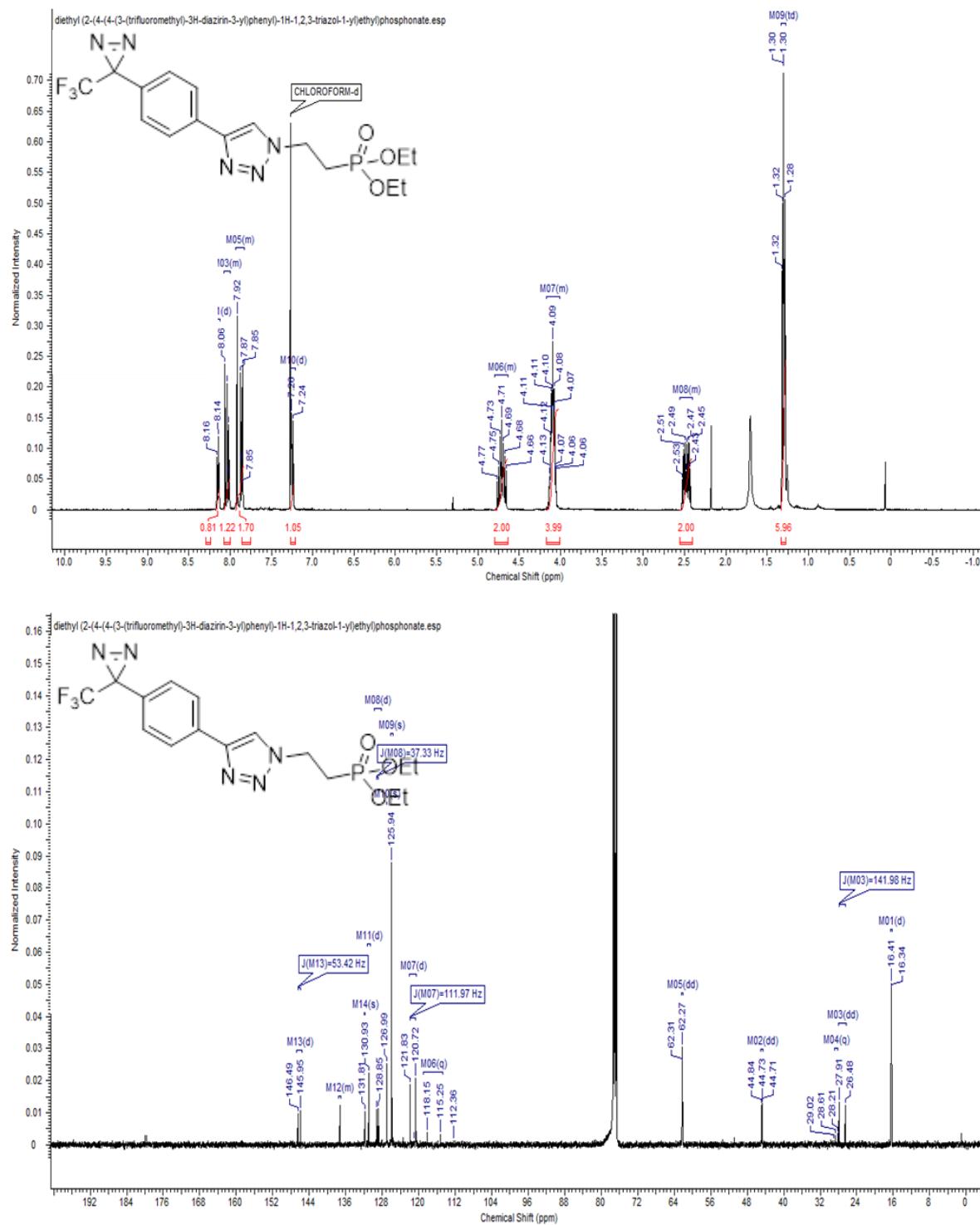
Compound 3b



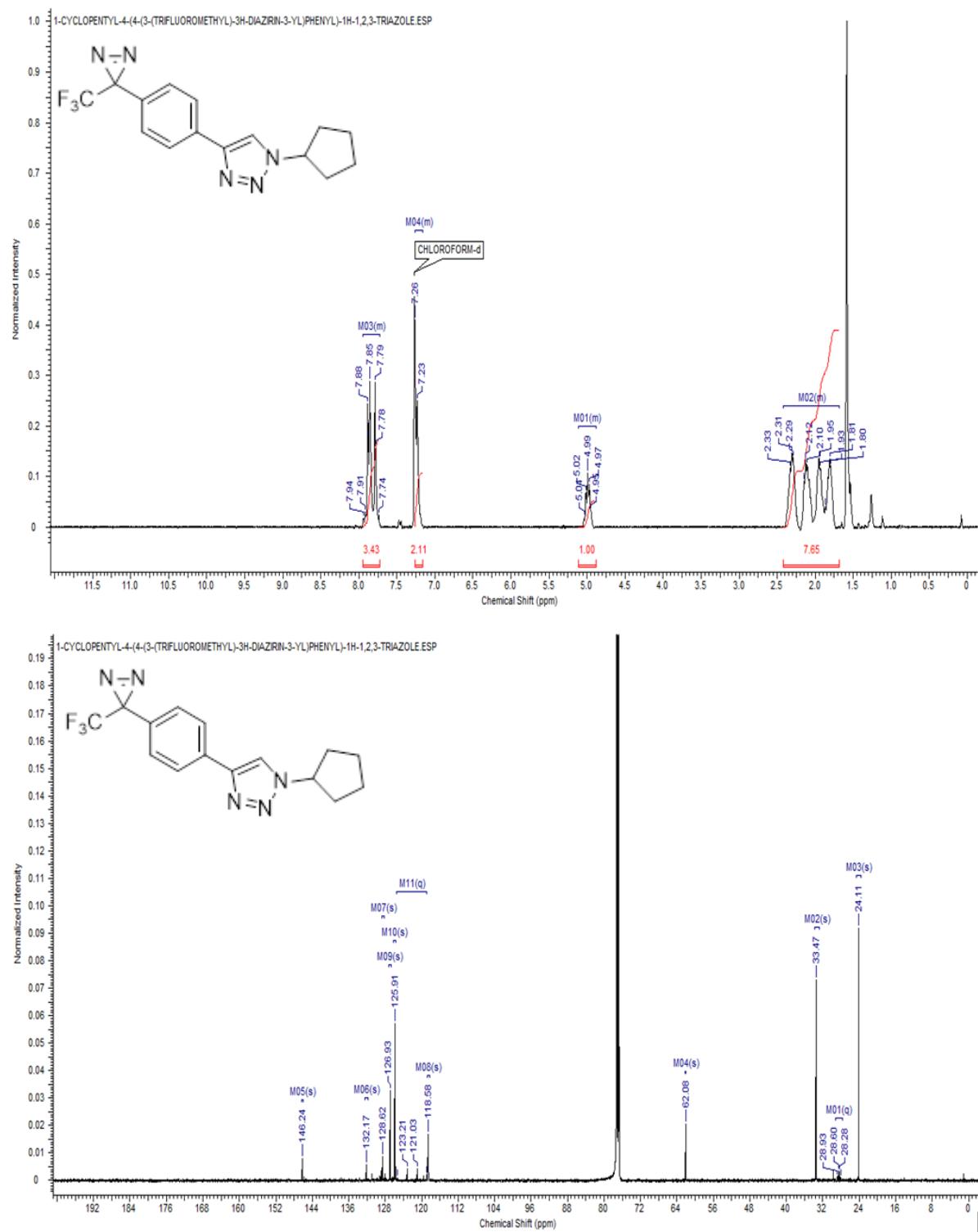
Compound 3c



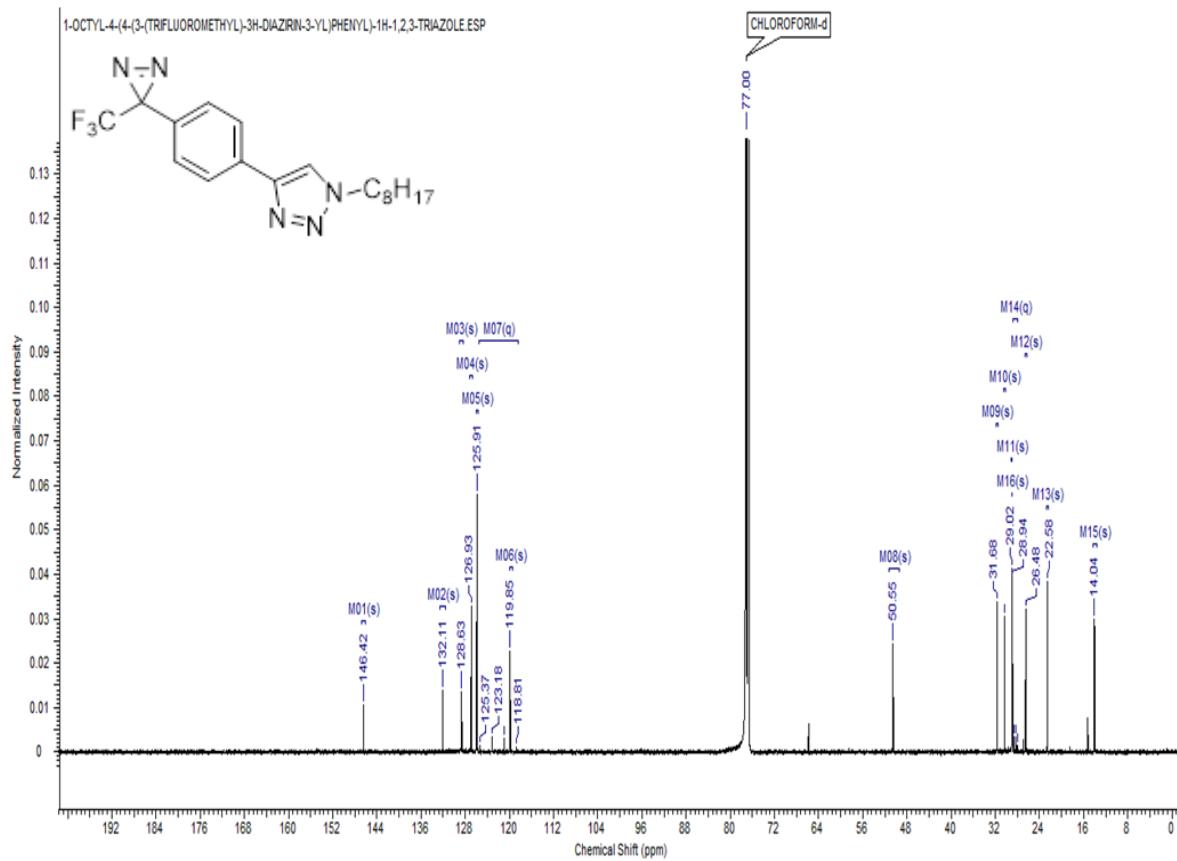
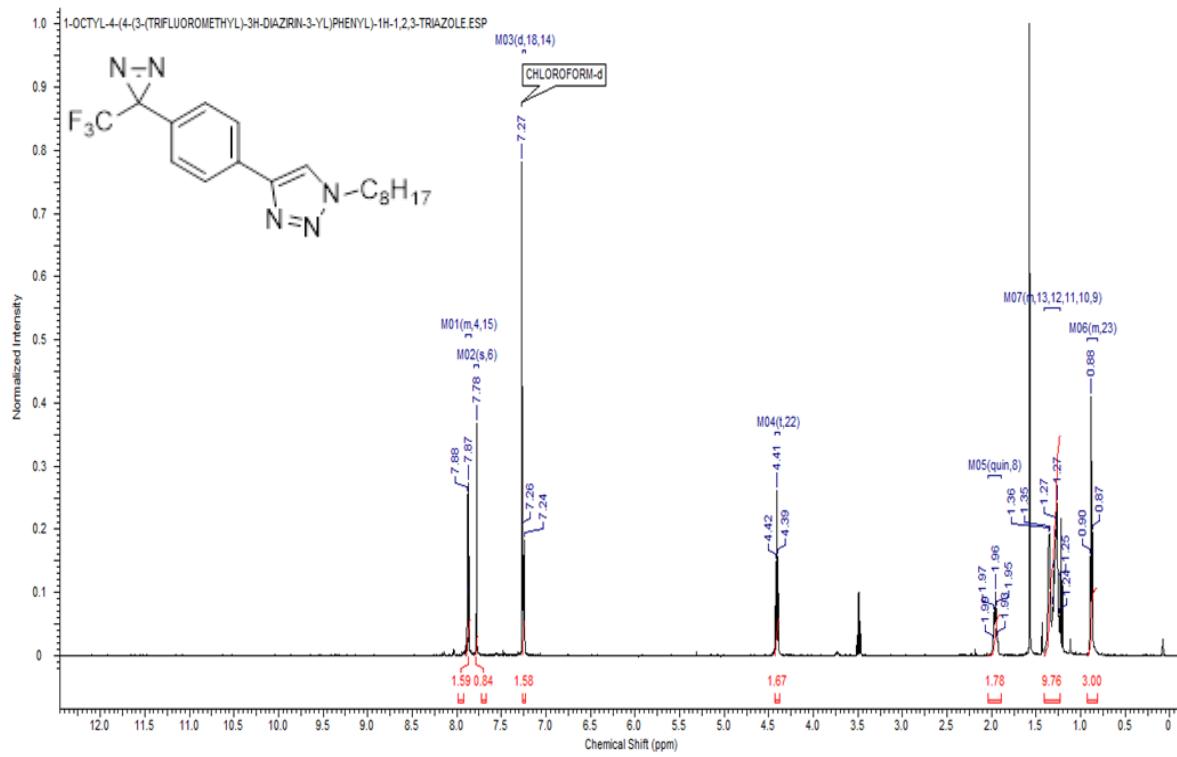
Compound 3d



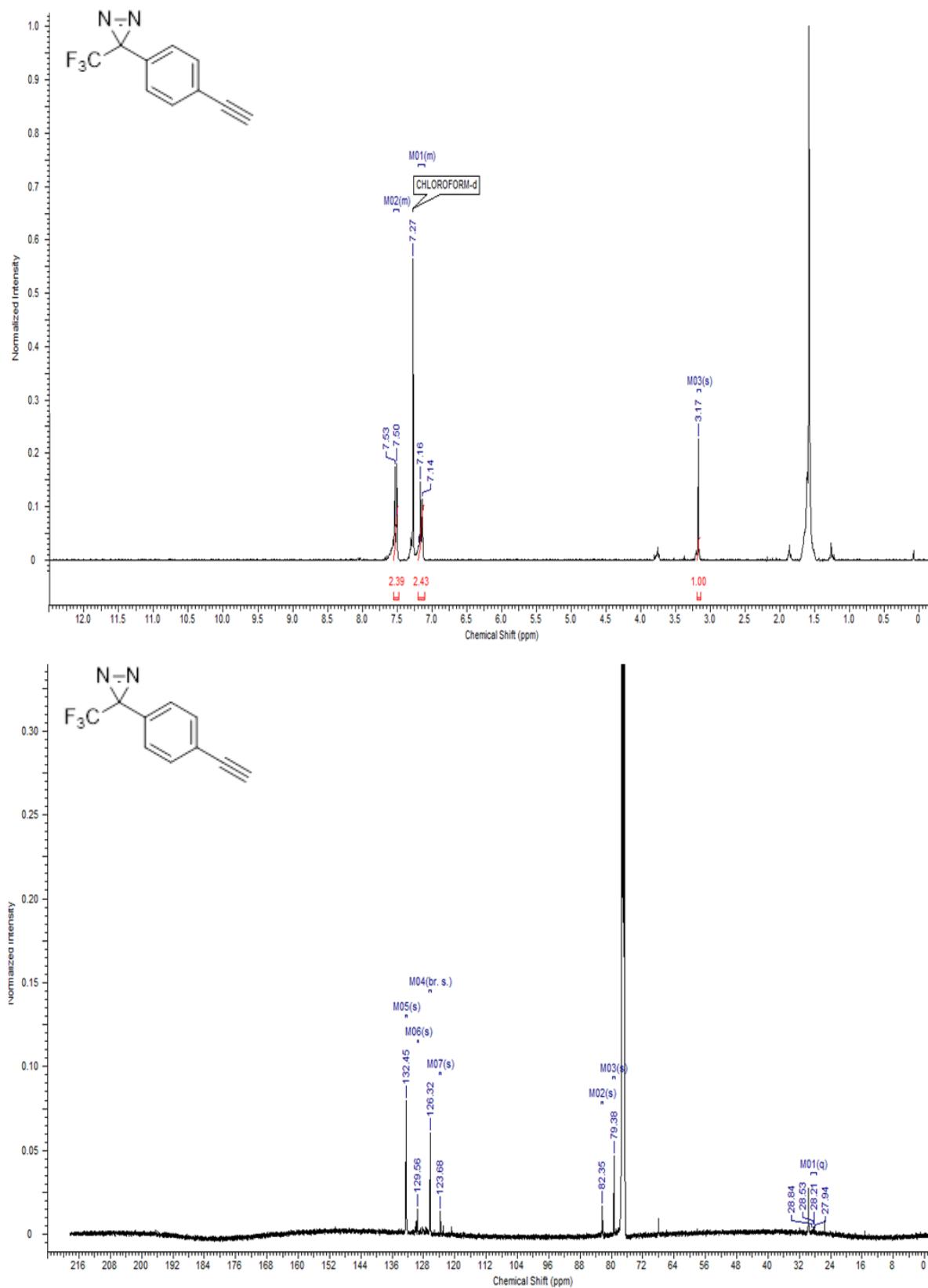
Compound 3e



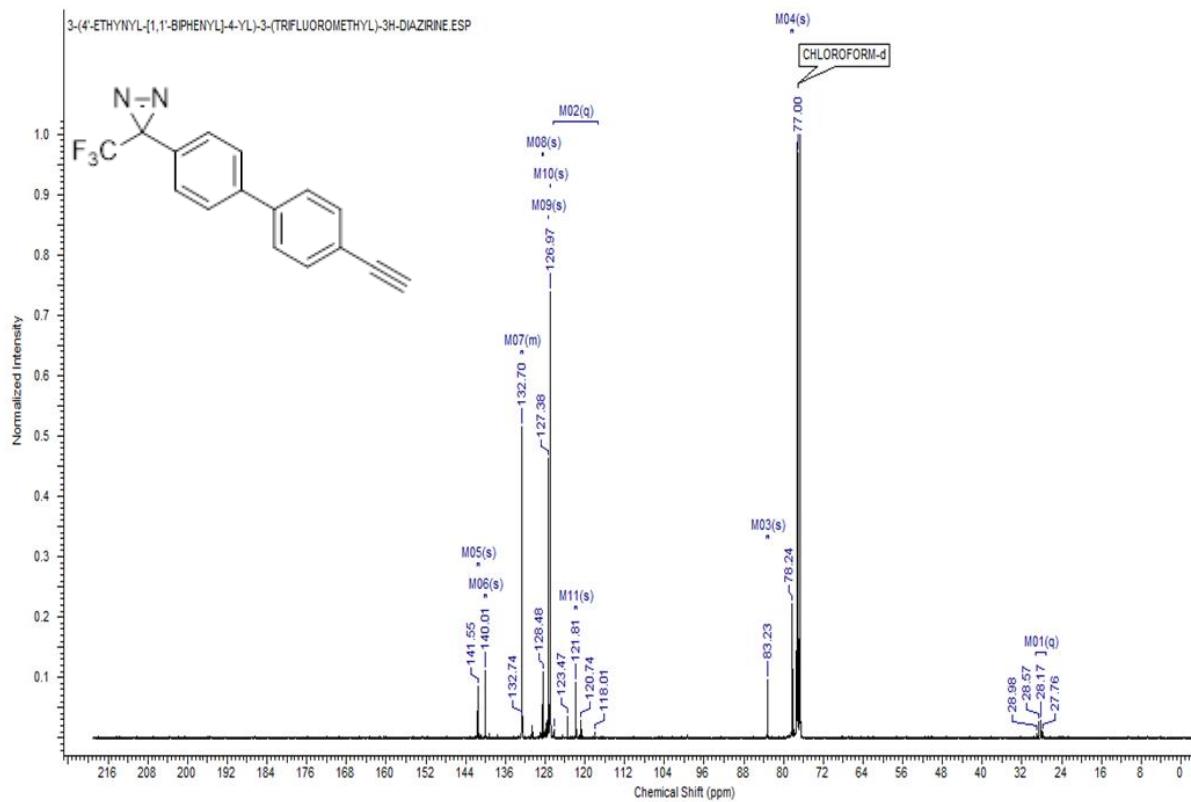
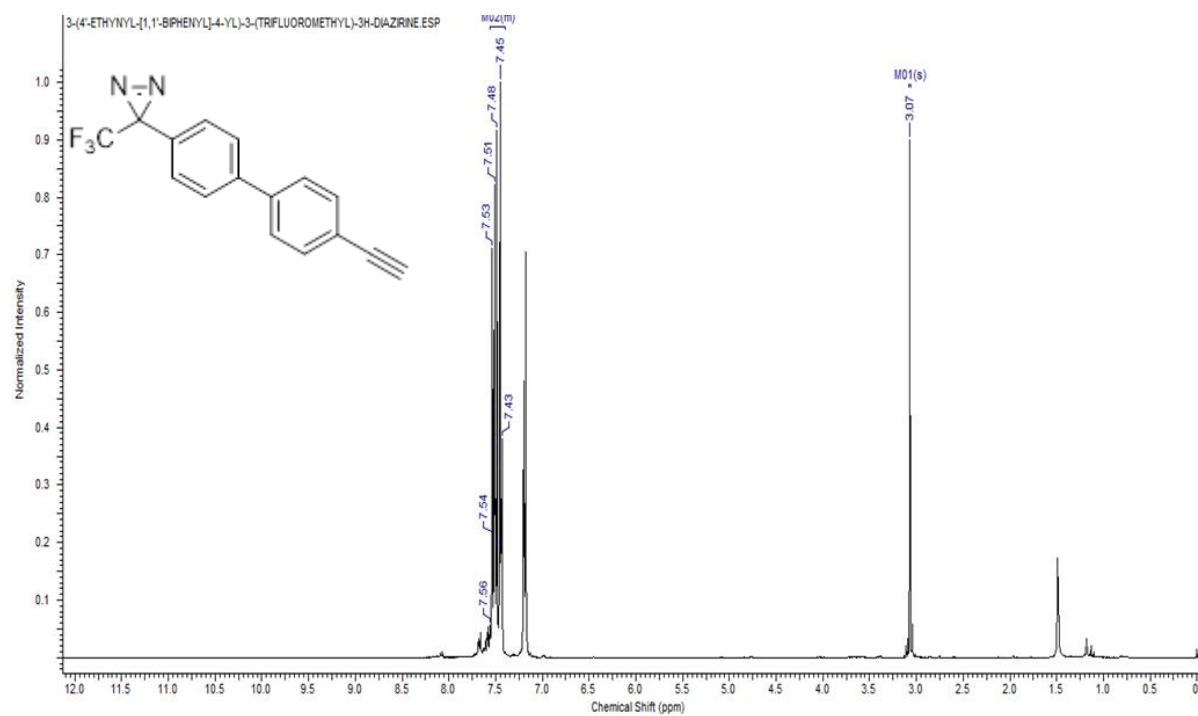
Compound 3f



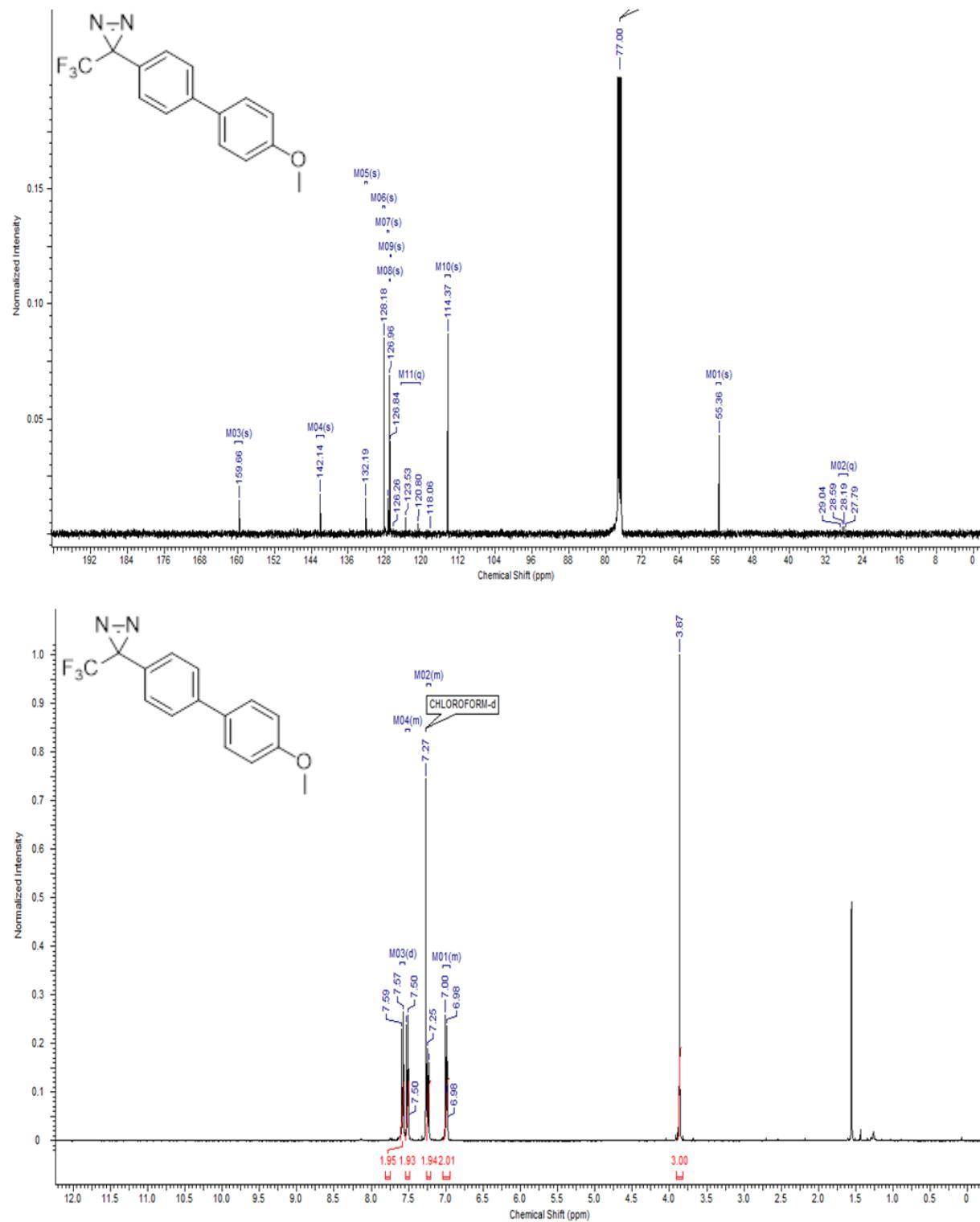
Compound 3g



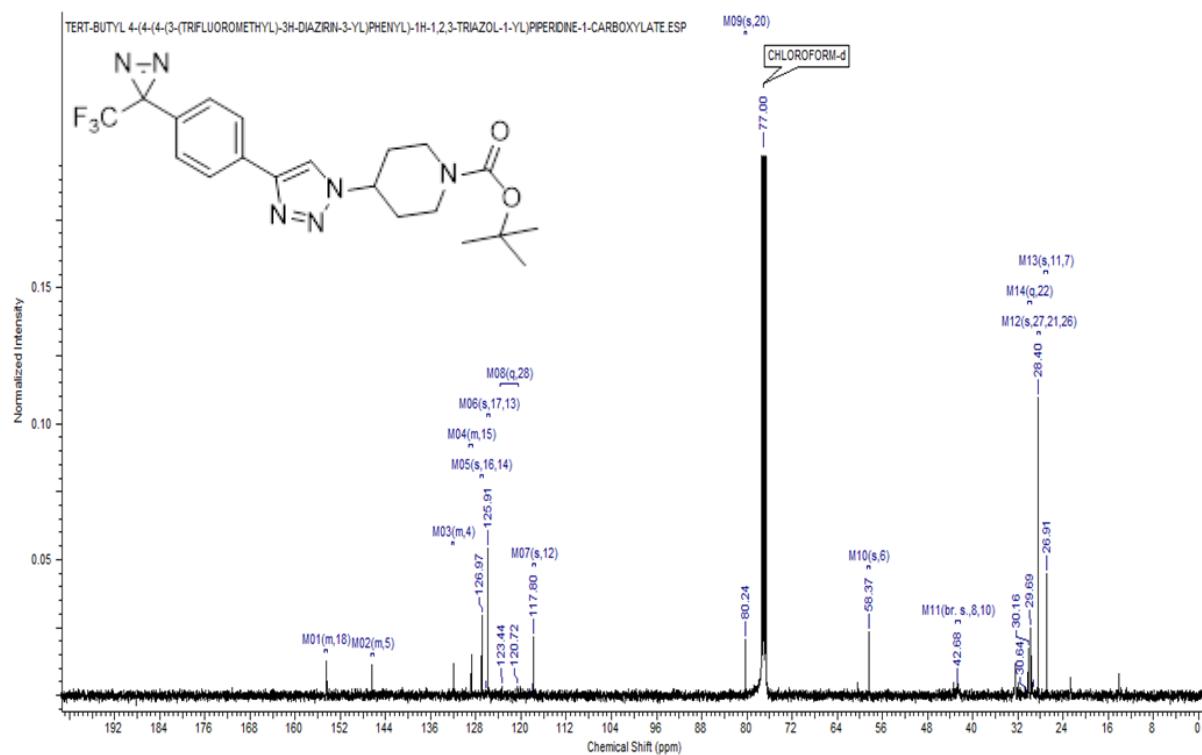
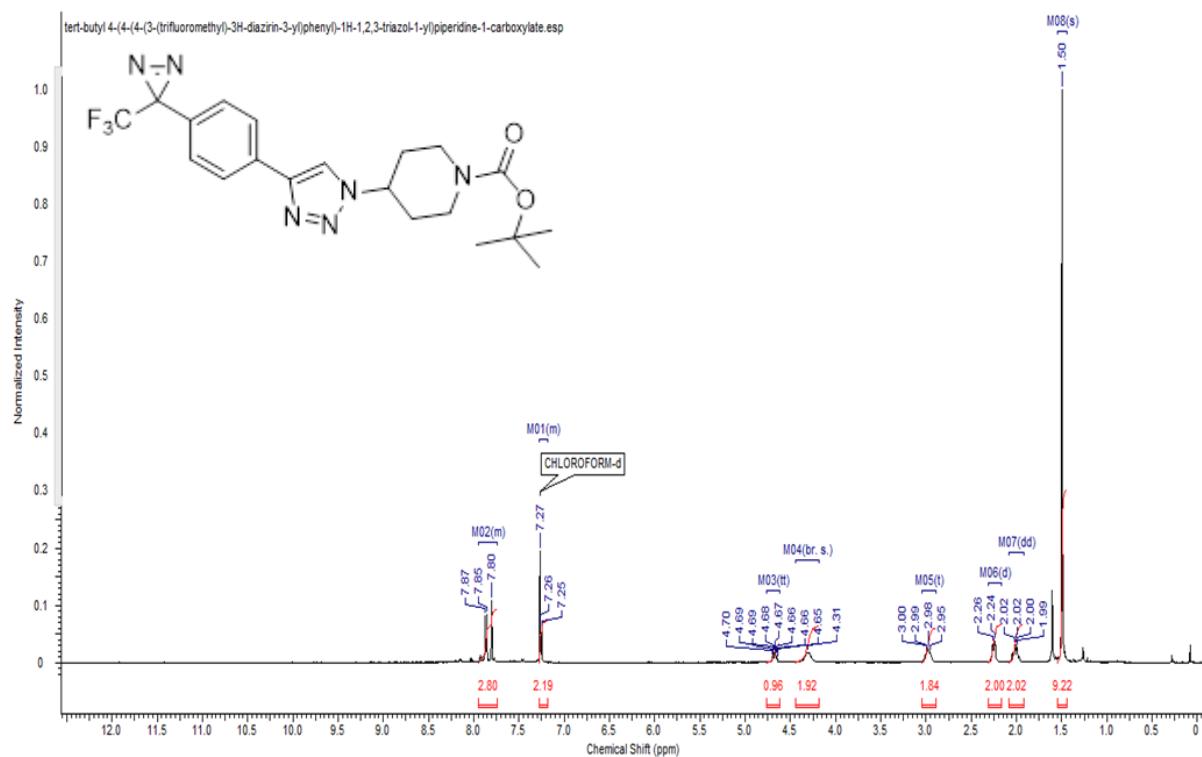
Compound 3h



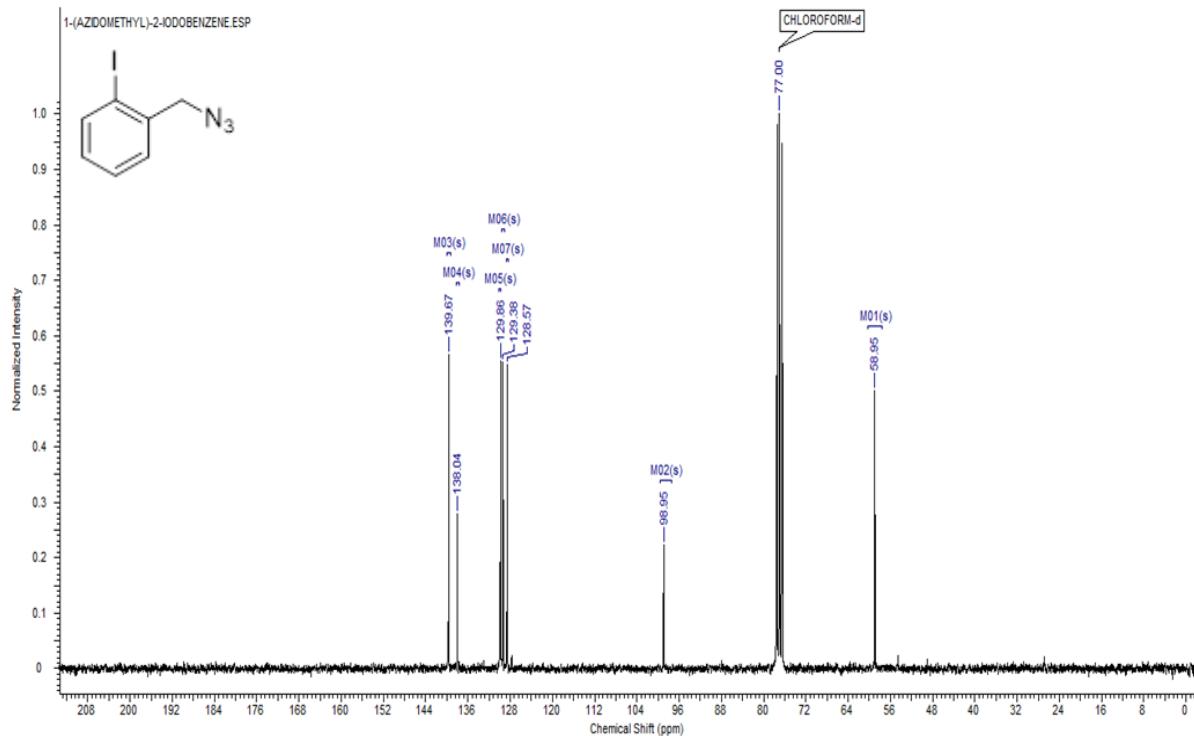
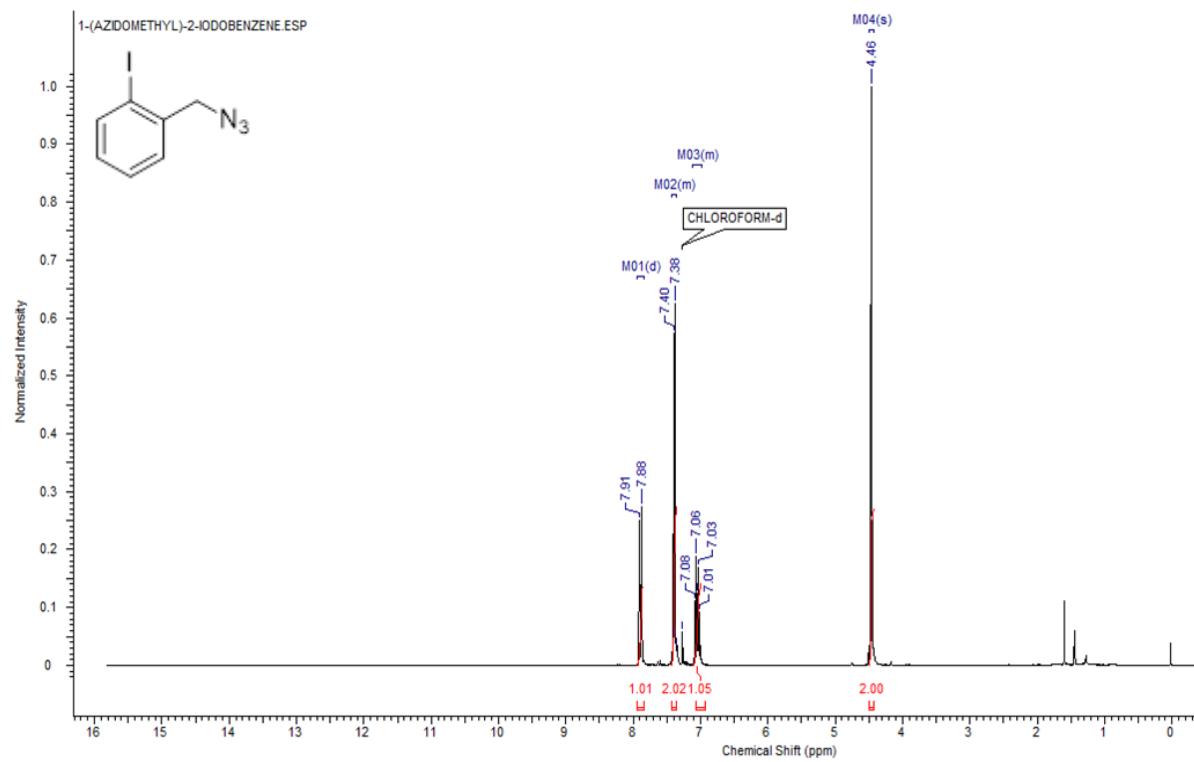
Compound 3i



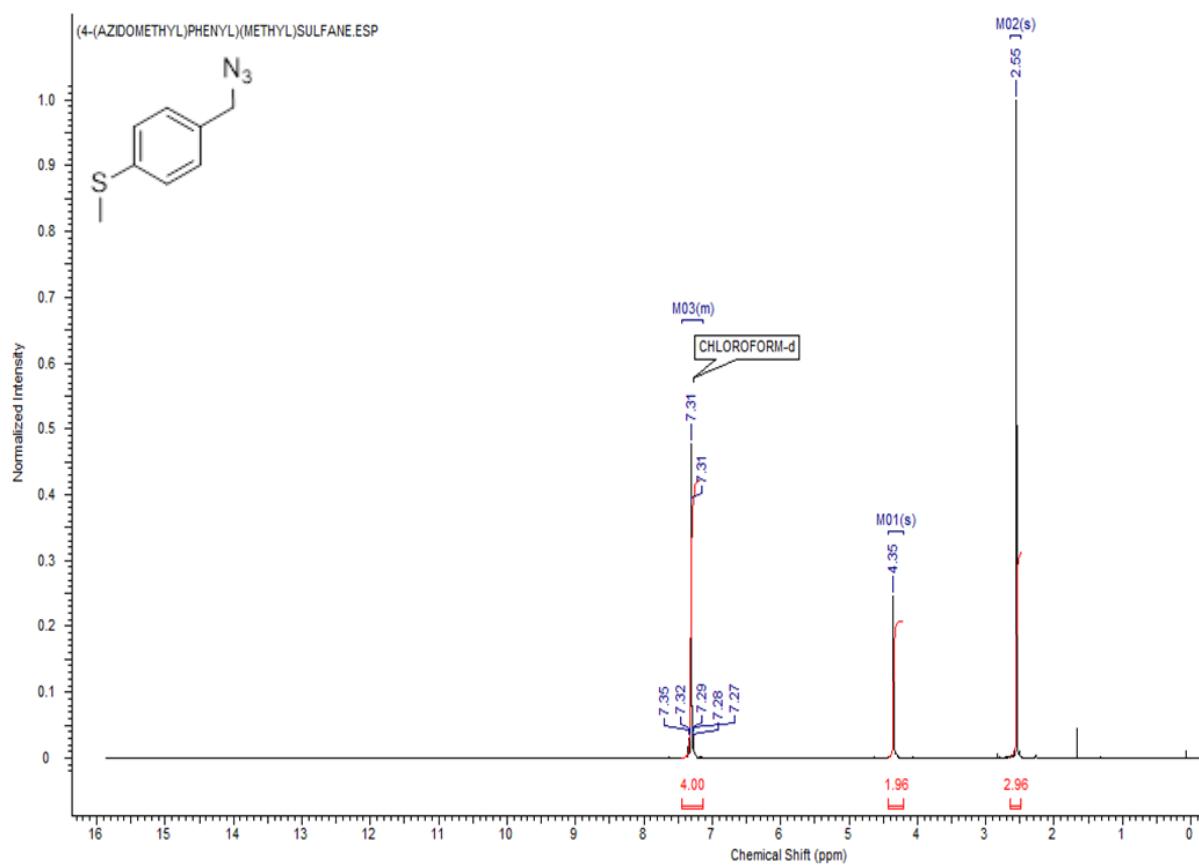
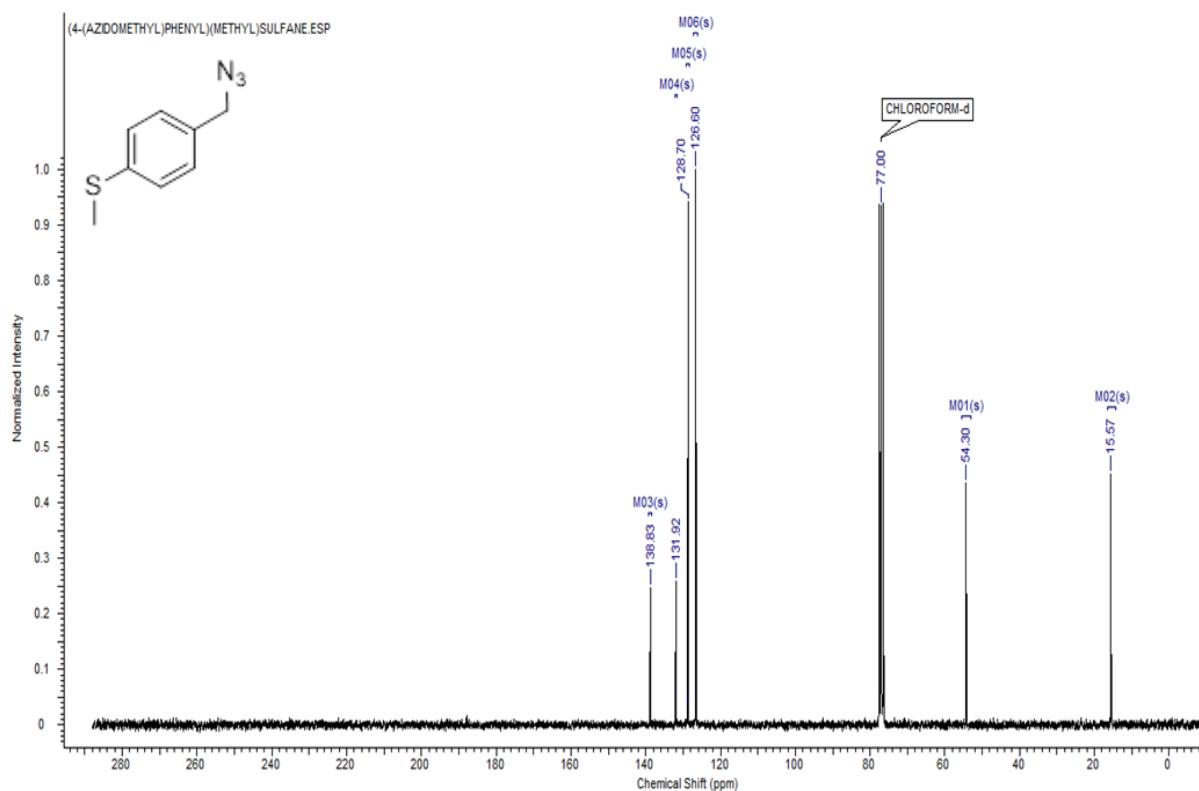
Compound 3j



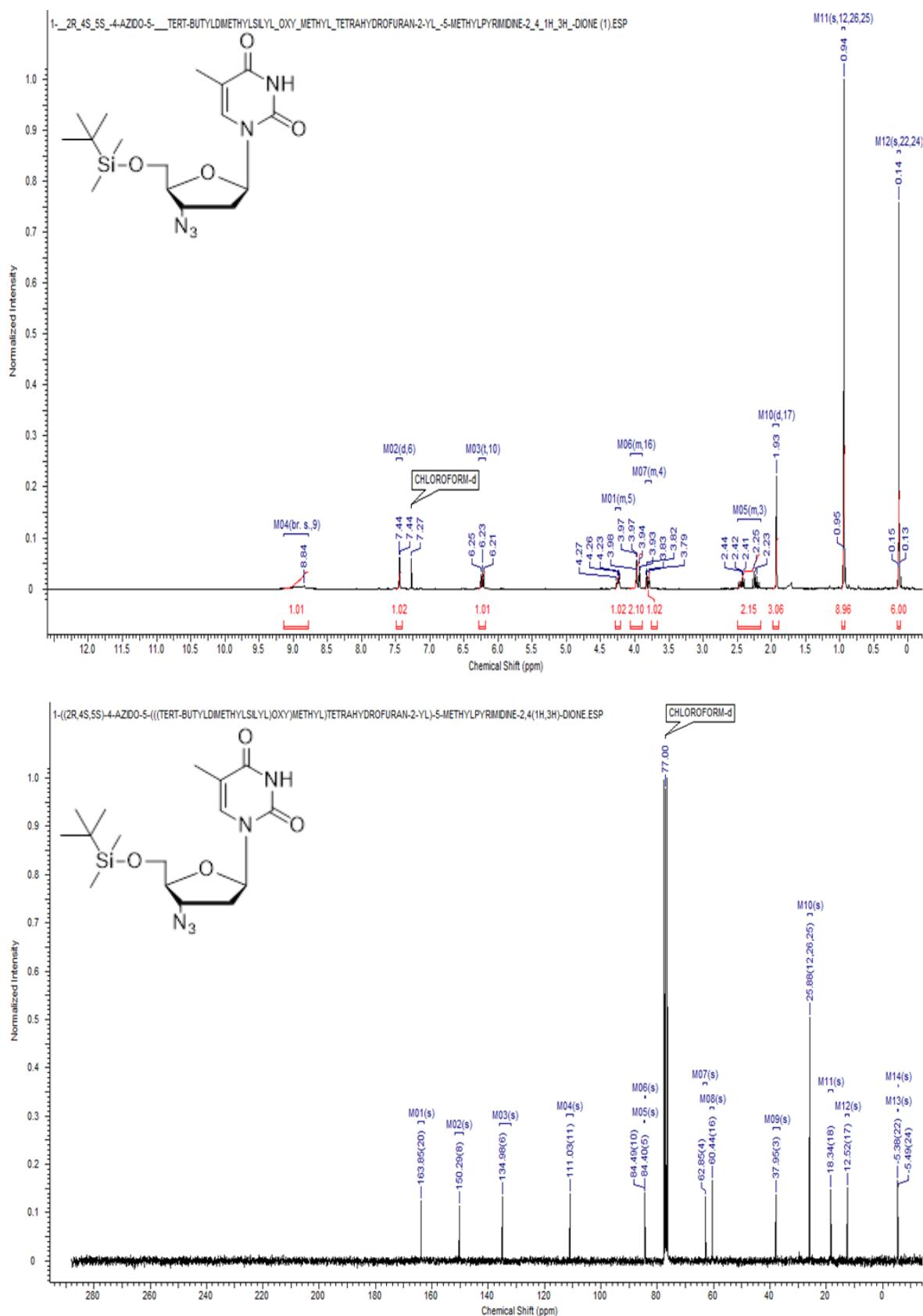
Compound 9a



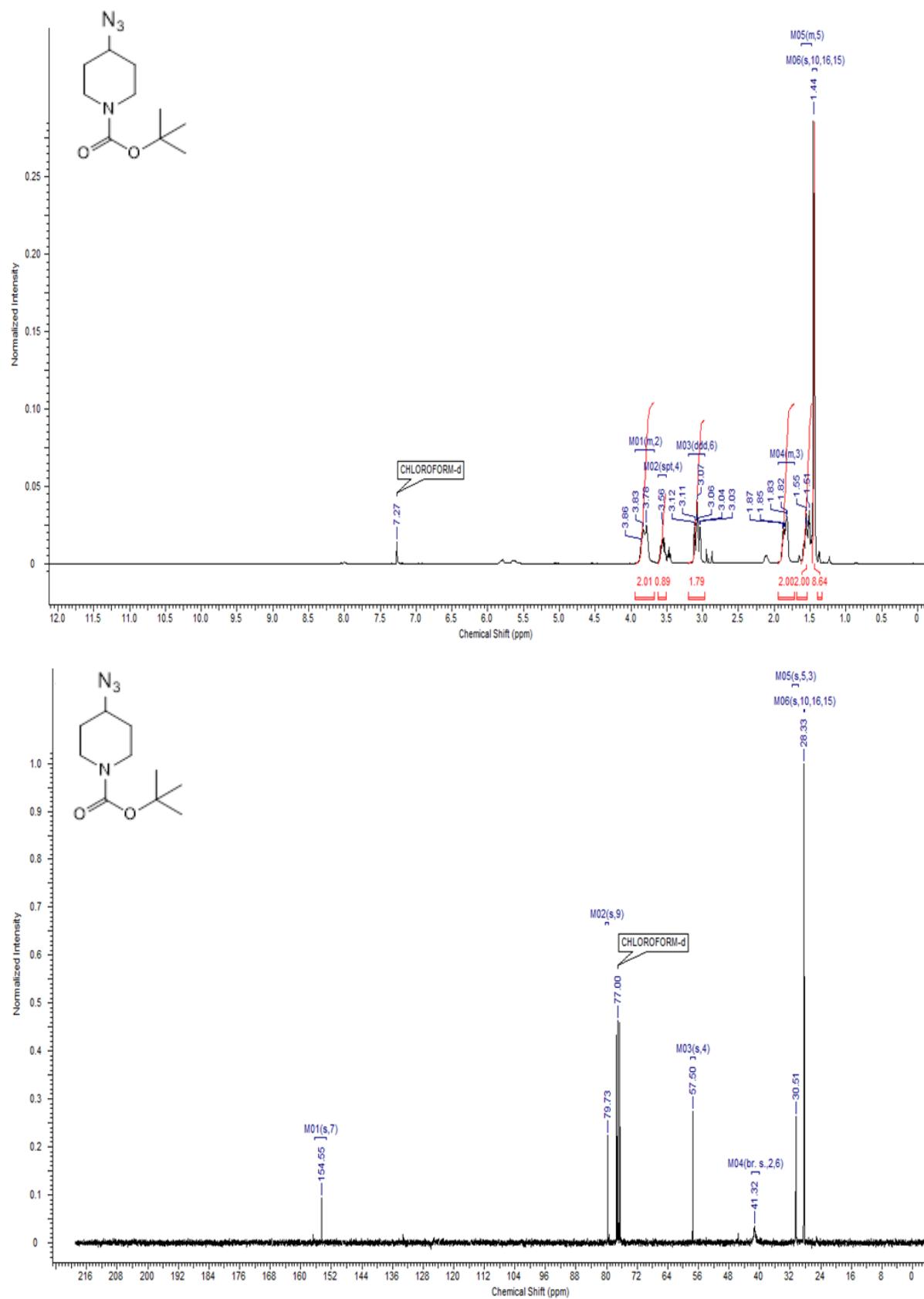
Compound 9b



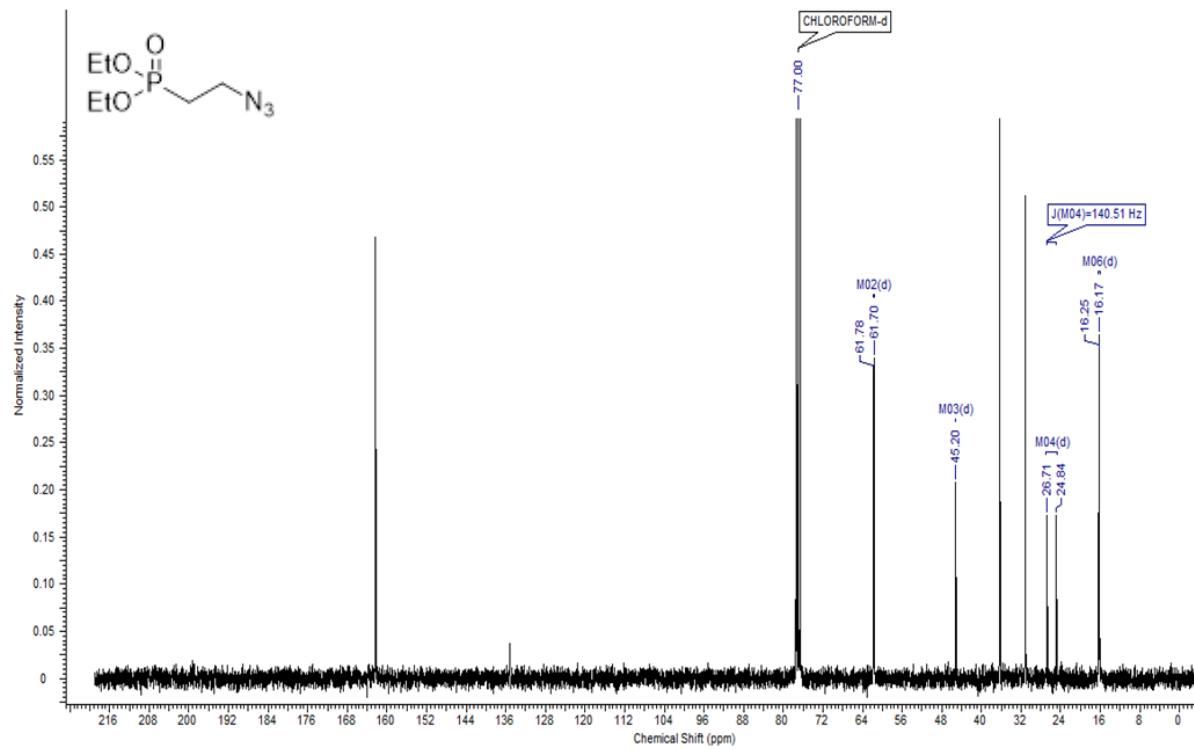
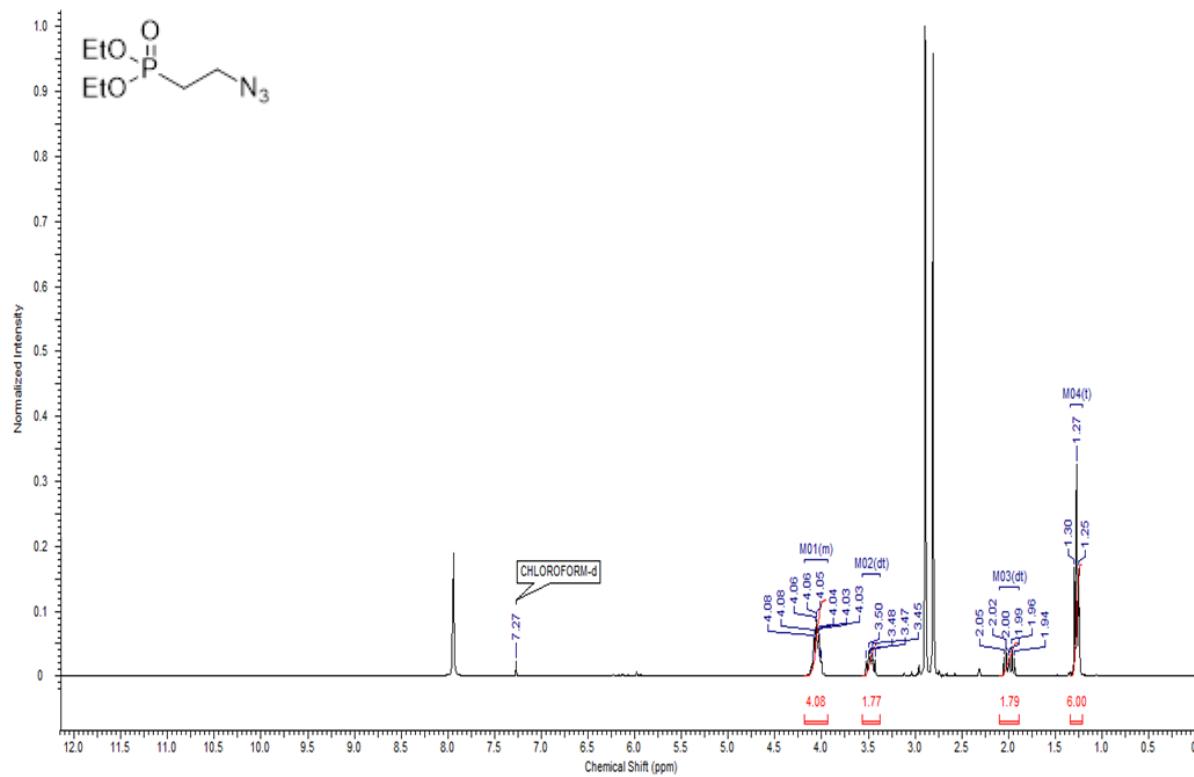
Compound 9d



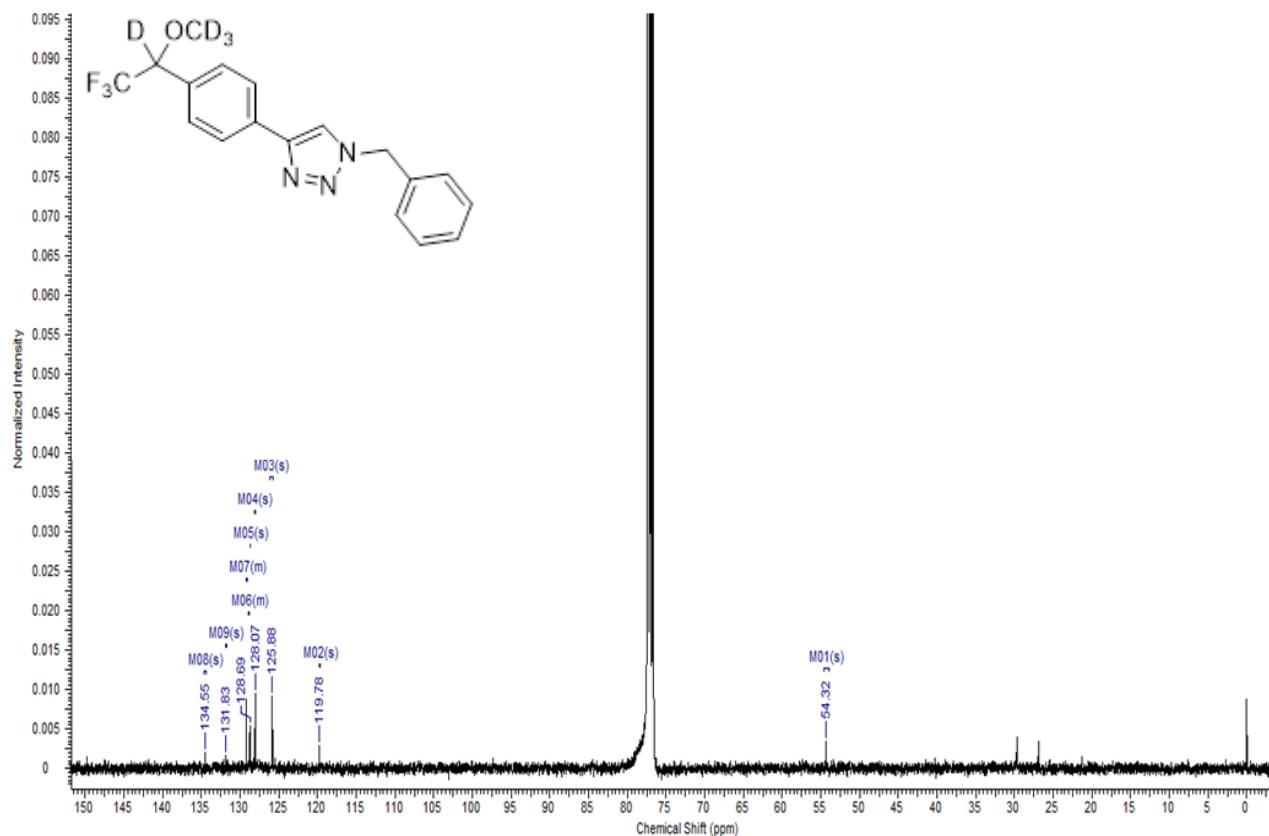
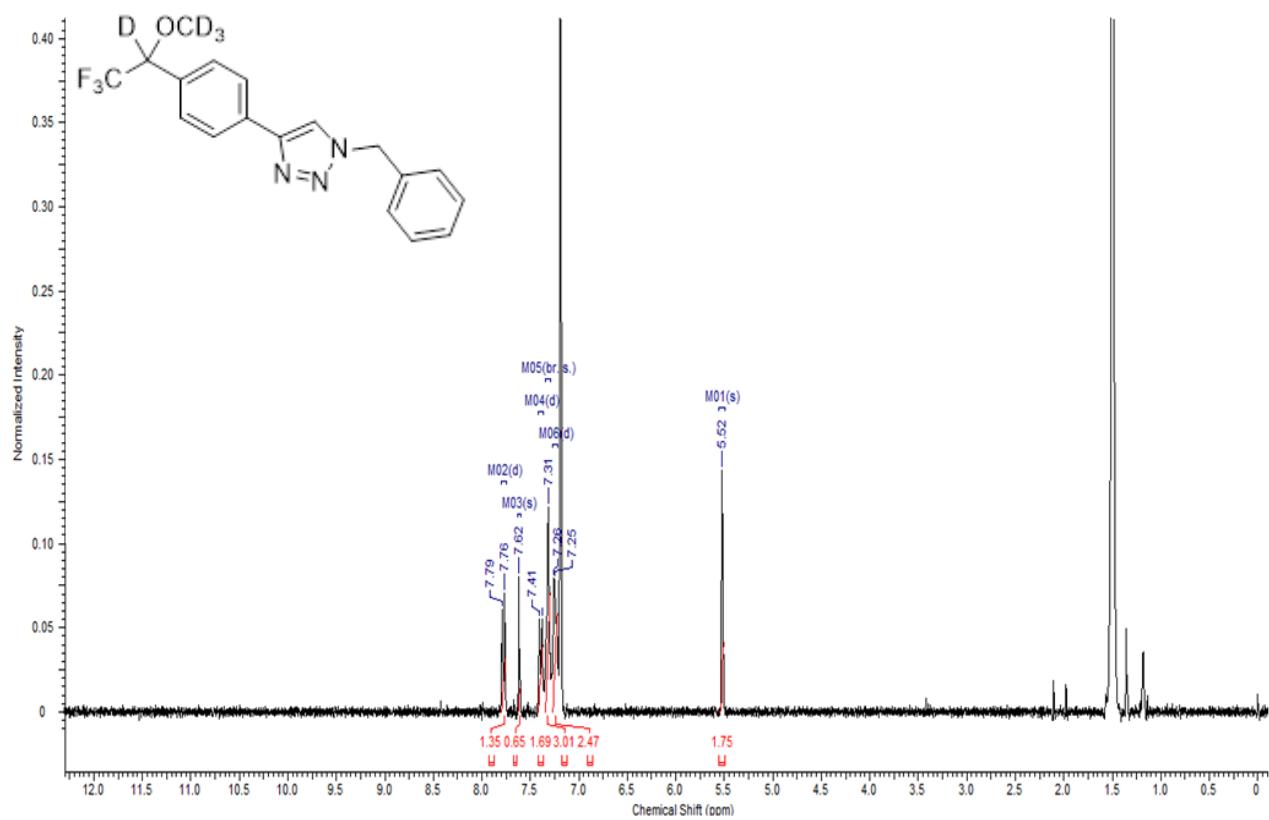
Compound 9e



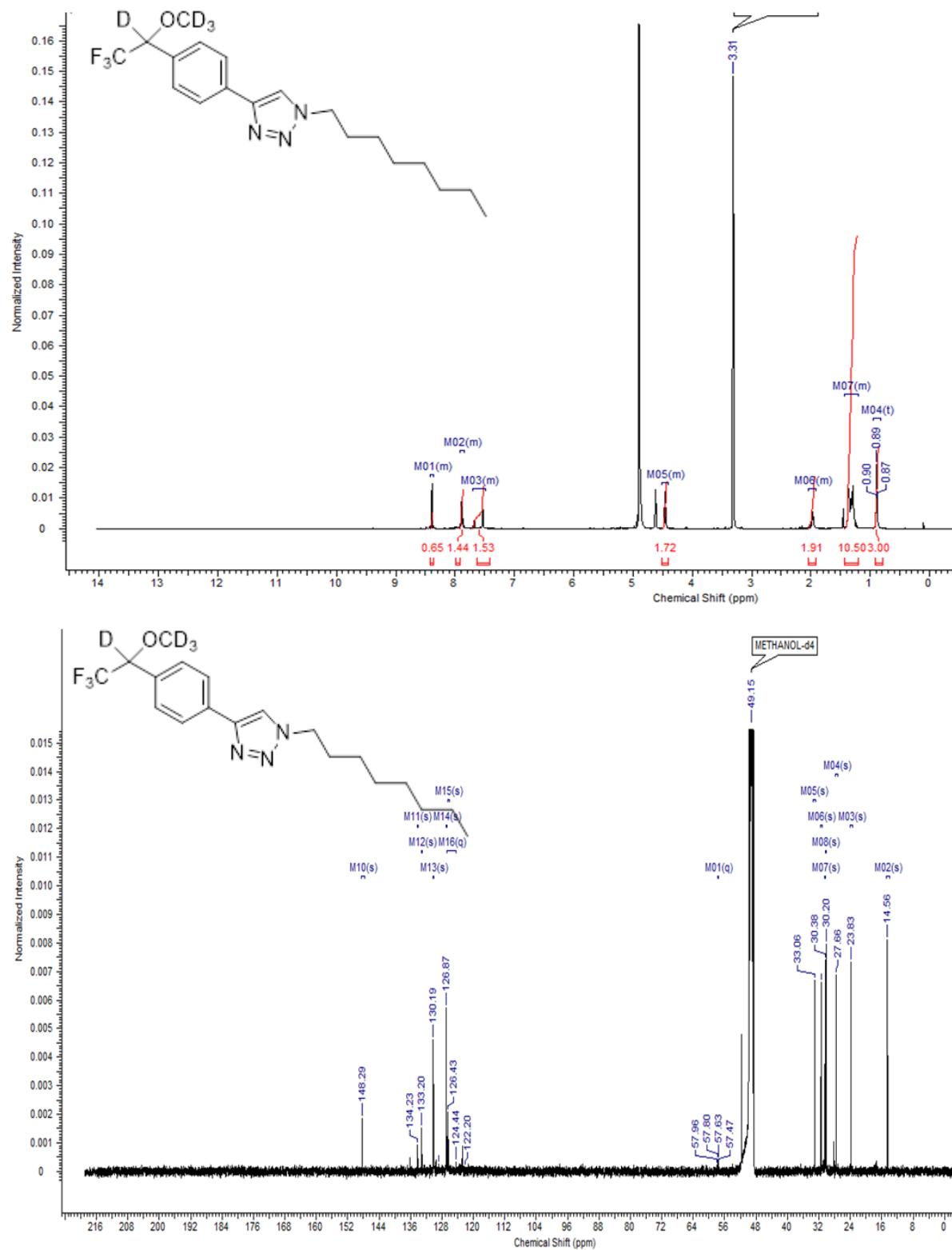
Compound 9f



Compound 10a



Compound 10b



* : SM = Starting Material

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