Supporting Information

EDA complex photoactivation of thianthrene-based radical precursors enables divergent access to functionalized saturated heterocycles

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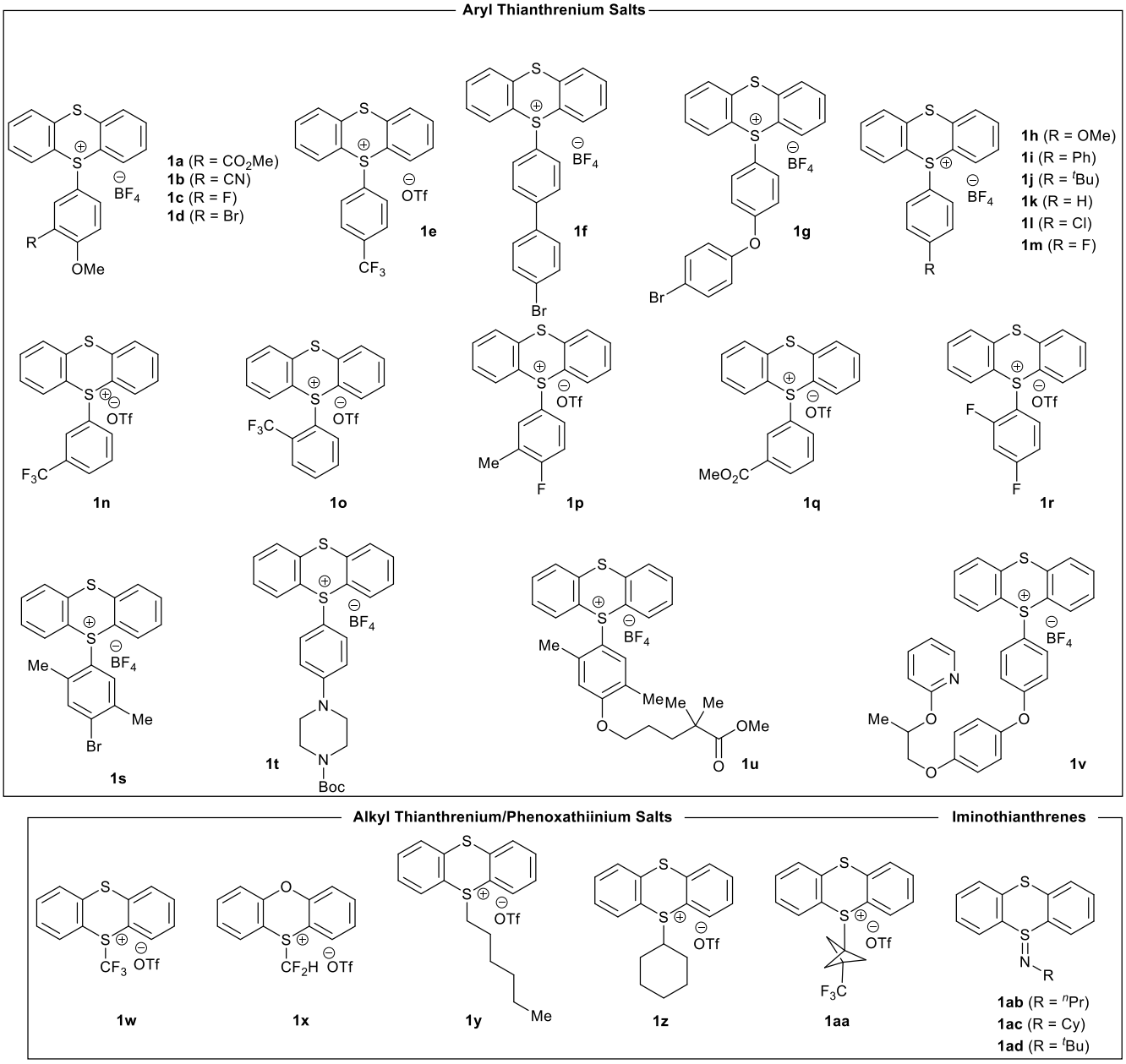
1. General Considerations

1.1 General: all chemical transformations requiring inert atmosphere were done using Schlenk line technique. For purple light irradiation, a Kessil PR160-purple LED lamp (30 W High Luminous DEX 2100 LED, λ_{max} = 390 nm) was placed 4 cm away from the reaction vials. Photoinduced reactions were performed using 4 or 8 mL Chemglass vials (15-425 Green Open Top Cap, TFE Septa). Reactions were monitored by TLC or NMR. TLC analysis was performed using hexanes/EtOAc as the eluent and visualized using phosphomolybdic acid and/or UV light. The UV-Vis spectra were recorded in a UV-Vis spectrophotometer Cary 60 at room temperature, with the appropriate solvent. The NMR experiments (^{1}H, ^{13}C, ^{19}F) were performed in the *Servei de Ressonància Magnètica Nuclear*, *Universitat Autònoma de Barcelona*, using NEO 400, NEO 500 or NEO 600 spectrometers at 298 K. Chemical shifts are referenced to residual, nondeuterated $CHCl_3$ (δ = 7.26 in ^{1}H NMR and 77.16 in ^{13}C NMR). The HRMS (ESI+) and elemental analyses were done by *Parque Científico Tecnológico* of Universidad de Burgos. HRMS was done using a Bruker microTOF-QII mass spectrometer (fly time analyzer) through positive electrospray ionization. IR spectra were recorded on an FT- IR Perkin Elmer using either neat oil or solid products. Melting points (°C) are uncorrected.

1.2 Chemicals: Deuterated NMR solvents were purchased from Eurisotop. Dry solvents were obtained from Aldrich and used as received. Bulk solvents were purchased from VWR. Chemicals were purchased from Chemosapiens and used as received unless specified.

2. List of Sulfonium Salts and Iminothianthrenes

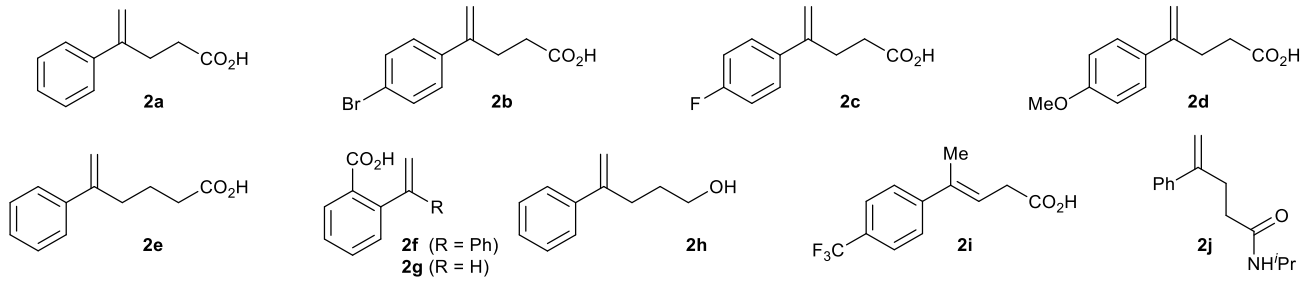
Sulfonium salts **1a-aa** and iminothianthrene **1ab-ad** were synthesized from the corresponding commercially available compounds, according to the literature procedure.[1,2,3,4,5]



[1] J. Li, R. Sang, W.-S. Ham, M. B. Plutaschack, F. Berger, S. Chabbra, A. Schnegg, C. Genicot, T. Ritter, *Nature Chem.* 2020*,* **12**, 56-62.
[2] F. Ye, F. Berger, H. Jia, J. Ford, A. Wortman, J. Börgel, C. Genicot, T. Ritter, *Angew. Chem. Int. Ed.* 2019, **58**, 14615-14619.
[3] X.-Y. Chen, Y.-N, Li, Y. Wu, J. Bai, Y. Guo, P. Wang*, J. Am. Chem. Soc.* 2023**, 145**, 10431-10440.
[4] X. Li, W. Si, Z. Liu, H. Qian, T. Wang, S. Leng, J. Sun, Y. Jiao, X. Zhang, *Org. Lett.* 2022, **24***,* 4070-4074.
[5] Q. Cheng, J. Chen, S. Lin, T. Ritter, *J. Am. Chem. Soc.* 2020, **142**, 17287-17293.

3. List of Radical acceptors

The radical acceptors **2a-j** were synthesized from the corresponding commercially available compounds, according to the literature procedure.[6,7]



4. Synthesis of Substituted Saturated Heterocycles: Reaction Workflow, Optimization and Characterization

A. Reaction Workflow

All photoredox reactions were performed with a Kessil PR160-purple LED lamp (30 W High Luminous DEX 2100 LED, λ_{max} = 390 nm). The lamp was placed 4 cm away from the reaction vials within a ventilated fume hood. A typical reaction setup is shown below in *Figure S1*.

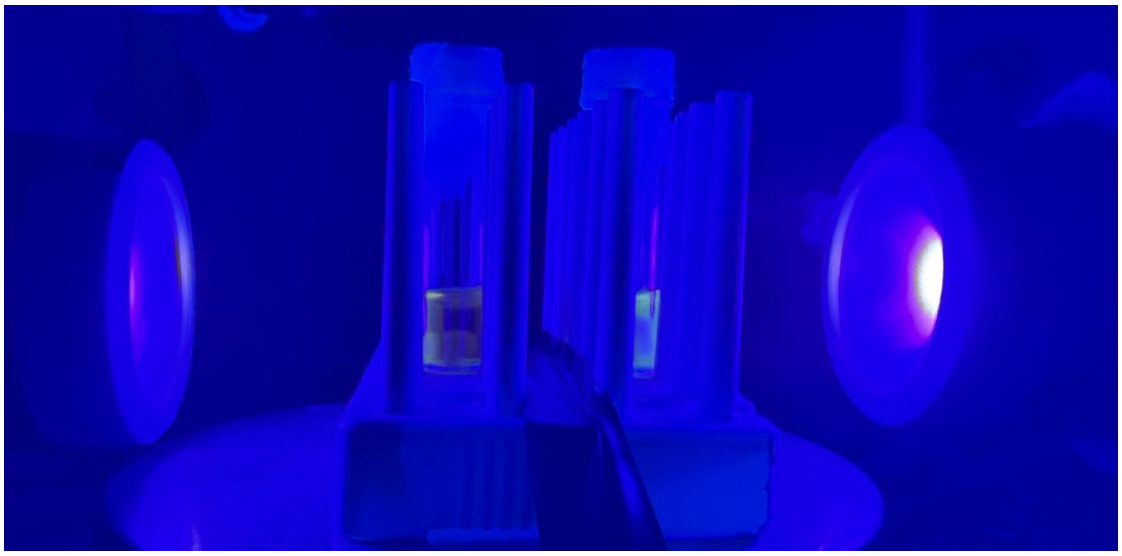
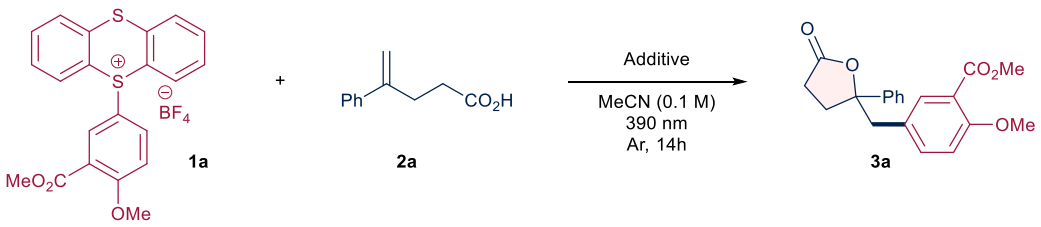


Figure S1. *Reaction setup for the photoinduced formation of heterocycles.*

B. Reaction Optimization

Table S1. Exploration of the optimal reaction conditions.

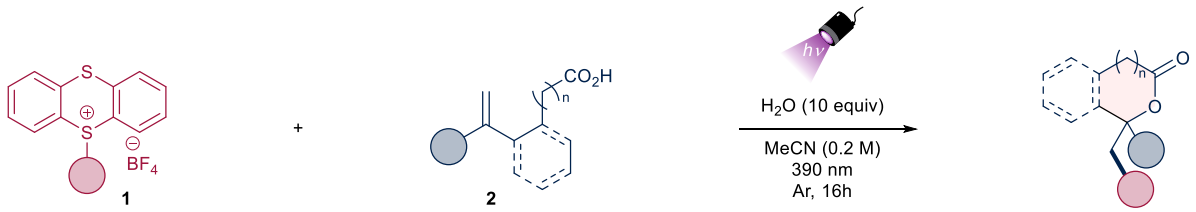
[6] B. N. Hemric, K. Shen, Q. Wang, *J. Am. Chem. Soc*. 2016, **138**, 5813-5816.
[7] R. Giri, S. Patra, D. Katayev, *ChemCatChem*, 2023**, 15**, e202201427.



Entry	Equiv **1a/2a**	Additive (equiv)	Yield (%)
1	1/2.5	DABCO (3.5)	34
2	1/2.5	DIPEA (3.5)	0
3	1/2.5	K_2CO_3 (3.5)	27
4	1.5/1	DABCO (3)	43
5	1.5/1	DABCO (2.0)	45
6	2/1	DABCO (2.0)	50
7 [a]	2/1	None	15
8 [a]	2/1	H_2O (10)	55
9 [a]	**2/1**	**H_2O (10)**	**72**
10 [a]	2/1	H_2O (5)	53
11 [a]	2/1	H_2O (15)	63
12 [a,b]	2/1	H_2O (10)	0

[a]0.2 M. [b]No light irradiation.

C. General Procedure:

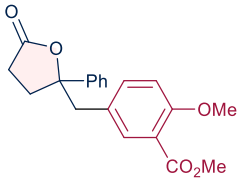


To an 8 mL vial equipped with a magnetic stir bar was added thianthrene-based radical precursor **1** (0.6 mmol, 2.0 equiv), radical acceptor **2** (0.3 mmol, 1.0 equiv), and H_2O (54 µL, 3.0 mmol, 10.0 equiv). The vial was then charged with dry ACN (1.5 mL, c = 0.2 M) and closed with a cap. The reaction mixture was irradiated for 14 h with a Kessil PR160-purple LED lamp (30 W High Luminous DEX 2100 LED, λ_{max} = 390 nm) as described in the "Workflow" section. The temperature of the reaction was maintained at approximately 25 °C via a fan. Upon completion, the reaction mixture was diluted with DCM, dried with Na_2SO_4 then the solvent was evaporatedunder reduced pressure.

The crude mixture was subjected to flash column chromatography purification using hexanes/EtOAc mixtures to yield the desired compound.

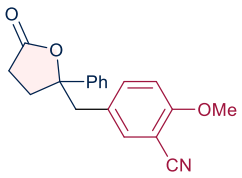
D. Characterization Data:

Methyl 2-Methoxy-5-((5-oxo-2-phenyltetrahydrofuran-2-yl)methyl)benzoate (3a)



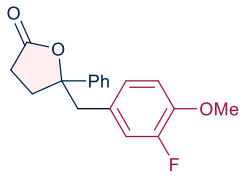
Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1a** (281.0 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2a** (52.9 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 3:2 Hexane:EtOAc), the title compound **3a** was obtained as a colorless oil (70.5 mg, 0.21 mmol, 69%). $\mathbf{R_f}$ = 0.40 (silica gel, *n*-hexane / EtOAc, 3:2 (v/v)); **^{1}H NMR** (500 MHz, $CDCl_3$), δ (ppm) = 7.49 (d, *J* = 2.4 Hz, 1H), 7.34 (m, 2H), 7.29 (s, 3H), 7.18 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.84 (d, *J* = 8.5 Hz, 1H), 3.86 (s, 6H), 3.20 (d, *J* = 14.2 Hz, 1H), 3.09 (d, *J* = 14.2 Hz, 1H), 2.56 – 2.43 (m, 2H), 2.39 – 2.32 (m, 1H), 2.19 (ddd, *J* = 17.7, 9.4, 5.9 Hz, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm) = 176.7, 166.9, 158.7, 143.5, 136.2, 134.0, 129.0, 128.2, 127.2, 125.3, 120.0, 112.4, 89.3, 56.5, 52.5, 48.0, 33.5, 29.2. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2950, 1776, 1724, 1599, 1491, 1434, 1301, 1244, 1301, 1244, 1164, 1129, 1081. **HRMS (ESI)** calcd for $C_{20}H_{21}O_5$ $[M+H]^+$: 341.1384, found 341.1388.

2-Methoxy-5-((5-oxo-2-phenyltetrahydrofuran-2-yl)methyl)benzonitrile (3b)



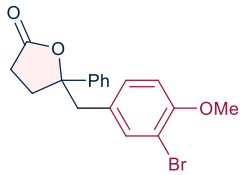
Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1b** (261.2 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2a** (52.9 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 1:1 Hexane:EtOAc), the title compound **3b** was obtained as a colorless oil (83.0 mg, 0.27 mmol, 90%). $\mathbf{R_f}$ = 0.33 (silica gel, *n*-hexane / EtOAc, 1:1 (v/v)); **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.34 – 7.28 (m, 3H), 7.25 – 7.20 (m, 3H), 7.12 (d, *J* = 2.3 Hz, 1H), 6.81 (d, *J* = 8.7 Hz, 1H), 3.88 (s, 3H), 3.18 (d, *J* = 14.3 Hz, 1H), 3.12 (d, *J* = 14.3 Hz, 1H), 2.54 – 2.46 (m, 2H), 2.38 (ddd, *J* = 10.2, 9.0, 7.0 Hz, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$), δ (ppm) = 176.4, 160.8, 142.6, 137.1, 135.7, 129.1, 128.5, 128.2, 125.2, 116.7, 111.6, 101.8, 89.0, 56.5, 47.7, 34.2, 29.0. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2927, 2225, 1770, 1608, 1580, 1502, 1445, 1417, 1267, 1168, 1124, 1017. **HRMS (ESI)** calcd for $C_{19}H_{18}NO_3$ $[M+H]^+$: 308.1281, found 308.1287.

5-(3-Fluoro-4-methoxybenzyl)-5-phenyldihydrofuran-2(3*H*)-one (3c)



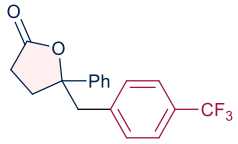
Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1c** (256.9 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2a** (52.9 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 3:1 Hexane:EtOAc), the title compound **3c** was obtained as a colorless oil (54.1 mg, 0.18 mmol, 60%). $\mathbf{R_f}$ = 0.45 (silica gel, *n*-hexane / EtOAc, 3:1 (v/v)); **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.33 (d, *J* = 6.7 Hz, 2H), 7.30 – 7.28 (m, 3H), 6.85 – 6.73 (m, 3H), 3.84 (s, 3H), 3.17 (d, *J* = 14.2 Hz, 1H), 3.05 (d, *J* = 14.2 Hz, 1H), 2.50 (m, 2H), 2.40 – 2.30 (m, 1H), 2.24 – 2.16 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$), δ (ppm) = 176.7, 152.3 (d, *J* = 247.5 Hz), 147.1 (d, *J* = 10.1 Hz), 143.4, 128.9, 128.3 (d, *J* = 7.1 Hz), 128.2, 126,9 (d, *J* = 3.0 Hz), 125.2, 118.6 (d, *J* = 18.2 Hz), 113.5 (d, *J* = 2.0 Hz), 89.2, 56.6, 48.1, 33.6, 29.2. **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$), δ (ppm) = -135.5. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 2936, 1768, 1515, 1444, 1271, 1223, 1165, 1125, 1051, 1024. **HRMS (ESI)** calcd for $C_{18}H_{18}FO_3$ $[M+H]^+$: 301.1234, found 301.1240.

5-(3-Bromo-4-methoxybenzyl)-5-phenyldihydrofuran-2(3*H*)-one (3d)



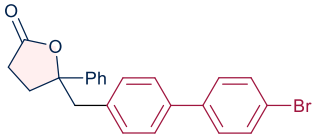
Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1d** (290.5 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2a** (52.9 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 3:1 Hexane:EtOAc), the title compound **3d** was obtained as a colorless oil (55.3 mg, 0.15 mmol, 51%). $\mathbf{R_f}$ = 0.35 (silica gel, *n*-hexane / EtOAc, 3:1 (v/v)); **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.38 – 7.27 (m, 5H), 7.22 (d, *J* = 2.1 Hz, 1H), 6.99 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 3.85 (s, 3H), 3.16 (d, *J* = 14.2 Hz, 1H), 3.04 (d, *J* = 14.3 Hz, 1H), 2.57 – 2.44 (m, 2H), 2.41 – 2.30 (m, 1H), 2.25 – 2.17 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$), δ (ppm) = 176.7, 155.4, 143.4, 135. 6, 131.2, 129.2, 128.9, 128.3, 125.2, 112.0, 111.6, 89.2, 56.6, 47.8, 33.6, 29.2. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 2922, 1769, 1602, 1495, 1442, 1279, 1254, 1165, 1053, 1018. **HRMS (ESI)** calcd for $C_{18}H_{18}BrO_3$ $[M+H]^+$: 361.0434, found 361.0436.

5-Phenyl-5-(4-(trifluoromethyl)benzyl)dihydrofuran-2(3*H*)-one (3e)



Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1e** (360.3 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2a** (52.9 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 3:1 Hexane:EtOAc), the title compound **3e** was obtained as a yellow oil (81.7 mg, 0.26 mmol, 85%). $\mathbf{R_f}$ = 0.35 (silica gel, *n*-hexane / EtOAc, 3:1 (v/v)); **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.46 (d, *J* = 8.0 Hz, 2H), 7.37 – 7.26 (m, 5H), 7.16 (d, *J* = 8.0 Hz, 2H), 3.31 (d, *J* = 14.0 Hz, 1H), 3.22 (d, *J* = 14.0 Hz, 1H), 2.53 (dd, *J* = 8.8, 7.3 Hz, 2H), 2.42 – 2.35 (m, 1H), 2.32 – 2.24 (m, 1H). **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$) δ (ppm) = -62.7. The data matches those previously reported.[8]

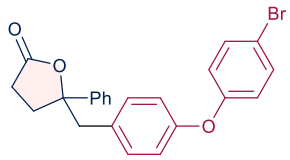
5-((4'-Bromo-[1,1'-biphenyl]-4-yl)methyl)-5-phenyldihydrofuran-2(3*H*)-one (3f)



Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1f** (206.4 mg, 0.40 mmol, 2.0 equiv) and radical acceptor **2a** (35.3 mg, 0.20 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 4:1 Hexane:EtOAc), the title compound **3f** was obtained as a yellow oil (80.4 mg, 0.20 mmol, 67%). $\mathbf{R_f}$ = 0.4 (silica gel, *n*-hexane / EtOAc, 4:1 (v/v)); **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.54 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 3.2 Hz, 2H), 7.42 (d, *J* = 3.2 Hz, 2H), 7.39 – 7.32 (m, 5H), 7.16 (d, *J* = 8.2 Hz, 2H), 3.30 (d, *J* = 14.1 Hz, 1H), 3.16 (d, *J* = 14.1 Hz, 1H), 2.61 – 2.54 (m, 1H), 2.54 – 2.45 (m, 1H), 2.40 – 2.31 (m, 1H), 2.23 – 2.14 (m, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm) = 176.8, 143.8, 140.0, 139.1, 135.0, 132.3, 131.7, 129.0, 129.0, 128.2, 127.2, 125.3, 122.0, 89.3, 48.8, 33.6, 29.3. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 3059, 2922, 1759, 1487, 1440, 1342, 1234, 1196, 1158, 1126, 1050, 1035. **HRMS (ESI)** calcd for $C_{23}H_{20}BrO_2$ $[M+H]^+$: 407.0641, found 407.0645.

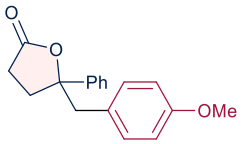
[8] Y. Gao, J. Xu, P. Zhang, H. Fang, G. Tang. Y. Zhao, *RSC Adv.* 2015, **5**, 36167-36170.

5-(4-(4-Bromophenoxy)benzyl)-5-phenyldihydrofuran-2(3*H*)-one (3g)



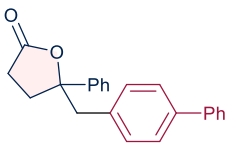
Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1g** (330.7 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2a** (52.9 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 4:1 Hexane:EtOAc), the title compound **3g** was obtained as a yellow oil (88.9 mg, 0.21 mmol, 70%). $\mathbf{R_f}$ = 0.40 (silica gel, *n*-hexane / EtOAc, 4:1 (v/v)); **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.42 (d, *J* = 8.8 Hz, 2H), 7.32 (m, 5H), 7.04 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 6.6 Hz, 2H), 6.84 (d, *J* = 6.6 Hz, 2H), 3.23 (d, *J* = 14.1 Hz, 1H), 3.12 (d, *J* = 14.2 Hz, 1H), 2.58 – 2.45 (m, 2H), 2.41 – 2.33 (m, 1H), 2.25 – 2.16 (m, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm) = 176.8, 156.9, 156.3, 143.6, 133.1, 132.5, 130.9, 128.9, 128.2, 125.3, 120.9, 119.2, 116.2, 89.4, 48.4, 33.7, 29.2. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2919, 1770, 1580, 1504, 1478, 1447, 1230, 1162, 1067. **HRMS (ESI)** calcd for $C_{23}H_{20}BrO_3$ $[M+H]^+$: 423.0590, found 423.0596.

5-(4-Methoxybenzyl)-5-phenyldihydrofuran-2(3*H*)-one (3h)



Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1h** (246.2 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2a** (52.9 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 3:1 Hexane:EtOAc), the title compound **3h** was obtained as a colorless oil (39.8 mg, 0.14 mmol, 47%). $\mathbf{R_f}$ = 0.45 (silica gel, *n*-hexane / EtOAc, 3:1 (v/v)); **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) = 7.39 – 7.31 (m, 4H), 7.31 – 7.27 (m, 1H), 7.03 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 3.77 (s, 3H), 3.20 (d, *J* = 14.2 Hz, 1H), 3.05 (d, *J* = 14.3 Hz, 1H), 2.57 – 2.52 (m, 1H), 2.45 – 2.40 (m, 1H), 2.34 – 2.28 (m 1H), 2.10 – 2.05 (m, 1H). The data matches those previously reported.[8]

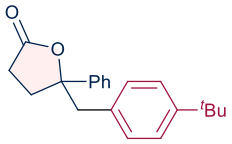
5-([1,1'-Biphenyl]-4-ylmethyl)-5-phenyldihydrofuran-2(3*H*)-one (3i)



Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1i** (273.8 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2a** (52.9 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 9:1

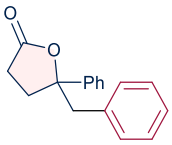
to 6:1 Hexane:EtOAc), the title compound **3i** was obtained as a yellow solid (81.8 mg, 0.25 mmol, 83%). $\mathbf{R_f}$ = 0.25 (silica gel, *n*-hexane / EtOAc, 6:1 (v/v)); **mp** = 58-60 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.58 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.38 – 7.30 (m, 6H), 7.18 (d, *J* = 8.1 Hz, 2H), 3.31 (d, *J* = 14.1 Hz, 1H), 3.16 (d, *J* = 14.1 Hz, 1H), 2.62 – 2.57 (m, 1H), 2.51 – 2.46 (m, 1H), 2.38 – 2.32 (m, 1H), 2.20 – 2.14 (m, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm) = 176.9, 143.9, 141.1, 140.4, 134.6, 131.6, 129.2, 128.9, 128.2, 127.8, 127.5, 127.4, 125.3, 89.4, 48.8, 33.5, 29.3. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 3021, 1765, 1485, 1446, 1224, 1166, 1115, 1052, 1004. **HRMS (ESI)** calcd for $C_{23}H_{21}O_2$ $[M+H]^+$: 329.1536, found 329.1541.

5-(4-(Tert-butyl)benzyl)-5-phenyldihydrofuran-2(3*H*)-one (3j)



Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1j** (299.2 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2a** (52.9 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 6:1 Hexane:EtOAc), the title compound **3j** was obtained as a white solid (61.6 mg, 0.20 mmol, 66%). $\mathbf{R_f}$ = 0.5 (silica gel, *n*-hexane / EtOAc, 4:1 (v/v)); **mp** = 105-108 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.37 – 7.35 (m, 4H), 7.29 (dd, *J* = 8.6, 2.2 Hz, 3H), 7.08 (d, *J* = 8.3 Hz, 2H), 3.25 (d, *J* = 14.1 Hz, 1H), 3.06 (d, *J* = 14.1 Hz, 1H), 2.60 – 2.53 (m, 1H), 2.46 – 2.38 (m, 1H), 2.34 – 2.25 (m, 1H), 2.05 – 1.96 (m, 1H), 1.30 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$), δ (ppm) = 177.0, 150.5, 144.4, 132.4, 130.8, 128.9, 128.1, 125.7, 125.2, 89.5, 48.7, 34.9, 33.2, 31.8, 29.3. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2956, 1760, 1513, 1449, 1361, 1259, 1225, 1187, 1173, 1049, 1002. **HRMS (ESI)** calcd for $C_{21}H_{25}O_2$ $[M+H]^+$: 309.1849, found 309.1851.

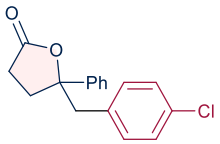
5-Benzyl-5-phenyldihydrofuran-2(3*H*)-one (3k)



Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1k** (265.5 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2a** (52.9 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 4:1 Hexane:EtOAc), the title compound **3k** was obtained as a yellow oil (46,9 mg, 0.19 mmol, 62%). $\mathbf{R_f}$ = 0.38 (silica gel, *n*-hexane / EtOAc, 4:1 (v/v)); **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.39 – 7.27 (m, 5H), 7.26 – 7.23

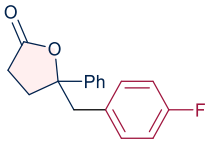
(m, 3H), 7.11 (dd, *J* = 6.8, 2.8 Hz, 2H), 3.27 (d, *J* = 14.0 Hz, 1H), 3.12 (d, *J* = 14.1 Hz, 1H), 2.60 – 2.53 (m, 1H), 2.49 – 2.42 (m, 1H), 2.36 – 2.27 (m, 1H), 2.12 – 2.03 (m, 1H). The data matches those previously reported.[9]

5-(4-Chlorobenzyl)-5-phenyldihydrofuran-2(3*H*)-one (3l)



Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1l** (286.2 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2a** (52.9 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 4:1 Hexane:EtOAc), the title compound **3l** was obtained as a yellow oil (59.8 mg, 0.21 mmol, 69%). $\mathbf{R_f}$ = 0.33 (silica gel, *n*-hexane / EtOAc, 4:1 (v/v)); **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) = 7.33 (d, *J* = 6.9 Hz, 2H), 7.31 – 7.27 (m, 3H), 7.21 – 7.16 (m, 2H), 7.01 – 6.97 (m, 2H), 3.21 (d, *J* = 14.2 Hz, 1H), 3.12 (d, *J* = 14.2 Hz, 1H), 2.53 – 2.47 (m, 2H), 2.40 – 2.32 (m, 1H), 2.26 – 2.20 (m, 1H). The data matches those previously reported.[9]

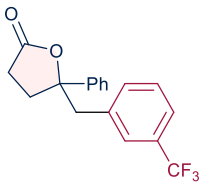
5-(4-Fluorobenzyl)-5-phenyldihydrofuran-2(3*H*)-one (3m)



Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1m** (276.3 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2a** (52.9 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 3:1 Hexane:EtOAc), the title compound **3m** was obtained as a yellow oil (55.1 mg, 0.20 mmol, 68%). $\mathbf{R_f}$ = 0.45 (silica gel, *n*-hexane / EtOAc, 3:1 (v/v)); **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) = 7.35 – 7.27 (m, 5H), 7.05 – 7.00 (m, 2H), 6.91 (t, *J* = 8.6 Hz, 2H), 3.22 (d, *J* = 14.3 Hz, 1H), 3.12 (d, *J* = 14.2 Hz, 1H), 2.57 – 2.45 (m, 2H), 2.39 – 2.33 (m, 1H), 2.23 – 2.17 (m, 1H). **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$) δ (ppm) = -115.6. The data matches those previously reported.[9]

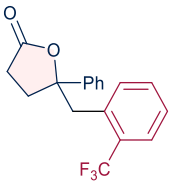
[9] W. Guo, H.-G. Cheng, L.-Y. Chen, J. Xuan, Z.-J. Feng, J.-R. Chen, L. Lu, *Adv. Synth. Catal.* 2014, **356**, 2787–2793.

5-Phenyl-5-(3-(trifluoromethyl)benzyl)dihydrofuran-2(3*H*)-one (3n)



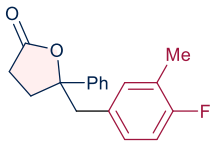
Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1n** (360.3 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2a** (52.9 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 3:1 Hexane:EtOAc), the title compound **3n** was obtained as a yellow oil (80.7 mg, 0.25 mmol, 84%). $\mathbf{R_f}$ = 0.38 (silica gel, *n*-hexane / EtOAc, 3:1 (v/v)); **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.47 (d, *J* = 7.8 Hz, 1H), 7.37 – 7.28 (m, 4H), 7.26 (m, 3H), 7.18 (s, 1H), 3.30 (d, *J* = 14.0 Hz, 1H), 3.22 (d, *J* = 14.0 Hz, 1H), 2.60 – 2.47 (m, 2H), 2.46 – 2.24 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ (ppm) = 176.2, 142.5, 136.2, 134.3, 130.7 (q, *J* = 31.5 Hz), 128.9, 128.8, 127.4 (q, *J* = 3.8 Hz), 125.1, 124.1 (q, *J* = 3.8 Hz), 122.1 (q, *J* = 273.4 Hz), 88.8, 48.7, 33.8, 28.9. **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$), δ (ppm) = -62.7. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 3062, 2925, 1773, 1494, 1448, 1326, 1159, 1117, 1073, 1003. **HRMS (ESI)** calcd for $C_{18}H_{16}F_3O_2$ $[M+H]^+$: 321.1097, found 321.1101.

5-Phenyl-5-(2-(trifluoromethyl)benzyl)dihydrofuran-2(3*H*)-one (3o)



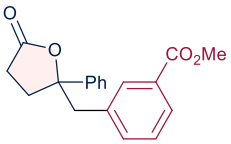
Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1o** (360.3 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2a** (52.9 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (9:1 to 3:1 Hexane:EtOAc), the title compound **3o** was obtained as a yellow oil (78.8 mg, 0.25 mmol, 82%). $\mathbf{R_f}$ = 0.35 (silica gel, *n*-hexane / EtOAc, 3:1 (v/v)); **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.66 (d, *J* = 7.9 Hz, 1H), 7.53 – 7.32 (m, 8H), 3.51 (d, *J* = 15.5 Hz, 1H), 3.42 (d, *J* = 15.5 Hz, 1H), 2.48 – 2.38 (m, 1H), 2.35 – 2.16 (m, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ (ppm) = 176.7, 143.8, 134.6, 133.5, 132.3, 130.0 (q, *J* = 29.0 Hz), 129.1, 128.4, 127.7, 126.5 (q, *J* = 6.3 Hz), 125.2, 125.0 (q, *J* = 274.7 Hz), 89.4, 43.5, 33.5, 29.0. **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$), δ (ppm) = -57.9. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 3063, 1776, 1606, 1447, 1308, 1230, 1155, 1105, 1061, 1037. **HRMS (ESI)** calcd for $C_{18}H_{16}F_3O_2$ $[M+H]^+$: 321.1097, found 321.1101.

5-(4-Fluoro-3-methylbenzyl)-5-phenyldihydrofuran-2(3*H*)-one (3p)



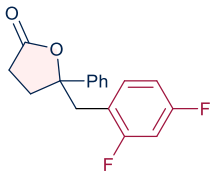
Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1p** (314.7 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2a** (52.9 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 3:1 Hexane:EtOAc), the title compound **3p** was obtained as a white solid (49.0 mg, 0.17 mmol, 57%). $\mathbf{R_f}$ = 0.48 (silica gel, *n*-hexane / EtOAc, 3:1 (v/v)); **mp** = 67-69 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.38 – 7.32 (m, 2H), 7.31 – 7.29 (m, 3H), 6.89 (d, *J* = 7.4 Hz, 1H), 6.88 – 6.80 (m, 2H), 3.18 (d, *J* = 14.1 Hz, 1H), 3.05 (d, *J* = 14.1 Hz, 1H), 2.57 – 2.43 (m, 2H), 2.34 (m, 1H), 2.22 – 2.10 (m, 4H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm) = 176.8, 161.1 (d, *J* = 245.7 Hz), 143.7, 134.2 (d, *J* = 5.0 Hz), 130.9, 129.8 (d, *J* = 7.6 Hz), 128.9, 128.2, 125.3, 125.0 (d, *J* = 22.7 Hz), 115.2 (d, *J* = 22.7 Hz), 89.3, 48.4, 33.5, 29.3, 14.9 (d, *J* = 3.8Hz). **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$), δ (ppm) = -120.1. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 2923, 1761, 1498, 1448, 1346, 1247, 1234, 1200, 1161, 1140, 1120, 1056. **HRMS (ESI)** calcd for $C_{18}H_{18}FO_2$ $[M+H]^+$: 285.1285, found 285.1290.

Methyl 3-((5-Oxo-2-phenyltetrahydrofuran-2-yl)methyl)benzoate (3q)



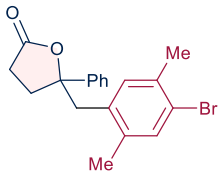
Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1q** (300.0 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2a** (52.9 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 3:1 Hexane:EtOAc), the title compound **3q** was obtained as a colorless oil (43.8 mg, 0.14 mmol, 47%). $\mathbf{R_f}$ = 0.33 (silica gel, *n*-hexane / EtOAc, 3:1 (v/v)); **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.90 (d, *J* = 7.5 Hz, 1H), 7.75 (s, 1H), 7.35 – 7.27 (m, 7H), 3.89 (s, 3H), 3.30 (d, *J* = 14.0 Hz, 1H), 3.20 (d, *J* = 14.1 Hz, 1H), 2.59 – 2.44 (m, 2H), 2.40 – 2.31 (m, 1H), 2.19 (ddd, *J* = 17.7, 9.2, 5.9 Hz, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm) = 176.6, 167.4, 143.3, 135.9, 135.7, 132.0, 130.6, 129.1, 129.0, 128.8, 128.3, 125.3, 89.1, 52.6, 48.8, 33.7, 29.1. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 2950, 1771, 1715, 1605, 1494, 1445, 1280, 1199, 1162, 1107, 1085, 1032, 1003. **HRMS (ESI)** calcd for $C_{19}H_{19}O_4$ $[M+H]^+$: 311.1278, found 311.1282.

5-(2,4-Difluorobenzyl)-5-phenyldihydrofuran-2(3*H*)-one (3r)



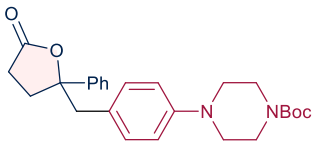
Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1r** (191.4 mg, 0.40 mmol, 2.0 equiv) and radical acceptor **2a** (35.3 mg, 0.20 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 6:1 Hexane:EtOAc), the title compound **3r** was obtained as a yellow oil (47.3 mg, 0.16 mmol, 82%). $\mathbf{R_f}$ = 0.33 (silica gel, *n*-hexane / EtOAc, 6:1 (v/v)); **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.40 – 7.27 (m, 5H), 7.03 (td, *J* = 8.7, 6.4 Hz, 1H), 6.81 – 6.67 (m, 2H), 3.27 (dd, *J* = 14.3, 1.5 Hz, 1H), 3.18 (dd, *J* = 14.4, 1.5 Hz, 1H), 2.57 – 2.47 (m, 2H), 2.47 – 2.24 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm) = 176.5, 162.6 (dd, *J* = 249.5, 12.6 Hz), 159.5 (dd, *J* = 248.2, 11.3 Hz), 143.1, 134.1 (dd, *J* = 6.3, 5.0 Hz), 129.0, 128.4, 125.2, 118.5 (dd, *J* = 15.1, 3.8 Hz), 111.7 (dd, *J* = 21.4, 3.8 Hz), 104.0 (dd, *J* = 25.2, 25.2 Hz), 89.1, 40.5, 33.7, 29.2. **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$), δ (ppm) = -111.0 (d, *J* = 7.5 Hz), -112.8 (d, *J* = 7.5 Hz). **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 3066, 1772, 1618, 1503, 1447, 1277, 1189, 1137, 1094. **HRMS (ESI)** calcd for $C_{17}H_{15}F_2O_2$ $[M+H]^+$: 289.1035, found 289.1038.

5-(4-Bromo-2,5-dimethylbenzyl)-5-phenyldihydrofuran-2(3*H*)-one (3s)



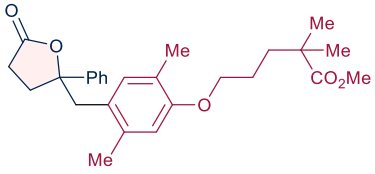
Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1s** (292.3 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2a** (52.9 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 3:1 Hexane:EtOAc), the title compound **3s** was obtained as a white solid (53.9 mg, 0.15 mmol, 50%). $\mathbf{R_f}$ = 0.58 (silica gel, *n*-hexane / EtOAc, 3:1 (v/v)); **mp** = 84-87 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) = 7.35 (d, *J* = 7.3 Hz, 2H), 7.33 – 7.28 (m, 4H), 6.91 (s, 1H), 3.16 (d, *J* = 14.4 Hz, 1H), 3.11 (d, *J* = 14.4 Hz, 1H), 2.51 (td, *J* = 8.7, 5.3 Hz, 2H), 2.38 – 2.33 (m, 1H), 2.29 – 2.22 (m, 4H), 2.09 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm) = 176.0, 143.2, 137.0, 134.9, 133.9, 133.8, 132.7, 128.5, 127.9, 124.9, 123.5, 89.2, 44.3, 33.1, 28.7, 22.2, 19.2. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 3059, 2922, 1759, 1487, 1440, 1342, 1234, 1196, 1158, 1126, 1050. **HRMS (ESI)** calcd for $C_{19}H_{20}BrO_2$ $[M+H]^+$: 359.6041, found 359.6045.

***Tert*-butyl 4-(4-((5-oxo-2-phenyltetrahydrofuran-2-yl)methyl)phenyl)piperazine-1-carboxylate (3t)**



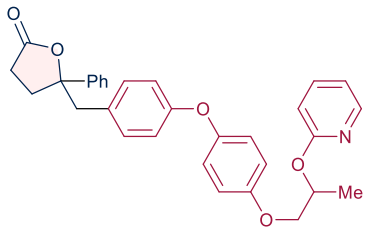
Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1t** (338.7 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2a** (52.9 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 1:1 Hexane:EtOAc), the title compound **3t** was obtained as a brown oil (52.3 mg, 0.12 mmol, 40%). $\mathbf{R_f}$ = 0.85 (silica gel, *n*-hexane / EtOAc, 1:1 (v/v)); **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) = 7.36 – 7.32 (m, 5H), 7.02 (d, *J* = 8.5 Hz, 2H), 6.83 – 6.79 (m, 2H), 3.56 (t, *J* = 5.2 Hz, 4H), 3.17 (s, 1H), 3.10 (s, 4H), 3.01 (d, *J* = 14.3 Hz, 1H), 2.56 – 2.51 (m,1H), 2.43 – 2.39 (m, 1H), 2.32 – 2.27 (m, 1H), 2.08 – 2.04 (m, 1H), 1.48 (s, 9H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm) = 176.6, 154.8, 150.2, 143.8, 131.4, 128.4, 127.6, 126.6, 124.7, 116.3, 89.2, 80.0, 49.3, 47.9, 32.8, 28.9, 28.8, 28.5. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2972, 1772, 1687, 1515, 1365, 1160, 1124, 1000. **HRMS (ESI)** calcd for $C_{26}H_{33}N_2O_4$ $[M+H]^+$: 437.2435, found 437.2442.

Methyl 6-(2,5-Dimethyl-4-((5-oxo-2-phenyltetrahydrofuran-2-yl)methyl)phenoxy)-2,2-dimethylhexanoate (3u)



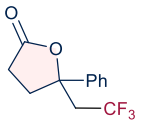
Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1u** (339.9 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2a** (52.9 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 4:1 Hexane:EtOAc), the title compound **3u** was obtained as a white solid (46.0 mg, 0.11 mmol, 35%). $\mathbf{R_f}$ = 0.35 (silica gel, *n*-hexane / EtOAc, 4:1 (v/v)); **mp =** 70-72 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.41 – 7.28 (m, 5H), 6.86 (s, 1H), 6.54 (s, 1H), 3.89 (s, 2H), 3.67 (s, 3H), 3.16 (d, *J* = 14.5 Hz, 1H), 3.05 (d, *J* = 14.5 Hz, 1H), 2.61 – 2.54 (m, 1H), 2.46 – 2.39 (m, 1H), 2.33 – 2.25 (m, 2H), 2.17 – 2.07 (m, 7H), 1.72 (s, 3H), 1.61 – 1.59 (m, 1H), 1.22 (m, 7H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm) = 178.8, 176.8, 156.5, 144.5, 136.5, 134.1, 128.9, 128.1, 125.2, 124.5, 113.5, 90.3, 68.4, 52.2, 44.8, 42.6, 37.6, 33.2, 29.3, 25.7, 20.4, 16.1. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2922, 1762, 1737, 1614, 1513, 1460, 1427, 1390, 1323, 1272, 1167, 1141, 1080. **HRMS (ESI)** calcd for $C_{28}H_{36}O_5Na$ $[M+Na]^+$: 475.2455, found 475.2455.

5-Phenyl-5-(4-(4-(2-(pyridin-2-yloxy)propoxy)phenoxy)benzyl)dihydrofuran-2(3*H*)-one (3v)



Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1v** (374.1 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2a** (52.9 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 4:1 Hexane:EtOAc with 4 % of NEt_3), the title compound **3v** was obtained as a colorless oil (50.7 mg, 0.13 mmol, 42%). $\mathbf{R_f}$ = 0.13 (silica gel, *n*-hexane / EtOAc, 4:1 (v/v)); **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 8.15 (dd, *J* = 5.2, 2.0 Hz, 1H), 7.57 (ddd, *J* = 8.8, 7.2, 2.0 Hz, 1H), 7.39 – 7.27 (m, 5H), 7.01 (d, *J* = 8.5 Hz, 2H), 6.92 (s, 4H), 6.88 – 6.84 (m, 1H), 6.81 (d, *J* = 8.6 Hz, 2H), 6.74 (d, *J* = 8.4 Hz, 1H), 5.58 (ddd, *J* = 11.7, 6.7, 5.2 Hz, 1H), 4.19 (dd, *J* = 9.9, 5.3 Hz, 1H), 4.07 (dd, *J* = 9.9, 4.8 Hz, 1H), 3.21 (d, *J* = 14.2 Hz, 1H), 3.07 (d, *J* = 14.2 Hz, 1H), 2.55 (ddd, *J* = 12.6, 9.5, 7.4 Hz, 1H), 2.45 (ddd, *J* = 12.5, 9.3, 6.1 Hz, 1H), 2.34 (ddd, *J* = 16.9, 9.3, 7.4 Hz, 1H), 2.15 (ddd, *J* = 17.5, 9.5, 6.0 Hz, 1H), 1.48 (d, *J* = 6.4 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$), δ (ppm) = 176.8, 163.6, 158.1, 155.7, 150.6, 147.3, 143.9, 139.2, 132.3, 129.4, 128.9, 128.2, 125.3, 121.2, 117.8, 117.2, 116.3, 112.2, 89.4, 71.5, 69.7, 48.4, 33.5, 29.3, 17.5. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 3056, 2930, 1771, 1594, 1569, 1495, 1469, 1430, 1285, 1216, 1165, 1079. **HRMS (ESI)** calcd for $C_{31}H_{30}NO_5$ $[M+H]^+$: 496.2118, found 496.2124.

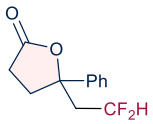
5-Phenyl-5-(2,2,2-trifluoroethyl)dihydrofuran-2(3*H*)-one (3w)



Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1w** (260.6 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2a** (52.9 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 3:1 Hexane:EtOAc), the title compound **3w** was obtained as a yellow solid (57.6 mg, 0.24 mmol, 79%). $\mathbf{R_f}$ = 0.28 (silica gel, *n*-hexane / EtOAc, 3:1 (v/v)); **^{1}H NMR** (500 MHz, $CDCl_3$), δ (ppm) = 7.40 (t, *J* = 4.6 Hz, 4H), 7.35 (td, *J* = 5.2, 3.4 Hz, 1H), 2.94 – 2.75 (m, 2H), 2.71 – 2.58 (m, 3H), 2.52 – 2.39 (m, 1H). **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$) δ (ppm) = -60.5. The data matches those previously reported.[10]

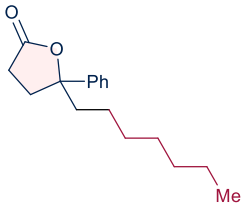
[10] R. Zhu, S. L. Buchwald, *J. Am. Chem. Soc*. 2012, **134**, 12462–12465.

5-(2,2-Difluoroethyl)-5-phenyldihydrofuran-2(3H)-one (3x)



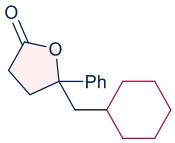
Prepared according to the *General Procedure* from the corresponding sulfonium salt **1x** (202.8 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2a** (52.9 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 0-20% EtOAc in Hexane), the title compound **3x** was obtained as a colorless oil (52.5 mg, 0.25 mmol, 82%). $\mathbf{R_f}$ = 0.35 (silica gel, *n*-hexane / EtOAc, 6:1 (v/v)); **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.44 – 7.29 (m, 5H), 5.70 (tt, *J* = 55.6, 4.7 Hz, 1H), 2.66 – 2.34 (m, 6H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$), δ (ppm) = 175.62, 141.2, 128.98, 128.4, 124.5, 114.7 (t, *J* = 239.5 Hz), 85.3, 45.9 (t, *J* = 21.7 Hz), 35.0, 28.0. **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$) δ (ppm) = -113.8, -113.9. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2985, 1774, 1494, 1407, 1191, 1114, 1063. **HRMS (ESI)** calcd for $C_{12}H_{13}F_2O_2$ $[M+H]^+$: 227.0878, found 227.0879.

5-Heptyl-5-phenyldihydrofuran-2(3*H*)-one (3y)



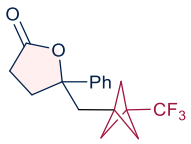
Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1y** (270.3 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2a** (52.9 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 6:1 Hexane:EtOAc), the title compound **3x** was obtained as a colorless oil (44.6 mg, 0.17 mmol, 57%). $\mathbf{R_f}$ = 0.60 (silica gel, *n*-hexane / EtOAc, 6:1 (v/v)); **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) = 7.41 – 7.23 (m, 5H), 2.62 – 2.52 (m, 1H), 2.49 – 2.40 (m, 3H), 1.99 – 1.89 (m, 2H), 1.38 – 1.28 (m, 1H), 1.26 – 1.12 (m, 8H), 1.10 – 1.01 (m, 1H), 0.84 (t, *J* = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$), δ (ppm) = 176.7, 143.1, 128.5, 127.5, 124.6, 89.6, 42.5, 35.1, 31.7, 29.6, 29.0, 28.7, 23.8, 22.6, 14.1. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2926, 2854, 1772, 1447, 1176, 1125, 1029. **HRMS (ESI)** calcd for $C_{17}H_{25}O_2$ $[M+H]^+$: 261.1849, found 261.1849.

5-(Cyclohexylmethyl)-5-phenyldihydrofuran-2(3*H*)-one (3z)



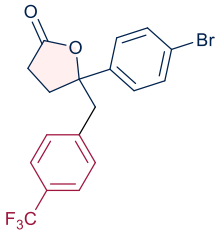
Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1z** (97.7 mg, 0.20 mmol, 2.0 equiv) and radical acceptor **2a** (17.6 mg, 0.10 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 7:1 Hexane:EtOAc), the title compound **3y** was obtained as a yellow oil (14.1 mg, 0.05 mmol, 55%). $\mathbf{R_f}$ = 0.50 (silica gel, *n*-hexane / EtOAc, 4:1 (v/v)); **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.44 – 7.26 (m, 5H), 2.61 – 2.47 (m, 1H), 2.46 – 2.31 (m, 3H), 1.94 (dd, *J* = 14.7, 5.0 Hz, 1H), 1.88 – 1.73 (m, 2H), 1.53 – 1.51 (m, 3H), 1.38 – 1.29 (m, 1H), 1.27 – 1.14 (m, 1H), 1.12 – 0.99 (m, 3H), 0.96 – 0.76 (m, 2H). The data matches those previously reported.[11]

5-Phenyl-5-((3-(trifluoromethyl)bicyclo[1.1.1]pentan-1-yl)methyl)dihydrofuran-2(3*H*)-one (3aa)



Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1aa** (262.9 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2a** (52.9 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 3:1 Hexane:EtOAc), the title compound **3z** was obtained as a yellow oil (38.3 mg, 0.12 mmol, 41%). $\mathbf{R_f}$ = 0.40 (silica gel, *n*-hexane / EtOAc, 3:1 (v/v)); **^{1}H NMR** (500 MHz, $CDCl_3$), δ (ppm) = 7.40 – 7.38 (m, 2H), 7.34 – 7.29 (m, 3H), 2.54 (ddd, *J* = 16.7, 8.7, 4.7 Hz, 1H), 2.45 (q, *J* = 8.8 Hz, 1H), 2.38 (dt, *J* = 13.0, 5.3 Hz, 3H), 2.22 (d, *J* = 15.1 Hz, 1H), 1.69 (d, *J* = 9.6 Hz, 3H), 1.55 (d, *J* = 9.5 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm) = 176.9, 142.6, 129.2, 128.4, 125.0, 122.8 (q, *J* = 275.9 Hz), 88.8, 50.5 (q, *J* = 2.5 Hz), 43.2, 38.4 (q, *J* = 39.1 Hz), 37.4, 36.8, 28.5. **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$), δ (ppm) = -73.4. **FT-IR** (cm^{-1}, neat, ATR), ṽ =2989, 2920, 1774, 1517, 1448, 1391, 1227, 1168, 1122, 1053. **HRMS (ESI)** calcd for $C_{17}H_{18}F_3O_2$ $[M+H]^+$: 311.1253, found 311.1254.

5-(4-Bromophenyl)-5-(4-(trifluoromethyl)benzyl)dihydrofuran-2(3*H*)-one (4a)

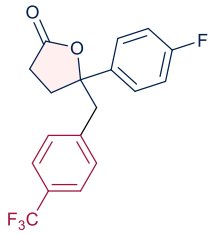


Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1e** (306.3 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2b** (76.5 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 3:1 Hexane:EtOAc), the title compound **4a** was obtained as a white solid (74.3 mg, 0.19 mmol, 62%). $\mathbf{R_f}$ = 0.25

[11] W. Sha, S. Ni, J. Han, Y. Pan, *Org. Lett.* 2017, **19**, 5900–5903.

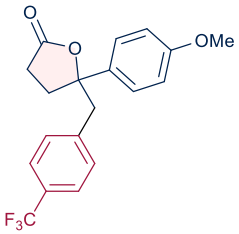
(silica gel, *n*-hexane / EtOAc, 3:1 (v/v)); **mp =** 93-95 ºC; **^{1}H NMR** (500 MHz, $CDCl_3$), δ (ppm) = 7.48 (d, *J* = 6.5 Hz, 2H), 7.47 (d, *J* = 6.5 Hz, 2H), 7.20 – 7.11 (m, 4H), 3.27 (d, *J* = 14.0 Hz, 1H), 3.20 (d, *J* = 14.0 Hz, 1H), 2.57 – 2.43 (m, 2H), 2.39 (dt, *J* = 17.1, 8.4 Hz, 1H), 2.30 (ddd, *J* = 17.6, 9.4, 5.7 Hz, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm) = 175.6, 141.6, 138.7, 131.7, 130.9, 129.5 (q, *J* = 32.8 H), 126.6, 125.2, 124.1 (q, *J* = 272.2 Hz), 122.1, 88.0, 48.2, 33.6, 28.5. **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$) δ (ppm) = -62.5. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2952, 1766, 1468, 1419, 1323, 1161, 1108. **HRMS (ESI)** calcd for $C_{18}H_{15}BrF_3O_2$ $[M+H]^+$: 399.0202, found 399.0202.

5-(4-Fluorophenyl)-5-(4-(trifluoromethyl)benzyl)dihydrofuran-2(3*H*)-one (4b)



Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1e** (306.3 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2c** (52.8 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 3:1 Hexane:EtOAc), the title compound **4b** was obtained as a yellow oil (75.1 mg, 0.22 mmol, 74%). **R_f** = 0.23 (silica gel, *n*-hexane / EtOAc, 3:1 (v/v)); **^{1}H NMR** (500 MHz, $CDCl_3$), δ (ppm) = 7.47 (d, *J* = 8.1 Hz, 2H), 7.25 – 7.19 (m, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 8.7 Hz, 1H), 7.01 (d, *J* = 8.7 Hz, 1H), 3.27 (d, *J* = 14.0 Hz, 1H), 3.20 (d, *J* = 14.0 Hz, 1H), 2.58 – 2.47 (m, 2H), 2.46 – 2.26 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm) = 176.7, 162.2 (d, *J* = 248.2 Hz), 138.6 (d, *J* = 84.4 Hz), 130.9, 129.4 (q, *J* = 32.8 Hz), 126.7 (d, *J* = 7.6 Hz), 125.1 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272.2 Hz), 115.6, 115.4, 88.1, 48.5, 33.7, 28.6. **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$) δ (ppm) = -62.6, -114.1. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 3058, 1775, 1604, 1510, 1419, 1322, 1277, 1157, 1065. **HRMS (ESI)** calcd for $C_{18}H_{15}F_4O_2$ $[M+H]^+$: 339.1003, found 339.1002.

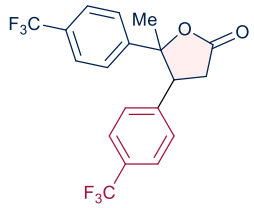
5-(4-Methoxyphenyl)-5-(4-(trifluoromethyl)benzyl)dihydrofuran-2(3*H*)-one (4c)



Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1e** (102.1 mg, 0.20 mmol, 2.0 equiv) and radical acceptor **2d** (20.6 mg, 0.10 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 4:1 Hexane:EtOAc), the title compound **4c** was obtained as a yellow oil (18.0 mg, 0.05 mmol, 51%). **R_f** = 0.19

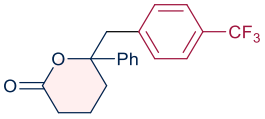
(silica gel, *n*-hexane / EtOAc, 4:1 (v/v)); **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) = 7.47 (d, *J* = 8.0 Hz, 2H), 7.20 – 7.16 (m, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 3.27 (d, *J* = 14.0 Hz, 1H), 3.20 (d, *J* = 14.0 Hz, 1H), 2.54 – 2.46 (m, 2H), 2.40 (ddd, *J* = 17.6, 9.6, 7.9 Hz, 1H), 2.30 (ddd, *J* = 17.6, 8.2, 6.4 Hz, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm) = 176.1, 159.2, 139.2, 134.3, 130.9, 129.3 (q, *J* = 32.8 Hz), 126.1, 125.0, 124.4 (q, *J* = 272.2 Hz), 113.2, 88.5, 55.3, 48.5, 33.6, 28.7. **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$), δ (ppm) = -62.5. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 2975, 1774, 1617, 1446, 1320, 1161, 1107, 1065, 1017. **HRMS (ESI)** calcd for $C_{19}H_{18}F_3O_3$ $[M+H]^+$: 351.1203, found 351.1205.

5-methyl-4,5-bis(4-(trifluoromethyl)phenyl)dihydrofuran-2(3H)-one (4d)



Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1e** (102.1 mg, 0.20 mmol, 2.0 equiv) and radical acceptor **2i** (61 mg, 0.25 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 4:1 Hexane:EtOAc), the title compound **4d** was obtained as a yellow oil (33.3 mg, 0.08 mmol, 36%). **R_f** = 0.62 (silica gel, *n*-hexane / EtOAc, 4:1 (v/v)); **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.72–7.67 (m, 4H), 7.50–7.46 (m, 3H), 7.32 (bs, 1H), 3.82 (t, *J* = 8.0 Hz, 1H), 2.98 (dd, *J* = 8.0, 2.4 Hz, 2H), 1.44 (s, 3H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$), δ (ppm) = 174.6, 147.6, 140.6, 128.7, 125.9 (m), 124.9, 124.7 (q, *J* = 272.2 Hz), 88.5, 52.6, 35.0, 23.9. **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$), δ (ppm) = -62.6, -62.7. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 3051, 1771, 1600, 1515, 1420, 1320, 1271, 1060. **HRMS (ESI)** calcd for $C_{19}H_{15}F_6O_2$ $[M+H]^+$: 389.0971, found 389.0975.

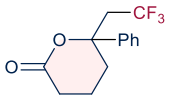
6-Phenyl-6-(4-(trifluoromethyl)benzyl)tetrahydro-2*H*-pyran-2-one (5a)



Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1e** (303.6 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2e** (57.1 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 4:1 Hexane:EtOAc), the title compound **5a** was obtained as a yellow oil (75.2 mg, 0.22 mmol, 75%). **R_f** = 0.25 (silica gel, *n*-hexane / EtOAc, 4:1 (v/v)); **^{1}H NMR** (500 MHz, $CDCl_3$), δ (ppm) = 7.46 (d, *J* = 8.0 Hz, 2H), 7.37 – 7.29 (m 3H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 3.24 (d, *J* = 13.8 Hz, 1H), 3.17 (d, *J* = 13.8 Hz, 1H), 2.40 – 2.34 (m, 3H), 1.92 (ddd, *J* = 14.1, 12.6, 4.6 Hz, 1H), 1.77 – 1.70 (m, 1H), 1.59 (dt, *J* = 13.4, 4.5 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$), δ (ppm) = 171.2, 142.3, 139.3, 131.2, 129.0, 128.7, 127.8, 125.2, 124.2 (q, *J* = 273.7 Hz), 124.8 (q, *J* = 3.0 Hz), 86.9, 50.0, 31.3, 29.0, 16.1. **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$), δ (ppm) = -62.5. **FT-IR**

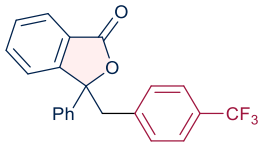
(cm^{-1}, neat, ATR), $\tilde{\nu}$ = 3060, 2955, 1733, 1617, 1447, 1417, 1321, 1236, 1160, 1109, 1065, 1041. **HRMS (ESI)** calcd for $C_{19}H_{18}F_3O_2$ $[M+H]^+$: 335.1253, found 335.1253.

6-Phenyl-6-(2,2,2-trifluoroethyl)tetrahydro-2*H*-pyran-2-one (5b)



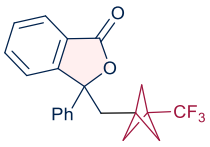
Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1w** (360.3 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2e** (57.1 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 4:1 Hexane:EtOAc), the title compound **5b** was obtained as a yellow solid (51.9 mg, 0.20 mmol, 67%). $\mathbf{R_f}$ = 0.25 (silica gel, *n*-hexane / EtOAc, 4:1 (v/v)); **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.48 – 7.29 (m, 5H), 2.88 – 2.67 (m, 2H), 2.56 – 2.37 (m, 3H), 2.25 (td, *J* = 13.4, 4.3 Hz, 1H), 1.81 (ddt, *J* = 15.4, 7.8, 3.9 Hz, 1H), 1.58 (qdd, *J* = 13.8, 7.4, 4.1 Hz, 1H). **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$) δ (ppm) = -59.8. The data matches those previously reported.[12]

3-Phenyl-3-(4-(trifluoromethyl)benzyl)isobenzofuran-1(3*H*)-one (6a)



Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1e** (303.6 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2f** (67.3 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 4:1 Hexane:EtOAc), the title compound **6a** was obtained as a yellow oil (93.3 mg, 0.25 mmol, 84%). $\mathbf{R_f}$ = 0.40 (silica gel, *n*-hexane / EtOAc, 4:1 (v/v)); **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.69 (t, *J* = 7.9 Hz, 2H), 7.64 (t, *J* = 7.9 Hz, 2H), 7.60 – 7.55 (m, 2H), 7.45 (td, *J* = 7.3, 1.1 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.36 – 7.32 (m, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 3.78 (d, *J* = 13.9 Hz, 1H), 3.63 (d, *J* = 14.0 Hz, 1H). **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$) δ (ppm) = -62.5. The data matches those previously reported.[13]

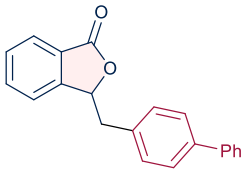
3-Phenyl-3-((3-(trifluoromethyl)bicyclo[1.1.1]pentan-1-yl)methyl)isobenzofuran-1(3*H*)-one (6b)



[12]Y. Yasu, Y. Arai, R. Tomita, T. Koike, M. Akita, *Org. Lett*. 2014, **16**, 780–783.
[13]D. Felipe-Blanco, J. C. Gonzalez-Gomez, *Eur. J. Org. Chem*. 2019, **2019**, 7735–7744.

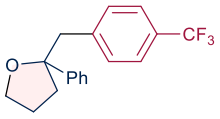
Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1aa** (262.9 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2f** (67.3 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 3:1 Hexane:EtOAc), the title compound **6b** was obtained as a yellow oil (73.1 mg, 0.20 mmol, 68%). $\mathbf{R_f}$ = 0.40 (silica gel, *n*-hexane / EtOAc, 3:1 (v/v)); **^{1}H NMR** (500 MHz, $CDCl_3$), δ (ppm) = 7.90 (d, *J* = 7.5 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.52 (dd, *J* = 10.9, 7.5 Hz, 4H), 7.38 – 7.29 (m, 3H), 2.82 (d, *J* = 15.3 Hz, 1H), 2.41 (d, *J* = 15.3 Hz, 1H), 1.62 (q, *J* = 9.7 Hz, 6H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm) = 176.9, 142.6, 129.2, 128.4, 125.0, 122.8 (q, *J* = 275.9 Hz), 88.8, 50.5 (q, *J* = 2.5 Hz), 43.2, 38.4 (q, *J* = 39.1 Hz), 37.4, 36.8, 28.5. **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$) δ (ppm) = -73.4. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2989, 2918, 1758, 1598, 1466, 1394, 1286, 1991, 1170, 1123, 1011. **HRMS (ESI)** calcd for $C_{21}H_{18}F_3O_2$ $[M+H]^+$: 359.1253, found 359.1258.

3-([1,1'-Biphenyl]-4-ylmethyl)isobenzofuran-1(3*H*)-one (7a)



Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1i** (273.6 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2g** (44.4 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 9:1 to 5:1 Hexane:EtOAc), the title compound **7a** was obtained as a yellow oil (31.5 mg, 0.10 mmol, 35%). $\mathbf{R_f}$ = 0.32 (silica gel, *n*-hexane / EtOAc, 5:1 (v/v)); **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) = 7.87 (d, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.60 – 7.57 (m, 2H), 7.54 (d, *J* = 7.9 Hz, 2H), 7.45 – 7.43 (m, 3H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.26 – 7.22 (m, 1H), 5.73 (t, *J* = 6.4 Hz, 1H), 3.31 (dd, *J* = 14.1, 6.8 Hz, 1H), 3.22 (dd, *J* = 14.1, 6.8 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$), δ (ppm) = 170.3, 149.1, 140.6, 140.1, 134.1, 133.8, 130.1, 128.8, 127.7, 127.4, 127.3, 127.0, 126.3, 125.8, 122.3, 81.2, 40.6. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 3026, 2851, 1756, 1598, 1486, 1442, 1347, 1284, 211, 1061. **HRMS (ESI)** calcd for $C_{21}H_{17}O_2$ $[M+H]^+$: 301.1223, found 301.1225.

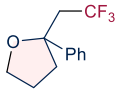
2-phenyl-2-(4-(trifluoromethyl)benzyl)tetrahydrofuran (8a)



Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1e** (303.6 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2h** (48.7 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 0 to 5 % EtOAc in Hexane), the title compound **8a** was obtained as a yellow oil (61.7 mg, 0.22 mmol, 75%). $\mathbf{R_f}$ = 0.08 (silica gel, *n*-hexane / EtOAc, 20:1 (v/v)); **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.41 (d, *J* = 8.0 Hz, 2H), 7.29 – 7.20 (m, 5H), 7.09 (d, *J* = 8.0 Hz, 2H), 3.98 – 3.79 (m, 2H), 3.15 (d, *J* = 13.4 Hz, 1H), 3.06 (d, *J* = 13.4 Hz, 1H), 2.26 – 2.17 (m, 1H), 2.14 – 2.05 (m, 1H), 1.80 – 1.69 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm) = 146.3,

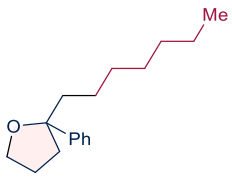
141.9, 131.0, 128.5 (q, J = 32.8 Hz), 128.1, 126.7, 125.5, 124.6, 124.5 (q, J = 272.2 Hz), 86.9, 67.8, 48.5, 37.5, 25.6. **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$) δ (ppm) = -62.3. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2975, 1617, 1320, 1161, 1107, 1065, 1017. **HRMS (ESI)** calcd for $C_{18}H_{18}F_3O$ $[M+H]^+$: 307.1304, found 307.1308.

2-Phenyl-2-(2,2,2-trifluoroethyl)tetrahydrofuran (8b)



Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1w** (260.6 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2h** (48.7 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 0 to 5 % EtOAc in Hexane), the title compound **8b** was obtained as a yellow oil (38.0 mg, 0.17 mmol, 55%). **R_f** = 0.2 (silica gel, *n*-hexane); **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.44 – 7.37 (m, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.29 – 7.23 (m, 1H), 4.10 – 4.01 (m, 1H), 3.96 – 3.89 (m, 1H), 2.80 – 2.56 (m, 2H), 2.37 – 2.29 (m, 1H), 2.26 – 2.12 (m, 1H), 2.05 – 1.91 (m, 1H), 1.85 – 1.72 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$), δ (ppm) = 144.6, 128.2, 127.1, 125.2, 125.1 (q, J = 279.7 Hz), 82.9, 67.8, 45.1 (q, J = 26.3 Hz), 38.1, 25.1. **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$) δ (ppm) = -60.5. The data matches those previously reported.[14]

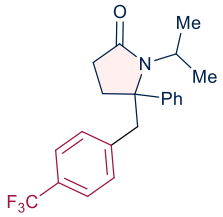
2-Heptyl-2-phenyltetrahydrofuran (8c)



Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1y** (270.3 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2h** (48.7 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from 0 to 5 % EtOAc in Hexane), the title compound **8c** was obtained as a yellow oil (43.6 mg, 0.18 mmol, 59%). **R_f** = 0.13 (silica gel, *n*-hexane); **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) = 7.38 – 7.29 (m, 4H), 7.24 – 7.17 (m, 1H), 3.97 (ddd, J = 7.5 Hz, 1H), 3.87 (ddd, J = 7.5 Hz, 1H), 2.17 (ddd, J = 12.6, 7.9, 4.9 Hz, 1H), 2.03 (dt, J = 12.6, 8.2 Hz, 1H), 1.95 – 1.90 (m, 1H), 1.83 – 1.70 (m, 3H), 1.30 – 1.14 (m, 9H), 1.07 – 0.97 (m, 1H), 0.84 (t, J = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm) = 146.9, 127.8, 126.3, 125.2, 86.9, 67.4, 67.1, 42.6, 31.8, 30.0, 29.2, 25.6, 24.5, 22.6, 14.1. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 3059, 2926, 2854, 1458, 1445, 1118, 1053, 1029. **HRMS (ESI)** calcd for $C_{17}H_{27}O$ $[M+H]^+$: 247.2056, found 247.2058.

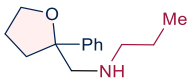
[14] Y. Wang, M. Jiang, J.-T. Liu, *Adv. Synth. Catal.* 2016, **358**, 1322 – 1327.

1-Isopropyl-5-phenyl-5-(4-(trifluoromethyl)benzyl)pyrrolidin-2-one (9a)



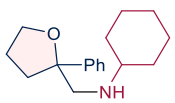
Prepared according to the *General Procedure* from the corresponding thianthrenium salt **1e** (306.3 mg, 0.60 mmol, 2.0 equiv) and radical acceptor **2j** (65.2 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (from hexanes to 4:1 Hexane:EtOAc), the title compound **9a** was obtained as a yellow oil (75.9 mg, 0.21 mmol, 70%). $\mathbf{R_f}$ = 0.52 (silica gel, *n*-hexane / EtOAc, 4:1 (v/v)); **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.62 – 7.17 (m, 9H), 3.96 (m, 1H), 2.41 – 2.10 (m, 6H), 1.09 – 0.89 (m, 6H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm) = 159.9, 143.3, 140.0, 130.9, 125.5, 124.9, 124.7, 123.4 (q, J = 273.0 Hz), 123.2, 121.0, 89.2, 48.1, 47.4, 34.6, 28.9, 24.0. **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$) δ (ppm) = -60.7. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 3457, 2968, 2880, 1765, 1446, 1251, 1165, 1029. **HRMS (ESI)** calcd for $C_{21}H_{23}F_3NO$ $[M+H]^+$: 362.1726, found 362.1730.

***N*-((2-Phenyltetrahydrofuran-2-yl)methyl)propan-1-amine (10a)**



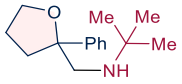
Adapted from the *General Procedure*, using the corresponding iminothianthrene **1ab** (164.0 mg, 0.60 mmol, 2.0 equiv), radical acceptor **2h** (48.7 mg, 0.30 mmol, 1.0 equiv) and $Bi(OTf)_3$ (236.2 mg, 0.36 mmol, 1.2 equiv). After chromatographic purification (from DCM to 4:1 DCM:MeOH), the title compound **10a** was obtained as a yellow oil (25.5 mg, 0.11 mmol, 39%). $\mathbf{R_f}$ = 0.25 (silica gel, DCM / MeOH, 50:1 (v/v)); **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) = 7.41 (m, 4H), 7.34 (m, 1H), 4.23 – 4.19 (m, 1H), 4.03 – 3.97 (m, 1H), 3.50 (d, J = 12.8 Hz, 1H), 3.14 (d, J = 12.8 Hz, 1H), 3.04 – 2.96 (m, 1H), 2.91 – 2.83 (m, 1H), 2.48 – 2.43 (m, 1H), 2.29 – 2.25 (m, 1H), 2.10 – 2.06 (m, 1H), 1.88 – 1.80 (m, 1H), 1.79 – 1.71 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H), NH not oberved. **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$), δ (ppm) = 142.8, 128.9, 128.0, 124.9, 83.9, 68.6, 55.3, 50.5, 35.9, 25.4, 19.5, 10.9. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ =3461, 2968, 2880, 1601, 1446, 1246, 1160, 1029. **HRMS (ESI)** calcd for $C_{14}H_{22}NO$ $[M+H]^+$: 220.1696, found 220.1700.

***N*-((2-Phenyltetrahydrofuran-2-yl)methyl)cyclohexanamine (10b)**



Adapted from the *General Procedure*, using the corresponding iminothianthrene **1ac** (188.1 mg, 0.60 mmol, 2.0 equiv), radical acceptor **2h** (48.7 mg, 0.30 mmol, 1.0 equiv) and $Bi(OTf)_3$ (236.2 mg, 0.36 mmol, 1.2 equiv). After chromatographic purification (from DCM to 4:1 DCM:MeOH), the title compound **10b** was obtained as a yellow oil (38.9 mg, 0.15 mmol, 50%). $\mathbf{R_f}$ = 0.13 (silica gel, DCM / MeOH, 50:1 (v/v)); **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) = 7.41 – 7.22 (m, 5H), 4.27 (s, 1H), 4.11 (ddd, *J* = 7.5 Hz, 1H), 3.93 (ddd, *J* = 7.5 Hz, 1H), 3.26 (d, *J* = 12.4 Hz, 1H), 3.01 (d, *J* = 12.4 Hz, 1H), 2.71 – 2.66 (m, 1H), 2.41 – 2.36 (m, 1H), 2.21 – 2.16 (m, 1H), 2.04 – 1.90 (m, 4H), 1.82 – 1.68 (m, 3H), 1.34 – 1.07 (m, 5H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm) = 144.6, 127.4, 125.1, 121,7, 85.0, 68.3, 58.0, 35.5, 31.1, 30.7, 25.4, 24.8, 24.7. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 3394, 2930, 1600, 1447, 1243, 1163, 1029. **HRMS (ESI)** calcd for $C_{17}H_{26}NO$ $[M+H]^+$: 260.2009, found 260.2014.

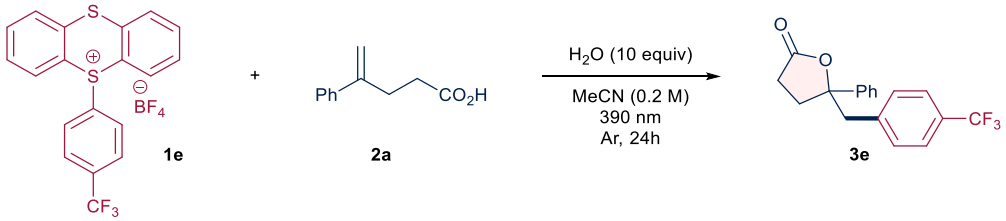
2-Methyl-*N*-((2-phenyltetrahydrofuran-2-yl)methyl)propan-2-amine (10c)



Adapted from the *General Procedure*, using the corresponding iminothianthrene **1ad** (172.5 mg, 0.60 mmol, 2.0 equiv), radical acceptor **2h** (48.7 mg, 0.30 mmol, 1.0 equiv) and $Bi(OTf)_3$ (236.2 mg, 0.36 mmol, 1.2 equiv). After chromatographic purification (from DCM to 4:1 DCM:MeOH), the title compound **10c** was obtained as a yellow oil (21.0 mg, 0.09 mmol, 30%). $\mathbf{R_f}$ = 0.20 (silica gel, DCM / MeOH, 50:1 (v/v)); **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.43 – 7.33 (m, 5H), 4.18 (ddd, *J* = 7.7 Hz, 1H), 3.94 (ddd, *J* = 7.7 Hz, 1H), 3.45 (d, *J* = 12.5 Hz, 1H), 2.97 (d, *J* = 12.5 Hz, 1H), 2.47 – 2.40 (m, 1H), 2.28 – 2.22 (m, 1H), 2.05 – 1.99 (m, 1H), 1.76 – 1.71 (m, 1H), 1.35 (s, 9H), NH not observed. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm) = 132.4, 128.8, 127.9, 125.0, 84.1, 68.2, 49.5, 34.2, 30.5, 26.3, 25.0. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 3451, 2945, 1660, 1450, 1247, 1161, 1029. **HRMS (ESI)** calcd for $C_{15}H_{24}NO$ $[M+H]^+$: 234.1852, found 234.1857.

*E. Large-Scale Synthesis of **3e***

Figure S2. Large-Scale synthesis reaction setup of **3e**.



To a 25 mL Schlenk with a magnetic stir bar, the corresponding carboxylic acid **2a** (1.5 mmol, 264.5 mg, 1.0 equiv), thianthrenium salt **1e** (3 mmol, 1.5315 g, 2.0 equiv), and H_2O (0.3 ml, 15 mmol, 10 equiv) were added. The Schlenk was charged with dry ACN (7.5 mL, c = 0.2 M) under an argon atmosphere. The reaction mixture was irradiated 24 h with a Kessil PR160-purple LED lamp (30 W High Luminous DEX 2100 LED, λ_{max} = 390 nm) as described in the "Workflow" section. The temperature of the reaction was maintained at approximately 25 °C via a fan. Once finished the reaction, the solvent was distilled, and the crude mixture was diluted with DCM, dried over with Na_2SO_4. The crude mixture was subjected to purification by column chromatography (9:1 to 3:1 Hexane:EtOAc), obtaining the title compound **3e** as a yellow oil (360.3 mg, 1.12 mmol, 75%).

5. Green Chemistry Metrics Calculations

When the reaction of large-scale was over, the solvent was recovered by distillation (7.0 mL, 5.41 g) and the crude mixture was subjected to purification by chromatography on silica gel (from 9:1 to 3:1 Hexane:EtOAc) to afford the desired product **3e** as yellow oil (360.3 mg, 1.12 mmol, 75%) and the major byproduct TT (642.0 mg, 99% yield). The reaction exhibits a moderate sustainability profile, with a Complete E Factor (CEF) of 4.1 and a carbon efficiency of 60%. While the CEF indicates a relatively low level of waste generation compared to many classical organic processes, the carbon efficiency suggests that a significant portion of the input carbon is still lost to byproducts or waste.

$$Complete\ E\ Factor\ (cEF) = \frac{\sum m\ (raw\ materials) + \sum m\ (reagents) + \sum m\ (solvents) - m(product)}{m\ (product)}$$

$$Complete\ E\ Factor\ (cEF) = \frac{1.5315 + 0{,}2645 + 0{,}30 + 5{,}7675 - 5{,}41 - 0{,}3603 - 0{,}6420}{0{,}3603} =$$

$$Complete\ E\ Factor\ (cEF) = 4.1\ kg\ waste\ per\ kg\ product$$

$$Carbon\ Efficiency = \frac{C(product)}{C(reagents)} \cdot 100 = \frac{18}{19 + 11} \cdot 100 = 60\%$$

6. Mechanistic Investigations

A. UV/vis Studies:

UV/vis absorption spectra were measured in a 1 cm quartz cuvette using a Genesys 150 UV/vis spectrophotometer from Thermo Scientific. Absorption spectra of individual reaction components and mixtures thereof were recorded. A bathochromic shift was observed for a mixture of thianthrenium salt **1e**, radical acceptor **2a**, in ACN (0.2 M) (*Figure S3*).

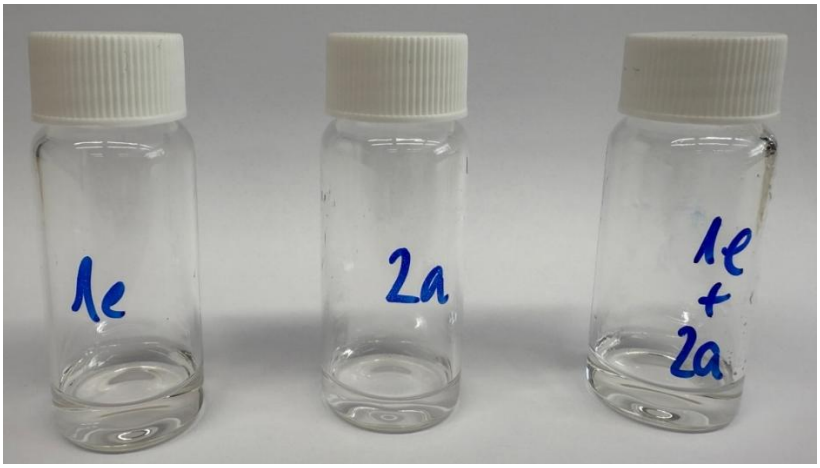


Figure S3. Visual appearance of reaction components and mixtures thereof

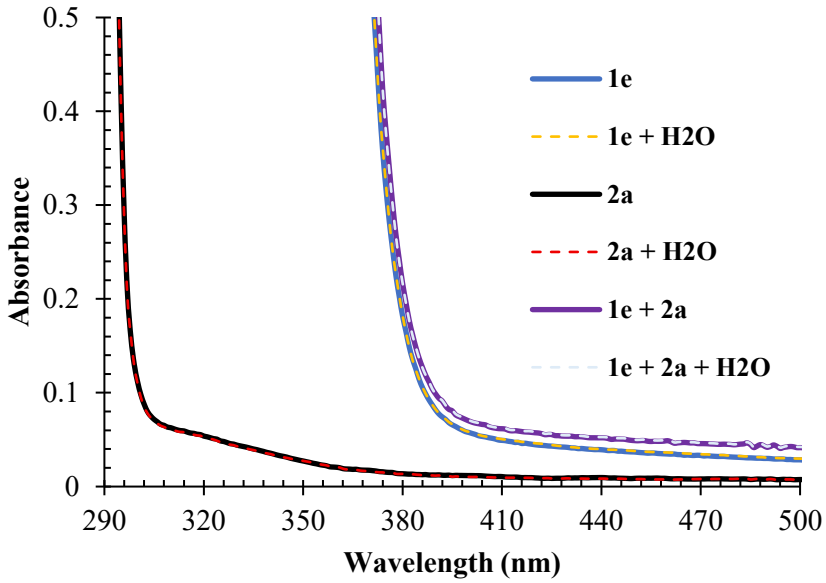


Figure S4. UV/vis absorption spectra of individual reaction components and a combination thereof. All spectra were measured in ACN and with a concentration of 0.08 M thianthrenium salt **1e**, 0.04 M radical acceptor **2a**, 0.4 M H_2O.

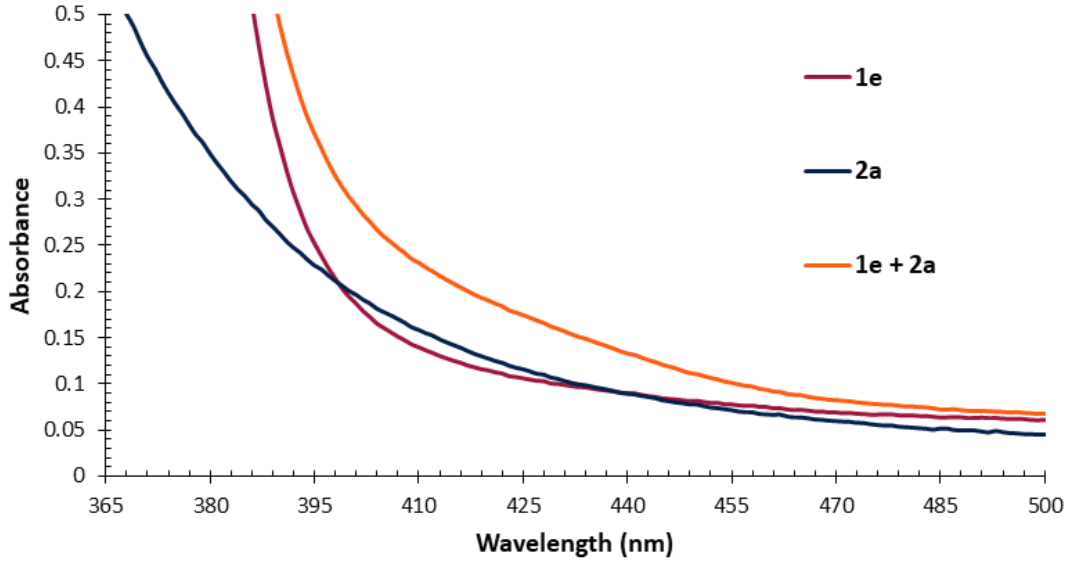
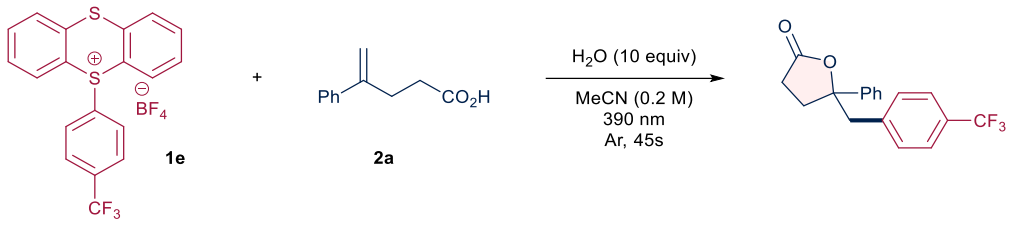


Figure S4-bis. UV/vis absorption spectra of individual reaction components and a combination thereof. All spectra were measured in DCM and with a concentration of 0.08 M thianthrenium salt **1e**, 0.04 M radical acceptor **2a**, 0.4 M H_2O.

B. Photochemical Quantum Yield

Thianthrenium salt **1e**, radical acceptor **2a** were used as model substrates to determinate the quantum yield of this transformation, using 1,3,5-trimethoxybenzene as internal standard in a proportion 1:1 with **2a**.



The quantum yield of the reaction is defined as:

$$\Phi(\text{reaction at 390 nm}) = \frac{\text{mol of formed product}}{\text{mol of photon flux} \cdot t \cdot f} \qquad (1)$$

where Φ is the quantum yield of the reaction, t is the time of the reaction (s), and f is the incident light absorbed by the EDA complex at 390 nm. The photon flux is calculated by standard ferrioxalate actinometry[4] (see Section *B.3*).

B.1. Incident light absorbed by the EDA complex

The fraction of light, f, absorbed was determined according to equation 2:

$$F = 1 - 10^{-A} \qquad (2)$$

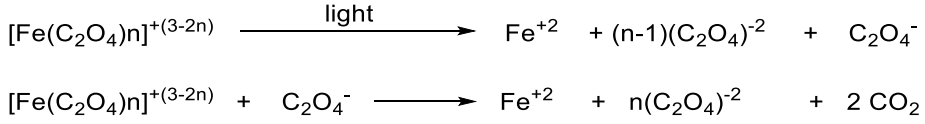
Where A is the absorbance of the EDA complex in DMSO at 390 nm. The wavelength of 390 nm was chosen based on the known absolute $\Phi(Fe^{+2})$ value. The absorbance of EDA complex was measured (0.4 M **1a**, 0.2 M **2a**) in ACN (0.5 mL) to a cuvette equipped with a Teflon-coated magnetic stir bar and stirred for 45 seconds. The absorbance was recorded. The absorbance (A) at 390 nm was determined to be >4, thus indicating the fraction of light absorbed is ~1 according to equation 2.

B.2. The photoredox reaction

The photoredox transformation was developed using the general procedure for 120 min (2 h). Afterwards, 1,3,5-trimethoxybenzene was added as internal standard, and the reaction was worked up. The yield of the reaction was determined by ^{1}H NMR, where 0.009 mmols (0.9%) of the desired compound were obtained.

B.3. Photon flux at 390 nm

Standard ferrioxalate actinometry was used to determine the photon flux of the spectrophotometer using equations 3 and 4. For the ferrioxalate actinometer, the production of iron(II) ions proceeds by the following reactions:[3]



The moles of Fe^{+2} formed are determined spectrophotometrically by development with 1,10-phenanthroline (phen) to form the red $[Fe(phen)_3]^{+2}$ moiety (λ = 390 nm).[3] The photon flux is defined as shown in equation 3:

$$\text{Photon flux} = \frac{\text{mol } Fe^{+2}}{\Phi(Fe^{+2}) \cdot t \cdot f} \qquad (3)$$

where Φ is the quantum yield for the ferrioxalate actinometer (1.01 at λ = 390 nm),[4] t is the time (s), f ~1, and the mol of Fe^{+2} are calculated according to equation 4.

$$\text{mol } (Fe^{+2}) = \frac{V \cdot \Delta A}{l \cdot \epsilon} \qquad (4)$$

where V is the total volume of the solution, ΔA is the difference in absorbance between irradiated and nonirradiated solutions, l is the path length (1.0 cm), and ε is the molar absorptivity at 390 nm (11110 L mol^{-1} cm^{-1}).[3]

B.4. Experimental

The following solutions were prepared in the dark (flasks were wrapped in aluminum foil) and stored in the dark at room temperature:

– Ferrioxalate solution (0.15 M): Ammonium ferrioxalate hydrate (1.284 g) was added to a flask wrapped in aluminum foil containing H_2SO_4 (20 mL, 0.05 M). The flask was stirred for complete solvation of the green solid in complete darkness. It is noteworthy that the solution should not be exposed to any incident light.

– Developer solution: 1,10-Phenanthroline (50 mg) and NaOAc (11.25 g) was added to a flask containing H_2SO_4 (50 mL, 0.5 M) and sonicated until completely solvated.

The absorbance of the non-irradiated sample. The buffered solution of phen (350 μL) was added to a ferrioxalate solution (2.0 mL) in a vial that had been covered with aluminum foil and with the lights of the laboratory switched off. The vial was capped and allowed to rest for 1 h and then transferred to a cuvette. The absorbance of the non-irradiated solution was measured at 390 nm to be 1.31 (average of two determinations, see *Figure S5*).

The absorbance of the irradiated sample. In a cuvette equipped with a stir bar was added the ferrioxalate solution (2.0 mL), and the stirred solution was irradiated for 45 s at λ = 390 nm with an excitation slit width = 10.0 nm. After irradiation, the buffered phen solution (350 μL) was added to the cuvette and allowed to rest for 1 h in the dark to allow the ferrous ions to coordinate completely to phen. The absorbance was measured at 390 nm to be 0.06 (average of two determinations, *Figure S5*).

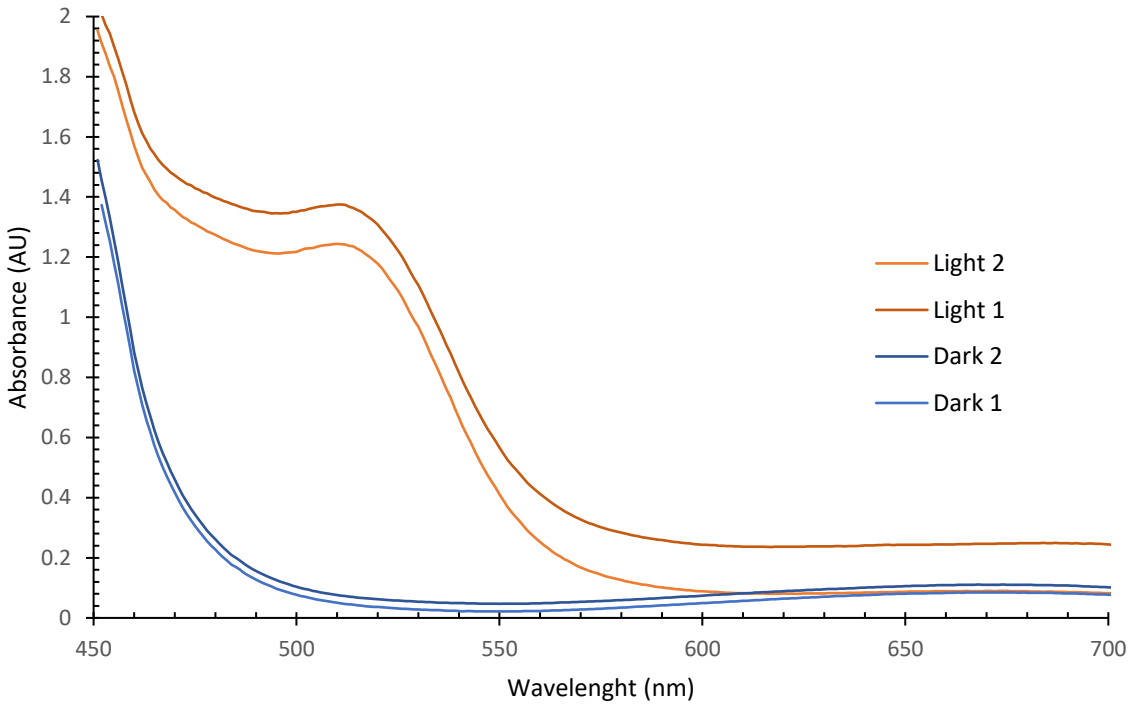


Figure S5. Absorption spectra for irradiated and non-irradiated samples of red $[Fe(phen)_3]^{+2}$

Photon flux sample calculation. Sample calculation:

$$\text{mol } (Fe^{+2}) = \frac{V \cdot \Delta A}{l \cdot \epsilon} \qquad (4)$$

$$\text{mol } (Fe^{+2}) = \frac{0.00235\ \text{L} \cdot 1.25}{1.0\ \text{cm} \cdot 11100\ \text{L} \cdot \text{mol}^{-1}\text{cm}^{-1}} = 2.64\text{x}10^{-7}\text{mol}$$

$$\text{Photon flux} = \frac{\text{mol } Fe^{+2}}{\Phi(Fe^{+2}) \cdot t \cdot f} \qquad (3)$$

$$\text{Photon flux} = \frac{2.64\text{x}10^{-7}\text{mol}}{1.01 \cdot 45\ \text{s} \cdot 1} = \mathbf{5.80x10^{-9}\ einstein\ s^{-1}}$$

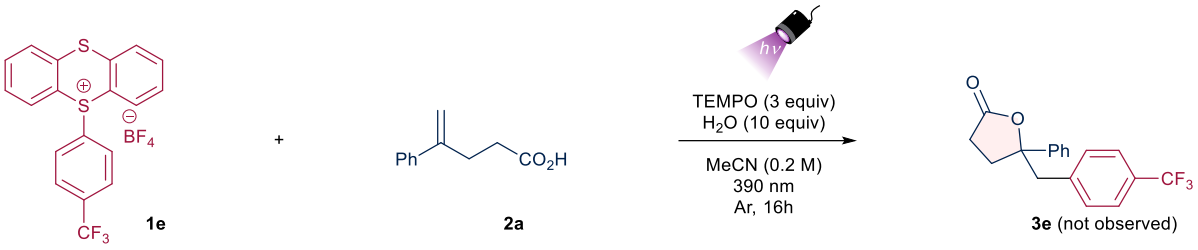
B.5. Quantum yield of the photoinduced transformation

Therefore, the quantum yield of the reaction was determined to be:

$$\Phi(\text{reaction at 390 nm}) = \text{mol of formed}\frac{\text{product}}{\text{mol of photon flux} \cdot t \cdot f} \qquad (1)$$

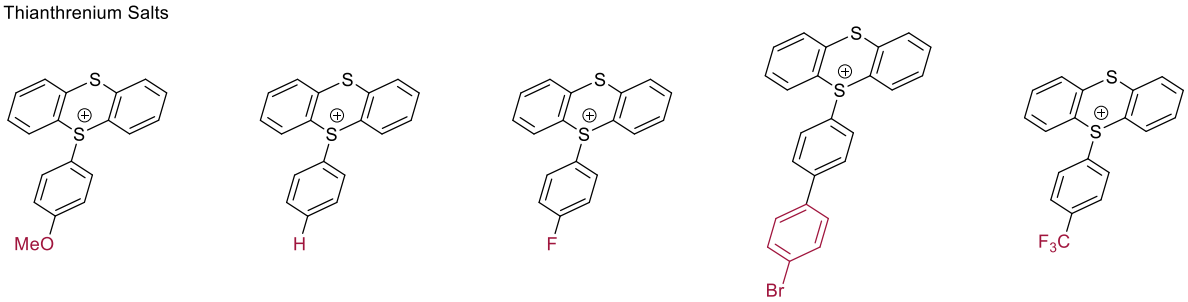
$$\mathbf{\Phi(reaction\ at\ 390\ nm)} = \frac{9.0\text{x}10^{-6}\ \text{mol}}{5.80\text{x}10^{-9}\ \text{einstein}\ \text{s}^{-1} \cdot 7200\ \text{s} \cdot 1} = \mathbf{0.2}$$

C. Radical Trapping Experiment:



To test the intermediacy of radical species, a trapping experiment was performed using TEMPO [(2,2,6,6-tetramethylpiperidin-1-yl)oxyl] as a radical scavenger. The reaction was performed according to the *General Procedure* with thianthrenium salt **1e** (102.1 mg, 0.2 mmol, 2.0 equiv), 4-phenylpent-4-enoic acid **2a** (17.6 mg, 0.1 mmol, 1.0 equiv), and H_2O (18 µL, 1.0 mmol, 10.0 equiv) in the presence of TEMPO (46.9 mg, 0.3 mmol, 3.0 equiv). After reaction time, the crude mixture was analyzed by ^{1}H-NMR, and we did not detect the formation of the compound **3e**.

D. Hammett Studies



To identify the nature of the reactive intermediate formed in the reaction, we obtained the Hammett plot. The reaction was done as described on the "*Workflow*" section, with radical acceptor (0.1 mmol, 1.0 equiv), corresponding thianthrenium salt (0.2 mmol, 2.0 equiv) and H_2O (1 mmol, 10 equiv). After 7 h of irradiation, an 1,3,5-Trimethoxybenzene (0.1 mmol) was added to the reaction mixture to determine the conversion.

Table S2. Data analysis for *para*-substituted Thianthrenium salt derivatives

Substituent on TT-Ar	Yield	ln(yield)	$\ln(\text{yield}_S)/\ln(\text{yield}_H)$	$\log(C_S/C_H)$	σ_p
CF_3	0.7	-0.3566749	0.3587	-0.445	0.54
p-Bromobiphenyl	0.42	-0.8675006	0.8725	-0.059	0.12
F	0.39	-0.9416085	0.94705	-0.023	0.06
H	0.37	-0.9942523	1	0	0.00
Me	0.21	-1.5606477	1.5696	0.1958	-0.17

E. DOSY2D Experiment

An DOSY 2D experiment was recorded for each individual reaction components and mixture thereof (0.1 mmol of each in 0.6 mL of CD_3CN).

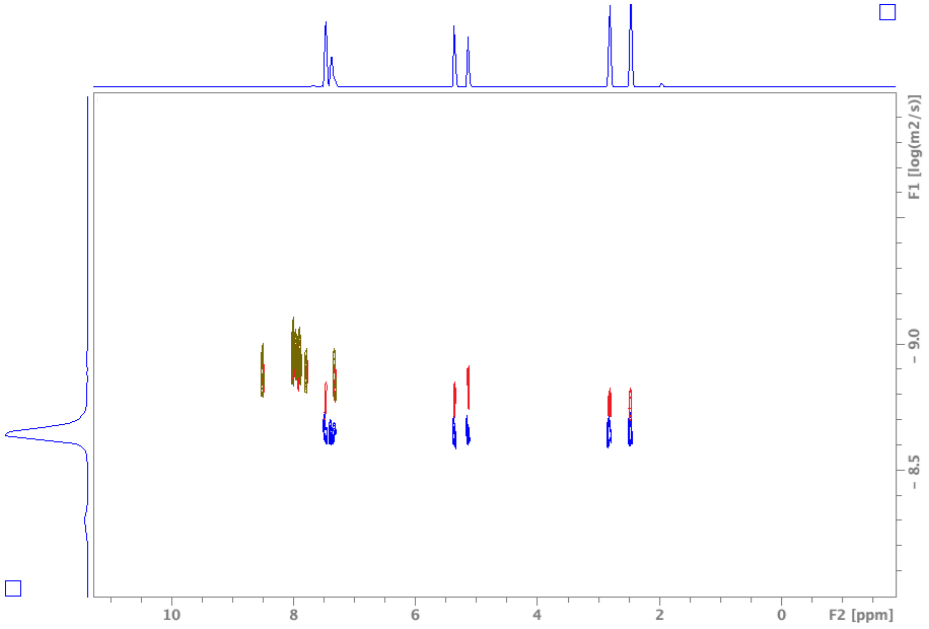
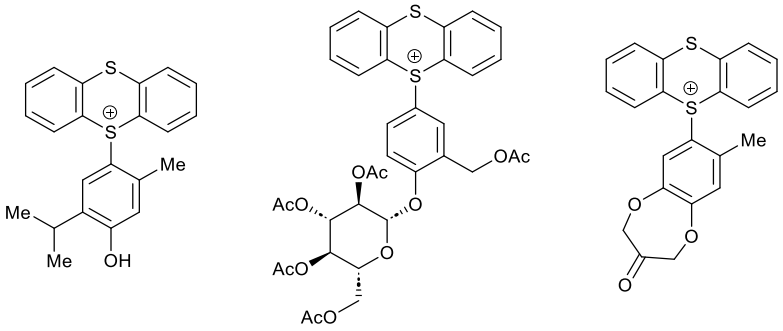


Figure S6. DOSY2D spectra of compound **1e** (**red**), radical acceptor **2a** (**blue**) and the mixture (**brown**).

F. Unsuccessful substrates



7. DFT

Computational Details

All the geometry optimizations and frequency calculations reported in this paper were obtained with the ORCA 6.0.1 program.[15] Electron correlation was partially taken into account using the B3LYP[16] functional in conjunction with the D3(BJ) dispersion correction suggested by Grimme et al.[17], the resolution-of-identity approach,[18] RI(JCOSX), and the double-ζ quality plus polarization functions def2-SVP[19] basis set for all atoms. Solvent effects (solvent = water) were taken into account by using the conductor-like polarizable continuum model (CPCM).[20] All species were characterized by frequency calculations: reactants and adducts exhibited positive definite Hessian matrices, while transition states showed a single negative eigenvalue in their diagonalized force constant matrices. This level is denoted CPCM-(RI)-B3LYP-D3(BJ)/def2-SVP.

[15] F. Neese, *Rev. Comput. Mol. Sci*., 2025, **15**, e70019.
[16] (a) A. D. Becke, *J. Chem. Phys.,* 1993, **98**, 5648−5652; (b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B,* 1988, **37**, 785−789; (c) S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.,* 1980, **58**, 1200−1211.
[17] (a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, H. *J. Chem. Phys*., 2010, **132**, 154104; (b) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem*., 2011, **32**, 1456−1465.
[18] F. Neese, *J. Comp. Chem*., 2003, **24**, 1740−1747.
[19] F. Weigend, R. Alhrichs, *Phys. Chem. Chem. Phys*., 2005, **7**, 3297-3305.
[20] V. Barone, M. Cossi, *J. Phys. Chem. A,* 1998, **102**, 1995-2001.

Conformational search for aggregate:

The Conformer-Rotamer Ensemble Sampling Tool (CREST)[21] was used to assess different supramolecular conformations for the aggregate formed upon mixing **1e** and **2a**. For this search, the semiempirical method GFN2-xTB[22] was used, and the methodology consisted of an extensive sampling of the conformational space starting from a guess species. The lower lying ensembles (see below) were fully optimized at the DFT level (CPCM-(RI)-B3LYP-D3(BJ)/def2-SVP)

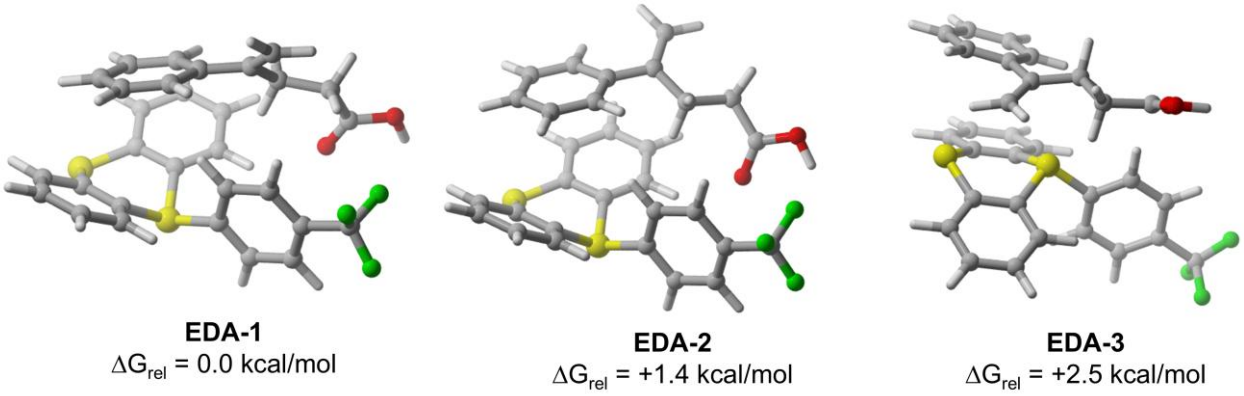


Figure S7. Global minima structures for the aggregate formed between **1e** and **2a**. Data computed at the CPCM-(RI)-B3LYP-D3(BJ)/def2-SVP level.

[21] (a) S. Grimme, *Chem. Theory Comput.,* 2019, **15**, 2847–2862; (b) P. Pracht, F. Bohle, S. Grimme, *Phys. Chem. Chem. Phys.*, 2020, **22**, 7169-7192; (c) P. Pracht, S. Grimme, C. Bannwarth, F. Bohle, S. Ehlert, G. Feldmann, J. Gorges, M. Müller, T. Neudecker, C. Plett, S. Spicher, P. Steinbach, P. A. Wesołowski, F. Zeller, *J. Chem. Phys.*, 2024, **160**, 114110-114128.

[22] C. Bannwarth, S. Ehlert, S. Grimme, *J. Chem. Theory Comput.*, 2019, **15***,* 1652–1671

Cartesian coordinates (in Å) and free energies (in a.u., at 298 K) of all the stationary points discussed in the text. All calculations have been performed at the CPCM-(RI)-B3LYP-D3(BJ)/def2-SVP level.

EDA-1: G= -2401.18396990

C	-2.324836000	0.519557000	-3.492491000
C	-3.019254000	0.002147000	-2.391672000
S	-4.030607000	-1.441801000	-2.631420000
C	-2.924082000	0.674841000	-1.167079000
S	-3.964028000	0.069017000	0.172942000
C	-3.666920000	-1.709844000	0.125749000
C	-3.749821000	-2.337852000	-1.121619000
C	-1.568058000	1.683497000	-3.360102000
C	-2.164903000	1.836818000	-1.019198000
C	-3.475303000	-2.424589000	1.307095000
C	-3.636654000	-3.732892000	-1.173639000
C	-3.457448000	-4.464133000	0.001846000
C	-3.370202000	-3.814320000	1.236046000
H	-3.406905000	-1.930012000	2.275693000
H	-3.677687000	-4.237336000	-2.141047000
H	-3.370803000	-5.551404000	-0.051893000
H	-3.214362000	-4.381615000	2.155368000

C	-1.481178000	2.337294000	-2.127806000
H	-2.372657000	-0.005421000	-4.448484000
H	-1.030530000	2.075093000	-4.226269000
H	-2.115877000	2.358945000	-0.063612000
H	-0.885066000	3.245771000	-2.023194000
C	-3.130567000	0.567988000	1.673759000
C	-1.745824000	0.437578000	1.808718000
C	-3.944897000	1.027737000	2.708730000
C	-1.164117000	0.781017000	3.023474000
C	-3.350462000	1.349662000	3.930822000
C	-1.968383000	1.221015000	4.082785000
H	-1.126885000	0.071415000	0.990405000
H	-5.023677000	1.123344000	2.574231000
H	-0.084039000	0.688356000	3.144833000
H	-3.968135000	1.702014000	4.757464000
C	-1.324149000	1.512695000	5.416414000
F	-1.120790000	0.372445000	6.114976000
F	-0.124507000	2.098001000	5.272556000
F	-2.079419000	2.311321000	6.183044000
C	-0.094935000	-2.682067000	-0.145424000
C	0.689024000	-1.755590000	0.567743000
C	-0.349764000	-2.508345000	-1.507591000

H	-0.952958000	-3.245512000	-2.040844000
C	1.182868000	-0.634132000	-0.127902000
C	0.152174000	-1.394307000	-2.184157000
H	1.755807000	0.121928000	0.413155000
H	-0.059860000	-1.253561000	-3.245498000
C	0.914689000	-0.452846000	-1.485645000
H	1.291083000	0.435724000	-1.998082000
H	-0.507687000	-3.555148000	0.361260000
C	0.943855000	-1.922713000	2.027096000
C	-0.183133000	-2.552228000	2.817321000
H	-0.258154000	-3.624075000	2.562921000
H	-1.127620000	-2.117204000	2.466643000
C	-0.118110000	-2.397076000	4.331786000
H	0.580348000	-3.101256000	4.807147000
H	0.238640000	-1.390205000	4.609394000
C	-1.473701000	-2.524545000	4.987390000
O	-2.540568000	-2.343151000	4.436261000
O	-1.378612000	-2.818750000	6.288190000
H	-2.277737000	-2.829159000	6.667217000
C	2.091695000	-1.505730000	2.590235000
H	2.894638000	-1.070326000	1.990383000
H	2.275333000	-1.597802000	3.662809000

EDA-2: G= -2401.18171075

C	-1.983944000	0.926414000	-3.659359000
C	-2.712721000	0.547617000	-2.524851000
S	-3.577770000	-1.005539000	-2.553770000
C	-2.756017000	1.426634000	-1.435443000
S	-3.843121000	0.970944000	-0.072328000
C	-3.394451000	-0.751768000	0.224133000
C	-3.331317000	-1.592101000	-0.893653000
C	-1.326604000	2.155930000	-3.692177000
C	-2.097303000	2.657174000	-1.452390000
C	-3.242091000	-1.230576000	1.524716000
C	-3.104856000	-2.957944000	-0.687692000
C	-2.969422000	-3.456192000	0.608526000
C	-3.030061000	-2.598310000	1.708576000
H	-3.276076000	-0.567383000	2.389443000
H	-3.022212000	-3.622229000	-1.549574000
H	-2.792071000	-4.523428000	0.756461000
H	-2.905562000	-2.984656000	2.721640000
C	-1.375741000	3.016734000	-2.591367000
H	-1.924909000	0.243121000	-4.508564000
H	-0.760687000	2.438045000	-4.582497000

H	-2.154365000	3.337752000	-0.602812000
H	-0.858198000	3.977585000	-2.615641000
C	-3.183410000	1.820981000	1.354156000
C	-1.811191000	1.825738000	1.623705000
C	-4.112725000	2.430637000	2.195673000
C	-1.363970000	2.456738000	2.776632000
C	-3.650654000	3.055386000	3.357268000
C	-2.285310000	3.061709000	3.642155000
H	-1.106176000	1.340587000	0.951045000
H	-5.178386000	2.414967000	1.961140000
H	-0.297606000	2.459281000	3.009437000
H	-4.360076000	3.530399000	4.035029000
C	-1.765833000	3.702409000	4.905822000
F	-1.183788000	2.786718000	5.712221000
F	-0.826997000	4.626782000	4.638798000
F	-2.732341000	4.299006000	5.615664000
C	0.217183000	-2.850660000	-0.554657000
C	0.453834000	-1.852502000	0.408465000
C	0.150260000	-2.541033000	-1.913577000
H	-0.050286000	-3.333944000	-2.638682000
C	0.615463000	-0.528520000	-0.044297000
C	0.308678000	-1.220911000	-2.345065000

H	0.823268000	0.269246000	0.670417000
H	0.241714000	-0.975857000	-3.406986000
C	0.542059000	-0.215227000	-1.403358000
H	0.660081000	0.821775000	-1.726103000
H	0.048625000	-3.879105000	-0.230968000
C	0.490426000	-2.179961000	1.861431000
C	-0.010337000	-1.094490000	2.788912000
H	-0.923911000	-0.674462000	2.348975000
H	0.712241000	-0.259441000	2.807052000
C	-0.316922000	-1.520529000	4.226351000
H	-0.881711000	-2.468217000	4.220119000
H	0.594556000	-1.682281000	4.816958000
C	-1.207493000	-0.511445000	4.913818000
O	-2.259869000	-0.109214000	4.459549000
O	-0.732202000	-0.102412000	6.094389000
H	-1.360462000	0.544596000	6.467956000
C	0.921006000	-3.374771000	2.303446000
H	1.299698000	-4.134779000	1.615851000
H	0.925016000	-3.629971000	3.365196000

EDA-3: G= -2401.17994410

C	-2.874152000	0.308223000	-3.110918000
C	-3.184942000	-0.094716000	-1.804672000
S	-3.546325000	-1.809976000	-1.537644000
C	-3.234384000	0.883018000	-0.804267000
S	-3.826803000	0.410704000	0.827888000
C	-2.986766000	-1.151009000	1.134234000
C	-2.915896000	-2.088984000	0.096527000
C	-2.639049000	1.652211000	-3.396300000
C	-2.987573000	2.230244000	-1.074211000
C	-2.536701000	-1.439411000	2.424516000
C	-2.364558000	-3.347817000	0.377958000
C	-1.923474000	-3.652570000	1.665553000
C	-2.004595000	-2.701666000	2.687740000
H	-2.610748000	-0.696828000	3.219664000
H	-2.280953000	-4.084147000	-0.424073000
H	-1.502644000	-4.639831000	1.868098000
H	-1.656160000	-2.938036000	3.694930000
C	-2.689052000	2.612392000	-2.381568000
H	-2.816764000	-0.443618000	-3.900424000
H	-2.407882000	1.949800000	-4.421284000

H	-3.046484000	2.977886000	-0.282658000
H	-2.501984000	3.664723000	-2.603533000
C	-2.996491000	1.550109000	1.929692000
C	-1.605899000	1.708422000	1.895859000
C	-3.812750000	2.254749000	2.812970000
C	-1.022776000	2.607525000	2.780809000
C	-3.211134000	3.153536000	3.699086000
C	-1.826943000	3.325237000	3.679603000
H	-0.989875000	1.145241000	1.193302000
H	-4.896141000	2.116842000	2.829850000
H	0.058819000	2.753189000	2.769912000
H	-3.830870000	3.715294000	4.398600000
C	-1.161227000	4.265964000	4.655410000
F	-0.566301000	3.587481000	5.655516000
F	-0.205074000	4.998932000	4.058114000
F	-2.032956000	5.117612000	5.216236000
C	-6.818985000	-0.974491000	-2.256400000
C	-6.720189000	-0.128363000	-1.133641000
C	-6.629956000	-0.487683000	-3.548743000
H	-6.707419000	-1.169874000	-4.399306000
C	-6.459716000	1.235227000	-1.367297000
C	-6.344428000	0.866440000	-3.758568000

H	-6.371484000	1.930234000	-0.531761000
H	-6.186506000	1.247141000	-4.770639000
C	-6.267837000	1.725620000	-2.661396000
H	-6.042296000	2.784600000	-2.806934000
H	-7.053101000	-2.030713000	-2.114157000
C	-6.837740000	-0.671677000	0.249914000
C	-7.273343000	0.296031000	1.327241000
H	-8.297690000	0.643785000	1.101676000
H	-6.652816000	1.202551000	1.274721000
C	-7.206180000	-0.228480000	2.757603000
H	-7.931979000	-1.030958000	2.949502000
H	-6.205501000	-0.654643000	2.956295000
C	-7.387860000	0.867898000	3.779164000
O	-6.995666000	2.010596000	3.646249000
O	-7.999516000	0.442833000	4.888923000
H	-8.035215000	1.183664000	5.523894000
C	-6.534786000	-1.955841000	0.518991000
H	-6.175857000	-2.632719000	-0.257457000
H	-6.616518000	-2.370678000	1.524748000

INT1: G= -1143.74925702

C	0.271469000	0.604938000	-4.390342000
C	0.118208000	1.297414000	-3.084867000
O	-1.729572000	-0.755754000	-2.723487000
C	0.137241000	0.405424000	-1.826822000
C	-1.129122000	-0.384981000	-1.580304000
H	-0.742970000	1.972763000	-3.062637000
H	0.312747000	1.031503000	-0.942594000
H	1.023355000	1.935200000	-3.025325000
H	0.964719000	-0.323190000	-1.864298000
O	-1.543391000	-0.683972000	-0.486628000
H	-2.518435000	-1.292925000	-2.517935000
C	-0.678899000	0.729230000	-5.433013000
C	-0.353949000	0.338471000	-6.770092000
C	-1.987718000	1.241999000	-5.175771000
C	-1.282935000	0.466187000	-7.785743000
C	-2.918061000	1.341649000	-6.196477000
C	-2.567398000	0.959935000	-7.500104000
H	0.640025000	-0.036238000	-7.006137000
H	-2.277571000	1.520069000	-4.164561000
H	-1.019727000	0.183927000	-8.806654000

H	-3.921453000	1.716210000	-5.986626000
H	-3.301922000	1.048392000	-8.304598000
C	1.557006000	-0.138962000	-4.584206000
H	2.116056000	-0.152898000	-3.636768000
H	2.160216000	0.494734000	-5.262880000
C	1.475622000	-1.545471000	-5.145616000
C	2.434527000	-1.981349000	-6.071556000
C	0.485459000	-2.439851000	-4.716949000
C	2.404256000	-3.284590000	-6.564602000
C	0.447754000	-3.744254000	-5.210515000
C	1.406536000	-4.167865000	-6.135461000
H	3.211066000	-1.292863000	-6.413462000
H	-0.269349000	-2.120453000	-3.996823000
H	3.157440000	-3.612177000	-7.283946000
H	-0.328050000	-4.431526000	-4.869806000
C	1.351911000	-5.555318000	-6.713531000
F	0.802534000	-5.561022000	-7.947853000
F	2.579909000	-6.095565000	-6.841367000
F	0.622081000	-6.396911000	-5.960278000

TS: G = -1143.73389218 (i = -252 cm-1)

C	0.094336000	1.475410000	0.626948000
C	0.234217000	2.446458000	1.779099000
O	-0.442690000	0.120674000	1.806439000
C	0.704080000	1.716439000	3.041445000
C	0.010104000	0.384650000	3.096327000
H	-0.725147000	2.947622000	1.959871000
H	0.492782000	2.281435000	3.959082000
H	0.957372000	3.215222000	1.460559000
H	1.787572000	1.508989000	3.029742000
O	-0.155676000	-0.384572000	3.990156000
H	-0.820948000	-0.766942000	1.627186000
C	-1.071137000	1.646505000	-0.260403000
C	-0.894227000	1.872674000	-1.638833000
C	-2.375779000	1.684466000	0.276740000
C	-1.996024000	2.120067000	-2.458844000
C	-3.472105000	1.900993000	-0.551505000
C	-3.285368000	2.122066000	-1.922266000
H	0.103422000	1.910514000	-2.073903000
H	-2.532583000	1.507354000	1.341673000
H	-1.840739000	2.312141000	-3.522603000

H	-4.478207000	1.902068000	-0.126607000
H	-4.147151000	2.302775000	-2.569157000
C	1.382475000	0.902811000	0.076067000
H	2.175485000	1.037198000	0.822192000
H	1.647553000	1.559619000	-0.769300000
C	1.351090000	-0.549036000	-0.361305000
C	1.830855000	-1.525831000	0.527673000
C	0.863946000	-0.957867000	-1.608878000
C	1.806201000	-2.876541000	0.189754000
C	0.836799000	-2.310591000	-1.956147000
C	1.302341000	-3.270907000	-1.056013000
H	2.233224000	-1.224686000	1.497972000
H	0.506313000	-0.225811000	-2.331896000
H	2.181208000	-3.621118000	0.895278000
H	0.454582000	-2.612273000	-2.932060000
C	1.289090000	-4.734327000	-1.404186000
F	2.535236000	-5.252542000	-1.425307000
F	0.594130000	-5.454744000	-0.499295000
F	0.741146000	-4.975191000	-2.607049000

INT2: G = -1143.73884637

C	0.181619000	0.183659000	-4.319701000
C	0.368572000	1.450882000	-3.463036000
O	-0.240542000	-0.781179000	-3.231014000
C	0.845221000	0.988114000	-2.085146000
C	0.266122000	-0.358953000	-1.844758000
H	-0.594404000	1.970659000	-3.374215000
H	0.557239000	1.654662000	-1.259919000
H	1.086901000	2.127196000	-3.942096000
H	1.940477000	0.854272000	-2.032571000
O	0.126568000	-1.112396000	-0.963565000
H	-0.228363000	-1.750715000	-3.413794000
C	-0.938599000	0.293652000	-5.330125000
C	-0.831264000	1.300628000	-6.302200000
C	-2.034688000	-0.575197000	-5.359593000
C	-1.804642000	1.429032000	-7.293753000
C	-3.008986000	-0.442505000	-6.354611000
C	-2.896340000	0.554965000	-7.324905000
H	0.019073000	1.986431000	-6.293029000
H	-2.149478000	-1.361750000	-4.613082000
H	-1.707877000	2.216194000	-8.045222000

H	-3.858942000	-1.128857000	-6.366621000
H	-3.657415000	0.653877000	-8.102649000
C	1.496580000	-0.340054000	-4.927066000
H	2.281461000	-0.328519000	-4.156453000
H	1.785829000	0.389475000	-5.696979000
C	1.361520000	-1.721747000	-5.517549000
C	1.665372000	-2.851747000	-4.740993000
C	0.870351000	-1.906687000	-6.818980000
C	1.469388000	-4.138621000	-5.244927000
C	0.679218000	-3.188871000	-7.331422000
C	0.973354000	-4.306061000	-6.541779000
H	2.065973000	-2.725412000	-3.731084000
H	0.631582000	-1.039021000	-7.436521000
H	1.703892000	-5.007907000	-4.627370000
H	0.294833000	-3.319685000	-8.343981000
C	0.803916000	-5.697130000	-7.089976000
F	1.985670000	-6.235174000	-7.461696000
F	0.274369000	-6.534491000	-6.176574000
F	0.004974000	-5.728729000	-8.170845000

INT1w: G = -1220.08163384

C	0.356895000	0.722673000	-4.426673000
C	0.174146000	1.428001000	-3.132812000
O	-1.661875000	-0.606886000	-2.839626000
C	0.172751000	0.553199000	-1.865511000
C	-1.048266000	-0.326320000	-1.697045000
H	-0.691999000	2.097060000	-3.137194000
H	0.248076000	1.199357000	-0.980387000
H	1.072856000	2.075248000	-3.065467000
H	1.049718000	-0.114927000	-1.831511000
O	-1.403829000	-0.758661000	-0.615847000
H	-2.422503000	-1.254622000	-2.649285000
C	-0.554488000	0.863306000	-5.503603000
C	-0.186006000	0.475200000	-6.829363000
C	-1.865511000	1.388651000	-5.290919000
C	-1.076021000	0.618752000	-7.877866000
C	-2.757182000	1.504245000	-6.344283000
C	-2.364107000	1.125695000	-7.636613000
H	0.812093000	0.091210000	-7.031170000
H	-2.189811000	1.659007000	-4.288163000
H	-0.778770000	0.338530000	-8.889963000

H	-3.763878000	1.887390000	-6.168296000
H	-3.068256000	1.226143000	-8.466467000
C	1.631784000	-0.049159000	-4.576130000
H	2.155031000	-0.078328000	-3.609146000
H	2.274342000	0.571970000	-5.229893000
C	1.540985000	-1.453030000	-5.144029000
C	2.529582000	-1.908989000	-6.028730000
C	0.513478000	-2.325642000	-4.761636000
C	2.491273000	-3.209778000	-6.527028000
C	0.467719000	-3.627810000	-5.261231000
C	1.455459000	-4.071017000	-6.144979000
H	3.335809000	-1.237585000	-6.334044000
H	-0.263996000	-1.990940000	-4.073685000
H	3.267544000	-3.552662000	-7.214204000
H	-0.338032000	-4.297659000	-4.957477000
C	1.401083000	-5.456473000	-6.727573000
F	0.981456000	-5.442444000	-8.011657000
F	2.612962000	-6.047020000	-6.730745000
F	0.565173000	-6.265752000	-6.053833000
O	-3.453651000	-2.260828000	-1.965982000
H	-3.085198000	-2.069268000	-1.082202000
H	-3.162875000	-3.170311000	-2.146698000

TSw: G = -1220.07750520 (i = -168 cm-1)

C	0.201110000	0.556149000	-4.146398000
C	0.312213000	1.708529000	-3.180187000
O	-0.855389000	-0.469918000	-2.713882000
C	0.382159000	1.234105000	-1.725111000
C	-0.666810000	0.163041000	-1.536771000
H	-0.533054000	2.394556000	-3.313100000
H	0.205350000	2.054518000	-1.017625000
H	1.223497000	2.263431000	-3.461885000
H	1.362809000	0.795820000	-1.475806000
O	-1.262268000	-0.124111000	-0.530446000
H	-1.691320000	-1.104040000	-2.794492000
C	-0.753998000	0.641468000	-5.242919000
C	-0.398380000	0.225295000	-6.545771000
C	-2.043837000	1.180521000	-5.025572000
C	-1.300447000	0.361737000	-7.597400000
C	-2.953165000	1.275540000	-6.071989000
C	-2.581125000	0.872589000	-7.361809000
H	0.595271000	-0.169962000	-6.748257000
H	-2.348013000	1.481902000	-4.022559000
H	-1.004972000	0.060859000	-8.604609000

H	-3.955318000	1.667478000	-5.886553000
H	-3.293710000	0.958687000	-8.185753000
C	1.413561000	-0.316364000	-4.240120000
H	1.844282000	-0.429647000	-3.233451000
H	2.141775000	0.327476000	-4.771570000
C	1.361577000	-1.666452000	-4.922917000
C	2.487974000	-2.081689000	-5.649661000
C	0.266978000	-2.537338000	-4.827863000
C	2.524271000	-3.329111000	-6.271380000
C	0.294144000	-3.785108000	-5.449677000
C	1.421990000	-4.184160000	-6.174098000
H	3.350379000	-1.415779000	-5.734603000
H	-0.626344000	-2.254502000	-4.278442000
H	3.409624000	-3.633563000	-6.832166000
H	-0.568145000	-4.448950000	-5.365356000
C	1.424739000	-5.505505000	-6.891711000
F	0.900915000	-5.402401000	-8.133359000
F	2.667047000	-6.002034000	-7.039210000
F	0.696448000	-6.435524000	-6.245215000
O	-2.849073000	-1.942469000	-3.028751000
H	-2.658466000	-2.890774000	-2.928798000
H	-3.170316000	-1.844779000	-3.941727000

INT2w: G = -1220.09594331

C	0.271197000	0.220775000	-4.295178000
C	0.521098000	1.522807000	-3.496342000
O	-0.051209000	-0.743719000	-3.225354000
C	0.993335000	1.040843000	-2.125847000
C	0.364551000	-0.317875000	-1.976368000
H	-0.423788000	2.075181000	-3.400497000
H	0.704784000	1.686329000	-1.285718000
H	1.246935000	2.164730000	-4.011584000
H	2.086128000	0.897209000	-2.076440000
O	0.207036000	-1.020742000	-1.021252000
H	-0.474413000	-2.167687000	-3.292490000
C	-0.913911000	0.336326000	-5.234110000
C	-0.795846000	1.168051000	-6.359576000
C	-2.127837000	-0.321214000	-5.004362000
C	-1.863032000	1.320643000	-7.245895000
C	-3.195755000	-0.172733000	-5.896330000
C	-3.067442000	0.644497000	-7.020986000
H	0.136937000	1.703080000	-6.550821000
H	-2.255495000	-0.954292000	-4.127521000
H	-1.751737000	1.970000000	-8.117735000

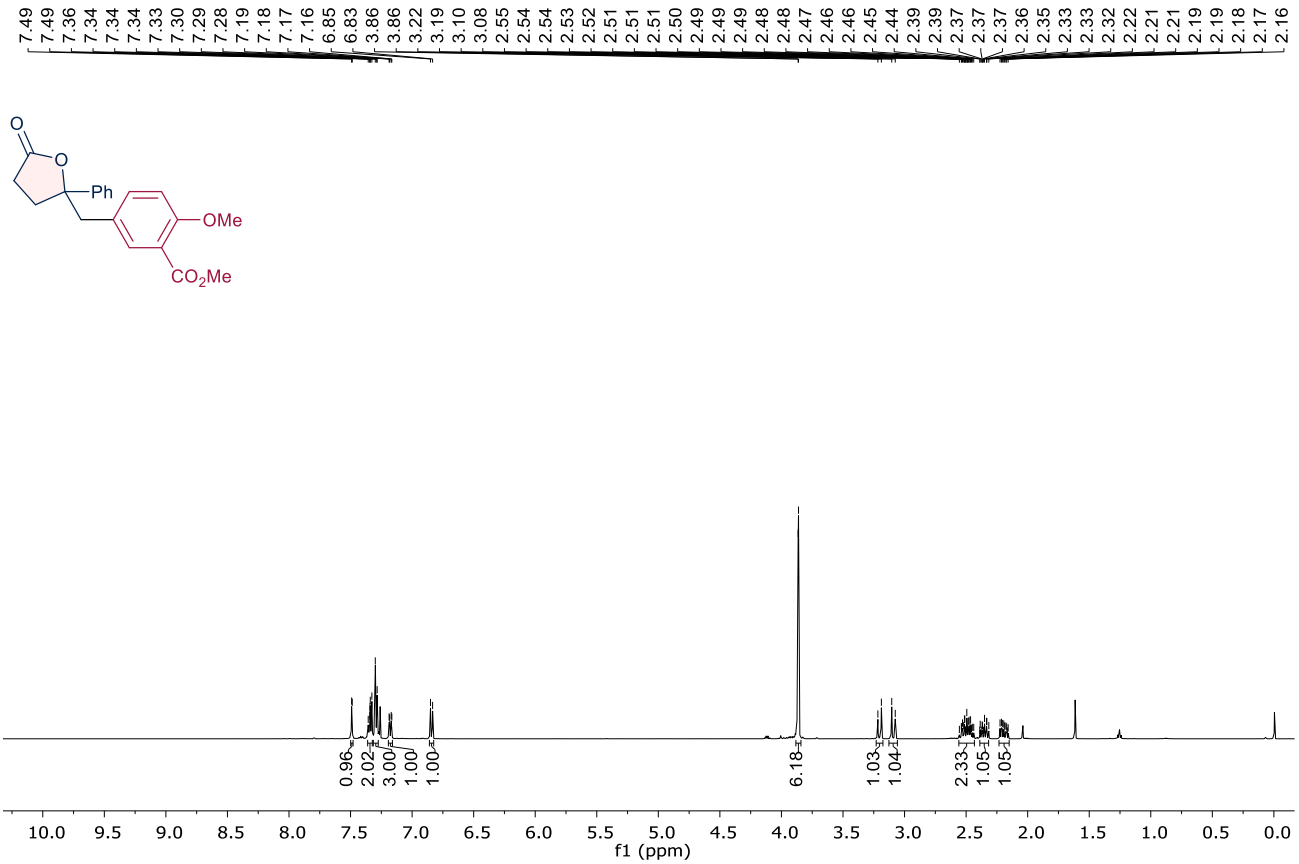
H	-4.132814000	-0.700991000	-5.703860000
H	-3.901505000	0.758788000	-7.717674000
C	1.555871000	-0.278434000	-4.993947000
H	2.388103000	-0.202134000	-4.278723000
H	1.773364000	0.418400000	-5.815269000
C	1.456425000	-1.693490000	-5.505156000
C	1.967765000	-2.753404000	-4.741007000
C	0.817408000	-1.987990000	-6.720338000
C	1.839755000	-4.075127000	-5.168823000
C	0.682995000	-3.305831000	-7.155452000
C	1.191249000	-4.352515000	-6.376990000
H	2.466600000	-2.540933000	-3.792243000
H	0.417376000	-1.178625000	-7.333053000
H	2.235874000	-4.888211000	-4.557900000
H	0.178662000	-3.519587000	-8.099407000
C	1.091456000	-5.772072000	-6.862301000
F	2.184287000	-6.139336000	-7.567753000
F	0.979976000	-6.648670000	-5.845954000
F	0.031761000	-5.961105000	-7.670552000
O	-0.782953000	-3.164548000	-3.249884000
H	-1.045603000	-3.467878000	-4.144752000
H	-1.566770000	-3.234884000	-2.664323000

lactone: G = -1143.36043028

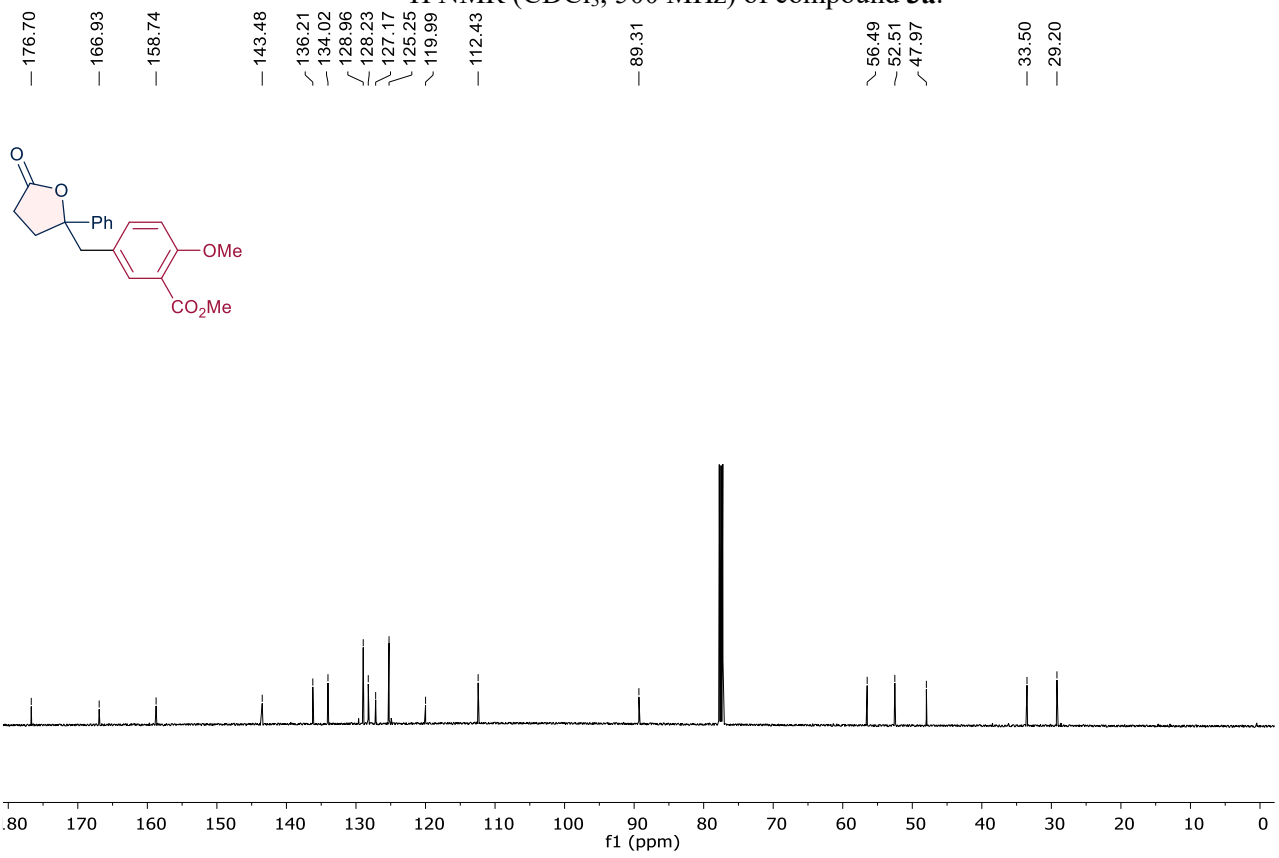
C	0.329758000	0.272208000	-4.220689000
C	0.602460000	1.636054000	-3.541062000
O	0.032589000	-0.614092000	-3.105978000
C	1.105183000	1.238892000	-2.155198000
C	0.479581000	-0.121922000	-1.928703000
H	-0.339598000	2.196964000	-3.460259000
H	0.826044000	1.927146000	-1.346105000
H	1.315996000	2.241031000	-4.115216000
H	2.199998000	1.109670000	-2.119196000
O	0.368275000	-0.744441000	-0.903213000
C	-0.855438000	0.282678000	-5.163784000
C	-0.910035000	1.247040000	-6.181241000
C	-1.868800000	-0.679932000	-5.083109000
C	-1.960314000	1.248697000	-7.101881000
C	-2.922061000	-0.676829000	-6.003552000
C	-2.971159000	0.284638000	-7.016473000
H	-0.123500000	2.001597000	-6.260982000
H	-1.829806000	-1.435748000	-4.298677000
H	-1.989270000	2.006607000	-7.888904000
H	-3.706347000	-1.434651000	-5.928497000

H	-3.793150000	0.284508000	-7.736863000
C	1.599293000	-0.267141000	-4.928616000
H	2.432888000	-0.234663000	-4.209982000
H	1.840251000	0.429863000	-5.744173000
C	1.432154000	-1.663549000	-5.466916000
C	1.662321000	-2.779247000	-4.647075000
C	0.992033000	-1.875701000	-6.781844000
C	1.455125000	-4.072740000	-5.124074000
C	0.783929000	-3.165732000	-7.269839000
C	1.013568000	-4.267295000	-6.438783000
H	2.003016000	-2.631894000	-3.619975000
H	0.802971000	-1.017940000	-7.430946000
H	1.634097000	-4.931052000	-4.473272000
H	0.438597000	-3.314171000	-8.294338000
C	0.844094000	-5.664355000	-6.964775000
F	2.019767000	-6.196309000	-7.370304000
F	0.351890000	-6.502135000	-6.030443000
F	0.014157000	-5.717422000	-8.023379000

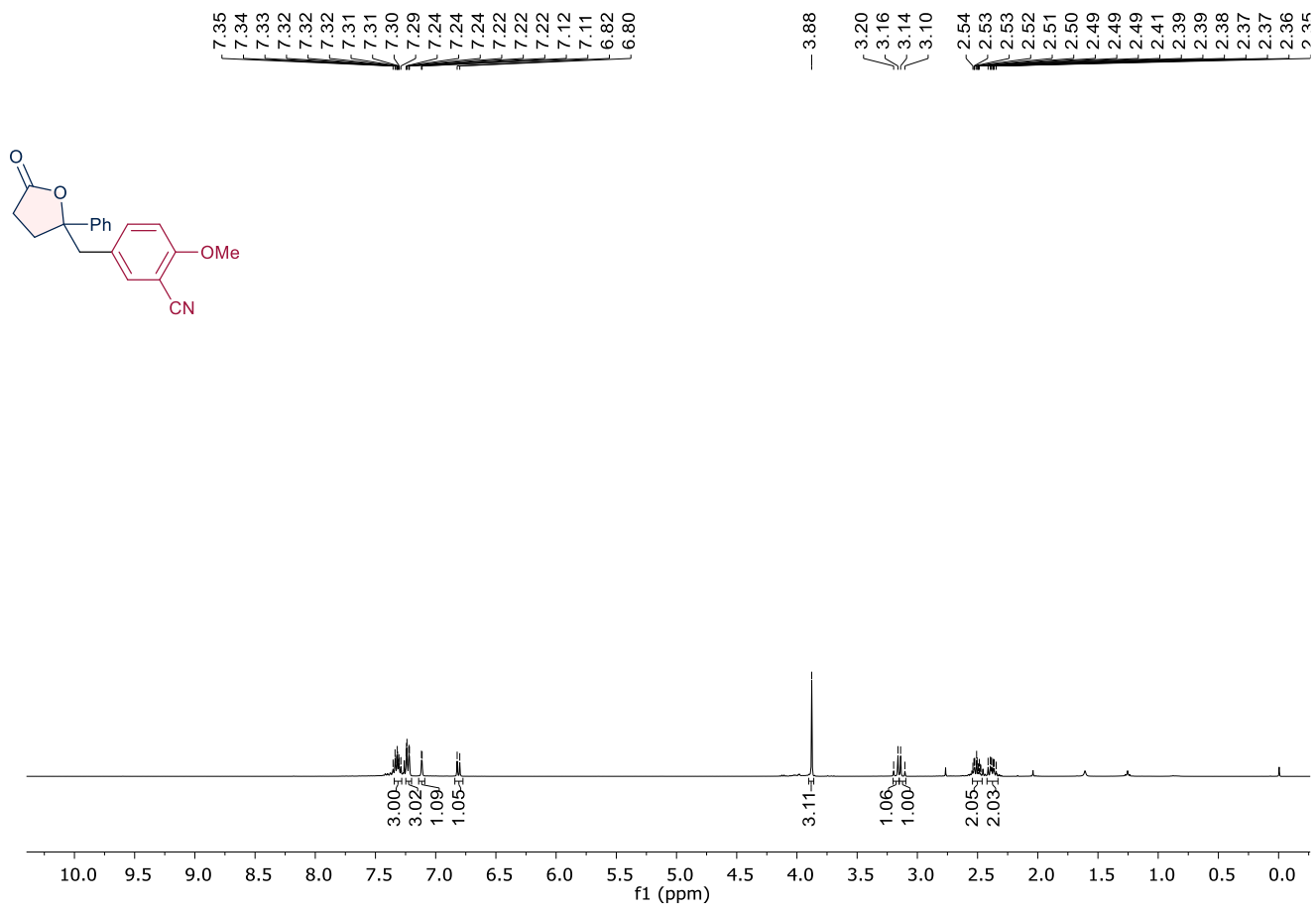
8. NMR spectra



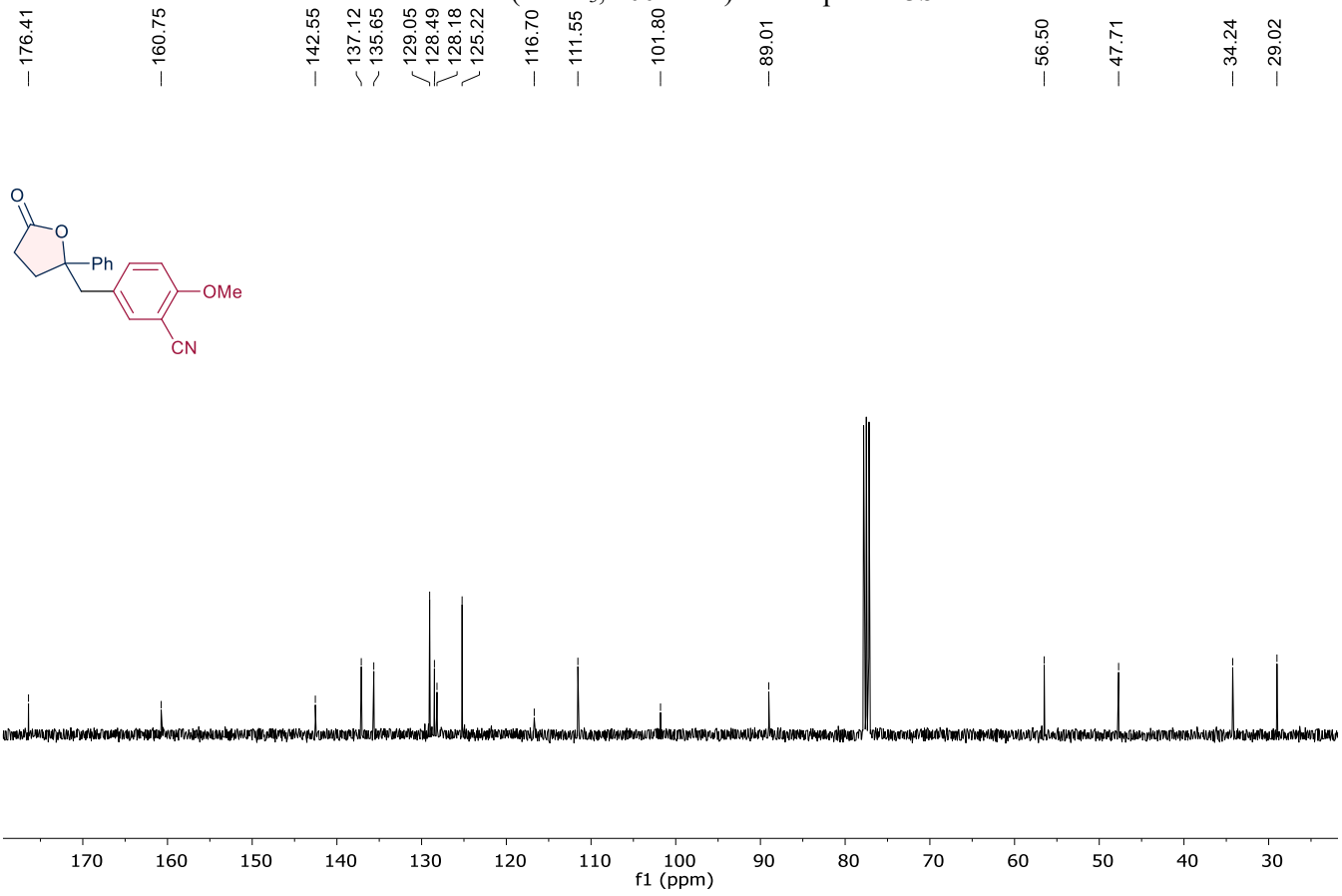
^{1}H NMR ($CDCl_3$, 500 MHz) of compound **3a**.



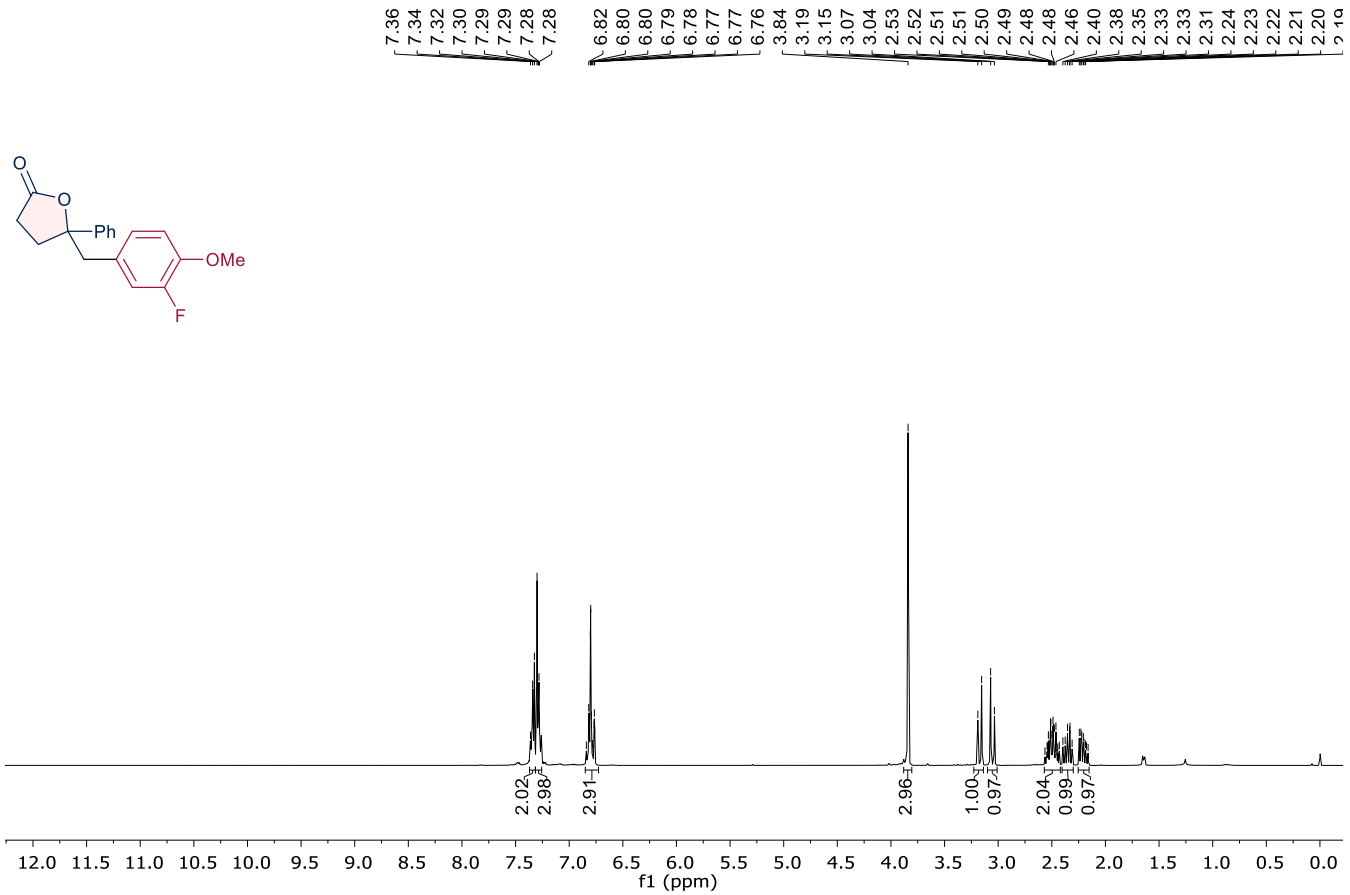
^{13}C NMR ($CDCl_3$, 126 MHz) of compound **3a**.



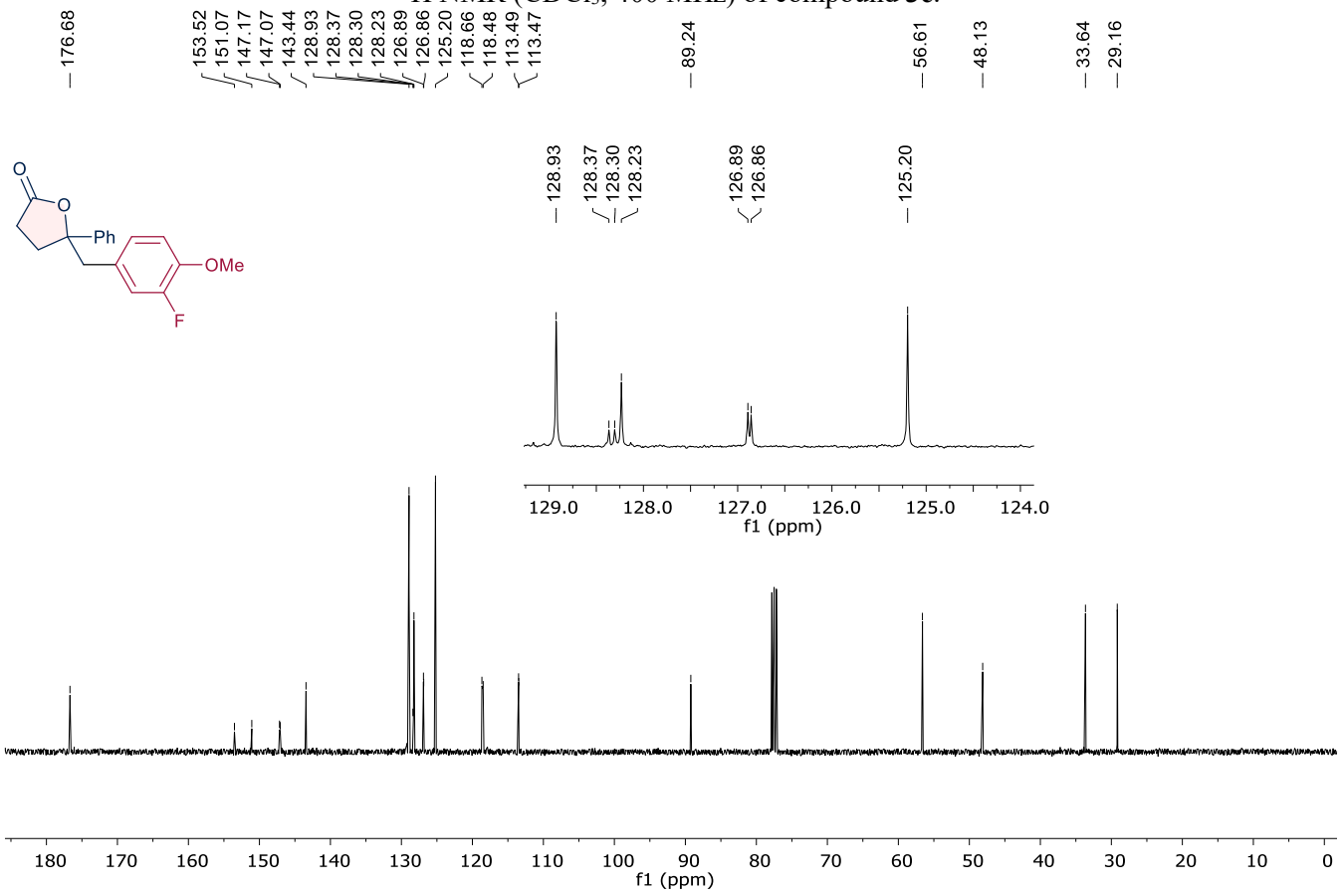
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3b**.



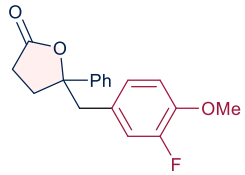
^{13}C NMR ($CDCl_3$, 101 MHz) of compound **3b**.



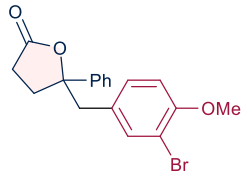
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3c**.



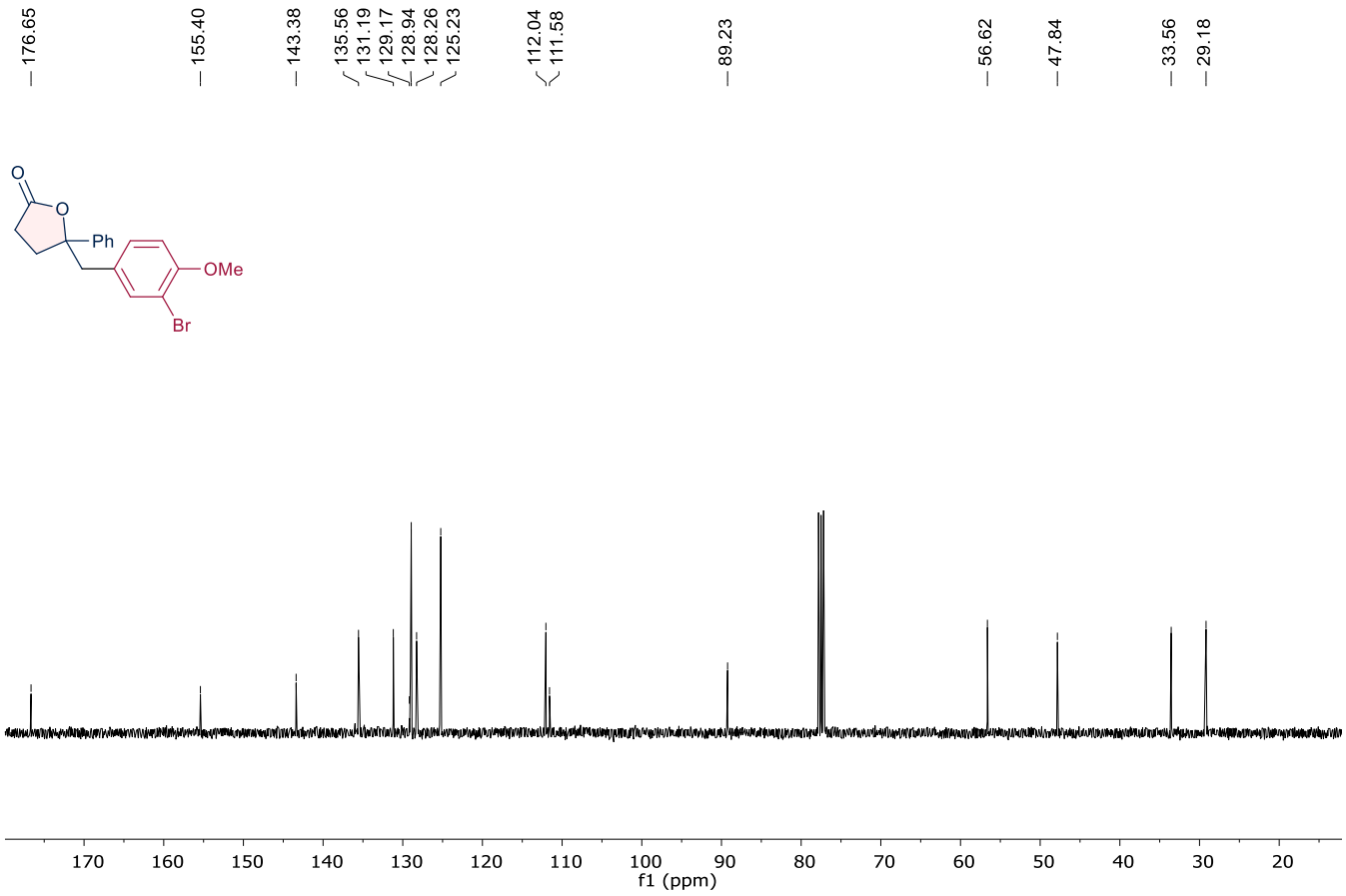
^{13}C NMR ($CDCl_3$, 101 MHz) of compound **3c**.



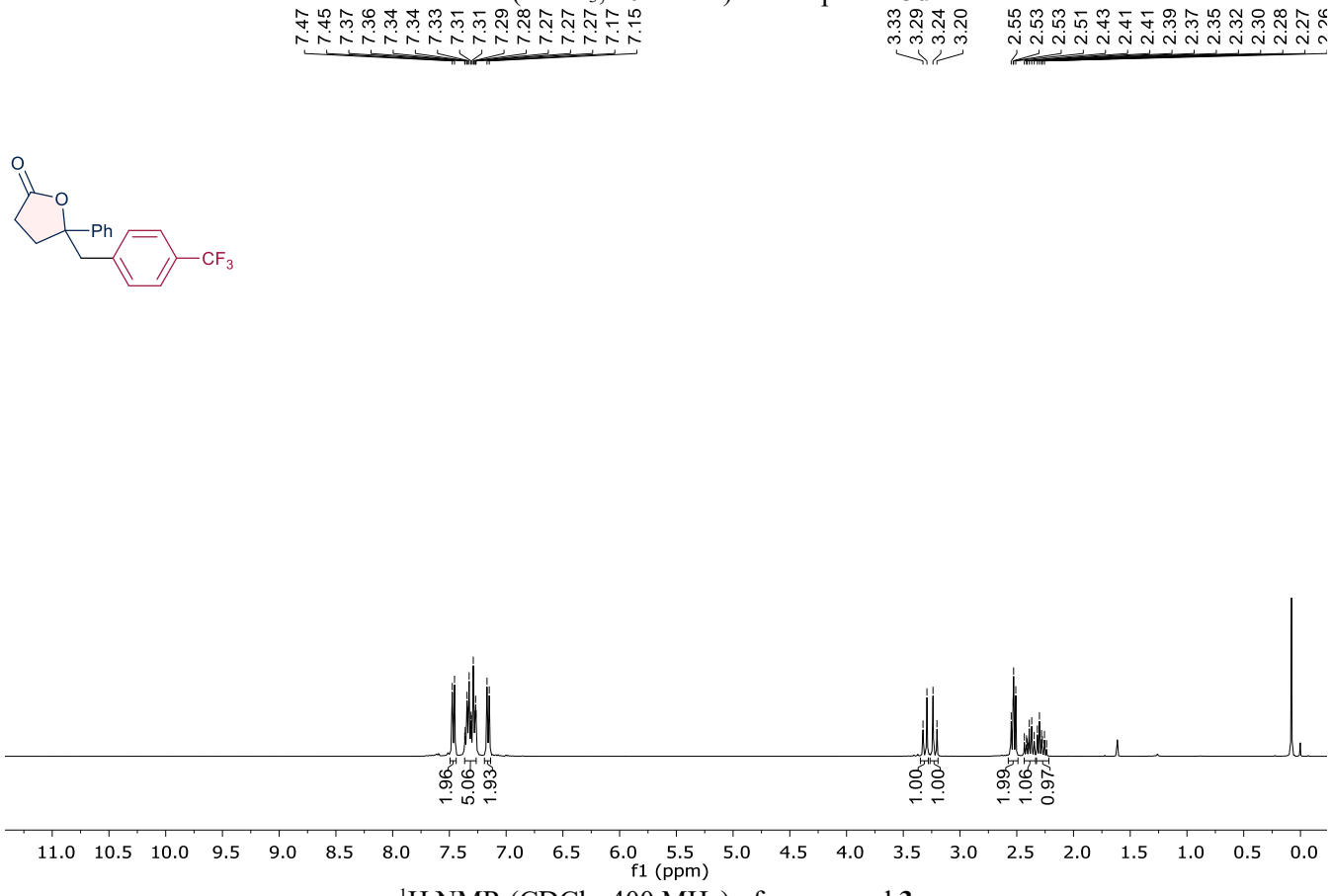
^{19}F NMR ($CDCl_3$, 377 MHz) of compound **3c**.



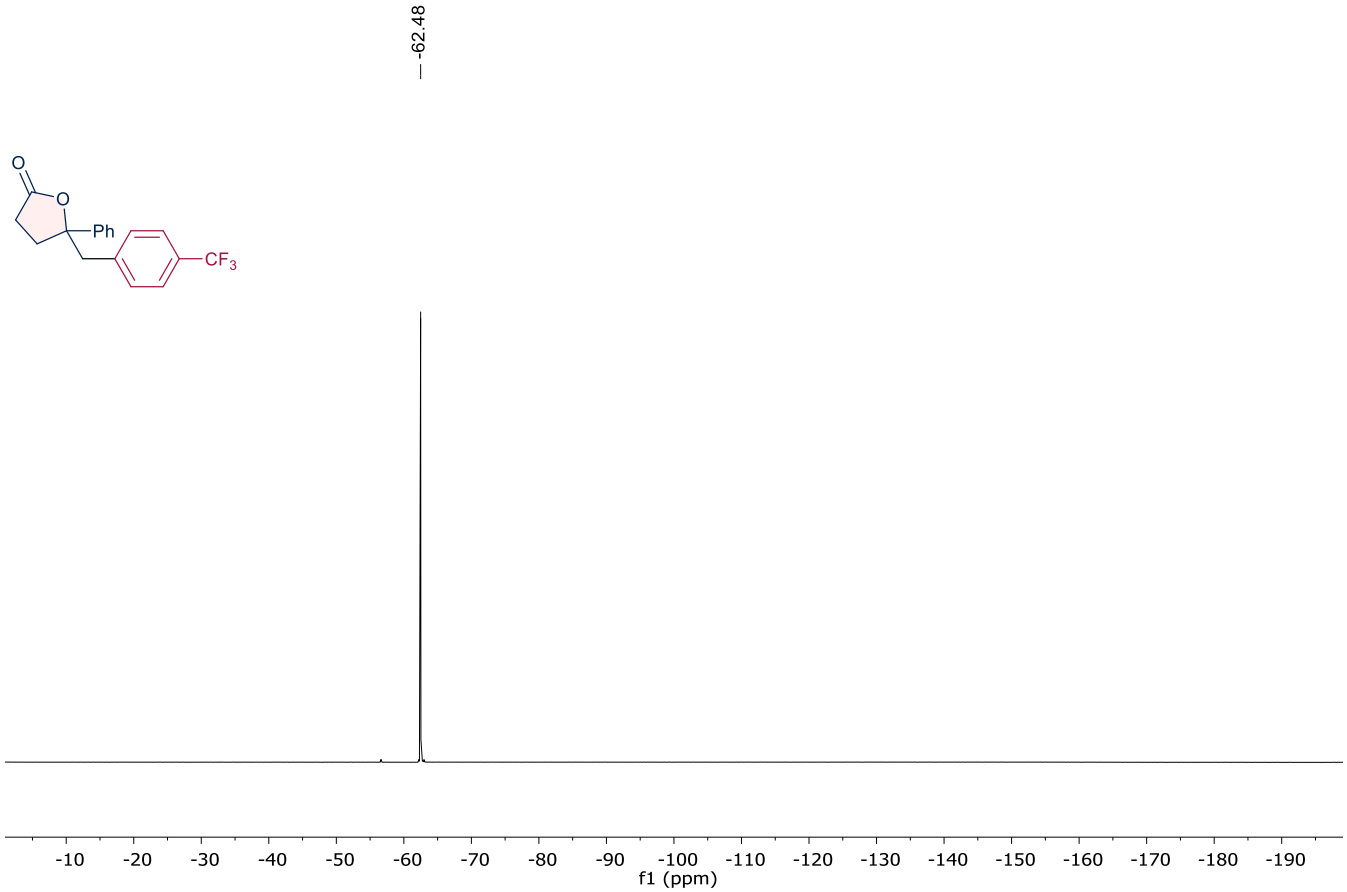
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3d**.



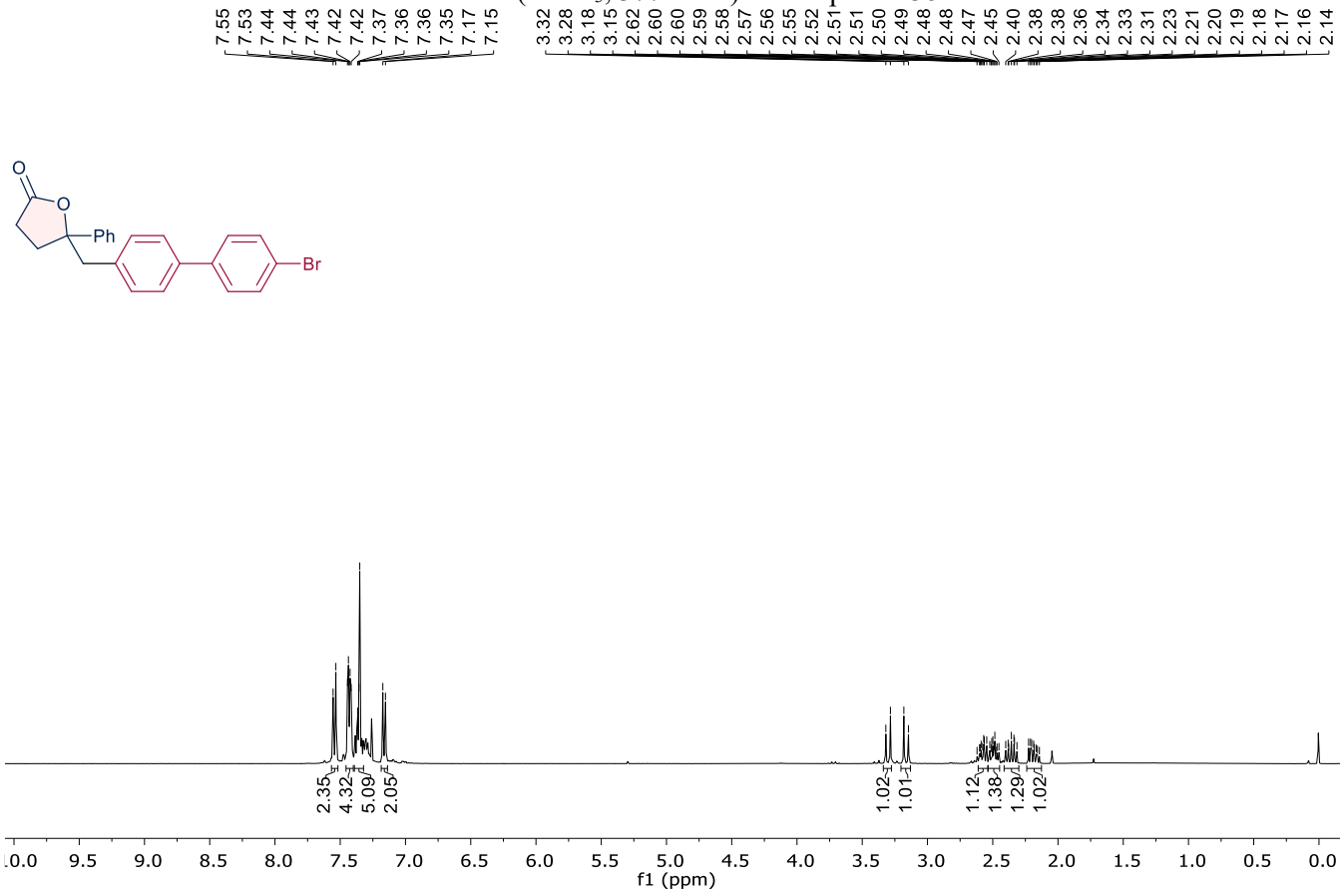
^{13}C NMR ($CDCl_3$, 101 MHz) of compound **3d**.



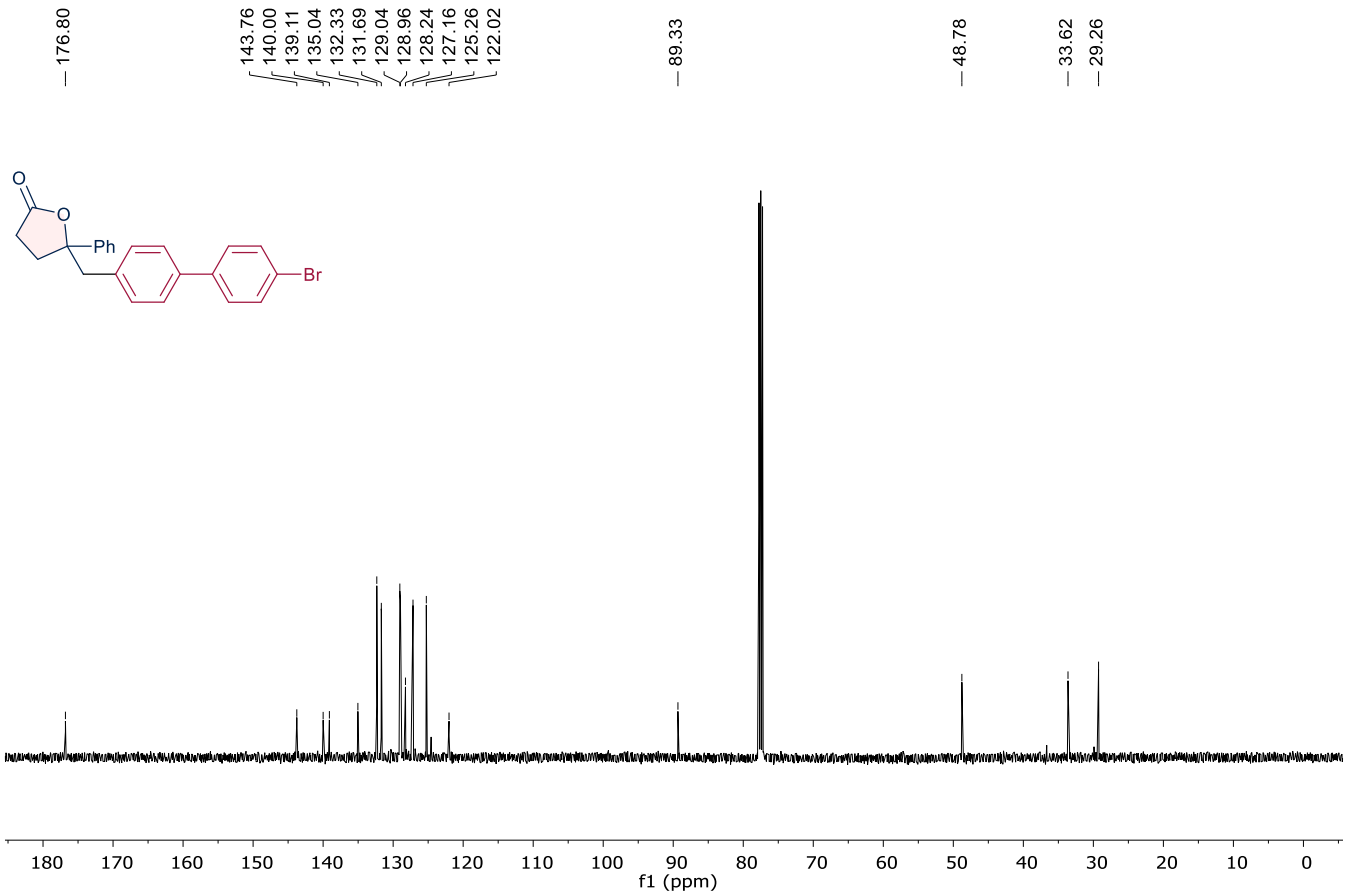
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3e**.



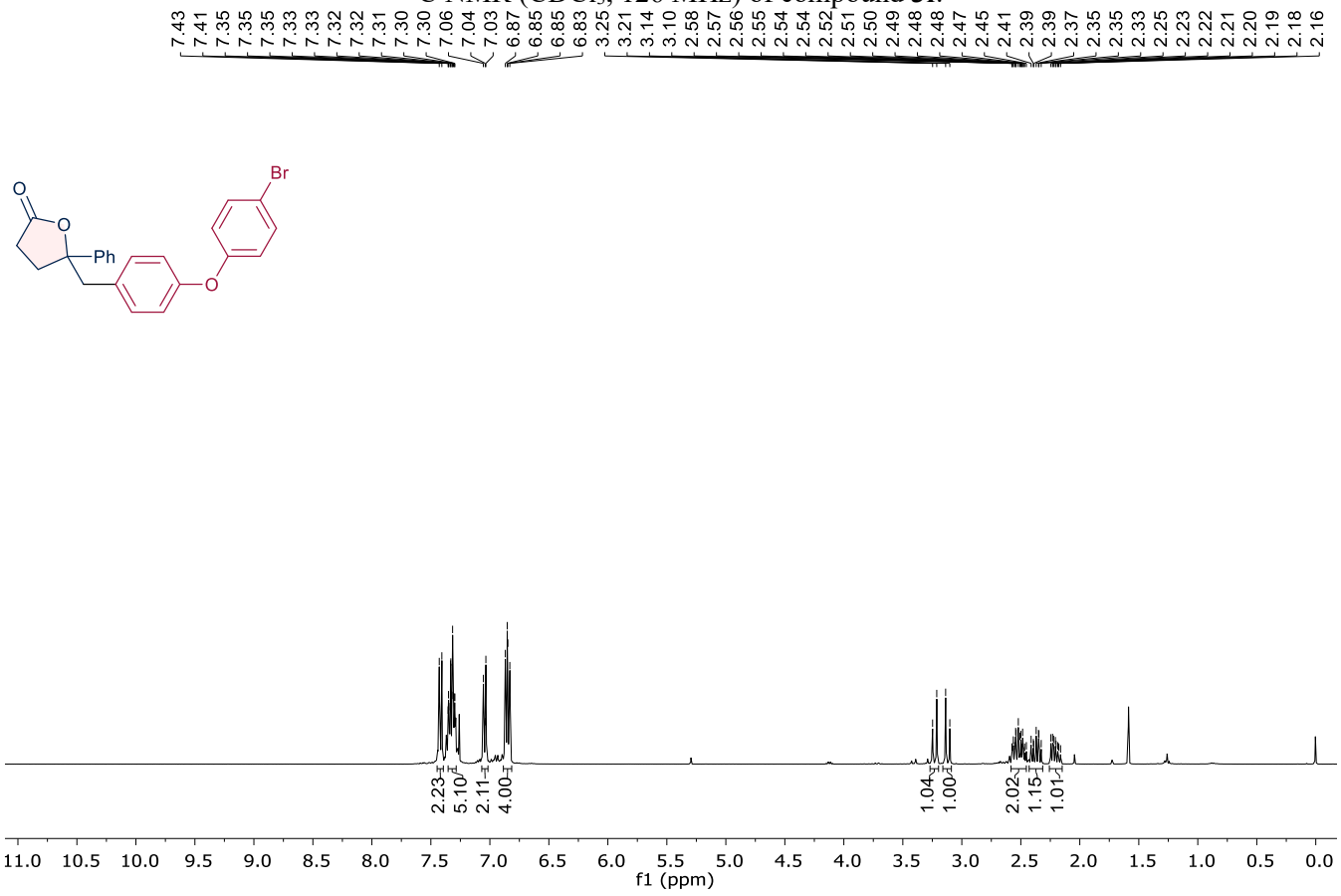
^{19}F NMR ($CDCl_3$, 377 MHz) of compound **3e**.



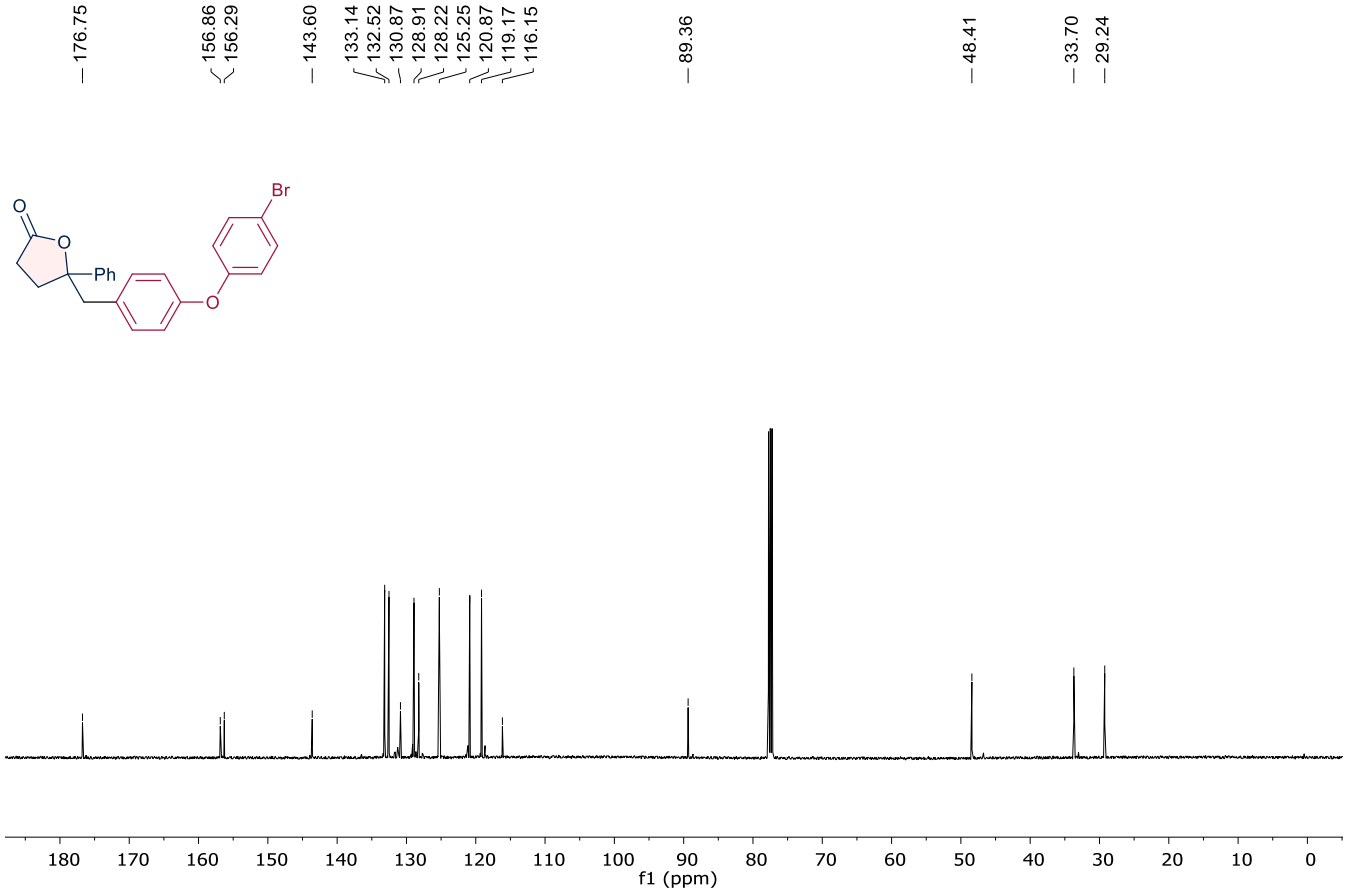
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3f**.



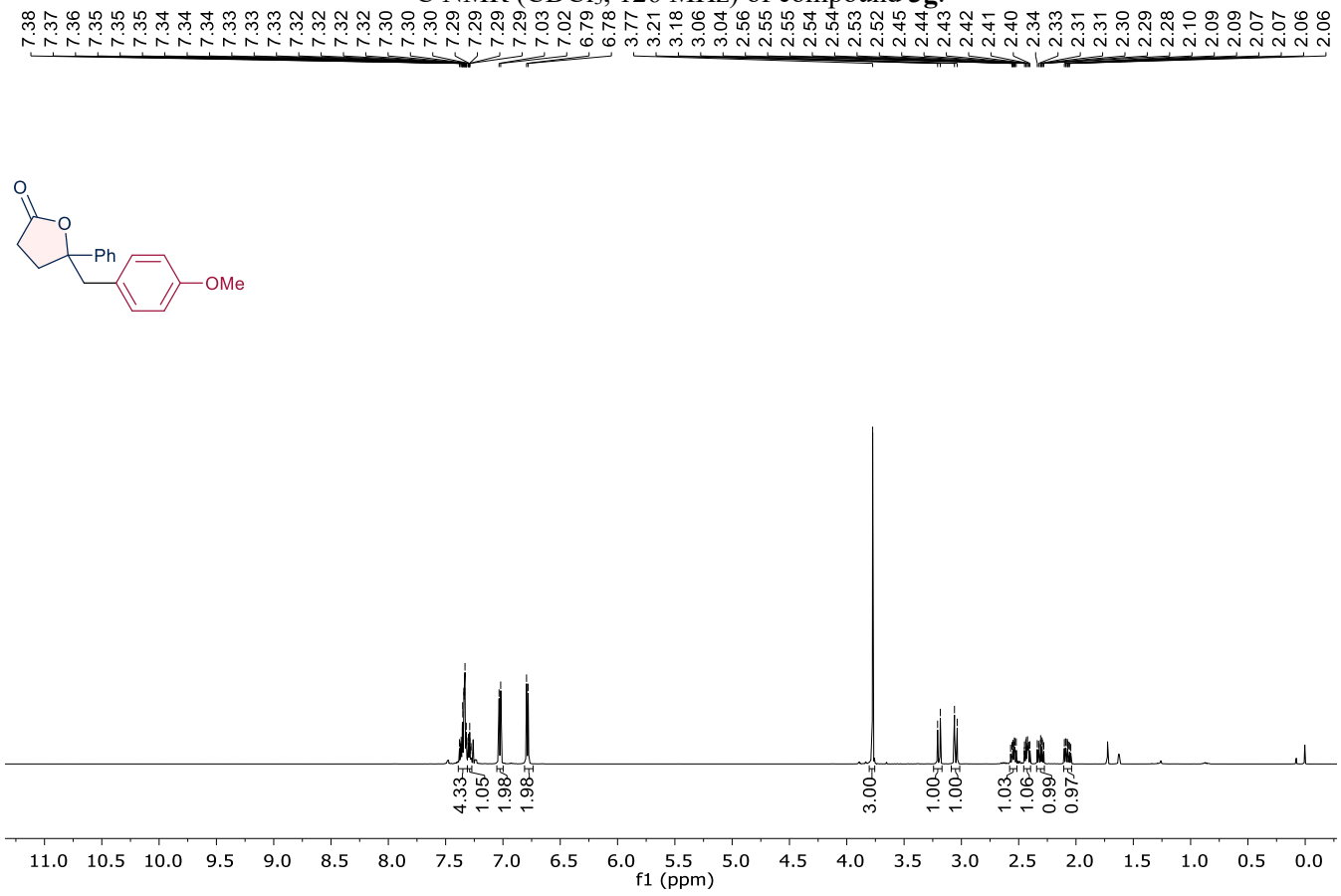
^{13}C NMR ($CDCl_3$, 126 MHz) of compound **3f**.



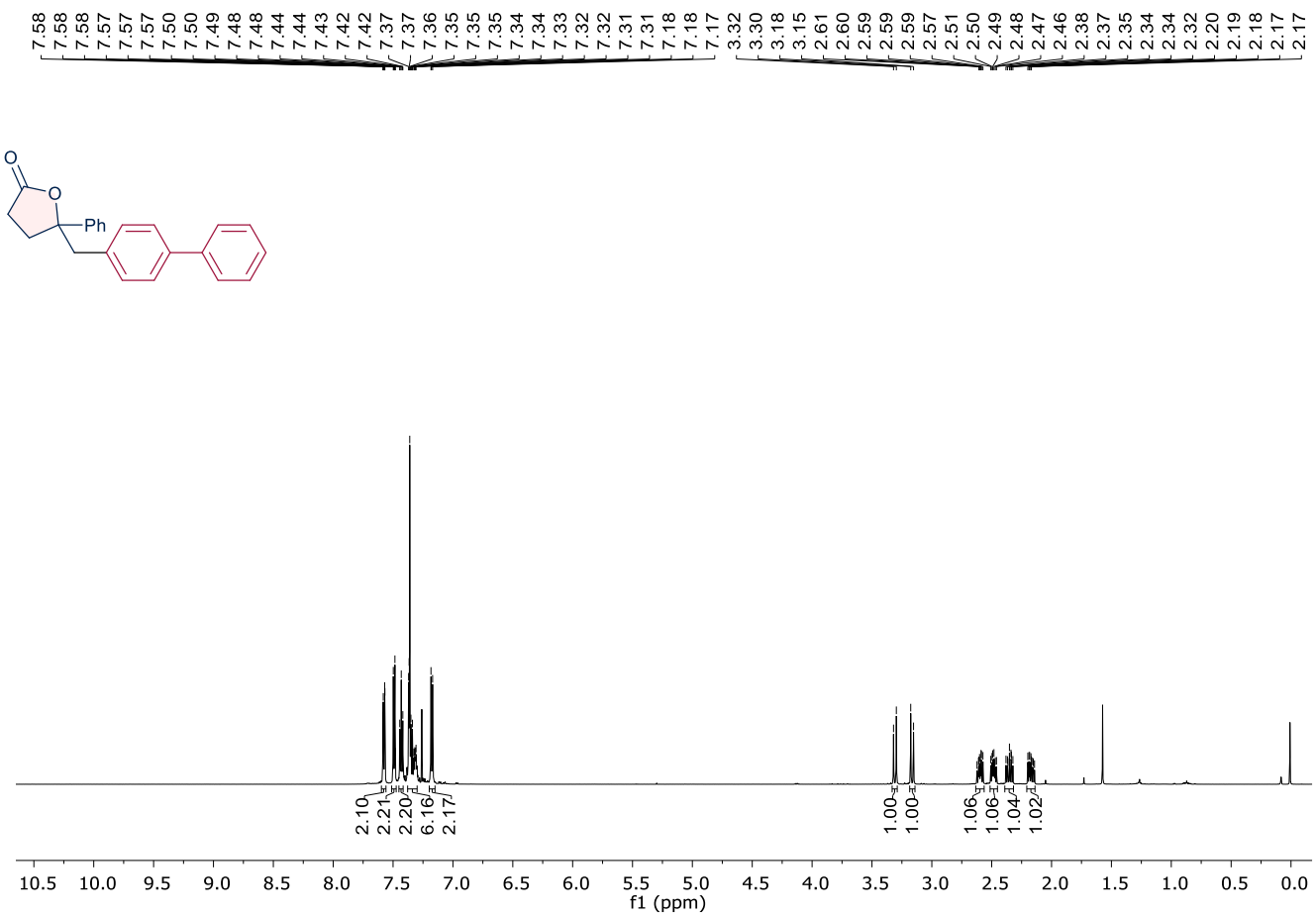
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3g**.



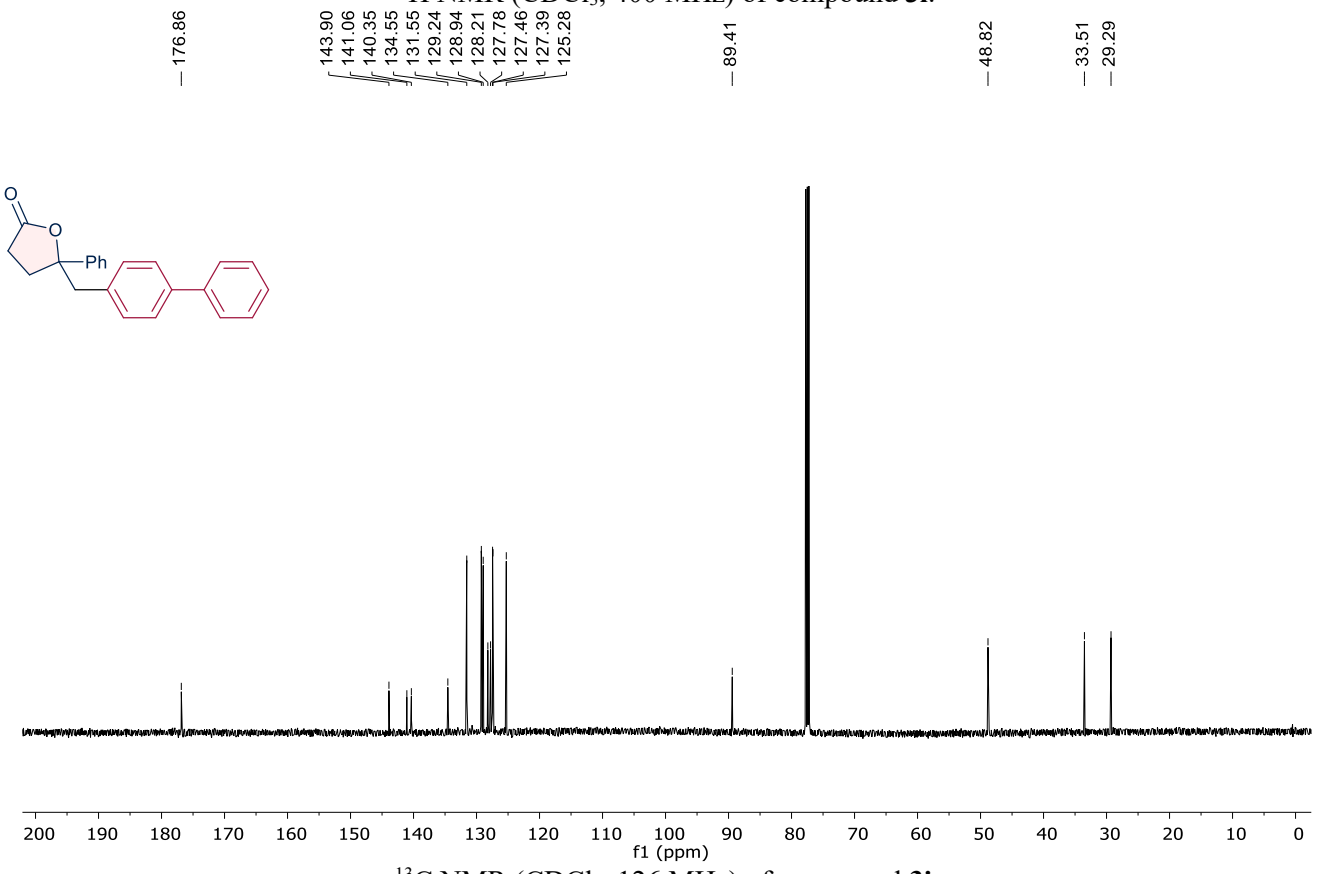
^{13}C NMR ($CDCl_3$, 126 MHz) of compound **3g**.



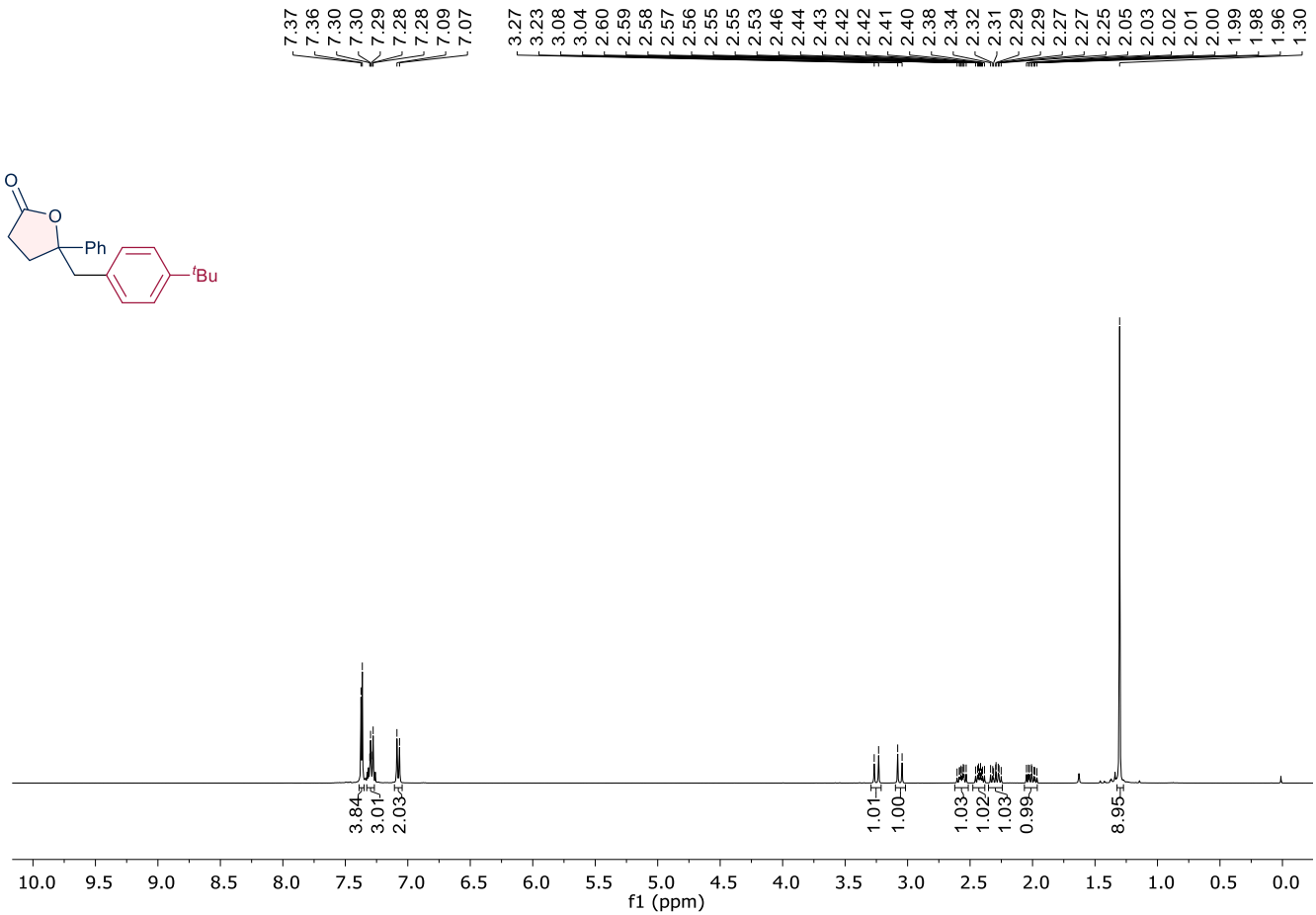
^{1}H NMR ($CDCl_3$, 600 MHz) of compound **3h**.



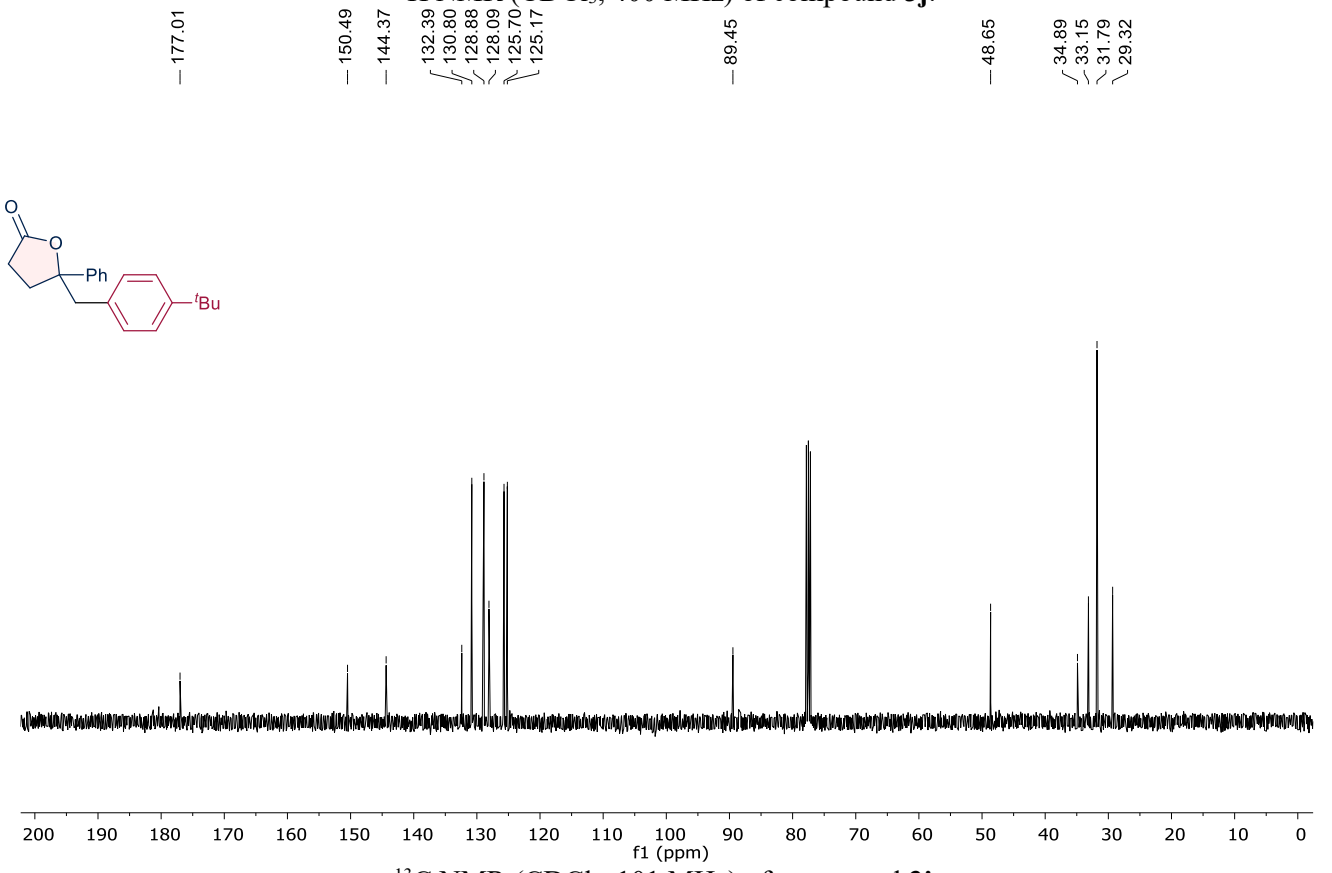
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3i**.



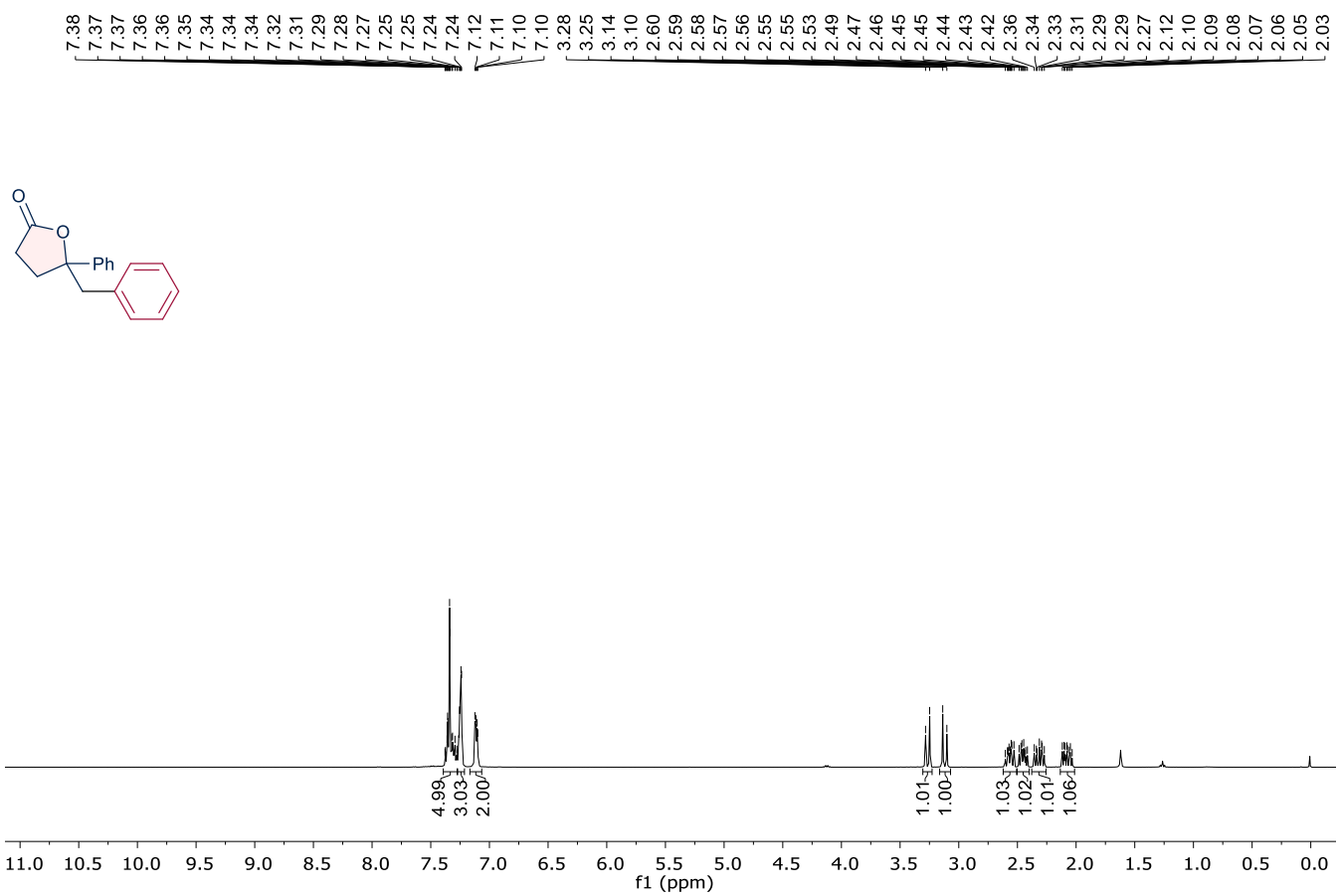
^{13}C NMR ($CDCl_3$, 126 MHz) of compound **3i**.



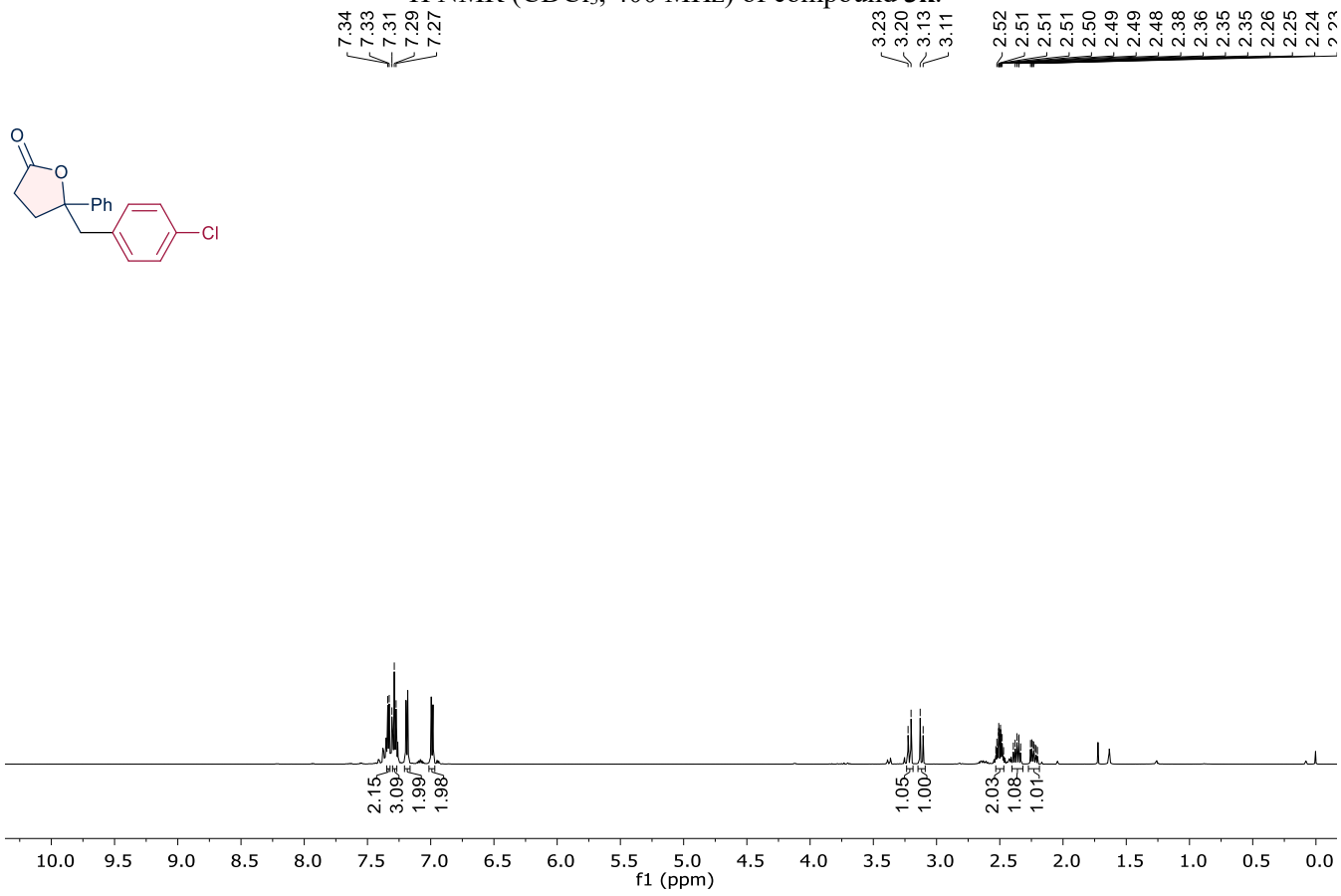
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3j**.



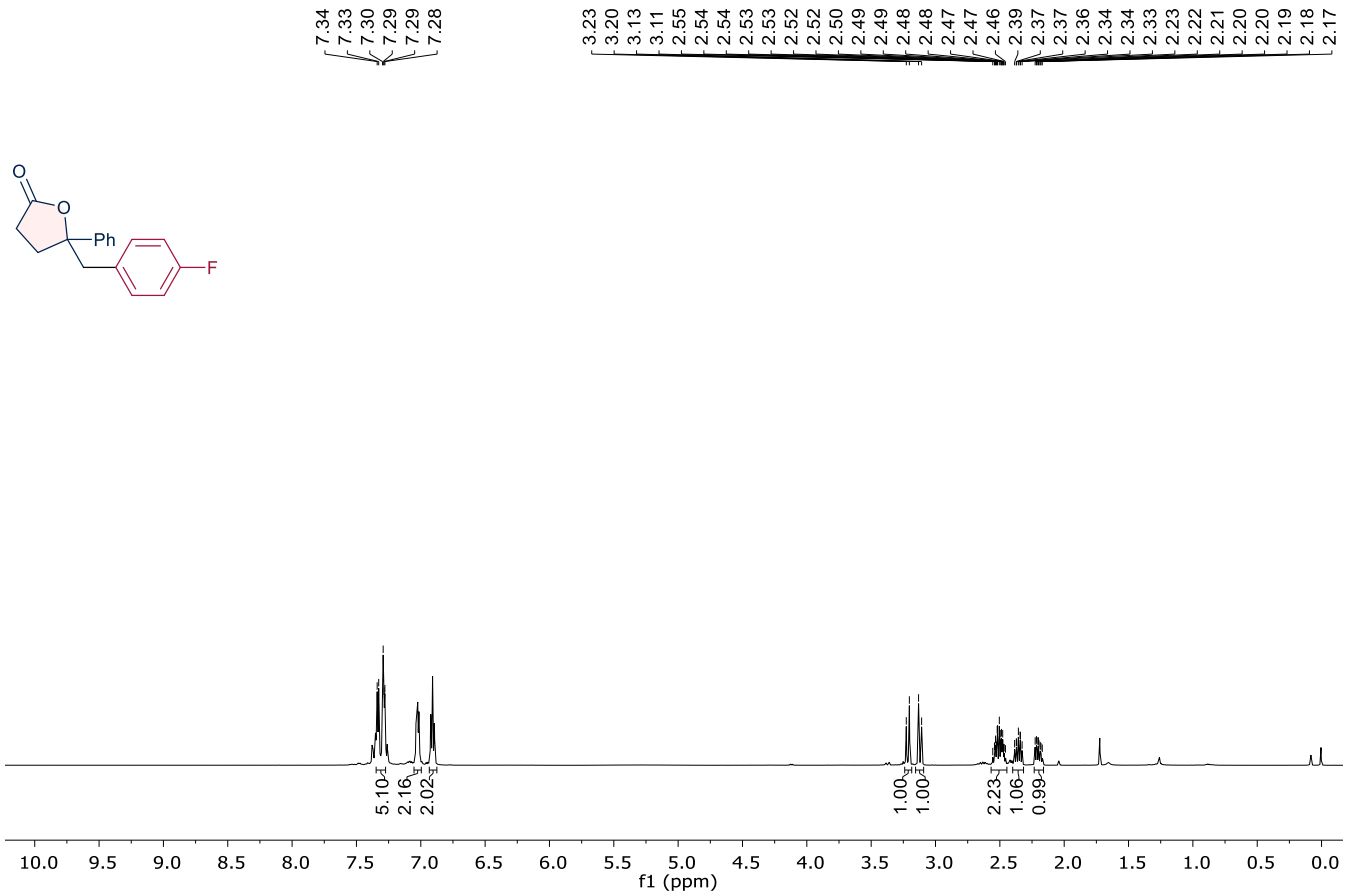
^{13}C NMR ($CDCl_3$, 101 MHz) of compound **3j**.



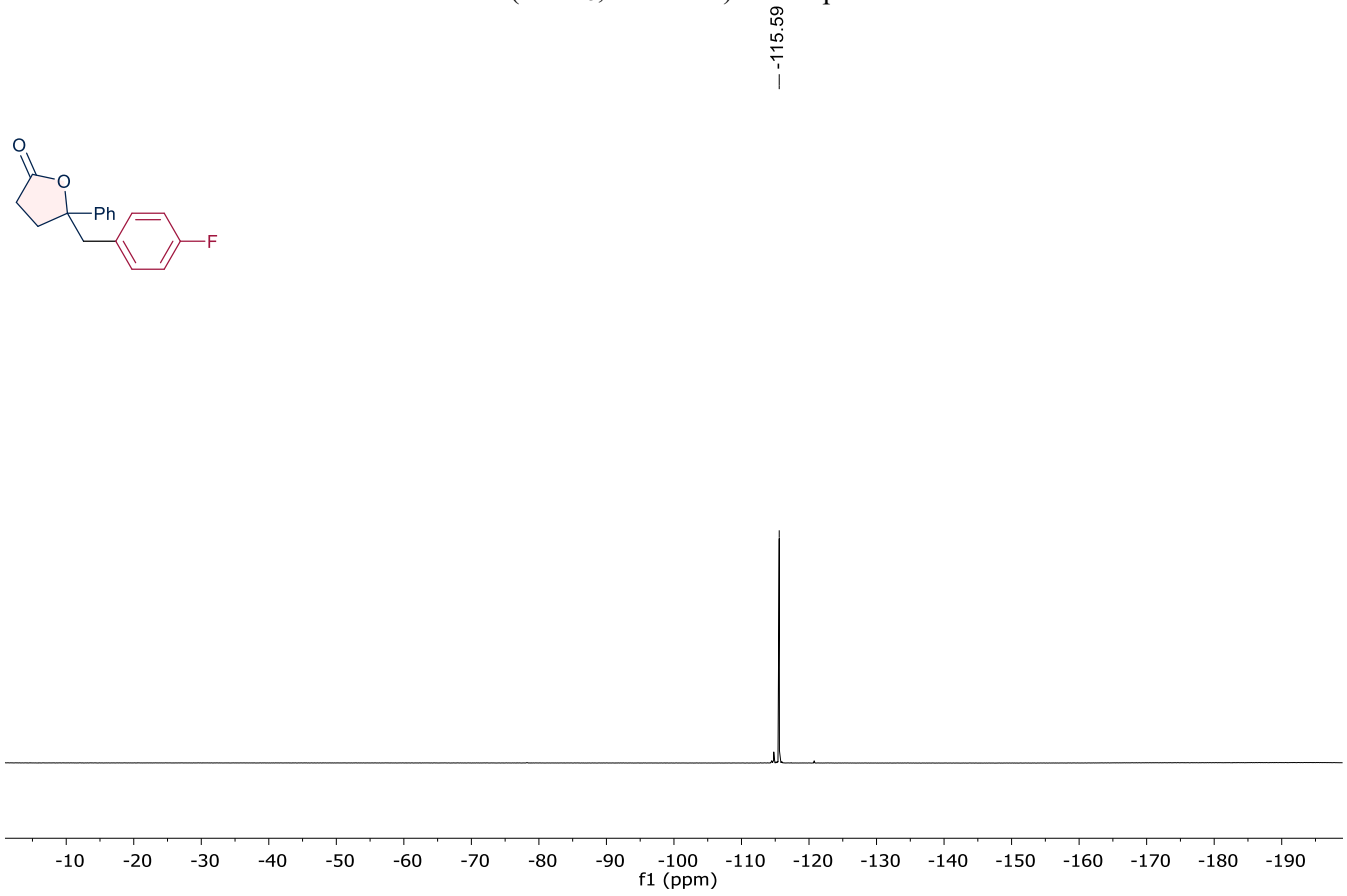
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3k**.



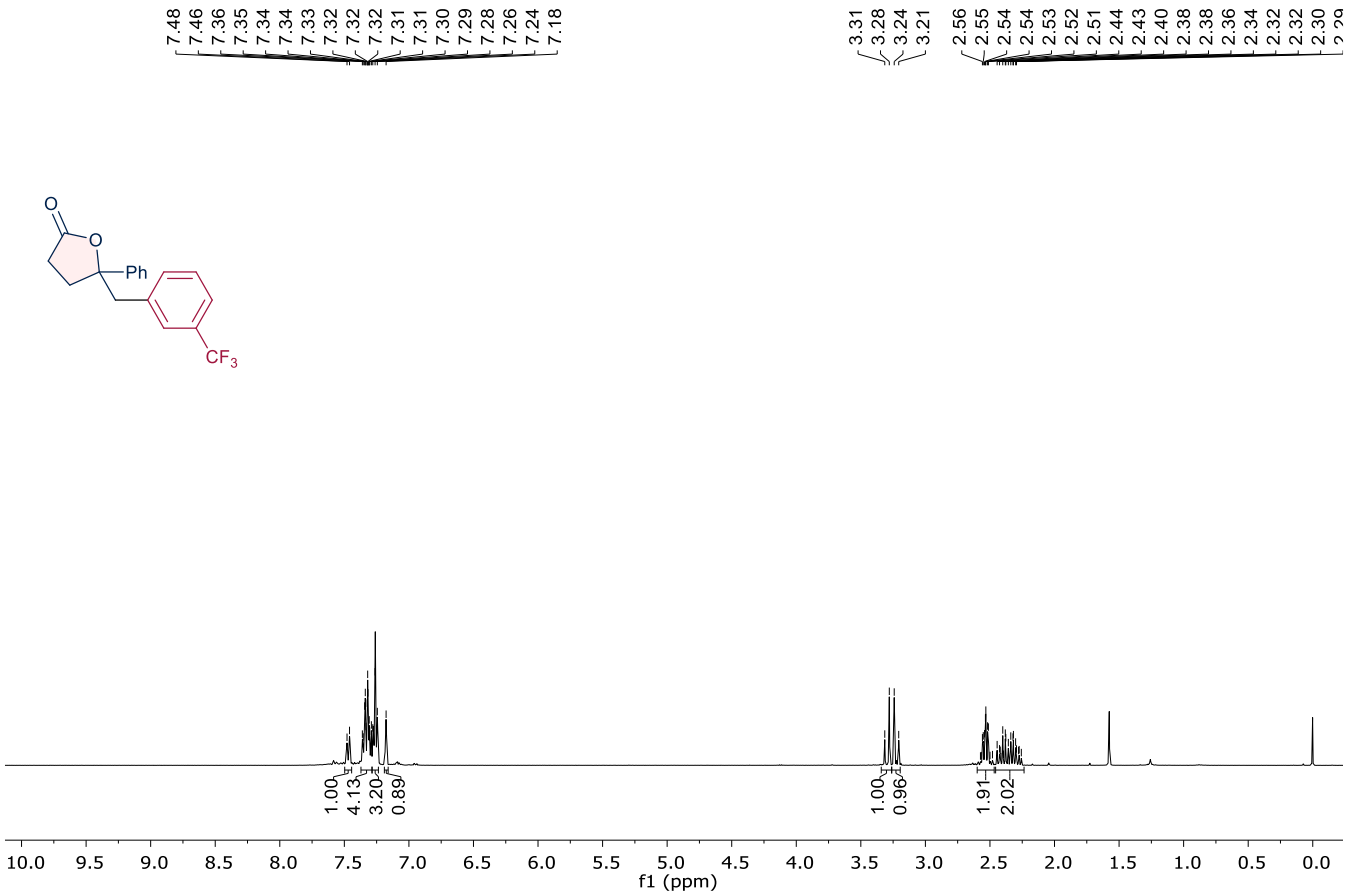
^{1}H NMR ($CDCl_3$, 600 MHz) of compound **3l**.



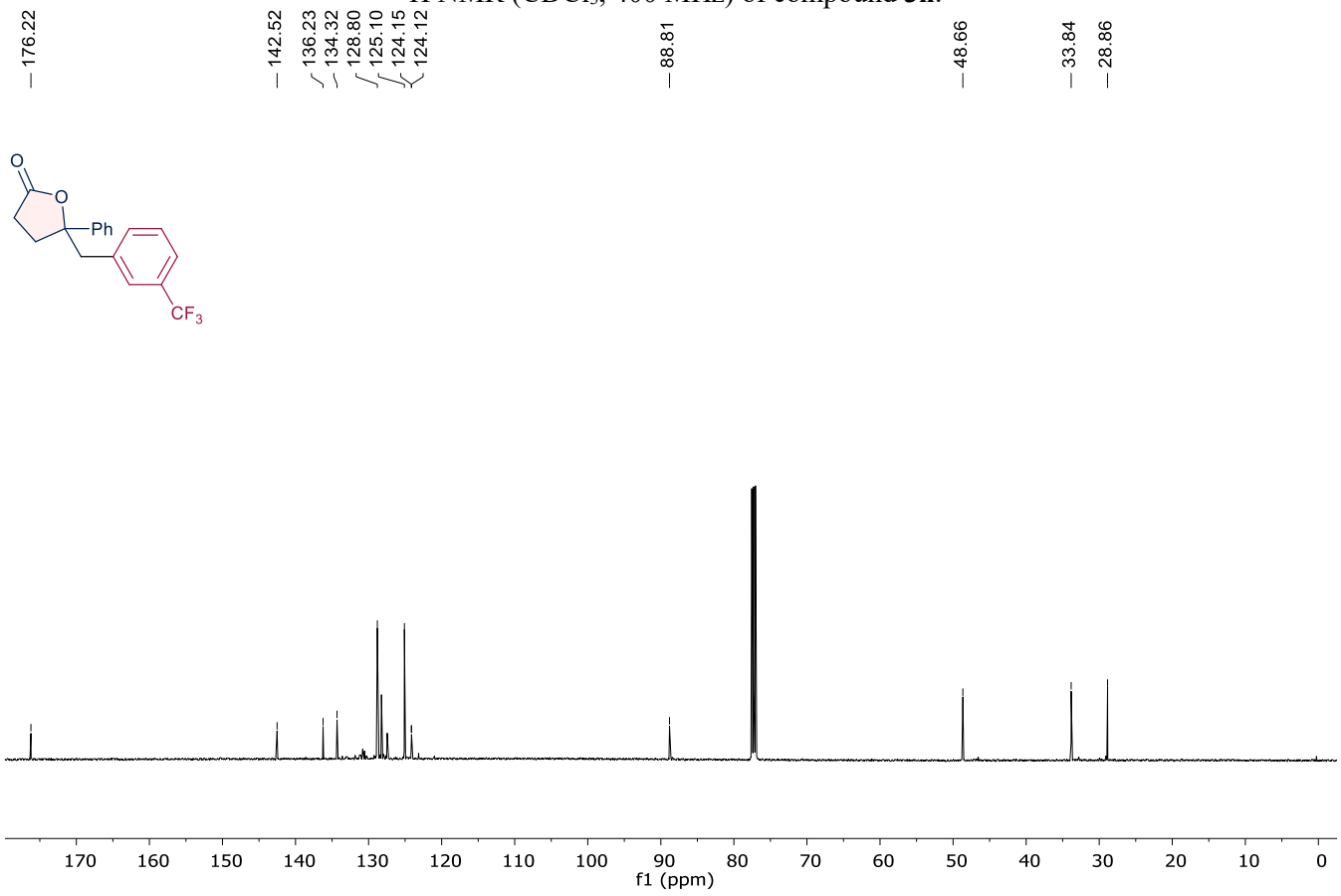
^{1}H NMR ($CDCl_3$, 600 MHz) of compound **3m**.



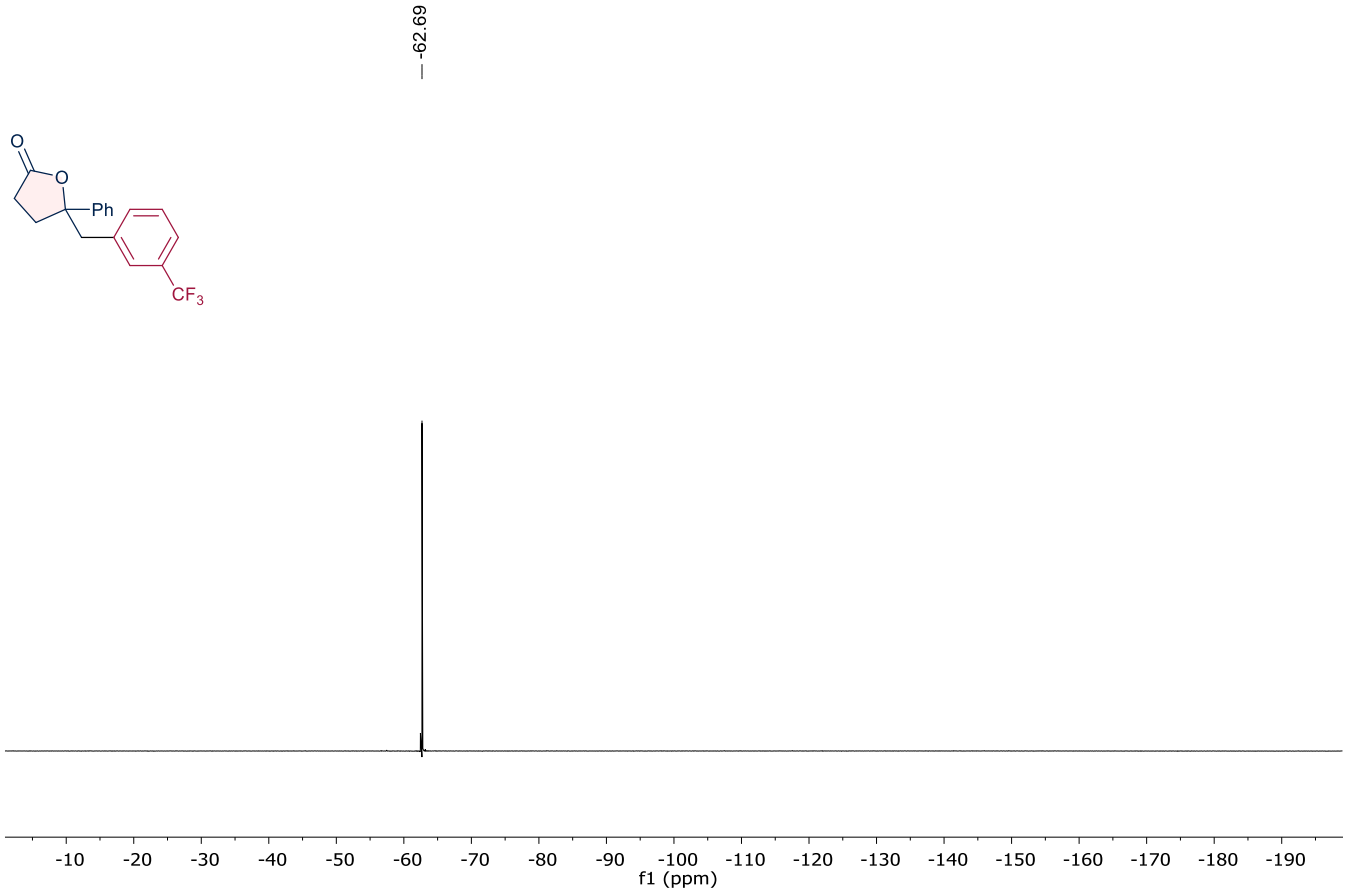
^{19}F NMR ($CDCl_3$, 377 MHz) of compound **3m**.



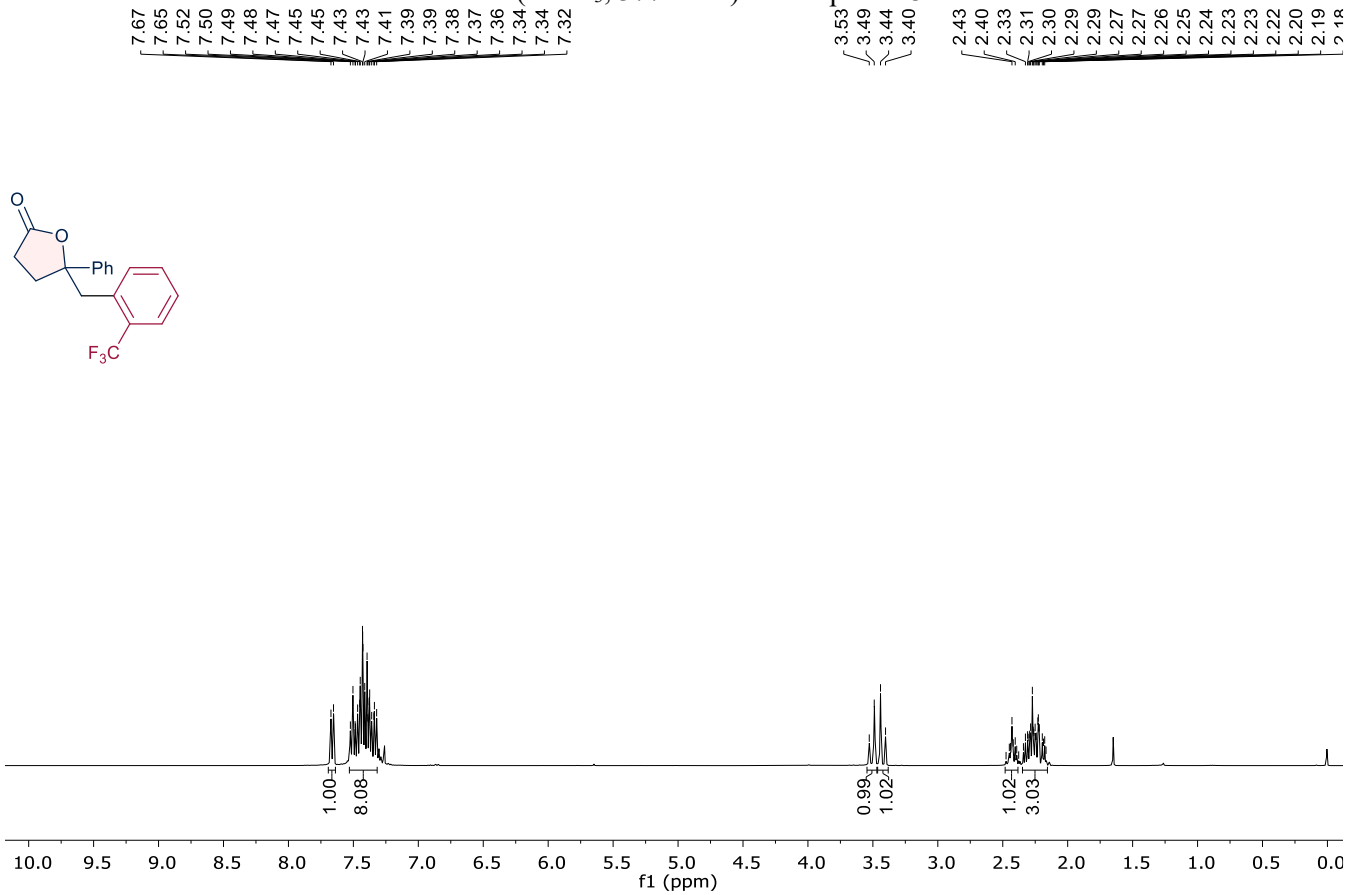
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3n**.



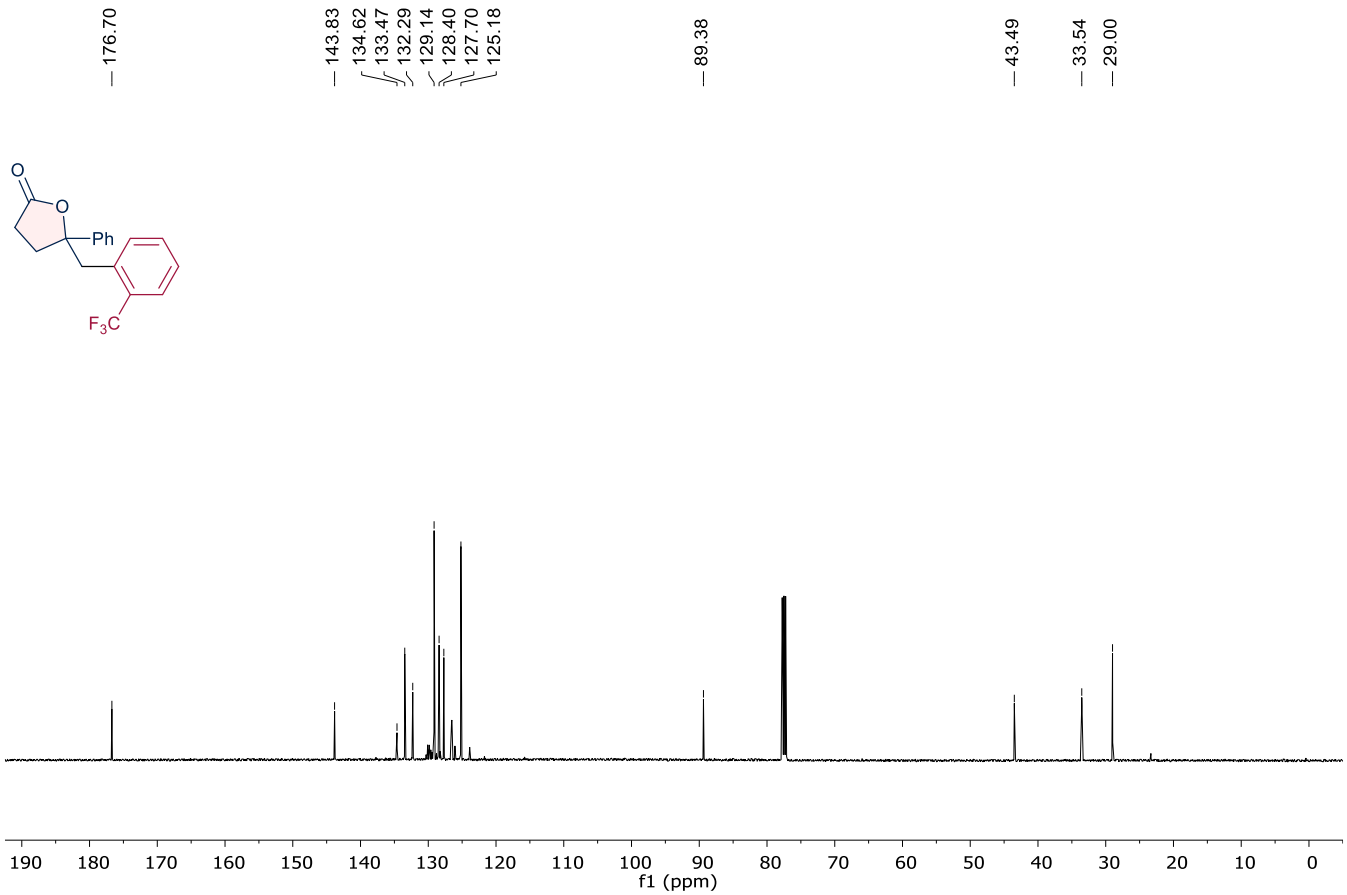
^{13}C NMR ($CDCl_3$, 126 MHz) of compound **3n**.



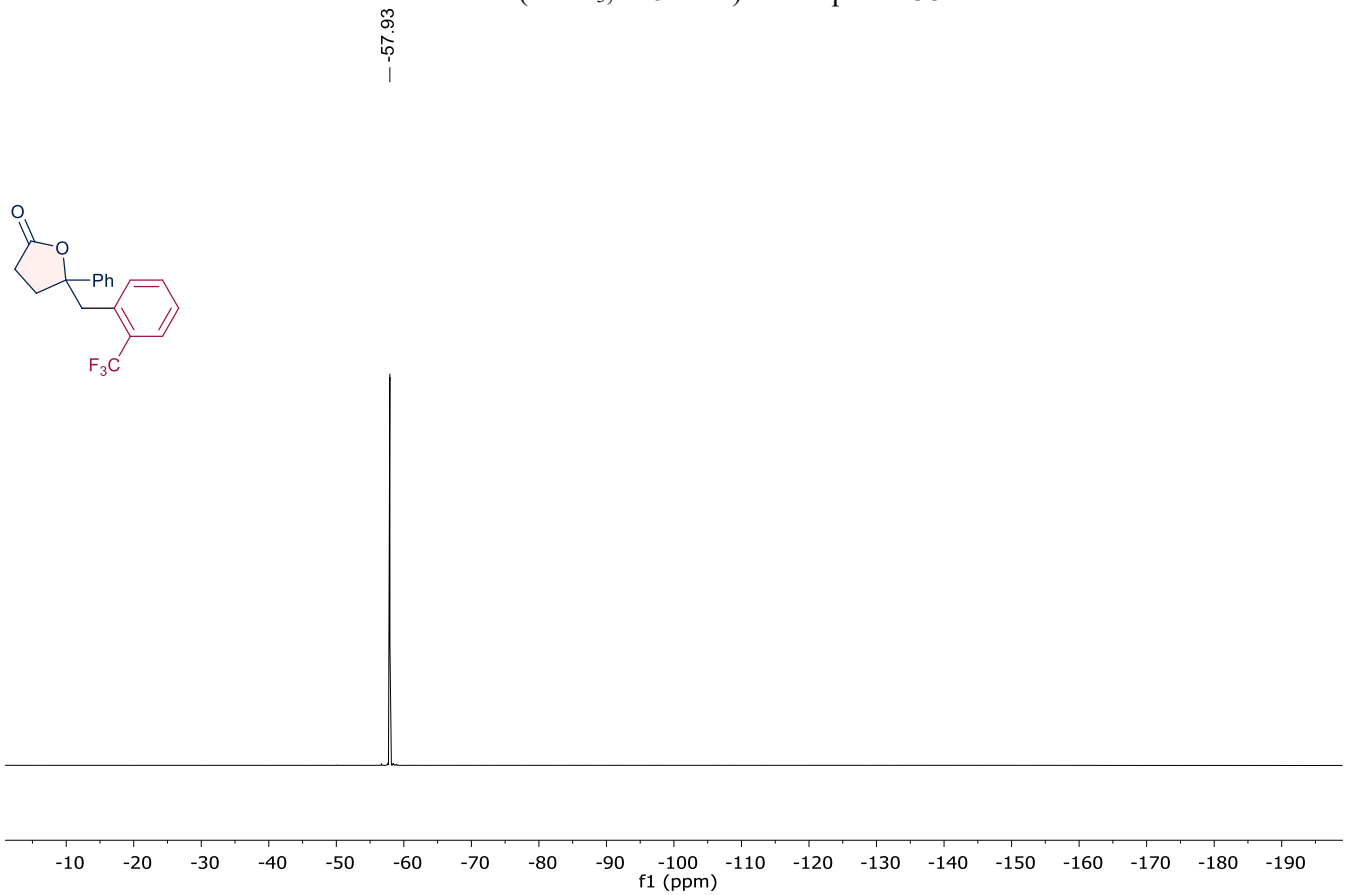
^{19}F NMR ($CDCl_3$, 377 MHz) of compound **3n**.



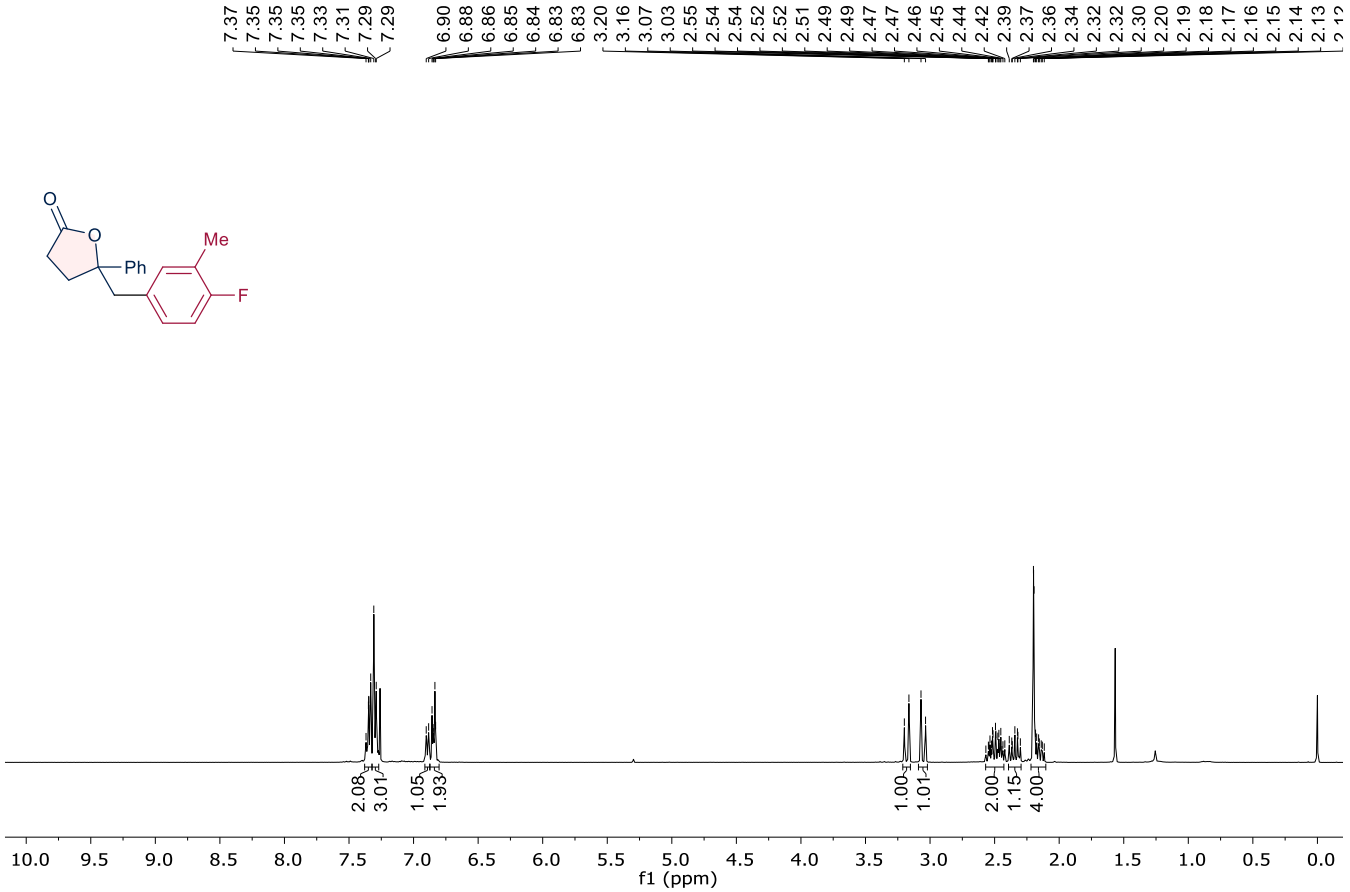
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3o**.



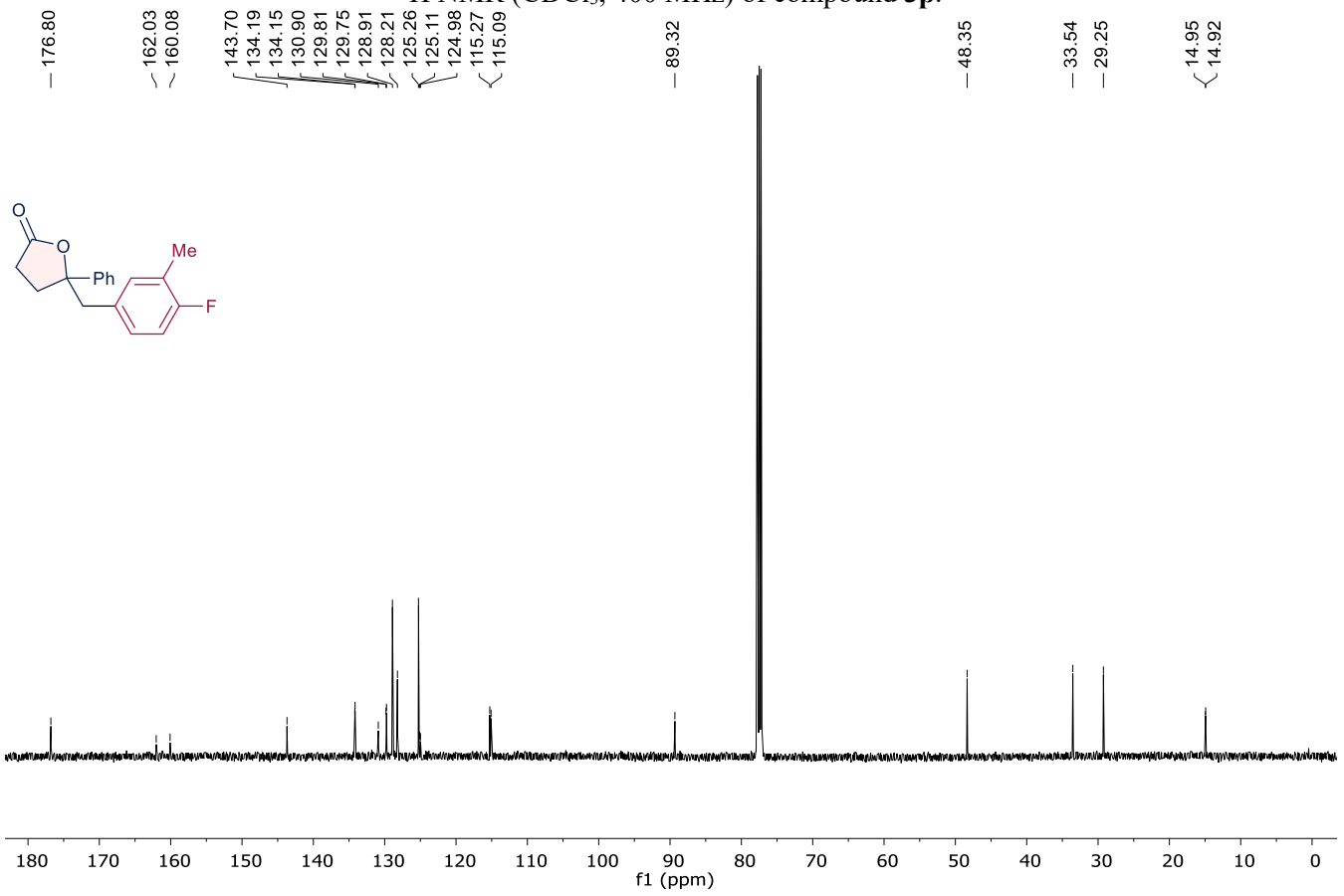
^{13}C NMR ($CDCl_3$, 126 MHz) of compound **3o**.



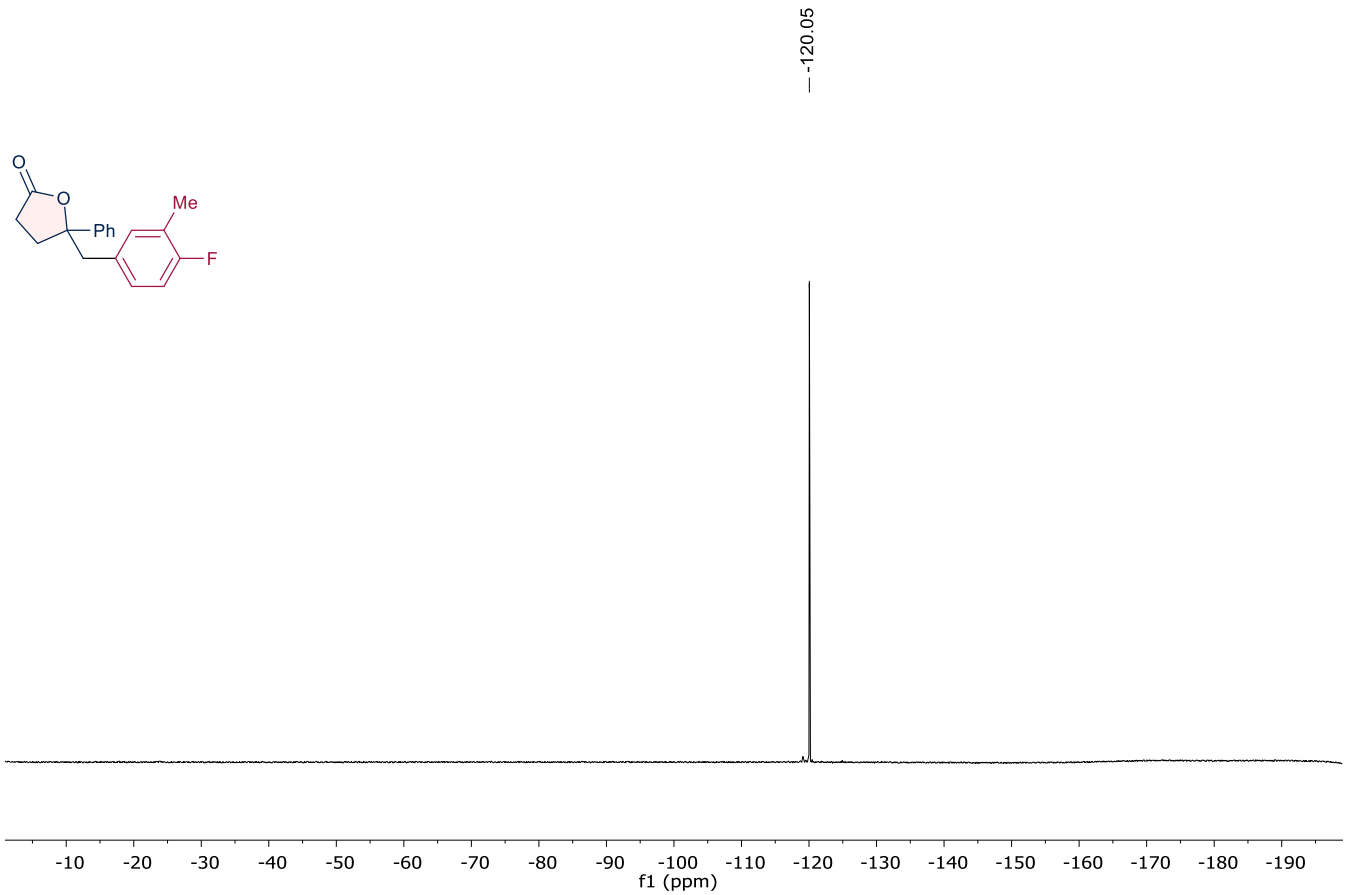
^{19}F NMR ($CDCl_3$, 377 MHz) of compound **3o**.



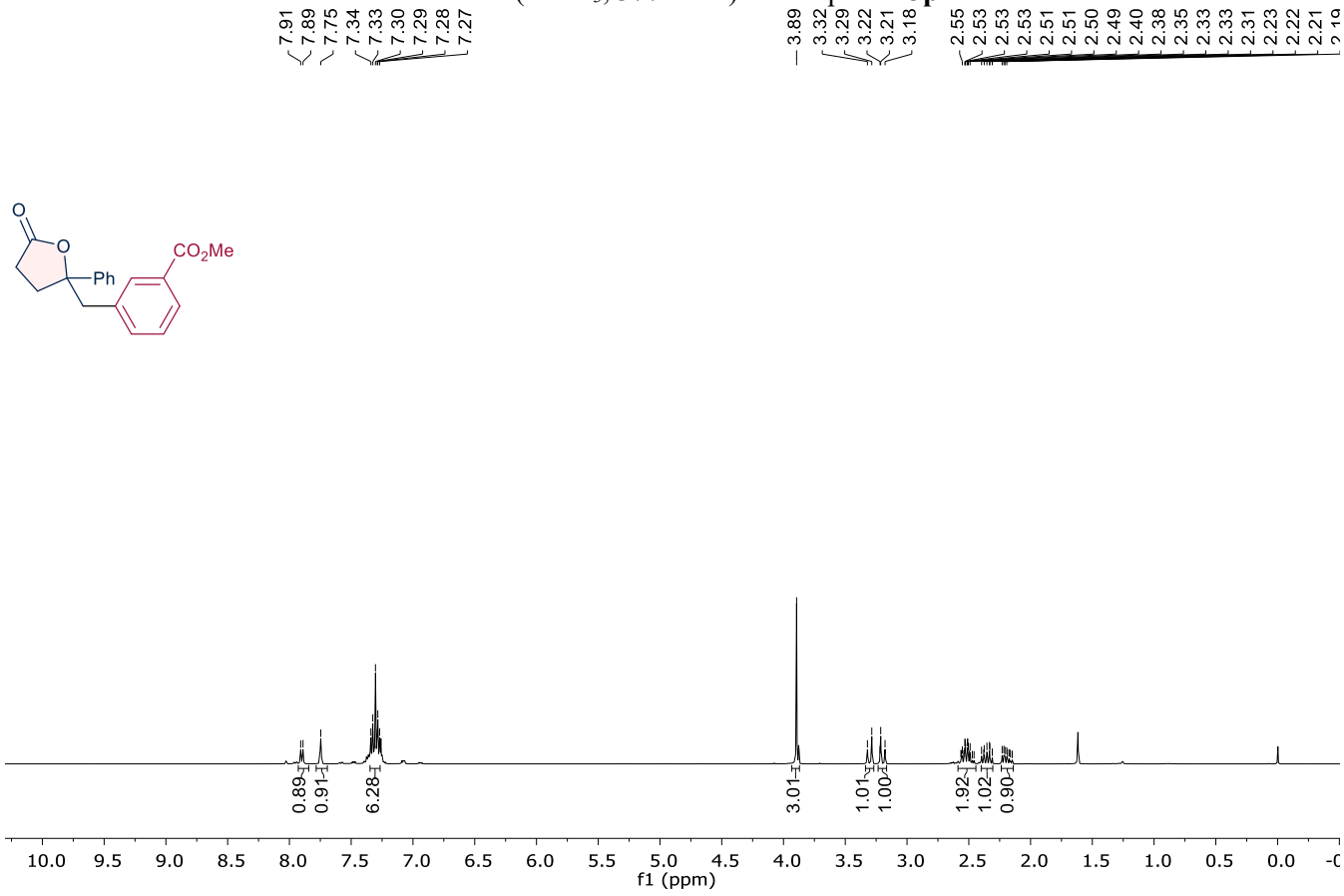
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3p**.



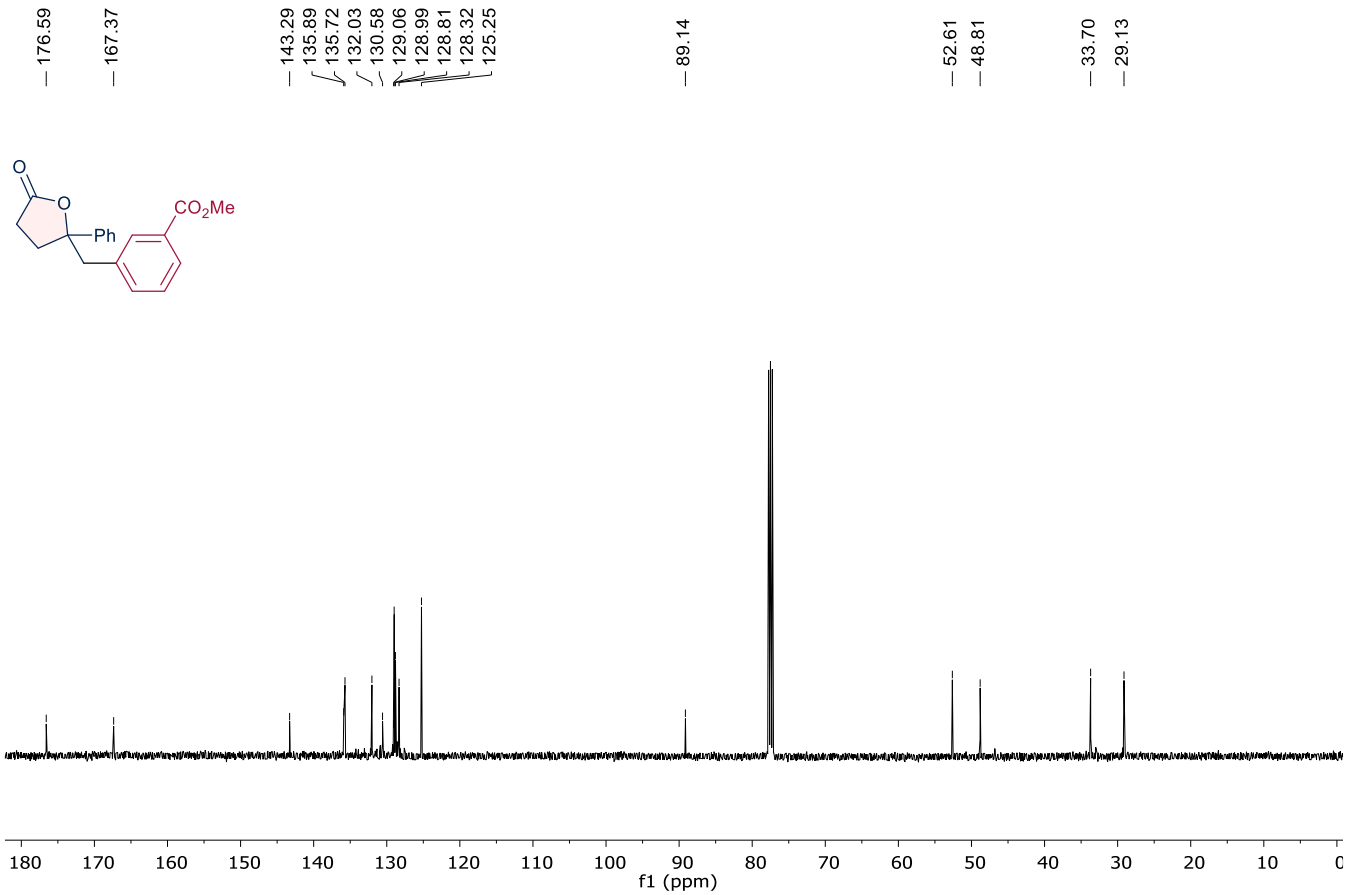
^{13}C NMR ($CDCl_3$, 126 MHz) of compound **3p**.



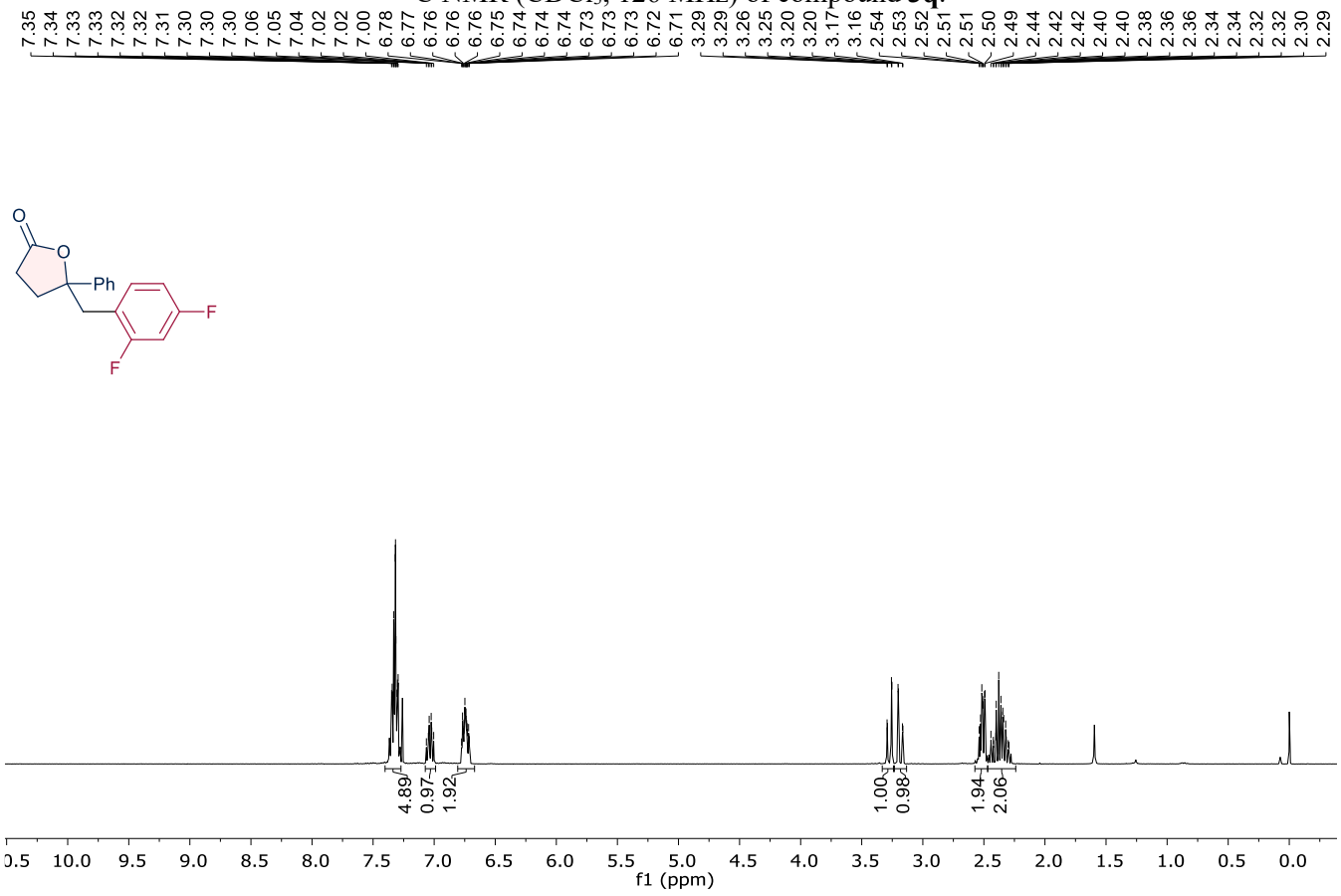
^{19}F NMR ($CDCl_3$, 377 MHz) of compound **3p**.



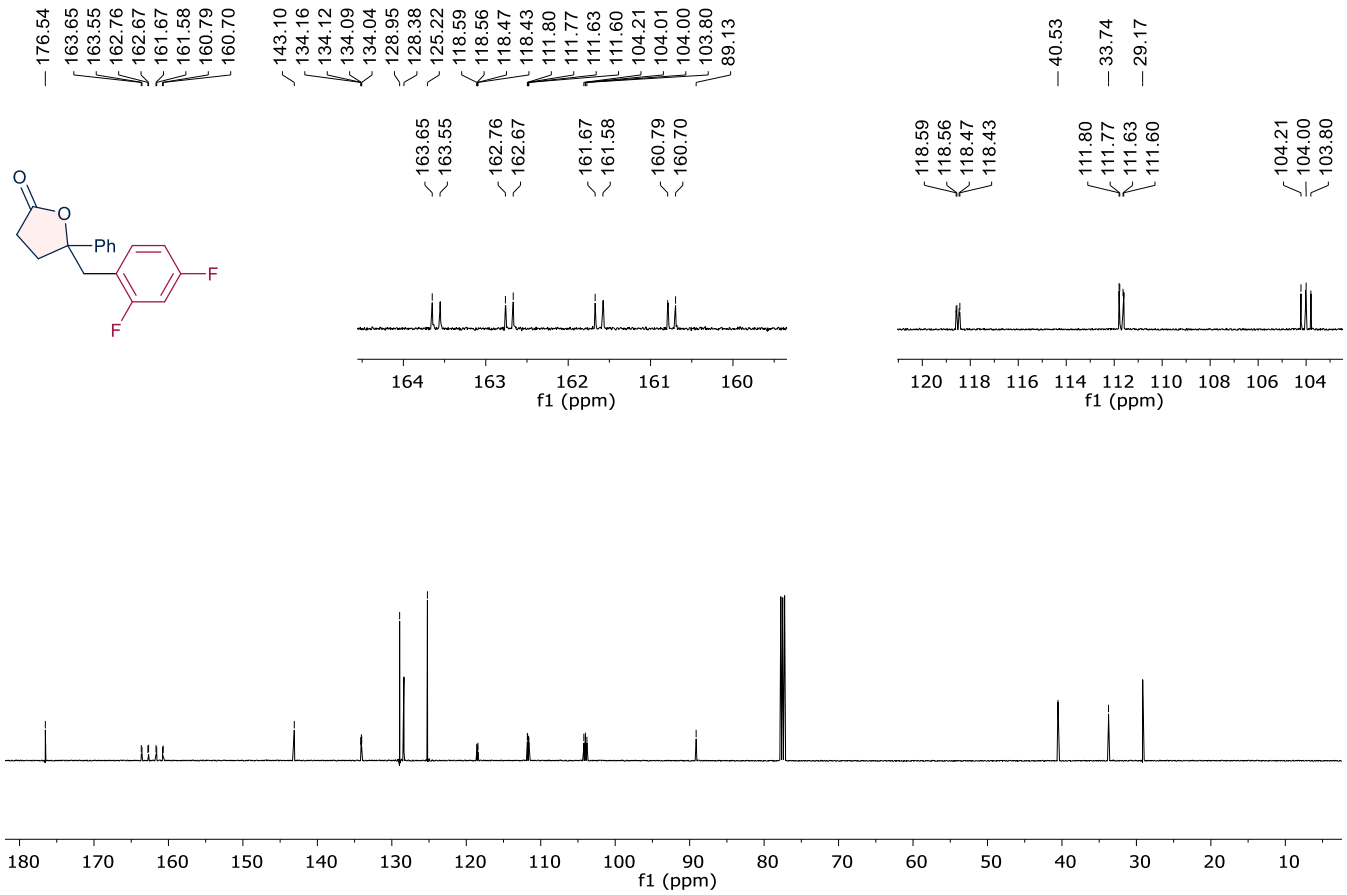
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3q**.



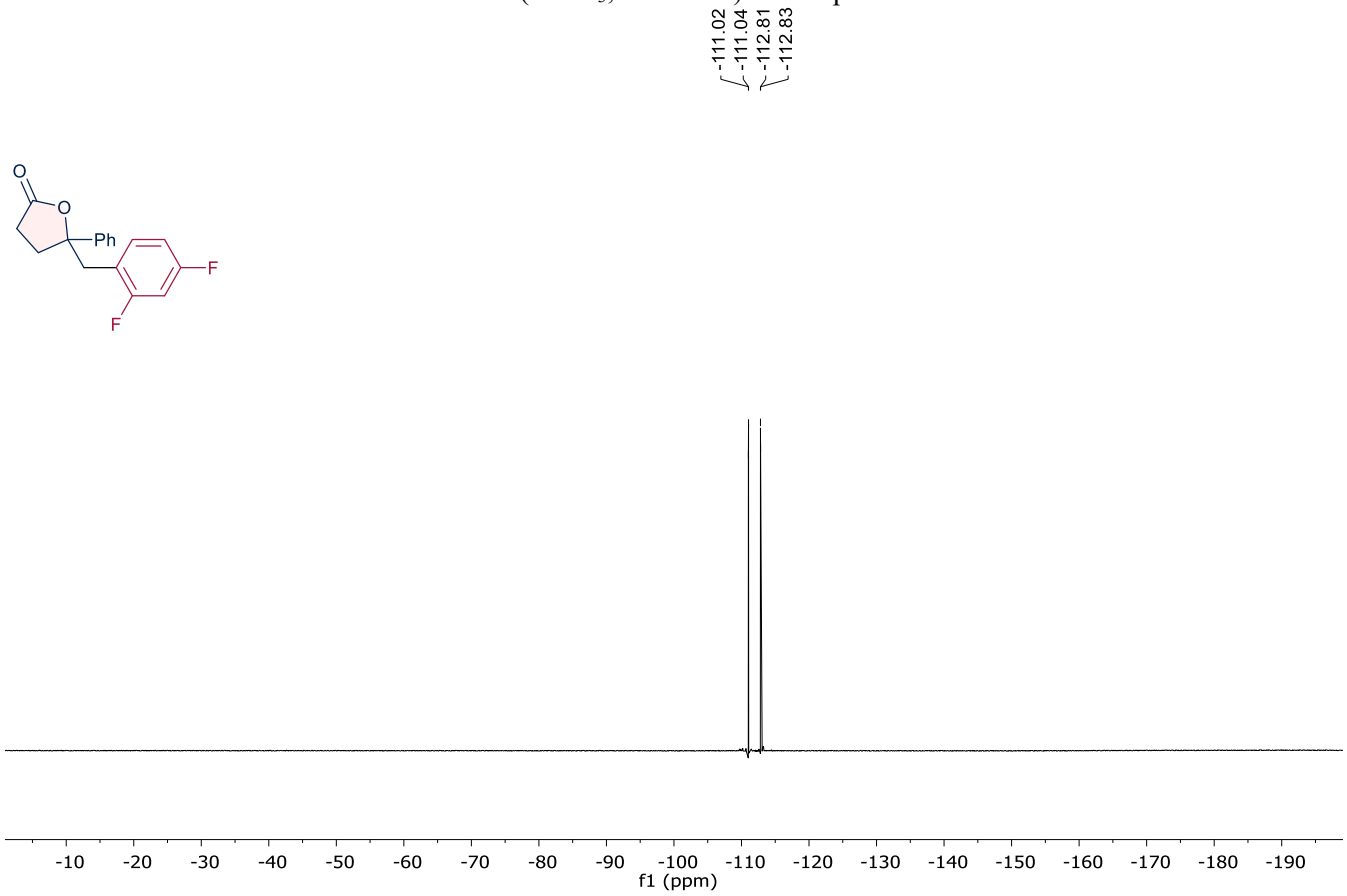
^{13}C NMR ($CDCl_3$, 126 MHz) of compound **3q**.



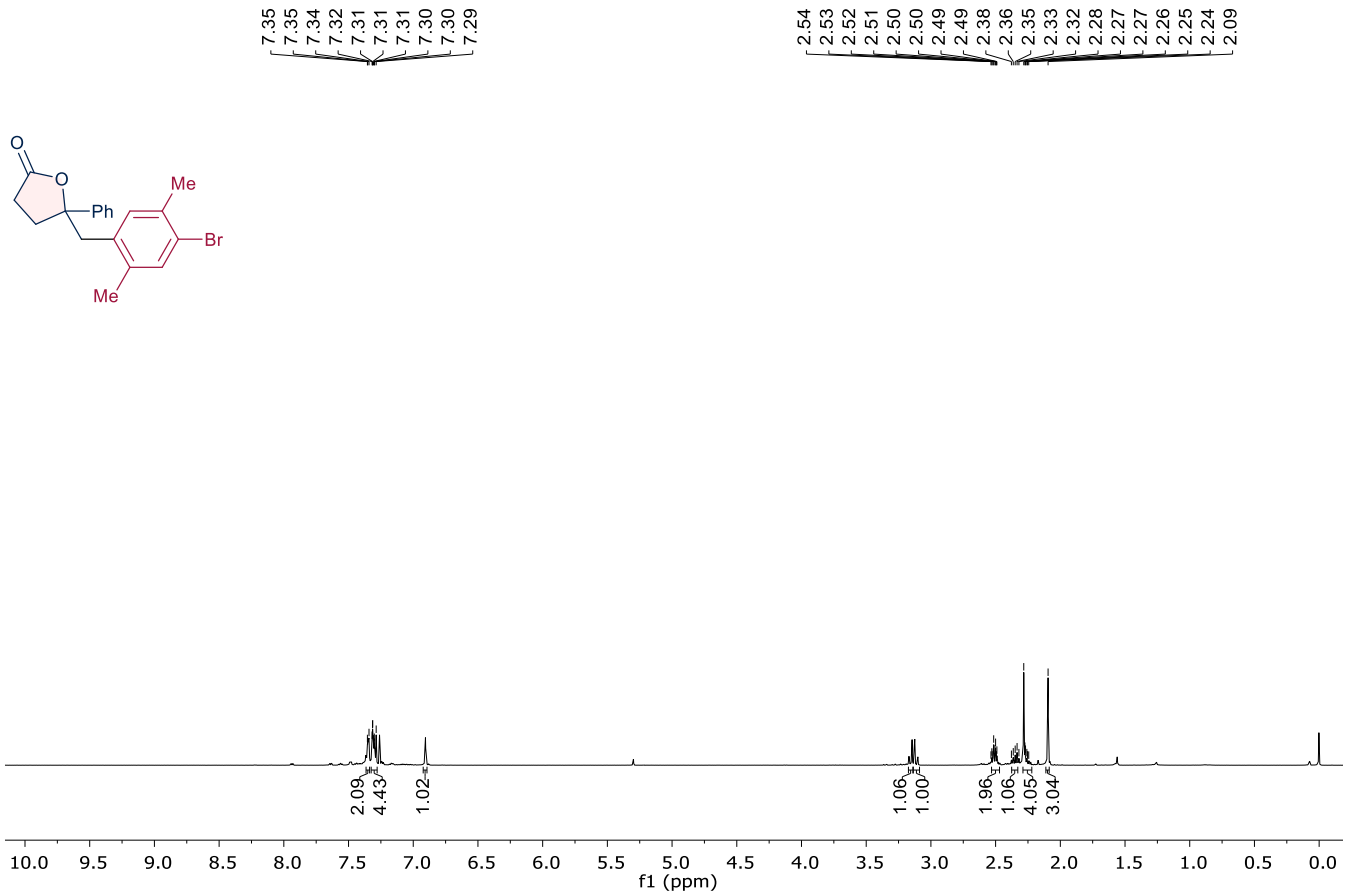
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3r**.



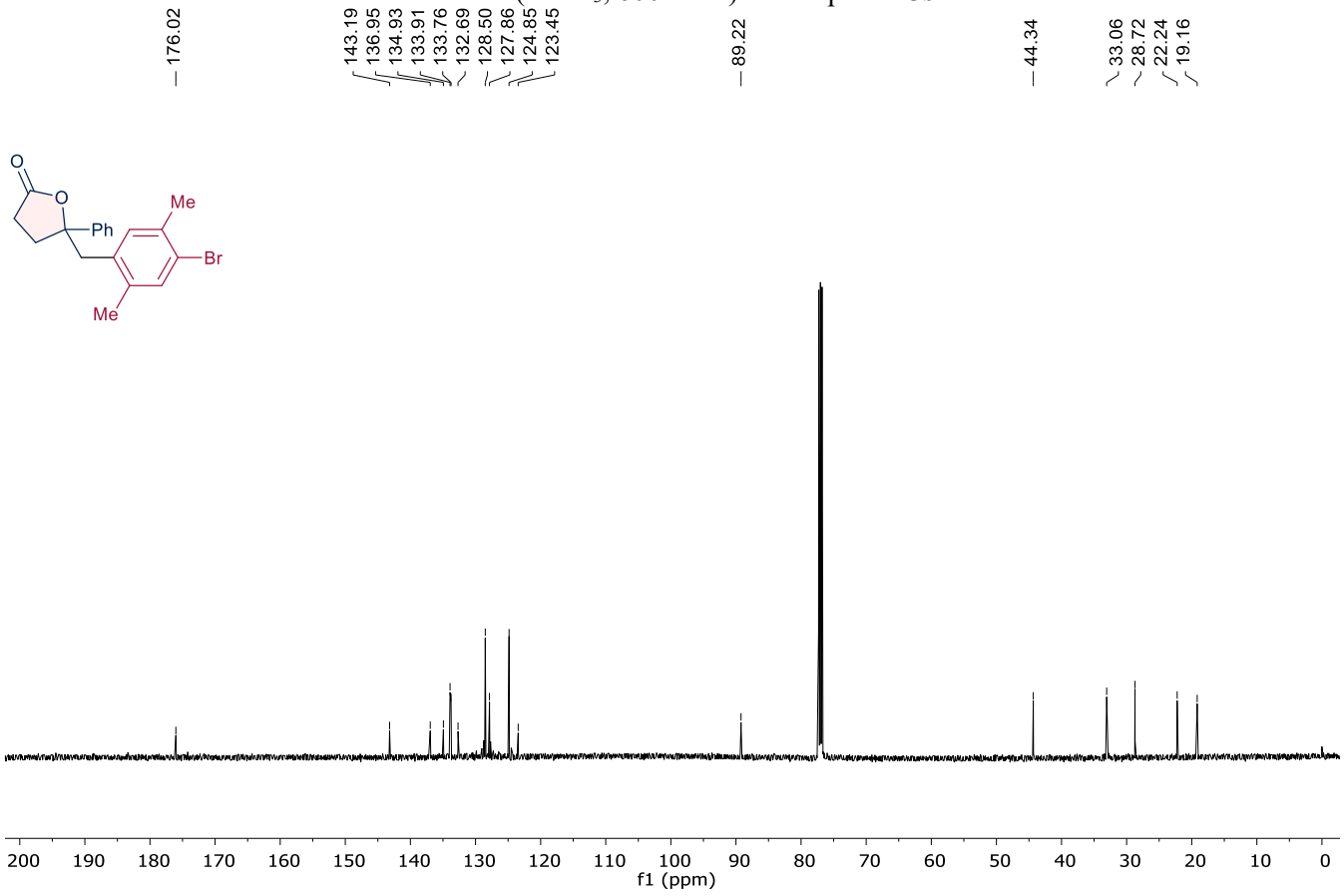
^{13}C NMR ($CDCl_3$, 126 MHz) of compound **3r**.



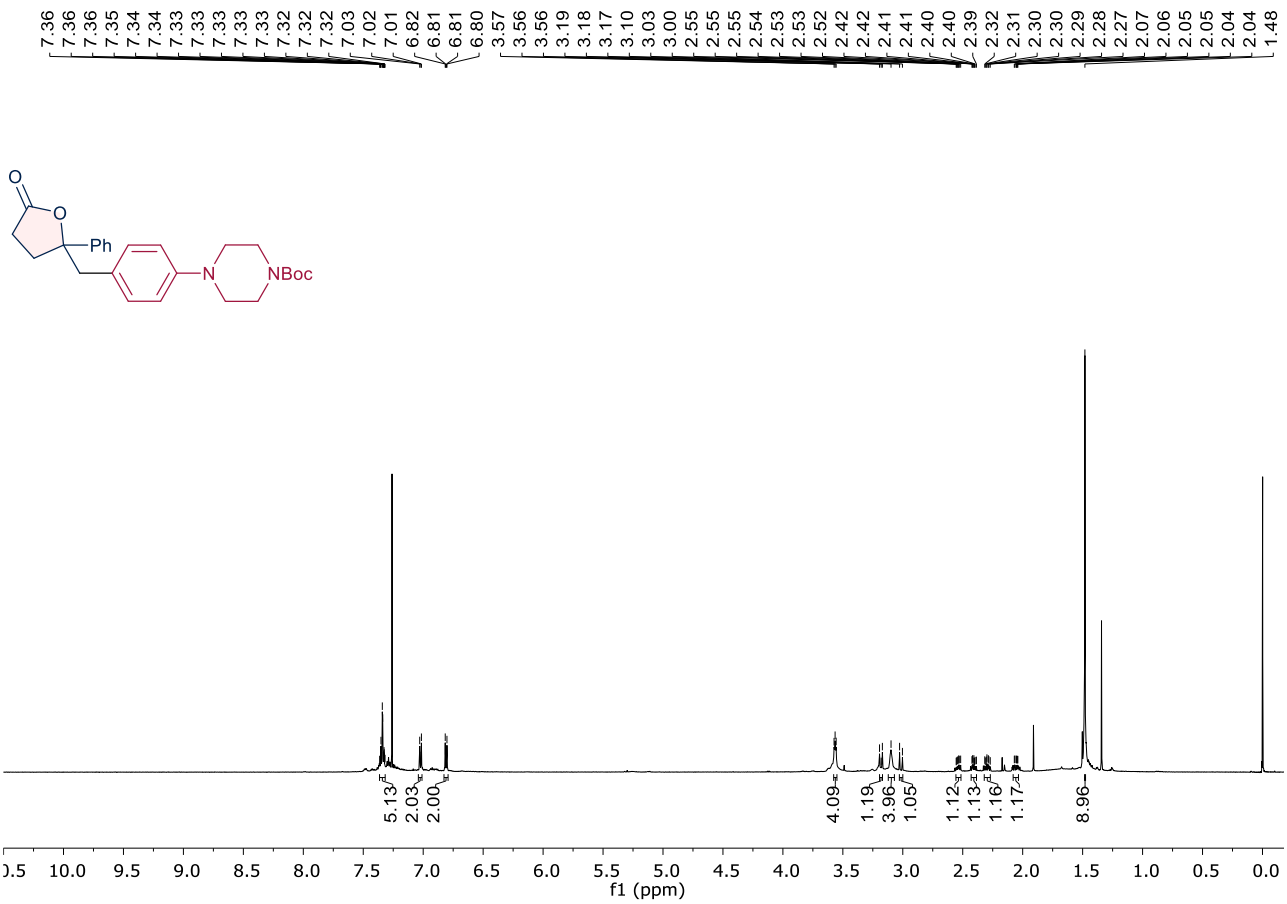
^{19}F NMR ($CDCl_3$, 377 MHz) of compound **3r**.



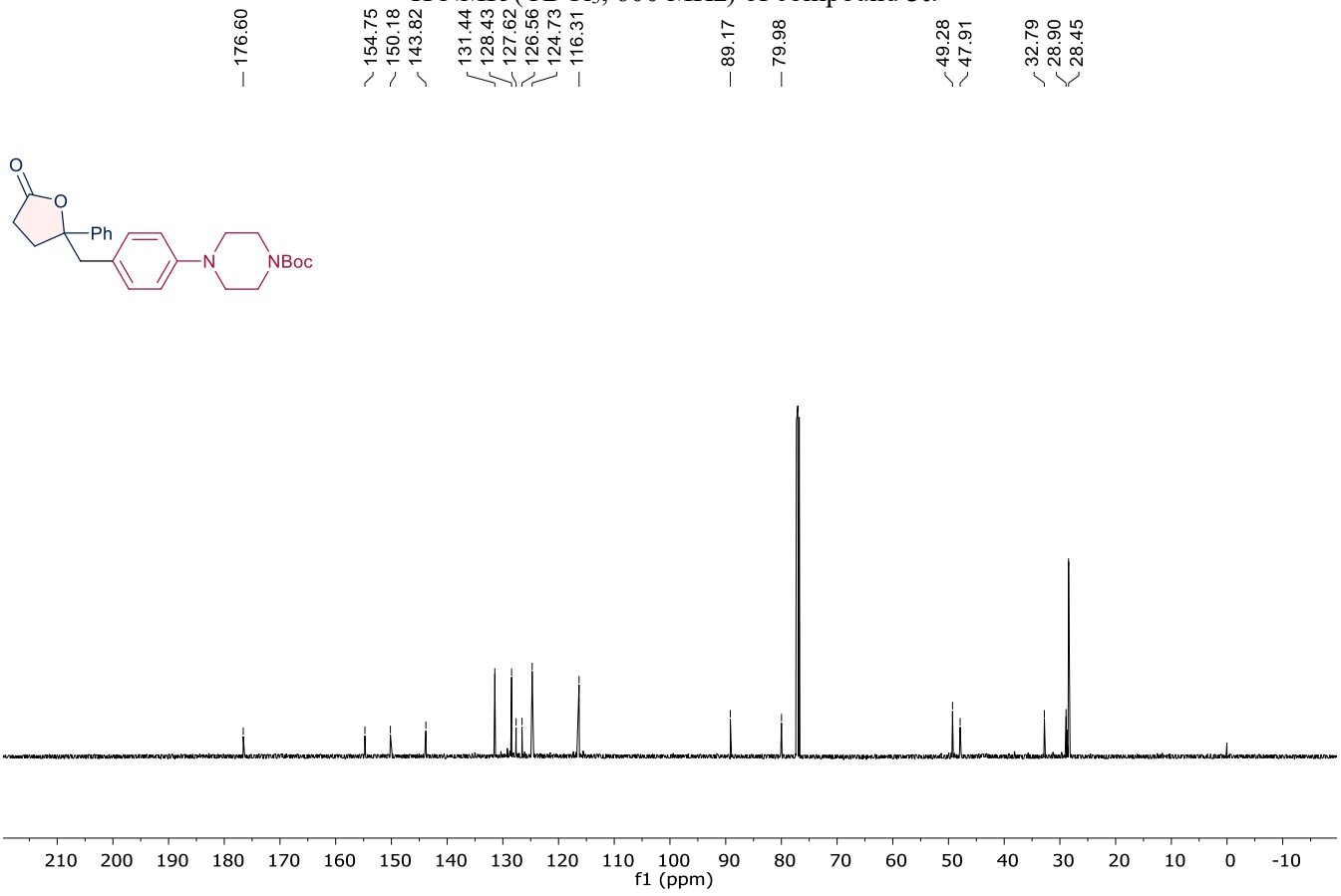
^{1}H NMR ($CDCl_3$, 600 MHz) of compound **3s**.



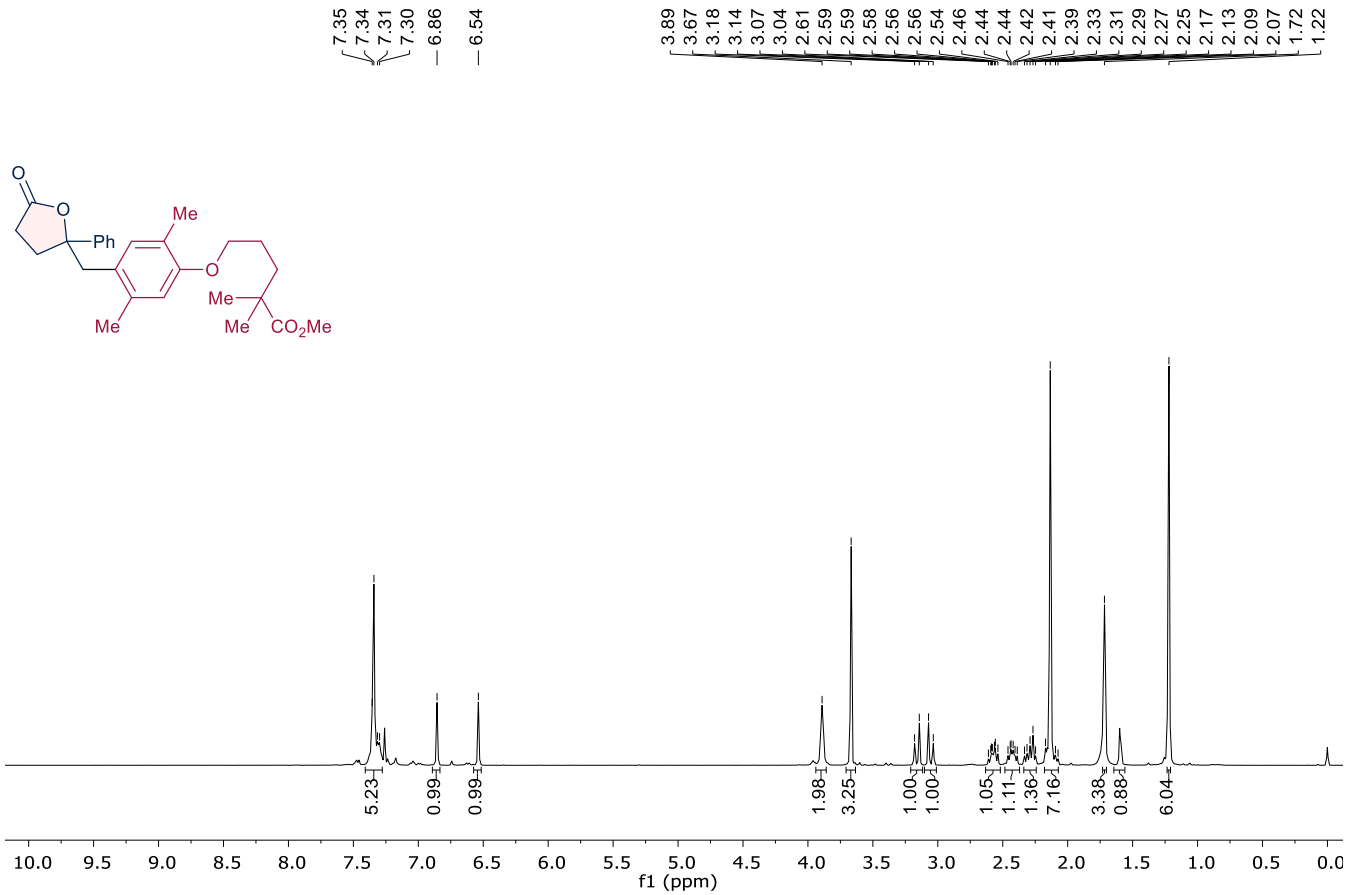
^{13}C NMR ($CDCl_3$, 126 MHz) of compound **3s**.



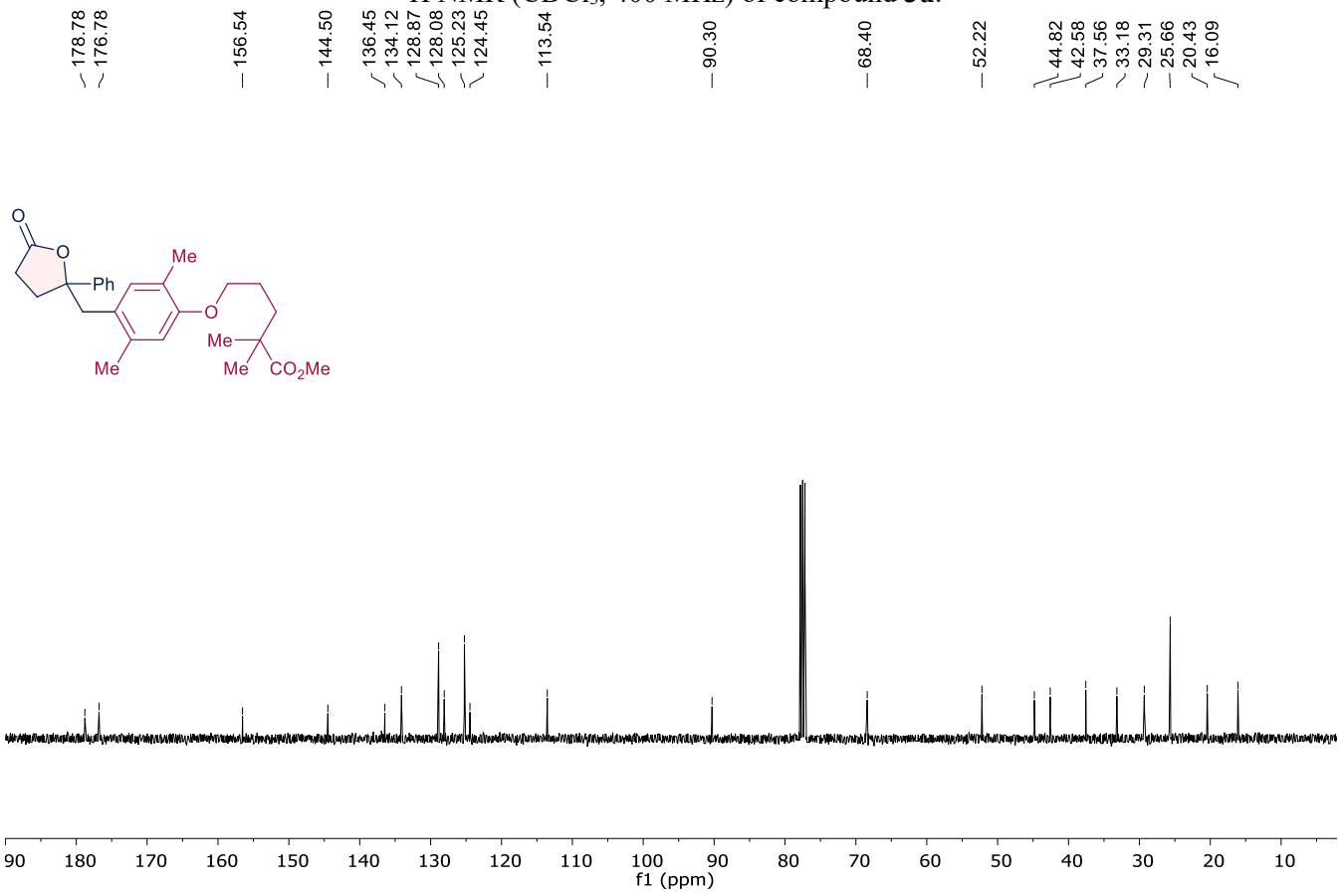
^{1}H NMR ($CDCl_3$, 600 MHz) of compound **3t**.



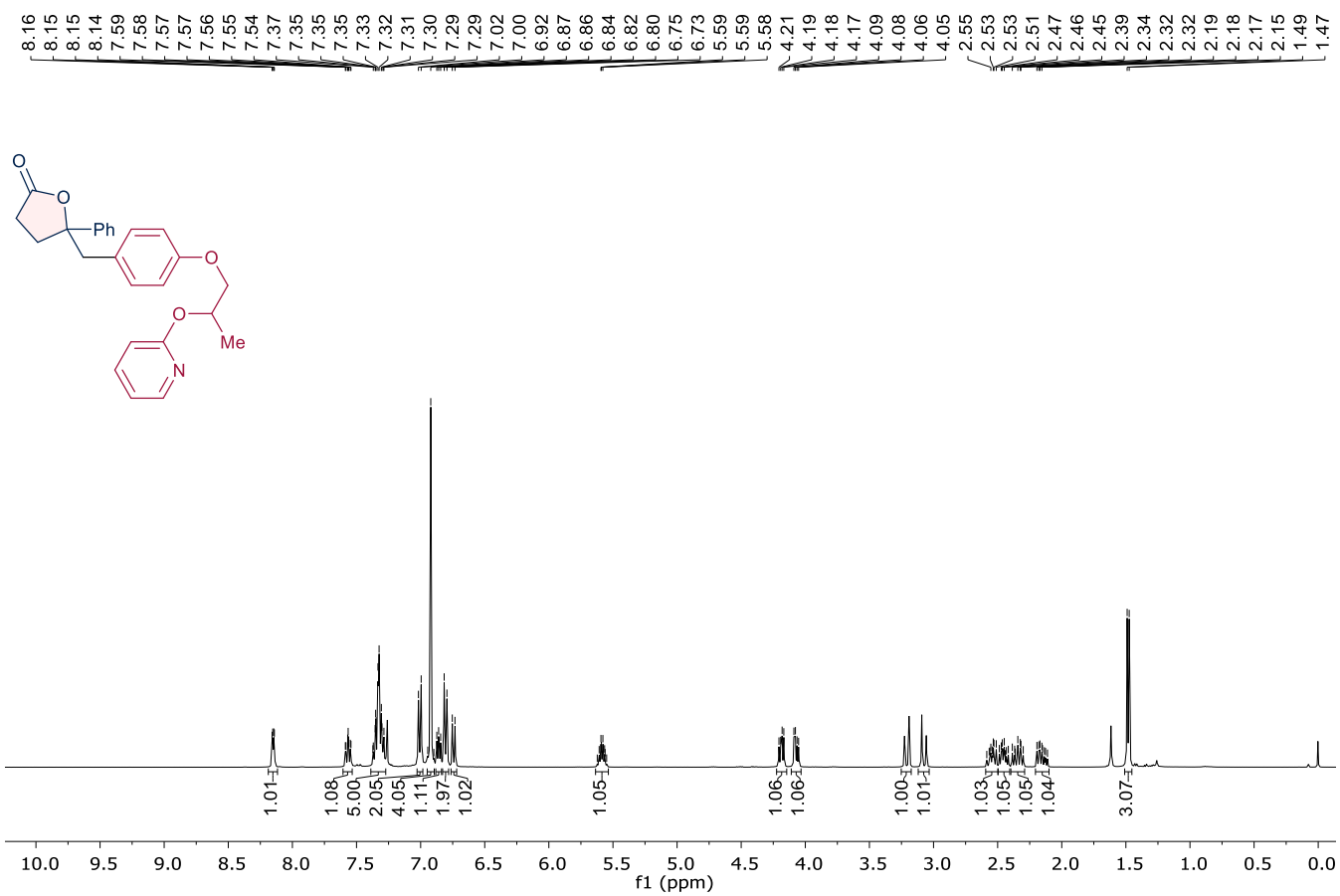
^{13}C NMR ($CDCl_3$, 126 MHz) of compound **3t**.



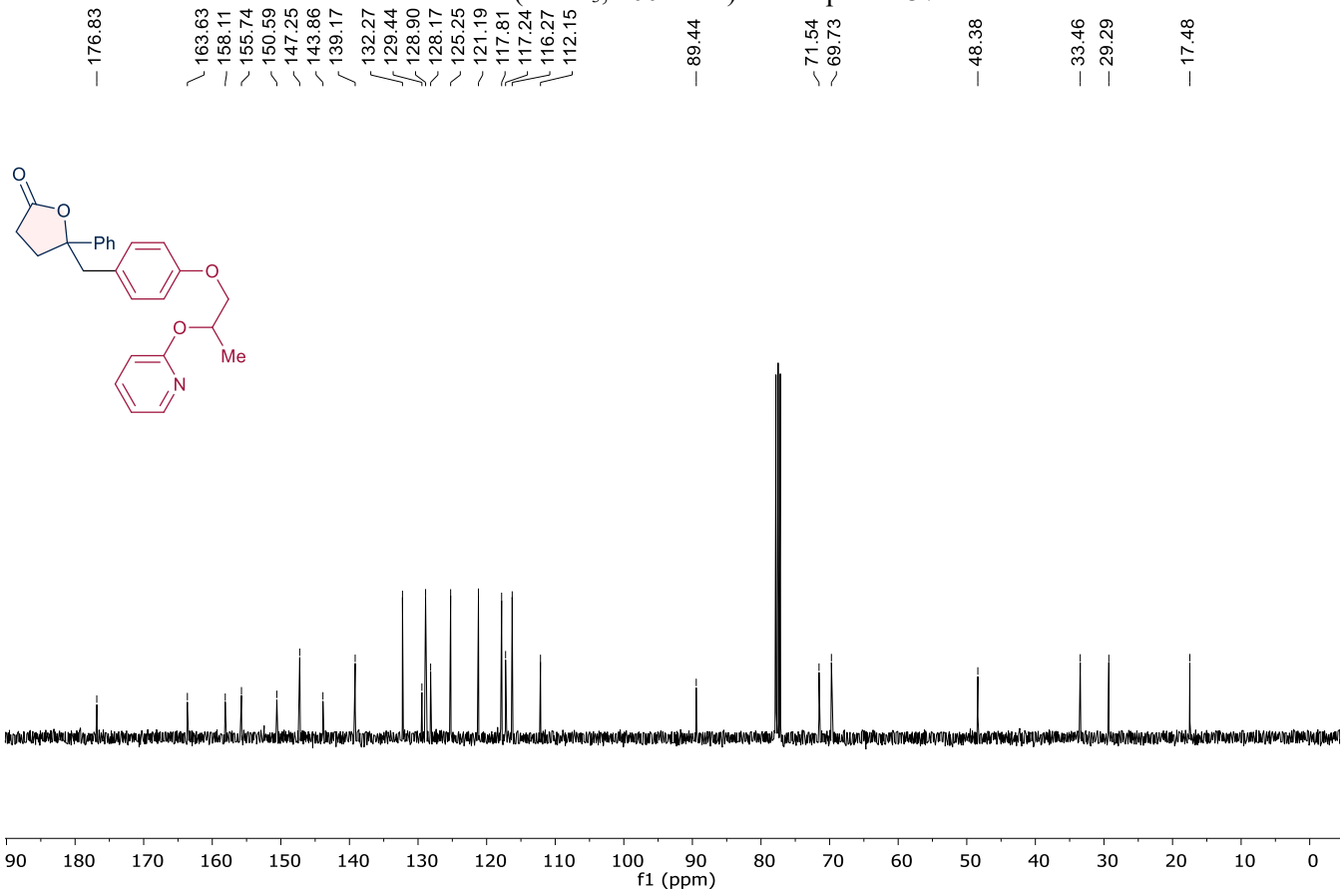
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3u**.



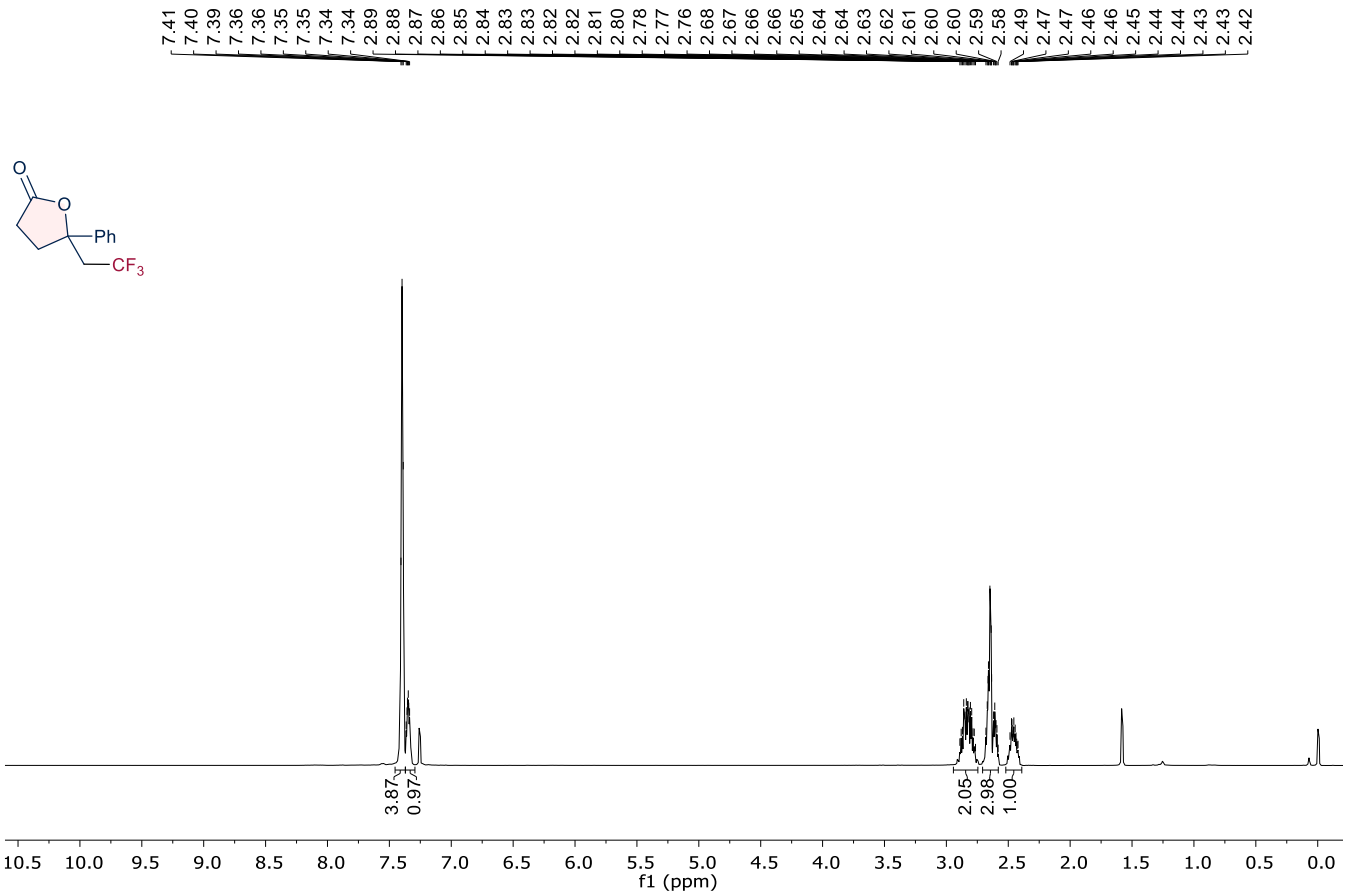
^{13}C NMR ($CDCl_3$, 126 MHz) of compound **3u**.



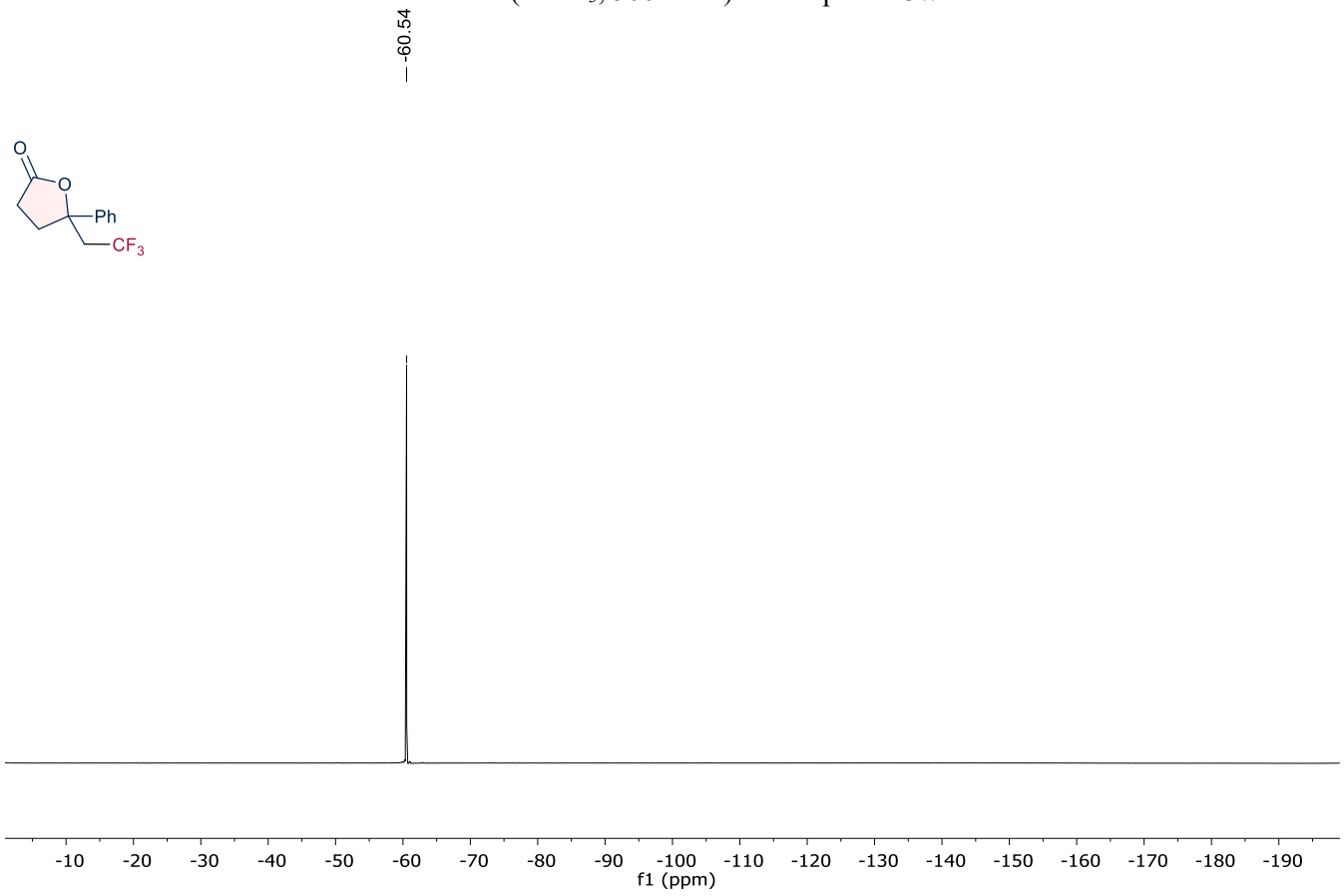
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3v**.



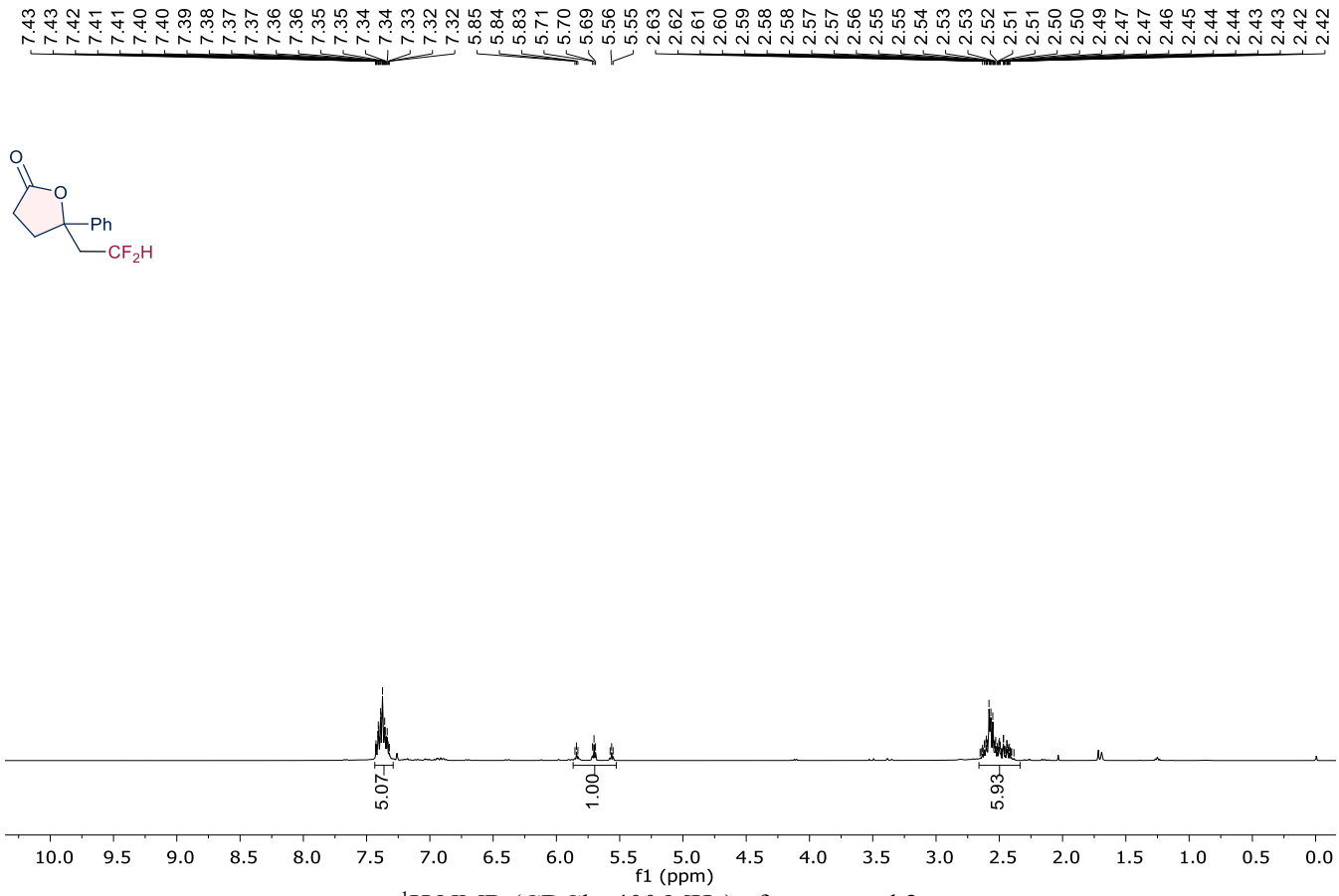
^{13}C NMR ($CDCl_3$, 101 MHz) of compound **3v**.



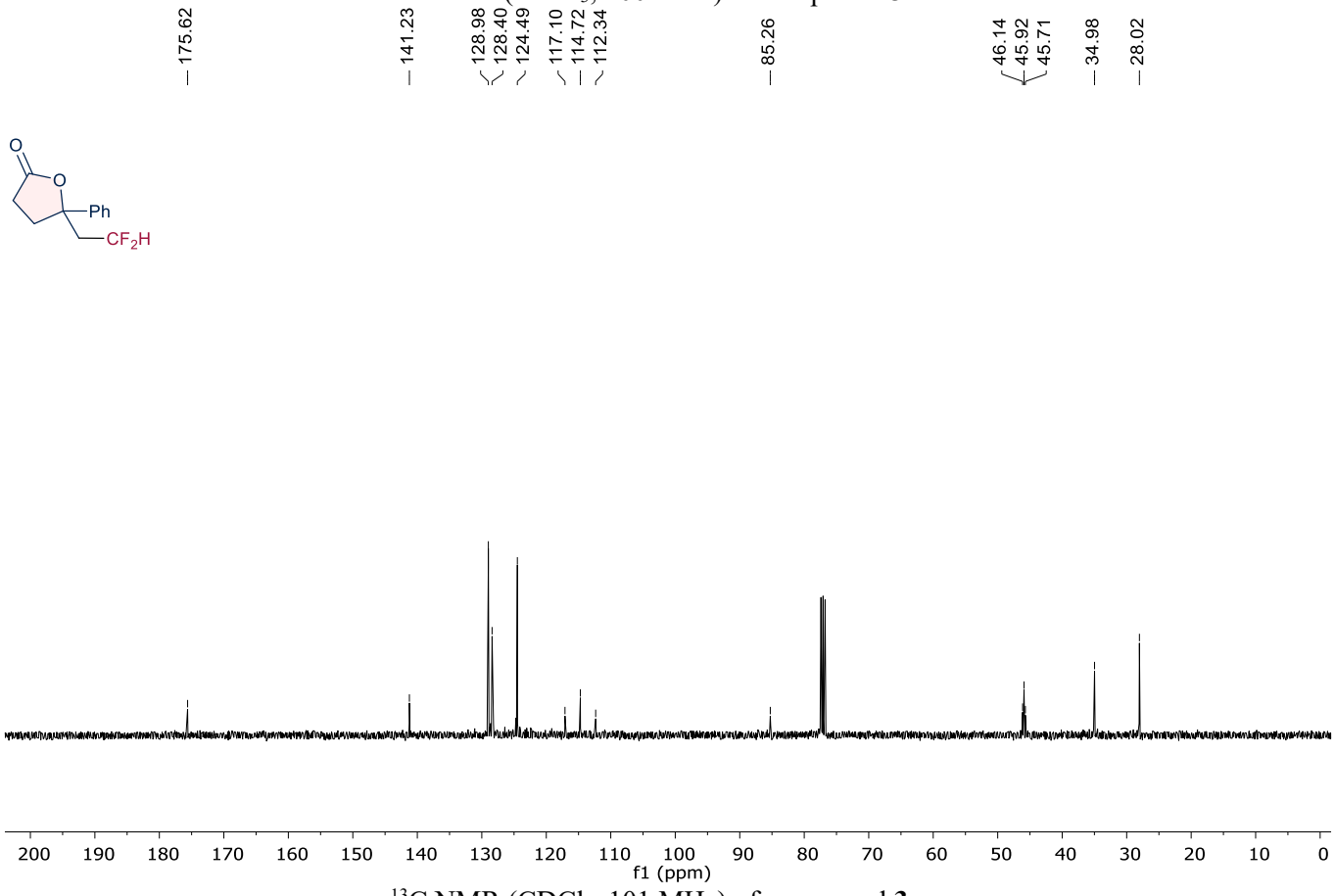
^{1}H NMR ($CDCl_3$, 500 MHz) of compound **3w**.



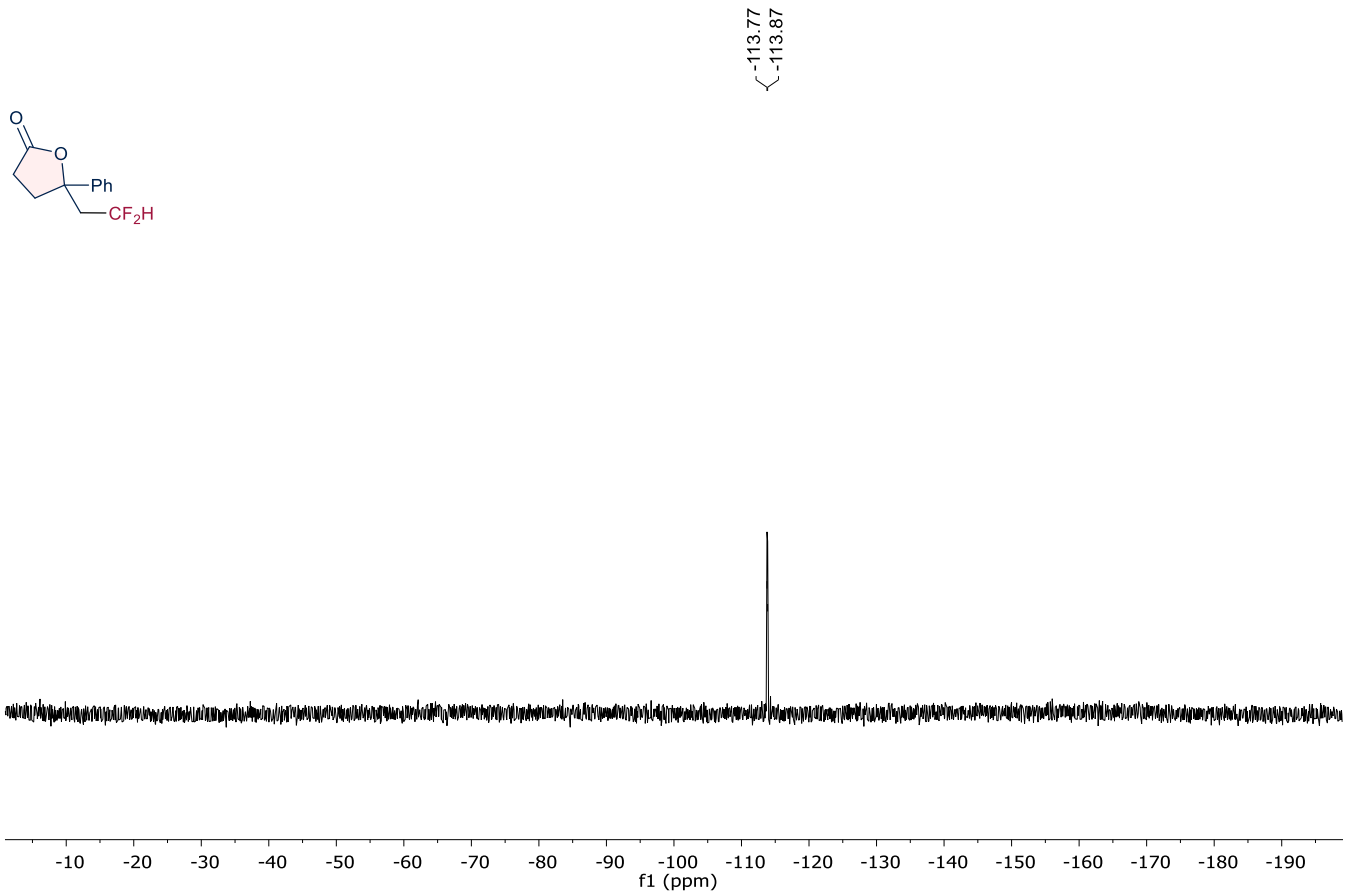
^{19}F NMR ($CDCl_3$, 377 MHz) of compound **3w**.



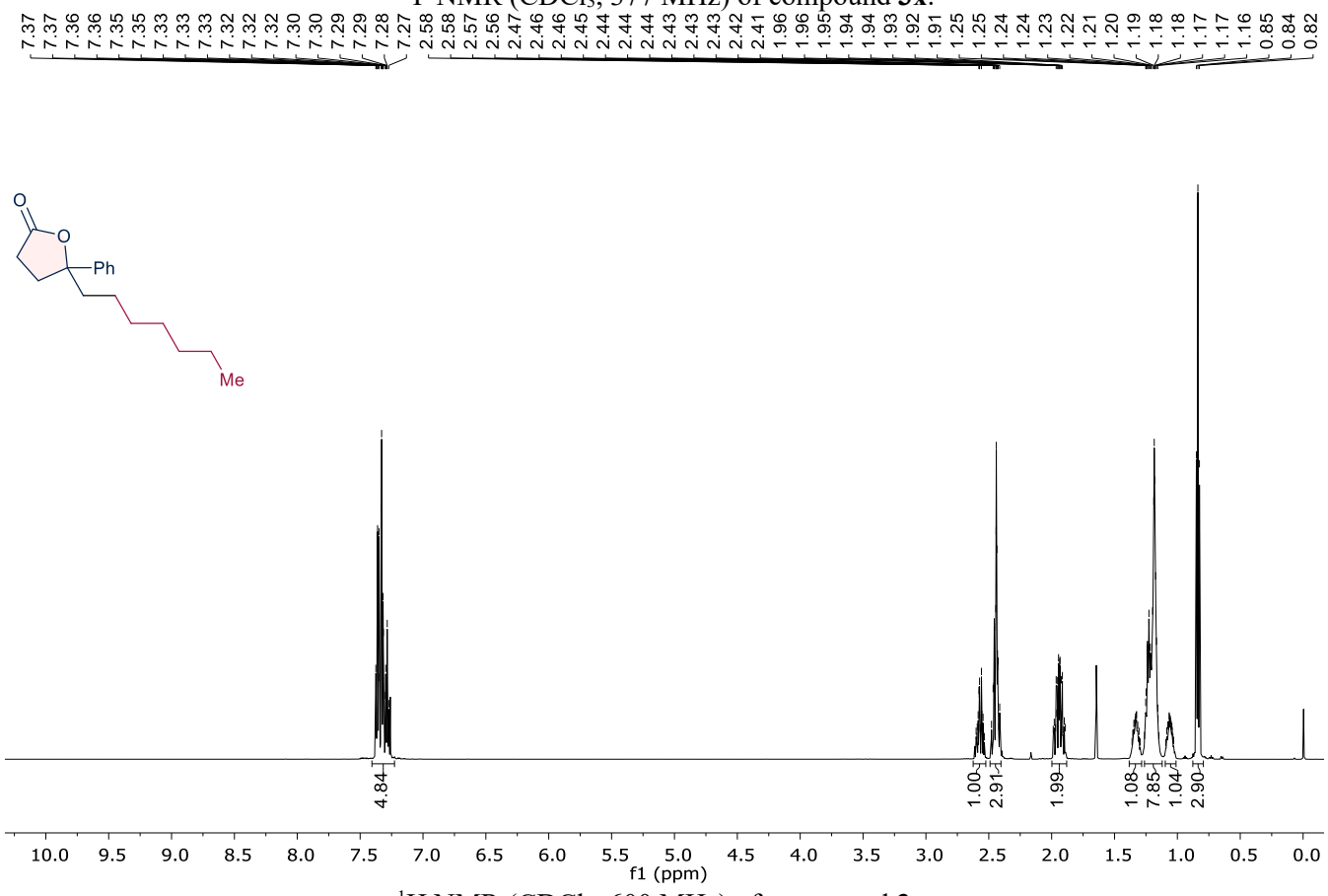
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3x**.



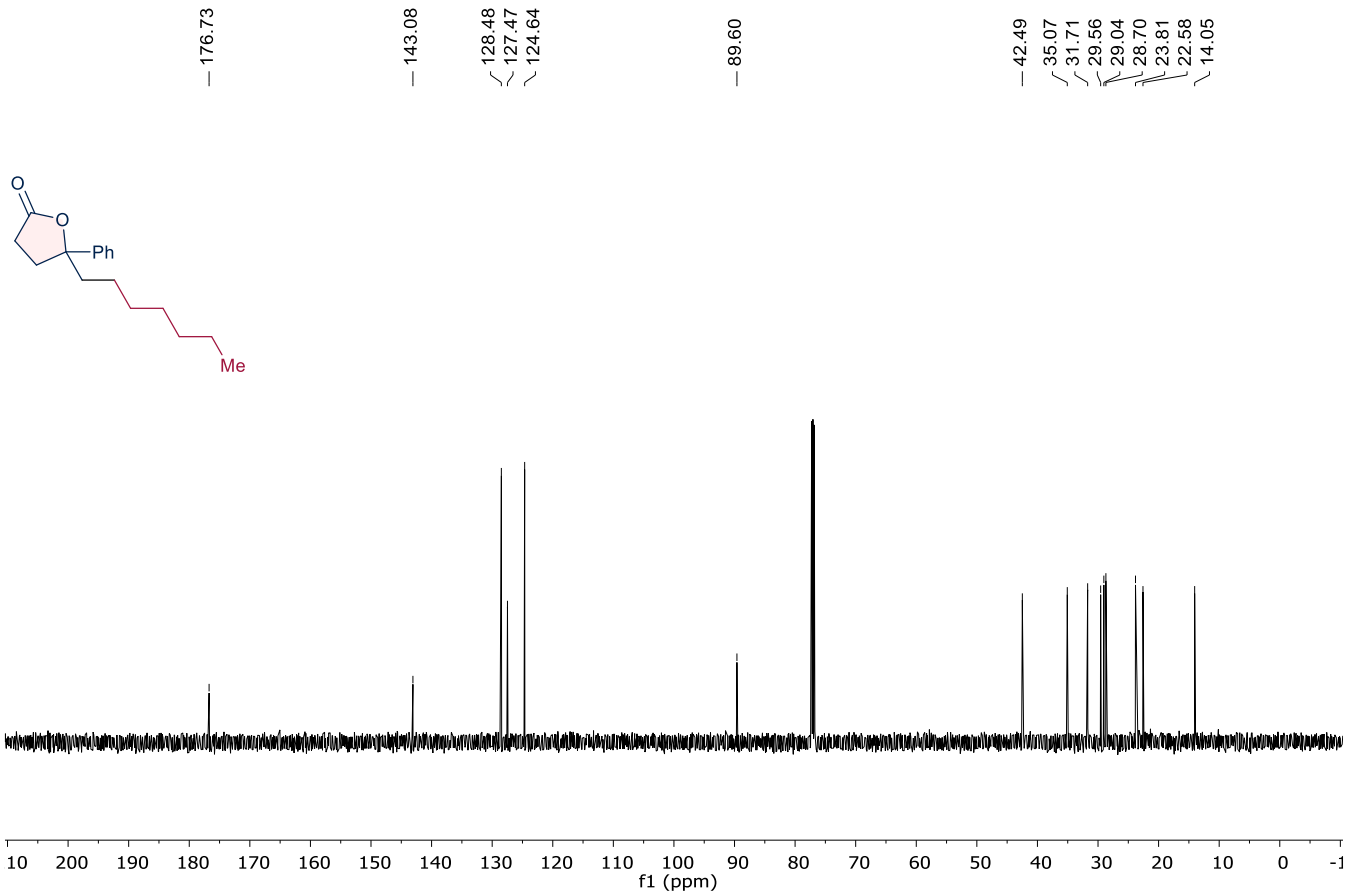
^{13}C NMR ($CDCl_3$, 101 MHz) of compound **3x**.



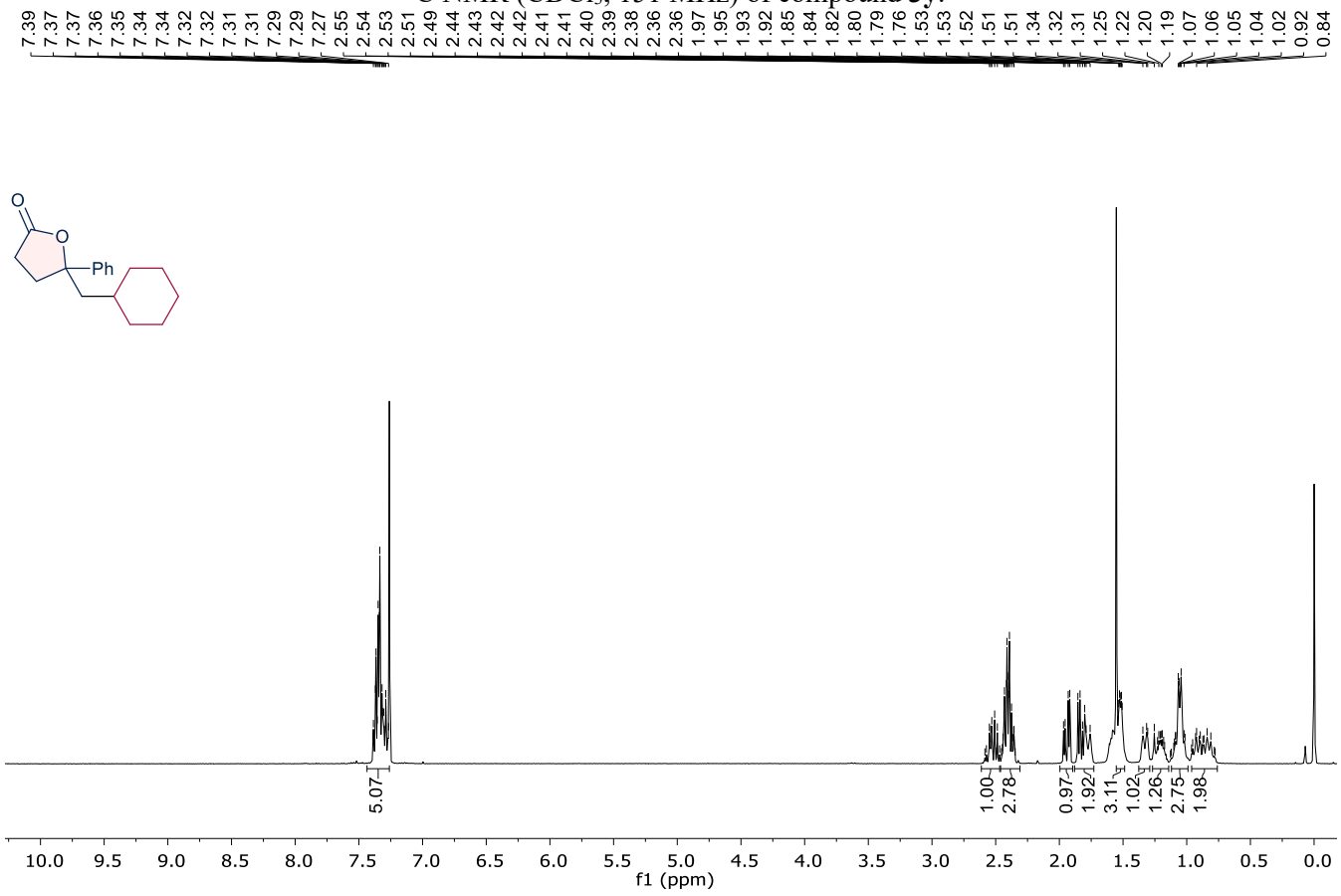
^{19}F NMR ($CDCl_3$, 377 MHz) of compound **3x**.



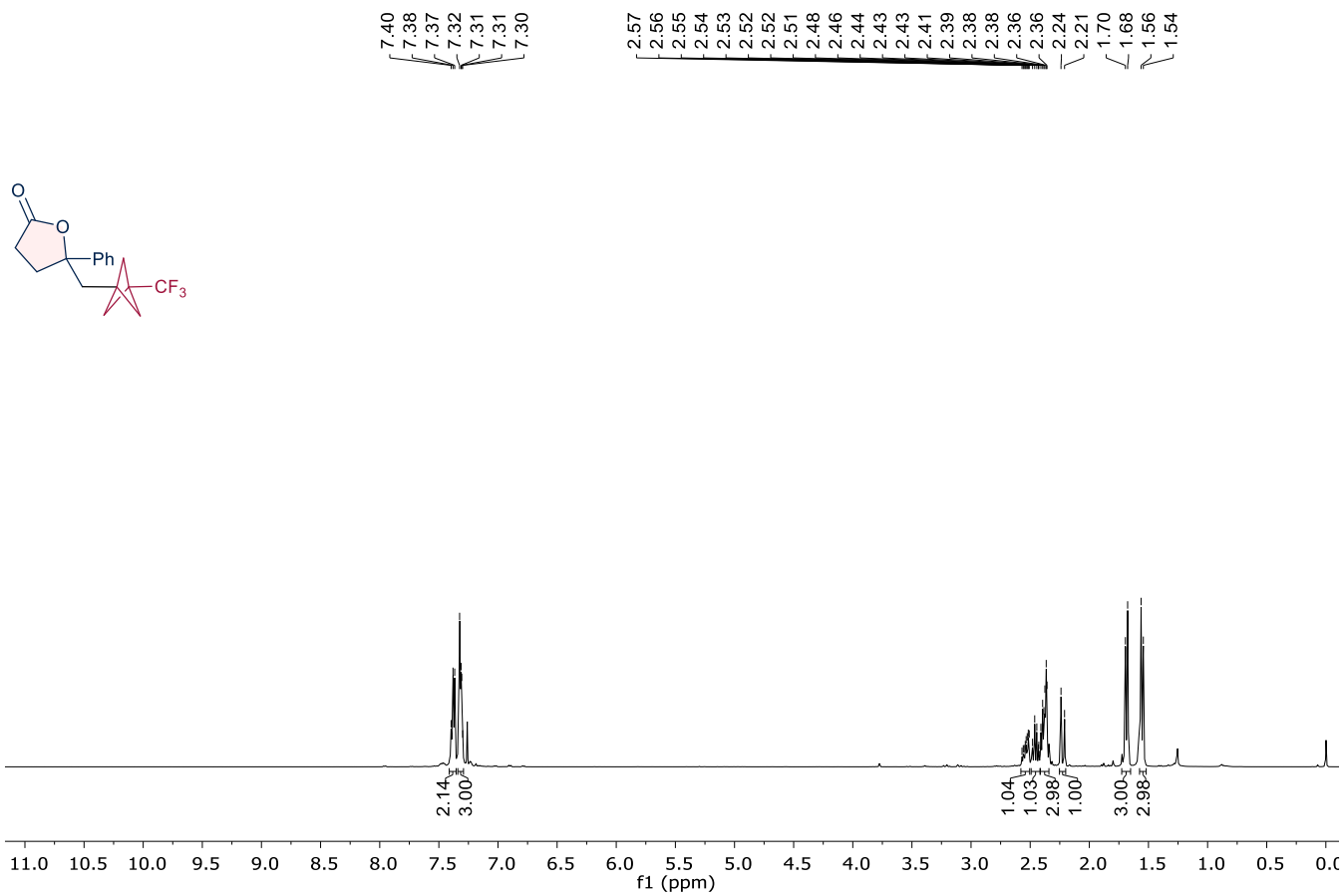
^{1}H NMR ($CDCl_3$, 600 MHz) of compound **3y**.



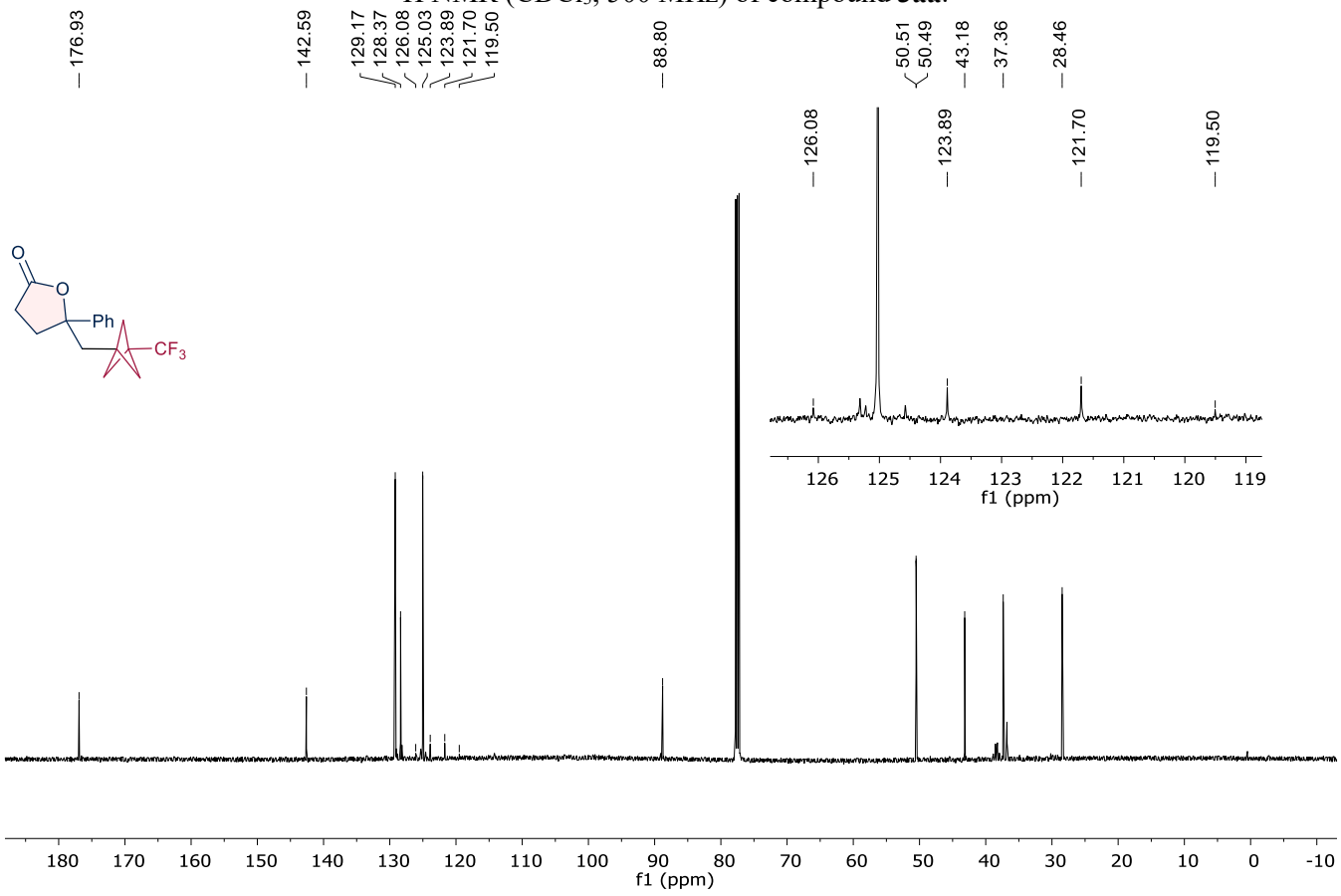
^{13}C NMR ($CDCl_3$, 151 MHz) of compound **3y**.



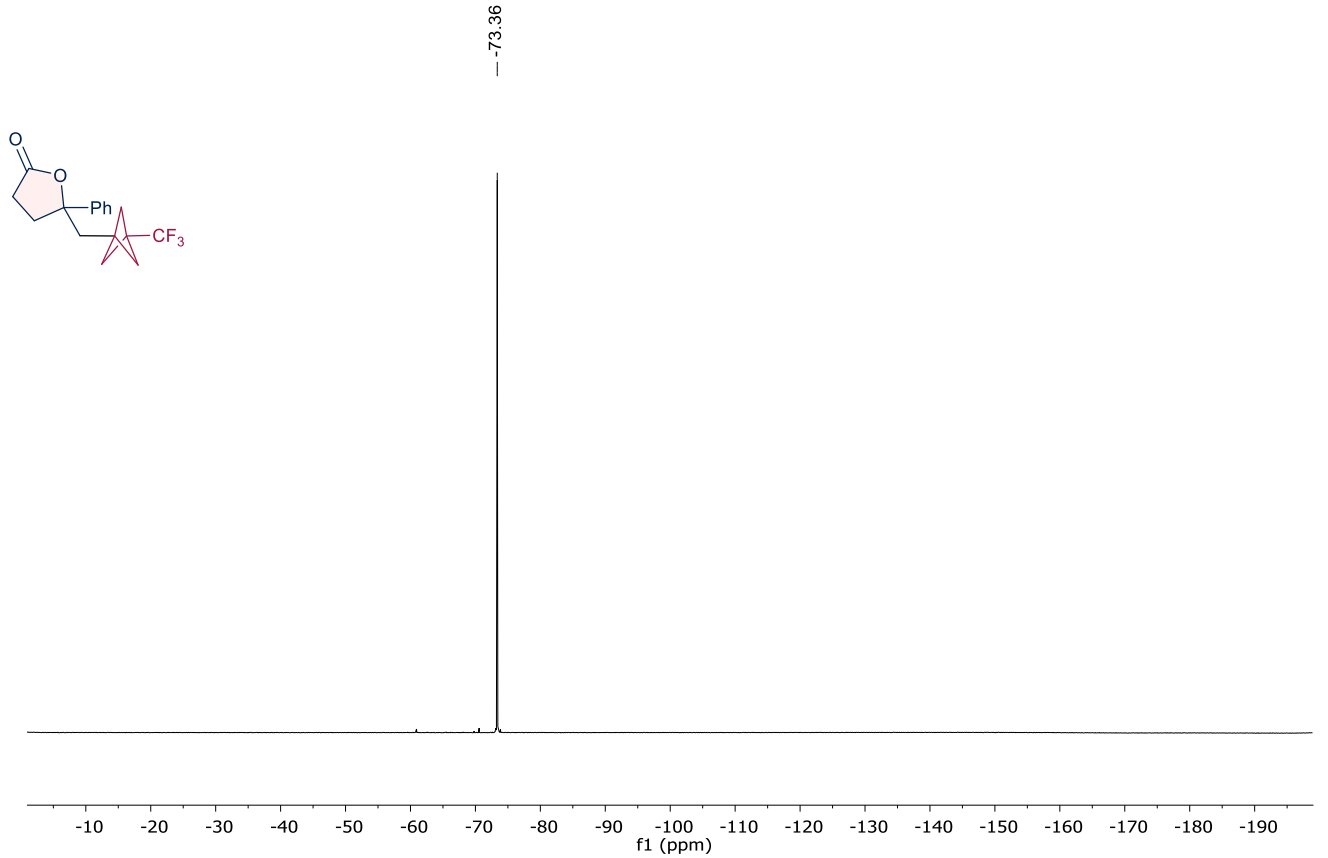
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3z**.



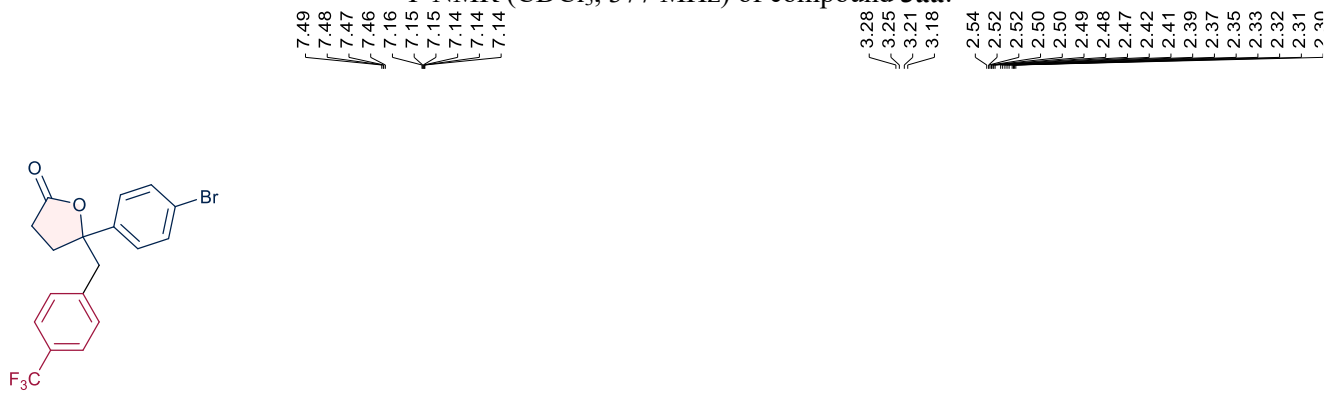
^{1}H NMR ($CDCl_3$, 500 MHz) of compound **3aa**.



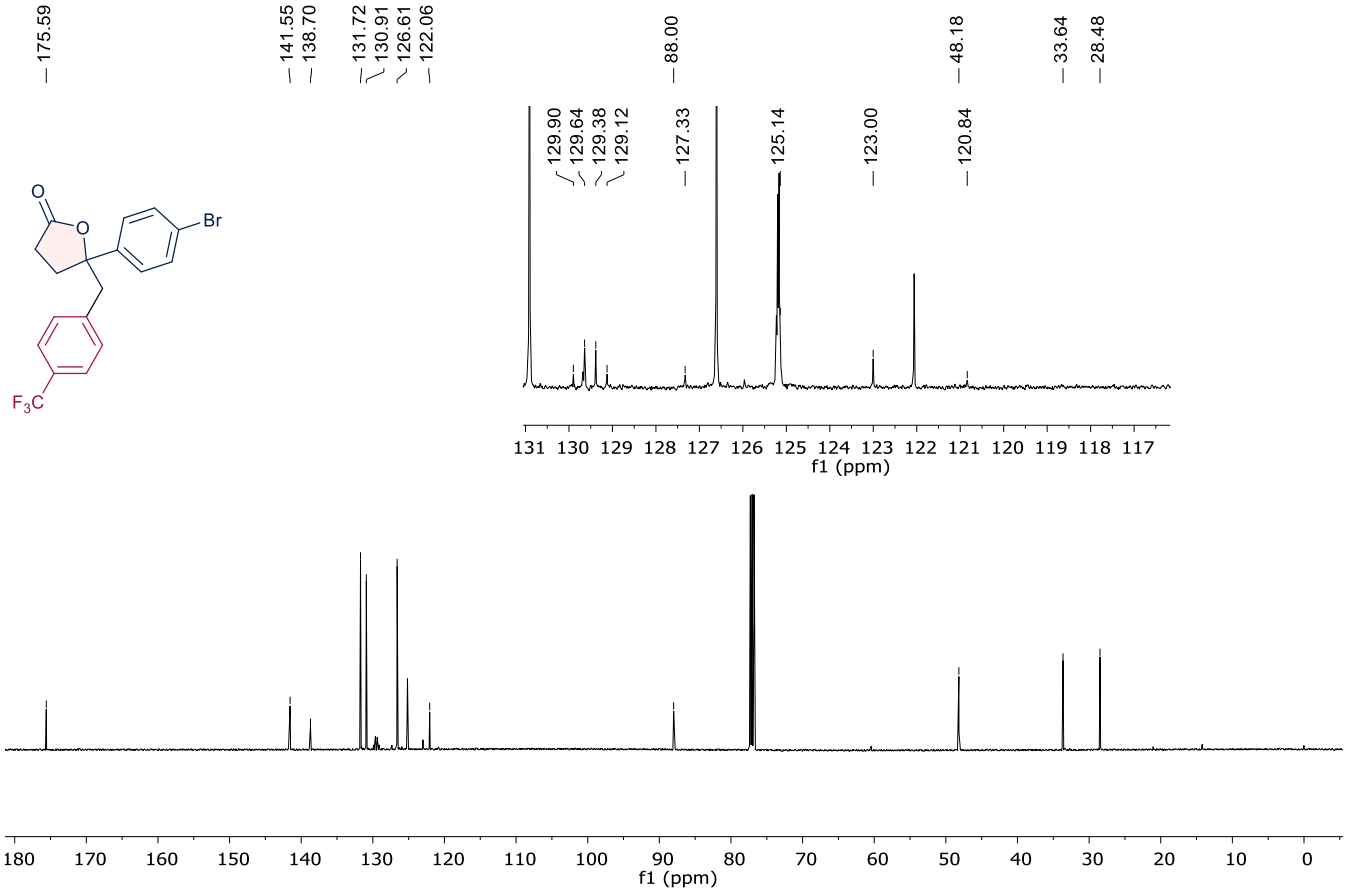
^{13}C NMR ($CDCl_3$, 126 MHz) of compound **3aa**.



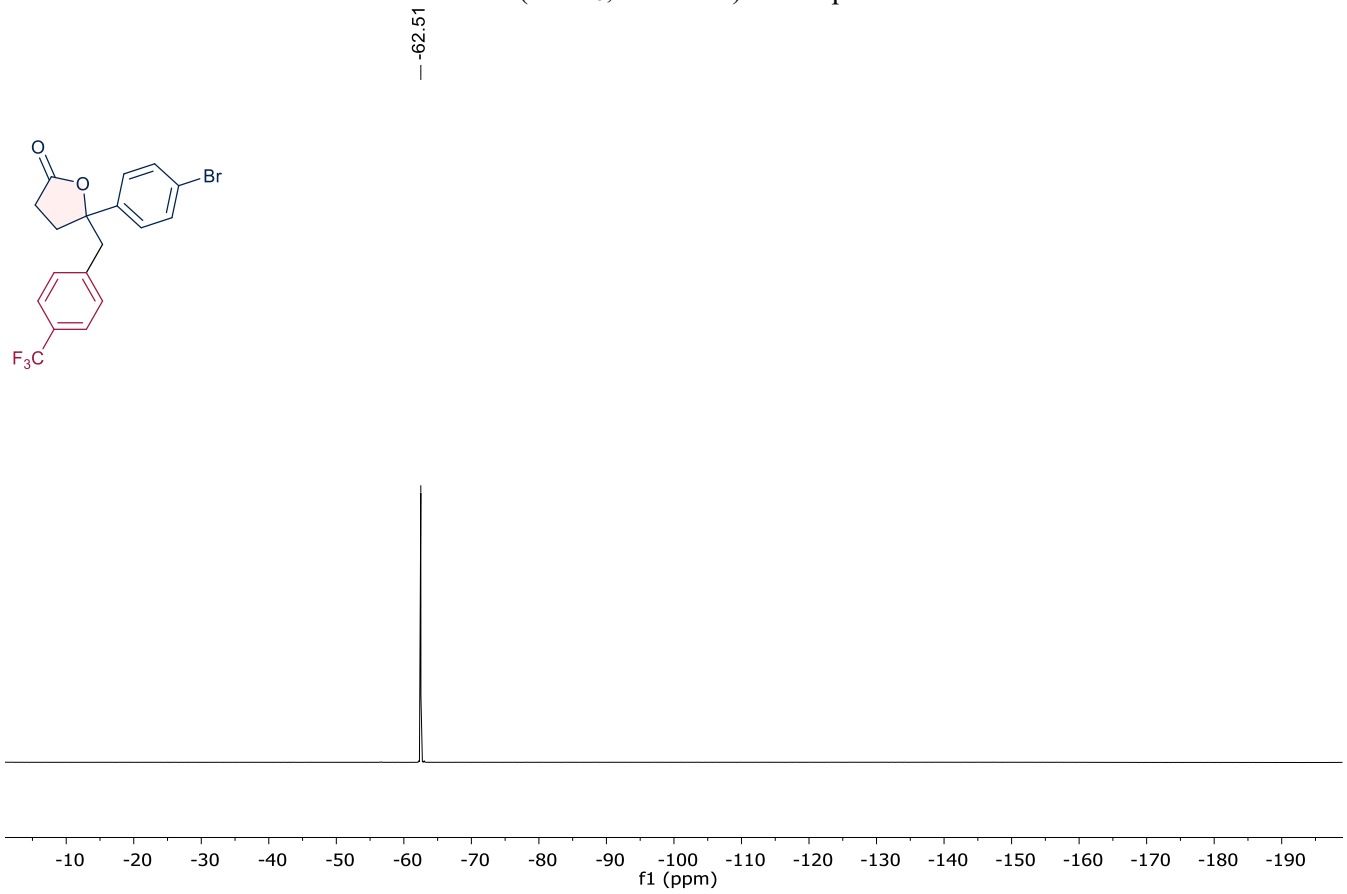
^{19}F NMR ($CDCl_3$, 377 MHz) of compound **3aa**.



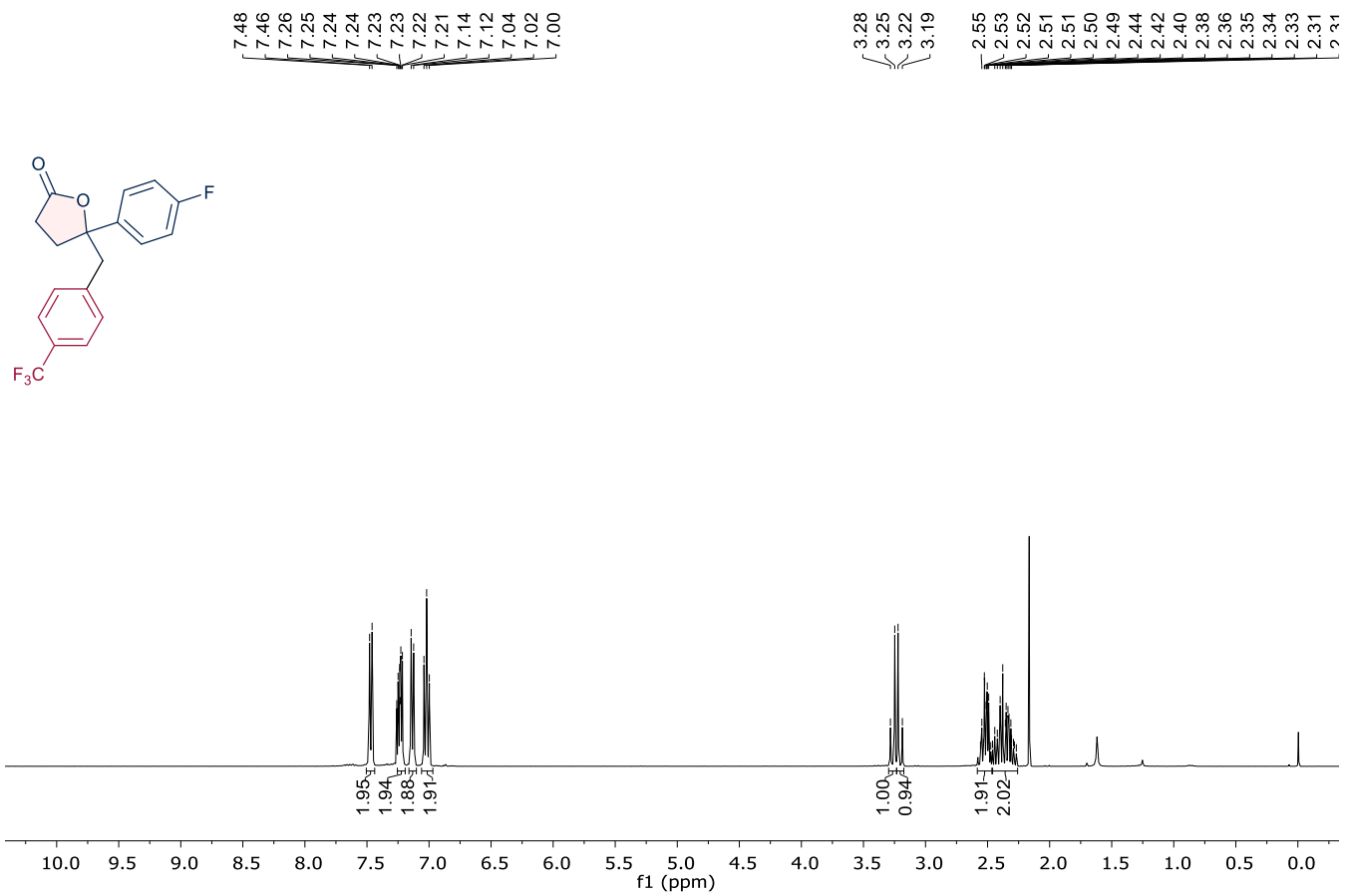
^{1}H NMR ($CDCl_3$, 500 MHz) of compound **4a**.



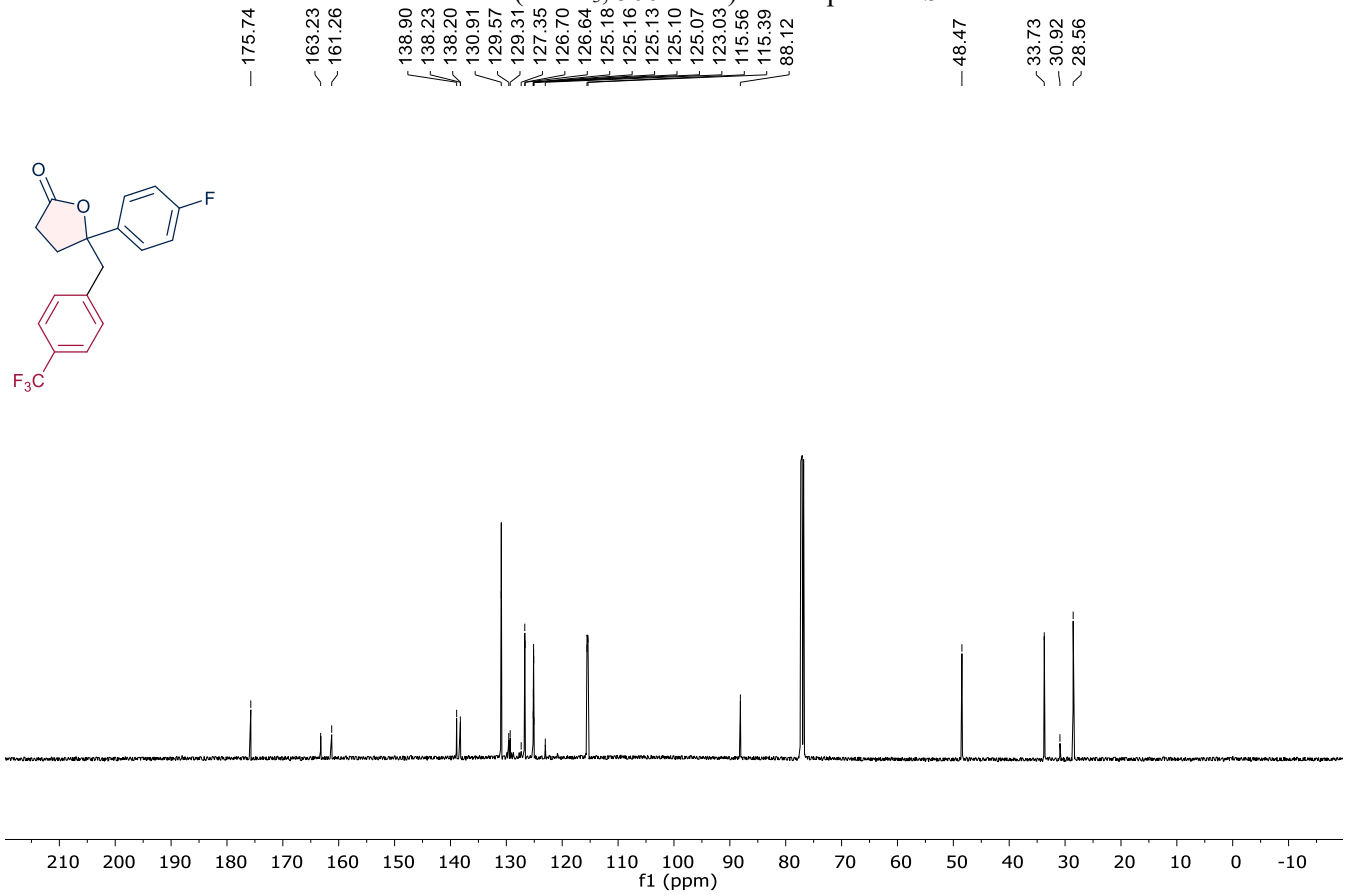
^{13}C NMR ($CDCl_3$, 126 MHz) of compound **4a**.



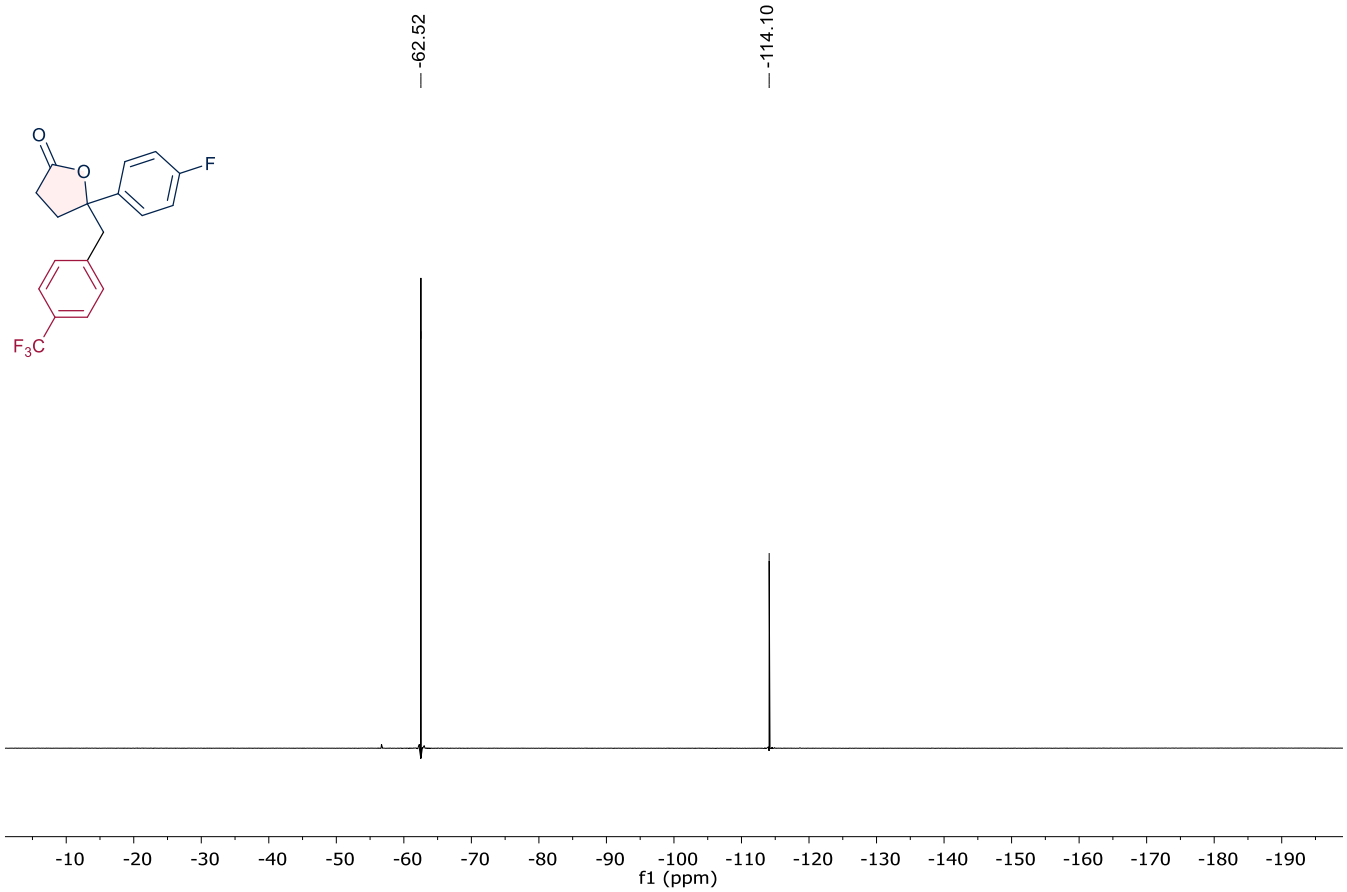
^{19}F NMR ($CDCl_3$, 377 MHz) of compound **4a**.



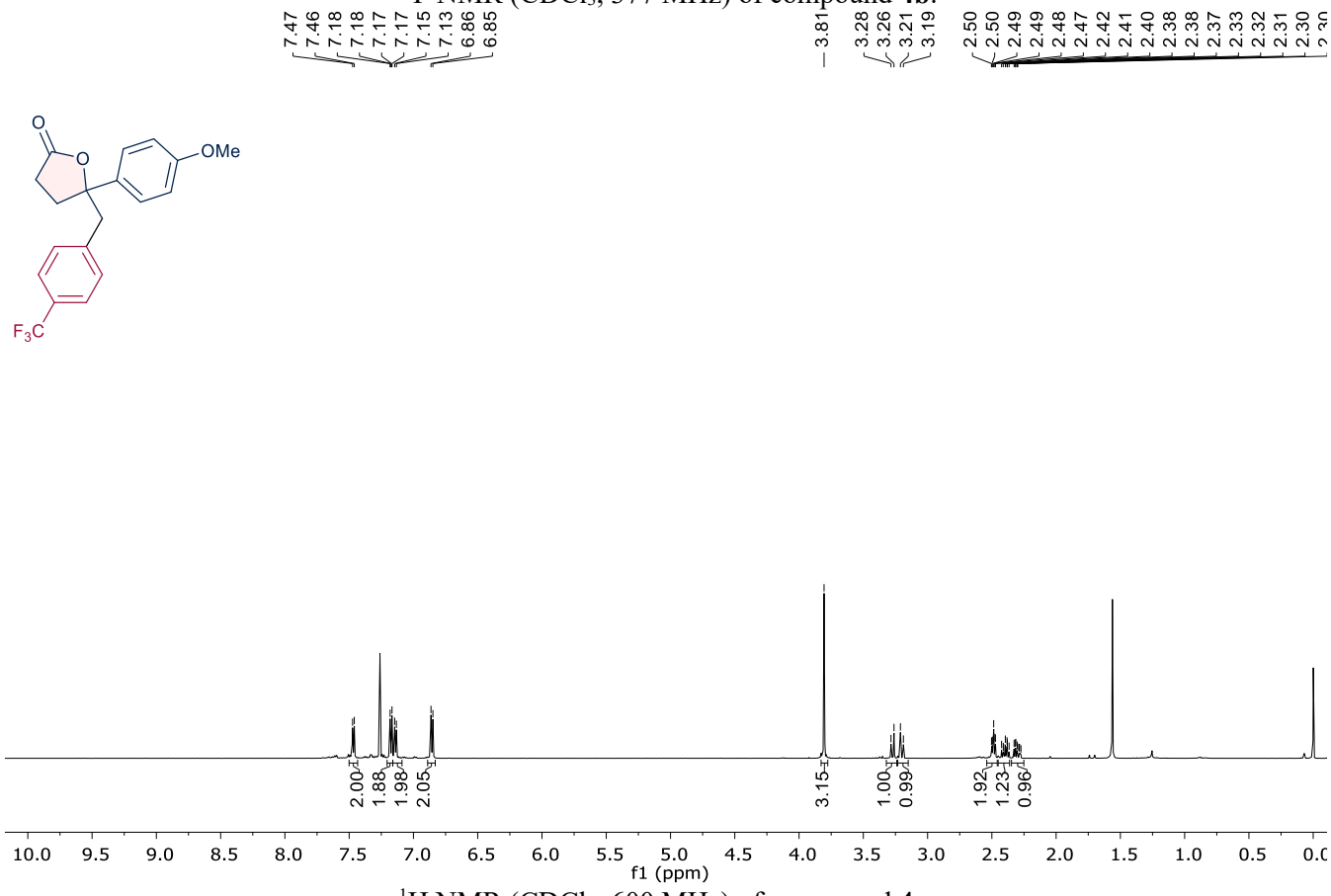
^{1}H NMR ($CDCl_3$, 500 MHz) of compound **4b**.



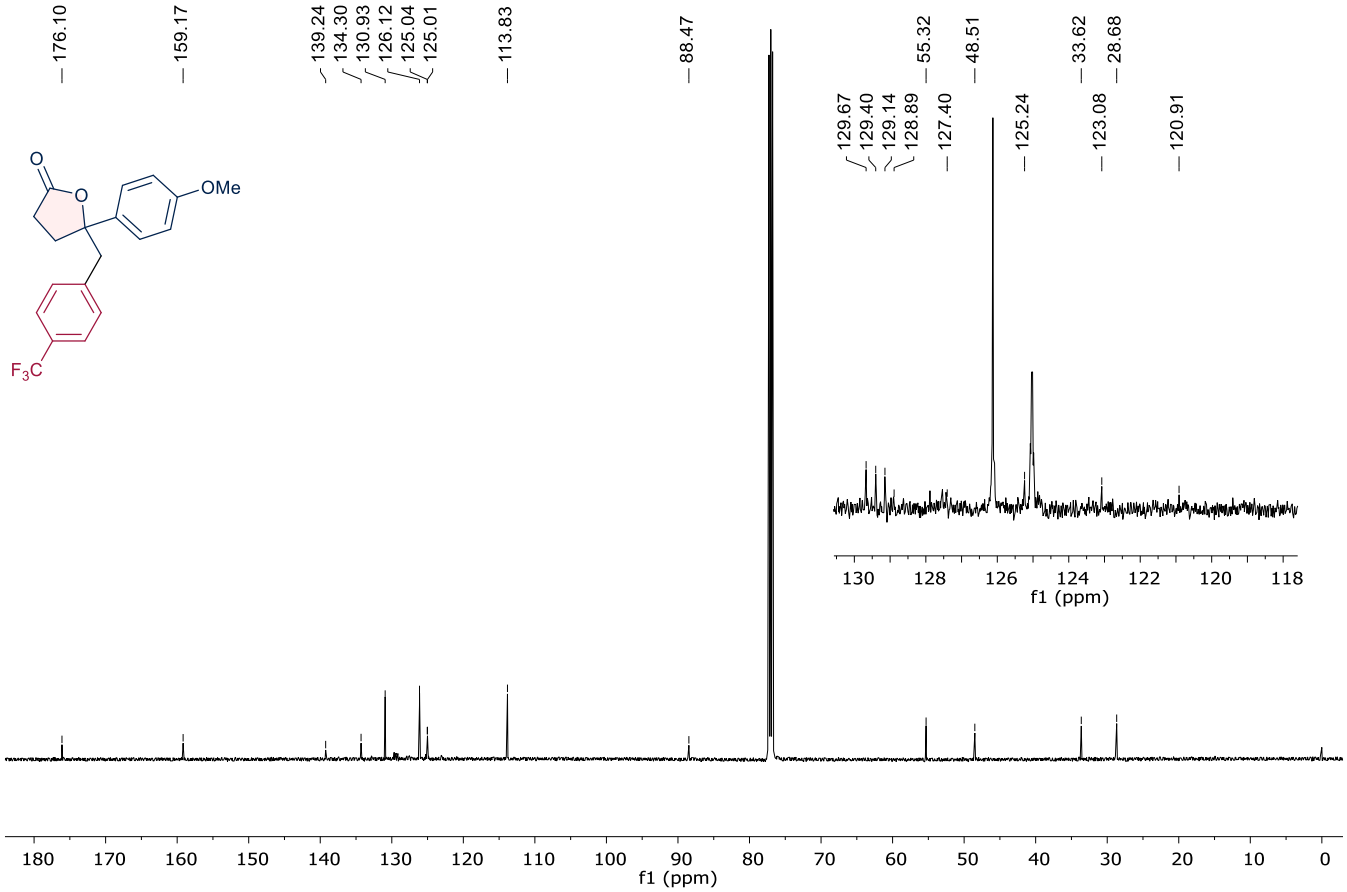
^{13}C NMR ($CDCl_3$, 126 MHz) of compound **4b**.



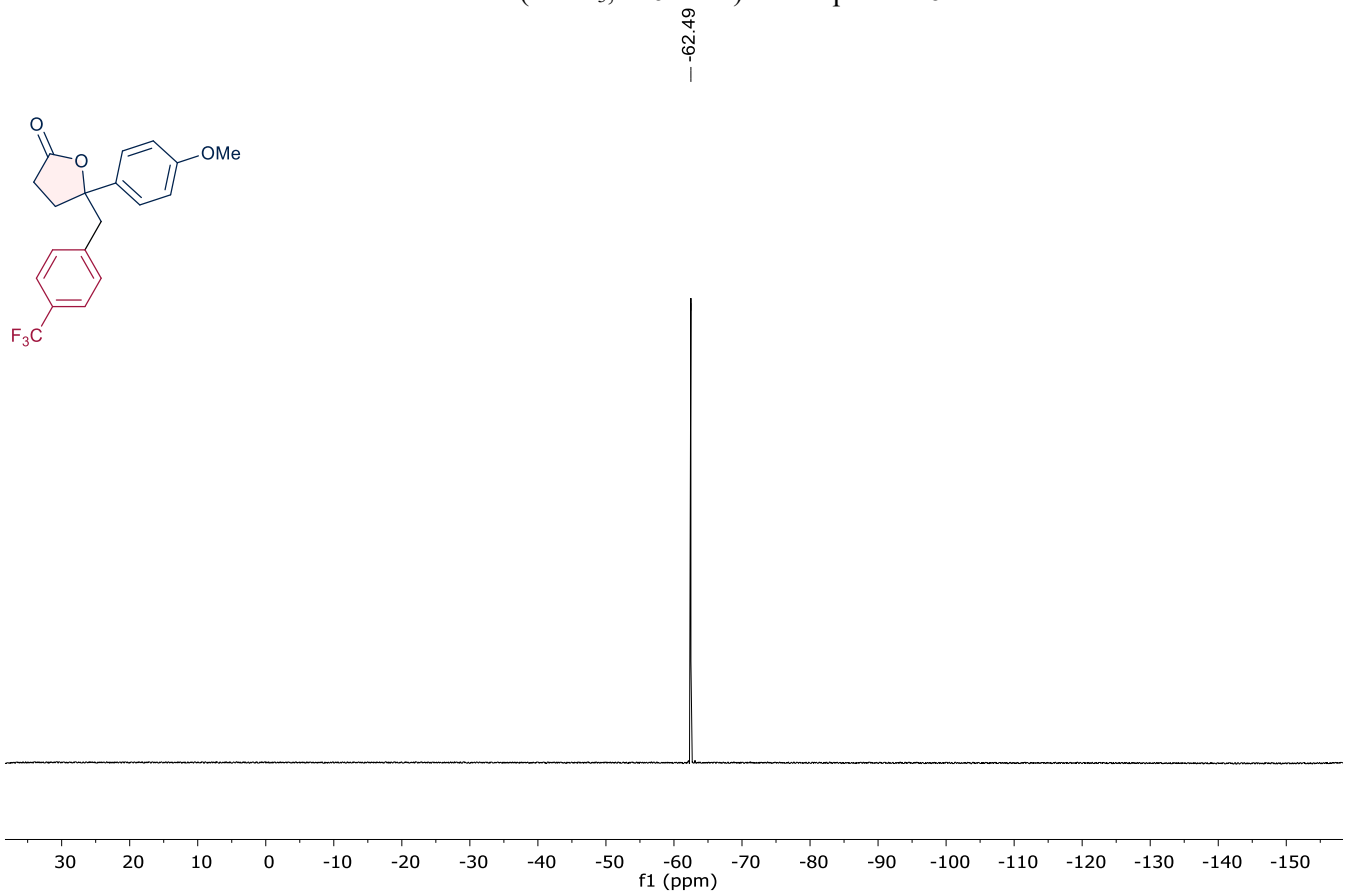
^{19}F NMR ($CDCl_3$, 377 MHz) of compound **4b**.



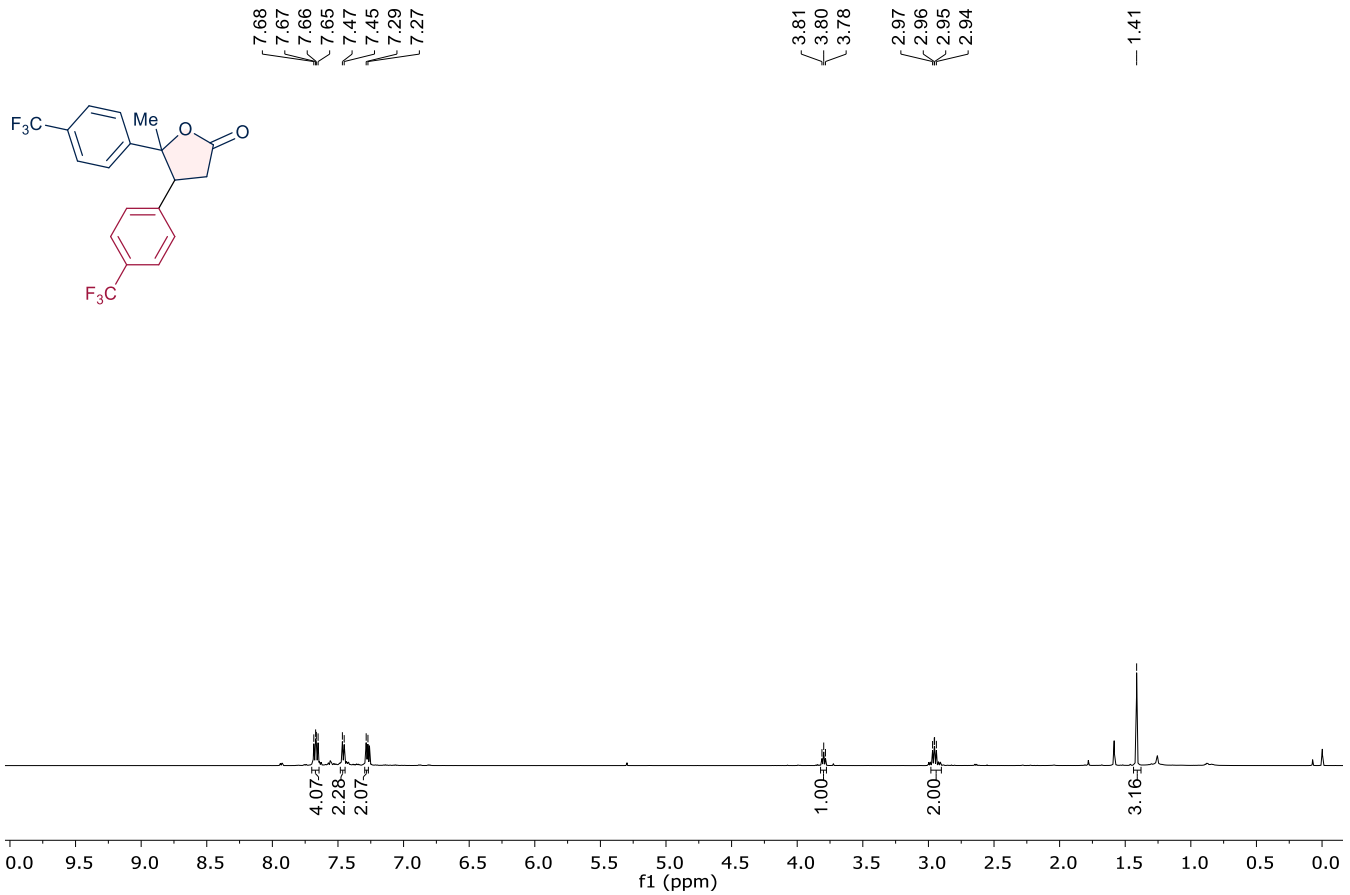
^{1}H NMR ($CDCl_3$, 600 MHz) of compound **4c**.



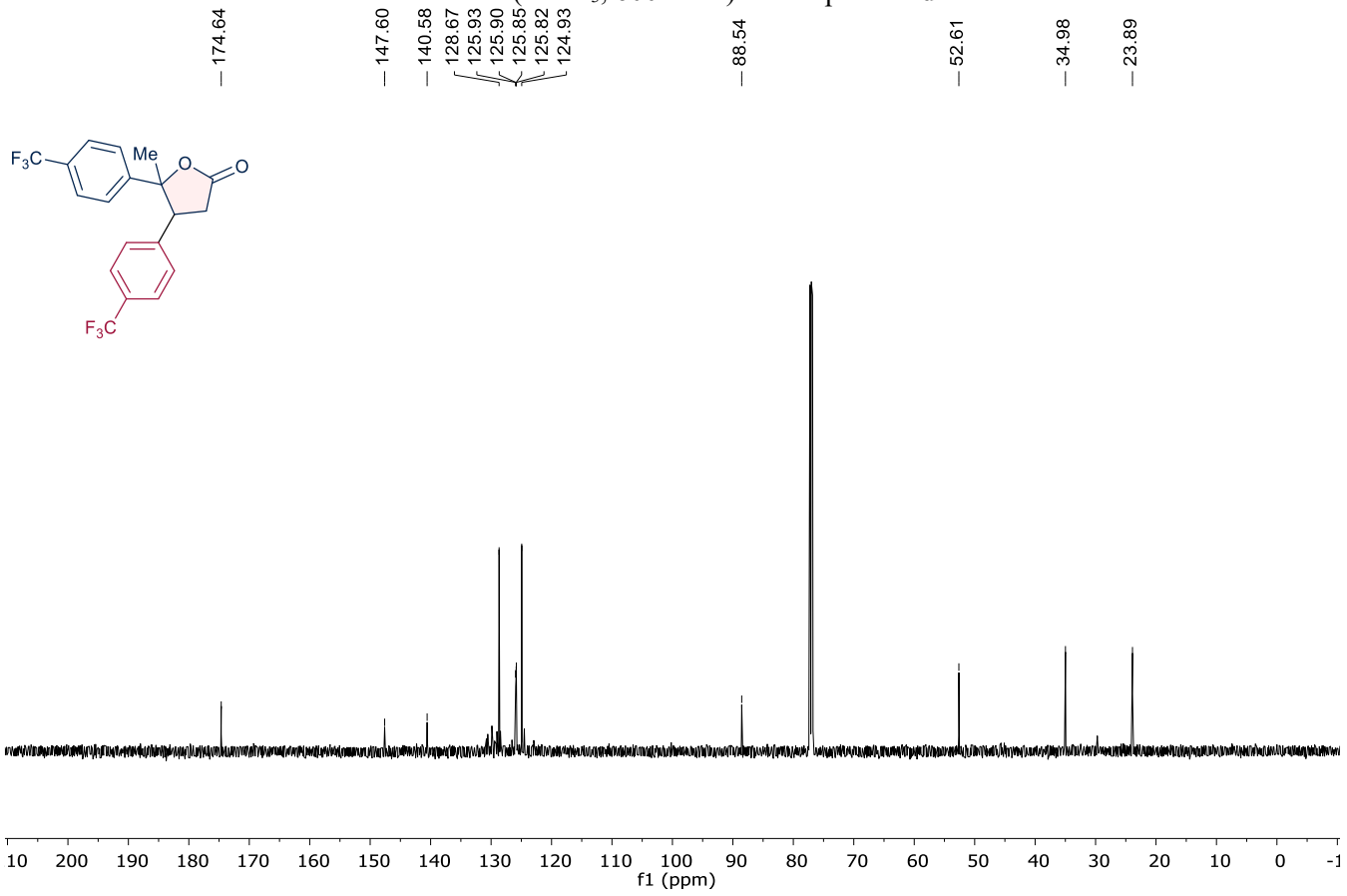
^{13}C NMR ($CDCl_3$, 126 MHz) of compound **4c**.



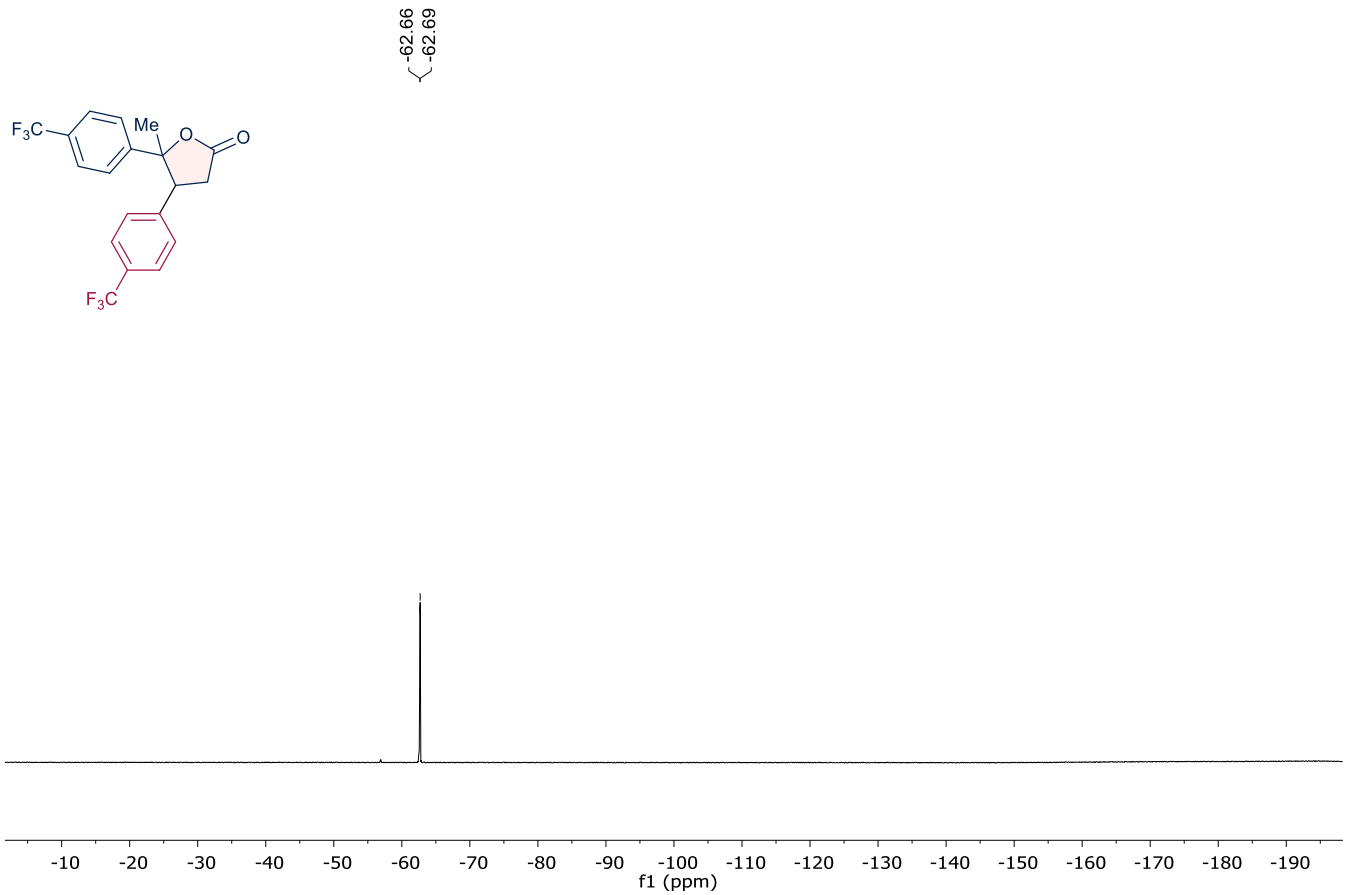
^{19}F NMR ($CDCl_3$, 282 MHz) of compound **4c**.



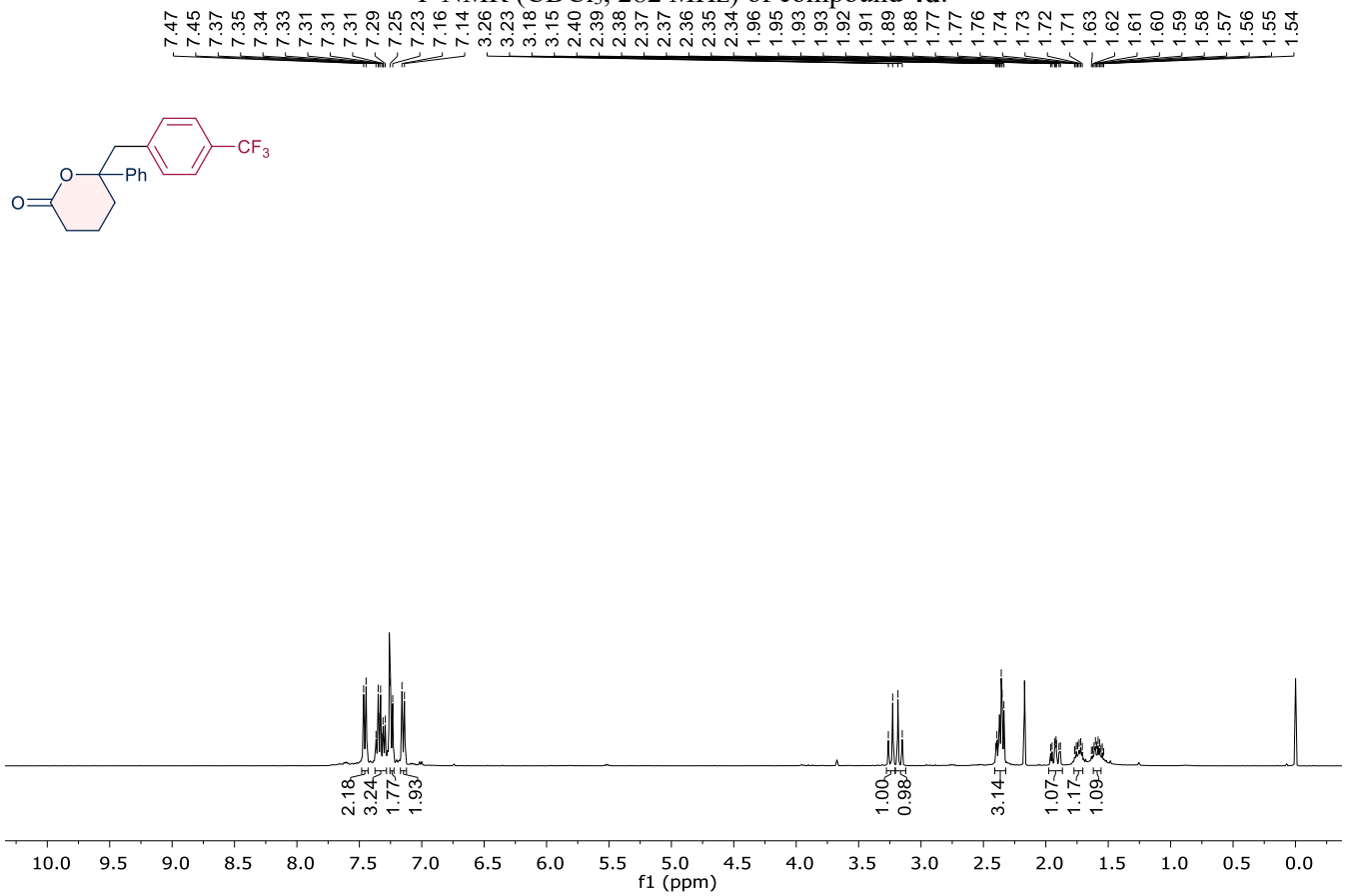
^{1}H NMR ($CDCl_3$, 600 MHz) of compound **4d**.



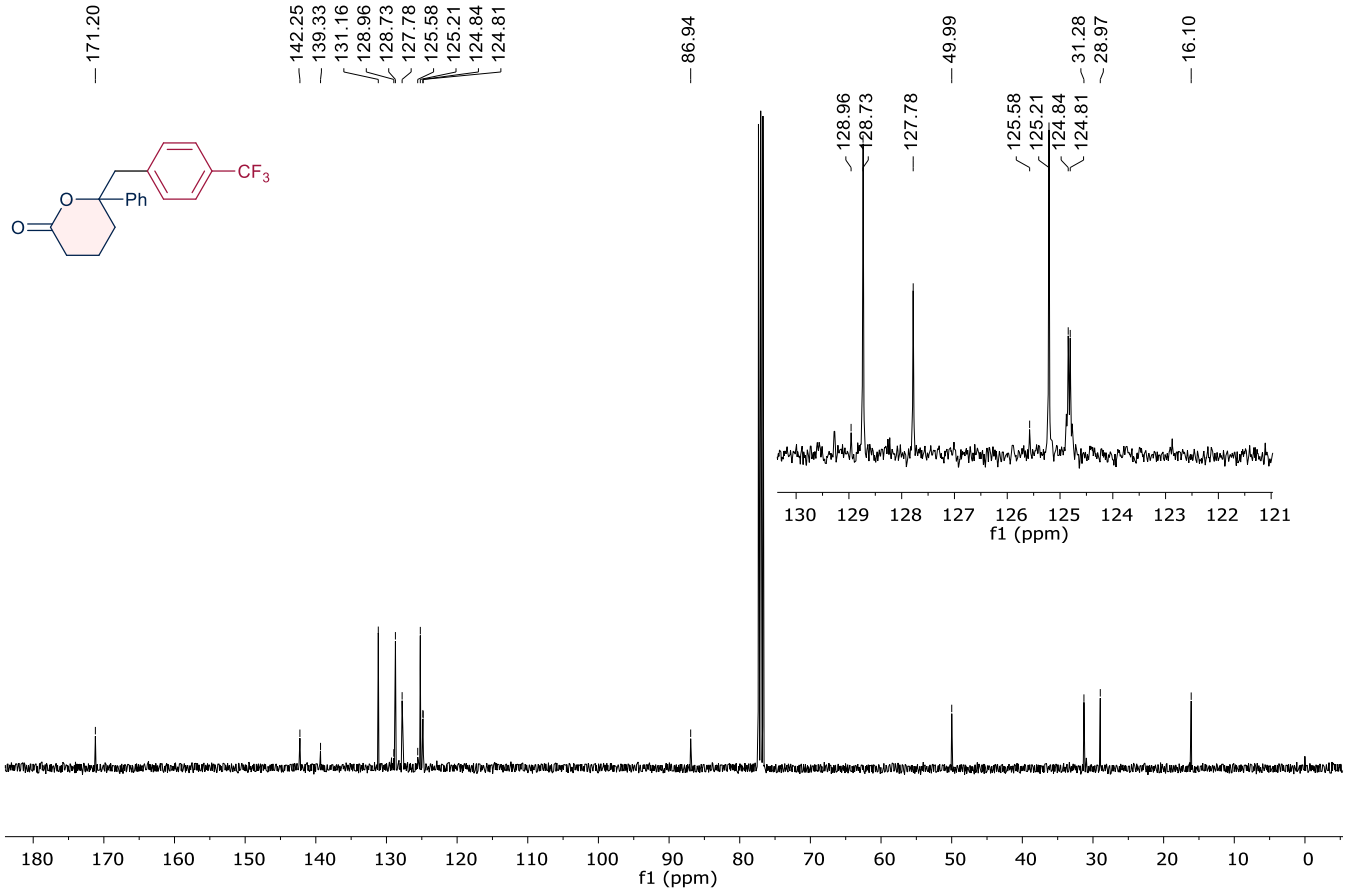
^{13}C NMR ($CDCl_3$, 151 MHz) of compound **4d**.



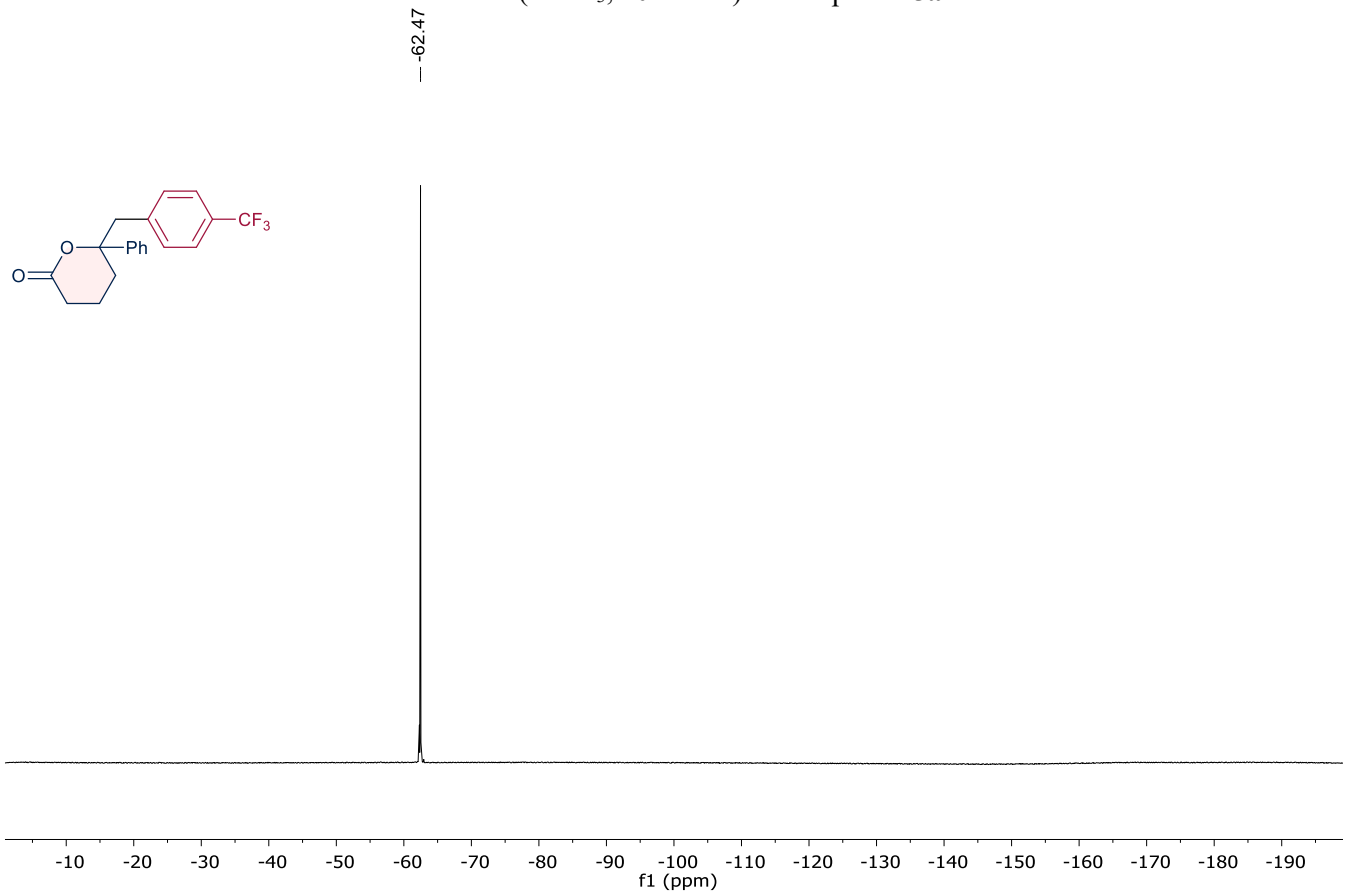
^{19}F NMR ($CDCl_3$, 282 MHz) of compound **4d**.



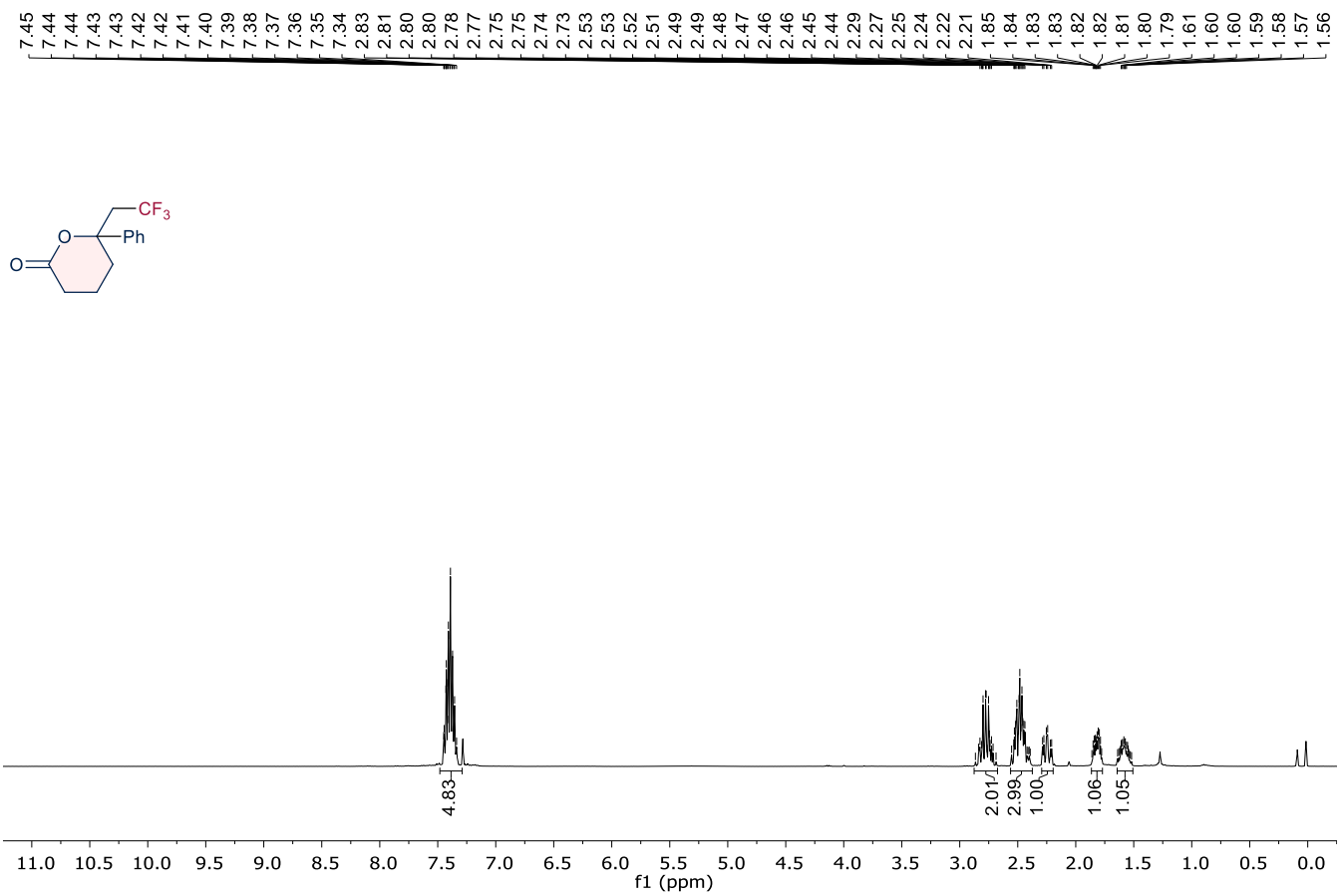
^{1}H NMR ($CDCl_3$, 500 MHz) of compound **5a**.



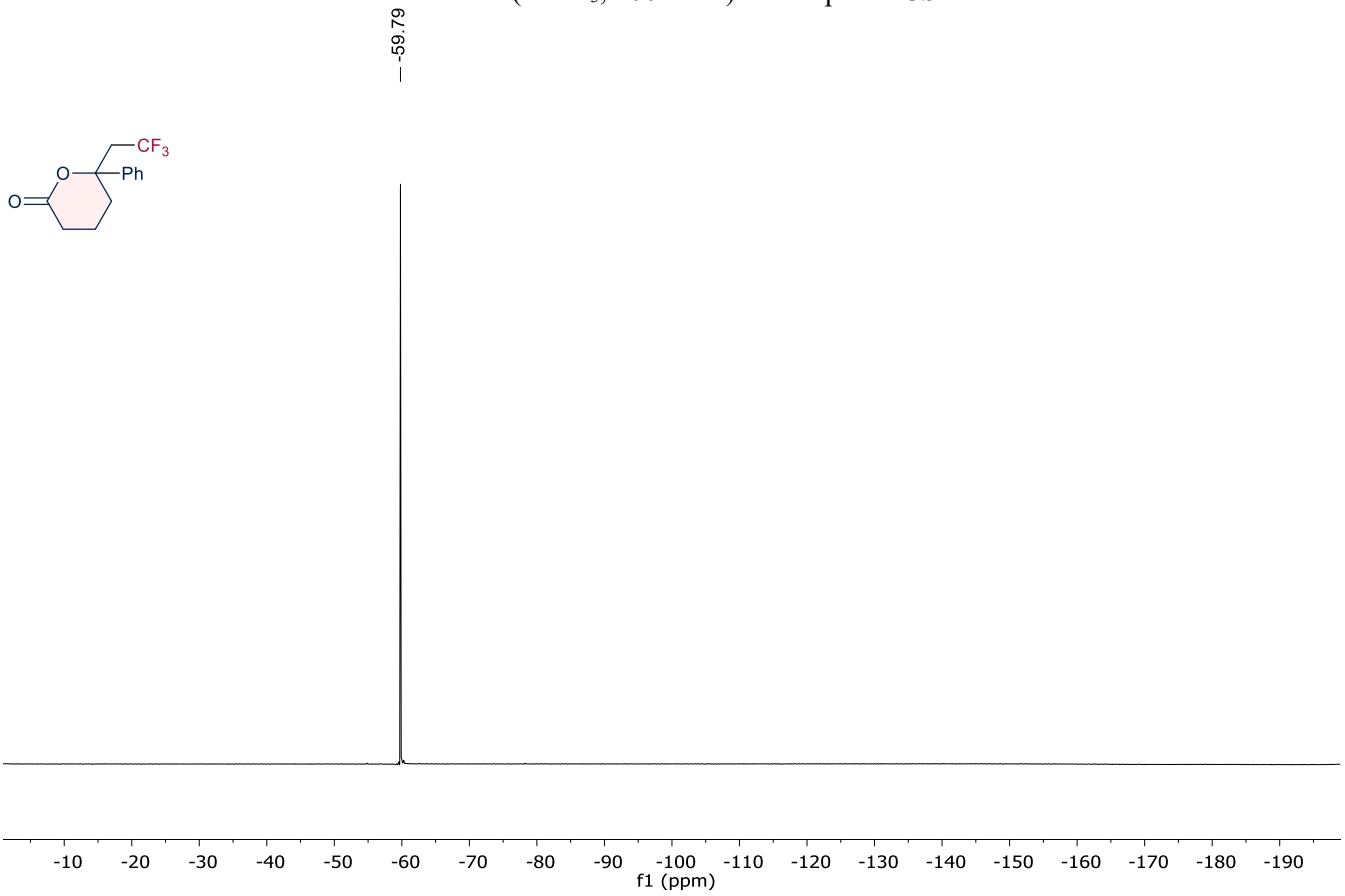
^{13}C NMR ($CDCl_3$, 101 MHz) of compound **5a**.



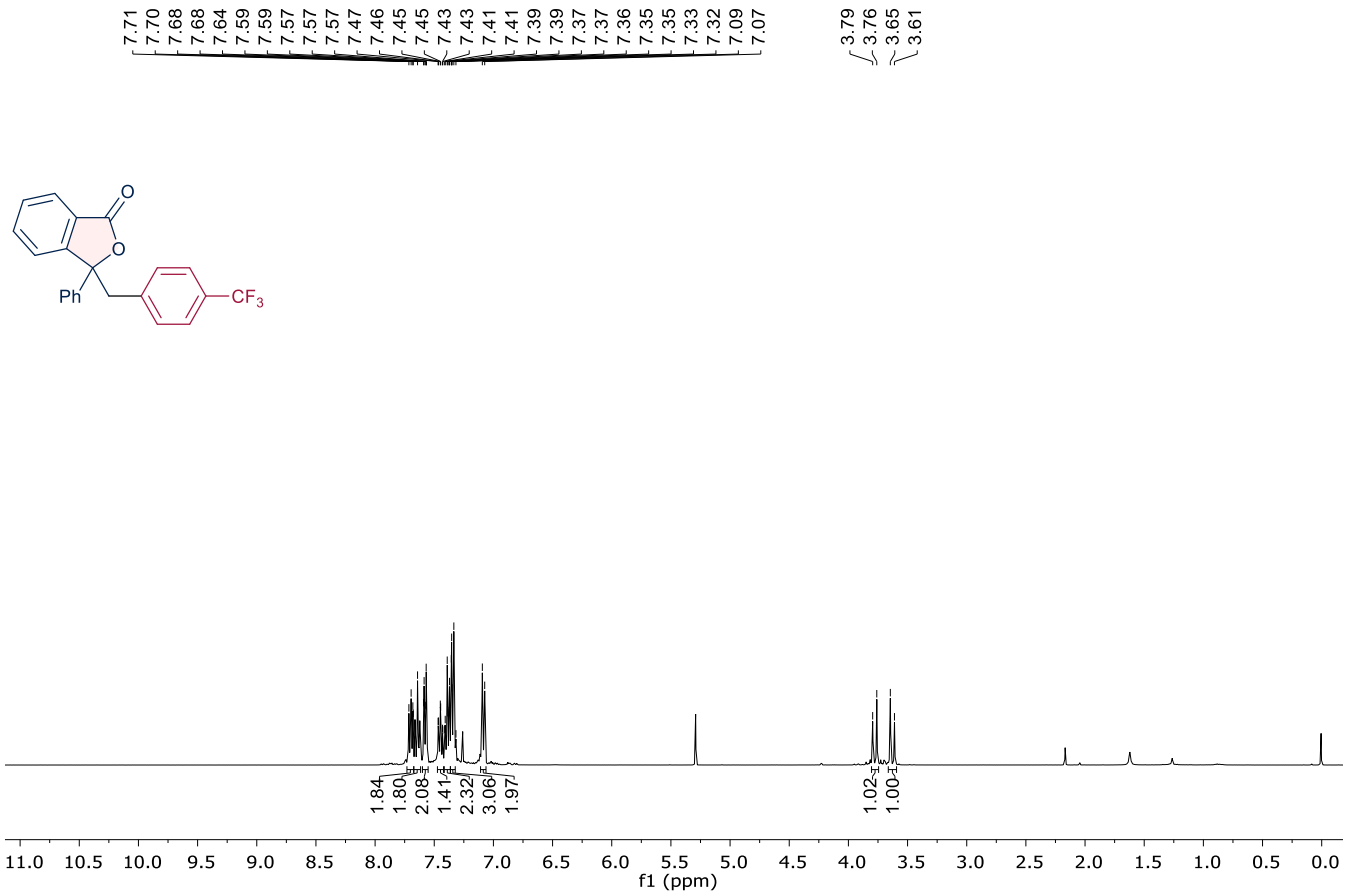
^{19}F NMR ($CDCl_3$, 377 MHz) of compound **5a**.



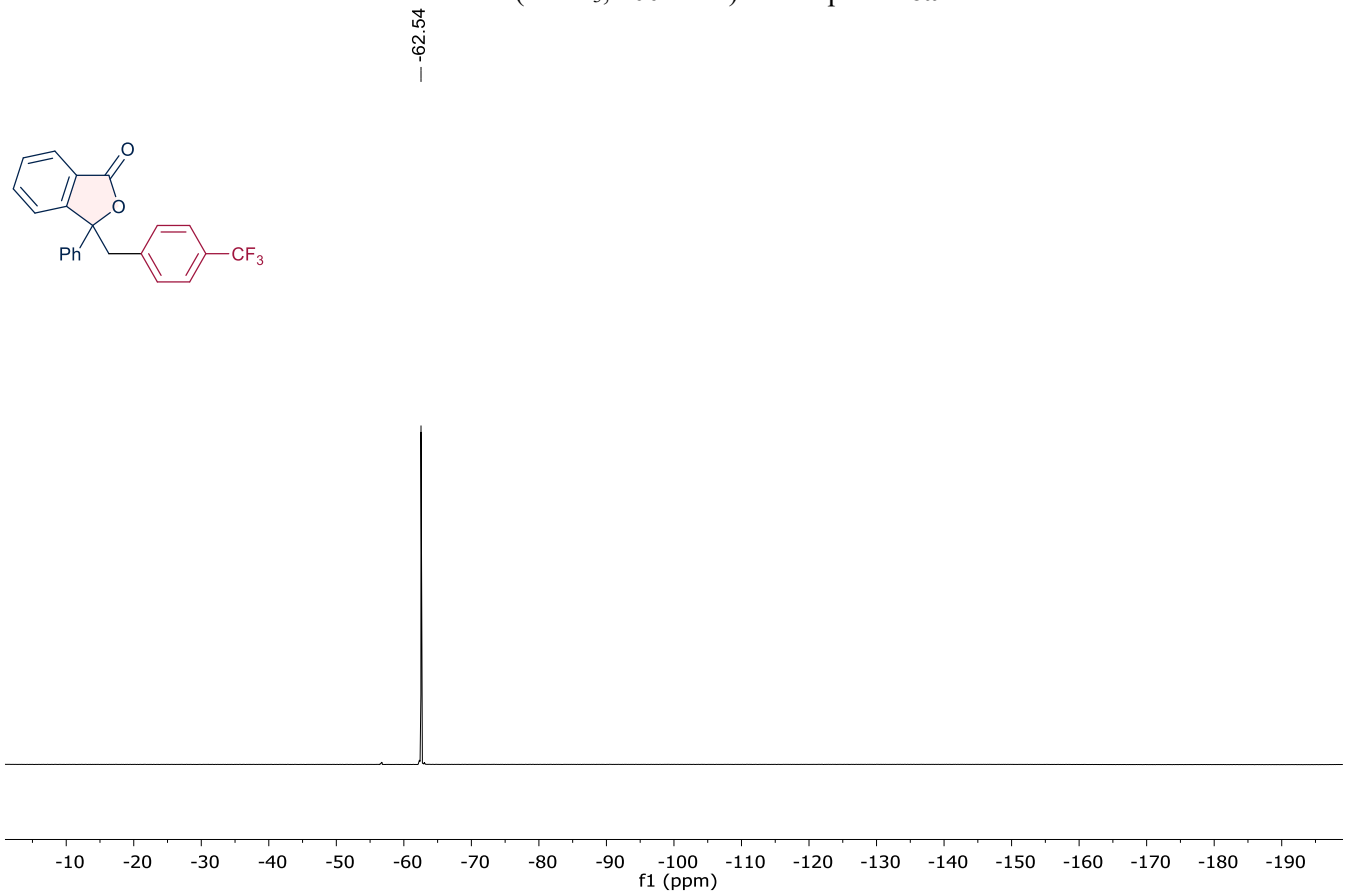
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **5b**.



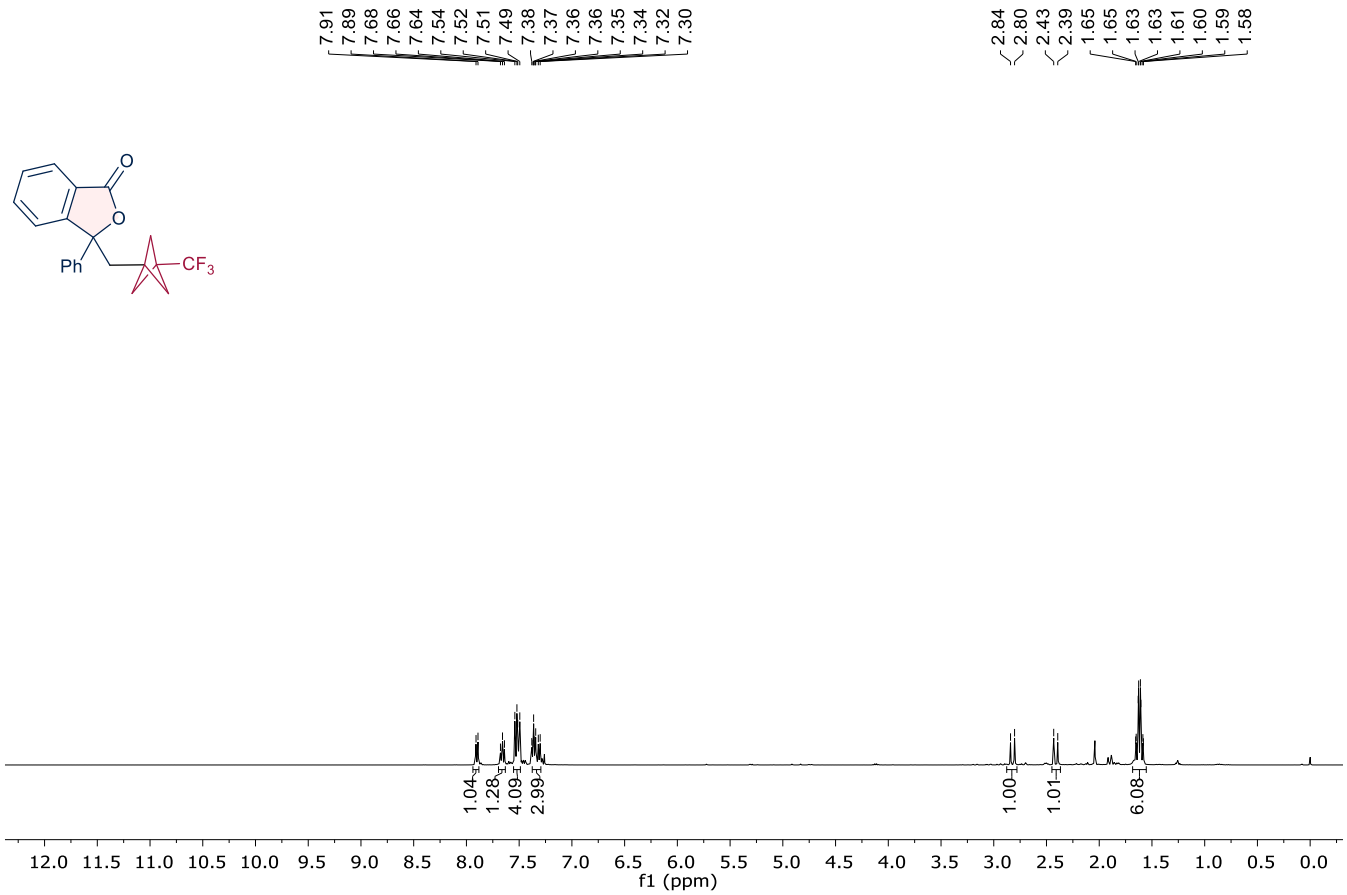
^{19}F NMR ($CDCl_3$, 377 MHz) of compound **5b**.



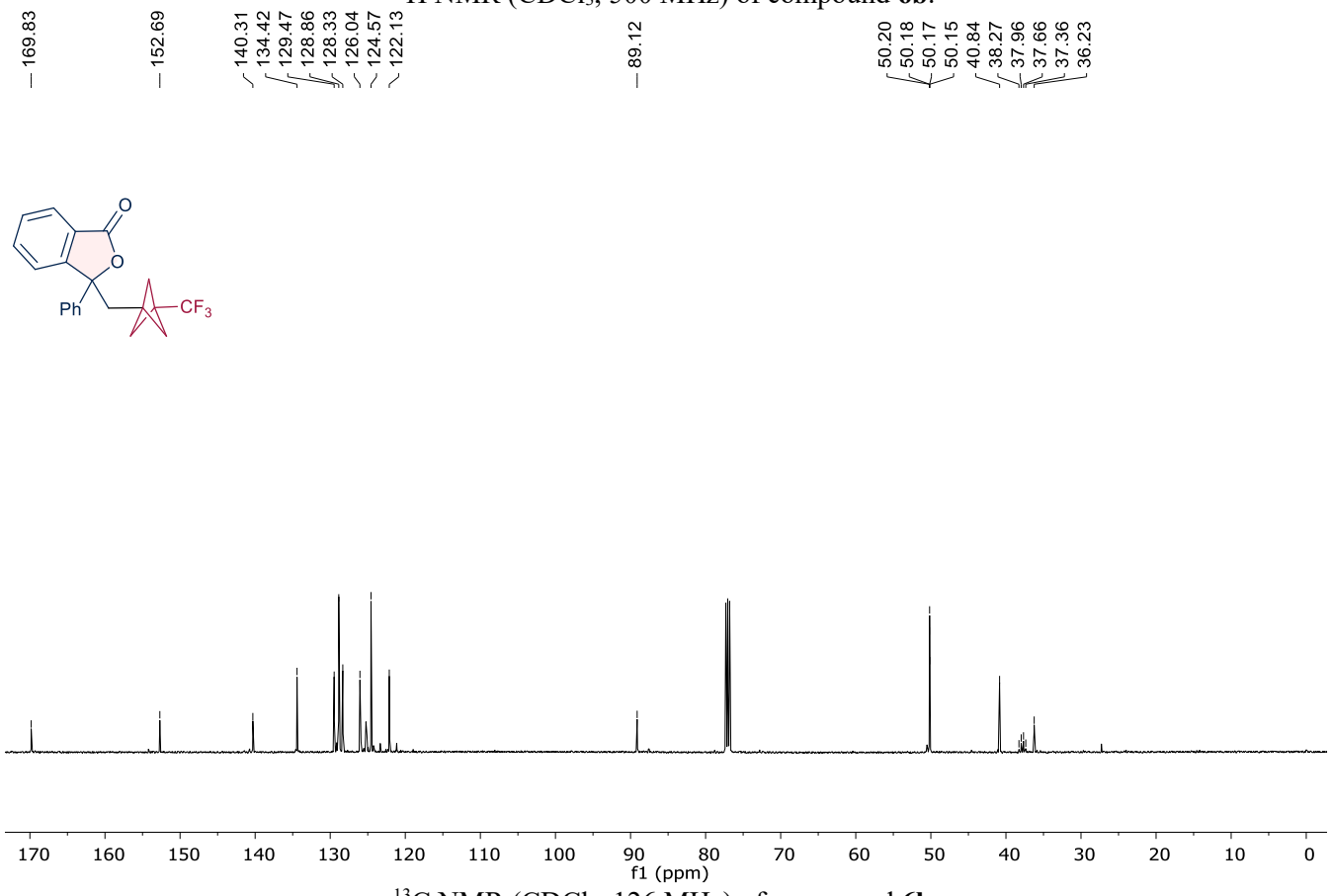
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **6a**.



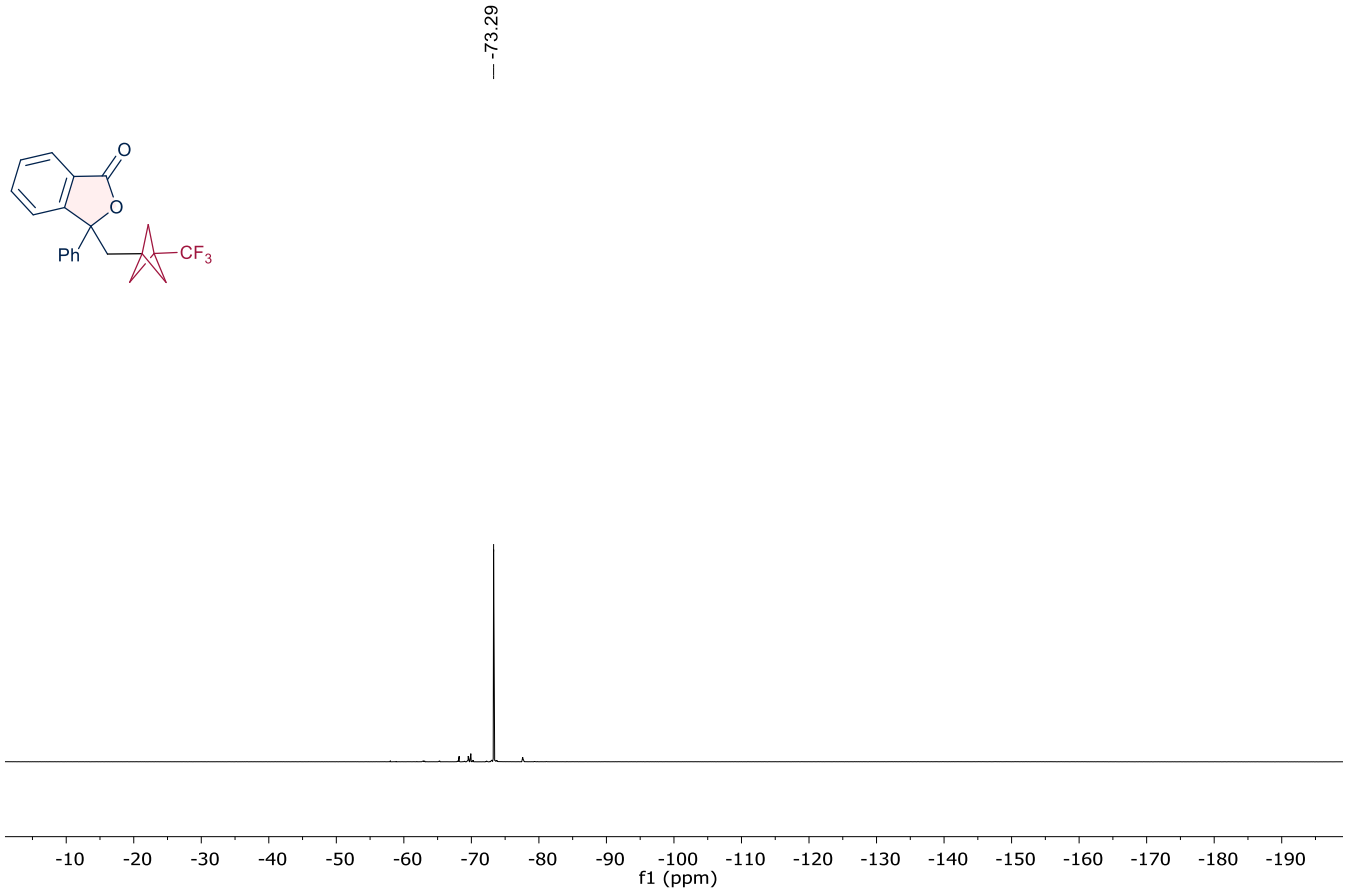
^{19}F NMR ($CDCl_3$, 377 MHz) of compound **6a**.



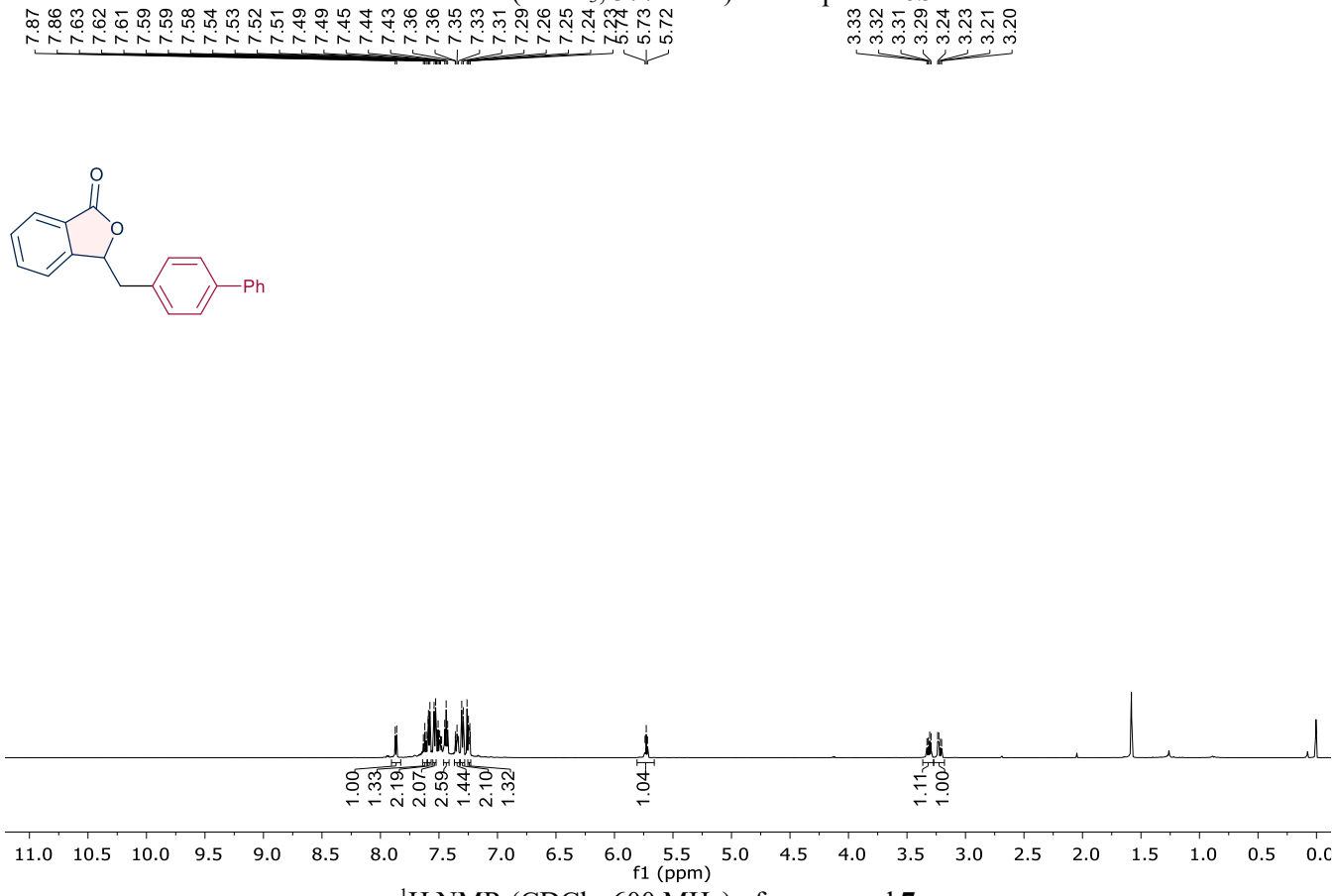
^{1}H NMR ($CDCl_3$, 500 MHz) of compound **6b**.



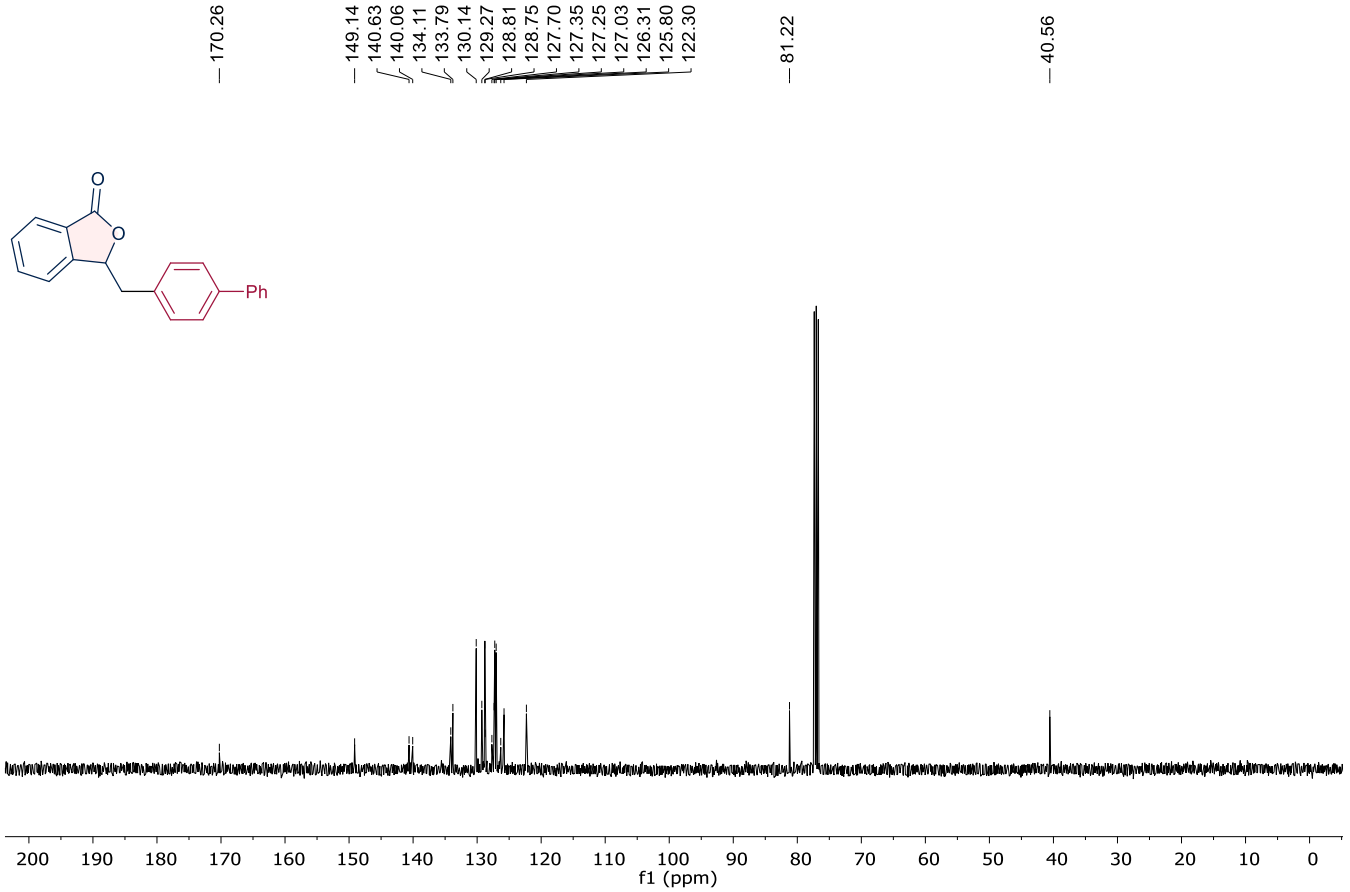
^{13}C NMR ($CDCl_3$, 126 MHz) of compound **6b**.



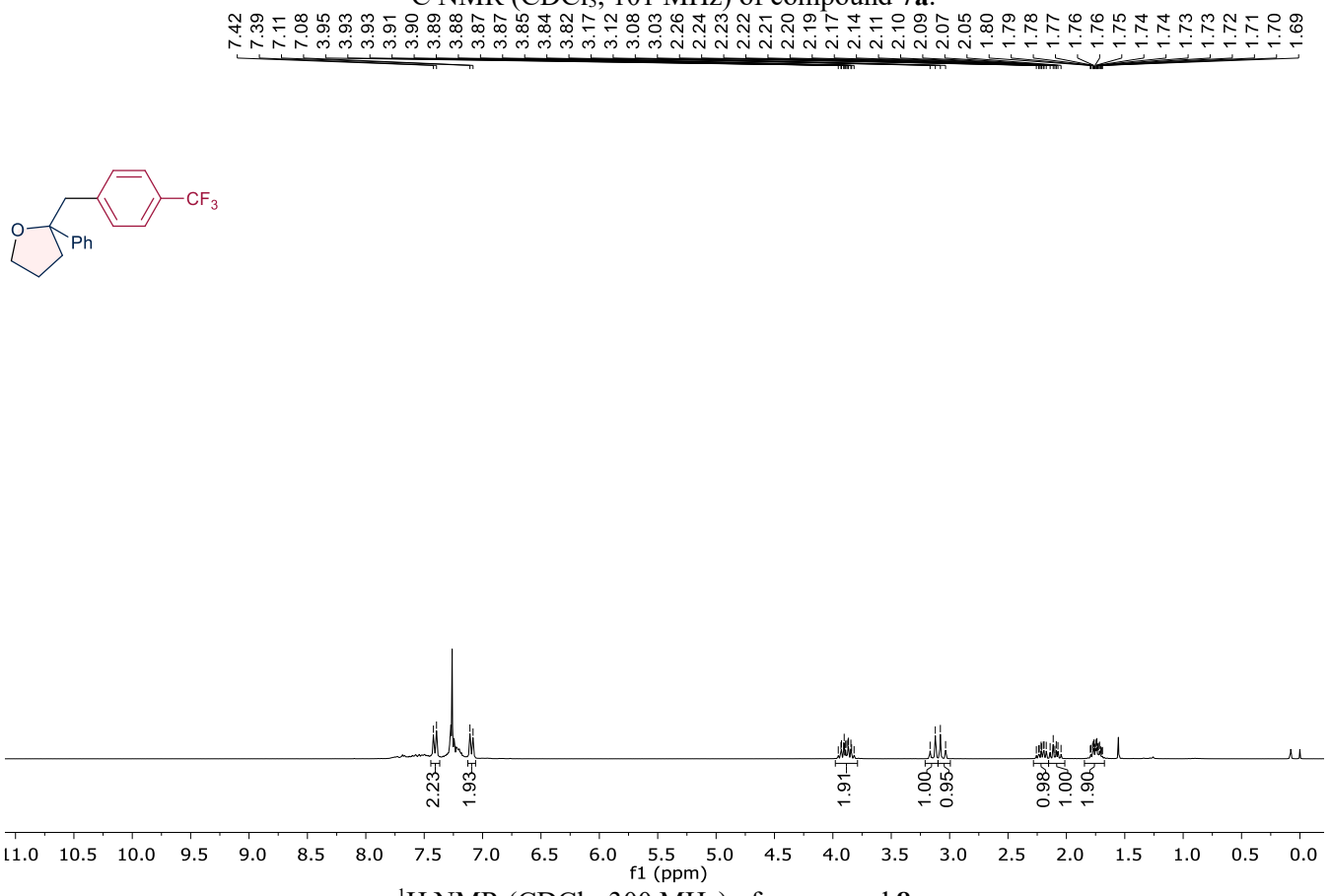
^{19}F NMR ($CDCl_3$, 377 MHz) of compound **6b**.



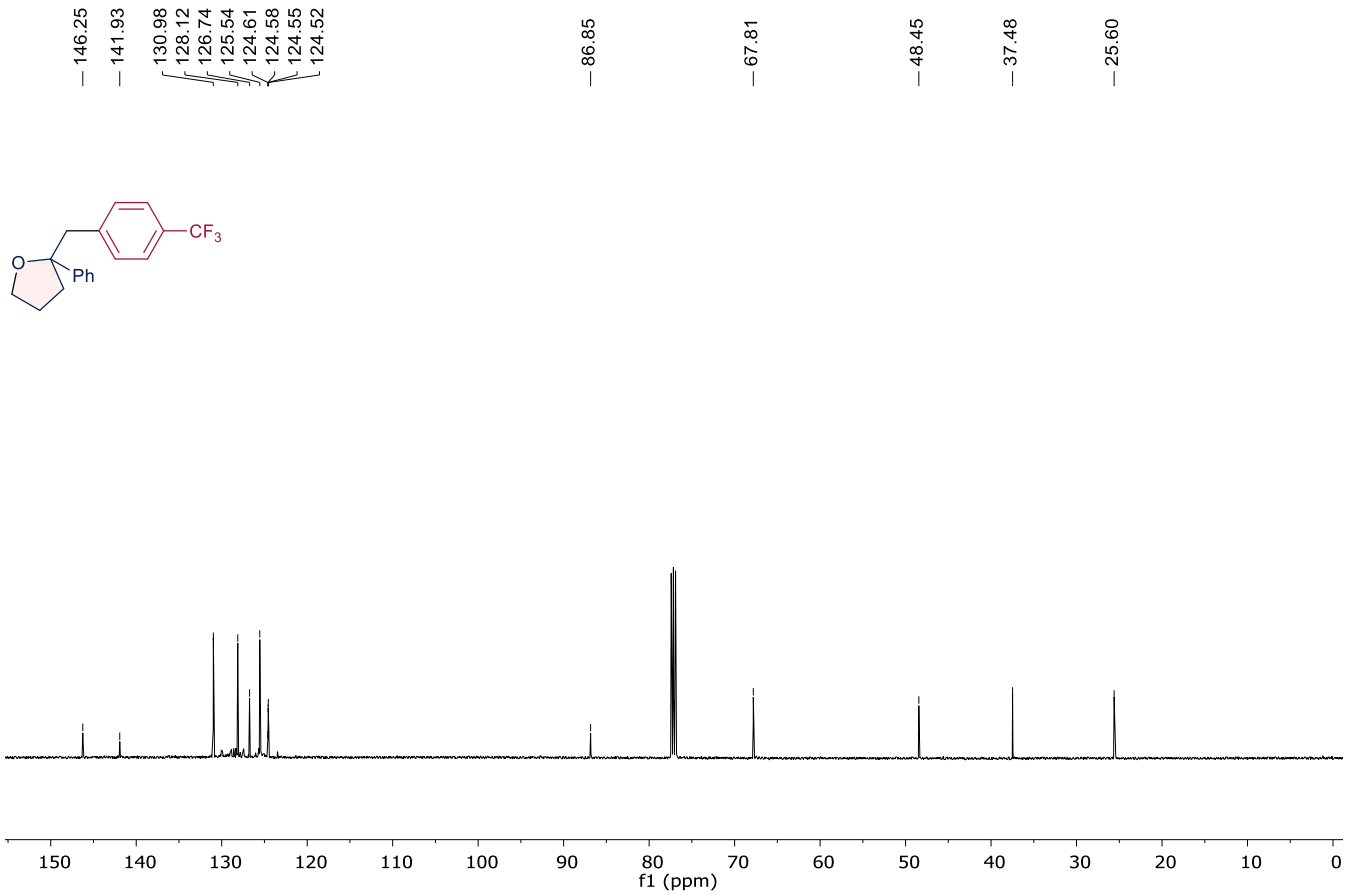
^{1}H NMR ($CDCl_3$, 600 MHz) of compound **7a**.



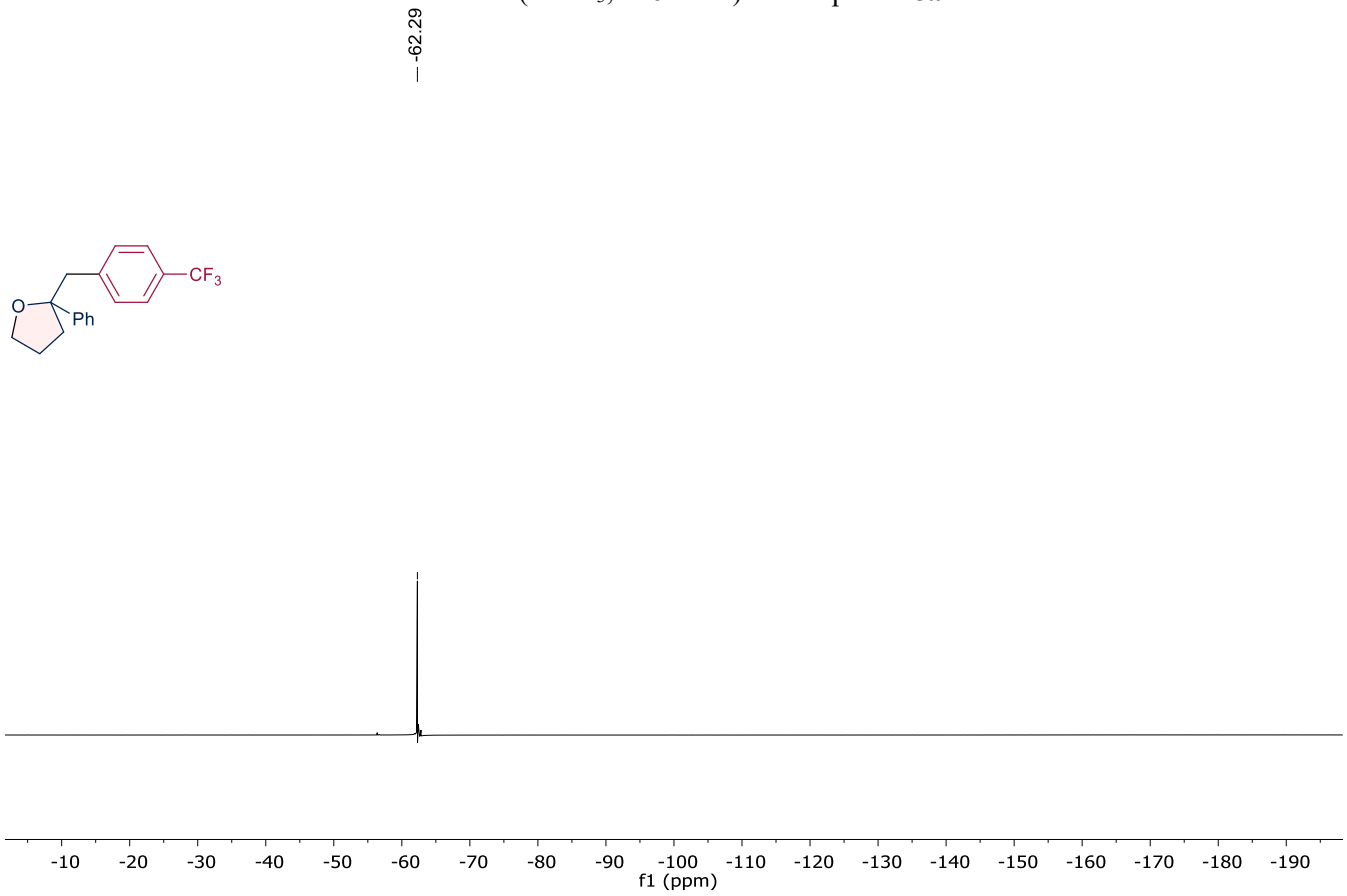
^{13}C NMR ($CDCl_3$, 101 MHz) of compound **7a**.



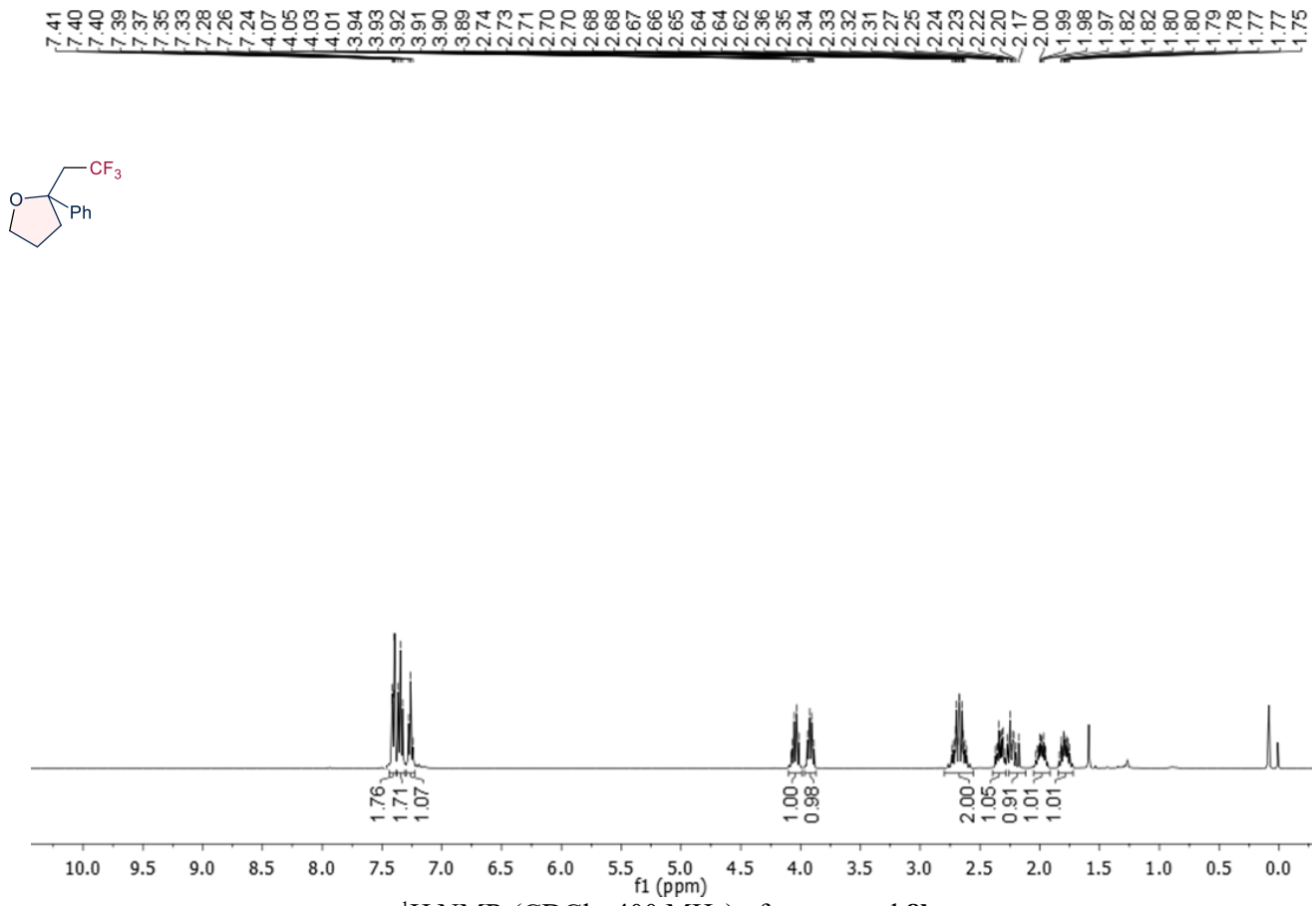
^{1}H NMR ($CDCl_3$, 300 MHz) of compound **8a**.



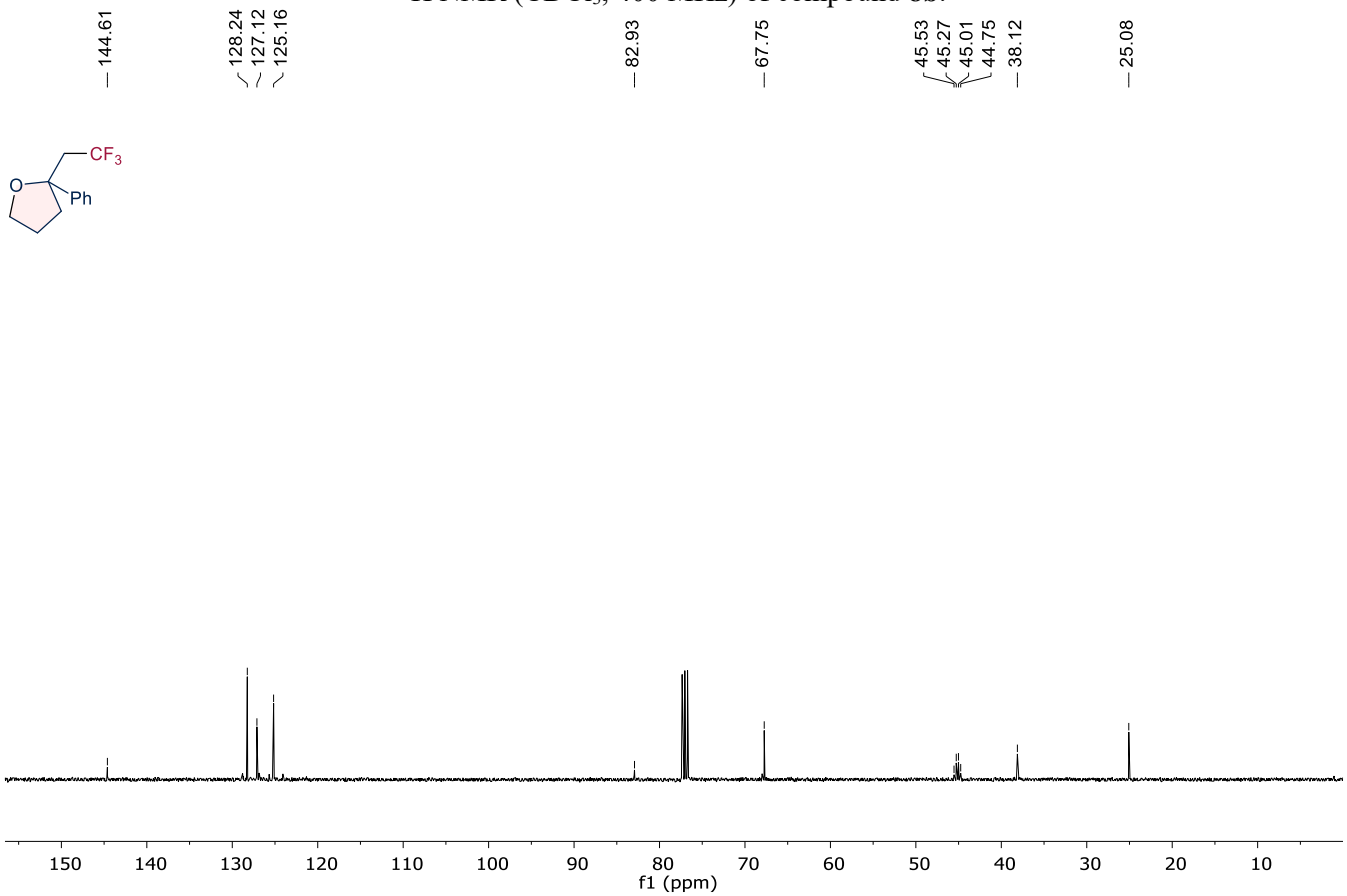
^{13}C NMR ($CDCl_3$, 126 MHz) of compound **8a**.



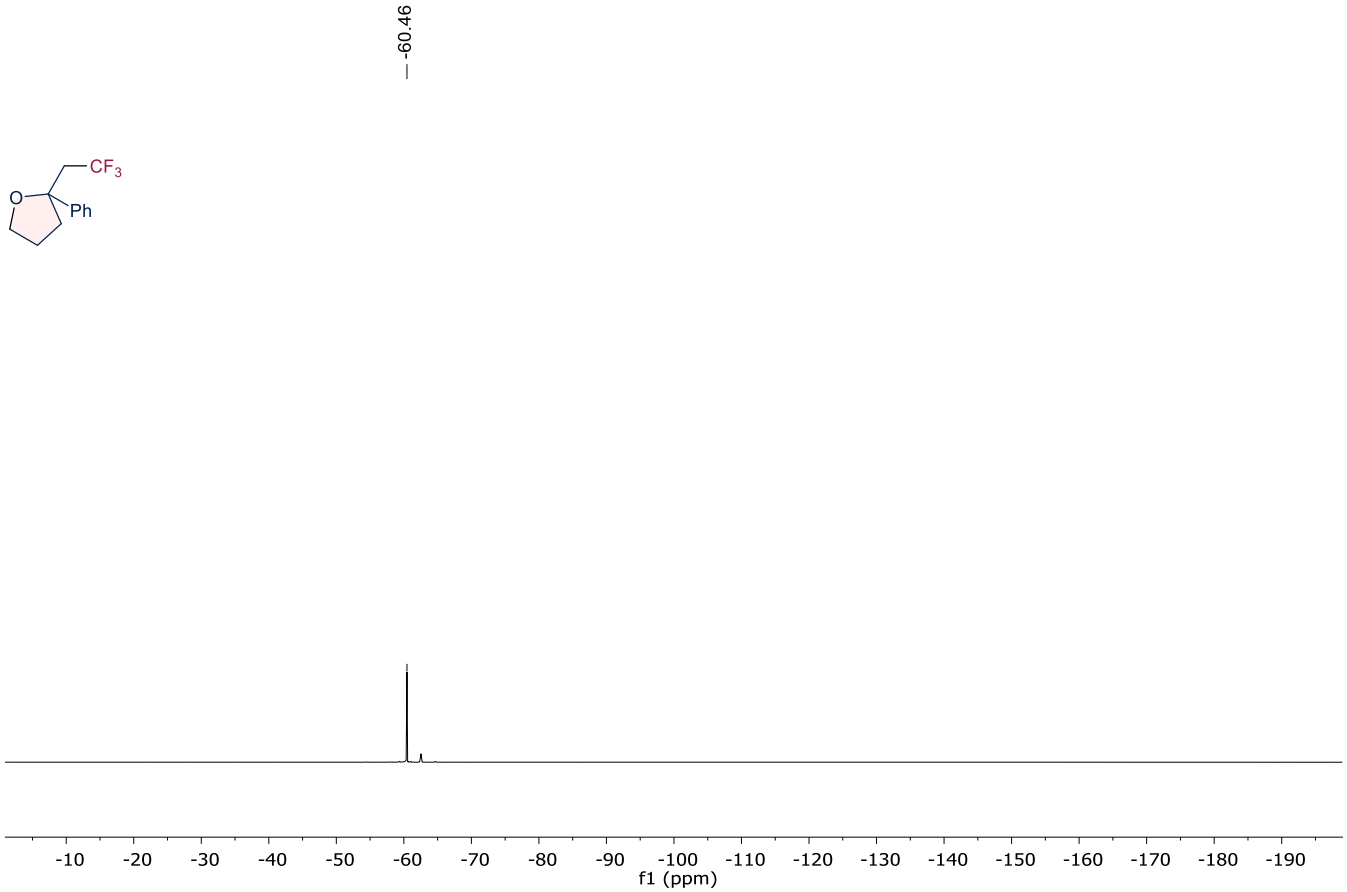
^{19}F NMR ($CDCl_3$, 282 MHz) of compound **8a**.



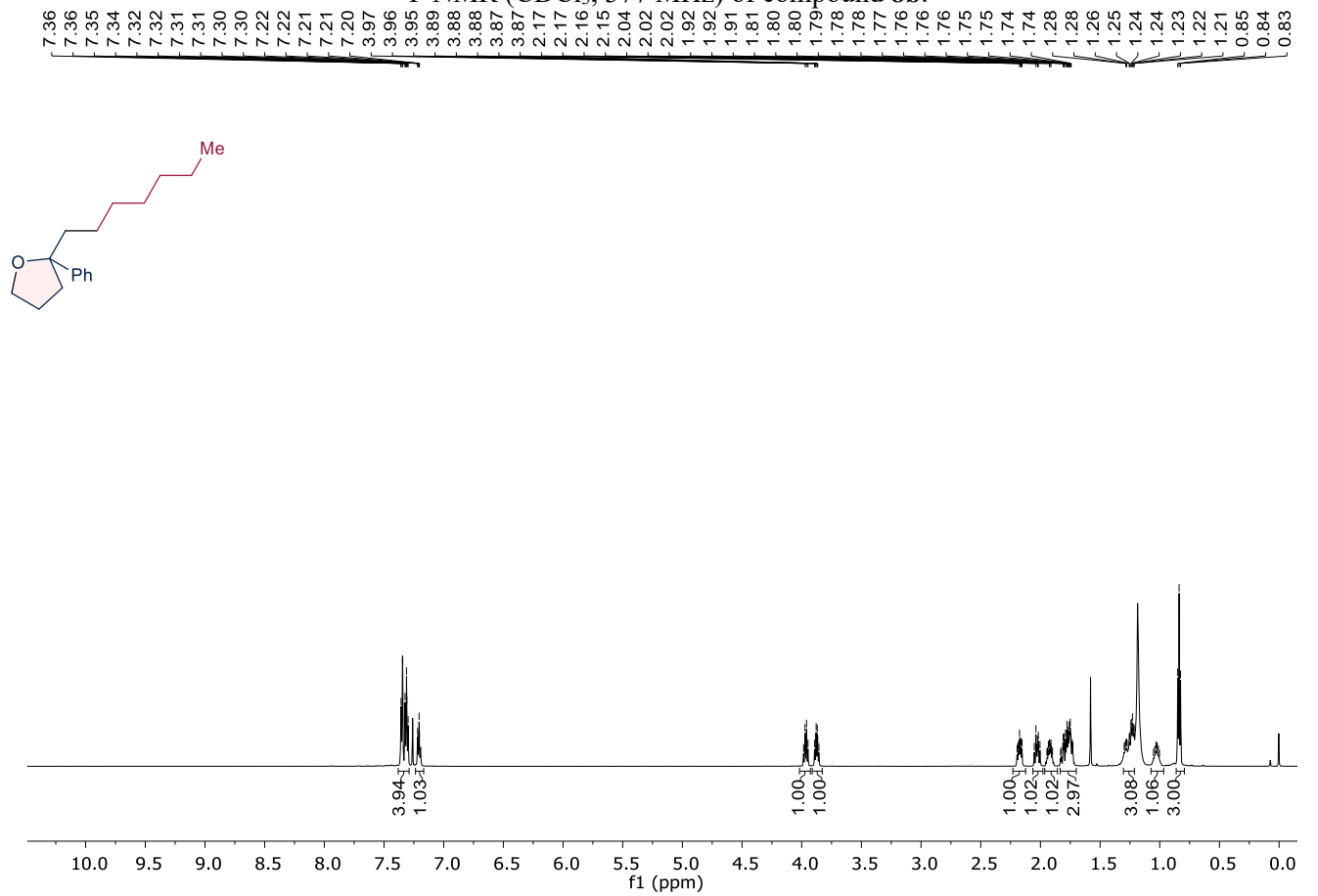
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **8b**.



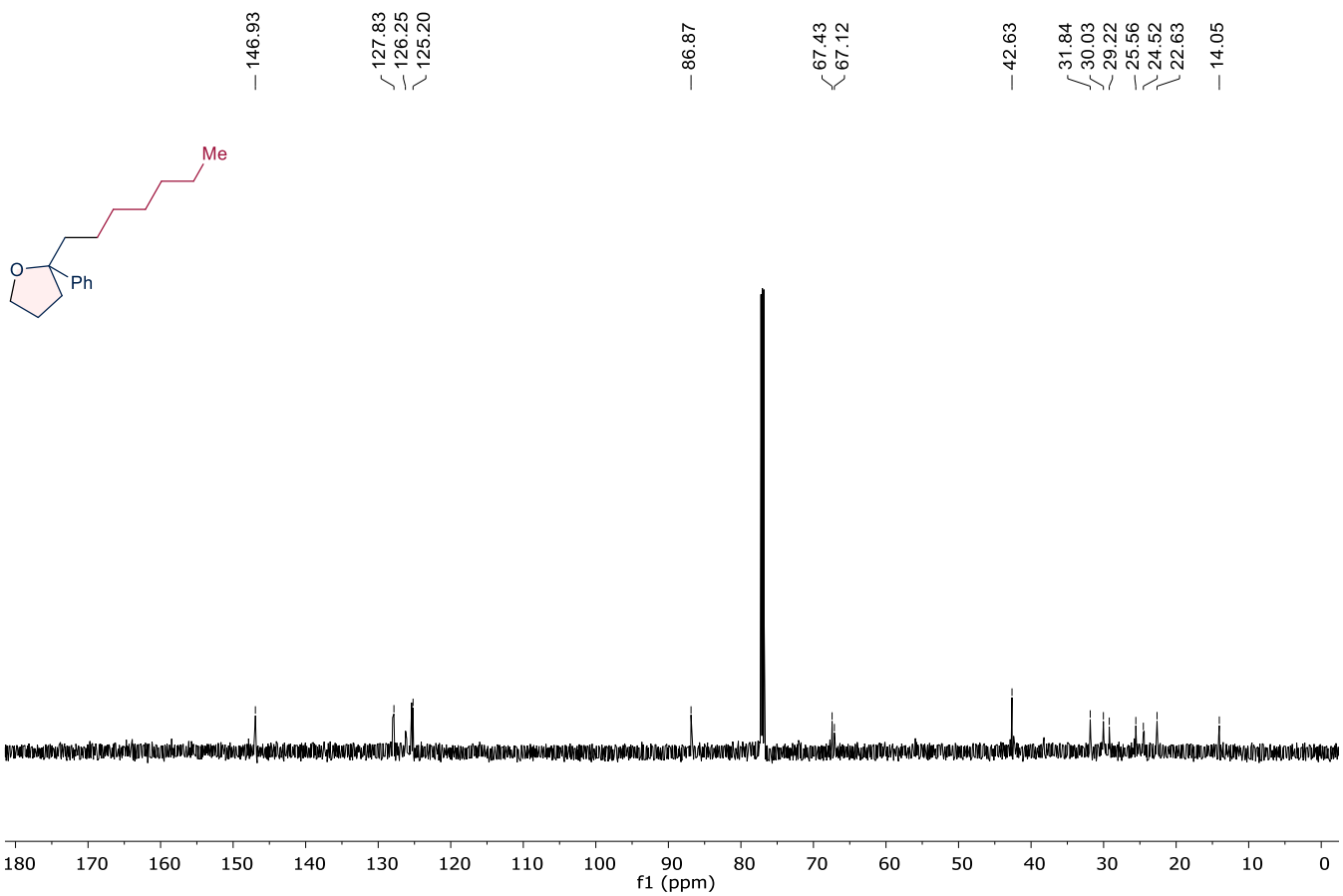
^{13}C NMR ($CDCl_3$, 1016 MHz) of compound **8b**.



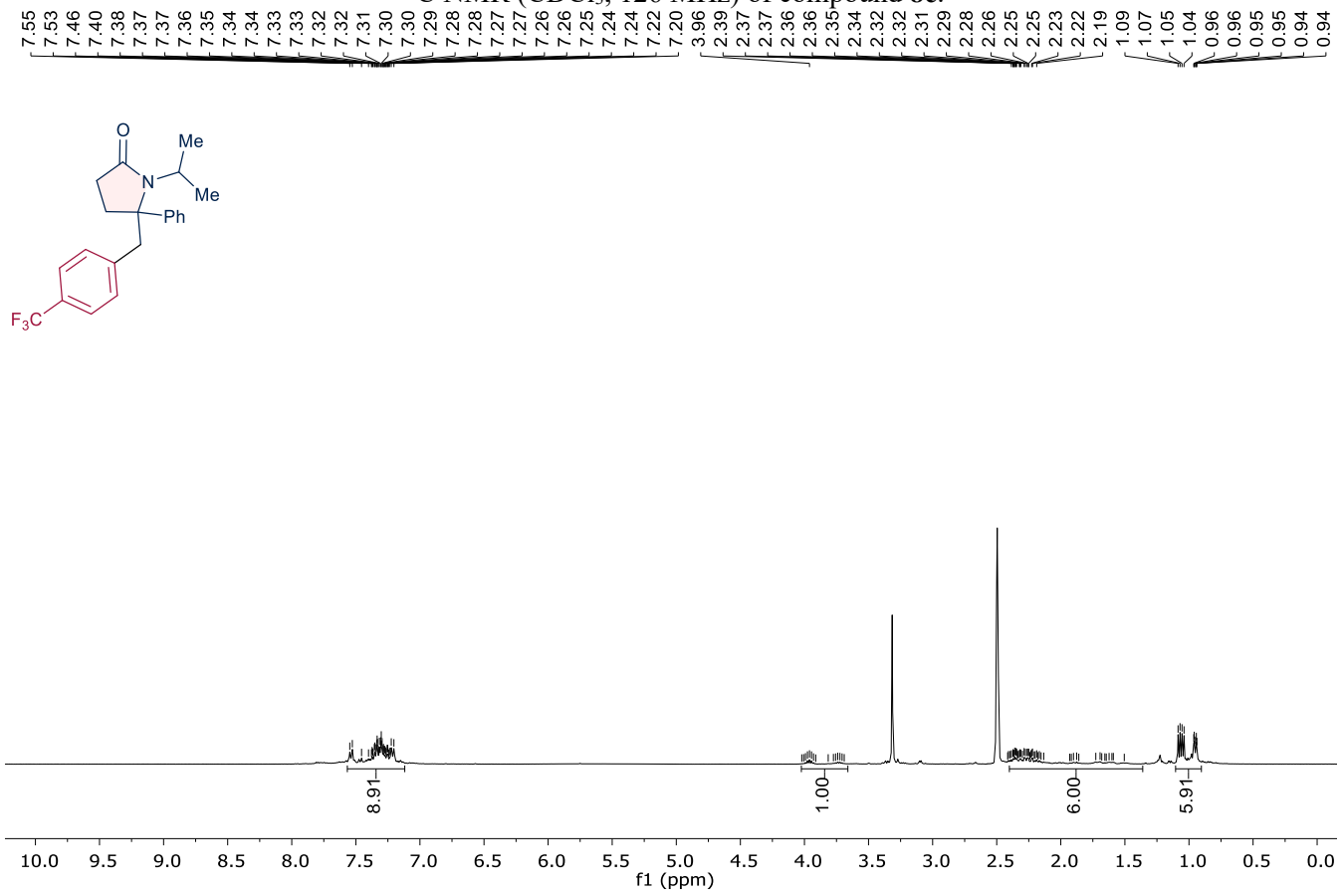
^{19}F NMR ($CDCl_3$, 377 MHz) of compound **8b**.



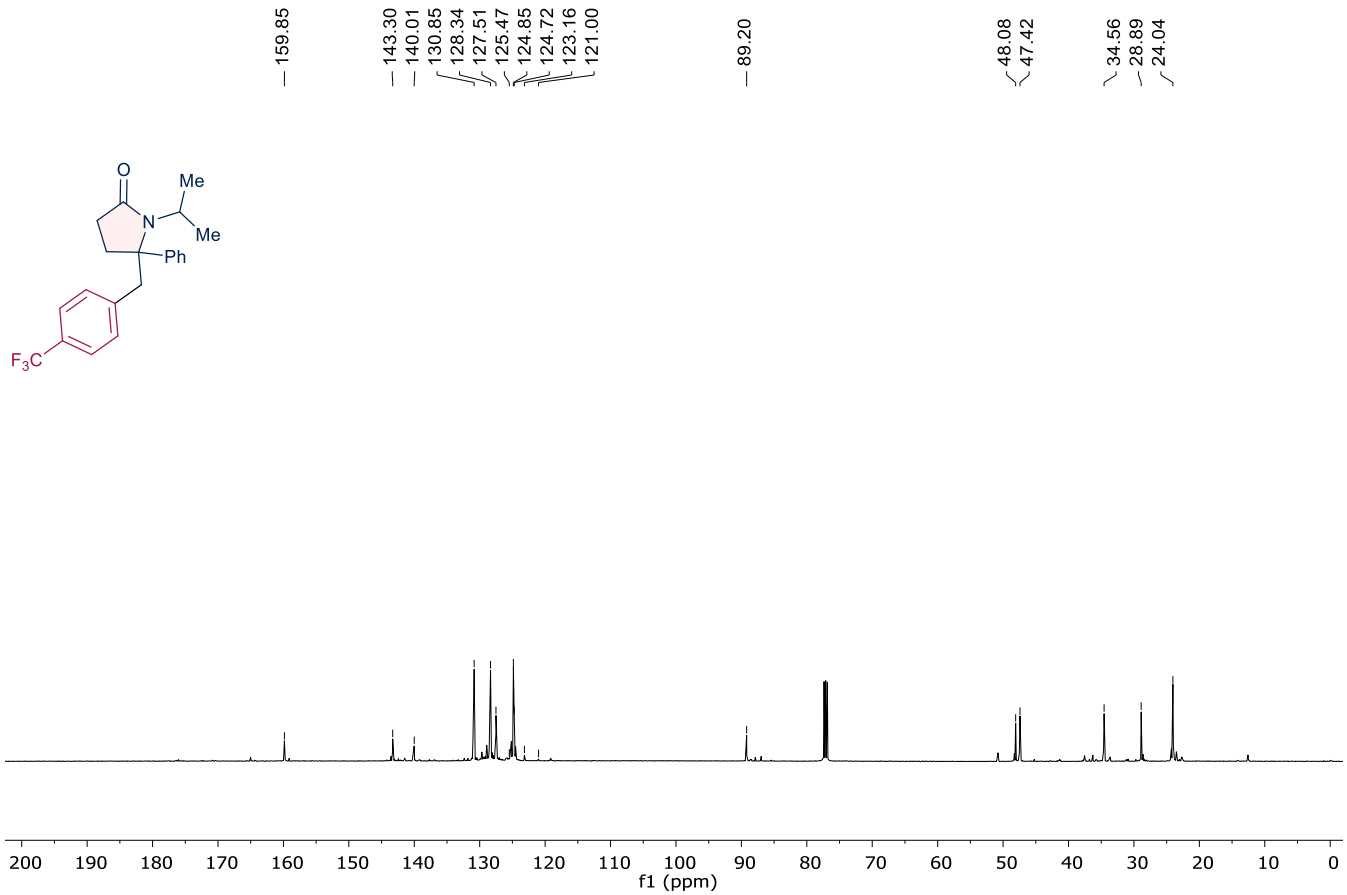
^{1}H NMR ($CDCl_3$, 600 MHz) of compound **8c**.



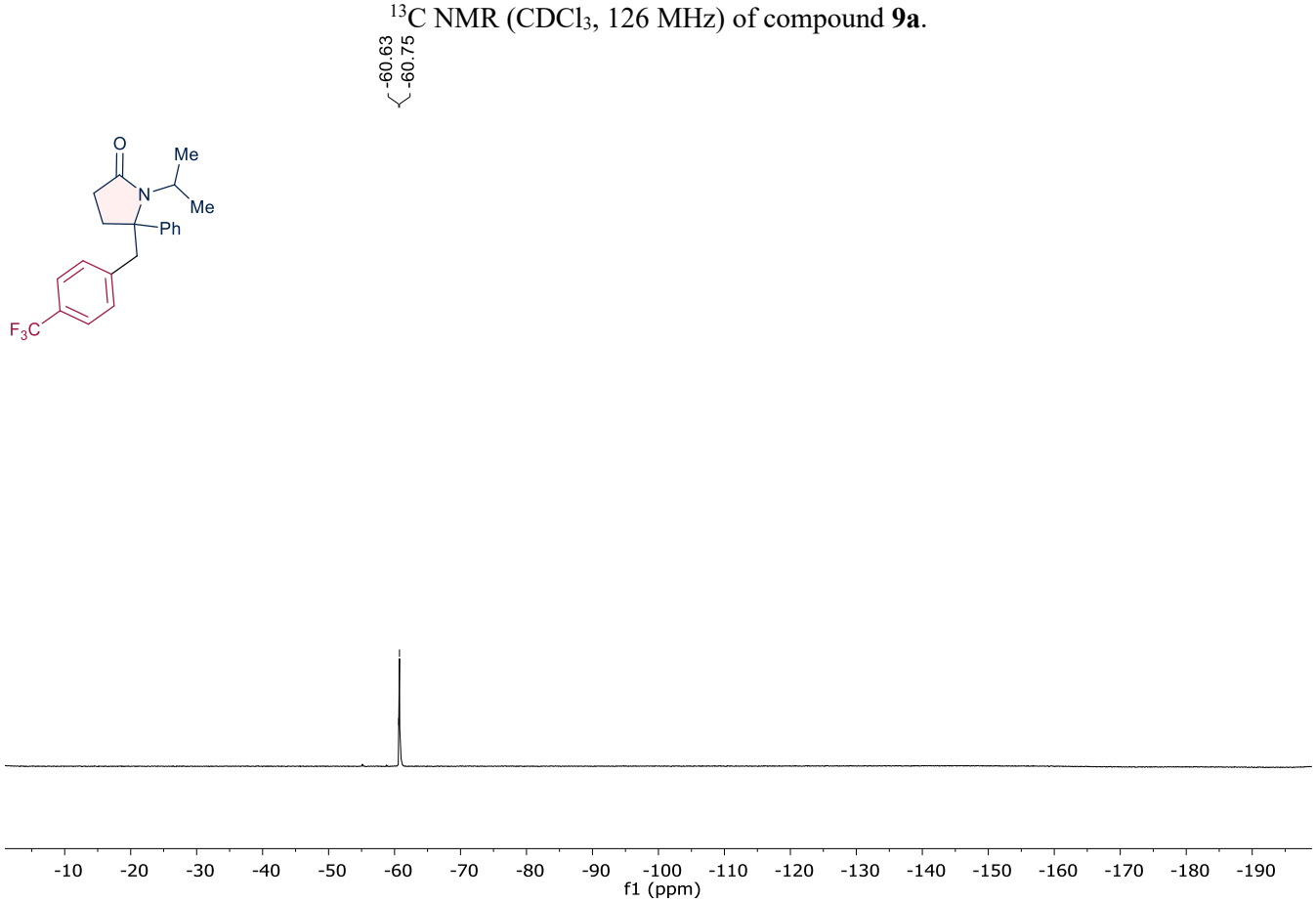
^{13}C NMR ($CDCl_3$, 126 MHz) of compound **8c**.



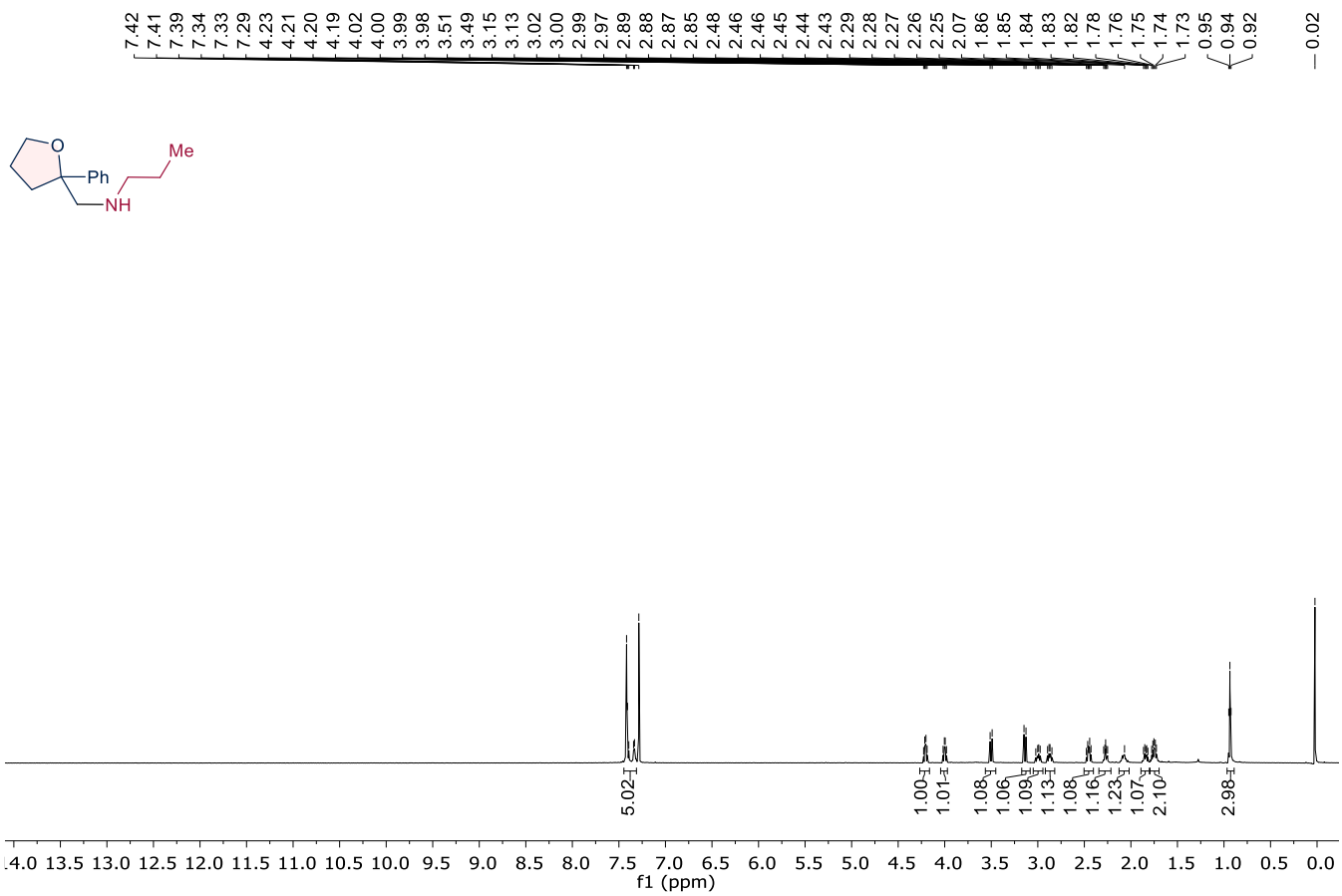
^{1}H NMR (d_6-DMSO, 400 MHz) of compound **9a**.



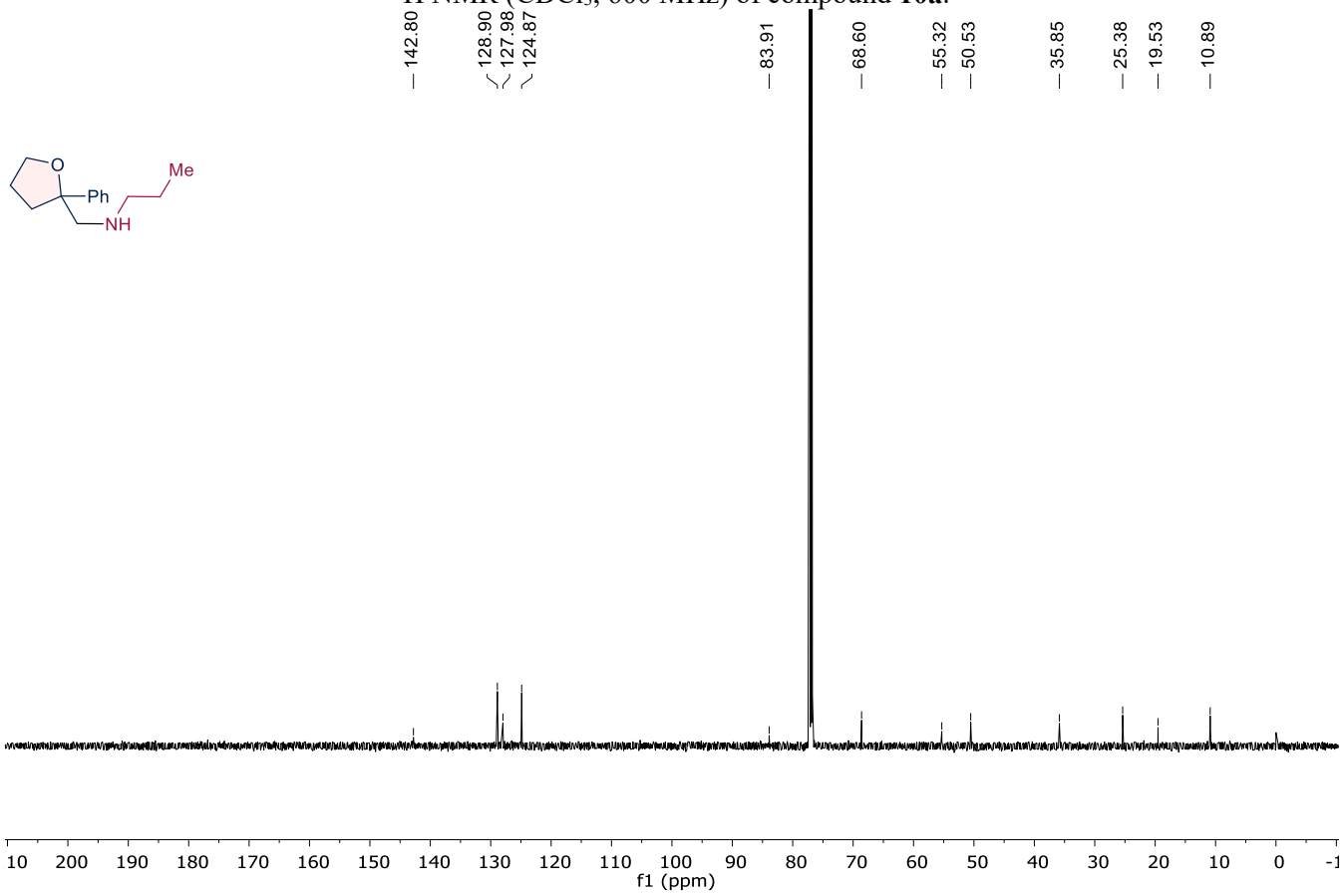
^{13}C NMR ($CDCl_3$, 126 MHz) of compound **9a**.



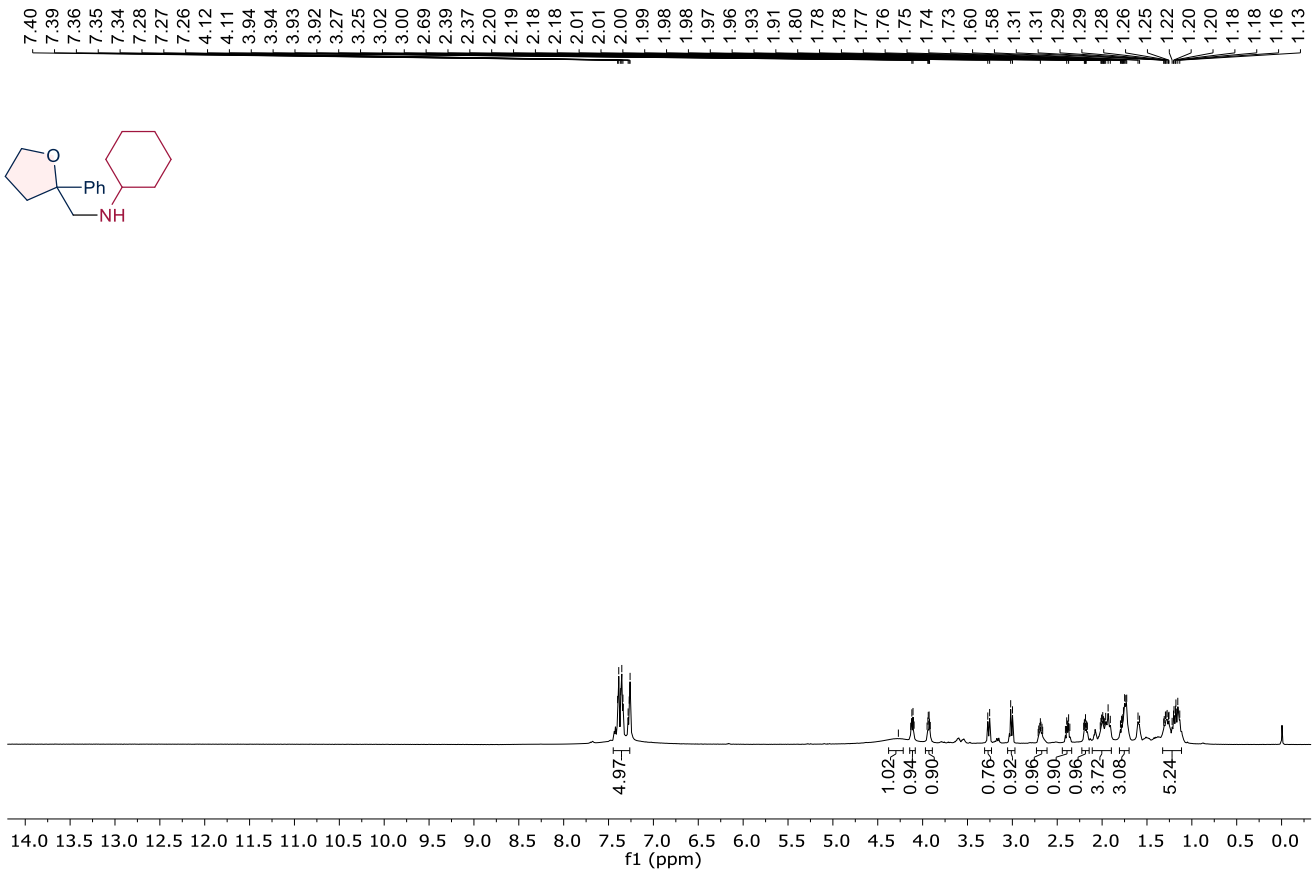
^{19}F NMR ($CDCl_3$, 377 MHz) of compound **9a**.



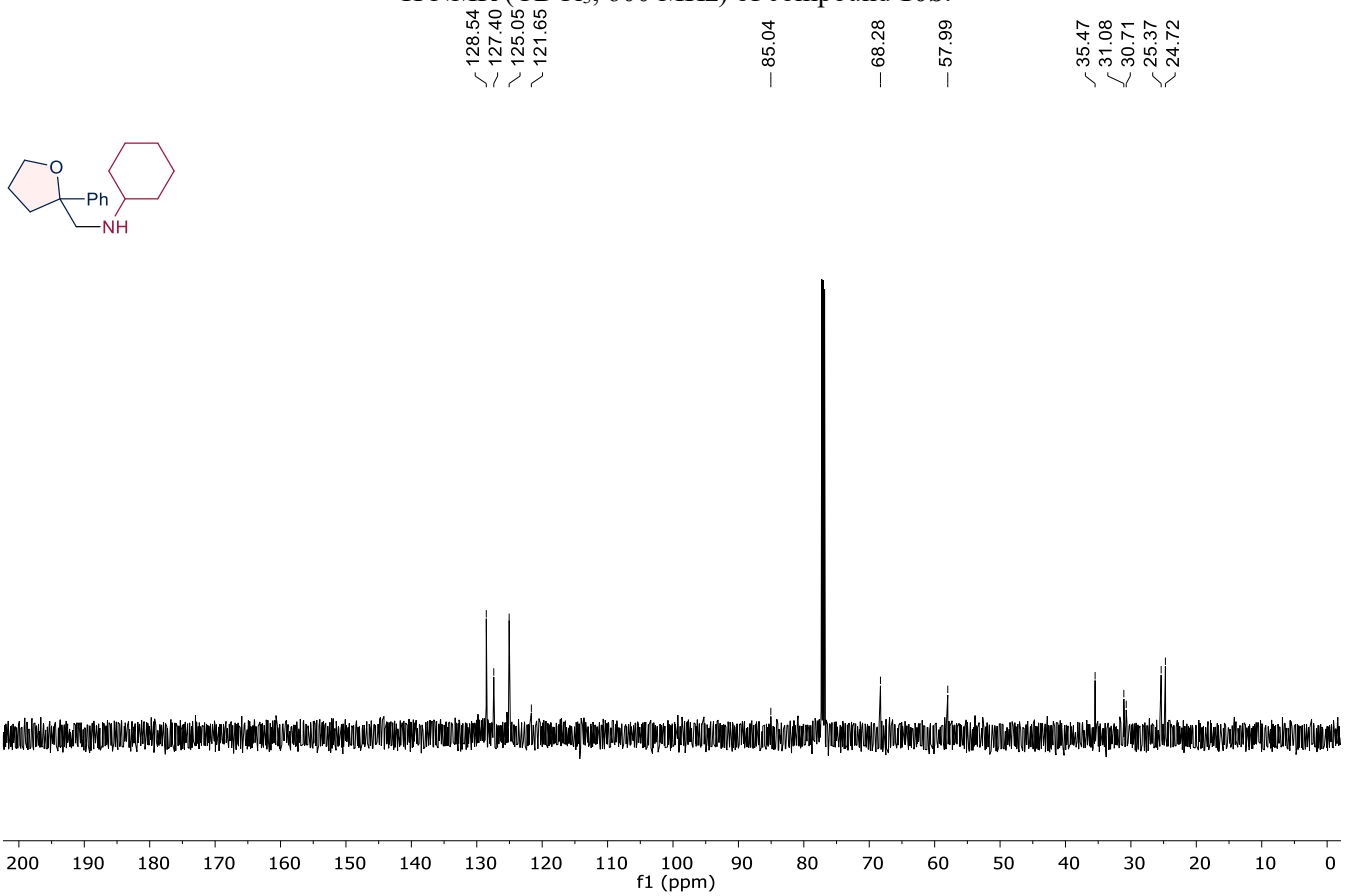
^{1}H NMR ($CDCl_3$, 600 MHz) of compound **10a**.



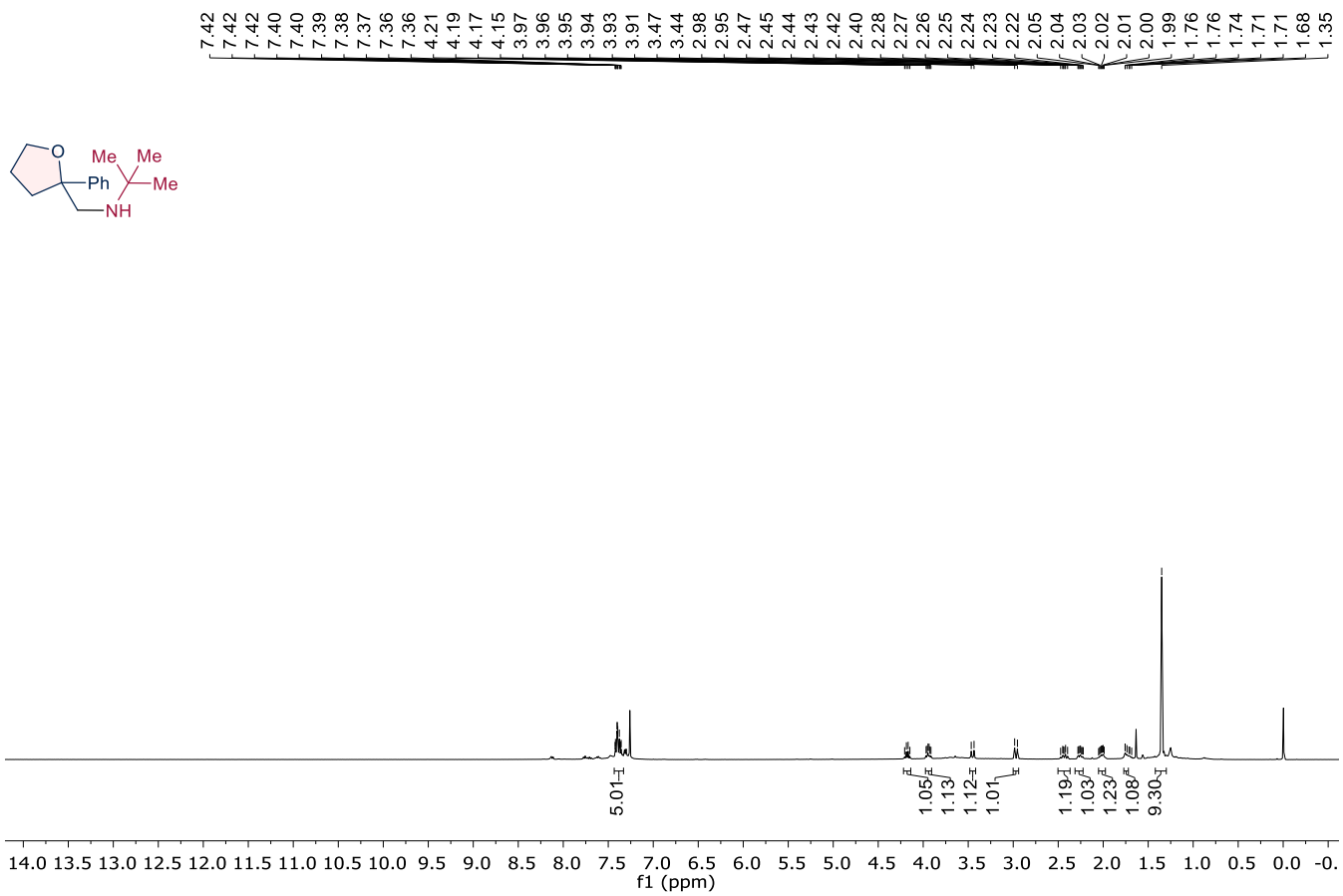
^{13}C NMR ($CDCl_3$, 151 MHz) of compound **10a**.



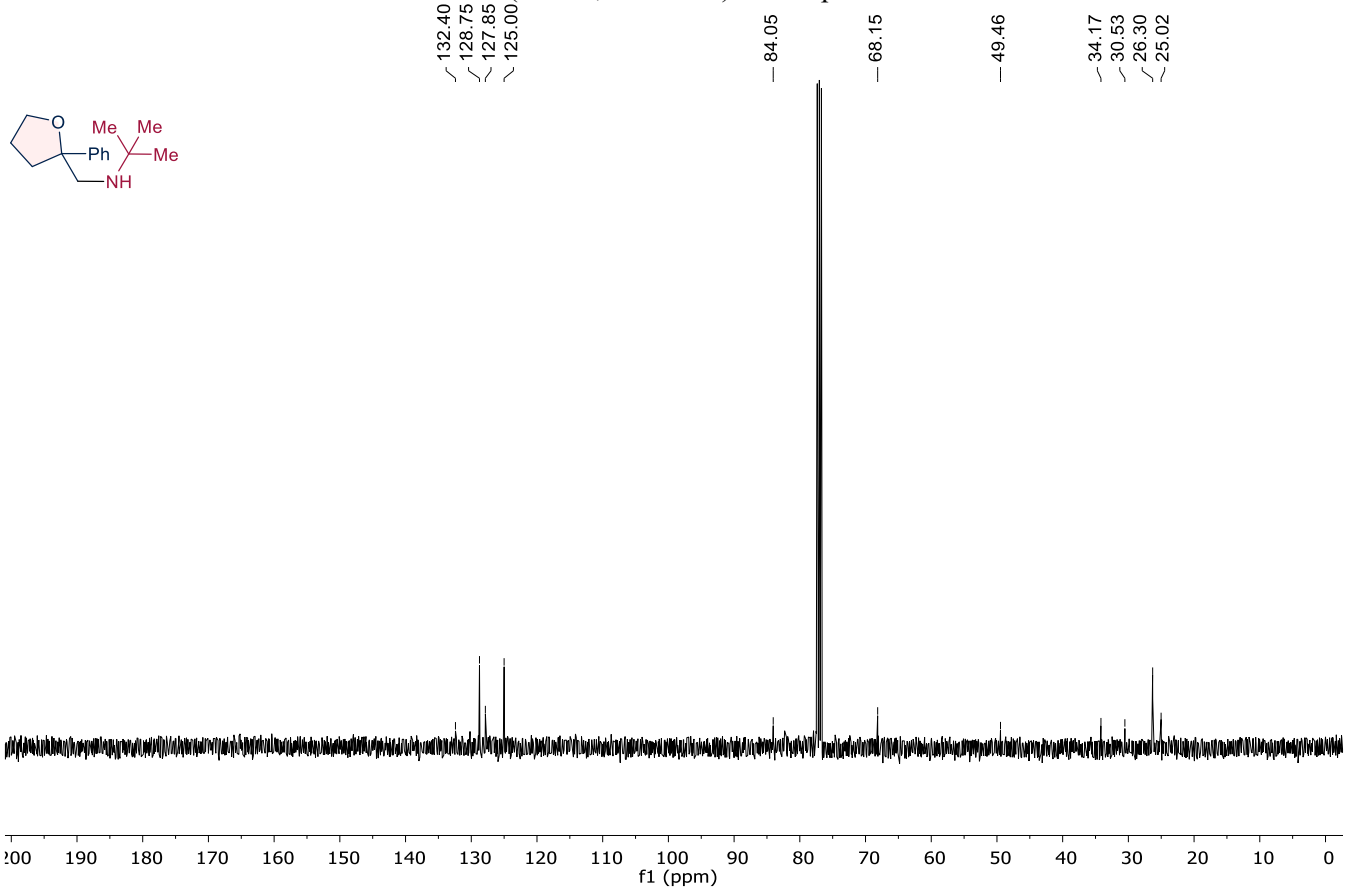
^{1}H NMR ($CDCl_3$, 600 MHz) of compound **10b**.



^{13}C NMR ($CDCl_3$, 151 MHz) of compound **10b**.



^{1}H NMR ($CDCl_3$, 400 MHz) of compound **10c**.



^{13}C NMR ($CDCl_3$, 151 MHz) of compound **10c**.