Supporting Information

for

Directed Regioselective Ortho,Ortho'-Magnesiations of Aromatics and Heterocycles using sBu$_2$Mg in Toluene

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Table of Content

1. General Information

All reactions were carried out under argon or nitrogen atmosphere in glassware dried with a heat gun (650 °C) under high vacuum (<1 mbar). Syringes which were used to transfer anhydrous solvents or reagents were purged thrice with argon or nitrogen prior to use. Indicated yields are isolated yields of compounds estimated to be >95% pure as determined by ^{1}H-NMR (25 °C) and capillary GC. Unless otherwise indicated, all reagents were obtained from commercial sources.

Solvents

Toluene was continuously refluxed and freshly distilled from sodium under nitrogen and stored over molecular sieves. THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen and stored over molecular sieves. Solvents for flash column chromatography were distilled prior to use.

Chromatography

Flash column chromatography was performed using SiO_2 60 (0.040-0.063 mm, 230-400 mesh ASTM) from Merck. Thin layer chromatography (TLC) was performed using aluminum plates covered with SiO_2 (Merck 60, F-254). Spots were visualized under UV light.

Analytical Data

^{1}H-NMR and **^{13}C-NMR** spectra were recorded on VARIAN Mercury 200, BRUKER ARX 300, VARIAN VXR 400 S and BRUKER AMX 600 instruments. Chemical shifts are reported as values in ppm relative to tetramethylsilane. $CDCl_3$ peaks were set to 7.26 ppm in ^{1}H NMR and 77.16 ppm in ^{13}C NMR experiments. The following abbreviations were used to characterize signal multiplicities: s (singlet), d (doublet), dd (doublet of doublets),t (triplet),q (quartet), hept (heptett)as well as m (multiplet).

Mass spectroscopy: High resolution (HRMS) and low resolution (MS) spectra were recorded on a FINNIGAN MAT 95Q instrument. Electron impact ionization (EI) was conducted with an ionization energy of 70 eV. For coupled gas chromatography/mass spectrometry, a HEWLETT-PACKARD HP 6890/MSD 5973 GC/MS system was used. Molecular fragments are reported starting at a relative intensity of 10-20%.

Infrared spectra (IR) were recorded from 4500 cm^{-1} to 650 cm^{-1}on a PERKIN ELMER Spectrum BX-59343 instrument. For detection a SMITHS DETECTION DuraSamplIR II Diamond ATR sensor was used. The main absorption peaks are reported in cm^{-1}.

Melting points (m.p.) were determined on a BÜCHI B-540 melting point apparatus and are uncorrected.

2. Reagents

All reagents were obtained from commercial sources and used without further purification unless otherwise stated.

***n*BuLi** and ***s*BuLi** solutions in hexane/cyclohexane were purchased from Albemarle and the concentration was determined by titration using 1,10-phenanthroline in THF with *i*PrOH.[1]

***s*BuMgCl** solution in Et_2O was purchased from Sigma-Aldrich and the concentration was determined by iodometric titration.

***s*Bu$_2$Mg**: A dry and argon-flushed Schlenk-flask equipped with a stirring bar and a septum, was charged with *s*BuMgCl (10.2 mL, 20 mmol, 1.95 M in Et_2O, 1.00 equiv). Then *s*BuLi (12.8 mL, 20 mmol, 1.56 M in cyclohexane, 1.00 equiv) was added at room temperature under vigorous stirring. The resulting suspension was stirred for 2 h at room temperature. The solvents were removed under vacuum followed by addition of dry toluene (40 mL). The resulting suspension was vigorously stirred and allowed to settle overnight. The colourless solution was carefully transferred by cannula using a syringe filter and titrated (benzoic acid and 4-(phenylazo)diphenylamine as indicator, 0.43-0.48 M, 96% yield) prior use.

^{1}H NMR (400 MHz, Toluene-d_8) δ (ppm) = 1.80 (pd, *J* = 7.2, 2.0 Hz, 4H), 1.45 (d, *J* = 7.9 Hz, 6H), 1.15 (t, *J* = 7.2 Hz, 6H), 0.02 (hept, *J* = 8.5 Hz, 2H).

Ph$_2$Mg[2], **(TMSCH$_2$)$_2$Mg**[3], ***t*Bu$_2$Mg**[4] and ***c*Hex$_2$Mg**[5] were prepared using the same procedure.

CuCN·2LiCl: A CuCN·2LiCl solution (1.00 M) was prepared by drying CuCN (80.0 mmol, 7.17 g) and LiCl (160 mmol, 6.77 g) in a Schlenk-flask under vacuum at 140 °C for 12 h. After cooling, dry THF (80 mL) was added and stirring was continued until the salts were dissolved.[6]

$ZnCl_2$: A $ZnCl_2$ solution (1.00 M) was prepared by drying $ZnCl_2$ (200 mmol, 27.3 g) in a Schlenk-flask under vacuum at 140 °C for 5 h. After cooling, dry THF (200 mL) was added and stirring continued until the salt was dissolved.

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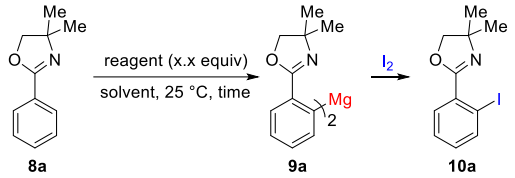
[1] J. Skotnitzki, A. Kremsmair, D. Keefer, Y. Gong, R. de Vivie-Riedle, P. Knochel, *Angew. Chem. Int. Ed.* **2020**, *59*, 320-324.
[2] I. Fujii, K. Semba, Q.-Z. Li, S. Sakaki, Y. Nakao, *J. Am. Chem. Soc.* **2020**, *142*, 11647-11652.
[3] J. Francos, S. Zaragoza-Calero, C. T. O'Hara, *Dalton Trans.* **2014**, *43*, 1408-1412.
[4] E. C. Ashby, G. E. Parris, *J. Am. Chem. Soc.* **1971**, *93*, 1206-1213.
[5] F. R. Jensen, K. L. Nakamaye, *J. Am. Chem. Soc.* **1968**, *90*, 3248-3250.
[6] P. Knochel, M. C. P. Yeh, S. C. Berk, J. Talbert, *J. Org. Chem.* **1988**, *53*, 2390-2392.

3. Optimization of the metalation

Table 1: Optimization of the metalation of oxazoline **8a**.



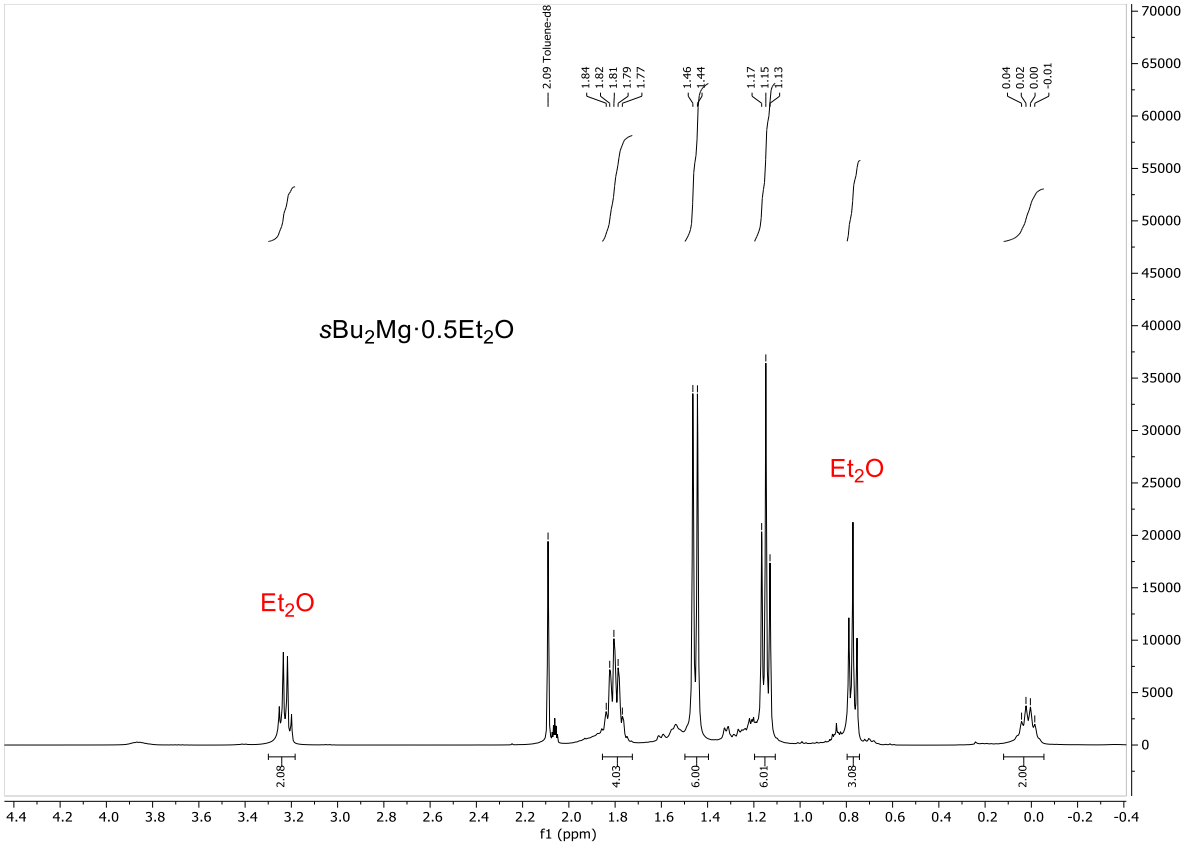
8a **9a** **10a**

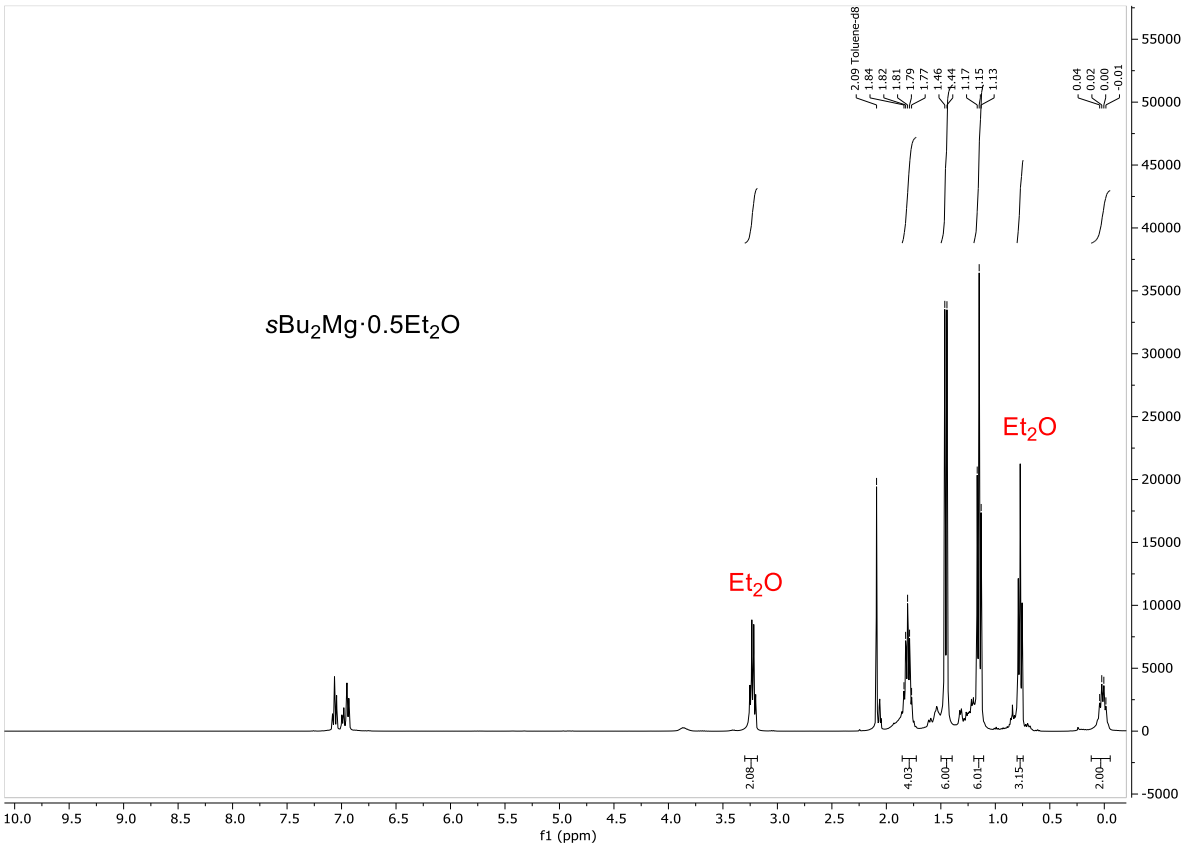
Entry	Reagent	Equivalents	Solvent	Time	Yield[a]
1	*s*BuMgCl	1.2	ether/toluene	1 h	0%
2	Ph_2Mg	0.6	toluene	1 h	0%
3	$(TMSCH_2)_2Mg$	0.6	toluene	1 h	0%
4	*t*Bu_2Mg	0.6	toluene	1 h	0%
5	*c*Hex_2Mg	0.6	toluene	0.5 h	26%
6	*c*Hex_2Mg	0.6	toluene	1 h	46%
7	*s*Bu_2Mg	0.6	cyclohexane	0.5 h	70%
8	*s*Bu_2Mg	0.6	cyclohexane	1 h	61%
9	*s*Bu_2Mg	0.55	toluene	0.5 h	62%
10	*s*Bu_2Mg	0.55	toluene	1 h	78%
11	*s*Bu_2Mg	0.6	toluene	0.5 h	74%
12	*s*Bu_2Mg	0.6	toluene	1 h	91%
13	*s*Bu_2Mg	0.6	toluene	1.5 h	85%
14	*s*Bu_2Mg	0.6	THF	1 h	73%

[a] Calibrated GC-yield using undecane as internal standard.

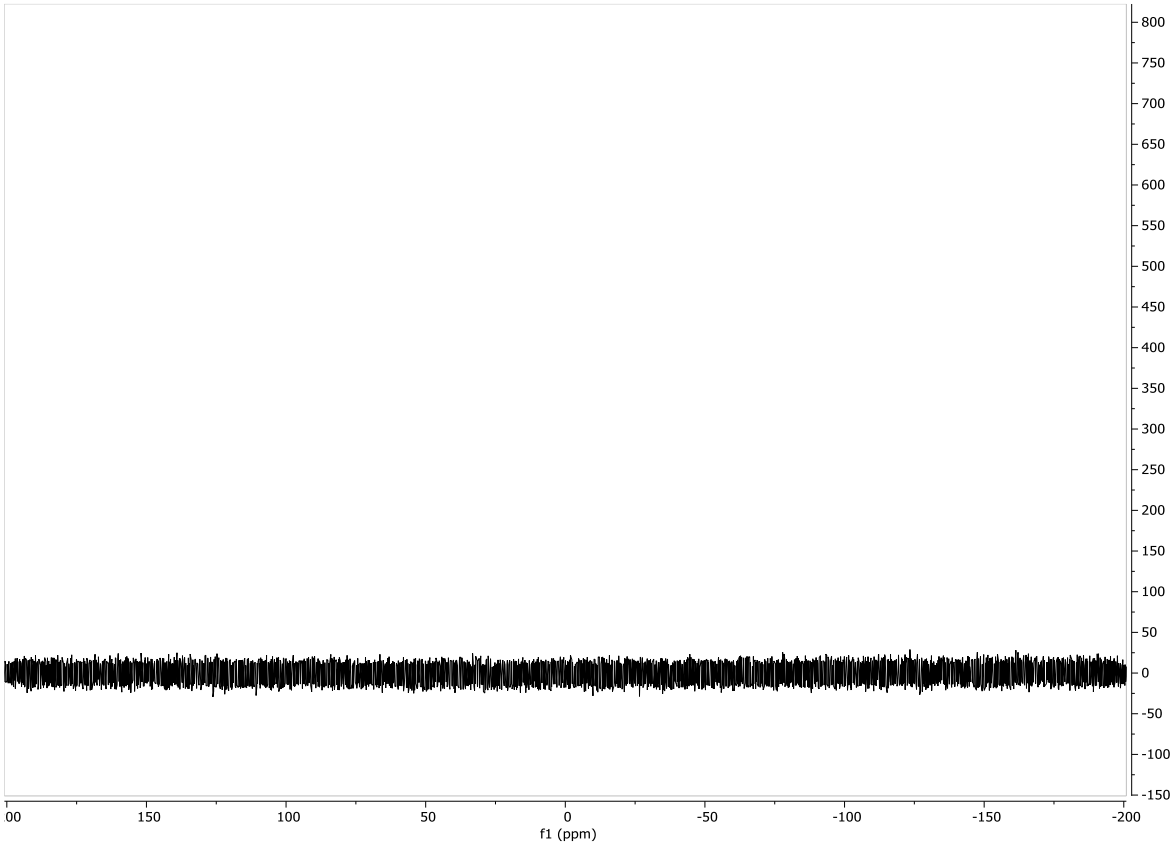
NMR studies on *s*Bu_2Mg:

The amount of complexed ether was determined as 0.5 equiv with respect to1.0 equiv *s*Bu_2Mg.

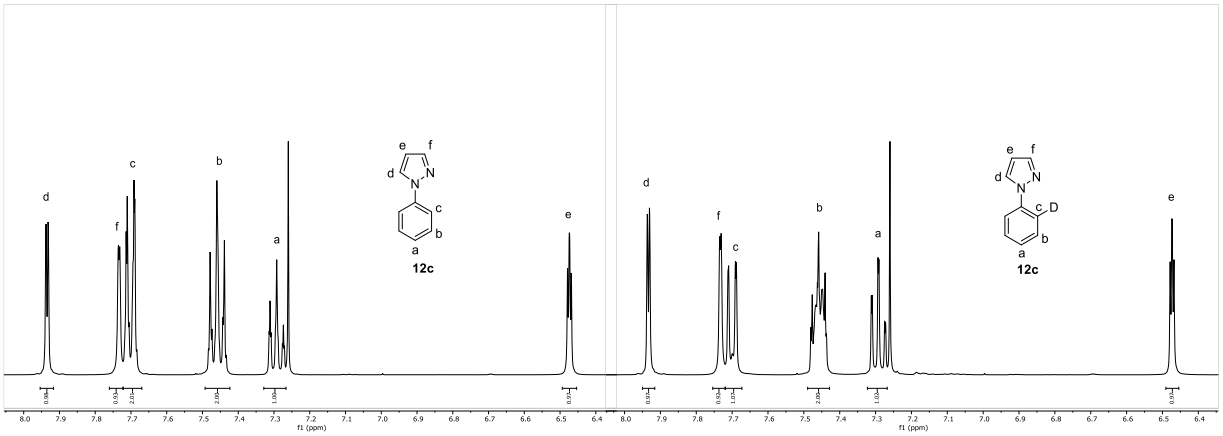




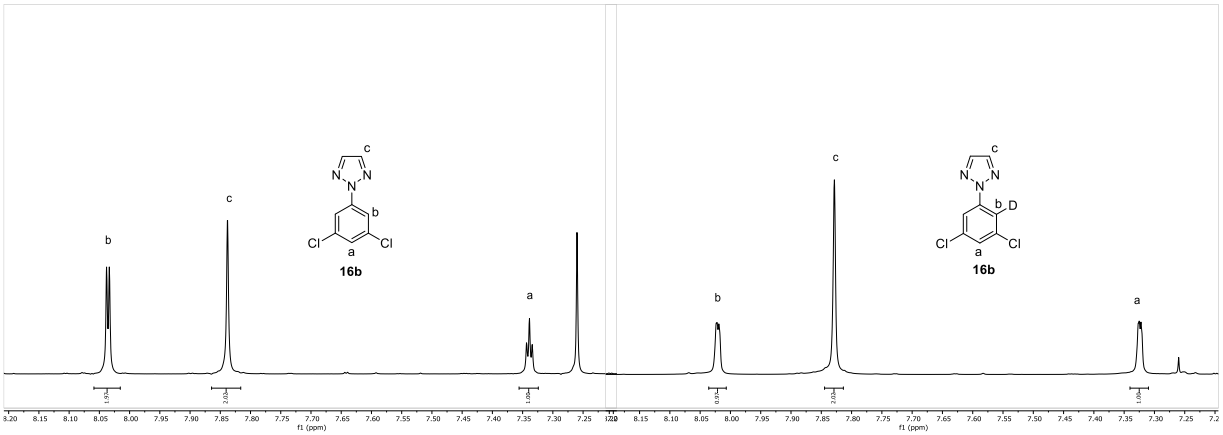
^{7}Li-NMR of *s*Bu_2Mg in toluene-d_8:



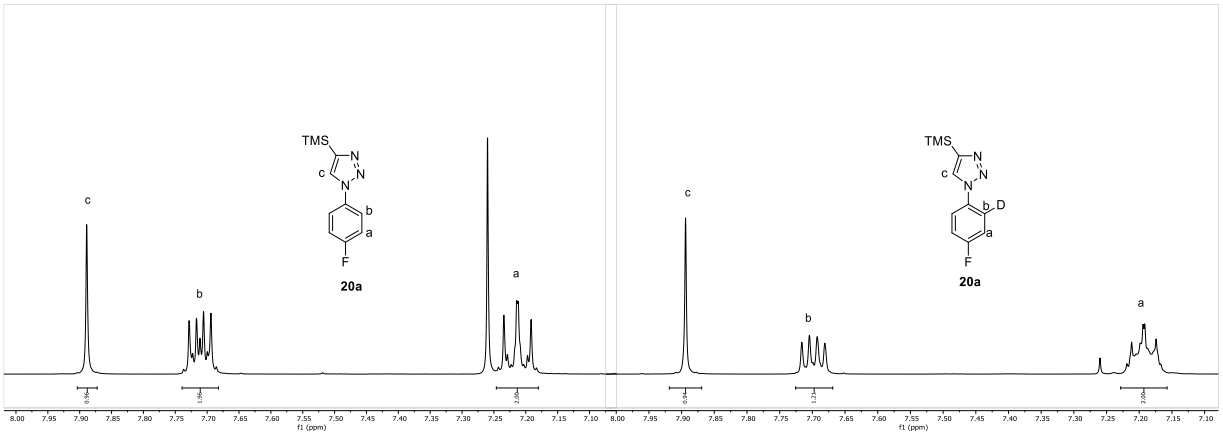
Deuterolysis experiments:



Metalation yield = 94%; Ratio c:d:f = 98:1:1.



Metalation yield = 100%; Ratio b:c = >99:1.



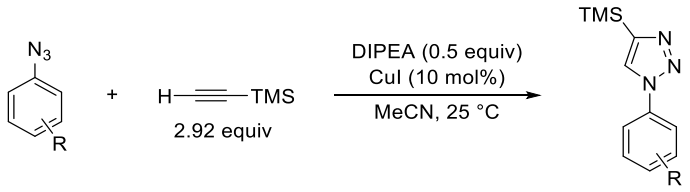
Metalation yield = 75%; Ratio b:c = 97:3.

4. Typical Procedures

Typical Procedure 1 (TP1): Regioselective metalation and functionalization using *s*Bu_2Mg

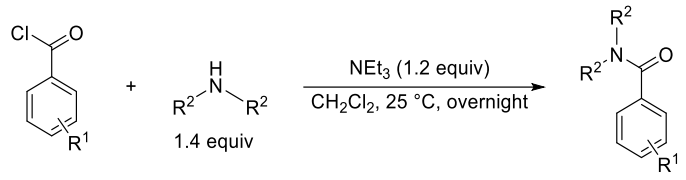
A dry and argon flushed Schlenk-tube, equipped with a magnetic stirring bar and a septum, was charged with the corresponding substrate (1.0 equiv) in dry toluene (0.5 M solution). The resulting solution was stirred at indicated temperature and *s*Bu_2Mg (0.60-0.80 equiv) was added dropwise. The completion of the metalation was checked by GC-analysis of reaction aliquots quenched with iodine, using undecane as internal standard. Subsequent reactions with electrophiles (1.2 equiv) were carried out under the indicated conditions. After complete conversion, the mixture was quenched with sat. aq. NH_4Cl solution and extracted with ethyl acetate (3 x 10 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated. Purification of the crude product by flash column chromatography using an indicated eluent afforded the corresponding title compounds.

Typical Procedure 2 (TP2): Preparation of 1-aryl-4-trimethylsilyl-1*H*-1,2,3-triazoles



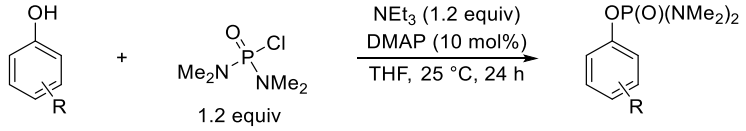
A dry and argon flushed Schlenk-tube, equipped with a magnetic stirring bar and a septum, was charged with the corresponding aromatic azide (30.0 mmol, 1.0 equiv) and dissolved in dry acetonitrile (20 mL). Copper(I)-iodide (3.0 mmol, 10 mol%), trimethylsilylacetylene (87.7 mmol, 2.92 equiv) and DIPEA (15.0 mmol, 0.5 equiv) were added and the reaction mixture was stirred for a indicated time at room temperature. The reaction mixture was quenched with water, filtered through a short pad of celite and extracted with ethyl acetate (3 x 30 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography.

Typical Procedure 3 (TP3): Preparation of aryl amides



A dry and argon flushed Schlenk-tube, equipped with a magnetic stirring bar and a septum, was charged with the corresponding aromatic acid chloride (20.0 mmol, 1.0 equiv) and dissolved in dry dichloromethane (20 mL). NEt_3 (24.0 mmol, 1.2 equiv) was added and the corresponding amine (28.0 mmol, 1.4 equiv) was added dropwise at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was quenched with sat. aq. $NaHCO_3$ solution and extracted with dichloromethane (3 x 30 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude products were purified by flash column chromatography.

Typical Procedure 4 (TP4): Preparation of aryl phosphordiamidate derivatives

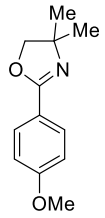


The described preparation was performed according to a modified literature procedure.[7] A dry and argon flushed Schlenk-tube, equipped with a magnetic stirring bar and a septum, was charged with the corresponding phenol (20.0 mmol, 1.0 equiv) and DMAP (2.0 mmol, 10 mol%) and subsequently dissolved in dry THF (20 mL). NEt_3 (24.0 mmol, 1.2 equiv) and *N,N,N',N'*-tetramethylphosphordiamidic chloride (24.0 mmol, 1.2 equiv) were added and the reaction mixture was stirred for 24 h at room temperature. The mixture was quenched with brine (20 mL) and extracted with ethyl acetate (3 x 30 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude products were purified by flash column chromatography.

[7] M. Balkenhohl, B. Heinz, T. Abegg, P. Knochel, *Org. Lett.* **2018**, *24*, 8057-8060.

5. Starting Materials

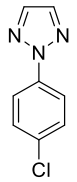
2-(4-Methoxyphenyl)-4,4-dimethyl-4,5-dihydrooxazole (8b)



2-(4-Methoxyphenyl)-4,4-dimethyl-4,5-dihydrooxazole (**8b**) was prepared according to a literature procedure.[8]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.92–7.87 (m, 2H), 6.93–6.88 (m, 2H), 4.09 (s, 2H), 3.84 (s, 3H), 1.38 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 162.0, 130.0, 120.2, 113.66, 79.1, 67.3, 55.3, 28.4.

2-(4-Chlorophenyl)-2*H*-1,2,3-triazole (16a)



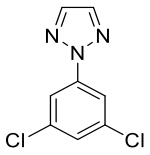
2-(4-Chlorophenyl)-2*H*-1,2,3-triazole (**16a**) was prepared according to modified literature procedures.[9] 4-chlorophenylhydrazine hydrochloride (8.95 g, 50.0 mmol, 1.0 equiv) was suspended in water (100 mL). Sodium acetate trihydrate (20.41 g, 150.0 mmol, 3.0 equiv) was added followed by dropwise addition of an aqueous solution of glyoxal (40% in water, 3.63 mL, 25.0 mmol, 0.5 equiv). The reaction mixture was vigorously stirred for 2 h. The yellow precipitate was filtrated, dried and used without further purification. A dry and argon flushed three-necked flask, equipped with a magnetic stirring bar, reflux condenser and a septum, was charged with the dry osazone and diluted in toluene (25 mL). Copper(II) triflate (0.27 g, 3 mol%) was added and the reaction mixture was heated to reflux for 48 h. The reaction mixture was cooled to room temperature, filtered through a short pad of celite and

[8] D. A. Gutierrez, W.-C. C. Lee, Y. Shen, J. J. Li, *Tetrahedron Lett.* **2016**, *57*, 5372-5376.
[9] (a) J. L. Riebsomer, *J. Org. Chem.* **1948**, *13*, 815-821. (b) G. F. Myachina, T. G. Ermakova, N. P. Kuznetsova, R. G. Sultangareev, L. I. Larina, L. V. Klyba, G. T. Suchanov, B. A. Trofimov, *Chem. Heterocycl. Cmpd.* **2010**, *46*, 79-81.

concentrated *in vacuo*. The crude product was purified by flash column chromatography (silica gel, *i*hexane/EtOAc = 99:1) affording 2-(4-Chlorophenyl)-2*H*-1,2,3-triazole as an orange solid (**16a**, 2.991 g, 16.7 mmol, 67% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.08–8.00 (m, 2H), 7.82 (s, 2H), 7.49–7.42 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 138.8, 136.2, 133.6, 129.8, 120.5.

2-(3,5-Dichlorophenyl)-2*H*-1,2,3-triazole (16b)

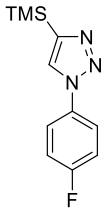


2-(3,5-Dichlorophenyl)-2*H*-1,2,3-triazole (**16b**) was prepared according to modified literature procedures.[10] 3,5-dichlorophenylhydrazine hydrochloride (14.16 g, 80.0 mmol, 1.0 equiv) was suspended in water (160 mL). Sodium acetate trihydrate (32.66 g, 240.0 mmol, 3.0 equiv) was added followed by dropwise addition of an aqueous solution of glyoxal (40% in water, 5.81 mL, 40.0 mmol, 0.5 equiv). The reaction mixture was vigorously stirred for 2 h. The yellow precipitate was filtrated, dried and used without further purification. A dry and argon flushed three-necked flask, equipped with a magnetic stirring bar, reflux condenser and a septum, was charged with the dry osazone and diluted in toluene (40 mL). Copper(II) triflate (0.95 g, 3 mol%) was added and the reaction mixture was heated to reflux for 48 h. The reaction mixture was cooled to room temperature, filtered through a short pad of celite and concentrated *in vacuo*. The crude product was purified by flash column chromatography (silica gel, *i*hexane/EtOAc = 99:1) affording 2-(3,5-dichlorophenyl)-2*H*-1,2,3-triazole as a brown solid (**16b**, 4.691 g, 22.0 mmol, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.04 (d, *J* = 1.9 Hz, 2H), 7.84 (s, 2H), 7.34 (t, *J* = 1.9 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 140.9, 136.4, 135.8, 127.4, 117.5.

[10] J. L. Riebsomer, *J. Org. Chem.* **1948**, *13*, 815-821; G. F. Myachina, T. G. Ermakova, N. P. Kuznetsova, R. G. Sultangareev, L. I. Larina, L. V. Klyba, G. T. Suchanov, B. A. Trofimov, *Chem. Heterocycl. Cmpd.* **2010**, *46*, 79-81.

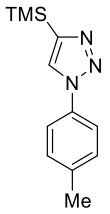
1-(4-Fluorophenyl)-4-(trimethylsilyl)-1*H*-1,2,3-triazole (20a)



1-(4-Fluorophenyl)-4-(trimethylsilyl)-1*H*-1,2,3-triazole (**20a**) was prepared according to **TP 2** using 1-azido-4-fluorobenzene. The reaction was complete after 48 h. The crude product was purified by flash column chromatography (silica gel, *i*hexane/EtOAc = 9:1) affording the desired compound as a pale brown solid (**20a**, 5.72 g, 24.3 mmol, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.89 (s, 1H), 7.74–7.68 (m, 2H), 7.24–7.18 (m, 2H), 0.38 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 163.2, 160.8, 147.3, 133.2, 133.1, 127.1, 122.5, 122.5, 116.5, 116.2, -1.4.
Analytical data was equivalent to literature.[11]

1-(*p*-Tolyl)-4-(trimethylsilyl)-1*H*-1,2,3-triazole (20c)

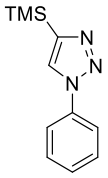


1-(*p*-Tolyl)-4-(trimethylsilyl)-1*H*-1,2,3-triazole (**20c**) was prepared according to **TP 2** using 1-azido-4-methylbenzene. The reaction was complete after 24 h. The crude product was purified by flash column chromatography (silica gel, *i*hexane/EtOAc = 9:1) affording the desired compound as a pale brown solid (**20c**, 4.33 g, 18.7 mmol, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.89 (s, 1H), 7.64–7.58 (m, 2H), 7.33–7.28 (m, 2H), 2.42 (s, 3H), 0.37 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 148.2, 139.6, 135.9, 131.2, 128.2, 121.8, 22.2, 0.0.
Analytical data was equivalent to literature.[11]

[11] F. H. Lutter, L. Grokenberger, L. A. Perego, D. Broggini, S. Lemaire, S. Wagschal, P. Knochel, *Nat. Comm.* **2020**, *11*, 4443.

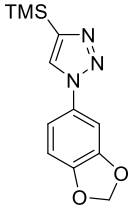
1-Phenyl-4-(trimethylsilyl)-1*H*-1,2,3-triazole (20d)



1-Phenyl-4-(trimethylsilyl)-1*H*-1,2,3-triazole (**20d**) was prepared according to **TP 2** using azidobenzene. The reaction was complete after 48 h. The crude product was purified by flash column chromatography (silica gel, *i*hexane/EtOAc = 6:1) affording the desired compound as a pale brown solid (**20d**, 4.35 g, 20.0 mmol, 67% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.94 (s, 1H), 7.78–7.70 (m, 2H), 7.56–7.47 (m, 2H), 7.47–7.38 (m, 1H), 0.38 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 147.3, 137.1, 129.8, 128.7, 127.3, 120.9, -0.9.
Analytical data was equivalent to literature.[11]

1-(Benzo[*d*][1,3]dioxol-5-yl)-4-(trimethylsilyl)-1*H*-1,2,3-triazole (20e)

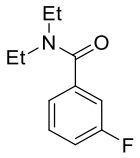


1-(Benzo[*d*][1,3]dioxol-5-yl)-4-(trimethylsilyl)-1*H*-1,2,3-triazole (**20e**) was prepared according to **TP 2** using 5-azidobenzo[*d*][1,3]dioxole. The reaction was complete after 48 h. The crude product was purified by flash column chromatography (silica gel, *i*hexane/EtOAc = 9:1) affording the desired compound as a pale brown solid (**20e**, 4.28 g, 16.4 mmol, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.83 (s, 1H), 7.24 (d, *J* = 2.2 Hz, 1H), 7.14 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 6.07 (s, 2H), 0.37 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 149.8, 149.3, 147.8, 132.3, 128.8, 115.7, 109.6, 104.1, 103.3, 0.0.
MS (EI, 70 eV): m/z (%) = 236 (39), 233 (17), 218 (100), 190 (23), 168 (11).

HRMS (EI) for $C_{12}H_{15}N_3O_2Si$: calc. $[M-CH_3N_2]^{2\bullet}$: 218.0637, found: 218.0629.
IR (Diamond-ATR, neat): $\tilde{\nu}/cm^{-1}$ = 3128 (vw), 2952 (w), 2897 (w), 1507 (m), 1484 (w), 1470 (m), 1463 (m), 1376 (w), 1246 (s), 1233 (m), 1205 (m), 1193 (m), 1170 (w), 1126 (m), 1108 (w), 1042 (s), 989 (m), 938 (m), 884 (m), 840 (vs), 818 (s), 806 (s), 799 (s), 756 (s), 726 (w), 690 (m).

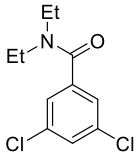
N,N-Diethyl-3-fluorobenzamide (23a)



N,N-Diethyl-3-fluorobenzamide (**23a**) was prepared according to **TP 3** using 3-fluorobenzoyl chloride and diethylamine. The crude product was purified by flash column chromatography (silica gel, *i*hexane/EtOAc = 4:1) affording the desired compound as a colorless liquid (**23a**, 3.87 g, 19.8 mmol, 99% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.36 (dtd, *J* = 7.5, 5.6, 2.3 Hz, 1H), 7.14 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.08 (ddt, *J* = 8.7, 7.0, 2.0 Hz, 2H), 3.63–3.15 (m, 4H), 1.35–1.02 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 169.8–161.3 (d, J = 847.21 Hz), 139.3 (d, *J* = 6.7 Hz), 130.3 (d, *J* = 8.1 Hz), 121.9 (d, *J* = 3.2 Hz), 116.2 (d, *J* = 21.0 Hz), 113.6 (d, *J* = 22.7 Hz).
Analytical data was equivalent to literature.[12]

3,5-Dichloro-*N,N*-diethylbenzamide (23b)

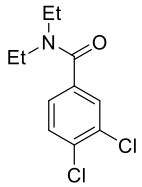


3,5-Dichloro-*N,N*-diethylbenzamide (**23b**) was prepared according to **TP 3** using 3,5-dichlorobenzoyl chloride and diethylamine. The crude product was purified by flash column chromatography (silica gel, *i*hexane/EtOAc = 4:1) affording the desired compound as a colorless solid (**23b**, 4.92 g, 20.0 mmol, 100% yield).

[12] R. J. Mills, N. J. Taylor, V. Snieckus, *J. Org. Chem.* **1989**, *54*, 4372.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.37 (t, *J* = 1.9 Hz, 1H), 7.23 (d, *J* = 1.9 Hz, 2H), 3.36 (dq, *J* = 115.6, 7.3 Hz, 4H), 1.16 (dt, *J* = 44.0, 7.4 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 168.2, 139.9, 135.3, 129.3, 124.8, 43.3, 39.5, 14.2, 12.8.
Analytical data was equivalent to literature.[13]

3,4-Dichloro-*N,N*-diethylbenzamide (23c)

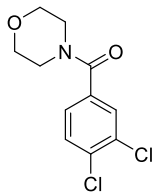


3,4-Dichloro-*N,N*-diethylbenzamide (**23c**) was prepared according to **TP 3** using 3,4-dichlorobenzoyl chloride and diethylamine. The crude product was purified by flash column chromatography (silica gel, *i*hexane/EtOAc = 4:1) affording the desired compound as a colorless oil (**23c**, 5.09 g, 20.0 mmol, 100% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.47 (dd, *J* = 5.1, 3.1 Hz, 2H), 7.20 (dd, *J* = 8.2, 1.9 Hz, 1H), 3.77–3.06 (m, 4H), 1.42–1.03 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 168.8, 137.0, 133.5, 132.9, 130.6, 128.6, 125.7, 43.4, 39.5, 14.2, 12.8.
Analytical data was equivalent to literature.[14]

[13] M. Demas, G. J. Javadi, L. M. Bradley, D. A. Hunt, *J. Org. Chem.* **2000**, *21*, 7201-7202.
[14] K. Shichijo, M. Fujitsuka, Y. Hisaeda, H. Shimakoshi, *J. Organomet. Chem.* **2020**, *907*, 121058.

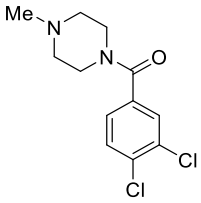
(3,4-Dichlorophenyl)(morpholino)methanone (23d)



(3,4-Dichlorophenyl)(morpholino)methanone (**23d**) was prepared according to **TP 3** using 3,4-dichlorobenzoyl chloride and morpholine. The crude product was purified by flash column chromatography (silica gel, *i*hexane/EtOAc = 4:1 to 1:1) affording the desired compound as a yellow solid (**23d**, 5.04 g, 19.3 mmol, 97% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.48–7.41 (m, 2H), 7.19–7.15 (m, 1H), 3.53 (d, *J* = 120.1 Hz, 8H).
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 168.0, 135.0, 134.4, 133.1, 130.7, 129.4, 126.4, 66.8.
Analytical data was equivalent to literature.[15]

(3,4-Dichlorophenyl)(4-methylpiperazin-1-yl)methanone (23e)



(3,4-Dichlorophenyl)(4-methylpiperazin-1-yl)methanone (**23e**) was prepared according to **TP 3** using 3,4-dichlorobenzoyl chloride and *N*-methylpiperazine. The crude product was purified by flash column chromatography (silica gel, *i*hexane/EtOAc = 1:1) affording the desired compound as an orange solid (**23e**, 5.217 g, 19.1 mmol, 95% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.53–7.47 (m, 2H), 7.24 (dd, *J* = 8.2, 2.0 Hz, 1H), 3.60 (d, *J* = 139.7 Hz, 4H), 2.32 (s, 7H).
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 167.8, 135.6, 134.1, 133.0, 130.6, 129.3, 126.4, 46.0.

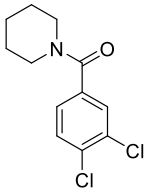
[15] A. Althammer, L. Ackermann, *Angew. Chem. Int. Ed.* **2007**, *46*, 1627-1629.

MS (EI, 70 eV): m/z (%) = 229 (28), 227 (46), 180 (14), 174 (52), 172 (82), 146 (12), 144 (19), 110 (23), 108 (69), 99 (20), 84 (10), 83 (16), 82 (18), 75 (17), 74 (22), 70 (67), 58 (34), 56 (22), 42 (32).

HRMS (EI) for $C_{12}H_{14}Cl_2N_2O$: calc. [M]: 272.0483, found: 272.0480.

IR (Diamond-ATR, neat): $\tilde{\nu}/cm^{-1}$ = 2946 (m), 2930 (m), 2859 (m), 1626 (vs), 1587 (m), 1553 (m), 1475 (m), 1461 (m), 1434 (vs), 1402 (m), 1377 (m), 1368 (m), 1352 (w), 1346 (w), 1287 (s), 1277 (s), 1258 (m), 1251 (s), 1235 (m), 1178 (w), 1148 (w), 1140 (w), 1132 (m), 1125 (m), 1105 (m), 1030 (m), 1003 (m), 954 (w), 895 (m), 881 (m), 851 (s), 835 (m), 807 (w), 793 (w), 781 (w), 753 (m), 710 (w), 670 (m), 660 (m).

(3,4-Dichlorophenyl)(piperidin-1-yl)methanone (23f)



(3,4-Dichlorophenyl)(piperidin-1-yl)methanone (**23f**) was prepared according to **TP 3** using 3,4-dichlorobenzoyl chloride and piperidine. The crude product was purified by flash column chromatography (silica gel, *i*hexane/EtOAc = 1:1) affording the desired compound as a white solid (**23f**, 4.827 g, 18.7 mmol, 94% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.50–7.43 (m, 2H), 7.21 (dd, *J* = 8.2, 1.9 Hz, 1H), 3.78–3.22 (m, 4H), 1.73–1.44 (m, 6H).

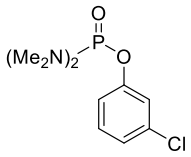
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 167.8, 136.3, 133.7, 132.9, 130.5, 129.1, 126.2, 48.8, 43.3, 26.5, 25.5, 24.5.

MS (EI, 70 eV): m/z (%) = 258 (63), 257 (12), 256 (100), 174 (15), 172 (24), 108 (15).

HRMS (EI) for $C_{12}H_{13}Cl_2NO$: calc. [M]: 257.0374, found: 257.0375.

IR (Diamond-ATR, neat): $\tilde{\nu}/cm^{-1}$ = 2950 (w), 2929 (m), 2868 (w), 2845 (w), 2794 (m), 2769 (w), 1630 (vs), 1585 (m), 1549 (w), 1476 (w), 1455 (m), 1438 (vs), 1373 (m), 1362 (m), 1295 (s), 1289 (s), 1275 (s), 1265 (m), 1253 (m), 1239 (m), 1204 (w), 1170 (m), 1141 (s), 1128 (s), 1089 (w), 1073 (w), 1052 (m), 1029 (vs), 1000 (s), 913 (m), 903 (m), 848 (vs), 840 (m), 790 (s), 777 (m), 750 (vs), 712 (w), 681 (m), 665 (m).

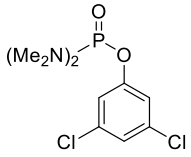
3-Chlorophenyl *N,N,N′,N′*-tetramethylphosphorodiamidate (23g)



3-Chlorophenyl *N,N,N′,N′*-tetramethylphosphorodiamidate (**23g**) was prepared according to **TP 4** using 3-chlorophenol. The crude product was purified by flash column chromatography (silica gel, *i*hexane/EtOAc = 1:1) affording the desired compound as a colorless liquid (**23g**, 3.37 g, 12.8 mmol, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.25–7.18 (m, 2H), 7.14–7.08 (m, 2H), 2.72 (d, *J* = 10.1 Hz, 12H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 151.9, 134.7, 130.3, 124.4, 120.7, 118.4, 36.7.
^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) = 16.1.
Analytical data was equivalent to literature.[16]

3,5-Dichlorophenyl *N,N,N′,N′*-tetramethylphosphorodiamidate (23h)



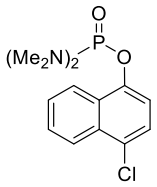
3,5-Dichlorophenyl *N,N,N′,N′*-tetramethylphosphorodiamidate (**23h**) was prepared according to **TP 4** using 3,5-dichlorophenol. The crude product was purified by flash column chromatography (silica gel, *i*hexane/EtOAc = 1:1) affording the desired compound as a colorless liquid (**23h**, 5.08 g, 17.1 mmol, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.11 (d, *J* = 1.0 Hz, 3H), 2.70 (d, *J* = 10.2 Hz, 12H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 152.4, 135.3, 124.6, 119.2, 36.6.
^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) = 16.3.
MS (EI, 70 eV): m/z (%) = 189 (29), 188 (47), 135 (100), 92 (11).
HRMS (EI) for $C_{10}H_{15}Cl_2N_2O_2P$: calc. [M- C_2H_6N]: 251.9748, found: 251.9740.

[16] C. J. Rohbogner, G. Clososki, P. Knochel, *Angew. Chem. Int. Ed.* **2008**, *47*, 1503-1507.

IR (Diamond-ATR, neat): $\tilde{\nu}$/cm^{-1} = 2928 (w), 2896 (w), 2811 (vw), 1582 (m), 1572 (s), 1455 (w), 1428 (m), 1305 (m), 1294 (m), 1246 (m), 1228 (m), 1218 (m), 1177 (m), 1096 (m), 1068 (w), 988 (s), 952 (vs), 847 (m), 830 (w), 809 (s), 787 (s), 756 (s), 674 (m), 665 (m).

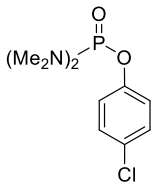
4-Chloronaphtyl *N,N,N′,N′*-tetramethylphosphorodiamidate (23i)



4-Chloronaphtyl *N,N,N′,N′*-tetramethylphosphorodiamidate (**23i**) was prepared according to **TP 4** using 4-chloronaphtol. The crude product was purified by flash column chromatography (silica gel, *i*hexane/EtOAc = 1:1) affording the desired compound as a colorless solid (**23i**, 5.82 g, 18.6 mmol, 93% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.31–8.17 (m, 2H), 7.63 (dddd, *J* = 19.5, 8.2, 6.9, 1.4 Hz, 2H), 7.51 (s, 2H), 2.80 (d, *J* = 10.1 Hz, 12H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) =146.4, 146.3, 131.6, 127.4, 126.7, 125.8, 124.7, 121.9, 114.3, 36.8.
^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) = 16.29.
MS (EI, 70 eV): m/z (%) = 312 (13), 149 (10), 135 (100).
HRMS (EI) for $C_{14}H_{18}ClN_2O_2P$: calc. [M]: 312.0794, found: 312.0787.
IR (Diamond-ATR, neat): $\tilde{\nu}$/cm^{-1} = 2923 (w), 2889 (w), 2847 (w), 2799 (w), 1593 (w), 1503 (w), 1477 (w), 1454 (m), 1417 (w), 1371 (m), 1313 (m), 1254 (m), 1222 (s), 1179 (m), 1147 (m), 1115 (w), 1047 (m), 1025 (w), 1000 (s), 984 (s), 950 (m), 856 (s), 836 (s), 759 (vs), 707 (m), 674 (m), 656 (m).
Melting point: M.p. = 111 °C

4-Chlorophenyl *N,N,N′,N′*-tetramethylphosphorodiamidate (23j)

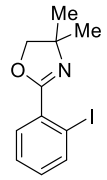


4-Chlorophenyl *N,N,N′,N′*-tetramethylphosphorodiamidate (**23j**) was prepared according to **TP 4** using 4-chlorophenol. The crude product was purified by flash column chromatography (silica gel, *i*hexane/EtOAc = 1:4) affording the desired compound as a yellow liquid (**23j**, 4.95 g, 18.8 mmol, 94% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.30–7.26 (m, 2H), 7.17–7.12 (m, 2H), 2.72 (d, *J* = 10.1 Hz, 12H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 150.0, 129.5, 129.3, 121.5, 36.6.
^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) = 16.24.
Analytical data was equivalent to literature.[16]

6. Preparation of compounds

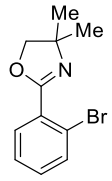
2-(2-Iodophenyl)-4,4-dimethyl-4,5-dihydrooxazole (10a)



According to **TP 1**, to a mixture of 4,4-dimethyl-2-phenyl-4,5-dihydrooxazole (**8a**, 85 µL, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.30 mmol, 0.6 equiv) at 25 °C. After 1 h, the reaction mixture was cooled to 0 °C and iodine (153 mg, 0.60 mmol, 1.2 equiv) dissolved in THF (1 mL) was added dropwise and the reaction mixture was stirred for 1 h. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 9:1) afforded the title compound as a yellow oil (**10a**, 143 mg, 0.40 mmol, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.90 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.57 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.37 (td, *J* = 7.6, 1.2 Hz, 1H), 7.10 (td, *J* = 7.7, 1.7 Hz, 1H), 4.14 (s, 2H), 1.42 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 162.8, 140.1, 134.2, 131.5, 130.5, 127.8, 94.7, 79.4, 68.2, 28.2.
MS (EI, 70 eV): m/z (%) = 300 (19), 286 (10), 285 (100), 257 (35), 229 (26), 228 (13), 144 (27), 131 (15), 130 (15), 103 (18).
HRMS (EI): for $C_{11}H_{12}INO$: calc. [M^+]: 300.9964; found: 300.9957.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 2964 (m), 2925 (w), 2888 (w), 1652 (m), 1584 (w), 1560 (w), 1461 (m), 1428 (m), 1382 (w), 1363 (m), 1349 (m), 1304 (s), 1248 (w), 1213 (m), 1187 (m), 1123 (w), 1081 (s), 1031 (s), 1023 (w), 1014 (s), 976 (w), 961 (s), 920 (m), 866 (w), 818 (w), 760 (s), 738 (w), 726 (vs), 707 (w), 694 (m).

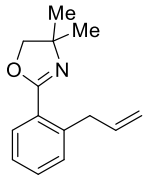
2-(2-Bromophenyl)-4,4-dimethyl-4,5-dihydrooxazole (10b)



According to **TP 1**, to a mixture of 4,4-dimethyl-2-phenyl-4,5-dihydrooxazole (**8a**, 85 µL, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.30 mmol, 0.6 equiv) at 25 °C. After 1 h, the reaction mixture was cooled to 0 °C and 1,2-dibromotetrachloroethane (244 mg, 0.60 mmol, 1.2 equiv) dissolved in THF (1 mL) was added dropwise and the reaction mixture was stirred for 1 h. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 9:1) afforded the title compound as a yellow oil (**10b**, 87 mg, 0.34 mmol, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.62 (ddd, *J* = 9.2, 7.7, 1.6 Hz, 2H), 7.32 (td, *J* = 7.5, 1.4 Hz, 1H), 7.26 (td, *J* = 7.7, 1.9 Hz, 1H), 4.13 (s, 2H), 1.41 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 162.2, 133.9, 131.9, 131.6, 130.7, 127.4, 122.2, 79.8, 68.4, 28.6.
MS (EI, 70 eV): m/z (%) = 240 (10), 239 (99), 238 (10), 237 (100), 224 (26), 222 (26), 211 (50), 209 (51), 184 (15), 183 (69), 182 (15), 181 (72), 180 (15), 130 (12), 103 (15).
HRMS (EI): for $C_{11}H_{12}BrNO$: calc. [M-H$^+$]: 252.0024; found: 252.0016.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3187 (w), 3068 (w), 2967 (m), 2929 (w), 2892 (w), 1655 (s), 1590 (w), 1565 (w), 1474 (m), 1462 (m), 1433 (m), 1383 (w), 1352 (m), 1310 (s), 1250 (m), 1214 (m), 1187 (m), 1128 (w), 1087 (s), 1024 (vs), 986 (m), 962 (s), 921 (m), 869 (w), 819 (w), 762 (vs), 730 (vs), 703 (m), 685 (m).

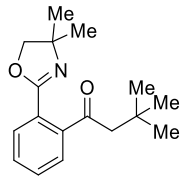
2-(2-Allylphenyl)-4,4-dimethyl-4,5-dihydrooxazole (10c)



According to **TP 1**, to a mixture of 4,4-dimethyl-2-phenyl-4,5-dihydrooxazole (**8a**, 85 µL, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.30 mmol, 0.6 equiv) at 25 °C. After 1 h, allyl bromide (52 µL, 0.60 mmol, 1.2 equiv) and CuCN·2LiCl (0.1 mL, 1.0 M in THF, 20 mol%) were added at -25 °C and the mixture was stirred for 1 h. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 9:1) afforded the title compound as a colorless oil (**10c**, 98 mg, 0.45 mmol, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.78 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.41 (td, *J* = 7.4, 1.5 Hz, 1H), 7.31–7.27 (m, 2H), 6.02 (ddt, *J* = 17.6, 9.6, 6.6 Hz, 1H), 5.07 (dtd, *J* = 14.9, 3.6, 1.9 Hz, 2H), 4.11 (s, 2H), 3.81 (dt, *J* = 6.6, 1.6 Hz, 2H), 1.42 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 162.6, 140.1, 137.5, 130.6, 130.2, 130.0, 126.0, 115.5, 78.7, 67.8, 38.3, 28.4.
MS (EI, 70 eV): m/z (%) = 214 (69), 201 (14), 200 (100), 176 (11), 160 (19), 158 (10), 146 (12), 143 (20), 142 (14), 130 (10), 129 (12), 128 (13), 117 (16), 116 (13), 115 (53).
HRMS (EI): for $C_{14}H_{17}NO$: calc. [M+]: 215.1310; found: 215.1304.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3075 (w), 2964 (m), 2928 (w), 2890 (w), 2382 (vw), 2303 (vw), 2205 (vw), 2131 (vw), 2051 (vw), 1934 (vw), 1638 (s), 1601 (w), 1575 (w), 1491 (w), 1462 (w), 1445 (w), 1409 (w), 1382 (w), 1363 (w), 1349 (m), 1305 (m), 1279 (w), 1248 (w), 1214 (w), 1189 (m), 1164 (w), 1121 (w), 1066 (w), 1050 (m), 1035 (vs), 992 (m), 967 (m), 914 (m), 869 (w), 820 (w), 773 (m), 747 (s), 730 (m), 696 (s), 672 (w).

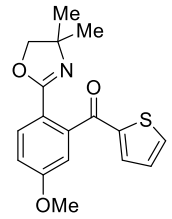
1-(2-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)phenyl)-3,3-dimethylbutan-1-one (10d)



According to **TP 1**, to a mixture of 4,4-dimethyl-2-phenyl-4,5-dihydrooxazole (**8a**, 85 µL, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.30 mmol, 0.6 equiv) at 25 °C. After 1 h, 3,3-dimethylbutanoyl chloride (81 mg, 0.60 mmol, 1.2 equiv) and CuCN·2LiCl (0.1 mL, 1.0 M in THF, 20 mol%) were added at -25 °C and the mixture was stirred for 12 h at 25 °C. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 9:1) afforded the title compound as a colorless oil (**10d**, 90 mg, 0.33 mmol, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.83–7.78 (m, 1H), 7.52–7.41 (m, 2H), 7.38 (dd, *J* = 7.4, 1.6 Hz, 1H), 4.07 (s, 2H), 2.74 (s, 2H), 1.38 (s, 6H), 1.03 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 204.7, 143.1, 130.7, 129.7, 129.6, 126.9, 125.9, 79.5, 68.1, 54.7, 31.4, 29.7, 28.1, 23.8.
MS (EI, 70 eV): m/z (%) = 216 (25), 203 (12), 202 (100), 186 (60), 160 (70), 148 (51), 146 (21), 130 (86).
HRMS (EI): for $C_{17}H_{23}NO_2$: calc. [M-CH_3]: 258.1494; found: 258.1487.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3066 (vw), 2957 (m), 2869 (m), 2361 (vw), 1709 (s), 1691 (m), 1653 (s), 1595 (w), 1574 (w), 1478 (m), 1463 (m), 1447 (w), 1398 (w), 1384 (m), 1363 (s), 1351 (s), 1312 (s), 1266 (m), 1249 (m), 1231 (s), 1215 (m), 1184 (s), 1122 (w), 1106 (w), 1073 (m), 1059 (m), 1044 (s), 1035 (s), 1008 (s), 989 (m), 964 (s), 912 (m), 869 (w), 818 (w), 770 (s), 745 (m), 697 (vs).

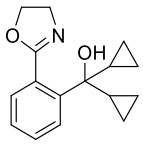
(2-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)-5-methoxyphenyl)(thiophen-2-yl)methanone (10e)



According to **TP 1**, to a mixture of 2-(4-methoxyphenyl)-4,4-dimethyl-4,5-dihydrooxazole (**8b**, 103 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.30 mmol, 0.6 equiv) at 40 °C. After 20 min, thiophene-2-carbonyl chloride (64 µL, 0.60 mmol, 1.2 equiv) and CuCN·2LiCl (0.1 mL, 1.0 M in THF, 20 mol%) were added at -25 °C and the mixture was stirred for 12 h at 25 °C. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 2:1) afforded the title compound as a yellow oil (**10e**, 142 mg, 0.45 mmol, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.91 (d, *J* = 8.6 Hz, 1H), 7.66 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.26 (d, *J* = 2.2 Hz, 1H), 7.07–6.99 (m, 3H), 3.87 (s, 3H), 3.71 (s, 2H), 1.13 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 188.6, 161.8, 144.7, 141.4, 134.0, 131.3, 127.9, 115.9, 113.1, 79.7, 55.6, 27.7.
MS (EI, 70 eV): m/z (%) = 315 (15), 287 (16), 286 (100), 271 (12), 270 (72), 259 (15), 231 (35), 216 (25), 201 (12), 160 (16).
HRMS (EI): for $C_{17}H_{17}NO_3S$: calc. [M+]: 315.0929; found: 315.0921.
IR (Diamond-ATR, neat): $\tilde{\nu}$/cm^{-1} = 3074 (vw), 2964 (w), 2927 (w), 2894 (w), 2839 (vw), 1716 (vw), 1647 (vs), 1600 (s), 1568 (m), 1509 (w), 1500 (m), 1460 (m), 1411 (s), 1383 (w), 1351 (s), 1319 (m), 1311 (m), 1294 (vs), 1231 (vs), 1184 (m), 1146 (w), 1109 (m), 1081 (w), 1060 (m), 1044 (m), 1025 (vs), 988 (w), 962 (m), 931 (m), 919 (m), 859 (m), 832 (m), 799 (s), 759 (s), 739 (s), 722 (s), 685 (m), 654 (w).

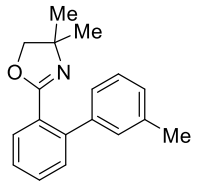
Dicyclopropyl(2-(4,5-dihydrooxazol-2-yl)phenyl)methanol (10f)



According to **TP 1**, to a mixture of 2-phenyl-4,5-dihydrooxazole (**8d**, 64 µL, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.30 mmol, 0.6 equiv) at 50 °C. After 1 h, dicyclopropyl ketone (74 µL, 0.60 mmol, 1.2 equiv) was added dropwise at 0 °C and the reaction mixture was stirred for 2 h at room temperature. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 1:2) afforded the title compound as a white solid (**10f**, 90 mg, 0.35 mmol, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.48 (d, J = 7.6 Hz, 1H), 7.08 (td, J = 7.5, 1.2 Hz, 1H), 7.01 (td, J = 7.5, 1.1 Hz, 1H), 6.93 (d, J = 7.5 Hz, 1H), 3.88 (s, 1H), 3.52 (t, J = 5.3 Hz, 2H), 3.23 (t, J = 5.3 Hz, 2H), 0.91 (tt, J = 8.3, 5.4 Hz, 2H), 0.19–0.05 (m, 4H), 0.00–-0.13 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 160.3, 148.7, 130.8, 129.9, 128.2, 123.1, 120.8, 88.8, 62.0, 49.2, 18.0, 1.0, 0.0.
MS (EI, 70 eV): m/z (%) = 227 (11), 226 (100), 216 (34), 198 (21), 185 (61), 184 (46), 172 (13), 128 (12).
HRMS (EI): for $C_{16}H_{19}NO_2$: calc. [M+]: 257.1416; found: 257.1412.
IR (Diamond-ATR, neat): $\tilde{\nu}$/cm^{-1} = 3178 (w), 3085 (w), 3004 (w), 2951 (w), 2921 (w), 2903 (w), 2856 (w), 1679 (vs), 1610 (w), 1479 (w), 1467 (m), 1427 (w), 1367 (w), 1357 (m), 1330 (w), 1303 (m), 1272 (m), 1132 (m), 1121 (m), 1111 (m), 1093 (m), 1075 (s), 1057 (m), 1043 (m), 1019 (s), 990 (w), 952 (s), 918 (m), 897 (m), 872 (m), 862 (m), 838 (w), 821 (w), 815 (w), 786 (m), 777 (s), 756 (s), 721 (m), 675 (s), 660 (w).
Melting point: M.p. = 86 °C.

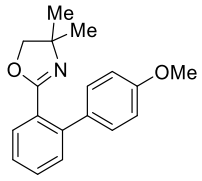
4,4-dimethyl-2-(3'-methyl-[1,1'-biphenyl]-2-yl)-4,5-dihydrooxazole (10g)



According to **TP 1**, to a mixture of 4,4-dimethyl-2-phenyl-4,5-dihydrooxazole (**8a**, 0.85 mL, 5.00 mmol, 1.0 equiv) in toluene (10 mL) was added *s*Bu_2Mg (3.00 mmol, 0.6 equiv) at 25 °C. After 1 h, the resulting diarylmagnesium was transmetalated with a $ZnCl_2$ solution (5.5 mL, 1.00 M in THF, 1.10 equiv) at 0 °C for 30 min. A dry and argon-flushed Schlenk-tube, equipped with a magnetic stirring bar and a septum was charged with Pd(dppf)Cl_2 (183 mg, 5 mol%) and 3-iodotoluene (0.53 mL, 4.15 mmol, 0.83 equiv).The freshly prepared arylzinc reagent was added and the reaction mixture was placed in an oil bath at 55 °C for 18 h. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 9:1) afforded the title compound as a colorless oil (**10g**, 1.03 g, 3.88 mmol, 93% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.71 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.48 (td, *J* = 7.5, 1.4 Hz, 1H), 7.37 (ddd, *J* = 14.6, 7.5, 1.4 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.25–7.19 (m, 2H), 7.18–7.12 (m, 1H), 3.83 (s, 2H), 2.38 (s, 3H), 1.31 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 141.7, 141.0, 137.5, 130.4, 130.1, 129.1, 128.0, 127.0, 125.5, 79.6, 67.5, 28.0, 21.5.
MS (EI, 70 eV): m/z (%) = 265 (19), 264 (100), 210 (13), 209 (18), 192 (14), 179 (28), 178 (14), 165 (22), 152 (10).
HRMS (EI): for $C_{18}H_{19}NO$: calc. [M^+]: 265.1467; found: 265.1461.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 2964 (m), 2944 (w), 2942 (w), 2939 (w), 2925 (m), 2922 (m), 2915 (w), 2912 (w), 2889 (w), 2886 (w), 1676 (w), 1656 (s), 1652 (s), 1606 (w), 1604 (w), 1600 (w), 1479 (w), 1473 (m), 1471 (m), 1462 (m), 1456 (m), 1446 (m), 1363 (m), 1349 (m), 1311 (m), 1212 (w), 1190 (w), 1188 (w), 1113 (w), 1076 (m), 1067 (w), 1065 (w), 1043 (s), 1041 (m), 1034 (s), 988 (w), 964 (m), 920 (w), 918 (w), 790 (m), 769 (m), 755 (vs), 699 (s).

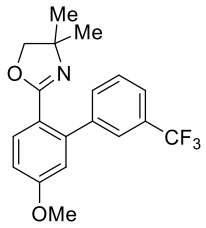
2-(4'-Methoxy-[1,1'-biphenyl]-2-yl)-4,4-dimethyl-4,5-dihydrooxazole (10h)



According to **TP 1**, to a mixture of 4,4-dimethyl-2-phenyl-4,5-dihydrooxazole (**8a**, 85 µL, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.30 mmol, 0.6 equiv) at 25 °C. After 1 h, the resulting diarylmagnesium was transmetalated with a $ZnCl_2$ solution (0.6 mL, 1.00 M in THF, 1.10 equiv) at 0 °C for 30 min. A dry and argon-flushed Schlenk-tube, equipped with a magnetic stirring bar and a septum was charged with Pd(dppf)Cl_2 (15 mg, 5 mol%) and 4-bromoanisole (53 µL, 0.42 mmol, 0.83 equiv).The freshly prepared arylzinc reagent was added and the reaction mixture was placed in an oil bath at 55 °C for 18 h. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 9:1) afforded the title compound as a yellow oil (**10h**, 89 mg, 0.32 mmol, 76% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.70 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.47 (td, *J* = 7.5, 1.5 Hz, 1H), 7.39–7.31 (m, 4H), 6.95–6.90 (m, 2H), 3.85 (s, 3H), 3.83 (s, 2H), 1.31 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 164.1, 158.9, 141.2, 133.6, 130.4, 130.2, 130.0, 129.4, 127.8, 126.7, 113.4, 79.5, 67.4, 55.3, 40.8, 28.0, 23.8.
MS (EI, 70 eV): m/z (%) = 281 (19), 280 (100), 225 (29), 195 (11).
HRMS (EI): for $C_{18}H_{19}NO_2$: calc. [M-H$^+$]: 280.1338; found: 280.1332.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3138 (vw), 3064 (vw), 2964 (m), 2892 (w), 2837 (w), 1652 (m), 1611 (m), 1580 (w), 1565 (vw), 1517 (s), 1483 (m), 1462 (m), 1446 (m), 1413 (vw), 1383 (w), 1363 (w), 1351 (m), 1295 (m), 1243 (vs), 1212 (m), 1177 (s), 1107 (w), 1075 (m), 1036 (vs), 1017 (m), 1001 (m), 988 (w), 963 (m), 920 (w), 869 (w), 832 (s), 804 (m), 761 (vs), 727 (m), 704 (m), 662 (w).

2-(5-methoxy-3'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)-4,4-dimethyl-4,5-dihydrooxazole (10i)



According to **TP 1**, to a mixture of 2-(4-methoxyphenyl)-4,4-dimethyl-4,5-dihydrooxazole (**8b**, 1.026 g, 5.00 mmol, 1.0 equiv) in toluene (10 mL) was added *s*Bu_2Mg (3.00 mmol, 0.6 equiv) at 40 °C. After 20 min, the resulting diarylmagnesium was transmetalated with a $ZnCl_2$ solution (5.5 mL, 1.00 M in THF, 1.10 equiv) at 0 °C for 30 min. A dry and argon-flushed Schlenk-tube, equipped with a magnetic stirring bar and a septum was charged with Pd(dppf)Cl_2 (183 mg, 5 mol%) and 1-iodo-3-(trifluoromethyl)benzene (0.60 mL, 4.15 mmol, 0.83 equiv).The freshly prepared arylzinc reagent was added and the reaction mixture was placed in an oil bath at 55 °C for 18 h. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/Et_2O = 1:1) afforded the title compound as a brown solid (**10i**, 1.62 g, 4.05 mmol, 98% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.76 (d, J = 8.6 Hz, 1H), 7.66–7.55 (m, 3H), 7.51 (t, J = 7.6 Hz, 1H), 6.93 (dd, J = 8.6, 2.6 Hz, 1H), 6.86 (d, J = 2.6 Hz, 1H), 3.86 (s, 3H), 3.76 (s, 2H), 1.26 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 162.7, 160.9, 141.8, 141.7, 132.0, 131.4, 131.3, 130.5, 130.1, 129.8, 129.5, 128.4, 125.3, 125.3, 125.2, 125.2, 125.1, 123.8, 123.8, 123.8, 123.7, 122.7, 120.1, 115.5, 112.8, 79.0, 67.2, 55.3, 27.8.

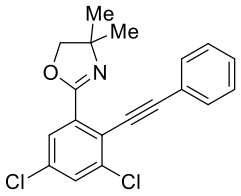
MS (EI, 70 eV): m/z (%) = 349 (20), 348 (100), 263 (38), 258 (18), 215 (14).

HRMS (EI): for $C_{19}H_{18}F_3NO_2$: calc. [M-H$^+$]: 348.1211; found: 348.1199.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 2988 (vw), 2974 (w), 2945 (w), 2942 (w), 2937 (vw), 2933 (vw), 2931 (vw), 2927 (vw), 2905 (vw), 2901 (vw), 2886 (w), 2843 (vw), 1635 (s), 1608 (s), 1579 (w), 1568 (w), 1513 (w), 1464 (m), 1448 (w), 1432 (w), 1423 (w), 1365 (w), 1350 (m), 1334 (s), 1314 (s), 1295 (s), 1276 (m), 1244 (m), 1212 (s), 1195 (m), 1178 (s), 1165 (vs), 1139 (s), 1110 (s), 1095 (s), 1080 (s), 1068 (s), 1034 (m), 1025 (vs), 1002 (w), 986 (m), 964 (m), 959 (m), 932 (m), 927 (m), 914 (m), 907 (m), 895 (s), 809 (s), 788 (m), 774 (vw), 771 (vw), 768 (vw), 758 (w), 743 (vw), 716 (m), 706 (m), 701 (vs), 687 (w), 664 (m).

Melting point: M.p. = 70 °C.

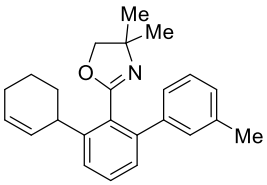
2-(3,5-dichloro-2-(phenylethynyl)phenyl)-4,4-dimethyl-4,5-dihydrooxazole (10j)



According to **TP 1**, to a mixture of 2-(3,5-dichlorophenyl)-4,4-dimethyl-4,5-dihydrooxazole (**8c**, 0.732 g, 3.00 mmol, 1.0 equiv) in toluene (6 mL) was added *s*Bu_2Mg (1.80 mmol, 0.6 equiv) at 25 °C. After 15 min, the resulting diarylmagnesium was transmetalated with a $ZnCl_2$ solution (3.6 mL, 1.00 M in THF, 1.10 equiv) at 0 °C for 30 min. Iodine (0.838 g, 3.30 mmol, 1.1 equiv) dissolved in THF (2 mL) was added and the reaction mixture was allowed to stir 1 h at 25 °C. A dry and argon-flushed Schlenk-tube, equipped with a magnetic stirring bar and a septum was charged with $Pd(dba)_2$ (52 mg, 3 mol%), CuI (23 mg, 4 mol%), tfp (42 mg, 6 mol%) and NEt_3 (10 mL). The freshly prepared arylzinc reagent followed by phenylacetylene (0.43 mL, 3.90 mmol, 1.3 equiv) were added and the reaction mixture was stirred overnight at 25 °C. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/Et_2O = 9:1) afforded the title compound as a yellow oil (**10j**, 633 mg, 1.84 mmol, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.73 (d, *J* = 2.1 Hz, 1H), 7.58–7.53 (m, 3H), 7.37 (tt, *J* = 4.0, 2.7 Hz, 3H), 4.17 (s, 2H), 1.42 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 160.3, 143.4, 138.1, 133.8, 131.7, 131.0, 129.0, 128.4, 128.2, 100.4, 84.1, 79.6, 68.3, 28.4.
MS (EI, 70 eV): m/z (%) = 344 (22), 342 (36), 331 (11), 330 (61), 329 (18), 328 (100), 326 (17), 289 (16), 253 (11), 238 (14), 237 (18), 207 (32), 201 (14), 190 (19), 163 (13), 158 (26), 156 (39), 43 (54), 42 (25).
HRMS (EI): for $C_{19}H_{15}Cl_2NO$: calc. [M-H$^+$]: 342.0452; found: 342.0445.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3079 (vw), 3057 (vw), 2965 (w), 2928 (w), 2892 (w), 2866 (vw), 2219 (w), 1651 (m), 1623 (m), 1596 (w), 1576 (m), 1541 (w), 1492 (m), 1475 (vw), 1461 (w), 1450 (m), 1442 (m), 1412 (m), 1382 (w), 1363 (w), 1347 (m), 1338 (w), 1296 (m), 1251 (w), 1214 (w), 1188 (m), 1157 (w), 1148 (w), 1116 (m), 1077 (w), 1063 (m), 1025 (vw), 988 (m), 969 (s), 915 (w), 893 (w), 891 (w), 861 (s), 819 (vw), 792 (m), 753 (vs), 729 (w), 688 (s), 672 (w), 667 (w).

4,4-dimethyl-2-(3''-methyl-1,2,3,4-tetrahydro-[1,1':3',1''-terphenyl]-2'-yl)-4,5-dihydrooxazole (11a)



According to **TP 1**, to a mixture of 4,4-dimethyl-2-(3'-methyl-[1,1'-biphenyl]-2-yl)-4,5-dihydrooxazole (**10g**, 133 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added sBu$_2$Mg (0.30 mmol, 0.6 equiv) at 60 °C. After 1 h, 3-bromocyclohexene (70 µL, 0.60 mmol, 1.2 equiv) and CuCN·2LiCl (0.1 mL, 1.0 M in THF, 20 mol%) were added at -25 °C and the mixture was stirred for 1 h. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 4:1) afforded the title compound as a colorless liquid (**11a**, 129 mg, 0.37 mmol, 74% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.40 (t, J = 7.7 Hz, 1H), 7.34–7.21 (m, 5H), 7.19–7.12 (m, 1H), 6.00–5.91 (m, 1H), 5.76 (dq, J = 10.3, 2.2 Hz, 1H), 3.88–3.80 (m, 2H), 3.77 (tq, J = 5.5, 2.7 Hz, 1H), 2.39 (s, 3H), 2.18–2.06 (m, 3H), 1.77 (tdd, J = 10.2, 6.8, 4.9 Hz, 1H), 1.66–1.54 (m, 2H), 1.20 (d, J = 16.2 Hz, 6H).

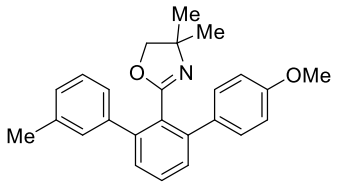
^{13}C NMR (101 MHz, CDCl$_3$): δ (ppm) = 161.7, 145.5, 142.1, 141.1, 137.2, 130.2, 129.7, 129.4, 128.6, 127.9, 127.8, 127.8, 127.4, 126.6, 125.9, 78.9, 67.8, 65.9, 38.7, 32.2, 27.9, 27.8, 25.0, 21.4, 21.2.

MS (EI, 70 eV): m/z (%) = 345 (22), 290 (40), 289 (20), 288 (100), 274 (17), 273 (14), 272 (15), 271 (17), 270 (13), 255 (14), 244 (10), 222 (23), 215 (22), 202 (22), 189 (12), 179 (13), 178 (13), 165 (21).

HRMS (EI): for $C_{24}H_{27}NO$: calc. [M-H$^+$]: 345.2093; found: 345.2085.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3027 (w), 3019 (w), 2965 (m), 2962 (m), 2960 (m), 2952 (w), 2949 (w), 2926 (m), 2923 (m), 2900 (w), 2898 (w), 2897 (w), 2895 (w), 2889 (w), 2886 (w), 2883 (w), 2878 (w), 2875 (w), 2872 (w), 2870 (w), 2868 (w), 2865 (w), 2862 (w), 2859 (w), 2856 (w), 2844 (w), 2834 (w), 1661 (s), 1606 (w), 1584 (w), 1577 (w), 1459 (m), 1447 (m), 1433 (w), 1363 (w), 1345 (w), 1313 (w), 1285 (m), 1274 (w), 1265 (w), 1253 (w), 1246 (w), 1208 (w), 1196 (w), 1188 (w), 1178 (w), 1175 (w), 1172 (w), 1095 (w), 1035 (vs), 1000 (w), 987 (w), 962 (m), 945 (w), 943 (w), 940 (w), 936 (w), 930 (w), 917 (m), 905 (w), 891 (w), 882 (w), 871 (w), 806 (w), 781 (s), 759 (s), 741 (m), 733 (w), 722 (m), 703 (vs).

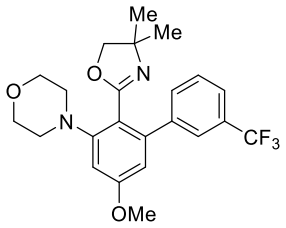
2-(4''-methoxy-3-methyl-[1,1':3',1''-terphenyl]-2'-yl)-4,4-dimethyl-4,5-dihydrooxazole (11b)



According to **TP 1**, to a mixture of 2-(4'-Methoxy-[1,1'-biphenyl]-2-yl)-4,4-dimethyl-4,5-dihydrooxazole (**10h**, 1.0 g, 3.55 mmol, 1.0 equiv) in toluene (10 mL) was added *s*Bu_2Mg (3.00 mmol, 0.6 equiv) at 60 °C. After 0.5 h, the resulting diarylmagnesium was transmetalated with a $ZnCl_2$ solution (3.91 mL, 1.00 M in THF, 1.10 equiv) at 0 °C for 30 min. A dry and argon-flushed Schlenk-tube, equipped with a magnetic stirring bar and a septum was charged with Pd(dppf)Cl_2 (132 mg, 5 mol%) and 3-iodotoluene (0.38 mL, 2.95 mmol, 0.83 equiv).The freshly prepared arylzinc reagent was added and the reaction mixture was placed in an oil bath at 55 °C for 16 h. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 4:1) afforded the title compound as a brown solid (**11b**, 0.914 g, 2.46 mmol, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.47 (dd, J = 8.1, 7.3 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.33 (d, J = 7.8 Hz, 2H), 7.28 (d, J = 1.4 Hz, 1H), 7.26 (d, J = 3.4 Hz, 3H), 7.18 – 7.11 (m, 1H), 6.94 – 6.88 (m, 2H), 3.84 (s, 3H), 3.62 (s, 2H), 2.36 (s, 3H), 0.96 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 159.0, 142.4, 141.8, 140.7, 137.3, 133.3, 130.1, 129.7, 129.3, 128.6, 128.3, 127.9, 127.8, 126.0, 113.3, 79.0, 67.6, 55.3, 27.4, 21.4.
MS (EI, 70 eV): m/z (%) = 371 (26), 370 (100), 298 (11).
HRMS (EI): for $C_{25}H_{25}NO_2$: calc. [M^+]: 371.1885; found: 371.1833.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 2972 (w), 2950 (w), 2928 (w), 2925 (w), 2919 (w), 2916 (w), 2914 (w), 2899 (w), 2878 (w), 2877 (w), 2864 (w), 2833 (w), 1658 (m), 1635 (w), 1610 (m), 1605 (m), 1587 (w), 1582 (w), 1574 (w), 1515 (s), 1461 (m), 1454 (s), 1441 (s), 1419 (w), 1403 (w), 1402 (w), 1382 (w), 1379 (w), 1364 (m), 1345 (w), 1303 (w), 1293 (m), 1289 (m), 1283 (m), 1242 (vs), 1212 (m), 1202 (w), 1186 (m), 1171 (s), 1150 (w), 1120 (w), 1106 (m), 1092 (m), 1077 (w), 1043 (m), 1036 (vs), 1010 (w), 987 (m), 978 (w), 964 (m), 931 (w), 920 (w), 907 (m), 888 (w), 865 (w), 833 (s), 821 (m), 809 (s), 803 (s), 792 (w), 786 (vs), 762 (s), 729 (w), 716 (w), 713 (m), 702 (s).
Melting point: M.p. = 84 °C.

4-(2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-5-methoxy-3'-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)morpholine (11c)



According to **TP 1**, to a mixture of 2-(5-methoxy-3'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)-4,4-dimethyl-4,5-dihydrooxazole (**10i**, 64 mg, 0.20 mmol, 1.0 equiv) in toluene (0.4 mL) was added *s*Bu_2Mg (0.12 mmol, 0.6 equiv) at 40 °C. After 0.5 h, the resulting diarylmagnesium was transmetalated with a $ZnCl_2$ solution (0.24 mL, 1.00 M in THF, 1.20 equiv) at 0 °C for 30 min. A dry and argon-flushed Schlenk-tube, equipped with a magnetic stirring bar and a septum was charged with $CoCl_2$ (1.3 mg, 5 mol%) and morpholino benzoate (50 mg, 0.24 mmol, 1.2 equiv).The freshly prepared arylzinc reagent was added and the reaction mixture was stirred at 25 °C for 2 h. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 1:1) afforded the title compound as a white solid (**11c**, 73 mg, 0.17 mmol, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.67 (d, J = 1.9 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.47 (t, J = 7.7 Hz, 1H), 6.68 (d, J = 2.4 Hz, 1H), 6.57 (d, J = 2.4 Hz, 1H), 3.82 (m, 9H), 3.13 – 3.01 (m, 4H), 1.07 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 161.1, 160.9, 153.8, 143.3, 141.6, 132.2, 130.6, 130.3, 130.0, 129.6, 128.4, 125.6, 125.6, 125.5, 125.5, 125.5, 124.2, 124.1, 124.1, 124.0, 122.8, 117.7, 109.5, 106.1, 78.8, 67.5, 67.4, 55.4, 53.1, 27.9.

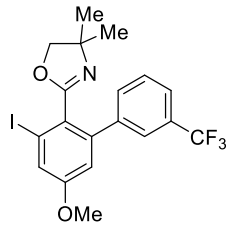
MS (EI, 70 eV): m/z (%) = 404 (46), 403 (29), 389 (58), 377 (16), 376 (17), 375 (77), 361 (23), 360 (26), 359 (39), 348 (75), 347 (26), 346 (54), 331 (26), 321 (38), 320 (33), 319 (100), 306 (19), 305 (22), 303 (45), 301 (36), 285 (17), 283 (19), 263 (50), 258 (28), 235 (19), 220 (25), 215 (20), 207 (33), 201 (19), 188 (18), 165 (18), 164 (20), 43 (58), 42 (22).

HRMS (EI): for $C_{23}H_{25}F_3N_2O_3$: calc. [M^+]: 434.1817; found: 434.1823.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 2963 (m), 1663 (m), 1591 (m), 1575 (m), 1466 (m), 1454 (m), 1437 (m), 1418 (m), 1362 (s), 1347 (m), 1331 (m), 1323 (s), 1315 (m), 1305 (m), 1292 (m), 1260 (m), 1236 (m), 1210 (m), 1198 (m), 1187 (w), 1175 (m), 1165 (s), 1148 (s), 1127 (vs), 1110 (vs), 1093 (s), 1075 (s), 1045 (m), 1027 (s), 982 (m), 964 (m), 927 (m), 922 (m), 916 (m), 910 (m), 870 (m), 863 (s), 856 (s), 816 (m), 806 (s), 768 (m), 757 (m), 706 (s).

Melting point: M.p. = 117 °C.

2-(3-iodo-5-methoxy-3'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)-4,4-dimethyl-4,5-dihydrooxazole (11d)



According to **TP 1**, to a mixture of 2-(5-methoxy-3'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)-4,4-dimethyl-4,5-dihydrooxazole (**10i**, 64 mg, 0.20 mmol, 1.0 equiv) in toluene (0.4 mL) was added sBu$_2$Mg (0.12 mmol, 0.6 equiv) at 40 °C. After 0.5 h, the reaction mixture was cooled to 0 °C and iodine (61 mg, 0.24 mmol, 1.2 equiv) dissolved in THF (1 mL) was added dropwise and the reaction mixture was stirred for 1 h. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 2:1) afforded the title compound as a yellow oil (**11d**, 74 mg, 0.16 mmol, 80% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.69 (dt, J = 1.9, 1.0 Hz, 1H), 7.64–7.56 (m, 2H), 7.50 (t, J = 7.7 Hz, 1H), 7.41 (d, J = 2.5 Hz, 1H), 6.85 (d, J = 2.5 Hz, 1H), 3.90 (s, 2H), 3.83 (s, 3H), 1.14 (s, 6H).

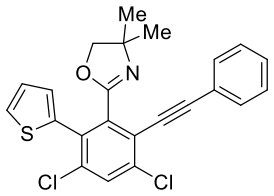
^{13}C NMR (101 MHz, CDCl$_3$): δ (ppm) = 162.2, 160.3, 142.9, 140.8, 132.1, 130.9, 130.6, 130.3, 130.0, 128.8, 126.7, 125.6, 125.6, 125.5, 125.5, 124.8, 124.7, 124.7, 124.6, 124.0, 122.8, 115.6, 97.6, 79.4, 68.1, 55.8, 27.7.

MS (EI, 70 eV): m/z (%) = 475 (18), 474 (93), 389 (14), 388 (100), 383 (24), 376 (22), 332 (21), 305 (11), 257 (11), 242 (16), 226 (12), 220 (10), 219 (12), 214 (11), 213 (15), 207 (27), 206 (15), 165 (14), 164 (24).

HRMS (EI): for $C_{19}H_{17}F_3INO_2$: calc. [M-H$^+$]: 474.0178; found: 474.0170.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3012 (vw), 2976 (w), 2972 (w), 2969 (w), 2945 (w), 2942 (w), 2935 (w), 2931 (w), 2912 (vw), 2904 (vw), 2902 (vw), 2880 (vw), 2865 (vw), 2858 (vw), 2841 (vw), 1736 (s), 1667 (m), 1590 (m), 1546 (m), 1492 (w), 1464 (m), 1436 (w), 1428 (w), 1395 (w), 1373 (m), 1359 (w), 1348 (w), 1331 (vs), 1305 (m), 1270 (m), 1238 (vs), 1214 (s), 1165 (s), 1158 (s), 1125 (vs), 1095 (m), 1082 (m), 1073 (s), 1044 (s), 1035 (s), 1024 (vs), 1002 (w), 985 (w), 960 (m), 937 (w), 918 (w), 904 (w), 874 (w), 861 (w), 856 (w), 845 (w), 827 (vw), 803 (s), 787 (w), 744 (w), 733 (w), 703 (s), 666 (s).

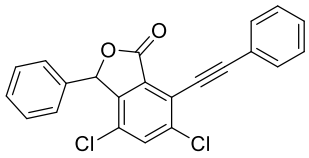
2-(3,5-dichloro-2-(phenylethynyl)-6-(thiophen-2-yl)phenyl)-4,4-dimethyl-4,5-dihydrooxazole (11e)



According to **TP 1**, to a mixture of 2-(3,5-dichloro-2-(phenylethynyl)phenyl)-4,4-dimethyl-4,5-dihydrooxazole (**10j**, 68 mg, 0.2 mmol, 1.0 equiv) in toluene (0.4 mL) was added *s*Bu_2Mg (0.12 mmol, 0.6 equiv) at 40 °C. After 0.5 h, the resulting diarylmagnesium was transmetalated with a $ZnCl_2$ solution (0.22 mL, 1.00 M in THF, 1.10 equiv) at 0 °C for 30 min. A dry and argon-flushed Schlenk-tube, equipped with a magnetic stirring bar and a septum was charged with Pd(dppf)Cl_2 (8 mg, 5 mol%) and 2-iodothiophene (16 µL, 0.17 mmol, 0.83 equiv).The freshly prepared arylzinc reagent was added and the reaction mixture was placed in an oil bath at 55 °C for 16 h. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 9:1) afforded the title compound as a white solid (**11e**, 66 mg, 0.15 mmol, 93% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.64 (s, 1H), 7.55–7.48 (m, 2H), 7.46–7.42 (m, 1H), 7.35 (qd, J = 4.4, 1.4 Hz, 3H), 7.07 (d, J = 3.2 Hz, 2H), 3.88 (s, 2H), 1.13 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 159.1, 136.6, 135.9, 135.1, 135.0, 132.3, 131.5, 130.8, 129.2, 128.9, 128.2, 126.9, 126.2, 122.2, 121.9, 98.6, 82.9, 79.5, 68.0, 29.5, 27.6.
MS (EI, 70 eV): m/z (%) = 281 (33), 266 (11), 265 (11), 225 (39), 209 (18), 208 (13), 207 (100), 191 (21), 43 (42), 42 (12).
HRMS (EI): for $C_{23}H_{17}Cl_2NOS$: calc. [M+]: 425.0408; found: 425.0396.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 2960 (m), 2958 (m), 2945 (m), 2921 (s), 2892 (m), 2887 (m), 2871 (w), 2866 (w), 2853 (m), 1740 (w), 1674 (m), 1492 (m), 1462 (m), 1447 (m), 1442 (m), 1424 (m), 1396 (w), 1363 (w), 1339 (w), 1307 (w), 1262 (m), 1237 (m), 1206 (s), 1177 (m), 1162 (m), 1093 (s), 1083 (m), 1069 (m), 1052 (m), 1033 (w), 1022 (w), 988 (m), 968 (s), 927 (w), 888 (m), 872 (w), 866 (m), 863 (w), 847 (m), 829 (w), 820 (w), 807 (m), 762 (s), 757 (s), 698 (s), 686 (vs), 667 (m).
Melting point: M.p. = 126 °C.

4,6-dichloro-3-phenyl-7-(phenylethynyl)isobenzofuran-1(3H)-one (11f)



According to **TP 1**, to a mixture of 2-(3,5-dichloro-2-(phenylethynyl)phenyl)-4,4-dimethyl-4,5-dihydrooxazole (**10j**, 68 mg, 0.2 mmol, 1.0 equiv) in toluene (0.4 mL) was added *s*Bu_2Mg (0.12 mmol, 0.6 equiv) at 40 °C. After 0.5 h, benzaldehyde (26 µL, 0.24 mmol, 1.2 equiv) was added dropwise at 0 °C and the reaction mixture was stirred for 1 h at room temperature. & M HCl (4 mL) was added and the reaction mixture was stirred at 25 °C overnight. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 98:2) afforded the title compound as a white solid (**11f**, 42 mg, 0.11 mmol, 56% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.77–7.70 (m, 2H), 7.68 (s, 1H), 7.46–7.35 (m, 6H), 7.26–7.21 (m, 2H), 6.30 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 166.5, 145.6, 138.5, 134.8, 133.7, 132.4, 129.9, 129.7, 129.0, 128.7, 128.6, 128.5, 128.2, 122.1, 120.7, 104.3, 81.2, 80.9.

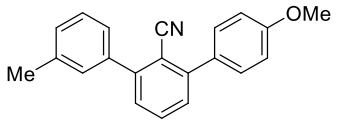
MS (EI, 70 eV): m/z (%) = 381 (14), 380 (61), 379 (22), 378 (100), 302 (13), 300 (20), 299 (21), 286 (12), 274 (51), 273 (12), 272 (79), 264 (12), 263 (67), 261 (36), 250 (30), 245 (12), 243 (19), 212 (23), 210 (69), 175 (19), 174 (46), 131 (24), 130 (15), 125 (18), 105 (92), 77 (25).

HRMS (EI): for $C_{22}H_{12}Cl_2O_2$: calc. [M+]: 378.0214; found: 378.0208.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3066 (w), 2961 (w), 2959 (w), 2945 (w), 2924 (w), 2922 (w), 2898 (w), 2896 (w), 2872 (w), 2869 (w), 2866 (w), 2864 (w), 2853 (w), 2210 (w), 1764 (m), 1754 (vs), 1733 (w), 1723 (w), 1720 (w), 1717 (w), 1700 (w), 1683 (w), 1674 (w), 1671 (w), 1669 (w), 1663 (w), 1652 (w), 1647 (w), 1492 (m), 1453 (s), 1441 (m), 1388 (w), 1322 (m), 1300 (w), 1270 (m), 1263 (m), 1210 (w), 1194 (s), 1178 (m), 1174 (m), 1167 (w), 1162 (w), 1158 (w), 1109 (w), 1106 (w), 1091 (vs), 1073 (m), 1069 (m), 1050 (w), 1038 (w), 1036 (w), 1026 (m), 1011 (w), 993 (w), 980 (s), 969 (w), 922 (w), 910 (m), 881 (m), 829 (w), 804 (m), 796 (m), 785 (m), 764 (m), 757 (vs), 723 (m), 710 (w), 709 (w), 701 (vs), 696 (m), 685 (s), 674 (m), 669 (w), 667 (w).

Melting point: M.p. = 148 °C.

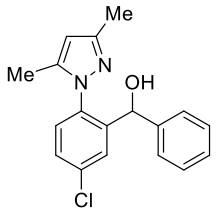
4''-methoxy-3-methyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (11g)



2-(4''-methoxy-3-methyl-[1,1':3',1''-terphenyl]-2'-yl)-4,4-dimethyl-4,5-dihydrooxazole (**11b**, 75 mg, 0.20 mmol, 1.0 equiv) was dissolved in $SOCl_2$ (2 mL) and DMF (1 mL) was added dropwise at 25 °C. The reaction mixture was refluxed for 2 h and subsequently cooled to 0 °C. Water was carefully added and the reaction mixture was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed in vacuo. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 98:2) afforded the title compound as a yellow solid (**11g**, 55 mg, 0.18 mmol, 92% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.63 (t, J = 7.8 Hz, 1H), 7.57–7.52 (m, 2H), 7.43 (ddd, J = 7.6, 6.4, 1.2 Hz, 2H), 7.40–7.38 (m, 3H), 7.28–7.26 (m, 1H), 7.05–7.00 (m, 2H), 3.87 (s, 3H), 2.44 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 160.0, 147.1, 146.6, 138.7, 138.3, 132.2, 131.0, 130.3, 129.8, 129.4, 128.6, 128.5, 128.4, 126.1, 118.3, 114.1, 110.2, 55.4, 21.5.
MS (EI, 70 eV): m/z (%) = 299 (100), 298 (55), 284 (31), 283 (11), 255 (27), 254 (20), 241 (29), 240 (26).
HRMS (EI): for $C_{21}H_{17}NO$: calc. [M+]: 299.1310; found: 299.1305.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3013 (vw), 2957 (w), 2953 (w), 2945 (w), 2921 (w), 2920 (w), 2896 (w), 2877 (w), 2874 (w), 2871 (w), 2853 (w), 2844 (w), 2220 (w), 1733 (vw), 1662 (w), 1660 (w), 1652 (w), 1609 (m), 1581 (w), 1577 (w), 1575 (w), 1559 (w), 1558 (vw), 1515 (s), 1496 (w), 1490 (w), 1475 (vw), 1455 (s), 1442 (m), 1436 (m), 1419 (w), 1404 (w), 1394 (w), 1375 (w), 1364 (w), 1323 (vw), 1307 (w), 1298 (m), 1283 (m), 1247 (s), 1211 (w), 1202 (w), 1178 (s), 1151 (w), 1121 (w), 1110 (m), 1093 (w), 1077 (w), 1067 (w), 1043 (m), 1024 (s), 999 (w), 988 (w), 985 (w), 980 (w), 964 (w), 950 (w), 932 (vw), 917 (w), 907 (w), 888 (w), 872 (w), 833 (m), 828 (s), 809 (m), 804 (m), 785 (vs), 770 (s), 751 (m), 735 (w), 726 (w), 717 (w), 712 (w), 703 (s).
Melting point: M.p. = 83 °C.

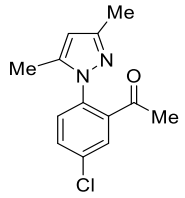
(5-Chloro-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)phenyl)(phenyl)methanol (14a)



According to **TP 1**, to a mixture of 1-(4-chlorophenyl)-3,5-dimethyl-1*H*-pyrazole (**12a**, 103 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.30 mmol, 0.6 equiv) at 40 °C. After 30 min, benzaldehyde (62 µL, 0.60 mmol, 1.2 equiv) was added dropwise at 0 °C and the reaction mixture was stirred for 1 h at room temperature. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 7:1) afforded the title compound as a white solid (**14a**, 135 mg, 0.43 mmol, 86% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.47 (d, *J* = 2.4 Hz, 1H), 7.35 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.23–7.13 (m, 3H), 7.09–7.05 (m, 3H), 5.77 (s, 1H), 5.61 (s, 1H), 2.27 (s, 3H), 1.78 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 149.1, 144.0, 141.6, 141.2, 130.5, 128.9, 128.2, 127.8, 127.0, 125.4, 106.4, 72.8, 13.3, 11.2.
MS (EI, 70 eV): m/z (%) = 314 (43), 313 (26), 312 (100), 311 (34), 310 (26), 297 (15), 295 (18), 294 (19), 283 (13), 282 (16), 280 (27), 266 (37), 255 (18), 234 (29), 232 (48), 229 (12), 228 (13), 216 (12), 207 (34), 151 (17), 104 (22), 82 (16), 77 (20), 76 (28), 62 (27), 57 (12).
HRMS (EI): for $C_{18}H_{17}ClN_2O$: calc. [M+]: 312.1029; found: 312.1033.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3166 (m), 3059 (w), 3030 (w), 2923 (m), 2853 (m), 2733 (w), 2663 (w), 2563 (w), 2479 (w), 2360 (w), 2243 (w), 1932 (w), 1735 (w), 1700 (w), 1670 (w), 1595 (w), 1573 (w), 1555 (m), 1492 (m), 1472 (m), 1455 (m), 1417 (m), 1397 (m), 1379 (m), 1371 (m), 1338 (w), 1317 (m), 1292 (w), 1269 (w), 1242 (m), 1195 (w), 1179 (m), 1161 (w), 1139 (w), 1121 (w), 1091 (m), 1077 (m), 1049 (m), 1035 (s), 1026 (m), 982 (w), 962 (w), 918 (w), 906 (m), 889 (m), 850 (w), 832 (s), 773 (s), 751 (s), 699 (vs), 671 (w), 658 (w).
Melting point: M.p. = 179 °C.

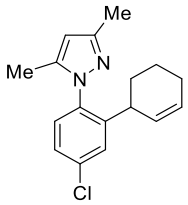
1-(5-Chloro-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)phenyl)ethan-1-one (14b)



According to **TP 1**, to a mixture of 1-(4-chlorophenyl)-3,5-dimethyl-1*H*-pyrazole (**12a**, 103 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.30 mmol, 0.6 equiv) at 40 °C. After 30 min, *N*-methoxy-*N*-methyl acetamide (65 µL, 0.60 mmol, 1.2 equiv) was added dropwise at 0 °C and the reaction mixture was stirred for 1 h at room temperature. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 6:1) afforded the title compound as an orange solid (**14b**, 92 mg, 0.37 mmol, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.67 (d, *J* = 2.4 Hz, 1H), 7.53 (dd, *J* = 8.4, 2.5 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 6.04 (s, 1H), 2.27 (s, 3H), 2.14 (d, *J* = 0.7 Hz, 3H), 1.90 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 198.9, 150.0, 140.8, 138.9, 134.8, 131.7, 129.1, 129.0, 107.2, 28.2, 13.4, 11.5.
MS (EI, 70 eV): m/z (%) = 235 (31), 234 (12), 233 (100).
HRMS (EI): for $C_{13}H_{13}ClN_2O$: calc. [M+]: 248.0716; found: 248.0713.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3070 (vw), 2922 (w), 2854 (w), 2360 (vw), 1700 (vw), 1684 (vs), 1637 (vw), 1593 (w), 1570 (w), 1558 (m), 1542 (vw), 1508 (w), 1492 (s), 1467 (m), 1441 (w), 1410 (m), 1396 (m), 1376 (w), 1362 (w), 1351 (m), 1288 (w), 1274 (m), 1256 (m), 1229 (s), 1178 (vw), 1131 (w), 1114 (vw), 1098 (m), 1082 (w), 1042 (vw), 1029 (m), 1012 (w), 976 (w), 890 (m), 835 (s), 811 (vs), 764 (w), 731 (w), 689 (w), 663 (vw).
Melting point: M.p. = 82 °C.

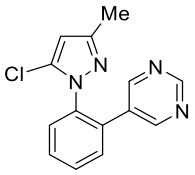
1-(5-Chloro-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-2-yl)-3,5-dimethyl-1*H*-pyrazole (14c)



According to **TP 1**, to a mixture of 1-(4-chlorophenyl)-3,5-dimethyl-1*H*-pyrazole (**12a**, 103 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.30 mmol, 0.6 equiv) at 40 °C. After 30 min, 3-bromocyclohexene (70 µL, 0.60 mmol, 1.2 equiv) and CuCN·2LiCl (0.1 mL, 1.0 M in THF, 20 mol%) were added at -25 °C and the mixture was stirred for 1 h. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 18:1) afforded the title compound as a yellow solid (**14c**, 129 mg, 0.45 mmol, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.34 (d, *J* = 2.4 Hz, 1H), 7.24 (dd, *J* = 8.3, 2.4 Hz, 1H), 7.11 (d, *J* = 8.3 Hz, 1H), 5.95 (s, 1H), 5.90 (ddt, *J* = 10.0, 5.1, 2.8 Hz, 1H), 5.59–5.53 (m, 1H), 3.15 (s, 1H), 2.27 (s, 3H), 2.12–1.95 (m, 5H), 1.83 (d, *J* = 12.0 Hz, 1H), 1.68 (ddt, *J* = 16.4, 5.9, 3.7 Hz, 1H), 1.54–1.35 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 148.7, 146.7, 140.5, 136.4, 134.9, 129.4, 129.3, 129.0, 128.9, 126.7, 105.3, 36.1, 31.4, 24.7, 21.1, 13.6, 11.5.
MS (EI, 70 eV): m/z (%) = 288 (23), 286 (77), 285 (30), 273 (30), 272 (18), 271 (100), 257 (22), 254 (17), 245 (17), 243 (57), 231 (34), 228 (23), 217 (27), 205 (22), 191 (15), 190 (26), 180 (15), 168 (17), 167 (29), 164 (16), 162 (52), 154 (18), 153 (15), 152 (23), 115 (17), 96 (15).
HRMS (EI): for $C_{17}H_{19}ClN_2$: calc. [M+]: 286.1237; found: 286.1233.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3021 (vw), 2933 (m), 2859 (w), 2839 (w), 2360 (vw), 1731 (w), 1595 (vw), 1569 (vw), 1553 (m), 1496 (s), 1470 (m), 1445 (w), 1433 (w), 1415 (m), 1389 (w), 1378 (w), 1365 (m), 1343 (w), 1310 (w), 1298 (vw), 1279 (vw), 1267 (vw), 1241 (w), 1220 (vw), 1184 (w), 1154 (vw), 1136 (w), 1118 (w), 1091 (m), 1077 (w), 1042 (w), 1028 (m), 1014 (w), 991 (w), 984 (w), 931 (vw), 910 (w), 898 (w), 883 (m), 859 (w), 832 (vs), 810 (w), 795 (m), 775 (w), 753 (w), 726 (m), 718 (m), 683 (vw), 669 (w), 662 (w).
Melting point: M.p. = 94 °C.

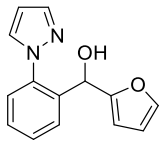
5-(2-(5-Chloro-3-methyl-1*H*-pyrazol-1-yl)phenyl)pyrimidine (14d)



According to **TP 1**, to a mixture of 5-chloro-3-methyl-1-phenyl-1*H*-pyrazole (**12b**, 96 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.40 mmol, 0.8 equiv) at 60 °C. After 20 min, the resulting diarylmagnesium was transmetalated with a $ZnCl_2$ solution (0.6 mL, 1.00 M in THF, 1.10 equiv) at 0 °C for 30 min. A dry and argon-flushed Schlenk-tube, equipped with a magnetic stirring bar and a septum was charged with $Pd(dppf)Cl_2$ (15 mg, 5 mol%) and 5-bromopyrimidine (67 mg, 0.42 mmol, 0.83 equiv).The freshly prepared arylzinc reagent was added and the reaction mixture was placed in an oil bath at 55 °C for 18 h. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 2:1) afforded the title compound as a yellow oil (**14d**, 72 mg, 0.27 mmol, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.15 (s, 1H), 8.51 (s, 2H), 7.73–7.51 (m, 4H), 6.07 (s, 1H), 2.28 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 156.9, 155.9, 150.5, 136.1, 132.8, 132.3, 130.4, 130.2, 130.1, 129.2, 128.5, 105.9, 14.0.
MS (EI, 70 eV): m/z (%) = 236 (15), 235 (100), 208 (14), 207 (10), 194 (15), 167 (18), 140 (16).
HRMS (EI): for $C_{14}H_{11}ClN_4$: calc. [M-H$^+$]: 269.0594; found: 269.0586.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3118 (vw), 3039 (w), 2929 (w), 2855 (vw), 1725 (vw), 1578 (w), 1549 (m), 1524 (s), 1497 (m), 1462 (m), 1421 (m), 1408 (vs), 1373 (m), 1362 (m), 1278 (w), 1187 (m), 1163 (w), 1117 (w), 1087 (w), 1011 (m), 1002 (m), 992 (m), 972 (w), 912 (w), 781 (m), 765 (vs), 750 (m), 726 (vs), 672 (w).

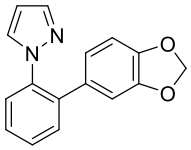
(2-(1*H*-Pyrazol-1-yl)phenyl)(furan-2-yl)methanol (14e)



According to **TP 1**, to a mixture of 1-phenyl-1*H*-pyrazole (**12c**, 65 µL, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.40 mmol, 0.8 equiv) at 40 °C. After 1 h, furfural (50 µL, 0.60 mmol, 1.2 equiv) was added dropwise at 0 °C and the reaction mixture was stirred for 1 h at room temperature. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 4:1) afforded the title compound as a brown solid (**14e**, 108 mg, 0.45 mmol, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.71 (dd, *J* = 1.9, 0.7 Hz, 1H), 7.65 (dd, *J* = 2.4, 0.7 Hz, 1H), 7.46–7.36 (m, 3H), 7.34–7.30 (m, 1H), 7.28–7.26 (m, 2H), 6.43 (t, *J* = 2.2 Hz, 1H), 6.27 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.18 (dt, *J* = 3.3, 1.0 Hz, 1H), 5.72 (d, *J* = 1.1 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 154.5, 141.6, 140.5, 139.2, 136.9, 130.6, 130.2, 129.1, 128.6, 125.1, 110.2, 107.2, 106.5, 68.3.
MS (EI, 70 eV): m/z (%) = 223 (30), 212 (29), 211 (100), 209 (29), 197 (51), 195 (26), 193 (39), 184 (80), 183 (59), 181 (19), 172 (18), 171 (47), 169 (30), 168 (16), 167 (30), 166 (25), 156 (29), 144 (17), 130 (25), 117 (21), 115 (37), 89 (17).
HRMS (EI): for $C_{14}H_{12}N_2O_2$: calc. [M+]: 240.0899; found: 240.0892.
IR (Diamond-ATR, neat): $\tilde{\nu}$/cm^{-1} = 3244 (w), 3240 (w), 3091 (w), 2923 (vw), 1601 (w), 1583 (vw), 1515 (w), 1490 (m), 1458 (w), 1424 (w), 1398 (m), 1331 (w), 1316 (m), 1283 (w), 1270 (w), 1211 (m), 1197 (m), 1182 (m), 1166 (vw), 1142 (m), 1129 (w), 1103 (vw), 1068 (w), 1056 (m), 1046 (s), 1026 (m), 1012 (s), 985 (w), 950 (m), 922 (m), 914 (w), 881 (w), 865 (w), 830 (w), 802 (m), 769 (s), 757 (vs), 732 (vs), 717 (s), 698 (m), 677 (w), 663 (m).
Melting point: M.p. = 91 °C.

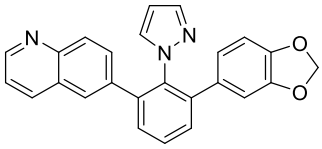
1-(2-(benzo[*d*][1,3]dioxol-5-yl)phenyl)-1H-pyrazole (14f)



According to **TP 1**, to a mixture of 1-phenyl-1*H*-pyrazole (**12c**, 0.65 mL, 5.00 mmol, 1.0 equiv) in toluene (10 mL) was added sBu$_2$Mg (0.40 mmol, 0.8 equiv) at 40 °C. After 1 h, the resulting diarylmagnesium was transmetalated with a $ZnCl_2$ solution (5.5 mL, 1.00 M in THF, 1.10 equiv) at 0 °C for 30 min. A dry and argon-flushed Schlenk-tube, equipped with a magnetic stirring bar and a septum was charged with Pd(dppf)Cl_2 (182 mg, 5 mol%) and 5-bromobenzo[d][1,3]dioxole (0.50 mL, 4.15 mmol, 0.83 equiv).The freshly prepared arylzinc reagent was added and the reaction mixture was placed in an oil bath at 55 °C for 18 h. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 9:1) afforded the title compound as a brown solid (**14f**, 879 mg, 3.33 mmol, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.65 (dd, J = 1.8, 0.7 Hz, 1H), 7.61–7.55 (m, 1H), 7.49–7.41 (m, 3H), 7.15 (dd, J = 2.4, 0.7 Hz, 1H), 6.74 (d, J = 8.0 Hz, 1H), 6.60 (dd, J = 8.0, 1.8 Hz, 1H), 6.54 (d, J = 1.7 Hz, 1H), 6.24 (dd, J = 2.4, 1.8 Hz, 1H), 5.95 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 147.7, 147.0, 140.3, 138.5, 136.4, 132.4, 131.3, 131.0, 128.3, 128.2, 126.6, 122.2, 108.9, 108.4, 106.5, 101.1.
MS (EI, 70 eV): m/z (%) = 264 (20), 263 (100), 205 (15).
HRMS (EI): for $C_{16}H_{12}N_2O_2$: calc. [M+]: 264.0899; found: 264.0891.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 2892 (w), 1733 (vw), 1607 (w), 1576 (vw), 1517 (m), 1505 (m), 1477 (vs), 1460 (s), 1435 (m), 1416 (m), 1393 (s), 1337 (m), 1329 (m), 1239 (s), 1218 (vs), 1192 (m), 1148 (w), 1126 (w), 1107 (m), 1097 (m), 1036 (s), 1021 (s), 1012 (m), 935 (s), 915 (m), 891 (m), 877 (m), 863 (w), 861 (w), 836 (vw), 809 (m), 749 (vs), 744 (vs), 726 (m), 715 (m), 701 (w), 699 (w), 694 (vw), 675 (w), 667 (w), 659 (w).
Melting point: M.p. = 97 °C.

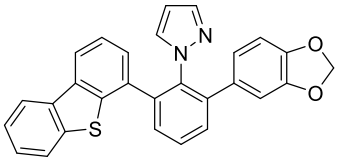
6-(3-(benzo[d][1,3]dioxol-5-yl)-2-(1H-pyrazol-1-yl)phenyl)quinolone (15a)



According to **TP 1**, to a mixture of 1-(2-(benzo[*d*][1,3]dioxol-5-yl)phenyl)-1H-pyrazole (**14f**, 53 mg, 0.20 mmol, 1.0 equiv) in toluene (0.4 mL) was added *s*Bu_2Mg (0.40 mmol, 0.8 equiv) at 60 °C. After 0.5 h, the resulting diarylmagnesium was transmetalated with a $ZnCl_2$ solution (0.24 mL, 1.00 M in THF, 1.10 equiv) at 0 °C for 30 min. A dry and argon-flushed Schlenk-tube, equipped with a magnetic stirring bar and a septum was charged with Pd(dppf)Cl_2 (8 mg, 5 mol%) and 6-iodoquinoline (43 mg, 0.17 mmol, 0.83 equiv).The freshly prepared arylzinc reagent was added and the reaction mixture was placed in an oil bath at 55 °C for 18 h. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 2:1) afforded the title compound as a brown oil (**15b**, 55 mg, 0.14 mmol, 84% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.88 (dd, J = 4.2, 1.7 Hz, 1H), 8.06 (dd, J = 8.3, 1.7 Hz, 1H), 7.92 (d, J = 8.8 Hz, 1H), 7.68–7.48 (m, 4H), 7.41–7.34 (m, 3H), 7.12 (d, J = 2.4 Hz, 1H), 6.71 (d, J = 8.0 Hz, 1H), 6.63 (dd, J = 8.0, 1.7 Hz, 1H), 6.57 (d, J = 1.8 Hz, 1H), 6.07 (t, J = 2.1 Hz, 1H), 5.93 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 150.6, 147.6, 147.4, 147.1, 140.3, 139.9, 139.7, 137.3, 136.7, 136.5, 132.5, 132.5, 130.7, 130.2, 130.0, 129.4, 129.1, 128.1, 127.4, 122.1, 121.5, 108.8, 108.3, 106.6, 101.2.
MS (EI, 70 eV): m/z (%) = 281 (17), 252 (14), 225 (41), 209 (20), 207 (64), 191 (17).
HRMS (EI): for $C_{25}H_{17}N_3O_2$: calc. [M+]: 391.1321; found: 391.1315.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 2955 (w), 2924 (m), 2855 (w), 1741 (m), 1517 (w), 1502 (m), 1492 (m), 1464 (s), 1435 (m), 1410 (w), 1390 (w), 1354 (w), 1341 (w), 1241 (m), 1227 (m), 1157 (m), 1154 (m), 1109 (m), 1091 (m), 1083 (m), 1037 (vs), 1022 (s), 976 (s), 937 (vs), 914 (vs), 870 (s), 841 (s), 829 (m), 799 (s), 763 (s), 754 (s), 736 (m), 731 (m), 698 (w), 673 (w), 668 (w).

1-(2-(benzo[d][1,3]dioxol-5-yl)-6-(dibenzo[b,d]thiophen-4-yl)phenyl)-1H-pyrazole (15b)



According to **TP 1**, to a mixture of 1-(2-(benzo[*d*][1,3]dioxol-5-yl)phenyl)-1H-pyrazole (**14f**, 53 mg, 0.20 mmol, 1.0 equiv) in toluene (0.4 mL) was added *s*Bu_2Mg (0.40 mmol, 0.8 equiv) at 60 °C. After 0.5 h, the resulting diarylmagnesium was transmetalated with a $ZnCl_2$ solution (0.24 mL, 1.00 M in THF, 1.10 equiv) at 0 °C for 30 min. A dry and argon-flushed Schlenk-tube, equipped with a magnetic stirring bar and a septum was charged with $Pd(dppf)Cl_2$ (8 mg, 5 mol%) and 4-iododibenzo[*b*,*d*]thiophene (53 mg, 0.17 mmol, 0.83 equiv).The freshly prepared arylzinc reagent was added and the reaction mixture was placed in an oil bath at 55 °C for 18 h. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 98:1) afforded the title compound as a white solid (**15b**, 51 mg, 0.12 mmol, 67% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.17–8.12 (m, 1H), 8.03 (dd, J = 7.9, 1.1 Hz, 1H), 7.84–7.78 (m, 1H), 7.67 (dd, J = 7.3, 1.9 Hz, 1H), 7.64–7.56 (m, 2H), 7.49–7.42 (m, 2H), 7.32–7.26 (m, 2H), 7.07–7.01 (m, 2H), 6.71 (d, J = 8.1 Hz, 1H), 6.66 (dd, J = 8.1, 1.7 Hz, 1H), 6.60 (d, J = 1.7 Hz, 1H), 5.92 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 147.2, 146.8, 140.0, 139.5, 139.3, 139.3, 138.7, 136.8, 135.7, 135.4, 133.1, 132.2, 131.9, 130.8, 129.1, 128.9, 126.7, 126.6, 124.3, 124.1, 122.5, 121.9, 121.6, 120.3, 108.6, 107.9, 105.7, 100.8.

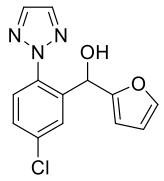
MS (EI, 70 eV): m/z (%) = 447 (26), 446 (74), 445 (100).

HRMS (EI): for $C_{28}H_{18}N_2O_2S$: calc. [M-H$^+$]: 445.1011; found: 445.1010.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 2962 (vw), 2959 (w), 2957 (w), 2954 (w), 2950 (vw), 2945 (vw), 2922 (w), 2918 (w), 2914 (w), 2901 (w), 2896 (w), 2892 (w), 2889 (w), 2887 (w), 2884 (w), 2882 (w), 2876 (w), 2874 (w), 2866 (w), 2864 (w), 2862 (w), 2853 (w), 1517 (w), 1502 (m), 1492 (m), 1480 (w), 1462 (m), 1440 (m), 1436 (m), 1419 (w), 1411 (w), 1392 (m), 1385 (w), 1339 (w), 1315 (w), 1304 (w), 1259 (w), 1257 (w), 1242 (m), 1227 (s), 1195 (w), 1178 (w), 1157 (vw), 1155 (vw), 1107 (w), 1084 (w), 1038 (s), 1022 (m), 937 (m), 911 (m), 894 (w), 890 (w), 882 (w), 877 (w), 874 (w), 872 (w), 870 (w), 868 (w), 865 (w), 863 (w), 804 (m), 793 (m), 749 (vs), 737 (m), 732 (m), 727 (m), 722 (s), 705 (m), 692 (w).

Melting point: M.p. = 152 °C.

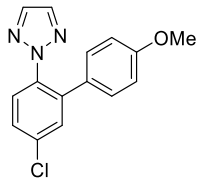
(5-Chloro-2-(2*H*-1,2,3-triazol-2-yl)phenyl)(furan-2-yl)methanol (18a)



According to **TP 1**, to a mixture of 2-(4-chlorophenyl)-2*H*-1,2,3-triazole (**16a**, 90 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.40 mmol, 0.8 equiv) at 40 °C. After 15 min, furfural (50 µL, 0.60 mmol, 1.2 equiv) was added dropwise at 0 °C and the reaction mixture was stirred for 1 h at room temperature. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 4:1) afforded the title compound as a brown oil (**18a**, 92 mg, 0.34 mmol, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.84 (s, 2H), 7.75–7.69 (m, 1H), 7.48–7.42 (m, 2H), 7.32 (dd, *J* = 1.9, 0.9 Hz, 1H), 6.28 (dd, *J* = 3.3, 1.9 Hz, 1H), 6.17 (dt, *J* = 3.3, 1.0 Hz, 1H), 5.98 (d, *J* = 0.9 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 153.3, 142.3, 137.0, 136.4, 135.7, 134.9, 129.8, 129.2, 126.2, 110.2, 107.3, 67.2.
MS (EI, 70 eV): m/z (%) = 277 (23), 275 (64), 260 (26), 259 (20), 258 (71), 257 (22), 248 (32), 247 (37), 246 (84), 231 (26), 230 (20), 228 (19), 221 (38), 220 (41), 219 (100), 208 (22), 207 (39), 206 (62), 204 (22), 202 (18), 192 (29), 191 (34), 164 (22), 163 (17), 140 (16), 124 (25), 123 (18), 115 (18), 95 (42), 81 (31), 75 (18), 70 (83), 63 (17), 43 (78), 42 (43), 41 (16).
HRMS (EI): for $C_{13}H_{10}ClN_3O_2$: calc. [M^+]: 275.0462; found: 275.0457.
IR (Diamond-ATR, neat): $\tilde{\nu}$/cm^{-1} = 3380 (w), 3143 (w), 3120 (w), 2923 (vw), 2852 (vw), 2363 (vw), 1794 (w), 1714 (w), 1700 (w), 1652 (w), 1594 (w), 1488 (s), 1410 (s), 1370 (w), 1290 (w), 1260 (w), 1225 (w), 1181 (m), 1148 (m), 1122 (w), 1100 (m), 1072 (m), 1049 (w), 1010 (s), 962 (s), 948 (vs), 902 (w), 883 (m), 819 (vs), 783 (m), 735 (s), 675 (w), 656 (vw).

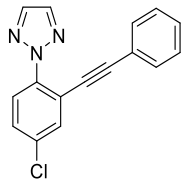
2-(5-Chloro-4'-methoxy-[1,1'-biphenyl]-2-yl)-2*H*-1,2,3-triazole (18b)



According to **TP 1**, to a mixture of 2-(4-chlorophenyl)-2*H*-1,2,3-triazole (**16a**, 539 mg, 3.00 mmol, 1.0 equiv) in toluene (6 mL) was added *s*Bu_2Mg (1.80 mmol, 0.6 equiv) at 40 °C. After 15 min, the resulting diarylmagnesium was transmetalated with a $ZnCl_2$ solution (3.3 mL, 1.00 M in THF, 1.10 equiv) at 0 °C for 30 min. A dry and argon-flushed Schlenk-tube, equipped with a magnetic stirring bar and a septum was charged with Pd(dppf)Cl_2 (110 mg, 5 mol%) and 4-bromoanisole (0.31 mL, 2.50 mmol, 0.83 equiv).The freshly prepared arylzinc reagent was added and the reaction mixture was placed in an oil bath at 55 °C for 18 h. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 9:1) afforded the title compound as a yellow oil (**18b**, 455 mg, 1.60 mmol, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.69 (s, 2H), 7.54 – 7.49 (m, 2H), 7.42 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.96–6.92 (m, 2H), 6.81–6.76 (m, 2H), 3.79 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 159.3, 139.1, 136.8, 135.3, 135.1, 131.0, 129.5, 129.2, 127.9, 127.6, 113.8, 55.2.
MS (EI, 70 eV): m/z (%) = 287 (11), 286 (31), 285 (36), 284 (100), 269 (10), 188 (22), 153 (18), 126 (10).
HRMS (EI): for $C_{15}H_{12}ClN_3O$: calc. [M+]: 285.0669; found: 285.0671.
IR (Diamond-ATR, neat): $\tilde{\nu}$/cm^{-1} = 3125 (vw), 3060 (vw), 3038 (vw), 3001 (vw), 2956 (w), 2932 (w), 2835 (w), 1609 (m), 1580 (w), 1516 (m), 1488 (s), 1462 (m), 1441 (w), 1410 (m), 1401 (m), 1368 (w), 1289 (m), 1250 (s), 1242 (s), 1178 (s), 1149 (m), 1128 (w), 1110 (m), 1099 (m), 1075 (m), 1056 (w), 1036 (m), 1024 (m), 1007 (w), 961 (s), 950 (s), 884 (w), 819 (vs), 776 (m), 745 (w), 728 (vw), 670 (w).

2-(4-Chloro-2-(phenylethynyl)phenyl)-2*H*-1,2,3-triazole (18c)



According to **TP 1**, to a mixture of 2-(4-chlorophenyl)-2*H*-1,2,3-triazole (**16a**, 539 mg, 3.00 mmol, 1.0 equiv) in toluene (6 mL) was added *s*Bu_2Mg (1.80 mmol, 0.6 equiv) at 40 °C. After 15 min, the further procedure was adopted and modified from literature.[17] The reaction mixture was cooled to -50 °C and CuCN·2LiCl (3.6 mL, 1.0 M in THF, 1.2 equiv) was added dropwise and the mixture was stirred for 25 min. (phenylethynyl)lithium (6.00 mmol; prepared by adding *n*BuLi (6.00 mmol) to a 0.5 M solution of phenylacetylen (6.00 mol) in THF at 0 °C and stirring for 30 min) was added dropwise to the resulting cuprate and the mixture was stirred for 1 h at -50 °C. The reaction mixture was cooled to -78 °C, and a solution of chloranil (959 mg, 3.90 mmol, 1.3 equiv) in dry THF (20 mL) was added slowly over a period of 45 min. The reaction mixture was then warmed to -50 °C and stirred for 3 h. Et_2O (30 mL) was poured into the crude reaction mixture and the reaction mixture was then filtered through celite and the residue washed with Et_2O (ca. 100 mL). The organic phase was washed with NH_4OH (2 M, 2 x 30 mL) and extracted with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 98:2) afforded the title compound as a brown oil (**18c**, 432 mg, 1.54 mmol, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) =7.90 (s, 2H), 7.71–7.66 (m, 2H), 7.45–7.40 (m, 3H), 7.33 (dd, *J* = 5.3, 2.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 139.2, 135.7, 134.1, 133.3, 131.6, 129.0, 128.9, 128.3, 125.9, 122.5, 119.7, 95.2, 84.6.

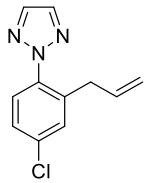
MS (EI, 70 eV): m/z (%) = 278 (20), 254 (32), 253 (16), 252 (100), 223 (12), 217 (31), 190 (41), 163 (19).

HRMS (EI): for $C_{16}H_{10}ClN_3$: calc. [M+]: 279.0563; found: 279.0559.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3284 (vw), 3061 (vw), 2966 (w), 2927 (vw), 2873 (vw), 2223 (w), 1683 (m), 1599 (w), 1571 (m), 1497 (s), 1484 (s), 1442 (m), 1406 (s), 1262 (w), 1149 (m), 1103 (s), 1068 (m), 1024 (w), 961 (s), 945 (s), 893 (m), 820 (vs), 753 (vs), 728 (s), 688 (vs), 669 (w).

[17] S. R. Dubbaka, M. Kienle, H. Mayr, P. Knochel, *Angew. Chem. Int. Ed.* **2007**, *46*, 9093-9096.

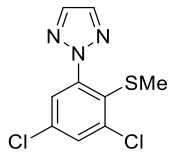
2-(2-Allyl-4-chlorophenyl)-2*H*-1,2,3-triazole (18d)



According to **TP 1**, to a mixture of 2-(4-chlorophenyl)-2*H*-1,2,3-triazole (**16a**, 539 mg, 3.00 mmol, 1.0 equiv) in toluene (6 mL) was added *s*Bu_2Mg (1.80 mmol, 0.6 equiv) at 40 °C. After 15 min, allyl bromide (0.31 mL, 3.60 mmol, 1.2 equiv) and CuCN·2LiCl (0.6 mL, 1.0 M in THF, 20 mol%) were added at -25 °C and the mixture was stirred for 1 h. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 98:2) afforded the title compound as a white solid (**18d**, 433 mg, 1.98 mmol, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.84 (s, 2H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.38–7.30 (m, 2H), 5.81 (ddt, *J* = 16.8, 10.1, 6.6 Hz, 1H), 5.06–4.93 (m, 2H), 3.48 (dt, *J* = 6.7, 1.6 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 138.2, 137.1, 135.8, 135.6, 135.2, 131.1, 127.6, 127.4, 117.4, 36.4.
MS (EI, 70 eV): m/z (%) = 206 (32), 205 (10), 204 (100), 164 (14), 155 (12), 128 (12), 115 (10).
HRMS (EI): for $C_{11}H_{10}ClN_3$: calc. [M+]: 219.0563; found: 219.0558.
IR (Diamond-ATR, neat): $\tilde{\nu}$/cm^{-1} = 3134 (w), 3121 (w), 3076 (vw), 2926 (w), 2856 (vw), 1882 (vw), 1854 (vw), 1635 (w), 1600 (w), 1490 (m), 1437 (w), 1414 (m), 1407 (m), 1375 (w), 1304 (w), 1255 (w), 1188 (w), 1157 (m), 1132 (m), 1103 (m), 1095 (m), 1070 (m), 1045 (w), 1005 (m), 956 (s), 945 (m), 920 (s), 883 (m), 871 (m), 815 (vs), 751 (m), 705 (w), 677 (m), 660 (w).
Melting point: M.p. = 63 °C.

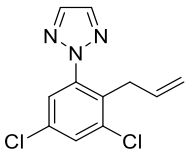
2-(3,5-Dichloro-2-(methylthio)phenyl)-2*H*-1,2,3-triazole (18e)



According to **TP 1**, to a mixture of 2-(3,5-dichlorophenyl)-2*H*-1,2,3-triazole (**16b**, 1.070 g, 5.00 mmol, 1.0 equiv) in toluene (10 mL) was added *s*Bu_2Mg (3.00 mmol, 0.6 equiv) at 25 °C. After 30 min, *S*-methyl methanethiosulfonate (0.57 mL, 6.00 mmol, 1.2 equiv) was added dropwise at 0 °C and the reaction mixture was stirred for 2 h at room temperature. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 98:2) afforded the title compound as a brown solid (**18e**, 1.062 g, 4.08 mmol, 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.90 (s, 2H), 7.61 (d, *J* = 2.3 Hz, 1H), 7.48 (d, *J* = 2.3 Hz, 1H), 2.24 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 144.7, 141.3, 135.9, 134.6, 131.8, 130.9, 126.3, 19.0.
MS (EI, 70 eV): m/z (%) = 260 (49), 258 (73), 245 (38), 243 (56), 227 (61), 225 (100), 205 (44), 203 (71), 202 (11), 191 (12), 190 (12), 189 (20), 188 (23), 168 (27), 167 (13), 160 (19), 158 (26), 141 (10), 123 (15), 119 (24), 92 (10), 78 (16), 69 (29).
HRMS (EI): for $C_9H_7Cl_2N_3S$: calc. [M+]: 258.9738; found: 258.9735.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3141 (vw), 3122 (vw), 3075 (w), 3059 (w), 2995 (vw), 2919 (w), 1768 (vw), 1738 (vw), 1574 (s), 1545 (m), 1439 (m), 1406 (s), 1346 (m), 1313 (w), 1249 (w), 1184 (w), 1146 (m), 1119 (m), 1067 (w), 1047 (w), 979 (m), 958 (vs), 899 (m), 885 (w), 870 (s), 828 (s), 821 (vs), 791 (s), 723 (m), 701 (w), 672 (w), 654 (w).
Melting point: M.p. = 53 °C.

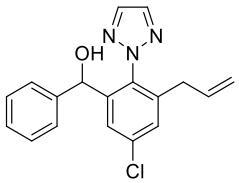
2-(2-Allyl-3,5-dichlorophenyl)-2*H*-1,2,3-triazole (18f)



According to **TP 1**, to a mixture of 2-(3,5-dichlorophenyl)-2*H*-1,2,3-triazole (**16b**, 1.070 g, 5.00 mmol, 1.0 equiv) in toluene (10 mL) was added *s*Bu_2Mg (3.00 mmol, 0.6 equiv) at 25 °C. After 30 min, allyl bromide (0.52 mL, 6.00 mmol, 1.2 equiv) and CuCN·2LiCl (1.0 mL, 1.0 M in THF, 20 mol%) were added at -25 °C and the mixture was stirred for 1 h. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 99:1) afforded the title compound as a red solid (**18f**, 1.150 g, 4.53 mmol, 91% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.86 (s, 2H), 7.55–7.49 (m, 2H), 5.79 (ddt, *J* = 16.3, 10.1, 6.2 Hz, 1H), 4.97 (dq, *J* = 10.2, 1.6 Hz, 1H), 4.87 (dq, *J* = 17.1, 1.7 Hz, 1H), 3.59 (dt, *J* = 6.1, 1.6 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 135.7, 133.7, 132.6, 132.0, 130.2, 125.2, 116.5, 32.8.
MS (EI, 70 eV): m/z (%) = 239 (62), 237 (100), 207 (20), 149 (15), 57 (11), 44 (67), 43 (42).
HRMS (EI): for $C_{11}H_9Cl_2N_3$: calc. [M+]: 253.0174; found: 253.0181.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3136 (w), 3084 (w), 2360 (w), 1733 (w), 1635 (m), 1589 (s), 1565 (m), 1466 (m), 1455 (m), 1447 (m), 1436 (m), 1428 (m), 1411 (s), 1283 (w), 1256 (w), 1184 (w), 1146 (m), 1129 (m), 1119 (m), 1076 (m), 1061 (m), 998 (m), 960 (s), 936 (m), 920 (s), 907 (s), 857 (vs), 825 (m), 818 (s), 807 (m), 782 (s), 705 (m), 672 (w).
Melting point: M.p. = 58 °C.

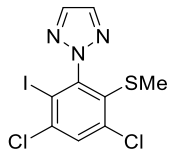
(3-Allyl-5-chloro-2-(2*H*-1,2,3-triazol-2-yl)phenyl)(phenyl)methanol (19a)



According to **TP 1**, to a mixture of 2-(2-allyl-4-chlorophenyl)-2*H*-1,2,3-triazole (**18d**, 110 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.40 mmol, 0.8 equiv) at 40 °C. After 15 min, benzaldehyde (62 µL, 0.60 mmol, 1.2 equiv) was added dropwise at 0 °C and the reaction mixture was stirred for 1 h at room temperature. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 9:1) afforded the title compound as a white solid (**19a**, 67 mg, 0.21 mmol, 42% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.84 (s, 2H), 7.40 (d, *J* = 2.4 Hz, 1H), 7.37–7.26 (m, 4H), 7.22–7.16 (m, 2H), 5.73 (ddt, *J* = 16.9, 10.0, 6.8 Hz, 1H), 5.43 (d, *J* = 4.2 Hz, 1H), 5.04 (dq, *J* = 10.1, 1.5 Hz, 1H), 4.95 (dq, *J* = 17.0, 1.6 Hz, 1H), 3.56–3.47 (m, 1H), 3.11 (dd, *J* = 6.8, 1.7 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 143.3, 140.9, 140.0, 136.1, 135.2, 134.6, 129.6, 128.2, 127.6, 127.1, 126.0, 117.3, 71.2, 35.6.
MS (EI, 70 eV): m/z (%) = 325 (13), 324 (25), 309 (22), 308 (37), 307 (72), 306 (21), 299 (24), 297 (78), 272 (17), 270 (16), 268 (100), 254 (16), 219 (36), 204 (15), 203 (49), 202 (34), 192 (15), 190 (66), 189 (19), 152 (17), 128 (16), 115 (21), 105 (75), 77 (48).
HRMS (EI): for $C_{18}H_{16}ClN_3O$: calc. [M+]: 325.0982; found: 325.0979.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3320 (m), 3132 (w), 3109 (m), 2955 (w), 2919 (m), 2849 (w), 1639 (w), 1589 (w), 1578 (w), 1456 (m), 1435 (m), 1418 (m), 1363 (w), 1315 (m), 1307 (w), 1227 (m), 1186 (w), 1153 (m), 1117 (w), 1061 (s), 1007 (m), 967 (s), 956 (s), 938 (m), 893 (m), 865 (m), 842 (m), 825 (m), 777 (m), 758 (m), 697 (vs), 684 (m), 668 (m).
Melting point: M.p. = 84 °C.

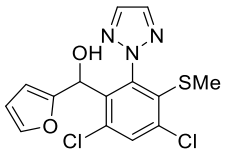
2-(3,5-Dichloro-2-iodo-6-(methylthio)phenyl)-2*H*-1,2,3-triazole (19b)



According to **TP 1**, to a mixture of 2-(3,5-dichloro-2-(methylthio)phenyl)-2*H*-1,2,3-triazole (**18e**, 130 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.40 mmol, 0.8 equiv) at 25 °C. After 10 min, the reaction mixture was cooled to 0 °C and iodine (153 mg, 0.60 mmol, 1.2 equiv) dissolved in THF (1 mL) was added dropwise and the reaction mixture was stirred for 1 h. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 98:2) afforded the title compound as a brown solid (**19b**, 169 mg, 0.44 mmol, 88% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.93 (s, 2H), 7.79 (s, 1H), 2.26 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 148.8, 140.8, 140.2, 135.5, 135.3, 131.2, 100.8, 18.9.
MS (EI, 70 eV): m/z (%) = 384 (100), 371 (13), 369 (21), 354 (26), 352 (35), 332 (21), 331 (11), 330 (33), 317 (33), 316 (12), 315 (38), 227 (11), 225 (16), 202 (21), 190 (17), 189 (13), 188 (24), 157 (12), 155 (16), 153 (41), 70 (43), 69 (33), 44 (12).
HRMS (EI): for $C_9H_6Cl_2IN_3S$: calc. [M+]: 384.8704; found: 384.8698.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3139 (vw), 3126 (w), 2920 (w), 2361 (vw), 1543 (w), 1517 (w), 1432 (m), 1411 (m), 1391 (s), 1277 (m), 1234 (w), 1160 (m), 1155 (s), 1131 (m), 1073 (m), 1062 (m), 1057 (m), 968 (m), 961 (vs), 872 (s), 823 (vs), 792 (m), 699 (w), 682 (w).
Melting point: M.p. = 97 °C.

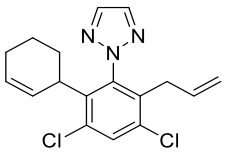
(4,6-Dichloro-3-(methylthio)-2-(2*H*-1,2,3-triazol-2-yl)phenyl)(furan-2-yl)methanol (19c)



According to **TP 1**, to a mixture of 2-(3,5-dichloro-2-(methylthio)phenyl)-2*H*-1,2,3-triazole (**18e**, 130 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.40 mmol, 0.8 equiv) at 25 °C. After 10 min, furfural (50 µL, 0.60 mmol, 1.2 equiv) was added dropwise at 0 °C and the reaction mixture was stirred for 1 h at room temperature. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 9:1) afforded the title compound as a yellow oil (**19c**, 136 mg, 0.38 mmol, 76% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.79 (s, 1H), 7.77–7.67 (m, 2H), 7.16 (dt, *J* = 1.8, 0.9 Hz, 1H), 6.11 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.06 (d, *J* = 9.9 Hz, 1H), 5.86–5.80 (m, 1H), 4.38 (d, *J* = 11.0 Hz, 1H), 2.21 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 152.7, 144.3, 141.7, 140.8, 136.6, 135.7, 135.5, 135.3, 132.8, 110.2, 105.3, 66.8, 19.0.
MS (EI, 70 eV): m/z (%) = 354 (100), 341 (15), 339 (27), 338 (15), 336 (16), 327 (15), 325 (22), 288 (23), 287 (30), 286 (33), 285 (41), 279 (17), 277 (24), 273 (13), 271 (24), 230 (12), 97 (12), 95 (61), 70 (94), 69 (22), 41 (23), 40 (16).
HRMS (EI): for $C_{14}H_{11}Cl_2N_3O_2S$: calc. [M^+]: 354.9949; found: 354.9944.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3410 (w), 3122 (w), 3066 (vw), 2980 (vw), 2925 (w), 1733 (m), 1562 (m), 1536 (m), 1505 (w), 1431 (s), 1410 (s), 1373 (m), 1241 (m), 1188 (w), 1143 (s), 1108 (s), 1045 (s), 1003 (s), 960 (vs), 905 (s), 883 (m), 823 (vs), 807 (m), 793 (m), 733 (vs), 702 (w).

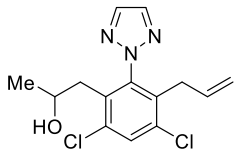
2-(3-Allyl-4,6-dichloro-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-2-yl)-2*H*-1,2,3-triazole (19d)



According to **TP 1**, to a mixture of 2-(2-allyl-3,5-dichlorophenyl)-2*H*-1,2,3-triazole (**18f**, 127 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added sBu$_2$Mg (0.30 mmol, 0.6 equiv) at 40 °C. After 20 min, 3-bromocyclohexene (70 µL, 0.60 mmol, 1.2 equiv) and CuCN·2LiCl (0.1 mL, 1.0 M in THF, 20 mol%) were added at -25 °C and the mixture was stirred for 1 h. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 99:1) afforded the title compound as a colorless oil (**19d**, 117 mg, 0.35 mmol, 70 % yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.89–7.71 (m, 2H), 7.60 (s, 1H), 5.67 (ddt, J = 16.6, 10.1, 6.4 Hz, 1H), 5.38–5.16 (m, 2H), 4.95 (dq, J = 10.1, 1.5 Hz, 1H), 4.81 (dq, J = 17.1, 1.7 Hz, 1H), 3.01–2.77 (m, 2H), 2.12–1.71 (m, 6H), 1.43 (d, J = 13.6 Hz, 1H).
^{13}C NMR (101 MHz, CDCl$_3$): δ (ppm) = 141.1, 140.6, 134.8, 133.5, 133.2, 133.0, 127.2, 116.8, 76.7, 38.7, 33.4, 27.8, 23.8, 22.7.
MS (EI, 70 eV): m/z (%) =334 (46), 332 (74), 320 (57), 318 (91), 305 (42), 304 (38), 298 (63), 280 (69), 279 (56), 278 (100), 277 (75), 276 (66), 265 (35), 264 (39), 243 (40), 242 (45), 241 (47), 240 (37), 238 (37), 236 (63), 234 (41), 229 (49), 214 (57), 207 (40), 206 (49), 204 (40), 201 (57), 180 (53), 178 (35), 165 (96), 153 (42), 152 (87), 139 (52).
HRMS (EI): for $C_{17}H_{17}Cl_2N_3$: calc. [M$^+$]: 333.0800; found: 333.0793.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3027 (vw), 2927 (vw), 2866 (vw), 2252 (vw), 1639 (vw), 1578 (vw), 1554 (vw), 1455 (vw), 1433 (vw), 1413 (vw), 1380 (vw), 1219 (vw), 1178 (vw), 1148 (vw), 1110 (vw), 1011 (vw), 994 (vw), 962 (w), 821 (w), 804 (vw), 652 (vw).

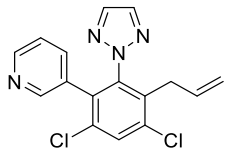
2-(3-Allyl-4,6-dichloro-2-(2*H*-1,2,3-triazol-2-yl)phenyl)propan-2-ol (19e)



According to **TP 1**, to a mixture of 2-(2-allyl-3,5-dichlorophenyl)-2*H*-1,2,3-triazole (**18f**, 51 mg, 0.20 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.12 mmol, 0.6 equiv) at 40 °C. After 20 min, the reaction mixture was cooled to 0 °C and CuI (8 mg, 5 mol%) was added and the reaction mixture was stirred for 1 h at 0 °C. Propylene oxide (42 µL, 0.24 mmol, 1.2 equiv) was added dropwise and the reaction mixture was stirred for further 4 h at 0 °C. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 4:1) afforded the title compound as a yellow oil (**19e**, 42 mg, 0.14 mmol, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.92 (s, 2H), 7.64 (s, 1H), 5.67 (ddt, *J* = 16.7, 10.1, 6.3 Hz, 1H), 4.94 (dq, *J* = 10.1, 1.5 Hz, 1H), 4.81 (dq, *J* = 17.0, 1.6 Hz, 1H), 4.07 (dtq, *J* = 12.5, 6.2, 3.3, 2.4 Hz, 1H), 3.14 (ddt, *J* = 15.0, 6.6, 1.5 Hz, 1H), 3.05–2.97 (m, 2H), 2.77 (dd, *J* = 14.1, 4.0 Hz, 1H), 1.95 (dd, *J* = 14.1, 9.5 Hz, 1H), 1.13 (d, *J* = 6.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 140.9, 135.4, 135.0, 133.6, 133.4, 133.2, 132.2, 116.8, 66.2, 38.6, 33.5, 24.5.
MS (EI, 70 eV): m/z (%) = 269 (25), 268 (13), 267 (39), 266 (11), 256 (11), 254 (62), 253 (14), 252 (100), 239 (10), 197 (12), 45 (17), 43 (14).
HRMS (EI): for $C_{14}H_{15}Cl_2N_3O$: calc. [M-H$^+$]: 310.0514; found: 310.0509.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3426 (w), 3080 (vw), 2969 (w), 2930 (w), 2360 (w), 1638 (w), 1581 (m), 1569 (w), 1558 (m), 1456 (m), 1436 (vs), 1411 (s), 1387 (w), 1374 (m), 1286 (w), 1206 (w), 1148 (m), 1110 (s), 1083 (m), 1050 (m), 987 (m), 960 (vs), 932 (s), 916 (s), 893 (m), 874 (m), 820 (s), 802 (m), 777 (m), 756 (w), 740 (w).

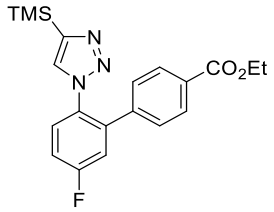
3-(3-Allyl-4,6-dichloro-2-(2*H*-1,2,3-triazol-2-yl)phenyl)pyridine (19f)



According to **TP 1**, to a mixture of 2-(2-allyl-3,5-dichlorophenyl)-2*H*-1,2,3-triazole (**18f**, 127 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.30 mmol, 0.6 equiv) at 40 °C. After 20 min, the resulting diarylmagnesium was transmetalated with a $ZnCl_2$ solution (0.6 mL, 1.00 M in THF, 1.10 equiv) at 0 °C for 30 min. A dry and argon-flushed Schlenk-tube, equipped with a magnetic stirring bar and a septum was charged with Pd(dppf)Cl_2 (15 mg, 5 mol%) and 3-bromopyridine (40 µL, 0.42 mmol, 0.83 equiv).The freshly prepared arylzinc reagent was added and the reaction mixture was placed in an oil bath at 55 °C for 18 h. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 2:1) afforded the title compound as a yellow oil (**19f**, 98 mg, 0.30 mmol, 71% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.45 (dd, *J* = 4.9, 1.7 Hz, 1H), 8.31 (dd, *J* = 2.3, 0.9 Hz, 1H), 7.76 (s, 1H), 7.57 (s, 2H), 7.44 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.15 (ddd, *J* = 7.9, 4.9, 0.9 Hz, 1H), 5.73 (ddt, *J* = 16.6, 10.0, 6.4 Hz, 1H), 4.98 (dq, *J* = 10.0, 1.5 Hz, 1H), 4.85 (dq, *J* = 17.1, 1.6 Hz, 1H), 3.18 (dt, *J* = 6.4, 1.6 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 149.9, 149.5, 141.1, 137.2, 136.3, 136.0, 135.9, 135.6, 133.4, 133.1, 132.4, 130.7, 122.9, 117.6, 33.9.
MS (EI, 70 eV): m/z (%) = 332 (14), 330 (22), 319 (11), 318 (12), 317 (63), 316 (23), 315 (100), 302 (11), 275 (11), 263 (18), 261 (23), 239 (12), 205 (11), 191 (11).
HRMS (EI): for $C_{16}H_{12}Cl_2N_4$: calc. [M^+]: 330.0439; found: 330.0434.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 2962 (vw), 2253 (vw), 2151 (vw), 2020 (vw), 1639 (vw), 1581 (vw), 1441 (vw), 1411 (vw), 1379 (vw), 1193 (vw), 1150 (vw), 1100 (vw), 1027 (vw), 962 (vw), 823 (vw), 664 (vw).

Ethyl 5'-fluoro-2'-(4-(trimethylsilyl)-1*H*-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (22a)



According to **TP 1**, to a mixture of 1-(4-fluorophenyl)-4-(trimethylsilyl)-1*H*-1,2,3-triazole (**20a**, 118 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.30 mmol, 0.6 equiv) at 25 °C. After 30 min, the resulting diarylmagnesium was transmetalated with a $ZnCl_2$ solution (0.6 mL, 1.00 M in THF, 1.10 equiv) at 0 °C for 30 min. A dry and argon-flushed Schlenk-tube, equipped with a magnetic stirring bar and a septum was charged with $Pd(dppf)Cl_2$ (15 mg, 5 mol%) and ethyl 4-bromobenzoate (69 µL, 0.42 mmol, 0.83 equiv).The freshly prepared arylzinc reagent was added and the reaction mixture was placed in an oil bath at 55 °C for 18 h. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 12:1) afforded the title compound as a yellow oil (**22a**, 148 mg, 0.39 mmol, 93% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.97–7.91 (m, 2H), 7.61 (dd, *J* = 9.6, 5.1 Hz, 1H), 7.26–7.22 (m, 2H), 7.12 (s, 1H), 7.12–7.08 (m, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 0.21 (s, 9H).

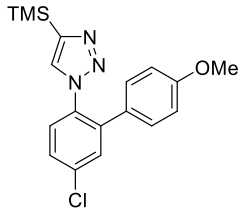
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 167.2, 165.3, 162.8, 147.8, 141.9, 139.9, 139.8, 132.5, 131.6, 131.1, 130.1, 130.0, 129.6, 118.9, 118.7, 117.4, 117.2, 62.5, 15.5, 0.0.

MS (EI, 70 eV): m/z (%) = 356 (10), 355 (28), 354 (31), 340 (17), 326 (13), 312 (12), 297 (13), 296 (54), 283 (14), 282 (48), 269 (13), 268 (50), 267 (100), 266 (13), 252 (18), 238 (19), 222 (16), 209 (12), 169 (14), 75 (15), 73 (20).

HRMS (EI) for $C_{20}H_{22}FN_3O_2Si$: calc. [M]: 383.1465, found: 383.1448.

IR (Diamond-ATR, neat): $\tilde{\nu}$/cm^{-1} = 3121 (vw), 3073 (vw), 2980 (vw), 2956 (w), 2900 (vw), 1713 (s), 1608 (w), 1588 (w), 1567 (w), 1517 (m), 1501 (m), 1478 (w), 1408 (w), 1391 (w), 1367 (w), 1271 (s), 1248 (s), 1200 (w), 1184 (m), 1147 (m), 1101 (s), 1034 (m), 1018 (m), 984 (m), 892 (w), 838 (vs), 775 (s), 758 (m), 737 (w), 705 (s), 670 (w).

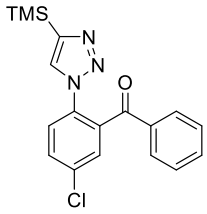
1-(5-Chloro-4'-methoxy-[1,1'-biphenyl]-2-yl)-4-(trimethylsilyl)-1*H*-1,2,3-triazole (22b)



According to **TP 1**, to a mixture of 1-(4-chlorophenyl)-4-(trimethylsilyl)-1*H*-1,2,3-triazole (**20b**, 126 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.30 mmol, 0.6 equiv) at 25 °C. After 30 min, the resulting diarylmagnesium was transmetalated with a $ZnCl_2$ solution (0.6 mL, 1.00 M in THF, 1.10 equiv) at 0 °C for 30 min. A dry and argon-flushed Schlenk-tube, equipped with a magnetic stirring bar and a septum was charged with $Pd(dppf)Cl_2$ (15 mg, 5 mol%) and 4-bromoanisole (53 µL, 0.42 mmol, 0.83 equiv).The freshly prepared arylzinc reagent was added and the reaction mixture was placed in an oil bath at 55 °C for 18 h. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 9:1) afforded the title compound as a yellow oil (**22b**, 101 mg, 0.28 mmol, 67% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.57 (d, *J* = 8.4 Hz, 1H), 7.49 (d, *J* = 2.3 Hz, 1H), 7.45 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.09 (s, 1H), 6.96–6.90 (m, 2H), 6.82–6.76 (m, 2H), 3.78 (s, 3H), 0.22 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 160.9, 147.6, 139.5, 136.6, 134.8, 132.3, 131.9, 130.8, 129.6, 129.3, 129.0, 115.3, 56.5, 0.0.
MS (EI, 70 eV): m/z (%) = 329 (30), 328 (25), 327 (84), 315 (24), 314 (20), 313 (74), 312 (12), 284 (21), 283 (17), 282 (56), 280 (21), 279 (100), 271 (17), 264 (10), 139 (18), 73 (24).
HRMS (EI): for $C_{18}H_{20}ClN_3OSi$: calc. [M^+]: 357.1064; found: 357.1059
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 2957 (w), 2900 (vw), 2838 (vw), 1609 (m), 1579 (vw), 1516 (m), 1496 (s), 1464 (m), 1443 (w), 1427 (w), 1378 (vw), 1292 (w), 1248 (s), 1201 (m), 1179 (m), 1149 (m), 1125 (w), 1112 (w), 1095 (w), 1042 (m), 1034 (m), 1008 (w), 996 (w), 982 (m), 884 (w), 832 (vs), 821 (vs), 775 (m), 758 (s), 725 (w), 708 (w), 698 (w), 680 (w), 659 (w).

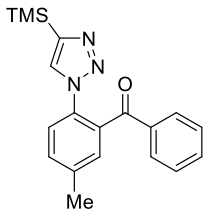
(5-Chloro-2-(4-(trimethylsilyl)-1*H*-1,2,3-triazol-1-yl)phenyl)(phenyl)methanone (22c)



According to **TP 1**, to a mixture of 1-(4-chlorophenyl)-4-(trimethylsilyl)-1*H*-1,2,3-triazole (**20b**, 126 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added sBu$_2$Mg (0.30 mmol, 0.6 equiv) at 25 °C. After 30 min, benzoyl chloride (70 µL, 0.60 mmol, 1.2 equiv) and CuCN·2LiCl (0.1 mL, 1.0 M in THF, 20 mol%) were added at -25 °C and the mixture was stirred for 12 h at room temperature. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 9:1) afforded the title compound as a yellow oil (**22c**, 103 mg, 0.29 mmol, 58% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.69–7.57 (m, 6H), 7.47 (ddt, *J* = 8.7, 7.1, 1.4 Hz, 1H), 7.34–7.28 (m, 2H), 0.19 (s, 9H).
^{13}C NMR (101 MHz, CDCl$_3$): δ (ppm) = 148.6, 137.2, 137.0, 136.8, 135.1, 132.9, 131.5, 131.2, 130.6, 129.8, 127.4, 0.0.
MS (EI, 70 eV): m/z (%) = 313 (30), 312 (18), 311 (100), 105 (52), 77 (29), 73 (10).
HRMS (EI) for $C_{18}H_{18}ClN_3OSi$: calc. [M]: 355.0908, found: 355.0914.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3117 (w), 2954 (w), 2854 (vw), 1733 (vw), 1658 (m), 1595 (w), 1583 (vw), 1573 (vw), 1497 (m), 1478 (w), 1449 (w), 1408 (w), 1394 (w), 1314 (w), 1278 (m), 1268 (m), 1247 (m), 1202 (m), 1176 (w), 1158 (w), 1136 (vw), 1113 (w), 1090 (w), 1069 (w), 1041 (m), 1025 (w), 1000 (w), 984 (m), 956 (w), 939 (vw), 904 (vw), 891 (vw), 833 (vs), 805 (m), 786 (m), 760 (m), 740 (m), 708 (s), 695 (m), 661 (w).

(5-Methyl-2-(4-(trimethylsilyl)-1*H*-1,2,3-triazol-1-yl)phenyl)(phenyl)methanone (22d)



According to **TP 1**, to a mixture of 1-(*p*-tolyl)-4-(trimethylsilyl)-1*H*-1,2,3-triazole (**20c**, 116 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.40 mmol, 0.8 equiv) at 40 °C. After 60 min, benzoyl chloride (70 µL, 0.60 mmol, 1.2 equiv) and CuCN·2LiCl (0.1 mL, 1.0 M in THF, 20 mol%) were added at -25 °C and the mixture was stirred for 12 h at room temperature. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 9:1) afforded the title compound as a yellow oil (**22d**, 93 mg, 0.28 mmol, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.61–7.40 (m, 7H), 7.31–7.27 (m, 2H), 2.50 (s, 3H), 0.19 (s, 9H).

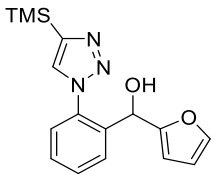
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 196.8, 148.2, 141.1, 137.7, 135.7, 134.6, 134.1, 133.6, 131.6, 130.5, 129.6, 126.0, 22.5, 0.0.

MS (EI, 70 eV): m/z (%) = 307 (22), 292 (26), 291 (100).

HRMS (EI) for $C_{19}H_{21}N_3OSi$: calc. [M]: 335.1454, found: 335.1477.

IR (Diamond-ATR, neat): $\tilde{\nu}$/cm^{-1} = 3080 (w), 2957 (w), 2923 (vw), 2852 (vw), 1730 (w), 1660 (s), 1605 (w), 1597 (w), 1581 (w), 1509 (m), 1450 (w), 1406 (w), 1318 (w), 1312 (w), 1287 (m), 1247 (m), 1211 (w), 1198 (m), 1179 (m), 1161 (w), 1108 (w), 1039 (m), 1002 (w), 982 (w), 976 (m), 971 (m), 958 (w), 932 (w), 908 (vw), 836 (vs), 824 (vs), 797 (m), 757 (m), 738 (s), 702 (vs), 686 (m), 662 (w).

Furan-2-yl(2-(4-(trimethylsilyl)-1H-1,2,3-triazol-1-yl)phenyl)methanol (22e)



According to **TP 1**, to a mixture of 1-phenyl-4-(trimethylsilyl)-1*H*-1,2,3-triazole (**20d**, 109 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.40 mmol, 0.8 equiv) at 40 °C. After 1 h, furfural (50 µL, 0.60 mmol, 1.2 equiv) was added dropwise at 0 °C and the reaction mixture was stirred for 1 h at room temperature. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 4:1) afforded the title compound as a slight yellow solid (**22e**, 126 mg, 0.40 mmol, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.67 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.58 (s, 1H), 7.55 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.49 (td, *J* = 7.6, 1.6 Hz, 1H), 7.33 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.24 (dd, *J* = 1.9, 0.9 Hz, 1H), 6.24 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.09 (dt, *J* = 3.3, 1.0 Hz, 1H), 5.74 (s, 1H), 0.37 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 155.3, 148.1, 143.1, 138.4, 136.6, 131.8, 131.3, 131.0, 130.3, 111.6, 108.3, 68.4, 0.0.

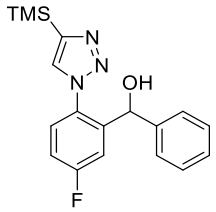
MS (EI, 70 eV): m/z (%) = 313 (17), 284 (14), 270 (15), 269 (13), 268 (56), 252 (18), 224 (12), 212 (18), 204 (21), 202 (22), 196 (88), 195 (16), 194 (17), 187 (15), 180 (17), 168 (10), 167 (31), 166 (33), 115 (22), 75 (74), 73 (100).

HRMS (EI) for $C_{16}H_{19}N_3O_2Si$: calc. [M]: 313.1247, found: 313.1234.

IR (Diamond-ATR, neat): $\tilde{\nu}$/cm^{-1} = 3272 (w), 3141 (vw), 2954 (w), 1500 (m), 1459 (w), 1390 (vw), 1347 (vw), 1251 (m), 1208 (m), 1183 (w), 1156 (w), 1148 (m), 1105 (w), 1072 (w), 1051 (m), 1029 (m), 1013 (m), 987 (w), 929 (w), 842 (vs), 807 (m), 760 (s), 747 (s), 731 (m), 709 (w), 680 (vw), 667 (w).

Melting point: M.p. = 107 °C.

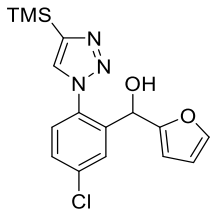
(5-Fluoro-2-(4-(trimethylsilyl)-1*H*-1,2,3-triazol-1-yl)phenyl)(phenyl)methanol (22f)



According to **TP 1**, to a mixture of 1-(4-fluorophenyl)-4-(trimethylsilyl)-1*H*-1,2,3-triazole (**20a**, 118 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.30 mmol, 0.6 equiv) at 25 °C. After 30 min, benzaldehyde (62 µL, 0.60 mmol, 1.2 equiv) was added dropwise at 0 °C and the reaction mixture was stirred for 1 h at room temperature. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 6:1) afforded the title compound as a white solid (**22f**, 118 mg, 0.35 mmol, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.43 (dd, *J* = 9.2, 2.9 Hz, 1H), 7.29 (s, 1H), 7.25–7.17 (m, 4H), 7.12 (ddd, *J* = 8.7, 7.5, 2.8 Hz, 1H), 7.07–7.02 (m, 2H), 5.79 (s, 1H), 0.31 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 165.7, 163.2, 147.6, 144.2, 144.1, 142.4, 132.3, 129.6, 129.1, 129.0, 128.9, 127.4, 117.8, 117.6, 116.7, 116.5, 72.8, 0.0.
MS (EI, 70 eV): m/z (%) = 313 (21), 312 (56), 298 (31), 296 (15), 256 (18), 239 (28), 236 (28), 225 (15), 224 (100), 223 (18), 222 (71) 220 (69), 207 (14), 204 (14), 198 (47), 183 (23), 170 (12), 75 (11), 73 (27).
HRMS (EI) for $C_{18}H_{20}FN_3OSi$: calc. [M]: 341.1360, found: 341.1366.
IR (Diamond-ATR, neat): $\tilde{\nu}$/cm^{-1} = 3223 (w), 3030 (vw), 2953 (w), 1618 (vw), 1594 (w), 1501 (m), 1488 (w), 1455 (w), 1421 (w), 1348 (vw), 1263 (m), 1250 (m), 1202 (m), 1152 (m), 1142 (m), 1099 (w), 1055 (m), 1044 (m), 1039 (m), 1017 (w), 989 (m), 957 (m), 917 (vw), 891 (w), 835 (vs), 822 (s), 765 (w), 749 (m), 744 (s), 702 (s), 663 (w), 656 (w).
Melting point: M.p. = 118 °C.

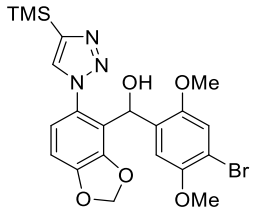
(5-Chloro-2-(4-(trimethylsilyl)-1*H*-1,2,3-triazol-1-yl)phenyl)(furan-2-yl)methanol (22g)



According to **TP 1**, to a mixture of 1-(4-chlorophenyl)-4-(trimethylsilyl)-1*H*-1,2,3-triazole (**20b**, 126 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.30 mmol, 0.6 equiv) at 25 °C. After 1 h, furfural (50 µL, 0.60 mmol, 1.2 equiv) was added dropwise at 0 °C and the reaction mixture was stirred for 1 h at room temperature. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 4:1) afforded the title compound as a colorless solid (**22g**, 134 mg, 0.39 mmol, 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.71 (d, *J* = 2.3 Hz, 1H), 7.51 (s, 1H), 7.44 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.28–7.25 (m, 2H), 6.25 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.08 (dt, *J* = 3.4, 0.9 Hz, 1H), 5.74 (s, 1H), 0.34 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 154.6, 148.2, 143.4, 140.1, 137.3, 134.8, 131.9, 130.8, 130.3, 128.0, 111.6, 108.8, 67.5, 0.0.
MS (EI, 70 eV): m/z (%) = 317 (16), 303 (11), 301 (25), 285 (11), 245 (10), 238 (10), 235 (15), 231 (21), 229 (68), 228 (20), 200 (13), 199 (13), 167 (15), 166 (18), 115 (10), 81 (21), 75 (75), 73 (100), 45 (12).
HRMS (EI): for $C_{16}H_{18}ClN_3O_2Si$: calc. [M+]: 347.0857; found: 347.0851.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3213 (w), 3142 (w), 2959 (w), 2360 (w), 1498 (m), 1484 (w), 1457 (w), 1406 (w), 1318 (w), 1298 (vw), 1286 (vw), 1251 (m), 1211 (m), 1183 (w), 1159 (w), 1152 (m), 1119 (w), 1092 (w), 1077 (vw), 1056 (m), 1043 (m), 1010 (m), 989 (w), 927 (w), 889 (w), 871 (w), 838 (vs), 817 (s), 806 (m), 786 (m), 757 (m), 742 (s), 713 (m), 681 (w), 657 (w).
Melting point: M.p. = 136 °C.

(4-Bromo-2,5-dimethoxyphenyl)(5-(4-(trimethylsilyl)-1*H*-1,2,3-triazol-1-yl)benzo[*d*][1,3]dioxol-4-yl)methanol (22h)



According to **TP 1**, to a mixture of 1-(benzo[*d*][1,3]dioxol-5-yl)-4-(trimethylsilyl)-1*H*-1,2,3-triazole (**20e**, 126 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added sBu$_2$Mg·(0.30 mmol, 0.6 equiv) at 25 °C. After 1 h, 4-bromo-2,5-dimethoxybenzaldehyde (147 mg, 0.60 mmol, 1.2 equiv) dissolved in toluene (1 mL) was added dropwise at 0 °C and the reaction mixture was stirred for 1 h at room temperature. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 4:1 to 1:1) afforded the title compound as a colorless solid (**22h**, 201 mg, 0.40 mmol, 80% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.23 (s, 1H), 6.80 (t, *J* = 4.1 Hz, 2H), 6.76 (s, 1H), 6.67 (d, *J* = 8.2 Hz, 1H), 6.14 (d, *J* = 13.9 Hz, 2H), 5.97 (s, 1H), 3.80 (s, 3H), 3.49 (s, 3H), 0.31 (s, 9H).

^{13}C NMR (101 MHz, CDCl$_3$): δ (ppm) = 150.6, 148.4, 132.4, 131.1, 130.0, 123.4, 120.9, 116.9, 111.2, 110.4, 108.6, 103.7, 65.8, 61.7, 57.5, 23.9, 22.3, 15.5, 0.0.

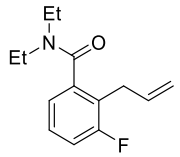
MS (EI, 70 eV): m/z (%) = 463 (14), 462 (11), 448 (10), 390 (12), 388 (18), 358 (13), 355 (12), 332 (23), 263 (19), 262 (97), 246 (47), 217 (25), 297 (24), 111 (11), 99 (11), 97 (23), 85 (46), 84 (11), 83 (23), 75 (50), 74 (11), 73 (93), 71 (61), 70 (14), 67 (10), 57 (83), 56 (17), 55 (32), 44 (100), 43 (57), 43 (33), 41 (24).

HRMS (EI): for $C_{21}H_{24}BrN_3O_5Si$: $[M-O]^{\bullet+}$: 489.0714, found: 489.0719.

IR (Diamond-ATR, neat): $\tilde{\nu}$/cm^{-1} = 3142 (w), 2359 (w), 1492 (s), 1453 (m), 1409 (w), 1378 (m), 1323 (m), 1275 (w), 1250 (m), 1241 (m), 1210 (s), 1180 (m), 1138 (w), 1071 (s), 1048 (s), 1034 (s), 1004 (m), 934 (w), 889 (w), 843 (vs), 817 (s), 761 (s), 736 (m), 709 (m), 668 (m).

Melting point: M.p. = 201 °C.

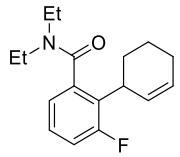
2-Allyl-*N*,*N*-diethyl-3-fluorobenzamide (25a)



According to **TP 1**, to a mixture of *N*,*N*-diethyl-3-fluorobenzamide (**23a**, 98 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added sBu$_2$Mg (0.30 mmol, 0.6 equiv) at 25 °C. After 30 min, allyl bromide (52 µL, 0.60 mmol, 1.2 equiv) and CuCN·2LiCl (0.1 mL, 1.0 M in THF, 20 mol%) were added at -25 °C and the mixture was stirred for 1 h. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 4:1) afforded the title compound as a colorless oil (**25a**, 73 mg, 0.31 mmol, 62% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.25–7.18 (m, 1H), 7.04 (ddd, *J* = 9.6, 8.2, 1.2 Hz, 1H), 6.97 (dd, *J* = 7.5, 1.2 Hz, 1H), 5.97–5.85 (m, 1H), 5.08–4.98 (m, 2H), 3.79 (s, 1H), 3.46–3.23 (m, 3H), 3.08 (p, *J* = 6.6 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, CDCl$_3$): δ (ppm) = 169.1, 169.1, 162.5, 160.1, 139.1, 139.0, 135.0, 135.0, 128.0, 127.9, 124.0, 123.8, 121.3, 121.3, 116.0, 115.7, 115.5, 43.0, 38.7, 30.7, 13.8, 12.7.
MS (EI, 70 eV): m/z (%) = 282 (10), 281 (61), 266 (32), 265 (13), 253 (13), 250 (10), 248 (13), 225 (23), 221 (20), 209 (12), 208 (12), 207 (92), 197 (17), 192 (13), 191 (19), 163 (31), 162 (100), 149 (12), 147 (24), 135 (18), 134 (58), 133 (76), 115 (48), 109 (16), 73 (33).
HRMS (EI): for $C_{14}H_{18}FNO$: calc. [M-H$^+$]: 234.1294; found: 234.1289.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3080 (vw), 2976 (w), 2936 (w), 2876 (vw), 1629 (vs), 1613 (m), 1578 (m), 1482 (m), 1456 (s), 1427 (s), 1381 (m), 1365 (m), 1348 (w),1315 (m), 1287 (s), 1244 (m), 1231 (m), 1220 (m), 1207 (w), 1186 (w), 1159 (w), 1130 (w), 1095 (m), 1070 (w), 1016 (w), 994 (w), 960 (w), 939 (w), 915 (m), 884 (w), 844 (m), 793 (s), 752 (m), 676 (w).

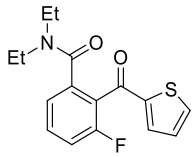
***N*,*N*-Diethyl-6-fluoro-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-2-carboxamide (25b)**



According to **TP 1**, to a mixture of *N*,*N*-diethyl-3-fluorobenzamide (**23a**, 976 mg, 5.00 mmol, 1.0 equiv) in toluene (10 mL) was added *s*Bu_2Mg (0.30 mmol, 0.6 equiv) at 25 °C. After 30 min, 3-bromocyclohexene (0.81 mL, 7.00 mmol, 1.4 equiv) and CuCN·2LiCl (1.0 mL, 1.0 M in THF, 20 mol%) were added at -25 °C and the mixture was stirred for 1 h. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 9:1 to 4:1) afforded the title compound as a pink oil (**25b**, 974 mg, 3.54 mmol, 71% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.19 (tt, *J* = 7.9, 4.8 Hz, 1H), 6.99 (ddt, *J* = 11.2, 8.2, 1.5 Hz, 1H), 6.92 (ddd, *J* = 7.7, 3.8, 1.2 Hz, 1H), 5.85–5.70 (m, 1H), 5.61 (dt, *J* = 9.7, 1.9 Hz, 1H), 3.87–3.03 (m, 5H), 2.20–1.72 (m, 5H), 1.66–1.52 (m, 1H), 1.23 (q, *J* = 7.3 Hz, 3H), 1.05 (dt, *J* = 11.5, 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 169.3, 163.2, 163.1, 160.7, 160.6, 139.0, 139.0, 139.0, 129.7, 129.5, 129.4, 129.0, 128.8, 128.0, 127.9, 127.8, 127.7, 127.3, 127.2, 121.3, 121.1, 116.5, 116.3, 116.1, 43.0, 42.8, 38.7, 38.4, 37.9, 36.7, 29.1, 28.8, 24.6, 24.5, 22.8, 13.9, 12.7, 12.5.
MS (EI, 70 eV): m/z (%) = 275 (29), 260 (23), 246 (17), 220 (30), 203 (17), 202 (100), 201 (86), 187 (17), 185 (35), 184 (62), 183 (54), 175 (18). 174 (14), 173 (17), 170 (11), 165 (32), 159 (25), 153 (11), 152 (13), 147 (25), 146 (42), 133 (37), 109 (12), 72 (13).
HRMS (EI): for $C_{17}H_{22}FNO$: calc. [M^+]: 275.1685; found: 275.1681.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3020 (w), 2971 (w), 2933 (m), 2874 (w), 2836 (w), 2363 (vw), 1629 (vs), 1609 (m), 1574 (w), 1479 (m), 1454 (s), 1425 (s), 1380 (m), 1364 (w), 1347 (w), 1315 (m), 1288 (s), 1265 (w), 1238 (m), 1222 (m), 1190 (w), 1160 (w), 1135 (w), 1119 (m), 1099 (w), 1067 (w), 1047 (w), 1014 (w), 987 (w), 952 (w), 928 (w), 900 (w), 878 (vw), 850 (w), 833 (m), 799 (s), 746 (s), 720 (m), 703 (w), 654 (vw).

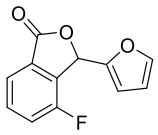
***N*,*N*-Diethyl-3-fluoro-2-(thiophene-2-carbonyl)benzamide (25c)**



According to **TP 1**, to a mixture of *N*,*N*-diethyl-3-fluorobenzamide (**23a**, 98 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.30 mmol, 0.6 equiv) at 25 °C. After 30 min, thiophene-2-carbonyl chloride (64 µL, 0.60 mmol, 1.2 equiv) and CuCN·2LiCl (0.1 mL, 1.0 M in THF, 20 mol%) were added at -25 °C and the mixture was stirred for 12 h at 25 °C. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 1:1) afforded the title compound as a yellow oil (**25c**, 97 mg, 0.32 mmol, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.72 (dd, *J* = 4.9, 1.2 Hz, 1H), 7.57–7.45 (m, 2H), 7.23–7.16 (m, 2H), 7.10 (dd, *J* = 4.9, 3.8 Hz, 1H), 3.40 (q, *J* = 7.1 Hz, 2H), 3.25 (q, *J* = 7.1 Hz, 2H), 1.10 (t, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 184.3, 167.9, 160.3, 157.8, 143.9, 138.7, 136.2, 135.5, 131.7, 128.4, 125.5, 125.4, 122.2, 116.6, 116.4, 43.4, 38.9, 13.7, 12.1.
MS (EI, 70 eV): m/z (%) = 234 (22), 233 (100), 213 (15), 205 (17), 189 (11), 186 (11), 185 (12), 157 (20), 133 (13), 110 (23), 72 (18).
HRMS (EI): for $C_{16}H_{16}FNO_2S$: calc. [M-H$^+$]: 304.0808; found: 304.0804.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3078 (vw), 2975 (w), 2935 (w), 2876 (vw), 1626 (vs), 1606 (s), 1572 (m), 1516 (m), 1483 (m), 1449 (s), 1429 (s), 1409 (vs), 1382 (m), 1355 (m), 1314 (m), 1283 (vs), 1243 (s), 1212 (m), 1165 (w), 1142 (w), 1123 (m), 1100 (w), 1081 (w), 1069 (w), 1048 (m), 1017 (w), 956 (w), 934 (w), 914 (w), 883 (m), 844 (s), 826 (w), 802 (s), 767 (m), 742 (s), 724 (s), 689 (w), 680 (w).

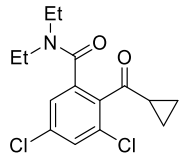
4-Fluoro-3-(furan-2-yl)isobenzofuran-1(3*H*)-one (25d)



According to **TP 1**, to a mixture of *N*,*N*-diethyl-3-fluorobenzamide (**23a**, 98 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.30 mmol, 0.6 equiv) at 25 °C. After 30 min, furfural (50 µL, 0.60 mmol, 1.2 equiv) was added dropwise at 0 °C and the reaction mixture was stirred for 1 h at room temperature. The reaction mixture was warmed to 60 °C and stirred for further 2 h. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 4:1) afforded the title compound as a red solid (**25d**, 83 mg, 0.38 mmol, 76% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.79 (d, *J* = 7.5 Hz, 1H), 7.66–7.58 (m, 1H), 7.46–7.36 (m, 2H), 6.54 (s, 1H), 6.46 (dd, *J* = 3.3, 0.7 Hz, 1H), 6.40 (dd, *J* = 3.3, 1.8 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 168.5, 158.3, 155.8, 147.0, 144.3, 132.3, 132.3, 132.1, 129.6, 121.7, 121.7, 121.3, 121.1, 111.1, 110.7, 73.1.
MS (EI, 70 eV): m/z (%) = 218 (47), 217 (11), 191 (10), 190 (85), 174 (57), 173 (23), 162 (32), 147 (10), 146 (100), 134 (11), 133 (33), 126 (10), 125 (11), 123 (24), 122 (19), 120 (21), 95 (11), 94 (17), 75 (10).
HRMS (EI): for $C_{12}H_7FO_3$: calc. [M+]: 218.0379; found: 218.0372.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 515 (vw), 3121 (vw), 3079 (vw), 2925 (vw), 2853 (vw), 1900 (vw), 1770 (s), 1764 (s), 1732 (w), 1725 (w), 1603 (m), 1501 (w), 1483 (s), 1386 (vw), 1342 (w), 1312 (w), 1288 (m), 1254 (m), 1245 (s), 1181 (w), 1156 (m), 1152 (m), 1083 (s), 1070 (m), 1050 (m), 1016 (m), 985 (m), 936 (m), 925 (s), 887 (m), 868 (m), 823 (s), 796 (w), 751 (s), 741 (vs), 668 (w).
Melting point: M.p. = 87 °C.

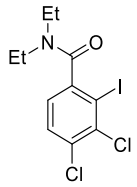
3,5-Dichloro-2-(cyclopropanecarbonyl)-*N*,*N*-diethylbenzamide (25e)



According to **TP 1**, to a mixture of 3,5-dichloro-*N*,*N*-diethylbenzamide (**23b**, 738 mg, 3.00 mmol, 1.0 equiv) in toluene (6 mL) was added *s*Bu_2Mg (2.40 mmol, 0.8 equiv) at 25 °C. After 10 min cyclopropanecarbonyl chloride (0.33 mL, 3.60 mmol, 1.2 equiv) and CuCN·2LiCl (0.6 mL, 1.0 M in THF, 20 mol%) were added at -25 °C and the mixture was stirred for 12 h at 25 °C. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 9:1) afforded the title compound as a white solid (**25e**, 675 mg, 2.15 mmol, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.43 (d, *J* = 1.9 Hz, 1H), 7.18 (d, *J* = 1.9 Hz, 1H), 3.45 (q, *J* = 7.1 Hz, 2H), 3.18 (q, *J* = 7.2 Hz, 2H), 2.39 (tt, *J* = 7.8, 4.5 Hz, 1H), 1.32–1.26 (m, 2H), 1.18–1.08 (m, 8H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 203.6, 167.2, 138.7, 137.4, 135.6, 131.7, 129.8, 124.6, 43.4, 39.1, 23.2, 14.0, 13.7, 12.3.
MS (EI, 70 eV): m/z (%) = 222 (38), 215 (30), 214 (21), 213 (49), 212 (33), 199 (20), 197 (30), 186 (28), 184 (44), 180 (10), 178 (32), 174 (20), 172 (32), 160 (13), 151 (13), 150 (24), 149 (38), 143 (12), 115 (25), 108 (13), 72 (100).
HRMS (EI): for $C_{15}H_{17}Cl_2NO_2$: calc. [M-H$^+$]: 312.0558; found: 312.0552.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3048 (w), 2972 (w), 2933 (w), 2362 (vw), 1680 (m), 1620 (vs), 1580 (m), 1551 (m), 1478 (m), 1455 (m), 1428 (m), 1371 (s), 1361 (m), 1346 (m), 1316 (m), 1285 (m), 1265 (w), 1228 (m), 1202 (m), 1183 (m), 1121 (w), 1103 (m), 1087 (m), 1063 (w), 1035 (m), 1015 (w), 984 (s), 949 (w), 928 (w), 861 (s), 829 (m), 795 (m), 762 (m), 729 (w).
Melting point: M.p. = 91 °C.

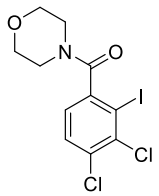
3,4-Dichloro-*N*,*N*-diethyl-2-iodobenzamide (25f)



According to **TP 1**, to a mixture of 3,4-dichloro-*N*,*N*-diethylbenzamide (**23c**, 123 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.30 mmol, 0.6 equiv) at 40 °C. After 10 min, the reaction mixture was cooled to 0 °C and iodine (153 mg, 0.60 mmol, 1.2 equiv) dissolved in THF (1 mL) was added dropwise and the reaction mixture was stirred for 1 h. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 4:1) afforded the title compound as a brown solid (**25f**, 134 mg, 0.36 mmol, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.49 (d, *J* = 8.1 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 1H), 3.84 (dtd, *J* = 14.3, 7.2, 0.9 Hz, 1H), 3.28 (dq, *J* = 14.1, 7.1 Hz, 1H), 3.22–3.02 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 168.9, 144.2, 137.9, 132.1, 130.5, 125.1, 98.7, 42.8, 39.0, 13.9, 12.2.
MS (EI, 70 eV): m/z (%) = 371 (16), 370 (14), 369 (21), 300 (43), 298 (75), 270 (11), 246 (24), 244 (27), 207 (15), 174 (12), 172 (19), 145 (11), 143 (19), 85 (11), 83 (16), 71 (17), 70 (11), 69 (20), 57 (35), 56 (23), 55 (14), 43 (100), 42 (27), 41 (12), 40 (15).
HRMS (EI): for $C_{11}H_{12}Cl_2INO$: calc. [M-H$^+$]: 369.9262; found: 369.9260.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 2996 (w), 2972 (w), 2932 (w), 2873 (w), 2365 (vw), 1888 (vw), 1609 (vs), 1568 (m), 1537 (w), 1520 (w), 1463 (m), 1444 (m), 1419 (s), 1384 (m), 1366 (m), 1343 (m), 1337 (m), 1319 (m), 1292 (s), 1247 (w), 1221 (m), 1201 (m), 1163 (m), 1147 (m), 1112 (m), 1108 (m), 1089 (m), 1068 (m), 1048 (m), 1012 (w), 950 (w), 895 (m), 820 (s), 800 (s), 777 (m), 760 (m), 713 (m), 659 (m).
Melting point: M.p. = 103 °C.

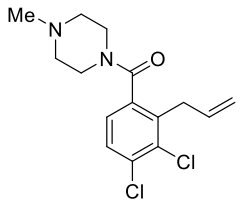
(3,4-Dichloro-2-iodophenyl)(morpholino)methanone (25g)



According to **TP 1**, to a mixture of (3,4-dichlorophenyl)(morpholino)methanone (**23d**, 130 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.30 mmol, 0.6 equiv) at -20 °C. After 2 h, iodine (153 mg, 0.60 mmol, 1.2 equiv) dissolved in THF (1 mL) was added dropwise and the reaction mixture was stirred for 1 h at 0 °C. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 4:1 to 1:1) afforded the title compound as a yellow solid (**25g**, 118 mg, 0.31 mmol, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.52 (d, *J* = 8.2 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 1H), 3.89-3.73 (m, 5H), 3.60 (ddd, *J* = 11.6, 6.3, 3.2 Hz, 1H), 3.28 (ddd, *J* = 13.4, 6.4, 3.3 Hz, 1H), 3.18 (ddd, *J* = 13.4, 6.6, 3.3 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 168.2, 143.1, 138.2, 132.7, 130.7, 125.2, 98.5, 66.6, 47.1, 42.0.
MS (EI, 70 eV): m/z (%) = 386 (22), 385 (25), 384 (35), 383 (32), 302 (11), 300 (63), 298 (100), 272 (15), 270 (20), 260 (12), 258 (19), 174 (15), 172 (24), 146 (10), 145 (20), 144 (16), 143 (30), 108 (25), 86 (38), 74 (18), 56 (37), 55 (19), 41 (12).
HRMS (EI): for $C_{11}H_{10}Cl_2INO_2$: calc. [M-H$^+$]: 384.9133; found: 384.9127.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3066 (vw), 2957 (m), 2869 (m), 2361 (vw), 1709 (s), 1691 (m), 1653 (s), 1595 (w), 1574 (w), 1478 (m), 1463 (m), 1447 (w), 1398 (w), 1384 (m), 1363 (s), 1351 (s), 1312 (s), 1266 (m), 1249 (m), 1231 (s), 1215 (m), 1184 (s), 1122 (w), 1106 (w), 1073 (m), 1059 (m), 1044 (s), 1035 (s), 1008 (s), 989 (m), 964 (s), 912 (m), 869 (w), 818 (w), 770 (s), 745 (m), 697 (vs).
Melting point: M.p. = 134 °C.

(2-Allyl-3,4-dichlorophenyl)(4-methylpiperazin-1-yl)methanone (25h)



According to **TP 1**, to a mixture of (3,4-dichlorophenyl)(4-methylpiperazin-1-yl)methanone (**23e**, 137 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg·(0.40 mmol, 0.8 equiv) at 0 °C. After 15 min, allyl bromide (52 µL, 0.60 mmol, 1.2 equiv) and CuCN·2LiCl (0.1 mL, 1.0 M in THF, 20 mol%) were added at -25 °C and the mixture was stirred for 1 h. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 1:1) afforded the title compound as a brown oil (**25h**, 104 mg, 0.33 mmol, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 7.38 (d, *J* = 8.1 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 5.88 (dddd, *J* = 17.3, 10.1, 7.4, 5.2 Hz, 1H), 5.13–4.98 (m, 2H), 3.87 (dd, *J* = 11.5, 6.0 Hz, 1H), 3.77–3.52 (m, 3H), 3.19 (dtdt, *J* = 13.2, 10.5, 7.1, 3.6 Hz, 2H), 2.46 (dtq, *J* = 18.7, 7.1, 3.5 Hz, 2H), 2.36–2.20 (m, 5H).

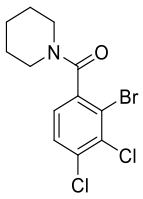
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 168.3, 137.5, 136.7, 134.5, 134.4, 134.3, 128.9, 125.3, 117.3, 55.4, 55.0, 47.6, 46.5, 42.0, 36.2.

MS (EI, 70 eV): m/z (%) = 281 (16), 225 (38), 209 (22), 208 (13), 207 (100), 192 (16), 191 (25), 151 (11), 150 (13), 149 (38), 133 (15), 115 (40), 99 (11), 97 (39), 85 (14), 73 (27), 70 (45), 56 (10), 42 (13).

HRMS (EI): for $C_{15}H_{18}Cl_2N_2O$: calc. [M^+]: 312.0796; found: 312.0790.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3077 (vw), 2936 (w), 2847 (w), 2791 (w), 2357 (w), 2331 (vw), 1717 (w), 1632 (vs), 1579 (m), 1460 (m), 1447 (m), 1427 (s), 1383 (m), 1291 (s), 1273 (s), 1266 (s), 1243 (m), 1171 (m), 1143 (m), 1122 (m), 1092 (w), 1071 (m), 1025 (m), 1000 (s), 915 (m), 894 (w), 824 (m), 777 (m), 668 (w).

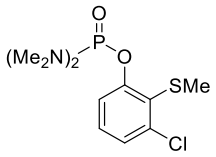
(2-Bromo-3,4-dichlorophenyl)(piperidin-1-yl)methanone (25i)



According to **TP 1**, to a mixture of (3,4-dichlorophenyl)(piperidin-1-yl)methanone (**23f**, 129 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.30 mmol, 0.6 equiv) at 0 °C. After 20 min, 1,2-dibromotetrachloroethane (244 mg, 0.60 mmol, 1.2 equiv) dissolved in THF (1 mL) was added dropwise and the reaction mixture was stirred for 1 h at 0 C°. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 4:1) afforded the title compound as a white solid (**25i**, 115 mg, 0.34 mmol, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.47 (d, *J* = 8.2 Hz, 1H), 7.08 (d, *J* = 8.2 Hz, 1H), 3.80–3.66 (m, 2H), 3.17 (qdd, *J* = 13.2, 7.1, 3.8 Hz, 2H), 1.66 (tt, *J* = 13.9, 5.4 Hz, 5H), 1.51–1.41 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 166.1, 139.2, 134.3, 133.9, 129.6, 125.4, 121.1, 47.8, 42.6, 26.2, 25.4, 24.4.
MS (EI, 70 eV): m/z (%) = 338 (14), 337 (40), 336 (32), 335 (85), 334 (21), 333 (50), 258 (41), 257 (10), 256 (65), 254 (44), 252 (100), 250 (59), 226 (13), 224 (29), 222 (17), 172 (15), 145 (11), 143 (18), 108 (15), 84 (16), 83 (11), 55 (23), 42 (22), 41 (22).
HRMS (EI): for $C_{12}H_{12}BrCl_2NO$: calc. [M-H$^+$]: 334.9479; found: 333.9389.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 2942 (m), 2921 (w), 2861 (m), 2353 (vw), 1630 (vs), 1572 (m), 1467 (m), 1458 (m), 1447 (m), 1441 (m), 1424 (vs), 1351 (m), 1284 (m), 1278 (m), 1272 (s), 1258 (m), 1250 (m), 1240 (m), 1188 (m), 1166 (m), 1146 (w), 1117 (m), 1059 (w), 1028 (m), 1004 (s), 955 (w), 932 (vw), 896 (m), 852 (m), 823 (vs), 790 (m), 762 (m), 730 (m), 721 (m), 667 (m).
Melting point: M.p. = 111 °C.

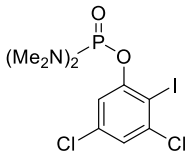
3-Chloro-2(methylsulfanyl)phenyl *N,N,N′,N′*-tetramethylphosphorodiamidate (25j)



According to **TP 1**, to a mixture of 3-Chlorophenyl *N,N,N′,N′*-tetramethylphosphorodiamidate (**23g**, 131 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.40 mmol, 0.8 equiv) at 40 °C. After 30 min, *S*-methyl methanethiosulfonate (57 µL, 0.60 mmol, 1.2 equiv) was added dropwise at 0 °C and the reaction mixture was stirred for 1 h at room temperature. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 9:1) afforded the title compound as a colorless oil (**25j**, 106 mg, 0.34 mmol, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.35 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.24–7.17 (m, 2H), 2.77 (d, *J* = 10.1 Hz, 12H), 2.41 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 153.8, 140.1, 130.3, 129.7, 125.5, 118.7, 36.7, 18.3.
^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) = 15.9.
MS (EI, 70 eV): m/z (%) = 265 (29), 264 (83), 263 (27), 261 (87), 200 (11), 173 (21), 154 (13), 135 (100), 92 (12).
HRMS (EI): for $C_{11}H_{18}ClN_2O_2PS$: calc. [M+]: 308.0515; found: 308.0506.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3471 (vw), 3065 (vw), 2994 (vw), 2923 (w), 2893 (w), 2851 (w), 2809 (w), 1589 (w), 1573 (w), 1564 (m), 1474 (w), 1438 (s), 1304 (m), 1220 (s), 1179 (m), 1107 (vw), 1068 (w), 987 (s), 929 (vs), 777 (s), 754 (s), 736 (m), 719 (m), 700 (vw), 682 (w), 667 (m).

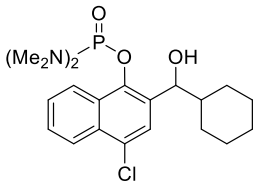
2-Iodo-3,5-Dichlorophenyl *N,N,N′,N′*-tetramethylphosphorodiamidate (25k)



According to **TP 1**, to a mixture of 3,5-Dichlorophenyl *N,N,N′,N′*-tetramethylphosphorodiamidate (**23h**, 148 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.30 mmol, 0.6 equiv) at 40 °C. After 1 h, iodine (153 mg, 0.60 mmol, 1.2 equiv) dissolved in THF (1 mL) was added dropwise and the reaction mixture was stirred for 1 h at 0 °C. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 1:1) afforded the title compound as a yellow oil (**25k**, 209 mg, 0.49 mmol, 98% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.44 (dd, J = 2.2, 1.1 Hz, 1H), 7.24 (d, J = 2.2 Hz, 1H), 2.75 (d, J = 10.3 Hz, 12H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 153.3, 140.1, 135.5, 124.5, 117.8, 92.0, 36.9.
^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) = 16.5.
MS (EI, 70 eV): m/z (%) = 297 (31), 295 (47), 135 (100), 44 (29).
HRMS (EI): for $C_{10}H_{14}Cl_2IN_2O_2P$: calc. [M-I]: 295.0170; found: 295.0173.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 2942 (m), 2921 (w), 2861 (m), 2353 (vw), 1630 (vs), 1572 (m), 1467 (m), 1458 (m), 1447 (m), 1441 (m), 1424 (vs), 1351 (m), 1284 (m), 1278 (m), 1272 (s), 1258 (m), 1250 (m), 1240 (m), 1188 (m), 1166 (m), 1146 (w), 1117 (m), 1059 (w), 1028 (m), 1004 (s), 955 (w), 932 (vw), 896 (m), 852 (m), 823 (vs), 790 (m), 762 (m), 730 (m), 721 (m), 667 (m).

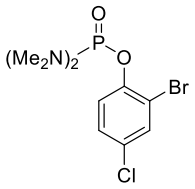
4-Chloro-2-(cyclohexyl(hydroxy)methyl)phenyl *N,N,N′,N′* tetramethylphosphorodiamidate (25l)



According to **TP 1**, to a mixture of 4-Chloronaphtyl *N,N,N′,N′*-tetramethylphosphorodiamidate (**23i**, 156 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.40 mmol, 0.8 equiv) at 60 °C. After 30 min, cyclohexan carboxaldehyde (73 µL, 0.60 mmol, 1.2 equiv) was added dropwise at 0 °C and the reaction mixture was stirred for 1 h at room temperature. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 2:1) afforded the title compound as a white solid (**25l**, 144 mg, 0.34 mmol, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.26–8.20 (m, 1H), 8.05–7.98 (m, 1H), 7.70 (s, 1H), 7.64–7.55 (m, 2H), 4.73 (d, *J* = 10.0 Hz, 1H), 2.89 (d, *J* = 10.0 Hz, 6H), 2.60 (d, *J* = 9.8 Hz, 6H), 2.49–2.40 (m, 1H), 1.97–1.78 (m, 2H), 1.71–1.52 (m, 2H), 1.38–1.04 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 142.9, 133.0, 130.8, 128.7, 128.4, 127.1, 126.5, 125.6, 124.7, 122.1, 71.6, 41.4, 36.9, 30.7, 26.5, 25.8.
^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) = 15.9.
MS (EI, 70 eV): m/z (%) = 270 (11), 254 (17), 219 (18), 191 (12), 135 (100).
HRMS (EI): for $C_{21}H_{30}ClN_2O_3P$: calc. [M-H_2O]: 406.1582; found: 406.1572.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3325 (w), 2951 (w), 2921 (s), 2851 (m), 2815 (w), 1743 (vw), 1597 (w), 1455 (w), 1449 (w), 1360 (m), 1307 (m), 1254 (w), 1213 (m), 1195 (s), 1160 (m), 1124 (m), 1083 (s), 1068 (m), 1027 (m), 995 (vs), 971 (m), 954 (m), 910 (w), 850 (s), 789 (m), 784 (w), 776 (s), 757 (s), 706 (s), 674 (w), 669 (w).
Melting point: M.p. = 155 °C.

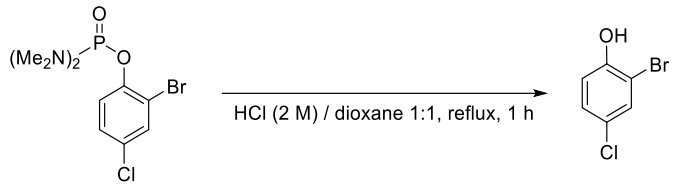
2-Bromo-4-Chlorophenyl *N,N,N′,N′*-tetramethylphosphorodiamidate (25m)



According to **TP 1**, to a mixture of 4-Chlorophenyl *N,N,N′,N′*-tetramethylphosphorodiamidate (**23j**, 657 mg, 2.50 mmol, 1.0 equiv) in toluene (5 mL) was added *s*Bu_2Mg (2.00 mmol, 0.8 equiv) at 60 °C. After 30 min, 1,2-dibromotetrachloroethane (1.14 g, 3.50 mmol, 1.4 equiv) dissolved in THF (5 mL) was added dropwise and the reaction mixture was stirred for 1 h at 0 C°. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 1:4) afforded the title compound as a yellow oil (**25m**, 699 mg, 2.10 mmol, 84% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.53 (dd, *J* = 2.5, 1.0 Hz, 1H), 7.44 (dd, *J* = 8.8, 1.1 Hz, 1H), 7.21 (dd, *J* = 8.8, 2.6 Hz, 1H), 2.73 (d, *J* = 10.2 Hz, 12H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 147.5, 132.8, 129.4, 128.5, 121.5, 114.7, 114.6, 36.7.
^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) = 16.1.
MS (EI, 70 eV): m/z (%) = 263 (20), 261 (63), 135 (100).
HRMS (EI): for $C_{10}H_{15}BrClN_2O_2P$: calc. [M+]: 339.9743; found: 339.9740.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3461 (vw), 3089 (vw), 2997 (vw), 2926 (w), 2895 (w), 2852 (w), 2810 (w), 2363 (vw), 1733 (vw), 1647 (vw), 1579 (vw), 1470 (vs), 1379 (w), 1304 (m), 1262 (m), 1223 (s), 1180 (m), 1149 (w), 1096 (w), 1068 (w), 1046 (m), 985 (vs), 904 (vs), 866 (m), 823 (m), 790 (vs), 758 (vs), 684 (s), 659 (w).

2-Bromo-4-chlorophenol (25n)

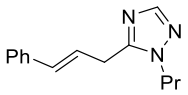


The procedure was adopted from literature.[18] 2-Bromo-4-Chlorophenyl *N,N,N′,N′*-tetramethylphosphorodiamidate (**23n**, 171 mg, 0.50 mmol, 1.0 equiv) was dissolved in a mixture of HCl (2 M) and dioxane (1:1, 5 mL). The reaction mixture was warmed to reflux for 1 h. The reaction mixture was extracted with Et_2O (3 x 10 mL). Purification by short path flash column chromatography (silica gel, *i*hexane/EtOAc = 4:1) afforded the title compound as a white solid (**25n**, 91 mg, 0.44 mmol, 88% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.40 (d, *J* = 2.5 Hz, 1H), 7.13 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.89 (d, *J* = 8.7 Hz, 1H), 5.40 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 150.9, 131.1, 129.0, 125.6, 116.6, 110.1.
Analytical data was equivalent to literature.[19]

[18] C. J. Rohbogner, S. Wirth, P. Knochel, *Org. Lett.* **2010**, *9*, 1984-1987.
[19] P. Suresh, S. Annalakshmi, K. Pitchumani, *Tetrahedron* **2007**, *63*, 4959-4967.

5-Cinnamyl-1-propyl-1*H*-1,2,4-triazole (25o)

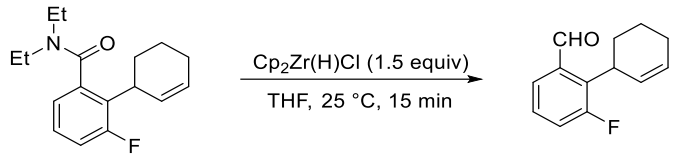


According to **TP 1**, to a mixture of 1-propyl-1*H*-1,2,4-triazole (**23k**, 56 mg, 0.50 mmol, 1.0 equiv) in toluene (1 mL) was added *s*Bu_2Mg (0.30 mmol, 0.6 equiv) at 0 °C. After 15 min, cinnamyl bromide, (118 mg, 0.60 mmol, 1.2 equiv) and CuCN·2LiCl (0.1 mL, 1.0 M in THF, 20 mol%) were added at -25 °C and the mixture was stirred for 1 h. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 1:1) afforded the title compound as a colorless oil (**25o**, 98 mg, 0.43 mmol, 86% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.91 (s, 1H), 7.42 – 7.28 (m, 6H), 6.53 (dt, *J* = 15.9, 1.7 Hz, 1H), 6.35 (dt, *J* = 15.9, 6.5 Hz, 1H), 4.11 (t, *J* = 7.2 Hz, 2H), 3.78 (dd, *J* = 6.5, 1.5 Hz, 2H), 1.93 (h, *J* = 7.4 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 153.0, 150.3, 136.4, 133.0, 128.6, 127.7, 126.3, 123.1, 49.9, 29.7, 23.2, 11.1.
MS (EI, 70 eV): m/z (%) = 227 (41), 226 (30), 212 (57), 199 (14), 198 (39), 184 (54), 170 (17), 157 (13), 145 (20), 144 (11), 136 (15), 130 (13), 129 (12), 128 (15), 125 (34), 117 (17), 116 (10), 115 (72), 110 (46), 97 (56), 96 (21), 91 (16), 84 (100), 83 (22).
HRMS (EI): for $C_{14}H_{17}N_3$: calc. [M+]: 227.1422; found: 227.1415.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3057 (w), 3026 (w), 2964 (m), 2930 (m), 2876 (w), 2853 (w), 1733 (w), 1598 (w), 1510 (m), 1482 (s), 1460 (m), 1448 (s), 1399 (m), 1384 (m), 1347 (w), 1274 (s), 1225 (w), 1184 (m), 1136 (m), 1040 (m), 1030 (m), 966 (vs), 927 (w), 899 (w), 876 (m), 806 (w), 770 (m), 732 (vs), 692 (vs), 676 (m).

7. Synthetic transformations

6-Fluoro-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-2-carbaldehyde (26a)

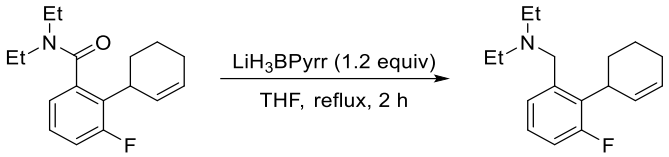


The title compound was prepared according to a literature procedure.[20] A dry and argon flushed Schlenk-tube, equipped with a magnetic stirring bar and a septum, was charged with $Cp_2Zr(H)Cl$ (77 mg, 0.30 mmol, 1.5 equiv). A solution of *N*,*N*-diethyl-6-fluoro-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-2-carboxamide (**25b**, 55 mg, 0.20 mmol, 1.0 equiv) in dry THF (1 mL) was added and the reaction mixture was stirred for 15 min at 25 °C. Purification by short path flash column chromatography (silica gel, *i*hexane/EtOAc = 4:1) afforded the title compound as a colorless oil (**26a**, 37 mg, 0.18 mmol, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 10.57 (s, 1H), 7.72 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.39–7.25 (m, 2H), 5.92–5.77 (m, 2H), 4.35 (h, *J* = 5.2, 3.9 Hz, 1H), 2.25–1.75 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 191.4, 162.4, 160.0, 136.5, 135.3, 130.3, 127.8, 127.7, 127.5, 125.4, 121.0, 120.8, 33.4, 31.8, 24.6, 22.9.
MS (EI, 70 eV): m/z (%) = 204 (14), 203 (13), 187 (11), 186 (81), 185 (69), 183 (13), 176 (24), 175 (100), 171 (33), 170 (14), 165 (51), 163 (37), 162 (40), 160 (17), 159 (19), 149 (35), 148 (12), 147 (44), 146 (42), 135 (20), 134 (13), 133 (64), 121 (14), 115 (16), 109 (16).
HRMS (EI): for $C_{13}H_{13}FO$: calc. [M+]: 204.0950; found: 204.0945.
IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3069 (vw), 3021 (vw), 2928 (w), 2859 (w), 2836 (w), 2764 (vw), 2732 (vw), 2363 (vw), 1687 (s), 1652 (vw), 1604 (m), 1574 (w), 1457 (m), 1447 (m), 1434 (w), 1396 (w), 1271 (w), 1239 (vs), 1221 (m), 1205 (m), 1192 (w), 1186 (w), 1135 (w), 1078 (vw), 1031 (vw), 987 (w), 950 (w), 929 (w), 899 (w), 876 (w), 847 (w), 791 (s), 776 (m), 760 (m), 744 (m), 735 (s), 720 (m), 679 (m).

[20] J. M. White, A. R. Tunoori, G. I. Georg, *J. Am. Chem. Soc.* **2000**, *122*, 11995-11996.

_N_-Ethyl-_N_-((6-fluoro-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-2-yl)methyl)ethanamine



The title compound was prepared according to a literature procedure.[21] A dry and argon flushed Schlenk-tube, equipped with a magnetic stirring bar and a septum, was charged with *N*,*N*-diethyl-6-fluoro-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-2-carboxamide (**25b**, 138 mg, 0.50 mmol, 1.0 equiv). Lithium pyrrolidinoborohydride (0.60 mL, 0.60 mmol, 1 M in THF, 1.2 equiv) was added dropwise and the reaction mixture was heated to reflux for 2 h. The reaction was quenched by slow addition of 3M HCl (2 mL). The aqueous layer was separated, layered with Et_2O and NaOH was added until the reaction mixture was strongly basic to litmus. The organic layer was separated, the aqueous layer extracted with Et_2O (3 x 10 mL) and the combined organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification of the crude product by flash column chromatography (silica gel, *i*hexane/EtOAc = 9:1 to 4:1) afforded the title compound as a colorless oil (114 mg, 0.44 mmol, 88% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.13–7.04 (m, 2H), 6.94–6.86 (m, 1H), 5.79–5.71 (m, 1H), 5.64 (ddt, *J* = 10.1, 3.0, 1.6 Hz, 1H), 3.97 (dtd, *J* = 9.8, 4.8, 2.4 Hz, 1H), 3.59 (d, *J* = 13.4 Hz, 1H), 3.49 (d, *J* = 13.4 Hz, 1H), 2.47 (p, *J* = 7.1 Hz, 4H), 2.23–1.61 (m, 6H), 1.01 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 140.3, 132.5, 132.4, 130.7, 126.6, 126.5, 125.9, 125.6, 114.9, 114.6, 56.2, 46.5, 35.1, 28.7, 24.7, 23.2, 11.8.

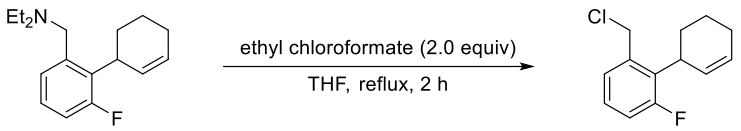
MS (EI, 70 eV): m/z (%) = 189 (14), 188 (29), 187 (16), 173 (30), 161 (11), 160 (98), 159 (100), 153 (10), 147 (49), 146 (48), 135 (11), 133 (36), 123 (18), 109 (11).

HRMS (EI): for $C_{17}H_{24}FN$: calc. [M+]: 261.1893; found: 261.1891.

IR (Diamond-ATR, neat): $\tilde{\nu}$ / cm^{-1} = 3019 (w), 2967 (s), 2930 (s), 2856 (m), 2834 (m), 2796 (m), 2722 (w), 1652 (vw), 1612 (w), 1577 (m), 1464 (vs), 1383 (m), 1371 (m), 1291 (m), 1239 (vs), 1220 (m), 1198 (m), 1164 (m), 1133 (m), 1118 (w), 1058 (m), 1003 (m), 928 (w), 899 (w), 876 (m), 847 (w), 804 (s), 790 (s), 764 (vs), 746 (vs), 734 (vs), 718 (s), 655 (w).

[21] G. B. Fisher, J. C. Fuller, J. Harrison, C. T. Goralski, B. Singaram, *Tetrahedron Lett.* **1993**, *34*, 1091-1094.

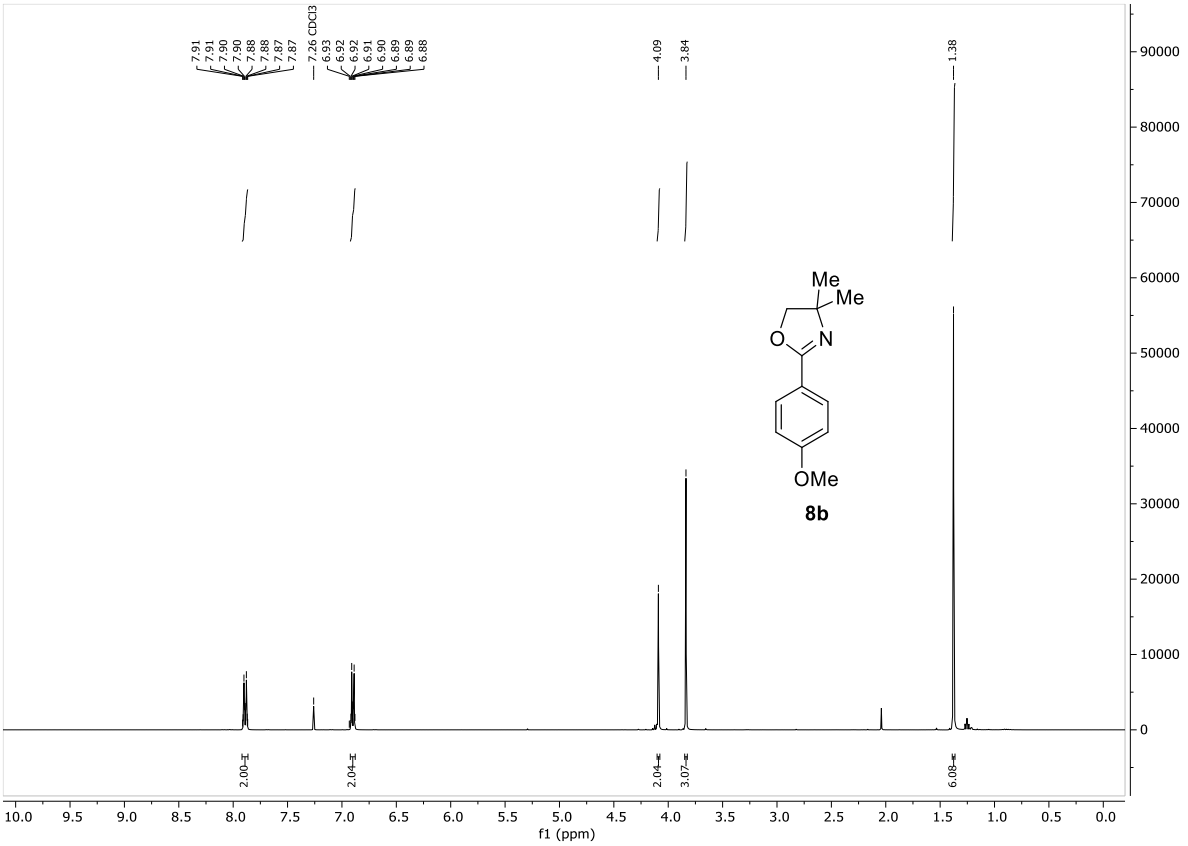
2'-(Chloromethyl)-6'-fluoro-1,2,3,4-tetrahydro-1,1'-biphenyl (26b)

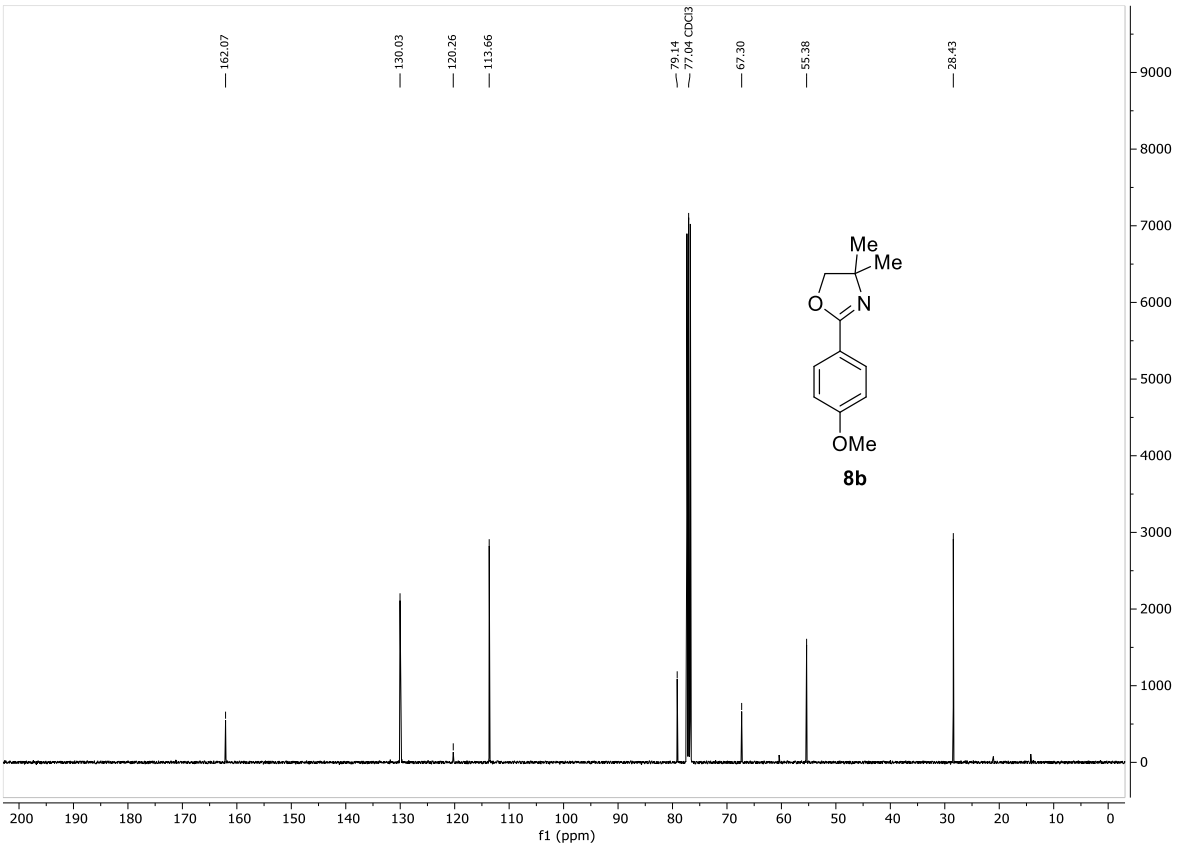


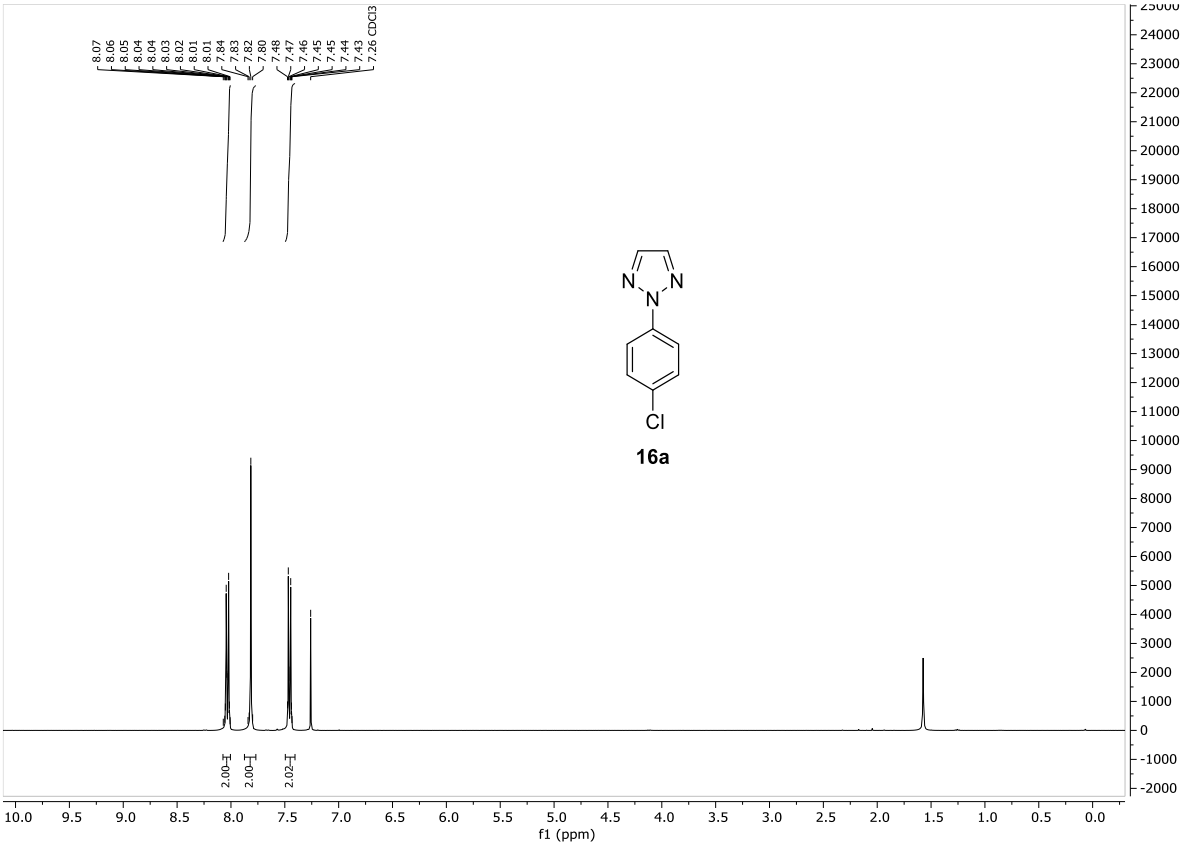
A dry and argon flushed Schlenk-tube, equipped with a magnetic stirring bar and a septum, was charged with *N*-ethyl-*N*-((6-fluoro-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-2-yl)methyl)ethanamine (69 mg, 0.26 mmol, 1.0 equiv) in dry THF (1 mL). Ethyl chloroformate (50 µL, 0.52 mmol, 2.0 equiv) was added dropwise and the reaction mixture was heated to reflux for 2 h. Purification by short path flash column chromatography (silica gel, *i*hexane/EtOAc = 98:2) afforded the title compound as a colorless oil (**26b**, 56 mg, 0.25 mmol, 97% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.22–7.12 (m, 2H), 7.00 (ddd, *J* = 10.9, 7.7, 1.8 Hz, 1H), 5.84 (ddt, *J* = 10.4, 5.3, 2.9 Hz, 1H), 5.69 (dp, *J* = 10.1, 1.6 Hz, 1H), 4.69 (s, 2H), 3.86 (ddh, J = 9.8, 4.8, 2.5 Hz, 1H), 2.27–2.07 (m, 2H), 2.05–1.68 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 163.1, 160.7, 137.8, 132.3, 132.1, 129.7, 127.7, 127.7, 127.1, 127.1, 126.5, 126.5, 116.7, 116.5, 43.9, 35.3, 29.3, 24.6, 23.0.
MS (EI, 70 eV): m/z (%) = 224 (22), 189 (27), 188 (16), 160 (24), 159 (16), 147 (46), 146 (21), 137 (13), 133 (21), 125 (18), 123 (18), 113 (14), 112 (21), 111 (34), 110 (13), 109 (28), 97 (48), 96 (22), 95 (44), 91 (15), 85 (39), 84 (23), 83 (53), 82 (19), 81 (47), 79 (18), 71 (61), 70 (30), 69 (58), 67 (30), 57 (100), 56 (28), 55 (73), 43 (85), 42 (72), 40 (53).
HRMS (EI): for $C_{13}H_{14}ClF$: calc. [M+]: 224.0768; found: 224.0773.

8. NMR Spectra



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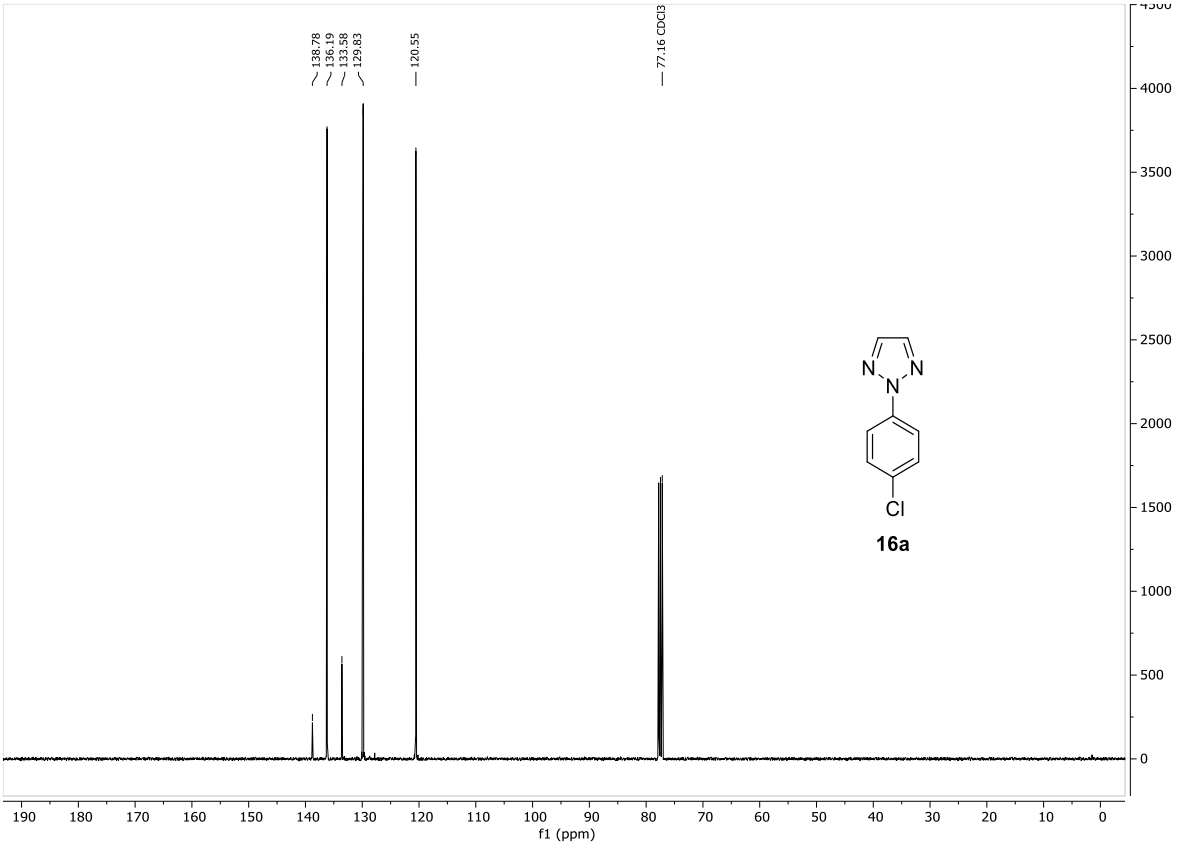
8.05
8.04
8.04
8.03
8.02
8.01
8.01
7.84
7.83
7.82
7.80
7.48
7.47
7.46
7.45
7.45
7.44
7.43
7.26 CDCl3
2.00
2.00
2.02
Cl
16a
f1 (ppm)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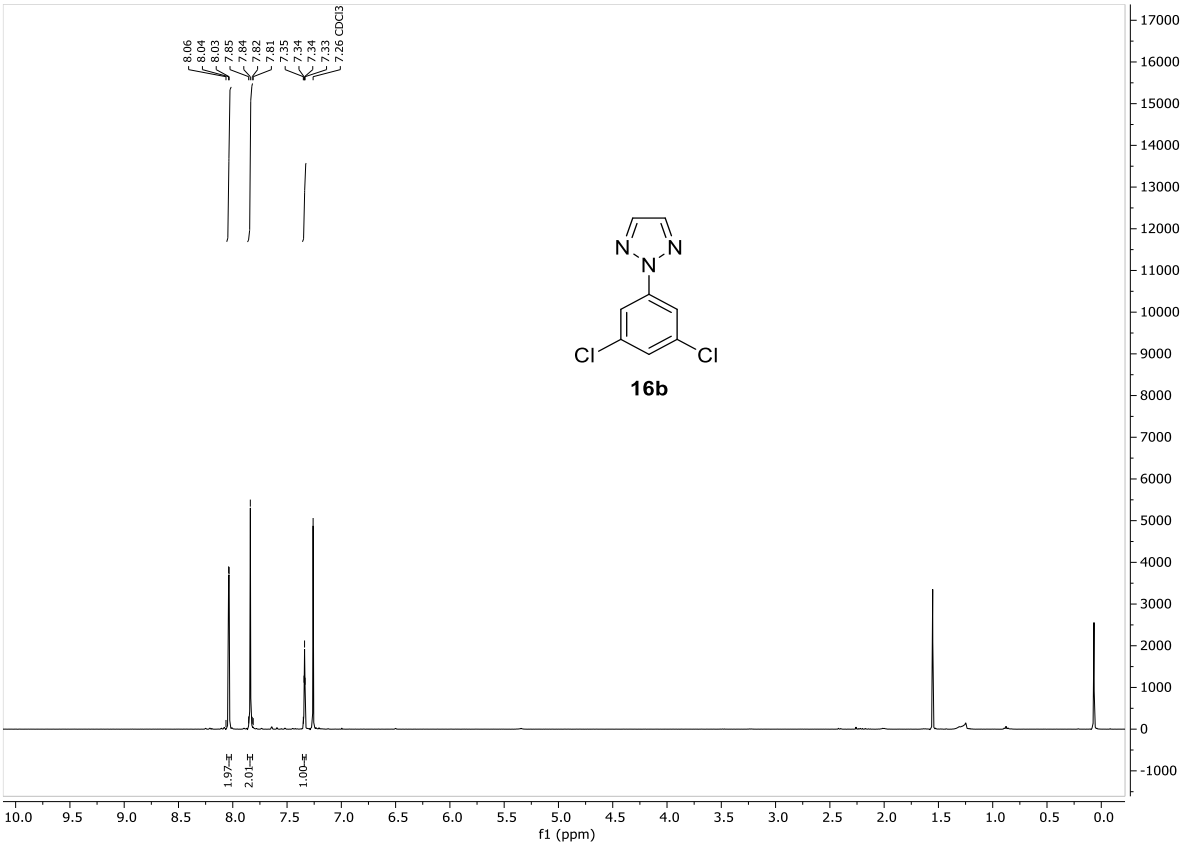
Cl
16a
f1 (ppm)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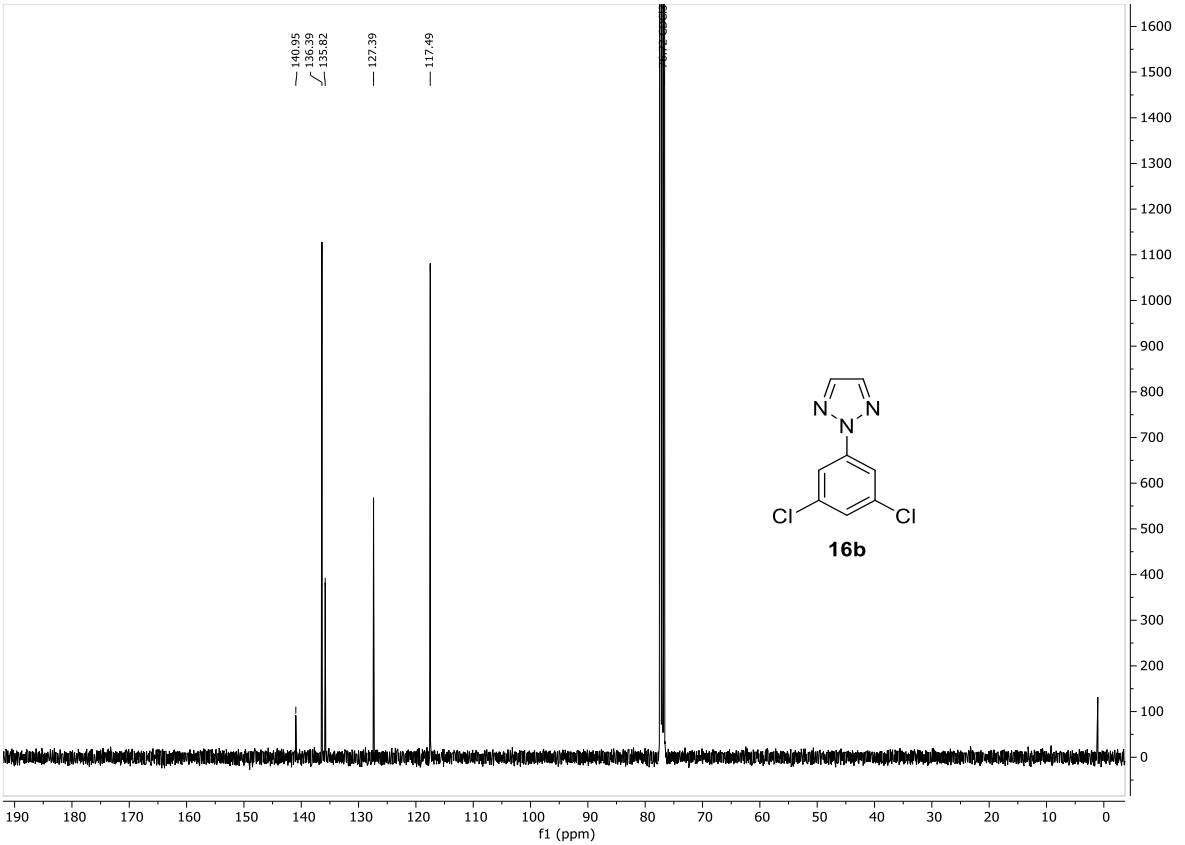
8.04
8.03
7.85
7.84
7.82
7.81
7.35
7.34
7.34
7.33
7.26 CDCl3
1.97
2.01
1.00
Cl
Cl
16b
f1 (ppm)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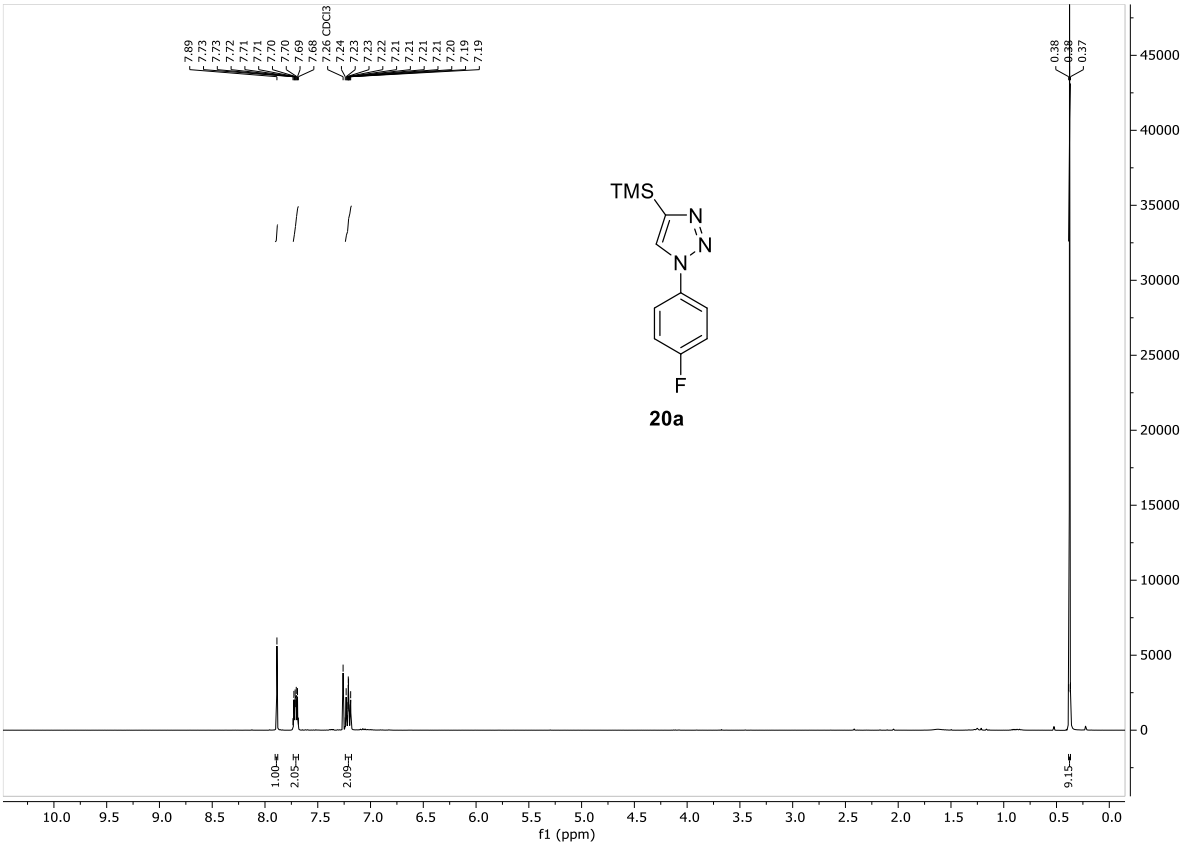
117.49
Cl
Cl
16b
f1 (ppm)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7.70
7.70
7.69
7.68
CDCl3
7.26
7.24
7.23
7.23
7.22
7.21
7.21
7.21
7.21
7.20
7.19
7.19
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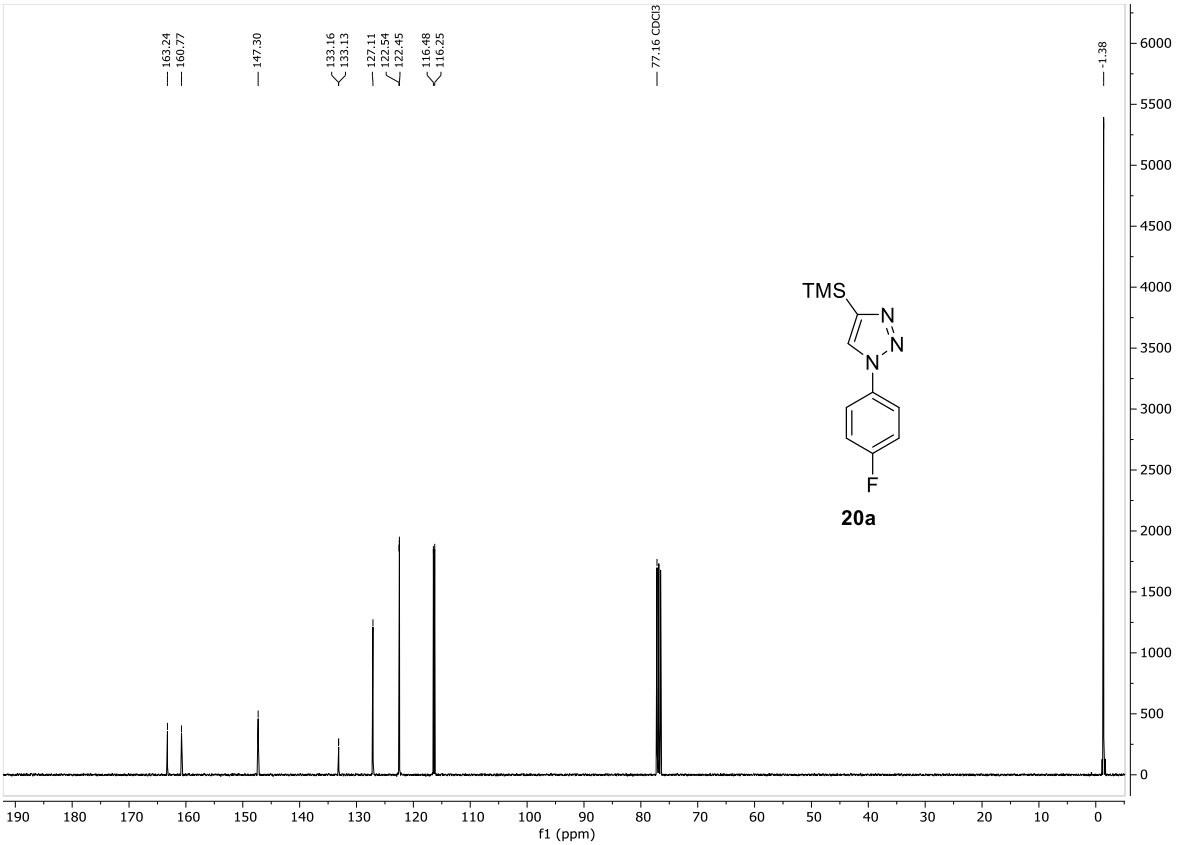
0.38
0.37
TMS
N
N
N
F
20a
1.00
2.05
2.09
9.15
f1 (ppm)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133.16
133.13
127.11
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122.45
116.48
116.25
77.16 CDCl3
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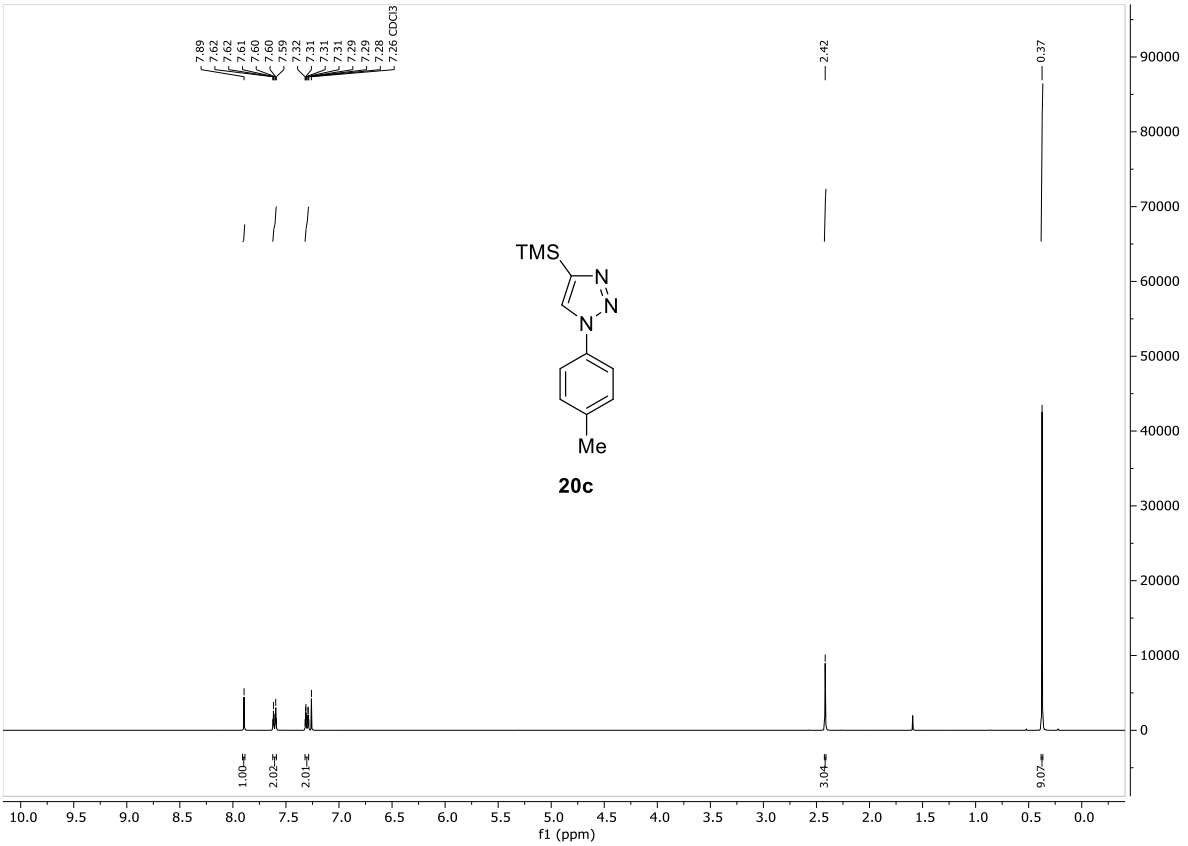
TMS
N
N
N
F
20a
f1 (ppm)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7.29
7.29
7.28
7.26 CDCl3
2.42
0.37
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N
N
Me
20c
1.00
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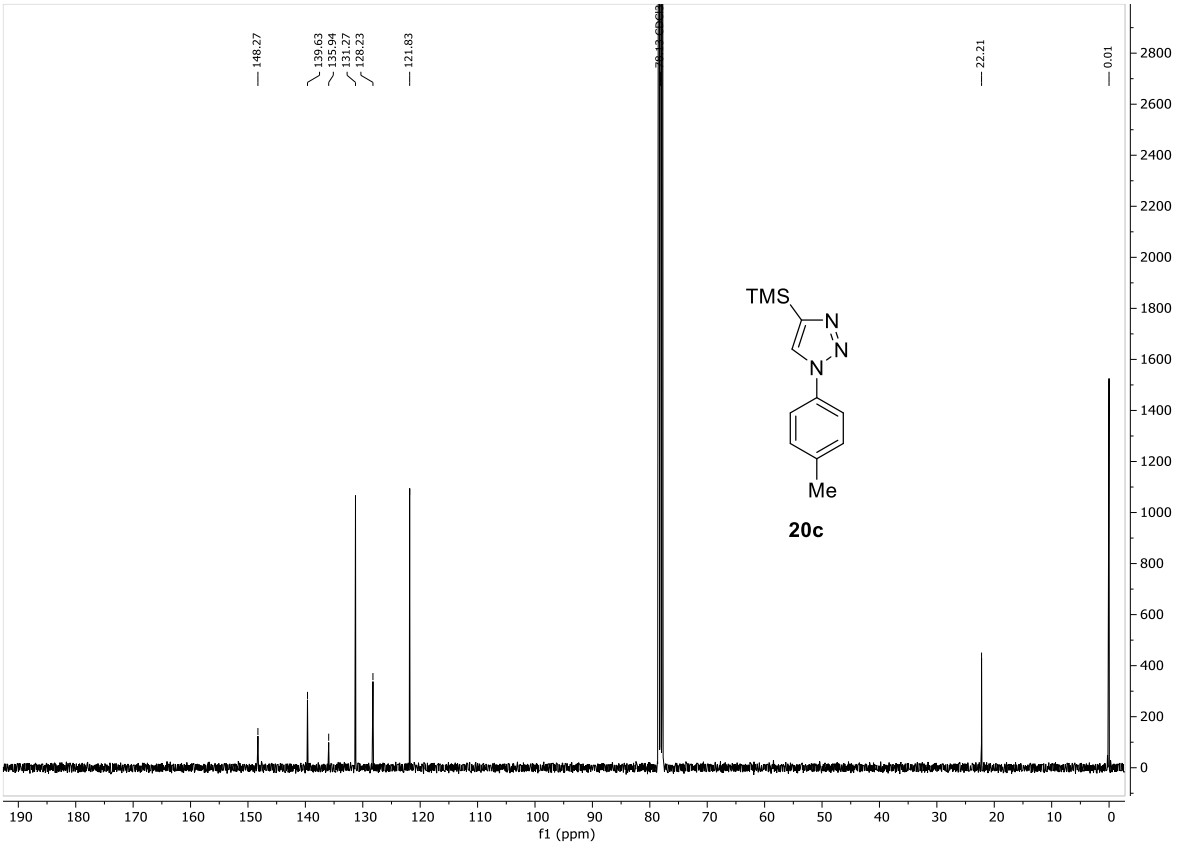
2.01
3.04
9.07
f1 (ppm)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121.83
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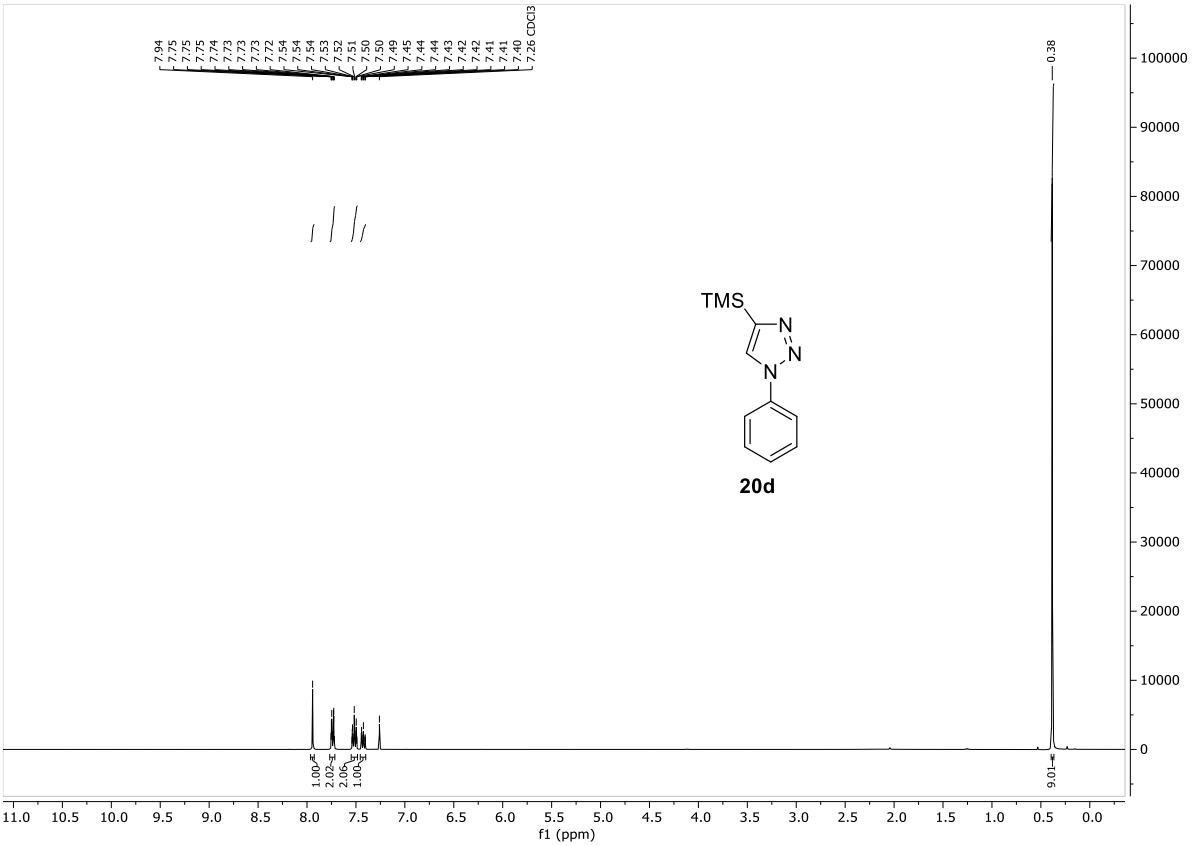
22.21
0.01
TMS
N
N
N
Me
20c
f1 (ppm)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7.51
7.50
7.50
7.49
7.45
7.44
7.44
7.43
7.42
7.42
7.41
7.41
7.40
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TMS
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N
N
20d
1.00
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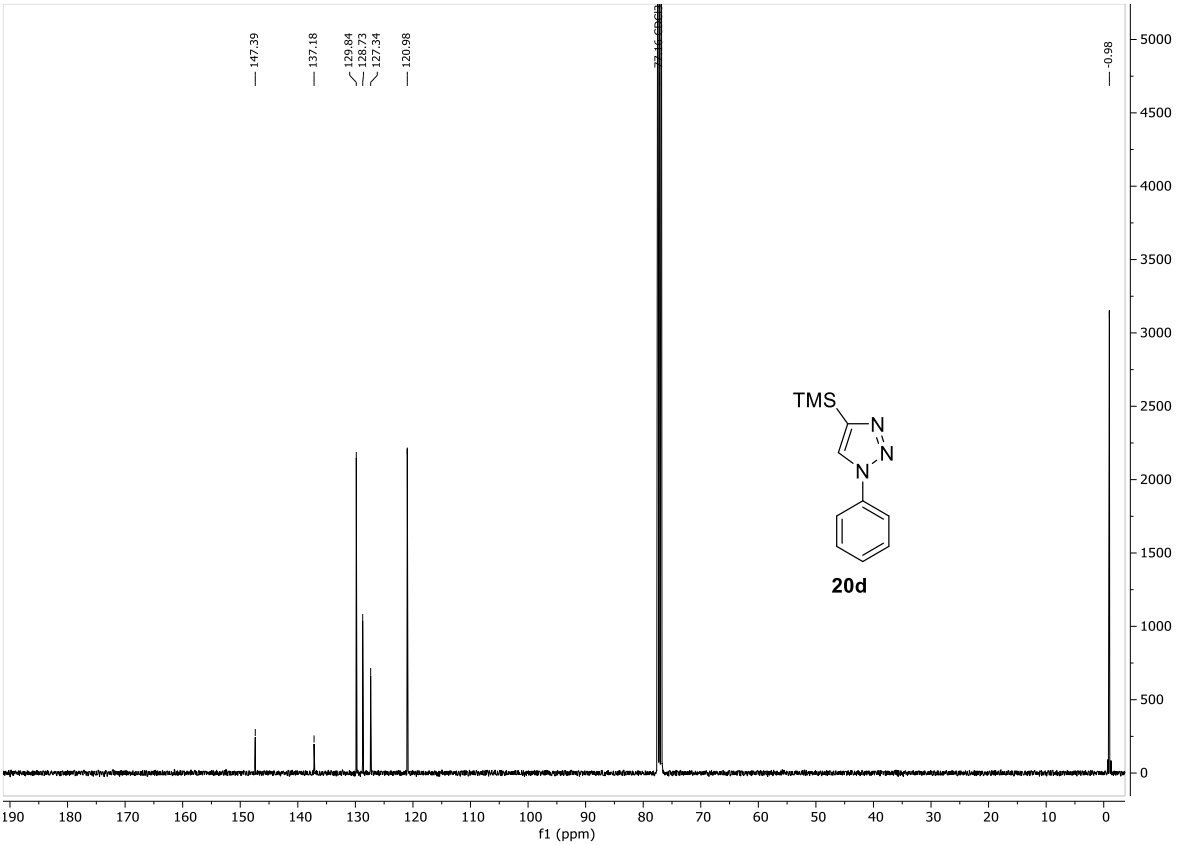
2.06
1.00
9.01
f1 (ppm)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TMS
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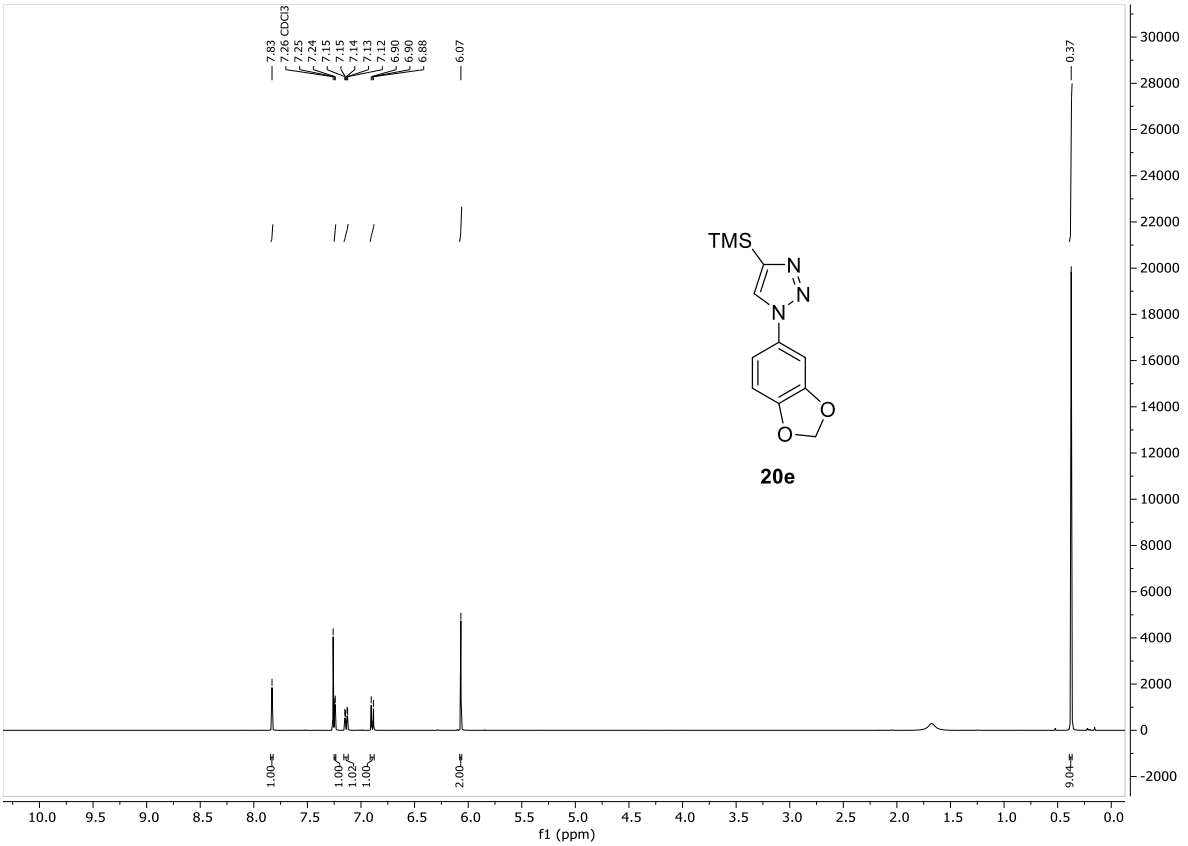
N
N
20d
f1 (ppm)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6.90
6.88
6.07
0.37
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N
O
O
20e
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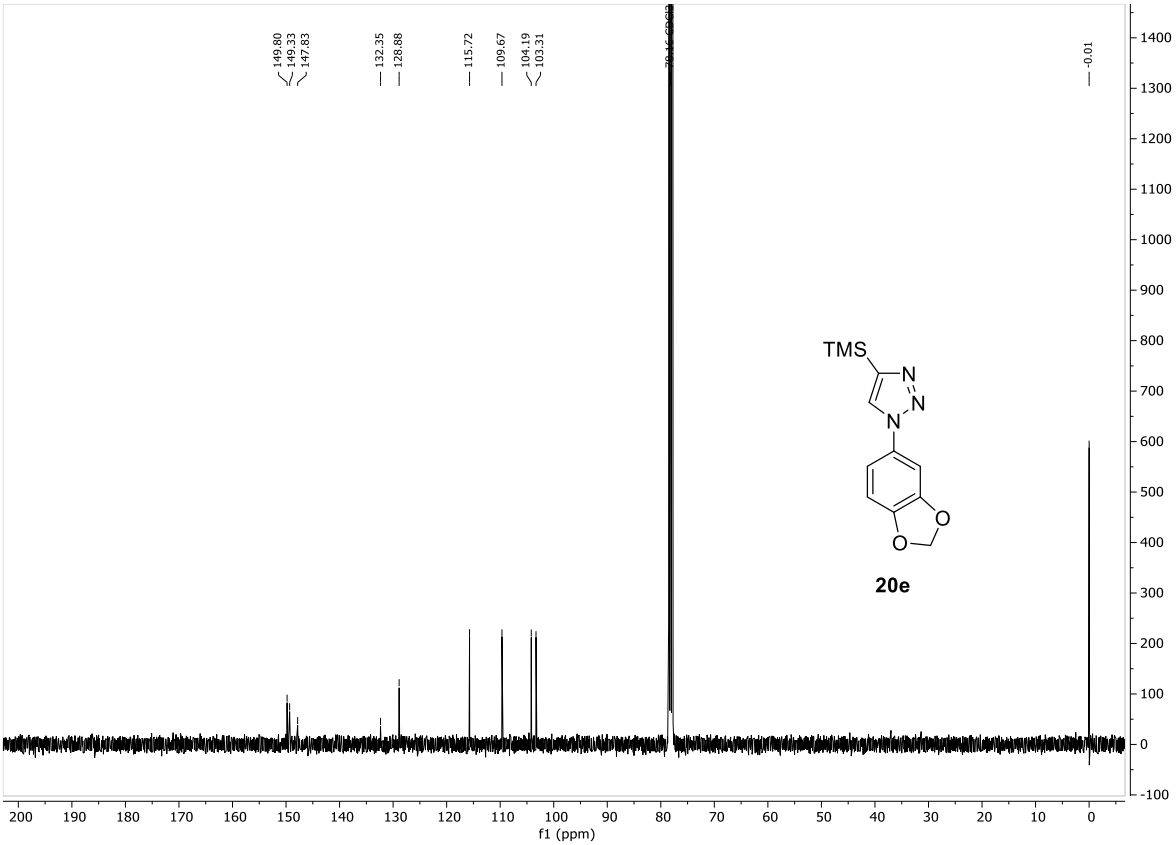
1.00
1.02
1.00
2.00
9.04
f1 (ppm)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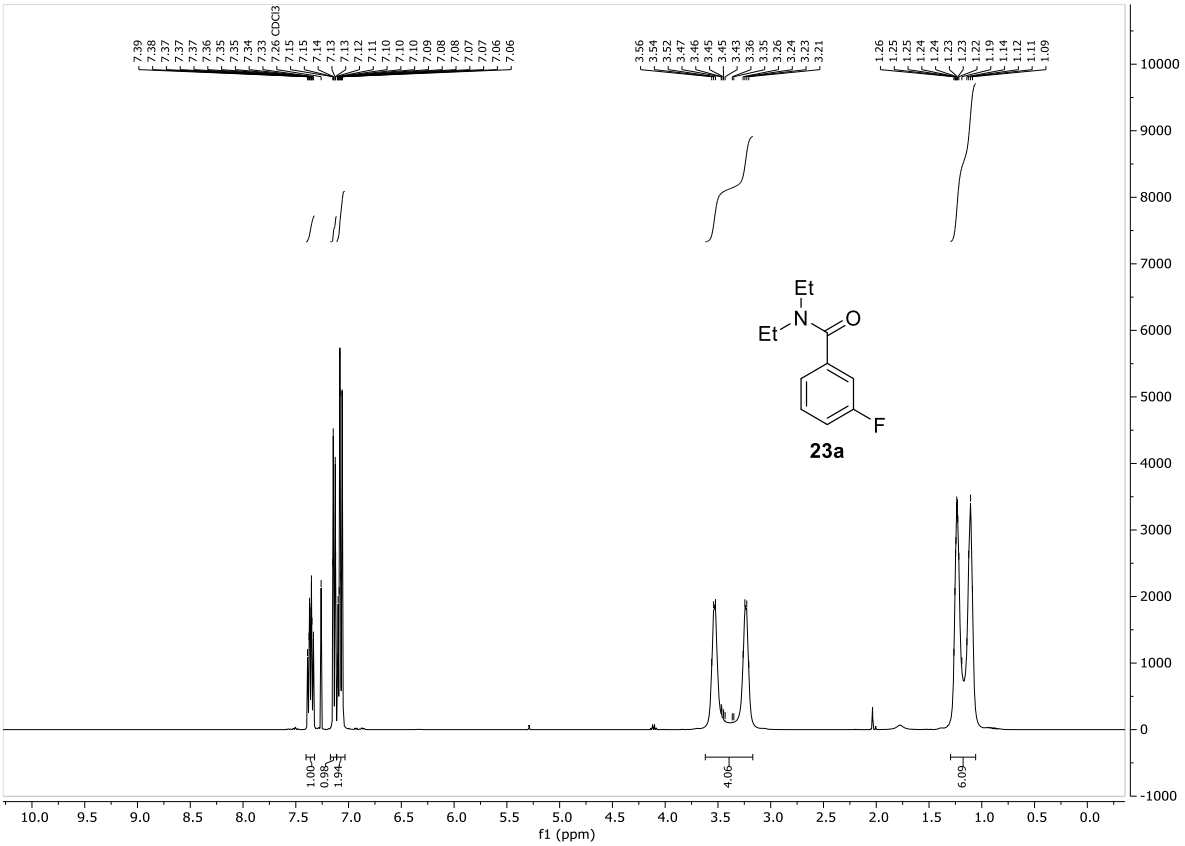
N
N
N
O
O
20e
f1 (ppm)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3.24
3.23
3.21
1.26
1.25
1.25
1.24
1.24
1.23
1.23
1.22
1.19
1.14
1.12
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O
Et
F
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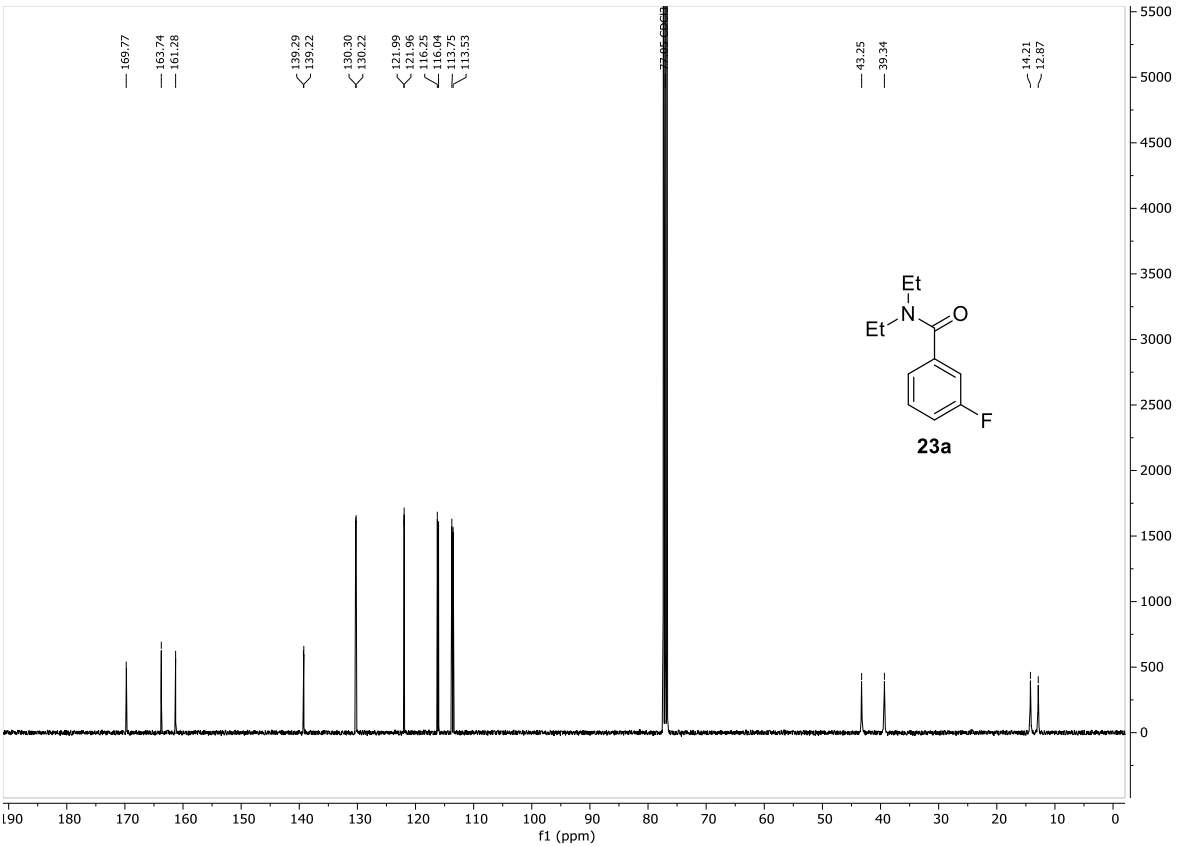
4.06
6.09
f1 (ppm)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14.21
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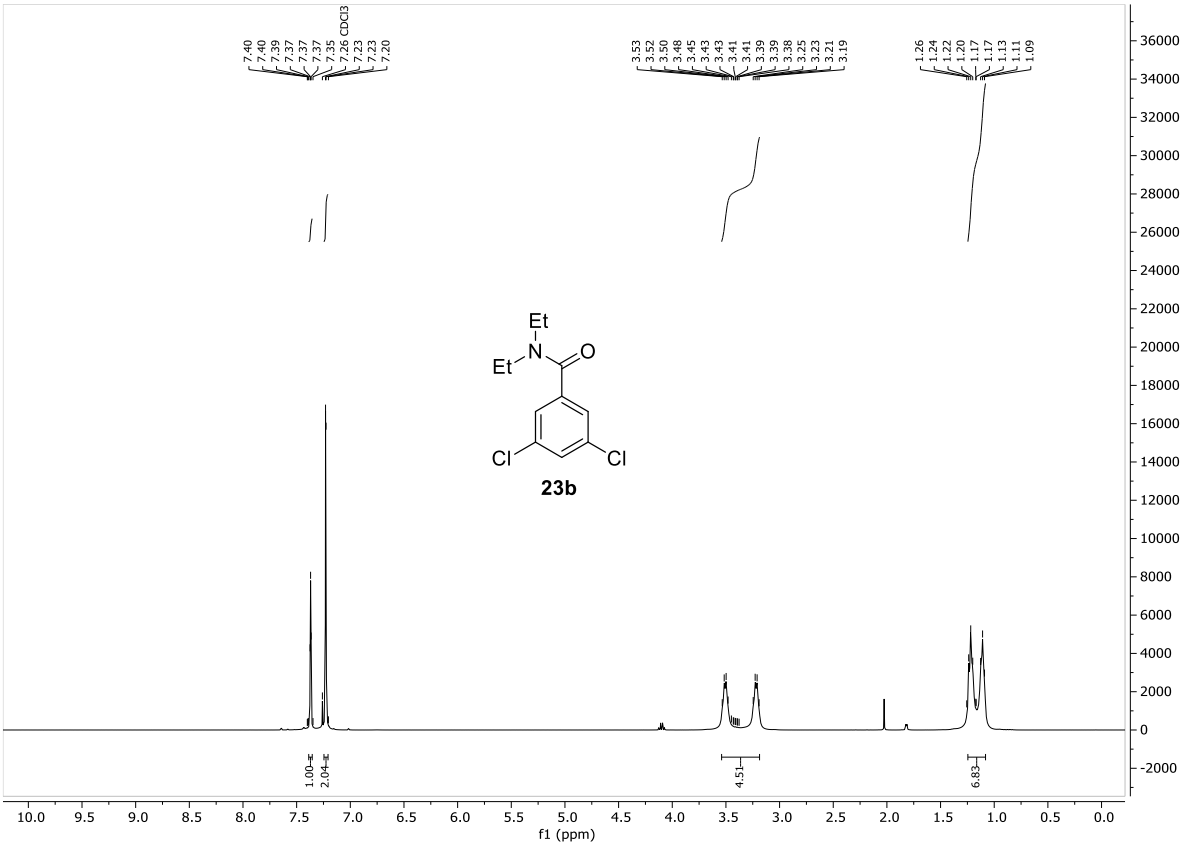
Et
N
O
Et
F
23a
f1 (ppm)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3.52
3.50
3.48
3.45
3.43
3.43
3.41
3.41
3.39
3.39
3.38
3.25
3.23
3.21
3.19
1.26
1.24
1.22
1.20
1.17
1.17
1.13
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N
O
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Cl
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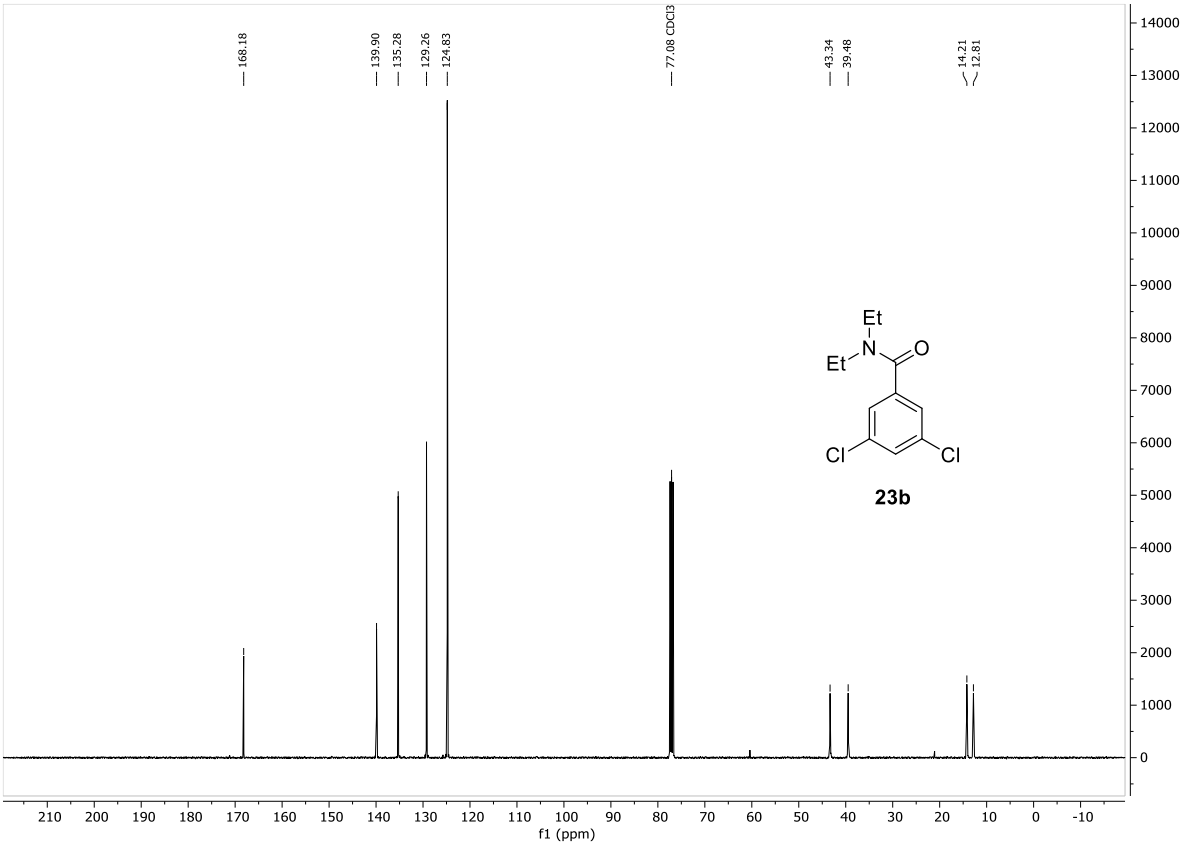
f1 (ppm)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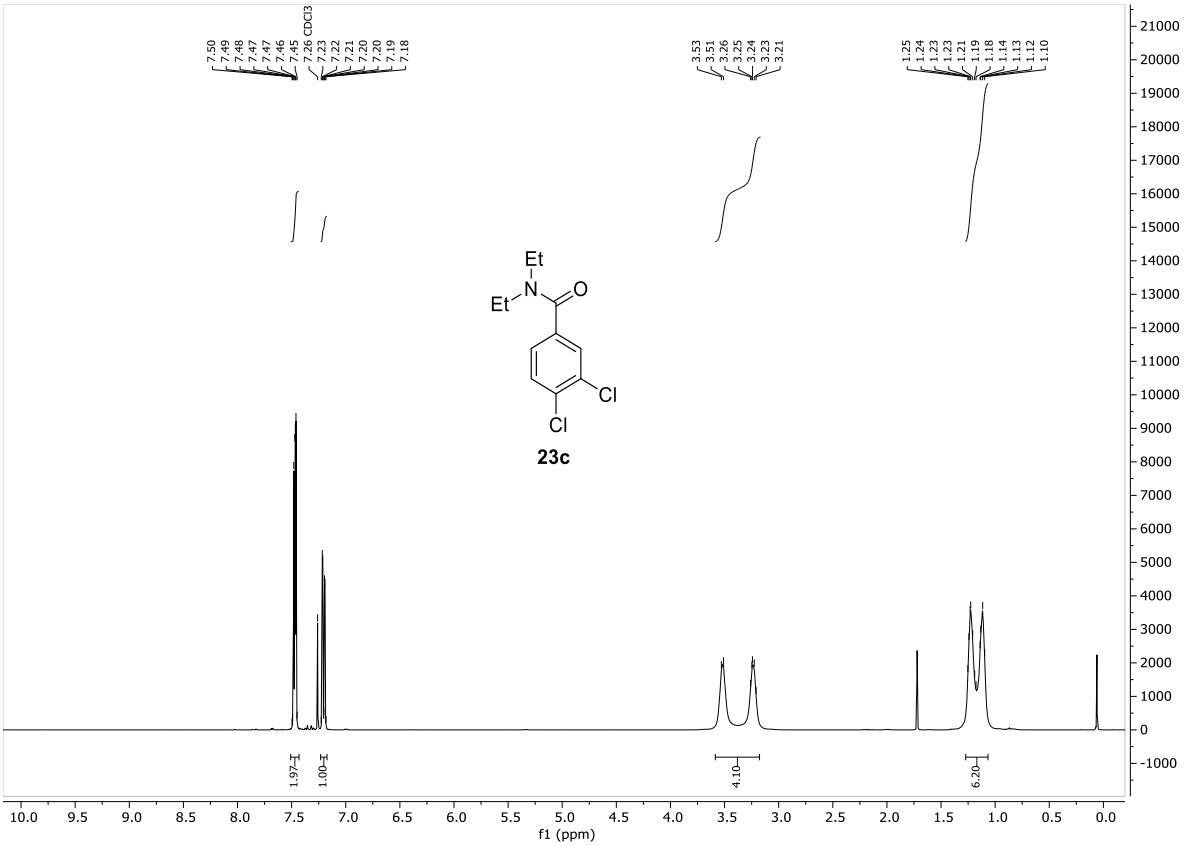
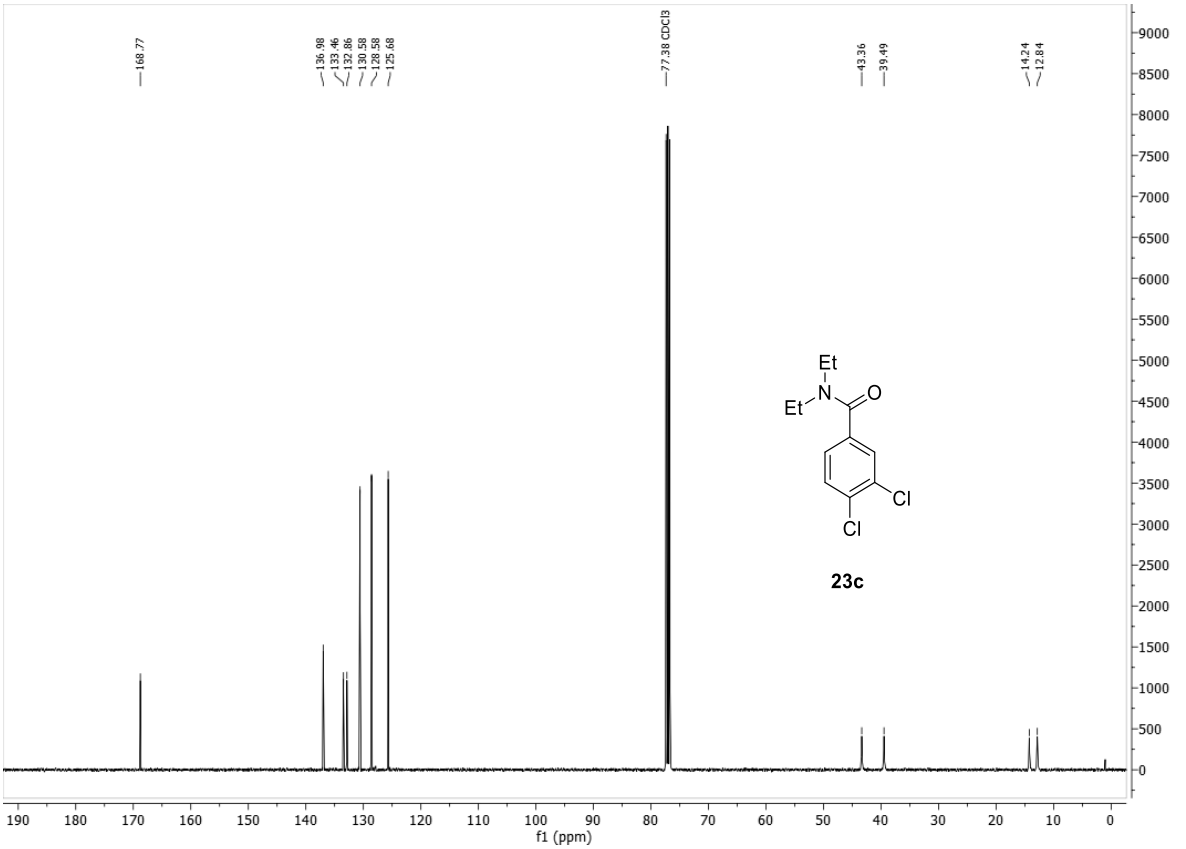
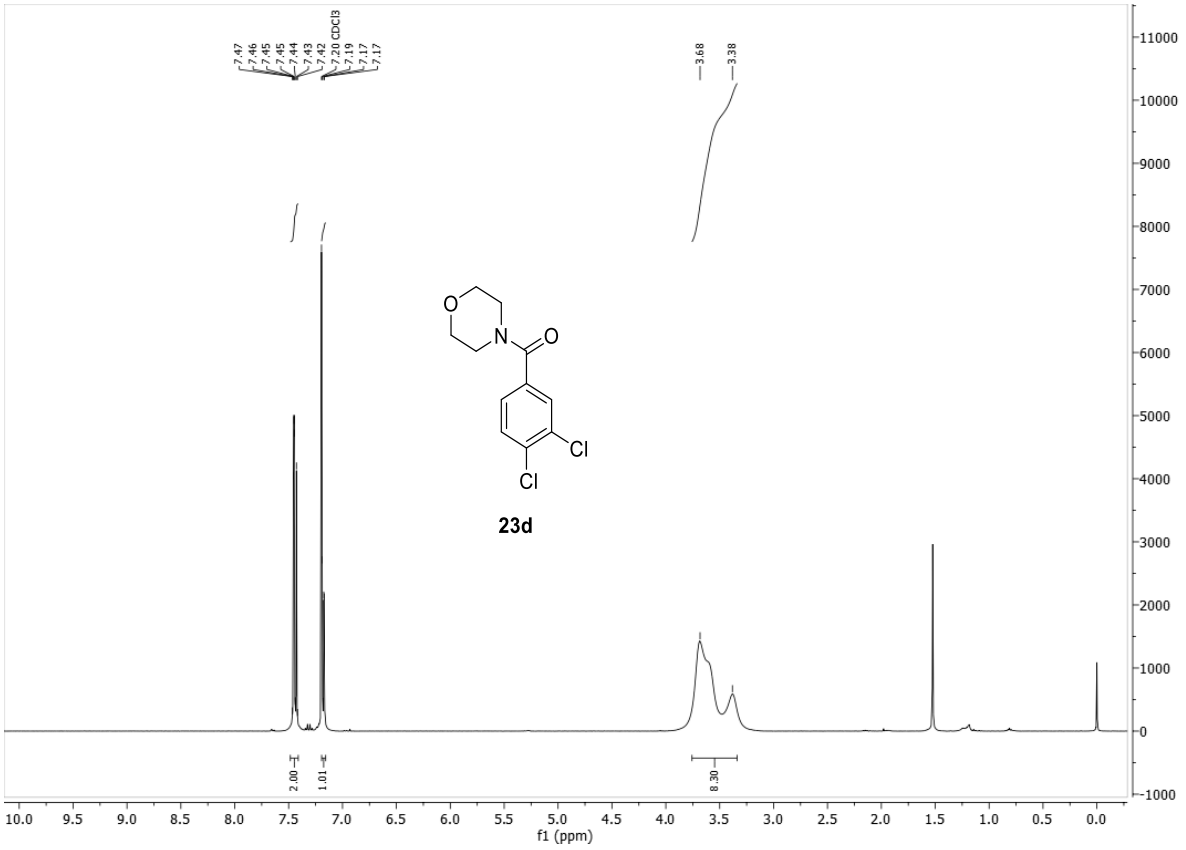
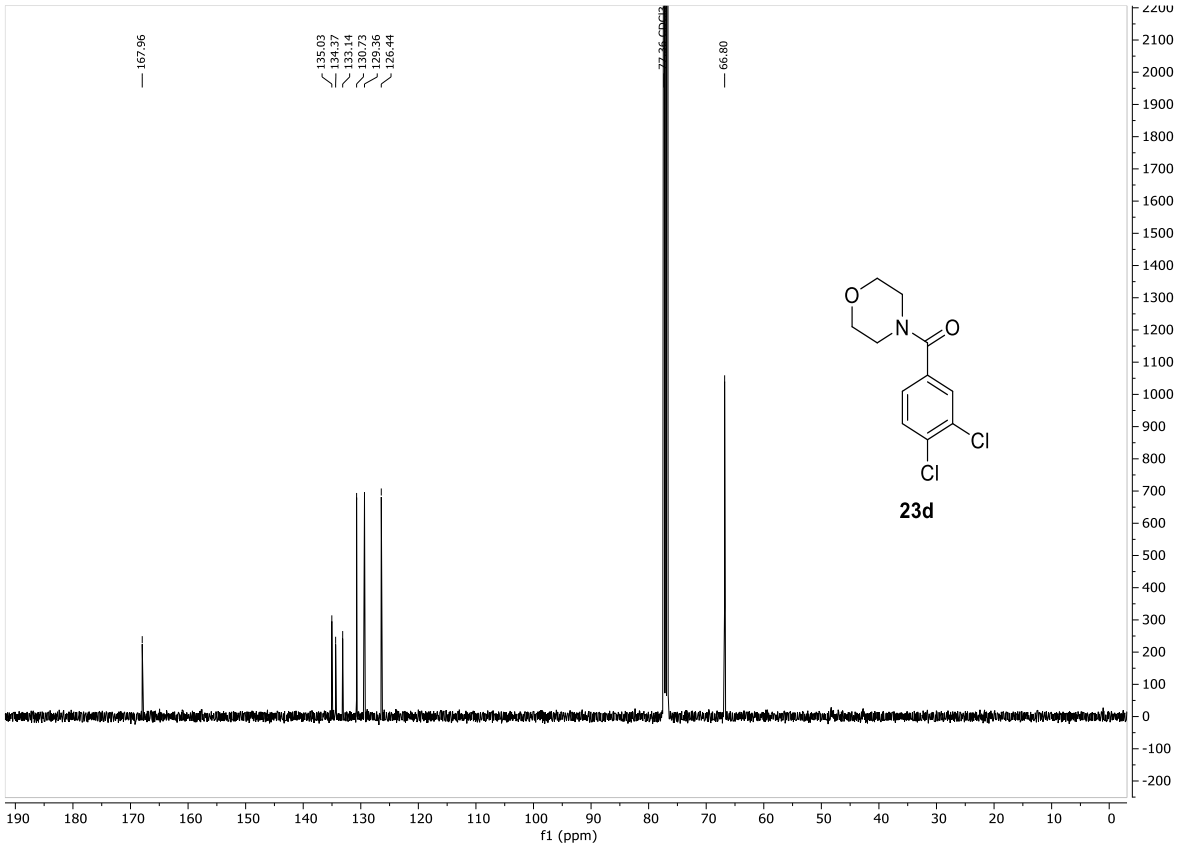
14.21
12.81
Et
N
O
Et
Cl
Cl
23b
f1 (ppm)


7.50
7.49
7.48
7.47
7.47
7.46
7.45
7.26 CDCl3
7.23
7.22
7.21
7.20
7.20
7.19
7.18
3.53
3.51
3.26
3.25
3.24
3.23
3.21
1.25
1.24
1.23
1.23
1.21
1.19
1.18
1.14
1.13
1.12
1.10
Et
N
Et
O
Cl
Cl
23c
1.97
1.00
4.10
6.20
f1 (ppm)

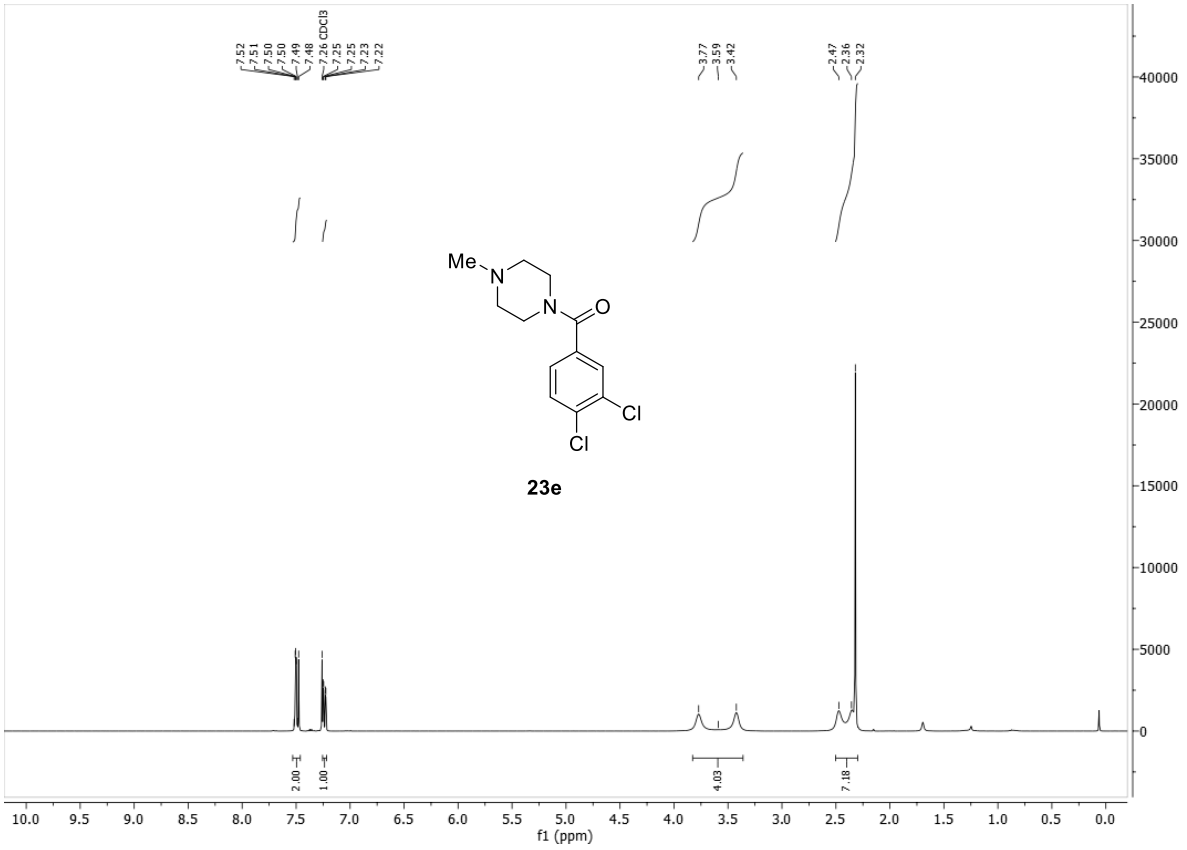

168.77
136.98
133.46
132.86
130.58
128.58
125.68
77.38 CDCl3
43.36
39.49
14.24
12.84
Et
N
Et
O
Cl
Cl
23c
f1 (ppm)


7.47
7.46
7.45
7.45
7.44
7.43
7.42
7.20 CDCl3
7.19
7.17
7.17
3.68
3.38
2.00
1.01
8.30
f1 (ppm)

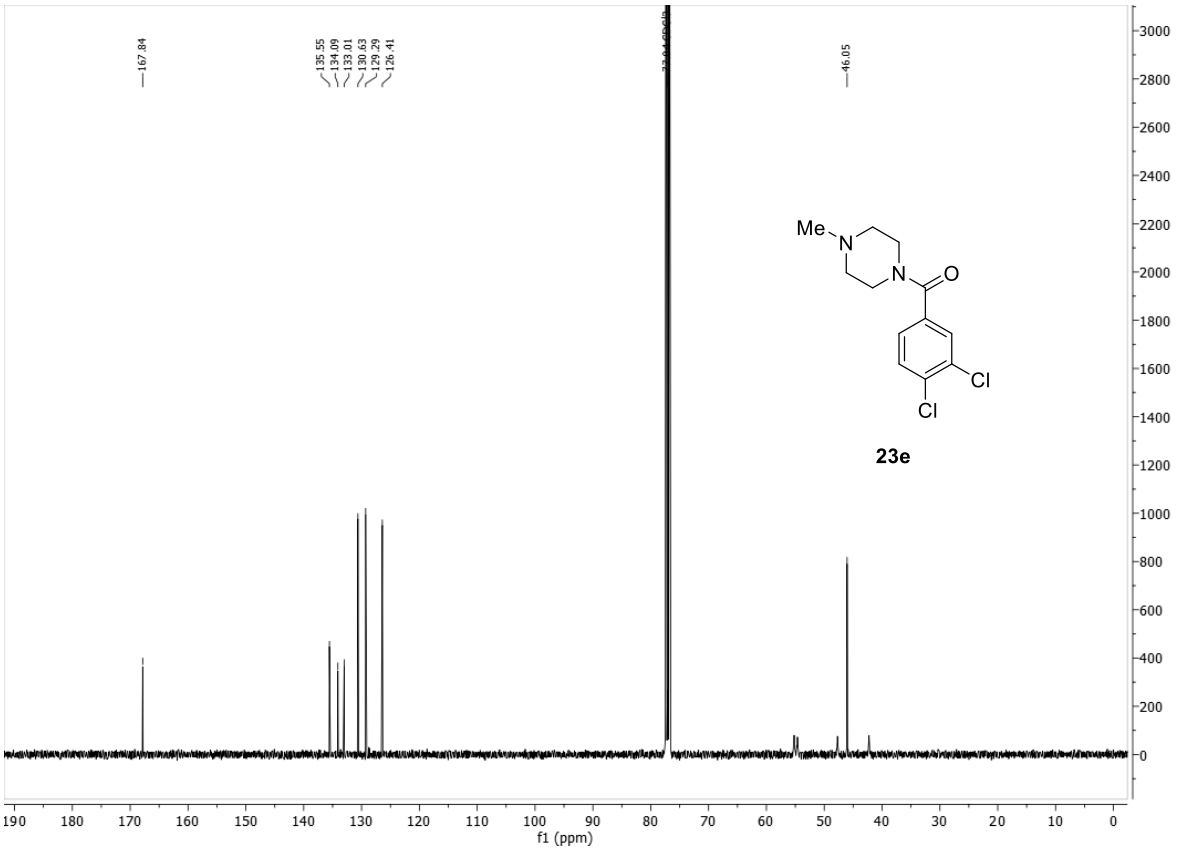
23d


167.96
135.03
134.37
133.14
130.73
129.36
126.44
77.36 CDCl3
66.80
f1 (ppm)

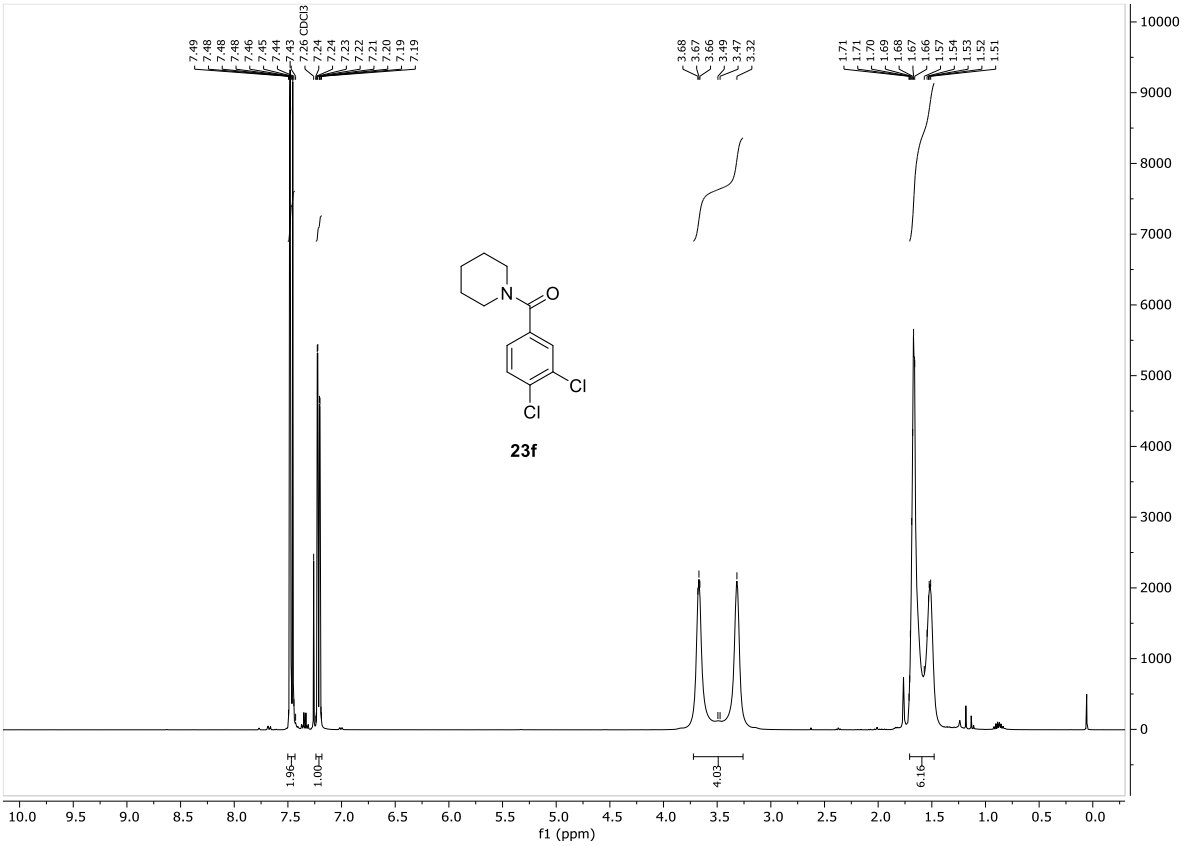
23d

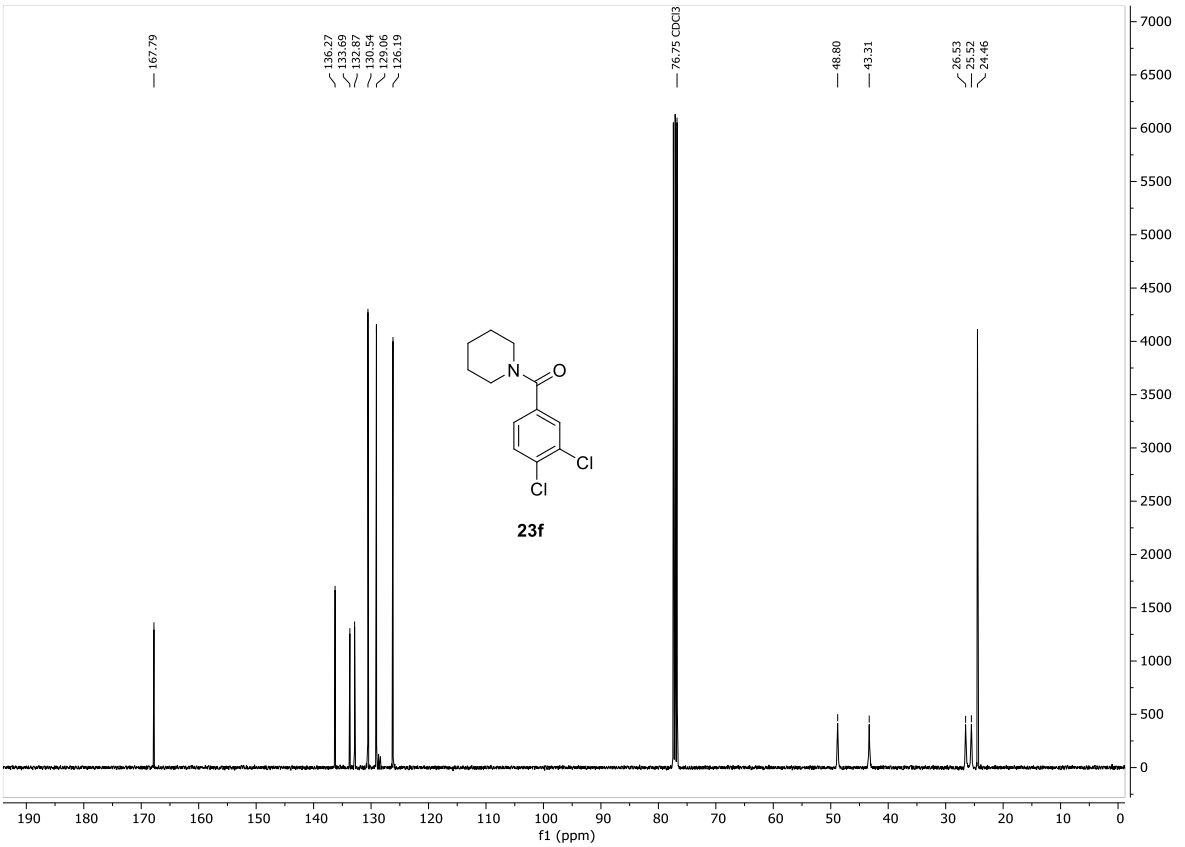

7.52
7.51
7.50
7.50
7.49
7.48
7.26 CDCl3
7.25
7.25
7.23
7.22
3.77
3.59
3.42
2.47
2.36
2.32
Me
N
N
O
Cl
Cl
2.00
1.00
4.03
7.18
f1 (ppm)

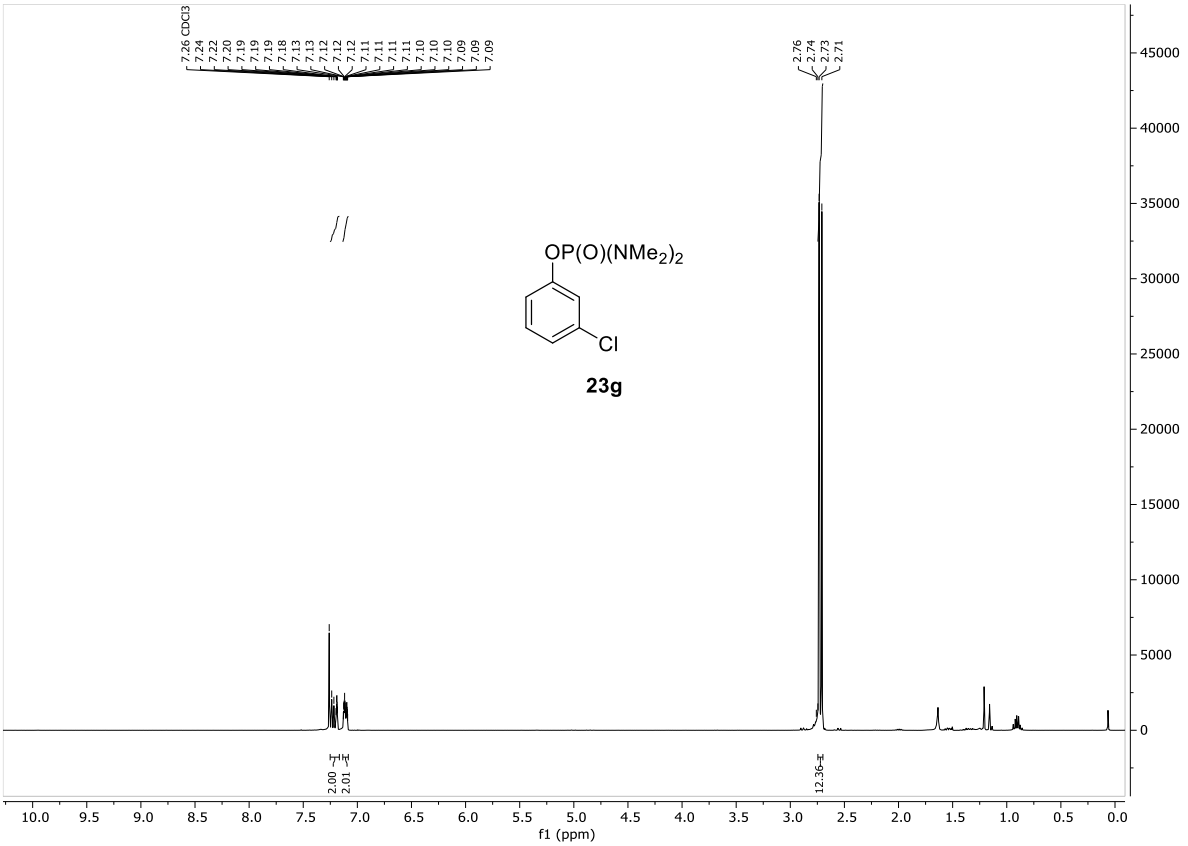
23e

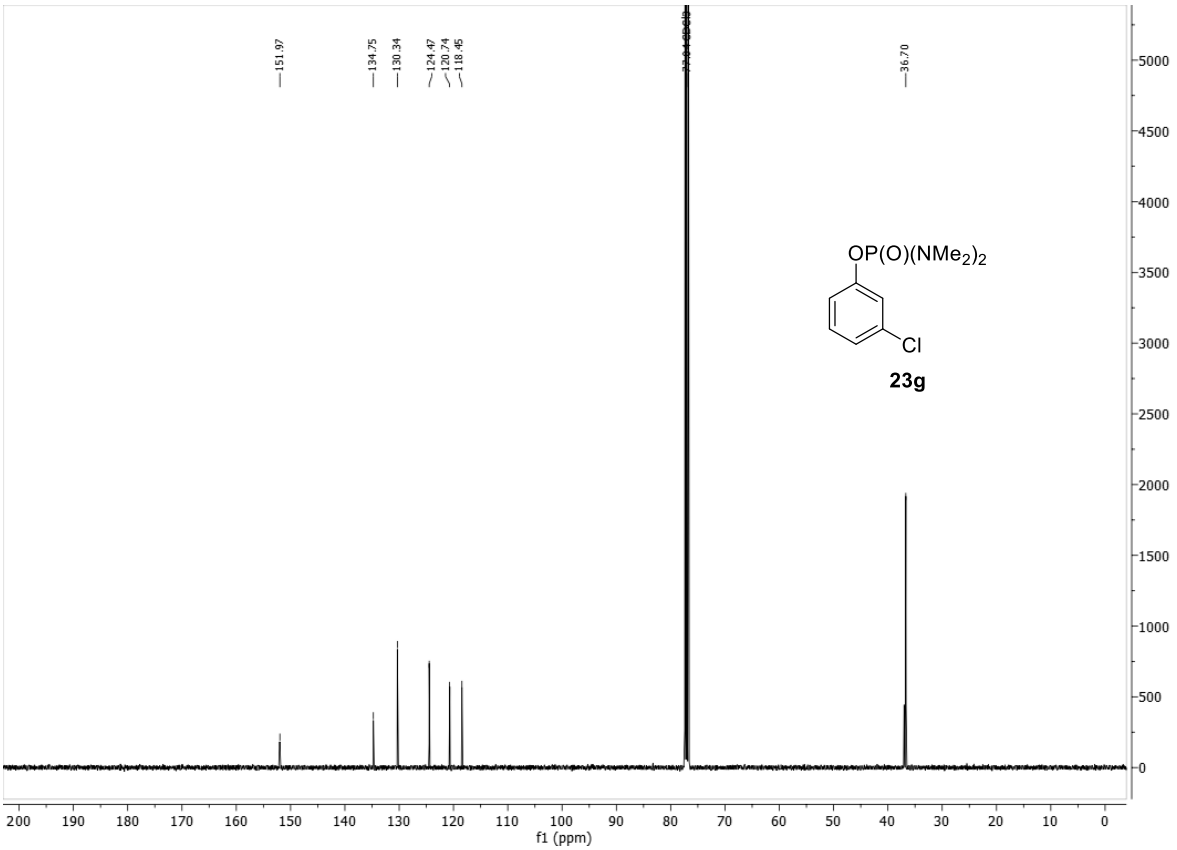

167.84
135.55
134.09
133.01
130.63
129.29
126.41
77.04 CDCl3
46.05
Me
N
N
O
Cl
Cl
f1 (ppm)

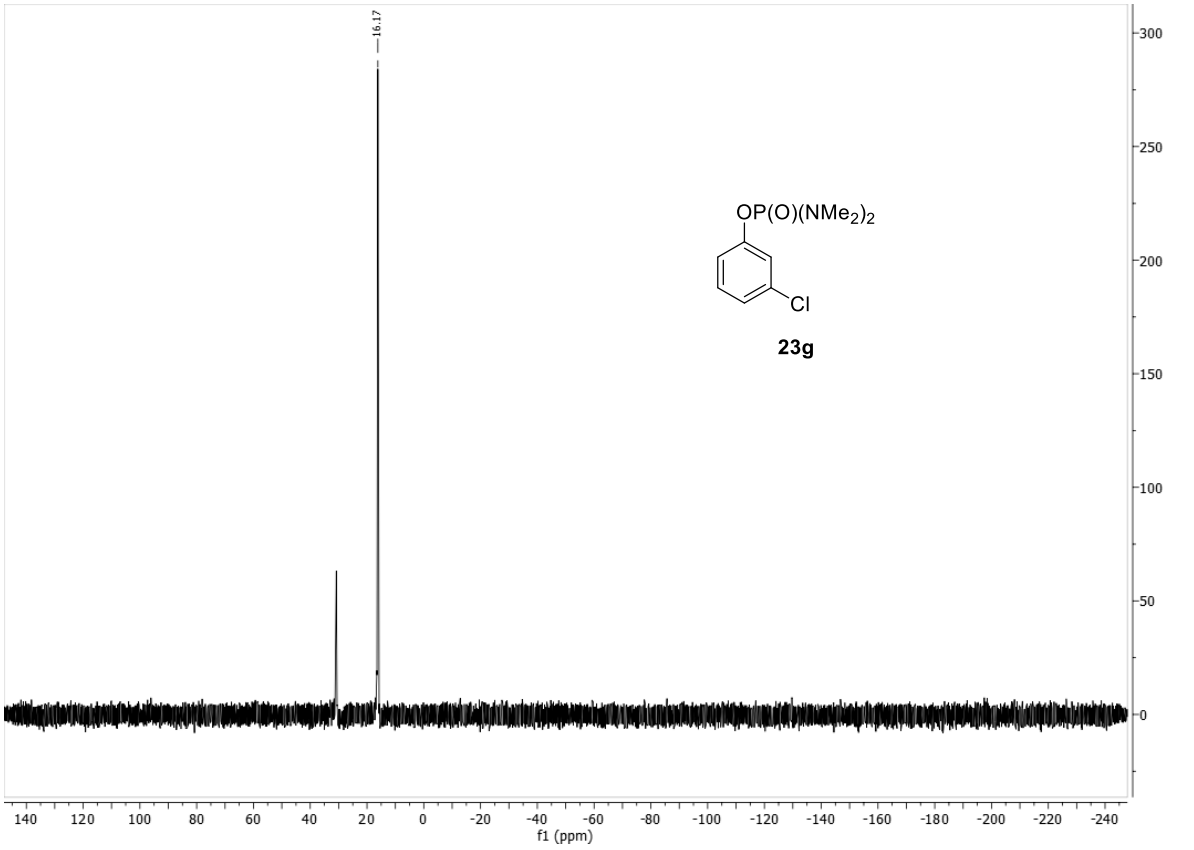
23e

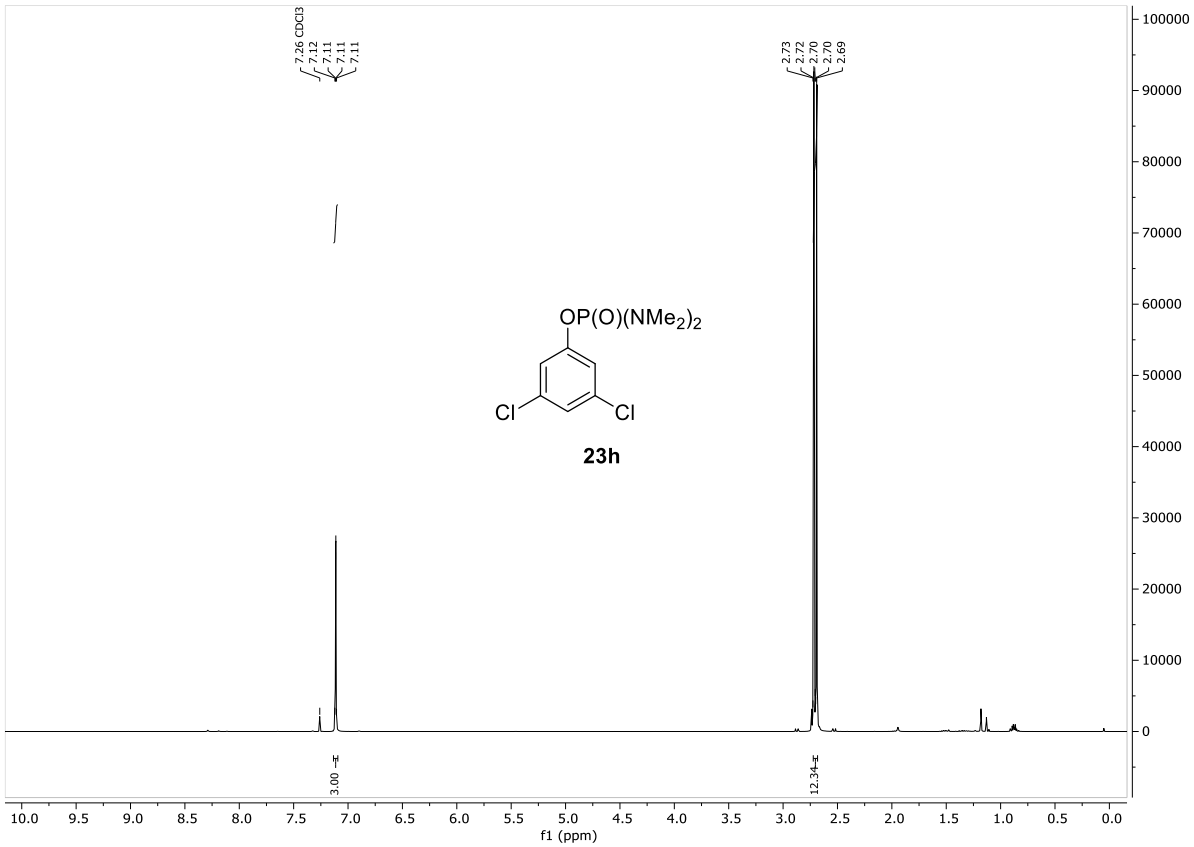

7.49
7.48
7.48
7.48
7.46
7.45
7.44
7.43
7.26 CDCl3
7.24
7.24
7.23
7.22
7.21
7.20
7.19
7.19
3.68
3.67
3.66
3.49
3.47
3.32
1.71
1.71
1.70
1.69
1.68
1.67
1.66
1.57
1.54
1.53
1.52
1.51
1.96
1.00
4.03
6.16
N
O
Cl
Cl
23f
f1 (ppm)

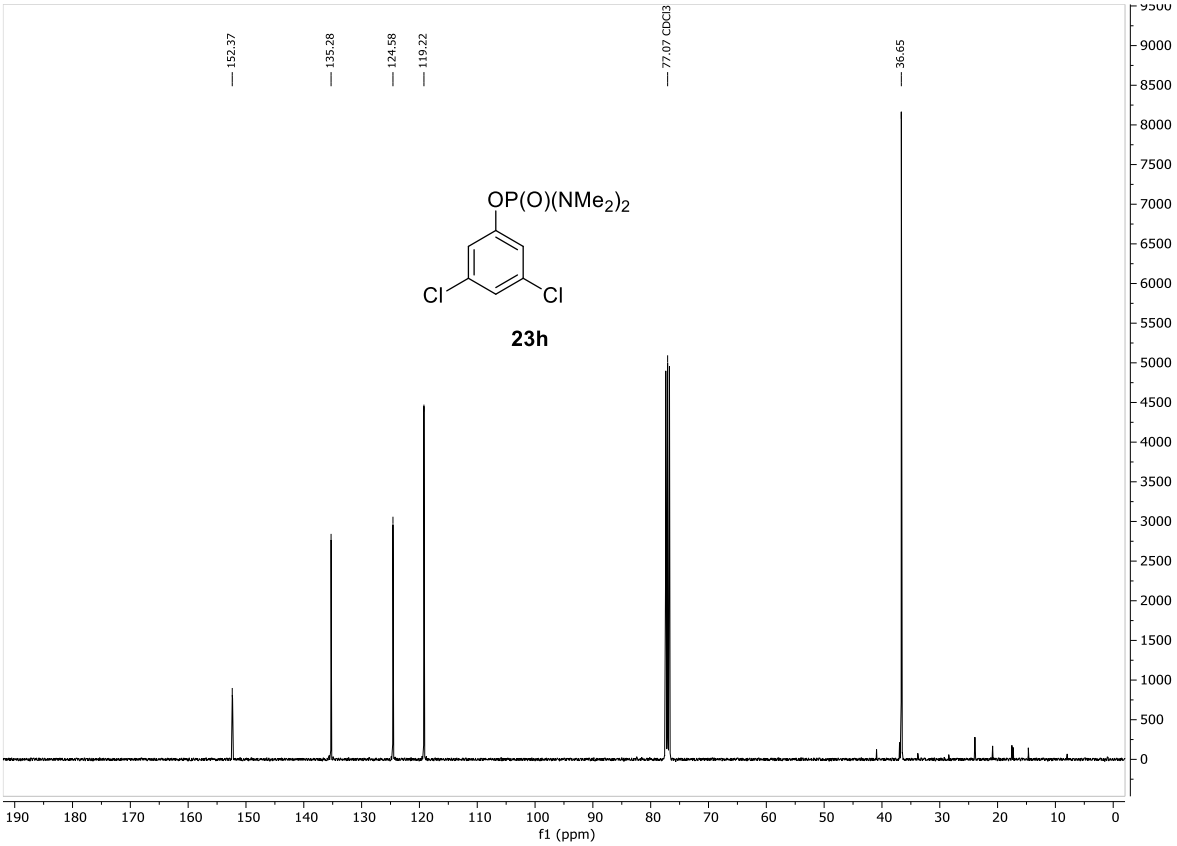

167.79
136.27
133.69
132.97
130.54
129.06
126.19
76.75 CDCl3
48.80
43.31
26.53
25.52
24.46
N
O
Cl
Cl
23f
f1 (ppm)

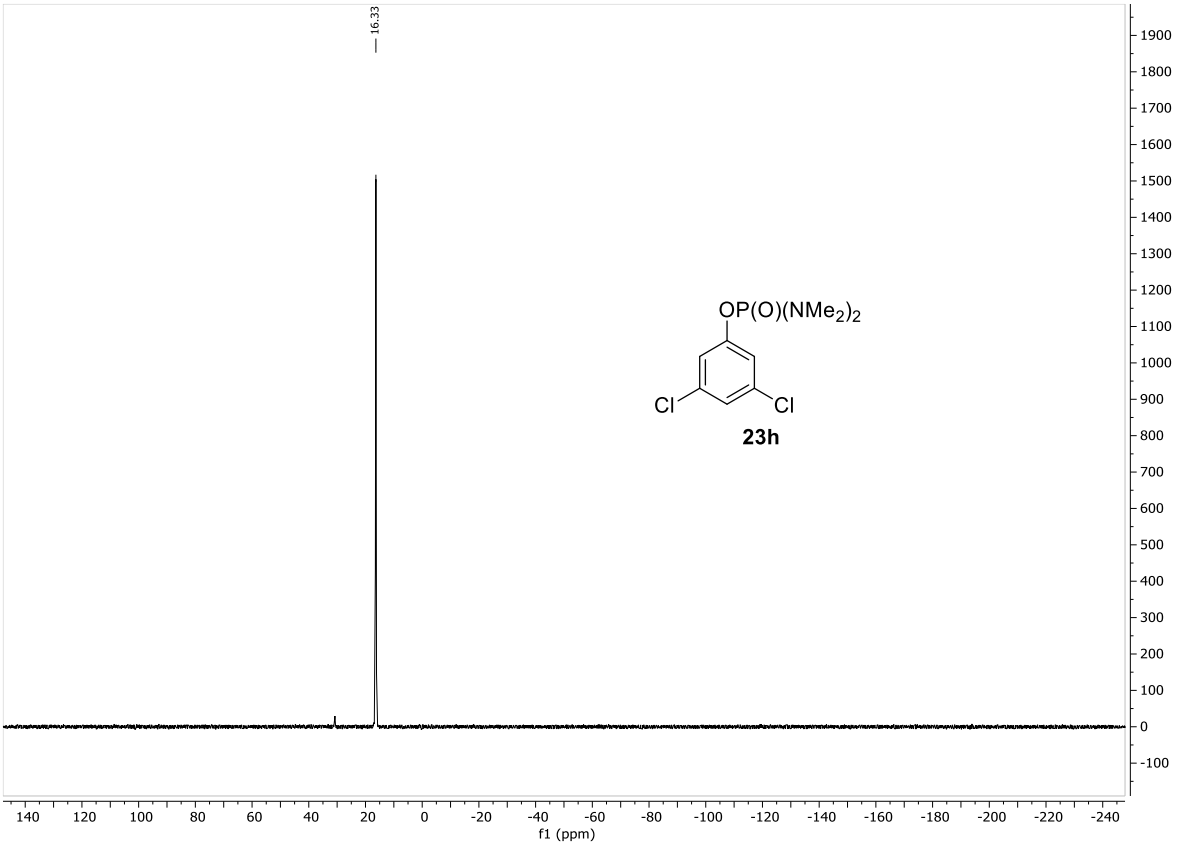

7.26 CDCl3
7.24
7.22
7.20
7.19
7.19
7.19
7.18
7.13
7.12
7.12
7.12
7.11
7.11
7.11
7.11
7.10
7.10
7.10
7.09
7.09
7.09
2.76
2.74
2.73
2.71
OP(O)(NMe2)2
Cl
23g
2.00
2.01
12.36
f1 (ppm)

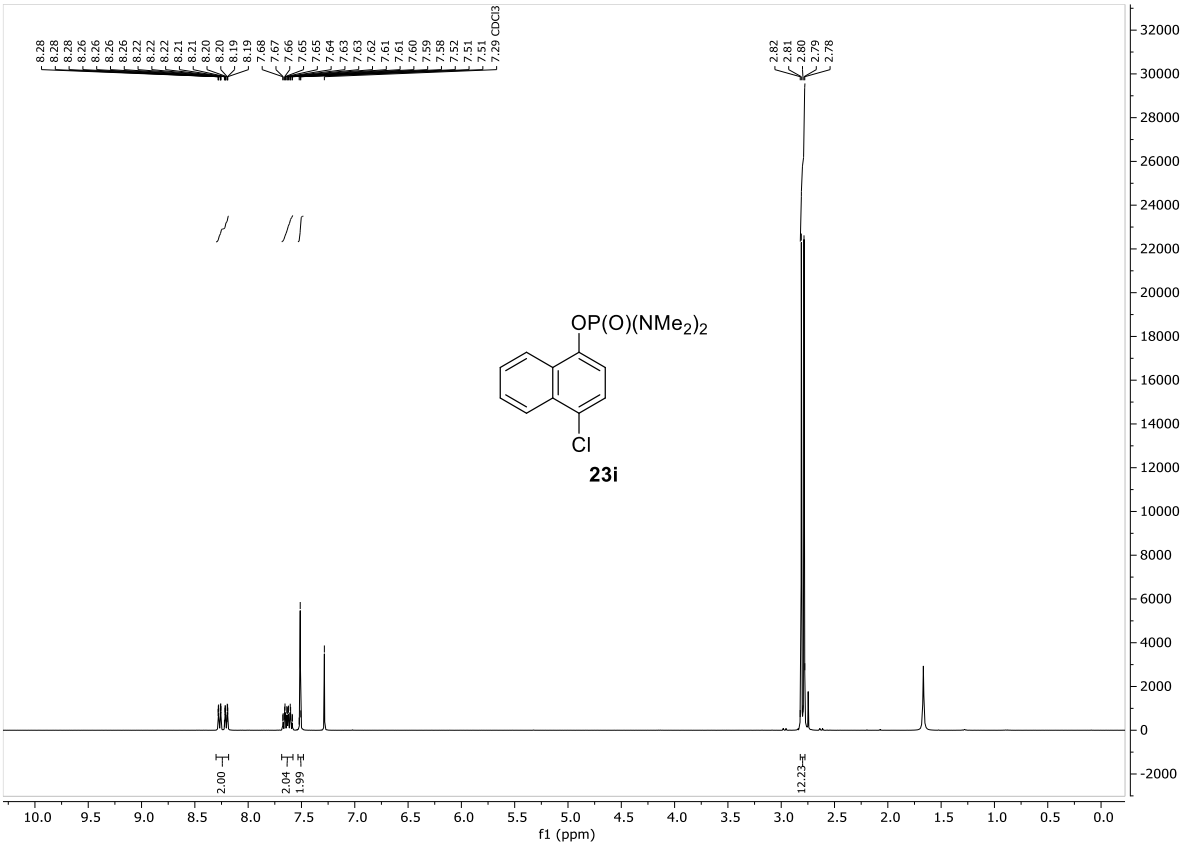

151.97
134.75
130.34
124.47
120.74
118.45
36.70
OP(O)(NMe2)2
Cl
23g
f1 (ppm)

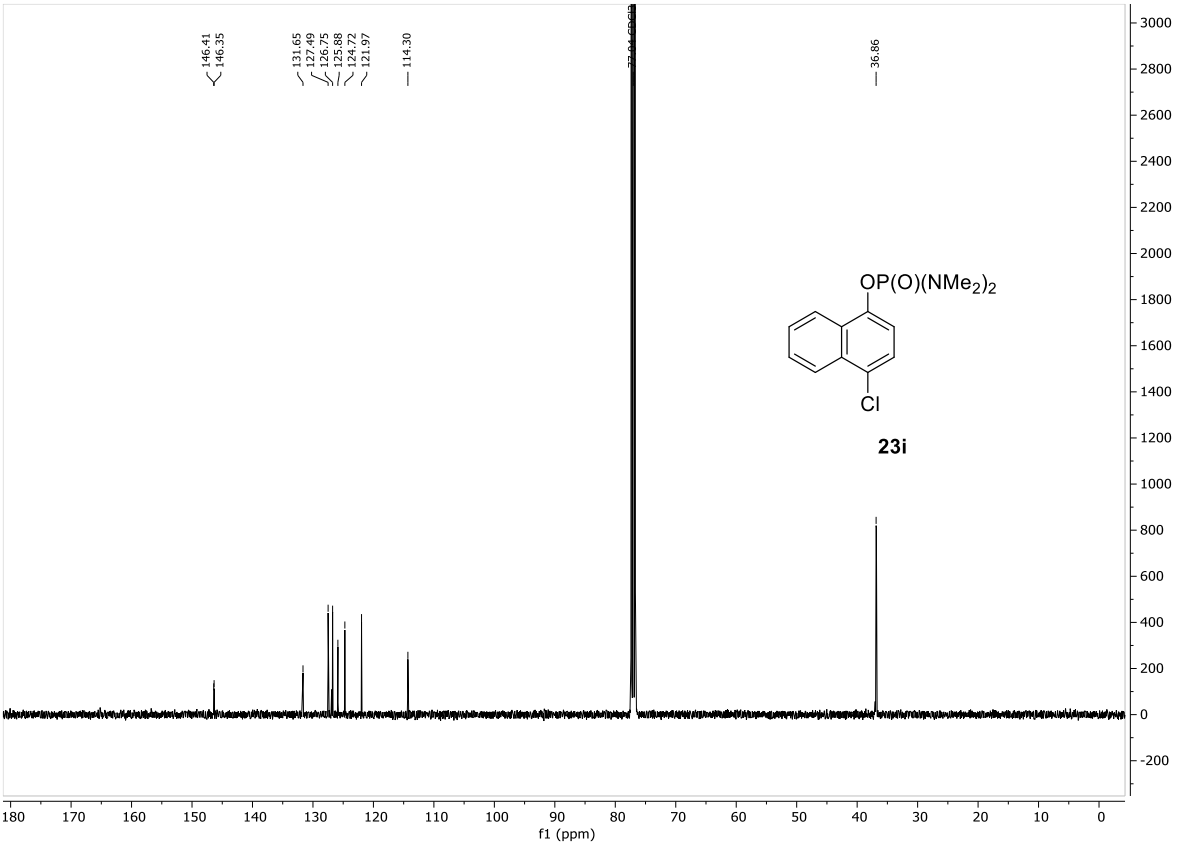

16.17
OP(O)(NMe2)2
Cl
23g
f1 (ppm)

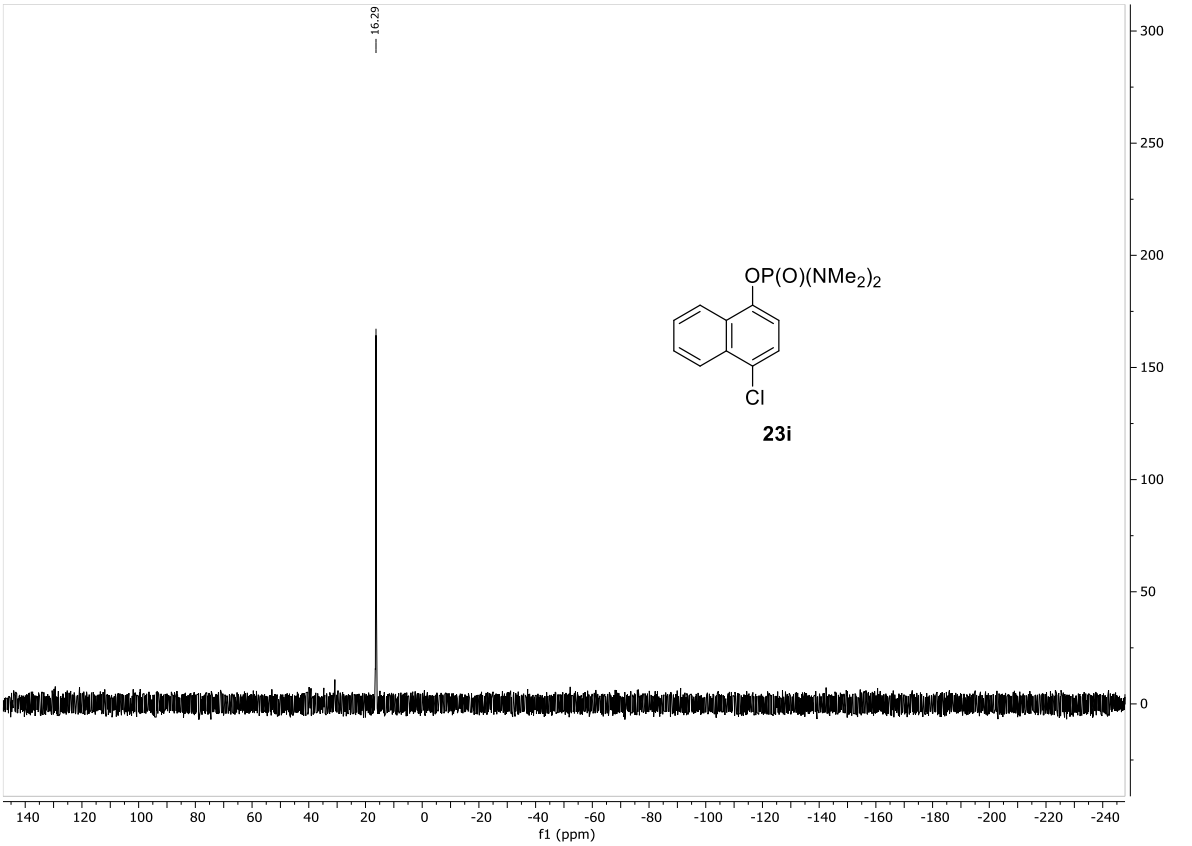

7.26 CDCl3
7.12
7.11
7.11
7.11
2.73
2.72
2.70
2.70
2.69
OP(O)(NMe2)2
Cl
Cl
23h
3.00
12.34
f1 (ppm)

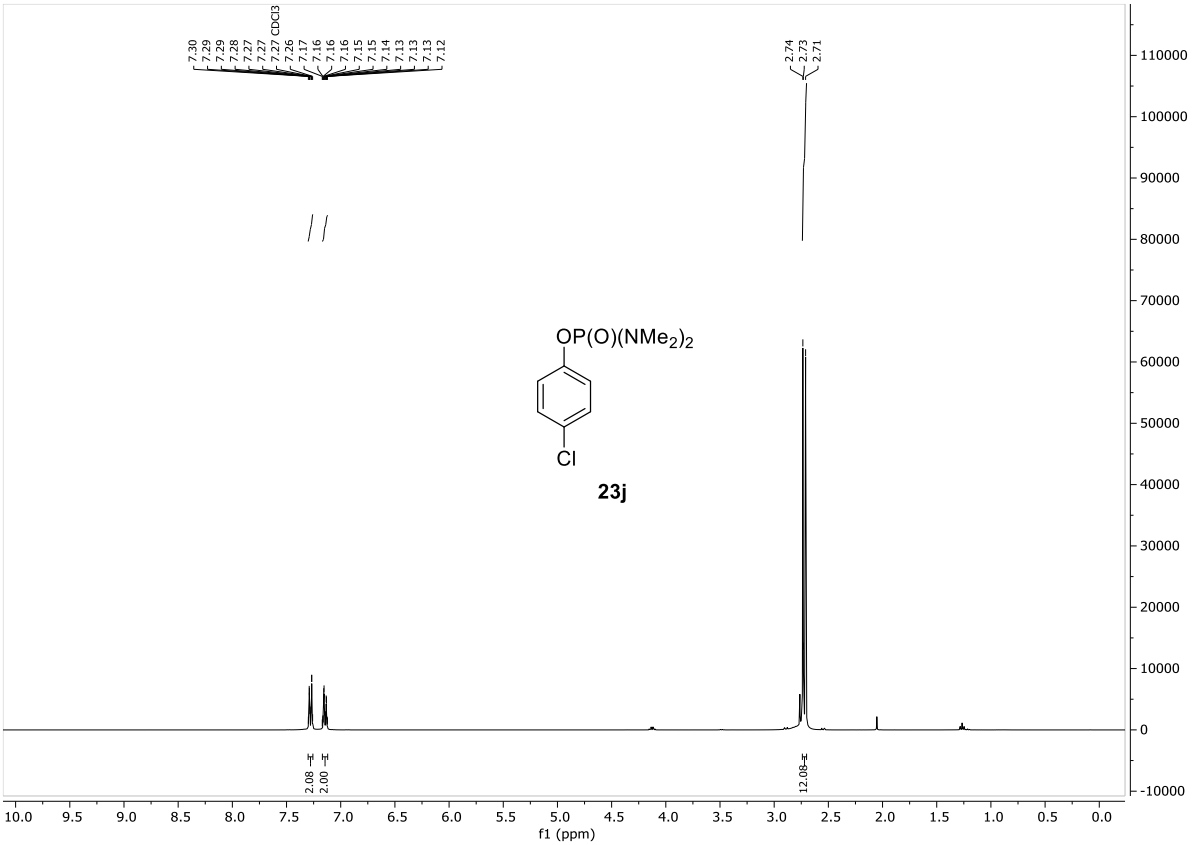

152.37
135.28
124.58
119.22
77.07 CDCl3
36.65
OP(O)(NMe2)2
Cl
Cl
23h
f1 (ppm)

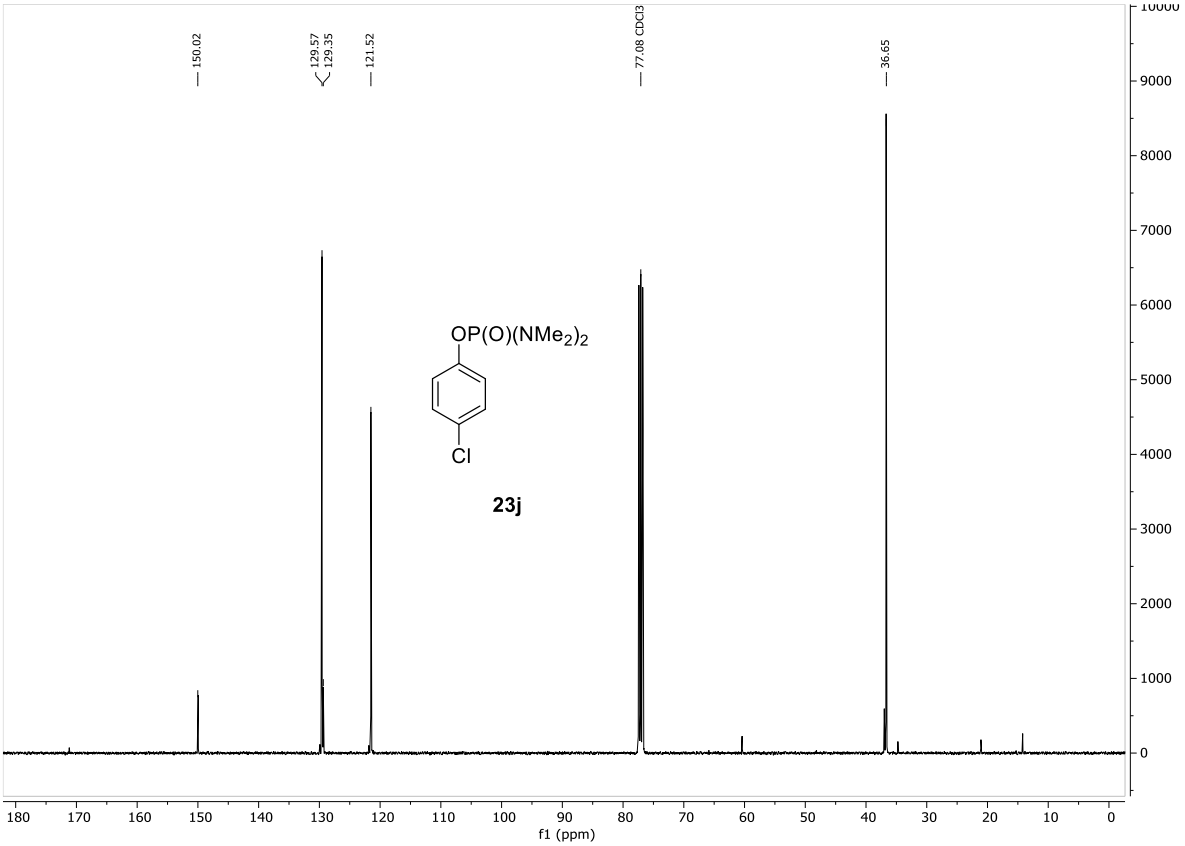

16.33
OP(O)(NMe2)2
Cl
Cl
23h
f1 (ppm)

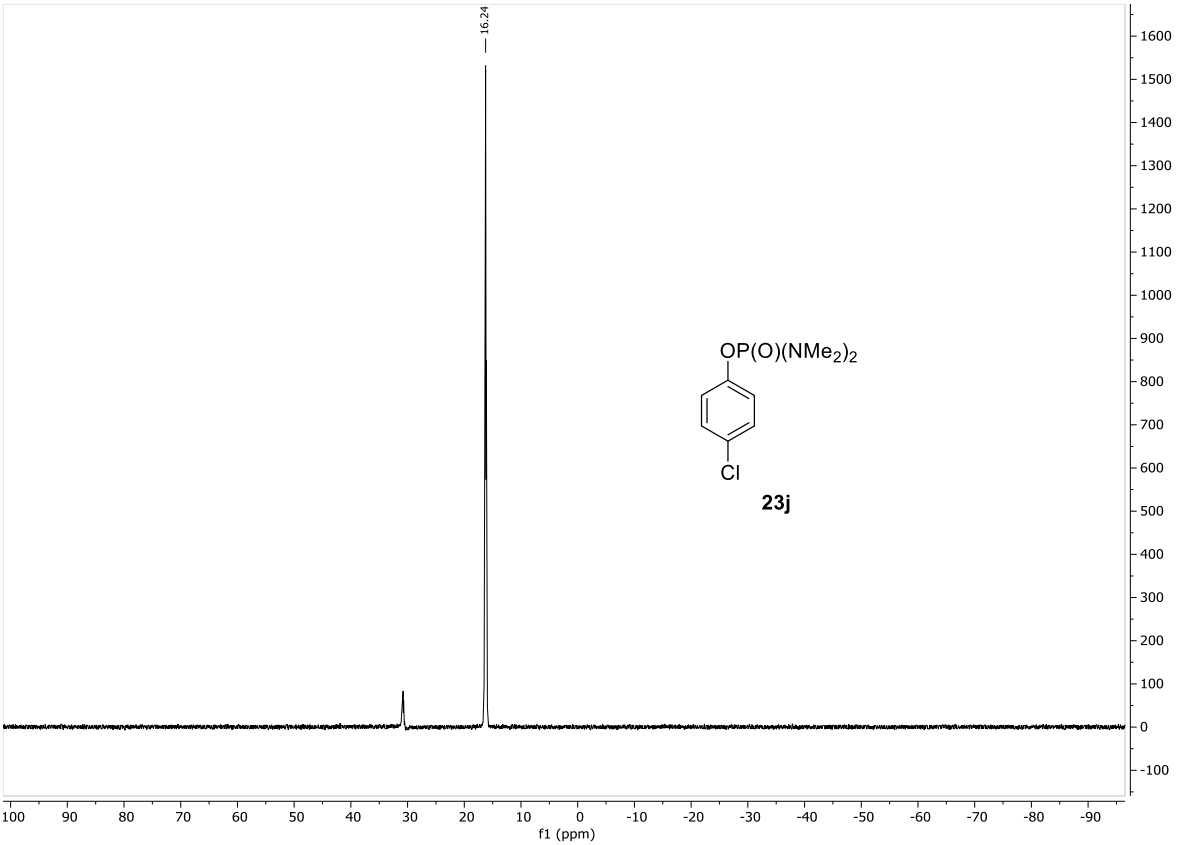

8.28
8.28
8.28
8.26
8.26
8.26
8.26
8.22
8.22
8.22
8.21
8.21
8.20
8.20
8.19
8.19
7.68
7.67
7.66
7.65
7.65
7.64
7.63
7.63
7.62
7.61
7.61
7.60
7.59
7.58
7.52
7.51
7.51
7.29
CDCl3
2.82
2.81
2.80
2.79
2.78
OP(O)(NMe2)2
Cl
23i
2.00
2.04
1.99
12.23
f1 (ppm)

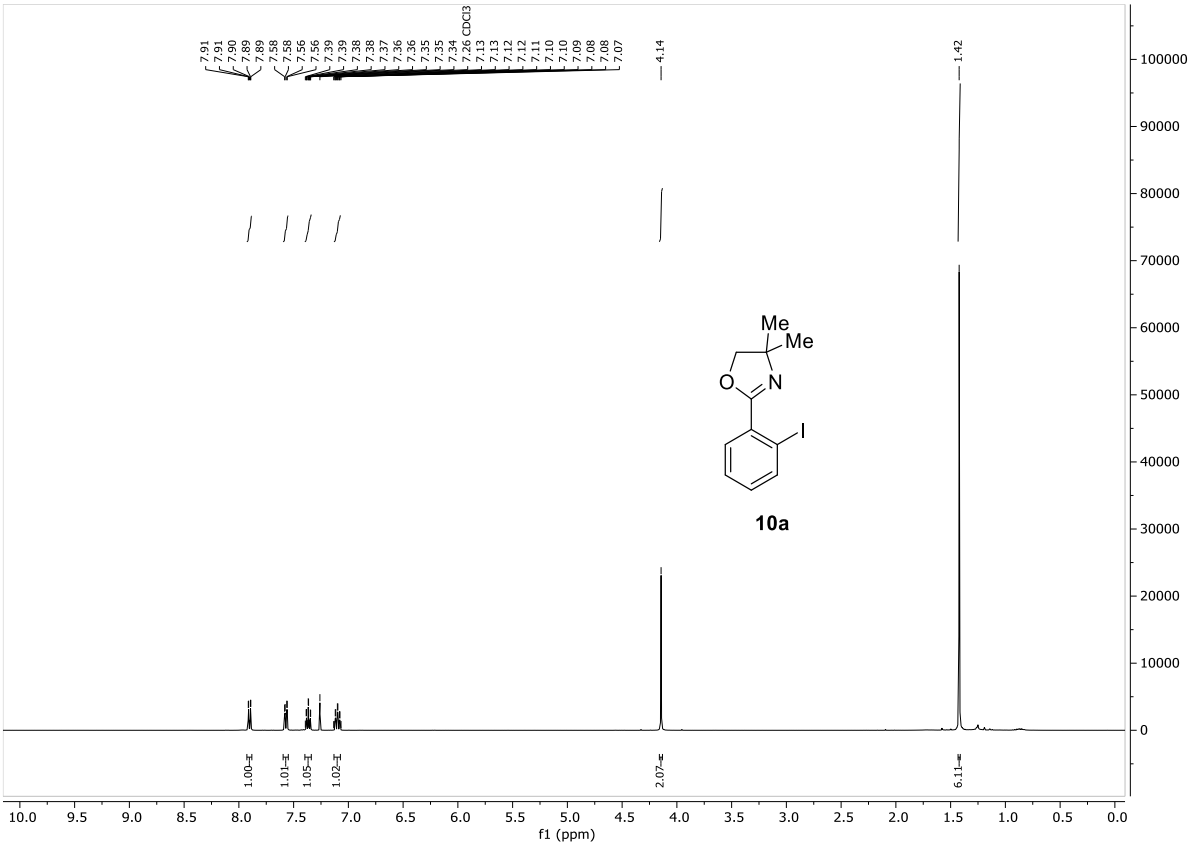

146.41
146.35
131.65
127.49
126.75
125.88
124.72
121.97
114.30
77.04 CDCl3
36.86
OP(O)(NMe2)2
Cl
23i
f1 (ppm)

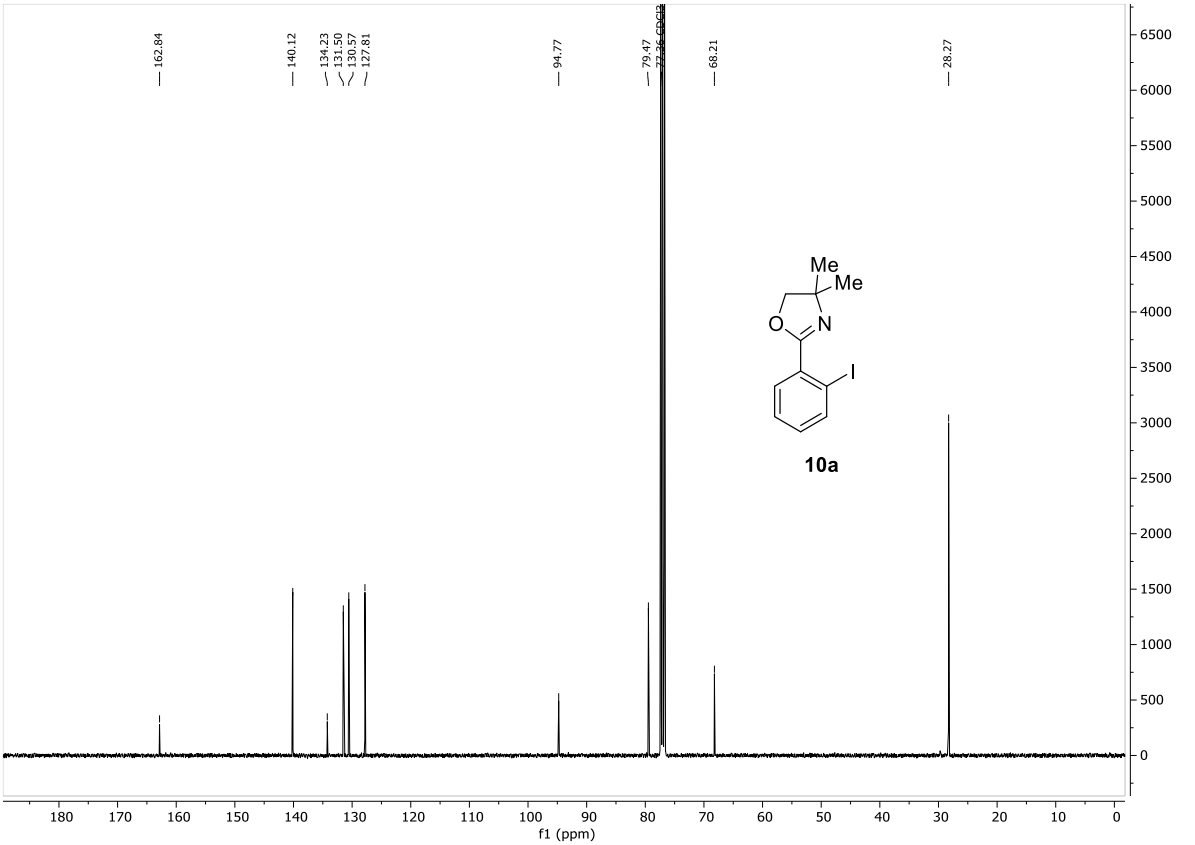

16.29
OP(O)(NMe2)2
Cl
23i
f1 (ppm)

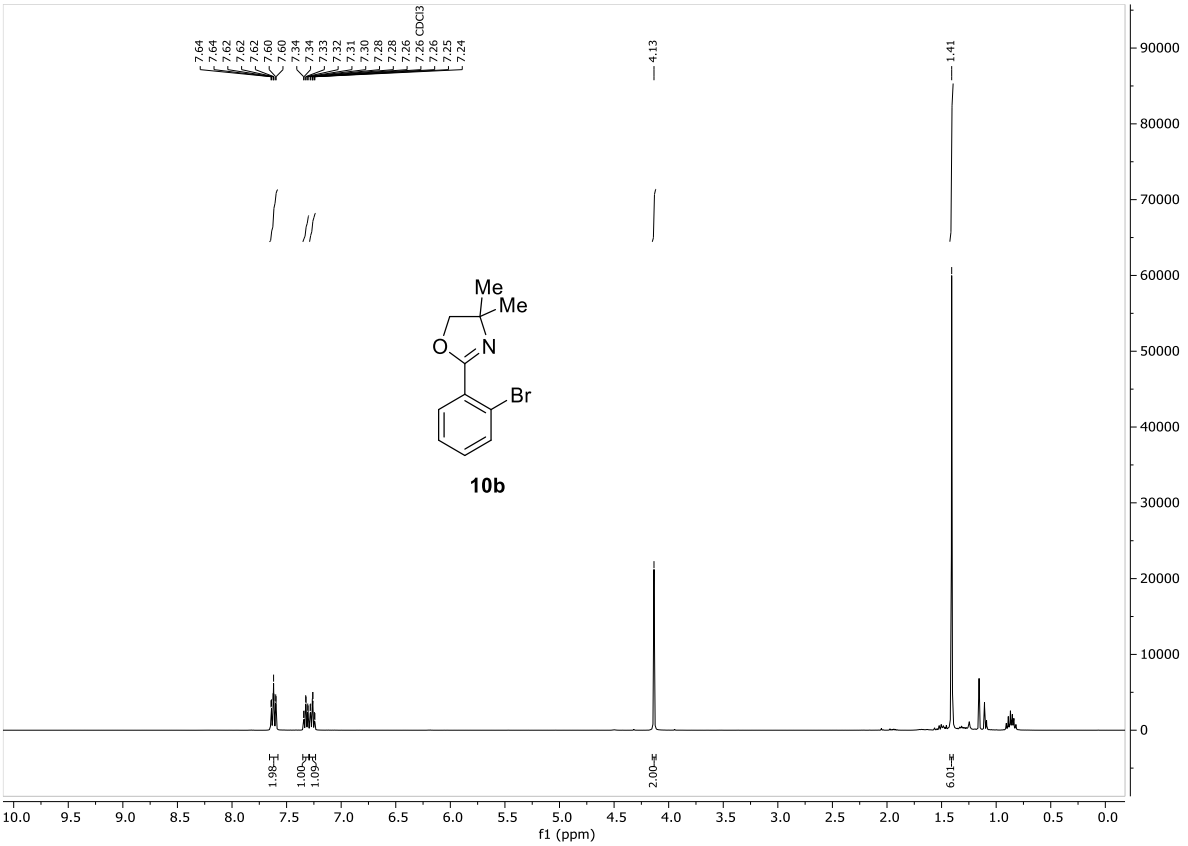

7.30
7.29
7.29
7.28
7.27
7.27
7.27 CDCl3
7.26
7.17
7.16
7.16
7.16
7.15
7.15
7.14
7.13
7.13
7.13
7.12
2.74
2.73
2.71
OP(O)(NMe2)2
Cl
23j
2.08
2.00
12.08
f1 (ppm)

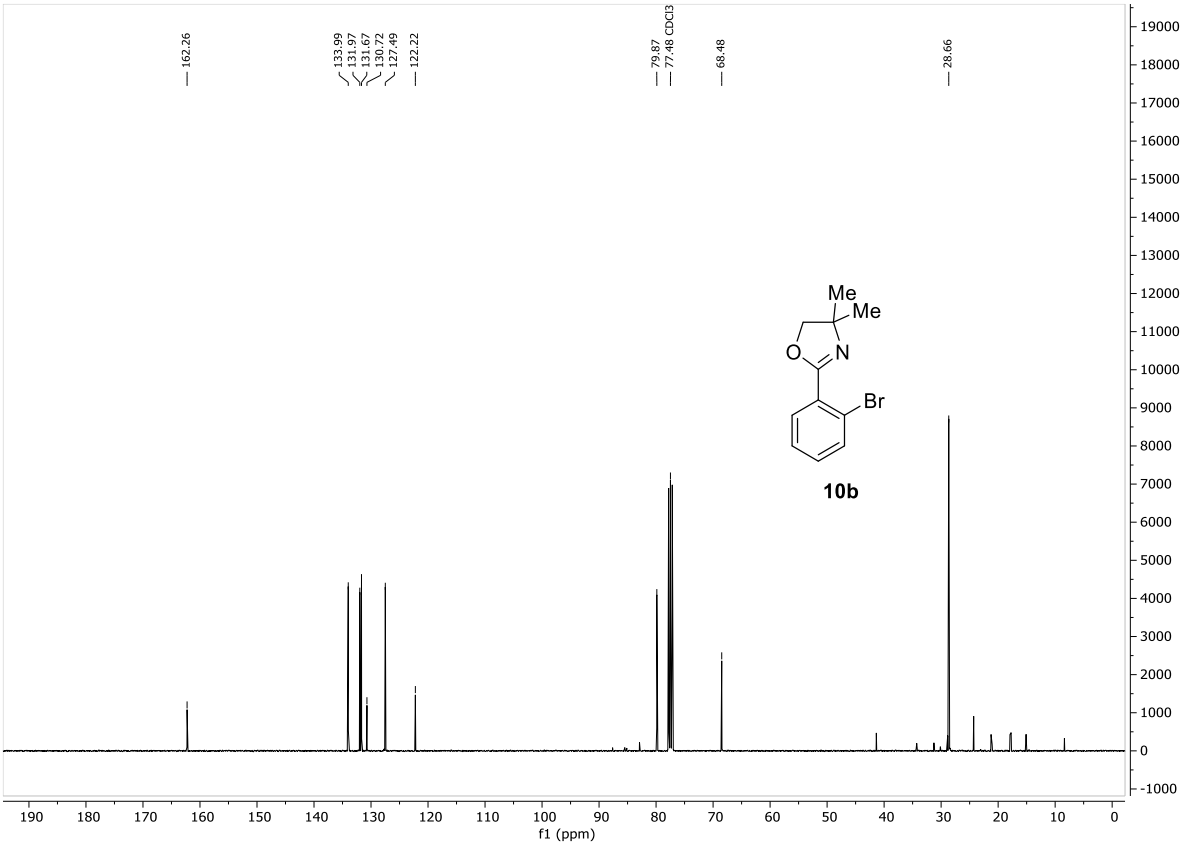

150.02
129.57
129.35
121.52
77.08 CDCl3
36.65
OP(O)(NMe2)2
Cl
23j
f1 (ppm)

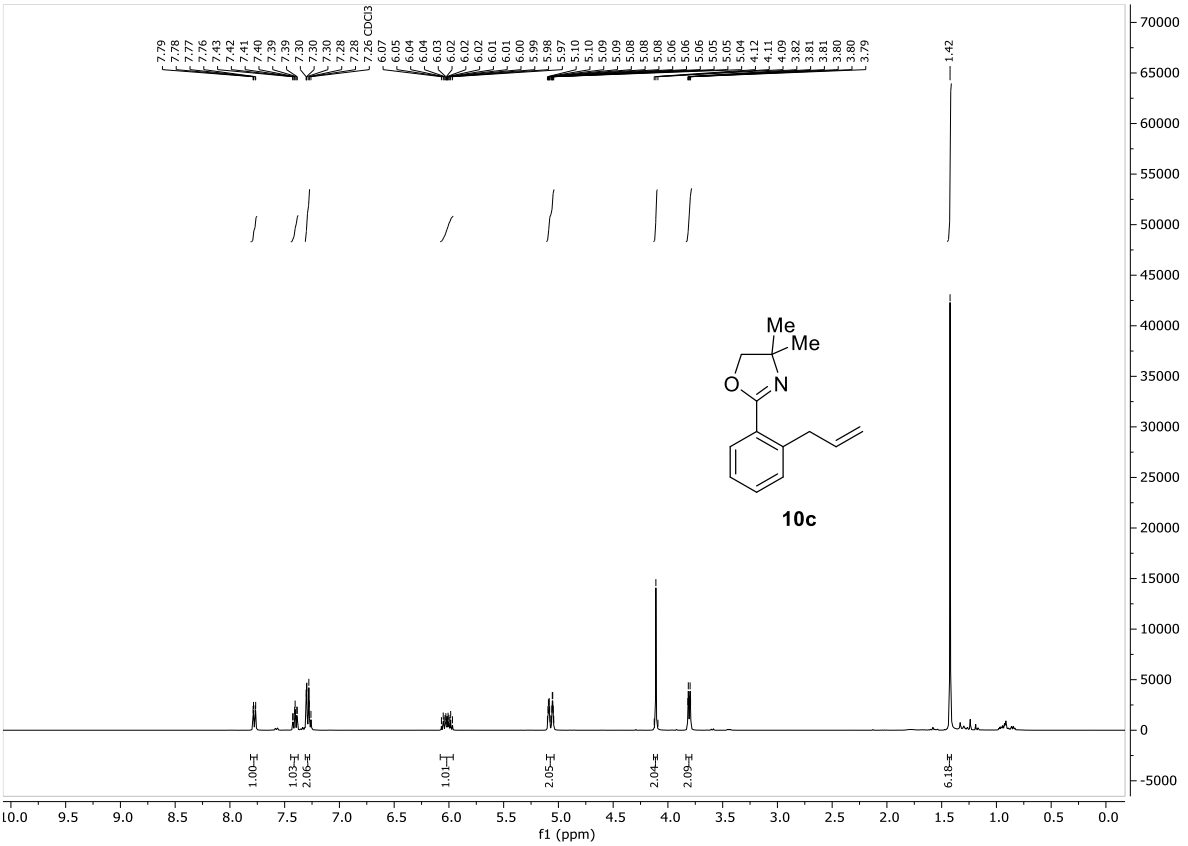

16.24
OP(O)(NMe2)2
Cl
23j
f1 (ppm)


7.91
7.91
7.90
7.89
7.89
7.58
7.58
7.56
7.56
7.39
7.39
7.38
7.38
7.37
7.36
7.36
7.35
7.35
7.34
CDCl3
7.26
7.13
7.13
7.12
7.12
7.11
7.10
7.10
7.09
7.08
7.08
7.07
4.14
1.42
1.00
1.01
1.05
1.02
2.07
6.11
Me
Me
O
N
I
10a
f1 (ppm)


162.84
140.12
134.23
131.50
130.57
127.81
94.77
79.47
77.36 CDCl3
68.21
28.27
Me
Me
O
N
I
10a
f1 (ppm)


7.64
7.64
7.62
7.62
7.62
7.60
7.60
7.34
7.34
7.33
7.32
7.31
7.30
7.28
7.28
7.26
7.26 CDCl3
7.26
7.25
7.24
4.13
1.41
Me
Me
O
N
Br
10b
1.98
1.00
1.09
2.00
6.01
f1 (ppm)


162.26
133.99
131.97
131.67
130.72
127.49
122.22
79.87
77.48 CDCl3
68.48
28.66
Me
Me
O
N
Br
10b
f1 (ppm)


7.79
7.78
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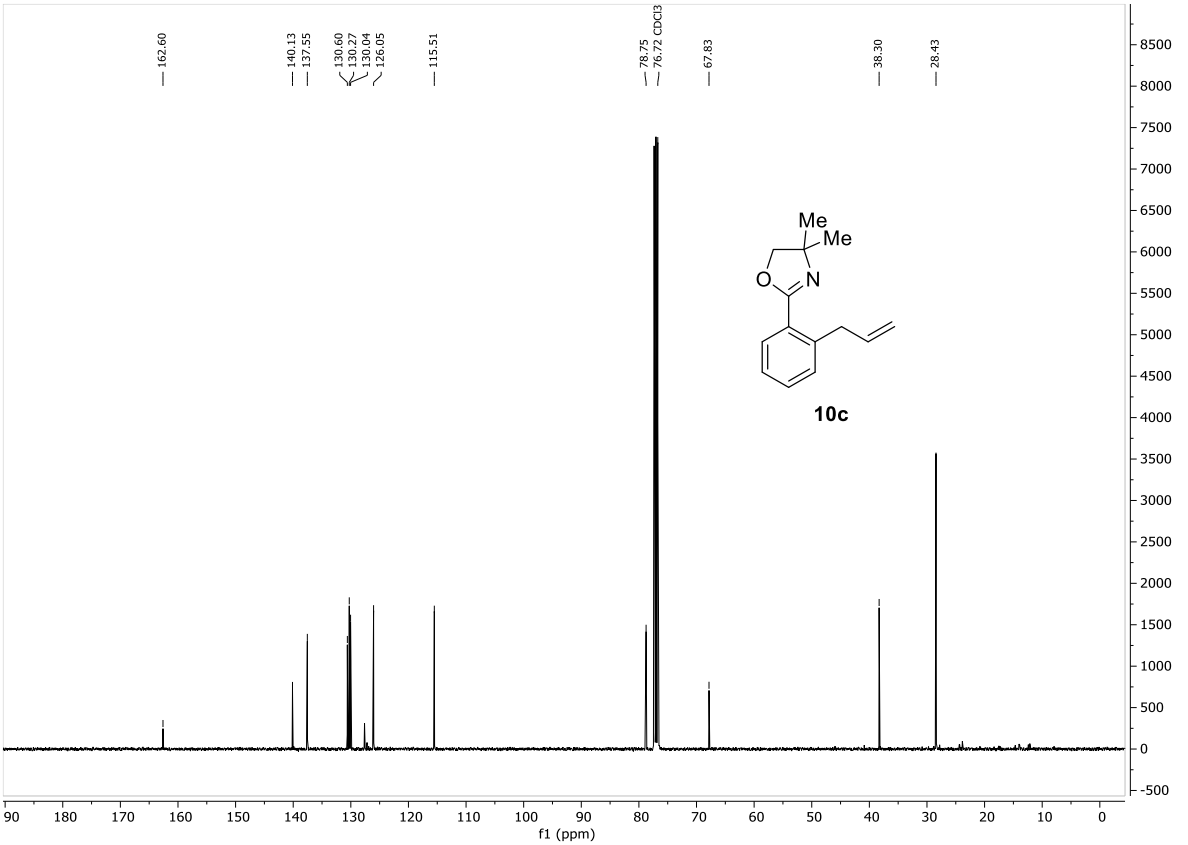
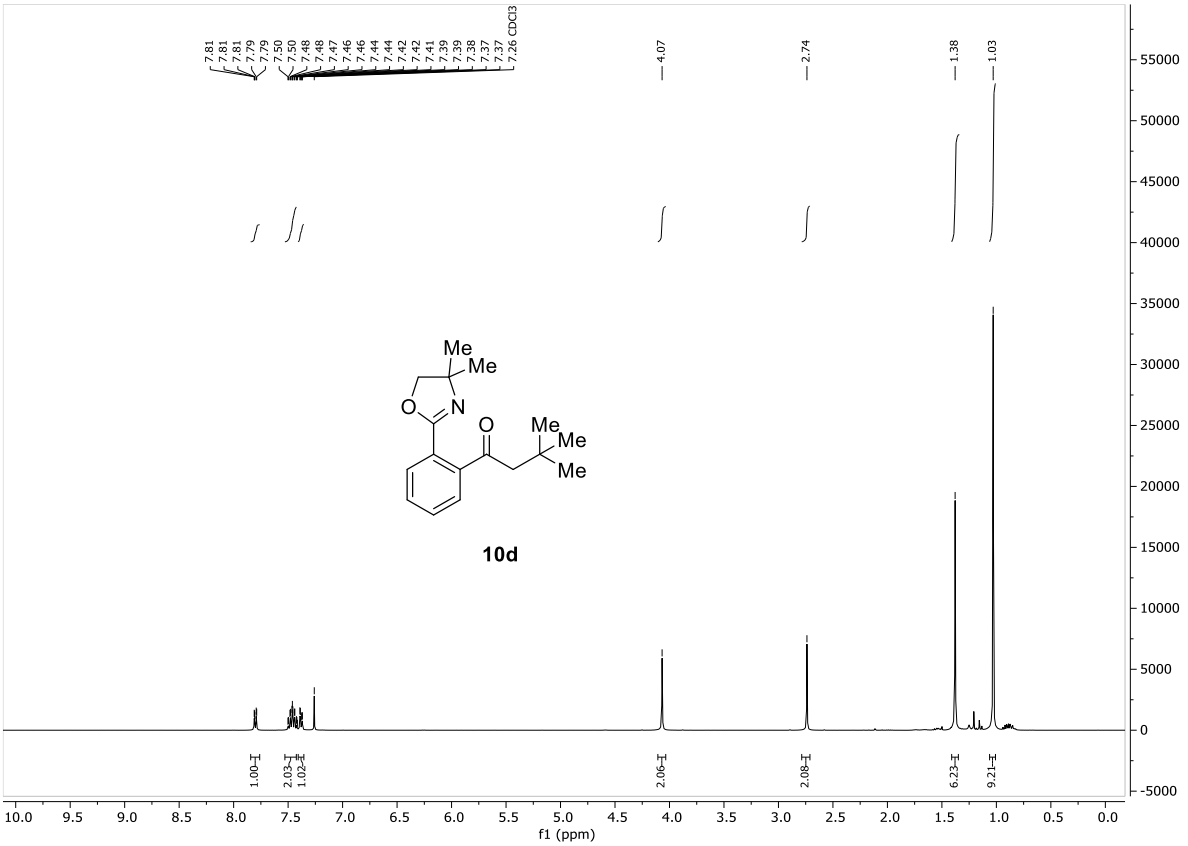
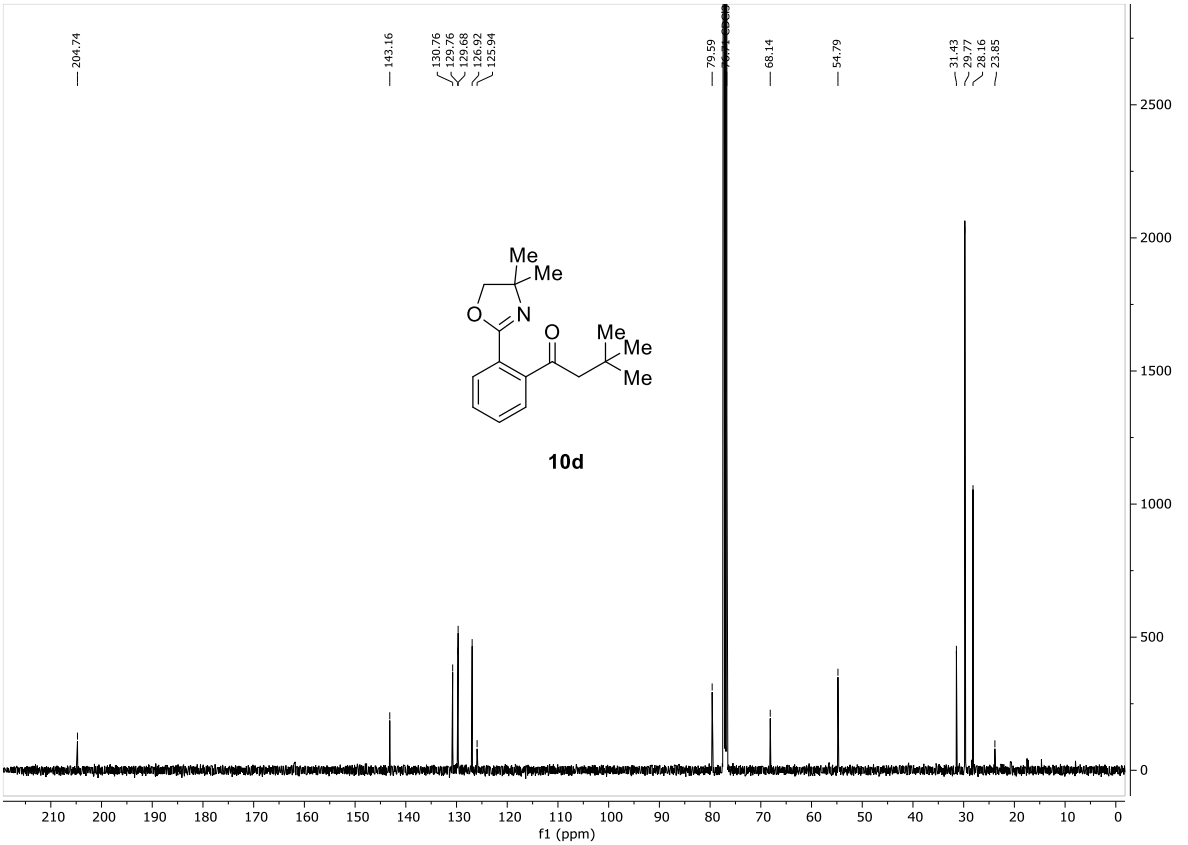
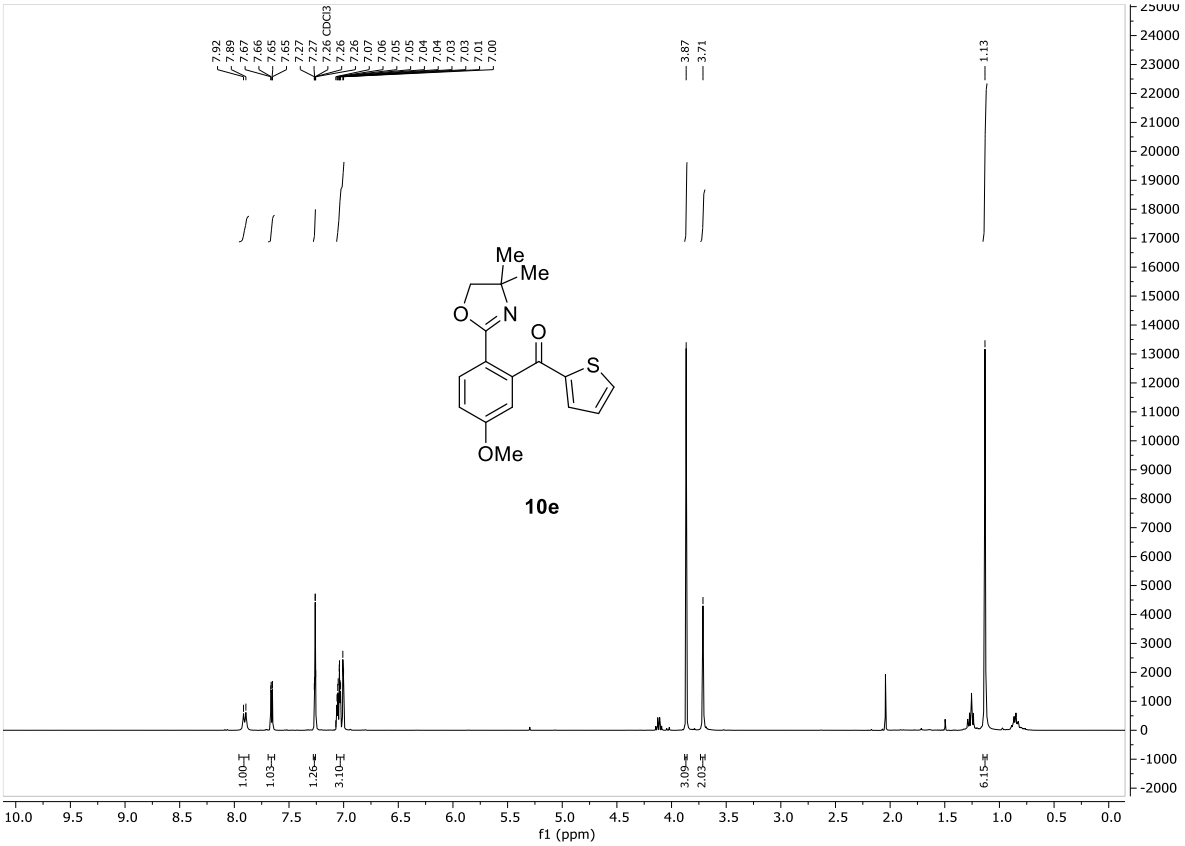
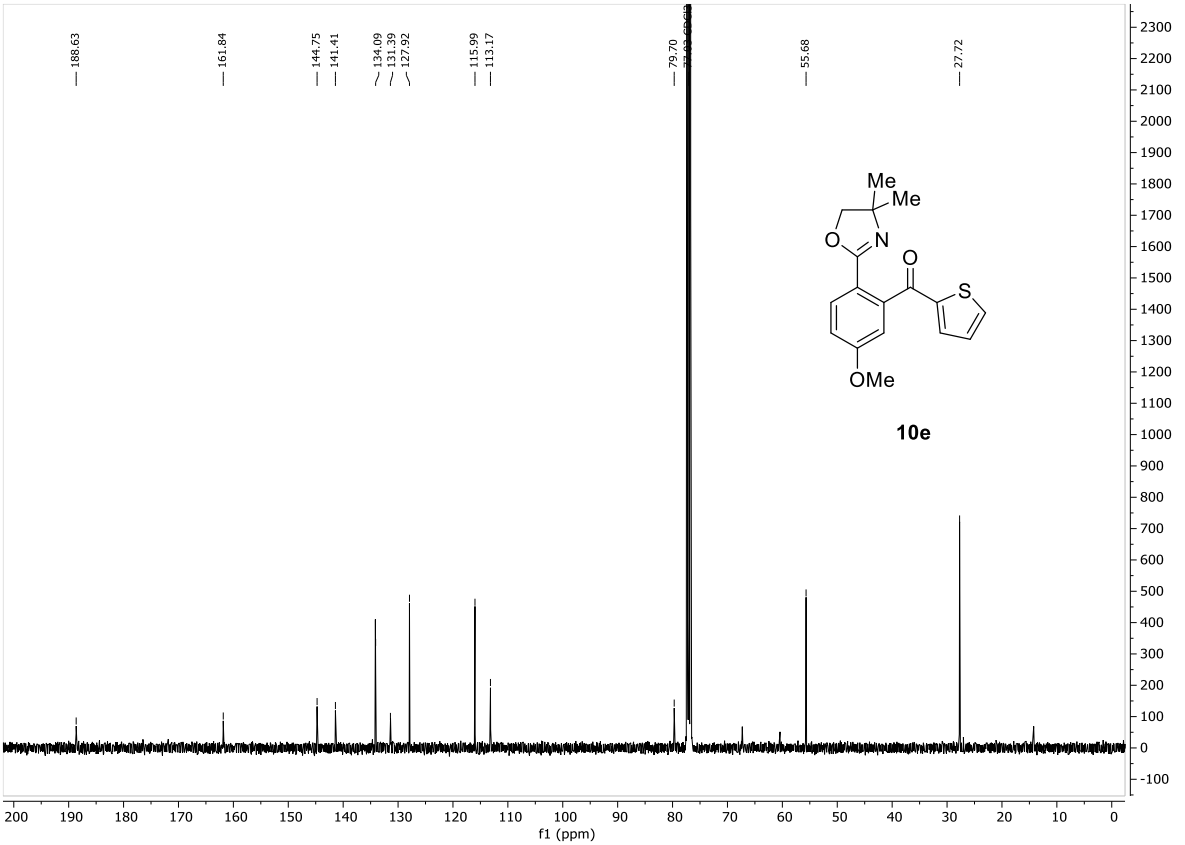
7.43
7.42
7.41
7.40
7.39
7.30
7.30
7.30
7.28
7.28
7.26 CDCl3
6.07
6.05
6.04
6.04
6.03
6.02
6.02
6.02
6.01
6.01
6.00
5.99
5.98
5.97
5.10
5.10
5.09
5.09
5.08
5.08
5.08
5.06
5.06
5.06
5.05
5.05
5.04
4.12
4.11
4.09
3.82
3.81
3.81
3.80
3.80
3.79
1.42
Me
Me
O
N
10c
1.00
1.03
2.06
1.01
2.05
2.04
2.09
6.18
f1 (ppm)

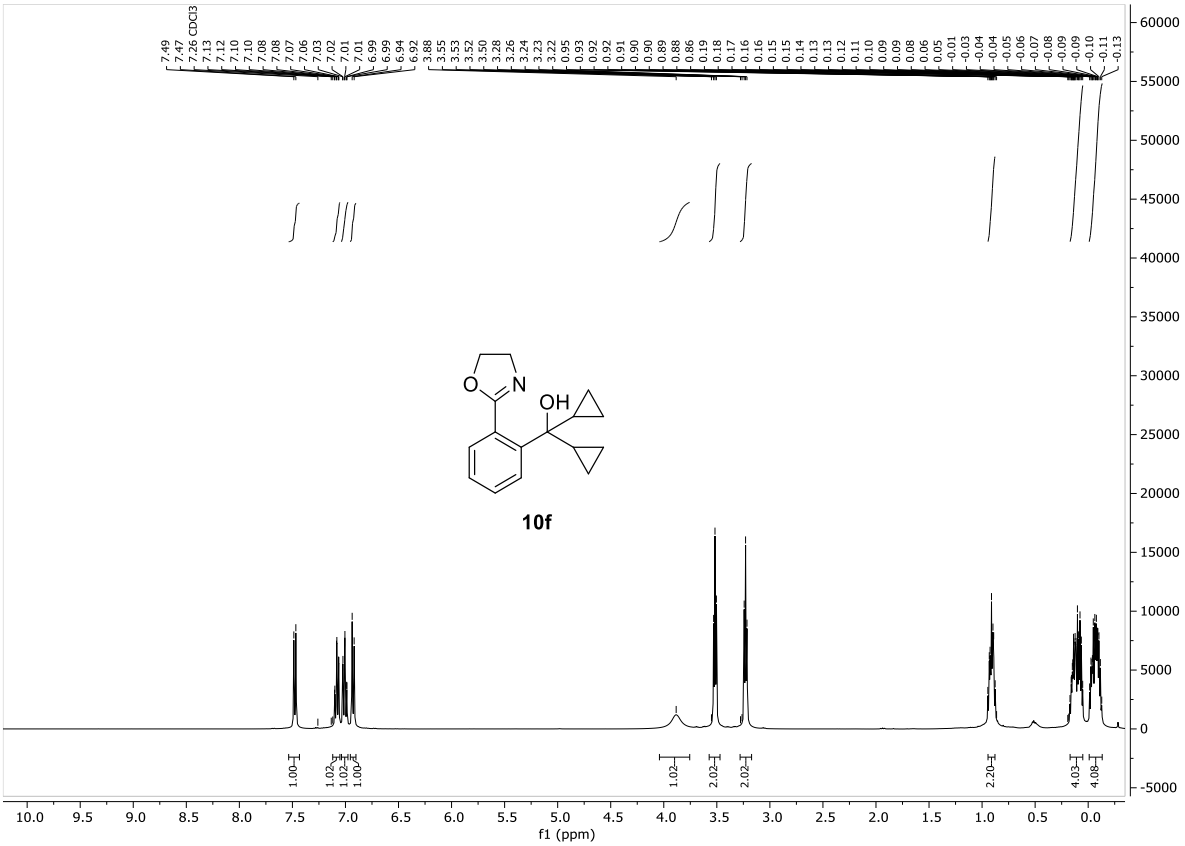

162.60
140.13
137.55
130.60
130.27
130.04
126.05
115.51
78.75
76.72 CDCl3
67.83
38.30
28.43
Me
Me
O
N
10c
f1 (ppm)

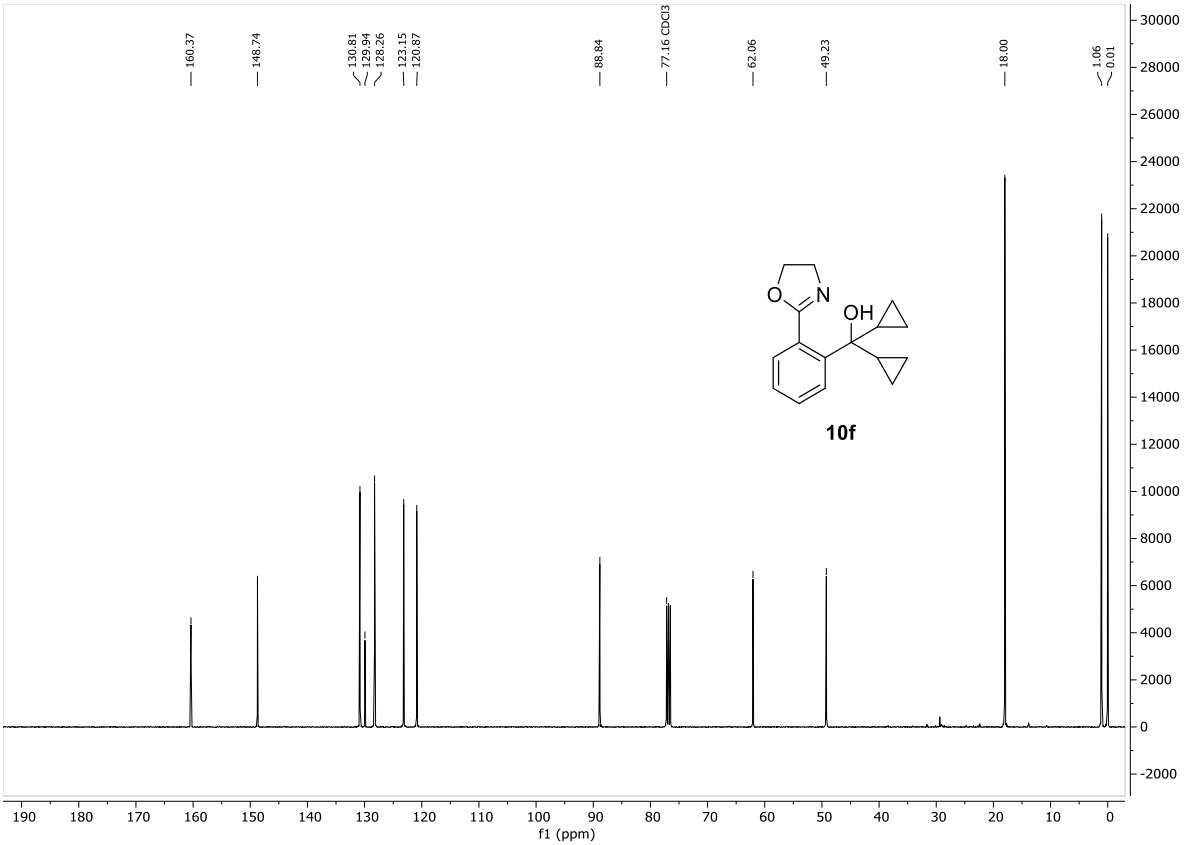

7.81
7.81
7.81
7.79
7.79
7.50
7.50
7.48
7.48
7.47
7.46
7.46
7.46
7.44
7.44
7.42
7.42
7.41
7.39
7.39
7.38
7.37
7.37
7.26 CDCl3
4.07
2.74
1.38
1.03
Me
Me
O
N
O
Me
Me
Me
10d
1.00
2.03
1.02
2.06
2.08
6.23
9.21
f1 (ppm)


204.74
143.16
130.76
129.76
129.68
126.92
125.94
79.59
68.14
54.79
31.43
29.77
28.16
23.85
Me
Me
O
N
O
Me
Me
Me
10d
f1 (ppm)


7.92
7.89
7.67
7.66
7.65
7.27
CDCl3
7.26
7.07
7.06
7.05
7.04
7.03
7.01
7.00
3.87
3.71
1.13
Me
Me
O
N
O
S
OMe
10e
1.00
1.03
1.26
3.10
3.09
2.03
6.15
f1 (ppm)


188.63
161.84
144.75
141.41
134.09
131.39
127.92
115.99
113.17
79.70
55.68
27.72
Me
Me
O
N
O
S
OMe
10e
f1 (ppm)


7.49
7.47
7.26 CDCl3
7.13
7.12
7.10
7.10
7.08
7.08
7.07
7.06
7.03
7.02
7.01
7.01
6.99
6.99
6.94
6.92
3.88
3.55
3.53
3.52
3.50
3.28
3.26
3.24
3.23
3.22
3.05
0.93
0.92
0.92
0.91
0.90
0.90
0.89
0.88
0.86
0.19
0.18
0.17
0.16
0.16
0.15
0.15
0.14
0.13
0.13
0.12
0.11
0.10
0.09
0.09
0.08
0.06
0.05
-0.01
-0.03
-0.04
-0.04
-0.05
-0.06
-0.07
-0.08
-0.09
-0.09
-0.10
-0.11
-0.13
O
N
OH
10f
1.00
1.02
1.02
1.00
1.02
2.02
2.02
2.20
4.03
4.08
f1 (ppm)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129.94
128.26
123.15
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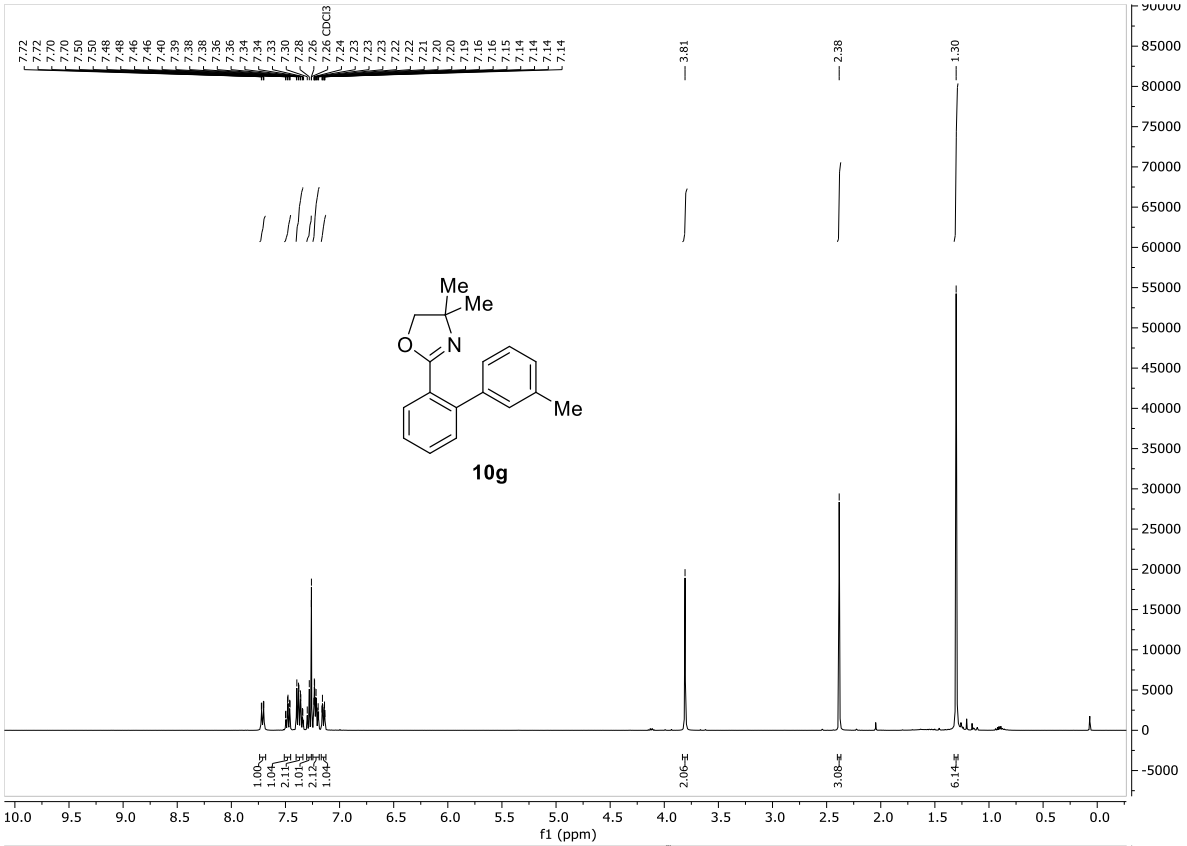
62.06
49.23
18.00
1.06
0.01
O
N
OH
10f
f1 (ppm)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Me
O
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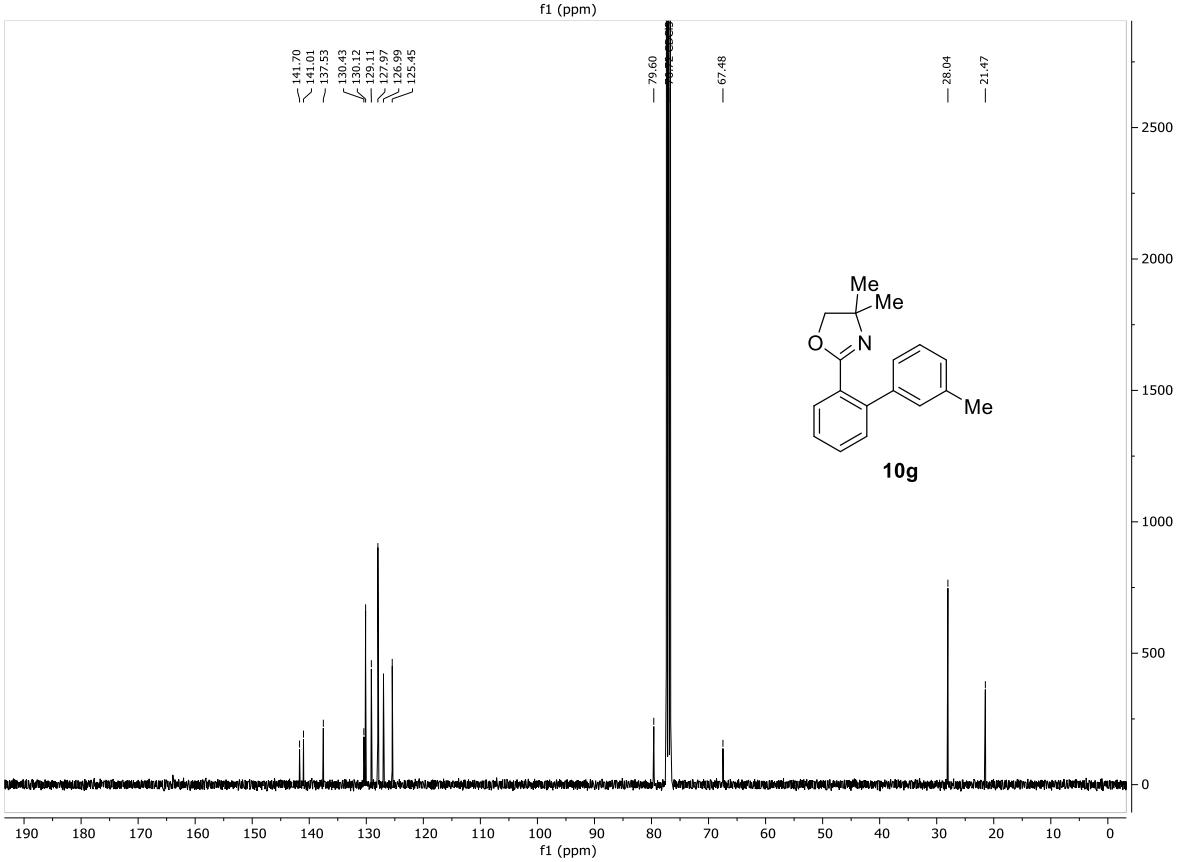
Me
10g
f1 (ppm)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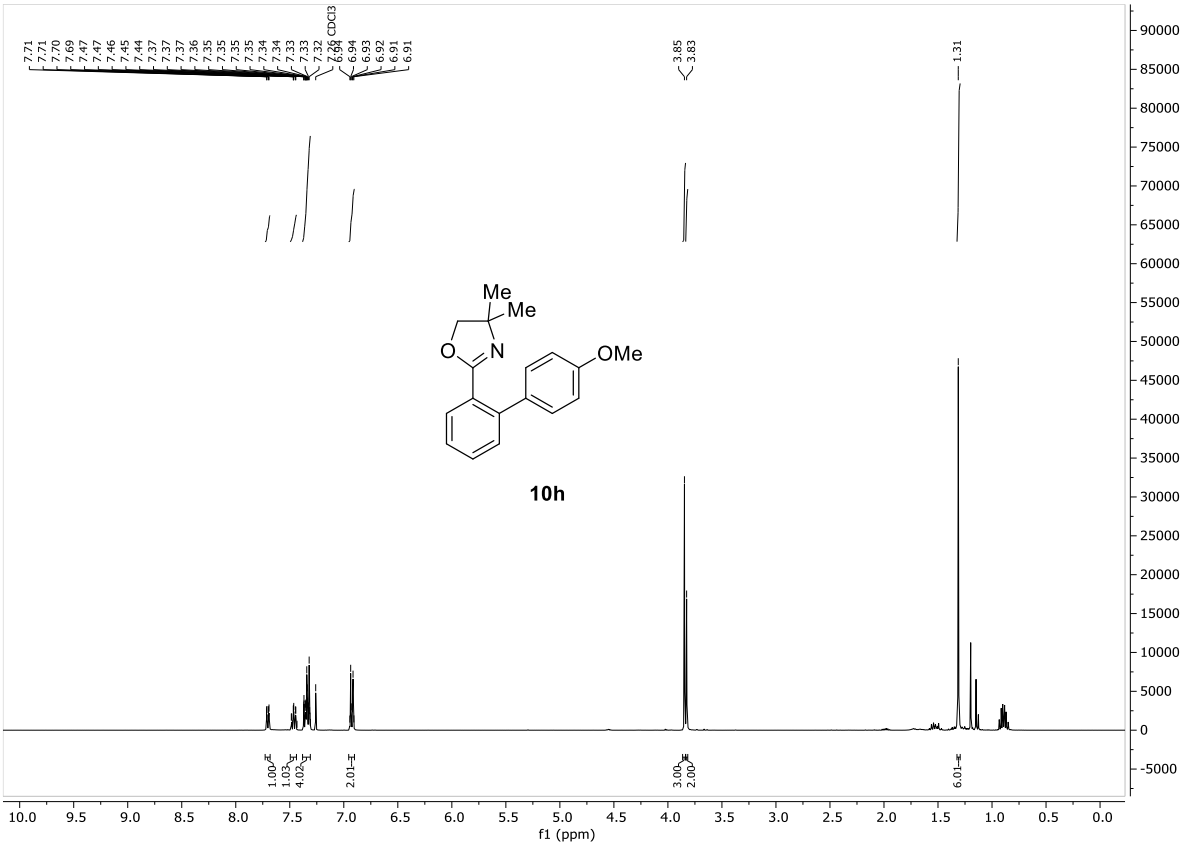
79.60
67.48
28.04
21.47
Me
Me
O
N
Me
10g
f1 (ppm)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7.37
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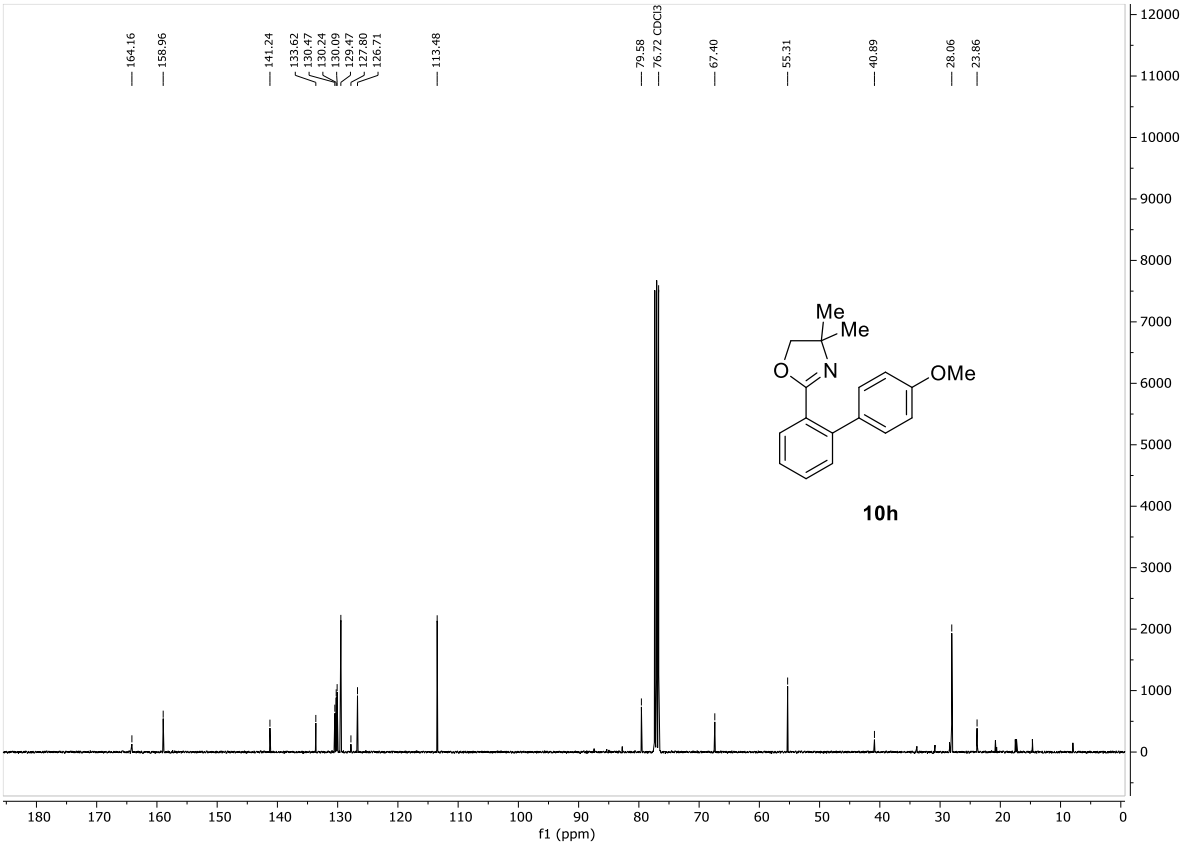
7.35
7.35
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.26 CDCl3
6.94
6.93
6.92
6.91
6.91
3.85
3.83
1.31
Me
Me
O
N
OMe
10h
1.00
1.03
4.02
2.01
3.00
2.00
6.01
f1 (ppm)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129.47
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113.48
79.58
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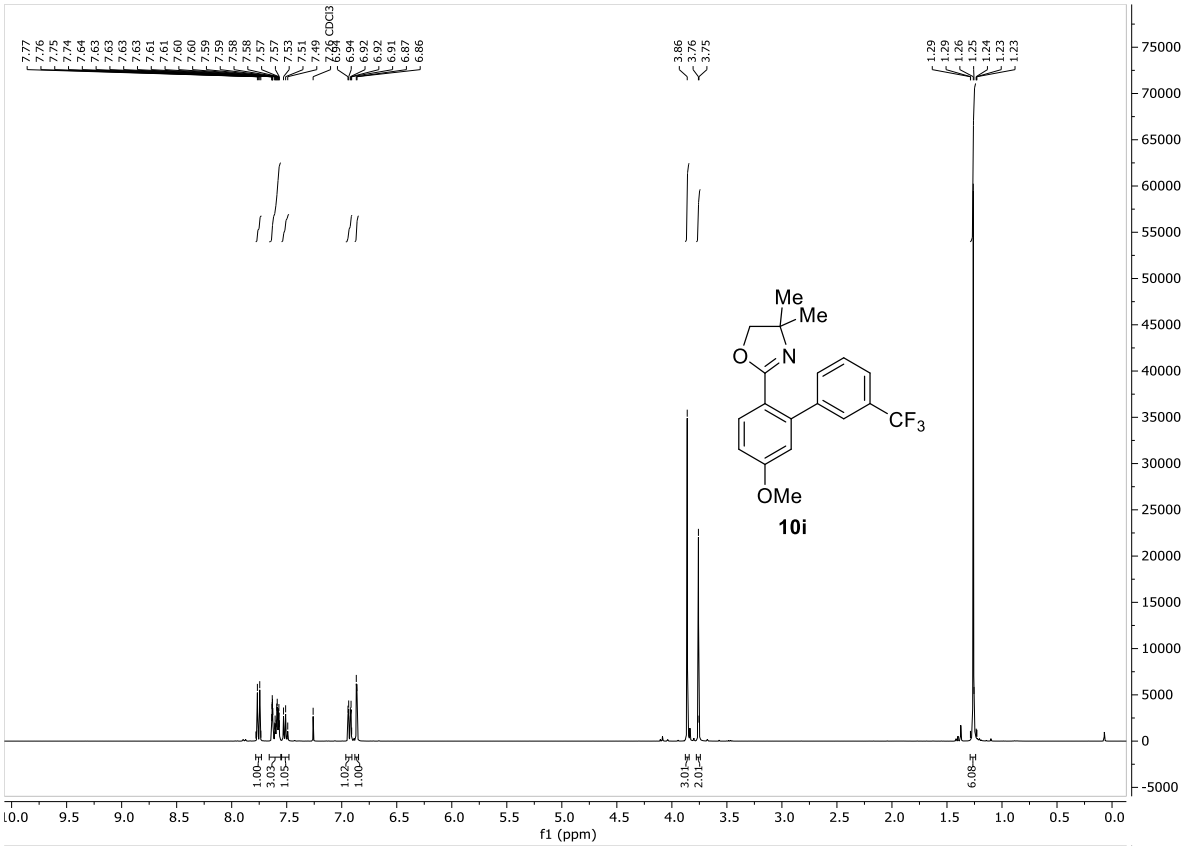
55.31
40.89
28.06
23.86
Me
Me
O
N
OMe
10h
f1 (ppm)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7.59
7.58
7.58
7.57
7.57
7.53
7.51
7.49
CDCl3
6.94
6.94
6.92
6.92
6.91
6.87
6.86
3.86
3.76
3.75
1.29
1.29
1.26
1.25
1.24
1.23
1.23
Me
Me
O
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CF3
OMe
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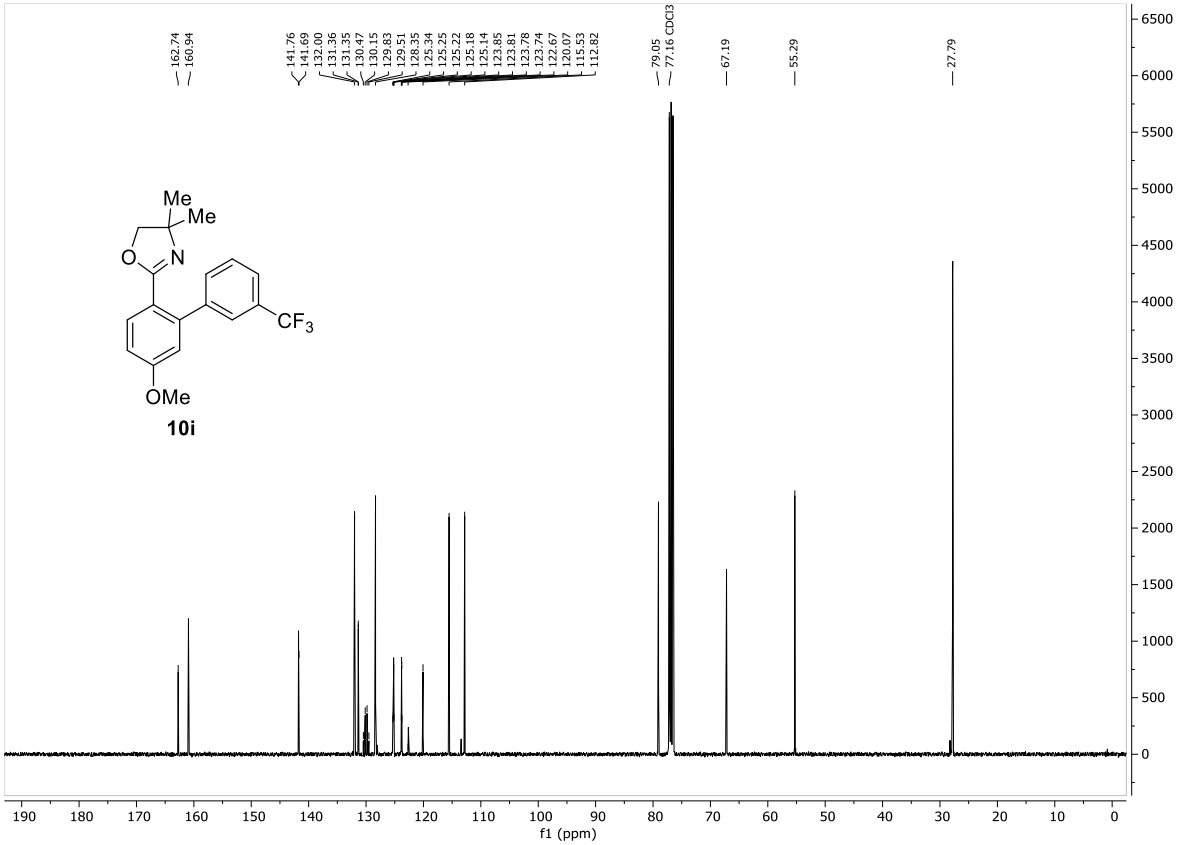
1.00
3.03
1.05
1.02
1.00
3.01
2.01
6.08
f1 (ppm)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125.22
125.18
125.14
123.85
123.81
123.78
123.74
122.67
120.07
115.53
112.82
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CDCl3
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27.79
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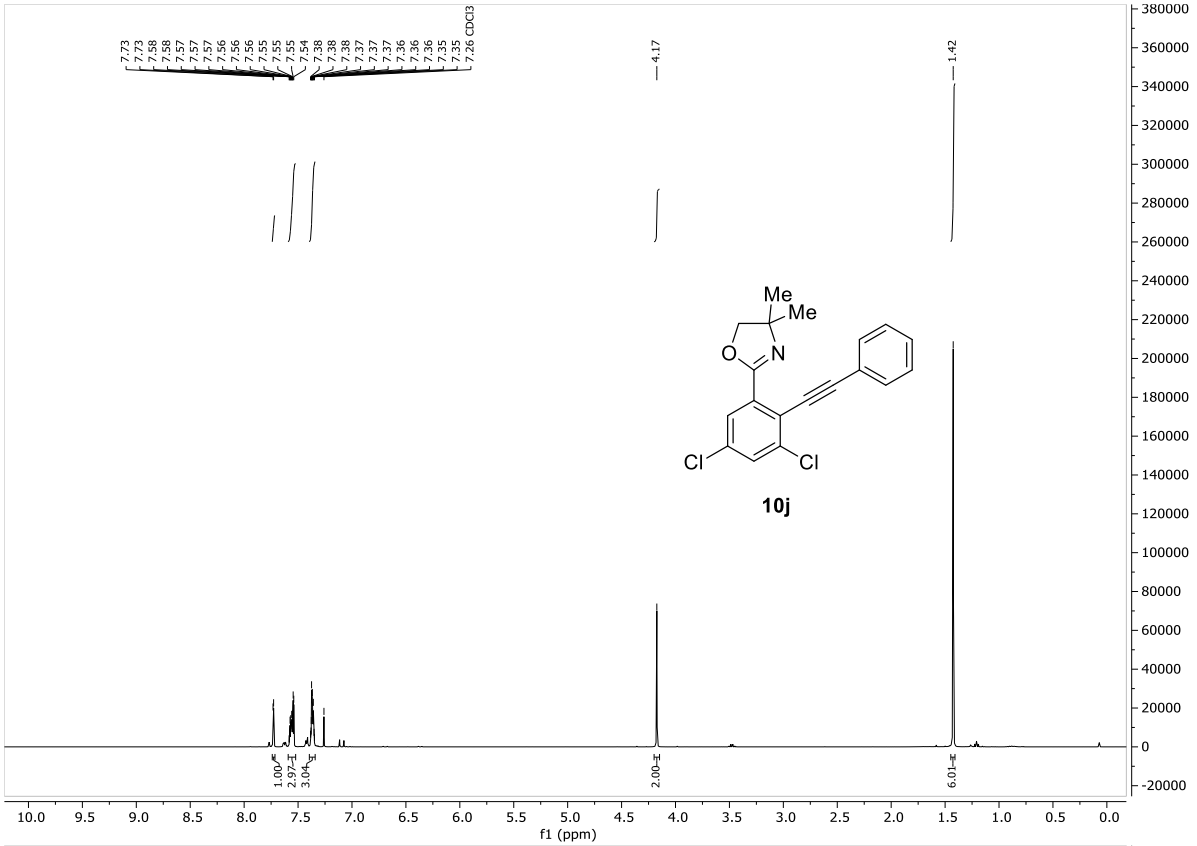
Me
O
N
CF3
OMe
10i
f1 (ppm)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7.54
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7.38
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7.37
7.37
7.37
7.36
7.36
7.36
7.35
7.35
7.26 CDCl3
4.17
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O
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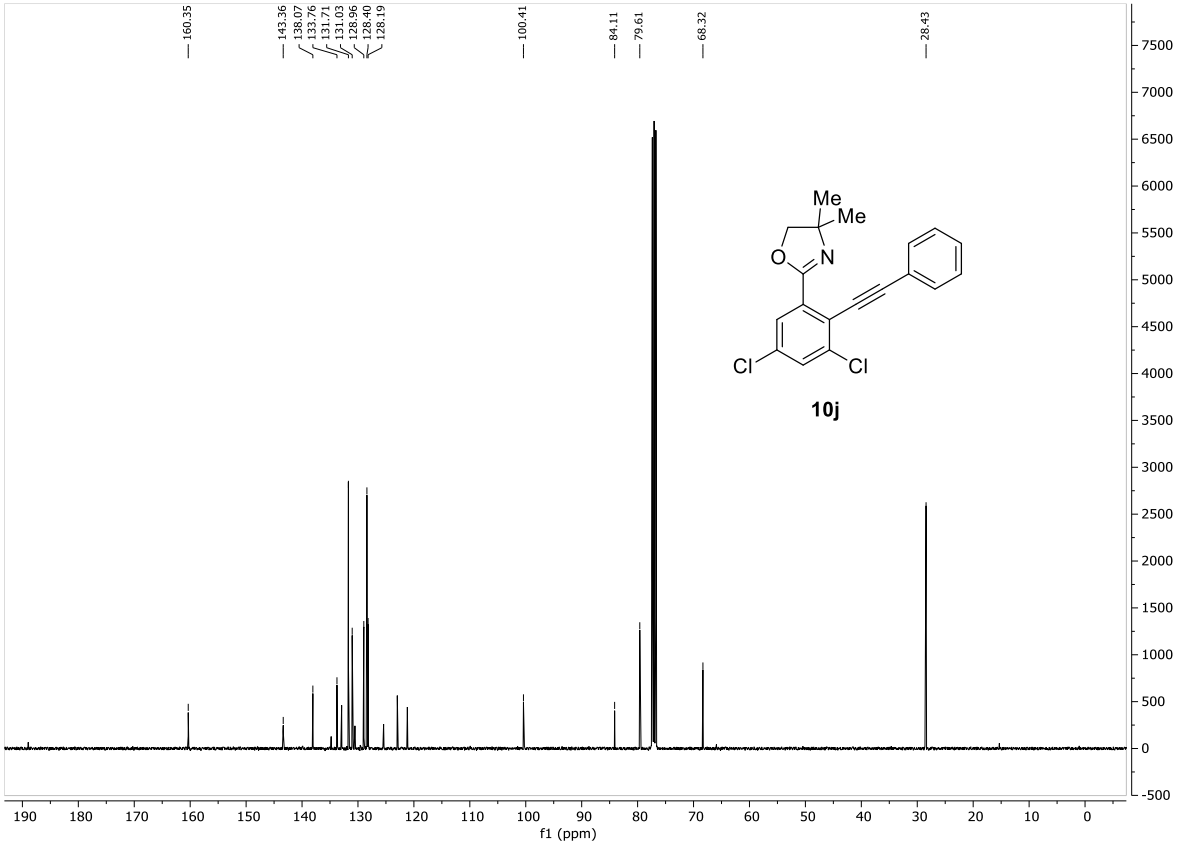
Cl
Cl
10j
1.00
2.97
3.04
2.00
6.01
f1 (ppm)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131.03
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128.40
128.19
100.41
84.11
79.61
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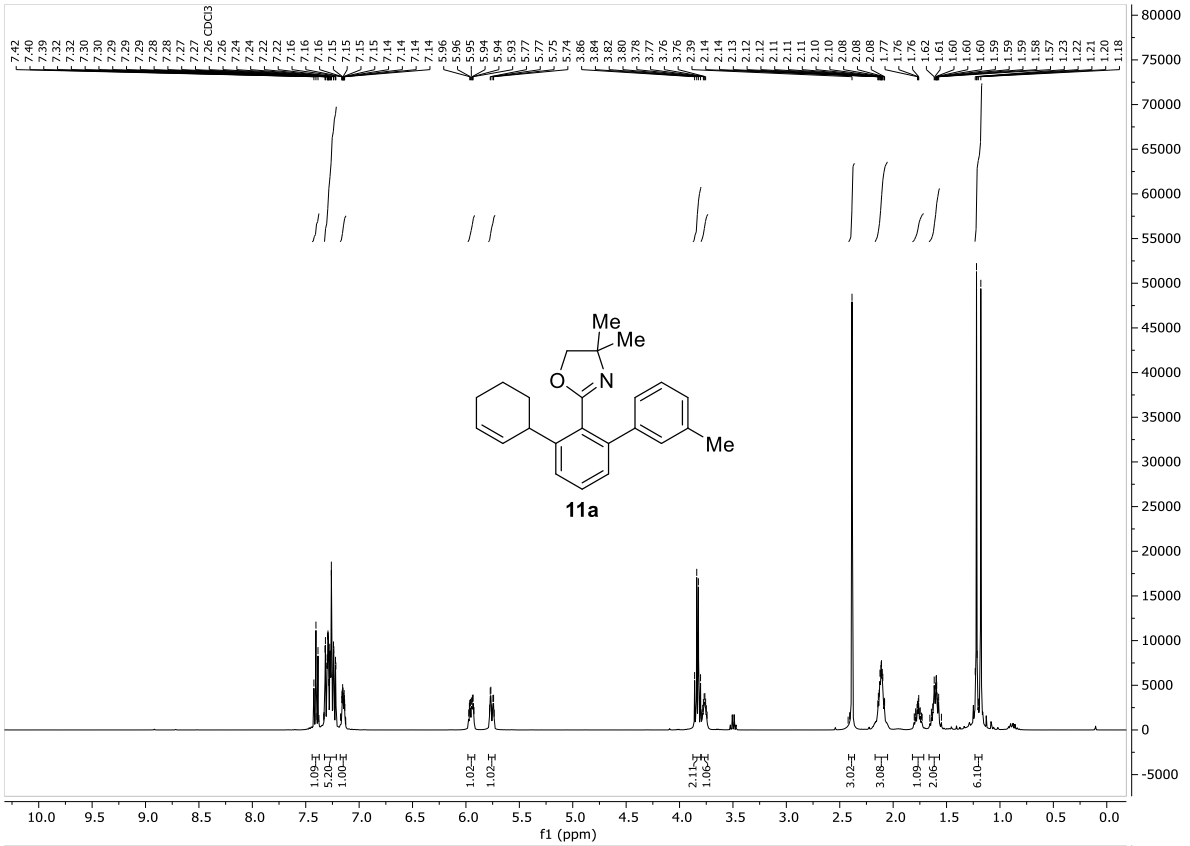
Me
Me
O
N
Cl
Cl
10j
f1 (ppm)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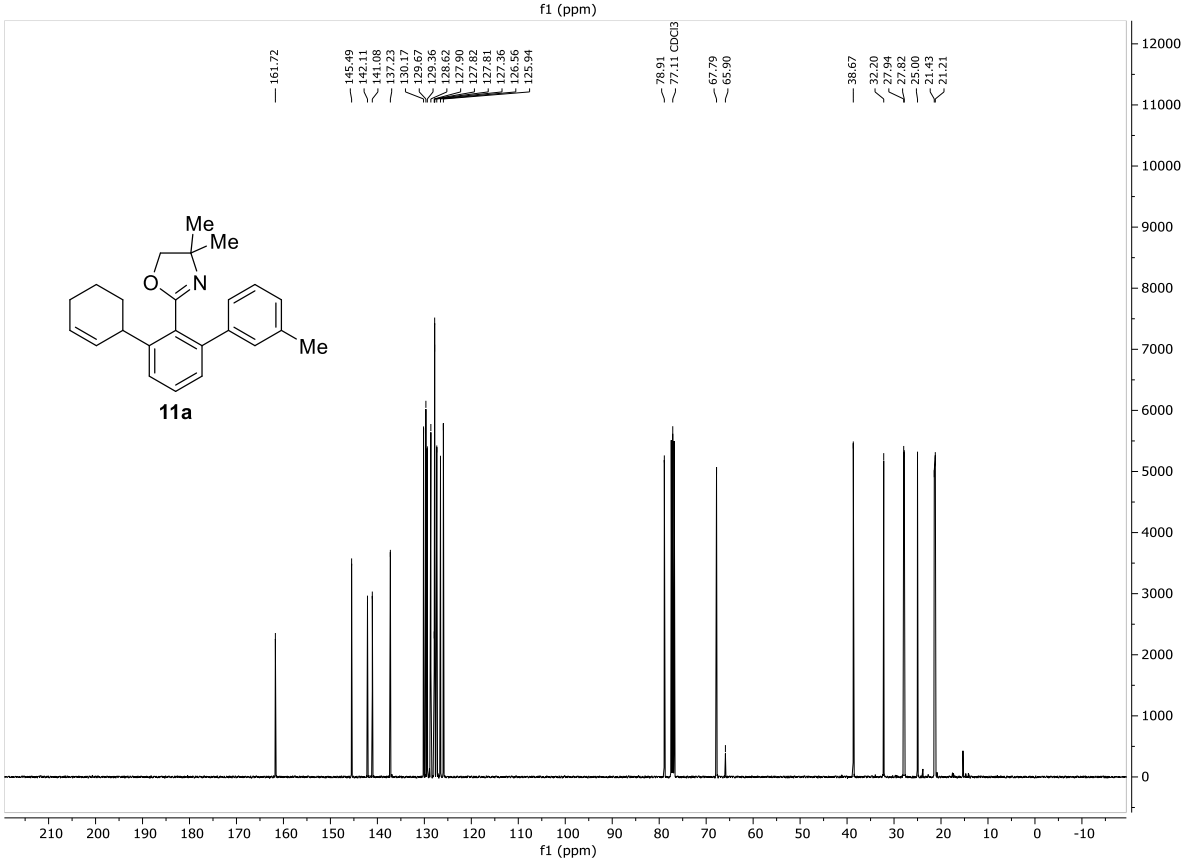
Me
O
N
Me
11a
f1 (ppm)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Me
O
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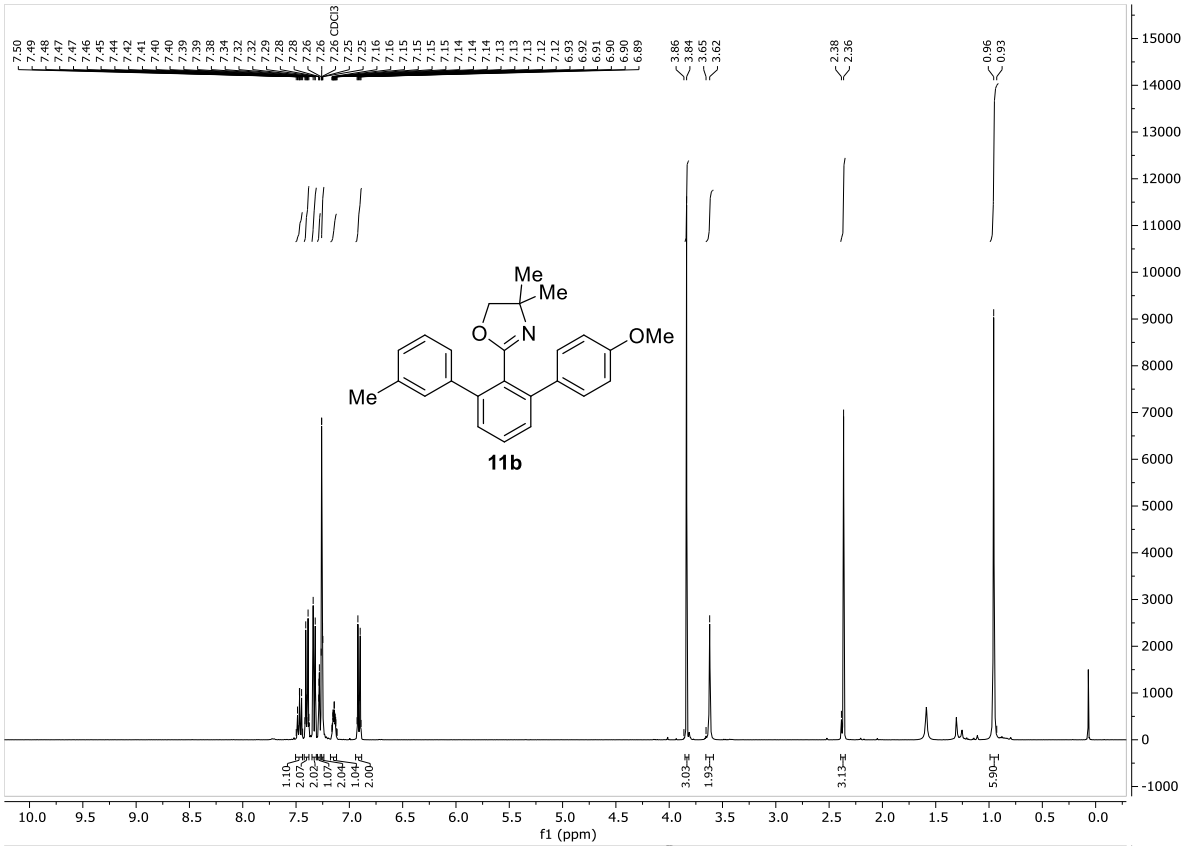
f1 (ppm)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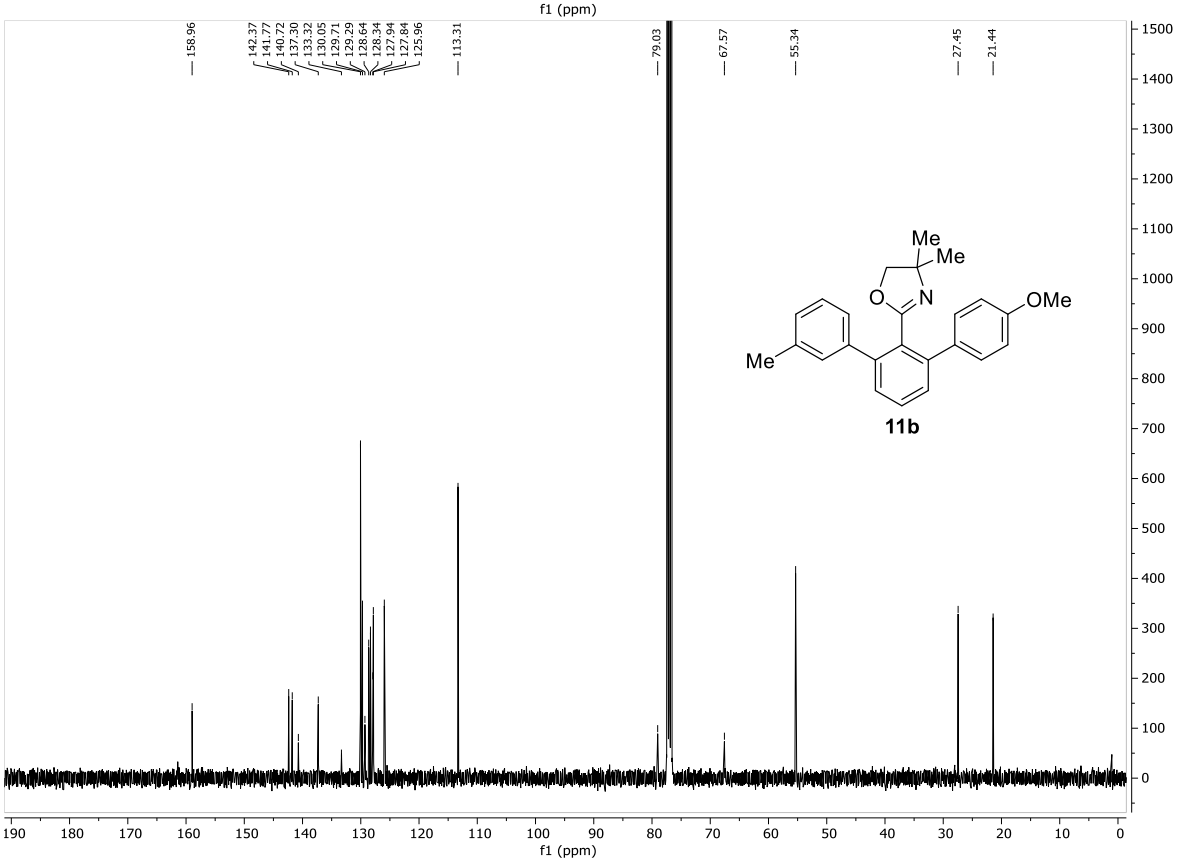
3.86 3.84 3.65 3.62
2.38 2.36
0.96 0.93
Me
Me
O
N
OMe
Me
11b
1.10 2.07 2.02 1.07 2.04 1.04 2.00
3.03 1.93 3.13 5.90
f1 (ppm)


158.96
142.37 141.77 140.72 137.30 133.32 130.05 129.71 129.29 128.64 128.34 127.94 127.84 125.96
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67.57
55.34
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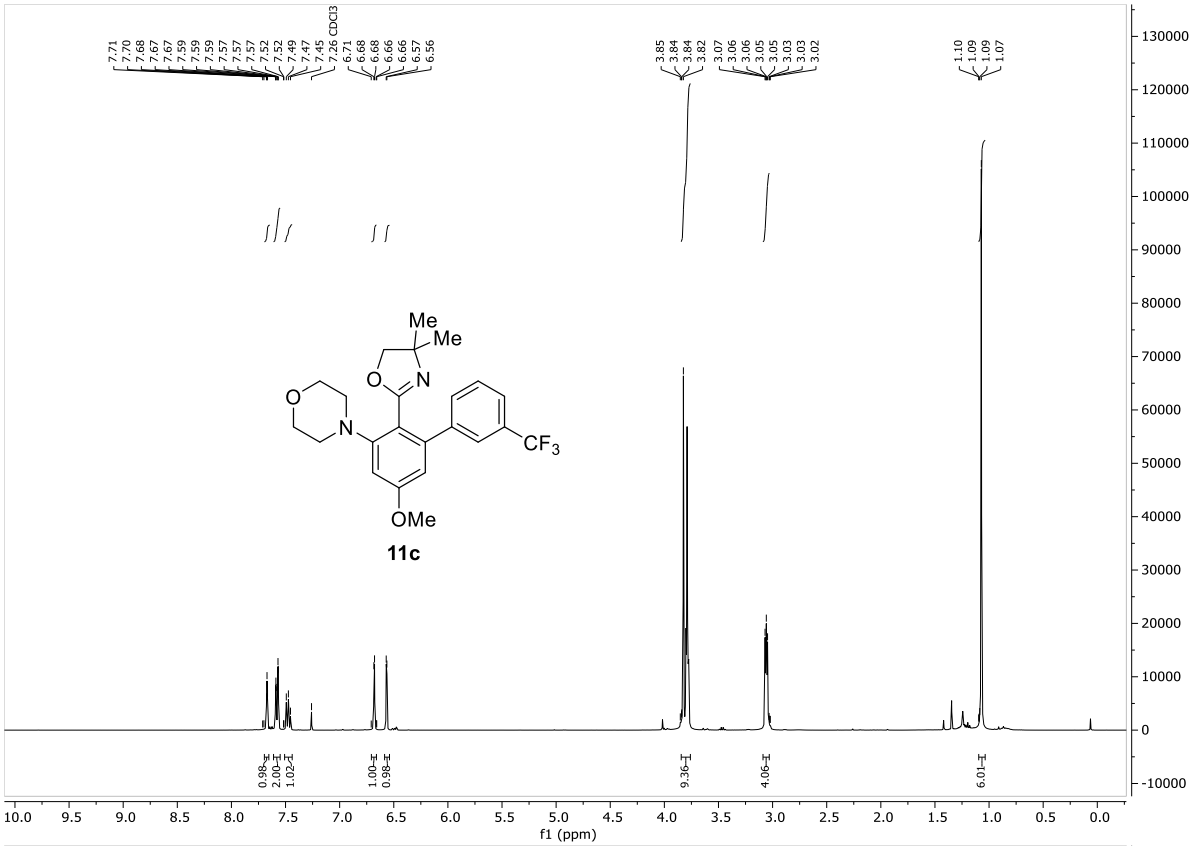
21.44
Me
Me
O
N
OMe
Me
11b
f1 (ppm)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7.52
7.49
7.47
7.45
7.26 CDCl3
6.71
6.68
6.68
6.66
6.66
6.57
6.56
3.85
3.84
3.84
3.82
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3.06
3.06
3.05
3.05
3.03
3.03
3.02
1.10
1.09
1.09
1.07
Me
Me
O
N
O
N
CF3
OMe
11c
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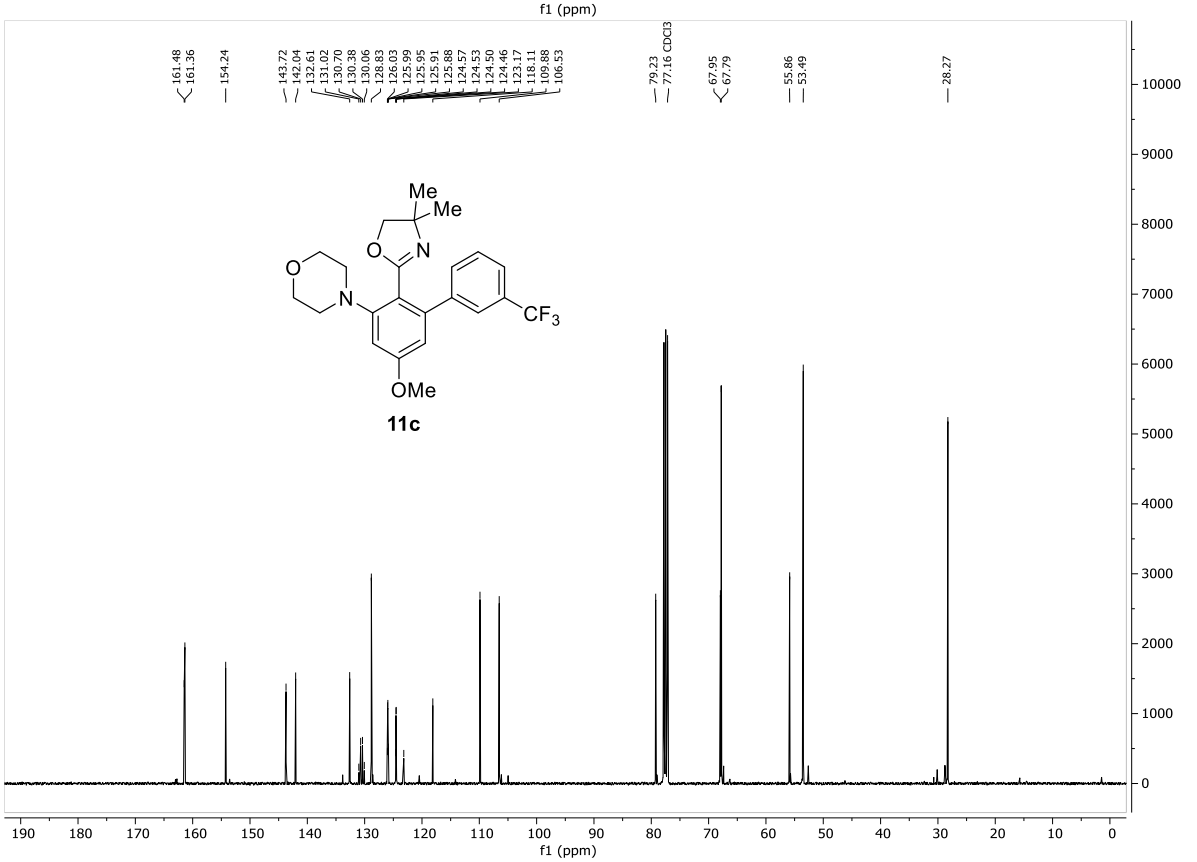
1.02
1.00
0.98
9.36
4.06
6.01
f1 (ppm)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126.03
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125.91
125.88
124.57
124.53
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124.46
123.17
118.11
109.88
106.53
79.23
77.16 CDCl3
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28.27
Me
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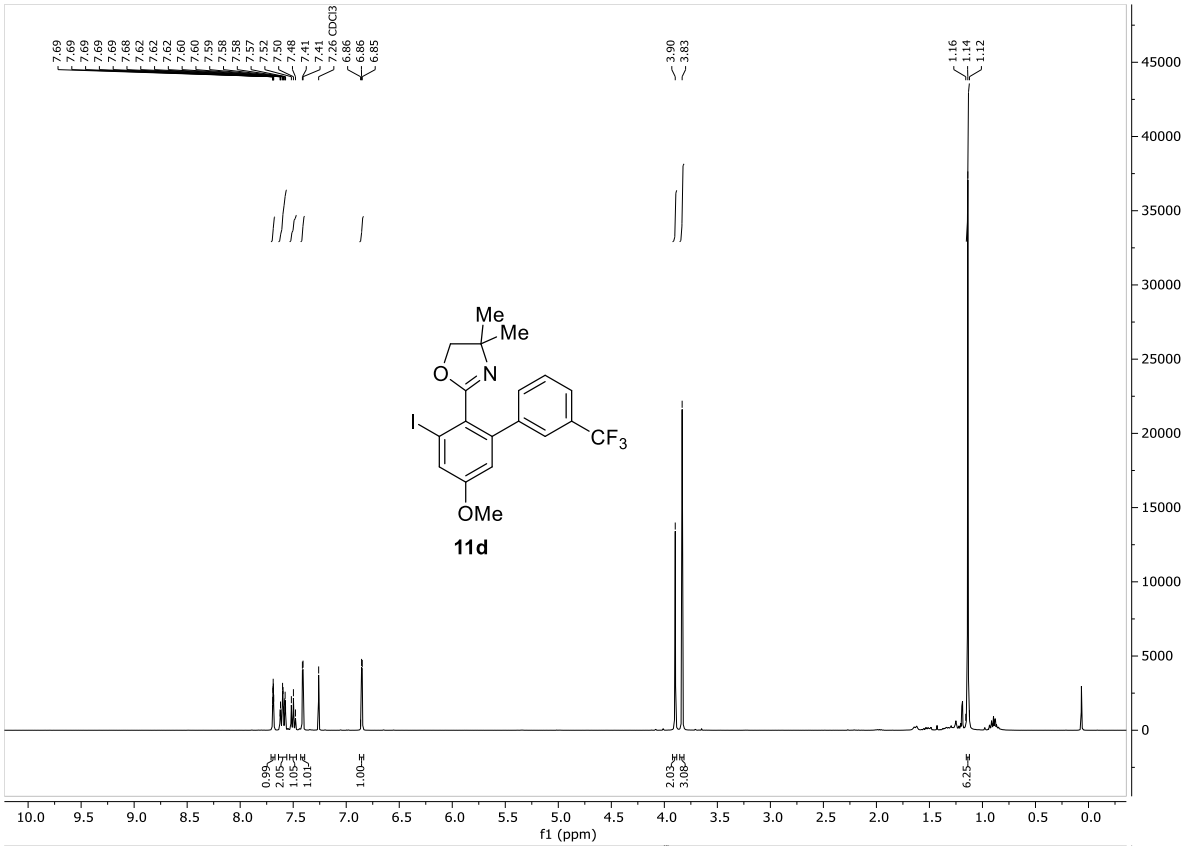
OMe
11c
f1 (ppm)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7.58
7.57
7.52
7.50
7.48
7.41
7.41
7.26 CDCl3
6.86
6.86
6.85
3.90
3.83
1.16
1.14
1.12
Me
Me
O
N
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2.03
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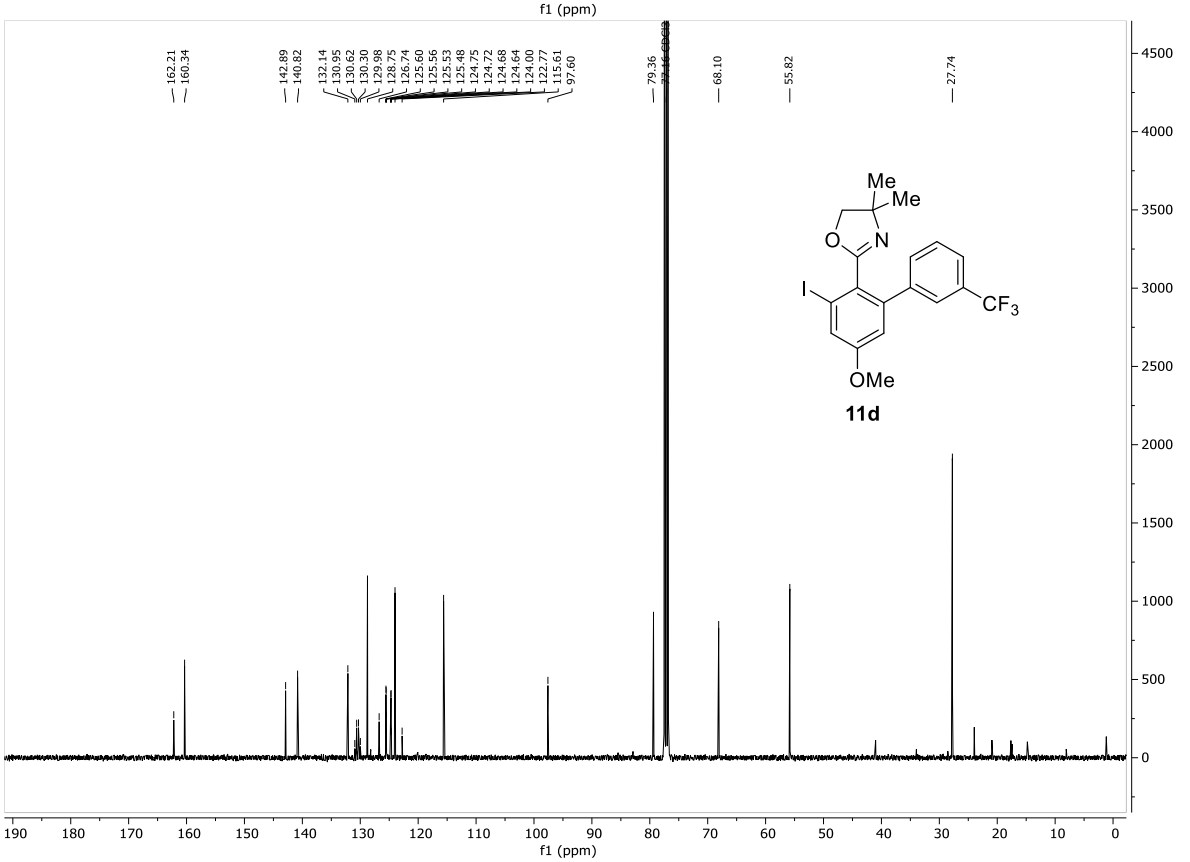
6.25
f1 (ppm)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124.00
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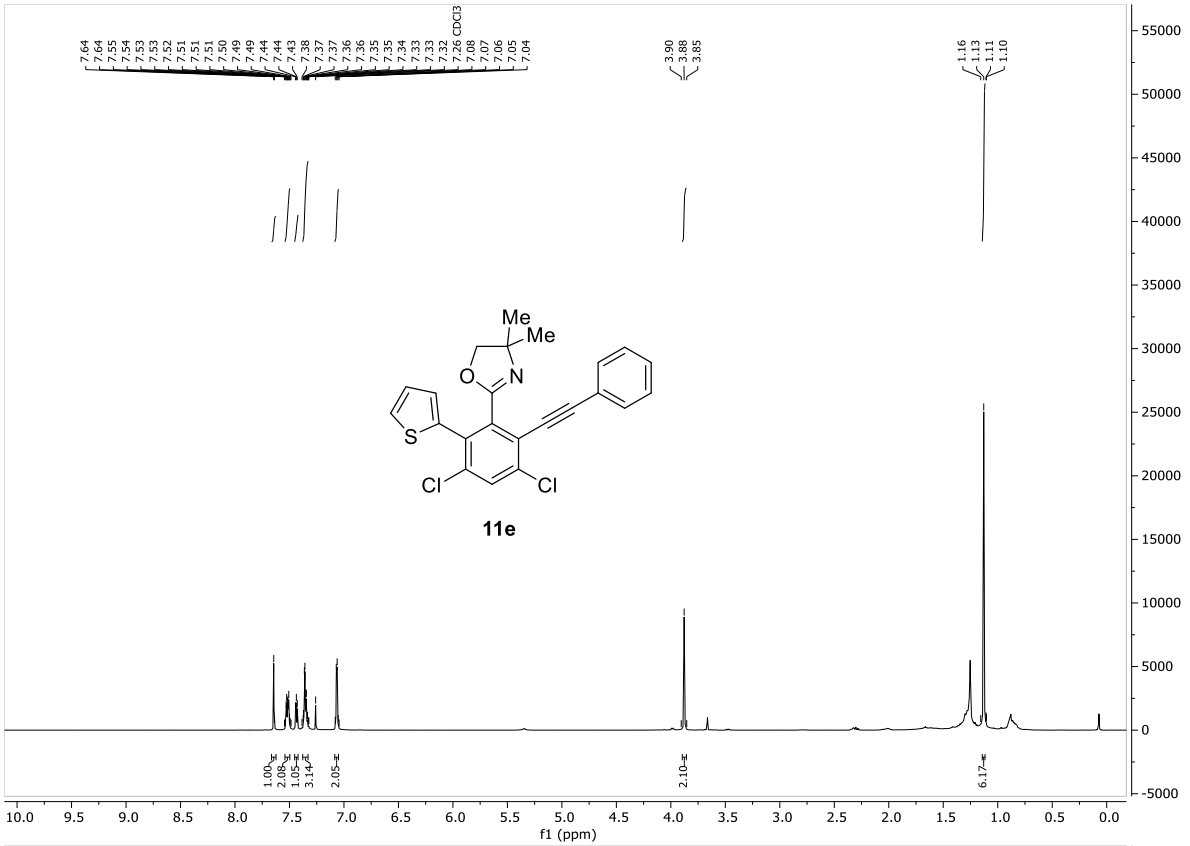
11d
f1 (ppm)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7.32
CDCl3
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7.07
7.06
7.05
7.04
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3.88
3.85
1.16
1.13
1.11
1.10
Me
Me
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Cl
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2.10
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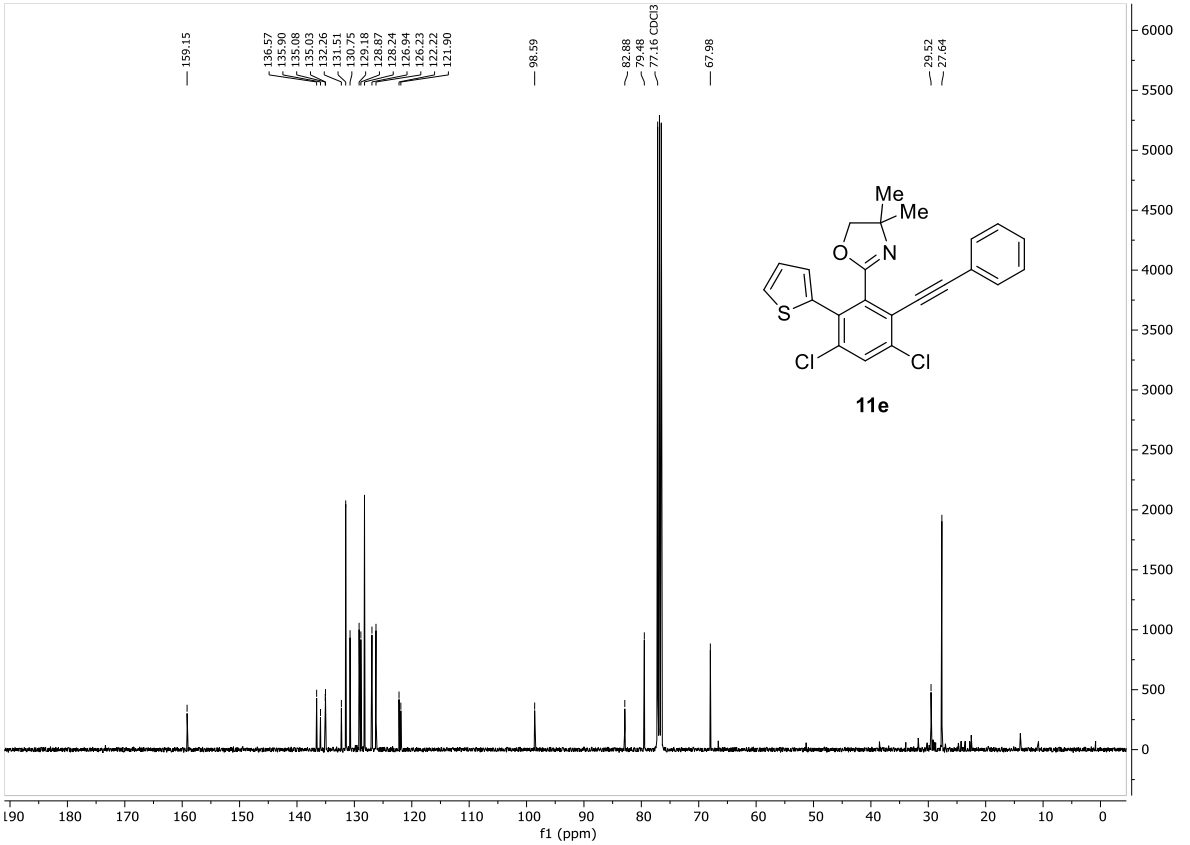
f1 (ppm)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128.24
126.94
126.23
122.22
121.90
98.59
82.88
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67.98
29.52
27.64
Me
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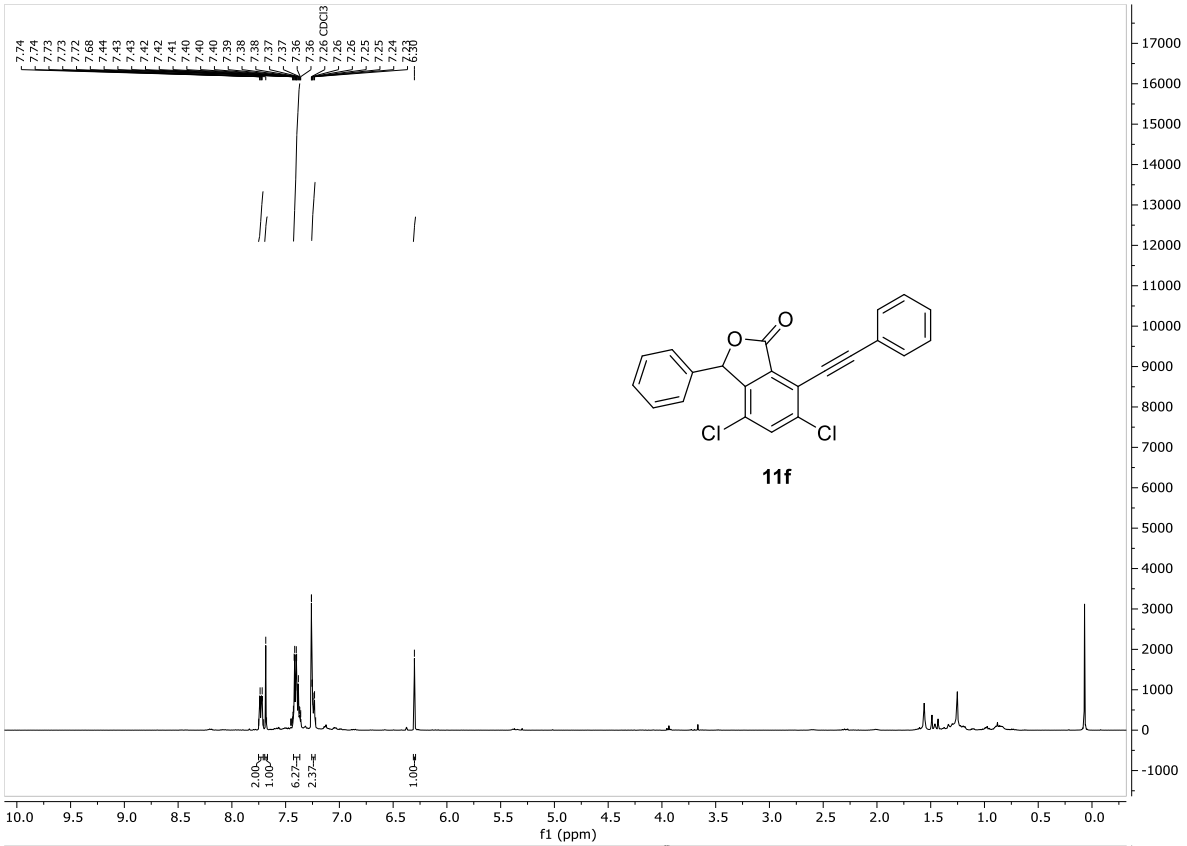
O
N
S
Cl
Cl
11e
f1 (ppm)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7.40
7.39
7.38
7.38
7.37
7.37
7.36
7.36
CDCl3
7.26
7.26
7.26
7.25
7.25
7.24
7.23
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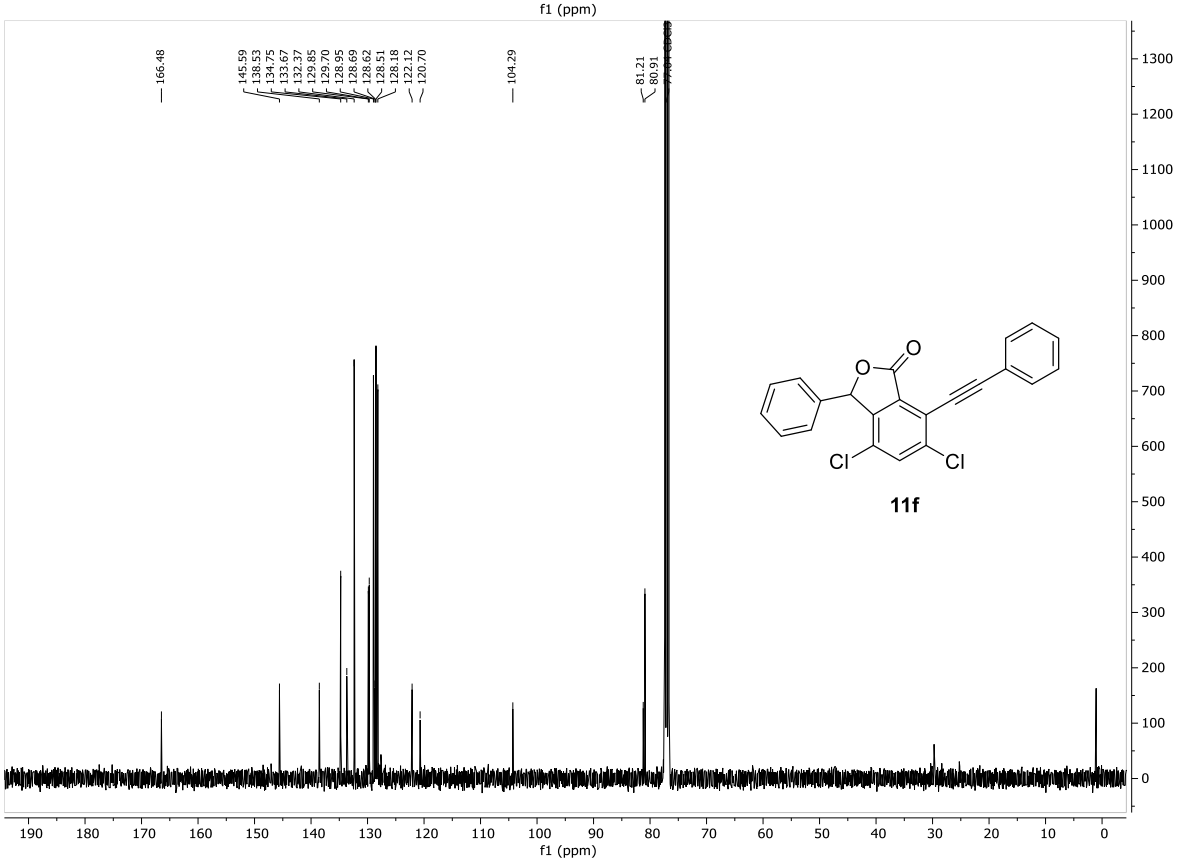
O
O
Cl
Cl
11f
2.00
1.00
6.27
2.37
1.00
f1 (ppm)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120.70
104.29
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O
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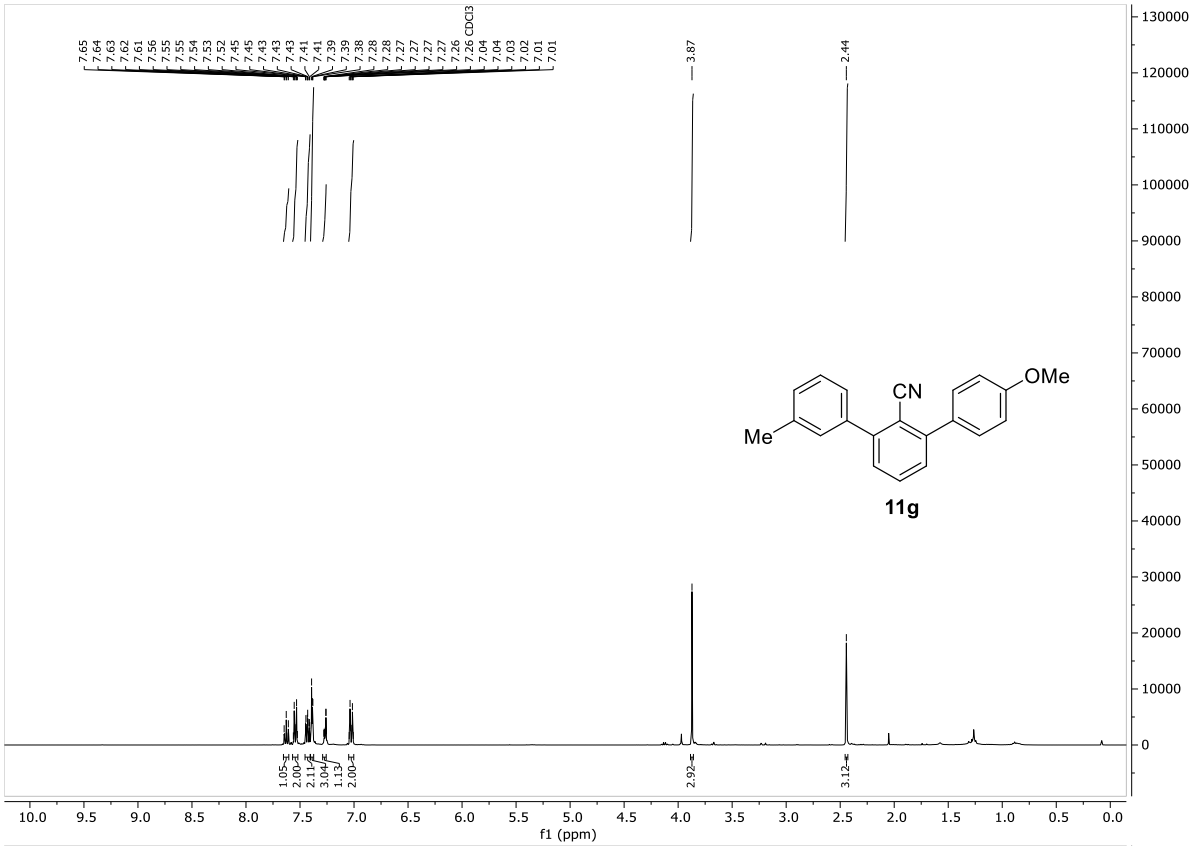
Cl
Cl
11f
f1 (ppm)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7.27
7.26
7.26
CDCl3
7.04
7.03
7.02
7.01
7.01
3.87
2.44
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2.00
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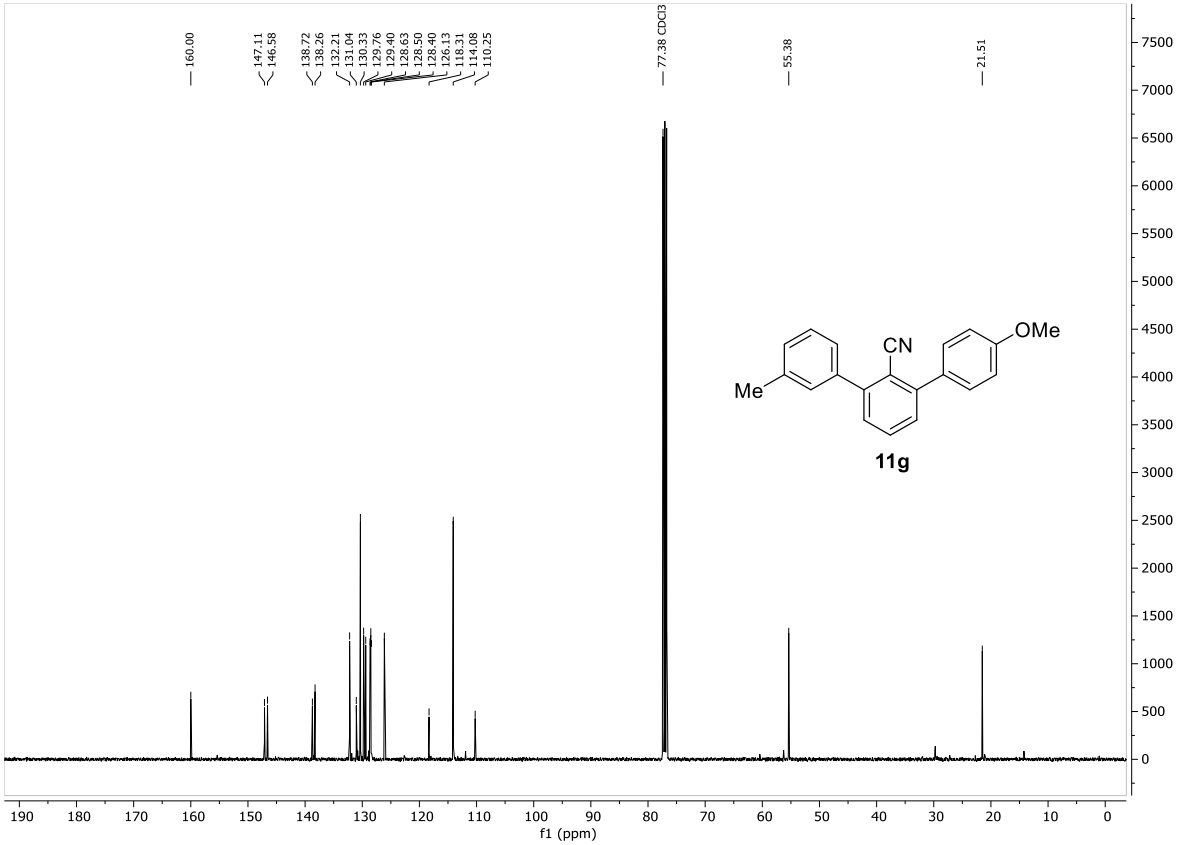
3.12
f1 (ppm)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128.63
128.50
128.40
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110.25
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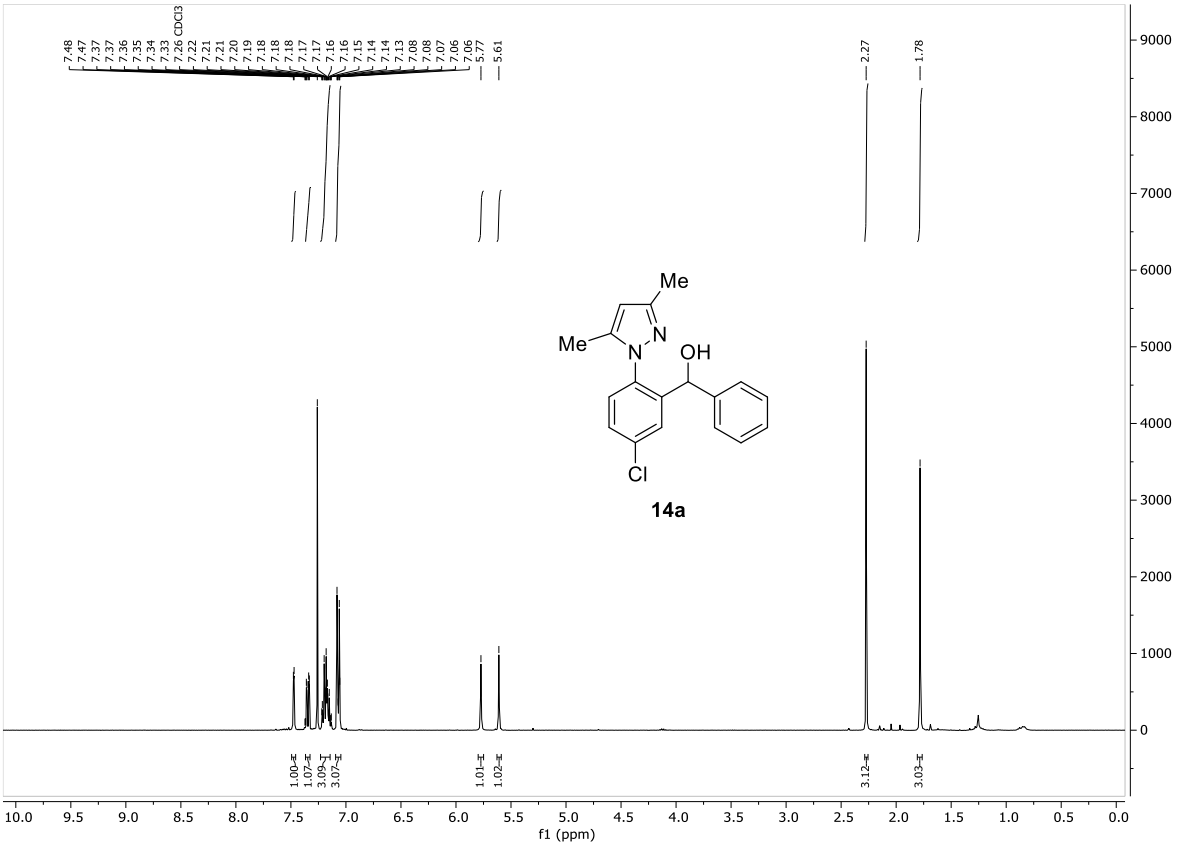
55.38
21.51
CN
OMe
Me
11g
f1 (ppm)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7.34
7.33
7.26 CDCl3
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7.08
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7.07
7.06
5.66
5.77
5.61
2.27
1.78
Me
Me
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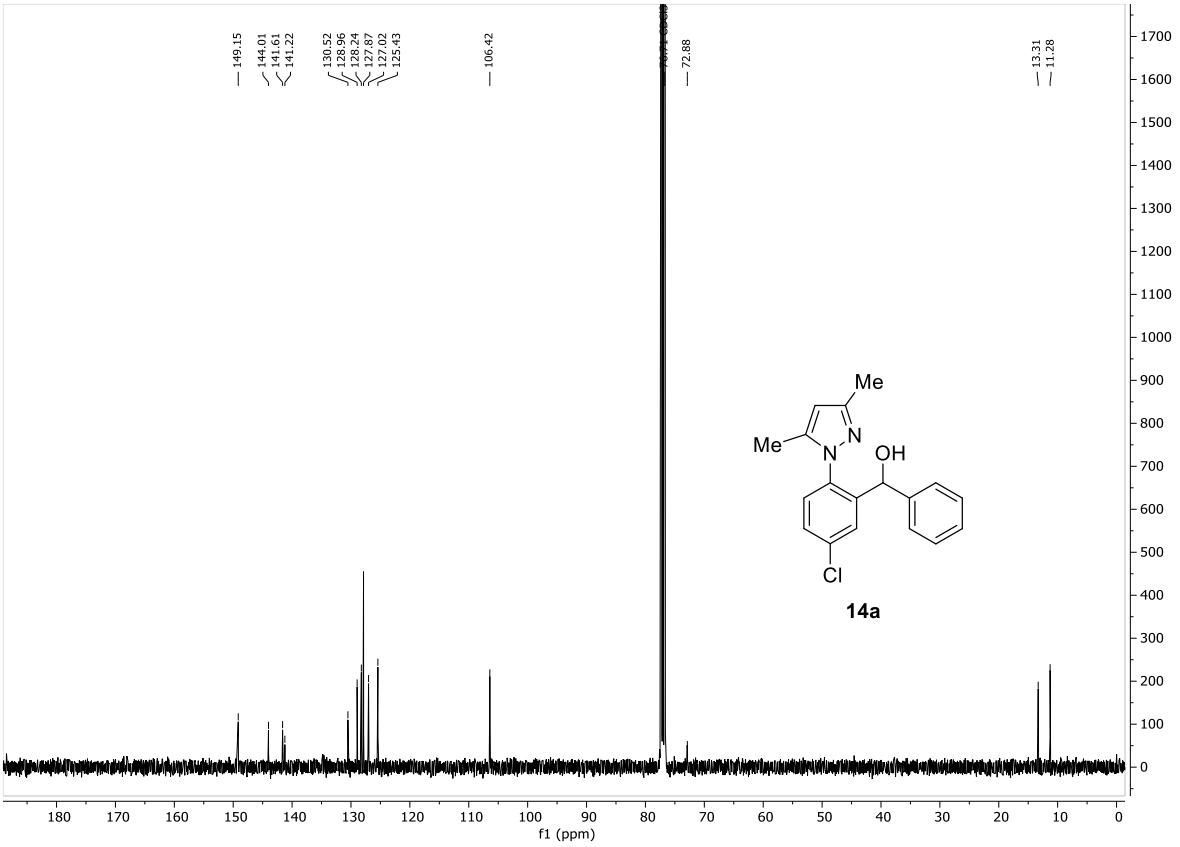
3.07
1.01
1.02
3.12
3.03
f1 (ppm)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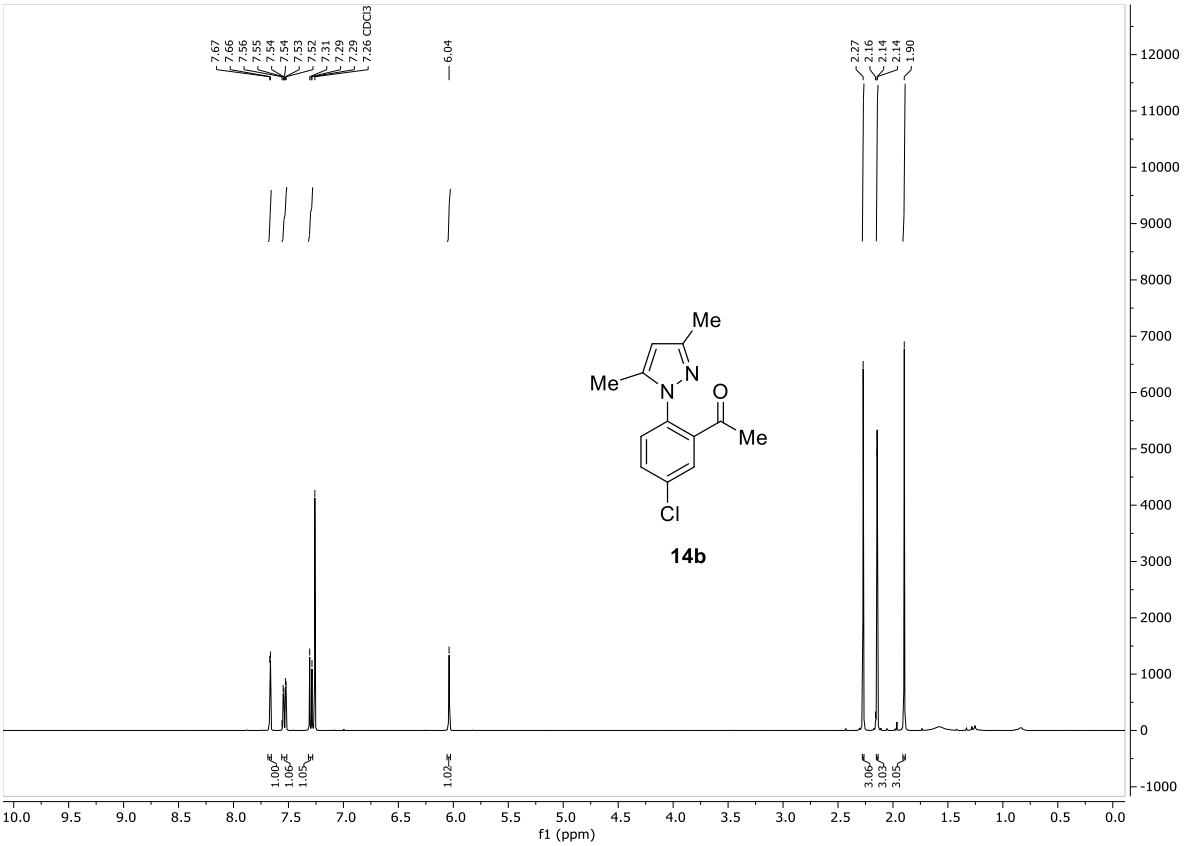
106.42
72.88
13.31
11.28
Me
Me
N
N
OH
Cl
14a
f1 (ppm)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7.29
7.29
7.26 CDCl3
6.04
2.27
2.16
2.14
2.14
1.90
Me
Me
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N
O
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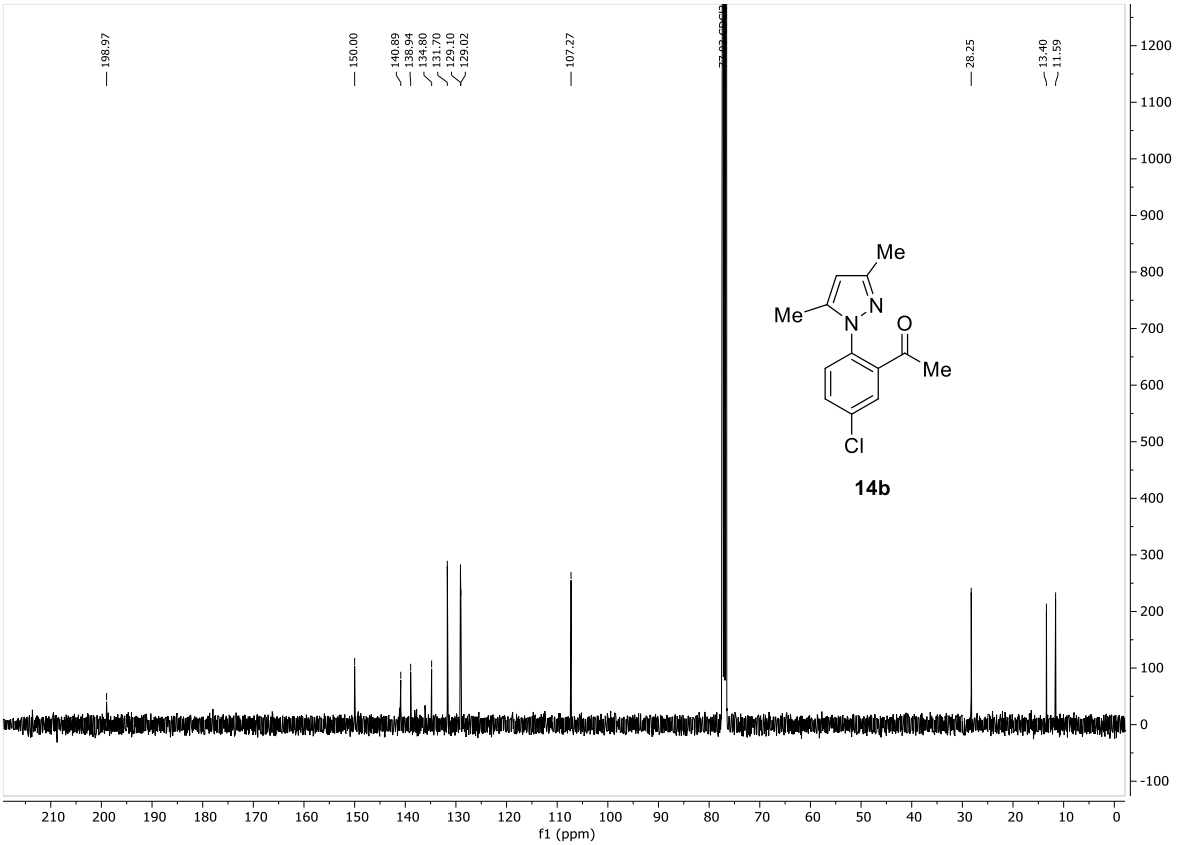
Cl
14b
1.00
1.06
1.05
1.02
3.06
3.03
3.05
f1 (ppm)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129.02
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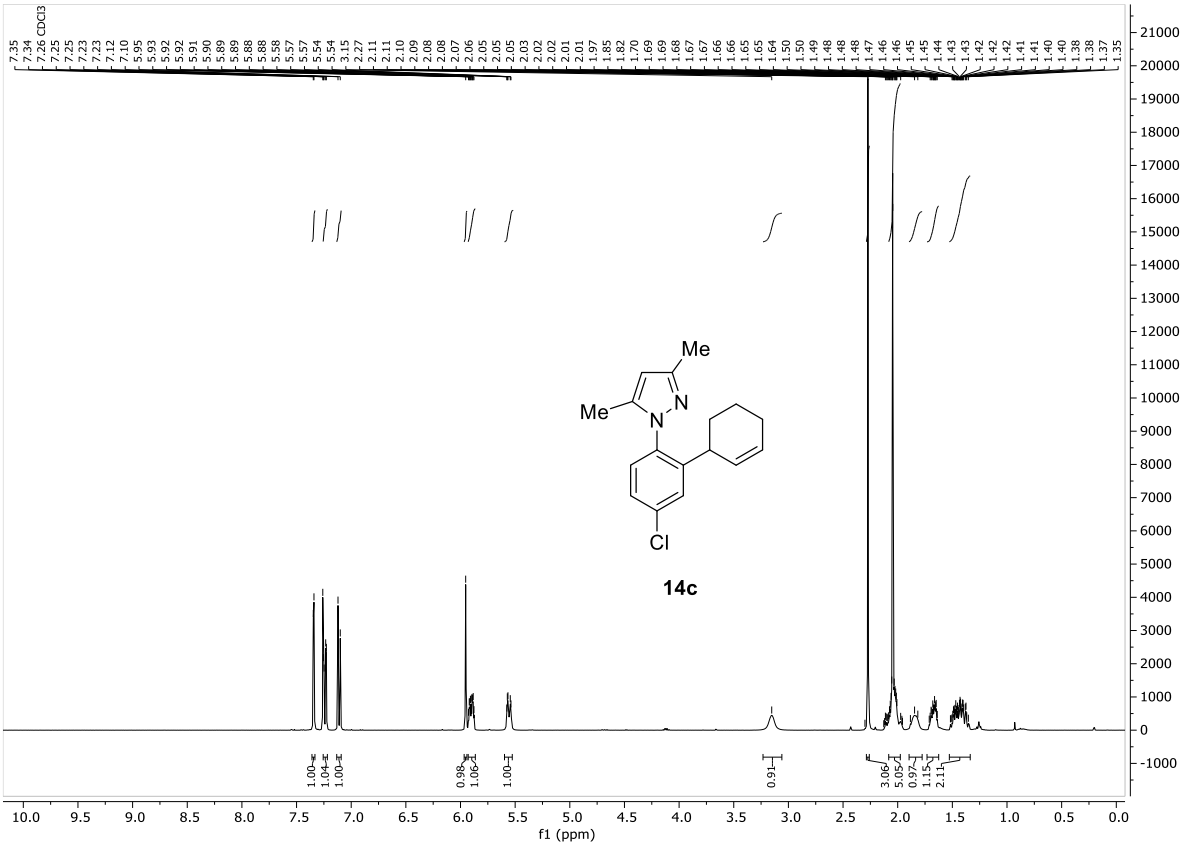
28.25
13.40
11.59
Me
Me
N
N
O
Me
Cl
14b
f1 (ppm)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14c
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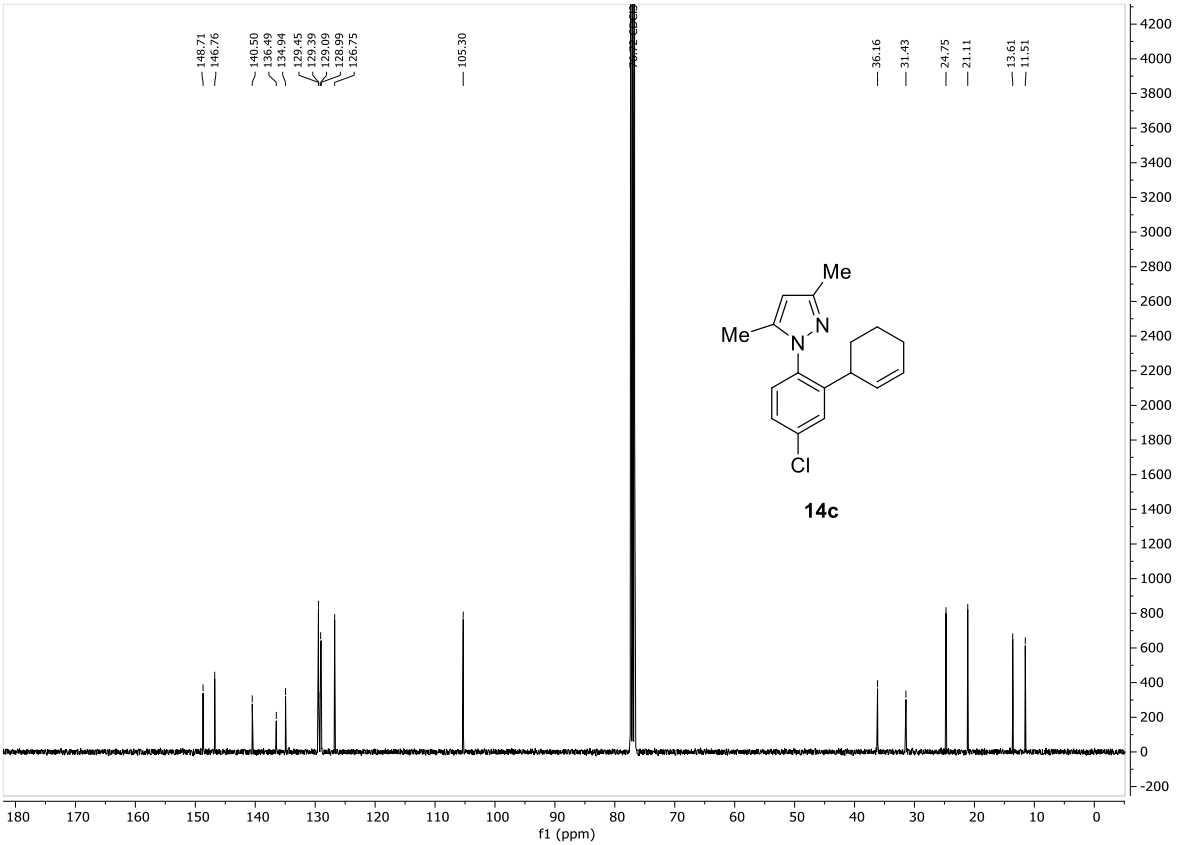
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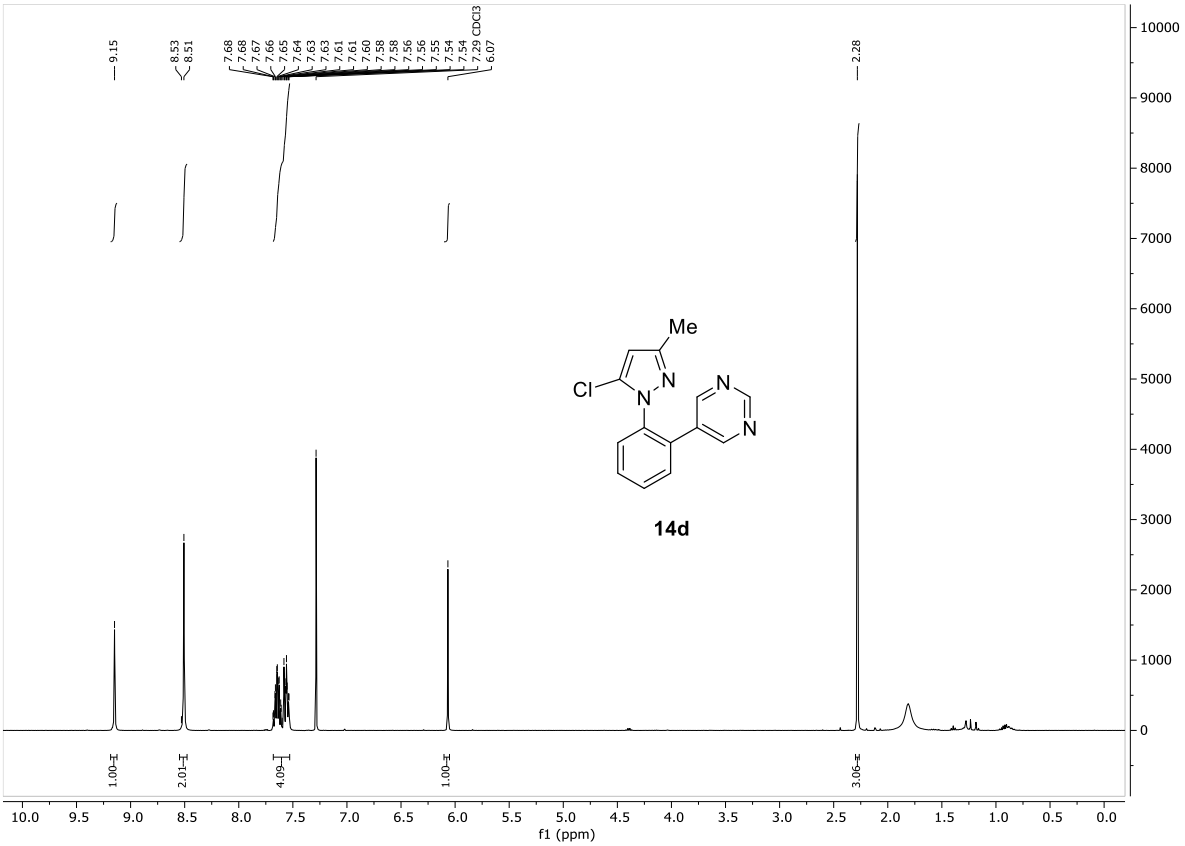
14c
f1 (ppm)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7.68
7.67
7.66
7.65
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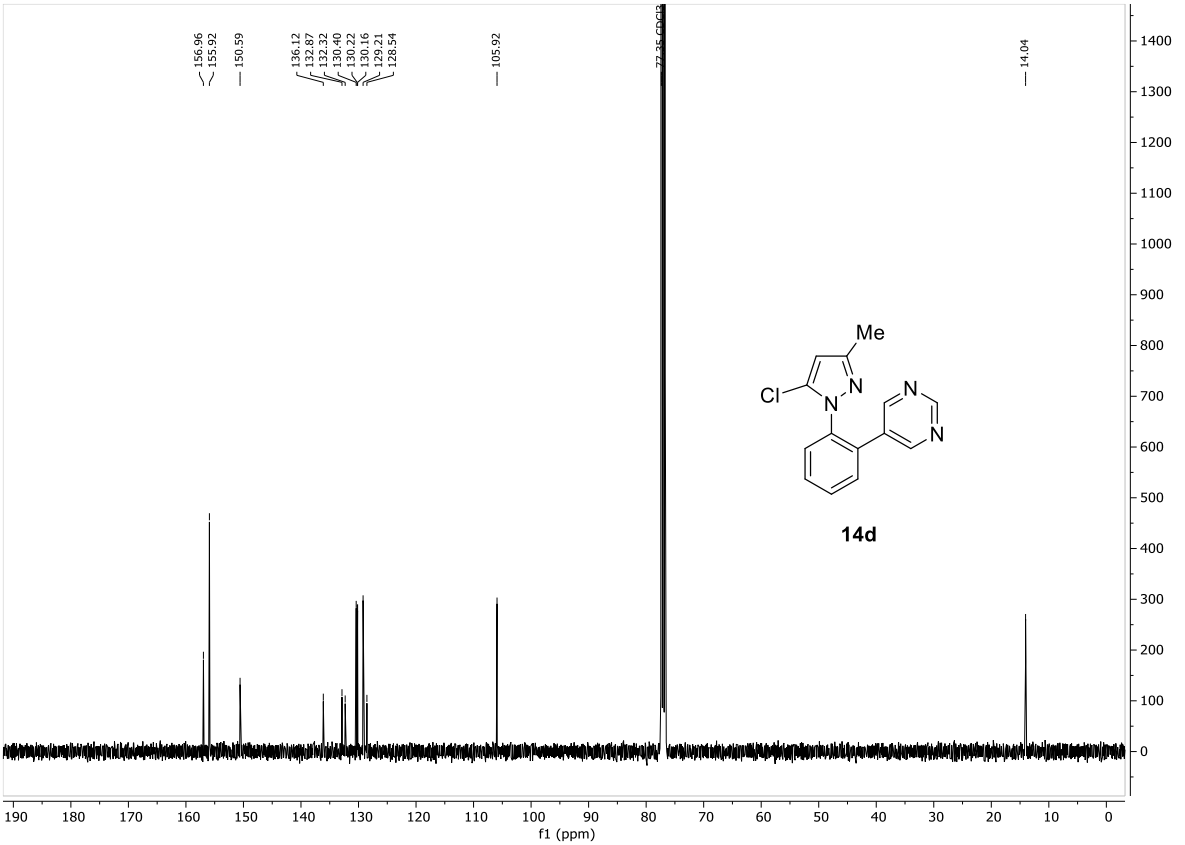
7.63
7.63
7.61
7.61
7.60
7.58
7.58
7.56
7.56
7.55
7.54
7.54
7.29 CDCl3
6.07
2.28
Me
Cl
N
N
N
N
14d
1.00
2.01
4.09
1.00
3.06
f1 (ppm)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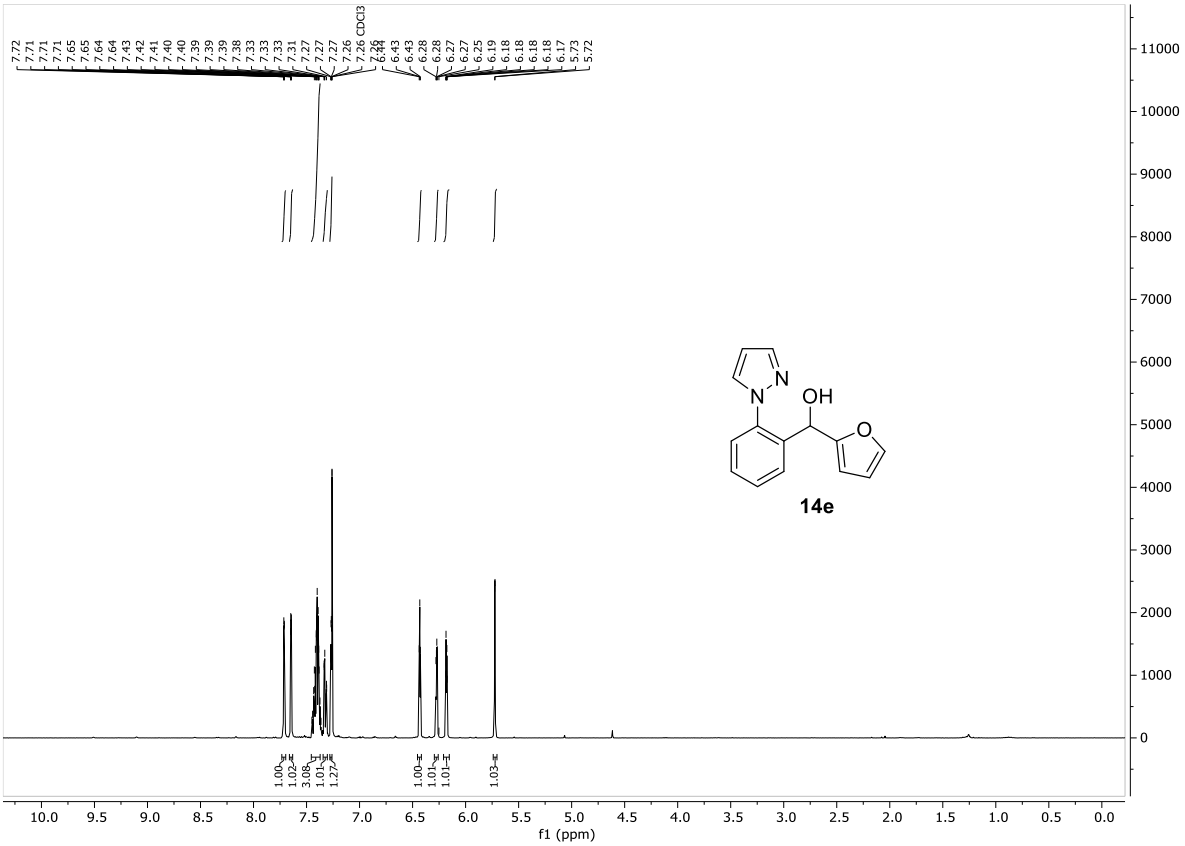
128.54
105.92
77.35 CDCl3
14.04
Me
Cl
N
N
N
N
14d
f1 (ppm)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7.40
7.39
7.39
7.39
7.38
7.33
7.33
7.33
7.31
7.27
7.27
7.27
7.26
7.26 CDCl3
6.43
6.43
6.28
6.28
6.27
6.27
6.25
6.19
6.18
6.18
6.18
6.18
6.17
5.73
5.72
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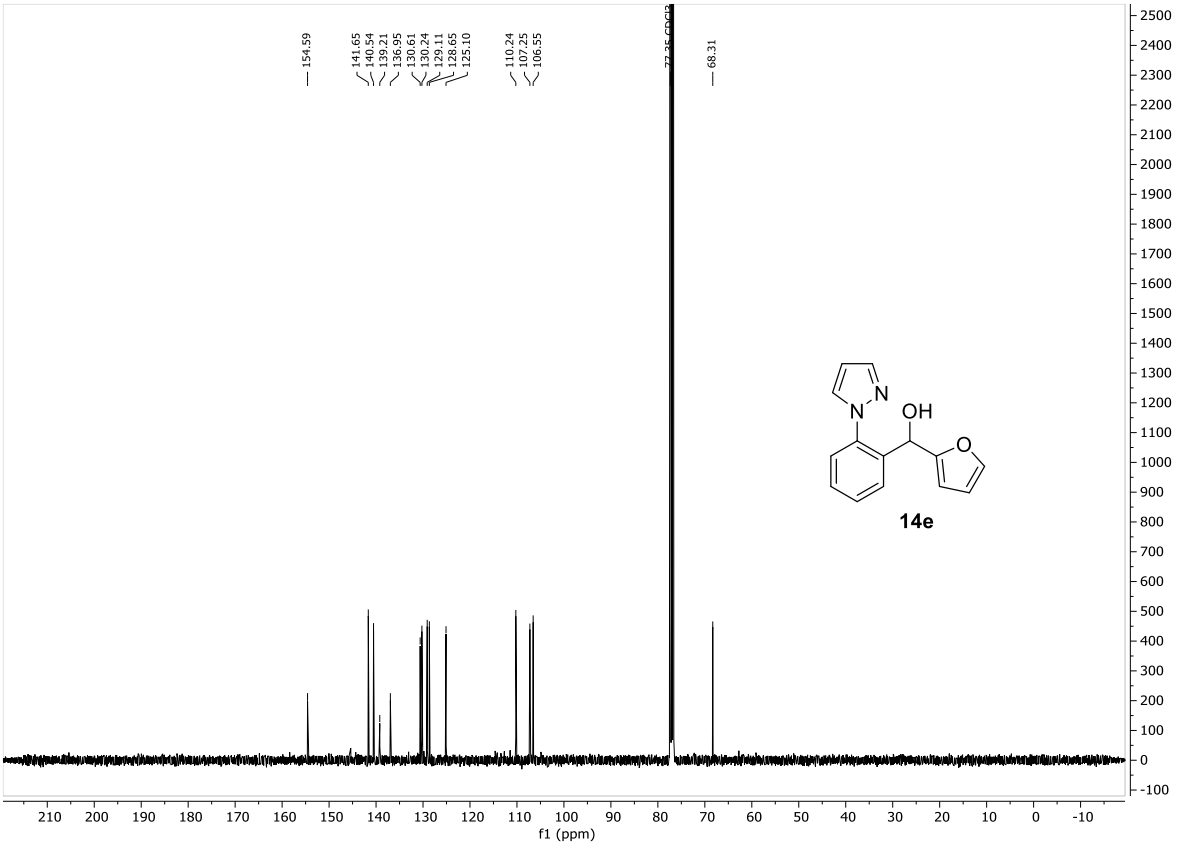
1.01
1.27
1.00
1.01
1.01
1.03
OH
O
14e
f1 (ppm)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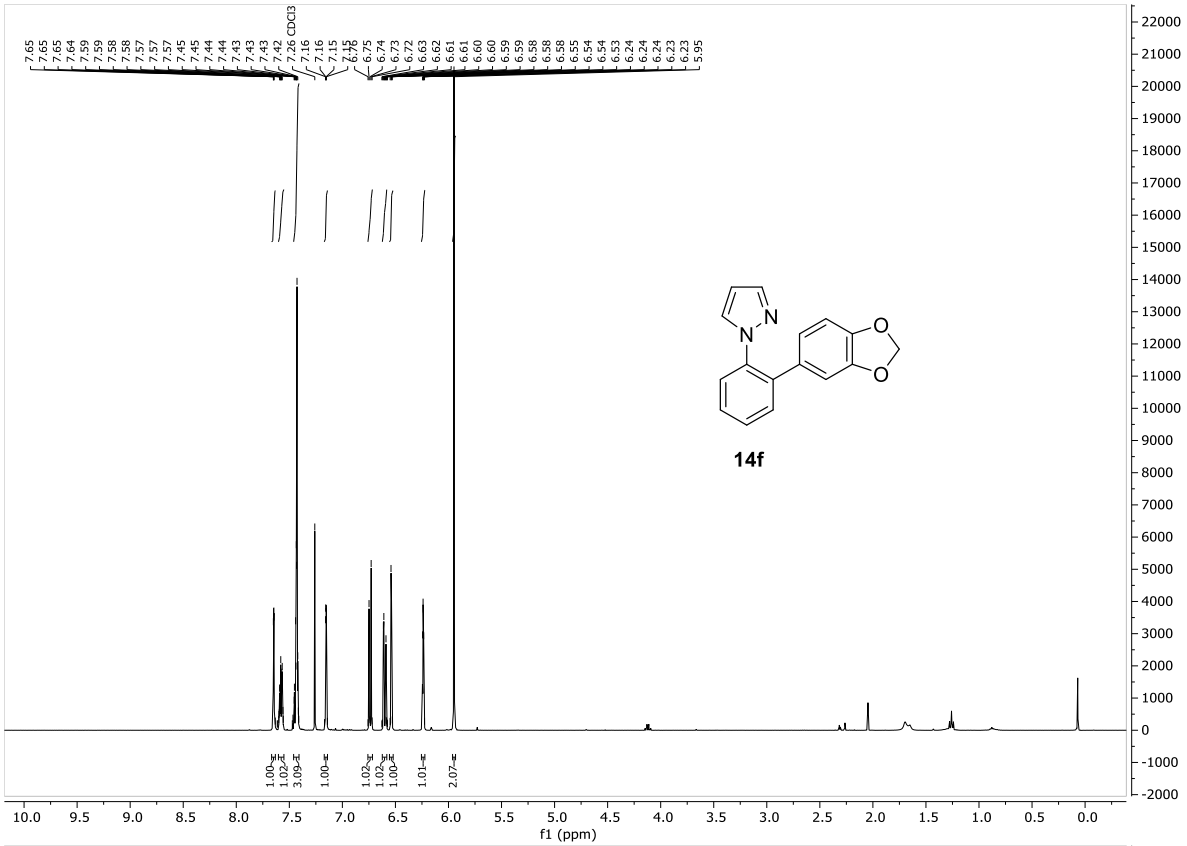
106.55
77.35 CDCl3
68.31
OH
O
14e
f1 (ppm)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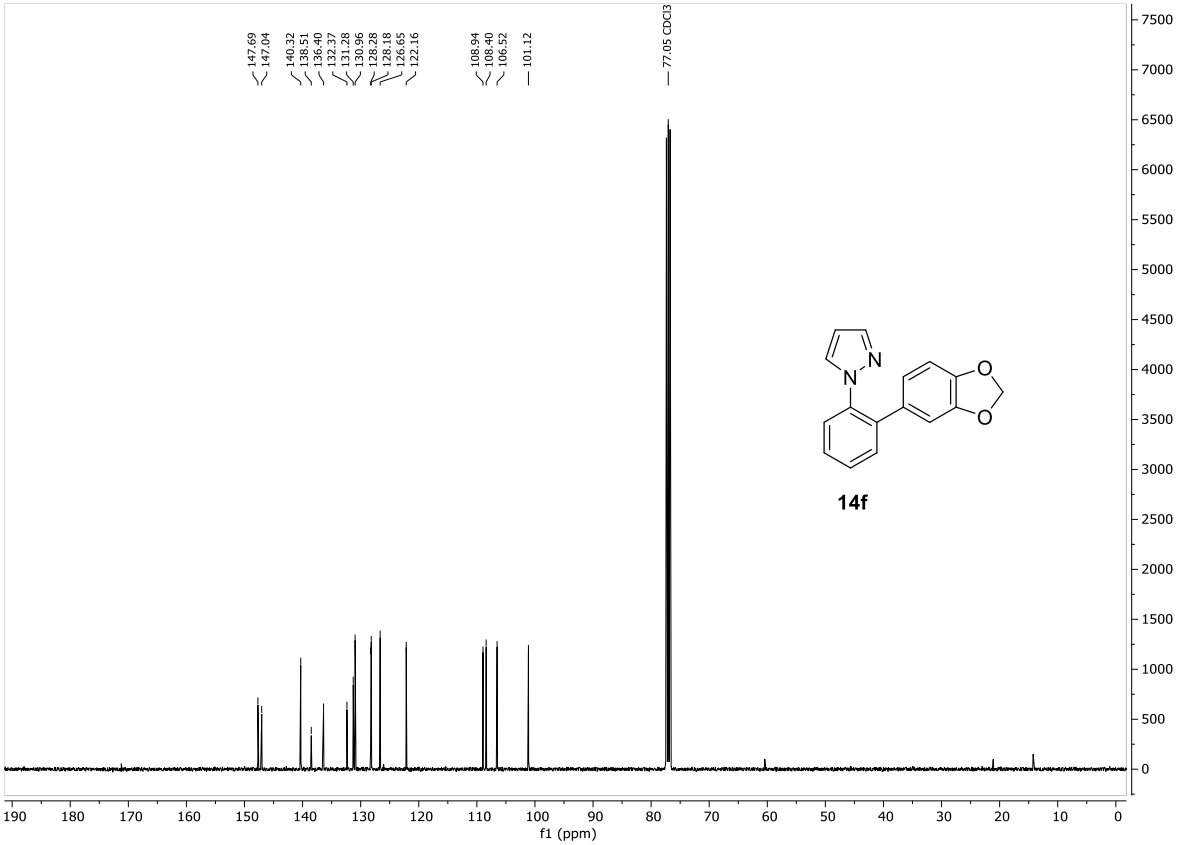
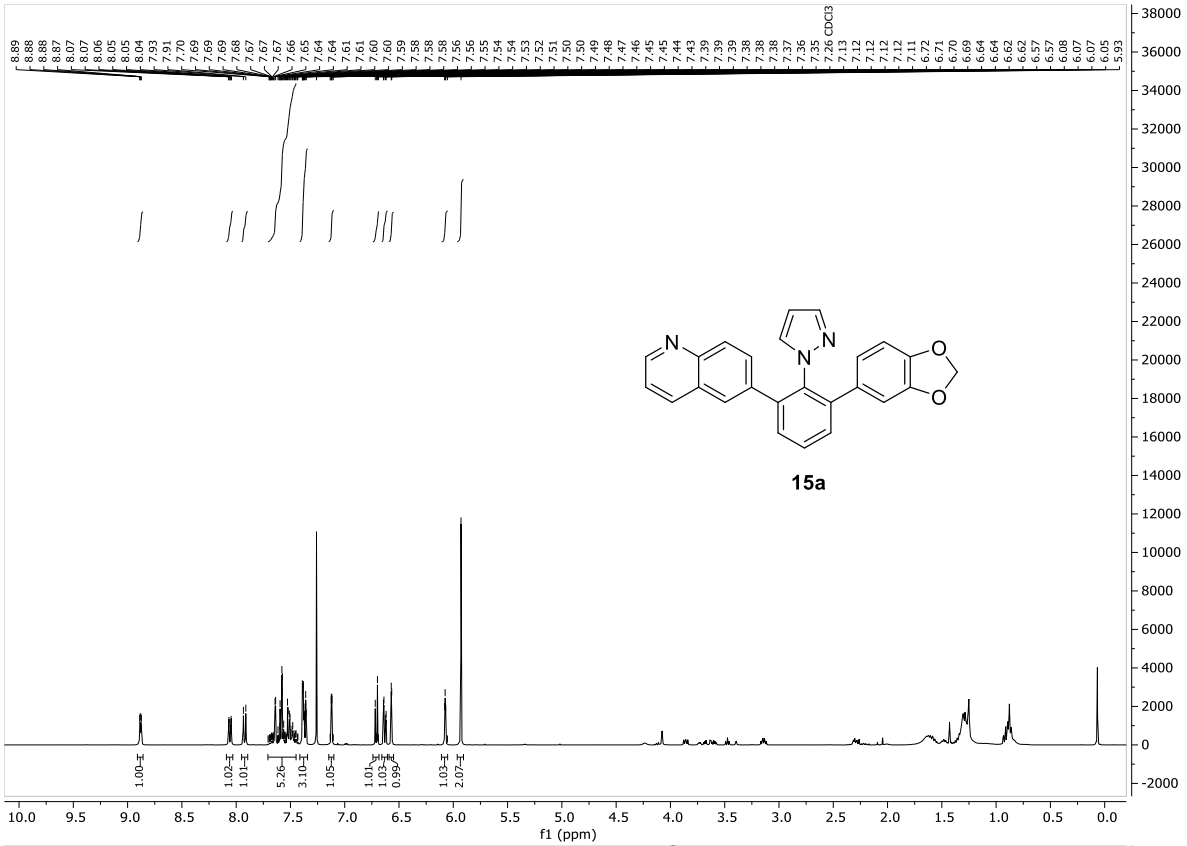
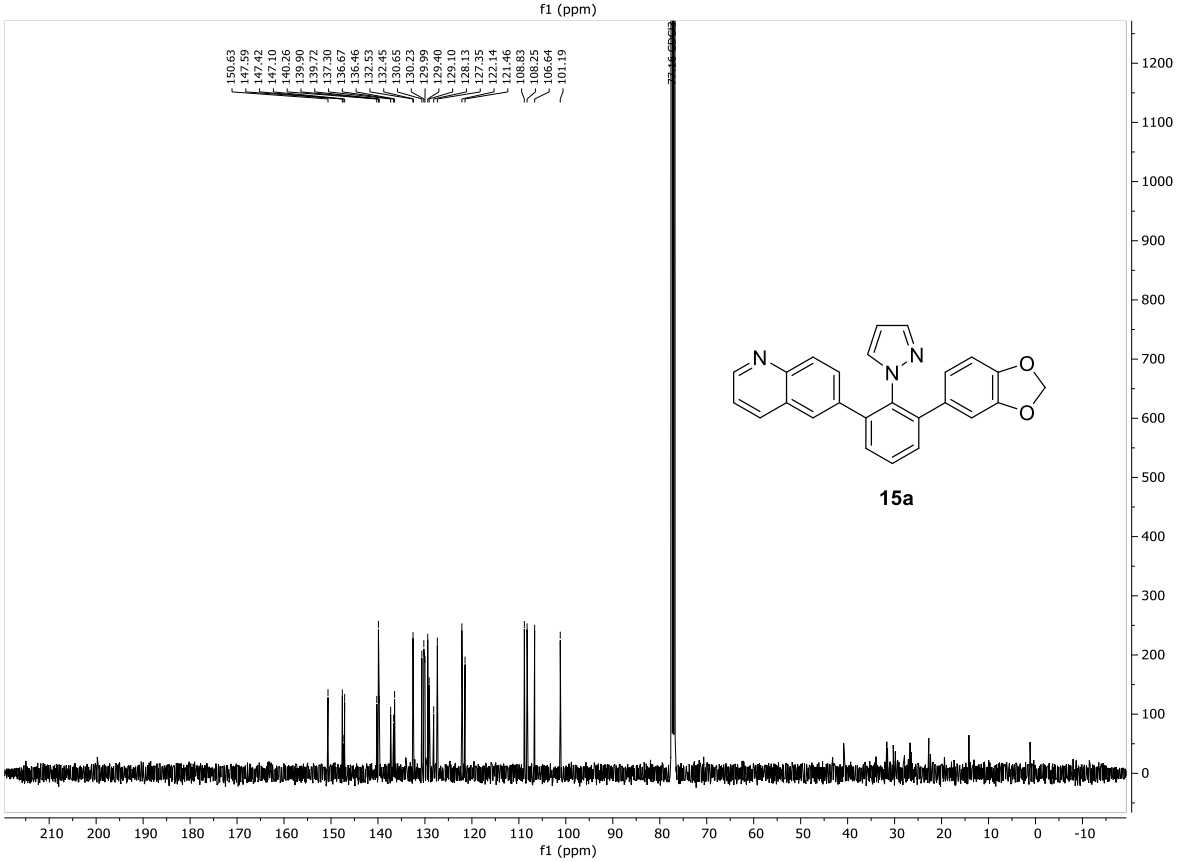
1.00 1.02 3.09 1.00 1.02 1.02 1.00 1.01 2.07
f1 (ppm)
14f


147.69 147.04 140.32 138.51 136.40 132.37 131.28 130.96 128.28 128.18 126.65 122.16 108.94 108.40 106.52 101.12 77.05 CDCl3
f1 (ppm)
14f


CDCl3
15a
f1 (ppm)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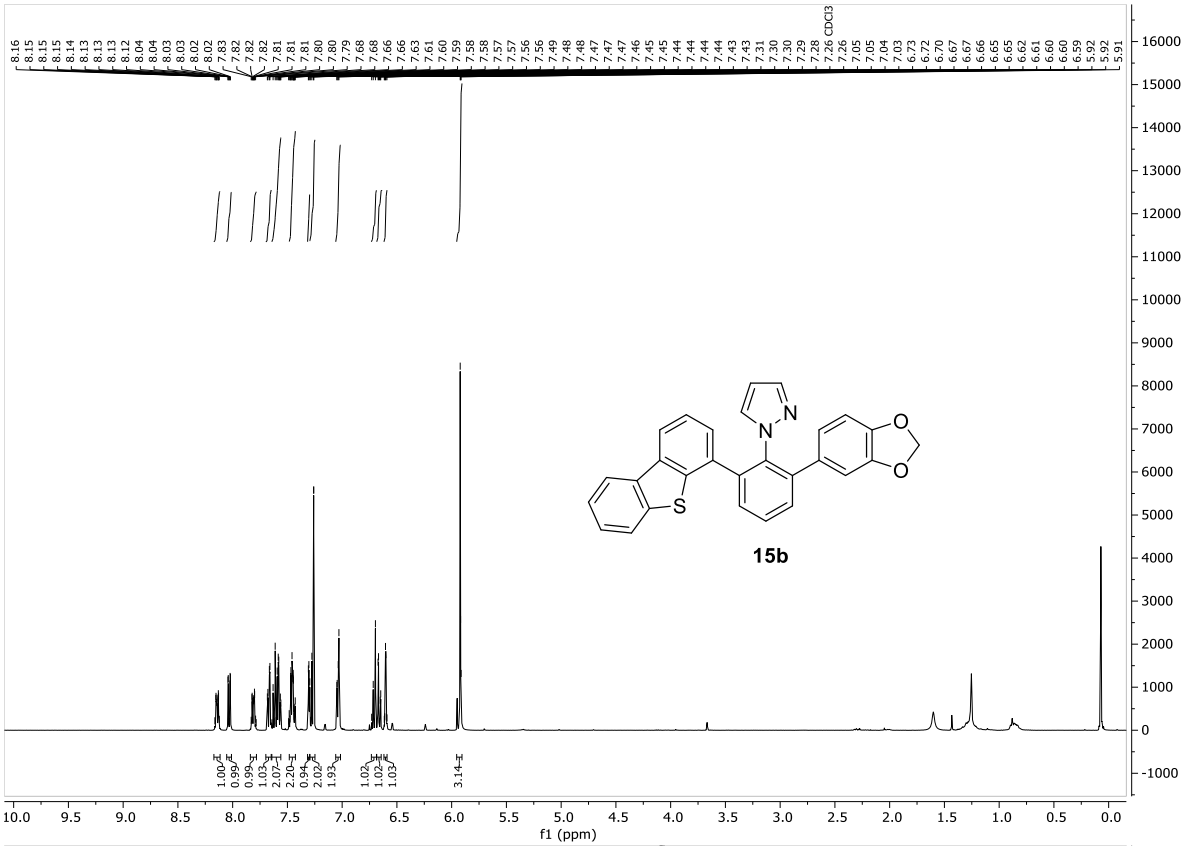
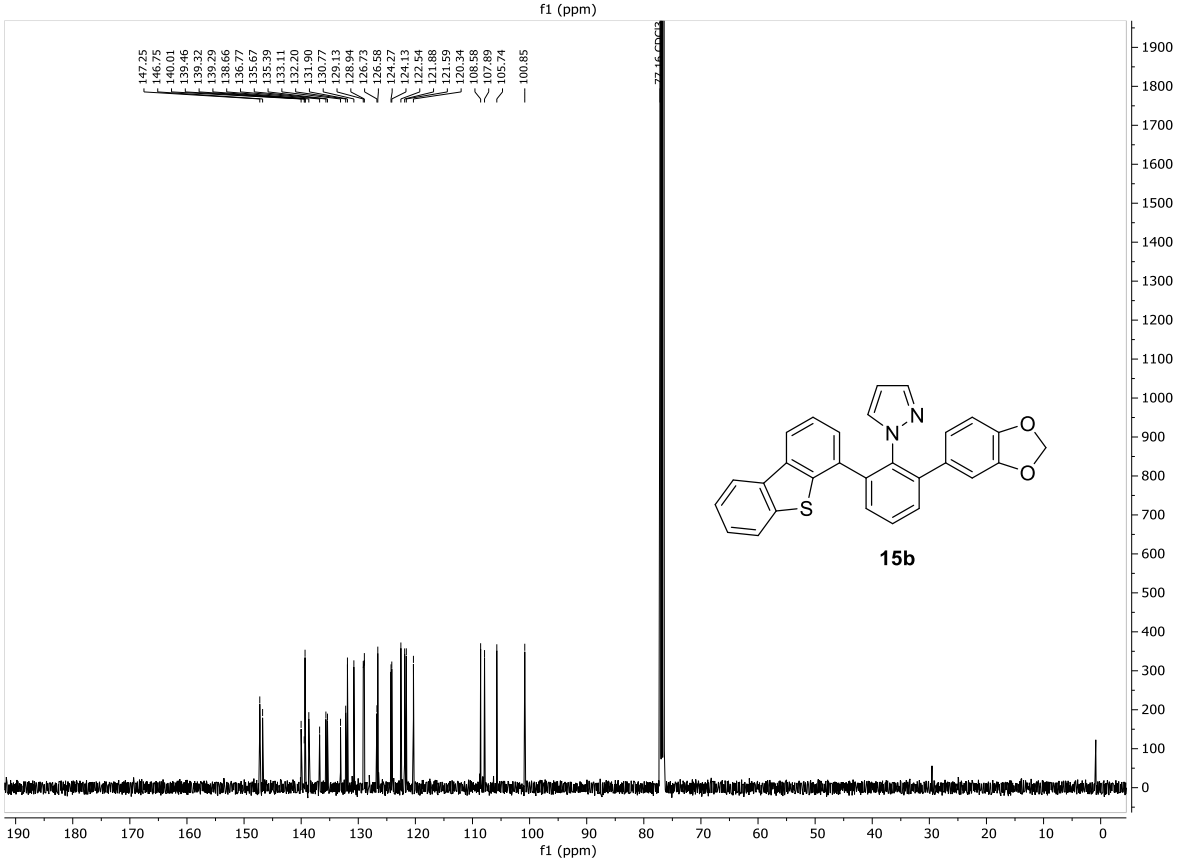
f1 (ppm)


CDCl3
15b
f1 (ppm)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139.29
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136.77
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133.11
132.20
131.90
130.77
129.13
128.94
126.73
126.58
124.27
124.13
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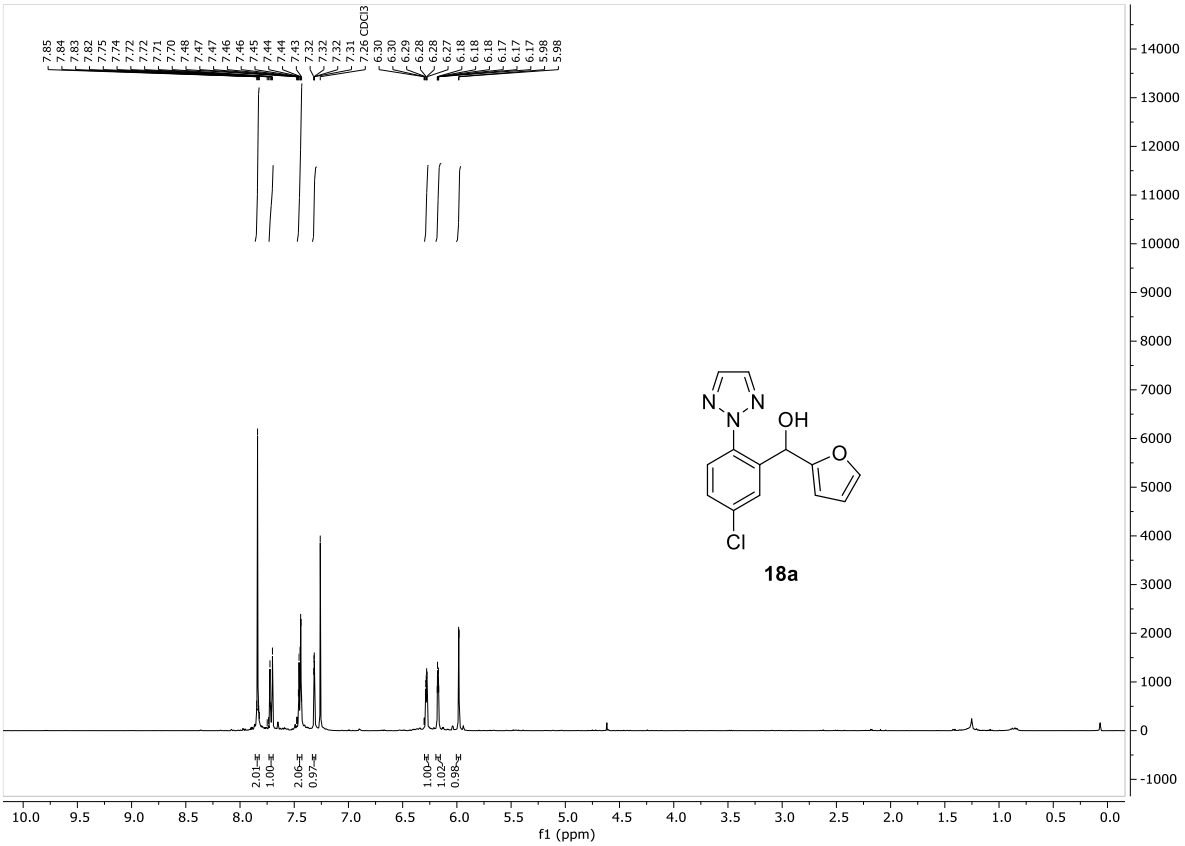
121.59
120.34
108.58
107.89
105.74
100.85
77.16 CDCl3
15b
f1 (ppm)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7.46
7.46
7.45
7.44
7.44
7.43
7.32
7.32
7.32
7.31
7.26 CDCl3
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6.30
6.29
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6.18
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6.18
6.17
6.17
6.17
5.98
5.98
2.01
1.00
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0.97
1.00
1.02
0.98
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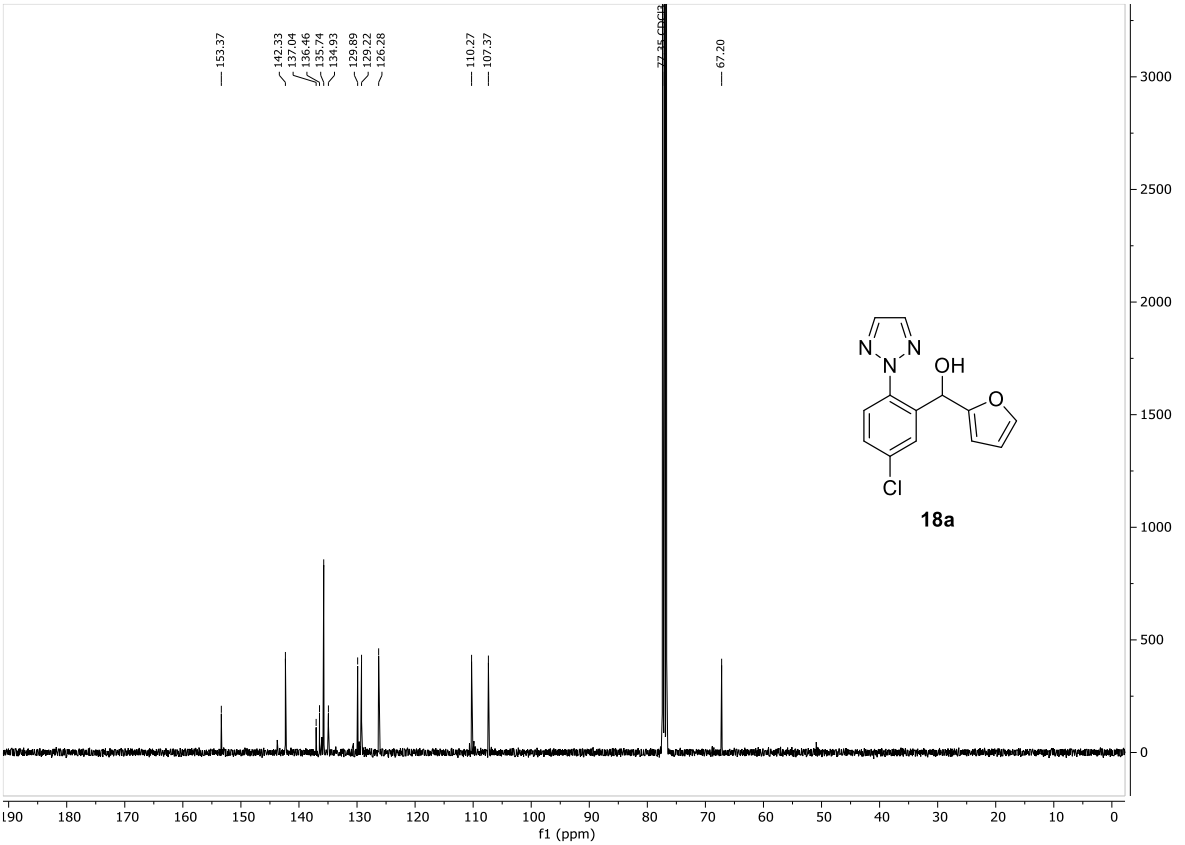
N
OH
O
Cl
18a
f1 (ppm)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142.33
137.04
136.46
135.74
134.93
129.89
129.22
126.28
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107.37
77.35 CDCl3
67.20
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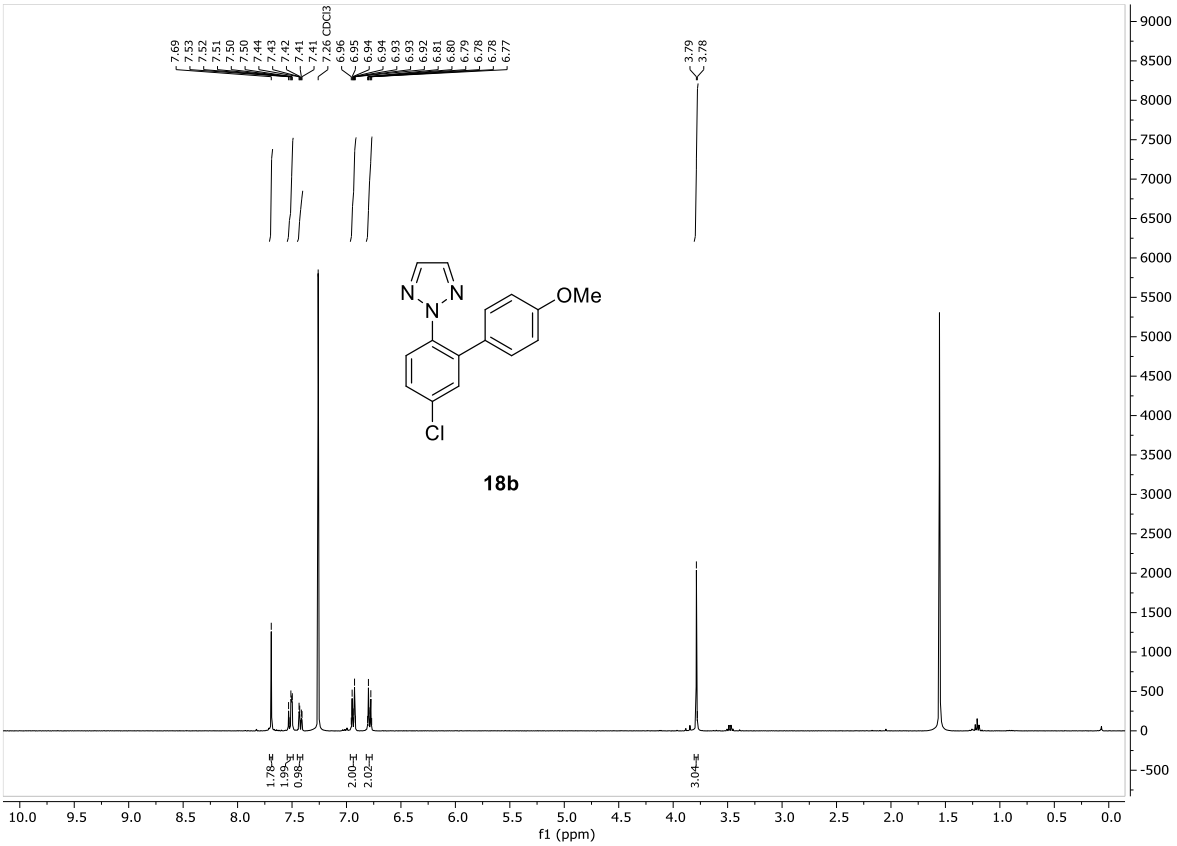
N
N
OH
O
Cl
18a
f1 (ppm)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7.43
7.42
7.41
7.41
CDCl3
7.26
6.96
6.95
6.94
6.94
6.93
6.93
6.92
6.81
6.80
6.79
6.78
6.78
6.77
3.79
3.78
OMe
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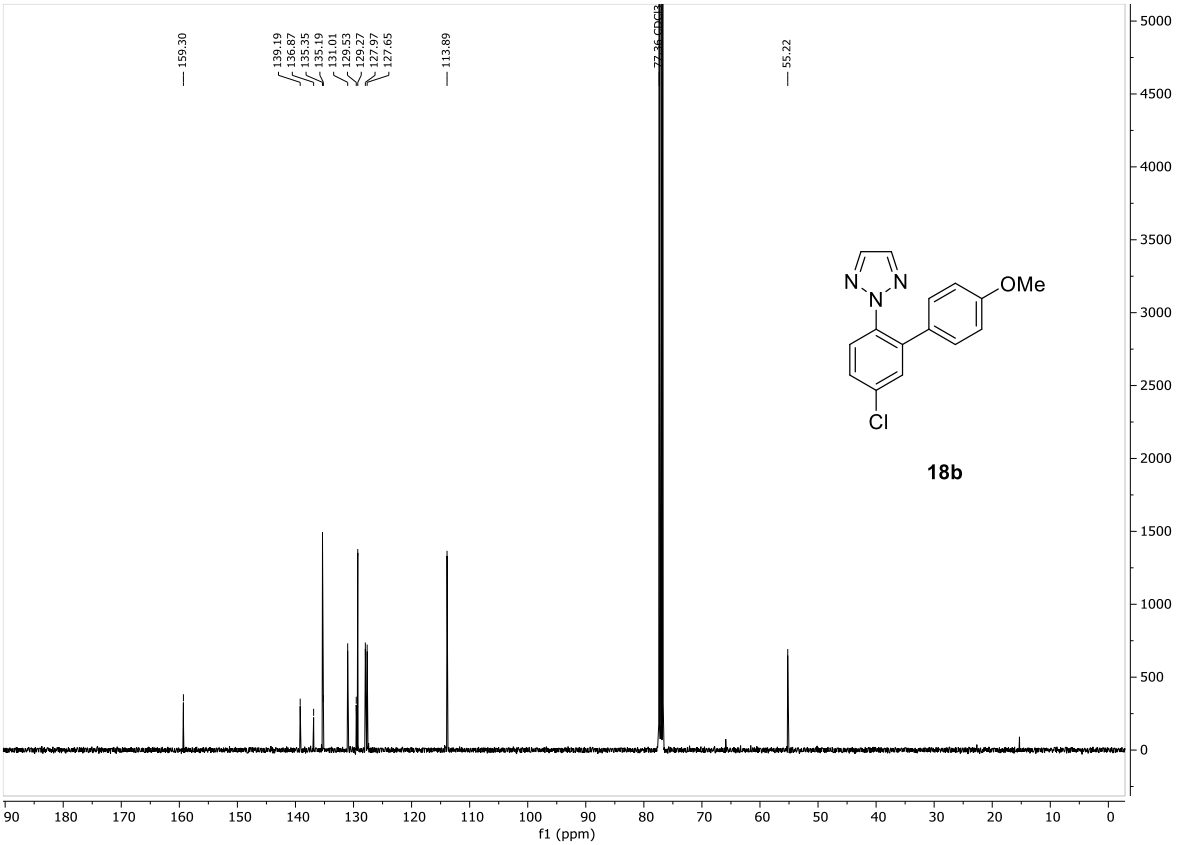
N
N
Cl
18b
1.78
1.99
0.98
2.00
2.02
3.04
f1 (ppm)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131.01
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113.89
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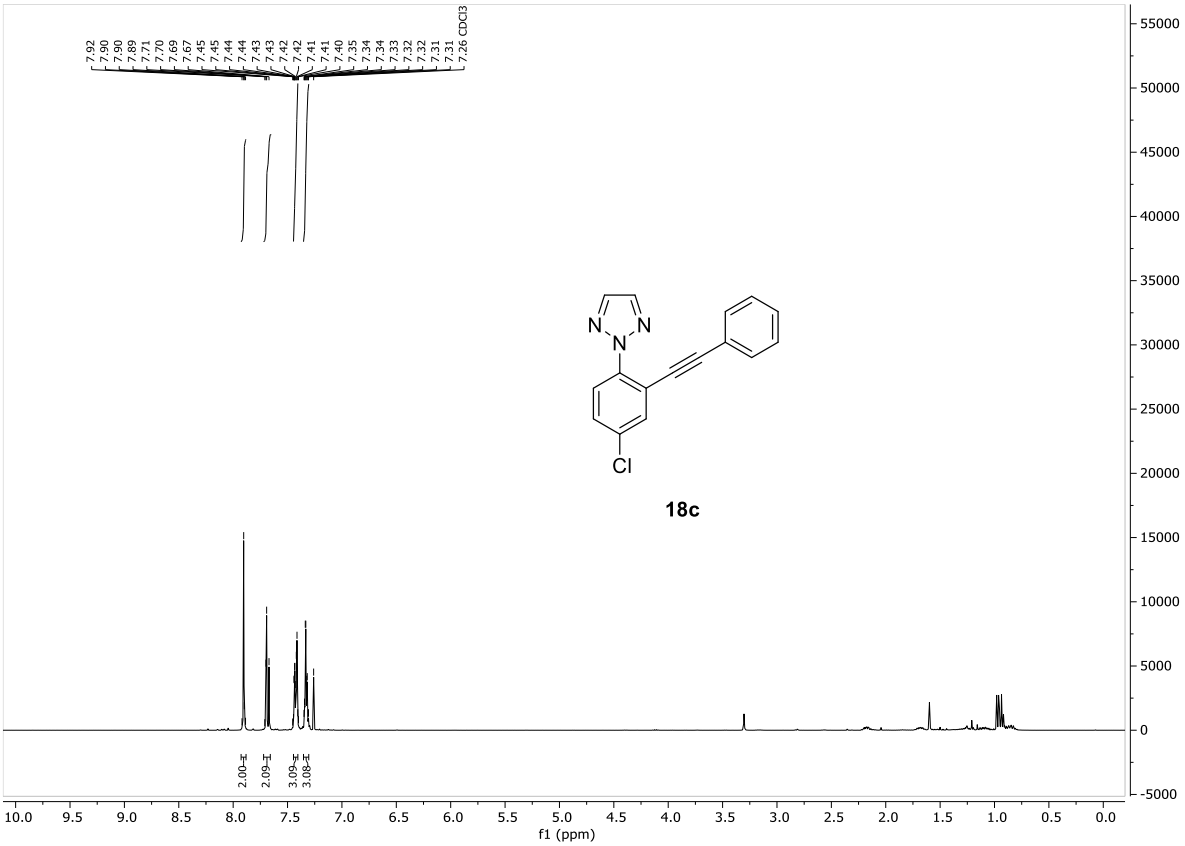
55.22
OMe
N
N
N
Cl
18b
f1 (ppm)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7.70
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7.44
7.44
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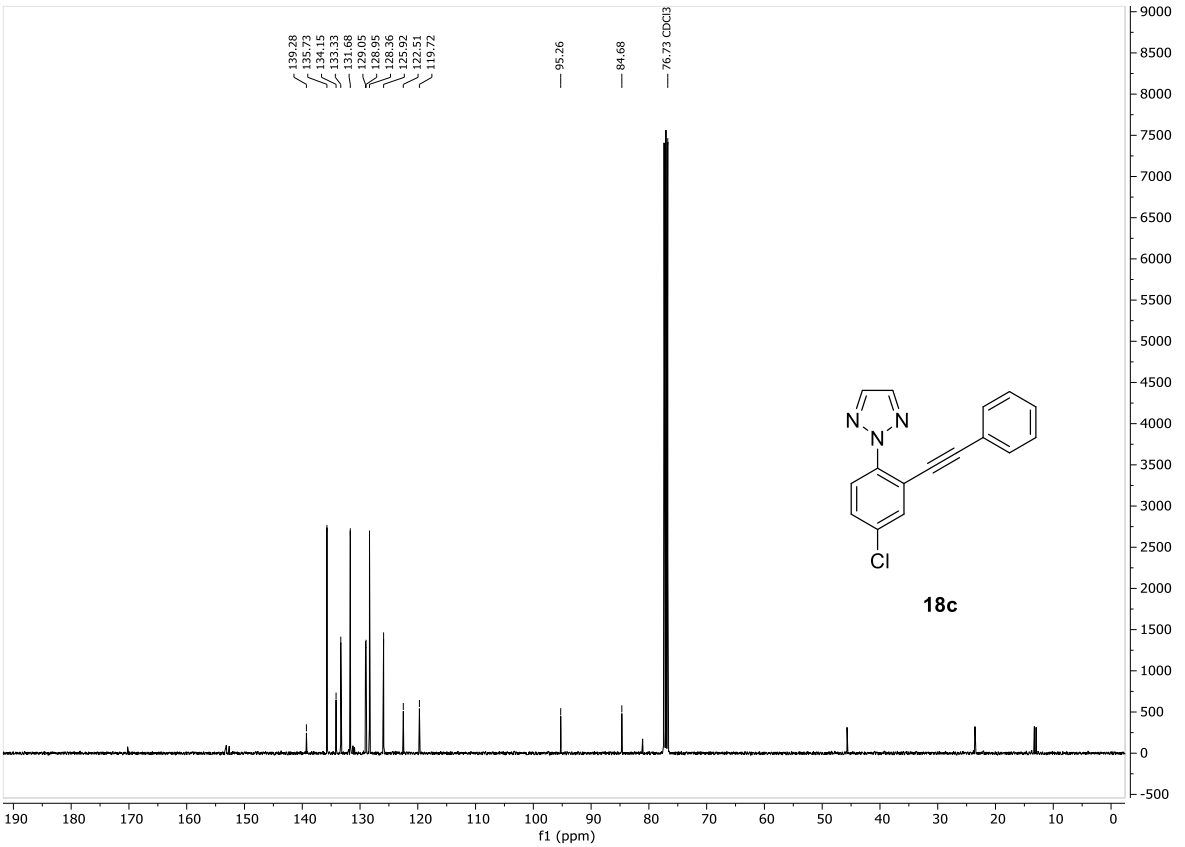
7.43
7.42
7.42
7.41
7.41
7.40
7.35
7.34
7.34
7.33
7.32
7.32
7.31
7.31
7.26 CDCl3
N
N
N
Cl
18c
2.00
2.09
3.09
3.08
f1 (ppm)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129.05
128.95
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119.72
95.26
84.68
76.73 CDCl3
N
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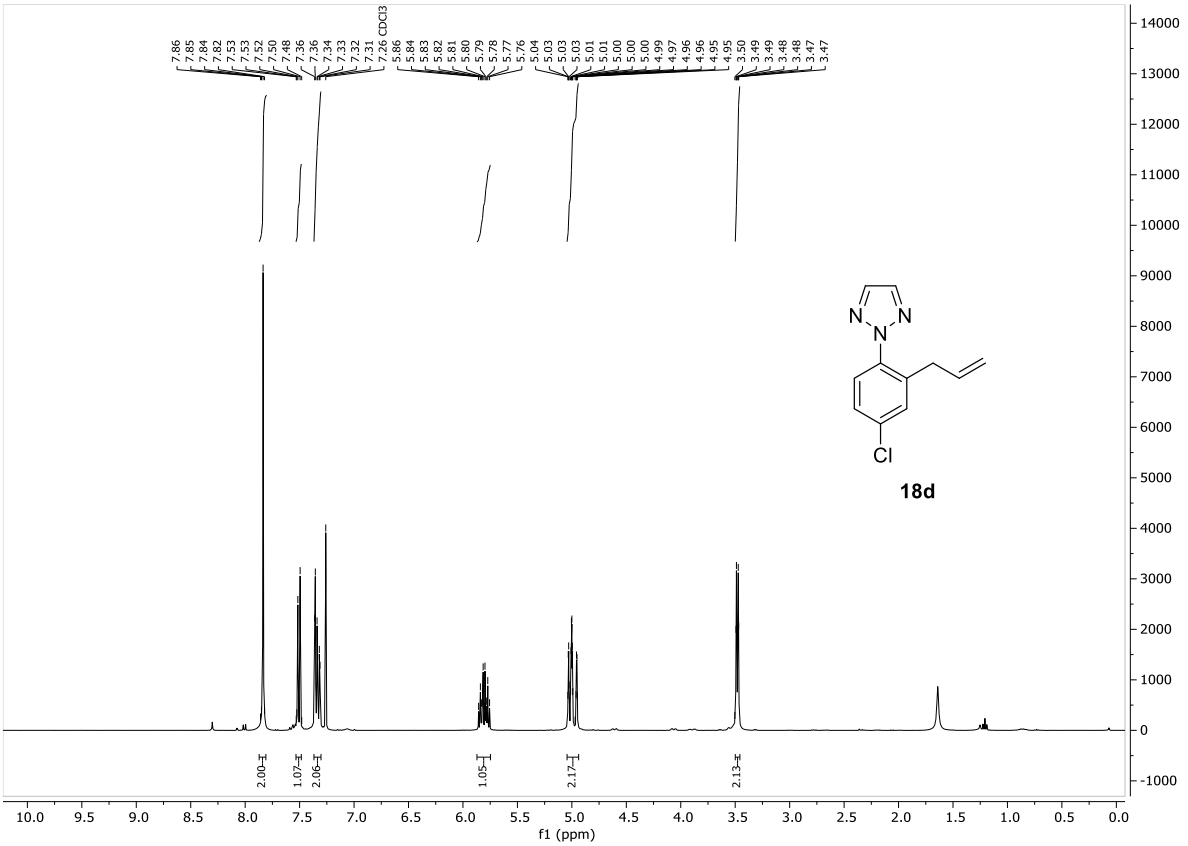
N
Cl
18c
f1 (ppm)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7.52
7.50
7.48
7.36
7.36
7.34
7.33
7.31
7.26
CDCl3
5.86
5.84
5.83
5.82
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5.80
5.79
5.78
5.77
5.76
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3.49
3.48
3.48
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2.06
1.05
2.17
2.13
N
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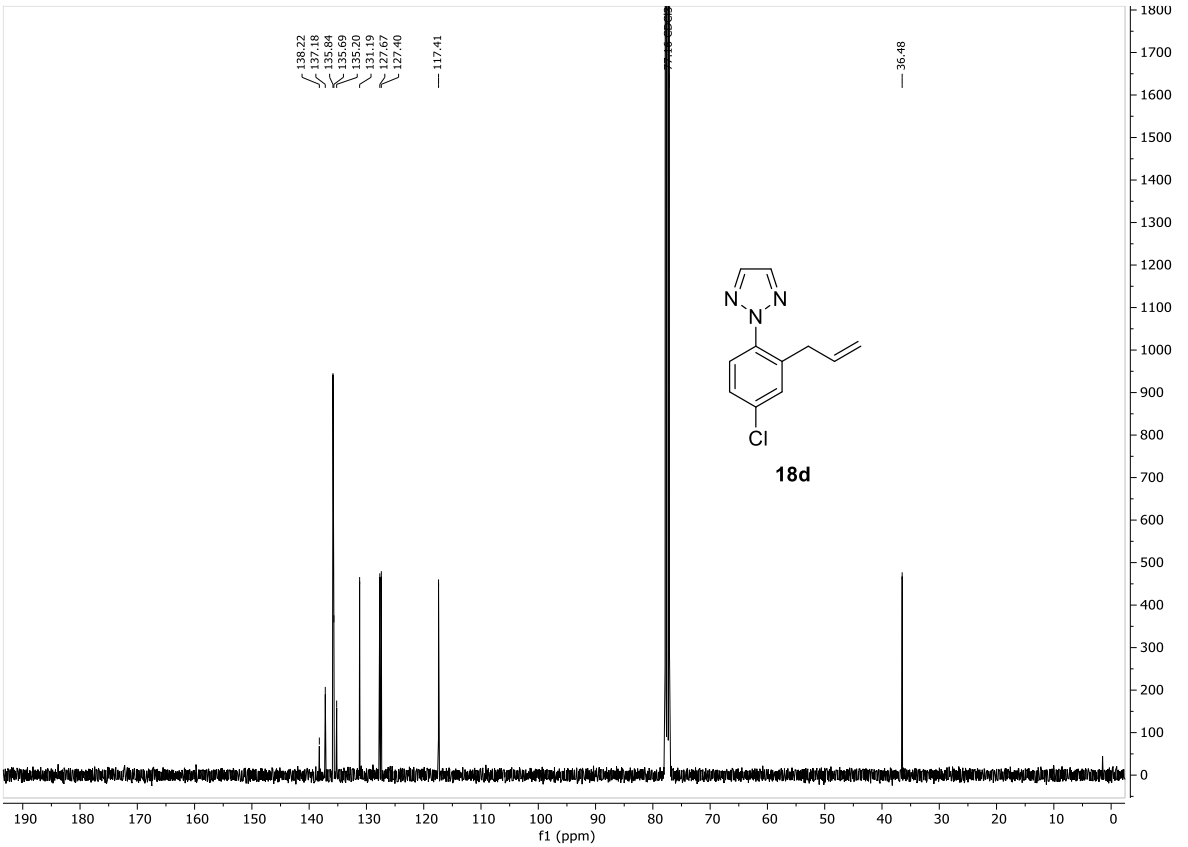
N
Cl
18d
f1 (ppm)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137.18
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121.67
127.40
117.41
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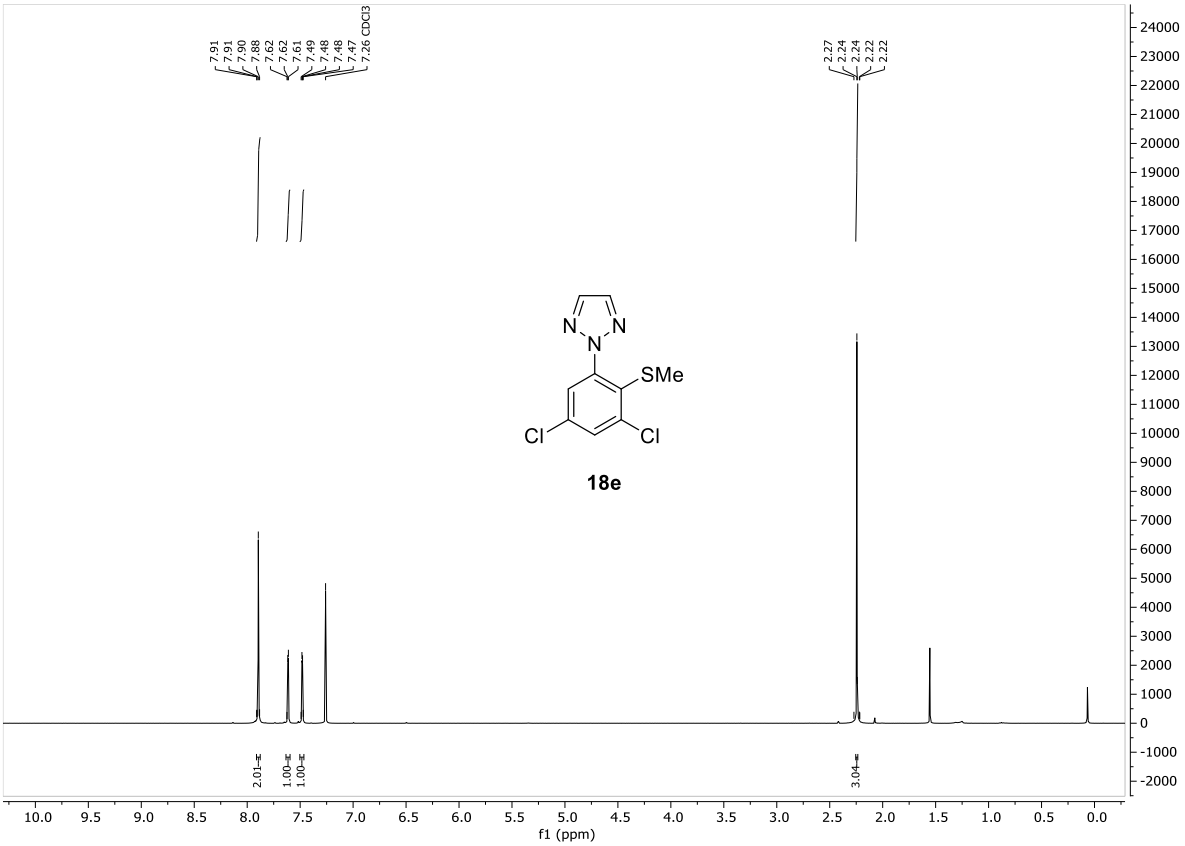
N
N
N
Cl
18d
f1 (ppm)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7.91
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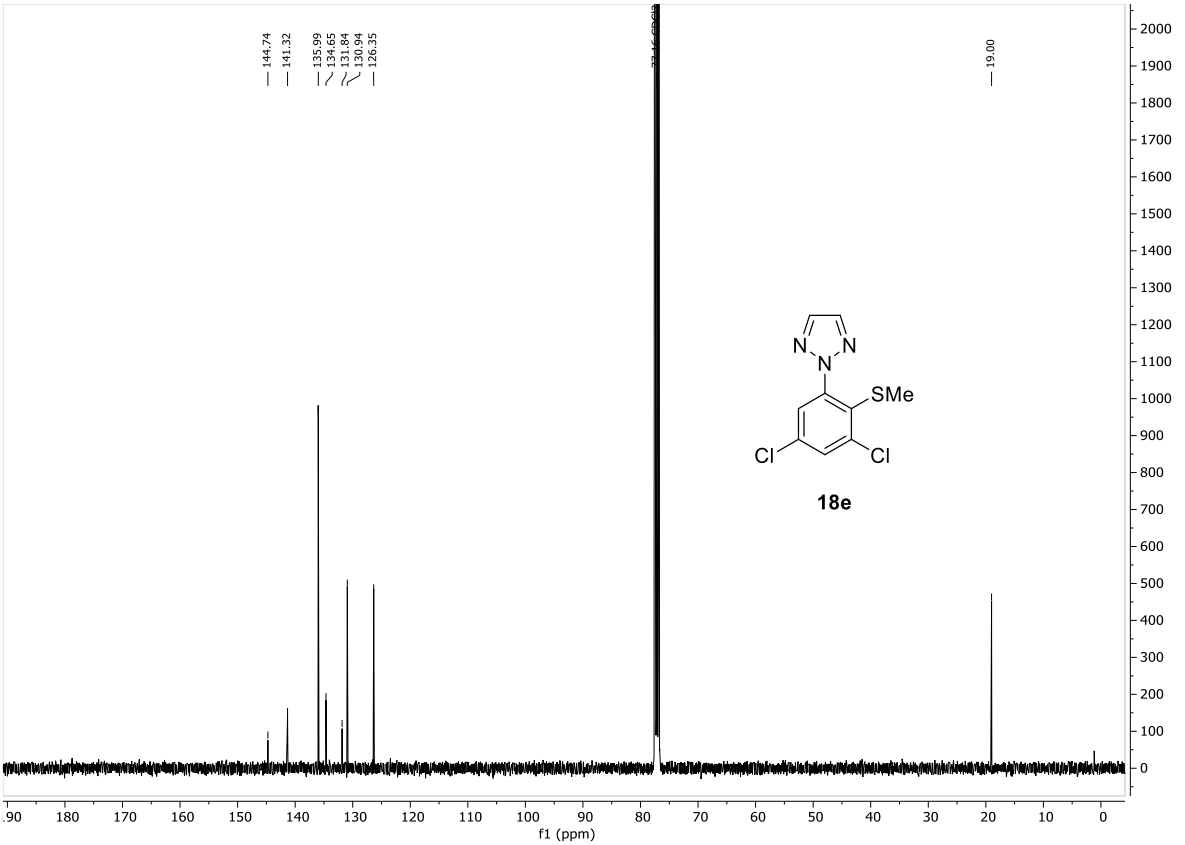
7.62
7.61
7.49
7.48
7.48
7.47
7.26 CDCl3
2.27
2.24
2.24
2.22
2.22
SMe
Cl
Cl
18e
2.01
1.00
1.00
3.04
f1 (ppm)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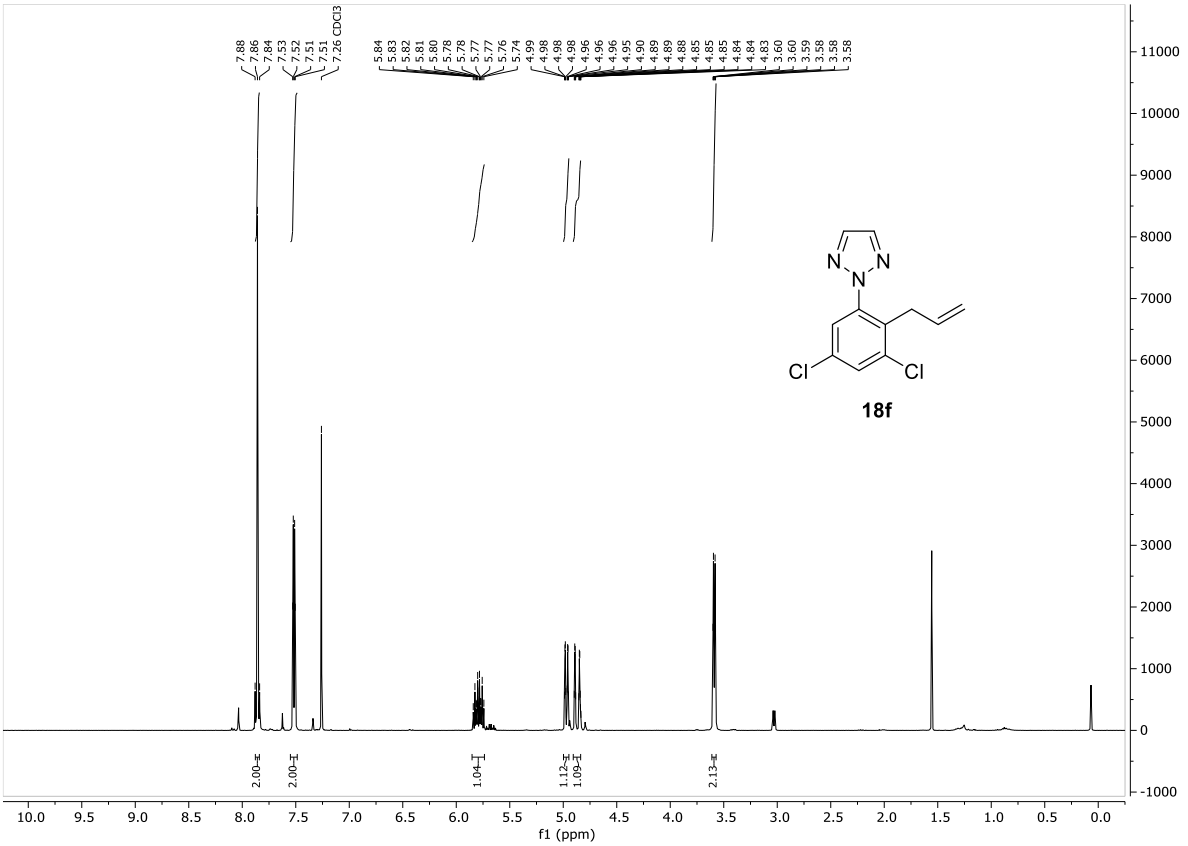
130.94
126.35
77.16 CDCl3
19.00
SMe
Cl
Cl
18e
f1 (ppm)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7.51
7.51
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5.83
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3.60
3.59
3.58
3.58
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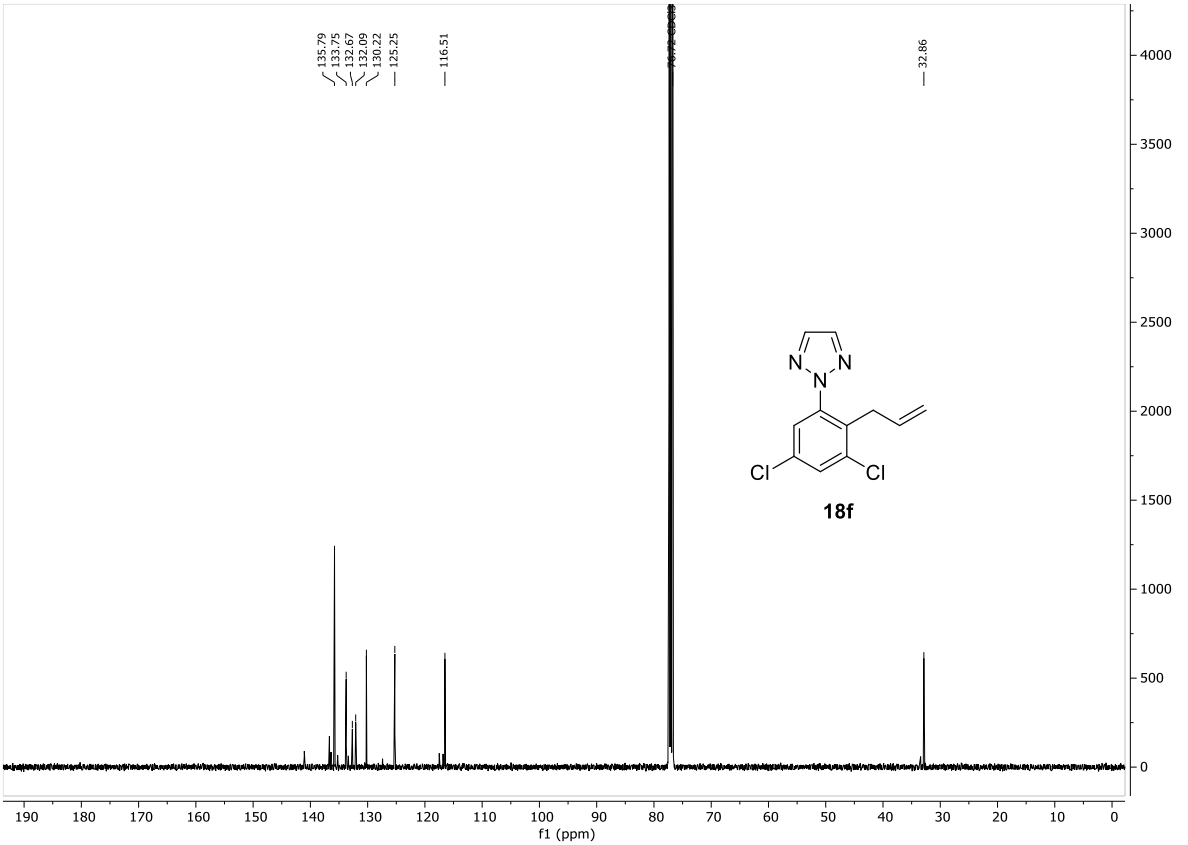
2.00
2.00
1.04
1.12
1.09
2.13
Cl
Cl
18f
f1 (ppm)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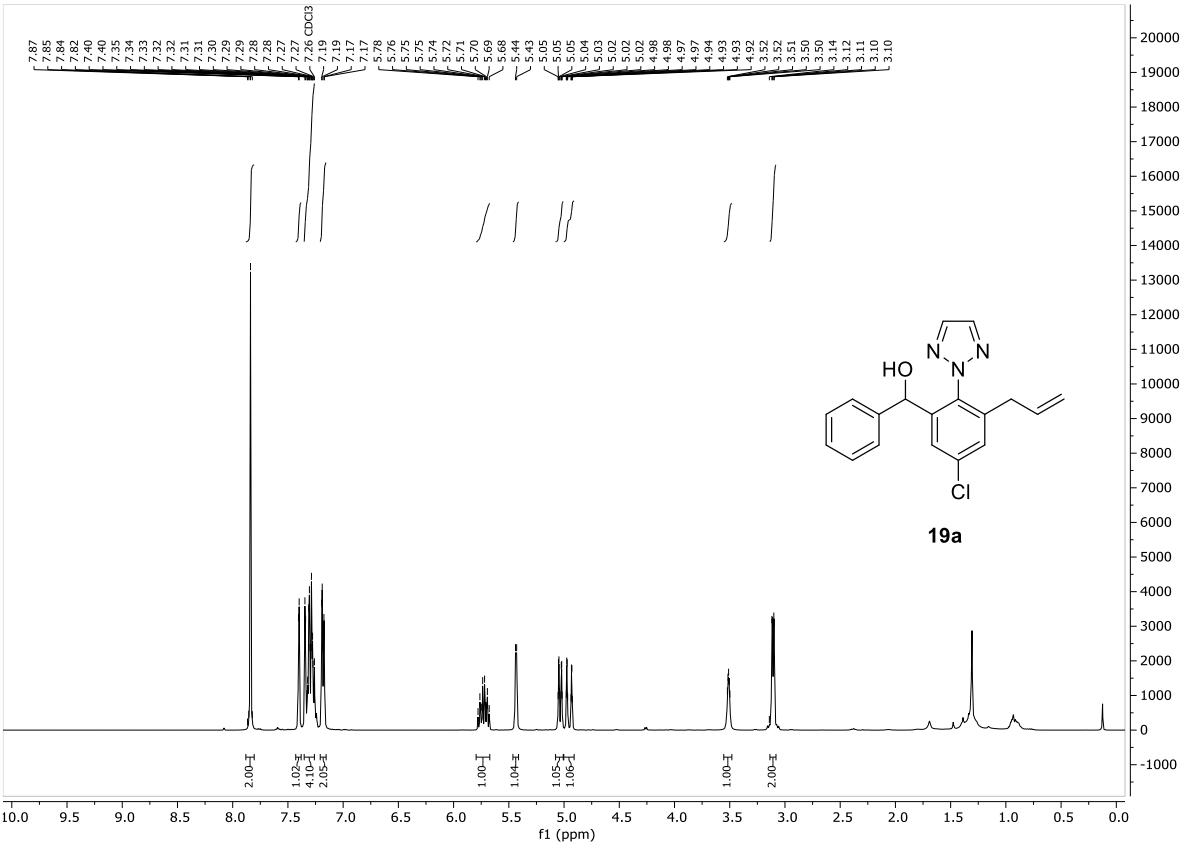
130.22
125.25
116.51
77.16 CDCl3
32.86
Cl
Cl
18f
f1 (ppm)


7.87 7.85 7.84 7.82 7.40 7.40 7.35 7.34 7.33 7.32 7.32 7.31 7.31 7.30 7.29 7.29 7.28 7.28 7.27 7.27 7.26 CDCl3 7.19 7.19 7.17 7.17
5.78 5.76 5.75 5.75 5.74 5.72 5.71 5.70 5.69 5.68 5.44 5.43 5.05 5.05 5.05 5.04 5.03 5.02 5.02 5.02 4.98 4.98 4.97 4.97 4.94 4.93 4.93 4.92 3.52 3.52 3.51 3.50 3.50 3.14 3.12 3.11 3.10 3.10
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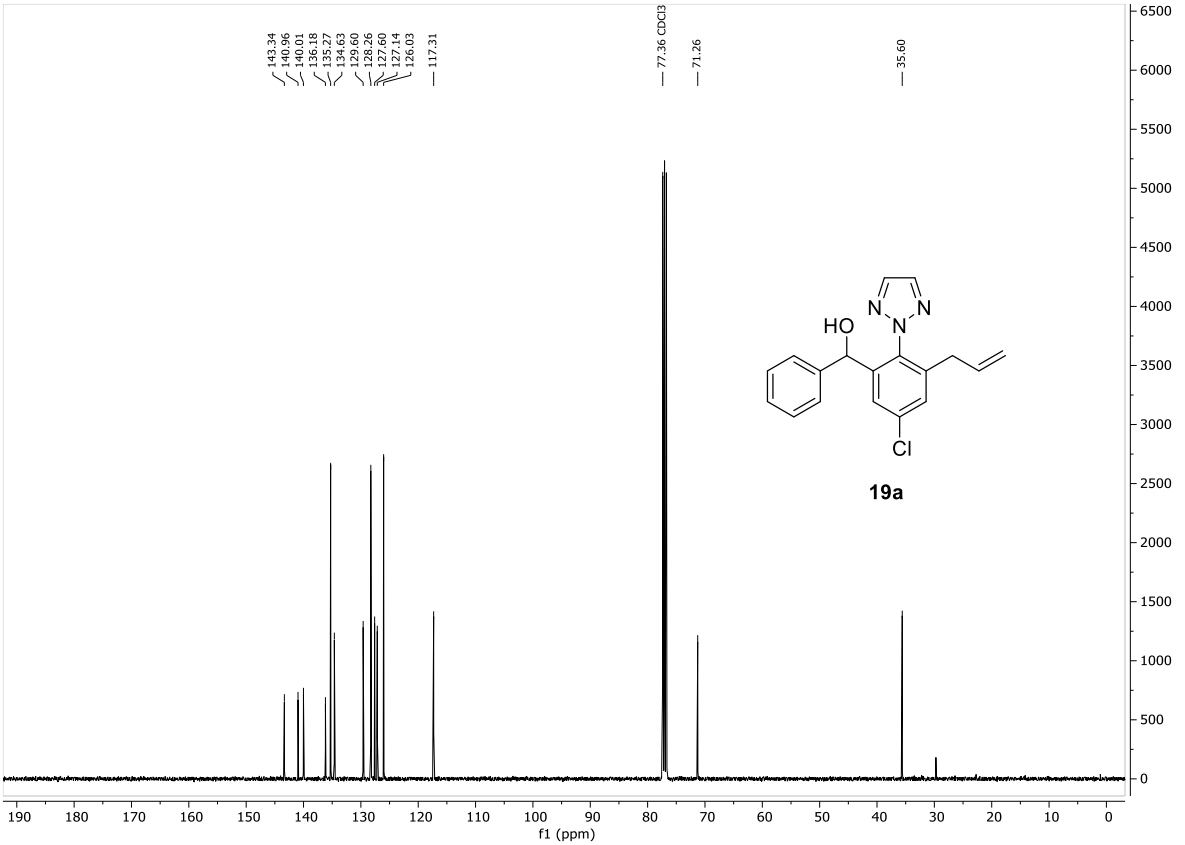
N
Cl
19a
2.00 1.02 4.10 2.05 1.00 1.04 1.05 1.06 1.00 2.00
f1 (ppm)


143.34 140.96 140.01 136.18 135.27 134.63 129.60 128.26 127.60 127.14 126.03 117.31
77.36 CDCl3 71.26 35.60
HO
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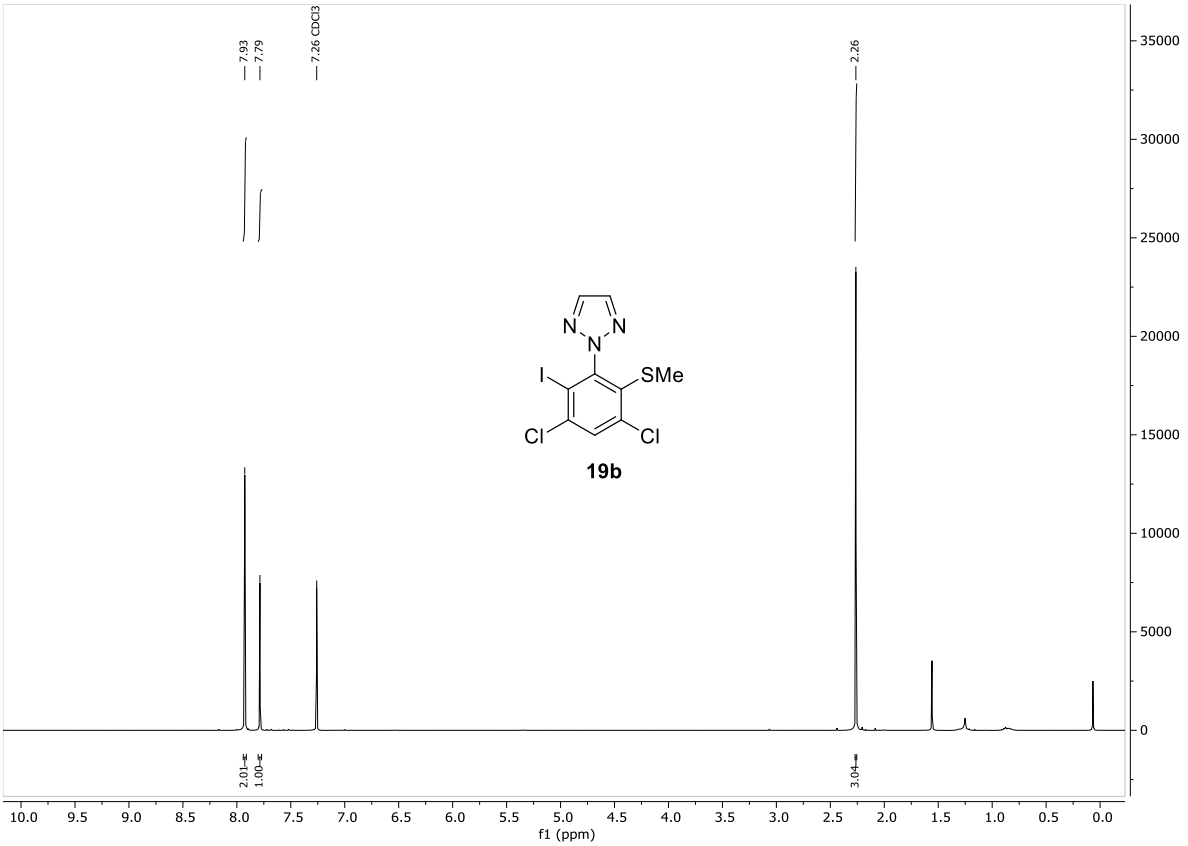
N
N
Cl
19a
f1 (ppm)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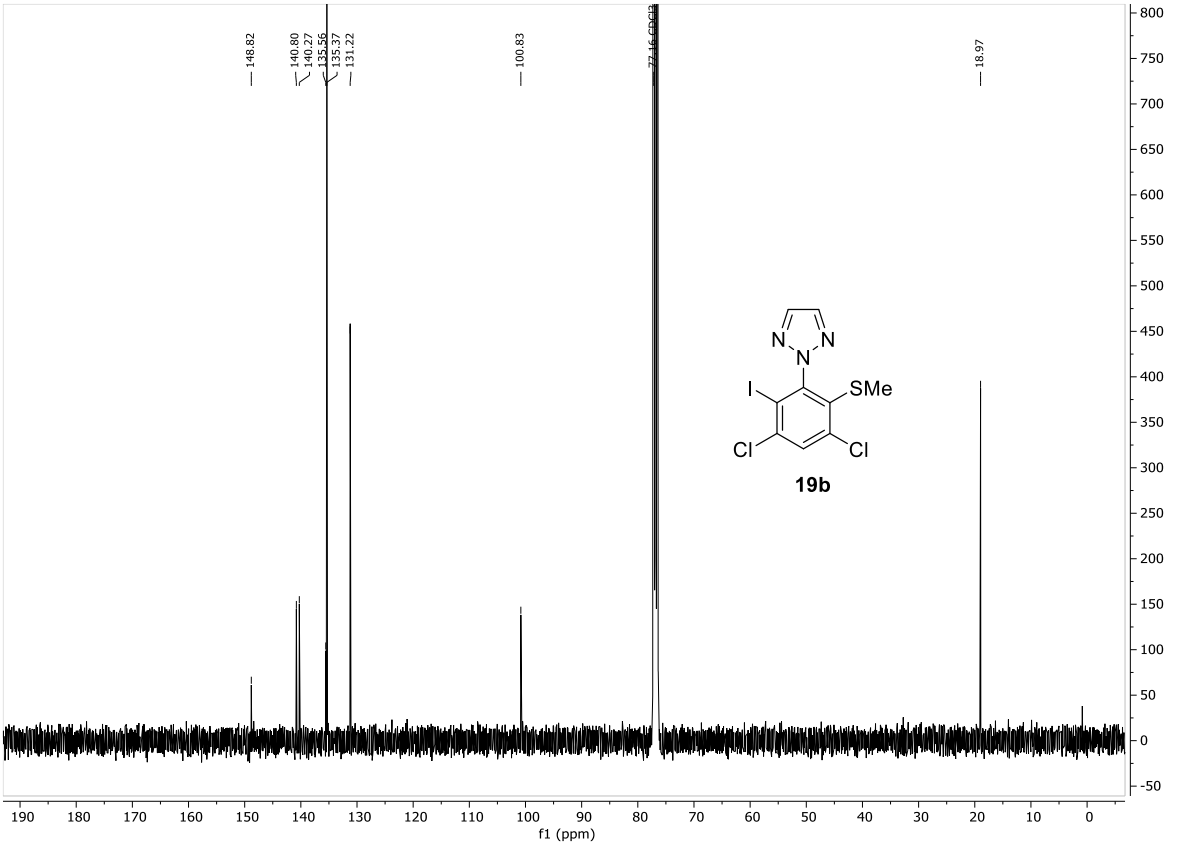
2.26
2.01
1.00
3.04
f1 (ppm)
I
SMe
Cl
Cl
19b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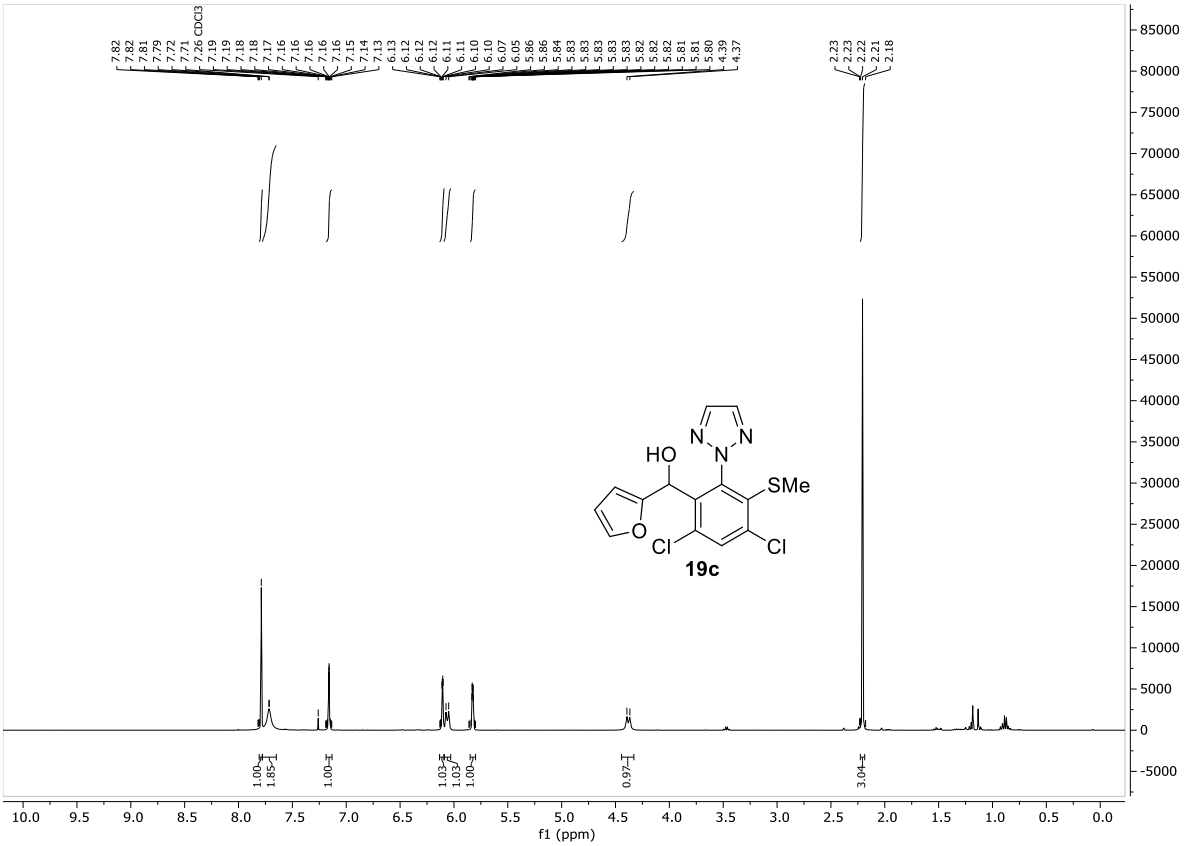
77.16 CDCl3
18.97
f1 (ppm)
I
SMe
Cl
Cl
19b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5.80
4.39
4.37
2.23
2.23
2.22
2.21
2.18
HO
N
N
N
SMe
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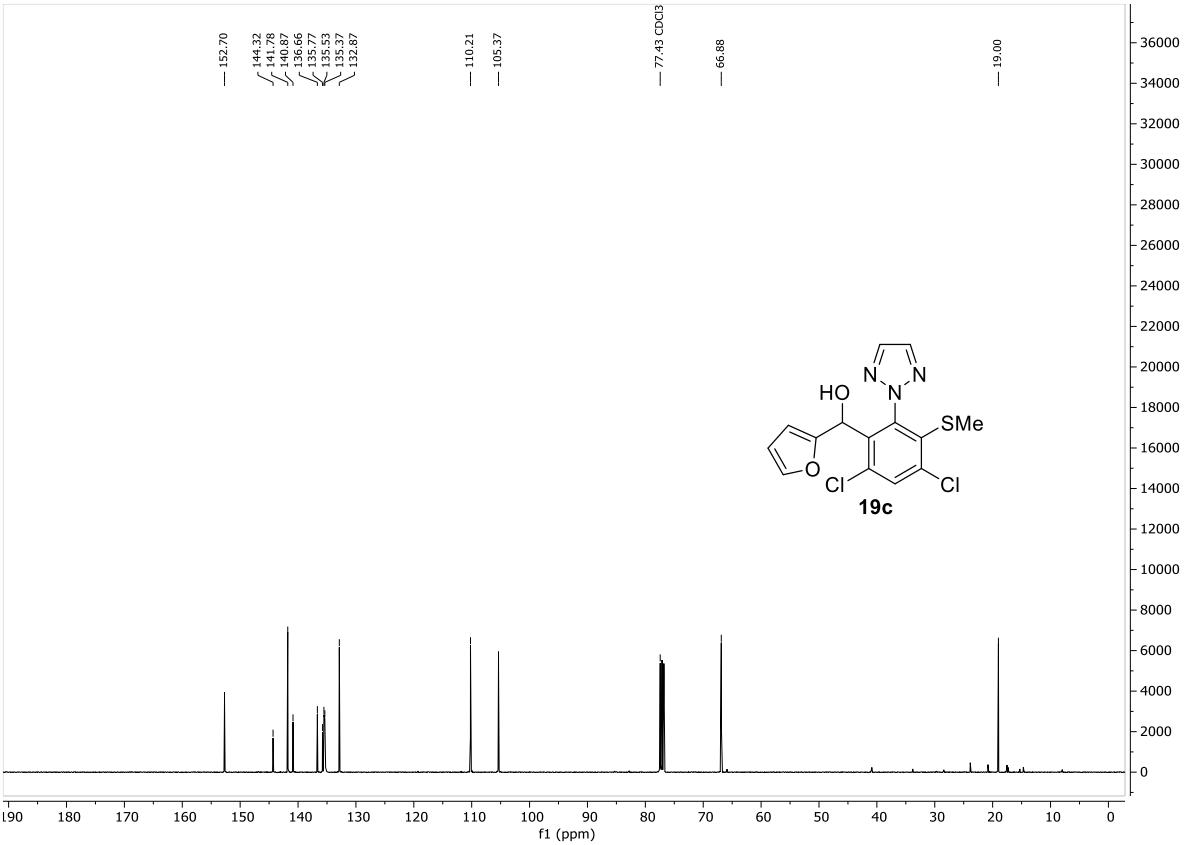
1.00
1.03
1.03
1.00
0.97
3.04
f1 (ppm)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135.77
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135.37
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110.21
105.37
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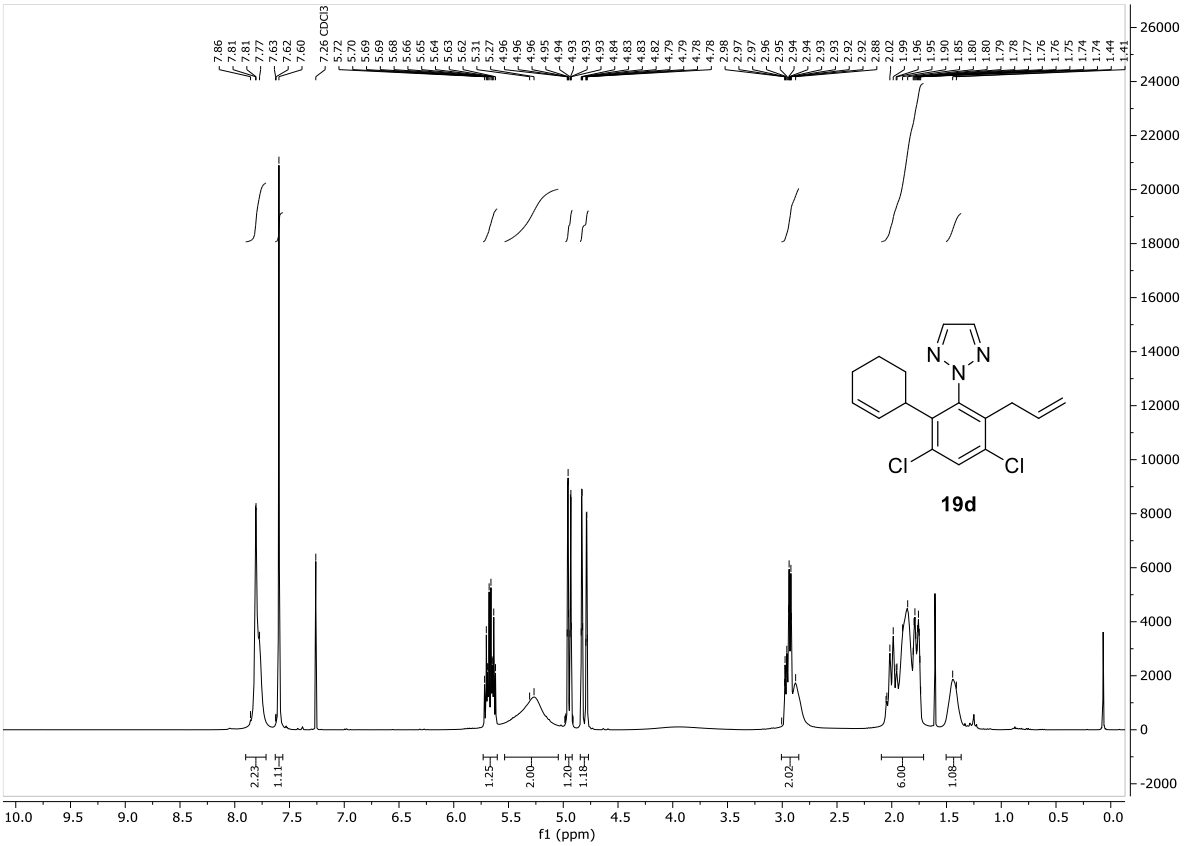
66.88
19.00
HO
N
N
N
SMe
O
Cl
Cl
19c
f1 (ppm)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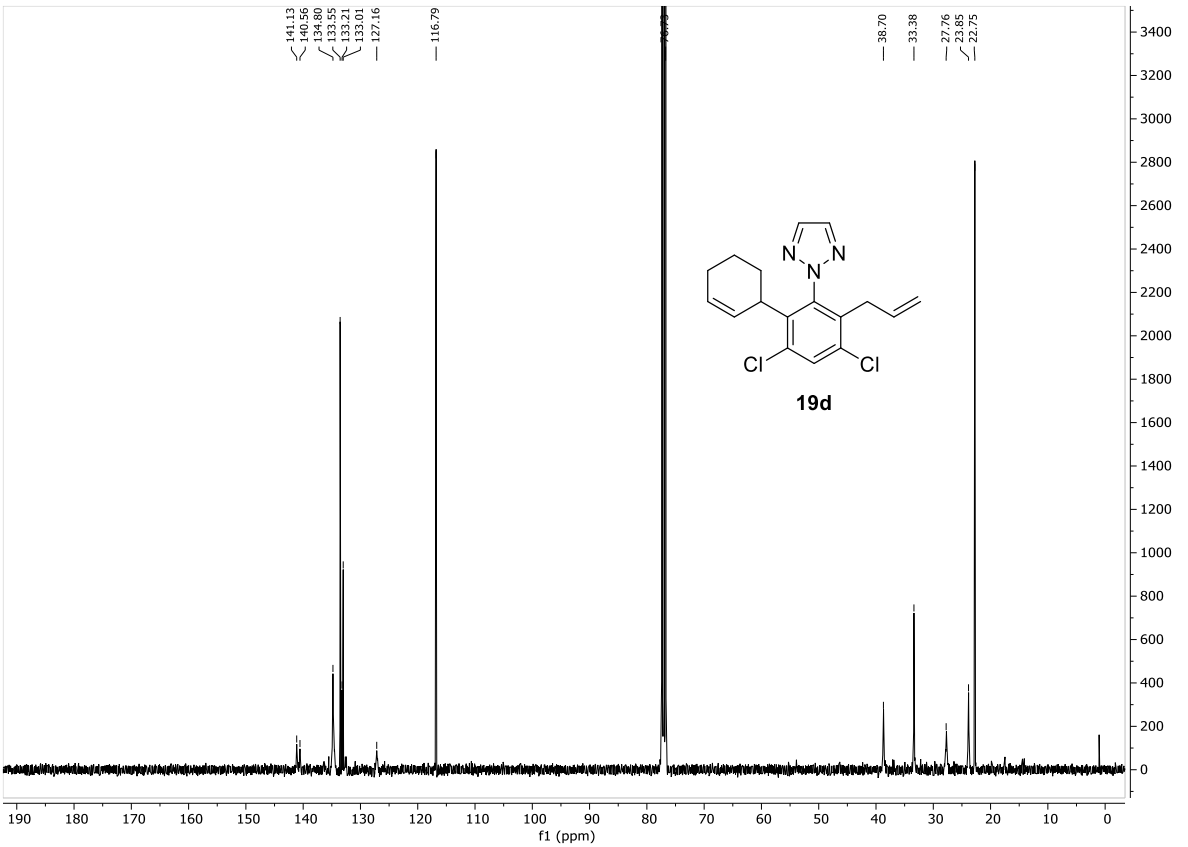
1.20
1.18
2.02
6.00
1.08
f1 (ppm)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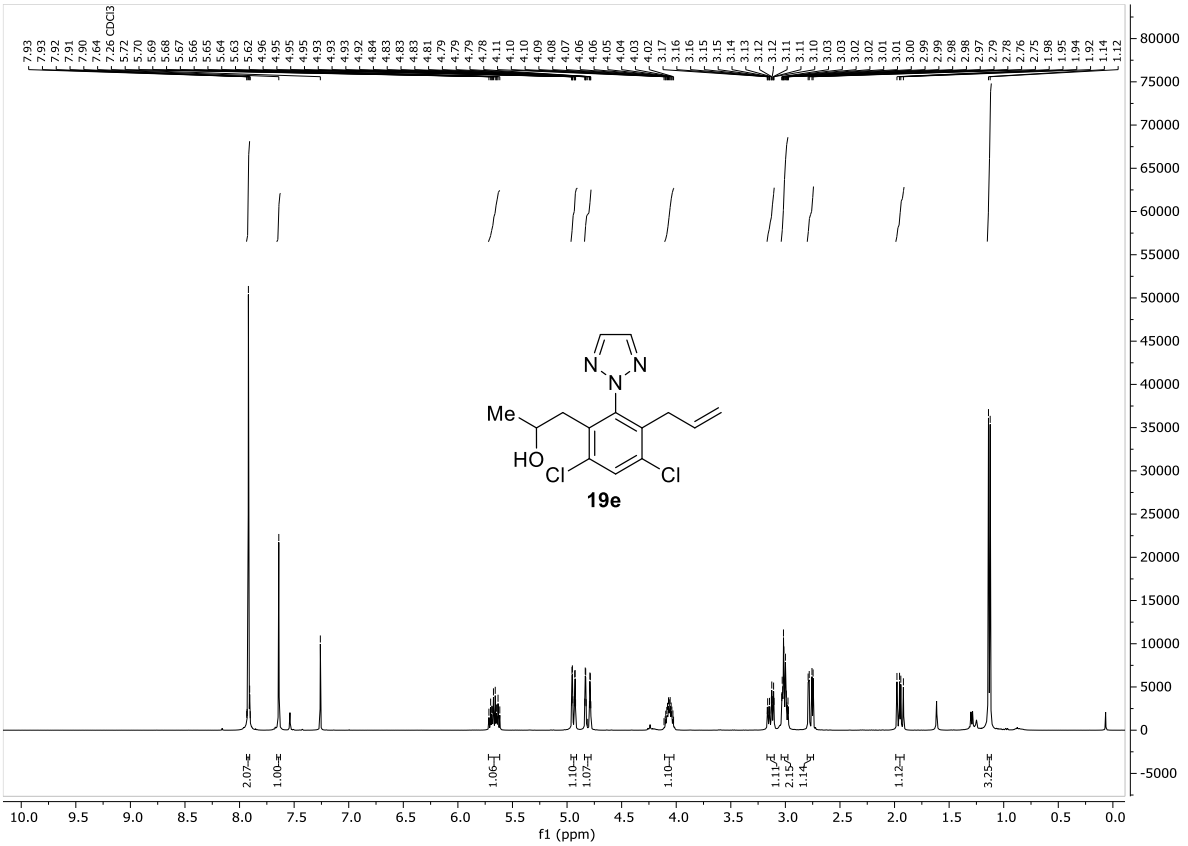
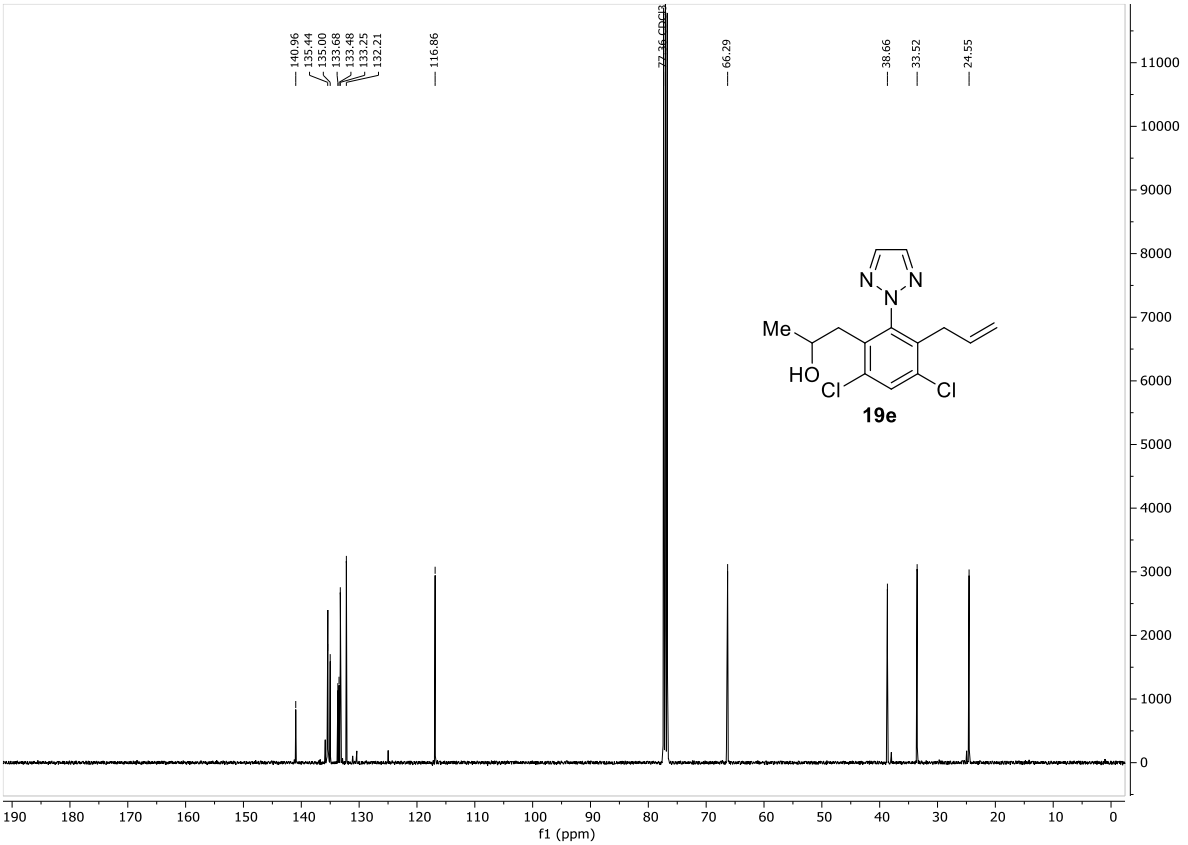
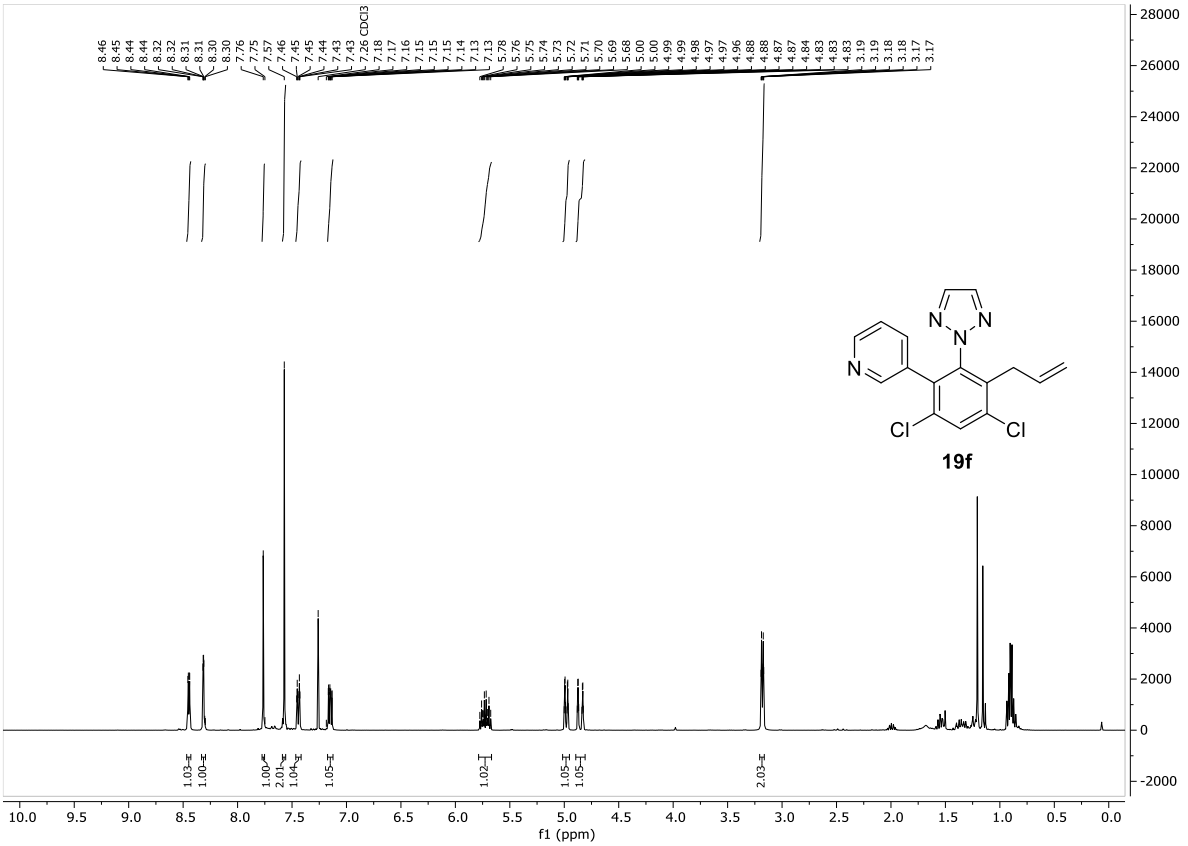
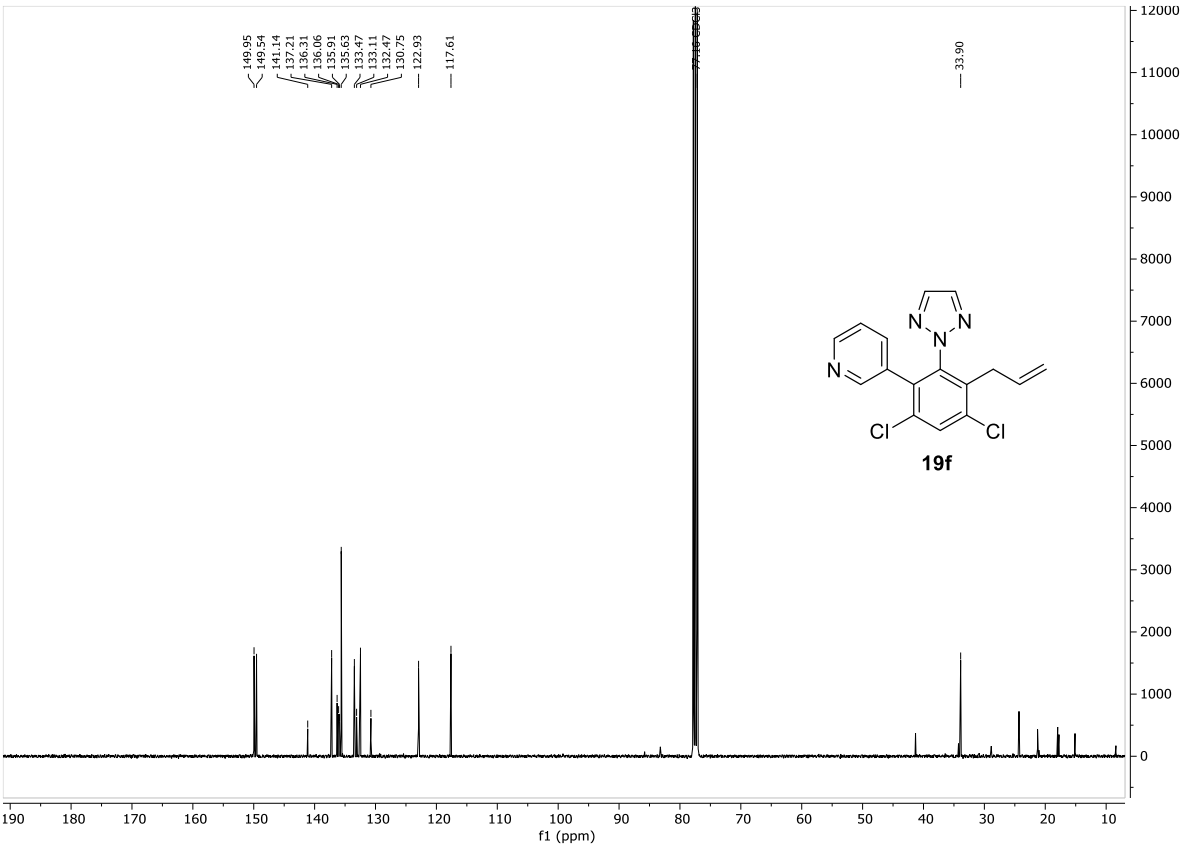
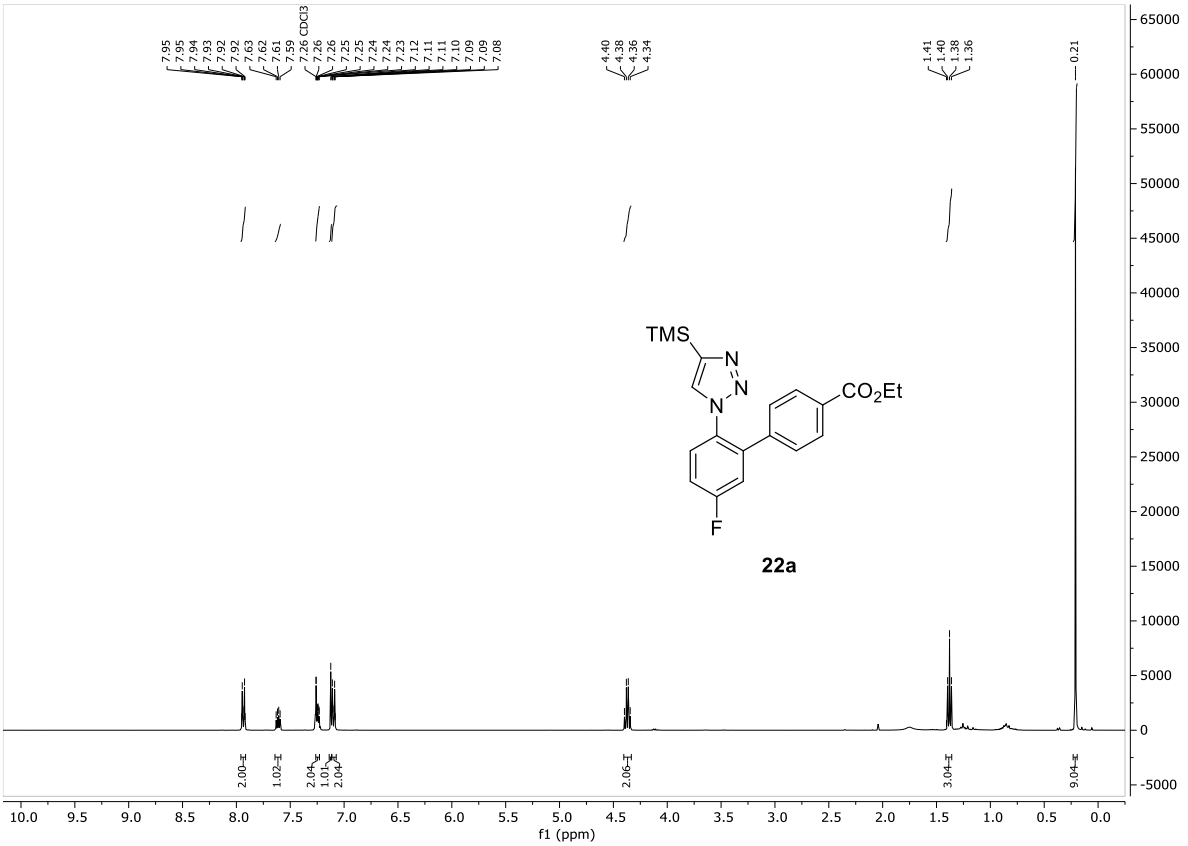
140.56
134.80
133.55
133.21
133.01
127.16
116.79
38.70
33.38
27.76
23.85
22.75
N
N
N
Cl
Cl
19d
f1 (ppm)


19e
f1 (ppm)


19e
f1 (ppm)


8.46 8.45 8.44 8.44 8.32 8.32 8.31 8.31 8.30 8.30 7.76 7.75 7.57 7.46 7.45 7.45 7.44 7.43 7.43 7.26 CDCl3 7.18 7.17 7.16 7.15 7.15 7.15 7.14 7.13 7.13 5.78 5.76 5.75 5.74 5.73 5.72 5.71 5.70 5.69 5.68 5.00 5.00 4.99 4.99 4.98 4.97 4.97 4.96 4.88 4.88 4.87 4.87 4.84 4.83 4.83 4.83 3.19 3.19 3.18 3.18 3.17 3.17
1.03 1.00 1.00 2.01 1.04 1.05 1.02 1.05 1.05 2.03
N N N N Cl Cl
19f
f1 (ppm)


149.95 149.54 141.14 137.21 136.31 136.06 135.91 135.63 133.47 133.11 132.47 130.75 122.93 117.61 77.16 33.90
N N N N Cl Cl
19f
f1 (ppm)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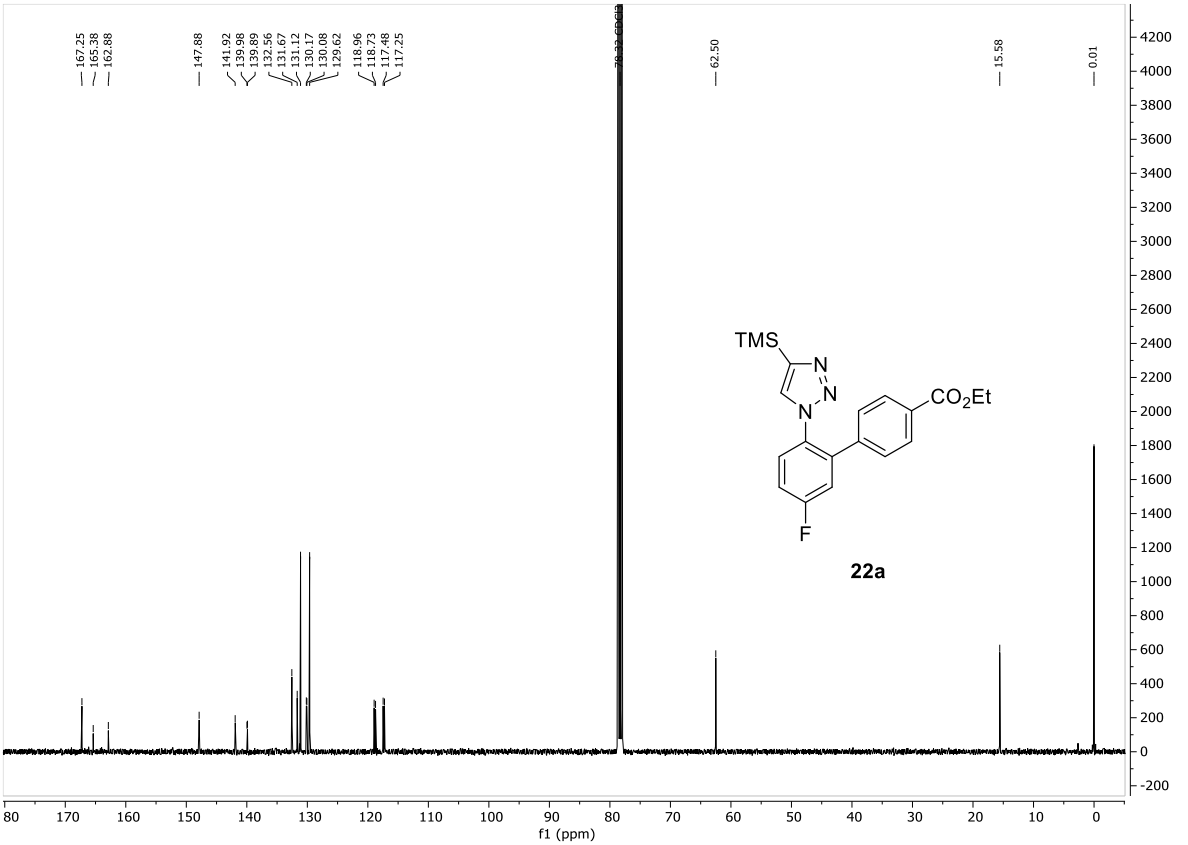
7.95
7.94
7.93
7.92
7.92
7.63
7.62
7.61
7.59
CDCl3
7.26
7.26
7.26
7.25
7.25
7.24
7.24
7.23
7.12
7.11
7.11
7.10
7.09
7.09
7.08
4.40
4.38
4.36
4.34
1.41
1.40
1.38
1.36
0.21
TMS
N
N
N
CO2Et
F
22a
2.00
1.02
2.04
1.01
2.04
2.06
3.04
9.04
f1 (ppm)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139.98
139.89
132.56
131.67
131.12
130.17
130.08
129.62
118.96
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117.48
117.25
62.50
15.58
0.01
TMS
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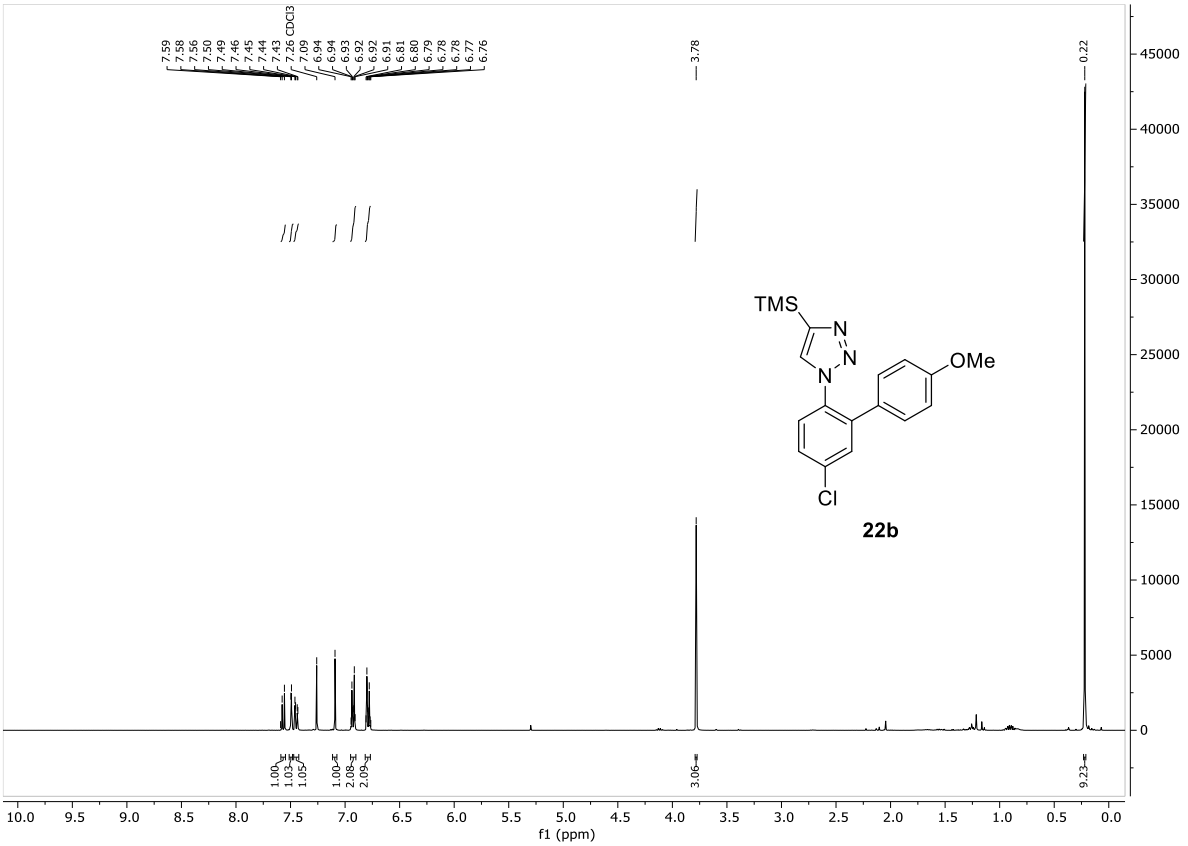
N
N
CO2Et
F
22a
f1 (ppm)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7.58
7.56
7.50
7.49
7.46
7.45
7.44
7.43
7.26 CDCl3
7.09
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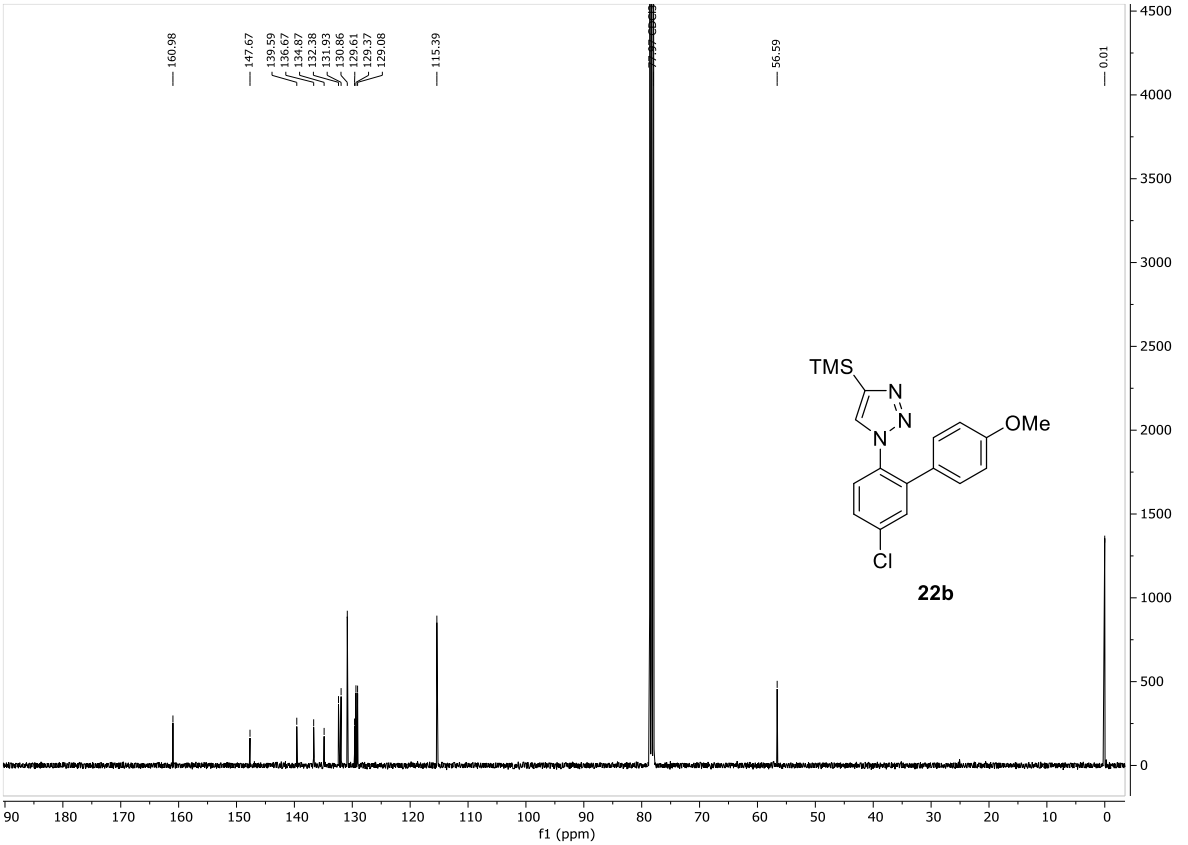
6.94
6.93
6.92
6.92
6.91
6.81
6.80
6.79
6.78
6.78
6.77
6.76
3.78
0.22
TMS
N
N
N
OMe
Cl
22b
1.00
1.03
1.05
1.00
2.08
2.09
3.06
9.23
f1 (ppm)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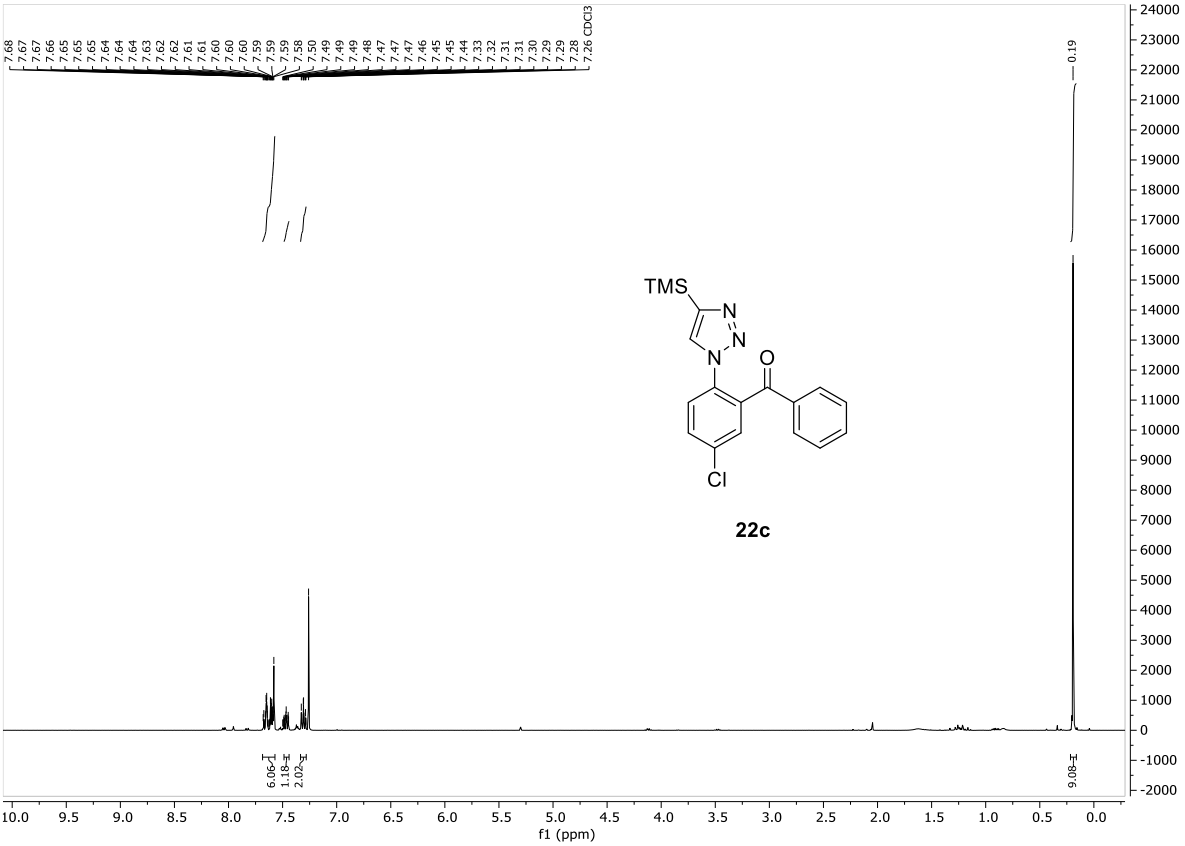
147.67
139.59
136.67
134.87
132.38
131.93
130.86
129.61
129.37
129.08
115.39
56.59
0.01
TMS
N
N
N
OMe
Cl
22b
f1 (ppm)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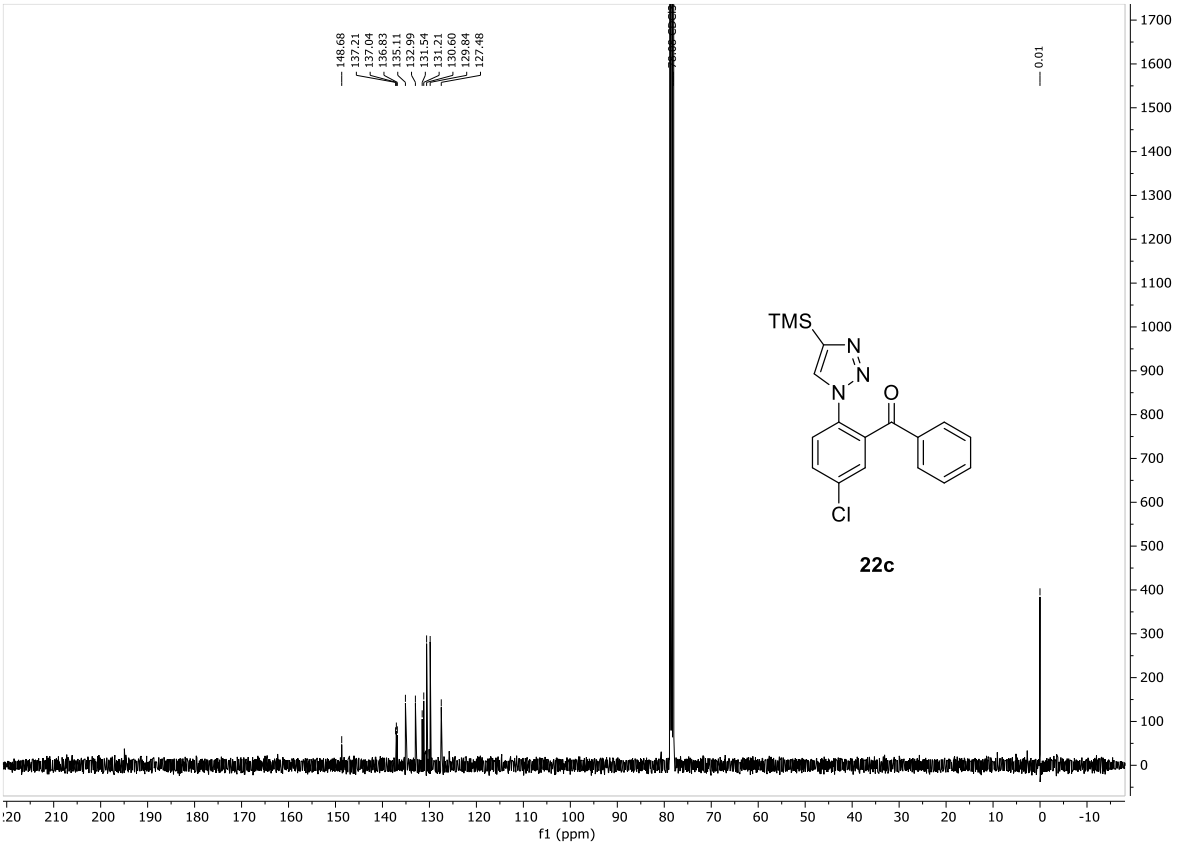
N
O
Cl
22c
f1 (ppm)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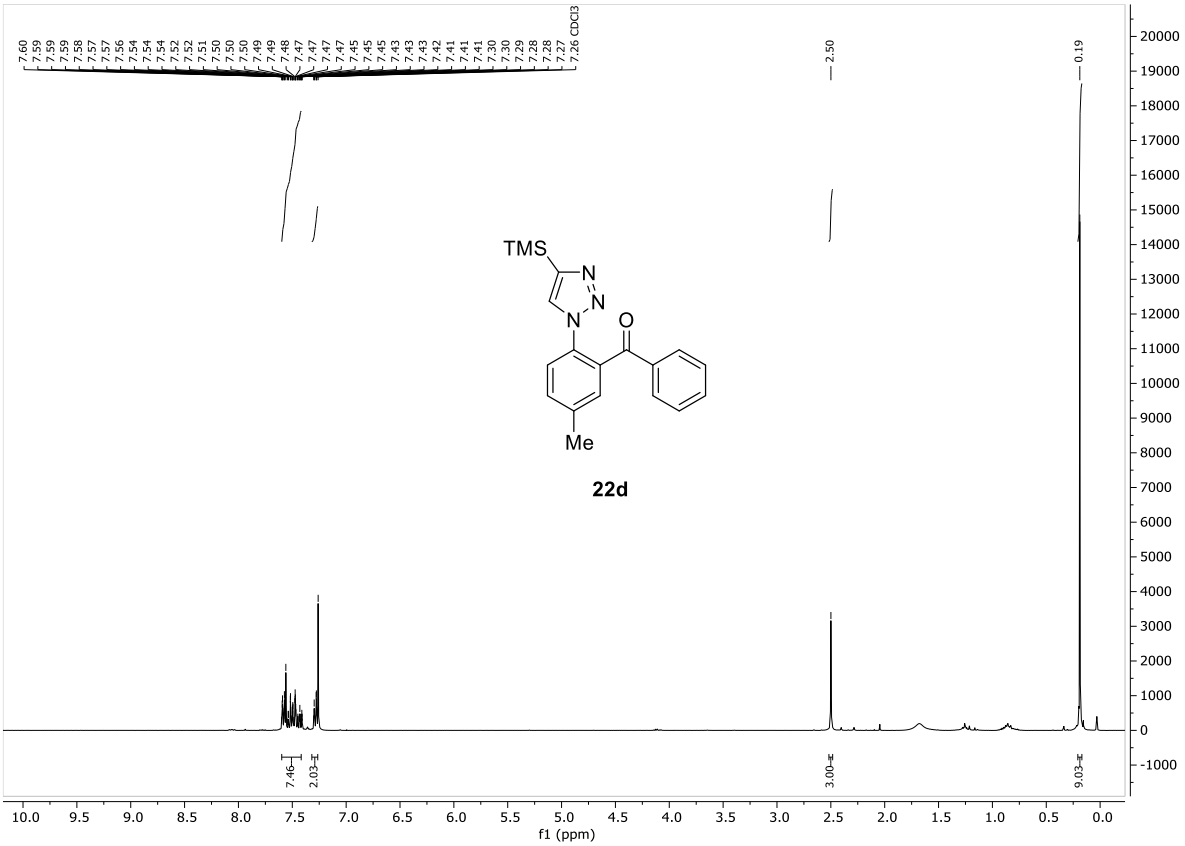
N
O
Cl
22c
f1 (ppm)


TMS
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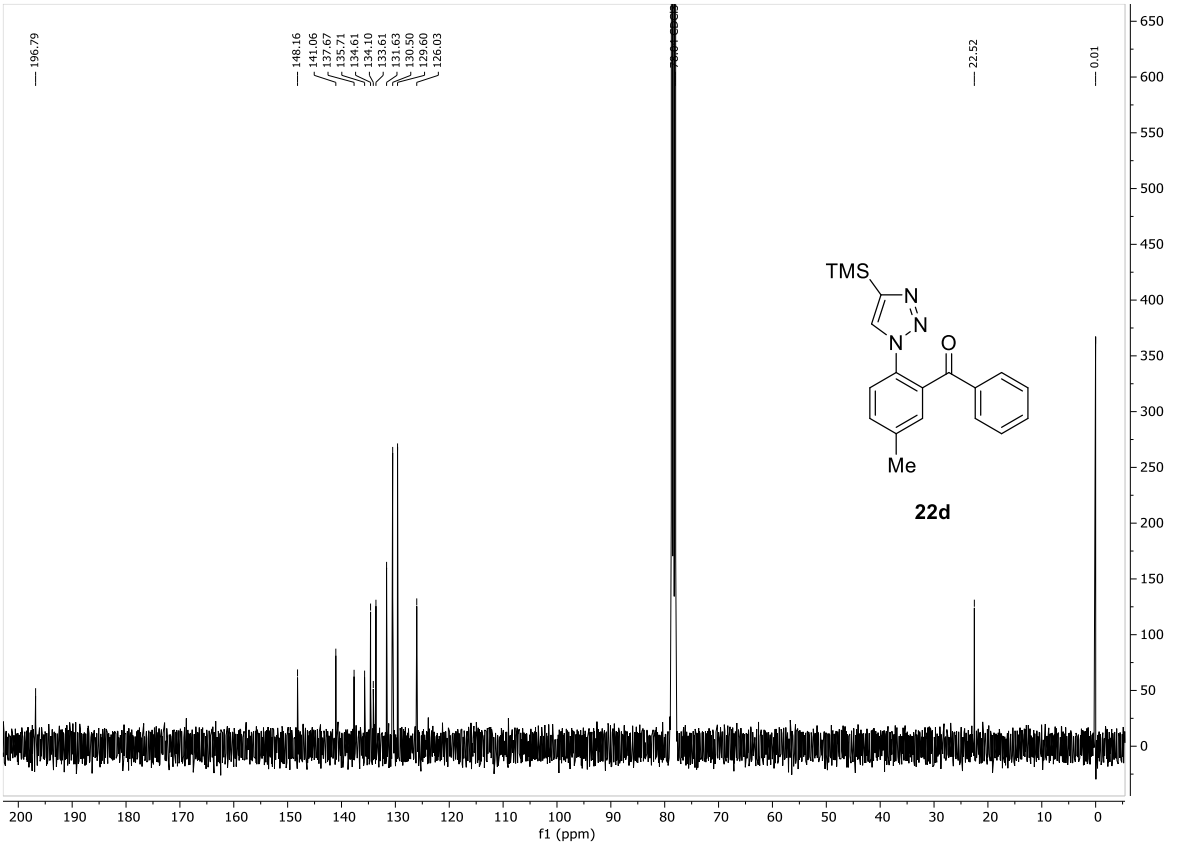
N
N
O
Me
22d
f1 (ppm)


TMS
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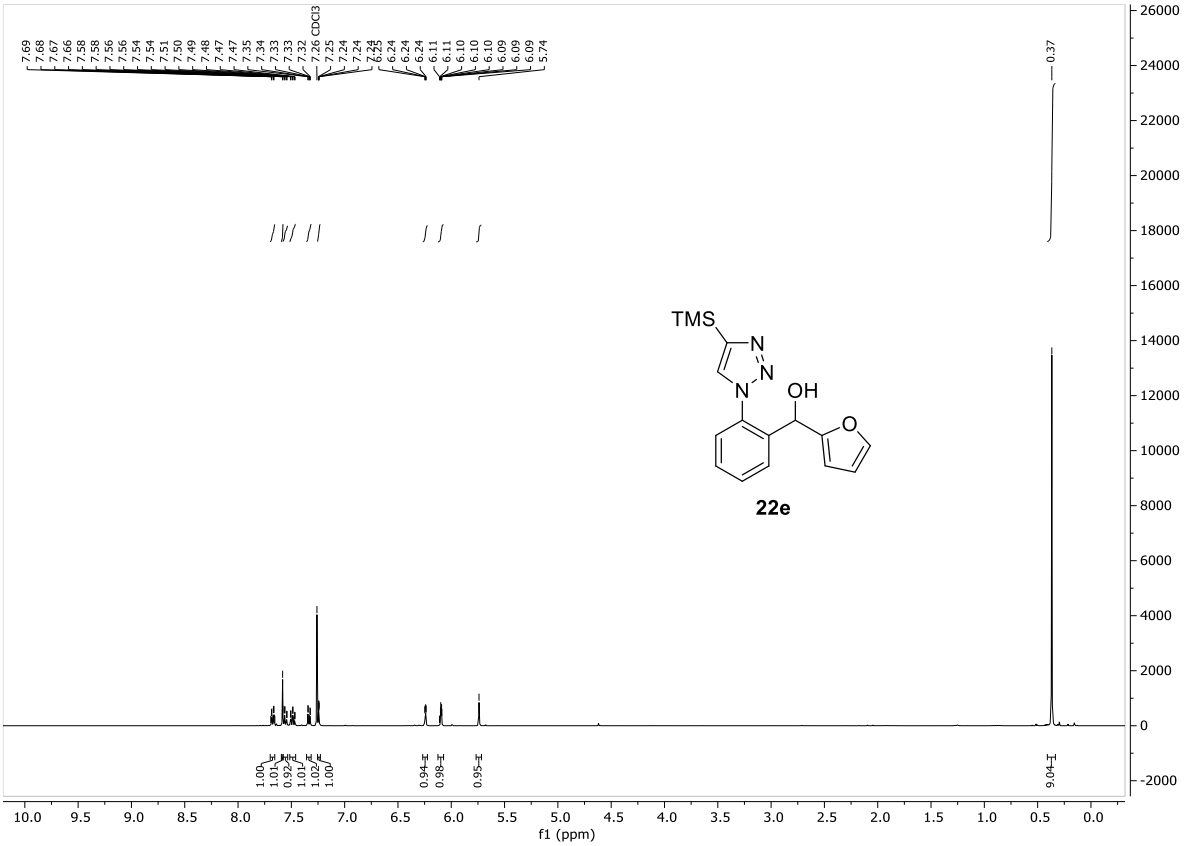
N
N
O
Me
22d
f1 (ppm)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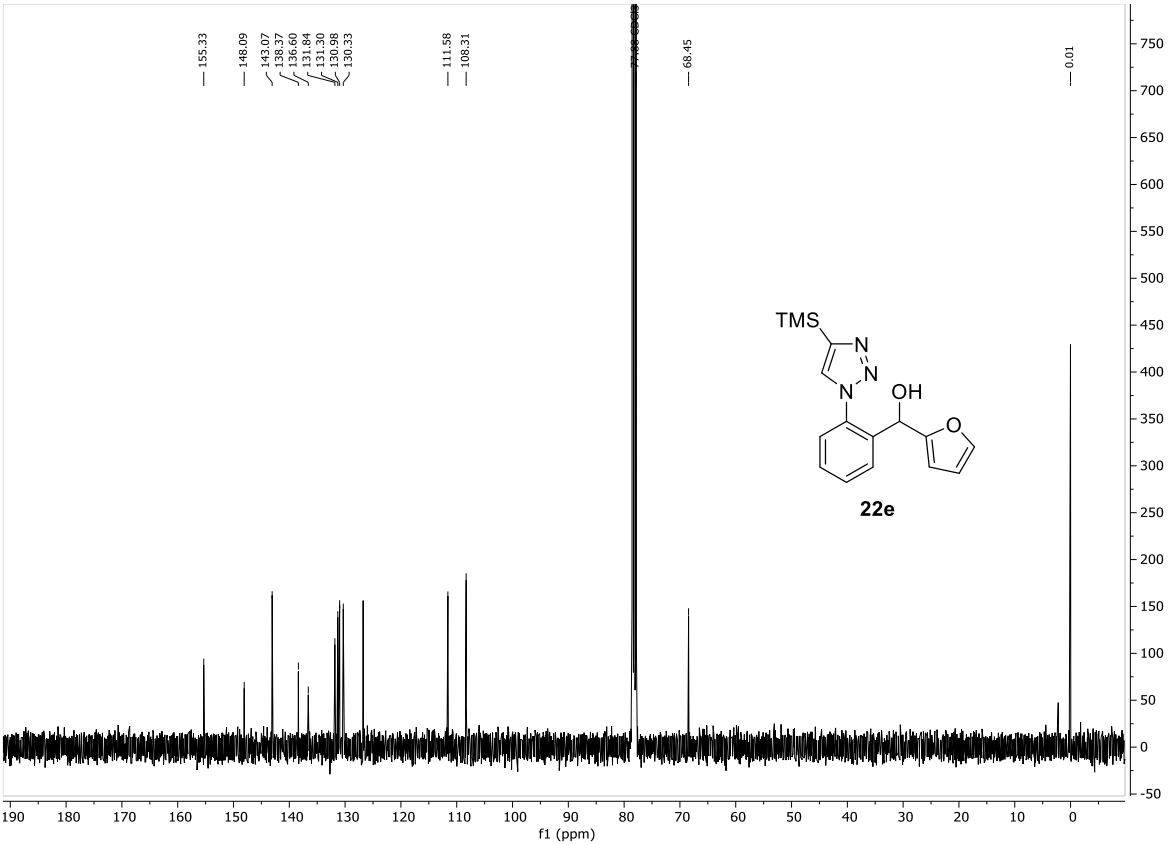
N
N
N
OH
O
22e
f1 (ppm)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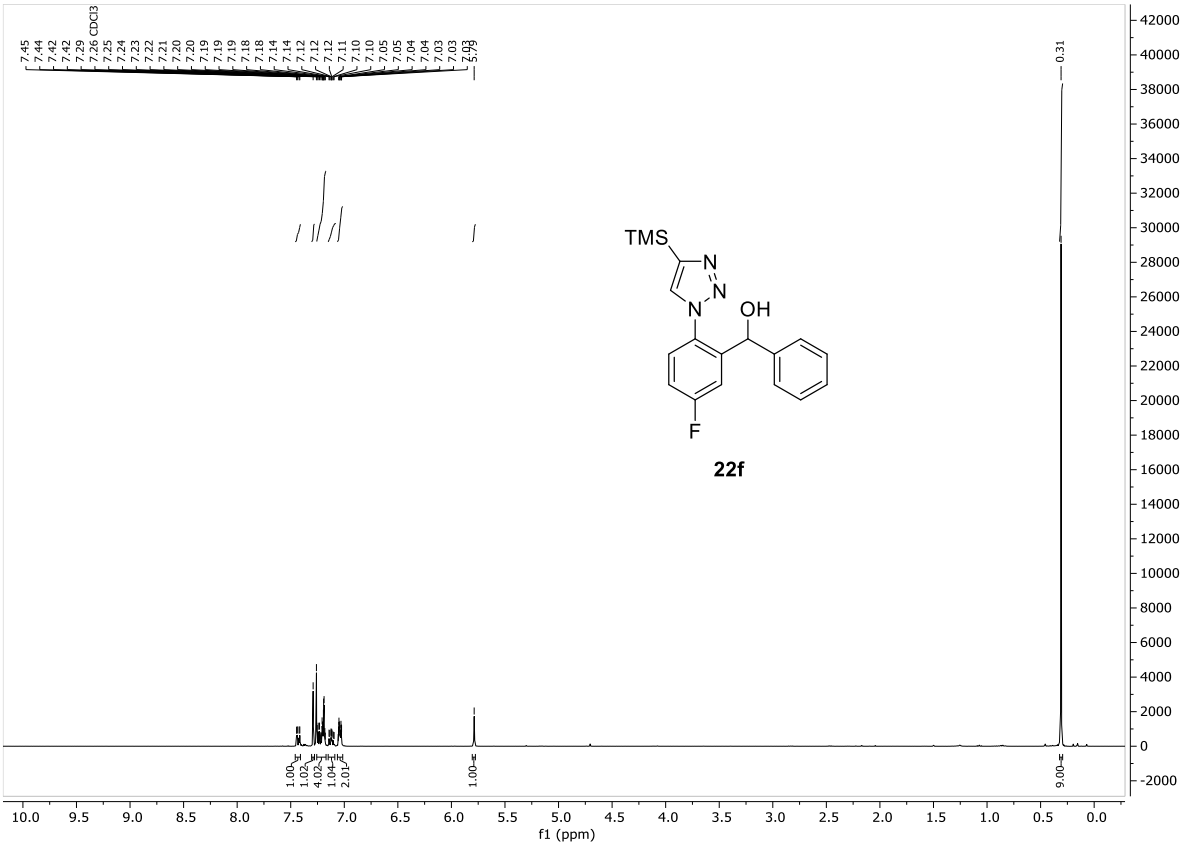
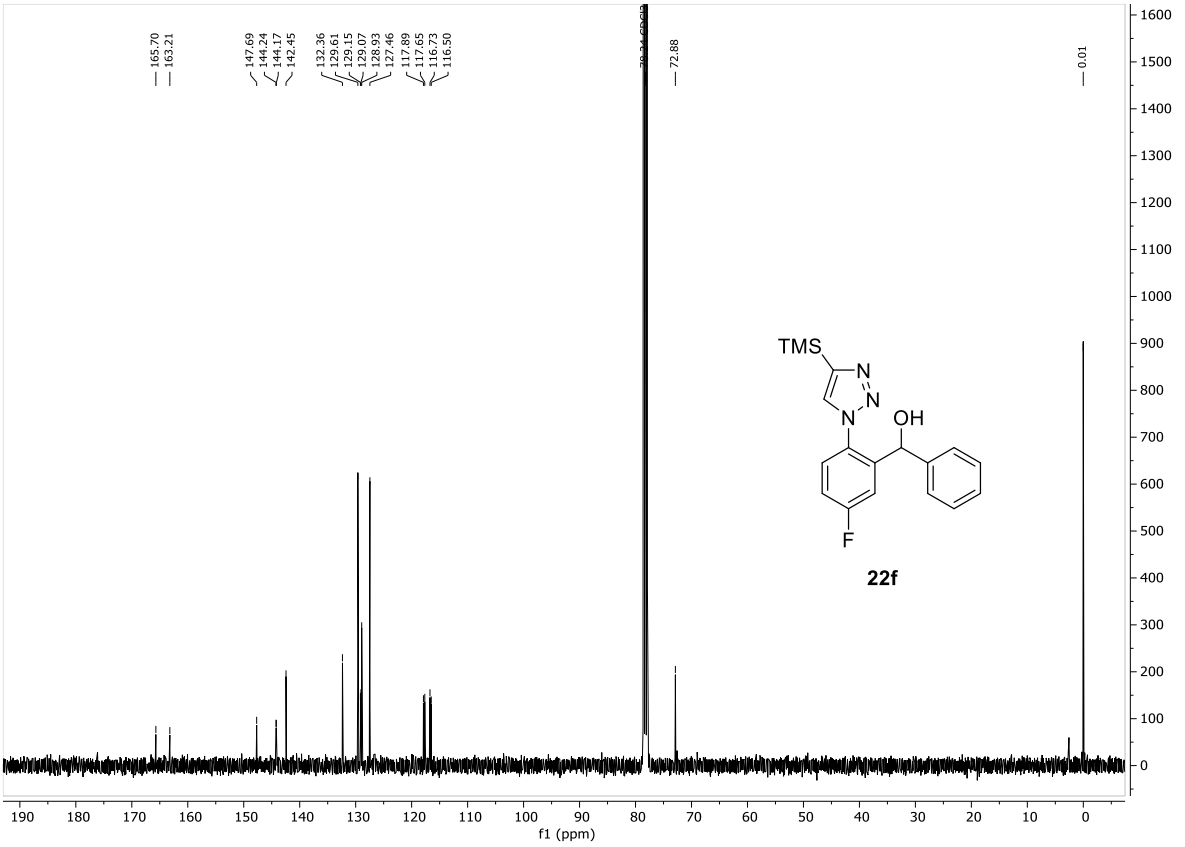
N
OH
O
22e
f1 (ppm)


TMS
N
N
N
OH
F
22f
f1 (ppm)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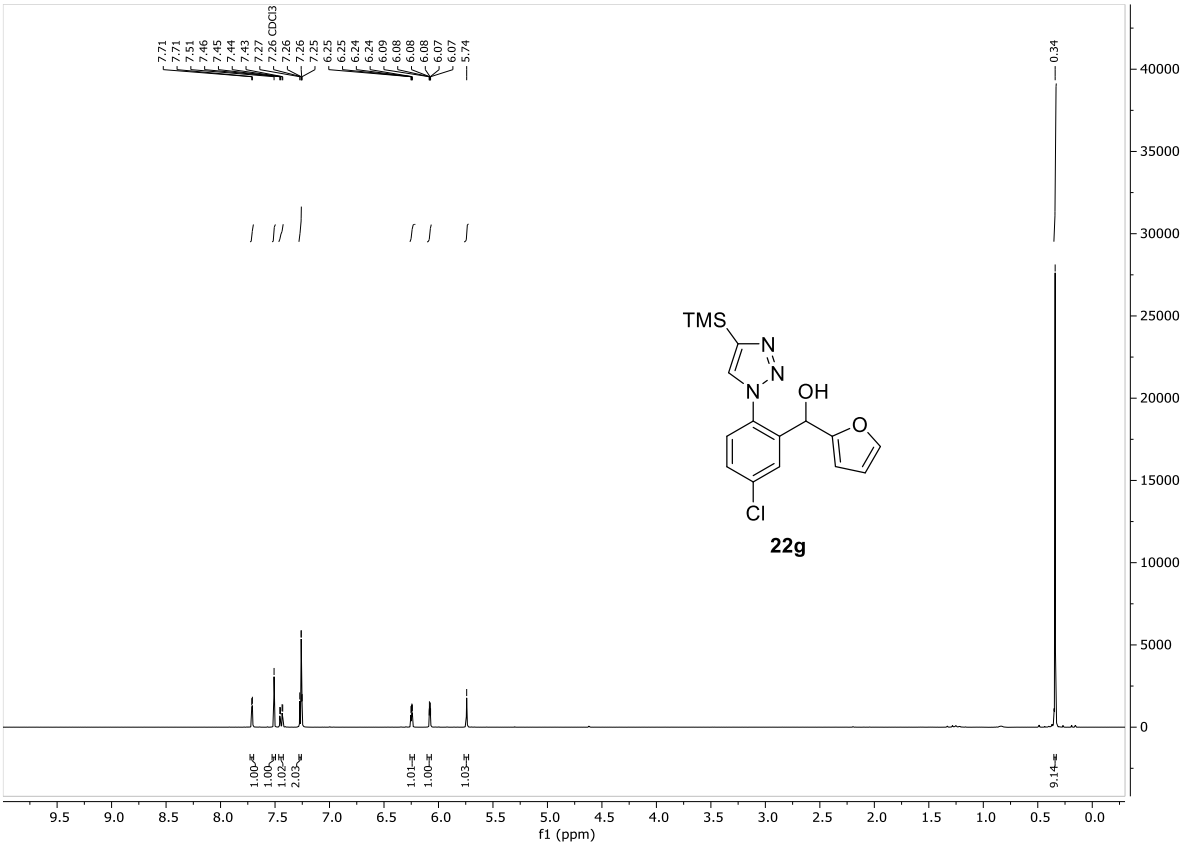
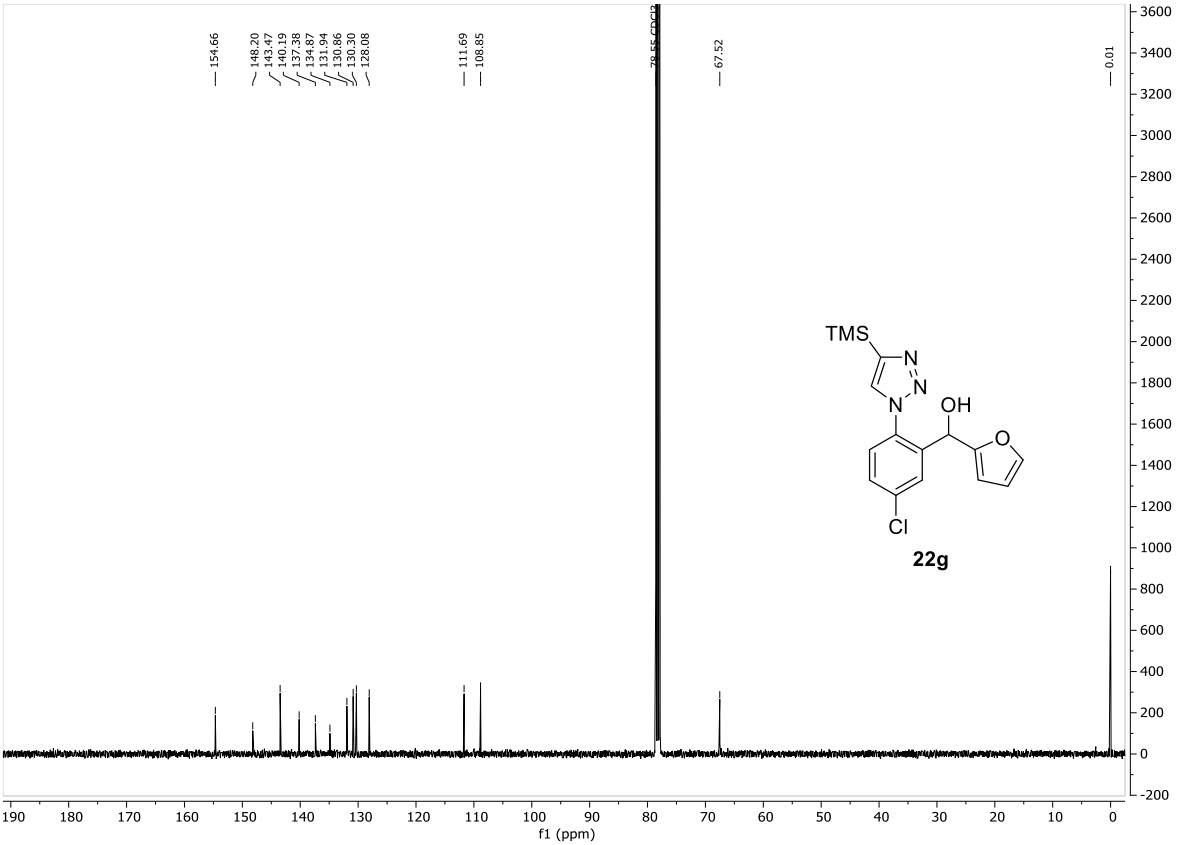
N
N
N
OH
F
22f
f1 (ppm)


7.71
7.71
7.51
7.46
7.45
7.44
7.43
7.27
CDCl3
7.26
7.26
7.26
7.25
6.25
6.25
6.24
6.24
6.09
6.08
6.08
6.08
6.07
6.07
5.74
0.34
TMS
N
N
N
OH
O
Cl
22g
1.00
1.00
1.02
2.03
1.01
1.00
1.03
9.14
f1 (ppm)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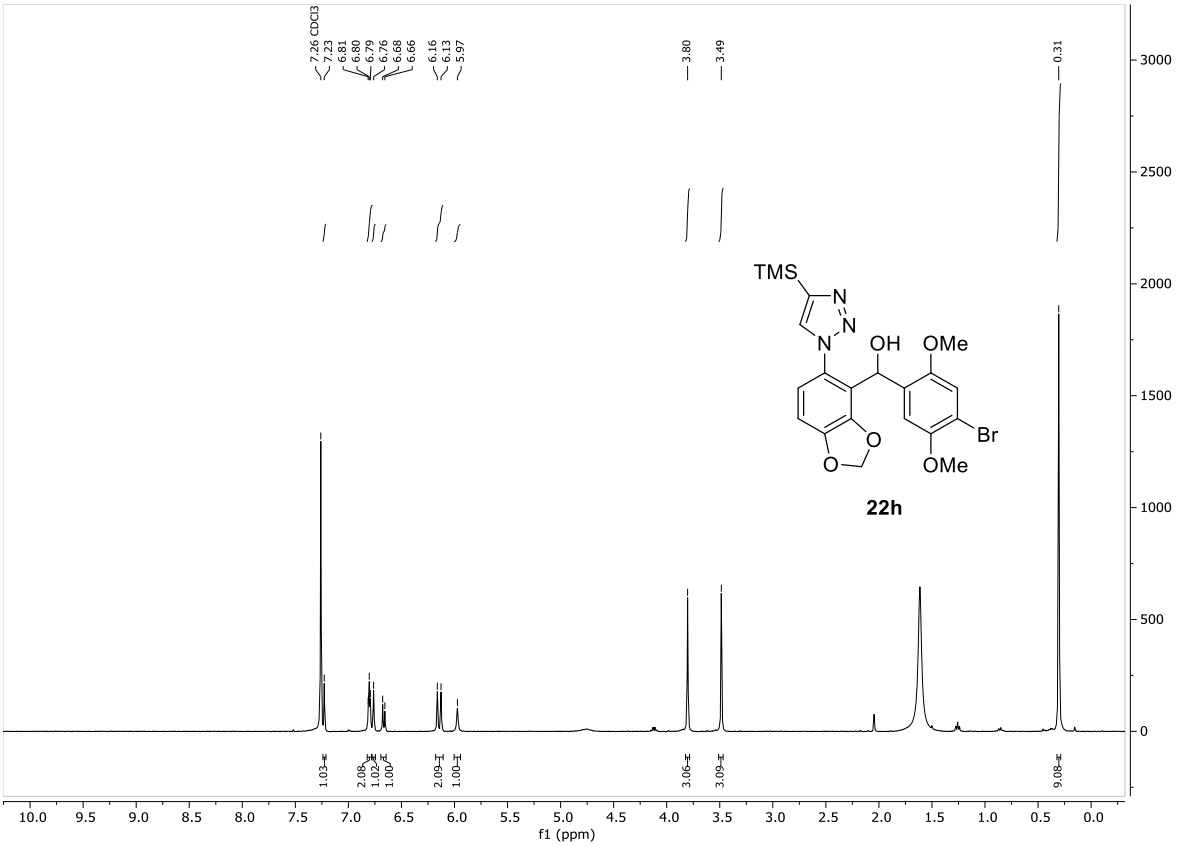
134.87
131.94
130.86
130.30
128.08
111.69
108.85
77.48
77.16
76.84
CDCl3
67.52
0.01
TMS
N
N
N
OH
O
Cl
22g
f1 (ppm)


7.26 CDCl3
7.23
6.81
6.80
6.79
6.76
6.68
6.66
6.16
6.13
5.97
3.80
3.49
0.31
TMS
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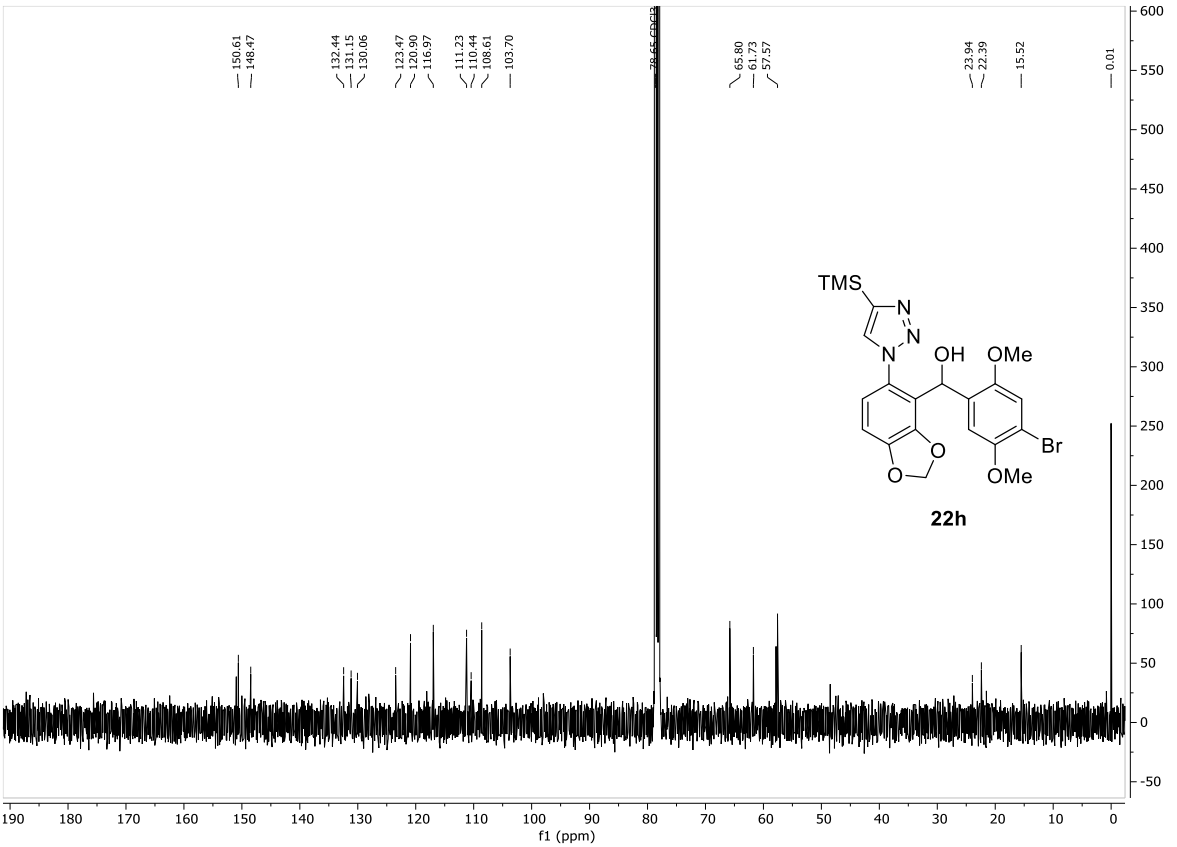
N
N
OH
OMe
Br
O
O
OMe
22h
f1 (ppm)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123.47
120.90
116.97
111.23
110.44
108.61
103.70
78.45 CDCl3
65.80
61.73
57.57
23.94
22.39
15.52
0.01
TMS
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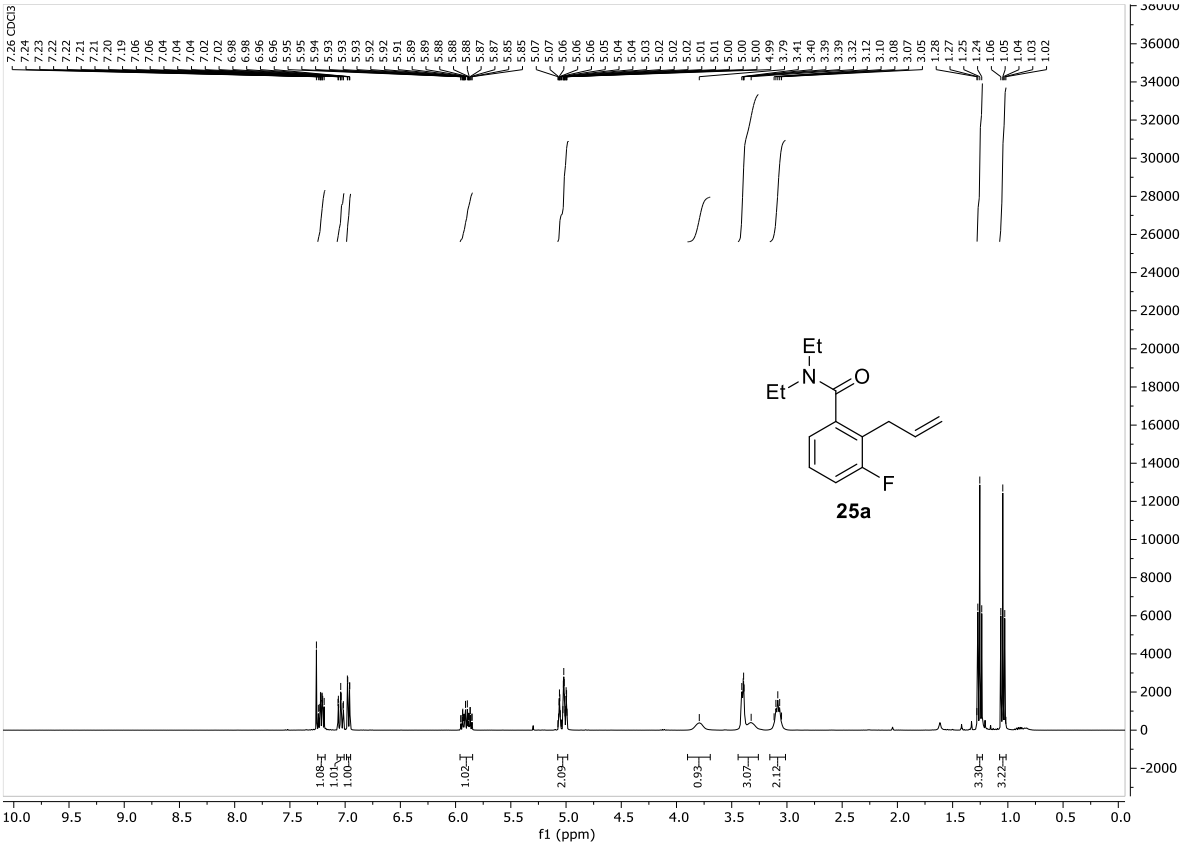
N
N
OH
OMe
Br
O
O
OMe
22h
f1 (ppm)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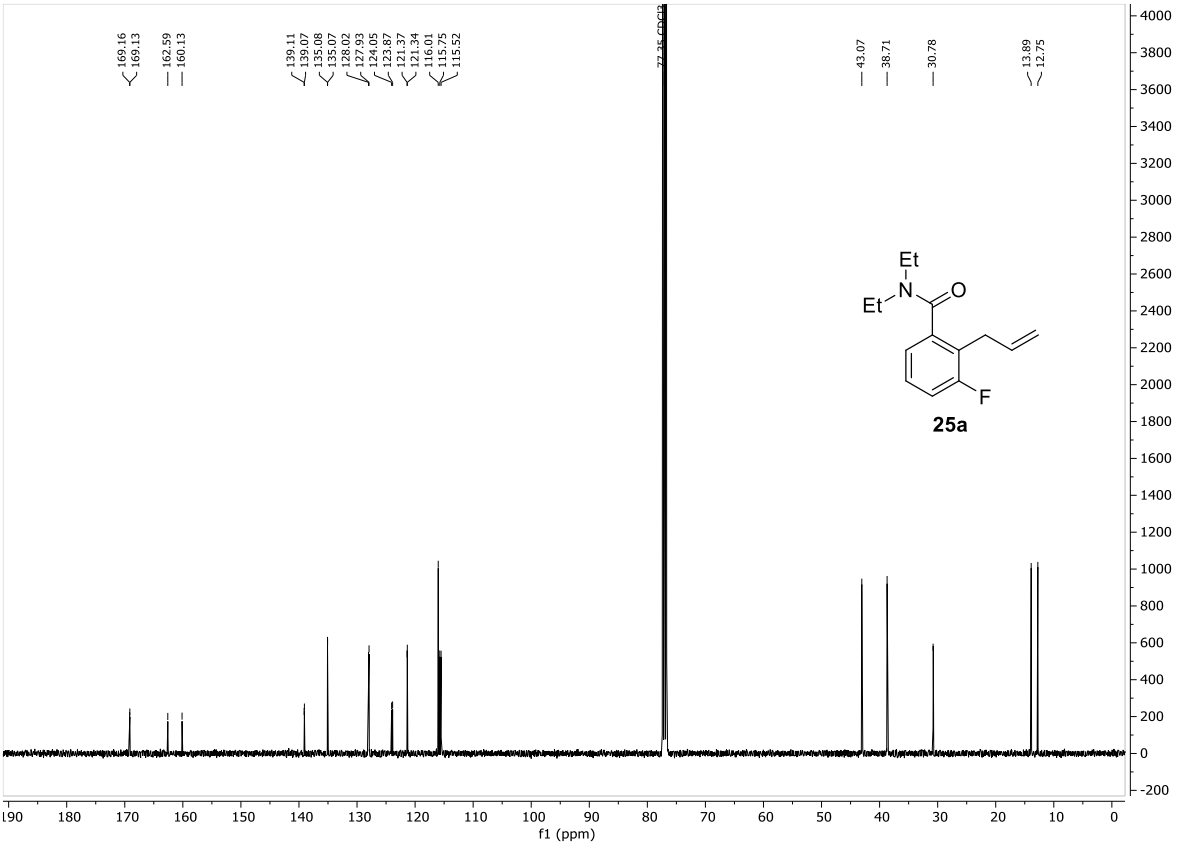
Et
O
F
25a
f1 (ppm)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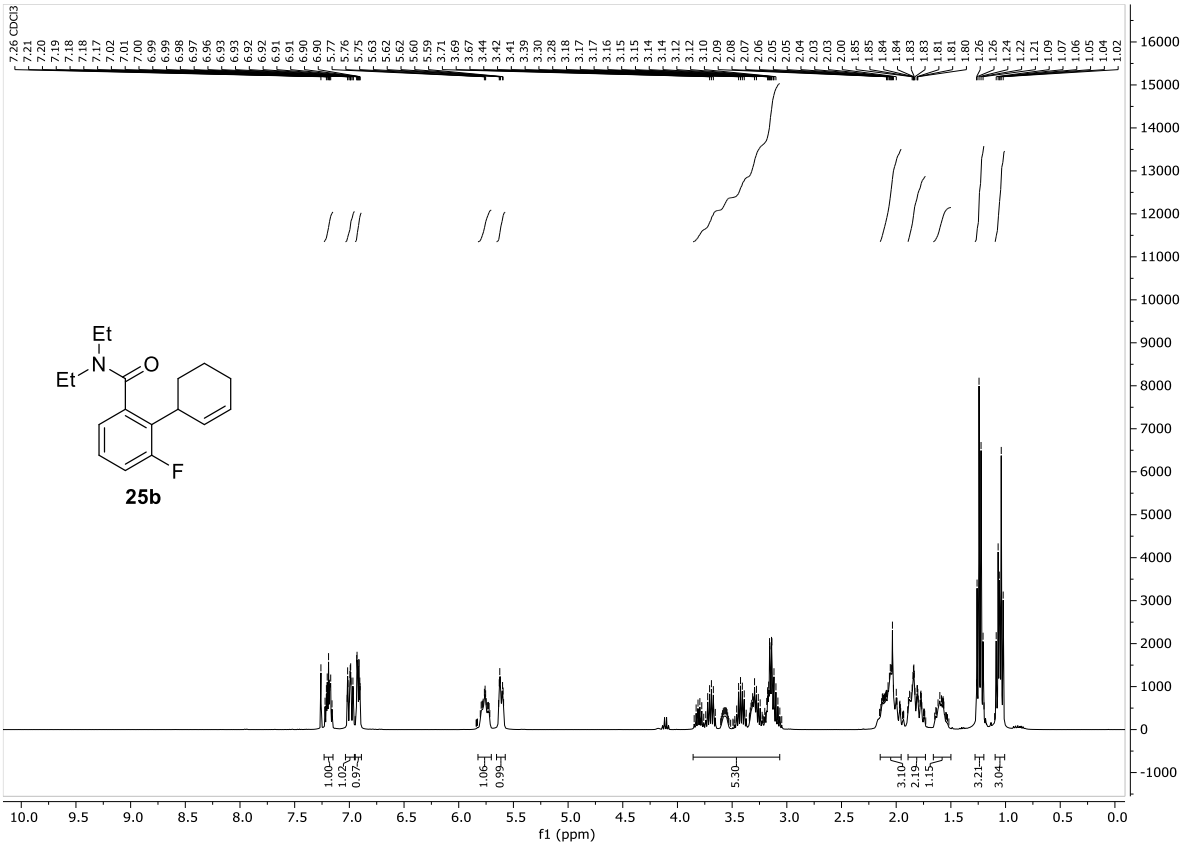
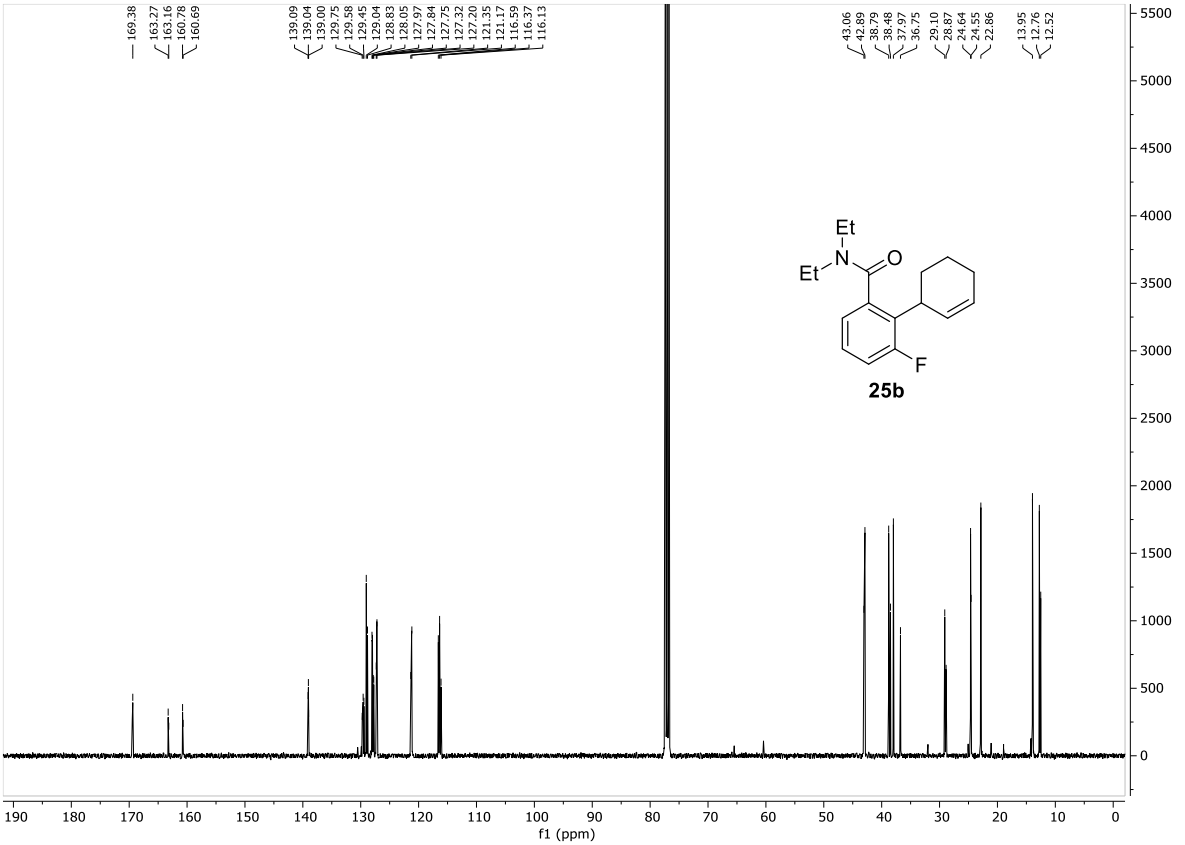
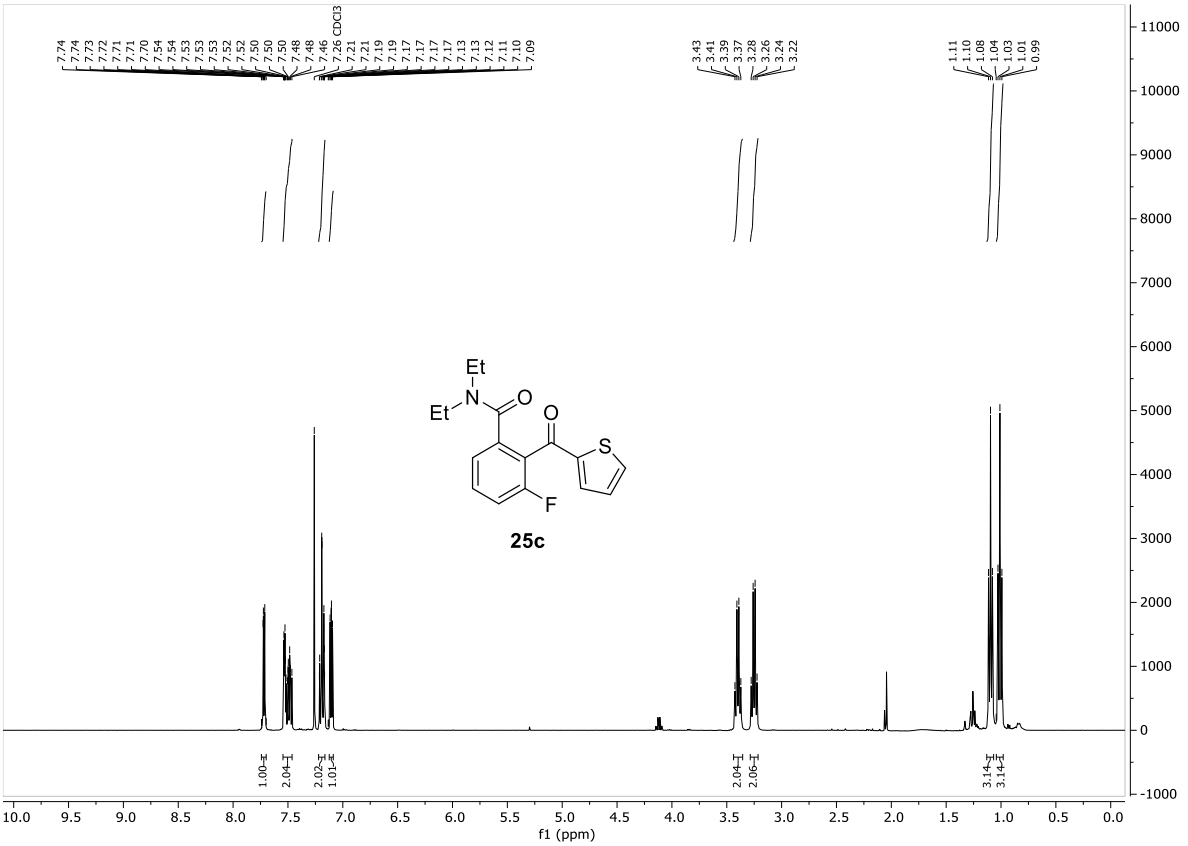
N
Et
O
F
25a
f1 (ppm)


Et
N
O
Et
F
25b
f1 (ppm)


Et
N
O
Et
F
25b
f1 (ppm)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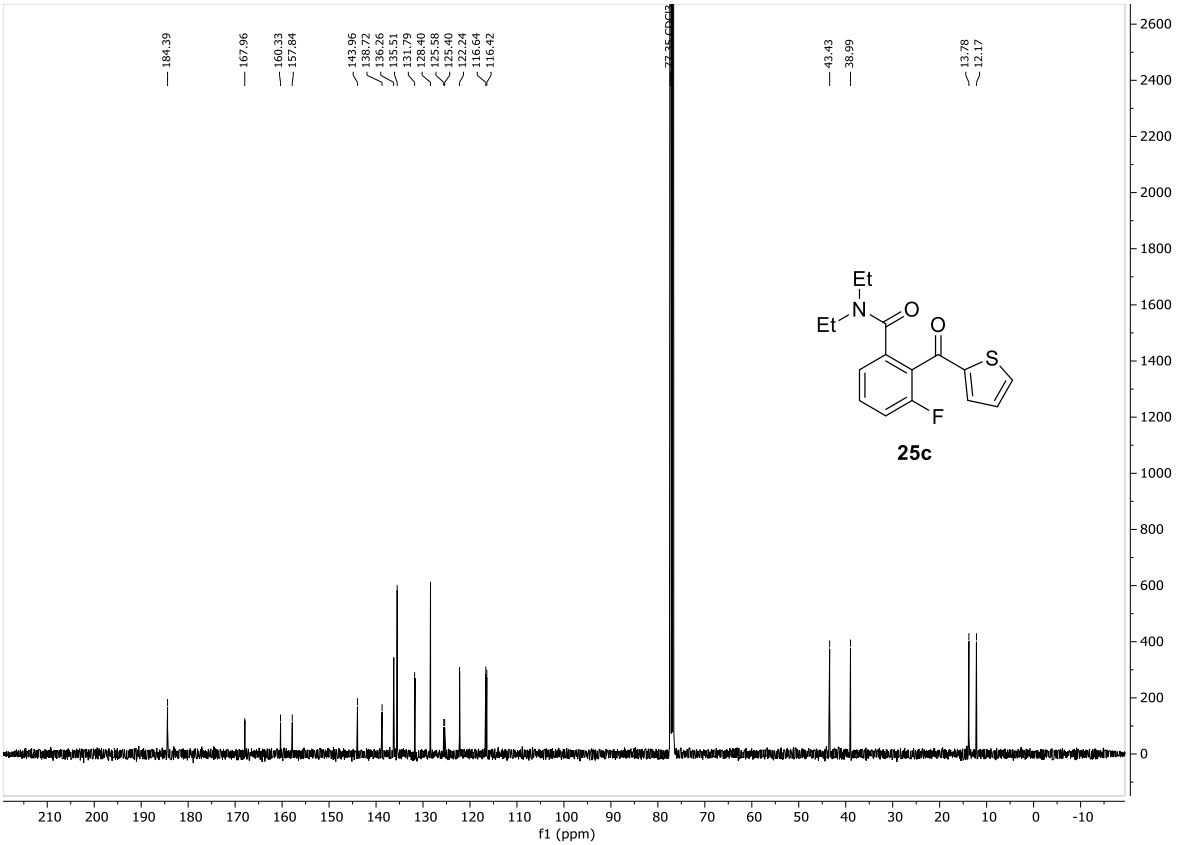
7.53
7.53
7.53
7.52
7.52
7.50
7.50
7.50
7.48
7.48
7.46
CDCl3
7.26
7.21
7.21
7.19
7.19
7.17
7.17
7.17
7.17
7.13
7.13
7.12
7.11
7.10
7.09
3.43
3.41
3.39
3.37
3.28
3.26
3.24
3.22
1.11
1.10
1.08
1.04
1.03
1.01
0.99
Et
N
Et
O
O
S
F
25c
1.00
2.04
2.02
1.01
2.04
2.06
3.14
3.14
f1 (ppm)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131.79
128.40
125.58
125.40
122.24
116.64
116.42
77.35 CDCl3
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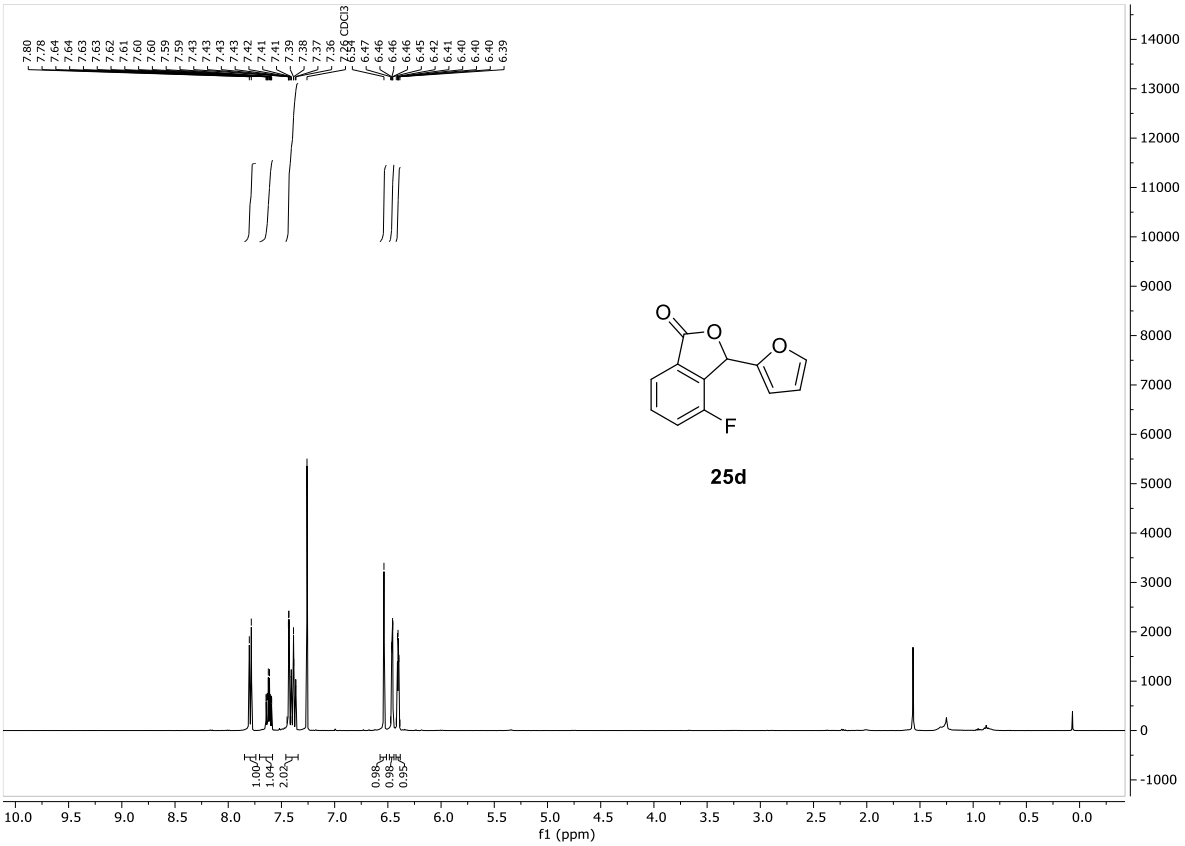
38.99
13.78
12.17
Et
N
Et
O
O
S
F
25c
f1 (ppm)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7.59
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7.43
7.43
7.43
7.43
7.42
7.41
7.41
7.39
7.38
7.37
7.36
7.26 CDCl3
6.47
6.46
6.46
6.46
6.45
6.42
6.41
6.40
6.40
6.40
6.39
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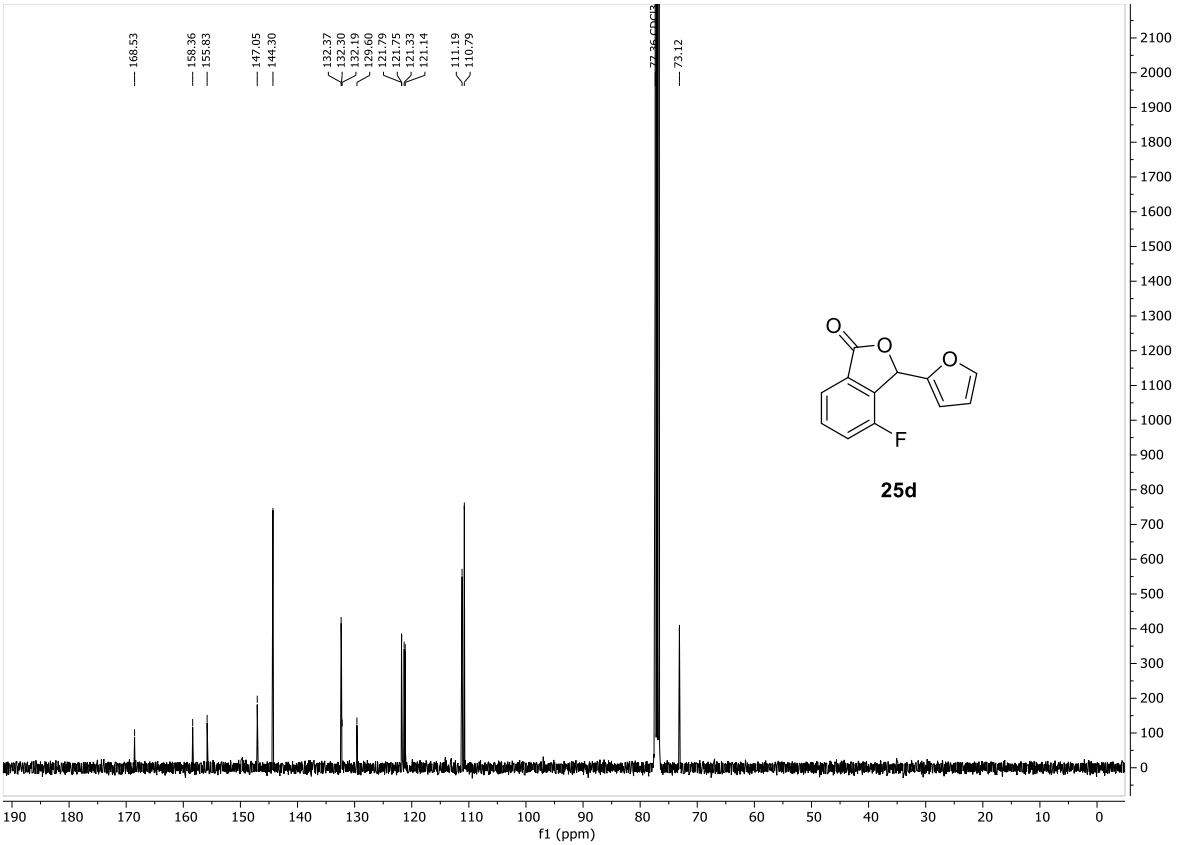
1.04
2.02
0.98
0.98
0.95
O
O
O
F
25d
f1 (ppm)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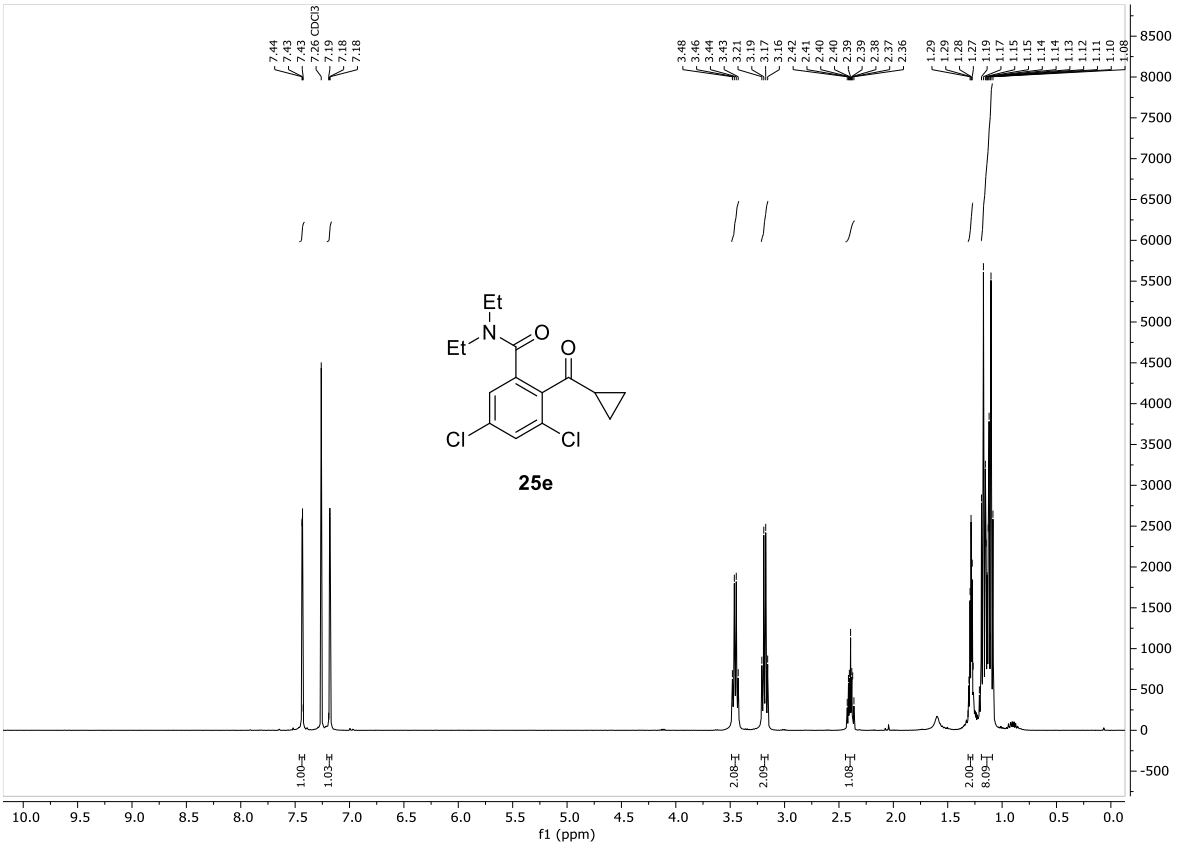
110.79
77.36 CDCl3
73.12
O
O
O
F
25d
f1 (ppm)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CDCl3
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7.18
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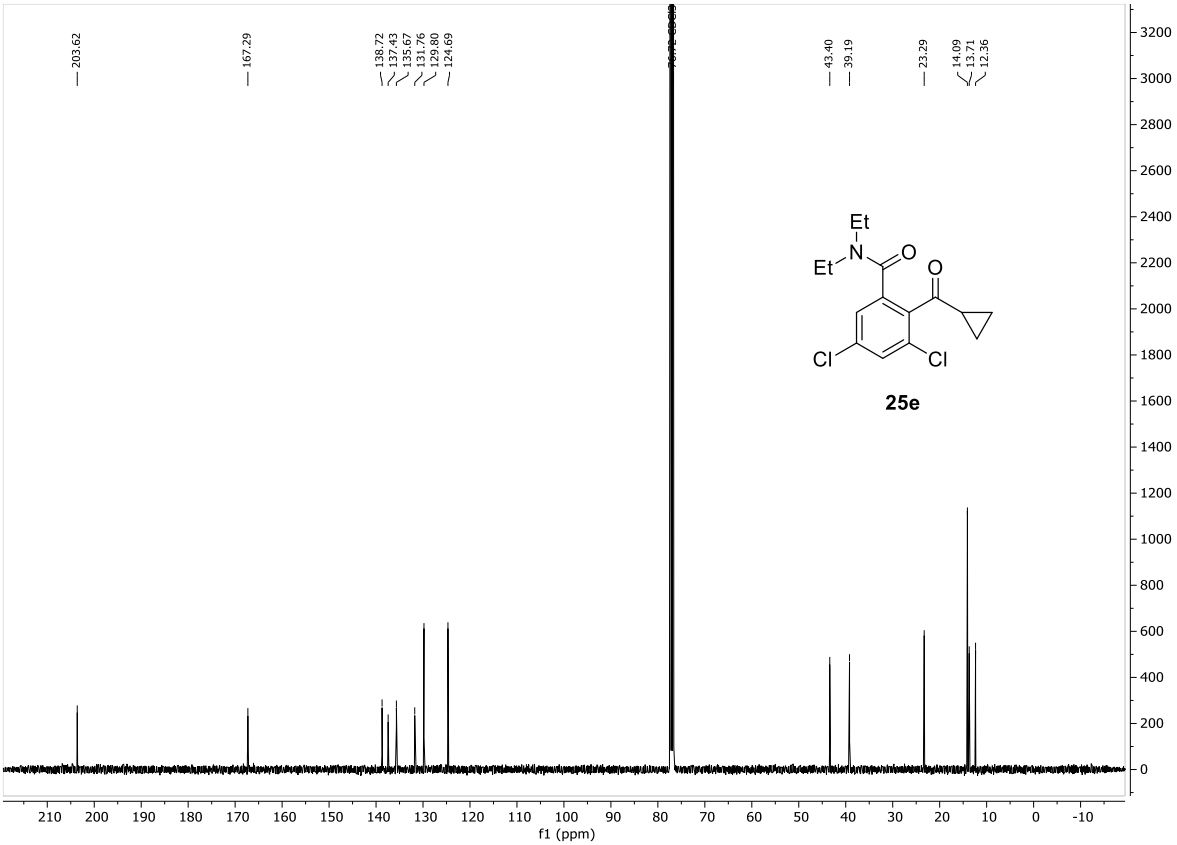
3.19
3.17
3.16
2.42
2.41
2.40
2.40
2.39
2.39
2.38
2.37
2.36
1.29
1.29
1.28
1.27
1.19
1.17
1.15
1.15
1.14
1.14
1.13
1.12
1.11
1.10
1.08
Et
N
Et
O
O
Cl
Cl
25e
1.00
1.03
2.08
2.09
1.08
2.00
8.09
f1 (ppm)


203.62
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137.43
135.67
131.76
129.80
124.69
77.16
43.40
39.19
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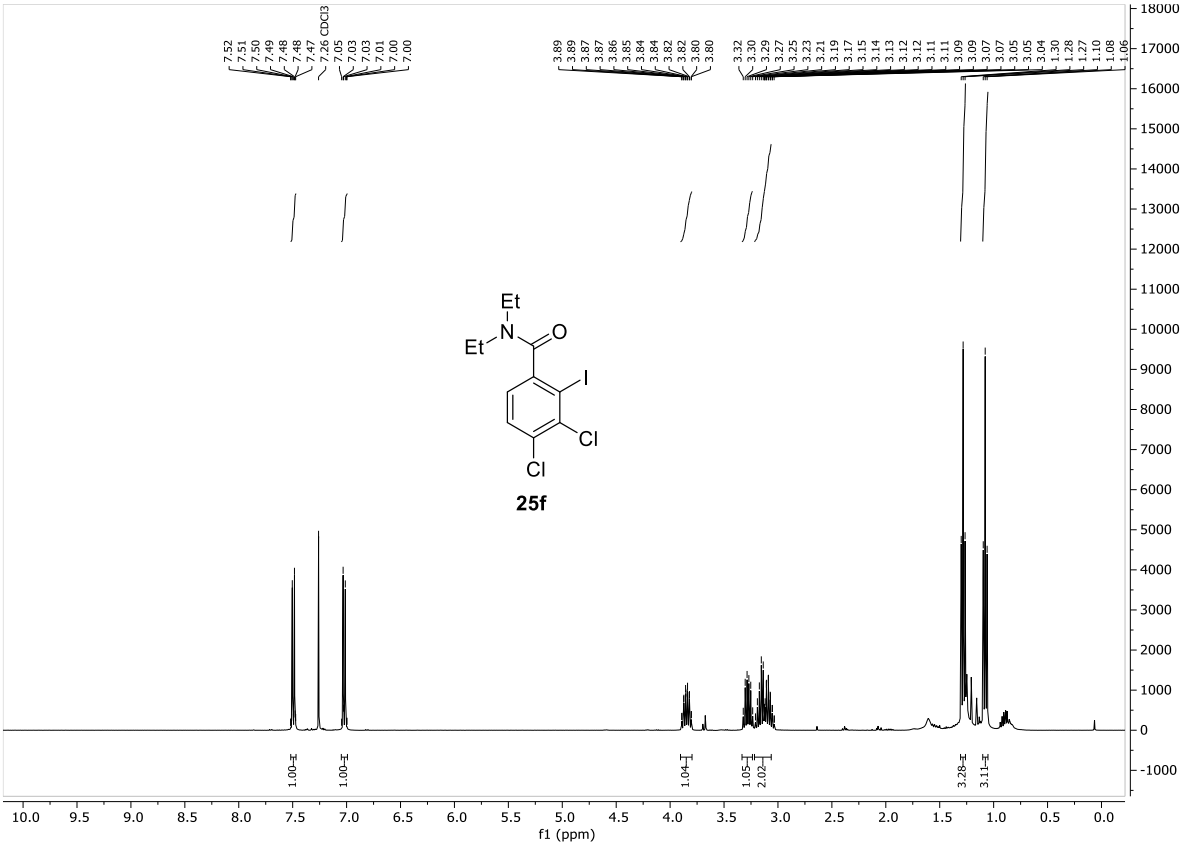
14.09
13.71
12.36
Et
N
Et
O
O
Cl
Cl
25e
f1 (ppm)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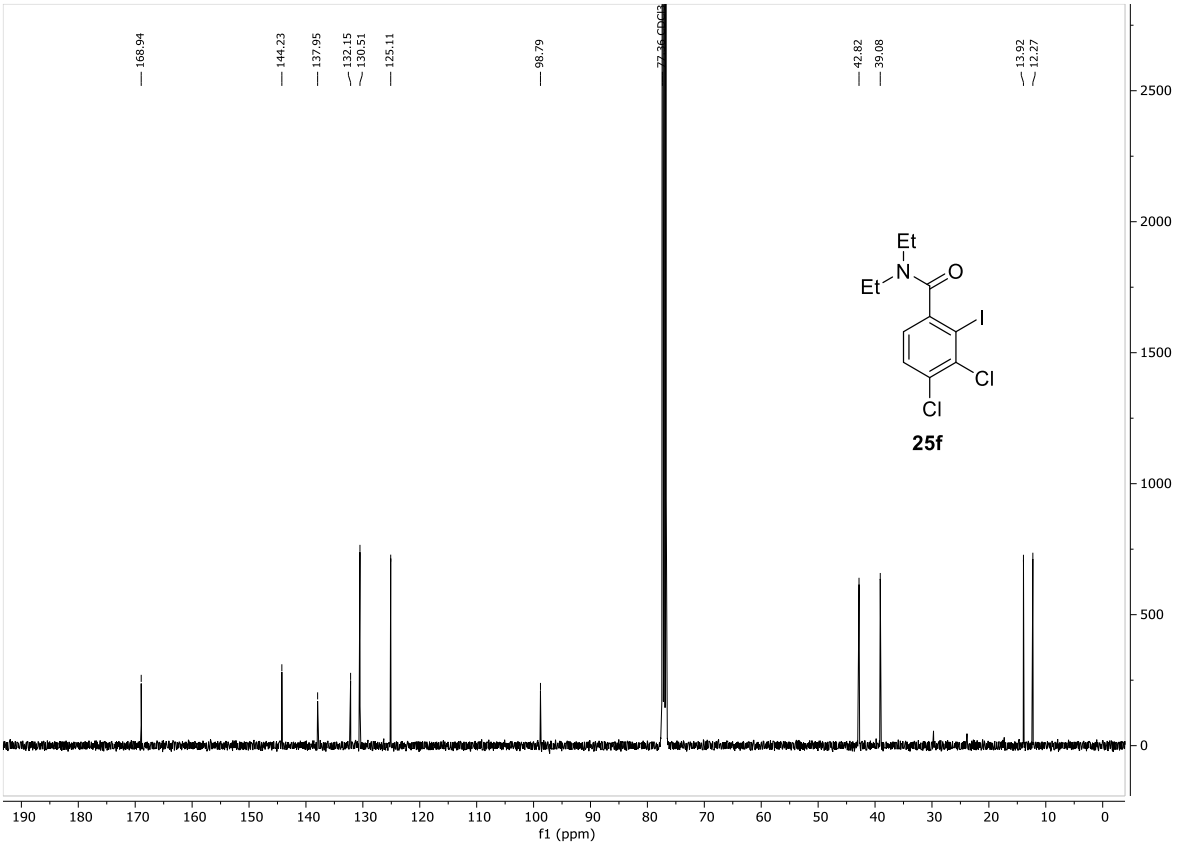
Et
O
I
Cl
Cl
25f
f1 (ppm)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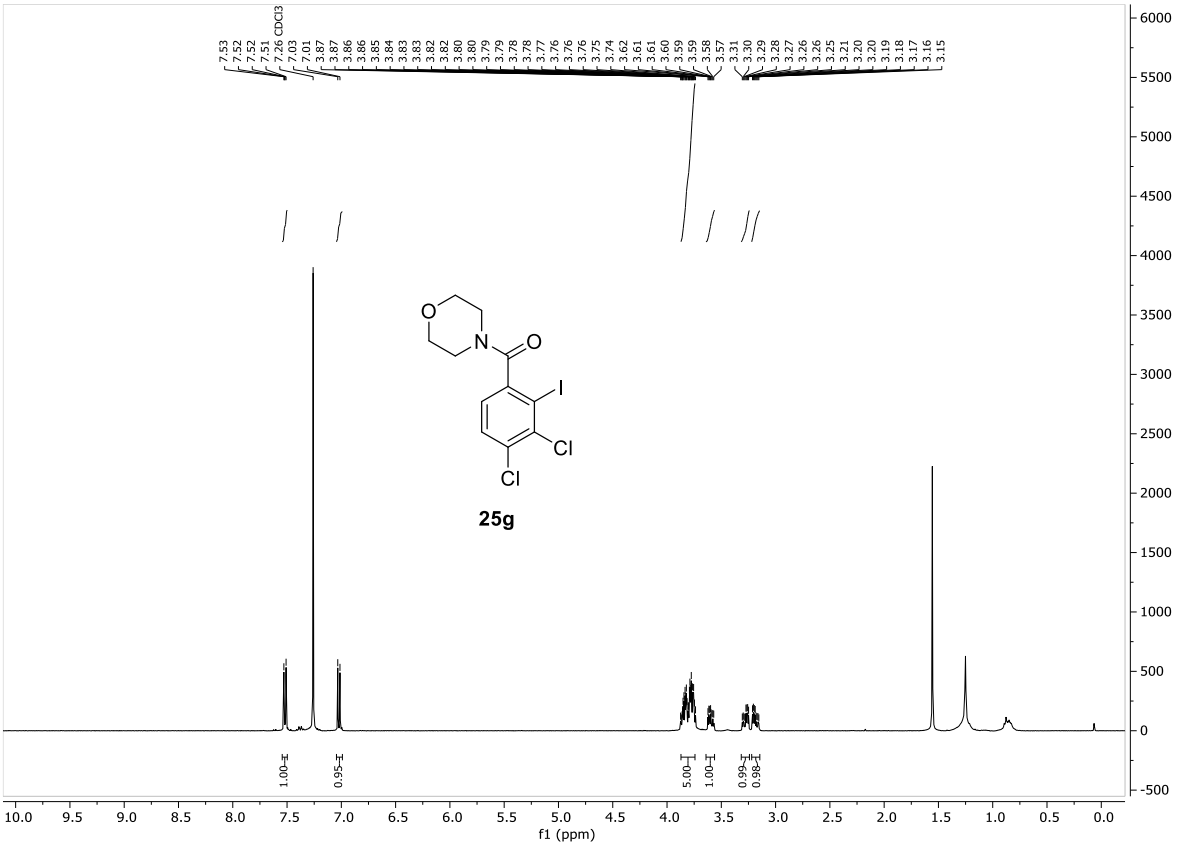
N
Et
O
I
Cl
Cl
25f
f1 (ppm)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7.52
7.51
7.26 CDCl3
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7.01
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3.87
3.86
3.86
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3.83
3.82
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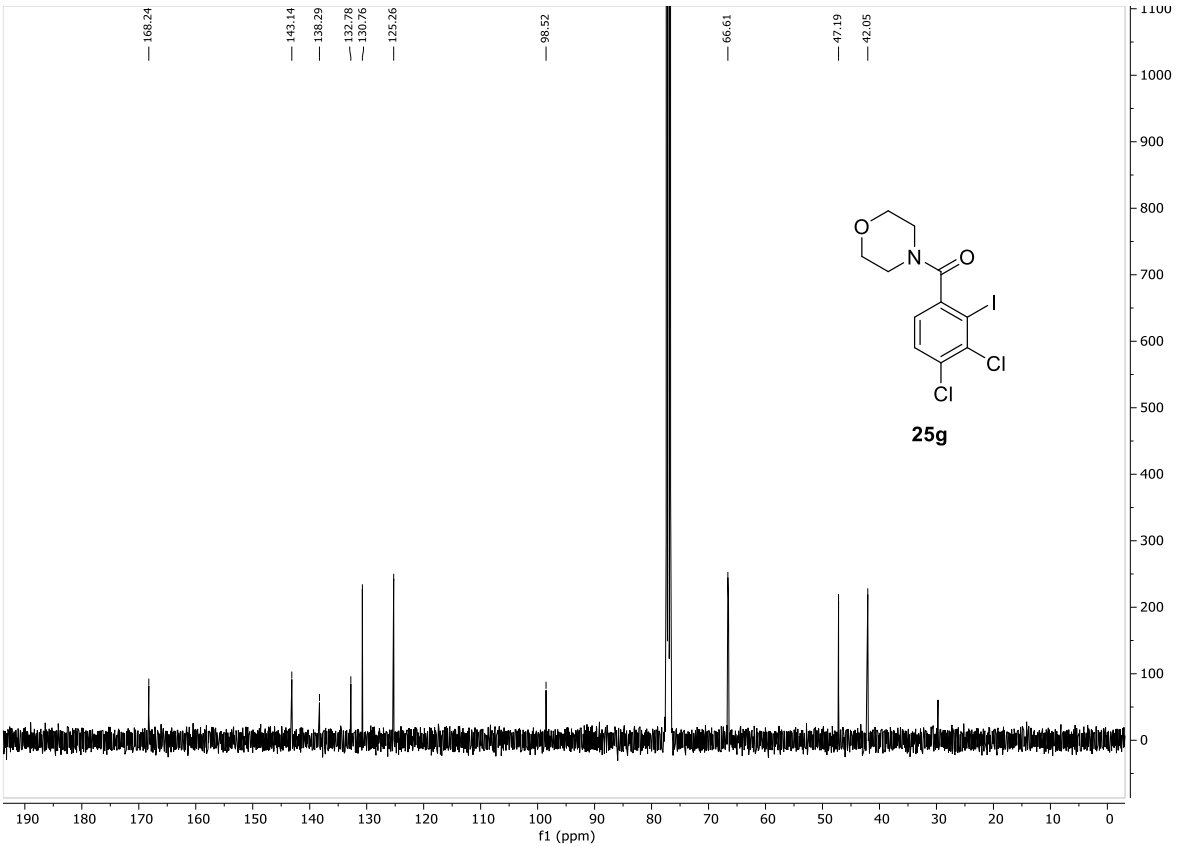
3.18
3.17
3.16
3.15
O
N
O
I
Cl
Cl
25g
1.00
0.95
5.00
1.00
0.99
0.98
f1 (ppm)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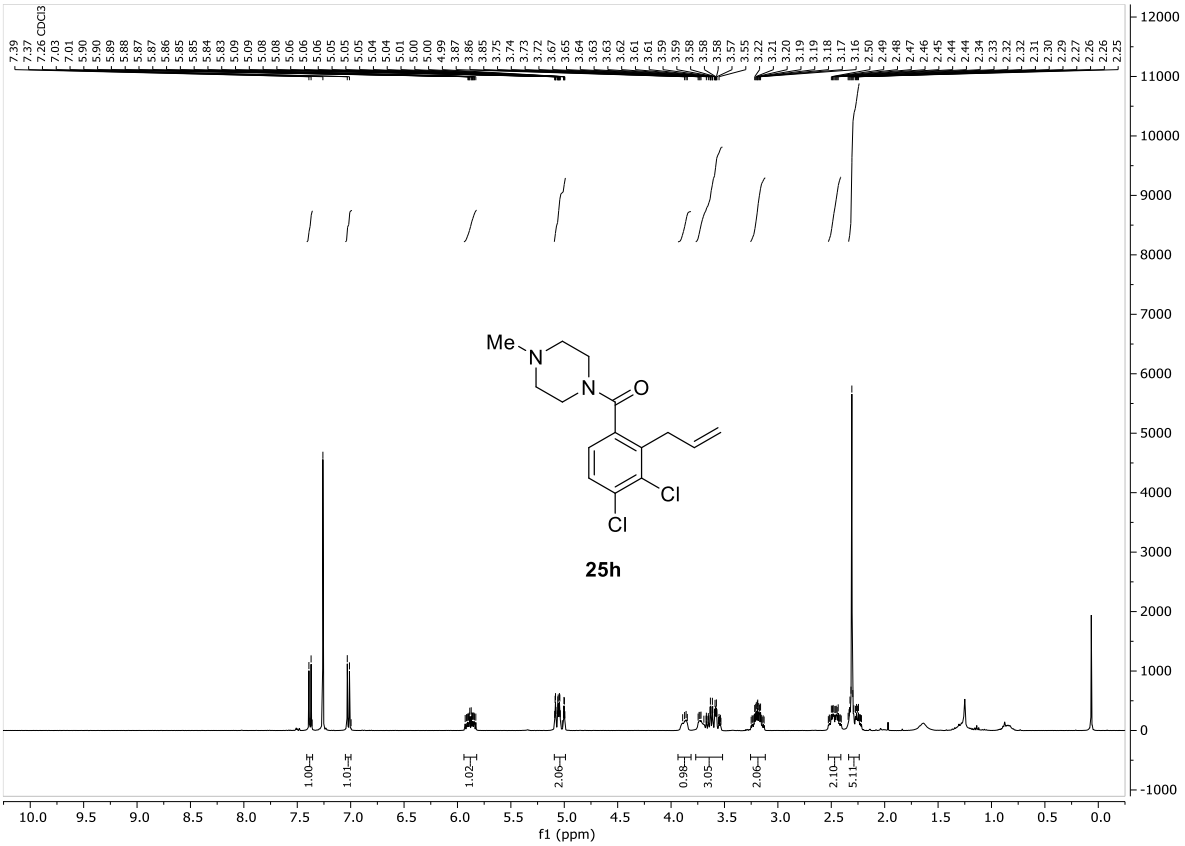
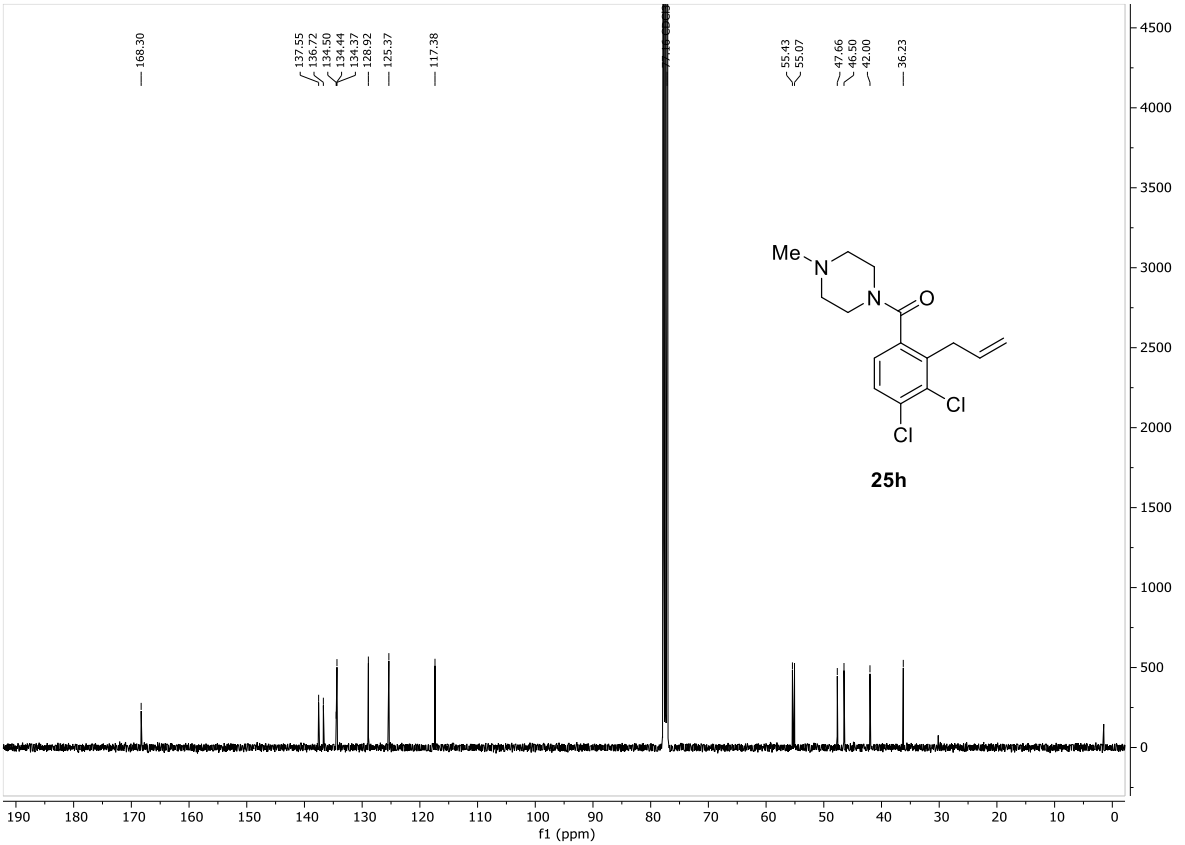
143.14
138.29
132.78
130.76
125.26
98.52
66.61
47.19
42.05
O
N
O
I
Cl
Cl
25g
f1 (ppm)


Me
N
N
O
Cl
Cl
25h
f1 (ppm)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134.37
128.92
125.37
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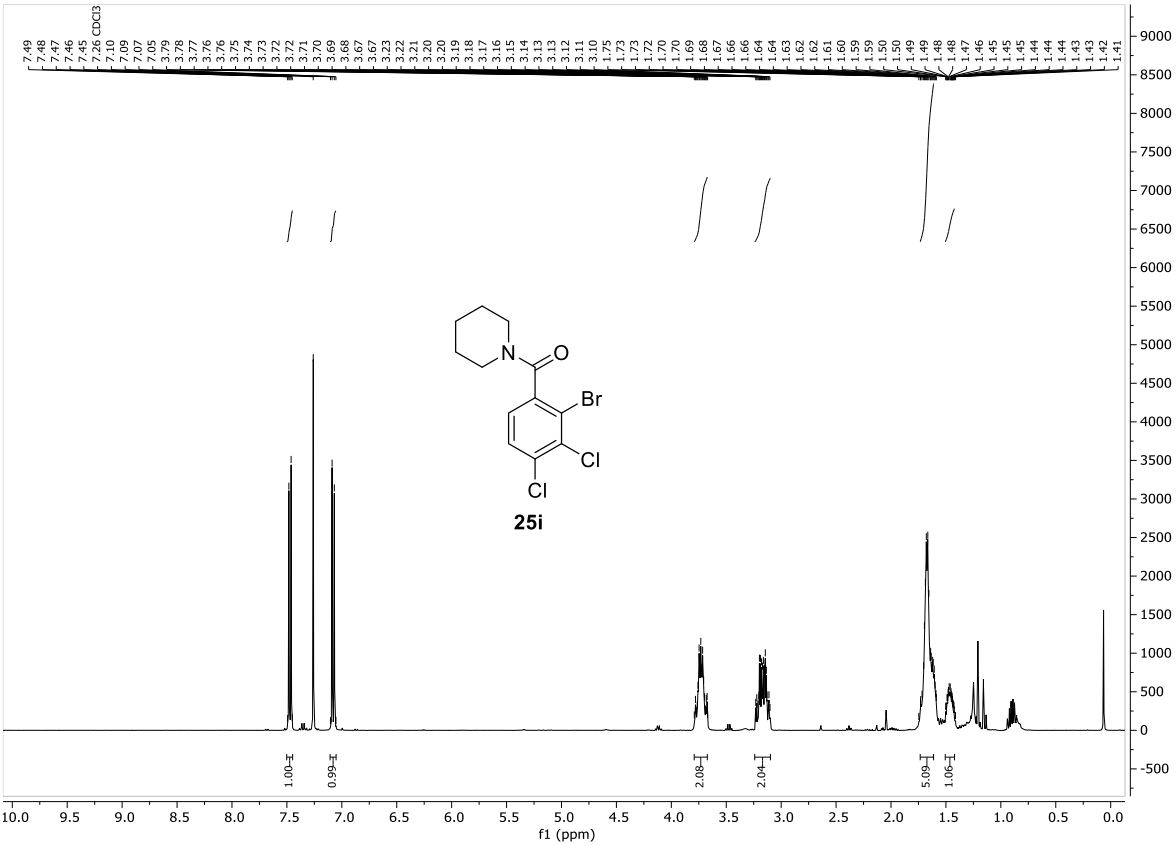
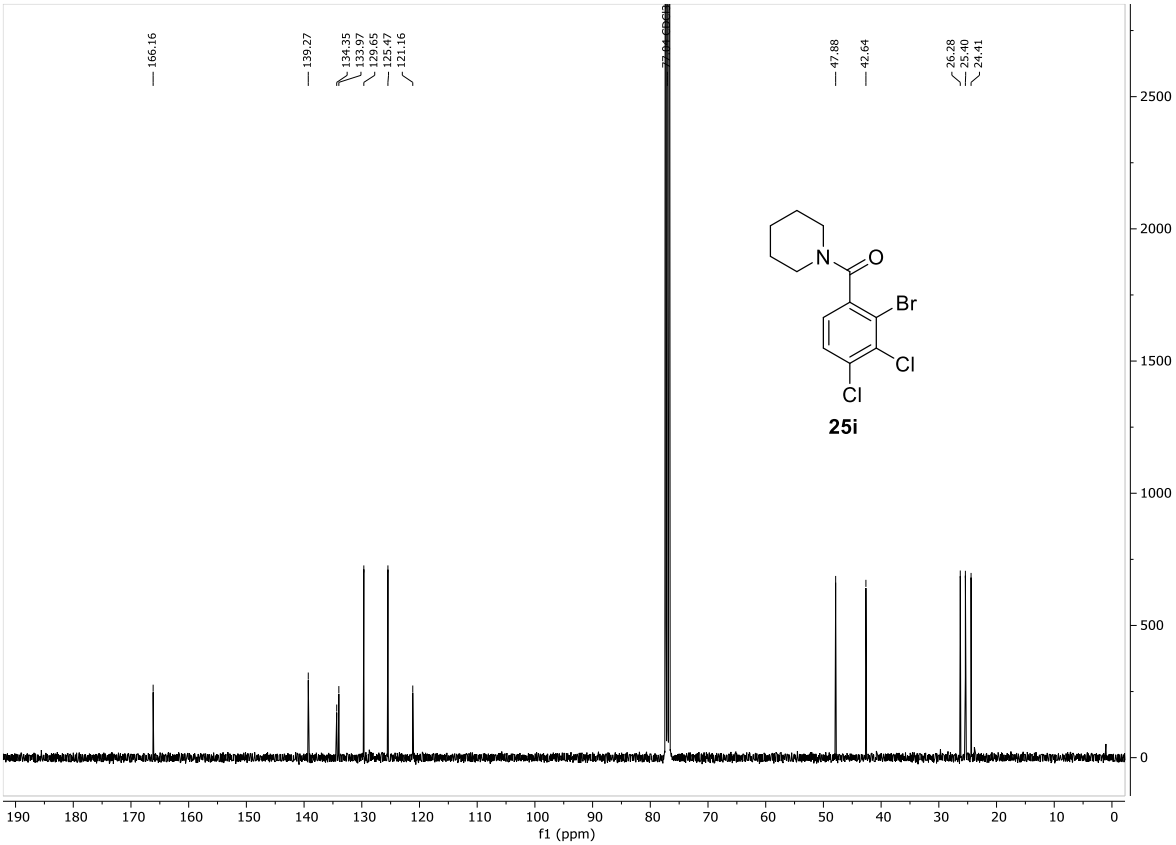
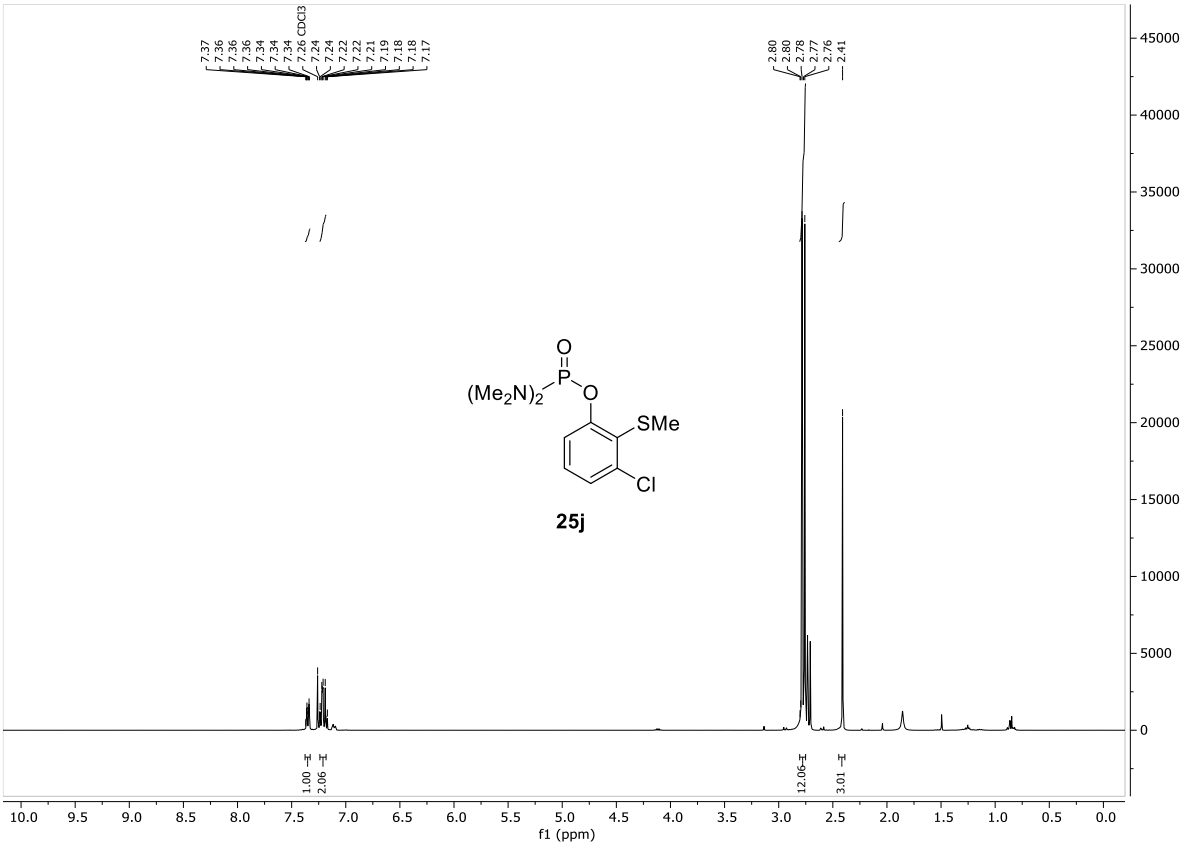
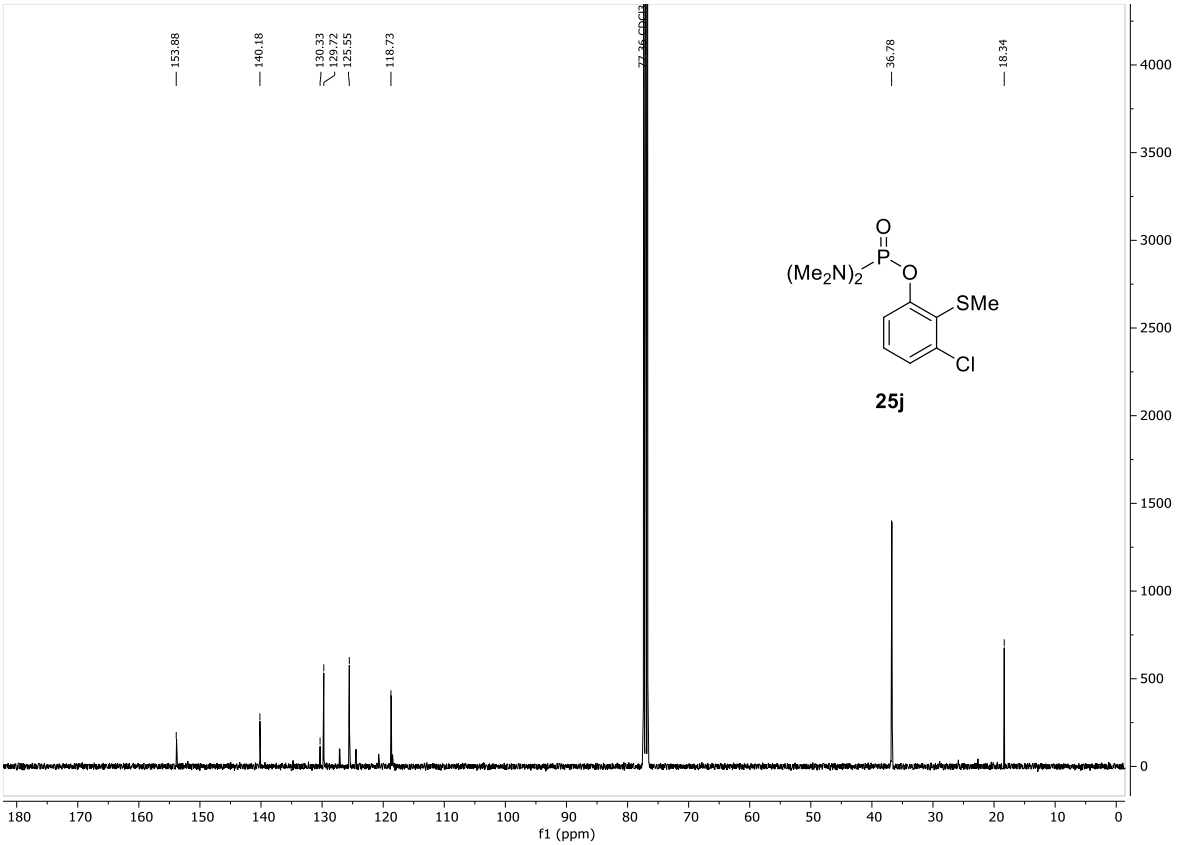
46.50
42.00
36.23
Me
N
N
O
Cl
Cl
25h
f1 (ppm)


7.49 7.48 7.47 7.46 7.45 7.26 CDCl3 7.10 7.09 7.07 7.05 3.79 3.78 3.77 3.76 3.76 3.75 3.74 3.73 3.72 3.72 3.71 3.70 3.69 3.68 3.67 3.67 3.23 3.22 3.21 3.20 3.20 3.19 3.18 3.17 3.16 3.15 3.14 3.13 3.13 3.12 3.11 3.10 1.75 1.73 1.73 1.72 1.70 1.70 1.69 1.68 1.67 1.66 1.66 1.64 1.64 1.63 1.62 1.62 1.61 1.60 1.59 1.59 1.50 1.50 1.49 1.49 1.48 1.48 1.47 1.46 1.45 1.45 1.45 1.44 1.44 1.44 1.43 1.43 1.42 1.41
N
O
Br
Cl
Cl
25i
1.00
0.99
2.08
2.04
5.09
1.06
f1 (ppm)


166.16
139.27
134.35
133.97
129.65
125.47
121.16
77.04 CDCl3
47.88
42.64
26.28
25.40
24.41
N
O
Br
Cl
Cl
25i
f1 (ppm)


7.37
7.36
7.36
7.36
7.34
7.34
7.34
7.26 CDCl3
7.24
7.24
7.22
7.22
7.21
7.19
7.18
7.18
7.17
2.80
2.80
2.78
2.77
2.76
2.41
O
P
O
(Me2N)2
SMe
Cl
25j
1.00
2.06
12.06
3.01
f1 (ppm)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140.18
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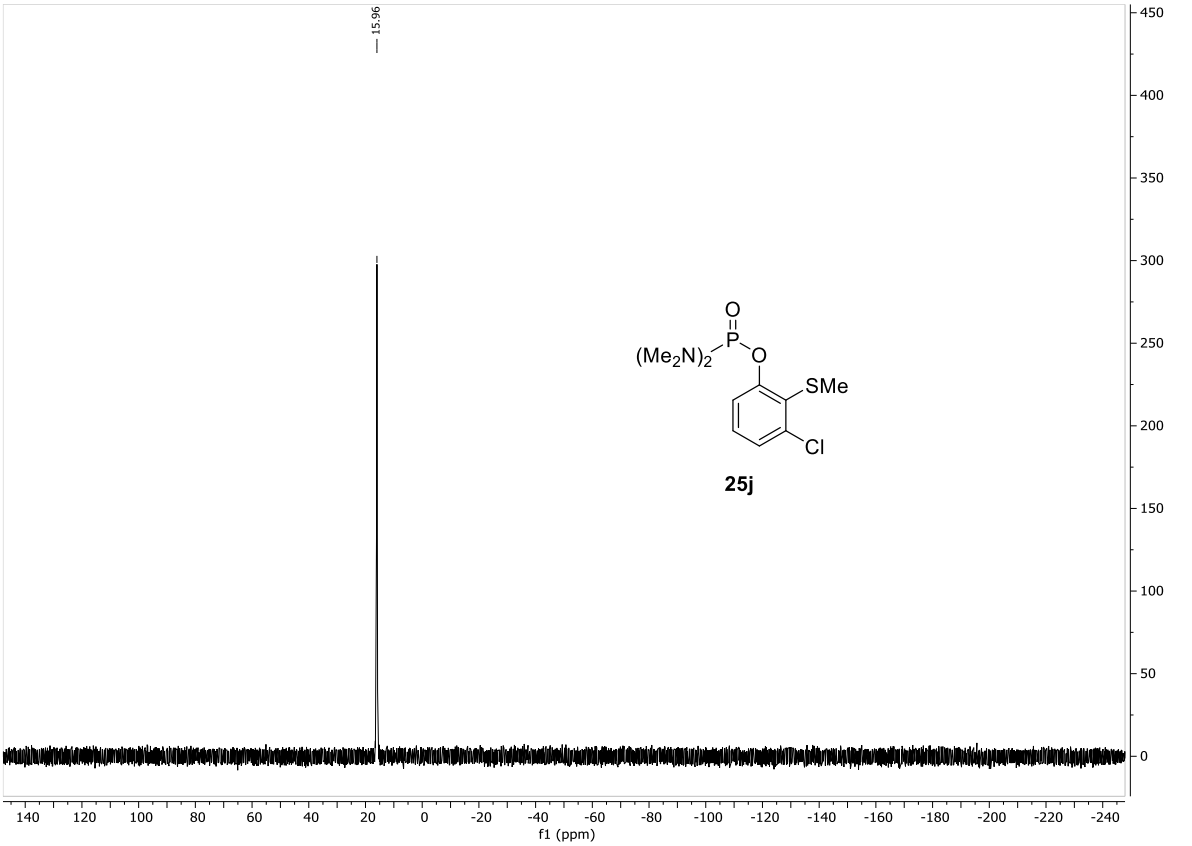
129.72
125.55
118.73
77.36 CDCl3
36.78
18.34
O
P
O
(Me2N)2
SMe
Cl
25j
f1 (ppm)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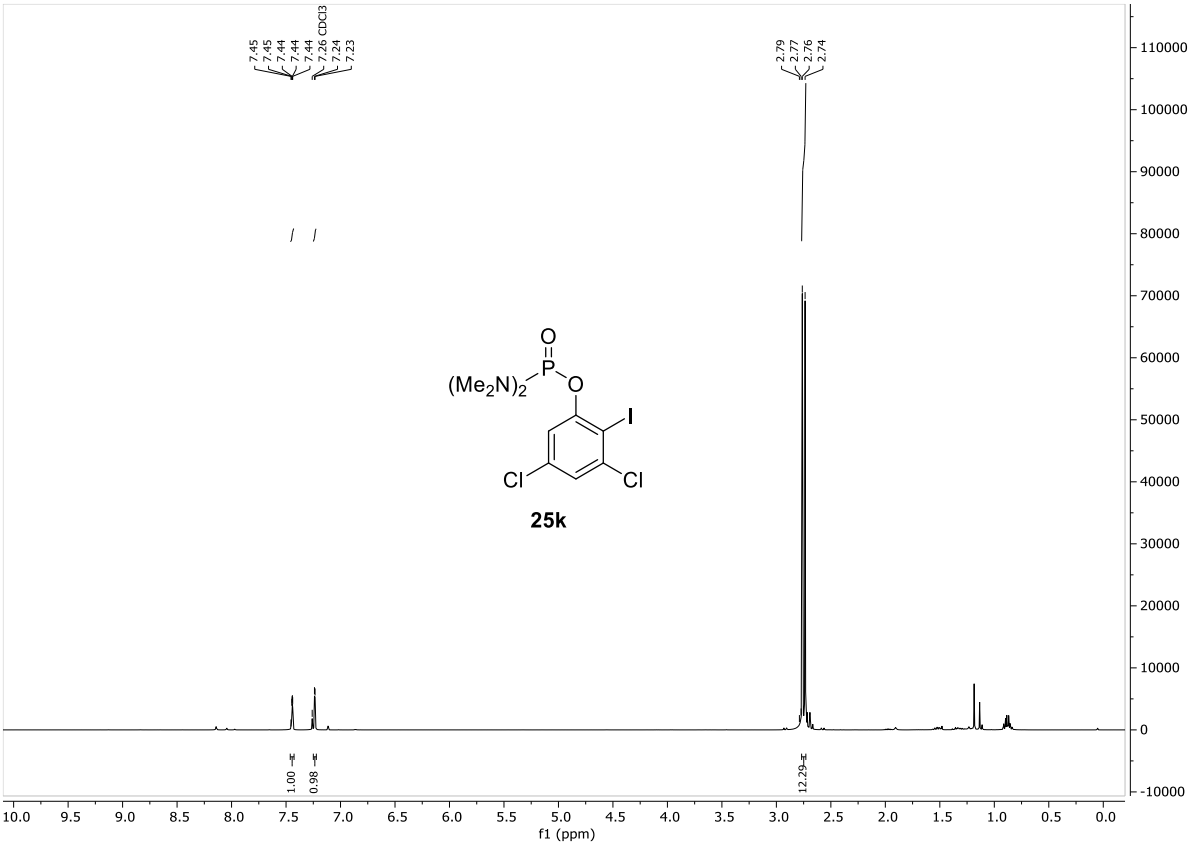
O
P
O
(Me2N)2
SMe
Cl
25j
f1 (ppm)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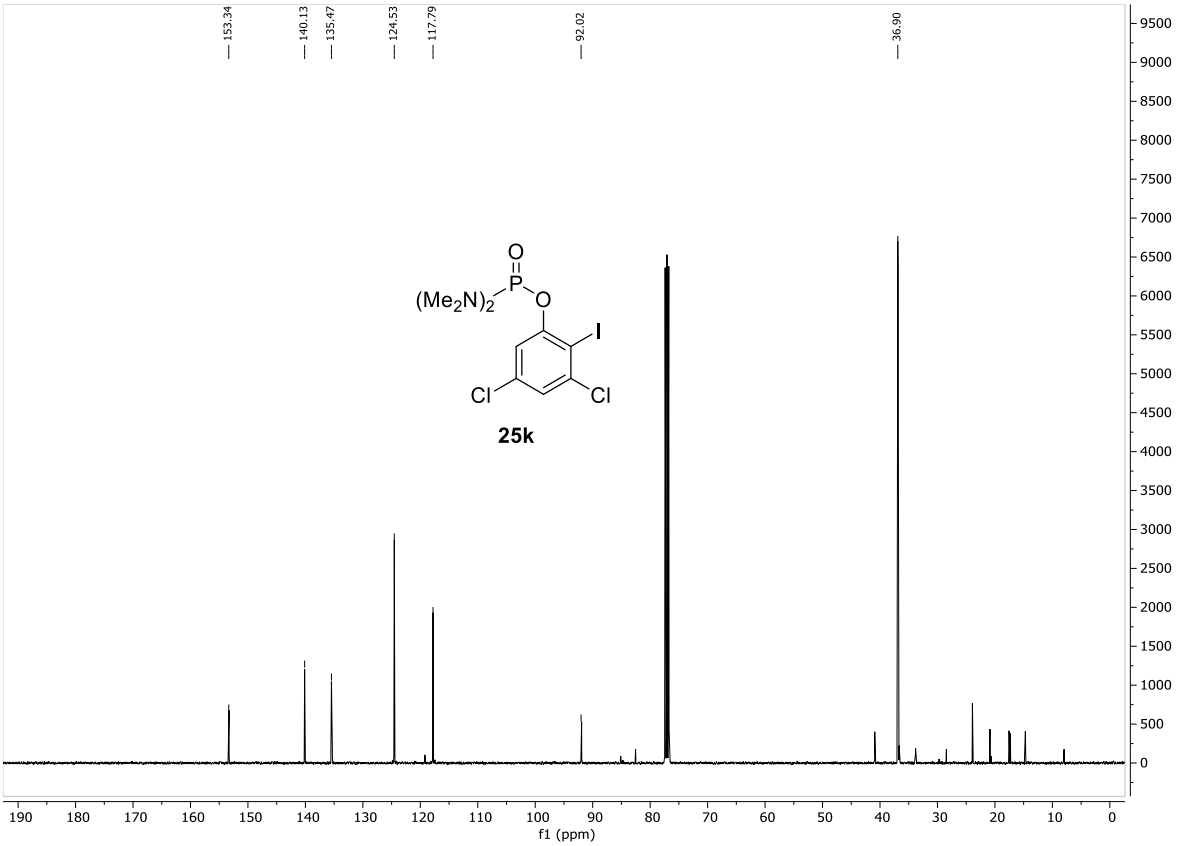
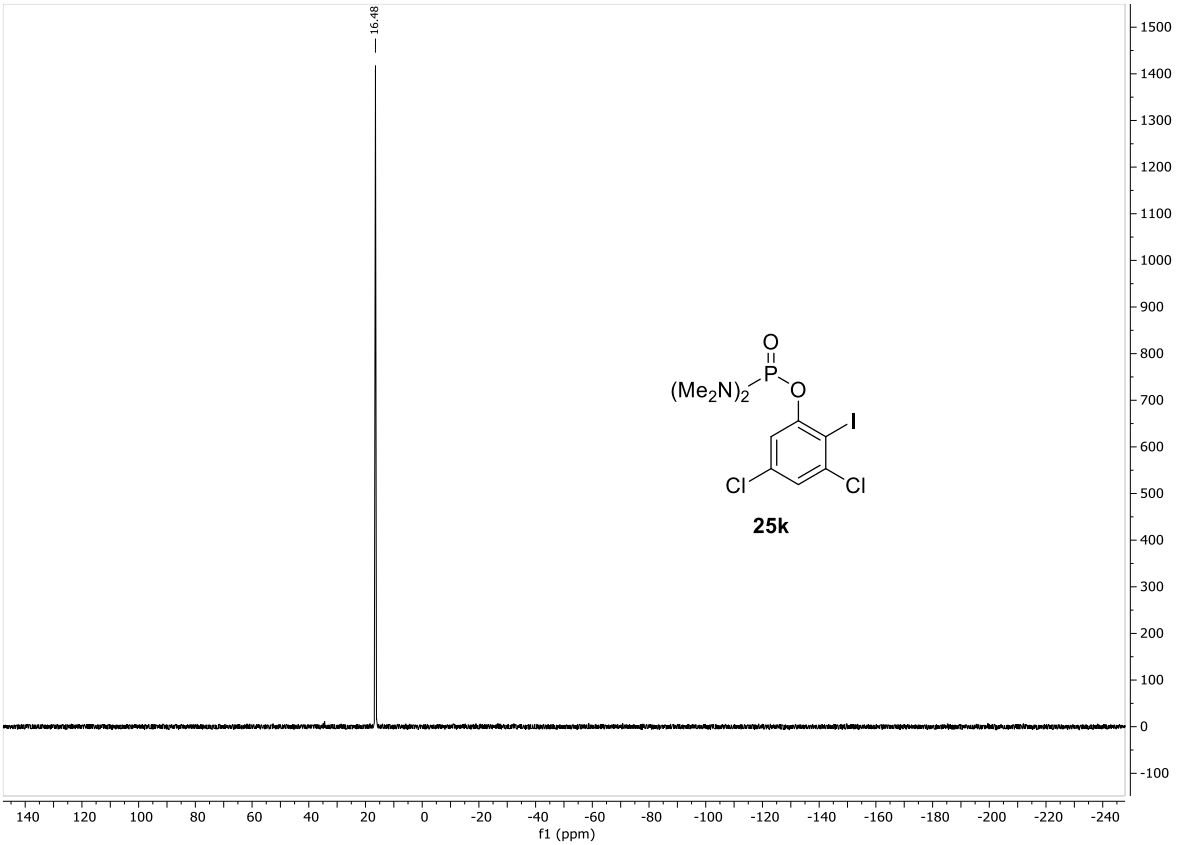
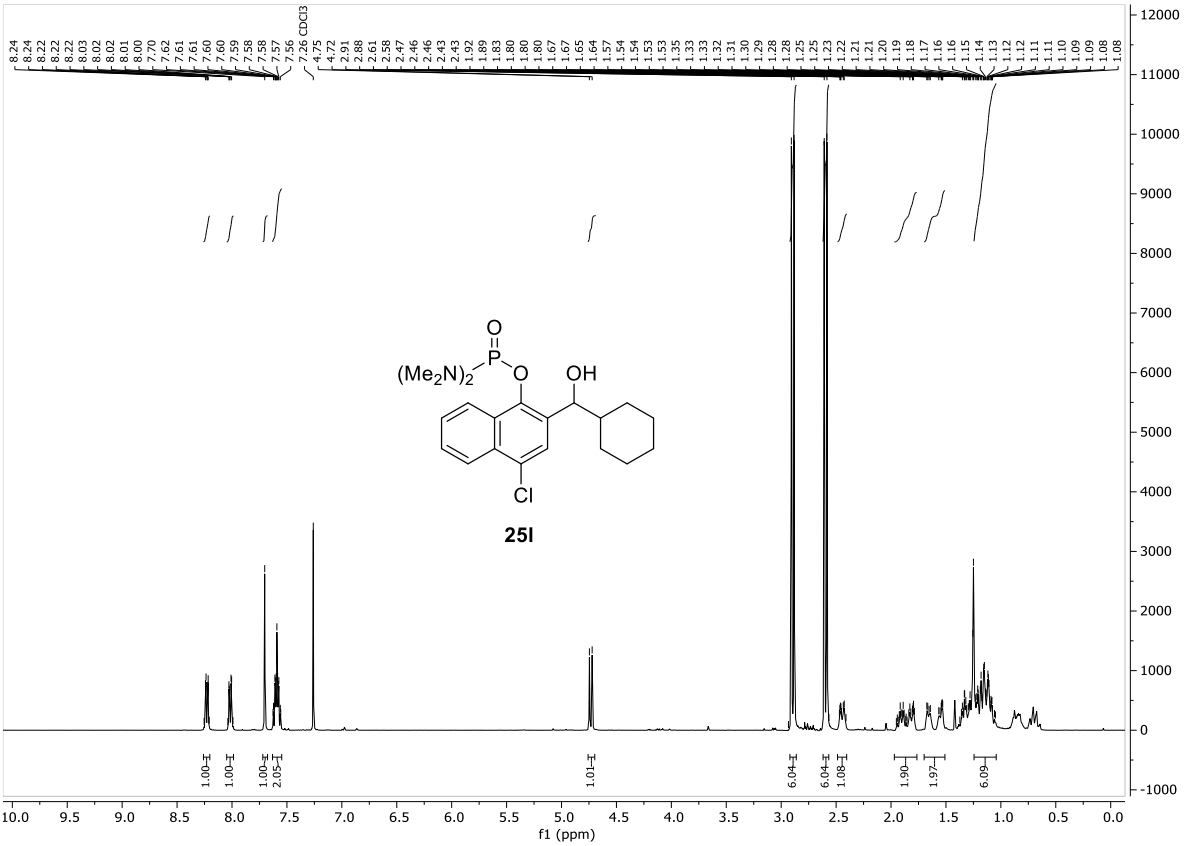
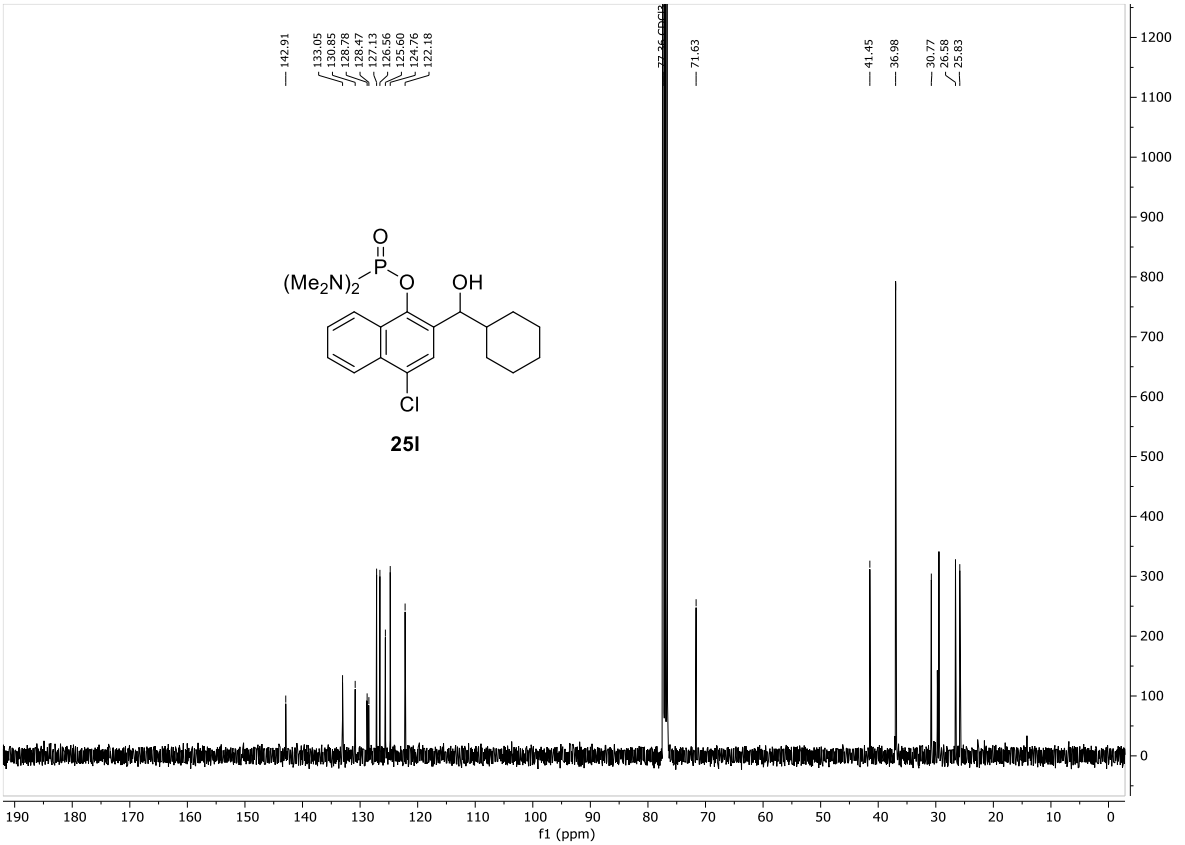
7.45
7.44
7.44
7.44
7.26 CDCl3
7.24
7.23
2.79
2.77
2.76
2.74
O
P
O
(Me2N)2
I
Cl
Cl
25k
1.00
0.98
12.29
f1 (ppm)


153.34
140.13
135.47
124.53
117.79
92.02
36.90
(Me2N)2
P
O
O
I
Cl
Cl
25k
f1 (ppm)


16.48
(Me2N)2
P
O
O
I
Cl
Cl
25k
f1 (ppm)


8.24 8.24 8.22 8.22 8.22 8.22 8.03 8.02 8.02 8.01 8.00 7.70 7.62 7.61 7.61 7.60 7.60 7.59 7.58 7.58 7.57 7.56 CDCl3 7.26 4.75 4.72 2.91 2.88 2.61 2.58 2.47 2.46 2.46 2.43 2.43 1.92 1.89 1.83 1.80 1.80 1.69 1.67 1.65 1.64 1.57 1.54 1.54 1.53 1.53 1.35 1.33 1.33 1.32 1.31 1.30 1.29 1.28 1.28 1.25 1.25 1.23 1.22 1.21 1.21 1.20 1.19 1.18 1.17 1.16 1.16 1.15 1.14 1.13 1.12 1.12 1.11 1.11 1.10 1.09 1.09 1.09 1.08 1.08
O
P
(Me2N)2
O
OH
Cl
25l
1.00 1.00 1.00 2.05 1.01 6.04 6.04 1.08 1.90 1.97 6.09
f1 (ppm)


142.91 133.05 130.85 128.78 128.47 127.13 126.56 125.60 124.76 122.18 77.36 CDCl3 71.63 41.45 36.98 30.77 26.58 25.83
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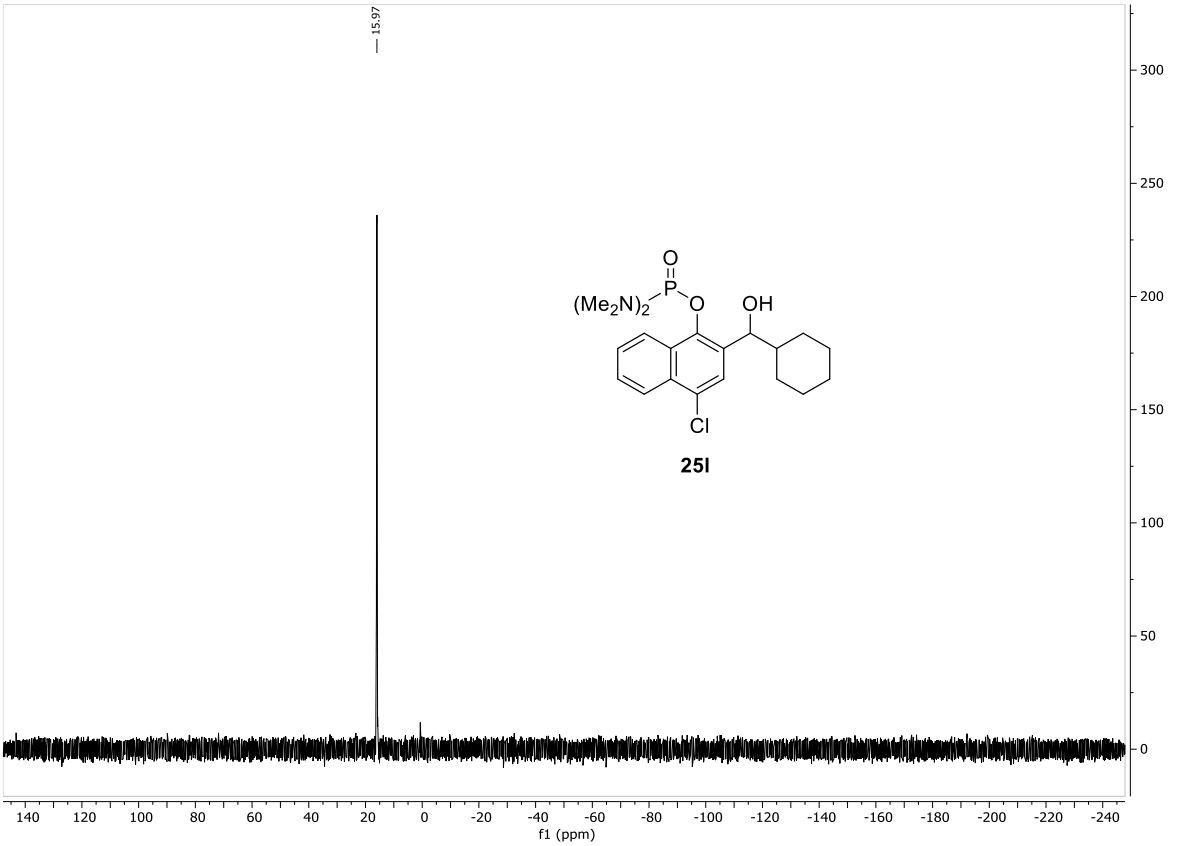
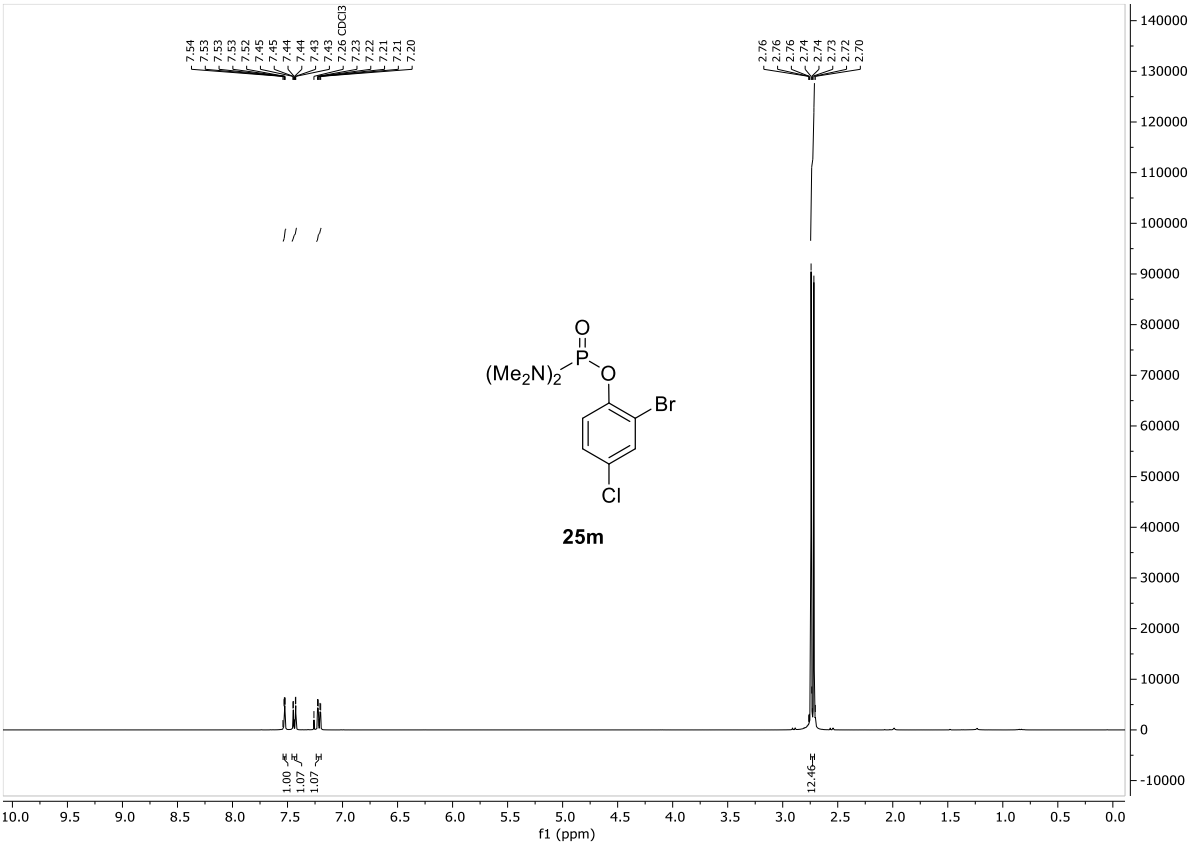
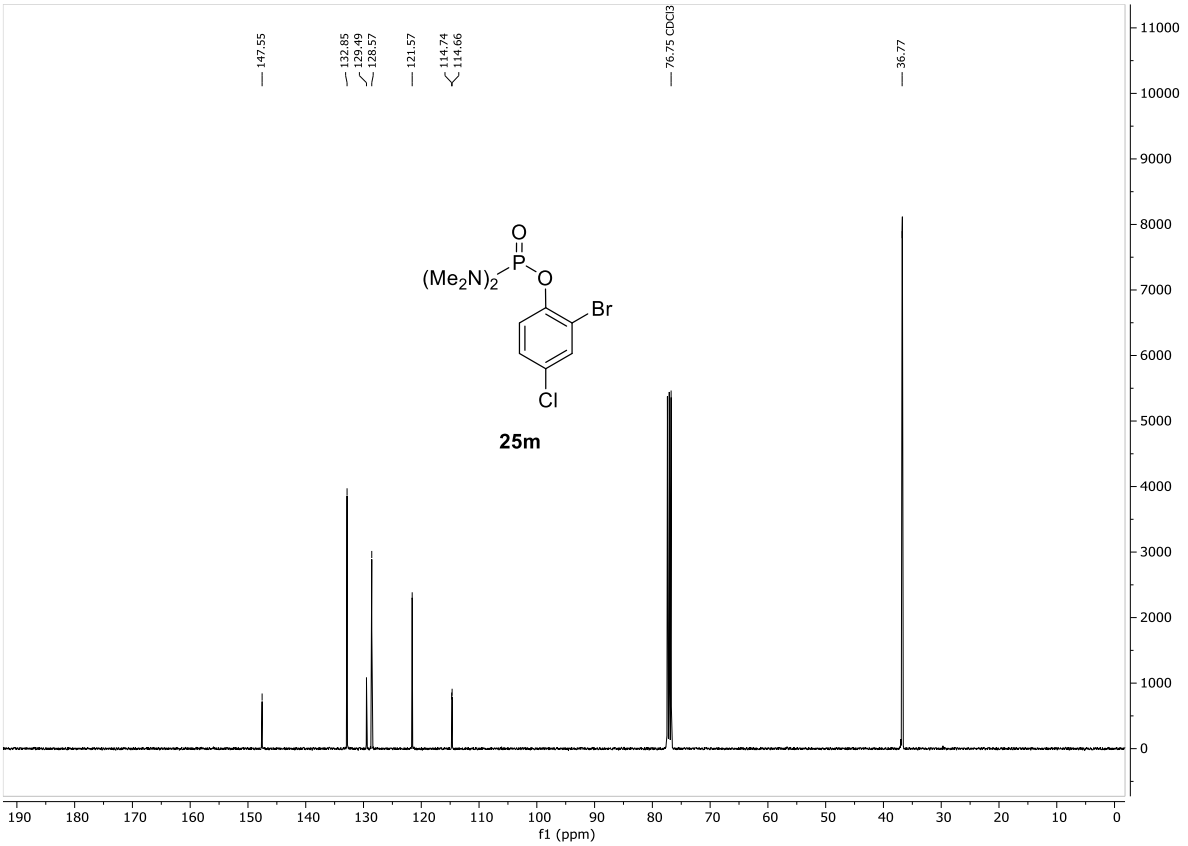
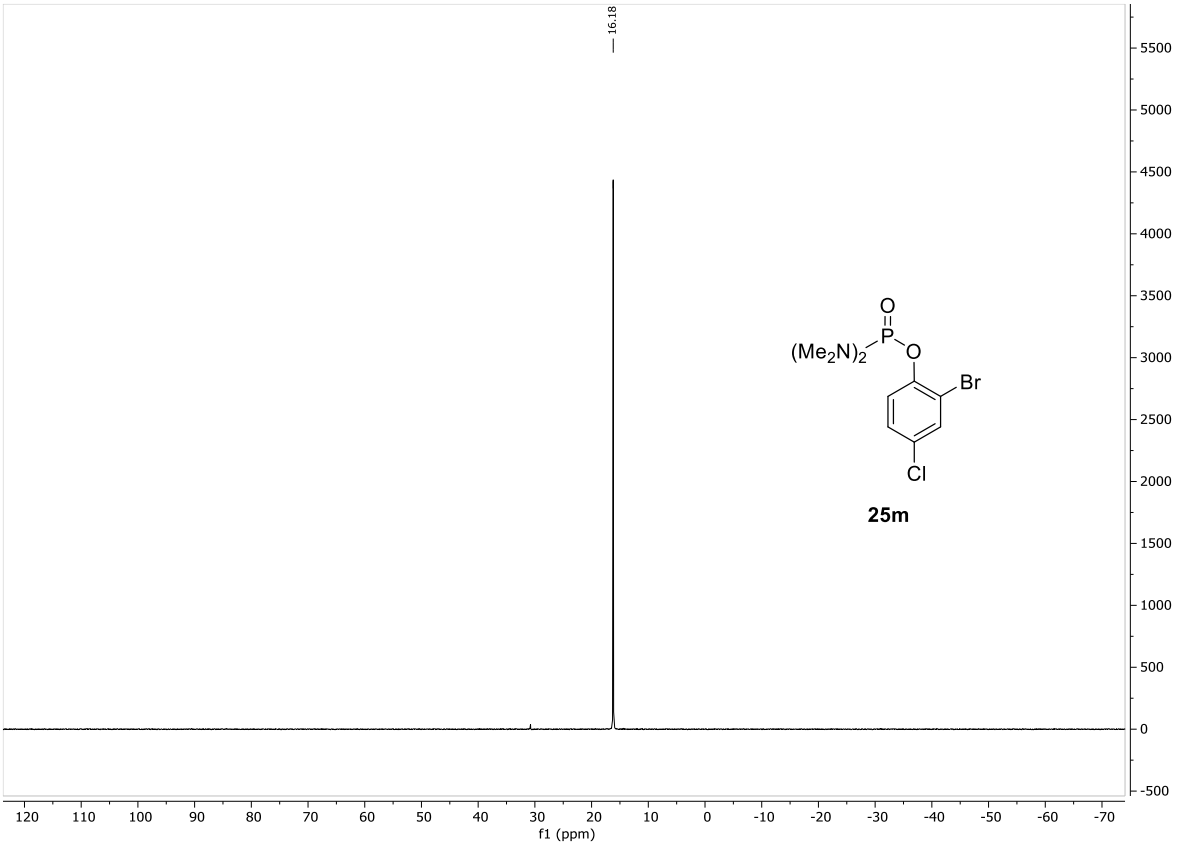
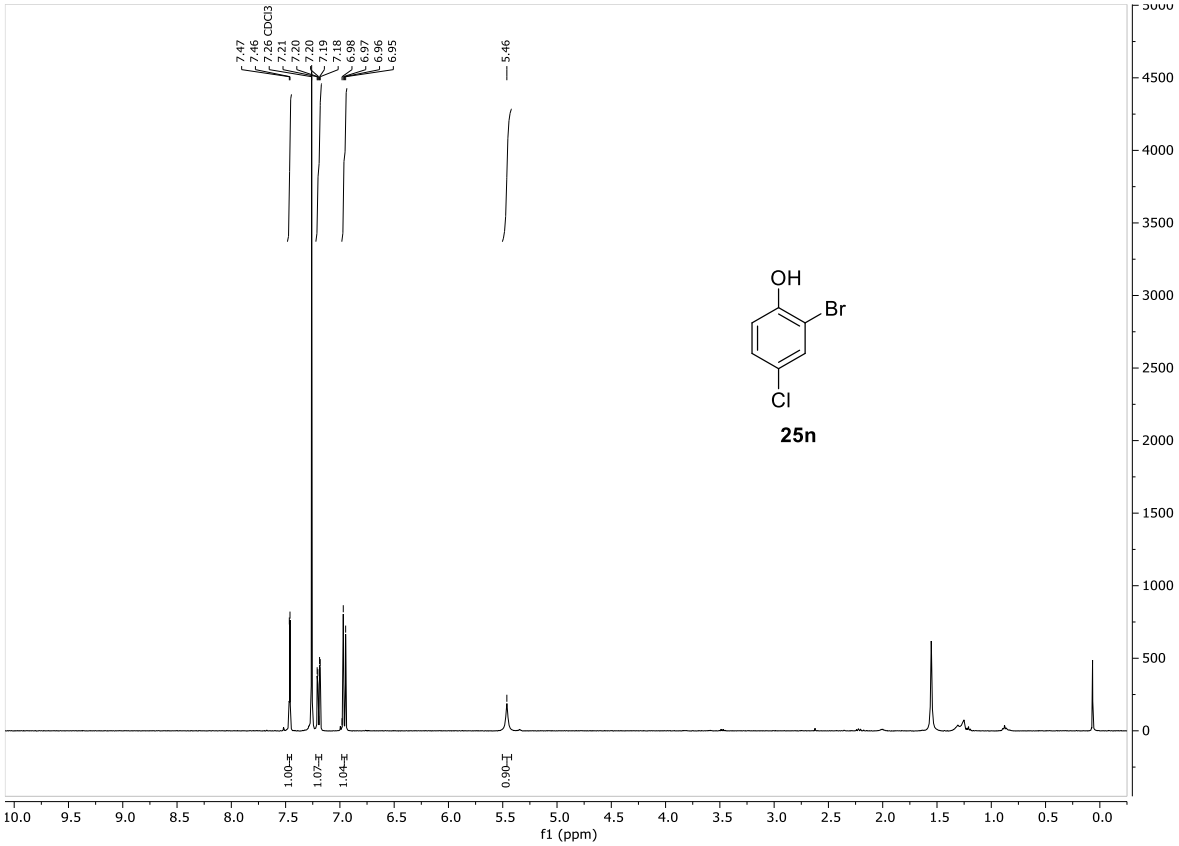
(Me2N)2
O
OH
Cl
25l
f1 (ppm)

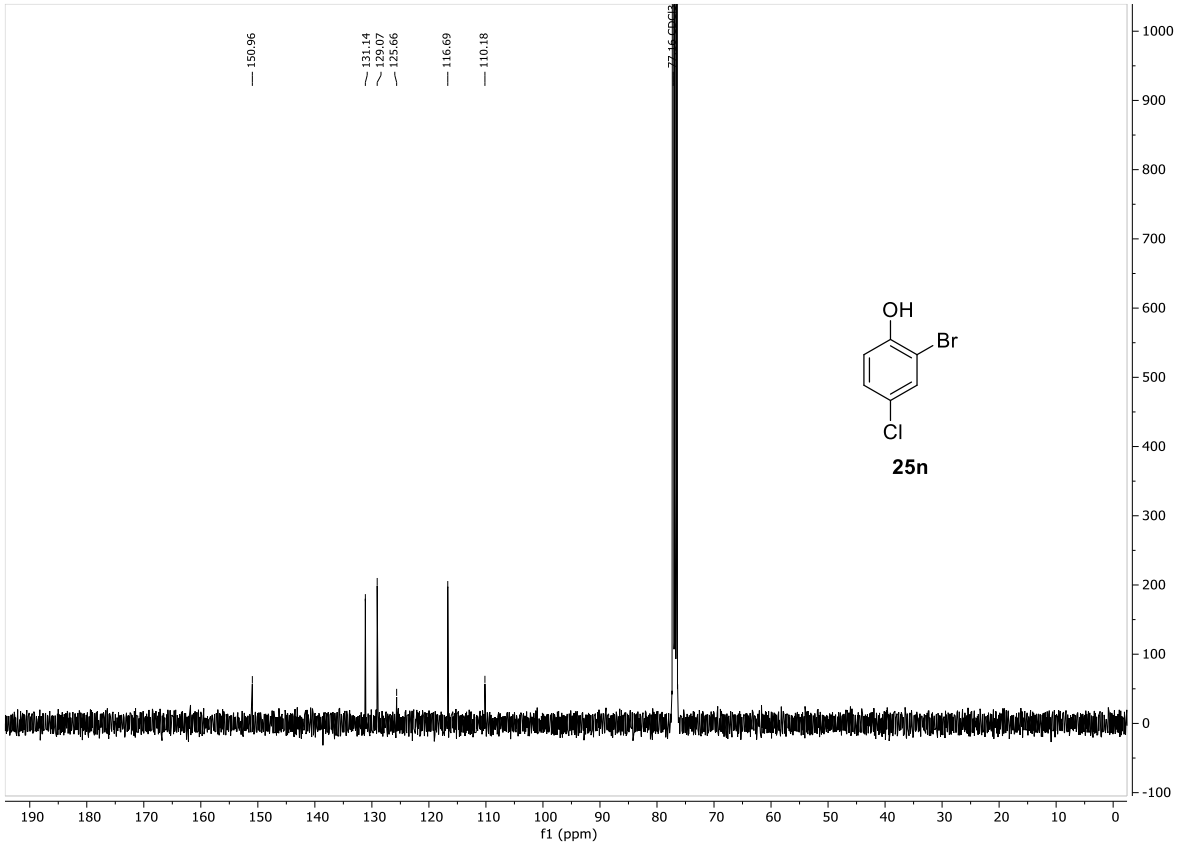

15.97
O
P
(Me2N)2
O
OH
Cl
25l
f1 (ppm)

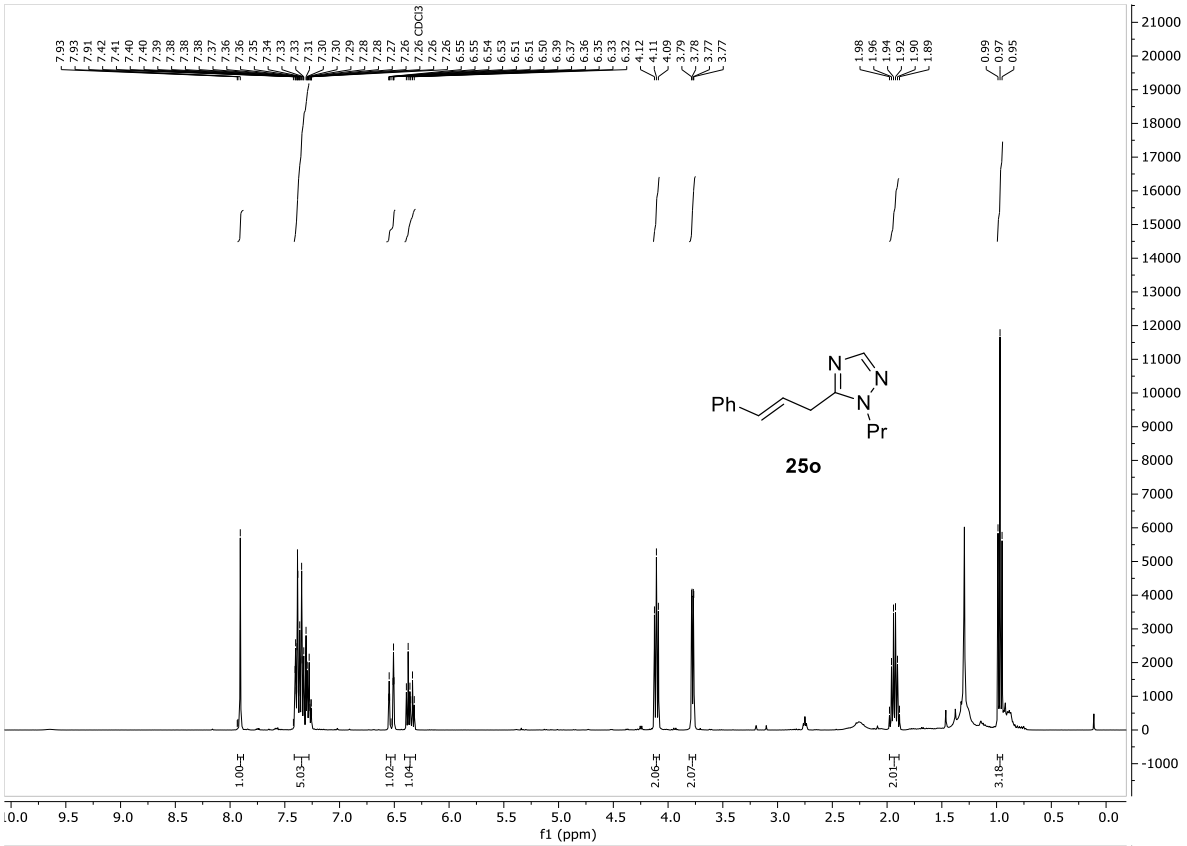

7.54
7.53
7.53
7.53
7.52
7.45
7.45
7.44
7.44
7.43
7.43
7.26 CDCl3
7.23
7.22
7.21
7.21
7.20
2.76
2.76
2.76
2.74
2.74
2.73
2.72
2.70
O
P
(Me2N)2
O
Br
Cl
25m
1.00
1.07
1.07
12.46
f1 (ppm)

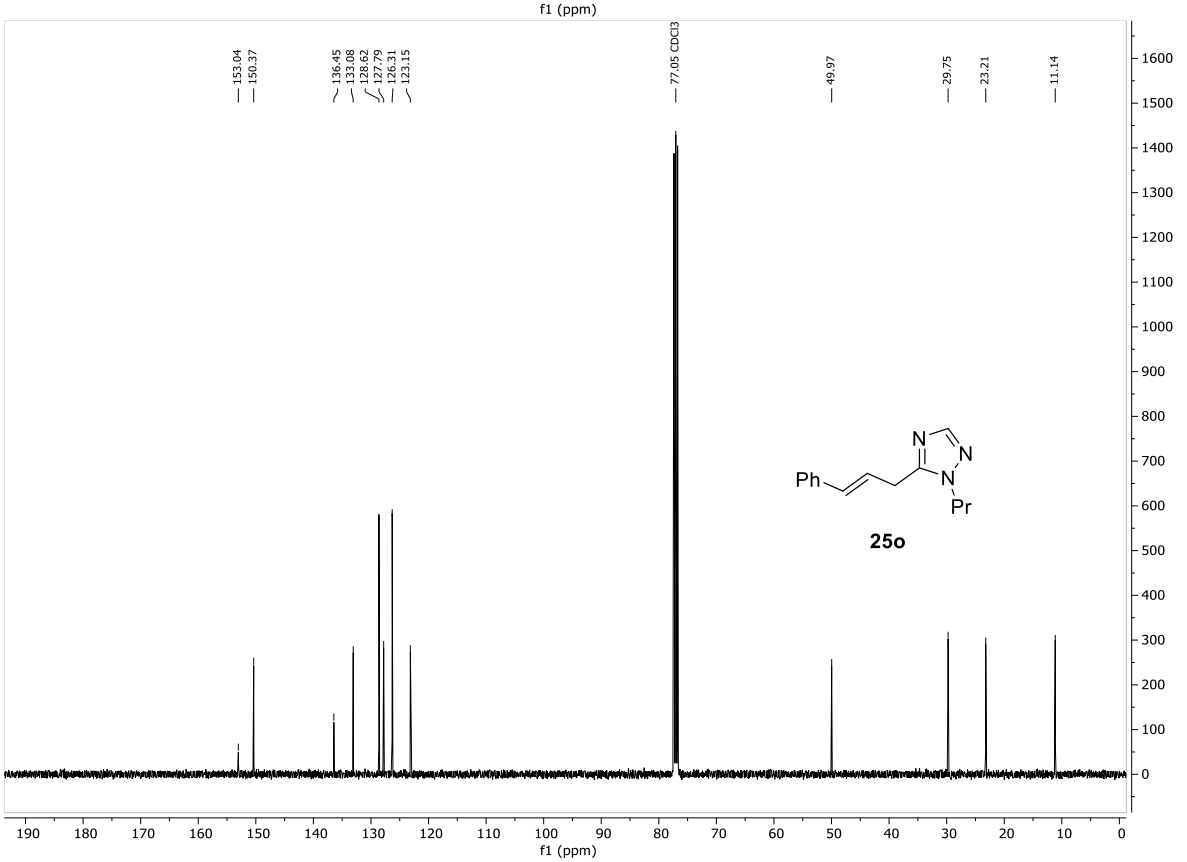

147.55
132.85
129.49
128.57
121.57
114.74
114.66
76.75 CDCl3
36.77
O
P
O
(Me2N)2
Br
Cl
25m
f1 (ppm)

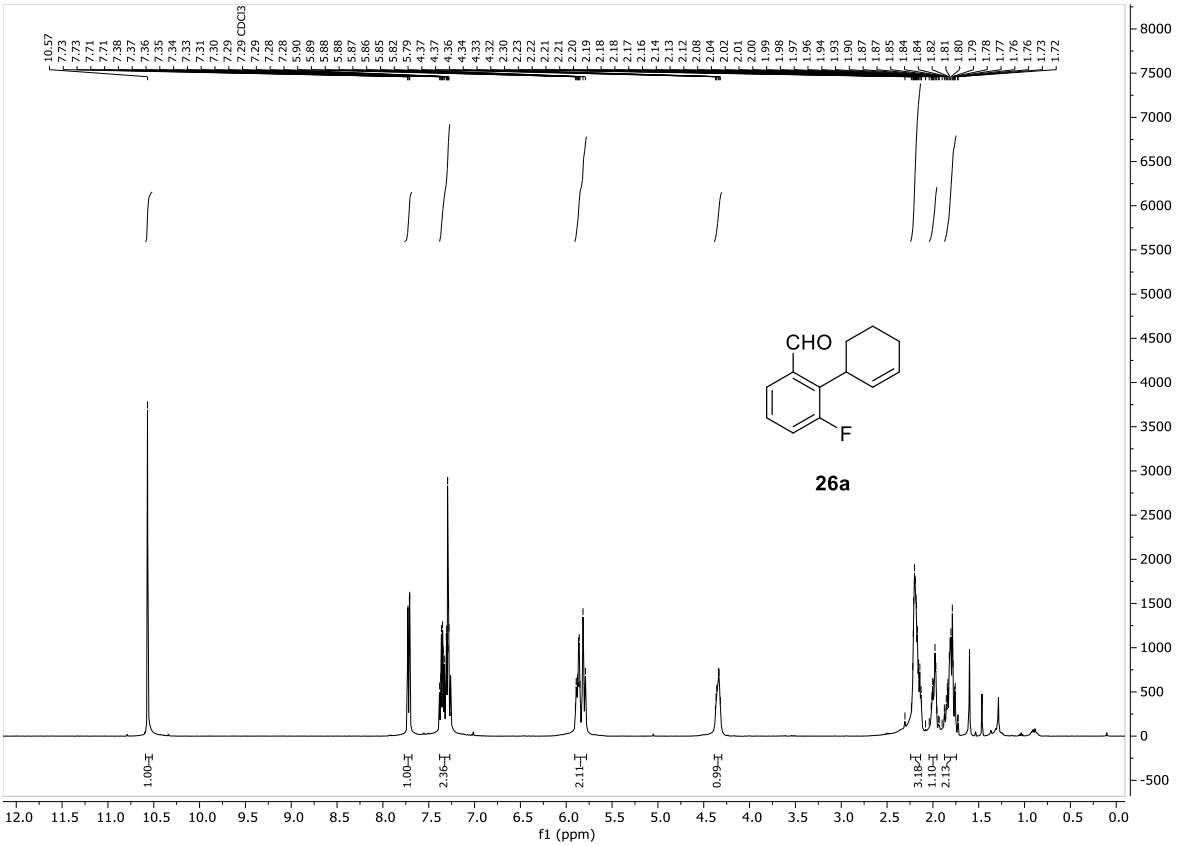

16.18
O
P
O
(Me2N)2
Br
Cl
25m
f1 (ppm)

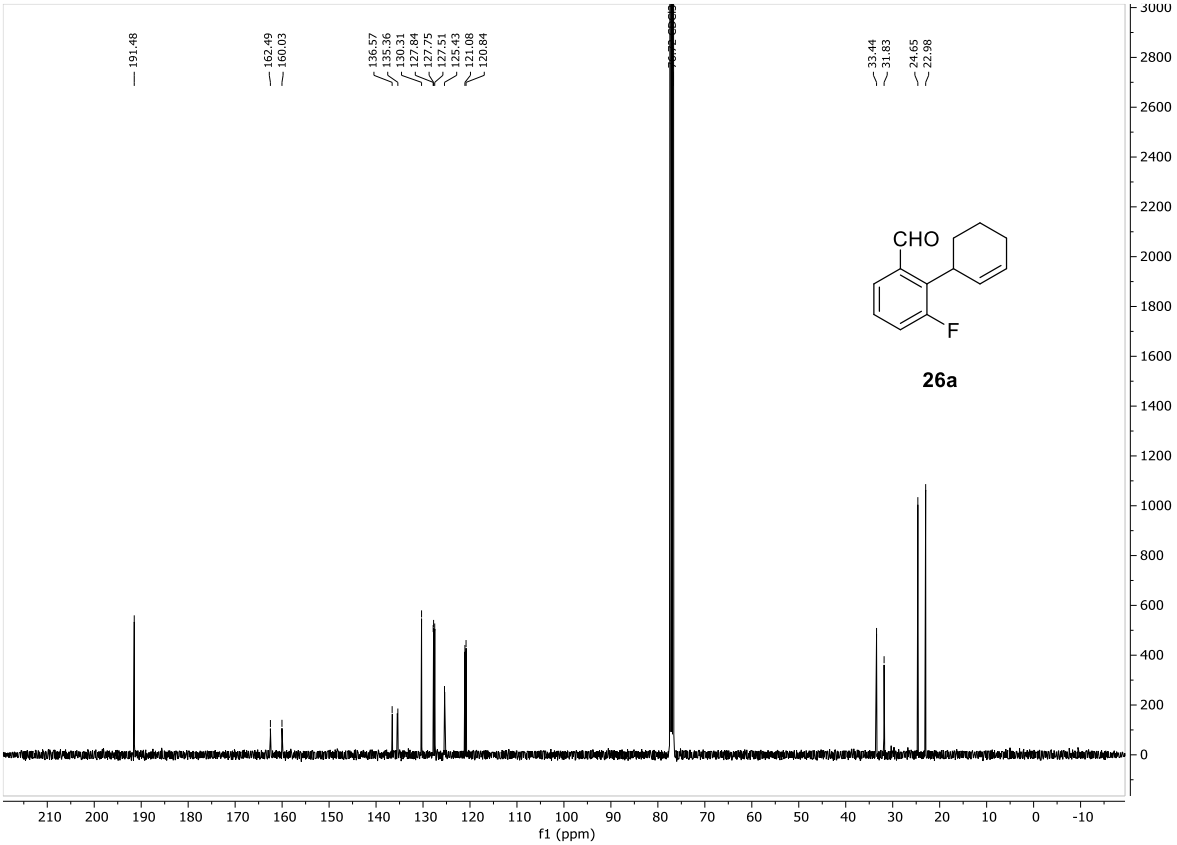

7.47
7.46
7.26 CDCl3
7.21
7.20
7.20
7.19
7.18
6.98
6.97
6.96
6.95
5.46
OH
Br
Cl
25n
1.00
1.07
1.04
0.90
f1 (ppm)

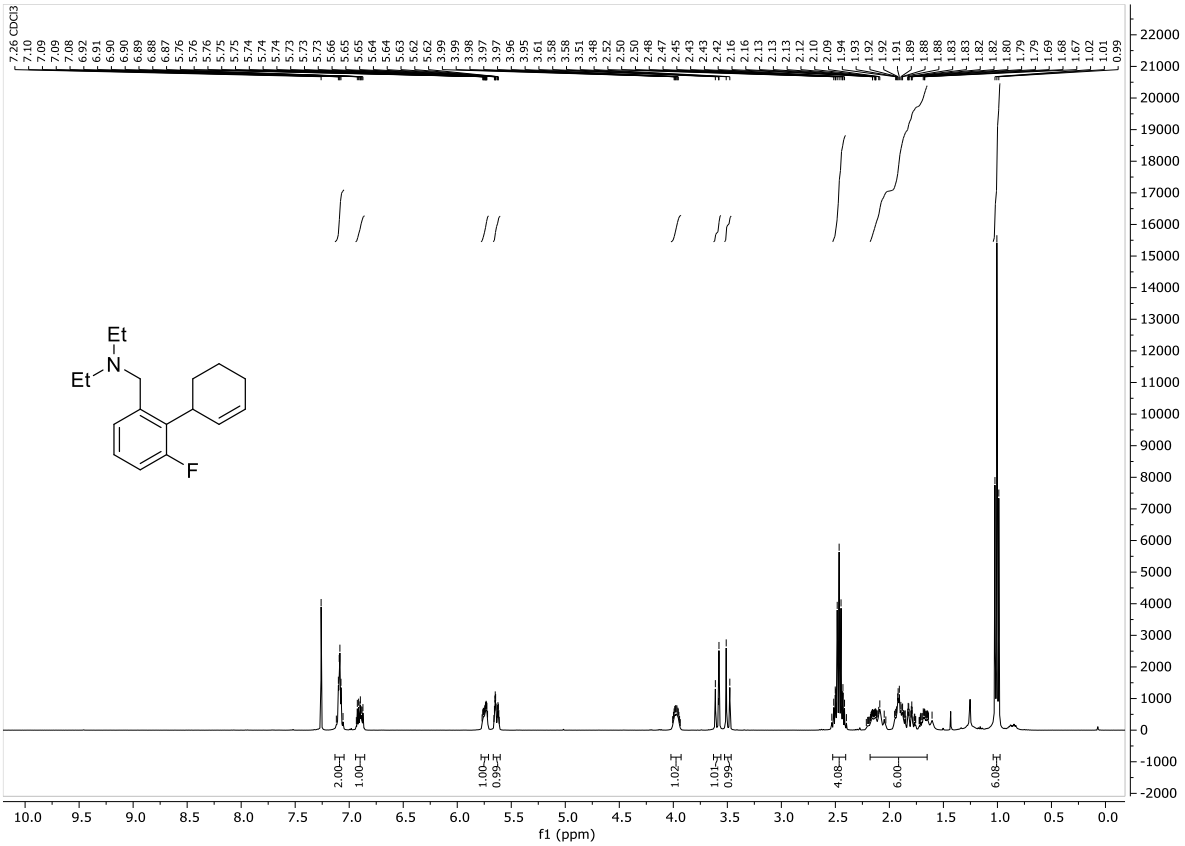

150.96
131.14
129.07
125.66
116.69
110.18
77.16 CDCl3
OH
Br
Cl
25n
f1 (ppm)

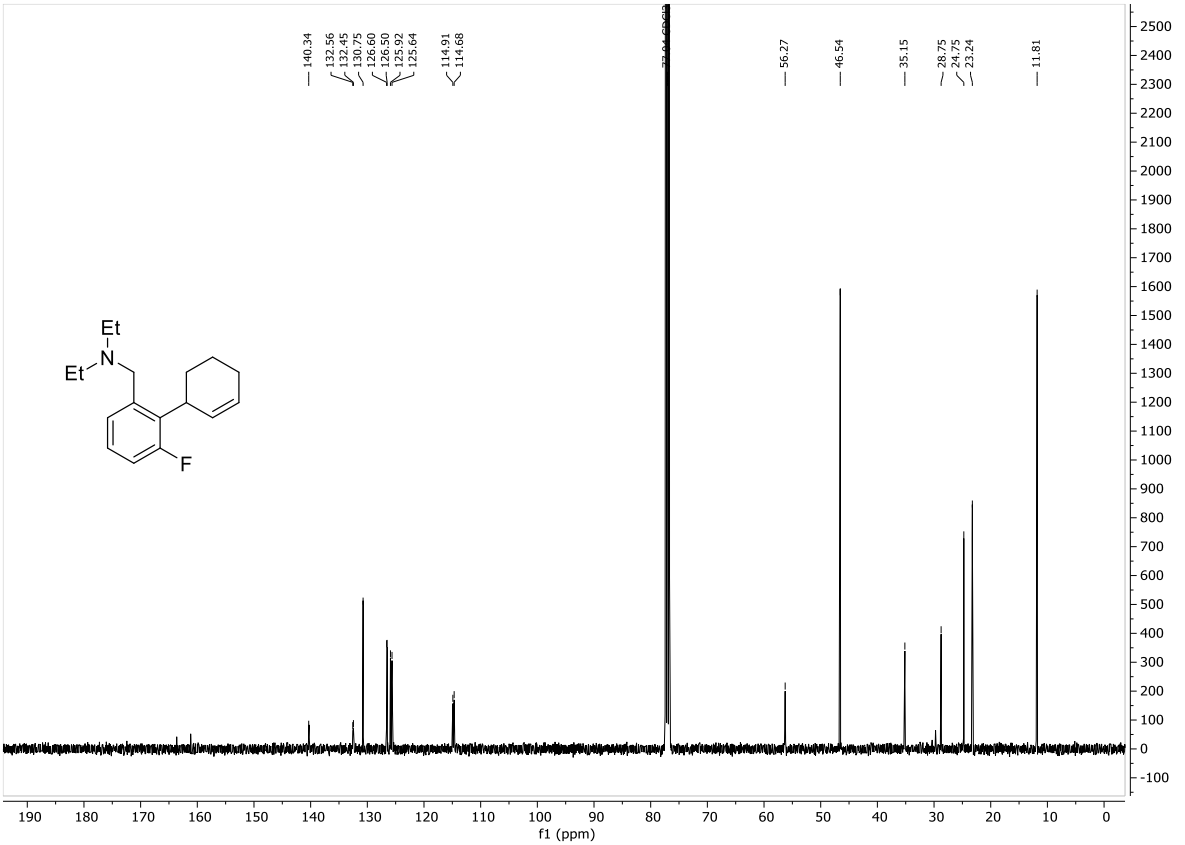

7.93 7.93 7.91 7.42 7.41 7.40 7.40 7.39 7.38 7.38 7.38 7.37 7.36 7.36 7.35 7.34 7.33 7.31 7.30 7.30 7.29 7.28 7.28 7.27 7.26 CDCl3 7.26 7.26 6.55 6.55 6.54 6.53 6.51 6.51 6.50 6.39 6.37 6.36 6.35 6.33 6.32 4.12 4.11 4.09 3.79 3.78 3.77 3.77
1.98 1.96 1.94 1.92 1.90 1.89
0.99 0.97 0.95
1.00 5.03 1.02 1.04 2.06 2.07 2.01 3.18
f1 (ppm)

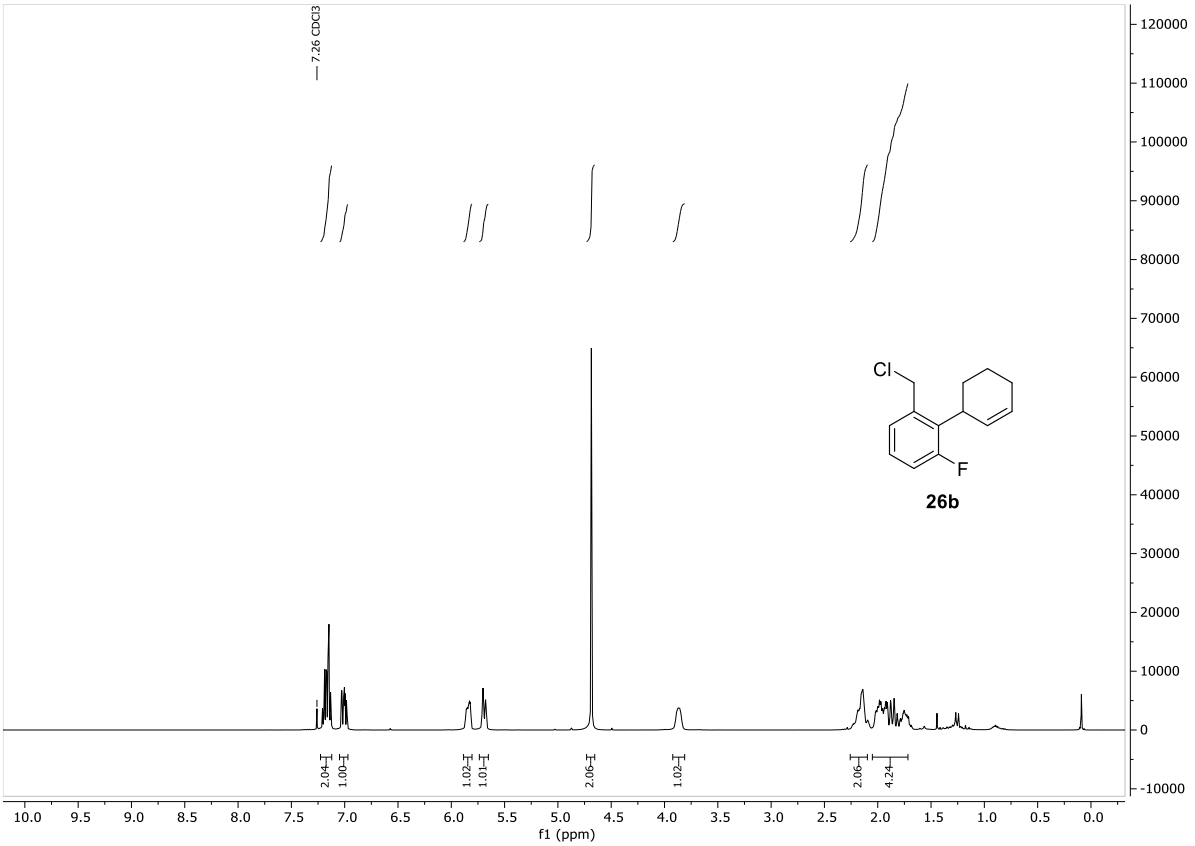

153.04 150.37 136.45 133.08 128.62 127.79 126.31 123.15 77.05 CDCl3 49.97 29.75 23.21 11.14
f1 (ppm)

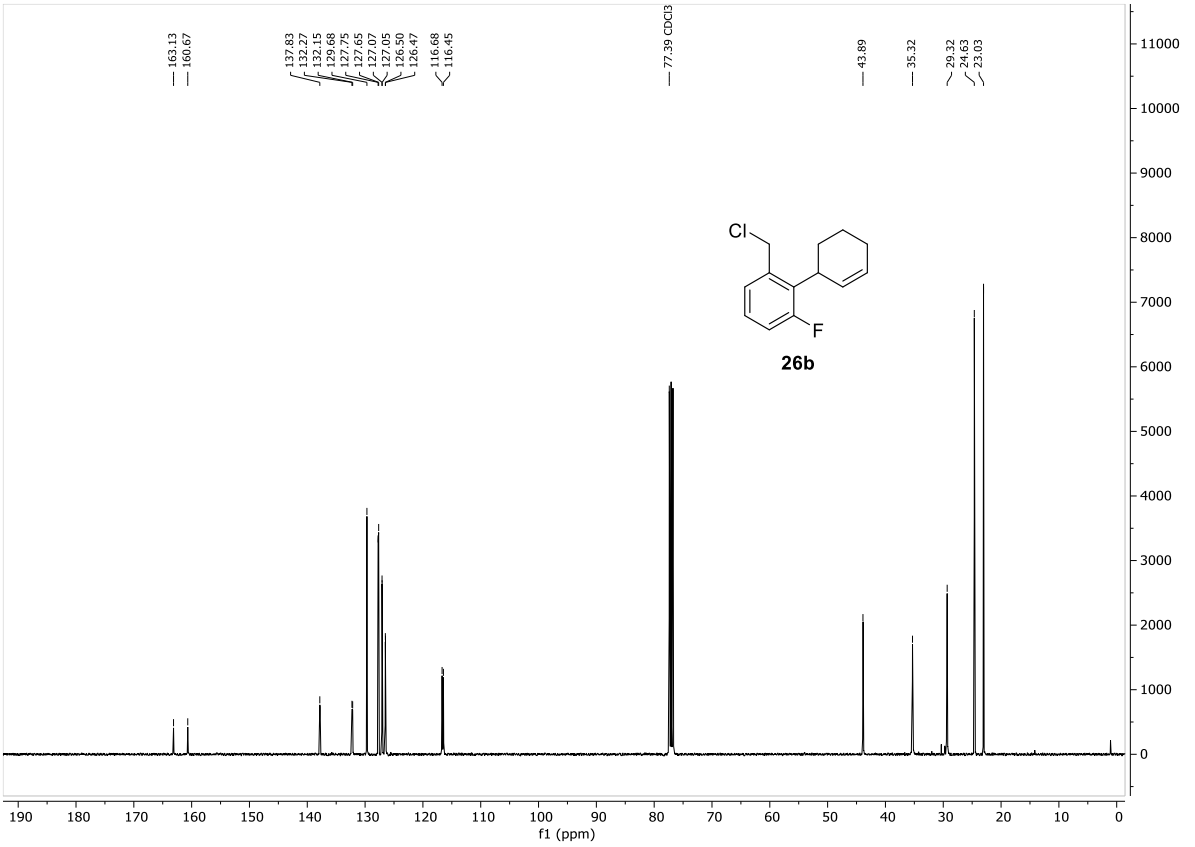

CHO
F
26a
f1 (ppm)


CHO
F
26a
f1 (ppm)


7.26 CDCl3
Et
N
Et
F
2.00
1.00
1.00
0.99
1.02
1.01
0.99
4.08
6.00
6.08
f1 (ppm)


140.34
132.56
132.45
130.75
126.60
126.50
125.92
125.64
114.91
114.68
56.27
46.54
35.15
28.75
24.75
23.24
11.81
Et
N
Et
F
f1 (ppm)


7.26 CDCl3
Cl
F
26b
2.04
1.00
1.02
1.01
2.06
1.02
2.06
4.24
f1 (ppm)


163.13
160.67
137.83
132.27
132.15
129.68
127.75
127.65
127.07
127.05
126.50
126.47
116.68
116.45
77.39 CDCl3
43.89
35.32
29.32
24.63
23.03
Cl
F
26b
f1 (ppm)

9. Single Crystal X-Ray Diffraction Studies

Single crystals of compound **22h**, suitable for X-ray diffraction, were obtained by slow evaporation of CH_2Cl_2 solution. The crystals were introduced into perfluorinated oil and a suitable single crystal was carefully mounted on the top of a thin glass wire. Data collection was performed with an Oxford Xcalibur 3 diffractometer equipped with a Spellman generator (50 kV, 40 mA) and a Kappa CCD detector, operating with Mo-K_α radiation (λ = 0.71071 Á).

Data collection and data reduction were performed with the CrysAlisPro software.[22] Absorption correction using the multiscan method[22] was applied. The structures were solved with SHELXS-97,[23] refined with SHELXL-97[24] and finally checked using PLATON.[25] Details for data collection and structure refinement are summarized in Table 1.

CCDC-2061336 contains supplementary crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

[22] Program package 'CrysAlisPro 1.171.40.82a (Rigaku OD, 2020)'.
[23] Sheldrick, G. M. (1997) SHELXS-97: *Program for Crystal Structure Solution*, University of Göttingen, Germany.
[24] Sheldrick, G. M. (1997) SHELXL-97: *Program for the Refinement of Crystal Structures*, University of Göttingen, Germany.
[25] Spek, A. L. (1999) PLATON: *A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands.

Table 2. Details for X-ray data collection and structure refinement for compound **22h**.

	22h
Empirical formula	$C_{21}H_{24}BrN_3O_5Si$
Formula mass	506.43
T[K]	123(2)
Crystal size [mm]	0.35 × 0.20 × 0.05
Crystal description	colorless block
Crystal system	triclinic
Space group	*P*-1
a [Å]	8.0355(4)
b [Å]	11.4221(6)
c [Å]	13.0590(5)
α [°]	105.984(4)
β [°]	104.098(4)
γ [°]	96.492(4)
V [Å^3]	1096.48(9)
Z	2
$\rho_{calcd.}$ [g cm^{-3}]	1.534
μ [mm^{-1}]	1.968
F(000)	520
Θ range [°]	2.72 – 25.24
Index ranges	-11 ≤ *h* ≤ 11
	-16 ≤ *k* ≤ 16
	-18 ≤ *l* ≤ 18
Reflns. collected	22400
Reflns. obsd.	4584
Reflns. unique	6683 (R_{int} = 0.0601)
R_1, wR_2 (2σ data)	0.0475, 0.0929
R_1, wR_2 (all data)	0.0826, 0.1078
GOOF on F^2	1.032
Peak/hole [e Å^{-3}]	0.757 / -0.430

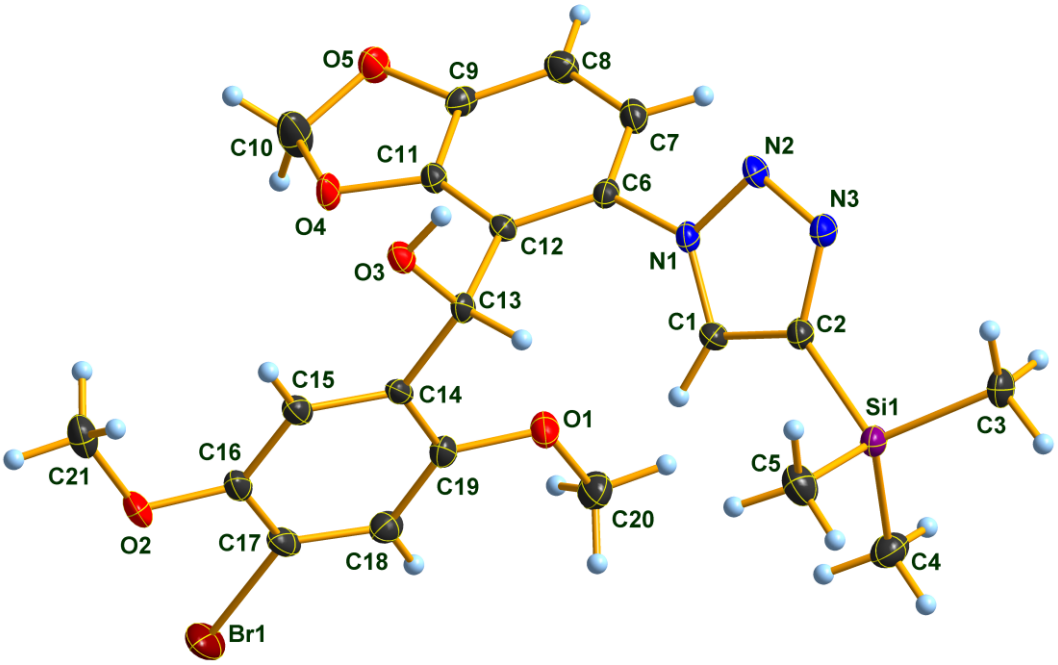


Figure 1. Molecular structure of compound **22h** in the crystal. DIAMOND[26] representation; thermal ellipsoids are drawn at 50 % probability level.

Table 3. Selected bond lengths (Å) of compound **22h**.

Br1 – C17	1.895(2)	O5 – C9	1.379(3)
O1 – C19	1.373(3)	O5 – C10	1.412(3)
O1 – C20	1.421(3)	C6 – C7	1.382(3)
N1 – C1	1.346(3)	C6 – C12	1.413(3)
N1 – N2	1.357(2)	C7 – C8	1.393(3)
N1 – C6	1.442(3)	C8 – C9	1.373(3)
C1 – C2	1.375(3)	C9 – C11	1.379(3)
Si1 – C5	1.852(3)	C12 – C11	1.379(3)
Si1 – C4	1.856(3)	C12 – C13	1.526(3)
Si1 – C3	1.861(2)	C13 – C14	1.522(3)
Si1 – C2	1.876(3)	C17 – C16	1.380(4)
N3 – N2	1.315(3)	C17 – C18	1.386(3)
N3 – C2	1.378(3)	C19 – C18	1.386(3)
O3 – C13	1.422(3)	C19 – C14	1.393(3)
O2 – C16	1.371(3)	C16 – C15	1.398(3)
O2 – C21	1.419(3)	C14 – C15	1.390(3)
O4 – C11	1.376(3)	O4 – C10	1.420(3)

[26] DIAMOND, Crystal Impact GbR., Version 3.2i

Table 4. Selected bond angles (°) of compound **22h**.

C19 – O1 – C20	118.3(2)	C8 – C9 – C11	122.1(2)
C1 – N1 – N2	110.7(2)	O5 – C9 – C11	109.5(2)
C1 – N1 – C6	130.8(2)	O5 – C10 – O4	108.9(2)
N2 – N1 – C6	118.5(2)	C11 – C12 – C6	113.8(2)
N1 – C1 – C2	106.4(2)	C11 – C12 – C13	119.5(2)
C5 – Si1 – C4	109.9(1)	C6 – C12 – C13	126.7(2)
C5 – Si1 – C3	109.9(1)	O4 – C11 – C12	126.2(2)
C4 – Si1 – C3	111.5(1)	O4 – C11 – C9	109.8(2)
C5 – Si1 – C2	108.8(1)	C12 – C11 – C9	123.9(2)
C4 – Si1 – C2	109.5(1)	O3 – C13 – C14	109.2(2)
C3 – Si1 – C2	107.3(1)	O3 – C13 – C12	109.4(2)
N2 – N3 – C2	110.6(2)	C14 – C13 – C12	111.9(2)
C1 – C2 – N3	106.1(2)	C16 – C17 – C18	122.1(2)
C1 – C2 – Si1	130.5(2)	C16 – C17 – Br1	119.7(2)
N3 – C2 – Si1	123.7(2)	C18 – C17 – Br1	118.1(2)
C16 – O2 – C21	117.3(2)	O1 – C19 – C18	123.5(2)
N3 – N2 – N1	106.3(2)	O1 – C19 – C14	115.7(2)
C11 – O4 – C10	104.3(2)	C18 – C19 – C14	120.8(2)
C9 – O5 – C10	104.6(2)	O2 – C16 – C17	117.6(2)
C7 – C6 – C12	122.4(2)	O2 – C16 – C15	124.3(2)
C7 – C6 – N1	116.7(2)	C17 – C16 – C15	118.1(2)
C12 – C6 – N1	120.8(2)	C15 – C14 – C19	119.0(2)
C6 – C7 – C8	122.0(2)	C15 – C14 – C13	121.2(2)
C9 – C8 – C7	115.7(2)	C19 – C14 – C13	119.7(2)
C8 – C9 – O5	128.3(2)	C14 – C15 – C16	121.1(2)
C19 – C18 – C17	118.8(2)		

Table 5. Selected torsion angles (°) of compound **22h**.

N2 – N1 – C1 – C2	0.6(3)	C13 – C12 – C11 – O4	0.7(3)
C6 – N1 – C1 – C2	177.8(2)	C6 – C12 – C11 – C9	0.1(3)
N1 – C1 – C2 – N3	-0.8(3)	C13 – C12 – C11 – C9	177.1(2)
N1 – C1 – C2 – Si1	175.0(2)	C8 – C9 – C11 – O4	175.8(2)
N2 – N3 – C2 – C1	0.7(3)	O5 – C9 – C11 – O4	-0.9(3)
N2 – N3 – C2 – Si1	-175.4(2)	C8 – C9 – C11 – C12	-1.0(4)
C5 – Si1 – C2 – C1	-76.1(3)	O5 – C9 – C11 – C12	-177.7(2)
C4 – Si1 – C2 – C1	44.0(3)	C11 – C12 – C13 – O3	-66.7(2)
C3 – Si1 – C2 – C1	165.1(2)	C6 – C12 – C13 – O3	109.8(2)
C5 – Si1 – C2 – N3	99.0(2)	C11 – C12 – C13 – C14	54.5(3)

C4 – Si1 – C2 – N3	-140.9(2)	C6 – C12 – C13 – C14	-129.0(2)
C3 – Si1 – C2 – N3	-19.8(2)	C20 – O1 – C19 – C18	-2.7(3)
C2 – N3 – N2 – N1	-0.3(2)	C20 – O1 – C19 – C14	178.1(2)
C1 – N1 – N2 – N3	-0.2(2)	C21 – O2 – C16 – C17	-164.7(2)
C6 – N1 – N2 – N3	-177.8(2)	C21 – O2 – C16 – C15	16.9(3)
C1 – N1 – C6 – C7	-131.2(3)	C18 – C17 – C16 – O2	-177.5(2)
N2 – N1 – C6 – C7	45.8(3)	Br1 – C17 – C16 – O2	3.9(3)
C1 – N1 – C6 – C12	49.8(3)	C18 – C17 – C16 – C15	1.1(4)
N2 – N1 – C6 – C12	-133.2(2)	Br1 – C17 – C16 – C15	-177.5(2)
C12 – C6 – C7 – C8	-0.2(4)	O1 – C19 – C14 – C15	-179.1(2)
N1 – C6 – C7 – C8	-179.2(2)	C18 – C19 – C14 – C15	1.6(3)
C6 – C7 – C8 – C9	-0.6(3)	O1 – C19 – C14 – C13	0.5(3)
C7 – C8 – C9 – O5	177.3(2)	C18 – C19 – C14 – C13	-178.7(2)
C7 – C8 – C9 – C11	1.2(3)	O3 – C13 – C14 – C15	-0.6(3)
C10 – O5 – C9 – C8	173.9(3)	C12 – C13 – C14 – C15	-121.8(2)
C10 – O5 – C9 – C11	-9.6(3)	O3 – C13 – C14 – C19	179.8(2)
C9 – O5 – C10 – O4	16.5(3)	C12 – C13 – C14 – C19	58.6(3)
C11 – O4 – C10 – O5	-17.0(3)	C19 – C14 – C15 – C16	-1.8(3)
C7 – C6 – C12 – C11	0.5(3)	C13 – C14 – C15 – C16	178.5(2)
N1 – C6 – C12 – C11	179.3(2)	O2 – C16 – C15 – C14	179.0(2)
C7 – C6 – C12 – C13	-176.2(2)	C17 – C16 – C15 – C14	0.5(4)
N1 – C6 – C12 – C13	2.7(3)	O1 – C19 – C18 – C17	-179.3(2)
C10 – O4 – C11 – C12	-172.3(2)	C14 – C19 – C18 – C17	-0.1(4)
C10 – O4 – C11 – C9	10.9(3)	C16 – C17 – C18 – C19	-1.3(4)
C6 – C12 – C11 – O4	-176.2(2)	Br1 – C17 – C18 – C19	177.4(2)

Single Crystal X-Ray Diffraction Studies

Single crystals of compound **19b**, suitable for X-ray diffraction, were obtained by slow evaporation of CH_2Cl_2 solution. The crystals were introduced into perfluorinated oil and a suitable single crystal was carefully mounted on the top of a thin glass wire. Data collection was performed with an Oxford Xcalibur 3 diffractometer equipped with a Spellman generator (50 kV, 40 mA) and a Kappa CCD detector, operating with Mo-K_α radiation (λ = 0.71071 Å).

Data collection and data reduction were performed with the CrysAlisPro software.[27] Absorption correction using the multiscan method[27] was applied. The structures were solved with SHELXS-97,[28] refined with SHELXL-97[29] and finally checked using PLATON.[30] Details for data collection and structure refinement are summarized in Table 5.

CCDC-2061337 contains supplementary crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

[27] Program package 'CrysAlisPro 1.171.40.82a (Rigaku OD, 2020)'.
[28] Sheldrick, G. M. (1997) SHELXS-97: *Program for Crystal Structure Solution*, University of Göttingen, Germany.
[29] Sheldrick, G. M. (1997) SHELXL-97: *Program for the Refinement of Crystal Structures*, University of Göttingen, Germany.
[30] Spek, A. L. (1999) PLATON: *A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands.

Table 6. Details for X-ray data collection and structure refinement for compound **19b**.

	19b
Empirical formula	$C_9H_6Cl_2IN_3S$
Formula mass	386.03
T[K]	123(2)
Crystal size [mm]	0.40 × 0.25 × 0.05
Crystal description	colorless platelet
Crystal system	orthorhombic
Space group	*Iba*2
a [Å]	29.5021(13)
b [Å]	9.0794(3)
c [Å]	9.4820(4)
α [°]	90.0
β [°]	90.0
γ [°]	90.0
V [Å^3]	2539.86(18)
Z	8
$\rho_{calcd.}$ [g cm^{-3}]	2.019
μ [mm^{-1}]	3.082
F(000)	1472
Θ range [°]	2.34 – 25.24
Index ranges	-36 ≤ *h* ≤ 36
	-11 ≤ *k* ≤ 11
	-11 ≤ *l* ≤ 11
Reflns. collected	15592
Reflns. obsd.	2254
Reflns. unique	2462 (R_{int} = 0.0560)
R_1, wR_2 (2σ data)	0.0317, 0.0722
R_1, wR_2 (all data)	0.0369, 0.0757
GOOF on F^2	1.059
Peak/hole [e Å^{-3}]	1.370 / -0.491

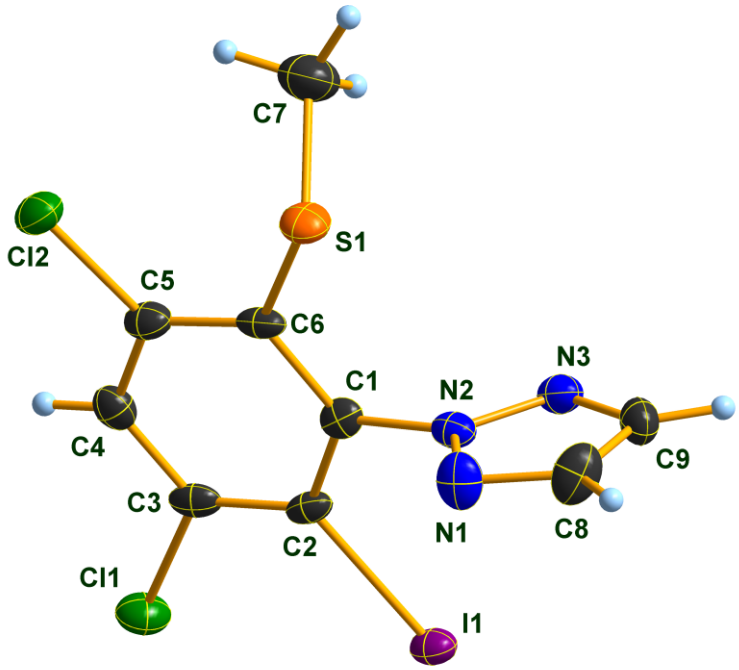


Figure 2. Molecular structure of compound **19b** in the crystal. DIAMOND[31] representation; thermal ellipsoids are drawn at 50 % probability level.

Table 7. Selected bond lengths (Å) of compound **19b**.

I1 – C2	2.095(7)	N3 – C9	1.323(10)
S1 – C6	1.779(9)	C3 – C4	1.381(11)
S1 – C7	1.798(10)	C4 – C5	1.390(11)
Cl1 – C3	1.745(8)	C6 – C5	1.386(12)
N1 – C8	1.311(12)	C8 – C9	1.374(17)
N1 – N2	1.332(9)	N2 – N3	1.330(9)
C1 – C2	1.408(11)	Cl2 – C5	1.733(8)
C1 – C6	1.411(11)	C2 – C3	1.379(11)
C1 – N2	1.412(10)		

Table 8. Selected bond angles (°) of compound **19b**.

C6 – S1 – C7	101.5(4)	C5 – C6 – C1	117.2(7)
C8 – N1 – N2	102.6(8)	C5 – C6 – S1	124.4(6)
C2 – C1 – C6	121.7(7)	C1 – C6 – S1	118.1(6)
C2 – C1 – N2	118.9(7)	C6 – C5 – C4	122.0(8)
C6 – C1 – N2	119.3(7)	C6 – C5 – Cl2	120.8(6)
N3 – N2 – N1	115.3(6)	C4 – C5 – Cl2	117.2(6)

[31] DIAMOND, Crystal Impact GbR., Version 3.2i.

N3 – N2 – C1	123.3(6)	N1 – C8 – C9	110.5(9)
N1 – N2 – C1	121.4(6)	N3 – C9 – C8	108.3(8)
C3 – C2 – C1	118.2(7)	C2 – C3 – C4	121.7(7)
C3 – C2 – I1	122.2(6)	C2 – C3 – Cl1	121.2(6)
C1 – C2 – I1	119.7(6)	C4 – C3 – Cl1	117.1(6)
C9 – N3 – N2	103.3(7)	C3 – C4 – C5	119.3(8)

Table 9. Selected torsion angles (°) of compound **19b**.

C8 – N1 – N2 – C1	-179.8(7)	C2 – C1 – C6 – C5	0.1(11)
C2 – C1 – N2 – N3	82.3(9)	N2 – C1 – C6 – C5	-175.0(6)
C6 – C1 – N2 – N3	-102.5(8)	C2 – C1 – C6 – S1	174.4(5)
C2 – C1 – N2 – N1	-96.3(9)	N2 – C1 – C6 – S1	-0.8(9)
C6 – C1 – N2 – N1	78.9(9)	C7 – S1 – C6 – C5	-66.7(7)
C6 – C1 – C2 – C3	-0.4(10)	C7 – S1 – C6 – C1	119.5(7)
N2 – C1 – C2 – C3	174.7(6)	C1 – C6 – C5 – C4	-0.5(11)
C6 – C1 – C2 – I1	180.0(5)	S1 – C6 – C5 – C4	-174.3(6)
N2 – C1 – C2 – I1	-4.9(9)	C1 – C6 – C5 – Cl2	175.9(6)
N1 – N2 – N3 – C9	-1.4(9)	S1 – C6 – C5 – Cl2	2.1(10)
C1 – N2 – N3 – C9	179.9(7)	C3 – C4 – C5 – C6	1.2(11)
C1 – C2 – C3 – C4	1.1(11)	C3 – C4 – C5 – Cl2	-175.4(6)
I1 – C2 – C3 – C4	-179.3(5)	N2 – N1 – C8 – C9	-1.(1)
C1 – C2 – C3 – Cl1	-175.1(5)	N2 – N3 – C9 – C8	0.7(9)
I1 – C2 – C3 – Cl1	4.5(9)	N1 – C8 – C9 – N3	0.2(11)
C2 – C3 – C4 – C5	-1.5(11)		