Electronic Supplementary Material (ESI) for ChemComm.

Defluorinative Arylation of Trifluoromethyl Alkenes via Photoredox Catalysis

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Supporting Information

Key to Abbreviated Terms:

4CzIPN: 2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile
Cl-4CzIPN: 2,4,5,6-tetrakis(3,6-dichloro-9H-carbazol-9-yl)isophthalonitrile
bpy: 2,2′-bipyridyl
dtbbpy: 4,4′-di-*tert*-butyl-2,2′-dipyridyl
ppy: 2-(pyridinyl)phenyl
LED: Light-emitting diode

General Considerations:

General: All chemical transformations requiring inert atmospheric conditions or vacuum distillation utilized Schlenk line techniques with a 4- or 5-port dual-bank manifold. Argon or nitrogen was used to provide such an atmosphere. LED irradiation was accomplished using the LED reactors described in our previous reports.[1] NMR spectra (^{1}H, ^{13}C, ^{19}F) were obtained at 298 K. ^{1}H NMR spectra were referenced to residual non-deuterated chloroform (δ 7.26) in $CDCl_3$, residual DMSO-d_5 (δ 2.50) in DMSO-d_6, acetone-d_5 (δ 2.09) in acetone-d_6, and residual MeCN-d_2 (δ 1.94) in MeCN-d_3. ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.3), DMSO-d_6 (δ 39.5), the carbonyl carbon of acetone (δ 205.9), or the nitrile carbon of MeCN-d_3 (δ 118.3), respectively. ^{19}F NMR spectra were referenced to hexafluorobenzene (δ –161.64)[2] as an internal standard and are run with C–F/C–H decoupling. Reactions were monitored by GC/MS, ^{1}H NMR, ^{19}F NMR and/or TLC on silica gel plates (60 Å porosity, 250 μm thickness). TLC analysis was performed using hexanes/EtOAc as the eluent and visualized using permanganate stain, Seebach's stain,[3] ninhydrin stain, and/or UV light. Silica plugs utilized flash silica gel (60 Å porosity, 32-63 μm). Flash chromatography was accomplished using an automated system (monitoring at 254 nm and 280 nm) with silica cartridges (60 Å porosity, 20-40 μm). Solvents were purified with drying cartridges through a solvent delivery system. Melting points (°C) are uncorrected.

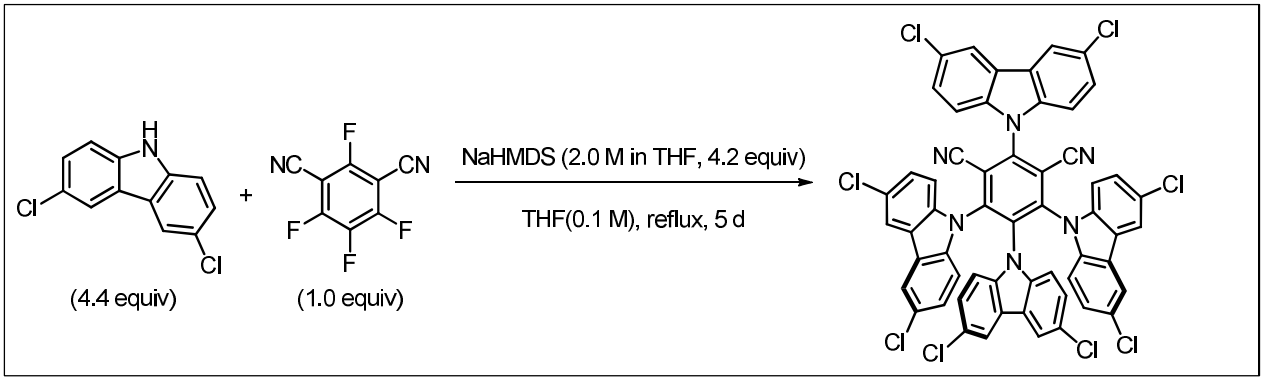
Chemicals: Deuterated NMR solvents were either used as purchased (MeCN-d_3, acetone-d_6, DMSO-d_6) or stored over 4Å molecular sieves and/or K_2CO_3 ($CDCl_3$). Na_2SO_4, $MgSO_4$, CH_2Cl_2, $CHCl_3$, EtOAc, pentane, hexanes, MeOH, Et_2O, and toluene were used as purchased. THF was purchased and dried *via* a solvent delivery system. DMF (99.8%, extra dry) and DMSO (99.8%, extra dry) were purchased from commercial sources and stored over 4 Å molecular sieves. The

[1] For information on these reactors and their construction see the supporting information of: (a) Patel, N. R.; Kelly, C. B.; Jouffroy, M.; Molander, G. A. *Org. Lett.* **2016**, *18*, 764. (b) Lin, K.; Wiles, R. J.; Kelly, C. B.; Davies, G. H. M.; Molander, G. A. *ACS Catal.* **2017**, *7*, 5129. (c) Milligan, J. A.; Phelan, J. P.; Polites, V. C.; Kelly, C. B.; Molander, G. A. *Org. Lett.* **2018**, *20*, 6840.
[2] Rosenau, C. P.; Jelier, B. J.; Gossert, A. D.; Togni, A. *Angew. Chem. Int. Ed.* **2018**, *57*, 9528.
[3] Seebach, D.; Imwinkelried, R; Stucky, G. *Helv. Chim. Acta* **1987**, *70*, 448.

transition metal photocatalyst [Ir{dFCF$_3$ppy}$_2$(bpy)]PF$_6$ was prepared in-house by the procedure outlined in our previous publications.[4] The organic photocatalyst 4CzIPN was prepared in-house by the procedure outlined in our previous publication.[5] The organic photocatalyst Cl-4CzIPN was prepared in-house by the procedure outlined here. The organic additive 1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-ol was prepared by the procedure outlined here. Trifluoromethyl-substituted alkenes were prepared in-house using the procedures outlined here (**1m**, **1s**) or as previously synthesized in earlier reports (**1a, 1n – 1r, 1t – 1x**).[6]All aryl halides were purchased from commercial suppliers and used without further purification. The oxoammonium salt 4-acetamido-2,2,6,6-tetramethyl-1-oxopiperidin-1-ium tetrafluoroborate ("Bobbitt's Salt") was prepared in the manner previously reported.[7]

Photochemistry: Irradiation of reaction vessels was accomplished using blue LEDs. LEDs were configured as outlined in the *Photochemical Reactor Design* section of our previous articles[1] or using two 34 W blue LED lamps with the sample positioned ~ 6 cm from each lamp.[1] A fan was employed to ensure reactions remained at or near rt when using LEDs.

Procedure for the Synthesis of Cl-4CzIPN Photocatalyst (4)



[4] Tellis, J. C.; Primer, D. P.; Molander, G. A. *Science* **2014**, *345*, 433.
[5] Patel, N. P.; Kelly, C. B.; Siegenfeld, A. P.; Molander, G. A. *ACS Catal.* **2017**, *7*, 1766.
[6] Phelan, J. P.; Lang, S. B.; Compton, J. S.; Kelly, C. B.; Dykstra, R.; Gutierrez, O.; Molander, G. A. *J. Am. Chem. Soc.* **2018**, *140*, 8037. Phelan, J. P.; Wiles, R. J.; Lang, S. B.; Kelly, C. B.; Molander, G. A. *Chem. Sci.* **2018**, *9*, 3215. Lang, S. B.; Wiles, R. W.; Kelly, C. B.; Molander, G. A. *Angew. Chem. Int. Ed.* **2017**, *56*, 15073.
[7] Mercadante, M. A.; Kelly, C. B.; Bobbitt, J. M.; Tilley, L. J.; Leadbeater, N. E. *Nat. Protoc.* **2013**, *8*, 666.

2,4,5,6-Tetrakis(3,6-dichloro-9H-carbazol-9-yl)isophthalonitrile (4)

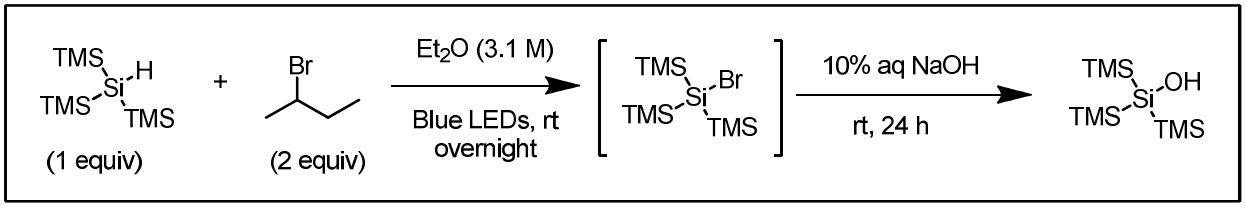
The following is a modification of the procedure developed by Waser et al.[8] To a flamed-dried 250 mL round-bottomed flask was added 3,6-dichloro-9H-carbazole (4.33 g, 17.6 mmol, 4.40 equiv) followed by anhyd THF (40 mL). The flask was sealed with a septum and placed under an Ar atmosphere *via* an Ar inlet needle. The flask was then cooled to 0 °C *via* an ice-water bath. After cooling for 15 min, the flask was charged with a solution of NaHMDS in THF (8.40 mL, 16.8 mmol, 2.00 M in THF). The solution immediately became brown-orange. The reaction mixture was stirred at 0 °C for 10 min after complete addition. The ice-water bath was removed, and the reaction mixture was stirred at rt for 30 min. After this time, 2,4,5,6-tetrafluoroisophthalonitrile (0.80 g, 4.0 mmol) was added all at once, turning the solution dark brown. The flask was then heated to reflux in an oil bath and stirred at this temperature for 5 d.

After this time, the reaction was cooled to rt and filtered using a large coarse fritted funnel. The solid material was then washed with anhyd Et_2O (~ 500 mL), and the filtrate was discarded. The product was then selectively eluted using $CHCl_3$ (~ 500 mL). The solvent was removed *in vacuo* by rotary evaporation, and the resulting solid was washed with a 75:25 mixture of pentane/acetone (2 X 100 mL) followed by pentane (100 mL). The neon yellow solid was dried under vacuum to give pure 2,4,5,6-tetrakis(3,6-dichloro-9H-carbazol-9-yl)isophthalonitrile (2.874 g, 68% yield).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.93 (dd, *J* = 8.7, 2.0 Hz, 2H), 7.32 (dd, *J* = 8.9, 2.0 Hz, 4H), 7.46 (d, *J* = 8.7 Hz, 2H), 7.69 (d, *J* = 8.9 Hz, 4H), 7.80 (d, *J* = 1.8 Hz, 2H), 7.85 - 7.89 (m, 2H), 8.08 (d, *J* = 8.7 Hz, 2H), 8.15 (d, *J* = 1.8 Hz, 4H), 8.60 (d, *J* = 1.8 Hz, 2H). **^{13}C NMR** (DMSO-d6, 125 MHz) δ 111.62 (C), 112.23 (C), 112.48 (C), 112.52 (C), 116.80 (C), 120.22 (C), 120.85 (C), 121.60 (C), 123.30 (C), 123.77 (C), 124.22 (C), 125.22 (C), 125.68 (C), 126.38 (C), 126.42 (C), 127.02 (C), 127.70 (C), 135.81 (C), 136.47 (C), 137.37 (C), 138.52 (C), 144.52 (C), 144.95 (C).

[8] Le Vaillant, F.; Garreau, M.; Nicolai, S.; Gryn'ova, G.; Corminboeuf, C.; Waser, J. *Chem. Sci.* **2018**, *9*, 5883.

Procedure for the Synthesis of Tris(trimethylsilyl)silanol (5)



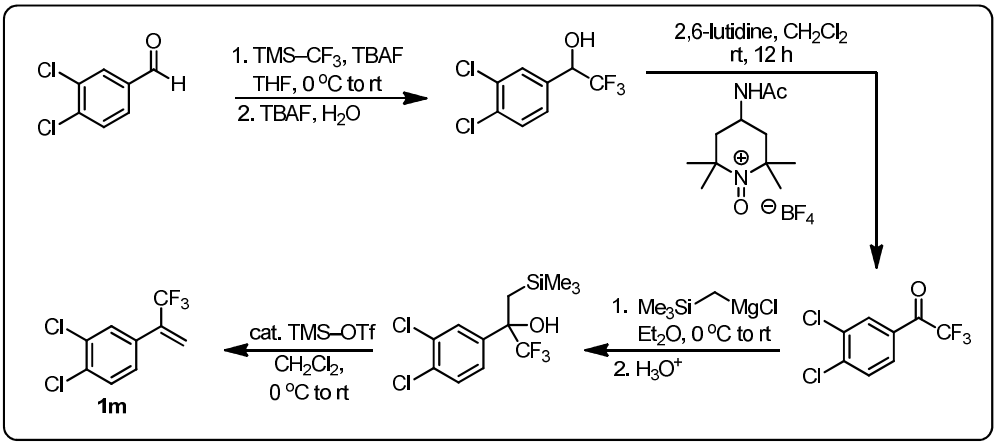
1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-ol (5)

To a 40-mL vial equipped with a magnetic stir bar was added TMS_3SiH (6.00 mL, 4.84 g, 19.4 mmol), 2-bromobutane (5.30 mL, 38.9 mmol, 2.00 equiv) and Et_2O (6.2 mL). The reaction vial was capped under air and irradiated with Kessil 34 W blue LEDs at rt for 12 h. After irradiation, the reaction vial was slowly opened to allow for a slow gas evolution. After gas evolution completed, the organic solution was poured into a round-bottom flask containing a 10% aq NaOH solution (20 mL), using additional Et_2O to ensure complete transfer. The reaction was allowed to stir at rt for an additional 24 h. After this time, the reaction was diluted with Et_2O and transferred to a separatory funnel. The layers were separated. The aqueous layer was extracted with Et_2O (2 × 20 mL). The combined organic layers were washed with brine (50 mL) and dried (Na_2SO_4). The solution was concentrated under vacuum *via* rotory evaporator to yield the crude silanol as a clear oil. Further purification was achieved *via* distillation under high vac (bp = 55 – 56 °C) to afford the pure silanol **5** as a clear, colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.18 (s, 27H). **^{13}C NMR** -0.28 (C).

Synthesis of Perfluoroalkyl-Substituted Alkenes

Preparation of 1,2-dichloro-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (1m)



Trifluoromethylation

1-(3,4-Dichlorophenyl)-2,2,2-trifluoroethanol

The following is a modification of the procedure outline by Kelly et al.[9] To a 150 mL round bottom flask equipped with a stir bar was added 3,4-dichlorobenzaldehyde (7.0 g, 0.040 mol, 1 equiv), THF (60 mL), and Me_3SiCF_3 (7.4 g, 0.052 mol, 1.3 equiv). The flask was sealed with a rubber septum and placed under an argon atmosphere *via* an inlet needle. The reaction mixture was cooled to 0 °C[10] in an ice-water bath. After stirring for approximately 10 min, TBAF (1.0 M in THF, 0.34 mL, 0.00034 mol, 0.010 equiv) was added dropwise *via* a syringe. After stirring for 10 min, the ice-bath was removed, and the solution was allowed to stir for approximately 8 h at rt.

To cleave the silyl ether formed by the reaction, H_2O (4.0 mL, 0.22 mol, ~ 5.5 equiv) was added *via* a syringe followed by TBAF (1 M in THF, 4 mL, 0.004 mol, 0.1 equiv). When the cleavage was judged to be complete,[11] the contents of the flask were transferred to a separatory funnel. Deionized H_2O (50 mL) and Et_2O (50 mL) were added, and the layers were partitioned. The aq layer was extracted with Et_2O (3 × 25 mL). The organic layers were combined, then washed once with deionized H_2O (100 mL) and brine (100 mL). The organic layer was dried (Na_2SO_4), and the

[9] Kelly, C. B.; Colthart, A. M.; Constant, B.D.; Corning, S.R.; Dubois, L. N. E.; Genovese, J.T.; Radziewicz, J. L.; Sletten, E. M.; Whitaker, K. R.; Tilley, L. J. *Org. Lett.* **2011**, *13*, 1646.

[10] Note that on small scales (< 20 mmol), the TBAF could be added relatively quickly. However, upon scale-up, the addition of TBAF is quite exothermic. It is recommended that the TBAF be added as slowly as possible, and/or cooling the reaction mixture to a temperature lower than that of 0 °C.

[11] It is recommended that this cleavage step be monitored by some form of spectroscopy or spectrometry (e.g., NMR or GC/MS).

solvent was removed *in vacuo* by rotary evaporation, affording crude 1-(3,4-dichlorophenyl)-2,2,2-trifluoroethanone. The crude product was purified by vacuum distillation (bp 79 – 81 °C @ 0.1 mmHg), giving the pure CF_3 alcohol (8.420 g, 86%) as a clear, pale-yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.00 (q, J = 6.5 Hz, 1H), 7.32 (d, J = 8.2 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.60 (s, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 71.8 (q, $J_{C\text{-}C\text{-}F}$ = 32.1 Hz, CH), 124.1 (q, $J_{C\text{-}F}$ =282.3 Hz, CF_3), 127.0 (CH), 129.6 (CH), 130.9 (CH), 133.2 (C), 134.1 (C), 134.1 (C).

^{19}F NMR ($CDCl_3$, 471 MHz) δ -78.38 (s, 3F).

FT-IR (cm^{-1}, neat, ATR) 3400, 1263, 1171, 1124, 1079, 1033, 814.

HRMS (ES+) calcd for $C_8H_5Cl_2F_3O$ $[M]^+$: 243.9670, found: 243.9673.

Oxidation

1-(3,4-Dichlorophenyl)-2,2,2-trifluoroethanone[12]

To a one-neck, 250 mL round bottom flask equipped with a stir bar was added 1-(3,4-dichlorophenyl)-2,2,2-trifluoroethanone (6.1 g, 0.025 mol, 1.0 equiv), 4-acetamido-2,2,6,6-tetramethyl-1-oxopiperidin-1-ium tetrafluoroborate (20 g, 0.066 mol, 2.6 equiv), and CH_2Cl_2 (63 mL). The mixture was allowed to stir at rt for approximately 5 min. At this time, 2,6-lutidine (6.03 g, 6.52 mL, 0.0562 mol, 2.25 equiv) was added all at once, and the flask was sealed with a rubber septum. The reaction mixture was stirred overnight at rt, gradually turning red. The solvent was removed *in vacuo* to afford a thick, red residue. To this thick residue was added Et_2O (~125 mL), causing immediate precipitation of the spent oxidant. The heterogeneous solution was allowed to stir for 10 min, and the solids were filtered off through a medium porosity fritted funnel, washing with Et_2O (~100 mL). The solids were saved for oxidant reclamation,[13] and the solvent was removed from the filtrate *in vacuo* by rotary evaporation. The crude liquid material was then loaded atop a silica gel plug. The plug was eluted with Et_2O (~ 100 mL) to remove any of the residual

[12] Matinez-Pardo, P.; Blay, G.; Vila, C.; Sanz-Marco, A.; Muñoz, M. C.; Pedro, J. R. *J. Org. Chem.* **2019**, *84*, 314.

[13] Regeneration of the oxoammonium salt from the nitroxide, 4-acetamido-(2,2,6,6-tetramethyl-piperidin-1-yl)oxyl, can be performed as outlined in the published protocol, see: Mercadante, M. A.; Kelly, C. B.; Bobbitt, J. M.; Tilley, L. J.; Leadbeater, N. E. *Nat. Protoc.* **2013**, *8*, 666. It is recommended that the nitroxide be recrystallized from EtOAc first to remove lutidinium tetrafluoroborate.

spent oxidant. The solvent was removed from the filtrate *in vacuo* by rotary evaporation to give pure trifluoromethyl ketone (6.00 g, 98%) as a clear, colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.66 (d, J = 8.4 Hz, 1H), 7.91 (dd, J = 8.4, 0.9 Hz, 1H), 8.16 (s, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 115.2 (q, $J_{C\text{-}F}$ = 291.4 Hz, CF_3), 127.8 (CH), 128.3 (C), 130.4 (CH), 130.7 (CH), 133.1 (C), 139.7 (C), 177.5 (q, $J_{C\text{-}C\text{-}F}$ = 36.7 Hz, C).

^{19}F NMR ($CDCl_3$, 471 MHz) δ -71.52 (s, 3F).

FT-IR (cm^{-1}, neat, ATR) 1723, 1208, 1180, 1140, 980, 960, 758, 722.

HRMS (ES+) calcd for $C_8H_3Cl_2F_3O$ $[M]^+$: 241.9513, found: 241.9509.

Grignard Alkylation

2-(3,4-Dichlorophenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol

This procedure is a modification of the procedure outlined by Hamlin et al.[14] To a 150 mL flame-dried round bottom flask equipped with a stir bar was added 1-(3,4-dichlorophenyl)-2,2,2-trifluoroethanone (6.1 g, 0.025 mol, 1.0 equiv) in anhyd Et_2O (31 mL). The flask was cooled to 0 °C *via* an ice-water bath for 5 min. After this time, Me_3SiCH_2MgCl (1.3 M in THF, 26 mL, 0.034 mol, 1.4 equiv) was added dropwise over 10 min *via* a syringe. The solution became bright yellow initially, then faded upon addition of the organomagnesium solution. After complete addition, the solution was stirred at 0 °C for 10 min, then warmed to rt. The reaction was allowed to stir at this temperature overnight.

After this time, the reaction mixture was cooled to 0 °C *via* an ice-water bath for 5 min. The reaction mixture was then *carefully* quenched dropwise with 2 M aq HCl (20 mL). ***CAUTION:*** *Exothermic, a vent needle is advisable*. After complete addition, the quenched reaction mixture was warmed to rt and transferred to a separatory funnel. Et_2O (50 mL) and deionized H_2O (50 mL) were added, and the layers were separated. The aq layer was extracted with Et_2O (3 × 25 mL). The combined organic layers were washed with 2 M aq HCl (50 mL), deionized H_2O (50 mL) and

[14] Hamlin, T. A.; Kelly, C. B.; Cywar, R. M.; Leadbeater, N. E. *J. Org. Chem.* **2014**, *79*, 1145.

finally brine (100 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation, affording the crude product. Further purification was achieved by vacuum distillation (bp 89 – 91 °C @ 0.1 mmHg) to afford the pure product 2-(3,4-dichlorophenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol (5.66 g, 68%) as a clear, colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ -0.13 (s, 9H), 1.45 (d, J = 15.4 Hz, 1H), 1.59 (d, J = 15.4 Hz, 1H), 2.30 (s, OH), 7.39 (dd, J = 8.4, 1.4 Hz, 1H), 7.43 - 7.47 (m, 1H), 7.68 (d, J = 1.8 Hz, 1H).
^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.1 (CH_3), 25.1 (CH_2), 77.1 (q, $J_{C\text{-}C\text{-}F}$ = 29.3 Hz, C), 125.7 (q, $J_{C\text{-}F}$ = 286.8 Hz, CF_3), 126.2 (CH), 129.0 (CH), 130.4 (CH), 132.8 (C), 133.0 (C), 138.6 (C).
^{19}F NMR ($CDCl_3$, 471 MHz) δ -81.94 (s, 3F).
FT-IR (cm^{-1}, neat, ATR) 1252, 1215, 1158, 992, 936, 839, 801.
HRMS (ES+) calcd for $C_{12}H_{15}Cl_2F_3OSi$ $[M]^+$: 330.0221, found: 330.0215.

Elimination

1,2-Dichloro-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (1m)[15]

To a 150 mL one neck round bottom flask equipped with a stir bar was added 2-(3,4-dichlorophenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol (4.97 g, 0.0150 mol, 1.00 equiv) and CH_2Cl_2 (60 mL).[16] The solution was cooled to 0 °C *via* an ice-water bath and stirred for 10 min at this temperature. After this time, TMSOTf (0.833 g, 0.679 mL, 3.75 mmol, 0.250 equiv) was added to the flask dropwise over 5 min. The reaction mixture was stirred at 0 °C for an additional 10 min upon complete addition of TMSOTf. The flask was then allowed to warm to rt and stirred for 2 h.After this time, the flask was cooled to rt and quenched with 75 mL of saturated aq $NaHCO_3$. The reaction mixture was transferred to a separatory funnel and diluted with Et_2O (~50 mL). The layers were separated, and the aq layer was extracted with Et_2O (3 × 25 mL). The combined organic layers were washed with saturated aq $NaHCO_3$ (50 mL), deionized H_2O (50 mL), and finally brine (50 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation to give the crude trifluoromethylalkene. Further purification was accomplished by

[15] Trost, B. M.; Debien, L. *J. Am. Chem. Soc.* **2015**, *137*, 11606.
[16] Hexanes can also be used in place of CH_2Cl_2.

eluting through a plug of silica gel and eluting with a 9:1 mixture of pentane/Et_2O, giving pure 1,2-dichloro-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1m)** (3.04 g, 84%) as a clear, yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.80 (d, *J* = 1.2 Hz, 1H), 6.02 (s, 1H), 7.29 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.47 (dd, *J* = 8.4, 0.5 Hz, 1H), 7.55 (d, *J* = 1.8 Hz, 1H).

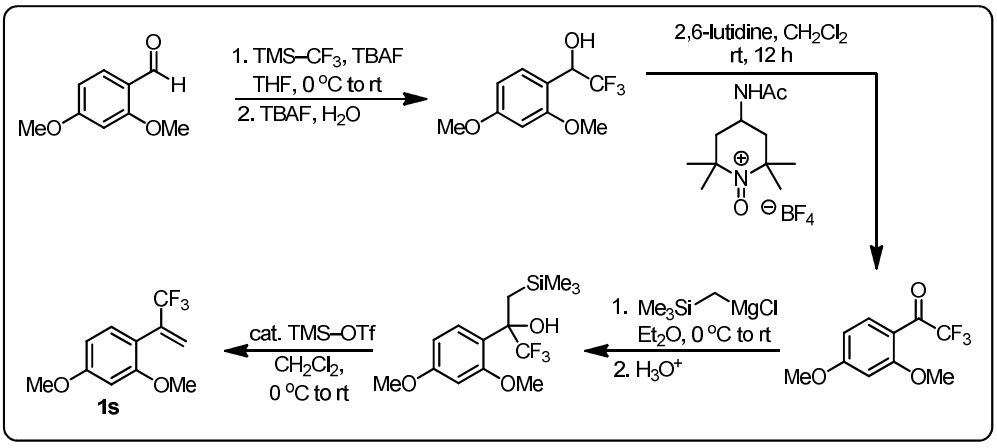
^{13}C NMR ($CDCl_3$, 125 MHz) δ 123.2 (q, $J_{C\text{-}F}$ = 273.1 Hz, CF_3), 121.9 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.5 Hz, CH_2), 126.9 (CH), 129.6 (CH), 130.8 (CH), 133.2 (C), 133.7 (two C's overlap[17]), 137.4 (q, $J_{C\text{-}C\text{-}F}$ = 31.2 Hz, C).

^{19}F NMR ($CDCl_3$, 471 MHz) δ -64.88 (s, 3F).

FT-IR (cm^{-1}, neat, ATR) 1476, 1348, 1193, 1170, 1120, 1089, 1079, 1032.

HRMS (ES+) calcd for $C_9H_5Cl_2F_3$ $[M]^+$: 239.9720, found: 239.9730.

Preparation of 2,4-dimethoxy-1-(3,3,3-trifluoroprop-1-en-2-yl)benzene (1s)



Trifluoromethylation

1-(2,4-Dimethoxyphenyl)-2,2,2-trifluoroethanol[18]

The following is a modification of the procedure outline by Kelly et al.[7] To a 150 mL round bottom flask equipped with a stir bar was added 2,4-dimethoxybenzaldehyde (6.7 g, 0.040 mol, 1.0 equiv), THF (60 mL), and Me_3SiCF_3 (7.4 g, 0.052 mol, 1.3 equiv). The flask was sealed with a rubber septum and placed under an argon atmosphere *via* an inlet needle. The reaction mixture was cooled

[17] Jiménez-Aquino, A.; Vega. J. A.; Trabanco, A. A.; Valdés, C. *Adv. Synth. Cat.* **2014**, *356*, 1079.

[18] Folleas, Benoit; Marek, I.; Normant, J.-F.; Jalmes, L. S. *Tetrahedron*, **1998**, *39*, 2973.

to 0 °C[8] in an ice-water bath. After stirring for approximately 10 min, TBAF (1 M in THF, 0.4 mL, 0.0004 mol, 0.01 equiv) was added dropwise *via* a syringe. After stirring for 10 min, the ice-bath was removed, and the solution was allowed to stir for approximately 8 h at rt.

To cleave the silyl ether formed by the reaction, H_2O (4 mL, 0.22 mol, ~ 5.5 equiv) was added *via* a syringe followed by TBAF (1 M in THF, 4 mL, 0.004 mol, 0.1 equiv). When the cleavage was judged to be complete,[9] the contents of the flask were transferred to a separatory funnel. Deionized H_2O (50 mL) and Et_2O (~50 mL) were added, and the layers were partitioned. The aq layer was extracted with Et_2O (3 × ~25 mL). The organic layers were combined, then washed once with deionized H_2O (50 mL) and brine (50 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation, affording crude 1-(2,4-dimethoxyphenyl)-2,2,2-trifluoroethanol. The crude product was purified by vacuum distillation (bp 99 –101 °C @ 0.1 mmHg), giving the pure CF_3 alcohol (7.86 g, 83%) as a clear, pale-yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.55 (br s, OH), 3.82 (s, 3H), 3.84 - 3.86 (m, 3H), 5.22 (q, J = 6.9 Hz, 1H), 6.50 (s, 1H), 6.53 (dd, J = 8.5, 1.7 Hz, 1H), 7.31 (d, J = 8.4 Hz, 1H).
^{13}C NMR ($CDCl_3$, 125 MHz) δ 55.6 (CH_3), 55.9 (CH_3), 69.0 (q, $J_{C\text{-}C\text{-}F}$ = 32.1 Hz, CH), 99.1 (CH), 105.2 (CH), 115.0 (C), 125.0 (q, $J_{C\text{-}F}$ = 283.2 Hz, CF_3), 130.1 (CH), 158.9 (C), 161.8 (C).
^{19}F NMR ($CDCl_3$, 471 MHz) δ -78.06 (s, 3F).
FT-IR (cm^{-1}, neat, ATR) 3450, 1510, 1262, 1209, 1158, 1125, 1064, 1031.
HRMS (ES+) calcd for $C_{10}H_{11}F_3O_3$ $[M]^+$: 236.0660, found: 236.0660.

Oxidation

1-(2,4-Dimethoxyphenyl)-2,2,2-trifluoroethanone[19]

To a one-neck, 250 mL round bottom flask equipped with a stir bar was added 1-(2,4-dimethoxyphenyl)-2,2,2-trifluoroethanol (5.9 g, 0.025 mol, 1.0 equiv), 4-acetamido-2,2,6,6-tetramethyl-1-oxopiperidin-1-ium tetrafluoroborate (19.5 g, 0.0650 mol, 2.60 equiv), and CH_2Cl_2 (63 mL). The mixture was allowed to stir at rt for approximately 5 min. At this time, 2,6-lutidine (6.03 g, 6.51 mL, 0.0563 mol, 2.25 equiv) was added all at once, and the flask was sealed with a

[19] Matador, E.; de Gracia Retamosa, M.; Jiménez-Sanches, A.; Monge, D.; Fernandez, R.; Lassaletta, J. M. *Eur. J. Org. Chem.* **2019**, *1*, 130.

rubber septum. The reaction mixture was stirred overnight at rt, gradually turning red. The solvent was removed *in vacuo* to afford a thick red residue. To this thick residue was added Et_2O (~75 mL), causing immediate precipitation of the spent oxidant. The heterogeneous solution was allowed to stir for 10 min, and the solids were filtered off through a medium porosity fritted funnel, washing with Et_2O (~100 mL). The solids were saved for oxidant reclamation,[11] and the solvent was removed from the filtrate *in vacuo* by rotary evaporation. The crude liquid material was then loaded atop a silica gel plug. The plug was eluted with Et_2O (~ 200 mL) to remove any of the residual spent oxidant. The solvent was removed from the filtrate *in vacuo* by rotary evaporation to give the pure trifluoromethyl ketone (5.83 g, 99%) as a clear yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.90 (s, 3H), 3.91 (s, 3H), 6.50 (d, J = 2.0 Hz, 1H), 6.58 (dd, J = 8.9, 2.1 Hz, 1H), 7.78 (d, J = 8.9 Hz, 1H).
^{13}C NMR ($CDCl_3$, 125 MHz) δ 55.6 (CH_3), 55.7 (CH_3), 98.5 (CH), 105.6 (C), 116.4 (q, $J_{C\text{-}F}$ = 291.4 Hz, CF_3), 114.0 (CH), 134.0 (CH), 162.4 (C), 166.2 (C), 179.5 (q, $J_{C\text{-}C\text{-}F}$ = 35.7 Hz, C).
^{19}F NMR ($CDCl_3$, 471 MHz) δ -72.88 (s, 3F).
FT-IR (cm^{-1}, neat, ATR) 1599, 1570, 1286, 1219, 1172, 1143, 1111, 1019.
HRMS (EI+) calcd for $C_{10}H_9F_3O_3$ $[M]^+$: 234.0504, found: 234.0506.

Grignard Alkylation

2-(2,4-Dimethoxyphenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol

This procedure is a modification of the procedure outlined by Hamlin et al.[12] To a 150 mL flame-dried round bottom flask equipped with a stir bar was added 1-(2,4-dimethoxyphenyl)-2,2,2-trifluoroethanone (5.9 g, 0.025 mol, 1.0 equiv) in anhyd Et_2O (30 mL). The flask was cooled to 0 °C *via* an ice-water bath for 5 min. After this time, Me_3SiCH_2MgCl (1.30 M in THF, 26.0 mL, 0.0337 mol, 1.35 equiv) was added dropwise over 10 min *via* a syringe. The solution became bright yellow initially, then faded upon addition of the organomagnesium solution. After complete addition, the solution was stirred at 0 °C for 10 min, then warmed to rt. The reaction was allowed to stir at this temperature overnight.

After this time, the reaction mixture was cooled to 0 °C *via* an ice-water bath for 5 min. The reaction mixture was then *carefully* quenched dropwise with 2 M aq HCl (20 mL). ***CAUTION:***

Exothermic, a vent needle is advisable. After complete addition, the quenched reaction mixture was warmed to rt and transferred to a separatory funnel. Et_2O (50 mL) and deionized H_2O (50 mL) were added, and the layers were separated. The aq layer was extracted with Et_2O (3 × 25 mL). The combined organic layers were washed with 2 M aq HCl (50 mL), deionized H_2O (50 mL) and finally brine (100 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation, affording the pure 2-(2,4-dimethoxyphenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol (6.97 g, 87%) as a clear, colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ -0.09 (s, 9H), 1.46 (d, J = 15.0 Hz, 1H), 1.58 (dd, J = 15.0, 2.3 Hz, 1H), 3.82 (s, 3H), 3.90 (s, 3H), 6.04 (br s, OH), 6.48 - 6.56 (m, 2H), 7.20 (d, J = 9.3 Hz, 1H).
^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.5 (CH_3), 23.1 (CH_2), 55.5 (CH_3), 56.6 (CH_3), 79.1 (q, $J_{C\text{-}C\text{-}F}$ = 29.3 Hz, C), 100.3 (CH), 105.5 (CH), 118.2 (CH), 126.5 (q, $J_{C\text{-}F}$ = 287.8 Hz, CF_3), 131.3 (C), 159.6 (C), 161.3 (C).
^{19}F NMR ($CDCl_3$, 471 MHz) δ -82.62 (s, 3F).
FT-IR (cm^{-1}, neat, ATR) 3460, 2950, 1259, 1208, 1159, 1133, 1082, 836.
HRMS (ES+) calcd for $C_{14}H_{21}F_3O_3Si$ $[M]^+$: 322.1212, found: 322.1227.

Elimination

2,4-Dimethoxy-1-(3,3,3-trifluoroprop-1-en-2-yl)benzene (1s)

To a 150 mL one neck round bottom flask equipped with a stir bar was added 2-(2,4-dimethoxyphenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol (4.84 g, 0.0150 mol, 1 equiv) and CH_2Cl_2 (60 mL).[14] The solution was cooled to 0 °C *via* an ice-water bath and stirred for 10 min at this temperature. After this time, TMSOTf (0.83 g, 0.68 mL, 3.75 mmol, 0.25 equiv) was added to the flask dropwise over 5 min. The reaction mixture was stirred at 0 °C for an additional 10 min upon complete addition of TMSOTf. The flask was allowed to warm to rt and stirred for 2 h. After this time, the flask was quenched with 50 mL of saturated aq $NaHCO_3$. The reaction mixture was transferred to a separatory funnel and diluted with Et_2O (~50 mL). The layers were separated, and the aq layer was extracted with Et_2O (3 × 50 mL). The combined organic layers were washed with saturated aq $NaHCO_3$ (50 mL), deionized H_2O (50 mL), and finally brine (~100 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation to give the crude trifluoromethylalkene. Further purification was accomplished by plugging through a pad of

silica, eluting with a mixture of 9:1 pentane/Et_2O, giving pure 2,4-dimethoxy-1-(3,3,3-trifluoroprop-1-en-2-yl)benzene **(1s)** (2.80 g, 80%) as a clear yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.80 (s, 3H), 3.83 (s, 3H), 5.62 (s, 1H), 6.04 (s, 1H), 6.45 - 6.52 (m, 2H), 7.14 (d, J = 8.1 Hz, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 55.4 (CH_3), 55.7 (CH_3), 99.1 (C), 104.6 (C), 116.1 (C), 123.6 (q, $J_{C\text{-}F}$ = 274.0 Hz, CF_3), 123.2 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.5 Hz, CH_2), 131.4 (CH), 136.0 (q, $J_{C\text{-}C\text{-}F}$ = 31.2 Hz, C), 158.9 (C), 161.8 (C).

^{19}F NMR ($CDCl_3$, 471 MHz) δ -65.56 (s, 3F).

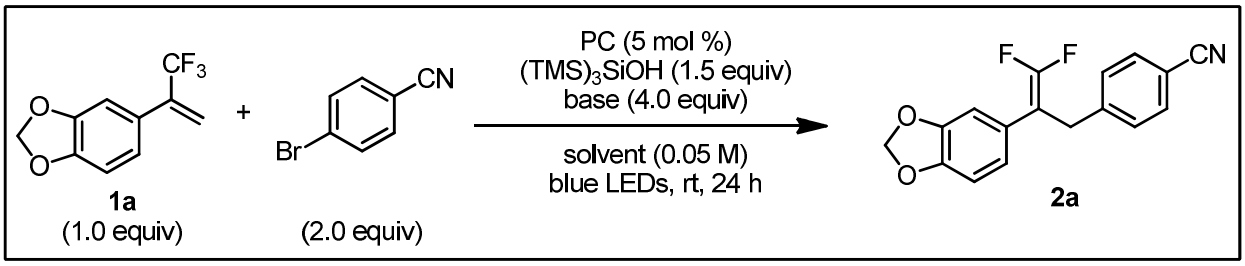
FT-IR (cm^{-1}, neat, ATR) 1609, 1509, 1305, 1210, 1190, 1158, 1117, 1075, 1033.

HRMS (ESI+) calcd for $C_{11}H_{11}F_3O_2$ $[M]^+$: 232.0711, found: 232.0716.

Optimization of Defluorinative Arylation with High Throughput Experimentation

High Throughput Experimentation was performed at the Penn/Merck Center for High Throughput Experimentation at the University of Pennsylvania. All solvents used in the screening center were dry and degassed. The screens were analyzed by UPLC with addition of an internal standard. The areas for the internal standard (IS), aryl bromide (ArBr), starting material (alkene), and product (P) from each of the screens are shown in the tables below. The ratios calculated are pertinent only to that specific screen; the ratios from one screen should not be quantitatively compared to those from a different screen. The results of the screens are illustrated in a heat map. Positive results (i.e., high product formation, low remaining starting material, etc.) are reflected with a green color, poor results are reflected with a red color.

Procedure for High Throughput Screen: Photocatalyst, Solvent, and Base Screen:



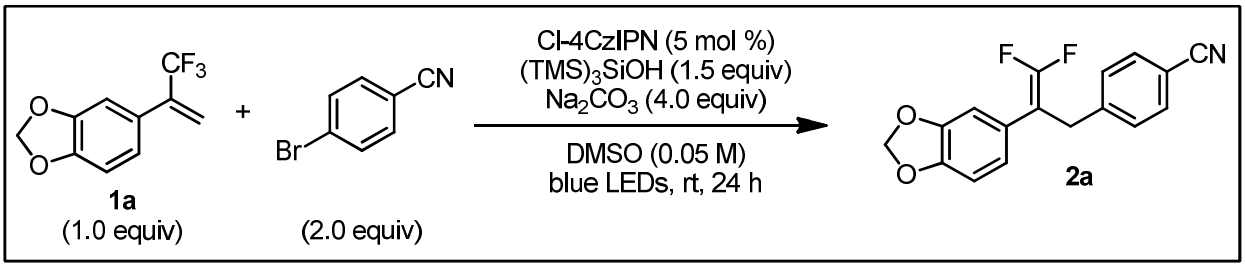
To a 96 well plate reactor containing 1 mL reaction vials equipped with a Teflon-coated magnetic stir bar in a glovebox was added sequentially: 1) slurry of base (rows 1-7) (4.0 equiv) in THF (200 μL); 2) photocatalyst (0.05 equiv) dissolved in acetone (50 μL). The solvent was then removed in the glovebox by Genovac evaporation before the following steps. Next, 1) TMG (row 8) (4.0 equiv), dosed neat; 2) solutions of trifluoromethylalkene **1a** (1.0 equiv), 4-bromobenzonitrile (2.0 equiv), and TMS_3SiOH (1.5 equiv) were dosed in the appropriate solvents designated by column (100 μL). The vials were sealed and stirred at rt under blue light irradiation for 24 h. After 24 h, the reactions were opened to air and diluted with 500 μL of MeCN. After stirring the diluted block for 15 min, 25 μL aliquots were then taken from the reaction vials and dosed into a 96-well UPLC block. These aliquots were further diluted by the addition of 700 μL of MeCN containing internal standard. The reaction mixtures were then analyzed by UPLC.

P/IS	Cl-4CzIPN						[Ir{dF(CF$_3$)ppy}$_2$(dCF$_3$bpy)](PF$_6$)					
	Acetone	MeCN	iPrOAc	DMSO	DMF	DME	Acetone	MeCN	iPrOAc	DMSO	DMF	DME
	1	2	3	4	5	6	7	8	9	10	11	12
NaOAc	0.82	1.28	1.62	0.97	0.76	0.59	1.71	1.68	0.99	0.29	0.49	0.21
Na_2CO_3	1.10	1.49	1.32	1.93	0.95	0.60	1.89	1.74	1.14	1.36	0.51	0.26
K_2CO_3	1.18	1.41	0.83	1.80	0.79	0.52	1.82	1.64	0.76	1.48	0.49	0.40
K_3PO_4	0.99	1.71	1.71	1.58	0.91	0.55	0.42	1.09	0.56	0.50	0.74	0.27
Cs_2CO_3	1.17	1.58	1.55	-	0.66	0.65	0.29	1.14	0.50	-	0.19	0.63
TMG	0.56	0.45	0.44	0.33	0.22	0.21	0.26	0.65	0.31	-	0.20	-

ArBr/IS	Cl-4CzIPN						[Ir{dF(CF$_3$)ppy}$_2$(dCF$_3$bpy)](PF$_6$)					
	Acetone	MeCN	iPrOAc	DMSO	DMF	DME	Acetone	MeCN	iPrOAc	DMSO	DMF	DME
	1	2	3	4	5	6	7	8	9	10	11	12
NaOAc	0.00	2.77	3.51	1.96	3.28	4.31	1.88	2.59	3.35	0.55	1.82	3.41
Na_2CO_3	0.70	3.35	3.98	3.19	3.36	2.51	1.99	3.20	3.53	2.53	3.14	3.25
K_2CO_3	1.17	2.76	3.45	3.35	2.24	2.58	1.54	2.83	3.17	1.36	1.75	2.17
K_3PO_4	0.05	2.13	3.49	2.87	2.83	2.62	1.78	2.81	3.67	1.12	0.77	2.78
Cs_2CO_3	0.11	1.22	3.12	-	0.00	2.56	0.40	2.36	3.74	-	0.00	1.47
TMG	2.43	3.12	3.13	1.83	2.59	4.01	2.75	2.76	3.65	-	2.24	-

Alkene/IS	Cl-4CzIPN						[Ir{dF(CF$_3$)ppy}$_2$(dCF$_3$bpy)](PF$_6$)					
	Acetone	MeCN	iPrOAc	DMSO	DMF	DME	Acetone	MeCN	iPrOAc	DMSO	DMF	DME
	1	2	3	4	5	6	7	8	9	10	11	12
NaOAc	0.00	1.06	1.18	0.45	1.09	0.08	0.36	0.50	2.09	2.13	2.32	2.31
Na_2CO_3	0.05	1.42	1.75	0.13	0.71	0.07	0.38	1.09	2.17	1.46	2.11	2.55
K_2CO_3	0.00	1.17	1.89	0.35	1.20	0.33	0.18	0.97	1.15	0.10	2.07	0.70
K_3PO_4	0.05	1.16	1.26	0.75	1.22	0.08	2.14	1.90	2.64	2.20	2.25	2.56
Cs_2CO_3	0.07	1.42	1.34	-	1.48	0.07	2.37	2.32	2.90	-	1.63	2.89
TMG	1.55	1.90	1.81	1.30	1.70	2.18	2.29	2.21	2.86	-	2.28	-

Control Studies Using Piperonyl Trifluoromethylalkene (1a) and 4-Bromobenzonitrile



Entry	Deviation from procedure	% Conversion to 2a[a]
1	*None*	98
2	*No Cl-4CzIPN*	0
3	*No TMS_3SiOH*	0

4	*No Base*	< 5
5	*No LEDs*	0

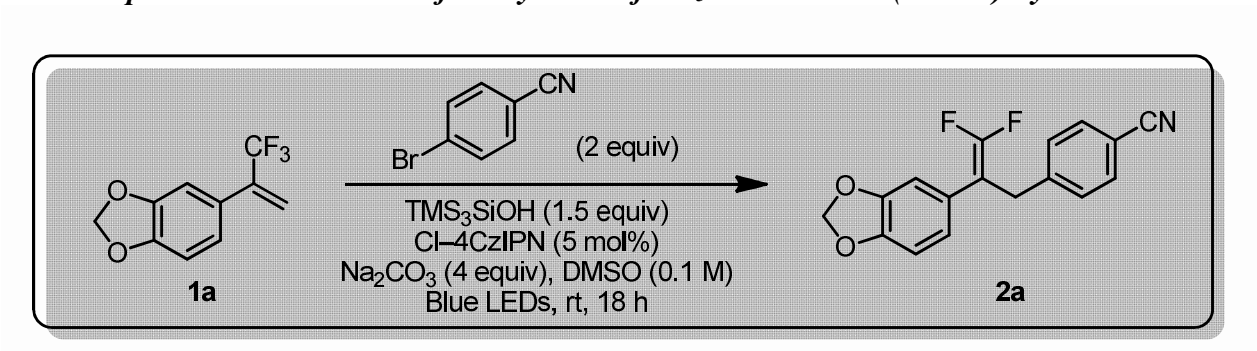
[a] Percent conversion was approximated based upon relative areas from the ^{19}F spectrum of a given run.

Procedure for Control Studies:

To 8 mL reaction vials equipped with stir bars was added Cl–4CzIPN (5.3 mg, 0.0050 mmol, 0.050 equiv), 4-bromobenzonitrile (36.4 mg, 0.200 mmol, 2.00 equiv), and Na_2CO_3 (42.4 mg, 0.400 mmol, 4.00 equiv). The vials were sealed with caps containing TFE-lined silicone septa and placed under an Ar atmosphere through evacuating and purging with Ar three times *via* an inlet needle. The vials were then charged with TMS_3SiOH (39.7 mg, 0.150 mmol, 1.50 equiv) and 1-(4-(2-(benzo[d][1,3]dioxol-5-yl)-3,3-difluoroallyl)phenyl)ethanone **1a** (2.16 mg, 0.100 mmol, 1.00 equiv) in anhyd DMSO (1 mL) *via* syringe. The caps were sealed with Parafilm©, and the solutions were irradiated with blue LEDs in the aforementioned photoreactor. The temperatures of the reactions were maintained at approximately 27 °C *via* a fan. The solutions were stirred vigorously while being irradiated. Reaction progress was monitored by ^{19}F NMR. The reaction for Entry 5 was allowed to stir at room temperature in ambient light.

Procedures for Defluorinative Arylation of Perfluoroalkyl-Substituted Alkenes

Representative Procedure for Arylation of CF_3 Alkenes with (Hetero)aryl Halides



4-(2-(Benzo[d][1,3]dioxol-5-yl)-3,3-difluoroallyl)benzonitrile (2a)

To a 20 mL reaction vial equipped with a stir bar was added Cl–4CzIPN (0.0532 g, 0.0500 mmol, 0.0500 equiv), 4-bromobenzonitrile (0.364 g, 2.00 mmol, 2.00 equiv), and Na_2CO_3 (0.424 g, 4.00 mmol, 4.00 equiv). The vial was sealed with a cap containing a TFE-lined silicone septum and placed under an Ar atmosphere through evacuating and purging with Ar three times *via* an inlet needle. The vial was then charged with TMS_3SiOH (0.397 g, 1.50 mmol, 1.50 equiv) and 5-(3,3,3-trifluoroprop-1-en-2-yl)benzo[d][1,3]dioxole **1a** (0.216 g, 1.00 mmol, 1.00 equiv) in anhyd DMSO (10 mL) *via* syringe. The cap was sealed with Parafilm©, and the now bright yellow solution was irradiated with blue LEDs in the aforementioned photoreactor. The temperature of the reaction was maintained at approximately 27 °C *via* a fan. The solution was stirred vigorously while being irradiated. Reaction progress was monitored by GC/MS and ^{19}F NMR. Once judged to be complete, the now dark red-brown solution was transferred to a separatory funnel and diluted with Et_2O (10 mL) and deionized H_2O (10 mL). The layers were separated, and the aq layer was extracted with Et_2O (5 × 10 mL). The combined organic layers were washed with saturated Na_2CO_3 (20 mL) followed by brine (20 mL). The combined organic layers were dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by SiO_2 chromatography (gradient hexanes to 80:20 hexanes/EtOAc) to give the desired product (**2a**) (0.224 g, 75%) as a clear, light yellow oil.

^1H NMR ($CDCl_3$, 500 MHz) δ 3.73 (s, 2H), 5.94 (s, 2H), 6.63 - 6.76 (m, 3H), 7.21 - 7.29 (m, 2H), 7.54 (d, J = 7.6 Hz, 2H).

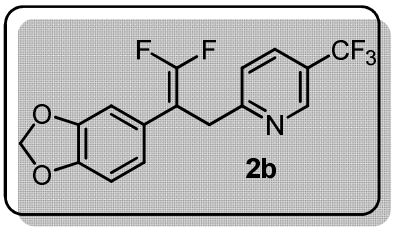
^{13}C NMR ($CDCl_3$, 125 MHz) δ 34.6 (CH_2), 90.9 (dd, $J_{C\text{-}C\text{-}F}$ = 21.1, 18.3 Hz, C), 101.5 (CH), 108.7 (C), 108.9 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, CH), 110.8 (CH), 119.0 (C), 122.1 (m, CH), 126.4 (CH), 129.3 (CH), 132.6 (C), 144.3 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.3 Hz, C), 147.3 (C), 148.1 (C), 154.6 (t, $J_{C\text{-}F}$ = 288.7 Hz, CF_2).

^{19}F NMR ($CDCl_3$, 471 MHz) δ -90.04 (ABq, Δδ = 0.04, J_{AB} = 39.9 Hz, 2F).

FT-IR (cm^{-1}, neat, ATR) 2850, 2229, 1727, 1490, 1241, 1038, 809, 729.

HRMS (EI+) calcd for $C_{17}H_{11}F_2NO_2$ $[M]^+$: 299.0758, found: 299.0753.

2-(2-(Benzo[d][1,3]dioxol-5-yl)-3,3-difluoroallyl)-5-(trifluoromethyl)pyridine, 2b Synthesis



2b

of 2-(2-(benzo[d][1,3]dioxol-5-yl)-3,3-difluoroallyl)-5-(trifluoromethyl)pyridine (0.073 g, 71%) was accomplished using the above procedure with ***the following modifications***: The reaction was conducted using 5-(3,3,3-trifluoroprop-1-en-2-yl)benzo[d][1,3]dioxole **1a** (64.8 mg, 0.300 mmol) and 2-bromo-5-(trifluoromethyl)pyridine (0.068 g, 0.300 mmol, 1 equiv).[20] Further purification was accomplished by SiO_2 column chromatography (gradient hexanes to 80:20 hexanes/EtOAc) to give the pure coupling product (**2b**) as a clear, light yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 3.95 (s, 2H), 5.93 (s, 2H), 6.69 - 6.76 (m, 1H), 6.76 - 6.80 (m, 1H), 6.83 (t, J = 1.2 Hz, 1H), 7.25 (d, J = 7.5 Hz, 1H), 7.79 (dd, J = 8.2, 2.1 Hz, 1H), 8.74 - 8.80 (m, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 37.0 (CH_2), 90.1 (dd, $J_{C\text{-}C\text{-}F}$ = 22.0, 15.6 Hz, C), 101.5 (CH_2), 108.6 (CH), 108.9 (dd, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 4.6, 2.8 Hz, CH), 123.9 (q, $J_{C\text{-}F}$ = 272.2 Hz, CF_3), 122.1 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, CH), 122.4 (CH), 125.0 (q, $J_{C\text{-}C\text{-}F}$ = 33.0 Hz, C), 126.6 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, C), 133.9 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, CH), 146.6 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, CH), 147.2 (C), 148.1 (C), 154.9 (dd, $J_{C\text{-}F}$ = 292.3, 288.7 Hz, CF_2), 162.8 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -89.13 (ABq, Δδ = 0.29, J_{AB} = 38.2 Hz, 2F), -62.20 (s, 3F). **FT-IR** (cm^{-1}, neat, ATR) 2900, 1725, 1506, 1325, 1242, 1125, 1077, 1039, 1017, 811. **HRMS** (EI+) calcd for $C_{16}H_{10}F_5NO_2$ $[M]^+$: 343.0632, found: 343.0627.

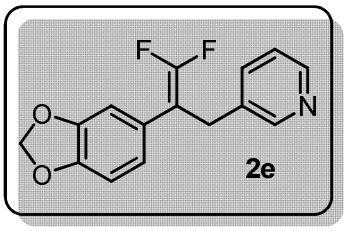
[20] The standard conditions resulted in some double addition byproduct.

5-(2-(Benzo[d][1,3]dioxol-5-yl)-3,3-difluoroallyl)-2-fluoropyridine, 2c Synthesis of 5-(2-(benzo[d][1,3]dioxol-5-yl)-3,3-difluoroallyl)-2-fluoropyridine (0.120 g, 82%) was accomplished using the above procedure with ***the following modifications***: The reaction was conducted using 5-(3,3,3-trifluoroprop-1-en-2-yl)benzo[d][1,3]dioxole **1a** (0.108 g, 0.500 mmol) and 5-bromo-2-fluoropyridine (0.176 g, 1.00 mmol, 2.0 equiv). Further purification was accomplished by SiO_2 column chromatography (gradient hexanes to 80:20 hexanes/EtOAc) to give the pure coupling product (**2c**) as a clear, light yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 3.65 (s, 2H), 5.94 (s, 2H), 6.64 - 6.70 (m, 2H), 6.72 - 6.76 (m, 1H), 6.81 (dd, J = 8.4, 2.9 Hz, 1H), 7.53 (td, J = 8.0, 2.4 Hz, 1H), 7.97 (s, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 30.9 (CH_2), 91.3 (dd, $J_{C\text{-}C\text{-}F}$ =20.9, 15.4 Hz, C), 101.5 (CH_2), 108.7 (CH), 109.0 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.2 Hz, CH), 109.6 (d, $J_{C\text{-}C\text{-}F}$ = 37.2 Hz, CH), 122.2 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.2 Hz, CH), 126.2 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 3.2 Hz, C), 131.8 (C), 141.2 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 7.3 Hz, CH), 147.3 (C), 147.4 (CH), 148.2 (C), 154.4 (dd, $J_{C\text{-}F}$ = 291.6, 287.9 Hz, CF_2), 162.8 (d, $J_{C\text{-}F}$ = 238.0 Hz, CF). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -90.39 (ABq, Δδ = 0.24, J_{AB} = 40.6 Hz, 2F), -70.79 (s, 1F). **FT-IR** (cm^{-1}, neat, ATR) 2900, 1728, 1597, 1504, 1239, 1037, 811. **HRMS** (EI+) calcd for $C_{15}H_{10}F_3NO_2$ $[M]^+$: 293.0664, found: 293.0671.

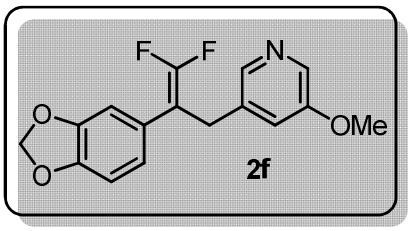
5-(2-(Benzo[d][1,3]dioxol-5-yl)-3,3-difluoroallyl)-1H-indole, 2d Synthesis of 5-(2-(benzo[d][1,3]dioxol-5-yl)-3,3-difluoroallyl)-1H-indole (0.074 g, 79%) was accomplished using the above procedure with ***the following modifications***: The reaction was conducted using 5-(3,3,3-trifluoroprop-1-en-2-yl)benzo[d][1,3]dioxole **1a** (0.216 g, 1.00 mmol) and 5-iodo-1H-indole (0.486 g, 2.00 mmol, 2.0 equiv); 10 mol % Cl-4CzIPN was used (31.9 mg). Further purification was accomplished by SiO_2 column chromatography (gradient hexanes to 80:20 hexanes/EtOAc) to give the pure coupling product (**2d**) as a clear, light yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 3.76 (s, 2H), 5.90 (s, 2H), 6.47 (br s, 1H), 6.67 - 6.72 (m, 1H), 6.73 - 6.78 (m, 2H), 7.00 (d, J = 8.2 Hz, 1H), 7.14 - 7.19 (m, 1H), 7.28 (d, J = 8.2 Hz, 1H), 7.41 (s, 1H), 8.06 (br s, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 34.4 (CH_2), 92.5 (dd, $J_{C\text{-}C\text{-}F}$ = 20.2, 14.7 Hz, C), 101.2 (CH_2), 102.4 (CH), 108.4 (CH), 109.2 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, CH), 111.3 (CH), 120.2 (CH), 122.2 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, CH), 122.8 (CH), 124.7 (CH), 127.7 (C), 128.2 (C), 129.9 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ =1.8 Hz, C), 134.8 (C), 146.8 (C), 147.7 (C), 154.5 (dd, $J_{C\text{-}F}$ = 289.6, 286.8 Hz, CF_2).

^{19}F NMR ($CDCl_3$, 471 MHz) δ -91.74 (ABq, Δδ = 0.07, J_{AB} = 43.1 Hz, 2F). **FT-IR** (cm^{-1}, neat, ATR) 3418, 2895, 1725, 1504, 1489, 1437, 1238, 1085, 1038, 1001, 907, 723. **HRMS** (EI+) calcd for $C_{18}H_{13}F_2NO_2$ $[M]^+$: 313.0914, found: 313.0909.

3-(2-(Benzo[d][1,3]dioxol-5-yl)-3,3-difluoroallyl)pyridine, 2e Synthesis of 3-(2-(benzo[d][1,3]dioxol-5-yl)-3,3-difluoroallyl)pyridine (0.218 g, 79%) was accomplished using the above procedure with ***the following modifications***: The reaction was conducted using 5-(3,3,3-trifluoroprop-1-en-2-yl)benzo[d][1,3]dioxole **1a** (0.216 g, 1.00 mmol) and 3-iodopyridine (0.410 g, 2.00 mmol, 2 equiv). Further purification was accomplished by SiO_2 column chromatography (gradient hexanes to 80:20 hexanes/EtOAc, then EtOAc) to give the desired coupling product (**2e**) as a clear, light orange oil, isolated with 5% impurity of inseparable trifluoromethylalkene. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 3.67 (s, 2H), 5.93 (s, 2H), 6.66 - 6.76 (m, 3H), 7.17 (dd, J = 7.6, 4.8 Hz, 1H), 7.44 (d, J = 7.3 Hz, 1H), 8.35 - 8.47 (m, 2H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 31.8 (CH_2), 91.2 (dd, $J_{C\text{-}C\text{-}F}$ = 20.2, 16.5 Hz, C), 101.4 (CH_2), 108.6 (CH), 109.0 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, CH), 122.2 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.2 Hz, CH), 123.6 (CH), 126.5 (C), 134.1 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.8 Hz, C), 135.9 (CH), 147.2 (C), 148.0 (C), 148.2 (CH), 150.0 (CH), 154.5 (dd, $J_{C\text{-}F}$ = 290.5, 288.7 Hz, CF_2). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -90.49 (ABq, Δδ = 0.06, J_{AB} = 40.9 Hz, 2F). **FT-IR** (cm^{-1}, neat, ATR) 2890, 1727, 1504, 1491, 1479, 1439, 1425, 1240, 1103, 1087, 1038, 935. **HRMS** (EI+) calcd for $C_{15}H_{11}F_2NO_2$ $[M]^+$: 275.0758, found: 275.0765.

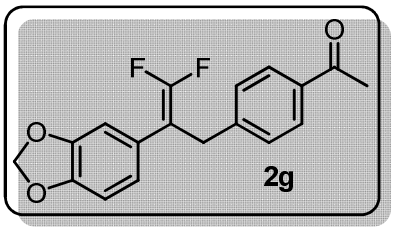


3-(2-(Benzo[d][1,3]dioxol-5-yl)-3,3-difluoroallyl)-5-methoxypyridine, 2f Synthesis of 3-(2-(benzo[d][1,3]dioxol-5-yl)-3,3-difluoroallyl)-5-methoxypyridine (55 mg, 60%) was accomplished using the above procedure with ***the following modifications***: The reaction was conducted using 5-(3,3,3-trifluoroprop-1-en-2-yl)benzo[d][1,3]dioxole **1a** (64.8 mg, 0.3 mmol) and 3-bromo-5-methoxypyridine (0.113 g, 0.600 mmol, 2.0 equiv). Further purification was accomplished by SiO_2 column chromatography (gradient hexanes to 80:20 hexanes/EtOAc, then EtOAc) to give the pure coupling product (**2f**) as a clear, light yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 3.66 (s, 2H), 3.80 (s, 3H), 5.94 (s, 2H), 6.67 - 6.75 (m, 3H), 6.94 (s, 1H), 8.02 (s, 1H), 8.14 (d, J = 2.4 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 100

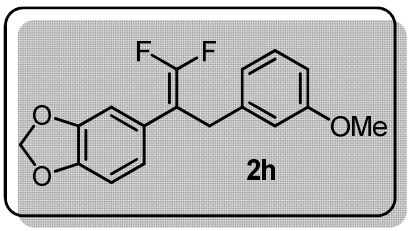


MHz) δ 31.7 (CH_2), 55.8 (CH_3), 91.1 (dd, $J_{C\text{-}C\text{-}F}$ = 20.2, 15.6 Hz, C), 101.5 (CH_2), 108.7 (CH), 109.0 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, CH), 121.1 (CH), 122.2 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.8 Hz, CH), 126.6 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, C), 135.0 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.8 Hz, C), 135.5 (CH), 142.3 (CH), 147.3 (C), 148.1 (C), 154.6 (dd, $J_{C\text{-}F}$ = 291.4, 288.7 Hz, CF_2), 156.0 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -90.41 (ABq, Δδ = 0.09, J_{AB} = 40.5 Hz, 2F). **FT-IR** (cm^{-1}, neat, ATR) 2926, 1730, 1589, 1490, 1440, 1040. **HRMS** (EI+) calcd for $C_{16}H_{13}F_2NO_3$ $[M]^+$: 305.0863, found: 305.0868.

1-(4-(2-(Benzo[d][1,3]dioxol-5-yl)-3,3-difluoroallyl)phenyl)ethanone, 2g Synthesis of 1-(4-(2-(benzo[d][1,3]dioxol-5-yl)-3,3-difluoroallyl)phenyl)ethanone (0.069 g, 73%) was accomplished using the above procedure with ***the following modifications***: The reaction was conducted using 5-(3,3,3-trifluoroprop-1-en-2-yl)benzo[d][1,3]dioxole **1a** (64.8 mg, 0.300 mmol) and 1-(4-iodophenyl)ethanone (147 mg, 0.600 mmol, 2.0 equiv) . Further purification was accomplished by SiO_2 column chromatography (gradient hexanes to 80:20 hexanes/EtOAc) to give the pure coupling product (**2g**) as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 2.55 (s, 3H), 3.72 (s, 2H), 5.92 (s, 2H), 6.67 - 6.73 (m, 3H), 7.23 (d, J = 8.2 Hz, 2H), 7.84 (d, J = 8.2 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 26.8 (CH_3), 34.4 (CH_2), 91.3 (t, $J_{C\text{-}C\text{-}F}$ = 17.9 Hz, C), 101.4 (CH_2), 108.6 (CH), 109.0 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, CH), 122.1 (q, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, CH), 126.8 (CH), 128.8 (CH), 128.9 (C), 135.8 (C), 144.3 (C), 147.1 (C), 148.0 (C), 154.6 (t, $J_{C\text{-}F}$ = 288.7 Hz, CF_2), 198.0 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -90.49 (app s, 2F). **FT-IR** (cm^{-1}, neat, ATR) 2890, 1726, 1681, 1504, 1490, 1266, 1240, 1088, 1038, 910, 809, 728. **HRMS** (EI+) calcd for $C_{18}H_{14}F_2O_3$ $[M]^+$: 316.0911, found: 316.0916.

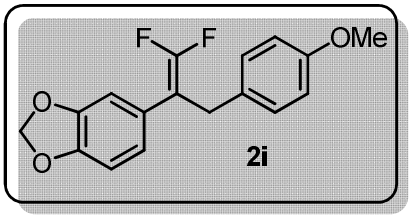


5-(1,1-Difluoro-3-(3-methoxyphenyl)prop-1-en-2-yl)benzo[d][1,3]dioxole, 2h Synthesis of 5-(1,1-difluoro-3-(3-methoxyphenyl)prop-1-en-2-yl)benzo[d][1,3]dioxole (0.055 g, 60%) was accomplished using the above procedure with ***the following modifications***: The reaction was conducted using 5-(3,3,3-trifluoroprop-1-en-2-yl)benzo[d][1,3]dioxole **1a** (64.8 mg, 0.300 mmol) and 1-bromo-3-methoxybenzene (0.112 g, 0.600 mmol, 2.0 equiv); 10 mol % of Cl-4CzIPN (31.9 mg) was used. Further purification was accomplished by SiO_2 column chromatography (gradient hexanes to 80:20 hexanes/EtOAc) to give

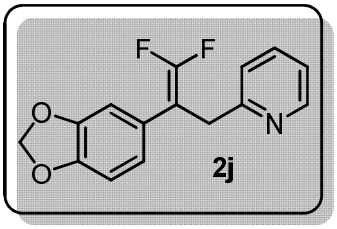


the pure coupling product (**2h**) as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 3.73 (s, 3H), 5.61 (s, 2H), 5.97 (s, 2H), 6.69 - 6.80 (m, 4H), 6.81 - 6.87 (m, 2H), 7.10 - 7.21 (m, 1H). **^{13}C NMR** (acetone-d6, 100 MHz) δ 34.1 (CH_2), 55.1 (CH_3), 92.6 (dd, $J_{C\text{-}C\text{-}F}$ = 21.8, 13.6 Hz, C), 101.9 (CH_2), 108.7 (CH), 109.3 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.3 Hz, CH), 112.2 (CH), 114.8 (CH), 121.2 (CH), 122.8 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.6 Hz, CH), 127.4 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 3.3 Hz, C), 130.0 (CH), 140.5 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, C), 147.6 (C), 148.4 (C), 154.8 (dd, $J_{C\text{-}F}$ = 288.8, 284.3 Hz, CF_2), 160.6 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -90.80 (ABq, Δδ = 0.25, J_{AB} = 46.0 Hz, 2F). **FT-IR** (cm^{-1}, neat, ATR) 2900, 1726, 1600, 1584, 1504, 1489, 1436, 1238, 1038, 811. **HRMS** (EI+) calcd for $C_{17}H_{14}F_2O_3$ $[M]^+$: 304.0911, found: 304.0900.

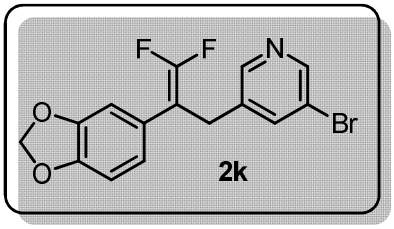
5-(1,1-Difluoro-3-(4-methoxyphenyl)prop-1-en-2-yl)benzo[d][1,3]dioxole, 2i Synthesis of 5-(1,1-difluoro-3-(4-methoxyphenyl)prop-1-en-2-yl)benzo[d][1,3]dioxole(0.192 g, 63%) was accomplished using the above procedure with ***the following modifications***: The reaction was conducted using 5-(3,3,3-trifluoroprop-1-en-2-yl)benzo[d][1,3]dioxole **1a** (0.216 g, 1.00 mmol) and 1-bromo-4-methoxypyridine (0.374 g, 2.00 mmol, 2.0 equiv). Further purification was accomplished by SiO_2 column chromatography (gradient hexanes to 90:10 hexanes/EtOAc) to give the desired coupling product (**2i**) as a clear, light yellow oil, isolated with an inseparable silanol byproduct impurity. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 3.60 (s, 2H), 3.76 (s, 3H), 5.92 (s, 2H), 6.70 - 6.74 (m, 3H), 6.78 (d, J = 8.5 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 33.6 (CH_2), 55.5 (CH_3), 92.1 (dd, $J_{C\text{-}C\text{-}F}$ = 20.2, 14.7 Hz, C), 101.3 (CH_2), 108.5 (CH), 109.2 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.2 Hz, CH), 114.2 (CH), 122.3 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, CH), 127.5 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, C), 129.5 (CH), 130.7 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.8 Hz, C), 147.0 (C), 147.9 (C), 154.5 (dd, $J_{C\text{-}F}$ = 289.6, 287.8 Hz, CF_2), 158.5 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -91.54 (ABq, Δδ = 0.07, J_{AB} = 42.7 Hz, 2F). **FT-IR** (cm^{-1}, neat, ATR) 2960, 1728, 1511, 1490, 1241, 1037, 841. **HRMS** (EI+) calcd for $C_{17}H_{14}F_2N_3$ $[M]^+$: 304.0911, found: 304.0914.



2-(2-(Benzo[d][1,3]dioxol-5-yl)-3,3-difluoroallyl)pyridine, 2j Synthesis of 2-(2-(benzo[d][1,3]dioxol-5-yl)-3,3-difluoroallyl)pyridine (0.055 g, 67%) was accomplished using the above procedure with ***the following modifications***: The reaction was conducted using 5-(3,3,3-trifluoroprop-1-en-2-yl)benzo[d][1,3]dioxole **1a** (64.8 mg, 0.300 mmol) and 2-iodopyridine (0.123 g, 0.600 mmol, 2.0 equiv). Further purification was accomplished by SiO_2 column chromatography (gradient hexanes to 70:30 hexanes/EtOAc) to give the coupling product (**2j**) as a clear, light yellow oil isolated with a 3% impurity of trifluoromethylalkene. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 3.87 (t, J = 2.1 Hz, 2H), 5.90 (s, 2H), 6.69 - 6.73 (m, 1H), 6.78 (dd, J = 8.1, 0.9 Hz, 1H), 6.80 - 6.83 (m, 1H), 7.09 (dd, J = 7.2, 5.1 Hz, 1H), 7.12 (d, J = 7.9 Hz, 1H), 7.54 (td, J = 7.6, 1.8 Hz, 1H), 8.51 (dd, J = 4.8, 0.7 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 37.0 (CH_2), 90.6 (dd, $J_{C\text{-}C\text{-}F}$ = 22.0, 15.6 Hz, C), 101.3 (CH_2), 108.5 (CH), 109.0 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, CH), 121.8 (CH), 122.1 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.2 Hz, CH), 122.7 (CH), 127.1 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, C), 136.8 (CH), 147.0 (C), 147.9 (C), 149.6 (CH), 154.8 (dd, $J_{C\text{-}F}$ = 292.3, 288.7 Hz, CF_2), 158.7 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -89.83 (ABq, Δδ = 0.25, J_{AB} = 39.6 Hz, 2F). **FT-IR** (cm^{-1}, neat, ATR) 2890, 1724, 1505, 1491, 1435, 1240, 1038, 811. **HRMS** (EI+) calcd for $C_{15}H_{11}F_2NO_2$ $[M]^+$: 275.0758, found: 275.0754.

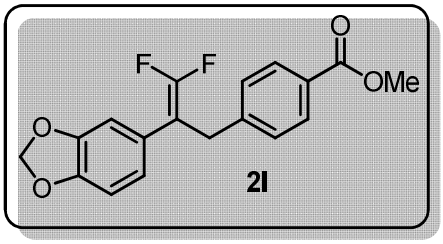


3-(2-(Benzo[d][1,3]dioxol-5-yl)-3,3-difluoroallyl)-5-bromopyridine, 2k Synthesis of 3-(2-(benzo[d][1,3]dioxol-5-yl)-3,3-difluoroallyl)-5-bromopyridine (0.049 g, 46%) was accomplished using the above procedure with ***the following modifications***: The reaction was conducted using 5-(3,3,3-trifluoroprop-1-en-2-yl)benzo[d][1,3]dioxole **1a** (64.8 mg, 0.300 mmol) and 1-bromo-3-iodobenzene (0.170 g, 0.600 mmol, 2 equiv); 10 mol % of Cl-4CzIPN (31.9 mg) was used. Further purification was accomplished by SiO_2 column chromatography (gradient hexanes to 70:30 hexanes/EtOAc) to give a 7.8:1 mixture of the aryl bromide to aryl iodide products (**2k**) as a clear, light orange oil. Spectral characterization for the major product: **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 3.66 (s, 2H), 5.95 (s, 2H), 6.62 - 6.80 (m, 4H), 7.60 (s, 1H), 8.31 (d, J = 1.4 Hz, 1H), 8.50 (d, J = 2.0 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 31.5 (CH_2), 90.7 (dd, $J_{C\text{-}C\text{-}F}$ = 21.1, 16.5 Hz, C), 101.6 (CH_2), 108.8 (CBr), 108.9 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, CH), 121.1 (CH), 122.2 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, CH), 126.0 (C), 136.1 (C), 138.7 (CH), 147.5 (C),

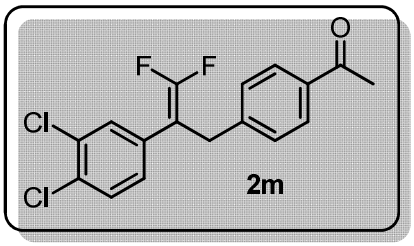


148.0 (CH), 148.2 (C), 149.3 (CH), 154.6 (dd, $J_{C\text{-}F}$ = 291.4, 288.7 Hz, CF_2). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -89.75 (ABq, Δδ = 0.12, J_{AB} = 39.5 Hz, 2F). **FT-IR** (cm^{-1}, neat, ATR) 2960, 1727, 1511, 1505, 1490, 1240, 1037, 907, 841, 810, 731. **HRMS** (EI+) calcd for aryl bromide: $C_{15}H_{10}BrF_2NO_2$ $[M]^+$: 352.9863, found: 352.9863. (EI+) calcd for aryl iodide: $C_{15}H_{10}F_2INO_2$ $[M]^+$: 400.9724, found: 400.9732.

Methyl 4-(2-(benzo[d][1,3]dioxol-5-yl)-3,3-difluoroallyl)benzoate, 2l Synthesis of methyl 4-(2-(benzo[d][1,3]dioxol-5-yl)-3,3-difluoroallyl)benzoate (0.129 g, 78%) was accomplished using the above procedure with ***the following modifications***: The reaction was conducted using 5-(3,3,3-trifluoroprop-1-en-2-yl)benzo[d][1,3]dioxole **1a** (0.108 g, 0.500 mmol) and methyl 4-iodobenzoate (0.262 g, 1.00 mmol, 2 equiv). Further purification was accomplished by SiO_2 column chromatography (gradient hexanes to 95:5 hexanes/EtOAc) to give the pure coupling product (**2l**) as a white, crystalline solid (mp = 42 – 44 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 3.72 (s, 2H), 3.89 (s, 3H), 5.93 (s, 2H), 6.62 - 6.77 (m, 3H), 7.21 (d, J = 8.1 Hz, 2H), 7.92 (d, J = 8.2 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 34.5 (CH_2), 52.2 (CH_3), 91.3 (dd, $J_{C\text{-}C\text{-}F}$ = 19.2, 17.4 Hz, C), 101.4 (CH_2), 108.5 (CH), 109.0 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, CH), 122.2 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.8 Hz, CH), 126.9 (C), 128.6 (CH), 128.8 (C), 130.1 (CH), 144.0 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.8 Hz, C), 147.1 (C), 148.0 (C), 154.6 (t, $J_{C\text{-}F}$ = 289.6 Hz, CF_2), 167.1 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -90.59 (app s, 2F). **FT-IR** (cm^{-1}, neat, ATR) 2890, 1717, 1490, 1435, 1277, 1240, 1106, 1087, 1038, 811. **HRMS** (EI+) calcd for $C_{18}H_{14}F_2O_4$ $[M]^+$: 332.0860, found: 332.0876.

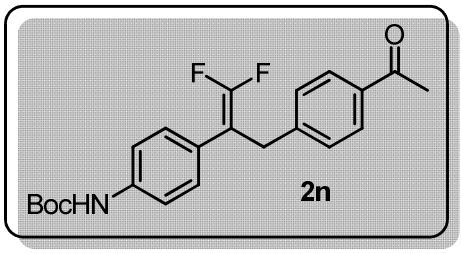


1-(4-(2-(3,4-Dichlorophenyl)-3,3-difluoroallyl)phenyl)ethanone, 2m Synthesis of 1-(4-(2-(3,4-dichlorophenyl)-3,3-difluoroallyl)phenyl)ethanone (0.139 g, 82%) was accomplished using the above procedure with ***the following modifications***: The reaction was conducted using 1,2-dichloro-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene **1m** (0.121 g, 0.500 mmol) and 1-(4-iodophenyl)ethanone (246 mg, 1.00 mmol, 2.0 equiv). Further purification was accomplished by SiO_2 column chromatography (gradient hexanes to 80:20 hexanes/EtOAc, then EtOAc) to give the pure coupling product (**2m**)



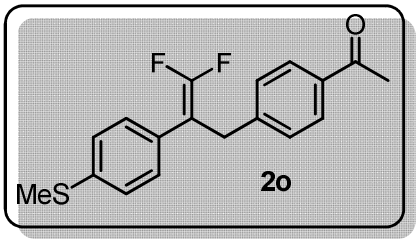
as a clear, light yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 2.56 (s, 3H), 3.76 (s, 2H), 7.06 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.32 - 7.38 (m, 2H), 7.86 (d, *J* = 8.2 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 26.8 (CH_3), 33.8 (CH_2), 90.2 (dd, $J_{C\text{-}C\text{-}F}$ = 22.9, 14.7 Hz, C), 127.7 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.2 Hz, CH), 128.7 (CH), 129.1 (CH), 130.3 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, CH), 130.7 (CH), 132.0 (C), 133.0 (C), 133.3 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 4.0 Hz, C), 136.1 (C), 143.4 - 143.5 (m, C), 154.9 (dd, $J_{C\text{-}F}$ = 294.2, 290.5 Hz, CF_2), 197.9 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -87.85 (ABq, Δδ = 0.22, J_{AB} = 34.6 Hz, 2F). **FT-IR** (cm^{-1}, neat, ATR) 2961, 1723, 1265, 1241, 1030, 1011, 818, 732. **HRMS** (EI+) calcd for $C_{17}H_{12}Cl_2F_2O$ $[M]^+$: 340.0233, found: 340.0241.

***tert*-Butyl (4-(3-(4-acetylphenyl)-1,1-difluoroprop-1-en-2-yl)phenyl)carbamate, 2n** Synthesis

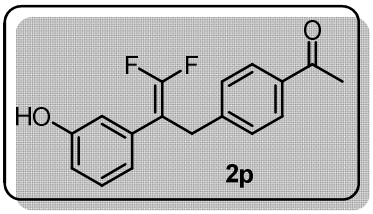


of *tert*-butyl (4-(3-(4-acetylphenyl)-1,1-difluoroprop-1-en-2-yl)phenyl)carbamate (0.139 g, 72%) was accomplished using the above procedure with ***the following modifications***: The reaction was conducted using *tert*-butyl (4-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)carbamate **1n** (0.144 g, 0.500 mmol) and 1-(4-iodophenyl)ethanone (246 mg, 1.00 mmol, 2.0 equiv). Further purification was accomplished by SiO_2 column chromatography (gradient hexanes to 70:30 hexanes/EtOAc) to give the pure coupling product (**2n**) as a clear, light yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.50 (s, 9H), 2.55 (s, 3H), 3.76 (s, 2H), 6.48 (br s, 1H), 7.16 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.83 (d, *J* = 8.1 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 26.7 (CH_3), 28.5 (CH_3), 34.0 (CH_2), 80.9 (C), 91.0 (dd, $J_{C\text{-}C\text{-}F}$ = 21.1, 14.7 Hz, C), 118.7 (CH), 127.6 (C), 128.7 (CH), 128.9 (CH), 129.0 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.2 Hz, CH), 135.7 (C), 137.9 (C), 144.5 (C), 152.8 (C), 154.6 (dd, $J_{C\text{-}F}$ = 292.3, 287.8 Hz, CF_2), 198.2 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -90.40 (ABq, Δδ = 0.27, J_{AB} = 40.2 Hz, 2F). **FT-IR** (cm^{-1}, neat, ATR) 3375, 2995, 1677, 1523, 1267, 1235, 1154, 729. **HRMS** (EI+) calcd for $C_{17}H_{15}F_2NO$ $[M–Boc+H]^+$: 287.1122, found: 287.1129.

1-(4-(3,3-Difluoro-2-(4-(methylthio)phenyl)allyl)phenyl)ethanone, 2o Synthesis of 1-(4-(3,3-difluoro-2-(4-(methylthio)phenyl)allyl)phenyl)ethanone (90.1 mg, 57%) was accomplished using the above procedure with ***the following modifications***: The reaction was conducted using methyl(4-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)sulfane **1o** (0.109 g, 0.500 mmol) and 1-(4-iodophenyl)ethanone (492 mg, 2.00 mmol, 2.0 equiv). Further purification was accomplished by SiO_2 column chromatography (gradient hexanes to 80:20 hexanes/EtOAc, then EtOAc) to give the pure coupling product (**2o**) as a pale yellow, crystalline solid (mp = 105 – 107 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 2.45 (s, 3H), 2.56 (s, 3H), 3.77 (s, 2H), 7.16 (s, 4H), 7.24 (d, J = 8.1 Hz, 2H), 7.84 (d, J = 8.1 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 15.6 (CH_3), 26.7 (CH_3), 33.9 (CH_2), 91.0 (dd, $J_{C\text{-}C\text{-}F}$ = 22.0, 14.7 Hz, C), 126.5 (CH), 128.7 (CH), 128.7 - 128.8 (m, CH), 128.9 (CH), 129.7 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, C), 135.8 (C), 138.2 (C), 144.2 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, C), 154.6 (dd, $J_{C\text{-}F}$ = 292.3, 287.8 Hz, CF_2), 197.8 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -89.67 (ABq, Δδ = 0.28, J_{AB} = 38.8 Hz, 2F). **FT-IR** (cm^{-1}, neat, ATR) 2935, 1723, 1678, 1266, 1240, 1088, 997, 818, 730. **HRMS** (EI+) calcd for $C_{18}H_{16}F_2OS$ $[M]^+$: 318.0890, found: 318.0892.

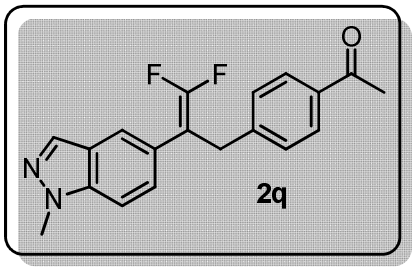


1-(4-(3,3-Difluoro-2-(3-hydroxyphenyl)allyl)phenyl)ethanone, 2p Synthesis of 1-(4-(3,3-difluoro-2-(3-hydroxyphenyl)allyl)phenyl)ethanone (91 mg, 63%) was accomplished using the above procedure with ***the following modifications***: The reaction was conducted using 3-(3,3,3-trifluoroprop-1-en-2-yl)phenol **1p** (94.1 mg, 0.500 mmol) and 1-(4-iodophenyl)ethanone (246 mg, 1.00 mmol, 2.0 equiv). Further purification was accomplished by SiO_2 column chromatography (gradient hexanes to 80:20 hexanes/EtOAc, then EtOAc) to give the pure coupling product (**2p**) as a clear, light yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 2.55 (s, 3H), 3.77 (s, 2H), 5.03 (br s, 1H), 6.68 - 6.76 (m, 2H), 6.83 (d, J = 7.8 Hz, 1H), 7.16 (t, J = 7.9 Hz, 1H), 7.25 (d, J = 8.7 Hz, 2H), 7.84 (d, J = 8.1 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 26.8 (CH_3), 34.1 (CH_2), 91.2 (t, $J_{C\text{-}C\text{-}F}$ = 18.2 Hz, C), 115.0 (CH), 115.5 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.2 Hz, CH), 120.6 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.6 Hz, CH), 128.8 (CH), 129.0 (CH), 129.9 (CH), 134.8 (C), 135.6 (C), 144.7 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, C), 154.8 (t, $J_{C\text{-}F}$ = 290.6 Hz, CF_2), 156.2 (C), 199.1 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -89.21 (ABq, Δδ = 0.03, J_{AB} = 38.2 Hz, 2F). **FT-IR** (cm^{-1}, neat, ATR) 3345, 1727, 1667,

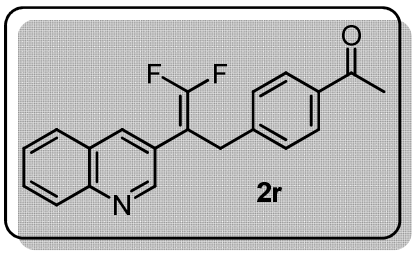


1606, 1583, 1360, 1264, 1182. **HRMS** (EI+) calcd for $C_{17}H_{14}F_2O_2$ $[M]^+$: 288.0962, found: 288.0965.

1-(4-(3,3-Difluoro-2-(1-methyl-1H-indazol-5-yl)allyl)phenyl)ethanone, 2q Synthesis of 1-(4-(3,3-difluoro-2-(1-methyl-1H-indazol-5-yl)allyl)phenyl)ethanone (0.125 g, 77%) was accomplished using the above procedure with ***the following modifications***: The reaction was conducted using 1-methyl-5-(3,3,3-trifluoroprop-1-en-2-yl)-1H-indazole **1q** (0.113 g, 0.500 mmol) and 1-(4-iodophenyl)ethanone (246 mg, 1.00 mmol, 2.0 equiv). Further purification was accomplished by SiO_2 column chromatography (gradient hexanes to 70:30 hexanes/EtOAc) to give the pure coupling product (**2q**) as a clear, light yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 2.54 (s, 3H), 3.83 (s, 2H), 4.04 (s, 3H), 7.24 (d, J = 7.9 Hz, 2H), 7.29 - 7.35 (m, 2H), 7.56 (s, 1H), 7.82 (d, J = 8.2 Hz, 2H), 7.91 (s, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 26.8 (CH_3), 34.8 (CH_2), 35.8 (CH_3), 91.6 (dd, $J_{C\text{-}C\text{-}F}$ = 22.0, 15.6 Hz, C), 109.3 (CH), 121.2 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.2 Hz, CH), 124.3 (C), 125.5 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, CH), 127.0 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 3.0 Hz, C), 128.8 (CH), 128.9 (CH), 133.1 (CH), 135.9 (C), 139.3 (C), 144.3 (C), 154.7 (dd, $J_{C\text{-}F}$ = 291.4, 287.8 Hz, CF_2), 197.9 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -91.00 (ABq, Δδ = 0.57, J_{AB} = 41.2 Hz, 2F). **FT-IR** (cm^{-1}, neat, ATR) 2953, 1725, 1679, 1266, 1235, 1157, 908, 727. **HRMS** (EI+) calcd for $C_{19}H_{16}F_2N_2O$ $[M]^+$: 326.1231, found: 326.1230.

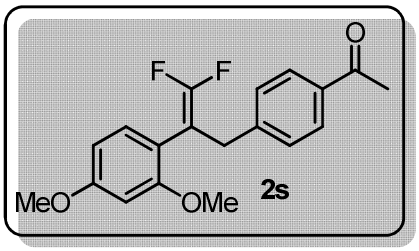


1-(4-(3,3-Difluoro-2-(quinolin-3-yl)allyl)phenyl)ethanone, 2r Synthesis of 1-(4-(3,3-difluoro-2-(quinolin-3-yl)allyl)phenyl)ethanone (0.128 g, 79%) was accomplished using the above procedure with ***the following modifications***: The reaction was conducted using 3-(3,3,3-trifluoroprop-1-en-2-yl)quinoline **1r** (0.112 g, 0.500 mmol) and 1-(4-iodophenyl)ethanone (246 mg, 1.00 mmol, 2.0 equiv); 10 mol % Cl-4CzIPN (53.2 mg) was used. Further purification was accomplished by SiO_2 column chromatography (gradient hexanes to 60:40 hexanes/EtOAc, then EtOAc) to give the desired coupling product (**2r**) as a clear, light yellow oil, isolated as 97% pure mixture of product and inseparable starting material. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 2.54 (s, 3H), 3.92 (s, 2H), 7.28 (d, J

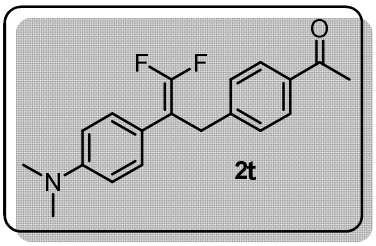


= 8.1 Hz, 2H), 7.53 (t, J = 7.6 Hz, 1H), 7.70 (t, J = 7.7 Hz, 1H), 7.73 (d, J = 8.2 Hz, 1H), 7.84 (d, J = 8.2 Hz, 2H), 7.97 (d, J = 1.8 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 8.83 (s, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 26.7 (CH_3), 33.9 (CH_2), 89.2 (dd, $J_{C\text{-}C\text{-}F}$ = 22.9, 14.7 Hz, C), 126.4 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 4.6 Hz, CH), 127.3 (CH), 127.7 (C), 128.0 (CH), 128.8 (CH), 129.0 (CH), 129.4 (CH), 130.1 (CH), 135.2 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 3.2 Hz, C), 136.1 (C), 143.4 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.8 Hz, C), 147.2 (C), 150.1 (dd, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 4.6, 2.7 Hz, CH), 155.2 (dd, $J_{C\text{-}F}$ = 294.2, 290.5 Hz, CF_2), 197.7 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -87.96 (ABq, Δδ = 0.84, J_{AB} = 34.7 Hz, 2F). **FT-IR** (cm^{-1}, neat, ATR) 2994, 1681, 1262, 1232, 909, 753, 728. **HRMS** (EI+) calcd for $C_{20}H_{15}F_2NO$ $[M]^+$: 323.1122, found: 323.1111.

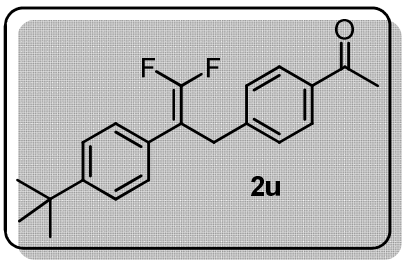
1-(4-(2-(2,4-Dimethoxyphenyl)-3,3-difluoroallyl)phenyl)ethanone, 2s Synthesis of 1-(4-(2-(2,4-dimethoxyphenyl)-3,3-difluoroallyl)phenyl)ethanone (0.130 g, 78%) was accomplished using the above procedure with ***the following modifications***: The reaction was conducted using 2,4-dimethoxy-1-(3,3,3-trifluoroprop-1-en-2-yl)benzene **1s** (0.116 g, 0.500 mmol) and 1-(4-iodophenyl)ethanone (246 mg, 1.00 mmol, 2.0 equiv). Further purification was accomplished by SiO_2 column chromatography (gradient hexanes to 80:20 hexanes/EtOAc, then EtOAc) to give the pure coupling product (**2s**) as a clear, light orange oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 2.54 (s, 3H), 3.69 (s, 2H), 3.72 - 3.78 (m, 6H), 6.36 (dd, J = 8.2, 2.0 Hz, 1H), 6.43 (d, J = 1.8 Hz, 1H), 6.83 (d, J = 8.4 Hz, 1H), 7.18 (d, J = 8.1 Hz, 2H), 7.80 (d, J = 8.1 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 26.7 (CH_3), 34.4 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 1.8 Hz, CH_2), 55.5 (CH_3), 55.6 (CH_3), 88.6 (dd, $J_{C\text{-}C\text{-}F}$ = 22.7, 18.2 Hz, C), 99.0 (CH), 104.5 (CH), 114.3 (dd, $J_{C\text{-}C\text{-}C\text{-}F}$ = 4.5, 1.8 Hz, C), 128.6 (CH), 129.1 (CH), 131.8 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 1.8 Hz, CH), 135.5 (C), 145.0 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, C), 154.0 (t, $J_{C\text{-}F}$ = 287.0 Hz, CF_2), 158.5 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 1.8 Hz, C), 161.0 (C), 198.1 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -92.96 (d, J = 41.2 Hz, 1F), -90.33 (d, J = 41.2 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 2945, 1681, 1606, 1508, 1264, 1236, 1208, 1159, 1097. **HRMS** (EI+) calcd for $C_{19}H_{18}F_2O_3$ $[M]^+$: 332.1224, found: 332.1230.



1-(4-(2-(4-(Dimethylamino)phenyl)-3,3-difluoroallyl)phenyl)ethanone, 2t Synthesis of 1-(4-(2-(4-(dimethylamino)phenyl)-3,3-difluoroallyl)phenyl)ethanone (54.3 mg, 57%) was accomplished using the above procedure with ***the following modifications***: The reaction was conducted using *N,N*-dimethyl-4-(3,3,3-trifluoroprop-1-en-2-yl)aniline **1t** (64.6 mg, 0.3 mmol) and 1-(4-bromophenyl)ethanone (199 mg, 0.600 mmol, 2.0 equiv). Further purification was accomplished by SiO_2 column chromatography (gradient hexanes to 85:15 hexanes/EtOAc, then EtOAc) to give the pure coupling product (**2t**) as a clear, light yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 2.55 (s, 3H), 2.92 (s, 6H), 3.76 (s, 2H), 6.64 (d, J = 8.5 Hz, 2H), 7.13 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H, overlaps with $CDCl_3$), 7.84 (d, J = 7.9 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 26.8 (CH_3), 34.1 (CH_2), 40.5 (CH_3), 90.9 (dd, $J_{C\text{-}C\text{-}F}$ = 21.1, 14.7 Hz, C), 112.4 (CH), 120.6 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, C), 128.7 (CH), 128.8 (CH), 129.1 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, CH), 135.7 (C), 145.0 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 1.8 Hz, C), 149.8 (C), 154.5 (dd, $J_{C\text{-}F}$ = 291.4, 286.8 Hz, CF_2), 198.0 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -91.67 (ABq, Δδ = 0.27, J_{AB} = 44.0 Hz, 2F). **FT-IR** (cm^{-1}, neat, ATR) 2965, 1680, 1607, 1524, 1358, 1267, 1234. **HRMS** (ES+) calcd for $C_{19}H_{20}F_2NO$ $[M+H]^+$: 316.1513, found: 316.1516.



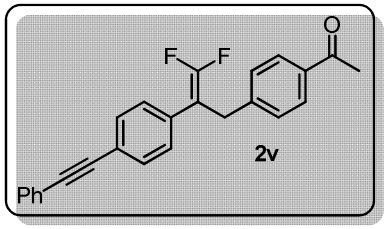
1-(4-(2-(4-(*tert*-Butyl)phenyl)-3,3-difluoroallyl)phenyl)ethanone, 2u Synthesis of 1-(4-(2-(4-(*tert*-butyl)phenyl)-3,3-difluoroallyl)phenyl)ethanone (96.9 mg, 59%) was accomplished using the above procedure with ***the following modifications***: The reaction was conducted using 1-(*tert*-butyl)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene **1u** (0.114 g, 0.500 mmol) and 1-(4-iodophenyl)ethanone (129 mg, 0.525 mmol, 1.05 equiv).[21] Further purification was accomplished by SiO_2 column chromatography (gradient hexanes to 90:10 hexanes/EtOAc) to give the desired coupling product (**2u**) as a clear, light yellow oil, isolated as a 96% pure mixture of product and trifluoromethylalkene. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.29 (s, 9H), 2.56 (s, 3H), 3.79 (s, 2H), 7.20 (d, J = 7.9 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 7.86 (d, J = 8.1 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 26.8 (CH_3), 31.5 (CH_3), 34.1 (C), 34.8 (CH_2), 91.0 (dd, $J_{C\text{-}C\text{-}F}$ = 21.1, 14.7 Hz, C), 125.7 (CH),



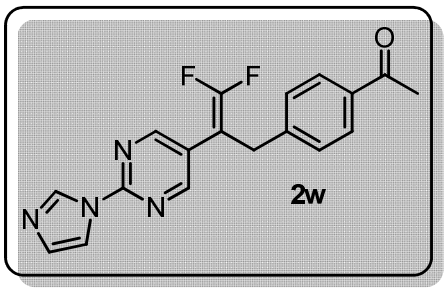
[21] The unreacted iodide was inseparable from the desired product so a reduced loading was used.

128.0 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, CH), 128.7 (CH), 129.0 (CH), 130.3 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 4.2 Hz, C), 135.8 (C), 144.7 (C), 150.7 (C), 154.9 (dd, $J_{C\text{-}F}$ = 292.3, 286.8 Hz, CF_2), 198.1 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -89.81 (ABq, Δδ = 0.46, J_{AB} = 39.3 Hz, 2F). **FT-IR** (cm^{-1}, neat, ATR) 2963, 1717, 1683, 1607, 1358, 1266, 1239, 1097, 998, 837. **HRMS** (EI+) calcd for $C_{21}H_{22}F_2O$ $[M]^+$: 328.1639, found: 328.1642.

1-(4-(3,3-Difluoro-2-(4-(phenylethynyl)phenyl)allyl)phenyl)ethanone, 2v Synthesis of 1-(4-(3,3-difluoro-2-(4-(phenylethynyl)phenyl)allyl)phenyl)ethanone (0.156 g, 84%) was accomplished using the above procedure with ***the following modifications***: The reaction was conducted using 1-(phenylethynyl)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene **1v** (0.136 g, 0.500 mmol) and 1-(4-iodophenyl)ethanone (246 mg, 1.00 mmol, 2.0 equiv). Further purification was accomplished by SiO_2 column chromatography (gradient hexanes to 80:20 hexanes/EtOAc, then EtOAc) to give the pure coupling product (**2v**) as a clear, light orange oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 2.57 (s, 3H), 3.81 (s, 2H), 7.25 (d, J = 7.9 Hz, 3H), 7.30 - 7.40 (m, 4H), 7.42 - 7.54 (m, 4H), 7.82 - 7.89 (m, 2H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 26.8 (CH_3), 33.8 (CH_2), 89.1 (C), 90.4 (C), 91.2 (dd, $J_{C\text{-}C\text{-}F}$ = 21.8, 14.5 Hz, C), 122.7 (C), 123.3 (C), 128.3 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.6 Hz, CH), 128.6 (CH), 128.6 (CH), 128.7 (CH), 129.0 (CH), 131.8 (CH), 131.9 (CH), 133.1 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 3.6 Hz, C), 135.9 (C), 144.1 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, C), 154.8 (dd, $J_{C\text{-}F}$ = 293.4, 288.8 Hz, CF_2), 198.0 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -88.53 (ABq, Δδ = 0.32, J_{AB} = 35.9 Hz, 2F). **FT-IR** (cm^{-1}, neat, ATR) 2981, 1723, 1683, 1607, 1358, 1267, 1243, 757. **HRMS** (EI+) calcd for $C_{25}H_{18}F_2O$ $[M]^+$: 372.1326, found: 372.1321.

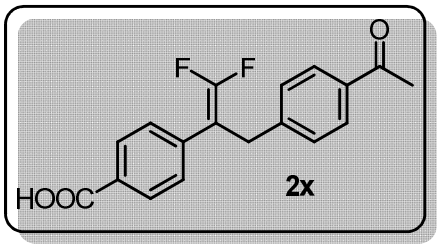


1-(4-(2-(2-(1H-imidazol-1-yl)pyrimidin-5-yl)-3,3-difluoroallyl)phenyl)ethanone, 2w Synthesis of 1-(4-(2-(2-(1H-imidazol-1-yl)pyrimidin-5-yl)-3,3-difluoroallyl)phenyl)ethanone (90.1 mg, 53%) was accomplished using the above procedure with ***the following modifications***: The reaction was conducted using 2-(1*H*-imidazol-1-yl)-5-(3,3,3-trifluoroprop-1-en-2-yl)pyrimidine **1w** (0.120 g, 0.500 mmol) and 1-(4-iodophenyl)ethanone (246 mg, 1.00 mmol, 2.0 equiv). Further purification was accomplished by SiO_2 column

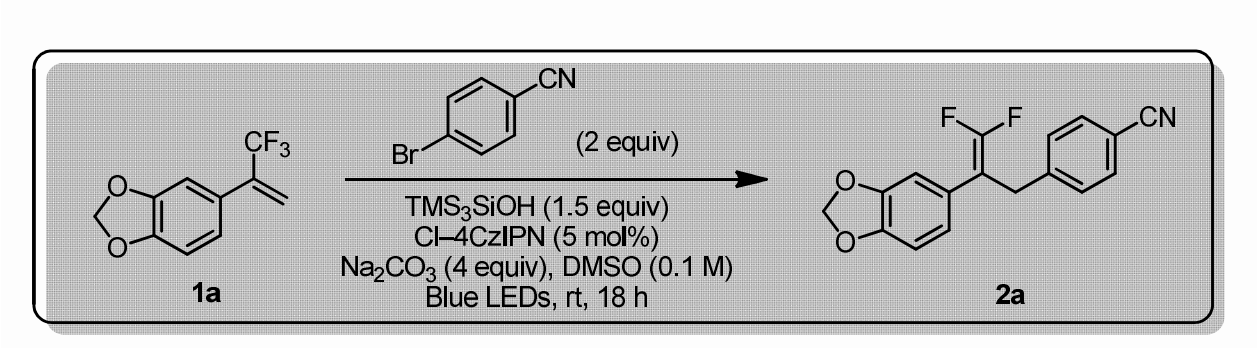


chromatography (gradient hexanes to EtOAc) to give the desired product (**2w**) as a clear, light yellow oil, isolated with a 5% impurity of inseparable trifluoromethylalkene. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 2.55 (s, 3H), 3.83 (s, 2H), 7.13 (s, 1H), 7.26 (d, J = 7.9 Hz, 2H), 7.80 (s, 1H), 7.88 (d, J = 8.1 Hz, 2H), 8.48 - 8.57 (m, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 26.8 (CH_3), 33.2 (CH_2), 86.1 (dd, $J_{C\text{-}C\text{-}F}$ = 24.7, 14.7 Hz, C), 116.7 (CH), 125.1 (C), 128.7 (CH), 129.3 (CH), 131.0 (CH), 136.4 (CH), 136.5 (C), 142.3 (C), 155.2 (dd, $J_{C\text{-}F}$ = 294.2, 292.3 Hz, CF_2), 153.6 (C), 157.9 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, CH), 197.6 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -85.89 (ABq, Δδ = 0.52, J_{AB} = 31.7 Hz, 2F). **FT-IR** (cm^{-1}, neat, ATR) 1682, 1474, 1456, 1263, 907, 726, 649. **HRMS** (EI+) calcd for $C_{18}H_{14}F_2N_4O$ $[M]^+$: 341.1214, found: 341.1213.

4-(3-(4-Acetylphenyl)-1,1-difluoroprop-1-en-2-yl)benzoic acid, 2x Synthesis of 4-(3-(4-acetylphenyl)-1,1-difluoroprop-1-en-2-yl)benzoic acid (66 mg, 42%) was accomplished using the above procedure with ***the following modifications***: The reaction was conducted using 4-(3,3,3-trifluoroprop-1-en-2-yl)benzoic acid **1x** (0.108 g, 0.500 mmol) and 1-(4-iodophenyl)ethanone (369 mg, 1.50 mmol, 3.0 equiv); 10 mol % of Cl-4CzIPN (53.2 mg) was used; the reaction was allowed to stir for 39 h. Further purification was accomplished by SiO_2 column chromatography (gradient 90:10 hexanes/EtOAc to 70:30 hexanes/EtOAc) to give the desired coupling product (**2x**) as a clear, light yellow oil, isolated with a 6% impurity of inseparable trifluoromethylalkene. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 2.56 (s, 3H), 3.84 (s, 2H), 7.24 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.1 Hz, 2H), 7.85 (d, J = 8.1 Hz, 2H), 8.03 (d, J = 8.5 Hz, 2H), 11.87 (br. s., OH). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 26.8 (CH_3), 33.8 (CH_2), 91.2 (dd, $J_{C\text{-}C\text{-}F}$ = 22.7, 13.6 Hz, C), 128.4 - 128.6 (CH), 128.7 (CH), 129.1 (CH), 130.7 (CH), 130.8 (C), 136.1 (C), 139.1 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.6 Hz, C), 143.7 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, C), 155.1 (dd, $J_{C\text{-}F}$ = 294.2, 291.6 Hz, CF_2), 171.3 (C), 198.0 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -87.17 (ABq, Δδ = 0.47, J_{AB} = 32.6 Hz, 2F). **FT-IR** (cm^{-1}, neat, ATR) 2924, 1683, 1607, 1413, 1265, 1242, 1182, 1098, 736. **HRMS** (ES+) calcd for $C_{18}H_{14}F_2O_3$ $[M]^+$: 316.0911, found: 316.0904.



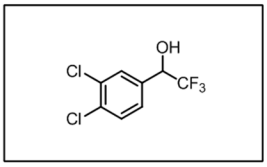
Procedure for Gram-Scale Defluorinative Arylation

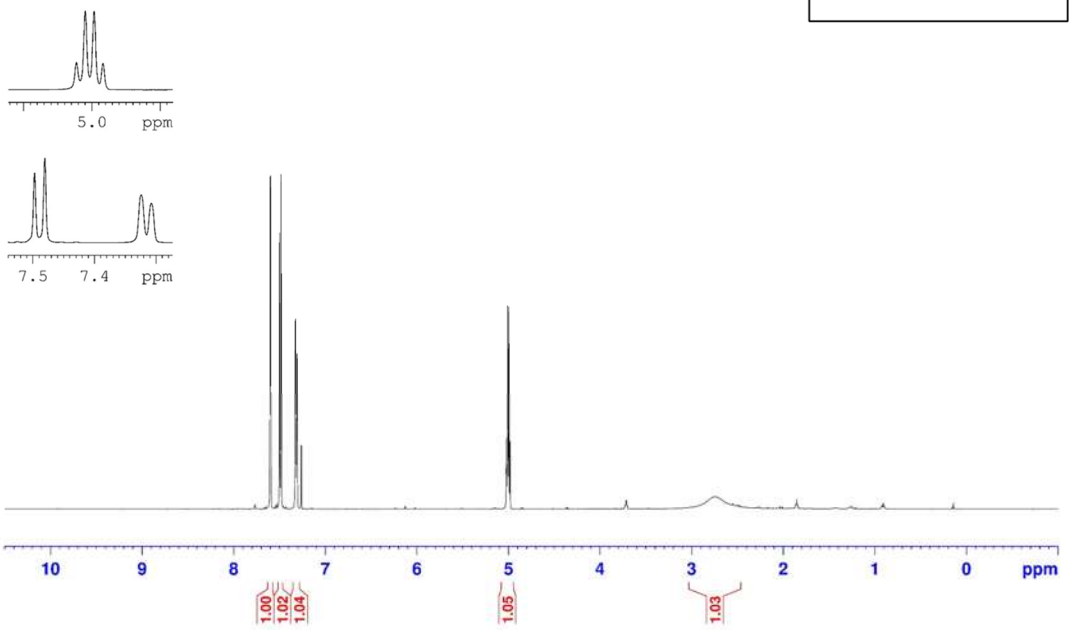


Gram scale procedure for the synthesis of ***(2a)***

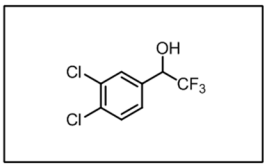
To a 100 mL round bottom flask equipped with a stir bar was added Cl–4CzIPN (0.133 g, 0.125 mmol, 0.0500 equiv), 4-bromobenzonitrile (0.910 g, 5.00 mmol, 2.00 equiv), and Na_2CO_3 (1.06 g, 10.0 mmol, 4.00 equiv). The flask was sealed with a rubber septum and placed under an Ar atmosphere through evacuating and purging with Ar three times *via* an inlet needle. The vial was then charged with TMS_3SiOH (0.992 g, 3.75 mmol, 1.50 equiv) and 5-(3,3,3-trifluoroprop-1-en-2-yl)benzo[d][1,3]dioxole **1a** (0.540 g, 2.50 mmol, 1.00 equiv) in anhyd DMSO (25 mL) *via* syringe. The now bright yellow solution was irradiated with blue LEDs in the aforementioned photoreactor. The temperature of the reaction was maintained at approximately 27 °C *via* a fan. The solution was stirred vigorously while being irradiated. Reaction progress was monitored by GC/MS and ^{19}F NMR. Once judged to be complete, the now dark red-brown solution was transferred to a separatory funnel and diluted with Et_2O (30 mL) and deionized H_2O (30 mL). The layers were separated, and the aq layer was extracted with Et_2O (5 × 20 mL). The combined organic layers were washed with saturated Na_2CO_3 (100 mL) followed by brine (100 mL). The combined organic layers were dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by SiO_2 chromatography (gradient hexanes to 80:20 hexanes/EtOAc) to give the desired product (**2a**) (0.523 g, 70%) as a clear, light yellow oil.

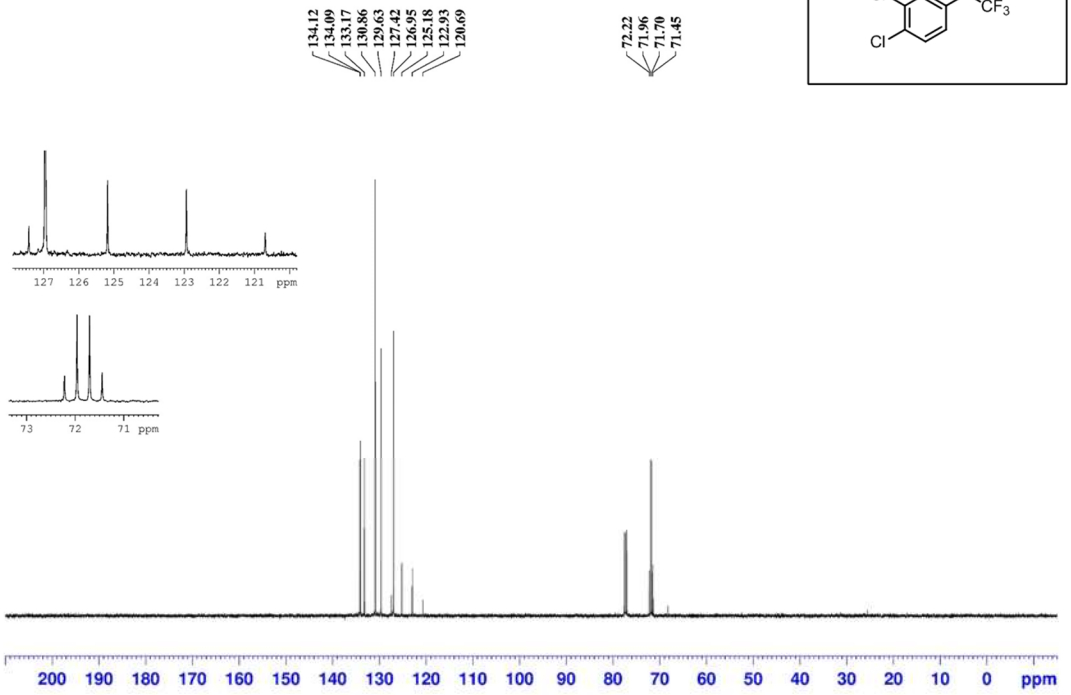
1–(3,4–Dichlorophenyl)–2,2,2–trifluoroethanol
500 MHz, CDCl3



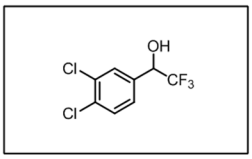


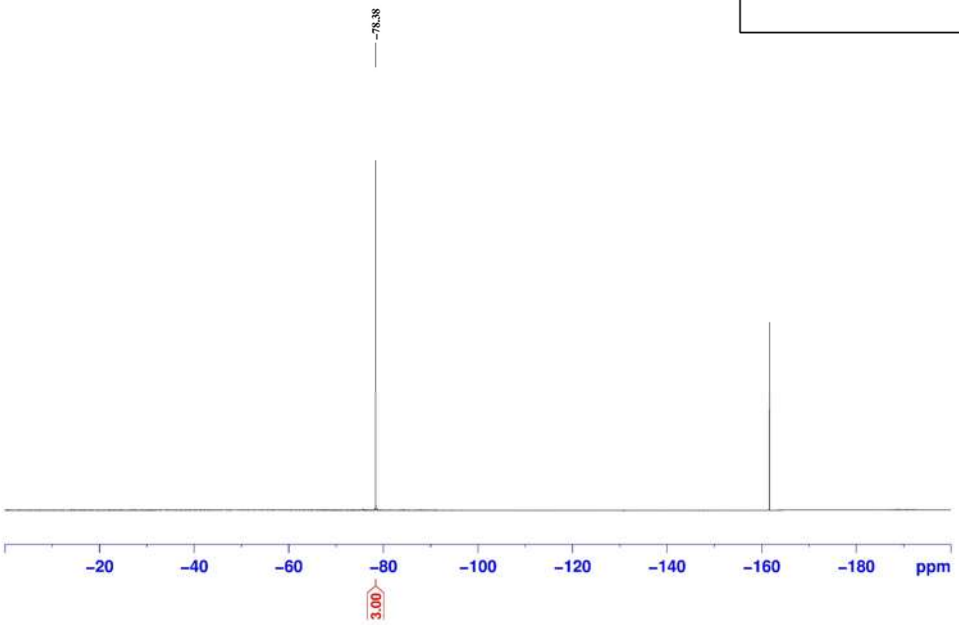
1–(3,4–Dichlorophenyl)–2,2,2–trifluoroethanol
125 MHz, CDCl3



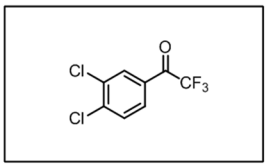


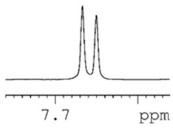
1–(3,4–Dichlorophenyl)–2,2,2–trifluoroethanol
471 MHz, CDCl3

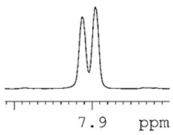


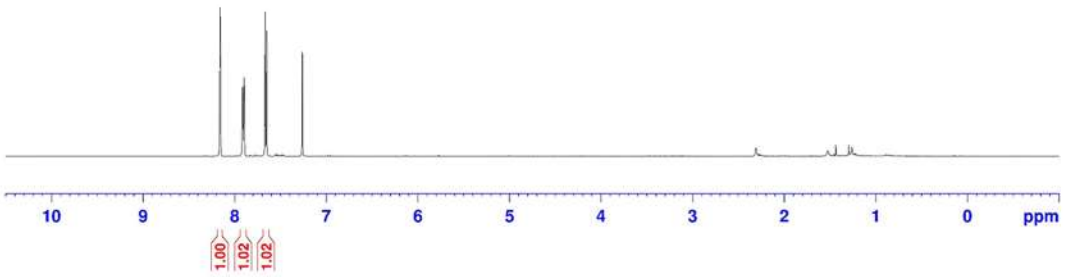


1–(3,4–Dichlorophenyl)–2,2,2–trifluoroethanone
500 MHz, CDCl3

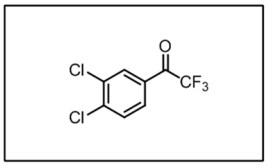


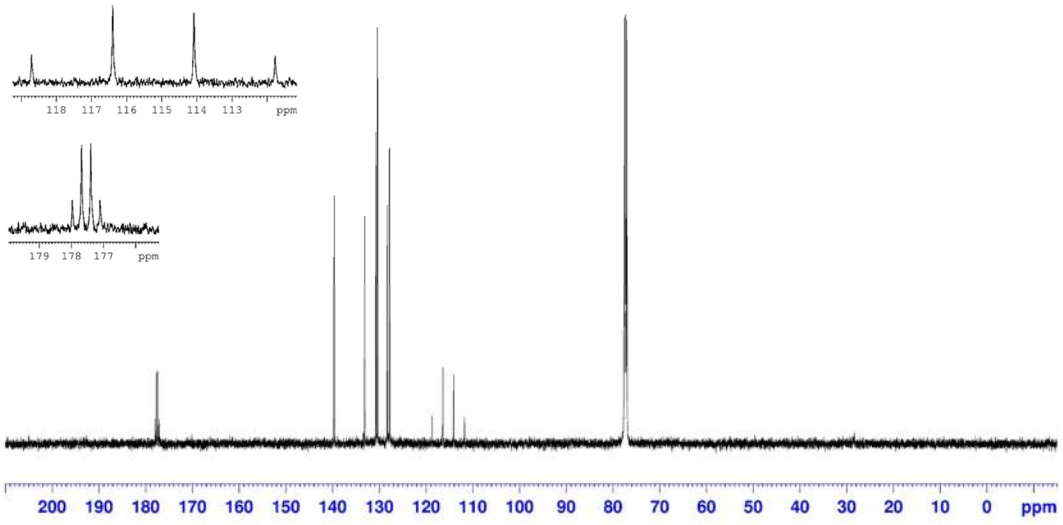




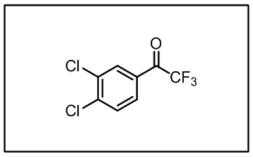


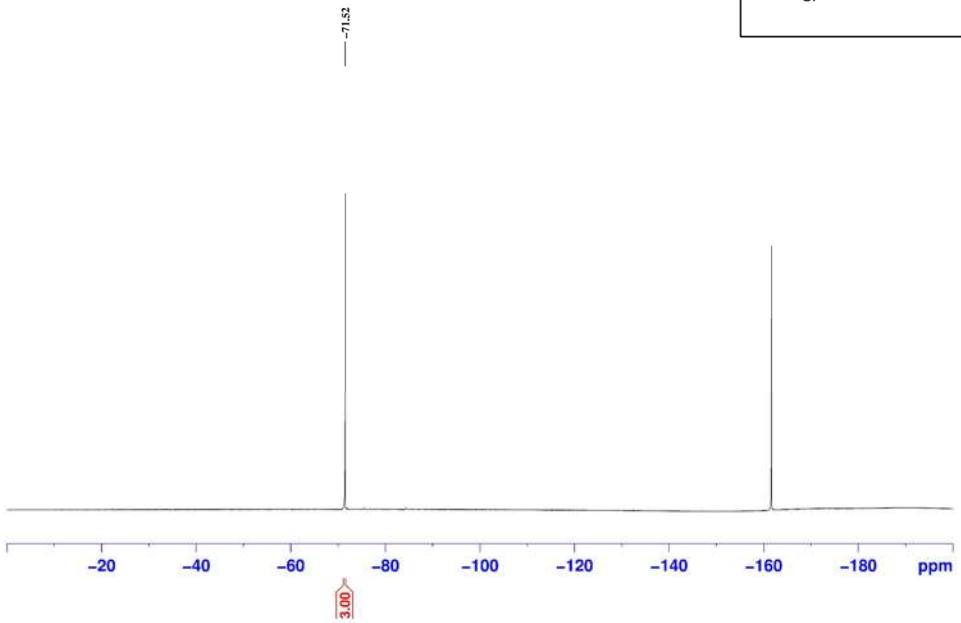
1–(3,4–Dichlorophenyl)–2,2,2–trifluoroethanone
125 MHz, CDCl3



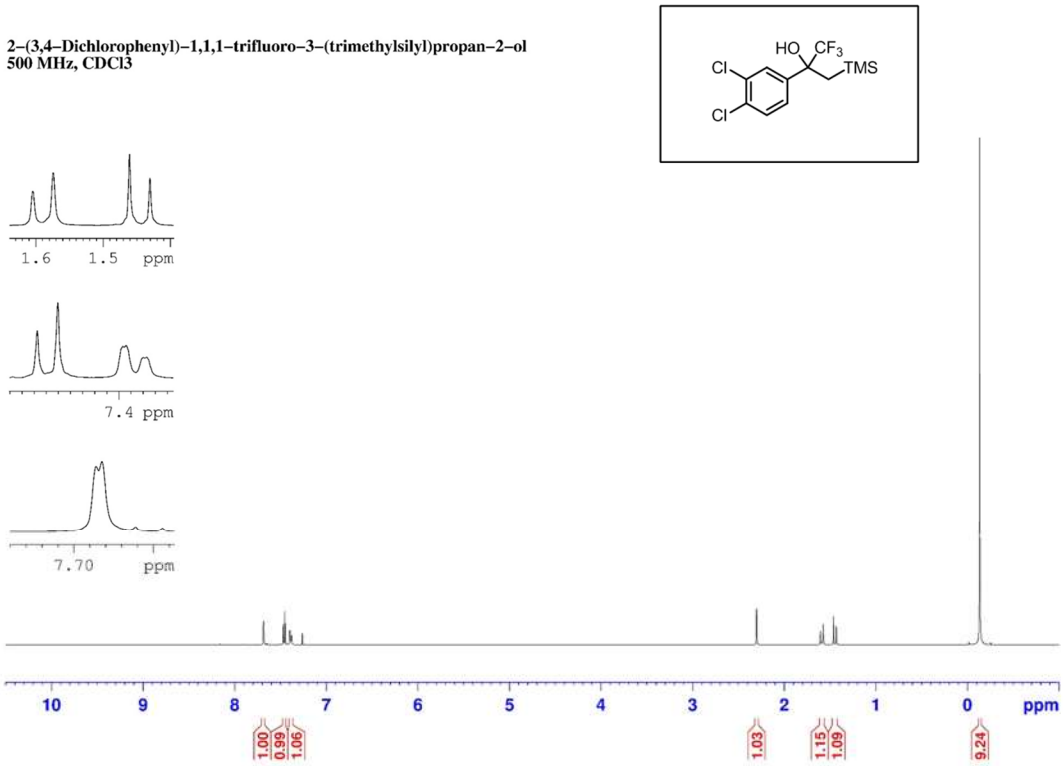


1–(3,4–Dichlorophenyl)–2,2,2–trifluoroethanone
471 MHz, CDCl3

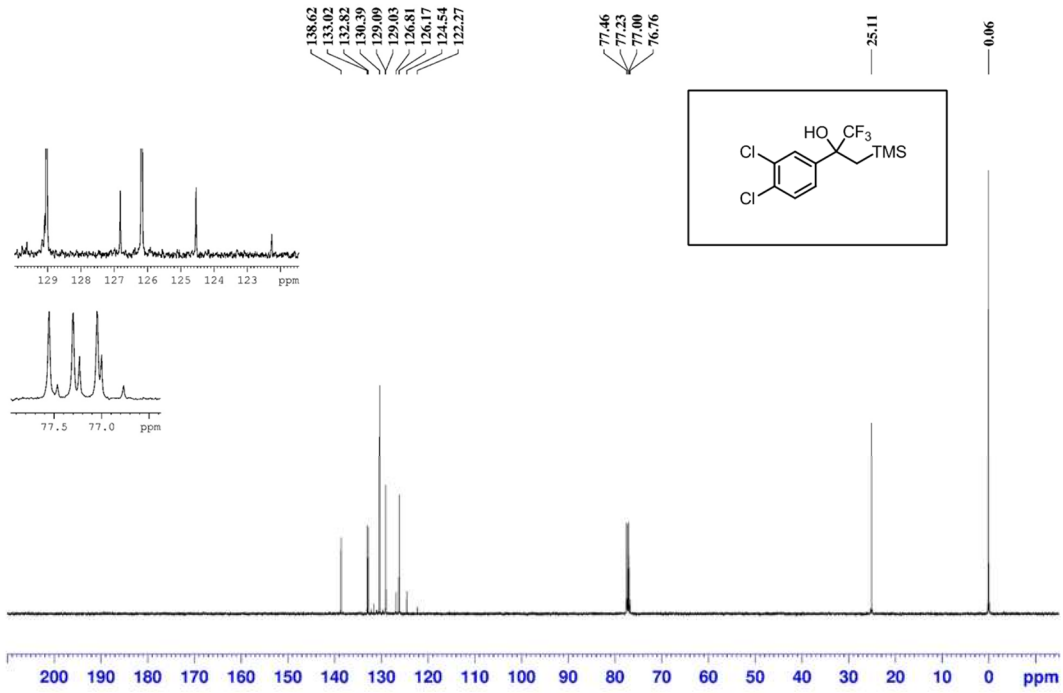




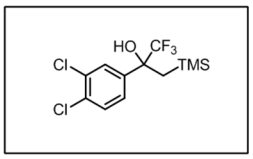
2–(3,4–Dichlorophenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol
500 MHz, CDCl3

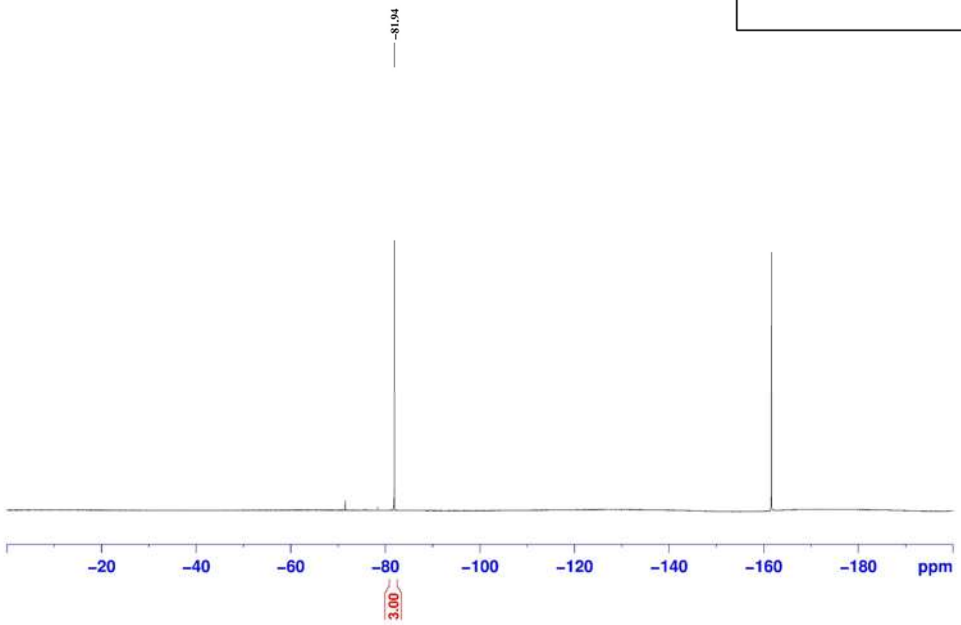


2–(3,4–Dichlorophenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol
125 MHz, CDCl3

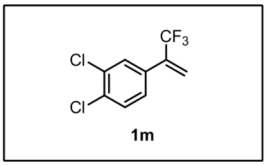


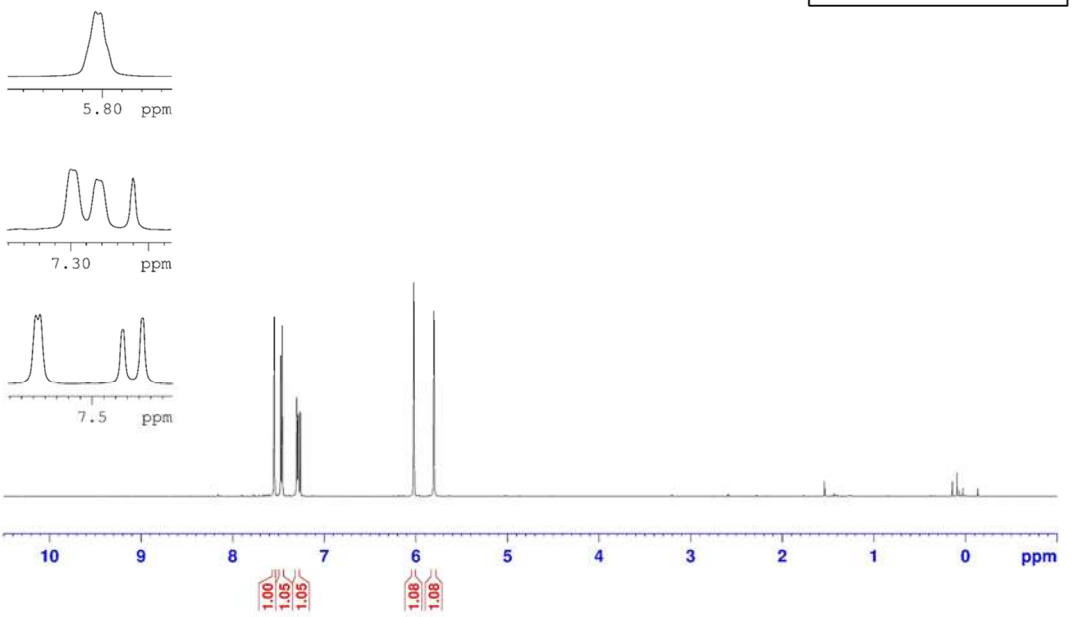
2–(3,4–Dichlorophenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol
471 MHz, CDCl3



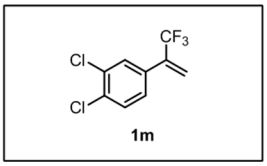


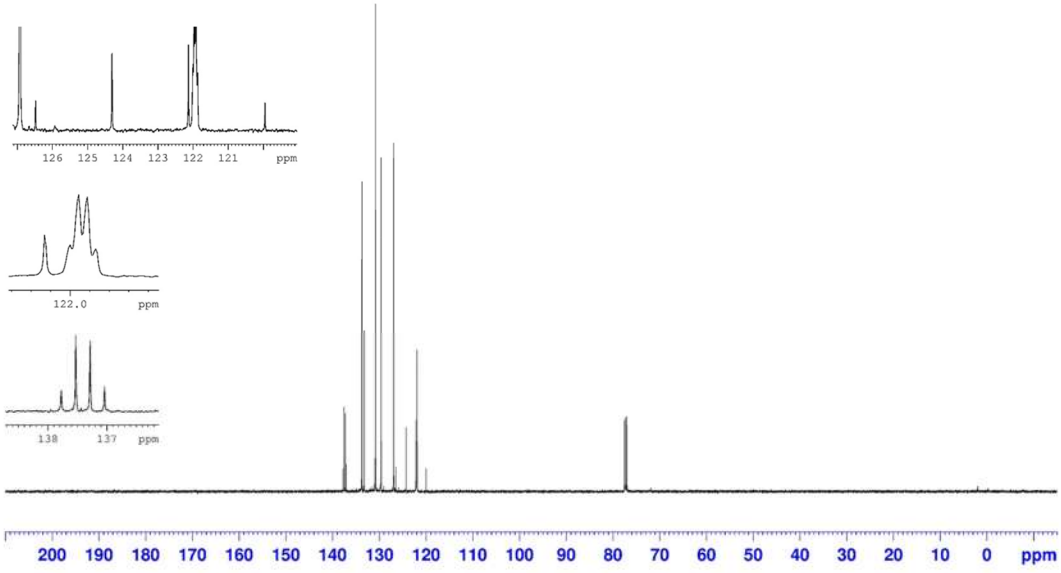
1,2–Dichloro–4–(3,3,3–trifluoroprop–1–en–2–yl)benzene
500 MHz, CDCl3



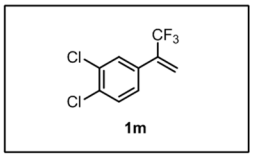


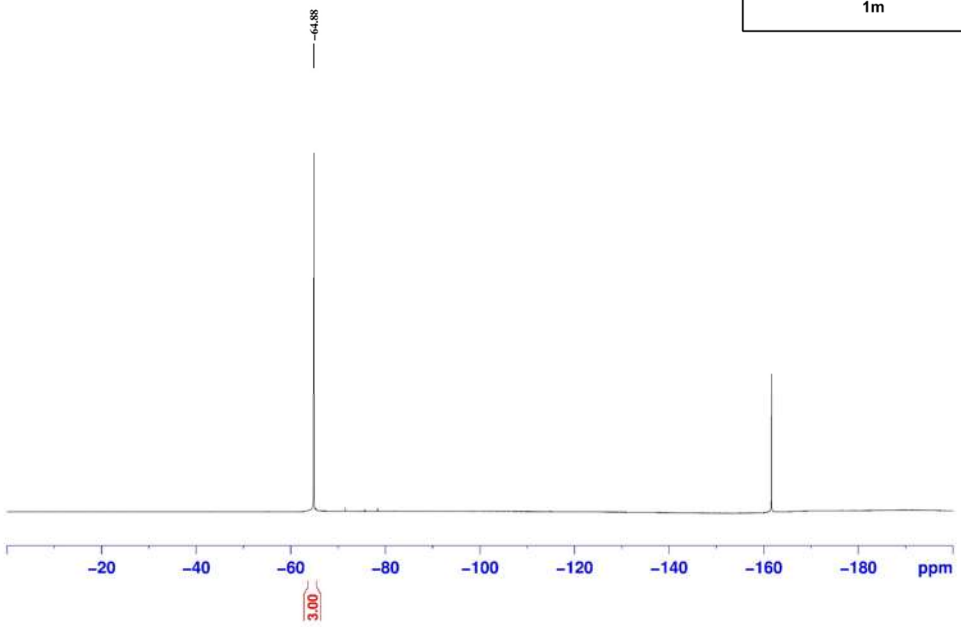
1,2–Dichloro–4–(3,3,3–trifluoroprop–1–en–2–yl)benzene
125 MHz, CDCl3



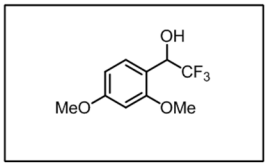


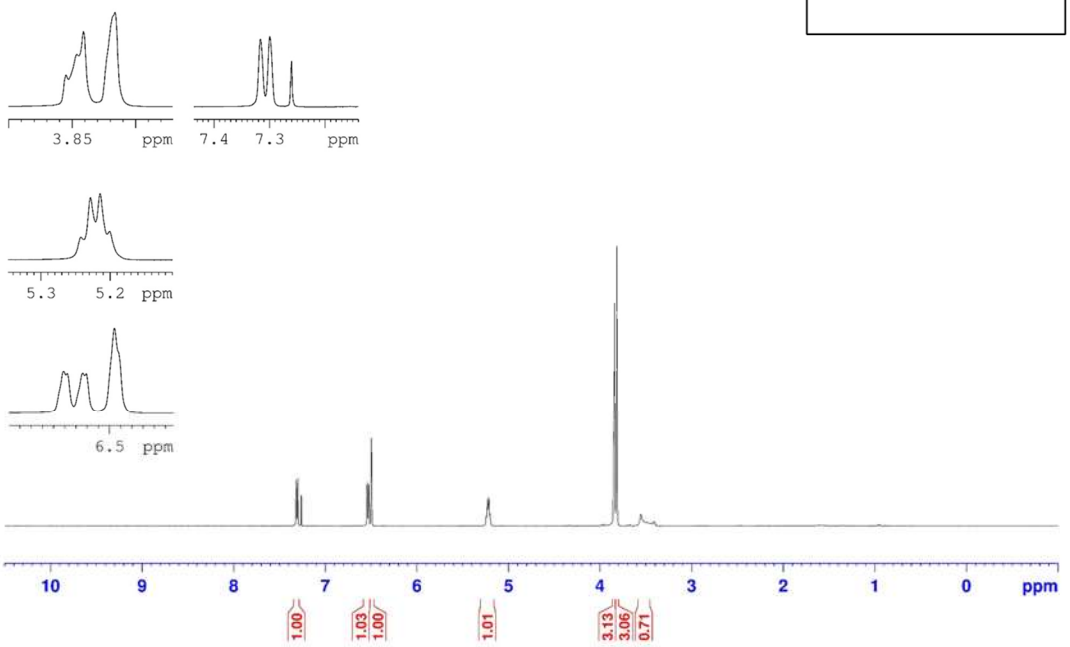
1,2–Dichloro–4–(3,3,3–trifluoroprop–1–en–2–yl)benzene
471 MHz, CDCl3



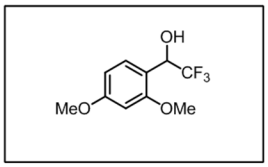


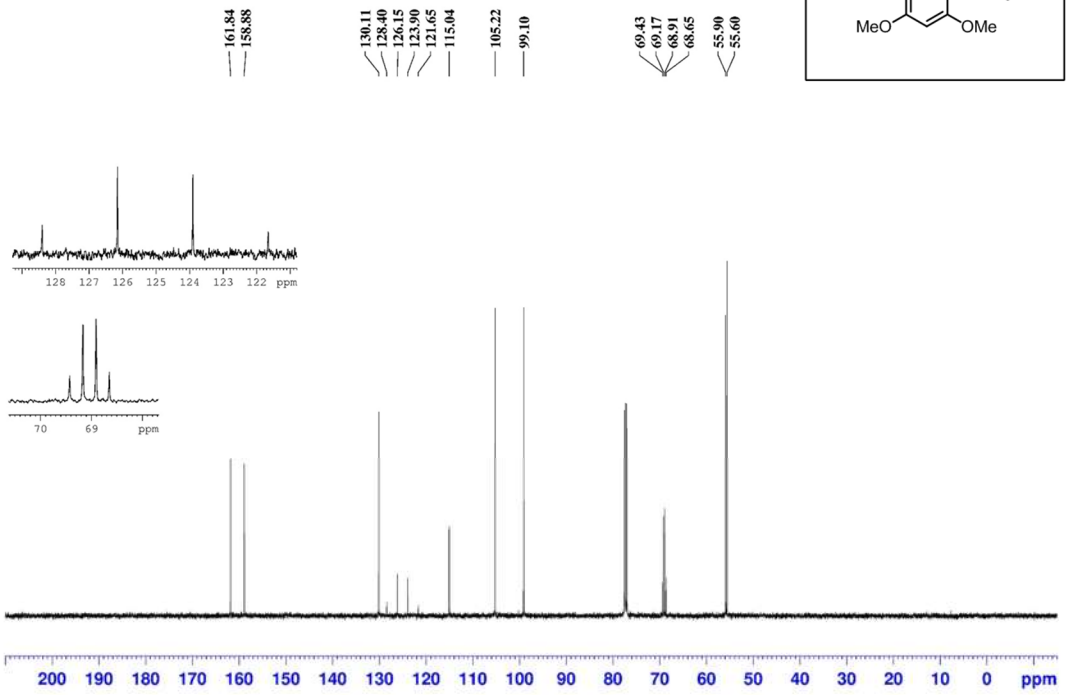
1–(2,4–Dimethoxyphenyl)–2,2,2–trifluoroethanol
500 MHz, CDCl3



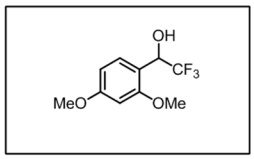


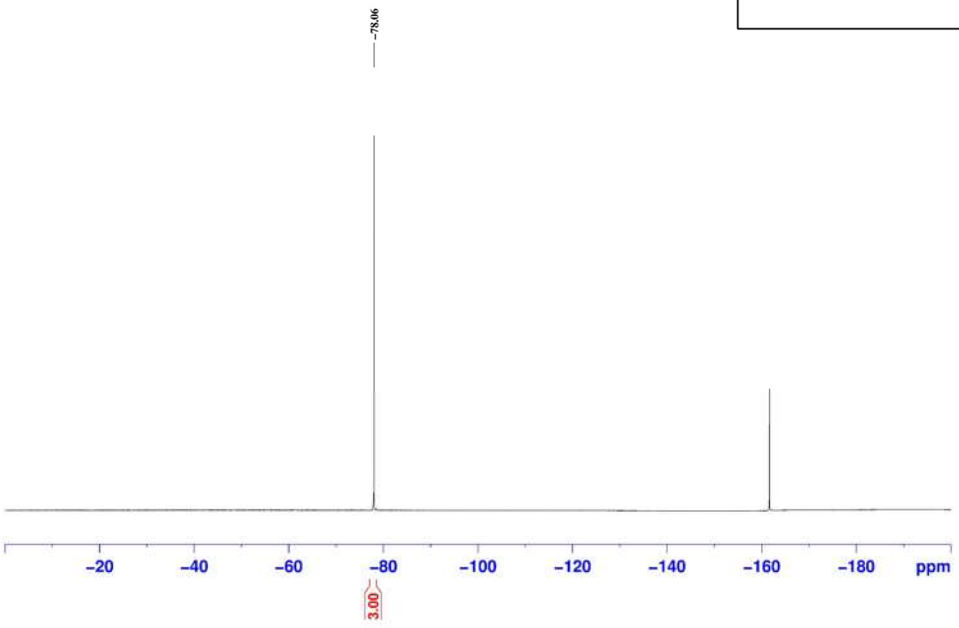
1–(2,4–Dimethoxyphenyl)–2,2,2–trifluoroethanol
125 MHz, CDCl3



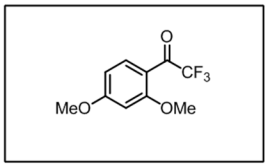


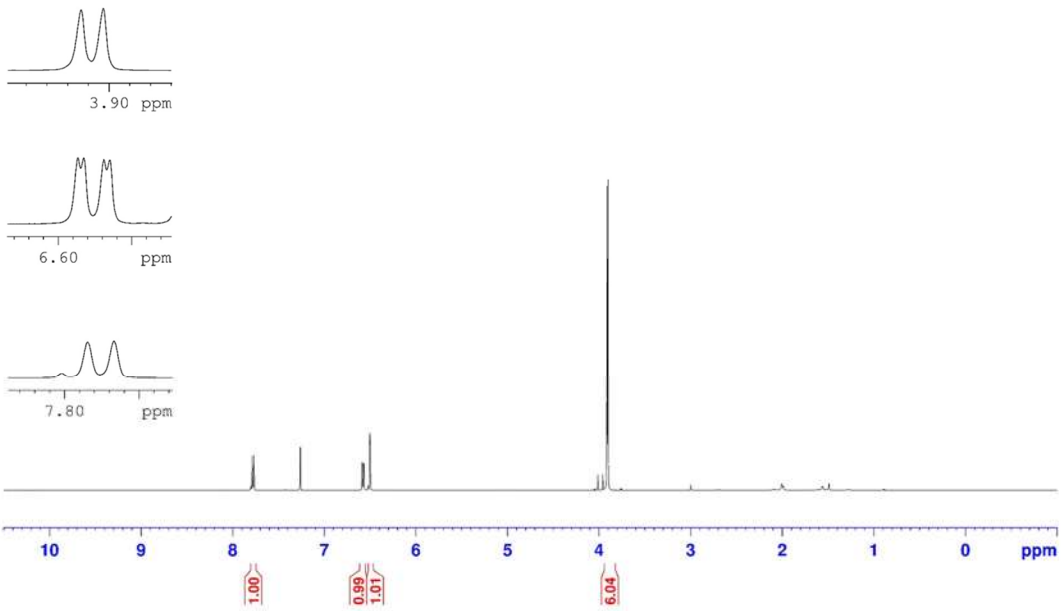
1–(2,4–Dimethoxyphenyl)–2,2,2–trifluoroethanol
471 MHz, CDCl3



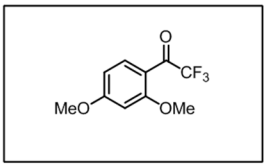


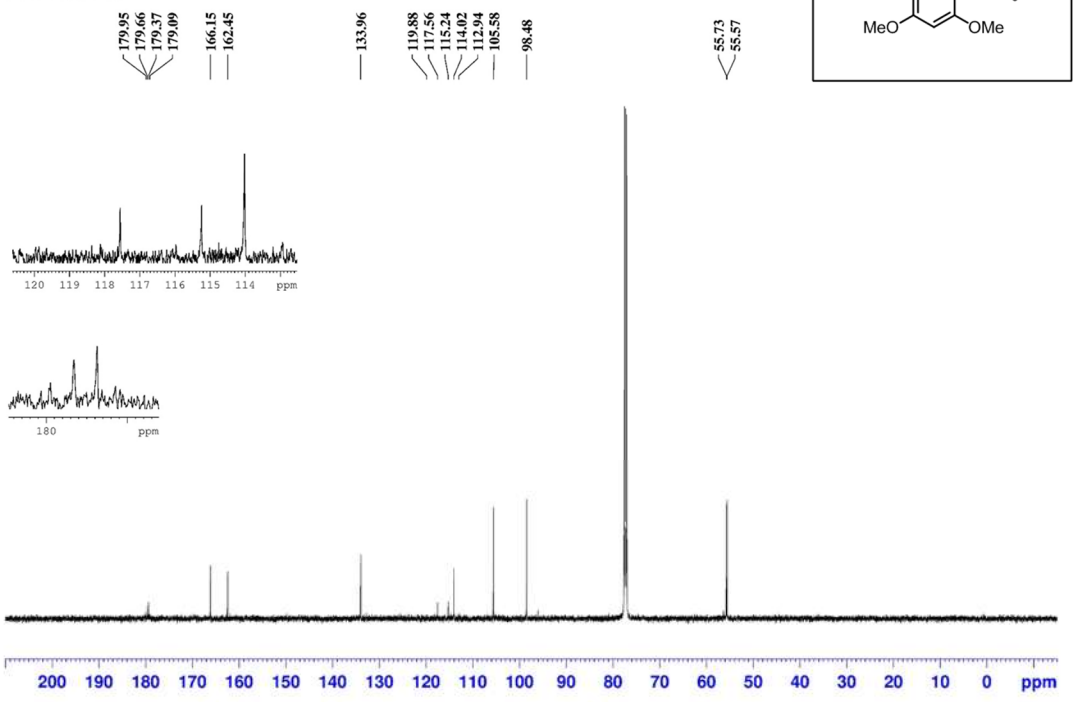
1–(2,4–Dimethoxyphenyl)–2,2,2–trifluoroethanone
500 MHz, CDCl3



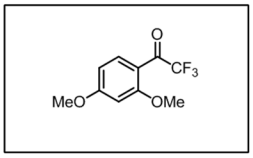


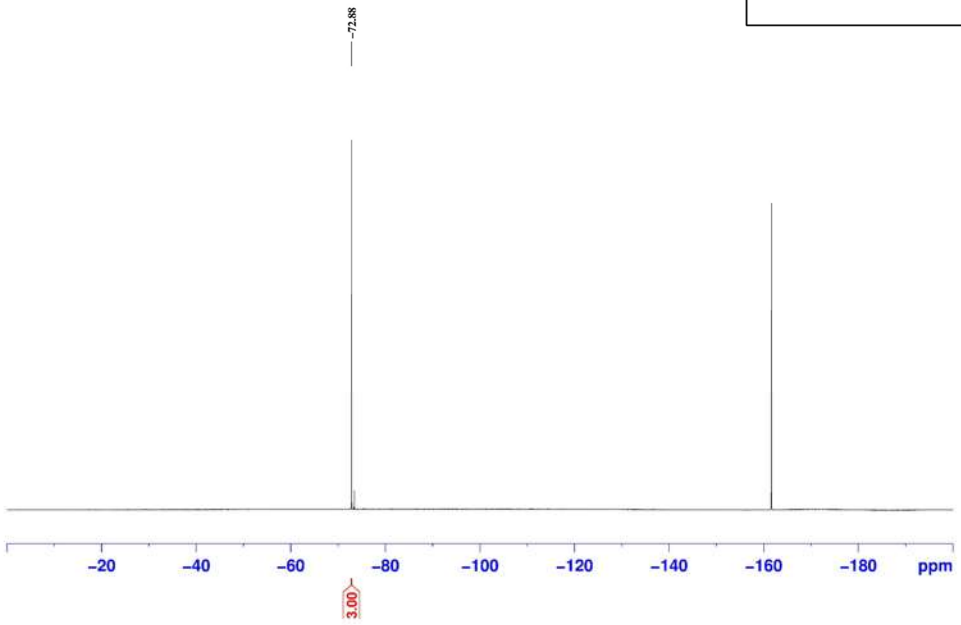
1–(2,4–Dimethoxyphenyl)–2,2,2–trifluoroethanone
125 MHz, CDCl3



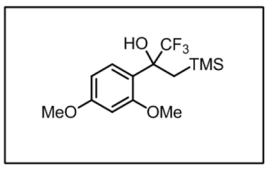


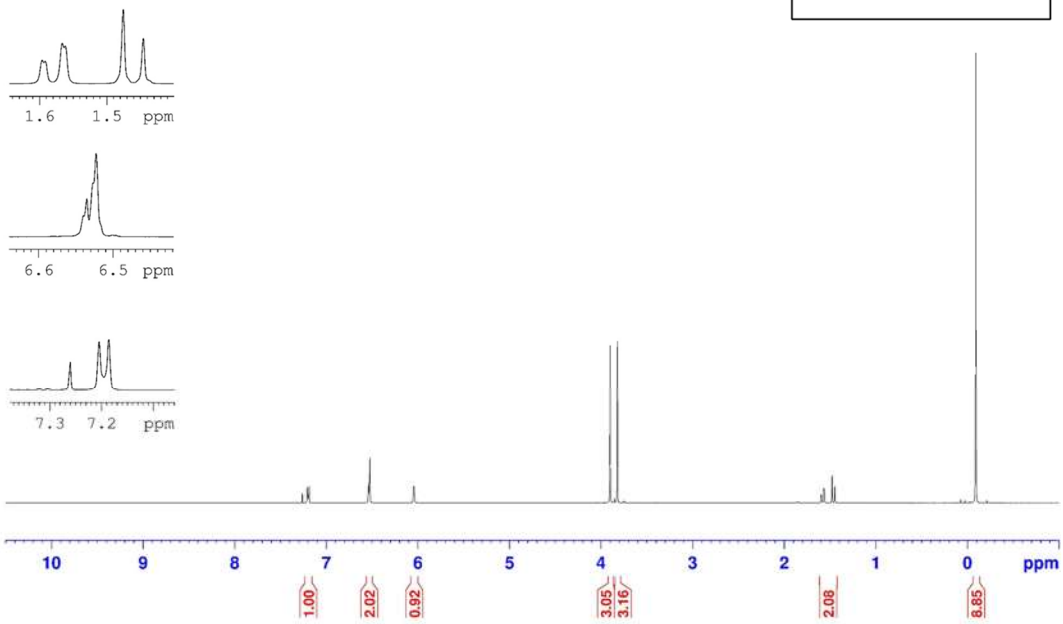
1–(2,4–Dimethoxyphenyl)–2,2,2–trifluoroethanone
471 MHz, CDCl3



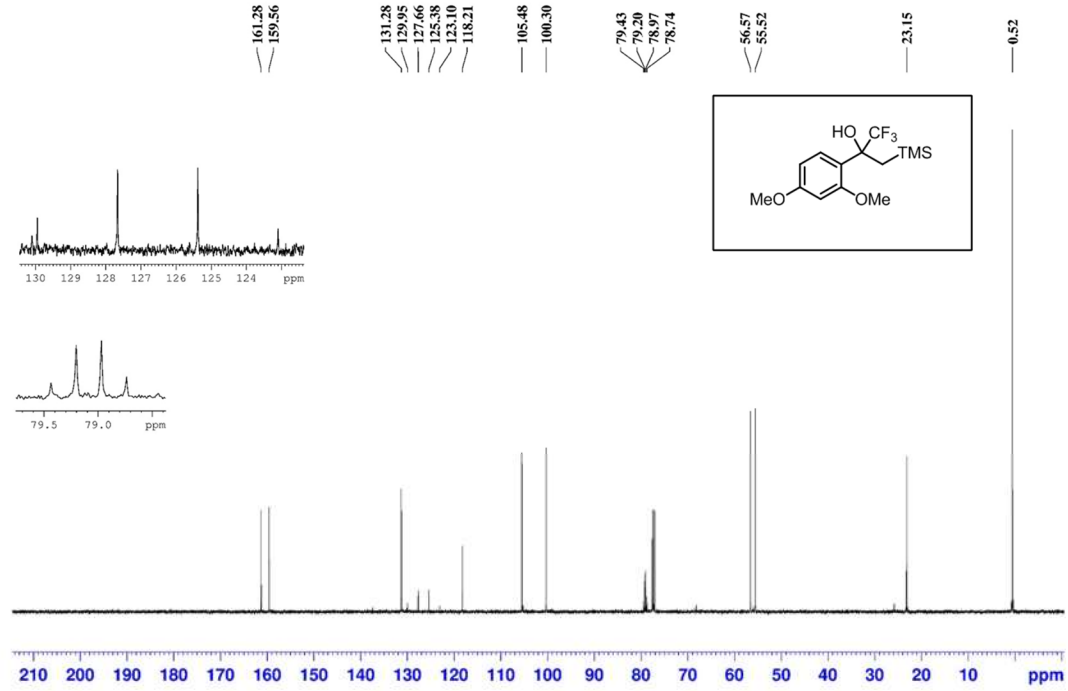


2–(2,4–Dimethoxyphenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol
500 MHz, CDCl3

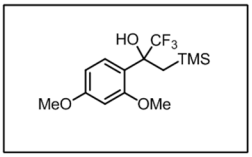


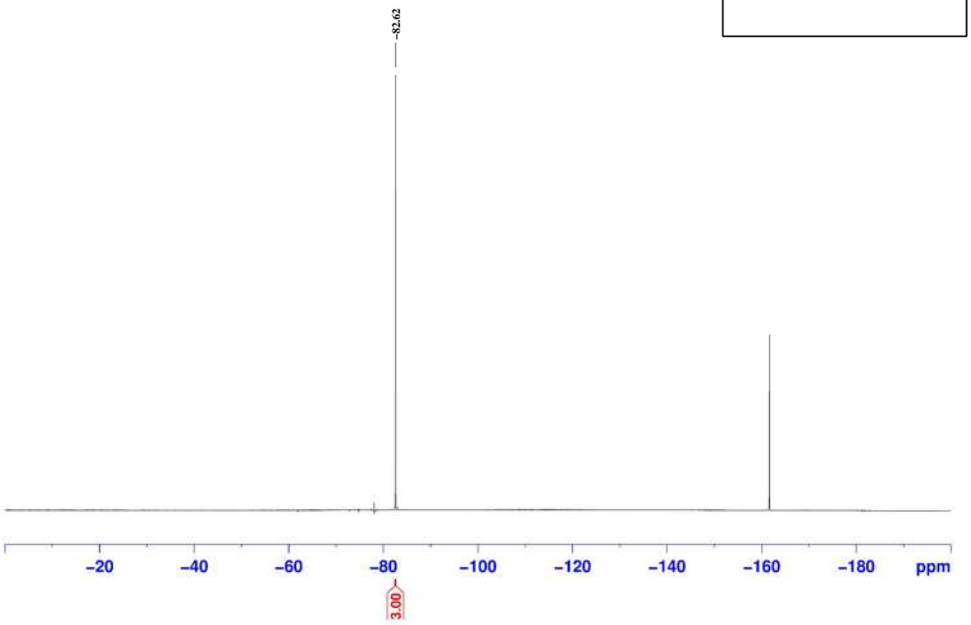


2–(2,4–Dimethoxyphenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol
125 MHz, CDCl3

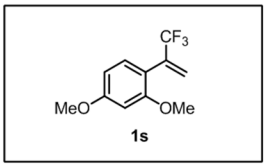


2–(2,4–Dimethoxyphenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol
471 MHz, CDCl3

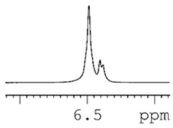


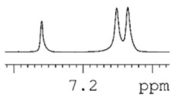


2,4–Dimethoxy–1–(3,3,3–trifluoroprop–1–en–2–yl)benzene
500 MHz, CDCl3

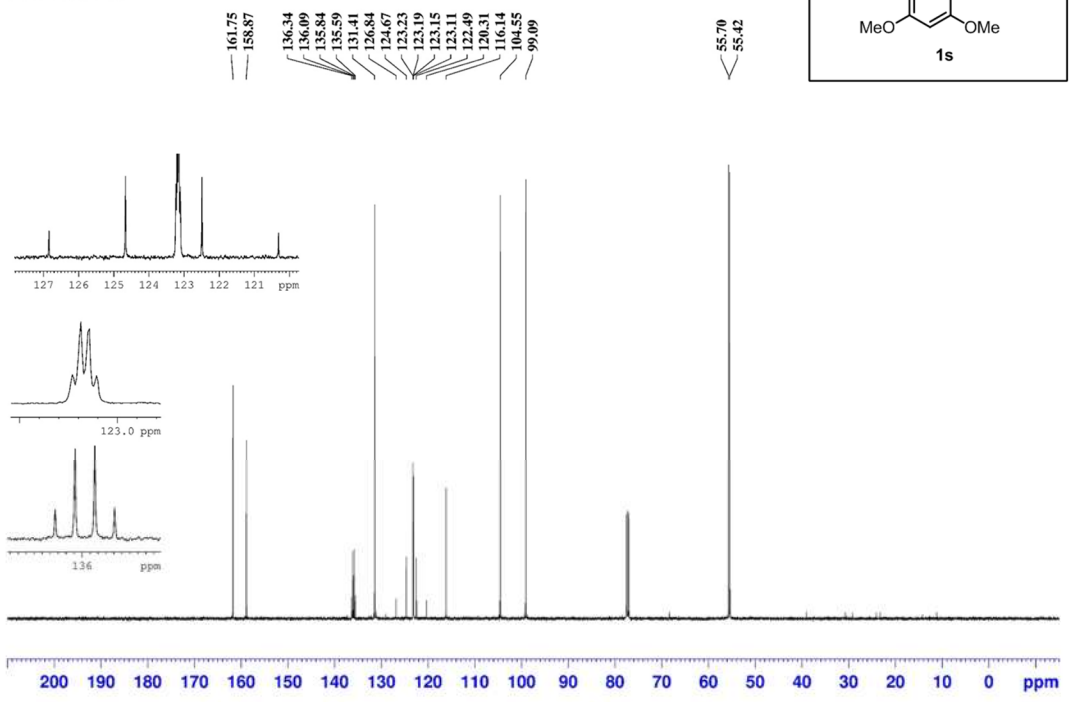


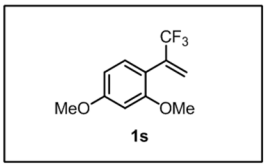
1s



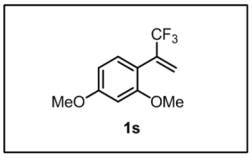


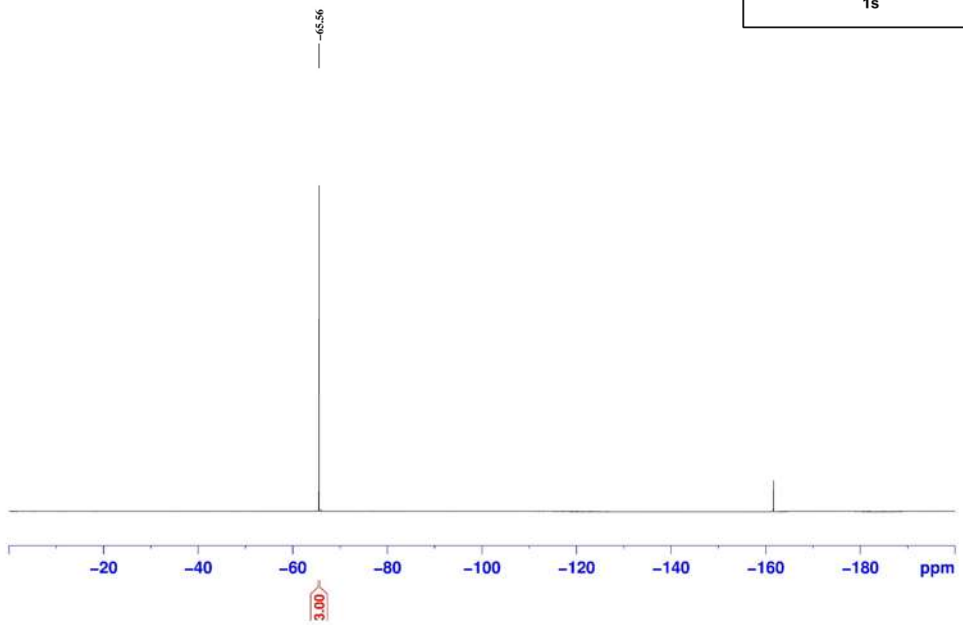
2,4–Dimethoxy–1–(3,3,3–trifluoroprop–1–en–2–yl)benzene
125 MHz, CDCl3



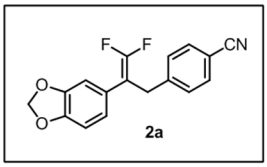


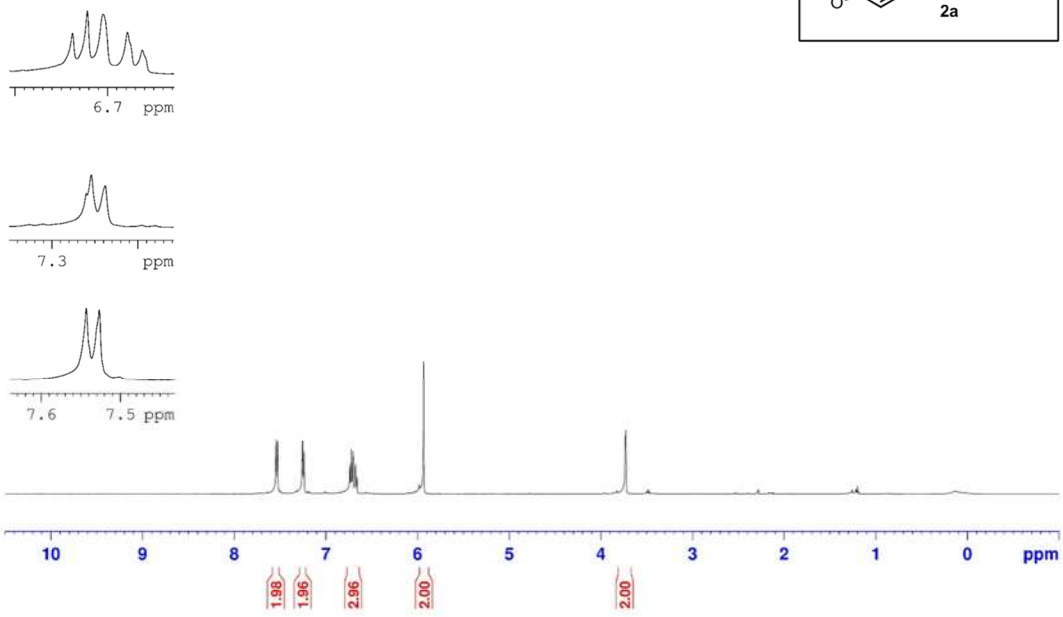
2,4–Dimethoxy–1–(3,3,3–trifluoroprop–1–en–2–yl)benzene
471 MHz, CDCl3



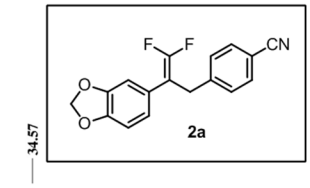


4–(2–(benzo[d][1,3]dioxol–5–yl)–3,3–difluoroallyl)benzonitrile
500 MHz, CDCl3





4–(2–(Benzo[d][1,3]dioxol–5–yl)–3,3–difluoroallyl)benzonitrile
125 MHz, CDCl3



156.93
154.64
152.33
148.09
147.30
144.26
144.24
144.23
132.60
129.33
126.44
122.10
119.04
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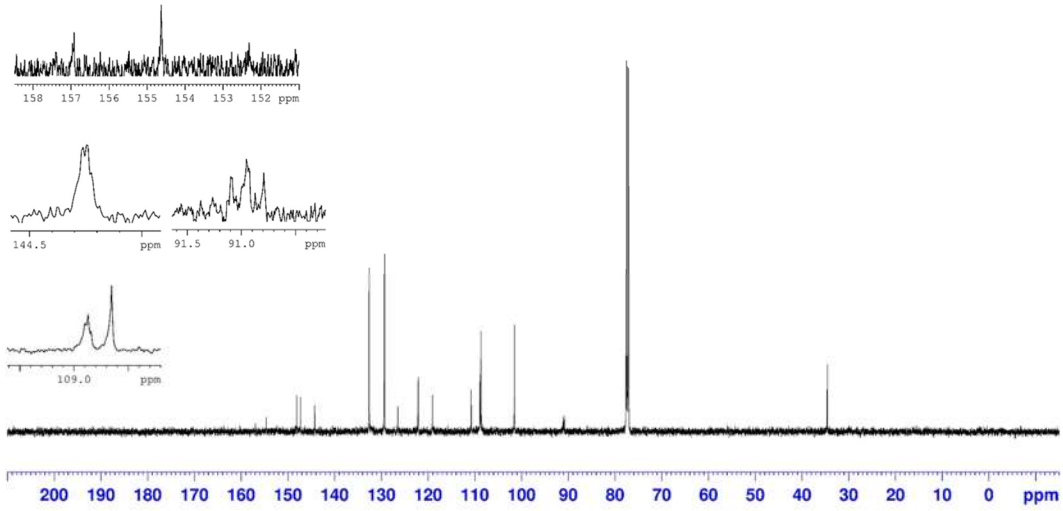
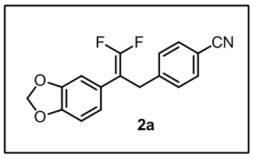
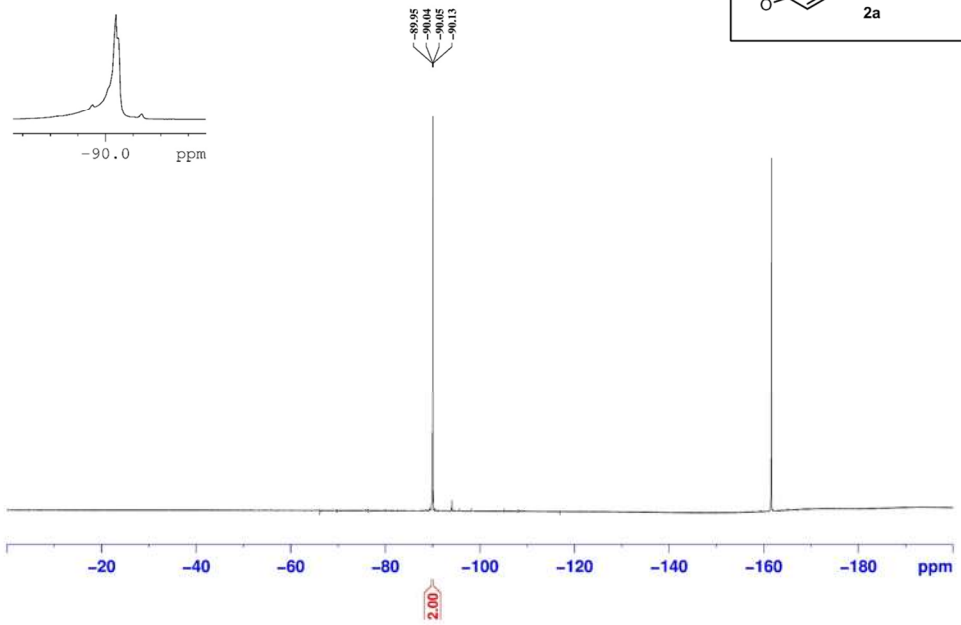
108.90
108.87
108.84
108.65
101.49
91.10
90.95
90.93
90.79
34.57

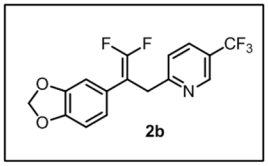


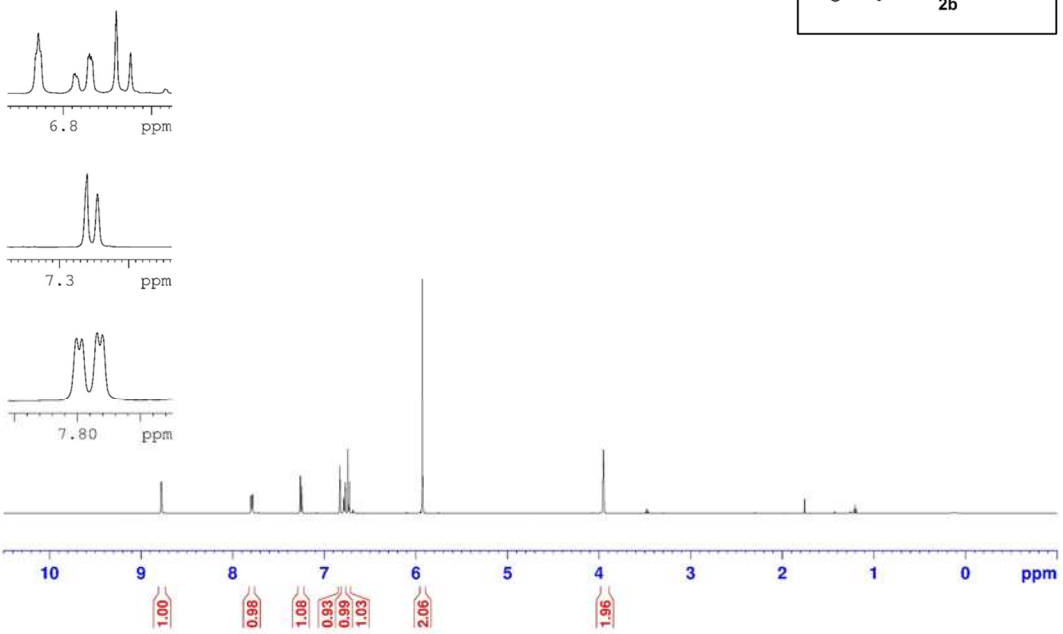
4–(2–(Benzo[d][1,3]dioxol–5–yl)–3,3–difluoroallyl)benzonitrile
471 MHz, CDCl3



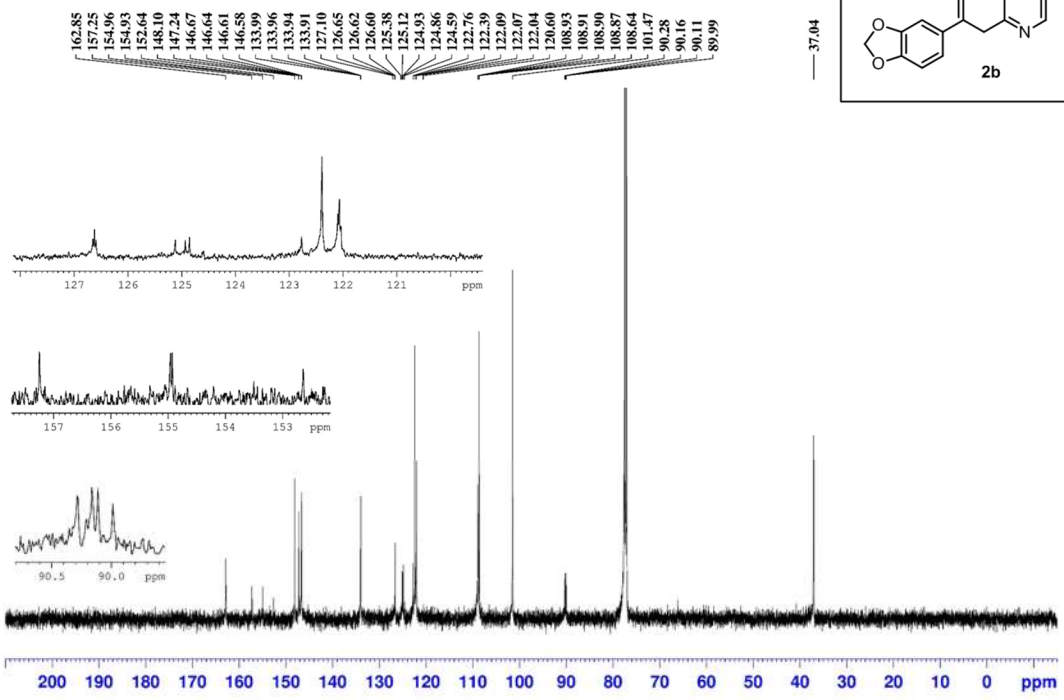


2–(2–(Benzo[d][1,3]dioxol–5–yl)–3,3–difluoroallyl)–5–(trifluoromethyl)pyridine
500 MHz, CDCl3

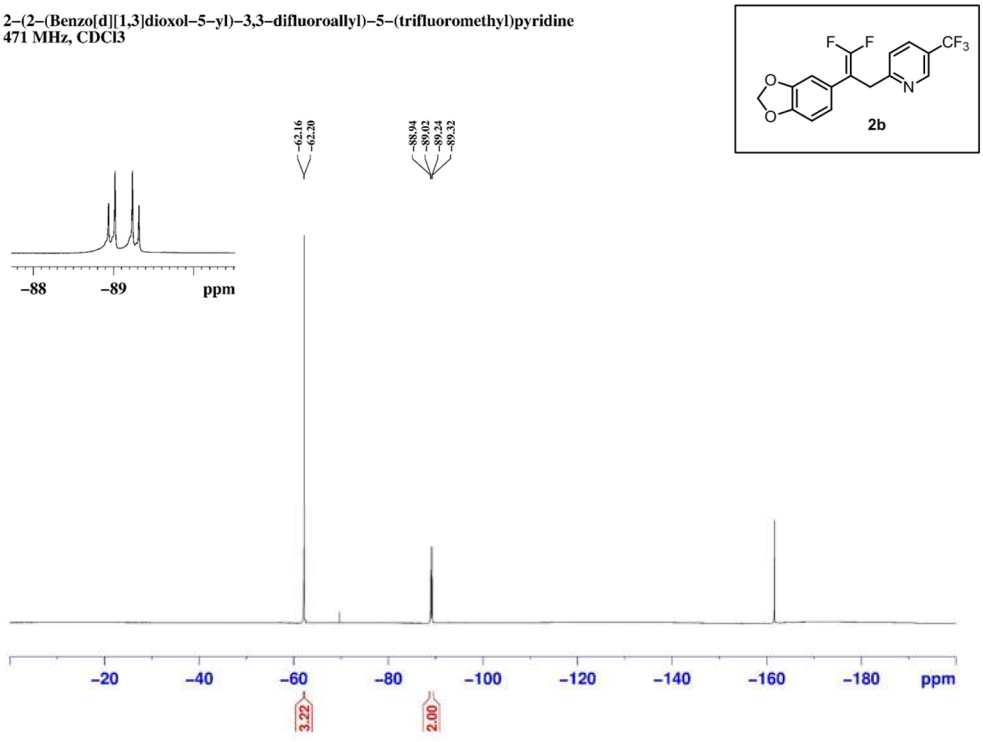




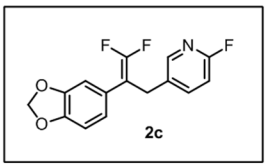
2–(2–(Benzo[d][1,3]dioxol–5–yl)–3,3–difluoroallyl)–5–(trifluoromethyl)pyridine
125 MHz, CDCl3

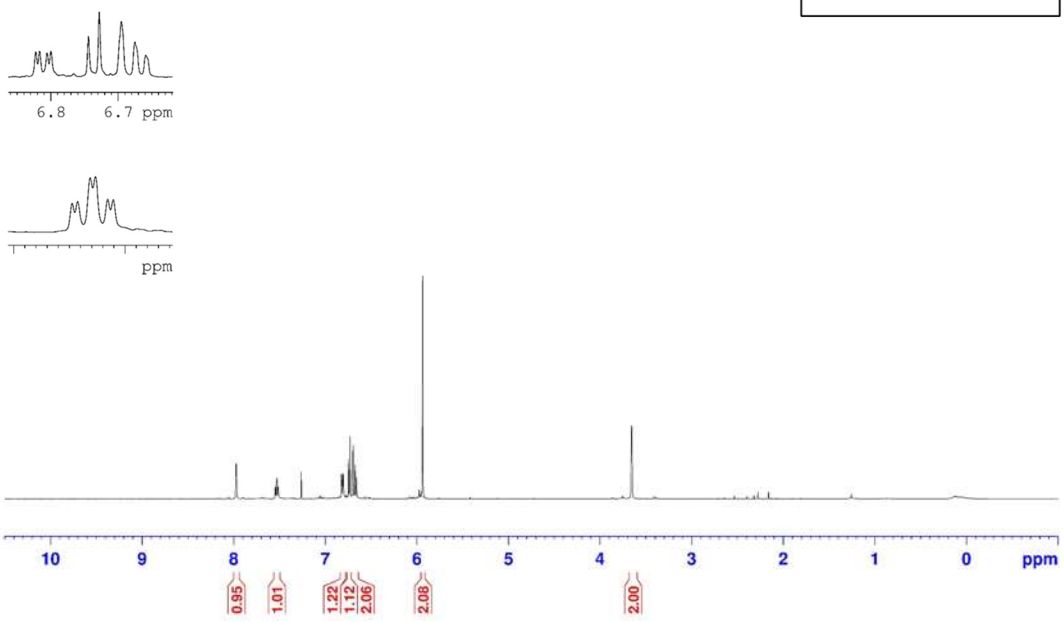


2–(2–(Benzo[d][1,3]dioxol–5–yl)–3,3–difluoroallyl)–5–(trifluoromethyl)pyridine
471 MHz, CDCl3

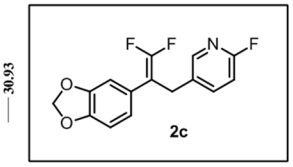


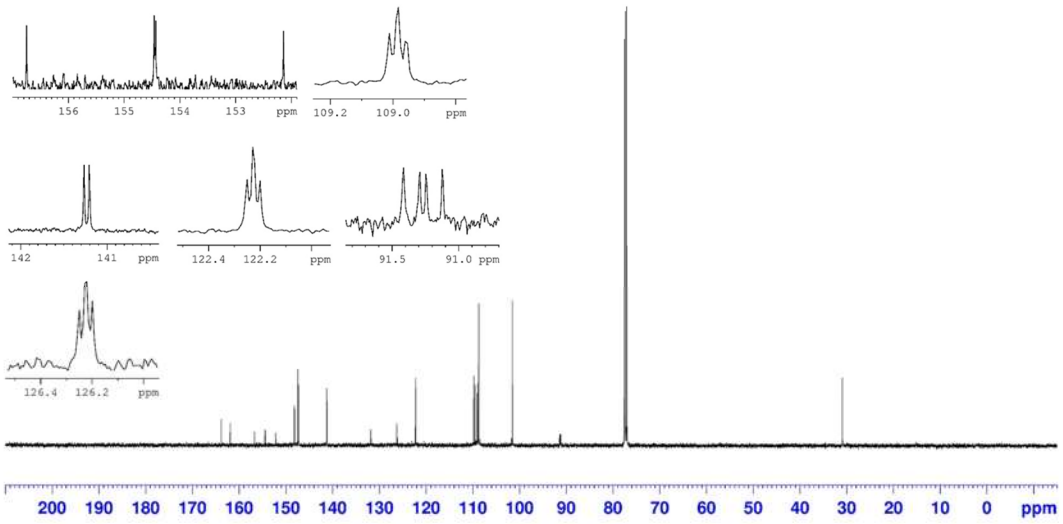
5–(2–(Benzo[d][1,3]dioxol–5–yl)–3,3–difluoroallyl)–2–fluoropyridine
500 MHz, CDCl3



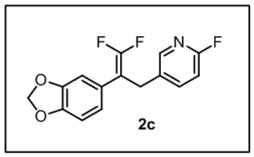


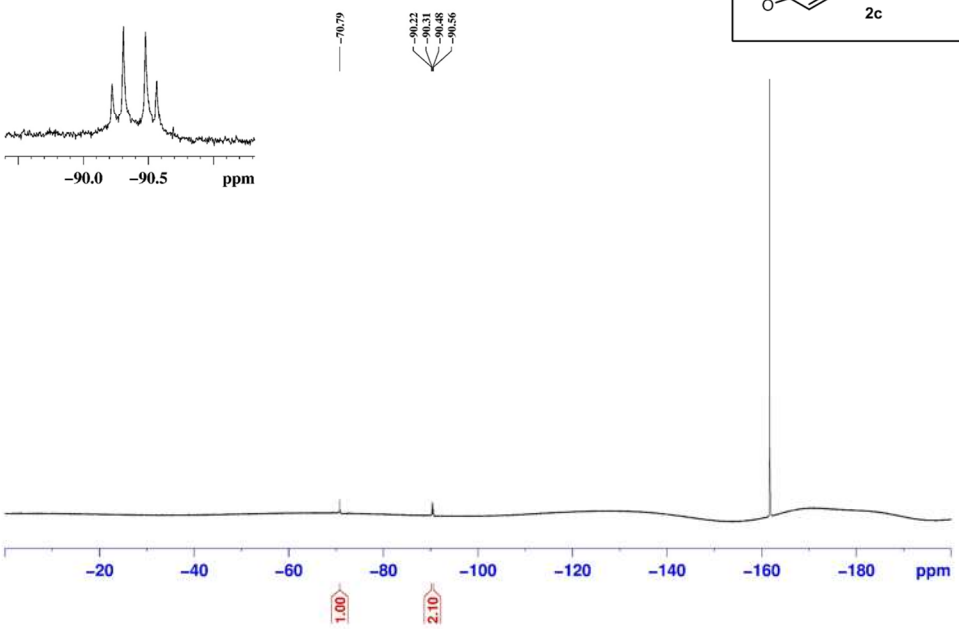
5–(2–(Benzo[d][1,3]dioxol–5–yl)–3,3–difluoroallyl)–2–fluoropyridine
125 MHz, CDCl3



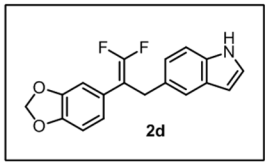


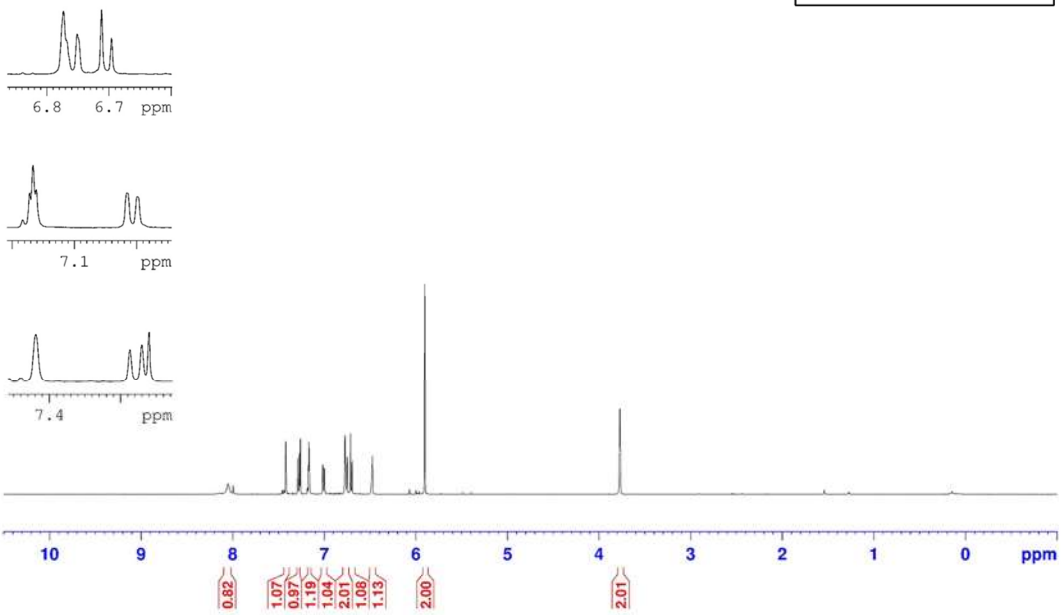
5−(2−(Benzo[d][1,3]dioxol−5−yl)−3,3−difluoroallyl)−2−fluoropyridine
471 MHz, CDCl3



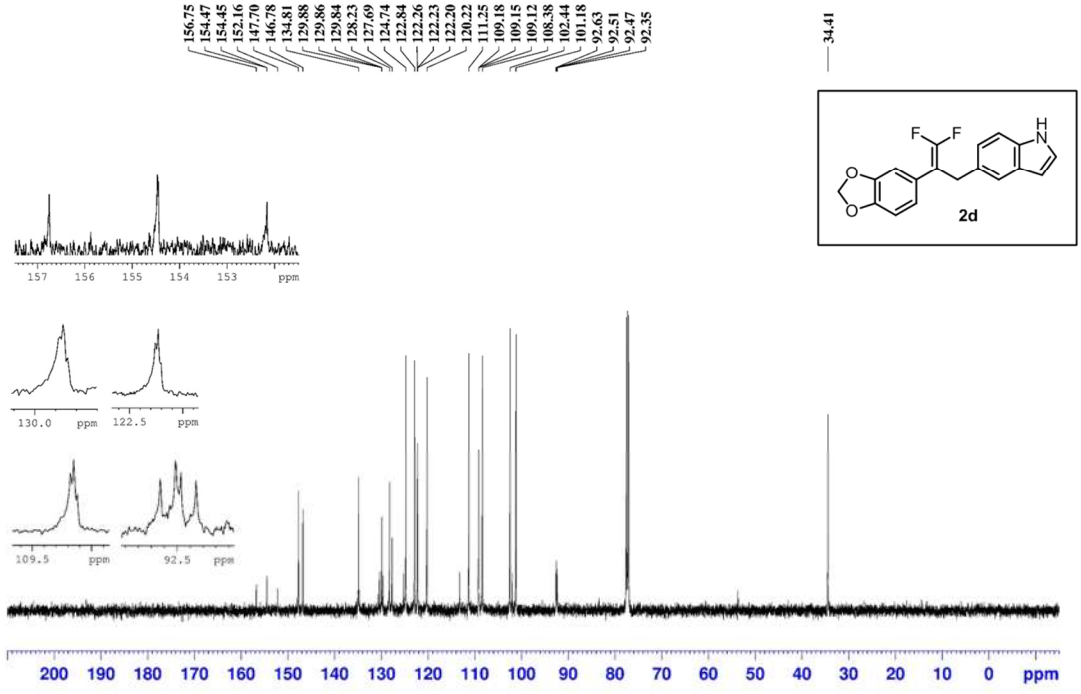


5−(2−(Benzo[d][1,3]dioxol−5−yl)−3,3−difluoroallyl)−1H−indole
500 MHz, CDCl3

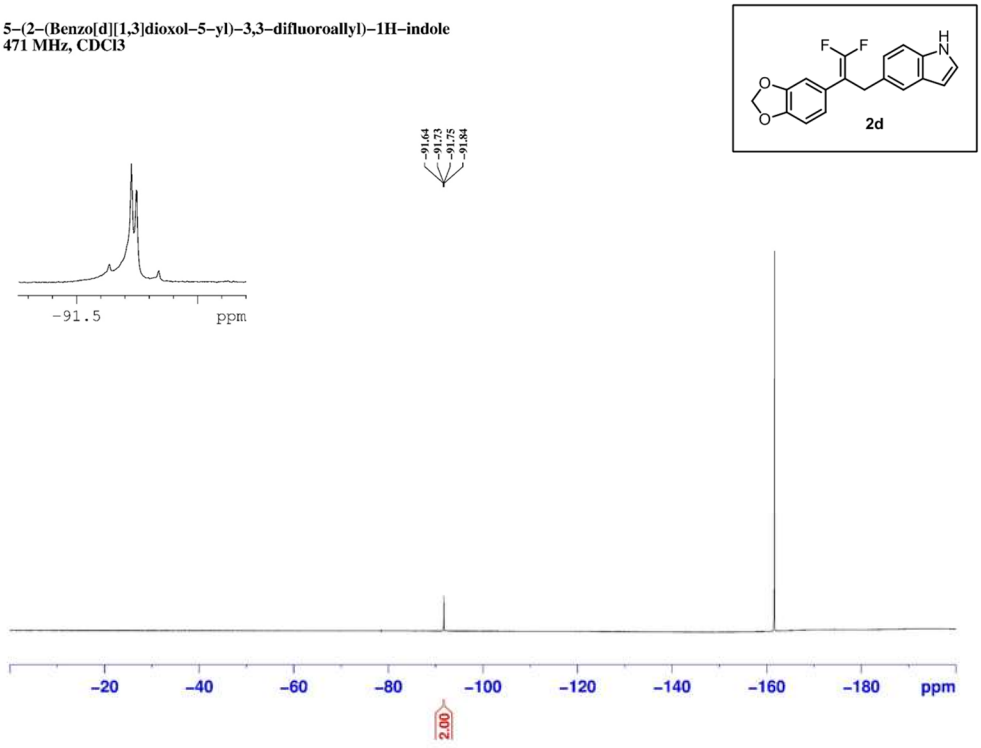




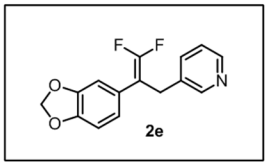
5–(2–(Benzo[d][1,3]dioxol–5–yl)–3,3–difluoroallyl)–1H–indole
125 MHz, CDCl3

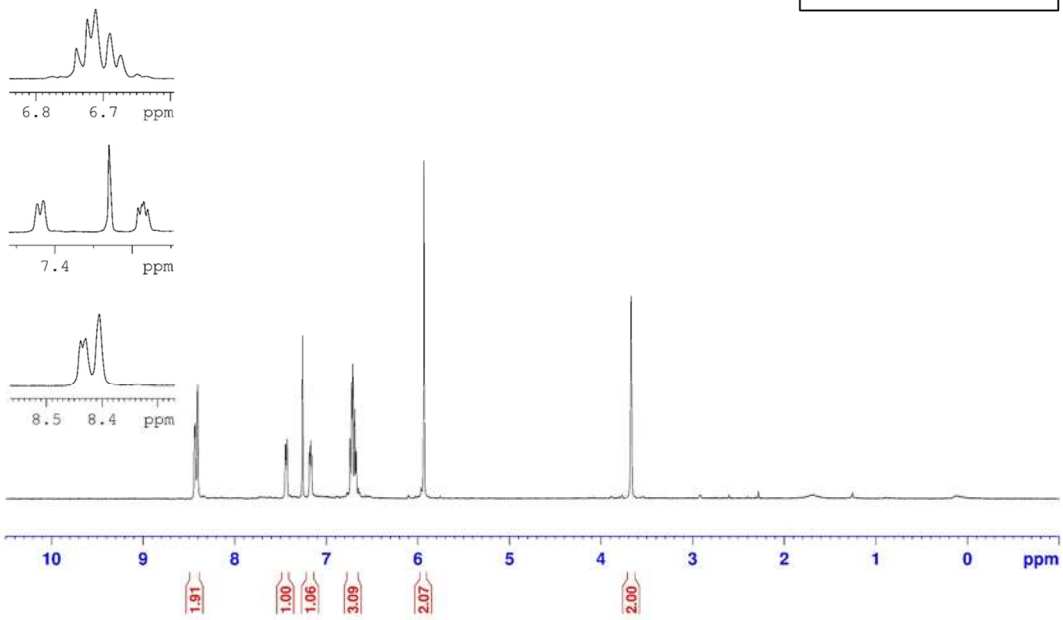


5–(2–(Benzo[d][1,3]dioxol–5–yl)–3,3–difluoroallyl)–1H–indole
471 MHz, CDCl3

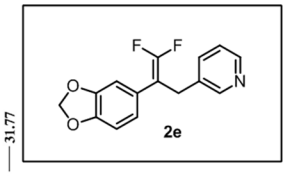


3–(2–(Benzo[d][1,3]dioxol–5–yl)–3,3–difluoroallyl)pyridine
500 MHz, CDCl3

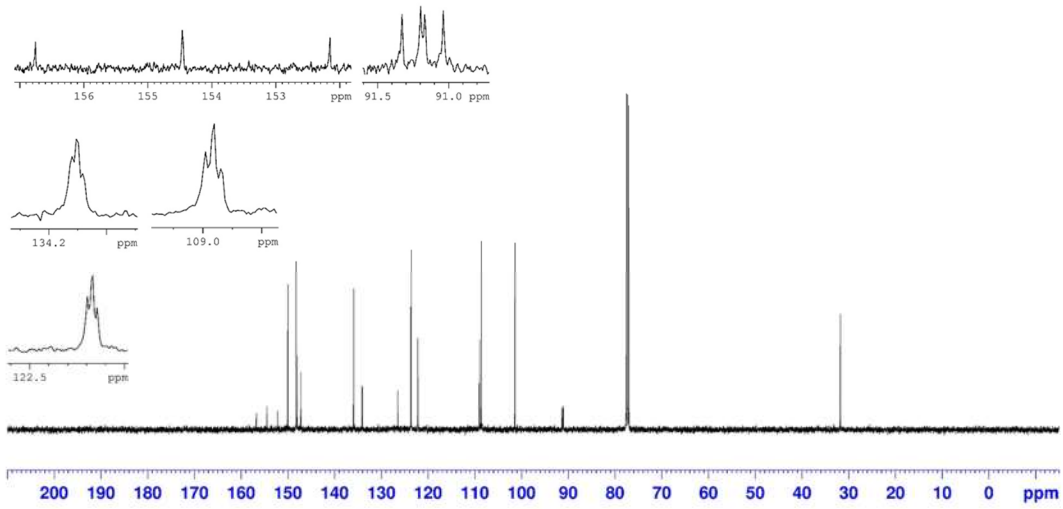




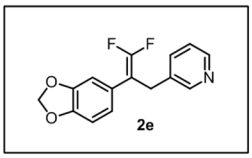
3–(2–(Benzo[d][1,3]dioxol–5–yl)–3,3–difluoroallyl)pyridine
125 MHz, CDCl3

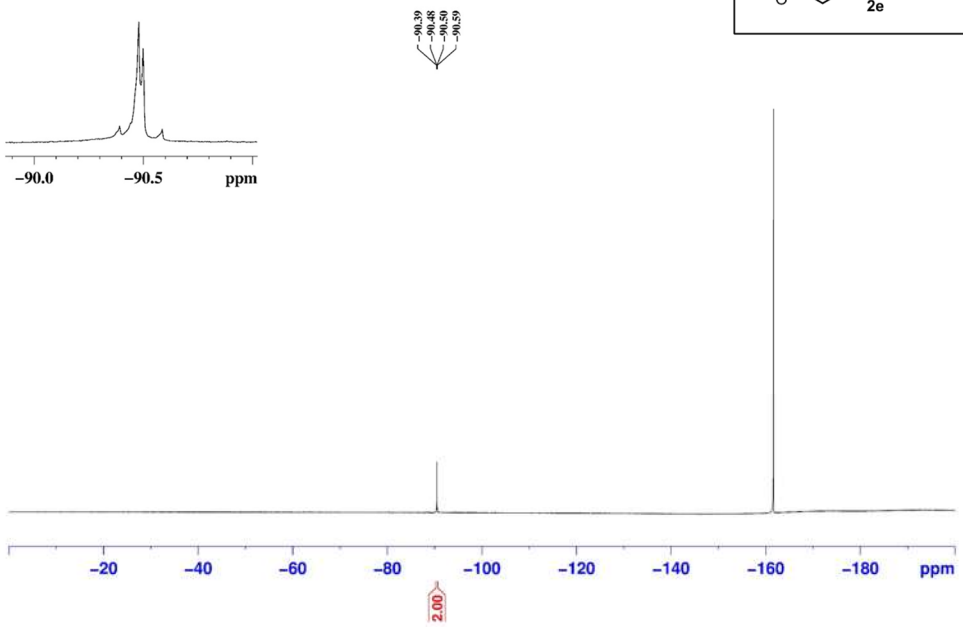


156.76
154.46
154.45
152.15
150.01
148.21
148.03
147.23
135.93
134.12
134.10
134.08
126.47
123.63
122.20
122.17
122.15
108.99
108.96
108.94
108.60
101.41
91.33
91.20
91.17
91.04
31.77

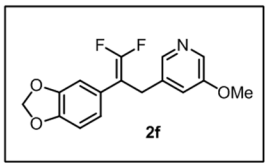


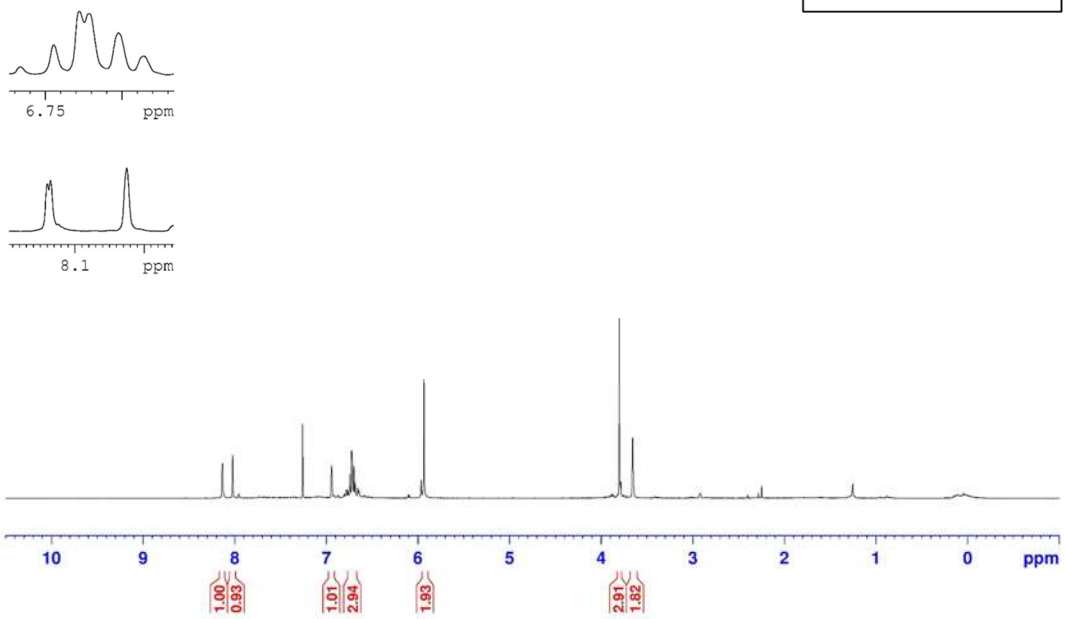
3–(2–(Benzo[d][1,3]dioxol–5–yl)–3,3–difluoroallyl)pyridine
471 MHz, CDCl3



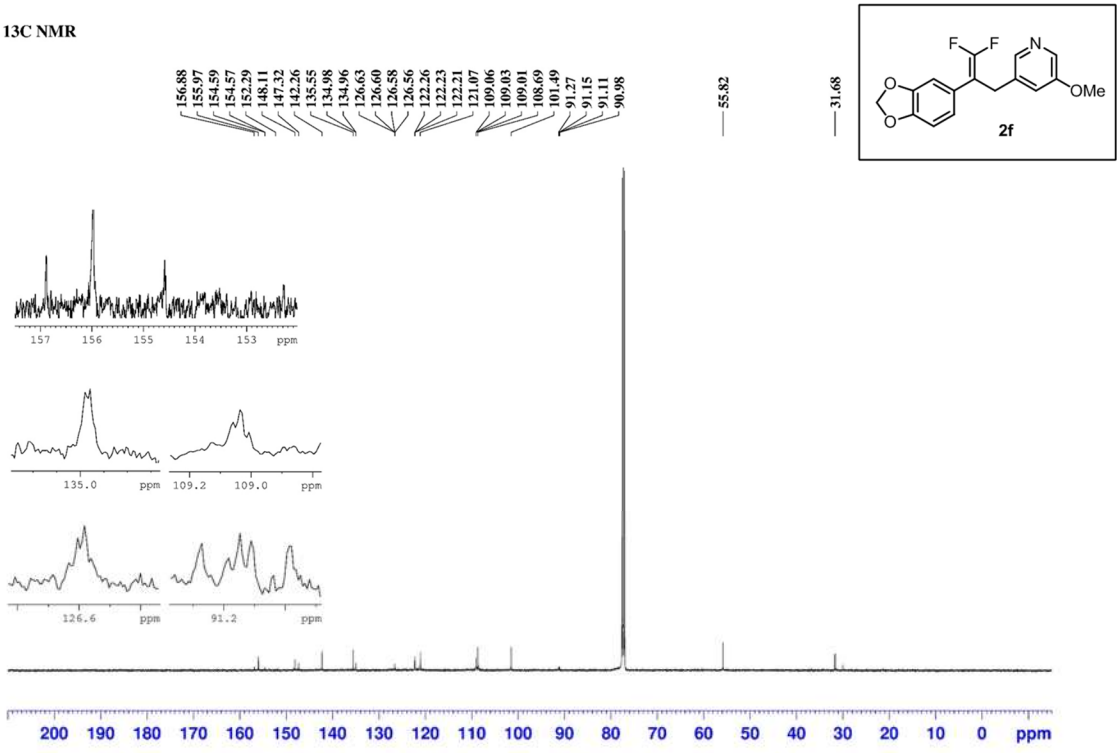


3–(2–(Benzo[d][1,3]dioxol–5–yl)–3,3–difluoroallyl)–5–methoxypyridine
500 MHz, CDCl3

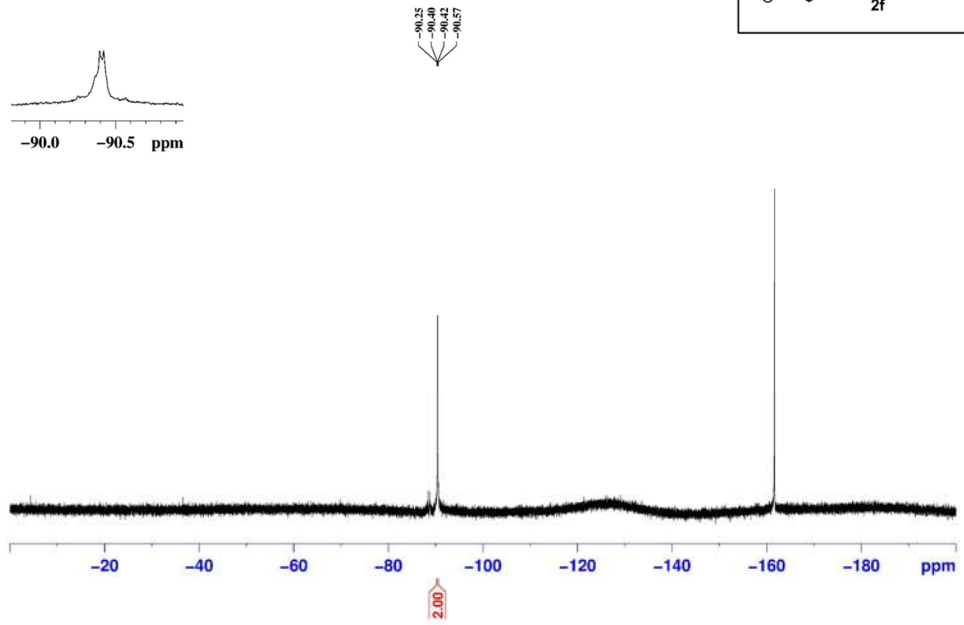




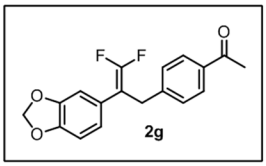
13C NMR

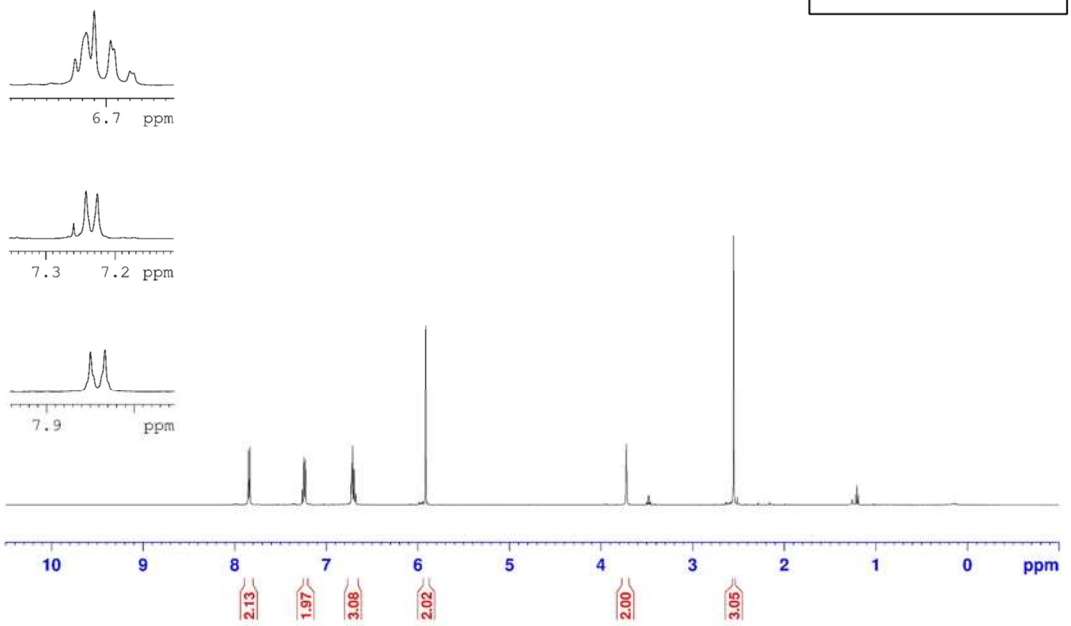


3–(2–(Benzo[d][1,3]dioxol–5–yl)–3,3–difluoroallyl)–5–methoxypyridine
282 MHz, CDCl3

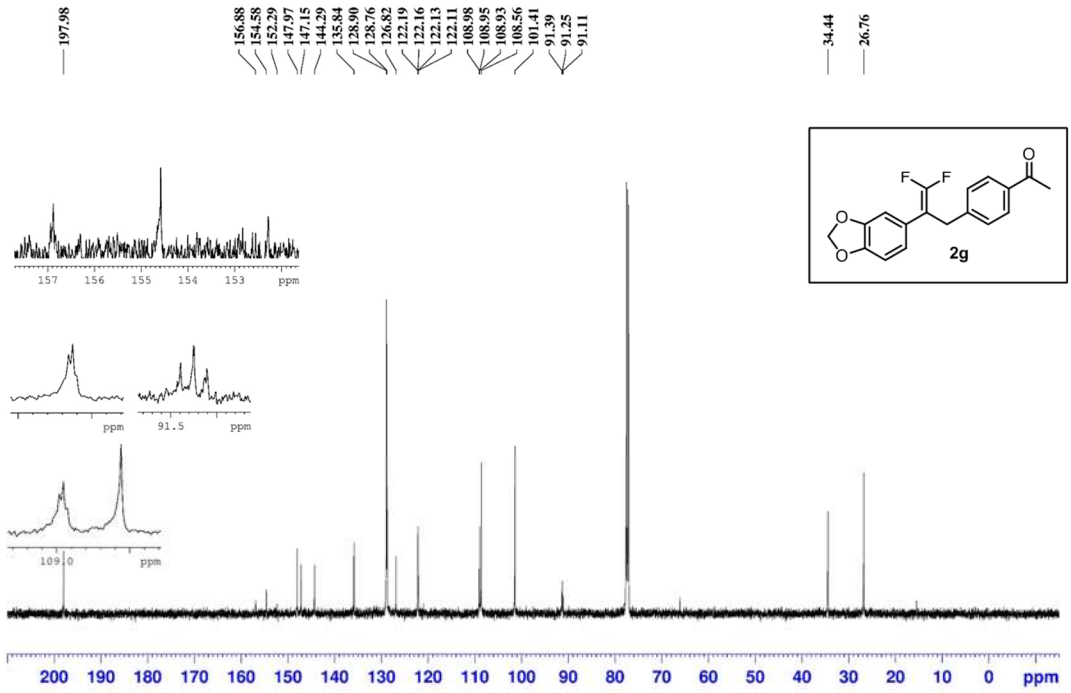


1–(4–(2–(Benzo[d][1,3]dioxol–5–yl)–3,3–difluoroallyl)phenyl)ethanone
500 MHz, CDCl3

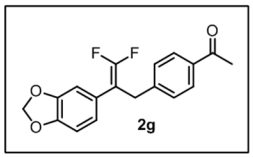


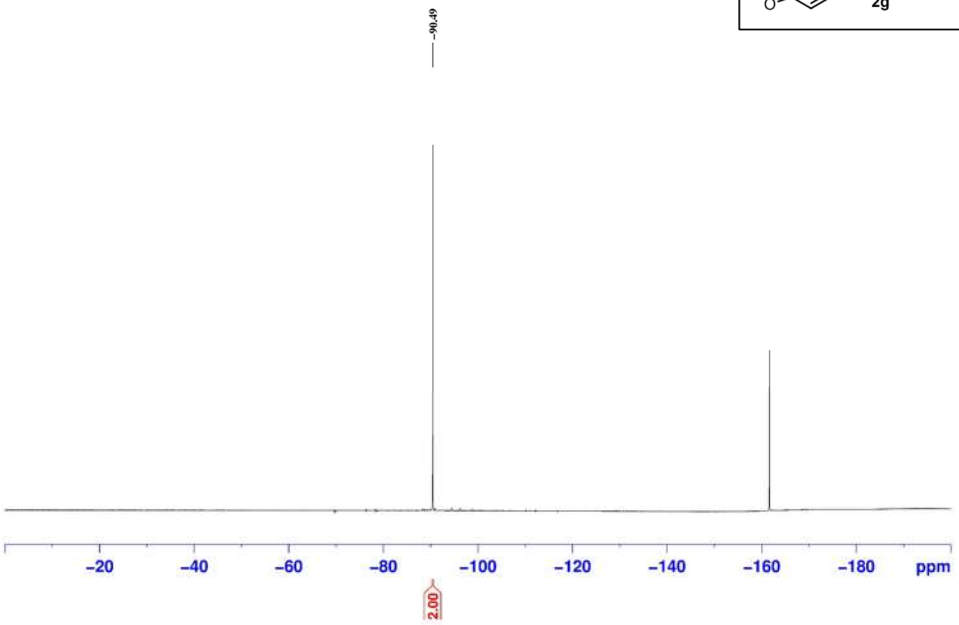


1–(4–(2–(Benzo[d][1,3]dioxol–5–yl)–3,3–difluoroallyl)phenyl)ethanone
125 MHz, CDCl3

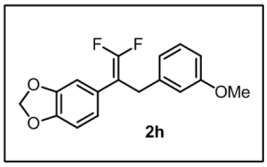


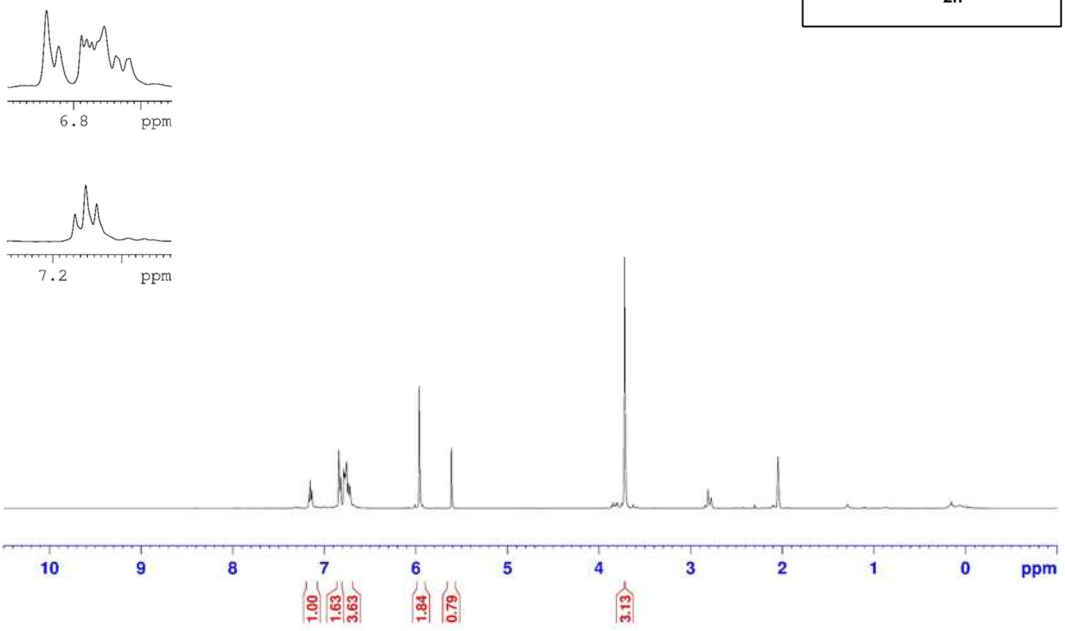
1–(4–(2–(Benzo[d][1,3]dioxol–5–yl)–3,3–difluoroallyl)phenyl)ethanone
471 MHz, CDCl3



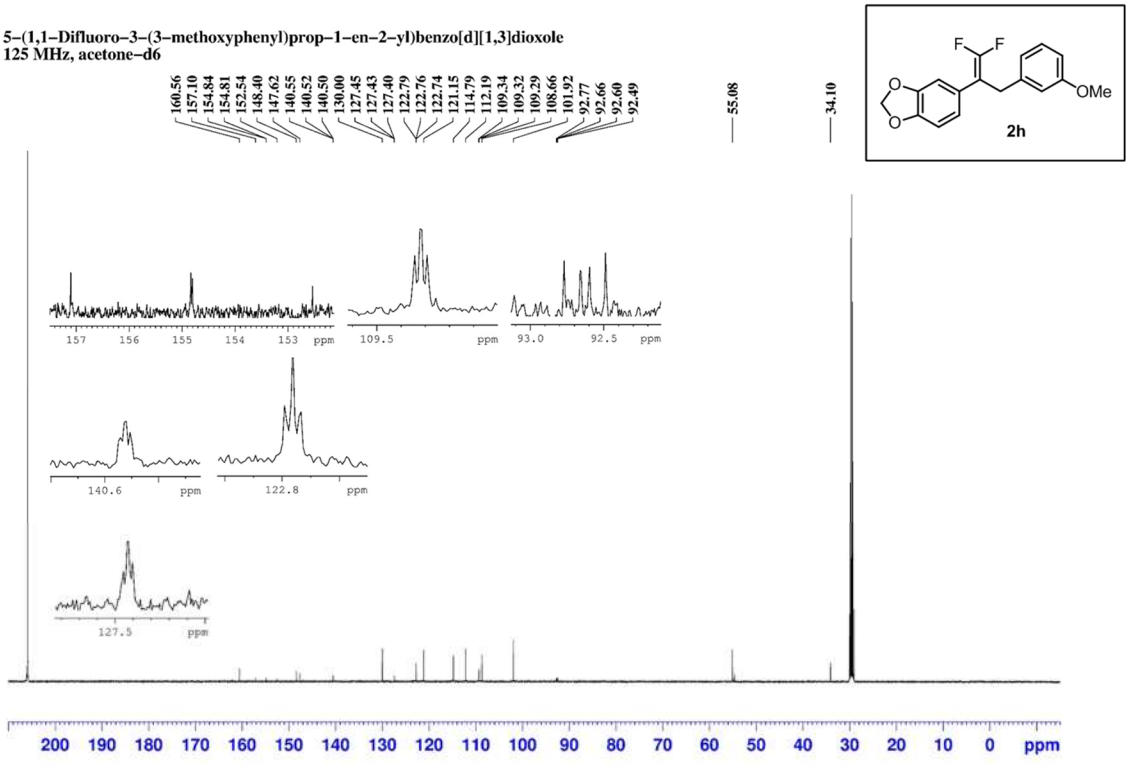


5–(1,1–Difluoro–3–(3–methoxyphenyl)prop–1–en–2–yl)benzo[d][1,3]dioxole
500 MHz, acetone–d6

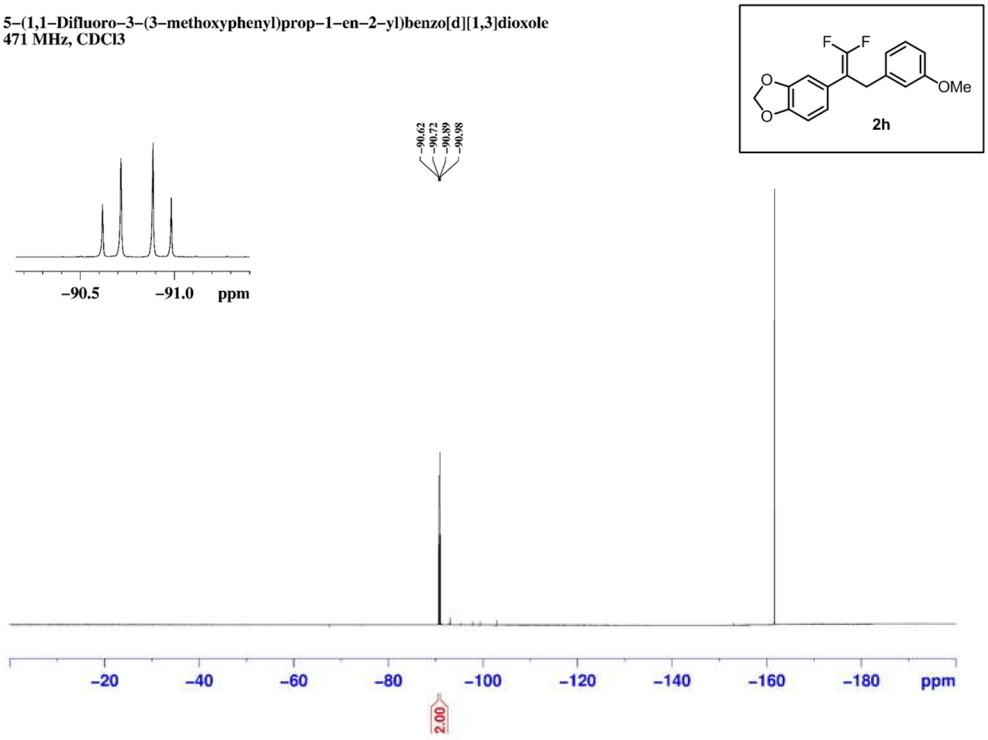




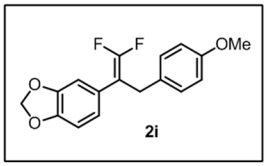
5–(1,1–Difluoro–3–(3–methoxyphenyl)prop–1–en–2–yl)benzo[d][1,3]dioxole
125 MHz, acetone–d6

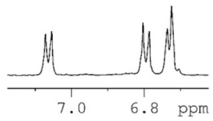


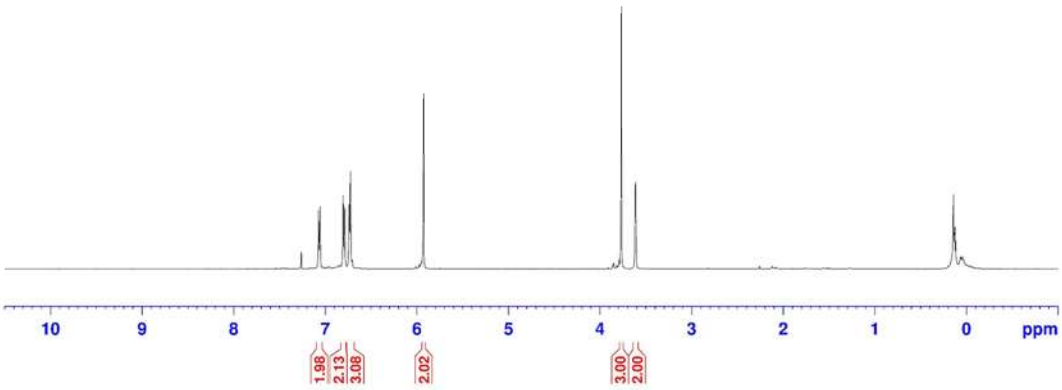
5–(1,1–Difluoro–3–(3–methoxyphenyl)prop–1–en–2–yl)benzo[d][1,3]dioxole
471 MHz, CDCl3



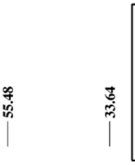
5–(1,1–Difluoro–3–(4–methoxyphenyl)prop–1–en–2–yl)benzo[d][1,3]dioxole
500 MHz, CDCl3

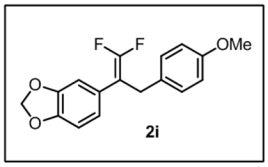


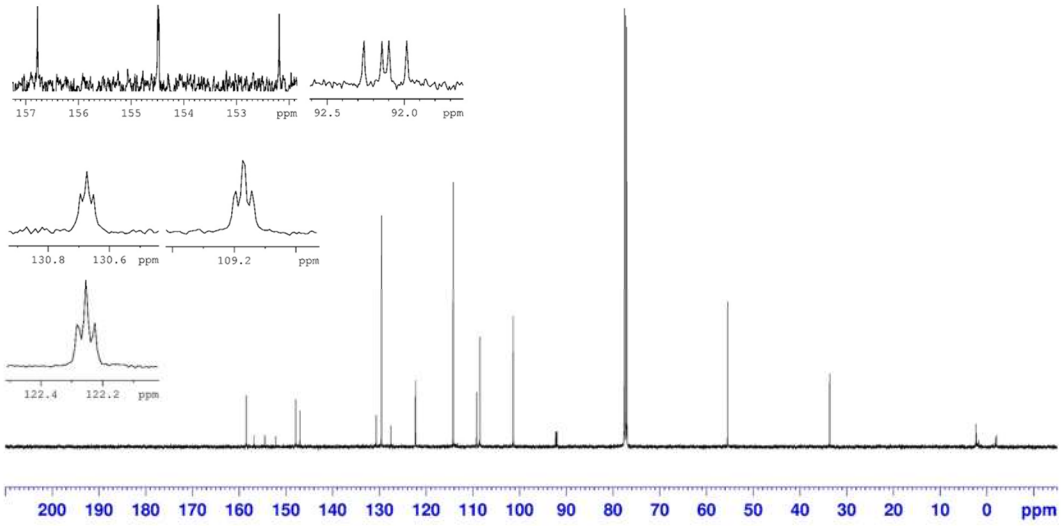




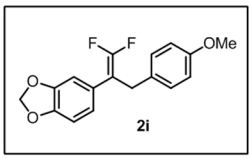
5–(1,1–Difluoro–3–(4–methoxyphenyl)prop–1–en–2–yl)benzo[d][1,3]dioxole
125 MHz, CDCl3

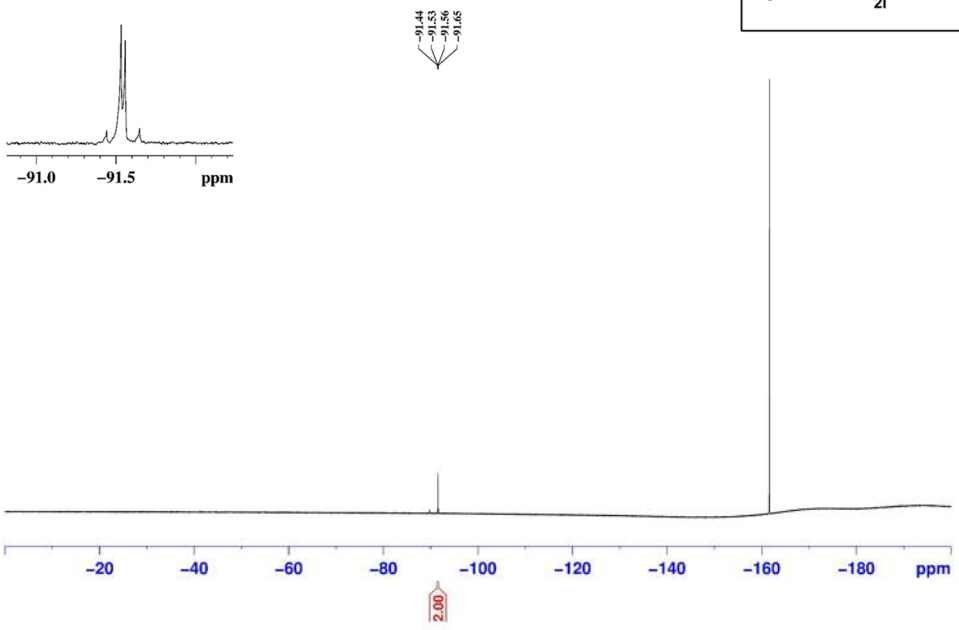




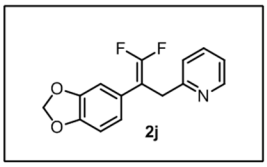


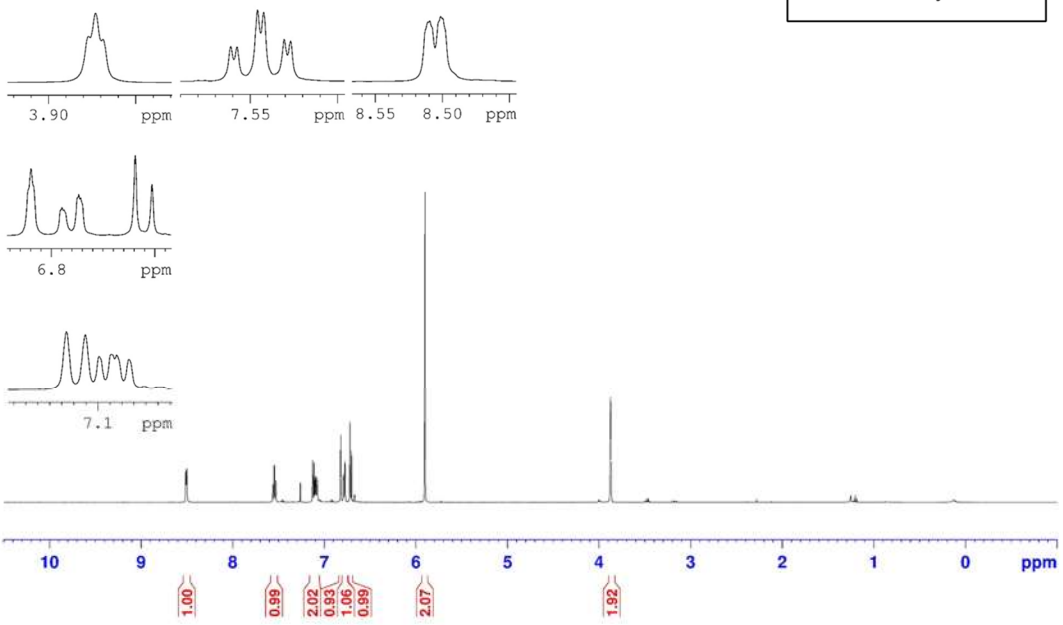
5–(1,1–Difluoro–3–(4–methoxyphenyl)prop–1–en–2–yl)benzo[d][1,3]dioxole
471 MHz, CDCl3



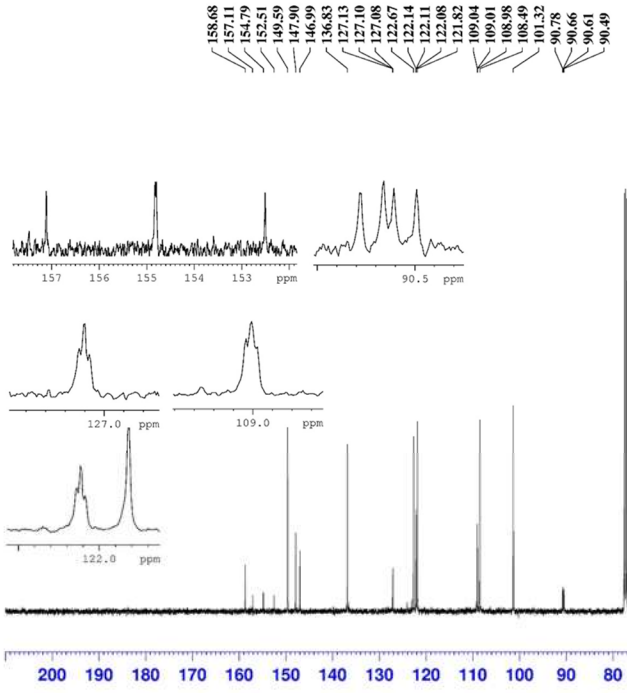


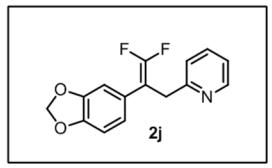
2–(2–(Benzo[d][1,3]dioxol–5–yl)–3,3–difluoroallyl)pyridine
500 MHz, CDCl3



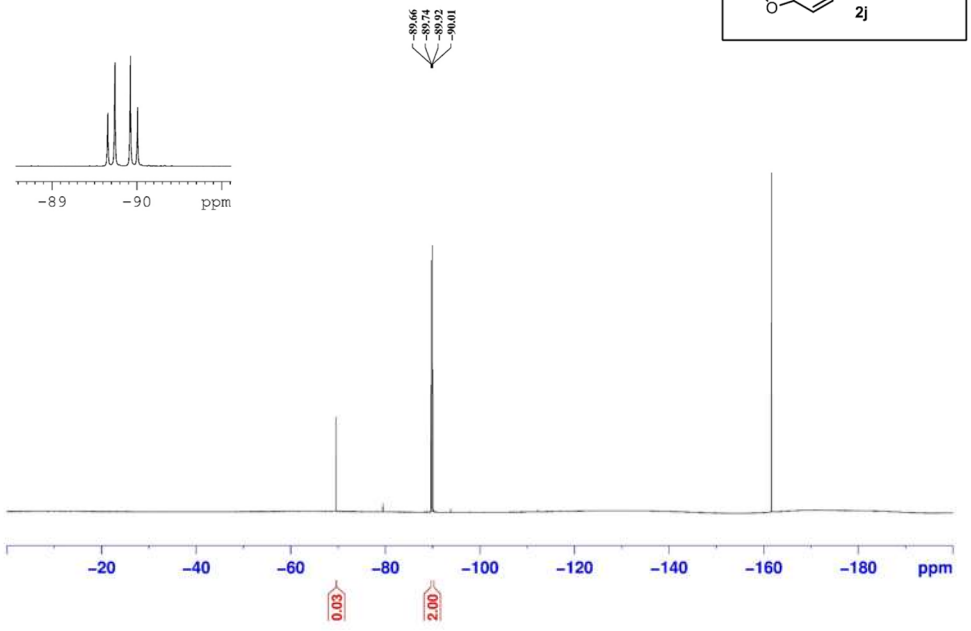


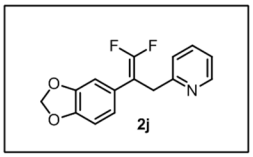
2–(2–(Benzo[d][1,3]dioxol–5–yl)–3,3–difluoroallyl)pyridine
125 MHz, CDCl3



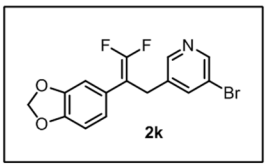


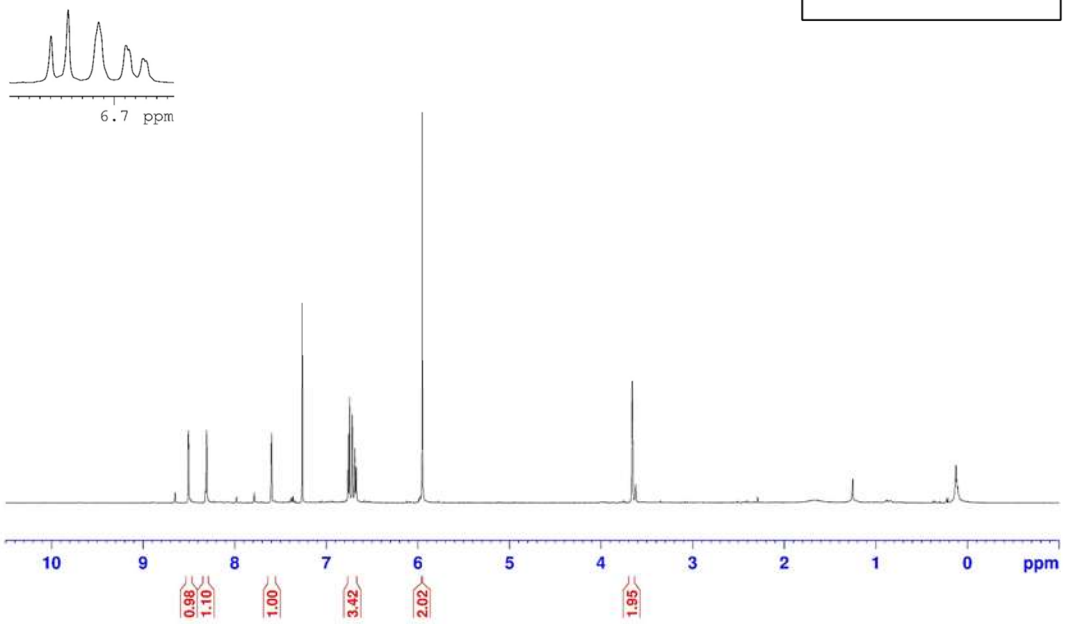
2–(2–(Benzo[d][1,3]dioxol–5–yl)–3,3–difluoroallyl)pyridine
471 MHz, CDCl3





3–(2–(Benzo[d][1,3]dioxol–5–yl)–3,3–difluoroallyl)–5–bromopyridine
500 MHz, CDCl3





3–(2–(Benzo[d][1,3]dioxol–5–yl)–3,3–difluoroallyl)–5–bromopyridine
125 MHz, CDCl3

156.90
154.60
154.58
152.29
149.28
148.23
147.95
147.48
138.75
136.08
126.03
122.20
122.17
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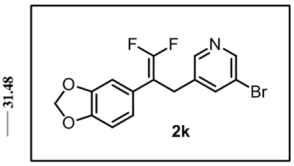
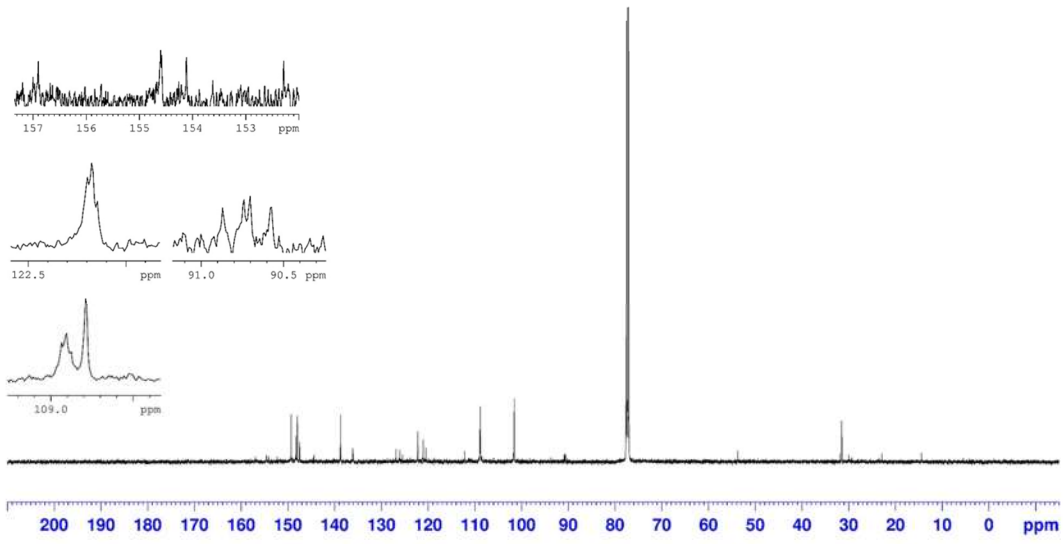
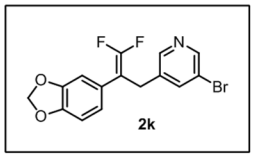
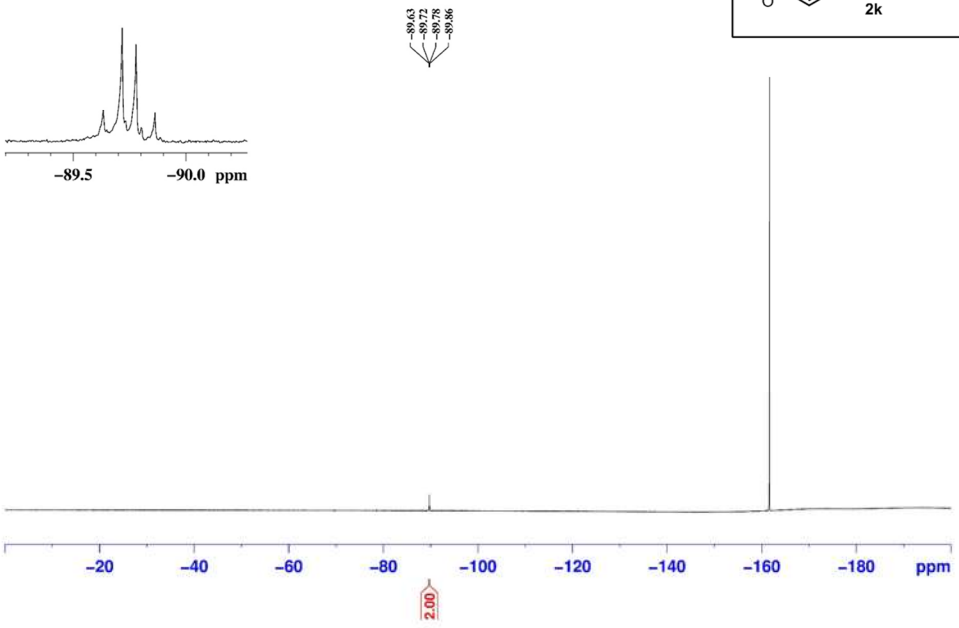




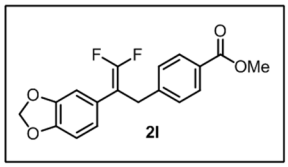
3–(2–(Benzo[d][1,3]dioxol–5–yl)–3,3–difluoroallyl)–5–bromopyridine
471 MHz, CDCl3



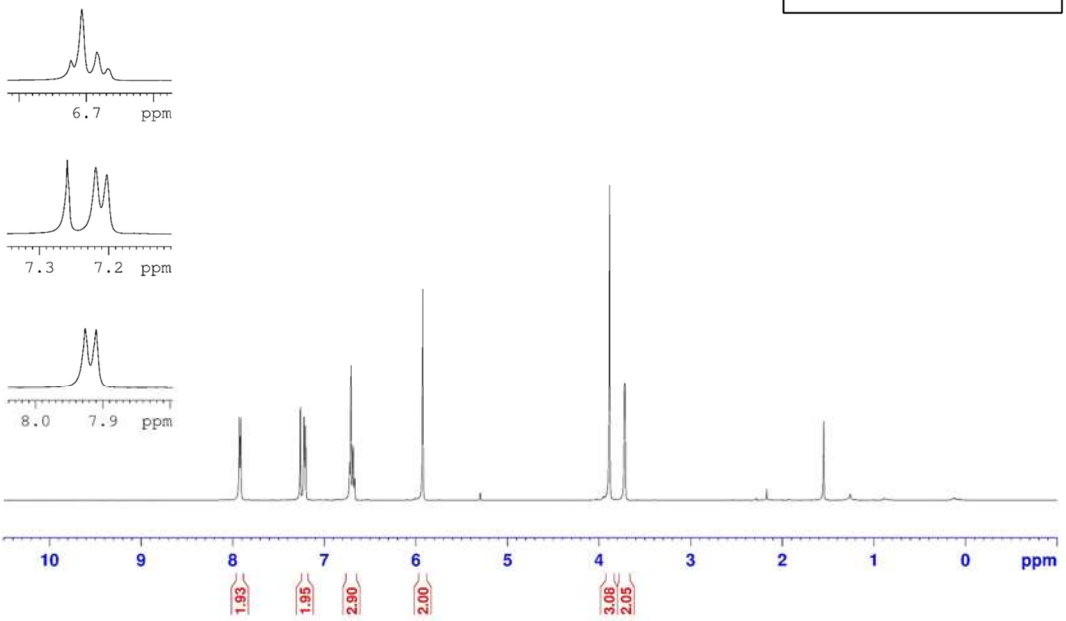
2k



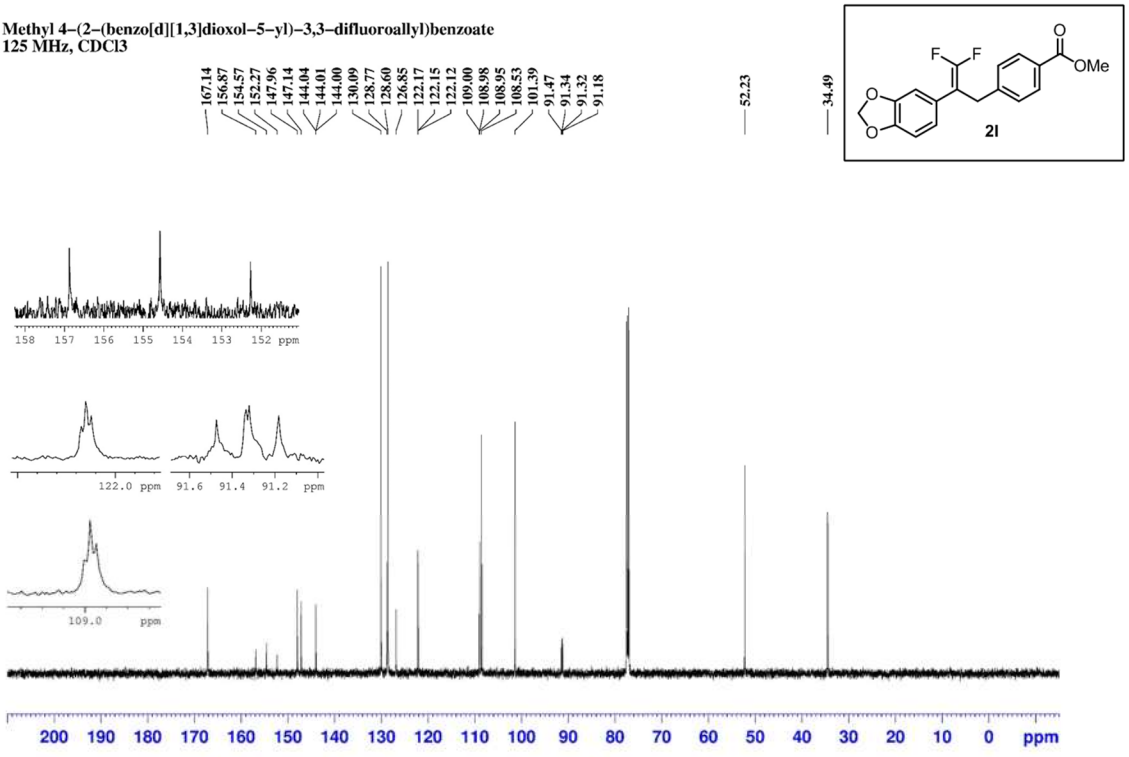
Methyl 4–(2–(benzo[d][1,3]dioxol–5–yl)–3,3–difluoroallyl)benzoate
500 MHz, CDCl3



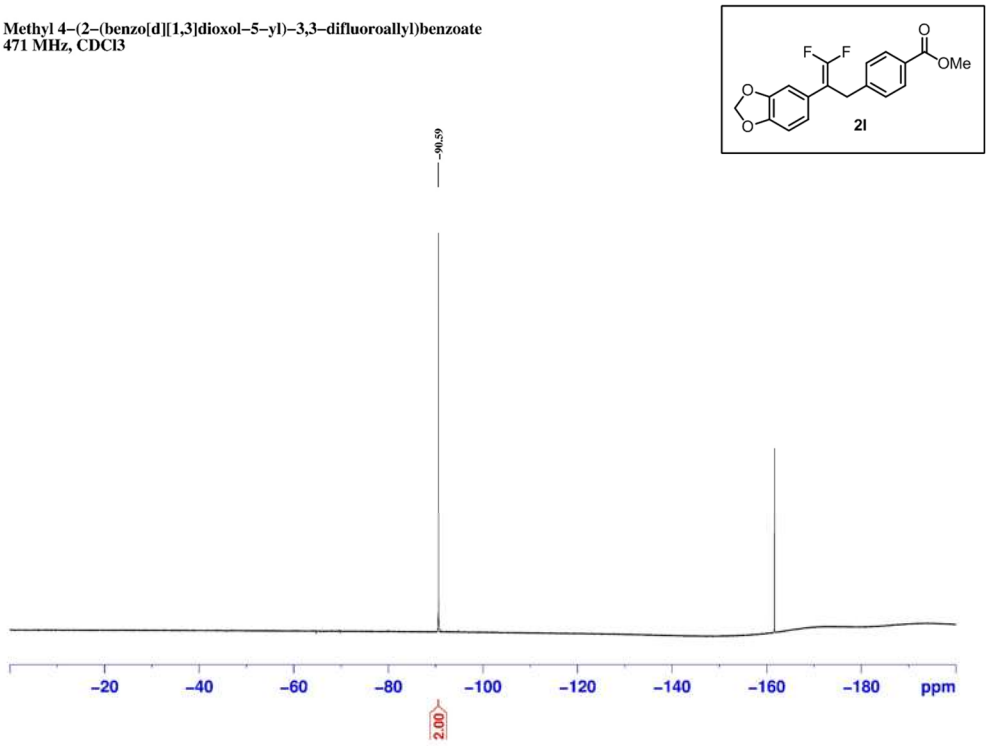
2l



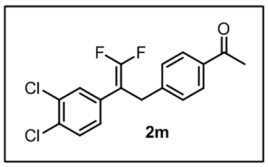
Methyl 4–(2–(benzo[d][1,3]dioxol–5–yl)–3,3–difluoroallyl)benzoate
125 MHz, CDCl3

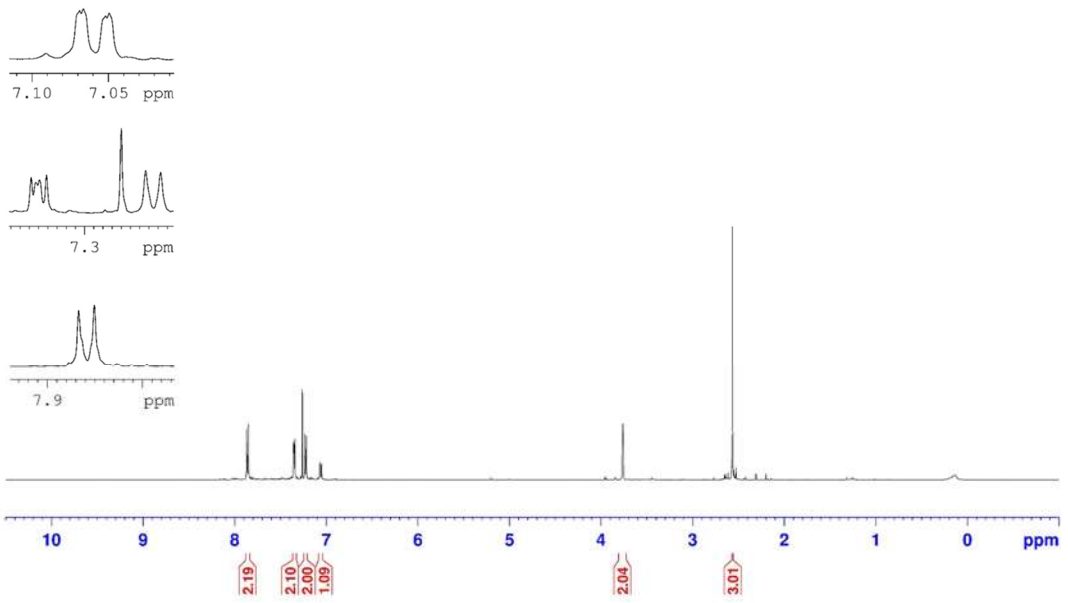


Methyl 4–(2–(benzo[d][1,3]dioxol–5–yl)–3,3–difluoroallyl)benzoate
471 MHz, CDCl3

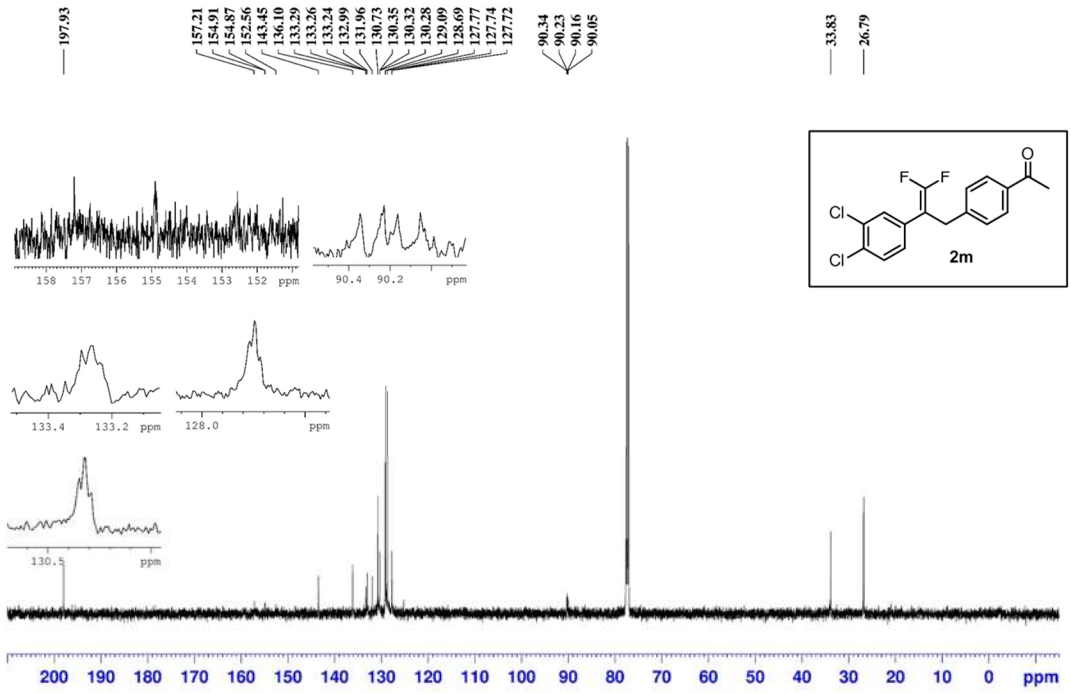


1–(4–(2–(3,4–Dichlorophenyl)–3,3–difluoroallyl)phenyl)ethanone
500 MHz, CDCl3

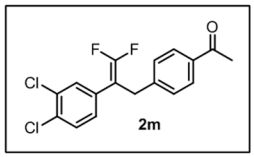


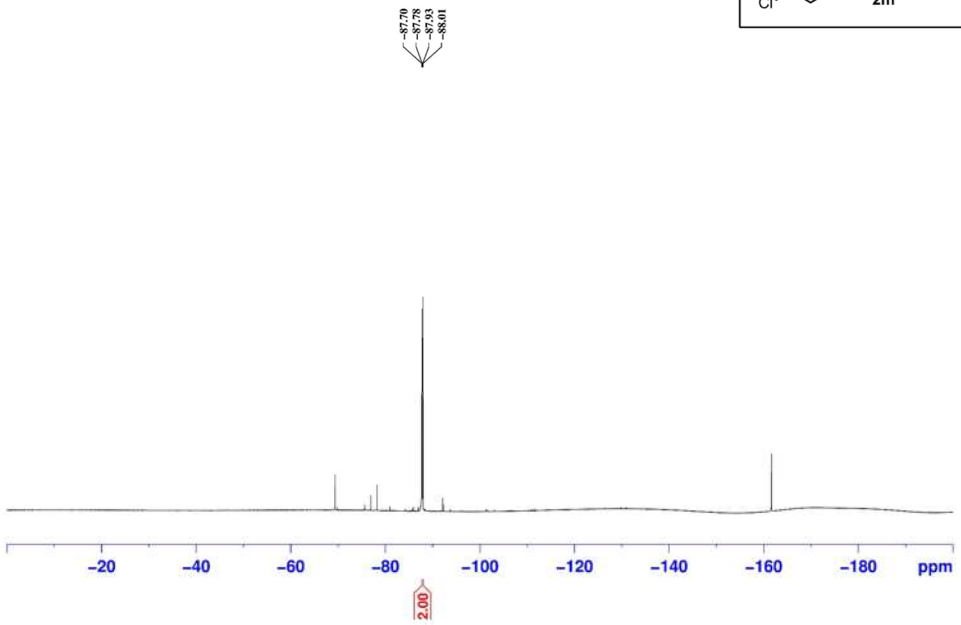


1–(4–(2–(3,4–Dichlorophenyl)–3,3–difluoroallyl)phenyl)ethanone
125 MHz, CDCl3

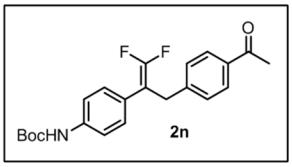


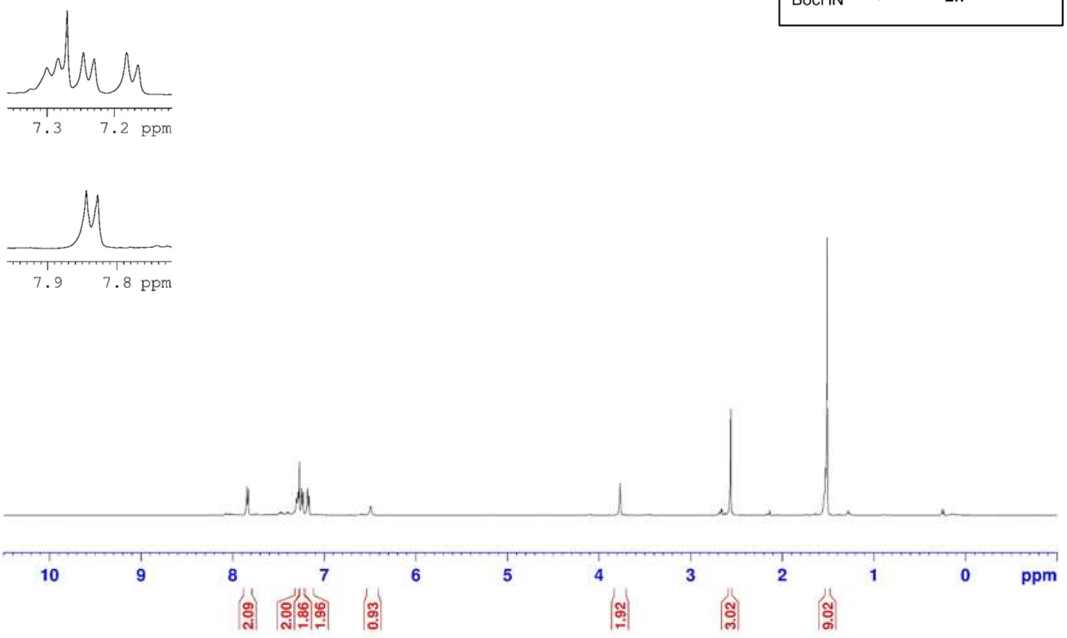
5–(1,1–Difluoro–3–(3–methoxyphenyl)prop–1–en–2–yl)benzo[d][1,3]dioxole
471 MHz, CDCl3



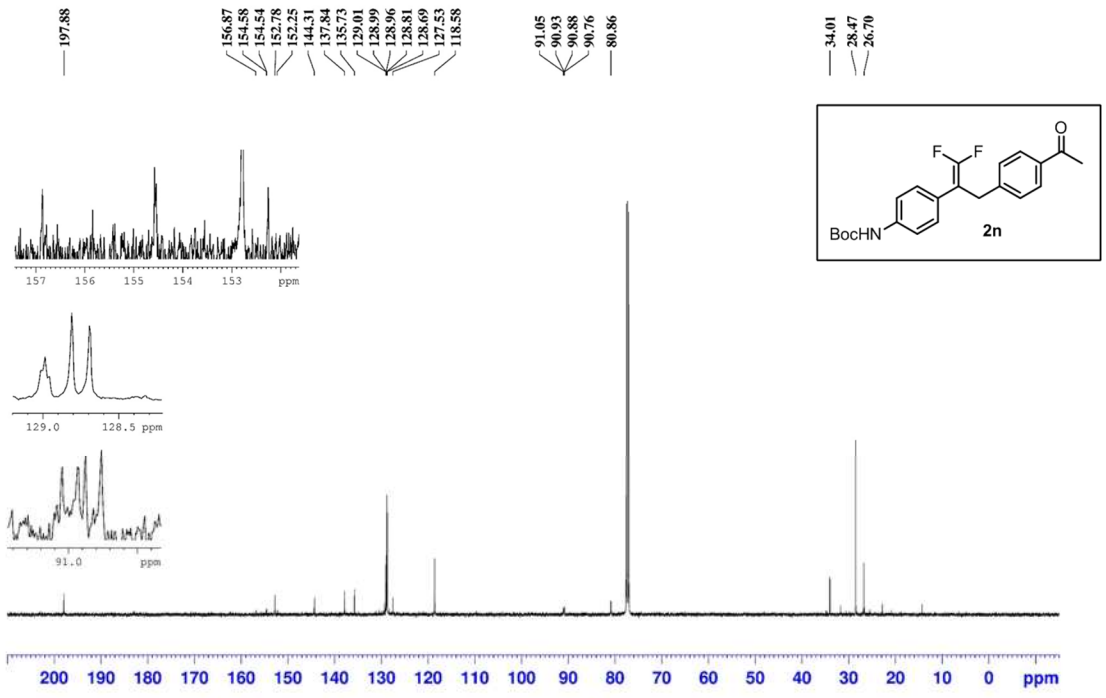


tert–Butyl (4–(3–(4–acetylphenyl)–1,1–difluoroprop–1–en–2–yl)phenyl)carbamate
500 MHz, CDCl3

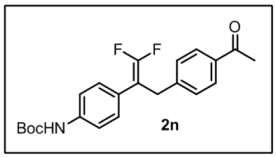


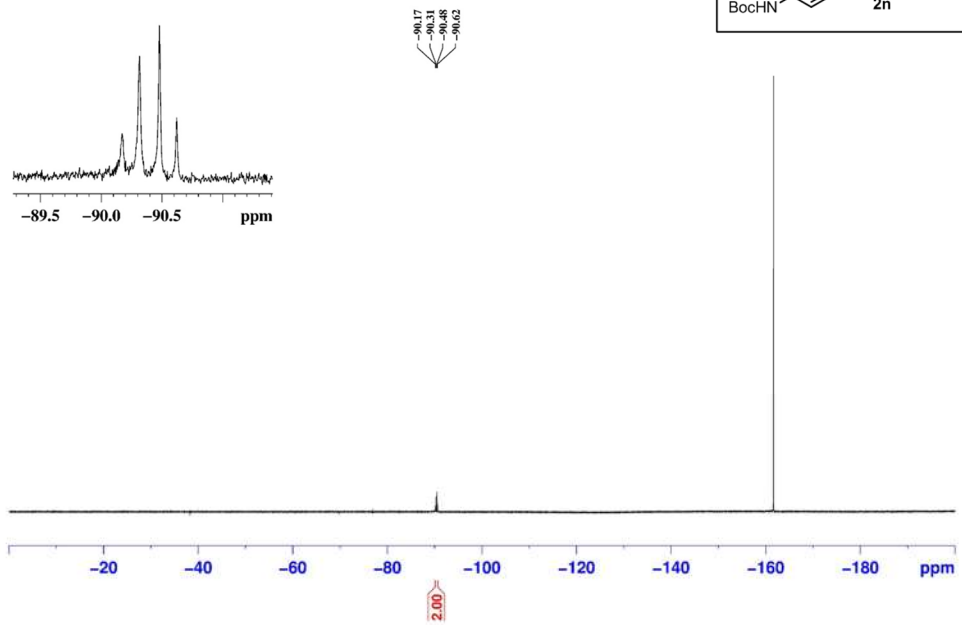


tert–Butyl (4–(3–(4–acetylphenyl)–1,1–difluoroprop–1–en–2–yl)phenyl)carbamate
125 MHz, CDCl3

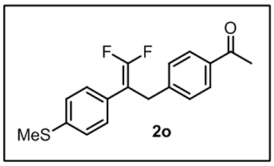


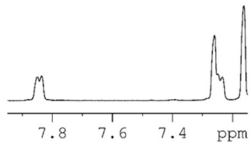
tert–Butyl (4–(3–(4–acetylphenyl)–1,1–difluoroprop–1–en–2–yl)phenyl)carbamate
282 MHz, CDCl3

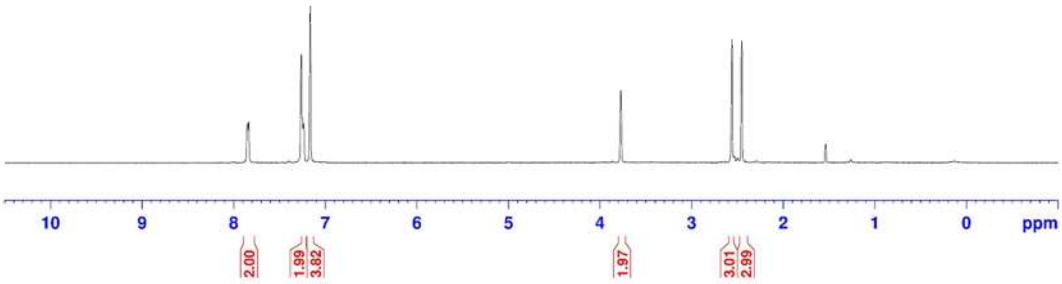




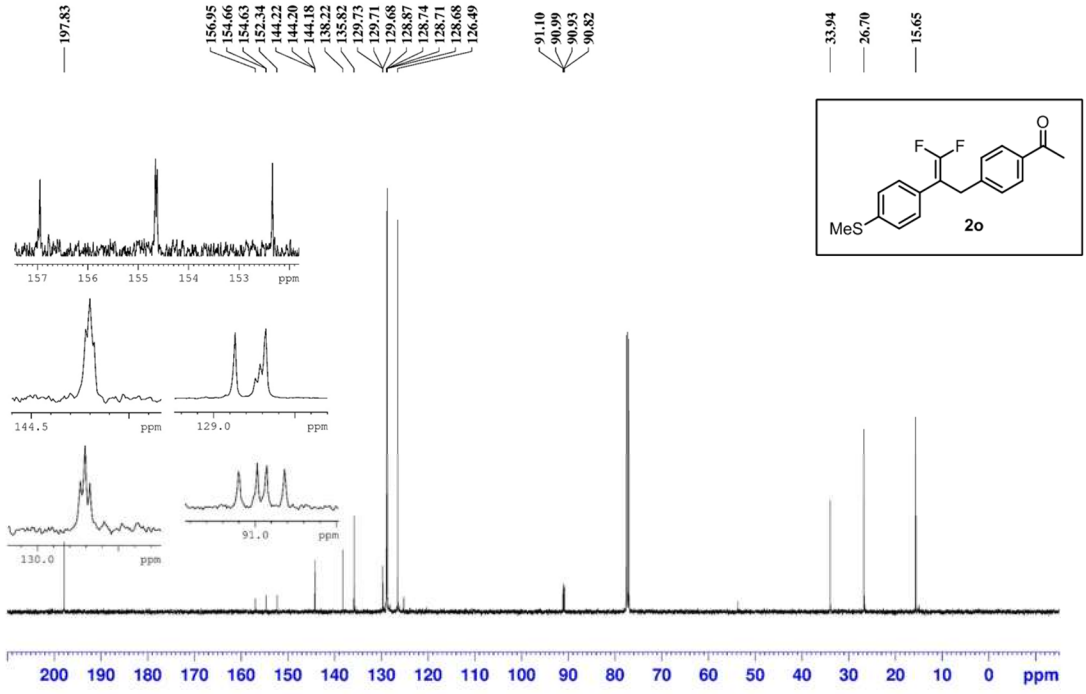
1–(4–(3,3–Difluoro–2–(4–(methylthio)phenyl)allyl)phenyl)ethanone
500 MHz, CDCl3



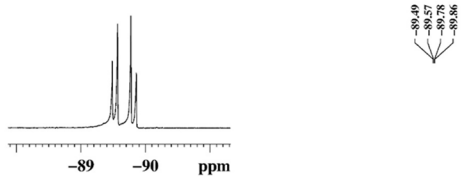


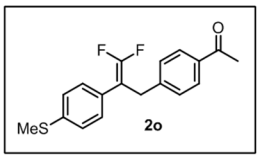


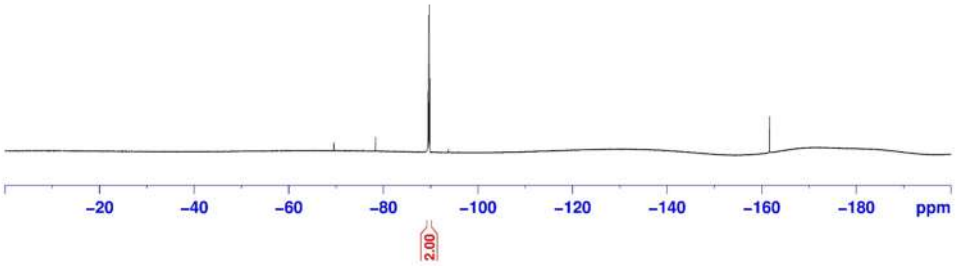
1–(4–(3,3–Difluoro–2–(4–(methylthio)phenyl)allyl)phenyl)ethanone
125 MHz, CDCl3



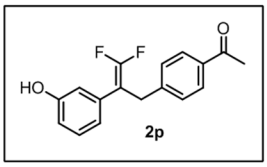
1–(4–(3,3–Difluoro–2–(4–(methylthio)phenyl)allyl)phenyl)ethanone
471 MHz, CDCl3

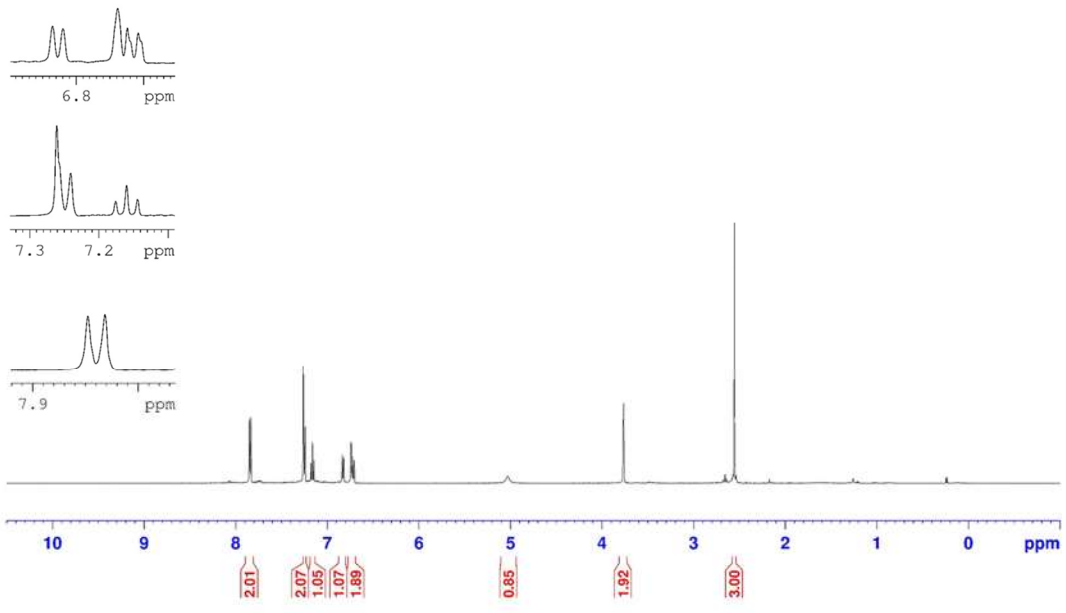




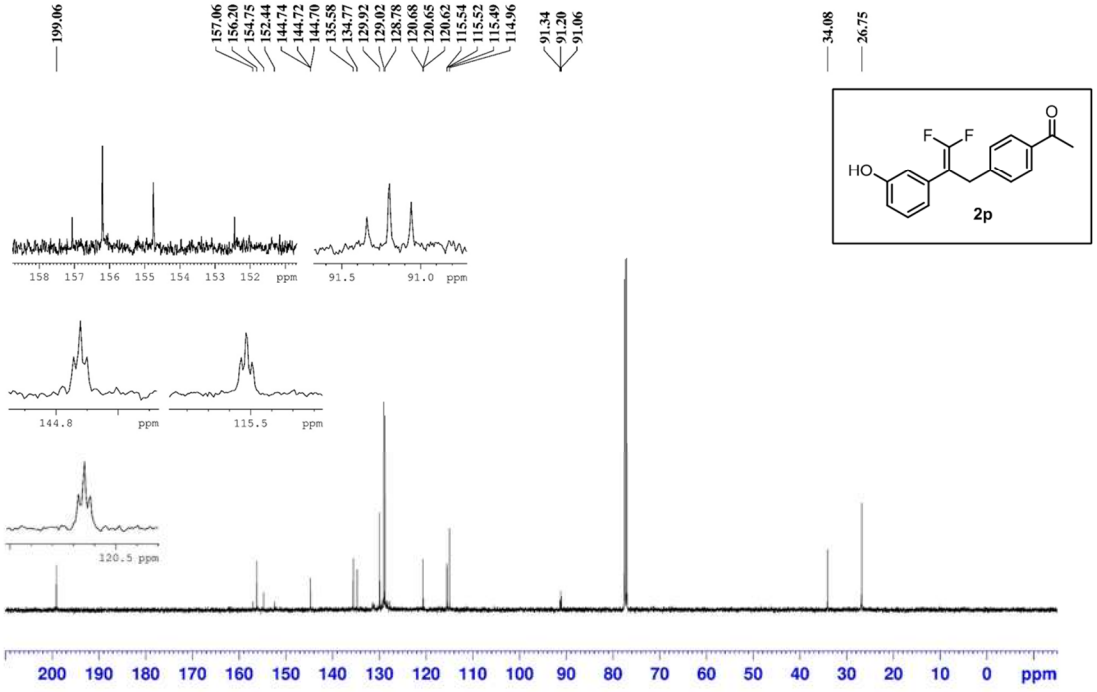


1–(4–(3,3–difluoro–2–(3–hydroxyphenyl)allyl)phenyl)ethanone
500 MHz, CDCl3

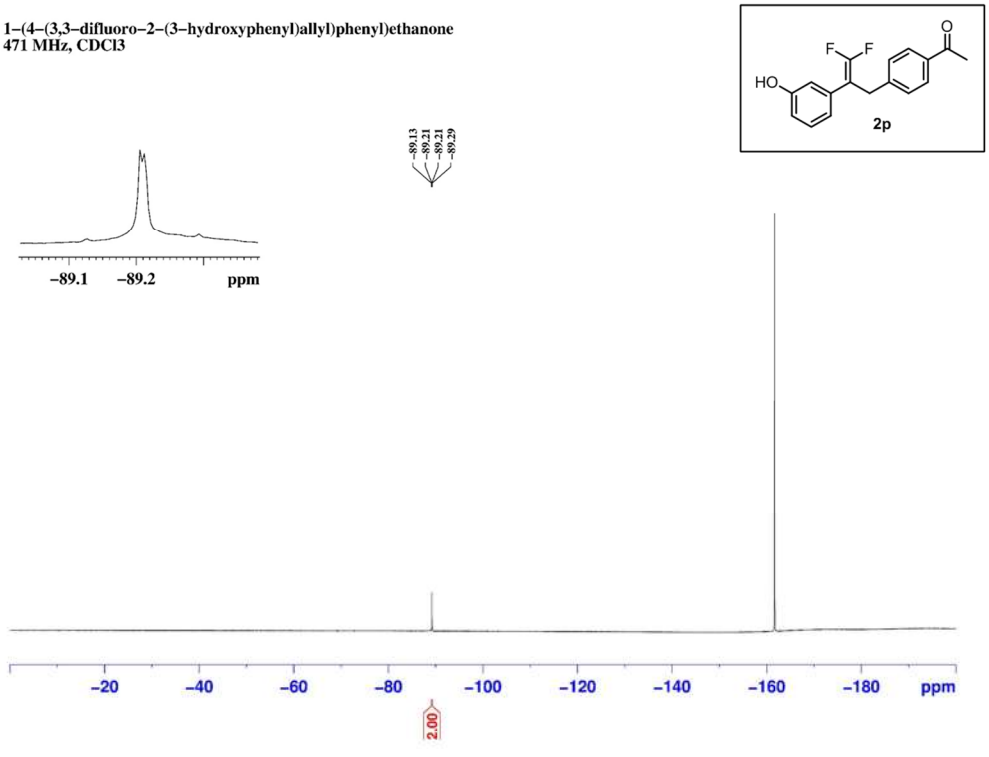




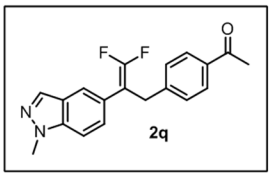
1–(4–(3,3–difluoro–2–(3–hydroxyphenyl)allyl)phenyl)ethanone
125 MHz, CDCl3

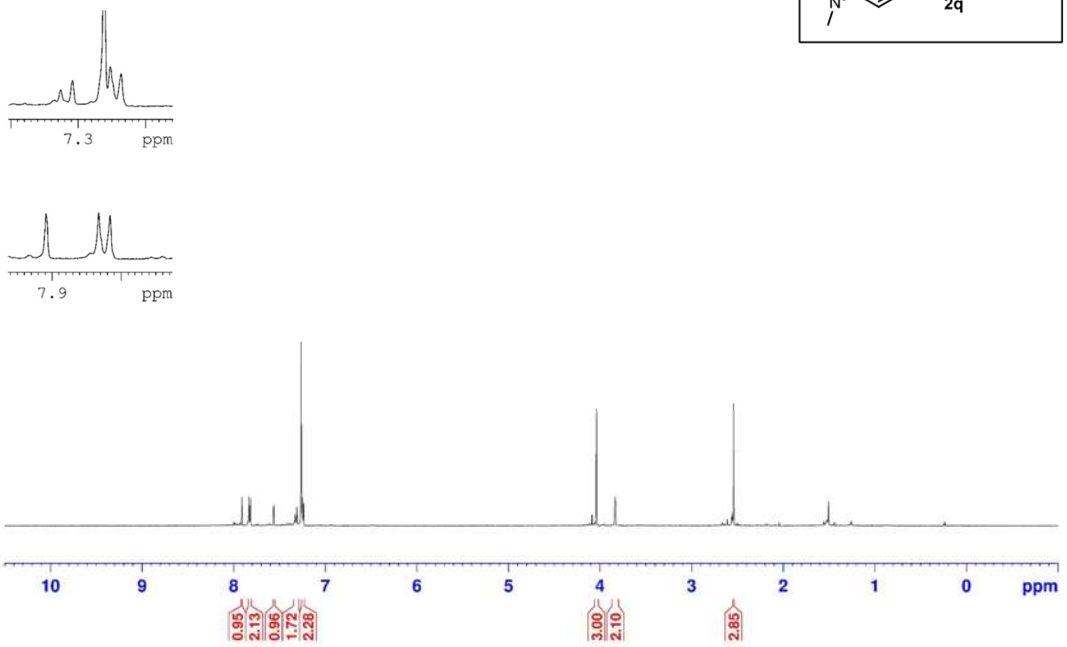


1–(4–(3,3–difluoro–2–(3–hydroxyphenyl)allyl)phenyl)ethanone
471 MHz, CDCl3

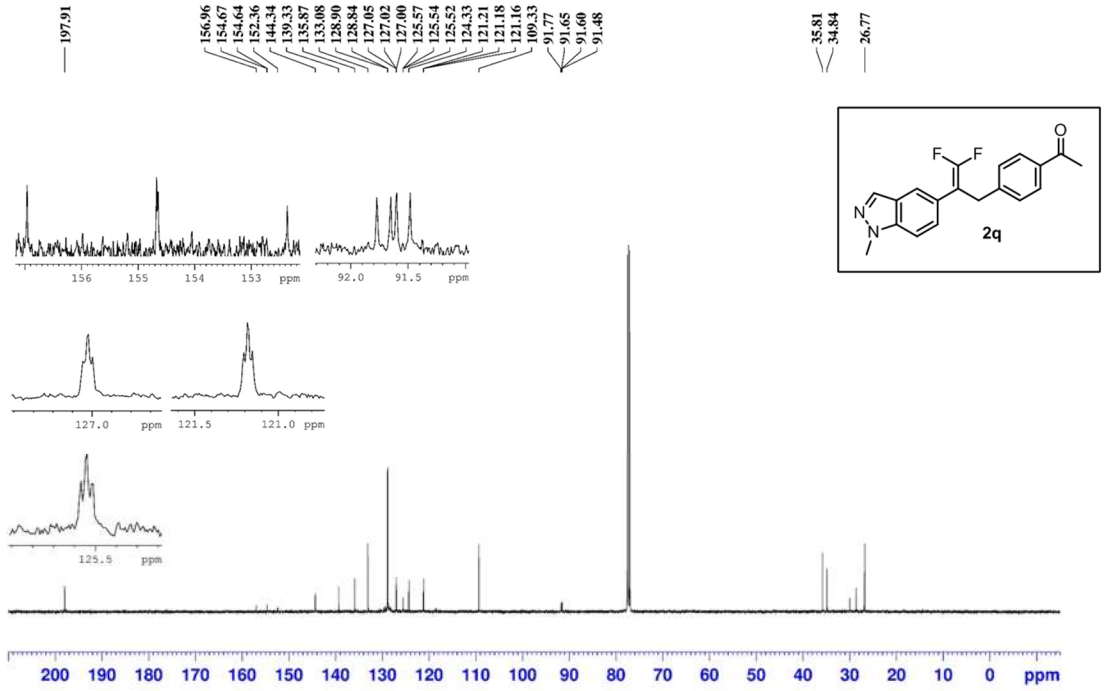


1–(4–(3,3–Difluoro–2–(1–methyl–1H–indazol–5–yl)allyl)phenyl)ethanone
500 MHz, CDCl3

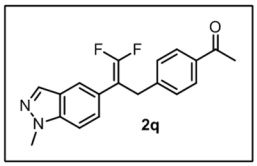


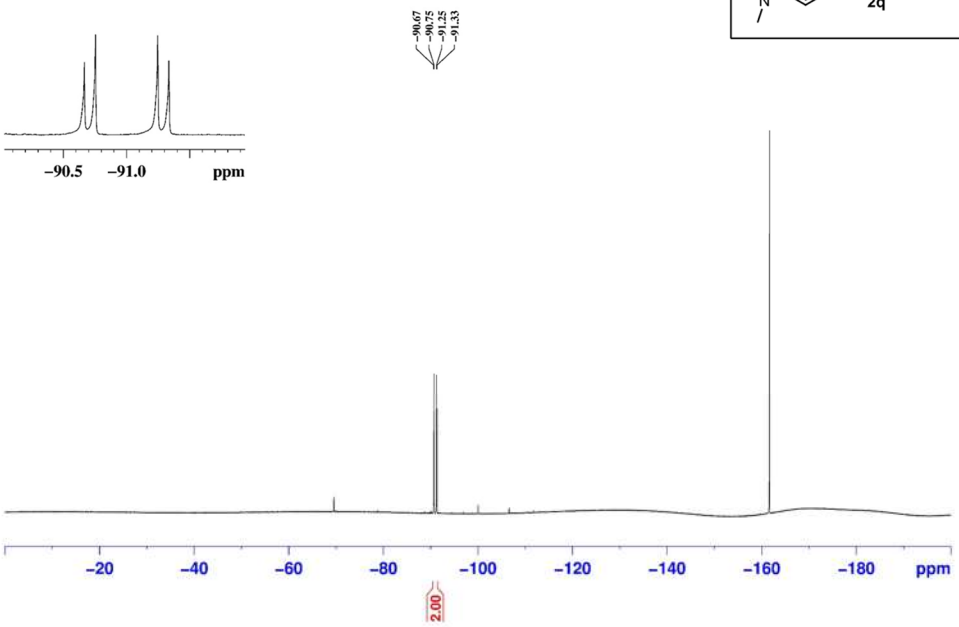


1–(4–(3,3–Difluoro–2–(1–methyl–1H–indazol–5–yl)allyl)phenyl)ethanone
125 MHz, CDCl3

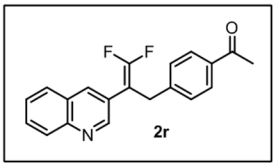


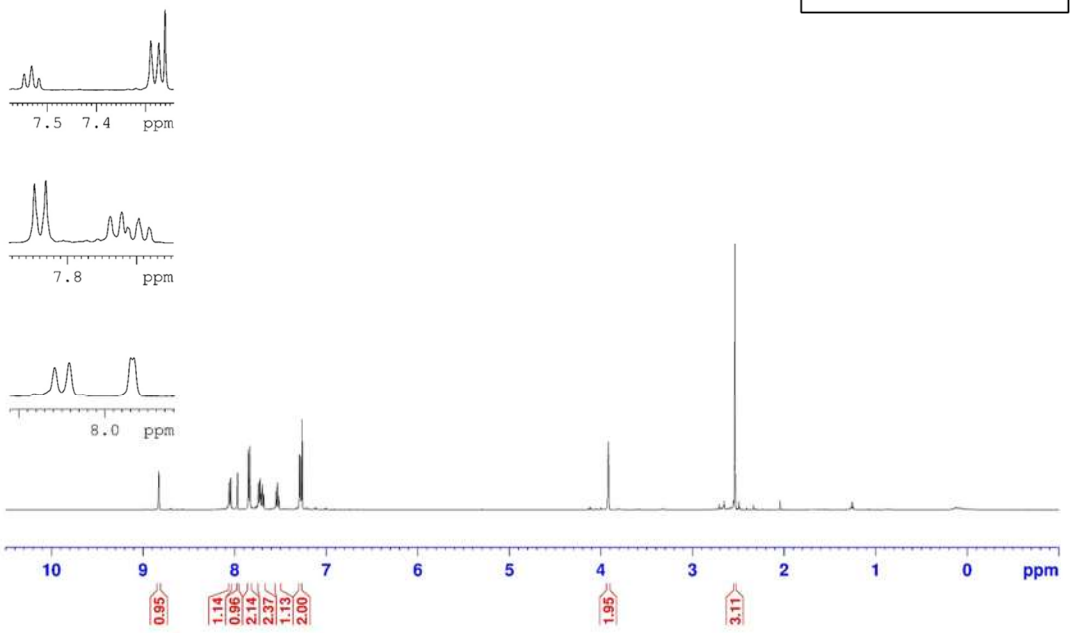
1–(4–(3,3–Difluoro–2–(1–methyl–1H–indazol–5–yl)allyl)phenyl)ethanone
471 MHz, CDCl3



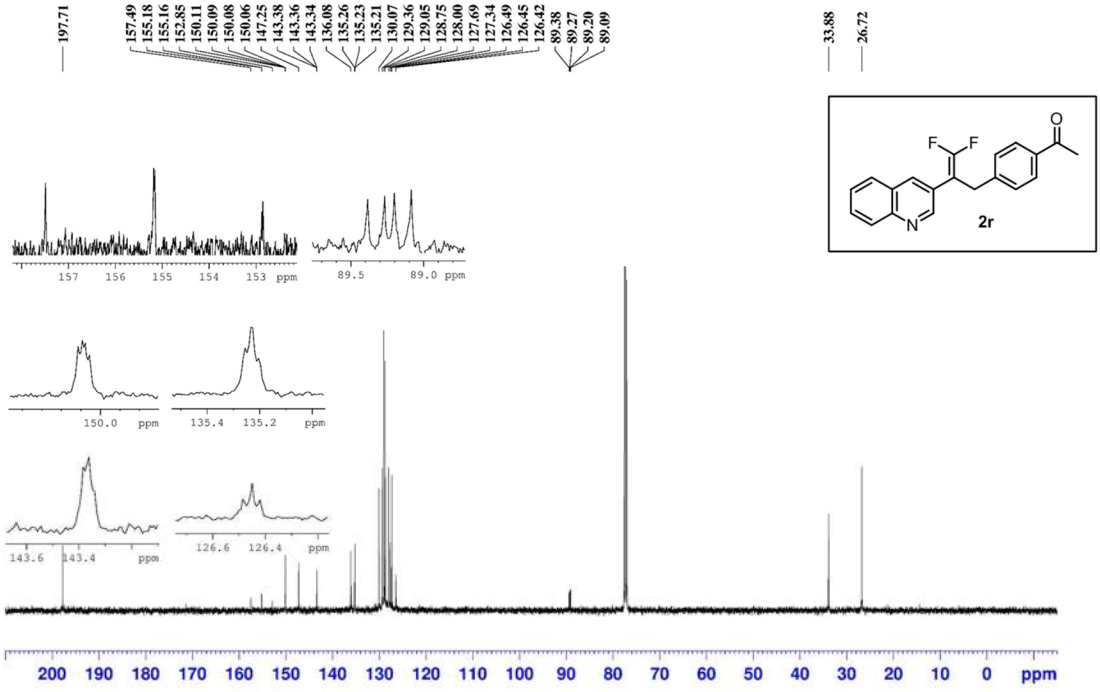


1–(4–(3,3–Difluoro–2–(quinolin–3–yl)allyl)phenyl)ethanone
500 MHz, CDCl3

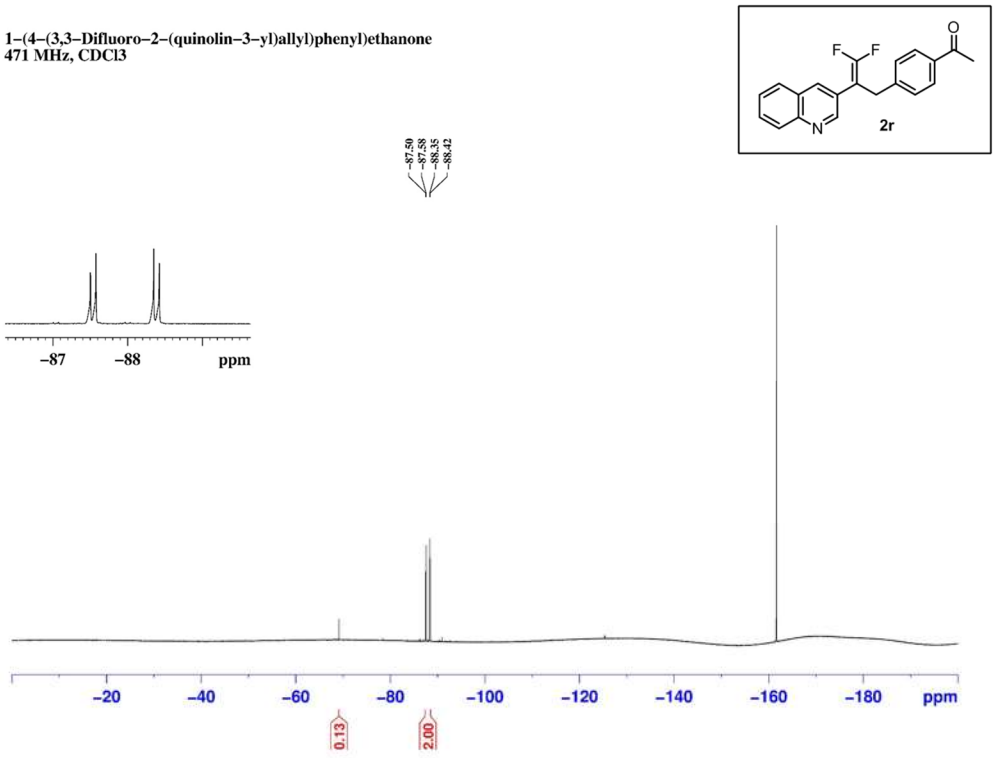




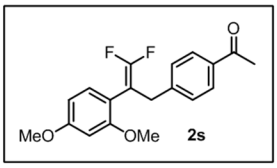
1–(4–(3,3–Difluoro–2–(quinolin–3–yl)allyl)phenyl)ethanone
125 MHz, CDCl3

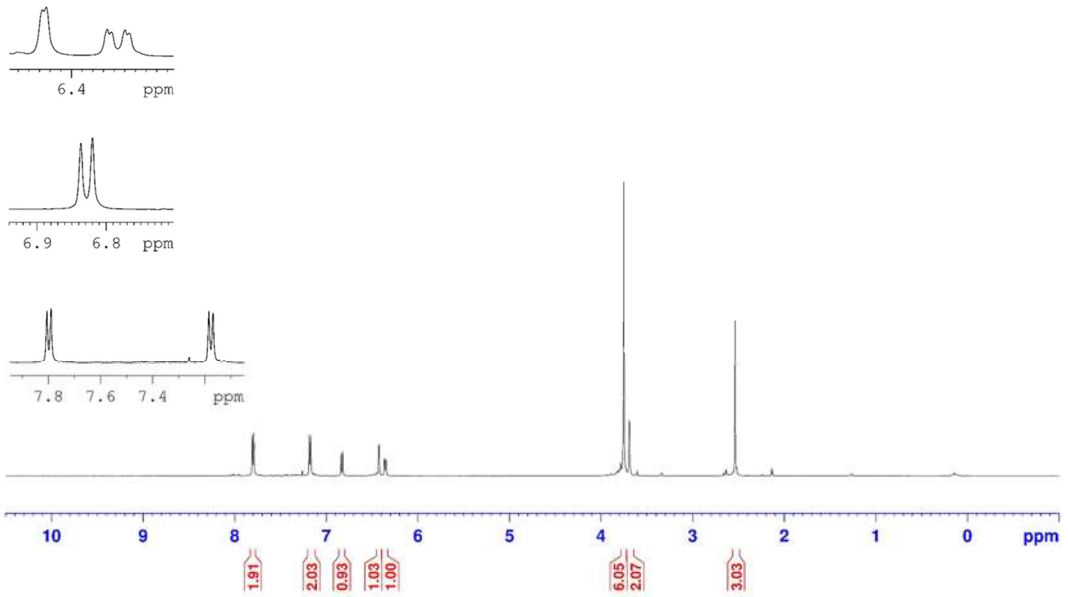


1–(4–(3,3–Difluoro–2–(quinolin–3–yl)allyl)phenyl)ethanone
471 MHz, CDCl3



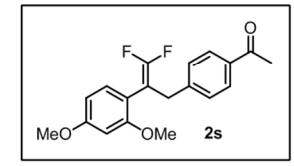
1–(4–(2–(2,4–Dimethoxyphenyl)–3,3–difluoroallyl)phenyl)ethanone
500 MHz, CDCl3



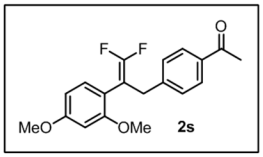


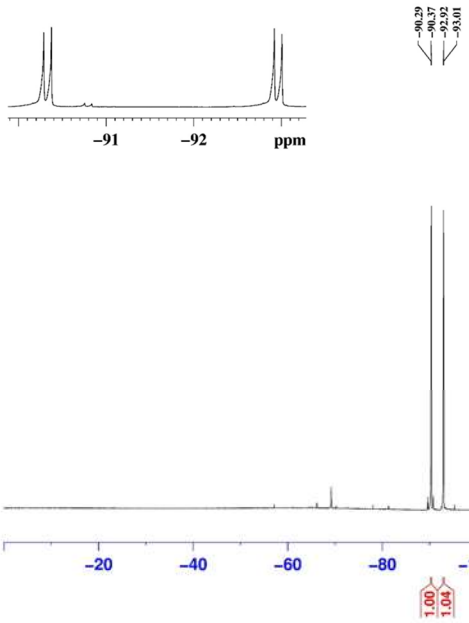
1–(4–(2–(2,4–Dimethoxyphenyl)–3,3–difluoroallyl)phenyl)ethanone
125 MHz, CDCl3

198.06
160.98
158.48
158.46
156.29
154.00
151.72
145.01
144.99
144.97
135.53
131.84
131.82
131.80
129.08
128.55
114.37
114.36
114.33
114.32
104.52
99.01
88.75
88.61
88.57
88.43
55.62
55.48
34.43
34.42
26.72

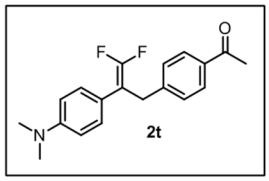


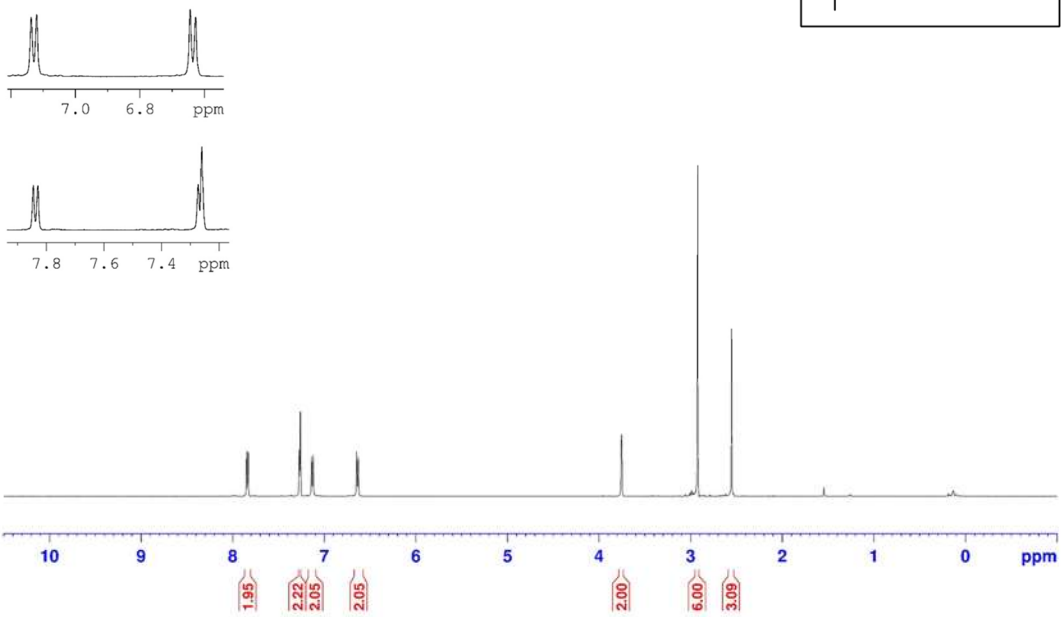
1–(4–(2–(2,4–Dimethoxyphenyl)–3,3–difluoroallyl)phenyl)ethanone
471 MHz, CDCl3



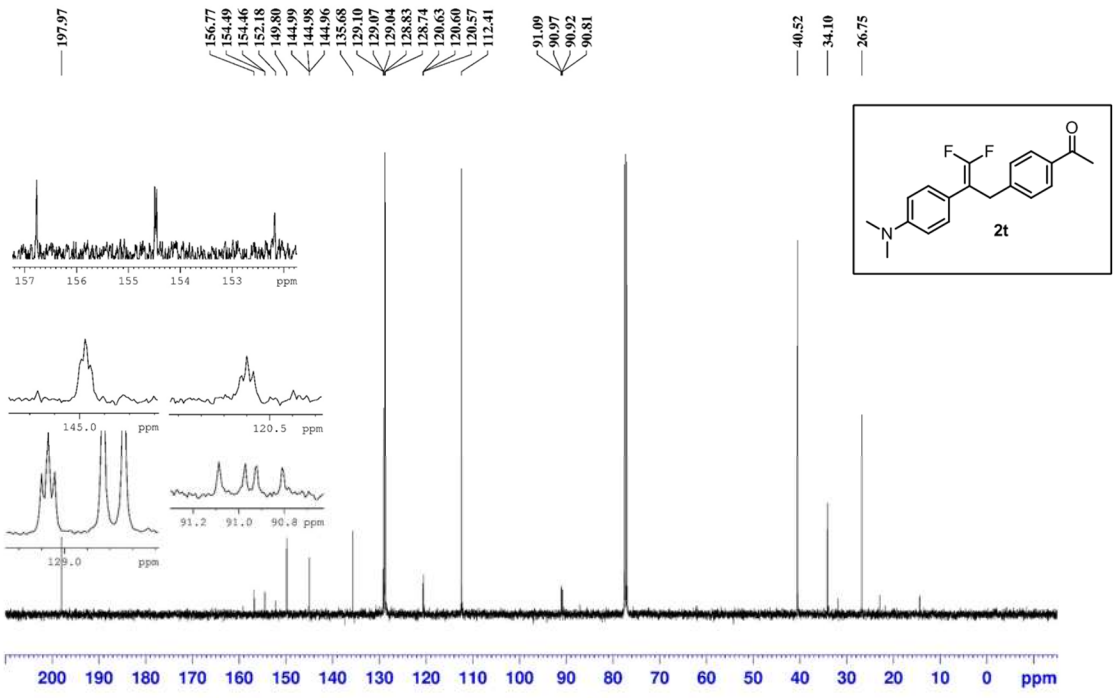


1–(4–(2–(4–(Dimethylamino)phenyl)–3,3–difluoroallyl)phenyl)ethanone
500 MHz, CDCl3

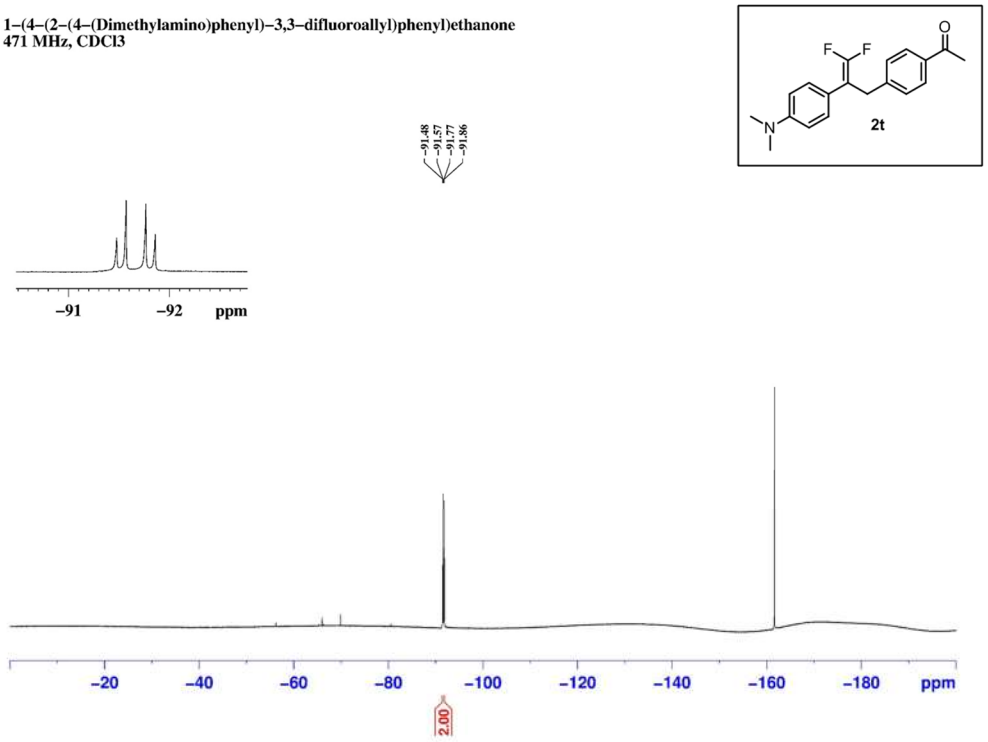




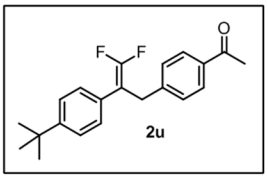
1–(4–(2–(4–(Dimethylamino)phenyl)–3,3–difluoroallyl)phenyl)ethanone
125 MHz, CDCl3

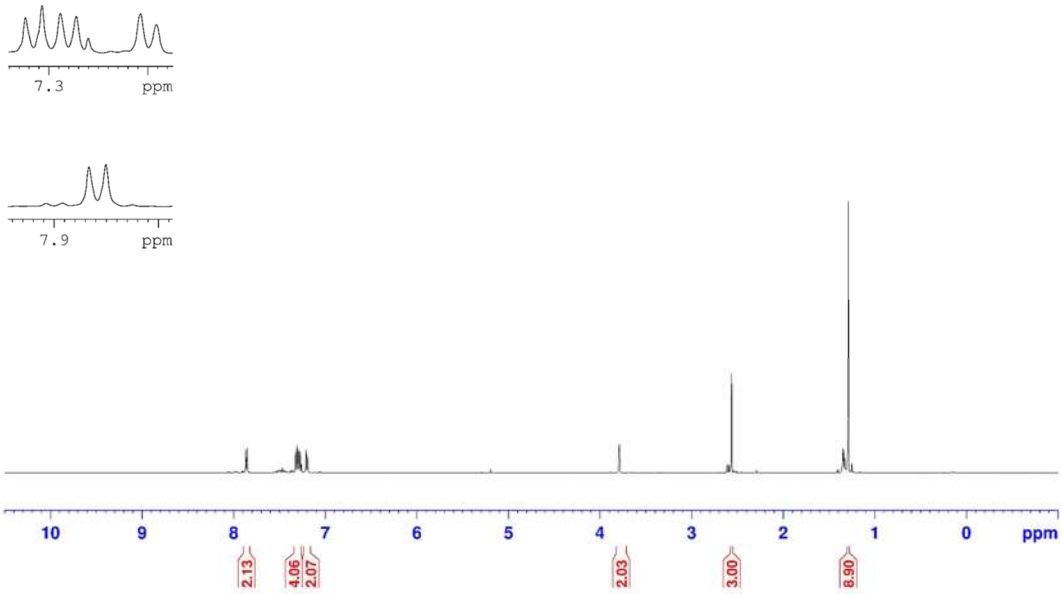


1–(4–(2–(4–(Dimethylamino)phenyl)–3,3–difluoroallyl)phenyl)ethanone
471 MHz, CDCl3

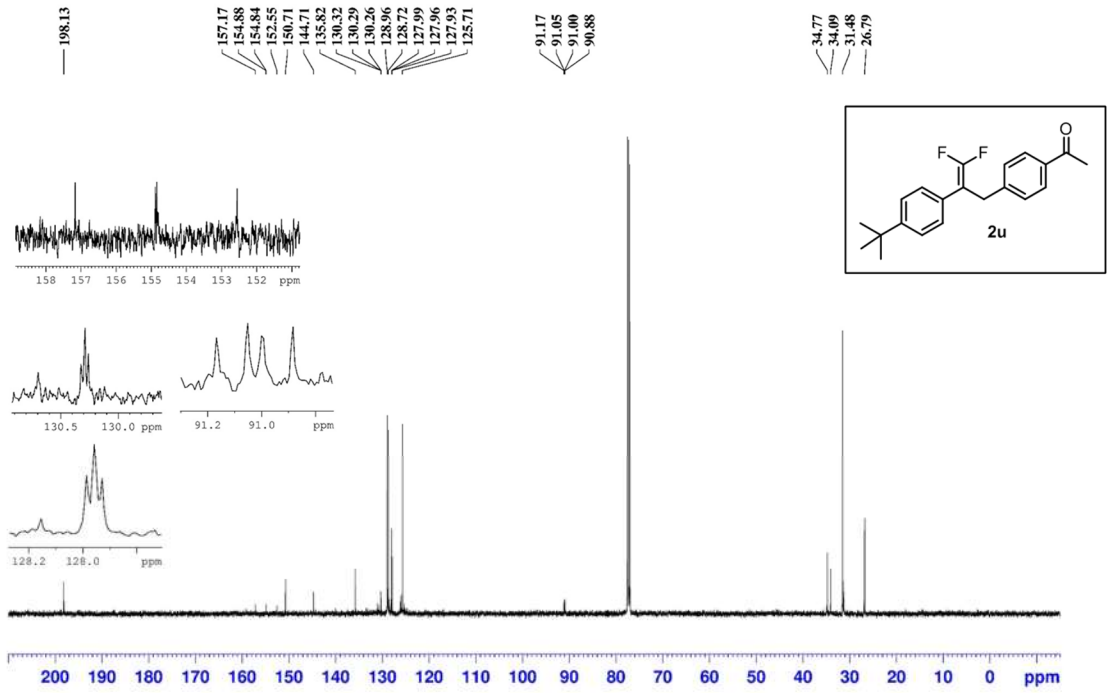


1–(4–(2–(4–(tert–Butyl)phenyl)–3,3–difluoroallyl)phenyl)ethanone
500 MHz, CDCl3

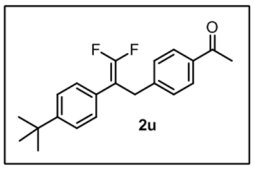


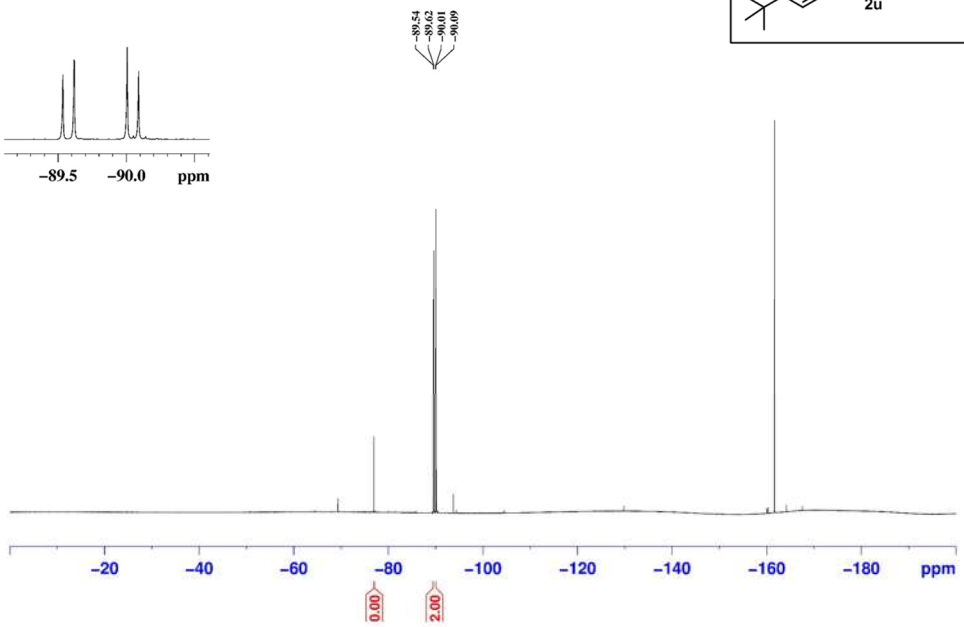


1–(4–(2–(4–(tert–Butyl)phenyl)–3,3–difluoroallyl)phenyl)ethanone
125 MHz, CDCl3

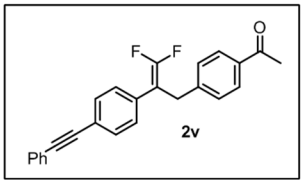


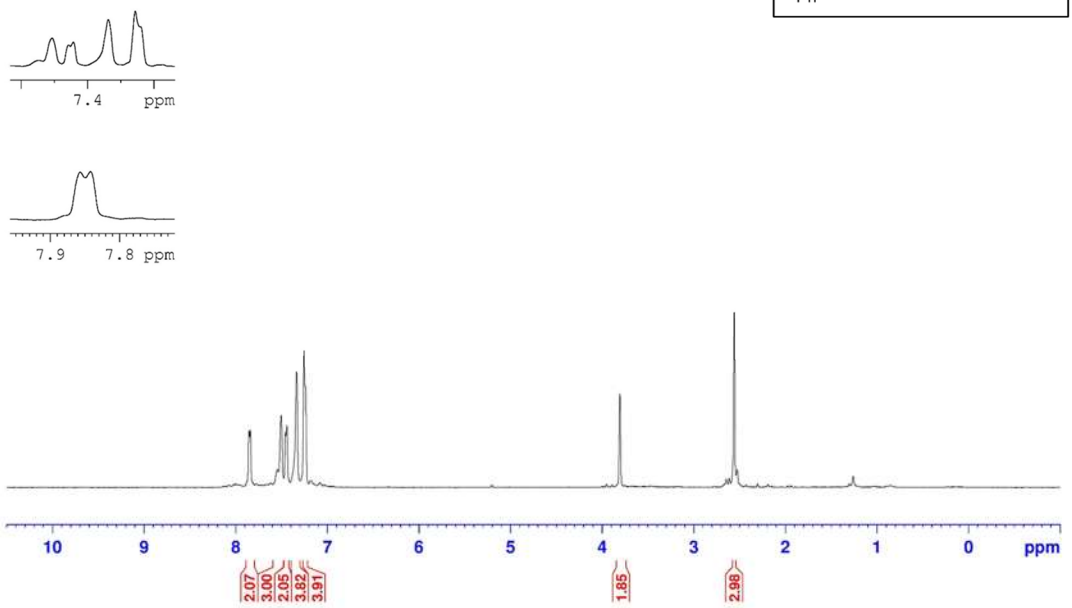
1-(4-(2-(4-(tert-Butyl)phenyl)-3,3-difluoroallyl)phenyl)ethanone
471 MHz, CDCl3



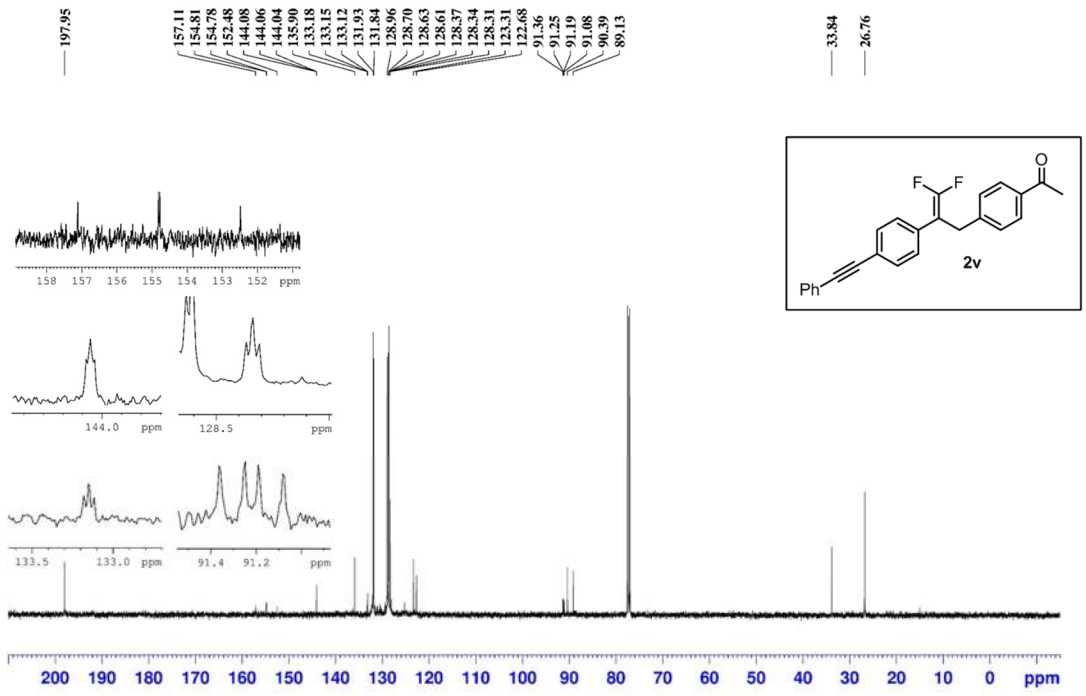


1-(4-(3,3-Difluoro-2-(4-(phenylethynyl)phenyl)allyl)phenyl)ethanone
500 MHz, CDCl3

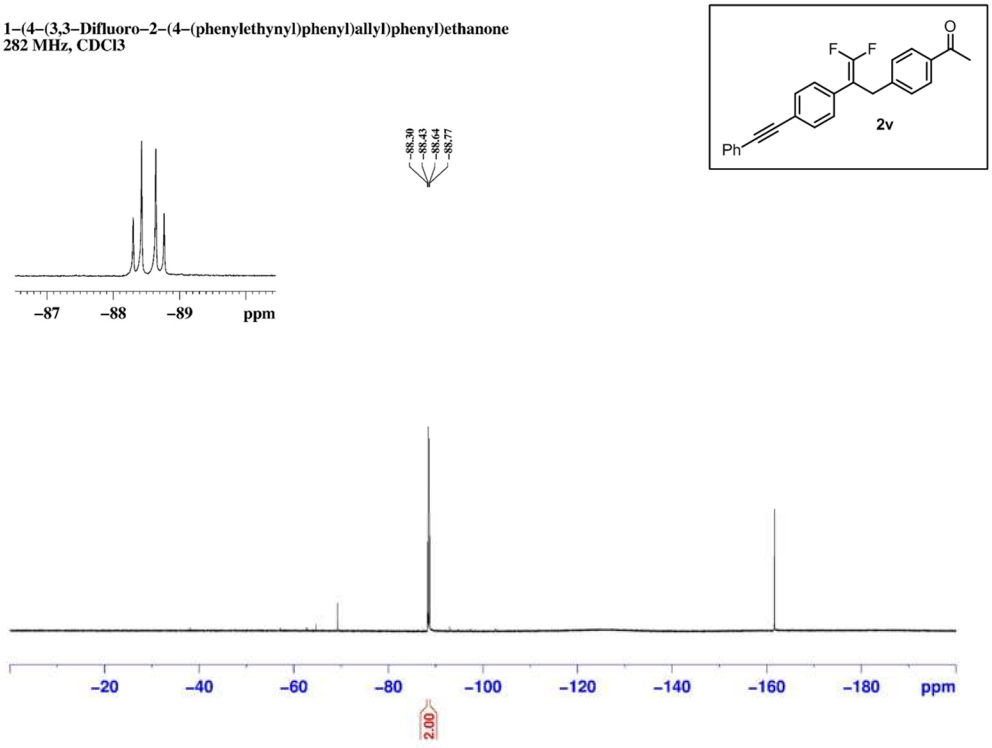




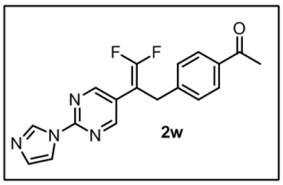
1–(4–(3,3–Difluoro–2–(4–(phenylethynyl)phenyl)allyl)phenyl)ethanone
125 MHz, CDCl3

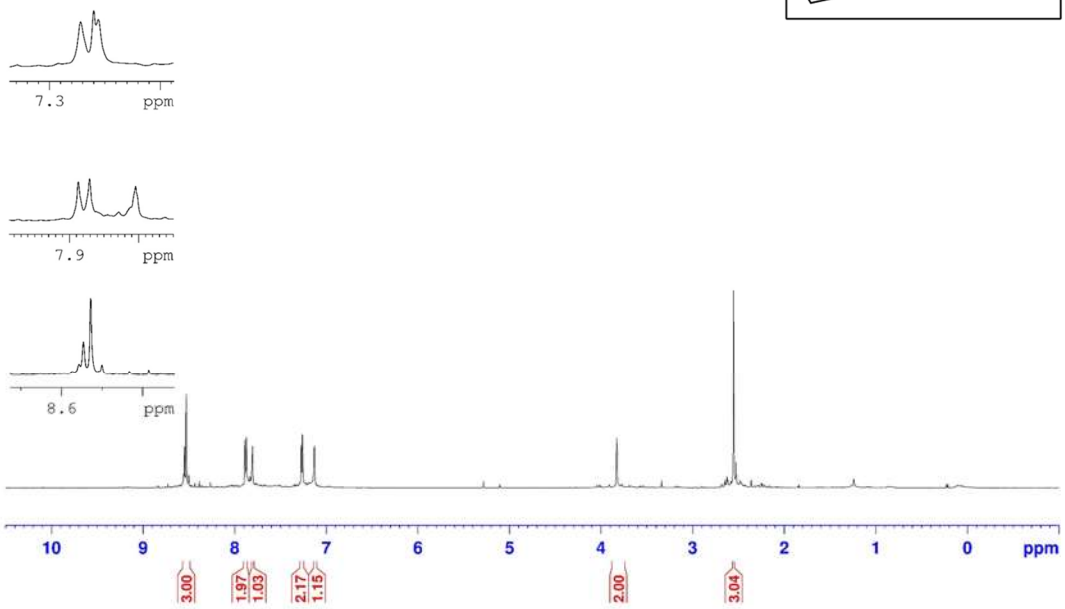


1–(4–(3,3–Difluoro–2–(4–(phenylethynyl)phenyl)allyl)phenyl)ethanone
282 MHz, CDCl3

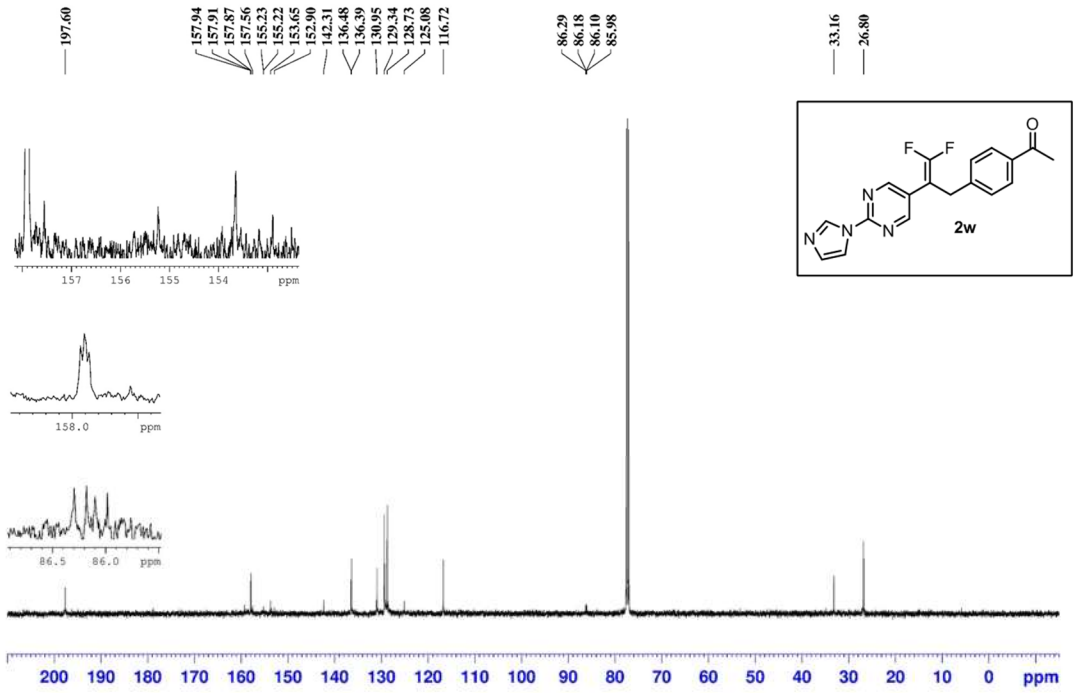


1–(4–(2–(2–(1H–imidazol–1–yl)pyrimidin–5–yl)–3,3–difluoroallyl)phenyl)ethanone
500 MHz, CDCl3

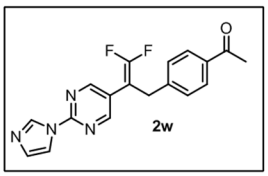


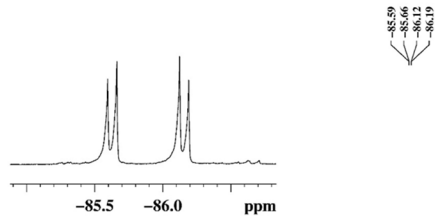


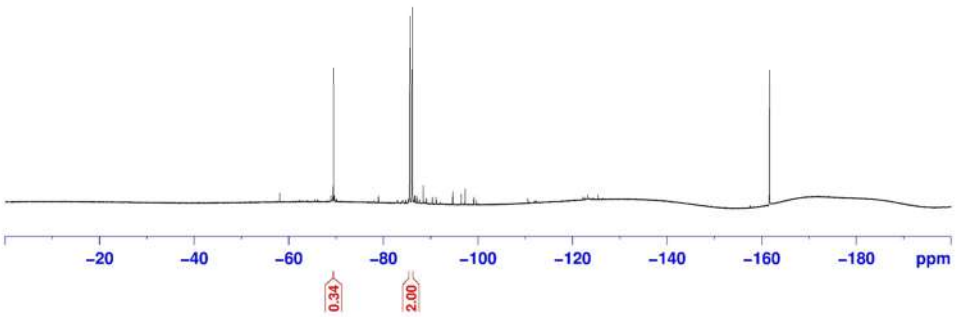
1–(4–(2–(2–(1H–imidazol–1–yl)pyrimidin–5–yl)–3,3–difluoroallyl)phenyl)ethanone
125 MHz, CDCl3



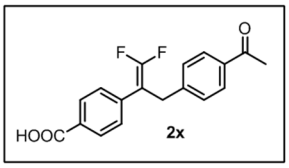
1−(4−(2−(2−(1H−imidazol−1−yl)pyrimidin−5−yl)−3,3−difluoroallyl)phenyl)ethanone
471 MHz, CDCl3

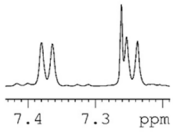


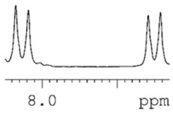


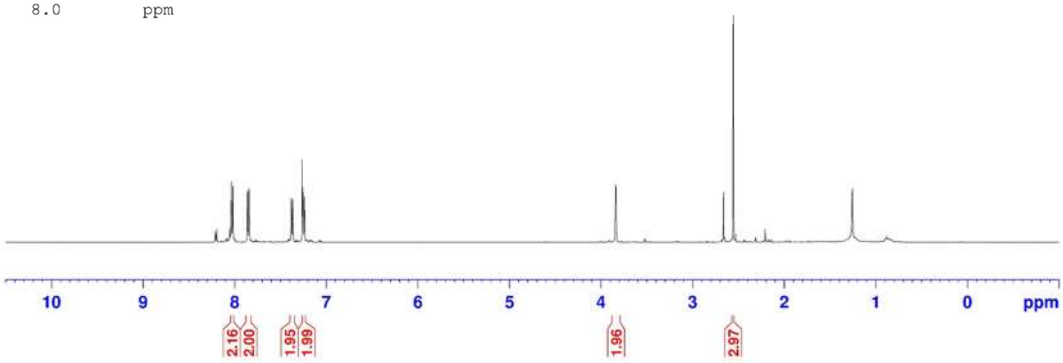


4−(3−(4−Acetylphenyl)−1,1−difluoroprop−1−en−2−yl)benzoic acid
500 MHz, CDCl3

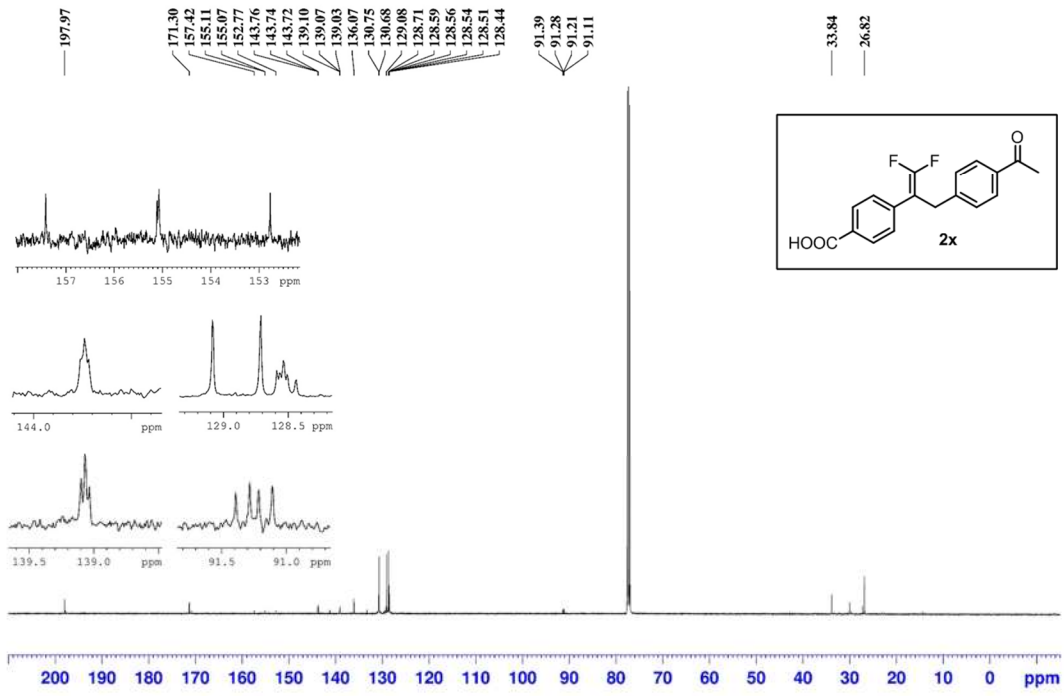




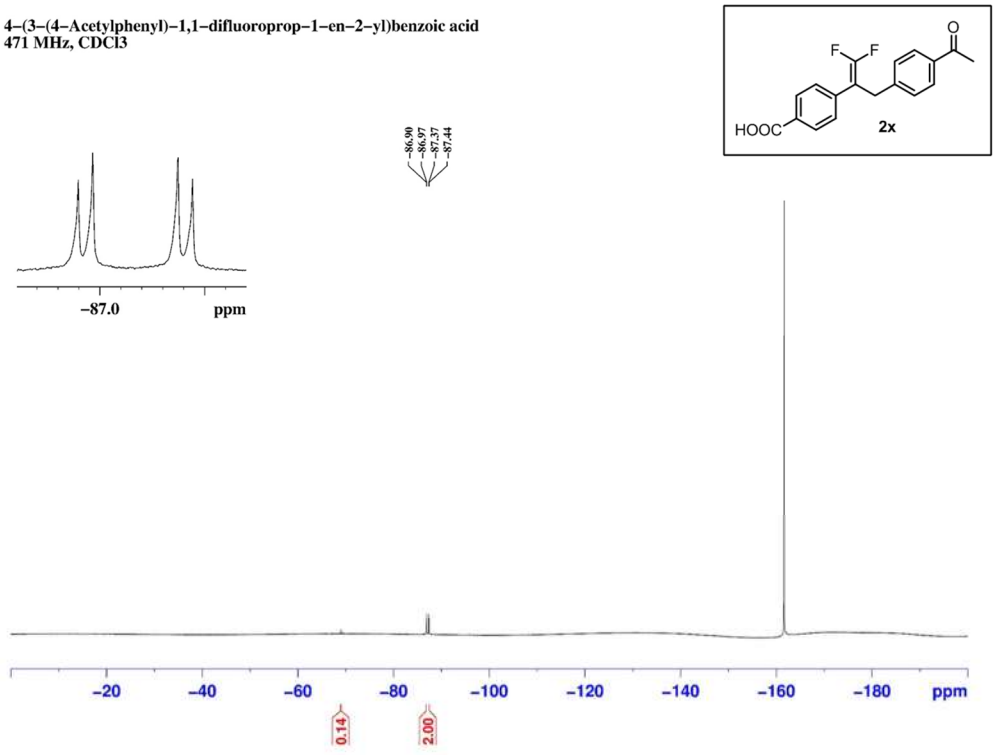




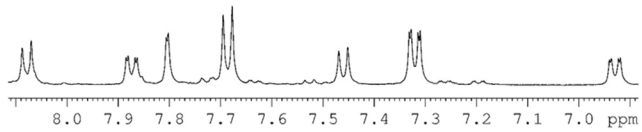
4–(3–(4–Acetylphenyl)–1,1–difluoroprop–1–en–2–yl)benzoic acid
125 MHz, CDCl3

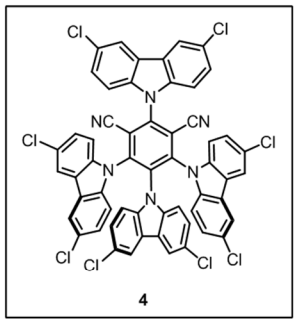


4–(3–(4–Acetylphenyl)–1,1–difluoroprop–1–en–2–yl)benzoic acid
471 MHz, CDCl3

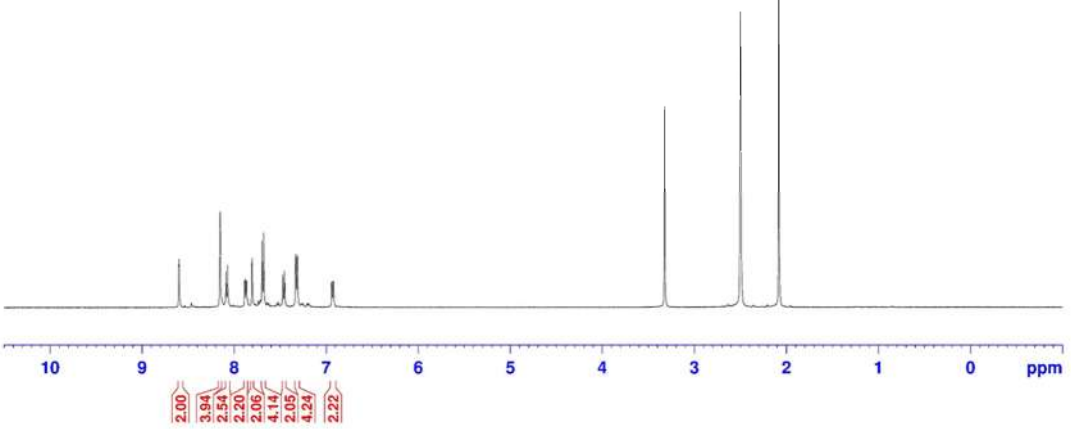


2,4,5,6–tetrakis(3,6–dichloro–9H–carbazol–9–yl)isophthalonitrile
DMSO–d6, 125 MHz

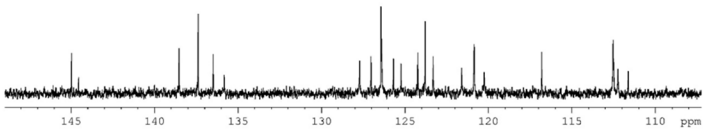


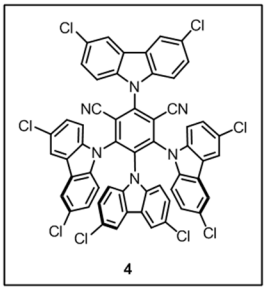


4



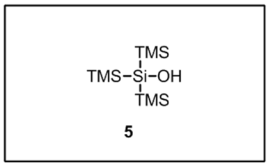
2,4,5,6–tetrakis(3,6–dichloro–9H–carbazol–9–yl)isophthalonitrile
DMSO–d6, 125 MHz

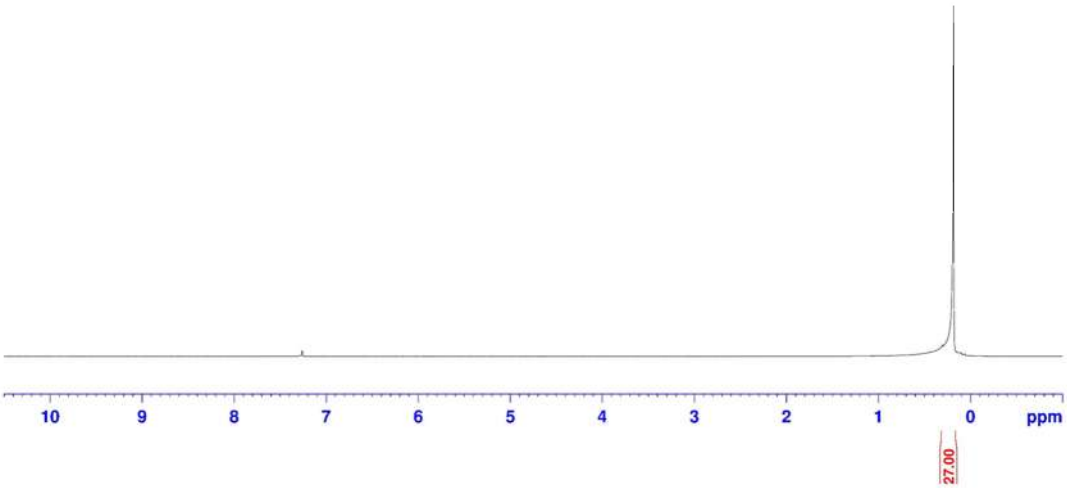




4

1,1,1,3,3,3−Hexamethyl−2−(trimethylsilyl)trisilan−2−ol
500 MHz, CDCl3





1,1,1,3,3,3−Hexamethyl−2−(trimethylsilyl)trisilan−2−ol
125 MHz, CDCl3