Supporting Information

Carbofluorination via a Palladium-Catalyzed Cascade Reaction

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I. General information

General Procedures. Unless otherwise noted, reactions were performed without the exclusion of air or moisture. Screens were performed in borosilicate vials, and all other reactions were performed in round-bottom flasks. Flasks were sealed with rubber septa or polyethylene caps. Stainless steel cannulae or syringes were used to transfer air- and moisture-sensitive reagents. Reactions using silver(I) fluoride were performed with the exclusion of light by wrapping reaction vessels in aluminum foil. Reactions were monitored by thin-layer chromatography (TLC) on EMD Silica Gel 60 F_{254} plates, visualizing with fluorescence quenching, potassium permanganate ($KMnO_4$), or ceric ammonium molybdate (CAM). Organic solutions were concentrated under reduced pressure using a rotary evaporator with an ice-water bath for volatile compounds. Manual column chromatography was performed using SiliCycle SiliaFlash F60 (40-53 μm, 60 Å). Automated column chromatography was performed using pre-packed silica gel cartridges on a Biotage SP4 (40–53 μm, 60 Å).

Materials. Commercial reagents were purchased from Sigma-Aldrich, Acros, Alfa Aesar, Oakwood, Strem, and TCI, and used as received with the following exceptions. Diethyl ether (Et_2O), dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), toluene, 1,4-dioxane, and benzene were dried by passing through activated alumina columns; acetonitrile (CH_3CN), *N*,*N*-

dimethylformamide (DMF), and pyridine were dried by passing through a column of activated molecular sieves.[1] Silver(I) fluoride, tris(dibenzylideneacetone)dipalladium, allylpalladium chloride dimer, and 2-(dicyclohexylphosphino)-2',4',6'-tri-i-propyl-1,1'-biphenyl (XPhos) were purchased from Strem and used as received. Tris[3,5-bis(trifluoromethyl)phenyl]phosphine [$P(3,5\text{-}CF_3\text{-}C_6H_3)_3$] was purchased from Alfa Aesar or prepared in one step from commercial materials.[2] Bis(3,5,3′,5′-dimethoxydibenzylideneacetone)palladium and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos) were purchased from Sigma-Aldrich and used as received. When used as a ligand in carbofluorinations, triphenylphosphine (PPh_3) was recrystallized from acetone (for other reactions, it was used as received). d_8-toluene was purchased from Sigma-Aldrich and dried over activated 4Å molecular sieves before use. If not used immediately after synthesis, allenes were stored at –30 ºC. Allene **4a** was purchased from Sigma-Aldrich. Allenes **1g**,[3] **1j**,[4] **4b**,[5] **4c**,[5] and **4d**[6] were prepared according to reported procedures. Complexes **8-I** and **8-F** were prepared according to reported procedures.[7]

Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker 500 AVANCE spectrometer (500 and 125 MHz, respectively). Chemical shifts for proton are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26, benzene = δ 7.16, toluene (Me) = δ 2.08, CH_2Cl_2 = δ 5.32, CH_3OH = δ 3.31). Chemical shifts for carbon are reported in ppm downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent residual peak ($CDCl_3$ = δ 77.16, C_6D_6 = δ 128.06, d_8-toluene (Me) = δ 20.43, CD_2Cl_2 = δ 53.84, CD_3OD = δ 49.00). Fluorine nuclear magnetic resonance (^{19}F NMR) spectra were recorded on a Bruker AVANCE 300 (282 MHz) or Varian Inova 400 (376 MHz) spectrometer; chemical shifts are reported in parts per million and are referenced to $CFCl_3$ (δ 0 ppm). Phosphorus nuclear magnetic resonance (^{31}P NMR) spectra were recorded on a Bruker AVANCE 500 (203 MHz) or 300 (121 MHz) spectrometer; chemical shifts are reported in parts per million and are referenced to H_3PO_4 (δ 0 ppm). NMR data are presented as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in Hertz (Hz), integration. Liquid chromatography/mass spectrometry (LC/MS) spectra were recorded on an Agilent 1260 Infinity system with 6120 Quadropole LC/MS. High-resolution mass spectra (HRMS) were obtained on an Agilent 6220 LC/MS using electrospray ionization time-of-flight (ESI-TOF) or Agilent 7200 GC/MS spectrometer using electron impact time-of-flight (EI-TOF). Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer Spectrum 100 and are reported in terms of frequency of absorption (cm^{-1}) and intensity (s = strong, m = moderate, w = weak, br = broad). High-performance liquid chromatography (HPLC) was performed on an Agilent 1200 series

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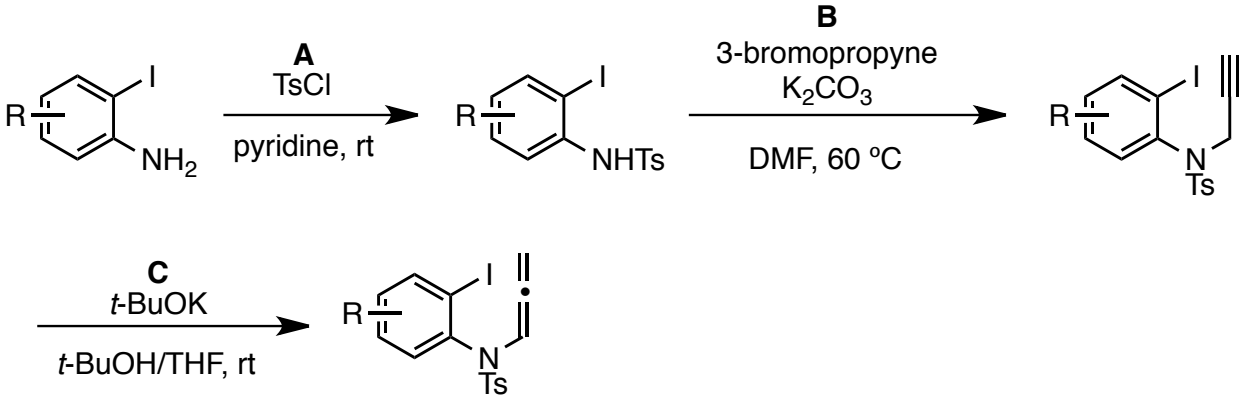
[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics,* **1996**, *15*, 1518–1520.
[2] Haji, S.; Erkey, C. *Tetrahedron* **2002**, *58*, 3929–3941.
[3] Grigg, R.; Sansano, J.; Santhakumar, V.; Sridharan, V.; Thangavelanthum, R.; Thornton-Pett, M.; Wilson, D. *Tetrahedron* **1997**, *53*, 11803–11826.
[4] Ma, S.; Negishi, E.-I. *J. Am. Chem. Soc.* **1995**, *117*, 6345–6357.
[5] Clavier, H.; Jeune, K. L.; de Riggi, I.; Tenaglia, A.; Buono, G. *Org. Lett.* **2011**, *13*, 308–311.
[6] Kuang, J.; Ma, S. *J. Org. Chem.* **2009**, *74*, 1763–1765.
[7] Pilon, M. C.; Grushin, V. V. *Organometallics* **1998**, *17*, 1774–1781.

instrument with a binary pump and a diode array detector, using Chiralcel OJ-H (25 cm x 0.46 cm) and Chiralpak AS-H (25 cm x 0.46 cm) columns.

II. Synthesis of substrates

Scheme S1. *Reaction sequence for preparation of allenes*

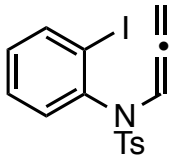


General procedure A for tosylation: To a solution of the aniline (1.00 equiv) in pyridine (1 M) at room temperature, *p*-toluenesulfonyl chloride (1.05 equiv) was added. The reaction mixture was allowed to stir at room temperature overnight. The reaction mixture was quenched with water, and the aqueous layer was extracted with dichloromethane (3x). The combined organic extracts were washed with aqueous copper sulfate (2x, 10% w/w). The organic layer was then dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography to afford the desired tosylamine.

General procedure B for propargylation: To a solution of tosylamine (1.00 equiv) and potassium carbonate (1.50 equiv) in DMF (0.4 M) at room temperature, 3-bromopropyne (1.20 equiv, 80% w/w in toluene) was added. The mixture was allowed to stir at 60 ºC overnight. After cooling to room temperature, the mixture was diluted with water and ethyl acetate. The aqueous layer was extracted with ethyl acetate (2x). The combined organic layers were washed with aqueous lithium chloride (10% w/w), dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography to afford the desired propargylamine.

General procedure C for isomerization to allene: To a solution of the propargylamine (1.00 equiv) in *tert*-butanol/tetrahydrofuran (0.5 M), potassium *tert*-butoxide (1.00 equiv) was added. The reaction mixture was then allowed to stir at room temperature. Upon completion (as determined by TLC),[8] the mixture was diluted with dichloromethane. The organic layer was washed with water and brine, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography to afford the desired allene.

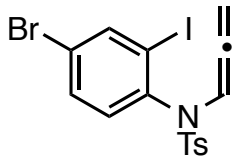
[8] For some isomerizations, product decomposition was observed with prolonged reaction time. These reactions should be monitored carefully, and reaction times should be heeded when provided.



***N*-(2-iodophenyl)-4-methyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (1a).** General procedure **B** was followed (with a modification in purification), using *N*-(2-iodophenyl)-4-methylbenzenesulfonamide[9] (4.00 g, 10.7 mmol), potassium carbonate (2.22 g, 16.1 mmol), 3-bromopropyne (1.39 mL, 12.9 mmol) and DMF (27 mL). The residue was purified by recrystallization from dichloromethane/hexanes to afford *N*-(2-iodophenyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (3.80 g, 9.24 mmol, 86% yield) as an off-white solid.

Then, general procedure **C** was followed (with a modification in purification), using *N*-(2-iodophenyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1.65 g, 4.00 mmol), potassium *tert*-butoxide (449 mg, 4.00 mmol) and *tert*-butanol/THF (1:1, 8 mL). The reaction was complete after 10 min. The residue was purified by passing through a plug of silica gel (30% ethyl acetate in hexanes) and concentrating the filtrate under reduced pressure. The obtained residue was triturated with pentanes, left at –30 ºC, and filtered through a fritted funnel to afford the title compound[10] (1.38 g, 3.36 mmol, 84% yield) as a yellow powder.

FTIR (thin film, cm^{-1}) 1596 (w), 1465 (m), 1438 (w), 1360 (s), 1278 (m), 1249 (w), 1165 (s), 1090 (m), 1018 (m), 971 (w), 941 (w), 814 (w); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dd, J = 8.0, 1.5 Hz, 1H), 7.72 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.26 (dt, J = 7.6, 1.5 Hz, 1H), 7.13 (t, J = 6.2 Hz, 1H), 7.07 (td, J = 7.7, 1.6 Hz, 1H), 6.79 (d, J = 8.2 Hz, 1H), 5.08 (dd, J = 10.1, 6.2 Hz, 1H), 5.01 (dd, J = 10.1, 6.2 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.23, 144.23, 140.35, 139.87, 136.03, 130.36, 130.22, 129.77, 128.60, 127.95, 102.03, 101.95, 87.82, 21.74; HRMS (ESI+) calculated for $C_{16}H_{15}INO_2S$ ($[M+H]^+$): 411.9868, found: 411.9855.



***N*-(4-bromo-2-iodophenyl)-4-methyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (1b).** General procedure **A** was followed, using 4-bromo-2-iodoaniline[11] (1.96 g, 6.58 mmol), *p*-toluenesulfonyl chloride (1.32 g, 6.91 mmol) and pyridine (6.6 mL). The residue was purified by automated column chromatography (100 g silica gel, 2→20% ethyl acetate in hexanes) to afford *N*-(4-bromo-2-iodophenyl)-4-methylbenzenesulfonamide (2.73 g, 6.04 mmol, 92% yield) as a brown solid.

Then, general procedure **B** was followed, using *N*-(4-bromo-2-iodophenyl)-4-methylbenzenesulfonamide (2.71 g, 6.00 mmol), potassium carbonate (1.24 g, 9.00 mmol), 3-bromopropyne (0.776 ml, 7.20 mmol) and DMF (15 mL). The residue was purified by automated column chromatography (50 g silica gel, 2→20% ethyl acetate in hexanes) to afford

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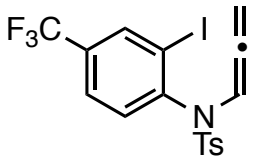
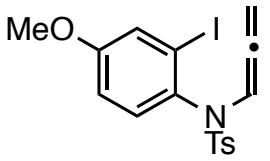
[9] Zenner, J. M.; Larock, R. C. *J. Org. Chem.* **1999**, *64*, 7312–7322.
[10] Fuwa, H.; Sasaki, M. *Org. Biomol. Chem.* **2007**, *5*, 2214–2218.
[11] (a) Kajigaeshi, S.; Kakinami, T.; Yamasaki, H.; Fujisaki, S.; Okamoto, T. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 600–602. (b) Chrétien, J.-M.; Zammattio, F.; Le Grognec, E.; Paris, M.; Cahingt, B.; Montavon, G.; Quintard, J.-P. *J. Org. Chem.* **2005**, *70*, 2870–2873.

N-(4-bromo-2-iodophenyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (2.83 g, 5.77 mmol, 96% yield) as a pink solid.
Finally, general procedure **C** was followed, using *N*-(4-bromo-2-iodophenyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (980 mg, 2.00 mmol), potassium *tert*-butoxide (224 mg, 2.00 mmol) and *tert*-butanol/THF (1:1, 6 mL). The reaction was complete after 6 h. The residue was purified by automated column chromatography (100 g silica gel, 7→9% ethyl acetate in hexanes) to afford the title compound (600 mg, 1.22 mmol, 61% yield) as a yellow powder.
FTIR (thin film, cm^{-1}) 1462 (w), 1362 (w), 1264 (m), 1166 (m), 1050 (w), 1019 (w), 814 (w); ^1H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, J = 2.3 Hz, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.28 – 7.40 (m, 3H), 7.07 (t, J = 6.2 Hz, 1H), 6.60 (d, J = 8.4 Hz, 1H), 5.08 (dd, J = 10.1, 6.1 Hz, 1H), 5.00 (dd, J = 10.1, 6.2 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.11, 144.58, 142.59, 139.21, 135.80, 131.95, 131.19, 129.98, 128.03, 123.51, 102.99, 101.84, 88.33, 21.85; HRMS (ESI+) calculated for $C_{16}H_{14}BrINO_2S$ ($[M+H]^+$): 489.8973, found: 489.8963.



***N*-(2-iodo-4-(trifluoromethyl)phenyl)-4-methyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (1c).** General procedure **A** was followed, using 2-iodo-4-(trifluoromethyl)aniline (2.87 g, 10.0 mmol), *p*-toluenesulfonyl chloride (2.00 g, 10.5 mmol) and pyridine (10 mL). The residue was purified by automated column chromatography (100 g silica gel, 5→28% ethyl acetate in hexanes) to afford *N*-(2-iodo-4-(trifluoromethyl)phenyl)-4-methylbenzenesulfonamide (3.45 g, 7.83 mmol, 78% yield) as a white solid.
Then, general procedure **B** was followed using *N*-(2-iodo-4-(trifluoromethyl)phenyl)-4-methylbenzenesulfonamide (3.45 g, 7.83 mmol), potassium carbonate (1.62 g, 11.8 mmol), 3-bromopropyne (1.05 mL, 9.40 mmol) and DMF (18 mL). The residue was purified by automated column chromatography (100 g silica gel, 2→20% ether in hexanes) to afford *N*-(2-iodo-4-(trifluoromethyl)phenyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (3.30 g, 6.89 mmol, 88% yield) as a white solid.
Finally, general procedure **C** was followed using *N*-(2-iodo-4-(trifluoromethyl)phenyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1.52 g, 3.17 mmol), potassium *tert*-butoxide (356 mg, 3.17 mmol) and *tert*-butanol/THF (1:1, 20 mL). The reaction was complete after 20 min. The residue was purified by automated column chromatography (50 g silica gel, 0.1→2% triethylamine in hexanes) to afford the title compound (1.23 g, 2.57 mmol, 81% yield) as a white solid.
FTIR (thin film, cm^{-1}) 1599 (w), 1495 (w), 1364 (w), 1318 (s), 1281 (w), 1168 (s), 1133 (m), 1079 (m), 907 (w), 721 (w), 664 (m); ^1H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.68 (d, J = 8.1 Hz, 2H), 7.49 (d, J = 8.2 Hz, 1H), 7.35 (d, J = 8.1 Hz, 2H), 7.07 (t, J = 6.2 Hz, 1H), 6.87 (d, J = 8.2 Hz, 1H), 4.98–5.10 (m, 2H), 2.47 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.16, 144.77, 143.50, 137.46 (q, ^3J = 3.8 Hz), 135.79, 132.10 (q, ^2J = 33.2 Hz), 130.57, 130.07, 128.03, 125.78 (q, ^3J = 3.6 Hz), 122.58 (q, ^1J = 273.1 Hz), 102.23, 101.64, 88.42, 21.86. HRMS (ESI+) calculated for $C_{17}H_{14}F_3INO_2S$ ($[M+H]^+$): 479.9742, found: 479.9754.

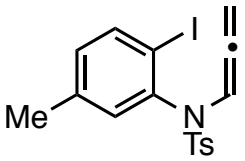


***N*-(2-iodo-4-methoxyphenyl)-4-methyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (1d).** General procedure **A** was followed, using 2-iodo-4-methoxyaniline[12] (2.49 g, 10.0 mmol), *p*-toluenesulfonyl chloride (2.00 g, 10.5 mmol) and pyridine (10 mL). The residue was purified by automated column chromatography (100 g silica gel, 5→40% ethyl acetate in hexanes) to afford *N*-(2-iodo-4-methoxyphenyl)-4-methylbenzenesulfonamide (3.83 g, 9.50 mmol, 95% yield) as a white solid.

Then, general procedure **B** was followed using *N*-(2-iodo-4-methoxyphenyl)-4-methylbenzenesulfonamide (2.01 g, 5.0 mmol), potassium carbonate (1.04 g, 7.5 mmol), 3-bromopropyne (650 µL, 6.0 mmol) and DMF (12.5 mL). The residue was purified by automated column chromatography (100 g silica gel, 5→40 % ethyl acetate in hexanes) to afford *N*-(2-iodo-4-methoxyphenyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (2.10 g, 4.75 mmol, 95% yield) as a white solid.

Finally, general procedure **C** was followed using *N*-(2-iodo-4-methoxyphenyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (555 mg, 1.25 mmol), potassium *tert*-butoxide (140 mg, 1.25 mmol) and THF (3 mL). The reaction was complete after 15 min. The residue was purified by automated column chromatography (50 g silica gel, 5→30% ethyl acetate in hexanes) to afford the title compound (392 mg, 0.89 mmol, 71% yield) as a white solid.

FTIR (thin film, cm^{-1}) 1709 (w), 1590 (m), 1564 (w), 1482 (m), 1438 (s), 1290(m), 1220 (m), 1163 (s), 1088 (m), 1025 (s), 908 (m), 812 (m), 727 (s); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 2.9 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.09 (t, J = 6.2 Hz, 1H), 6.73 (dd, J = 8.8, 2.9 Hz, 1H), 6.60 (d, J = 8.8 Hz, 1H), 5.06 (dd, J = 10.1, 6.2 Hz, 1H), 4.98 (dd, J = 10.1, 6.2 Hz, 1H), 3.77 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.25, 159.74, 144.22[13], 136.09, 132.54, 129.82, 128.00, 125.00, 114.51, 102.51, 102.41, 87.90, 55.76, 21.81; HRMS (ESI+) calculated for $C_{17}H_{17}INO_3S$ ($[M+H]^+$): 441.9974, found: 441.9966.



***N*-(2-iodo-5-methylphenyl)-4-methyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (1e).** General procedure **A** was followed, using 2-iodo-5-methylaniline[14] (980 mg, 4.21 mmol), *p*-toluenesulfonyl chloride (0.842 g, 4.42 mmol) and pyridine (4 mL). The residue was purified by automated column chromatography (50 g silica gel, 0→20% ethyl acetate in hexanes) to afford *N*-(2-iodo-5-methylphenyl)-4-methylbenzenesulfonamide (1.59 g, 4.11 mmol, 98% yield) as a white solid.

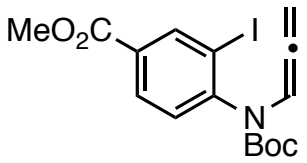
Then, general procedure **B** was followed, using *N*-(2-iodo-5-methylphenyl)-4-methylbenzenesulfonamide (1.58 g, 4.08 mmol), potassium carbonate (846 mg, 6.12 mmol), 3-bromopropyne (0.528 mL, 4.90 mmol) and DMF (10 mL). The residue was purified by

[12] Lizos, D. E.; Murphy, J. A. *Org. Biomol. Chem*. **2003**, *1*, 117–122.
[13] Two quaternary carbons are overlapping.
[14] Wetzel, A.; Gagosz, F. *Angew. Chem., Int. Ed.* **2011**, *50*, 7354–7358.

automated column chromatography (50 g silica gel, 0→25% ethyl acetate in hexanes) to afford *N*-(2-iodo-5-methylphenyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1.65 g, 3.88 mmol, 95% yield) as a yellow solid.

Finally, general procedure **C** was followed, using *N*-(2-iodo-5-methylphenyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (851 mg, 2.00 mmol), potassium *tert*-butoxide (224 mg, 2.00 mmol) and *tert*-butanol/THF (1:1, 4 mL). The reaction was complete after 10 min. The residue was purified by automated column chromatography (100 g silica gel, 0→10→15% ethyl acetate in hexanes, with 1% triethylamine) to afford the title compound (571 mg, 1.34 mmol, 67% yield) as a yellow solid.

FTIR (thin film, cm^{-1}) 1597 (w), 1494 (w), 1471 (m), 1397 (w), 1359 (m), 1288 (w), 1265 (w), 1199 (w), 1185 (w), 1165 (s), 1133 (m), 1090 (m), 1018 (m), 979 (m), 886 (w), 812 (m); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, J = 8.1 Hz, 1H), 7.69 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.06 (t, J = 6.2 Hz, 1H), 6.85 (dd, J = 8.1, 2.1 Hz, 1H), 6.63 (d, J = 2.0 Hz, 1H), 5.06 (dd, J = 10.0, 6.2 Hz, 1H), 4.98 (dd, J = 10.0, 6.1 Hz, 1H), 2.46 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.43, 144.28, 139.94, 139.77, 139.03, 136.37, 131.33, 131.33, 129.77, 128.17, 101.98, 97.44, 87.79, 21.81, 20.93; HRMS (ESI+) calculated for $C_{17}H_{17}INO_2S$ ($[M+H]^+$): 426.0025, found: 426.0010.



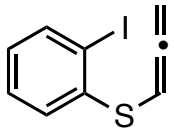
Methyl 4-((*tert*-butoxycarbonyl)(propa-1,2-dien-1-yl)amino)-3-iodobenzoate (1f). To a solution of methyl 4-amino-3-iodobenzoate (1.0 g, 3.6 mmol, 1.0 equiv) in THF (30 mL) was added Boc anhydride (2.36 g, 10.8 mmol, 3.0 equiv) followed by 4-dimethylaminopyridine (40 mg, 0.36 mmol, 0.1 equiv). The solution was stirred at reflux for 12 h before concentrating under reduced pressure and partitioning between 0.5 N hydrochloric acid and ethyl acetate. The aqueous layer was extracted with ethyl acetate and the combined organic phases were washed with brine, dried over sodium sulfate, filtered, and concentrated to afford methyl 4-(bis((tert-butoxy)carbonyl)amino)-3-iodobenzoate as a white solid.

Crude methyl 4-(bis((tert-butoxy)carbonyl)amino)-3-iodobenzoate was dissolved in methanol (11 mL), treated with potassium carbonate (498 mg, 3.6 mmol, 1.0 equiv) and stirred at reflux for 2 h. The mixture was concentrated under reduced pressure and partitioned between 0.5 N hydrochloric acid and ethyl acetate. The aqueous phase was extracted with ethyl acetate, and the combined organic phases were washed with brine (50 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by automated column chromatography (100 g silica gel, 5→20% ethyl acetate in hexanes) to afford methyl 4-((*tert*-butoxycarbonyl)amino)-3-iodobenzoate[15] (1.17 g, 3.10 mmol, 86% over 2 steps) as a white solid.

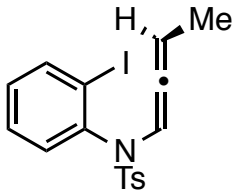
Then, general procedure **B** was followed using methyl 4-((*tert*-butoxycarbonyl)amino)-3-iodobenzoate (974 mg, 2.58 mmol), potassium carbonate (535 mg, 3.87 mmol), 3-bromopropyne (345 μL, 3.10 mmol) and DMF (7 mL). The residue was purified by automated column chromatography (25 g silica gel, 2→13% ether in hexanes) to afford methyl 4-((*tert*-butoxycarbonyl)(prop-2-yn-1-yl)amino)-3-iodobenzoate (1.05 g, 2.54 mmol, 98% yield) as a white solid.

[15] Darnbrough, S.; Mervic, M.; Condon; S. M.; Burns, C. J. *Synth. Comm*. **2001**, *31*, 3273–3280.

Finally, general procedure **C** was followed using methyl 4-((*tert*-butoxycarbonyl)(prop-2-yn-1-yl)amino)-3-iodobenzoate (625 mg, 1.5 mmol), potassium *tert*-butoxide (168 mg, 1.5 mmol) and THF (3 mL). The reaction was complete after 3 min. The residue was purified by automated column chromatography (25 g silica gel, 3→25% ether in hexanes) to afford the title compound (405 mg, 1.07 mmol, 65% yield) as a white solid.
FTIR (thin film, cm^{-1}) 2976 (w), 1710 (s), 1591 (m), 1518 (w), 1478 (m), 1435 (w), 1367 (m), 1286 (s), 1248 (s), 1159 (s), 1115 (m), 849 (w), 765 (w); ^1H NMR (500 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.27–7.35 (m, 2H), 4.98–5.05 (m, 2H), 3.93 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.43, 165.27 , 150.98 , 146.09, 140.66, 130.79, 130.21, 129.56, 100.80, 99.51, 87.49, 82.19, 52.66, 28.27; HRMS (ESI+) calculated for $C_{11}H_{11}INO_2$ ($[M–Boc+H+H]^+$): 315.9434, found: 315.9424.



(2-iodophenyl)(propa-1,2-dien-1-yl)sulfane (1h). Prepared in analogy to a literature procedure.[16] A solution of (2-iodophenyl)(prop-2-yn-1-yl)sulfane[17] (850 mg, 3.1 mmol, 1.0 equiv) in *tert*-butanol (30 mL) was treated with aqueous sodium hydroxide (10% w/w, 1.11 mL, 2.79 mmol, 0.9 equiv) and heated at reflux for 30 min. After cooling to room temperature, the reaction mixture was diluted with ether and washed with water, aqueous ammonium chloride, and brine. The organic layer was dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by manual column chromatography (silica gel, 1→4% ether in hexanes) to afford the title compound (565 mg, 2.06 mmol, 66% yield) as a colorless oil.[18]
FTIR (thin film, cm^{-1}) 2910 (w), 1557 (m), 1567 (w), 1439 (s), 1424 (m), 1254 (w), 1091 (w), 1007 (s), 732 (s); ^1H NMR (500 MHz, $CDCl_3$) δ 7.79 (dd, J = 7.9, 1.3 Hz, 1H), 7.25–7.45 (m, 2H), 6.89 (ddd, J = 7.9, 7.0, 2.0 Hz, 1H), 5.92 (t, J = 6.2 Hz, 1H), 5.01 (d, J = 6.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.00, 141.36, 139.55, 128.82, 127.77, 127.27, 97.66, 81.18, 78.67; HRMS (ESI+) calculated for C_9H_7IS ($[M]^+$): 273.9313, found: 273.9309.



(+/–)

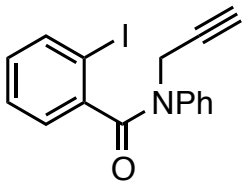
(+/–)-*N*-(buta-1,2-dien-1-yl)-*N*-(2-iodophenyl)-4-methylbenzenesulfonamide (1i). General procedure **B** was followed, substituting 1-bromo-2-butyne as the electrophile, and using *N*-(2-iodophenyl)-4-methylbenzenesulfonamide[9] (1.12 g, 3.0 mmol), potassium carbonate (622 mg, 4.5 mmol), 1-bromo-2-butyne (315 μL, 3.6 mmol) and DMF (7 mL). The residue was purified

[16] Yeo, S.-K.; Shiro, M.; Kanematsu, K. *J. Org. Chem*. **1994**, *59*, 1621–1632.
[17] Arnau, N.; Moreno-Mafias, M.; Pleixats, R. *Tetrahedron* **1993**, *49*, 11019–11028.
[18] This allene is particularly unstable. Despite storing at –30 ºC, fast decomposition was observed. Ideally, it should be used as soon as possible after synthesis.

by automated column chromatography (100 g silica gel, 5→20% ethyl acetate in hexanes) to afford *N*-(but-2-yn-1-yl)-*N*-(2-iodophenyl)-4-methylbenzenesulfonamide (1.24 g, 2.91 mmol, 97% yield) as a white solid.

Then, general procedure **C** was followed using *N*-(but-2-yn-1-yl)-*N*-(2-iodophenyl)-4-methylbenzenesulfonamide (1.13 g, 2.67 mmol), potassium *tert*-butoxide (300 mg, 2.67 mmol) and *tert*-butanol/THF (1:1, 5.3 mL). The reaction showed no additional conversion after 24 h. The residue was purified by automated column chromatography (100 g silica gel, 4→40% ethyl acetate in hexanes) to afford the title compound (397 mg, 0.93 mmol, 35% yield) as a white solid and as a mixture of two rotamers in a 1:1 ratio.[19]

FTIR (thin film, cm^{-1}) 2920 (w), 1597 (w), 1465 (m), 1398 (w), 1355 (m), 1265 (w), 1160 (s), 1090 (m), 1019 (m), 858 (w), 813 (m), 735 (w), 711 (s); ^1H NMR (500 MHz, C_6D_6) δ 7.69 (d, J = 8.2 Hz, 2H), 7.61 (t, J = 7.7 Hz, 1H), 7.27–7.32 (m, 1H), 6.87 (dd, J = 18.4, 7.9 Hz, 2H), 6.76 (t, J = 7.6 Hz, 1H), 6.71 (d, J = 8.2 Hz, 1H), 6.40–6.44 (m, 1H), 5.12–5.18 (m, 1H), 1.85 (s, 3H), 1.31 (dd, J = 6.9, 2.7 Hz, 1.5H), 1.13 (dd, J = 6.9, 2.7 Hz, 1.5H); ^{13}C NMR (125 MHz, C_6D_6) δ 196.36, 196.18, 143.66, 143.62, 141.21, 141.05, 140.55, 140.54, 137.56, 137.27, 130.95, 130.95, 130.44, 130.12, 129.77, 129.71, 128.58, 128.48, 128.36, 128.36, 102.93, 102.28, 102.11, 102.06, 99.44, 99.00, 21.21, 21.20, 15.47, 15.40; HRMS (ESI+) calculated for $C_{17}H_{17}INO_2S$ ($[M+H]^+$) 426.0025, found: 426.0026.



2-iodo-*N*-phenyl-*N*-(prop-2-yn-1-yl)benzamide (S1). Prepared in analogy to a published procedure.[20] To a solution of 2-iodobenzoyl chloride (3.57 g, 13.4 mmol, 1 equiv) in dichloromethane (5 mL) at 0 °C, *N*-(prop-2-yn-1-yl)aniline[21] (1.76 g, 13.4 mmol, 1 equiv), followed by triethylamine (1.63 g, 2.24 ml, 16.1 mmol, 1.2 equiv) in dichloromethane (12 mL), were added. After stirring at room temperature for 12 h, the reaction mixture was quenched with water (50 mL). The organic layer was separated, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by automated column chromatography (100 g silica gel, 2→40% ethyl acetate in hexanes) to afford the title compound (3.29 g, 9.11 mmol, 68% yield) as a yellow solid.

FTIR (thin film, cm^{-1}) 1652 (s), 1595 (w), 1586 (w), 1493 (m), 1421 (m), 1383 (m), 1300 (m), 1265 (m), 1163 (w), 1018 (w), 984 (w), 765 (m); ^1H NMR (500 MHz, CD_3OD) δ 7.69 (dd, J = 8.0, 1.1 Hz, 1H), 7.32–7.47 (m, 2H), 7.05–7.33 (m, 5H), 6.85–7.01 (m, 1H), 4.70 (d, J = 2.5 Hz, 2H), 2.72 (t, J = 2.5 Hz, 1H); ^{13}C NMR (125 MHz, CD_3OD) δ 171.84, 142.91, 142.32, 140.37, 131.26, 130.06, 129.78, 129.33, 129.25, 128.55, 94.04, 79.20, 74.09, 39.68; HRMS (ESI+) calculated for $C_{16}H_{13}INO$ ($[M+H]^+$): 362.0042, found: 362.0028.

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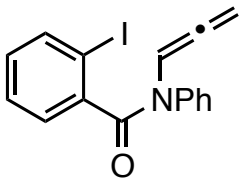
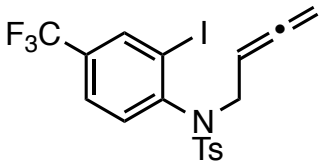
[19] 75% yield based on recovered starting material.

[20] Fretwell, P.; Grigg, R.; Sansano, J. M.; Sridharan, V.; Sukirthalingam, S.; Wilson, D.; Redpath, J. *Tetrahedron* **2000**, *56*, 7525–7539.

[21] Majumdar, K.; Nandi, R.; Ganai, S.; Taher, A. *Synlett* **2011**, 116–120.



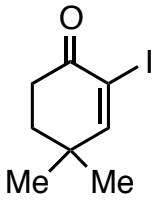
2-iodo-*N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzamide (1k). Prepared in analogy to a published procedure.[20] To a solution of 2-iodo-*N*-phenyl-*N*-(prop-2-yn-1-yl)benzamide (2.02 g, 5.6 mmol, 1 equiv) in DMF (12.5 ml) at room temperature, sodium hydroxide (269 mg, 6.72 mmol, 1.2 equiv) was added. After stirring at room temperature overnight, dichloromethane (25 mL) was added to the reaction mixture. The organic layer was washed with water (25 mL) and aqueous lithium chloride (10% w/w, 25 mL). The organic layer was then dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by automated column chromatography (100 g silica gel, 2→20% ethyl acetate in hexanes) to afford the title compound (800 mg, 2.22 mmol, 40% yield) as a yellow oil.[22]
FTIR (thin film, cm^{-1}) 1651 (s), 1596 (w), 1585 (w), 1491 (m), 1465 (m), 1439 (m), 1365 (s), 1324 (s), 1279 (m), 1264 (m), 1169 (w), 1040 (w), 1016 (m), 875 (w), 764 (m); ^{1}H NMR (500 MHz, CD_3OD) δ 7.66–7.76 (m, 2H), 7.29–7.34 (m, 2H), 7.12–7.27 (m, 5H), 6.87–6.97 (m, 1H), 5.12 (d, J = 6.4 Hz, 2H); ^{13}C NMR (125 MHz, CD_3OD) 202.89, 168.75, 141.51, 138.88, 138.70, 129.91, 128.57, 128.52, 128.44, 128.13, 127.13, 100.04, 92.70, 85.92; HRMS (ESI+) calculated for $C_{16}H_{13}INO$ ($[M+H]^+$): 362.0042, found: 362.0029.



***N*-(buta-2,3-dien-1-yl)-*N*-(2-iodo-4-(trifluoromethyl)phenyl)-4-methylbenzenesulfonamide (1l).** Prepared in analogy to a published procedure.[6] A suspension of *N*-(2-iodo-4-(trifluoromethyl)phenyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide[23] (479 mg, 1.0 mmol, 1.0 equiv), diisopropylamine (163 µL, 1.2 mmol, 1.2 equiv), copper(I) bromide (44 mg, 0.30 mmol, 0.3 equiv), and 37% aqueous formaldehyde (125 µL, 1.6 mmol, 1.6 equiv) in dioxane (2 mL) was warmed from room temperature to reflux. After 4 h, the reaction mixture was cooled to room temperature, and acetic acid (2.5 mL, 1 N) was added. The resulting mixture was allowed to stir vigorously for 10 min before extracting three times with ether. The combined organic layers were then washed with aqueous sodium bicarbonate (saturated), dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by automated column chromatography (50 g silica gel, 3→30% ethyl acetate in hexanes) to afford the title compound (296 mg, 0.60 mmol, 60% yield) as a white solid.
FTIR (thin film, cm^{-1}) 1955 (w), 1598 (w), 1354 (m), 1317 (s), 1163 (s), 1131 (s), 1079 (s), 1026 (w), 905 (w), 850 (w), 815 (w), 718 (m), 656 (m); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, J = 2.1 Hz, 1H), 7.67 (d, J = 8.0 Hz, 2H), 7.55 (dd, J = 8.3, 2.1 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.3 Hz, 1H), 5.07–5.25 (m, 1H), 4.58 (dt, J = 6.5, 2.2 Hz, 2H), 4.20–4.22 (m, 2H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.09, 145.92, 144.35, 137.46, 136.18, 131.82 (q, ^{2}J = 33.2

[22] 63% yield based on recovered starting material.
[23] See procedure for the synthesis of **1c**.

Hz), 131.34, 129.63, 128.21, 125.76, 121.63 (q, ^{1}J = 273.1 Hz), 103.49, 85.41, 76.44, 50.90, 21.80; HRMS (ESI+) calculated for $C_{18}H_{16}F_3INO_2S$ ($[M+H]^+$): 493.9889, found: 493.9889.



2-iodo-4,4-dimethylcyclohex-2-enone (5b). To a solution of 4,4-dimethylcyclohex-2-enone (1.24 g, 10.0 mmol, 1.0 equiv) in CH_2Cl_2/pyridine (1:1, 24 mL) at 0 °C, iodine (3.04 g, 12 mmol, 1.2 equiv) was added portionwise over 10 min. After stirring at room temperature for 12 h, the brown solution was poured into aqueous sodium thiosulfate (saturated) and ether. The layers were separated, and the organic phase was washed with hydrochloric acid (1 N, 2x), dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by automated column chromatography (100 g silica gel, 4→5% ethyl acetate in hexanes) to afford 2-iodo-4,4-dimethylcyclohex-2-enone (2.2 g, 8.8 mmol, 88% yield) as a white solid.
FTIR (thin film, cm^{-1}) 2959 (w), 2926 (w), 2864 (w), 1686 (s), 1583 (m), 1466 (w), 1416 (w), 1364 (w), 1319 (m), 1275 (w), 1142 (m), 1014 (w), 991 (w), 957 (m), 800 (m); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (s, 1H), 2.67 (t, J = 6.9 Hz, 2H), 1.92 (t, J = 6.9 Hz, 2H), 1.19 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.18, 168.22, 101.93, 38.16, 36.07, 33.47, 27.48; HRMS (ESI+) calculated for $C_8H_{12}IO$ ($[M+H]^+$): 250.9933, found: 250.9929.

III. Procedure for reaction optimization (Table 1)

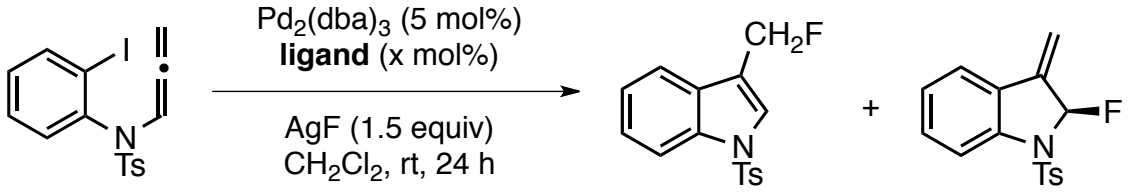
A 0.1 M stock solution was prepared in dichloromethane (1 mL/rxn), containing *N*-(2-iodophenyl)-4-methyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (**1a**, 0.1 mmol/rxn, 1 equiv) and naphthalene (5 mg/rxn, 0.4 equiv). An aliquot was reserved for measurement of the initial ratio by LC/MS. To oven-dried 1-dram borosilicate vials, tris(dibenzylideneacetone)dipalladium (4.6 mg, 0.005 mmol), the appropriate ligand (0.01 mmol for bidentate ligands, 0.02 mmol for monodentate ligands), and the appropriate fluoride source[24] (0.15 mmol) were added. Three times, the vials were purged under high vacuum and filled with nitrogen. Then, each vial was charged with stock solution (1 mL). After stirring at 700 rpm for 24 h (with the vials covered in aluminum foil), half of each reaction mixture was filtered through a short plug of silica gel, eluting with ether. Conversion and yield were determined by LC/MS using a commercial column (a response factor was calculated using ^{1}H NMR). The other half of the reaction mixture was filtered through a short plug of Celite, eluting with $CDCl_3$. Regioselectivity was determined by ^{19}F NMR (linear product: –208 ppm, branched product: –141 ppm).

[24] Reactions with KF and CsF were set up in a glovebox due to the hygroscopicity of these salts. Reactions with AgF in the glovebox gave comparable results to those set up on the benchtop.

IV. Additional reaction optimization

For the reactions in this section, procedures similar to those in section III were used.

Table S1. *Evaluation of additional conditions for the carbofluorination of* **1a**

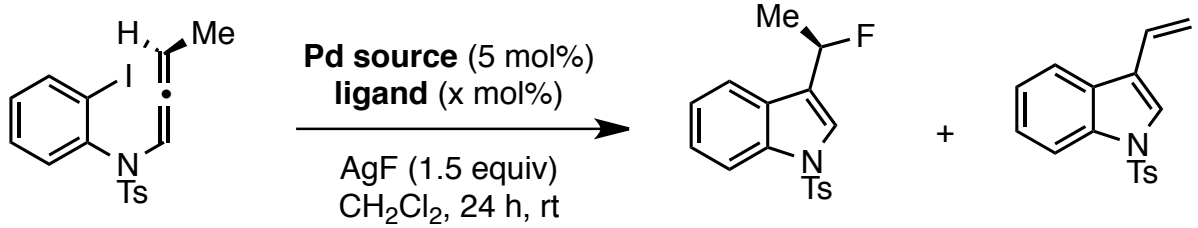


1a **2a** (+/–)-**3a**

entry	ligand (mol%)	yield (%)[a]	2a:3a[b]
1	Xantphos (10)	14	1:2
2	BINAP (10)	10	nd[c]
3	dppp (10)	12	nd[c]
4	P(4-CF_3-C_6H_4)$_3$ (20)	49	>20:1
5[d]	P(3,5-CF_3-C_6H_3)$_3$ (20)	21	2:1
6	none [with $Pd_2(dba)_3$]	47	5:1
7	no Pd, no ligand	0	nd[c]

[a] Combined yield of **2a** and **3a**, determined by HPLC using naphthalene as a quantitative internal standard. [b] Determined by ^{19}F NMR. [c] Not determined. [d] Toluene as solvent.

Table S2. *Evaluation of reaction conditions for disubstituted allene* **1i**

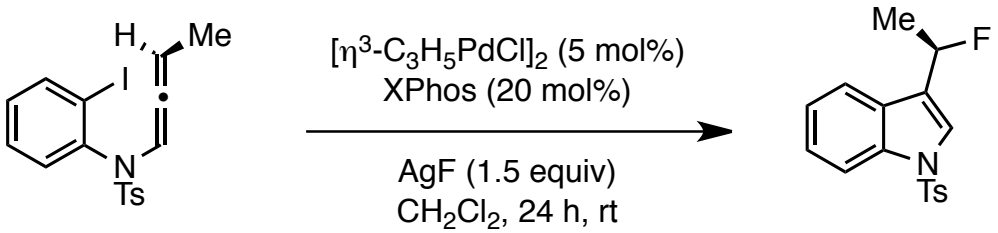


(+/–)-**1i** (+/–)-**2i** **diene**

entry	ligand (mol%)	Pd source	yield (%)[a]	2i:diene[b]
1	Xantphos (10)	$Pd_2(dba)_3$	33	1:5
2	dppf (10)	$Pd_2(dba)_3$	69	0:1
3	P(3,5-CF_3-C_6H_3)$_3$ (30)	$Pd_2(dba)_3$	65	2:1
4	XPhos (20)	$Pd_2(dba)_3$	62	3:1
5	XPhos (20)	[η^3-$C_3H_5PdCl]_2$	64	4:1

[a] Combined yield of **2i** and **3i**, determined by HPLC using naphthalene as a quantitative internal standard; yields are not corrected by a response factor; 100% conversion was observed in all cases. [b] Determined by ^{1}H NMR.

Scheme S2. *Racemization in the carbofluorination of enantioenriched allene* **1i**

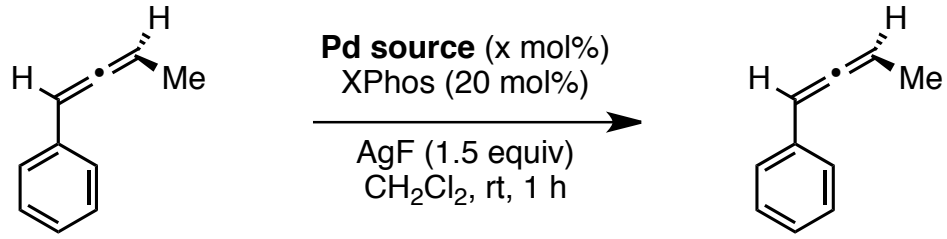


1i
95% ee[a]

2i
73% yield
4% ee[b]

[a] Enantiomers separated by preparative chiral HPLC. Configurations drawn are arbitrary.
[b] Determined by chiral HPLC, assay conditions: Chiralpak AS-H, 5% hexanes/isopropanol, 1 mL/min, t_R(enantiomer 1) = 13.2 min, t_R(enantiomer 2) = 16.7 min, t_R(diene) = 12.2 min.

Table S3. *Investigation of the racemization of a disubstituted allene*[a]



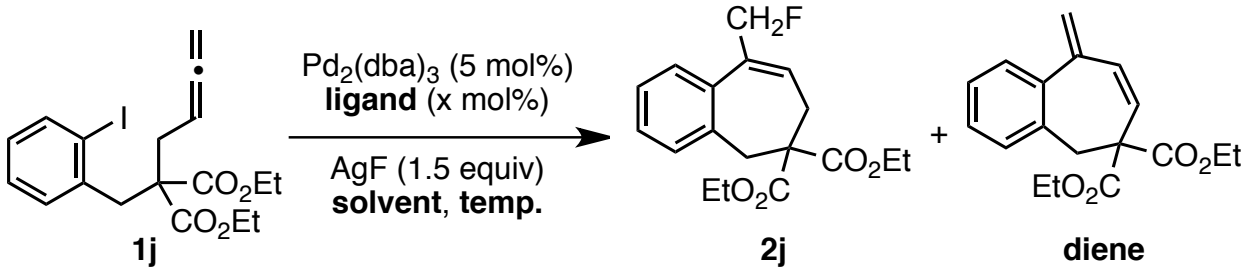
S2 **S2**

entry	Pd source (mol%)	AgF present?	ee (%)[b]
1	$Pd(PPh_3)_4$ (10)	no	35
2	$Pd(PPh_3)_4$ (10)	yes	55
3	$[\eta^3\text{-}C_3H_5PdCl]_2$ (5)	no	88
4	$[\eta^3\text{-}C_3H_5PdCl]_2$ (5)	yes	25

[a] **S2** was prepared in 98% ee by a literature procedure.[25] [b] Determined by chiral HPLC: Chiralcel OJ-H, 1% hexanes/isopropanol, 1 mL/min.

[25] Myers, A. G.; Zheng, B. *J. Am. Chem. Soc.* **1996,** *118,* 4492–4493.

Table S4. *Evaluation of reaction conditions for substrate* ***1j***



1j **2j** **diene**

entry	ligand (mol%)	solvent	temp. (°C)	conv (%)[a]	2j:diene[b]
1	P(3,5-CF_3-C_6H_3)$_3$ (30)	CH_2Cl_2	rt	30	0:1
2	XPhos (20)	CH_2Cl_2	rt	20	0:1
3	XPhos (20)	toluene	60 °C	100	1:5
4	BINAP (20)	toluene	40 °C	40	nd[c]
5	dppf (10)	toluene	40 °C	50	0:1
6	(*S,S*)-DACH-Naphthyl Trost (10)	toluene	40 °C	30	0:1
7	P(3,5-CF_3-C_6H_3)$_3$ (30)	toluene	40 °C	50	0:1
8	Xantphos (10)	toluene	40 °C	60	2:1
9	PPh_3 (30)	toluene	40 °C	73	3:1

[a] Determined by HPLC using naphthalene as a quantitative internal standard. [b] Determined by ^{1}H NMR. [c] Not determined since only degradation was observed.

V. Procedure for intramolecular carbofluorination (Table 2)

General procedure D for intramolecular carbofluorination of amines (Table 2, conditions A). After cooling to room temperature in a desiccator, an oven-dried flask was charged with the iodoallene (1.0 equiv), silver(I) fluoride (1.5 equiv), P(3,5-CF_3-C_6H_3)$_3$ (20 mol%), and tris(dibenzylideneacetone)dipalladium (5 mol%). Three times, the flask was purged under high vacuum and filled with nitrogen,[26] before charging with dichloromethane (0.1 M) and removing the nitrogen line. The reaction mixture was allowed to stir at room temperature, covered in aluminum foil, for 24 h.[27] The reaction mixture was then filtered through a pad of Celite, eluting with dichloromethane. After concentrating the filtrate under reduced pressure, the residue was purified by manual column chromatography[28] to afford the desired product. Yields for at least two runs were obtained.

General procedure E for intramolecular carbofluorination of ethers and thioethers (Table 2, conditions B). After cooling to room temperature in a desiccator, an oven-dried flask was charged with the iodoallene (1.0 equiv). A separate oven-dried flask was charged with silver(I) fluoride (1.5 equiv), XPhos (20 mol%), and tris(dibenzylideneacetone)dipalladium (5 mol%). Three times, each flask was purged under high vacuum and filled with nitrogen.[26] The flask with the iodoallene was then charged with toluene (0.1 M), and the appropriate amount (1 equiv) of this solution was transferred via syringe to the flask with the other reagents, under nitrogen. After removing the nitrogen line, the reaction mixture was allowed to stir at 60 ºC, covered in aluminum foil, for 2–3 h.[27] After cooling to room temperature, the reaction mixture was filtered through a pad of Celite, eluting with dichloromethane. After concentrating the filtrate under reduced pressure, the residue was purified by manual column chromatography[28] to afford the desired product. Yields for at least two runs were obtained.

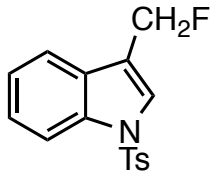
General procedure F for intramolecular carbofluorination for forming 6- and 7-membered rings (Table 2, conditions C). After cooling to room temperature in a desiccator, an oven-dried flask was charged with the iodoallene (1.0 equiv), silver(I) fluoride (1.5 equiv), PPh_3 (30 mol%), and tris(dibenzylideneacetone)dipalladium (5 mol%). Three times, the flask was purged under high vacuum and filled with nitrogen,[26] before charging with toluene (0.1 M) and removing the nitrogen line. The reaction mixture was allowed to stir at 40 ºC, covered in aluminum foil, for 24 h.[27] After cooling to room temperature, the reaction mixture was filtered through a pad of Celite, eluting with dichloromethane. After concentrating the filtrate under reduced pressure, the residue was purified by manual column chromatography[28] to afford the desired product. Yields for at least two runs were obtained.

Note: The heterogeneity of the reaction was found to have a large impact on the outcome (rate

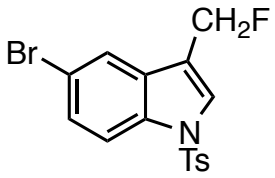
[26] For reproducible reactions, this procedure is recommended. Reactions set up without the exclusion of air or moisture often provided comparable results but were not always consistent.
[27] Since halting the reaction to remove a sample for TLC analysis resulted in suboptimal results, carbofluorinations were run for the indicated time (even though some were complete in less time).
[28] Chromatography was performed on silica gel pre-treated with triethylamine to limit product decomposition.

and yield). Ideally, carbofluorinations should be conducted in a round-bottom flask with an egg-shaped stirbar, magnetically stirring at a rate of 600–800 rpm.

Note: The carbofluorination products were obtained in ≥95% purity, since impurities derived from the ligand or dibenzylideneacetone (dba) were sometimes difficult to remove. The amounts of these impurities are noted when present, and the reported yields were calculated by removing the mass of any impurities from the total mass isolated.

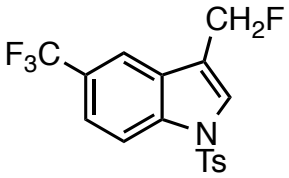


3-(fluoromethyl)-1-tosyl-1*H*-indole (2a). General procedure **D** was followed, using *N*-(2-iodophenyl)-4-methyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (206 mg, 0.5 mmol), P(3,5-CF_3-C_6H_3)$_3$ (67 mg, 0.1 mmol), silver(I) fluoride (95 mg, 0.75 mmol), tris(dibenzylideneacetone)dipalladium (23 mg, 0.025 mmol), and dichloromethane (5 mL). Purification by manual column chromatography (silica gel, 0→5→10→15% ethyl acetate in hexanes, with 2% triethylamine) afforded the title compound (119 mg, 95% w/w with dba, 0.373 mmol, 75% yield) as a yellow solid. A second run provided 100 mg, 0.330 mmol, 66% yield; average yield was 71%.
FTIR (thin film, cm^{-1}) 1596 (w), 1447 (m), 1374 (m), 1281 (m), 1265 (w), 1189 (m), 1172 (s), 1138 (m), 1121 (s), 1102 (m), 1084 (m), 973 (s), 812 (m), 774 (w), 671 (s); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 8.3 Hz, 1H), 7.79 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 4.7 Hz, 1H), 7.62 (J = 7.7 Hz, 1H), 7.36 (dt, J = 7.4, 0.9 Hz, 1H), 7.22–7.31 (m, 3H), 5.51 (dm, J = 48.3 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.41, 135.18 (d, ^{2}J = 22.2 Hz), 130.15, 129.35, 127.05, 125.99 (d, ^{3}J = 9.4 Hz), 125.37, 123.72, 119.88, 117.80, 117.64, 113.77, 76.57 (d, ^{1}J = 162.8 Hz), 21.76; ^{19}F NMR (282 MHz, $CDCl_3$) δ –207.35 (m); HRMS (ESI+) calculated for $C_{16}H_{15}FNO_2S$ ($[M+H]^+$): 304.0808, found: 304.0813.

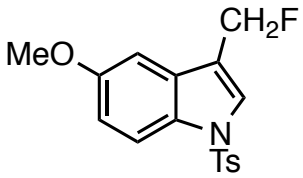


5-bromo-3-(fluoromethyl)-1-tosyl-1*H*-indole (2b). General procedure **D** was followed, substituting allylpalladium chloride dimer (5 mol%) as catalyst and using a shorter reaction time (12 h), and using *N*-(4-bromo-2-iodophenyl)-4-methyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (245 mg, 0.5 mmol), P(3,5-CF_3-C_6H_3)$_3$ (67 mg, 0.1 mmol), silver(I) fluoride (95 mg, 0.75 mmol), allylpalladium chloride dimer (9.1 mg, 0.025 mmol), and dichloromethane (5 mL). The reaction was stopped after 12 h. Purification by manual column chromatography (silica gel, 0→7→20% ethyl acetate in hexanes, with 2% triethylamine) afforded the title compound (159 mg, 97% w/w with ligand, 0.403 mmol, 81% yield) as a yellow solid. A second run provided 164 mg (96% w/w with ligand), 0.412 mmol, 82% yield; average yield was 82%.

FTIR (thin film, cm^{-1}) 1596 (w), 1441 (m), 1374 (m), 1295 (w), 1189 (m), 1174 (s), 1150 (m), 1126 (s), 1109 (m), 1088 (w), 971 (m), 799 (m), 676 (m), 664 (s); ^1H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, J = 8.8 Hz, 1H), 7.76–7.78 (m, 1H), 7.74–7.76 (m, 2H), 7.64 (d, J = 4.5 Hz, 1H), 7.45 (dd, J = 8.8, 1.9 Hz, 1H), 7.23–7.26 (m, 2H), 5.47 (d, J = 48.3 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 146.50, 134.97, 134.37, 131.52, 130.64, 128.57, 127.64 (d, ^3J = 9.1 Hz), 127.35, 123.10, 117.61 (d, ^2J = 19.9 Hz), 117.50, 115.61, 76.68 (d, ^1J = 162.3 Hz), 21.89; ^{19}F NMR (282 MHz, $CDCl_3$) δ –207.91 (m); HRMS (ESI+) calculated for $C_{16}H_{13}BrNO_2S$ ($[M–F]^+$): 361.9850, found: 361.9837.

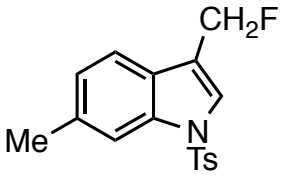


3-(fluoromethyl)-1-tosyl-5-(trifluoromethyl)-1H-indole (2c). General procedure **D** was followed using *N*-(2-iodo-4-(trifluoromethyl)phenyl)-4-methyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (144 mg, 0.30 mmol), P(3,5-CF_3-C_6H_3)$_3$ (40.2 mg, 0.60 mmol), silver(I) fluoride (57 mg, 0.45 mmol), tris(dibenzylideneacetone)dipalladium (13.7 mg, 0.015 mmol), and dichloromethane (3.0 mL). Purification by manual column chromatography (silica gel, 2→5→10% triethylamine in hexanes) afforded the title compound (70 mg, 0.19 mmol, 63% yield) as a white solid. A second run provided 78 mg, 0.21 mmol, 70% yield; average yield was 67%.
FTIR (thin film, cm^{-1}) 2925 (w), 1622 (w), 1569 (w), 1449 (w), 1377 (m), 1355 (w), 1313 (s), 1282 (m), 1170 (s), 1105 (s), 1123 (s), 1060 (m), 813 (w), 703 (w), 667 (s); ^1H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, J = 8.6 Hz, 1H), 7.91 (s, 1H), 7.80 (d, J = 8.2 Hz, 2H), 7.75 (d, J = 4.5 Hz, 1H), 7.60 (dd, J = 8.6 Hz, 1H), 7.27 (d, J = 8.1 Hz, 2H), 5.54 (d, J = 48.1 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.99, 136.71, 134.74, 130.37, 129.05, 127.46 (d, ^2J= 9.0 Hz), 127.09, 126.19 (q, ^2J = 32.5 Hz), 124.49 (q, ^1J = 272.2 Hz), 123.40, 122.19 (q, ^3J = 3.5 Hz), 117.66 (q, ^3J = 4.1 Hz), 114.12, 76.18 (d, ^1J = 163.7 Hz), 21.80; ^{19}F NMR (282 MHz, $CDCl_3$) δ –61.27 (s), –208.11 (m); HRMS (ESI+) calculated for $C_{17}H_{14}F_3NO_2S$ ($[M–F]^+$): 352.0619, found: 352.0616.

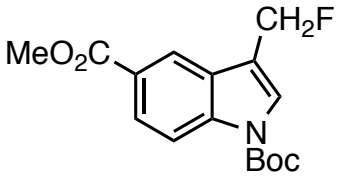


3-(fluoromethyl)-5-methoxy-1-tosyl-1H-indole (2d). General procedure **D** was followed, using *N*-(2-iodo-4-methoxyphenyl)-4-methyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (132 mg, 0.30 mmol), P(3,5-CF_3-C_6H_3)$_3$ (40.2 mg, 0.06 mmol), silver(I) fluoride (57 mg, 0.45 mmol), tris(dibenzylideneacetone)dipalladium (13.7 mg, 0.015 mmol), and dichloromethane (3 mL). Purification by manual column chromatography (silica gel, 0→2→5→10% ethyl acetate in hexanes, with 2% triethylamine) afforded the title compound (80 mg, 0.24 mmol, 80% yield) as a white solid. A second run provided 72 mg, 0.22 mmol, 72% yield; average yield was 76%.
FTIR (thin film, cm^{-1}) 2925 (w), 1614 (w), 1597 (w), 1477 (m), 1450 (m), 1436 (m), 1370 (s), 1215 (s), 1170 (s), 1097 (m), 1119 (s), 1030 (s), 975 (s), 885 (m), 807 (m), 736 (m), 705 (s); ^1H

NMR (500 MHz, $CDCl_3$) δ 7.87 (d, J = 9.1 Hz, 1H), 7.75 (d, J = 8.1 Hz, 2H), 7.60 (d, J = 4.8 Hz, 1H), 7.22 (d, J = 8.1 Hz, 2H), 7.02 (d, J = 2.5 Hz, 1H), 6.96 (dd, J = 9.1, 2.5 Hz, 1H), 5.48 (d, ^{2}J = 48.5 Hz, 2H), 3.83 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.75, 145.31, 135.05, 130.37, 129.91, 130.10 126.95, 126.68, 126.75, 117.71 (d, ^{2}J = 19.8 Hz), 114.70 (d, ^{3}J = 4.3 Hz), 101.87, 76.60 (d, ^{1}J = 162.5 Hz), 55.81, 21.73; ^{19}F NMR (282 MHz, $CDCl_3$) δ –207.18 (m); HRMS (ESI+) calculated for $C_{17}H_{17}FNO_3S$ ($[M+H]^+$): 334.0913, found: 334.0905.

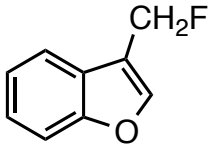


3-(fluoromethyl)-6-methyl-1-tosyl-1*H*-indole (2e). General procedure **D** was followed, using *N*-(2-iodo-5-methylphenyl)-4-methyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (213 mg, 0.5 mmol), P(3,5-CF_3-C_6H_3)$_3$ (67 mg, 0.1 mmol), silver(I) fluoride (95 mg, 0.75 mmol), tris(dibenzylideneacetone) dipalladium (23 mg, 0.025 mmol), and dichloromethane (5 mL). Purification by manual column chromatography (silica gel, 0→5→10% ethyl acetate in hexanes, with 2% triethylamine) afforded the title compound (125 mg, 97% w/w with dba and ligand, 0.382 mmol, 76% yield) as a yellow solid. A second run provided 124 mg (98% w/w with dba and ligand), 0.383 mmol, 77% yield; average yield was 77%.
FTIR (thin film, cm^{-1}) 1374 (w), 1265 (m), 1175 (m), 1113 (w), 981 (w), 812 (w), 673 (m); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75–7.81 (m, 3H), 7.57 (d, J = 4.8 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.22 –7.26 (m, 2H), 7.09–7.13 (m, 1H), 5.48 (d, J = 48.4 Hz, 2H), 2.48 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.29, 135.69, 135.61, 135.23, 130.13, 127.07, 126.98, 125.34 (d, ^{3}J = 9.5 Hz), 125.27, 119.43, 117.68 (d, ^{2}J = 19.6 Hz), 113.80, 76.65 (d, ^{1}J = 162.5 Hz), 22.14, 21.76; ^{19}F NMR (282 MHz, $CDCl_3$) δ –207.29 (m); HRMS (ESI+) calculated for $C_{17}H_{17}FNO_2S$ ($[M+H]^+$): 318.0964, found: 318.09

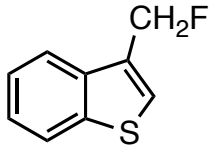


1-*tert*-butyl 5-methyl 3-(fluoromethyl)-1H-indole-1,5-dicarboxylate (2f). General procedure **D** was followed, using methyl 4-((*tert*-butoxycarbonyl)(propa-1,2-dien-1-yl)amino)-3-iodobenzoate (125 mg, 0.30 mmol), P(3,5-CF_3-C_6H_3)$_3$ (40.2 mg, 0.06 mmol), silver(I) fluoride (57 mg, 0.45 mmol), tris(dibenzylideneacetone)dipalladium (13.7 mg, 0.015 mmol), and dichloromethane (3.0 mL). Purification by manual column chromatography (silica gel, 0→2→5% ether in hexanes, with 2% triethylamine) afforded the title compound (65 mg, 0.21 mmol, 70% yield) as a yellow solid. A second run provided 63 mg, 0.20 mmol, 68% yield; average yield was 69 %.
FTIR (thin film, cm^{-1}) 2955 (w), 1741 (s), 1720 (s), 1617 (w), 1449 (m), 1389 (m), 1356 (m), 1281 (s), 1240 (s), 1155 (s), 1077(s), 972 (w), 768 (w); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (d, J = 1.7 Hz, 1H), 8.20 (d, J = 8.8 Hz, 1H), 8.07 (dd, J = 8.8, 1.7 Hz, 1H), 7.74 (d, J = 4.8 Hz, 1H), 5.57 (d, J = 48.5 Hz, 2H), 3.95 (s, 3H), 1.68 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.46, 149.23, 138.42, 128.93, 127.22 (d, ^{3}J = 8.8 Hz), 126.42, 125.14, 121.67, 116.63 (d, ^{2}J = 19.5 Hz),

115.25, 85.00, 76.40 (d, ^{1}J= 162.5 Hz), 52.31, 28.26. ^{19}F NMR (282 MHz, $CDCl_3$) δ –206.30 (m); HRMS (ESI+) calculated for $C_{16}H_{19}FNO_4$ ([M+H]$^+$): 308.1298, found: 308.1291.

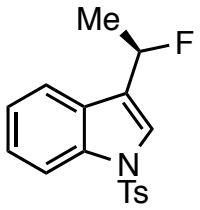


3-(fluoromethyl)benzofuran (2g). General procedure **E** was followed (with a change in workup, as noted below), using 1-iodo-2-(propa-1,2-dien-1-yloxy)benzene[3,29] (258 mg, 1.0 mmol), XPhos (95 mg, 0.2 mmol), silver(I) fluoride (190 mg, 1.50 mmol), tris(dibenzylideneacetone) dipalladium (46 mg, 0.05 mmol), and toluene (10 mL). Reaction time was 3 h. Upon cooling to room temperature, the reaction mixture was loaded directly onto a column of silica gel. Purification by manual column chromatography (silica gel, 0→5% ether in pentanes, with 1% triethylamine) afforded the title compound (94.0 mg, 95% w/w with pentanes, 0.595 mmol, 59% yield) as a colorless oil. A second run provided 84.0 mg (98% w/w with pentanes) 0.548 mmol, 55% yield; average yield was 57%.
FTIR (thin film, cm^{-1}) 2959 (w), 1583 (m), 1452 (s), 1377 (w), 1282 (w), 1190 (m), 1108 (s), 1078 (m), 963 (s), 857 (m), 820 (w), 743 (s); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 5.2 Hz, 1H), 7.69 (d, J = 7.7 Hz, 1H), 7.52 (d, J = 8.1 Hz, 1H), 7.33–7.38 (m, 1H), 7.28–7.33 (m, 1H), 5.55 (d, J = 48.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 155.70, 144.32 (d, ^{3}J = 10.0 Hz), 126.52, 123.32, 119.95, 116.69 (d, ^{2}J = 20.0 Hz), 111.84, 75.42 (d, ^{1}J = 162.4 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ –208.33 (m); HRMS (EI+) calculated for C_9H_7FO ([M$^{\bullet}$]+): 150.0481, found: 150.0475.



3-(fluoromethyl)benzo[b]thiophene (2h). General procedure **E** was followed using (2-iodophenyl)(propa-1,2-dien-1-yl)sulfane[29] (137 mg, 0.5 mmol), XPhos (48 mg, 0.1 mmol), silver(I) fluoride (95 mg, 0.75 mmol), tris(dibenzylideneacetone)dipalladium (23 mg, 0.025 mmol), and toluene (5 mL). Reaction time was 2 h. Purification by manual column chromatography (silica gel, 0→1% ether in pentanes, with 1% triethylamine) afforded the title compound (51.5 mg, 0.31 mmol, 62% yield) as a colorless oil. A second run provided 45 mg, 0.27 mmol, 54% yield; average yield was 58%.
FTIR (thin film, cm^{-1}) 2954 (w), 2888 (w), 1529 (w), 1461 (m), 1430 (m), 1370 (w), 1235 (w), 1138 (w), 1097 (m), 1052 (w), 962 (s), 839 (m), 794 (m), 757 (s), 732 (s); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84–7.94 (m, 2H), 7.53 (d, J = 4.1 Hz, 1H), 7.37–7.48 (m, 2H), 5.63 (d, J = 48.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.63, 137.73, 131.57 (d, ^{2}J = 18.13 Hz), 127.25 (d, ^{3}J = 9.12 Hz), 124.96, 124.68, 122.99, 122.03, 78.75 (d, ^{1}J = 164.7 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ –208.08 (m); HRMS (ESI+) calculated for C_9H_7S ([M–F]$^+$): 147.0268, found: 147.0269.

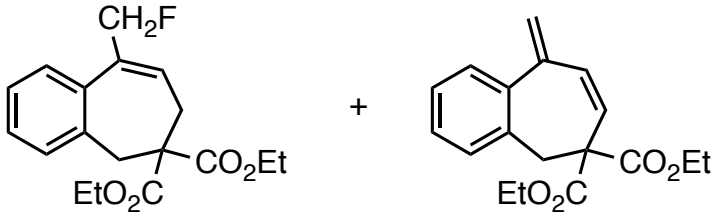
[29] Note: this allene was found to be unstable, even when stored at low temperature. Therefore, carbofluorinations were performed immediately or shortly after purification of the allene.



(+/–)

(+/–)-3-(1-fluoroethyl)-1-tosyl-1H-indole (2i). General procedure **D** was followed, substituting XPhos (20 mol%) as ligand and allylpalladium chloride dimer (5 mol%) as catalyst, and using *N*-(buta-1,2-dien-1-yl)-*N*-(2-iodophenyl)-4-methylbenzenesulfonamide (128 mg, 0.30 mmol), XPhos (28.7 mg, 0.06 mmol), silver(I) fluoride (57 mg, 0.45 mmol), allylpalladium chloride dimer (5.5 mg, 0.015 mmol), and dichloromethane (3 mL). Purification by manual column chromatography (silica gel, 2→10→20% ether in hexanes, with 2% triethylamine) afforded the title compound (70 mg, 0.22 mmol, 73% yield) as a yellow solid. A second run provided 67 mg, 0.21 mmol, 70% yield; average yield was 72%.

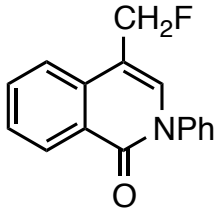
FTIR (thin film, cm^{-1}) 2923 (w), 1597 (w), 1447 (m), 1367 (s), 1293 (w), 1188 (m), 1172 (s), 1126 (s), 1088 (m), 958 (m), 811 (m), 745 (s), 662 (s); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, J = 8.3 Hz, 1H), 7.81 (d, J = 8.1 Hz, 2H), 7.67 (d, J = 7.7 Hz, 1H), 7.60 (d, J = 3.1 Hz, 1H), 7.37 (t, J = 7.7 Hz, 1H), 7.33–7.22 (m, 3H), 5.92 (dq, J = 47.8, 6.4 Hz, 1H), 2.38 (s, 3H), 1.81 (dd, J = 23.3, 6.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.32, 135.35, 135.13, 130.11, 128.70 (^{3}J = 2.1 Hz), 127.02, 125.19, 123.53, 123.23 (d, ^{3}J = 9.1 Hz), 122.76 (d, ^{2}J = 22.4 Hz), 120.41, 113.77, 85.05 (d, ^{1}J = 162.7 Hz), 21.75, 21.00 (d, ^{2}J = 24.2 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ –166.54 (m); HRMS (ESI+) calculated for $C_{17}H_{16}NO_2S$ ($[M–F]^+$): 298.0902, found: 298.0897.



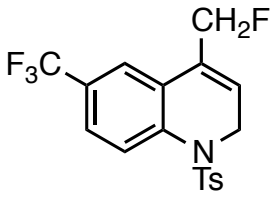
diethyl 9-(fluoromethyl)-5H-benzo[7]annulene-6,6(7H)-dicarboxylate (2j). General procedure **F** was followed, using diethyl 2-(buta-2,3-dien-1-yl)-2-(2-iodobenzyl)malonate[4] (129 mg, 0.30 mmol), PPh_3 (23.6 mg, 0.09 mmol), silver(I) fluoride (57 mg, 0.45 mmol), tris(dibenzylideneacetone)dipalladium (13.7 mg, 0.015 mmol), and toluene (3 mL). Purification by manual column chromatography (silica gel, 0→5→10% ether in hexanes, with 2% triethylamine) afforded the title compound (66 mg, 88% w/w with diene, 0.18 mmol, 60% yield) as a colorless oil. A second run provided 70 mg (87% w/w with diene), 0.19 mmol, 63% yield; average yield was 62%.

FTIR (thin film, cm^{-1}) 2979 (w), 1731 (s), 1449 (w), 1270 (m), 1257 (m), 1212 (m), 1087 (w), 1040 (w), 765 (w); ^{1}H NMR (500 MHz, $CDCl_3$, diene indicated by *) δ 7.19-7.40 (m, 4H, 4H*), 6.52 (d, J = 12.0 Hz, 1H*), 5.44–5.48 (m, 1H), 5.83 (d, J = 12.0 Hz, 1H*), 5.45 (s, 1H*), 5.37 (s, 1H*), 5.15 (d, J = 47.6 Hz, 2H), 4.16–4.25 (m, 4H), 4.12 (q, J = 7.12 Hz, 4H*), 3.45 (s, 2H*), 3.12 (s, 2H), 2.41 (dd, J = 7.1, 3.3 Hz, 2H), 1.26 (t, J = 7.12 Hz, 6H), 1.18 (t, J = 7.12 Hz, 6H*); ^{13}C NMR (125 MHz, $CDCl_3$, diene indicated by *) δ 171.14, 171.14*, 145.20*, 141.16*, 137.63*, 138.40 (d, ^{2}J = 14.7 Hz), 137.22, 137.13, 133.69*, 131.11, 130.03*, 129.7 (d, ^{3}J = 10.5 Hz), 127.97*, 127.81*, 127.71, 127.20*, 127.16, 126.49*, 126.12, 121.48*, 85.08 (d, ^{1}J= 159.8

Hz), 68.06 (d, ^{5}J = 3.7 Hz), 61.73*, 61.94, 39.02*, 37.72, 30.81, 14.22, 14.14*; ^{19}F NMR (282 MHz, $CDCl_3$) δ –207.86 (m); HRMS (ESI+) calculated for $C_{18}H_{22}FO_4$([M+H]$^+$): 321.1504, found: 321.1503.



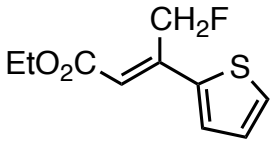
4-(fluoromethyl)-2-phenylisoquinolin-1(2*H*)-one (2k). General procedure **F** was followed, using 2-iodo-*N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzamide (181 mg, 0.5 mmol), PPh_3 (39.3 mg, 0.15 mmol), silver(I) fluoride (95 mg, 0.75 mmol), tris(dibenzylideneacetone)dipalladium (23 mg, 0.025 mmol), and dichloromethane (5 mL). Purification by manual column chromatography (silica gel, 0→15→25% ethyl acetate in hexanes, with 2% triethylamine) afforded the title compound (53 mg, 0.209 mmol, 42% yield) as a yellow solid. A second run provided 48 mg, 0.190 mmol, 38% yield; average yield was 40%. FTIR (thin film, cm^{-1}) 1666 (s), 1595 (w), 1493 (m), 1329 (w), 1265 (s), 1132 (w), 1071 (w), 970 (m), 896 (w), 774 (m); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (dd, J = 8.0, 0.8 Hz, 1H), 7.75–7.85 (m, 2H), 7.59 (ddd, J = 8.1, 6.9, 1.3 Hz, 1H), 7.50–7.55 (m, 2H), 7.41–7.47 (m, 3H), 7.34 (d, J = 4.7 Hz, 1H), 5.50 (d, J = 48.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.13, 140.95, 135.64, 134.11 (d, ^{3}J = 9.8 Hz), 133.20, 129.58, 128.98, 128.58, 127.84, 126.97, 126.52, 123.19, 111.66 (d, ^{2}J = 18.2 Hz), 81.07 (d, ^{1}J = 166.1 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ –202.78 (m); HRMS (ESI+) calculated for $C_{16}H_{13}FNO$ ([M+H]$^+$): 254.0981, found: 254.0981.



4-(fluoromethyl)-1-tosyl-1,2-dihydroquinoline (2l). General procedure **F** was followed, using *N*-(buta-2,3-dien-1-yl)-*N*-(2-iodo-4-(trifluoromethyl)phenyl)-4-methylbenzenesulfonamide (148 mg, 0.3 mmol), PPh_3 (23.6 mg, 0.09 mmol), silver(I) fluoride (57 mg, 0.45 mmol), tris(dibenzylideneacetone)dipalladium (13.7 mg, 0.015 mmol), and toluene (3 mL). Purification by manual column chromatography (silica gel, 0→5→10% ethyl acetate in hexanes, with 2% triethylamine) afforded the title compound (60 mg, 0.16 mmol, 52% yield) as a white solid. A second run provided 62 mg, 0.16 mmol, 54% yield; average yield was 53%.
FTIR (thin film, cm^{-1}) 2926 (w), 1598 (w), 1493 (w), 1435 (w), 1356 (m), 1318 (s), 1225 (m), 1170 (s), 1120 (s), 1080 (s), 1036 (m), 1075 (m), 854 (m), 813 (m), 736 (s), 706 (s), 688 (s), 656 (s); ^{1}H NMR (500 MHz, $CDCl_3$) 7.85 (d, J = 8.4 Hz, 1H), 7.60 (d, J = 8.4 Hz, 1H), 7.42 (s, 1H), 7.28 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 8.2 Hz, 2H), 5.77 (d, J = 4.9 Hz, 1H), 4.76 (d, J = 47.3 Hz, 2H), 4.47 (t, J = 4.9 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.35, 138.45, 135.74, 130.79 (d, ^{2}J = 16.0 Hz), 129.51, 128.94 (q, ^{2}J = 32.8 Hz), 128.57, 127.71, 127.23, 126.07 (d, ^{3}J = 10.0 Hz), 125.50 (q, ^{3}J = 3.7 Hz), 123.84 (q, ^{1}J = 272.5 Hz), 120.58, 81.34 (d, ^{1}J = 168.6 Hz), 44.92, 21.65; ^{19}F NMR (282 MHz, $CDCl_3$) δ –62.43 (s), –213.93 (m); HRMS (ESI+) calculated for $C_{18}H_{16}F_4NO_2S$ ([M+H]$^+$): 368.0838, found: 368.0838.

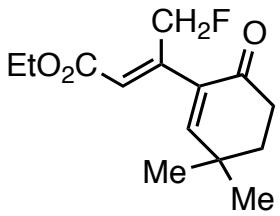
VI. Procedure for intermolecular reaction (Table 3)

General procedure G for intermolecular carbofluorination. After cooling to room temperature in a desiccator, an oven-dried flask was charged with, silver(I) fluoride (1.5 equiv), PPh_3 (30 mol%), and tris(dibenzylideneacetone)dipalladium (5 mol%). Three times, the flask was purged under high vacuum and filled with nitrogen,[26] before charging with toluene (30% of total volume). The reaction mixture was stirred for 10 min at room temperature. After cooling to room temperature in a desiccator, a second oven-dried flask was charged with the allene (1.0 equiv) and the iodide (1.5 equiv), before charging with toluene (70% of total volume). The solution containing the allene and iodide was then added to the solution containing silver(I) fluoride, PPh_3, and tris(dibenzylideneacetone)dipalladium (in total, 0.1 M in toluene). The nitrogen line was then removed and the reaction mixture was allowed to stir at 50 ºC, covered in aluminum foil, for 24 h.[27] After cooling to room temperature, the reaction mixture was then filtered through a pad of Celite, eluting with dichloromethane. After concentrating the filtrate under reduced pressure, the residue was purified by manual column chromatography[28] to afford the desired product. Yields for at least two runs were obtained.

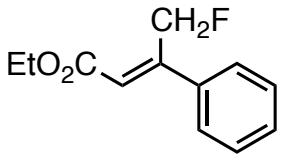


(*E*)-ethyl 4-fluoro-3-(thiophen-2-yl)but-2-enoate (6a). General procedure **G** was followed, using ethyl buta-2,3-dienoate (116 µL, 1.0 mmol), 2-iodothiophene (166 µL, 1.5 mmol), PPh_3 (79 mg, 0.30 mmol), silver(I) fluoride (190 mg, 1.5 mmol), tris(dibenzylideneacetone)dipalladium (45.8 mg, 0.05 mmol), and toluene (10 mL). Purification by manual column chromatography (silica gel, 0→1→8% ether in hexanes, with 1% triethylamine) afforded the title compound (129 mg, 0.60 mmol, 60% yield) as a colorless oil. A second run provided 139 mg, 0.65 mmol, 65% yield; average yield was 63%. For both runs, the regioselectivity was determined to be >20:1 linear:branched and the *E*:*Z* ratio >20:1 by ^{1}H NMR and ^{19}F NMR of the crude reaction mixture and of the pure product. The geometry of the double bond was determined using NOE experiments.

FTIR (thin film, cm^{-1}) 2982 (w), 1709 (s), 1631 (m), 1447 (w), 1377 (w), 1339 (w), 1289 (w), 1174 (s), 1016 (m), 990 (m), 769 (m), 694 (s); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (dd, J = 3.8, 2.0 Hz, 1H), 7.37 (dd, J = 5.1, 2.0 Hz, 1H), 7.08 (dd, J = 5.1, 3.8 Hz, 1H), 6.33 (s, 1H), 5.89 (d, J = 47.1 Hz, 2H), 4.22 (q, J = 7.1 Hz, 2H), 1.32 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.63 (d, ^{4}J = 2.5 Hz), 145.10 (d, ^{2}J = 15.2 Hz), 140.73, 129.05 (d, ^{3}J = 3.5 Hz), 128.30, 127.85, 117.59, 78.53 (d, ^{1}J = 165.3 Hz), 60.80, 14.38; ^{19}F NMR (282 MHz, $CDCl_3$) δ –216.79 (m); HRMS (ESI+) calculated for $C_{10}H_{11}O_2S$ ($[M–F]^+$): 195.0480, found: 195.0485.



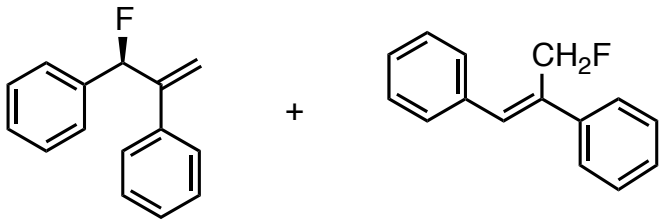
(*Z*)- and (*E*)-ethyl 3-(3,3-dimethyl-6-oxocyclohex-1-enyl)-4-fluorobut-2-enoate (6b). General procedure **G** was followed, substituting Xantphos (10 mol%) as ligand[30] and bis(3,5,3′,5′-dimethoxydibenzylideneacetone)palladium (10 mol%) as catalyst,[31] and using ethyl buta-2,3-dienoate (116 μL, 1.0 mmol), 2-iodo-4,4-dimethylcyclohex-2-enone (188 mg, 1.5 mmol), Xantphos (57.6 mg, 0.10 mmol), silver(I) fluoride (190 mg, 1.5 mmol), bis(3,5,3′,5′-dimethoxydibenzylideneacetone)palladium (81.5 mg, 0.10 mmol), and toluene (10 mL). Purification by manual column chromatography (silica gel, 0→1→5% ether in hexanes, with 1% triethylamine) afforded the title compound (150 mg, 0.59 mmol, 59% yield) as a colorless oil and as mixture of *E* and *Z* isomers in 1.3:1.0 ratio in favor of the *Z* isomer. A second run provided 155 mg, 0.61 mmol, 61% yield and the same *Z*:*E* ratio; average yield was 60%. For both runs, the regioselectivity was determined to be >20:1 linear:branched and the *Z*:*E* ratio 1.3:1.0 by ^{1}H NMR and ^{19}F NMR of the crude reaction mixture and of the pure product. The geometry of the double bond of the major product was determined using NOE experiments showing that the linear product is trans for the olefinic H and the CH_2F group.
FTIR (thin film, cm^{-1}) 2959 (w), 2926 (w), 2865 (w), 1710 (m), 1687 (s), 1584 (m), 1467 (m), 1364 (m), 1320 (m), 1287 (w), 1173 (m), 1142 (m), 1114 (w), 1016 (m), 992 (m), 957 (m), 907 (w), 886 (w), 801 (m), 724 (s); ^{1}H NMR (500 MHz, $CDCl_3$, *E* isomer indicated by *) δ 6.63 (s, 1H*), 6.41 (s, 1H), 6.08 (d, J = 1.9 Hz, 1H), 5.78 (d, J = 1.7 Hz, 1H*), 5.66 (dd, J = 47.5, 1.9 Hz, 2H*), 4.86 (dd, J = 46.6, 1.9 Hz, 2H), 4.17 (q, J = 7.1 Hz, 2H*), 4.10 (q, J = 7.1 Hz, 2H), 2.57 (t, J = 6.9 Hz, 2H), 2.53 (t, J = 6.9 Hz, 2H*), 1.88–1.93 (m, 2H, 2H*), 1.28 (t, J = 7.1 Hz, 3H*), 1.24 (t, J = 7.1 Hz, 3H), 1.20 (s, 6H, 6H*); ^{13}C NMR (125 MHz, $CDCl_3$, *E* isomer indicated by *) δ 197.34*, 196.83, 165.40*, 165.20, 157.68*,156.09, 154.71* (d, ^{2}J = 21.4 Hz), 148.53 (d, ^{2}J = 14.0 Hz), 136.23* (d, ^{3}J = 4.4 Hz), 132.93 (d, ^{3}J = 3.0 Hz), 118.53 (d, ^{3}J = 10.4 Hz), 110.01* (d, ^{3}J = 4.0 Hz), 83.93* (d, ^{1}J = 162.7 Hz), 83.77 (d, ^{1}J = 180.3 Hz), 60.69*, 60.32, 35.95, 35.88*, 34.83*, 34.83, 33.57*, 33.34, 27.93*, 27.75, 14.36, 14.36*; ^{19}F NMR (282 MHz, $CDCl_3$, *E* isomer indicated by *) δ –217.20 (m), –219.22* (m); HRMS (ESI+) calculated for $C_{14}H_{19}O_3$([M–F]$^{+}$): 235.1334, found: 235.1339.



(*Z*)-ethyl 4-fluoro-3-phenylbut-2-enoate (6c). General procedure **G** was followed, using ethyl buta-2,3-dienoate (116 μL, 1.0 mmol), iodobenzene (116 μL, 1.5 mmol), PPh_3 (79 mg, 0.30 mmol), silver(I) fluoride (190 mg, 1.5 mmol), tris(dibenzylideneacetone)dipalladium (45.8 mg, 0.05 mmol), and toluene (10 mL). Purification by manual column chromatography (silica gel, 0→1% ether in hexanes, with 1% triethylamine) afforded the title compound (129 mg, 0.62 mmol, 62% yield) as a colorless oil. A second run provided 127 mg, 0.61 mmol, 61% yield; average yield was 62%. For both runs, the regioselectivity was determined to be >20:1 linear:branched and the *Z*:*E* ratio >20:1 by ^{1}H NMR and ^{19}F NMR of the crude reaction mixture and of the pure product. The geometry of the double bond was determined using NOE

[30] PPh_3 as ligand did not afford the desired product. Analysis of the crude ^{1}H NMR showed complete conversion and the formation of multiple unidentifiable products.
[31] This catalyst was used since dba co-eluted with the allylic fluoride by column chromatography.

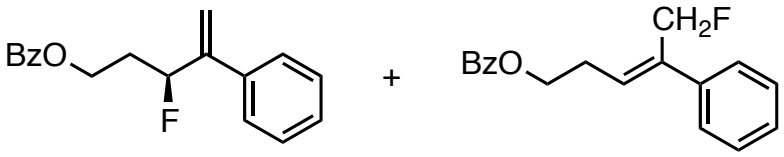
experiments showing that the linear product is trans for the olefinic H and the CH_2F group.
FTIR (thin film, cm^{-1}) 2981 (w), 1708 (s), 1630 (m), 1447 (w), 1377 (w), 1339 (w), 1288 (w), 1259 (w), 1174 (s), 1016 (m), 880 (m), 769 (m), 694 (s); ^1H NMR (500 MHz, $CDCl_3$) 7.48–7.52 (m, 2H), 7.37-7.46 (m, 3H), 6.17 (d, J = 1.2 Hz, 1H), 5.91 (dd, J = 47.5, 1.2 Hz, 2H), 4.24 (q, J = 7.1 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.73 (d, ^4J = 2.4 Hz), 153.30 (d, ^2J = 17.2 Hz), 137.47 (d, ^3J = 2.5 Hz), 129.56, 128.68, 127.42, 120.21 (d, ^3J = 5.0 Hz), 79.19 (d, ^1J = 164.2 Hz), 60.76, 14.29; ^{19}F NMR (282 MHz, $CDCl_3$) δ –216.79 (m); HRMS (ESI+) calculated for $C_{12}H_{14}FO_2$ ($[M+H]^+$): 209.0978, found: 209.0975.



(+/–)

(+/–)-(1-fluoroprop-2-ene-1,2-diyl)dibenzene (7d), (*Z*)-(3-fluoroprop-1-ene-1,2-diyl)dibenzene (6d). General procedure **G** was followed, using propa-1,2-dienylbenzene[5] (116 mg, 1.0 mmol), 2-iodobenzene (166 μL, 1.5 mmol), PPh_3 (79 mg, 0.30 mmol), silver(I) fluoride (190 mg, 1.5 mmol), tris(dibenzylideneacetone)dipalladium (45.8 mg, 0.05 mmol), and toluene (10 mL). Purification by manual column chromatography (silica gel, 0→1% ether in hexanes, with 1% triethylamine) afforded the title compound (159 mg, 0.75 mmol, 75% yield) as a colorless oil. A second run provided 163 mg, 0.77 mmol, 77% yield; average yield was 76%. The regioselectivity was determined to be 1.5:1.0 branched:linear by ^1H NMR and ^{19}F NMR of the crude reaction mixture and of the pure product. The *Z*:*E* ratio of the linear product was 10:1 by ^1H NMR and ^{19}F NMR of the crude reaction mixture, but only the *Z* isomer was observed after chromatography. The geometry of the double bond for the linear product **6d** was inferred from other experiments, as NOE experiments were inconclusive on this mixture of products.
FTIR (thin film, cm^{-1}) 3058 (w), 3029 (w), 1599 (w), 1575 (w), 1495 (m), 1466 (w), 1383 (w), 1260 (w), 1197 (w), 1107 (w), 990 (m), 952 (m), 915 (m), 848.10 (w), 777 (m), 759 (m), 694 (s); ^1H NMR (300 MHz, $CDCl_3$, linear isomer indicated by *) δ 7.22–7.62 (m, 10H, 11H*), 6.35 (d, J = 46.7 Hz, 1H), 5.65 (s, 1H), 5.49 (s, 1H), 5.39 (d, J = 47.8 Hz, 2H*); ^{13}C NMR (125 MHz, $CDCl_3$, linear isomer indicated by *, ‡ indicates peaks which could not be attributed with certainty) 146.58 (d, ^2J = 19.4 Hz), 140.36*, 138.13, 138.00 (d, ^2J = 18.63 Hz), 137.36* (d, ^3J = 3.6 Hz), 135.88* (d, ^2J = 12.4 Hz), 134.96 (d, ^3J = 9.2 Hz), 129.19‡, 129.16‡, 128.77‡, 128.62‡, 128.58‡, 128.46‡, 128.03‡, 127.94‡, 127.13‡, 127.09‡, 127.03‡, 126.37‡, 115.79 (d, ^3J = 9.9 Hz), 94.39 (d, ^1J = 175.0 Hz), 80.71* (d, ^1J = 162.6 Hz); ^{19}F NMR (282 MHz, $CDCl_3$, linear isomer indicated by *) δ –167.10 (m), –204.48* (m); HRMS (ESI+) calculated for $C_{15}H_{13}$ ($[M–F]^+$): 193.1017, found 193.1018.
Spectral data of the branched product were in agreement with literature values.[32]

[32] Luo, H.-Q.; Loh, T.-P. *Tetrahedron Lett.* **2009**, 50, 1554–1556.



(+/–)

(+/–)-3-fluoro-4-phenylpent-4-enyl benzoate (6e), (*Z*)-5-fluoro-4-phenylpent-3-en-1-yl benzoate (7e). General procedure **G** substituting bis(3,5,3′,5′-dimethoxydibenzylideneacetone)palladium (10 mol%),[31] was followed, using penta-3,4-dien-1-yl benzoate[5] (94 mg, 0.5 mmol), 2-iodobenzene (83 μL, 0.75 mmol), PPh_3 (39.5 mg, 0.15 mmol), silver(I) fluoride (95 mg, 0.75 mmol), bis(3,5,3′,5′-dimethoxydibenzylideneacetone)palladium (40.8 mg, 0.05 mmol), and toluene (5 mL). Purification by manual column chromatography (silica gel, 0→2→8% ether in hexanes, with 1% triethylamine) afforded the branched product (66 mg, 0.23 mmol, 47% yield) and the linear product (33 mg, 0.12 mmol, 23% yield), 70% yield in total. A second run provided the branched product (68 mg, 0.24 mmol, 48% yield) and the linear product (34 mg, 0.12 mmol, 24% yield) as two colorless oils, 72% yield in total; average yield was 71%. The regioselectivity was determined to be 2:1 branched:linear and the *Z*:*E* ratio 4.5:1.0 by ^{1}H NMR and ^{19}F NMR of the crude reaction mixture, but only the *Z* isomer was observed after chromatography. The geometry of the double bond of the linear product **6e** was determined using NOE experiments showing that the linear product is trans for the olefinic H and the CH_2F group.

(+/–)-3-fluoro-4-phenylpent-4-enyl benzoate (7e), branched product. FTIR (thin film, cm^{-1}) 2926 (w), 1717 (s), 1602 (w), 1495 (w), 1451 (w), 1315 (w), 1270 (s), 1176 (w), 1110 (m), 1069 (m), 1027 (m), 912 (m), 778 (m), 702 (s); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97–8.11 (m, 2H), 7.54–7.61 (m, 1H), 7.30–7.47 (m, 7H), 5.59 (dt, J = 47.8, 6.2 Hz, 1H), 5.44-5.48 (m, 2H), 4.45 (td, J = 6.4, 1.9 Hz, 2H), 2.09–2.25 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.52, 146.71 (d, ^{2}J = 16.2 Hz), 138.13 (d, ^{3}J = 2.8 Hz), 133.16, 130.16, 129.68, 128.71, 128.52, 128.25, 126.95, 115.08 (d, ^{3}J = 10.9 Hz), 91.51 (d, ^{1}J = 174.6 Hz), 61.15 (d, ^{3}J = 4.1 Hz), 33.87 (d, ^{2}J = 22.9 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ –180.21 (m); HRMS (ESI+) calculated for $C_{18}H_{17}O_2$ ($[M–F]^+$): 265.1229, found: 265.1231.

(*Z*)-5-fluoro-4-phenylpent-3-en-1-yl benzoate (6e), linear product. FTIR (thin film, cm^{-1}) 2923, 1715 (s), 1602 (w), 1451 (w), 1383 (w), 1314 (w), 1268 (s), 1176 (w), 1108 (m), 1070 (m), 1026 (m), 966 (m), 764 (w), 709 (s); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00–8.06 (m, 2H), 7.27–7.46 (m, 7H,), 6.13 (td, J = 7.6, 3.9 Hz, 1H), 5.33 (d, J = 47.8 Hz, 2H), 4.46 (t, J = 6.6 Hz, 2H), 4.36 (t, J = 6.6 Hz, 2H), 2.84 (ddd, 2H, J = 14.2, 6.7, 4.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.69, 140.19, 137.70 (d, ^{2}J = 13.3 Hz), 133.09, 130.80 (d, ^{3}J = 8.4 Hz), 130.15, 129.70, 128.65, 128.54, 127.70, 126.28, 79.79 (d, ^{1}J = 163.7 Hz), 64.01, 28.37; ^{19}F NMR (282 MHz, $CDCl_3$) δ –208.94 (m); HRMS (ESI+) calculated for $C_{18}H_{17}O_2$($[M–F]^+$): 265.1229, found: 265.1227.

VII. Procedure and information for stoichiometric experiments (Scheme 2)

Complex **8-I** was prepared as in ref. 7 and recrystallized from dichloromethane/hexanes before use.[33] Complex **8-F** was prepared from the hydroxo palladium dimer and triethylamine-trihydrofluoride, followed by recrystallization from dichloromethane/toluene (as in ref. 7).[34] In our hands, this procedure afforded complex **8-F** in >95% purity, by ^{31}P NMR. For optimal stability, **8-F** was stored in a nitrogen-filled glovebox; when stored in air, this compound turned from white to brown.

Carbofluorinations with these complexes in the presence of AgF provided comparable results when set up on the benchtop or in a nitrogen-filled glovebox. Reactions of **8-F** in the absence of AgF were set up in a nitrogen-filled glovebox to ensure reproducibility.

*For reactions with AgF with **8-F** or **8-I** on the benchtop:*
A 0.1 M stock solution was prepared in d_8-toluene (0.5 mL/rxn), containing undeca-1,2-diene[6] (**4d**, 0.05 mmol/rxn, 1 equiv) and methyl benzoate (2.5 ug/rxn, 0.4 equiv). An aliquot was reserved for measurement of the initial ratio by ^{1}H NMR. To oven-dried 16x100 mm threaded culture tubes, **8-F** or **8-I** (0.05 mmol, 1 equiv), dimethyl fumarate (7.2 mg, 0.05 mmol, 1 equiv), and silver(I) fluoride (19 mg, 0.15 mmol, 3 equiv) were added. Three times, the vials were purged under high vacuum and filled with nitrogen. Then, each vial was charged with stock solution (0.5 mL). After stirring at 600 rpm for 12 h at 50 ºC (with the vials covered in aluminum foil), the reaction mixtures were cooled to room temperature and filtered through short plugs of Celite, eluting with d_8-toluene. Conversion and yield were determined by ^{1}H NMR, and the regioselectivity was determined by ^{19}F NMR. By ^{1}H NMR, the mass balance consisted of diene byproducts.

For reactions with **8-F** with AgF, the following yields were obtained: 28%, 24%, 18% (23% average)
For reactions with **8-I** with AgF, the following yields were obtained: 48%, 51% (50% average)

The following peaks in the ^{1}H NMR spectra were monitored: 8.03 (m, *o*-C**H**, methyl benzoate), 6.30 (d, C**H**CPhCH$_2$, diene), 5.38 (m, terminal C**H$_2$**, branched carbofluorination product), 5.22 (dm, C**H**F, branched carbofluorination product), 5.05 (m, **H**CCCH$_2$, allene), 4.61 (dt, HCCC**H$_2$**, allene), 3.48 (s, C**H$_3$**, methyl benzoate), 0.89 (t, terminal-C**H$_3$** for allene and allene-derived products).
The following peaks in the ^{19}F NMR spectra were monitored: –178.50 (m, **6f**, branched), –206.97 (m, **7f**, *Z* isomer, linear), –207.96 (m, **7f**, *E* isomer, linear).

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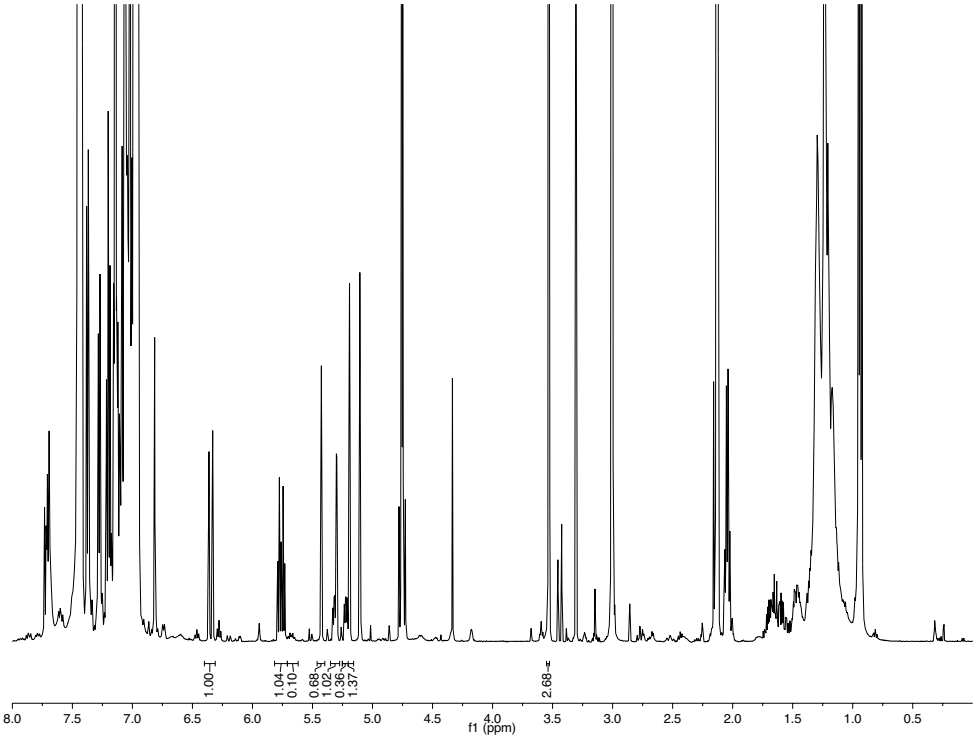
[33] Characterization: Garrou, P. E.; Heck, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 4115–4127.
[34] The procedure for I/F exchange with AgF reported by Grushin also provides **8-F**. In our hands, this method afforded material with silver-derived impurities that caused irreproducible results in the carbofluorination.

A representative spectrum is provided here:



*To monitor the conversion of **8-I** to **8-F**:*
The same procedure as above was followed with **8-I** (^{31}P NMR δ 23.48) as the palladium complex. After 30 min, the reaction was allowed to cool to room temperature and filtered through a short plug of Celite, eluting with d_8-toluene. By ^{1}H NMR, conversion of the allene was determined to be 13% and the yield of the carbofluorination product 6%. By ^{31}P NMR, none of **8-I** remained (**8-F**, δ 19.38, and the Pd(0) product complex, δ 26.17, were the major signals observed).

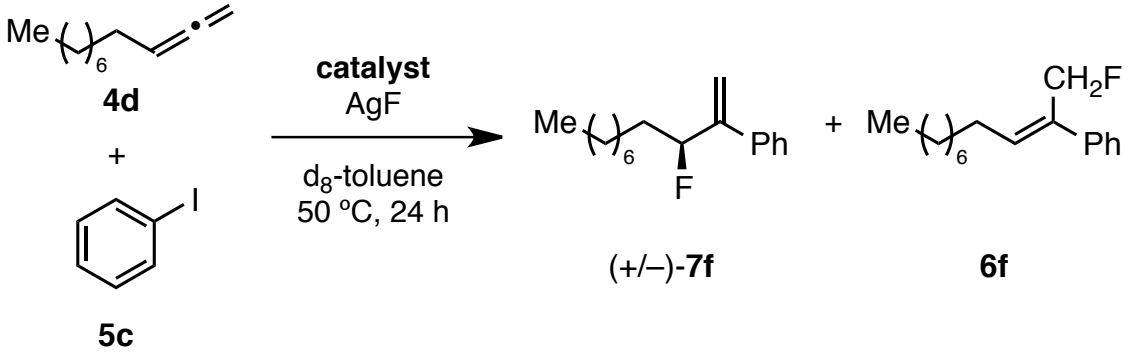
*For reactions with **8-F** (without AgF) in the glovebox:*
In a nitrogen-filled glovebox, a 16x100 mm threaded culture tube was charged with *trans*-bis(triphenylphosphine)phenylpalladium fluoride (**8-F**, 36 mg, 0.05 mmol) and dimethyl fumarate (7.2 mg, 1 equiv). The tube was sealed with Teflon on the thread before removing from the glovebox. Outside the glovebox, a 0.1 M stock solution was prepared in d_8-toluene (0.5 mL/rxn), containing undeca-1,2-diene (**4d**, 0.05 mmol/rxn, 1 equiv) and methyl benzoate (2.5 ug/rxn, 0.4 equiv). An aliquot was reserved for measurement of the initial ratio by ^{1}H NMR. The reaction tube was charged with stock solution (0.5 mL). After stirring at 600 rpm for 24 h at 50 ºC (with the vial covered in aluminum foil), the reaction mixture was cooled to room temperature and filtered through a short plug of Celite, eluting with d_8-toluene. Conversion and yield were determined by ^{1}H NMR, and the regioselectivity was determined by ^{19}F NMR. By ^{1}H NMR, the mass balance consisted of diene byproducts.

For reactions with **8-F** without AgF, the following yields were obtained: 29%, 39% (average 34%)

*Catalytic reactions with **4d**:*

A 0.1 M stock solution was prepared in d_8-toluene (0.5 mL/rxn), containing undeca-1,2-diene (**4d**, 0.05 mmol/rxn, 1 equiv) and methyl benzoate (2.5 ug/rxn, 0.4 equiv). An aliquot was reserved for measurement of the initial ratio by ^{1}H NMR. To oven-dried 16x100 mm threaded culture tubes, the appropriate catalyst (see below) and silver(I) fluoride (9.5 mg, 0.075 mmol, 1.5 equiv) were added. Three times, the vials were purged under high vacuum and filled with nitrogen. Then, each vial was charged with stock solution (0.5 mL), followed by iodobenzene (8.4 µL, 15 mg, 0.075 mmol, 1.5 equiv). After stirring at 600 rpm for 24 h at 50 ºC (with the vials covered in aluminum foil), the reaction mixtures were cooled to room temperature and filtered through short plugs of Celite, eluting with d_8-toluene. Conversion and yield were determined by ^{1}H NMR, and the regioselectivity was determined by ^{19}F NMR. By ^{1}H NMR, the mass balance consisted of diene byproducts.

Table S5.** Catalytic carbofluorinations with allene **4d** and iodide **5c



entry	catalyst	yield (%)[a]	7f:6f[b]	*Z*:*E* for 6f[b]
1	**8-I** (10 mol%)	78	1.6:1.0	5:1
2	**8-F** (10 mol%)	77	1.5:1.0	5:1
3	$Pd_2(dba)_3$ (5 mol%) and PPh_3 (30 mol%)	69	1.4:1.0	4:1

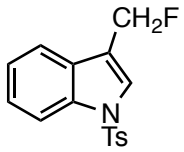
[a] Combined yield of **7f** and **6f**, determined by ^{1}H NMR using methyl benzoate as a quantitative internal standard [b] Determined by ^{19}F NMR.

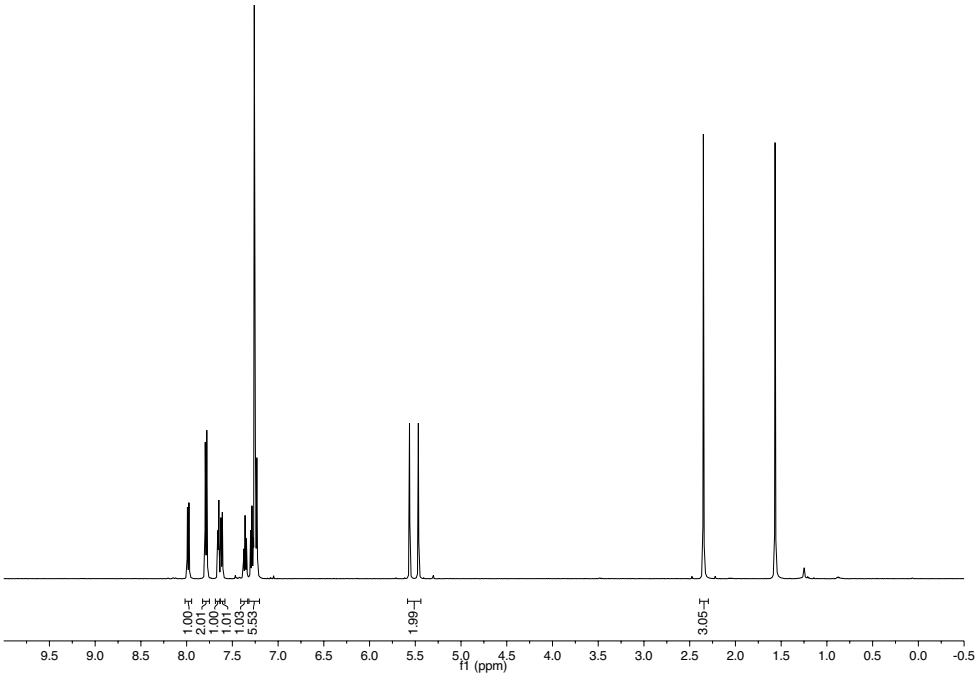
To characterize products **7f** and **6f**, the reaction mixtures from entries 1 and 2 (above) were combined and filtered through a short plug of silica gel, eluting with pentanes. The solution was then concentrated under reduced pressure to remove most of the non-deuterated solvent. The NMR spectra contain a mixture of isomers and dienes, with residual iodobenzene. When identifiable, peaks are indicated as follows: branched isomer indicated by ^, *Z* linear isomer indicated by *, *E* linear isomer indicated by ‡, dienes indicated by #. Integrations are given relative to 1H for the branched isomer.

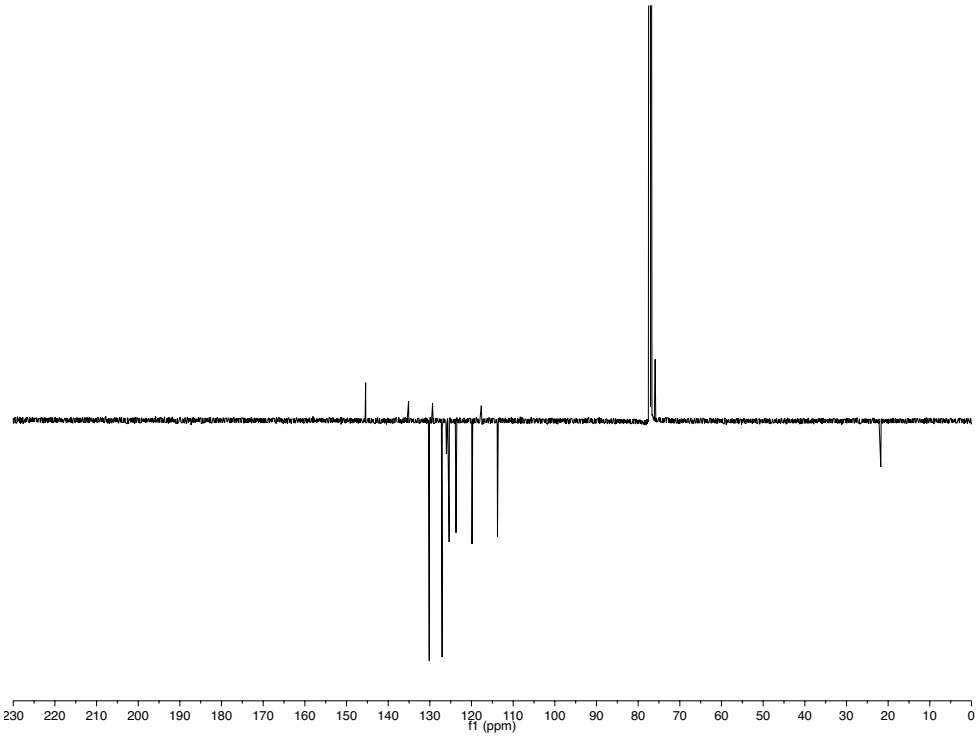
^{1}H NMR (500 MHz, d_8-toluene) δ 7.30–7.41 (m, 3.5H), 7.20–7.26 (m, 2H), 7.11–7.18 (m, 2.5H), 7.04–7.09 (m, 4H), 6.83–6.88 (m, 1H), 6.58–6.63 (m, 2H), 6.29# (d, J = 15.6 Hz, 0.25H), 5.89 (td, J = 7.7, 3.3 Hz, 0.5H), 5.65–5.74 (m, 0.4H), 5.36–5.39^ (m, 1H), 5.23–5.25 (m, 1H), 5.21^ (ddd, J = 47.8, 7.5, 4.0 Hz, 1H), 5.13–5.15 (m, 0.25H), 5.04–5.07 (m, 0.8H), 4.95–4.98 (m, 0.5H), 4.76‡ (dm, J = 48.0 Hz, 0.2H), 4.27 (s, 1H), 0.8–2.1 (m, alkyl H); ^{13}C NMR (125 MHz,

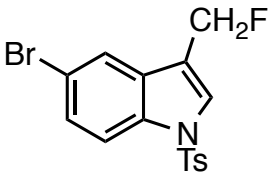
d_8-toluene) δ 148.81, 148.45, 148.32, 141.22, 139.19 (d, ^3J = 3.0 Hz), 137.68, 136.16* (d, ^2J = 8.5 Hz), 135.53^ (d, ^2J = 13.1 Hz), 134.65, 133.14‡ (d, ^2J = 10.0 Hz), 132.07, 130.20, 129.13, 128.61, 128.46, 127.53, 127.45, 127.32, 127.27, 127.17, 126.38, 125.36, 114.69, 113.99, 113. 91, 94.59, 94.37^ (d, ^1J = 175.2 Hz), 86.96‡ (d, ^1J = 170.2 Hz), 79.27* (d, ^1J = 164.4 Hz), 65.89, 34.96, 34.90, 34.72, 33.34, 32.37, 32.29, 32.26, 32.05, 30.06 (d, ^3J = 2.9 Hz), 29.97, 29.92, 29.79, 29.70, 29.67, 28.77 (d, ^3J = 2.5 Hz), 25.40^ (d, ^3J = 3.5 Hz), 23.16, 23.12, 23.11, 22.79, 15.55, 14.37, 14.35, 14.27; ^{19}F NMR (282 MHz, d_8-toluene) δ –178.50^ (m), –206.97‡ (m), –207.96* (m); HRMS (ESI+) calculated for $C_{17}H_{25}$ ($[M–F]^+$): 229.1956, found: 229.1959.

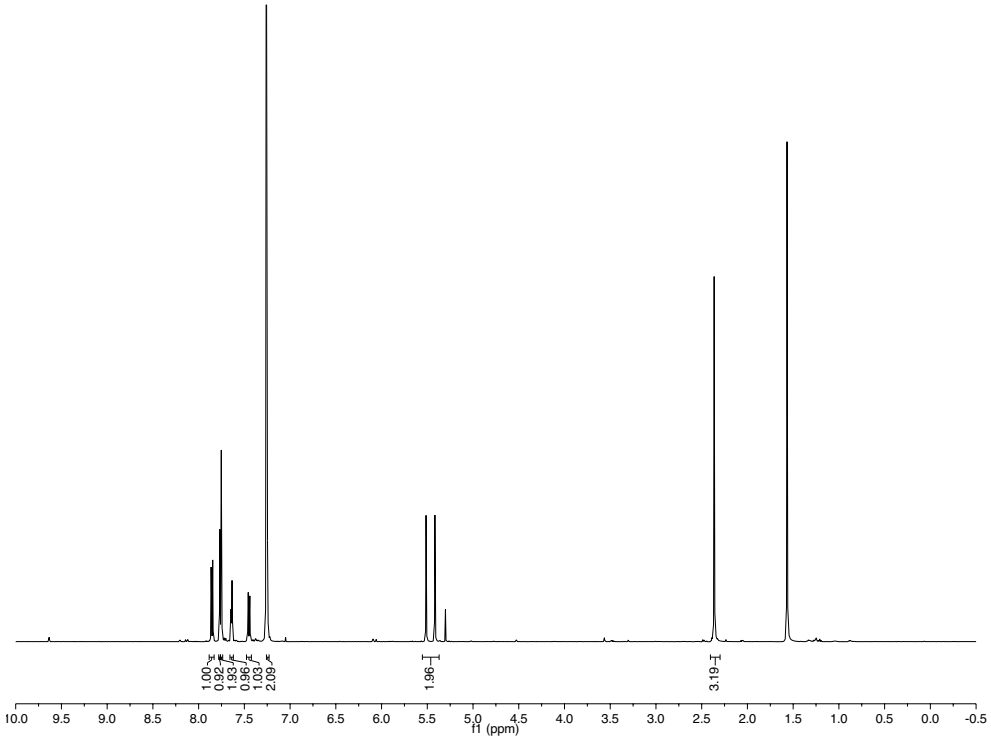
VIII. NMR Spectra








CH2F
Br
N
Ts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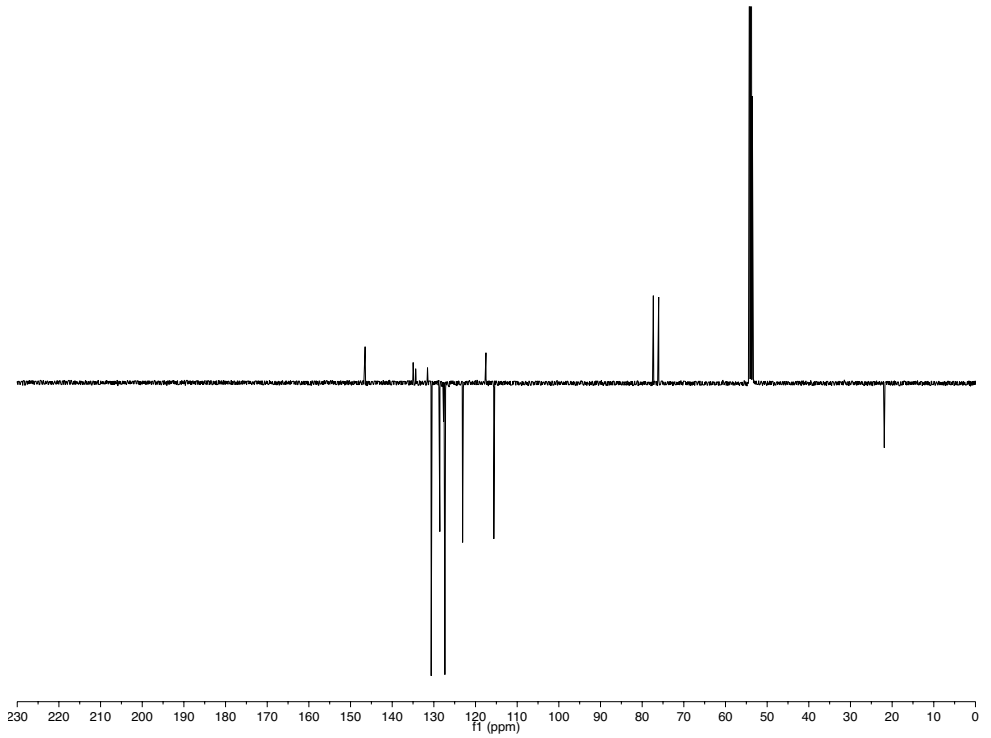
0.92
1.93
0.96
1.03
2.09
1.96
3.19
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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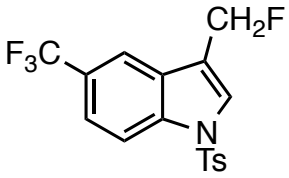
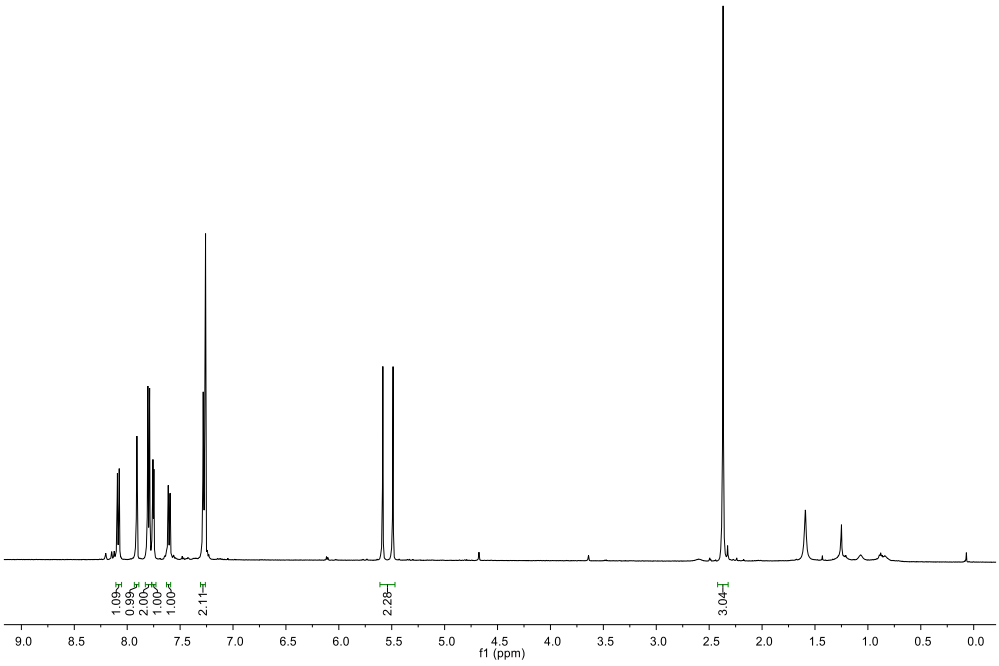
f1 (ppm)


CH2F
F3C
N
Ts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0.99
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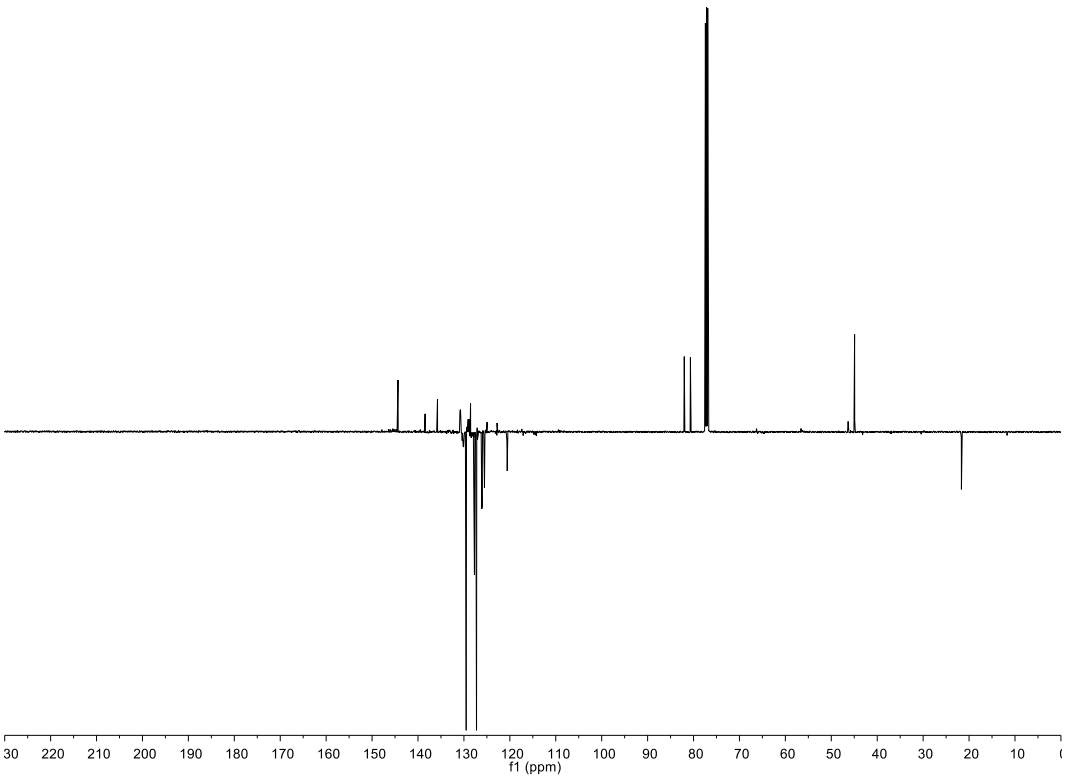
1.00
1.00
2.11
2.28
3.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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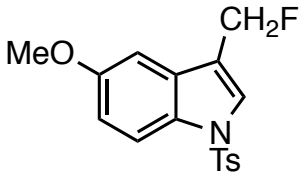
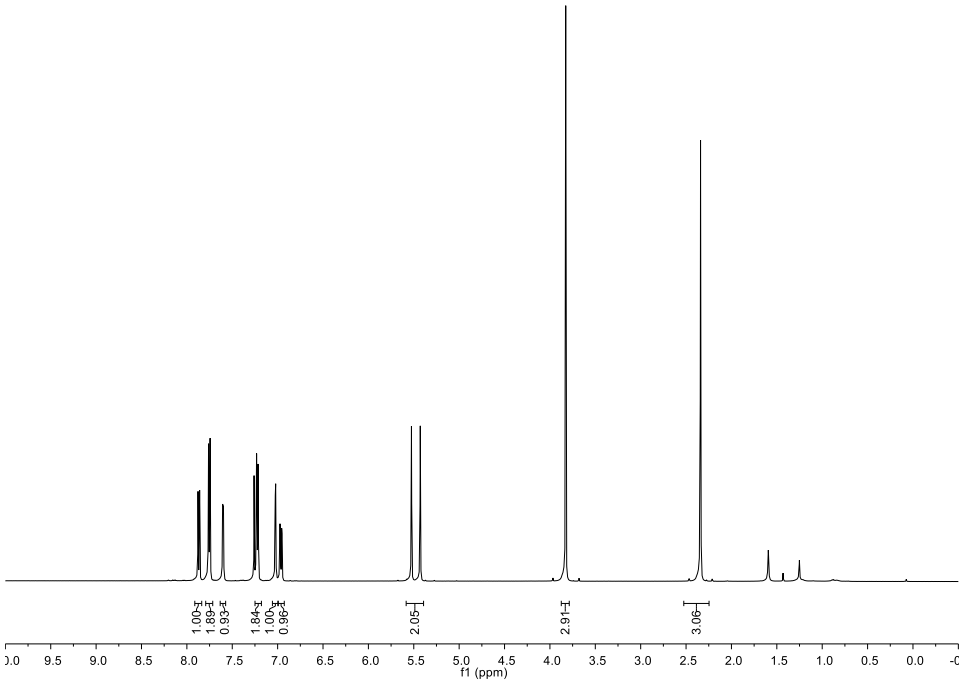
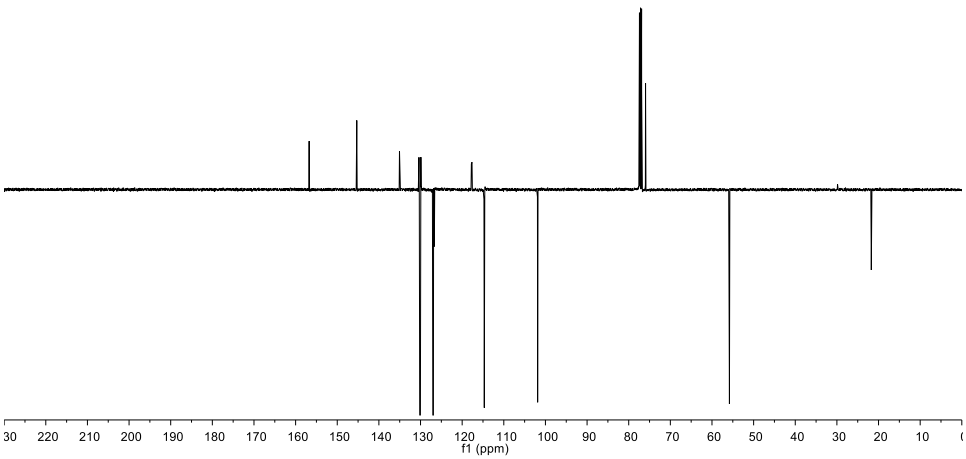
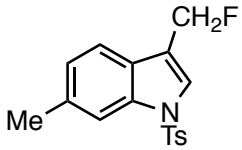
f1 (ppm)

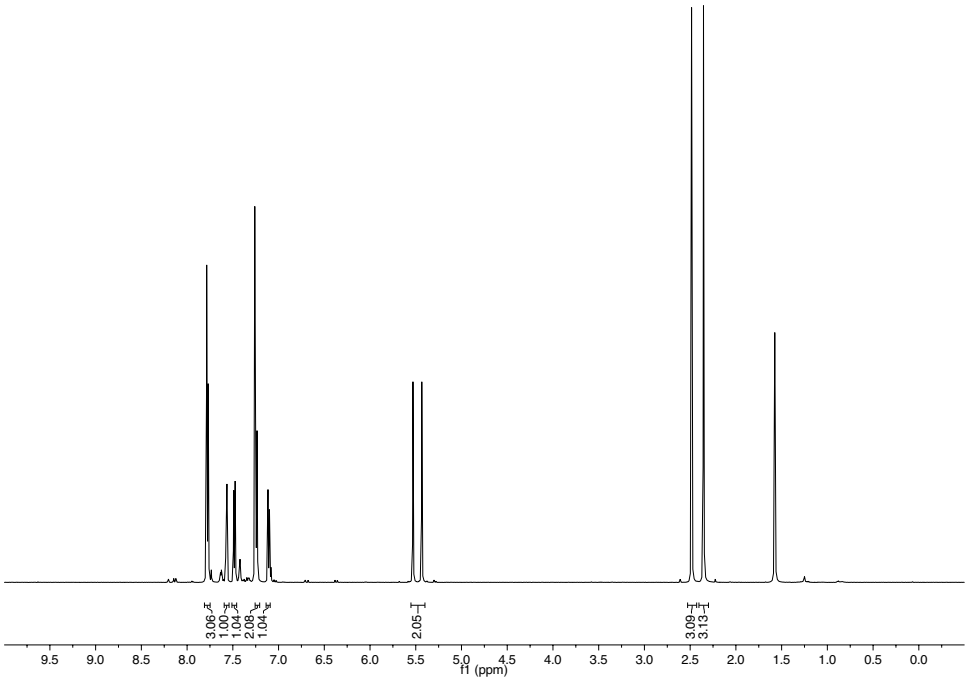


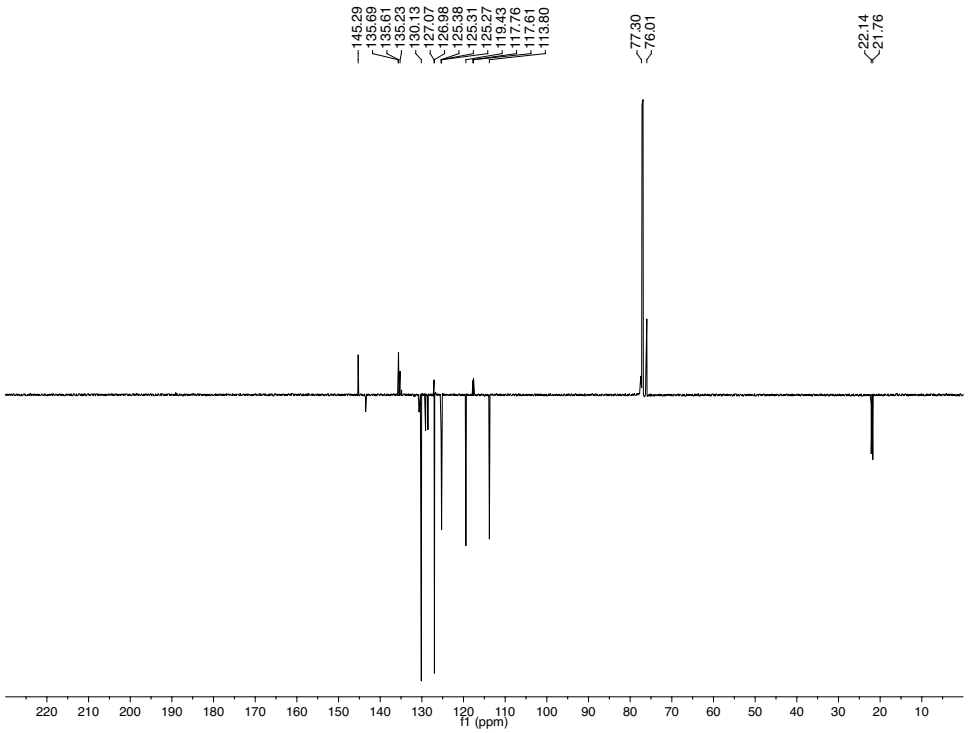


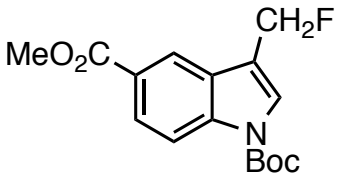


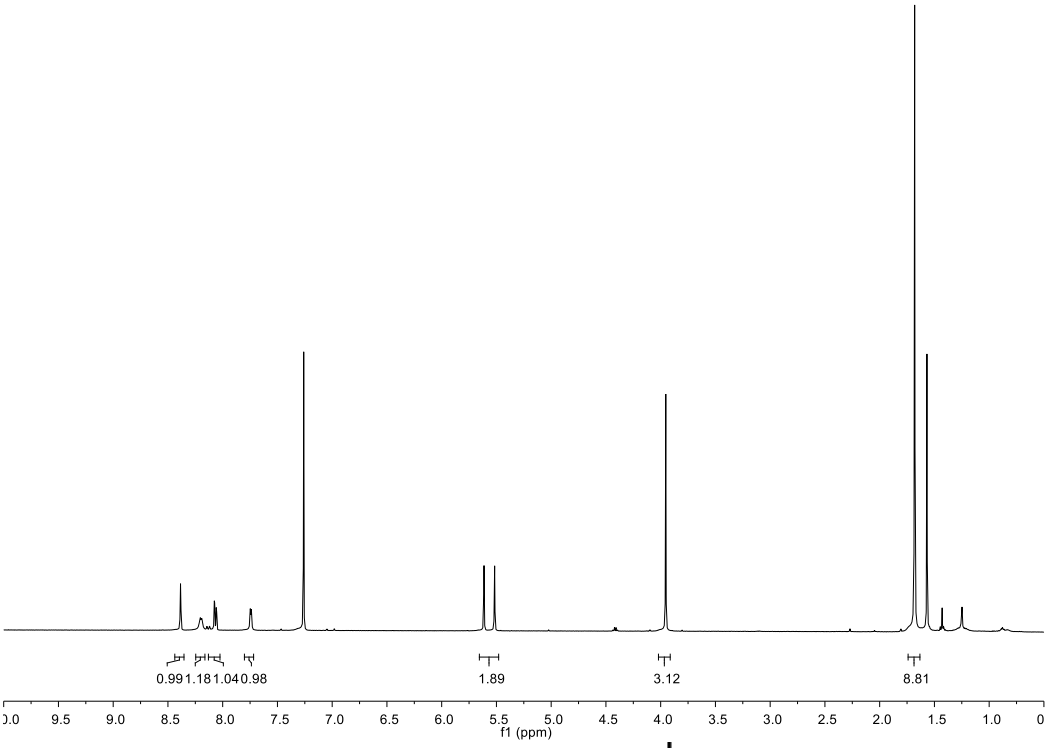


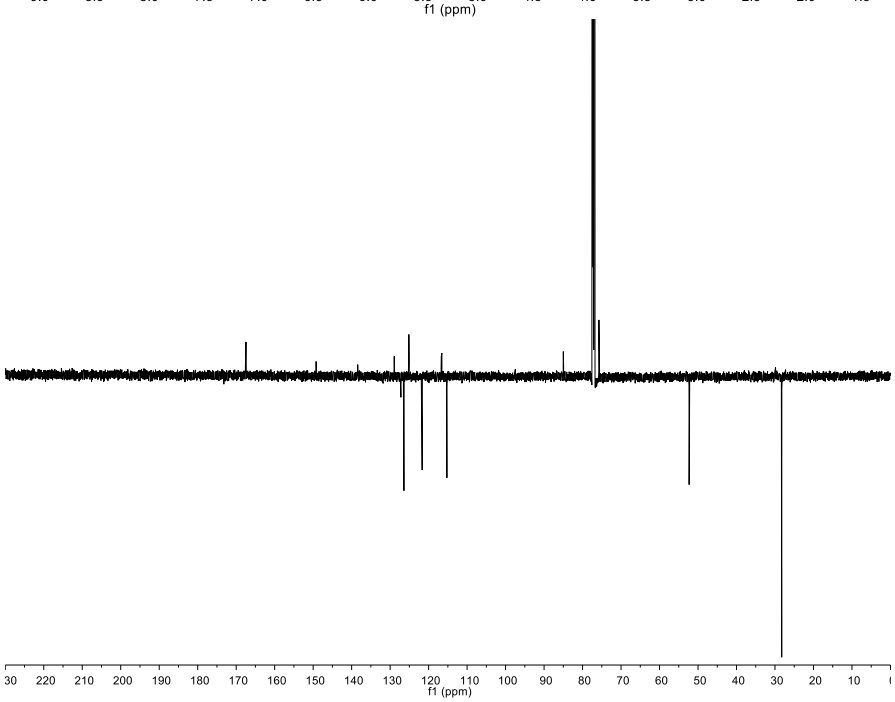
(unmarked peaks indicate dba or ligand impurities)

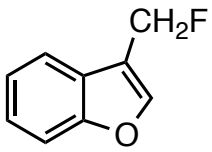


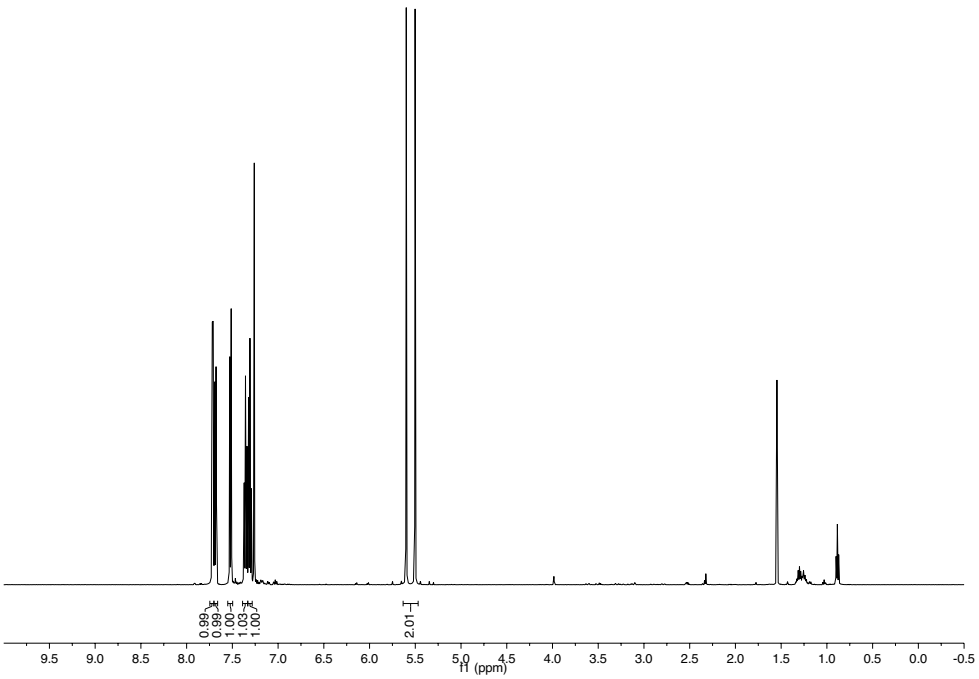


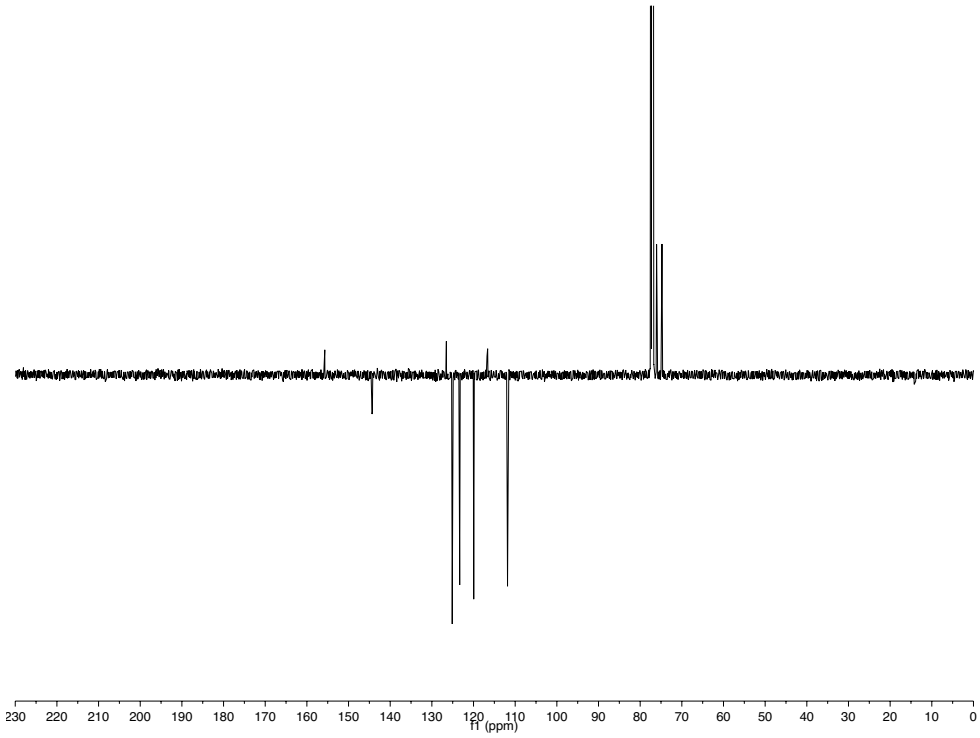


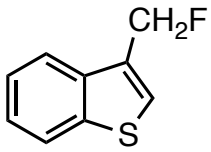


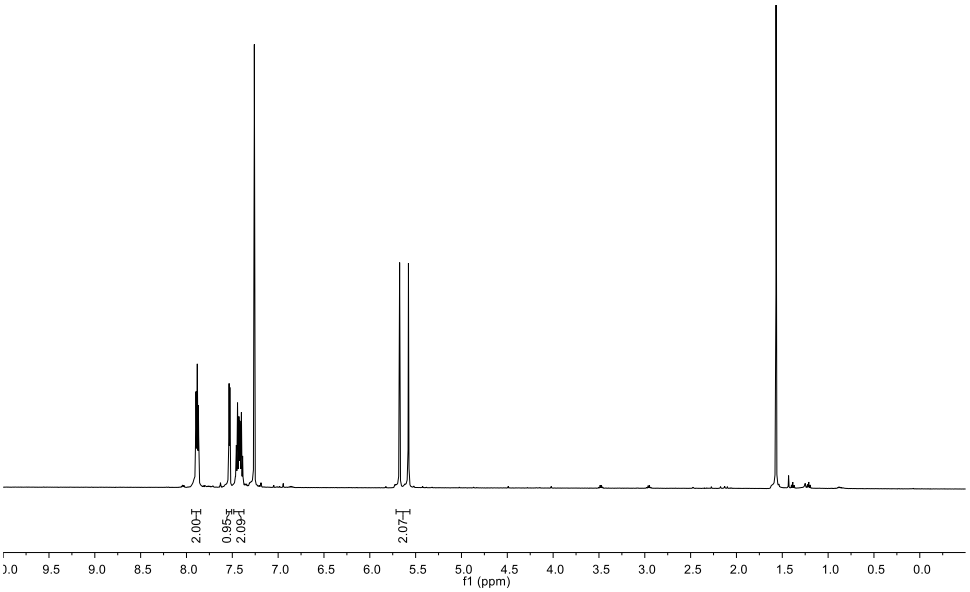


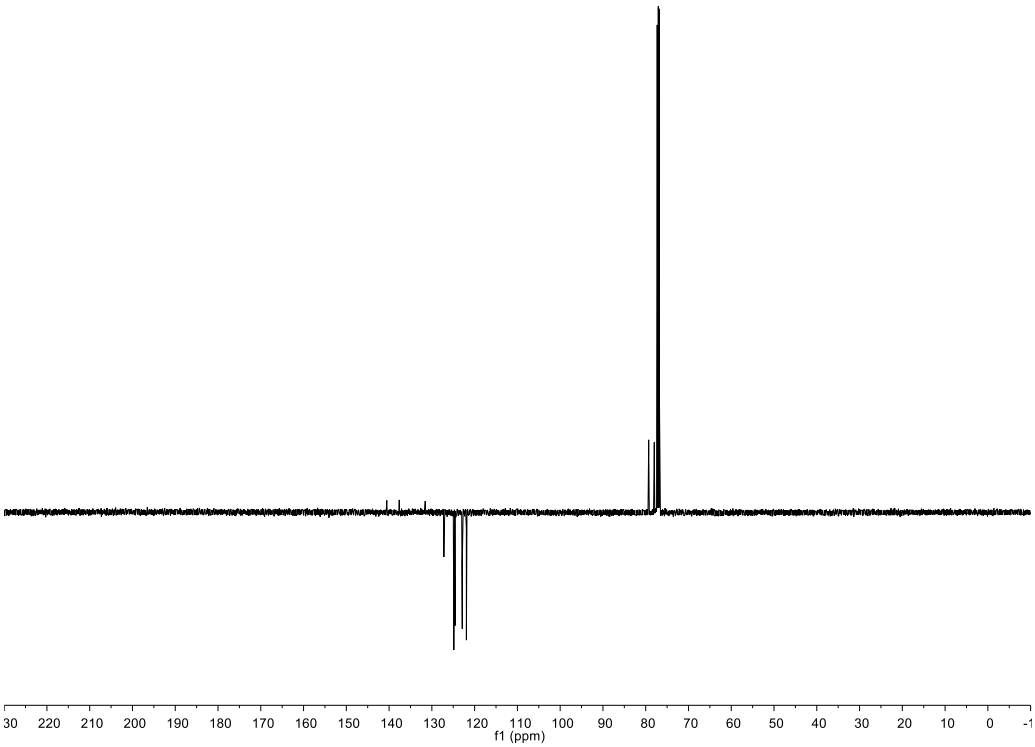

CH2F
O

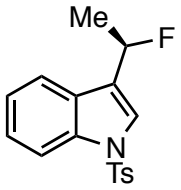

0.99
0.99
1.00
1.03
1.00
2.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

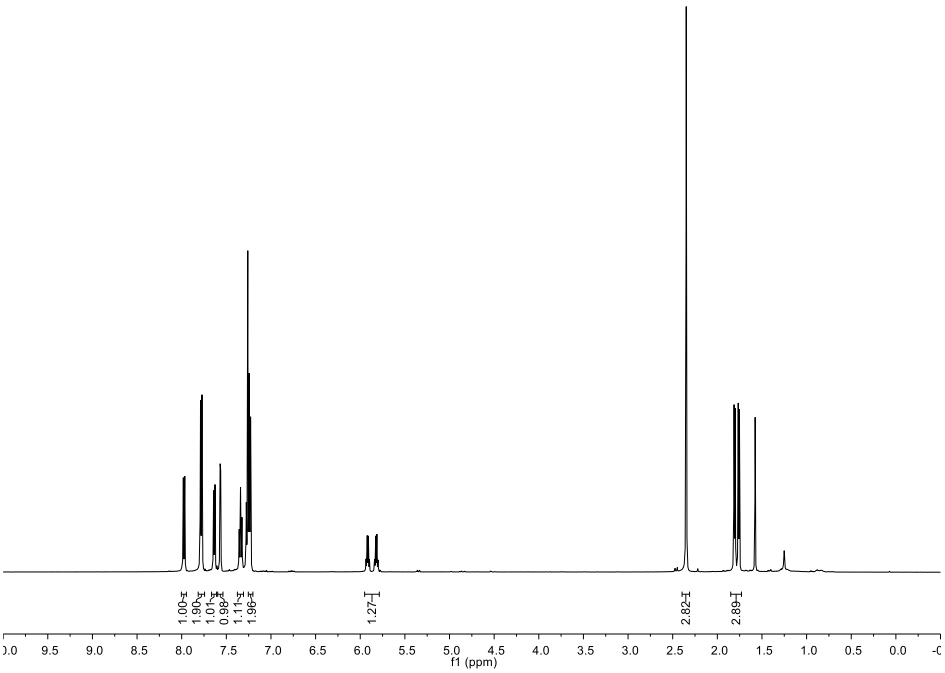


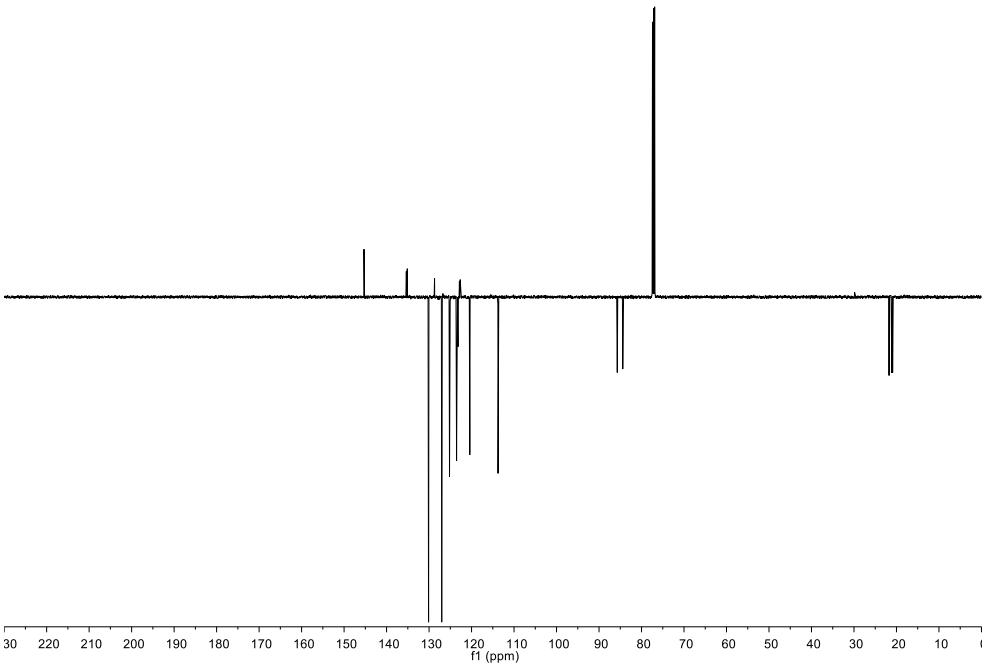


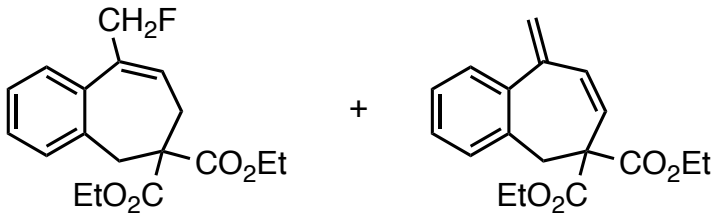


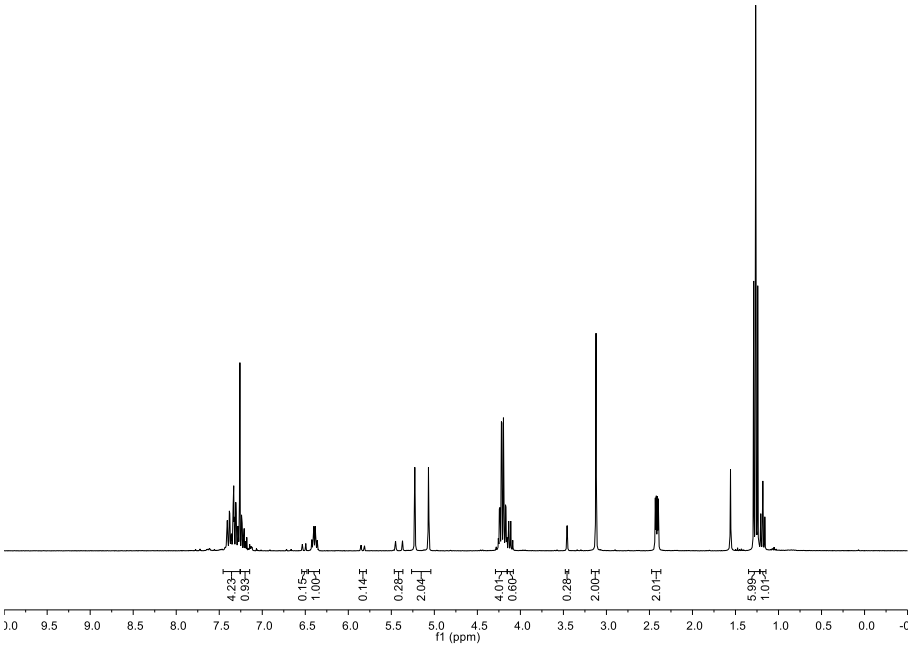

Me
F
N
Ts

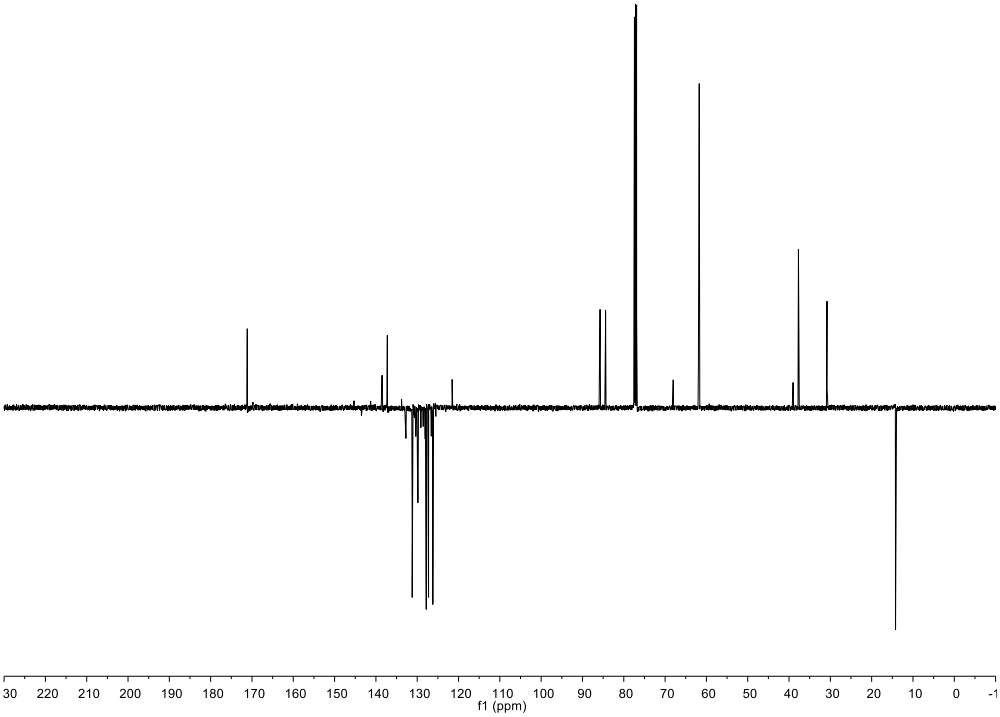
(+/–)

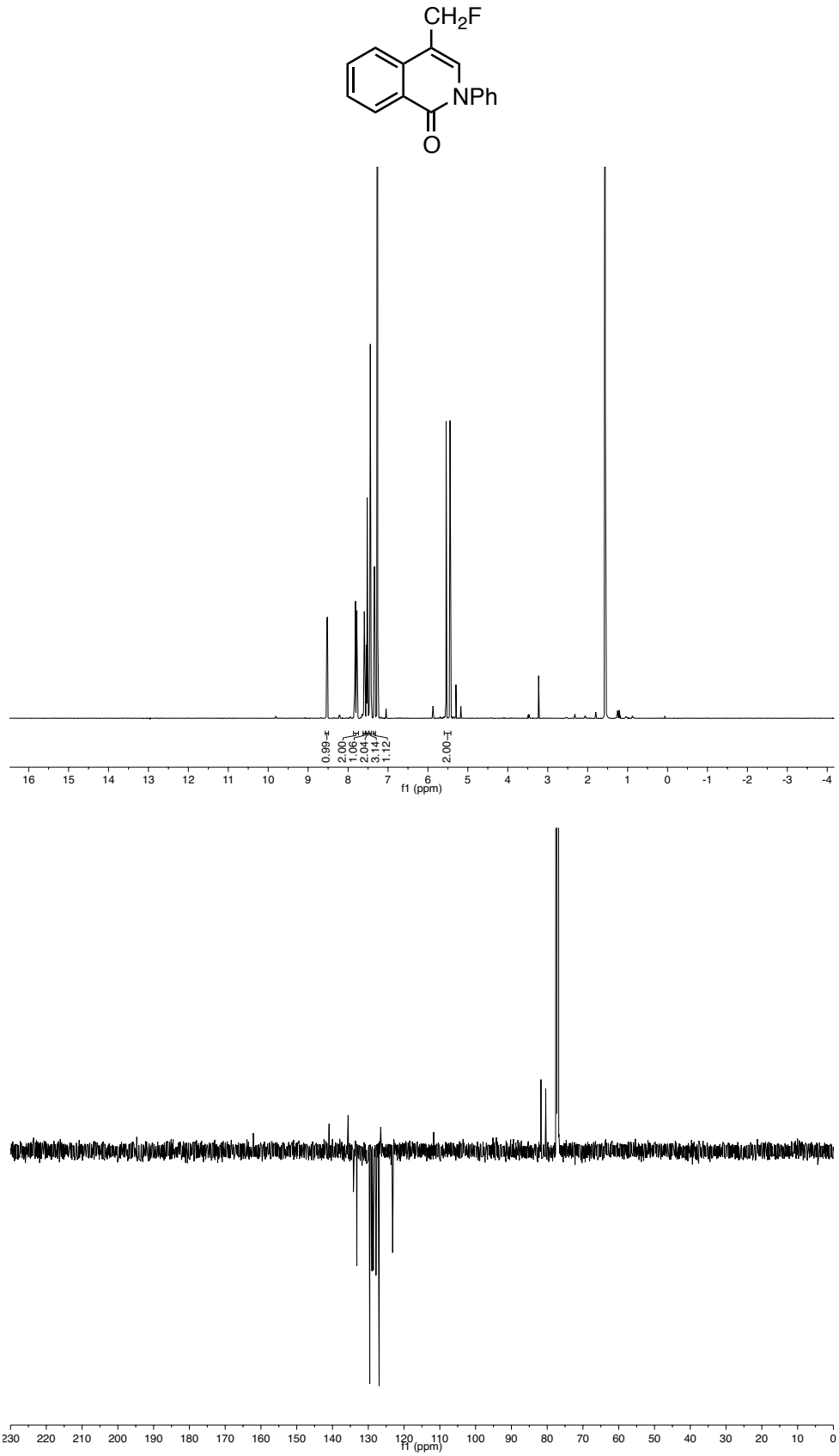

1.00
1.90
1.01
0.98
1.11
1.96
1.27
2.82
2.89
f1 (ppm)

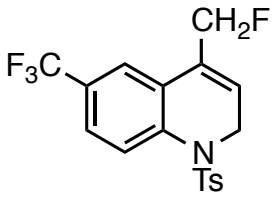

f1 (ppm)

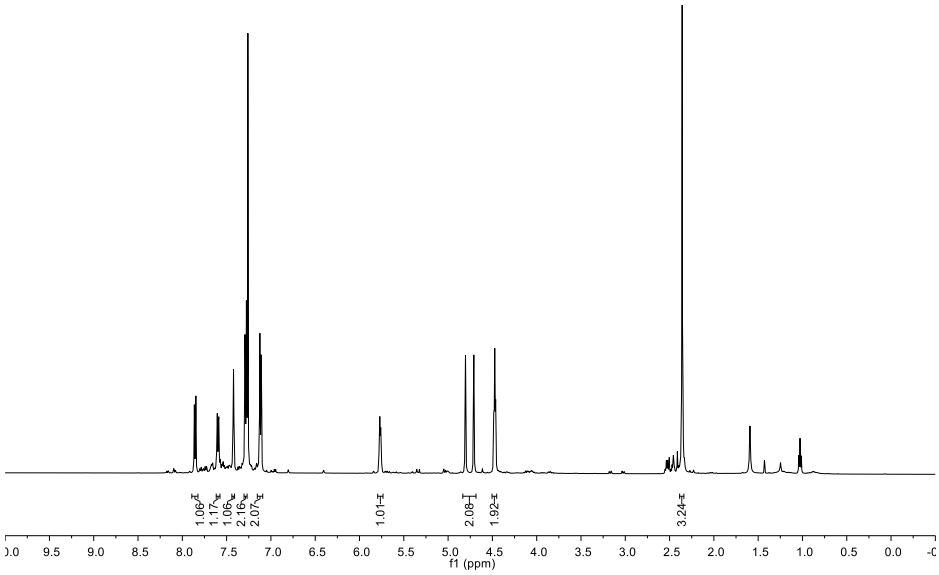


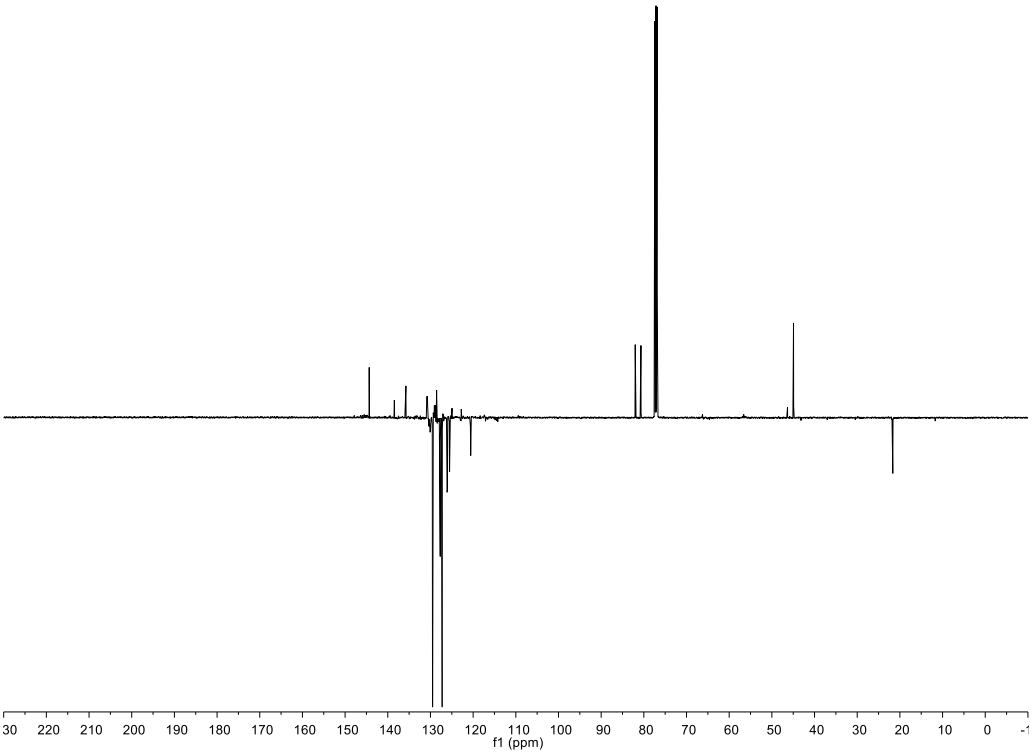


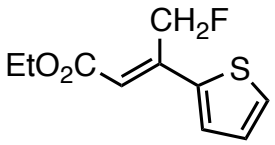


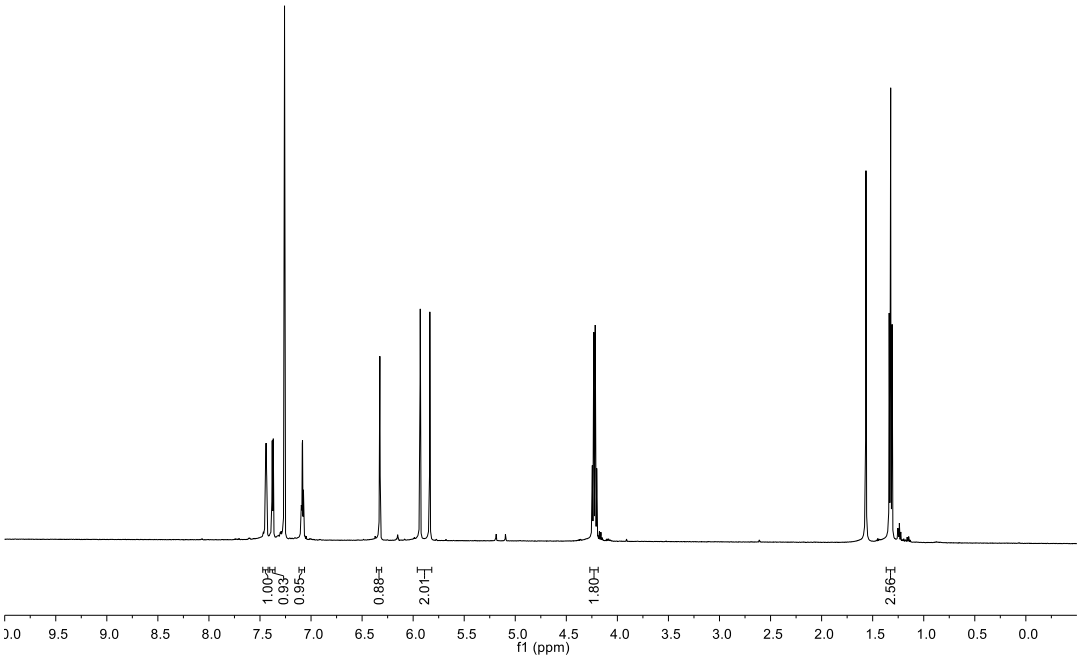

CH2F
NPh
O
0.99
2.00
1.06
2.04
3.14
1.12
2.00
f1 (ppm)
f1 (ppm)

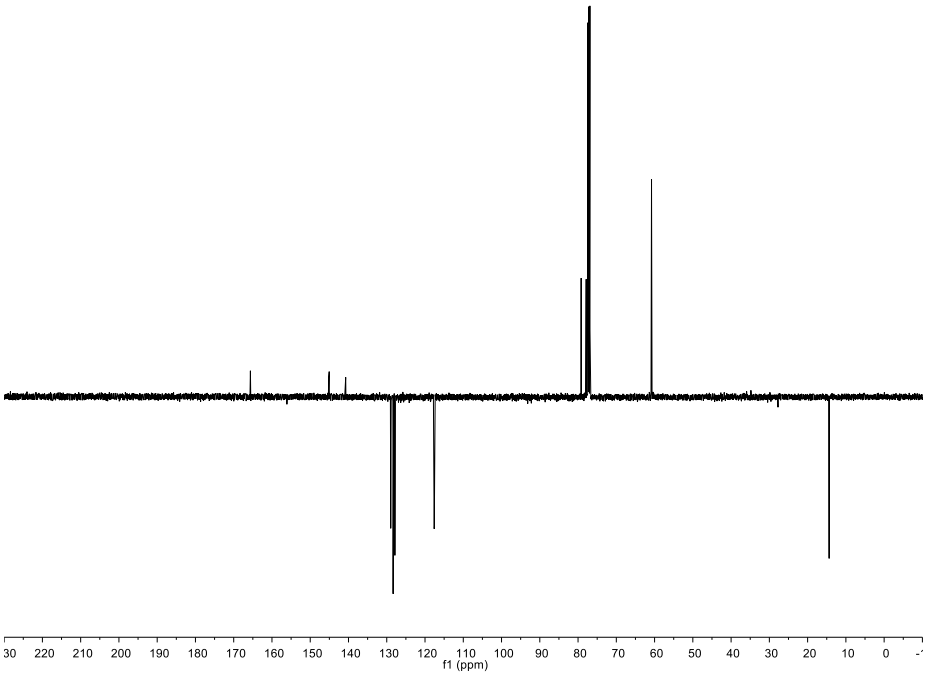




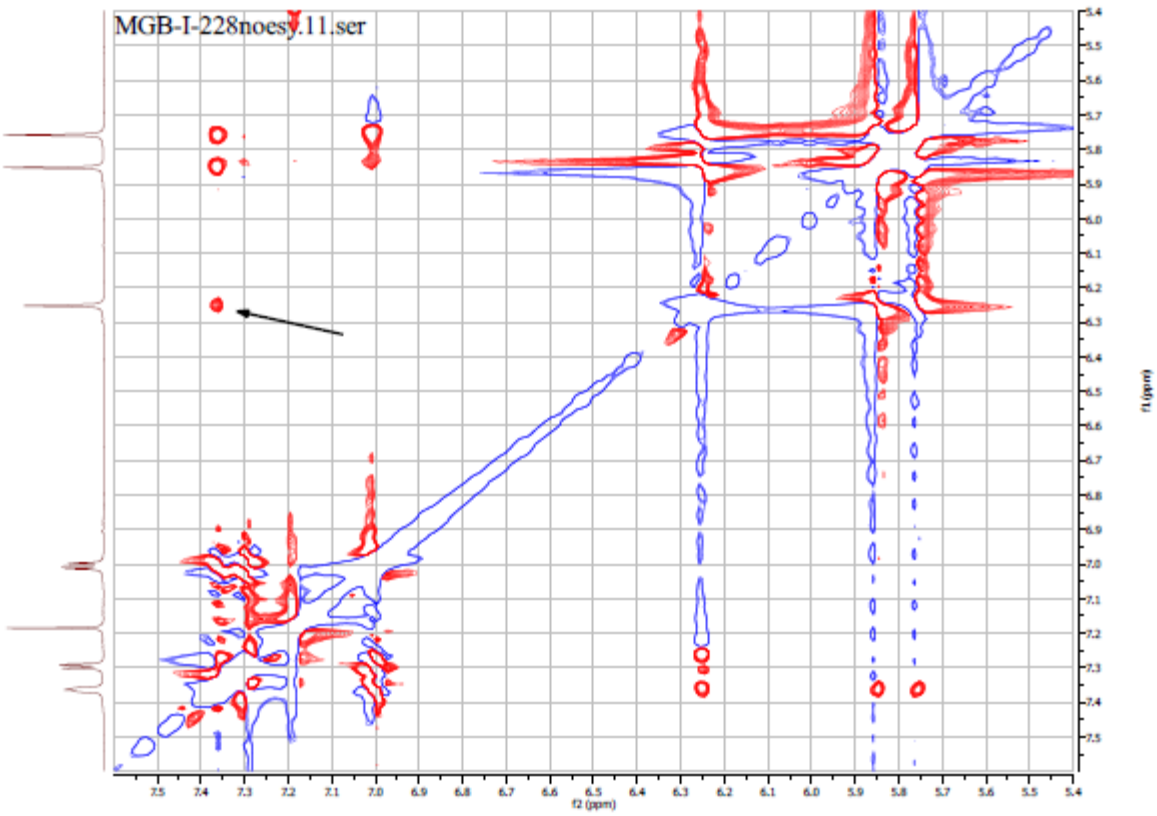


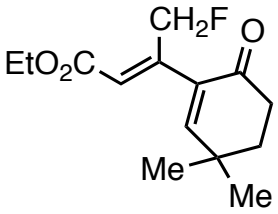

CH2F
EtO2C
S

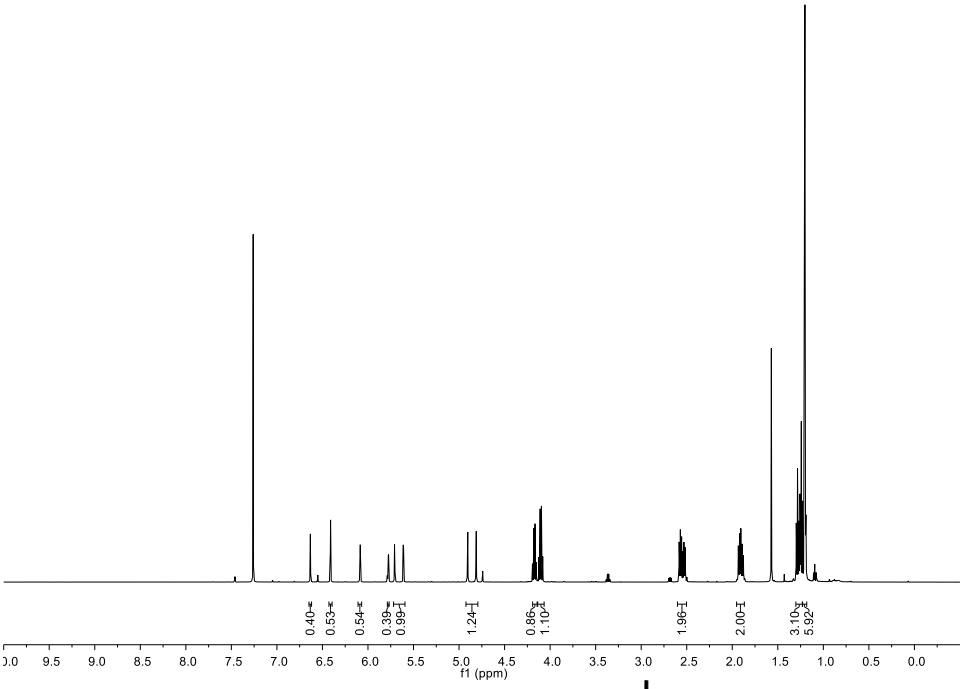

1.00
0.93
0.95
0.88
2.01
1.80
2.56
f1 (ppm)

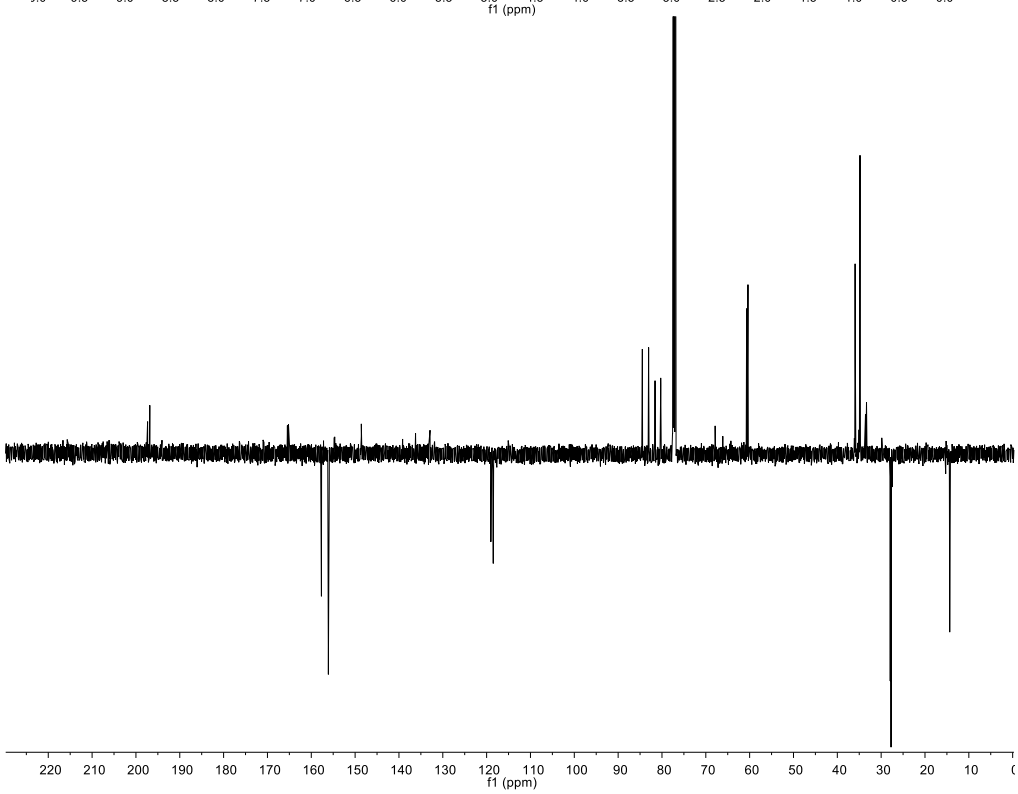

f1 (ppm)

NOE experiments for the product **6a**

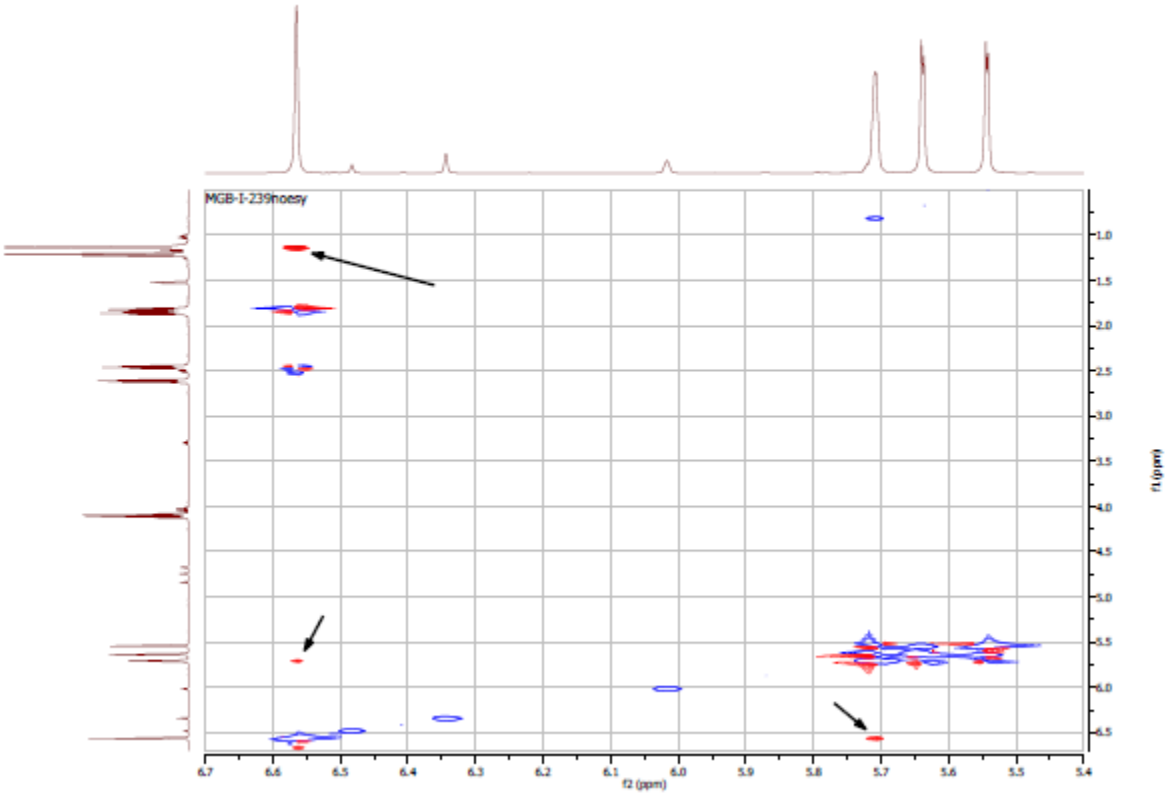


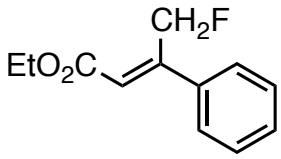


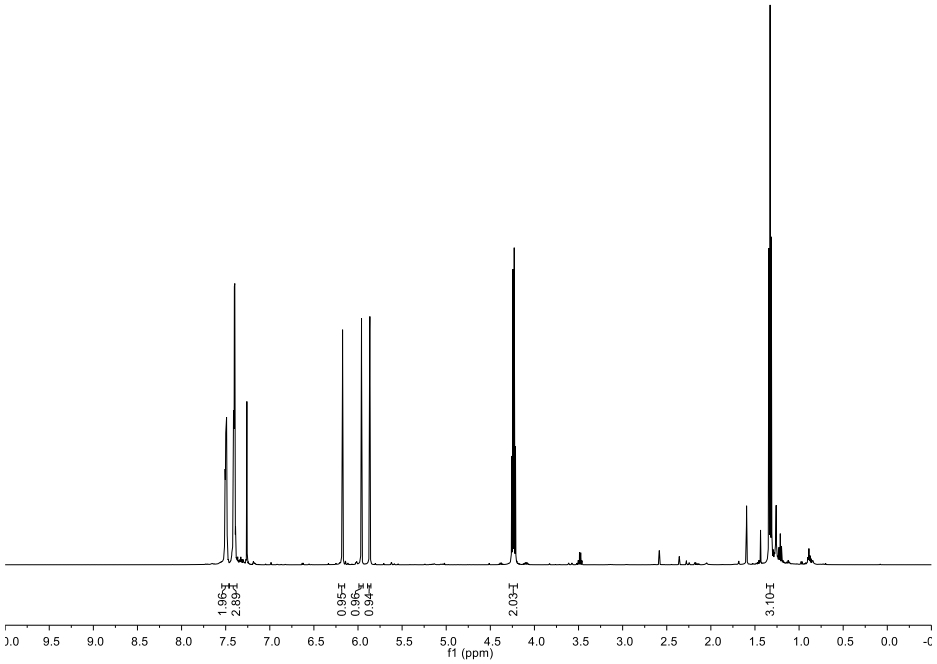


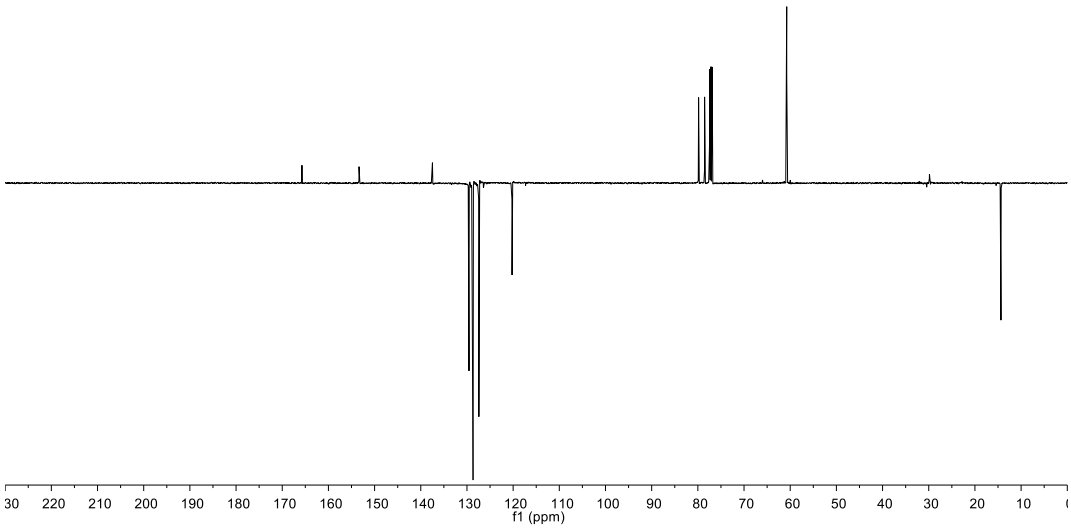


NOE experiments for the product **6b**

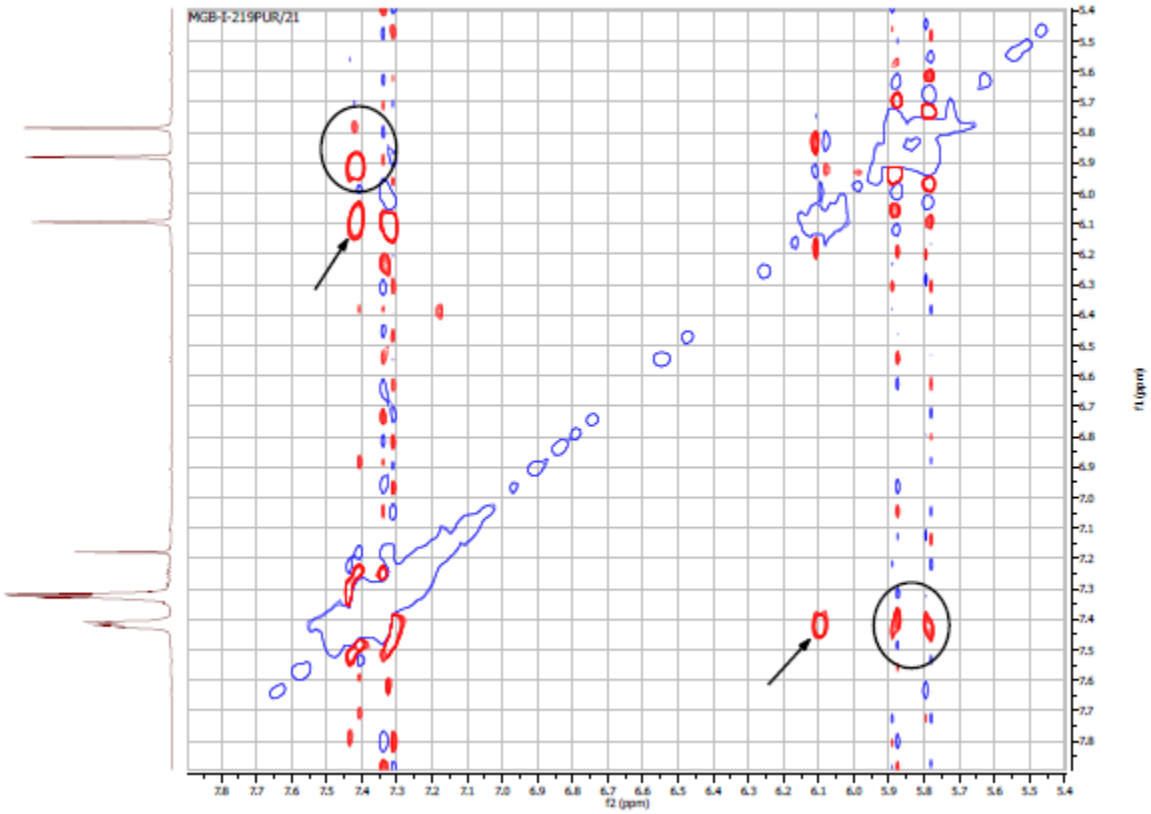


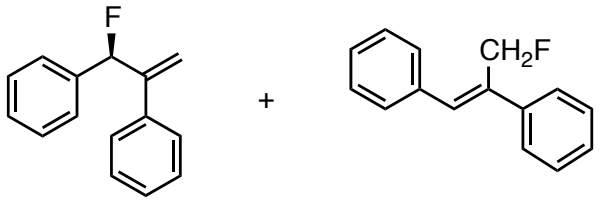




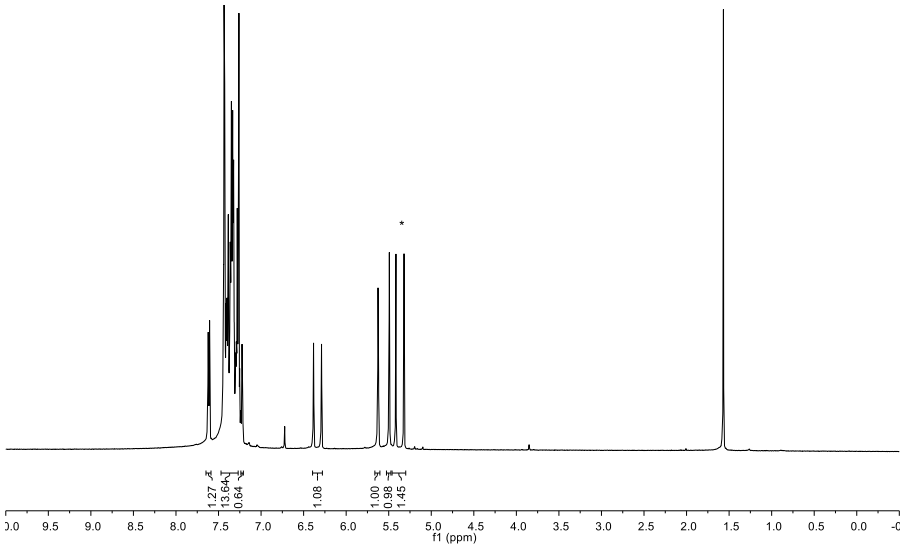


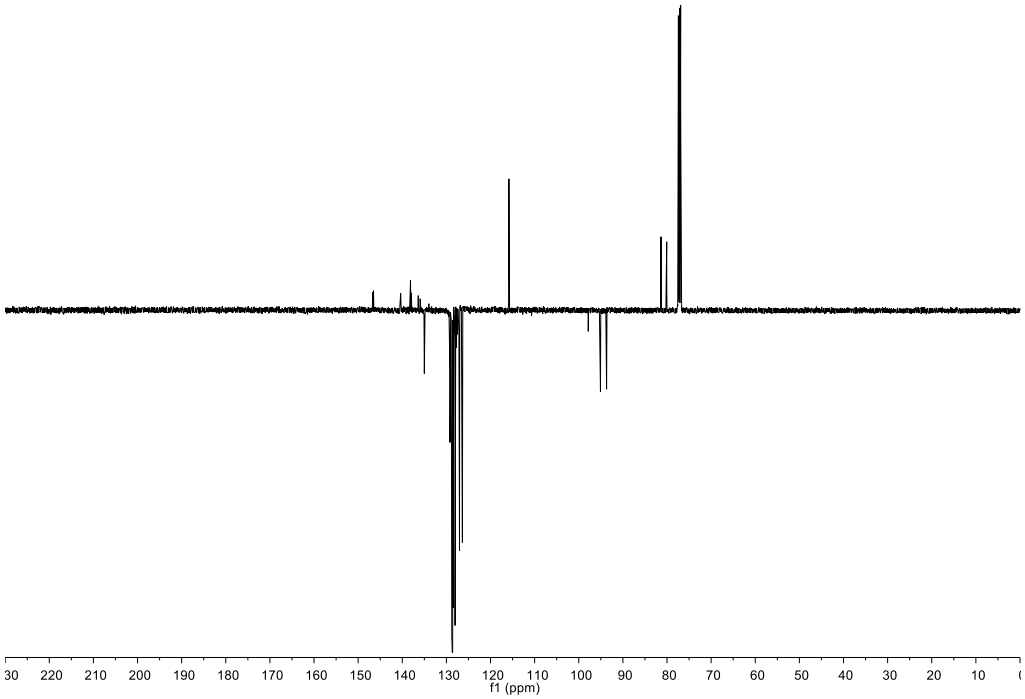
NOE experiments for the product **6c**

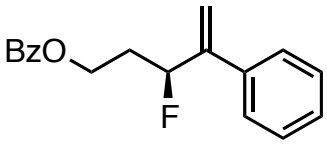




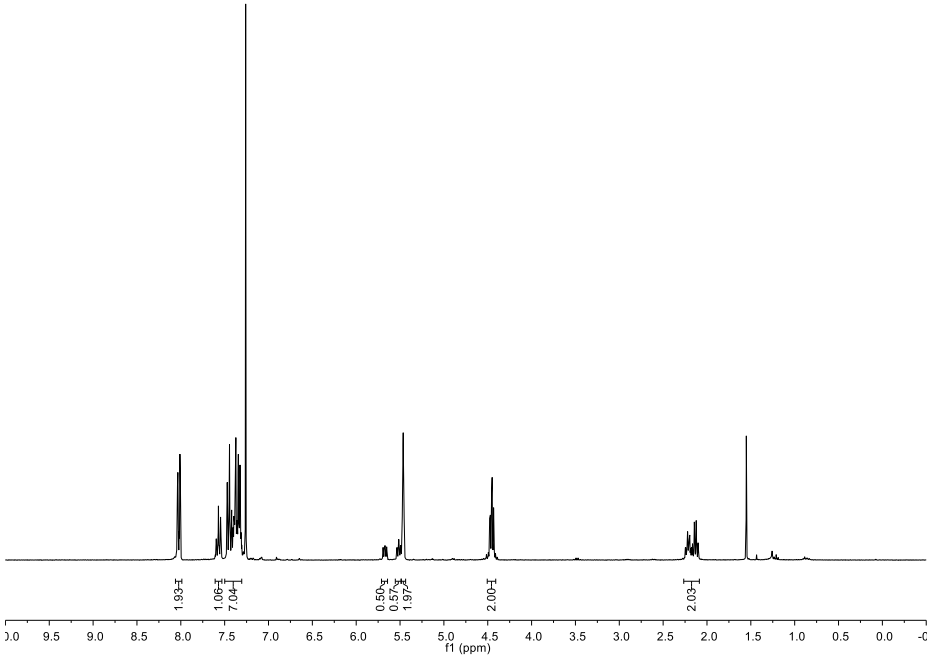
(+/–)

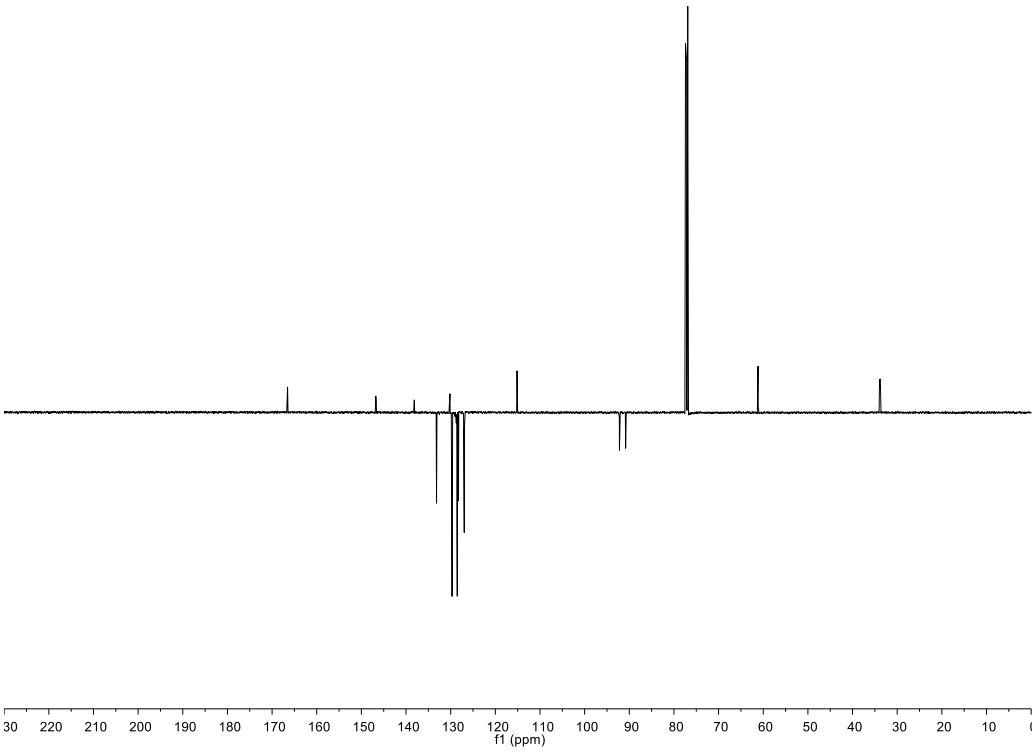


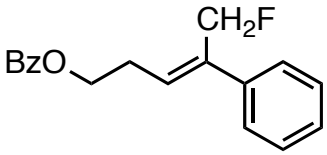


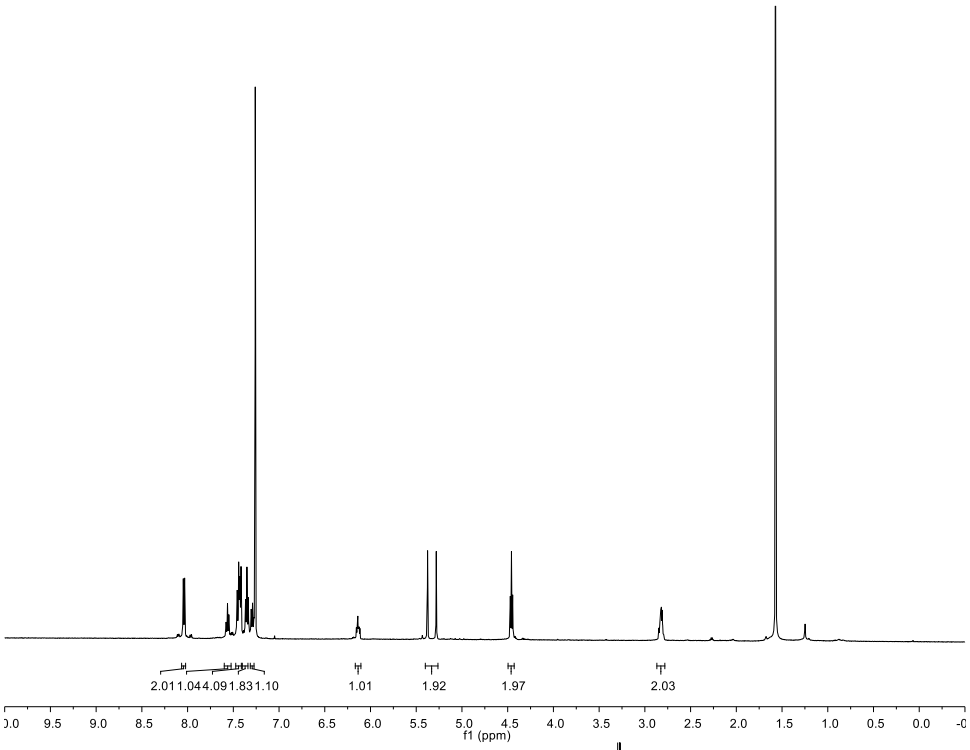


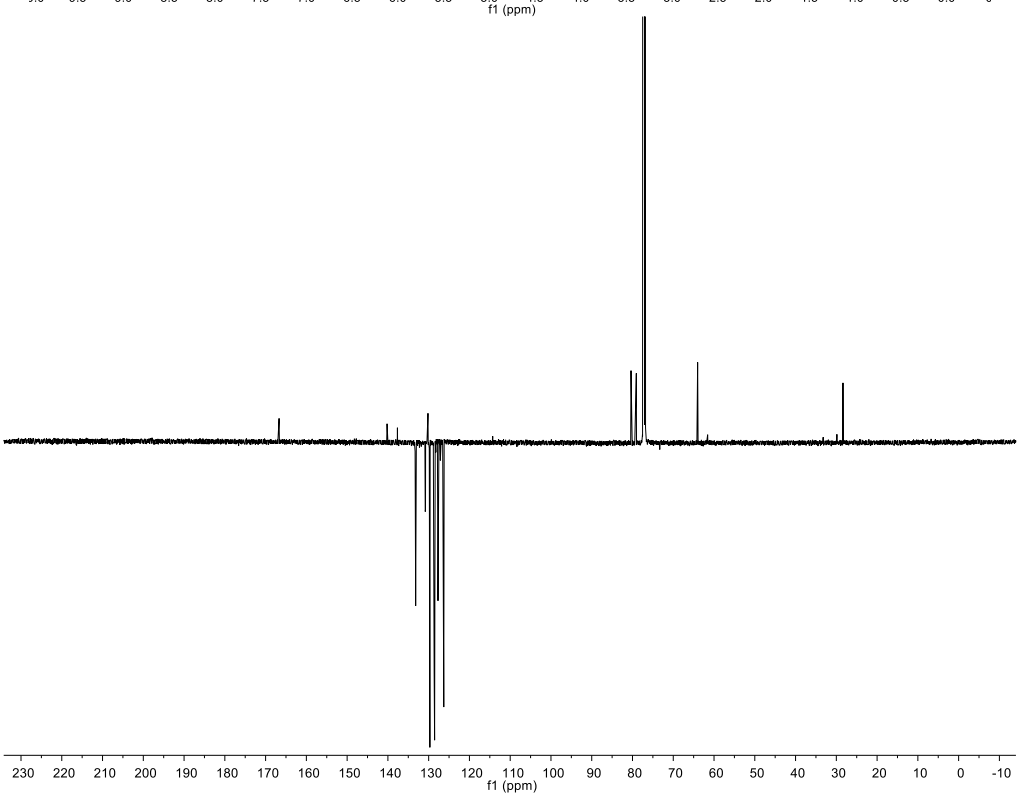
(+/–)



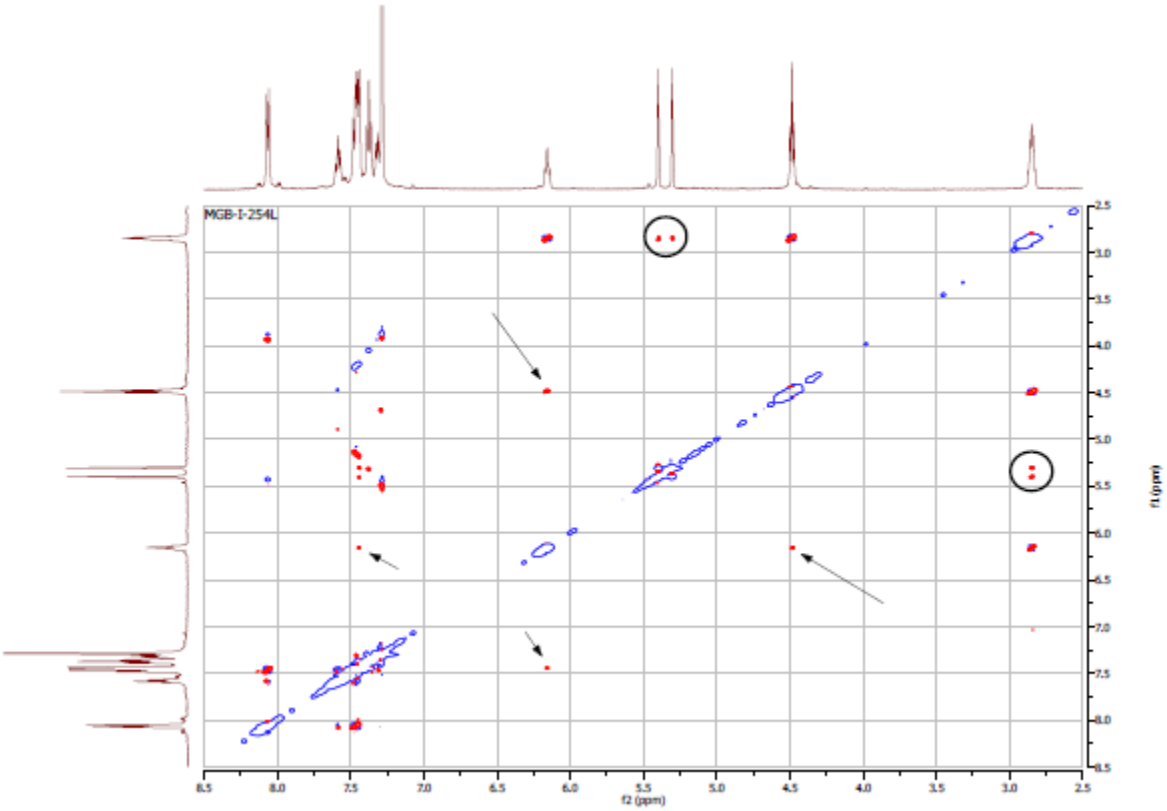


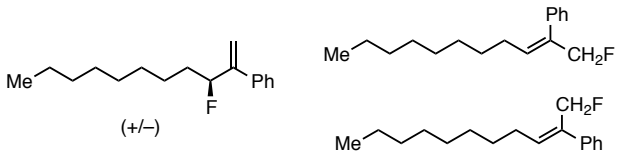

CH2F
BzO


2.01 1.04 4.09 1.83 1.10
1.01
1.92
1.97
2.03
f1 (ppm)


f1 (ppm)

NOE experiments for the product **6e**





(dienes and iodobenzene also present)