Palladium-catalyzed asymmetric 1,6-addition of diarylphosphines to *α,β,γ,δ*-unsaturated sulfonic esters: controlling regioselectivity by rational selection of electron-withdrawing groups

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Supporting Information

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General Methods

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under nitrogen. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian instrument (300 MHz, 75 MHz and 121Hz; 400 MHz, 100 MHz and 162 MHz, respectively). ^{1}H, ^{13}C NMR chemical shifts are reported vs tetramethylsilane signal or residual protio solvent signals.

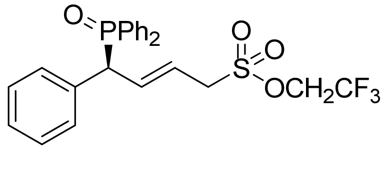
Toluene and THF were distilled over sodium benzophenone ketyl under nitrogen. Dichloromethane and tert-amyl alcohol was distilled over CaH_2 under nitrogen.

The pincer-PdOAc catalysts[1], diarylphosphine[2] and *α*,*β*-unsaturated sulfonic esters[3] were synthesized following the literature procedures. All other chemicals and solvents were purchased from commercial company and used as received.

Experimental Details and Characterization Data

General Experimental Procedures for Table 2.

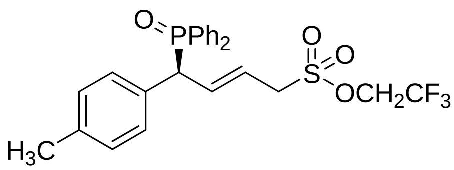
Diarylphosphine (0.20 mmol) was added to a solution of (*S*,*S*)-Pd catalyst (6.7 mg, 10 μmol Pd) and *α*,*β*,*γ*,*δ*-unsaturated sulfonic ester **1** (0.21 mmol) in toluene (4.0 mL) at −60 °C (realized with a refrigerated bath circulator), then the resulting solution was stirred for 24 h at the same temperature. The reaction was quenched with 30% H_2O_2 aqueous solution (0.1 mL) and concentrated under vacuum. The residue was purified by silica gel chromatography with CH_2Cl_2/MeOH = 100/1 to afford the 1,6-adduct.



Entry 1. White solid. (80.2 mg; 81% yield). The ee was determined on a Daicel Chiralcel OD column with hexane/2-propanol = 70/30, flow = 0.7 mL/min. Retention times: 12.2 min [(*R*)-enantiomer], 14.1 min [(*S*)-enantiomer]. 94% ee. $[\alpha]^{20}_{D}$ = −12.1

(c 0.500, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4.

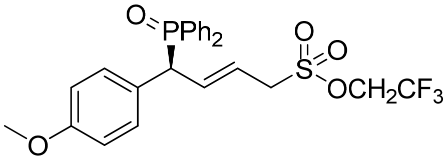
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89-7.83 (m, 2H, Ar), 7.61-7.45 (m, 5H, Ar), 7.40-7.35 (m, 1H, Ar), 7.29-7.18 (m, 7H, Ar), 6.36-6.16 (m, 1H, olefin), 5.58-5.48 (m, 1H, olefin), 4.33-4.21 (m, 3H), 3.89-3.76 (m, 2H, CH_2S). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.7 (d, J_{CP} = 6.4 Hz), 134.5 (d, J_{CP} = 5.7 Hz), 132.3 (d, J_{CP} = 2.7 Hz), 131.8 (d, J_{CP} = 3.0 Hz), 131.6 (d, J_{CP} = 8.7 Hz), 131.19 (d, J_{CP} = 8.8 Hz), 131.16 (d, J_{CP} = 96.1 Hz), 131.0 (d, J_{CP} = 97.2 Hz), 129.4 (d, J_{CP} = 5.7 Hz), 128.9 (d, J_{CP} = 10.3 Hz), 128.85, 128.4 (d, J_{CP} = 11.8 Hz), 127.7 (d, J_{CP} = 2.3 Hz), 121.9 (q, J_{CF} = 277.8 Hz), 119.8 (d, J_{CP} = 11.0 Hz), 65.1 (q, J_{CF} = 37.8 Hz), 55.0 (d, J_{CP} = 1.9 Hz), 51.6 (d, J_{CP} = 64.5 Hz). $^{31}P\{^{1}H\}$ NMR (161 MHz, $CDCl_3$): δ 28.2 (s). HRMS (ESI) calcd for $C_{24}H_{23}F_3O_4PS$ $(M+H)^+$: 495.1001, found: 495.1002.



Entry 2. White solid. (79.1 mg; 78% yield). The ee was determined on a Daicel Chiralpak AD column with hexane/2-propanol = 90/10, flow = 1.0 mL/min. Retention times: 86.7 min [(*R*)-enantiomer], 98.5 min [(*S*)-enantiomer]. 94% ee. $[\alpha]^{20}_{D} = -5.2$ (c 0.50, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4.

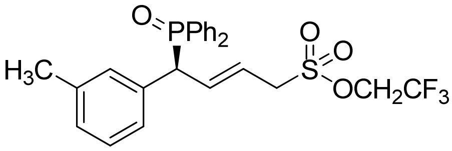
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86-7.82 (m, 2H, Ar), 7.56-7.48 (m, 5H, Ar), 7.40-7.35 (m, 1H, Ar), 7.31-7.25 (m, 2H, Ar), 7.15 (d, *J* = 7.6 Hz, 2H, Ar), 7.02 (d, *J* = 7.6 Hz, 2H, Ar), 6.36-6.16 (m, 1H, olefin), 5.55-5.46 (m, 1H, olefin), 4.33-4.15 (m, 3H), 3.89-3.75 (m, 2H, CH_2S), 2.26 (s, 3H, Me). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.5 (d, J_{CP} = 2.3 Hz), 137.0 (d, J_{CP} = 6.0 Hz), 132.2 (d, J_{CP} = 3.0 Hz), 131.8 (d, J_{CP} = 2.7 Hz), 131.6 (d, J_{CP} = 8.8 Hz), 131.4 (d, J_{CP} = 6.1 Hz), 131.31 (d, J_{CP} = 89.0 Hz), 131.29 (d, J_{CP} = 9.1 Hz), 130.21 (d, J_{CP} = 96.9 Hz), 129.6 (d, J_{CP} = 1.5 Hz), 129.3 (d, J_{CP} = 5.7 Hz), 128.9 (d, J_{CP} = 11.4 Hz), 128.4 (d, J_{CP} = 11.8 Hz), 121.9 (q, J_{CF} = 277.7 Hz), 119.6 (d, J_{CP} = 11.0 Hz), 65.1 (q, J_{CF} = 38.2 Hz), 55.0 (d, J_{CP} = 1.9 Hz), 51.2 (d,

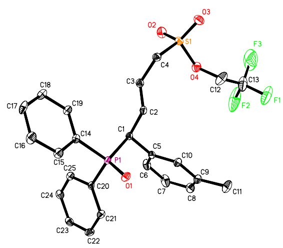
J_{CP} = 64.8 Hz). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ 28.2 (s). HRMS (ESI) calcd for $C_{25}H_{25}F_3O_4PS$ $(M+H)^+$:509.1158, found: 509.1156.



Entry 3. White solid. (66.3 mg; 63% yield). The ee was determined on a Daicel Chiralcel OD column with hexane/2-propanol = 85/15, flow = 1.0 mL/min. Retention times: 15.4 min [(*R*)-enantiomer], 26.6 min [(*S*)-enantiomer]. 96% ee. $[\alpha]^{20}_D$ = −18.4 (c 0.50, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4.

^1H NMR (400 MHz, $CDCl_3$): δ 7.86-7.82 (m, 2H, Ar), 7.56-7.46 (m, 5H, Ar), 7.40-7.35 (m, 1H, Ar), 7.31-7.25 (m, 2H, Ar), 7.15 (dd, *J* = 6.8 and 1.6 Hz, 2H, Ar), 6.75 (d, *J* = 8.8 Hz, 2H, Ar), 6.32-6.22 (m, 1H, olefin), 5.55-5.46 (m, 1H, olefin), 4.31-4.15 (m, 3H), 3.87-3.75 (m, 2H, CH_2S), 3.75 (s, 3H, OMe). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0 (d, J_{CP} = 2.3 Hz), 136.8 (d, J_{CP} = 6.1 Hz), 132.2 (d, J_{CP} = 2.7 Hz), 131.8 (d, J_{CP} = 3.0 Hz), 131.6 (d, J_{CP} = 8.3 Hz), 131.21 (d, J_{CP} = 9.1 Hz), 131.18 (d, J_{CP} = 99.1 Hz), 131.0 (d, J_{CP} = 96.5 Hz), 130.5 (d, J_{CP} = 5.7 Hz), 128.9 (d, J_{CP} = 11.3 Hz), 128.4 (d, J_{CP} = 11.7 Hz), 126.5 (d, J_{CP} = 6.1 Hz), 121.9 (q, J_{CF} = 278.1 Hz), 119.6 (d, J_{CP} = 11.0 Hz), 114.3 (d, J_{CP} = 1.9 Hz), 65.1 (q, J_{CF} = 37.8 Hz), 55.2, 54.9 (d, J_{CP} = 1.2 Hz), 50.6 (d, J_{CP} = 65.2 Hz). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ 28.2 (s). HRMS (ESI) calcd for $C_{25}H_{25}F_3O_5PS$ $(M+H)^+$: 525.1107, found: 525.1106.

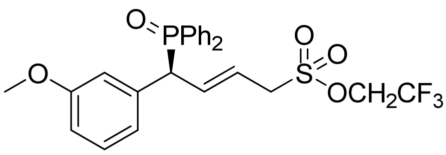




Entry 4. White solid. (88.3 mg; 87% yield). The ee was determined on a Daicel Chiralpak AD column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention

times: 18.7 min [(*R*)-enantiomer], 20.8 min [(*S*)-enantiomer]. 93% ee. $[\alpha]^{20}_{D} = -11.9$ (c 0.500, CH_2Cl_2), The absolute configuration was determined as *S* according to the X-ray crystal diffraction analysis of the product.

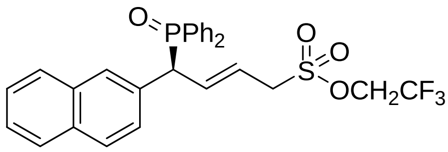
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.82 (m, 2H, Ar), 7.55-7.46 (m, 5H, Ar), 7.40-7.35 (m, 1H, Ar), 7.31-7.25 (m, 2H, Ar), 7.10-7.00 (m, 3H, Ar), 7.00 (d, J = 7.2 Hz, 1H, Ar), 6.35-6.28 (m, 1H, olefin), 5.57-5.48 (m, 1H, olefin), 4.32-4.15 (m, 3H), 3.88-3.75 (m, 2H, CH_2S), 2.23 (s, 3H, Me). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5 (d, J_{CP} = 1.9 Hz), 136.7 (d, J_{CP} = 6.3 Hz), 134.3 (d, J_{CP} = 5.9 Hz), 132.2 (d, J_{CP} = 3.0 Hz), 131.8 (d, J_{CP} = 3.0 Hz), 131.6 (d, J_{CP} = 8.2 Hz), 131.3 (d, J_{CP} = 9.0 Hz), 131.2 (d, J_{CP} = 99.1 Hz), 131.0 (d, J_{CP} = 96.9 Hz), 130.0 (d, J_{CP} = 5.6 Hz), 128.9 (d, J_{CP} = 11.5 Hz), 128.7 (d, J_{CP} = 1.5 Hz), 128.4 (d, J_{CF} = 2.3 Hz), 128.3 (d, J_{CP} = 11.9 Hz), 126.4 (d, J_{CP} = 6.0 Hz), 121.9 (q, J_{CF} = 278.3 Hz), 119.7 (d, J_{CP} = 11.2 Hz), 65.1 (q, J_{CF} = 38.1 Hz), 55.0 (d, J_{CP} = 1.5 Hz), 51.6 (d, J_{CP} = 64.3 Hz), 21.4. ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$): δ 28.1 (s). HRMS (ESI) calcd for $C_{25}H_{25}F_3O_4PS$ $(M+H)^+$: 509.1158, found: 509.1162.



Entry 5. White solid. (82.1 mg; 78% yield). The ee was determined on a Daicel Chiralpak AD column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 24.8 min [(*R*)-enantiomer], 30.7 min [(*S*)-enantiomer]. 95% ee. The absolute configuration was assigned by analogy with Table 2, entry 4.

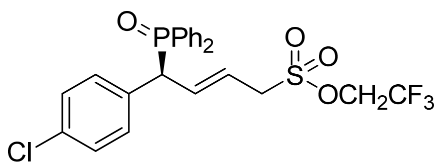
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88-7.82 (m, 2H, Ar), 7.55-7.46 (m, 5H, Ar), 7.40-7.35 (m, 1H, Ar), 7.31-7.25 (m, 2H, Ar), 7.13 (t, J = 8.0 Hz, 1H, Ar), 6.86-6.79 (m, 2H, Ar), 6.73 (d, J = 8.4 Hz, 1H, Ar), 6.35-6.28 (m, 1H, olefin), 5.55-5.48 (m, 1H, olefin), 4.32-4.15 (m, 3H), 3.88-3.75 (m, 2H, CH_2S), 3.68 (s, 3H, OMe). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8 (d, J_{CP} = 1.6 Hz), 136.6 (d, J_{CP} = 6.5 Hz), 136.0 (d, J_{CP} = 5.6 Hz), 132.3 (d, J_{CP} = 2.6 Hz), 131.9 (d, J_{CP} = 3.1 Hz), 131.6 (d, J_{CP} = 8.4 Hz), 131.3 (d, J_{CP} = 9.1 Hz), 131.2 (d, J_{CP} = 99.2 Hz), 131.0 (d, J_{CP} = 96.9 Hz), 129.8 (d,

J_{CP} = 1.6 Hz), 128.9 (d, J_{CP} = 11.7 Hz), 128.4 (d, J_{CP} = 11.7 Hz), 121.9 (q, J_{CF} = 278.1 Hz), 121.8 (d, J_{CP} = 6.0 Hz), 119.8 (d, J_{CP} = 11.0 Hz), 114.7 (d, J_{CP} = 5.7 Hz), 113.6 (d, J_{CP} = 2.3 Hz), 65.1 (q, J_{CF} = 38.3 Hz), 55.3, 55.0 (d, J_{CP} = 1.9 Hz), 51.7 (d, J_{CP} = 64.5 Hz). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ 28.2 (s). HRMS (ESI) calcd for $C_{25}H_{25}F_3O_5PS$ $(M+H)^+$: 525.1107, found: 525.1107.



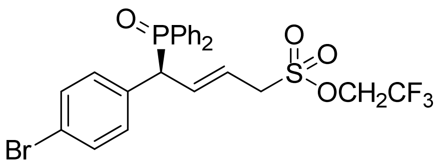
Entry 6. White solid. (95.0 mg; 87% yield). The ee was determined on a Daicel Chiralpak IC column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 19.1 min [(*R*)-enantiomer], 25.2 min [(*S*)-enantiomer]. 90% ee. $[\alpha]^{20}_{D}$ = −6.4 (c 0.50, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4.

^1H NMR (400 MHz, $CDCl_3$): δ 7.91-7.83 (m, 2H, Ar), 7.75-7.68 (m, 4H, Ar), 7.60-7.35 (m, 5H, Ar), 7.45-7.37 (m, 3H, Ar), 7.31 (t, *J* = 7.6 Hz, 1H, Ar), 7.22 (dd, *J* = 7.6 and 2.8 Hz, 2H, Ar), 6.45-6.37 (m, 1H, olefin), 5.60-5.52 (m, 1H, olefin), 4.50 (t, *J* = 9.2 Hz, 1H, PCH), 4.32-4.17 (m, 2H, OCH_2), 3.87-3.75 (m, 2H, CH_2S). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.6 (d, J_{CP} = 6.3 Hz), 133.4 (d, J_{CP} = 1.9 Hz), 132.6 (d, J_{CP} = 1.5 Hz), 132.3 (d, J_{CP} = 2.6 Hz), 132.1 (d, J_{CP} = 6.0 Hz), 131.9 (d, J_{CP} = 2.6 Hz), 131.6 (d, J_{CP} = 8.5 Hz), 131.2 (d, J_{CP} = 8.9 Hz), 131.1 (d, J_{CP} = 98.4 Hz), 131.05 (d, J_{CP} = 97.3 Hz), 128.9 (d, J_{CP} = 11.6 Hz), 128.62 (d, J_{CP} = 8.2 Hz), 128.60, 128.4 (d, J_{CP} = 11.9 Hz), 127.9, 127.7, 127.1 (d, J_{CP} = 4.8 Hz), 126.4, 126.2, 121.9 (q, J_{CF} = 277.9 Hz), 120.0 (d, J_{CP} = 11.2 Hz), 65.0 (q, J_{CF} = 38.1 Hz), 55.9 (d, J_{CP} = 1.4 Hz), 51.7 (d, J_{CP} = 64.4 Hz). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ 32.1 (s). HRMS (ESI) calcd for $C_{28}H_{25}F_3O_4PS$ $(M+H)^+$: 545.1158, found: 545.1161.



Entry 7. White solid. (89.7 mg; 85% yield). The ee was determined on a Daicel Chiralpak IC column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 13.2 min [(*R*)-enantiomer], 17.0 min [(*S*)-enantiomer]. 88% ee. $[\alpha]^{20}{}_{D} = -20.7$ (c 0.500, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4.

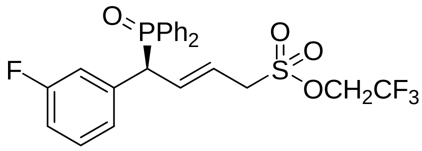
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.81 (m, 2H, Ar), 7.58-7.45 (m, 5H, Ar), 7.41-7.35 (m, 1H, Ar), 7.35-7.28 (m, 2H, Ar), 7.24-7.17 (m, 4H, Ar), 6.32-6.21 (m, 1H, olefin), 5.56-5.46 (m, 1H, olefin), 4.30-4.15 (m, 3H), 3.87-3.75 (m, 2H, CH_2S). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.2 (d, J_{CP} = 6.4 Hz), 133.7 (d, J_{CP} = 2.6 Hz), 133.1 (d, J_{CP} = 6.1 Hz), 132.4 (d, J_{CP} = 2.6 Hz), 132.1 (d, J_{CP} = 2.7 Hz), 131.6 (d, J_{CP} = 8.8 Hz), 131.1 (d, J_{CP} = 9.1 Hz), 130.9 (d, J_{CP} = 99.2 Hz), 130.7 (d, J_{CP} = 5.3 Hz), 130.67 (d, J_{CP} = 97.6 Hz), 129.04 (d, J_{CP} = 3.7 Hz), 128.99 (d, J_{CP} = 9.4 Hz), 121.9 (q, J_{CF} = 278.1 Hz), 120.2 (d, J_{CP} = 11.0 Hz), 64.9 (q, J_{CF} = 37.7 Hz), 54.9 (d, J_{CP} = 1.9 Hz), 51.9 (d, J_{CP} = 64.1 Hz). ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$): δ 27.9 (s). HRMS (ESI) calcd for $C_{24}H_{22}ClF_3O_4PS$ $(M+H)^+$: 529.0612, found: 529.0616.



Entry 8. White solid. (99.5 mg; 87% yield). The ee was determined on a Daicel Chiralpak AD column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 40.3 min [(*S*)-enantiomer], 53.1 min [(*R*)-enantiomer]. 93% ee. $[\alpha]^{20}{}_{D} = -25.9$ (c 0.500, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4.

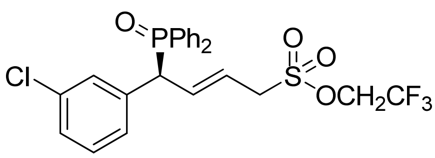
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89-7.83 (m, 2H, Ar), 7.61-7.48 (m, 5H, Ar), 7.40-7.38 (m, 1H, Ar), 7.35-7.30 (m, 4H, Ar), 7.15 (d, *J* = 6.8 Hz, 2H, Ar), 6.30-6.22 (m, 1H, olefin), 5.58-5.46 (m, 1H, olefin), 4.33-4.24 (m, 3H), 3.89-3.76 (m, 2H, CH_2S). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.5 (d, J_{CP} = 6.8 Hz), 132.0 (d, J_{CP} = 2.7 Hz), 131.9 (d, J_{CP} = 2.6 Hz), 131.4 (d, J_{CP} = 97.7 Hz), 131.1 (d, J_{CP} = 8.7 Hz), 131.07 (d, J_{CP} = 8.8 Hz), 128.8 (d, J_{CP} = 13.3 Hz), 128.7 (d, J_{CP} = 12.9 Hz), 121.9 (q, J_{CF} =

277.7 Hz), 120.3 (d, J_{CP} = 2.1 Hz), 64.6 (q, J_{CF} = 37.8 Hz), 54.7, 45.9 (d, J_{CP} = 68.0 Hz), 20.7 (d, J_{CP} = 2.6 Hz), 12.4 (d, J_{CP} = 13.3 Hz). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ 27.9 (s). HRMS (ESI) calcd for $C_{24}H_{22}BrF_3O_4PS$ $(M+H)^+$: 573.0106, found: 573.0114.



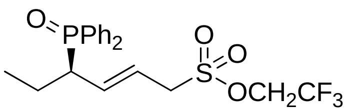
Entry 9. White solid. (86.9 mg; 86% yield). The ee was determined on a Daicel Chiralpak IC column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 12.1 min [(*R*)-enantiomer], 14.5 min [(*S*)-enantiomer]. 92% ee. $[\alpha]^{20}_D = -15.4$ (c 0.500, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4.

^1H NMR (400 MHz, $CDCl_3$): δ 7.89-7.83 (m, 2H, Ar), 7.60-7.46 (m, 5H, Ar), 7.40-7.38 (m, 1H, Ar), 7.35-7.28 (m, 2H, Ar), 7.19-7.15 (m, 1H, Ar), 7.04 (d, *J* = 8.0 Hz, 1H, Ar), 7.15 (dd, *J* = 9.2 and 1.6 Hz, 1H, Ar), 6.89 (t, *J* = 8.0 Hz, 1H, Ar), 6.30-6.22 (m, 1H, olefin), 5.54-5.46 (m, 1H, olefin), 4.33-4.21 (m, 3H), 3.89-3.76 (m, 2H, CH_2S). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7 (dd, J_{CF} = 246.9 Hz, J_{CP} = 1.9 Hz), 137.0 (dd, *J* = 7.4 and 5.9 Hz), 136.0 (d, J_{CP} = 6.3 Hz), 132.4 (d, J_{CP} = 2.6 Hz), 132.0 (d, J_{CP} = 2.6 Hz), 131.5 (d, J_{CP} = 8.6 Hz), 131.1 (d, J_{CP} = 9.0 Hz), 130.8 (d, J_{CP} = 99.5 Hz), 130.6 (d, J_{CP} = 96.9 Hz), 130.3 (dd, *J* = 9.3 and 2.6 Hz), 129.0 (d, J_{CP} = 11.5 Hz), 128.5 (d, J_{CP} = 11.9 Hz), 125.1 (dd, *J* = 6.0 and 3.0 Hz), 121.9 (q, J_{CF} = 277.9 Hz), 120.2 (d, *J* = 10.7 Hz), 116.4 (dd, *J* = 12.3 and 5.9 Hz), 114.6 (dd, *J* = 21.2 and 1.2 Hz), 64.9 (hept, J_{CF} = 38.2 Hz), 54.8 (d, J_{CP} = 1.4 Hz), 51.3 (dd, J_{CP} = 63.9 Hz, J_{CF} = 1.8 Hz). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ 27.9 (s). HRMS (ESI) calcd for $C_{24}H_{22}F_4O_4PS$ $(M+H)^+$: 513.0907, found: 513.0911.



Entry 10. White solid. (86.5 mg; 82% yield). The ee was determined on a Daicel Chiralpak IC column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 12.0 min [(*R*)-enantiomer], 14.1 min [(*S*)-enantiomer]. 89% ee. $[\alpha]^{20}_{D} = -20.7$ (c 0.500, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4.

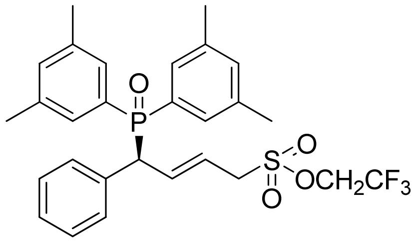
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88-7.83 (m, 2H, Ar), 7.61-7.46 (m, 5H, Ar), 7.43-7.38 (m, 1H, Ar), 7.34-7.28 (m, 2H, Ar), 7.23-7.12 (m, 4H, Ar), 6.32-6.22 (m, 1H, olefin), 5.58-5.48 (m, 1H, olefin), 4.35-4.24 (m, 3H), 3.89-3.77 (m, 2H, CH_2S). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.6 (d, J_{CP} = 5.9 Hz), 135.9 (d, J = 6.3 Hz), 134.5 (d, J_{CP} = 1.9 Hz), 132.4 (d, J_{CP} = 2.9 Hz), 132.1 (d, J_{CP} = 3.0 Hz), 131.6 (d, J_{CP} = 8.6 Hz), 131.1 (d, J_{CP} = 8.9 Hz), 130.8 (d, J_{CP} = 99.5 Hz), 130.5 (d, J_{CP} = 98.4 Hz), 130.0 (d, J =1.5 Hz), 129.5 (d, J_{CP} = 5.5 Hz), 129.0 (d, J_{CP} = 11.9 Hz), 128.5 (d, J = 11.9 Hz), 127.8 (d, J = 2.3 Hz), 127.5 (d, J = 5.6 Hz), 121.9 (q, J_{CF} = 277.9 Hz), 120.3 (d, J = 10.8 Hz), 64.9 (hept, J_{CF} = 37.8 Hz), 54.8 (d, J_{CP} = 1.1 Hz), 51.3 (d, J_{CP} = 63.6 Hz). $^{31}P\{^{1}H\}$ NMR (161 MHz, $CDCl_3$): δ 28.0 (s). HRMS (ESI) calcd for $C_{24}H_{22}ClF_3O_4PS$ $(M+H)^+$: 529.0612, found: 529.0615.



Entry 11. White solid. (74.8 mg; 84% yield). The ee was determined on a Daicel Chiralpak IC column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 18.2 min [(*R*)-enantiomer], 19.9 min [(*S*)-enantiomer]. 71% ee. $[\alpha]^{20}_{D} = -12.7$ (c 0.500, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4.

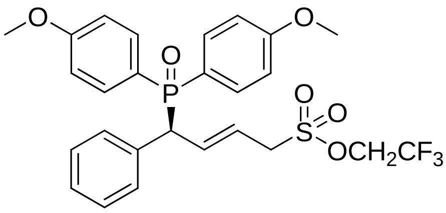
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-7.50 (m, 4H, Ar), 7.52-7.45 (m, 6H, Ar), 5.89-5.82 (m, 1H, olefin), 5.56-5.48 (m, 1H, olefin), 4.40-4.33 (m, 2H, OCH_2), 3.91-3.77 (m, 2H, CH_2S), 3.08-2.95 (m, 1H, PCH), 1.79-1.65 (m, 2H), 0.92 (t, J_{CH} = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.6 (d, J_{CP} = 5.9 Hz), 135.9 (d, J = 6.3 Hz), 134.5 (d, J_{CP} = 1.9 Hz), 132.4 (d, J_{CP} = 2.9 Hz), 132.1 (d, J_{CP} = 3.0 Hz), 131.6 (d, J_{CP} = 8.6 Hz), 131.1 (d, J_{CP} = 8.9 Hz), 130.8 (d, J_{CP} = 99.5 Hz), 130.5 (d, J_{CP} = 98.4

Hz), 130.0 (d, J =1.5 Hz), 129.5 (d, J_{CP} = 5.5 Hz), 129.0 (d, J_{CP} = 11.9 Hz), 128.5 (d, J = 11.9 Hz), 127.8 (d, J = 2.3 Hz), 127.5 (d, J = 5.6 Hz), 121.9 (q, J_{CF} = 277.9 Hz), 120.3 (d, J = 10.8 Hz), 64.9 (hept, J_{CF} = 37.8 Hz), 54.8 (d, J_{CP} = 1.1 Hz), 51.3 (d, J_{CP} = 63.6 Hz). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ 28.0 (s). HRMS (ESI) calcd for $C_{20}H_{23}F_3O_4PS$ $(M+H)^+$: 447.1001, found: 447.0999.



Entry 12. White solid. (95.5 mg; 87% yield). The ee was determined on a Daicel Chiralpak IC column with hexane/2-propanol = 85/15, flow = 1.0 mL/min. Retention times: 12.7 min [(*R*)-enantiomer], 16.6 min [(*S*)-enantiomer]. 86% ee. $[\alpha]^{20}_D = -14.5$ (c 0.50, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4.

^1H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, J = 11.2 Hz, 2H, Ar), 7.28-7.18 (m, 6H, Ar), 7.04 (d, J = 11.2 Hz, 2H, Ar), 6.97 (s, 1H, Ar), 6.34-6.26 (m, 1H, olefin), 5.58-5.47 (m, 1H, olefin), 4.32-4.15 (m, 3H), 3.87-3.77 (m, 2H, CH_2S), 2.73 (s, 6H, Me), 2.17 (s, 6H, Me). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.6 (d, J_{CP} = 11.9 Hz), 137.9 (d, J = 12.3 Hz), 137.0 (d, J_{CP} = 6.3 Hz), 134.8 (d, J_{CP} = 6.0 Hz), 133.9 (d, J_{CP} = 3.0 Hz), 133.4 (d, J_{CP} = 3.0 Hz), 131.1 (d, J_{CP} = 98.8 Hz), 130.8 (d, J_{CP} = 96.2 Hz), 129.5 (d, J_{CP} = 5.6 Hz), 129.1 (d, J =8.2 Hz), 128.8 (d, J_{CP} = 8.9 Hz), 128.7 (d, J_{CP} = 2.8 Hz), 127.5 (d, J_{CP} = 2.2 Hz), 121.9 (q, J_{CF} = 277.9 Hz), 119.6 (d, J = 11.1 Hz), 65.2 (q, J_{CF} = 38.1 Hz), 55.0 (d, J_{CP} = 1.1 Hz), 51.4 (d, J_{CP} = 63.6 Hz), 21.4 (d, J_{CP} = 0.8 Hz), 21.2 (d, J_{CP} = 0.7 Hz). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ 28.8 (s). HRMS (ESI) calcd for $C_{28}H_{31}F_3O_4PS$ $(M+H)^+$: 551.1627, found: 551.1626.



Entry 13. White solid. (95.0 mg; 86% yield). The ee was determined on a Daicel Chiralpak AS column with hexane/2-propanol = 85/15, flow = 1.0 mL/min. Retention times: 41.8 min [(*R*)-enantiomer], 54.8 min [(*S*)-enantiomer]. 76% ee. $[\alpha]^{20}_{D} = -8.6$ (c 0.50, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (t, J = 8.8 Hz, 2H, Ar), 7.36 (dd, J = 10.4 and 8.8 Hz, 2H, Ar), 7.26-7.20 (m, 5H, Ar), 7.02 (d, J = 6.8 Hz, 2H, Ar), 6.78 (d, J = 6.8 Hz, 2H, Ar), 6.36-6.28 (m, 1H, olefin), 5.55-5.47 (m, 1H, olefin), 4.30-4.19 (m, 3H), 3.86 (s, 3H, OMe), 3.84-3.78 (m, 2H, CH_2S), 3.76 (s, 3H, OMe). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.6 (d, J_{CP} = 2.6 Hz), 162.2 (d, J = 3.0 Hz), 137.2 (d, J_{CP} = 6.3 Hz), 135.0 (d, J_{CP} = 6.0 Hz), 133.4 (d, J_{CP} = 10.0 Hz), 133.1 (d, J_{CP} = 10.0 Hz), 129.5 (d, J_{CP} = 5.6 Hz), 128.8 (d, J_{CP} = 1.8 Hz), 127.5 (d, J_{CP} = 2.3 Hz), 122.7 (d, J =105.4 Hz), 122.1 (d, J_{CP} = 104.3 Hz), 121.9 (q, J_{CF} = 277.9 Hz), 119.4 (d, J = 10.4 Hz), 114.4 (d, J = 12.2 Hz), 113.9 (d, J = 12.6 Hz), 65.1 (q, J_{CF} = 38.1 Hz), 55.4, 55.3, 55.0 (d, J_{CP} = 1.1 Hz), 52.3 (d, J_{CP} = 65.1 Hz). ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$): δ 28.6 (s). HRMS (ESI) calcd for $C_{26}H_{27}F_3O_6PS$ $(M+H)^+$: 555.1213, found: 555.1212.

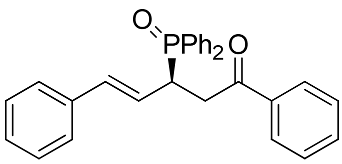


Table 1, Entry 1. White solid. (81.0 mg; 93% yield). The ee was determined on a Daicel Chiralpak IC column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 14.3 min [(*S*)-enantiomer], 17.2 min [(*R*)-enantiomer]. 93% ee. The absolute configuration was assigned by analogy with the literature example (Pincer Pd-catalyzed asymmetric 1,4-addition of diarylphosphines to *α*,*β*-unsaturated enones).[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93-7.88 (m, 4H, Ar), 7.83-7.76 (m, 2H, Ar), 7.56-7.38 (m, 9H, Ar), 7.23-7.12 (m, 5H, Ar), 6.43 (dd, *J* = 16.0 and 4.0 Hz, 1H, olefin), 6.15 (ddd, *J* = 16.0, 9.2 and 6.8 Hz, 1H, olefin), 4.22-4.10 (m, 1H), 3.69 (ddd, *J* = 18.0, 10.4 and 4.4 Hz, 1H), 3.30 (ddd, *J* = 18.0, 11.6 and 2.4 Hz, 1H). ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$): δ 34.6 (s). HRMS (ESI) calcd for $C_{29}H_{26}O_2P$ $(M+H)^+$: 437.1665, found: 437.1666.

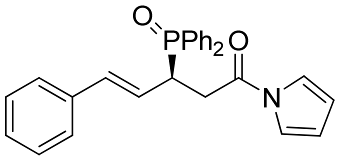


Table 1, Entry 2. (CAS: 1334387-70-0). White solid. (76.2 mg; 90% yield). The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 25.3 min [(*S*)-enantiomer], 33.1 min [(*R*)-enantiomer]. 96% ee. The absolute configuration was assigned by analogy with the literature example (Pincer Pd-catalyzed asymmetric 1,4-addition of diarylphosphines to *α*,*β*-unsaturated *N*-acylpyrroles).[4]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (t, J_{HH} = 8.8 Hz, 2H, Ar), 7.79 (dd, *J* = 10.0 and 8.0 Hz, 2H, Ar), 7.57-7.16 (m, 13H), 6.45 (dd, *J* = 15.6 and 3.6 Hz, 1H, olefin), 6.25 (s, 2H), 6.13 (ddd, *J* = 15.6, 8.8 and 2.4 Hz, 1H, olefin), 4.06 (q, *J* = 8.8 Hz, 1H), 3.41 (ddd, J_{HH} = 17.2 and 10.0 Hz, J_{HP} = 4.4 Hz, 1H), 3.21 (ddd, J_{HH} = 16.8 and 2.0 Hz, J_{HP} = 10.8 Hz, 1H). ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$): δ 33.7 (s).

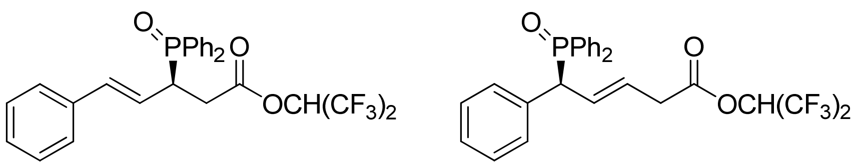


Table 1, Entry 3. White solid. (64.1 mg; 61% combined yield). 1.4-adduct : 1.6-adduct = 1 : 2.

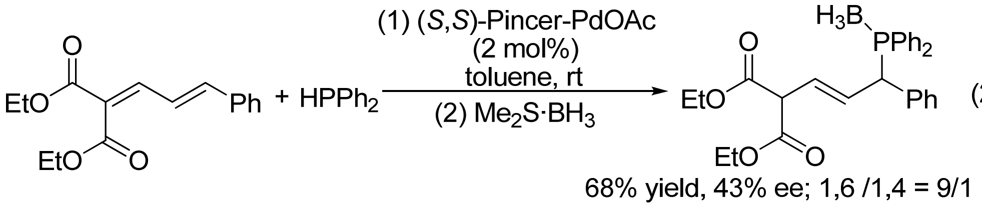
The ee of 1,4-adduct was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 6.6 min [(*S*)-enantiomer], 11.0 min [(*R*)-enantiomer]. 61% ee. The absolute configuration was assigned by analogy with the literature examples (Pincer Pd-catalyzed asymmetric 1,4-addition of diarylphosphines to *α,β*-unsaturated carboxylic esters).[5]

^{1}H NMR (400 MHz, $CDCl_3$) for 1,4-adduct: δ 6.35 (dd, *J* = 16.0 and 4.4 Hz, 1H, olefin), 6.02 (ddd, *J* = 16.0, 8.8 and 6.4 Hz, 1H, olefin), 3.83-3.74 (m, 1H), 3.07 (ddd, *J* = 16.4 and 8.8 and 3.6 Hz, 1H), 2.94 (ddd, *J* = 16.4, 11.2 and 5.2 Hz, 1H). ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$): δ 33.5 (s). HRMS (ESI) calcd for $C_{26}H_{22}F_6O_3P$ $(M+H)^+$: 527.1205, found: 527.1201.

The ee of 1,6-adduct was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 8.6 min [(*R*)-enantiomer], 9.6 min [(*S*)-enantiomer]. 71% ee. The absolute configuration was assigned by analogy with Table 2, entry 4.

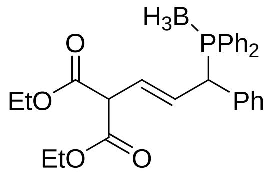
^{1}H NMR (400 MHz, $CDCl_3$) for 1,6-adduct: δ 6.15-6.06 (m, 1H, olefin), 5.71-5.63 (m, 1H), 5.60-5.48 (m, 1H), 4.26 (t, *J* = 9.6 Hz, 1H), 3.24-3.10 (m, 2H). ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$): δ 33.0 (s). HRMS (ESI) calcd for $C_{26}H_{22}F_6O_3P$ $(M+H)^+$: 527.1205, found: 527.1201.

Experimental Procedures for the 1,6-Addition Reaction in Eq. 2



(2)

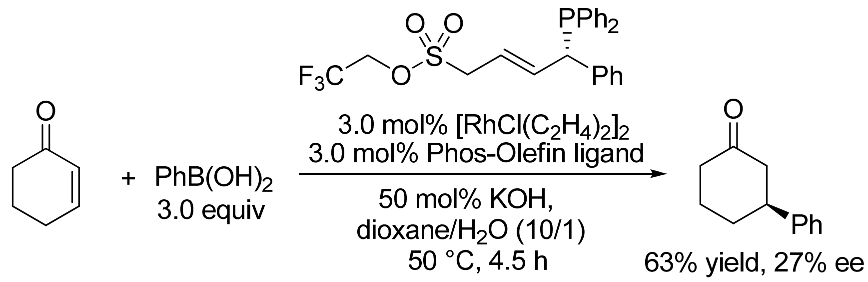
Diphenylphosphine (18.6 mg, 0.10 mmol) was added to a solution of (*S,S*)-Pd catalyst (1.4 mg, 2 μmol Pd) and [(2E)-3-phenyl-2-propenylidene]- diethyl ester (32.9 mg, 0.12 mmol) in toluene (2.0 mL) at room temperature, then the resulting solution was stirred for 17 h. The reaction was quenched with $Me_2S{\cdot}BH_3$ (0.15 mL; 2 M in THF) and concentrated under vacuum. The residue was purified by silica gel chromatography with hexane/EtOAc = 10/1 to afford the 1,6-adduct as a white solid.



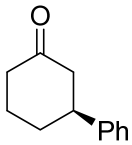
White solid. (32.0 mg; 68% yield). The ee was determined on a Daicel Chiralpak AD column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 7.8 min [major enantiomer], 8.7 min [minor enantiomer]. 43% ee. $[\alpha]^{20}_{D}$ = 7.3 (c 1.00, CH_2Cl_2),

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (t, J = 8.8 Hz, 2H, Ar), 7.52-7.32 (m, 6H, Ar), 7.30-7.26 (m, 2H, Ar), 7.20-7.10 (m, 5H, Ar), 6.17 (ddd, J = 15.2, 9.6 and 6.4 Hz, 1H, olefin), 5.71 (ddd, J = 15.2, 9.6 and 3.2 Hz, 1H, olefin), 4.44 (dd, J = 15.2 and 9.6 Hz, 1H), 4.12 (q, J = 7.2 Hz, 2H), 4.10-4.00 (m, 2H), 3.96 (d, J = 9.2 Hz, 1H), 1.19 (t, J = 7.2 Hz, 3H), 1.18 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.5 (d, J_{CP} = 1.9 Hz), 167.3 (d, J = 2.6 Hz), 135.3 (d, J_{CP} = 1.5 Hz), 133.5 (d, J_{CP} = 8.4 Hz), 132.9 (d, J_{CP} = 8.4 Hz), 131.4 (d, J_{CP} = 2.2 Hz), 131.3, 131.0 (d, J_{CP} = 2.6 Hz), 129.4 (d, J_{CP} = 4.9 Hz), 128.6 (d, J_{CP} = 9.8 Hz), 128.3 (d, J = 9.8 Hz), 128.1 (d, J_{CP} = 2.3 Hz), 127.8 (d, J_{CP} = 52.6 Hz), 127.3 (d, J_{CP} = 2.7 Hz), 127.1 (q, J_{CF} = 52.7 Hz), 126.1 (d, J = 11.0 Hz), 61.7, 52.2 (q, J_{CF} = 1.5 Hz), 48.0 (d, J_{CP} = 29.9 Hz), 13.94, 13.93. $^{31}P\{^{1}H\}$ NMR (161 MHz, $CDCl_3$): δ 24.7 (m). HRMS (ESI) calcd for $C_{28}H_{36}BNO_4P$ $(M+NH_4)^+$: 491.2506, found: 491.2511.

Experimental Procedure for Rhodium-Catalyzed 1,4-Addition of Phenylboronic Acid to Cyclohexenone

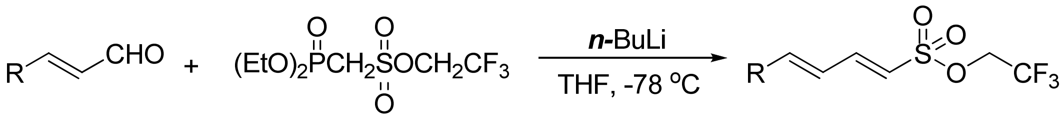


A mixture of $[RhCl(C_2H_4)]_2$ (1.2 mg, 6 μmol Rh) and the allylic phosphine (2.9 mg, 6 μmol; Table 2, Entry 1) in dioxane (2 mL) was stirred at room temperature for 20 min. Then, 0.50 M aqueous KOH (0.20 mL, 0.10 mmol) wa added into it, followed by the addition of cyclohexenone (119.2 mg, 0.20 mmol) and $PhB(OH)_2$ (73.2 mg, 0.60 mmol). The solution was stirred for 4.5 h at 50 °C, and was then passed through a pad of silica gel with EtOAc, and the solvent was removed under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane to afford the 1,4-adduct .

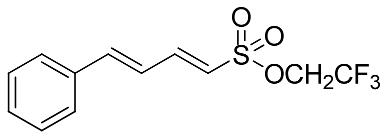


(CAS 57344-86-2). (22.0 mg; 63% yield). ^{1}H NMR data of the product are identical with the reported data of the product in literature.[6] The ee was determined on a Daicel Chiralcel OD column with hexane/2-propanol = 98/2, flow = 1.0 mL/min. Retention times: 12.8 min [(*S*)-enantiomer], 13.6 min [(*R*)-enantiomer]. 27% ee.

Genernal Procedures for the Preparation of *α,β,γ,δ*-Unsaturated Sulfonic Esters

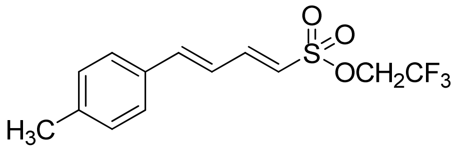


n-BuLi (1.92 mmol; 2.5 M in hexane) was added to a solution of 2,2,2-trifluoroethyl (diethoxyphosphoryl)methanesulfonate (0.6 g, 1.92 mmol) in THF at −78 °C and stirred for 20 min. Aldehyde (1.6 mmol) was added to it, and the resulting solution was allowed to warm to room temperature slowly an stirred at room temperature for 20 h. After quenching with AcOH (0.2 mL), the mixture was extracted with EtOAc, dried over $MgSO_4$, filtered and concentrated under vacuum. The residue was purified by silica gel chromatography with hexane/EtOAc = 30/1 to afford product as a white solid.

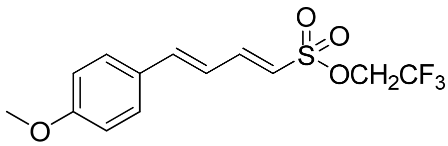


(0.42 g; 89% yield). ^{1}H NMR (300MHz, $CDCl_3$): δ 7.50-7.46 (m, 2H), 7.42-7.36 (m, 4H), 7.03 (d, J_{HH} = 15.0 Hz, 1H, olefin), 6.87-6.78 (m, 1H, olefin), 6.35 (d, J_{HH} = 15.0

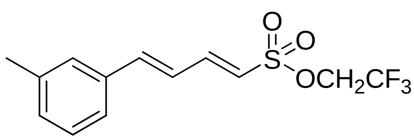
Hz, 1H, olefin), 4.42 (q, J_{HF} = 7.8 Hz, 2H, OCH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.7, 145.0, 135.0, 130.3, 129.1, 127.8, 122.7, 122.1 (q, J_{CF} = 277.8 Hz), 120.3, 64.6 (q, J_{CF} = 38.0 Hz). HRMS (ESI) calcd for $C_{12}H_{15}F_3NO_3S$ $(M+NH_4)^+$: 310.0719, found: 310.0726.



(0.38 g; 77% yield). ^1H NMR (300MHz, $CDCl_3$): δ 7.36-7.28 (m, 3H), 7.12-7.09 (m, 2H), 6.92 (d, J_{HH} = 15.0 Hz, 1H, olefin), 6.74-6.65 (m, 1H, olefin), 6.22 (d, J_{HH} =15.0 Hz, 1H, olefin), 4.32 (q, J_{HF} = 8.1 Hz, 2H, OCH_2), 2.28 (s, 3H, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.0, 145.1, 140.8, 132.3, 129.8, 127.8, 122.1 (q, J_{CF} = 277.8 Hz), 121.8, 120.5, 64.6 (q, J_{CF} = 38.0 Hz), 21.5. HRMS (ESI) calcd for $C_{13}H_{13}F_3NaO_3S$ $(M+Na)^+$: 329.0430, found: 329.0417.

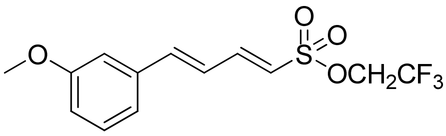


(0.39 g; 76% yield). ^1H NMR (300MHz, $CDCl_3$): δ 7.46-7.37 (m, 3H), 7.01 (d, J_{HH} = 15.0 Hz, 1H, olefin), 6.93-6.90 (m, 2H, Ar), 6.77-6.68 (m, 1H, olefin), 6.28 (d, J_{HH} =15.0 Hz, 1H, olefin), 4.41 (q, J_{HF} = 8.1 Hz, 2H, OCH_2), 3.85 (s, 3H, OMe). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.5, 147.3, 144.9, 129.5, 127.8, 122.3 (q, J_{CF} = 277.8 Hz), 120.6, 119.5, 114.6, 64.6 (q, J_{CF} = 38.0 Hz), 55.5. HRMS (ESI) calcd for $C_{13}H_{17}F_3NO_4S$ $(M+NH_4)^+$: 340.0825, found: 340.0817.

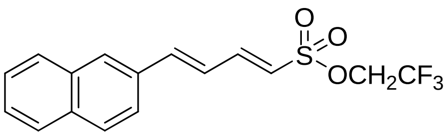


(0.37 g; 76% yield). ^1H NMR (300MHz, $CDCl_3$): δ 7.46-7.38 (m, 1H), 7.30-7.25 (m, 3H), 7.20-7.18 (m, 1H), 7.02 (d, J_{HH} = 15.0 Hz, 1H, olefin), 6.88-6.79 (m, 1H, olefin), 6.33 (d, J_{HH} =15.0 Hz, 1H, olefin), 4.42 (q, J_{HF} = 7.8 Hz, 2H, OCH_2), 2.37 (s, 3H, Me).

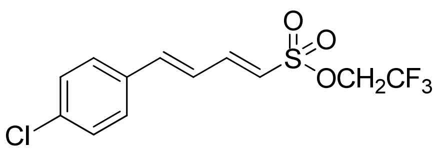
^{13}C NMR (75 MHz, $CDCl_3$): δ 146.8, 145.3, 138.9, 135.0, 131.2, 129.0, 128.5, 125.1, 122.6, 122.1 (q, J_{CF} = 277.8 Hz), 121.0, 64.6 (q, J_{CF} = 37.5 Hz), 21.4. HRMS (ESI) calcd for $C_{13}H_{17}F_3NO_3S$ $(M+NH_4)^+$: 324.0876, found: 324.0879.



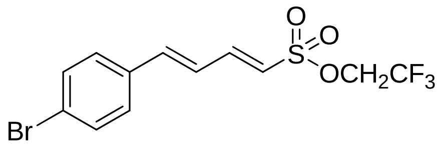
(0.38 g; 76% yield). ^{1}H NMR (300MHz, $CDCl_3$): δ 7.45-7.29 (m, 2H), 7.09-6.78 (m, 5H), 6.35 (d, J_{HH} = 14.7 Hz, 1H, olefin), 4.42 (q, J_{HF} = 7.2 Hz, 2H, OCH_2), 3.83 (s, 3H, OMe). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.1, 146.5, 144.9, 136.4, 130.1, 123.1, 122.3 (q, J_{CF} = 277.8 Hz), 121.4, 120.5, 116.0, 112.9, 64.6 (q, J_{CF} = 38.6 Hz), 55.4. HRMS (ESI) calcd for $C_{13}H_{17}F_3NO_4S$ $(M+NH_4)^+$: 340.0825, found: 340.0829.



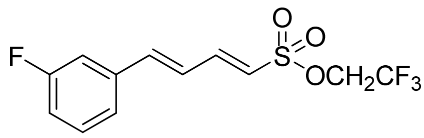
(0.27 g; 50% yield). ^{1}H NMR (300MHz, $CDCl_3$): δ 7.74-7.71 (m, 4H), 7.51-7.31 (m, 4H), 7.03 (d, J_{HH} = 15.0 Hz, 1H, olefin), 6.84-6.75 (m, 1H, olefin), 6.25 (d, J_{HH} =15.0 Hz, 1H, olefin), 4.34 (q, J_{HF} = 7.8 Hz, 2H, OCH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.7, 145.1, 134.2, 133.4, 132.5, 129.6, 128.9, 128.6, 127.9, 127.5, 127.0, 123.3, 123.0, 122.2, 122.3 (q, J_{CF} = 277.8 Hz), 64.6 (q, J_{CF} = 37.4 Hz). HRMS (ESI) calcd for $C_{16}H_{17}F_3NO_3S$ $(M+NH_4)^+$: 360.0876, found: 360.0879.



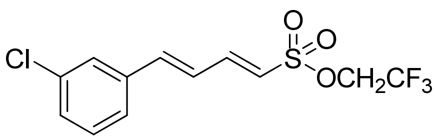
(0.38 g; 72% yield). ^{1}H NMR (300MHz, $CDCl_3$): δ 7.35-7.46 (m, 5H), 7.01 (d, J_{HH} = 15.0 Hz, 1H, olefin), 6.78-6.86 (m, 1H, olefin), 6.38 (d, J_{HH} =15.0 Hz, 1H, olefin), 4.43 (q, J_{HF} = 7.8 Hz, 2H, OCH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.2, 143.5, 136.2, 133.5, 129.4, 129.0, 123.3, 122.1 (q, J_{CF} = 277.9 Hz), 121.9, 64.7 (q, J_{CF} = 38.0 Hz). HRMS (ESI) calcd for $C_{12}H_{14}ClF_3NO_3S$ $(M+NH_4)^+$: 344.0330, found: 344.0331.



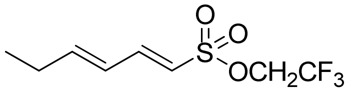
(0.36 g; 61% yield). ^{1}H NMR (300MHz, $CDCl_3$): δ 7.54-7.51 (m, 2H), 7.45-7.34 (m, 3H), 6.99 (d, J_{HH} = 15.0 Hz, 1H, olefin), 6.88-6.79 (m, 1H, olefin), 6.38 (d, J_{HH} =15.0 Hz, 1H, olefin), 4.43 (q, J_{HF} = 7.8 Hz, 2H, OCH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.1, 143.5, 133.9, 132.4, 129.2, 124.6, 123.4, 122.1 (q, J_{CF} = 277.9 Hz), 122.1, 64.7 (q, J_{CF} = 38.0 Hz). HRMS (ESI) calcd for $C_{12}H_{10}BrF_3NaO_3S$ $(M+Na)^+$: 392.9378, found: 392.9362.



(0.35 g; 77% yield). ^{1}H NMR (300MHz, $CDCl_3$): δ 7.46-7.33 (m, 2H), 7.27-7.17 (m, 2H), 7.10-6.98 (m, 2H), 6.88-6.79 (m, 1H, olefin), 6.40 (d, J_{HH} =15.0 Hz, 1H, olefin), 4.44 (q, J_{HF} = 7.8 Hz, 2H, OCH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.1 (d, J_{CF} = 247.1 Hz), 145.9, 143.4 (d, J_{CF} = 2.9 Hz), 137.2 (d, J_{CF} = 8.0 Hz), 130.7 (d, J_{CF} = 8.4 Hz), 124.0, 123.8 (d, J_{CF} = 2.8 Hz), 122.4, 122.1 (q, J_{CF} = 278.3 Hz), 117.1 (d, J_{CF} = 21.2 Hz), 114.0 (d, J_{CF} = 22.4 Hz), 64.7 (q, J_{CF} = 38.0 Hz). HRMS (ESI) calcd for $C_{12}H_{14}F_4NO_3S$ $(M+NH_4)^+$: 328.0625, found: 328.0631.

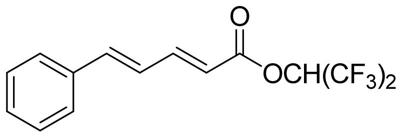


(0.6 g; 69% yield). ^{1}H NMR (300MHz, $CDCl_3$): δ 7.47-7.34 (m, 5H), 6.98 (d, J_{HH} = 15.0 Hz, 1H, olefin), 6.88-6.80 (m, 1H, olefin), 6.40 (d, J_{HH} =15.0 Hz, 1H, olefin), 4.40 (q, J_{HF} = 8.1 Hz, 2H, OCH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.9, 143.1, 136.8, 135.1, 130.4, 130.1, 127.5, 126.0, 124.1, 122.5, 122.1 (q, J_{CF} = 277.9 Hz), 64.7 (q, J_{CF} = 38.0 Hz). HRMS (ESI) calcd for $C_{12}H_{14}ClF_3NO_3S$ $(M+NH_4)^+$: 344.0330, found: 344.0333.



(0.23 g; 60% yield). ^{1}H NMR (300MHz, $CDCl_3$): δ 7.30-7.22 (m, 1H, olefin), 6.45-6.35 (m, 1H, olefin), 6.24-6.16 (m, 2H, olefin), 4.39 (q, J_{HF} = 7.8 Hz, 2H, OCH_2), 2.31-2.22 (m, 2H, $=CCH_2$), 1.08 (t, J_{HH} = 7.5 Hz, 3H, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.4, 147.3, 124.5, 120.8, 122.1 (q, J_{CF} = 208.5 Hz), 64.4 (q, J_{CF} = 28.3 Hz), 26.1, 12.3. HRMS (ESI) calcd for $C_8H_{12}F_3O_3S$ $(M+H)^+$: 245.0454, found: 245.0452.

The substrate **1f** was prepared from the corresponding acyl chloride with hexafluoro isopropanol in the presence of Et_3N following the literature procedure.



71% yield. ^{1}H NMR (300MHz, $CDCl_3$): δ 7.66 (dd, J_{HH} = 15.3 and 10.2 Hz, 1H, olefin), 7.53-7.50 (m, 2H, Ar), 7.46-7.40 (m, 3H, Ar), 7.02-6.85 (m, 2H, olefin), 6.06 (q, J_{HH} = 15.3 Hz, 1H, olefin), 6.08-5.98 (m, 1H, OCH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.5, 149.1, 143.4, 135.7, 129.9, 129.0, 127.7, 125.5, 122.7, 120.9 (q, J_{CF} = 282.9 Hz), 116.9, 66.6 (sept, J_{CF} = 34.7 Hz). MS (ESI): 324.8 (M^+).

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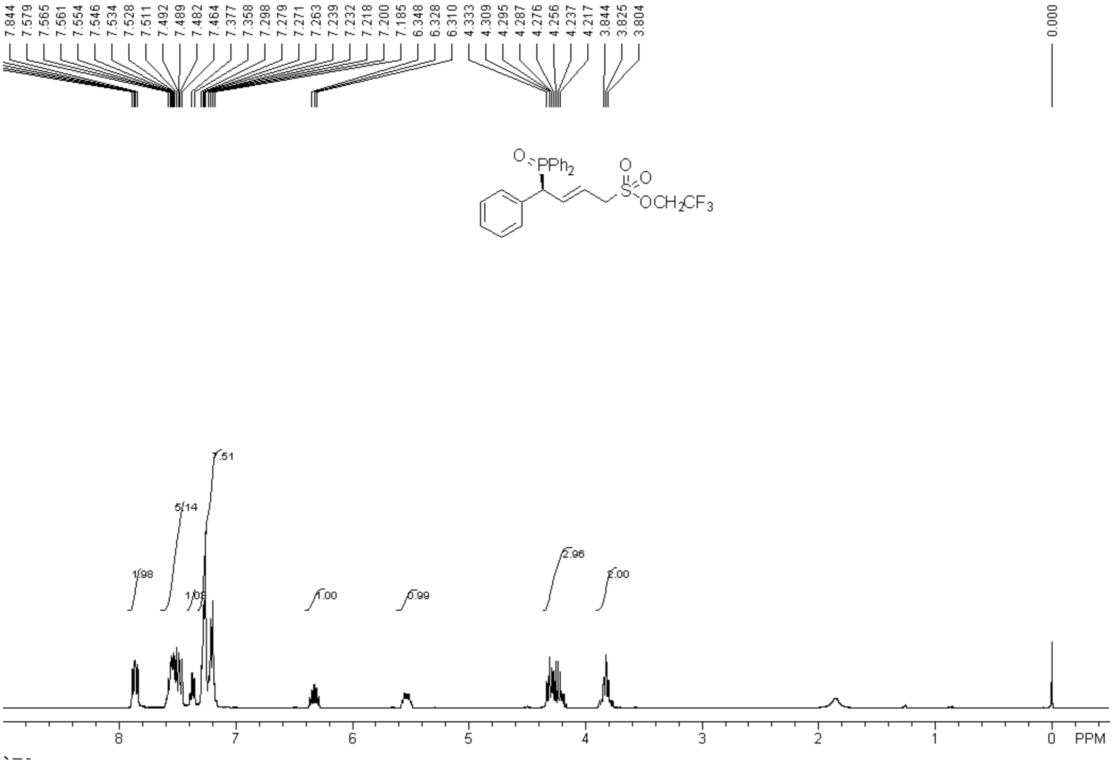
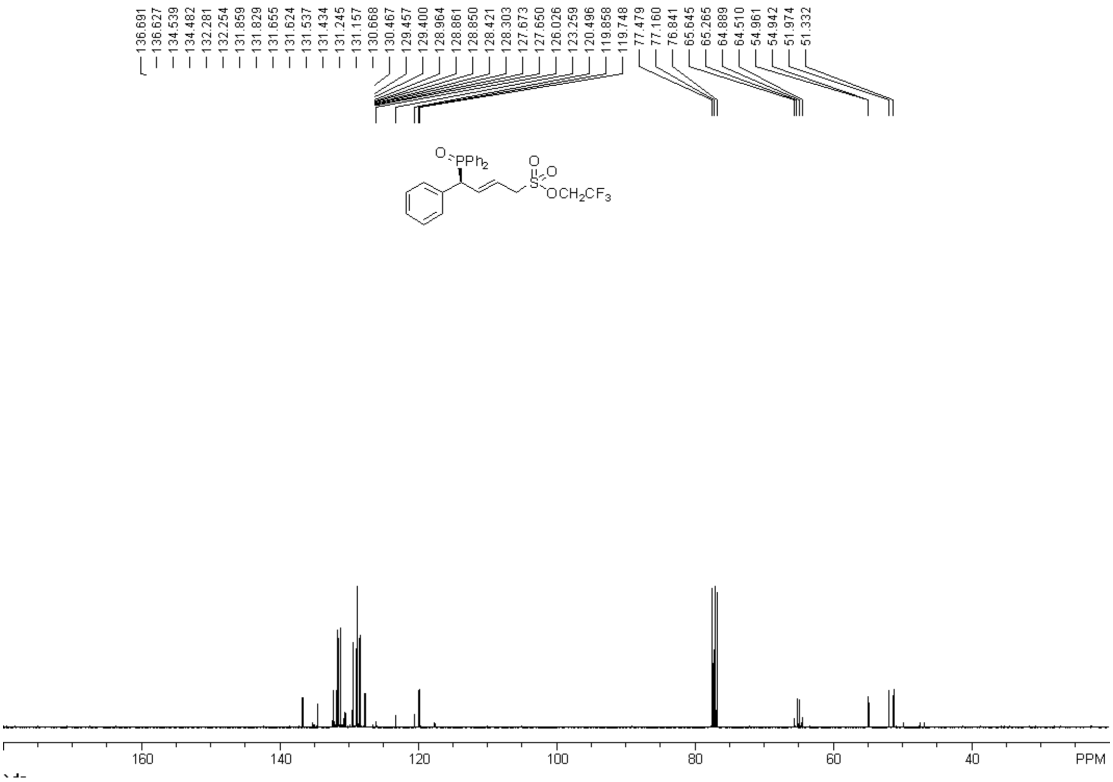
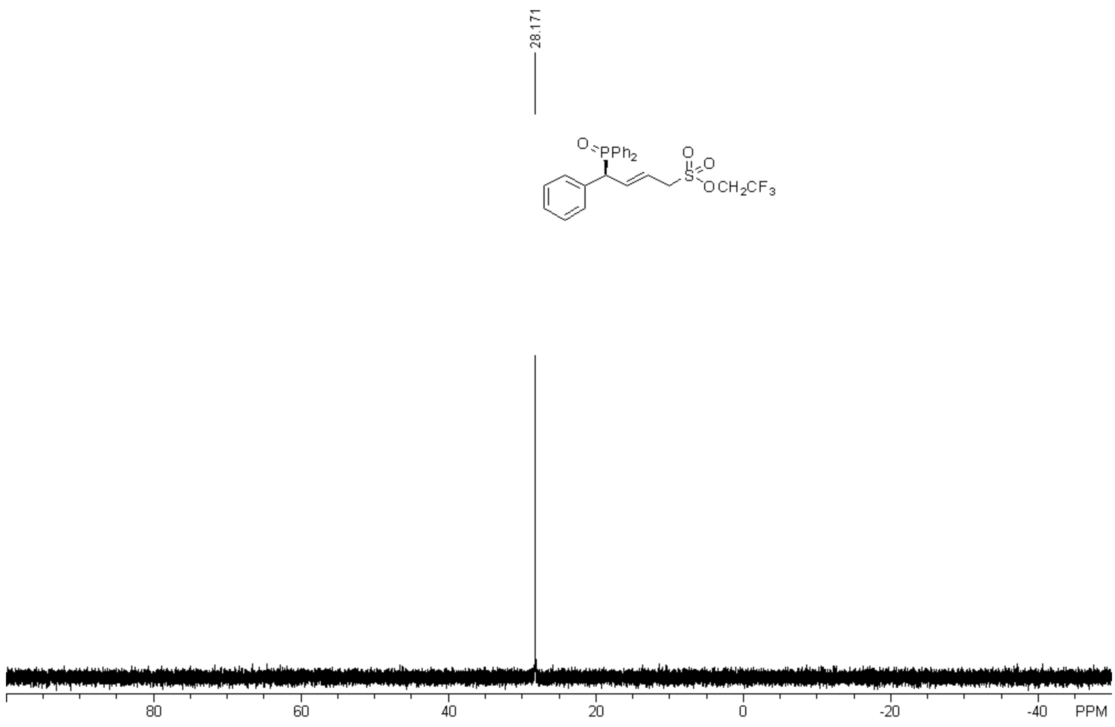
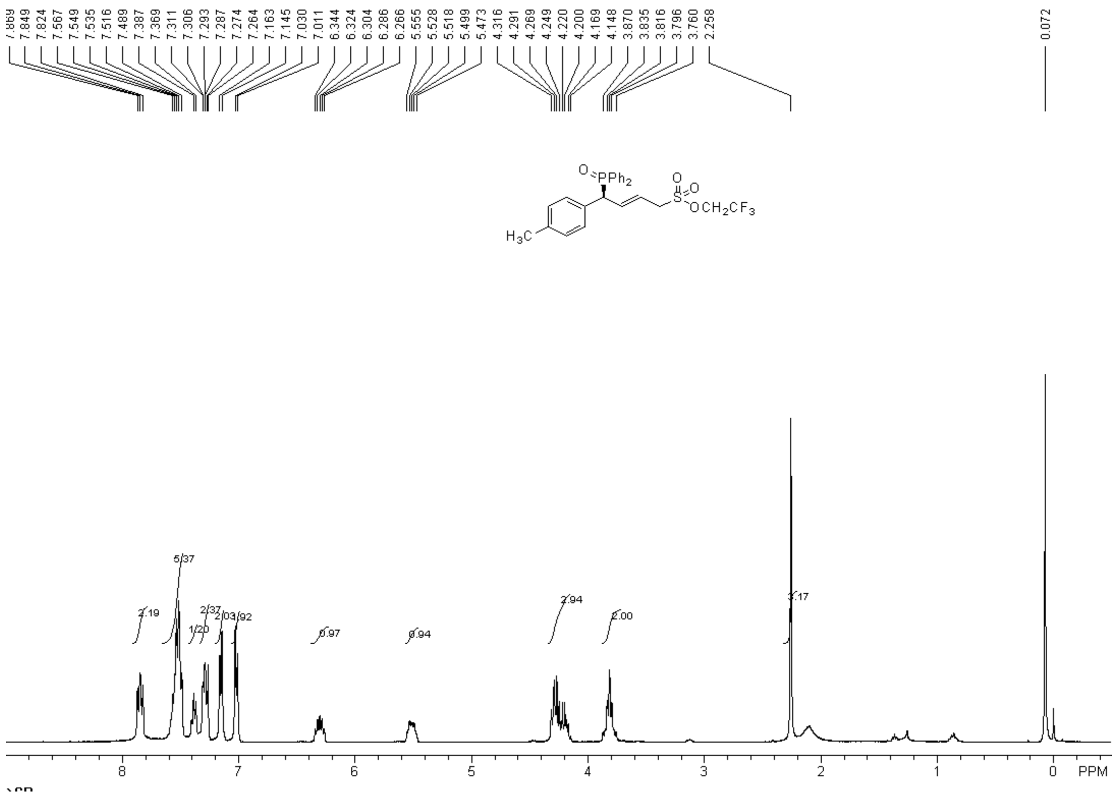
NMR Spectra

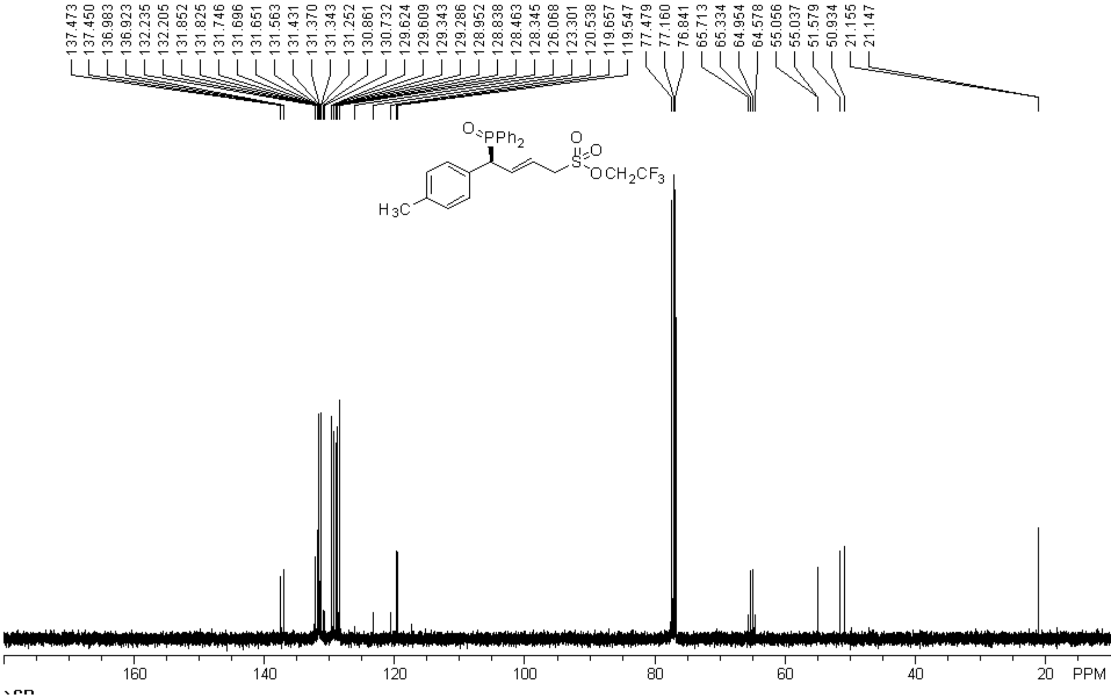




Electronic Supplementary Material (ESI) for Chemical Communications



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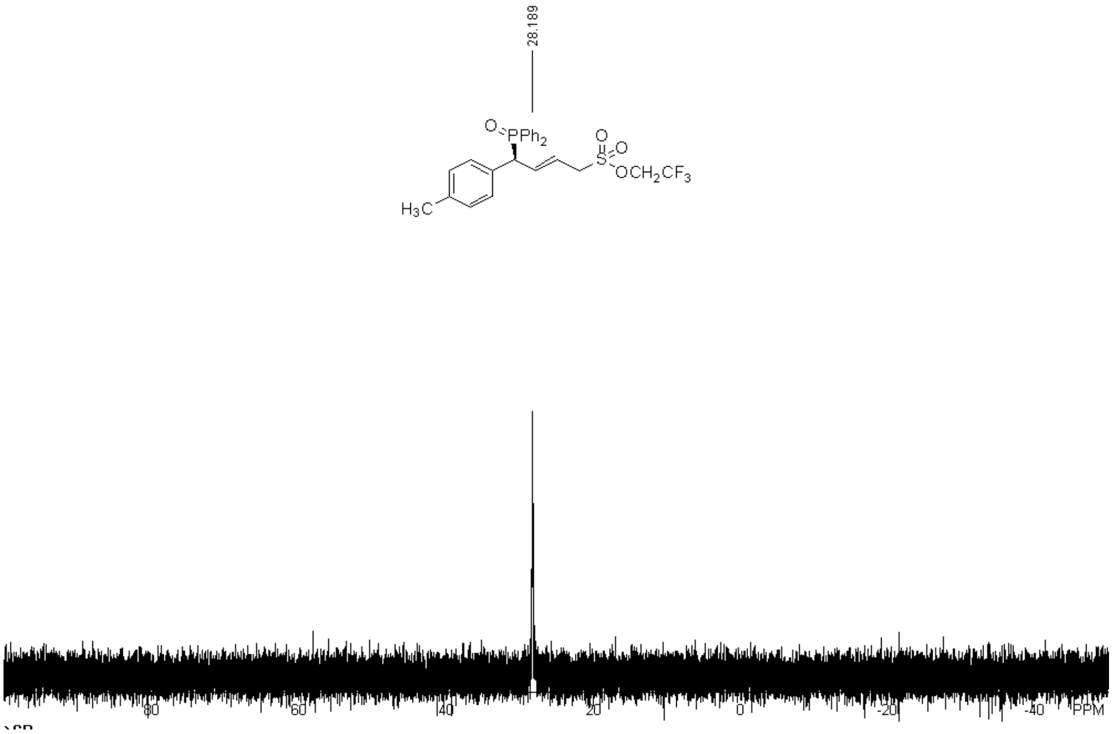
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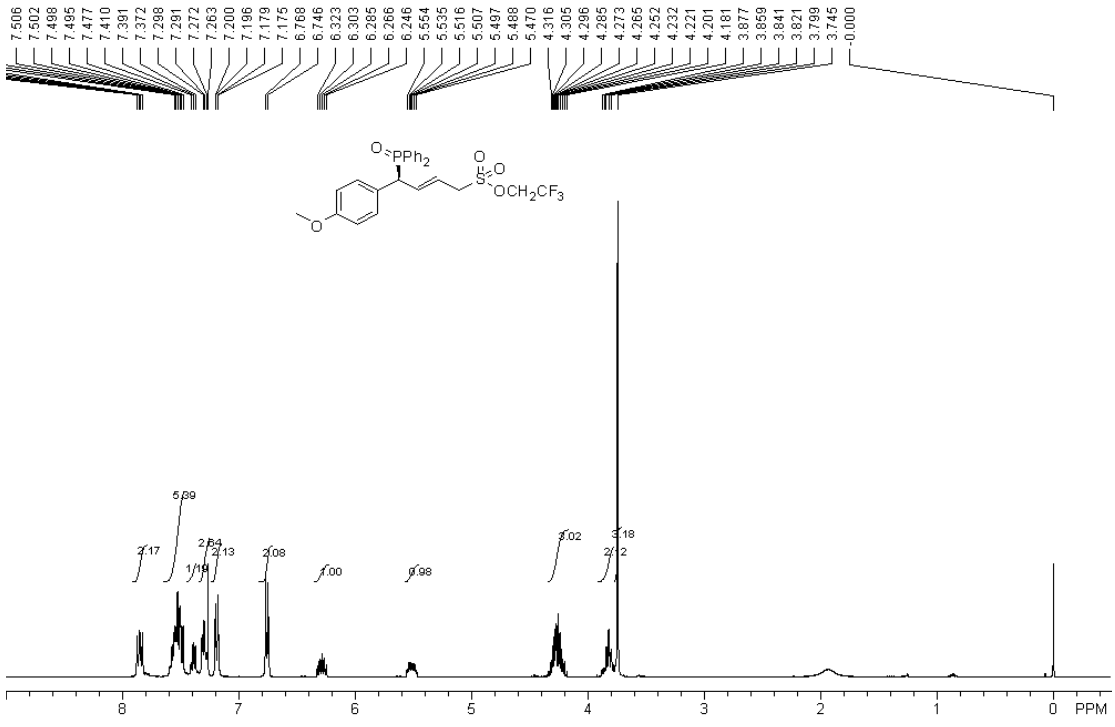
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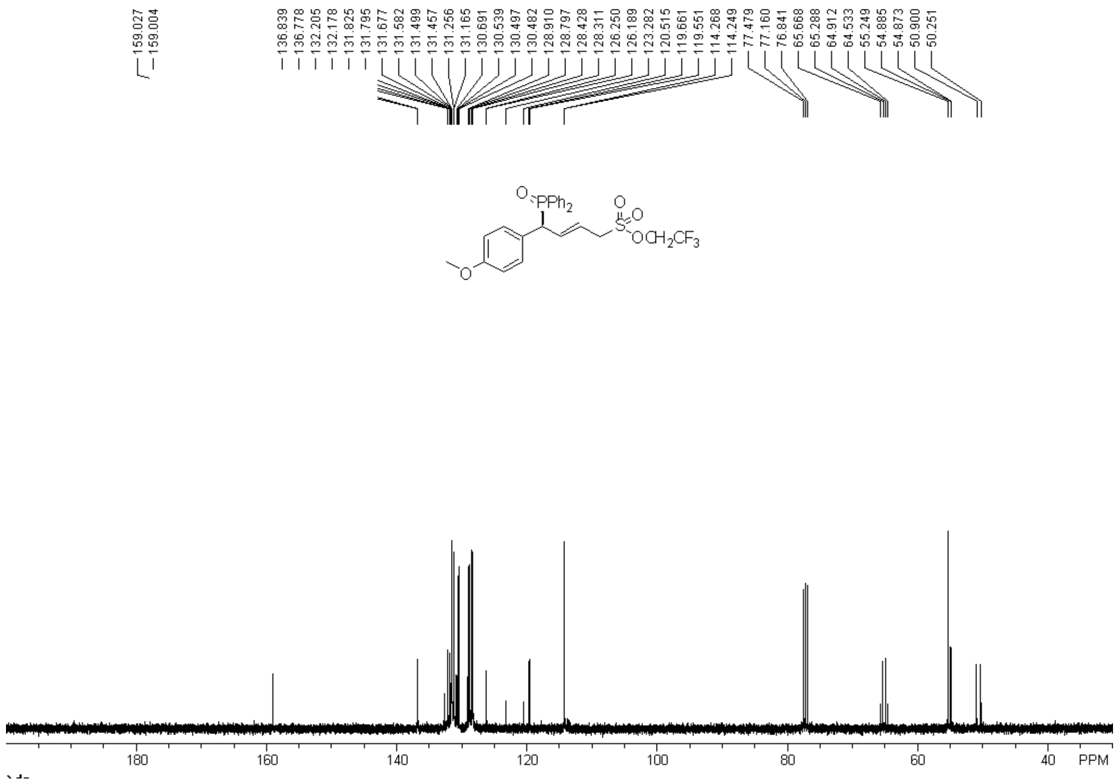
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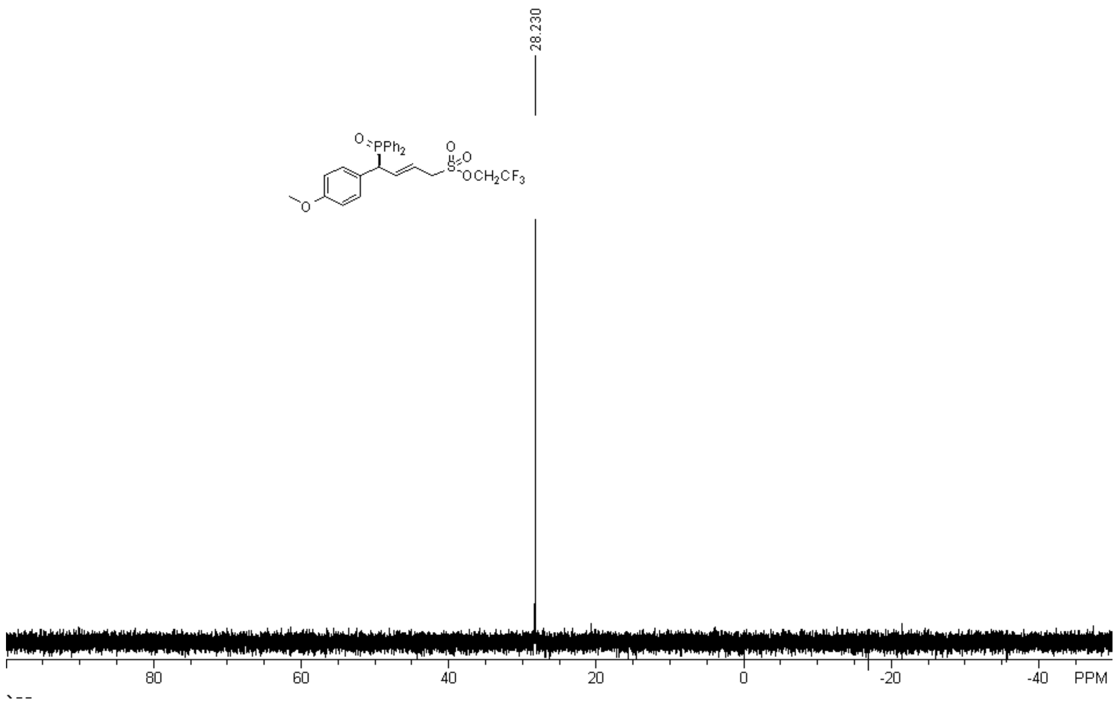
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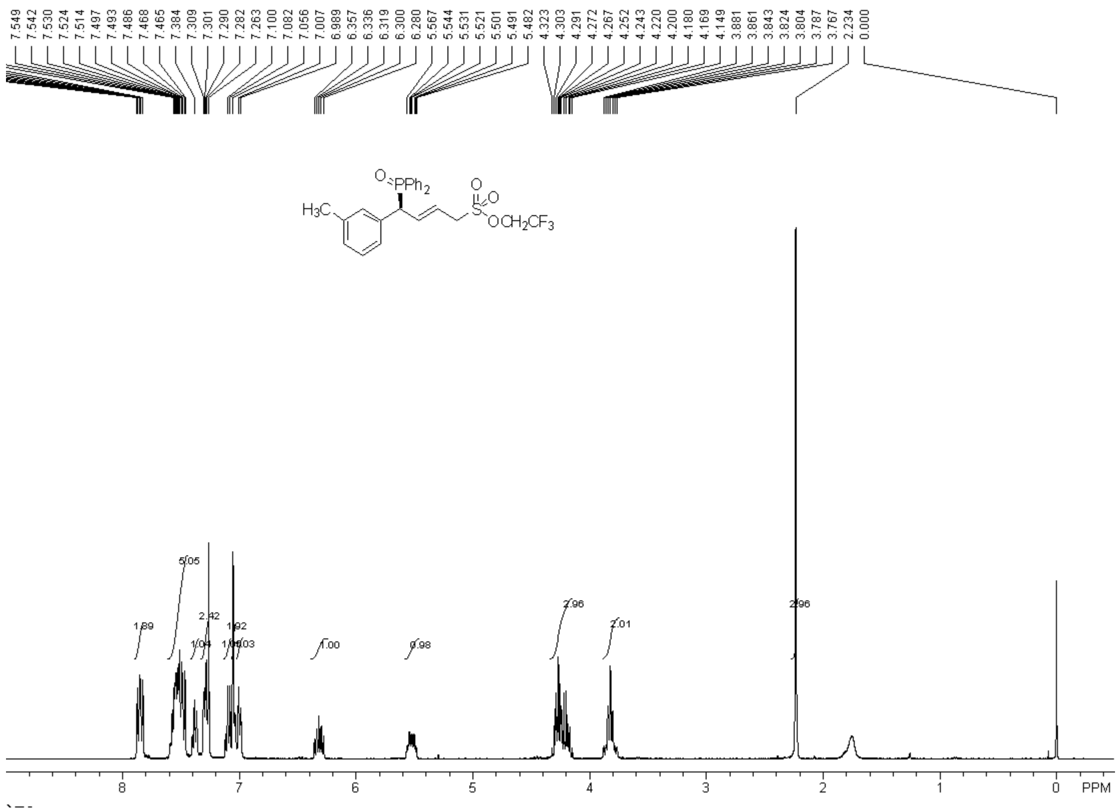
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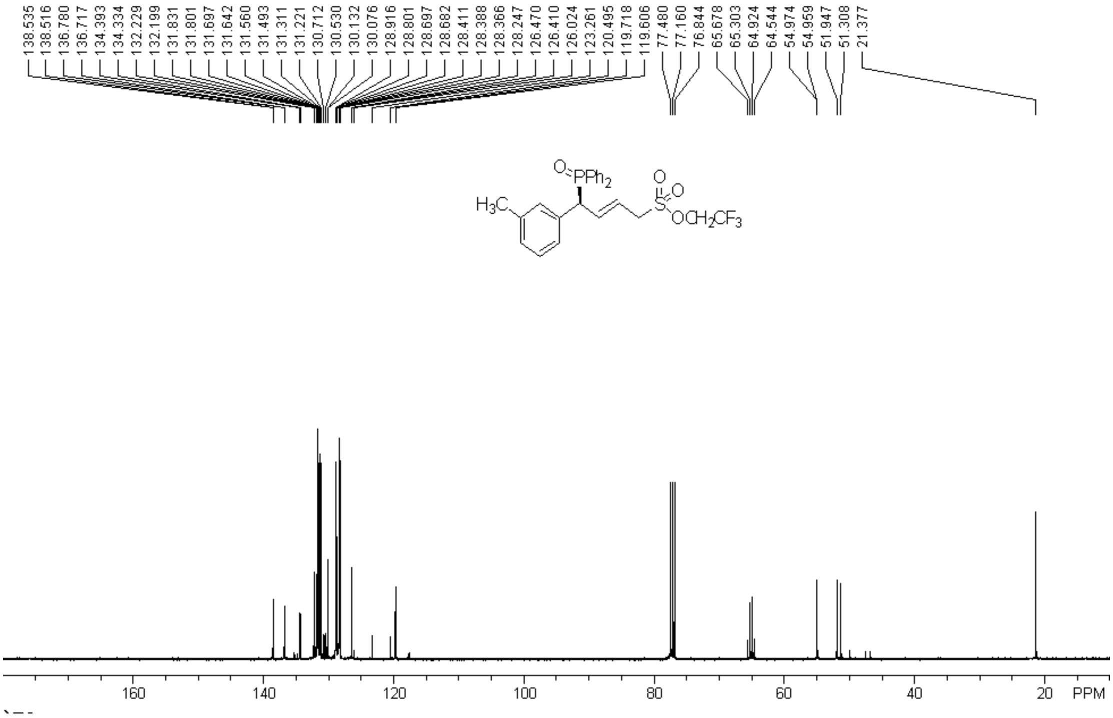
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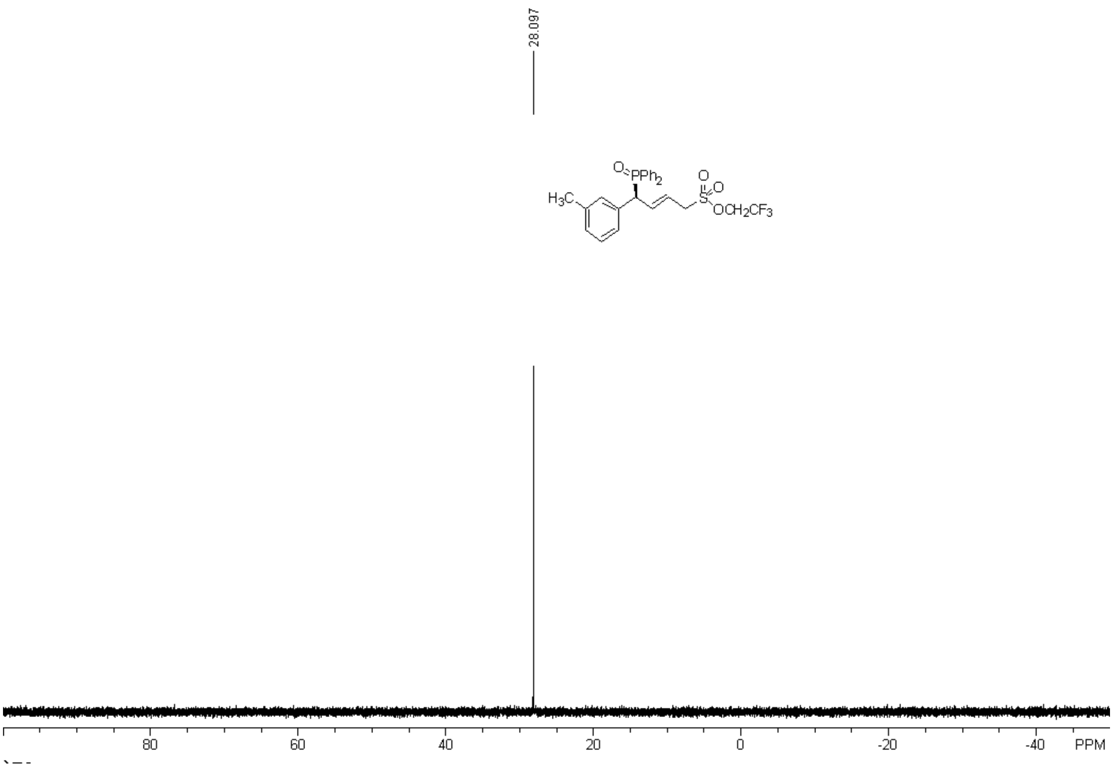
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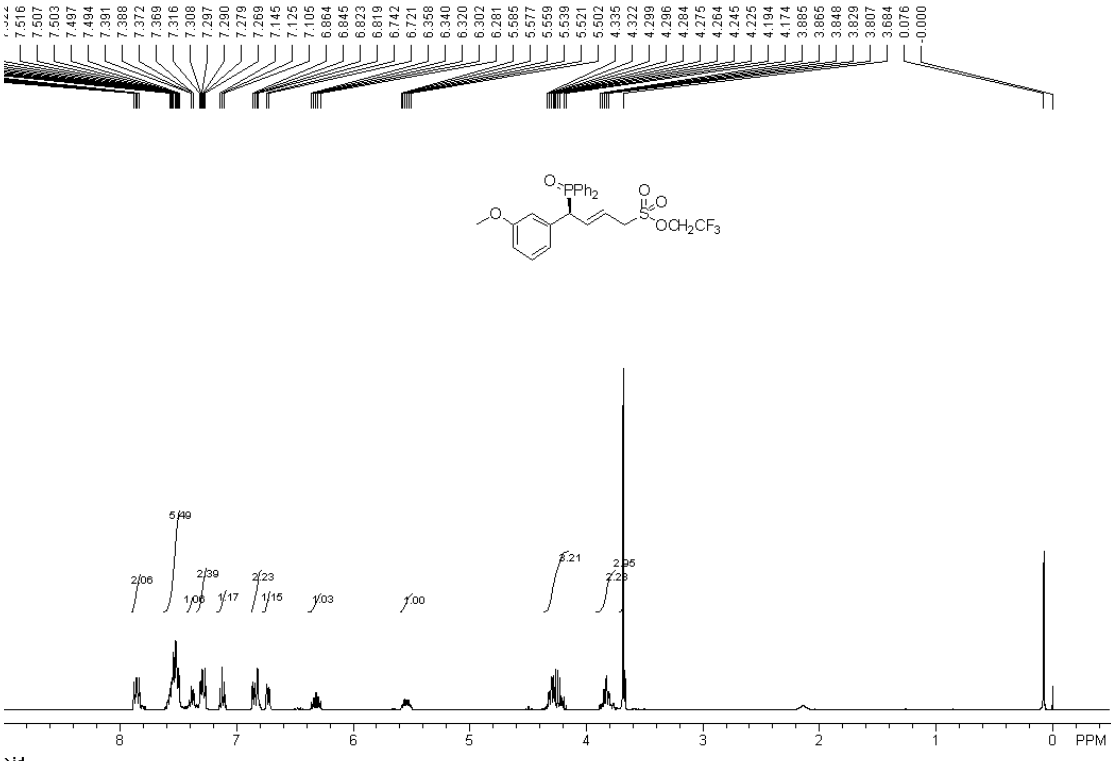
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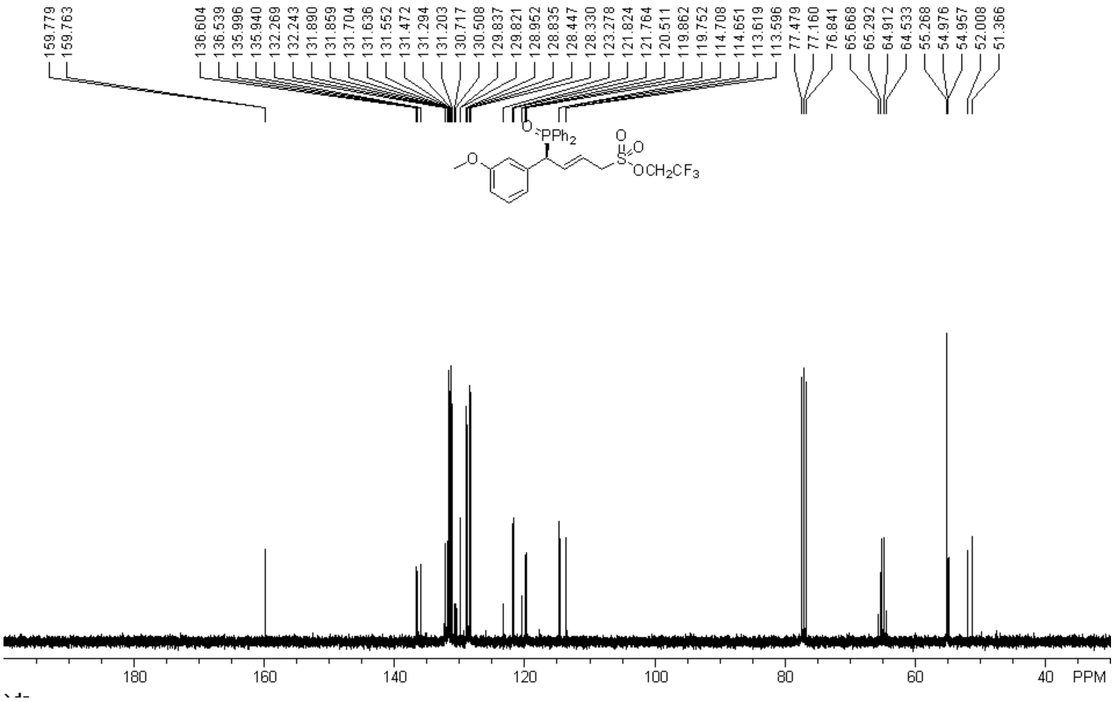
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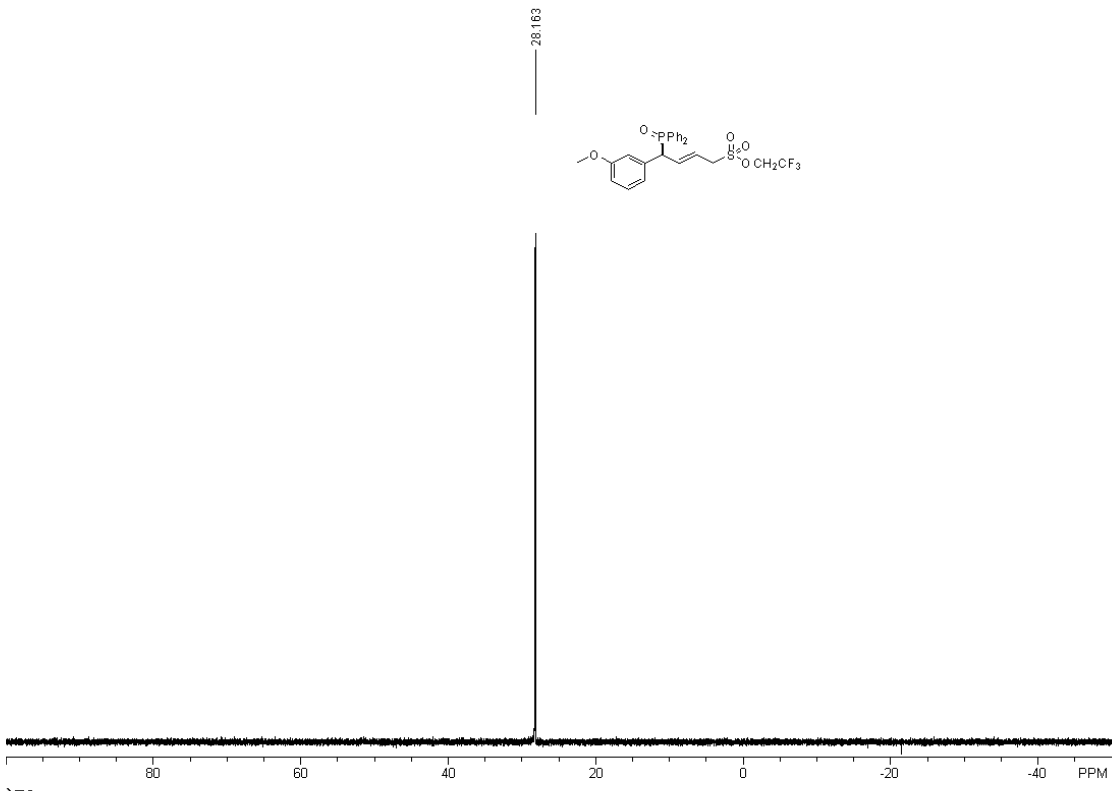
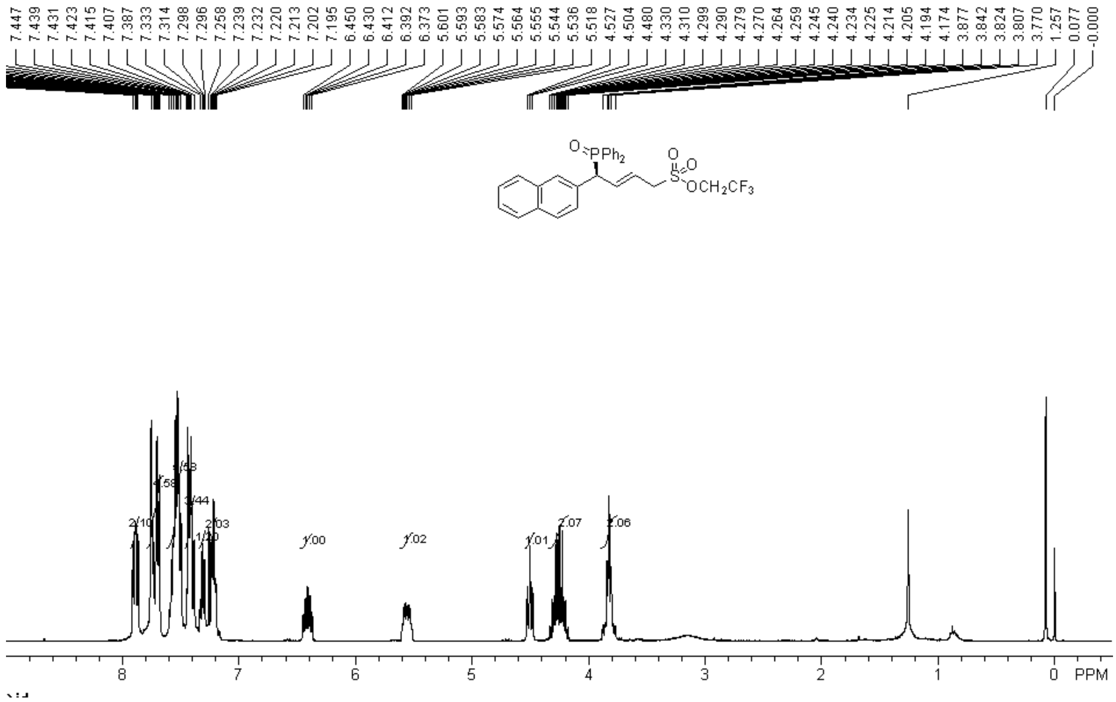
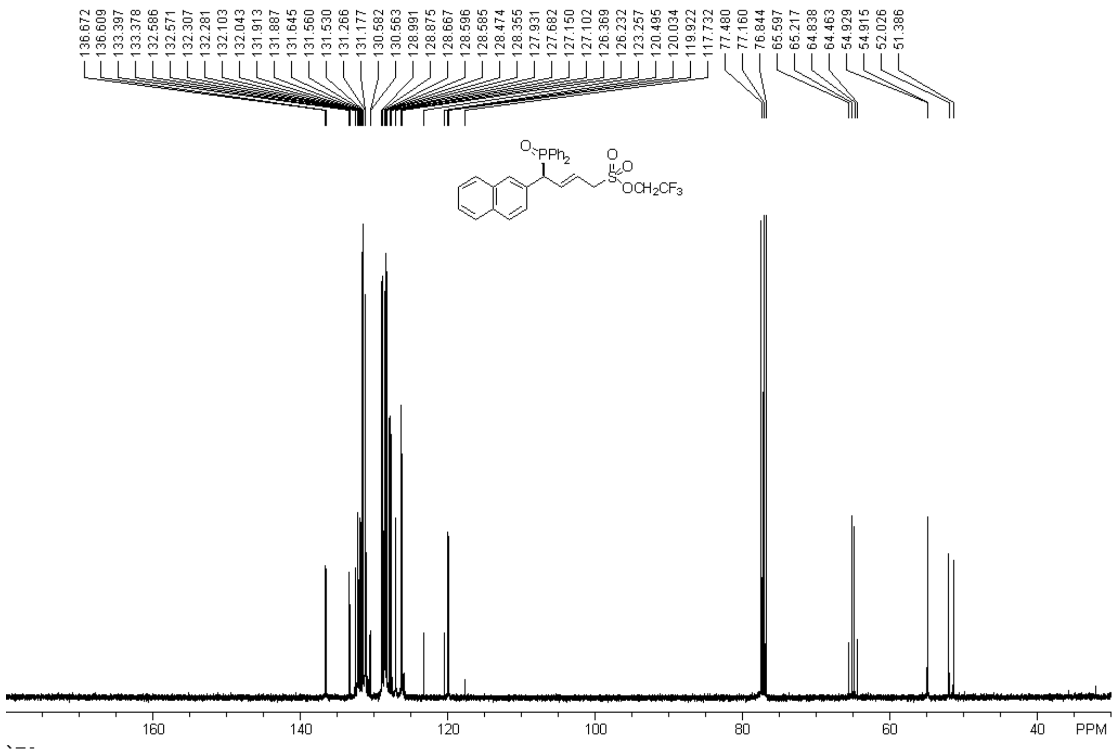
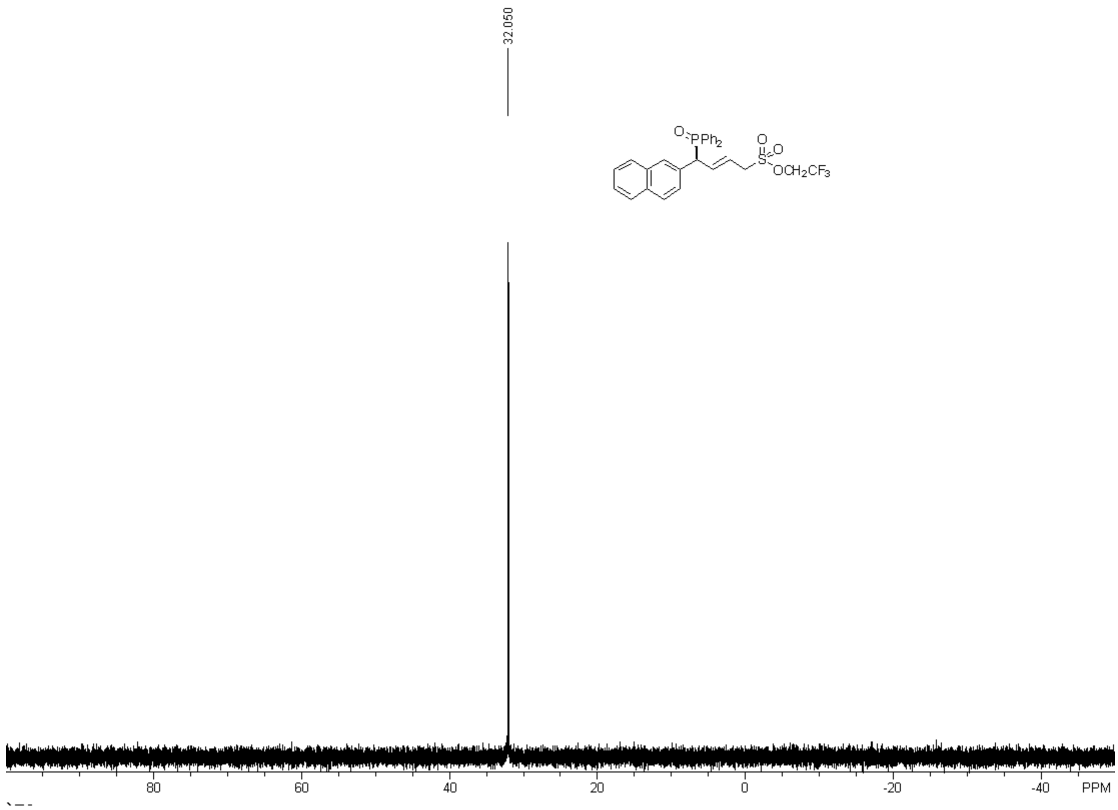
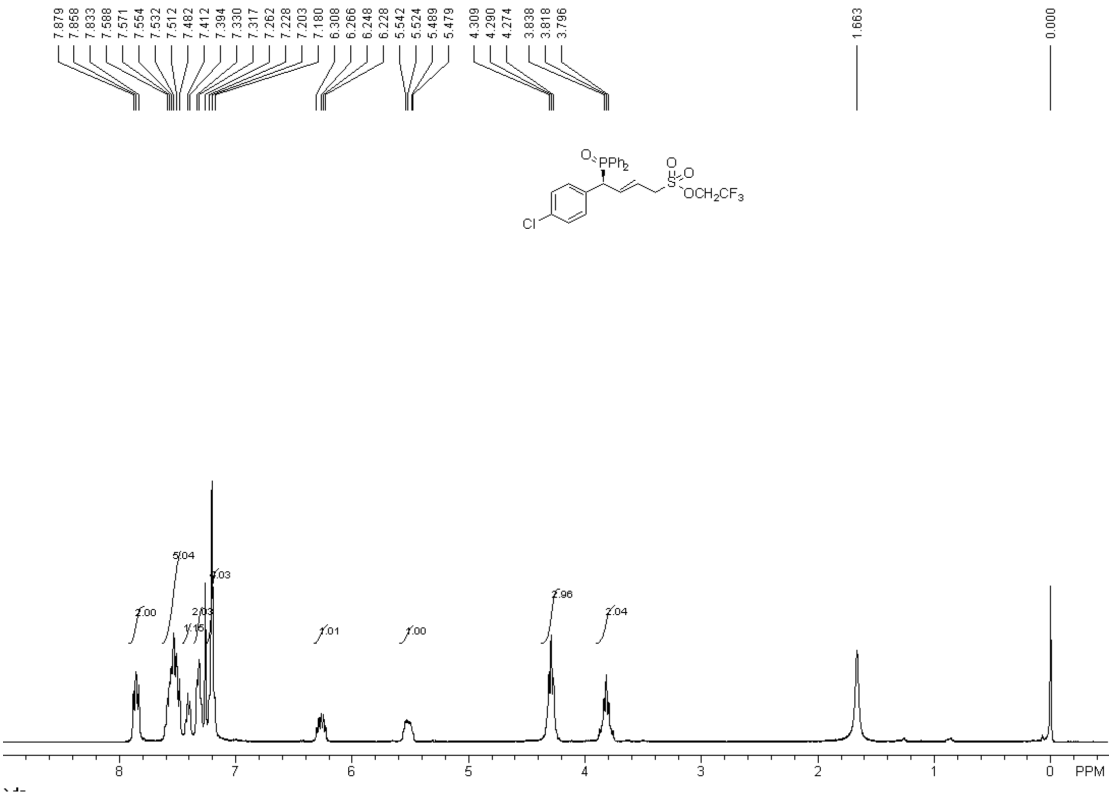
Electronic Supplementary Material (ESI) for Chemical Communications







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1.663
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Cl
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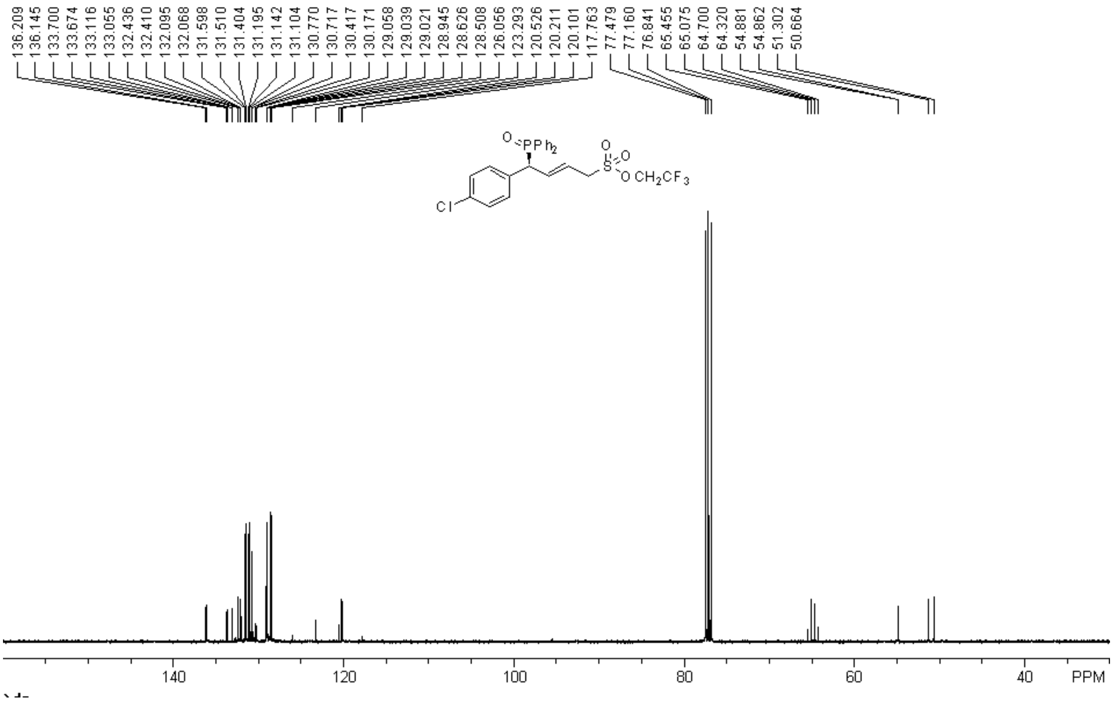
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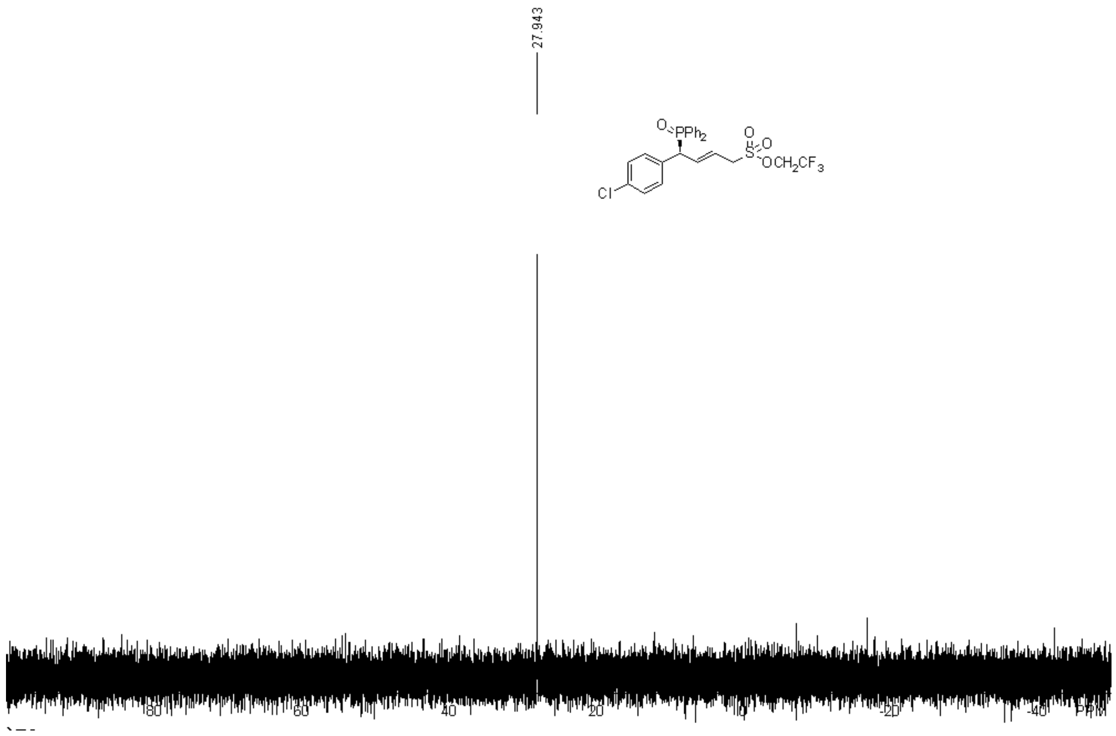
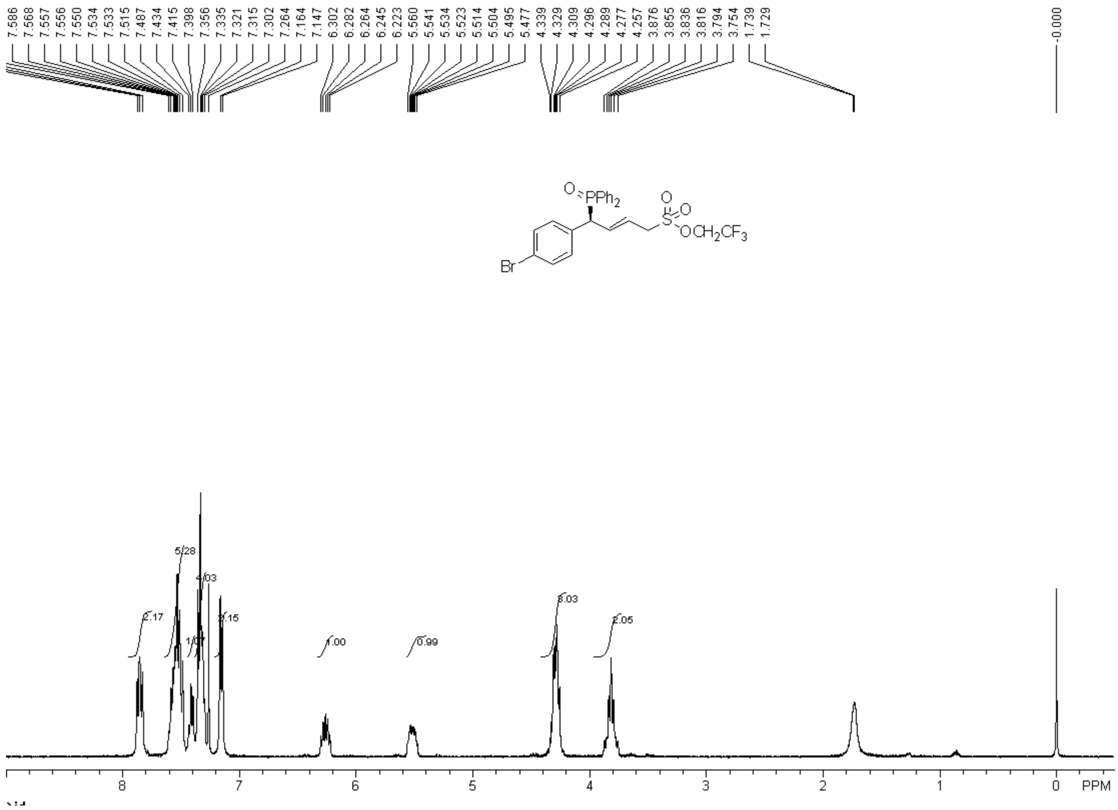
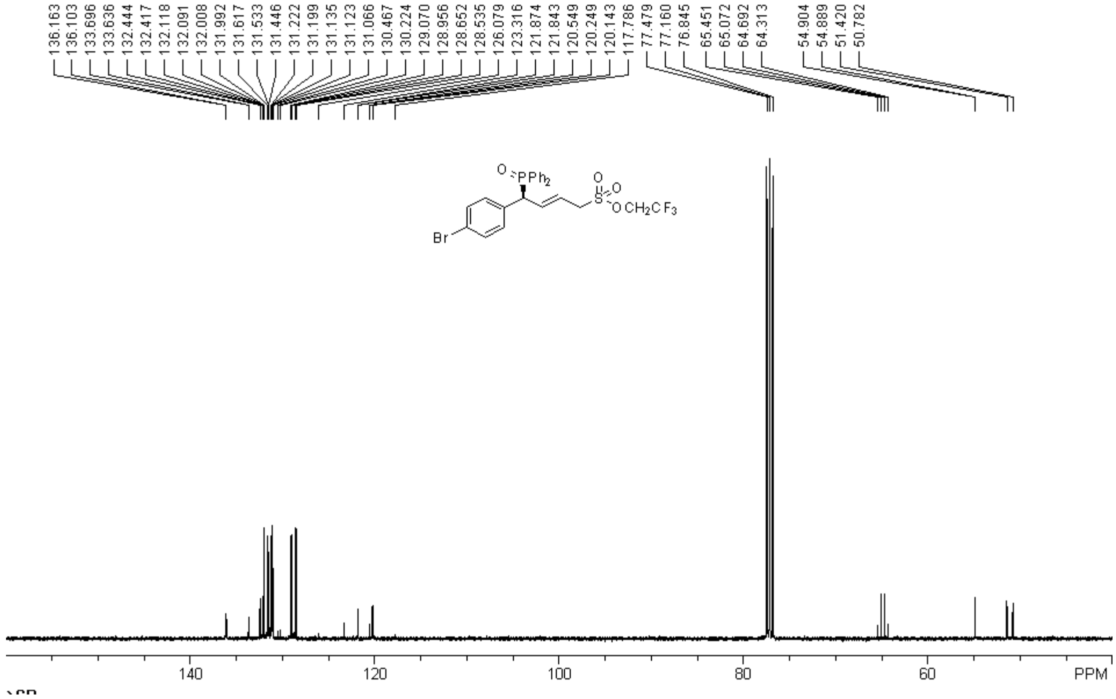
OCH2CF3
Cl
140 120 100 80 60 40 PPM

Electronic Supplementary Material (ESI) for Chemical Communications



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130.224
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128.652
128.535
126.079
123.316
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120.549
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Br
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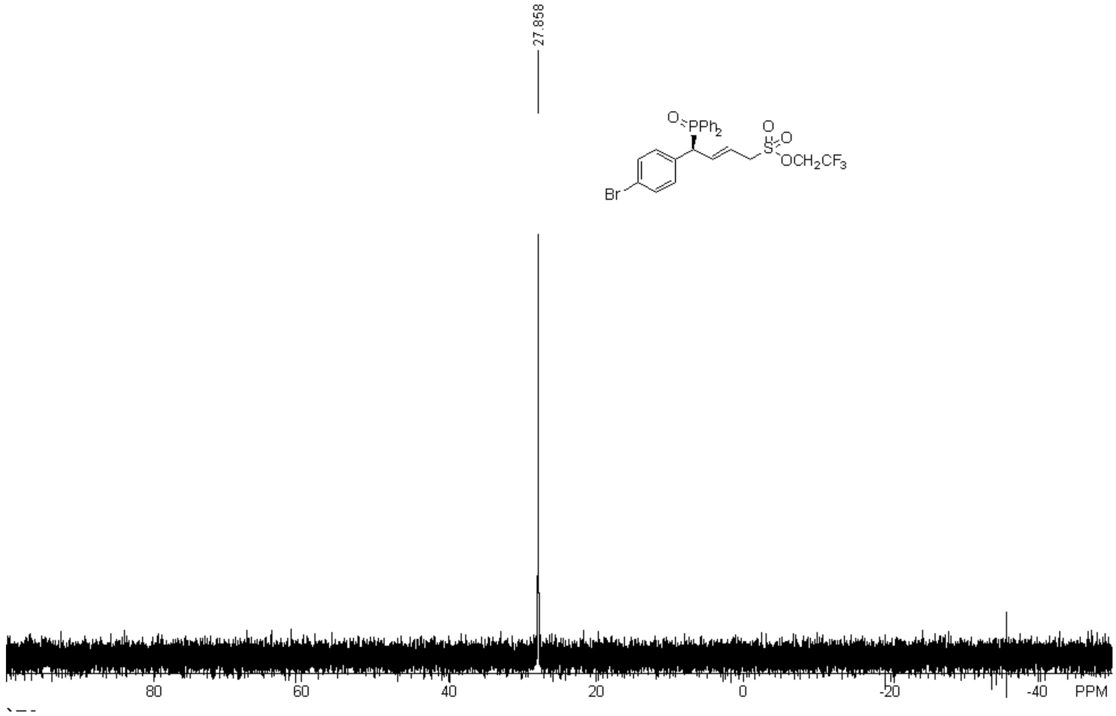
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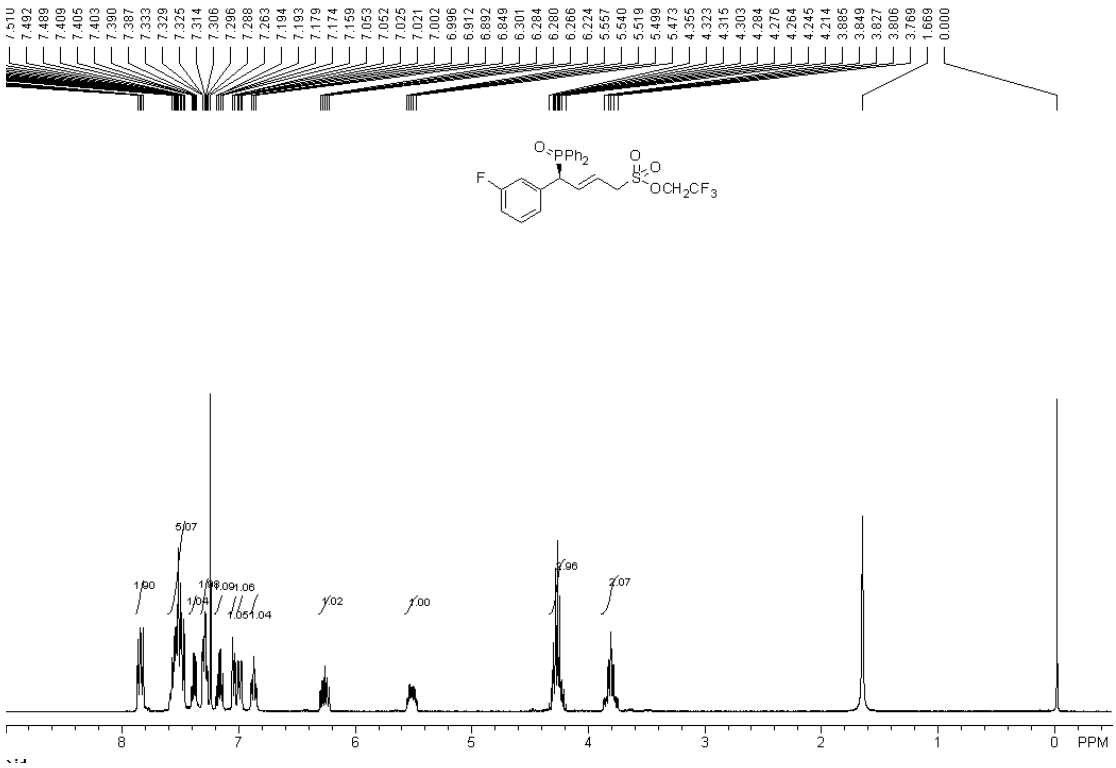
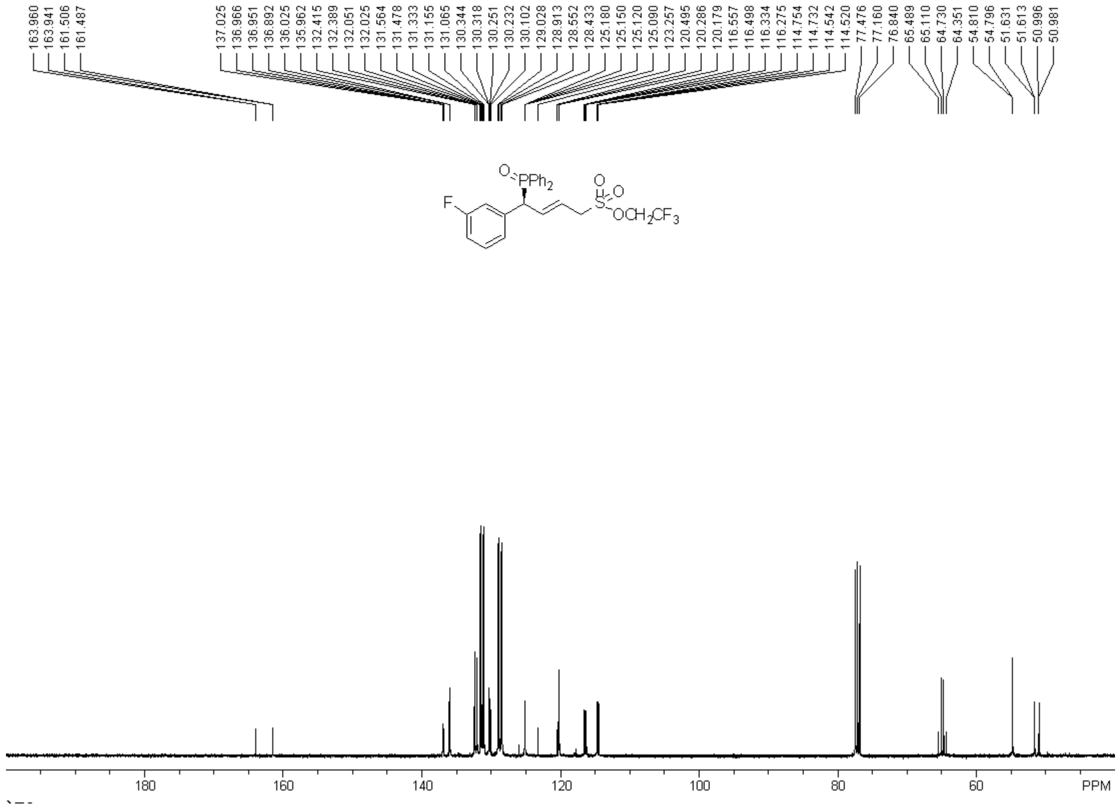
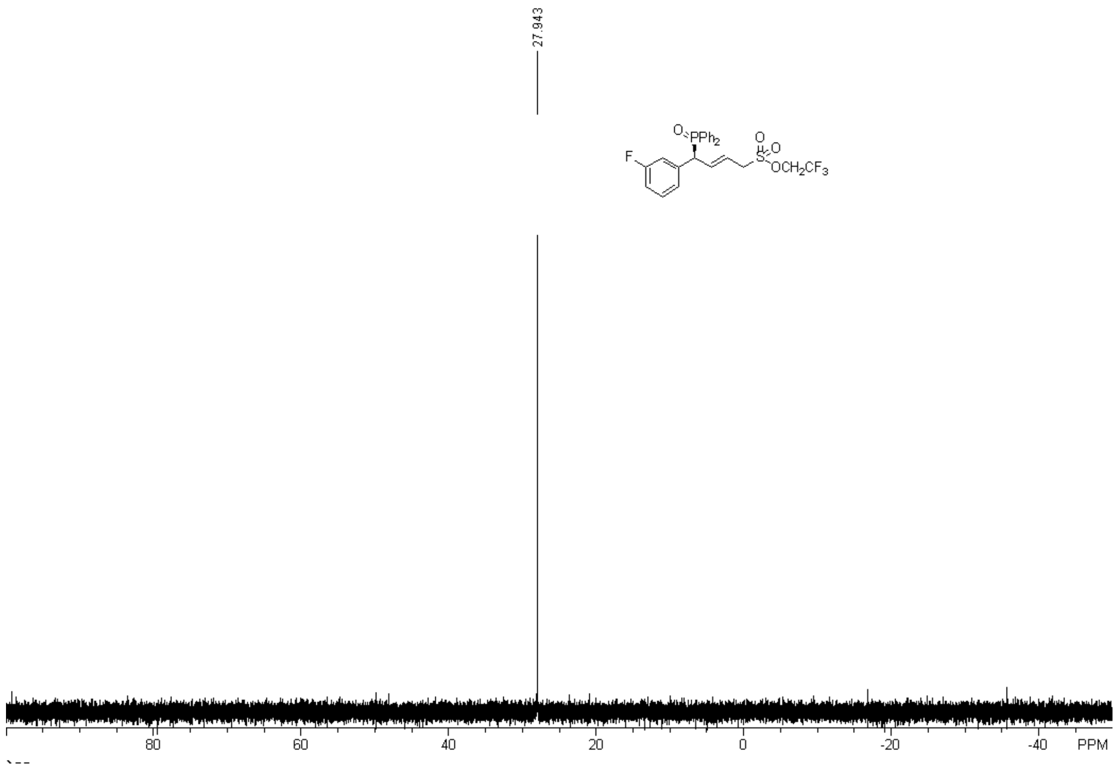
Electronic Supplementary Material (ESI) for Chemical Communications



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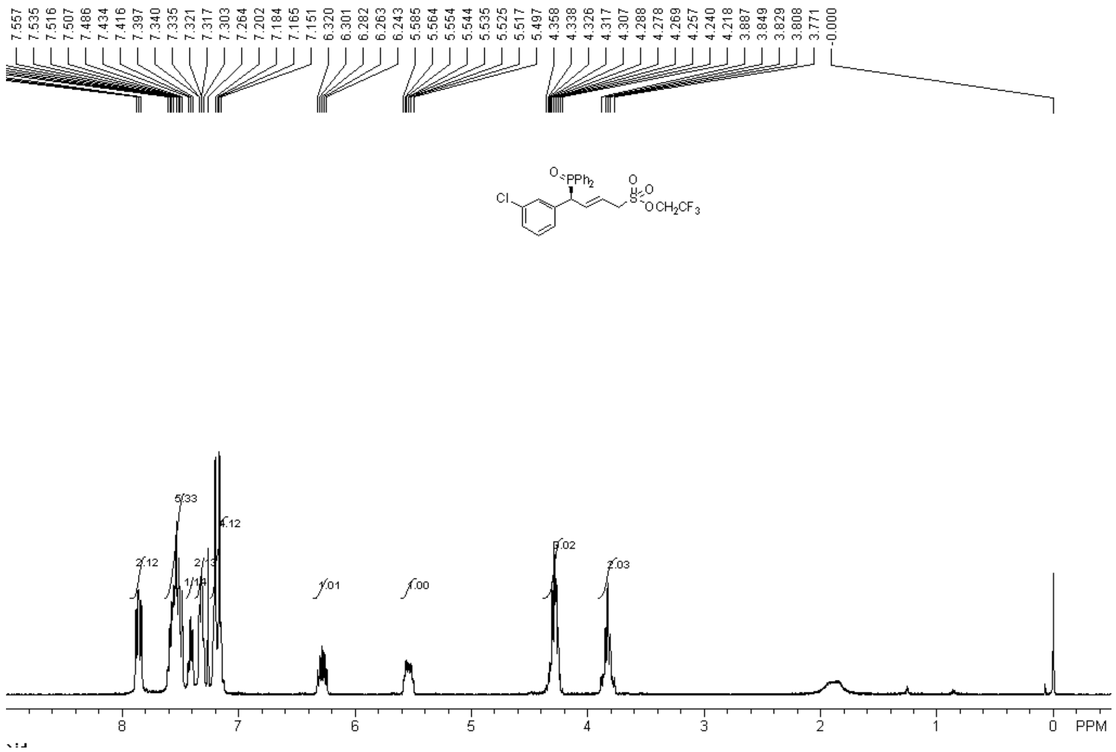
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7.303
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7.202
7.184
7.165
7.151
6.320
6.301
6.282
6.263
6.243
5.585
5.564
5.554
5.544
5.535
5.525
5.517
5.497
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4.338
4.326
4.317
4.307
4.288
4.278
4.269
4.257
4.240
4.218
3.887
3.849
3.829
3.808
3.771
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PPh2
Cl
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1.00
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5
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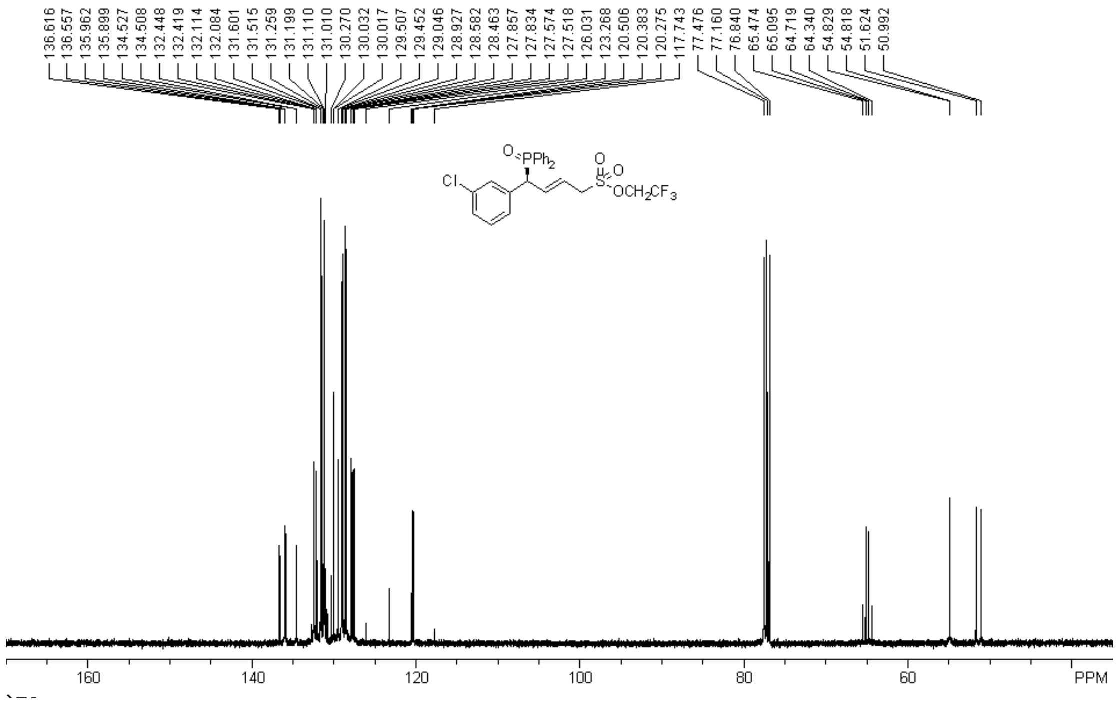
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76.840
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65.095
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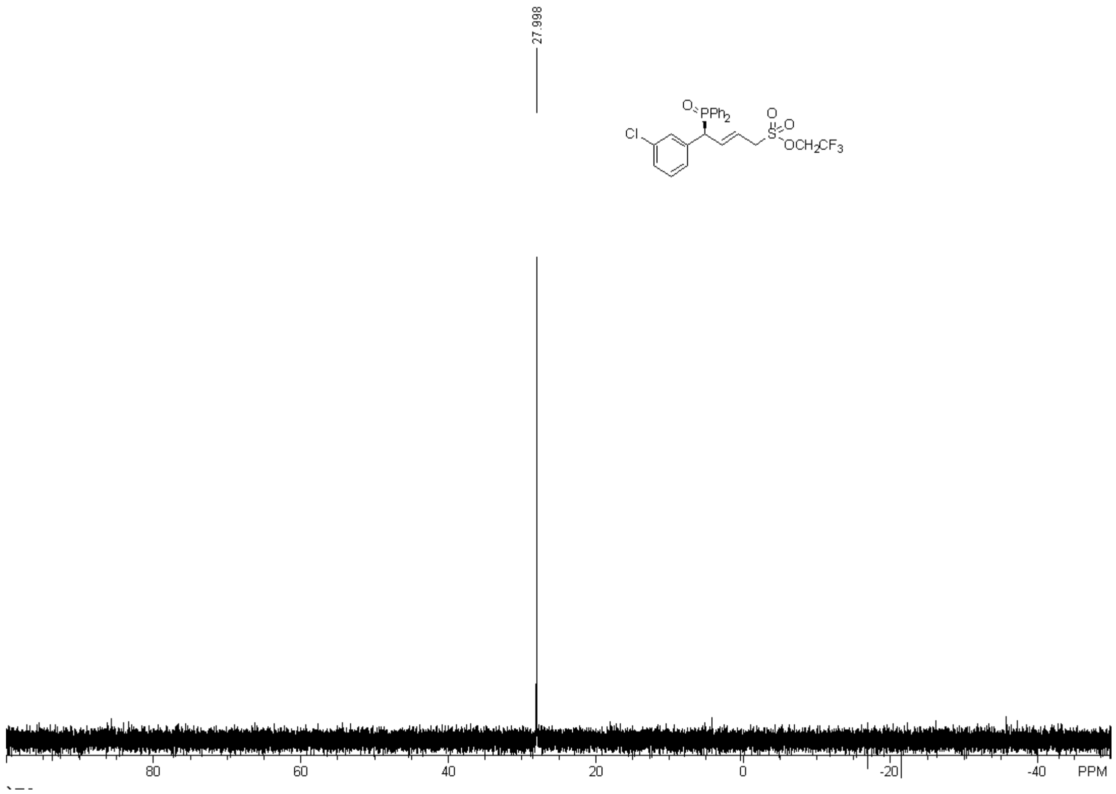
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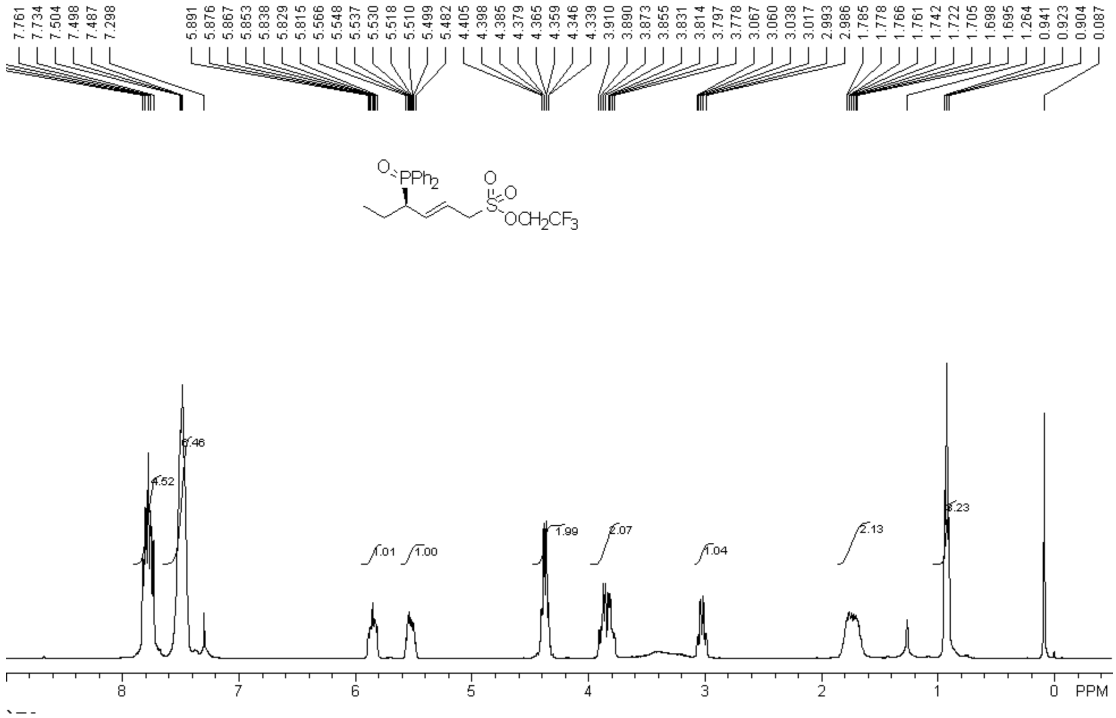
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4.405
4.398
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4.365
4.359
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4.339
3.910
3.890
3.873
3.855
3.831
3.814
3.797
3.778
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3.060
3.038
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2.993
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1.766
1.761
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1.722
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1.695
1.264
0.941
0.923
0.904
0.087
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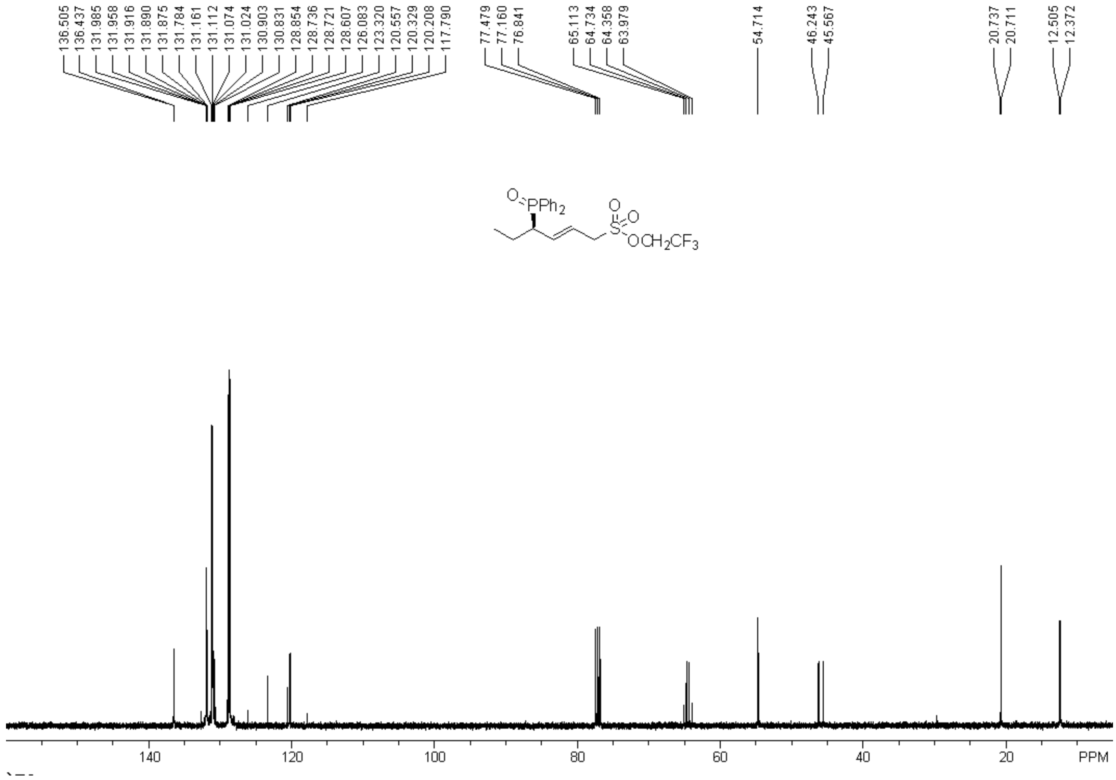
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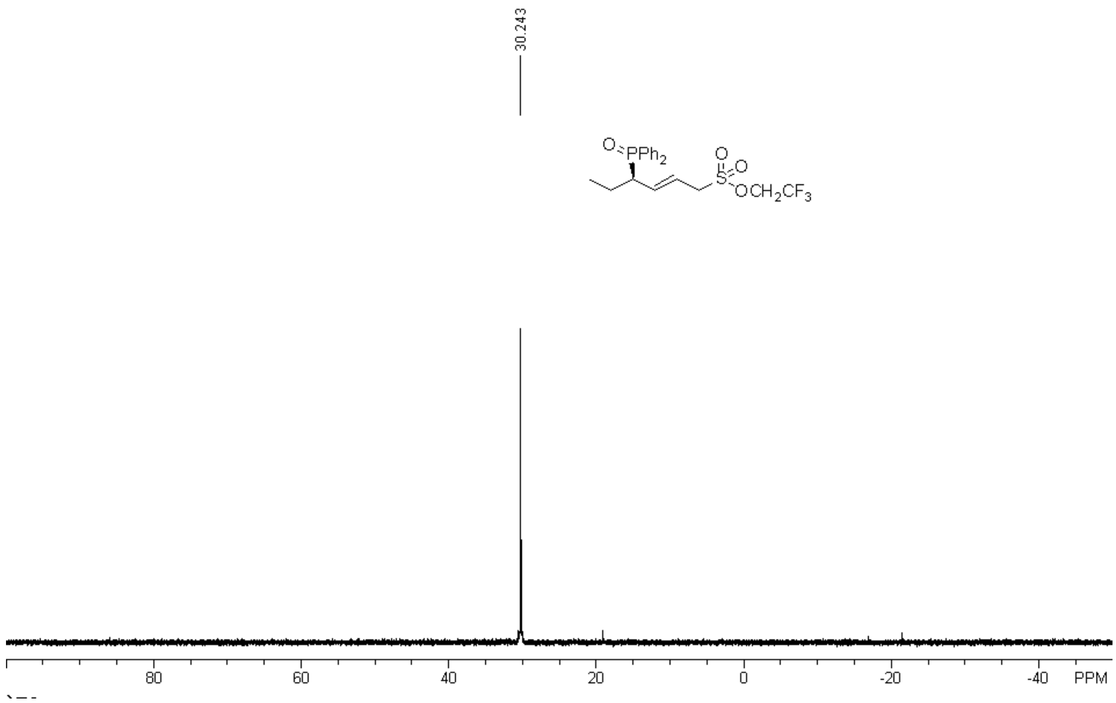
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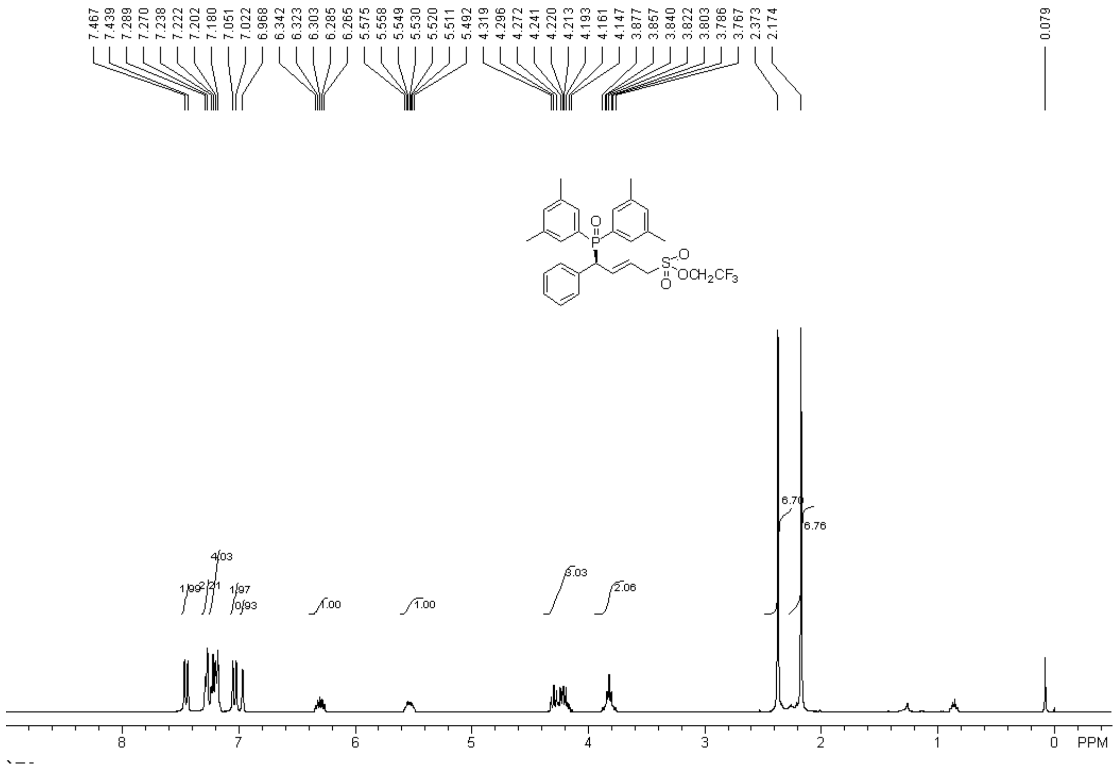
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6.285
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4.272
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4.213
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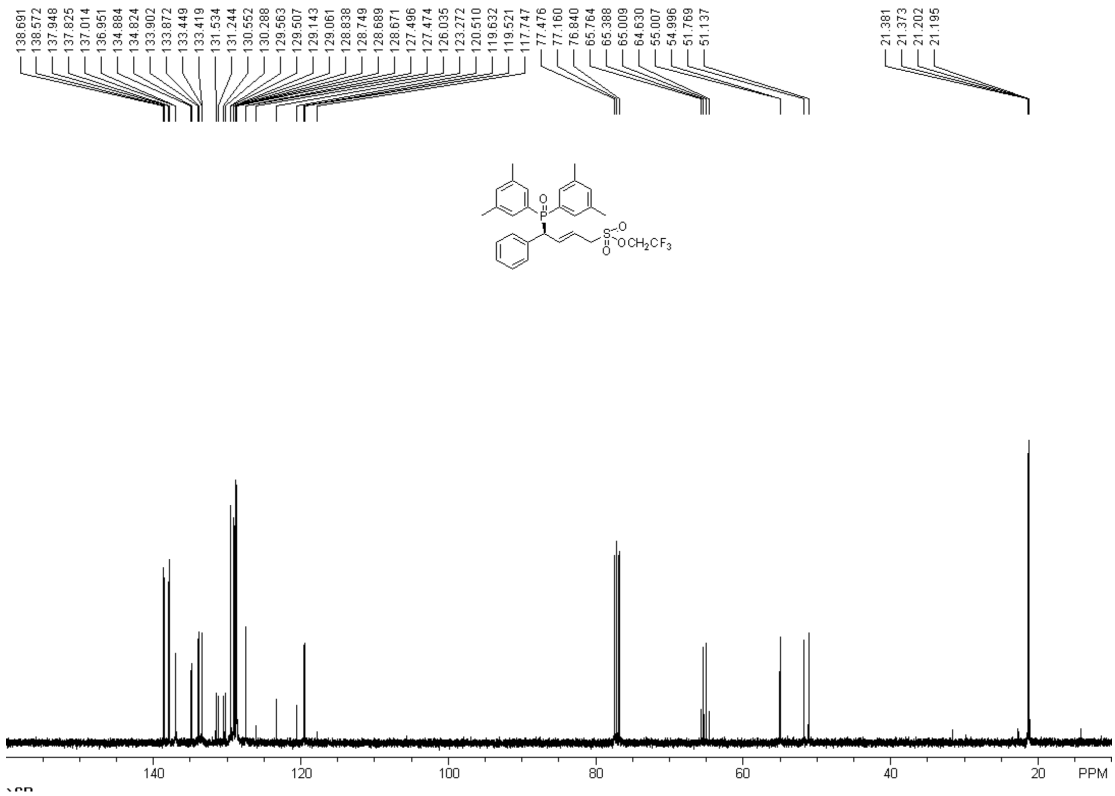
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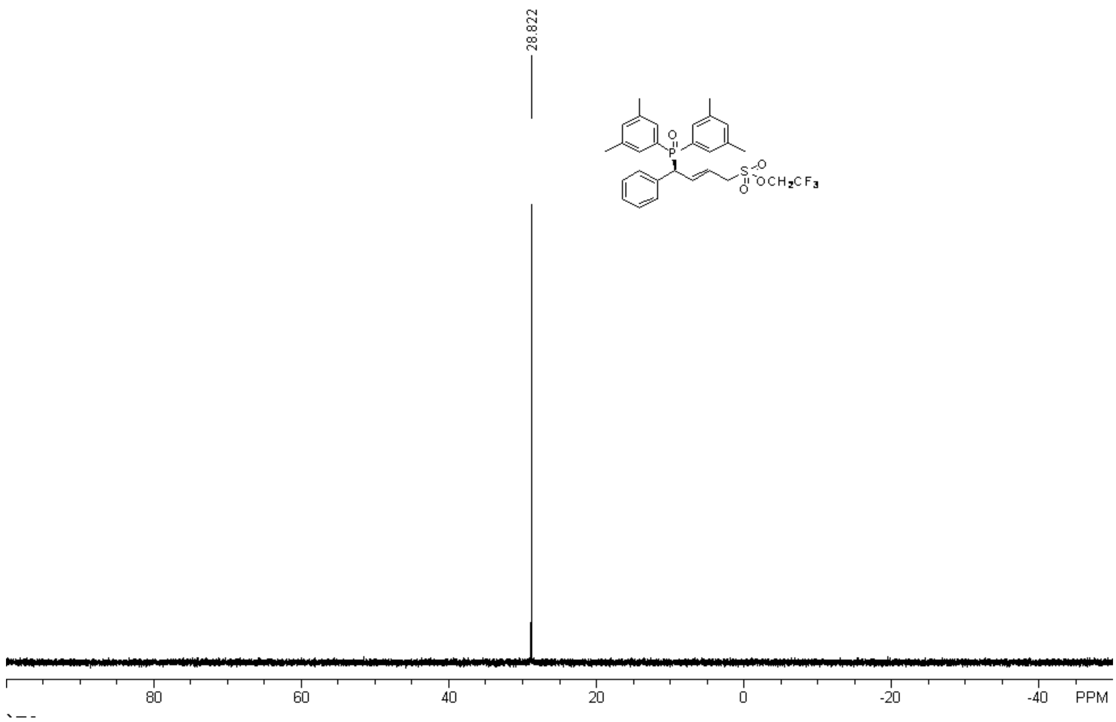
PPM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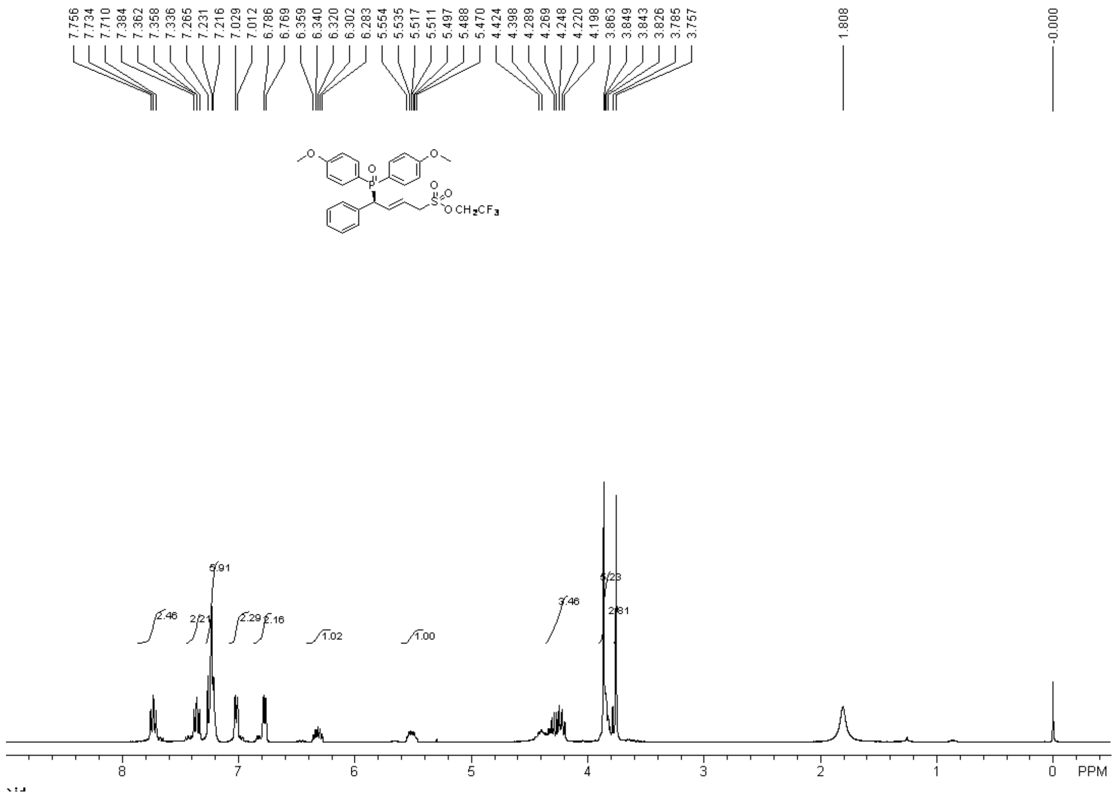

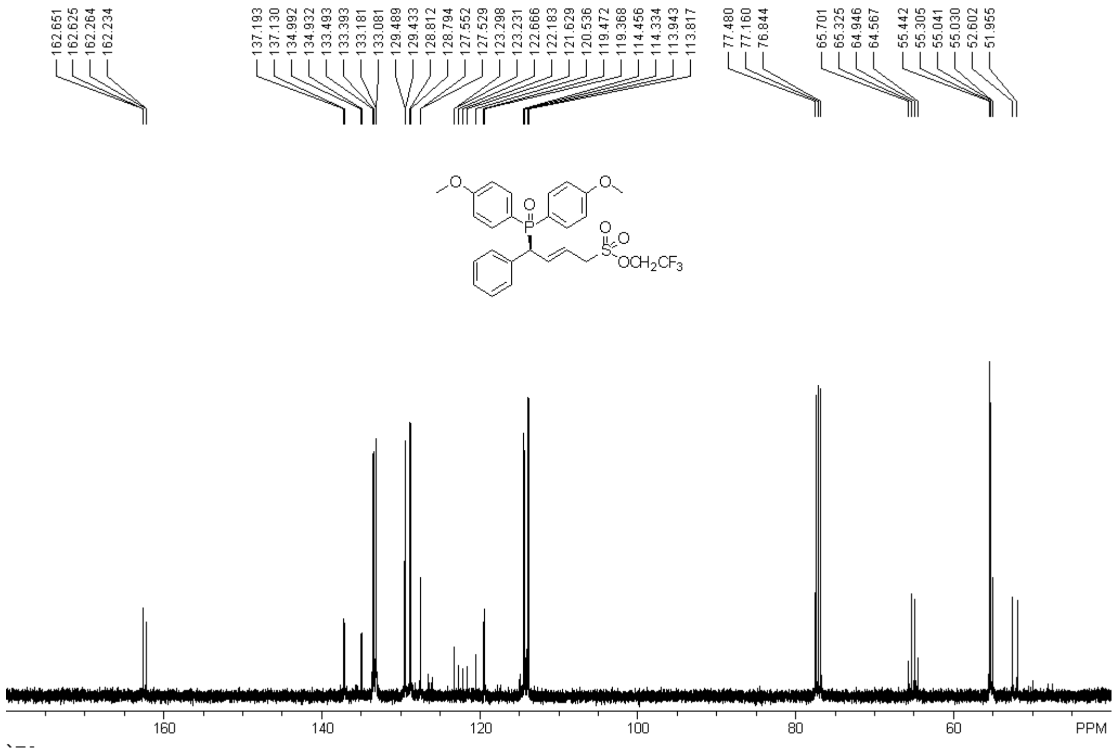

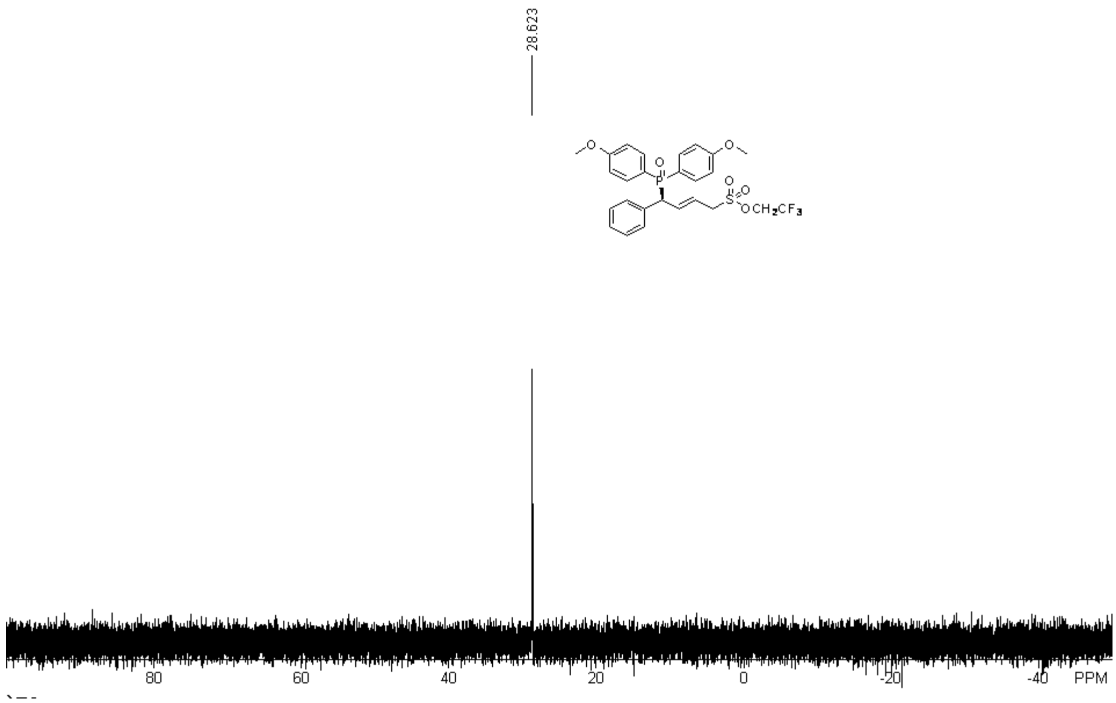
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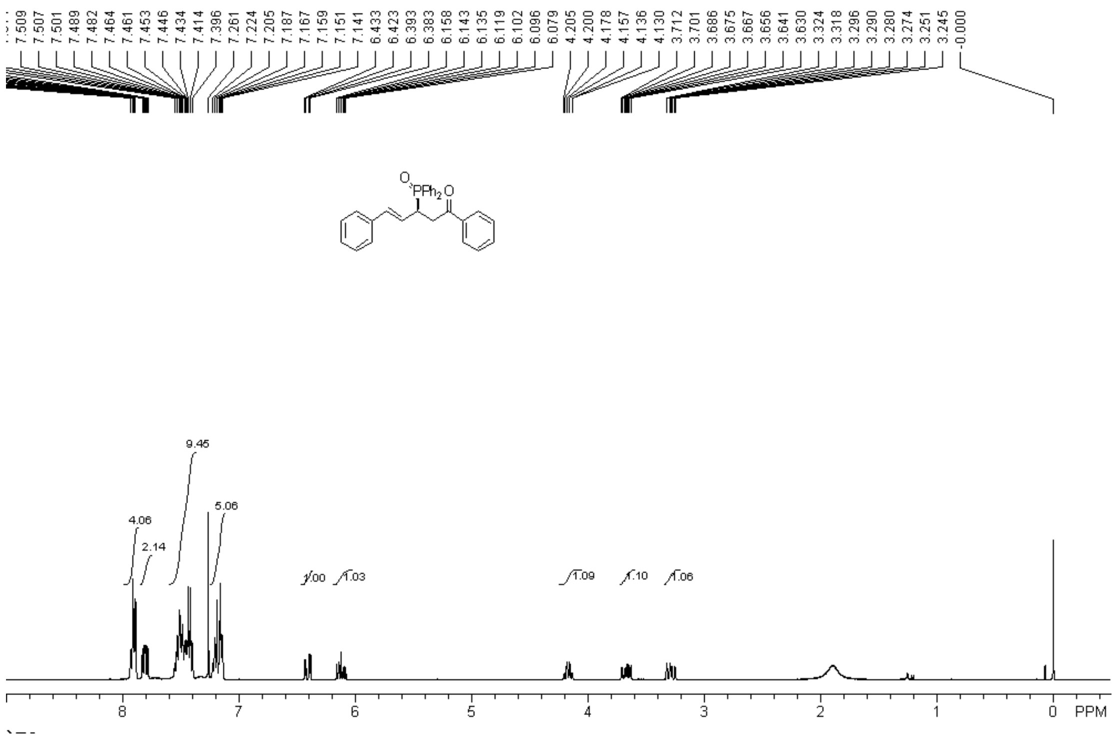
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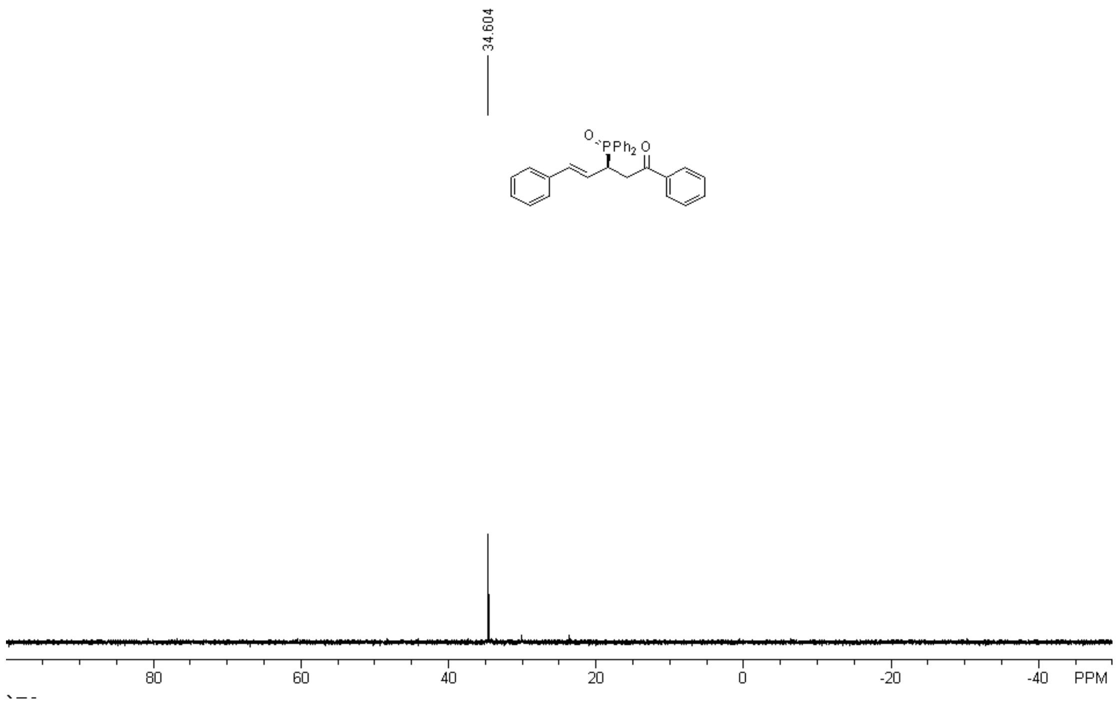
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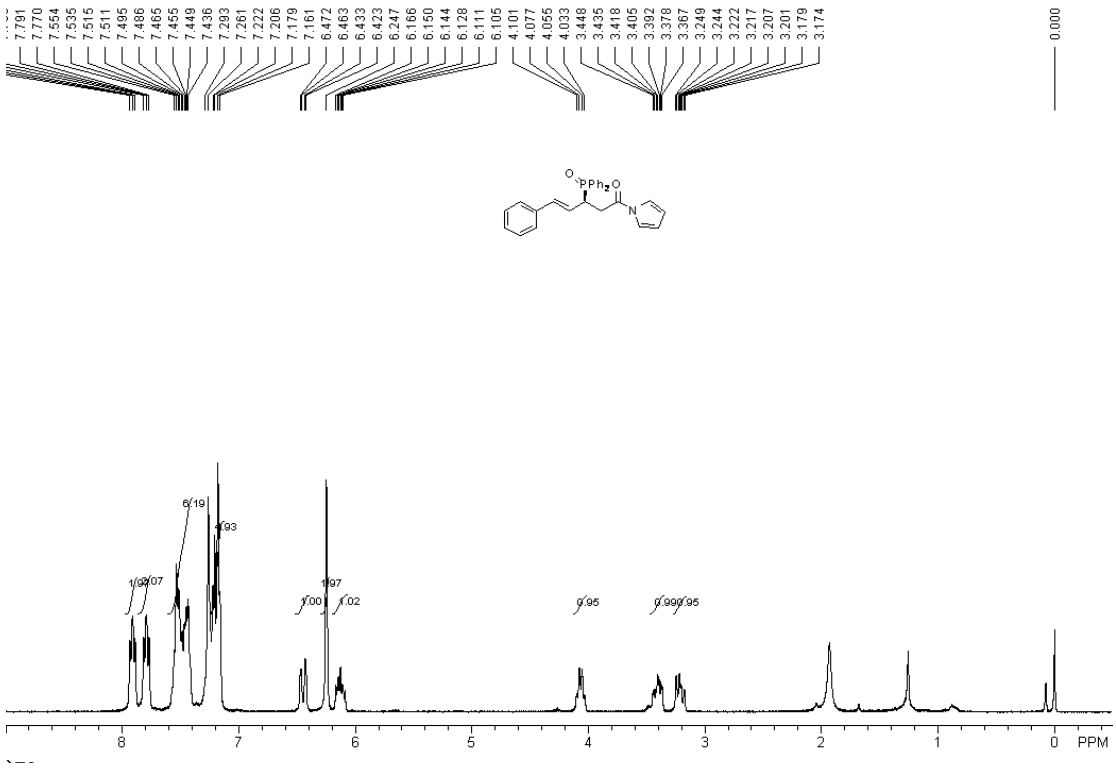
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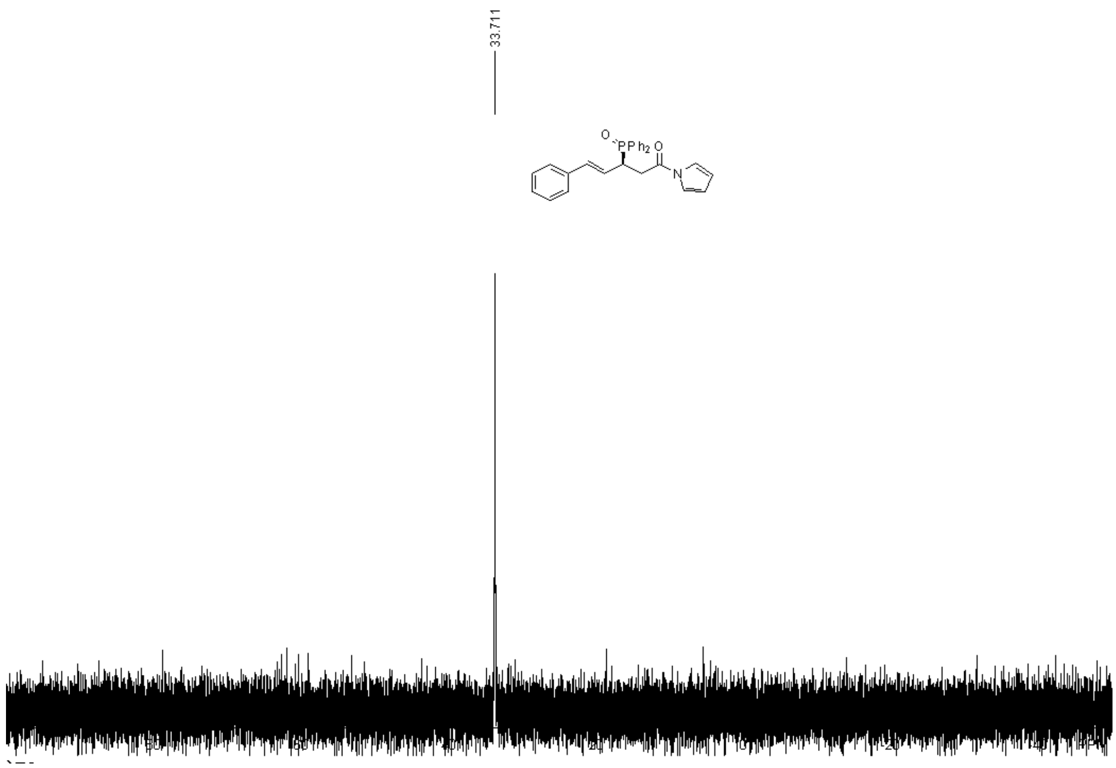
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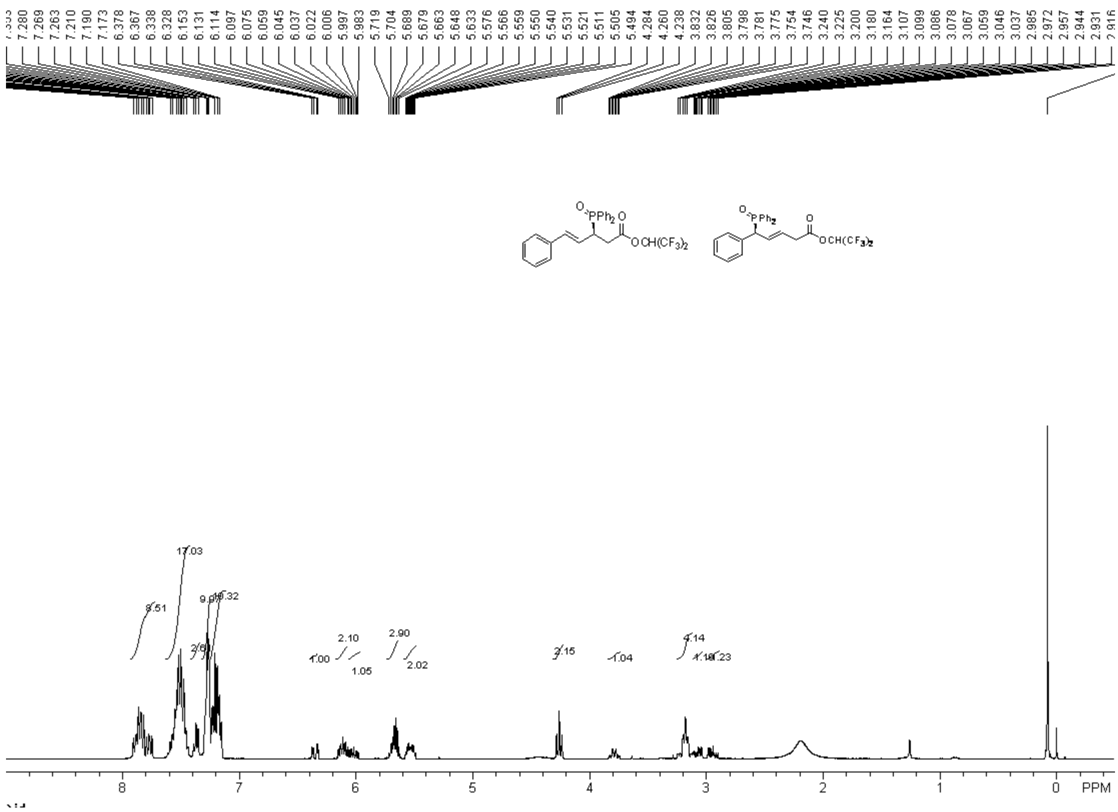
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OCH(CF3)2
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2
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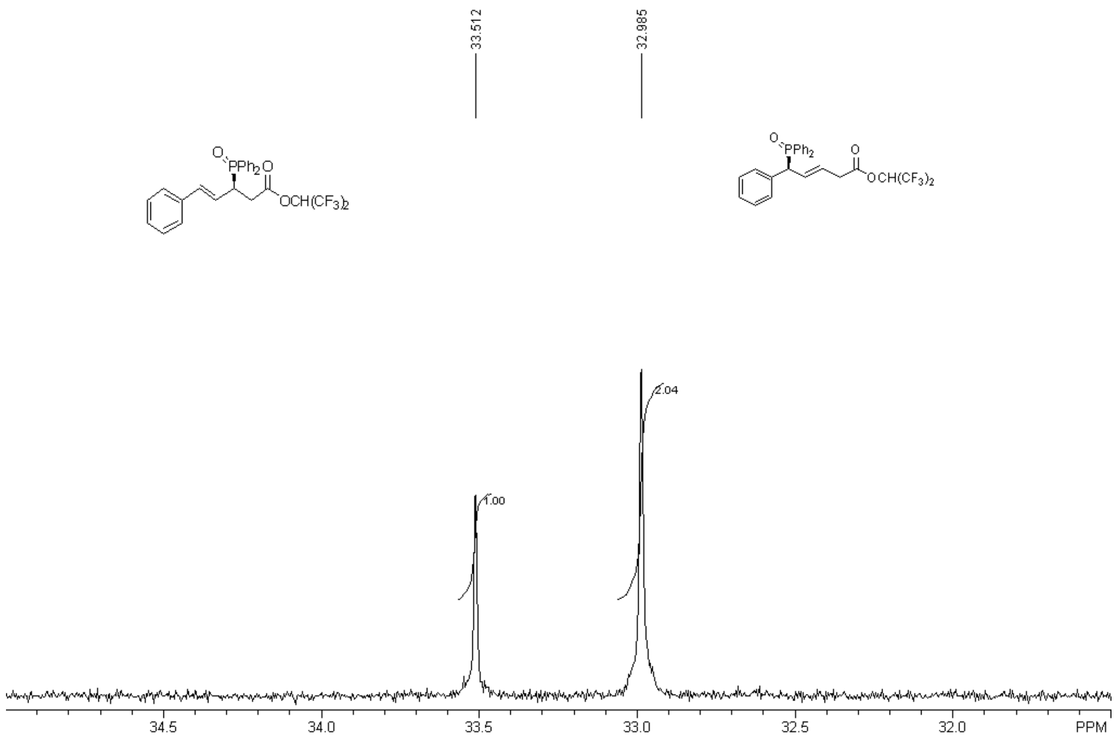
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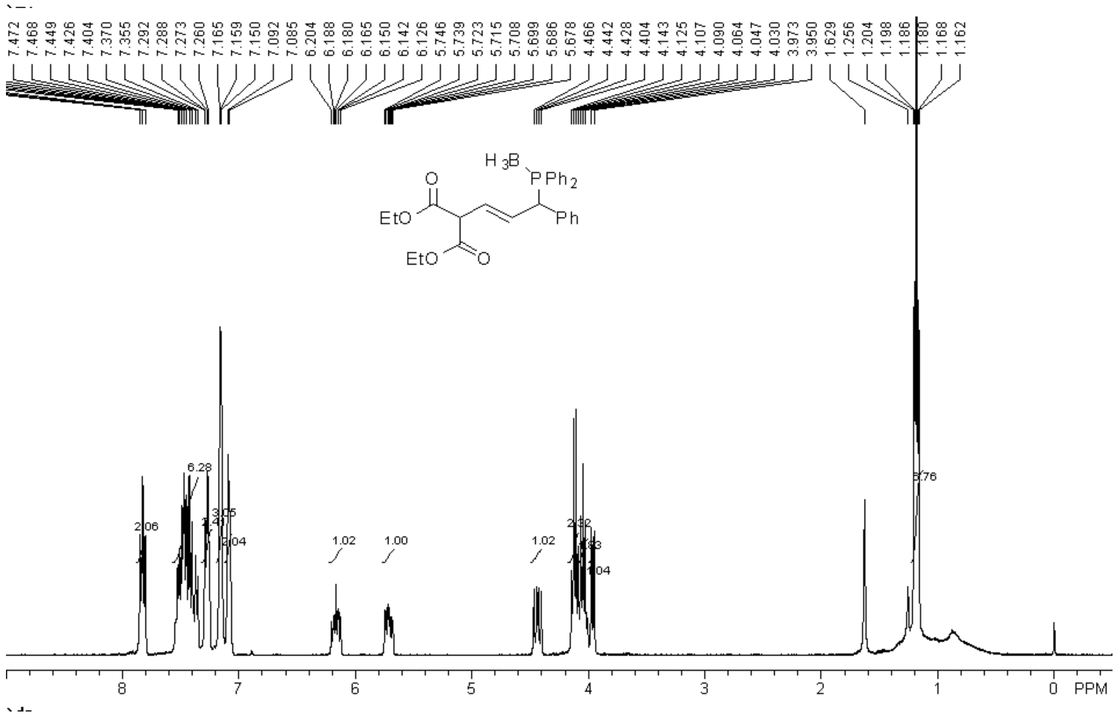
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EtO
EtO
Ph
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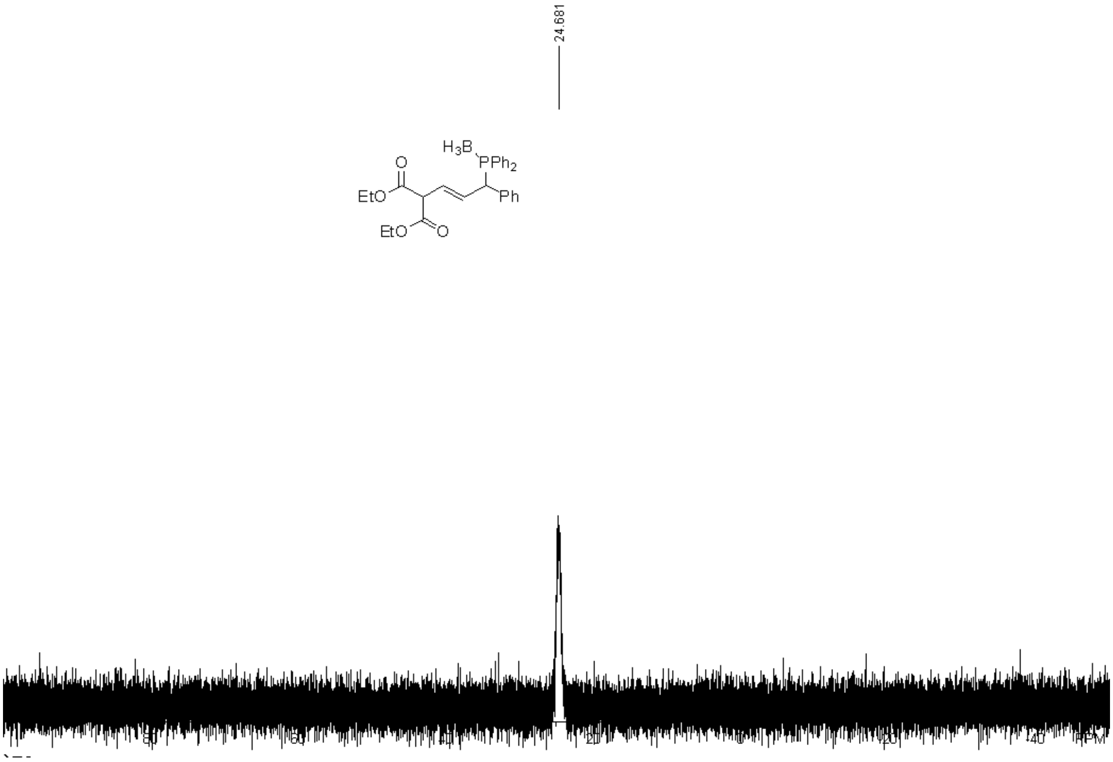
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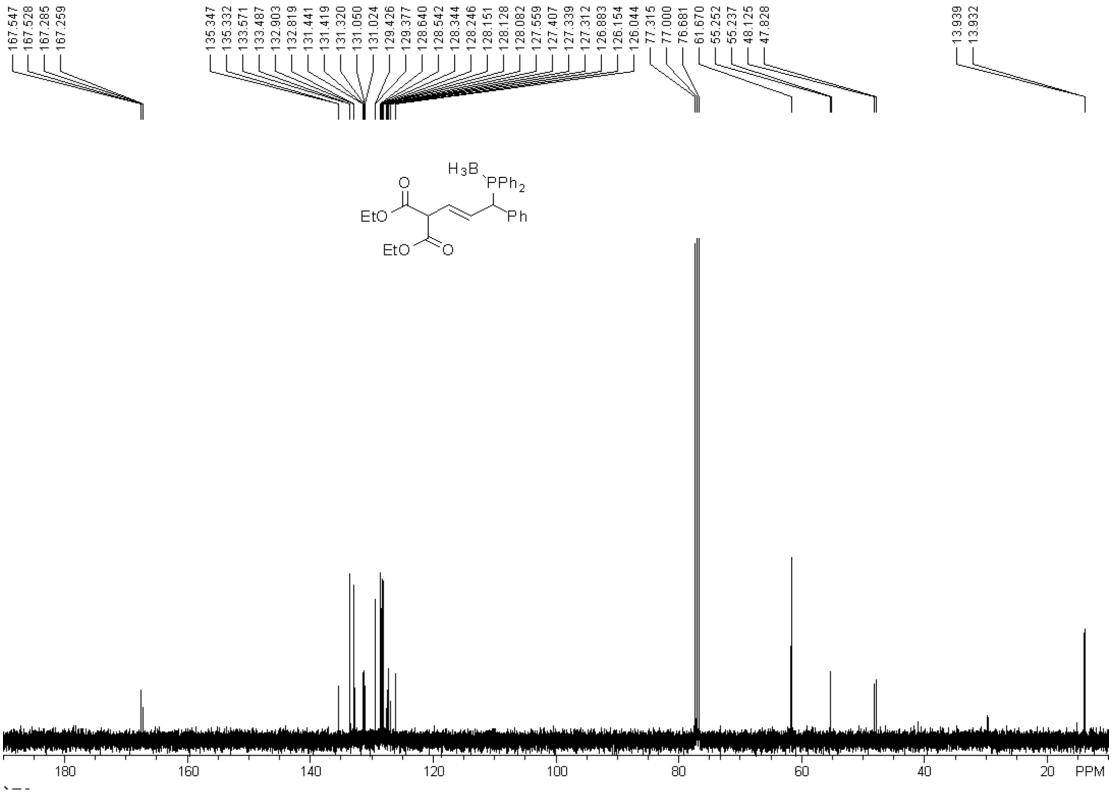
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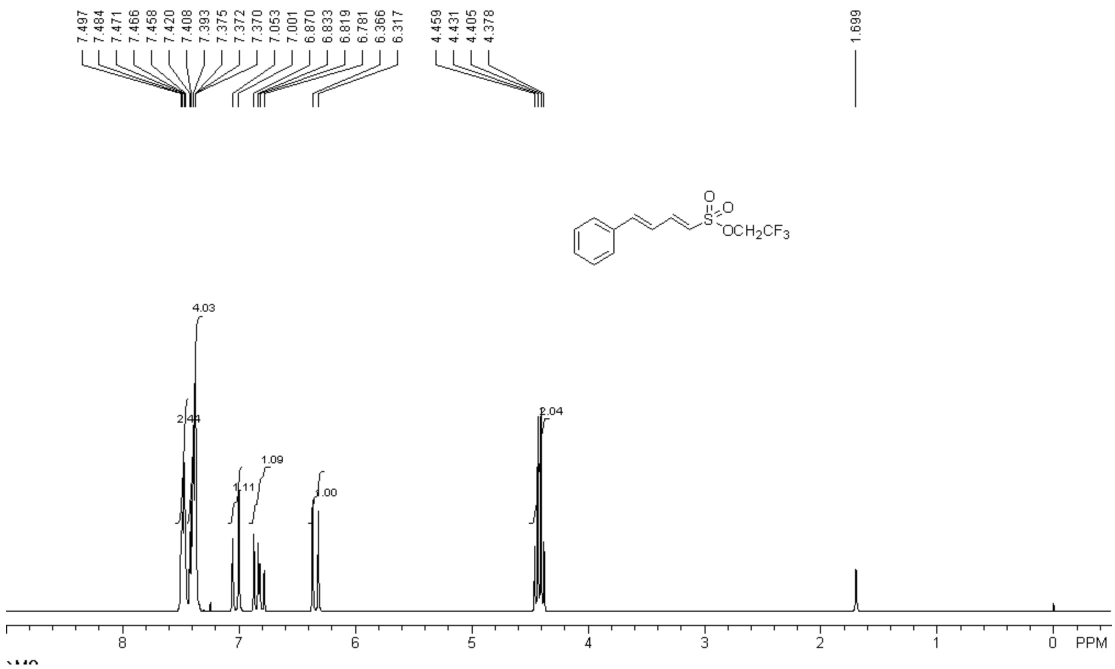
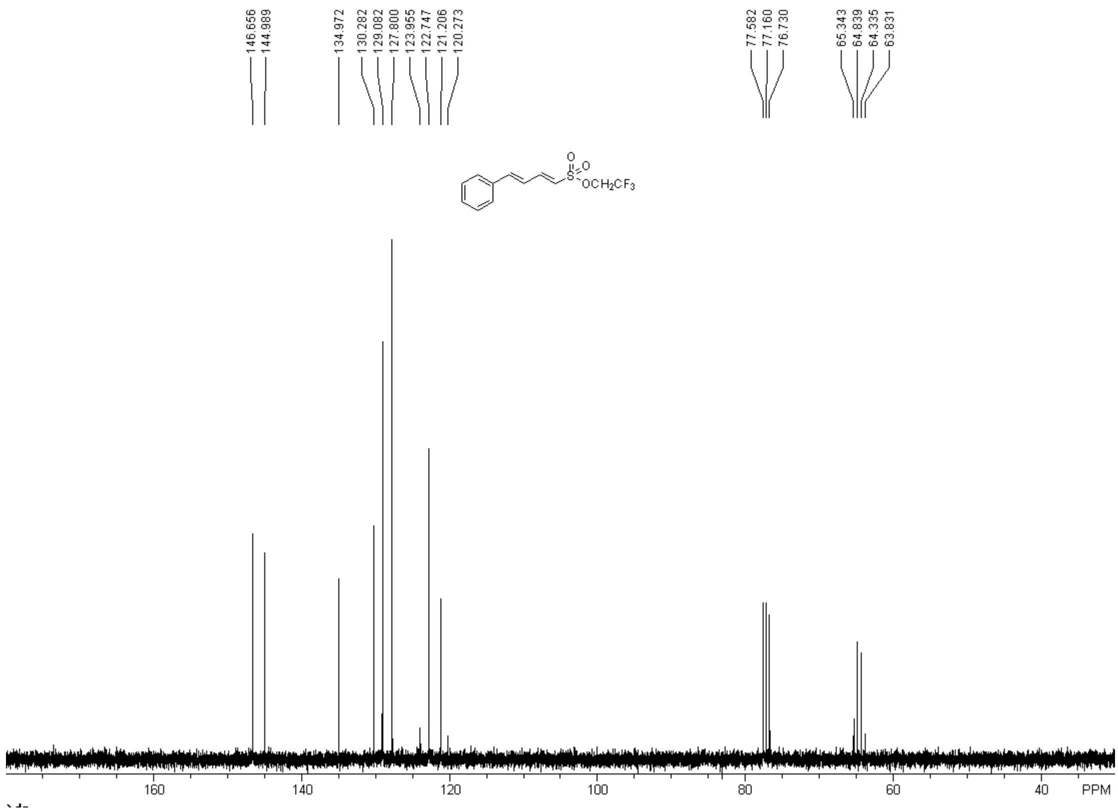
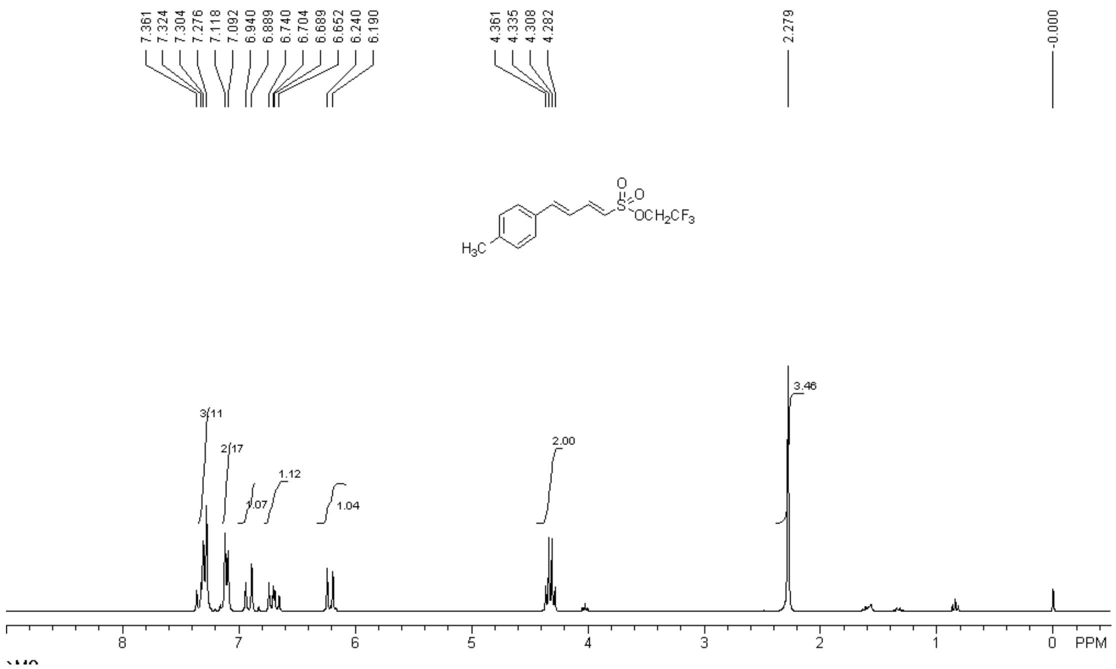
Electronic Supplementary Material (ESI) for Chemical Communications



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6.704
6.689
6.652
6.240
6.190
4.361
4.335
4.308
4.282
2.279
-0.000
OCH2CF3
H3C
3.11
2.17
1.12
1.07
1.04
2.00
3.46
8
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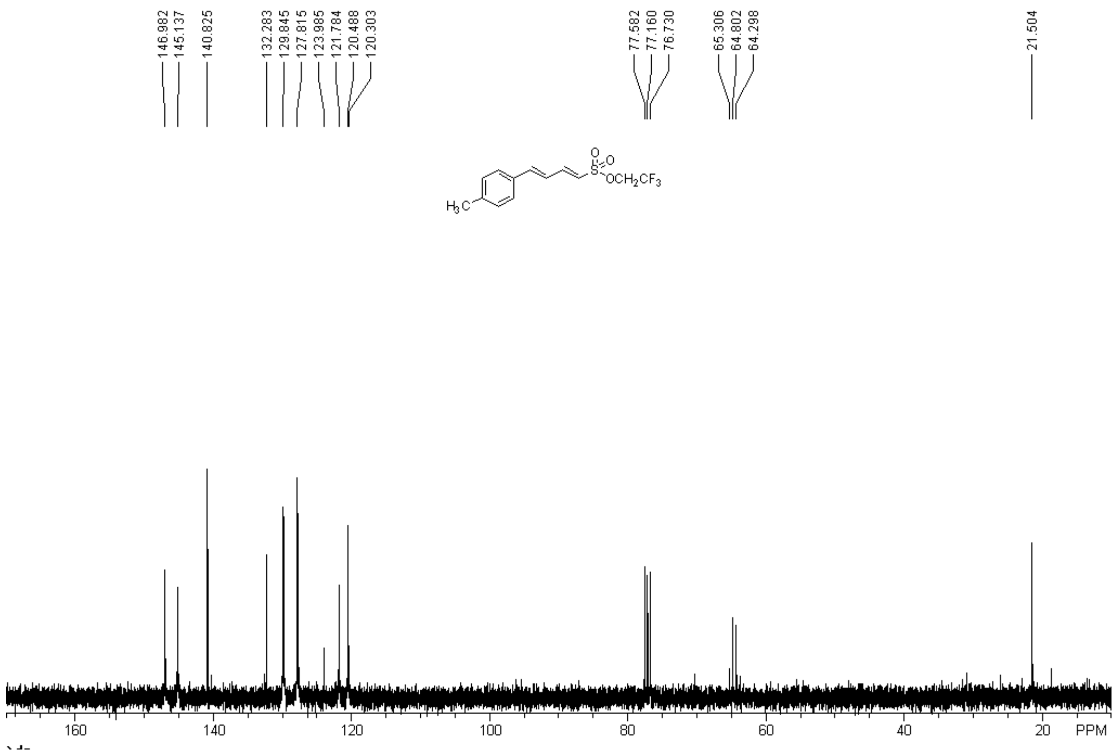
6
5
4
3
2
1
0
PPM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77.582
77.160
76.730
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64.802
64.298
21.504
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H3C
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120
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80
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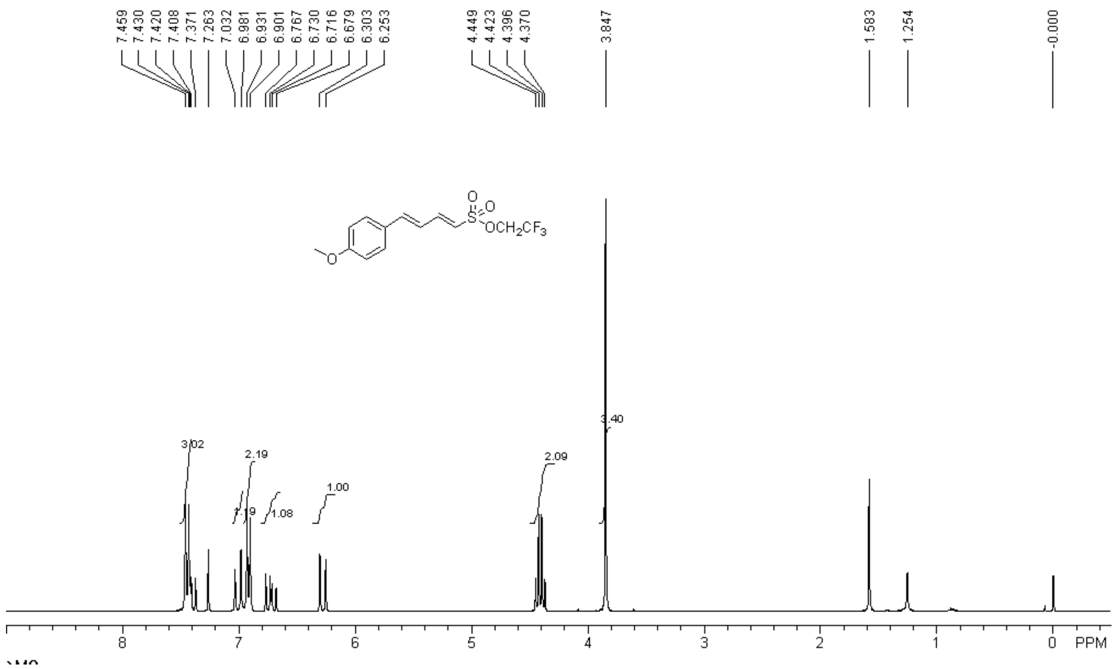
20
PPM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6.716
6.679
6.303
6.253
4.449
4.423
4.396
4.370
3.847
1.583
1.254
-0.000
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3.02
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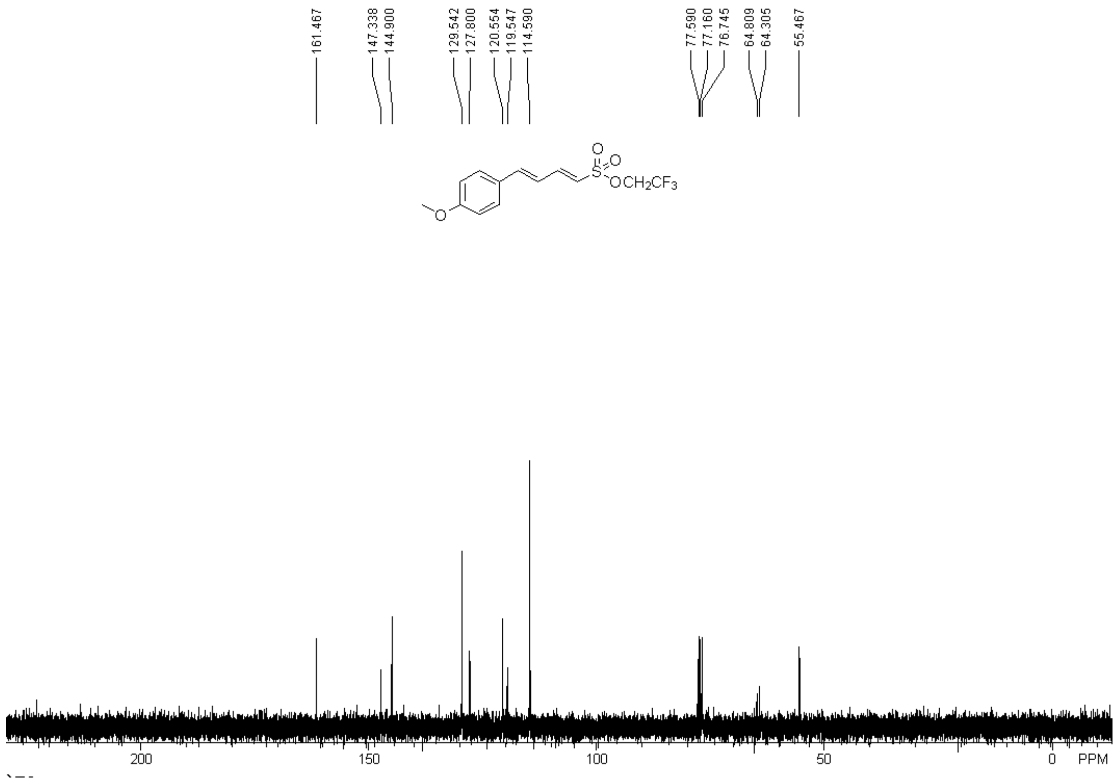
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119.547
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64.305
55.467
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150
100
50
0
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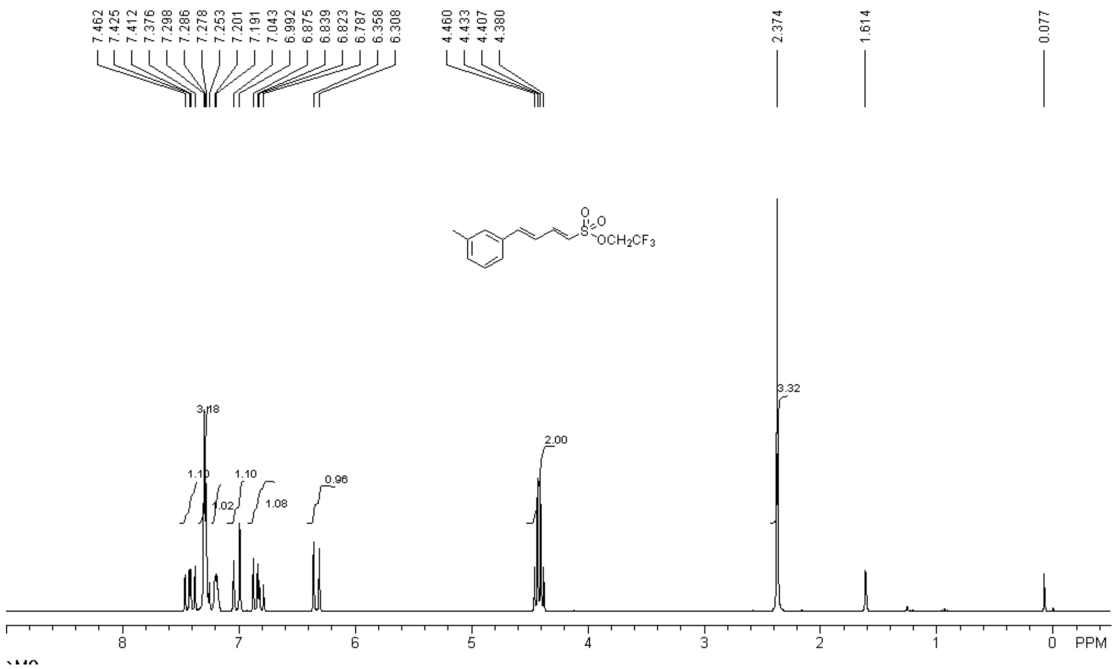
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7.253
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6.875
6.839
6.823
6.787
6.358
6.308
4.460
4.433
4.407
4.380
2.374
1.614
0.077
OCH2CF3
3.18
1.10
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1.10
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2.00
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6
5
4
3
2
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0
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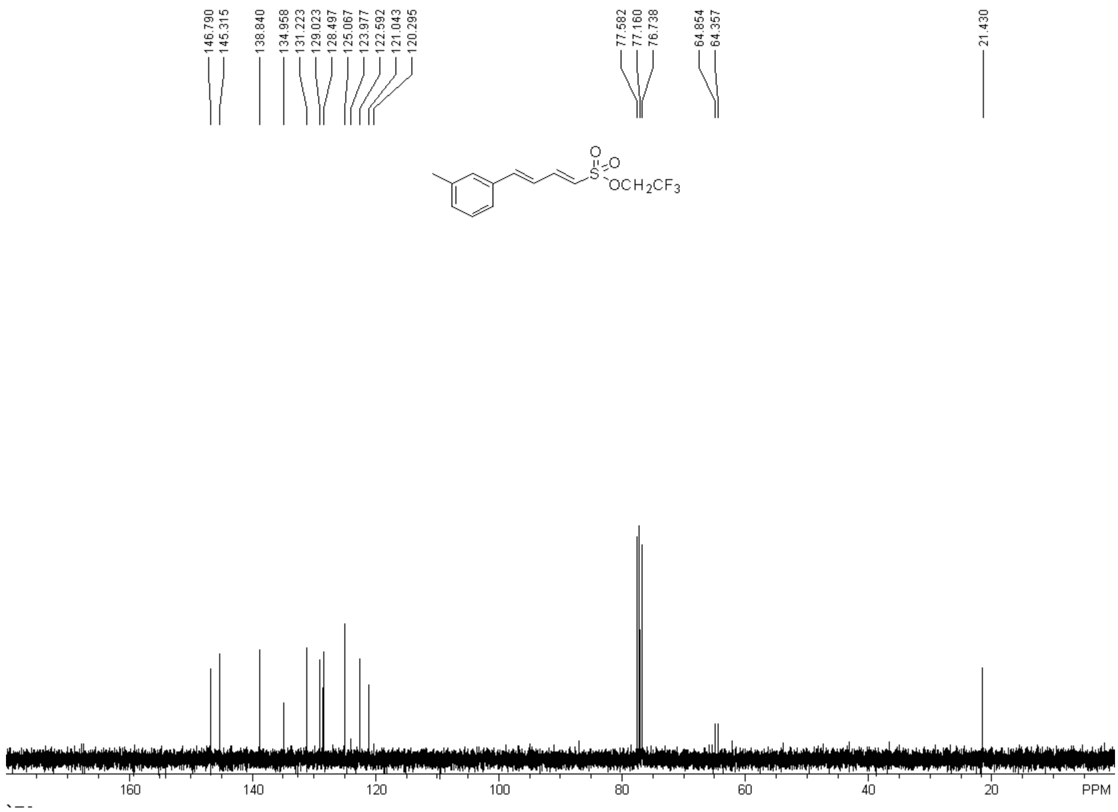
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138.840
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128.497
125.067
123.977
122.592
121.043
120.295
77.582
77.160
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64.854
64.357
21.430
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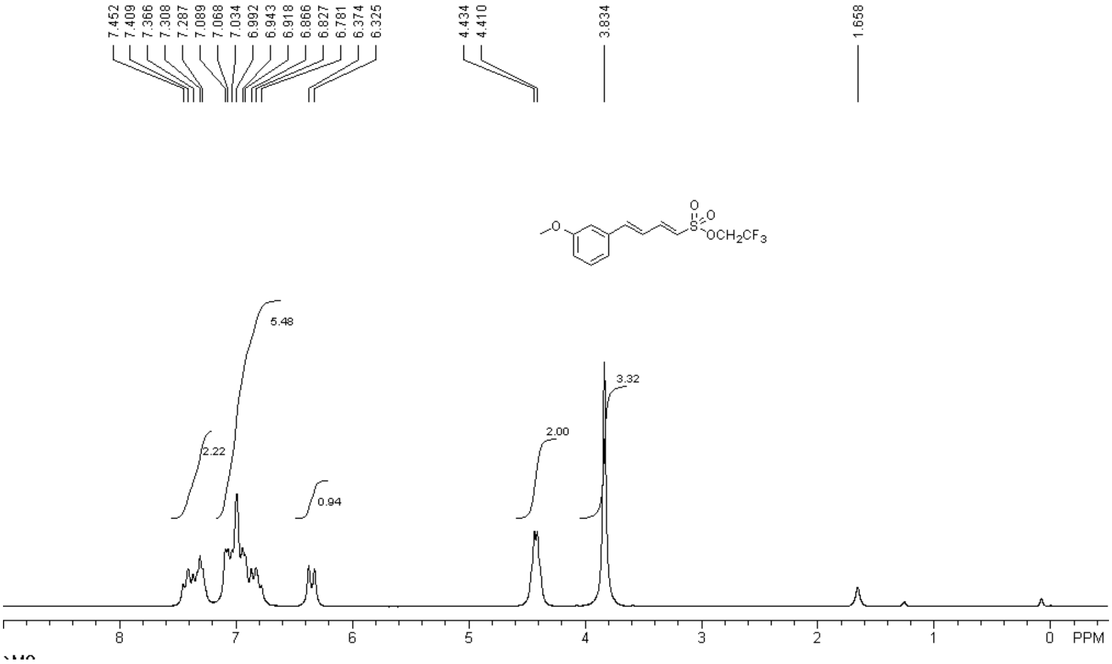
140
120
100
80
60
40
20
PPM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7.366
7.308
7.287
7.089
7.068
7.034
6.992
6.943
6.918
6.866
6.827
6.781
6.374
6.325
4.434
4.410
3.834
1.658
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2.22
2.00
0.94
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4
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2
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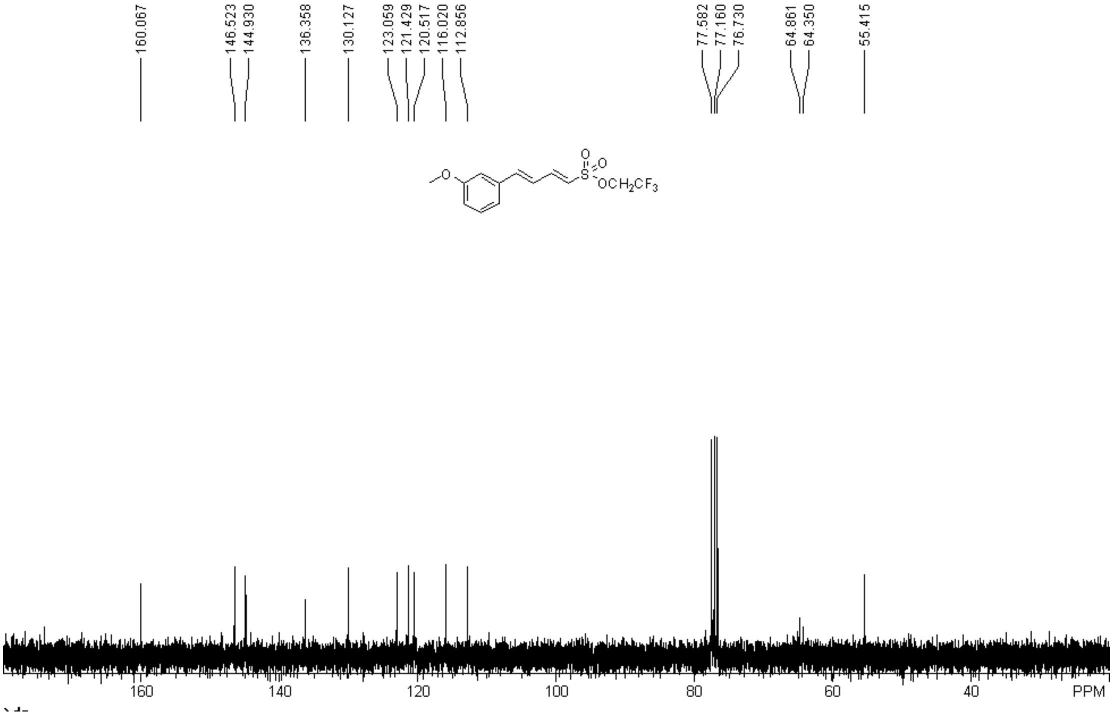
PPM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136.358
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123.059
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120.517
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112.856
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77.160
76.730
64.861
64.350
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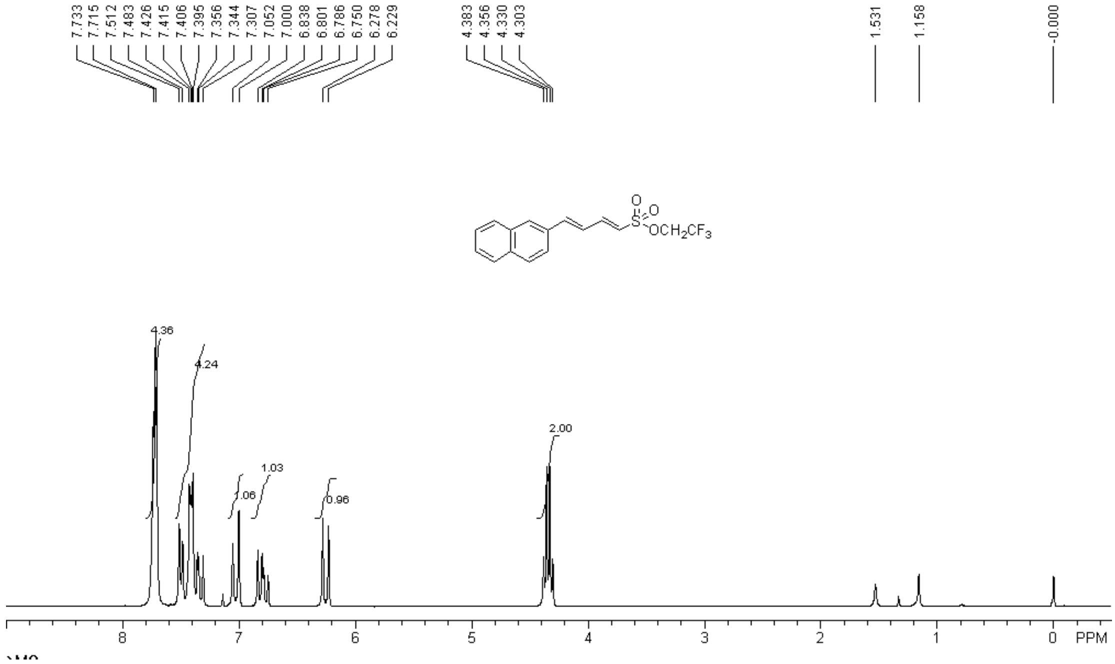
140
120
100
80
60
40
PPM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7.426
7.415
7.406
7.395
7.356
7.344
7.307
7.052
7.000
6.838
6.801
6.786
6.750
6.278
6.229
4.383
4.356
4.330
4.303
1.531
1.158
-0.000
OCH2CF3
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1.03
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2.00
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6
5
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2
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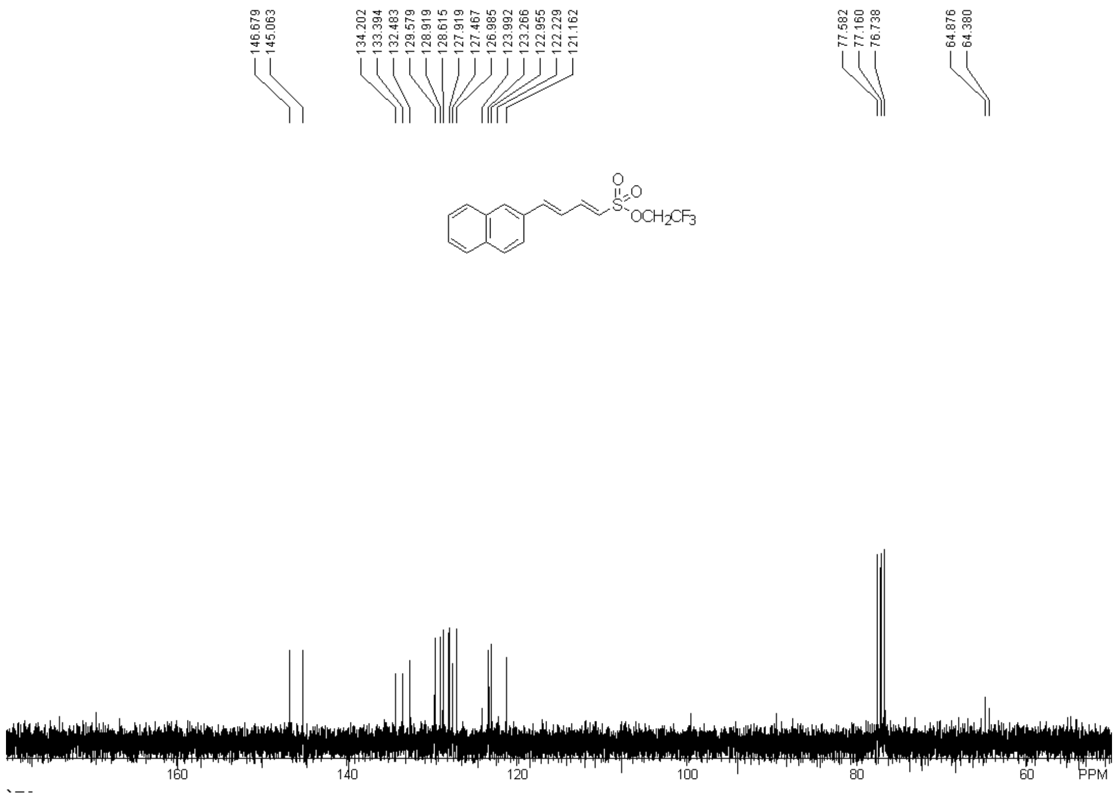
0
PPM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123.992
123.266
122.955
122.229
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76.738
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64.380
OCH2CF3
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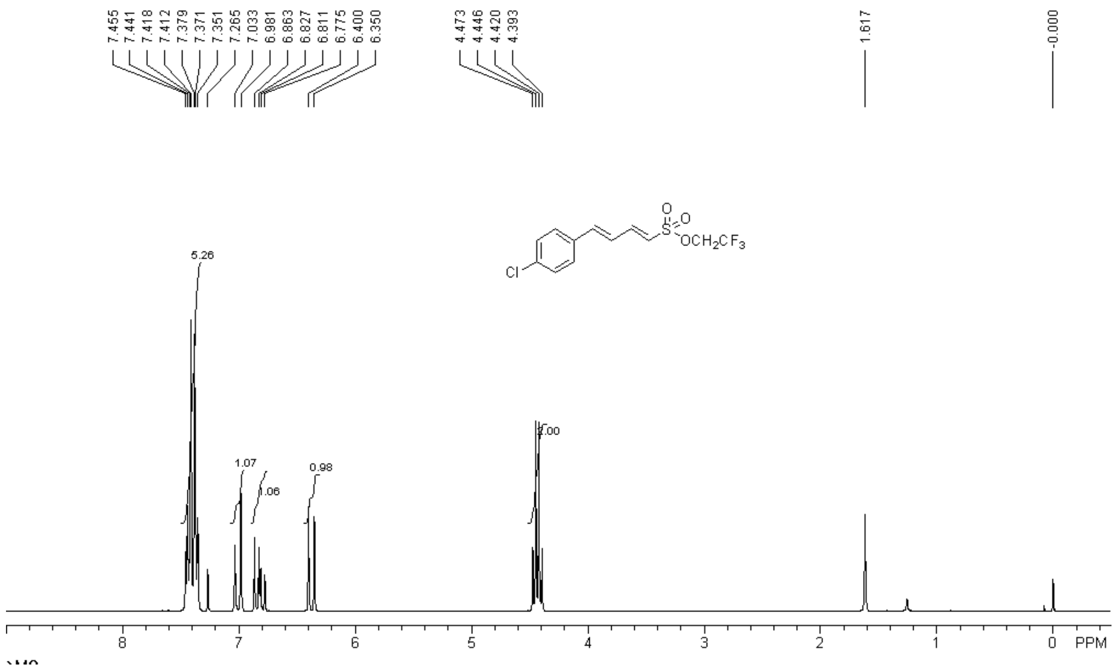
120
100
80
60
PPM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7.265
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6.981
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6.827
6.811
6.775
6.400
6.350
4.473
4.446
4.420
4.393
1.617
-0.000
Cl
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0.98
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8
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6
5
4
3
2
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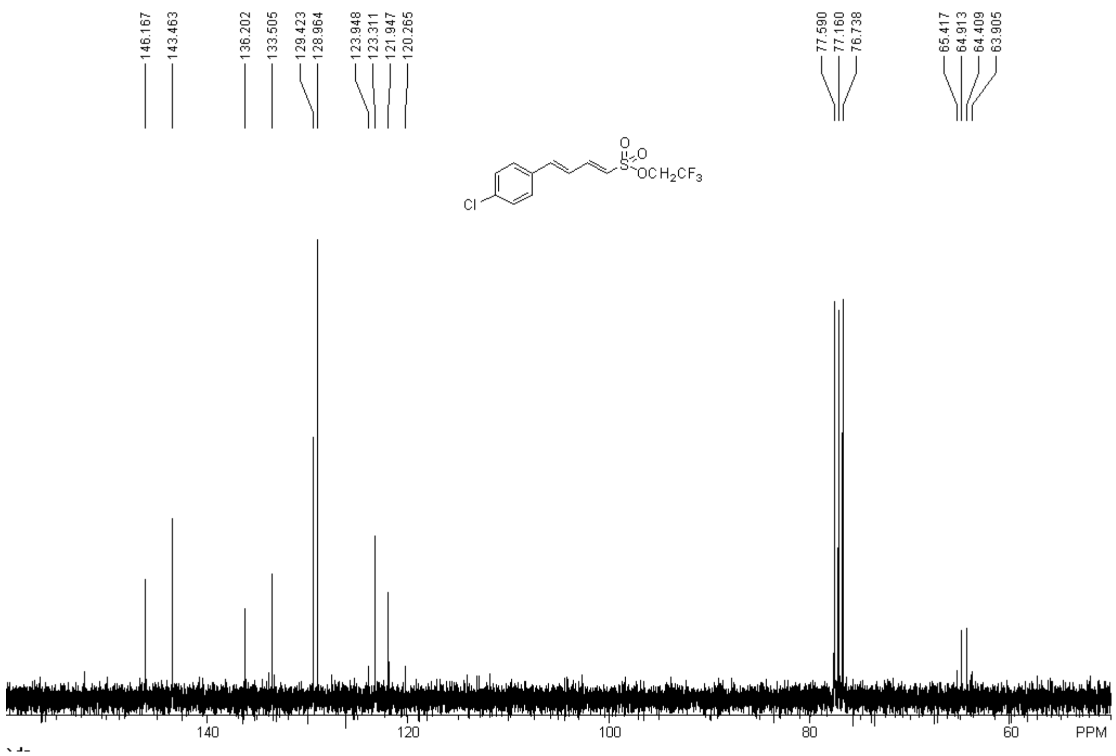
0
PPM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129.423
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123.311
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120.265
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77.160
76.738
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64.913
64.409
63.905
Cl
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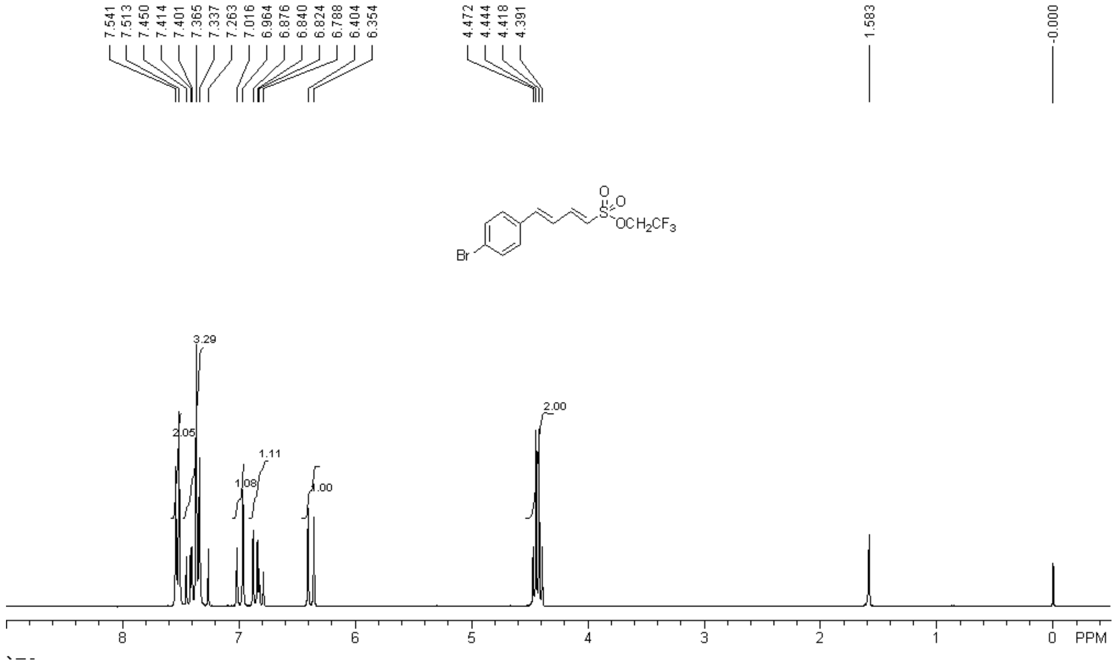
120
100
80
60
PPM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7.401
7.365
7.337
7.263
7.016
6.964
6.876
6.840
6.824
6.788
6.404
6.354
4.472
4.444
4.418
4.391
1.583
-0.000
Br
OCH2CF3
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1.08
1.11
1.00
2.00
8
7
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5
4
3
2
1
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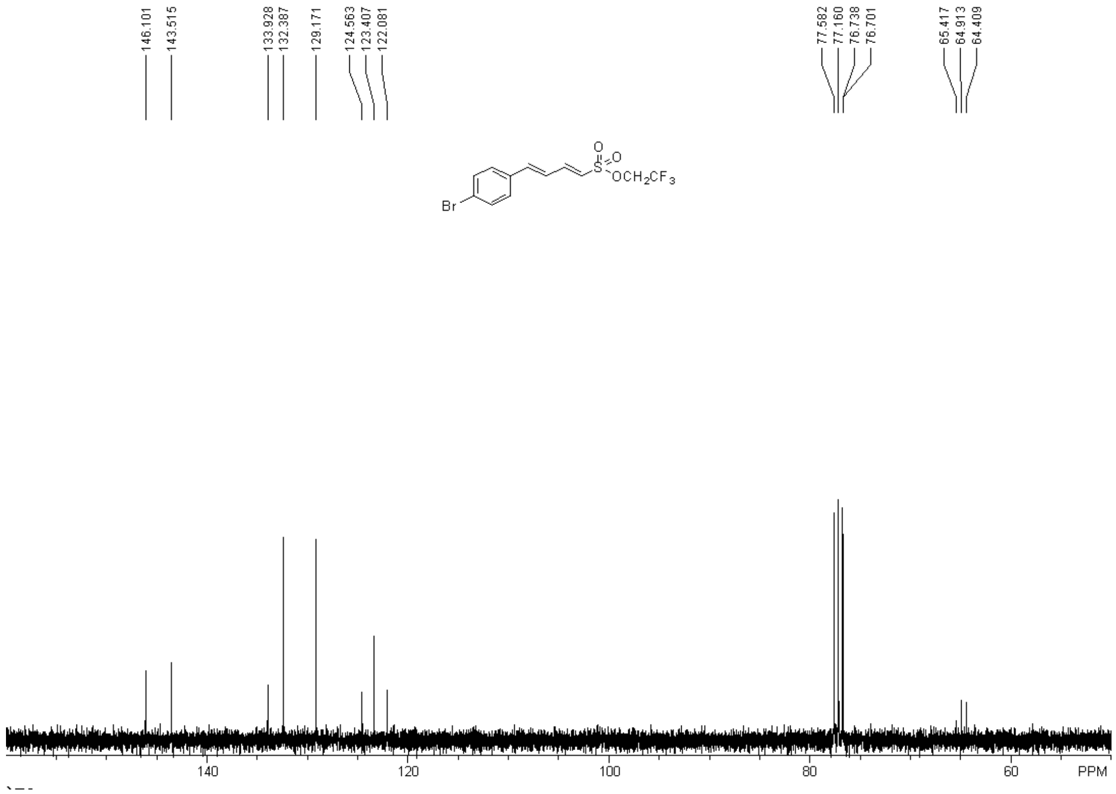
PPM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123.407
122.081
77.582
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76.738
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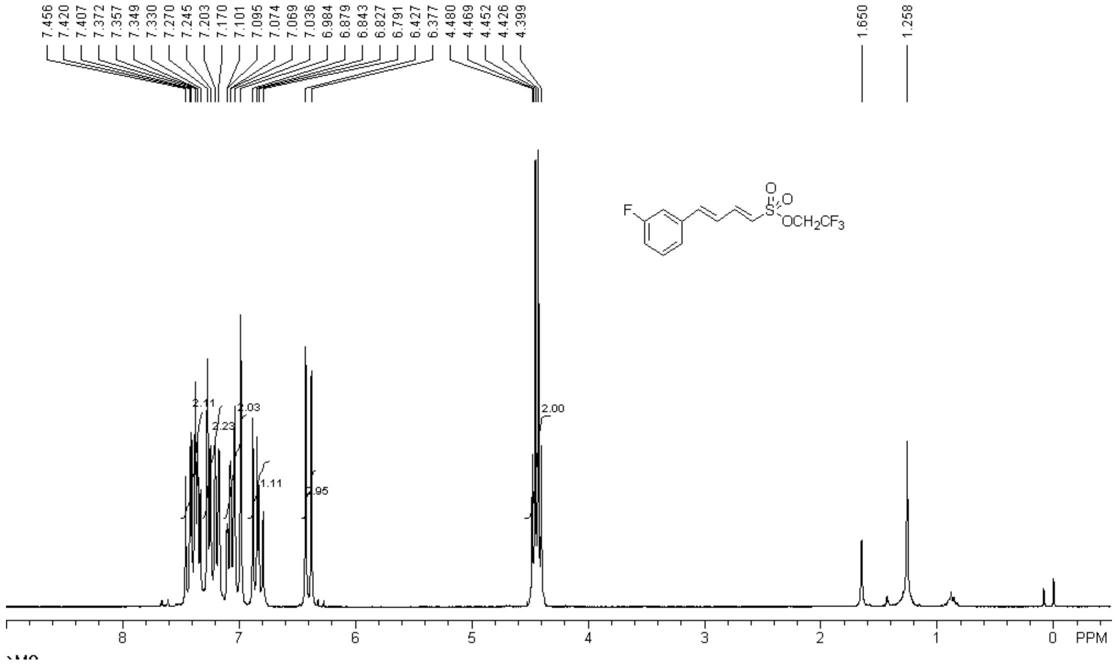
65.417
64.913
64.409
Br
OCH2CF3
140
120
100
80
60
PPM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7.270
7.245
7.203
7.170
7.101
7.095
7.074
7.069
7.036
6.984
6.879
6.843
6.827
6.791
6.427
6.377
4.480
4.469
4.452
4.426
4.399
1.650
1.258
F
O
S
O
OCH2CF3
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1.11
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2.00
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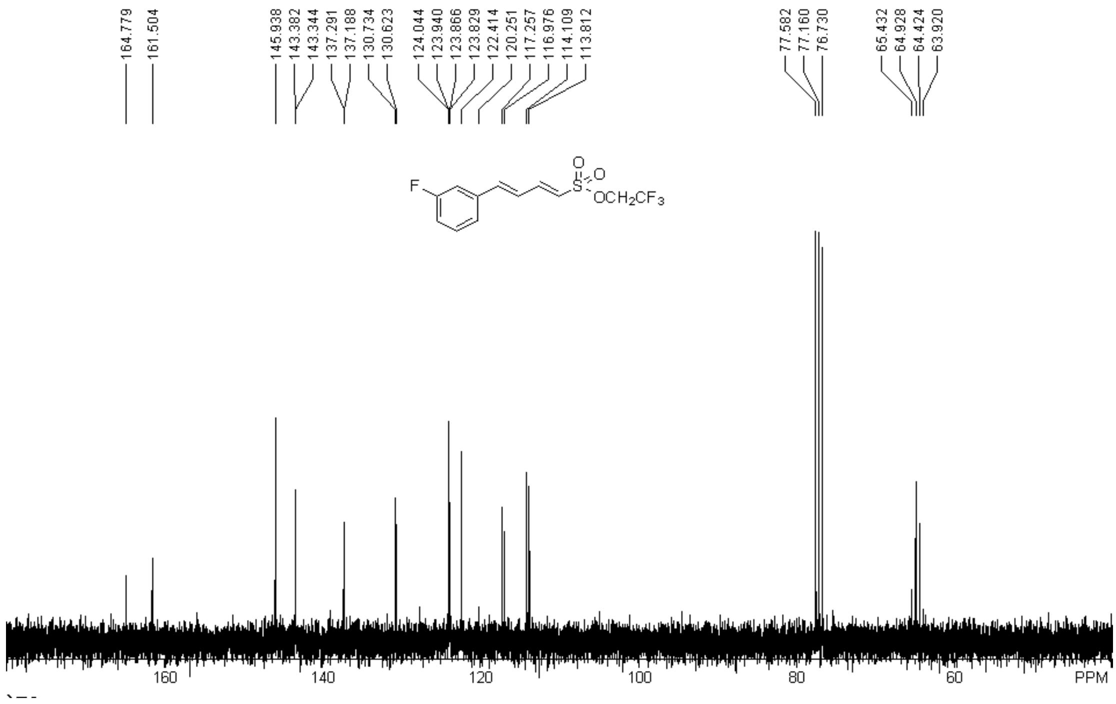
4
3
2
1
0
PPM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123.940
123.866
123.829
122.414
120.251
117.257
116.976
114.109
113.812
77.582
77.160
76.730
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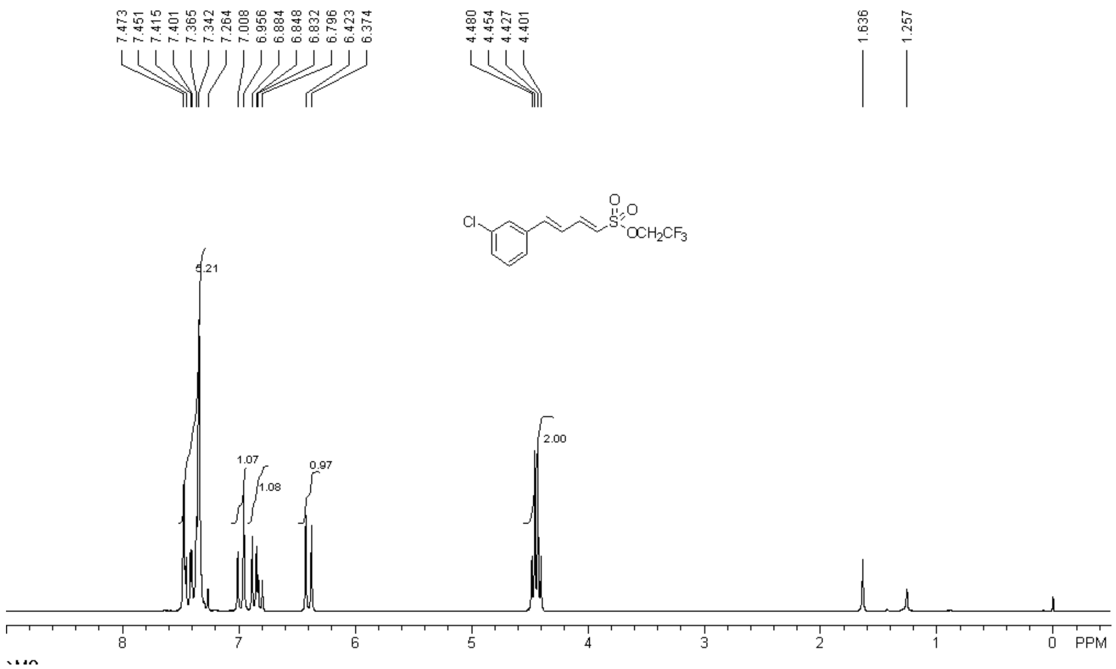
100
80
60
PPM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7.008
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6.884
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6.832
6.796
6.423
6.374
4.480
4.454
4.427
4.401
1.636
1.257
Cl
O
S
O
OCH2CF3
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1.08
0.97
2.00
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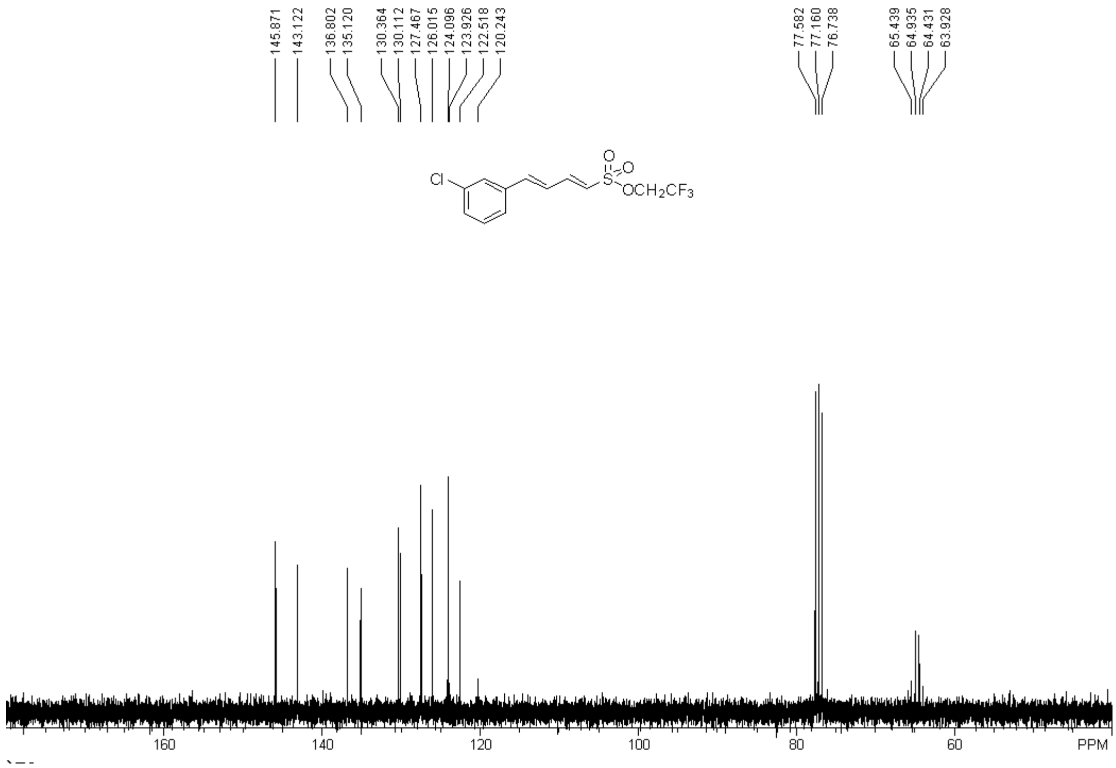
7
6
5
4
3
2
1
0
PPM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77.582
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76.738
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63.928
Cl
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S
O
OCH2CF3
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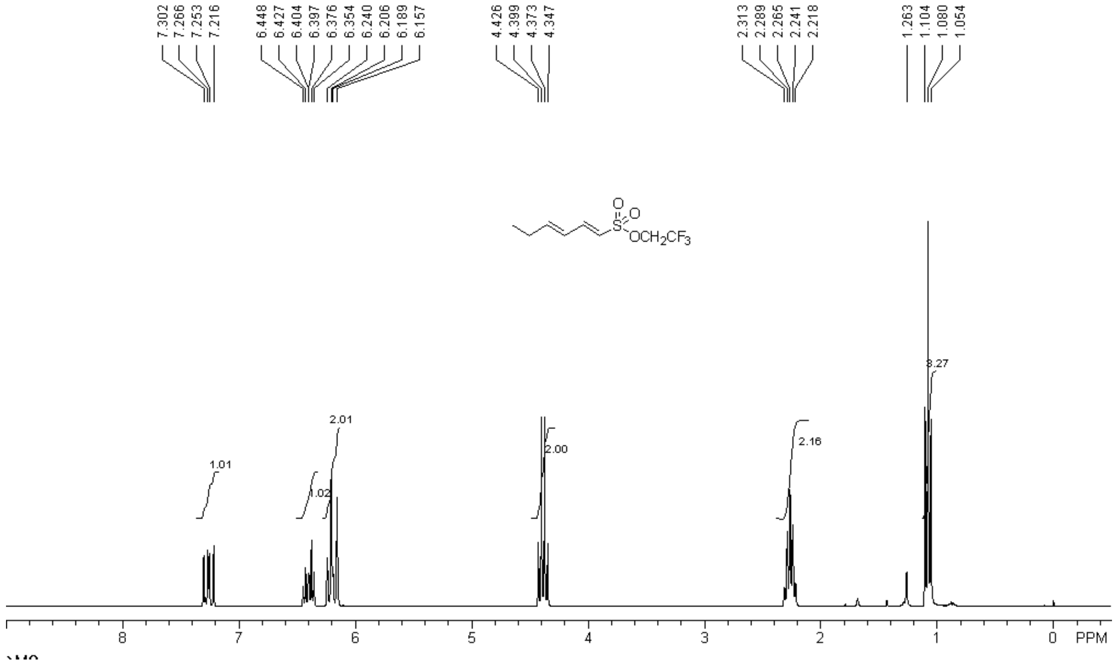
140
120
100
80
60
PPM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6.189
6.157
4.426
4.399
4.373
4.347
2.313
2.289
2.265
2.241
2.218
1.263
1.104
1.080
1.054
OCH2CF3
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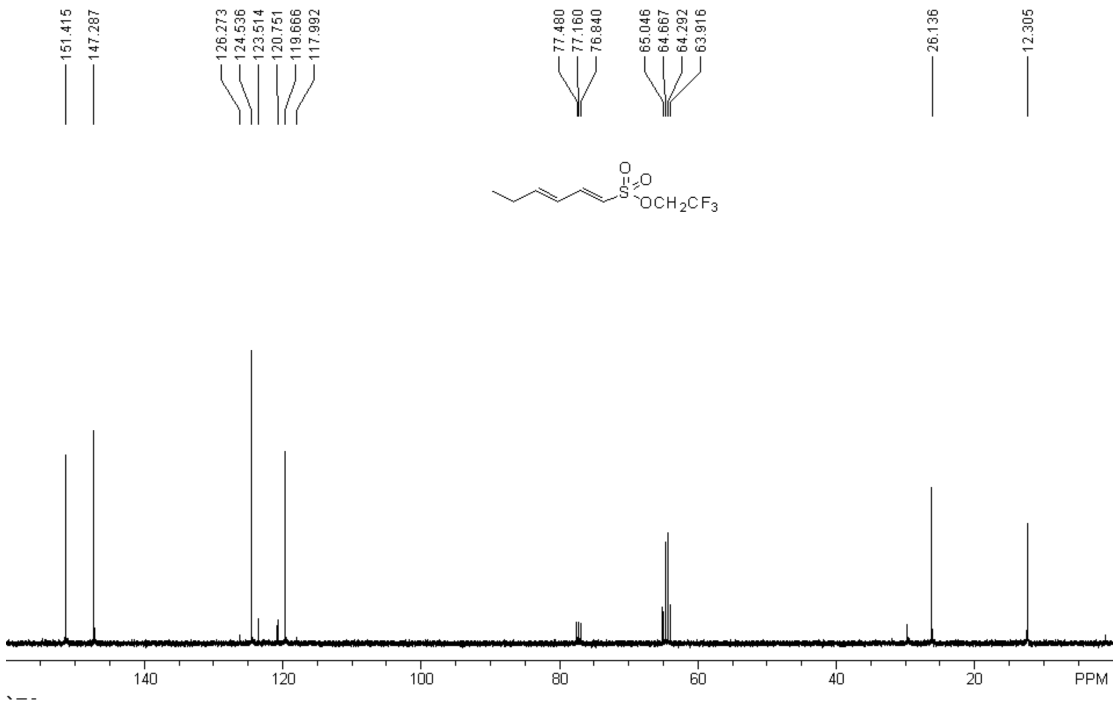
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117.992
77.480
77.160
76.840
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26.136
12.305
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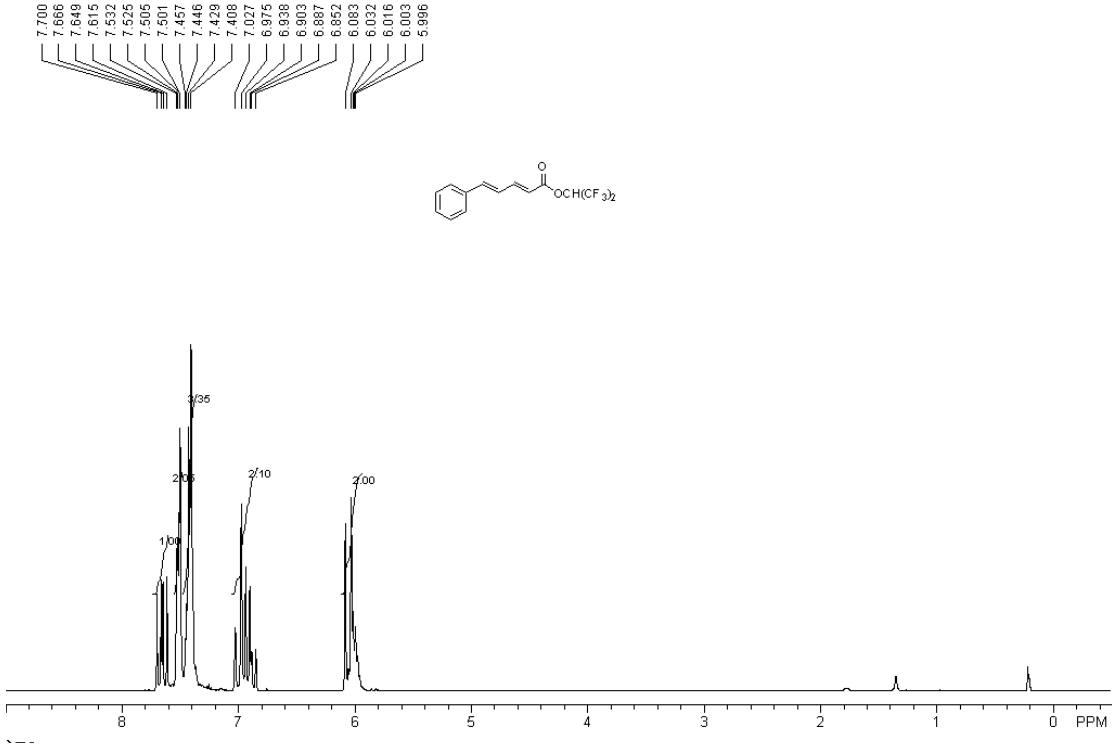
120
100
80
60
40
20
PPM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7.027
6.975
6.938
6.903
6.887
6.852
6.083
6.032
6.016
6.003
5.996
OCH(CF3)2
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2.10
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1.00
8
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6
5
4
3
2
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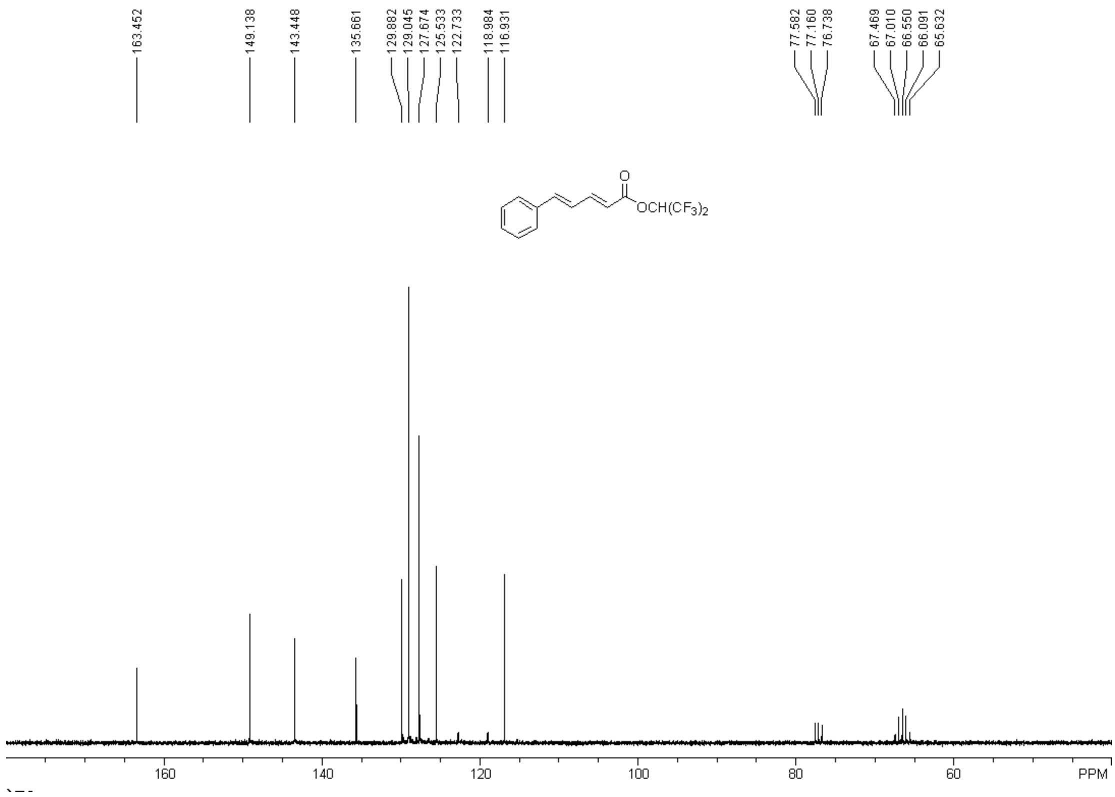
PPM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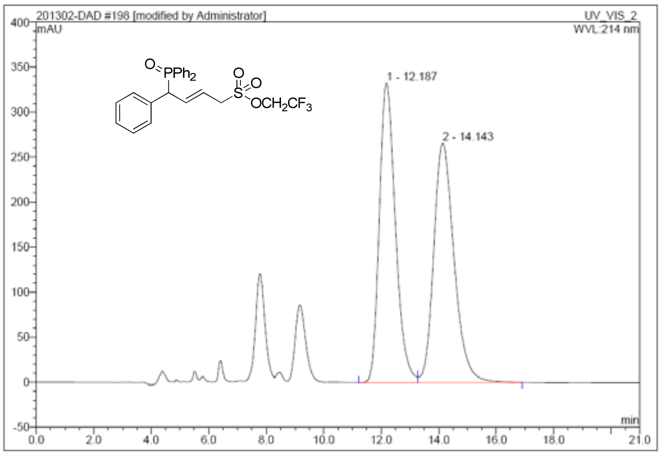
77.160
76.738
67.469
67.010
66.550
66.091
65.632
OCH(CF3)2
160
140
120
100
80
60
PPM

HPLC Chart

198 CJZ-5-6+- OD-H 73 214 0.7

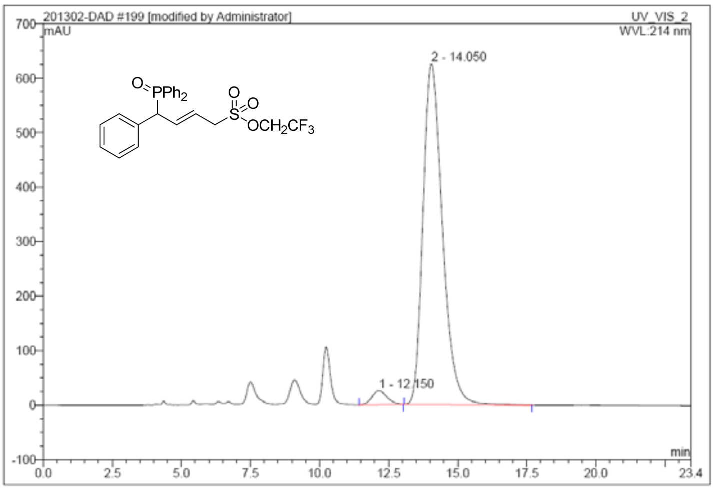
Sample Name:	CJZ-5-6+- OD-H 73 214 0.7	*Injection Volume:*	8.0
Vial Number:	RA2	*Channel:*	UV_VIS_2
Sample Type:	unknown	*Wavelength:*	214.0
Control Program:	test-dad	*Bandwidth:*	4
Quantif. Method:	WXL	*Dilution Factor:*	1.0000
Recording Time:	2013-3-25 10:13	*Sample Weight:*	1.0000
Run Time (min):	21.00	*Sample Amount:*	1.0000



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.19	n.a.	333.231	216.146	49.71	n.a.	BM
2	14.14	n.a.	265.955	218.711	50.29	n.a.	MB
Total:			599.185	434.856	100.00	0.000	

199 CJZ-6-9-2 OD-H 73 214 0.7

Sample Name:	CJZ-6-9-2 OD-H 73 214 0.7	*Injection Volume:*	4.0
Vial Number:	RA1	*Channel:*	UV_VIS_2
Sample Type:	unknown	*Wavelength:*	214.0
Control Program:	test-dad	*Bandwidth:*	4
Quantif. Method:	WXL	*Dilution Factor:*	1.0000
Recording Time:	2013-3-25 10:36	*Sample Weight:*	1.0000
Run Time (min):	23.44	*Sample Amount:*	1.0000



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.15	n.a.	25.745	16.234	3.08	n.a.	BMB*
2	14.05	n.a.	625.605	510.931	96.92	n.a.	BMB*
Total:			651.350	527.165	100.00	0.000	

==== Shimadzu LCsolution Analysis Report ====

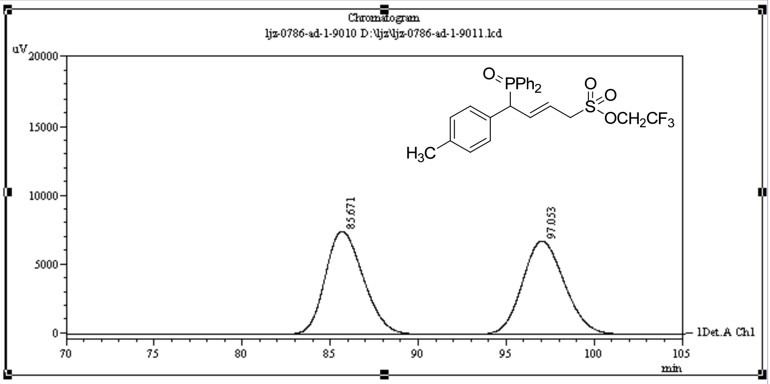
D:\ljz\ljz-0786-ad-1-9011.lcd

Sample Name : ljz-0786-ad-1-9010 Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	85.671	1121298	7476	49.948
2	97.053	1123618	6766	50.052
Total		2244915	14241	100.000

==== Shimadzu LCsolution Analysis Report ====

D:\ljz\ljz-0782-ad-1-9010.lcd

Sample Name : ljz-0782-ad-1-9010 Date:

Column: The mobile phase:

Velocity: The detection wavelength:

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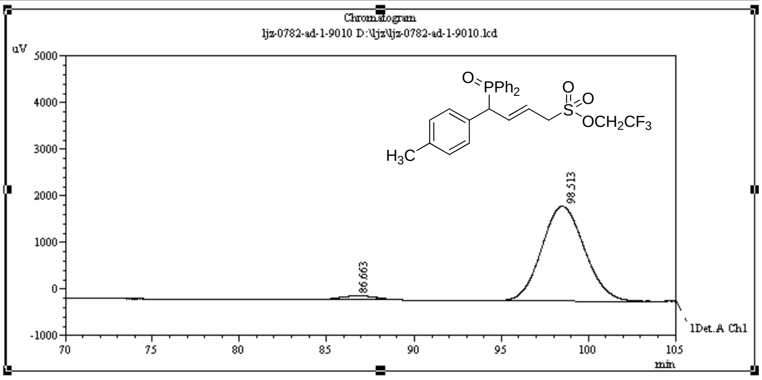


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	86.663	11584	89	3.217
2	98.513	348468	2036	96.783
Total		360051	2125	100.000

==== Shimadzu LCsolution Analysis Report ====

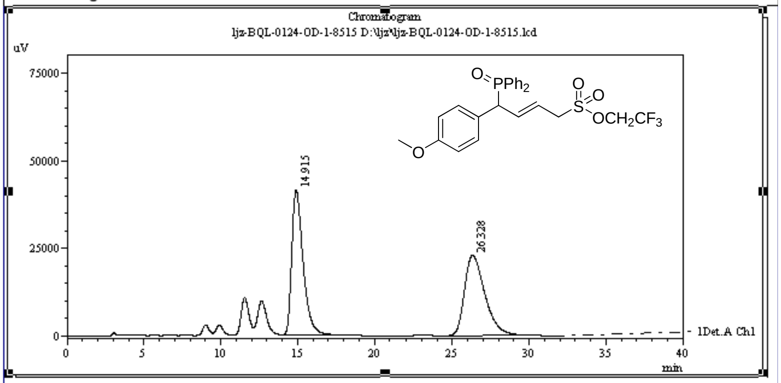
D:\ljz\ljz-BQL-0124-OD-1-8515.lcd

Sample Name : ljz-BQL-0124-OD-1-8515 Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	14.915	2116586	41234	50.126
2	26.328	2105977	22883	49.874
Total		4222563	64116	100.000

==== Shimadzu LCsolution Analysis Report ====

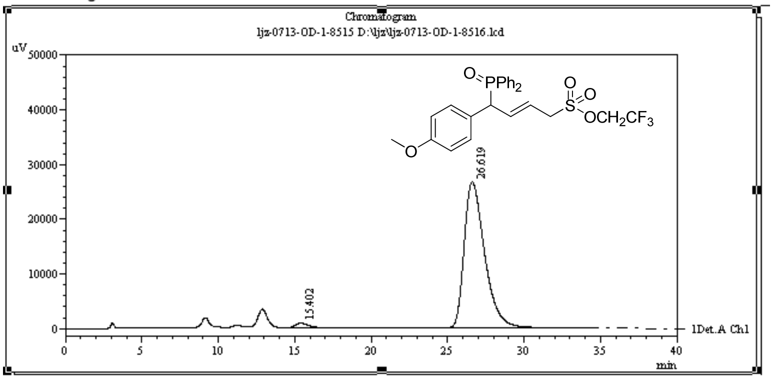
D:\ljz\ljz-0713-OD-1-8516.lcd

Sample Name : ljz-0713-OD-1-8515 Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	15.402	51452	870	2.042
2	26.619	2468763	26684	97.958
Total		2520215	27553	100.000

==== Shimadzu LCsolution Analysis Report ====

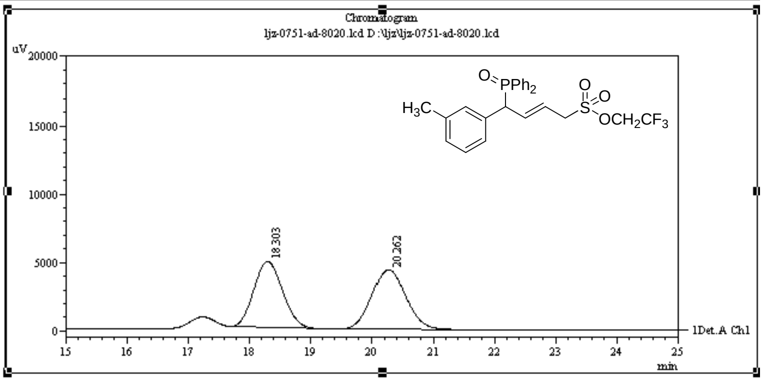
D:\ljz\ljz-0751-ad-8020.lcd

Sample Name : ljz-0751-ad-8020.lcd Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	18.303	158374	4822	48.913
2	20.262	165412	4359	51.087
Total		323785	9181	100.000

==== Shimadzu LCsolution Analysis Report ====

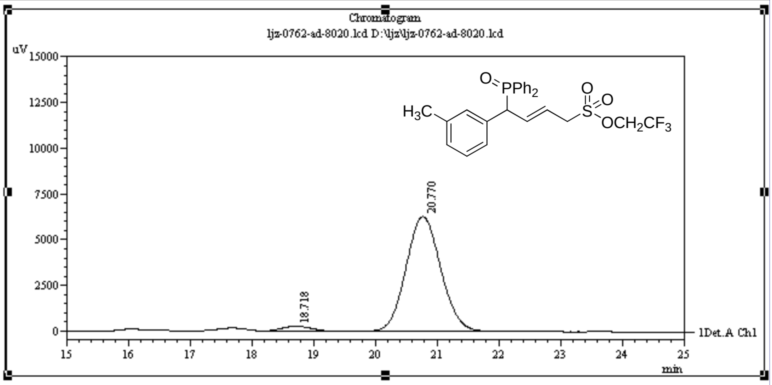
D:\ljz\ljz-0762-ad-8020.lcd

Sample Name : ljz-0762-ad-8020.lcd Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	18.718	8676	266	3.429
2	20.770	244361	6262	96.571
Total		253037	6527	100.000

==== Shimadzu LCsolution Analysis Report ====

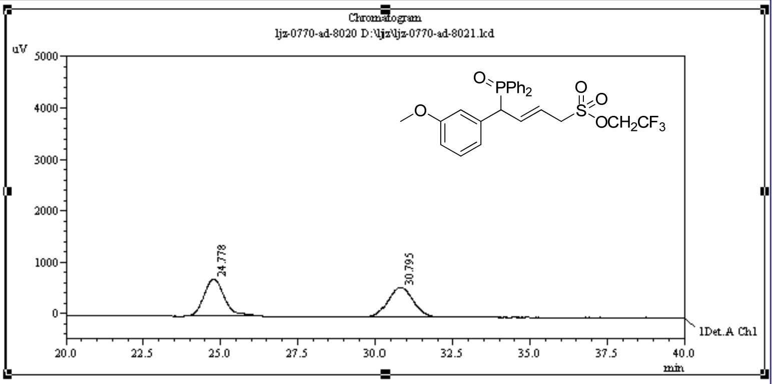
D:\ljz\ljz-0770-ad-8021.lcd

Sample Name : ljz-0770-ad-8020 Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	24.778	31716	714	49.636
2	30.795	32182	578	50.364
Total		63898	1292	100.000

==== Shimadzu LCsolution Analysis Report ====

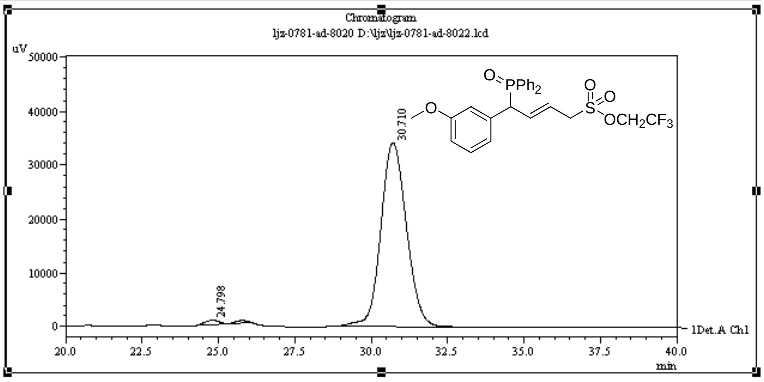
D:\ljz\ljz-0781-ad-8022.lcd

Sample Name : ljz-0781-ad-8020 Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	24.798	48131	882	2.353
2	30.710	1997251	34210	97.647
Total		2045382	35092	100.000

==== Shimadzu LCsolution Analysis Report ====

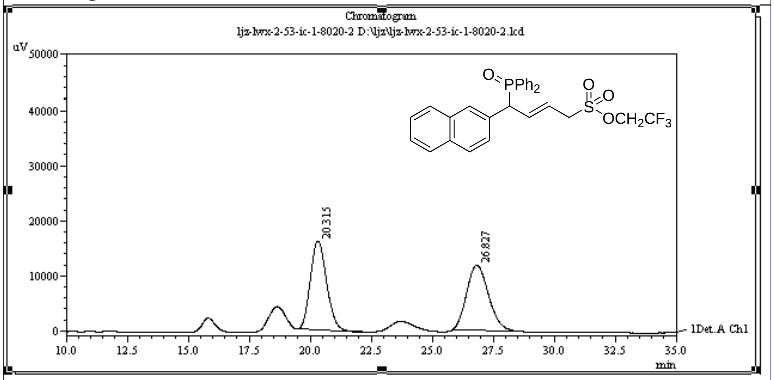
D:\ljz\ljz-lwx-2-53-ic-1-8020-2.lcd

Sample Name : ljz-lwx-2-53-ic-1-8020-2 Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	20.315	747934	16171	50.511
2	26.827	732805	11821	49.489
Total		1480739	27992	100.000

==== Shimadzu LCsolution Analysis Report ====

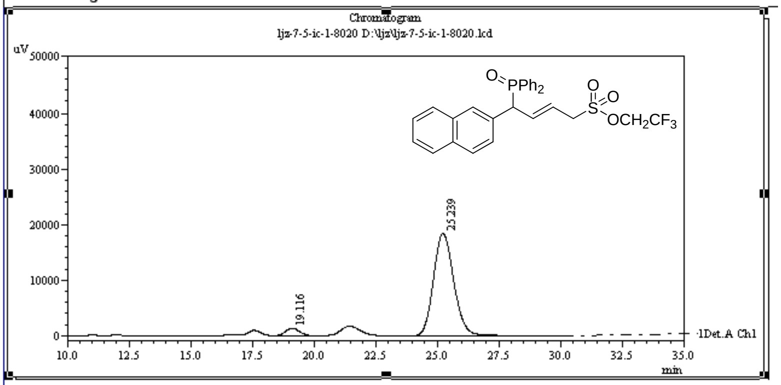
D:\ljz\ljz-7-5-ic-1-8020.lcd

Sample Name : ljz-7-5-ic-1-8020 Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	19.116	54091	1357	4.812
2	25.239	1069963	18529	95.188
Total		1124055	19885	100.000

==== Shimadzu LCsolution Analysis Report ====

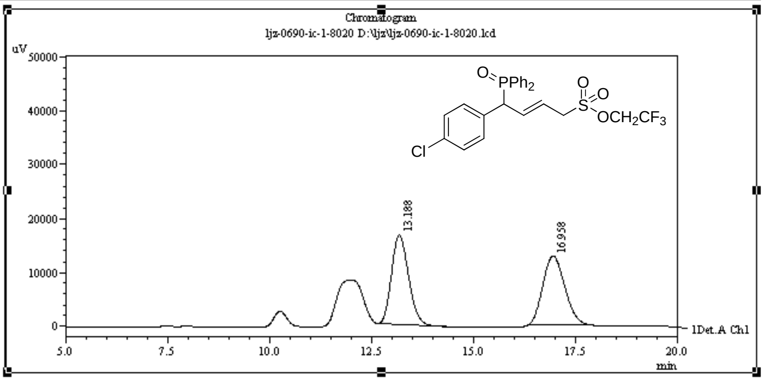
D:\ljz\ljz-0690-ic-1-8020.lcd

Sample Name : ljz-0690-ic-1-8020 Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	13.188	482165	16568	50.532
2	16.958	472009	12722	49.468
Total		954175	29290	100.000

==== Shimadzu LCsolution Analysis Report ====

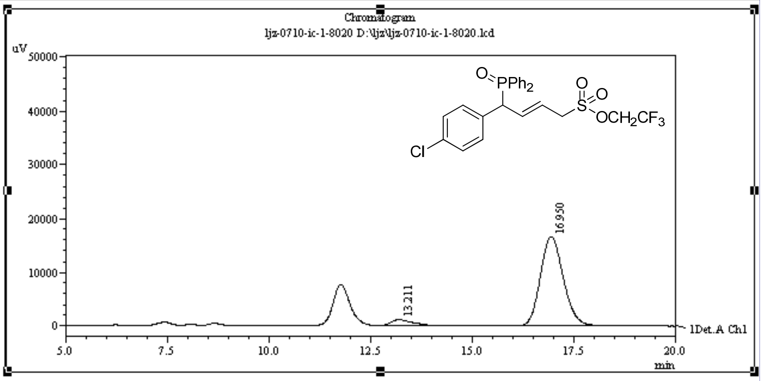
D:\ljz\ljz-0710-ic-1-8020.lcd

Sample Name : ljz-0710-ic-1-8020 Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	13.211	40916	1100	5.872
2	16.950	655904	16654	94.128
Total		696819	17754	100.000

==== Shimadzu LCsolution Analysis Report ====

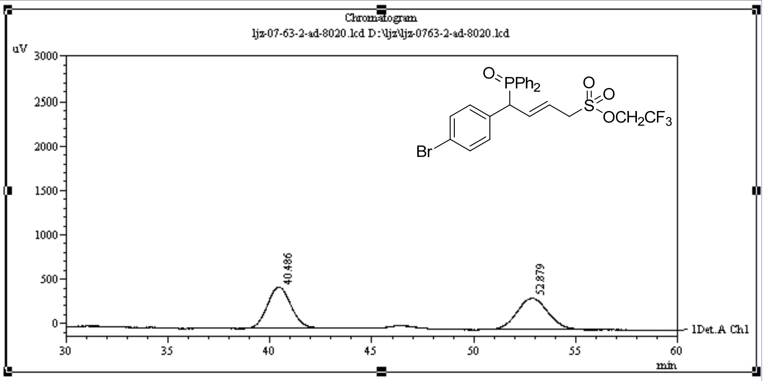
D:\ljz\ljz-0763-2-ad-8020.lcd

Sample Name : ljz-07-63-2-ad-8020.lcd Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	40.486	36759	461	49.550
2	52.879	37426	355	50.450
Total		74185	816	100.000

==== Shimadzu LCsolution Analysis Report ====

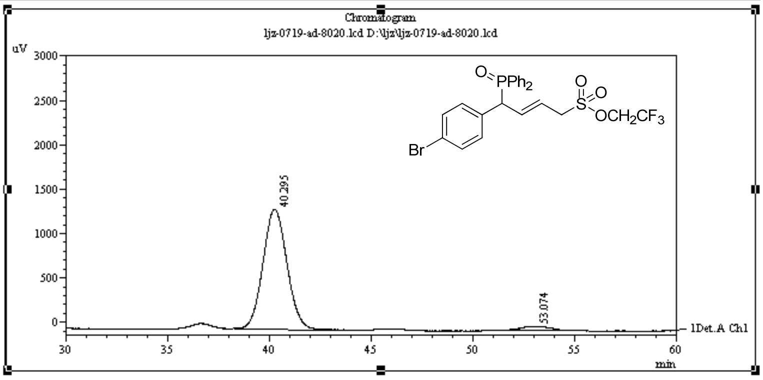
D:\ljz\ljz-0719-ad-8020.lcd

Sample Name : ljz-0719-ad-8020.lcd Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	40.295	110539	1352	96.593
2	53.074	3899	44	3.407
Total		114438	1395	100.000

==== Shimadzu LCsolution Analysis Report ====

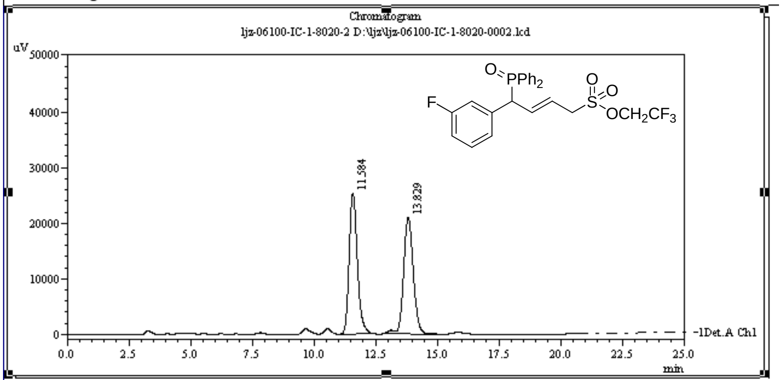
D:\ljz\ljz-06100-IC-1-8020-0002.lcd

Sample Name : ljz-06100-IC-1-8020-2 Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	11.584	585552	25324	50.393
2	13.829	576421	20965	49.607
Total		1161974	46290	100.000

==== Shimadzu LCsolution Analysis Report ====

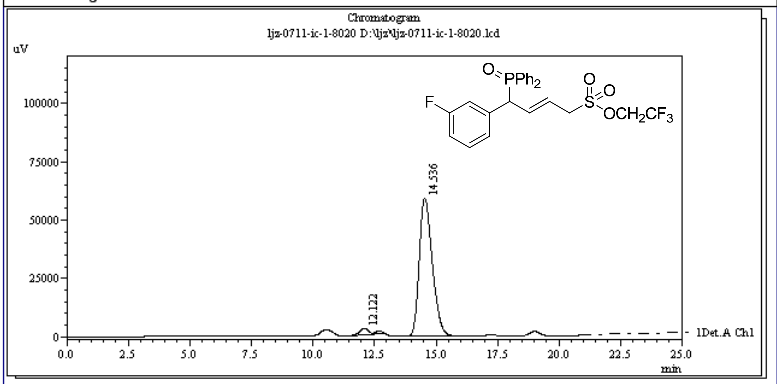
D:\ljz\ljz-0711-ic-1-8020.lcd

Sample Name : ljz-0711-ic-1-8020 Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.122	88232	2795	3.902
2	14.536	2173127	59121	96.098
Total		2261359	61916	100.000

==== Shimadzu LCsolution Analysis Report ====

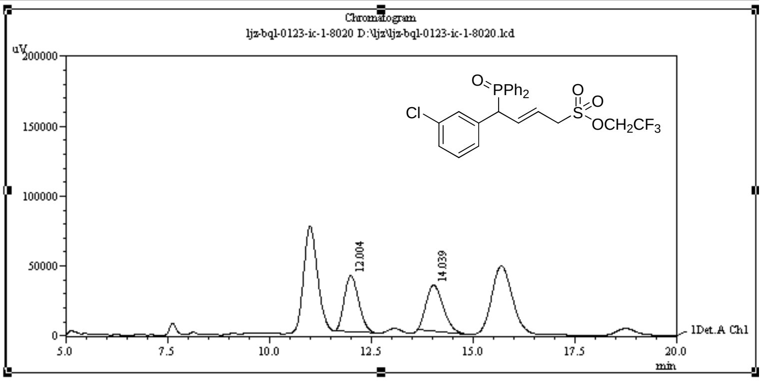
D:\ljz\ljz-bql-0123-ic-1-8020.lcd

Sample Name : ljz-bql-0123-ic-1-8020 Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.004	972842	39924	50.056
2	14.039	970650	33031	49.944
Total		1943492	72955	100.000

==== Shimadzu LCsolution Analysis Report ====

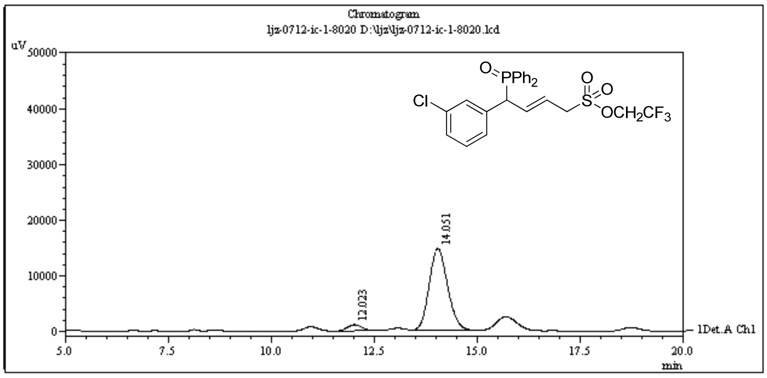
D:\ljz\ljz-0712-ic-1-8020.lcd

Sample Name : ljz-0712-ic-1-8020 Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.023	27063	1110	5.582
2	14.051	457746	14729	94.418
Total		484809	15840	100.000

==== Shimadzu LCsolution Analysis Report ====

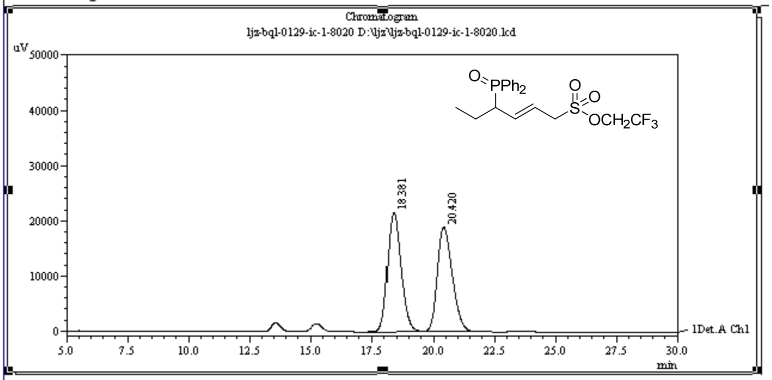
D:\ljz\ljz-bql-0129-ic-1-8020.lcd

Sample Name : ljz-bql-0129-ic-1-8020 Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	18.381	807585	21517	50.072
2	20.420	805261	18863	49.928
Total		1612846	40380	100.000

==== Shimadzu LCsolution Analysis Report ====

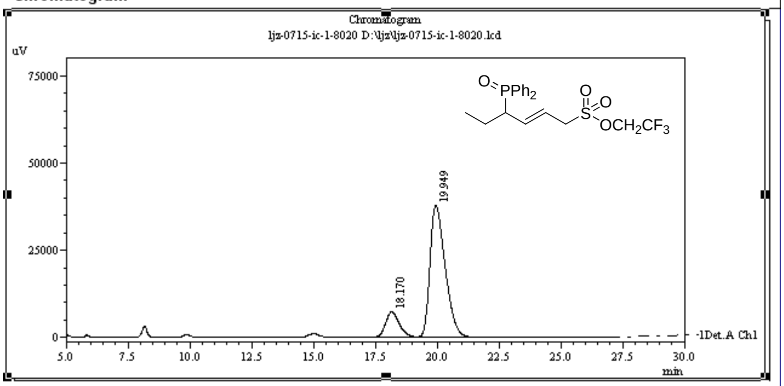
D:\ljz\ljz-0715-ic-1-8020.lcd

Sample Name : ljz-0715-ic-1-8020 Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	18.170	273575	7206	14.539
2	19.949	1608048	37614	85.461
Total		1881623	44820	100.000

==== Shimadzu LCsolution Analysis Report ====

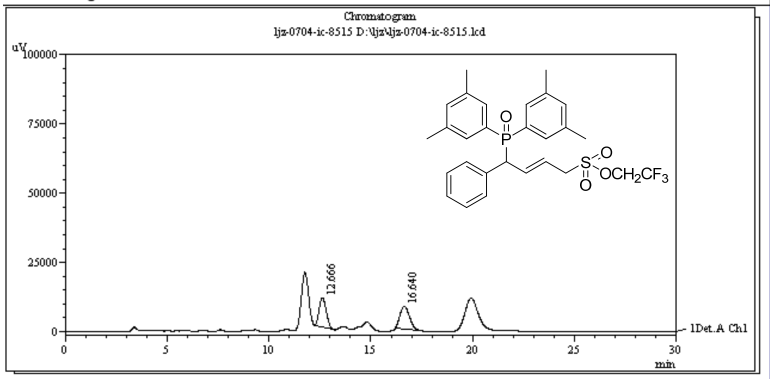
D:\ljz\ljz-0704-ic-8515.lcd

Sample Name : ljz-0704-ic-8515 Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.666	252616	10469	49.140
2	16.640	261458	8112	50.860
Total		514074	18581	100.000

==== Shimadzu LCsolution Analysis Report ====

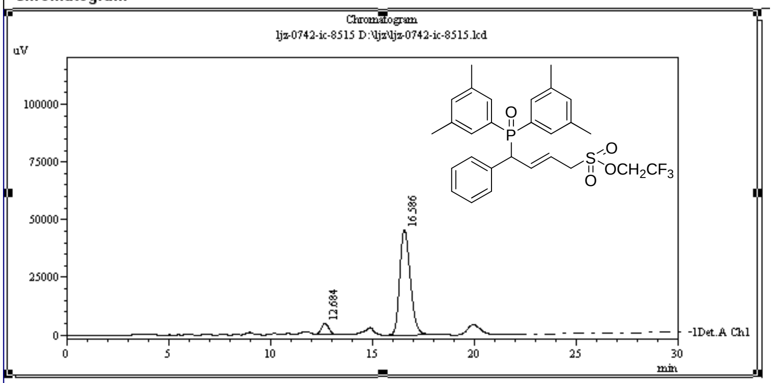
D:\ljz\ljz-0742-ic-8515.lcd

Sample Name : ljz-0742-ic-8515 Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.684	121656	4847	6.861
2	16.586	1651367	45608	93.139
Total		1773023	50455	100.000

==== Shimadzu LCsolution Analysis Report ====

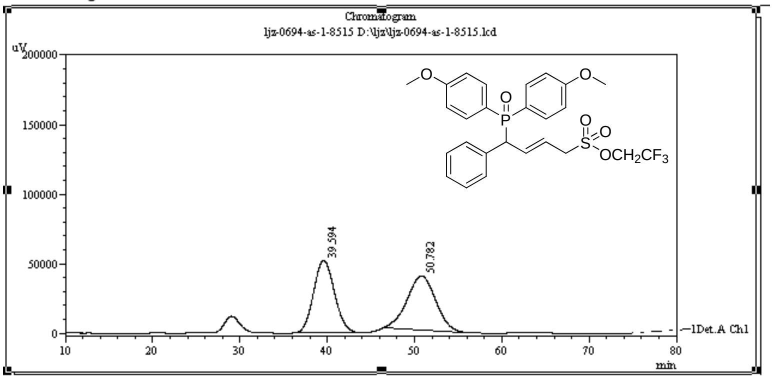
D:\ljz\ljz-0694-as-1-8515.lcd

Sample Name : ljz-0694-as-1-8515 Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	39.594	8701891	52084	49.564
2	50.782	8855048	38892	50.436
Total		17556940	90976	100.000

==== Shimadzu LCsolution Analysis Report ====

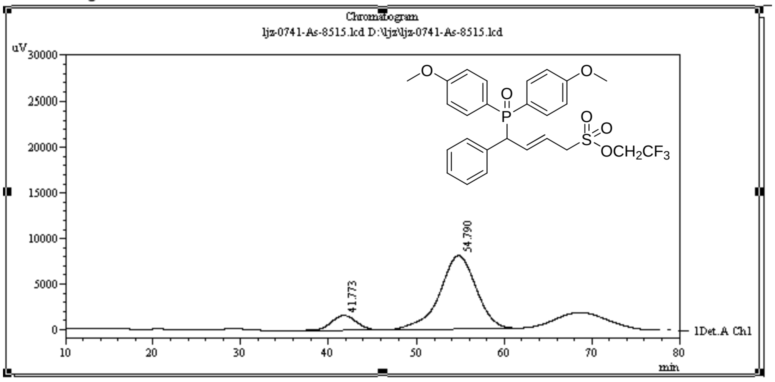
D:\ljz\ljz-0741-As-8515.lcd

Sample Name : ljz-0741-As-8515.lcd Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	41.773	322026	1628	12.075
2	54.790	2344904	8065	87.925
Total		2666929	9693	100.000

==== Shimadzu LCsolution Analysis Report ====

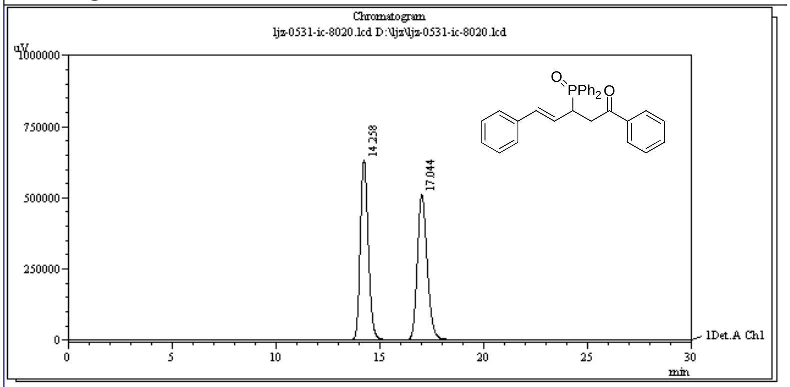
D:\ljz\ljz-0531-ic-8020.lcd

Sample Name : ljz-0531-ic-8020.lcd Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	14.258	16826752	632342	49.889
2	17.044	16901672	509331	50.111
Total		33728425	1141673	100.000

==== Shimadzu LCsolution Analysis Report ====

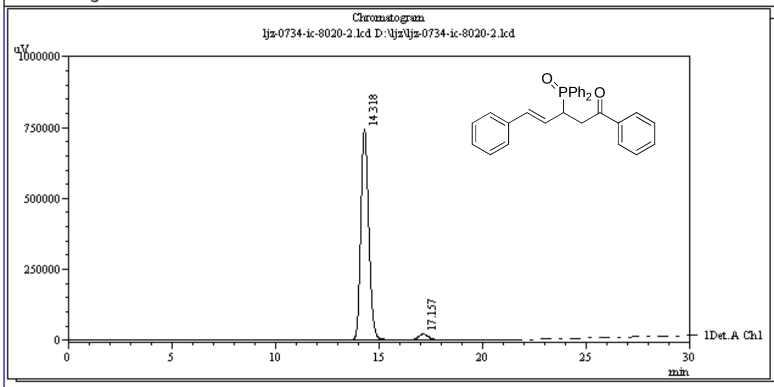
D:\ljz\ljz-0734-ic-8020-2.lcd

Sample Name : ljz-0734-ic-8020-2.lcd Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	14.318	19746403	742746	96.592
2	17.157	696782	20714	3.408
Total		20443185	763461	100.000

==== Shimadzu LCsolution Analysis Report ====

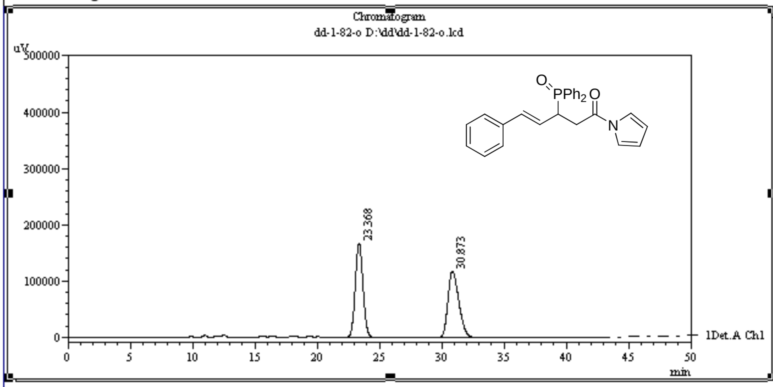
D:\dd\dd-1-82-o.lcd

Sample Name : dd-1-82-o Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



Peak Table

Detector A Ch1 245nm

Peak#	Ret. Time	Area	Height	Area %
1	23.368	7239253	167694	50.109
2	30.873	7207858	118112	49.891
Total		14447111	285806	100.000

==== Shimadzu LCsolution Analysis Report ====

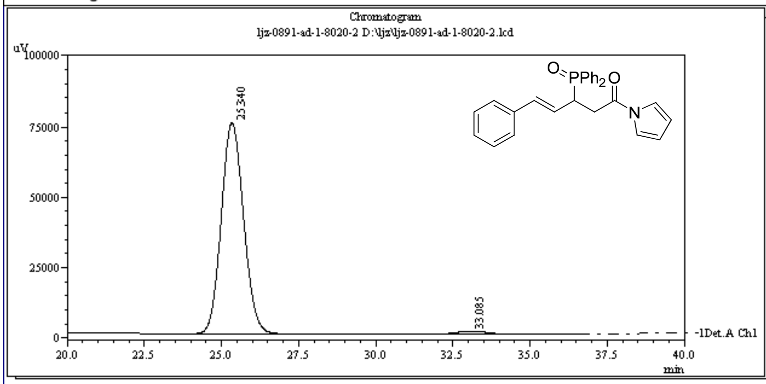
D:\ljz\ljz-0891-ad-1-8020-2.lcd

Sample Name : ljz-0891-ad-1-8020-2 Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	25.340	3784791	75085	97.958
2	33.085	78891	1145	2.042
Total		3863682	76230	100.000

==== Shimadzu LCsolution Analysis Report ====

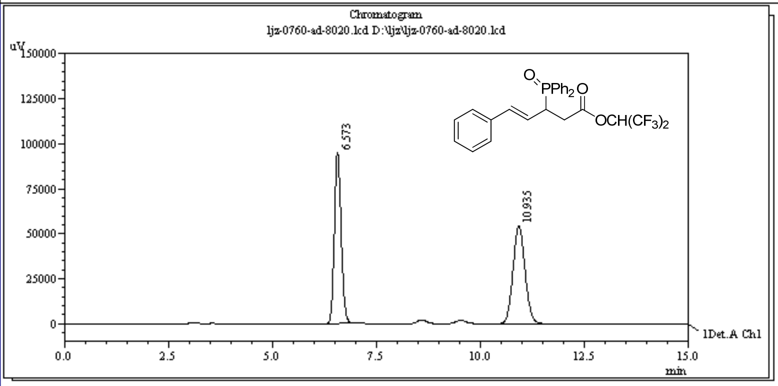
D:\ljz\ljz-0760-ad-8020.lcd

Sample Name : ljz-0760-ad-8020.lcd Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	6.573	1090506	95029	49.861
2	10.935	1096586	54173	50.139
Total		2187092	149202	100.000

==== Shimadzu LCsolution Analysis Report ====

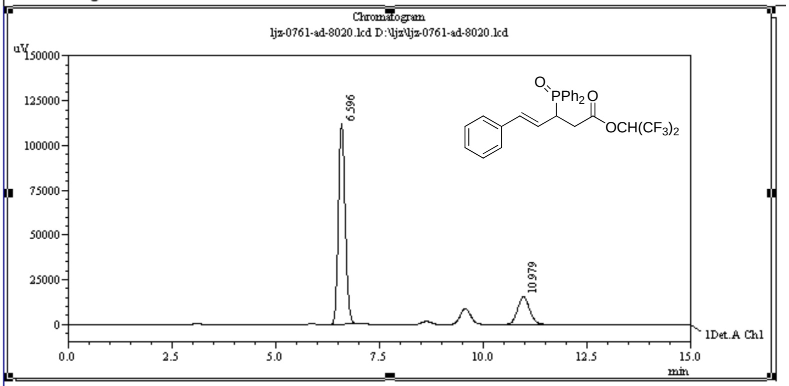
D:\ljz\ljz-0761-ad-8020.lcd

Sample Name : ljz-0761-ad-8020.lcd Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	6.596	1288561	112030	80.476
2	10.979	312612	15386	19.524
Total		1601173	127416	100.000

==== Shimadzu LCsolution Analysis Report ====

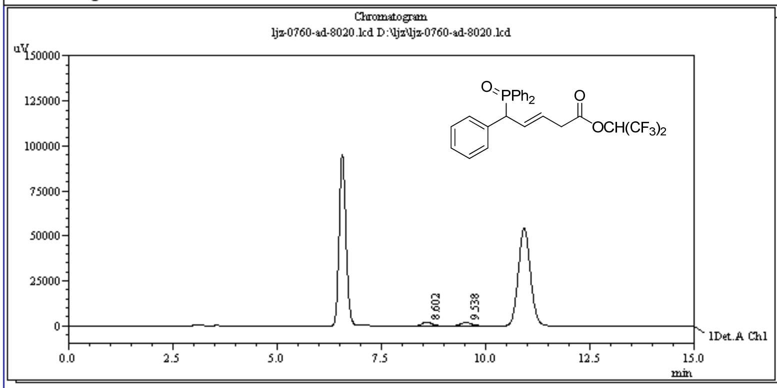
D:\ljz\ljz-0760-ad-8020.lcd

Sample Name : ljz-0760-ad-8020.lcd Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	8.602	33674	2150	50.553
2	9.538	32937	1835	49.447
Total		66611	3985	100.000

==== Shimadzu LCsolution Analysis Report ====

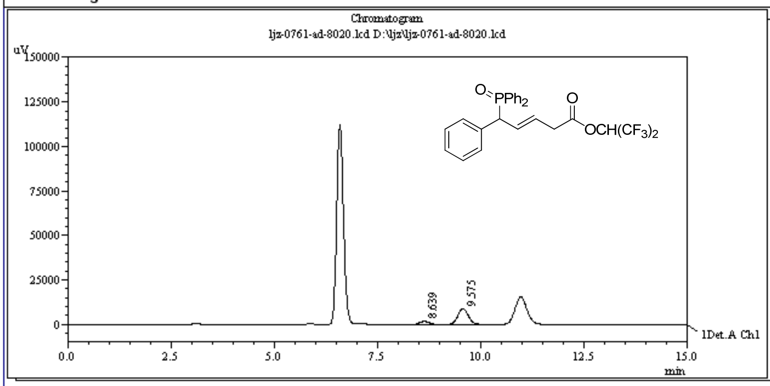
D:\ljz\ljz-0761-ad-8020.lcd

Sample Name : ljz-0761-ad-8020.lcd Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	8.639	27189	1740	14.624
2	9.575	158735	8940	85.376
Total		185924	10680	100.000

==== Shimadzu LCsolution Analysis Report ====

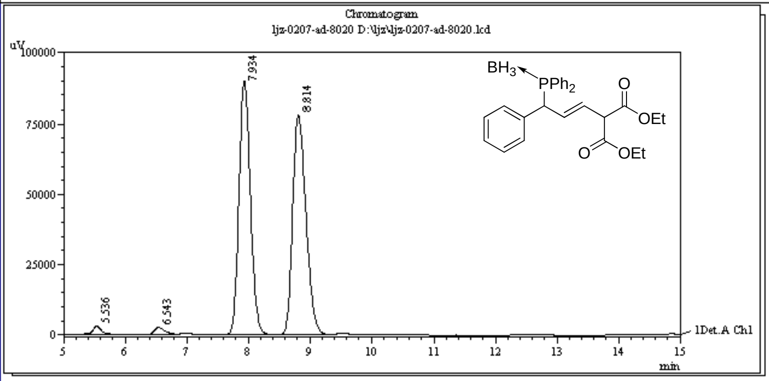
D:\ljz\ljz-0207-ad-8020.lcd

Sample Name : ljz-0207-ad-8020 Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	5.536	24469	2821	1.025
2	6.543	28686	2477	1.202
3	7.934	1162773	89968	48.728
4	8.814	1170348	78056	49.045
Total		2386276	173323	100.000

==== Shimadzu LCsolution Analysis Report ====

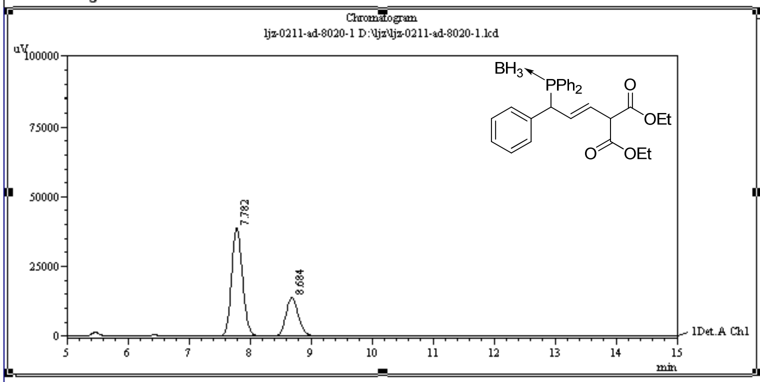
D:\ljz\ljz-0211-ad-8020-1.lcd

Sample Name : ljz-0211-ad-8020-1 Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.782	481121	38673	71.306
2	8.684	193605	13868	28.694
Total		674727	52542	100.000

==== Shimadzu LCsolution Analysis Report ====

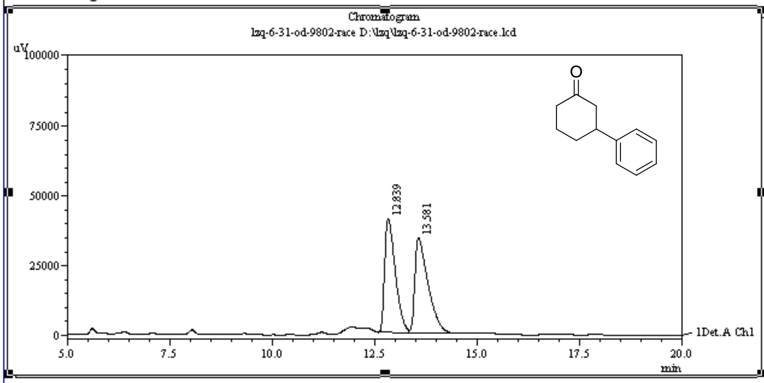
D:\lzq\lzq-6-31-od-9802-race.lcd

Sample Name : lzq-6-31-od-9802-race Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.839	736049	40835	48.989
2	13.581	766435	34146	51.011
Total		1502485	74980	100.000

==== Shimadzu LCsolution Analysis Report ====

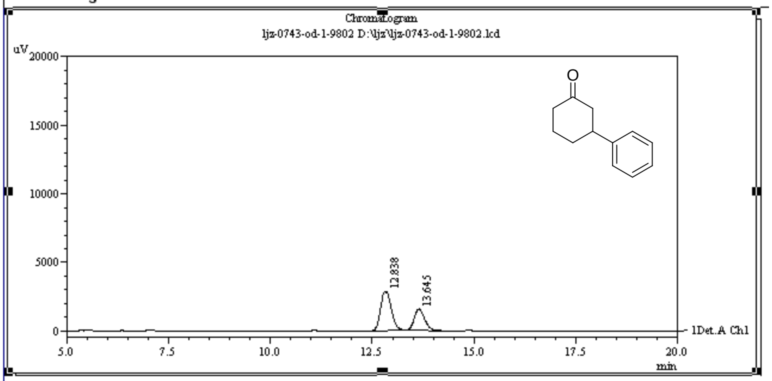
D:\ljz\ljz-0743-od-1-9802.lcd

Sample Name : ljz-0743-od-1-9802 Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>

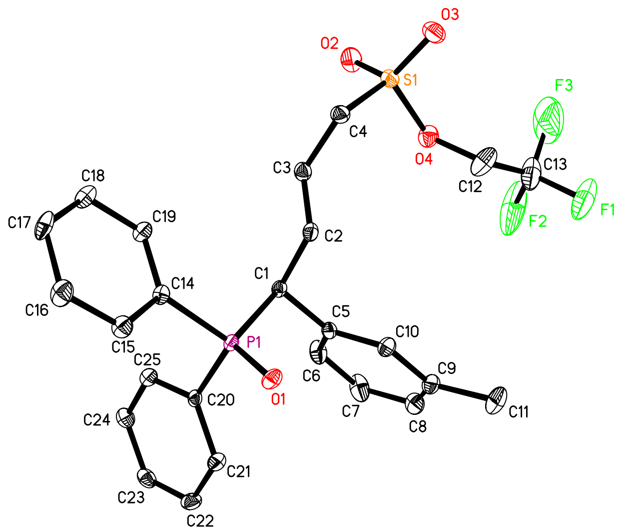


Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.838	47118	2839	63.070
2	13.645	27589	1550	36.930
Total		74708	4389	100.000

X-ray Data



1.6-adduct in Table 2, Entry 4

Table 1. Crystal data and structure refinement for mo_dm13397_0m.

Identification code	mo_dm13397_0m	
Empirical formula	C25 H24 F3 O4 P S	
Formula weight	508.47	
Temperature	140(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 5.6851(12) Å	α= 90°.
	b = 16.633(4) Å	β= 99.518(4)°.
	c = 13.304(3) Å	γ = 90°.
Volume	1240.7(4) Å^3	
Z	2	
Density (calculated)	1.361 Mg/m^3	
Absorption coefficient	0.246 mm^{-1}	
F(000)	528	
Crystal size	0.390 x 0.150 x 0.100 mm^3	
Theta range for data collection	1.552 to 30.606°.	
Index ranges	-8<=h<=8, -23<=k<=23, -19<=l<=17	
Reflections collected	12282	
Independent reflections	6964 [R(int) = 0.0457]	
Completeness to theta = 25.242°	100.0 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7461 and 0.6580
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6964 / 19 / 308
Goodness-of-fit on F^2	1.029
Final R indices [I>2sigma(I)]	R1 = 0.0513, wR2 = 0.1135
R indices (all data)	R1 = 0.0691, wR2 = 0.1236
Absolute structure parameter	-0.06(6)
Extinction coefficient	n/a
Largest diff. peak and hole	0.455 and -0.275 e.Å