Supporting Information

An intramolecular Heck reaction of enol ethers involving β-alkoxyl elimination followed by the β-hydride elimination process: access to (*Z*)-orthoformyl/keto-cinnamates†

Manman Sun,‡[a] Haibo Wu,‡[b] Haijian Wu[a] and Zhiming Wang*[a]

[a] Advanced Research Institute and Department of Chemistry, Taizhou University, 1139 Shifu Avenue, Taizhou 318000, P. R. China

[b] The Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology (Ministry of Education), Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China

‡ These authors contributed equally to this work

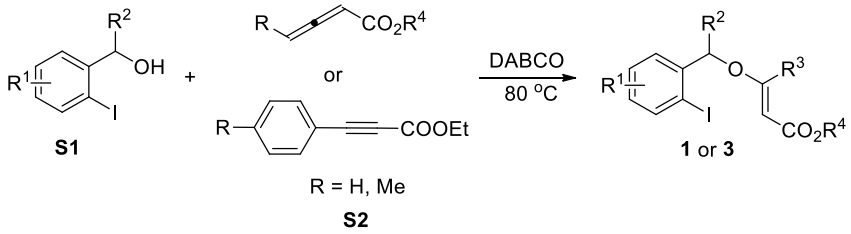
zhiming@tzc.edu.cn, wzmmol@hotmail.com

General Information

All reactions were performed under a N_2 atmosphere in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Organic solutions were concentrated under reduced pressure on a rotary evaporator or an oil pump. Reactions were monitored through thin layer chromatography (TLC) on silica gel–precoated glass plates. Chromatograms were visualized by fluorescence quenching under UV light at 254 nm. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (200–300 mesh). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a Bruker Avance 300 MHz NMR spectrometer (referenced internally to Me_4Si). Chemical shifts (δ, ppm) are reported relative to tetramethylsilane (TMS) with the resonance of the nondeuterated solvent or TMS as the internal standard. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet; d = doublet; q = quartet; m = multiplet), coupling constant (Hz), and integral. Data for ^{13}C NMR spectra are reported in terms of chemical shift. Accurate mass measurements were performed using a Varian instrument with the ESI-MS technique.

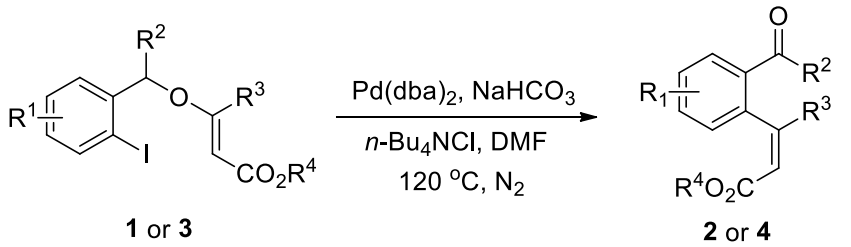
Experimental Procedure

General procedure for the synthesis of substrates 1 and 3:



To a mixture of alcohol (**S1**) (0.5 mmol) and allenoate or alkynoate (**S2**) (0.6 mmol) was added DABCO (2.8 mg). The reaction mixture was stirred at 80 ℃ until the substrate alcohol or allene was consumed (TLC monitored). The resulting mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate, 40:1) to give the desired product.[1]

General procedure for the synthesis of (*Z*)-*ortho*-formyl-cinnamates 2 and (*Z*)-*ortho*-keto-cinnamates 4:



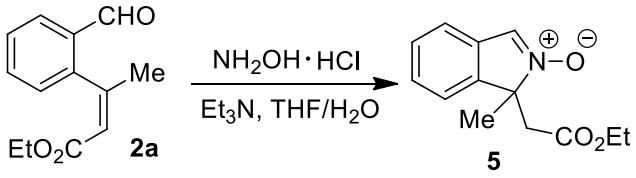
An oven-dried Schlenk tube was charged with **1** or **3** (0.5 mmol), $Pd(dba)_2$ (14.4 mg, 0.025 mmol), $NaHCO_3$ (84 mg, 1.0 mmol), *n*-Bu_4NCl (139 mg, 0.5 mmol) and dry DMF (2 mL) under N_2. The mixture was stirred at 120 ℃ for 4 h. After the reaction was cooled, H_2O (10 mL) was added. The resulting mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed sequentially with water and saturated NaCl solution, dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was loaded onto a silica gel column and separated chromatographically (petroleum ether/ethyl acetate, 20:1) to give the desired product.

Procedure for synthesis of compound 2a on 5 mmol scale:

An oven-dried Schlenk tube was charged with **1a** (1.73 g, 5 mmol), $Pd(dba)_2$ (144 mg, 0.25 mmol), $NaHCO_3$ (840 mg, 10 mmol), *n*-Bu_4NCl (1.39 g, 5 mmol) and dry DMF (20 mL) under N_2. The mixture was stirred at 120 ℃ for 4 h. After the reaction was

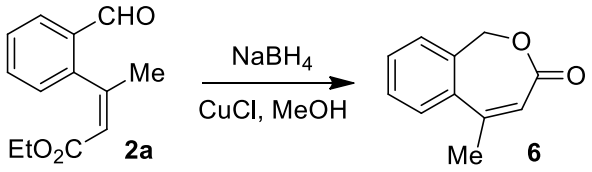
cooled, H_2O (50 mL) was added. The resulting mixture was extracted with EtOAc (3 × 100 mL). The combined organic layers were washed sequentially with water and saturated NaCl solution, dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was loaded onto a silica gel column and separated chromatographically (petroleum ether/ethyl acetate, 20:1) to give the desired product **2a** (828 mg, 76%).

Procedure for synthesis of compound 5:



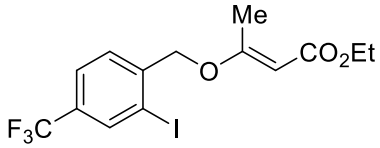
$NH_2OH·HCl$ (34.7 mg, 0.5 mmol) was added to a solution of **2a** (109 mg, 0.5 mmol), Et_3N (101 mg, 1.0 mmol) in 5:1 THF:H_2O (5 mL) at room temperature. The reaction was stirred for 3 h. The H_2O layer was extracted with two portions of DCM, the combined organic layer dried ($MgSO_4$), and the solvent was removed under reduced pressure to afford the nitrone product **5** (102.5 mg, 88%) as a yellow oil without no further purification.[2]

Procedure for synthesis of compound 6:



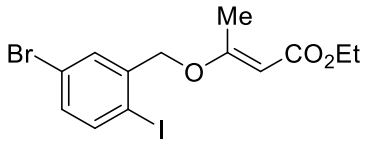
2a (109 mg, 0.5 mmol) was added to a solution of $NaBH_4$ (152 mg, 4 mmol), CuCl (74 mg, 0.75 mmol) in MeOH (10 mL) at 0 ^oC. After stirred for 30 minutes, the reaction mixture was filtered and extracted with Et_2O. The extract was washed with water, dried (Na_2SO_4), and evaporated under vacuum. Flash chromatography of the residue on silica gel (petroleum ether/ethyl acetate, 20:1) gave product **6** (66.1 mg, 76%).[3]

Characterization Data



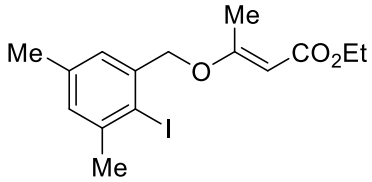
Ethyl (*E*)-3-((2-iodo-4-(trifluoromethyl)benzyl)oxy)but-2-enoate (**1d**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.64 (d, J = 8.1 Hz, 1H), 7.54 (d, J = 8.1 Hz, 1H), 5.15 (s, 1H), 4.83 (s, 2H), 4.16 (q, J = 7.2 Hz, 2H), 2.41 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.1, 167.5, 141.9, 136.1 (q, J = 2.2 Hz), 131.7 (q, J = 19.8 Hz), 128.5, 125.3 (q, J = 2.1 Hz), 122.8 (q, J = 162.6 Hz), 96.4, 92.9, 73.2, 59.6, 18.9, 14.4.



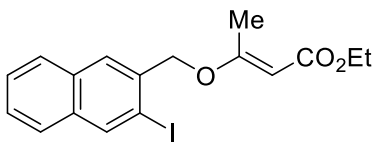
Ethyl (*E*)-3-((5-bromo-2-iodobenzyl)oxy)but-2-enoate (**1f**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 (d, J = 8.4 Hz, 1H), 7.54 (s, 1H), 7.17 (d, J = 8.4 Hz, 1H), 5.14 (s, 1H), 4.75 (s, 2H), 4.23-4.12 (m, 2H), 2.40 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.2, 166.6, 139.5, 138.8, 131.8, 130.5, 121.8, 93.9, 91.7, 72.0, 58.6, 17.9, 13.4.



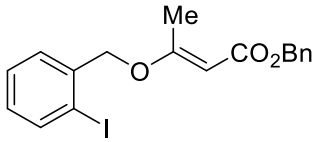
Ethyl (*E*)-3-((2-iodo-3,5-dimethylbenzyl)oxy)but-2-enoate (**1i**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.05 (s, 1H), 7.03 (s, 1H), 5.17 (s, 1H), 4.82 (s, 2H), 4.16 (q, J = 7.2 Hz, 2H), 2.45 (s, 3H), 2.40 (s, 3H), 2.30 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.8, 166.9, 141.2, 137.0, 136.9, 129.5, 126.1, 99.9, 91.2, 73.8, 58.4, 28.0, 19.8, 18.0, 13.4.



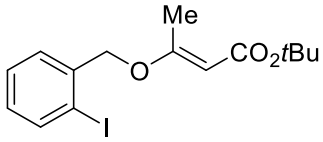
Ethyl (*E*)-3-((3-iodonaphthalen-2-yl)methoxy)but-2-enoate (**1j**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.41 (s, 1H), 7.86-7.81 (m, 2H), 7.76-7.71 (m, 1H), 7.53-7.50 (m, 2H), 5.23 (s, 1H), 4.95 (s, 2H), 4.18 (q, J = 7.2 Hz, 2H), 2.49 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.7, 166.8, 137.9, 133.4, 132.8, 131.5, 127.0, 126.9, 126.1, 125.9, 125.5, 93.3, 91.4, 72.8, 58.5, 18.0, 13.4.



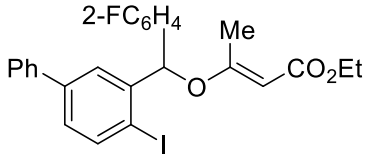
Benzyl (*E*)-3-((2-iodobenzyl)oxy)but-2-enoate (**1k**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86 (d, J = 7.8 Hz, 1H), 7.44-7.33 (m, 7H), 7.07-7.02 (m, 1H), 5.25 (s, 1H), 5.17 (s, 2H), 4.81 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.3, 167.6, 139.5, 137.7, 136.6, 129.9, 128.9, 128.6, 128.5, 128.3, 128.1, 97.8, 92.1, 73.9, 65.6, 19.1.



tert-Butyl (*E*)-3-((2-iodobenzyl)oxy)but-2-enoate (**1l**)

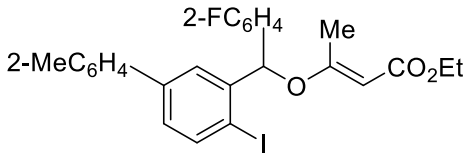
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86 (d, J = 7.8 Hz, 1H), 7.43-7.34 (m, 2H), 7.07-7.01 (m, 1H), 5.10 (s, 1H), 4.78 (s, 2H), 2.36 (s, 3H), 1.50 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.6, 166.3, 138.4, 137.0, 128.8, 128.0, 127.4, 96.8, 93.1, 78.4, 72.6, 27.4, 17.8.



Ethyl (*E*)-3-((2-fluorophenyl)(4-iodo-[1,1'-biphenyl]-3-yl)methoxy)but-2-enoate (**3d**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96 (d, J = 8.4 Hz, 1H), 7.56-7.53 (m, 3H), 7.48-7.37 (m, 4H), 7.30 (dd, J = 8.4, 2.4 Hz, 1H), 7.22-7.12 (m, 3H), 6.65 (s, 1H), 5.12 (s, 1H), 4.17-4.09 (m, 2H), 2.48 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.3, 167.7, 160.7 (d, J = 247.8 Hz), 141.7, 140.5, 140.4, 139.6, 130.6 (d, J = 8.2 Hz), 129.1 (d, J = 4.4 Hz), 129.0, 128.9, 128.0, 127.0, 126.9, 125.2 (d, J = 13.4 Hz), 124.4 (d, J = 3.5 Hz), 115.8 (d, J = 21.2 Hz), 97.4, 94.5, 78.7 (d, J = 2.8 Hz), 59.6,

19.1, 14.4.

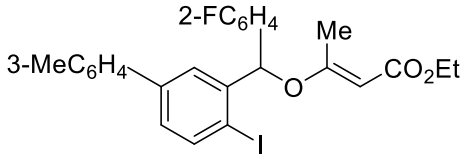


Ethyl

(*E*)-3-((2-fluorophenyl)(4-iodo-2'-methyl-[1,1'-biphenyl]-3-yl)methoxy)but-2-enoate

(**3e**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (d, J = 8.1 Hz, 1H), 7.36-7.30 (m, 1H), 7.25-7.22 (m, 3H), 7.20-7.08 (m, 5H), 7.03 (dd, J = 8.1, 2.1 Hz, 1H), 6.54 (s, 1H), 5.02 (s, 1H), 4.09 (q, J = 7.2 Hz, 2H), 2.38 (s, 3H), 2.18 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4, 167.9, 160.7 (d, J = 247.6 Hz), 142.3, 140.4, 140.0, 139.9, 135.3, 131.1, 130.7, 130.6 (d, J = 8.2 Hz), 129.7, 129.6, 129.1 (d, J = 3.2 Hz), 127.9, 126.2, 125.3 (d, J = 13.4 Hz), 124.5 (d, J = 3.6 Hz), 115.9 (d, J = 21.2 Hz), 97.1, 94.6, 78.7 (d, J = 2.8 Hz), 59.7, 20.4, 19.1, 14.5.

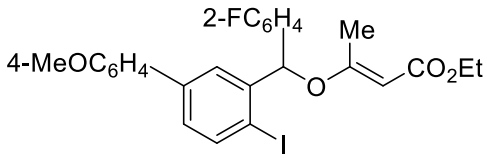


Ethyl

(*E*)-3-((2-fluorophenyl)(4-iodo-3'-methyl-[1,1'-biphenyl]-3-yl)methoxy)but-2-enoate

(**3f**)

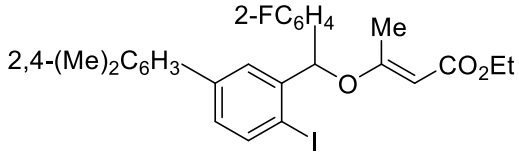
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81 (d, J = 8.4 Hz, 1H), 7.38 (d, J = 2.1 Hz, 1H), 7.22-7.14 (m, 5H), 7.08-7.01 (m, 4H), 6.48 (s, 1H), 4.95 (s, 1H), 4.02-3.95 (m, 2H), 2.32 (s, 3H), 2.30 (s, 3H), 1.12 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4, 167.8, 160.8 (d, J = 247.9 Hz), 141.9, 140.5, 140.4, 139.7, 138.7, 130.6 (d, J = 8.2 Hz), 129.1 (d, J = 3.2 Hz), 129.0, 128.9, 128.8, 127.8, 127.1, 125.2 (d, J = 13.5 Hz), 124.4 (d, J = 3.5 Hz), 124.2, 115.9 (d, J = 21.2 Hz), 97.3, 94.6, 78.8 (d, J = 2.8 Hz), 59.6, 21.6, 19.1, 14.4.



Ethyl

(*E*)-3-((2-fluorophenyl)(4-iodo-4'-methoxy-[1,1'-biphenyl]-3-yl)methoxy)but-2-enoat e (**3g**)

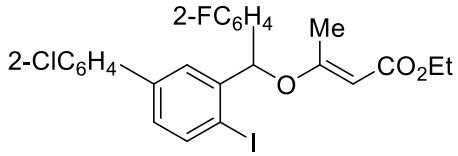
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.4 Hz, 1H), 7.47-7.43 (m, 3H), 7.39-7.32 (m, 1H), 7.24 (dd, *J* = 8.1, 2.4 Hz, 1H), 7.19-7.09 (m, 3H), 6.99-6.94 (m, 2H), 6.56 (s, 1H), 5.04 (s, 1H), 4.09 (q, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 2.42 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4, 167.9, 160.8 (d, *J* = 247.8 Hz), 159.7, 141.4, 140.5, 140.4, 132.2, 130.6 (d, *J* = 8.2 Hz), 129.2 (d, *J* = 3.2 Hz), 128.5, 128.1, 126.7, 125.3 (d, *J* = 13.4 Hz), 124.5 (d, *J* = 3.4 Hz), 115.9 (d, *J* = 21.2 Hz), 114.5, 96.6, 94.6, 78.8 (d, *J* = 2.9 Hz), 59.6, 55.5, 19.1, 14.5.



Ethyl

(*E*)-3-((2-fluorophenyl)(4-iodo-2',4'-dimethyl-[1,1'-biphenyl]-3-yl)methoxy)but-2-eno ate (**3h**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.1 Hz, 1H), 7.37-7.31 (m, 1H), 7.18-7.00 (m, 8H), 6.53 (s, 1H), 5.01 (s, 1H), 4.09 (q, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 2.35 (s, 3H), 2.14 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.3, 167.8, 160.6 (d, *J* = 247.6 Hz), 142.2, 139.8, 139.7, 137.6, 137.4, 135.0, 131.4, 131.0, 130.4 (d, *J* = 8.2 Hz), 129.6, 129.5, 128.9 (d, *J* = 3.2 Hz), 126.7, 125.2 (d, *J* = 13.3 Hz), 124.4 (d, *J* = 3.4 Hz), 115.8 (d, *J* = 21.2 Hz), 96.7, 94.4, 78.6 (d, *J* = 2.8 Hz), 59.5, 21.1, 20.2, 19.0, 14.4.

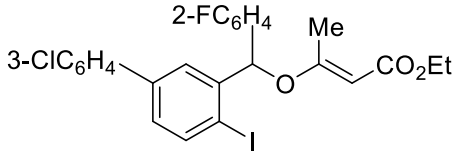


Ethyl

(*E*)-3-((2'-chloro-4-iodo-[1,1'-biphenyl]-3-yl)(2-fluorophenyl)methoxy)but-2-enoate (**3i**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.1 Hz, 1H), 7.47-7.44 (m, 1H), 7.37-7.30

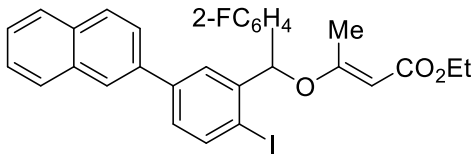
(m, 5H), 7.16-7.09 (m, 4H), 6.56 (s, 1H), 5.02 (s, 1H), 4.09 (q, *J* = 7.2 Hz, 2H), 2.38 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4, 167.9, 160.8 (d, *J* = 247.6 Hz), 140.0, 139.9, 139.7, 139.0, 132.4, 131.2, 130.6 (d, *J* = 8.2 Hz), 130.3, 129.8, 129.3, 129.2, 127.2, 125.2 (d, *J* = 13.6 Hz), 124.5 (d, *J* = 3.4 Hz), 115.9 (d, *J* = 21.2 Hz), 98.0, 94.6, 78.5 (d, *J* = 2.9 Hz), 59.7, 19.2, 14.5.



Ethyl

(*E*)-3-((3'-chloro-4-iodo-[1,1'-biphenyl]-3-yl)(2-fluorophenyl)methoxy)but-2-enoate (**3j**)

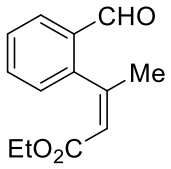
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.4 Hz, 1H), 7.47-7.44 (m, 2H), 7.36-7.31 (m, 4H), 7.22 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.16-7.08 (m, 3H), 6.57 (s, 1H), 5.04 (s, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.3, 167.8, 160.8 (d, *J* = 247.9 Hz), 141.6, 140.9, 140.6, 140.3, 135.0, 130.7 (d, *J* = 8.2 Hz), 130.3, 129.1 (d, *J* = 3.0 Hz), 128.8, 128.0, 127.1, 127.0, 125.2, 125.1 (d, *J* = 13.6 Hz), 124.5 (d, *J* = 3.6 Hz), 115.9 (d, *J* = 21.1 Hz), 98.2, 94.6, 78.8 (d, *J* = 2.7 Hz), 59.6, 19.1, 14.4.



Ethyl

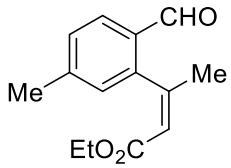
(*E*)-3-((2-fluorophenyl)(2-iodo-5-(naphthalen-2-yl)phenyl)methoxy)but-2-enoate (**3l**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00-7.97 (m, 2H), 7.91-7.85 (m, 3H), 7.66-7.62 (m, 2H), 7.53-7.50 (m, 2H), 7.43-7.36 (m, 2H), 7.22-7.12 (m, 3H), 6.63 (s, 1H), 5.09 (s, 1H), 4.15-4.08 (m, 2H), 2.46 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.3, 167.8, 160.8 (d, *J* = 247.9 Hz), 141.6, 140.9, 140.6, 140.3, 135.0, 130.7 (d, *J* = 8.2 Hz), 130.0, 129.1 (d, *J* = 3.0 Hz), 128.8, 128.1, 127.1, 127.0, 125.2, 125.1 (d, *J* = 13.6 Hz), 124.5 (d, *J* = 3.6 Hz), 115.9 (d, *J* = 21.1 Hz), 98.2, 94.6, 78.7 (d, *J* = 2.7 Hz), 59.6, 19.1, 14.5.



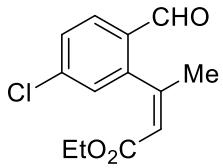
Ethyl (*Z*)-3-(2-formylphenyl)but-2-enoate (**2a**)

88.3 mg, 81% yield; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.05 (s, 1H), 7.93 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.59 (td, *J* = 7.5, 1.2 Hz, 1H), 7.49-7.44 (m, 1H), 7.14 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.10 (s, 1H), 3.92 (q, *J* = 7.2 Hz, 2H), 2.22 (s, 3H), 1.02 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.4, 165.2, 153.5, 144.7, 133.9, 132.4, 129.3, 127.9, 127.7, 120.2, 60.1, 28.1, 14.0; HRMS (ESI): $[M + H]^+$ calcd for $C_{13}H_{15}O_3^+$: *m*/*z* 219.1016, found: 219.1014. The *Z* stereochemistry was confirmed by NOESY (δ 6.10 and 2.22).



Ethyl (*Z*)-3-(2-formyl-5-methylphenyl)but-2-enoate (**2b**)

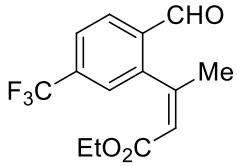
91.6 mg, 79% yield; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.99 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 6.94 (s, 1H), 6.08 (s, 1H), 3.93 (q, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 2.21 (s, 3H), 1.03 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.1, 165.3, 153.8, 144.9, 144.8, 130.2, 129.5, 128.8, 128.2, 119.9, 60.0, 28.1, 22.0, 14.0; HRMS (ESI): $[M + H]^+$ calcd for $C_{14}H_{17}O_3^+$: *m*/*z* 233.1172, found: 233.1172. Spectral data were consistent with data reported in the literature.[4]



Ethyl (*Z*)-3-(5-chloro-2-formylphenyl)but-2-enoate (**2c**)

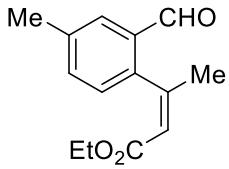
94.5 mg, 75% yield; colorless oil; ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.91 (s, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.38 (s, 1H), 6.16 (s, 1H), 3.86 (q, *J* = 7.2 Hz, 2H), 2.20 (s, 3H), 0.97 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6):

δ 190.6, 164.3, 152.2, 145.8, 138.6, 131.0, 130.5, 127.9, 127.6, 119.9, 59.5, 27.0, 13.8; HRMS (ESI): $[M + H]^+$ calcd for $C_{13}H_{14}ClO_3^+$: *m*/*z* 253.0626, found: 253.0621.



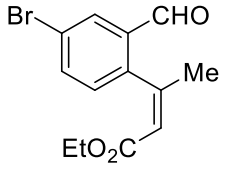
Ethyl (*Z*)-3-(2-formyl-5-(trifluoromethyl)phenyl)but-2-enoate (**2d**)

93.0 mg, 65% yield; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.09 (s, 1H), 8.04 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.42 (s, 1H), 6.16 (q, *J* = 1.5 Hz, 1H), 3.97-3.89 (m, 2H), 2.25 (d, *J* = 1.5 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.1, 164.8, 151.2, 145.0, 135.0 (q, *J* = 31.6 Hz), 129.9 (q, *J* = 207.0 Hz), 129.2, 124.8 (q, *J* = 2.9 Hz), 124.7, (q, *J* = 2.9 Hz), 122.3, 121.2, 60.2, 27.8, 13.7; HRMS (ESI): $[M + H]^+$ calcd for $C_{14}H_{14}F_3O_3^+$: *m*/*z* 287.0890, found: 287.0886.



Ethyl (*Z*)-3-(2-formyl-4-methylphenyl)but-2-enoate (**2e**)

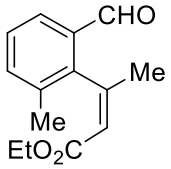
96.3 mg, 83% yield; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.01 (s, 1H), 7.74 (s, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 6.09 (s, 1H), 3.94 (q, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 2.07 (s, 3H), 1.06 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.6, 165.3, 153.8, 141.9, 137.8, 134.8, 132.3, 129.6, 127.6, 120.1, 60.0, 28.3, 21.2, 14.1; HRMS (ESI): $[M + H]^+$ calcd for $C_{14}H_{17}O_3^+$: *m*/*z* 233.1172, found: 233.1170.



Ethyl (*Z*)-3-(4-bromo-2-formylphenyl)but-2-enoate (**2f**)

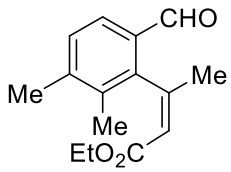
102.1 mg, 69% yield; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.96 (s, 1H), 8.05

(d, J = 2.1 Hz, 1H), 7.70 (dd, J = 8.1, 2.1 Hz, 1H), 7.04 (d, J = 8.1 Hz, 1H), 6.12 (q, J = 1.5 Hz, 1H), 3.95 (q, J = 7.1 Hz, 2H), 2.20 (d, J = 1.5 Hz, 3H), 1.07 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.8, 165.0, 152.0, 143.4, 136.7, 133.8, 131.7, 129.4, 122.1, 120.8, 60.3, 28.0, 14.0; HRMS (ESI): $[M + Na]^+$ calcd for $C_{13}H_{13}BrNaO_3^+$: m/z 318.9940, found: 318.9939.



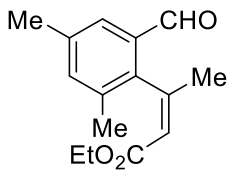
Ethyl (*Z*)-3-(2-formyl-6-methylphenyl)but-2-enoate (**2g**)

84.7 mg, 73% yield; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.02 (s, 1H), 7.76 (d, J = 7.6 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 6.17 (s, 1H), 3.92 (q, J = 7.2 Hz, 2H), 2.23 (s, 3H), 2.17 (s, 3H), 1.01 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.9, 165.1, 153.0, 144.2, 135.8, 134.5, 131.9, 127.5, 127.2, 120.8, 60.0, 26.9, 18.7, 14.0; HRMS (ESI): $[M + H]^+$ calcd for $C_{14}H_{17}O_3^+$: m/z 233.1172, found: 233.1172.



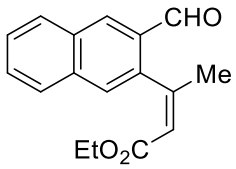
Ethyl (*Z*)-3-(6-formyl-2,3-dimethylphenyl)but-2-enoate (**2h**)

92.3 mg, 75% yield; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.95 (s, 1H), 7.68 (d, J = 7.8 Hz, 1H), 7.24 (d, J = 7.8 Hz, 1H), 6.18 (q, J = 1.2 Hz, 1H), 3.97-3.86 (m, 2H), 2.35 (s, 3H), 2.16 (s, 3H), 2.12 (s, 3H), 1.01 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.6, 164.0, 152.5, 143.0, 131.7, 128.9, 128.1, 125.9, 120.0, 58.8, 26.2, 20.1, 14.2, 12.8; HRMS (ESI): $[M + H]^+$ calcd for $C_{15}H_{19}O_3^+$: m/z 247.1329, found: 247.1330.



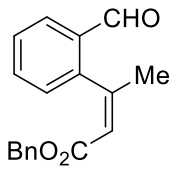
Ethyl (*Z*)-3-(2-formyl-4,6-dimethylphenyl)but-2-enoate (**2i**)

83.6 mg, 68% yield; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.98 (s, 1H), 7.57 (s, 1H), 7.28 (s, 1H), 6.16 (q, *J* = 1.5 Hz, 1H), 3.94 (q, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 2.19 (s, 3H), 2.15 (d, *J* = 1.5 Hz, 3H), 1.04 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.0, 165.2, 153.4, 141.5, 137.2, 136.8, 134.4, 131.9, 127.6, 120.7, 60.0, 27.1, 21.0, 18.6, 14.1; HRMS (ESI): $[M + H]^+$ calcd for $C_{15}H_{19}O_3^+$: *m*/*z* 247.1329, found: 247.1330.



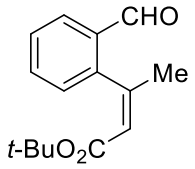
Ethyl (*Z*)-3-(3-formylnaphthalen-2-yl)but-2-enoate (**2j**)

91.2 mg, 68% yield; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.16 (s, 1H), 8.43 (s, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.64-7.55 (m, 3H), 6.13 (q, *J* = 1.5 Hz, 1H), 3.89 (q, *J* = 7.2 Hz, 2H), 2.29 (d, *J* = 1.5 Hz, 3H), 0.98 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.5, 164.4, 153.5, 137.8, 134.6, 132.5, 130.7, 130.2, 128.5, 128.2, 126.8, 125.9, 125.4, 118.4, 58.8, 26.9, 12.9; HRMS (ESI): $[M + H]^+$ calcd for $C_{17}H_{17}O_3^+$: *m*/*z* 269.1172, found: 269.1171.



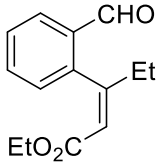
Benzyl (*Z*)-3-(2-formylphenyl)but-2-enoate (**2k**)

107.8 mg, 77% yield; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.96 (s, 1H), 7.81 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.50 (td, *J* = 7.5, 1.2 Hz, 1H), 7.36 (td, *J* = 7.5, 0.9 Hz, 1H), 7.22-7.19 (m, 3H), 7.08-7.04 (m, 3H), 6.08 (q, *J* = 1.2 Hz, 1H), 4.85 (s, 2H), 2.15 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.2, 163.8, 153.3, 143.2, 134.6, 132.8, 131.2, 128.5, 127.4, 127.2, 127.1, 126.8, 126.5, 118.5, 64.9, 27.0; HRMS (ESI): $[M + H]^+$ calcd for $C_{18}H_{17}O_3^+$: *m*/*z* 281.1172, found: 281.1174.



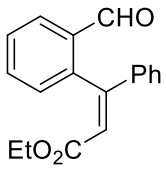
tert-Butyl (*Z*)-3-(2-formylphenyl)but-2-enoate (**2l**)

87.3 mg, 71% yield; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.06 (s, 1H), 7.92 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.58 (td, *J* = 7.5, 1.2 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.14 (dd, *J* = 7.8, 0.9 Hz, 1H), 6.02 (q, *J* = 1.5 Hz, 1H), 2.18 (d, *J* = 1.5 Hz, 3H), 1.13 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.3, 163.6, 149.3, 144.3, 132.8, 131.2, 127.4, 126.7, 126.6, 121.6, 79.3, 27.0, 26.7; HRMS (ESI): $[M + Na]^+$ calcd for $C_{15}H_{18}NaO_3^+$: *m*/*z* 269.1148, found: 269.1148.



Ethyl (Z)-3-(2-formylphenyl)pent-2-enoate (**2m**)

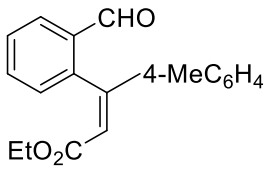
77.7 mg, 67% yield; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.02 (s, 1H), 7.93 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.58 (td, *J* = 7.5, 1.5 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.12 (dd, *J* = 7.5, 0.9 Hz, 1H), 6.07 (q, *J* = 1.5 Hz, 1H), 3.91 (q, *J* = 7.2 Hz, 2H), 2.52-2.43 (m, 2H), 1.11 (t, *J* = 7.2 Hz, 3H), 1.01 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.3, 165.4, 158.3, 144.2, 133.6, 132.7, 128.7, 127.9, 127.7, 118.5, 60.0, 34.1, 13.9, 11.7; HRMS (ESI): $[M + H]^+$ calcd for $C_{14}H_{17}O_3^+$: *m*/*z* 233.1172, found: 233.1177.



Ethyl (*Z*)-3-(2-formylphenyl)-3-phenylacrylate (**2n**)

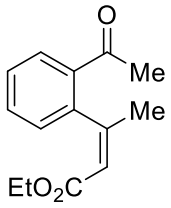
100.8 mg, 72% yield; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.15 (s, 1H), 7.96 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.61-7.47 (m, 2H), 7.34-7.23 (m, 6H), 6.03 (s, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 1.18 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.2, 165.5, 152.7, 145.4, 138.8, 134.5, 133.7, 130.8, 129.4, 129.2, 129.1, 128.5, 128.2, 123.0,

60.7, 14.1; HRMS (ESI): $[M + H]^+$ calcd for $C_{18}H_{17}O_3^+$: *m*/*z* 281.1172, found: 281.1170.



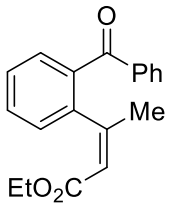
Ethyl (Z)-3-(2-formylphenyl)-3-(*p*-tolyl)acrylate (**2o**)

100.0 mg, 68% yield; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.12 (s, 1H), 7.95 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.57 (td, *J* = 7.5, 1.5 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.31 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.14 (s, 4H), 5.99 (s, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 2.35 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.2, 164.5, 151.8, 144.5, 138.2, 134.8, 133.4, 132.5, 129.6, 128.3, 127.9, 127.8, 127.2, 121.1, 59.5, 20.3, 13.0; HRMS (ESI): $[M + H]^+$ calcd for $C_{19}H_{19}O_3^+$: *m*/*z* 295.1329, found: 295.1327.



Ethyl (*Z*)-3-(2-acetylphenyl)but-2-enoate (**4a**)

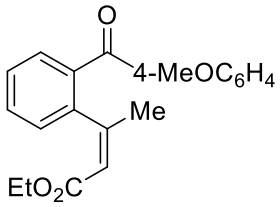
88.2 mg, 76% yield; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.49 (td, *J* = 7.5, 1.5 Hz, 1H), 7.39 (td, *J* = 7.5, 1.5 Hz, 1H), 7.06 (dd, *J* = 7.5, 0.9 Hz, 1H), 5.85 (s, 1H), 3.91 (q, *J* = 7.2 Hz, 2H), 2.56 (s, 3H), 2.20 (s, 3H), 1.05 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.7, 165.8, 158.5, 142.1, 136.1, 131.9, 129.1, 127.8, 127.3, 116.4, 59.6, 28.4, 27.5, 14.1; HRMS (ESI): $[M + H]^+$ calcd for $C_{14}H_{17}O_3^+$: *m*/*z* 233.1172, found: 233.1173.



Ethyl (*Z*)-3-(2-benzoylphenyl)but-2-enoate (**4b**)

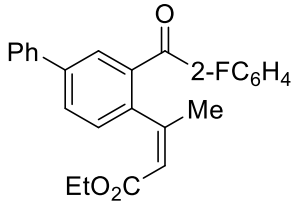
105.8 mg, 72% yield; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84-7.81 (m, 2H),

7.56-7.50 (m, 2H), 7.45-7.33 (m, 4H), 7.20 (d, J = 7.6 Hz, 1H), 5.79 (s, 1H), 3.87 (q, J = 7.2 Hz, 2H), 2.24 (s, 3H), 1.01 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.5, 165.4, 156.6, 142.1, 137.7, 137.0, 132.9, 130.9, 130.7, 129.6, 128.2, 127.6, 126.5, 118.1, 59.7, 28.1, 14.1; HRMS (ESI): $[M + H]^+$ calcd for $C_{19}H_{19}O_3^+$: m/z 295.1329, found: 295.1329.



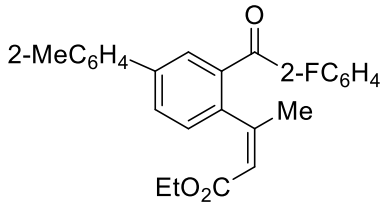
Ethyl (*Z*)-3-(2-(4-methoxybenzoyl)phenyl)but-2-enoate (**4c**)

113.4 mg, 70% yield; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82 (d, J = 7.8 Hz, 1H), 7.52-7.47 (m, 1H), 7.42-7.32 (m, 2H), 7.20-7.17 (m, 1H), 6.90 (d, J = 7.8 Hz, 1H), 5.78 (s, 1H), 3.90-3.83 (m, 5H), 2.22 (s, 2H), 1.01 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.3, 165.4, 163.6, 156.6, 141.6, 137.5, 133.1, 130.5, 130.4, 129.1, 127.6, 126.5, 118.2, 113.4, 59.7, 55.6, 28.2, 14.1; HRMS (ESI): $[M + H]^+$ calcd for $C_{20}H_{21}O_4^+$: m/z 325.1434, found: 325.1435.

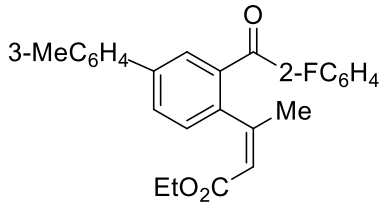


Ethyl (*Z*)-3-(3-(2-fluorobenzoyl)-[1,1'-biphenyl]-4-yl)but-2-enoate (**4d**)

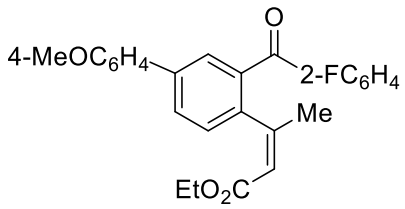
133.9 mg, 69% yield; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (dd, J = 8.1, 1.8 Hz, 1H), 7.71 (s, 1H), 7.65 (td, J = 7.5, 1.8 Hz, 1H), 7.58-7.51 (m, 3H), 7.47-7.36 (m, 3H), 7.28 (d, J = 7.8 Hz, 1H), 7.24-7.13 (m, 2H), 5.89 (q, J = 1.5 Hz, 1H), 3.98 (q, J = 7.2 Hz, 2H), 2.26 (d, J = 1.5 Hz, 3H), 1.10 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.8, 165.5, 161.0 (d, J = 203.5 Hz), 156.3, 141.3, 140.0, 139.9, 137.2, 133.8 (d, J = 6.7 Hz), 132.2, 130.3, 129.0, 128.9, 128.4, 127.8, 127.3 (d, J = 7.4 Hz), 127.2, 124.0 (d, J = 2.9 Hz), 118.1, 116.5 (d, J = 17.0 Hz), 59.8, 27.7, 14.1; HRMS (ESI): $[M + H]^+$ calcd for $C_{25}H_{22}FO_3^+$: m/z 389.1547, found: 389.1545.



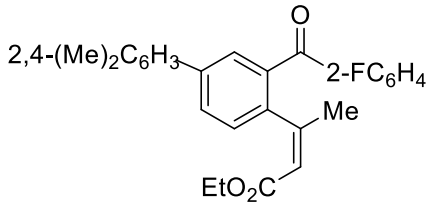
Ethyl (*Z*)-3-(3-(2-fluorobenzoyl)-2'-methyl-[1,1'-biphenyl]-4-yl)but-2-enoate (**4e**) 132.7 mg, 66% yield; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61 (td, J = 7.5, 1.8 Hz, 1H), 7.52-7.43 (m, 3H), 7.25-7.08 (m, 7H), 5.89 (q, J = 1.5 Hz, 1H), 3.97 (q, J = 7.2 Hz, 2H), 2.27 (s, 3H), 2.27 (d, J = 1.5 Hz, 3H), 1.08 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.8, 165.7, 160.9 (d, J = 253.8 Hz), 156.5, 141.1, 140.6, 136.3, 135.5, 133.7 (d, J = 8.5 Hz), 132.5, 132.1 (d, J = 2.1 Hz), 131.3, 131.2, 130.6, 129.9, 127.9, 127.8, 127.3 (d, J = 12.2 Hz), 126.0, 124.0 (d, J = 3.7 Hz), 118.1, 116.5 (d, J = 21.5 Hz), 59.8, 27.8, 20.6, 14.1; HRMS (ESI): $[M + H]^+$ calcd for $C_{26}H_{24}FO_3^+$: m/z 403.1704, found: 403.1706. The *Z* stereochemistry was confirmed by NOESY (δ 5.89 and 2.27).



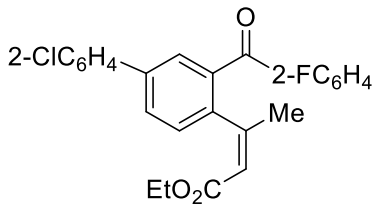
Ethyl (*Z*)-3-(3-(2-fluorobenzoyl)-3'-methyl-[1,1'-biphenyl]-4-yl)but-2-enoate (**4f**) 134.7 mg, 67% yield; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73 (dd, J = 7.8, 1.8 Hz, 1H), 7.67 (s, 1H), 7.62 (td, J = 7.5, 1.8 Hz, 1H), 7.54-7.46 (m, 1H), 7.35-7.30 (m, 3H), 7.25-7.11 (m, 4H), 5.85 (q, J = 1.2 Hz, 1H), 3.96 (q, J = 7.2 Hz, 2H), 2.39 (s, 3H), 2.23 (d, J = 1.2 Hz, 3H), 1.07 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.9, 165.6, 161.1 (d, J = 254.5 Hz), 156.4, 141.2, 140.2, 140.0, 138.6, 137.2, 133.8 (d, J = 8.6 Hz), 132.3 (d, J = 2.0 Hz), 130.4, 129.0, 128.9, 128.6, 128.3, 128.1, 127.2 (d, J = 11.8 Hz), 124.4, 124.0 (d, J = 3.8 Hz), 118.1, 116.6 (d, J = 21.5 Hz), 59.8, 27.7, 21.6, 14.1; HRMS (ESI): $[M + H]^+$ calcd for $C_{26}H_{24}FO_3^+$: m/z 403.1704, found: 403.1703.



Ethyl (*Z*)-3-(3-(2-fluorobenzoyl)-4'-methoxy-[1,1'-biphenyl]-4-yl)but-2-enoate (**4g**) 131.7 mg, 63% yield; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71 (dd, J = 7.8, 1.8 Hz, 1H), 7.65-7.59 (m, 2H), 7.52-7.46 (m, 3H), 7.24-7.11 (m, 3H), 6.97-6.94 (m, 2H), 5.86 (q, J = 1.5 Hz, 1H), 3.96 (q, J = 7.2 Hz, 2H), 3.83 (s, 3H), 2.23 (d, J = 1.5 Hz, 3H), 1.08 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.9, 165.6, 161.0 (d, J = 254.5 Hz), 159.5, 156.5, 140.7, 139.7, 137.2, 133.7 (d, J = 8.6 Hz), 132.4, 132.2 (d, J = 2.0 Hz), 129.9, 128.6, 128.3, 128.2, 127.3 (d, J = 11.9 Hz), 124.0 (d, J = 3.7 Hz), 118.0, 116.6 (d, J = 21.5 Hz), 114.4, 59.8, 55.4, 27.7, 14.1; HRMS (ESI): $[M + H]^+$ calcd for $C_{26}H_{24}FO_4^+$: m/z 419.1653, found: 419.1654. The *Z* stereochemistry was confirmed by NOESY (δ 5.86 and 2.23).

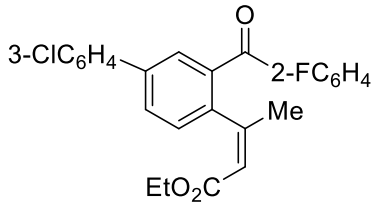


Ethyl (*Z*)-3-(3-(2-fluorobenzoyl)-2',4'-dimethyl-[1,1'-biphenyl]-4-yl)but-2-enoate (**4h**) 131.0 mg, 63% yield; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62 (td, J = 7.5, 1.8 Hz, 1H), 7.51-7.43 (m, 3H), 7.24-7.04 (m, 6H), 5.90 (q, J = 1.2 Hz, 1H), 3.98 (q, J = 7.2 Hz, 2H), 2.35 (s, 3H), 2.28 (d, J = 1.2 Hz, 3H), 2.25 (s, 3H), 1.08 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.8, 165.6, 160.9 (d, J = 253.7 Hz), 159.5, 140.9, 140.5, 137.7, 137.5, 136.2, 135.3, 133.6 (d, J = 8.6 Hz), 132.6, 132.0 (d, J = 2.0 Hz), 131.4, 131.3, 129.8, 127.8, 127.3 (d, J = 12.2 Hz), 126.7, 124.0 (d, J = 3.7 Hz), 118.0, 116.4 (d, J = 21.4 Hz), 59.7, 27.8, 21.1, 20.5, 14.1; HRMS (ESI): $[M + H]^+$ calcd for $C_{27}H_{26}FO_3^+$: m/z 417.1860, found: 417.1861. The *Z* stereochemistry was confirmed by NOESY (δ 5.90 and 2.28).



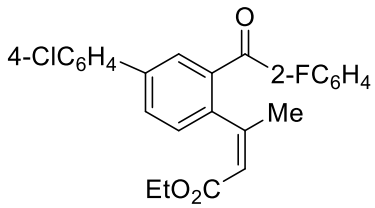
Ethyl (*Z*)-3-(2'-chloro-3-(2-fluorobenzoyl)-[1,1'-biphenyl]-4-yl)but-2-enoate (**4i**)

132.9 mg, 63% yield; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65-7.57 (m, 3H), 7.51-7.43 (m, 2H), 7.36-7.28 (m, 3H), 7.26-7.09 (m, 3H), 5.88 (q, *J* = 1.5 Hz, 1H), 3.96 (q, *J* = 7.2 Hz, 2H), 2.26 (d, *J* = 1.5 Hz, 3H), 1.06 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.6, 165.6, 161.0 (d, *J* = 254.6 Hz), 156.3, 141.9, 139.2, 138.0, 136.3, 133.8 (d, *J* = 8.6 Hz), 132.7, 132.6, 132.2 (d, *J* = 2.0 Hz), 131.6, 131.4, 130.2, 129.1, 127.8, 127.2 (d, *J* = 12.0 Hz), 127.1, 124.0 (d, *J* = 3.7 Hz), 118.2, 116.6 (d, *J* = 21.4 Hz), 59.8, 27.8, 14.1; HRMS (ESI): $[M + H]^+$ calcd for $C_{25}H_{21}ClFO_3^+$: *m*/*z* 423.1158, found: 423.1161. The *Z* stereochemistry was confirmed by NOESY (δ 5.88 and 2.26).



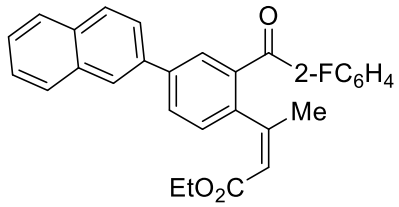
Ethyl (*Z*)-3-(3'-chloro-3-(2-fluorobenzoyl)-[1,1'-biphenyl]-4-yl)but-2-enoate (**4j**)

141.4 mg, 67% yield; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.65-7.59 (m, 2H), 7.54-7.50 (m, 2H), 7.43-7.33 (m, 3H), 7.26-7.12 (m, 3H), 5.86 (q, *J* = 1.5 Hz, 1H), 3.96 (q, *J* = 7.2 Hz, 2H), 2.23 (d, *J* = 1.5 Hz, 3H), 1.08 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.7, 165.5, 161.1 (d, *J* = 254.6 Hz), 156.1, 142.0, 141.8, 138.7, 137.5, 134.9, 134.0 (d, *J* = 8.7 Hz), 132.3 (d, *J* = 1.8 Hz), 130.3, 130.2, 128.8, 128.6, 127.9, 127.4, 127.0 (d, *J* = 11.6 Hz), 125.4, 124.1 (d, *J* = 3.7 Hz), 118.3, 116.7 (d, *J* = 21.4 Hz), 59.9, 27.7, 14.2; HRMS (ESI): $[M + H]^+$ calcd for $C_{25}H_{21}ClFO_3^+$: *m*/*z* 423.1158, found: 423.1160. The *Z* stereochemistry was confirmed by NOESY (δ 5.86 and 2.23).



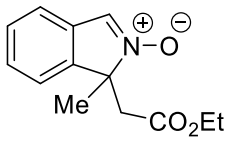
Ethyl (*Z*)-3-(4'-chloro-3-(2-fluorobenzoyl)-[1,1'-biphenyl]-4-yl)but-2-enoate (**4k**)

149.8 mg, 71% yield; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71 (dd, J = 7.8, 1.8 Hz, 1H), 7.64 (s, 1H), 7.62 (td, J = 7.5, 1.8 Hz, 1H), 7.53-7.45 (m, 3H), 7.38 (d, J = 8.7 Hz, 2H), 7.26-7.11 (m, 3H), 5.86 (q, J = 1.5 Hz, 1H), 3.96 (q, J = 7.2 Hz, 2H), 2.23 (d, J = 1.5 Hz, 3H), 1.08 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.7, 165.5, 161.0 (d, J = 254.6 Hz), 156.2, 141.7, 138.8, 138.4, 137.4, 134.0, 133.9 (d, J = 8.5 Hz), 132.2 (d, J = 2.0 Hz), 130.1, 129.2, 128.7, 128.6, 128.5, 128.4, 124.0 (d, J = 3.8 Hz), 118.2, 116.6 (d, J = 21.5 Hz), 59.8, 27.7, 14.2; HRMS (ESI): $[M + H]^+$ calcd for $C_{25}H_{21}ClFO_3^+$: m/z 423.1158, found: 423.1156.



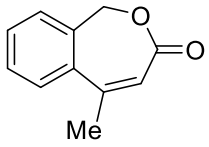
Ethyl (Z)-3-(2-(2-fluorobenzoyl)-4-(naphthalen-2-yl)phenyl)but-2-enoate (**4l**)

133.6 mg, 61% yield; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 (d, J = 1.5 Hz, 1H), 7.91-7.84 (m, 4H), 7.82 (s, 1H), 7.70-7.63 (m, 2H), 7.53-7.48 (m, 3H), 7.30 (d, J = 7.8 Hz, 1H), 7.23-7.13 (m, 2H), 5.88 (q, J = 1.5 Hz, 1H), 3.98 (q, J = 7.2 Hz, 2H), 2.26 (d, J = 1.5 Hz, 3H), 1.09 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.9, 165.6, 161.1 (d, J = 254.6 Hz), 156.4, 141.4, 140.0, 137.4, 137.3, 133.9 (d, J = 8.6 Hz), 133.6, 132.8, 132.3 (d, J = 1.8 Hz), 130.6, 129.3, 128.7, 128.5, 128.3, 127.8, 127.2 (d, J = 11.8 Hz), 126.6, 126.3, 126.1, 125.4, 124.0 (d, J = 3.8 Hz), 118.2, 116.6 (d, J = 21.5 Hz), 59.9, 27.7, 14.2; HRMS (ESI): $[M + H]^+$ calcd for $C_{29}H_{24}FO_3^+$: m/z 439.1704, found: 439.1704. The *Z* stereochemistry was confirmed by NOESY (δ 5.88 and 2.26).



1-(2-Ethoxy-2-oxoethyl)-1-methyl-1H-isoindole 2-oxide (**5**)

102.5 mg, 88% yield; yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (s, 1H), 7.38-7.32 (m, 4H), 3.99-3.88 (m, 2H), 3.02 (s, 2H), 1.61 (s, 3H), 1.02 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.6, 142.8, 133.3, 132.8, 128.9, 127.8, 121.6, 120.4, 60.7, 40.9, 29.8, 24.4, 14.0; HRMS (ESI): $[M + H]^+$ calcd for $C_{13}H_{16}NO_3^+$: m/z 234.1125, found: 234.1123.



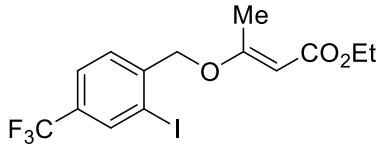
5-Methylbenzo[c]oxepin-3(1H)-one (**6**)

66.1 mg, 76% yield; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53-7.51 (m, 2H), 7.44-7.42 (m, 2H), 6.33 (q, J = 1.5 Hz, 1H), 5.02 (s, 2H), 2.36 (d, J = 1.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.0, 147.8, 137.7, 134.8, 129.6, 128.8, 126.9, 120.5, 68.6, 23.9; HRMS (ESI): $[M + H]^+$ calcd for $C_{11}H_{11}O_2^+$: m/z 175.0754, found: 175.0751.

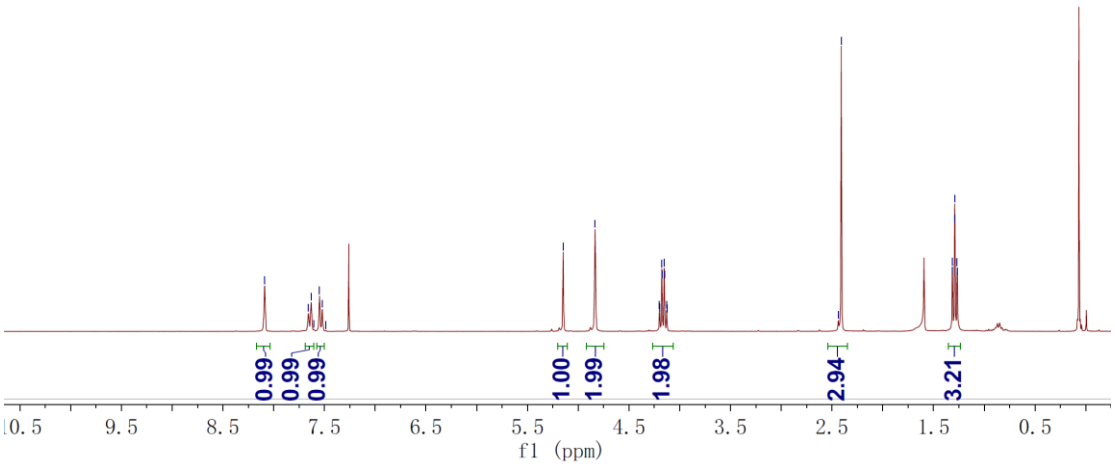
References

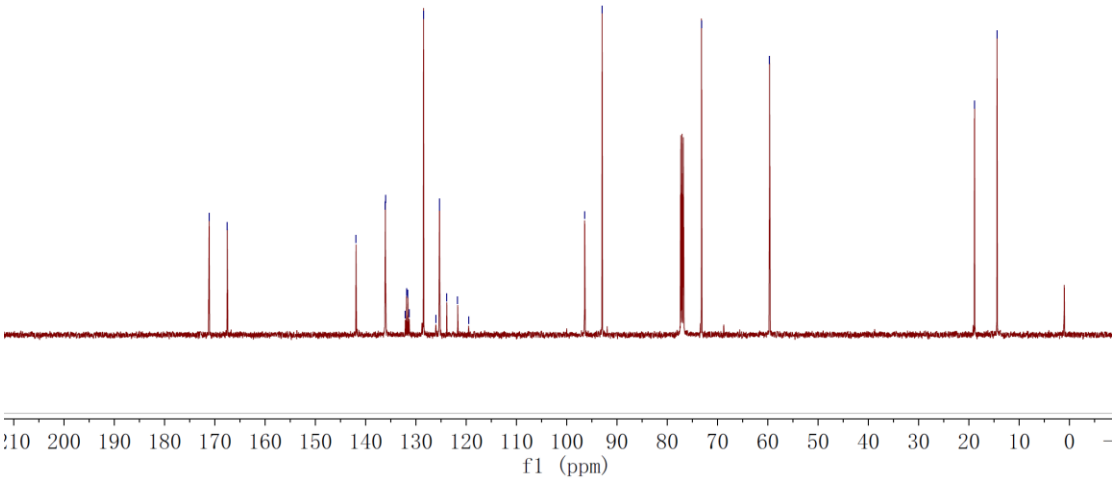
1. W. Feng, H. Wu, H. Qian, Z. Li, X. Sun and Z. Wang, *J. Chem. Res.*, 2016, **40**, 364.
2. L. R. Peacock, R. S. L. Chapman, A. C. Sedgwick, M. F. Mahon, D. Amans and S. D. Bull, *Org. Lett.*, 2015, **17**, 994.
3. M. Narisada, I. Horibe, F. Watanabe and K. Takeda, *J. Org. Chem.*, 1989, **54**, 5308.
4. S. W. Youn, H. S. Song and J. H. Park, *Org. Lett.*, 2014, **16**, 1028.

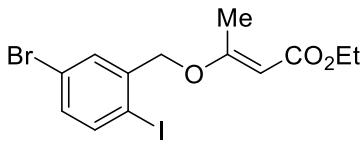
Copies of ^{1}H NMR, ^{13}C NMR and NOESY spectra



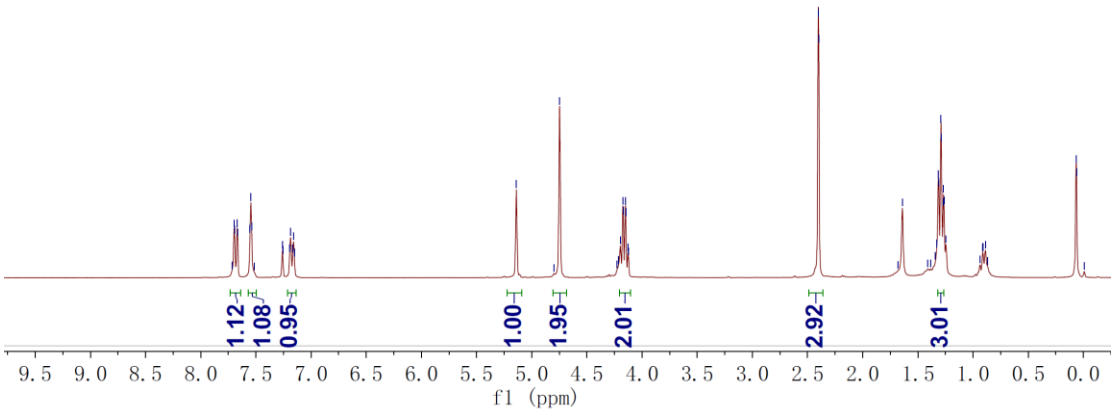
(**1d**)

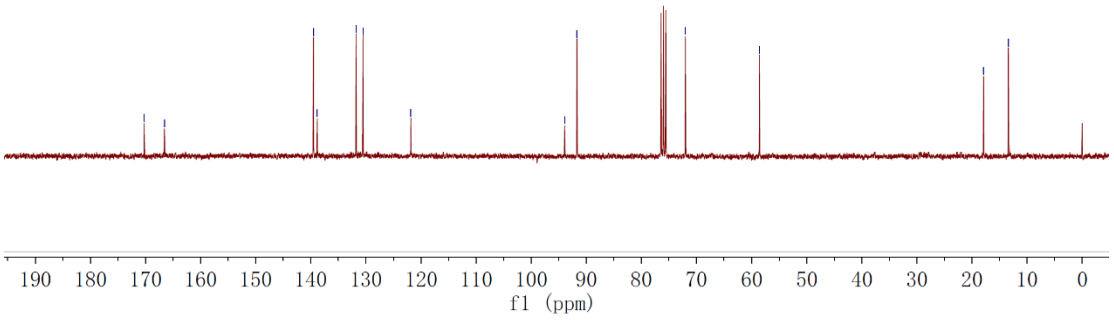


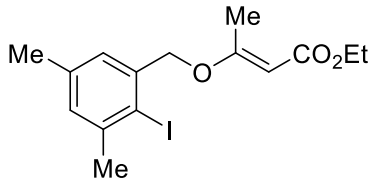



Me
Br
O
CO_2Et
I

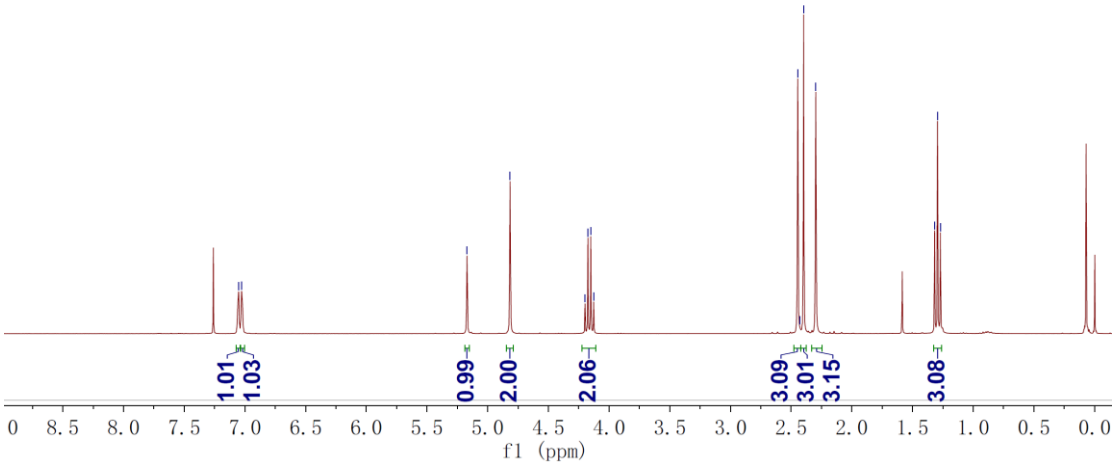
(**1f**)

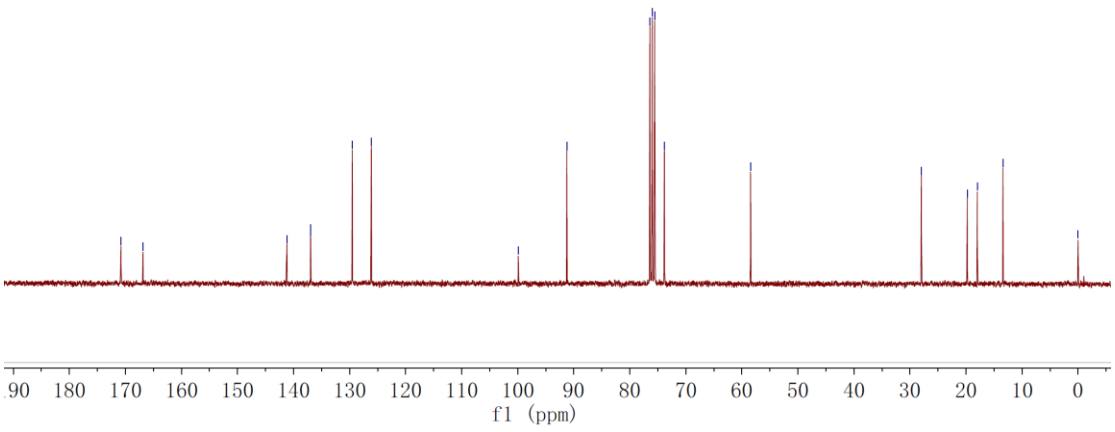

1.12
1.08
0.95
1.00
1.95
2.01
2.92
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

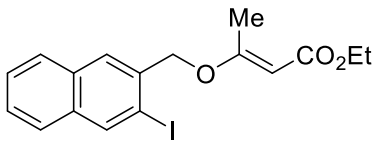

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
Me
CO2Et
O
I
Me

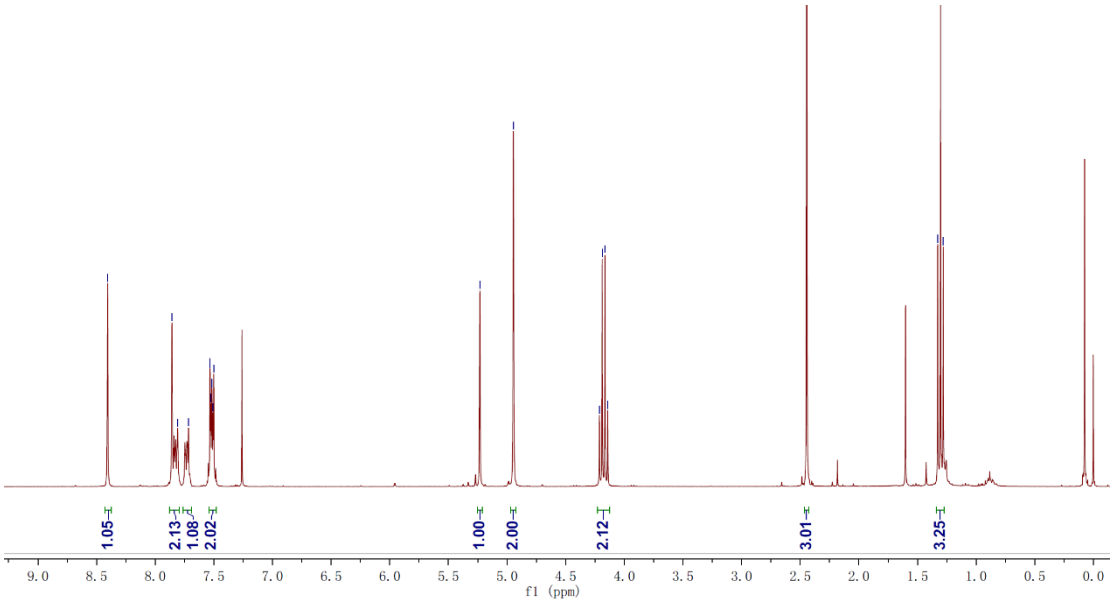
(1i)

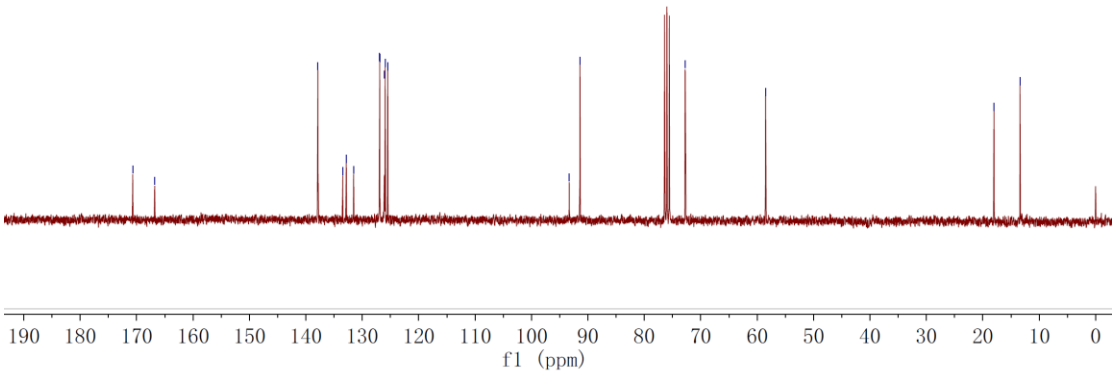

1.01
1.03
0.99
2.00
2.06
3.09
3.01
3.15
3.08
0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

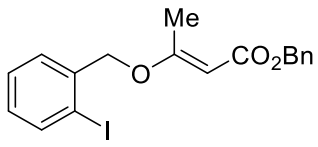

90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
CO2Et
O
I

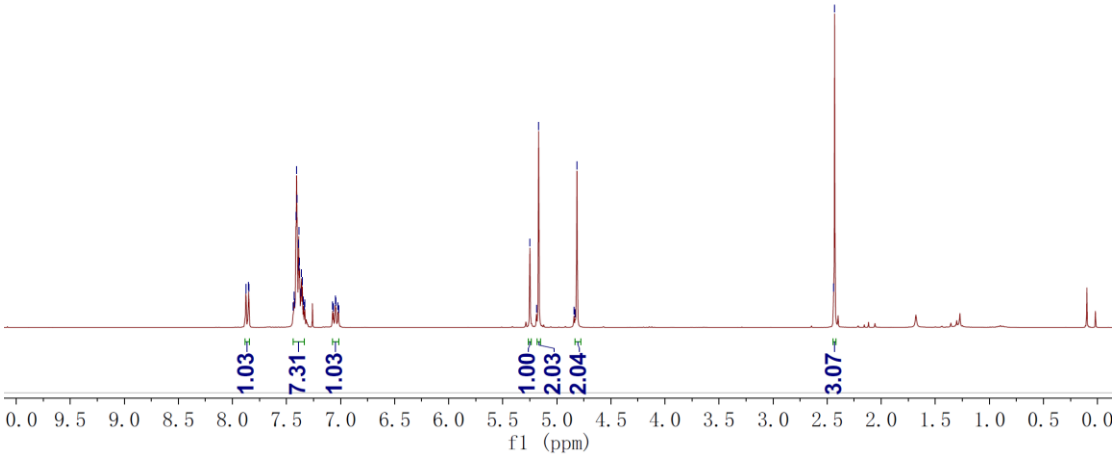
(1j)

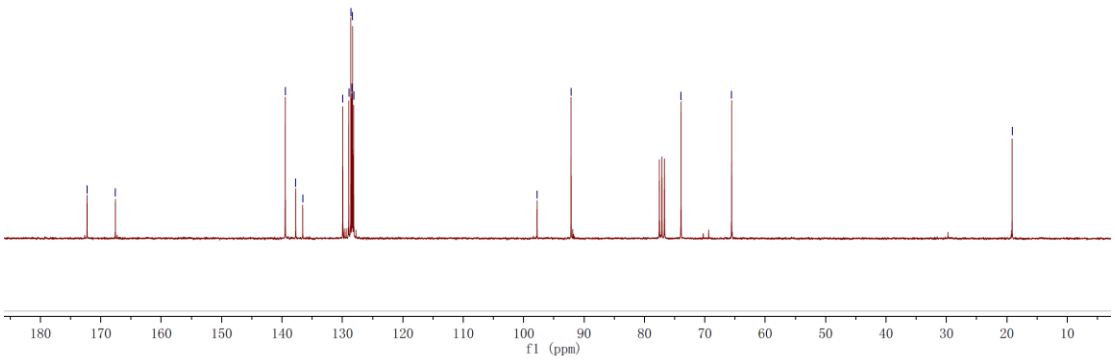

1.05
2.13
1.08
2.02
1.00
2.00
2.12
3.01
3.25
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

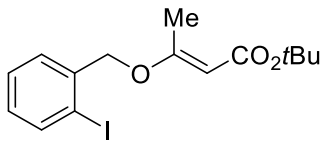

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
CO2Bn
O
I

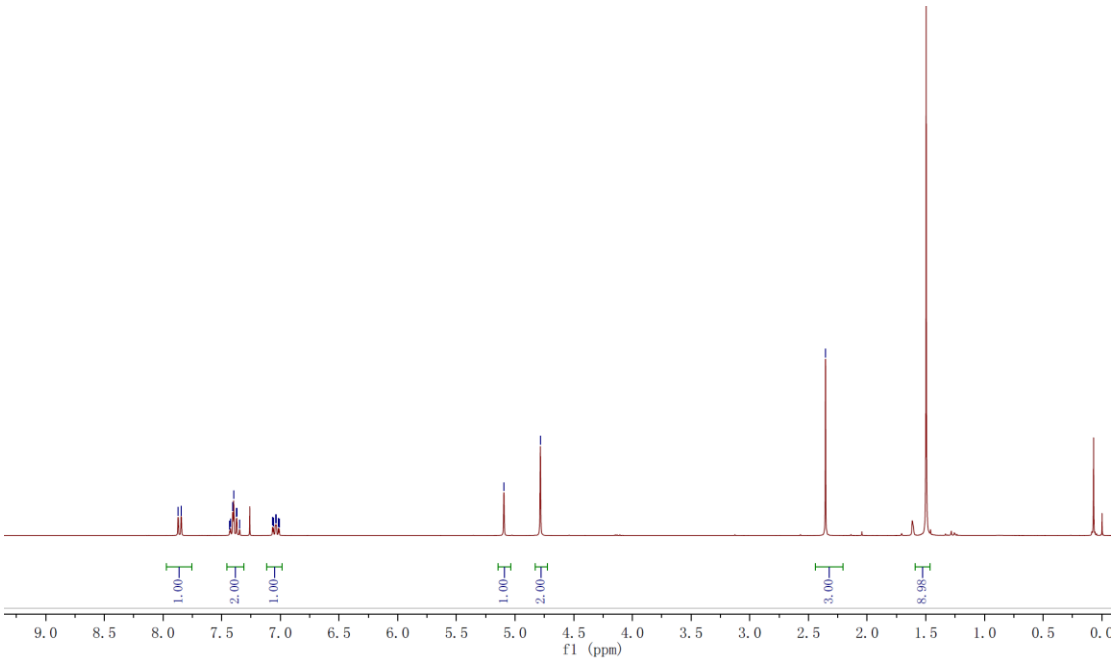
(1k)

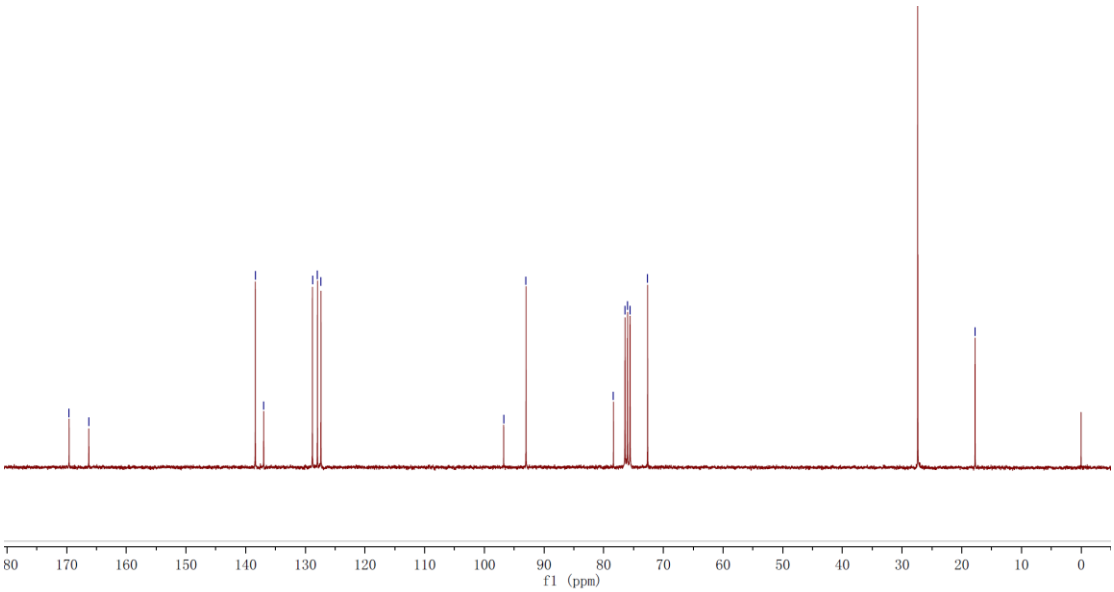

1.03
7.31
1.03
1.00
2.03
2.04
3.07
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

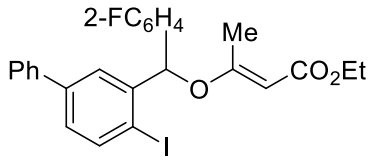

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Me
O
CO2tBu
I

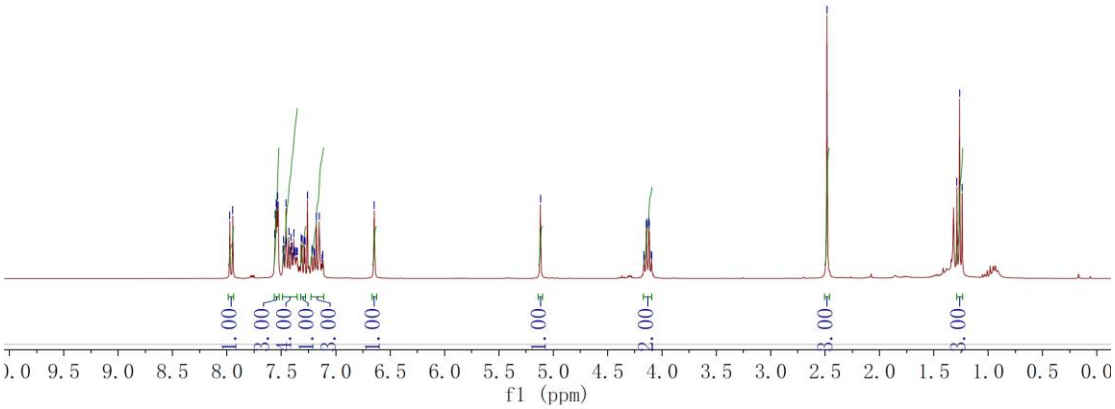
(1l)

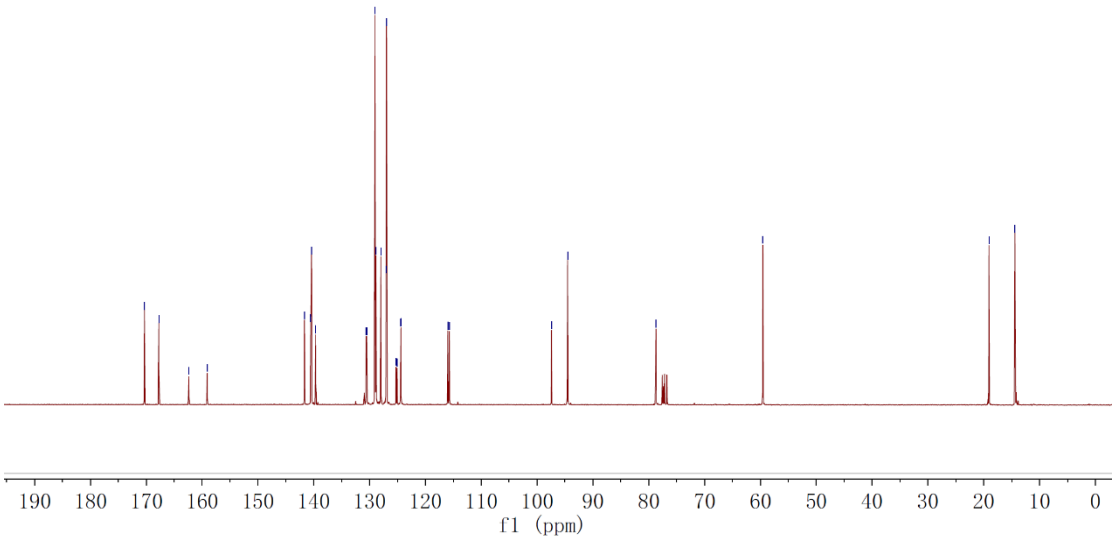

1.00
2.00
1.00
1.00
2.00
3.00
8.98
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

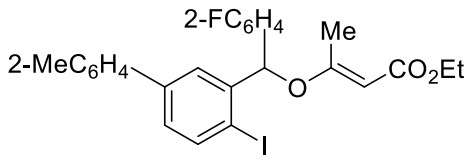

80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


2-FC6H4
Me
Ph
O
CO2Et
I

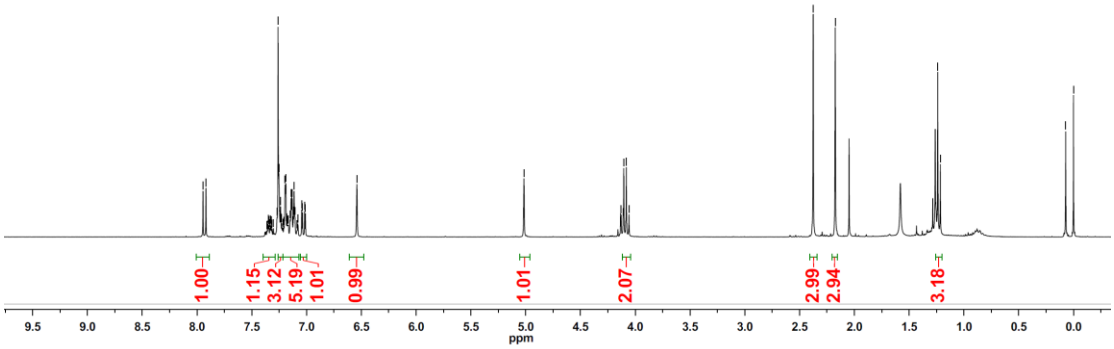
(3d)

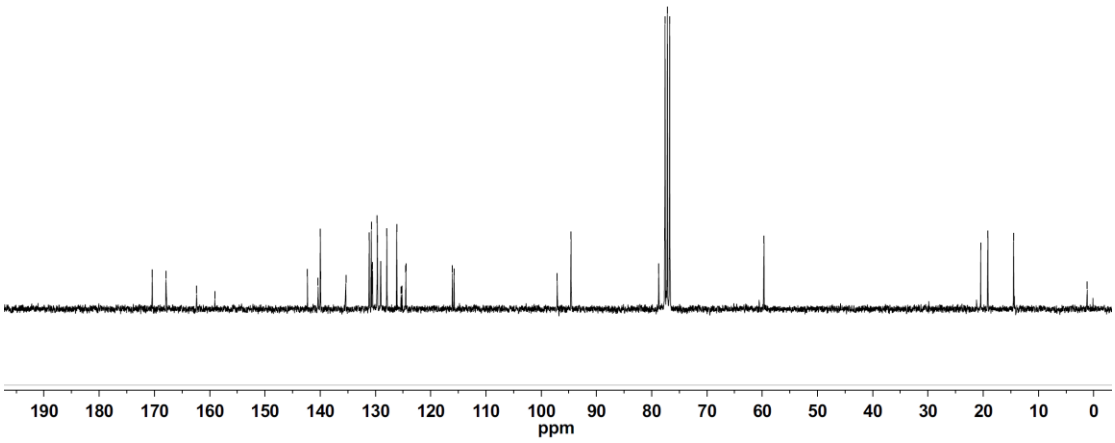

1.00
3.00
1.00
1.00
3.00
1.00
1.00
2.00
3.00
3.00
f1 (ppm)

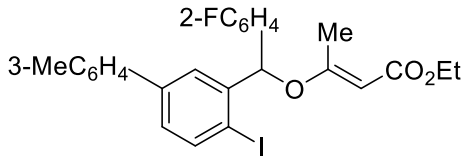

f1 (ppm)


2-FC6H4
Me
2-MeC6H4
O
CO2Et
I

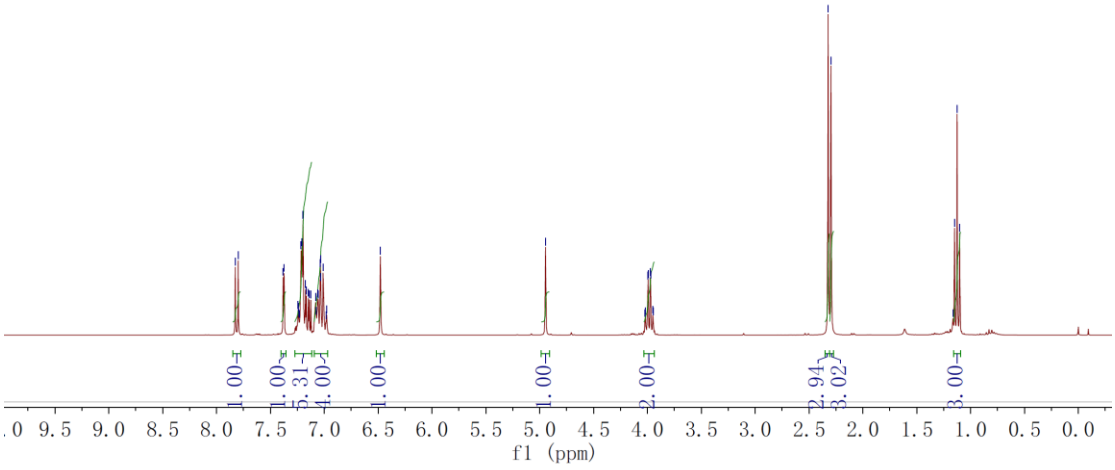
(3e)

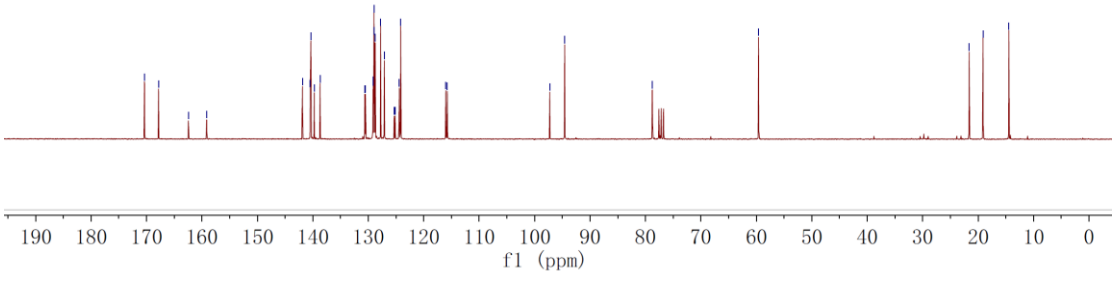

1.00
1.15
3.12
5.19
1.01
0.99
1.01
2.07
2.99
2.94
3.18
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

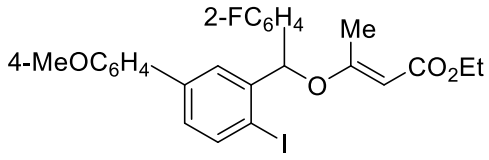

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


2-FC6H4
Me
3-MeC6H4
O
CO2Et
I

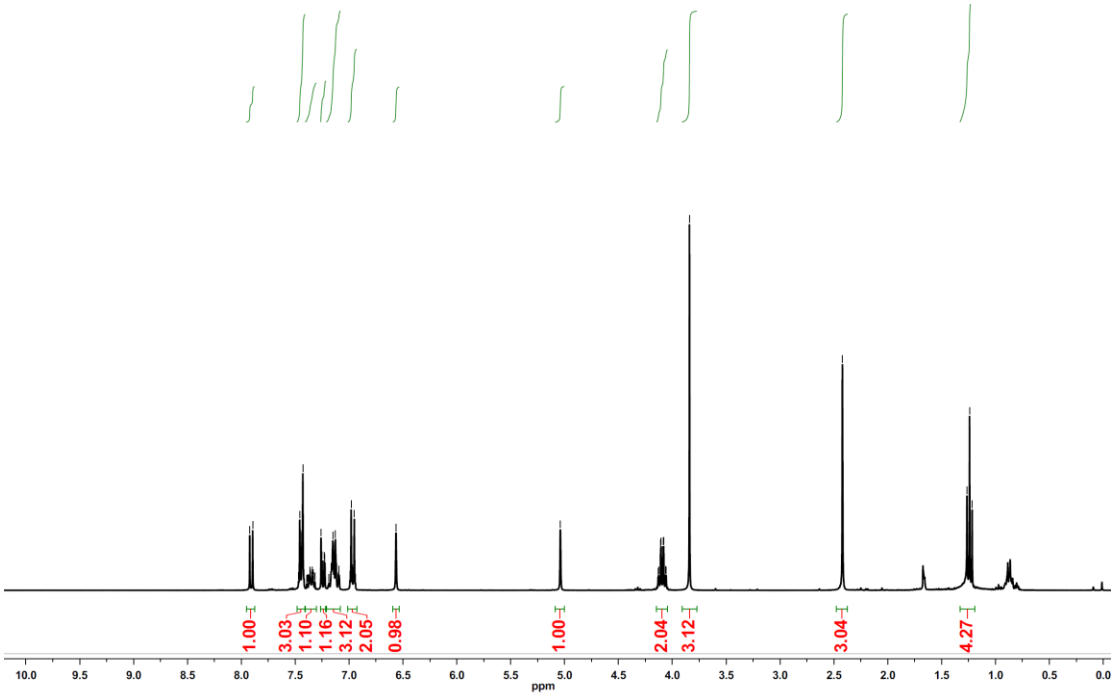
(3f)

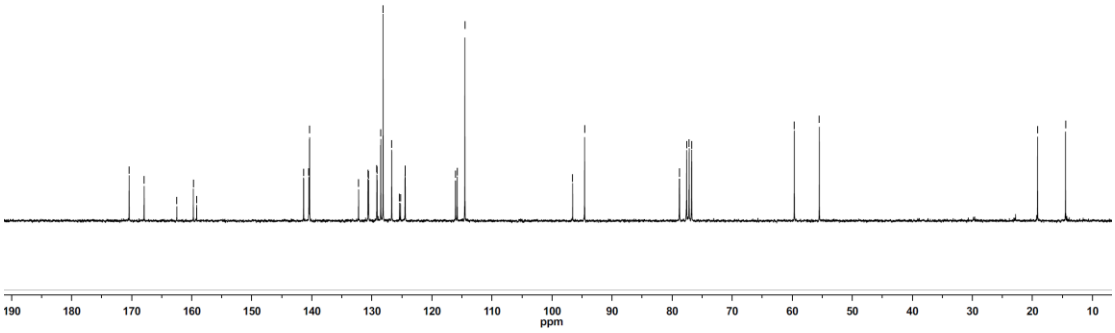

1.00
1.00
5.31
4.00
1.00
1.00
2.00
2.94
3.02
3.00
f1 (ppm)

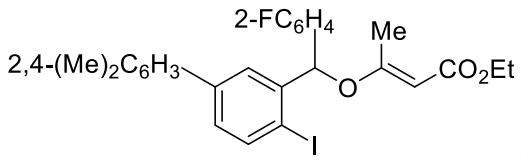

f1 (ppm)


2-FC6H4
Me
4-MeOC6H4
O
CO2Et
I

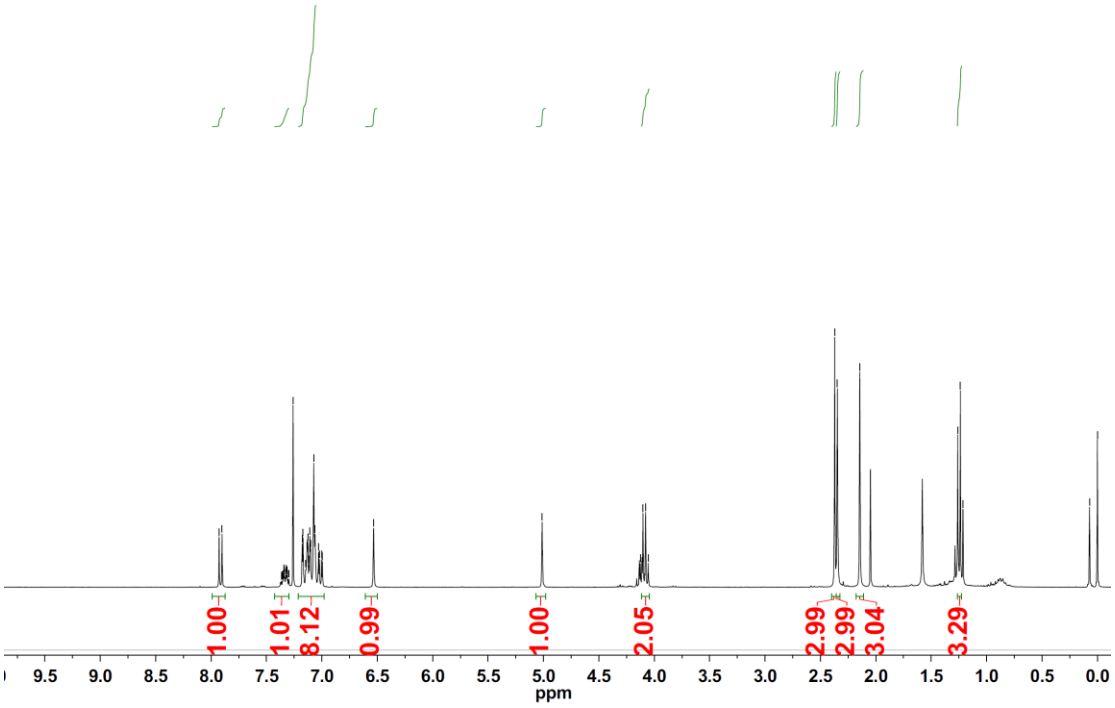
(3g)

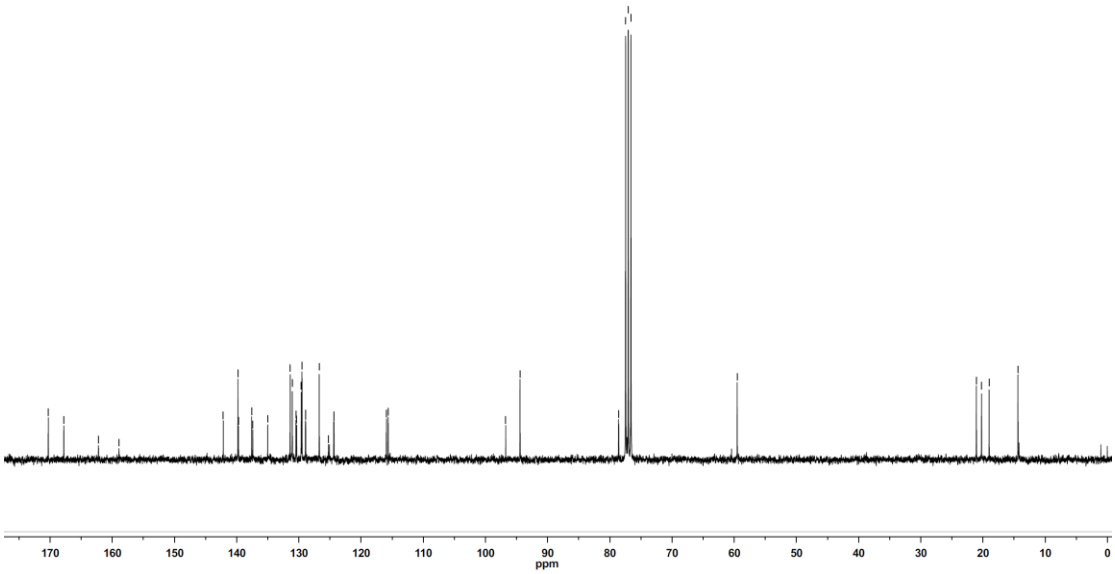

1.00
3.03
1.10
1.16
3.12
2.05
0.98
1.00
2.04
3.12
3.04
4.27
ppm

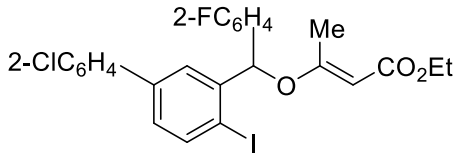

ppm


2-FC6H4
Me
2,4-(Me)2C6H3
O
CO2Et
I

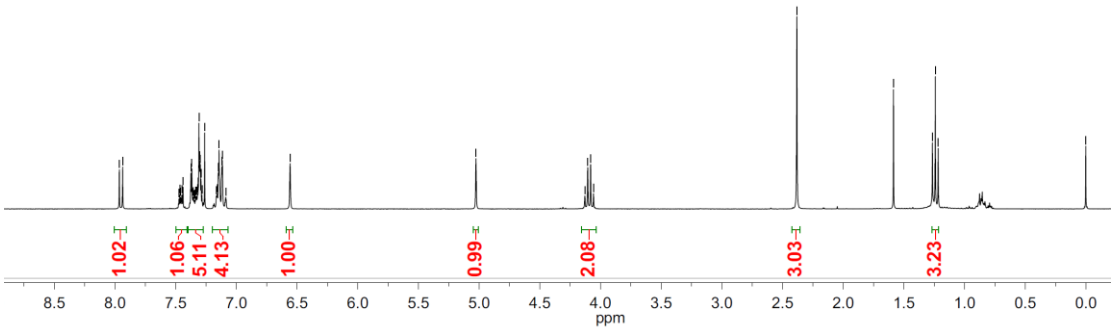
(3h)

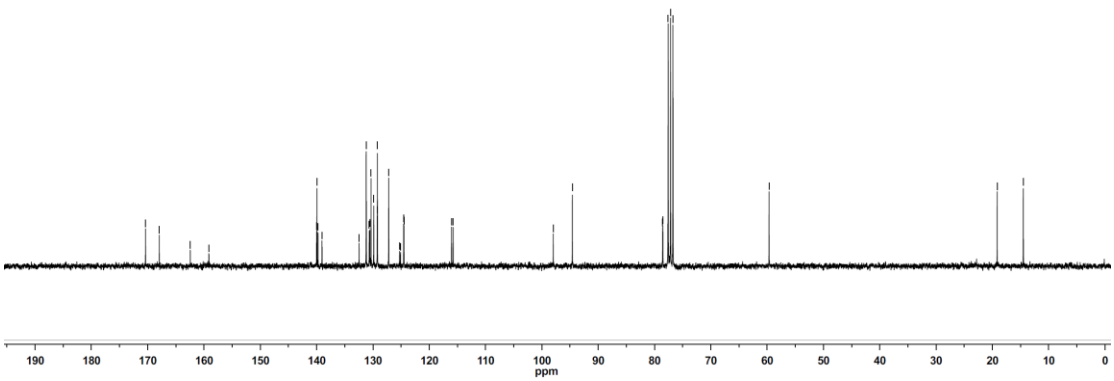

1.00
1.01
8.12
0.99
1.00
2.05
2.99
2.99
3.04
3.29
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

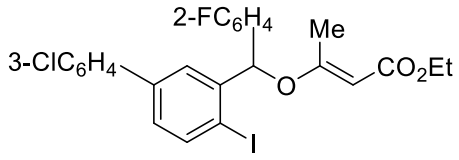

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


2-FC6H4
Me
2-ClC6H4
O
CO2Et
I

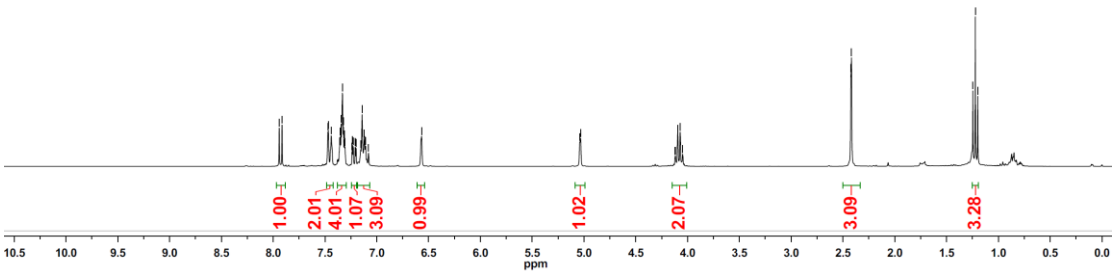
(3i)

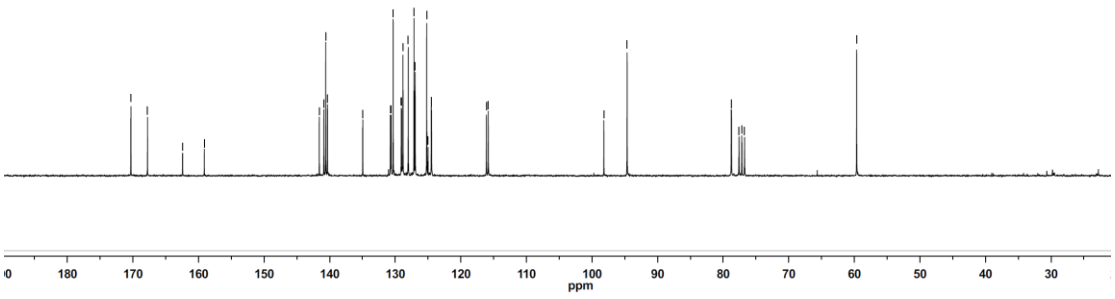

1.02
1.06
5.11
4.13
1.00
0.99
2.08
3.03
3.23
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

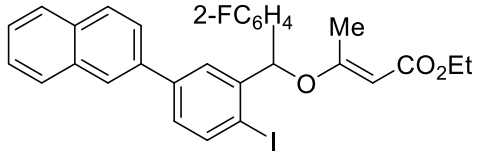

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


2-FC6H4
Me
3-ClC6H4
O
CO2Et
I

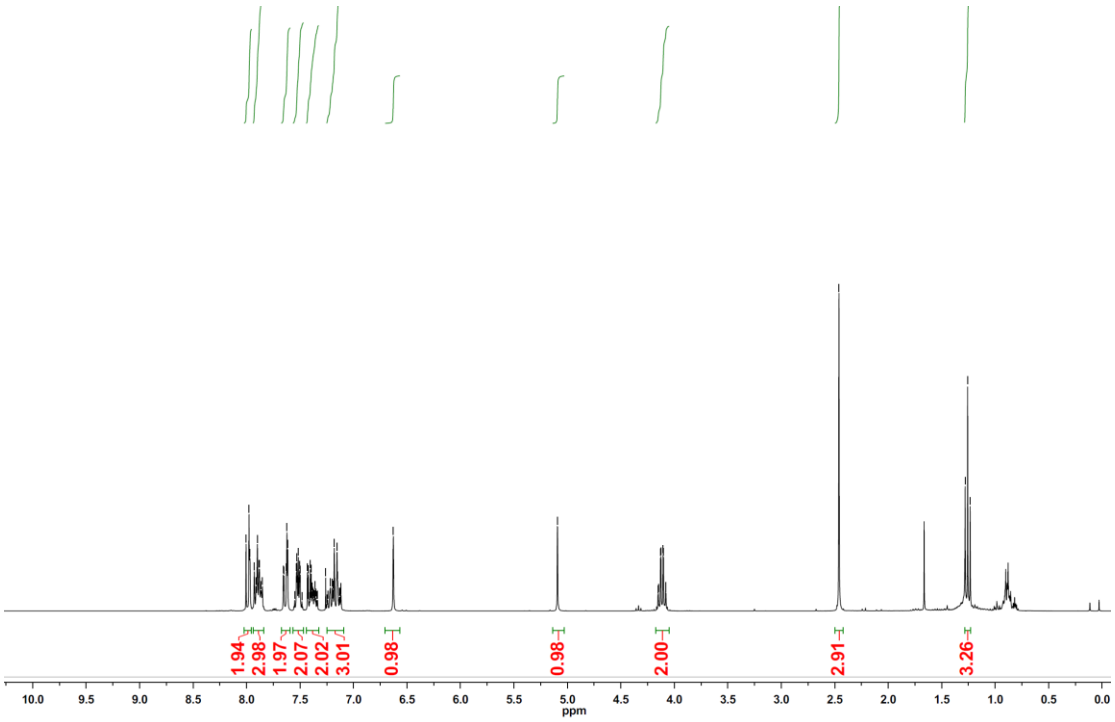
(3j)

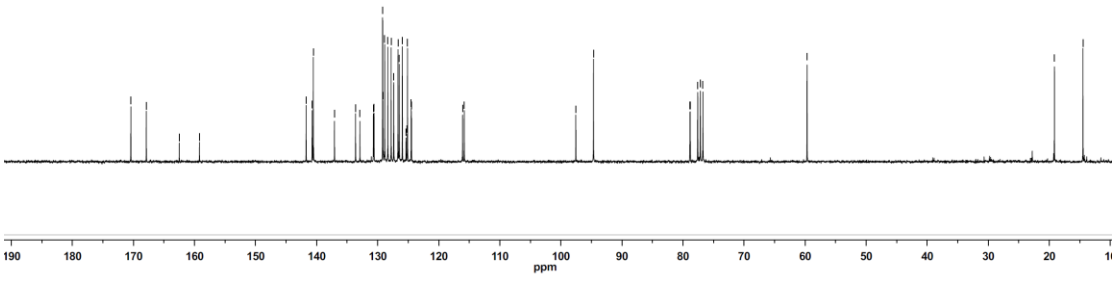

1.00
2.01
4.01
1.07
3.09
0.99
1.02
2.07
3.09
3.28
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

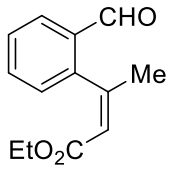

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30
ppm


2-FC6H4
Me
CO2Et
O
I

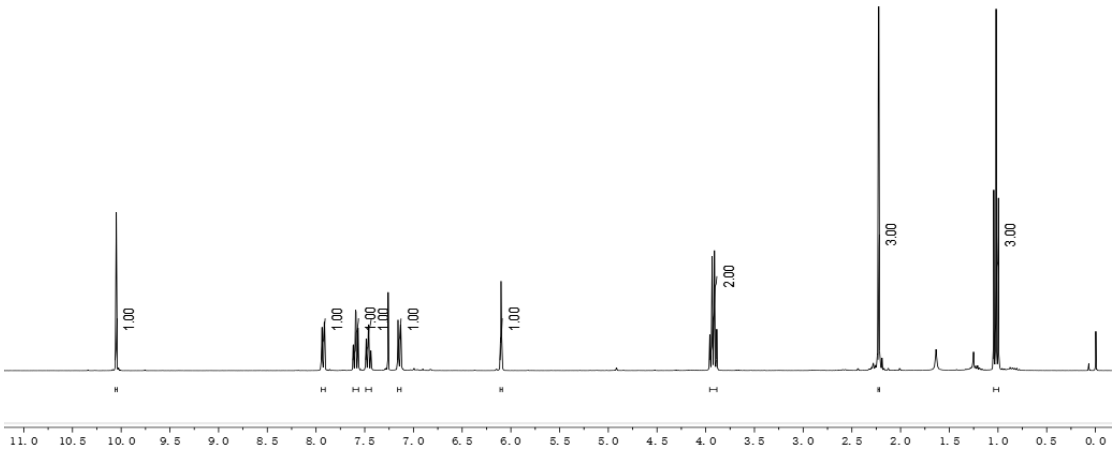
(3l)

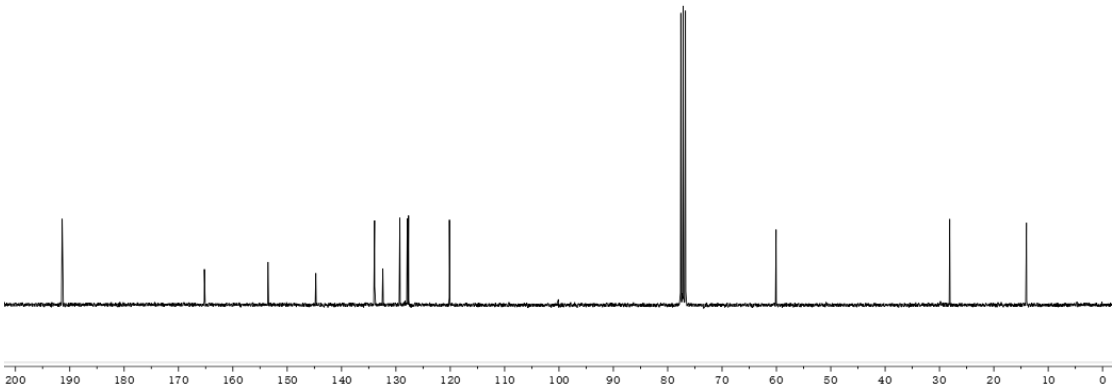

1.94
2.98
1.97
2.07
2.02
3.01
0.98
0.98
2.00
2.91
3.26
ppm

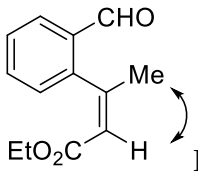

ppm


CHO
Me
EtO2C

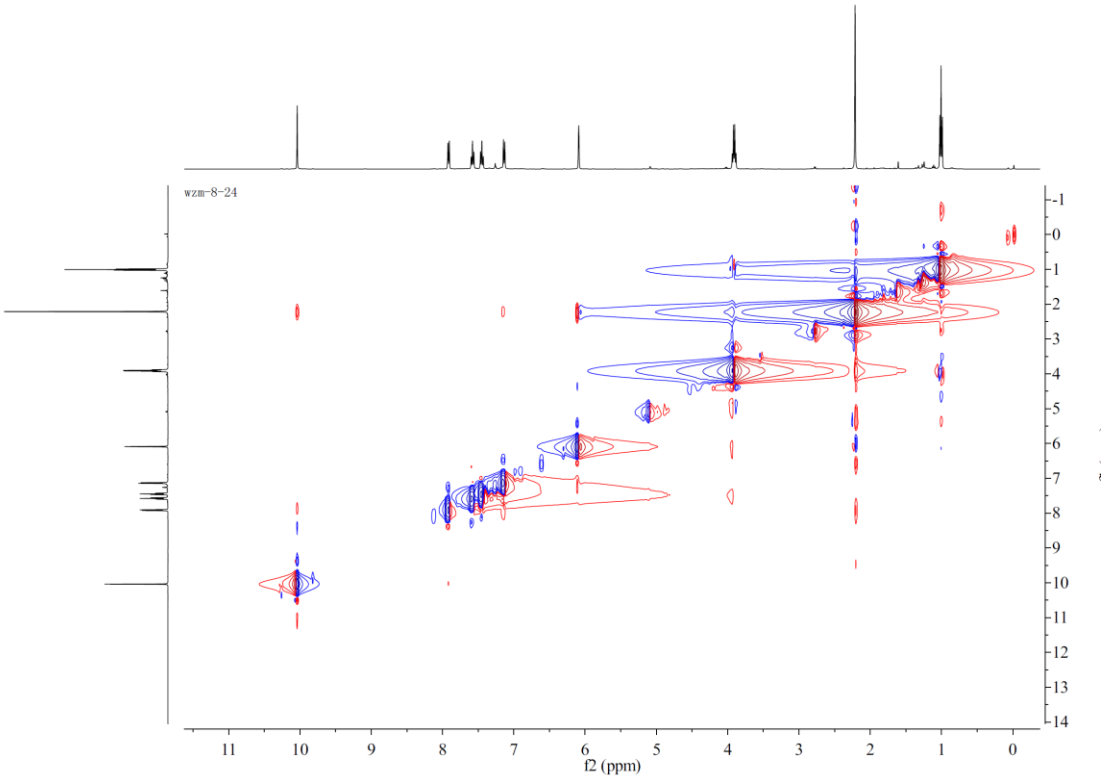
(**2a**)

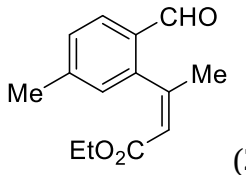

1.00
1.00
1.00
1.00
1.00
1.00
2.00
3.00
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

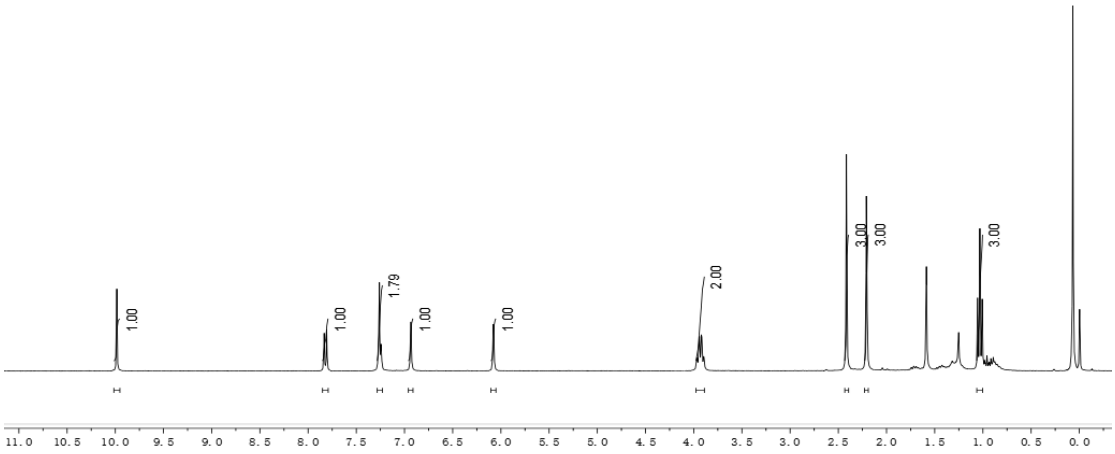


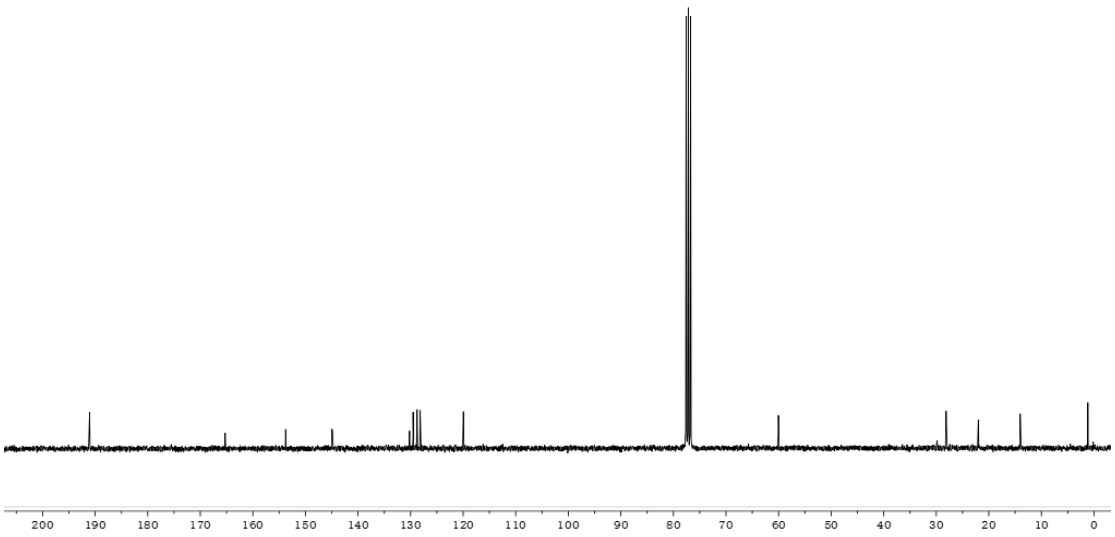
NOESY (δ 6.10 and 2.22)

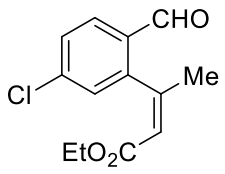



CHO
Me
Me
EtO2C

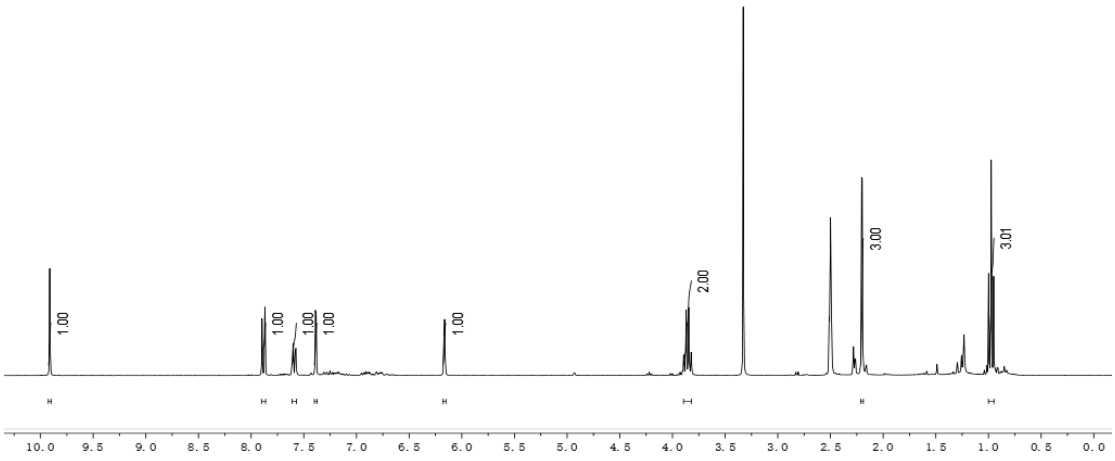
(2b)

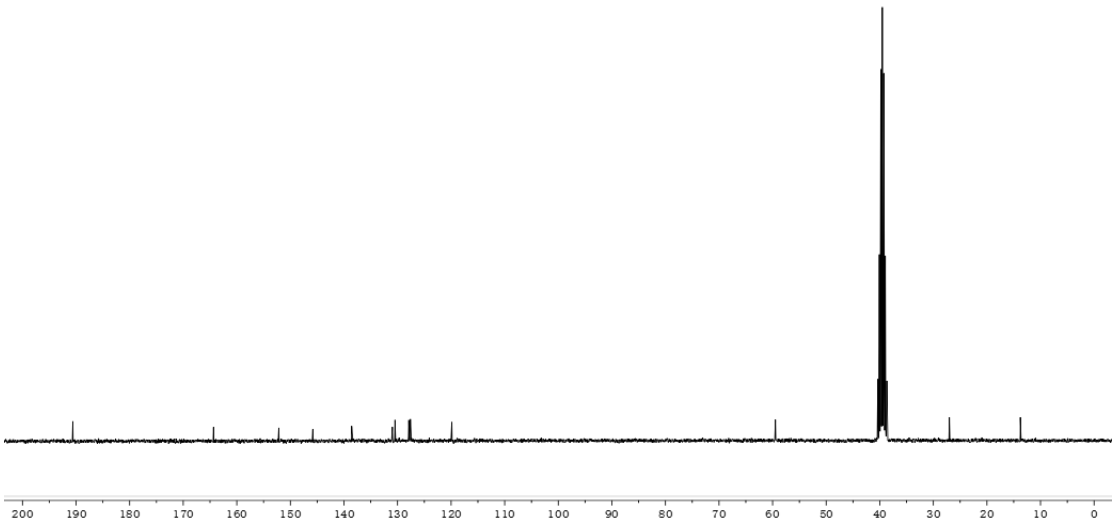

1.00
1.00
1.79
1.00
1.00
2.00
3.00
3.00
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

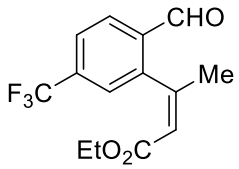

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


CHO
Me
Cl
EtO2C

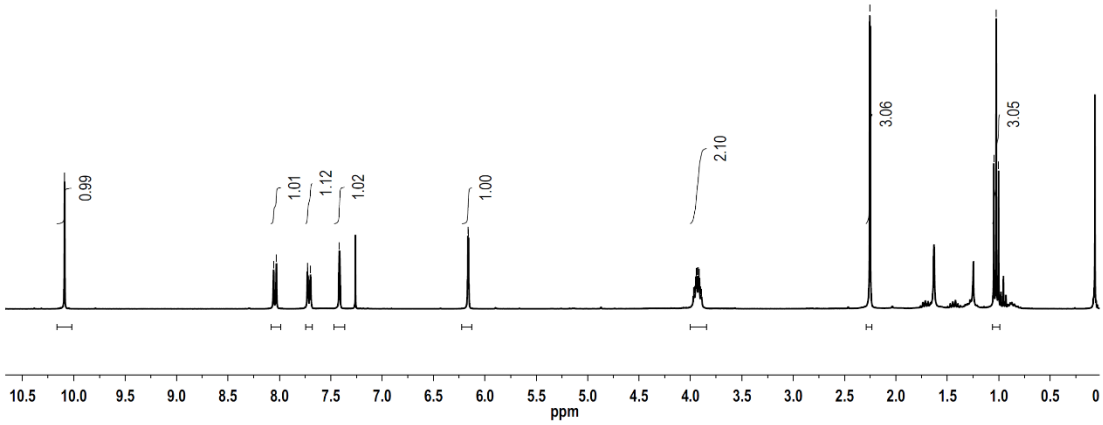
(**2c**)

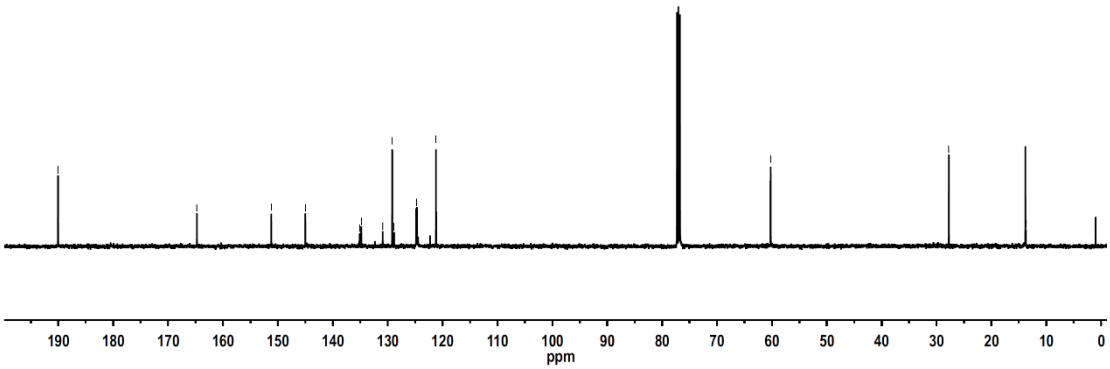

1.00
1.00
1.00
1.00
1.00
2.00
3.00
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

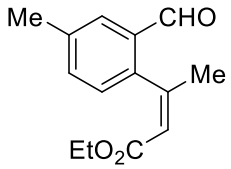

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


CHO
Me
F3C
EtO2C

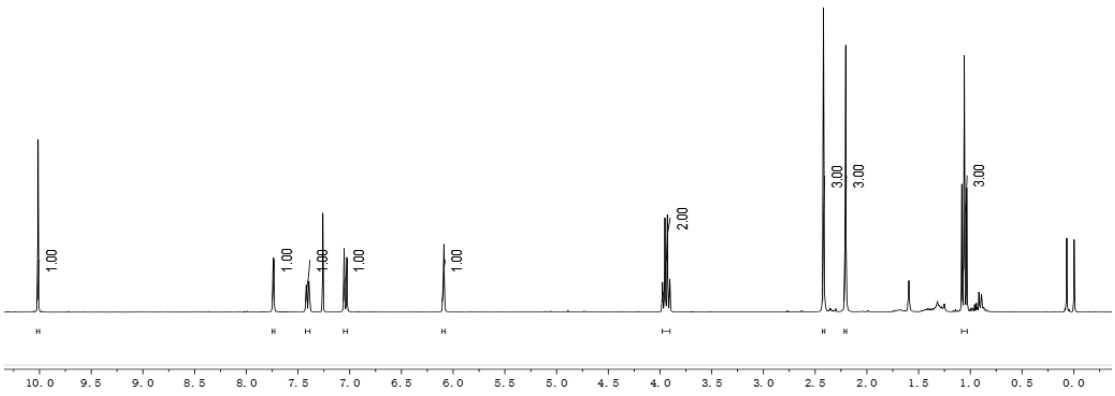
(**2d**)

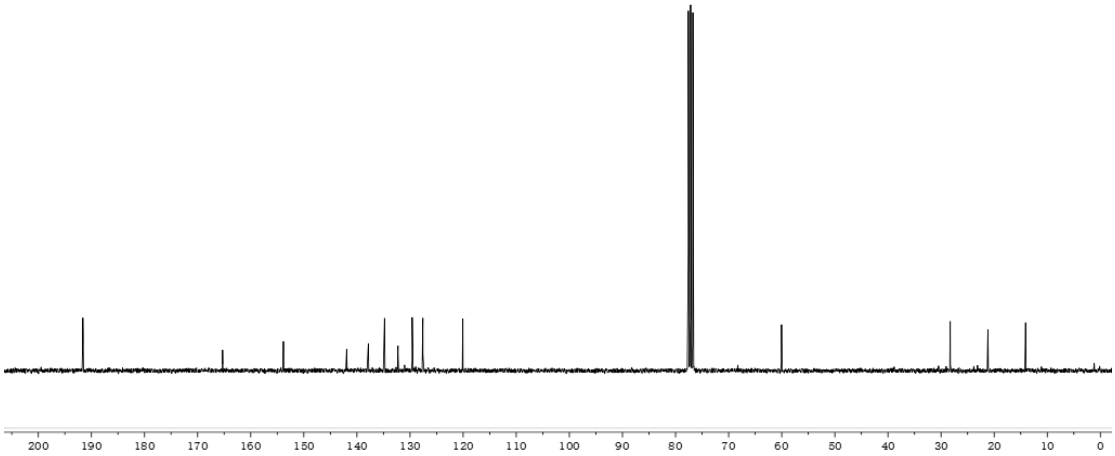

0.99
1.01
1.12
1.02
1.00
2.10
3.06
3.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
ppm

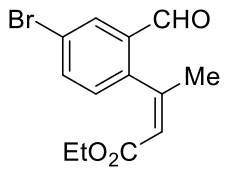

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


Me
CHO
Me
EtO2C

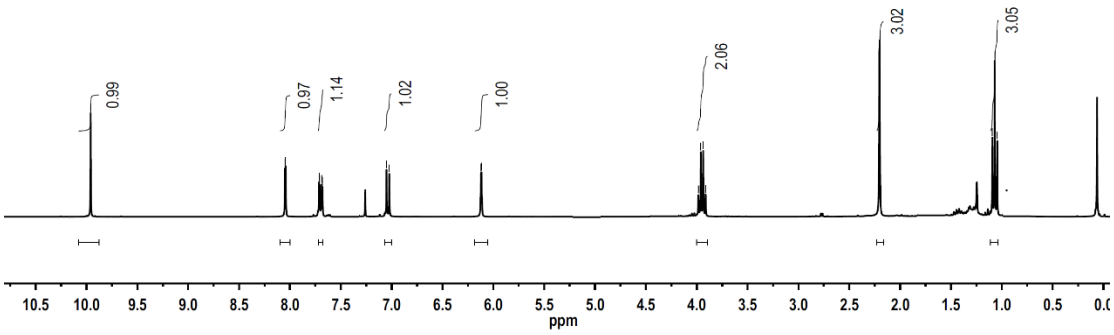
(**2e**)

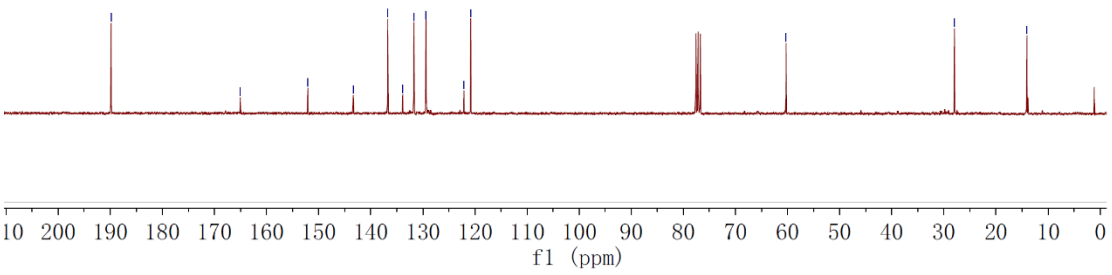

1.00
1.00
1.00
1.00
1.00
2.00
3.00
3.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

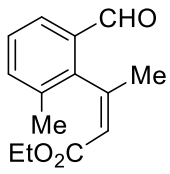

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


Br
CHO
Me
EtO2C

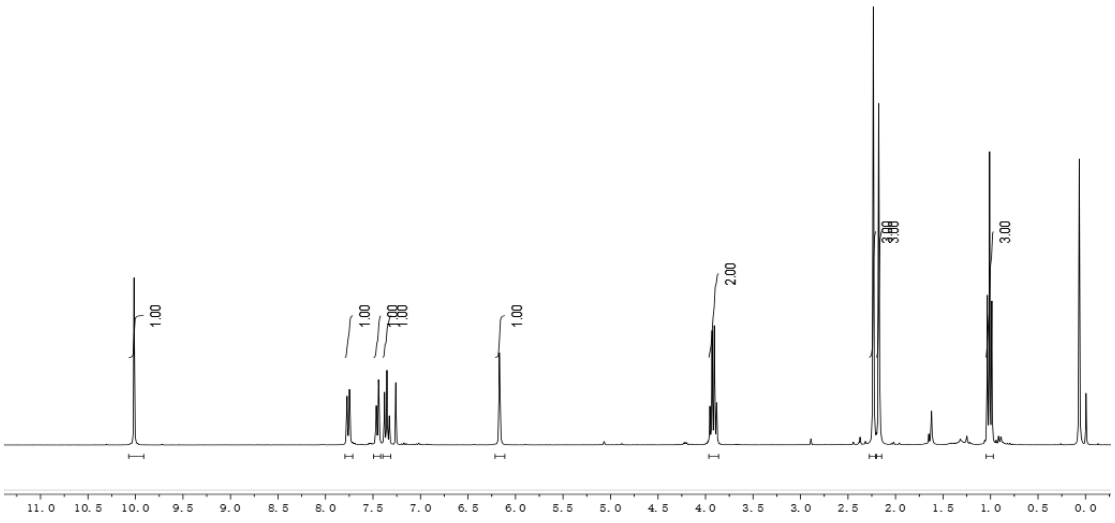
(2f)

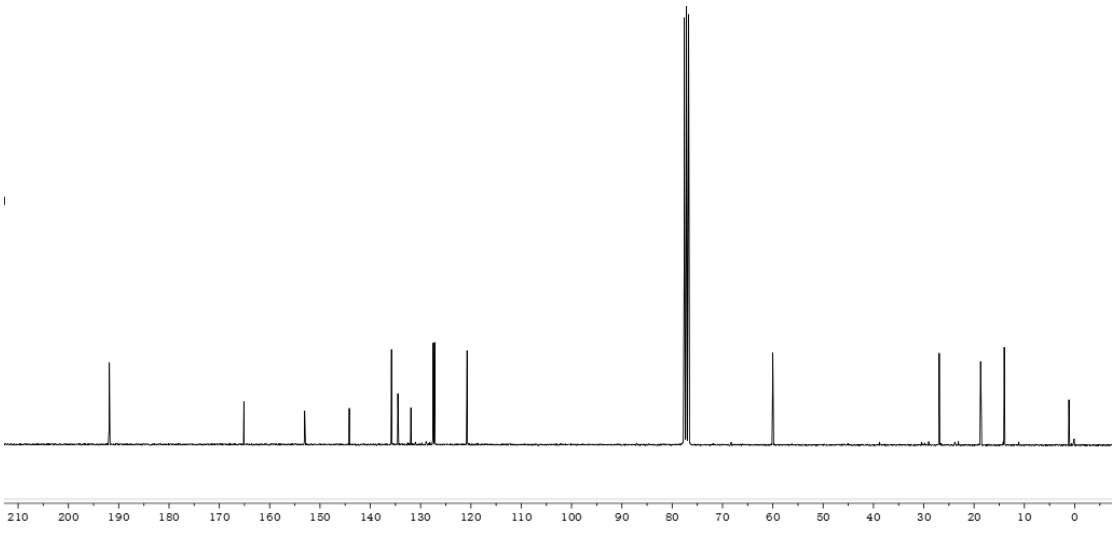

0.99
0.97
1.14
1.02
1.00
2.06
3.02
3.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

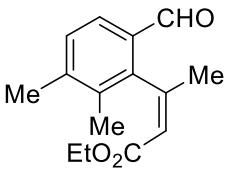

10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


CHO
Me
Me
EtO2C

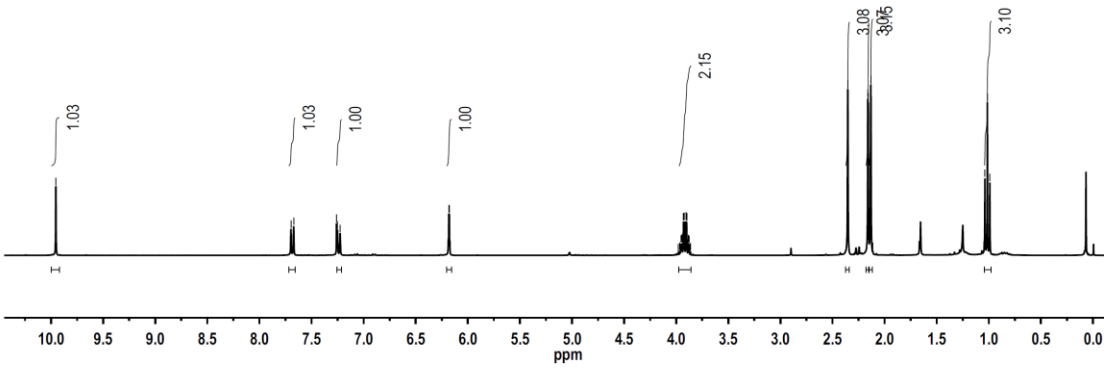
(**2g**)

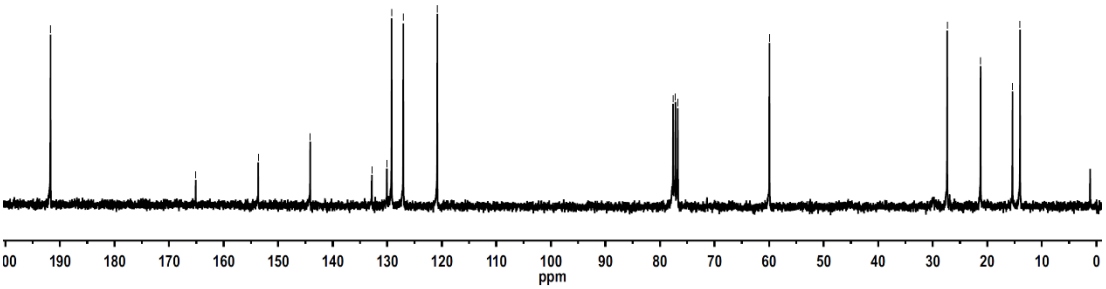

1.00
1.00
1.00
1.00
2.00
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

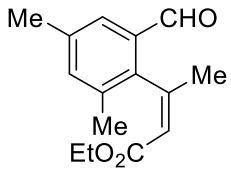

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


CHO
Me
Me
Me
EtO2C

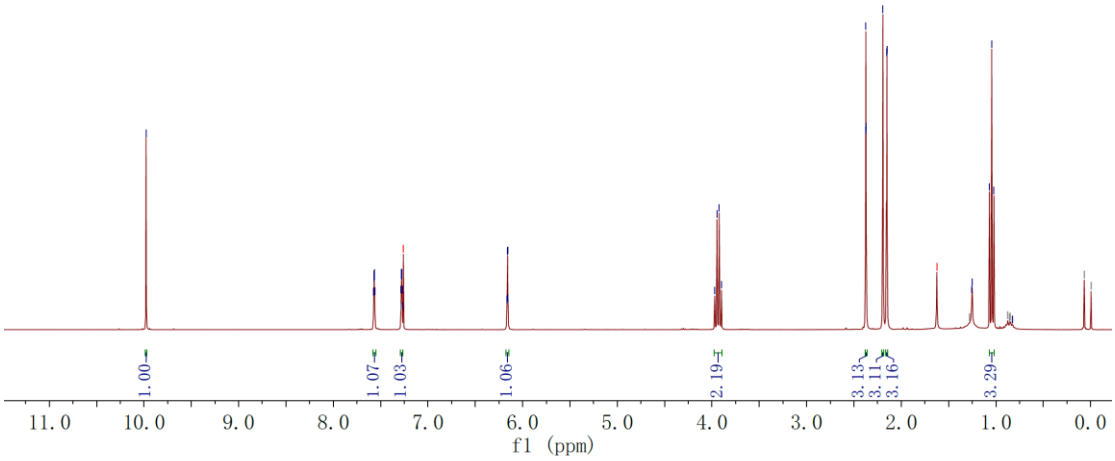
(2h)

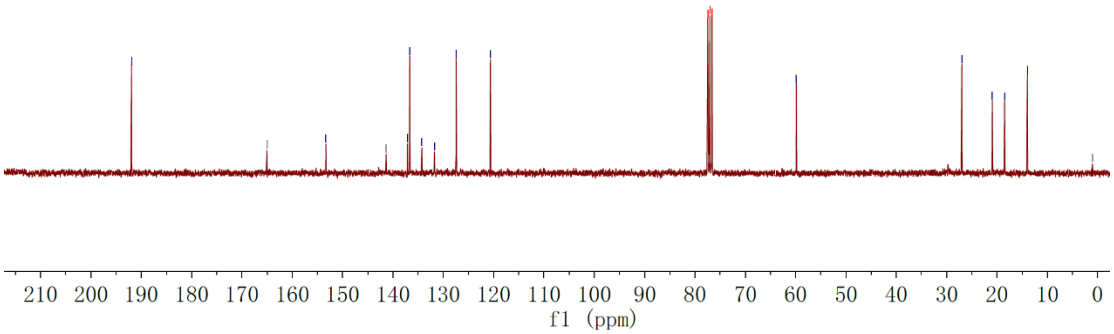

1.03
1.03
1.00
1.00
2.15
3.08
3.05
3.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

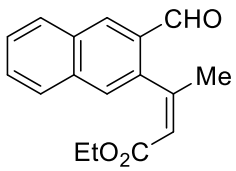

00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


Me
CHO
Me
Me
EtO2C

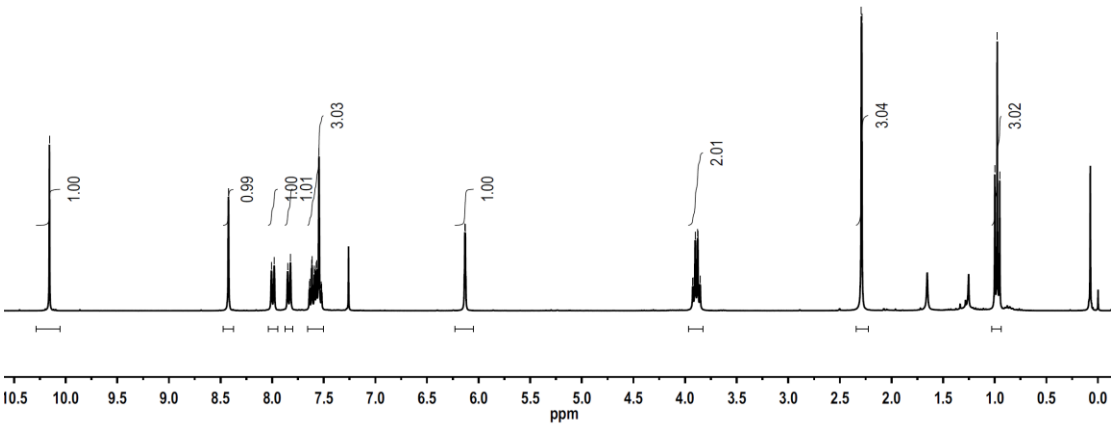
(2i)

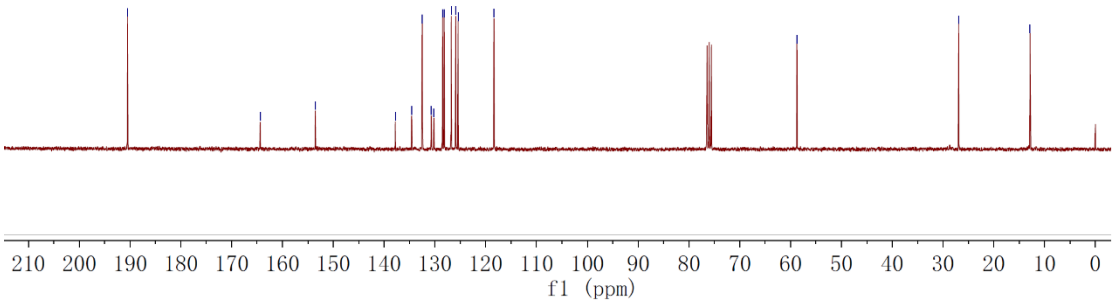

1.00
1.07
1.03
1.06
2.19
3.13
3.11
3.16
3.29
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

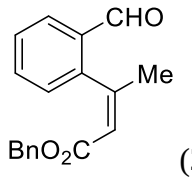

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


CHO
Me
EtO2C

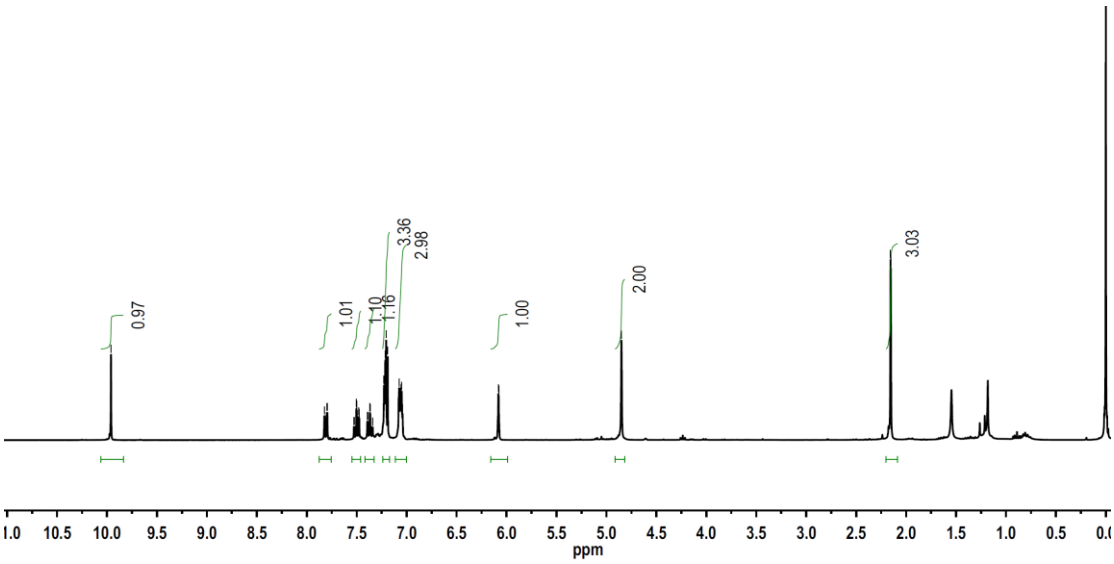
(2j)

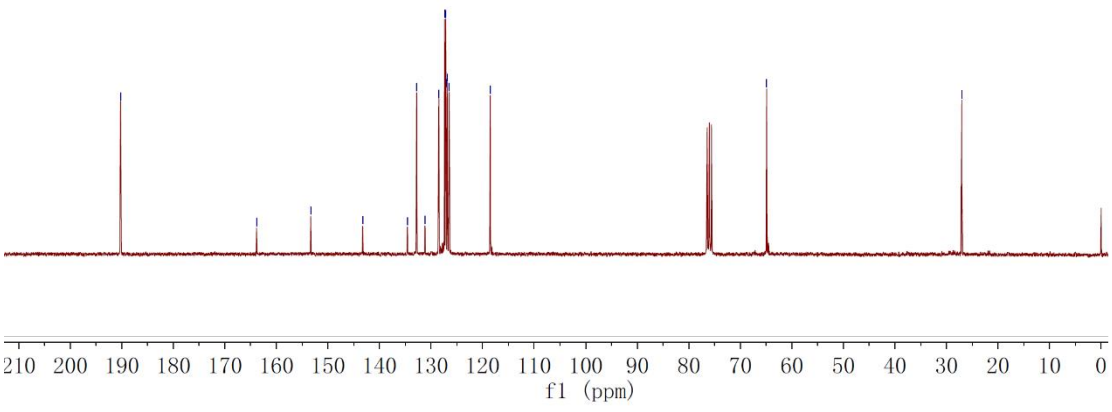

1.00
0.99
1.00
1.01
3.03
1.00
2.01
3.04
3.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

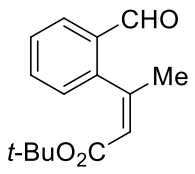

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



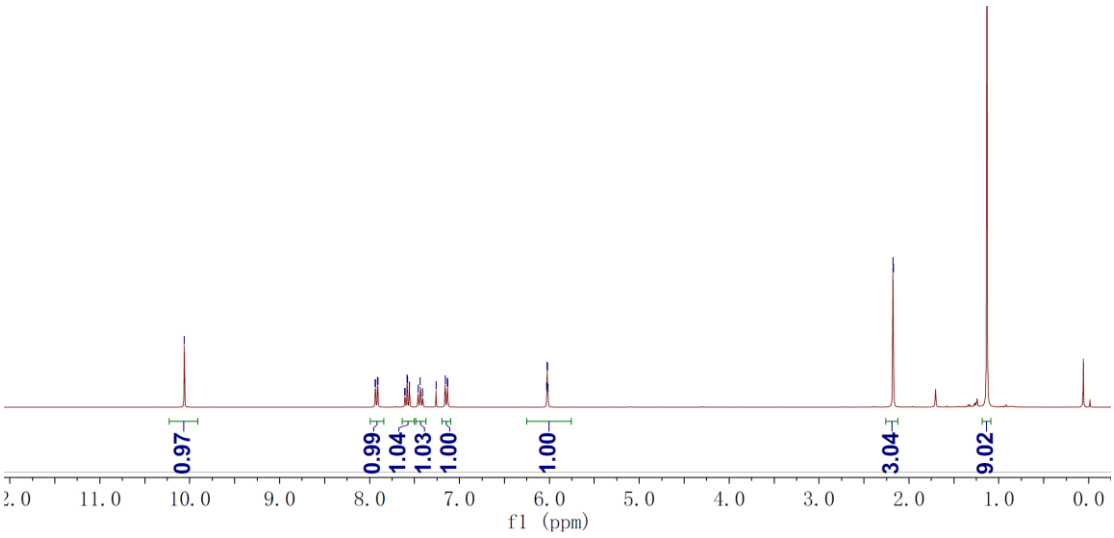
(**2k**)

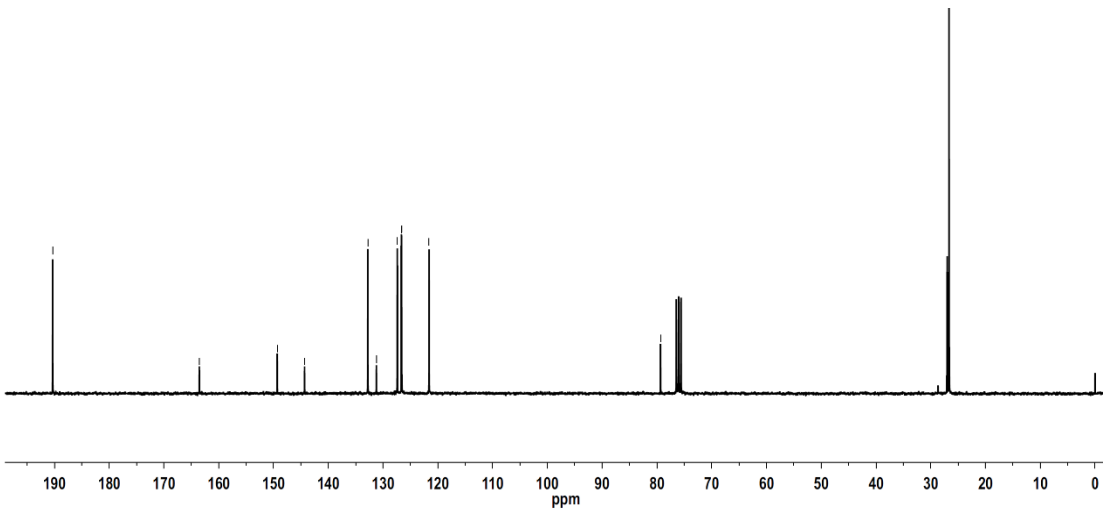


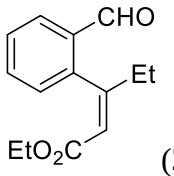



CHO
Me
t-BuO2C

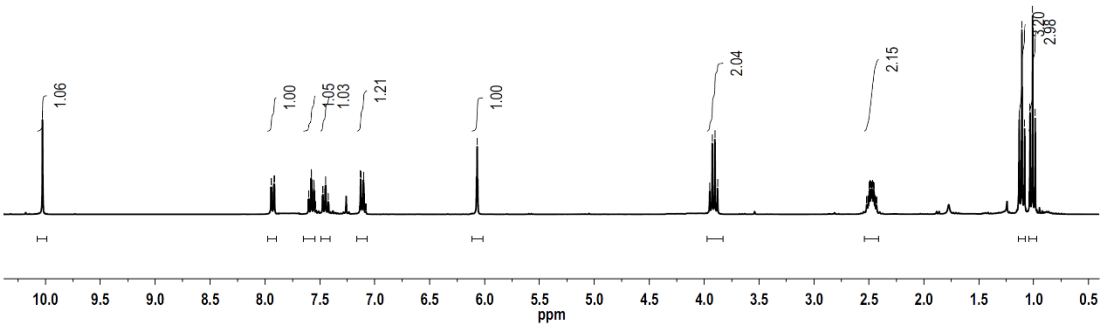
(**2l**)

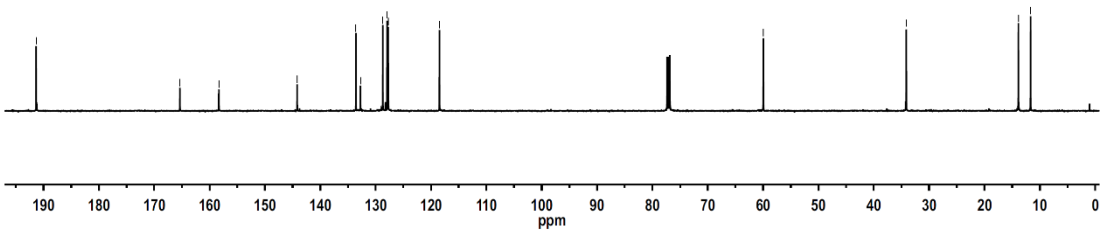

0.97
0.99
1.04
1.03
1.00
1.00
3.04
9.02
2.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

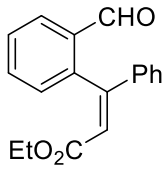

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


CHO
Et
EtO2C

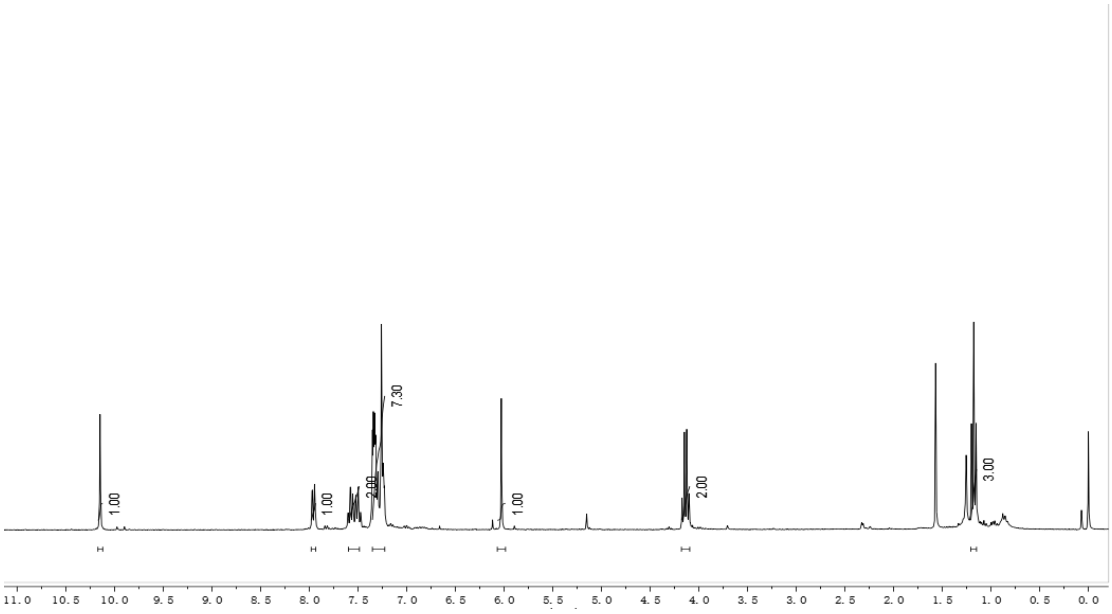
(**2m**)

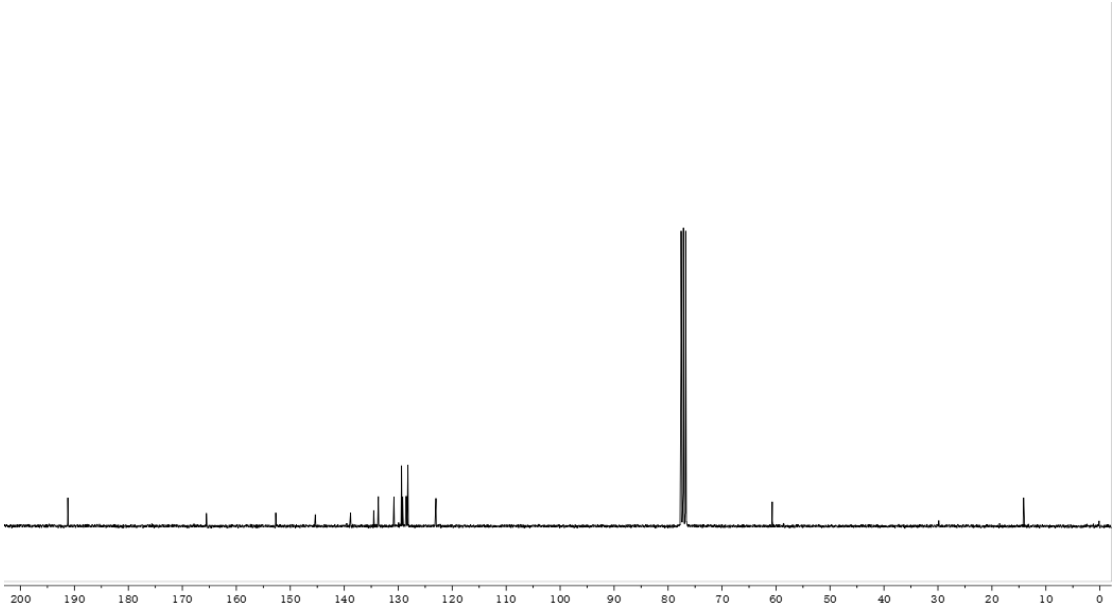

1.06
1.00
1.05
1.03
1.21
1.00
2.04
2.15
3.20
2.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

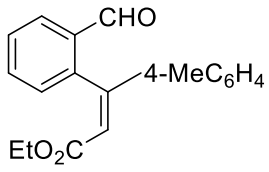

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



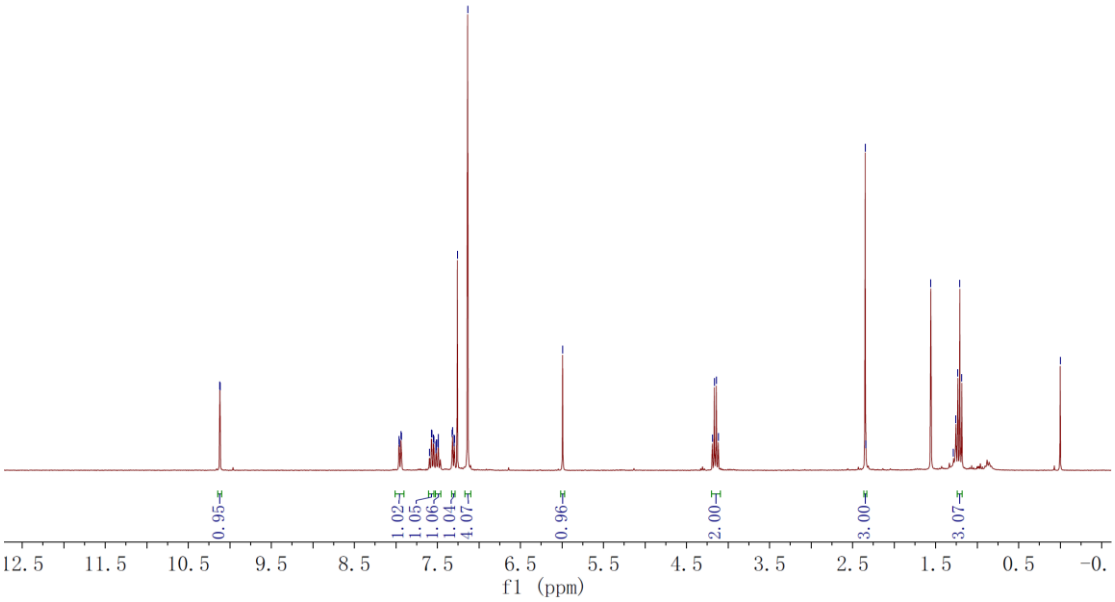
(2n)

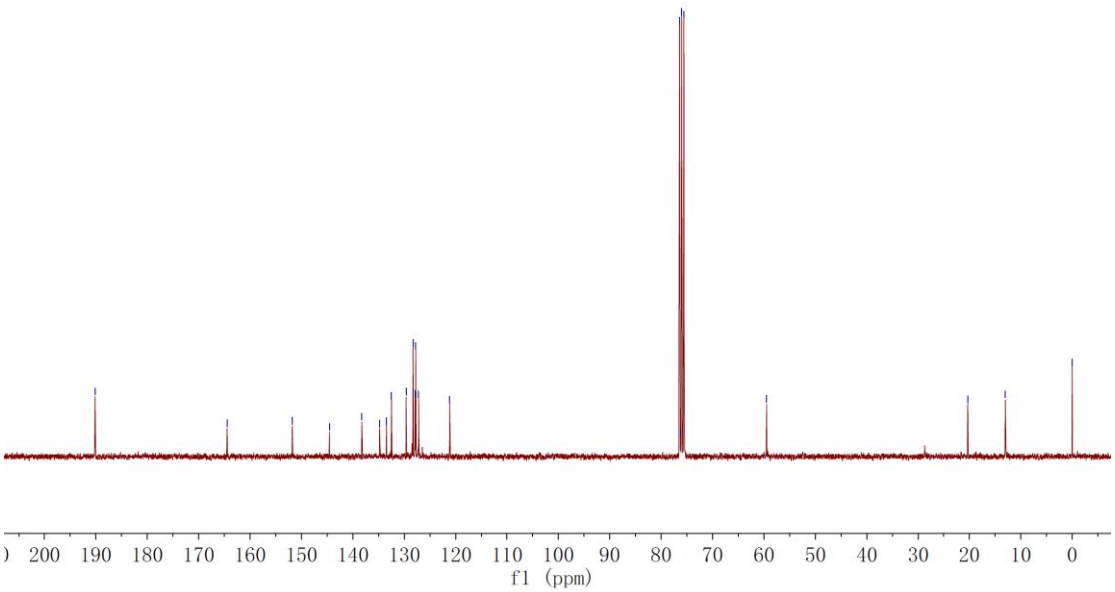


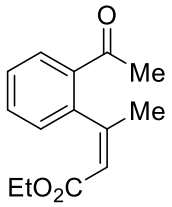



CHO
4-MeC6H4
EtO2C

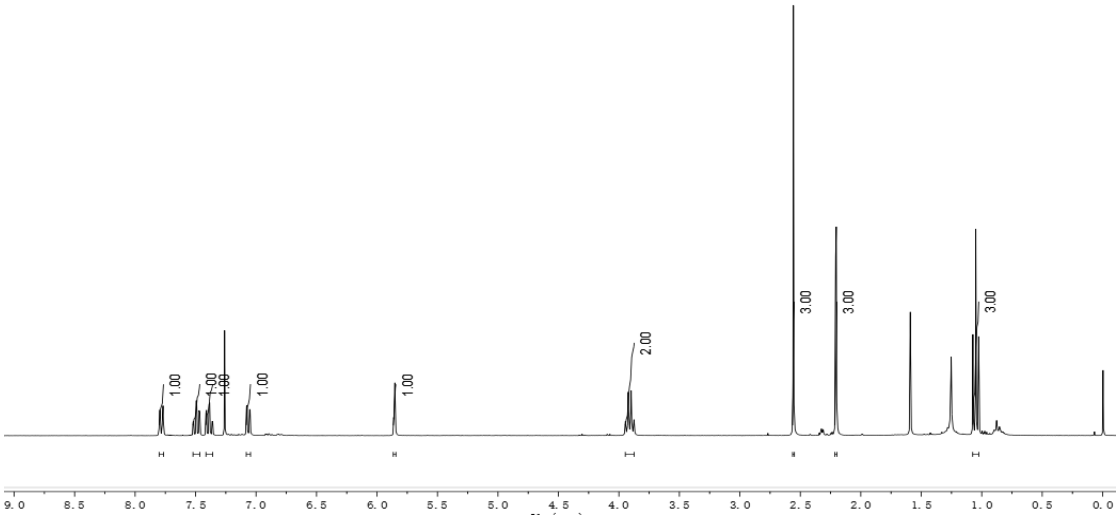
(**2o**)

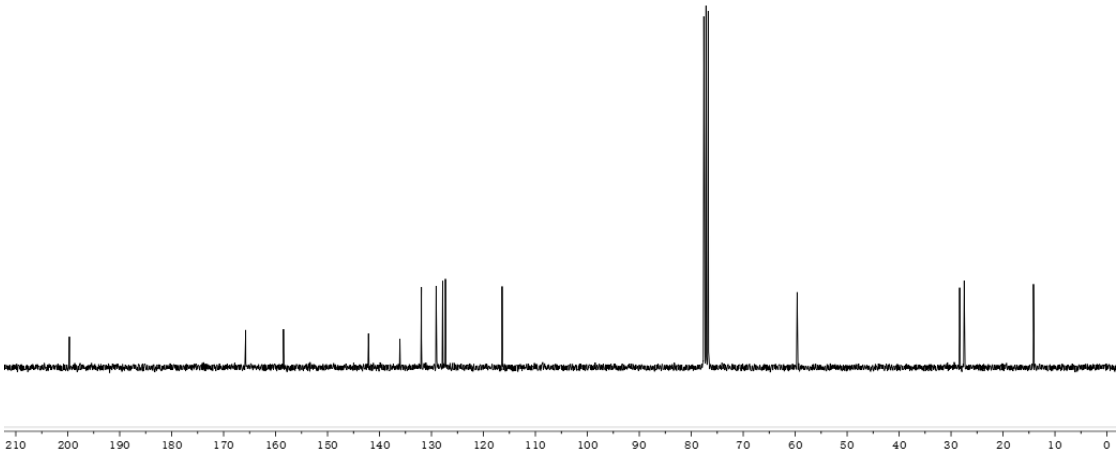

0.95
1.02
1.05
1.06
1.04
4.07
0.96
2.00
3.00
3.07
12.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.
f1 (ppm)

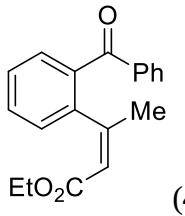

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
Me
Me
EtO2C

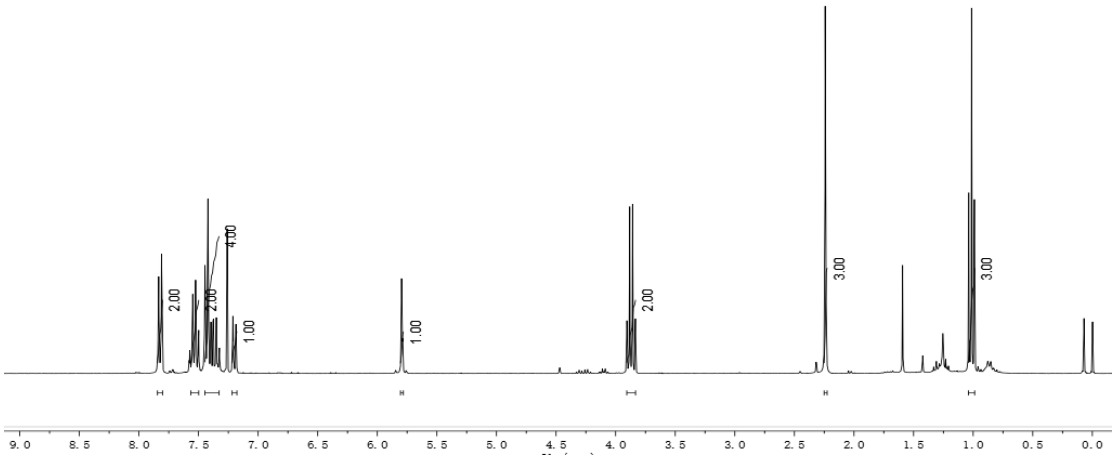
(**4a**)

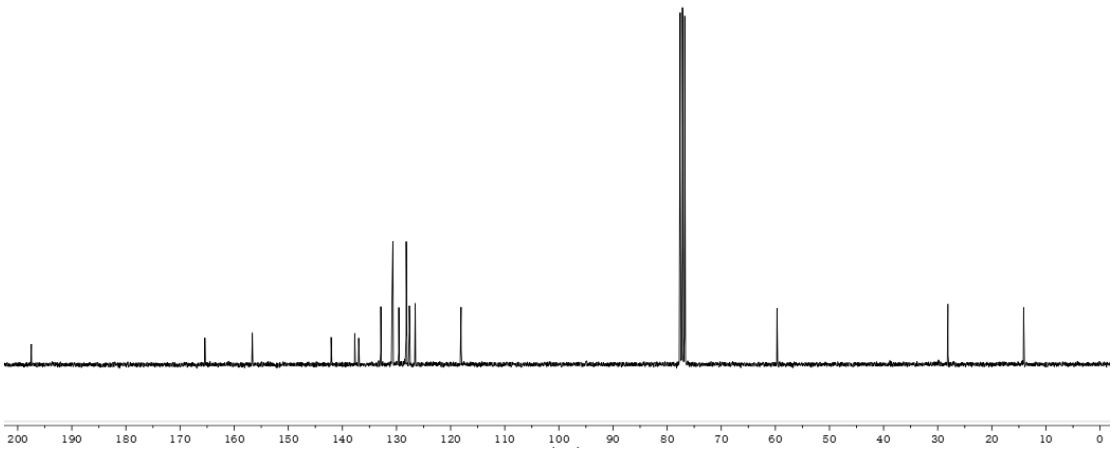

1.00
1.00
1.00
1.00
1.00
2.00
3.00
3.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

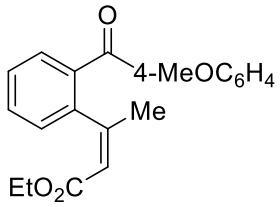

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



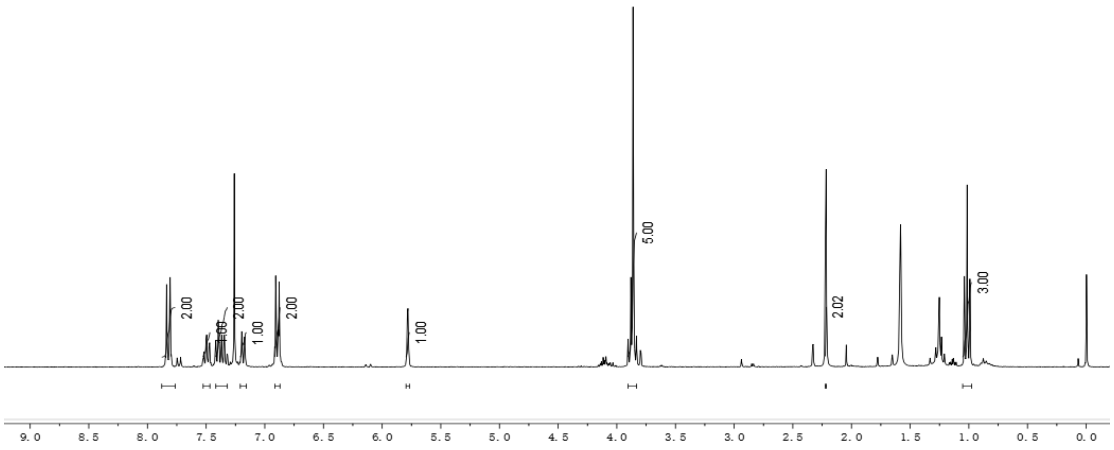
(**4b**)

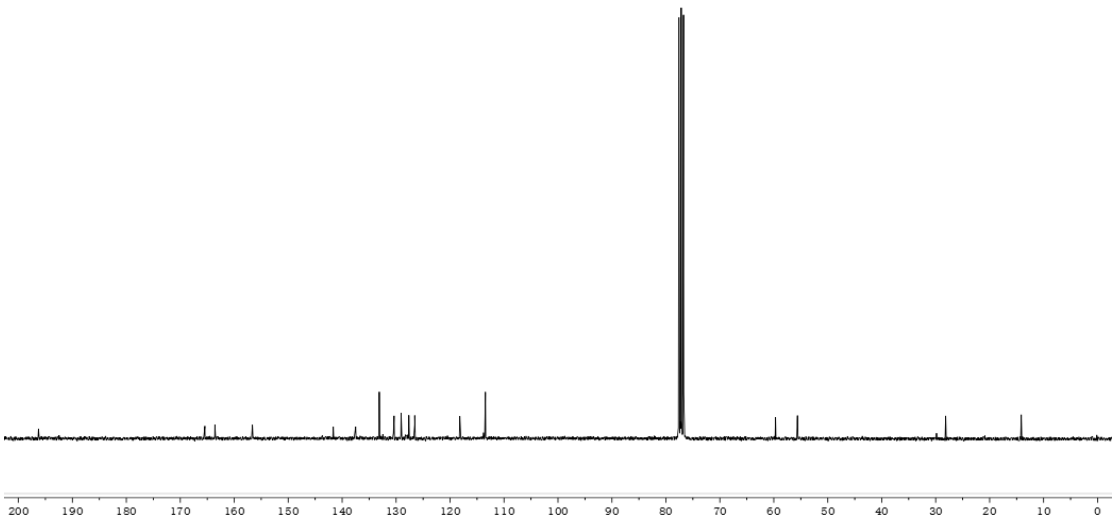


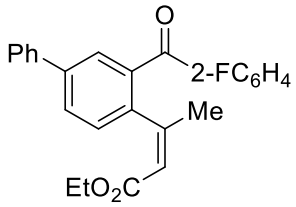



O
4-MeOC6H4
Me
EtO2C

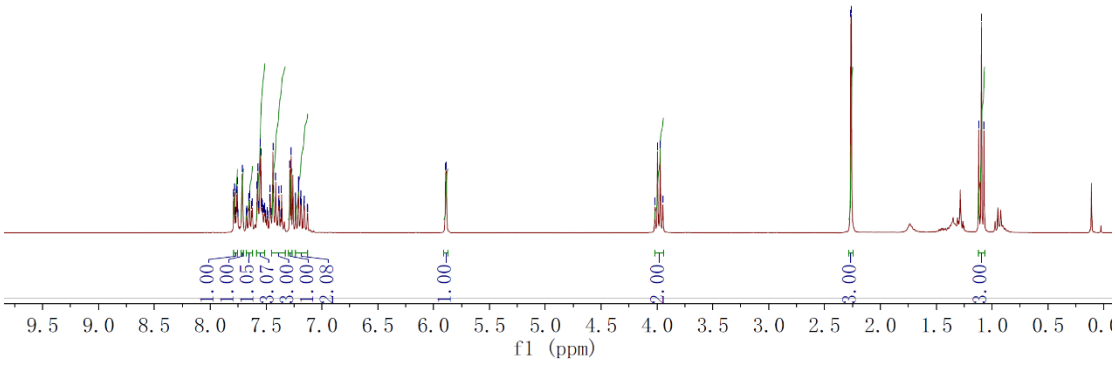
(**4c**)

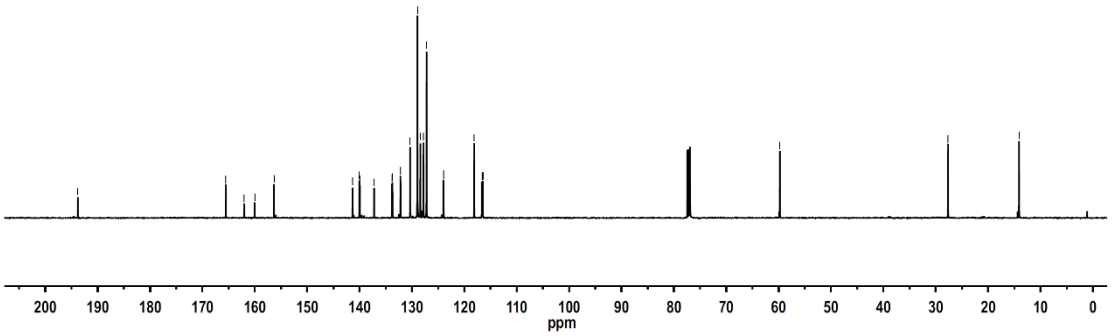

2.00
2.00
1.00
2.00
1.00
5.00
2.02
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

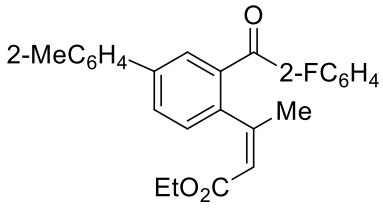

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


O
Ph
2-FC6H4
Me
EtO2C

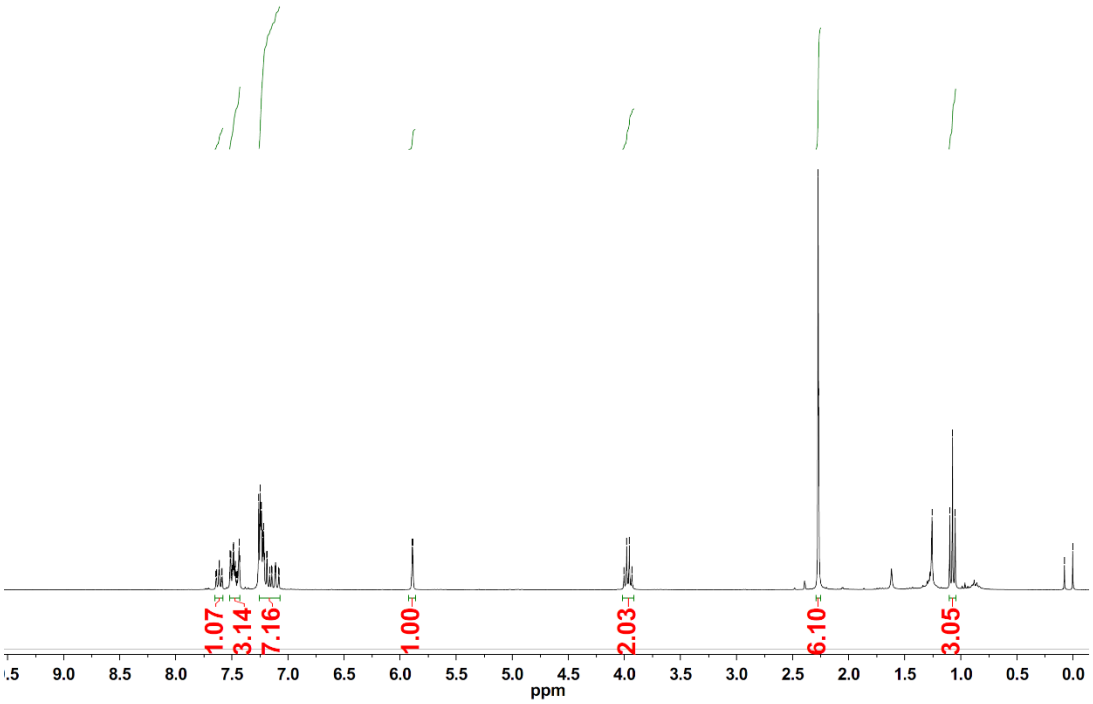
(**4d**)

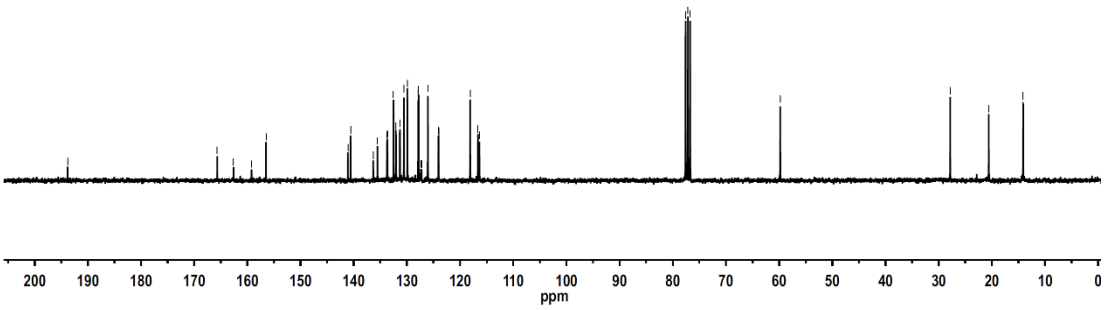

1.00
1.00
1.05
3.07
3.00
1.00
2.08
1.00
2.00
3.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

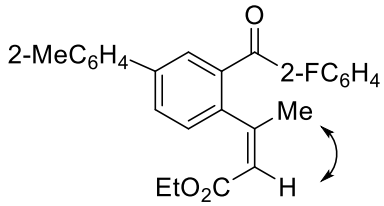

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


O
2-MeC6H4
2-FC6H4
Me
EtO2C

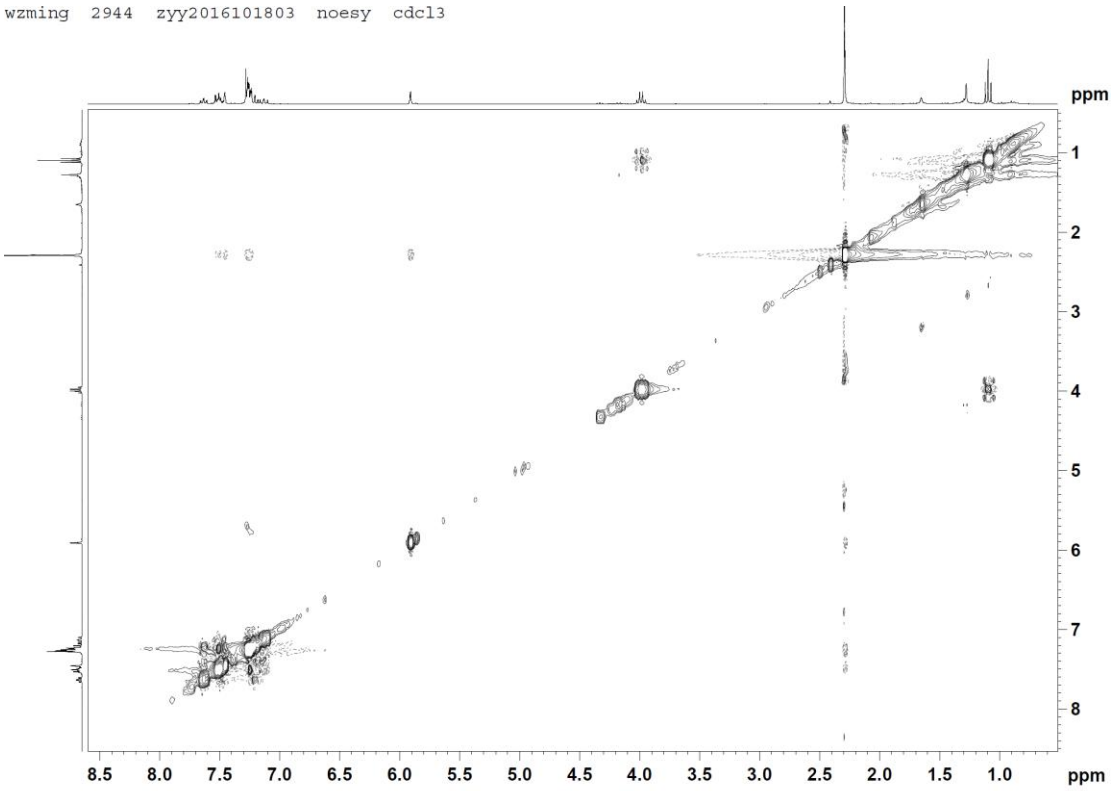
(**4e**)

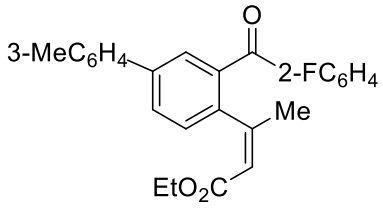

1.07
3.14
7.16
1.00
2.03
6.10
3.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

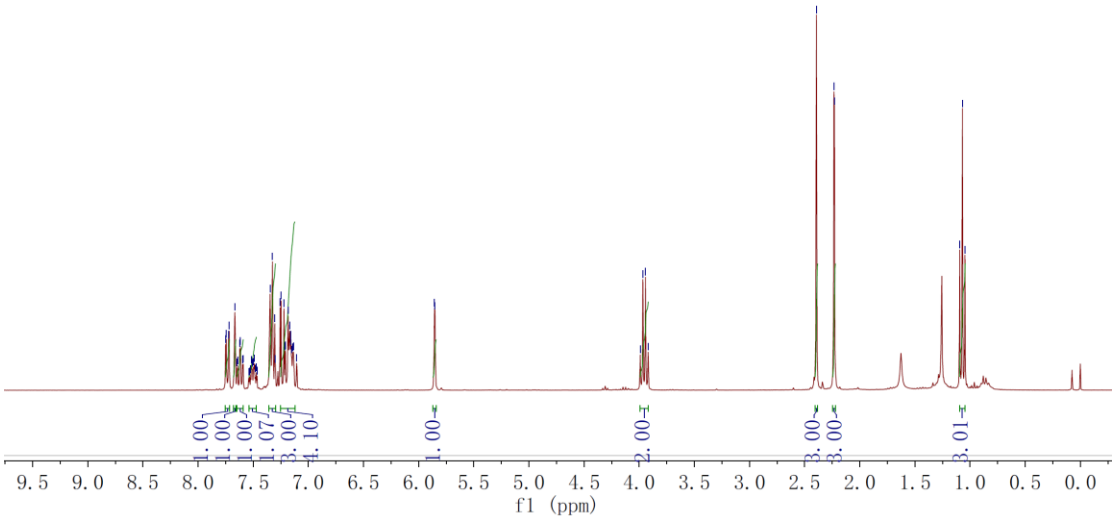


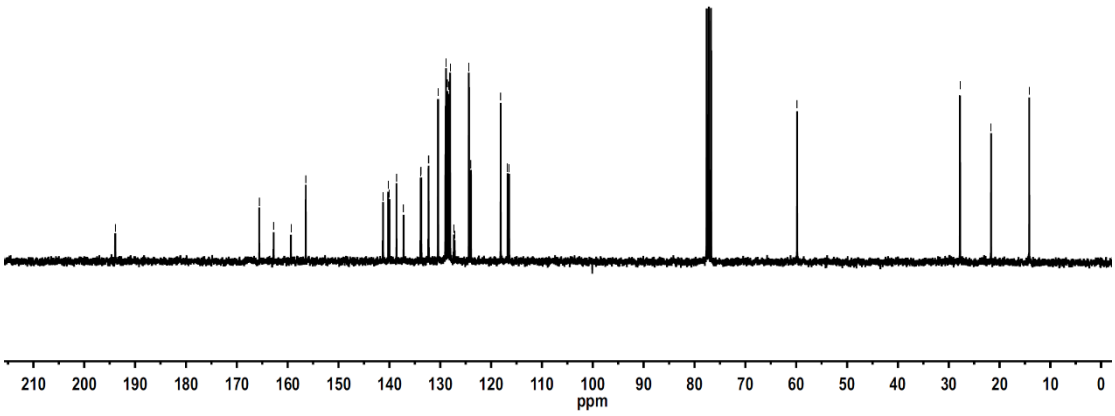
NOESY (δ 5.89 and 2.27)

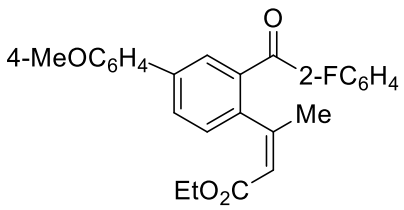



O
3-MeC6H4
2-FC6H4
Me
EtO2C

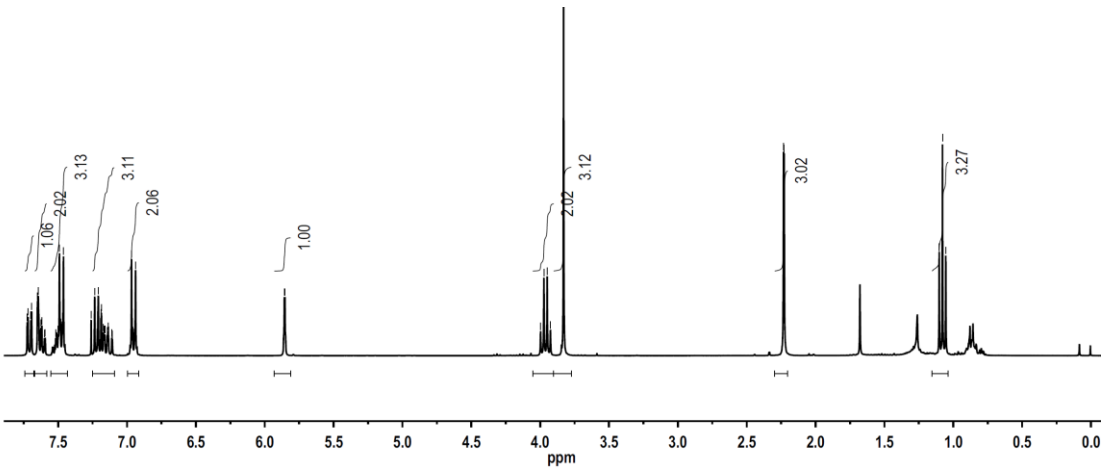
(**4f**)

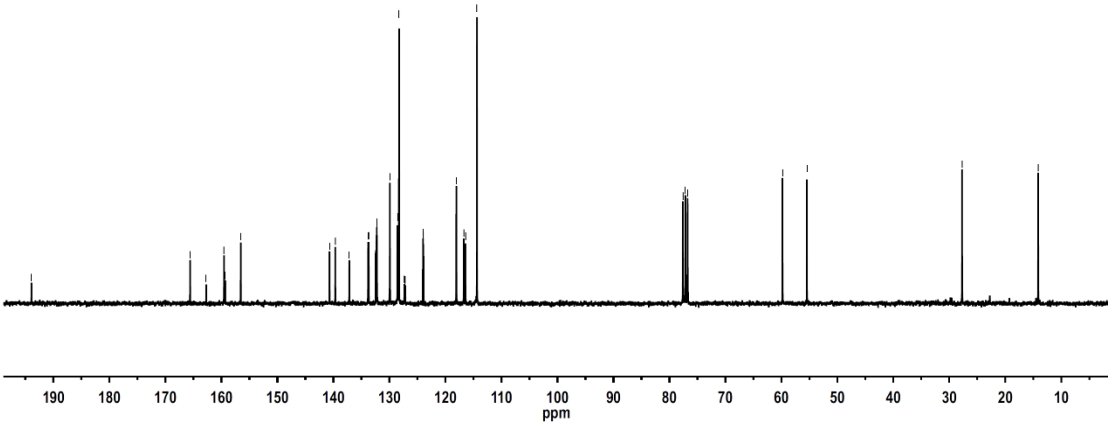

1.00
1.00
1.00
1.07
3.00
4.10
1.00
2.00
3.00
3.00
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

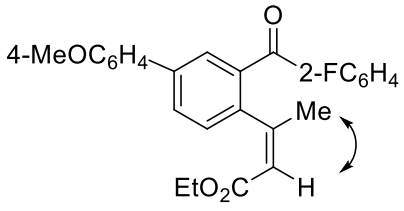

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


O
4-MeOC6H4
2-FC6H4
Me
EtO2C

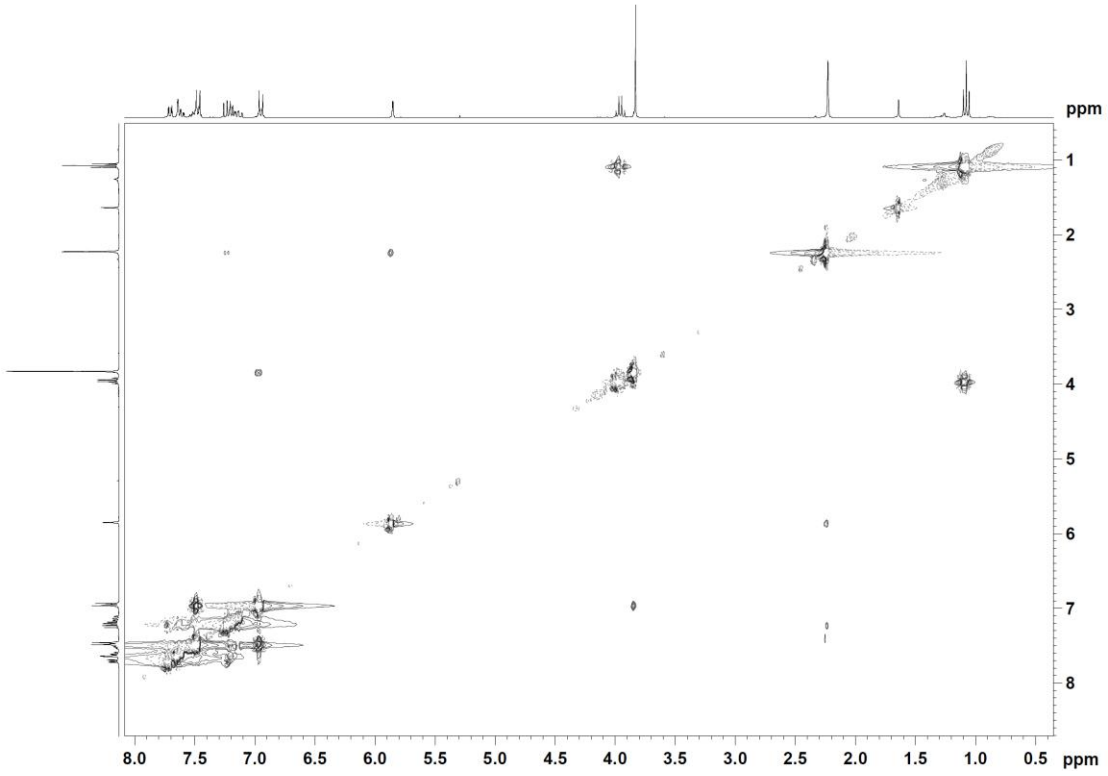
(**4g**)

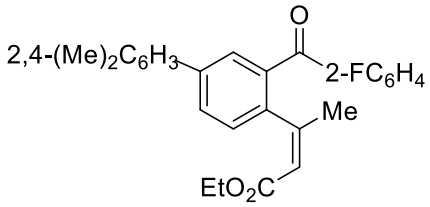

1.06
2.02
3.13
3.11
2.06
1.00
2.02
3.12
3.02
3.27
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

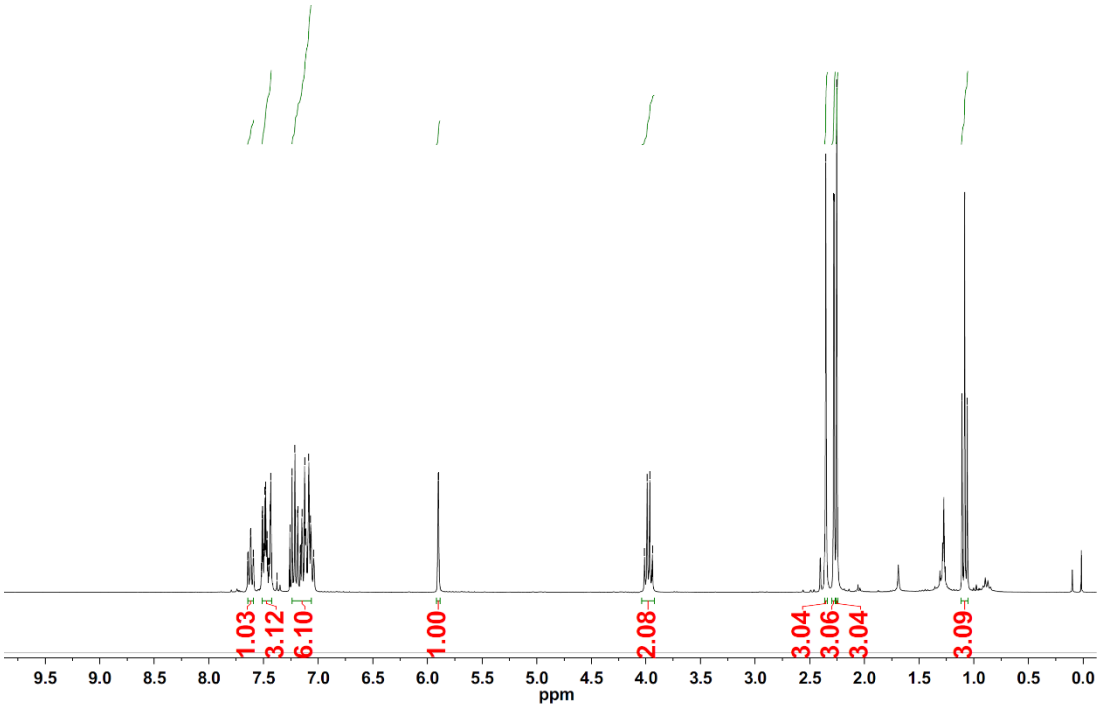


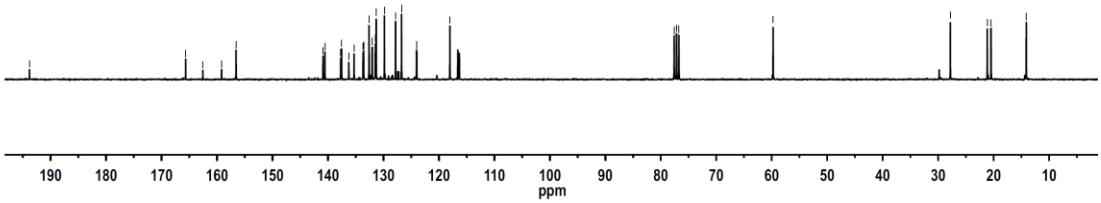
NOESY (δ 5.86 and 2.23)

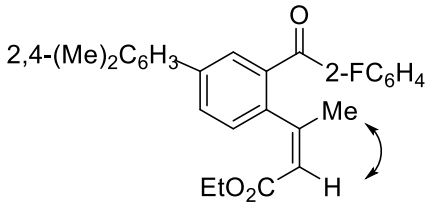



O
2,4-(Me)2C6H3
2-FC6H4
Me
EtO2C

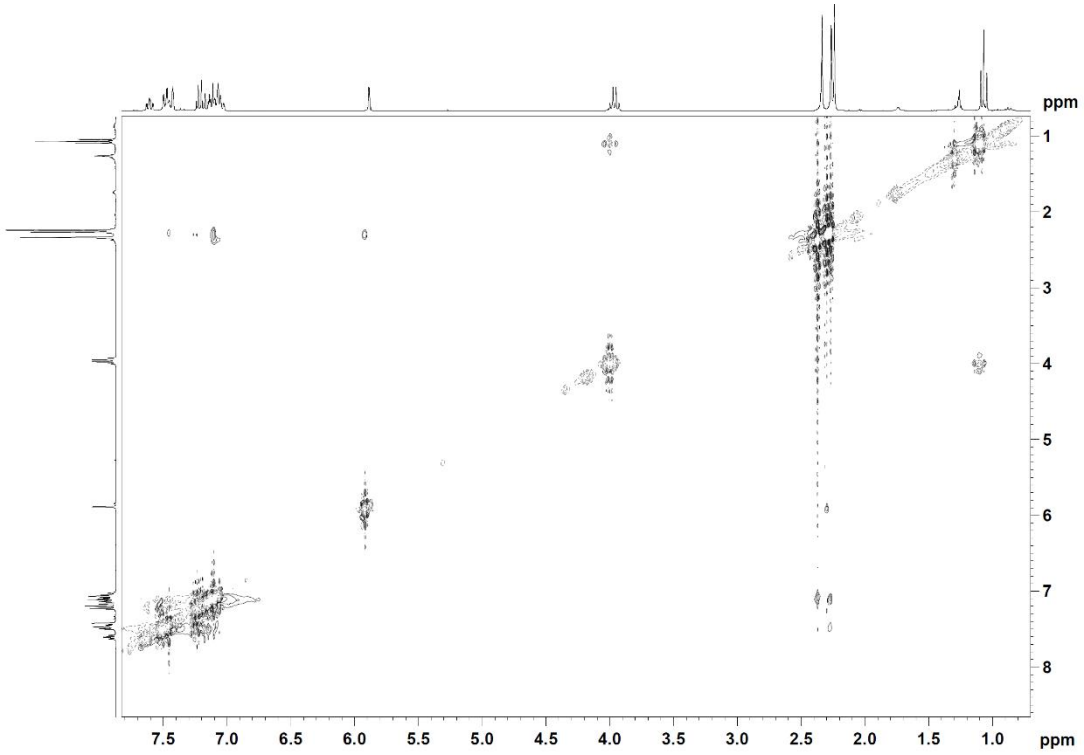
(**4h**)

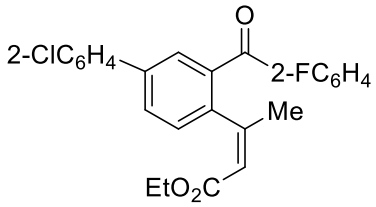

1.03
3.12
6.10
1.00
2.08
3.04
3.06
3.04
3.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

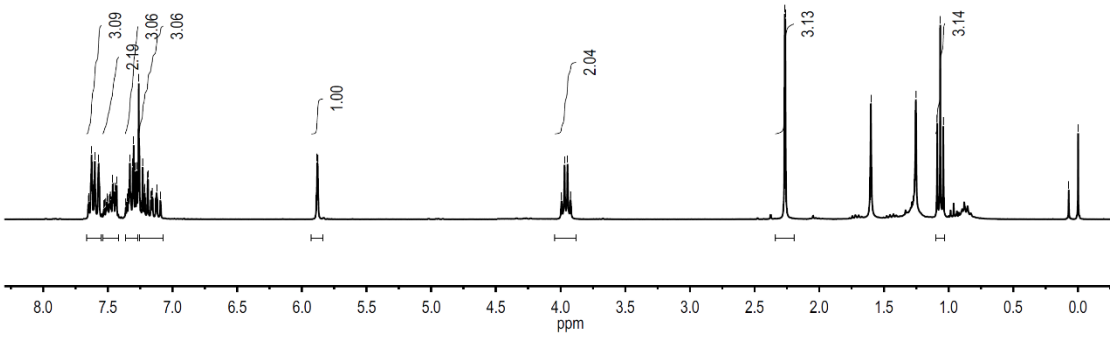


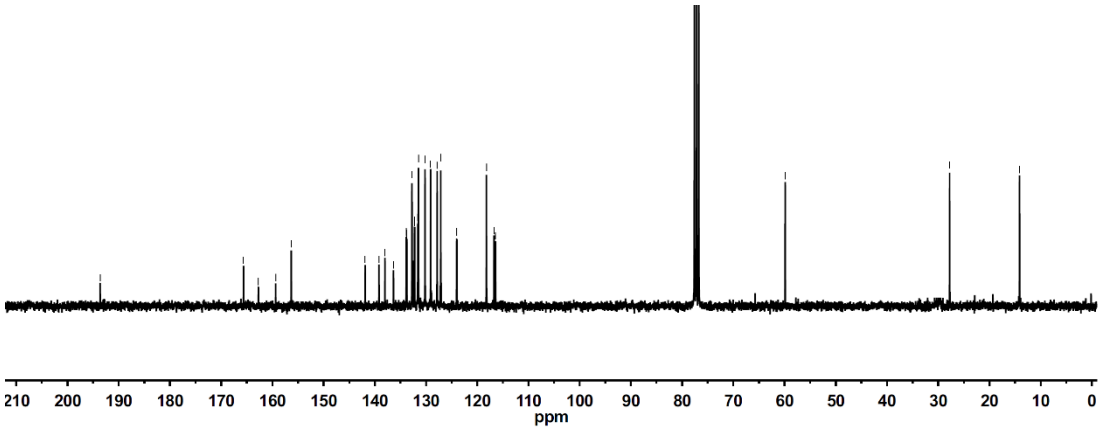
NOESY (δ 5.90 and 2.28)

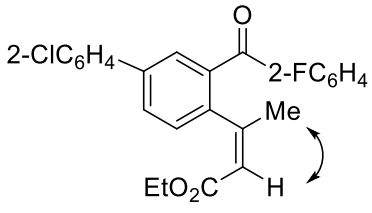



O
2-ClC6H4
2-FC6H4
Me
EtO2C

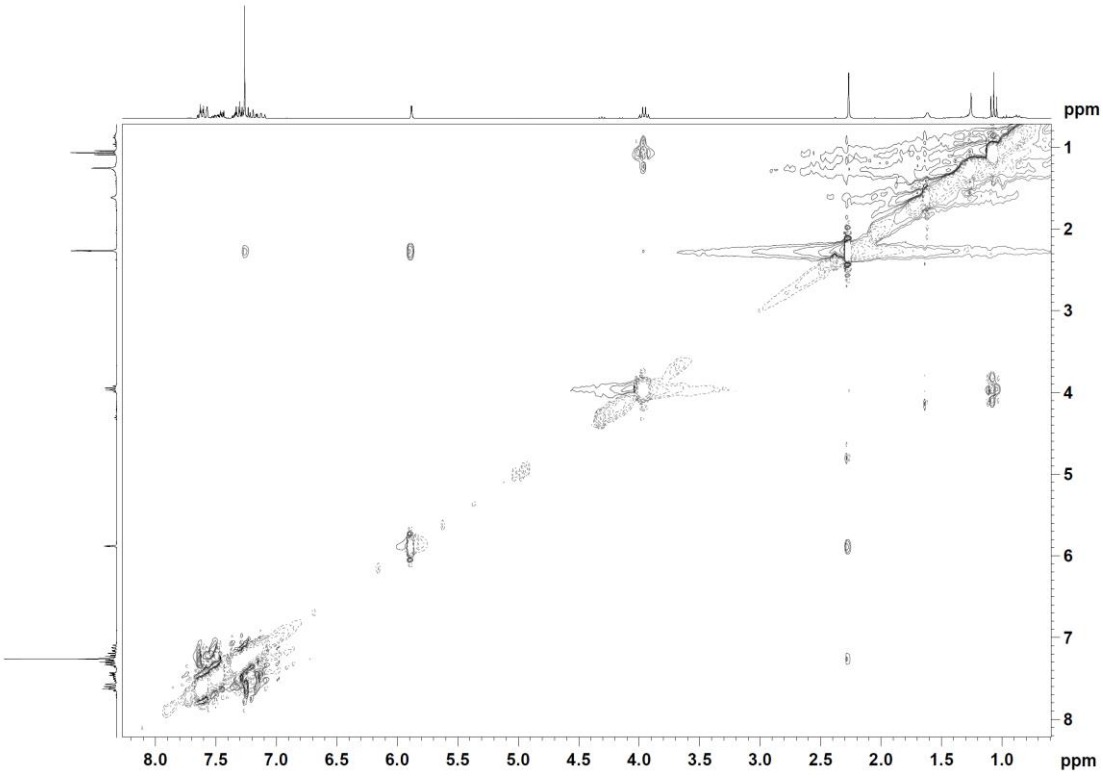
(**4i**)

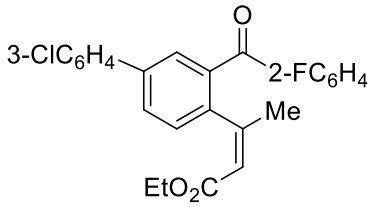

3.09
3.06
2.19
3.06
1.00
2.04
3.13
3.14
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


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

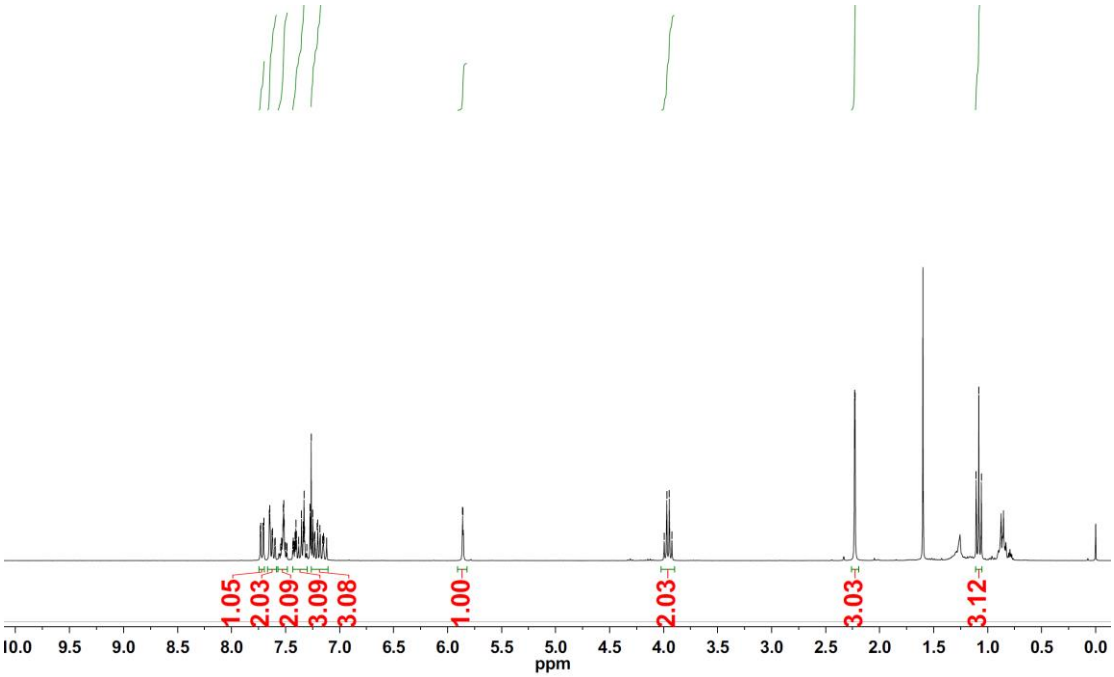


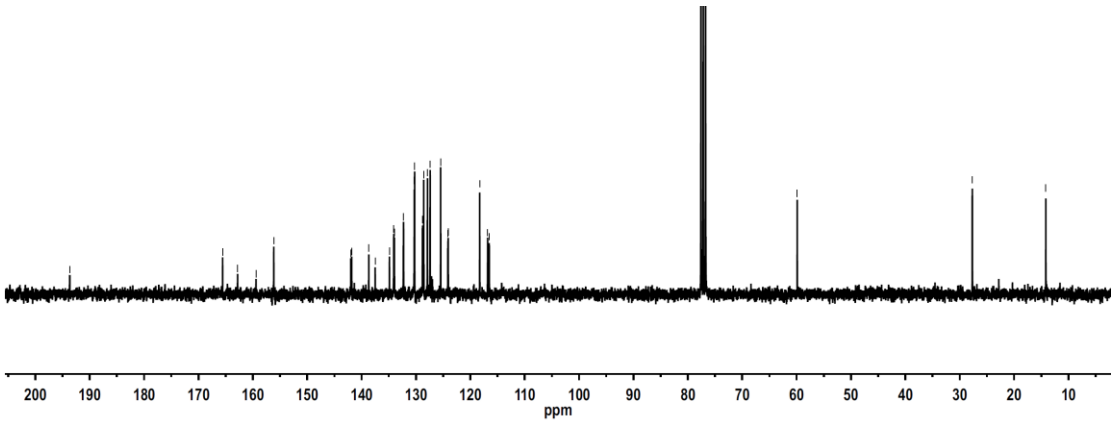
NOESY (δ 5.88 and 2.26)

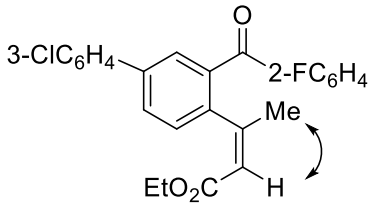



O
3-ClC6H4
2-FC6H4
Me
EtO2C

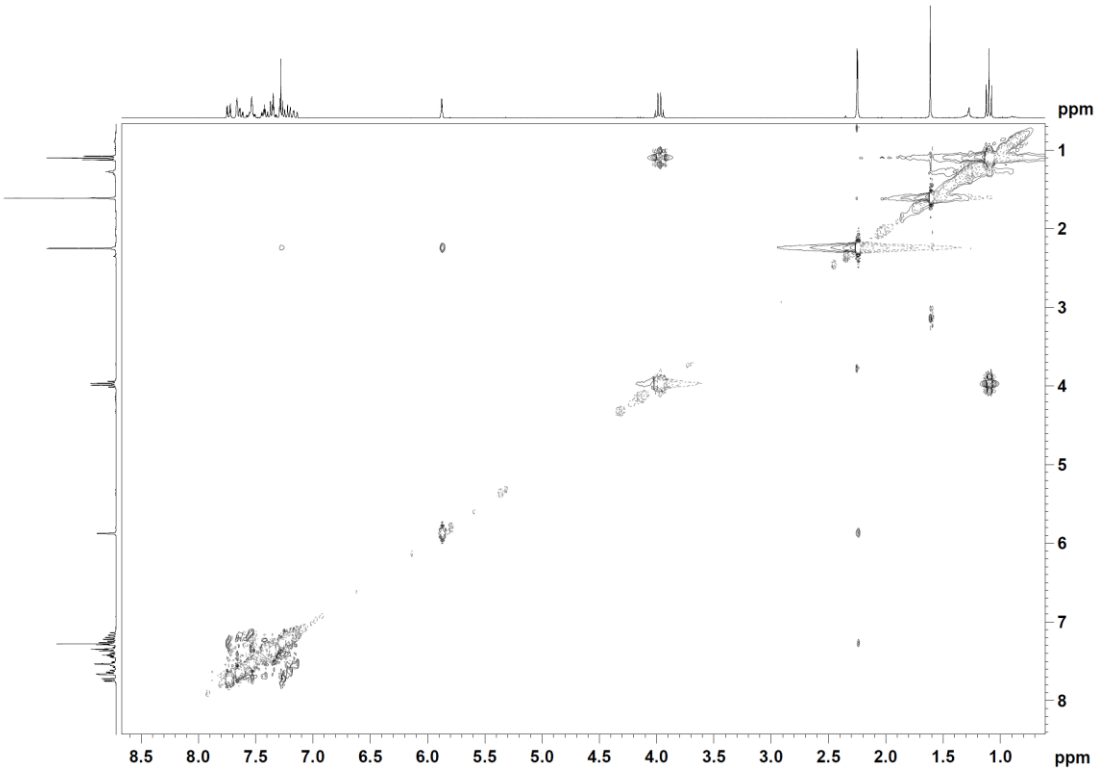
(**4j**)

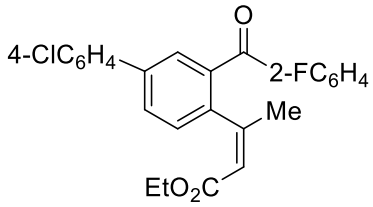

1.05
2.03
2.09
3.09
3.08
1.00
2.03
3.03
3.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

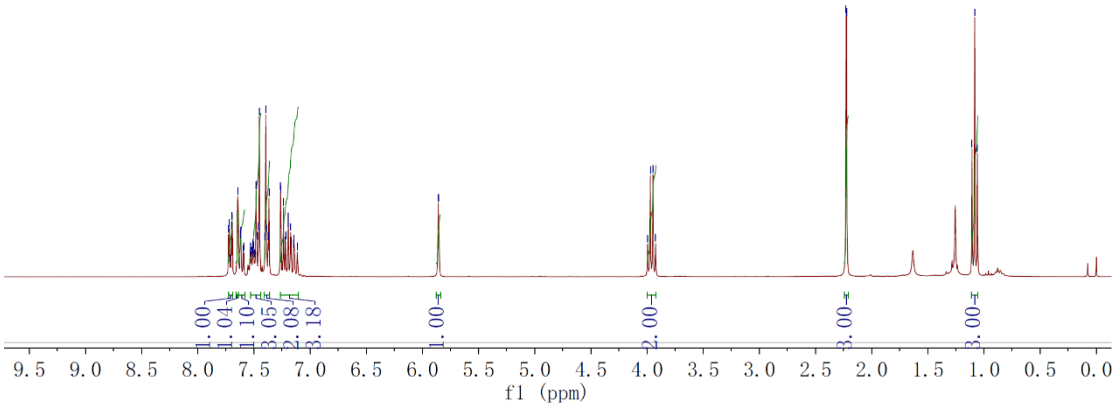


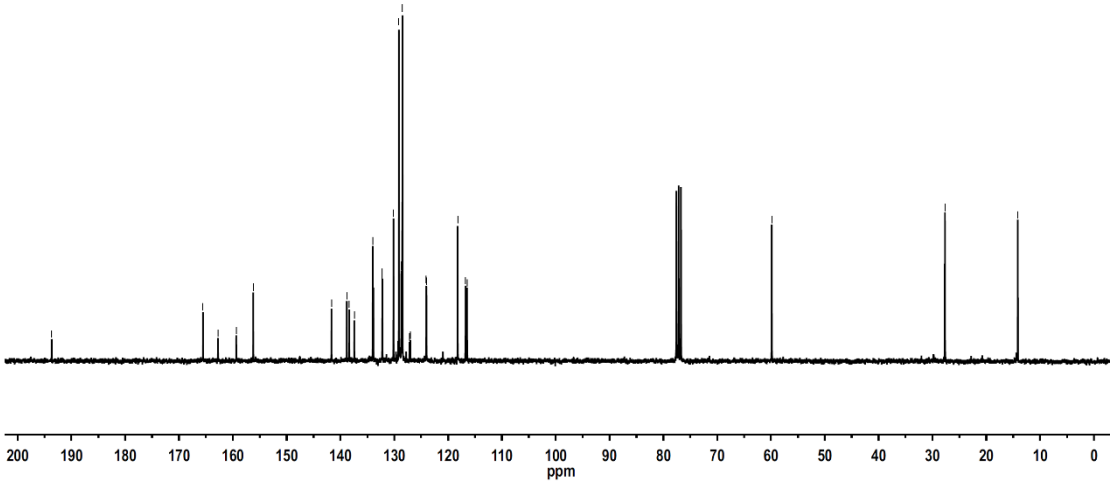
NOESY (δ 5.86 and 2.23)

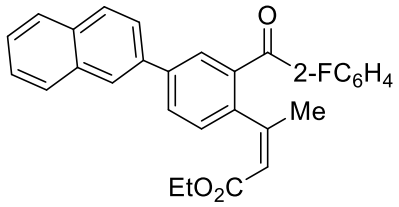



O
4-ClC6H4
2-FC6H4
Me
EtO2C

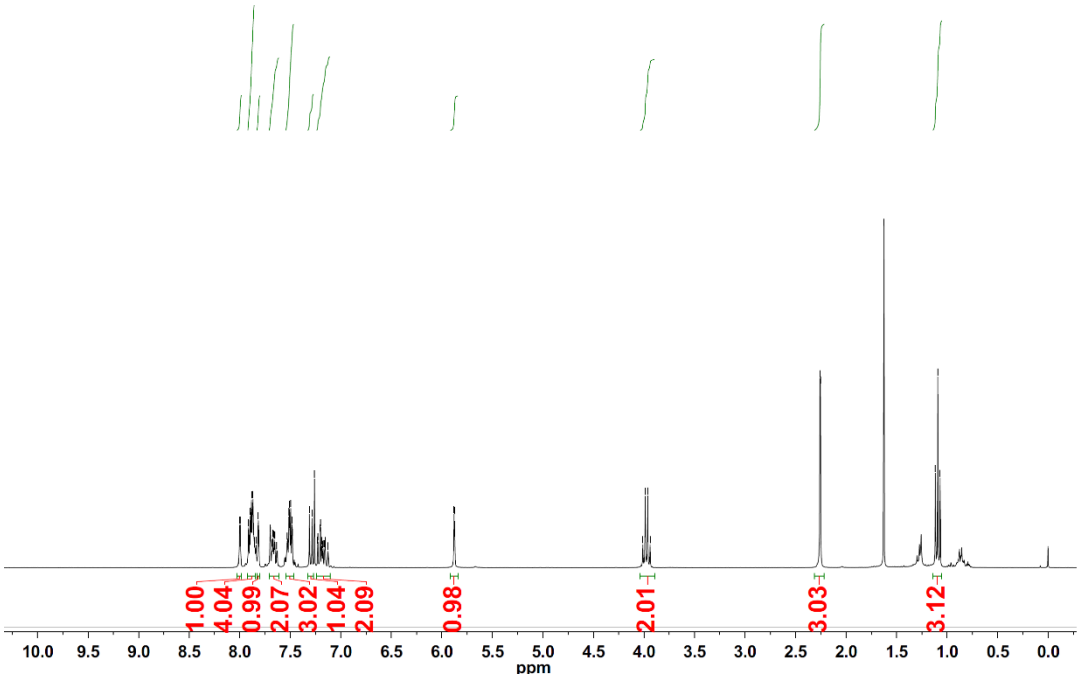
(4k)

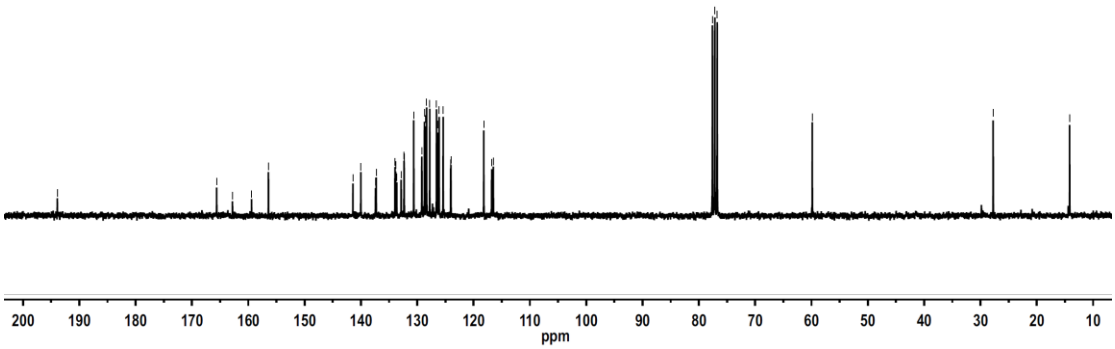

1.00
1.04
1.10
3.05
2.08
3.18
1.00
2.00
3.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

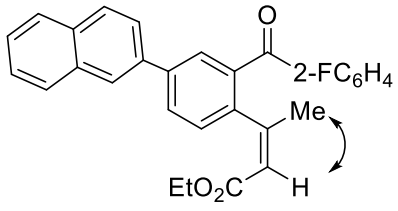

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


O
2-FC6H4
Me
EtO2C

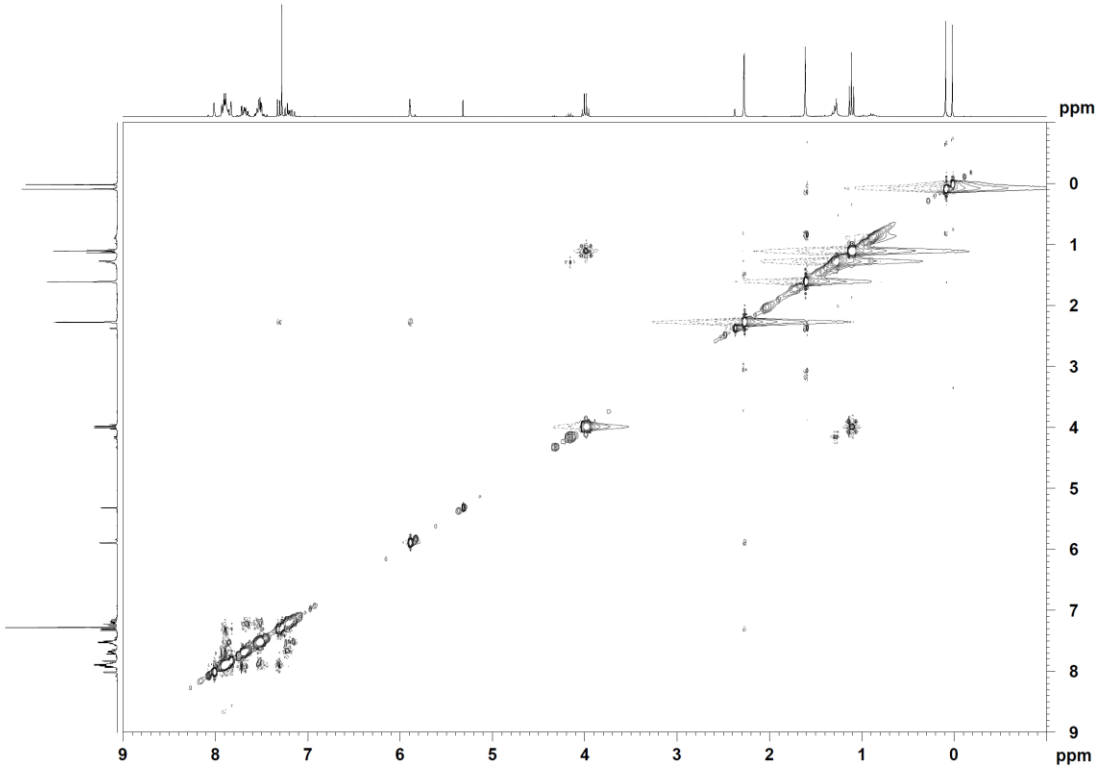
(**4l**)

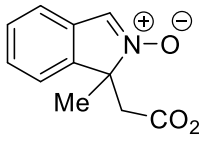

1.00
4.04
0.99
2.07
3.02
1.04
2.09
0.98
2.01
3.03
3.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

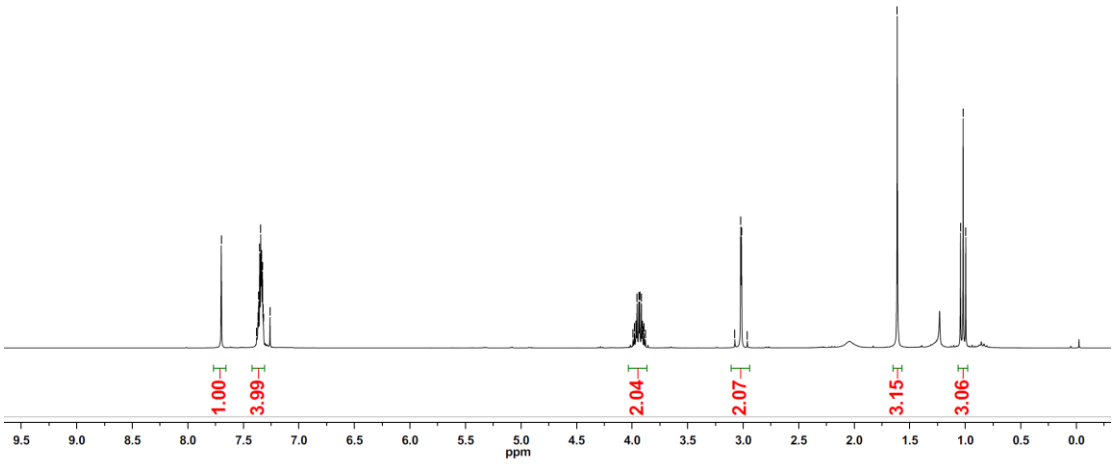


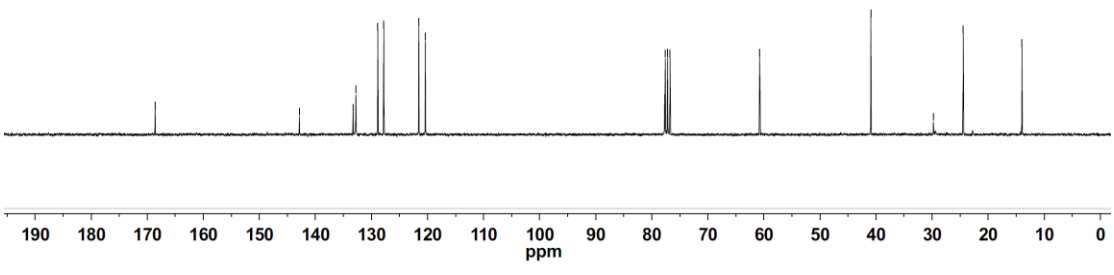
NOESY (δ 5.88 and 2.26)

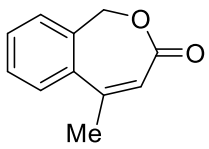



N–O
Me
CO2Et

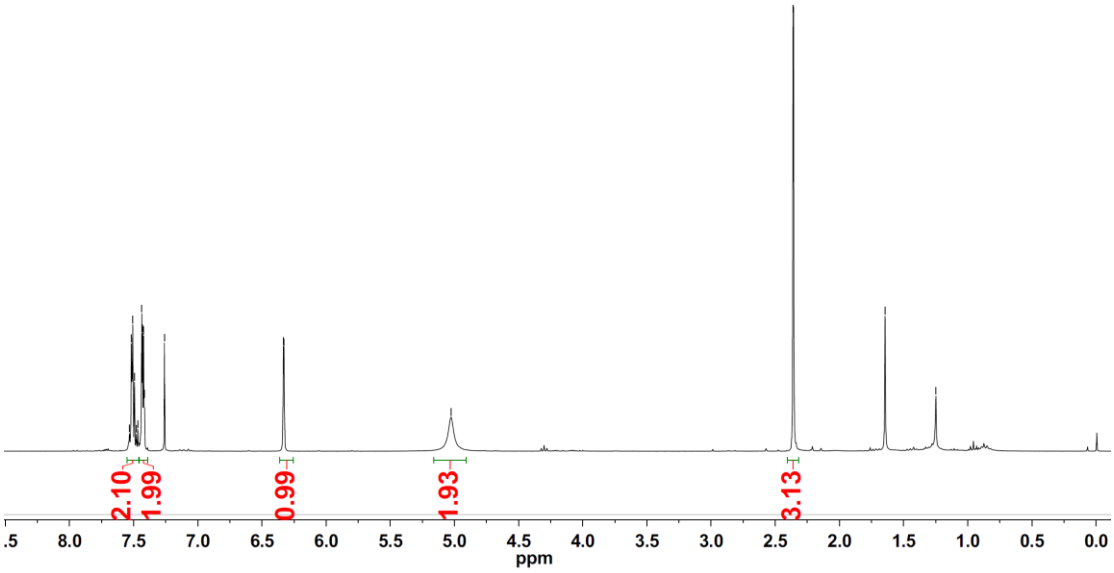
(5)

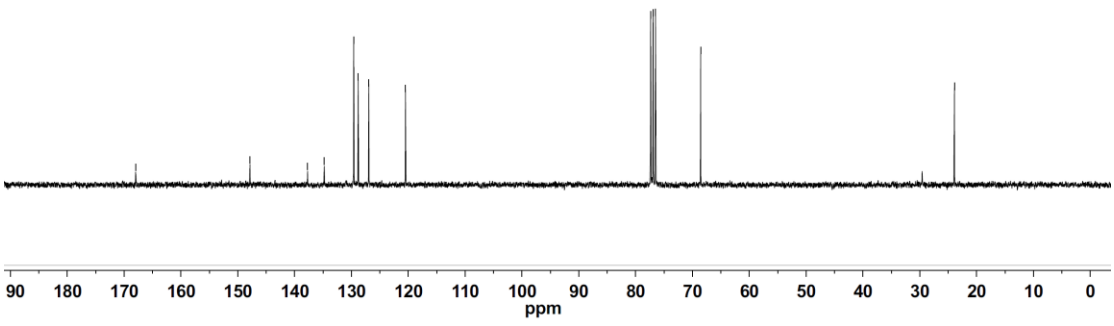

1.00
3.99
2.04
2.07
3.15
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


O
O
Me

(6)


2.10
1.99
0.99
1.93
3.13
.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
ppm


90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm