Organocatalyzed Trifunctionalization of Alkynyl 1,2-Diones for the Concise Synthesis of Acyloxy Allylidene Malonates and γ-Alkylidenebutenolides

Li Chen,[a,b] Shengtong Niu,[a] Shouang Lan,[a] Wenjun Liu,[a] Shuang Yang*[a] and Xinqiang Fang*[a]

[a]State Key Laboratory of Structural Chemistry, and Key Laboratory of Coal to Ethylene Glycol and Its Related Technology, Center for Excellence in Molecular Synthesis, Fujian Institute of Research on the Structure of Matter, University of Chinese Academy of Sciences, Fuzhou 350100, China.

[b]College of Chemistry and Materials Science, Fujian Normal University, Fuzhou 350007, China..

Table of Contents

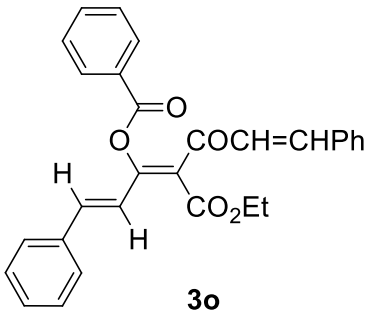
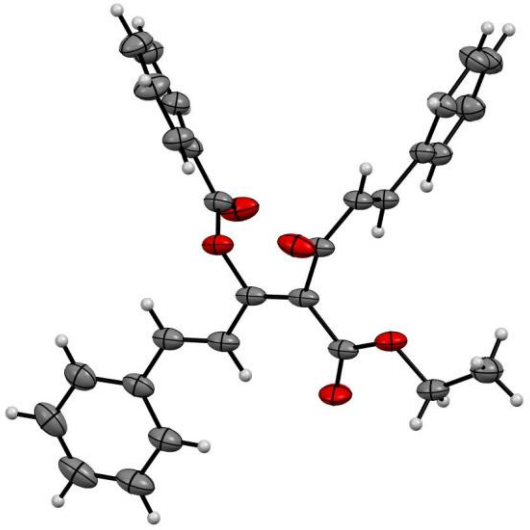
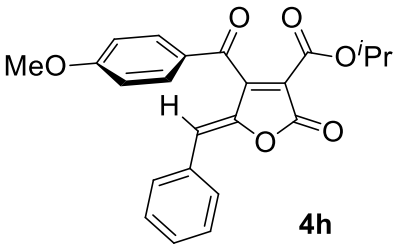
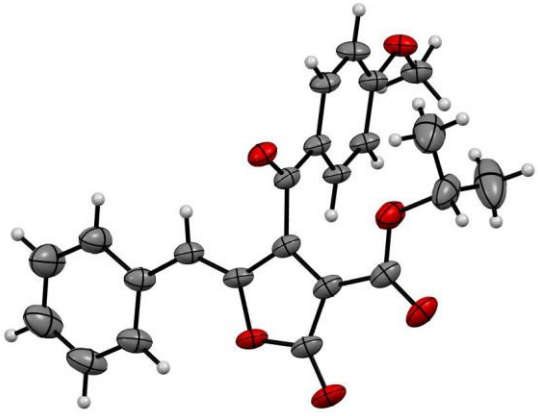
I. General Information.

Commercially available chemicals were directly used without further purification, unless otherwise mentioned, all experiments and manipulations involving air- or moisture-sensitive compounds were performed using standard Schlenk technique. All solvents were purified and dried using typical procedures. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker AVANCE III HD400 (400 MHz) and ECZ600S (600 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ = 0.00 ppm). ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets); m (multiplet), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker AVANCE III HD400 (101 MHz) and ECZ600S (151 MHz) spectrometers. High resolution mass spectral analysis (HRMS) was performed on Thermo Fisher Scientific Q Exactive Plus Hybrid Quadrupole-Orbitrap Mass Spectrometer. X-ray crystallography analysis was performed on Agilent Super Nova X-ray diffractionmeter. Analytical thin-layer chromatography (TLC) was carried out on WFH-203 F254 pre-coated silica gel plate

(0.2 mm thickness). Visualization was performed using a UV lamp or 2,4-Dinitrophenylhydrazine or potassium permanganate stain or phosphomolybdic acid.

II. X-ray crystallographic analysis

Method for single crystals cultivation: a pure solid sample (10−20 mg) was dissolved in dichloromethane/ethyl acetate/THF (1 mL) in a vial at room temperature, and petroleum ether/hexane (2 mL) was added into the above solution slowly while keeping the sample completely dissolved. The vial was properly sealed with parafilm and kept at room temperature to allow the slow evaporation of the solvents until a single crystal was obtained.

 **3o**	
 **4h**	

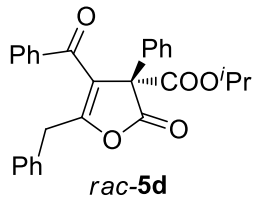
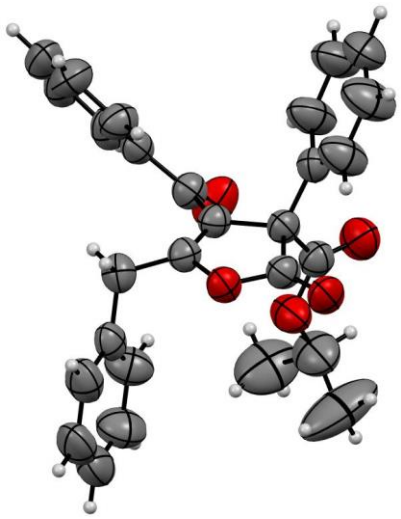
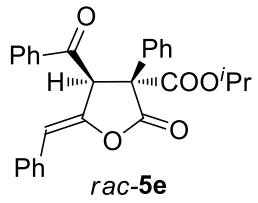
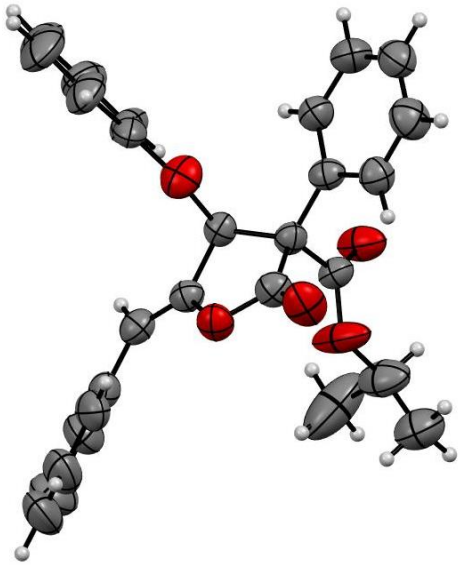
 *rac*-**5d**	
 *rac*-**5e**	

Table S1 Crystal data and structure refinement for 3o

Identification code	3o 2131560
Empirical formula	$C_{29}H_{24}O_5$
Formula weight	452.51
Temperature/K	149.98(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.1359(3)
b/Å	10.8744(3)
c/Å	12.1839(2)
α/°	83.076(2)
β/°	88.393(2)
γ/°	84.055(2)

Volume/Å^3	1195.00(6)
Z	2
ρ_{calc}g/cm^3	1.2575
μ/mm^{-1}	0.693
F(000)	477.6
Crystal size/mm^3	0.2 ×0.05 ×0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.3 to 148.48
Index ranges	-8 ≤ h ≤ 11, -13 ≤ k ≤ 13, -14 ≤ l ≤ 15
Reflections collected	12060
Independent reflections	4710 [R_{int} = 0.0544, R_{sigma} = 0.0501]
Data/restraints/parameters	4710/0/308
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0510, wR_2 = 0.1428
Final R indexes [all data]	R_1 = 0.0558, wR_2 = 0.1498
Largest diff. peak/hole / e Å^{-3}	0.21/-0.29

Table S2 Crystal data and structure refinement for 4h

Identification code	4h 2131561
Empirical formula	$C_{23}H_{20}O_6$
Formula weight	392.39
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	Pccn
a/Å	12.0593(7)
b/Å	16.1161(10)
c/Å	20.7106(9)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4025.1(4)
Z	8
ρ_{calc}g/cm^3	1.295
μ/mm^{-1}	0.494
F(000)	1648.0
Crystal size/mm^3	0.2 ×0.2 ×0.2
Radiation	GaKα (λ = 1.3414)
2Θ range for data collection/°	7.428 to 122.024
Index ranges	-15 ≤ h ≤ 15, -19 ≤ k ≤ 20, -22 ≤ l ≤ 26
Reflections collected	52295
Independent reflections	4591 [R_{int} = 0.0705, R_{sigma} = 0.0298]
Data/restraints/parameters	4591/0/266
Goodness-of-fit on F^2	1.070
Final R indexes [I>=2σ (I)]	R_1 = 0.0670, wR_2 = 0.1843
Final R indexes [all data]	R_1 = 0.0804, wR_2 = 0.2027

Largest diff. peak/hole / e $Å^{-3}$	0.41/-0.29

Table S3 Crystal data and structure refinement for 5d

Identification code	5d 2131562
Empirical formula	$C_{28}H_{24}O_5$
Formula weight	440.47
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	Pbca
a/Å	16.277(3)
b/Å	14.959(3)
c/Å	19.366(4)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	4715.6(16)
Z	8
$\rho_{calc}g/cm^3$	1.241
μ/mm^{-1}	0.085
F(000)	1856.0
Crystal size/mm^3	0.3 × 0.25 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.206 to 55.118
Index ranges	$-19 \le h \le 21$, $-19 \le k \le 19$, $-25 \le l \le 24$
Reflections collected	66511
Independent reflections	5394 [R_{int} = 0.0564, R_{sigma} = 0.0222]
Data/restraints/parameters	5394/268/300
Goodness-of-fit on F^2	1.004
Final R indexes [I>=2σ (I)]	R_1 = 0.0931, wR_2 = 0.1925
Final R indexes [all data]	R_1 = 0.1053, wR_2 = 0.2006
Largest diff. peak/hole / e $Å^{-3}$	0.35/-0.24

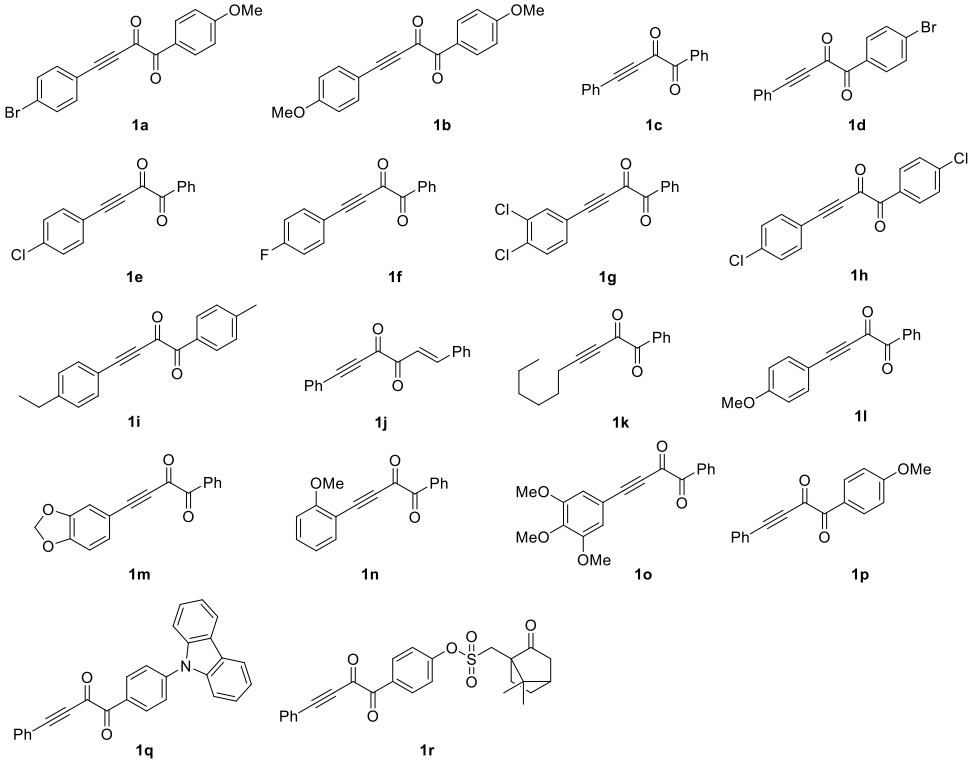
Table S4 Crystal data and structure refinement for 5e

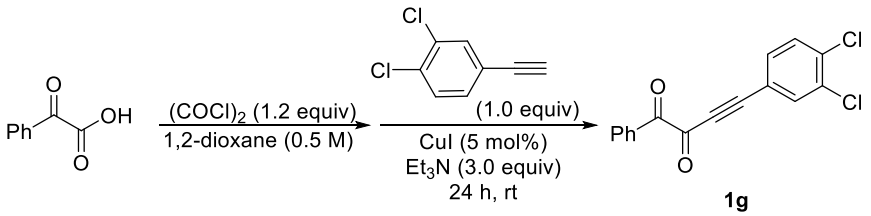
Identification code	5e 2131563
Empirical formula	$C_{28}H_{24}O_5$
Formula weight	440.47
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	20.333(4)
b/Å	6.4811(13)
c/Å	35.365(7)
α/°	90
β/°	90
γ/°	90

Volume/Å^3	4660.4(16)
Z	8
ρ_{calc}g/cm^3	1.256
μ/mm^{-1}	0.086
F(000)	1856.0
Crystal size/mm^3	0.3 ×0.25 ×0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.304 to 48.33
Index ranges	-23 ≤ h ≤ 23, -6 ≤ k ≤ 7, -33 ≤ l ≤ 40
Reflections collected	42005
Independent reflections	6627 [R_{int} = 0.1130, R_{sigma} = 0.0410]
Data/restraints/parameters	6627/1/600
Goodness-of-fit on F^2	1.119
Final R indexes [I>=2σ (I)]	R_1 = 0.0592, wR_2 = 0.1427
Final R indexes [all data]	R_1 = 0.0738, wR_2 = 0.1542
Largest diff. peak/hole / e Å^{-3}	0.38/-0.28

III. Typical procedure for the substrate synthesis

Substrates **1a**–**1f**, **1h**–**1l**, **1p** and **1q** are known compounds and were prepared according to the literature reports. [1-4]

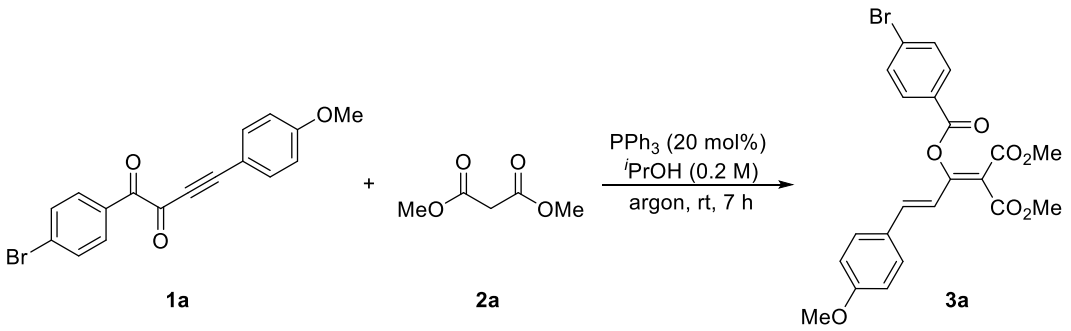




1g

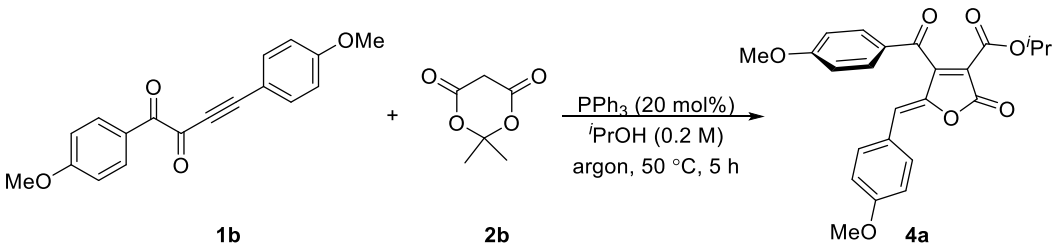
In a 50 mL of round bottom flask, phenylglyoxylic acid (10.0 mmol) was dissolved in 20 mL of 1,4-dioxane. To this solution oxalyl chloride (12.0 mmol, 1.2 equiv) was added dropwise to the reaction mixture at room temperature and the mixture was stirred at 50 ℃ for 4 h. Then the mixture was cooled to room temperature. CuI (95 mg, 0.50 mmol, 5 mol%), 1,2-dichloro-4-ethynylbenzene (10.0 mmol, 1 equiv), and dry triethylamine (30.0 mmol, 3 equiv) were successively added to the mixture, and stirring at room temperature was continued for 24 h. After complete conversion, water (50 mL) was added and the mixture was extracted with CH_2Cl_2 (2 × 15 mL). Drying of the organic phase with anhydrous Na_2SO_4 and subsequent evaporation gave crude products. The crude products were purified through a silica gel column using petroleum ether-ethyl acetate mixture (95:5 v/v) as eluent to obtain **1g** (1.7g, 56% yield). substrates **1g** ,**1m**−**1o**, **1r** were synthesized using the same method.

IV. Typical procedures for the reaction.



1a **2a** **3a**

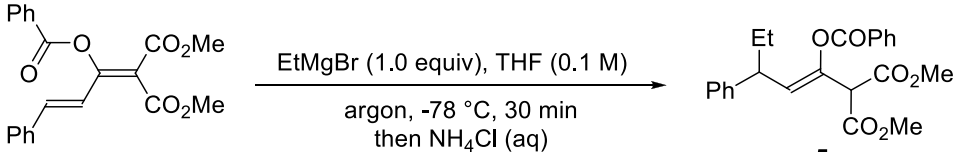
1a (68 mg, 0.2 mmol), **2a** (70 uL, 0.6 mmol), and Ph_3P (10.6 mg, 0.04 mmol) was add to ^{i}PrOH (1 mL) at room temperature under argon atmosphere. The reaction system was stirred for 7 h. the solvent was removed under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, v:v = 5:1) to give the product **3a** (72 mg, 76% yield). Compounds **3b**−**3q** were synthesized using the same method.



1b 2b 4a

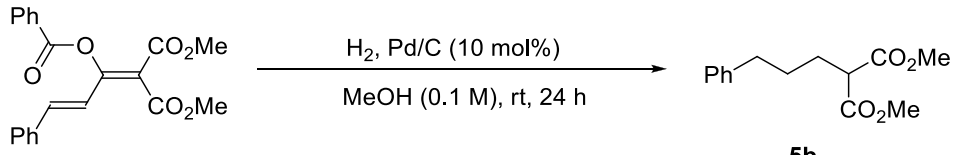
1b (59 mg, 0.2 mmol), **2b** (86 mg, 0.6 mmol), and Ph_3P (10.6 mg, 0.04 mmol) was add to ^{i}PrOH (1 mL) at 50 ^{o}C under argon atmosphere. The reaction system was stirred for 5 h. the solvent was removed under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, v:v = 3:1) to give the product **4a** (61 mg, 72% yield). Compounds **4b**−**4q** were synthesized using the same method.

V. Procedures for the product derivatizations.



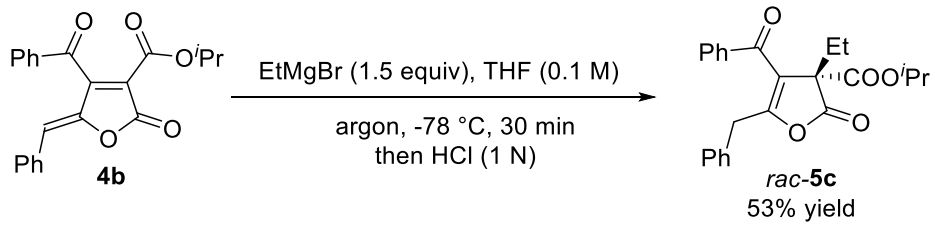
3b *rac*-**5a** 82% yield

3b (37 mg, 0.1 mmol) was dissolved in THF (1 mL) and the solution was cooled down to -78 ^{o}C. EtMgBr (0.1 mL, 0.1 mmol, 1 M in THF) was added. The reaction mixture was stirred at -78 ^{o}C for 30 minutes. The mixture was quenched by saturated aqueous NH_4Cl and extracted with ethyl acetate (3×5 mL). The organic solvent was removed under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, v:v = 5:1) to give the product **5a** (33 mg, 82% yield).

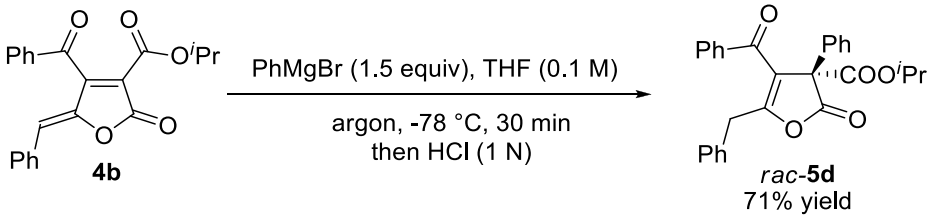


3b **5b** 62% yield

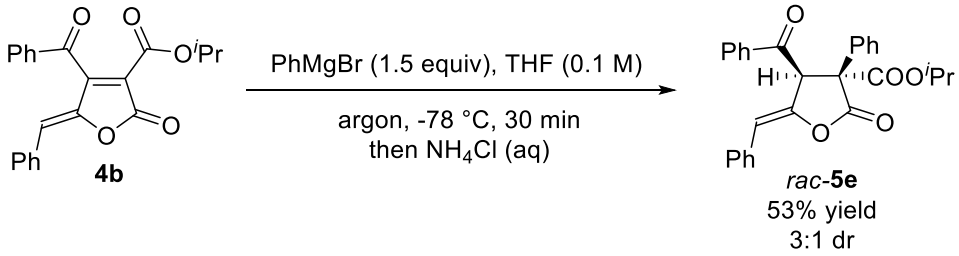
A flame dried vial was cooled under a stream of N_2 and charged with **3b** (90 mg, 0.24 mmol), MeOH (2.4 mL), and Pd/C (26 mg, 0.024 mmol, 10% Pd). The vial was sparged with a balloon of hydrogen gas, then stirred under a balloon of hydrogen gas for 24 h. The reaction mixture was loaded onto a short plug of celite, and the plug was washed with ethyl acetate (3×2 mL). The organic solvent was removed under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, v:v = 10:1) ro afford colorless oil **5b** (38 mg, 62% yield)



4b (56 mg, 0.15 mmol) was dissolved in THF (1.5 mL) and the solution was cooled down to -78 ^{o}C. EtMgBr (0.23 mL, 0.23 mmol, 1 M in THF) was added. The reaction mixture was stirred at -78 ^{o}C for 40 minutes. The mixture was quenched by aqueous HCl (1 N) and extracted with ethyl acetate (3×5 mL). The organic solvent was removed under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, v:v = 10:1) to give product **5c** (31mg, 53% yield).

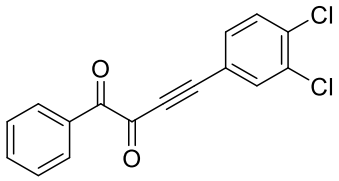


4b (56 mg, 0.15 mmol) was dissolved in THF (1.5 mL) and the solution was cooled down to -78 ^{o}C. PhMgBr (0.23 mL, 0.23 mmol, 1 M in THF) was added. The reaction mixture was stirred at -78 ^{o}C for 40 minutes. The mixture was quenched by aqueous HCl (1 N) and extracted with ethyl acetate (3×5 mL). The organic solvent was removed under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, v:v = 10:1) to give product **5d** (47 mg, 71% yield).



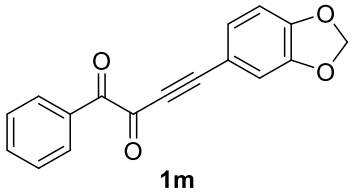
4b (74 mg, 0.2 mmol) was dissolved in THF (2 mL) and the solution was cooled down to -78 ^{o}C. PhMgBr (0.3 mL, 0.3 mmol, 1 M in THF) was added. The reaction mixture was stirred at -78 ^{o}C for 40 minutes. The mixture was quenched by saturated aqueous NH_4Cl and extracted with ethyl acetate (3×5 mL). The organic solvent was removed under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, v:v = 10:1) to give product **5e** (47 mg, 53% yield, 3:1 dr).

VI. Characterizations of new compounds



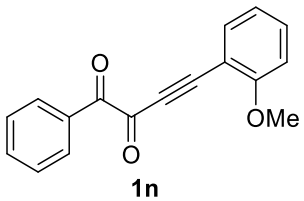
1g

1,4-bis(4-methoxyphenyl)but-3-yne-1,2-dione (1g): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow solid, mp 85−87 ℃, 1.7 g, 56% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10−8.07 (m, 2H), 7.75 (d, *J* = 1.2 Hz, 1H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.57−7.46 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 187.9, 177.8, 136.7, 135.2, 135.0, 133.4, 132.5, 131.5, 131.0, 130.7, 129.1, 119.2, 95.4, 88.0. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{16}H_8Cl_2O_2H^+$ 302.9974; Found 302.9978. IR (KBr thin film, cm^{-1}): ν 3072, 2988, 2196, 1676, 1646, 1459, 1375, 1129, 1111, 947, 828, 690, 673, 650.



1m

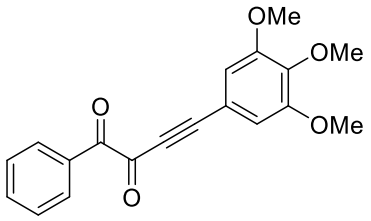
1,4-bis(4-methoxyphenyl)but-3-yne-1,2-dione (1m): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), yellow solid, mp 79−81 ℃, 0.97 g, 33% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09−8.06 (m, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 2H), 7.26−7.23 (m, 1H), 7.07−7.04 (m, 1H), 6.83 (d, *J* = 8.1 Hz, 1H), 6.05 (d, *J* = 0.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.6, 178.4, 151.1, 147.8, 134.8, 131.7, 130.5, 130.3, 128.9, 113.0, 112.1, 109.0, 102.0, 100.4, 86.9. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{17}H_{10}O_4H^+$ 279.0652; Found 279.0655. IR (KBr thin film, cm^{-1}): ν 2989, 2899, 2184, 1670, 1642, 1593, 1487, 1442, 1257, 1216, 1039, 935, 886, 859, 808, 676, 612.



1n

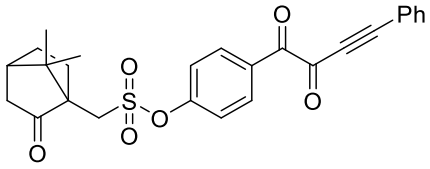
1,4-bis(4-methoxyphenyl)but-3-yne-1,2-dione (1n): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), yellow solid, mp 48−50 ℃, 1.4 g, 53% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.8 Hz, 2H), 7.66 (d, *J* = 7.3 Hz, 1H), 7.59−7.44 (m, 4H), 6.99−6.90 (m, 2H), 3.90 (d, *J* = 2.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.7, 178.6, 162.2, 135.6, 134.8, 133.7,

131.8, 130.5, 128.9, 120.7, 111.0, 108.5, 97.1, 91.3, 55.9. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{17}H_{12}O_3H^+$ 265.0859; Found 265.0862. IR (KBr thin film, cm^{-1}): ν 2948, 2842, 2176, 1680, 1638, 1693, 1487, 1449, 1254, 1096, 926, 754, 714, 675.



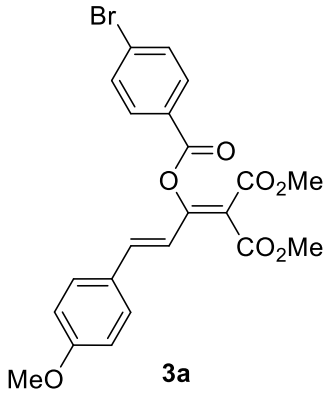
1o

1,4-bis(4-methoxyphenyl)but-3-yne-1,2-dione (1o): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), yellow solid, mp 68−70 ℃, 1.1 g, 35% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.5 Hz, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 2H), 6.90 (s, 2H), 3.91 (s, 3H), 3.87 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.5, 178.3, 153.2, 141.9, 134.9, 131.6, 130.5, 128.9, 113.7, 111.1, 99.9, 86.8, 61.1, 56.3. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{19}H_{16}O_5H^+$ 325.1071; Found 325.1074. IR (KBr thin film, cm^{-1}): ν 2949, 2842, 2178, 1670, 1643, 1574, 1449, 1410, 1237, 1123, 1101, 001, 836, 679, 638.



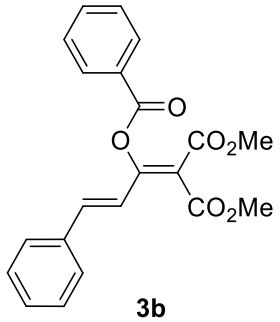
1r

1,4-bis(4-methoxyphenyl)but-3-yne-1,2-dione (1r): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), yellow liquid, 1.6 g, 34% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.7 Hz, 2H), 7.67 (d, *J* = 7.5 Hz, 2H), 7.55−7.40 (m, 5H), 3.86 (d, *J* = 15.0 Hz, 1H), 3.25 (d, *J* = 15.0 Hz, 1H), 2.57−2.40 (m, 2H), 2.18−1.97 (m, 3H), 1.79−1.71 (m, 1H), 1.52−1.45 (m, 1H), 1.16 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 213.9, 186.7, 177.7, 154.0, 133.8, 132.8, 131.9, 130.3, 128.9, 122.5, 119.2, 99.7, 87.1, 58.2, 48.6, 48.1, 42.9, 42.5, 27.0, 25.3, 20.0, 19.8. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{26}H_{24}O_6SH^+$ 465.1366; Found 465.1370. IR (KBr thin film, cm^{-1}): ν 2967, 2360, 2342, 2191, 1744, 1654, 1595, 1374, 1147, 1105, 856, 759, 688, 516.



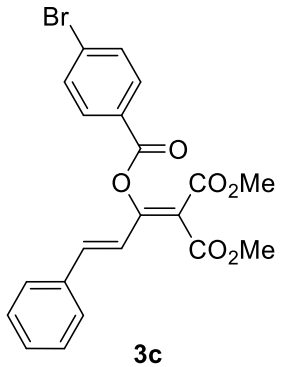
3a

dimethyl (*E*)-2-(1-((4-bromobenzoyl)oxy)-3-(4-methoxyphenyl)allylidene)malonate (3a): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), yellow solid, mp 151−153 ℃, 72 mg, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.6 Hz, 2H), 7.68 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 15.8 Hz, 1H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 15.8 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 3.82 (s, 3H), 3.64 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.5, 163.9, 162.8, 161.4, 158.6, 139.2, 132.2, 131.8, 129.9, 129.4, 127.7, 127.4, 116.8, 115.2, 114.3, 55.4, 52.7, 52.5. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{22}H_{19}BrO_7H^+$ 475.0387; Found 475.0390. IR (KBr thin film, cm^{-1}): ν 3091, 3007, 2932, 2835, 1745, 1731, 1577, 1490, 1213, 1167, 819, 745.



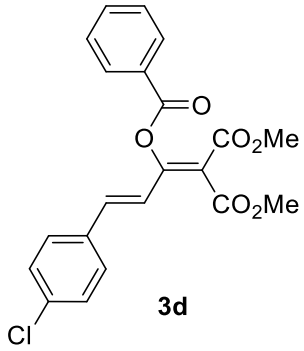
3b

dimethyl (*E*)-2-(1-(benzoyloxy)-3-phenylallylidene)malonate (3b): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), yellow solid, mp 99−101 ℃, 42 mg, 55% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.70−7.66 (m, 2H), 7.56−7.53 (m, 2H), 7.49−7.48 (m, 2H), 7.36−7.33 (m, 3H), 7.08 (d, *J* = 15.9 Hz, 1H), 3.88 (s, 3H), 3.64 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.4, 164.0, 163.5, 158.5, 139.5, 135.1, 134.2, 130.5, 130.2, 128.9, 128.4, 128.3, 119.4, 116.6, 52.8, 52.6. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{21}H_{18}O_6H^+$ 367.1176; Found 367.1181. IR (KBr thin film, cm^{-1}): ν 3092, 3022, 2945, 2873, 1739, 1716, 1616, 1585, 1218, 1046, 751, 706.



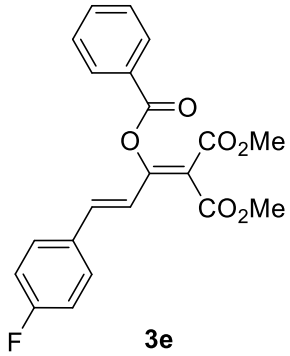
3c

dimethyl (*E*)-2-(1-((4-bromobenzoyl)oxy)-3-phenylallylidene)malonate (3c): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), yellow solid, mp 111−113 ℃, 59 mg, 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.6 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 15.9 Hz, 1H), 7.49−7.47 (m, 2H), 7.35−7.34 (m, 3H), 7.05 (d, *J* = 15.9 Hz, 1H), 3.89 (s, 3H), 3.65 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 163.7, 162.8, 158.1, 139.4, 134.9, 132.2, 131.8, 130.2, 129.5, 128.8, 128.2, 127.3, 119.1, 116.5, 52.8, 52.5. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{21}H_{17}BrO_6H^+$ 445.0281; Found 445.0279. IR (KBr thin film, cm^{-1}): ν 3085, 3013, 2938, 2867, 1728, 1584, 1484, 1173, 1060, 757, 685.



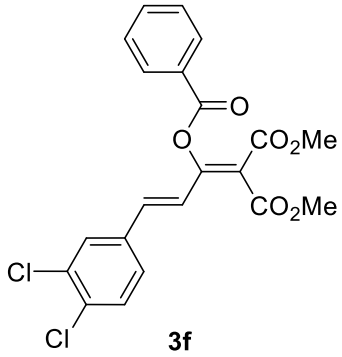
3d

dimethyl (*E*)-2-(1-(benzoyloxy)-3-(4-chlorophenyl)allylidene)malonate (3d): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), yellow solid, mp 94−96 ℃, 44 mg, 55% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 8.1, 1.1 Hz, 2H), 7.69−7.66 (m, 2H), 7.56−7.52 (m, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.00 (d, *J* = 15.9 Hz, 1H), 3.88 (s, 3H), 3.64 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 163.9, 163.4, 158.1, 137.8, 135.9, 134.2, 133.5, 130.4, 129.3, 129.1, 128.9, 128.2, 119.8, 116.9, 52.8, 52.6. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{21}H_{17}ClO_6H^+$ 401.0786; Found 401.0791. IR (KBr thin film, cm^{-1}): ν 3098, 3025, 2924, 2823, 1720, 1620, 1260, 1082, 703, 697.



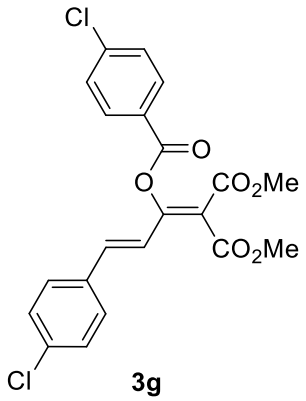
3e

dimethyl (*E*)-2-(1-(benzoyloxy)-3-(4-fluorophenyl)allylidene)malonate (3e): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), yellow solid, mp 93−95 ℃, 50 mg, 66% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17−8.15 (m, 2H), 7.68−7.66 (m, 1H), 7.61 (d, *J* = 15.9 Hz, 1H), 7.54−7.52 (m, 2H), 7.47−7.44 (m, 2H), 7.03−7.00 (m, 3H), 3.87 (s, 3H), 3.63 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 163.9, 163.9 (d, *J* = 88.0 Hz), 162.5, 158.3, 138.0, 134.2, 131.3 (d, *J* = 3.3 Hz), 130.4, 130.0 (d, *J* = 8.5 Hz), 128.8, 128.3, 119.1 (d, *J* = 2.3 Hz), 116.5, 116.0 (d, *J* = 22.1 Hz), 52.7, 52.5. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{21}H_{17}FO_6H^+$ 385.1082; Found 385.1086. IR (KBr thin film, cm^{-1}): ν 3094, 3013, 2956, 2877, 1714, 1573, 1217, 1058, 1013, 699.



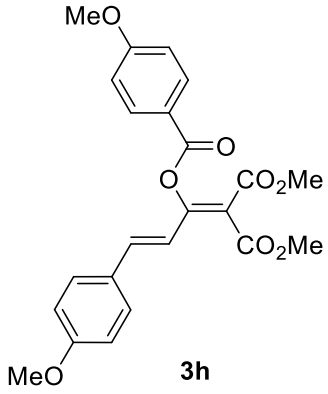
3f

dimethyl (*E*)-2-(1-(benzoyloxy)-3-(3,4-dichlorophenyl)allylidene)malonate (3f): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), yellow solid, mp 91−93 ℃, 52 mg, 60% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17−8.15 (m, 2H), 7.72−7.68 (m, 2H), 7.56−7.53 (m, 3H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.32 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.94 (d, *J* = 15.9 Hz, 1H), 3.89 (s, 3H), 3.64 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.2, 163.9, 163.5, 157.7, 136.5, 135.1, 134.4, 133.9, 133.3, 130.9, 130.5, 129.8, 129.0, 128.1, 127.0, 121.1, 117.7, 52.9, 52.7. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{21}H_{16}Cl_2O_6H^+$ 435.0397; Found 435.0400. IR (KBr thin film, cm^{-1}): ν 3078, 3033, 2920, 2850, 1732, 1619, 1216, 1082, 1044, 698.



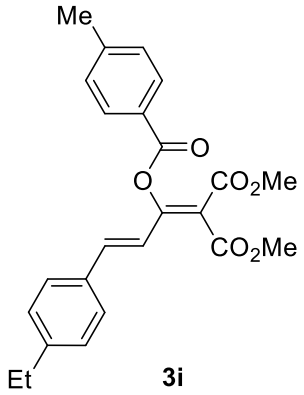
3g

dimethyl (*E*)-2-(1-((4-chlorobenzoyl)oxy)-3-(4-chlorophenyl)allylidene)malonate（3g）: purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), yellow solid, mp 134−136 ℃, 64 mg, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 15.9 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 15.9 Hz, 1H), 3.88 (s, 3H), 3.65 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 163.7, 162.6, 157.8, 140.9, 137.9, 136.0, 133.4, 131.7, 129.3, 129.1, 126.7, 119.7, 116.9, 52.8, 52.6. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{21}H_{16}Cl_2O_6H^+$ 435.0397; Found 435.0401. IR (KBr thin film, cm^{-1}): ν 3111, 2956, 2923, 2850, 1721, 1584, 1219, 1075, 1010, 815.



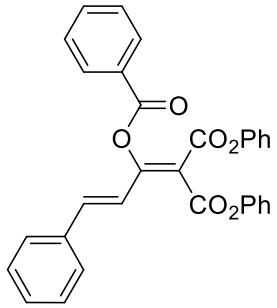
3h

dimethyl (*E*)-2-(1-((4-methoxybenzoyl)oxy)-3-(4-methoxyphenyl)allylidene) malonate (3h): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), yellow solid, mp 115−117 ℃, 60 mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 15.8 Hz, 1H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.05−6.99 (m, 3H), 6.86 (d, *J* = 8.7 Hz, 2H), 3.91 (s, 3H), 3.87 (s, 3H), 3.82 (s, 3H), 3.63 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.7, 164.4, 164.3, 163.3, 161.3, 159.2 139.3, 132.7, 129.9, 128.0, 120.7, 117.2, 115.3, 114.4, 114.2, 55.7, 55.5, 52.6, 52.5. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{23}H_{22}O_8H^+$ 427.1387; Found 427.1389. IR (KBr thin film, cm^{-1}): ν 3096, 2948, 2920, 2843, 1727, 1582, 1510, 1252, 1164, 1077, 1020, 979, 825, 757.



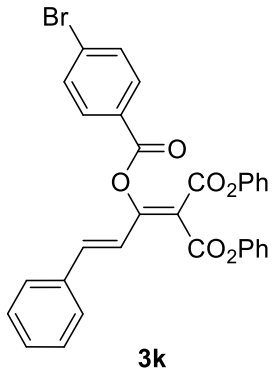
3i

dimethyl (*E*)-2-(3-(4-ethylphenyl)-1-((4-methylbenzoyl)oxy)allylidene)malonate (3i): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), yellow solid, mp 104−106 ℃, 45 mg, 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 15.8 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 15.8 Hz, 1H), 3.87 (s, 3H), 3.63 (s, 3H), 2.64 (q, *J* = 7.6 Hz, 2H), 2.47 (s, 3H), 1.22 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.5, 164.2, 163.6, 158.9, 146.9, 145.1, 139.6, 132.7, 130.5, 129.6, 128.5, 128.4, 125.7, 118.5, 116.0, 52.7, 52.6, 28.9, 21.9, 15.4. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{24}H_{24}O_6H^+$ 409.1646; Found 409.1649. IR (KBr thin film, cm^{-1}): ν 3032, 2954, 1718, 1592, 1224, 1175, 1080, 1061, 1014, 824, 739.



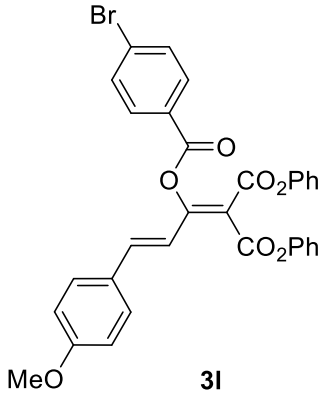
3j

diphenyl (E)-2-(1-(benzoyloxy)-3-phenylallylidene)malonate (3j): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), white solid, mp 117−119 ℃, 45 mg, 46% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.5 Hz, 2H), 7.90 (d, *J* = 15.8 Hz, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.57−7.52 (m, 4H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.36−7.30 (m, 8H), 7.22−7.16 (m, 2H), 7.02 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.4, 162.6, 162.2, 160.7, 150.5, 150.4, 141.0, 134.9, 134.4, 130.7, 130.6, 129.8, 129.6, 129.0, 128.5, 128.2, 126.5, 126.3, 121.6, 121.4, 119.2, 115.6. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{31}H_{22}O_6H^+$ 491.1489; Found 491.1494. IR (KBr thin film, cm^{-1}): ν 3059, 3042, 2923, 2857, 1743, 1592, 1483, 1337, 1194, 1124, 1069, 741, 689, 494.



3k

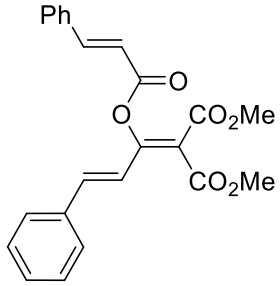
diphenyl (*E*)-2-(1-((4-bromobenzoyl)oxy)-3-phenylallylidene)malonate (3k): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), yellow solid, mp 93−95 ℃, 88 mg, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.5 Hz, 2H), 7.85 (d, *J* = 15.8 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.53−7.51 (m, 2H), 7.48−7.44 (m, 2H), 7.37−7.29 (m, 5H), 7.27−7.19 (m, 5H), 7.04 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.8, 162.6, 162.0, 160.5, 150.5, 150.3, 141.1, 134.8, 132.4, 132.1, 130.7, 129.9, 129.8, 129.7, 129.1, 128.5, 127.1, 126.5, 126.3, 121.6, 121.4, 119.0, 115.6. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{31}H_{21}BrO_6H^+$ 591.0414; Found 591.0419. IR (KBr thin film, cm^{-1}): ν 3082, 3061, 2997, 2846, 1741, 1483, 1190, 1131, 1069, 936, 742, 687, 492.



3l

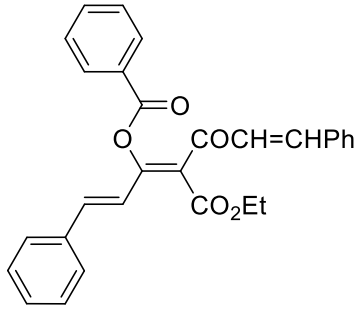
Diphenyl (*E*)-2-(1-((4-bromobenzoyl)oxy)-3-(4methoxyphenyl)allylidene) malonate (3l): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), yellow solid, mp 144−146 ℃, 76 mg, 63% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 15.8 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.48−7.44 (m, 4H), 7.33−7.29 (m, 3H), 7.25 (d, *J* = 8.8 Hz, 1H), 7.21−7.15 (m, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.9, 162.8, 162.2, 161.8, 161.1, 150.5, 150.4, 140.9, 132.4, 132.1, 130.4, 129.8, 129.6, 127.6, 127.2, 126.4, 126.2, 121.6, 121.4, 116.7, 114.5, 114.2, 55.5. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{32}H_{23}BrO_7H^+$ 599.0700; Found 599.0706. IR (KBr thin film, cm^{-1}): ν 3087, 2924,

2839, 1732, 1584, 1484, 1168, 1052, 1006, 959, 741, 687.



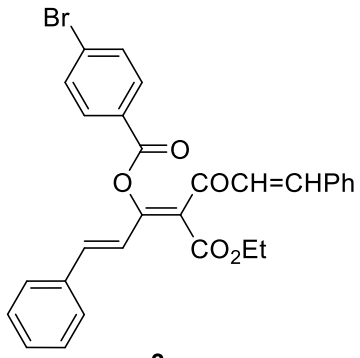
3m

dimethyl 2-((*E*)-1-(cinnamoyloxy)-3-phenylallylidene)malonate (3m): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), yellow solid, mp 121−123 ℃, 22 mg, 27% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 16.0 Hz, 1H), 7.66−7.60 (m, 3H), 7.52−7.50 (m, 2H), 7.45−7.44 (m, 3H), 7.36−7.34 (m, 3H), 7.08 (d, *J* = 15.8 Hz, 1H), 6.64 (d, *J* = 16.0 Hz, 1H), 3.87 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.4, 164.1, 163.5, 158.2, 148.1, 139.4, 135.1, 133.9, 131.2, 130.1, 129.2, 128.9, 128.6, 128.2, 119.4, 116.6, 115.8, 52.7, 52.7. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}O_6H^+$ 393.1333; Found 393.1337. IR (KBr thin film, cm^{-1}): ν 3082, 2985, 1731, 1582, 1168, 1052, 1006, 959, 741, 687.



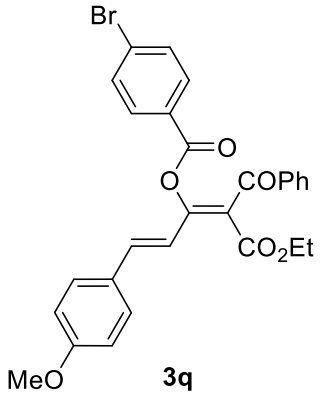
3o

(1*E*,3*E*,6*E*)-4-(ethoxycarbonyl)-5-oxo-1,7-diphenylhepta-1,3,6-trien-3-yl benzoate (3o): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), yellow solid, mp 154−156 ℃, 78 mg, 86% yield, 8:1 *E*/*Z*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 16.0 Hz, 1H), 8.06−8.03 (m, 2H), 7.62−7.48 (m, 6H), 7.46−7.42 (m, 2H), 7.38−7.34 (m, 6H), 7.01 (d, *J* = 16.0 Hz, 1H), 6.78 (d, *J* = 16.2 Hz, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 164.1, 163.7, 157.5, 146.1, 138.5, 135.3, 134.3, 134.1, 130.8, 130.4, 129.9, 128.9, 128.8, 128.7, 128.5, 128.2, 128.1, 126.6, 122.6, 119.6, 61.6, 14.2. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{29}H_{24}O_5H^+$ 453.1697; Found 453.1700. IR (KBr thin film, cm^{-1}): ν 3023, 2924, 1731, 1581, 1484, 1168, 1052, 1006, 959, 741, 686.



3p

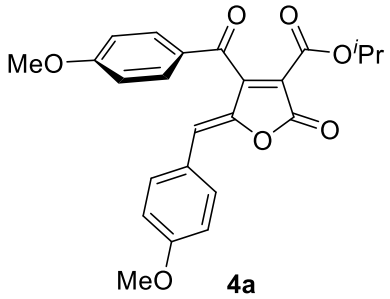
(1*E*,3*E*,6*E*)-4-(ethoxycarbonyl)-5-oxo-1,7-diphenylhepta-1,3,6-trien-3-yl 4-bromobenzoate (3p): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), yellow solid, mp 174−176 ℃, 69 mg, 65% yield, 4:1 *E*/*Z*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 16.0 Hz, 1H), 7.90 (d, *J* = 8.5 Hz, 2H), 7.60−7.48 (m, 7H), 7.39−7.34 (m, 6H), 6.98 (d, *J* = 16.0 Hz, 1H), 6.77 (d, *J* = 16.2 Hz, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 164.1, 163.0, 157.2, 146.1, 138.6, 135.2, 134.2, 132.1, 131.8, 130.8, 130.0, 129.5, 129.0, 128.9, 128.5, 128.1, 127.1, 126.4, 122.6, 119.4, 61.6, 14.2. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{29}H_{23}BrO_5H^+$ 531.0802; Found 531.0804. IR (KBr thin film, cm^{-1}): ν 3023, 2924, 1731, 1581, 1484, 1168, 1052, 1006, 959, 741, 686.



3q

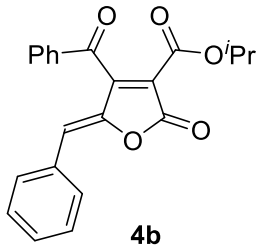
(1*E*,3*E*)-5-ethoxy-4-(4-methoxybenzoyl)-1-(4-methoxyphenyl)-5-oxopenta-1,3-dien-3-yl 4-bromobenzoate (3q): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), yellow solid, mp 129−131 ℃, 90 mg, 80% yield, 1:1 *E*/*Z*. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15−8.12 (m, 4H), 7.72−7.70 (m, 2H), 7.26−7.24 (m, 2H), 7.02−6.98 (m, 3H), 6.79−6.77 (m, 2H), 6.54 (d, *J* = 15.4 Hz, 1H), 4.01 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 3.77 (s, 3H), 0.96 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.0, 164.2, 163.6, 162.7, 161.1, 155.3, 137.8, 132.2, 131.9, 130.4, 129.6, 129.2, 128.0, 127.6, 120.8, 117.4, 114.3, 114.2, 61.0, 55.6, 55.3, 13.9. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{29}H_{25}BrO_7H^+$ 565.0856; Found 565.0859. IR (KBr thin film, cm^{-1}): ν 3093, 3033, 2924, 1731, 1580,

1484, 1168, 1052, 1006, 959, 741, 686.



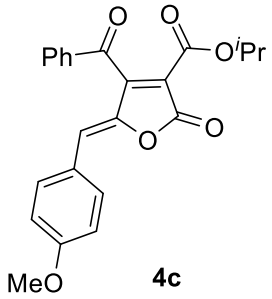
4a

isopropyl (*Z*)-4-(4-methoxybenzoyl)-5-(4-methoxybenzylidene)-2-oxo-2,5-dihydrofuran-3-carboxylate (4a): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1), yellow solid, mp 172−174 ℃, 61 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.09 (s, 1H), 5.00−4.94 (m, 1H), 3.89 (s, 3H), 3.84 (s, 3H), 0.97 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 187.5, 165.1, 164.1, 162.0, 159.2, 158.7, 142.8, 134.1, 131.8, 128.6, 125.1, 120.2, 115.3, 114.7, 114.4, 69.6, 55.8, 55.5, 21.2. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{24}H_{22}O_7H^+$ 423.1438; Found 423.1442. IR (KBr thin film, cm^{-1}): ν 3109, 2926, 1731, 1580, 1484, 1247, 1167, 1052, 1006, 959, 822, 741, 687.



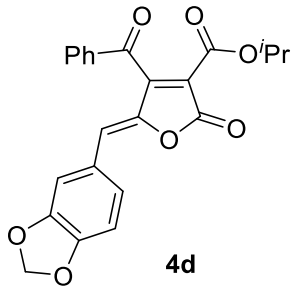
4b

isopropyl (*Z*)-4-benzoyl-5-benzylidene-2-oxo-2,5-dihydrofuran-3-carboxylate (4b): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1), yellow solid, mp 154−156 ℃, 31 mg, 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.4 Hz, 2H), 7.81−7.79 (m, 2H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.42−7.40 (m, 3H), 6.13 (s, 1H), 5.01−4.95 (m, 1H), 0.95 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.9, 162.6, 157.7, 157.4, 143.1, 134.2, 134.1, 131.0, 130.9, 130.1, 128.3, 128.2, 128.1, 118.9, 116.2, 69.0, 20.1. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{22}H_{18}O_5H^+$ 363.1227; Found 363.1231. IR (KBr thin film, cm^{-1}): ν 3057, 2977, 2941, 1784, 1719, 1680, 1569, 1384, 1283, 1176, 1103, 956, 784, 688.



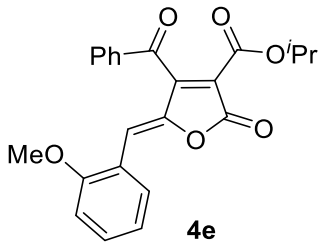
4c

isopropyl (*Z*)-4-benzoyl-5-(4-methoxybenzylidene)-2-oxo-2,5-dihydrofuran-3-carboxylate (4c): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1), yellow solid, mp 133−135 ℃, 53 mg, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 2H), 7.77 (d, *J* = 8.9 Hz, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.10 (s, 1H), 4.99−4.93 (m, 1H), 3.85 (s, 3H), 0.93 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.3, 164.0, 162.1, 159.0, 158.2, 142.6, 135.4, 135.0, 134.1, 129.3, 129.1, 125.1, 120.4, 115.6, 114.8, 69.8, 55.5, 21.1. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}O_6H^+$ 393.1333; Found 393.1335. IR (KBr thin film, cm^{-1}): ν 3042, 2974, 2942, 2848, 1783, 1664, 1547, 1290, 1242, 1162, 1103, 829, 674.



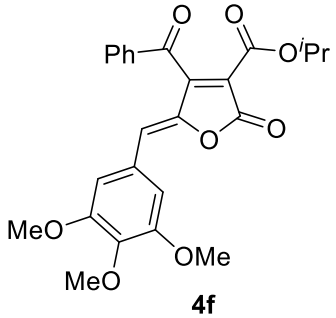
4d

isopropyl (*Z*)-5-(benzo[d][1,3]dioxol-5-ylmethylene)-4-benzoyl-2-oxo-2,5-dihydrofuran-3-carboxylate (4d): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1), yellow solid, mp 122−124 ℃, 69 mg, 85% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95–7.93 (m, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.56–7.51 (m, 3H), 7.17 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.81 (d, *J* = 8.2 Hz, 1H), 6.05 (s, 1H), 6.04 (s, 2H), 5.02–4.90 (m, 1H), 0.93 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.2, 163.8, 159.0, 158.2, 150.6, 148.7, 142.8, 135.5, 135.1, 129.4, 129.2, 128.9, 126.7, 120.4, 115.9, 110.8, 109.0, 102.1, 77.3, 21.2. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{23}H_{18}O_7H^+$ 407.1125; Found 407.1129. IR (KBr thin film, cm^{-1}): ν 3037, 2980, 2918, 2850, 1715, 1670, 1250, 1104, 1023, 960, 757.



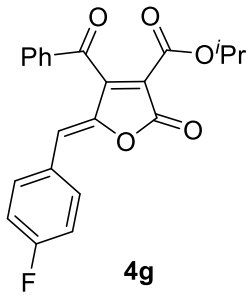
4e

isopropyl (*Z*)-4-benzoyl-5-(2-methoxybenzylidene)-2-oxo-2,5-dihydrofuran-3-carboxylate (4e): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1), yellow solid, mp 145−147 ℃, 36 mg, 46% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29 (dd, *J* = 8.0, 1.7 Hz 1H), 7.96–7.94 (m, 2H), 7.70–7.66 (m, 1H), 7.56–7.52 (m, 2H), 7.39–7.36 (m, 1H), 7.04–7.02 (m, 1H), 6.85 (dd, *J* = 8.4, 0.9 Hz, 1H), 6.73 (s, 1H), 4.99–4.95 (m, 1H), 3.77 (s, 3H), 0.94 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.2, 164.0, 159.1, 158.7, 158.6, 143.9, 135.6, 135.0, 133.0, 132.7, 129.4, 129.2, 121.4, 116.5, 114.4, 110.8, 69.9, 55.7, 21.2. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}O_6H^+$ 393.1333; Found 393.1336. IR (KBr thin film, cm^{-1}): ν 3069, 2986, 2936, 2836, 1781, 1670, 1558, 1254, 1164, 1106, 999, 759, 691.



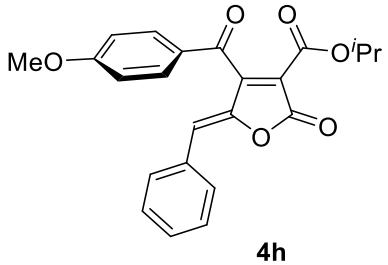
4f

isopropyl (*Z*)-4-benzoyl-2-oxo-5-(3,4,5-trimethoxybenzylidene)-2,5-dihydrofuran-3-carboxylate (4f): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1), yellow solid, mp 118−120 ℃, 47 mg, 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.6 Hz, 2H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.04 (s, 2H), 6.04 (s, 1H), 5.00–4.93 (m, 1H), 3.91 (s, 3H), 3.88 (s, 6H), 0.93 (d, *J* = 6.2 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.2, 163.6, 158.9, 158.2, 153.4, 143.6, 141.3, 135.4, 135.2, 129.4, 129.3, 127.5, 120.2, 116.4, 109.4, 70.0, 61.2, 56.4, 21.2. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{25}H_{24}O_8H^+$ 453.1544; Found 453.1545. IR (KBr thin film, cm^{-1}): ν 3037, 2985, 2936, 2843, 1795, 1706, 1568, 1282, 1125, 1099, 991, 696.



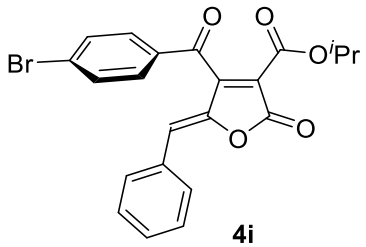
4g

isopropyl (*Z*)-4-benzoyl-5-(4-fluorobenzylidene)-2-oxo-2,5-dihydrofuran-3-carboxylate (4g): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1), yellow solid, mp 161−163 ℃, 40 mg, 53% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.4 Hz, 2H), 7.80 (dd, *J* = 8.8, 5.5 Hz, 2H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.09 (t, *J* = 8.6 Hz, 2H), 6.09 (s, 1H), 5.00−4.94 (m, 1H), 0.94 (d, *J* = 6.2 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.0, 164.1 (d, *J* = 255.0 Hz), 163.6, 158.8, 158.4, 143.8, 135.3, 134.1 (d, *J* = 8.7 Hz), 129.4, 129.3, 128.5 (d, *J* = 3.6 Hz), 118.6, 117.1, 116.6, 116.5, 70.2, 21.2. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{22}H_{17}FO_5H^+$ 381.1133; Found 381.1136. IR (KBr thin film, cm^{-1}): ν 3056, 2977, 2939, 2851, 1787, 1672, 1573, 1234, 1159, 1102, 998, 692.



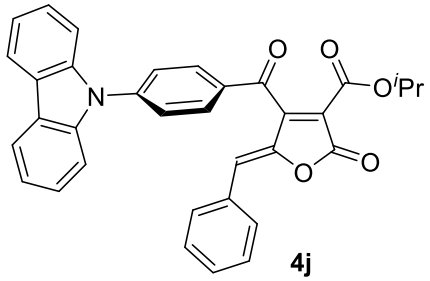
4h

isopropyl (*Z*)-5-benzylidene-4-(4-methoxybenzoyl)-2-oxo-2,5-dihydrofuran-3-carboxylate (4h): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1), yellow solid, mp 127−129 ℃, 42 mg, 54% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.7 Hz, 2H), 7.80−7.77 (m, 2H), 7.44−7.36 (m, 3H), 7.00 (d, *J* = 8.6 Hz, 2H), 6.12 (s, 1H), 5.02−4.94 (m, 1H), 3.90 (s, 3H), 0.99 (d, *J* = 6.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.2, 165.2, 163.8, 158.9, 158.9, 144.3, 132.1, 131.8, 131.0, 129.1, 128.5, 119.8, 116.9, 114.5, 69.9, 55.8, 21.2. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}O_6H^+$ 393.1333; Found 393.1338 IR (KBr thin film, cm^{-1}): ν 3064, 2984, 2943, 2837, 1790, 1596, 1570, 1249, 1168, 1100, 994, 680.



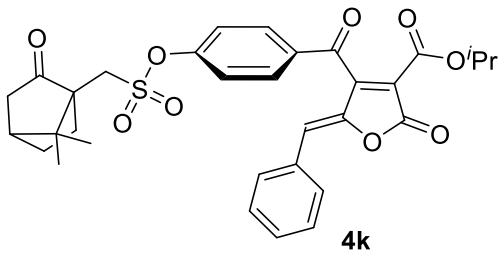
4i

isopropyl (*Z*)-5-benzylidene-4-(4-bromobenzoyl)-2-oxo-2,5-dihydrofuran-3-carboxylate (4i): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1), yellow solid, mp 186−188 ℃, 51 mg, 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.76 (m, 4H), 7.74–7.66 (m, 2H), 7.45–7.38 (m, 3H), 6.09 (s, 1H), 5.04–4.96 (m, 1H), 1.01 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.0, 163.3, 158.7, 158.0, 144.0, 134.0, 132.6, 131.9, 131.2, 130.7, 130.6, 129.1, 120.1, 117.4, 70.2, 21.3. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{22}H_{17}BrO_5H^+$ 441.0332; Found 441.0338. IR (KBr thin film, cm^{-1}): ν 3057, 2977, 2923, 2857, 1783, 1663, 1567, 1286, 1173, 1105, 998, 759, 673.



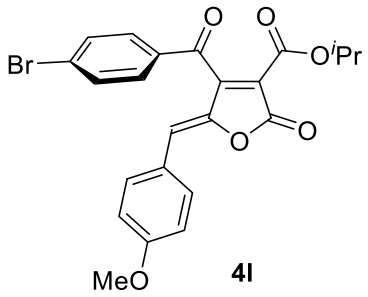
4j

isopropyl (*Z*)-4-(4-(9H-carbazol-9-yl)benzoyl)-5-benzylidene-2-oxo-2,5-dihydrofuran-3-carboxylate compound with methane (1:1) (4j): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1), yellow solid, mp 173−175 ℃, 44 mg, 40% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.4 Hz, 2H), 8.15 (d, *J* = 7.7 Hz, 2H), 7.89–7.79 (m, 4H), 7.52–7.49 (m, 2H), 7.48–7.40 (m, 5H), 7.34 (t, *J* = 7.4 Hz, 2H), 6.24 (s, 1H), 5.11–5.05 (m, 1H), 1.08 (d, *J* = 6.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.7, 163.5, 158.9, 158.3, 144.1, 139.8, 133.3, 132.0, 132.0, 131.2, 131.1, 129.2, 126.7, 126.4, 124.2, 121.1, 120.6, 120.1, 117.4, 109.7, 70.1, 21.3. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{34}H_{25}NO_5H^+$ 528.1805; Found 528.1811. IR (KBr thin film, cm^{-1}): ν 3051, 2987, 2937, 2853, 1796, 1596, 1449, 1288, 1168, 1099, 992, 751.



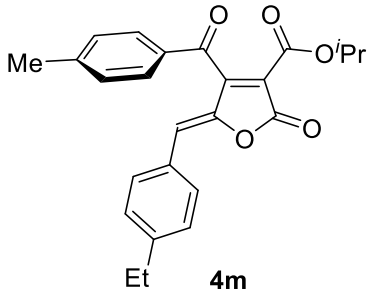
4k

isopropyl (Z)-5-benzylidene-4-(4-((((7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methyl)sulfonyl)oxy)benzoyl)-2-oxo-2,5-dihydrofuran-3-carboxylate (4k): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1), yellow liquid, 53 mg, 45% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.7 Hz, 2H), 7.76–7.73 (m, 2H), 7.43 (d, *J* = 8.7 Hz, 2H), 7.37–7.31 (m, 3H), 6.05 (s, 1H), 4.97–4.90 (m, 1H), 3.79 (d, *J* = 15.0 Hz, 1H), 3.19 (d, *J* = 15.0 Hz, 1H), 2.51–2.41 (m, 1H), 2.37 (dt, *J* = 18.6, 4.1 Hz, 1H), 2.10 (t, *J* = 4.4 Hz, 1H), 2.08–2.00 (m, 1H), 1.93 (d, *J* = 18.6 Hz, 1H), 1.72–1.64 (m, 1H), 1.45–1.38 (m, 1H), 1.09 (s, 3H), 0.93 (d, *J* = 6.3 Hz, 6H), 0.85 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 213.9, 187.7, 163.4, 158.79, 158.0, 154.0, 144.0, 133.8, 132.1, 132.0, 131.4, 131.3, 129.2, 122.9, 120.3, 117.4, 70.4, 58.2, 48.7, 48.2, 42.9, 42.5, 29.8, 27.0, 25.2, 21.3, 20.0, 19.8. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{32}H_{32}O_9SH^+$ 593.1840; Found 593.1843. IR (KBr thin film, cm^{-1}): ν 2961, 2923, 2853, 1786, 1595, 1374, 1148, 1006, 865, 788, 696.



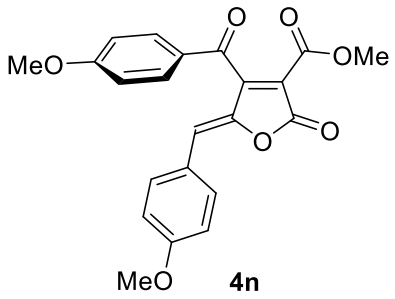
4l

isopropyl (*Z*)-4-(4-bromobenzoyl)-5-(4-methoxybenzylidene)-2-oxo-2,5-dihydrofuran-3-carboxylate (4l): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1), yellow solid, mp 212−214 ℃, 57 mg, 60% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.77 (d, *J* = 8.9 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.06 (s, 1H), 5.01−4.97 (m, 1H), 3.86 (s, 3H), 0.99 (d, *J* = 6.2 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 188.4, 163.8, 162.4, 159.1, 157.8, 142.5, 134.3, 132.6, 130.7, 125.1, 120.6, 115.8, 114.9, 70.0, 55.6, 21.4. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{23}H_{19}BrO_6H^+$ 471.0438; Found 471.0440. IR (KBr thin film, cm^{-1}): ν 2969, 2923, 2823, 1782, 16775, 1583, 1374, 1286, 1148, 1103, 1004, 869, 786.



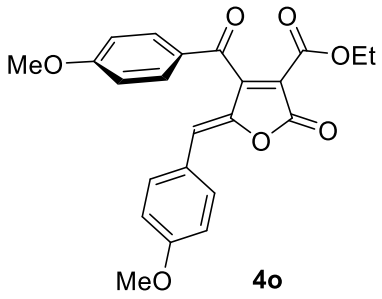
4m

isopropyl (*Z*)-4-benzoyl-2-oxo-5-(3,4,5-trimethoxybenzylidene)-2,5-dihydrofuran-3-carboxylate (4m): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1), yellow solid, mp 105−107 ℃, 50 mg, 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 6.10 (s, 1H), 5.01−4.94 (m, 1H), 2.66 (q, *J* = 7.6 Hz, 2H), 2.45 (s, 3H), 1.23 (t, *J* = 7.6 Hz, 3H), 0.96 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.6, 163.9, 159.0, 158.7, 148.3, 146.5, 143.7, 133.0, 132.1, 129.8, 129.7, 129.5, 128.7, 120.3, 116.4, 69.8, 29.0, 22.0, 21.2, 15.1. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{25}H_{24}O_5H^+$ 405.1697; Found 405.1699. IR (KBr thin film, cm^{-1}): ν 3045, 2963, 2931, 2871, 1797, 1669, 1576, 1287, 1175, 1108, 998, 827, 775.



4n

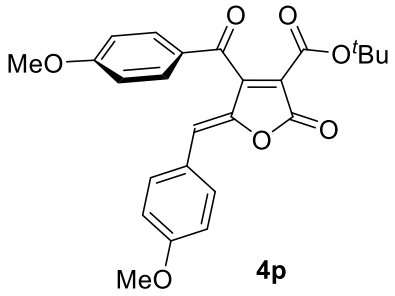
methyl (*Z*)-4-(4-methoxybenzoyl)-5-(4-methoxybenzylidene)-2-oxo-2,5-dihydrofuran-3-carboxylate (4n): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1), yellow solid, mp 187−189 ℃, 49 mg, 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.7 Hz, 2H), 7.76 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.10 (s, 1H), 3.89 (s, 3H), 3.85 (s, 3H), 3.71 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.5, 165.1, 164.0, 162.2, 160.5, 160.2, 142.9, 134.2, 131.8, 128.3, 125.0, 120.7, 115.1, 114.8, 114.5, 55.7, 55.5, 52.6. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{22}H_{18}O_7H^+$ 395.1125; Found 395.1129. IR (KBr thin film, cm^{-1}): ν 2959, 2920, 2849, 1667, 1599, 1509, 1251, 1163, 1020, 832, 773.



4o

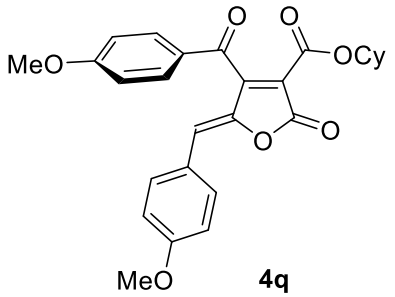
ethyl (*Z*)-4-(4-methoxybenzoyl)-5-(4-methoxybenzylidene)-2-oxo-2,5-dihydrofuran-3-carboxylate (4o): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1), yellow solid, mp 180−182 ℃, 56 mg, 71%

yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.8 Hz, 2H), 7.76 (d, *J* = 8.9 Hz, 2H), 6.99 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.10 (s, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 3.85 (s, 3H), 1.03 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.5, 165.1, 164.1, 162.1, 159.8, 159.4, 142.8, 134.1, 131.8, 128.5, 125.1, 120.4, 115.2, 114.7, 114.4, 61.7, 55.7, 55.5, 13.7. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}O_7H^+$ 409.1282; Found 409.1286. IR (KBr thin film, cm^{-1}): ν 3043, 2989, 2921, 2845, 1783, 1600, 1553, 1510, 1248, 1164, 1018, 831, 801.



4p

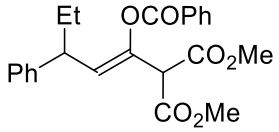
tert-butyl (*Z*)-4-(4-methoxybenzoyl)-5-(4-methoxybenzylidene)-2-oxo-2,5-dihydrofuran-3-carboxylatee (4p): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1), yellow solid, mp 204−206 ℃, 56 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.6 Hz, 2H), 7.75 (d, *J* = 8.7 Hz, 2H), 7.00 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.06 (s, 1H), 3.90 (s, 3H), 3.84 (s, 3H), 1.21 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.5, 165.1, 164.4. 161.9, 158.7, 157.8, 142.7, 133.9, 131.9, 128.6, 125.2, 119.8, 116.2, 114.7, 114.4, 83.4, 55.8, 55.5, 27.6; HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{25}H_{24}O_7H^+$ 437.1595; Found 437.1596. IR (KBr thin film, cm^{-1}): ν 3042, 2991, 2924, 2849, 1778, 1552, 1378, 1247, 1145, 1006, 969, 829, 576.



4q

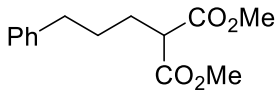
cyclohexyl (*Z*)-4-(4-methoxybenzoyl)-5-(4-methoxybenzylidene)-2-oxo-2,5-dihydrofuran-3-carboxylate (4q): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1), yellow solid, mp 150−152 ℃, 62 mg, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.7 Hz, 2H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.08 (s, 1H), 4.84–4.78 (m, 1H), 3.91 (s, 3H), 3.86 (s, 3H), 1.61–1.57 (m, 2H), 1.52–1.43 (m, 2H), 1.42–1.38 (m, 1H), 1.28– 1.10 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.5, 165.1, 164.1, 162.0, 159.2,

158.6, 142.8, 134.0, 131.9, 128.5, 125.1, 120.1, 115.5, 114.7, 114.4, 74.3, 55.8, 55.5, 30.9, 25.2, 23.2. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{27}H_{26}O_7H^+$ 463.1751; Found 463.1757. IR (KBr thin film, cm^{-1}): ν 2931, 2849, 1773, 1599, 1553, 1509, 1250, 1162, 997, 828.



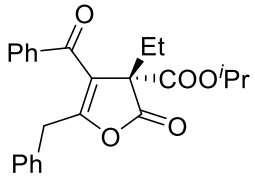
5a

dimethyl (Z)-2-(1-(benzoyloxy)-3-phenylpent-1-en-1-yl)malonate (5a): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), colorless oil, 33 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11–8.03 (m, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.31–7.25 (m, 2H), 7.20 (d, *J* = 7.6 Hz, 3H), 5.74 (d, *J* = 9.7 Hz, 1H), 4.39 (s, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 3.55–3.40 (m, 1H), 1.92–1.67 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 166.8, 164.3, 143.3, 139.3, 133.6, 130.1, 129.0, 128.6, 128.4, 127.5, 127.0, 126.3, 56.1, 53.0, 53.0, 44.0, 29.1, 12.0. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{24}O_6Na^+$ 419.1465; Found 419.1463. IR (KBr thin film, cm^{-1}): ν 2963, 2921, 2834, 1735, 1430, 1260, 1238, 1162, 1064, 1023, 704.



5b

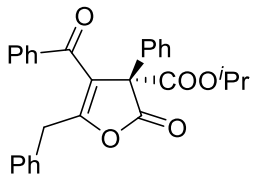
dimethyl 2-(3-phenylpropyl)malonate (5b)[5]**:** purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 38 mg, 62% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30–7.26 (m, 2H), 7.20–7.15 (m, 3H), 3.73 (s, 6H), 3.38 (t, *J* = 7.6 Hz, 1H), 2.64 (t, *J* = 7.5 Hz, 2H), 2.00–1.89 (m, 2H), 1.68–1.62 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 141.6, 128.4, 128.4, 125.9, 52.5, 51.6, 35.5, 29.1, 28.5. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{18}O_4Na^+$ 273.1097; Found 273.1104. IR (KBr thin film, cm^{-1}): ν 1603, 1496, 1453, 1435, 1343, 1197, 1144, 1056, 1003, 914, 806, 748, 699.



5c

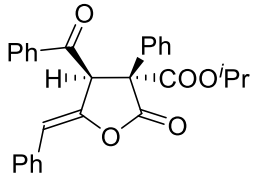
isopropyl 4-benzoyl-5-benzyl-3-ethyl-2-oxo-2,3-dihydrofuran-3-carboxylate (5c): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 21 mg, 53% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.73 (m,

2H), 7.65–7.58 (m, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.30–7.22 (m, 3H), 7.06–7.03 (m, 2H), 5.11–5.03 (m, 1H), 3.65 (d, *J* = 15.4 Hz, 1H), 3.57 (d, *J* = 15.4 Hz, 1H), 2.44–2.24 (m, 2H), 1.21–1.13 (m, 6H), 0.90 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.2, 172.4, 166.0, 162.0, 138.7, 134.3, 133.3, 129.0, 128.8, 128.8, 128.7, 127.4, 119.2, 70.4, 62.6, 34.5, 25.8, 21.5, 9.1. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{24}H_{24}O_5H^+$ 393.1697; Found 393.1693. IR (KBr thin film, cm^{-1}): ν 2979, 2935, 2360, 1809, 1743, 1635, 1352, 1226, 1104, 1066, 939, 696.



5d

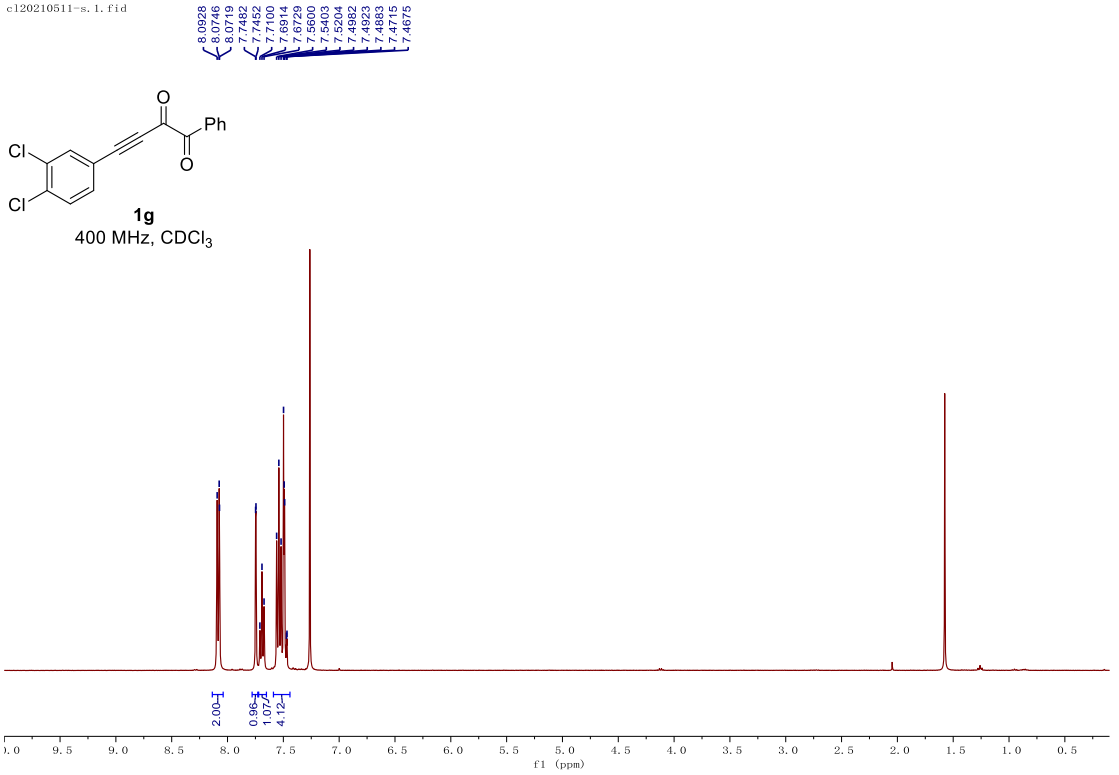
isopropyl 5-ethyl-2-oxo-5-phenyl-4-(2-phenylacetyl)-2,5-dihydrofuran-3-carboxylate (5d): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), white solid, mp 152−154 ℃, 47 mg, 71% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84–7.78 (m, 2H), 7.66–7.60 (m, 1H), 7.54–7.47 (m, 4H), 7.39–7.32 (m, 3H), 7.32–7.19 (m, 3H), 7.12–7.00 (m, 2H), 5.20–5.12 (m, 1H), 3.74 (d, *J* = 15.4 Hz, 1H), 3.60 (d, *J* = 15.4 Hz, 1H), 1.22 (d, *J* = 6.3 Hz, 3H), 1.17 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.8, 171.0, 165.5, 161.8, 138.3, 134.1, 133.5, 133.2, 129.1, 129.0, 128.9, 128.7, 128.6, 128.4, 127.5, 121.0, 71.0, 65.1, 34.5, 21.5, 21.4. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{24}O_5Na^+$ 463.1516; Found 463.1516. IR (KBr thin film, cm^{-1}): ν 2984, 1797, 1744, 1639, 1449, 1328, 1211, 1142, 1101, 973, 699, 663.

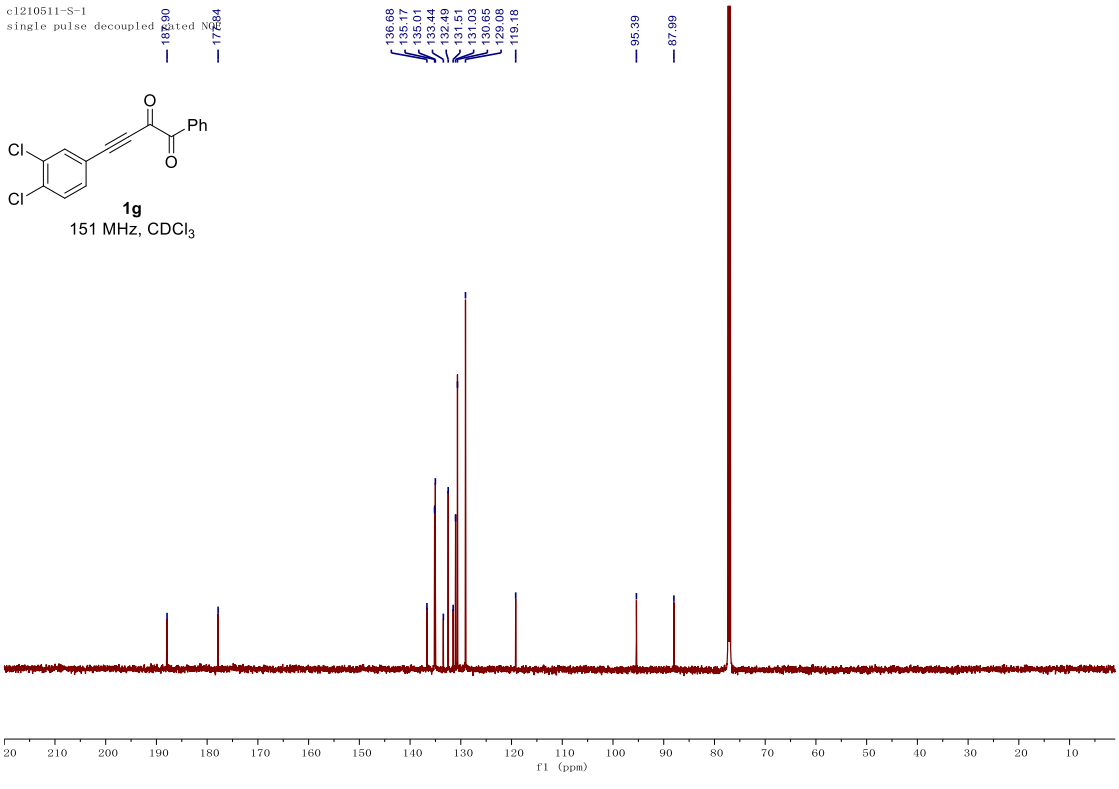


5e

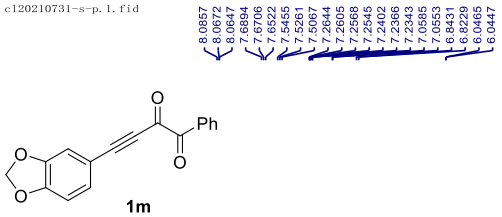
carboxylate (5e): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), white solid, mp 156−158 ℃, 47 mg, 53% yield, 3:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.92 (m, 2H), 7.64–7.59 (m, 3H), 7.58–7.54 (m, 2H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.25–7.18 (m, 4H), 5.95 (s, 1H), 5.68 (s, 1H), 5.09–5.00 (m, 1H), 1.20 (d, *J* = 6.3 Hz, 3H), 1.12 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.6, 168.7, 166.6, 142.8, 135.4, 134.3, 133.1, 132.5, 129.1, 128.9, 128.7, 128.6, 128.3, 127.6, 127.5, 108.2, 71.9, 62.2, 55.4, 21.4, 21.1. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{24}O_5Na^+$ 463.1516; Found 463.1509. IR (KBr thin film, cm^{-1}): ν 2984, 1805, 1728, 1670, 1447, 1222, 1081, 976, 686.

VII. ^{1}H NMR and ^{13}C NMR spectra of substrates and products



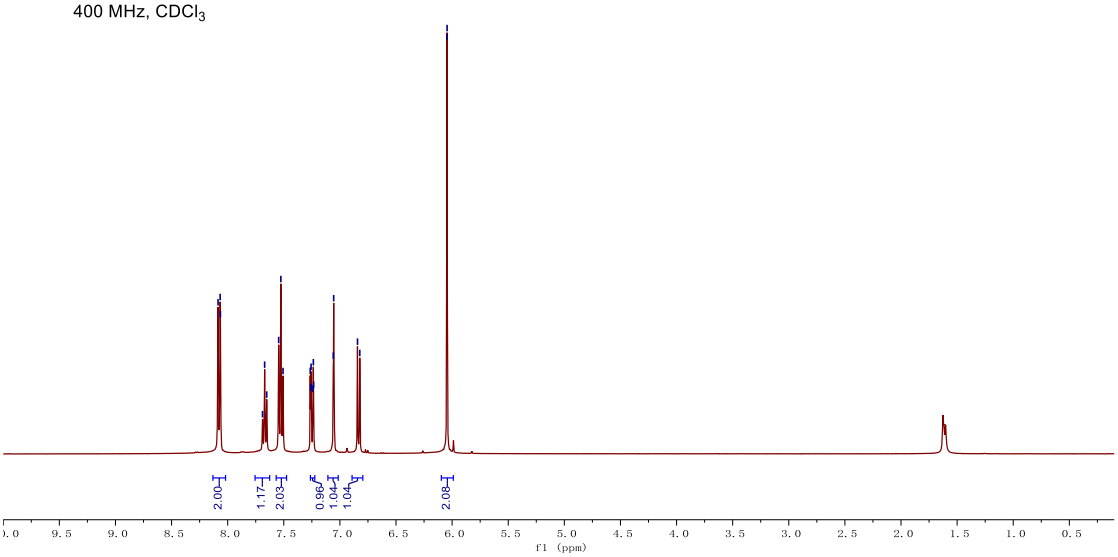


c120210731-s-p.1.fid

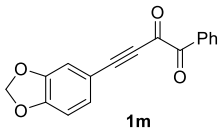


1m

400 MHz, $CDCl_3$

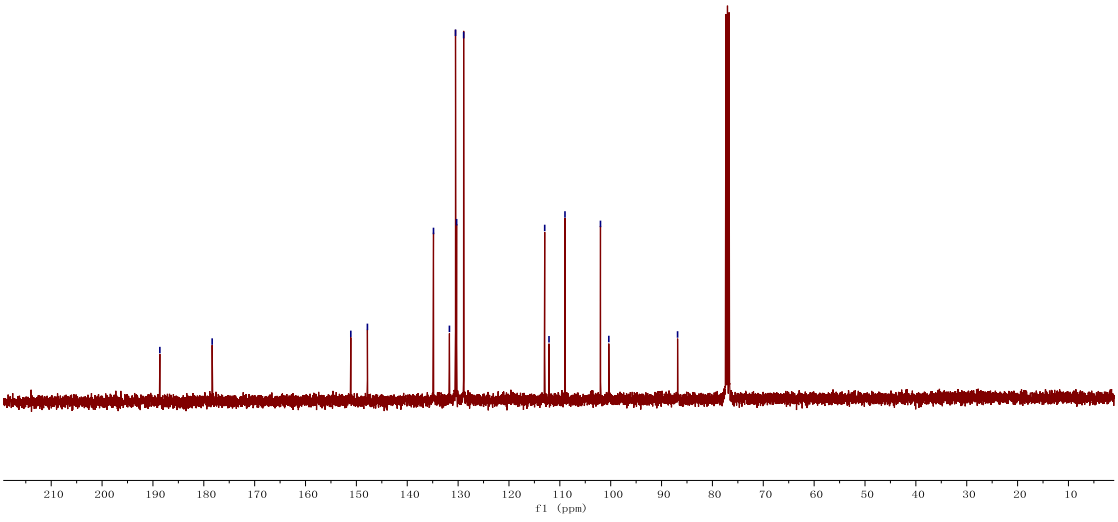


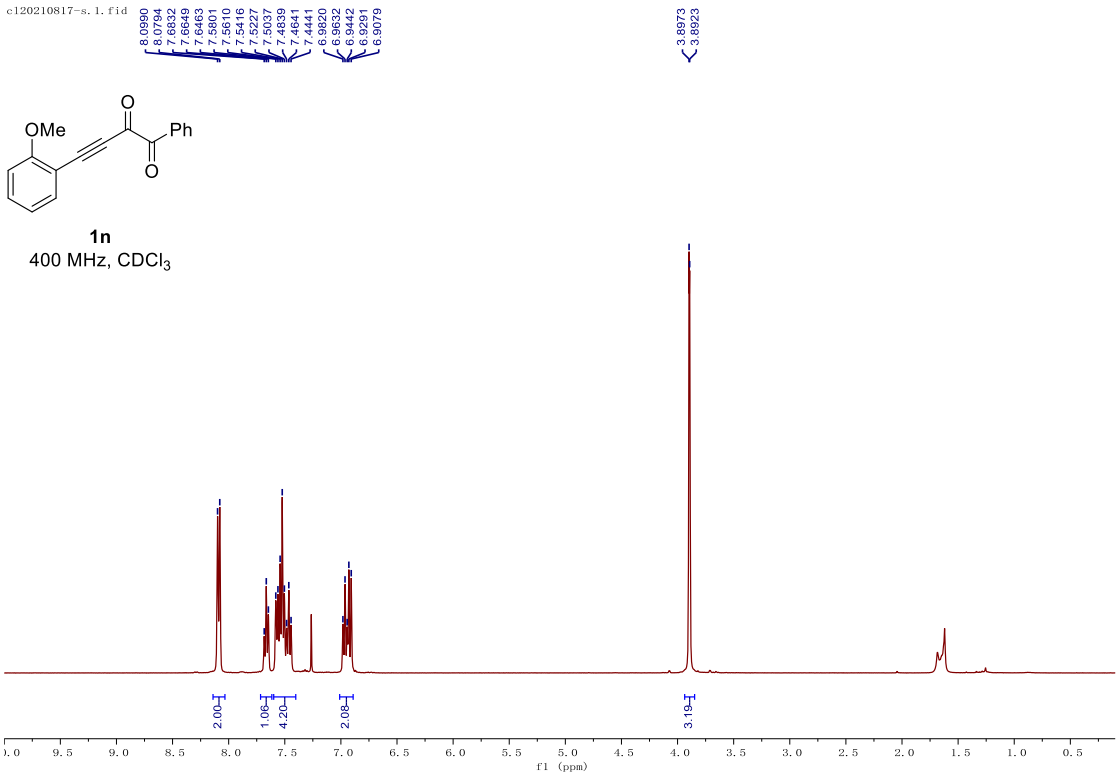
c120210809-s.1.fid



1m

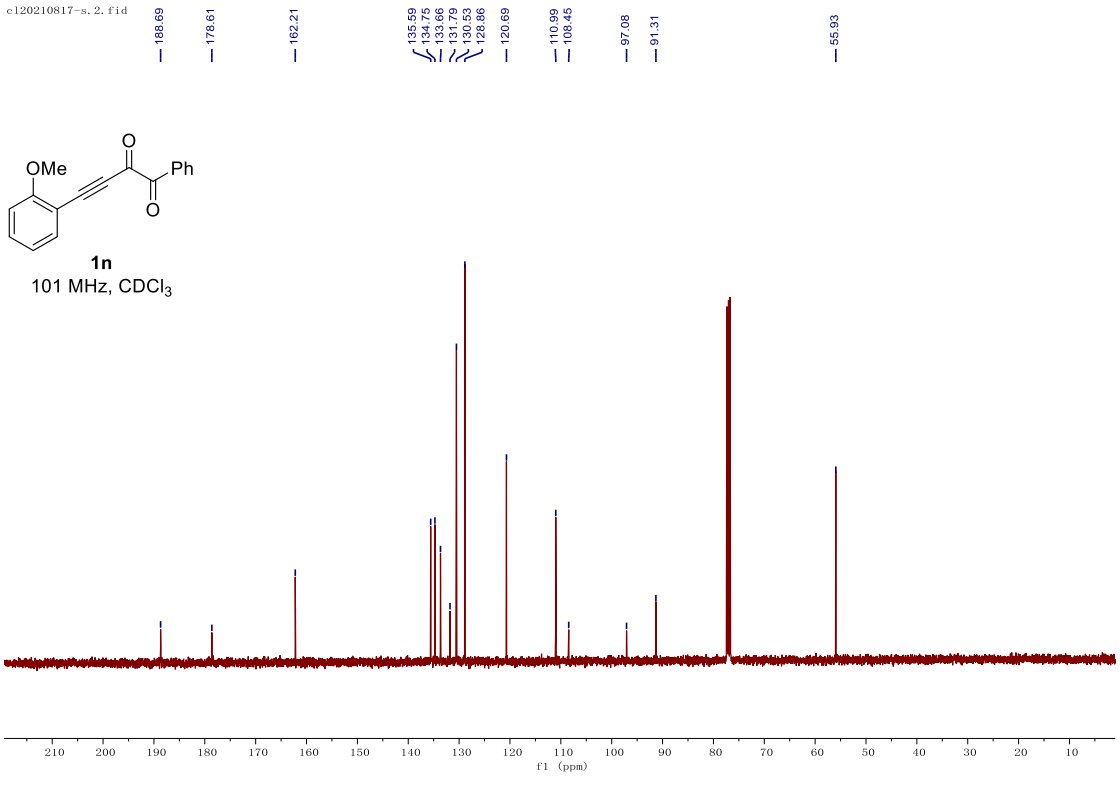
101 MHz, $CDCl_3$





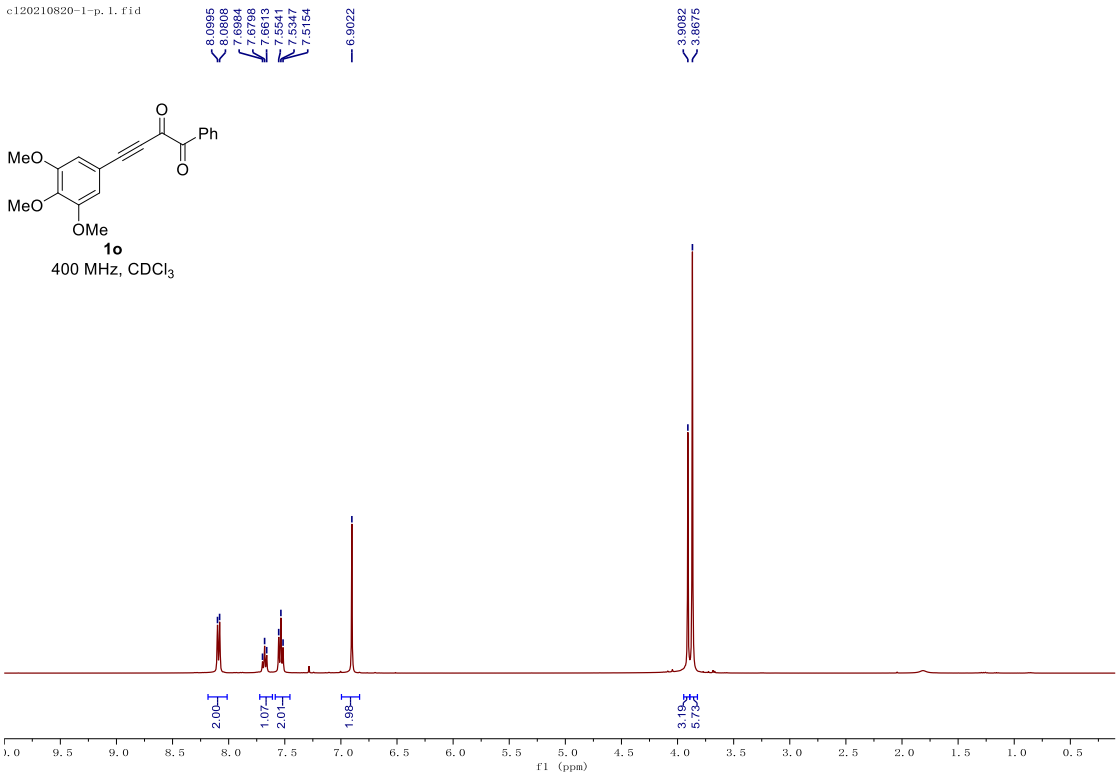
1n

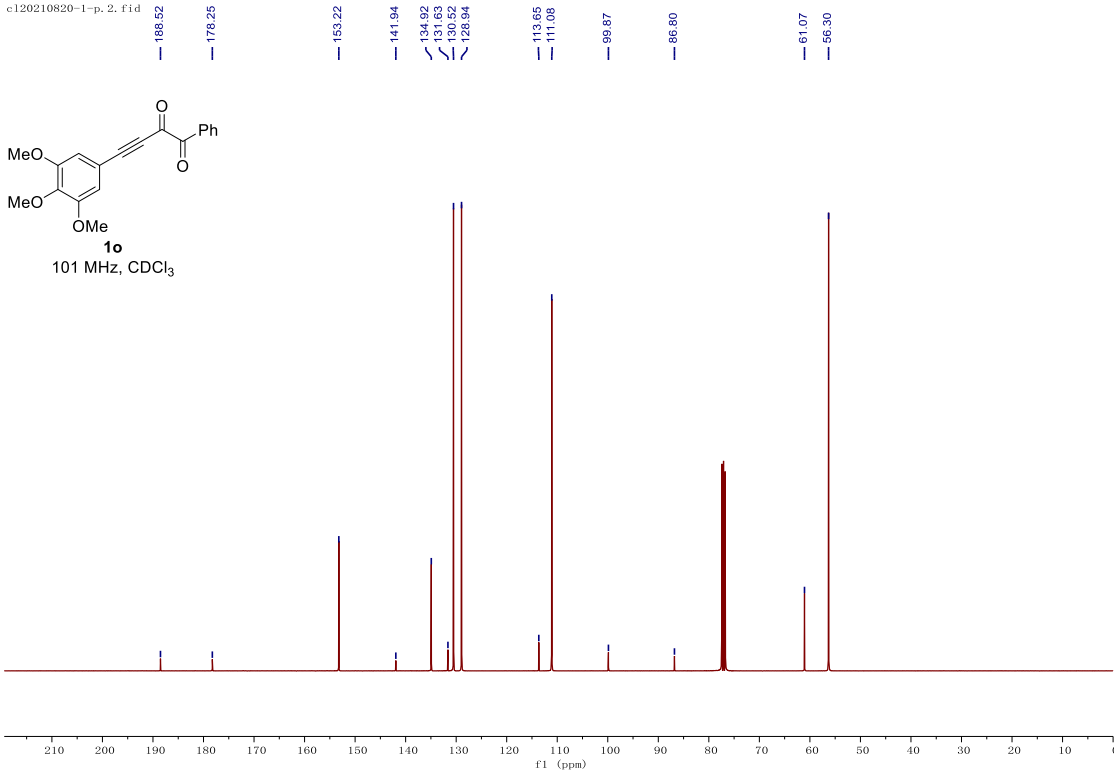
400 MHz, $CDCl_3$

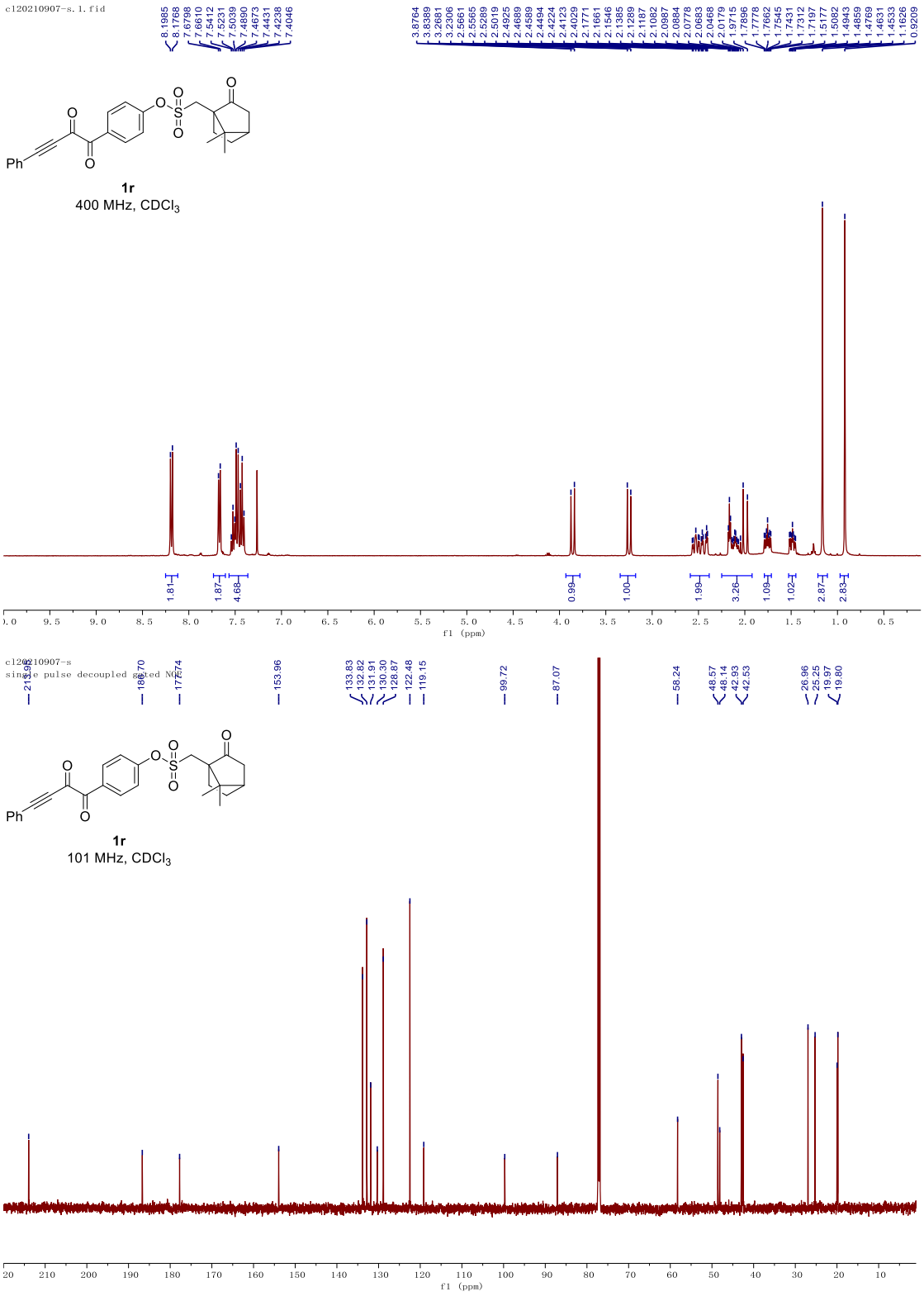


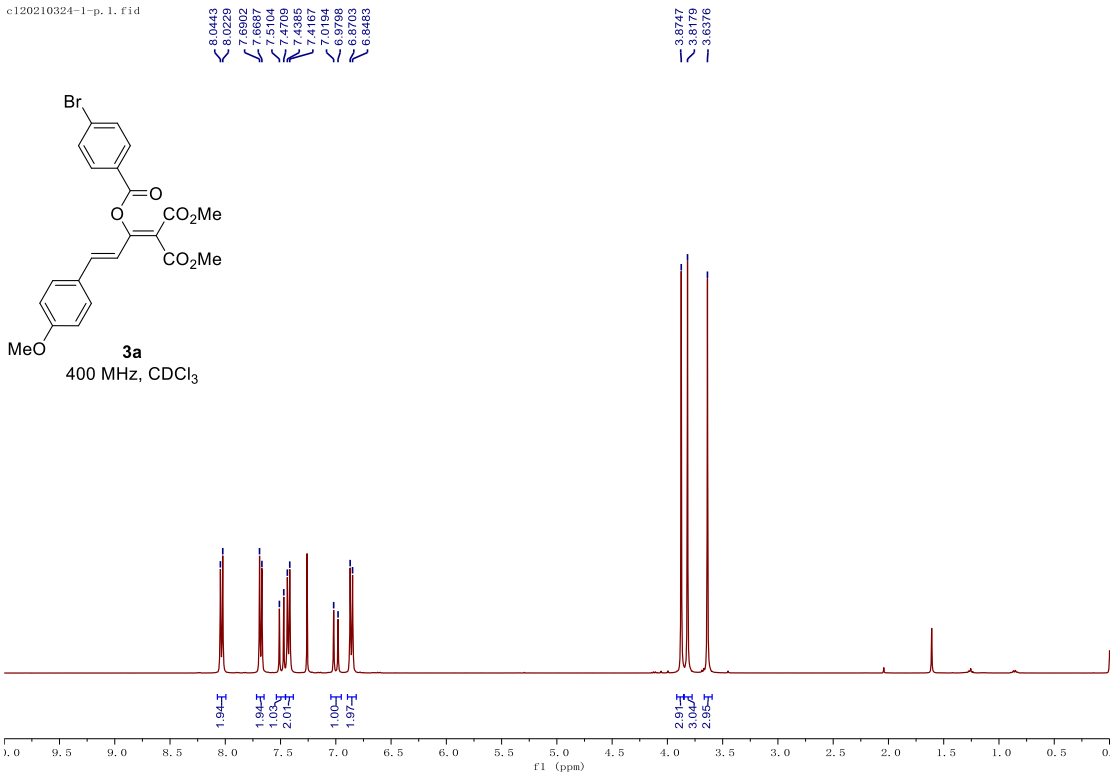
1n

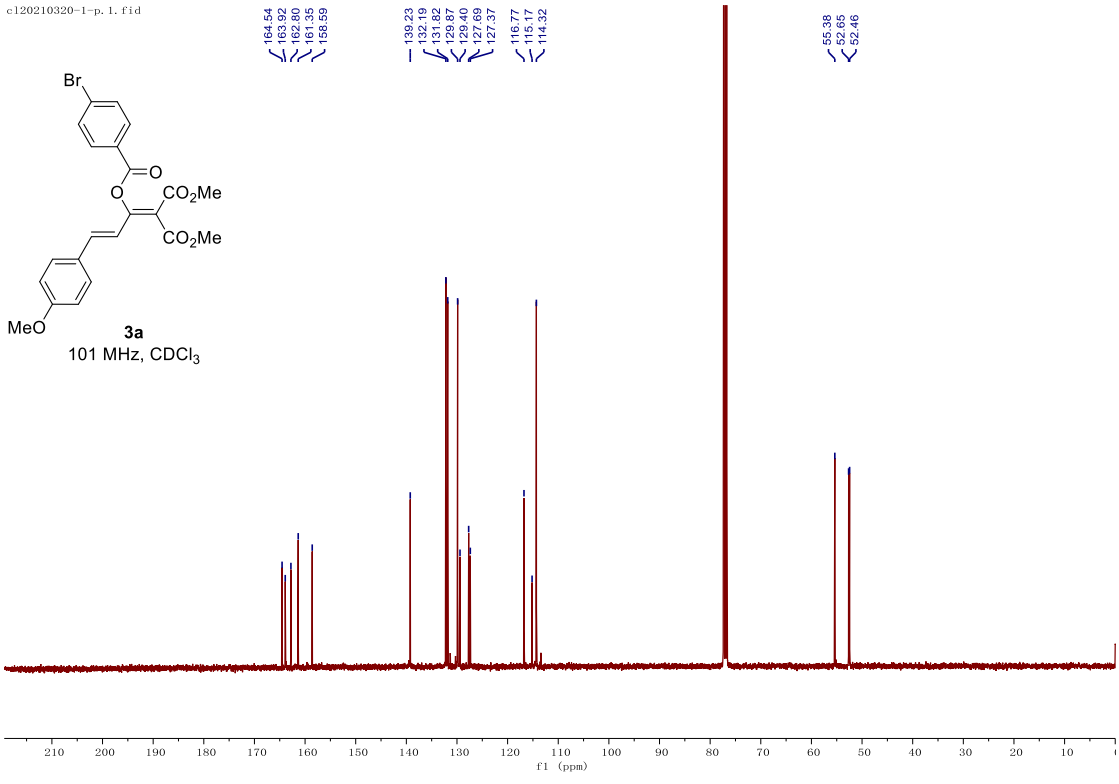
101 MHz, $CDCl_3$

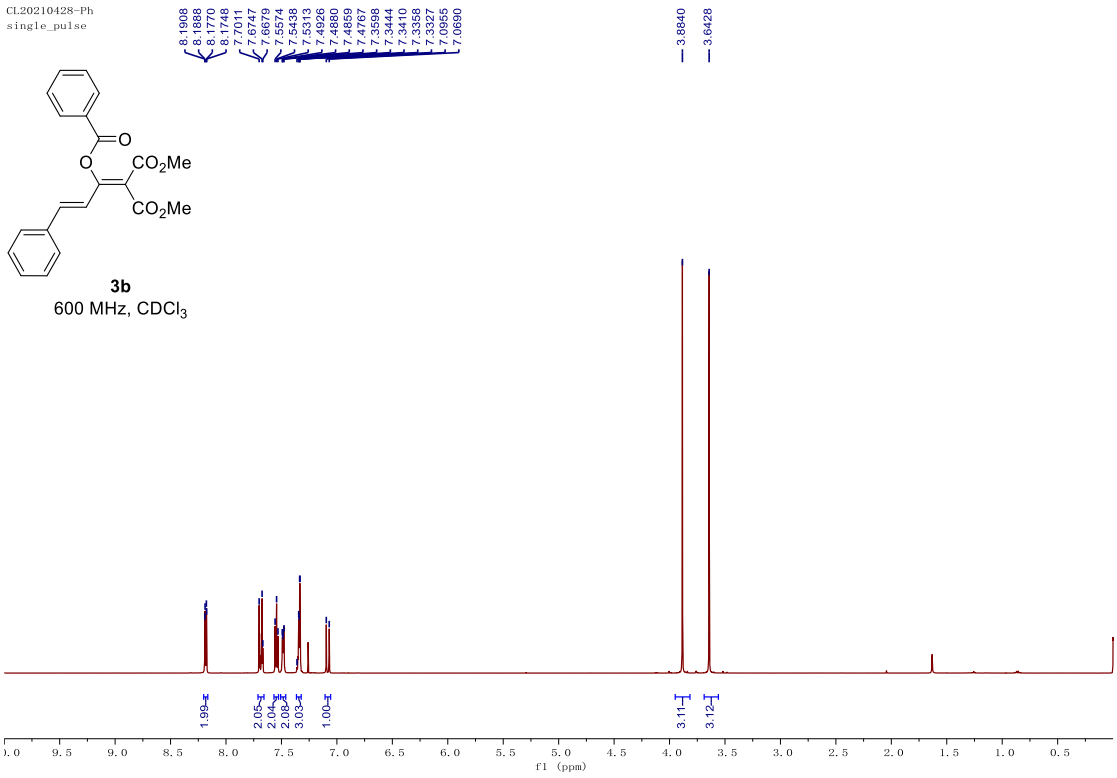

c120210820-1-p.1.fid
8.0995
8.0808
7.6984
7.6798
7.6613
7.5541
7.5347
7.5154
6.9022
3.9082
3.8675
MeO
MeO
OMe
O
Ph
O
1o
400 MHz, CDCl3
2.00
1.07
2.01
1.98
3.19
5.73
f1 (ppm)

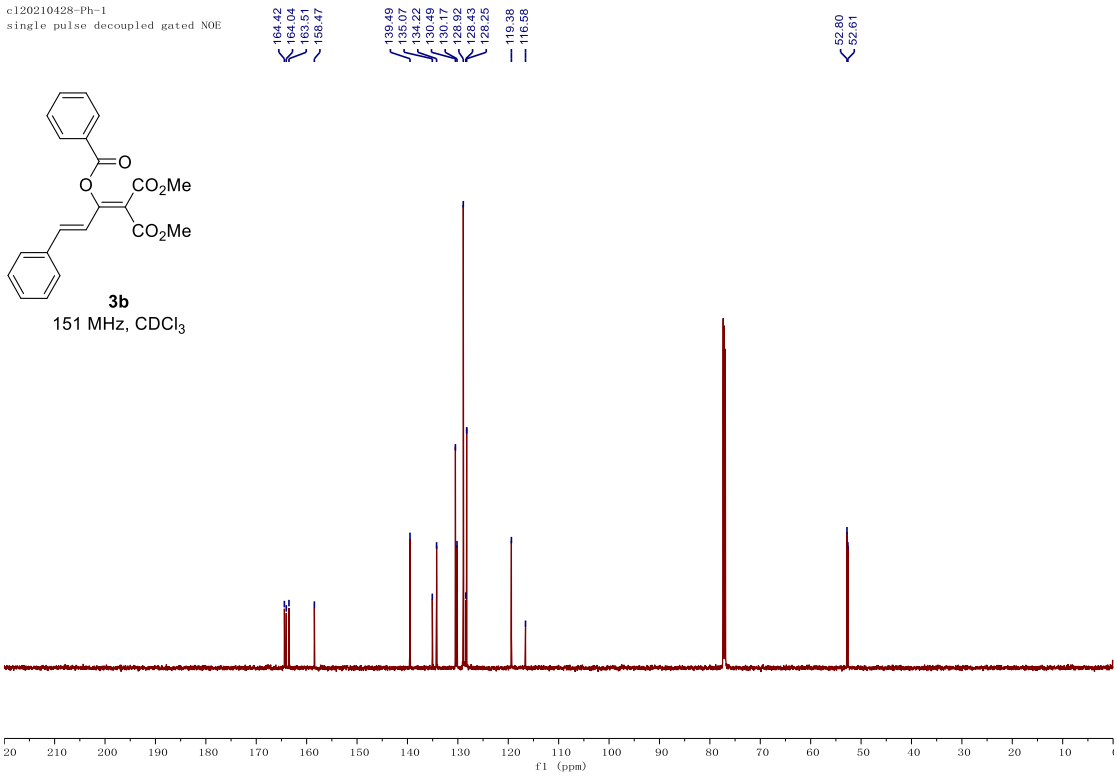

c120210820-1-p.2.fid
188.52
178.25
153.22
141.94
134.92
131.63
130.52
128.94
113.65
111.08
99.87
86.80
61.07
56.30
MeO
MeO
OMe
O
Ph
O
1o
101 MHz, CDCl3
f1 (ppm)

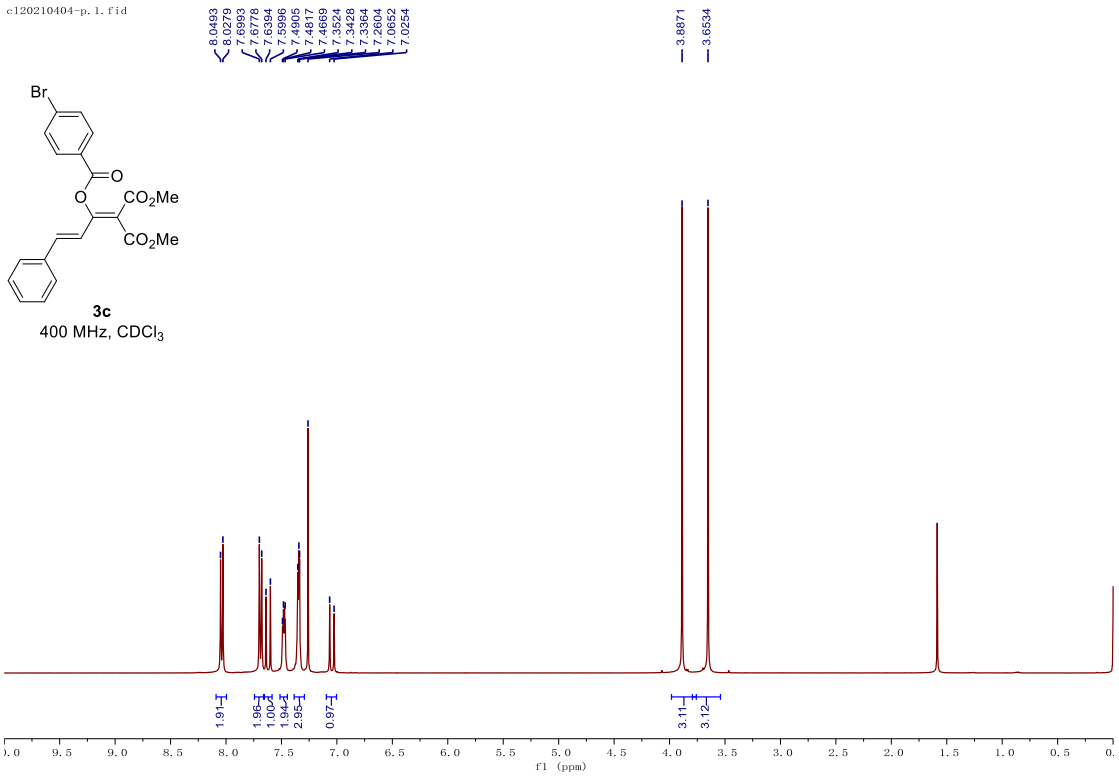

c120210907-s.1.fid
8.1985
8.1768
7.6798
7.6610
7.5412
7.5231
7.5039
7.4890
7.4673
7.4431
7.4238
7.4046
3.8764
3.8389
3.2681
3.2306
2.5661
2.5565
2.5289
2.5019
2.4925
2.4689
2.4589
2.4494
2.4224
2.4123
2.4029
2.1771
2.1661
2.1546
2.1385
2.1289
2.1187
2.1082
2.0987
2.0884
2.0778
2.0683
2.0468
2.0179
1.9715
1.7896
1.7778
1.7662
1.7545
1.7431
1.7312
1.7197
1.5177
1.5082
1.4943
1.4859
1.4759
1.4631
1.4531
1.1626
0.9209
O
O
O
O
S
O
O
Ph
1r
400 MHz, CDCl3
1.81
1.87
4.68
0.99
1.00
1.99
3.26
1.09
1.02
2.87
2.83
f1 (ppm)
c120210907-s
single pulse decoupled gated NOE
213.98
180.70
177.74
153.96
133.83
132.82
131.91
131.30
128.87
122.48
119.15
99.72
87.07
58.24
48.57
48.14
42.93
42.53
26.96
25.25
19.97
19.80
O
O
O
O
S
O
O
Ph
1r
101 MHz, CDCl3
f1 (ppm)

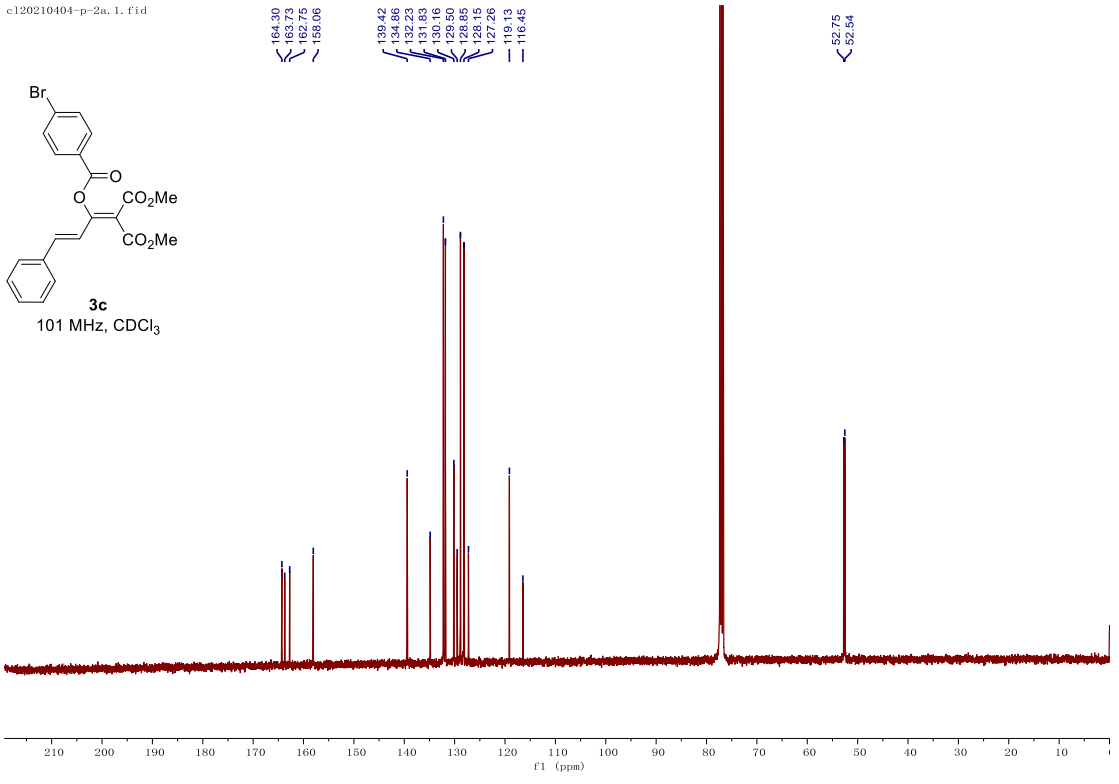

c120210324-1-p.1.fid
8.0443
8.0229
7.6902
7.6687
7.5104
7.4709
7.4385
7.4167
7.0194
6.9798
6.8703
6.8483
3.8747
3.8179
3.6376
Br
O
O
CO2Me
CO2Me
MeO
3a
400 MHz, CDCl3
1.94
1.94
1.03
2.01
1.00
1.97
2.91
3.04
2.95
f1 (ppm)

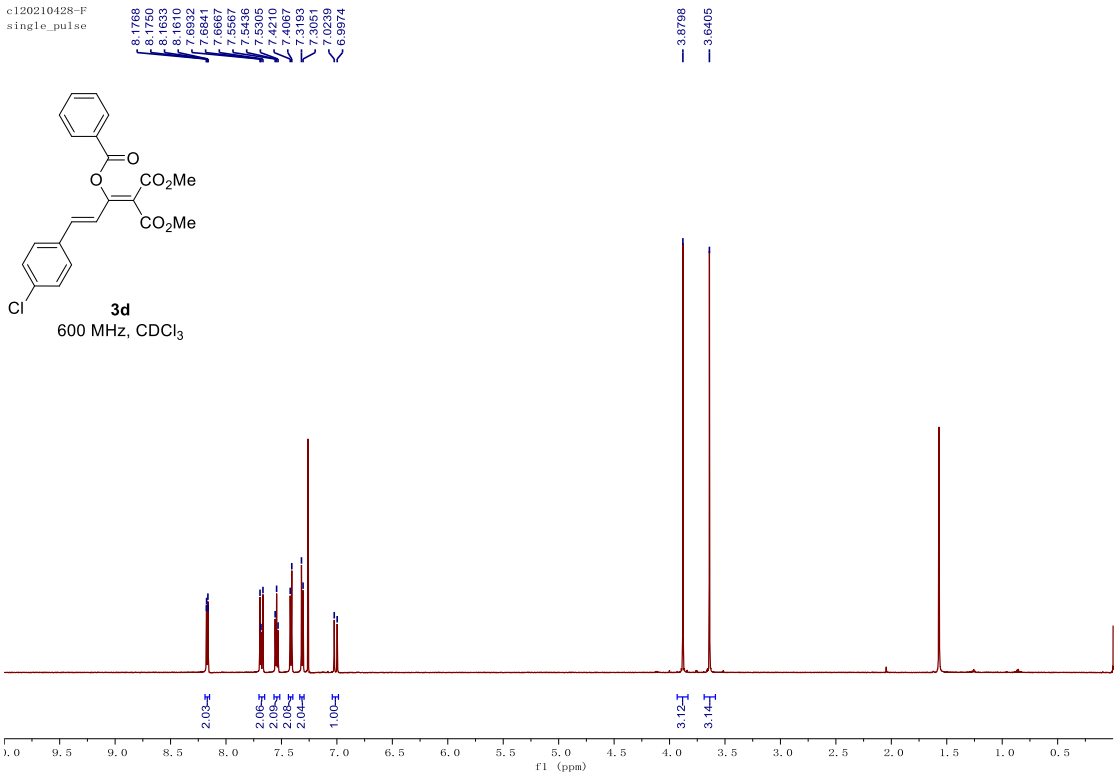

c120210320-1-p.1.fid
164.54
163.92
163.60
161.35
158.59
139.23
132.19
131.82
131.37
129.40
127.69
127.37
116.77
115.17
114.32
55.38
52.65
52.46
Br
O
O
CO2Me
CO2Me
MeO
3a
101 MHz, CDCl3
f1 (ppm)

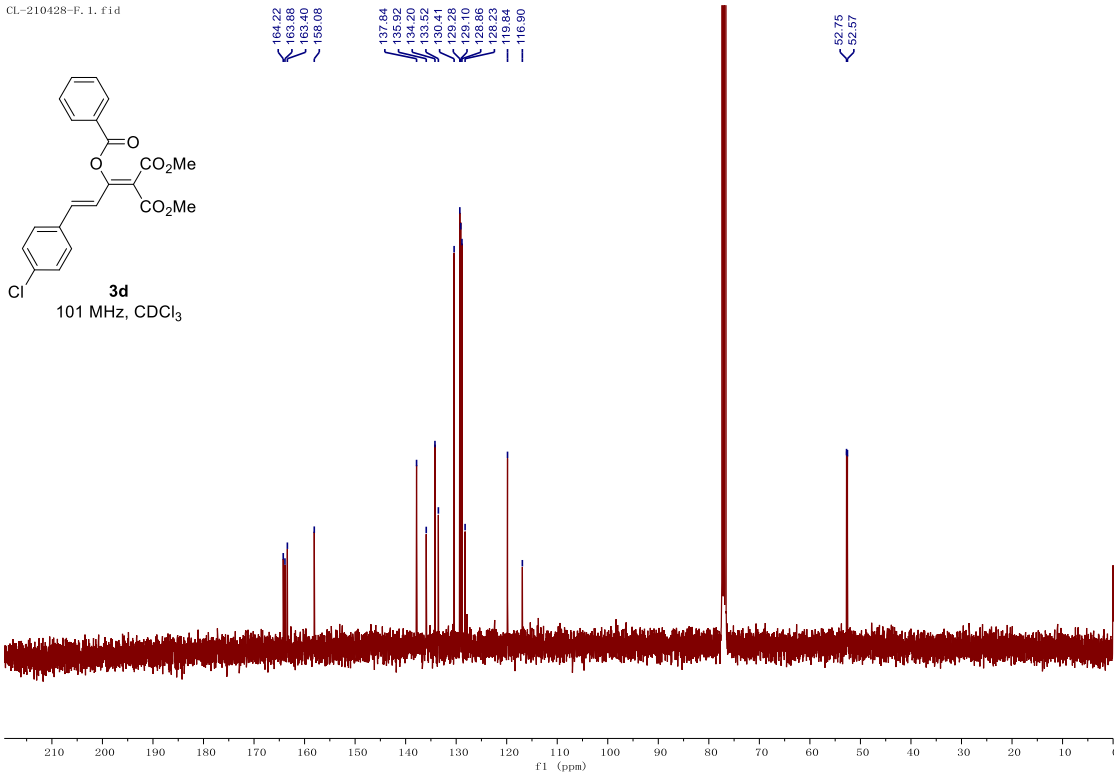

CL20210428-Ph
single_pulse
8.1908
8.1888
8.1770
8.1748
7.7011
7.6747
7.6679
7.5574
7.5438
7.5313
7.4926
7.4880
7.4859
7.4767
7.3598
7.3444
7.3410
7.3358
7.3327
7.0955
7.0690
3.8840
3.6428
O
O
CO2Me
CO2Me
3b
600 MHz, CDCl3
1.99
2.05
2.04
2.08
3.03
1.00
3.11
3.12
f1 (ppm)

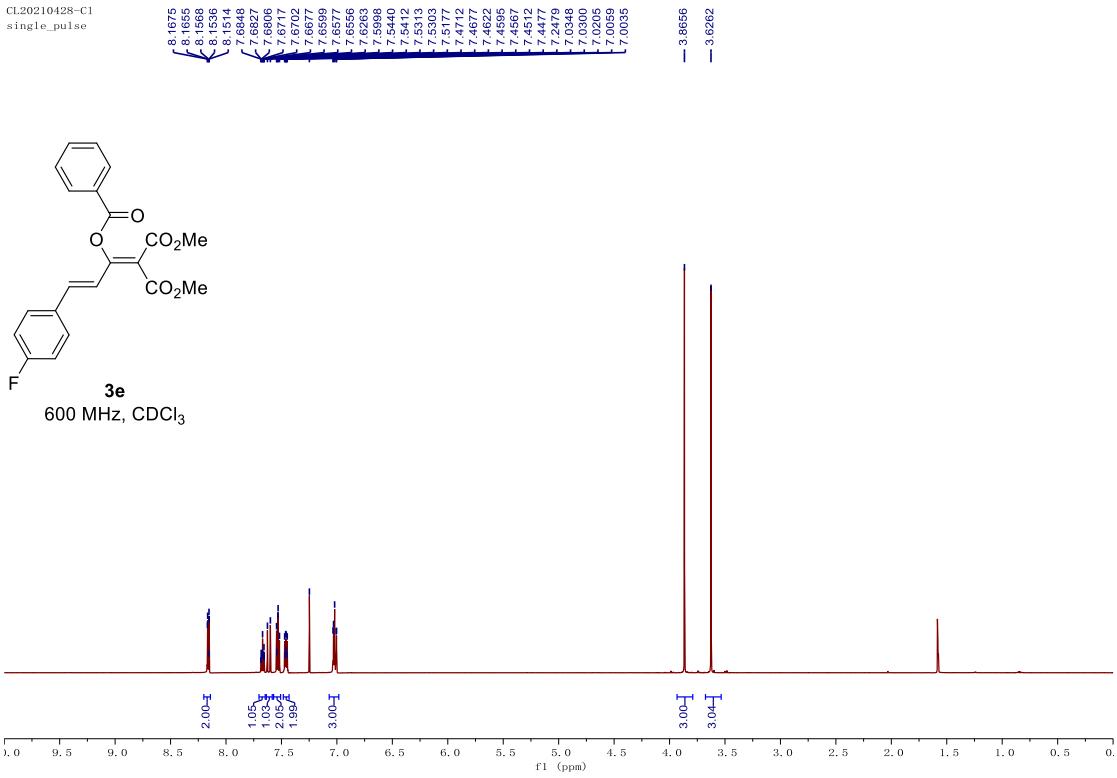

c120210428-Ph-1
single pulse decoupled gated NOE
164.42
164.04
163.51
158.47
139.49
135.07
134.22
130.49
130.17
128.92
128.43
128.25
119.38
116.58
52.80
52.61
O
O
CO2Me
CO2Me
3b
151 MHz, CDCl3
f1 (ppm)

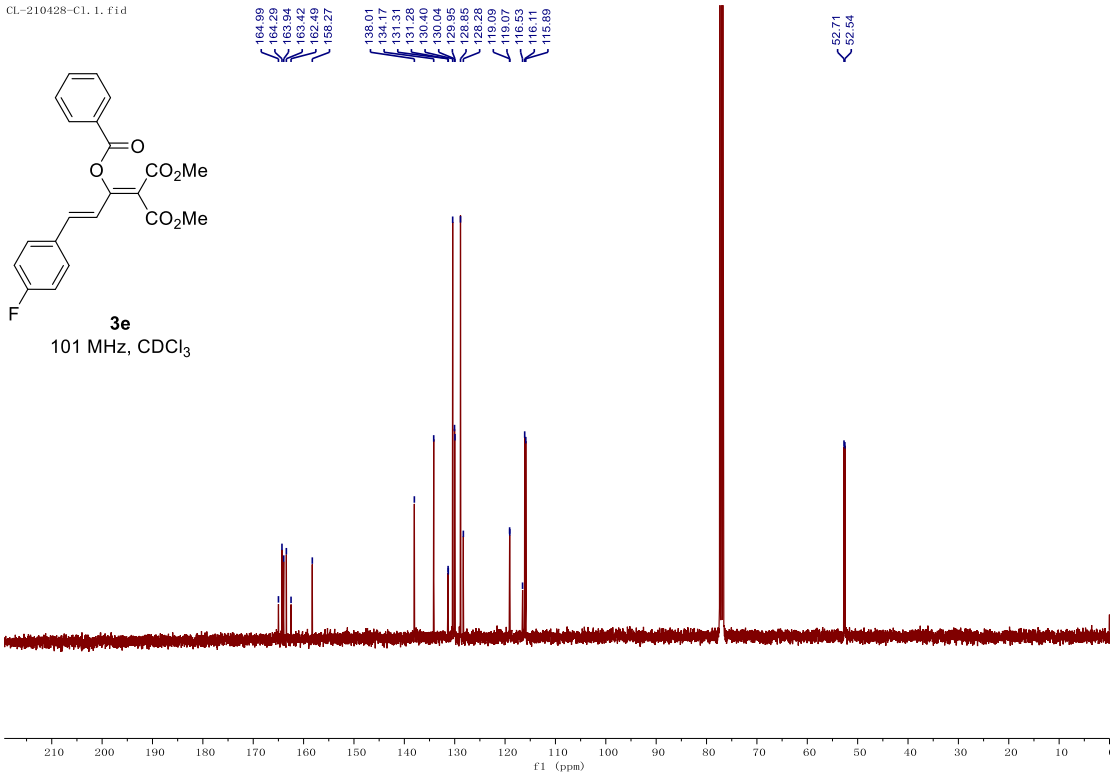

c120210404-p.1.fid
8.0493
8.0279
7.6993
7.6778
7.6394
7.4906
7.4817
7.4669
7.3524
7.3428
7.3364
7.2604
7.0652
7.0254
3.8871
3.6534
Br
O
O
CO2Me
CO2Me
3c
400 MHz, CDCl3
1.91
1.96
1.00
1.94
2.95
0.97
3.11
3.12
f1 (ppm)

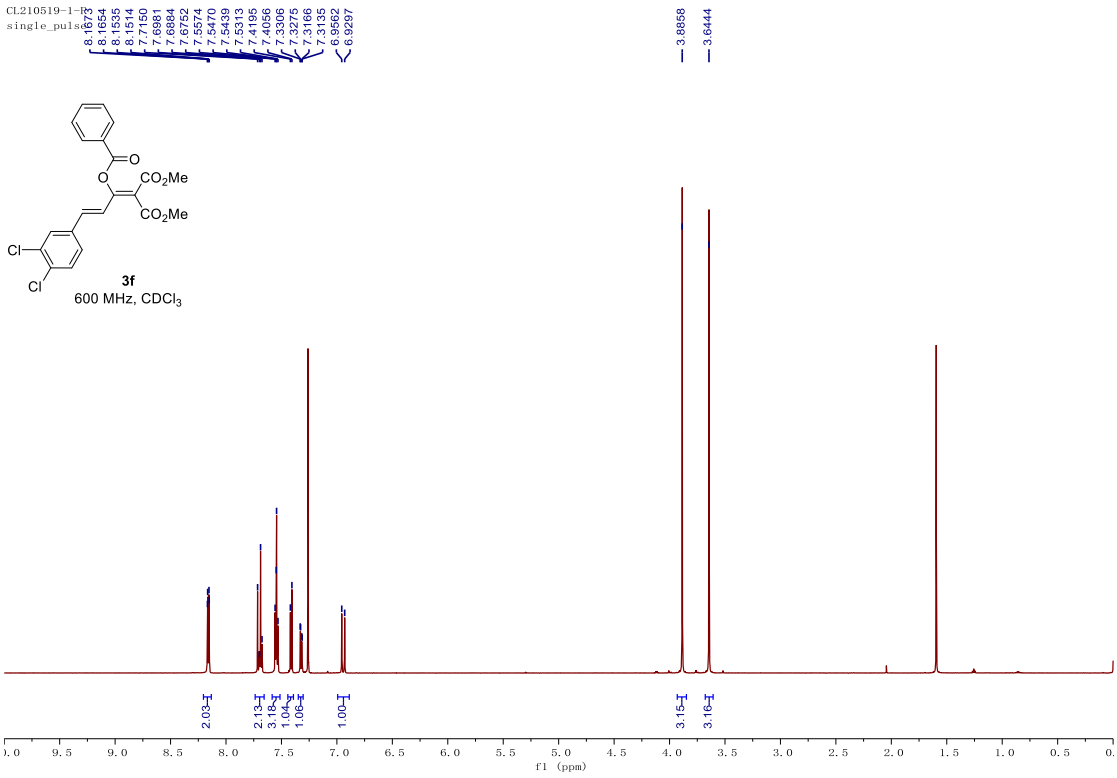

c120210404-p-2a.1.fid
164.30
163.73
162.75
158.06
139.42
134.86
132.23
131.83
130.16
129.55
128.85
128.45
127.26
119.13
116.45
52.75
52.54
Br
O
O
CO2Me
CO2Me
3c
101 MHz, CDCl3
f1 (ppm)

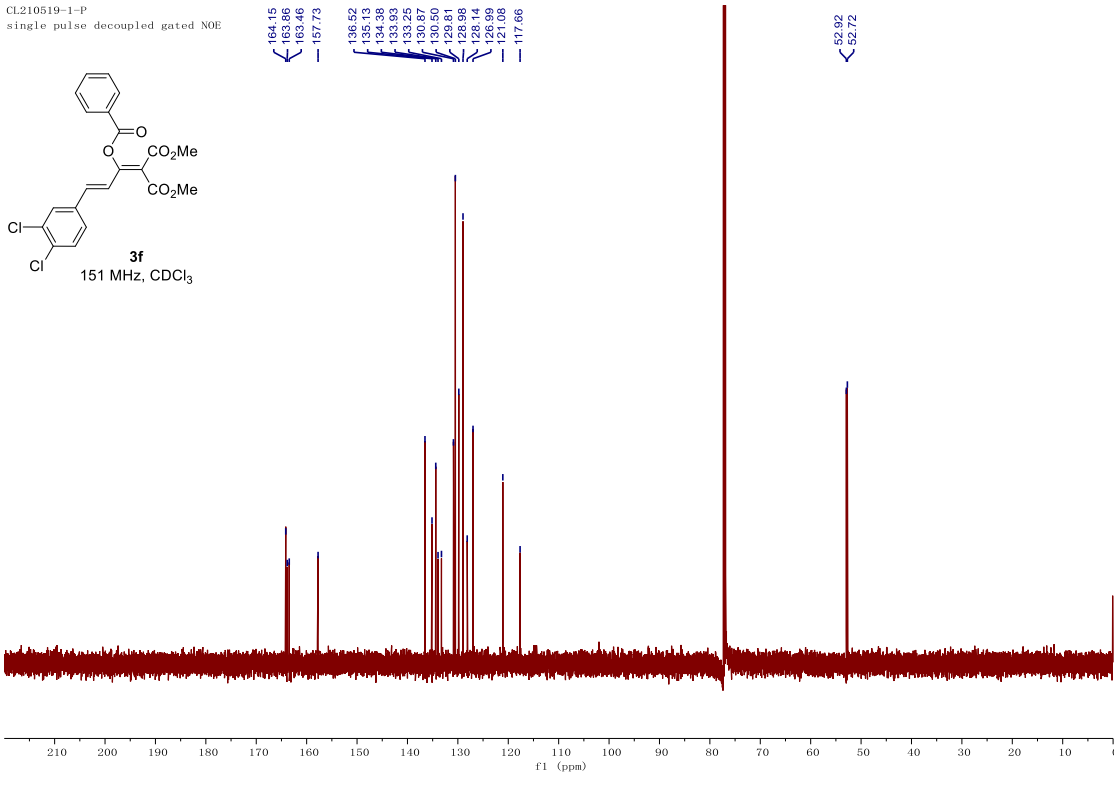

c120210428-F
single_pulse
8.1768
8.1750
8.1633
8.1610
7.6932
7.6841
7.6667
7.5567
7.5436
7.5305
7.4210
7.4067
7.3193
7.3051
7.0239
6.9974
3.8798
3.6405
O
O
CO2Me
CO2Me
Cl
3d
600 MHz, CDCl3
2.03
2.06
2.09
2.08
2.04
1.00
3.12
3.14
f1 (ppm)

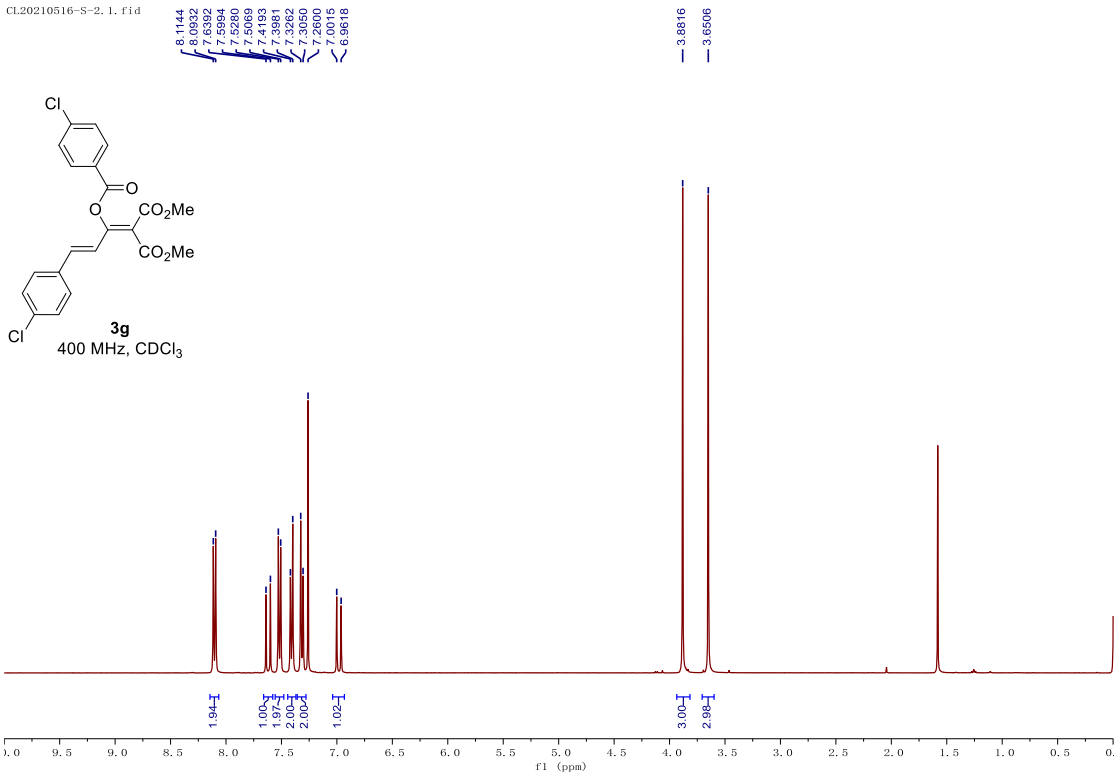

CL-210428-F.1.fid
164.22
163.88
163.40
158.08
137.84
135.92
134.20
133.52
130.41
129.28
129.10
128.86
128.23
119.64
116.90
52.75
52.57
O
O
CO2Me
CO2Me
Cl
3d
101 MHz, CDCl3
f1 (ppm)

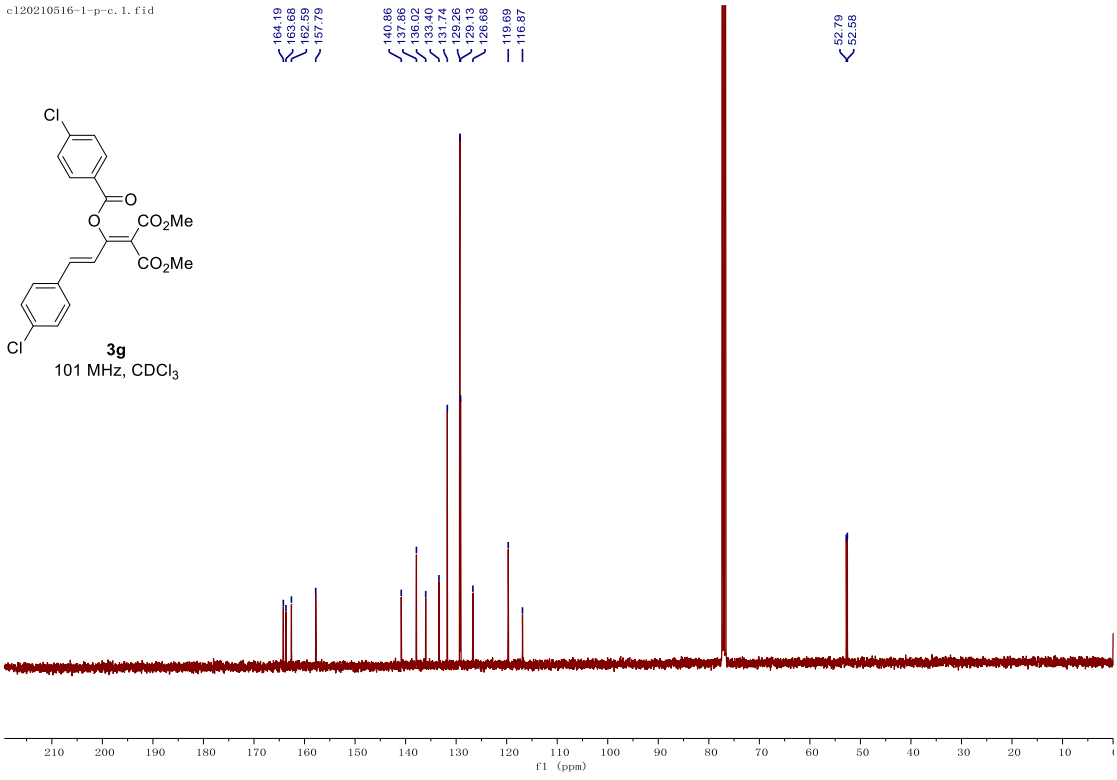

CL20210428-Cl
single_pulse
8.1675
8.1655
8.1568
8.1536
8.1514
7.6848
7.6827
7.6696
7.6717
7.6702
7.6677
7.6599
7.6577
7.6556
7.6263
7.5998
7.5440
7.5412
7.5313
7.5303
7.5177
7.4712
7.4677
7.4622
7.4595
7.4567
7.4512
7.4477
7.2479
7.0348
7.0300
7.0205
7.0059
7.0035
3.8656
3.6262
O
O
CO2Me
CO2Me
F
3e
600 MHz, CDCl3
2.00
1.05
1.03
2.05
1.99
3.00
3.00
3.04
f1 (ppm)

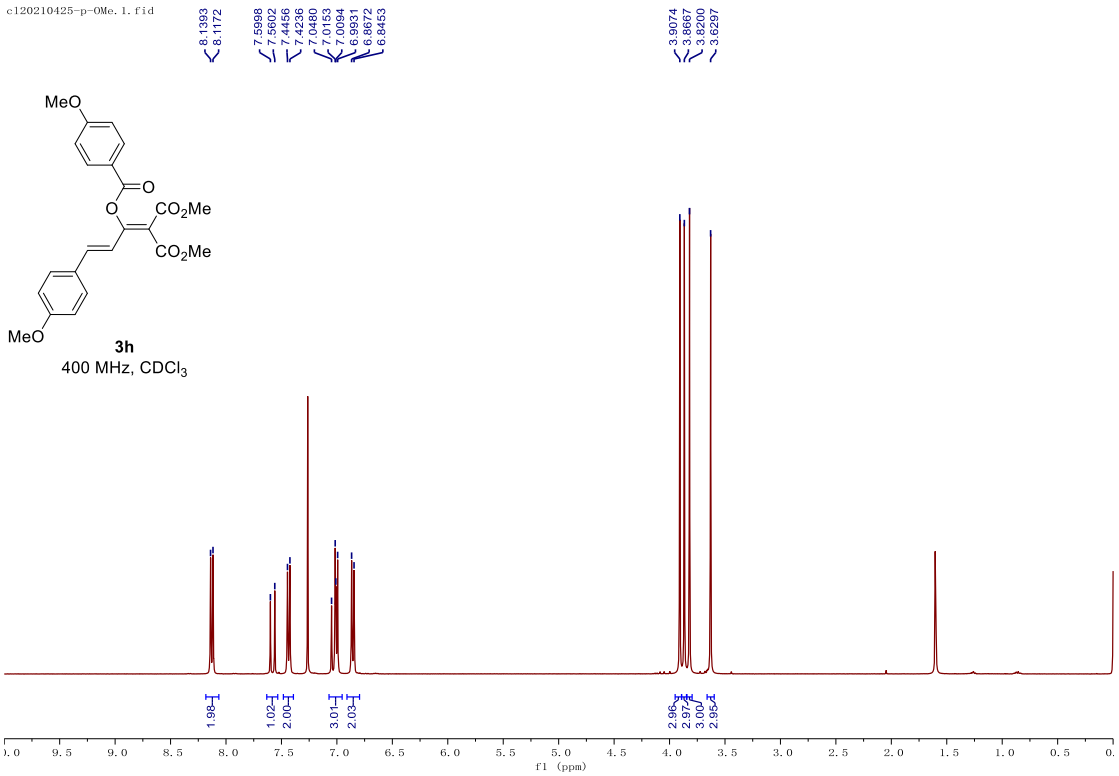

CL-210428-Cl.1.fid
164.99
164.29
163.94
163.42
162.49
158.27
138.01
134.17
131.31
131.28
130.40
130.04
129.95
128.85
128.28
119.09
119.07
116.53
116.11
115.89
52.71
52.54
O
O
CO2Me
CO2Me
F
3e
101 MHz, CDCl3
f1 (ppm)

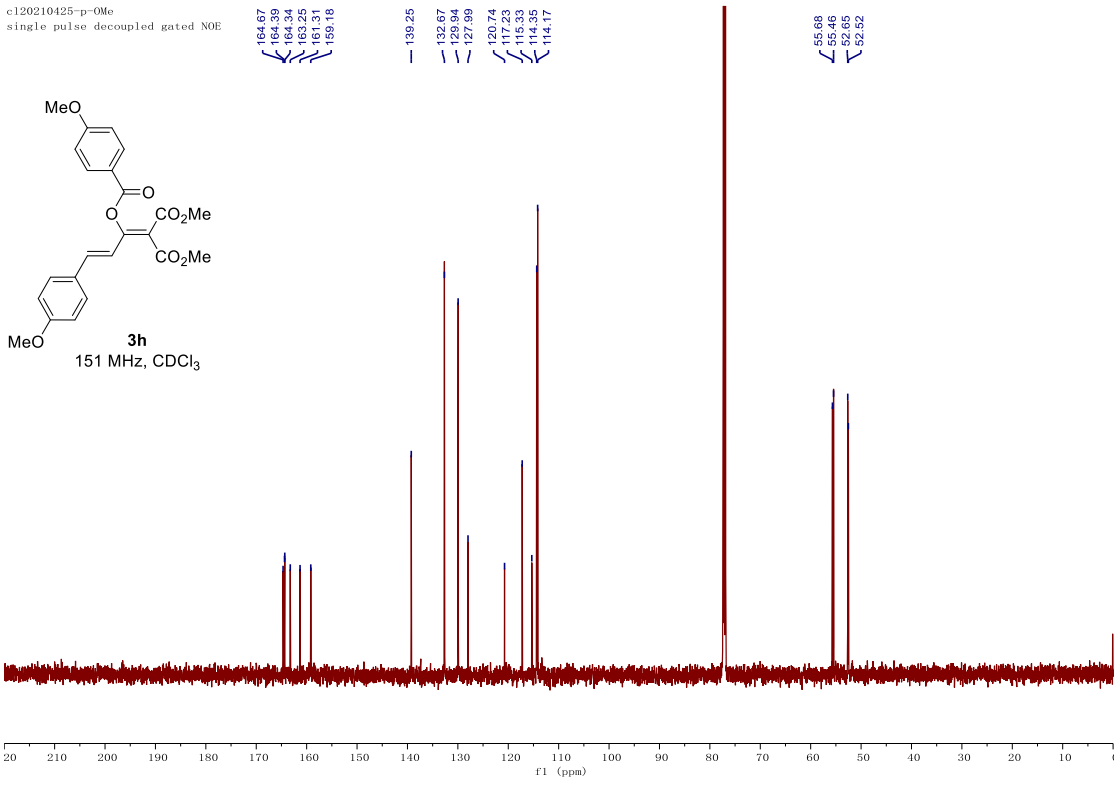

CL210519-1-P
single_pulse
8.1673
8.1654
8.1535
8.1514
7.7150
7.6981
7.6884
7.6752
7.5474
7.5470
7.5439
7.5313
7.4195
7.4056
7.3306
7.3275
7.3166
7.3135
6.9562
6.9297
3.8858
3.6444
O
O
CO2Me
CO2Me
Cl
Cl
3f
600 MHz, CDCl3
2.03
2.13
3.18
1.04
1.06
1.00
3.15
3.16
f1 (ppm)

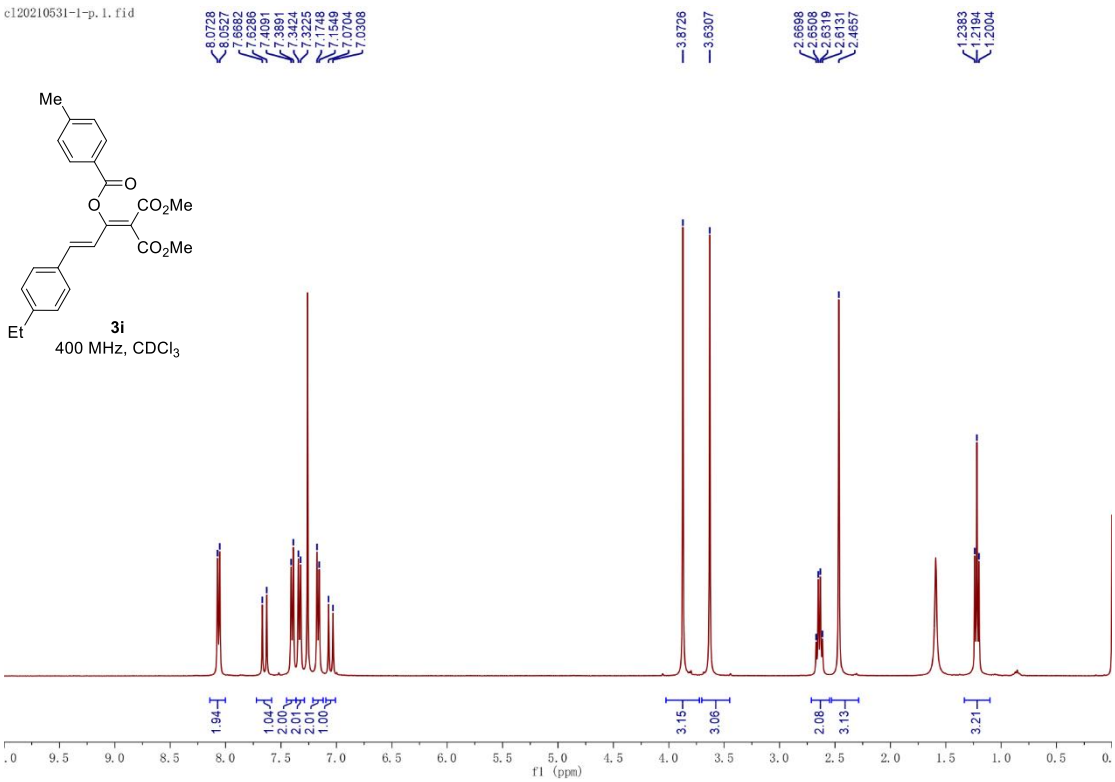

CL210519-1-P
single pulse decoupled gated NOE
164.15
163.86
163.46
157.73
136.52
135.13
134.38
134.03
133.25
130.67
130.50
129.81
128.98
128.14
126.99
121.08
117.66
52.92
52.72
O
O
CO2Me
CO2Me
Cl
Cl
3f
151 MHz, CDCl3
f1 (ppm)

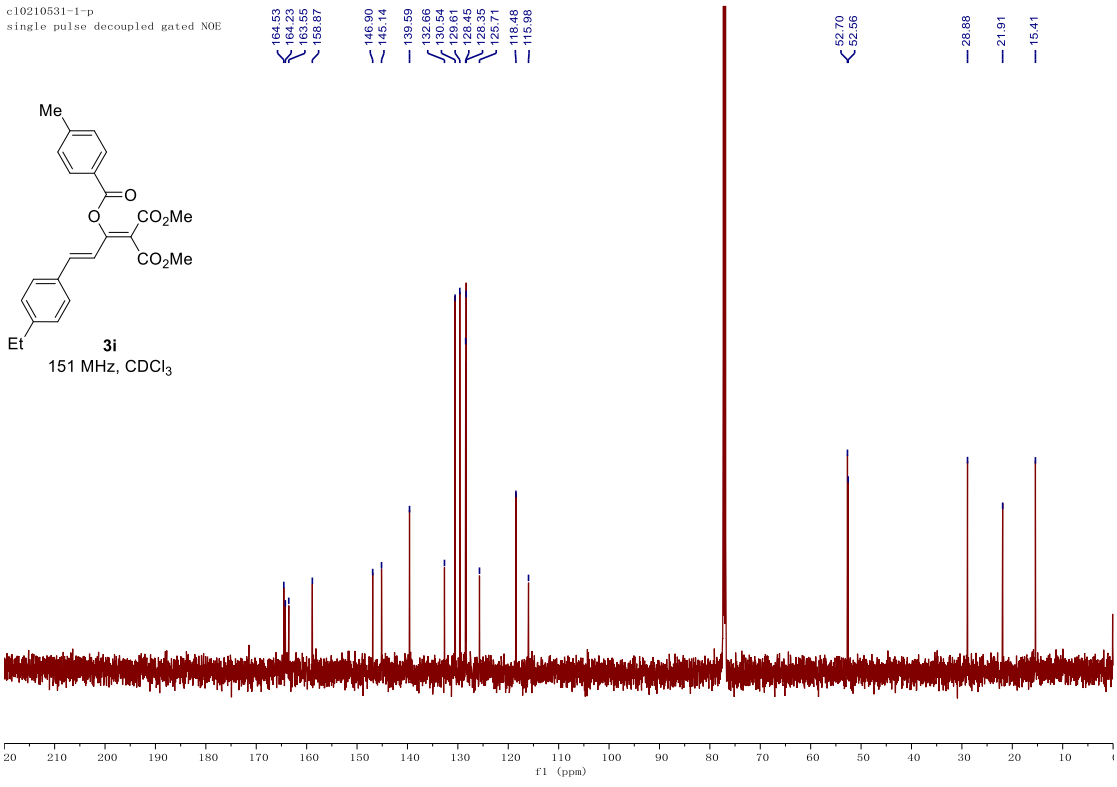

CL20210516-S-2.1.fid
8.1144
8.0932
7.6392
7.5994
7.5280
7.5069
7.4193
7.3981
7.3262
7.3050
7.2600
7.0015
6.9618
3.8816
3.6506
Cl
O
O
CO2Me
CO2Me
Cl
3g
400 MHz, CDCl3
1.94
1.00
1.97
2.00
2.00
1.02
3.00
2.98
f1 (ppm)

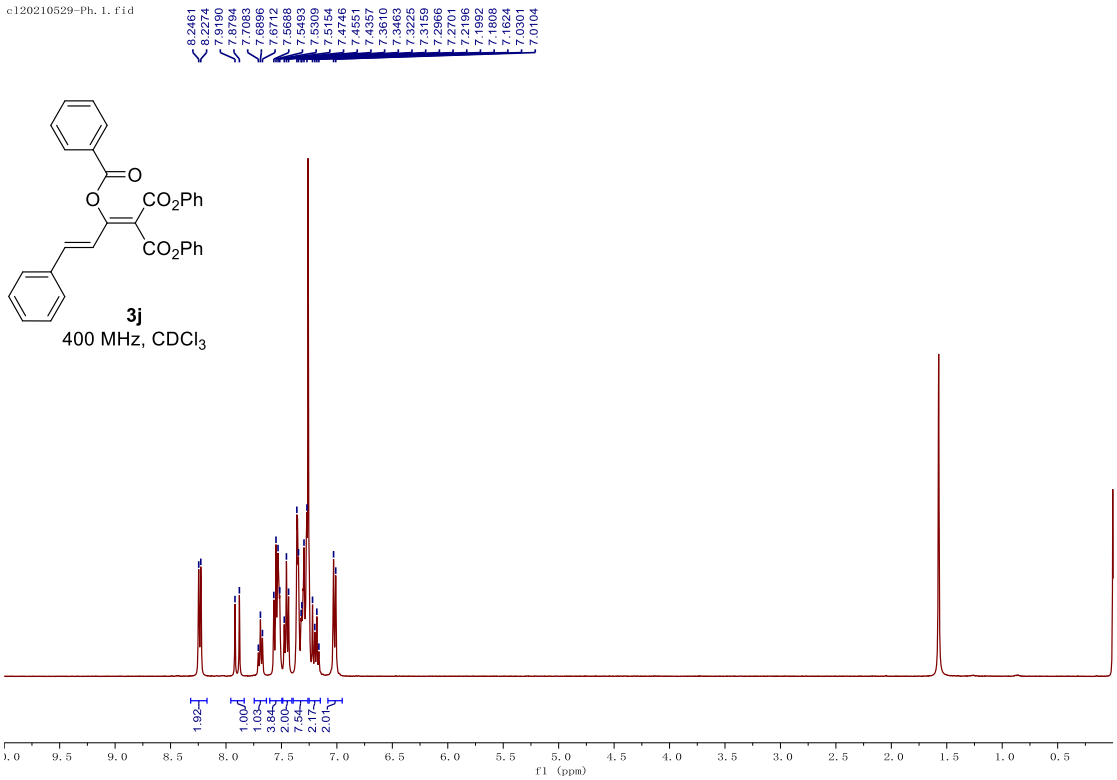

c120210516-1-p-c.1.fid
164.19
163.68
162.59
157.79
140.86
137.86
136.02
133.40
131.74
129.26
129.13
126.68
119.69
116.87
52.79
52.58
Cl
O
O
CO2Me
CO2Me
Cl
3g
101 MHz, CDCl3
f1 (ppm)

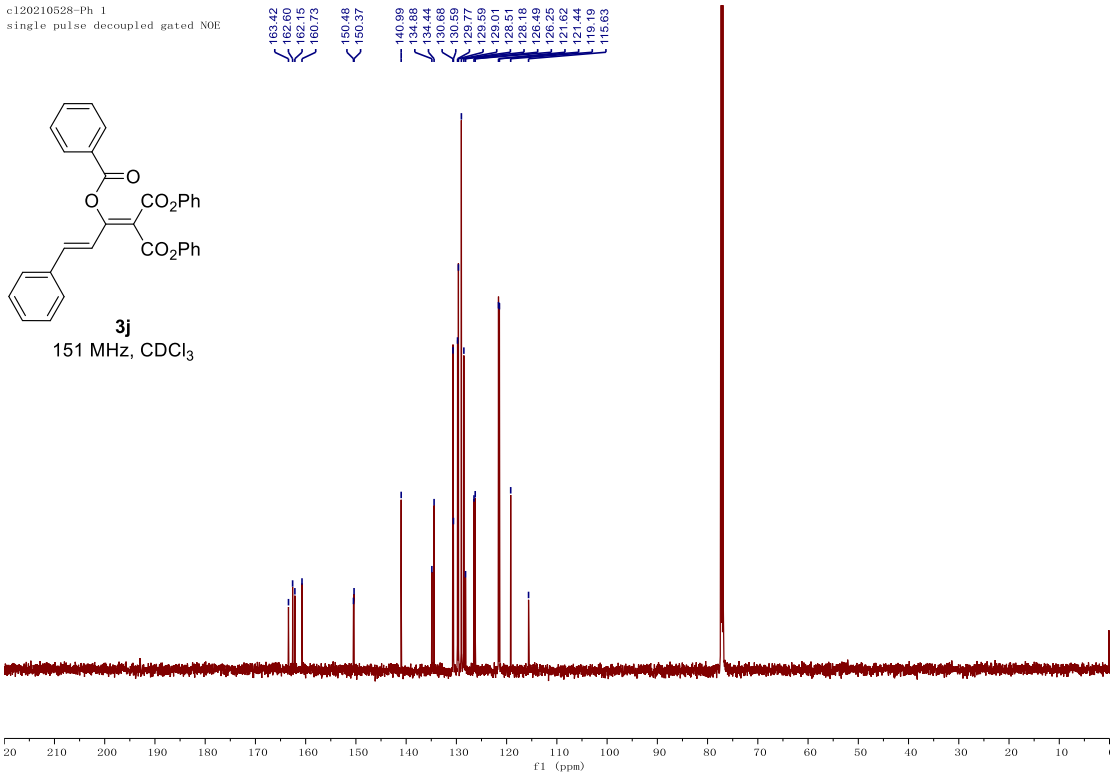

c120210425-p-OMe.1.fid
8.1393
8.1172
7.5998
7.5602
7.4456
7.4236
7.0480
7.0153
7.0094
6.9931
6.8672
6.8453
3.9074
3.8667
3.8200
3.6297
MeO
O
O
CO2Me
CO2Me
MeO
3h
400 MHz, CDCl3
1.98
1.02
2.00
3.01
2.03
2.96
2.97
3.00
2.95
f1 (ppm)

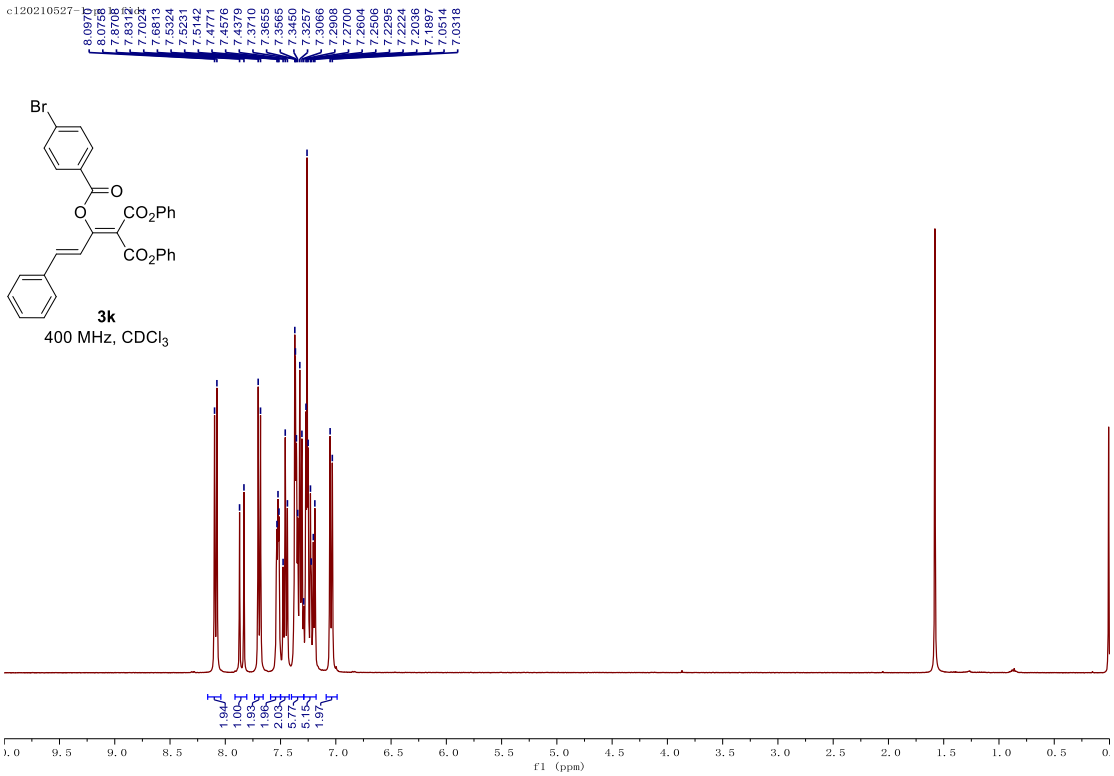

c120210425-p-OMe
single pulse decoupled gated NOE
164.67
164.39
164.34
163.25
161.31
159.18
139.25
132.67
129.94
127.99
120.74
117.23
115.33
114.35
114.17
55.68
55.46
52.65
52.52
MeO
O
O
CO2Me
CO2Me
MeO
3h
151 MHz, CDCl3
f1 (ppm)

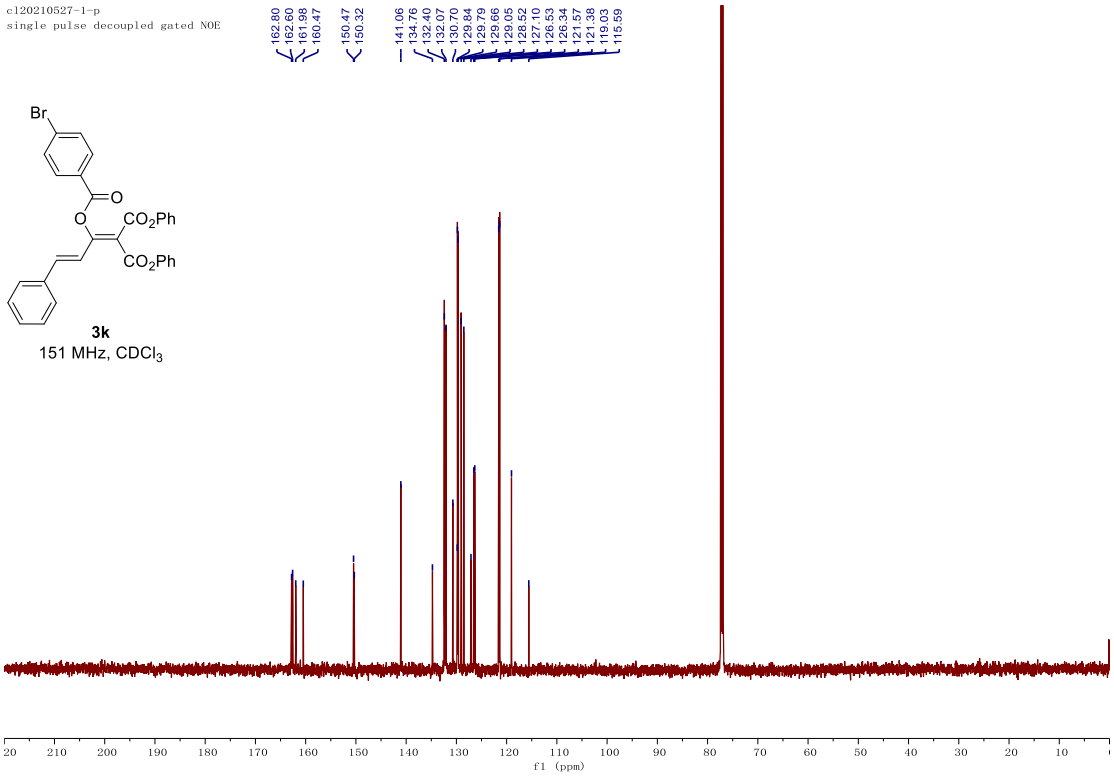

cl20210531-1-p.1.fid
8.0728
8.0527
7.6682
7.6286
7.4091
7.3891
7.3424
7.3225
7.1748
7.1549
7.0704
7.0308
3.8726
3.6307
2.6698
2.6508
2.6319
2.6131
2.4857
1.2383
1.2194
1.2004
Me
O
O
CO2Me
CO2Me
Et
3i
400 MHz, CDCl3
1.94
1.04
2.00
2.01
2.01
1.00
3.15
3.06
2.08
3.13
3.21
f1 (ppm)

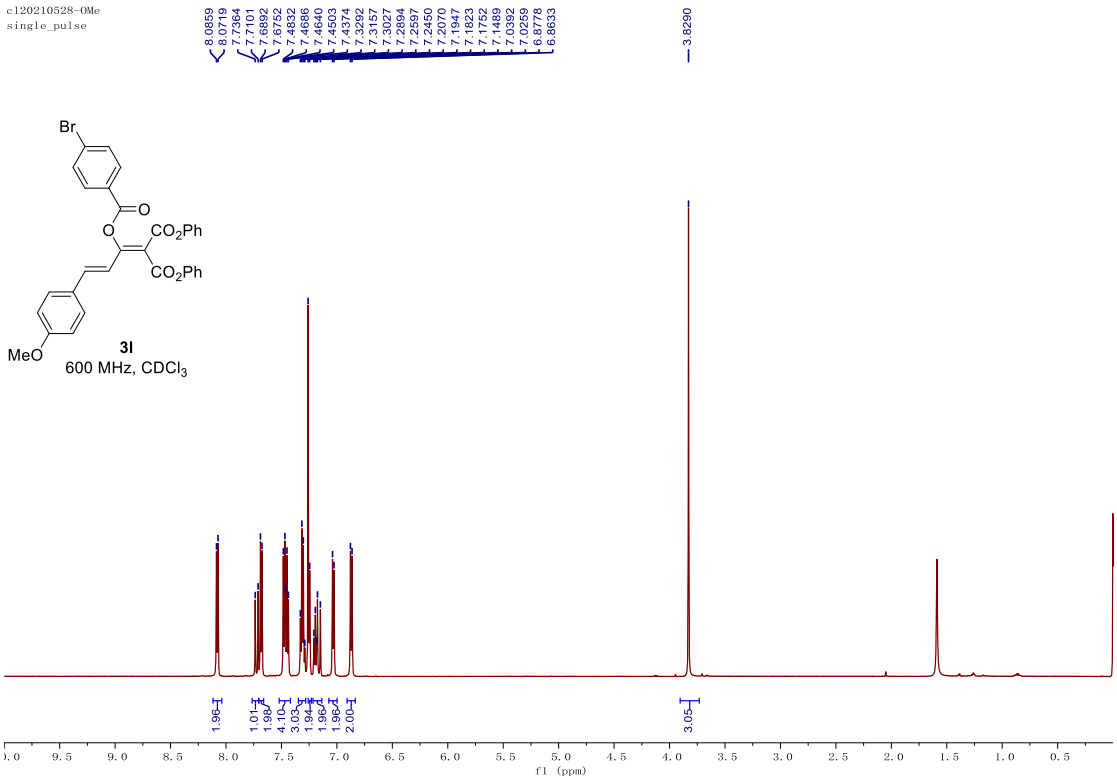

cl0210531-1-p
single pulse decoupled gated NOE
164.53
164.23
163.55
158.87
146.90
145.14
139.59
132.66
130.54
129.61
128.45
128.35
125.71
118.48
115.98
52.70
52.56
28.88
21.91
15.41
Me
O
O
CO2Me
CO2Me
Et
3i
151 MHz, CDCl3
f1 (ppm)

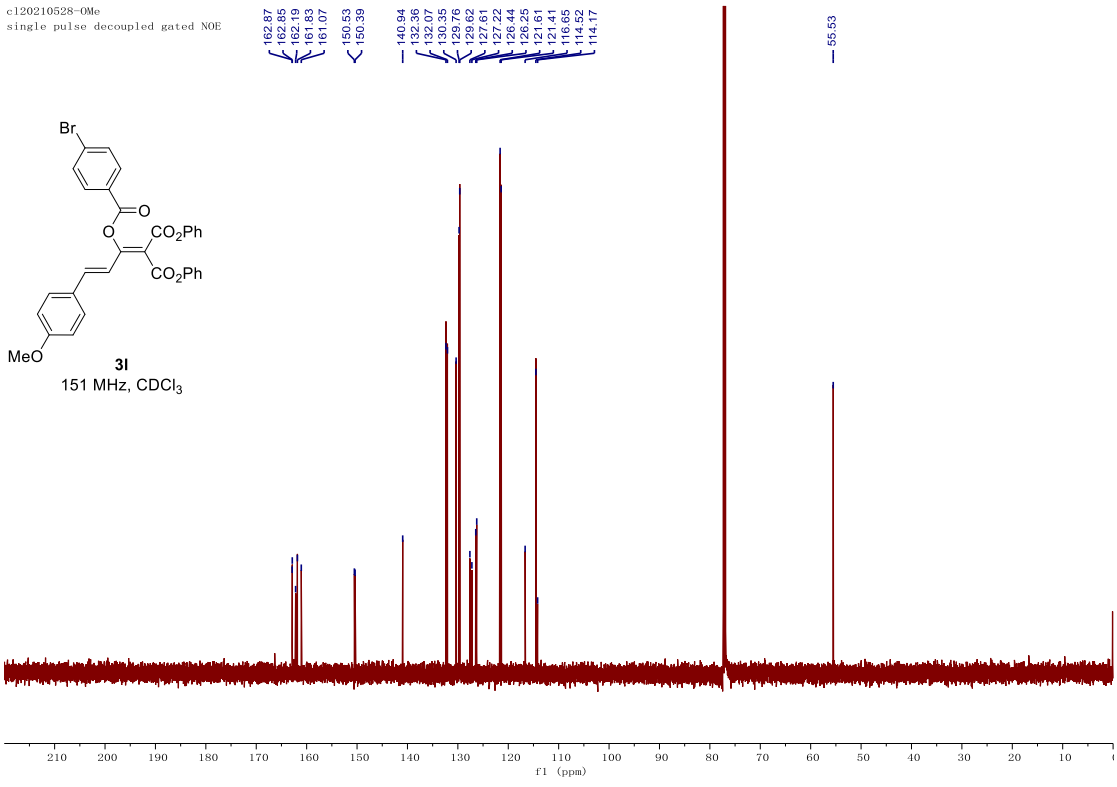

c120210529-Ph.1.fid
8.2461
8.2274
7.9190
7.8794
7.7083
7.6896
7.6712
7.5688
7.5493
7.5309
7.5154
7.4746
7.4551
7.4357
7.3610
7.3463
7.3225
7.3159
7.2966
7.2701
7.2196
7.1992
7.1608
7.1624
7.0301
7.0104
O
O
CO2Ph
CO2Ph
3j
400 MHz, CDCl3
1.92
1.00
1.03
3.84
2.00
7.54
2.17
2.01
f1 (ppm)

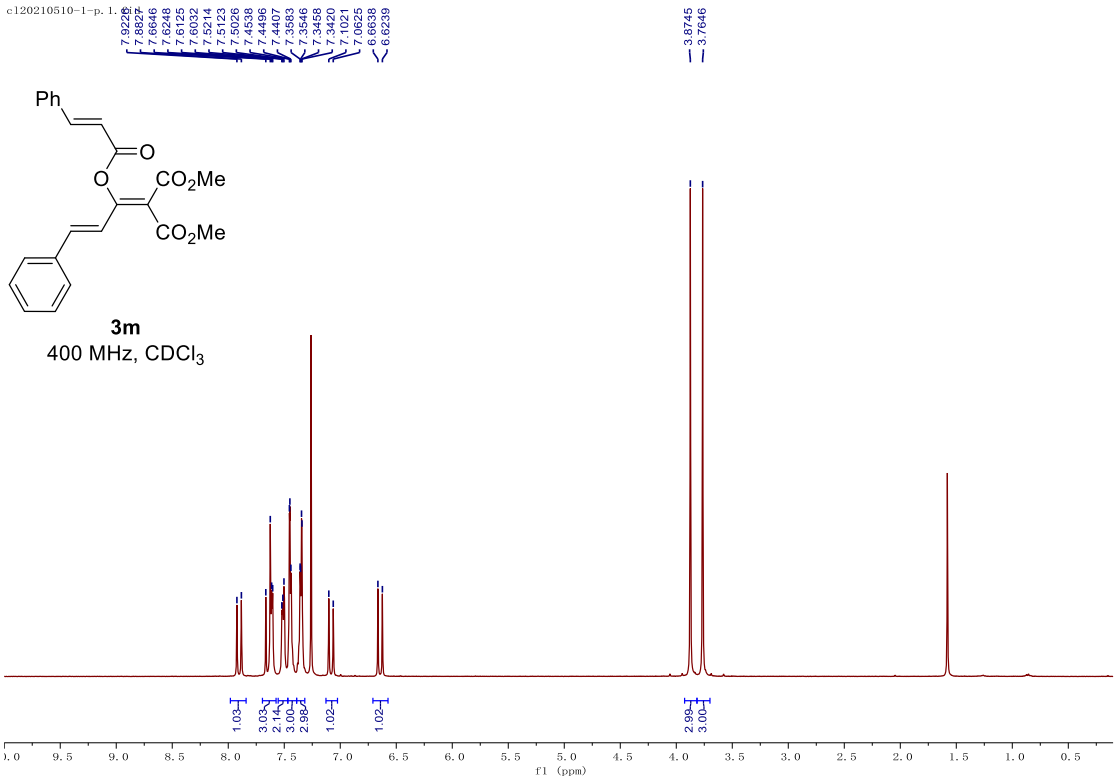

c120210528-Ph 1
single pulse decoupled gated NOE
163.42
162.60
162.15
160.73
150.48
150.37
140.99
134.88
134.44
130.68
130.59
129.77
129.59
129.01
128.51
128.18
126.49
126.25
121.62
121.44
119.19
115.83
O
O
CO2Ph
CO2Ph
3j
151 MHz, CDCl3
f1 (ppm)

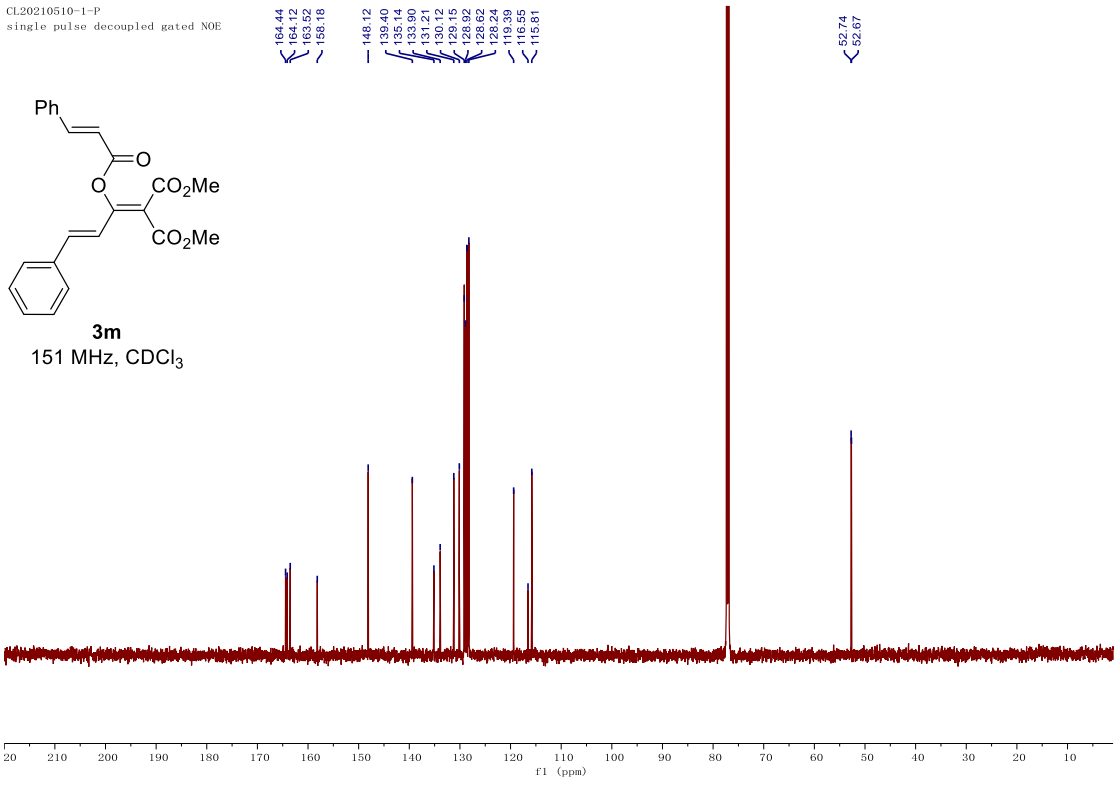

c120210527-1-p
Br
O
O
CO2Ph
CO2Ph
3k
400 MHz, CDCl3
f1 (ppm)

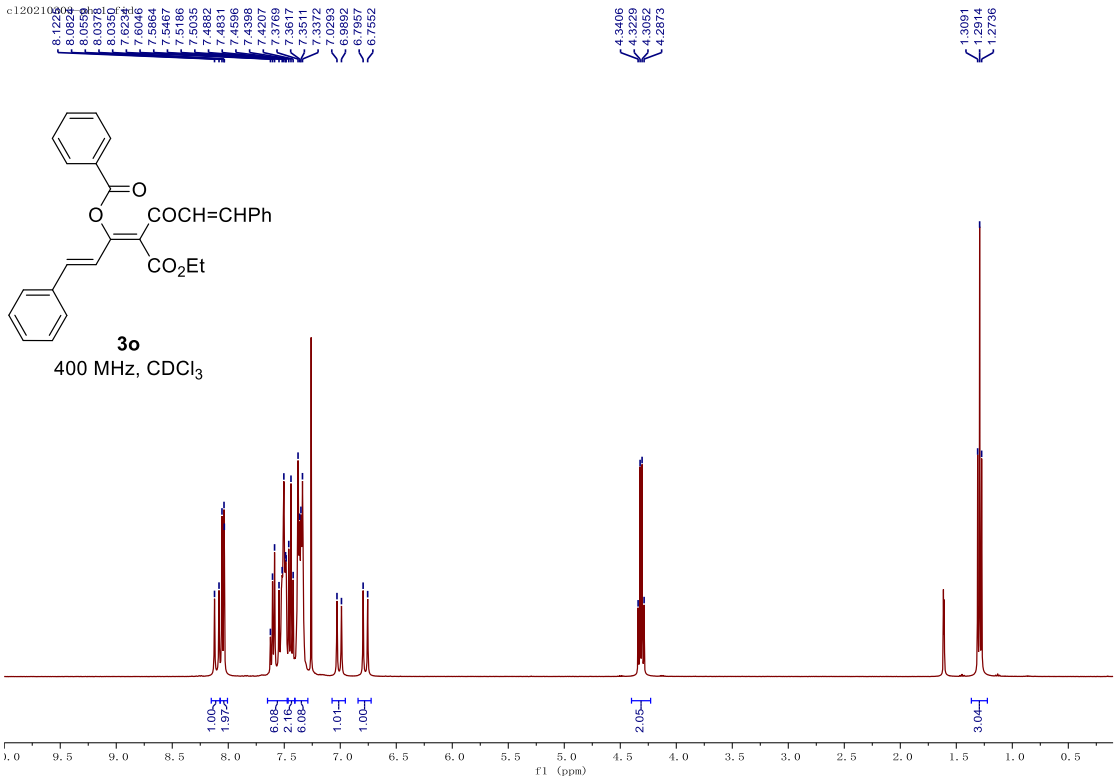

c120210527-1-p
single pulse decoupled gated NOE
Br
O
O
CO2Ph
CO2Ph
3k
151 MHz, CDCl3
f1 (ppm)

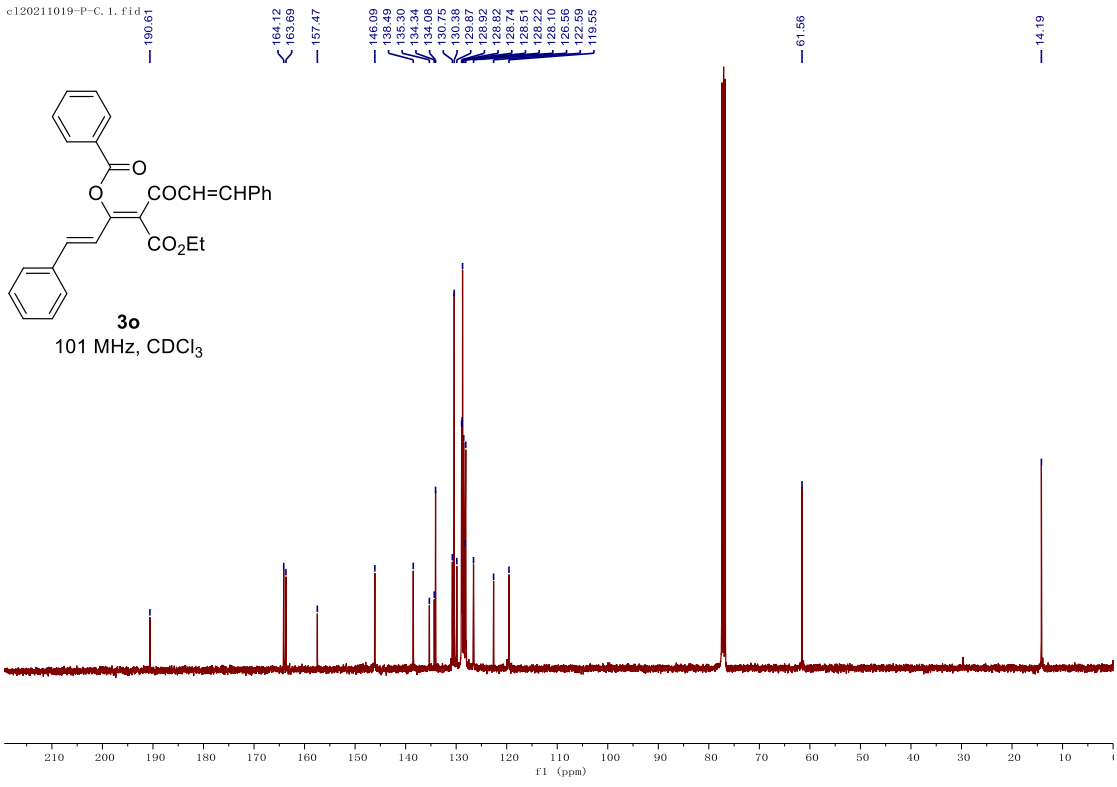

c120210528-OMe
single_pulse
8.0859
8.0719
7.7364
7.7101
7.6892
7.6752
7.4832
7.4686
7.4640
7.4503
7.4374
7.3292
7.3157
7.3027
7.2894
7.2597
7.2450
7.2070
7.1947
7.1823
7.1752
7.1489
7.0392
7.0259
6.8778
6.8633
3.8290
Br
O
O
CO2Ph
CO2Ph
MeO
3l
600 MHz, CDCl3
1.96
1.01
1.90
4.10
3.03
1.94
1.96
1.96
2.00
3.05
f1 (ppm)

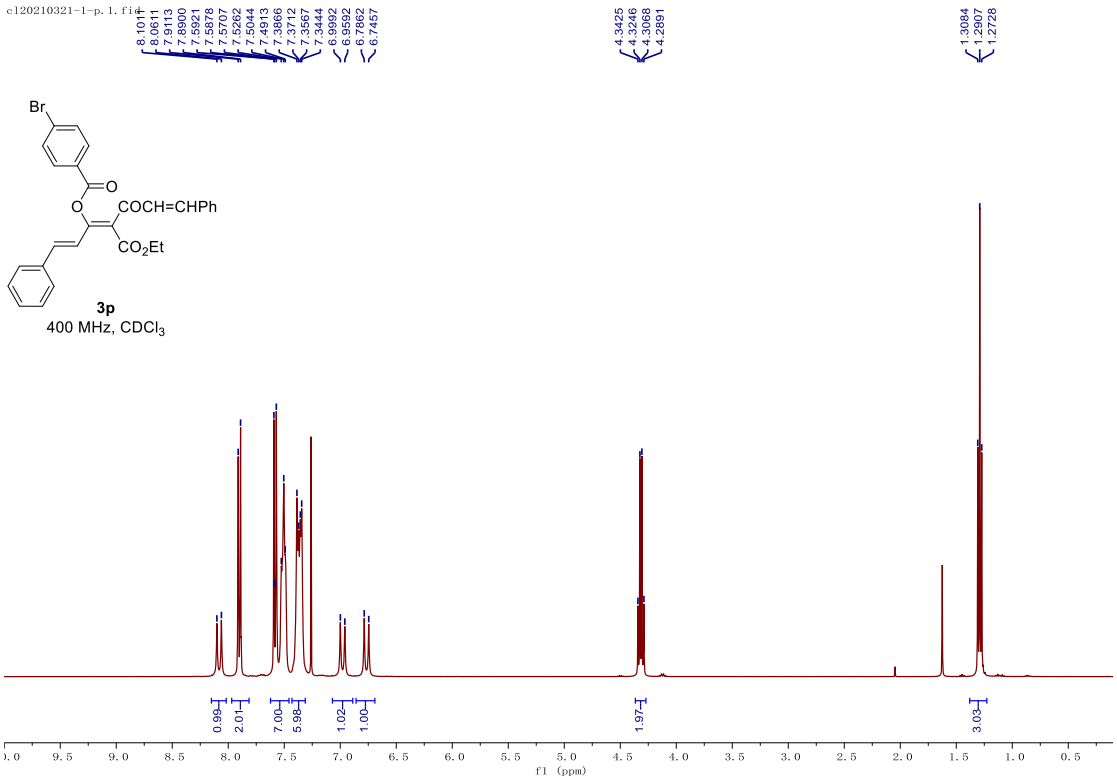

c120210528-OMe
single pulse decoupled gated NOE
162.87
162.85
162.19
161.83
161.07
150.53
150.39
140.94
132.36
132.07
130.35
129.76
129.62
127.61
127.22
126.44
126.25
121.61
121.41
116.65
114.52
114.17
55.53
Br
O
O
CO2Ph
CO2Ph
MeO
3l
151 MHz, CDCl3
f1 (ppm)

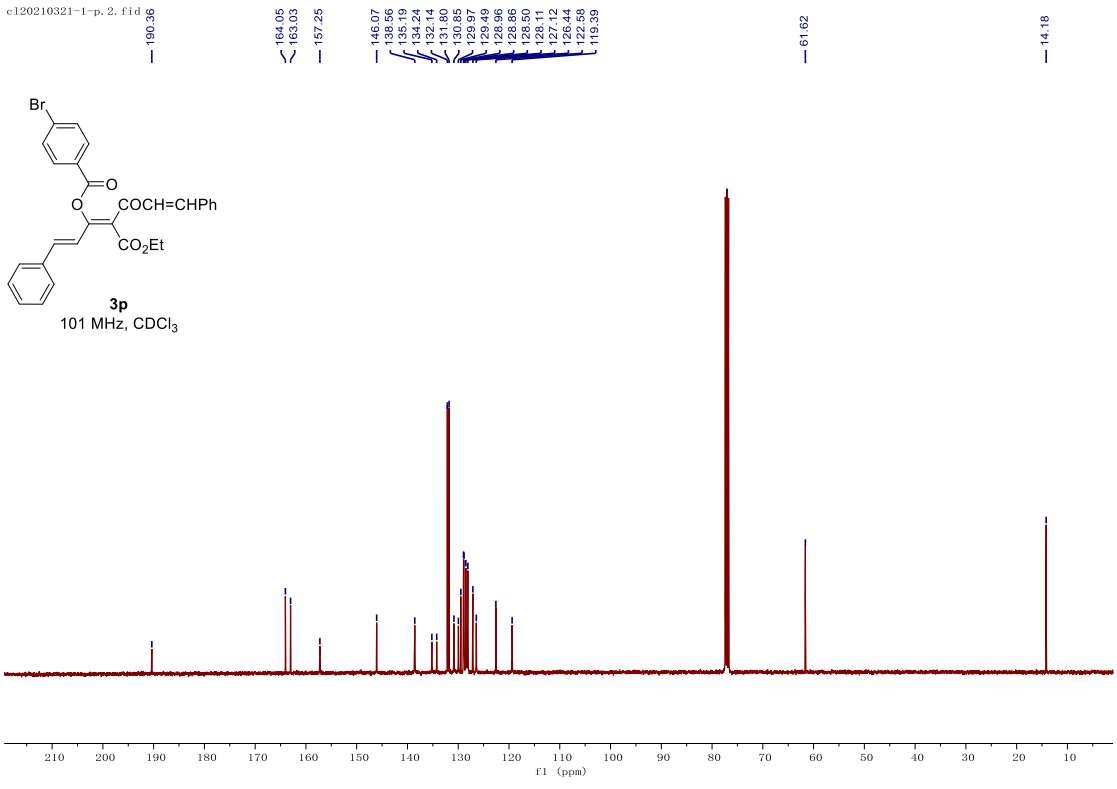

c120210510-1-p. 1.
7.9226
7.8827
7.6646
7.6248
7.6125
7.6032
7.5214
7.5123
7.5026
7.4538
7.4496
7.4407
7.3583
7.3546
7.3458
7.3420
7.1021
7.0625
6.6638
6.6239
3.8745
3.7646
Ph
O
O
CO2Me
CO2Me
3m
400 MHz, CDCl3
1.03
3.03
2.14
3.00
2.98
1.02
1.02
2.99
3.00
f1 (ppm)

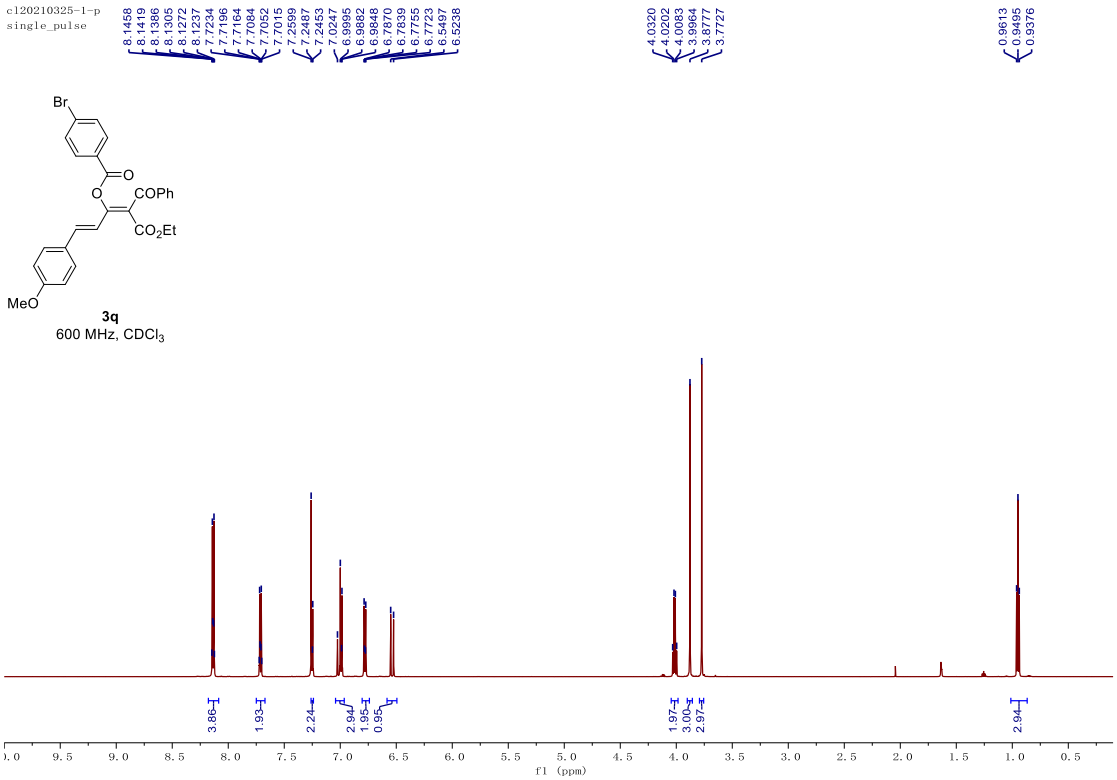

CL20210510-1-P
single pulse decoupled gated NOE
164.44
164.12
163.52
158.18
148.12
139.40
135.14
133.90
131.21
130.12
129.15
128.92
128.62
128.24
119.39
116.55
115.81
52.74
52.67
Ph
O
O
CO2Me
CO2Me
3m
151 MHz, CDCl3
f1 (ppm)

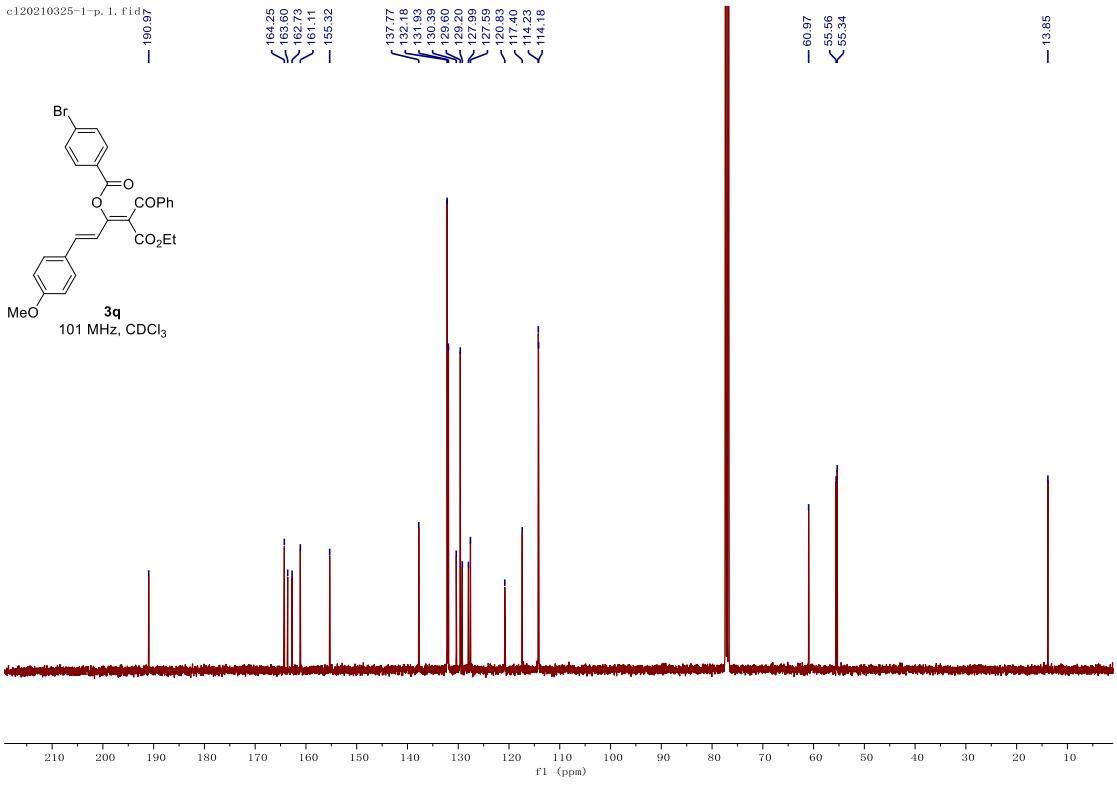

c120210304
8.1225
8.0824
8.0559
8.0378
8.0350
7.6234
7.6046
7.5864
7.5467
7.5186
7.5035
7.4882
7.4831
7.4596
7.4398
7.4207
7.3769
7.3617
7.3511
7.3372
7.0293
6.9892
6.7957
6.7552
4.3406
4.3229
4.3052
4.2873
1.3091
1.2914
1.2736
O
O
COCH=CHPh
CO2Et
3o
400 MHz, CDCl3
1.00
1.97
6.08
2.16
6.08
1.01
1.00
2.05
3.04
f1 (ppm)

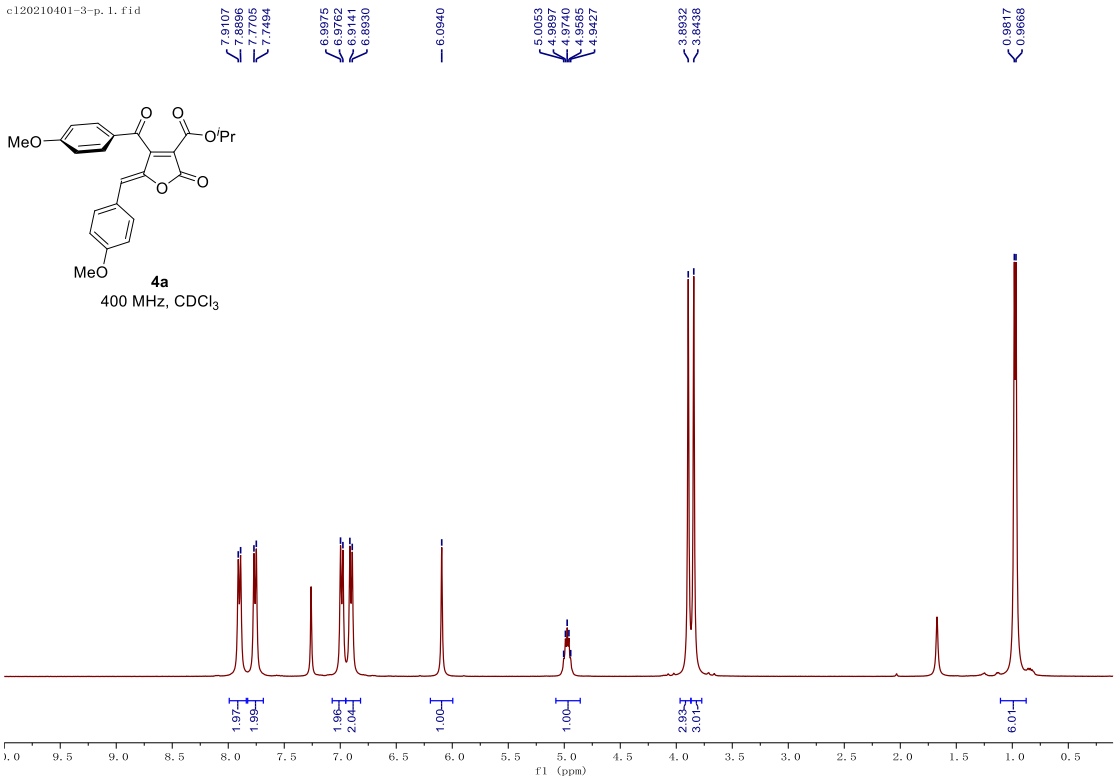

c120211019-P-C.1.fid
190.61
164.12
163.69
157.47
146.09
138.49
135.30
134.34
134.08
130.75
130.38
129.87
128.92
128.82
128.74
128.51
128.22
128.10
126.56
122.59
119.55
61.56
14.19
O
O
COCH=CHPh
CO2Et
3o
101 MHz, CDCl3
f1 (ppm)

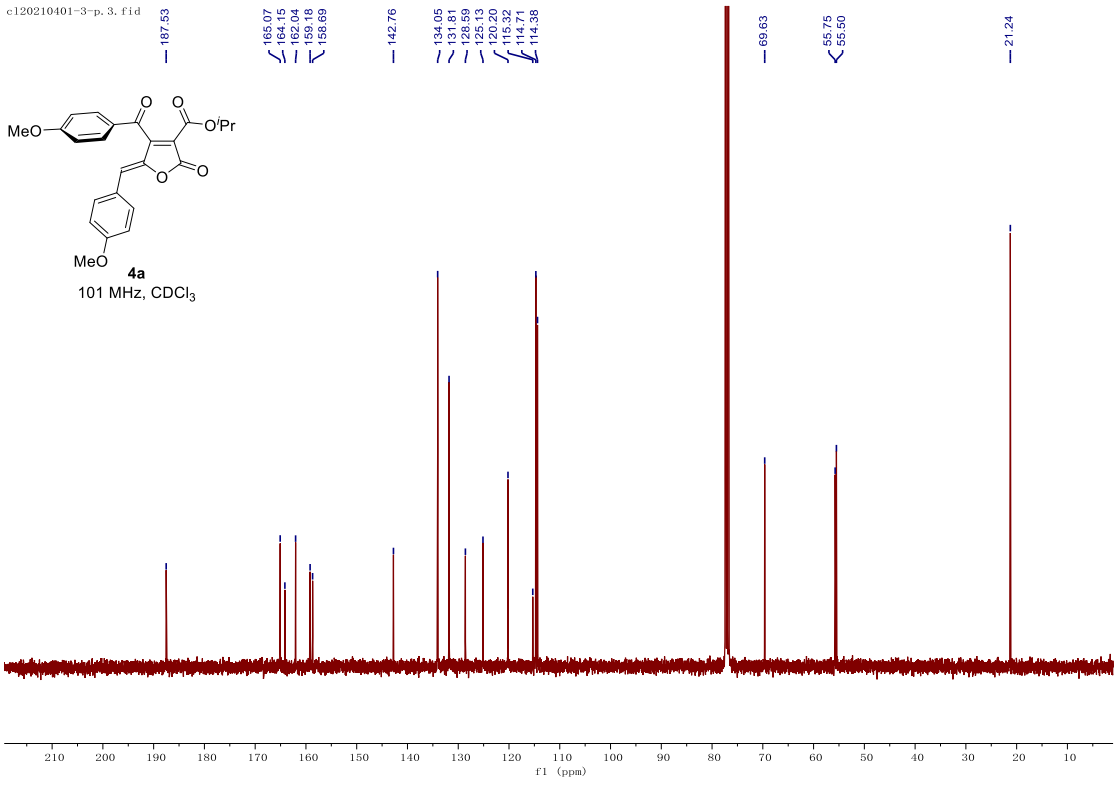

c120210321-1-p.1.fid
8.1014
8.0611
7.9113
7.8900
7.5921
7.5878
7.5707
7.5262
7.5044
7.4913
7.3866
7.3712
7.3567
7.3444
6.9992
6.9592
6.7862
6.7457
4.3425
4.3246
4.3068
4.2891
1.3084
1.2907
1.2728
Br
O
O
COCH=CHPh
CO2Et
3p
400 MHz, CDCl3
0.99
2.01
7.00
5.98
1.02
1.00
1.97
3.03
f1 (ppm)

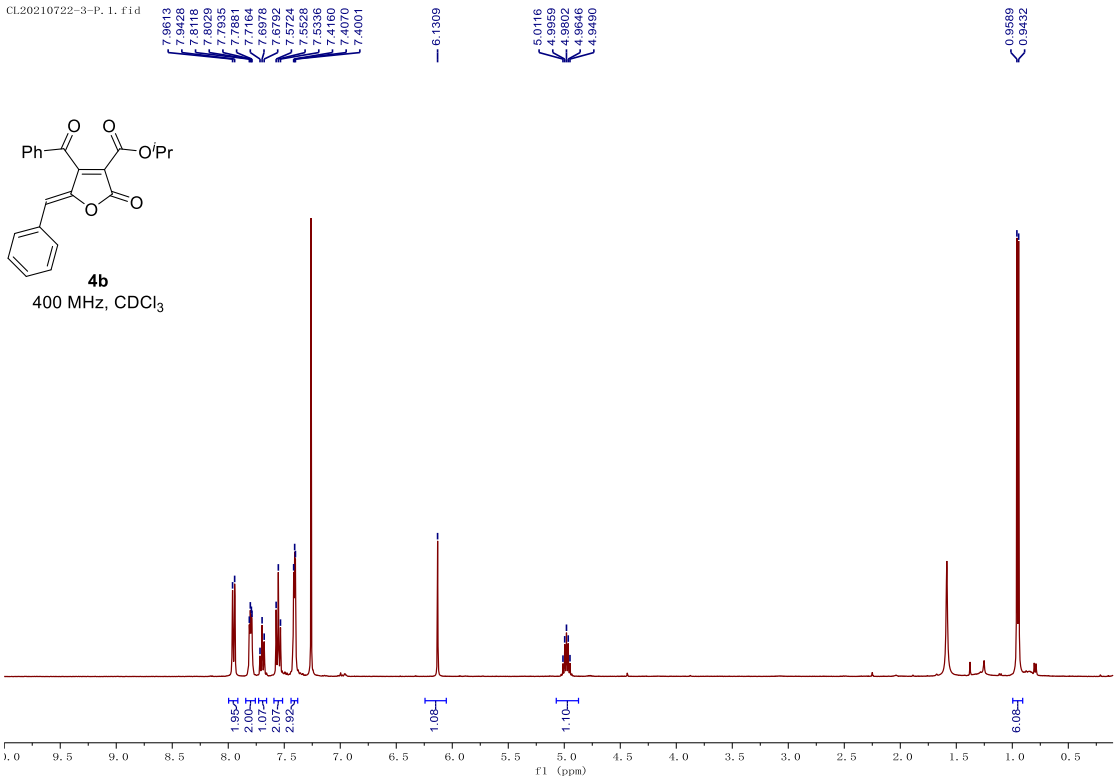

c120210321-1-p.2.fid
190.36
164.05
163.03
157.25
146.07
138.56
135.19
134.24
132.14
131.80
130.85
129.97
129.49
128.96
128.86
128.50
128.11
127.12
126.44
122.58
119.39
61.62
14.18
Br
O
O
COCH=CHPh
CO2Et
3p
101 MHz, CDCl3
f1 (ppm)

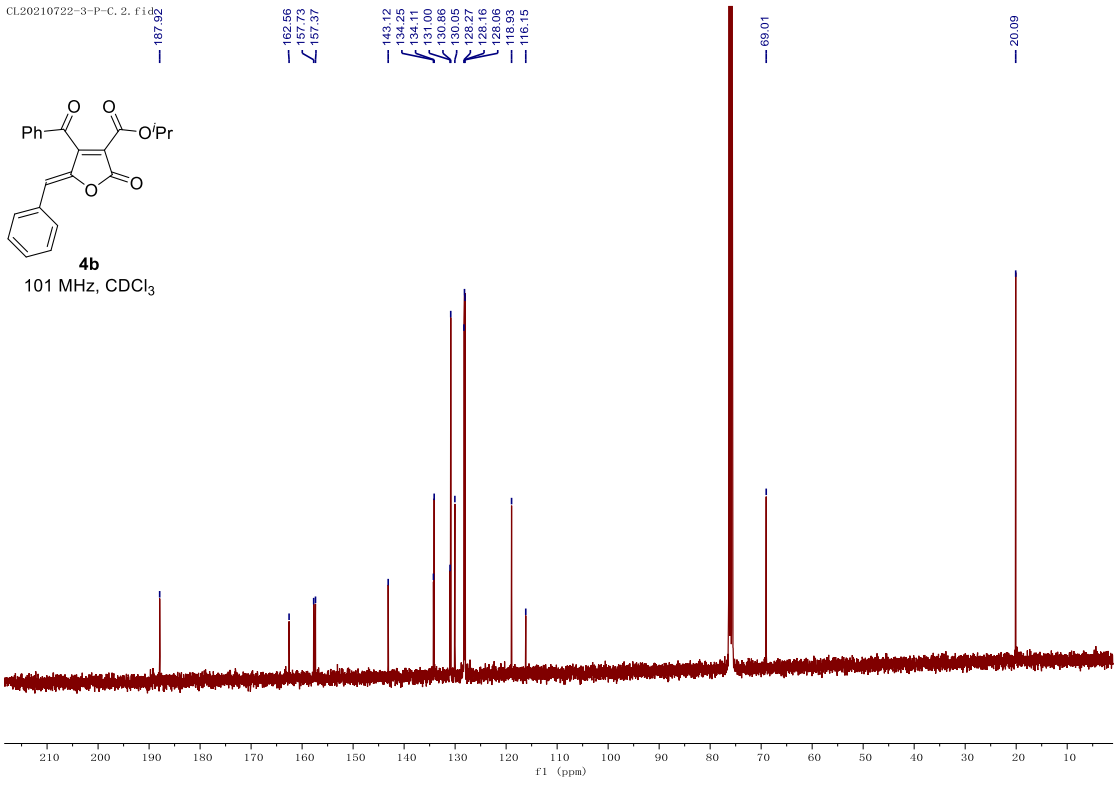

c120210325-1-p
single_pulse
8.1458
8.1419
8.1386
8.1305
8.1272
8.1237
7.7234
7.7196
7.7164
7.7084
7.7052
7.7015
7.2599
7.2487
7.2453
7.0247
6.9995
6.9882
6.9848
6.7870
6.7839
6.7755
6.7723
6.5497
6.5238
4.0320
4.0202
4.0083
3.9964
3.8777
3.7727
0.9613
0.9495
0.9376
Br
O
O
COPh
CO2Et
MeO
3q
600 MHz, CDCl3
3.86
1.93
2.24
2.94
1.95
0.95
1.97
3.00
2.97
2.94
f1 (ppm)

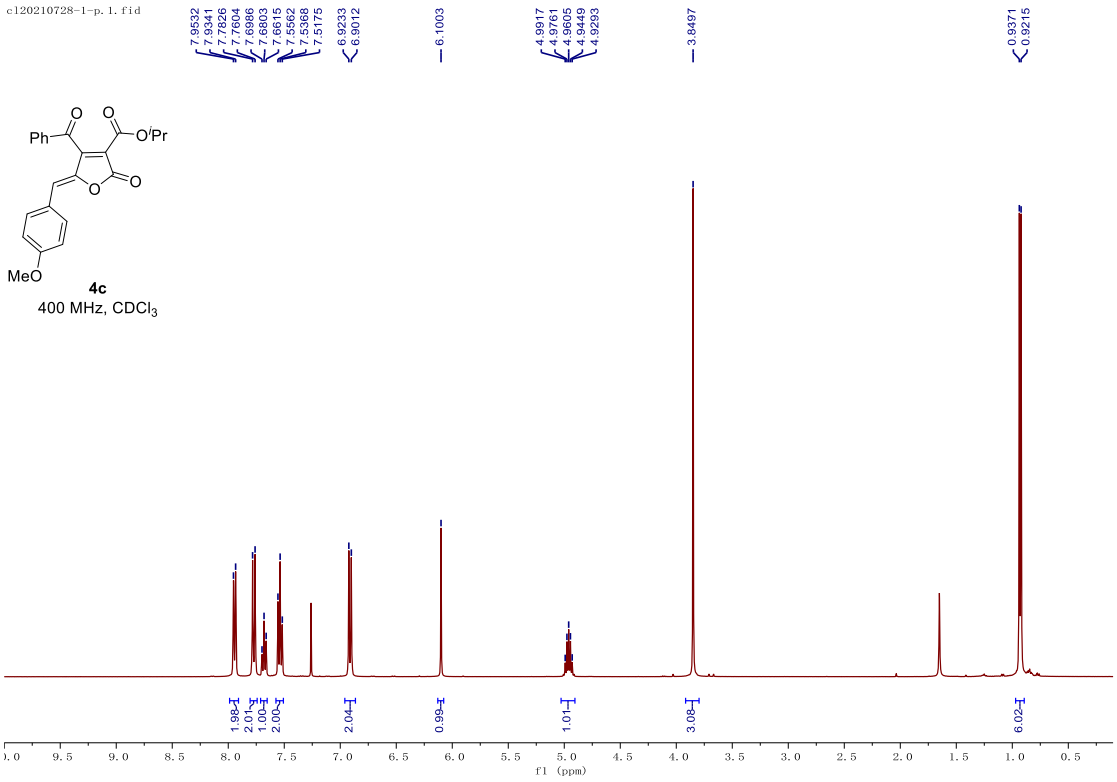

c120210325-1-p.1.fid
190.97
164.25
163.60
162.73
161.11
155.32
137.77
132.18
131.93
130.39
129.60
129.20
127.99
127.59
120.83
117.40
114.23
114.18
60.97
55.56
55.34
13.85
Br
O
O
COPh
CO2Et
MeO
3q
101 MHz, CDCl3
f1 (ppm)

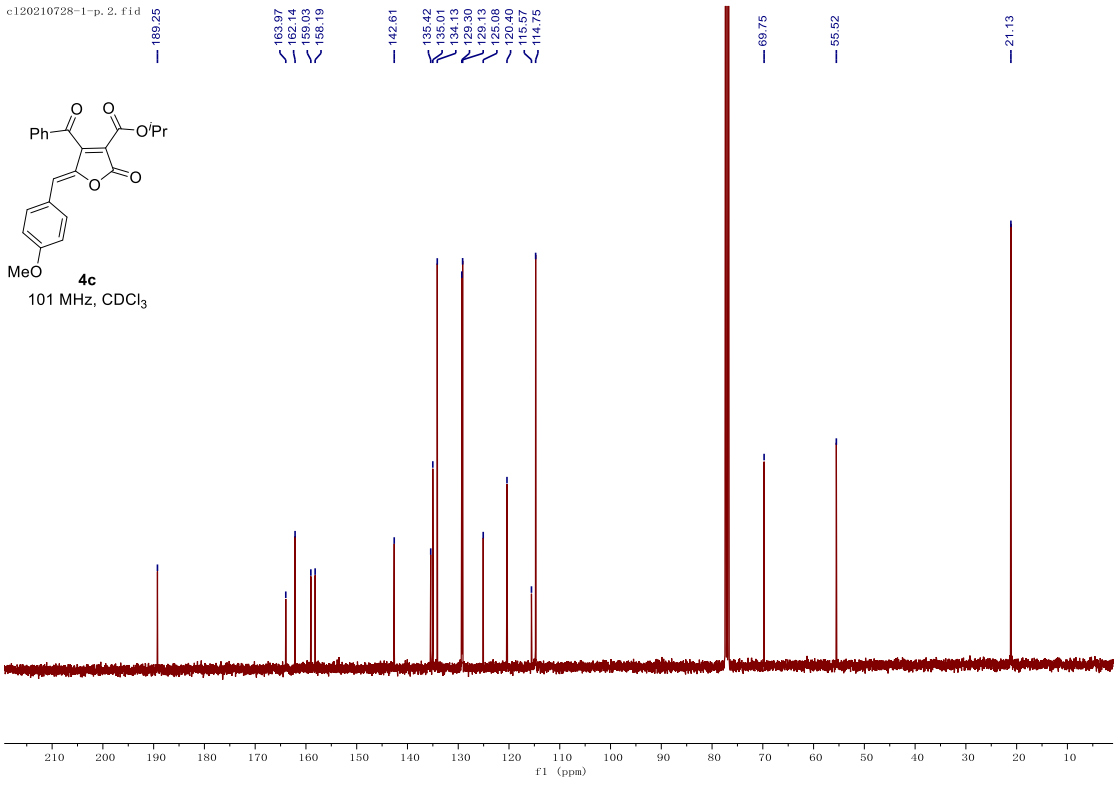

c120210401-3-p.1.fid
7.9107
7.8896
7.7705
7.7494
6.9975
6.9762
6.9141
6.8930
6.0940
5.0053
4.9897
4.9740
4.9585
4.9427
3.8932
3.8438
0.9817
0.9668
MeO
O
O
O
O
O
O
MeO
4a
400 MHz, CDCl3
1.97
1.99
1.96
2.04
1.00
1.00
2.93
3.01
6.01
f1 (ppm)

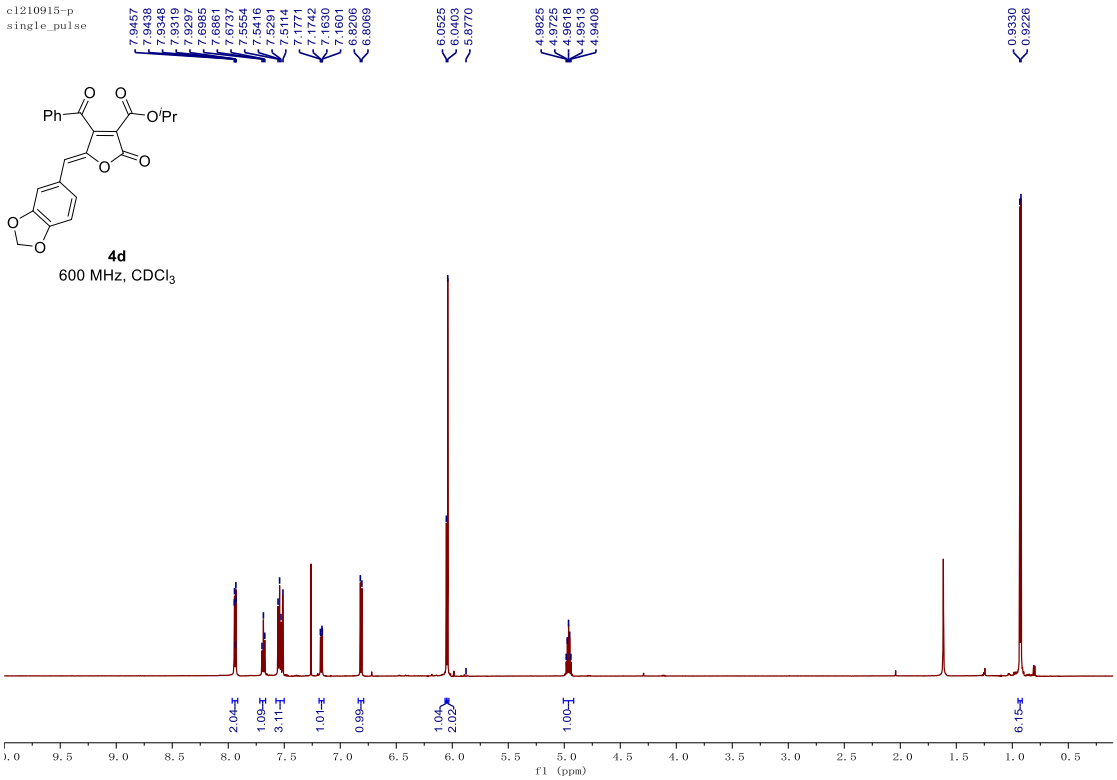

c120210401-3-p.3.fid
187.53
165.07
164.15
162.04
159.18
158.69
142.76
134.05
131.81
128.59
125.13
120.20
115.32
114.71
114.38
69.63
55.75
55.50
21.24
MeO
O
O
O
O
O
O
MeO
4a
101 MHz, CDCl3
f1 (ppm)

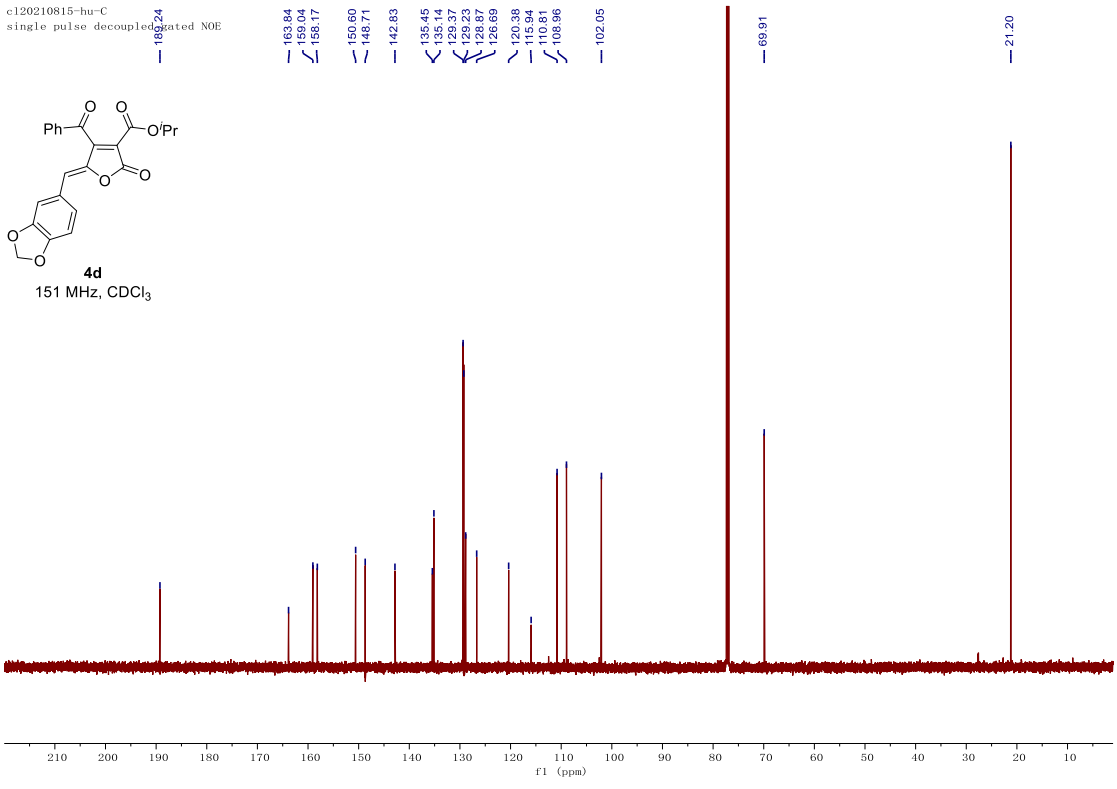

CL20210722-3-P.1.fid
7.9613
7.9428
7.8118
7.8029
7.7935
7.7881
7.7164
7.6978
7.6792
7.5724
7.5528
7.5336
7.4160
7.4070
7.4001
6.1309
5.0116
4.9959
4.9802
4.9646
4.9490
0.9589
0.9432
Ph
O
O
O
O
O
O
iPr
4b
400 MHz, CDCl3
1.95
2.00
1.07
2.07
2.92
1.08
1.10
6.08
f1 (ppm)

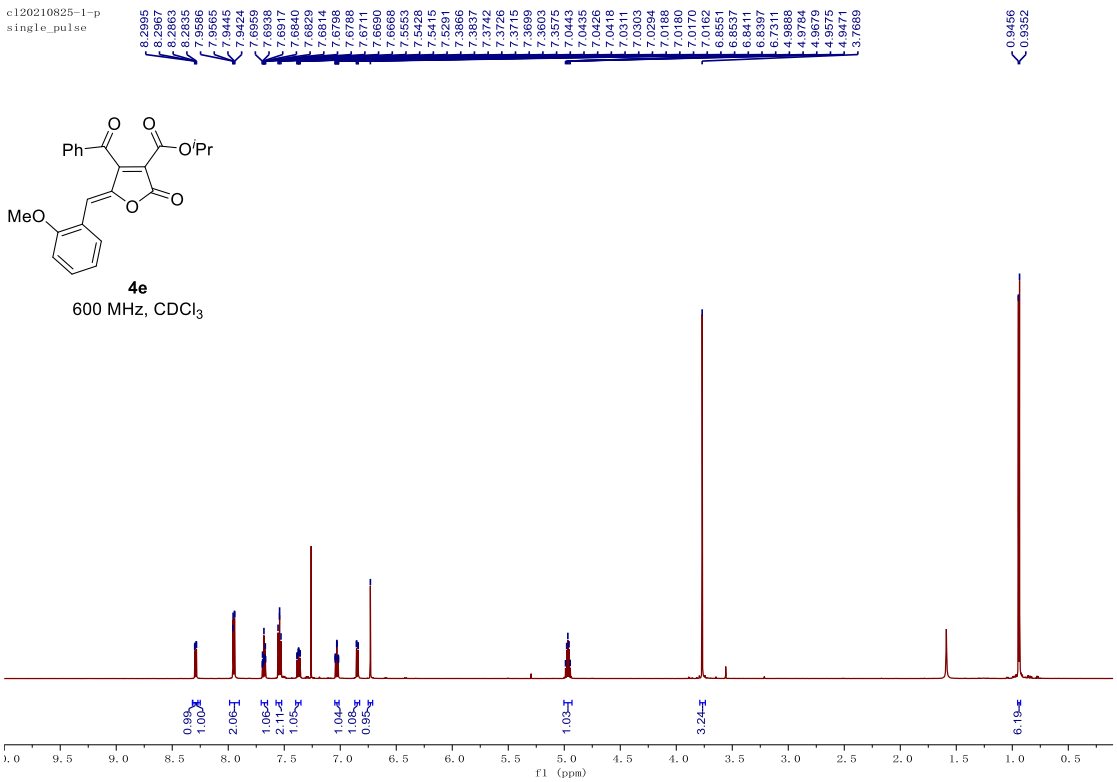

CL20210722-3-P-C.2.fid
187.92
162.56
157.73
157.37
143.12
134.25
134.11
131.00
130.86
130.05
128.27
128.16
128.06
118.93
116.15
69.01
20.09
Ph
O
O
O
O
O
O
iPr
4b
101 MHz, CDCl3
f1 (ppm)

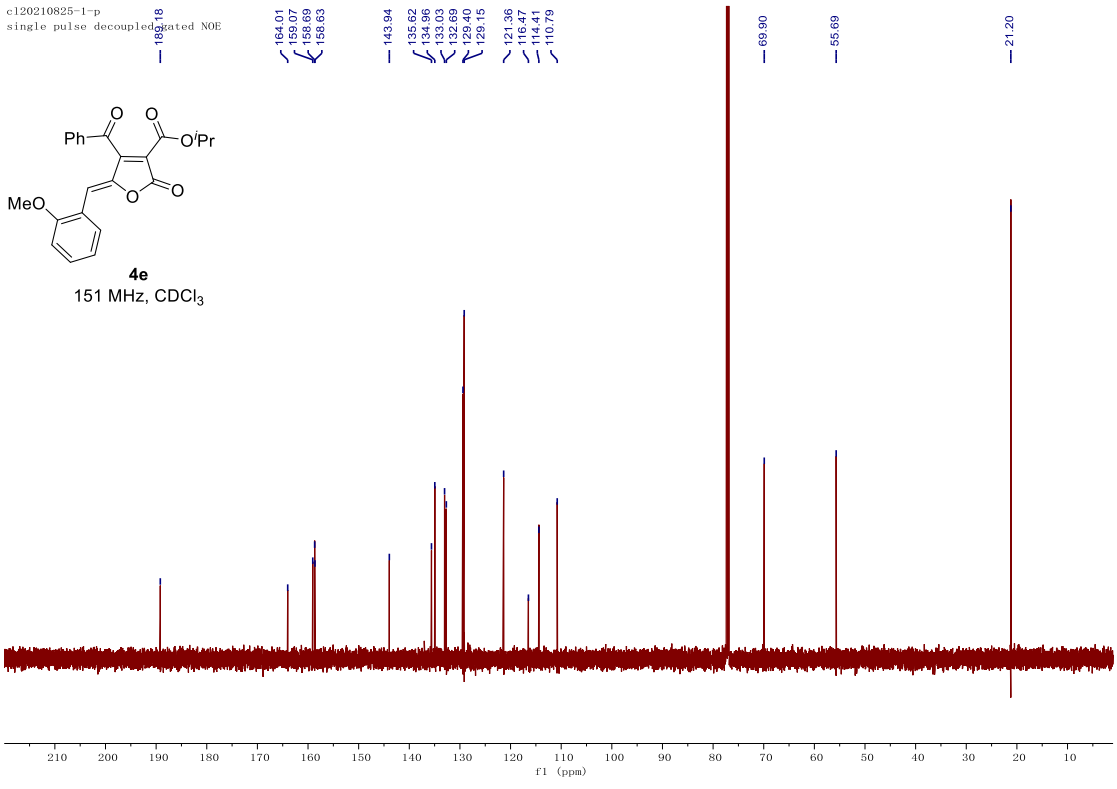

c120210728-1-p.1.fid
7.9532
7.9341
7.7826
7.7604
7.6986
7.6803
7.6615
7.5562
7.5368
7.5175
6.9233
6.9012
6.1003
4.9917
4.9761
4.9605
4.9449
4.9293
3.8497
0.9371
0.9215
Ph
O
O
O
O
O
O
Me
4c
400 MHz, CDCl3
1.98
2.01
1.00
2.00
2.04
0.99
1.01
3.08
6.02
f1 (ppm)

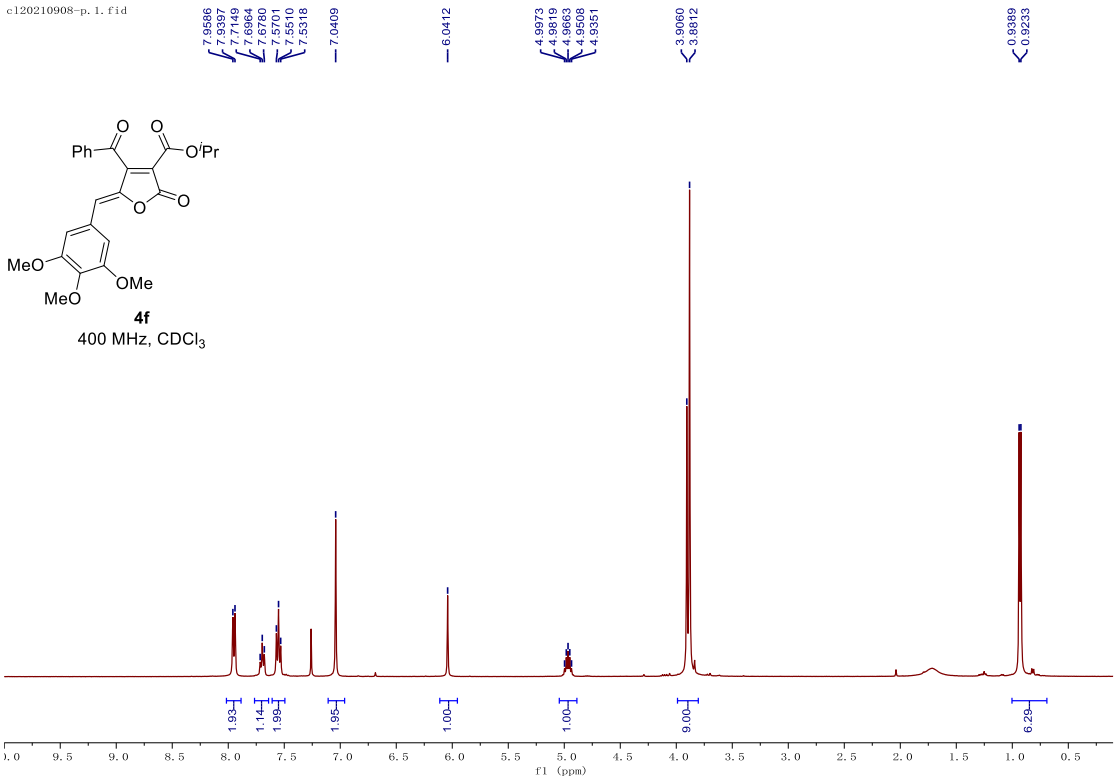

c120210728-1-p.2.fid
189.25
163.97
162.14
159.03
158.19
142.61
135.42
135.01
134.13
129.30
129.13
125.08
120.40
115.57
114.75
69.75
55.52
21.13
Ph
O
O
O
O
O
O
Me
4c
101 MHz, CDCl3
f1 (ppm)

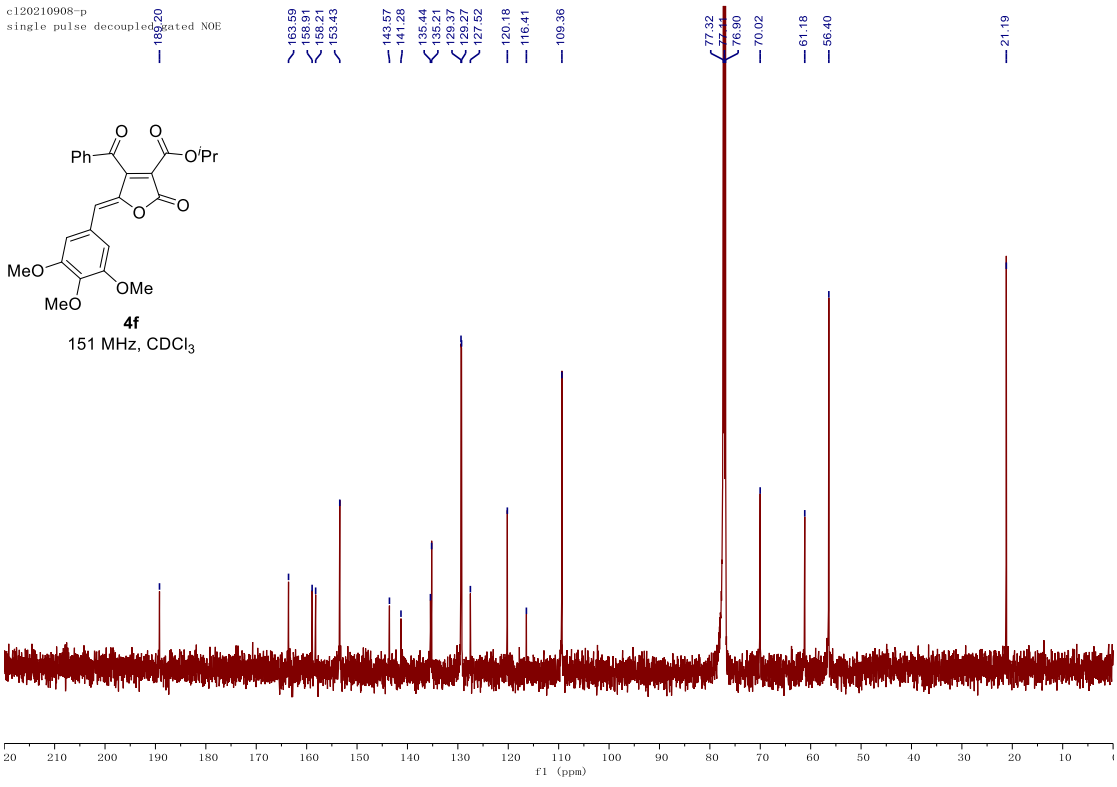

c1210915-p
single_pulse
7.9457
7.9438
7.9348
7.9319
7.9297
7.6985
7.6861
7.6737
7.5554
7.5416
7.5291
7.5114
7.1771
7.1742
7.1630
7.1601
6.8206
6.8069
6.0525
6.0403
5.8770
4.9825
4.9725
4.9618
4.9513
4.9408
0.9330
0.9226
Ph
O
O
O
O
O
O
O
4d
600 MHz, CDCl3
2.04
1.09
3.11
1.01
0.99
1.04
2.02
1.00
6.15
f1 (ppm)

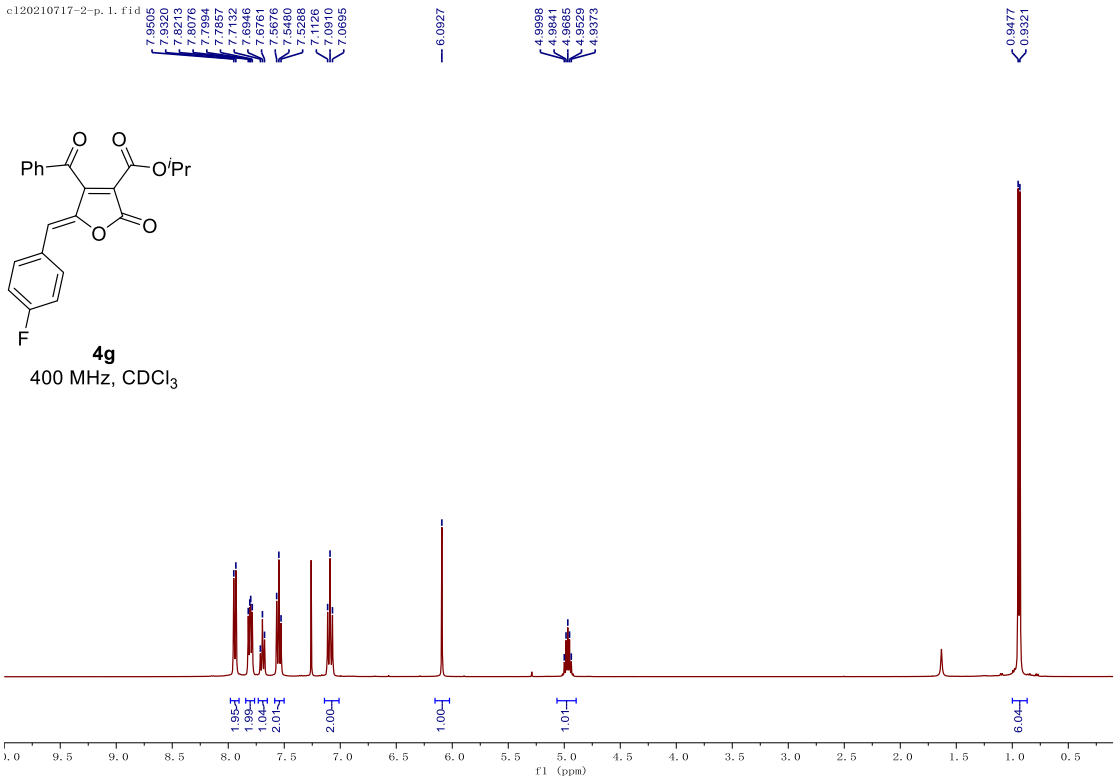

c120210815-hu-C
single pulse decoupled gated NOE
183.24
163.84
159.04
158.17
150.60
148.71
142.83
135.45
135.14
129.37
129.23
128.87
126.69
120.38
115.94
110.81
108.96
102.05
69.91
21.20
Ph
O
O
O
O
O
O
O
4d
151 MHz, CDCl3
f1 (ppm)

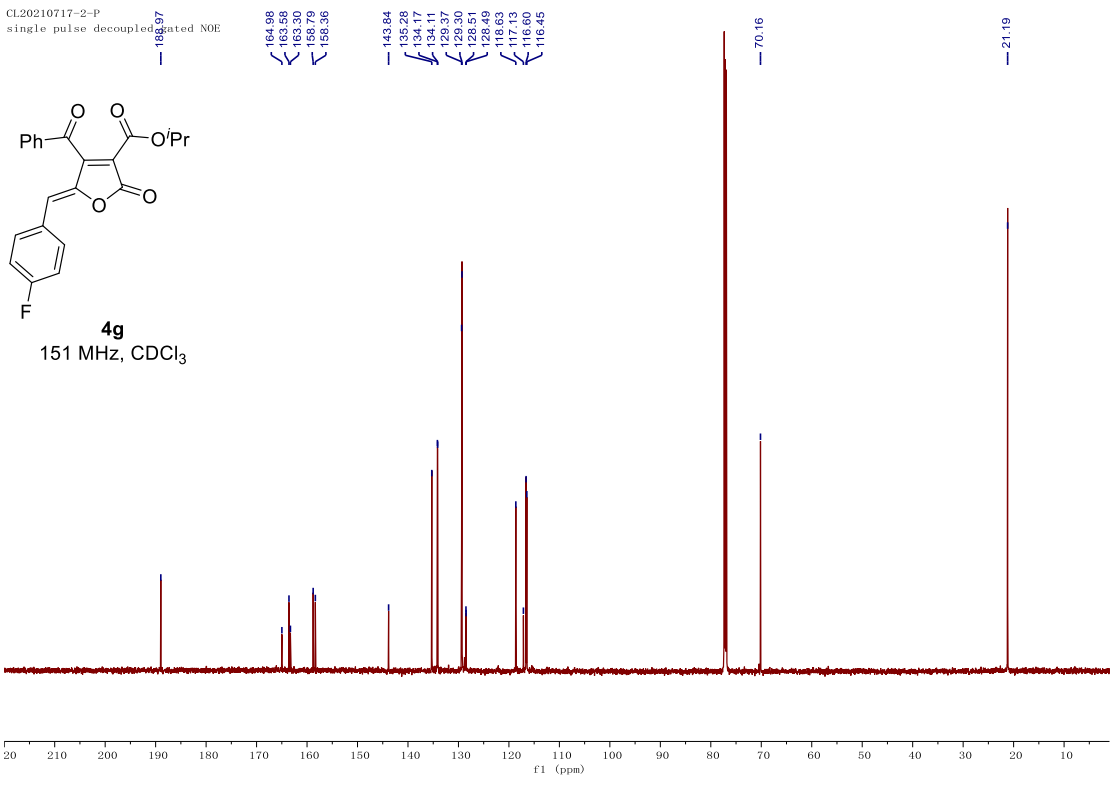

c120210825-1-p
single_pulse
8.2995
8.2967
8.2863
8.2835
7.9586
7.9565
7.9445
7.9424
7.6959
7.6938
7.6917
7.6840
7.6829
7.6814
7.6798
7.6788
7.6711
7.6690
7.6668
7.5553
7.5428
7.5415
7.5291
7.3866
7.3837
7.3742
7.3726
7.3715
7.3699
7.3603
7.3575
7.0443
7.0435
7.0426
7.0418
7.0311
7.0303
7.0294
7.0188
7.0180
7.0170
7.0162
6.8551
6.8537
6.8411
6.8397
6.7311
4.9888
4.9784
4.9679
4.9575
4.9471
3.7689
0.9456
0.9352
Ph
O
O
O
iPr
O
MeO
4e
600 MHz, CDCl3
0.99
1.00
2.06
1.06
2.11
1.05
1.04
1.08
0.95
1.03
3.24
6.19
f1 (ppm)

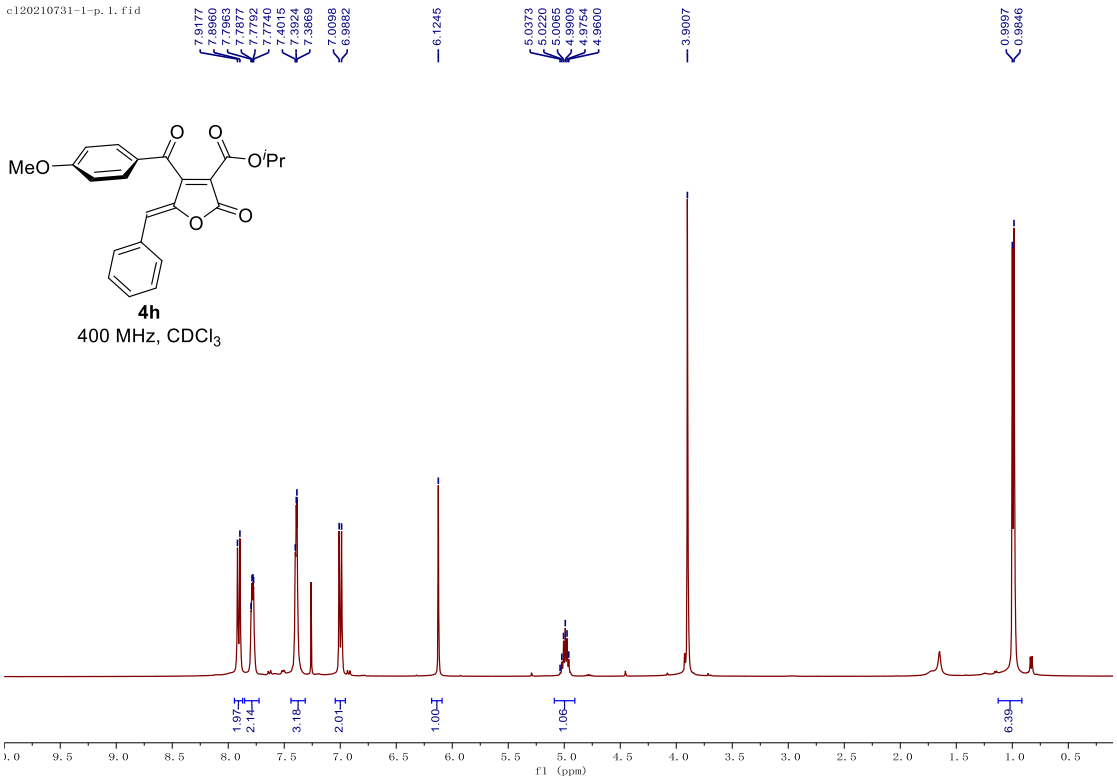

c120210825-1-p
single pulse decoupled gated NOE
183.18
164.01
159.07
158.69
158.63
143.94
135.62
134.96
133.03
132.69
129.40
129.15
121.36
116.47
114.41
110.79
69.90
55.69
21.20
Ph
O
O
O
iPr
O
MeO
4e
151 MHz, CDCl3
f1 (ppm)

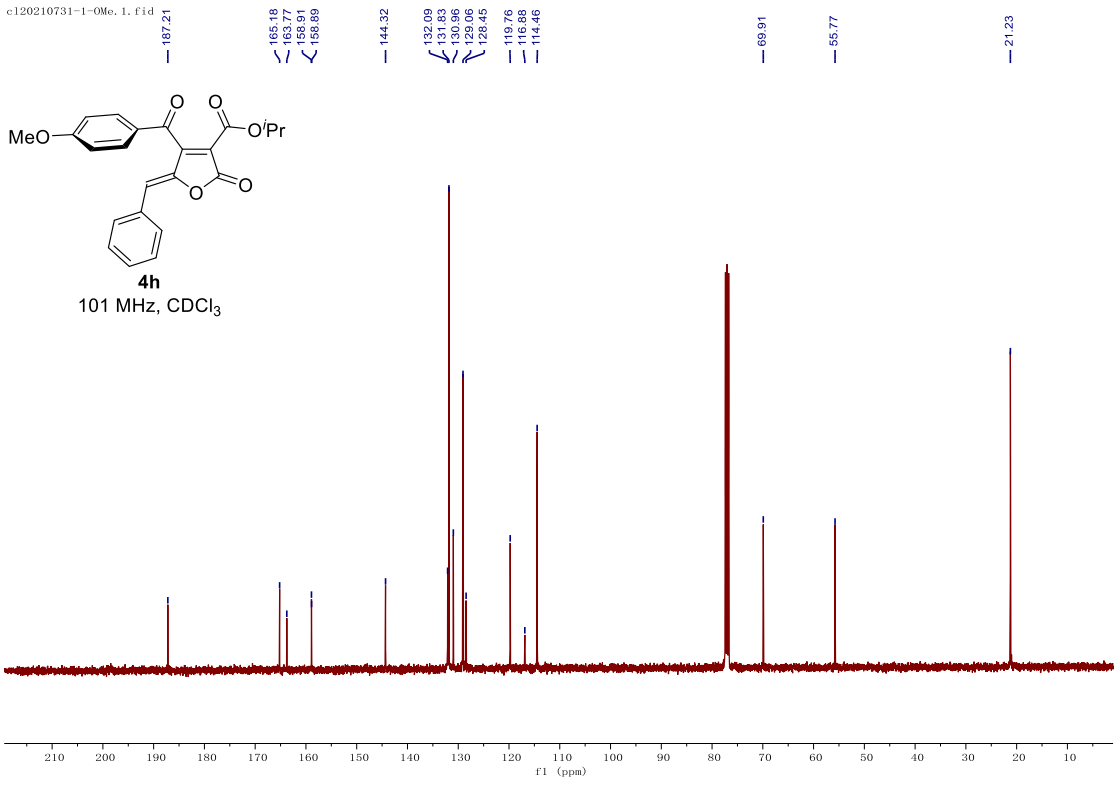

c120210908-p.1.fid
7.9586
7.9397
7.7149
7.6964
7.6780
7.5701
7.5510
7.5318
7.0409
6.0412
4.9973
4.9819
4.9663
4.9508
4.9351
3.9060
3.8812
0.9389
0.9233
Ph
O
O
O
O
O
O
iPr
MeO
MeO
OMe
4f
400 MHz, CDCl3
1.93
1.14
1.99
1.95
1.00
1.00
9.00
6.29
f1 (ppm)

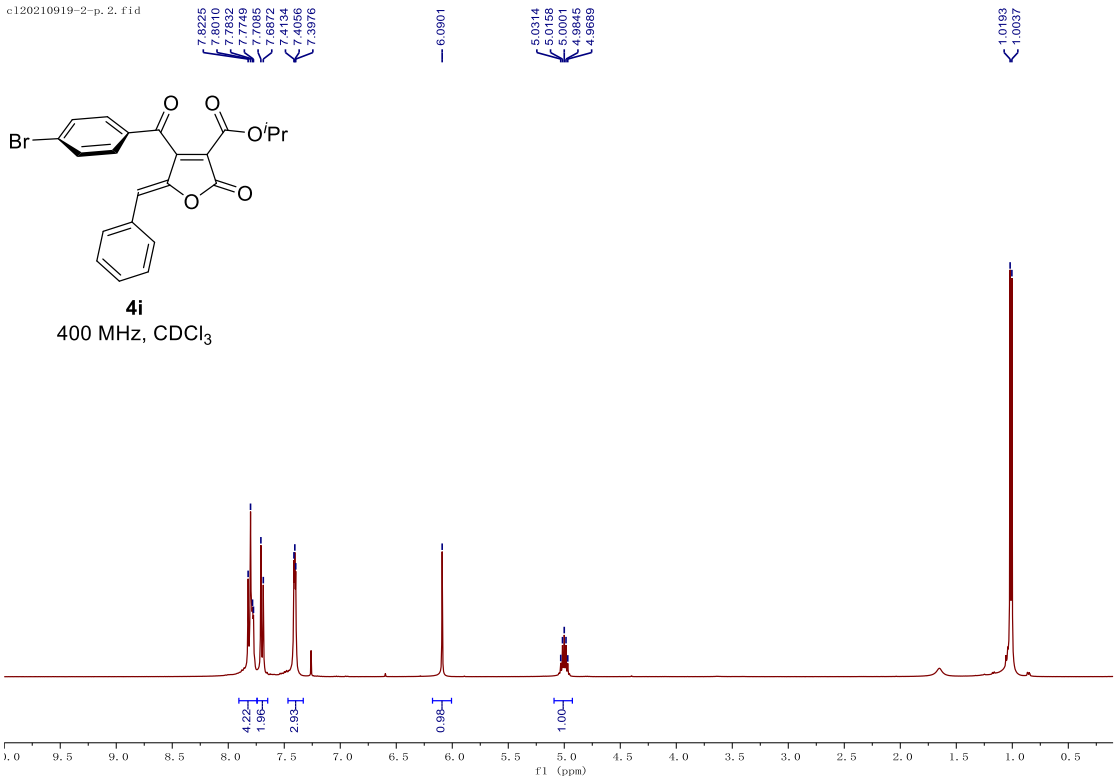

c120210908-p
single pulse decoupled gated NOE
183.20
163.59
158.91
158.21
153.43
143.57
141.28
135.44
135.21
129.37
129.27
127.52
120.18
116.41
109.36
77.32
77.11
76.90
70.02
61.18
56.40
21.19
Ph
O
O
O
O
O
O
iPr
MeO
MeO
OMe
4f
151 MHz, CDCl3
f1 (ppm)

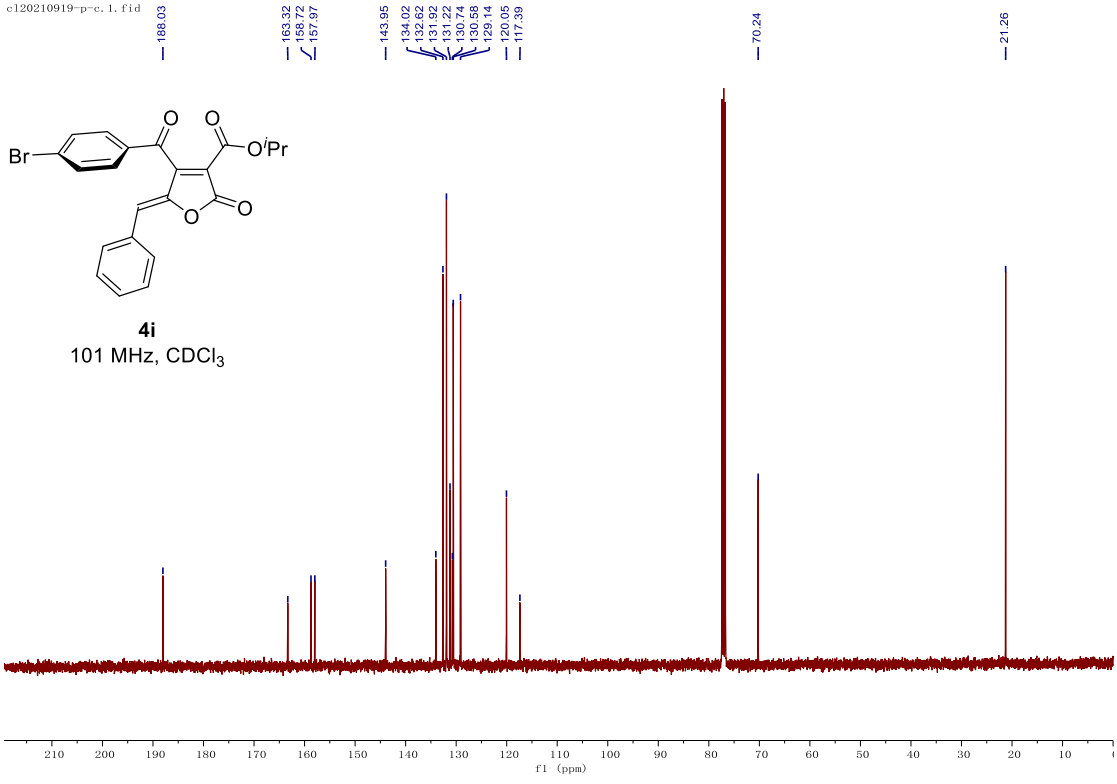

c120210717-2-p.1.fid
7.9505
7.9320
7.8213
7.8076
7.7994
7.7857
7.7132
7.6946
7.6761
7.5676
7.5480
7.5288
7.1126
7.0910
7.0695
6.0927
4.9998
4.9841
4.9685
4.9529
4.9373
0.9477
0.9321
Ph
O
O
O
O
O
O
F
4g
400 MHz, CDCl3
1.95
1.99
1.04
2.01
2.00
1.00
1.01
6.04
f1 (ppm)

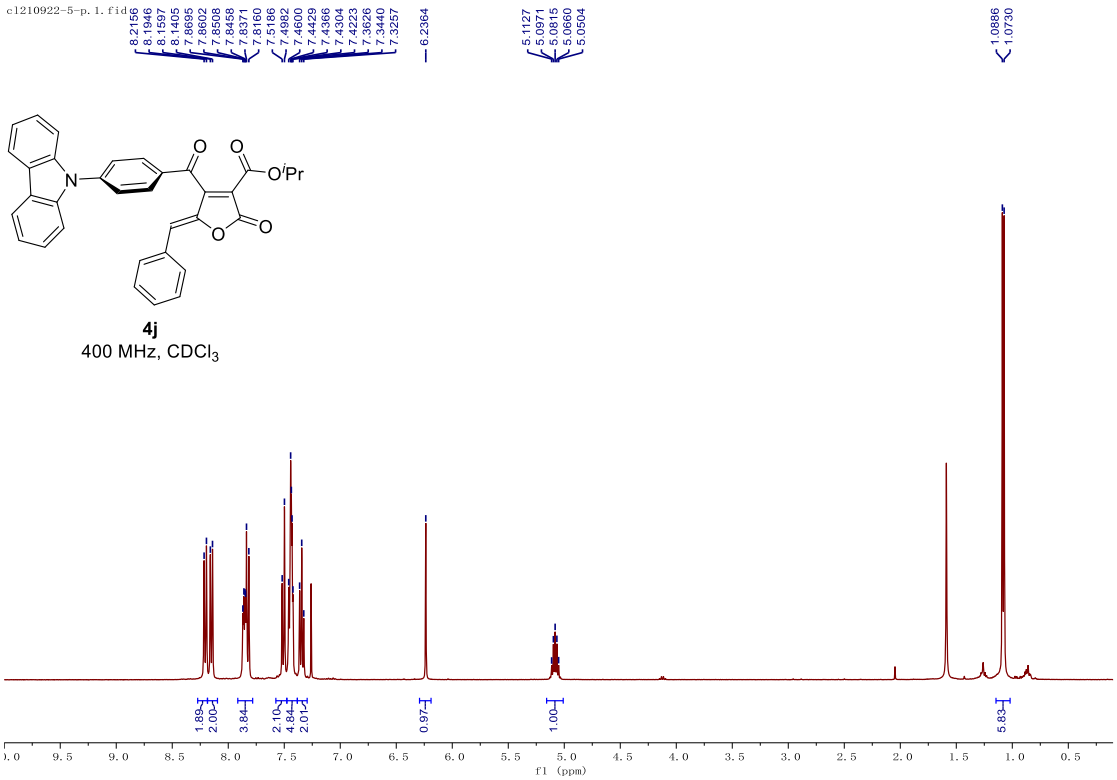

CL20210717-2-P
single pulse decoupled gated NOE
188.97
164.98
163.58
163.30
158.79
158.36
143.84
135.28
134.17
134.11
129.37
129.30
128.51
128.49
118.63
117.13
116.60
116.45
70.16
21.19
Ph
O
O
O
O
O
O
F
4g
151 MHz, CDCl3
f1 (ppm)

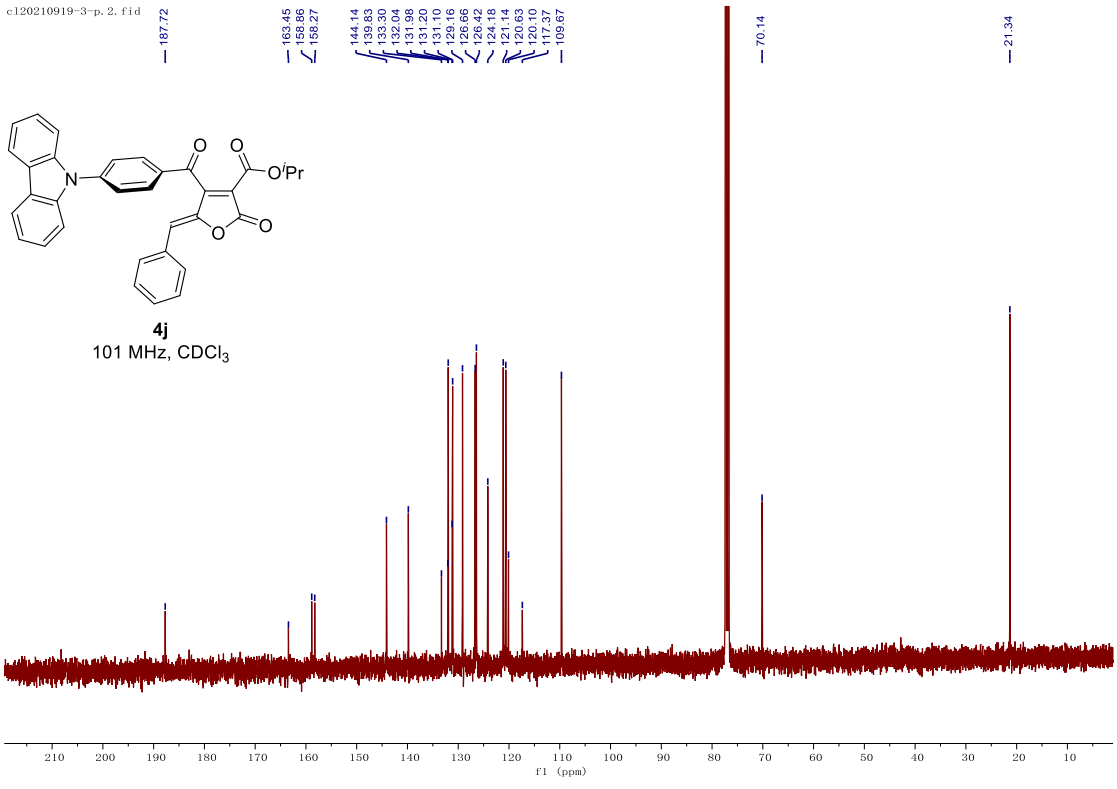

c120210731-1-p.1.fid
7.9177
7.8960
7.7963
7.7777
7.7792
7.7740
7.4015
7.3924
7.3869
7.0098
6.9882
6.1245
5.0373
5.0220
5.0065
4.9909
4.9754
4.9600
3.9007
0.9997
0.9846
MeO
O
O
O
O
O
O
iPr
4h
400 MHz, CDCl3
1.97
2.14
3.16
2.01
1.00
1.06
6.39
f1 (ppm)

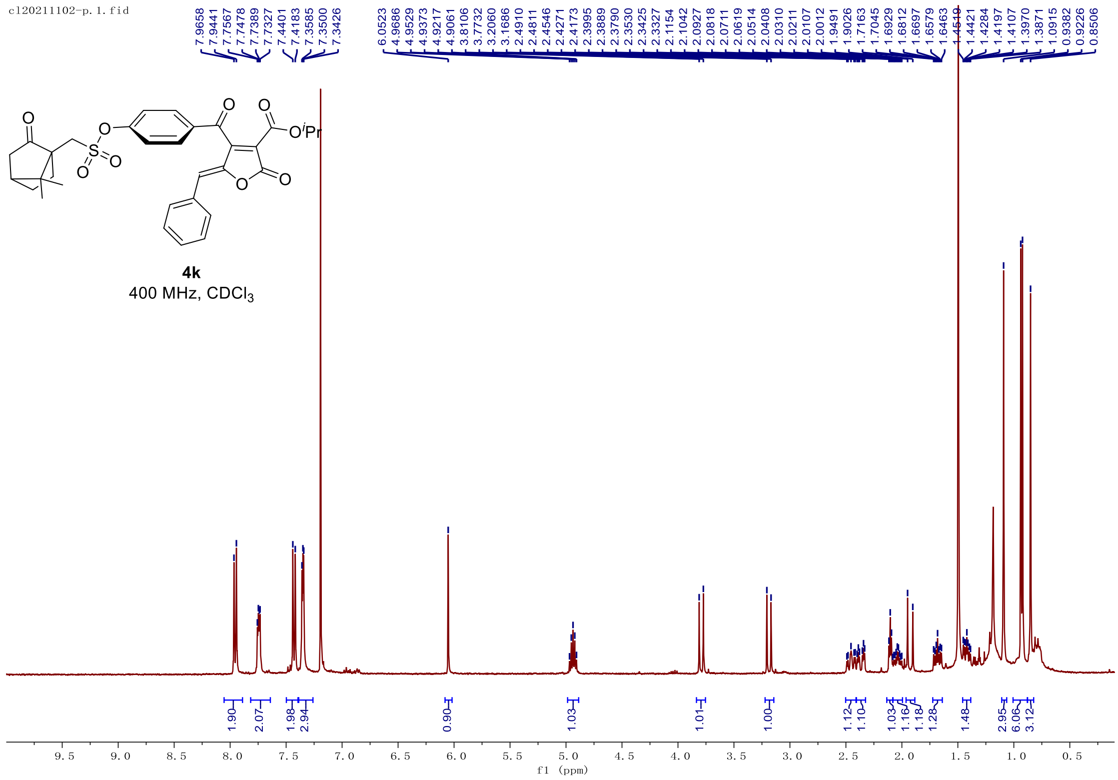

c120210731-1-OMe.1.fid
187.21
165.18
163.77
158.91
158.89
144.32
132.09
131.83
130.96
129.06
128.45
119.76
116.88
114.46
69.91
55.77
21.23
MeO
O
O
O
O
O
O
iPr
4h
101 MHz, CDCl3
f1 (ppm)

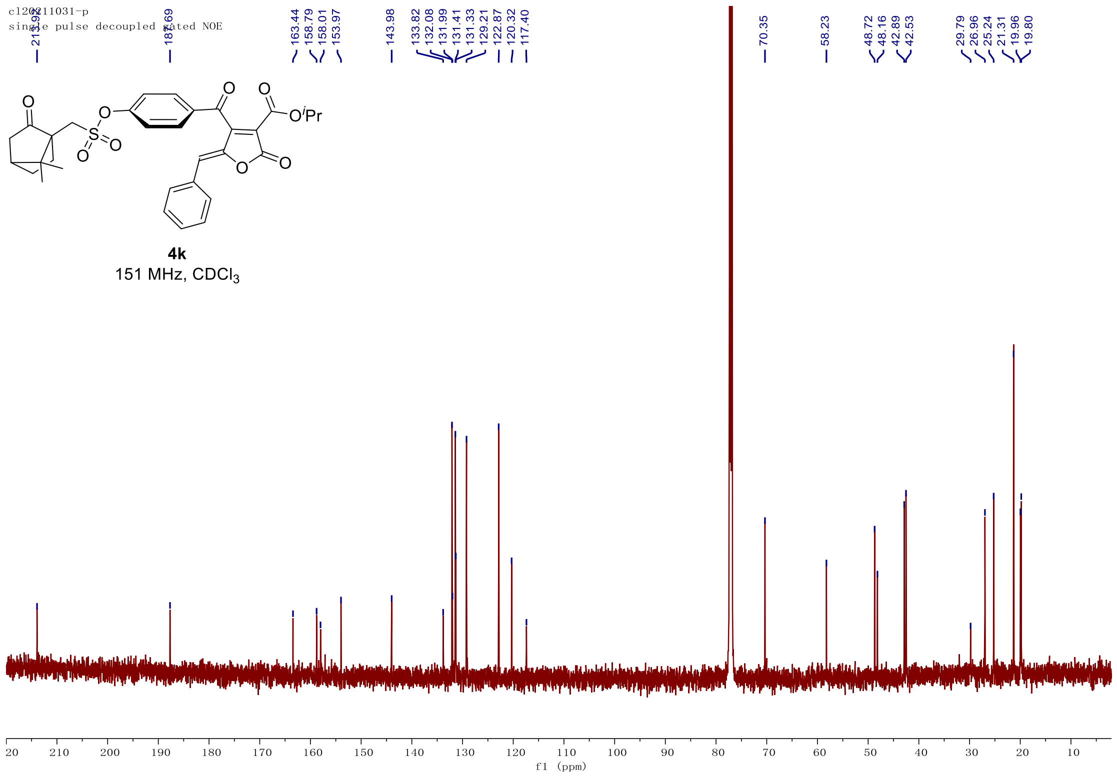

c120210919-2-p.2.fid
7.8225
7.8010
7.7832
7.7749
7.7085
7.6872
7.4134
7.4056
7.3976
6.0901
5.0314
5.0158
5.0001
4.9845
4.9689
1.0193
1.0037
Br
O
O
O
O
O
O
iPr
4i
400 MHz, CDCl3
4.22
1.96
2.93
0.98
1.00
f1 (ppm)

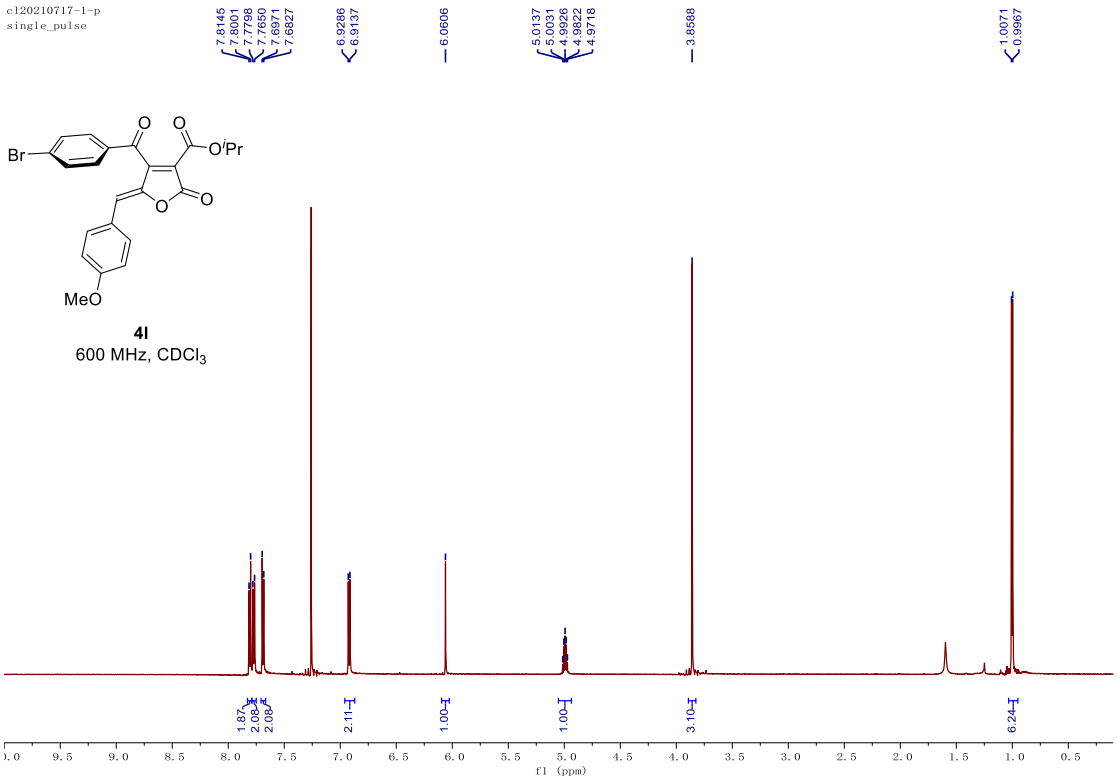

c120210919-p-c.1.fid
188.03
163.32
158.72
157.97
143.95
134.02
132.62
131.92
131.22
130.74
130.58
129.14
120.05
117.39
70.24
21.26
Br
O
O
O
O
O
O
iPr
4i
101 MHz, CDCl3
f1 (ppm)

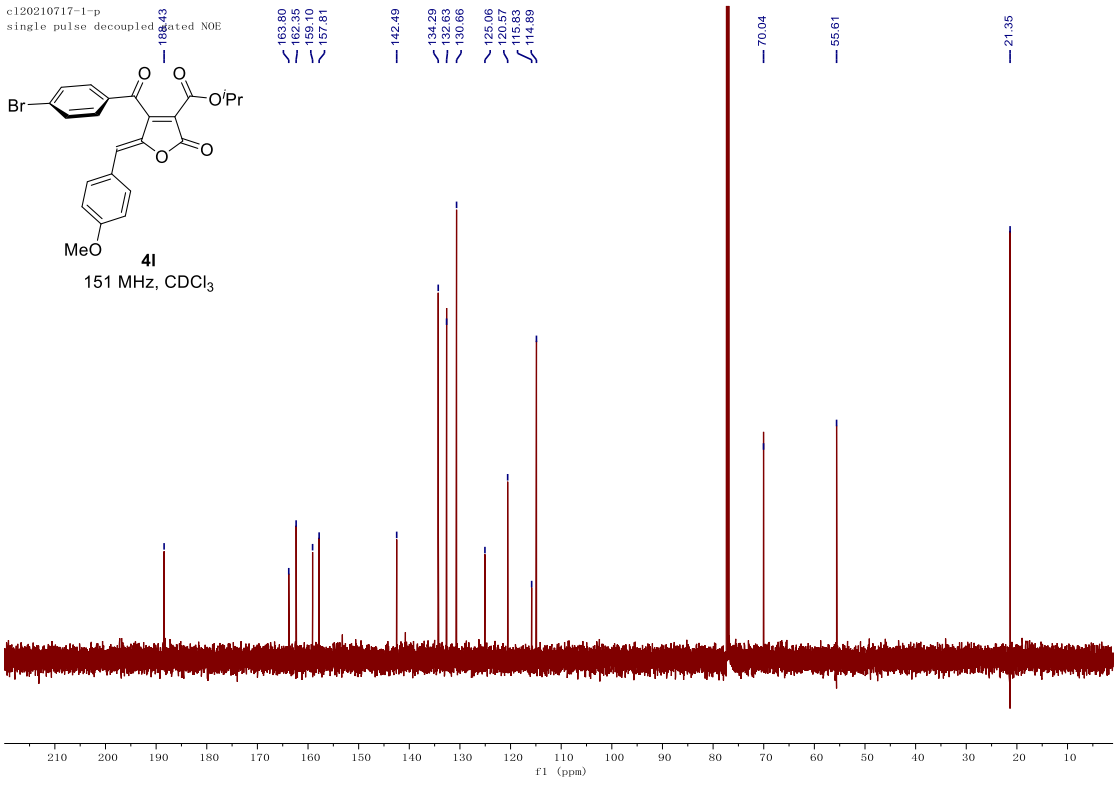

c1210922-5-p.1.fid
8.2156
8.1946
8.1597
8.1405
7.8695
7.8602
7.8508
7.8458
7.8371
7.8160
7.5186
7.4982
7.4600
7.4429
7.4366
7.4304
7.4223
7.3626
7.3440
7.3257
6.2364
5.1127
5.0971
5.0815
5.0660
5.0504
1.0886
1.0730
O
O
O^{i}Pr
N
O
O
4j
400 MHz, CDCl$_3$
1.88
2.00
3.84
2.10
4.84
2.01
0.97
1.00
5.83
f1 (ppm)

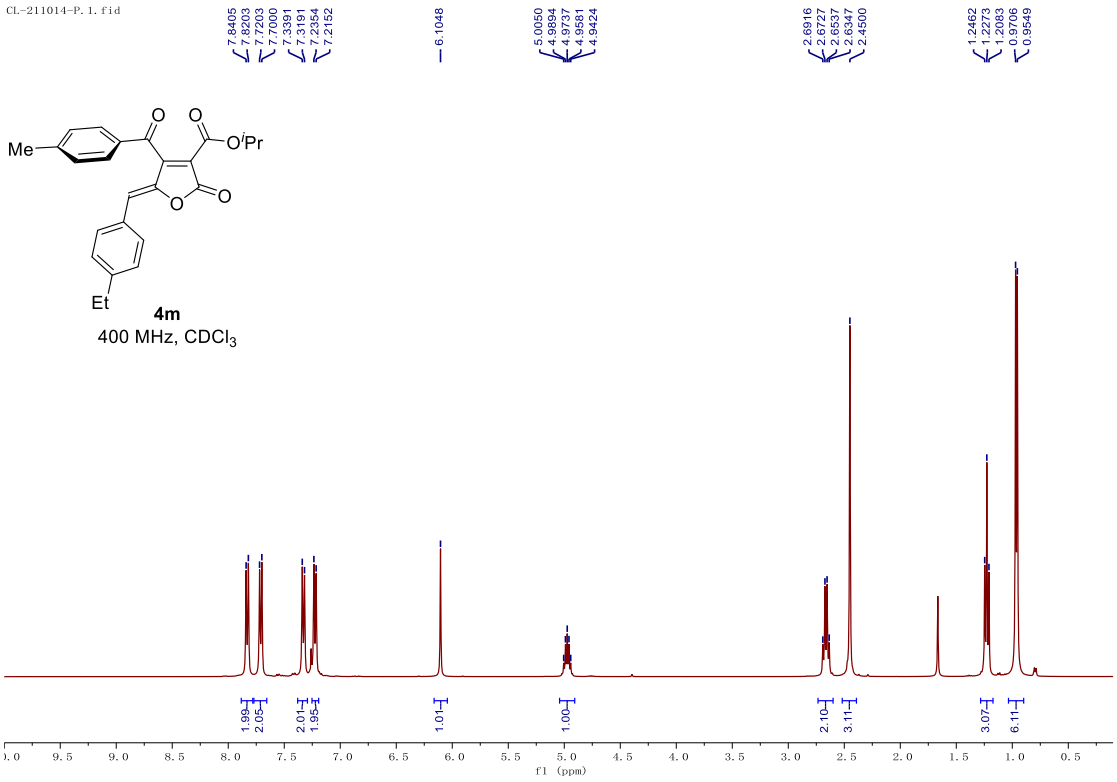

c120210919-3-p.2.fid
187.72
163.45
158.86
158.27
144.14
139.83
133.30
132.04
131.98
131.20
131.10
129.16
128.66
126.42
124.18
121.14
120.63
120.10
117.37
109.67
70.14
21.34
O
O
O^{i}Pr
N
O
O
4j
101 MHz, CDCl$_3$
f1 (ppm)

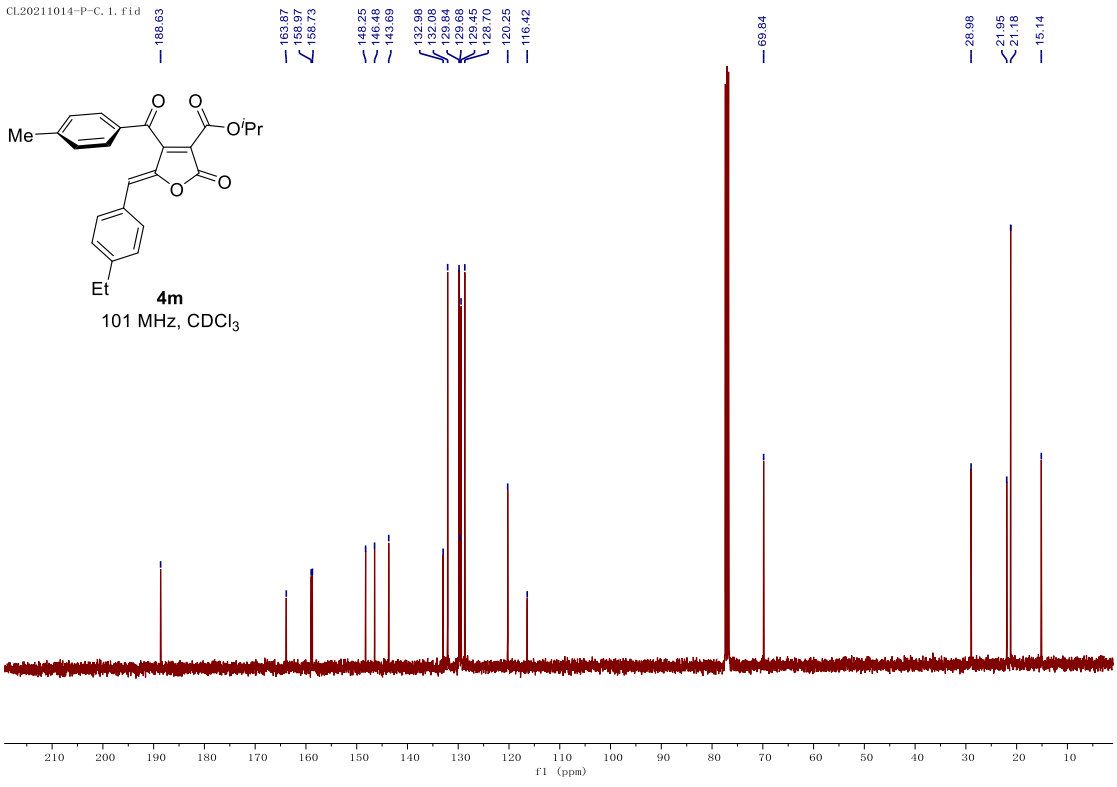

cl20211102-p.1.fid
4k
400 MHz, CDCl3
f1 (ppm)

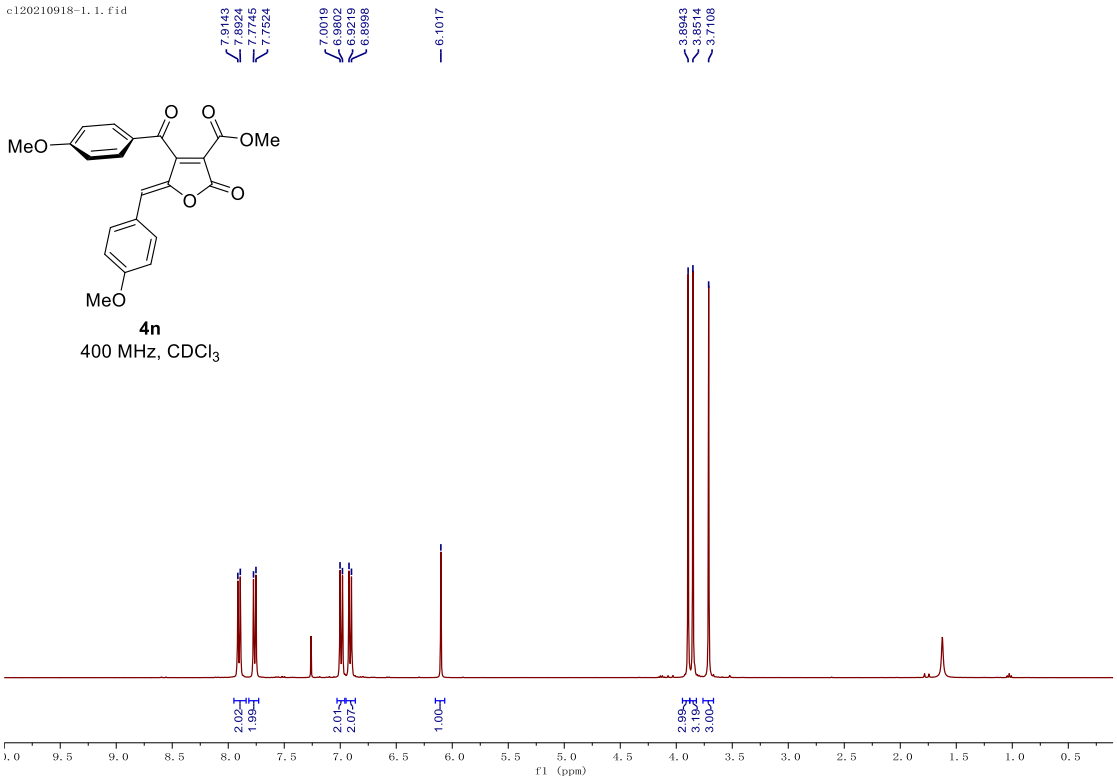

cl20211031-p
4k
151 MHz, CDCl3
f1 (ppm)

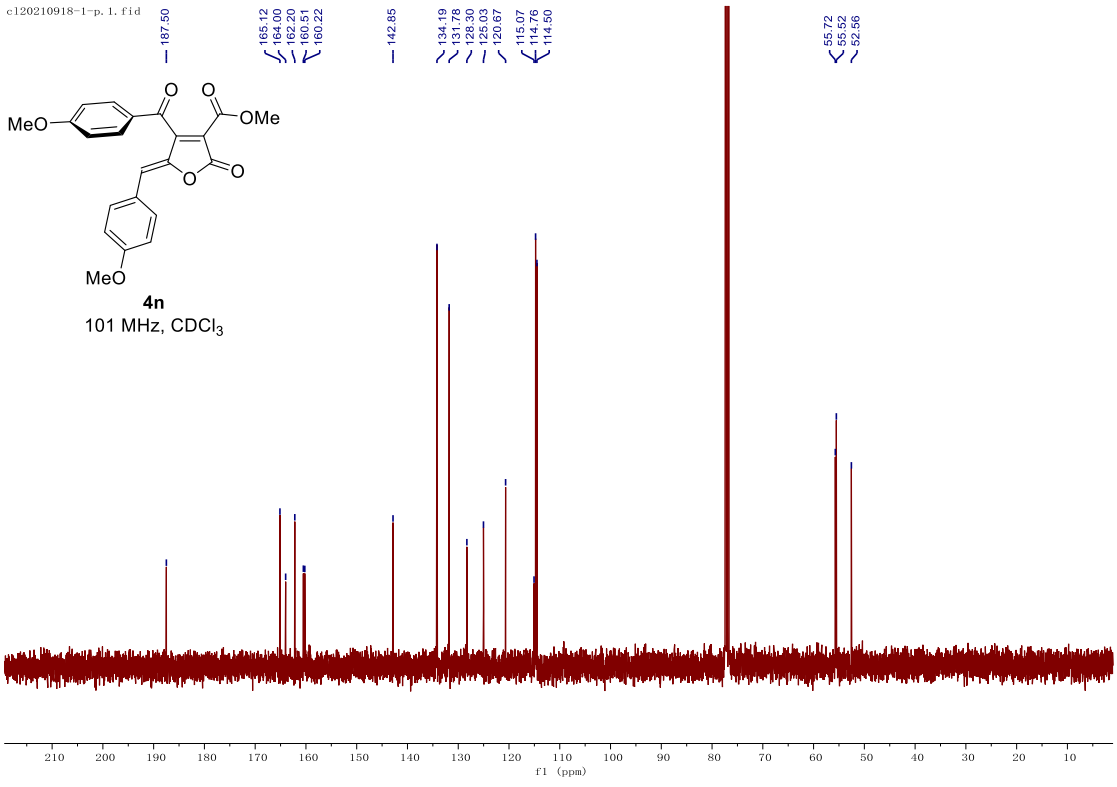

c120210717-1-p
single_pulse
7.8145
7.8001
7.7798
7.7650
7.6971
7.6827
6.9286
6.9137
6.0606
5.0137
5.0031
4.9926
4.9822
4.9718
3.8588
1.0071
0.9967
Br
O
O
O
O
O
O
O
O
iPr
MeO
4l
600 MHz, CDCl3
1.87
2.08
2.08
2.11
1.00
1.00
3.10
6.24
f1 (ppm)

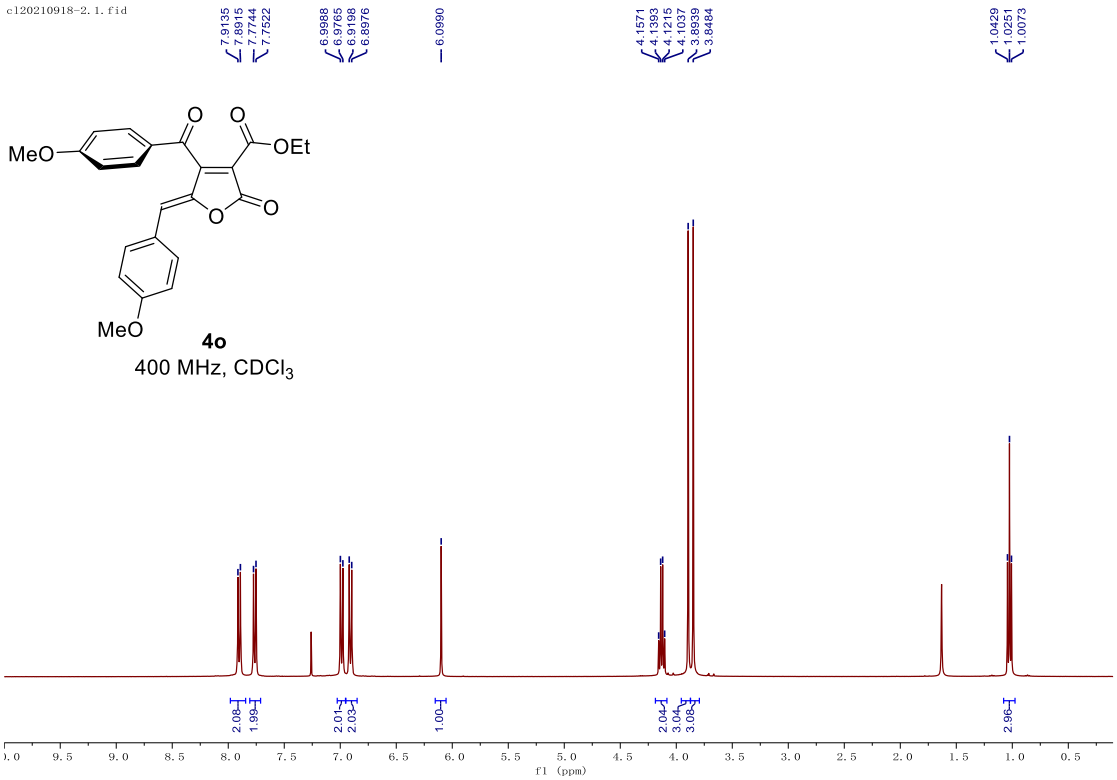

c120210717-1-p
single pulse decoupled gated NOE
188.43
163.80
162.35
159.10
157.81
142.49
134.29
132.63
130.66
125.06
120.57
115.83
114.89
70.04
55.61
21.35
Br
O
O
O
O
O
O
O
O
iPr
MeO
4l
151 MHz, CDCl3
f1 (ppm)

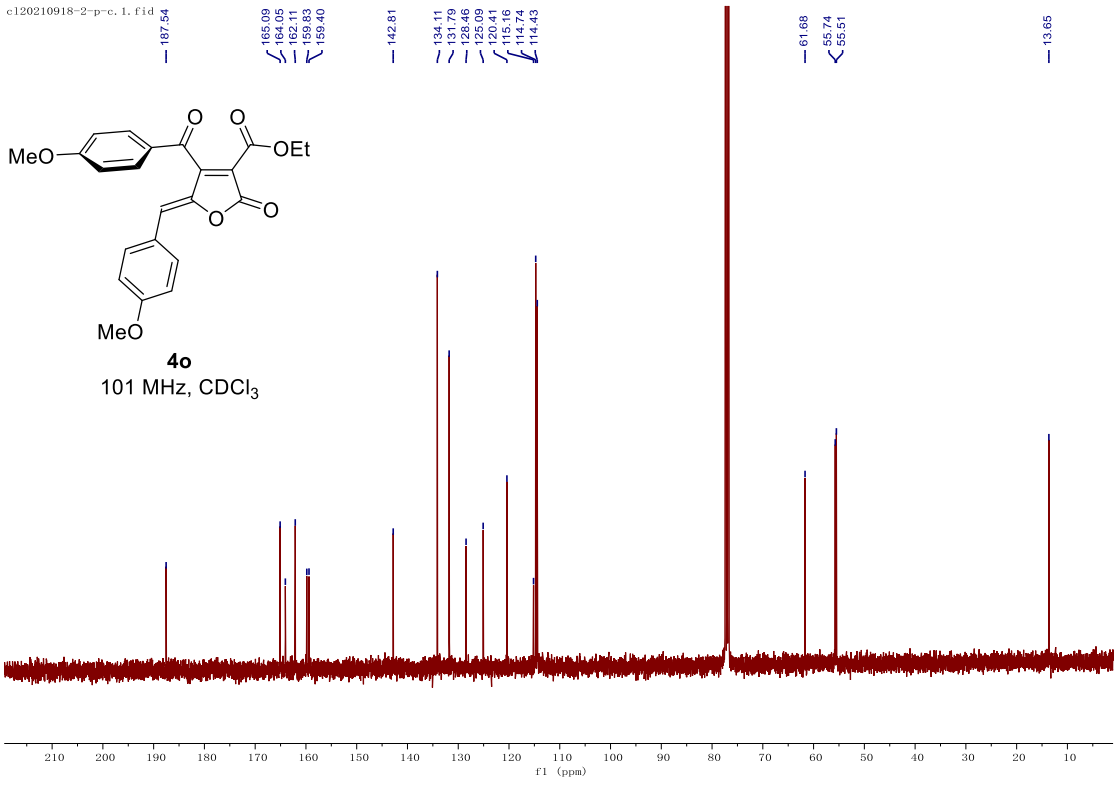

CL-211014-P. 1. fid
7.8405
7.8203
7.7203
7.7000
7.3391
7.3191
7.2354
7.2152
6.1048
5.0050
4.9894
4.9737
4.9581
4.9424
2.6916
2.6727
2.6537
2.6347
2.4500
1.2462
1.2273
1.2083
0.9706
0.9549
Me
O
O
O^{i}Pr
O
O
Et
4m
400 MHz, CDCl$_3$
1.99
2.05
2.01
1.96
1.01
1.00
2.10
3.11
3.07
6.11
f1 (ppm)

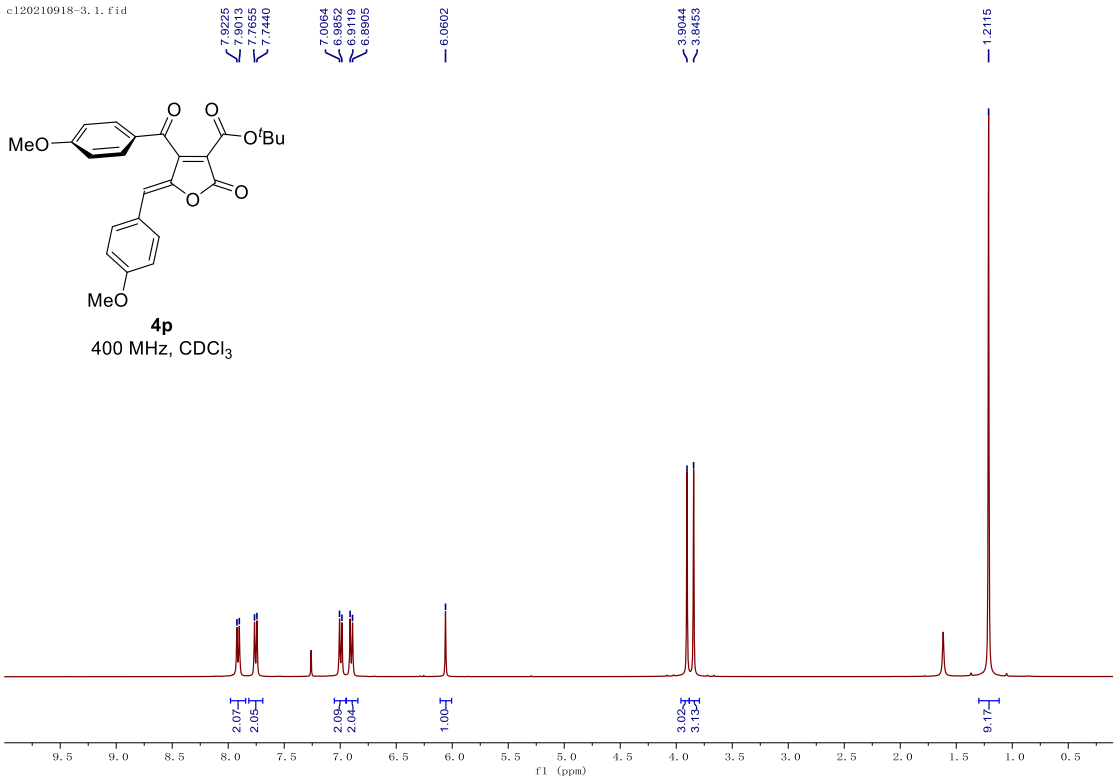

CL20211014-P-C. 1. fid
188.63
163.87
158.97
158.73
148.25
146.48
143.69
132.98
132.08
129.84
129.68
129.45
128.70
120.25
116.42
69.84
28.98
21.95
21.18
15.14
Me
O
O
O^{i}Pr
O
O
Et
4m
101 MHz, CDCl$_3$
f1 (ppm)

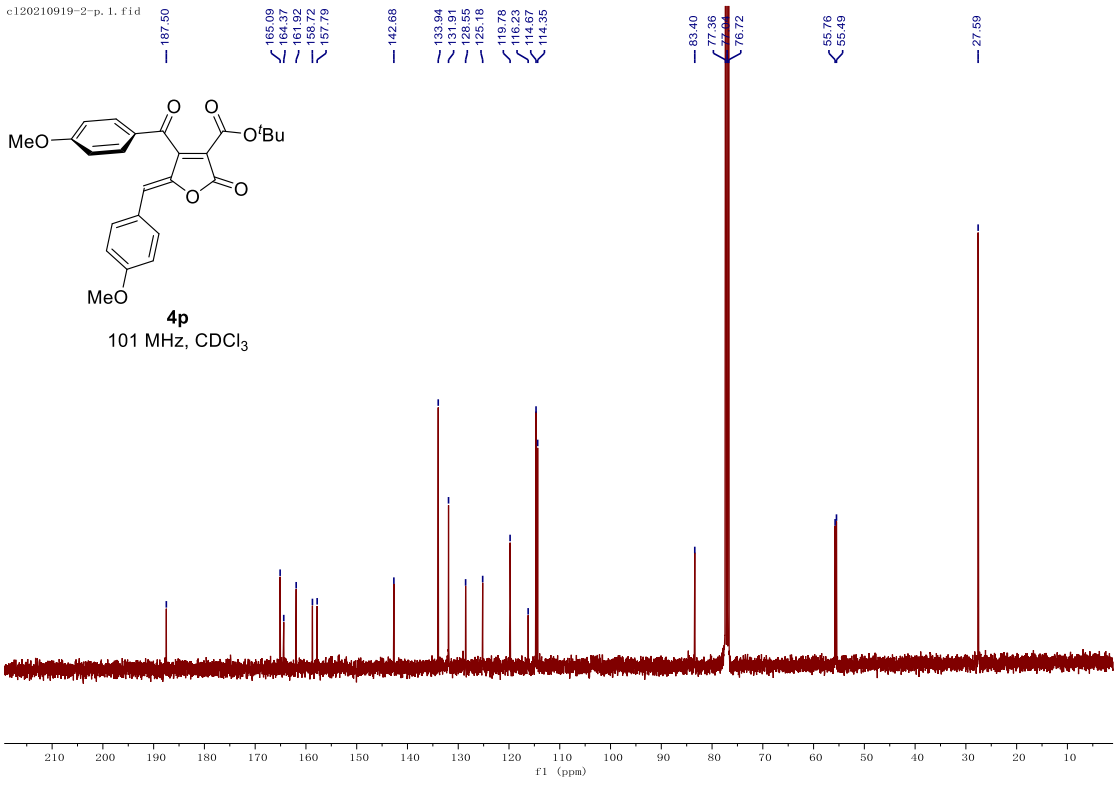

c120210918-1.1.fid
7.9143
7.8924
7.7745
7.7524
7.0019
6.9802
6.9219
6.8998
6.1017
3.8943
3.8514
3.7108
MeO
OMe
O
O
O
O
MeO
4n
400 MHz, CDCl3
2.02
1.98
2.01
2.07
1.00
2.98
3.19
3.00
f1 (ppm)

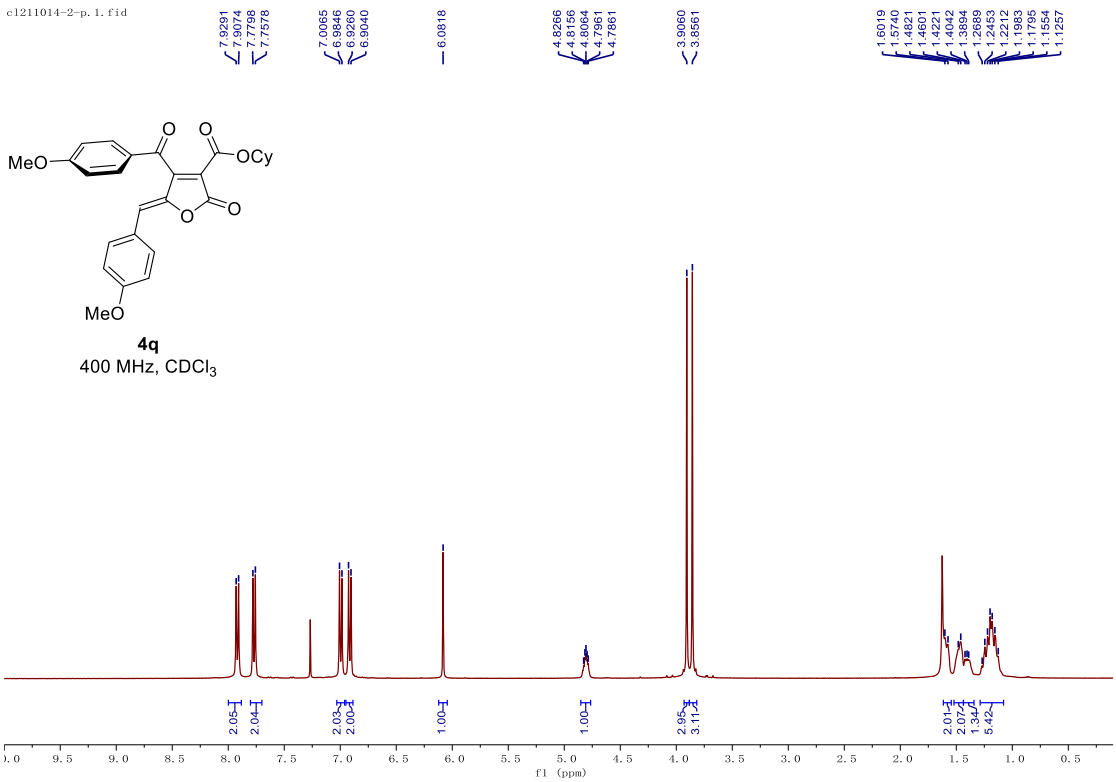

c120210918-1-p.1.fid
187.50
165.12
164.00
162.20
160.51
160.22
142.85
134.19
131.78
128.30
125.03
120.67
115.07
114.76
114.50
55.72
55.52
52.56
MeO
OMe
O
O
O
O
MeO
4n
101 MHz, CDCl3
f1 (ppm)

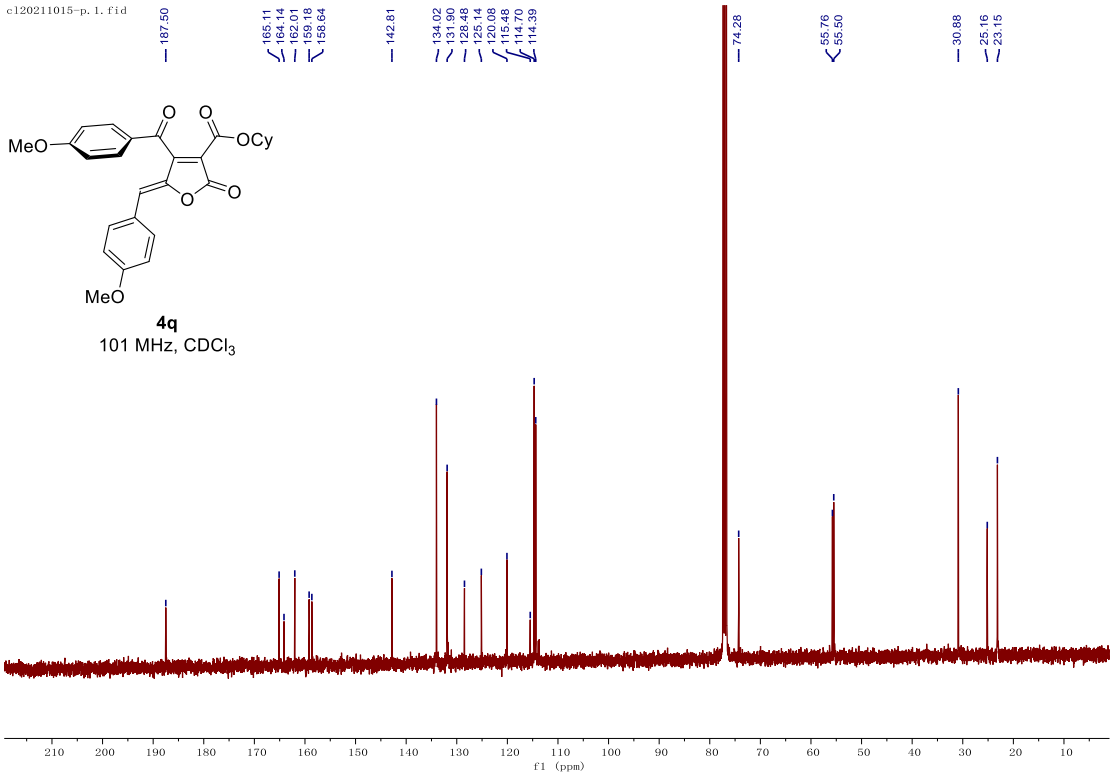

c120210918-2_1_fid
7.9135
7.8915
7.7744
7.7522
6.9988
6.9765
6.9198
6.8976
6.0990
4.1571
4.1393
4.1215
4.1037
3.8939
3.8484
1.0429
1.0251
1.0073
MeO
OEt
O
O
O
O
MeO
4o
400 MHz, CDCl3
2.08
1.99
2.01
2.03
1.00
2.04
3.04
3.08
2.96
f1 (ppm)


c120210918-2-p-c_1_fid
187.54
165.09
164.05
162.11
159.83
159.40
142.81
134.11
131.79
128.46
125.09
120.41
115.16
114.74
114.43
61.68
55.74
55.51
13.65
MeO
OEt
O
O
O
O
MeO
4o
101 MHz, CDCl3
f1 (ppm)

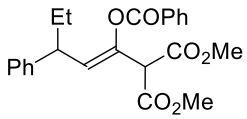

c120210918-3.1.fid
7.9225
7.9013
7.7655
7.7440
7.0064
6.9952
6.9119
6.8905
6.0602
3.9044
3.8453
1.2115
MeO
O
O
O
O
O
tBu
MeO
4p
400 MHz, CDCl3
2.07
2.05
2.09
2.04
1.00
3.02
3.13
9.17
f1 (ppm)


c120210919-2-p.1.fid
187.50
165.09
164.37
161.92
158.72
157.79
142.68
133.94
131.91
128.55
125.18
119.78
116.23
114.67
114.35
83.40
77.36
77.04
76.72
55.76
55.49
27.59
MeO
O
O
O
O
O
tBu
MeO
4p
101 MHz, CDCl3
f1 (ppm)


c1211014-2-p.1.fid
7.9291
7.9074
7.7798
7.7578
7.0065
6.9846
6.9260
6.9040
6.0818
4.8266
4.8156
4.8064
4.7961
4.7861
3.9060
3.8561
1.6019
1.5740
1.4821
1.4601
1.4221
1.4042
1.3894
1.2689
1.2453
1.2212
1.1983
1.1795
1.1554
1.1257
MeO
OCy
O
MeO
4q
400 MHz, CDCl3
2.05
2.04
2.03
2.00
1.00
1.00
2.95
3.11
2.01
2.07
1.34
5.42
f1 (ppm)

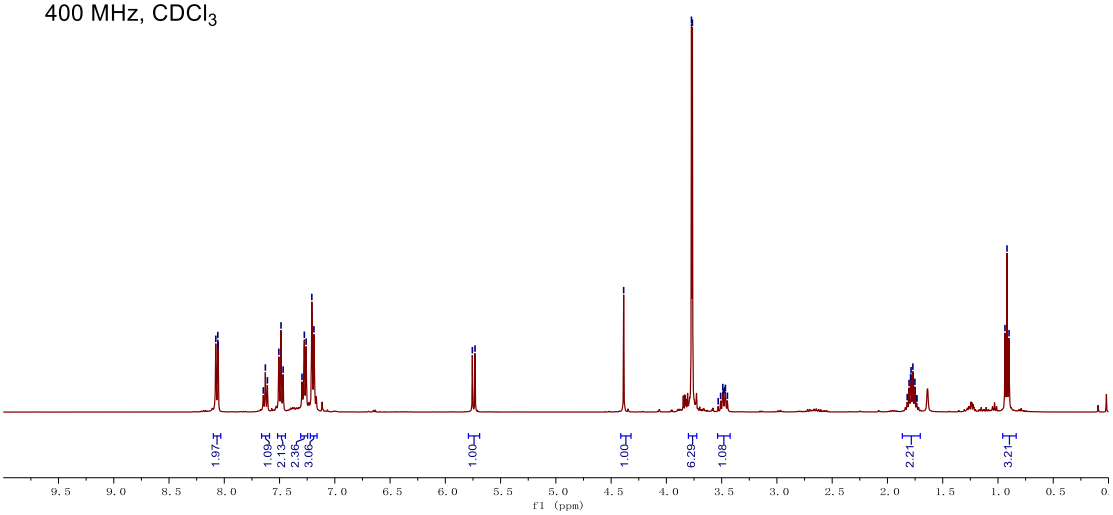

c120211015-p.1.fid
187.50
165.11
164.14
162.01
159.18
158.64
142.81
134.02
131.90
128.48
125.14
120.08
115.48
114.70
114.39
74.28
55.76
55.50
30.88
25.16
23.15
MeO
OCy
O
MeO
4q
101 MHz, CDCl3
f1 (ppm)

c120211112-4.1.fid

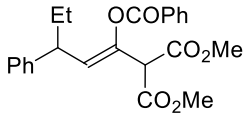


5a

400 MHz, $CDCl_3$

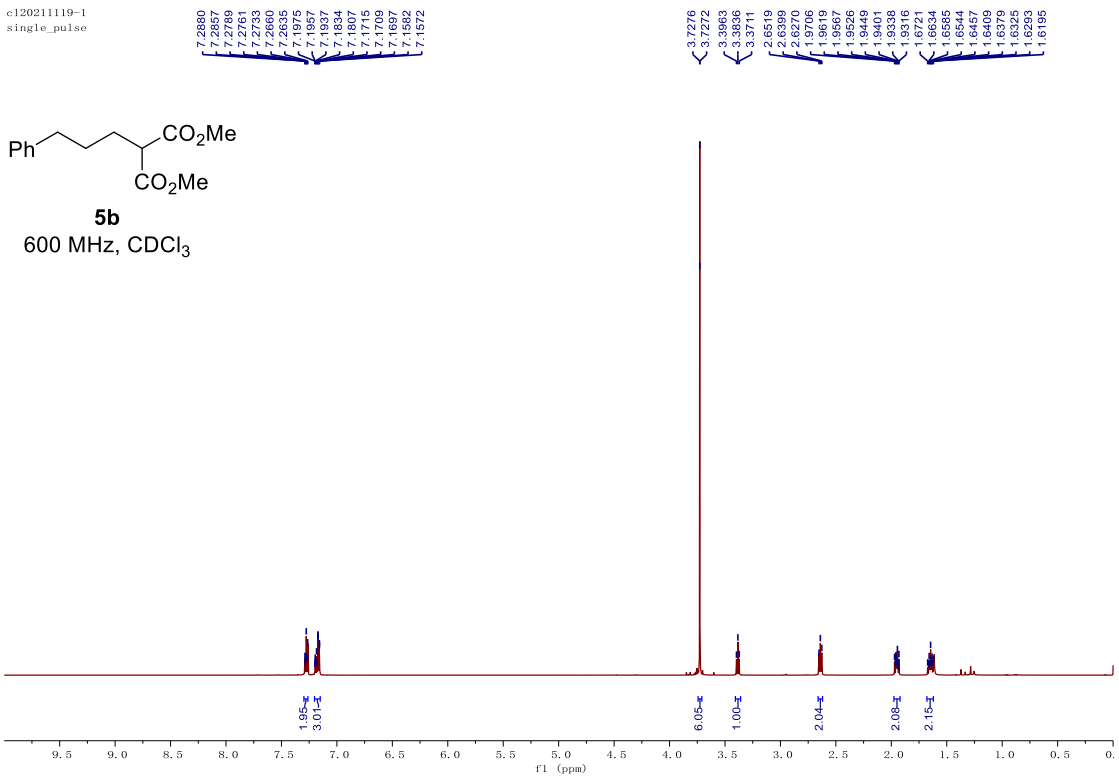


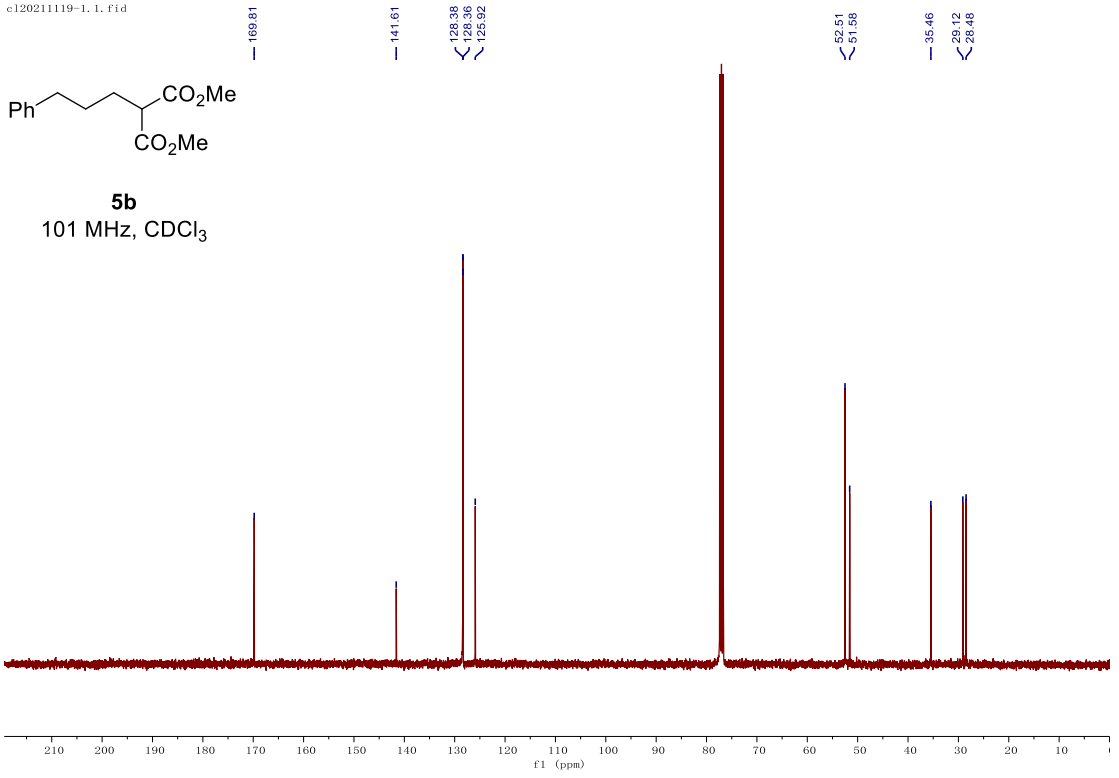
c120211112-4-C.1.fid

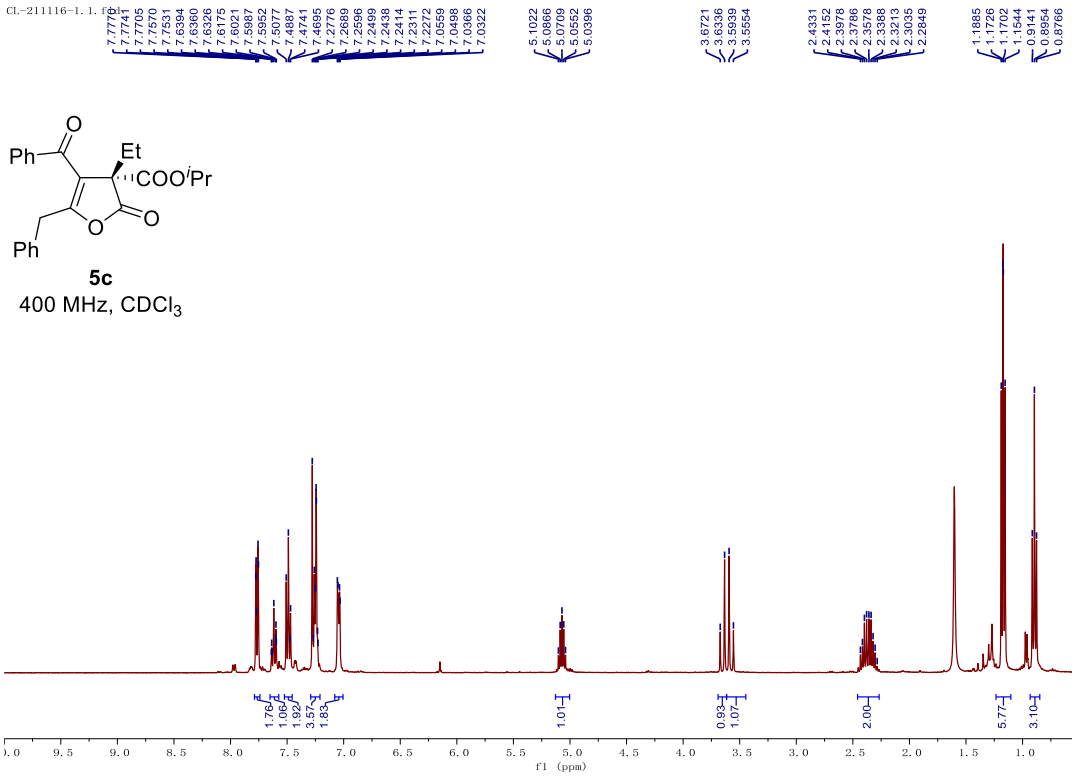


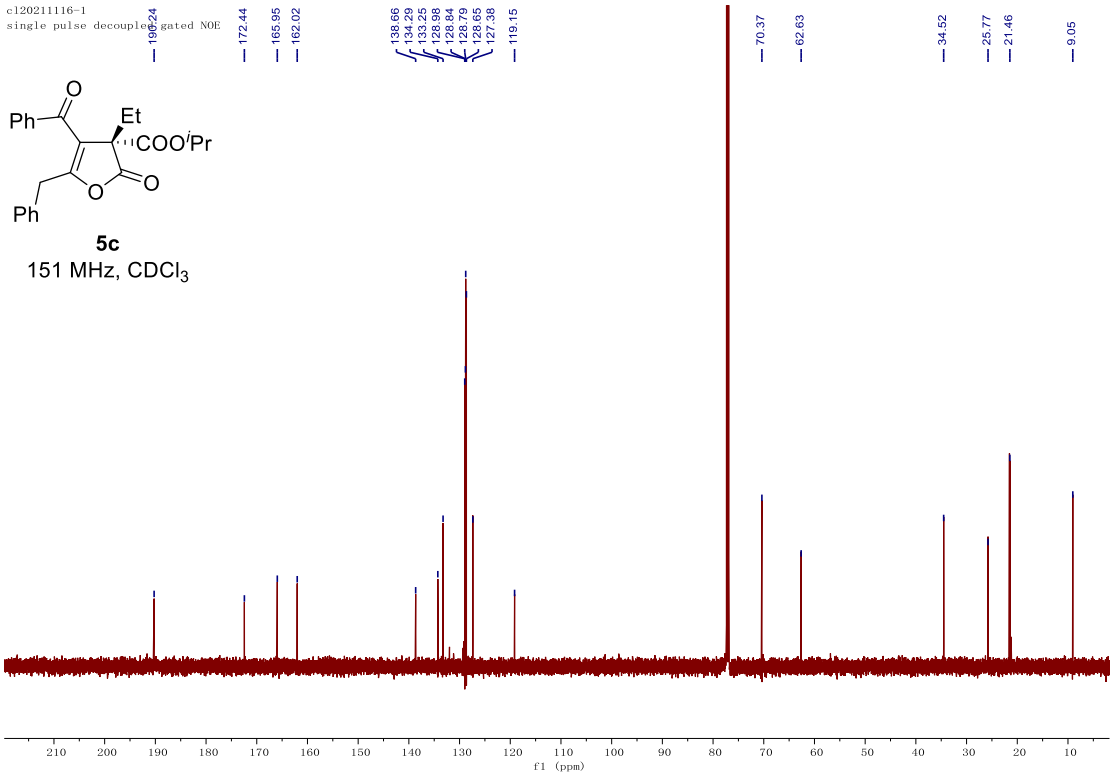
5a

101 MHz, $CDCl_3$

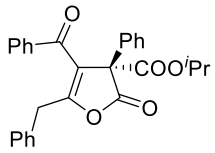

c120211119-1
single_pulse
7.2880
7.2857
7.2789
7.2761
7.2733
7.2660
7.2635
7.1975
7.1957
7.1937
7.1884
7.1697
7.1715
7.1709
7.1697
7.1582
7.1572
3.7276
3.7272
3.3963
3.3836
3.3711
2.6519
2.6399
2.6270
1.9706
1.9619
1.9567
1.9526
1.9449
1.9401
1.9338
1.9316
1.6721
1.6634
1.6585
1.6544
1.6457
1.6409
1.6379
1.6325
1.6293
1.6195
Ph
CO2Me
CO2Me
5b
600 MHz, CDCl3
1.95
3.01
6.05
1.00
2.04
2.08
2.15
f1 (ppm)


c120211119-1.1.fid
169.81
141.61
128.38
128.36
125.92
52.51
51.58
35.46
29.12
28.48
Ph
CO2Me
CO2Me
5b
101 MHz, CDCl3
f1 (ppm)


CL-211116-1.1.fid
7.7761
7.7741
7.7705
7.7570
7.7531
7.6394
7.6360
7.6326
7.6175
7.6021
7.5987
7.5952
7.5077
7.4887
7.4741
7.4695
7.2776
7.2689
7.2596
7.2499
7.2438
7.2414
7.2311
7.2272
7.0559
7.0498
7.0366
7.0322
5.1022
5.0866
5.0709
5.0552
5.0396
3.6721
3.6336
3.5939
3.5554
2.4331
2.4152
2.3978
2.3786
2.3578
2.3388
2.3213
2.3035
2.2849
1.1885
1.1726
1.1702
1.1544
0.9141
0.8954
0.8766
Ph
O
Et
COO^{i}Pr
O
O
Ph
5c
400 MHz, CDCl$_3$
1.76
1.06
1.92
3.57
1.83
1.01
0.93
1.07
2.00
5.77
3.10
f1 (ppm)

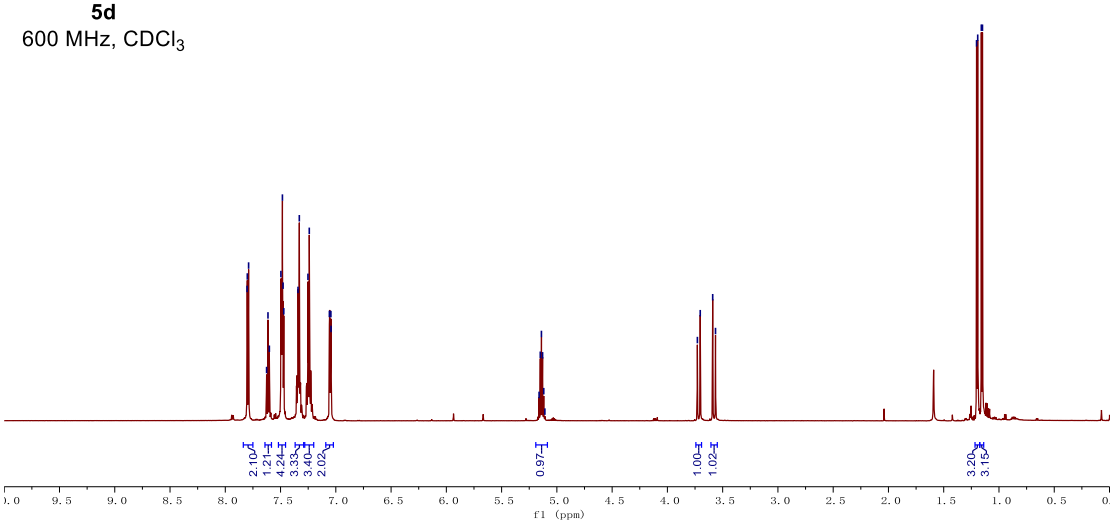

c120211116-1
single pulse decoupled gated NOE
190.24
172.44
165.95
162.02
138.66
134.29
133.25
128.88
128.84
128.79
128.65
127.38
119.15
70.37
62.63
34.52
25.77
21.46
9.05
Ph
O
Et
COO^{i}Pr
O
O
Ph
5c
151 MHz, CDCl$_3$
f1 (ppm)

c120211128-1
single_pulse

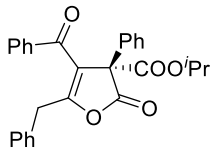


5d

600 MHz, $CDCl_3$

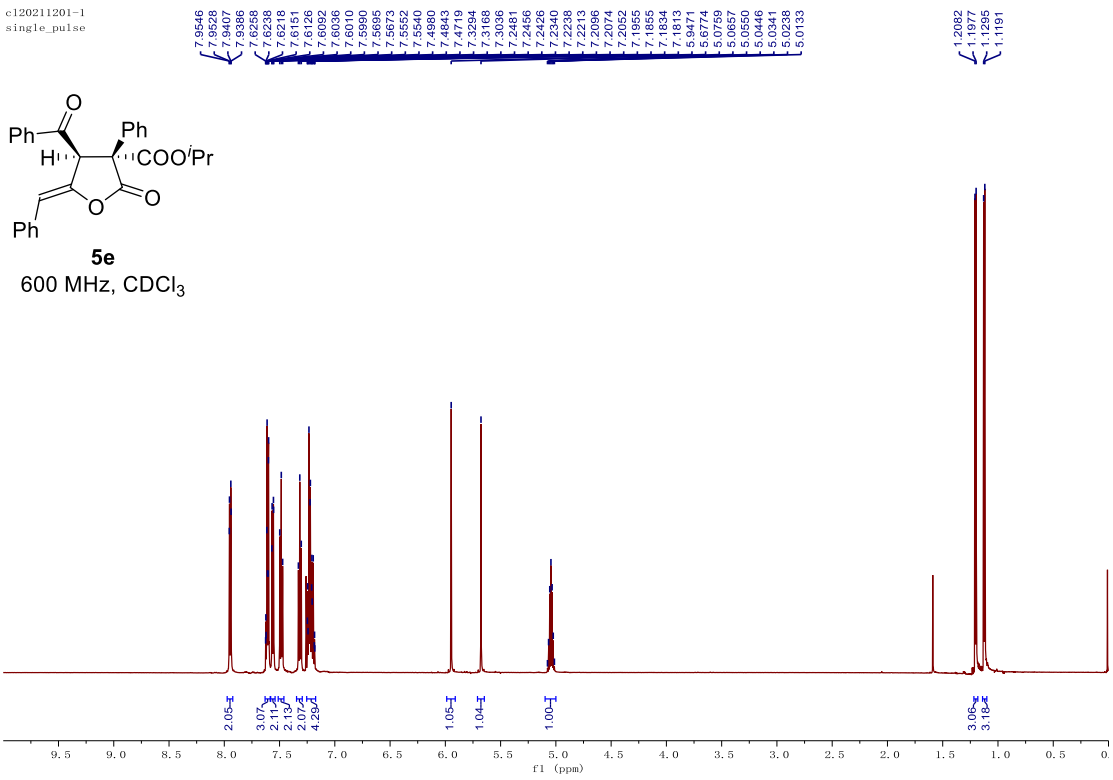


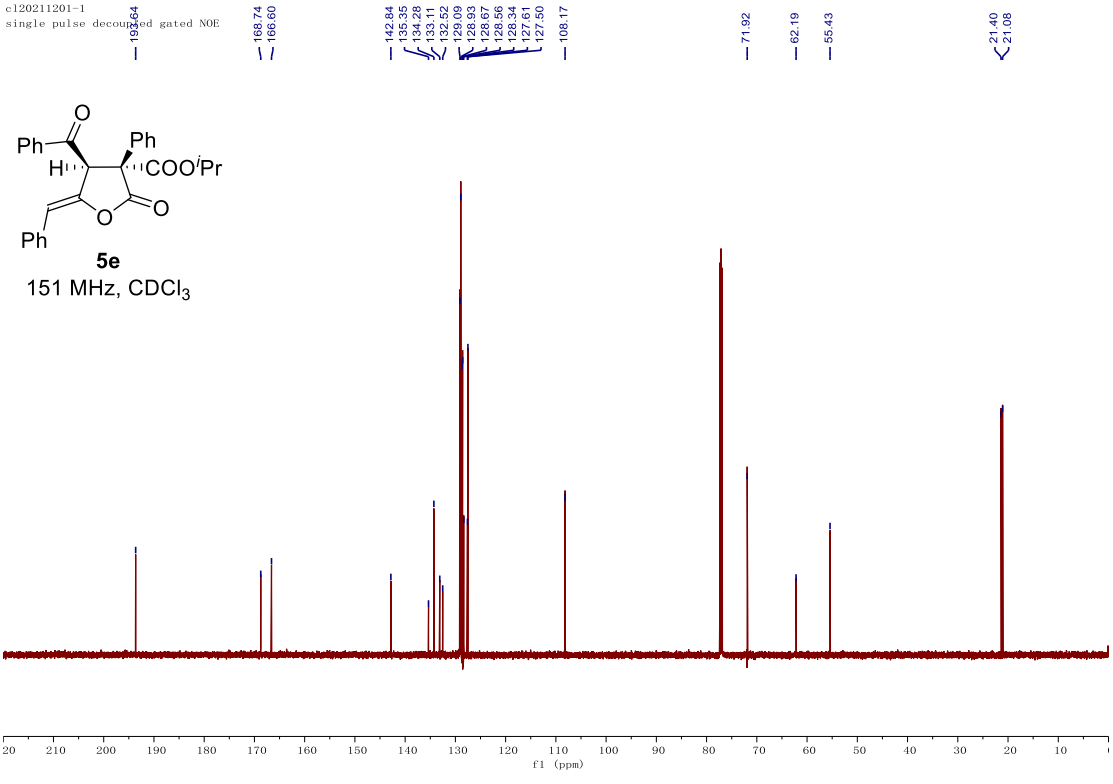
c120211128-1
single pulse decoupled gated NOE



5d

151 MHz, $CDCl_3$


c120211201-1
single_pulse
7.9546
7.9528
7.9407
7.9386
7.6258
7.6238
7.6218
7.6151
7.6126
7.6092
7.6036
7.6010
7.5990
7.5695
7.5673
7.5552
7.5540
7.4980
7.4843
7.4719
7.3294
7.3168
7.3036
7.2481
7.2456
7.2426
7.2340
7.2238
7.2213
7.2096
7.2074
7.2052
7.1955
7.1855
7.1834
7.1813
5.9471
5.6774
5.0759
5.0657
5.0550
5.0446
5.0341
5.0238
5.0133
1.2082
1.1977
1.1295
1.1191
Ph
O
H
Ph
COO^{i}Pr
O
O
Ph
5e
600 MHz, CDCl$_3$
2.05
3.07
2.11
2.13
2.07
4.29
1.05
1.04
1.00
3.06
3.18
f1 (ppm)


c120211201-1
single pulse decoupled gated NOE
193.64
168.74
166.60
142.84
135.35
134.28
133.11
132.52
129.09
128.93
128.67
128.56
128.34
127.61
127.50
108.17
71.92
62.19
55.43
21.40
21.08
Ph
O
H
Ph
COO^{i}Pr
O
O
Ph
5e
151 MHz, CDCl$_3$
f1 (ppm)

Reference

1. Kong, X.; Song, J.; Liu, J.; Meng, M.; Yang, S.; Zeng, M.; Zhan, X.; Li, C.; Fang, X. *Chem. Comm.* **2018,** *54*, 4266–4269.
2. Zhang, Z.; Jiang, X. *Org. Lett*. **2014**, *16*, 4400–4403.
3. Chen, Z.; Yu, F.; Liu, R.; Lin, X.; Yang, S.; Liu, J.; Chen, B.; Nagaraju, S.; Zeng, M.; Ding, C.; Fang, X. *Org. Lett*. **2020**, *22*, 2381–2385.
4. Kong, X; Yu, F; Chen, Z; Gong, F; Yang, S; Liu, J; Luo B; Fang, X. *Sci. China Chem*. **2021**,*64*, 991–998.
5. Guyon, C; Duclos, M; Sutter, M; Métay, E; Lemaire, M. *Org. Biomol. Chem*. **2015**, *13*, 7067-7075