Supporting Information

Copper-Catalyzed Cloke-Wilson Rearrangement for the Synthesis of Dihydrofurans Containing Tetrasubstituted Carbon Atoms

Qinqin Cui,[§,a] Shouang Lan,[§,b] Xiang Lei,[b] Chao Xu,[b] Chunyun Jiang,[b] Lili Zhao,[b,c] Liyuan Zhou,[b,c] Jinggong Liu,[d] Cheng-Zhi Gu,*[a] Shuang Yang,*[b] and Xinqiang Fang*[b]

[a] Shihezi University, Shihezi 832000, China.

[b] State Key Laboratory of Structural Chemistry, Center for Excellence in Molecular Synthesis, Fujian Institute of Research on the Structure of Matter, University of Chinese Academy of Sciences, Fuzhou 350100, China.

[c] Fujian Normal University, Fuzhou 350108, China.

[d] State Key Laboratory of Traditional Chinese Medicine Syndrome, The Second Affiliated Hospital of Guangzhou University of Chinese Medicine, Guangzhou 510120, China.

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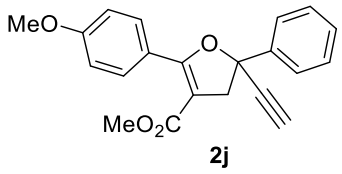
I. General Information

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), a JEOL ECZ400S (400 MHz) and a ECZ600S (600 MHz). Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ = 0.00 ppm) or chloroform (δ = 7.26 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), a JEOL ECZ400S (101 MHz) and a ECZ600S (151 MHz). 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 potassium permanganate stain.

II. X-Ray Crystallographic Analysis

Method for single crystals cultivation: a pure solid sample (10–20 mg) was dissolved in dichloromethane/ethyl acetate (1 mL) in a vial at room temperature, and petroleum ether/hexane (1 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.



2j

50% probability level

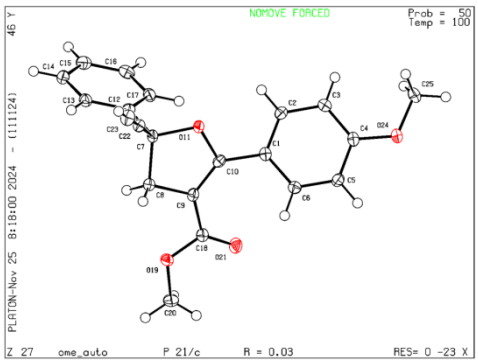
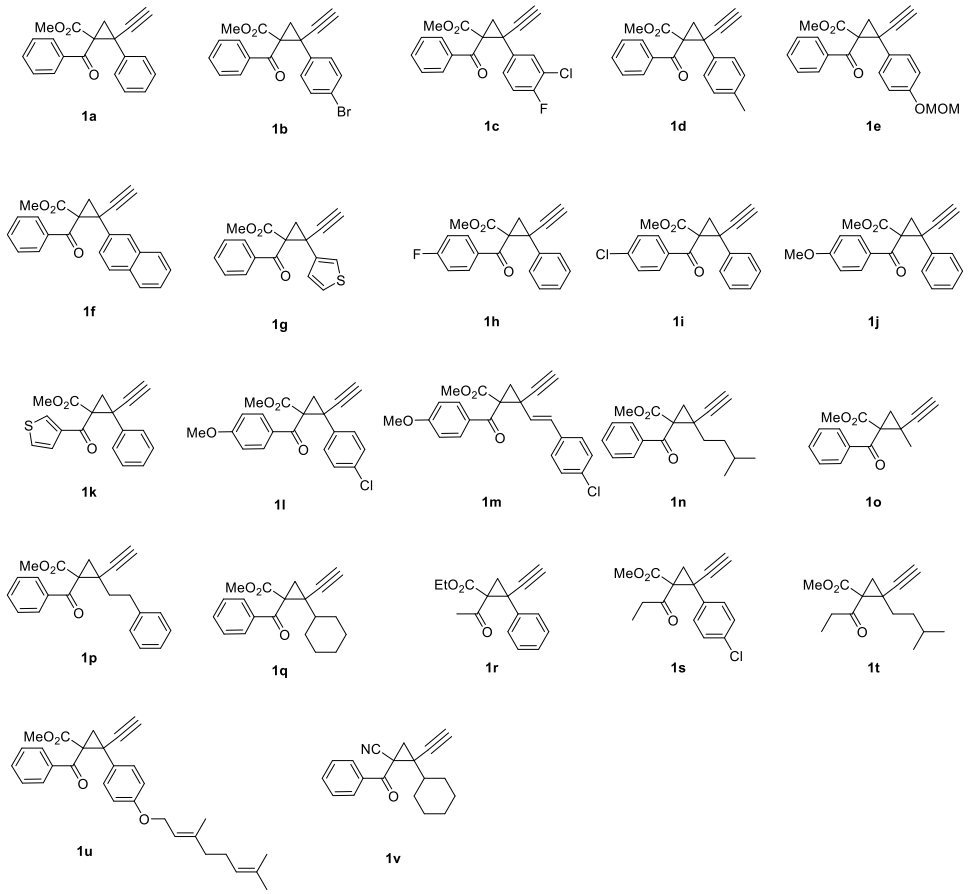


Table S1: Crystal data and structure refinement for 2j

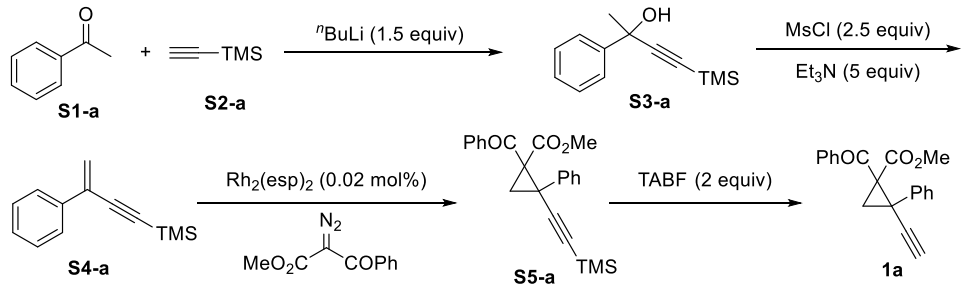
Identification code	2j
Empirical formula	$C_{21}H_{18}O_4$
Formula weight	334.35

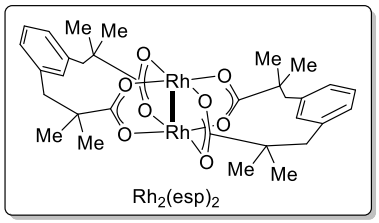
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.2453(6)
b/Å	9.2017(3)
c/Å	21.5805(5)
α/°	90
β/°	90.328(3)
γ/°	90
Volume/Å^3	1635.98(14)
Z	4
ρ_{calc}g/cm^3	1.357
μ/mm^{-1}	0.485
F(000)	704.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	GaKα (λ = 1.3405)
2Θ range for data collection/°	7.128 to 110.07
Index ranges	$-9 \leq h \leq 10$, $-11 \leq k \leq 11$, $-18 \leq l \leq 26$
Reflections collected	16570
Independent reflections	3092 [R_{int} = 0.0248, Rsigma = 0.0177]
Data/restraints/parameters	3092/0/229
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R1 = 0.0316, wR2 = 0.0782
Final R indexes [all data]	R1 = 0.0349, wR2 = 0.0805
Largest diff. peak/hole / e Å^{-3}	0.23/-0.18

III. Typical Procedures for the Preparation of Substrates



1. Typical procedures for the preparation of substrates 1a−1v





A 50 mL flask was purged with argon and charged with **S2-a** (15 mmol, 2.1 mL) and dry-THF (15.0 mL). The solution was cooled down to –78 ºC. ^{n}BuLi (15 mmol, 2.5 M in hexane, 6.0 mL) was added dropwise. The mixture was stirred at –78 ºC for 30 min, then **S1-a** (10 mmol, 1.2 mL) in THF (5.0 mL) was added by syringe. The

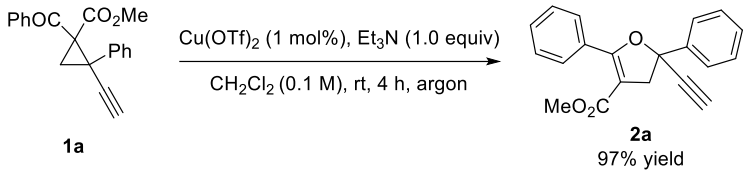
result mixture was allowed to reach room temperature within 1 h. Then, the reaction was quenched with aqueous NH_4Cl solution and extracted with ethyl acetate (3×30 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure to get **S3-a** without purification.

S3-a (10 mmol, 2.184 g) was dissolved in CH_2Cl_2 (20 mL) and cooled to 0 ºC, and Et_3N (50 mmol, 7.0 mL) was added followed by MsCl (25 mmol, 1.9 mL). The reaction mixture was allowed to stir at 0 °C for 30 min and then quenched with aqueous $NaHCO_3$ solution. The mixture was extracted with CH_2Cl_2 (2×40 mL). The combined organic fractions were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash aluminum oxide chromatography (petroleum ether) to afford **S4-a** as yellow oil (1.460 g, 73% yield). ^1H NMR (600 MHz, $CDCl_3$) δ 7.69–7.65 (m, 2H), 7.40–7.35 (m, 2H), 7.35–7.30 (m, 1H), 5.95 (s, 1H), 5.74 (s, 1H), 0.28 (s, 9H). Spectral data agreed with those reported previously by Malcolmson et al.[1]

CH_2Cl_2 (36.5 mL) was added to **S4-a** (7.3 mmol, 1.460 g) in a 100 mL two-necked flask equipped with a stir bar at room temperature under argon atmosphere. After 10 min, the reaction mixture was cooled to 0 °C. Then, $Rh_2(esp)_2$ (1.5 μmol, 1.1 mg) and methyl 2-diazo-3-oxo-3-phenylpropanoate (11 mmol, 2.234 g) was added to the mixture. After stirred at room temperature for 3 h, the reaction was quenched with H_2O and extracted with CH_2Cl_2 (3×20 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1) to afford **S5-a** as yellow oil (1.859 g, 68% yield).

To a solution of **S5-a** (5 mmol, 1.859 g) in THF (25 mL) was added TBAF (10 mmol, 3.150 g) at room temperature. When the reaction was completed as monitored by TLC, the mixture was quenched with saturated NH_4Cl solution. The product was extracted with ethyl acetate (3×25 mL), and dried over anhydrous Na_2SO_4. After filtration and evaporation in vacuo, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1) to afford the product **1a** (1.216 g, 80% yield, 1:1 dr).

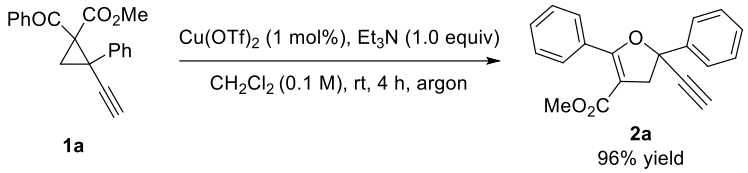
IV. Typical Procedure of the Synthesis of Compounds 2



1a **2a**
97% yield

To a solution of **1a** (0.1 mmol, 30.4 mg) and $Cu(OTf)_2$ (0.001 mmol, 0.36 mg) in CH_2Cl_2 (1.0 mL) was added Et_3N (0.1 mmol, 13.9 μL) at room temperature under argon atmosphere. After stirring for 4 h, the reaction mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1) to afford the product **2a** (29.6 mg, 97% yield).

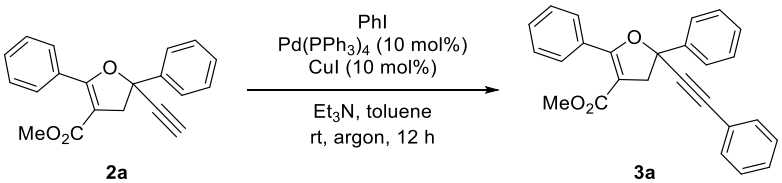
V. Gram-scale Reaction of 2a



1a **2a**
96% yield

To a solution of **1a** (3.3 mmol, 1.0 g) and $Cu(OTf)_2$ (0.033 mmol, 23.8 mg) in CH_2Cl_2 (33 mL) was added Et_3N (3.3 mmol, 0.46 mL) at room temperature under argon atmosphere. After stirring for 4 h, the reaction was quenched with aqueous NH_4Cl solution and extracted with CH_2Cl_2 (3×20 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1) to afford the product **2a** (963.4 mg, 96% yield).

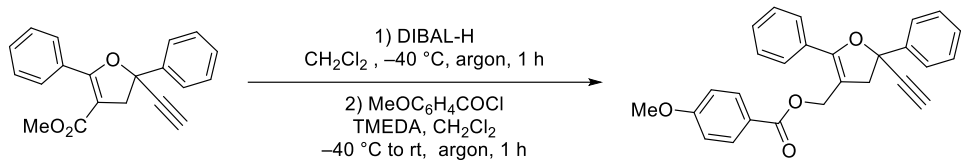
VI. Procedures for the Product Derivatizations



2a **3a**
71% yield

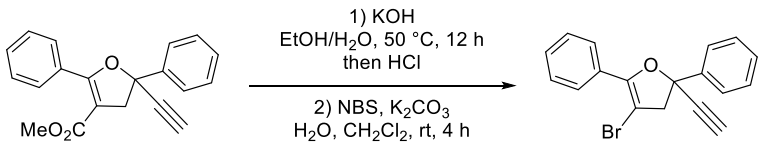
2a (0.2 mmol, 60.8 mg), iodobenzene (0.24 mmol, 26.8 μL), $Pd(PPh_3)_4$ (0.02 mmol, 23.0 mg), and CuI (0.02 mmol, 3.8 mg) were added successively to a Schlenk tube charged with a stirring bar at room temperature under argon atmosphere. Et_3N

(1.0 mL) and toluene (1.0 mL) were added by a syringe and the resulting solution was then stirred at room temperature for 12 h and monitored by TLC. The crude mixture was passed through a short pad of silica gel, washed with ethyl acetate (20 mL), and evaporated under reduced pressure. The residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1) to afford the desired product **3a** (53.8 mg, 71% yield) as yellow oil.



2a **3b**
82% yield

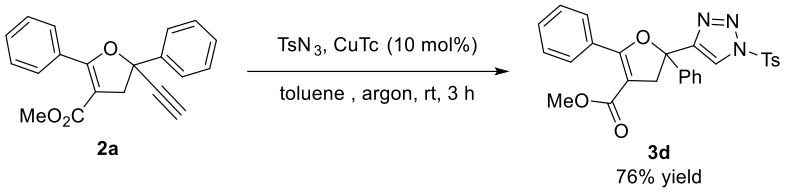
To a dry 10 mL flask was added a solution of **2a** (0.2 mmol, 60.8 mg) in CH_2Cl_2 (1.0 mL). The reaction mixture was stirred at –40 °C. DIBAL-H (0.6 mmol, 1 M in hexane, 0.6 mL) was added to the mixture under argon. The reaction was stirred at –40 °C for 1 h. Then the reaction was quenched by H_2O and extracted with CH_2Cl_2 (3×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. To the residue in dry CH_2Cl_2 (0.5 mL) was added 4-methoxybenzoyl chloride (0.4 mmol, 68.2 mg) in CH_2Cl_2 (0.5 mL) and TMEDA (0.2 mmol, 30 μL) at –40 ºC. The mixture was slowly warmed to room temperature and stirred for 1 h. Then the reaction was quenched with aqueous NH_4Cl solution and extracted with CH_2Cl_2 (3×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, v:v = 15:1) to afford the product **3b** (67.1 mg, 82% yield) as yellow oil.



2a **3c**
73% yield

To a dry 10 mL flask with **2a** (0.2 mmol, 60.8 mg) was added EtOH (0.50 mL) and aqueous KOH solution (0.6 mmol, 1.2 M, 0.50 mL). The resulting mixture was stirred at 50 ºC for 12 h. After this time, aqueous HCl solution (1.2 mmol, 1.0 M, 1.2

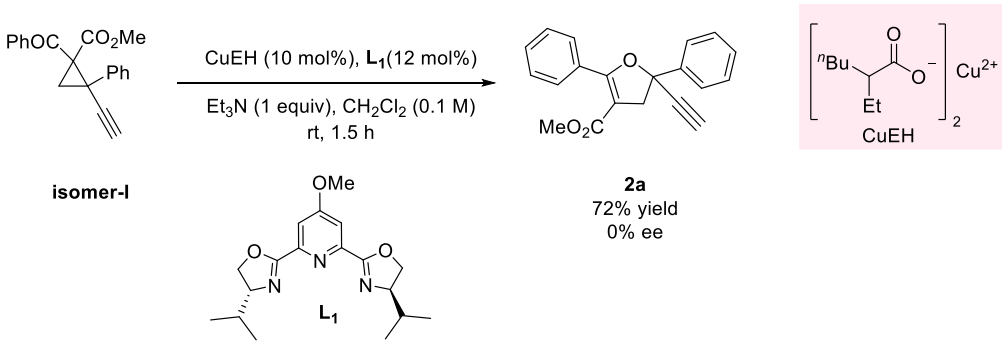
mL) was added and the solution was then extracted with EtOAc (3×10 mL). The combined organic layer was dried over Na_2SO_4, filtered and evaporated under reduced pressure. To the residue in CH_2Cl_2 (2.0 mL) with a stirring bar was added K_2CO_3 (0.2 mmol, 27.6 mg) at room temperature under argon atmosphere. After 10 min, NBS (0.2 mmol, 35.6 mg) was added followed by addition of H_2O (0.4 mmol, 7.2 μL). When the reaction was completed as monitored by TLC, the reaction was quenched by $Na_2S_2O_3$ and extracted with CH_2Cl_2 (3×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, v:v = 10:1) to afford the product **3c** (47.6 mg, 73% yield) as yellow oil.



2a **3d**
76% yield

To a dry 10 mL flask was added the solution of **2a** (0.2 mmol, 60.8 mg) and CuTc (0.02 mmol, 3.8 mg) in toluene (0.4 mL) at room temperature under argon atmosphere. The solution was allowed to stir until a pale yellow color was obtained. At this time, TsN_3 (0.2 mmol, 40.7 μL) was added dropwise carefully and slowly. After stirring for 3 h, the reaction mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1) to afford the product **3d** (76.6 mg, 76% yield).

VII. Asymmetric Catalysis



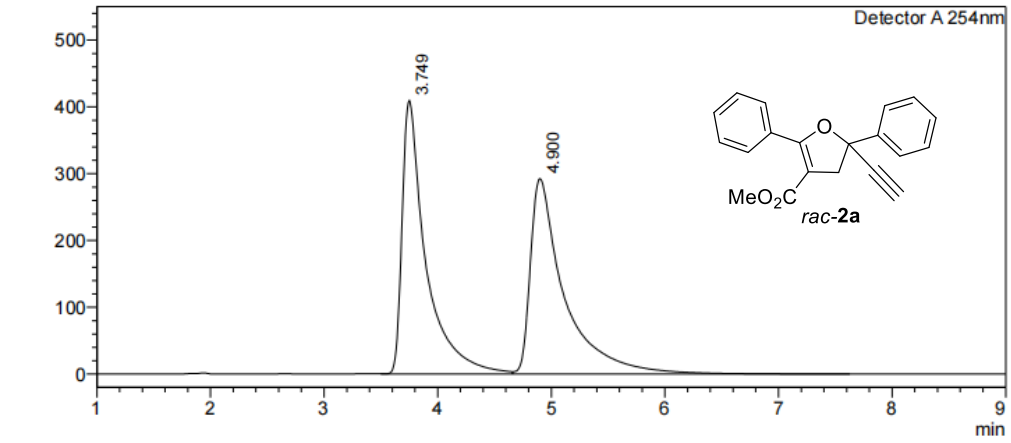
isomer-I **2a**
72% yield
0% ee

CH_2Cl_2 (0.5 mL) was added to CuEH (0.01 mmol, 3.5 mg,) and **L1** (0.012 mmol, 4.0 mg) in a Schlenk tube at room temperature under argon atmosphere. After stirred

at 38 °C for 30 min, the solution was cooled to room temperature within 30 min. Then, a solution of singe **isomer-I** (0.1 mmol, 30.4 mg) and Et_3N (0.1 mmol, 13.9 μL) in CH_2Cl_2 (0.5 mL) was added to the mixture via a syringe. After stirring for 1.5 h, the reaction mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1) to afford the product **2a** (21.8 mg, 72% yield, 0% ee).

L1 are known compounds and were prepared according to the literature reports.[2]

<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	3.749	5951075	409535	49.393			
2	4.900	6097392	292552	50.607		V	
Total		12048468	702087				

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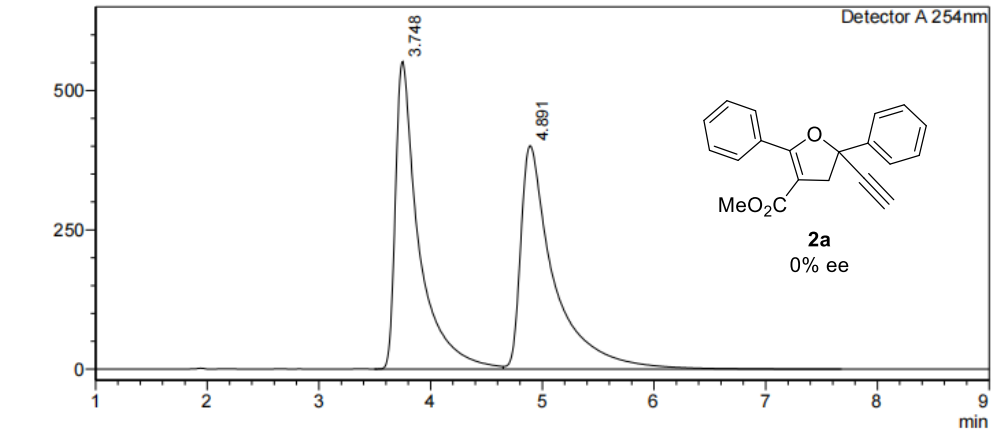

<Peak Table>

Detector A 254nm

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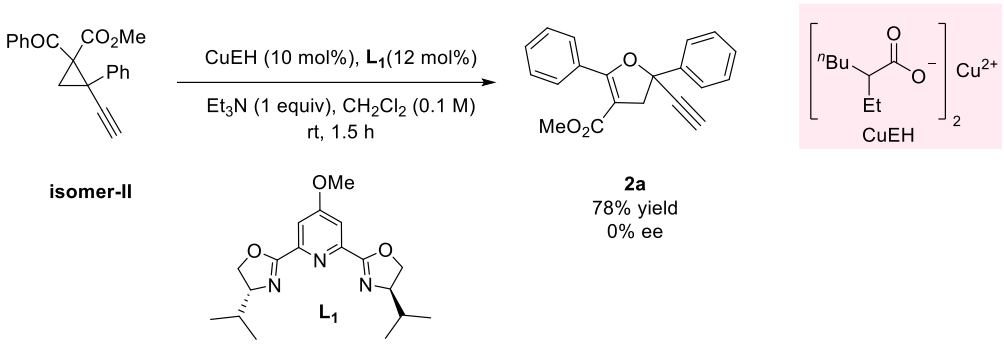

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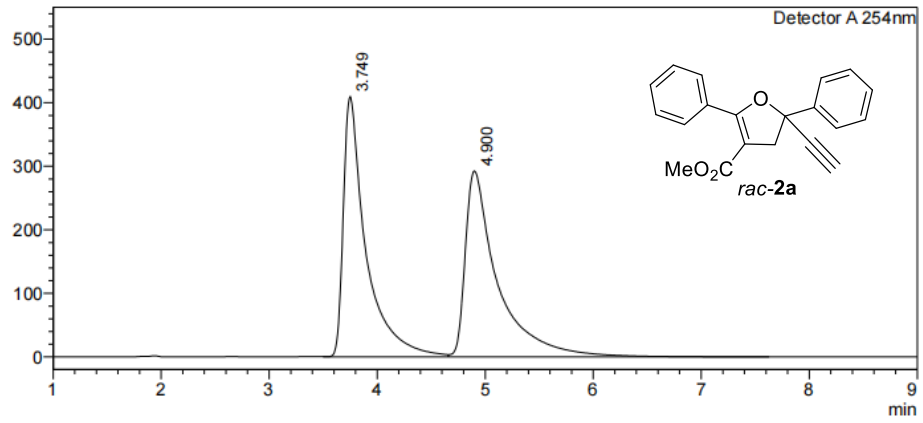
mV



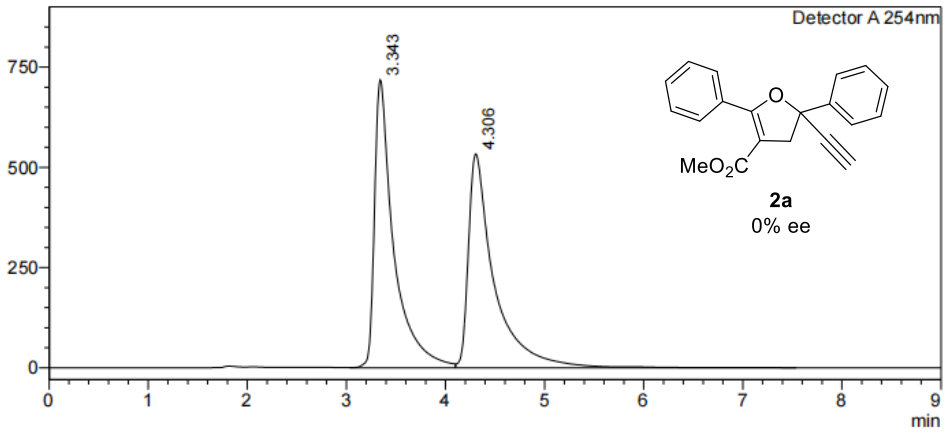
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	3.749	5951075	409535	49.393			
2	4.900	6097392	292552	50.607		V	
Total		12048468	702087				

<Chromatogram>

mV



<Peak Table>

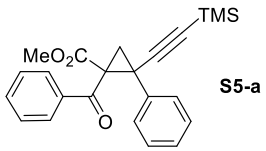
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	3.343	9715425	717922	50.117			
2	4.306	9670196	533266	49.883		V	
Total		19385621	1251188				

References

[1] Adamson, N. J.; Park, S.; Zhou, P. F.; Nguyen, A. L.; Malcomson, S. J. *Org. Lett.* **2020**, *22*, 2032–2037.
[2] Konowalchuk, D. J.; Hall, D. G. *Angew. Chem. Int. Ed*. **2023**, *62*, e202313503.

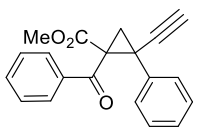
VIII. Characterizations of New Compounds



S5-a

Methyl 1-benzoyl-2-phenyl-2-((trimethylsilyl)ethynyl)cyclopropane-1-carboxylate (S5-a):

The general procedure was followed using **S4-a** (7.3 mmol, 1.460 g), $Rh_2(esp)_2$ (1.5 μmol, 1.1 mg) and methyl 2-diazo-3-oxo-3-phenylpropanoate (11 mmol, 2.234 g) in CH_2Cl_2 (36.5 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), amorphous white solid, mp 63–68 ºC, 1.859 g, 68% yield, 1:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$, after column 1:0.7 dr) δ 8.15–8.10 (m, 1.4H), 7.74–7.67 (m, 2H), 7.59 (d, *J* = 7.7 Hz, 2H), 7.55–7.49 (m, 1.4H), 7.44–7.37 (m, 2.4H), 7.37–7.32 (m, 0.7H), 7.32–7.26 (m, 4.1H), 7.13–6.99 (m, 3H), 3.70 (s, 3H), 3.35 (s, 2.1H), 2.68 (d, *J* = 5.9 Hz, 1H), 2.58 (d, *J* = 5.4 Hz, 0.7H), 2.47 (d, *J* = 5.9 Hz, 1H), 2.38 (d, *J* = 5.4 Hz, 0.7H), 0.23 (s, 9H), -0.23 (s, 6.3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.2, 191.6, 167.8, 167.6, 136.8, 136.3, 135.2, 134.3, 133.2, 133.1, 129.9, 129.6, 129.1, 128.4, 128.2, 128.08, 128.05, 127.9, 127.7, 105.3, 104.4, 88.1, 87.7, 52.7, 52.5, 48.2, 46.3, 33.2, 32.9, 24.7, 23.8, 0.2, -0.6. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{24}O_3SiNa$ 399.1387; Found 399.1388. IR (KBr thin film, cm^{-1}): ν 2958, 2164, 1730, 1678, 1448, 1224, 914, 838, 747, 688.

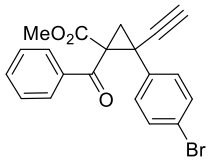


1a

Methyl 1-benzoyl-2-ethynyl-2-phenylcyclopropane-1-carboxylate (1a):

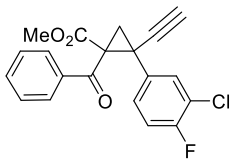
The general procedure was followed using **S5-a** (5 mmol, 1.859 g) and TBAF (10 mmol, 3.150 g) in THF (25 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), amorphous white solid, mp 66–70 ºC, 1.216 g, 80%

yield, 1:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$, after column 1:1 dr) δ 8.11–8.07 (m, 2H), 7.74–7.67 (m, 2H), 7.63–7.56 (m, 3H), 7.54–7.48 (m, 2H), 7.43–7.38 (m, 3H), 7.36–7.32 (m, 1H), 7.31–7.25 (m, 4H), 7.10–6.99 (m, 3H), 3.68 (s, 3H), 3.33 (s, 3H), 2.73 (d, *J* = 5.9 Hz, 1H), 2.59 (d, *J* = 5.4 Hz, 1H), 2.45 (s, 1H), 2.40–2.34 (m, 2H), 1.99 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 191.1, 168.2, 167.5, 136.7, 136.1, 135.3, 133.9, 133.3, 133.1, 129.5, 129.3, 129.0, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 83.6, 82.8, 71.3, 71.2, 52.8, 52.6, 47.0, 45.8, 31.92, 31.88, 24.5, 23.8. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{16}O_3Na$ 327.0992; Found 327.0991. IR (KBr thin film, cm^{-1}): ν 3264, 2956, 1727, 1681, 1436, 1323, 1227, 1138, 742, 689.



1b

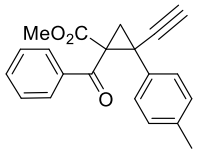
Methyl 1-benzoyl-2-(4-bromophenyl)-2-ethynylcyclopropane-1-carboxylate (1b): The general procedure was followed using **S5-b** (5 mmol, 2.275 g) and TBAF (10 mmol, 3.150 g) in THF (25 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), amorphous yellow solid, mp 95–97 ºC, 1.608 g, 84% yield, 1:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$, after column 1:1.7 dr) δ 8.04 (d, *J* = 7.7 Hz, 3.4H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.63–7.58 (m, 1.7H), 7.55–7.48 (m, 6.8H), 7.47–7.42 (m, 4.4H), 7.34–7.29 (m, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.16 (d, *J* = 8.6 Hz, 2H), 3.68 (s, 3H), 3.38 (s, 5.1H), 2.66 (d, *J* = 5.9 Hz, 1H), 2.54 (d, *J* = 5.5 Hz, 1.7H), 2.46 (s, 1H), 2.41–2.35 (m, 2.7H), 2.00 (s, 1.7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.5, 190.8, 168.0, 167.4, 136.5, 136.1, 134.4, 133.42, 133.39, 133.3, 131.6, 131.2, 130.7, 130.0, 129.4, 129.2, 128.5, 128.2, 122.3, 122.1, 83.1, 82.3, 71.6, 71.5, 52.9, 52.7, 46.9, 45.7, 31.3, 24.7, 23.9. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{15}BrO_3Na$ 405.0097 (100.0%), 407.0076 (97.3%); Found 405.0096 (100.0%), 407.0076 (97.3%). IR (KBr thin film, cm^{-1}): ν 3260, 2956, 1727, 1680, 1435, 1246, 1221, 1009, 724, 688, 658.



1c

Methyl 1-benzoyl-2-(3-chloro-4-fluorophenyl)-2-ethynylcyclopropane-1-carboxylate (1c):

The general procedure was followed using **S5-c** (5 mmol, 2.140 g) and TBAF (10 mmol, 3.150 g) in THF (25 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), amorphous yellow solid, mp 101–104 ºC, 1.021 g, 57% yield, 1:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$, after column 1:1.4 dr) δ 8.02 (d, *J* = 7.3 Hz, 2.8H), 7.71 (d, *J* = 7.3 Hz, 2H), 7.64–7.57 (m, 2.8H), 7.54–7.49 (m, 2.8H), 7.48–7.42 (m, 2.4H), 7.41–7.37 (m, 1H), 7.36–7.30 (m, 2H), 7.18–7.13 (m, 1.4H), 7.10–7.04 (m, 1H), 6.86–6.79 (m, 1H), 3.69 (s, 3H), 3.40 (s, 4.2H), 2.60 (d, *J* = 6.0 Hz, 1H), 2.52 (d, *J* = 5.5 Hz, 1.4H), 2.48 (s, 1H), 2.40 (d, *J* = 6.0 Hz, 1H), 2.36 (d, *J* = 5.6 Hz, 1.4H), 2.04 (s, 1.4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.1, 190.7, 167.8, 167.3, 157.8 (C-F, d, $^{1}J_{C\text{-}F}$ = 250.3 Hz), 157.4 (C-F, d, $^{1}J_{C\text{-}F}$ = 250.4 Hz), 136.3, 135.9, 133.48, 133.46, 132.5 (C-F, d, $^{4}J_{C\text{-}F}$ = 3.5 Hz), 131.5 (C-F, d, $^{4}J_{C\text{-}F}$ = 3.6 Hz), 131.4, 131.1, 129.3, 129.1, 128.8 (C-F, d, $^{3}J_{C\text{-}F}$ = 7.2 Hz), 128.5, 128.2, 127.7 (C-F, d, $^{3}J_{C\text{-}F}$ = 7.5 Hz), 121.0 (C-F, d, $^{2}J_{C\text{-}F}$ = 18.2 Hz), 120.7 (C-F, d, $^{2}J_{C\text{-}F}$ = 18.1 Hz), 116.5 (C-F, d, $^{2}J_{C\text{-}F}$ = 21.4 Hz), 116.0 (C-F, d, $^{2}J_{C\text{-}F}$ = 21.4 Hz), 82.8, 82.0, 71.9, 52.9, 52.8, 46.8, 45.6, 30.64, 30.60, 24.9, 23.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ –115.7, –116.2. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{14}ClFO_3Na$ 379.0508 (100.0%), 381.0478 (32.0%); Found 379.0512 (100.0%), 381.0483 (32.0%). IR (KBr thin film, cm^{-1}): ν 3233, 1726, 1676, 1500, 1436, 1329, 1218, 750, 710, 689, 622.

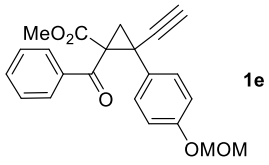


1d

Methyl 1-benzoyl-2-ethynyl-2-(*p*-tolyl)cyclopropane-1-carboxylate (1d):

The general procedure was followed using **S5-d** (5 mmol, 1.950 g) and TBAF (10 mmol, 3.150 g) in THF (25 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 1.103 g, 69% yield, 1:0.7 dr. ^{1}H NMR (400

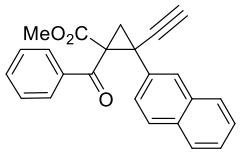
MHz, $CDCl_3$, after column 1:1 dr) δ 8.08 (d, *J* = 7.7 Hz, 2H), 7.71 (d, *J* = 7.9 Hz, 2H), 7.56–7.50 (m, 1H), 7.50–7.40 (m, 4H), 7.36–7.30 (m, 1H), 7.25–7.20 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 4H), 6.83 (d, *J* = 8.0 Hz, 2H), 3.58 (s, 3H), 3.26 (s, 3H), 2.69 (d, *J* = 5.8 Hz, 1H), 2.53 (d, *J* = 5.4 Hz, 1H), 2.42 (s, 1H), 2.37–2.26 (m, 5H), 2.06 (s, 3H), 1.93 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.6, 190.7, 167.9, 167.2, 137.6, 137.2, 136.5, 136.0, 133.0, 132.8, 132.0, 130.7, 129.2, 129.0, 128.9, 128.6, 128.5, 128.1, 127.9, 127.7, 83.5, 82.8, 71.0, 70.9, 52.4, 52.2, 46.6, 45.5, 31.6, 31.5, 24.2, 23.4, 21.0, 20.6. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{18}O_3Na$ 341.1148; Found 341.1146. IR (KBr thin film, cm^{-1}): ν 3252, 2952, 1734, 1679, 1433, 1240, 1043, 792, 752, 690.



1e

Methyl 1-benzoyl-2-ethynyl-2-(4-(methoxymethoxy)phenyl)cyclopropane-1-carboxylate (1e):

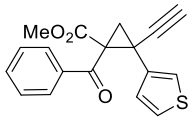
The general procedure was followed using **S5-e** (5 mmol, 2.180 g) and TBAF (10 mmol, 3.150 g) in THF (25 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 1.321 g, 73% yield, 1:0.2 dr. ^1H NMR (400 MHz, $CDCl_3$, after column single diastereoisomer) δ 8.08 (d, *J* = 7.6 Hz, 2H), 7.66–7.57 (m, 1H), 7.55–7.45 (m, 4H), 7.07 (d, *J* = 7.8 Hz, 2H), 5.20 (q, *J* = 6.8 Hz, 2H), 3.49 (s, 3H), 3.37 (s, 3H), 2.55 (d, *J* = 4.8 Hz, 1H), 2.36 (d, *J* = 5.1 Hz, 1H), 1.99 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 167.6, 157.2, 136.8, 133.3, 130.2, 129.5, 128.4, 116.1, 94.6, 83.8, 71.1, 56.3, 52.6, 45.9, 31.6, 24.8. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{20}O_5Na$ 387.1203; Found 387.1206. IR (KBr thin film, cm^{-1}): ν 3282, 2953, 1732, 1677, 1511, 1434, 1236, 1149, 1077, 994, 795, 688.



1f

Methyl 1-benzoyl-2-ethynyl-2-(naphthalen-2-yl)cyclopropane-1-carboxylate (1f):

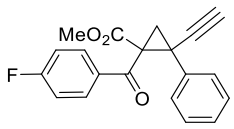
The general procedure was followed using **S5-f** (5 mmol, 2.130 g) and TBAF (10 mmol, 3.150 g) in THF (25 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 15:1), amorphous yellow solid, mp 115–119 ºC, 1.330 g, 75% yield, 1:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$, after column 1:1.3 dr) δ 8.08 (d, *J* = 7.6 Hz, 2.6H), 7.93 (s, 1.3H), 7.84–7.76 (m, 3.9H), 7.68–7.52 (m, 7.8H), 7.51–7.39 (m, 7.4H), 7.33–7.27 (m, 2.6H), 7.19–7.14 (m, 2H), 3.63 (s, 3H), 3.22 (s, 3.9H), 2.80 (d, *J* = 5.8 Hz, 1H), 2.68 (d, *J* = 5.4 Hz, 1.3H), 2.46–2.35 (m, 3.3H), 1.98 (s, 1.3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 191.0, 168.3, 167.5, 136.7, 136.2, 133.4, 133.2, 133.1, 133.0, 132.8, 132.7, 132.6, 131.6, 129.5, 129.2, 128.5, 128.3, 128.22, 128.18, 128.1, 128.0, 127.81, 127.77, 127.5, 127.1, 126.6, 126.50, 126.49, 126.4, 126.2, 83.6, 82.9, 76.8, 71.5, 71.4, 52.9, 52.6, 47.0, 45.9, 32.1, 24.8, 24.0. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{24}H_{19}O_3$ 355.1329; Found 355.1331. IR (KBr thin film, cm^{-1}): ν 3303, 3265, 1673, 1324, 1252, 1208, 1094, 819, 773, 697, 608.



1g

Methyl 1-benzoyl-2-ethynyl-2-(thiophen-3-yl)cyclopropane-1-carboxylate (1g):

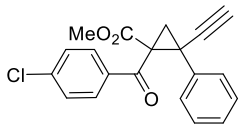
The general procedure was followed using **S5-g** (5 mmol, 1.910 g) and TBAF (10 mmol, 3.150 g) in THF (25 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), amorphous yellow solid, mp 67–70 ºC, 992 mg, 64% yield, 1:0.5 dr. ^{1}H NMR (400 MHz, $CDCl_3$, after column 1:0.25 dr) δ 8.05 (d, *J* = 7.7 Hz, 0.5H), 7.74 (d, *J* = 7.6 Hz, 2H), 7.62–7.57 (m, 0.25H), 7.52–7.47 (m, 0.5H), 7.46–7.39 (m, 1.25H), 7.35–7.27 (m, 2.5H), 7.05–6.99 (m, 1H), 6.96–6.91 (m, 1H), 6.84 (d, *J* = 4.9 Hz, 1H), 3.68 (s, 3H), 3.39 (s, 0.75H), 2.54–2.50 (m, 1.25H), 2.48 (s, 1H), 2.45–2.39 (m, 1.25H), 1.99 (s, 0.25H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 191.6, 168.0, 167.2, 136.7, 136.0, 135.84, 135.75, 133.3, 133.2, 129.6, 129.4, 128.4, 128.1, 128.0, 127.5, 125.7, 125.6, 124.6, 123.5, 83.0, 82.1, 71.2, 52.8, 52.7, 46.9, 46.1, 28.5, 27.8, 25.6. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{14}O_3SNa$ 333.0556; Found 333.0559. IR (KBr thin film, cm^{-1}): ν 3280, 2957, 1727, 1678, 1435, 1318, 1242, 1225, 757,687, 671.



1h

Methyl 2-ethynyl-1-(4-fluorobenzoyl)-2-phenylcyclopropane-1-carboxylate (1h):

The general procedure was followed using **S5-h** (5 mmol, 1.970 g) and TBAF (10 mmol, 3.150 g) in THF (25 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 1.208 g, 75% yield, 1:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$, after column 1:1 dr) δ 8.12–8.02 (m, 2H), 7.72–7.64 (m, 2H), 7.52 (d, *J* = 7.7 Hz, 2H), 7.40–7.32 (m, 2H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 2H), 7.18–7.09 (m, 2H), 7.06–6.95 (m, 3H), 6.93–6.84 (m, 2H), 3.63 (s, 3H), 3.27 (s, 3H), 2.68 (d, *J* = 5.9 Hz, 1H), 2.55 (d, *J* = 5.4 Hz, 1H), 2.42 (s, 1H), 2.35 (d, *J* = 5.9 Hz, 1H), 2.31 (d, *J* = 5.4 Hz, 1H), 1.95 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 189.5, 167.8, 167.1, 165.7 (C-F, d, $^{1}J_{C\text{-}F}$ = 256.3 Hz), 165.4 (C-F, d, $^{1}J_{C\text{-}F}$ = 256.4 Hz), 135.0, 133.6, 133.0 (C-F, d, $^{4}J_{C\text{-}F}$ = 2.5 Hz), 132.4 (C-F, d, $^{4}J_{C\text{-}F}$ = 2.3 Hz), 132.1 (C-F, d, $^{3}J_{C\text{-}F}$ = 9.4 Hz), 132.0 (C-F, d, $^{3}J_{C\text{-}F}$ = 9.3 Hz), 128.8, 128.4, 128.2, 128.0, 127.88, 127.86, 115.5 (C-F, d, $^{2}J_{C\text{-}F}$ = 22.1 Hz), 115.0 (C-F, d, $^{2}J_{C\text{-}F}$ = 22.1 Hz), 83.4, 82.4, 71.4, 71.3, 52.7, 52.5, 47.0, 45.7, 31.9, 31.8, 24.3, 23.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ –104.6, –104.7. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{15}FO_3Na$ 345.0897; Found 345.0906. IR (KBr thin film, cm^{-1}): ν 3282, 2952, 1729, 1672, 1596, 1433, 1229, 1138, 840, 737, 696.

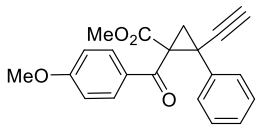


1i

Methyl 1-(4-chlorobenzoyl)-2-ethynyl-2-phenylcyclopropane-1-carboxylate (1i):

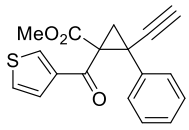
The general procedure was followed using **S5-i** (5 mmol, 2.050 g) and TBAF (10 mmol, 3.150 g) in THF (25 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 15:1), amorphous white solid, mp 96–101 ºC, 1.184 g, 70% yield, 1:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$, after column single diastereoisomer) δ 8.03 (d, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.45–7.38 (m, 2H), 7.38–7.32 (m, 1H), 3.35 (s, 3H), 2.60 (d, *J* = 5.4 Hz, 1H), 2.38 (d, *J* = 5.4 Hz, 1H), 2.00 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.0, 167.2, 139.7, 135.1, 135.0,

131.0, 128.9, 128.8, 128.6, 128.3, 83.5, 71.4, 52.6, 45.8, 32.1, 24.4. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{15}ClO_3Na$ 361.0602 (100.0%), 363.0572 (32.0%); Found 361.0604 (100.0%), 363.0575 (32.0%). IR (KBr thin film, cm^{-1}): ν 3258, 2949, 1740, 1674, 1587, 1429, 1328, 1215, 934, 756, 696, 664.



1j

Methyl 2-ethynyl-1-(4-methoxybenzoyl)-2-phenylcyclopropane-1-carboxylate (1j): The general procedure was followed using **S5-j** (5 mmol, 2.030 g) and TBAF (10 mmol, 3.150 g) in THF (25 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), amorphous white solid, mp 83–85 ºC, 1.086 g, 65% yield, 1:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$, after column 1:0.7 dr) δ 8.08 (d, *J* = 8.9 Hz, 1.4H), 7.70 (d, *J* = 8.9 Hz, 2H), 7.57 (d, *J* = 7.1 Hz, 1.4H), 7.44–7.37 (m, 1.4H), 7.34 (d, *J* = 7.2 Hz, 0.7H), 7.31–7.27 (m, 2H), 7.13–7.03 (m, 3H), 7.00 (d, *J* = 8.9 Hz, 1.4H), 6.76 (d, *J* = 8.9 Hz, 2H), 3.91 (s, 2.1H), 3.80 (s, 3H), 3.69 (s, 3H), 3.35 (s, 2.1H), 2.71 (d, *J* = 5.8 Hz, 1H), 2.58 (d, *J* = 5.4 Hz, 0.7H), 2.44 (s, 1H), 2.37 (d, *J* = 5.8 Hz, 1H), 2.33 (d, *J* = 5.4 Hz, 0.7H), 2.00 (s, 0.7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.2, 189.3, 168.2, 167.5, 163.7, 163.4, 135.4, 134.0, 131.9, 131.8, 129.6, 129.2, 128.9, 128.4, 128.03, 127.96, 127.9, 127.7, 113.6, 113.1, 83.7, 82.9, 71.1, 71.0, 55.5, 55.4, 52.7, 52.5, 46.9, 45.7, 31.54, 31.47, 24.4, 23.6. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{18}O_4Na$ 357.1097; Found 357.1099. IR (KBr thin film, cm^{-1}): ν 3298, 2962, 1727, 1657, 1594, 1449, 1225, 1223, 1170, 1026, 934, 840, 696.

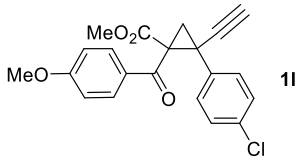


1k

Methyl 2-ethynyl-2-phenyl-1-(thiophene-3-carbonyl)cyclopropane-1-carboxylate (1k):

The general procedure was followed using **S5-k** (5 mmol, 1.910 g) and TBAF (10 mmol, 3.150 g) in THF (25 mL). Purified by chromatography on silica gel (petroleum

ether/ethyl acetate, v:v = 10:1), amorphous yellow solid, mp 67–70 ºC, 1.395 g, 90% yield, 1:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$, after column 1:1 dr) δ 8.27–8.21 (m, 1H), 7.93–7.86 (m, 1H), 7.69–7.63 (m, 1H), 7.56–7.50 (m, 2H), 7.43–7.31 (m, 4H), 7.30–7.26 (m, 3H), 7.14–7.04 (m, 4H), 3.74 (s, 3H), 3.37 (s, 3H), 2.69 (d, *J* = 5.9 Hz, 1H), 2.58 (d, *J* = 5.4 Hz, 1H), 2.41 (s, 1H), 2.37 (d, *J* = 5.9 Hz, 1H), 2.32 (d, *J* = 5.4 Hz, 1H), 2.04 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 185.8, 185.0, 168.0, 167.2, 141.6, 141.4, 135.4, 134.2, 134.0, 133.9, 128.8, 128.6, 128.2, 128.1, 128.04, 127.96, 127.9, 127.6, 125.9, 125.3, 83.5, 82.9, 71.2, 71.1, 53.0, 52.7, 48.3, 46.9, 31.5, 24.2, 23.4. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{14}O_3SNa$ 333.0556; Found 333.0566. IR (KBr thin film, cm^{-1}): ν 3280, 2951, 1731, 1662, 1508, 1433, 1410, 1277, 1133, 756, 694.

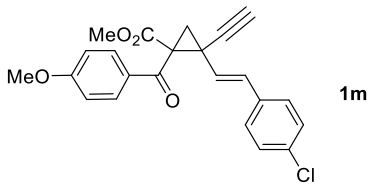


1l

Methyl 2-(4-chlorophenyl)-2-ethynyl-1-(4-methoxybenzoyl)cyclopropane-1-carboxylate (1l):

The general procedure was followed using **S5-l** (5 mmol, 2.200 g) and TBAF (10 mmol, 3.150 g) in THF (25 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 1.435 g, 78% yield, 1:0.7 dr. ^{1}H NMR (400 MHz, $CDCl_3$, after column 1:1.3 dr) δ 8.03 (d, *J* = 8.8 Hz, 2.6H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2.6H), 7.36 (d, *J* = 8.4 Hz, 2.6H), 7.22 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2.6H), 6.78 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3.9H), 3.81 (s, 3H), 3.68 (s, 3H), 3.38 (s, 3.9H), 2.63 (d, *J* = 5.8 Hz, 1H), 2.53 (d, *J* = 5.4 Hz, 1.3H), 2.45 (s, 1H), 2.37 (d, *J* = 5.9 Hz, 1H), 2.33 (d, *J* = 5.4 Hz, 1.3H), 2.01 (s, 1.3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.9, 189.1, 168.1, 167.6, 163.8, 163.7, 134.1, 134.0, 133.7, 133.0, 131.8, 131.7, 130.3, 129.5, 129.1, 128.6, 128.2, 113.7, 113.4, 83.3, 82.5, 71.5, 71.4, 55.6, 55.5, 52.9, 52.7, 47.0, 45.7, 31.0, 30.9, 24.7, 23.9. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{17}ClO_4Na$ 391.0708 (100.0%), 393.0678 (32.0%); Found 391.0707 (100.0%), 393.0679 (32.0%). IR (KBr

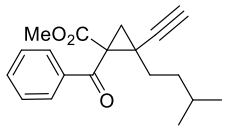
thin film, cm^{-1}): ν 3286, 2952, 1731, 1667, 1596, 1494, 1316, 1248, 1169, 1022, 830, 612.



1m

Methyl (*E*)-2-(4-chlorostyryl)-2-ethynyl-1-(4-methoxybenzoyl)cyclopropane-1-carboxylate (1m):

The general procedure was followed using **S5-m** (5 mmol, 2.330 g) and TBAF (10 mmol, 3.150 g) in THF (25 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), amorphous yellow solid, mp 131–135 ºC, 1.478 g, 75% yield, 1:0.16 dr. ^{1}H NMR (400 MHz, $CDCl_3$, after column single diastereoisomer) δ 7.92–7.85 (m, 2H), 7.20–7.08 (m, 2H), 7.00–6.92 (m, 2H), 6.91–6.84 (m, 3H), 5.34 (d, *J* = 15.6 Hz, 1H), 3.82 (s, 3H), 3.68 (s, 3H), 2.53 (s, 1H), 2.38 (d, *J* = 5.4 Hz, 1H), 2.08 (d, *J* = 5.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 168.0, 163.9, 134.9, 133.4, 132.1, 131.9, 129.4, 128.7, 127.6, 127.3, 113.8, 79.9, 73.2, 55.6, 52.9, 45.8, 30.0, 26.7. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}ClO_4$ 395.1045 (100.0%), 397.1015 (32.0%); Found 395.1054 (100.0%), 397.1021 (32.0%). IR (KBr thin film, cm^{-1}): ν 3264, 2947, 1726, 1677, 1597, 1288, 1260, 1169, 930, 818, 702, 666.

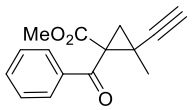


1n

Methyl 1-benzoyl-2-ethynyl-2-isopentylcyclopropane-1-carboxylate (1n):

The general procedure was followed using **S5-n** (5 mmol, 1.850 g) and TBAF (10 mmol, 3.150 g) in THF (25 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 15:1), colorless oil, 1.100g, 74% yield, >20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.4 Hz, 2H), 7.62–7.53 (m, 1H), 7.52–7.42 (m, 2H), 3.61 (s, 3H), 2.25 (s, 1H), 2.01 (d, *J* = 4.8 Hz, 1H), 1.71 –1.53 (m, 3H), 1.47–1.27 (m, 2H), 0.85–0.65 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.7, 168.8, 136.8, 133.6, 129.4, 128.6, 82.6, 70.4, 52.7, 43.6, 36.6, 33.6, 28.4, 27.7, 25.8, 22.8, 22.4. HRMS

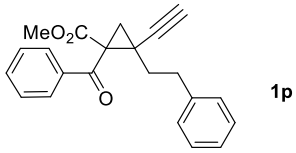
(ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{22}O_3Na$ 321.1461; Found 321.1468. IR (KBr thin film, cm^{-1}): ν 3276, 2953, 1736, 1679, 1423, 1214, 1143, 1110, 798, 689.



1o

Methyl 1-benzoyl-2-ethynyl-2-methylcyclopropane-1-carboxylate (1o):

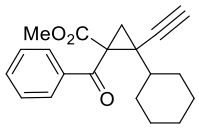
The general procedure was followed using **S5-o** (5 mmol, 1.570 g) and TBAF (10 mmol, 3.150 g) in THF (25 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), amorphous white solid, mp 50–54 ºC, 908 mg, 75% yield, >20:1 dr. ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.8 Hz, 2H), 7.61–7.55 (m, 1H), 7.52–7.43 (m, 2H), 3.61 (s, 3H), 2.27 (s, 1H), 2.02 (d, *J* = 4.9 Hz, 1H), 1.69 (d, *J* = 4.9 Hz, 1H), 1.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.6, 168.8, 136.8, 133.6, 129.2, 128.7, 83.6, 69.9, 52.6, 43.0, 26.6, 23.2, 22.4. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{14}O_3Na$ 265.0835; Found 265.0839. IR (KBr thin film, cm^{-1}): ν 3274, 2951, 1727, 1683, 1500, 1338, 1244, 1216, 800, 754, 688.



1p

Methyl 1-benzoyl-2-ethynyl-2-phenethylcyclopropane-1-carboxylate (1p):

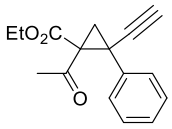
The general procedure was followed using **S5-p** (5 mmol, 2.020 g) and TBAF (10 mmol, 3.150 g) in THF (25 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), amorphous white solid, mp 112–116 ºC, 979 mg, 59% yield, >20:1 dr. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.3 Hz, 2H), 7.62–7.54 (m, 1H), 7.51–7.43 (m, 2H), 7.25–7.19 (m, 2H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.11 (d, *J* = 7.1 Hz, 2H), 3.64 (s, 3H), 3.09–2.98 (m, 1H), 2.88–2.76 (m, 1H), 2.39 (s, 1H), 2.07–1.96 (m, 2H), 1.53 (d, *J* = 5.1 Hz, 1H), 1.17–1.02 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 168.7, 140.9, 136.6, 133.6, 129.3, 128.7, 128.5, 126.2, 82.3, 71.1, 52.7, 43.1, 37.7, 33.7, 27.8, 25.9. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{20}O_3Na$ 355.1305; Found 355.1310. IR (KBr thin film, cm^{-1}): ν 3257, 2951, 1722, 1683, 1448, 1432, 1284, 792, 749, 687.



1q

Methyl 1-benzoyl-2-cyclohexyl-2-ethynylcyclopropane-1-carboxylate (1q):

The general procedure was followed using **S5-q** (5 mmol, 1.910 g) and TBAF (10 mmol, 3.150 g) in THF (25 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), amorphous yellow solid, mp 97–101 ºC, 899 mg, 58% yield, >20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.9 Hz, 2H), 7.60–7.51 (m, 1H), 7.48–7.39 (m, 2H), 3.61 (s, 3H), 2.18 (s, 1H), 2.07 (d, *J* = 4.8 Hz, 1H), 1.97–1.87 (m, 1H), 1.74–1.68 (m, 1H), 1.65–1.43 (m, 6H), 1.21–0.94 (m, 3H), 0.92–0.81 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.0, 168.9, 136.8, 133.5, 129.2, 128.5, 81.7, 70.6, 52.9, 44.5, 42.1, 33.7, 30.9, 30.1, 26.5, 26.1, 25.92, 25.86. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{22}O_3Na$ 333.1461; Found 333.1464. IR (KBr thin film, cm^{-1}): ν 3283, 2932, 1730, 1685, 1448, 1287, 1208, 1125, 756, 695, 646.

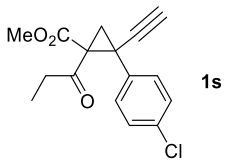


1r

Ethyl 1-acetyl-2-ethynyl-2-phenylcyclopropane-1-carboxylate (1r):

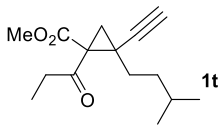
The general procedure was followed using **S5-r** (5 mmol, 1.640 g) and TBAF (10 mmol, 3.150 g) in THF (25 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 25:1), colorless oil, 845 mg, 66% yield, 1:1.2 dr. ^{1}H NMR (400 MHz, $CDCl_3$, after column 1.15:1 dr) δ 7.40 (d, *J* = 6.9 Hz, 2H), 7.38–7.28 (m, 6.45H), 7.28–7.22 (m, 2.3H), 4.31 (q, *J* = 7.1 Hz, 2.3H), 3.80–3.65 (m, 2H), 2.67 (s, 3H), 2.62 (d, *J* = 5.6 Hz, 1.15H), 2.41 (d, *J* = 5.5 Hz, 1H), 2.31 (d, *J* = 5.5 Hz, 1H), 2.27 (s, 1.15H), 2.23–2.18 (m, 2.15H), 2.08 (s, 3.45H), 1.35 (t, *J* = 7.1 Hz, 3.45H), 0.81 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.6, 198.2, 167.3, 166.3, 135.8, 134.2, 128.8, 128.6, 128.4, 128.2, 128.1, 83.4, 83.2, 70.3, 70.1, 61.9, 61.4, 50.2, 49.5, 33.7, 32.6, 30.5, 30.4, 22.7, 22.3, 14.2, 13.5. HRMS (ESI-Quadrupole-Orbitrap)

m/z: $[M + Na]^+$ Calcd for $C_{16}H_{16}O_3Na$ 279.0992; Found 279.0996. IR (KBr thin film, cm^{-1}): ν 3283, 2982, 1703, 1359, 1303, 1244, 1204, 1100, 1021, 742, 696.



1s

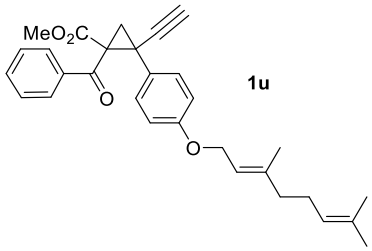
Methyl 2-(4-chlorophenyl)-2-ethynyl-1-propionylcyclopropane-1-carboxylate (1s): The general procedure was followed using **S5-s** (5 mmol, 1.810 g) and TBAF (10 mmol, 3.150 g) in THF (25 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 870 mg, 60% yield, 1:1.4 dr. ^{1}H NMR (400 MHz, $CDCl_3$, after column 1:1 dr) δ 7.39–7.26 (m, 8H), 3.86 (s, 3H), 3.36 (s, 3H), 3.20–3.07 (m, 1H), 3.07–2.96 (m, 1H), 2.82–2.69 (m, 1H), 2.61 (d, *J* = 5.6 Hz, 1H), 2.46–2.34 (m, 3H), 2.29 (s, 1H), 2.24 (d, *J* = 5.6 Hz, 1H), 2.21 (s, 1H), 1.20 (t, *J* = 7.2 Hz, 3H), 0.69 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 201.9, 200.7, 167.8, 166.8, 134.4, 134.14, 134.07, 133.0, 130.2, 130.1, 128.7, 128.6, 83.2, 82.9, 70.6, 70.3, 52.8, 52.4, 50.2, 49.2, 36.5, 36.1, 33.0, 31.8, 23.0, 22.9, 8.4, 7.8. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{15}ClO_3Na$ 313.0602 (100.0%), 315.0572 (32.0%); Found 313.0610 (100.0%), 315.0580 (32.0%). IR (KBr thin film, cm^{-1}): ν 3266, 2982, 1742, 1693, 1495, 1435, 1312, 1256, 1171, 1092, 836, 724, 687.



1t

Methyl 2-ethynyl-2-isopentyl-1-propionylcyclopropane-1-carboxylate (1t): The general procedure was followed using **S5-t** (5 mmol, 1.610 g) and TBAF (10 mmol, 3.150 g) in THF (25 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 15:1), colorless oil, 738 mg, 59% yield, 1:0.3 dr. ^{1}H NMR (400 MHz, $CDCl_3$, after column 1:0.25 dr) δ 3.75 (s, 3H), 3.73 (s, 0.75H), 2.98–2.71 (m, 2.5H), 2.08 (s, 1H), 1.96 (d, *J* = 4.9 Hz, 0.25H), 1.85 (d, *J* = 4.8 Hz, 1H), 1.76 (d, *J* = 4.8 Hz, 1H), 1.70 (s, 0.25H), 1.66 (d, *J* = 5.1 Hz, 0.25H), 1.58–1.39 (m, 3.75H), 1.38–1.28 (m, 1.25H), 1.28–1.15 (m, 1.25H), 1.11–1.01 (m, 3.75H), 0.88–0.79 (m, 7.5H).^{13}C NMR (101 MHz, $CDCl_3$) δ 202.9, 168.8, 168.7, 83.7, 83.5, 69.7, 69.2,

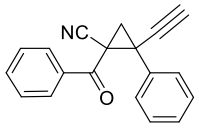
52.62, 52.57, 47.1, 46.5, 36.7, 36.6, 36.4, 35.7, 31.3, 30.7, 29.8, 29.1, 27.94, 27.87, 25.53, 25.50, 22.82, 22.76, 22.4, 8.5, 8.1. HRMS (ESI-Quadrupole-Orbitrap) m/z: [M + Na]$^+$ Calcd for $C_{15}H_{22}O_3Na$ 273.1461; Found 273.1469. IR (KBr thin film, cm^{-1}): ν 3290, 2955, 1731, 1698, 1409, 1309, 1215, 1205, 1116, 762, 666, 555.



1u

Methyl (*E*)-1-benzoyl-2-(4-((3,7-dimethylocta-2,6-dien-1-yl)oxy)phenyl)-2-ethynylcyclopropane-1-carboxylate (1u):

The general procedure was followed using **S5-u** (5 mmol, 2.640 g) and TBAF (10 mmol, 3.150 g) in THF (25 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 30:1), red oil, 1.230 g, 54% yield, 1:1.6 dr. ^{1}H NMR (600 MHz, $CDCl_3$, after column single diastereoisomer) δ 8.11–8.06 (m, 2H), 7.63–7.58 (m, 1H), 7.55–7.47 (m, 4H), 6.97–6.92 (m, 2H), 5.53–5.47 (m, 1H), 5.14–5.07 (m, 1H), 4.55 (d, *J* = 6.6 Hz, 2H), 3.36 (s, 3H), 2.56 (d, *J* = 5.3 Hz, 1H), 2.35 (d, *J* = 5.3 Hz, 1H), 2.16–2.11 (m, 2H), 2.11–2.07 (m, 2H), 1.98 (s, 1H), 1.74 (s, 3H), 1.69 (s, 3H), 1.61 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.2, 167.6, 158.8, 141.5, 136.8, 133.3, 132.0, 130.1, 129.6, 128.4, 127.0, 123.9, 119.4, 114.6, 83.9, 71.0, 65.0, 52.6, 45.9, 39.7, 31.7, 26.4, 25.9, 24.7, 17.9, 16.8. HRMS (ESI-Quadrupole-Orbitrap) m/z: [M + Na]$^+$ Calcd for $C_{30}H_{32}O_4Na$ 479.2193; Found 479.2199. IR (KBr thin film, cm^{-1}): ν 3286, 2916, 1712, 1681, 1510, 1448, 1325, 1236, 1177, 1093, 830, 753, 690.

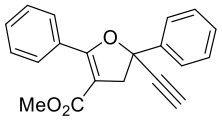


1v

1-benzoyl-2-ethynyl-2-phenylcyclopropane-1-carbonitrile (1v):

The general procedure was followed using **S5-v** (5 mmol, 1.715 g) and TBAF (10 mmol, 3.150 g) in THF (25 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 7:1), amorphous yellow solid, mp 85–90 ºC, 501 mg, 37%

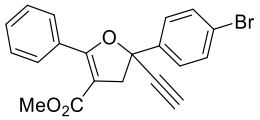
yield, 1:0.6 dr. ^{1}H NMR (600 MHz, $CDCl_3$, after column 1:0.5 dr) δ 8.00 (d, *J* = 7.4 Hz, 2H), 7.90 (d, *J* = 7.4 Hz, 1H), 7.69–7.62 (m, 3H), 7.59–7.50 (m, 4.5H), 7.49–7.43 (m, 2H), 7.40–7.35 (m, 1H), 7.22–7.15 (m, 1.5H), 3.15 (d, *J* = 5.9 Hz, 0.5H), 2.89 (d, *J* = 6.2 Hz, 1H), 2.67 (s, 0.5H), 2.52 (d, *J* = 6.2 Hz, 1H), 2.24 (d, *J* = 6.0 Hz, 0.5H), 2.15 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 187.8, 186.7, 134.8, 134.7, 134.3, 134.2, 133.5, 131.4, 129.4, 129.30, 129.27, 129.1, 129.0, 128.81, 128.77, 128.6, 127.9, 118.8, 117.3, 82.2, 79.9, 72.7, 72.1, 36.9, 35.2, 35.1, 34.4, 24.7, 23.7. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{13}NONa$ 294.0889; Found 294.0887. IR (KBr thin film, cm^{-1}): ν 3226, 2923, 2240, 1678, 1448, 1282, 1017, 779, 721, 689.



2a

Methyl 5-ethynyl-2,5-diphenyl-4,5-dihydrofuran-3-carboxylate (2a):

The general procedure was followed using **1a** (0.1 mmol, 30.4 mg, 1:1 dr), $Cu(OTf)_2$ (0.001 mmol, 0.36 mg) and Et_3N (0.1 mmol, 13.9 μL) in CH_2Cl_2 (1.0 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 29.6 mg, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.5 Hz, 2H), 7.66 (d, *J* = 7.9 Hz, 2H), 7.50–7.40 (m, 5H), 7.39–7.34 (m, 1H), 3.81 (d, *J* = 15.4 Hz, 1H), 3.70 (s, 3H), 3.54 (d, *J* = 15.4 Hz, 1H), 2.86 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 163.6, 141.8, 130.8, 129.6, 129.3, 128.7, 128.6, 127.8, 125.1, 101.5, 84.0, 82.5, 75.8, 51.3, 48.6. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{16}O_3Na$ 327.0992; Found 327.0990. IR (KBr thin film, cm^{-1}): ν 3246, 2953, 1700, 1623, 1491, 1447, 1275, 1235, 1091, 1066, 1018, 764, 694.

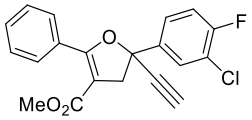


2b

Methyl 5-(4-bromophenyl)-5-ethynyl-2-phenyl-4,5-dihydrofuran-3-carboxylate (2b):

The general procedure was followed using **1b** (0.1 mmol, 38.3 mg, 1:1.7 dr), $Cu(OTf)_2$ (0.001 mmol, 0.36 mg) and Et_3N (0.1 mmol, 13.9 μL) in CH_2Cl_2 (1.0 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1),

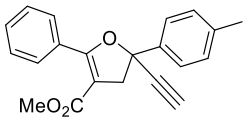
amorphous yellow solid, mp 90–93 ºC, 34.5 mg, 90% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.8 Hz, 2H), 7.56–7.49 (m, 4H), 7.49–7.41 (m, 3H), 3.78 (d, J = 15.4 Hz, 1H), 3.69 (s, 3H), 3.47 (d, *J* = 15.4 Hz, 1H), 2.86 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9, 163.4, 140.9, 131.9, 131.0, 129.6, 129.1, 127.9, 127.0, 122.8, 101.5, 83.6, 82.0, 76.1, 51.4, 48.5. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{15}BrO_3Na$ 405.0097 (100.0%), 407.0076 (97.3%); Found 405.0101 (100.0%), 407.0080 (97.3%). IR (KBr thin film, cm^{-1}): ν 3288, 2947, 1701, 1626, 1435, 1246, 1234, 1091, 1071, 790, 755, 693.



2c

Methyl 5-(3-chloro-4-fluorophenyl)-5-ethynyl-2-phenyl-4,5-dihydrofuran-3-carboxylate (2c):

The general procedure was followed using **1c** (0.1 mmol, 35.6 mg, 1:1.4 dr), $Cu(OTf)_2$ (0.001 mmol, 0.36 mg) and Et_3N (0.1 mmol, 13.9 μL) in CH_2Cl_2 (1.0 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 32.8 mg, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.3 Hz, 2H), 7.69 (d, *J* = 6.6 Hz, 1H), 7.53–7.49 (m, 1H), 7.48–7.42 (m, 3H), 7.21–7.13 (m, 1H), 3.78 (d, *J* = 15.5 Hz, 1H), 3.70 (s, 3H), 3.46 (d, *J* = 15.5 Hz, 1H), 2.89 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 163.3, 158.1 (C-F, d, $^{1}J_{C\text{-}F}$ = 251.6 Hz), 138.9 (C-F, d, $^{4}J_{C\text{-}F}$ = 3.7 Hz), 131.1, 129.6, 129.0, 128.0, 127.9, 125.2 (C-F, d, $^{3}J_{C\text{-}F}$ = 7.6 Hz), 121.4 (C-F, d, $^{2}J_{C\text{-}F}$ = 18.0 Hz), 116.9 (C-F, d, $^{2}J_{C\text{-}F}$ = 21.6 Hz), 101.5, 83.3, 81.4, 76.4, 51.4, 48.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ –115.5. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{14}ClFO_3Na$ 379.0508 (100.0%), 381.0478 (32.0%); Found 379.0511 (100.0%), 381.0482 (32.0%). IR (KBr thin film, cm^{-1}): ν 3293, 2949, 1700, 1626, 1494, 1434, 1344, 1244, 1091, 1074, 752, 691.

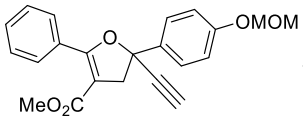


2d

Methyl 5-ethynyl-2-phenyl-5-(p-tolyl)-4,5-dihydrofuran-3-carboxylate (2d):

The general procedure was followed using **1d** (0.1 mmol, 31.8 mg, 1:1 dr), $Cu(OTf)_2$ (0.001 mmol, 0.36 mg) and Et_3N (0.1 mmol, 13.9 μL) in CH_2Cl_2 (1.0 mL). Purified

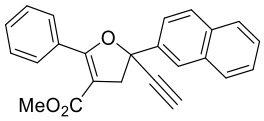
by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 30.5 mg, 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.90 (m, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.50–7.41 (m, 3H), 7.23 (d, *J* = 8.1 Hz, 2H), 3.79 (d, *J* = 15.4 Hz, 1H), 3.70 (s, 3H), 3.54 (d, *J* = 15.4 Hz, 1H), 2.85 (s, 1H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 163.6, 138.9, 138.5, 130.8, 129.6, 129.4, 127.8, 125.1, 101.5, 84.2, 82.5, 75.6, 51.3, 48.5, 21.2. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{18}O_3Na$ 341.1148; Found 341.1146. IR (KBr thin film, cm^{-1}): ν 3284, 2948, 1702, 1625, 1493, 1434, 1343, 1233, 1090, 816, 753, 691.



2e

Methyl 5-ethynyl-5-(4-(methoxymethoxy)phenyl)-2-phenyl-4,5-dihydrofuran-3-carboxylate (2e):

The general procedure was followed using **1e** (0.1 mmol, 36.4 mg, single diastereoisomer), $Cu(OTf)_2$ (0.001 mmol, 0.36 mg) and Et_3N (0.1 mmol, 13.9 μL) in CH_2Cl_2 (1.0 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 33.1 mg, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.86 (m, 2H), 7.57 (d, *J* = 8.7 Hz, 2H), 7.48–7.38 (m, 3H), 7.06 (d, *J* = 8.7 Hz, 2H), 5.19 (s, 2H), 3.76 (d, *J* = 15.4 Hz, 1H), 3.68 (s, 3H), 3.55–3.45 (m, 4H), 2.85 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.1, 163.6, 157.5, 135.1, 130.8, 129.6, 129.4, 127.9, 126.7, 116.3, 101.5, 94.4, 84.2, 82.4, 75.7, 56.2, 51.3, 48.4. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{20}O_5Na$ 387.1203; Found 387.1206. IR (KBr thin film, cm^{-1}): ν 3283, 2949, 1706, 1609, 1509, 1493, 1435, 1233, 1150, 1091, 1073, 753, 692.

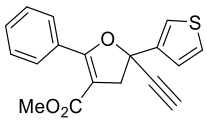


2f

Methyl 5-ethynyl-5-(naphthalen-2-yl)-2-phenyl-4,5-dihydrofuran-3-carboxylate (2f):

The general procedure was followed using **1f** (0.1 mmol, 35.4 mg, 1:1.3 dr), $Cu(OTf)_2$ (0.002 mmol, 0.72 mg) and Et_3N (0.1 mmol, 13.9 μL) in CH_2Cl_2 (1.0 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1),

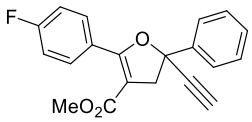
amorphous white solid, mp 70–75 ºC, 32.7 mg, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.97 (d, *J* = 7.8 Hz, 2H), 7.94–7.83 (m, 3H), 7.71 (d, *J* = 8.6 Hz, 1H), 7.56–7.50 (m, 2H), 7.50–7.41 (m, 3H), 3.87 (d, *J* = 15.4 Hz, 1H), 3.71 (s, 3H), 3.63 (d, *J* = 15.4 Hz, 1H), 2.93 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.1, 163.7, 138.9, 133.3, 133.0, 130.9, 129.7, 129.4, 129.0, 128.6, 127.9, 127.8, 126.73, 126.68, 124.2, 123.0, 101.7, 84.1, 82.7, 76.1, 51.3, 48.5. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{18}O_3Na$ 377.1148; Found 377.1150. IR (KBr thin film, cm^{-1}): ν 3283, 2947, 1704, 1626, 1492, 1434, 1342, 1240, 1190, 1090, 817, 748, 691.



2g

Methyl 5-ethynyl-2-phenyl-5-(thiophen-3-yl)-4,5-dihydrofuran-3-carboxylate (2g):

The general procedure was followed using **1g** (0.1 mmol, 31.0 mg, 1:0.25 dr), $Cu(OTf)_2$ (0.001 mmol, 0.36 mg) and Et_3N (0.1 mmol, 13.9 μL) in CH_2Cl_2 (1.0 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), red oil, 27.0 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.1 Hz, 2H), 7.52 (s, 1H), 7.47–7.32 (m, 4H), 7.24 (d, *J* = 4.9 Hz, 1H), 3.78–3.65 (m, 4H), 3.55 (d, *J* = 15.4 Hz, 1H), 2.83 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 163.5, 142.6, 130.9, 129.6, 129.3, 127.9, 127.3, 125.3, 122.7, 101.5, 83.8, 79.8, 75.1, 51.3, 47.4. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{14}O_3SNa$ 333.0556; Found 333.0558. IR (KBr thin film, cm^{-1}): ν 3283, 2948, 1705, 1628, 1434, 1361, 1236, 1191, 1091, 846, 790, 755, 691.

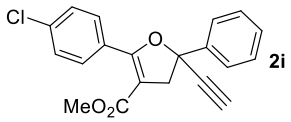


2h

Methyl 5-ethynyl-2-(4-fluorophenyl)-5-phenyl-4,5-dihydrofuran-3-carboxylate (2h):

The general procedure was followed using **1h** (0.1 mmol, 32.2 mg, 1:1 dr), $Cu(OTf)_2$ (0.001 mmol, 0.36 mg) and Et_3N (0.1 mmol, 13.9 μL) in CH_2Cl_2 (1.0 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1),

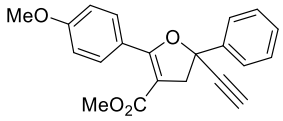
amorphous yellow solid, mp 56–59 ºC, 31.2 mg, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04–7.94 (m, 2H), 7.64 (d, *J* = 7.4 Hz, 2H), 7.47–7.33 (m, 3H), 7.18–7.05 (m, 2H), 3.80 (d, *J* = 15.4 Hz, 1H), 3.70 (s, 3H), 3.53 (d, *J* = 15.4 Hz, 1H), 2.87 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1 (C-F, d, $^{1}J_{C\text{-}F}$ = 252.8 Hz), 163.8 (C-F, d, $^{1}J_{C\text{-}F}$ = 257.2 Hz), 141.7, 132.0 (C-F, d, $^{3}J_{C\text{-}F}$ = 8.6 Hz), 128.8, 128.7, 125.4 (C-F, d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 125.1, 115.0 (C-F, d, $^{2}J_{C\text{-}F}$ = 21.8 Hz), 101.4, 84.0, 82.5, 75.9, 51.4, 48.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ –108.4. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{15}FO_3Na$ 345.0897; Found 345.0899. IR (KBr thin film, cm^{-1}): ν 3292, 2949, 1710, 1636, 1505, 1430, 1238, 1093, 953, 764, 699.



2i

Methyl 2-(4-chlorophenyl)-5-ethynyl-5-phenyl-4,5-dihydrofuran-3-carboxylate (2i):

The general procedure was followed using **1i** (0.1 mmol, 33.8 mg, single diastereoisomer), $Cu(OTf)_2$ (0.001 mmol, 0.36 mg) and Et_3N (0.1 mmol, 13.9 μL) in CH_2Cl_2 (1.0 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 15:1), amorphous white solid, mp 54–60 ºC, 30.8 mg, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.9 Hz, 2H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.46–7.34 (m, 5H), 3.79 (d, *J* = 15.5 Hz, 1H), 3.70 (s, 3H), 3.52 (d, *J* = 15.5 Hz, 1H), 2.87 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.9, 162.3, 141.6, 136.9, 131.0, 128.8, 128.7, 128.2, 127.7, 125.1, 102.0, 83.9, 82.7, 76.0, 51.4, 48.6. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{15}ClO_3Na$ 361.0602 (100.0%), 363.0572 (32.0%); Found 361.0603 (100.0%), 363.0574 (32.0%). IR (KBr thin film, cm^{-1}): ν 3249, 2947, 1690, 1611, 1489, 1430, 1241, 1089, 1073, 840, 757, 696.

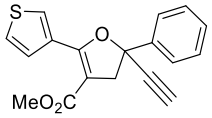


2j

Methyl 5-ethynyl-2-(4-methoxyphenyl)-5-phenyl-4,5-dihydrofuran-3-carboxylate (2j):

The general procedure was followed using **1j** (0.1 mmol, 33.4 mg, 1:0.7 dr), $Cu(OTf)_2$ (0.01 mmol, 3.60 mg) and Et_3N (0.1 mmol, 13.9 μL) in CH_2Cl_2 (1.0 mL). Purified by

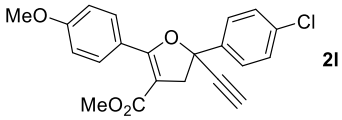
chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), amorphous white solid, mp 107–111 ºC, 32.6 mg, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.45–7.32 (m, 3H), 6.94 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 3.78 (d, *J* = 15.3 Hz, 1H), 3.70 (s, 3H), 3.50 (d, *J* = 15.2 Hz, 1H), 2.84 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 163.6, 161.7, 142.0, 131.5, 128.7, 128.6, 125.1, 121.7, 113.3, 99.9, 84.3, 82.2, 75.6, 55.5, 51.3, 48.7. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{18}O_4Na$ 357.1097; Found 357.1095. IR (KBr thin film, cm^{-1}): ν 3285, 2931, 1709, 1620, 1510, 1429, 1246, 1233, 1176, 1092, 859, 754, 690.



2k

Methyl 5-ethynyl-5-phenyl-2-(thiophen-3-yl)-4,5-dihydrofuran-3-carboxylate (2k):

The general procedure was followed using **1k** (0.1 mmol, 31.0 mg, 1:1 dr), $Cu(OTf)_2$ (0.02 mmol, 7.20 mg) and Et_3N (0.1 mmol, 13.9 μL) in CH_2Cl_2 (1.0 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 12.4 mg, 40% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.56–8.50 (m, 1H), 7.88–7.84 (m, 1H), 7.63–7.58 (m, 2H), 7.42–7.38 (m, 2H), 7.37–7.34 (m, 1H), 7.33–7.31 (m, 1H), 3.77 (d, *J* = 15.4 Hz, 1H), 3.73 (s, 3H), 3.47 (d, *J* = 15.4 Hz, 1H), 2.82 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.2, 158.5, 142.0, 131.1, 130.3, 128.8, 128.6, 125.1, 124.8, 100.2, 84.2, 82.1, 75.6, 51.4, 48.7. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{14}O_3SNa$ 333.0556; Found 333.0561. IR (KBr thin film, cm^{-1}): ν 3264, 2922, 1698, 1618, 1434, 1358, 1100, 1076, 923, 853, 757, 690.

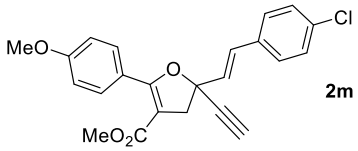


2l

Methyl 5-(4-chlorophenyl)-5-ethynyl-2-(4-methoxyphenyl)-4,5-dihydrofuran-3-carboxylate (2l):

The general procedure was followed using **1l** (0.1 mmol, 36.8 mg, 1:1.3 dr), $Cu(OTf)_2$ (0.001 mmol, 0.36 mg) and Et_3N (0.1 mmol, 13.9 μL) in CH_2Cl_2 (1.0 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless

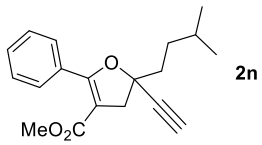
oil, 33.1 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 3.76 (d, *J* = 15.3 Hz, 1H), 3.69 (s, 3H), 3.43 (d, *J* = 15.3 Hz, 1H), 2.84 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 163.4, 161.8, 140.6, 134.5, 131.5, 128.9, 126.7, 121.4, 113.3, 99.9, 83.8, 81.6, 75.9, 55.5, 51.3, 48.6. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{21}H_{18}ClO_4$ 369.0888 (100.0%), 371.0859 (32.0%); Found 313.0897 (100.0%), 315.0869 (32.0%). IR (KBr thin film, cm^{-1}): ν 3283, 2950, 1706, 1609, 1509, 1493, 1233, 1150, 1091, 1074, 832, 753, 692.



2m

Methyl (*E*)-5-(4-chlorostyryl)-5-ethynyl-2-(4-methoxyphenyl)-4,5-dihydrofuran-3-carboxylate (2m):

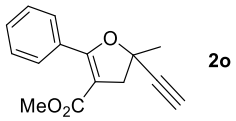
The general procedure was followed using **1m** (0.1 mmol, 39.4 mg, single diastereoisomer), $Cu(OTf)_2$ (0.001 mmol, 0.36 mg) and Et_3N (0.1 mmol, 13.9 μL) in CH_2Cl_2 (1.0 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), amorphous white solid, mp 90–93 ºC, 37.6 mg, 95% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92–7.85 (m, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 6.7 Hz, 2H), 6.96 (d, *J* = 15.8 Hz, 1H), 6.94–6.88 (m, 2H), 6.38 (d, *J* = 15.8 Hz, 1H), 3.84 (s, 3H), 3.70 (s, 3H), 3.55 (d, *J* = 15.2 Hz, 1H), 3.34 (d, *J* = 15.2 Hz, 1H), 2.84 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.4, 163.5, 161.6, 134.23, 134.21, 131.4, 130.8, 129.0, 128.5, 128.4, 121.6, 113.2, 100.0, 82.4, 81.0, 76.2, 55.5, 51.3, 46.0. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{19}ClO_4Na$ 417.0864 (100.0%), 419.0835 (32.0%); Found 417.0872 (100.0%), 419.0842 (32.0%). IR (KBr thin film, cm^{-1}): ν 3295, 2950, 1696, 1507, 1237, 1177, 1093, 756, 687, 617.



2n

Methyl 5-ethynyl-5-isopentyl-2-phenyl-4,5-dihydrofuran-3-carboxylate (2n):

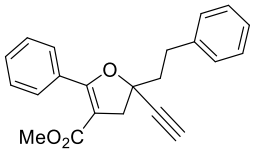
The general procedure was followed using **1n** (0.1 mmol, 29.8 mg, single diastereoisomer), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg) and Et_3N (0.1 mmol, 13.9 μL) in CH_2Cl_2 (1.0 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 30:1), colorless oil, 28.3 mg, 95% yield. ^1H NMR (600 MHz, $CDCl_3$) δ 7.82–7.77 (m, 2H), 7.44–7.37 (m, 3H), 3.68 (s, 3H), 3.38 (d, *J* = 15.1 Hz, 1H), 3.15 (d, *J* = 15.1 Hz, 1H), 2.63 (s, 1H), 2.03–1.97 (m, 1H), 1.92–1.85 (m, 1H), 1.64–1.58 (m, 1H), 1.56–1.48 (m, 1H), 1.48–1.40 (m, 1H), 0.94 (d, *J* = 6.6 Hz, 6H).^{13}C NMR (151 MHz, $CDCl_3$) δ 165.4, 163.8, 130.7, 129.7, 129.5, 127.8, 101.4, 84.4, 82.4, 74.1, 51.2, 44.4, 38.9, 33.1, 28.2, 22.7, 22.6. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{22}O_3Na$ 321.1461; Found 321.1465. IR (KBr thin film, cm^{-1}): ν 3288, 2952, 1893, 1627, 1599, 1493, 1434, 1247, 1090, 1071, 798, 754, 691.



2o

Methyl 5-ethynyl-5-methyl-2-phenyl-4,5-dihydrofuran-3-carboxylate (2o):

The general procedure was followed using **1o** (0.1 mmol, 24.2 mg, single diastereoisomer), $Cu(OTf)_2$ (0.01 mmol, 3.60 mg) and Et_3N (0.1 mmol, 13.9 μL) in CH_2Cl_2 (1.0 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 15:1), amorphous white solid, mp 52–54 ºC, 20.3 mg, 84% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.82–7.74 (m, 2H), 7.46–7.35 (m, 3H), 3.67 (s, 3H), 3.45 (d, *J* = 15.1 Hz, 1H), 3.12 (d, *J* = 15.1 Hz, 1H), 2.63 (s, 1H), 1.76 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 163.7, 130.7, 129.6, 129.5, 127.8, 101.4, 85.1, 78.9, 73.3, 51.2, 45.8, 28.4. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{14}O_3Na$ 265.0835; Found 265.0840. IR (KBr thin film, cm^{-1}): ν 3239, 2953, 1699, 1634, 1433, 1350, 1260, 1238, 1183, 1100, 1057, 768, 692.

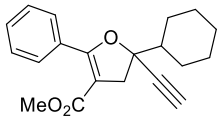


2p

Methyl 5-ethynyl-5-phenethyl-2-phenyl-4,5-dihydrofuran-3-carboxylate (2p):

The general procedure was followed using **1p** (0.1 mmol, 33.2 mg, single diastereoisomer), $Cu(OTf)_2$ (0.02 mmol, 7.20 mg) and Et_3N (0.1 mmol, 13.9 μL) in

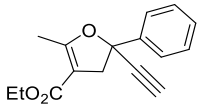
CH_2Cl_2 (1.0 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 31.5 mg, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.0 Hz, 2H), 7.46–7.35 (m, 3H), 7.33–7.26 (m, 2H), 7.25–7.16 (m, 3H), 3.67 (s, 3H), 3.44 (d, *J* = 15.2 Hz, 1H), 3.18 (d, *J* = 15.2 Hz, 1H), 3.02–2.86 (m, 2H), 2.69 (s, 1H), 2.40–2.26 (m, 1H), 2.25–2.11 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 163.7, 141.1, 130.7, 129.54, 129.50, 128.6, 128.5, 127.8, 126.2, 101.4, 83.9, 81.8, 74.7, 51.2, 44.6, 42.8, 30.8. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{20}O_3Na$ 355.1305; Found 355.1309. IR (KBr thin film, cm^{-1}): ν 3282, 2948, 1690, 1626, 1493, 1434, 1247, 1189, 1093, 1070, 1023, 752, 691.



2q

Methyl 5-cyclohexyl-5-ethynyl-2-phenyl-4,5-dihydrofuran-3-carboxylate (2q):

The general procedure was followed using **1q** (0.1 mmol, 31.0 mg, single diastereoisomer), $Cu(OTf)_2$ (0.02 mmol, 7.20 mg) and Et_3N (0.1 mmol, 13.9 μL) in CH_2Cl_2 (1.0 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), amorphous yellow solid, mp 56–61 ºC, 29.5 mg, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.76 (m, 2H), 7.45–7.35 (m, 3H), 3.67 (s, 3H), 3.31–3.18 (m, 2H), 2.60 (s, 1H), 2.14–2.00 (m, 1H), 1.87–1.76 (m, 4H), 1.75–1.68 (m, 1H), 1.33–1.19 (m, 5H).^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 163.9, 130.6, 129.8, 129.5, 127.8, 101.5, 85.6, 83.8, 74.5, 51.2, 47.1, 42.6, 27.3, 27.2, 26.3, 26.1, 25.9. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{22}NaO_3$ 333.1461; Found 333.1466. IR (KBr thin film, cm^{-1}): ν 3248, 2930, 1701, 1630, 1599, 1449, 1244, 1089, 1071, 971, 753.

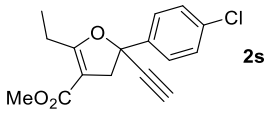


2r

Ethyl 5-ethynyl-2-methyl-5-phenyl-4,5-dihydrofuran-3-carboxylate (2r):

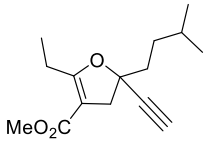
The general procedure was followed using **1r** (0.1 mmol, 25.6 mg, 1.15:1 dr), $Cu(OTf)_2$ (0.01 mmol, 3.60 mg) and Et_3N (0.1 mmol, 13.9 μL) in CH_2Cl_2 (1.0 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 15:1), yellow oil, 23.1 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.2 Hz,

2H), 7.45–7.28 (m, 3H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.57 (d, *J* = 14.8 Hz, 1H), 3.27 (d, *J* = 14.8 Hz, 1H), 2.82 (s, 1H), 2.33 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 166.2, 165.6, 142.0, 128.7, 128.6, 125.0, 101.6, 84.2, 82.9, 75.6, 59.9, 47.1, 14.5, 14.3. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{16}O_3Na$ 279.0992; Found 279.0995. IR (KBr thin film, cm^{-1}): ν 3286, 2980, 1695, 1651, 1448, 1380, 1342, 1279, 1226, 1088, 962, 757, 696.



2s

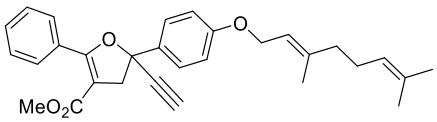
Methyl 5-(4-chlorophenyl)-2-ethyl-5-ethynyl-4,5-dihydrofuran-3-carboxylate (2s): The general procedure was followed using **1s** (0.1 mmol, 29.0 mg, 1:1 dr), $Cu(OTf)_2$ (0.01 mmol, 3.60 mg) and Et_3N (0.1 mmol, 13.9 μL) in CH_2Cl_2 (1.0 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 30:1), yellow oil, 26.7 mg, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 3.70 (s, 3H), 3.54 (d, *J* = 14.8 Hz, 1H), 3.21 (d, *J* = 14.8 Hz, 1H), 2.87–2.68 (m, 3H), 1.21 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.0, 165.6, 140.7, 134.5, 128.9, 126.5, 100.3, 83.7, 82.3, 75.9, 51.2, 47.2, 21.3, 11.2. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{15}ClO_3Na$ 313.0602 (100.0%), 315.0572 (32.0%); Found 313.0607 (100.0%), 315.0576 (32.0%). IR (KBr thin film, cm^{-1}): ν 3293, 2949, 1698, 1645, 1490, 1435, 1350, 1214, 1092, 1040, 827, 760.



2t

Methyl 2-ethyl-5-ethynyl-5-isopentyl-4,5-dihydrofuran-3-carboxylate (2t): The general procedure was followed using **1t** (0.1 mmol, 25.0 mg, 1:0.25 dr), $Cu(OTf)_2$ (0.02 mmol, 7.20 mg) and Et_3N (0.1 mmol, 13.9 μL) in CH_2Cl_2 (1.0 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 22.2 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 (s, 3H), 3.13 (d, *J* = 14.5 Hz, 1H), 2.89 (d, *J* = 14.5 Hz, 1H), 2.78–2.53 (m, 3H), 1.93–1.81 (m, 1H), 1.80–1.69 (m, 1H), 1.59–1.51 (m, 1H), 1.48–1.30 (m, 2H), 1.12 (t, *J* = 7.5 Hz, 3H),

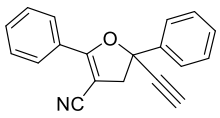
0.90 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 166.1, 100.0, 84.5, 82.7, 73.9, 51.0, 42.8, 38.9, 33.0, 28.1, 22.7, 21.4, 11.2. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{22}O_3Na$ 273.1461; Found 273.1464. IR (KBr thin film, cm^{-1}): ν 3291, 2953, 1701, 1642, 1435, 1367, 1353, 1254, 1095, 1027, 990, 762, 659.



2u

Methyl (*E*)-5-(4-((3,7-dimethylocta-2,6-dien-1-yl)oxy)phenyl)-5-ethynyl-2-phenyl-4,5-dihydrofuran-3-carboxylate (2u):

The general procedure was followed using **1u** (0.1 mmol, 45.6 mg, single diastereoisomer), $Cu(OTf)_2$ (0.001 mmol, 0.36 mg) and Et_3N (0.1 mmol, 13.9 μL) in CH_2Cl_2 (1.0 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), colorless oil, 41.6 mg, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.87 (m, 2H), 7.57 (d, *J* = 8.7 Hz, 2H), 7.46–7.38 (m, 3H), 6.94 (d, *J* = 8.8 Hz, 2H), 5.49 (t, *J* = 6.3 Hz, 1H), 5.10 (t, *J* = 6.0 Hz, 1H), 4.56 (d, *J* = 6.5 Hz, 2H), 3.76 (d, *J* = 15.4 Hz, 1H), 3.69 (s, 3H), 3.53 (d, *J* = 15.4 Hz, 1H), 2.85 (s, 1H), 2.19–2.06 (m, 4H), 1.75 (s, 3H), 1.69 (s, 3H), 1.62 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 163.6, 159.2, 141.5, 133.7, 131.9, 130.8, 129.6, 129.4, 127.8, 126.6, 123.9, 119.4, 114.7, 101.5, 84.2, 82.5, 75.7, 65.0, 51.3, 48.4, 39.6, 26.4, 25.8, 17.8, 16.8. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{32}O_4Na$ 479.2193; Found 479.2198. IR (KBr thin film, cm^{-1}): ν 3287, 2915, 1708, 1609, 1509, 1435, 1343, 1232, 1176, 1091, 829, 752, 692.

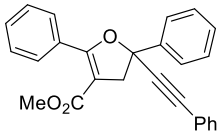


2v

5-ethynyl-2,5-diphenyl-4,5-dihydrofuran-3-carbonitrile (2v):

The general procedure was followed using **1v** (0.1 mmol, 27.1 mg, 1:0.5 dr), $Cu(OTf)_2$ (0.001 mmol, 0.36 mg) and Et_3N (0.1 mmol, 13.9 μL) in CH_2Cl_2 (1.0 mL). Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 6:1), amorphous white solid, mp 97–99 ºC, 22.2 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09–8.02 (m, 2H), 7.64–7.58 (m, 2H), 7.56–7.46 (m, 3H), 7.46–7.35 (m,

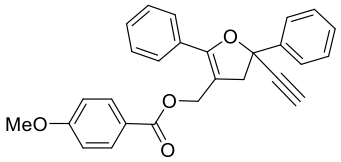
3H), 3.72 (d, *J* = 14.9 Hz, 1H), 3.45 (d, *J* = 14.9 Hz, 1H), 2.91 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.5, 140.7, 131.9, 129.1, 129.0, 128.9, 127.6, 127.4, 125.1, 116.9, 84.3, 82.9, 78.9, 76.8, 48.4. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{13}NONa$ 294.0889; Found 294.0890. IR (KBr thin film, cm^{-1}): ν 3256, 2923, 2201, 1621, 1493, 1448, 1343, 1232, 1182, 1076, 776, 710, 691.



3a

Methyl 2,5-diphenyl-5-(phenylethynyl)-4,5-dihydrofuran-3-carboxylate (3a):

Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 53.8 mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.7 Hz, 2H), 7.73 (d, *J* = 7.7 Hz, 2H), 7.55–7.50 (m, 2H), 7.49–7.41 (m, 5H), 7.40–7.31 (m, 4H), 3.90 (d, *J* = 15.4 Hz, 1H), 3.71 (s, 3H), 3.61 (d, *J* = 15.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 163.8, 142.6, 132.0, 130.8, 129.7, 129.5, 129.0, 128.8, 128.5, 128.4, 127.9, 125.3, 122.2, 101.5, 89.3, 87.5, 83.4, 51.3, 48.8. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{26}H_{21}O_3$ 348.1485; Found 348.1485. IR (KBr thin film, cm^{-1}): ν 2961, 1706, 1627 1257, 1238, 1091, 1070, 1017, 890, 797, 753, 688.

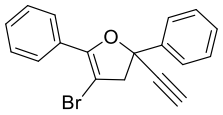


3b

(5-ethynyl-2,5-diphenyl-4,5-dihydrofuran-3-yl)methyl 4-methoxybenzoate (3b):

Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 15:1), yellow oil, 67.1 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.5 Hz, 2H), 7.75–7.63 (m, 4H), 7.48–7.38 (m, 5H), 7.37–7.33 (m, 1H), 6.93 (d, *J* = 8.6 Hz, 2H), 5.11 (d, *J* = 12.5 Hz, 1H), 5.06 (d, *J* = 12.5 Hz, 1H), 3.86 (s, 3H), 3.69 (d, *J* = 15.5 Hz, 1H), 3.40 (d, *J* = 15.5 Hz, 1H), 2.81 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 163.5, 153.4, 142.9, 131.8, 130.0, 129.5, 128.7, 128.6, 128.3, 127.9, 125.1, 122.6, 113.8, 103.9, 85.2, 81.3, 74.7, 60.7, 55.6, 51.0. HRMS (ESI-Quadrupole-

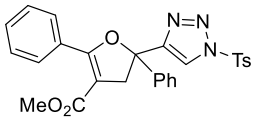
Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{26}H_{21}O_4$ 397.1434; Found 397.1445. IR (KBr thin film, cm^{-1}): ν 3287, 2934, 1734, 1605, 1447, 1372, 1252, 1166, 1093, 1042, 770, 696.



3c

4-bromo-2-ethynyl-2,5-diphenyl-2,3-dihydrofuran (3c):

Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 47.6 mg, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 6.4 Hz, 2H), 7.65 (d, *J* = 7.4 Hz, 2H), 7.49–7.32 (m, 6H), 3.74 (d, *J* = 15.5 Hz, 1H), 3.46 (d, *J* = 15.5 Hz, 1H), 2.82 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1, 142.3, 129.4, 128.8, 128.6, 128.3, 127.4, 125.1, 86.7, 84.6, 80.6, 75.2, 55.4. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{18}H_{14}BrO$ 325.0223; Found 325.0223. IR (KBr thin film, cm^{-1}): ν 3287, 2921, 1492, 1446, 1237, 1066, 1015, 902, 757, 691, 666.



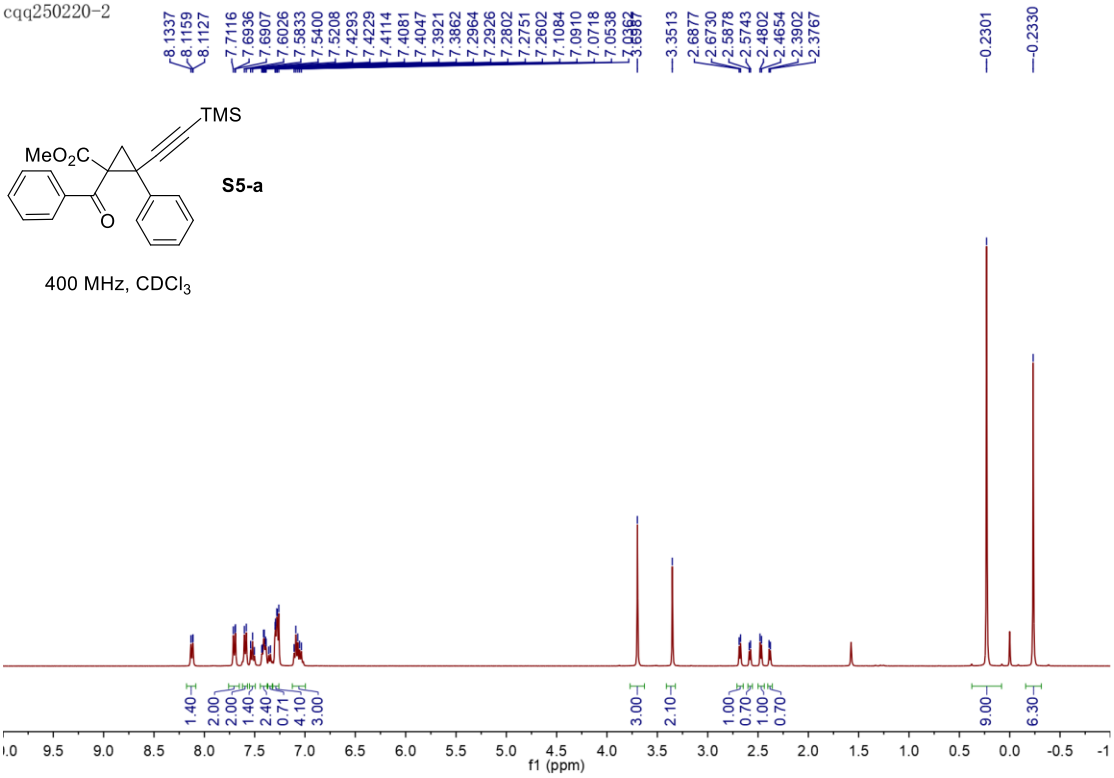
3d

Methyl 2,5-diphenyl-5-(1-tosyl-1*H*-1,2,3-triazol-4-yl)-4,5-dihydrofuran-3-carboxylate (3d):

Purified by chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), amorphous white solid, mp 166–168 ºC, 76.6 mg, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.2 Hz, 2H), 7.95–7.86 (m, 3H), 7.53 (d, *J* = 7.5 Hz, 2H), 7.50–7.42 (m, 3H), 7.42–7.29 (m, 5H), 4.21 (d, *J* = 15.5 Hz, 1H), 3.70–3.60 (m, 4H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 163.1, 151.5, 147.7, 143.3, 132.7, 130.9, 130.6, 129.5, 129.3, 129.0, 128.8, 128.3, 128.0, 125.1, 121.4, 102.3, 85.4, 51.3, 45.5, 22.0. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{27}H_{24}N_3O_5S$ 502.1431; Found 502.1431. IR (KBr thin film, cm^{-1}): ν 3148, 2947, 1702, 1633, 1391, 1358, 1244, 1195, 1101, 989, 743, 694, 672, 587.

IX. NMR Spectra of New Compounds

cqq250220-2



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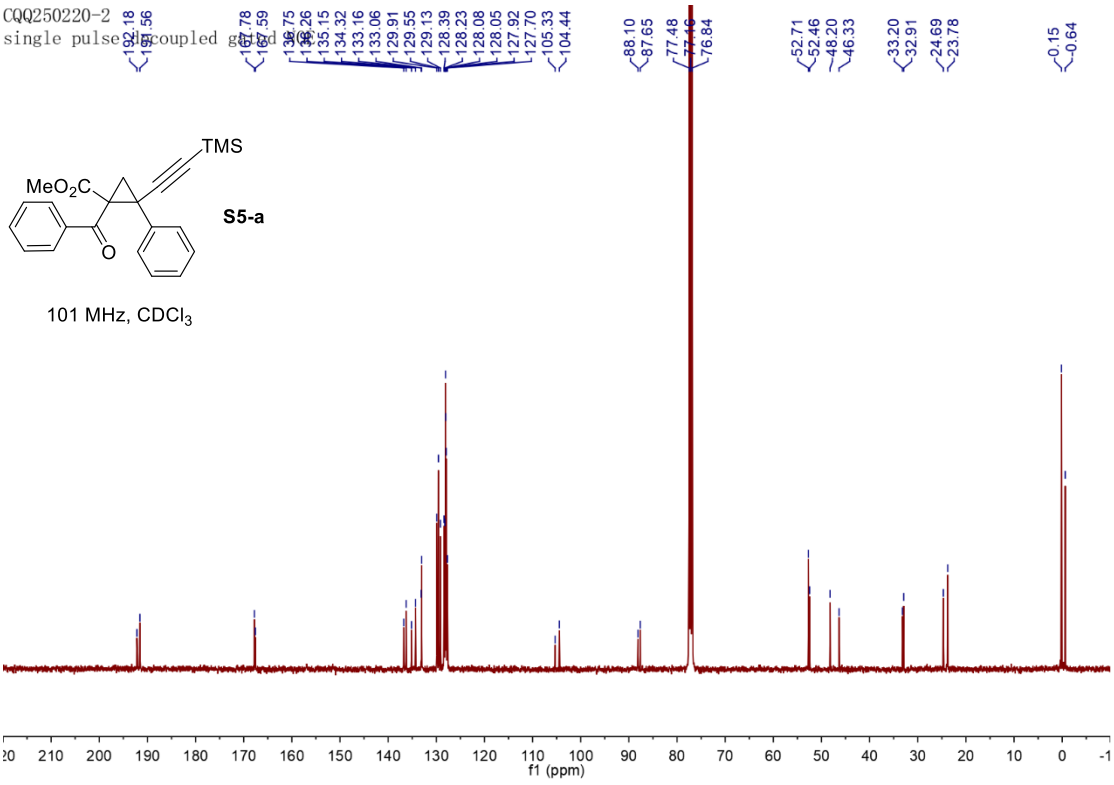
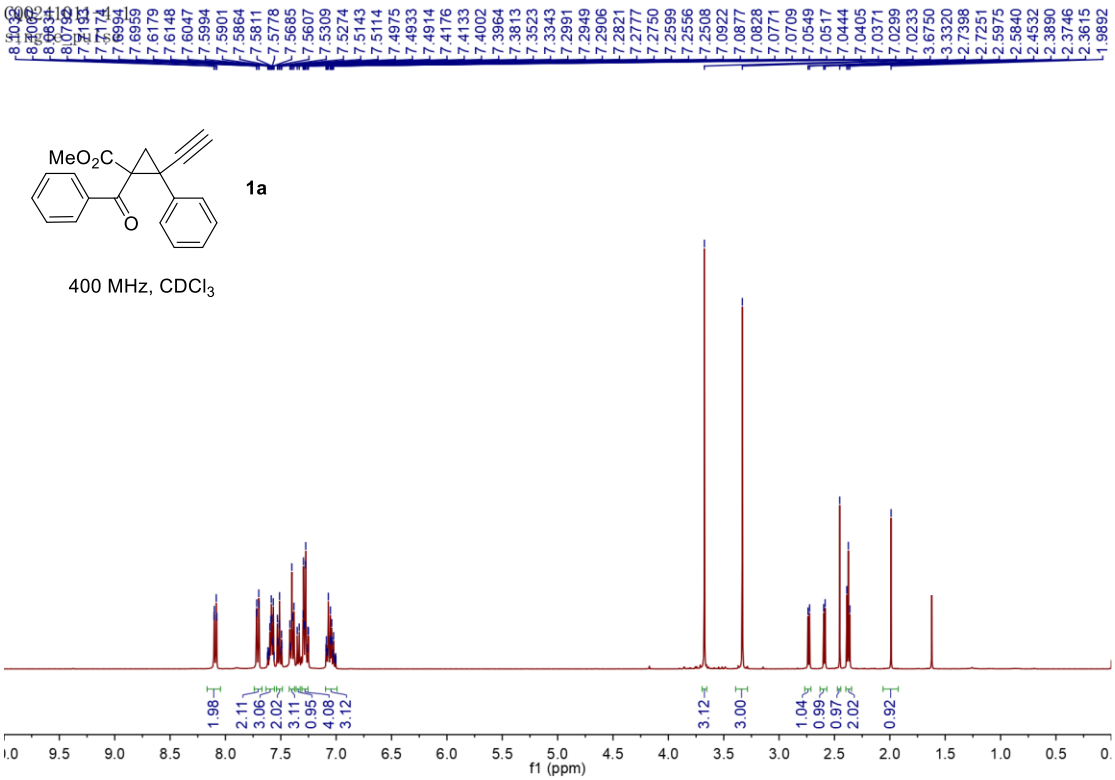
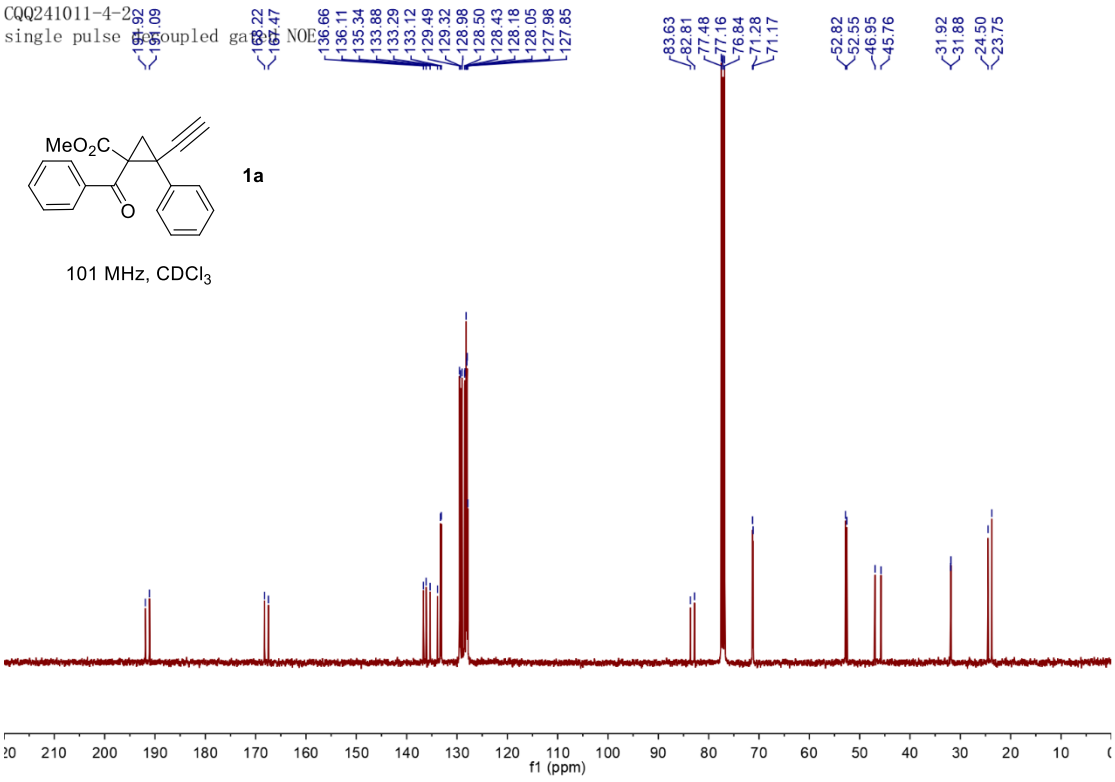
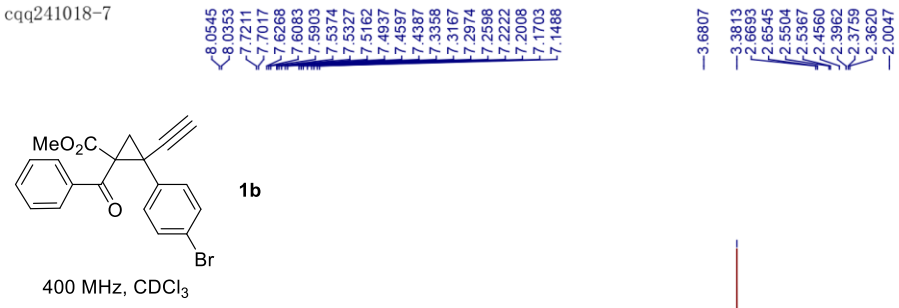
single pulse decoupled gated




MeO2C
O
1a
400 MHz, CDCl3
f1 (ppm)

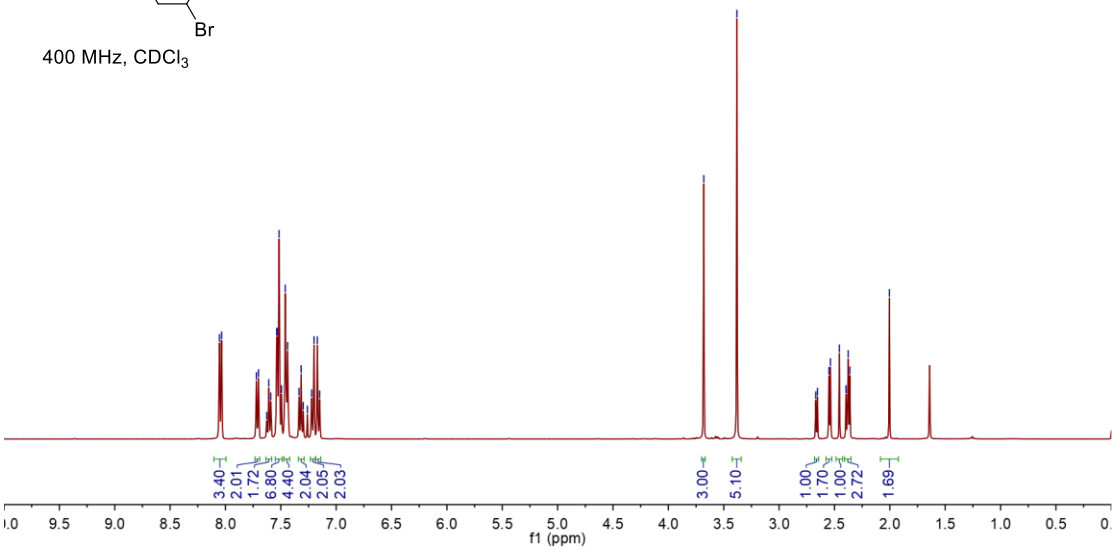

CQQ241011-4-2
single pulse decoupled gated NOE
MeO2C
O
1a
101 MHz, CDCl3
f1 (ppm)

cqq241018-7

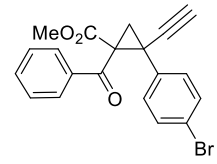


1b

400 MHz, $CDCl_3$

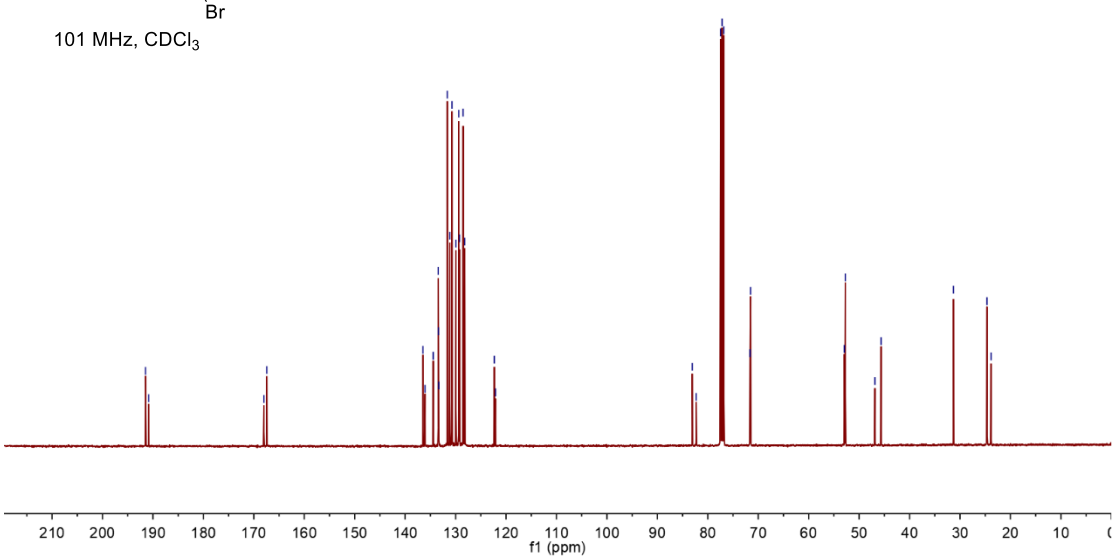


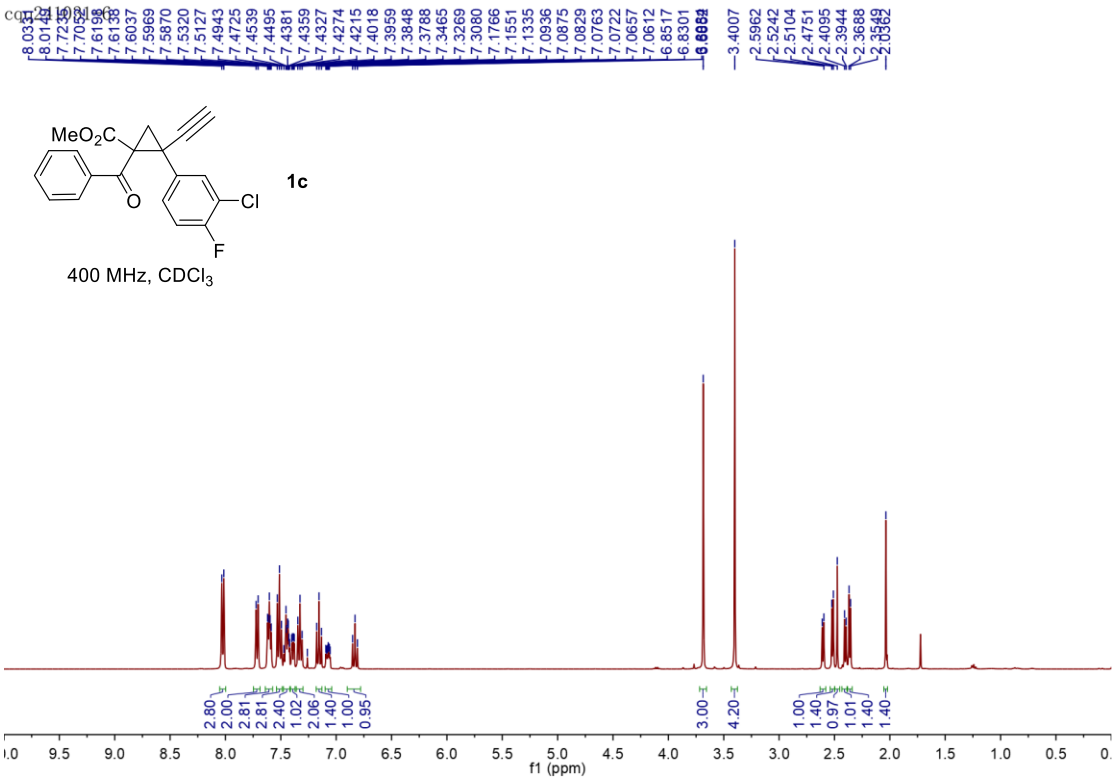
cqq241018-7

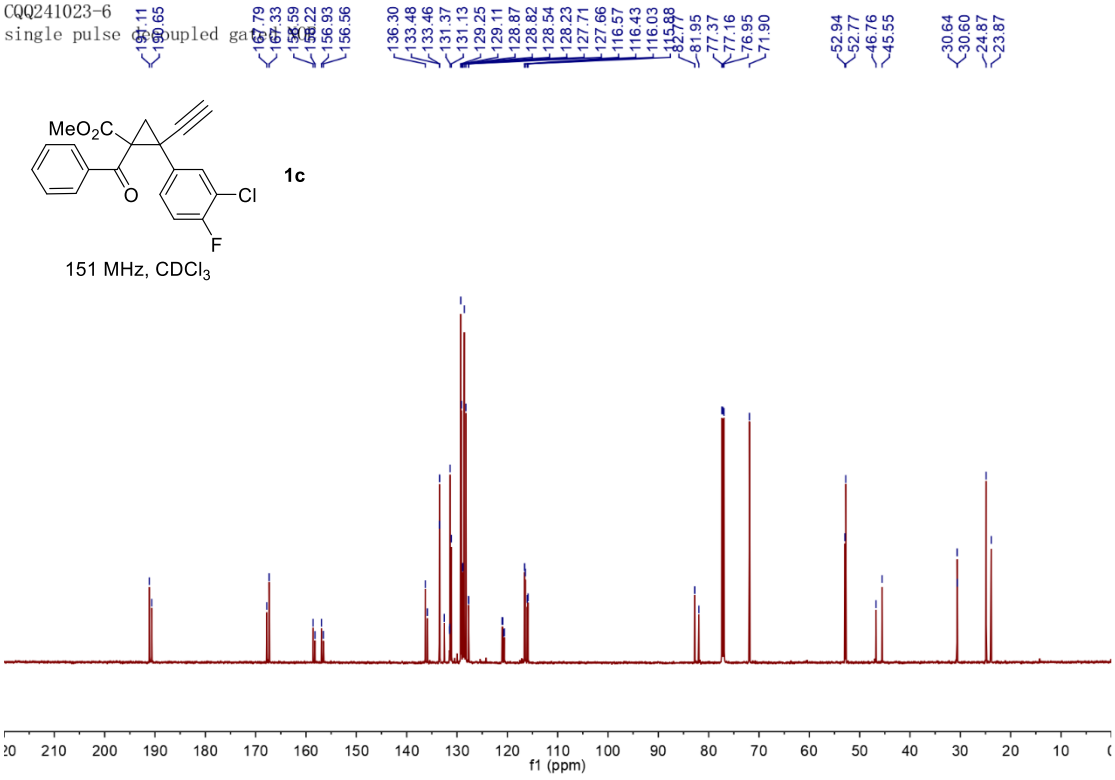


1b

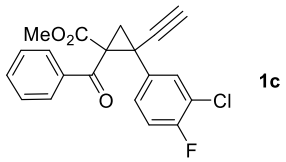
101 MHz, $CDCl_3$




MeO2C
O
Cl
F
1c
400 MHz, CDCl3
f1 (ppm)


CQQ241023-6
single pulse decoupled gated
MeO2C
O
Cl
F
1c
151 MHz, CDCl3
f1 (ppm)

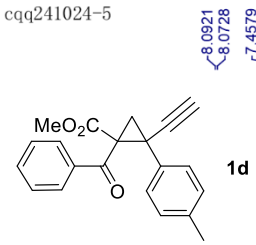
cqq241026-2



1c

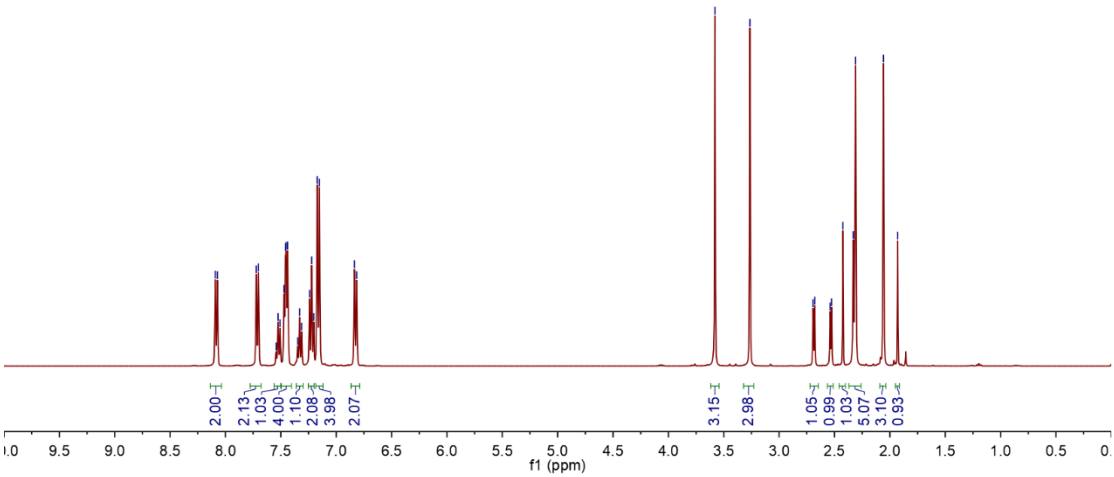
376 MHz, $CDCl_3$

cqq241024-5

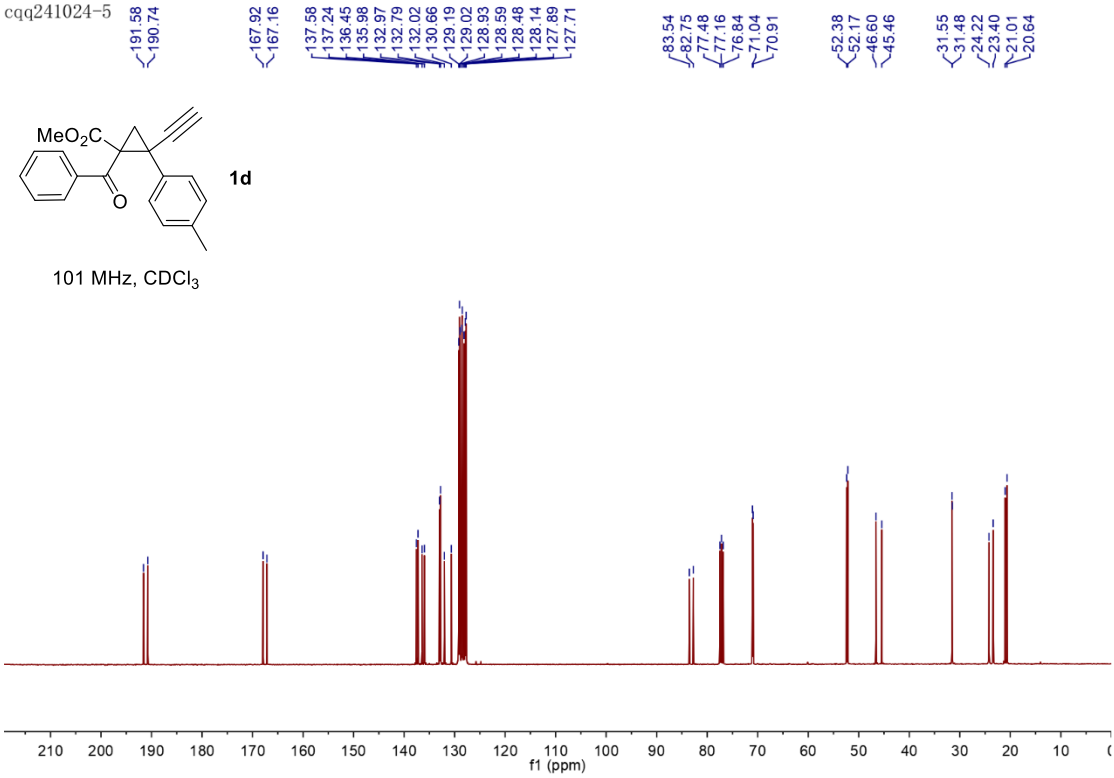


1d

400 MHz, $CDCl_3$



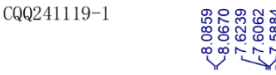
cqq241024-5

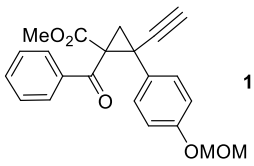


1d

101 MHz, $CDCl_3$

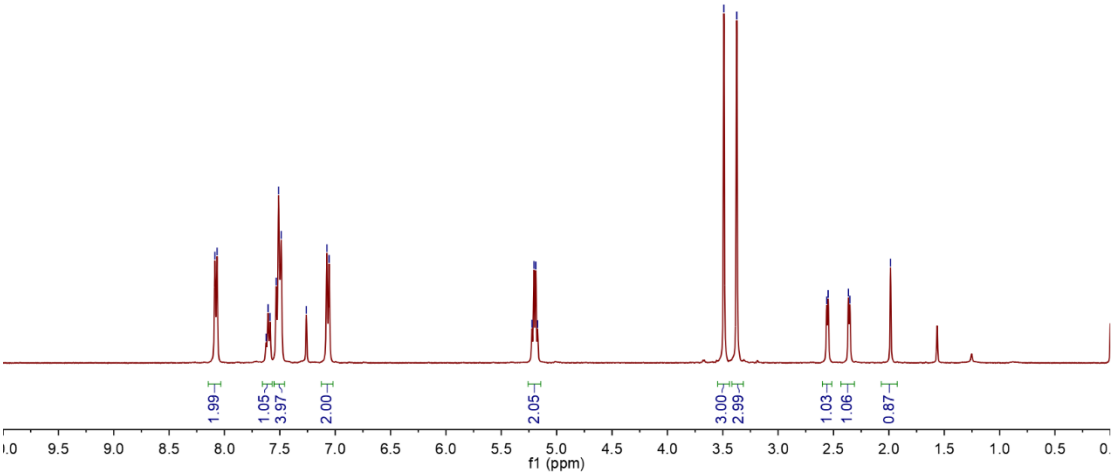
CQQ241119-1



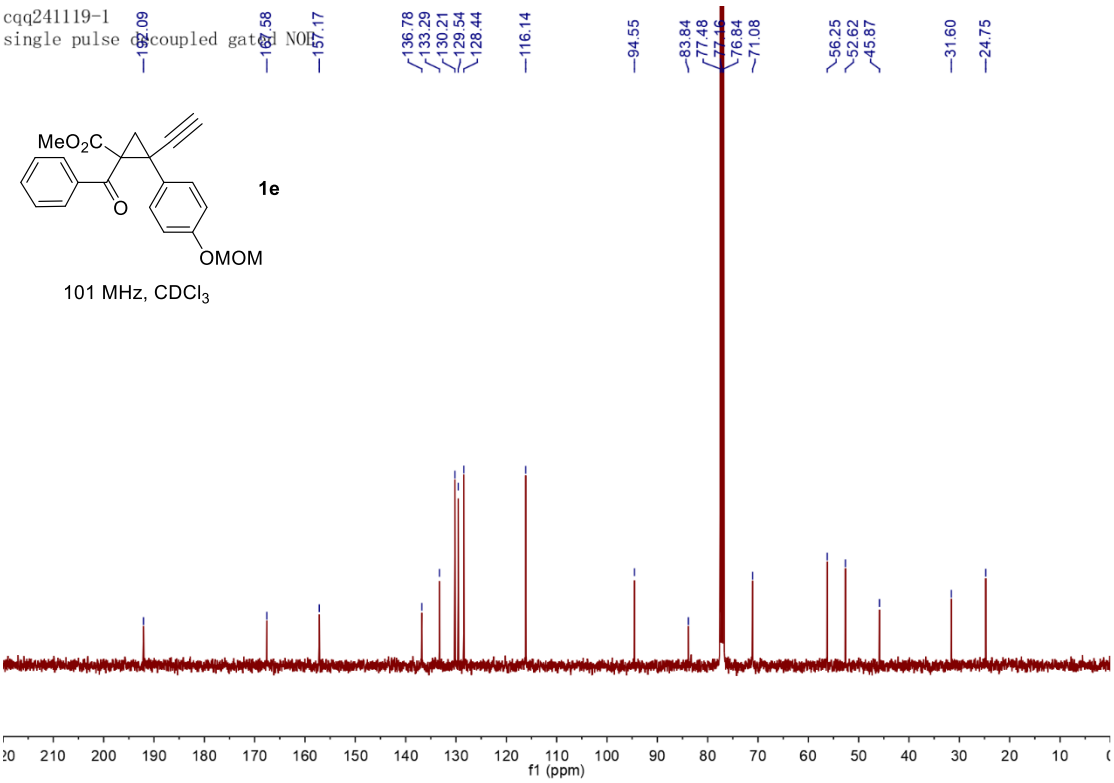


1e

400 MHz, $CDCl_3$

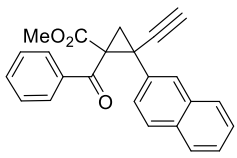


cqq241119-1
single pulse decoupled gated NOE



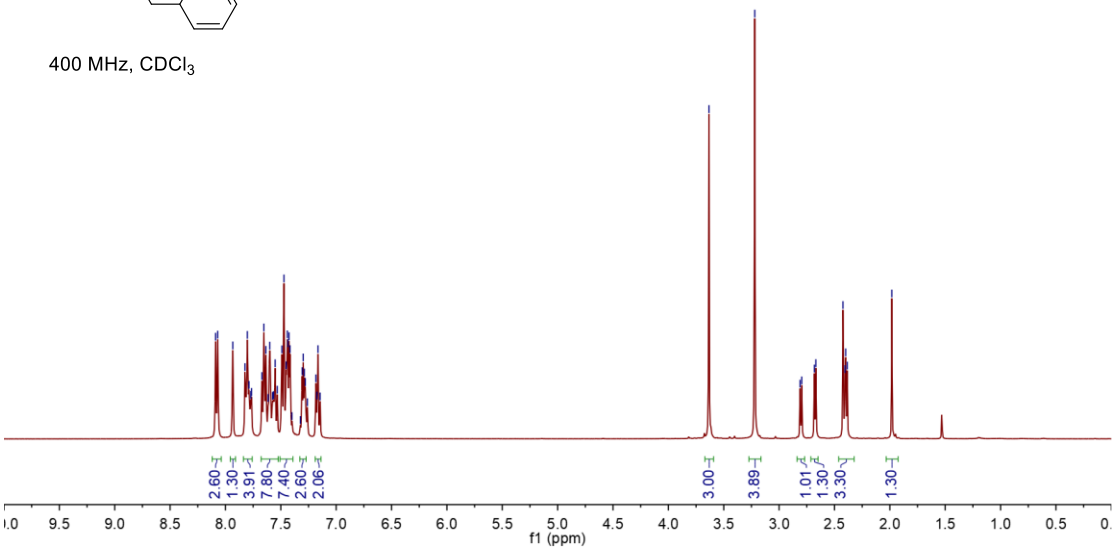
1e

101 MHz, $CDCl_3$

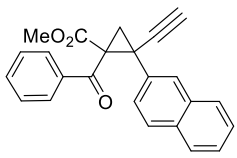


1f

400 MHz, $CDCl_3$

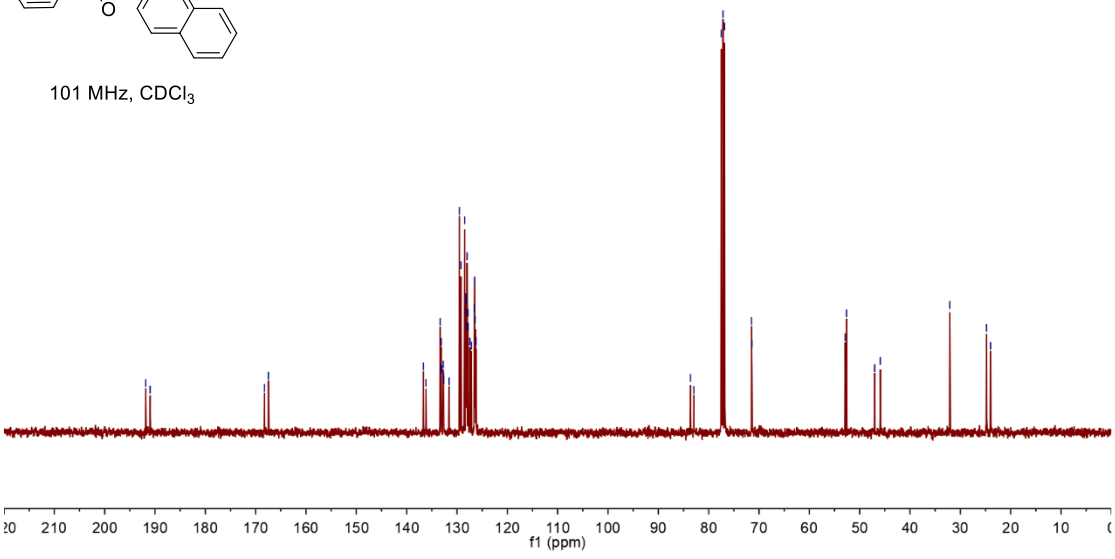


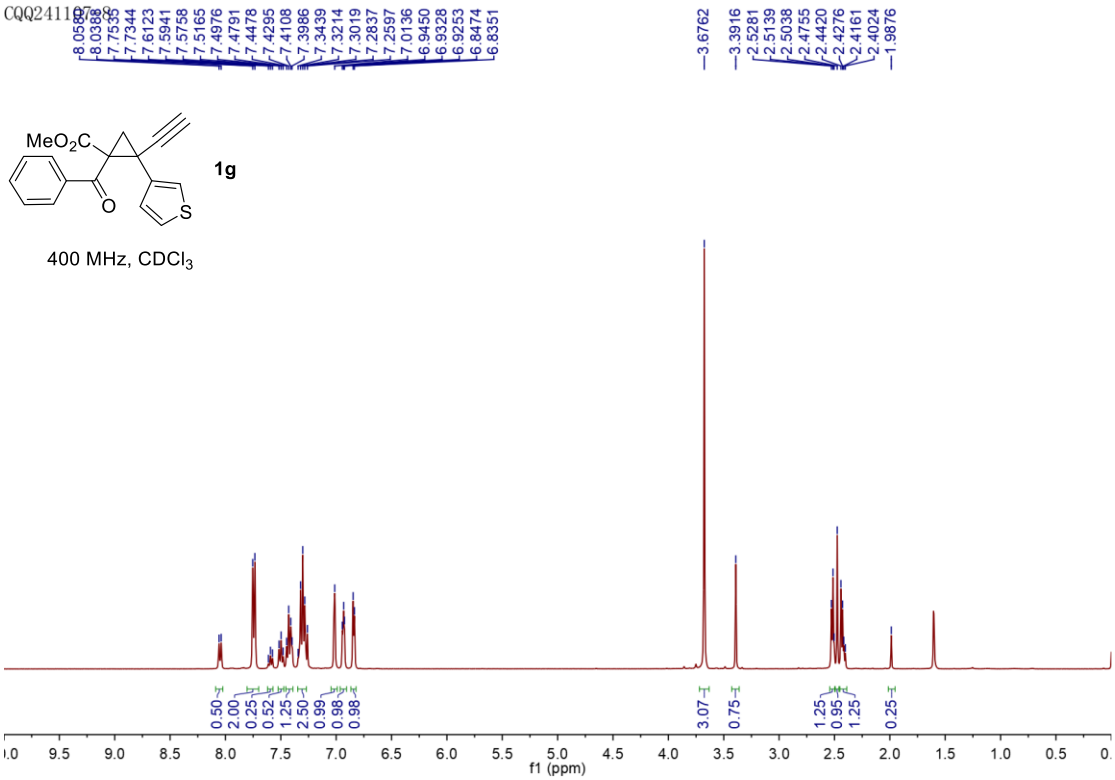
cqq241029-5
single pulse decoupled gated NOE

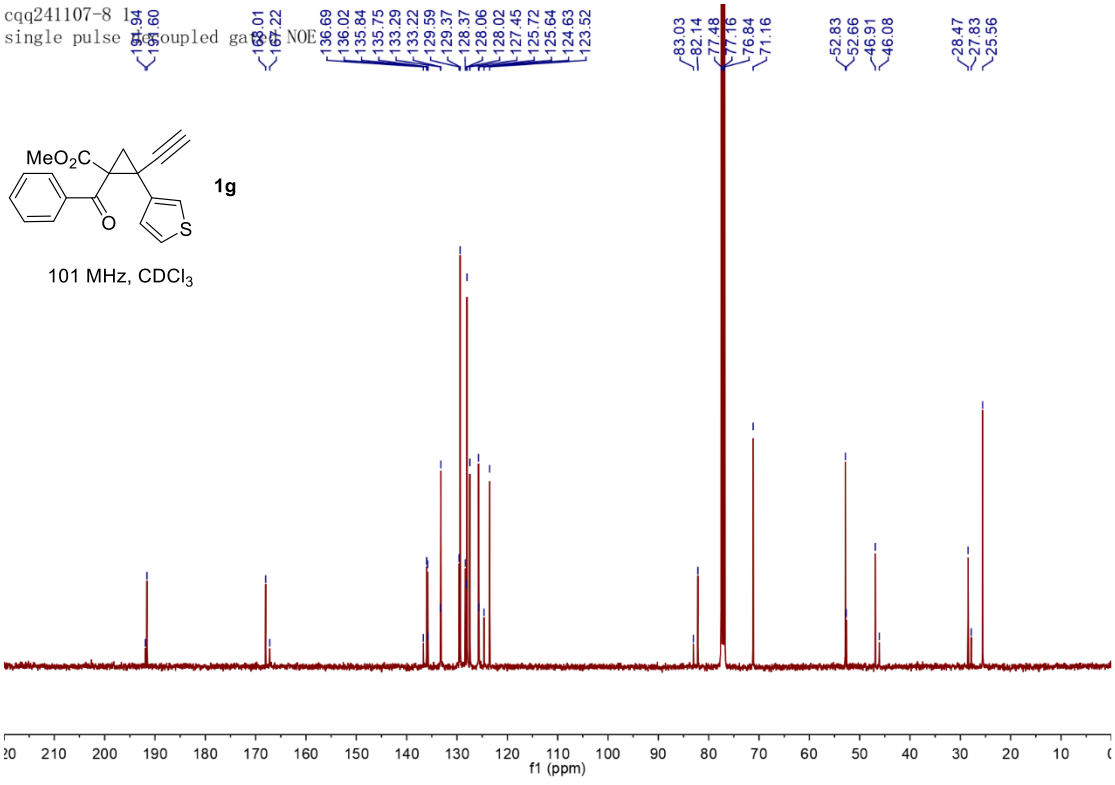


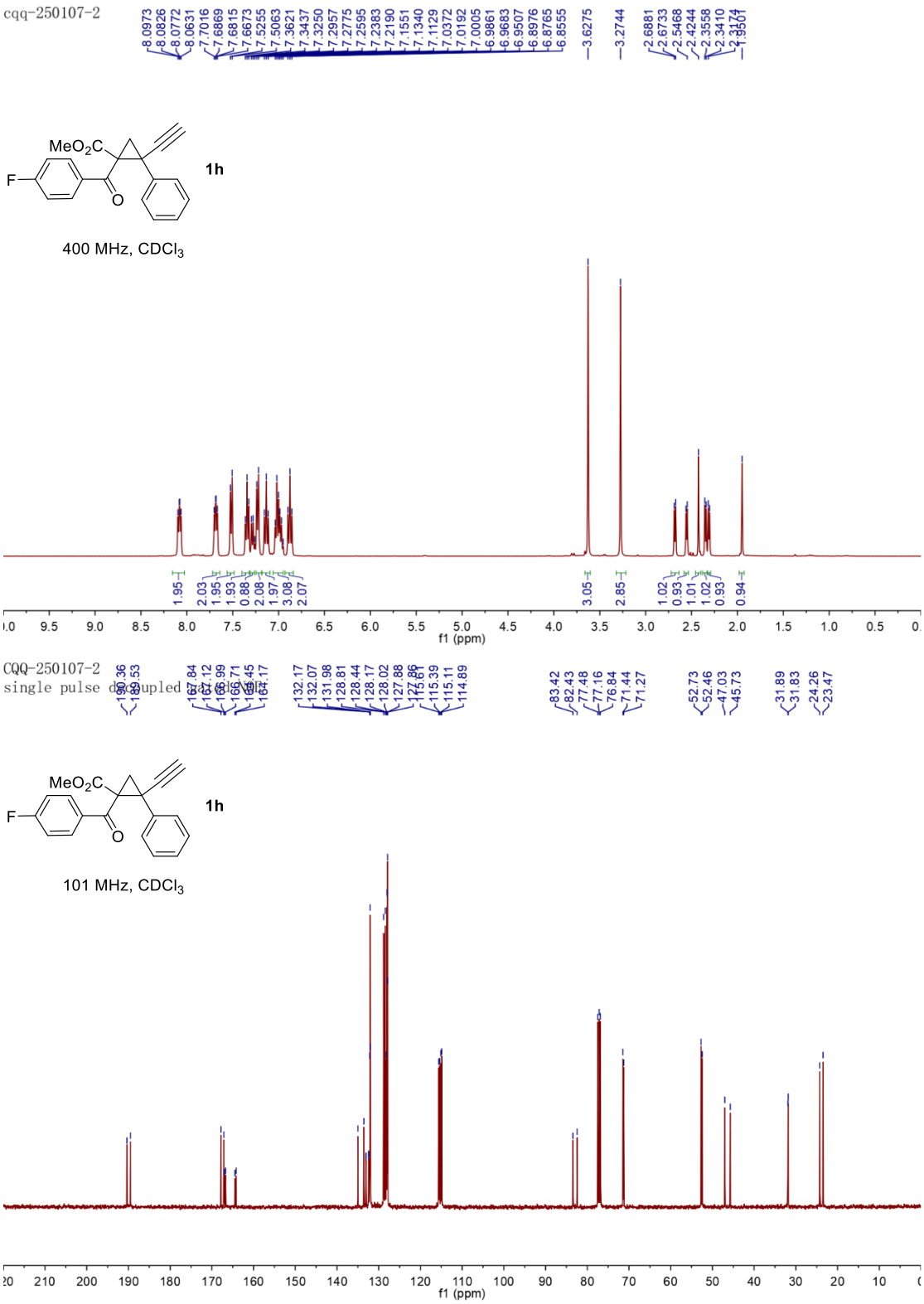
1f

101 MHz, $CDCl_3$

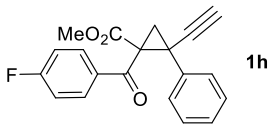



MeO2C
O
S
1g
400 MHz, CDCl3
f1 (ppm)


MeO2C
O
S
1g
101 MHz, CDCl3
f1 (ppm)


cqq-250107-2
8.0973
8.0826
8.0772
8.0631
7.7016
7.6869
7.6815
7.6673
7.5255
7.5063
7.3621
7.3437
7.3250
7.2957
7.2775
7.2595
7.2383
7.2190
7.1551
7.1340
7.1129
7.0372
7.0192
7.0005
6.9861
6.9683
6.9507
6.8976
6.8765
6.8555
3.6275
3.2744
2.6881
2.6733
2.5468
2.4244
2.3558
2.3410
MeO2C
F
O
1h
400 MHz, CDCl3
1.95
2.03
1.95
1.93
0.88
2.08
1.97
3.08
2.07
3.05
2.85
1.02
0.93
1.01
1.02
0.93
0.94
f1 (ppm)
CQQ-250107-2
single pulse decoupled
150.36
148.53
132.17
132.07
131.98
128.81
128.44
128.17
128.02
115.39
115.11
114.89
83.42
82.43
77.48
77.16
76.84
71.44
71.27
52.73
52.46
47.03
45.73
31.89
31.83
24.26
23.47
MeO2C
F
O
1h
101 MHz, CDCl3
f1 (ppm)

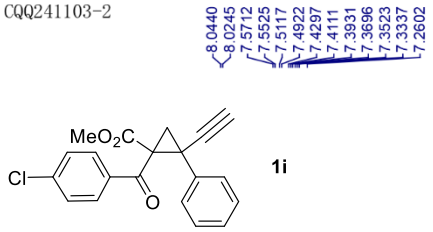
cqq250107-2



1h

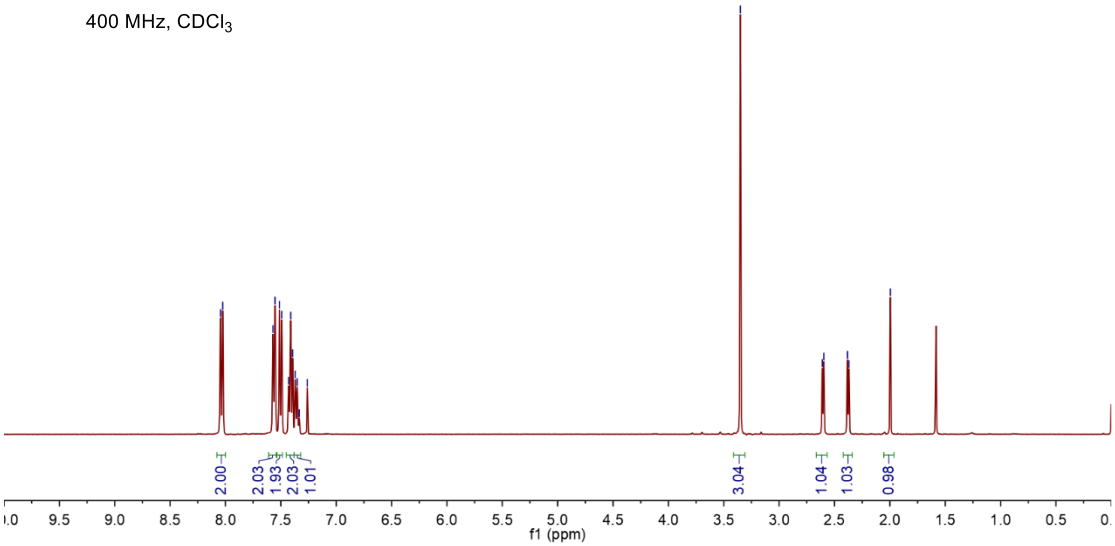
376 MHz, $CDCl_3$

CQQ241103-2

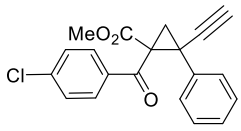


1i

400 MHz, $CDCl_3$

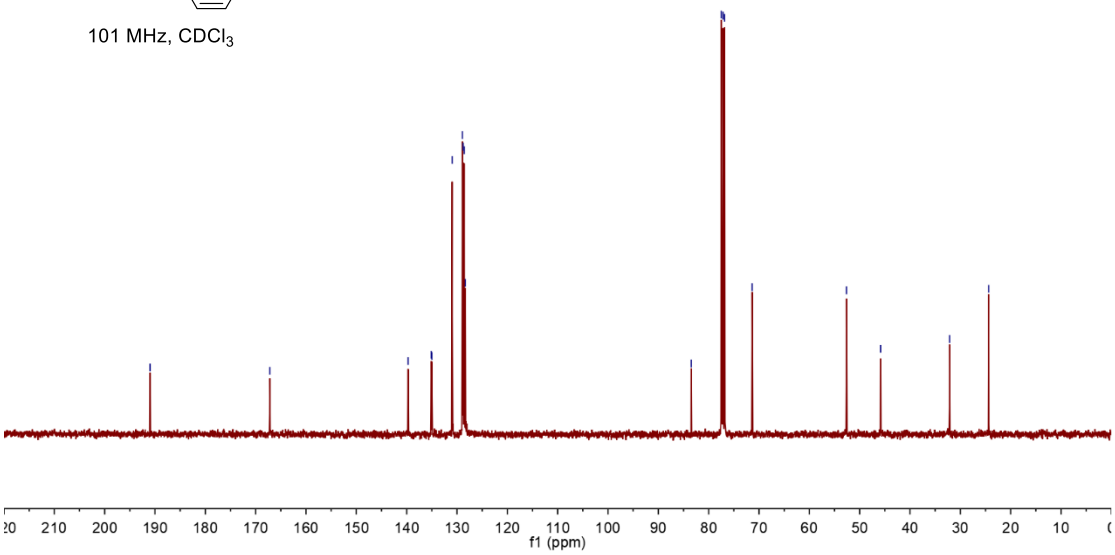


CQQ241102-1
single pulse decoupled gated NOE

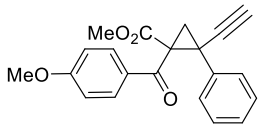


1i

101 MHz, $CDCl_3$

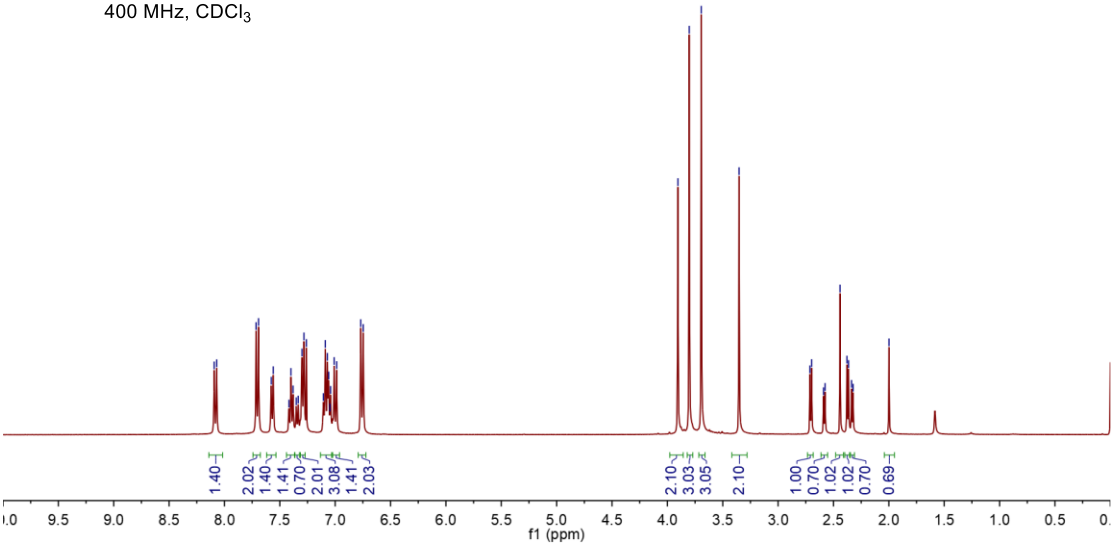


cqq-241109-3

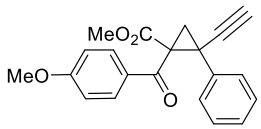


1j

400 MHz, $CDCl_3$

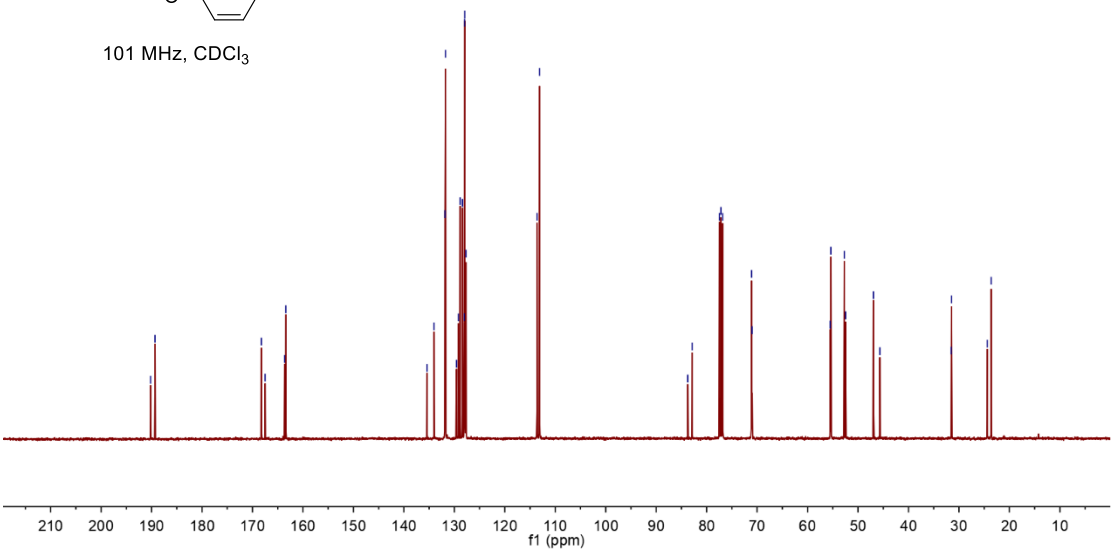


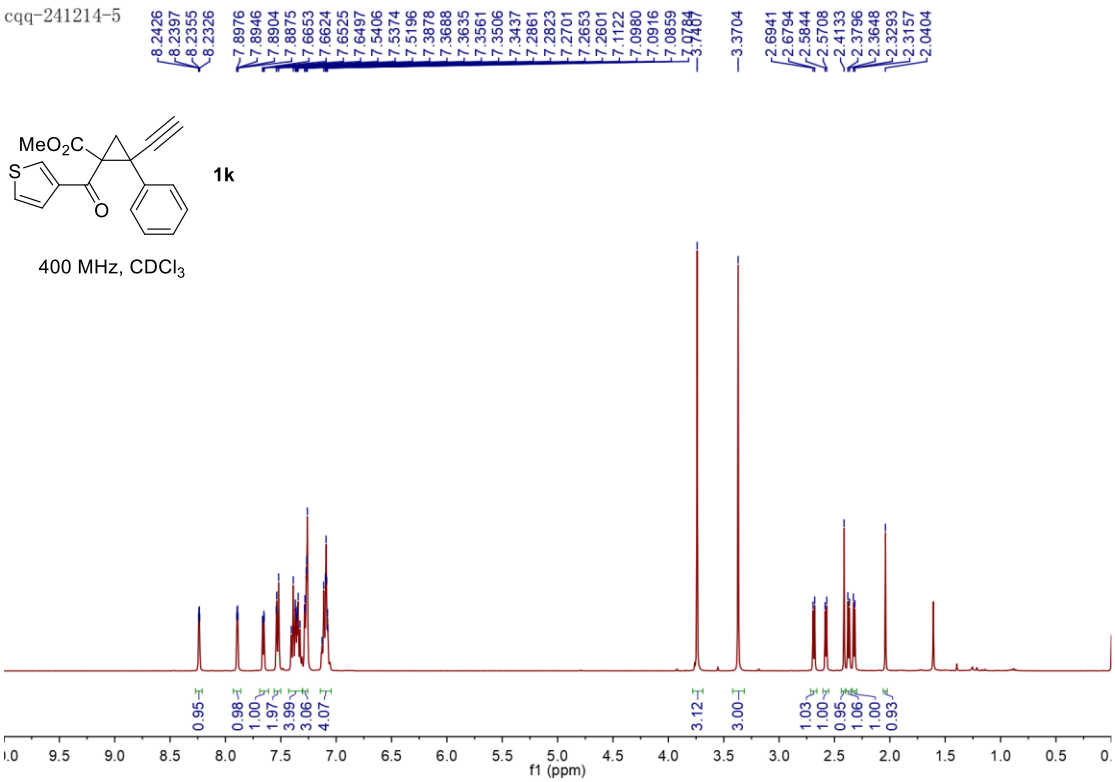
cqq241108-4

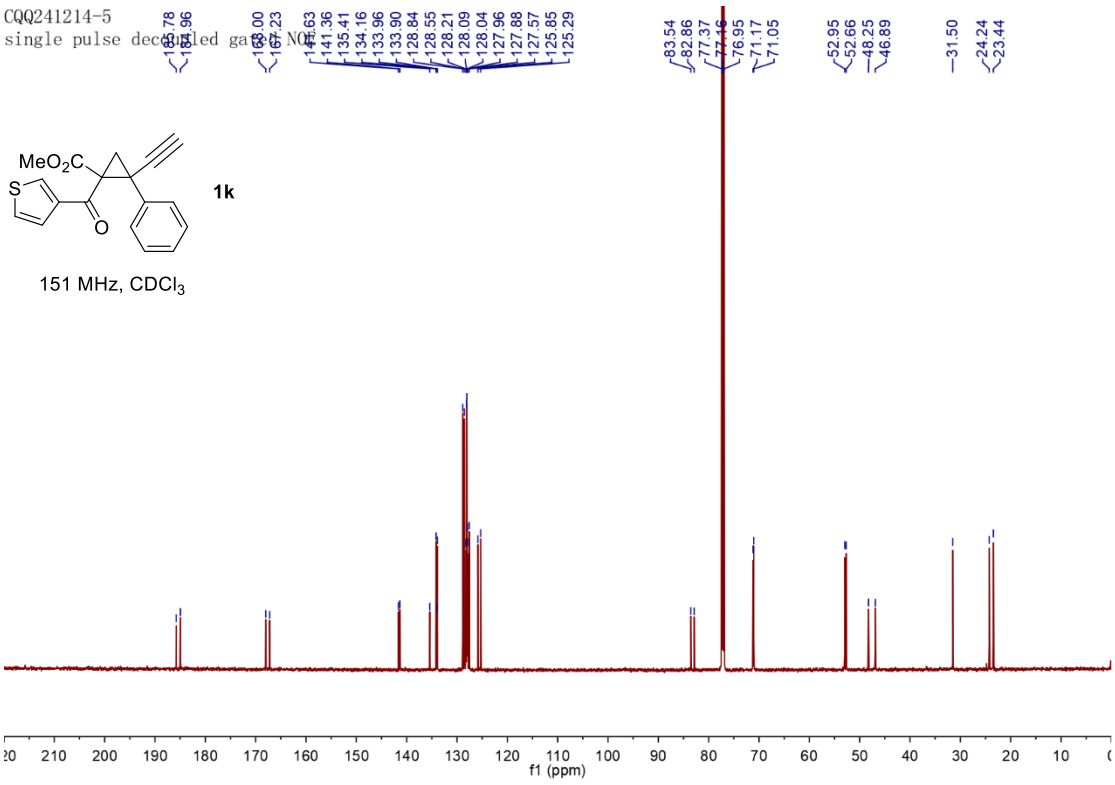


1j

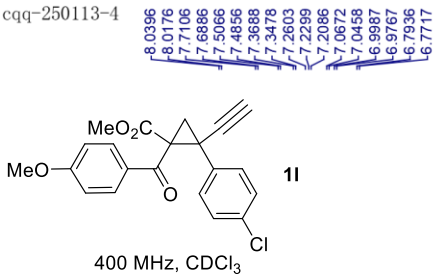
101 MHz, $CDCl_3$




cqq-241214-5
MeO2C
S
O
1k
400 MHz, CDCl3
f1 (ppm)


CQQ241214-5
single pulse decoupled gated NOE
MeO2C
S
O
1k
151 MHz, CDCl3
f1 (ppm)

cqq-250113-4

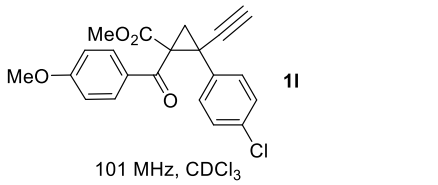


1l

400 MHz, $CDCl_3$

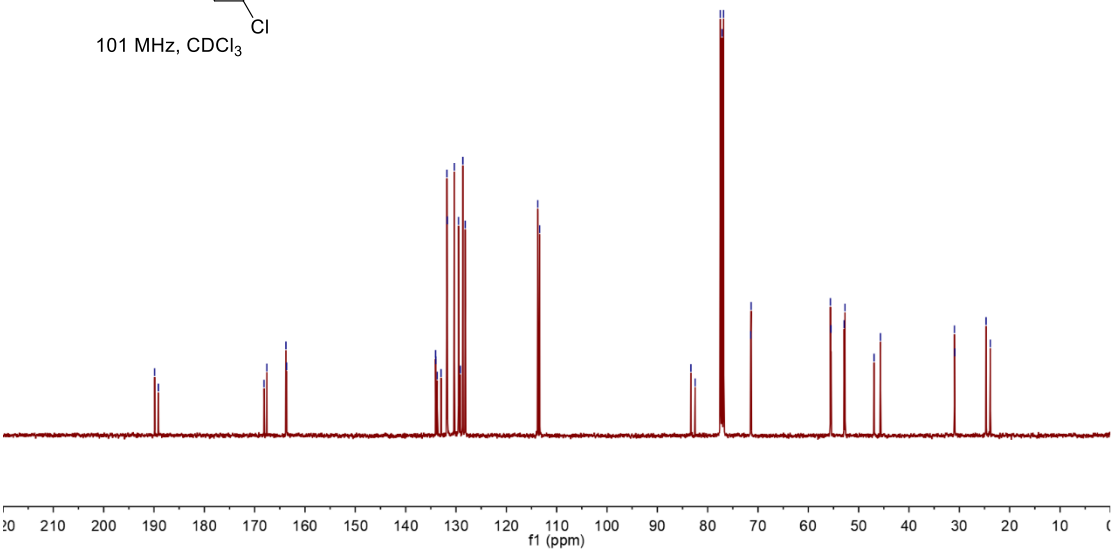
CQQ241113-4

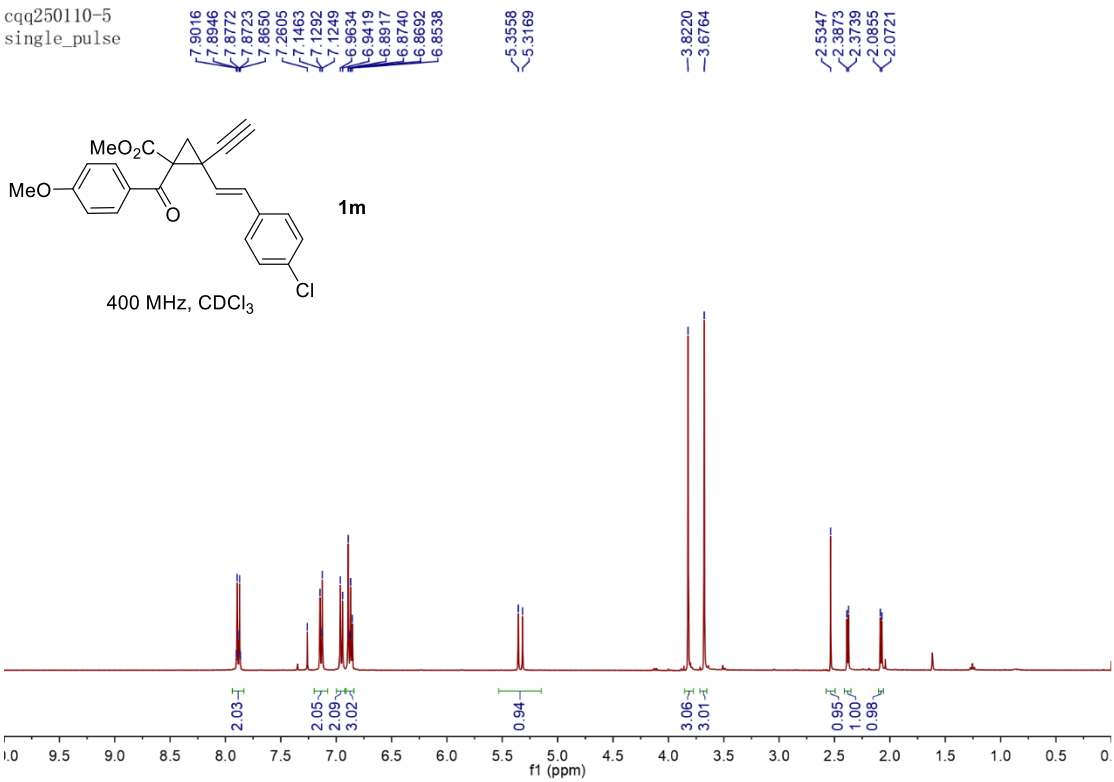
single pulse decoupled gated DEPTH

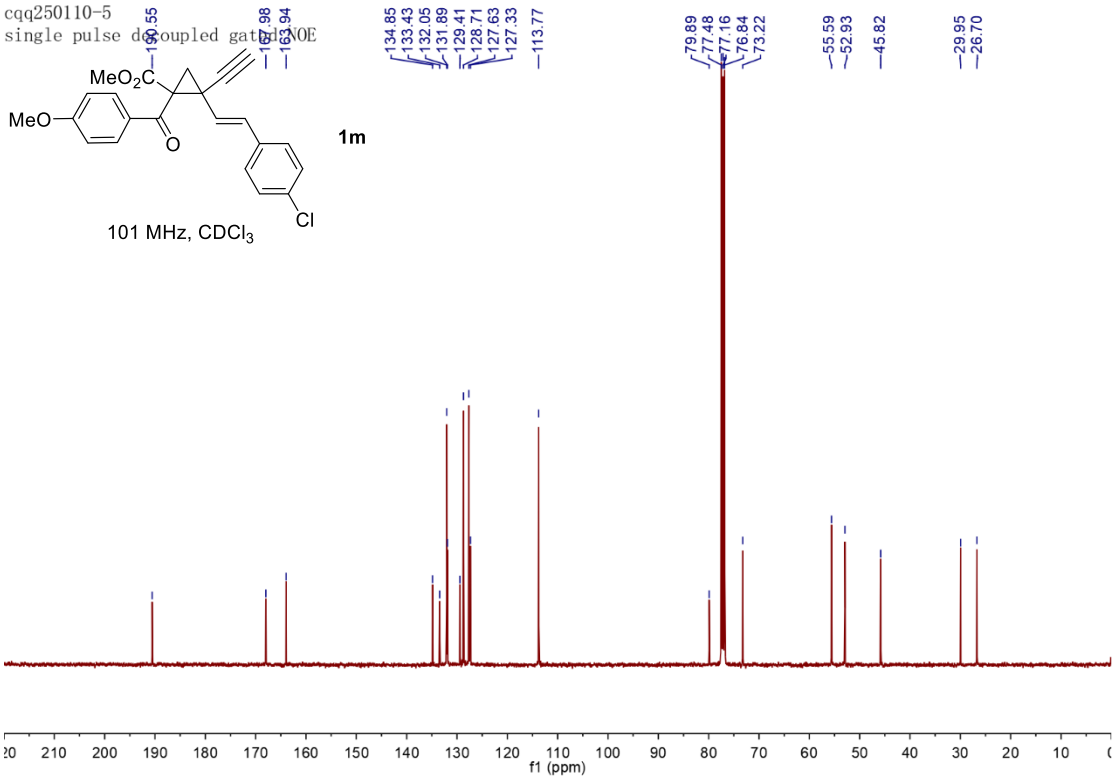


1l

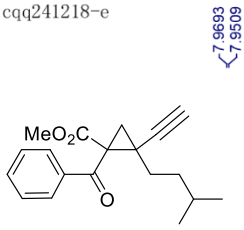
101 MHz, $CDCl_3$




cqq250110-5
single_pulse
7.9016
7.8946
7.8772
7.8723
7.8650
7.2605
7.1463
7.1292
7.1249
6.9634
6.9419
6.8917
6.8740
6.8692
6.8538
5.3558
5.3169
3.8220
3.6764
2.5347
2.3873
2.3739
2.0855
2.0721
MeO2C
MeO
O
Cl
1m
400 MHz, CDCl3
2.03
2.05
2.09
3.02
0.94
3.06
3.01
0.95
1.00
0.98
f1 (ppm)

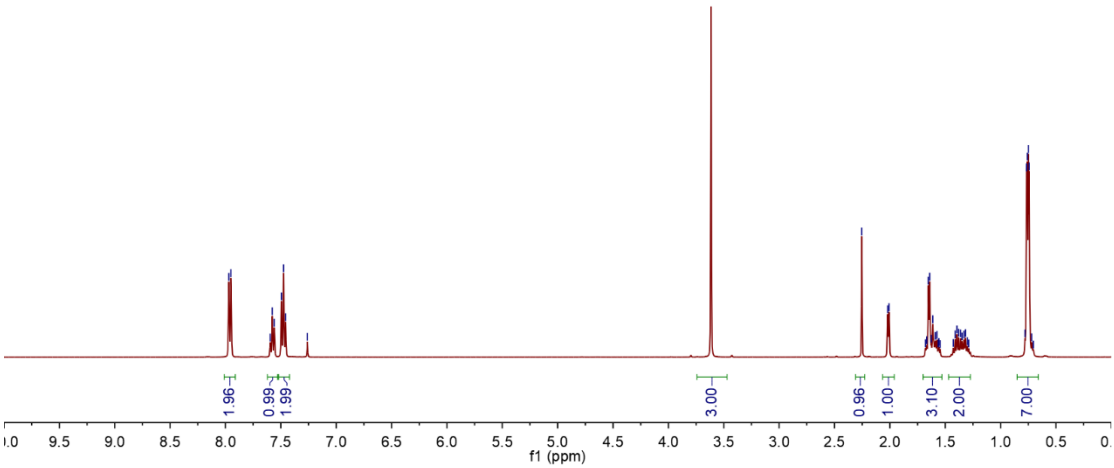

cqq250110-5
single pulse decoupled gated NOE
190.55
167.98
163.94
134.85
133.43
132.05
131.89
129.41
128.71
127.63
127.33
113.77
79.89
77.48
77.16
76.84
73.22
55.59
52.93
45.82
29.95
26.70
MeO2C
MeO
O
Cl
1m
101 MHz, CDCl3
f1 (ppm)

cqq241218-e

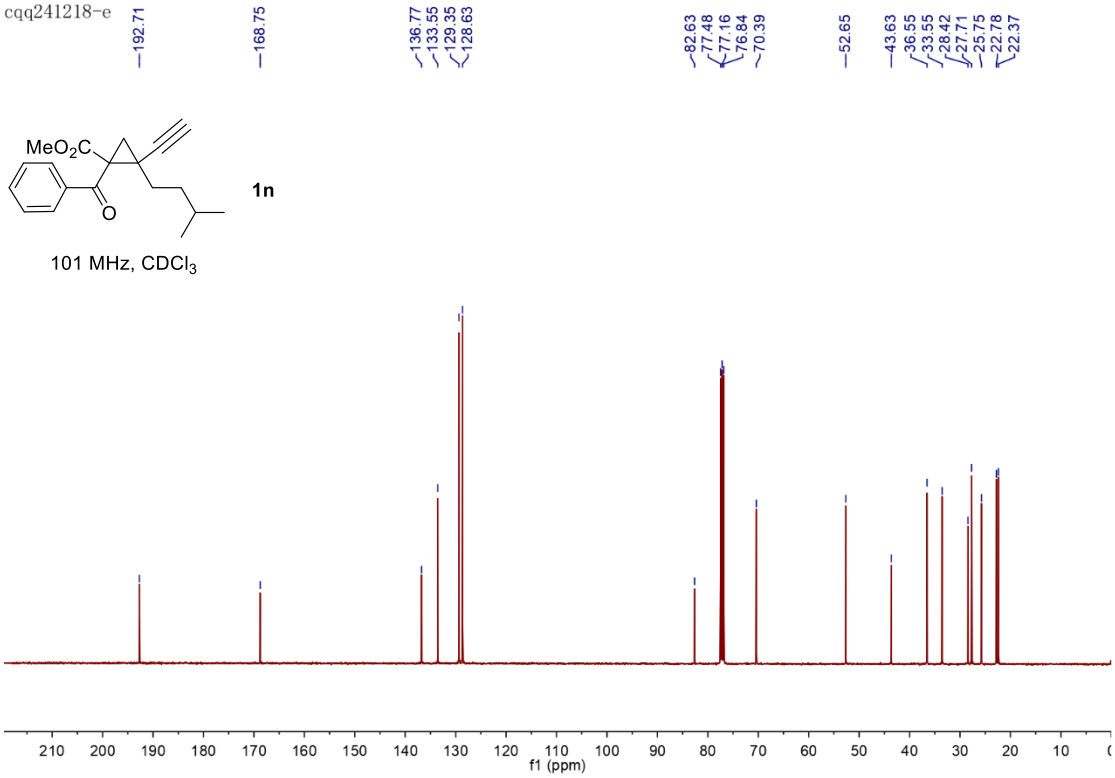


1n

400 MHz, $CDCl_3$



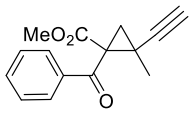
cqq241218-e



1n

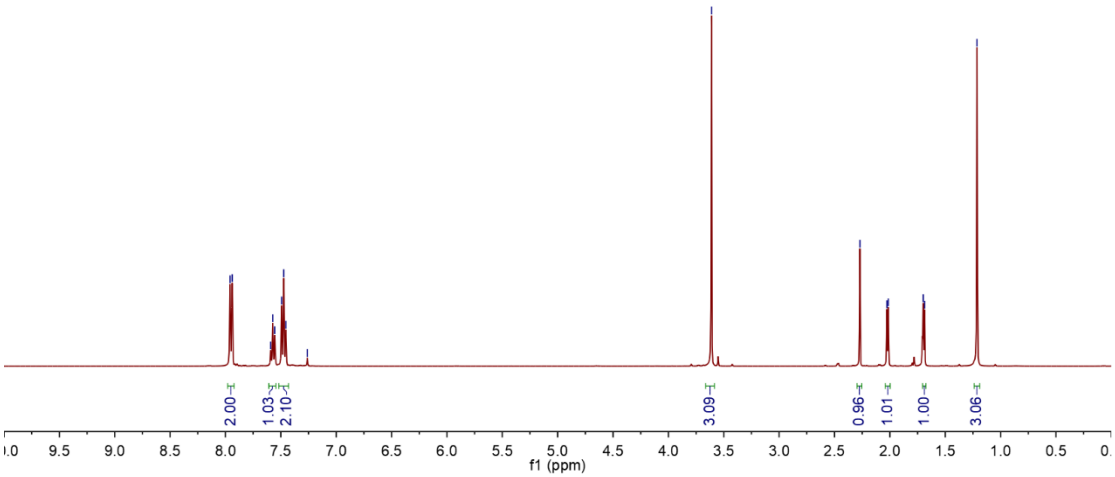
101 MHz, $CDCl_3$

cqq241120-2

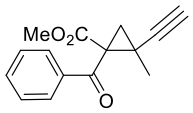


1o

400 MHz, $CDCl_3$

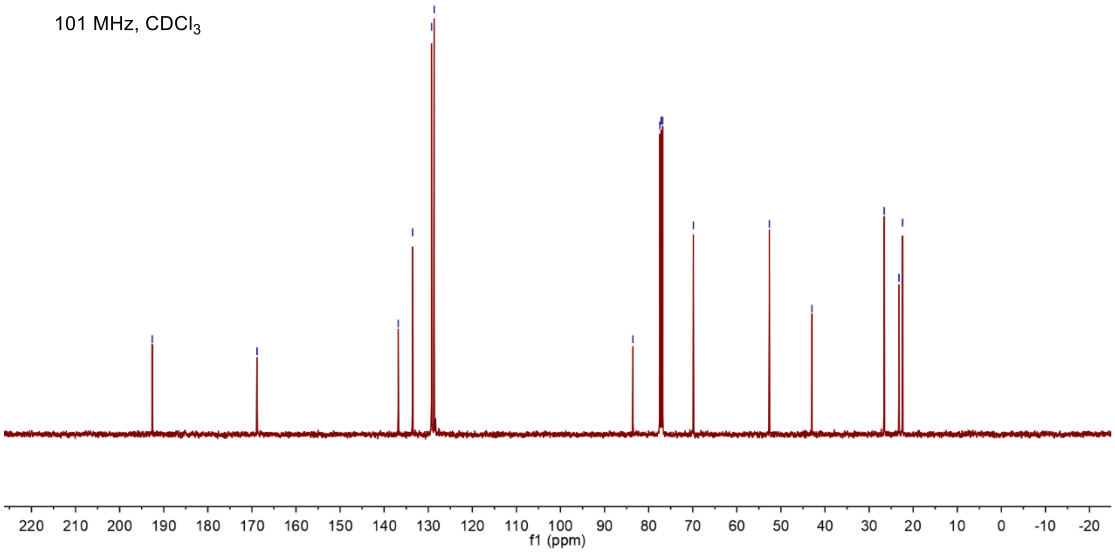


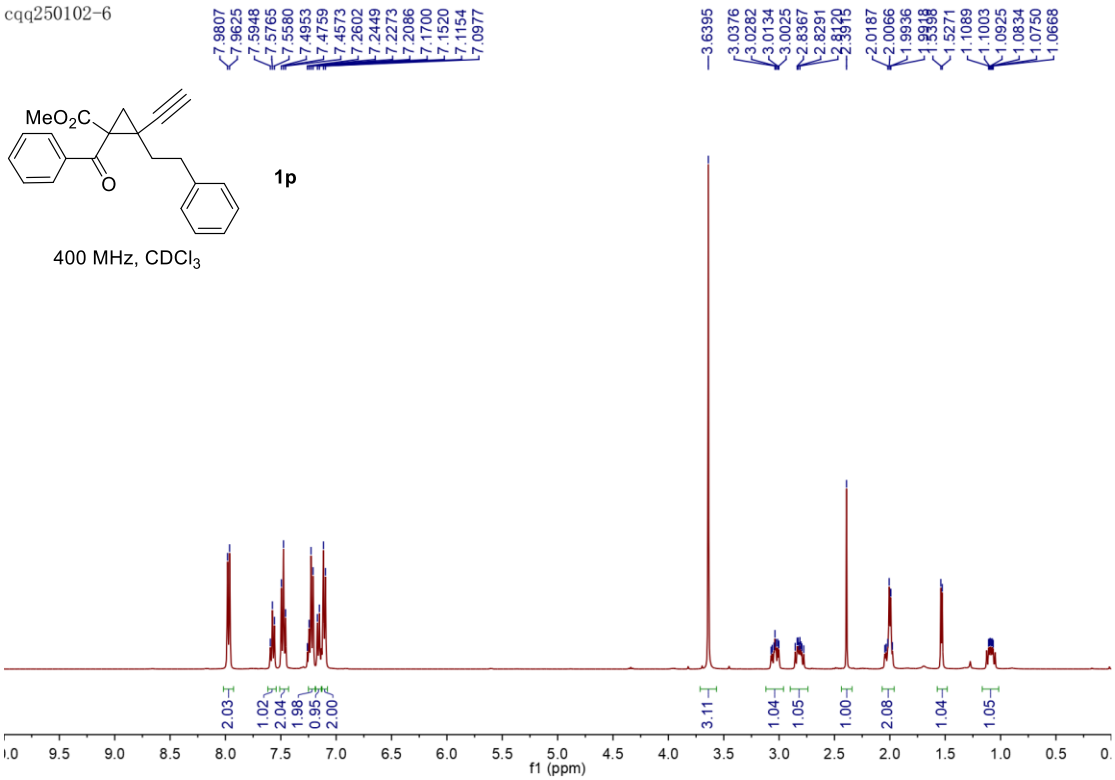
cqq241120-2
single pulse decoupled gated NOE

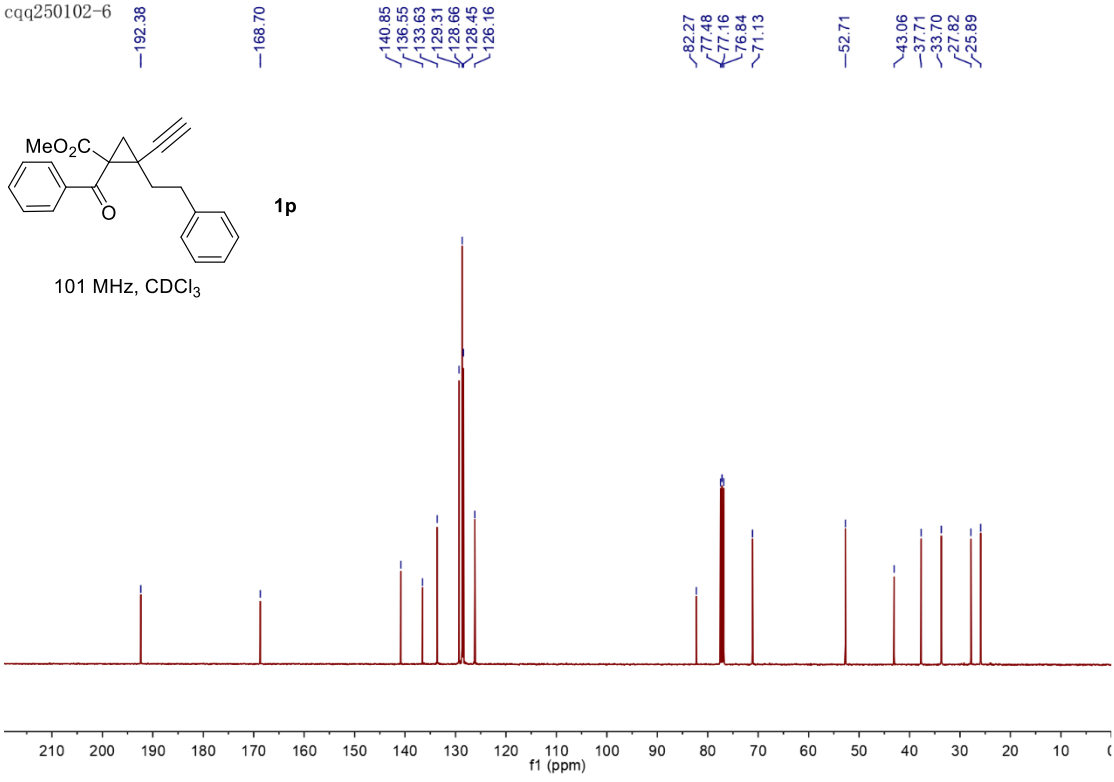


1o

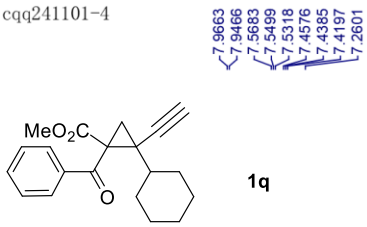
101 MHz, $CDCl_3$




cqq250102-6
7.9807
7.9625
7.5948
7.5765
7.5580
7.4953
7.4759
7.4573
7.2602
7.2449
7.2273
7.2086
7.1700
7.1520
7.1154
7.0977
3.6395
3.0376
3.0282
3.0134
3.0025
2.8367
2.8291
2.3915
2.0187
2.0066
1.9936
1.5271
1.1089
1.1003
1.0925
1.0834
1.0750
1.0668
MeO2C
O
1p
400 MHz, CDCl3
2.03
1.02
2.04
1.98
0.95
2.00
3.11
1.04
1.05
1.00
2.08
1.04
1.05
f1 (ppm)


cqq250102-6
192.38
168.70
140.85
136.55
133.63
129.31
128.66
128.45
126.16
82.27
77.48
77.16
76.84
71.13
52.71
43.06
37.71
33.70
27.82
25.89
MeO2C
O
1p
101 MHz, CDCl3
f1 (ppm)

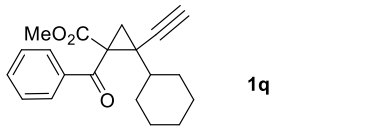
cqq241101-4



1q

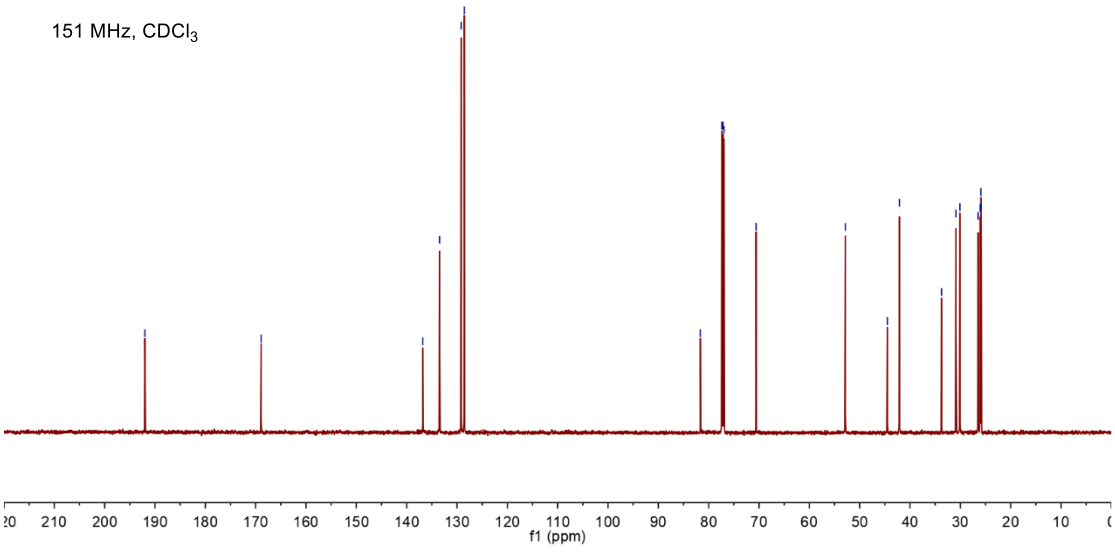
400 MHz, $CDCl_3$

CCQQ241101-4
single pulse decoupled gated NOE

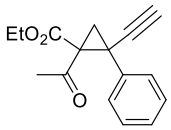


1q

151 MHz, $CDCl_3$

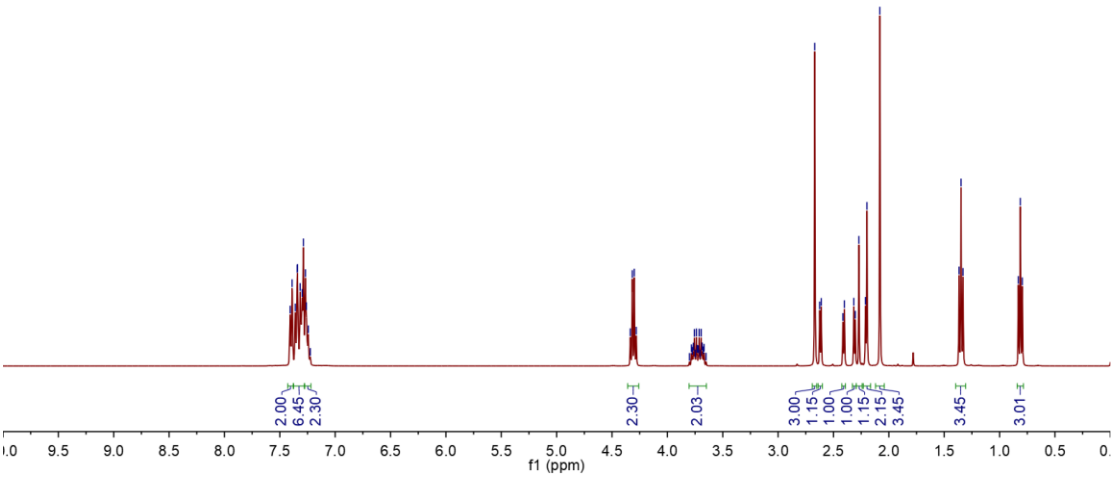


cqq241218-d

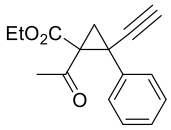


1r

400 MHz, $CDCl_3$



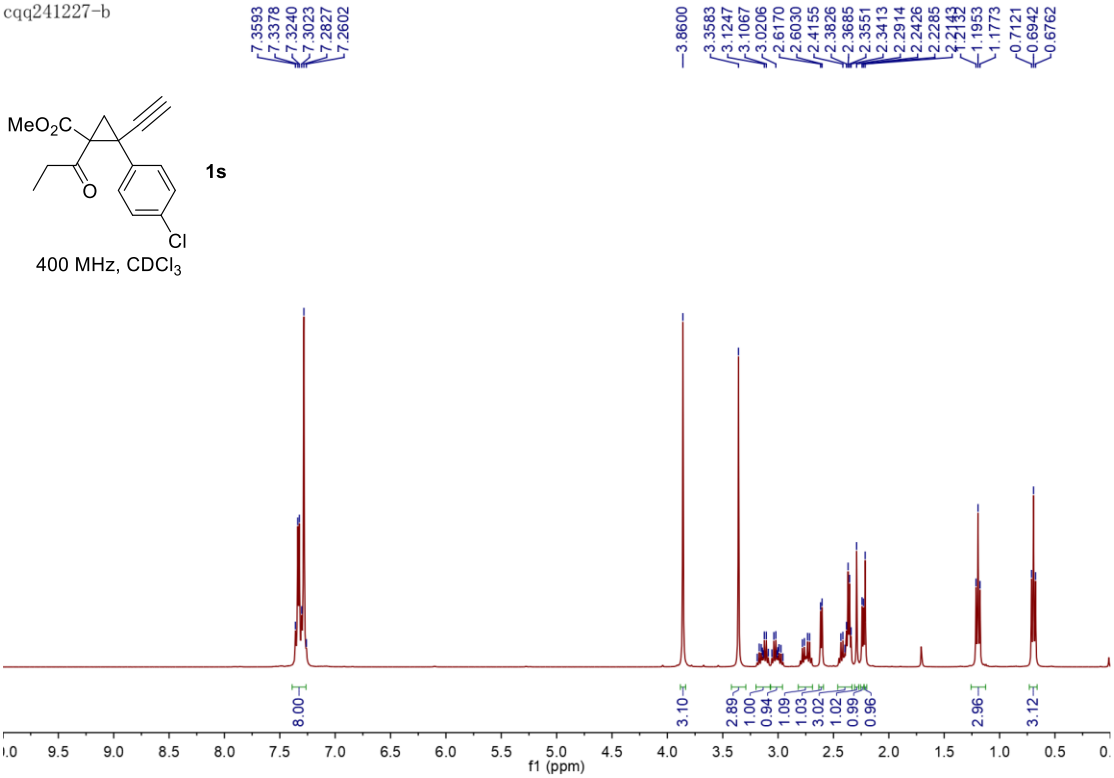
cqq241218



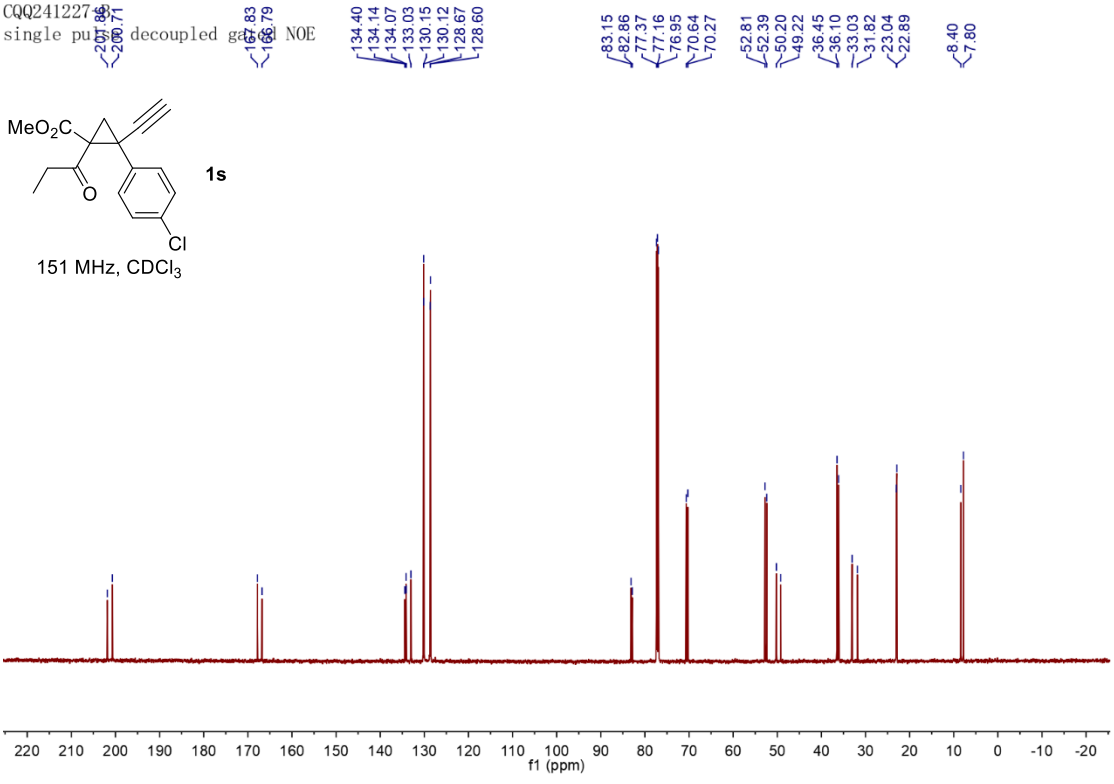
1r

101 MHz, $CDCl_3$

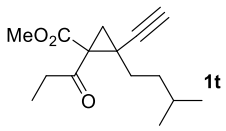
cqq241227-b



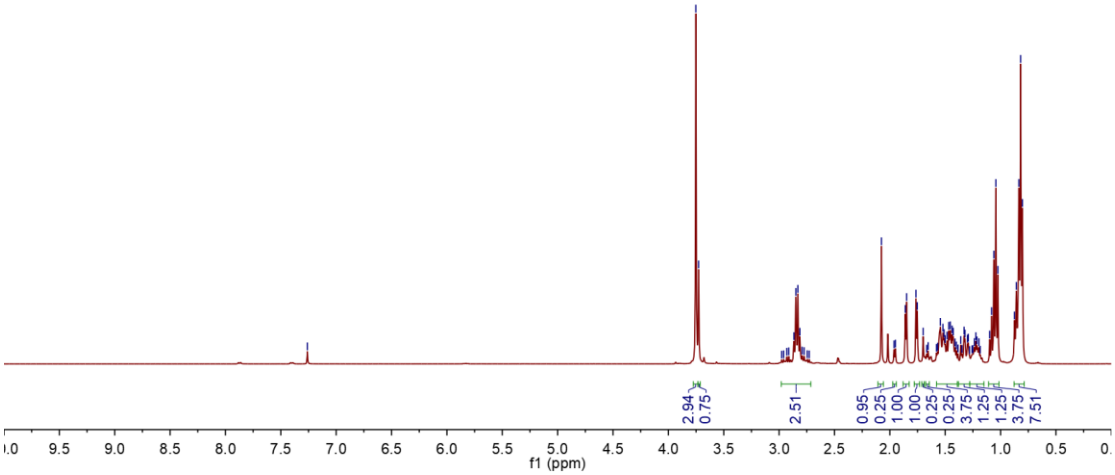
CQQ241227-b
single pulse decoupled gated NOE



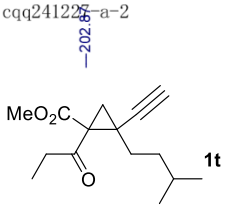
cqq241227-a



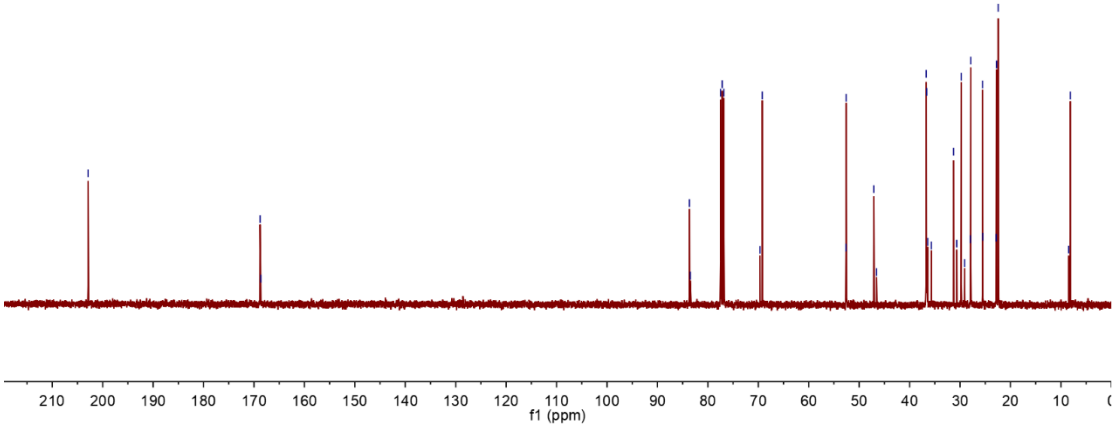
400 MHz, $CDCl_3$

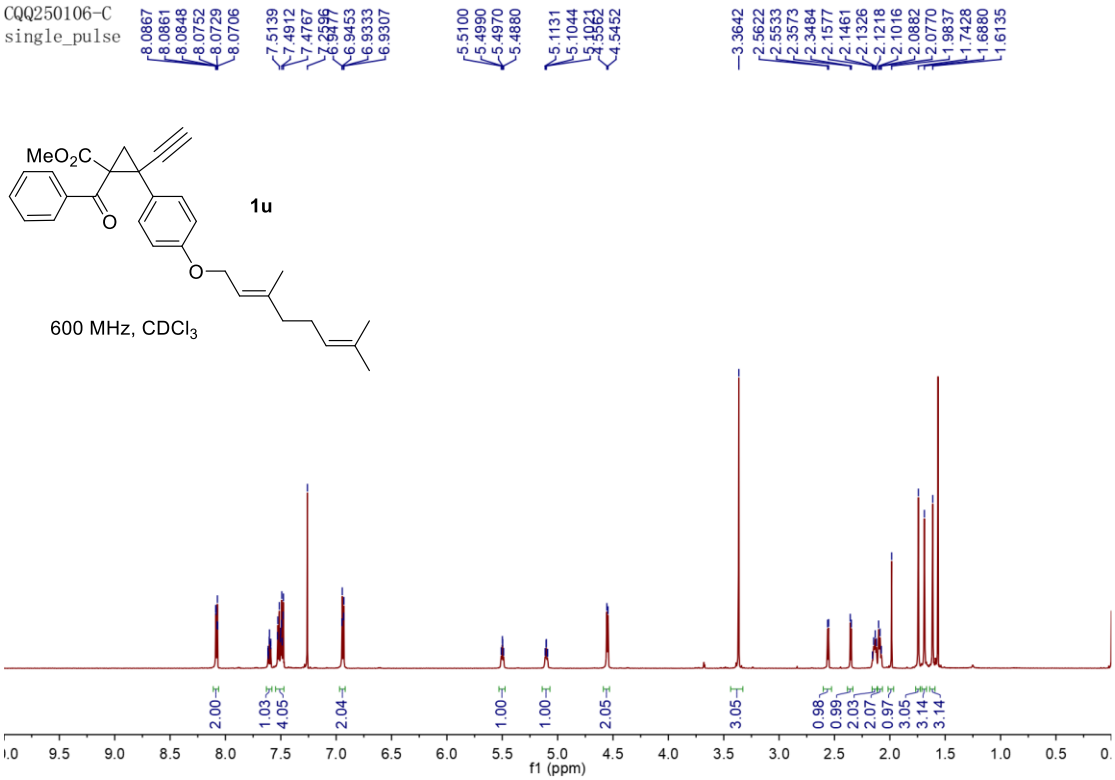


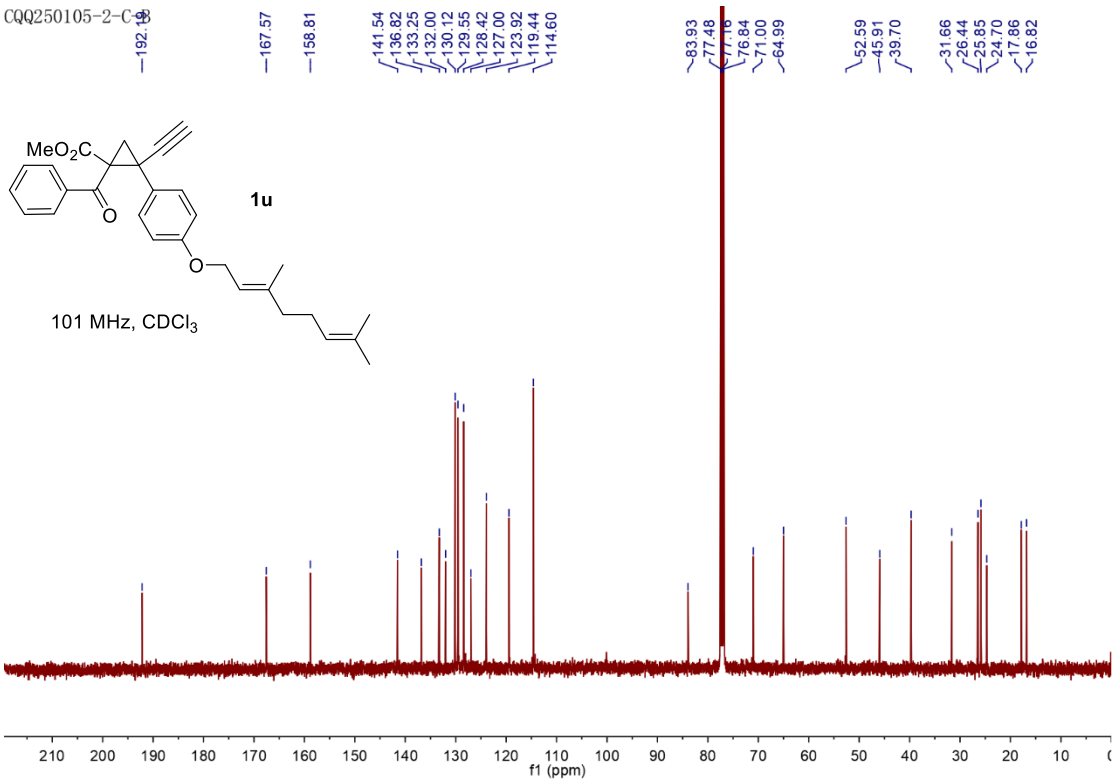
cqq241227-a-2

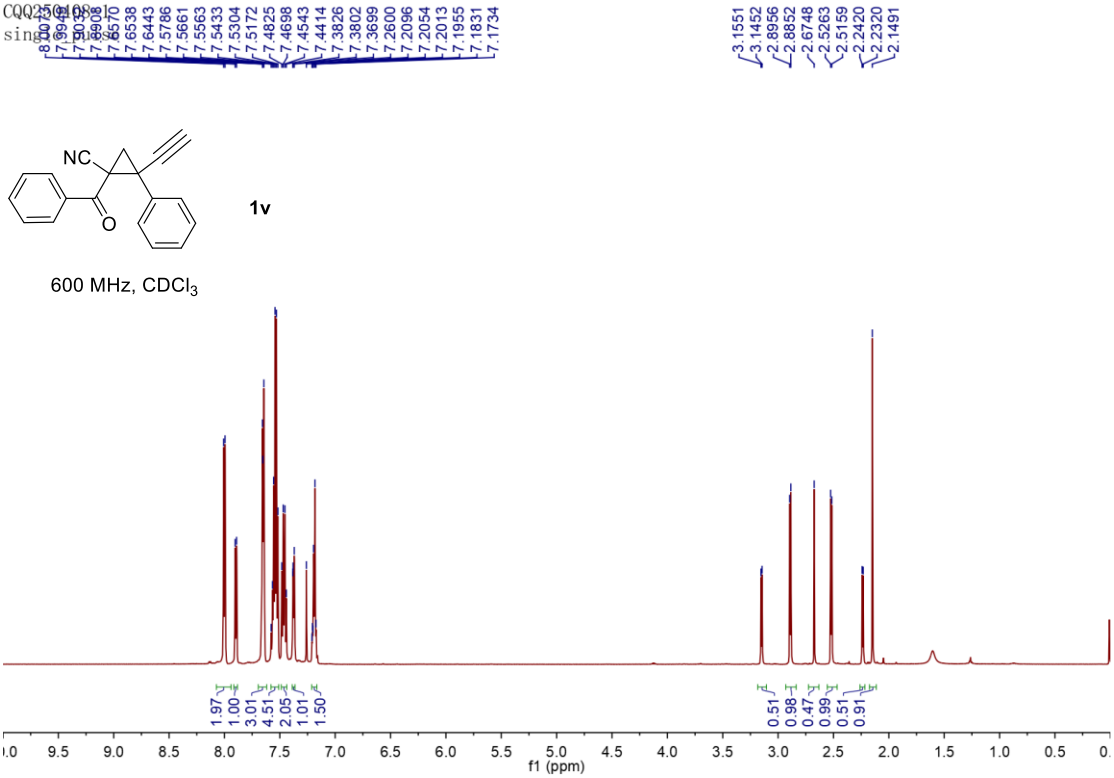


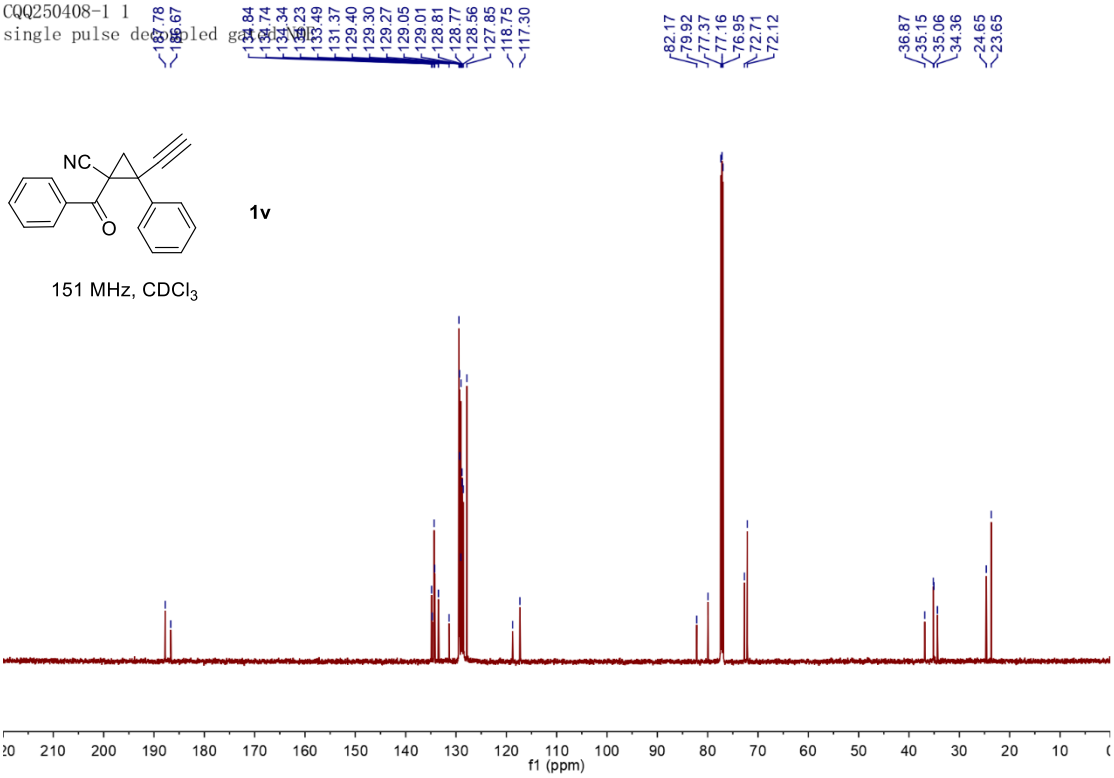
101 MHz, $CDCl_3$



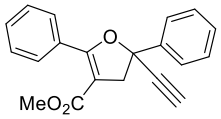

CQQ250106-C
single_pulse
1u
600 MHz, CDCl3
f1 (ppm)


CQQ250105-2-C-3
1u
101 MHz, CDCl3
f1 (ppm)


NC
O
1v
600 MHz, CDCl3
f1 (ppm)

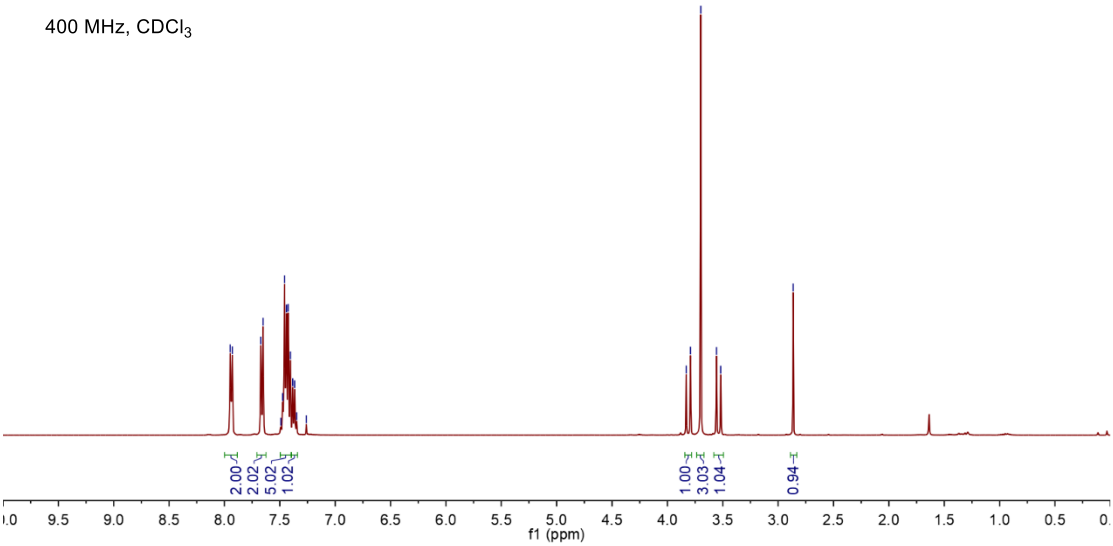

NC
O
1v
151 MHz, CDCl3
f1 (ppm)

cqq241017-3

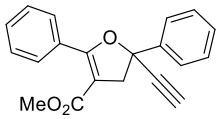


2a

400 MHz, $CDCl_3$

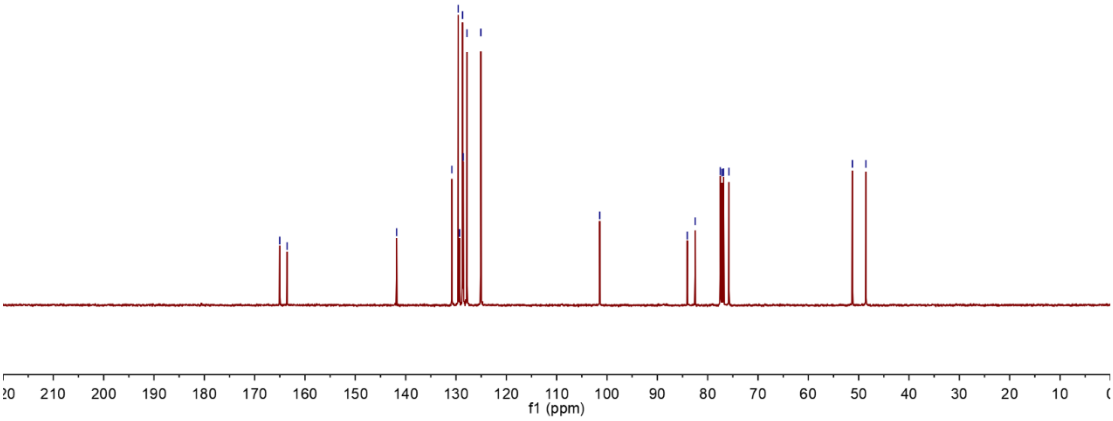


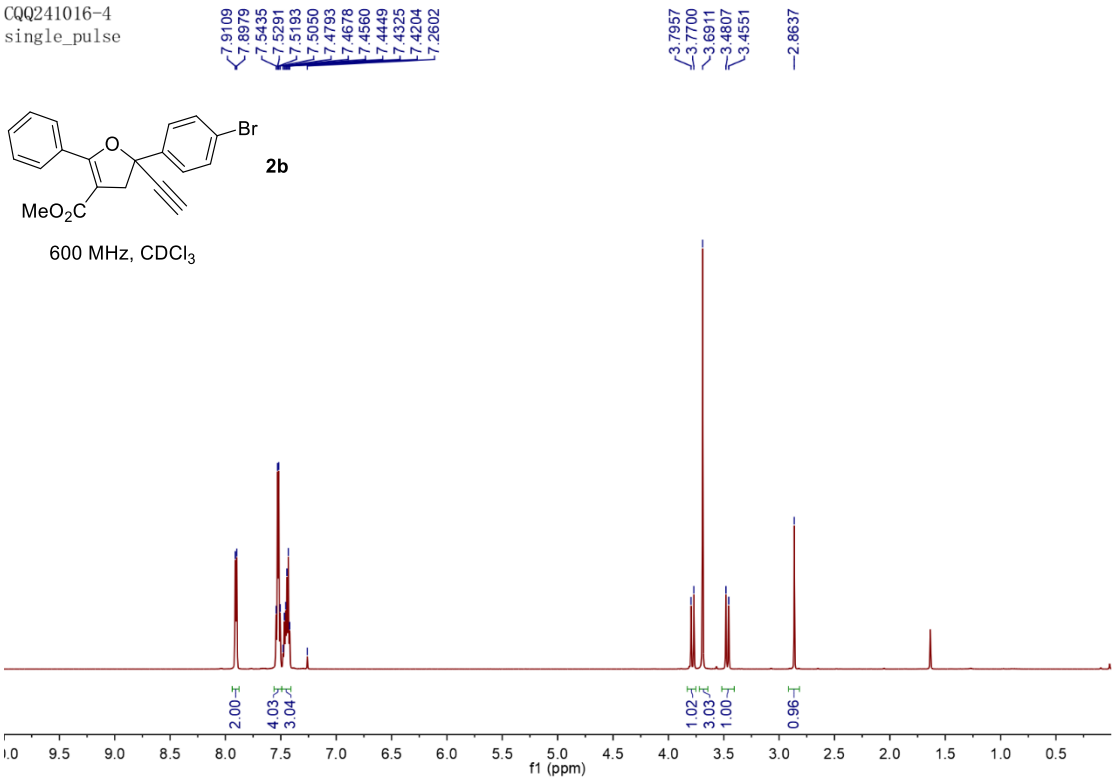
CQQ241011-3
single pulse decoupled gated NOE

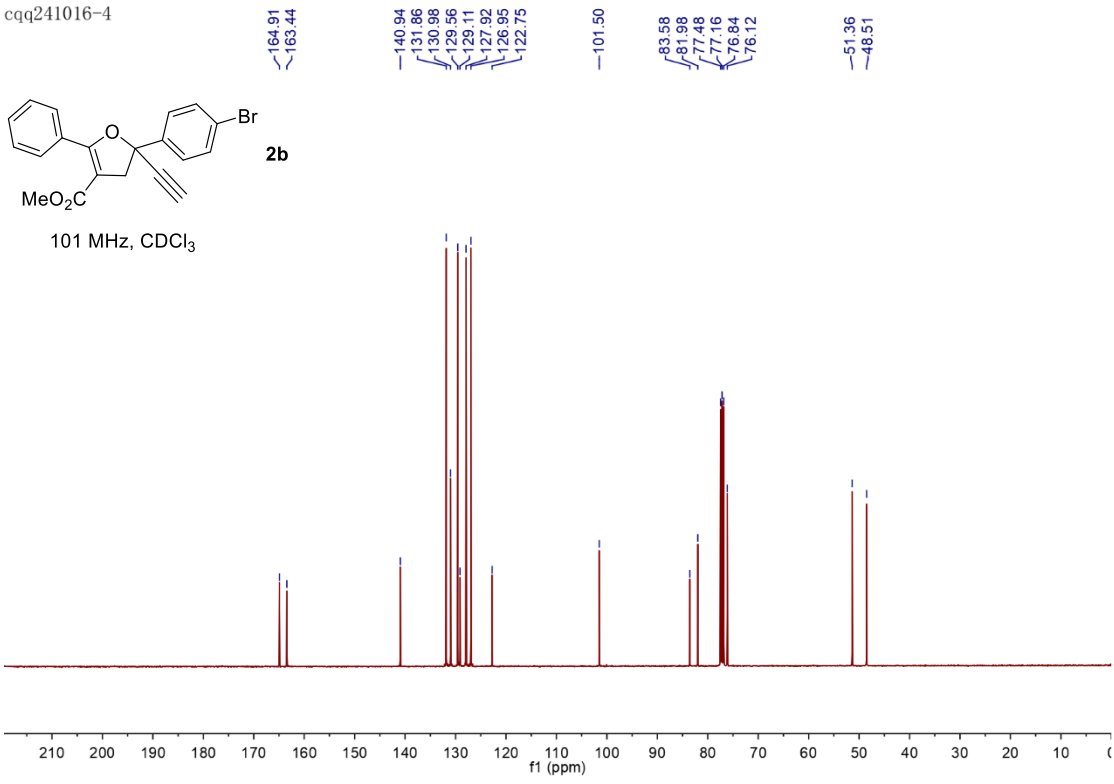


2a

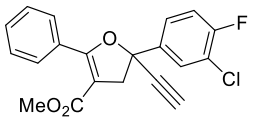
101 MHz, $CDCl_3$




CQQ241016-4
single_pulse
7.9109
7.8979
7.5435
7.5291
7.5193
7.5050
7.4793
7.4678
7.4560
7.4449
7.4325
7.4204
7.2602
3.7957
3.7700
3.6911
3.4807
3.4551
2.8637
Br
O
MeO2C
2b
600 MHz, CDCl3
2.00
4.03
3.04
1.02
3.03
1.00
0.96
f1 (ppm)

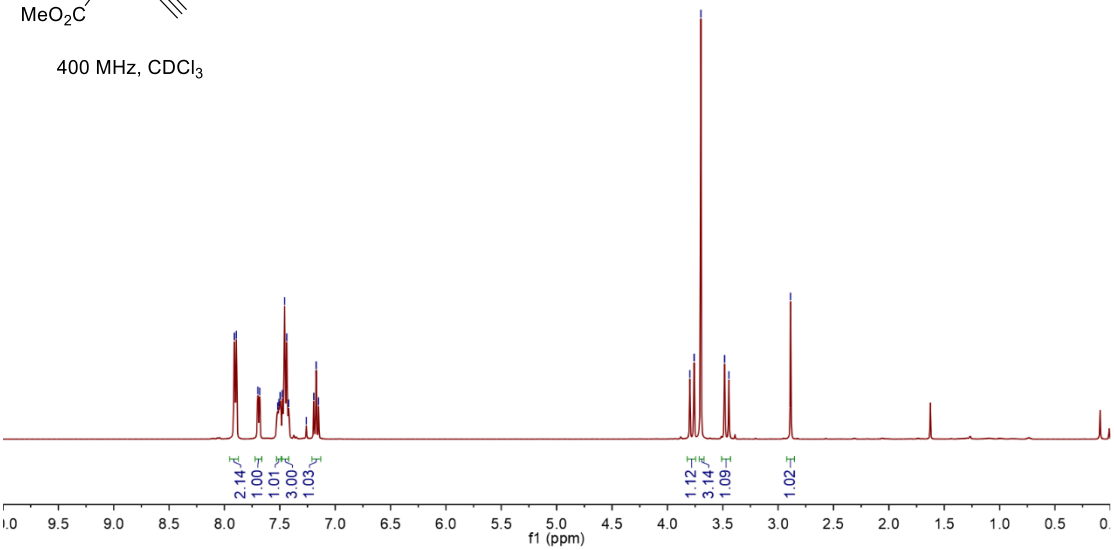

cqq241016-4
164.91
163.44
140.94
131.86
130.98
129.56
129.11
127.92
126.95
122.75
101.50
83.58
81.98
77.48
77.16
76.84
76.12
51.36
48.51
Br
O
MeO2C
2b
101 MHz, CDCl3
f1 (ppm)

cqq-241025-2

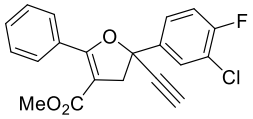


2c

400 MHz, $CDCl_3$

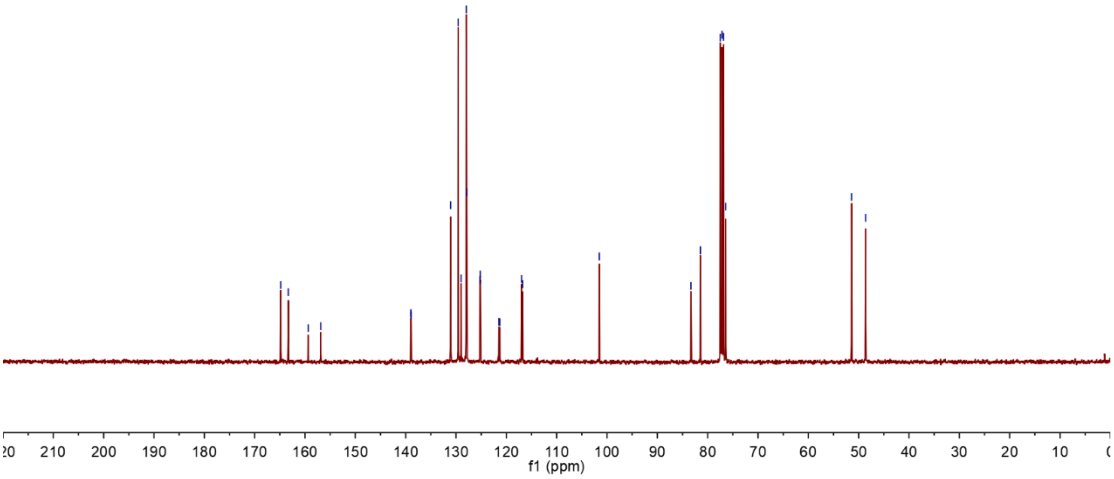


cqq241025-2
single pulse decoupled gated

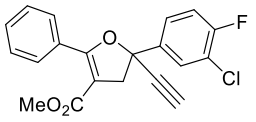


2c

101 MHz, $CDCl_3$

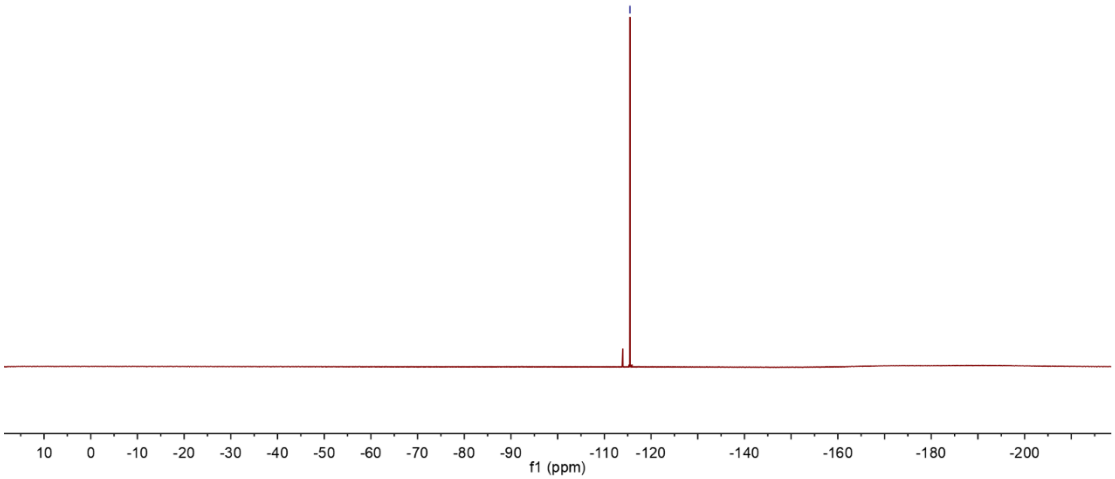


cqq241025-5

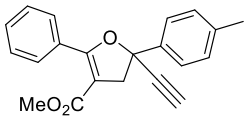


2c

376 MHz, $CDCl_3$

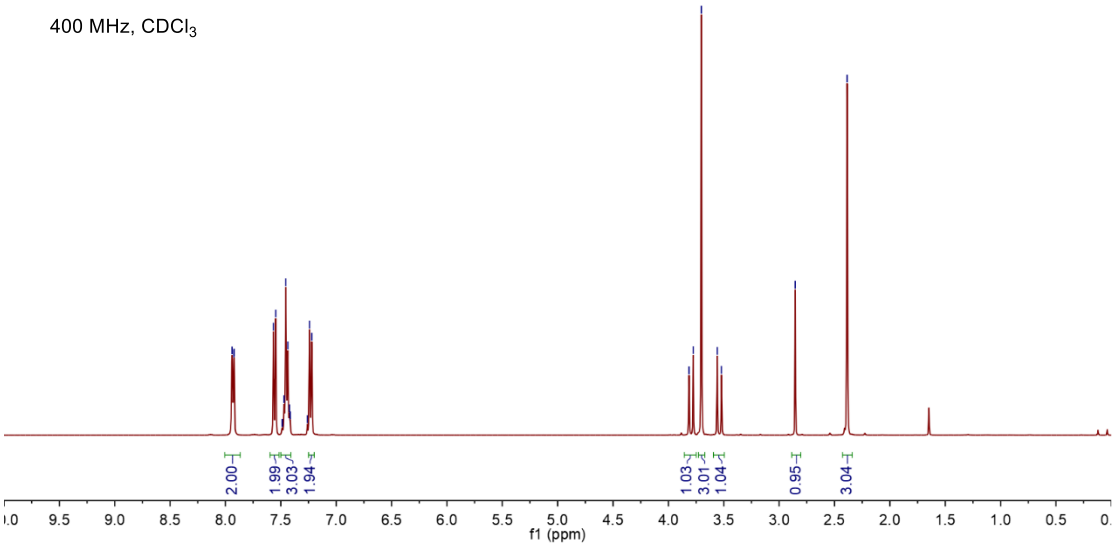


CQQ241025-4

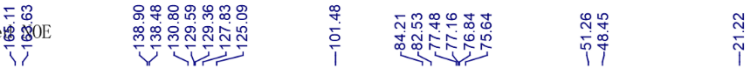


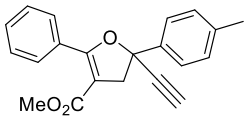
2d

400 MHz, $CDCl_3$



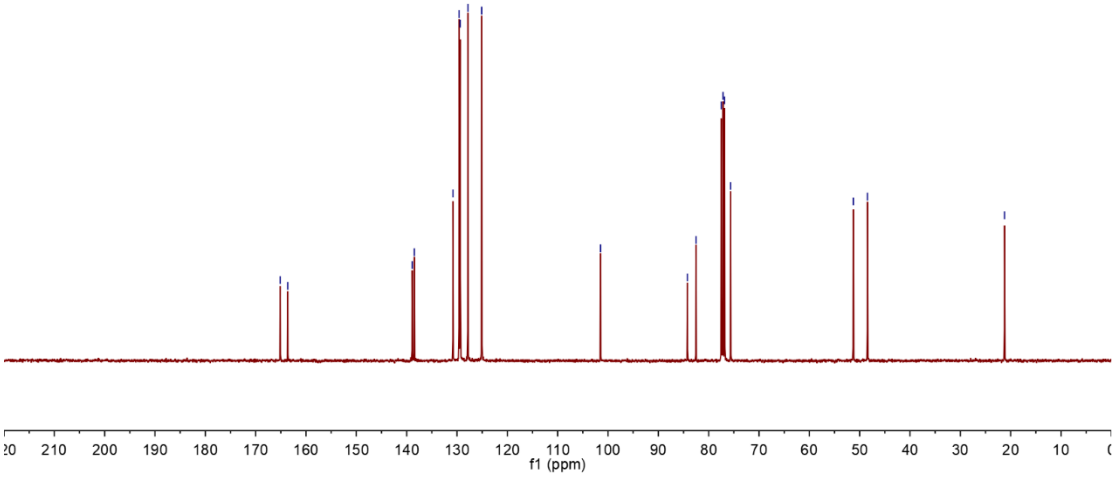
cqq241025-4
single pulse decoupled gated NOE



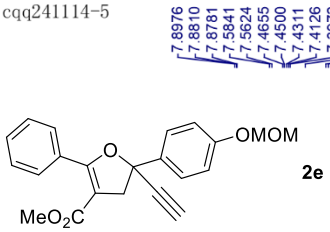


2d

101 MHz, $CDCl_3$

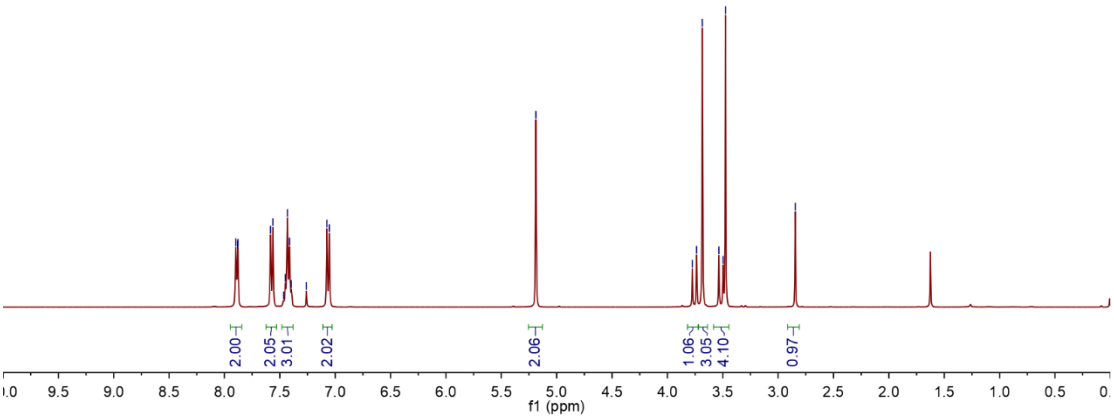


cqq241114-5

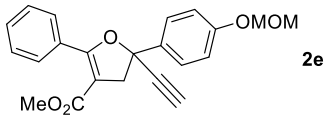


2e

400 MHz, $CDCl_3$



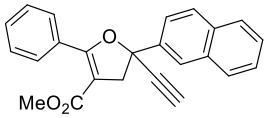
CQQ241114-5-C
single pulse decoupled gated



2e

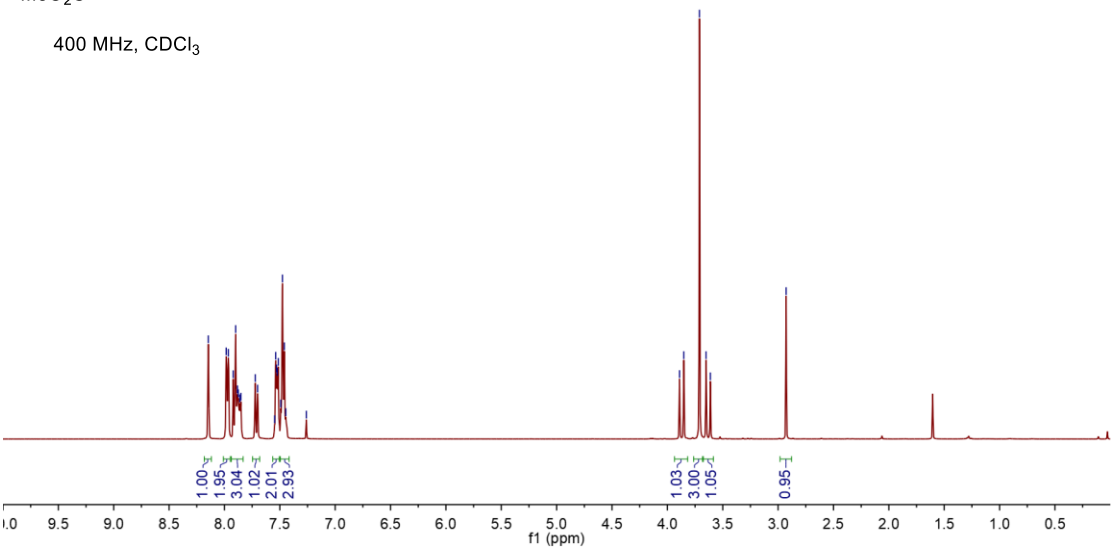
151 MHz, $CDCl_3$

cqq241030

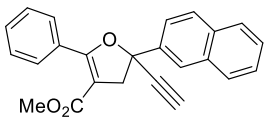


2f

400 MHz, $CDCl_3$

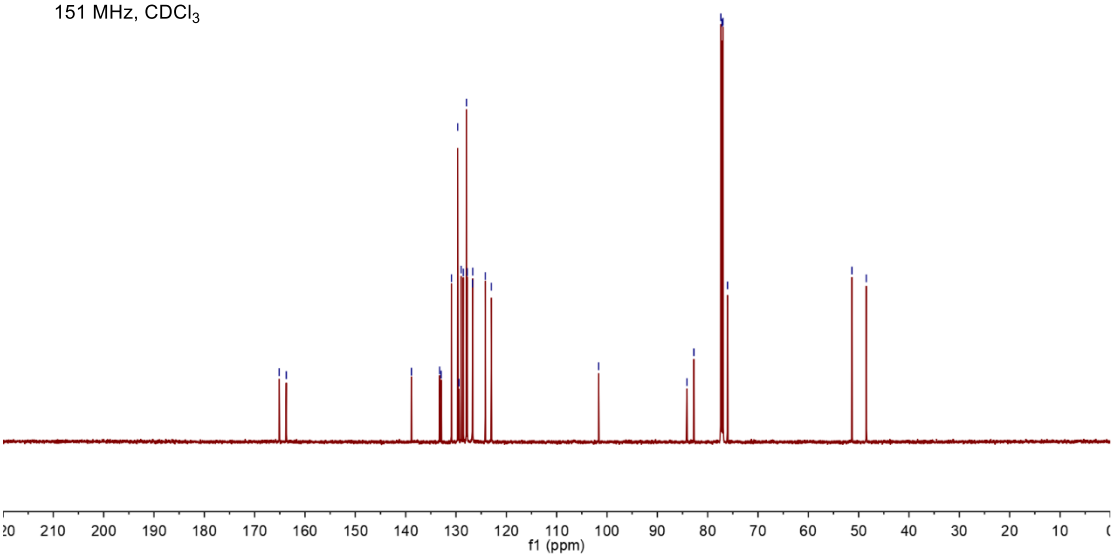


CQQ241030-3
single pulse decoupled gated NOE

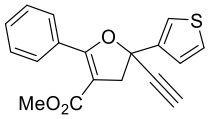


2f

151 MHz, $CDCl_3$

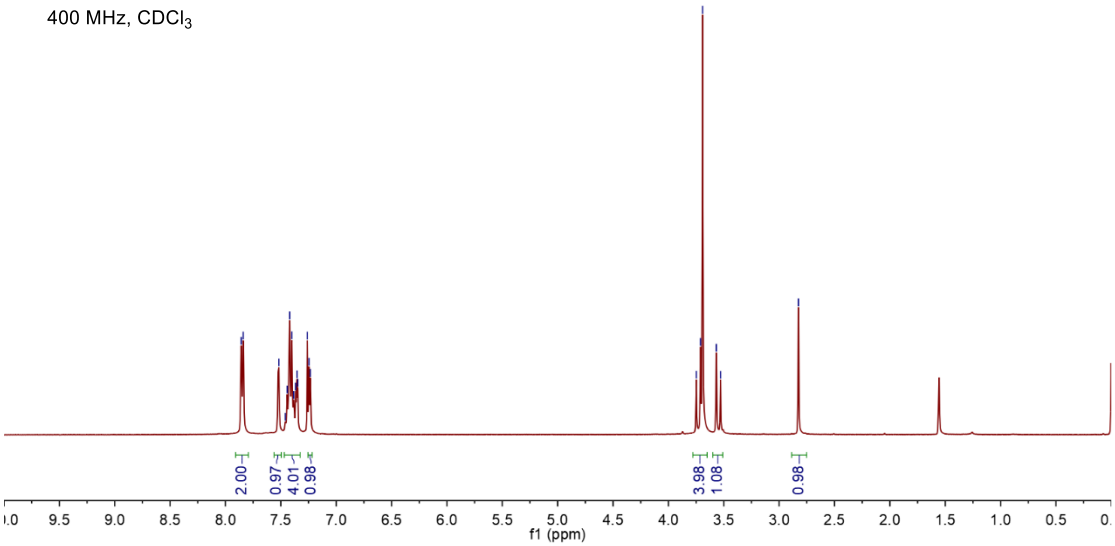


cqq-241109-1

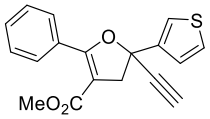


2g

400 MHz, $CDCl_3$



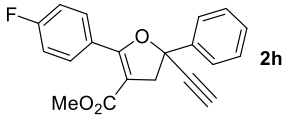
CQQ241108-3
single pulse decoupled gated NOE



2g

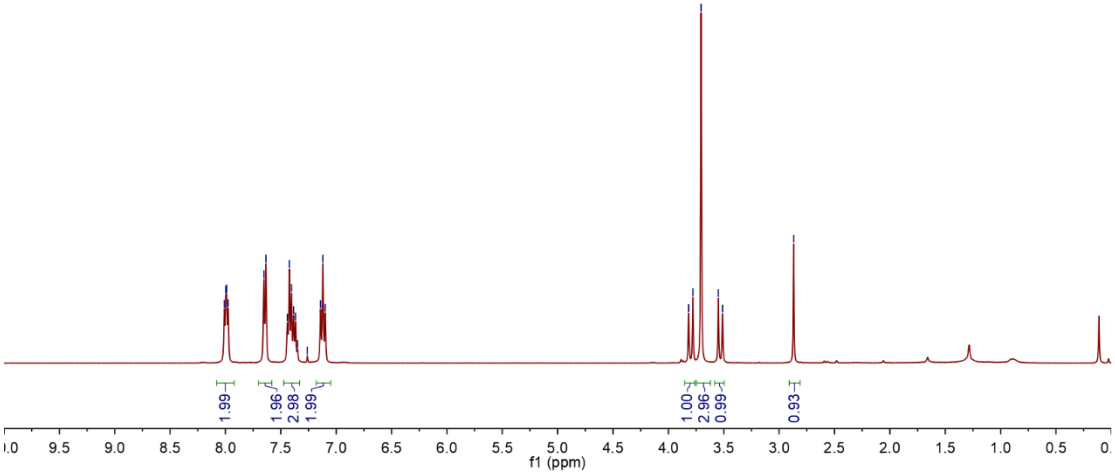
101 MHz, $CDCl_3$

cqq250107-4

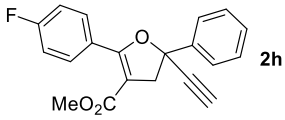


2h

400 MHz, $CDCl_3$

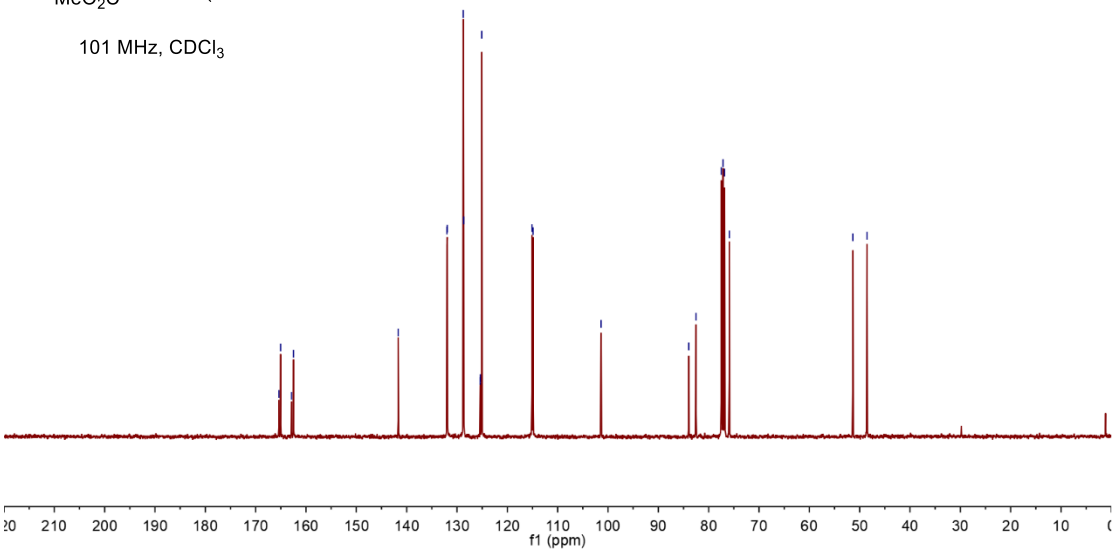


CQQ-250107-4
single pulse decoupled gated

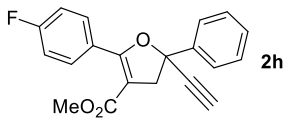


2h

101 MHz, $CDCl_3$



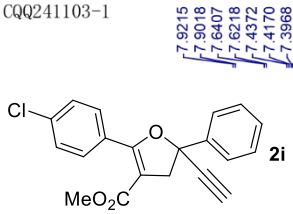
cqq250107-4



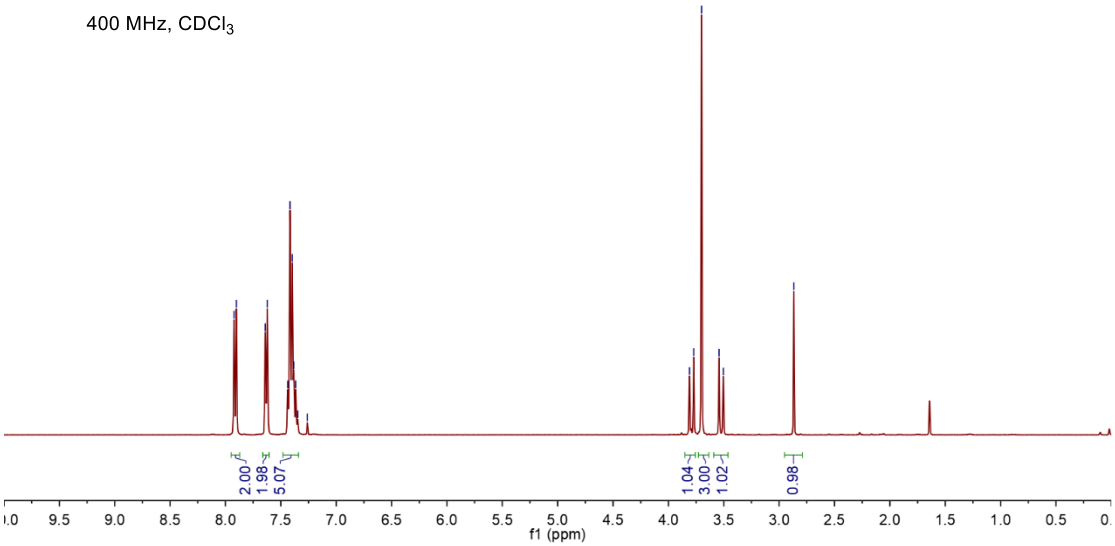
2h

376 MHz, $CDCl_3$

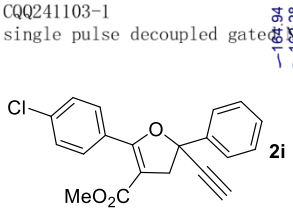
CQQ241103-1



400 MHz, $CDCl_3$

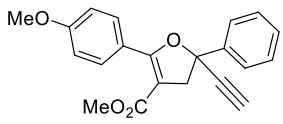


CQQ241103-1
single pulse decoupled gated NOE



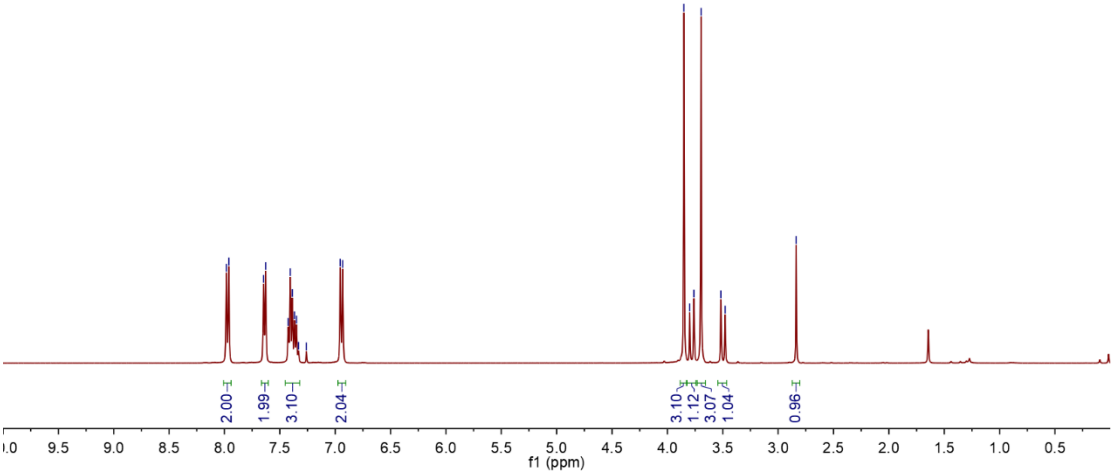
151 MHz, $CDCl_3$

cqq241111-2

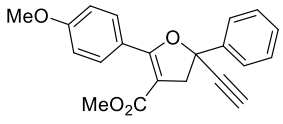


2j

400 MHz, $CDCl_3$

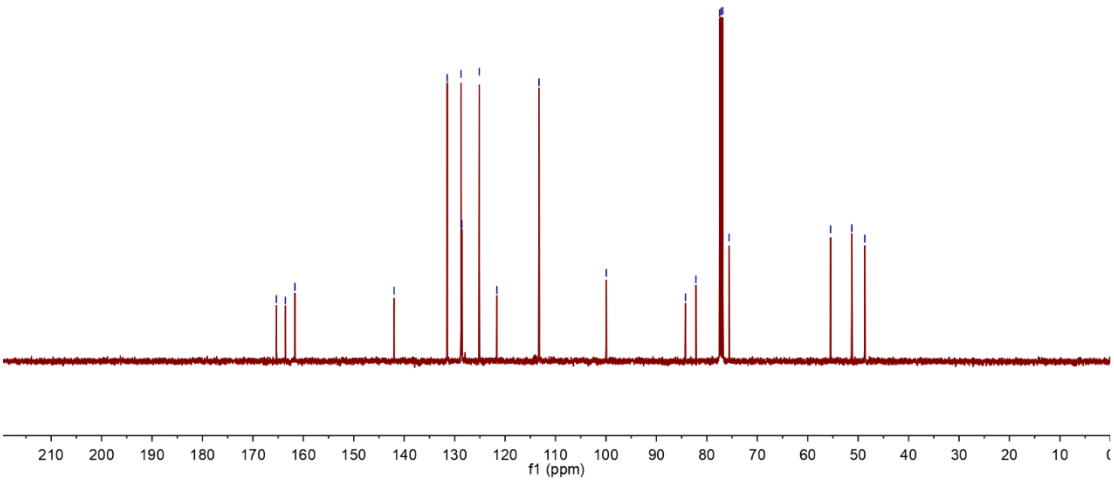


cqq241110-2

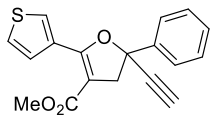


2j

101 MHz, $CDCl_3$

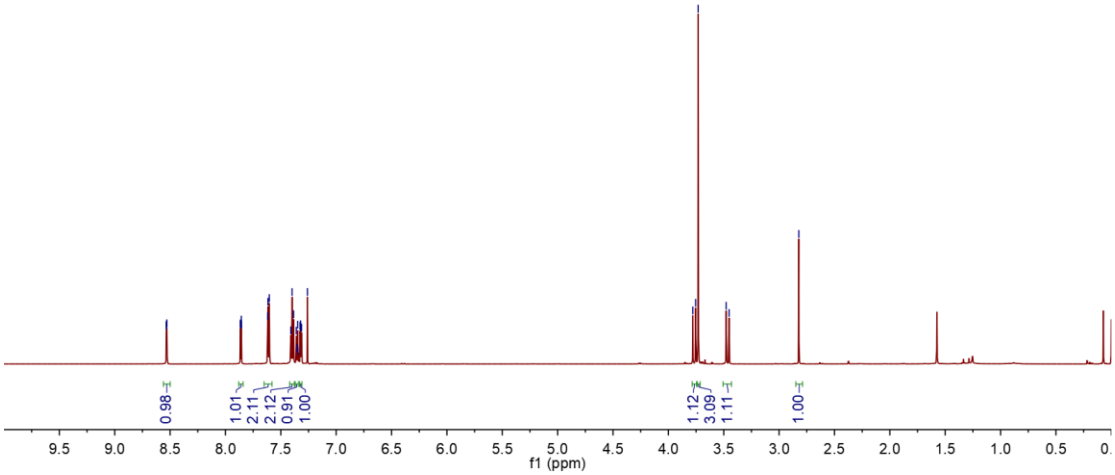


CQQ241219-5
single_pulse

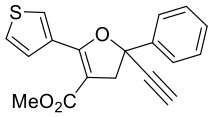


2k

400 MHz, $CDCl_3$

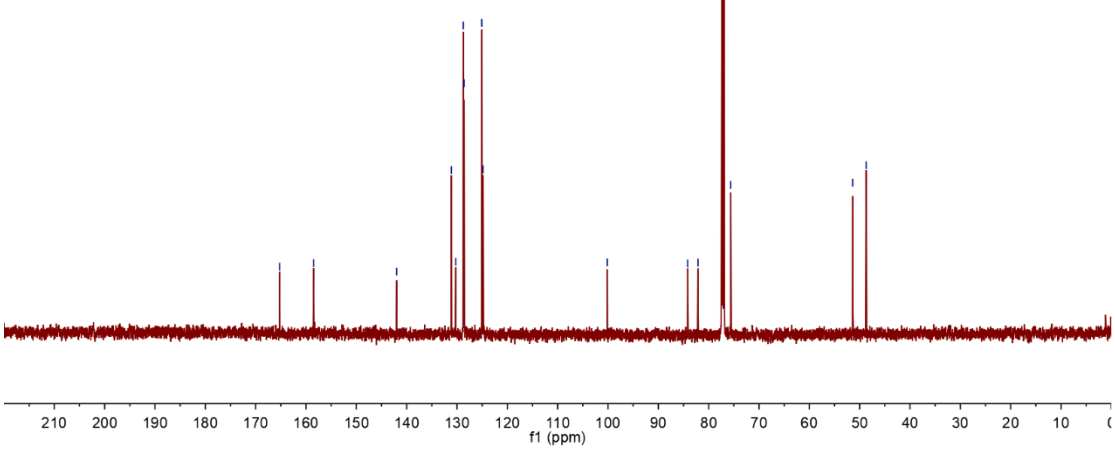


CQQ241219-5
single pulse decoupled gated NOE

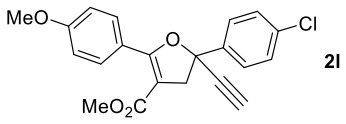


2k

151 MHz, $CDCl_3$



cqq241115-2



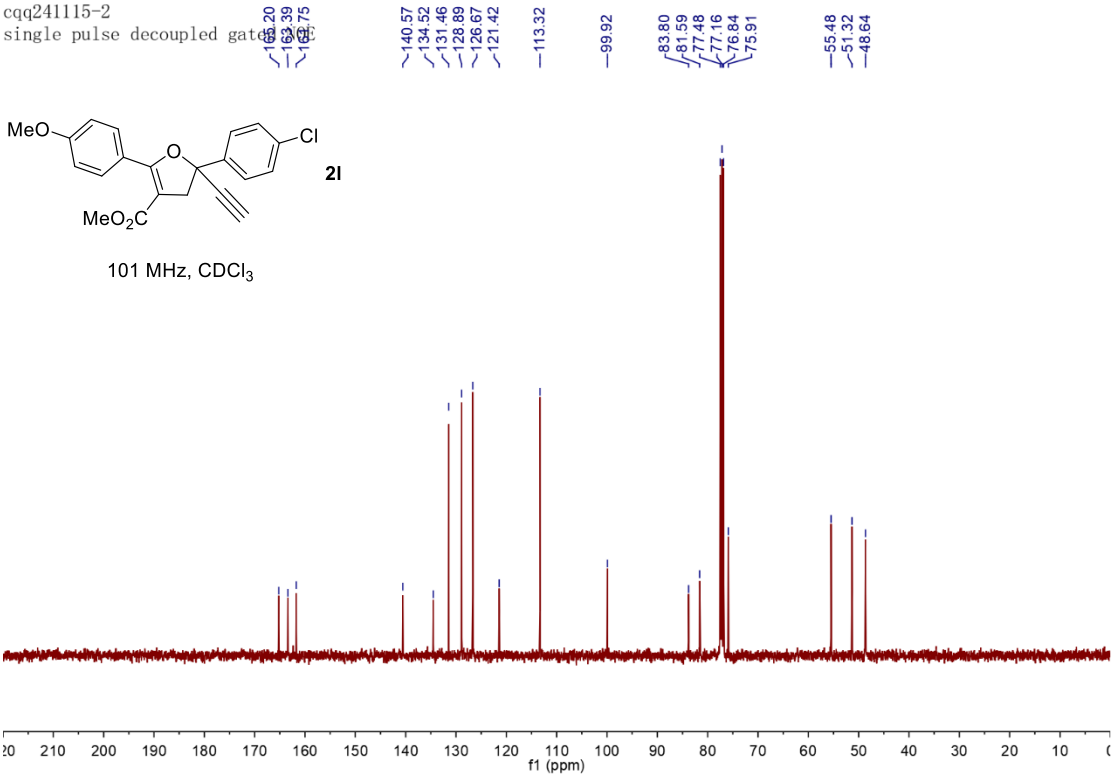
2l

400 MHz, $CDCl_3$

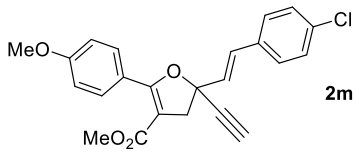
cqq241115-2
single pulse decoupled gated DE

2l

101 MHz, $CDCl_3$

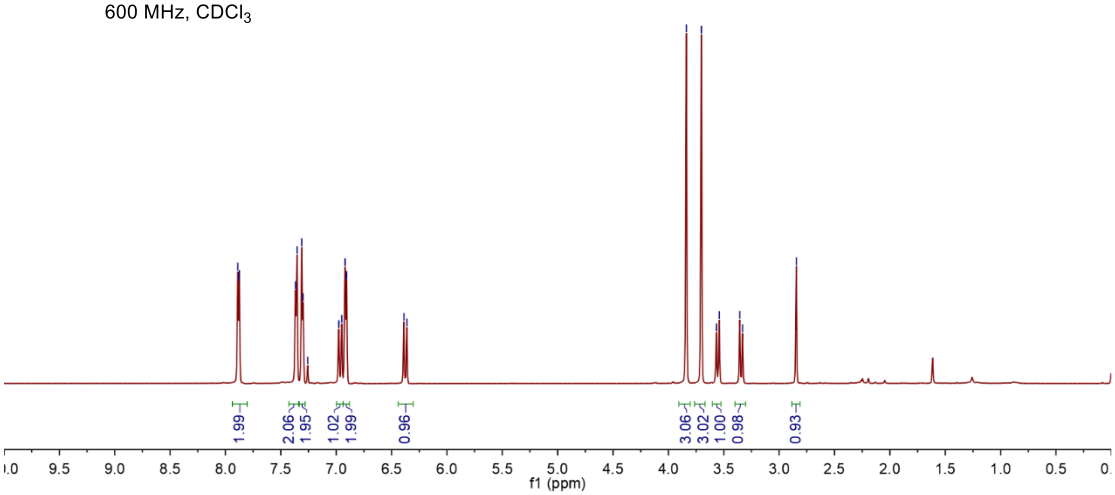


CQQ-250112-2
single_pulse

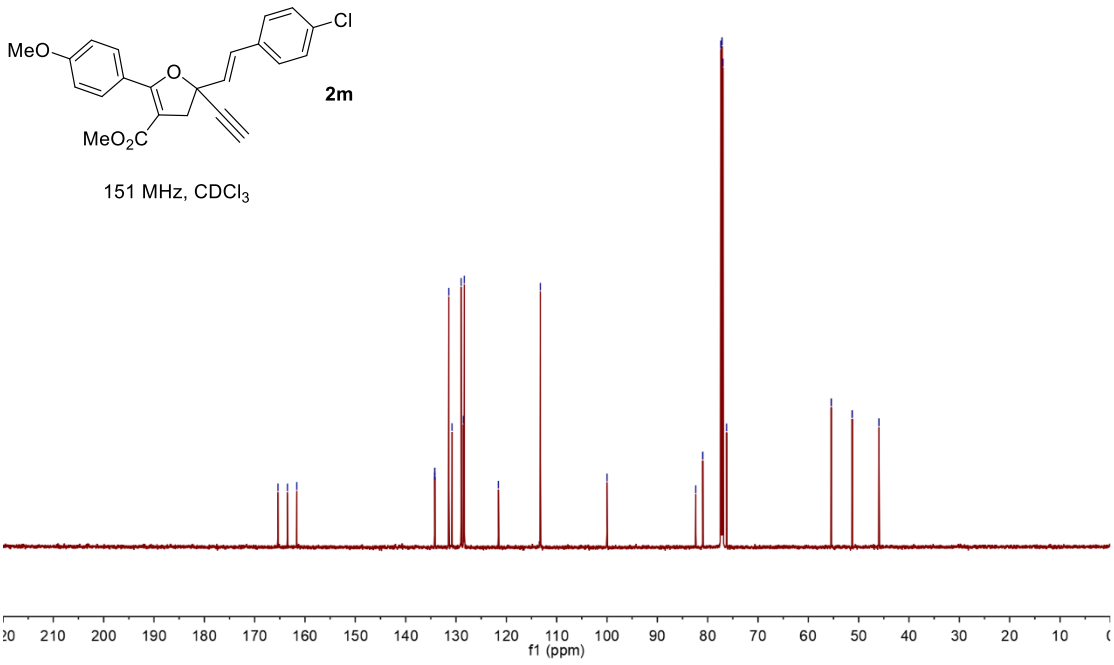


2m

600 MHz, $CDCl_3$



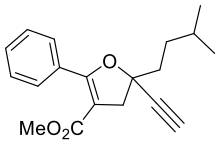
CQQ-250112-2
single pulse decoupled gated DE



2m

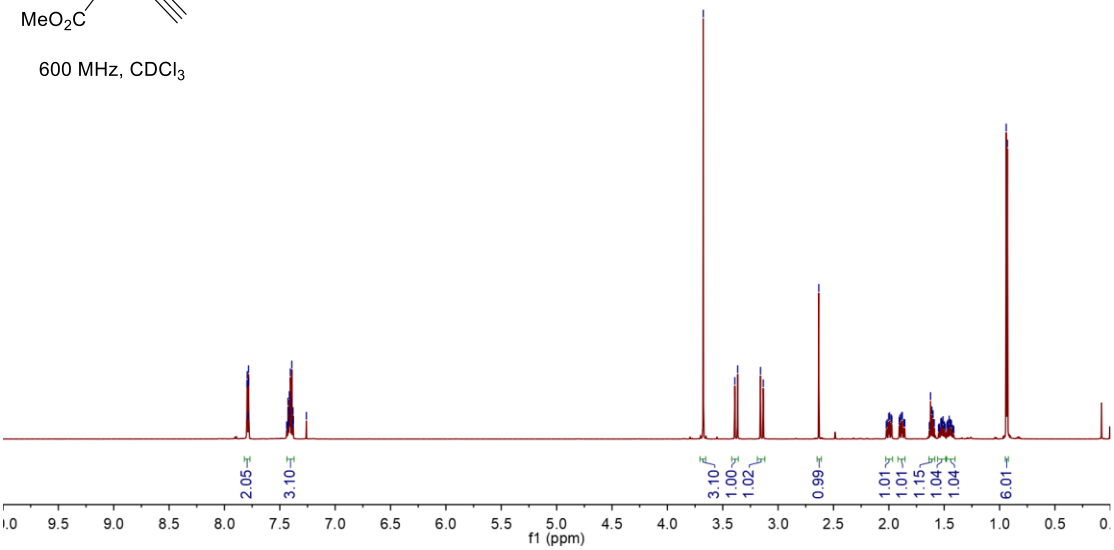
151 MHz, $CDCl_3$

CQQ241221-5
single_pulse

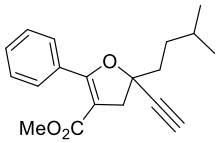


2n

600 MHz, $CDCl_3$

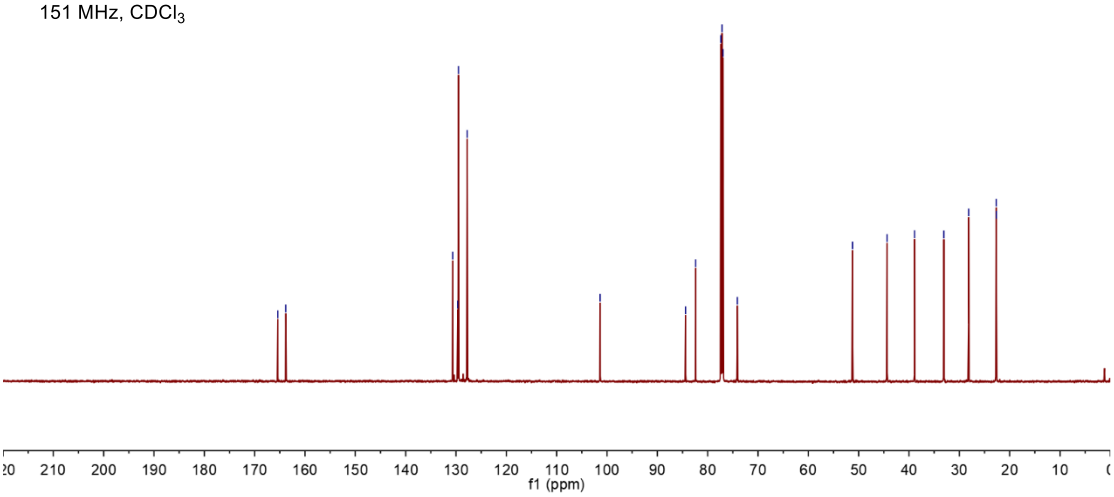


CQQ241221-5
single pulse decoupled gated NOE

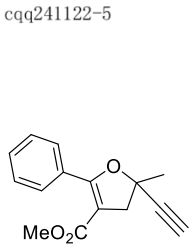


2n

151 MHz, $CDCl_3$



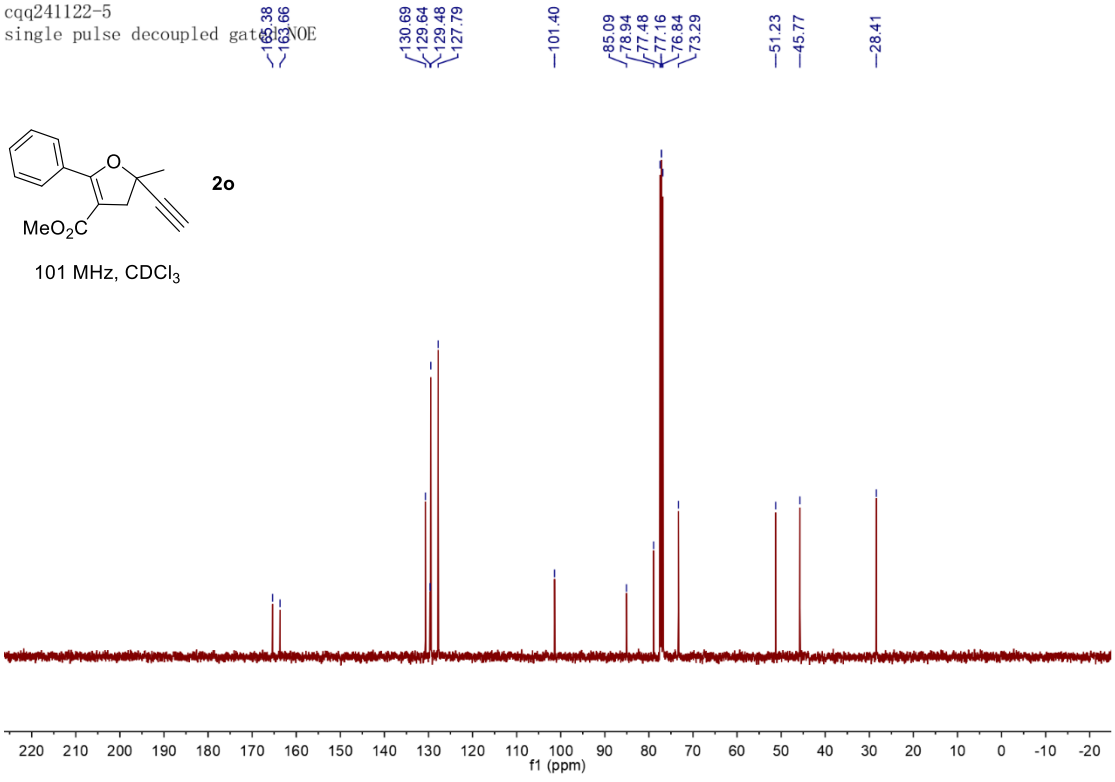
cqq241122-5



2o

400 MHz, $CDCl_3$

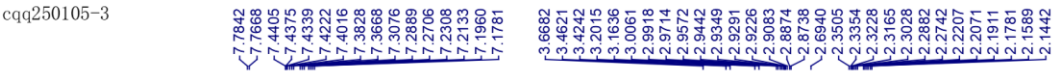
cqq241122-5
single pulse decoupled gated NOE

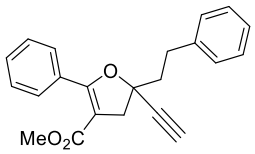


2o

101 MHz, $CDCl_3$

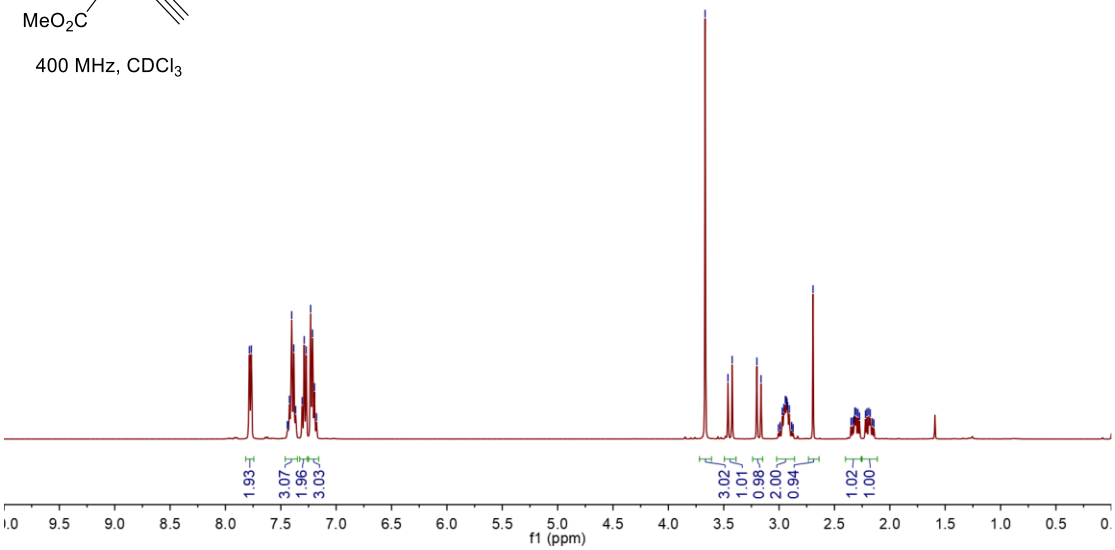
cqq250105-3



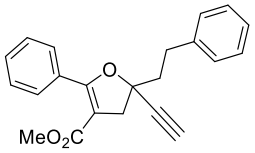


2p

400 MHz, $CDCl_3$

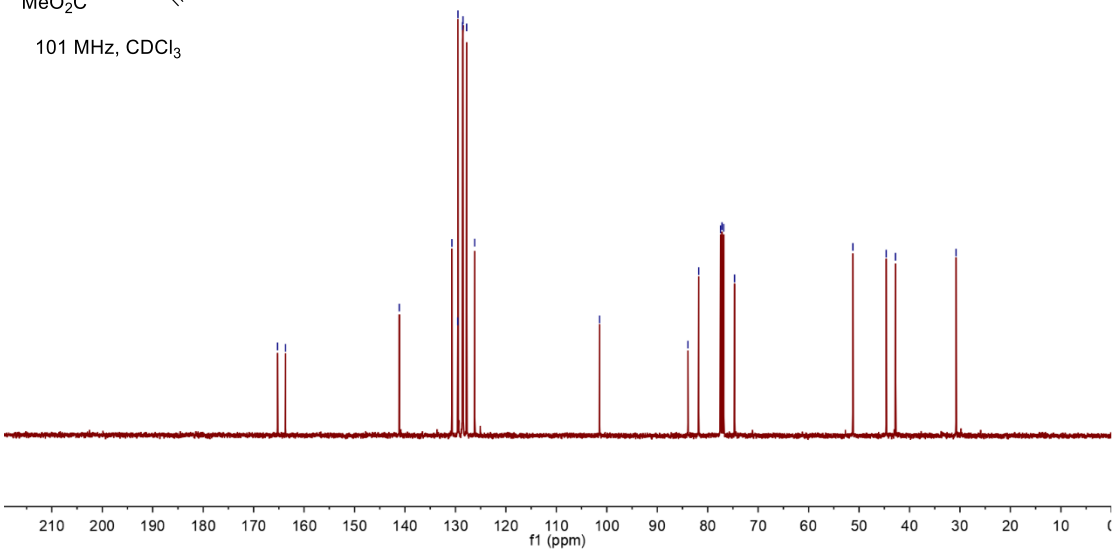


cqq250104-3

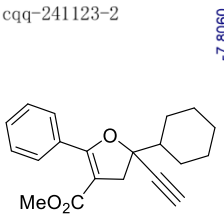


2p

101 MHz, $CDCl_3$



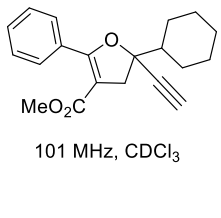
cqq-241123-2



2q

400 MHz, $CDCl_3$

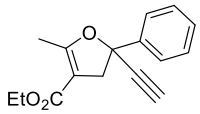
cqq241123-2



2q

101 MHz, $CDCl_3$

cqq241220-a

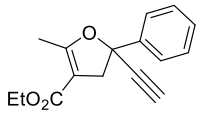


2r

400 MHz, $CDCl_3$

CQQ241220-B

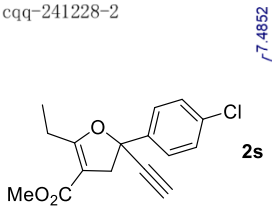
single pulse decoupled gated NOE



2r

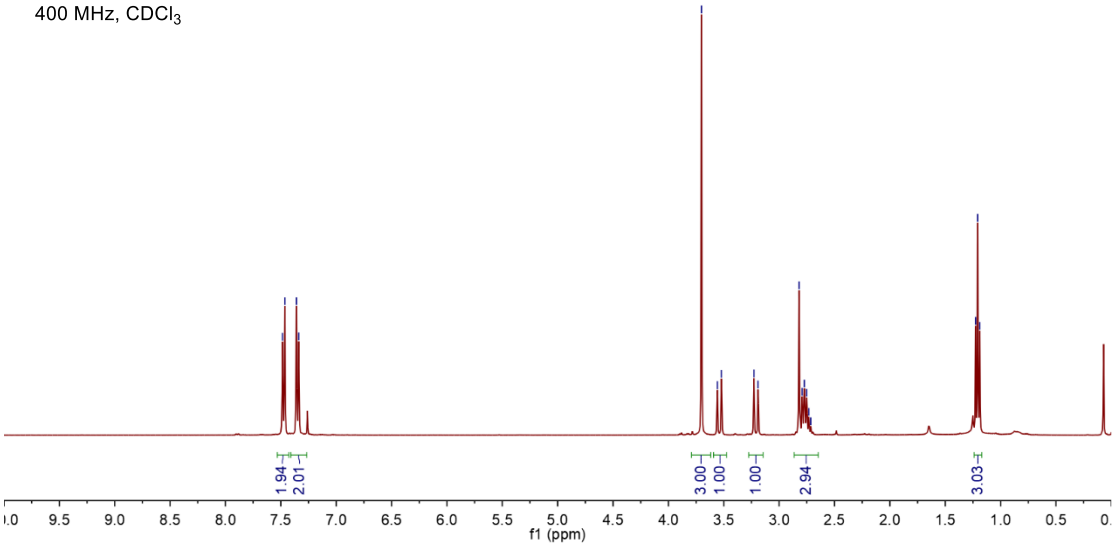
151 MHz, $CDCl_3$

cqq-241228-2



2s

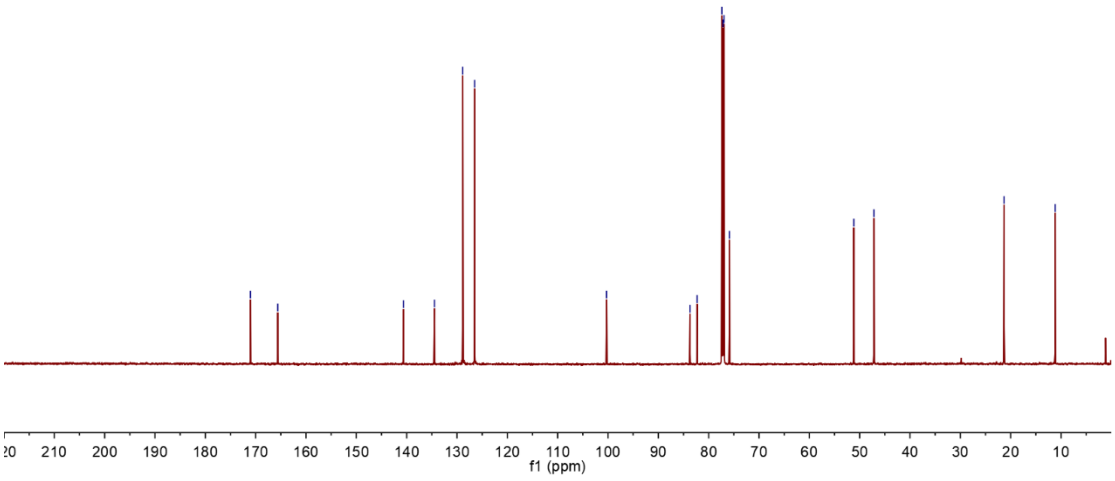
400 MHz, $CDCl_3$



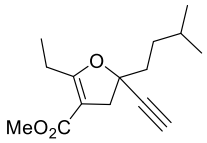
CQQ41228-2
single pulse decoupled gated NOE

2s

151 MHz, $CDCl_3$

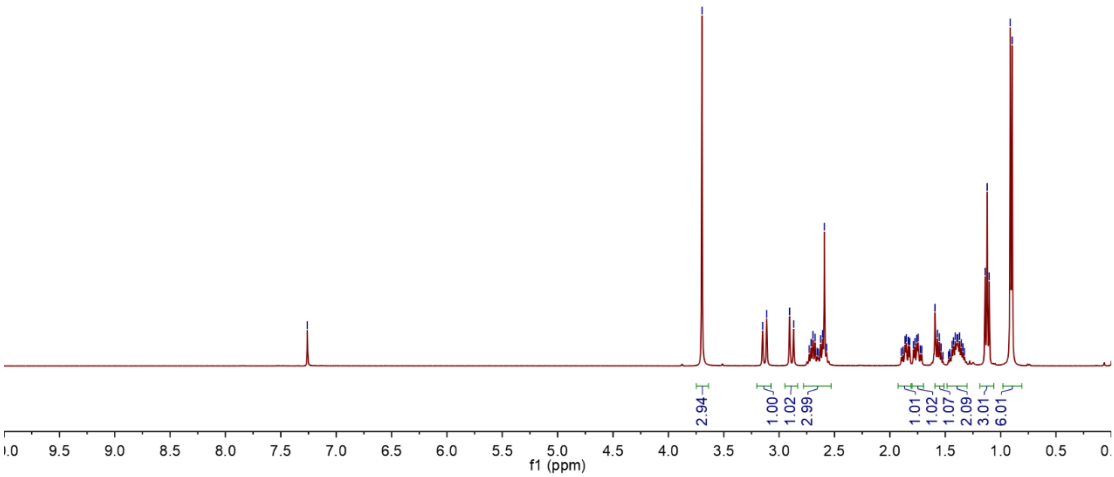


cqq241229-a

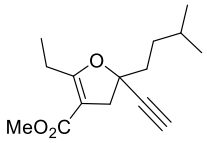


2t

400 MHz, $CDCl_3$



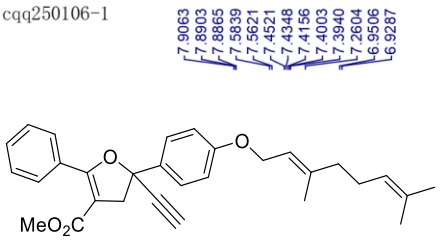
cqq241229-a



2t

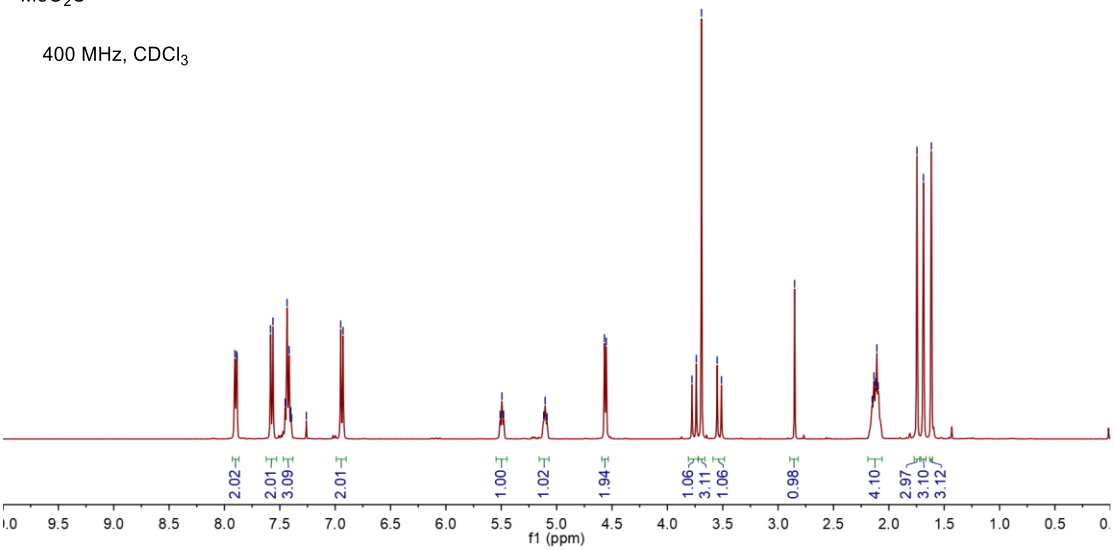
101 MHz, $CDCl_3$

cqq250106-1

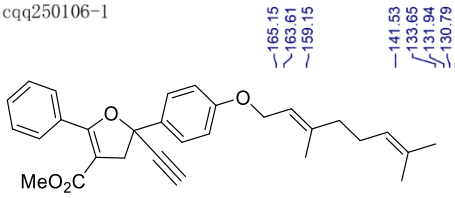


2u

400 MHz, $CDCl_3$

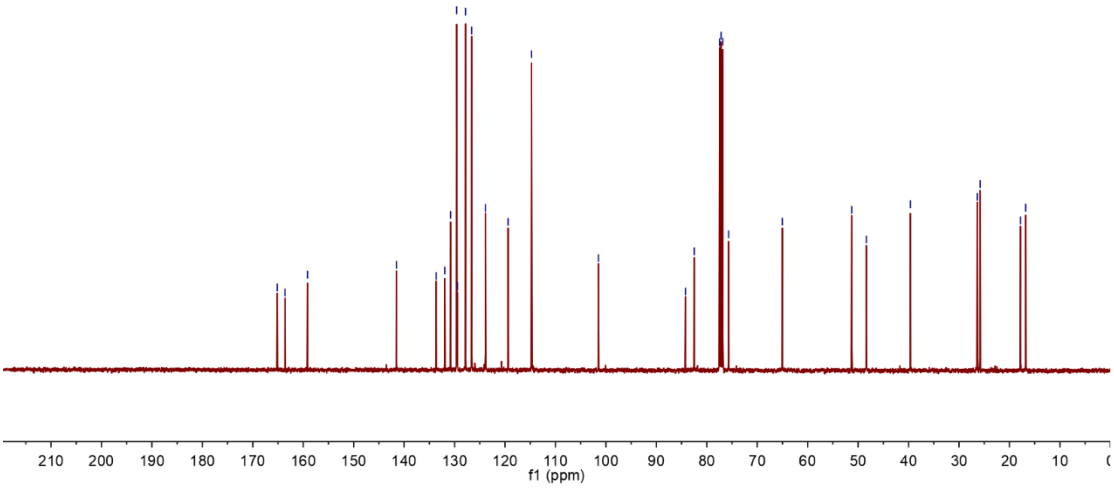


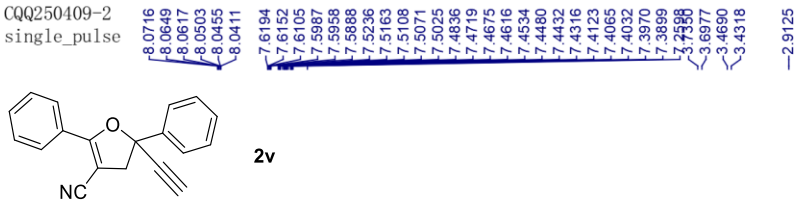
cqq250106-1



2u

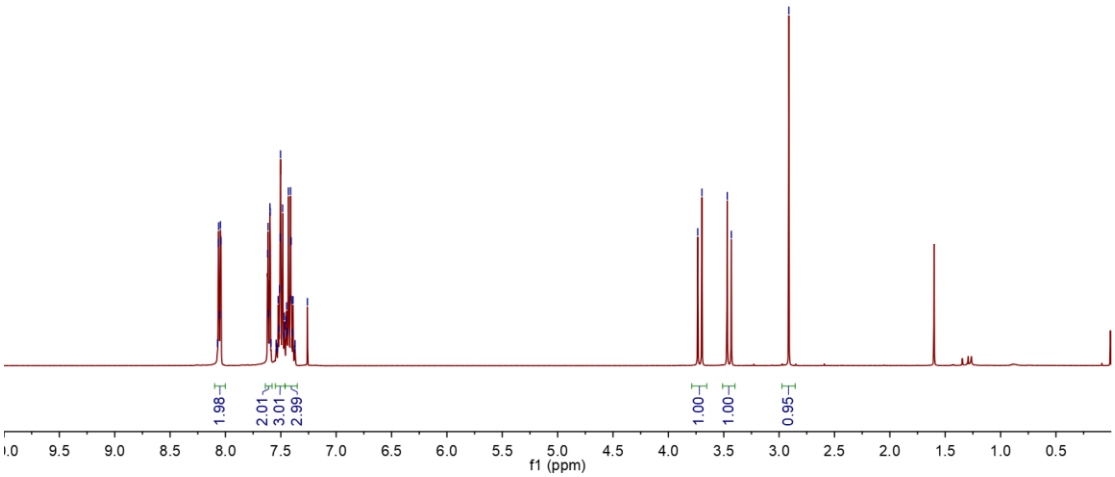
101 MHz, $CDCl_3$

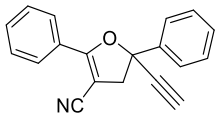




2v

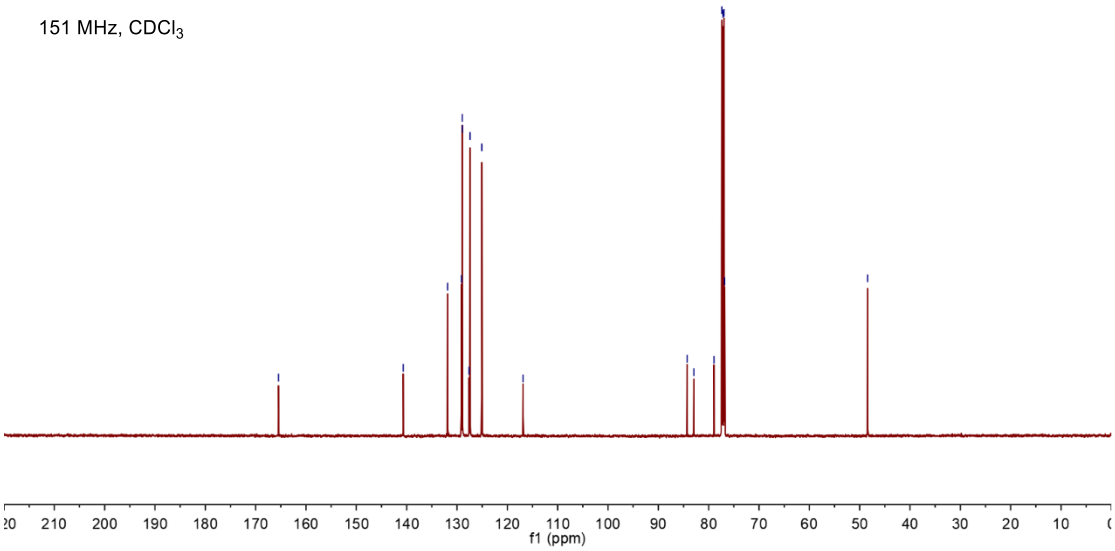
400 MHz, $CDCl_3$



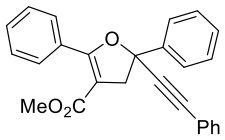


2v

151 MHz, $CDCl_3$

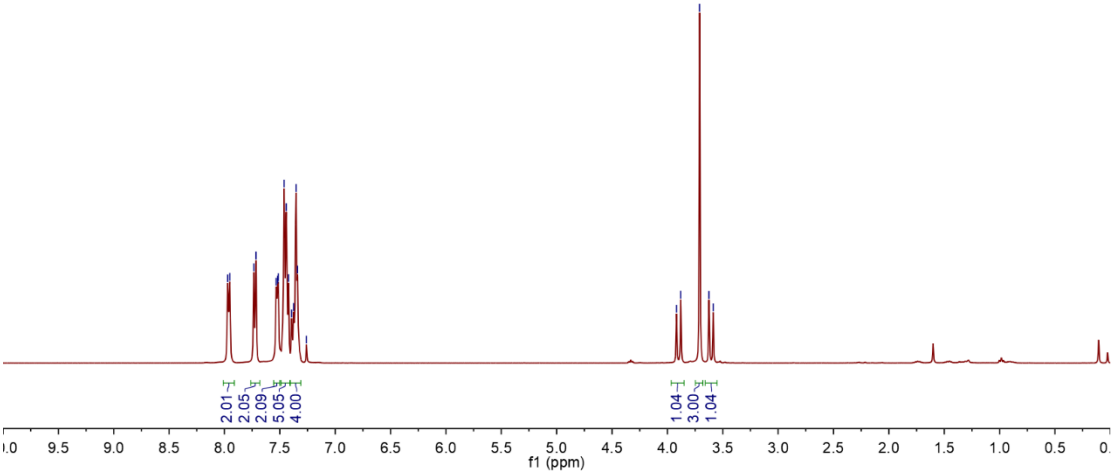


cqq250116-3

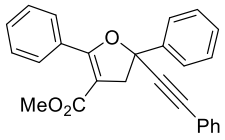


3a

400 MHz, $CDCl_3$

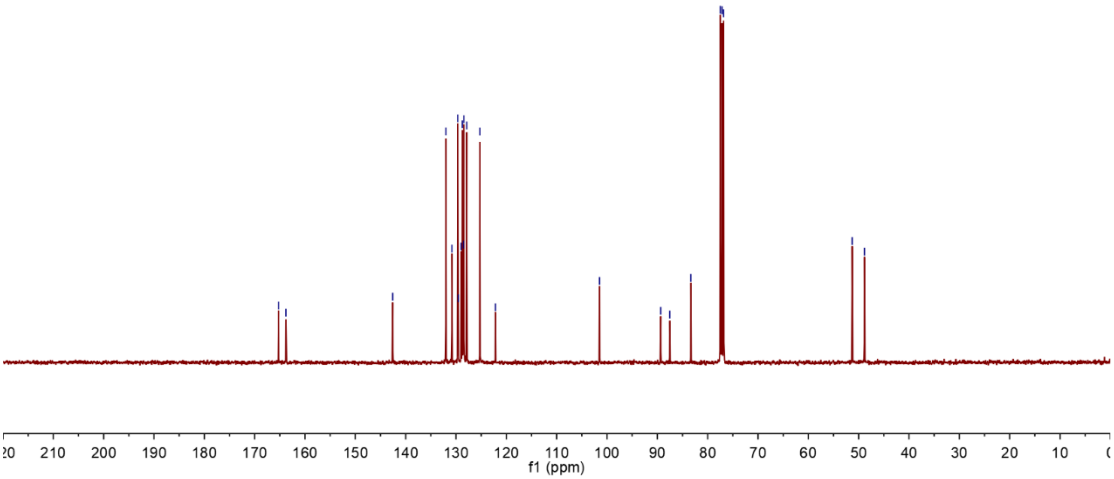


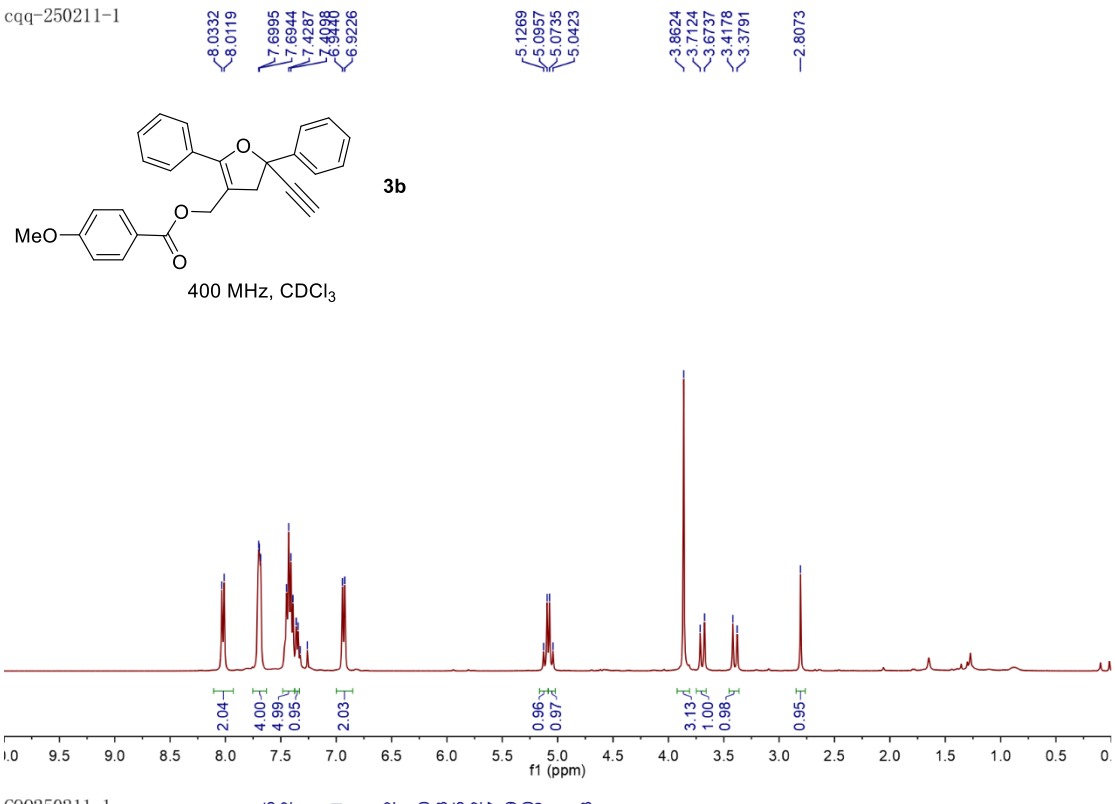
CQQ250116-3-C
single pulse decoupled gated NOE

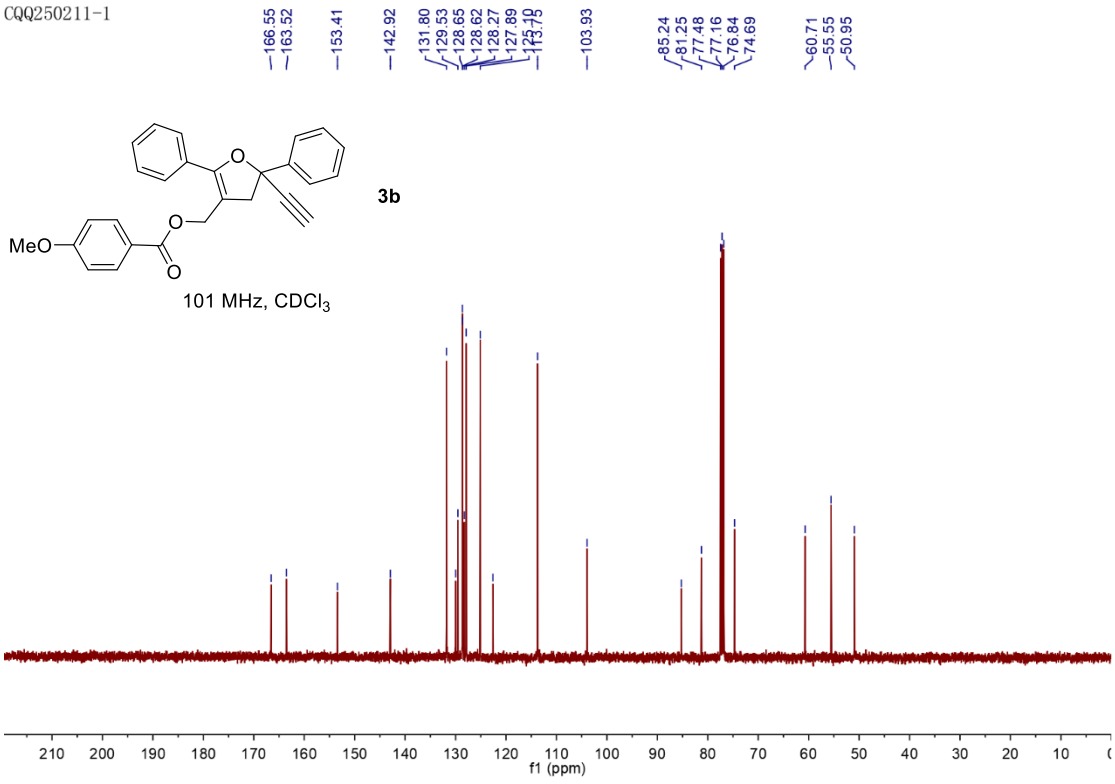


3a

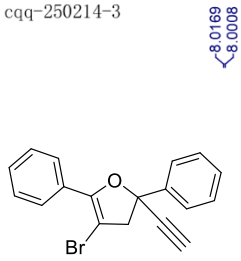
101 MHz, $CDCl_3$




cqq-250211-1
8.0332
8.0119
7.6995
7.6944
7.4287
6.9226
5.1269
5.0957
5.0735
5.0423
3.8624
3.7124
3.6737
3.4178
3.3791
2.8073
MeO
3b
400 MHz, CDCl3
2.04
4.00
4.99
0.95
2.03
0.96
0.97
3.13
1.00
0.98
0.95
f1 (ppm)

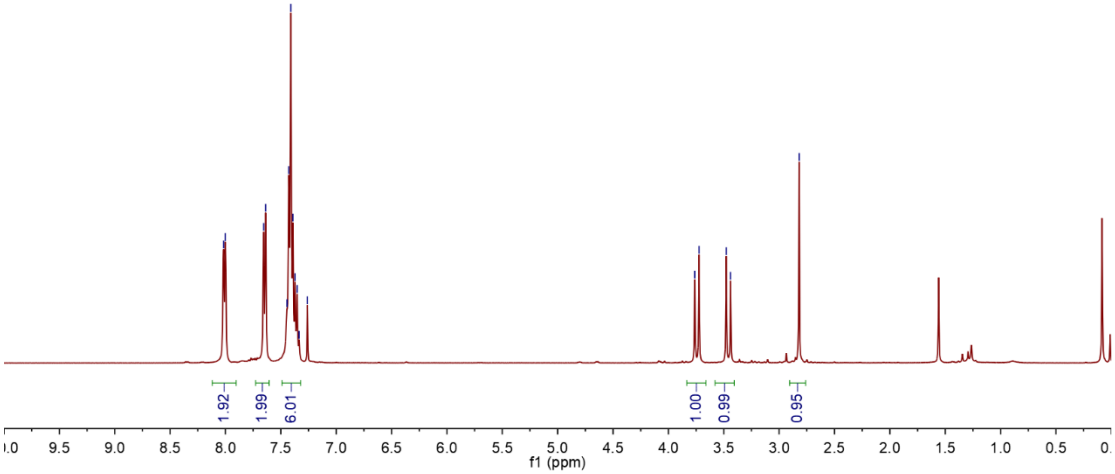

CQQ250211-1
166.55
163.52
153.41
142.92
131.80
129.53
128.65
128.62
128.27
127.89
103.93
85.24
81.25
77.48
77.16
76.84
74.69
60.71
55.55
50.95
MeO
3b
101 MHz, CDCl3
f1 (ppm)

cqq-250214-3

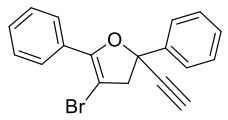


3c

400 MHz, $CDCl_3$



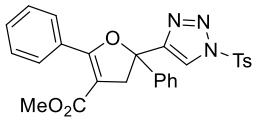
CQQ250214-3
single pulse decoupled gated NOE



3c

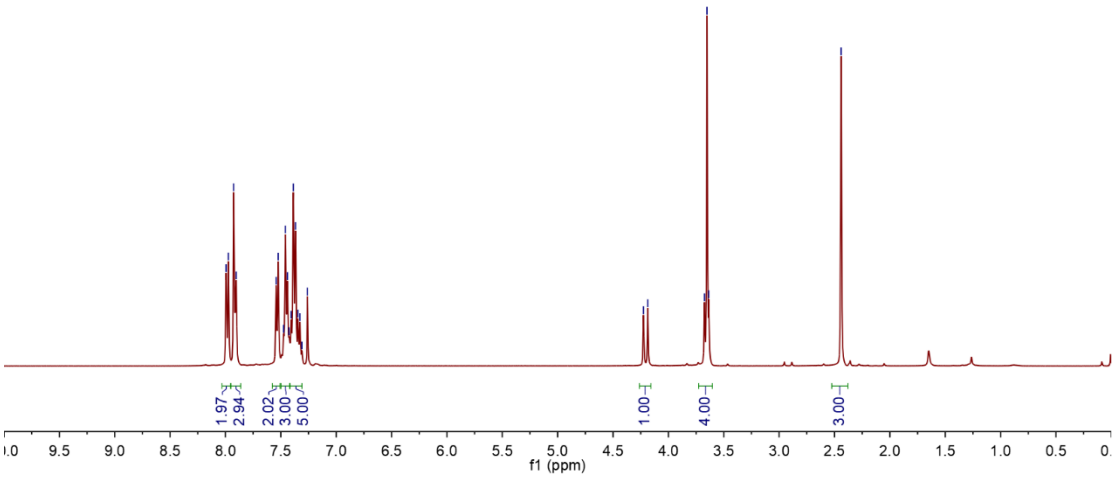
101 MHz, $CDCl_3$

CQQ250213-5

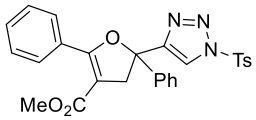


3d

400 MHz, $CDCl_3$



CQQ250213-5



3d

101 MHz, $CDCl_3$