Electronic Supplementary Information (ESI)

AgOTf-Catalyzed Sequential Synthesis of 4-Isoquinolone via Oxidative Ring Opening of Aziridines and Aza-Michael Addition

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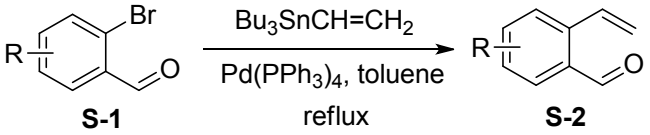
General Information

The ^{1}H NMR and ^{13}C NMR were recorded with Bruker 400 MHz spectrometer instruments in $CDCl_3$. The chemical shifts (δ) were measured in ppm and with the solvents as references (For $CDCl_3$, ^{1}H: δ=7.26 ppm, ^{13}C δ = 77.00 ppm). All solvents were obtained from commercial sources and were purified according to standard procedures. Purification of products was accomplished by flash chromatography using silica gel (200~300 mesh). Thin layer chromatography (TLC) was performed on Merck silica gel GF254 plates and visualized by UV-light (254 nm). Melting points were obtained on a Yanaco-241 apparatus and are uncorrected. IR spectra were recorded on a MAGNA-560 spectrometer made by Nicolet Company. HRMS were recorded on VG ZAB-HS mass spectrometer with ESI resource. Bs (4-bromobenzenesulfonyl); Ns (4-nitrobenzenesulfonyl); Ts (p-toluenesulfonyl).

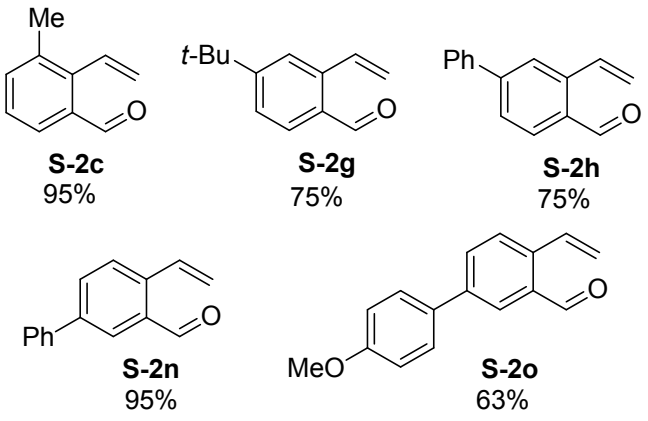
Synthesis of aldehydes S-2

General Procedure A



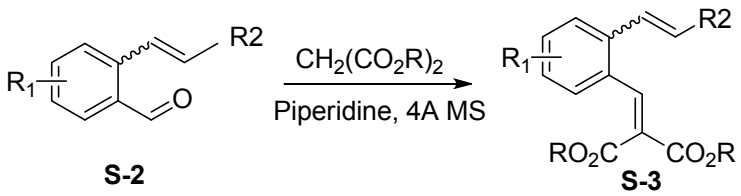
To a solution of $Pd(PPh_3)_4$ (1.2 mmol) in toluene (100 mL) was added aldehyde **S-1** (40 mmol) and tributylvinylstannane (48 mmol). The resulting solution was refluxed for 12 h. The reaction was quenched with water and extracted with Et_2O. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography to afford aldehyde **S-2**.

The unknown aldehydes including **S-2c, S-2g, S-2h, S-2n** and **S-2o** were synthesized from **S-1c**[1], **S-1g**[2], **S-1h**[3], **S-1n**[3] and **S-1o**[3] according to *General Procedure A*.



Synthesis of alkenes S-3

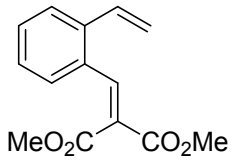
General Procedure B



S-2 **S-3**

Piperidine (1 mL) and 4Å MS (8 g) was added to the solution of aldehyde **S-2** (20 mmol), malonic ester (26 mmol) in toluene (20 mL) at room temperature. Then the mixture was stirred at 65 °C for 8 h. After filtration, the mixture was extracted with EtOAc (100 mL) and dried over Na_2SO_4. The solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate, 25:1) to afford product **S-3**.

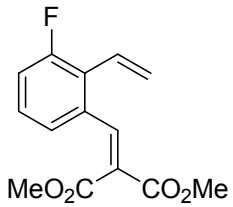
Dimethyl 2-(2-vinylbenzylidene)malonate **S-3a**



S-3a

S-3a was synthesized from aldehyde **S-2a**[4] according to *General Procedure B*. Yield: 76%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.31 (dq, *J* = 29.6, 7.4 Hz, 3H), 6.90 (dd, *J* = 17.3, 11.0 Hz, 1H), 5.64 (d, *J* = 17.3 Hz, 1H), 5.44 (d, *J* = 11.0 Hz, 1H), 3.86 (s, 3H), 3.71 (s, 3H); the analytical data were in accordance with those reported in our previous work[5].

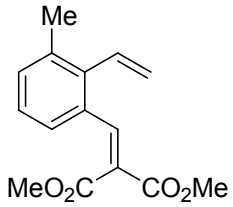
Dimethyl 2-(3-fluoro-2-vinylbenzylidene)malonate **S-3b**



S-3b

S-3b was synthesized from aldehyde **S-2b**[4] according to *General Procedure B*. Yield: 72%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.21 (dd, *J* = 13.4, 7.7 Hz, 1H), 7.10 (dd, *J* = 17.3, 8.2 Hz, 2H), 6.78 (dd, *J* = 17.7, 11.6 Hz, 1H), 5.69 (d, *J* = 11.6 Hz, 1H), 5.60 (d, *J* = 17.7 Hz, 1H), 3.86 (s, 3H), 3.71 (s, 3H).

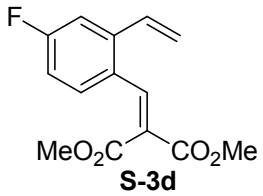
Dimethyl 2-(3-methyl-2-vinylbenzylidene)malonate **S-3c**



S-3c

S-3c was synthesized from aldehyde **S-2c** according to *General Procedure B*. Yield: 46%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.25 – 7.19 (m, 2H), 7.19 – 7.12 (m, 1H), 6.80 (dd, *J* = 17.6, 11.3 Hz, 1H), 5.69 (dd, *J* = 11.3, 1.5 Hz, 1H), 5.26 (dd, *J* = 17.6, 1.5 Hz, 1H), 3.84 (s, 3H), 3.72 (s, 3H), 2.32 (s, 3H).

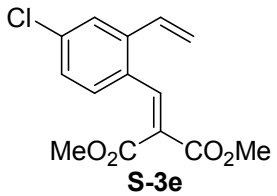
Dimethyl 2-(4-fluoro-2-vinylbenzylidene)malonate **S-3d**



S-3d

S-3d was synthesized from aldehyde **S-2d**[4] according to *General Procedure B*. Yield: 77%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.31 (dd, J = 8.6, 5.7 Hz, 1H), 7.19 (dd, *J* = 9.8, 2.6 Hz, 1H), 6.98 – 6.89 (m, 1H), 6.86 (dd, *J* = 17.2, 11.0 Hz, 1H), 5.66 (d, *J* = 17.3 Hz, 1H), 5.49 (d, *J* = 11.0 Hz, 1H), 3.86 (s, 3H), 3.73 (s, 3H); the analytical data were in accordance with those reported in our previous work[5].

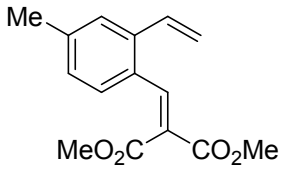
Dimethyl 2-(4-chloro-2-vinylbenzylidene)malonate **S-3e**



S-3e

S-3e was synthesized from aldehyde **S-2e**[6] according to *General Procedure B*. Yield: 47%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.38 (s, 1H), 7.19 – 6.97 (m, 2H), 6.73 (dd, *J* = 17.2, 11.1 Hz, 1H), 5.57 (d, *J* = 17.3 Hz, 1H), 5.39 (d, *J* = 11.0 Hz, 1H), 3.76 (s, 3H), 3.62 (s, 3H); the analytical data were in accordance with those reported in our previous work[5].

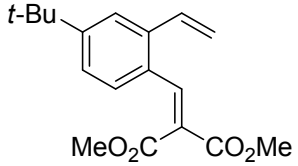
Dimethyl 2-(4-methyl-2-vinylbenzylidene)malonate **S-3f**



S-3f

S-3f was synthesized from aldehyde **S-2f**[4] according to *General Procedure B*. Yield: 65%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.31 – 7.25 (m, 1H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.06 (d, *J* = 8.1 Hz, 1H), 6.89 (dd, *J* = 17.3, 11.0 Hz, 1H), 5.61 (d, *J* = 17.3 Hz, 1H), 5.42 (d, *J* = 11.0 Hz, 1H), 3.85 (s, 3H), 3.73 (s, 3H), 2.36 (s, 3H); the analytical data were in accordance with those reported in our previous work[5].

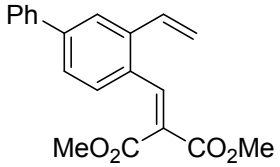
Dimethyl 2-(4-methyl-2-vinylbenzylidene)malonate **S-3g**



S-3g

S-3g was synthesized from aldehyde **S-2g** according to *General Procedure B*. Yield: 72%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.51 (s, 1H), 7.30 (d, J = 1.1 Hz, 2H), 6.96 (dd, J = 17.4, 11.0 Hz, 1H), 5.63 (dd, J = 17.3, 0.9 Hz, 1H), 5.47 (dd, J = 11.0, 0.9 Hz, 1H), 3.88 (s, 3H), 3.78 (s, 3H), 1.35 (s, 9H).

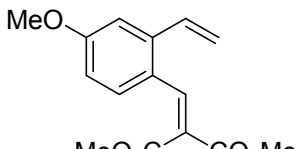
Dimethyl 2-((3-vinyl-[1,1'-biphenyl]-4-yl)methylene)malonate **S-3h**



S-3h

S-3h was synthesized from aldehyde **S-2h** according to *General Procedure B*. Yield: 59%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.71 (d, *J* = 1.8 Hz, 1H), 7.61 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.52 – 7.33 (m, 5H), 6.97 (dd, *J* = 17.3, 11.0 Hz, 1H), 5.70 (dd, *J* = 17.3, 0.9 Hz, 1H), 5.50 (dd, *J* = 11.0, 0.9 Hz, 1H), 3.87 (s, 3H), 3.76 (s, 3H).

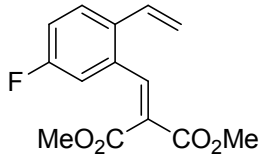
Dimethyl 2-(4-methoxy-2-vinylbenzylidene)malonate **S-3i**



S-3i

S-3i was synthesized from aldehyde **S-2i**[7] according to *General Procedure B*. Yield: 57%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.35 – 7.22 (m, 1H), 6.99 (d, *J* = 2.6 Hz, 1H), 6.92 (dd, *J* = 17.3, 11.0 Hz, 1H), 6.79 (dd, *J* = 8.7, 2.6 Hz, 1H), 5.62 (dd, *J* = 17.3, 0.9 Hz, 1H), 5.46 (dd, *J* = 11.0, 0.9 Hz, 1H), 3.84 (s, 3H), 3.84 (s, 3H), 3.76 (s, 3H).

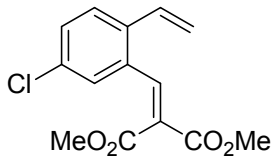
Dimethyl 2-(5-fluoro-2-vinylbenzylidene)malonate **S-3j**



S-3j

S-3j was synthesized from aldehyde **S-2j**[4] according to *General Procedure B*. Yield: 62%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.46 (dd, J = 8.6, 5.7 Hz, 1H), 7.09 – 6.98 (m, 2H), 6.81 (dd, J = 17.3, 11.0 Hz, 1H), 5.57 (d, J = 17.3 Hz, 1H), 5.40 (d, J = 11.0 Hz, 1H), 3.85 (s, 3H), 3.74 (s, 3H).

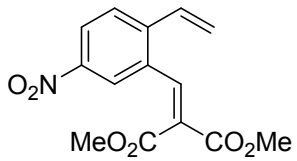
Dimethyl 2-(5-chloro-2-vinylbenzylidene)malonate **S-3k**



S-3k

S-3k was synthesized from aldehyde **S-2k**[4] according to *General Procedure B*. Yield: 84%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.49 – 7.11 (m, 3H), 6.85 (dd, *J* = 17.3, 11.0 Hz, 1H), 5.66 (d, *J* = 17.3 Hz, 1H), 5.48 (d, *J* = 11.0 Hz, 1H), 3.90 (s, 3H), 3.79 (s, 3H); the analytical data were in accordance with those reported in our previous work[5].

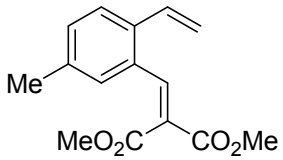
Dimethyl 2-(5-nitro-2-vinylbenzylidene)malonate **S-3l**



S-3l

S-3l was synthesized from aldehyde **S-2l**[4] according to *General Procedure B*. Yield: 74%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.92 (m, 1H), 7.89 (s, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 6.99 (dd, *J* = 17.5, 11.4 Hz, 1H), 5.77 (d, *J* = 11.4 Hz, 1H), 5.40 (d, *J* = 17.5 Hz, 1H), 3.86 (s, 3H), 3.72 (s, 3H); the analytical data were in accordance with those reported in our previous work[5].

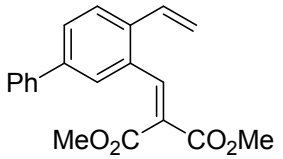
Dimethyl 2-(5-methyl-2-vinylbenzylidene)malonate **S-3m**



S-3m

S-3m was synthesized from aldehyde **S-2m**[8] according to *General Procedure B*. Yield: 56%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.40 (d, J = 7.9 Hz, 1H), 7.18 (s, 1H), 7.11 (s, 1H), 6.87 (dd, J = 17.3, 11.0 Hz, 1H), 5.59 (d, J = 17.3 Hz, 1H), 5.38 (d, J = 11.0 Hz, 1H), 3.86 (s, 3H), 3.72 (s, 3H), 2.32 (s, 3H).

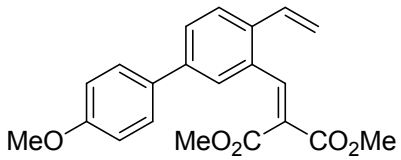
Dimethyl 2-((4-vinyl-[1,1'-biphenyl]-3-yl)methylene)malonate **S-3n**



S-3n

S-3n was synthesized from aldehyde **S-2n** according to *General Procedure B*. Yield: 76%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.65 – 7.52 (m, 5H), 7.50 – 7.41 (m, 2H), 7.36 (dd, *J* = 8.1, 6.4 Hz, 1H), 6.93 (dd, *J* = 17.3, 11.0 Hz, 1H), 5.70 (d, *J* = 17.3 Hz, 1H), 5.46 (d, *J* = 11.0 Hz, 1H), 3.88 (s, 3H), 3.72 (s, 3H).

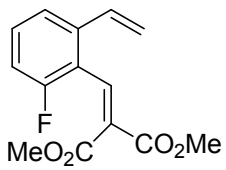
Dimethyl 2-((4'-methoxy-4-vinyl-[1,1'-biphenyl]-3-yl)methylene)malonate **S-3o**



S-3o

S-3o was synthesized from aldehyde **S-2o** according to *General Procedure B*. Yield: 49%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.52 (dd, *J* = 21.5, 8.0 Hz, 5H), 6.97 (d, *J* = 8.5 Hz, 2H), 6.92 (dd, *J* = 17.4, 11.1 Hz, 1H), 5.67 (d, *J* = 17.3 Hz, 1H), 5.44 (d, *J* = 11.0 Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.71 (s, 3H).

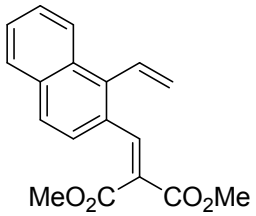
Dimethyl 2-(2-fluoro-6-vinylbenzylidene)malonate **S-3p**



S-3p

S-3p was synthesized from aldehyde **S-2p**[4] according to *General Procedure B*. Yield: 71%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.36 – 7.29 (m, 2H), 7.05 – 6.95 (m, 1H), 6.77 (dd, J = 17.3, 11.0 Hz, 1H), 5.68 (d, J = 17.3 Hz, 1H), 5.43 (d, J = 11.0 Hz, 1H), 3.87 (s, 3H), 3.68 (s, 3H).

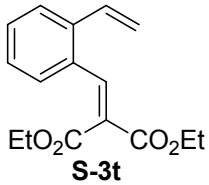
Dimethyl 2-((1-vinylnaphthalen-2-yl)methylene)malonate **S-3q**



S-3q

S-3q was synthesized from aldehyde **S-2q**[9] according to *General Procedure B*. Yield: 76%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.15 – 8.08 (m, 1H), 7.86 – 7.80 (m, 1H), 7.74 (d, J = 8.5 Hz, 1H), 7.59 – 7.49 (m, 2H), 7.47 – 7.39 (m, 1H), 7.32 – 7.21 (m, 1H), 5.93 (d, J = 11.3 Hz, 1H), 5.46 (d, J = 17.5 Hz, 1H), 3.87 (s, 3H), 3.74 (s, 3H).

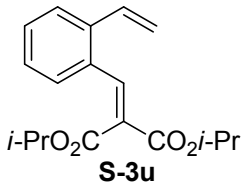
Diethyl 2-(2-vinylbenzylidene)malonate **S-3t**



S-3t

S-3t was synthesized from aldehyde **S-2a**[4] according to *General Procedure B*. Yield: 90%; yellow oil; the analytical data were in accordance with those reported in the literature[10].

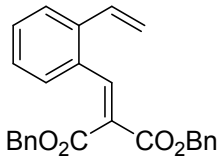
Diisopropyl 2-(2-vinylbenzylidene)malonate **S-3u**



S-3u

S-3u was synthesized from aldehyde **S-2a**[4] according to *General Procedure B*. Yield: 88%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.49 (d, J = 7.7 Hz, 1H), 7.34 (dd, J = 13.1, 7.4 Hz, 2H), 7.22 (dt, J = 7.5, 3.8 Hz, 1H), 6.90 (dd, J = 17.4, 11.0 Hz, 1H), 5.65 (dd, J = 17.4, 1.0 Hz, 1H), 5.41 (dd, J = 11.0, 1.0 Hz, 1H), 5.13 (ddt, J = 24.0, 12.5, 6.3 Hz, 2H), 1.32 (d, J = 6.3 Hz, 6H), 1.16 (d, J = 6.3 Hz, 6H).

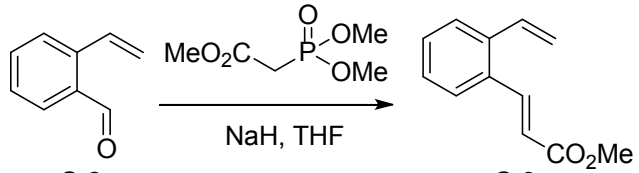
Dibenzyl 2-(2-vinylbenzylidene)malonate **S-3v**



S-3v

S-3v was synthesized from aldehyde **S-2a**[4] according to *General Procedure B*. Yield: 68%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.60 – 7.03 (m, 14H), 6.87 (dd, J = 17.3, 11.0 Hz, 1H), 5.61 (d, J = 17.0 Hz, 1H), 5.40 (d, J = 11.0 Hz, 1H), 5.29 (s, 2H), 5.15 (s, 2H).

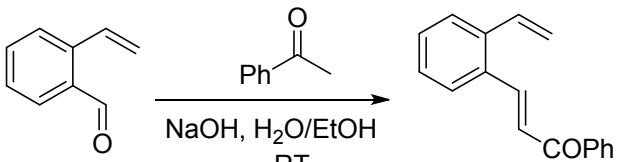
(E)-Methyl 3-(2-vinylphenyl)acrylate **S-3w**



S-2a **S-3w**

S-3w was synthesized synthesized according to the literature procedure[11]. Yield: 54%; yellow oil; the analytical data were in accordance with those reported in the literature [11].

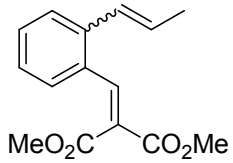
(E)-Methyl 3-(2-vinylphenyl)acrylate **S-3x**



S-2a **S-3x**

S-3x was synthesized synthesized according to the literature procedure[12]. Yield: 60%; yellow oil; the analytical data were in accordance with those reported in the literature[12].

Dimethyl 2-(2-(prop-1-en-1-yl)benzylidene)malonate **S-3y**

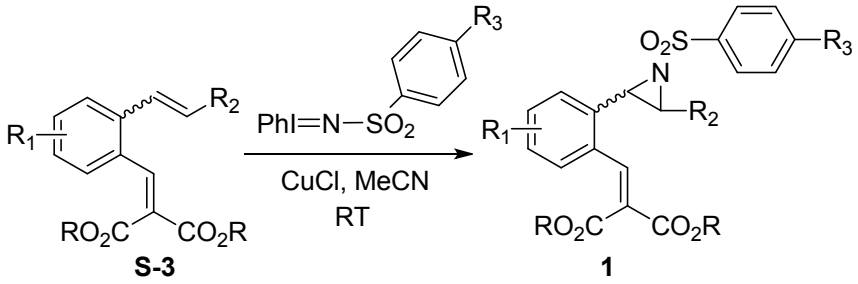


S-3y

S-3y was synthesized from aldehyde **S-2y**[13] according to *General Procedure B*. Yield: 59%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.92 (s, 1H), 7.47 – 7.13 (m, 8H), 6.59 – 6.44 (m, 2H), 6.16 – 6.03 (m, 1H), 5.96 (dq, J = 11.5, 7.1 Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.76 (s, 3H), 3.71 (s, 3H),1.92 (dd, J = 6.6, 1.6 Hz, 3H), 1.66 (dd, J = 7.1, 1.7 Hz, 3H).

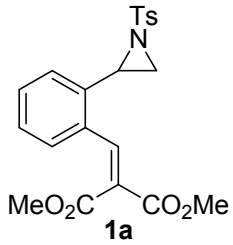
Synthesis of aziridines 1

General Procedure C



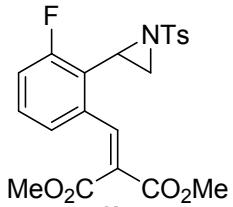
Under an argon atmosphere, CuCl (0.75 mmol, 15% cat.) was added to a suspension of alkene **S-3** (5 mmol), PhI=NSO_2Ar (7.5 mmol) in MeCN (50 mL) at room temperature. The reaction mixture was stirred overnight, then diluted with ethyl acetate (300 mL), and washed with brine (100 mL), dried over Na_2SO_4, and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate, 5:1) to afford aziridine **1**.

Dimethyl 2-(2-(1-tosylaziridin-2-yl)benzylidene)malonate **1a**



1a was synthesized from **S-3a** according to *General Procedure C*. Yield: 66%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.90 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.32 – 7.24 (m, 4H), 3.89 (s, 3H), 3.86 (dd, *J* = 7.1, 4.5 Hz, 1H), 3.69 (s, 3H), 3.01 (d, *J* = 7.2 Hz, 1H), 2.45 (s, 3H), 2.31 (d, *J* = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.20, 163.92, 144.90, 140.54, 134.60, 134.21, 132.73, 130.23, 129.85, 128.78, 128.26, 128.09, 127.63, 126.82, 52.84, 52.53, 38.77, 35.59, 21.68; the analytical data were in accordance with those reported in our previous work[5].

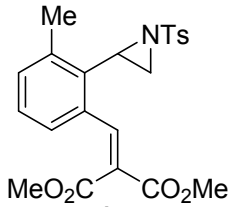
Dimethyl 2-(3-fluoro-2-(1-tosylaziridin-2-yl)benzylidene)malonate **1b**



1b

1b was synthesized from **S-3b** according to *General Procedure C*. Yield: 33%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.20 (m, 1H), 7.02 (dd, *J* = 20.2, 8.4 Hz, 2H), 3.92 (dd, *J* = 7.3, 4.5 Hz, 1H), 3.88 (s, 3H), 3.63 (s, 3H), 2.93 (d, *J* = 7.3 Hz, 1H), 2.47 (d, *J* = 4.5 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.90, 163.84, 161.56 (d, *J* = 249.9 Hz), 144.86, 141.97 (d, *J* = 3.2 Hz), 135.81 (d, *J* = 3.3 Hz), 134.38, 129.79, 129.72, 128.81, 128.24, 124.06 (d, *J* = 3.5 Hz), 120.91 (d, *J* = 12.7 Hz), 116.83 (d, *J* = 22.0 Hz), 52.72, 52.42, 34.76 (d, *J* = 4.9 Hz), 34.20 (d, *J* = 3.9 Hz), 21.66; HRMS (ESI) Calcd for $C_{21}H_{21}FNO_6S(M+H)^+$: 434.1068; Found: 434.1066; IR (neat): *v*= 556, 717, 916, 1080, 1161, 1236, 1329, 1363, 1438, 1734, 3421 cm^{-1}.

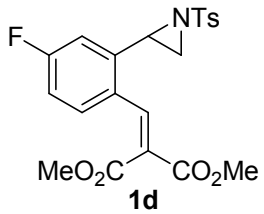
Dimethyl 2-(3-methyl-2-(1-tosylaziridin-2-yl)benzylidene)malonate **1c**



1c

1c was synthesized from **S-3c** according to *General Procedure C*. Yield: 11%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.87 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.19 – 7.12 (m, 2H), 7.02 (dd, *J* = 5.6, 3.5 Hz, 1H), 3.96 (dd, *J* = 7.2, 4.6 Hz, 1H), 3.86 (s, 3H), 3.60 (s, 3H), 2.88 (d, *J* = 7.2 Hz, 1H), 2.44 (s, 3H), 2.44 (s, 3H), 2.18 (d, *J* = 4.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.28, 164.21, 144.84, 144.52, 138.48, 134.69, 133.63, 131.94, 131.52, 129.74, 128.20, 128.04, 127.22, 126.13, 52.57, 52.30, 38.43, 35.24, 21.64, 20.06; HRMS (ESI) Calcd for $C_{22}H_{24}NO_6S(M+H)^+$: 430.1319; Found: 430.1324; IR (neat): *v*= 573, 720, 816, 915, 1070, 1090, 1161, 224, 1268, 1328, 1361, 1438, 1595, 1630, 1733, 2954, 3448 cm^{-1}.

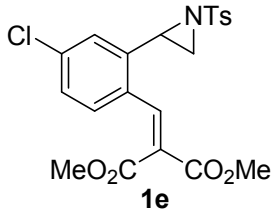
Dimethyl 2-(4-fluoro-2-(1-tosylaziridin-2-yl)benzylidene)malonate **1d**



1d

1d was synthesized from **S-3d** according to *General Procedure C.* Yield: 49%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.90 (d, *J* = 7.9 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.27 (d, *J* = 5.1 Hz, 1H), 6.96 (dd, *J* = 13.6, 8.8 Hz, 2H), 3.89 (s, 3H), 3.87 – 3.78 (m, 1H), 3.71 (s, 3H), 3.03 (d, *J* = 7.2 Hz, 1H), 2.46 (s, 3H), 2.28 (d, *J* = 4.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.09, 163.81, 163.60 (d, *J* = 251.5 Hz), 145.12, 139.16, 137.32 (d, *J* = 8.5 Hz), 134.38, 129.91, 129.80, 128.80, 128.65 (d, *J* = 3.1 Hz), 128.06, 115.48 (d, *J* = 21.9 Hz), 114.10 (d, *J* = 23.5 Hz), 52.87, 52.60, 38.08, 35.90, 21.67; the analytical data were in accordance with those reported in our previous work[5].

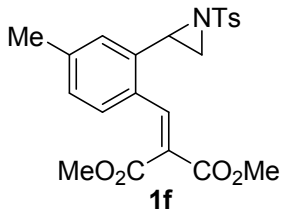
Dimethyl 2-(4-chloro-2-(1-tosylaziridin-2-yl)benzylidene)malonate **1e**



1e

1e was synthesized from **S-3e** according to *General Procedure C.* Yield: 49%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 6.5 Hz, 3H), 3.86 (s, 3H), 3.80 (dd, *J* = 6.9, 4.5 Hz, 1H), 3.68 (s, 3H), 2.98 (d, *J* = 7.2 Hz, 1H), 2.43 (s, 3H), 2.26 (d, *J* = 4.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.84, 163.63, 145.08, 139.08, 136.29, 136.11, 134.21, 131.03, 129.84, 129.18, 128.93, 128.43, 128.00, 126.96, 52.83, 52.58, 37.81, 35.78, 21.60; the analytical data were in accordance with those reported in our previous work[5].

Dimethyl 2-(4-methyl-2-(1-tosylaziridin-2-yl)benzylidene)malonate **1f**

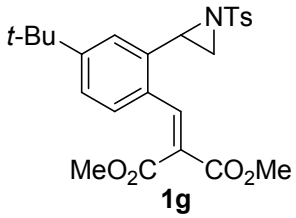


1f

1f was synthesized from **S-3f** according to *General Procedure C.* Yield: 48%; yellow oil; ^{1}H

NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.90 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 1H), 7.04 (d, *J* = 6.2 Hz, 2H), 3.86 (d, *J* = 3.6 Hz, 3H), 3.86 – 3.81 (m, 1H), 3.70 (s, 3H), 2.98 (d, *J* = 7.2 Hz, 1H), 2.45 (s, 3H), 2.29 (d, *J* = 4.4 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.50, 164.06, 144.89, 140.84, 140.30, 134.45, 134.15, 129.80, 129.65, 129.03, 128.08, 127.68, 127.61, 127.52, 52.74, 52.52, 38.59, 35.64, 21.64, 21.36; the analytical data were in accordance with those reported in our previous work[5].

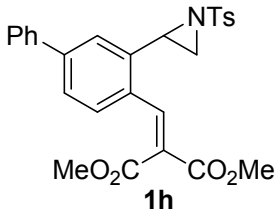
Dimethyl 2-(4-(tert-butyl)-2-(1-tosylaziridin-2-yl)benzylidene)malonate **1g**



1g

1g was synthesized from **S-3g** according to *General Procedure C*. Yield: 37%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.22 (s, 2H), 7.07 (s, 1H), 3.87 (s, 3H), 3.81 – 3.76 (m, 1H), 3.73 (s, 3H), 3.07 (d, *J* = 7.2 Hz, 1H), 2.44 (s, 3H), 2.35 (d, *J* = 4.4 Hz, 1H), 1.16 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.59, 164.12, 153.83, 144.88, 139.80, 134.71, 133.97, 129.83, 129.34, 128.09, 127.47, 127.40, 125.28, 124.28, 52.74, 52.53, 39.62, 34.91, 34.78, 30.82, 21.59; HRMS (ESI) Calcd for $C_{25}H_{30}NO_6S$ $(M+H)^+$: 472.1788; Found: 472.1792; IR (neat): *v*= 566, 673, 721, 755, 936, 1069, 1092, 1162, 1219, 1265, 1330, 1373, 1438, 1603, 1630, 1734, 2958, 3453 cm^{-1}.

Dimethyl 2-((3-(1-tosylaziridin-2-yl)-[1,1'-biphenyl]-4-yl)methylene)malonate **1h**

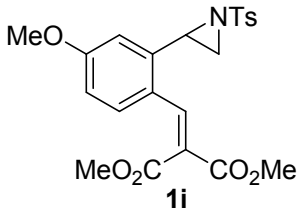


1h

1h was synthesized from **S-3h** according to *General Procedure C*. Yield: 66%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.93 (d, *J* = 8.3 Hz, 2H), 7.53 – 7.31 (m, 10H), 3.94 – 3.84 (m, 4H), 3.74 (s, 3H), 3.07 (d, *J* = 7.2 Hz, 1H), 2.45 (s, 3H), 2.37 (d, *J* = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.42, 164.02, 144.98, 143.06, 139.81, 139.46, 134.92, 134.64, 131.30, 129.89, 128.85, 128.27, 128.25, 128.18, 128.09, 126.97, 126.78, 125.66, 52.87, 52.64, 38.99, 35.46, 21.68; HRMS (ESI) Calcd for $C_{27}H_{26}NO_6S(M+H)^+$: 492.1475; Found: 492.1477; IR

(neat): v= 1069, 1092, 1160, 1219, 1261, 1329, 1378, 1438, 1601, 1733, 2923, 2955, 3447 cm^{-1}.

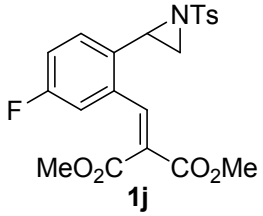
Dimethyl 2-(4-methoxy-2-(1-tosylaziridin-2-yl)benzylidene)malonate **1i**



1i

1i was synthesized from **S-3i** according to *General Procedure C*. Yield: 72%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.92 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 1.6 Hz, 1H), 6.80 – 6.72 (m, 2H), 3.88 (s, 3H), 3.87 – 3.83 (m, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 3.06 (d, *J* = 7.2 Hz, 1H), 2.46 (s, 3H), 2.31 (d, *J* = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.87, 164.28, 161.31, 144.96, 139.44, 136.73, 134.58, 129.85, 129.47, 128.12, 126.28, 124.60, 114.11, 112.19, 55.28, 52.71, 52.56, 38.85, 35.63, 21.66; HRMS (ESI) Calcd for $C_{22}H_{24}NO_7S(M+H)^+$: 446.1268; Found: 446.1266; IR (neat): *v*= 561, 615, 669, 720, 1091, 1161, 1223, 1327, 1379, 1437, 1603, 1732, 3417 cm^{-1}.

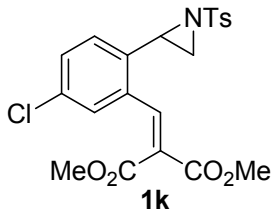
Dimethyl 2-(5-fluoro-2-(1-tosylaziridin-2-yl)benzylidene)malonate **1j**



1j

1j was synthesized from **S-3j** according to *General Procedure C*. Yield: 58%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.19 (m, 1H), 7.02 – 6.93 (m, 2H), 3.89 (s, 3H), 3.80 (dd, *J* = 7.0, 4.4 Hz, 1H), 3.73 (s, 3H), 2.98 (d, *J* = 7.1 Hz, 1H), 2.45 (s, 3H), 2.27 (d, *J* = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.62, 163.57, 162.03 (d, J = 248.5 Hz), 144.98, 138.93, 134.48 (d, J = 8.9 Hz), 130.10 (d, J = 2.9 Hz), 129.84, 129.77, 128.87 (d, J = 8.6 Hz), 128.02, 117.00 (d, J = 21.4 Hz), 114.54 (d, J = 23.3 Hz), 52.90, 52.62, 38.10, 35.60, 21.63; HRMS (ESI) Calcd for $C_{21}H_{21}FNO_6S(M+H)^+$: 434.1068; Found: 434.1065; IR (neat): *v*= 573, 665, 721, 818, 911, 989, 1070, 1162, 1222, 1275, 1329, 1378, 1439, 1495, 1589, 1633, 1735, 2955, 3447cm^{-1}.

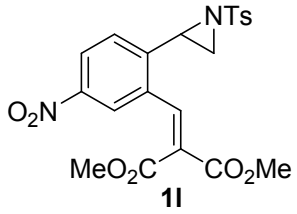
Dimethyl 2-(5-chloro-2-(1-tosylaziridin-2-yl)benzylidene)malonate **1k**



1k

1k was synthesized from **S-3k** according to *General Procedure C.* Yield: 62%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 7.7 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 1H), 3.90 (s, 3H), 3.80 (dd, *J* = 7.1, 4.4 Hz, 1H), 3.73 (s, 3H), 3.00 (d, *J* = 7.1 Hz, 1H), 2.46 (s, 3H), 2.28 (d, *J* = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.59, 163.58, 145.05, 138.91, 134.38, 134.22, 134.18, 132.68, 130.08, 129.88, 128.24, 128.05, 127.47, 52.96, 52.62, 38.12, 35.65, 21.67; the analytical data were in accordance with those reported in our previous work[5].

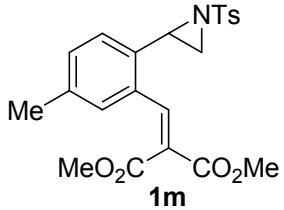
Dimethyl 2-(5-nitro-2-(1-tosylaziridin-2-yl)benzylidene)malonate **1l**



1l

1l was synthesized from **S-3l** according to *General Procedure C.* Yield: 40%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 2.0 Hz, 1H), 8.11 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.97 (s, 1H), 7.88 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 3.91 (s, 3H), 3.87 (dd, *J* = 7.2, 4.4 Hz, 1H), 3.77 (s, 3H), 3.06 (d, *J* = 7.2 Hz, 1H), 2.45 (s, 3H), 2.30 (d, *J* = 4.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.12, 163.29, 147.49, 145.33, 141.07, 137.65, 134.14, 134.02, 131.32, 129.97, 128.07, 124.55, 122.69, 53.08, 52.76, 37.91, 35.90, 21.66; the analytical data were in accordance with those reported in our previous work[5].

Dimethyl 2-(5-methyl-2-(1-tosylaziridin-2-yl)benzylidene)malonate **1m**

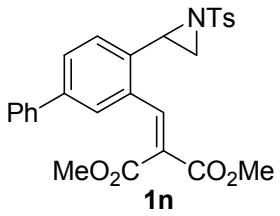


1m

1m was synthesized from **S-3m** according to *General Procedure C.* Yield: 29%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.88 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 7.10 (d,

J = 2.6 Hz, 2H), 7.06 (s, 1H), 3.88 (s, 3H), 3.82 (dd, J = 6.9, 4.6 Hz, 1H), 3.69 (s, 3H), 2.98 (d, J = 7.0 Hz, 1H), 2.44 (s, 3H), 2.29 – 2.27 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.28, 163.98, 144.82, 140.69, 138.14, 134.65, 132.56, 131.29, 130.99, 129.81, 128.44, 128.15, 128.06, 126.75, 52.79, 52.43, 38.72, 35.53, 21.65, 21.03; HRMS (ESI) Calcd for $C_{22}H_{24}NO_6S(M+H)^+$: 430.1319; Found: 430.1324; IR (neat): *v*= 572, 665, 720, 818, 908, 1070, 1092, 1161, 1226, 1268, 1327, 1378, 1438, 1630, 1734, 3454 cm^{-1}.

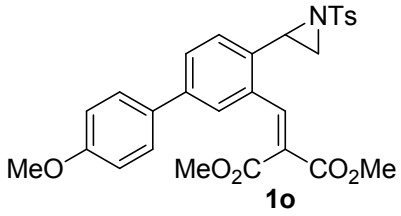
Dimethyl 2-((4-(1-tosylaziridin-2-yl)-[1,1'-biphenyl]-3-yl)methylene)malonate **1n**



1n

1n was synthesized from **S-3n** according to *General Procedure C.* Yield: 52%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.54 – 7.46 (m, 4H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.37 (dd, *J* = 7.6, 3.5 Hz, 3H), 7.31 (d, *J* = 8.6 Hz, 1H), 3.93 – 3.87 (m, 4H), 3.68 (s, 3H), 3.04 (d, *J* = 7.2 Hz, 1H), 2.45 (s, 3H), 2.35 (d, *J* = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.19, 163.90, 144.93, 141.19, 140.50, 139.47, 134.58, 133.12, 133.04, 129.86, 129.06, 128.94, 128.73, 128.09, 127.88, 127.31, 126.82, 126.33, 52.86, 52.59, 38.63, 35.64, 21.68; HRMS (ESI) Calcd for $C_{27}H_{26}NO_6S(M+H)^+$: 492.1475; Found: 492.1477; IR (neat): *v*= 1072, 1160, 1221, 1256, 1328, 1378, 1438, 1598, 1630, 1733, 3448 cm^{-1}.

Dimethyl 2-((4'-methoxy-4-(1-tosylaziridin-2-yl)-[1,1'-biphenyl]-3-yl)methylene)malonate **1o**

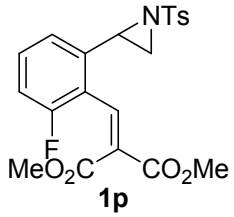


1o

1o was synthesized from **S-3o** according to *General Procedure C.* Yield: 64%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.52 – 7.35 (m, 6H), 7.28 (s, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H), 3.89 – 3.86 (m, 1H), 3.84 (s, 3H), 3.68 (s, 3H), 3.03 (d, *J* = 7.2 Hz, 1H), 2.45 (s, 3H), 2.34 (d, *J* = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.26, 163.94, 159.56, 144.90, 140.78, 140.61, 134.62, 133.08, 132.35, 131.93, 129.85, 128.95, 128.24, 128.09, 127.88, 127.27, 125.84, 114.38, 55.34, 52.85, 52.59, 38.68, 35.62, 21.69; HRMS (ESI)

Calcd for $C_{28}H_{28}NO_7S(M+H)^+$: 522.1581; Found: 522.1580; IR (neat): *v*= 1027, 1071, 1160, 1250, 1327, 1378, 1438, 1492, 1520, 1606, 1732, 2923, 2954, 3447 cm^{-1}.

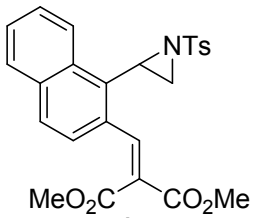
Dimethyl 2-(2-fluoro-6-(1-tosylaziridin-2-yl)benzylidene)malonate **1p**



1p

1p was synthesized from **S-3p** according to *General Procedure C.* Yield: 46%; yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.3 Hz, 2H), 7.81 (s, 1H), 7.36 (d, J = 8.1 Hz, 2H), 7.26 – 7.22 (m, 1H), 7.07 – 6.94 (m, 2H), 3.90 (s, 3H), 3.78 (dd, J = 7.1, 4.4 Hz, 1H), 3.67 (s, 3H), 2.97 (d, J = 7.2 Hz, 1H), 2.45 (s, 3H), 2.28 (d, J = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.79, 163.97, 159.04 (d, J = 249.8 Hz), 144.98, 136.11, 135.95 (d, J = 2.7 Hz), 134.48, 131.64 (d, J = 2.3 Hz), 131.01 (d, J = 9.3 Hz), 129.85, 128.07, 112.18 (d, J = 3.0 Hz), 121.25 (d, J = 16.3 Hz), 115.37 (d, J = 22.6 Hz), 52.90, 52.33, 38.39 (d, J = 3.6 Hz), 35.76, 21.66; HRMS (ESI) Calcd for $C_{21}H_{21}FNO_6S(M+H)^+$: 434.1068; Found: 434.1069; IR (neat): *v*= 558, 668, 722, 797, 891, 953, 1075, 1161, 1225, 1269, 1329, 1379, 1439, 1463, 1600, 1731, 2955, 3447 cm^{-1}.

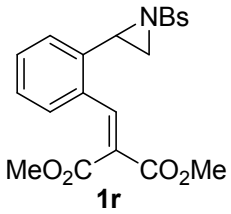
Dimethyl 2-((1-(1-tosylaziridin-2-yl)naphthalen-2-yl)methylene)malonate **1q**



1q

1q was synthesized from **S-3q** according to *General Procedure C.* Yield: 21%; yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.45 (d, *J* = 7.9 Hz, 1H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.85 – 7.81 (m, 1H), 7.76 (d, *J* = 8.6 Hz, 1H), 7.56 (qd, *J* = 6.8, 3.6 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 6.1 Hz, 1H), 4.39 (dd, *J* = 7.1, 4.6 Hz, 1H), 3.90 (s, 3H), 3.60 (s, 3H), 3.08 (d, *J* = 7.2 Hz, 1H), 2.45 (s, 3H), 2.31 (d, *J* = 4.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.26, 164.31, 144.99, 144.44, 134.54, 133.64, 131.72, 131.27, 129.80, 129.63, 128.94, 128.53, 128.31, 127.78, 127.27, 127.05, 125.12, 124.60, 52.67, 52.39, 37.89, 35.64, 21.67; HRMS (ESI) Calcd for $C_{25}H_{24}NO_6S(M+H)^+$: 466.1319; Found: 466.1325; IR (neat): *v*= 469, 556, 615, 661, 716, 818, 911, 988, 1072, 1160, 1219, 1259, 1327, 1382, 1436, 1621, 1731, 2923, 2953, 3416 cm^{-1}.

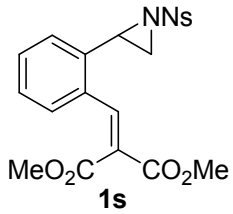
Dimethyl 2-(2-(1-((4-bromophenyl)sulfonyl)aziridin-2-yl)benzylidene)malonate **1r**



1r

1r was synthesized from **S-3a** according to *General Procedure C*. Yield: 45%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.90 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.36 – 7.24 (m, 4H), 3.99 – 3.85 (m, 4H), 3.71 (s, 3H), 3.06 (d, *J* = 7.2 Hz, 1H), 2.38 (d, *J* = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.10, 163.87, 140.47, 136.75, 133.72, 132.82, 132.55, 130.25, 129.51, 129.13, 128.96, 128.44, 127.73, 126.62, 52.86, 52.54, 39.10, 35.79; the analytical data were in accordance with those reported in our previous work[5].

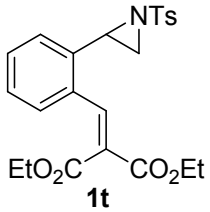
Dimethyl 2-(2-(1-((4-nitrophenyl)sulfonyl)aziridin-2-yl)benzylidene)malonate **1s**



1s

1s was synthesized from **S-3a** according to *General Procedure C*. Yield: 55%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 8.6 Hz, 2H), 8.25 (d, *J* = 8.6 Hz, 2H), 8.07 (s, 1H), 7.33 (dt, *J* = 9.9, 4.3 Hz, 3H), 7.23 (d, *J* = 7.2 Hz, 1H), 4.03 (dd, *J* = 7.1, 4.6 Hz, 1H), 3.91 (s, 3H), 3.71 (s, 3H), 3.15 (d, *J* = 7.2 Hz, 1H), 2.47 (d, *J* = 4.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.01, 163.82, 150.74, 143.53, 140.33, 133.19, 132.92, 130.28, 129.36, 129.17, 128.68, 127.86, 126.45, 124.42, 52.90, 52.58, 39.58, 36.11; the analytical data were in accordance with those reported in our previous work[5].

Diethyl 2-(2-(1-tosylaziridin-2-yl)benzylidene)malonate **1t**

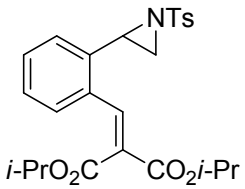


1t

1t was synthesized from **S-3t** according to *General Procedure C*. Yield: 70%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.90 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.31 –

7.23 (m, 4H), 4.35 (q, *J* = 7.1 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.86 (dd, *J* = 6.9, 4.6 Hz, 1H), 3.00 (d, *J* = 7.2 Hz, 1H), 2.45 (s, 3H), 2.31 (d, *J* = 4.4 Hz, 1H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.64, 163.52, 144.86, 140.01, 134.59, 134.03, 132.96, 129.98, 129.82, 129.73, 128.13, 128.07, 127.81, 126.64, 61.87, 61.50, 38.82, 35.56, 21.65, 14.11, 13.72; the analytical data were in accordance with those reported in our previous work[5].

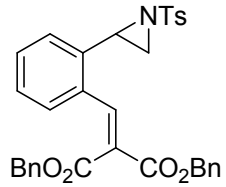
Diisopropyl 2-(2-(1-tosylaziridin-2-yl)benzylidene)malonate **1u**



1u

1u was synthesized from **S-3u** according to *General Procedure C.* Yield: 36%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.93 – 7.85 (m, 2H), 7.39 – 7.28 (m, 3H), 7.27 – 7.19 (m, 3H), 5.17 (dt, J = 12.5, 6.3 Hz, 1H), 5.06 (dt, J = 12.5, 6.3 Hz, 1H), 3.85 (dd, J = 7.2, 4.4 Hz, 1H), 2.99 (d, J = 7.2 Hz, 1H), 2.44 (s, 3H), 2.30 (d, J = 4.4 Hz, 1H), 1.34 (dd, J = 6.3, 2.0 Hz, 6H), 1.12 (dd, J = 6.3, 2.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.18, 163.05, 144.82, 139.16, 134.55, 133.98, 133.00, 130.53, 129.85, 129.81, 128.06, 127.90, 126.57, 69.58, 69.12, 38.83, 35.53, 21.73, 21.64, 21.34; HRMS (ESI) Calcd for $C_{25}H_{30}NO_6S(M+H)^+$: 472.1788; Found: 472.1790; IR (neat): *v*= 570, 666, 718, 766, 817, 846, 913, 1063, 1104, 1162, 1225, 1262, 1330, 1379, 1456, 1598, 1631, 1726, 2935, 2982, 3440 cm^{-1}.

Dibenzyl 2-(2-(1-tosylaziridin-2-yl)benzylidene)malonate **1v**

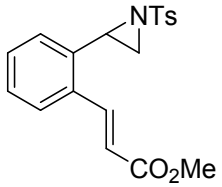


1v

1v was synthesized from **S-3v** according to *General Procedure C.* Yield: 51%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.40 – 7.27 (m, 8H), 7.25 – 7.15 (m, 5H), 7.06 (d, *J* = 6.8 Hz, 3H), 5.32 (s, 2H), 5.11 (s, 2H), 3.81 (dd, *J* = 7.1, 4.4 Hz, 1H), 2.95 (d, *J* = 7.2 Hz, 1H), 2.42 (s, 3H), 2.23 (d, *J* = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.33, 163.25, 144.83, 141.11, 135.29, 134.70, 134.52, 134.07, 132.67, 130.12, 129.80, 128.98, 128.62, 128.47, 128.44, 128.37, 128.31, 128.23, 128.13, 128.04, 127.81, 126.66, 67.41, 67.36, 38.79,

35.44, 21.64; HRMS (ESI) Calcd for $C_{33}H_{30}NO_6S(M+H)^+$: 568.1788; Found: 568.1792; IR (neat): *v*= 488, 569, 664, 697, 744, 814, 911, 981, 1061, 1090, 1161, 1201, 1256, 1294, 1328, 1383, 1453, 1596, 1629, 1731, 3451.8 cm^{-1}.

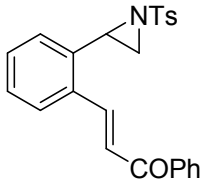
(E)-methyl 3-(2-(1-tosylaziridin-2-yl)phenyl)acrylate **1w**



1w

1w was synthesized from **S-3w** according to *General Procedure C.* Yield: 70%; yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 15.8 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 2H), 7.58 – 7.50 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.21 (m, 3H), 6.41 (d, *J* = 15.8 Hz, 1H), 3.99 (dd, *J* = 7.1, 4.5 Hz, 1H), 3.86 (s, 3H), 3.08 (d, *J* = 7.2 Hz, 1H), 2.47 (s, 3H), 2.31 (d, *J* = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.86, 144.88, 140.49, 134.57, 134.19, 133.45, 130.23, 129.83, 128.41, 128.06, 127.00, 126.49, 120.72, 51.87, 38.81, 35.77, 21.66; the analytical data were in accordance with those reported in our previous work[5].

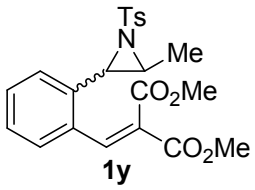
(E)-1-phenyl-3-(2-(1-tosylaziridin-2-yl)phenyl)prop-2-en-1-one **1x**



1x

1x was synthesized from **S-3x** according to *General Procedure C.* Yield: 52%; yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 15.5 Hz, 1H), 8.07 – 7.99 (m, 2H), 7.90 (d, *J* = 8.3 Hz, 2H), 7.71 – 7.66 (m, 1H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.51 (dd, *J* = 19.4, 11.7 Hz, 3H), 7.38 – 7.27 (m, 5H), 4.00 (dd, *J* = 7.2, 4.5 Hz, 1H), 3.06 (d, *J* = 7.2 Hz, 1H), 2.43 (s, 3H), 2.33 (d, *J* = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.87, 144.88, 140.30, 137.86, 134.81, 134.46, 134.05, 133.07, 130.44, 129.85, 128.72, 128.56, 128.42, 128.15, 127.24, 126.54, 124.68, 38.90, 35.76, 21.67; HRMS (ESI) Calcd for $C_{24}H_{22}NO_3S$ $(M+H)^+$: 404.1315; Found: 404.1319; IR (neat): *v*= 452, 556, 668, 692, 715, 742, 764, 836, 907, 978, 1015, 1098, 1161, 1215, 1287, 1322, 1385, 1445, 1484, 1594, 1658, 3447 cm^{-1}.

Dimethyl 2-(2-(3-methyl-1-tosylaziridin-2-yl)benzylidene)malonate **1y**

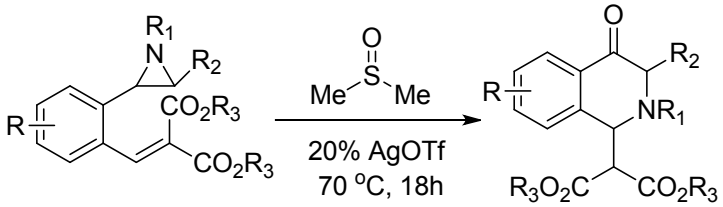


1y

1y was synthesized from **S-3y** according to *General Procedure C.* Yield: 27%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.95 (s, 0.33H), 7.90 (t, *J* = 7.5 Hz, 2.66H), 7.27 (tt, *J* = 8.6, 7.8 Hz, 7H), 6.93 (d, *J* = 5.0 Hz, 1H), 3.97 (d, *J* = 7.3 Hz, 0.33H), 3.93 – 3.84 (m, 5H), 3.71 (s, 4H), 3.31 – 3.23 (m, 0.33H), 2.88 – 2.78 (m, 1H), 2.46 (s, 1H), 2.45 (s, 3H), 1.88 (d, *J* = 5.9 Hz, 3H), 0.94 (d, *J* = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.21, 163.92, 144.69, 144.28, 140.49, 140.22, 137.42, 135.03, 132.44, 132.30, 130.23, 130.06, 129.82, 129.66, 128.65, 128.30, 128.05, 127.90, 127.52, 127.42, 126.53, 52.84, 52.55, 48.26, 47.05, 44.48, 41.57, 21.67, 21.64, 13.91, 12.07; HRMS (ESI) Calcd for $C_{22}H_{24}NO_6S$ $(M+H)^+$: 430.1319; Found: 430.1314; IR (neat): *v*= 884, 1068, 1091, 1159, 1217, 1263, 1321, 1632, 1736, 3464 cm^{-1}.

Synthesis of 2,3-Dihydro-4(1H)-isoquinolones 2

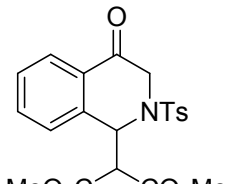
General Procedure D



1 **2**

In the open air, AgOTf (0.04 mmol, 20% cat.) was added to a solution of aziridine **1** (0.2 mmol) in dimethyl sulfoxide (4 mL) at room temperature. The reaction mixture was stirred at 70 °C for 18h. Then the reaction mixture was cooled to room temperature and poured into water (20 mL) and extracted with ethyl acetate (5 × 10 mL). The combined organic extract was washed with brine (20 mL), dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate, 5:1) to afford product **2**.

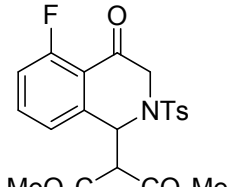
Dimethyl 2-(4-oxo-2-tosyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate **2a**



2a

White solid; mp: 140~143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.1 Hz, 1H), 7.44 – 7.39 (m, 1H), 7.39 – 7.32 (m, 3H), 7.23 (d, *J* = 7.3 Hz, 1H), 6.93 (d, *J* = 8.1 Hz, 2H), 5.93 (d, *J* = 9.8 Hz, 1H), 4.52 (d, *J* = 20.1 Hz, 1H), 4.30 (d, *J* = 20.1 Hz, 1H), 3.90 (d, *J* = 9.8 Hz, 1H), 3.83 (s, 3H), 3.61 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.18, 166.25, 143.80, 138.21, 134.91, 134.10, 129.46, 129.03, 128.54, 127.71, 127.12, 126.90, 58.04, 55.17, 53.38, 52.90, 50.30, 21.31; HRMS (ESI) Calcd for $C_{21}H_{22}NO_7S$ $(M+H)^+$: 432.1111; Found: 432.1116; IR (neat): *v*= 539, 567, 672, 771, 944, 1024, 1089, 1167, 1247, 1300, 1346, 1435, 1598, 1693, 1739, 1765, 2924, 2956, 3450 cm^{-1}.

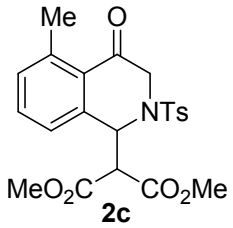
Dimethyl 2-(5-fluoro-4-oxo-2-tosyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate **2b**



2b

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, *J* = 8.0 Hz, 3H), 7.20 (d, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.96 – 6.86 (m, 1H), 5.90 (d, *J* = 9.9 Hz, 1H), 4.50 (d, *J* = 20.3 Hz, 1H), 4.23 (d, *J* = 20.4 Hz, 1H), 3.86 (d, *J* = 10.0 Hz, 1H), 3.83 (s, 3H), 3.62 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.69, 166.08, 166.01, 160.98 (d, *J* = 268.7 Hz), 144.09, 140.18, 135.48 (d, *J* = 10.1 Hz), 134.93, 129.62, 127.07, 123.81 (d, *J* = 3.9 Hz), 117.92, 117.88 (d, *J* = 6.6 Hz), 117.10 (d, *J* = 21.2 Hz), 57.73, 55.22 (d, *J* = 1.4 Hz), 53.44, 52.97, 50.81, 21.31; HRMS (ESI) Calcd for $C_{21}H_{21}FNO_7S$ $(M+H)^+$: 450.1017; Found: 450.1017; IR (neat): *v*= 1096, 1261, 1349, 1465, 1607, 1696, 1741, 1768, 2963, 3418 cm^{-1}.

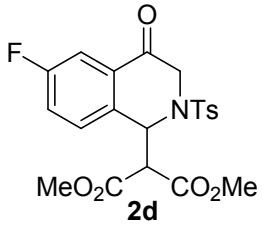
Dimethyl 2-(5-methyl-4-oxo-2-tosyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate **2c**



2c

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.3 Hz, 2H), 7.23 (dd, *J* = 12.5, 6.8 Hz, 2H), 7.00 (d, *J* = 6.6 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 2H), 5.85 (d, *J* = 10.3 Hz, 1H), 4.44 (dd, *J* = 20.4, 1.2 Hz, 1H), 4.24 (d, *J* = 20.4 Hz, 1H), 3.85 (d, *J* = 11.4 Hz, 4H), 3.60 (s, 3H), 2.28 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.70, 166.19, 166.15, 143.55, 141.37, 138.76, 134.83, 133.08, 132.27, 129.25, 127.35, 126.94, 126.11, 57.99, 56.38, 53.38, 52.85, 51.25, 21.96, 21.23; HRMS (ESI) Calcd for $C_{22}H_{24}NO_7S$ $(M+H)^+$: 446.1268; Found: 446.1261; IR (neat): *v*= 1029, 1092, 1145, 1167, 1231, 1252, 1281, 1357, 1433, 1595, 1682, 1761, 2924, 2957, 3456 cm^{-1}.

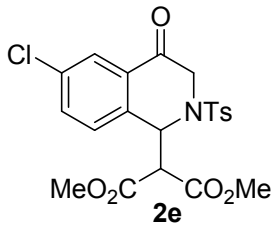
Dimethyl 2-(6-fluoro-4-oxo-2-tosyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate **2d**



2d

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 8.6, 5.0 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.27 – 7.22 (m, 1H), 7.13 (td, *J* = 8.3, 2.8 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 5.93 (d, *J* = 9.7 Hz, 1H), 4.54 (d, *J* = 20.2 Hz, 1H), 4.30 (d, *J* = 20.2 Hz, 1H), 3.89 (d, *J* = 9.8 Hz, 1H), 3.84 (s, 3H), 3.64 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.34, 166.27, 166.15, 162.40 (d, J = 250.8 Hz), 144.15, 134.83, 134.25 (d, J = 3.4 Hz), 131.05 (d, J = 6.5 Hz), 130.17(d, J = 7.4 Hz), 129.58, 127.15, 121.19 (d, J = 22.2 Hz), 113.15 (d, J = 22.6 Hz), 57.98, 54.61, 53.45, 53.01, 50.04, 21.32; HRMS (ESI) Calcd for $C_{21}H_{21}FNO_7S$ $(M+H)^+$: 450.1017; Found: 450.1021; IR (neat): *v*= 544, 586, 668, 723, 1023, 1088, 1165, 1246, 1273, 1352, 1435, 1492, 1601, 1699, 1731, 2955, 3447 cm^{-1}.

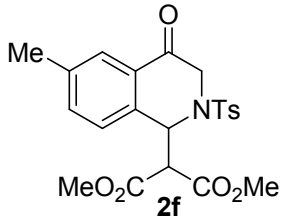
Dimethyl 2-(6-chloro-4-oxo-2-tosyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate **2e**



2e

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.35 (d, *J* = 8.3 Hz, 4H), 6.98 (d, *J* = 8.0 Hz, 2H), 5.89 (d, *J* = 9.7 Hz, 1H), 4.52 (d, *J* = 20.2 Hz, 1H), 4.28 (d, *J* = 20.2 Hz, 1H), 3.88 (d, *J* = 9.8 Hz, 1H), 3.83 (s, 3H), 3.63 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.25, 166.19, 166.06, 144.31, 136.35, 135.14, 134.70, 133.77, 130.37, 129.60, 127.12, 126.66, 57.79, 54.70, 53.44, 53.02, 50.18, 21.32; HRMS (ESI) Calcd for $C_{21}H_{21}ClNO_7S$ $(M+H)^+$: 466.0722; Found: 466.0725; IR (neat): *v*= 538, 575, 676, 722, 807, 843, 898, 940, 1021, 1090, 1136, 1169,1252, 1304, 1355, 1408, 1438, 1594, 1695, 1766, 2959, 3474 cm^{-1}.

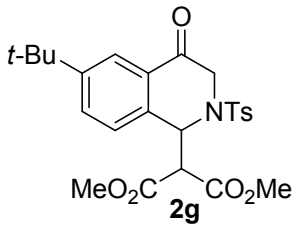
Dimethyl 2-(6-methyl-4-oxo-2-tosyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate **2f**



2f

White solid; mp: 108~111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 3H), 7.23 (s, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 5.89 (d, *J* = 9.9 Hz, 1H), 4.48 (d, *J* = 20.1 Hz, 1H), 4.26 (d, *J* = 20.1 Hz, 1H), 3.87 (d, *J* = 9.9 Hz, 1H), 3.82 (s, 3H), 3.61 (s, 3H), 2.26 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.50, 166.27, 143.71, 138.78, 135.33, 134.96, 134.83, 129.40, 128.82, 127.67, 127.14, 127.05, 58.06, 55.09, 53.33, 52.87, 50.27, 21.29, 20.87; HRMS (ESI) Calcd for $C_{22}H_{24}NO_7S$ $(M+H)^+$: 446.1268; Found: 446.1265; IR (neat): *v*= 545, 613, 667, 728, 946, 1031, 1088, 1144, 1166, 1253, 1306, 1353, 1435, 1611, 1687, 1739, 1764, 3456 cm^{-1}.

Dimethyl 2-(6-(tert-butyl)-4-oxo-2-tosyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate **2g**

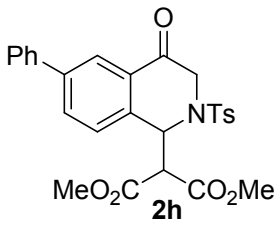


2g

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 2.0 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.31 (dd, *J* = 16.9, 8.2 Hz, 3H), 6.89 (d, *J* = 8.0 Hz, 2H), 5.90 (d, *J* = 10.2 Hz, 1H), 4.51 (d, *J* = 20.2 Hz,

1H), 4.28 (d, *J* = 20.2 Hz, 1H), 3.89 (d, *J* = 10.2 Hz, 1H), 3.85 (s, 3H), 3.64 (s, 3H), 2.20 (s, 3H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.56, 166.28, 166.27, 152.15, 143.38, 135.31, 134.93, 131.29, 129.34, 128.63, 127.70, 127.23, 123.38, 58.07, 55.14, 53.40, 52.90, 50.41, 34.70, 31.00, 21.36; HRMS (ESI) Calcd for $C_{25}H_{30}NO_7S$ $(M+H)^+$: 488.1737; Found: 488.1739; IR (neat): *v*= 587, 666, 1088, 1165, 1249, 1302, 1361, 1634, 1739, 2960, 3454 cm^{-1}.

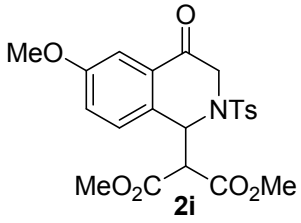
Dimethyl 2-(4-oxo-6-phenyl-2-tosyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate **2h**



2h

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 2.0 Hz, 1H), 7.65 (dd, *J* = 8.0, 2.1 Hz, 1H), 7.54 – 7.31 (m, 8H), 6.93 (d, *J* = 8.0 Hz, 2H), 5.97 (d, *J* = 10.0 Hz, 1H), 4.56 (dd, *J* = 20.2, 1.0 Hz, 1H), 4.33 (d, *J* = 20.2 Hz, 1H), 3.94 (d, *J* = 10.0 Hz, 1H), 3.86 (s, 3H), 3.65 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.37, 166.31, 166.24, 143.90, 141.78, 138.92, 136.78, 134.92, 132.36, 129.49, 129.45, 128.99, 128.51, 128.22, 127.22, 126.82, 125.18, 58.03, 55.18, 53.43, 52.97, 50.45, 21.27; HRMS (ESI) Calcd for $C_{27}H_{26}NO_7S$ $(M+H)^+$: 508.1424; Found: 508.1424; IR (neat): *v*= 1091, 1163, 1256, 1309, 1356, 1438, 1603, 1696, 1739, 2923, 2956, 3448 cm^{-1}.

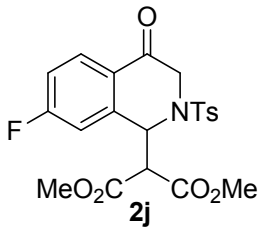
Dimethyl 2-(6-methoxy-4-oxo-2-tosyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate **2i**



2i

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 1H), 7.04 (d, *J* = 2.8 Hz, 1H), 7.03 – 6.86 (m, 3H), 5.89 (d, *J* = 9.9 Hz, 1H), 4.49 (d, *J* = 20.1 Hz, 1H), 4.27 (d, *J* = 20.1 Hz, 1H), 3.87 (d, *J* = 9.9 Hz, 1H), 3.83 (s, 3H), 3.74 (s, 3H), 3.62 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.30, 166.36, 166.32, 159.68, 143.68, 135.06, 130.86, 130.22, 129.48, 129.23, 127.23, 121.76, 109.29, 58.21, 55.51, 54.92, 53.34, 52.89, 50.16, 21.30; HRMS (ESI) Calcd for $C_{22}H_{24}NO_8S$ $(M+H)^+$: 462.1217; Found: 462.1214; IR (neat): *v*= 1091, 1164, 1289, 1354, 1437, 1498, 1605, 1738, 2849, 2924, 2956, 3449 cm^{-1}.

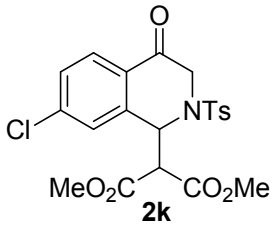
Dimethyl 2-(7-fluoro-4-oxo-2-tosyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate **2j**



2j

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 8.7, 5.8 Hz, 1H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.12 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.00 (d, *J* = 8.1 Hz, 2H), 6.92 (td, *J* = 8.4, 2.4 Hz, 1H), 5.89 (d, *J* = 9.8 Hz, 1H), 4.52 (d, *J* = 20.1 Hz, 1H), 4.27 (d, *J* = 20.1 Hz, 1H), 3.89 (d, *J* = 9.8 Hz, 1H), 3.84 (s, 3H), 3.66 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.72, 166.21, 166.03, 165.59 (d, J = 258.7 Hz), 144.08, 141.41 (d, J = 8.8 Hz), 134.90, 130.20 (d, J = 9.7 Hz), 129.55, 127.19, 125.79 (d, J = 3.3 Hz), 116.09 (d, J = 22.2 Hz), 114.90 (d, J = 23.6 Hz), 57.85, 54.81, 53.48, 53.09, 50.13, 21.34; HRMS (ESI) Calcd for $C_{21}H_{21}FNO_7S$ $(M+H)^+$: 450.1017; Found:450.1021; IR (neat): *v*= 554, 678, 728, 818, 916, 1020, 1090, 1165, 1250, 1279, 1357,1437,1491,1606, 1697, 1739.6, 2957, 3451 cm^{-1}.

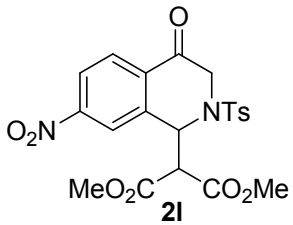
Dimethyl 2-(7-chloro-4-oxo-2-tosyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate **2k**



2k

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.4 Hz, 1H), 7.39 (dd, *J* = 8.1, 5.0 Hz, 3H), 7.21 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.00 (d, *J* = 8.1 Hz, 2H), 5.85 (d, *J* = 9.7 Hz, 1H), 4.52 (d, *J* = 20.2 Hz, 1H), 4.28 (d, *J* = 20.2 Hz, 1H), 3.88 (d, *J* = 9.7 Hz, 1H), 3.83 (s, 3H), 3.66 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.25, 166.14, 166.03, 144.17, 140.63, 139.87, 134.81, 129.55, 128.93, 128.53, 127.89, 127.49, 127.22, 57.80, 54.68, 53.48, 53.11, 50.24, 21.36; HRMS (ESI) Calcd for $C_{21}H_{21}ClNO_7S$ $(M+H)^+$: 466.0722; Found: 466.0723; IR (neat): *v*= 548, 671, 1027, 1088, 1165, 1279, 1358, 1437, 1594, 1739, 2957, 3445 cm^{-1}.

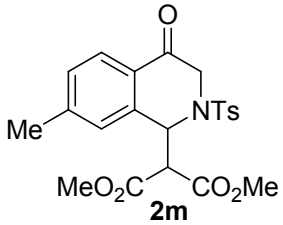
Dimethyl 2-(7-nitro-4-oxo-2-tosyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate **2l**



2l

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 2.0 Hz, 1H), 8.07 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.82 (d, *J* = 8.5 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.01 (d, *J* = 8.1 Hz, 2H), 5.99 (d, *J* = 9.3 Hz, 1H), 4.62 (d, *J* = 19.9 Hz, 1H), 4.36 (d, *J* = 20.3 Hz, 1H), 3.93 (d, *J* = 9.3 Hz, 1H), 3.83 (s, 3H), 3.68 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 189.93, 166.05, 165.94, 150.26, 144.51, 140.03, 134.81, 133.24, 129.76, 128.53, 127.26, 123.19, 123.14, 57.61, 54.55, 53.57, 53.31, 50.43, 21.36; HRMS (ESI) Calcd for $C_{21}H_{21}N_2O_9S$ $(M+H)^+$: 477.0962; Found: 477.0965; IR (neat): *v*= 551, 674, 1166, 1354, 1535, 1632, 1738, 3461 cm^{-1}.

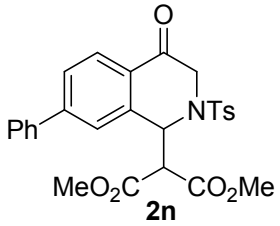
Dimethyl 2-(7-methyl-4-oxo-2-tosyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate **2m**



2m

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 7.9 Hz, 2H), 7.14 (s, 1H), 7.05 (d, *J* = 7.9 Hz, 1H), 6.95 (d, *J* = 7.9 Hz, 2H), 5.87 (d, *J* = 9.8 Hz, 1H), 4.48 (d, *J* = 20.0 Hz, 1H), 4.26 (d, *J* = 20.1 Hz, 1H), 3.89 (d, *J* = 9.7 Hz, 1H), 3.83 (s, 3H), 3.62 (s, 3H), 2.34 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.95, 166.32, 145.41, 143.77, 138.40, 135.08, 129.38, 128.02, 127.24, 127.11, 126.79, 58.06, 55.17, 53.34, 52.85, 50.23, 21.85, 21.34; HRMS (ESI) Calcd for $C_{22}H_{24}NO_7S$ $(M+H)^+$: 446.1268; Found: 446.1269; IR (neat): *v*= 555, 673, 814, 1025, 1091, 1164, 1260, 1354, 1609, 1690, 1740, 3461 cm^{-1}.

Dimethyl 2-(4-oxo-7-phenyl-2-tosyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate **2n**

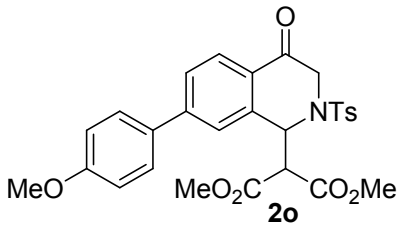


2n

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 1.7 Hz, 1H), 7.56 – 7.38 (m, 8H), 6.93 (d, *J* = 8.0 Hz, 2H), 5.96 (d, *J* = 9.9 Hz, 1H), 4.56 (dd, *J* = 20.1, 0.9 Hz, 1H),

4.33 (d, *J* = 20.1 Hz, 1H), 3.94 (d, *J* = 9.9 Hz, 1H), 3.86 (s, 3H), 3.61 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.95, 166.32, 166.27, 146.71, 143.87, 138.95, 138.76, 135.01, 129.44, 129.19, 128.87, 127.77, 127.60, 127.26, 127.12, 127.00, 126.33, 58.05, 55.39, 53.42, 52.95, 50.40, 21.33; HRMS (ESI) Calcd for $C_{27}H_{26}NO_7S$ $(M+H)^+$: 508.1424; Found: 508.1426; IR (neat): *v*= 1089, 1164, 1258, 1293, 1356, 1438, 1602, 1739, 2923, 2955, 3449 cm^{-1}.

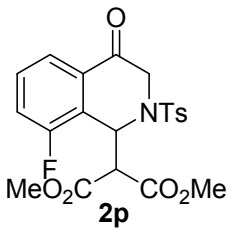
Dimethyl 2-(7-(4-methoxyphenyl)-4-oxo-2-tosyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate **2o**



2o

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.2 Hz, 1H), 7.57 – 7.36 (m, 6H), 7.02 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 7.9 Hz, 2H), 5.94 (d, *J* = 10.1 Hz, 1H), 4.54 (d, *J* = 20.0 Hz, 1H), 4.31 (d, *J* = 20.1 Hz, 1H), 3.93 (d, *J* = 9.9 Hz, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 3.60 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.85, 166.35, 166.29, 160.44, 146.28, 143.83, 138.77, 135.04, 131.24, 129.42, 128.30, 127.63, 127.27, 127.18, 126.32, 125.58, 114.65, 58.06, 55.44, 53.40, 52.92, 50.37, 21.33; HRMS (ESI) Calcd for $C_{28}H_{28}NO_8S$ $(M+H)^+$: 538.1530; Found: 538.1539; IR (neat): *v*= 1091, 1163, 1253, 1294, 1355, 1437, 1599, 1689, 1738, 2923, 2956, 3448 cm^{-1}.

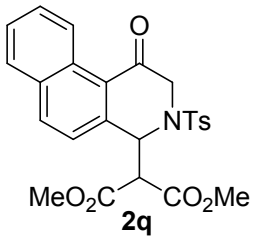
Dimethyl 2-(8-fluoro-4-oxo-2-tosyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate **2p**



2p

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.40 (m, 3H), 7.26 – 7.20 (m, 1H), 7.20 – 7.13 (m, 1H), 6.98 (d, J = 8.1 Hz, 2H), 6.09 (d, J = 8.2 Hz, 1H), 4.52 (d, J = 20.1, 0.7 Hz, 1H), 4.41 (d, J = 20.1 Hz, 1H), 4.08 (d, J = 8.2 Hz, 1H), 3.74 (s, 3H), 3.71 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.39 (d, J = 4.3 Hz), 166.53, 165.99, 157.81 (d, J = 248.8 Hz), 144.06, 134.88, 131.40 (d, J = 2.9 Hz), 129.65, 129.57 (d, J = 8.4 Hz), 126.96, 124.84 (d, J = 16.1 Hz), 122.49 (d, J = 3.3 Hz), 120.54 (d, J = 21.4 Hz), 56.23, 53.10, 53.04, 50.60, 49.72, 21.32; HRMS (ESI) Calcd for $C_{21}H_{21}FNO_7S$ $(M+H)^+$: 450.1017; Found:450.1020; IR (neat): *v*= 1032, 1160, 1260, 1380, 1461, 1602, 1741, 2852, 2922, 2957, 3434 cm^{-1}.

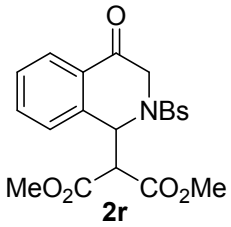
Dimethyl 2-(1-oxo-3-tosyl-1,2,3,4-tetrahydrobenzo[f]isoquinolin-4-yl)malonate **2q**



2q

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.55 – 7.46 (m, 2H), 7.32 – 7.28 (m, 2H), 6.66 (d, *J* = 6.8 Hz, 2H), 6.00 (d, *J* = 10.0 Hz, 1H), 4.66 (d, *J* = 20.5 Hz, 1H), 4.42 (d, *J* = 20.5 Hz, 1H), 3.98 (d, *J* = 10.2 Hz, 1H), 3.89 (s, 3H), 3.61 (s, 3H), 1.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.81, 166.21, 166.19, 143.77, 139.52, 135.09, 134.69, 133.40, 129.96, 129.37, 129.31, 128.15, 126.90, 126.72, 126.14, 125.14, 124.36, 58.10, 56.94, 53.47, 52.93, 51.76, 20.74; HRMS (ESI) Calcd for $C_{25}H_{24}NO_7S$ $(M+H)^+$: 482.1268; Found: 482.1265; IR (neat): *v*= 547, 665, 809, 1093, 1160, 1261, 1354, 1382, 1598, 1737, 2924, 2957, 3457 cm^{-1}.

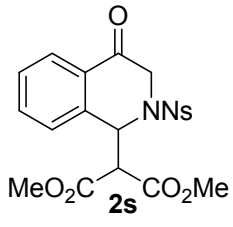
Dimethyl 2-(2-((4-bromophenyl)sulfonyl)-4-oxo-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate **2r**



2r

White solid; mp: 129~133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.46 (td, *J* = 7.6, 1.4 Hz, 1H), 7.39 – 7.33 (m, 3H), 7.32 – 7.25 (m, 3H), 5.91 (d, *J* = 9.9 Hz, 1H), 4.52 (dd, *J* = 20.2, 0.9 Hz, 1H), 4.34 (d, *J* = 20.1 Hz, 1H), 3.93 (d, *J* = 9.9 Hz, 1H), 3.84 (s, 3H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.73, 166.12, 166.10, 137.92, 136.90, 134.28, 132.13, 128.92, 128.51, 128.04, 127.75, 127.11, 57.89, 55.30, 53.42, 52.97, 50.36; HRMS (ESI) Calcd for $C_{20}H_{19}BrNO_7S$ $(M+H)^+$: 496.0060; Found: 496.0064; IR (neat): *v*= 552, 593, 641, 747, 1089, 1169, 1207, 1247, 1349, 1436, 1574, 1635, 1695, 1738, 2958, 3461 cm^{-1}.

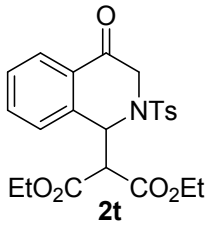
Dimethyl 2-(2-((4-nitrophenyl)sulfonyl)-4-oxo-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate **2s**



2s

White solid; mp: 114~117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.98 (m, 2H), 7.73 – 7.69 (m, 2H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.47 (td, *J* = 7.6, 1.3 Hz, 1H), 7.41 (d, *J* = 7.2 Hz, 1H), 7.29 (dd, *J* = 7.6, 1.1 Hz, 1H), 5.94 (d, *J* = 9.9 Hz, 1H), 4.57 (d, *J* = 20.1 Hz, 1H), 4.40 (d, *J* = 20.1 Hz, 1H), 3.94 (d, *J* = 9.9 Hz, 1H), 3.85 (s, 3H), 3.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.10, 166.00, 149.86, 143.69, 137.78, 134.47, 129.28, 128.80, 128.38, 127.80, 127.19, 124.02, 57.82, 55.43, 53.52, 53.09, 50.43; HRMS (ESI) Calcd for $C_{20}H_{19}N_2O_9S$ $(M+H)^+$: 463.0806; Found: 463.0808; IR (neat): *v*= 469, 547, 626, 647, 740, 772, 1015, 1088, 1169, 1204, 1243, 1266, 1313, 1352, 1436, 1536, 1602, 1696, 1735, 3462 cm^{-1}.

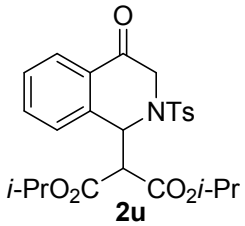
Diethyl 2-(4-oxo-2-tosyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate **2t**



2t

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.7 Hz, 1H), 7.42 (dd, *J* = 4.0, 1.9 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.25 – 7.21 (m, 1H), 6.92 (d, *J* = 8.1 Hz, 2H), 5.94 (d, *J* = 9.7 Hz, 1H), 4.53 (d, *J* = 20.1 Hz, 1H), 4.38 – 4.26 (m, 3H), 4.16 – 3.98 (m, 2H), 3.86 (d, *J* = 9.7 Hz, 1H), 2.22 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.12 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.35, 165.93, 143.70, 138.40, 134.96, 134.02, 129.43, 129.08, 128.41, 127.87, 127.12, 126.81, 62.57, 62.10, 58.30, 55.14, 50.41, 21.30, 13.98, 13.78; HRMS (ESI) Calcd for $C_{23}H_{26}NO_7S$ $(M+H)^+$: 460.1424; Found: 460.1427; IR (neat): *v*= 497, 538, 563, 616, 671, 770, 935, 1029, 1090, 1164, 1254, 1299, 1356, 1597, 1683, 1734, 1757, 3457 cm^{-1}.

Diisopropyl 2-(4-oxo-2-tosyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate **2u**

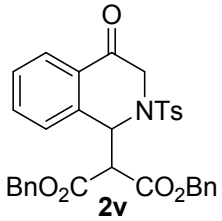


2u

White solid; mp: 110~112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.8 Hz, 1H), 7.49 – 7.37 (m, 2H), 7.34 (d, J = 8.3 Hz, 2H), 7.21 (dd, J = 10.7, 4.4 Hz, 1H), 6.89 (d, J = 8.1 Hz, 2H), 5.93 (d, J = 9.6 Hz, 1H), 5.15 (dt, J = 12.5, 6.3 Hz, 1H), 4.93 (dt, J = 12.5, 6.3 Hz, 1H), 4.52 (dd, J = 20.1, 0.9 Hz, 1H), 4.36 (d, J = 20.1 Hz, 1H), 3.78 (d, J = 9.6 Hz, 1H), 2.21 (s, 3H), 1.36 (d, J = 6.3 Hz,

3H), 1.30 (d, J = 6.3 Hz, 3H), 1.14 (d, J = 6.2 Hz, 3H), 1.04 (d, J = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.50, 165.57, 165.55, 143.62, 138.56, 134.96, 133.96, 129.40, 129.11, 128.29, 128.07, 127.13, 126.74, 70.40, 69.94, 58.66, 55.00, 50.54, 21.60, 21.54, 21.40, 21.31; HRMS (ESI) Calcd for $C_{25}H_{30}NO_7S$ $(M+H)^+$: 488.1737; Found: 488.1737; IR (neat): *v*= 562, 672, 938, 1008, 1106, 1164, 1246, 1269, 1296, 1355, 1383, 1599, 1688, 1732, 2986, 3454 cm^{-1}.

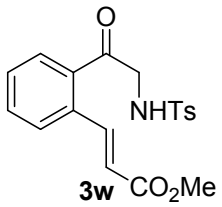
Dibenzyl 2-(4-oxo-2-tosyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate **2v**



2v

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.7 Hz, 1H), 7.37 – 7.16 (m, 13H), 7.11 (d, *J* = 7.2 Hz, 2H), 6.91 (d, *J* = 7.9 Hz, 2H), 5.98 (d, *J* = 9.7 Hz, 1H), 5.28 (d, *J* = 12.0 Hz, 1H), 5.15 (d, *J* = 12.1 Hz, 1H), 5.00 (dd, *J* = 30.0, 12.1 Hz, 2H), 4.49 (d, *J* = 20.1 Hz, 1H), 4.27 (d, *J* = 20.1 Hz, 1H), 3.96 (d, *J* = 9.6 Hz, 1H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.15, 165.63, 165.60, 143.76, 138.10, 134.89, 134.70, 134.40, 134.05, 129.44, 129.01, 128.59, 128.52, 128.43, 128.38, 127.72, 127.14, 126.83, 68.22, 67.77, 58.15, 55.18, 50.32, 21.29; HRMS (ESI) Calcd for $C_{33}H_{30}NO_7S$ $(M+H)^+$: 584.1737; Found: 584.1741; IR (neat): *v*= 497, 564, 670, 699, 744, 1006, 1090, 1165, 1262, 1295, 1354, 1599, 1695, 1736, 3457 cm^{-1}.

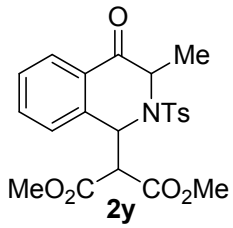
(E)-methyl 3-(2-(2-(4-methylphenylsulfonamido)acetyl)phenyl)acrylate **3w**



3w

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 15.9 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 4.2 Hz, 2H), 7.56 (dt, *J* = 8.1, 4.3 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 6.34 (d, *J* = 15.9 Hz, 1H), 5.72 (t, *J* = 4.2 Hz, 1H), 4.50 (d, *J* = 4.7 Hz, 2H), 3.90 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.73, 166.66, 143.89, 143.30, 135.97, 135.89, 133.69, 133.36, 129.84, 129.60, 128.86, 128.59, 127.17, 121.38, 51.85, 50.11, 21.48; HRMS (ESI) Calcd for $C_{19}H_{20}NO_5S$ $(M+H)^+$: 374.1057; Found: 374.1060; IR (neat): *v*= 513, 548, 664, 771, 813, 844, 970, 1099, 1162, 1198, 1282, 1327, 1444, 1597, 1630, 1697, 3457 cm^{-1}.

Dimethyl 2-(3-methyl-4-oxo-2-tosyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate **2y**

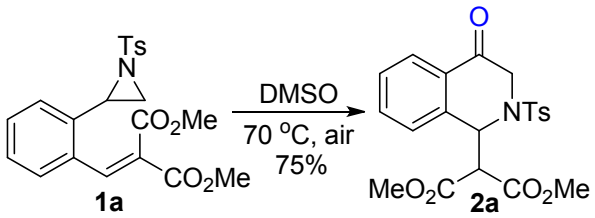


2y

The major diastereoisomer of compound **2y** was isolated. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.4 Hz, 1H), 7.42 (dd, *J* = 13.7, 7.8 Hz, 3H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 2H), 5.96 (d, *J* = 9.8 Hz, 1H), 4.48 (q, *J* = 7.3 Hz, 1H), 3.88 (s, 3H), 3.78 (d, *J* = 9.8 Hz, 1H), 3.49 (s, 3H), 2.24 (s, 3H), 1.73 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.86, 166.14, 165.96, 143.74, 138.57, 135.15, 133.61, 129.44, 129.28, 128.75, 127.39, 127.19, 125.99, 60.69, 58.34, 55.20, 53.21, 52.68, 21.34, 20.36; HRMS (ESI) Calcd for $C_{22}H_{24}NO_7S$ $(M+H)^+$: 446.1268; Found: 446.1275; IR (neat): *v*= 802, 1025, 1097, 1261, 1383, 1602, 2922, 2962, 3431 cm^{-1}.

<u>The control experiments for mechanistic studies</u>

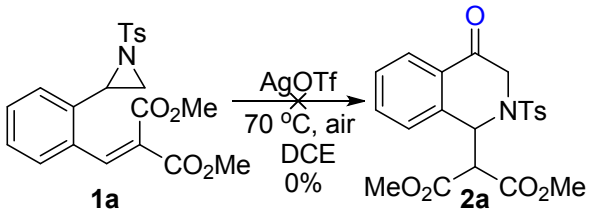
*The sequential reaction of **1a** in the absence of AgOTf:*



1a **2a**

In the open air, a solution of aziridine **1a** (0.2 mmol, 83 mg) in DMSO (4 mL) was stirred at 70 °C for 18h. Then the reaction mixture was cooled to room temperature and poured into water (20 mL) and extracted with ethyl acetate (5 × 10 mL). The combined organic extract was washed with brine (20 mL), dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate, 5:1) to afford product **2a** (0.15 mmol, 65mg) in 75% yield.

*The sequential reaction of **1a** using DCE instead of DMSO as the solvent:*

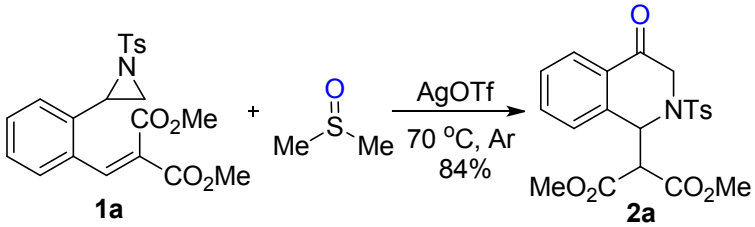


1a **2a**

In the open air, AgOTf (0.04 mmol, 20% cat.) was added to a solution of aziridine **1** (0.2 mmol,

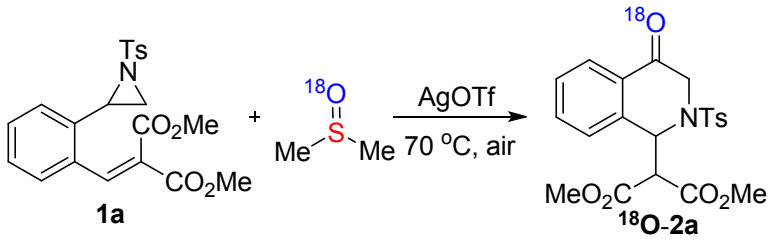
83 mg) in DCE (4 mL) at room temperature. The reaction mixture was stirred at 70 °C for 18h. Then the reaction mixture was cooled to room temperature and poured into water (20 mL) and extracted with ethyl acetate (5 × 10 mL). The combined organic extract was washed with brine (20 mL), dried over Na_2SO_4 and evaporated under reduced pressure. The residue was analyzed by ^1H NMR. The crude spectrum of this reaction system indicated that no desired product **2a** was afforded.

*The sequential reaction of **1a** using degassed and dry DMSO in Ar:*



Under argon atmosphere, to an oven-dried Schlenk tube was added AgOTf (0.04 mmol, 20% cat.), aziridine **1a** (0.2 mmol, 83 mg) and degassed and dry DMSO (4 mL) at room temperature. Then the system was evacuated under vacuum and back-filled with argon (repeated twice). The reaction mixture was stirred at 70 °C for 18h. Then the reaction mixture was cooled to room temperature and poured into water (20 mL) and extracted with ethyl acetate (5 × 10 mL). The combined organic extract was washed with brine (20 mL), dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate, 5:1) to afford product **2a** (0.168 mmol, 73mg) in 84% yield.

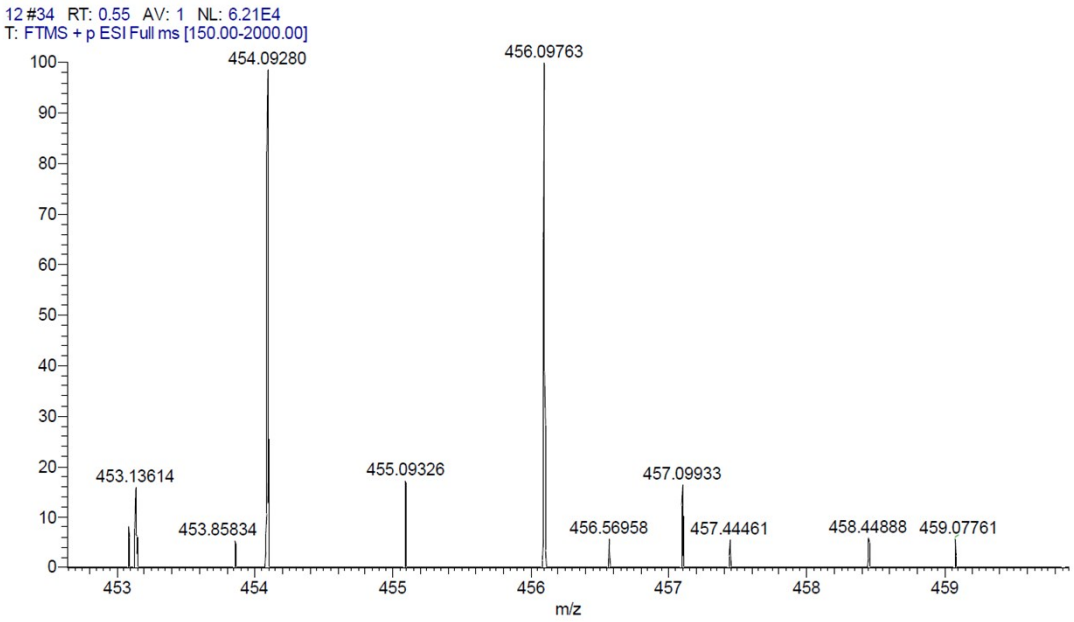
^{18}O Labeling experiment:



Method for preparation of ^{18}O labeled DMSO[14]: Solid dimethylsulfur dibromide (20 g, 90 mmol) was added portion wise over 15 min to a vigorously stirred solution of triethylamine (25.2 ml, 180 mmol, freshly distilled from sodium hydroxide) and ^{18}O-labeled water (97 atom % ^{18}O) (0.8 mL, 11 mmol) in 60 ml of tetrahydrofuran (freshly distilled from sodium metal). The temperature of the reaction was maintained below 50 °C by occasional cooling in ice. The precipitate of triethylamine hydrobromide was removed by centrifugation and washed twice with

ether. The combined yellow supernatant and washings were dried on high vacuum pressure pump at room temperature (15 mm) to remove the solvent and was given 1.6 g of a pale yellow liquid. Without further purification, the sequential reaction of **1a** was performed using newly prepared ^{18}O-DMSO according to *General procedure D*. The ratio of ^{18}O-**2a** and **2a** was determined as 1.1:1, suggesting that DMSO acts as the oxygen donor in the reaction. ^{18}O-**2a**: HRMS (ESI) Calcd for $C_{21}H_{21}NNaO_6{}^{18}OS$ $(M+Na)^+$, 456.0973, Found, 456.0976. **2a:** HRMS (ESI) Calcd for $C_{21}H_{21}NNaO_7S$ $(M+ Na)^+$, 454.0931, Found, 454.0928.

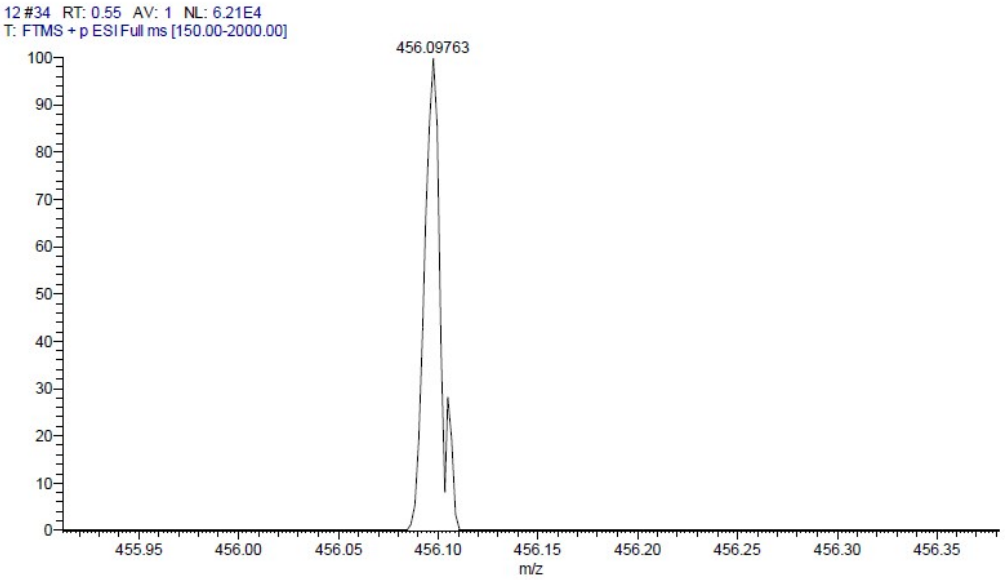
HRMS for ^{18}O-**2a** and **2a**:



^{18}O-**2a** : **2a** = 6.21E4 : 6.13E4 = 1.10305.

The ratio of ^{18}O-**2a** and **2a** was calculated according to the following two spectrums:

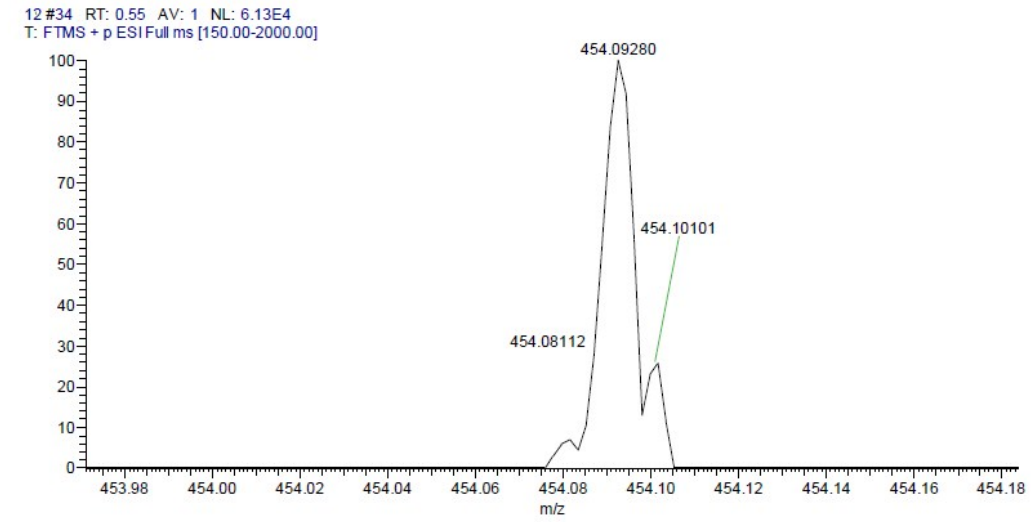
Spectrum 1:



SPECTRUM - simulation :

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
456.09763	456.09785	-0.48	-1.0	C7 H23 O12 [18]O N6 Na S
	456.09734	0.64	11.5	C21 H21 O6 [18]O N Na S

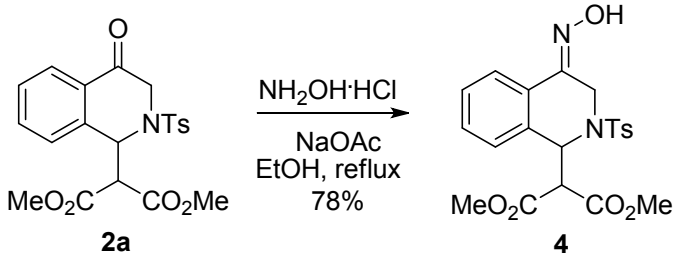
Spectrum 2:



SPECTRUM - simulation :

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
454.09280	454.09309	-0.64	17.0	C20 H15 O2 N8 Na S
	454.09309	-0.65	11.5	C21 H21 O7 N Na S

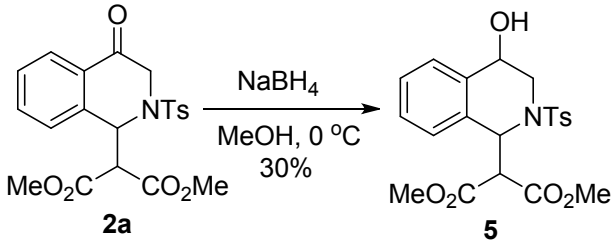
Synthesis of compound 4



2a **4**

To a solution of ketone **2a** (120 mg, 0.278 mmol) in EtOH (0.67 mL) was added a soluition of hydroxylamine hydrochloride (48 mg, 0.695 mmol) and NaOAc (28.7mg, 0.139 mmol) in H_2O (0.33 mL). The reaction mixture was reflux overnight. After cooling to the room temperature, the reaction mixture was extract with EtOAc (20 mL×2), washed with brine (10 mL), dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to afford product **4** (78%, 0.216 mmol, 97mg). The stereochemistry of compound **4** was not determined. White solid; mp: 156~159 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.26 – 7.21 (m, 1H), 7.17 (td, *J* = 7.5, 1.3 Hz, 1H), 7.09 (td, *J* = 7.6, 1.4 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 2H), 5.78 (d, *J* = 10.6 Hz, 1H), 5.08 (dd, *J* = 20.5, 1.2 Hz, 1H), 4.42 (d, *J* = 20.5 Hz, 1H), 3.86 (s, 3H), 3.79 (d, *J* = 10.7 Hz, 1H), 3.61 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.33, 166.25, 148.93, 143.38, 135.04, 132.98, 129.46, 129.16, 128.21, 128.08, 127.07, 127.05, 123.96, 57.58, 55.81, 53.34, 52.78, 40.13, 21.33; HRMS (ESI) Calcd for $C_{21}H_{23}N_2O_7S$ $(M+H)^+$: 447.1220; Found: 447.1220; IR (neat): *v*= 572, 674, 1091, 1144, 1167, 1359, 1384, 1435, 1599, 1763, 3437 cm^{-1}.

Synthesis of compound 5



2a **5**

To a solution of ketone **2a** (80mg, 0.186 mmol) in MeOH (1 mL) was added (14mg, 0.372 mmol) of sodium borohydride in small portions with stirring and external cooling. When the addition was complete, stirring was continued for 2 hours at room temperature. The solution was poured into 10 ml of water and stirred for 2 hours. The solid formed was filtered and extracted with EtOAc (20

mL×2). The combined organic extract was washed with brine (10 mL), dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to afford product **5** (30%, 0.056 mmol, 24 mg). The stereochemistry of compound **5** was not determined. White solid; mp: 108~112 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.4 Hz, 2H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.31 – 7.22 (m, 5H), 5.91 (d, *J* = 7.3 Hz, 1H), 4.63 (d, *J* = 7.6 Hz, 1H), 3.98 – 3.81 (m, 3H), 3.70 (s, 3H), 3.49 (s, 3H), 2.62 (d, *J* = 9.6 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.32, 166.95, 144.02, 136.09, 135.34, 132.69, 129.93, 129.64, 128.66, 128.12, 127.75, 126.66, 64.45, 58.60, 54.12, 52.95, 52.60, 47.20, 21.53; HRMS (ESI) Calcd for $C_{21}H_{24}NO_7S$ $(M+H)^+$: 434.1268; Found: 434.1270; IR (neat): *v*= 550, 577, 664, 1091, 1127, 1164, 1240, 1301, 1340, 1728, 3459, 3567 cm^{-1}.

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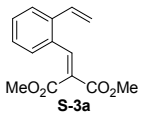
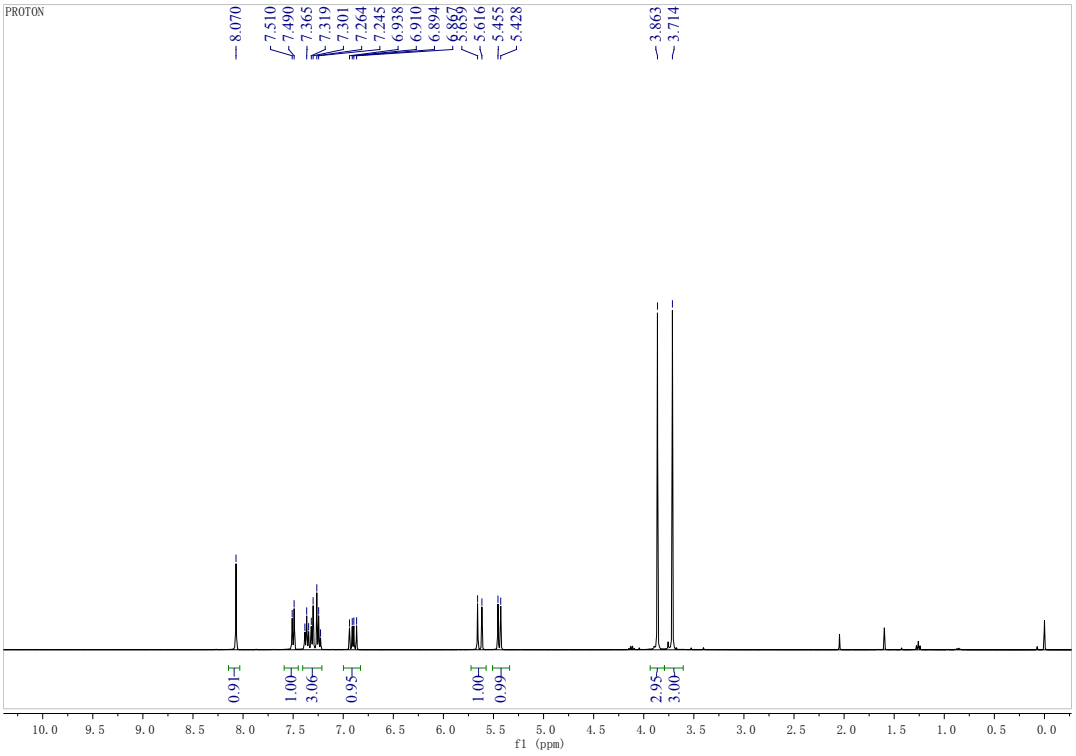
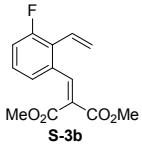
NMR Spectra

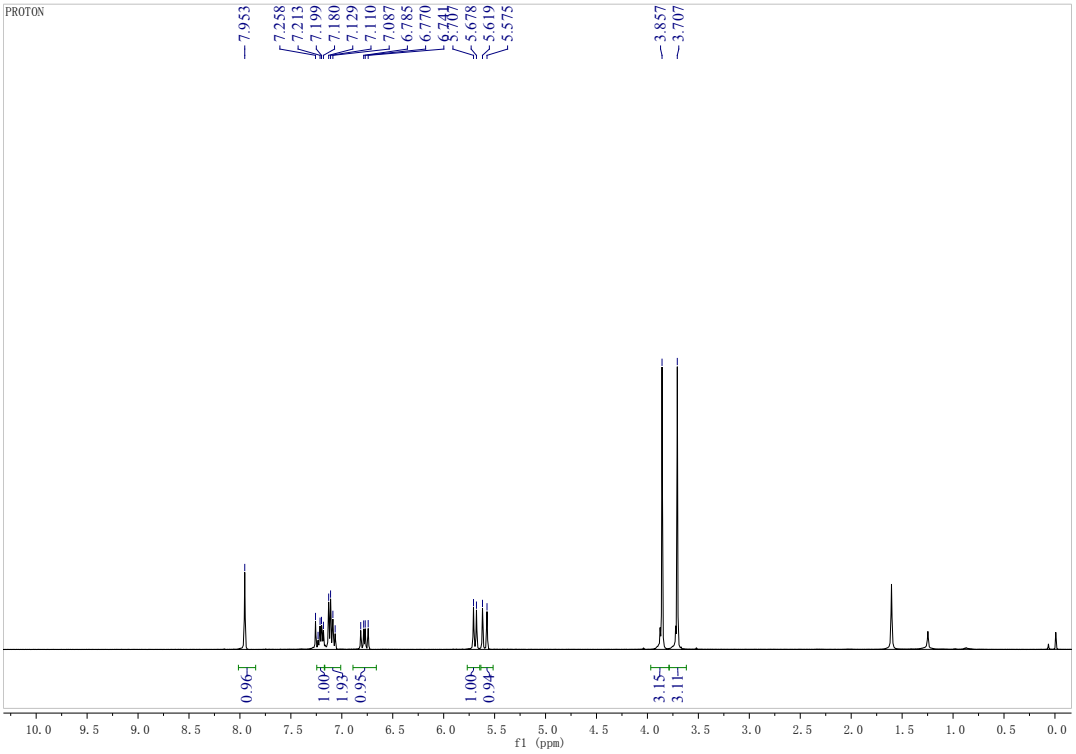


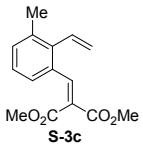
S-3a



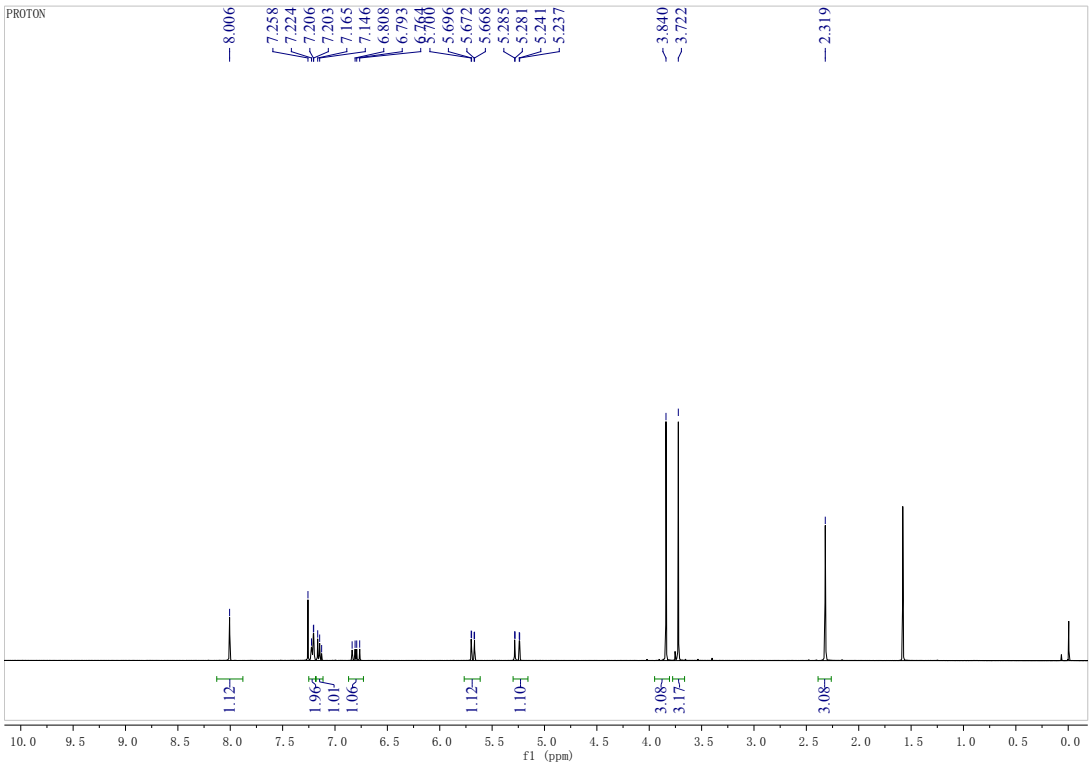


S-3b




Me
MeO2C
CO2Me

S-3c


PROTON
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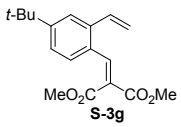
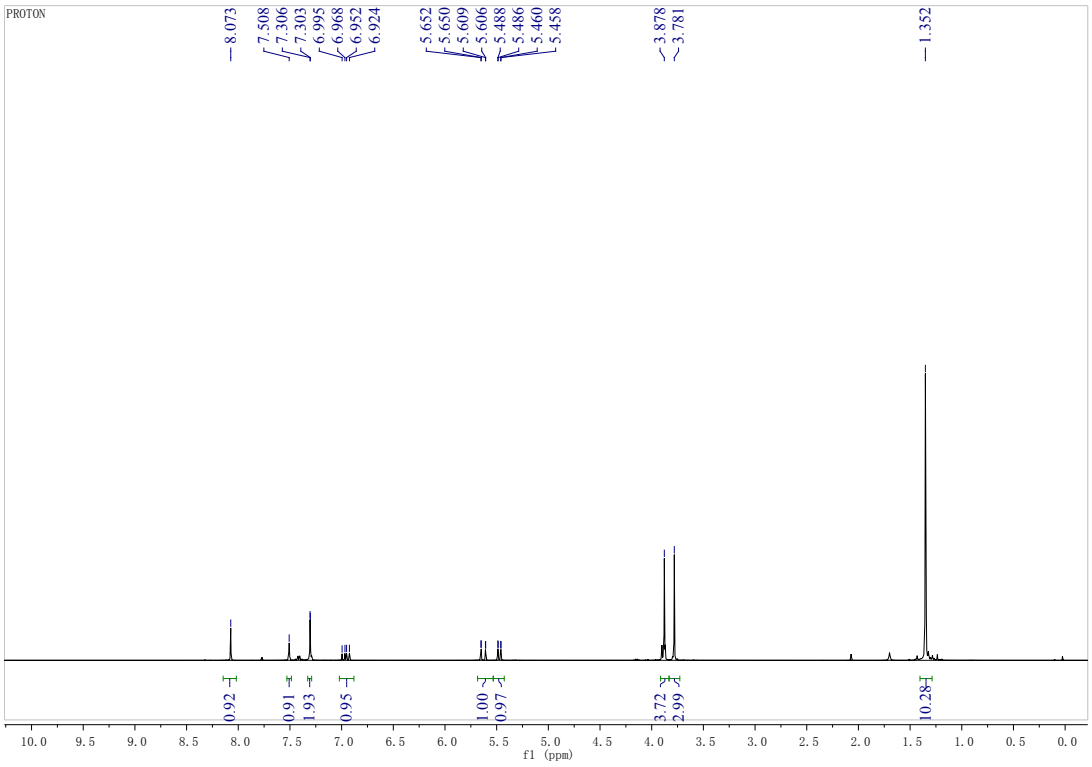
7.224
7.206
7.203
7.165
7.146
6.808
6.793
6.764
6.760
5.696
5.672
5.668
5.285
5.281
5.241
5.237
3.840
3.722
2.319
1.12
1.96
1.01
1.06
1.12
1.10
3.08
3.17
3.08
f1 (ppm)


t-Bu
MeO2C
CO2Me

S-3g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8.073
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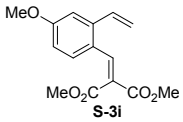
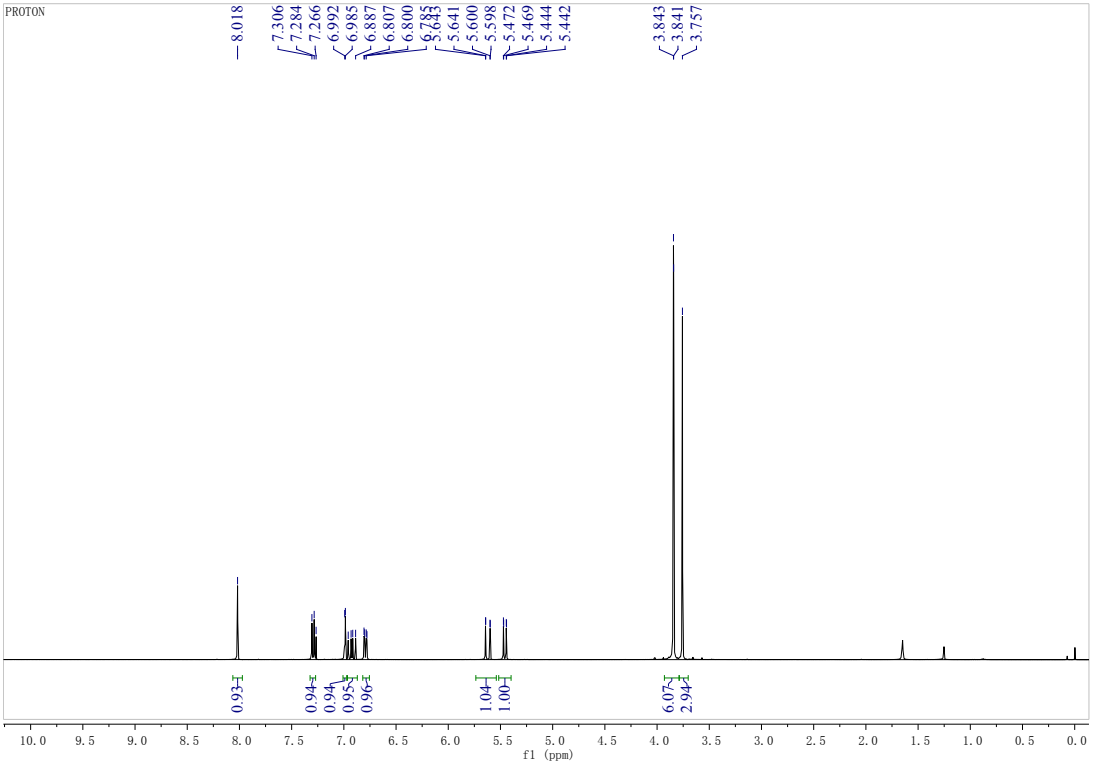
7.306
7.303
6.995
6.968
6.952
6.924
5.652
5.650
5.609
5.606
5.488
5.486
5.460
5.458
3.878
3.781
1.352
0.92
0.91
1.93
0.95
1.00
0.97
3.72
2.99
10.28
f1 (ppm)


MeO
MeO2C
CO2Me

S-3i


PROTON
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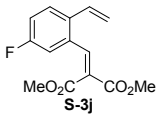
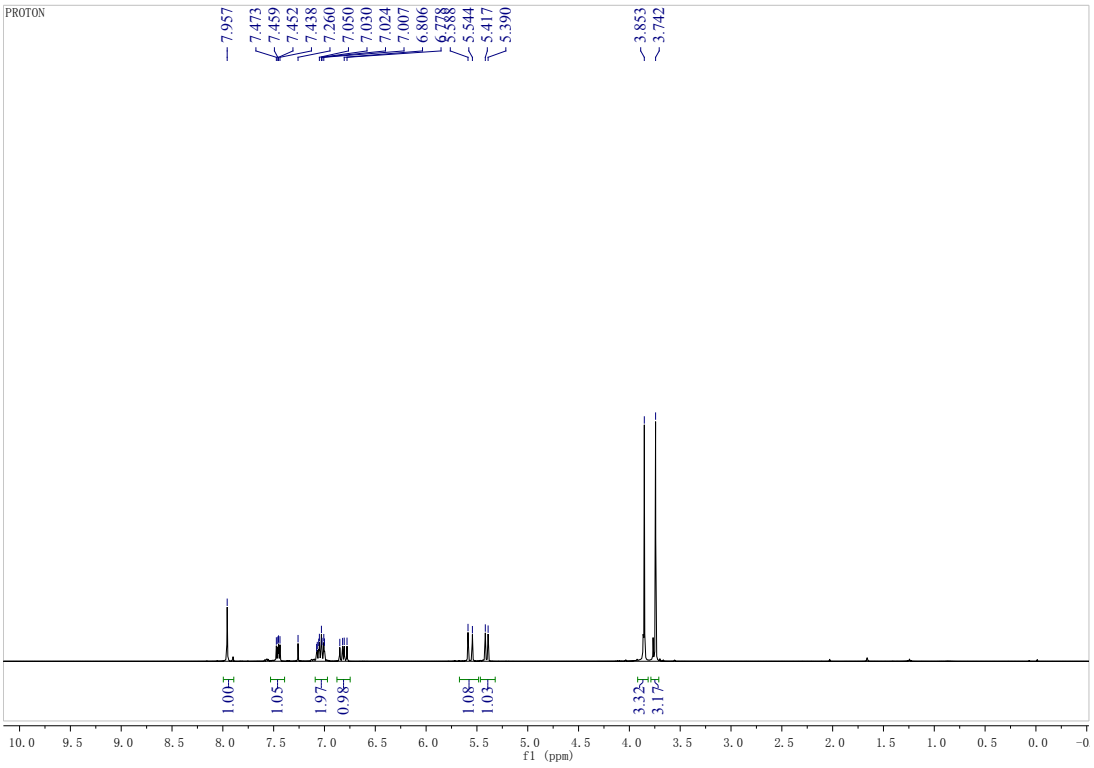
7.266
6.992
6.985
6.887
6.807
6.800
6.785
6.643
5.641
5.600
5.598
5.472
5.469
5.444
5.442
3.843
3.841
3.757
0.93
0.94
0.94
0.95
0.96
1.04
1.00
6.07
2.94
f1 (ppm)


F
MeO2C
CO2Me

S-3j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7.957
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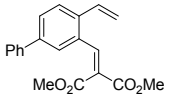
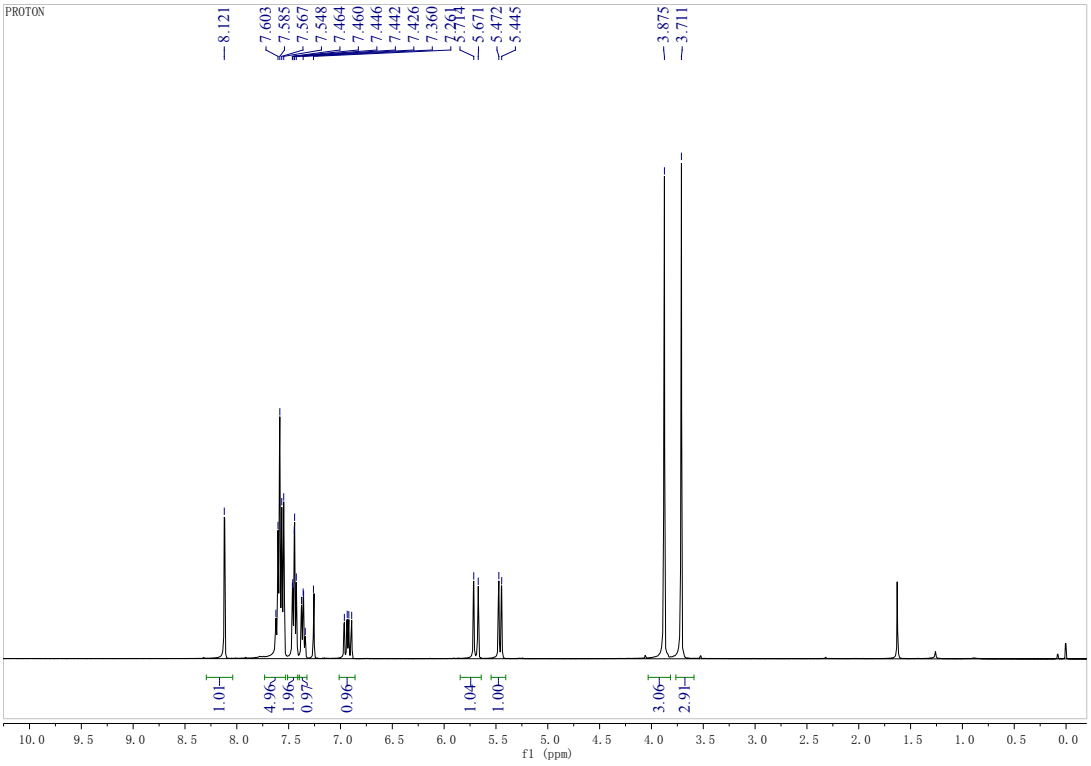
7.459
7.452
7.438
7.260
7.050
7.030
7.024
7.007
6.806
6.788
5.544
5.417
5.390
3.853
3.742
1.00
1.05
1.97
0.98
1.08
1.03
3.32
3.17
f1 (ppm)


Ph
MeO2C
CO2Me

S-3n


PROTON
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7.585
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7.548
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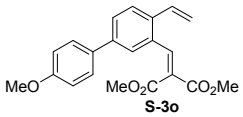
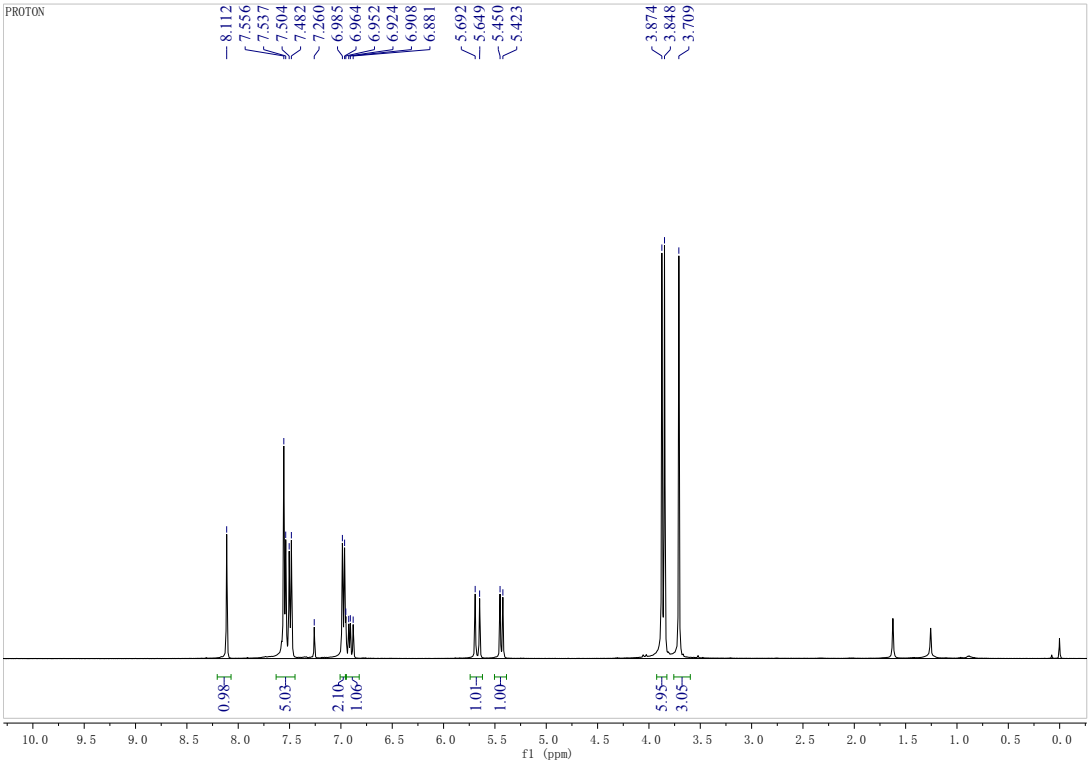
7.460
7.446
7.442
7.426
7.360
5.671
5.472
5.445
3.875
3.711
1.01
4.96
1.96
0.97
0.96
1.04
1.00
3.06
2.91
f1 (ppm)


MeO
MeO2C
CO2Me

S-3o


PROTON
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7.482
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6.952
6.924
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6.881
5.692
5.649
5.450
5.423
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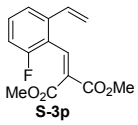
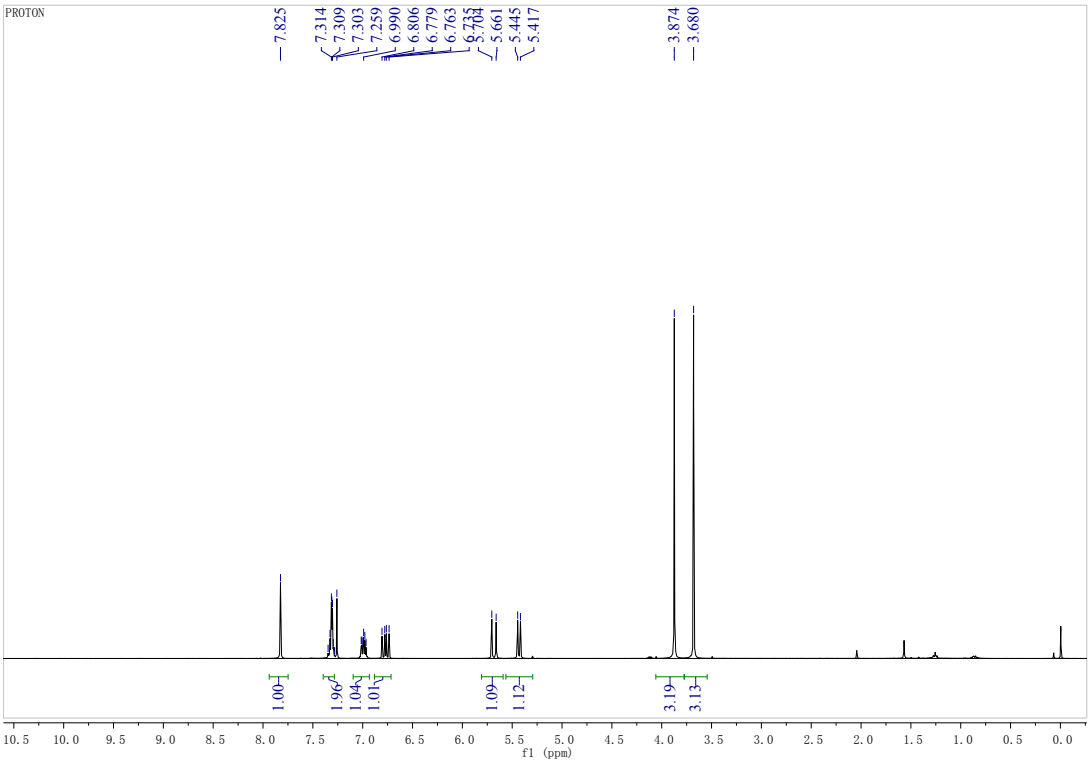
f1 (ppm)


F
MeO2C
CO2Me

S-3p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7.309
7.303
7.259
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6.806
6.779
6.763
5.704
5.661
5.445
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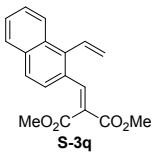
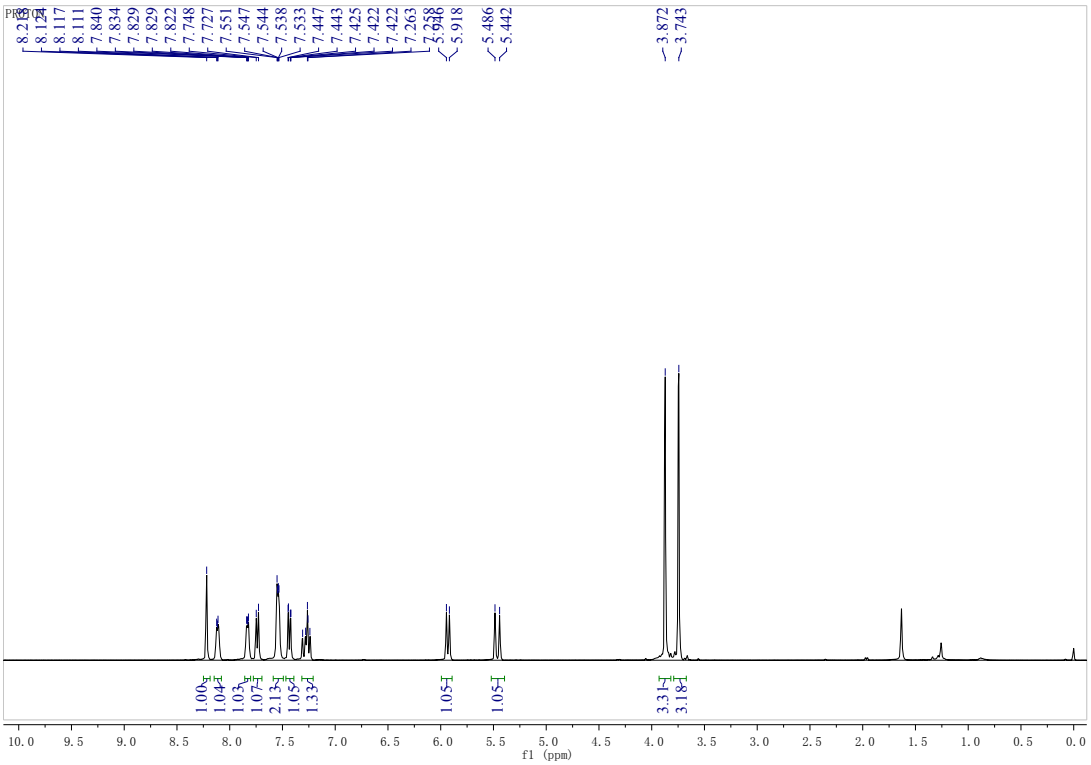
1.09
1.12
3.19
3.13
f1 (ppm)


MeO2C
CO2Me

S-3q


PROTON
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7.834
7.829
7.829
7.822
7.748
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7.544
7.538
7.533
7.447
7.443
7.425
7.422
7.422
7.263
5.946
5.918
5.486
5.442
3.872
3.743
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1.04
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1.07
2.13
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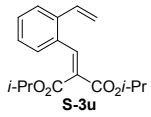
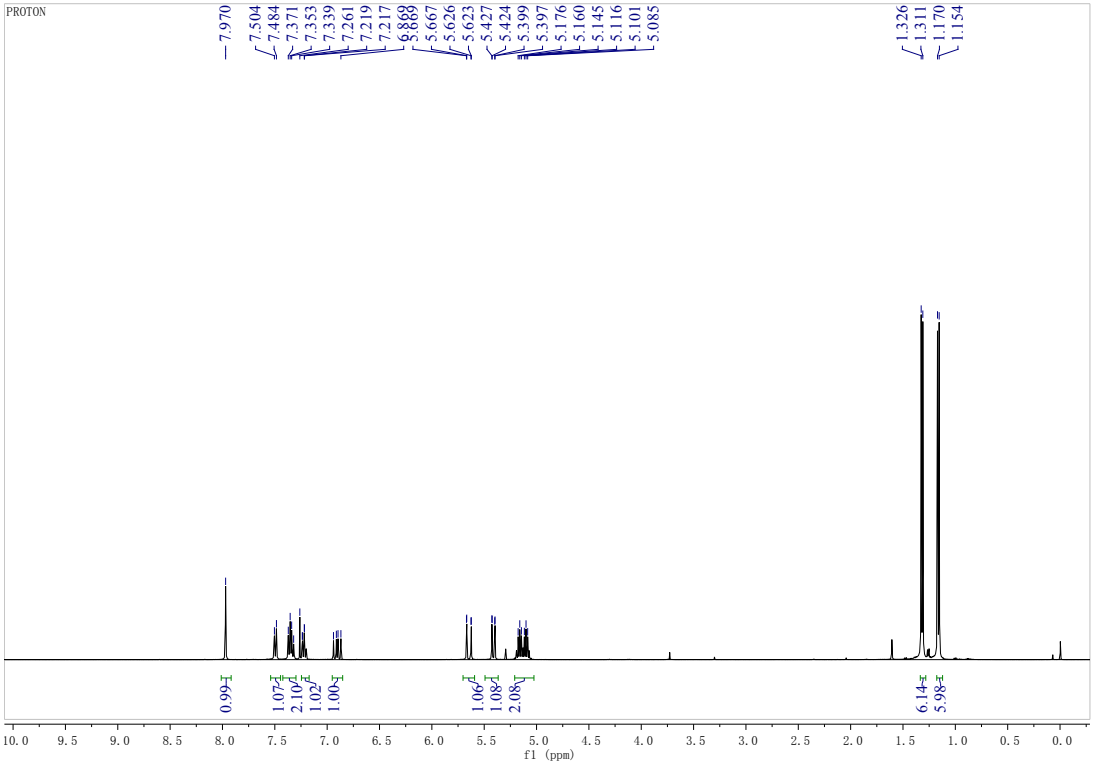
1.05
3.31
3.18
f1 (ppm)


i-PrO2C
CO2i-Pr

S-3u


PROTON
7.970
7.504
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7.339
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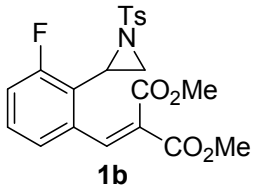
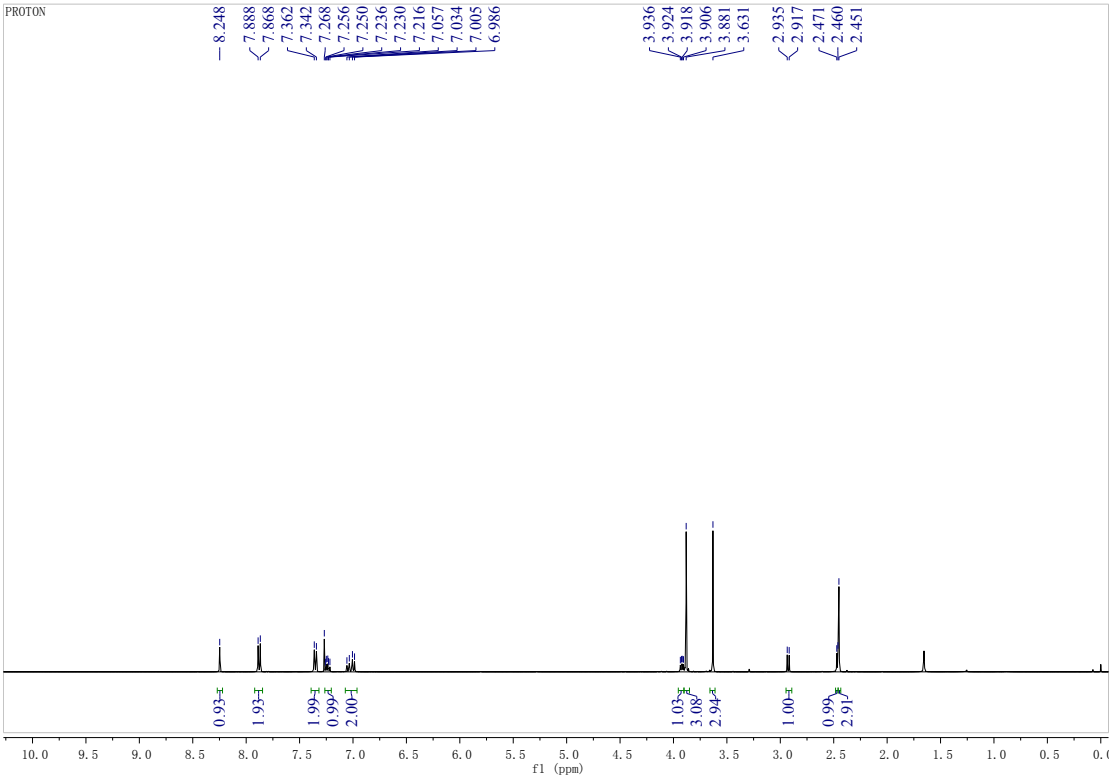
7.219
7.217
6.869
6.869
5.667
5.626
5.623
5.427
5.424
5.399
5.397
5.176
5.160
5.145
5.116
5.101
5.085
1.326
1.311
1.170
1.154
0.99
1.07
2.10
1.02
1.00
1.06
1.08
2.08
6.14
5.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Ts
N
F
CO2Me
CO2Me

1b


PROTON
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7.342
7.268
7.256
7.250
7.236
7.230
7.216
7.057
7.034
7.005
6.986
3.936
3.924
3.918
3.906
3.881
3.631
2.935
2.917
2.471
2.460
2.451
0.93
1.93
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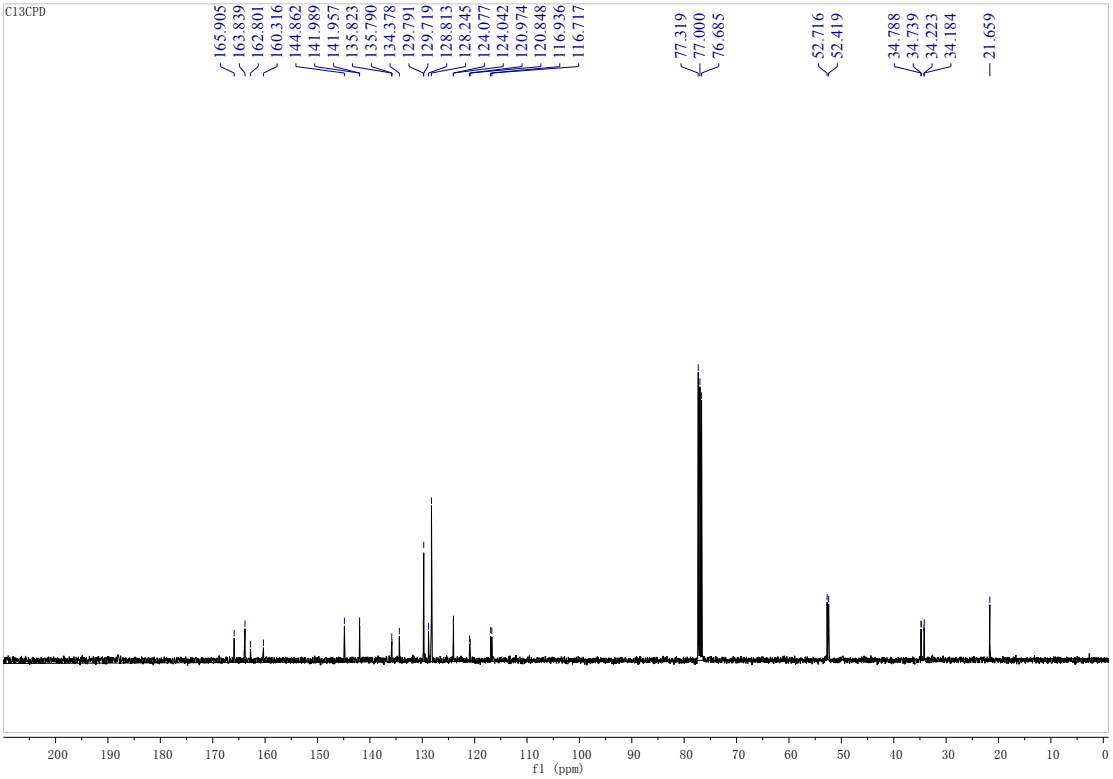
0.99
2.00
1.03
3.08
2.94
1.00
0.99
2.91
f1 (ppm)


C13CPD
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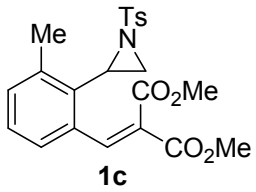
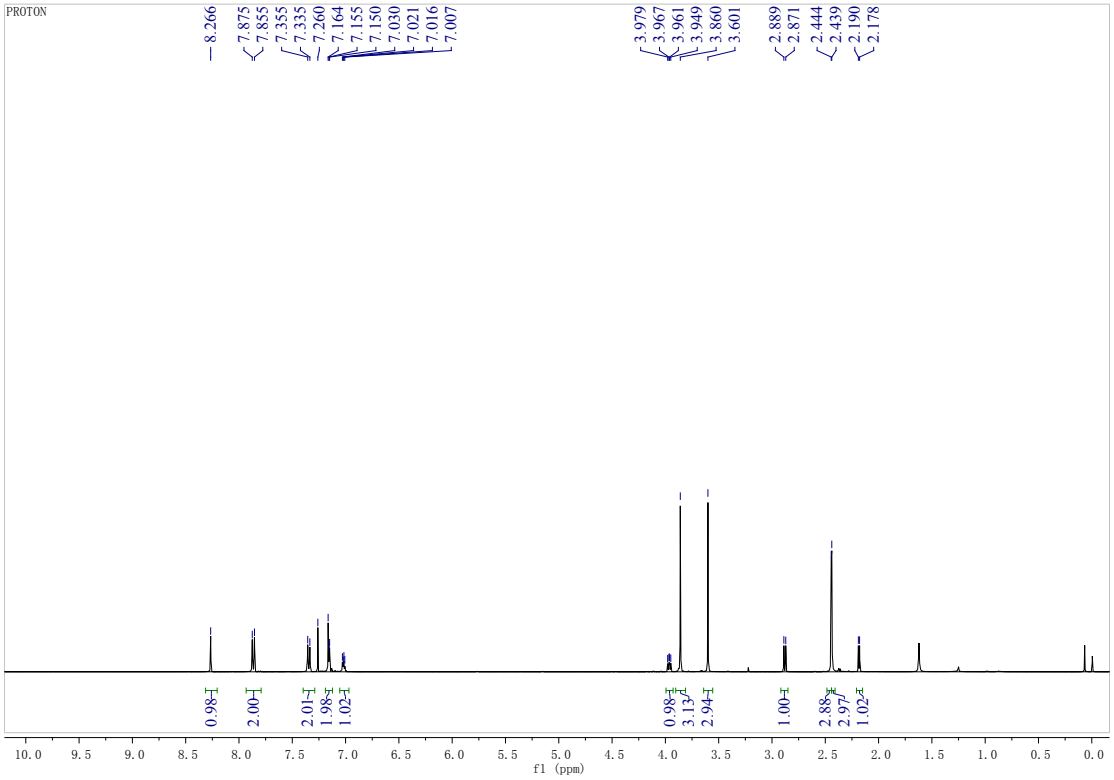
163.839
162.801
160.316
144.862
141.989
141.957
135.823
135.790
134.378
129.791
129.719
128.813
128.245
124.077
124.042
120.974
120.848
116.936
116.717
77.319
77.000
76.685
52.716
52.419
34.788
34.739
34.223
34.184
21.659
f1 (ppm)


Ts
N
Me
CO2Me
CO2Me

1c


PROTON
8.266
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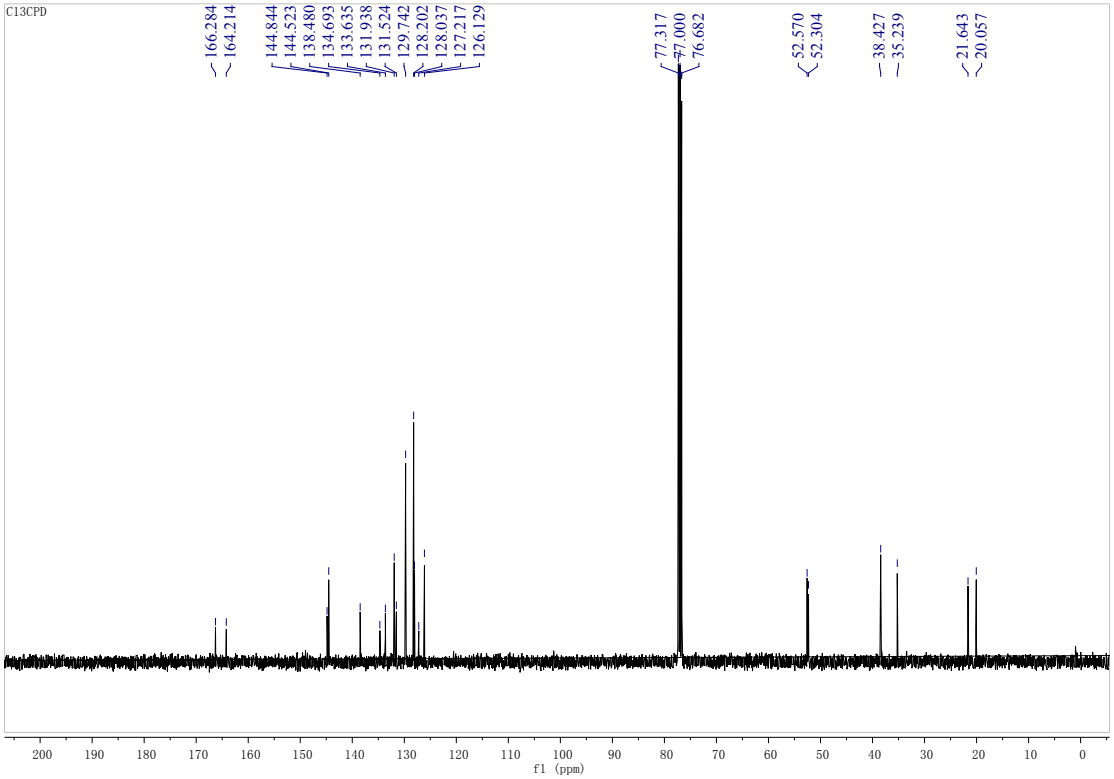
7.335
7.260
7.164
7.155
7.150
7.030
7.021
7.016
7.007
3.979
3.967
3.961
3.949
3.860
3.601
2.889
2.871
2.444
2.439
2.190
2.178
0.98
2.00
2.01
1.98
1.02
0.98
3.13
2.94
1.00
2.88
2.97
1.02
f1 (ppm)


C13CPD
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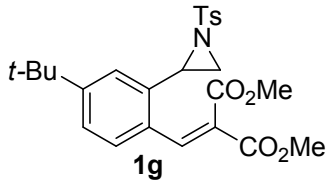
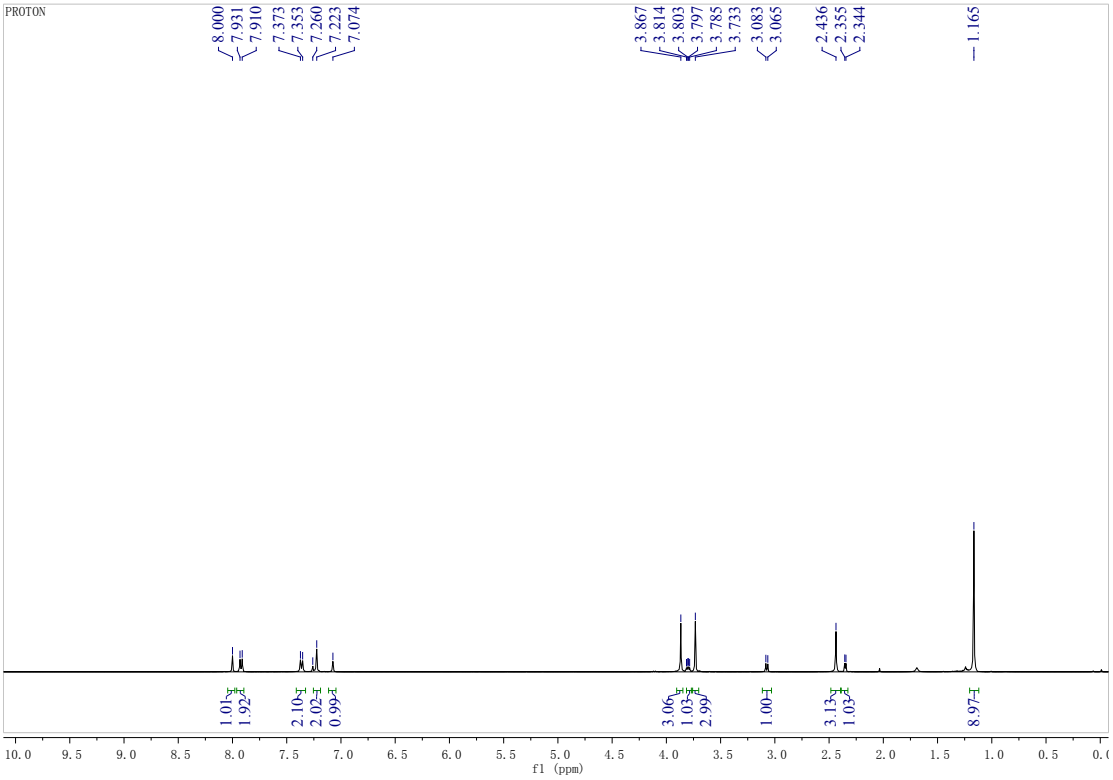
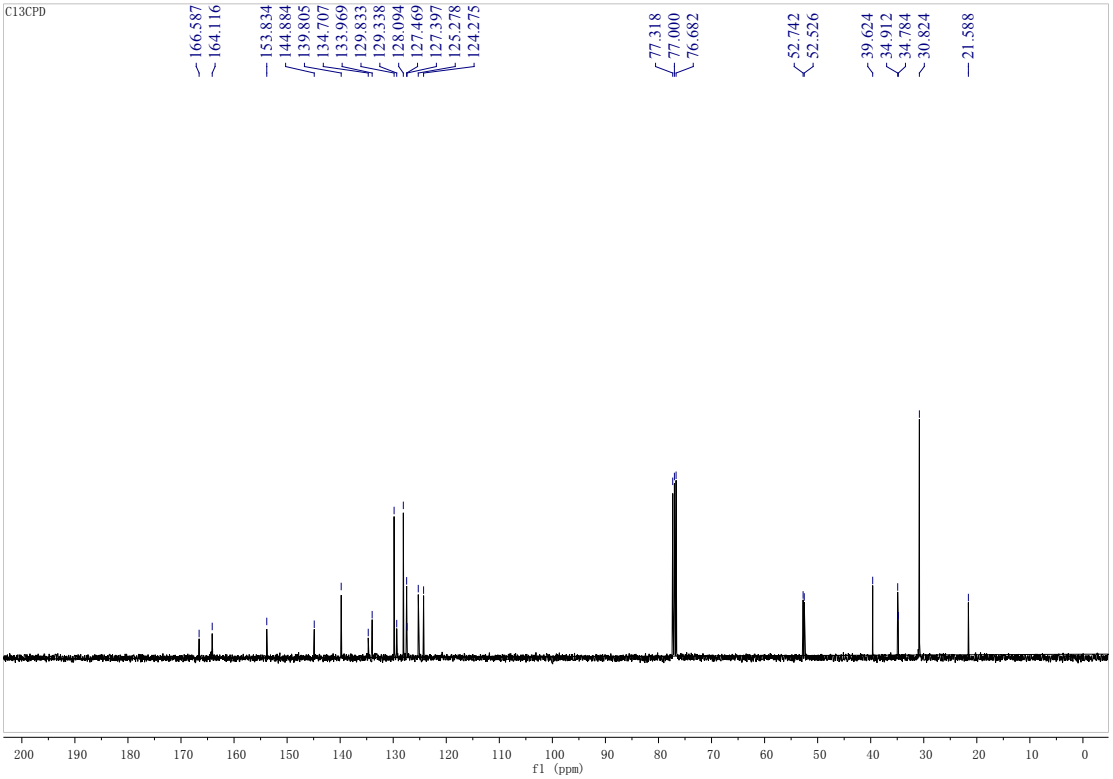
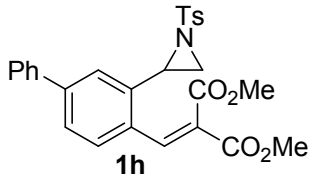
164.214
144.844
144.523
138.480
134.693
133.635
131.938
131.524
129.742
128.202
128.037
127.217
126.129
77.317
77.000
76.682
52.570
52.304
38.427
35.239
21.643
20.057
f1 (ppm)


Ts
N
t-Bu
CO2Me
CO2Me

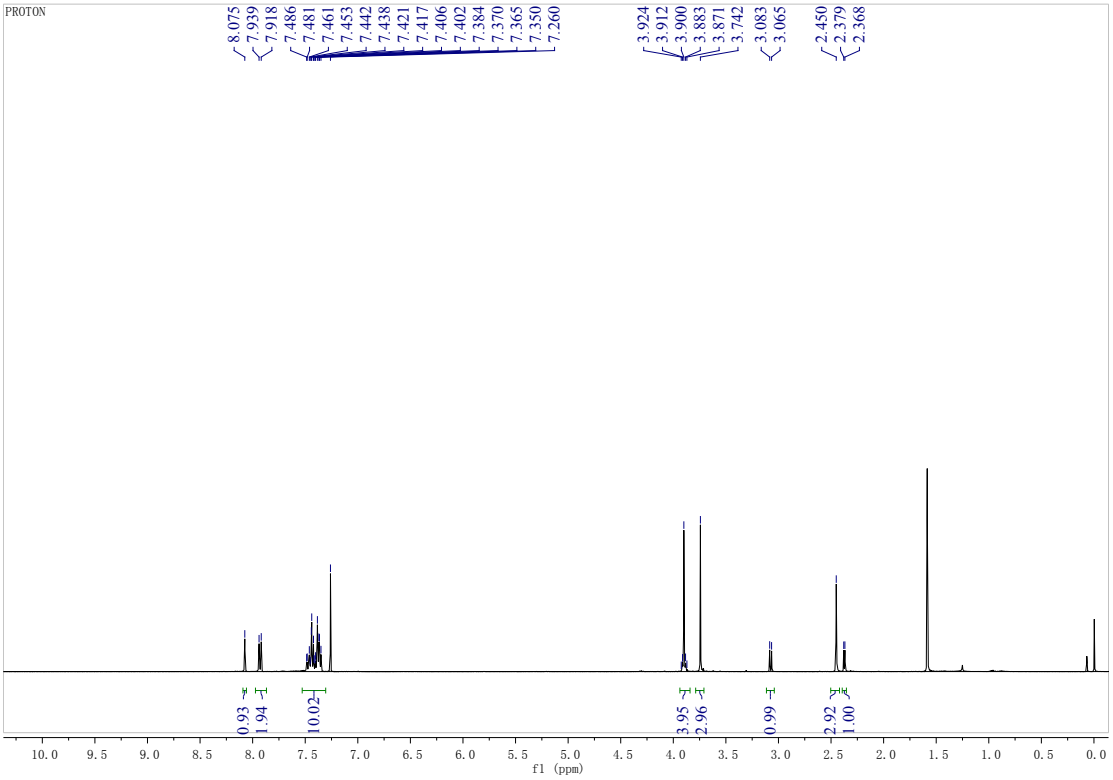
1g

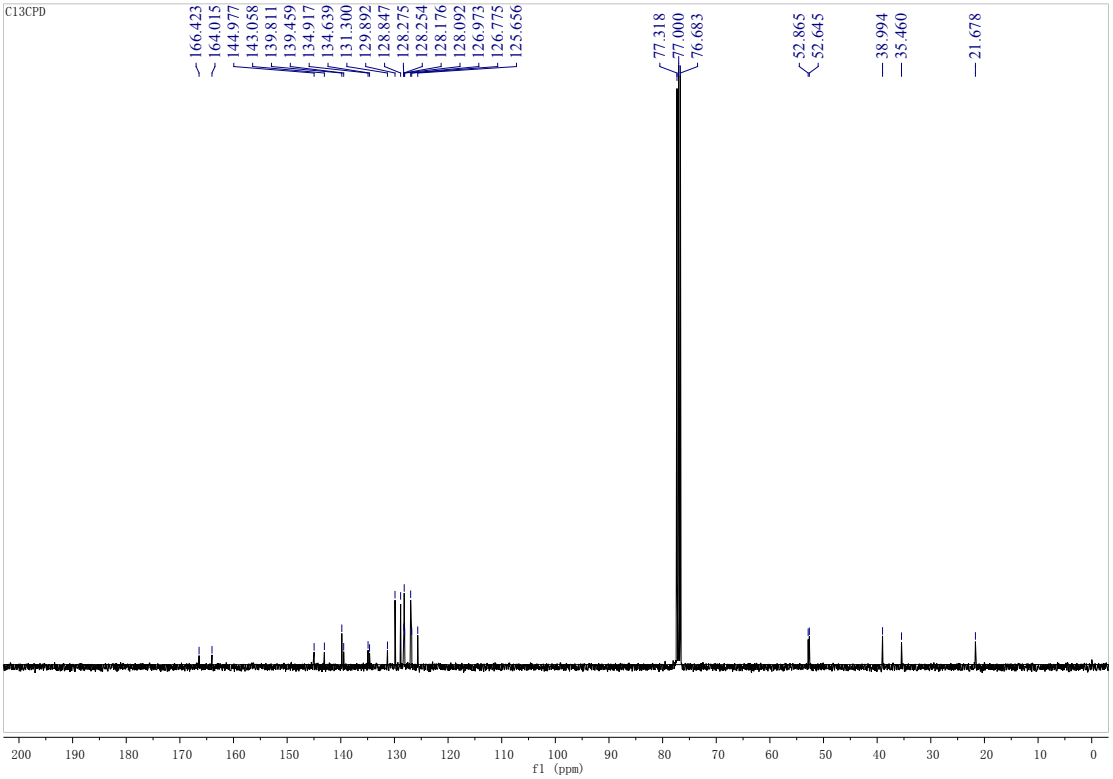

PROTON
8.000
7.931
7.910
7.373
7.353
7.260
7.223
7.074
3.867
3.814
3.803
3.797
3.785
3.733
3.083
3.065
2.436
2.355
2.344
1.165
1.01
1.92
2.10
2.02
0.99
3.06
1.03
2.99
1.00
3.13
1.03
8.97
f1 (ppm)

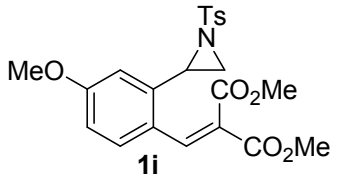

C13CPD
166.587
164.116
153.834
144.884
139.805
134.707
133.969
129.833
129.338
128.094
127.469
127.397
125.278
124.275
77.318
77.000
76.682
52.742
52.526
39.624
34.912
34.784
30.824
21.588
f1 (ppm)


Ts
N
Ph
CO2Me
CO2Me

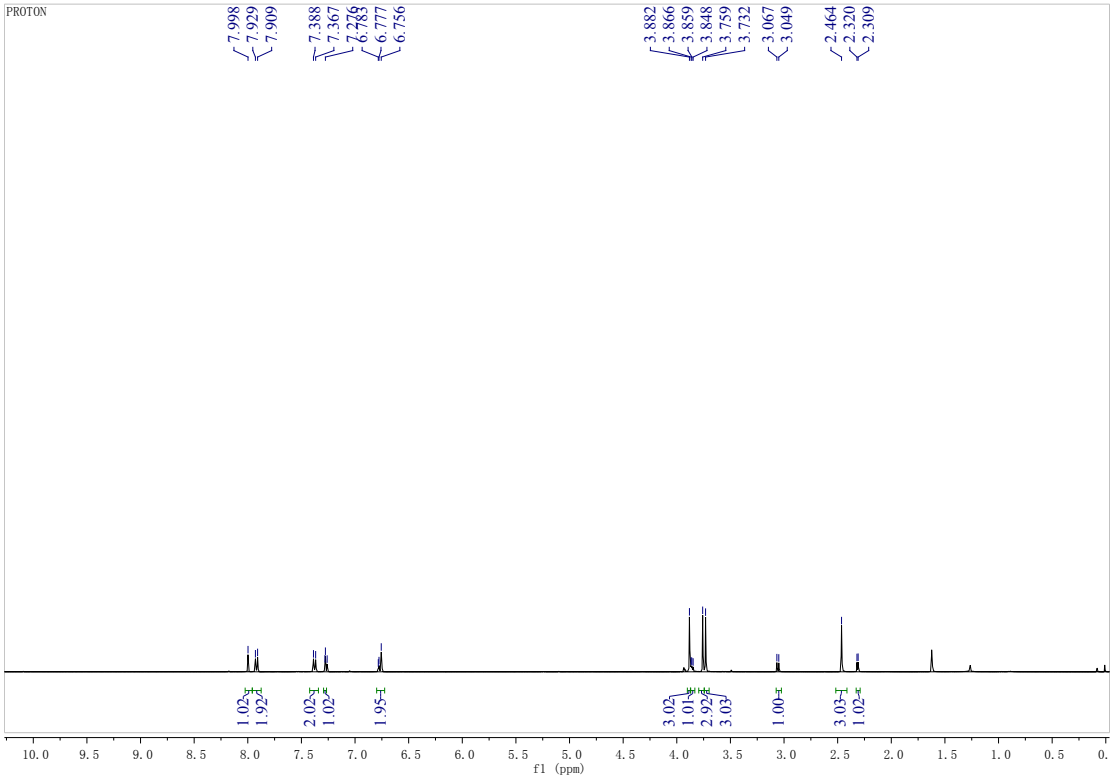
1h

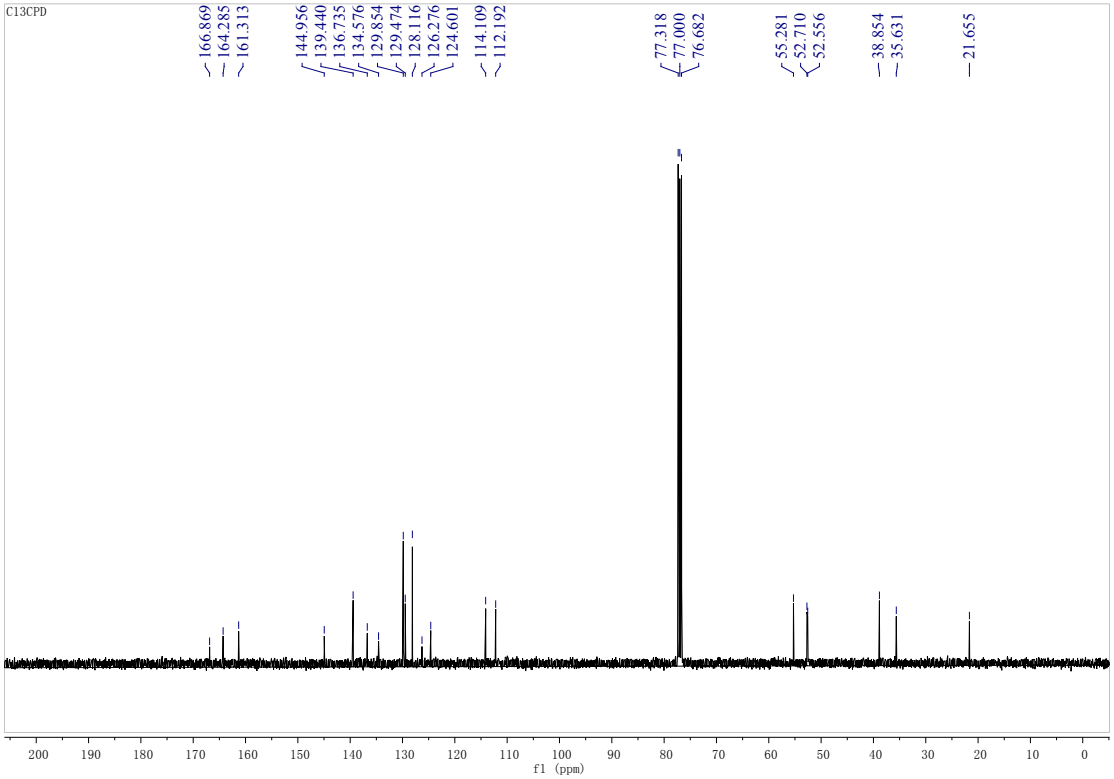

PROTON
8.075
7.939
7.918
7.486
7.481
7.461
7.453
7.442
7.438
7.421
7.417
7.406
7.402
7.384
7.370
7.365
7.350
7.260
3.924
3.912
3.900
3.883
3.871
3.742
3.083
3.065
2.450
2.379
2.368
0.93
1.94
10.02
3.95
2.96
0.99
2.92
1.00
f1 (ppm)

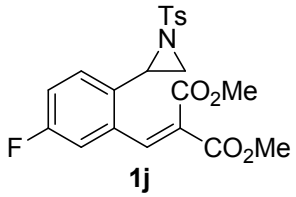

C13CPD
166.423
164.015
144.977
143.058
139.811
139.459
134.917
134.639
131.300
129.892
128.847
128.275
128.254
128.176
128.092
126.973
126.775
125.656
77.318
77.000
76.683
52.865
52.645
38.994
35.460
21.678
f1 (ppm)


Ts
N
MeO
CO2Me
CO2Me

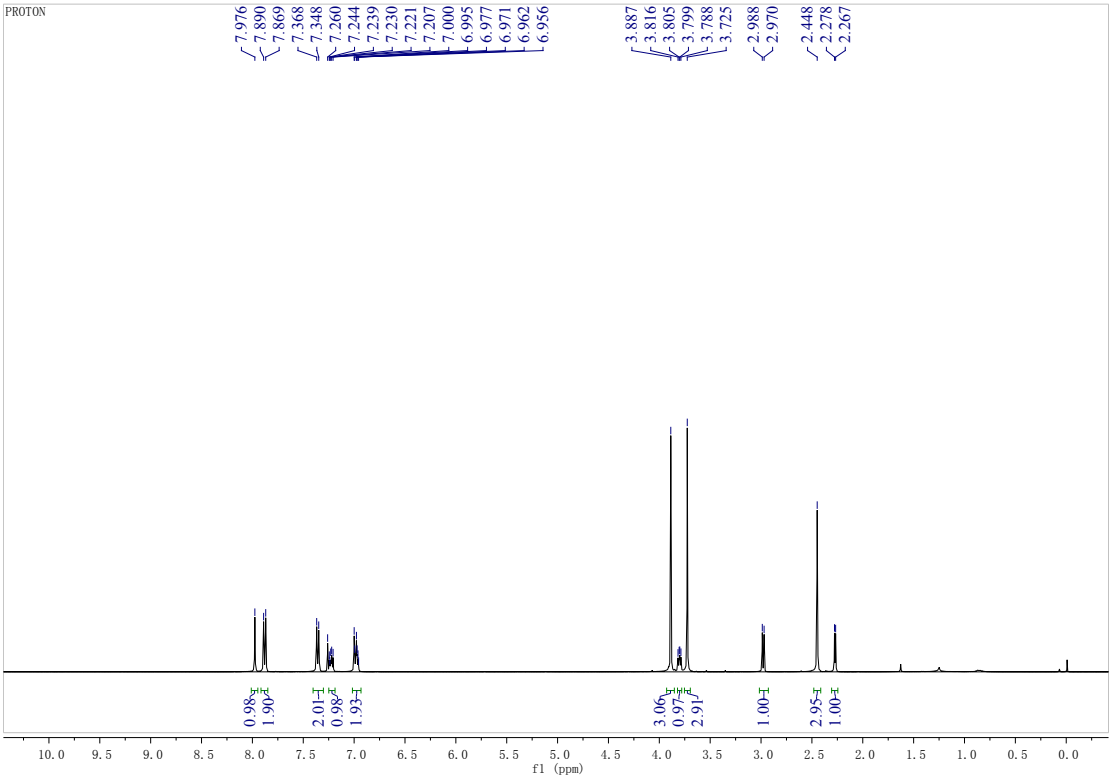
1i

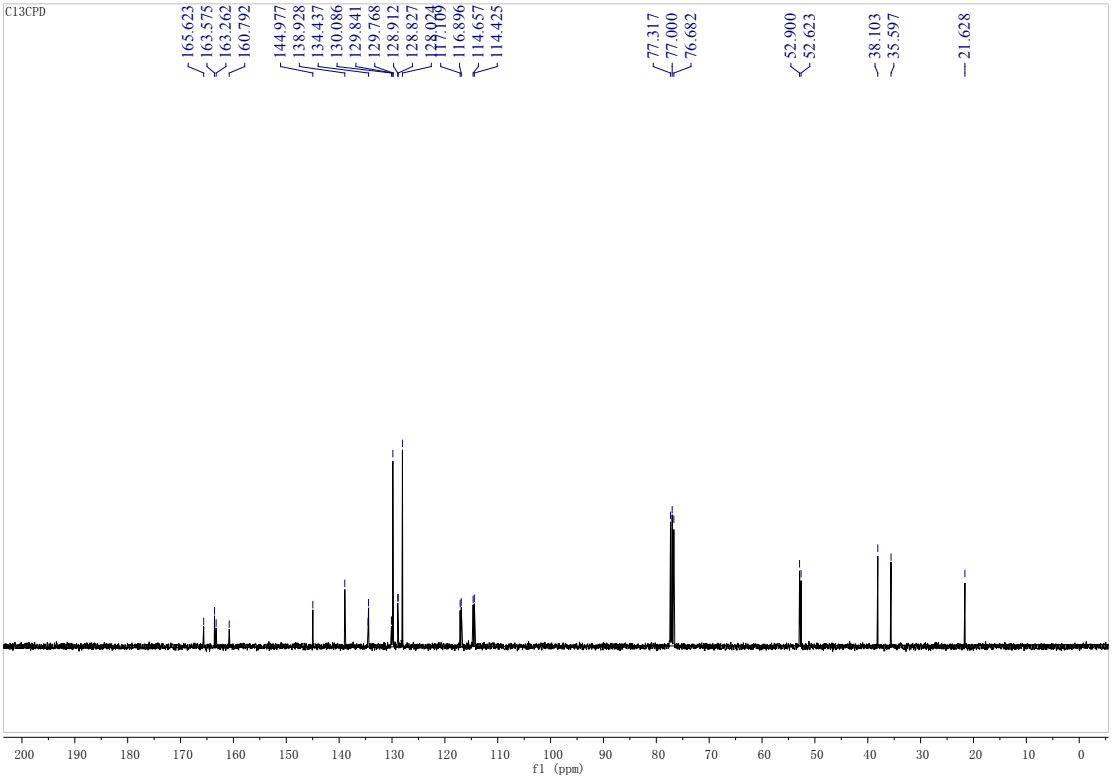

PROTON
7.998
7.929
7.909
7.388
7.367
7.276
6.788
6.777
6.756
3.882
3.866
3.859
3.848
3.759
3.732
3.067
3.049
2.464
2.320
2.309
1.02
1.92
2.02
1.02
1.95
3.02
1.01
2.92
3.03
1.00
3.03
1.02
f1 (ppm)

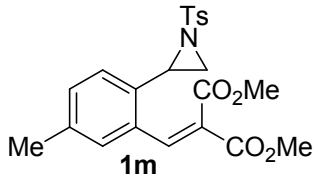

C13CPD
166.869
164.285
161.313
144.956
139.440
136.735
134.576
129.854
129.474
128.116
126.276
124.601
114.109
112.192
77.318
77.000
76.682
55.281
52.710
52.556
38.854
35.631
21.655
f1 (ppm)


Ts
N
CO2Me
F
CO2Me

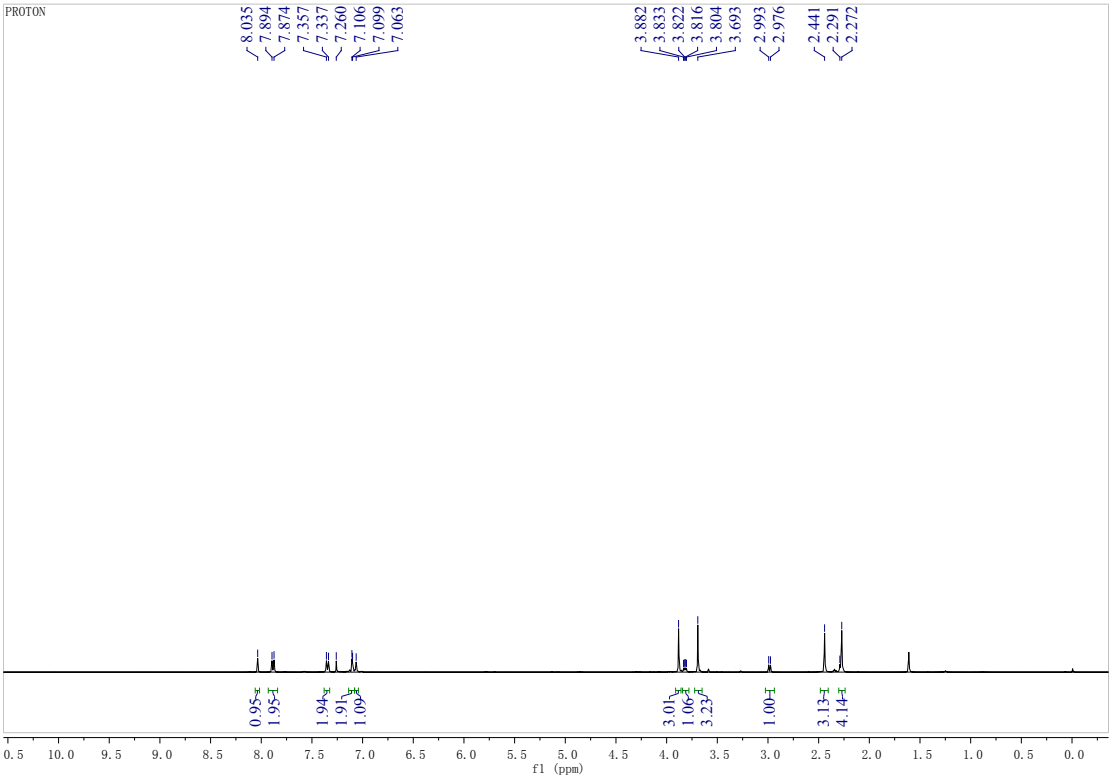
1j

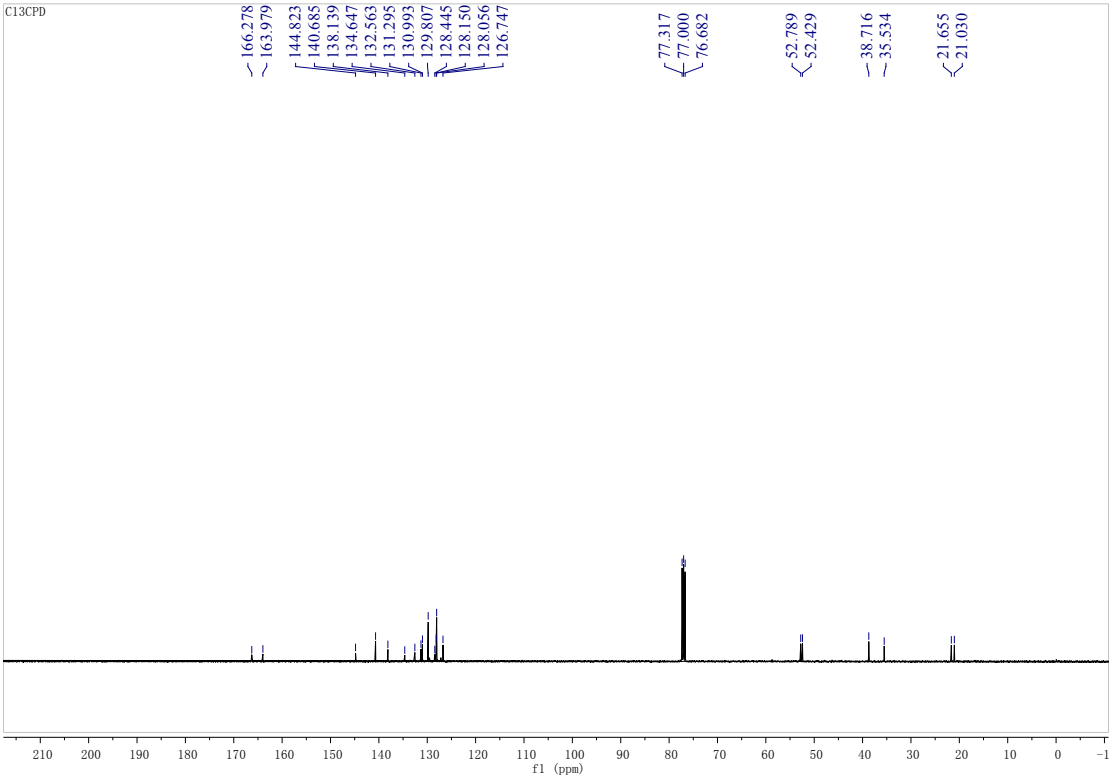

PROTON
7.976
7.890
7.869
7.368
7.348
7.260
7.244
7.239
7.230
7.221
7.207
7.000
6.995
6.977
6.971
6.962
6.956
3.887
3.816
3.805
3.799
3.788
3.725
2.988
2.970
2.448
2.278
2.267
0.98
1.90
2.01
0.98
1.93
3.06
0.97
2.91
1.00
2.95
1.00
f1 (ppm)

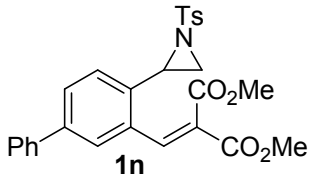

C13CPD
165.623
163.575
163.262
160.792
144.977
138.928
134.437
130.086
129.841
129.768
128.912
128.827
128.024
117.109
116.896
114.657
114.425
77.317
77.000
76.682
52.900
52.623
38.103
35.597
21.628
f1 (ppm)


Ts
N
CO2Me
Me
CO2Me

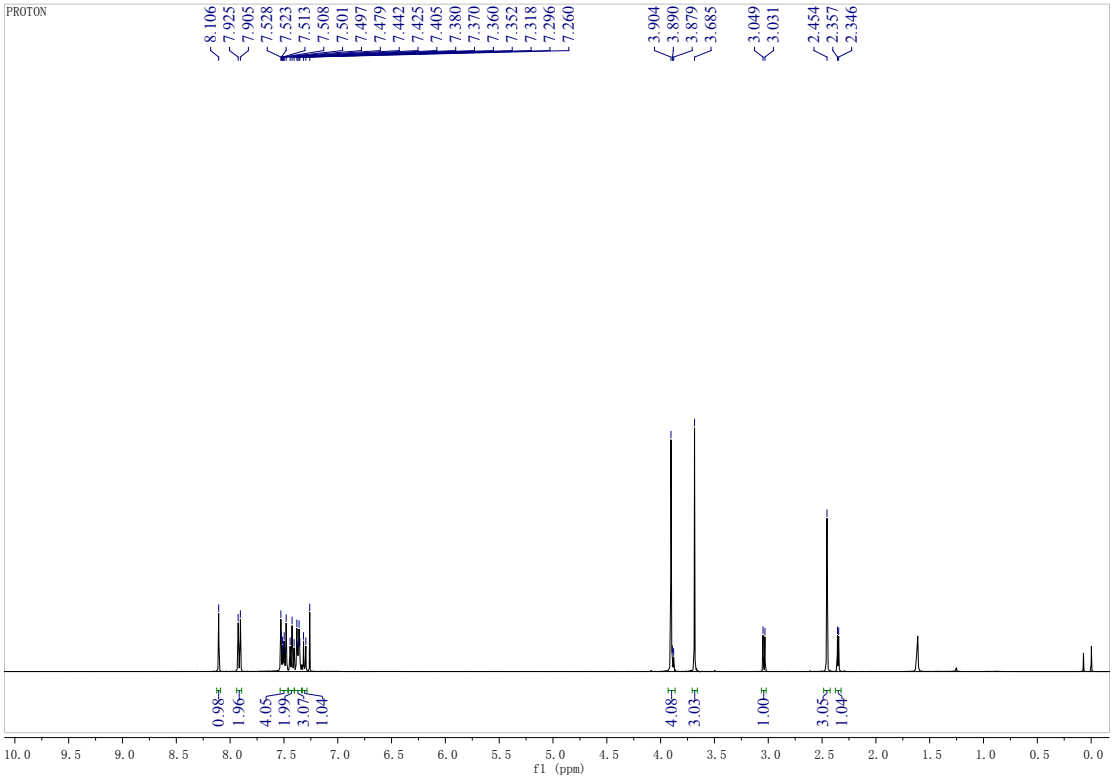
1m

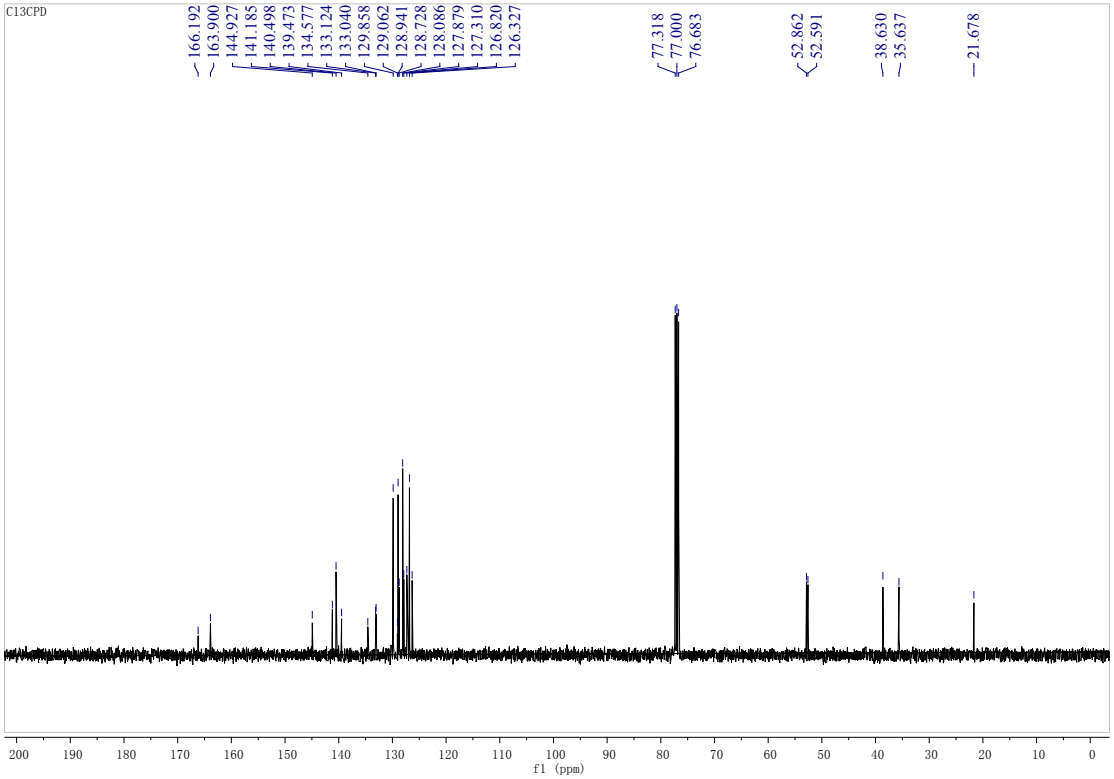

PROTON
8.035
7.894
7.874
7.357
7.337
7.260
7.106
7.099
7.063
3.882
3.833
3.822
3.816
3.804
3.693
2.993
2.976
2.441
2.291
2.272
0.95
1.95
1.94
1.91
1.09
3.01
1.06
3.23
1.00
3.13
4.14
f1 (ppm)

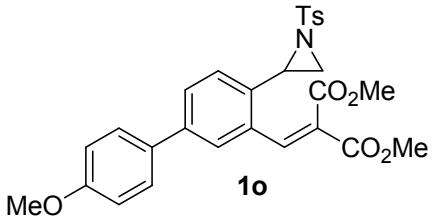

C13CPD
166.278
163.979
144.823
140.685
138.139
134.647
132.563
131.295
130.993
129.807
128.445
128.150
128.056
126.747
77.317
77.000
76.682
52.789
52.429
38.716
35.534
21.655
21.030
f1 (ppm)


Ts
N
CO2Me
Ph
CO2Me

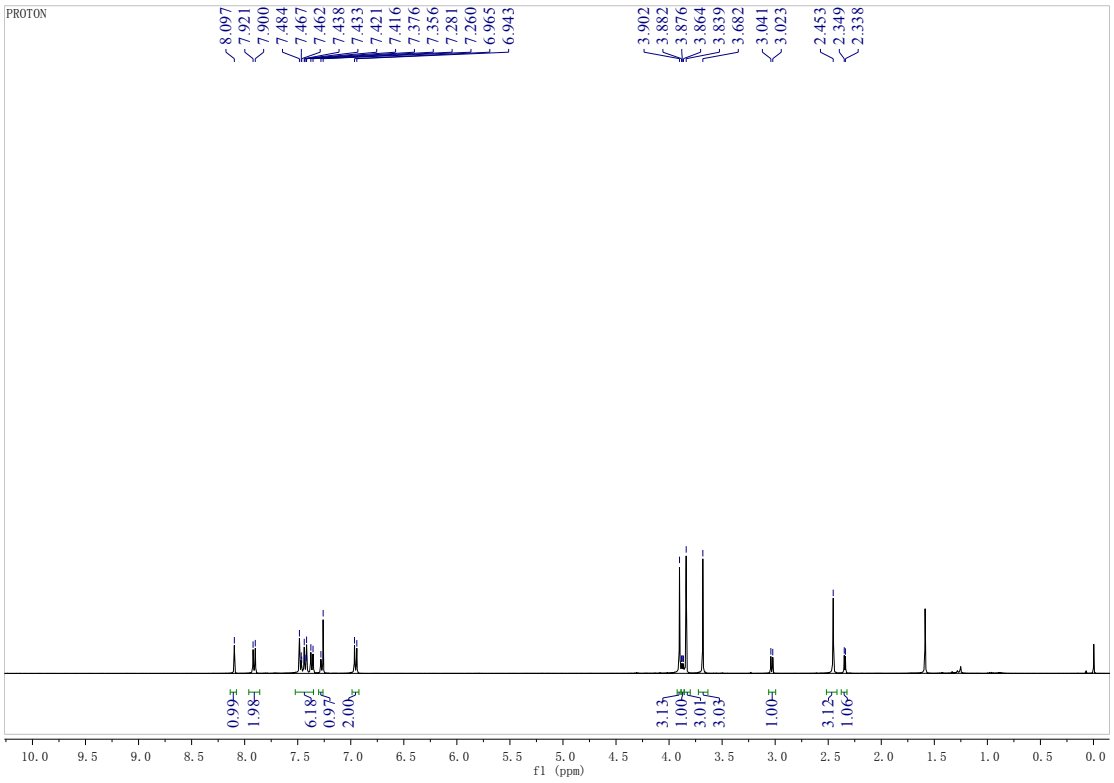
1n

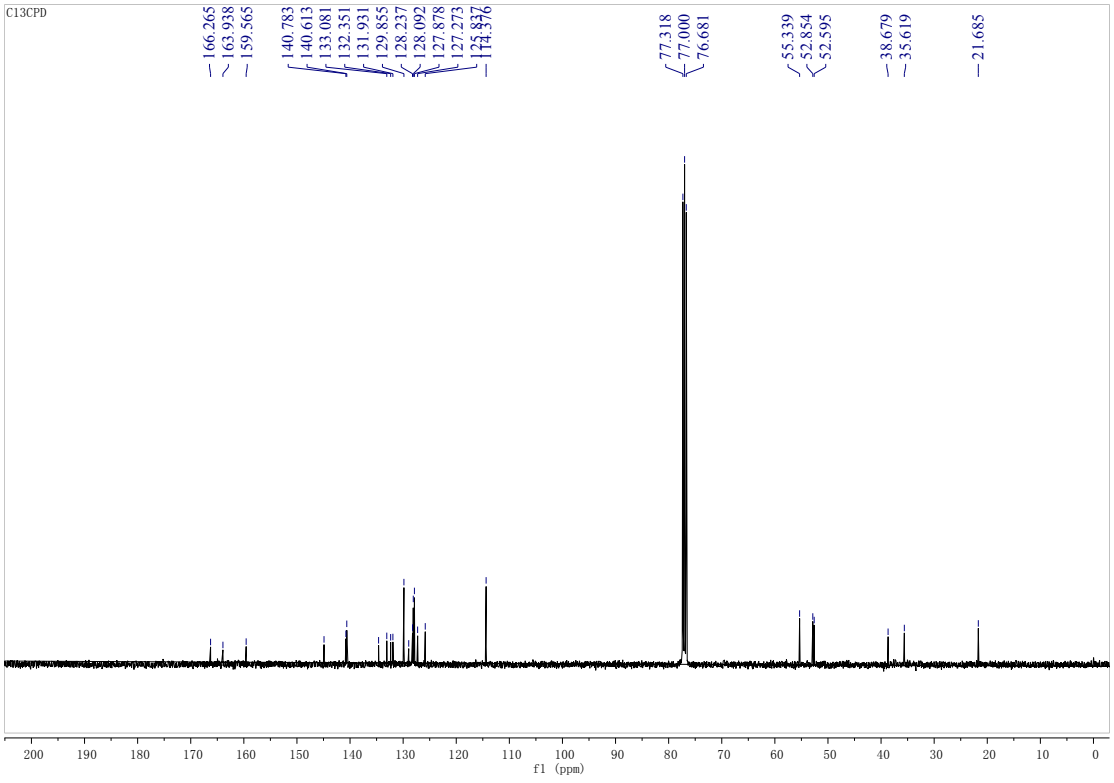

PROTON
8.106
7.925
7.905
7.528
7.523
7.513
7.508
7.501
7.497
7.479
7.442
7.425
7.405
7.380
7.370
7.360
7.352
7.318
7.296
7.260
3.904
3.890
3.879
3.685
3.049
3.031
2.454
2.357
2.346
0.98
1.96
4.05
1.99
3.07
1.04
4.08
3.03
1.00
3.05
1.04
f1 (ppm)

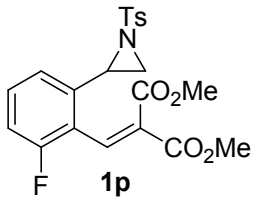

C13CPD
166.192
163.900
144.927
141.185
140.498
139.473
134.577
133.124
133.040
129.858
129.062
128.941
128.728
128.086
127.879
127.310
126.820
126.327
77.318
77.000
76.683
52.862
52.591
38.630
35.637
21.678
f1 (ppm)


Ts
N
CO2Me
CO2Me
MeO

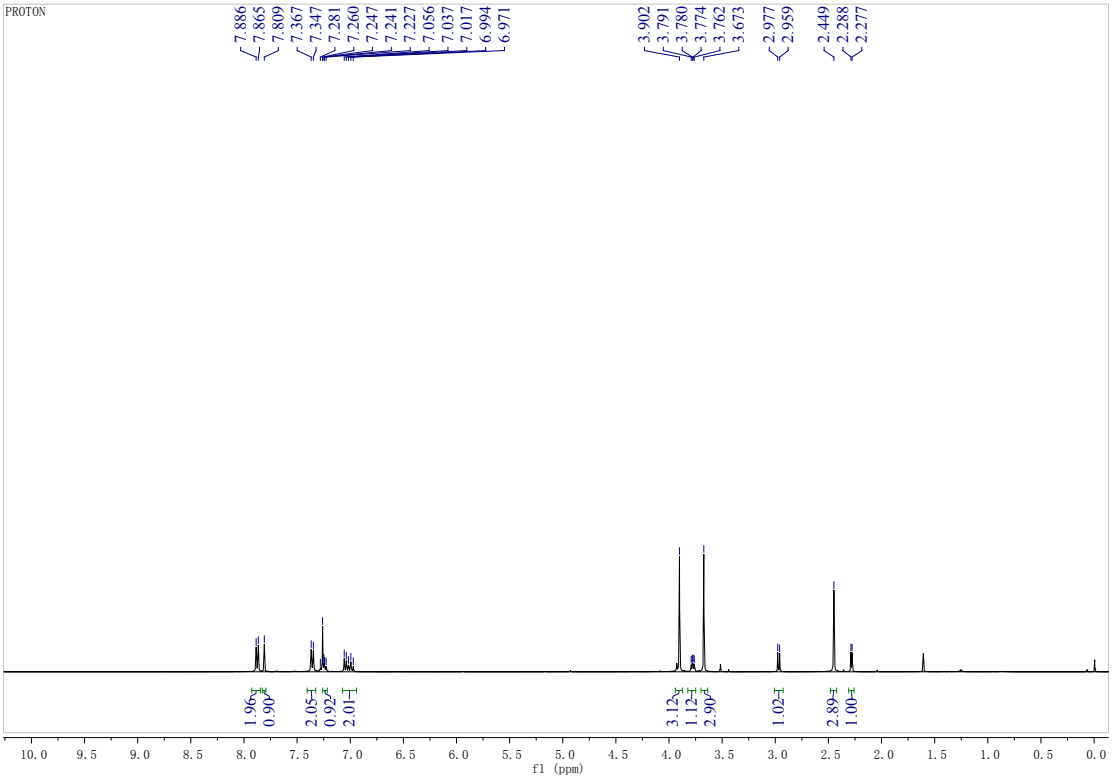
1o

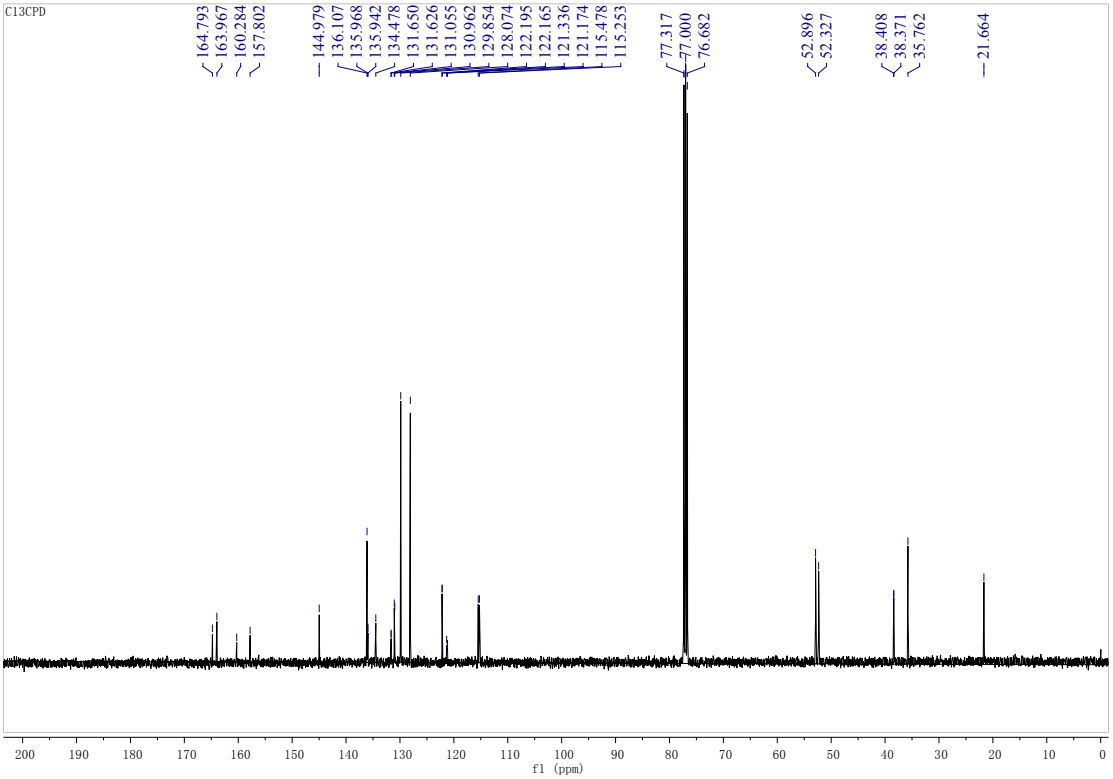

PROTON
8.097
7.921
7.900
7.484
7.467
7.462
7.438
7.433
7.421
7.416
7.376
7.356
7.281
7.260
6.965
6.943
3.902
3.882
3.876
3.864
3.839
3.682
3.041
3.023
2.453
2.349
2.338
0.99
1.98
6.18
0.97
2.00
3.13
1.00
3.01
3.03
1.00
3.12
1.06
f1 (ppm)

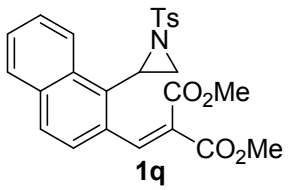

C13CPD
166.265
163.938
159.565
140.783
140.613
133.081
132.351
131.931
129.855
128.237
128.092
127.878
127.273
77.318
77.000
76.681
55.339
52.854
52.595
38.679
35.619
21.685
f1 (ppm)


Ts
N
CO2Me
CO2Me
F

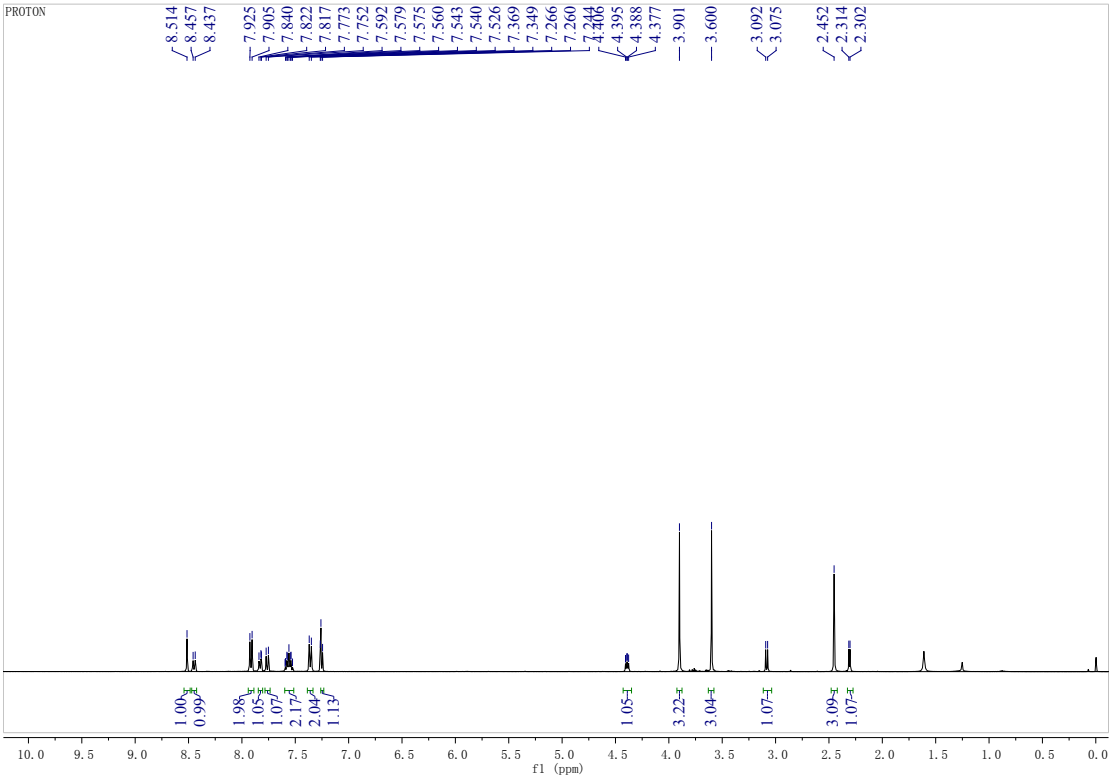
1p

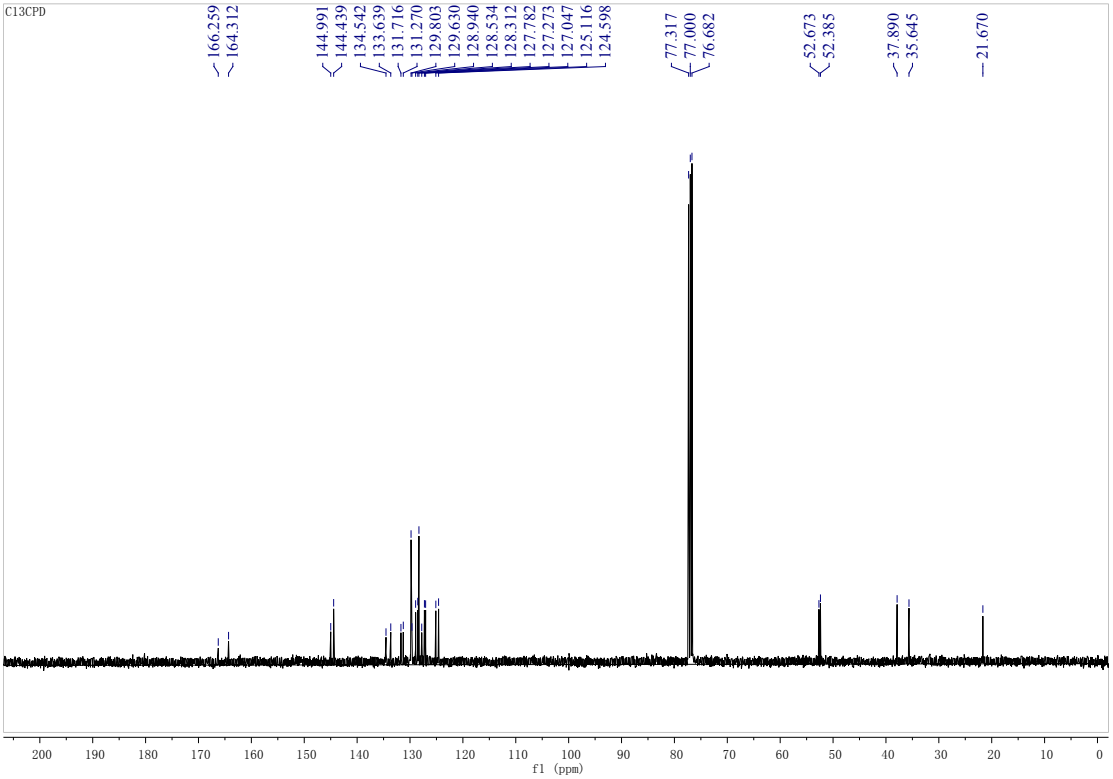

PROTON
7.886
7.865
7.809
7.367
7.347
7.281
7.260
7.247
7.241
7.227
7.056
7.037
7.017
6.994
6.971
3.902
3.791
3.780
3.774
3.762
3.673
2.977
2.959
2.449
2.288
2.277
1.96
0.90
2.05
0.92
2.01
3.12
1.12
2.90
1.02
2.89
1.00
f1 (ppm)

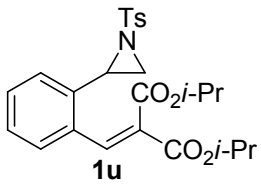

C13CPD
164.793
163.967
160.284
157.802
144.979
136.107
135.968
135.942
134.478
131.650
131.626
131.055
130.962
129.854
128.074
122.195
122.165
121.336
121.174
115.478
115.253
77.317
77.000
76.682
52.896
52.327
38.408
38.371
35.762
21.664
f1 (ppm)


Ts
N
CO2Me
CO2Me

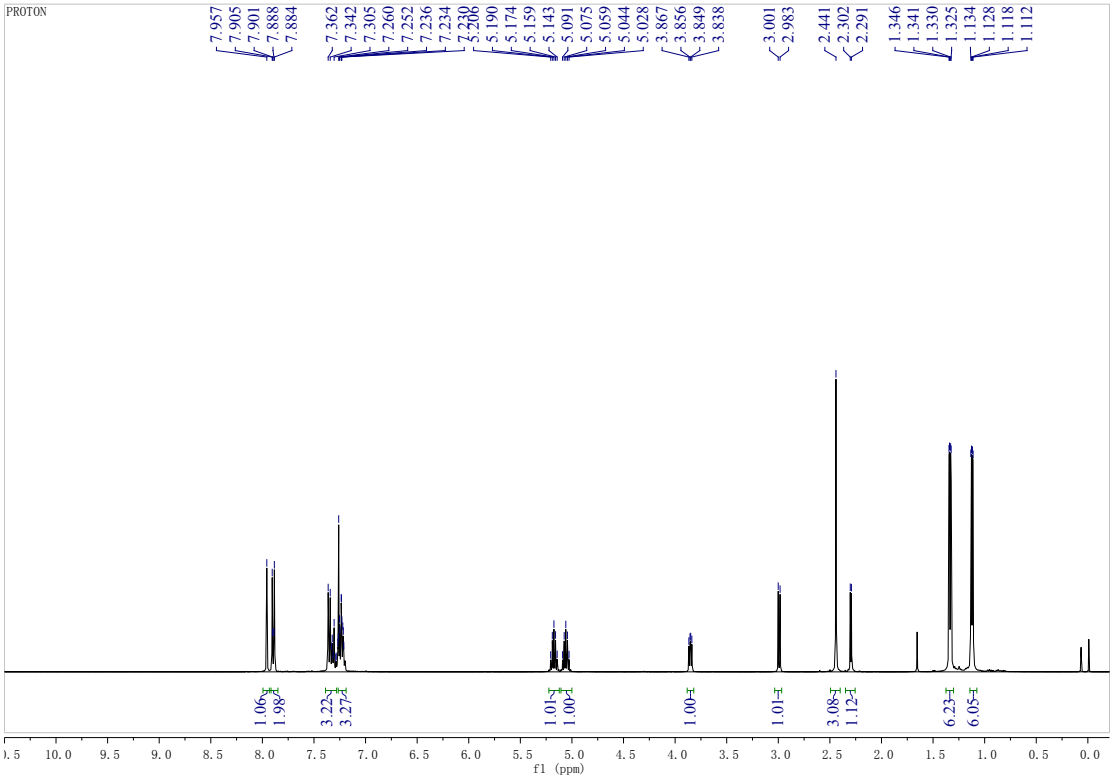
1q

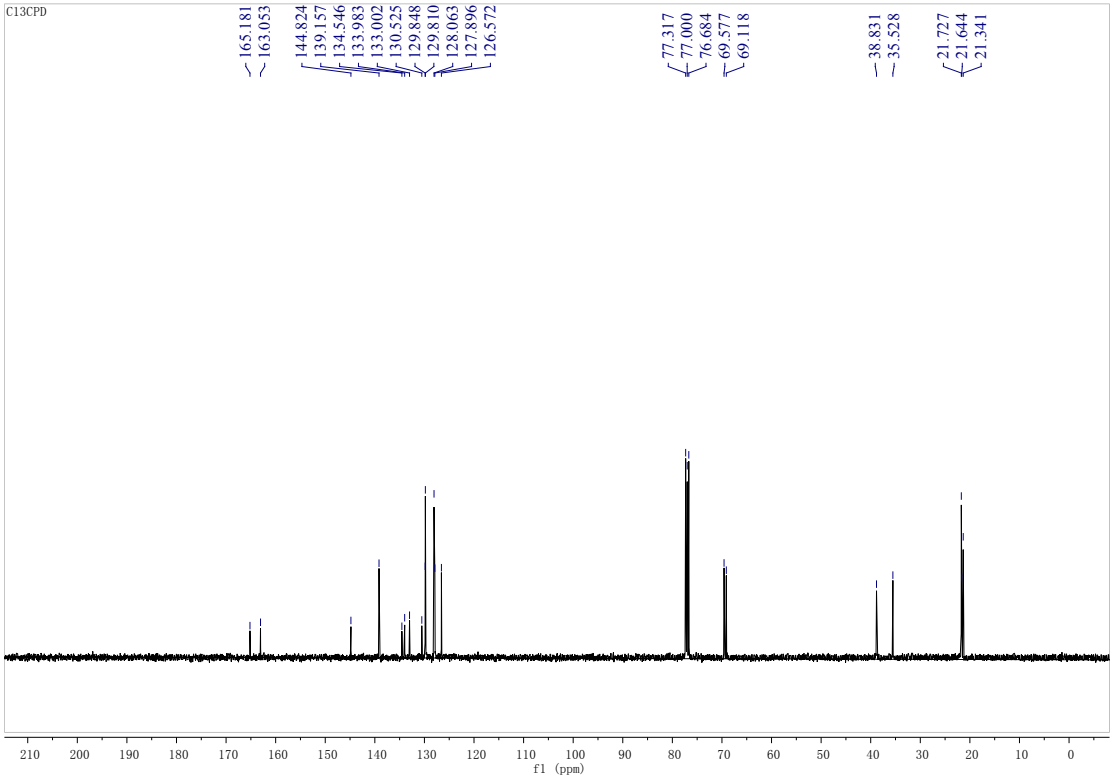

PROTON
8.514
8.457
8.437
7.925
7.905
7.840
7.822
7.817
7.773
7.752
7.592
7.579
7.575
7.560
7.543
7.540
7.526
7.369
7.349
7.266
7.260
4.395
4.388
4.377
3.901
3.600
3.092
3.075
2.452
2.314
2.302
1.00
0.99
1.98
1.05
1.07
2.17
2.04
1.13
1.05
3.22
3.04
1.07
3.09
1.07
f1 (ppm)

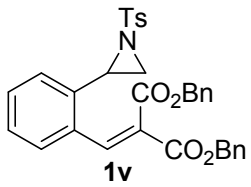

C13CPD
166.259
164.312
144.991
144.439
134.542
133.639
131.716
131.270
129.803
129.630
128.940
128.534
128.312
127.782
127.273
127.047
125.116
124.598
77.317
77.000
76.682
52.673
52.385
37.890
35.645
21.670
f1 (ppm)


Ts
N
CO2i-Pr
CO2i-Pr

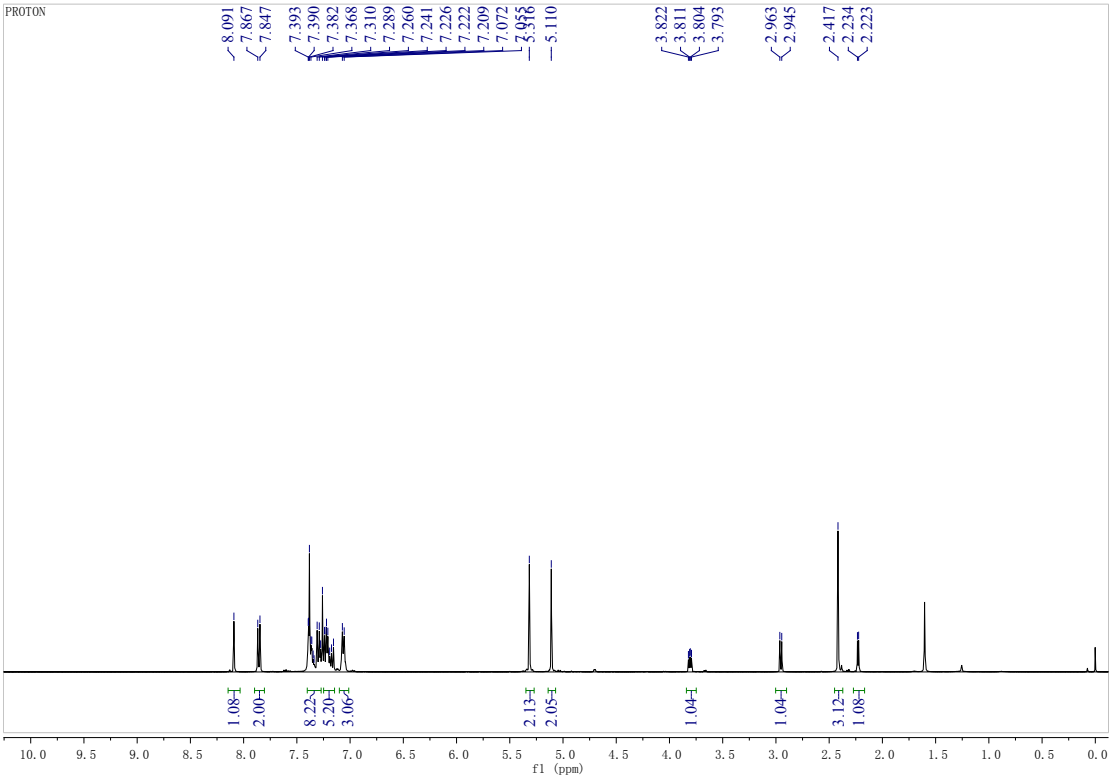
1u

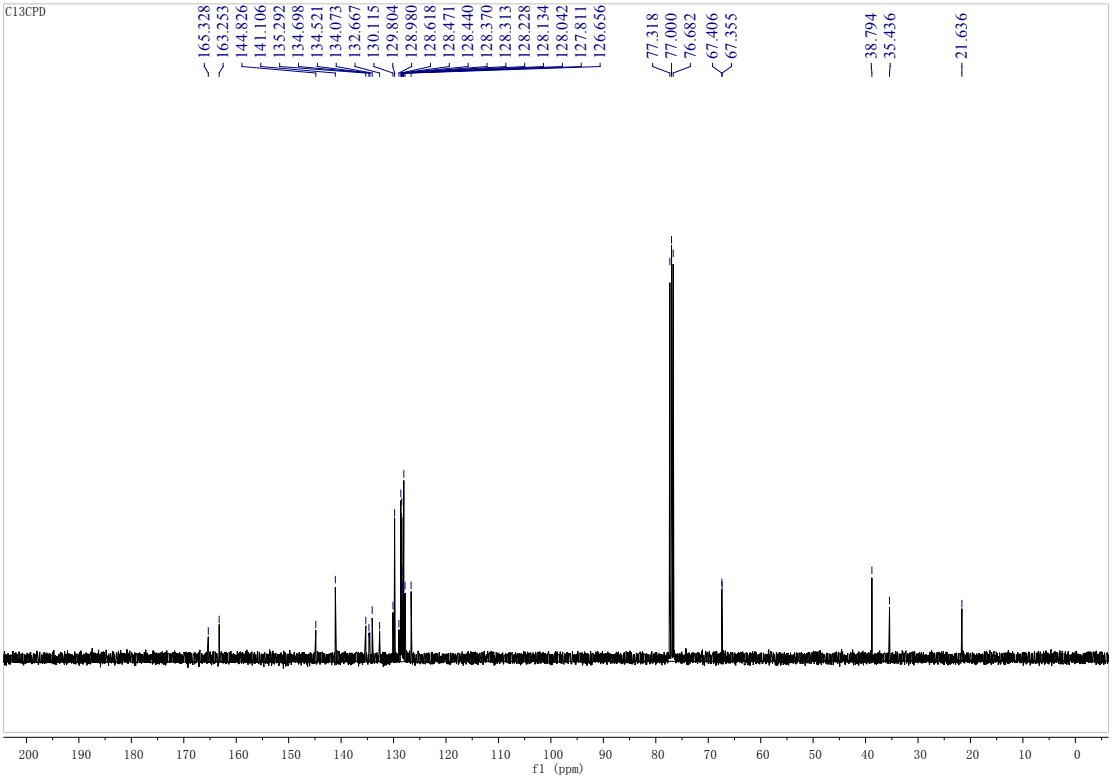

PROTON
7.957
7.905
7.901
7.888
7.884
7.362
7.342
7.305
7.260
7.252
7.236
7.234
7.230
5.208
5.190
5.174
5.159
5.143
5.091
5.075
5.059
5.044
5.028
3.867
3.856
3.849
3.838
3.001
2.983
2.441
2.302
2.291
1.346
1.341
1.330
1.325
1.134
1.128
1.118
1.112
1.06
1.98
3.22
3.27
1.01
1.00
1.00
1.01
3.08
1.12
6.23
6.05
f1 (ppm)

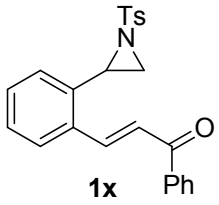

C13CPD
165.181
163.053
144.824
139.157
134.546
133.983
133.002
130.525
129.848
129.810
128.063
127.896
126.572
77.317
77.000
76.684
69.577
69.118
38.831
35.528
21.727
21.644
21.341
f1 (ppm)


Ts
N
CO2Bn
CO2Bn

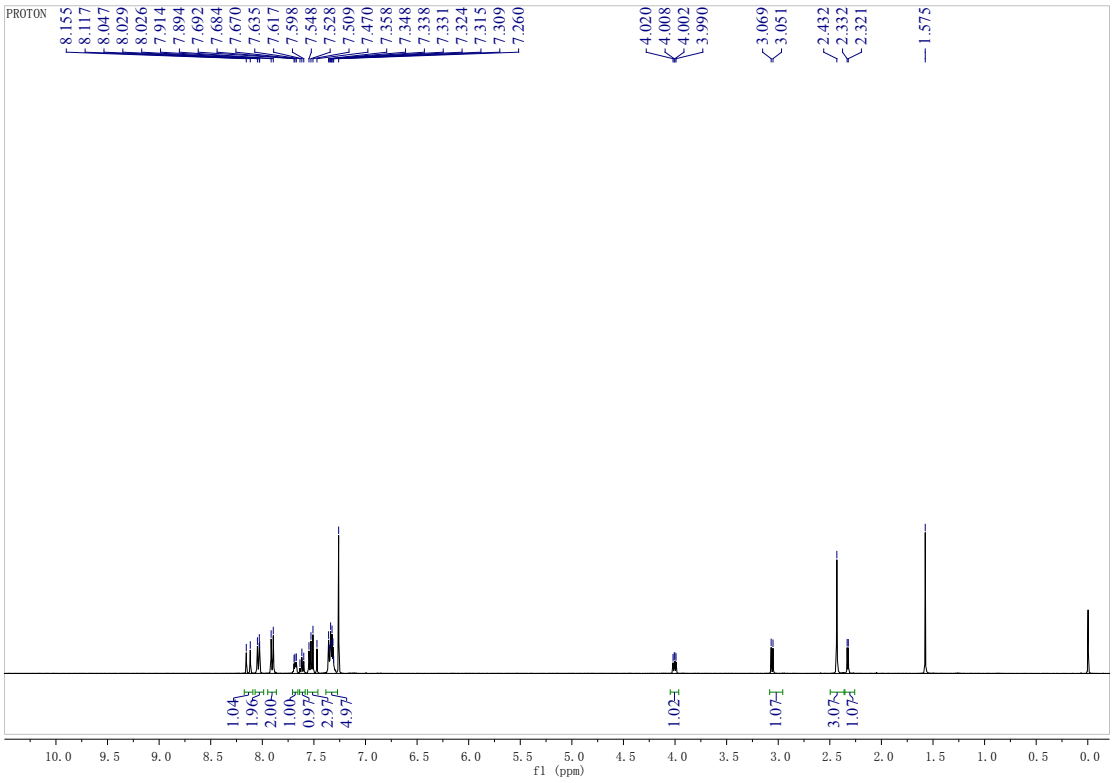
1v

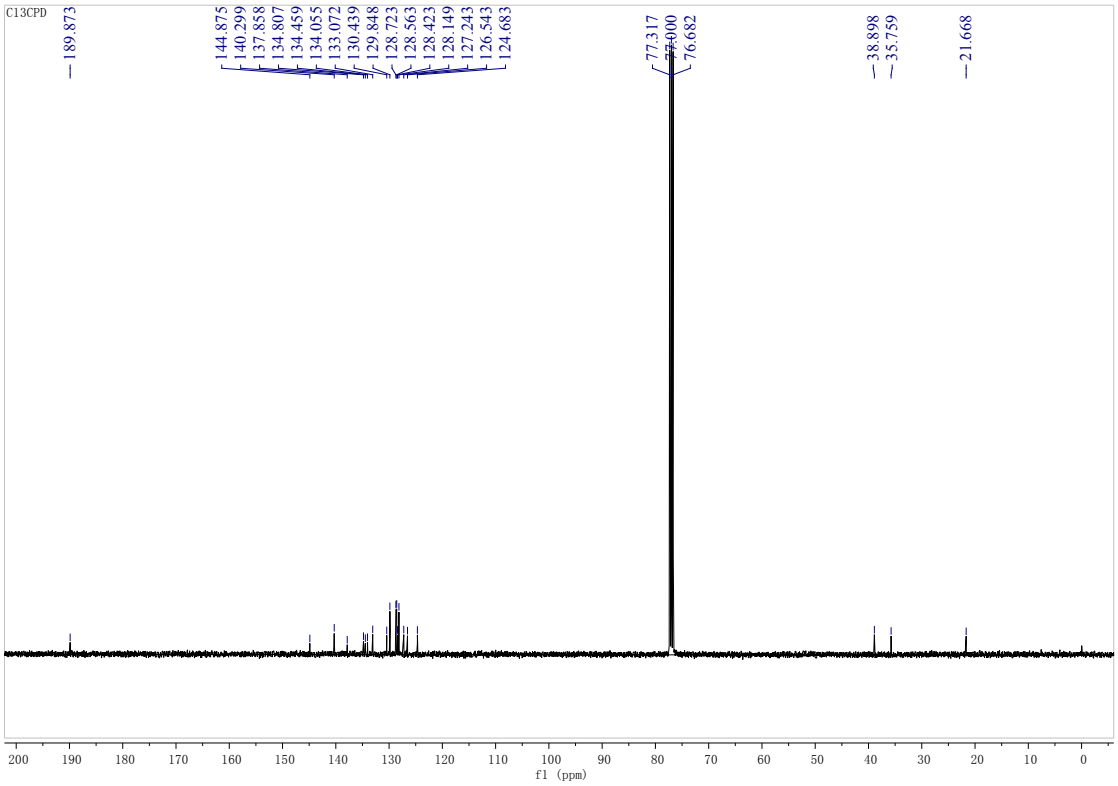

PROTON
8.091
7.867
7.847
7.393
7.390
7.382
7.368
7.310
7.289
7.260
7.241
7.226
7.222
7.209
7.072
5.116
5.110
3.822
3.811
3.804
3.793
2.963
2.945
2.417
2.234
2.223
1.08
2.00
8.22
5.20
3.06
2.13
2.05
1.04
1.04
3.12
1.08
f1 (ppm)

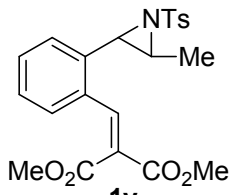

C13CPD
165.328
163.253
144.826
141.106
135.292
134.698
134.521
134.073
132.667
130.115
129.804
128.980
128.618
128.471
128.440
128.370
128.313
128.228
128.134
128.042
127.811
126.656
77.318
77.000
76.682
67.406
67.355
38.794
35.436
21.636
f1 (ppm)


Ts
N
O
Ph

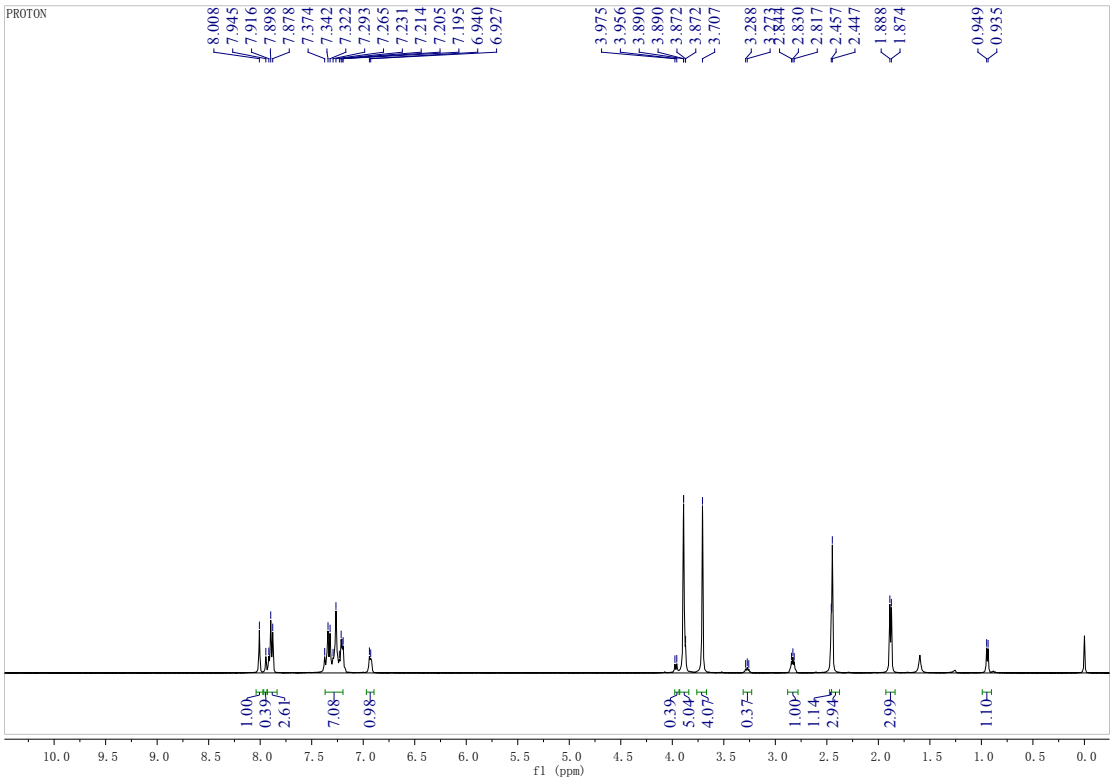
1x

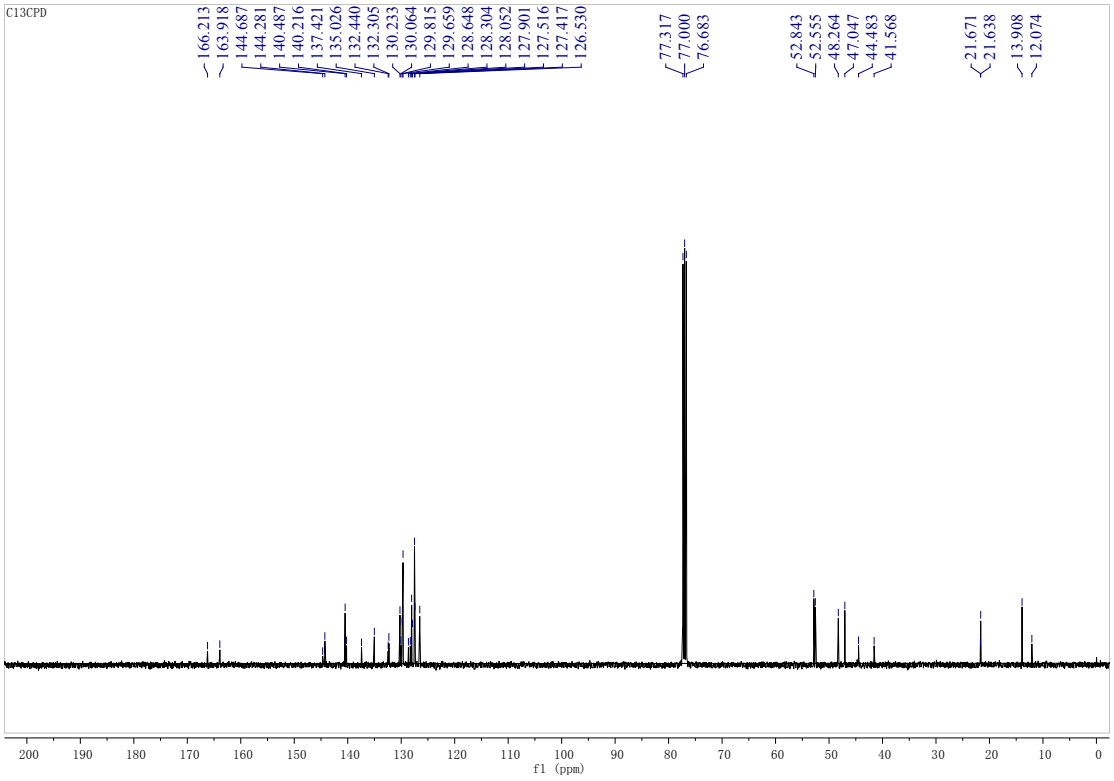

PROTON
8.155
8.117
8.047
8.029
8.026
7.914
7.894
7.692
7.684
7.670
7.635
7.617
7.598
7.548
7.528
7.509
7.470
7.358
7.348
7.338
7.331
7.324
7.315
7.309
7.260
4.020
4.008
4.002
3.990
3.069
3.051
2.432
2.332
2.321
1.575
1.04
1.96
2.00
1.00
0.97
2.97
4.97
1.02
1.07
3.07
1.07
f1 (ppm)

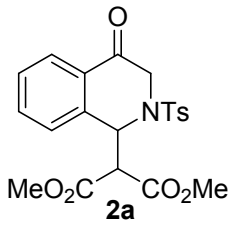

C13CPD
189.873
144.875
140.299
137.858
134.807
134.459
134.055
133.072
130.439
129.848
128.723
128.563
128.423
128.149
127.243
126.543
124.683
77.317
77.000
76.682
38.898
35.759
21.668
f1 (ppm)


NTs
Me
MeO2C
CO2Me

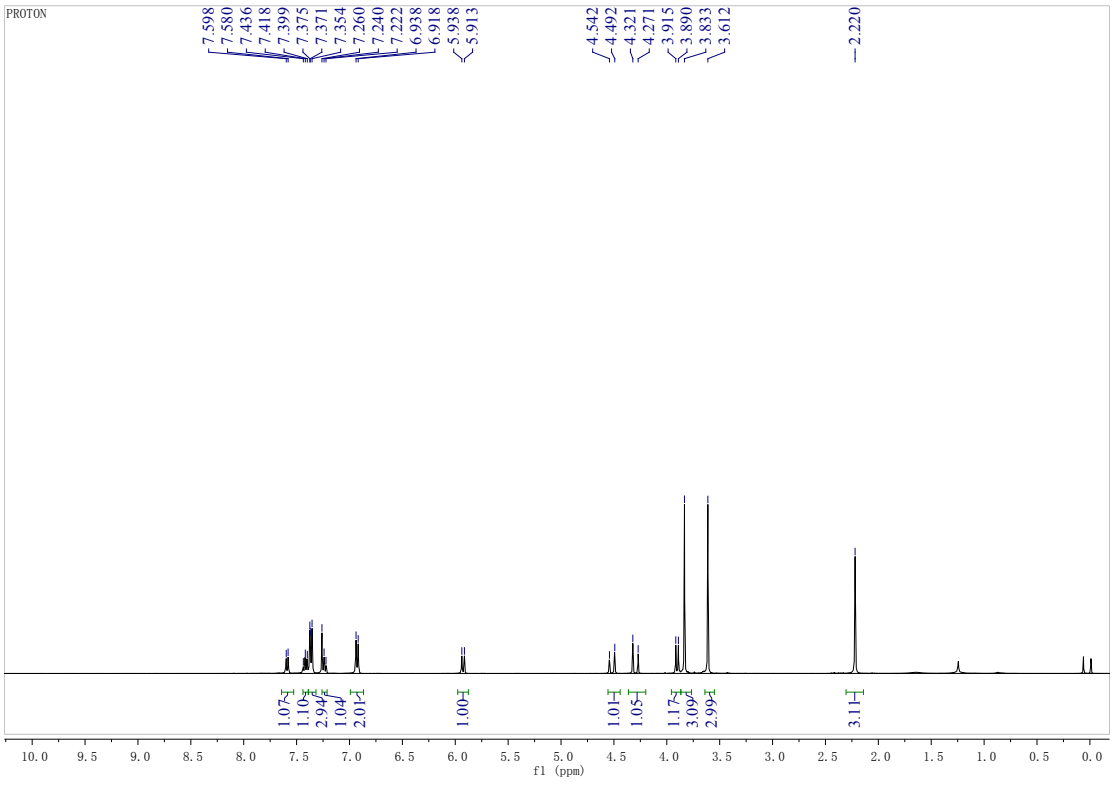
1y

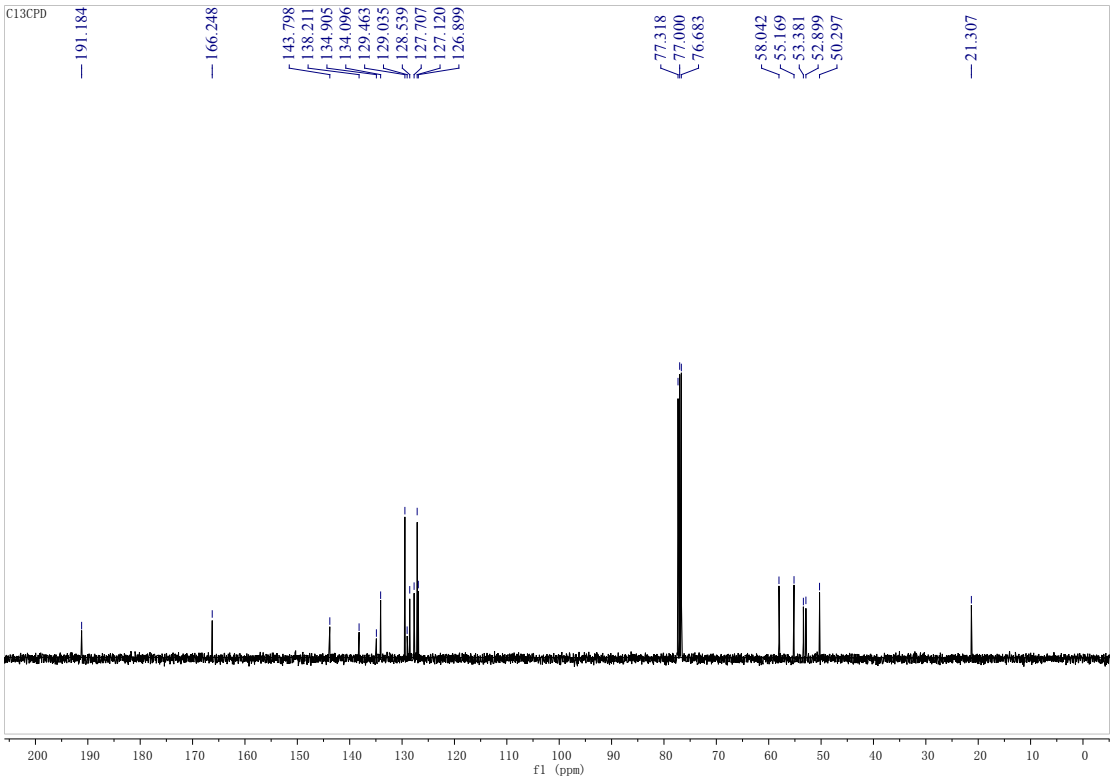

PROTON
8.008
7.945
7.916
7.898
7.878
7.374
7.342
7.322
7.293
7.265
7.231
7.214
7.205
7.195
6.940
6.927
3.975
3.956
3.890
3.890
3.872
3.872
3.707
3.288
3.273
2.844
2.830
2.817
2.457
2.447
1.888
1.874
0.949
0.935
1.00
0.39
2.61
7.08
0.98
0.39
5.04
4.07
0.37
1.00
1.14
2.94
2.99
1.10
f1 (ppm)

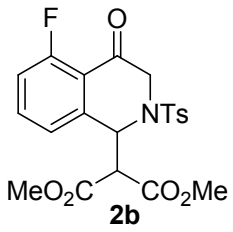

C13CPD
166.213
163.918
144.687
144.281
140.487
140.216
137.421
135.026
132.440
132.305
130.233
130.064
129.815
129.659
128.648
128.304
128.052
127.901
127.516
127.417
126.530
77.317
77.000
76.683
52.843
52.555
48.264
47.047
44.483
41.568
21.671
21.638
13.908
12.074
f1 (ppm)


O
NTs
MeO2C
CO2Me

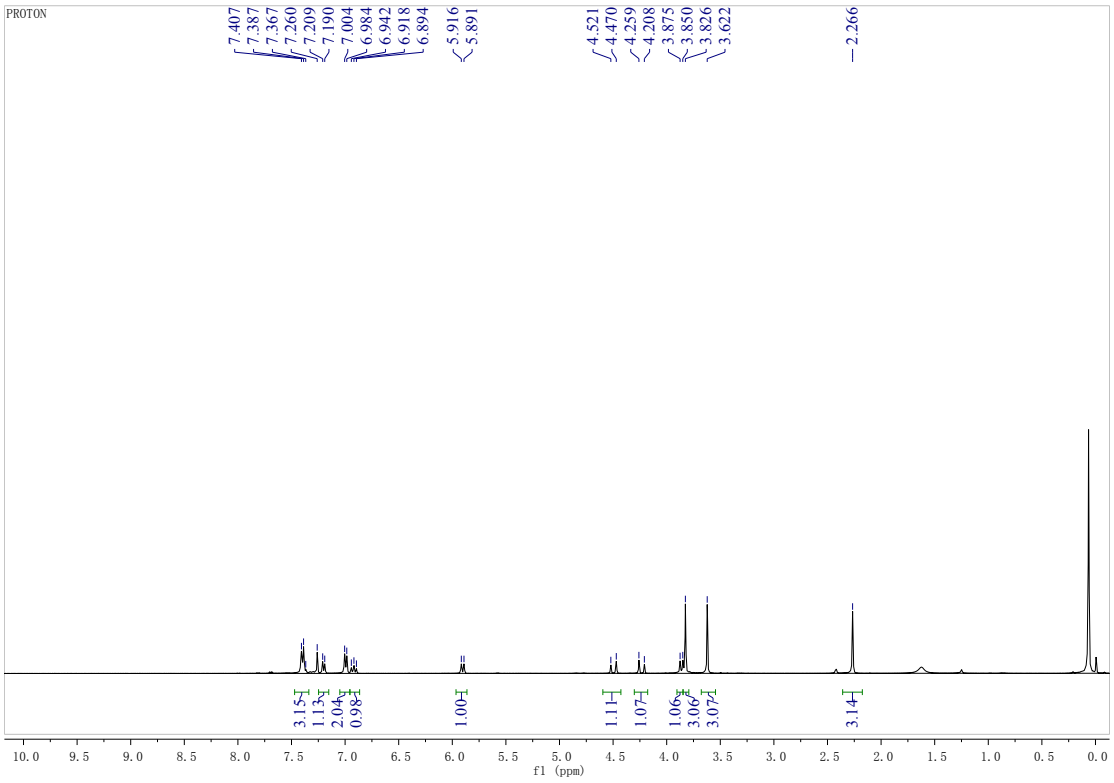
2a

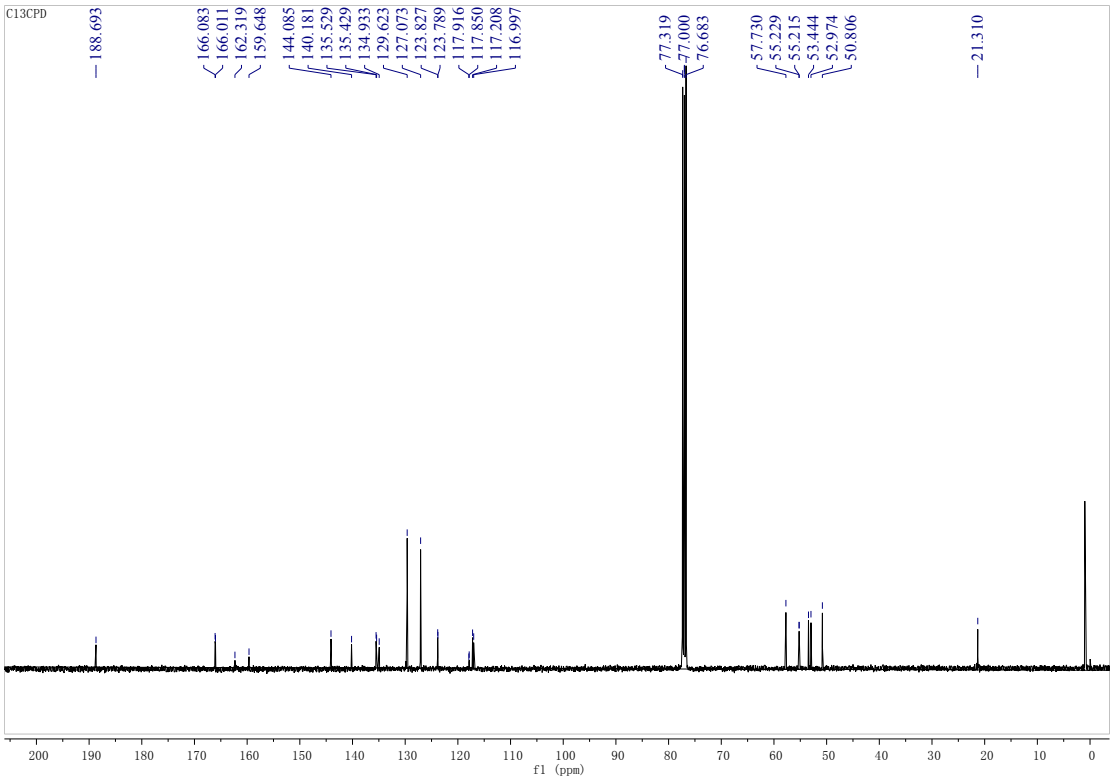

PROTON
7.598
7.580
7.436
7.418
7.399
7.375
7.371
7.354
7.260
7.240
7.222
6.938
6.918
5.938
5.913
4.542
4.492
4.321
4.271
3.915
3.890
3.833
3.612
2.220
1.07
1.10
2.94
1.04
2.01
1.00
1.01
1.05
1.17
3.09
2.99
3.11
f1 (ppm)

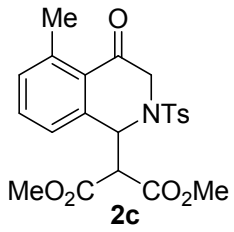

C13CPD
191.184
166.248
143.798
138.211
134.905
134.096
129.463
129.035
128.539
127.707
127.120
126.899
77.318
77.000
76.683
58.042
55.169
53.381
52.899
50.297
21.307
f1 (ppm)


F
O
NTs
MeO2C
CO2Me

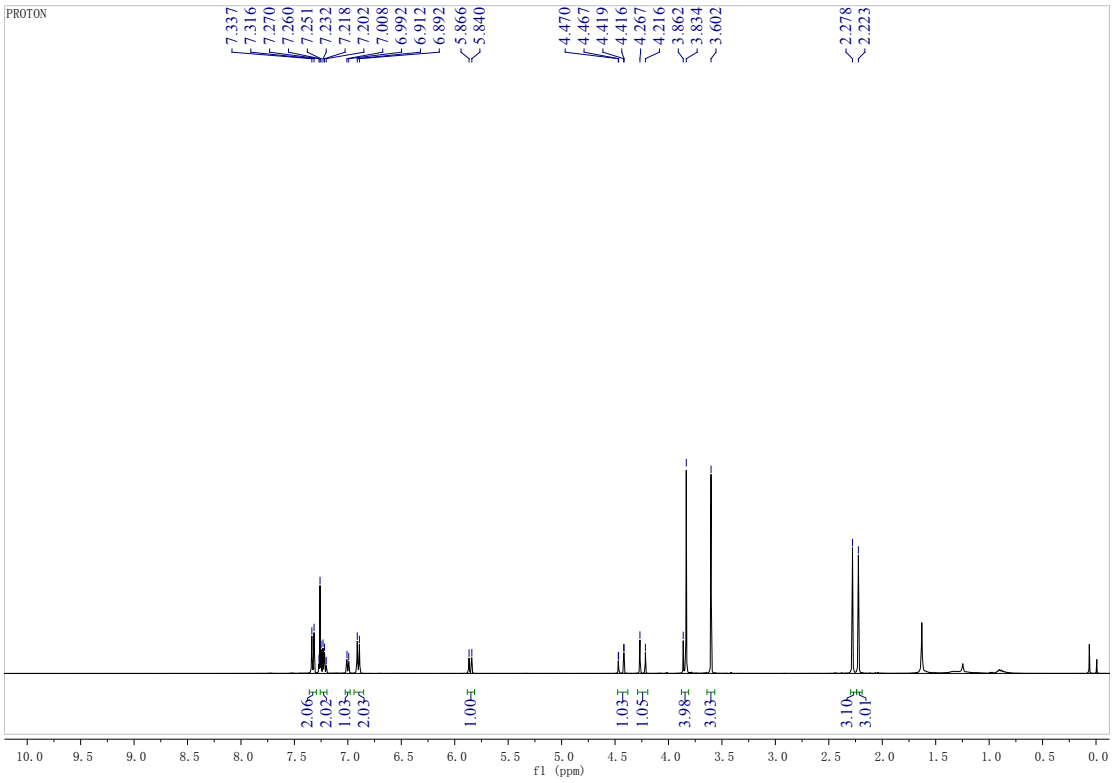
2b

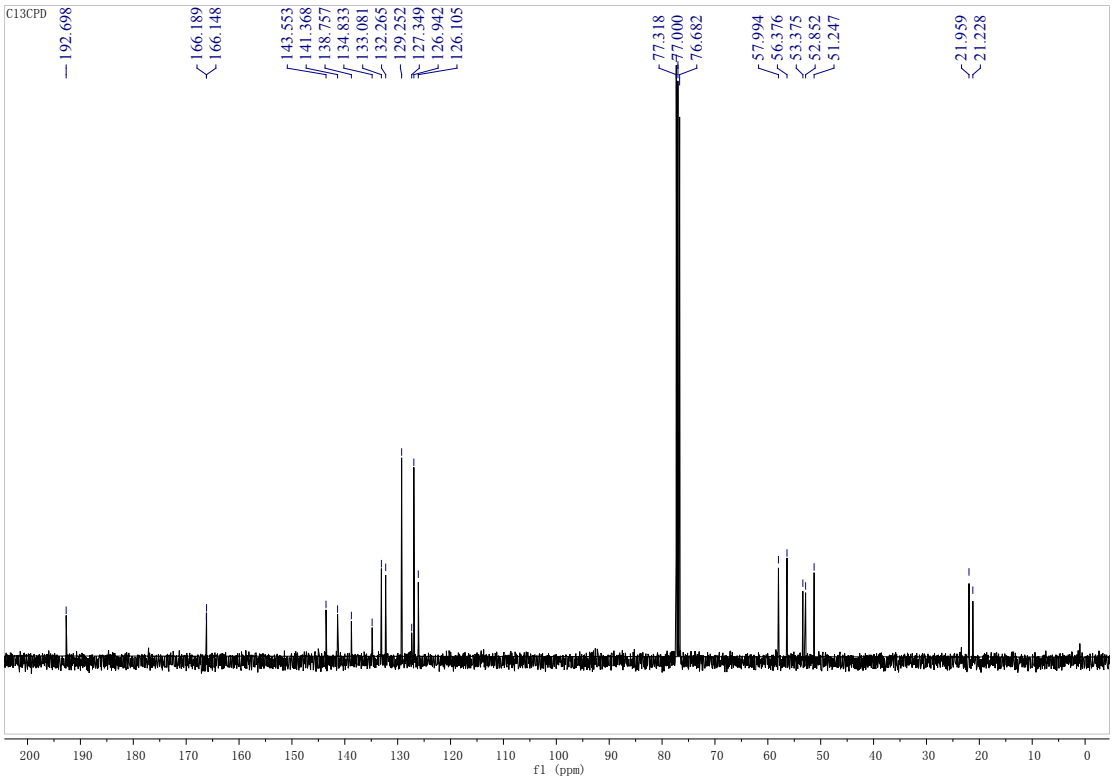

PROTON
7.407
7.387
7.367
7.260
7.209
7.190
7.004
6.984
6.942
6.918
6.894
5.916
5.891
4.521
4.470
4.259
4.208
3.875
3.850
3.826
3.622
2.266
3.15
1.13
2.04
0.98
1.00
1.11
1.07
1.06
3.06
3.07
3.14
f1 (ppm)

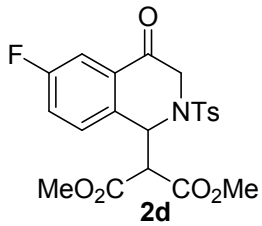

C13CPD
188.693
166.083
166.011
162.319
159.648
144.085
140.181
135.529
135.429
134.933
129.623
127.073
123.827
123.789
117.916
117.850
117.208
116.997
77.319
77.000
76.683
57.730
55.229
55.215
53.444
52.974
50.806
21.310
f1 (ppm)


Me
O
NTs
MeO2C
CO2Me

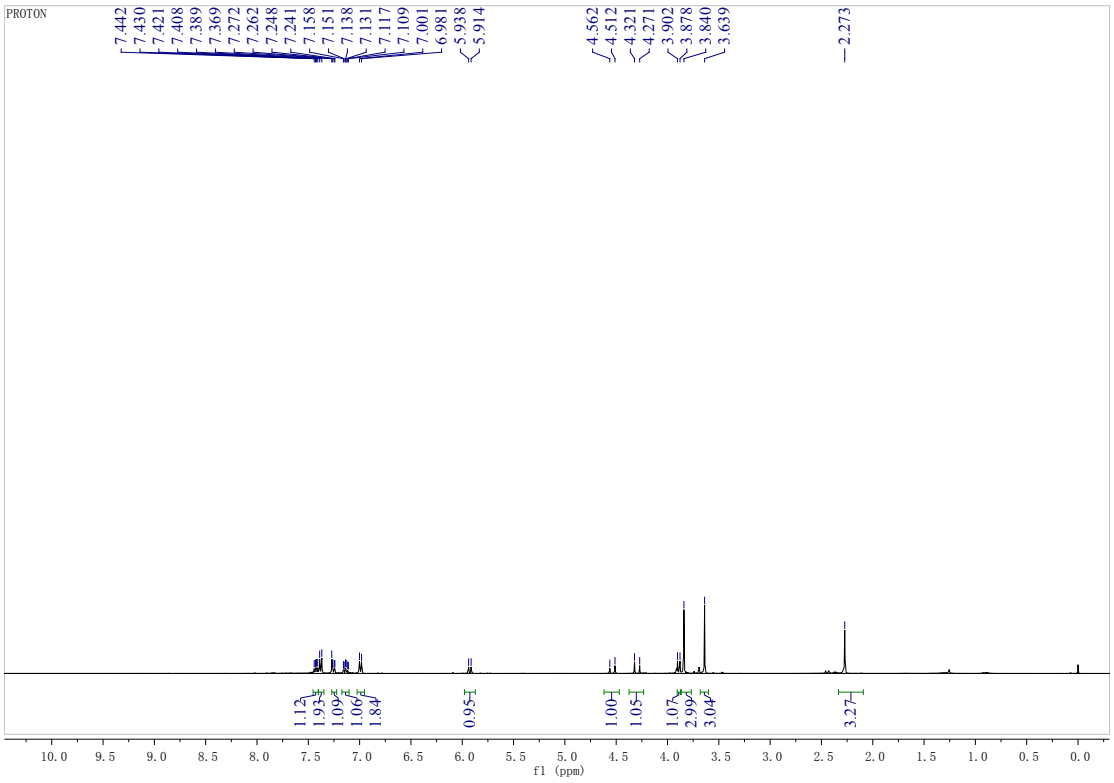
2c

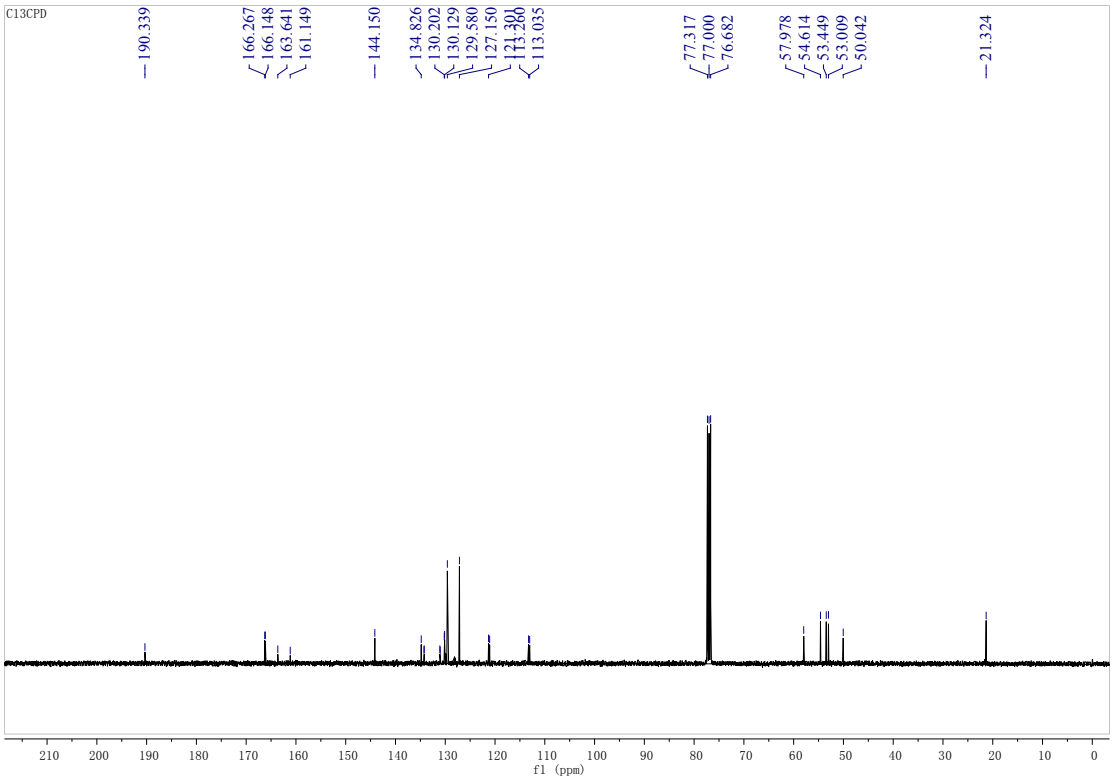

PROTON
7.337
7.316
7.270
7.260
7.251
7.232
7.218
7.202
7.008
6.992
6.912
6.892
5.866
5.840
4.470
4.467
4.419
4.416
4.267
4.216
3.862
3.834
3.602
2.278
2.223
2.06
2.02
1.03
2.03
1.00
1.03
1.05
3.98
3.03
3.10
3.01
f1 (ppm)

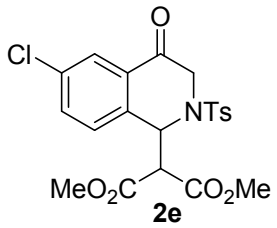

C13CPD
192.698
166.189
166.148
143.553
141.368
138.757
134.833
133.081
132.265
129.252
127.349
126.942
126.105
77.318
77.000
76.682
57.994
56.376
53.375
52.852
51.247
21.959
21.228
f1 (ppm)


O
F
NTs
MeO2C
CO2Me

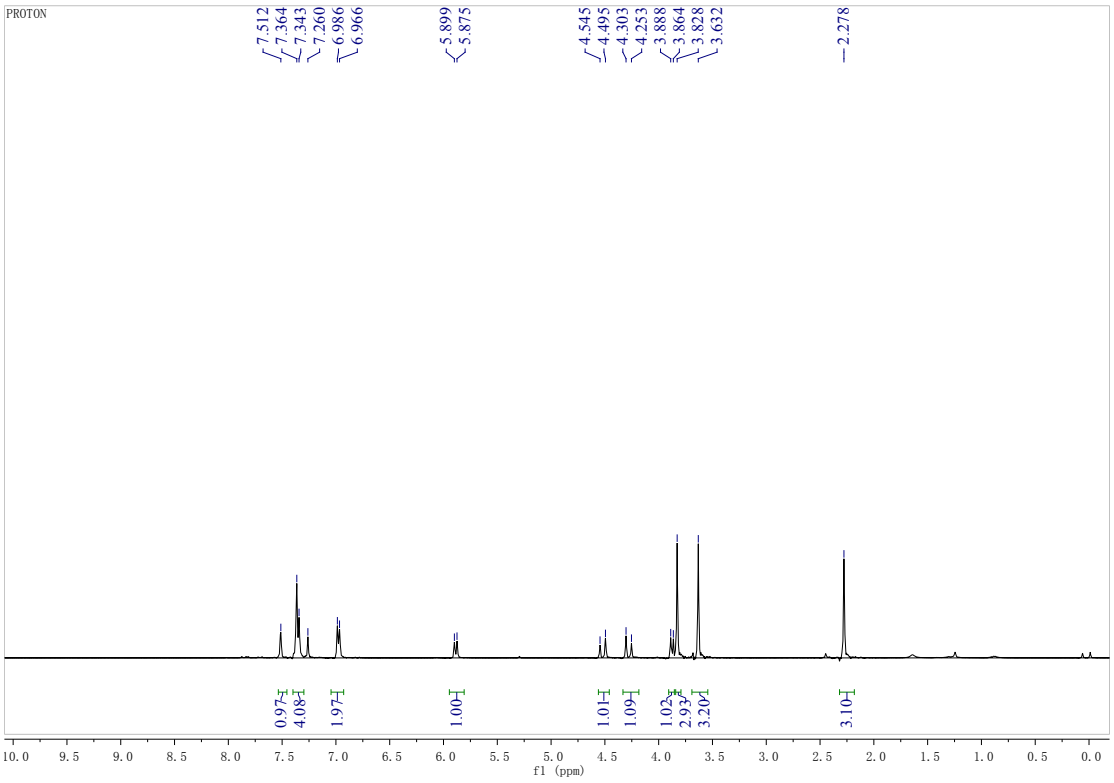
2d

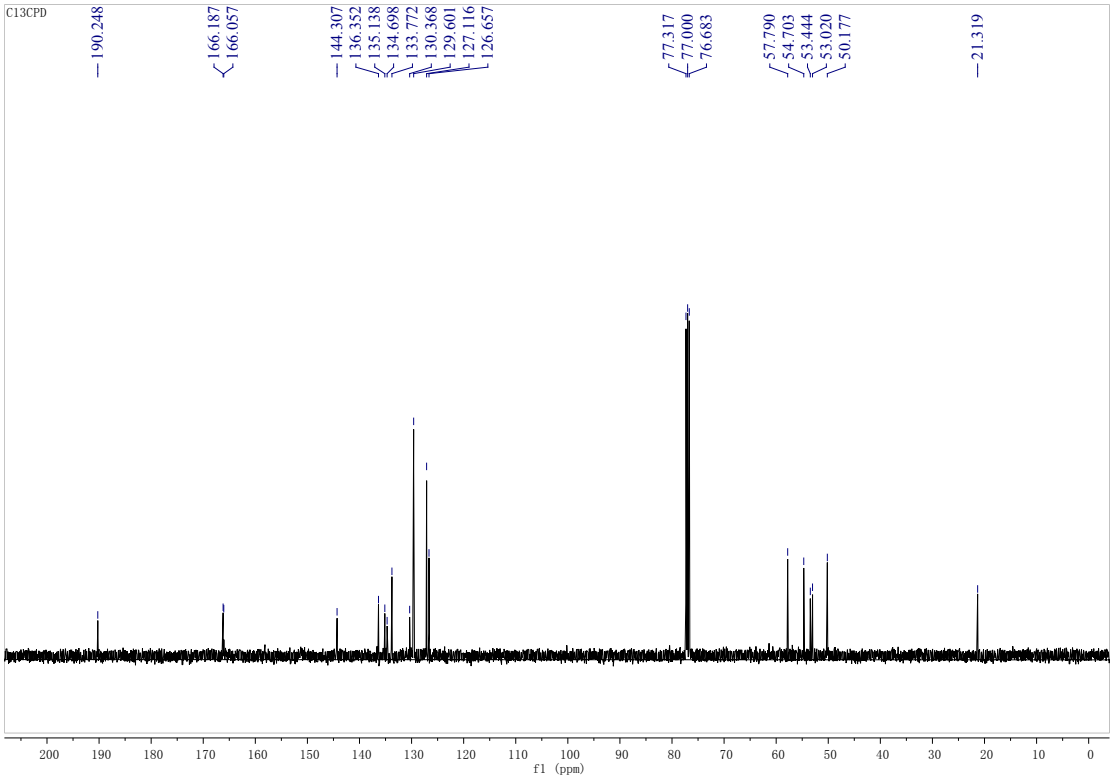

PROTON
7.442
7.430
7.421
7.408
7.389
7.369
7.272
7.262
7.248
7.241
7.158
7.151
7.138
7.131
7.117
7.109
7.001
6.981
5.938
5.914
4.562
4.512
4.321
4.271
3.902
3.878
3.840
3.639
2.273
1.12
1.93
1.09
1.06
1.84
0.95
1.00
1.05
1.07
2.99
3.04
3.27
f1 (ppm)

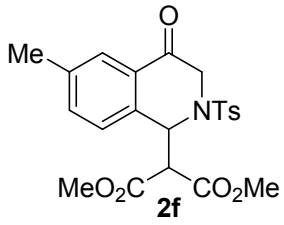

C13CPD
190.339
166.267
166.148
163.641
161.149
144.150
134.826
130.202
130.129
129.580
127.150
113.035
77.317
77.000
76.682
57.978
54.614
53.449
53.009
50.042
21.324
f1 (ppm)


O
Cl
NTs
MeO2C
CO2Me

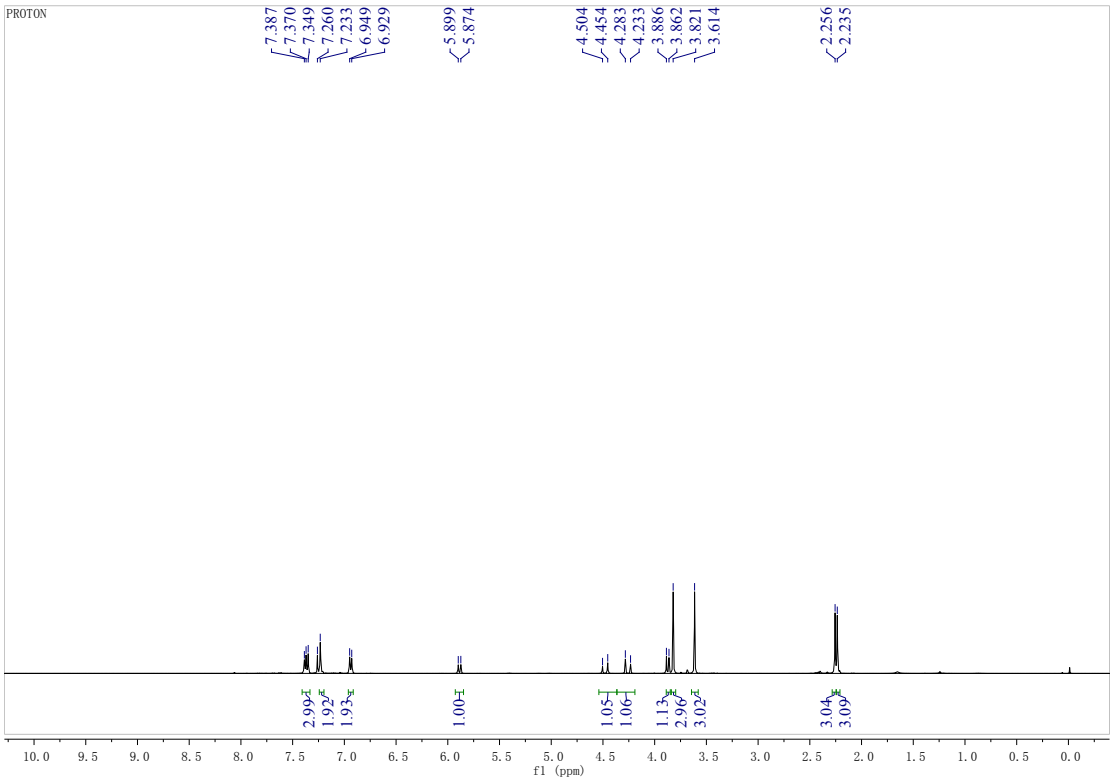
2e

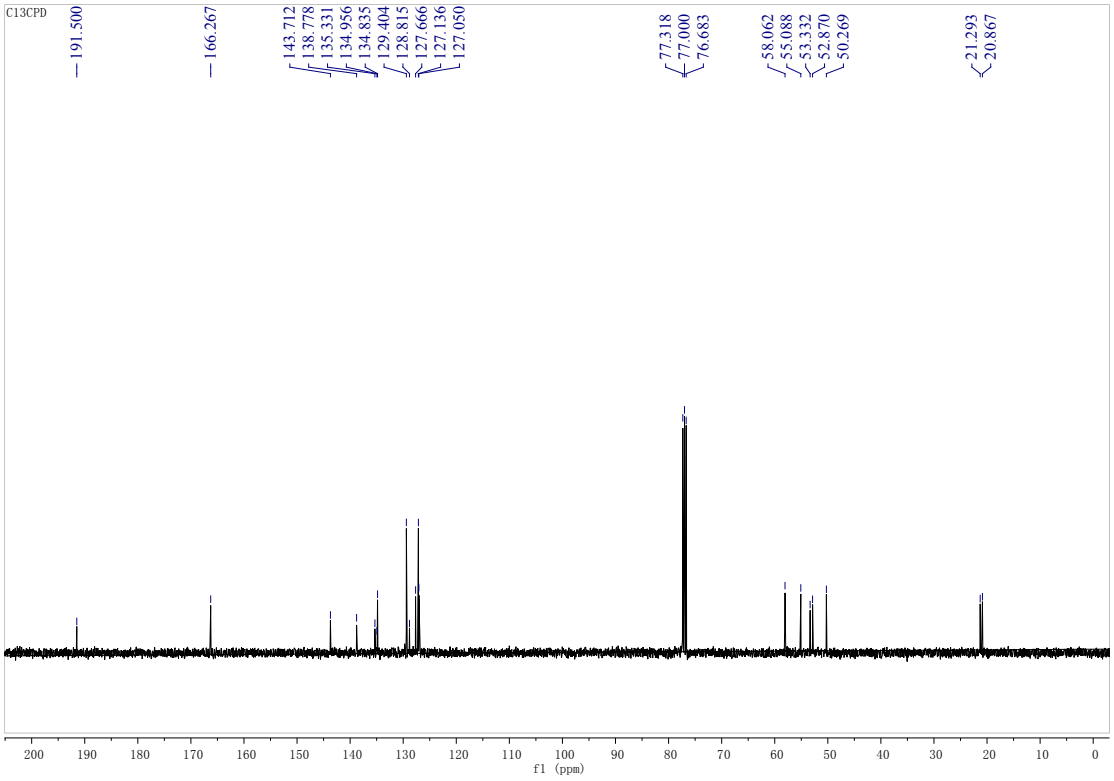

PROTON
7.512
7.364
7.343
7.260
6.986
6.966
5.899
5.875
4.545
4.495
4.303
4.253
3.888
3.864
3.828
3.632
2.278
0.97
4.08
1.97
1.00
1.01
1.09
1.02
2.93
3.20
3.10
f1 (ppm)

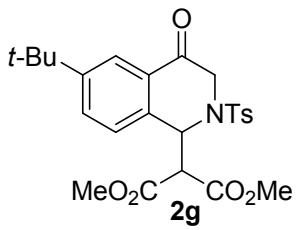

C13CPD
190.248
166.187
166.057
144.307
136.352
135.138
134.698
133.772
130.368
129.601
127.116
126.657
77.317
77.000
76.683
57.790
54.703
53.444
53.020
50.177
21.319
f1 (ppm)


O
Me
NTs
MeO2C
CO2Me

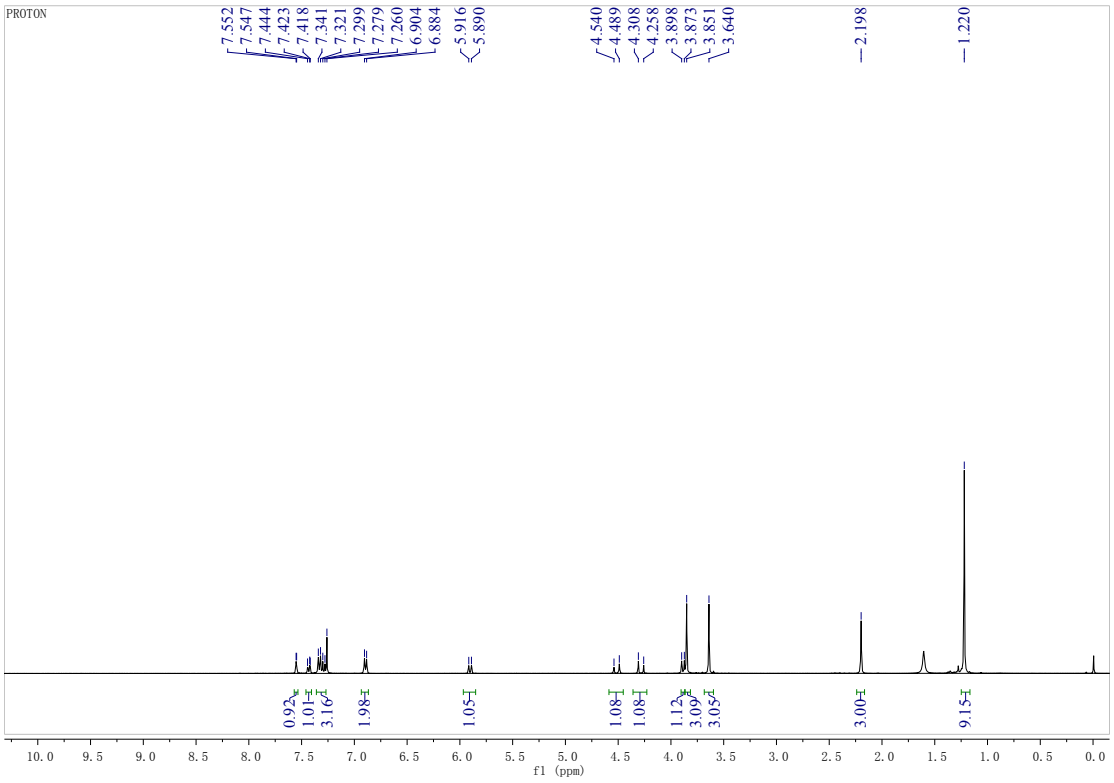
2f

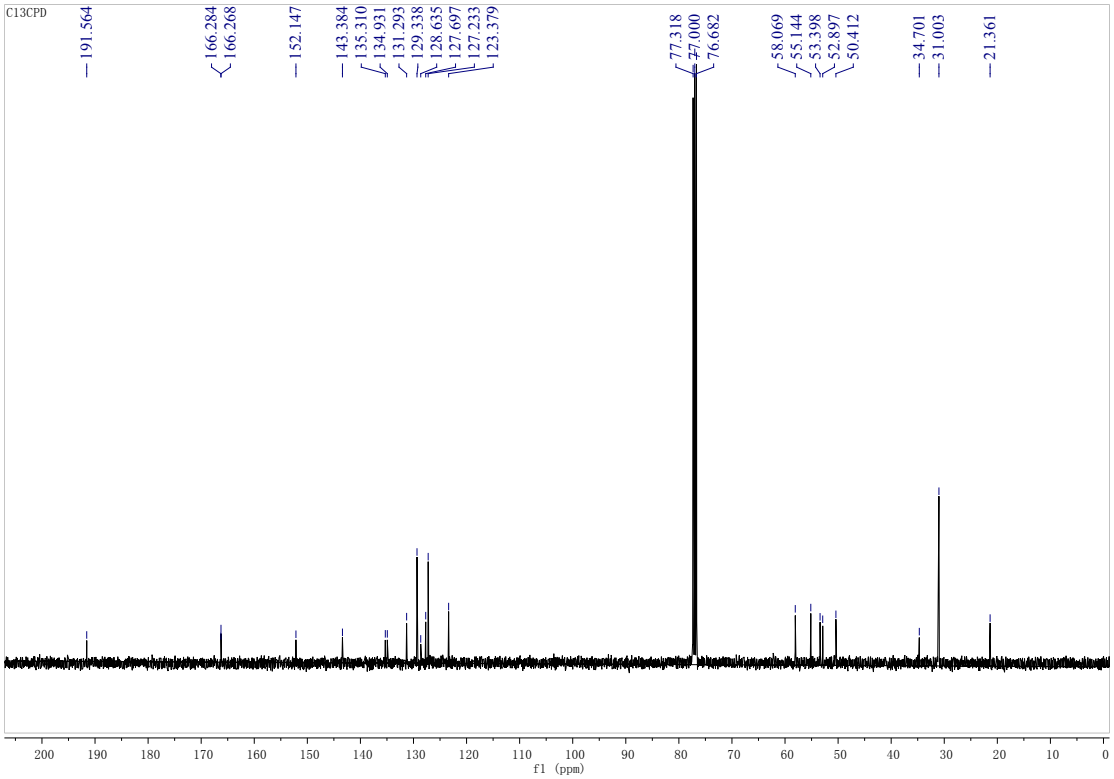

PROTON
7.387
7.370
7.349
7.260
7.233
6.949
6.929
5.899
5.874
4.504
4.454
4.283
4.233
3.886
3.862
3.821
3.614
2.256
2.235
2.99
1.92
1.93
1.00
1.05
1.06
1.13
2.96
3.02
3.04
3.09
f1 (ppm)

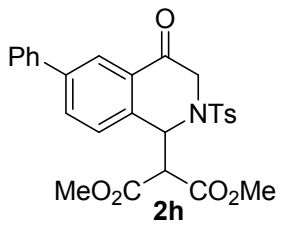

C13CPD
191.500
166.267
143.712
138.778
135.331
134.956
134.835
129.404
128.815
127.666
127.136
127.050
77.318
77.000
76.683
58.062
55.088
53.332
52.870
50.269
21.293
20.867
f1 (ppm)


O
t-Bu
NTs
MeO2C
CO2Me

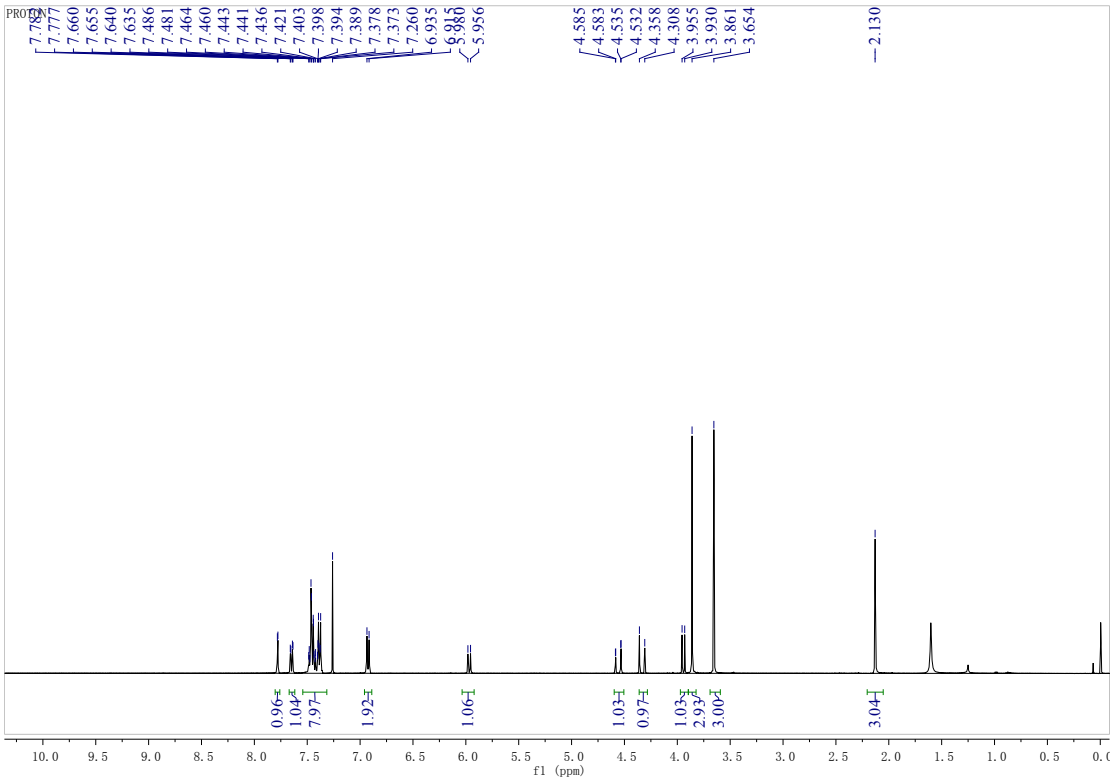
2g

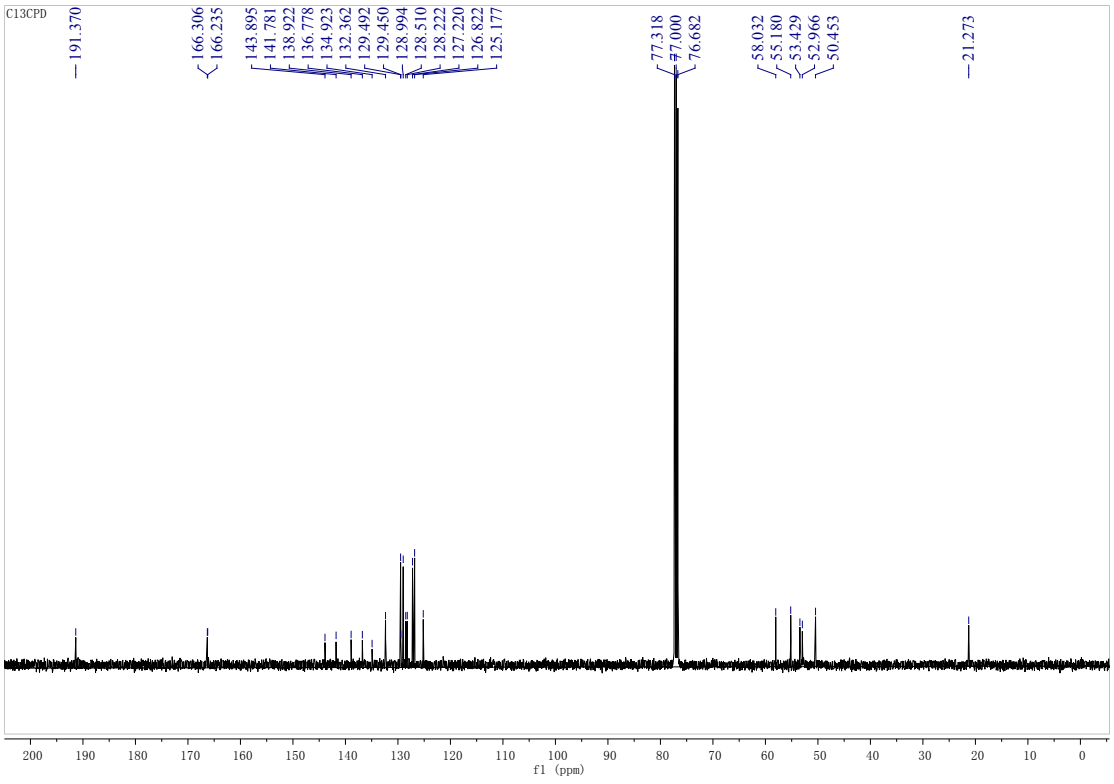

PROTON
7.552
7.547
7.444
7.423
7.418
7.341
7.321
7.299
7.279
7.260
6.904
6.884
5.916
5.890
4.540
4.489
4.308
4.258
3.898
3.873
3.851
3.640
2.198
1.220
0.92
1.01
3.16
1.98
1.05
1.08
1.08
1.12
3.09
3.05
3.00
9.15
f1 (ppm)

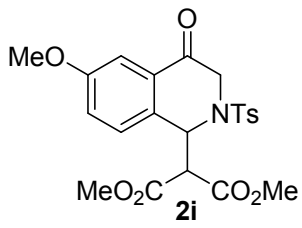

C13CPD
191.564
166.284
166.268
152.147
143.384
135.310
134.931
131.293
129.338
128.635
127.697
127.233
123.379
77.318
77.000
76.682
58.069
55.144
53.398
52.897
50.412
34.701
31.003
21.361
f1 (ppm)


O
Ph
NTs
MeO2C
CO2Me

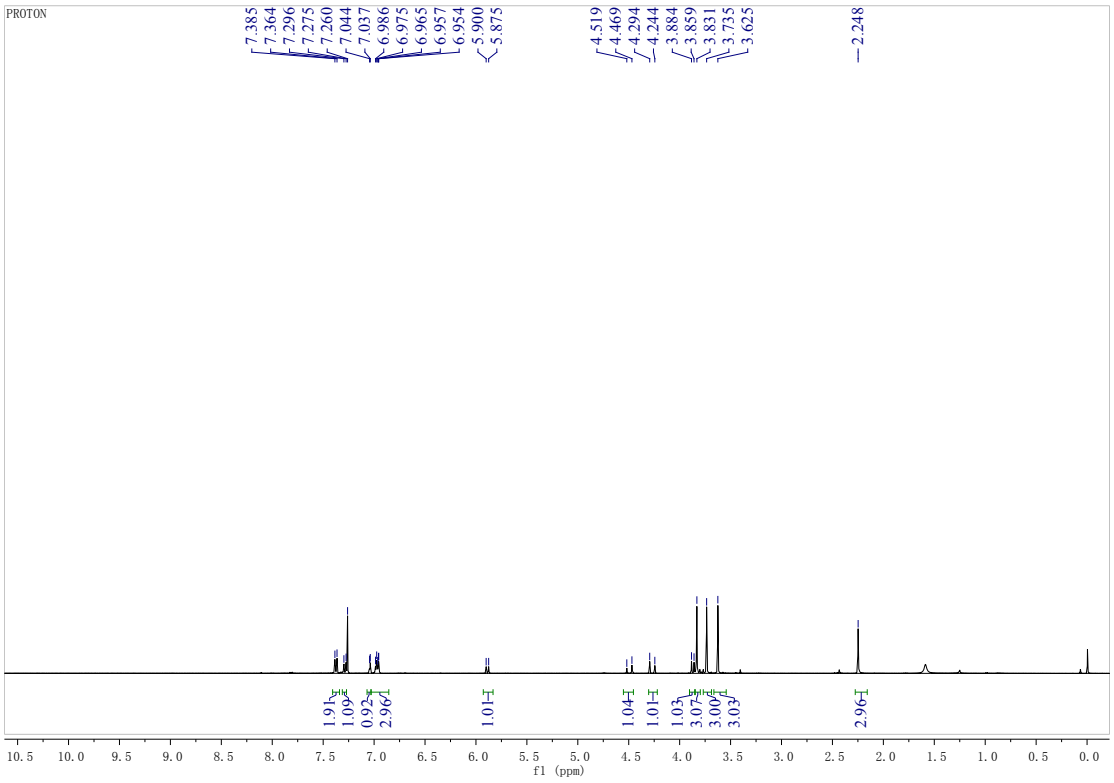
2h

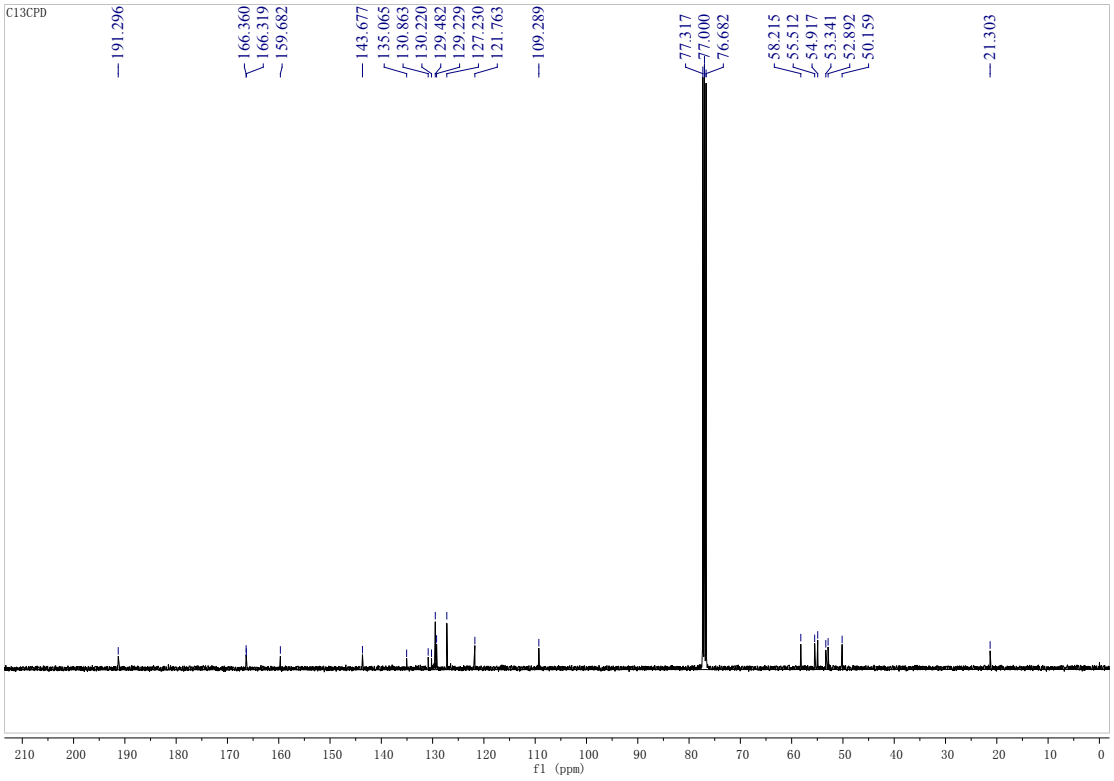

PROTON
7.782
7.777
7.660
7.655
7.640
7.635
7.486
7.481
7.464
7.460
7.443
7.441
7.436
7.421
7.403
7.398
7.394
7.389
7.378
7.373
7.260
6.935
6.915
5.956
4.585
4.583
4.535
4.532
4.358
4.308
3.955
3.930
3.861
3.654
2.130
0.96
1.04
7.97
1.92
1.06
1.03
0.97
1.03
2.93
3.00
3.04
f1 (ppm)

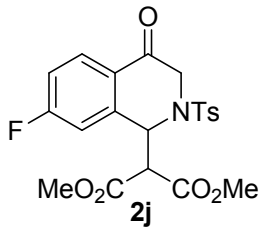

C13CPD
191.370
166.306
166.235
143.895
141.781
138.922
136.778
134.923
132.362
129.492
129.450
128.994
128.510
128.222
127.220
126.822
125.177
77.318
77.000
76.682
58.032
55.180
53.429
52.966
50.453
21.273
f1 (ppm)


O
MeO
NTs
MeO2C
CO2Me

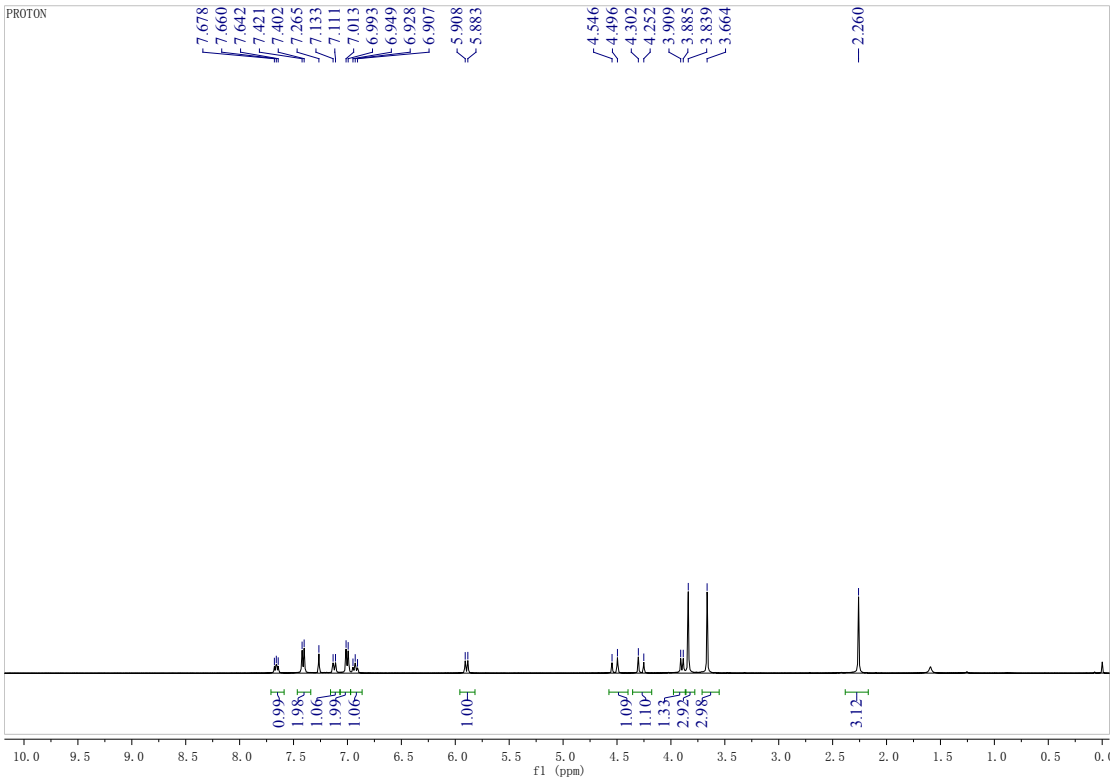
2i

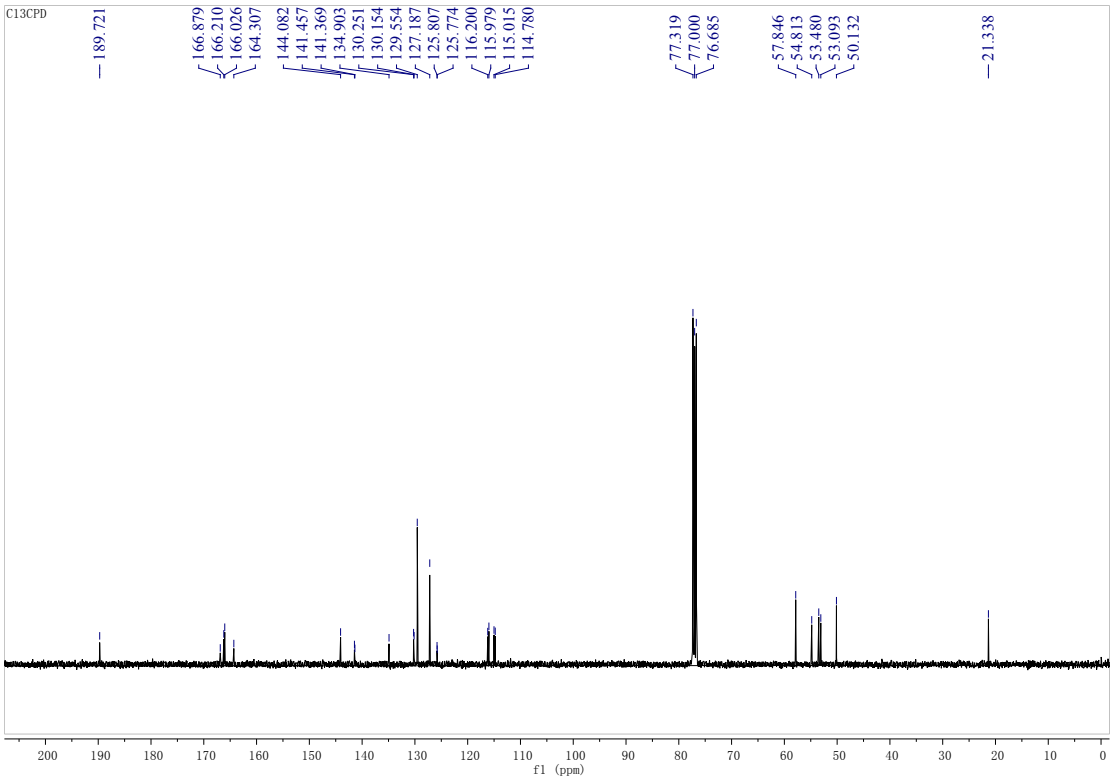

PROTON
7.385
7.364
7.296
7.275
7.260
7.044
7.037
6.986
6.975
6.965
6.957
6.954
5.900
5.875
4.519
4.469
4.294
4.244
3.884
3.859
3.831
3.735
3.625
2.248
1.91
1.09
0.92
2.96
1.01
1.04
1.01
1.03
3.07
3.00
3.03
2.96
f1 (ppm)

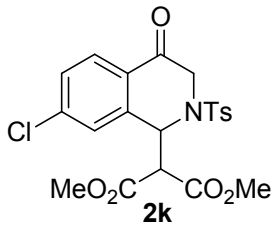

C13CPD
191.296
166.360
166.319
159.682
143.677
135.065
130.863
130.220
129.482
129.229
127.230
121.763
109.289
77.317
77.000
76.682
58.215
55.512
54.917
53.341
52.892
50.159
21.303
f1 (ppm)


O
NTs
F
MeO2C
CO2Me

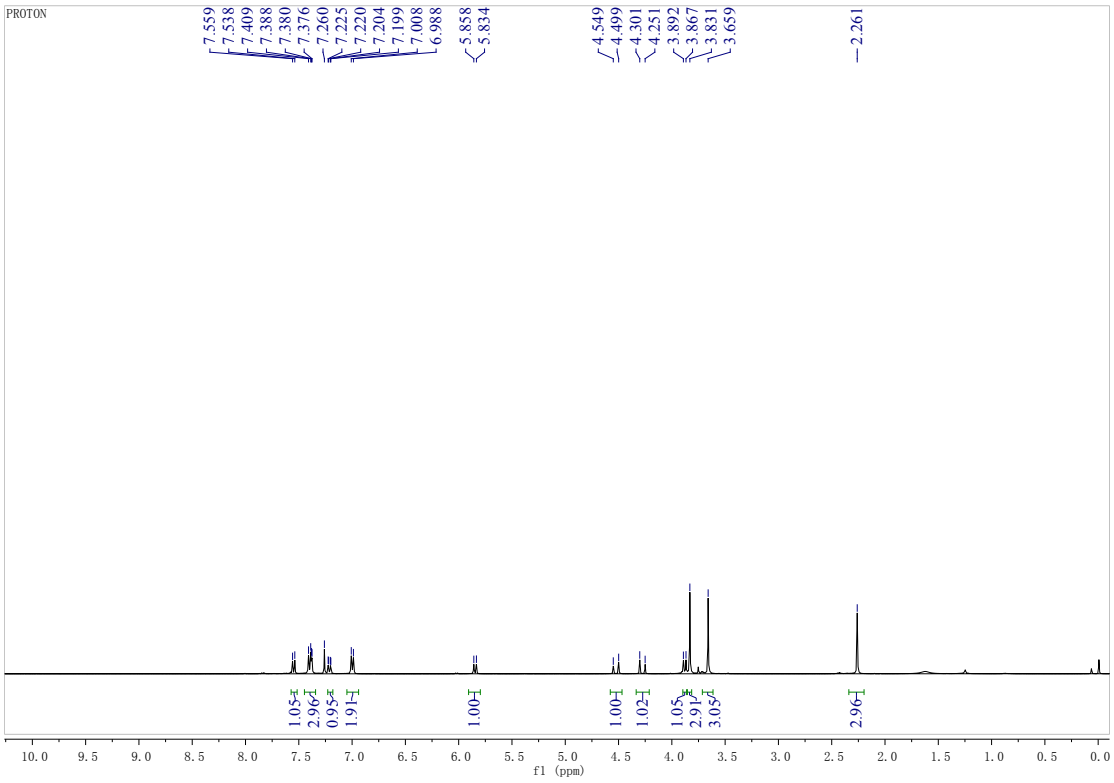
2j

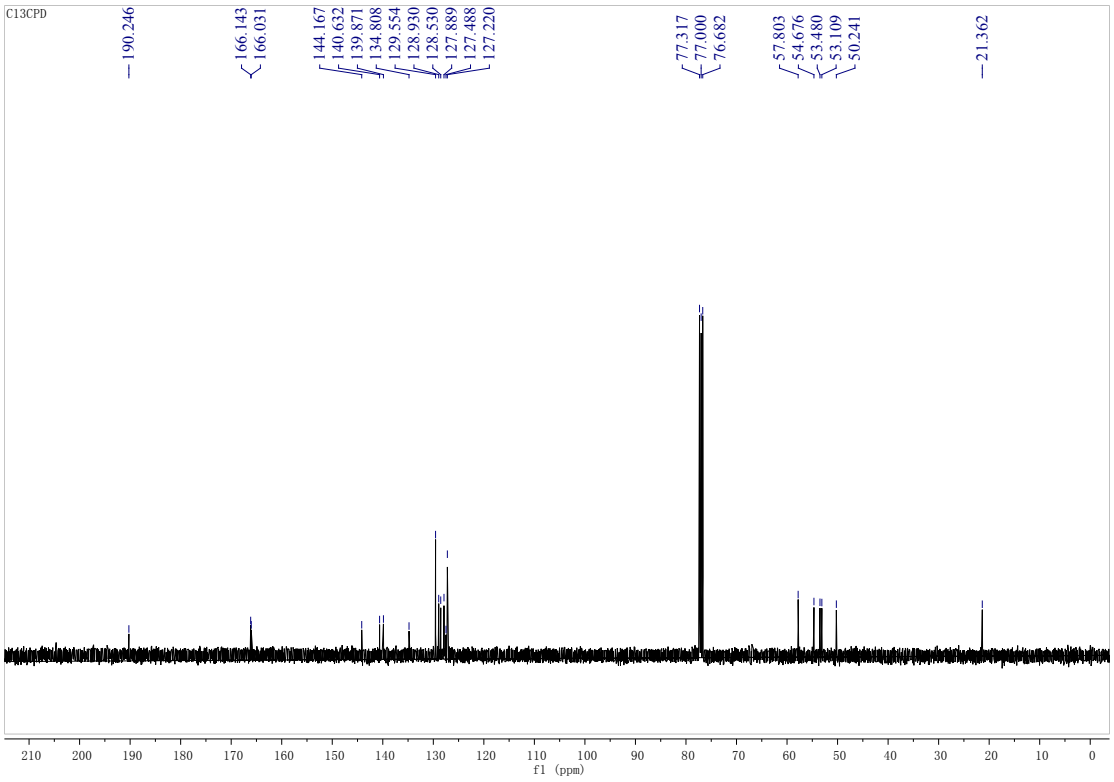

PROTON
7.678
7.660
7.642
7.421
7.402
7.265
7.133
7.111
7.013
6.993
6.949
6.928
6.907
5.908
5.883
4.546
4.496
4.302
4.252
3.909
3.885
3.839
3.664
2.260
0.99
1.98
1.06
1.99
1.06
1.00
1.09
1.10
1.33
2.92
2.98
3.12
f1 (ppm)

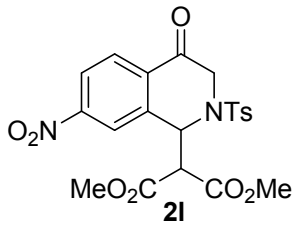

C13CPD
189.721
166.879
166.210
166.026
164.307
144.082
141.457
141.369
134.903
130.251
130.154
129.554
127.187
125.807
125.774
116.200
115.979
115.015
114.780
77.319
77.000
76.685
57.846
54.813
53.480
53.093
50.132
21.338
f1 (ppm)


O
NTs
Cl
MeO2C
CO2Me

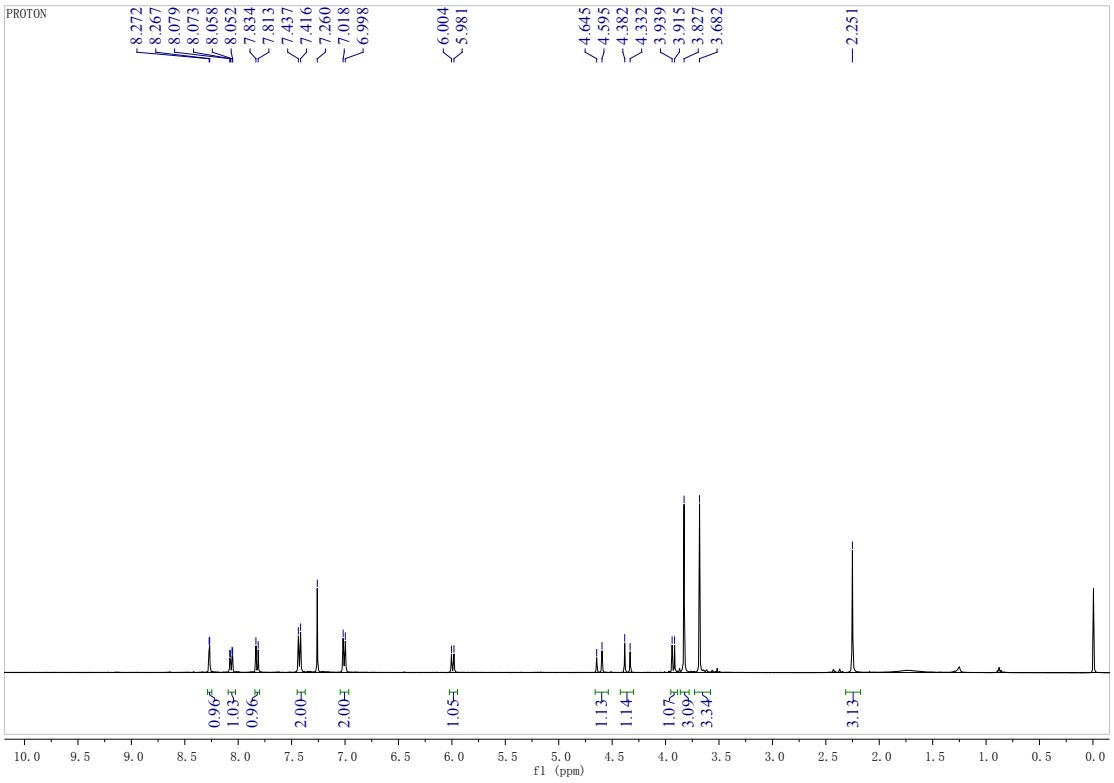
2k

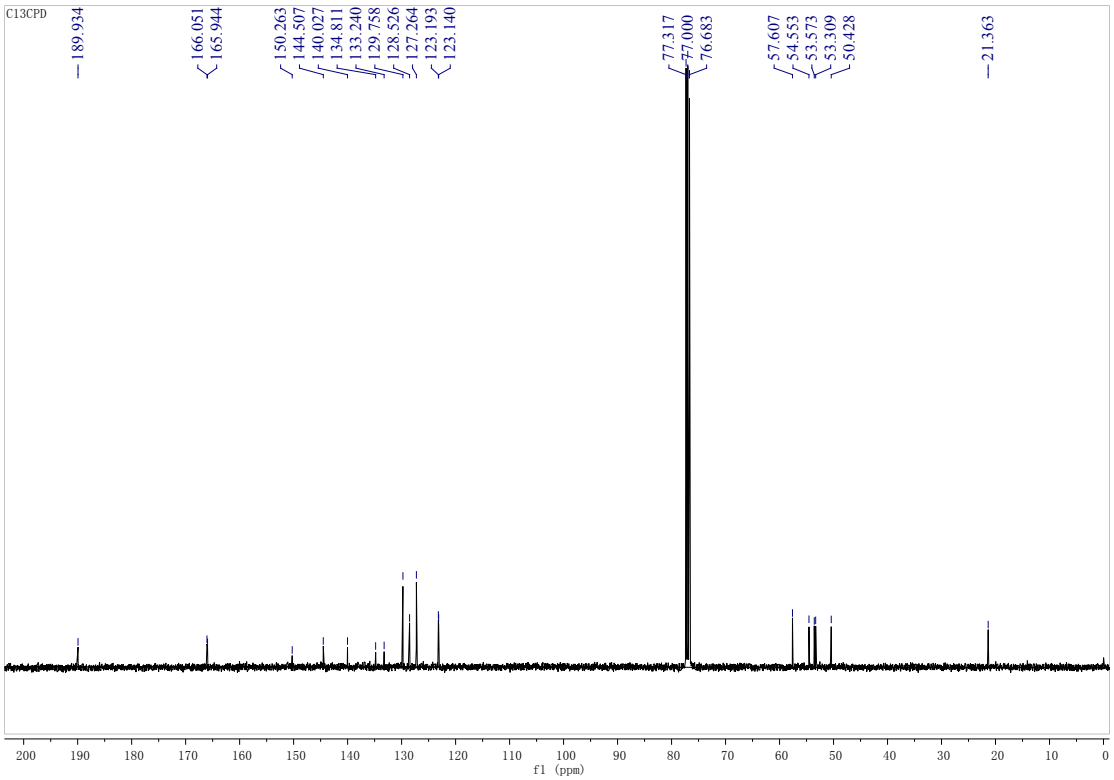

PROTON
7.559
7.538
7.409
7.388
7.380
7.376
7.260
7.225
7.220
7.204
7.199
7.008
6.988
5.858
5.834
4.549
4.499
4.301
4.251
3.892
3.867
3.831
3.659
2.261
1.05
2.96
0.95
1.91
1.00
1.00
1.02
1.05
2.91
3.05
2.96
f1 (ppm)

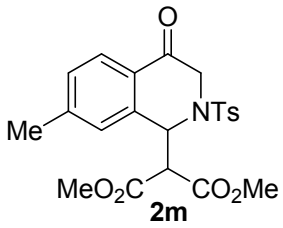

C13CPD
190.246
166.143
166.031
144.167
140.632
139.871
134.808
129.554
128.930
128.530
127.889
127.488
127.220
77.317
77.000
76.682
57.803
54.676
53.480
53.109
50.241
21.362
f1 (ppm)


O
NTs
O_2N
MeO_2C
CO_2Me

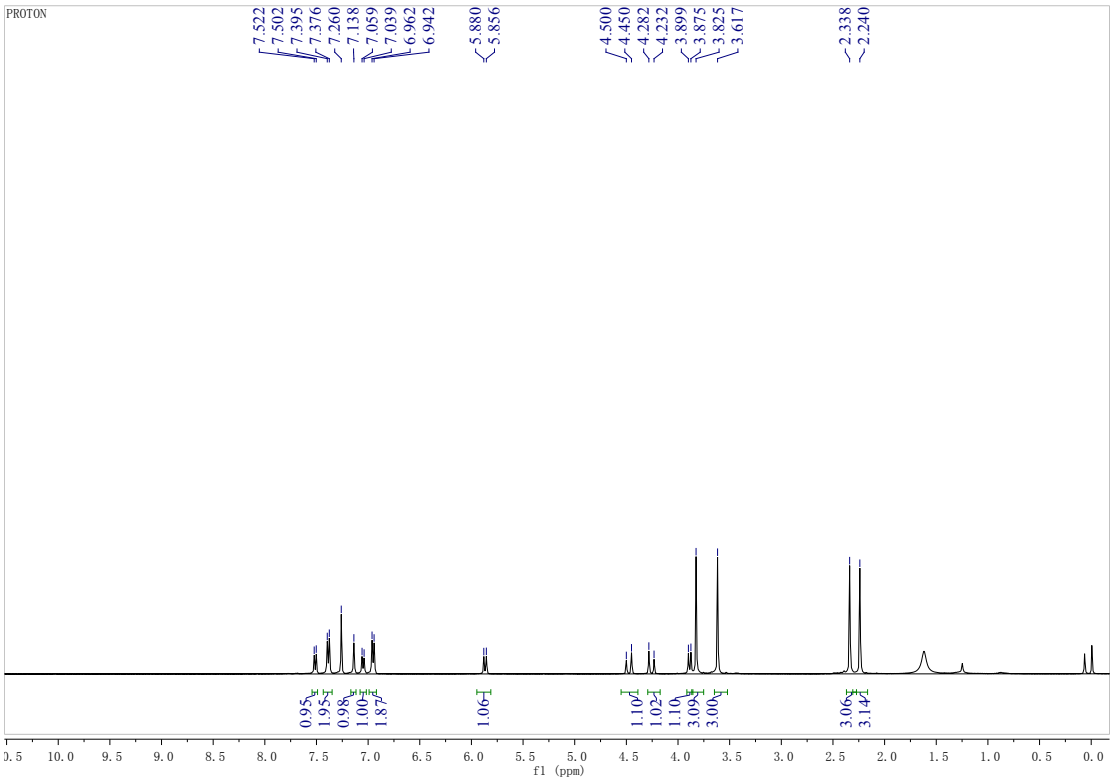
2l

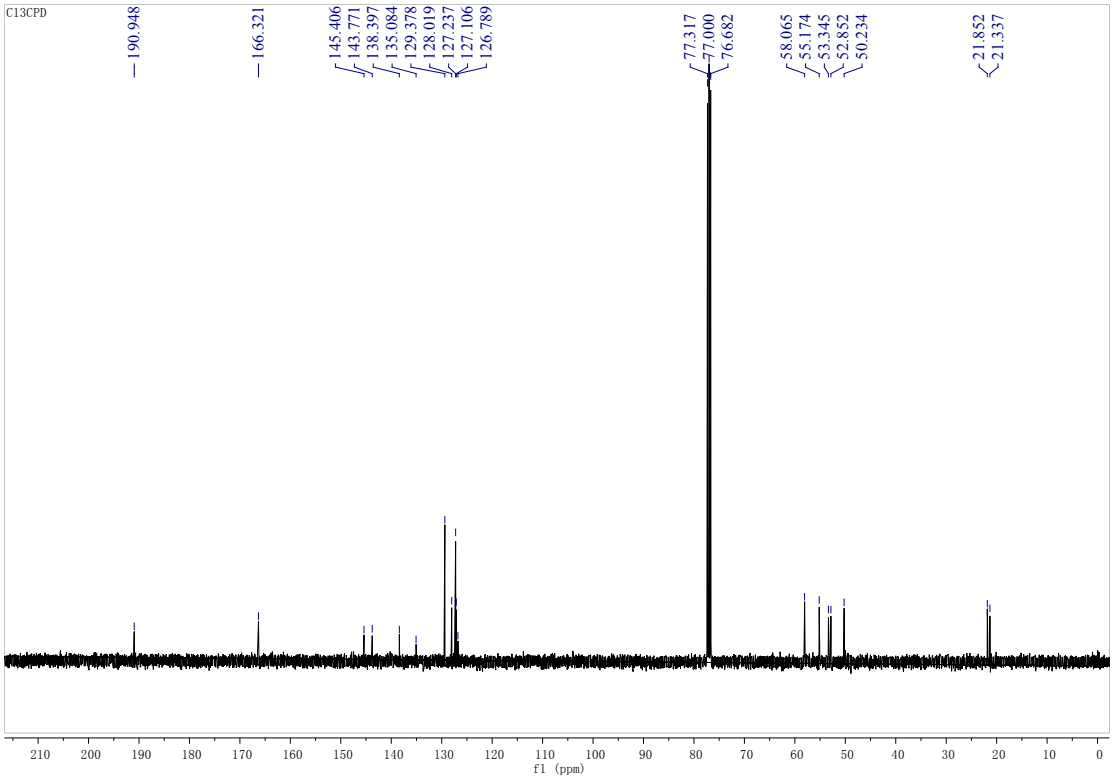

PROTON
8.272
8.267
8.079
8.073
8.058
8.052
7.834
7.813
7.437
7.416
7.260
7.018
6.998
6.004
5.981
4.645
4.595
4.382
4.332
3.939
3.915
3.827
3.682
2.251
0.96
1.03
0.96
2.00
2.00
1.05
1.13
1.14
1.07
3.09
3.34
3.13
f1 (ppm)

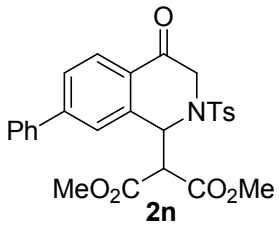

C13CPD
189.934
166.051
165.944
150.263
144.507
140.027
134.811
133.240
129.758
128.526
127.264
123.193
123.140
77.317
77.000
76.683
57.607
54.553
53.573
53.309
50.428
21.363
f1 (ppm)


O
NTs
Me
MeO2C
CO2Me

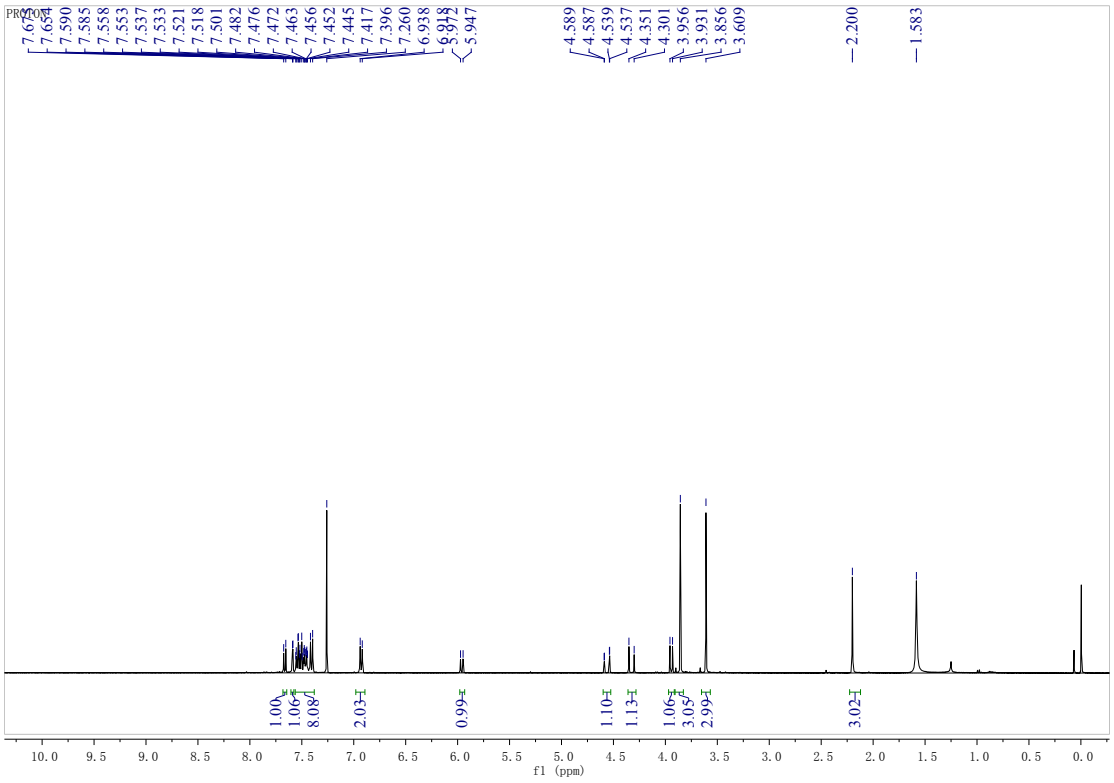
2m

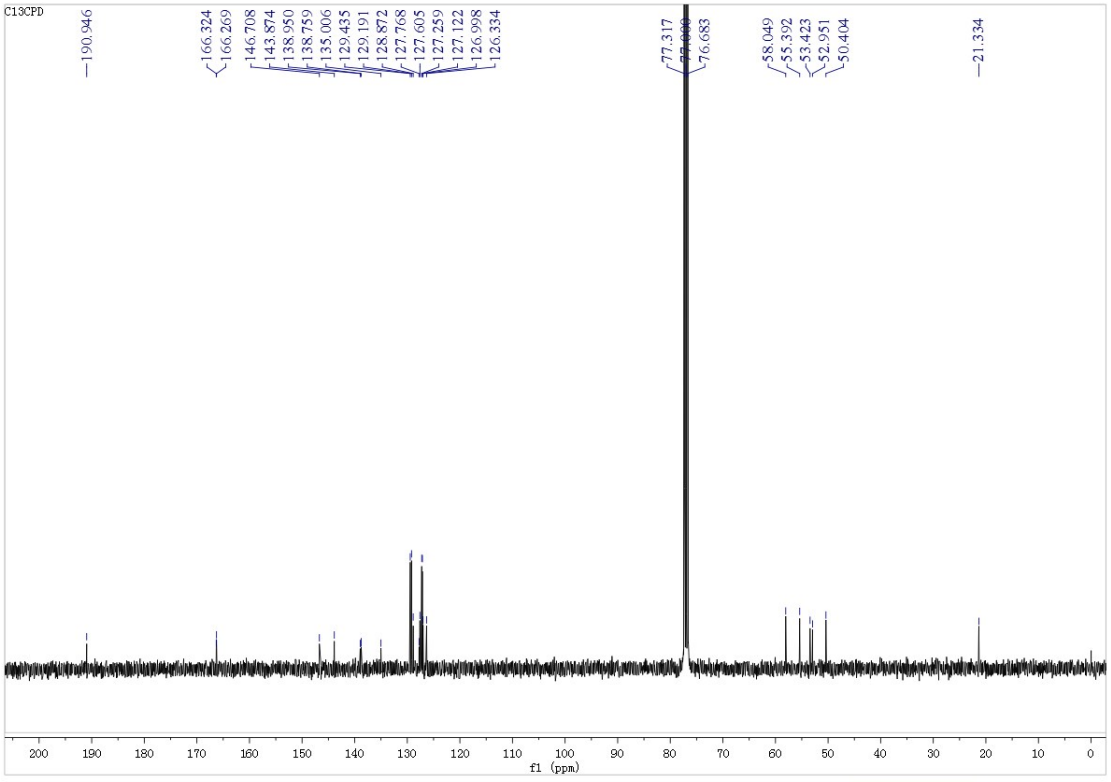

PROTON
7.522
7.502
7.395
7.376
7.260
7.138
7.059
7.039
6.962
6.942
5.880
5.856
4.500
4.450
4.282
4.232
3.899
3.875
3.825
3.617
2.338
2.240
0.95
1.95
0.98
1.00
1.87
1.06
1.10
1.02
1.10
3.09
3.00
3.06
3.14
f1 (ppm)

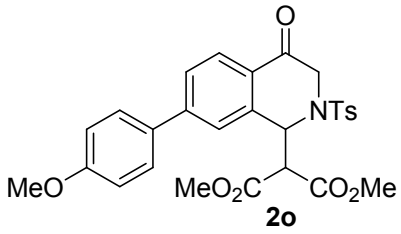

C13CPD
190.948
166.321
145.406
143.771
138.397
135.084
129.378
128.019
127.237
127.106
126.789
77.317
77.000
76.682
58.065
55.174
53.345
52.852
50.234
21.852
21.337
f1 (ppm)


O
NTs
Ph
MeO2C
CO2Me

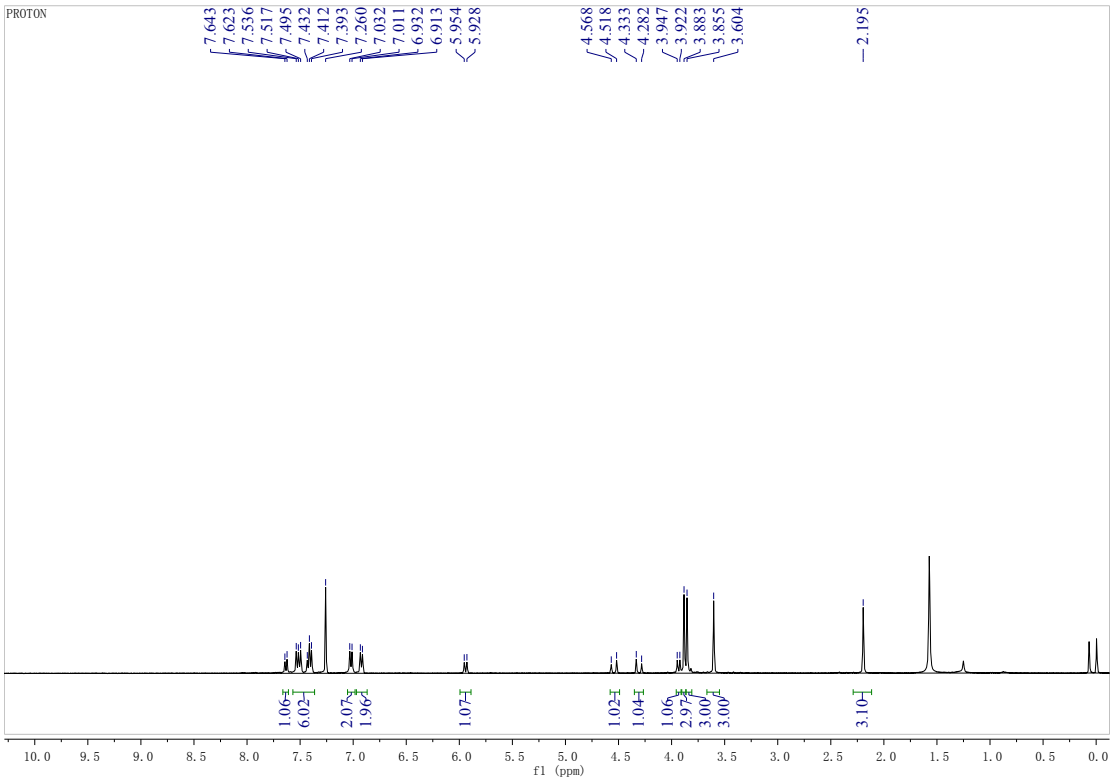
2n

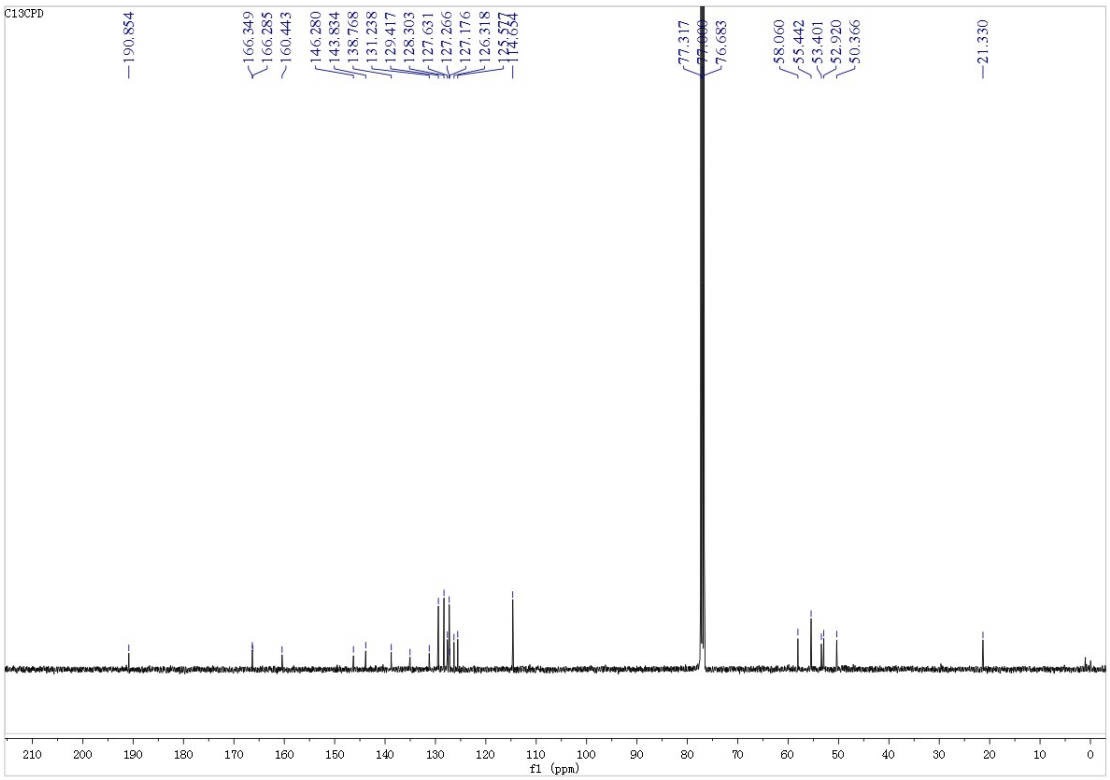

7.672
7.654
7.590
7.585
7.558
7.553
7.537
7.533
7.521
7.518
7.501
7.482
7.476
7.472
7.463
7.456
7.452
7.445
7.417
7.396
7.260
6.938
6.918
5.972
5.947
4.589
4.587
4.539
4.537
4.351
4.301
3.956
3.931
3.856
3.609
2.200
1.583
1.00
1.06
8.08
2.03
0.99
1.10
1.13
1.06
3.05
2.99
3.02
f1 (ppm)

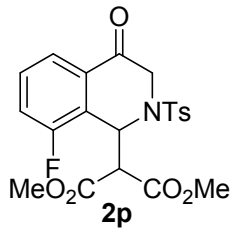

C13CPD
190.946
166.324
166.269
146.708
143.874
138.950
138.759
135.006
129.435
129.191
128.872
127.768
127.605
127.259
127.122
126.998
126.334
77.317
76.683
58.049
55.392
53.423
52.951
50.404
21.334
f1 (ppm)


O
NTs
MeO
MeO2C
CO2Me

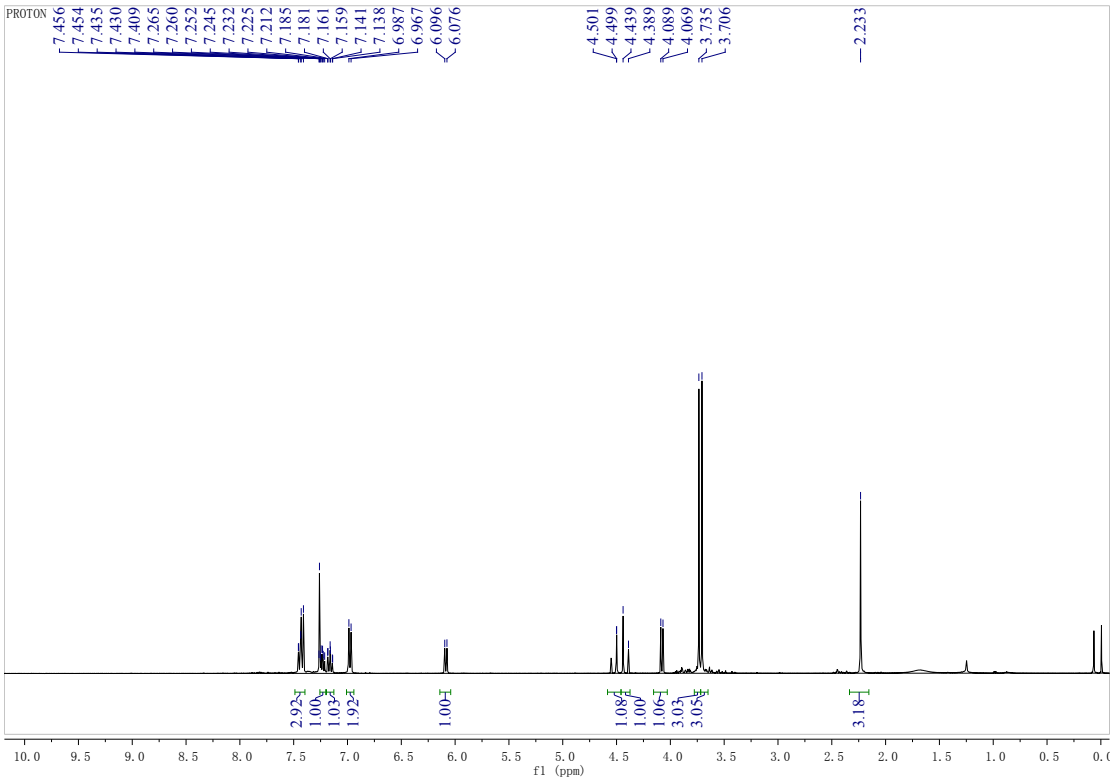
2o

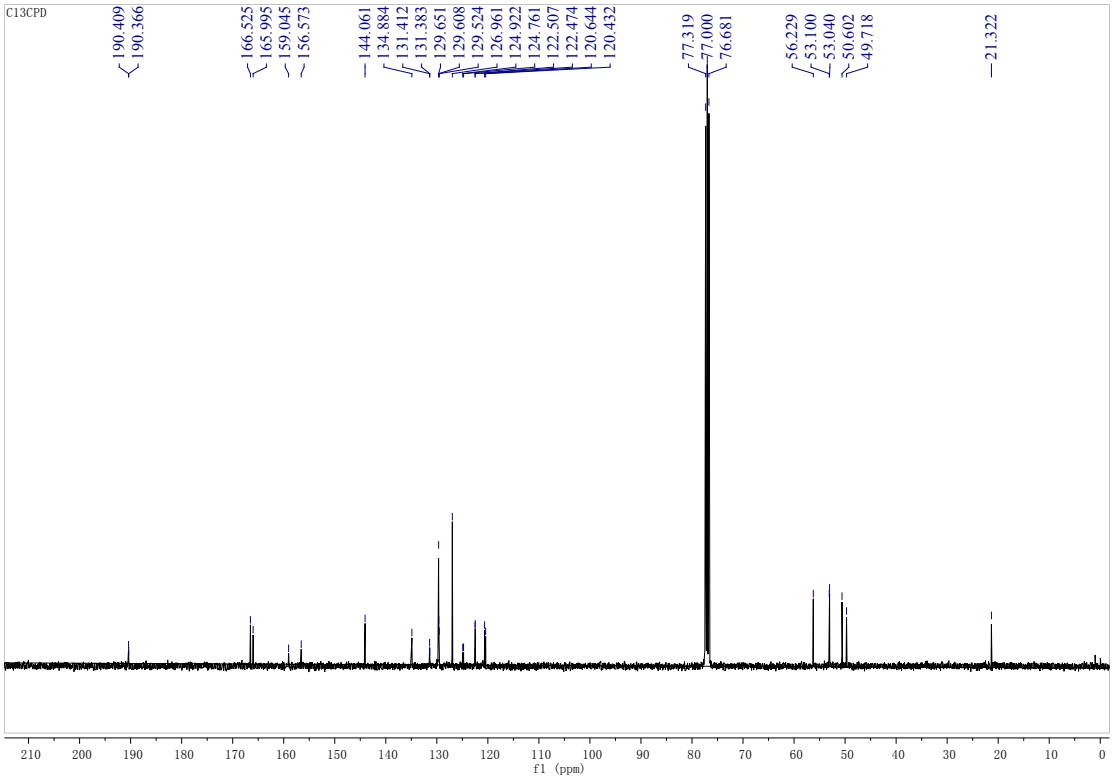

PROTON
7.643
7.623
7.536
7.517
7.495
7.432
7.412
7.393
7.260
7.032
7.011
6.932
6.913
5.954
5.928
4.568
4.518
4.333
4.282
3.947
3.922
3.883
3.855
3.604
2.195
1.06
6.02
2.07
1.96
1.07
1.02
1.04
1.06
2.97
3.00
3.00
3.10
f1 (ppm)

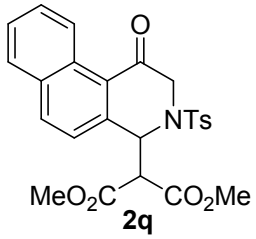

C13CPD
190.854
166.349
166.285
160.443
146.280
143.834
138.768
131.238
129.417
128.303
127.631
127.266
127.176
126.318
125.577
114.654
77.317
77.000
76.683
58.060
55.442
53.401
52.920
50.366
21.330
f1 (ppm)


O
NTs
F
MeO2C
CO2Me

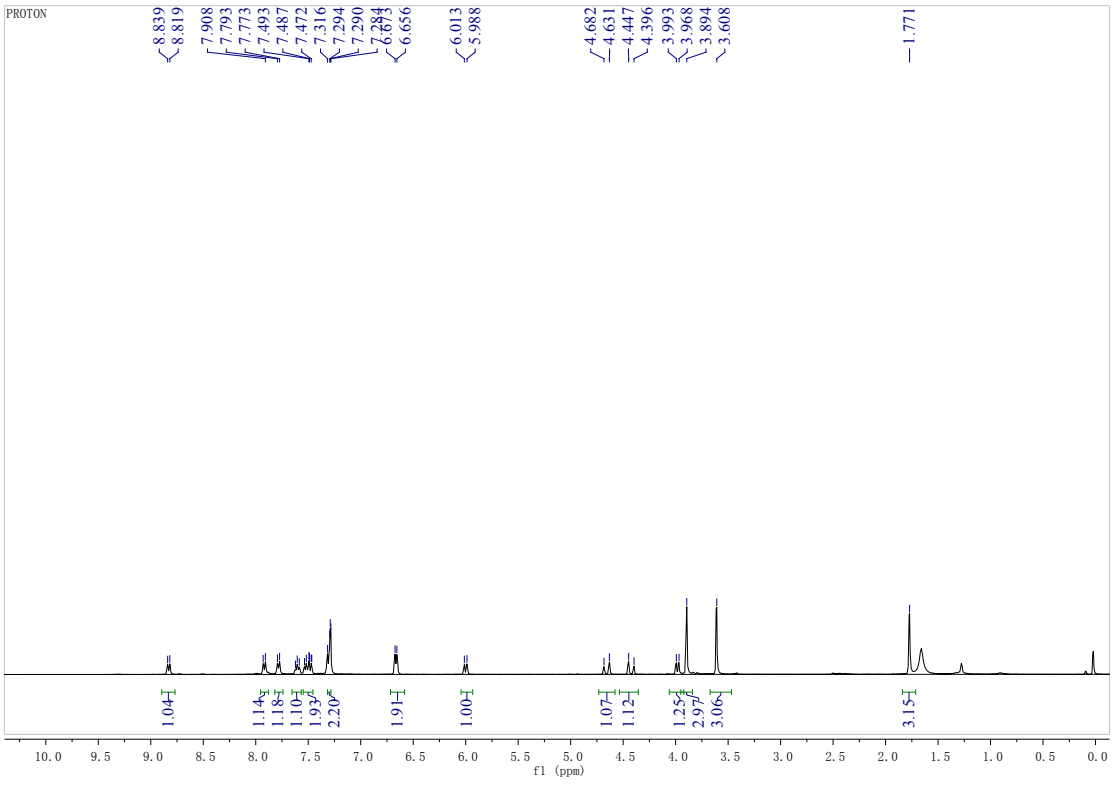
2p

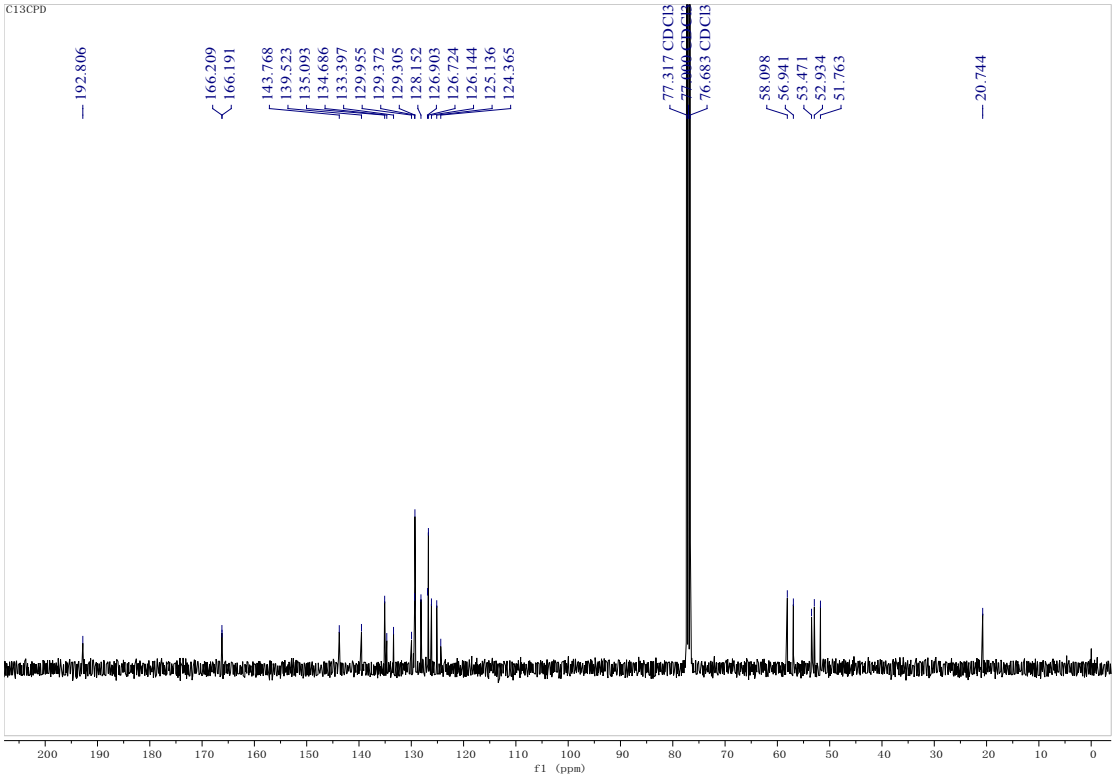

PROTON
7.456
7.454
7.435
7.430
7.409
7.265
7.260
7.252
7.245
7.232
7.225
7.212
7.185
7.181
7.161
7.159
7.141
7.138
6.987
6.967
6.096
6.076
4.501
4.499
4.439
4.389
4.089
4.069
3.735
3.706
2.233
2.92
1.00
1.03
1.92
1.00
1.08
1.00
1.06
3.03
3.05
3.18
f1 (ppm)

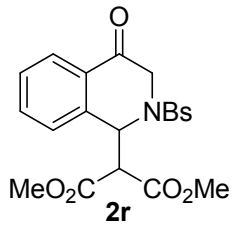

C13CPD
190.409
190.366
166.525
165.995
159.045
156.573
144.061
134.884
131.412
131.383
129.651
129.608
129.524
126.961
124.922
124.761
122.507
122.474
120.644
120.432
77.319
77.000
76.681
56.229
53.100
53.040
50.602
49.718
21.322
f1 (ppm)


O
NTs
MeO2C
CO2Me

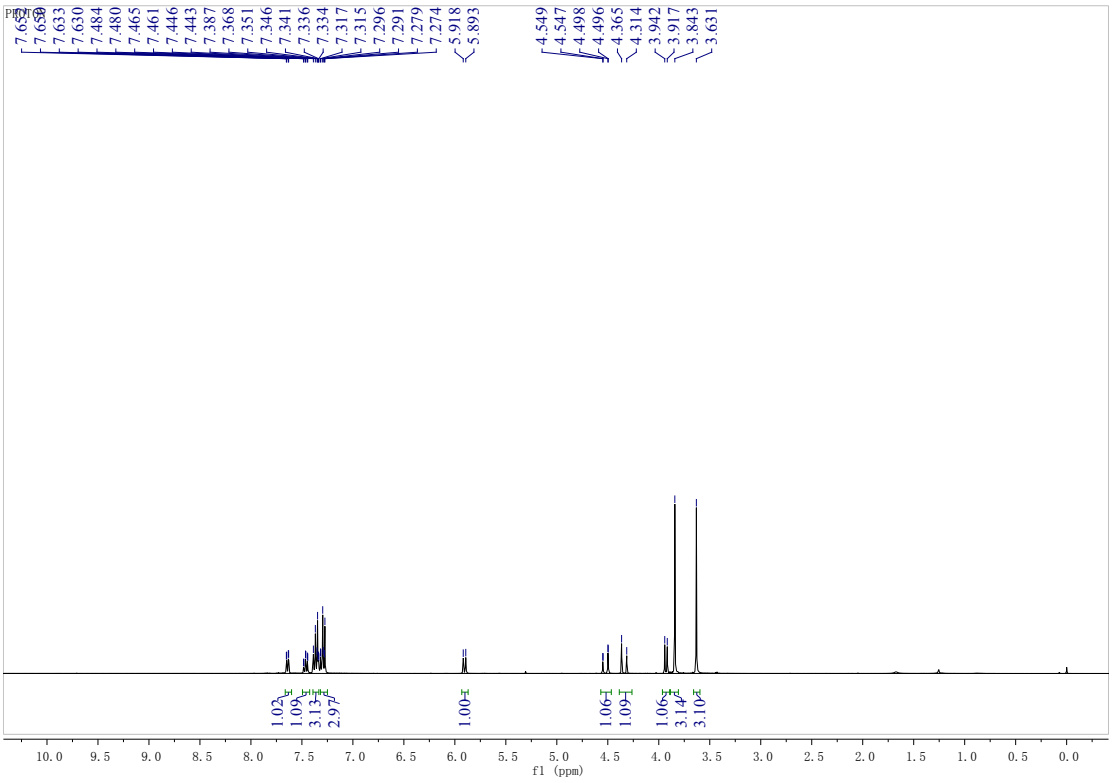
2q

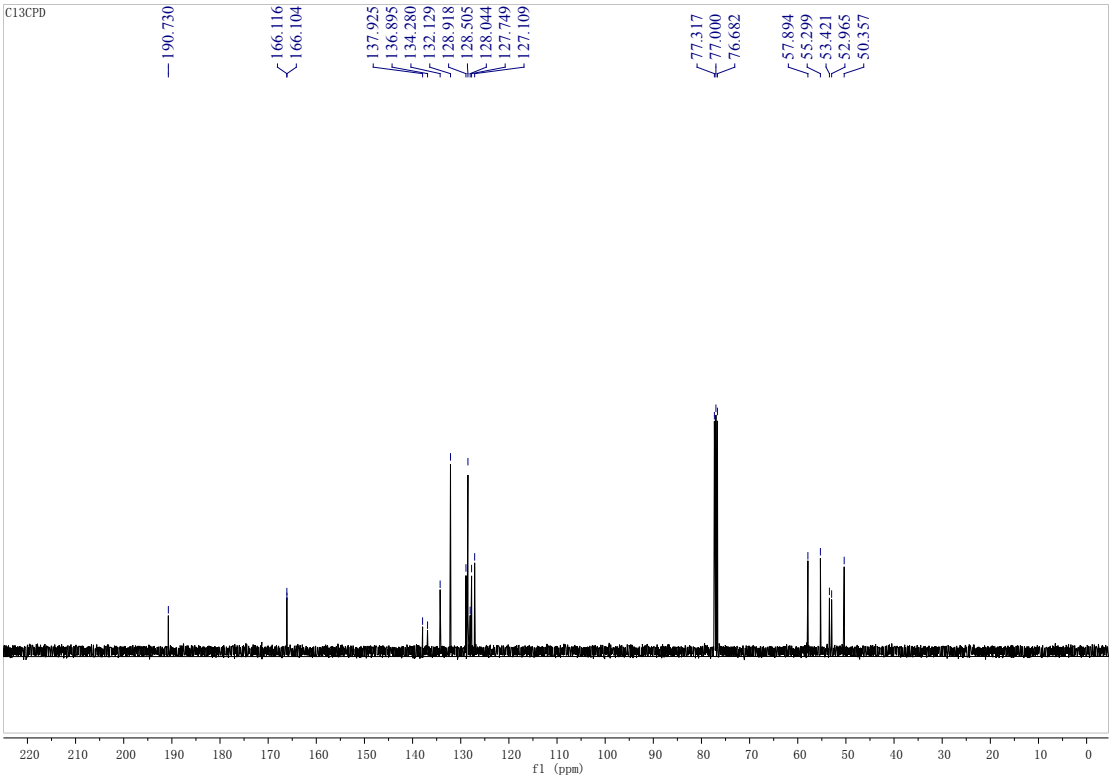

PROTON
8.839
8.819
7.908
7.793
7.773
7.493
7.487
7.472
7.316
7.294
7.290
7.284
6.673
6.656
6.013
5.988
4.682
4.631
4.447
4.396
3.993
3.968
3.894
3.608
1.771
1.04
1.14
1.18
1.10
1.93
2.20
1.91
1.00
1.07
1.12
1.25
2.97
3.06
3.15
f1 (ppm)

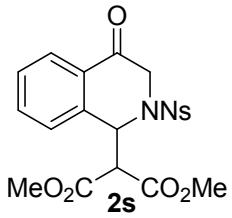

C13CPD
192.806
166.209
166.191
143.768
139.523
135.093
134.686
133.397
129.955
129.372
129.305
128.152
126.903
126.724
126.144
125.136
124.365
77.317 CDCl3
77.000 CDCl3
76.683 CDCl3
58.098
56.941
53.471
52.934
51.763
20.744
f1 (ppm)

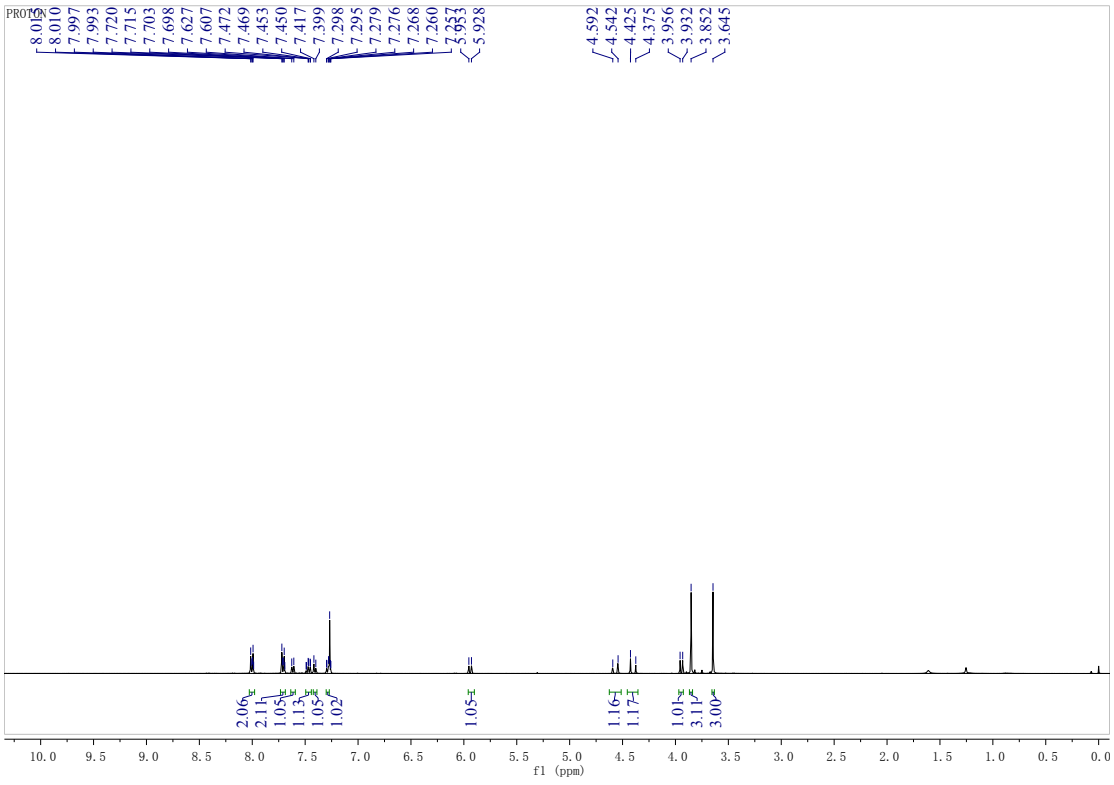

O
NBs
MeO2C
CO2Me

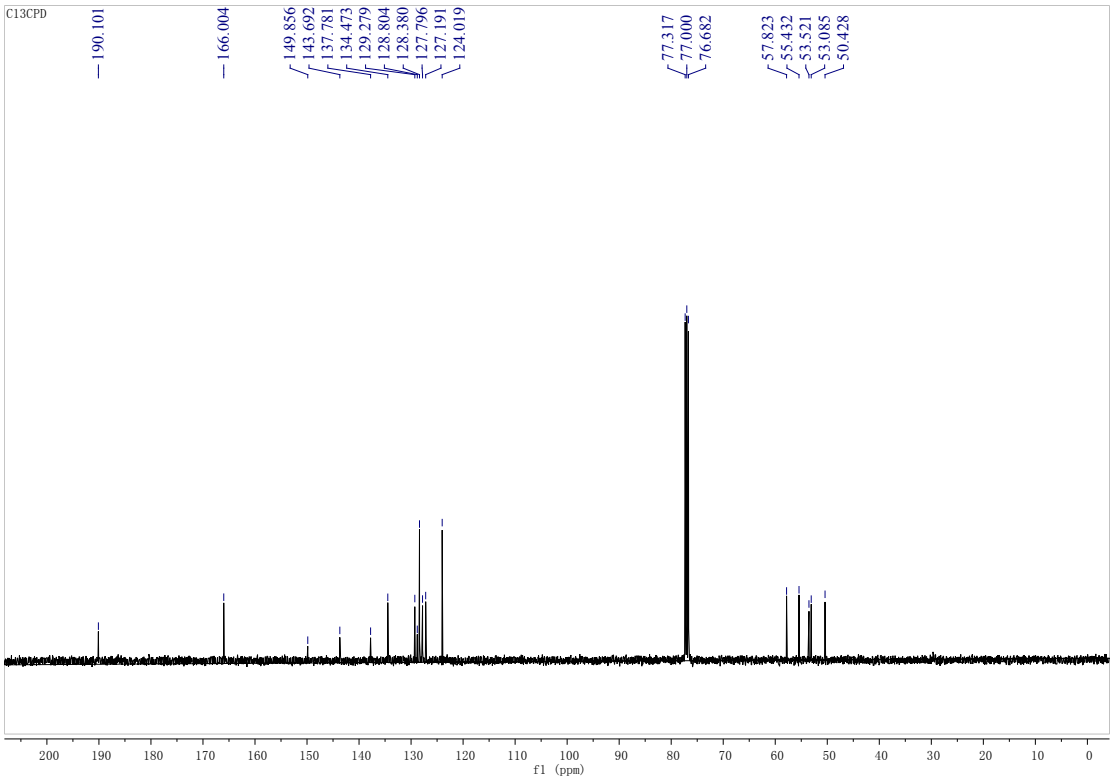
2r

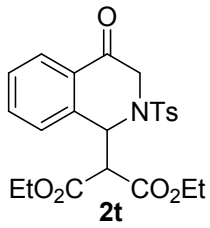

PROTON
7.652
7.650
7.633
7.630
7.484
7.480
7.465
7.461
7.446
7.443
7.387
7.368
7.351
7.346
7.341
7.336
7.334
7.317
7.315
7.296
7.291
7.279
7.274
5.918
5.893
4.549
4.547
4.498
4.496
4.365
4.314
3.942
3.917
3.843
3.631
1.02
1.09
3.13
2.97
1.00
1.06
1.09
1.06
3.14
3.10
f1 (ppm)


C13CPD
190.730
166.116
166.104
137.925
136.895
134.280
132.129
128.918
128.505
128.044
127.749
127.109
77.317
77.000
76.682
57.894
55.299
53.421
52.965
50.357
f1 (ppm)

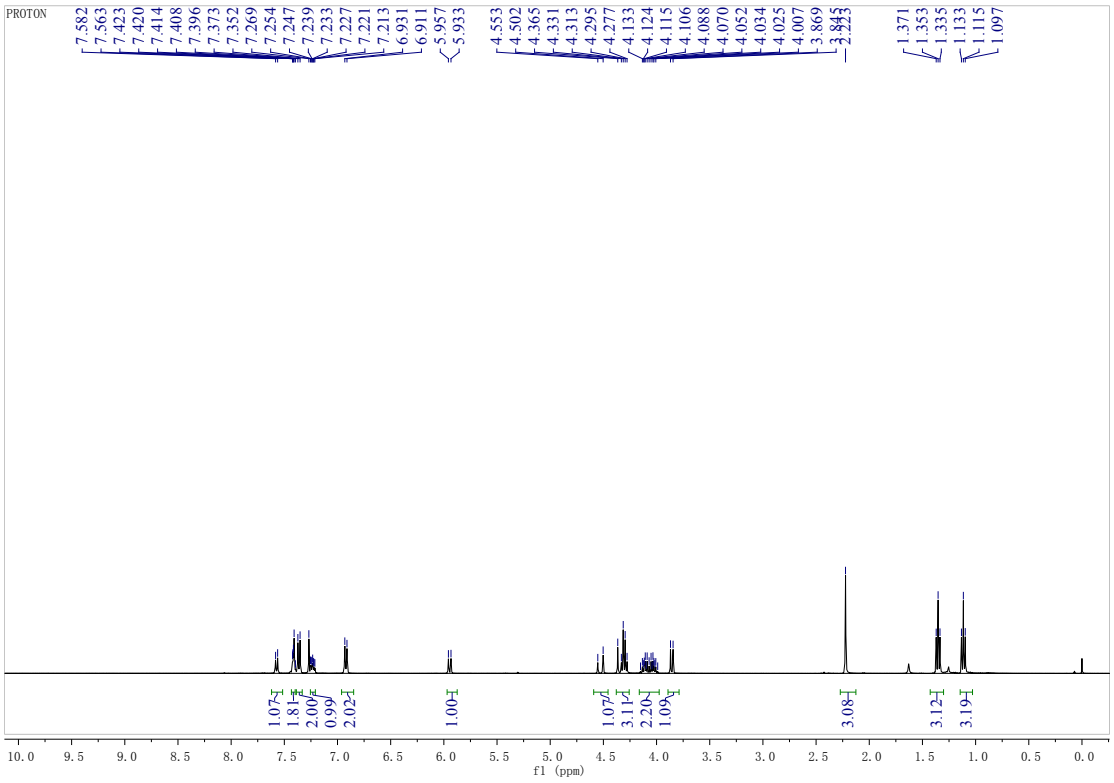

O
NNs
MeO2C
CO2Me
2s

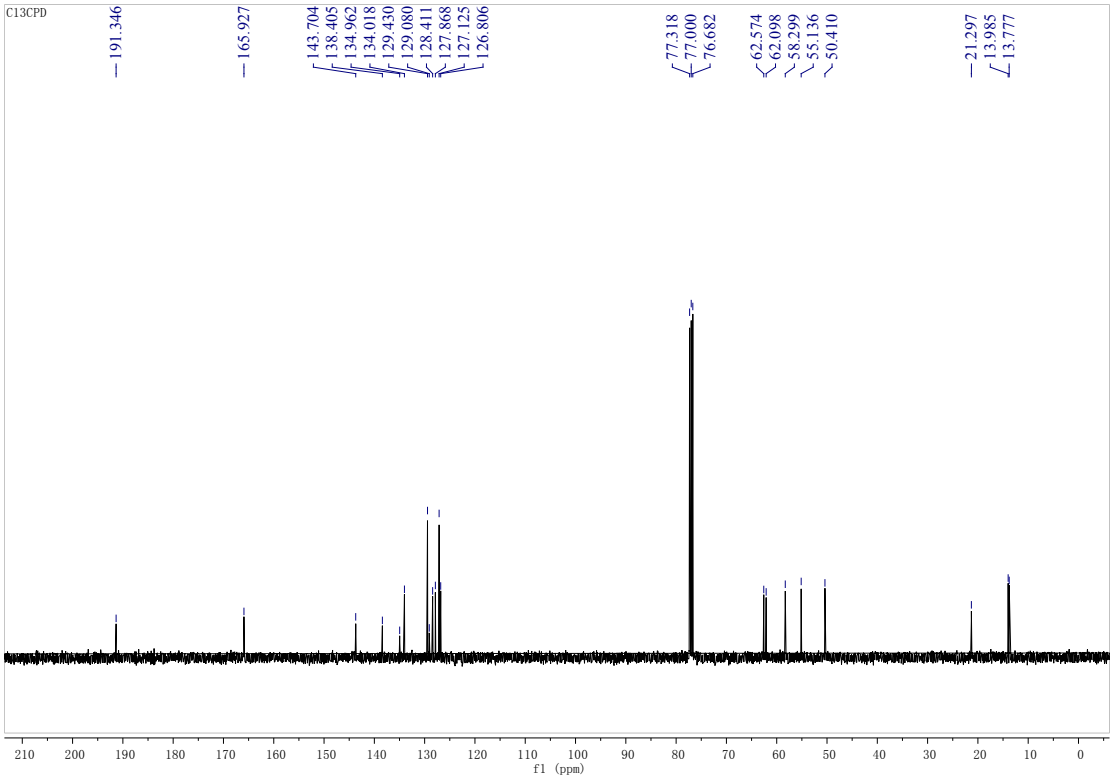

PROTON
8.015
8.010
7.997
7.993
7.720
7.715
7.703
7.698
7.627
7.607
7.472
7.469
7.453
7.450
7.417
7.399
7.298
7.295
7.279
7.276
7.268
7.260
5.953
5.928
4.592
4.542
4.425
4.375
3.956
3.932
3.852
3.645
2.06
2.11
1.05
1.13
1.05
1.02
1.05
1.16
1.17
1.01
3.11
3.00
f1 (ppm)

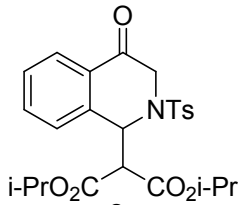

C13CPD
190.101
166.004
149.856
143.692
137.781
134.473
129.279
128.804
128.380
127.796
127.191
124.019
77.317
77.000
76.682
57.823
55.432
53.521
53.085
50.428
f1 (ppm)


O
NTs
EtO2C
CO2Et

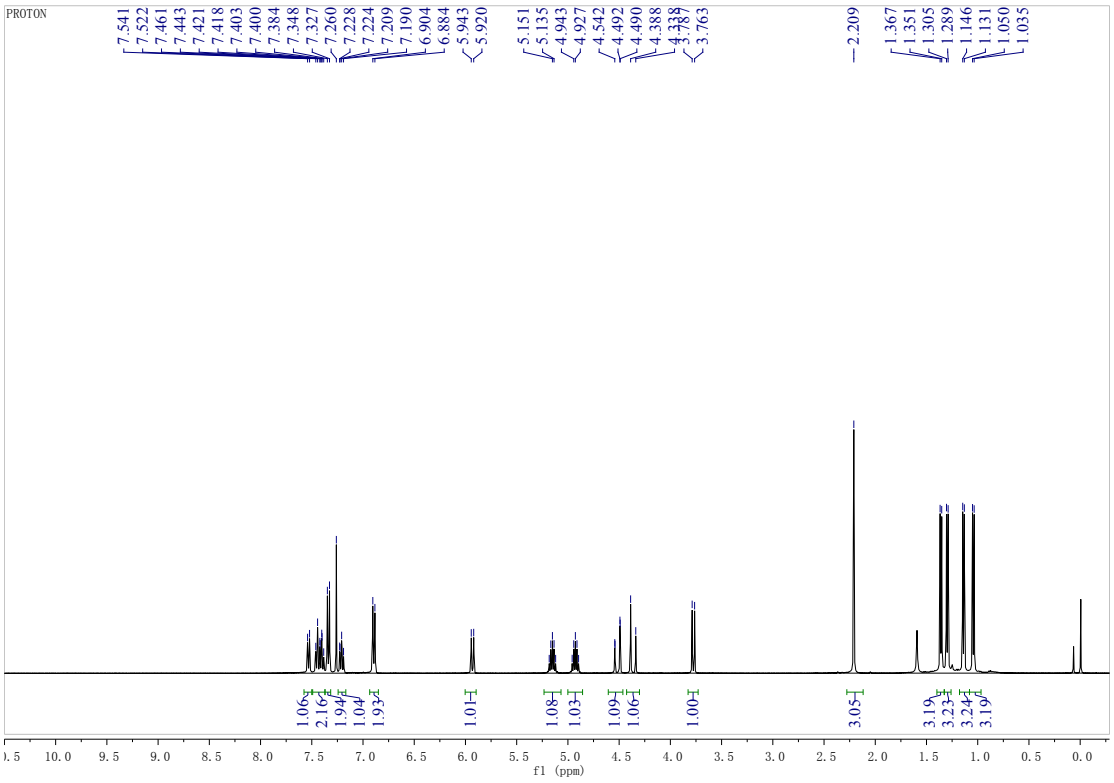
2t

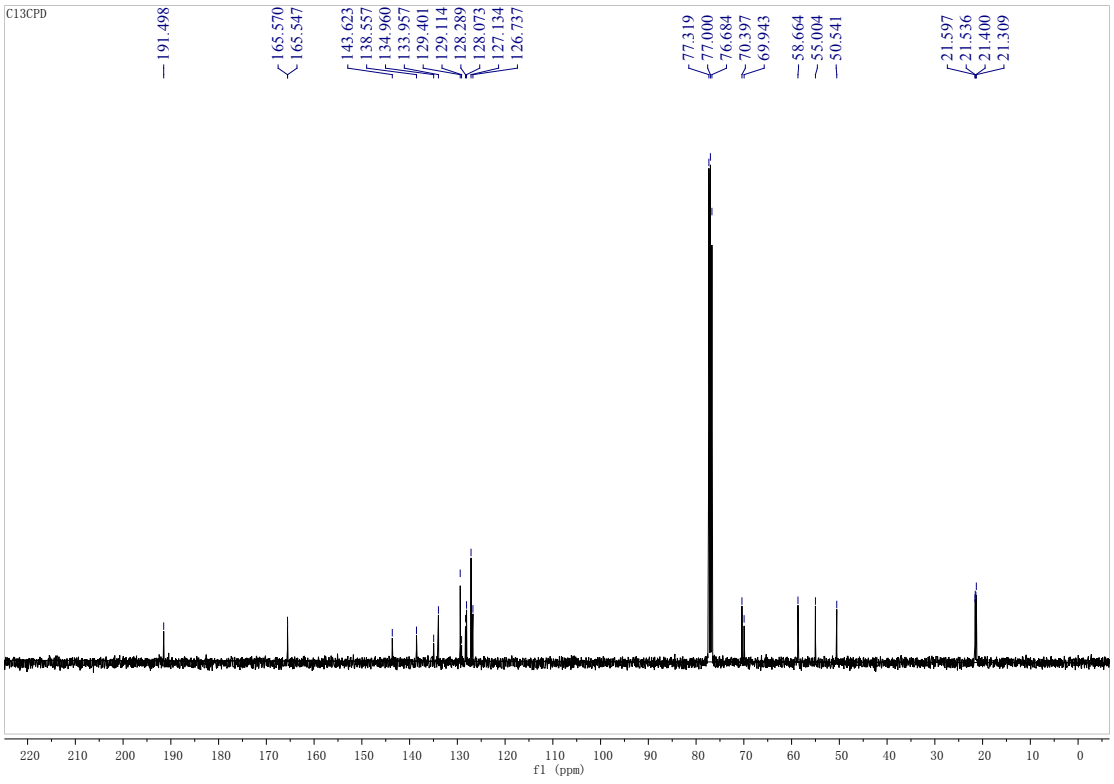

PROTON
7.582
7.563
7.423
7.420
7.414
7.408
7.396
7.373
7.352
7.269
7.254
7.247
7.239
7.233
7.227
7.221
7.213
6.931
6.911
5.957
5.933
4.553
4.502
4.365
4.331
4.313
4.295
4.277
4.133
4.124
4.115
4.106
4.088
4.070
4.052
4.034
4.025
4.007
3.869
3.845
2.223
1.371
1.353
1.335
1.133
1.115
1.097
1.07
1.81
2.00
0.99
2.02
1.00
1.07
3.11
2.20
1.09
3.08
3.12
3.19
f1 (ppm)

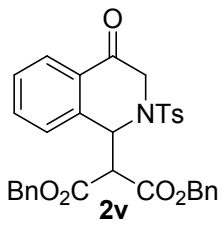

C13CPD
191.346
165.927
143.704
138.405
134.962
134.018
129.430
129.080
128.411
127.868
127.125
126.806
77.318
77.000
76.682
62.574
62.098
58.299
55.136
50.410
21.297
13.985
13.777
f1 (ppm)


O
NTs
i-PrO2C
CO2i-Pr

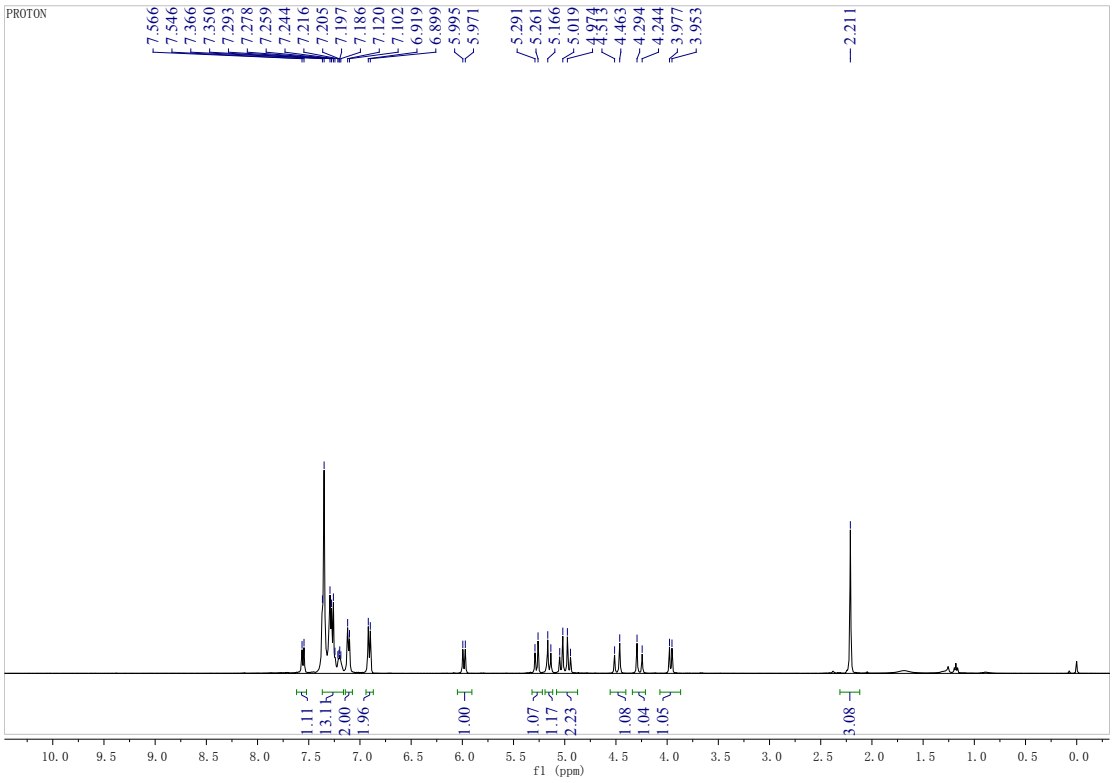
2u

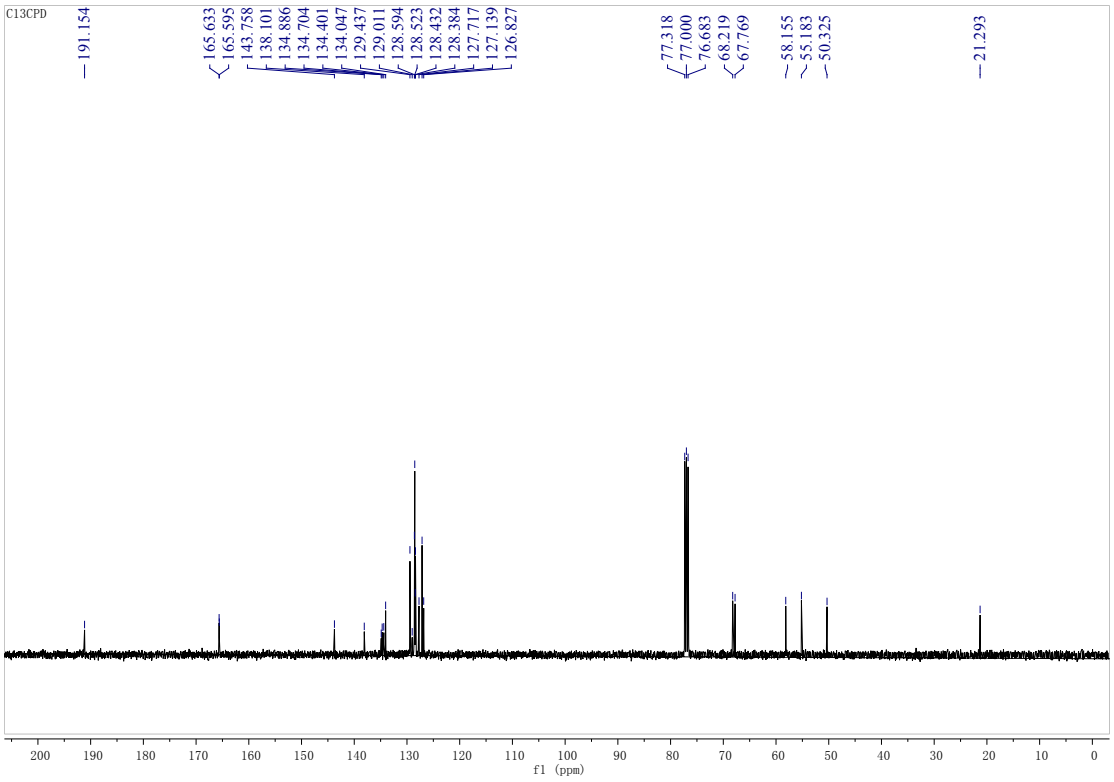

PROTON
7.541
7.522
7.461
7.443
7.421
7.418
7.403
7.400
7.384
7.348
7.327
7.260
7.228
7.224
7.209
7.190
6.904
6.884
5.943
5.920
5.151
5.135
4.943
4.927
4.542
4.492
4.490
4.388
3.763
2.209
1.367
1.351
1.305
1.289
1.146
1.131
1.050
1.035
1.06
2.16
1.94
1.04
1.93
1.01
1.08
1.03
1.09
1.06
1.00
3.05
3.19
3.23
3.24
3.19
f1 (ppm)

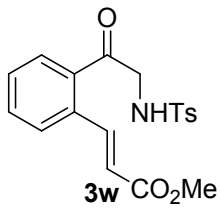

C13CPD
191.498
165.570
165.547
143.623
138.557
134.960
133.957
129.401
129.114
128.289
128.073
127.134
126.737
77.319
77.000
76.684
70.397
69.943
58.664
55.004
50.541
21.597
21.536
21.400
21.309
f1 (ppm)

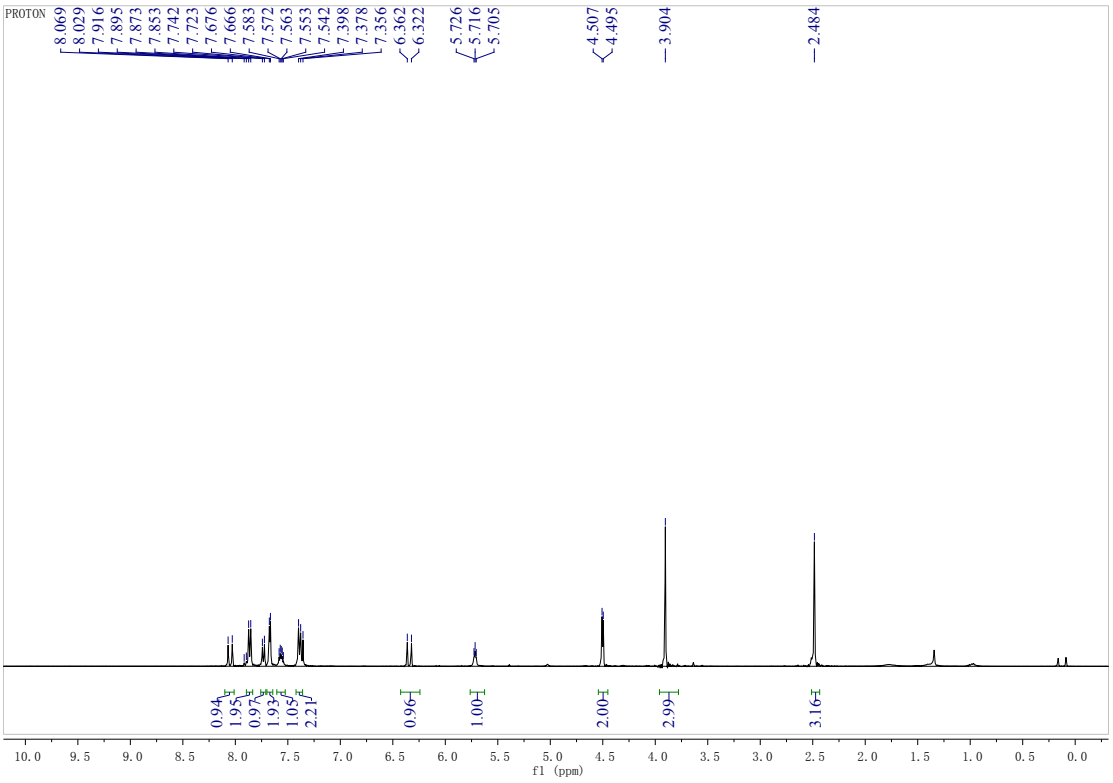

O
NTs
BnO2C
CO2Bn

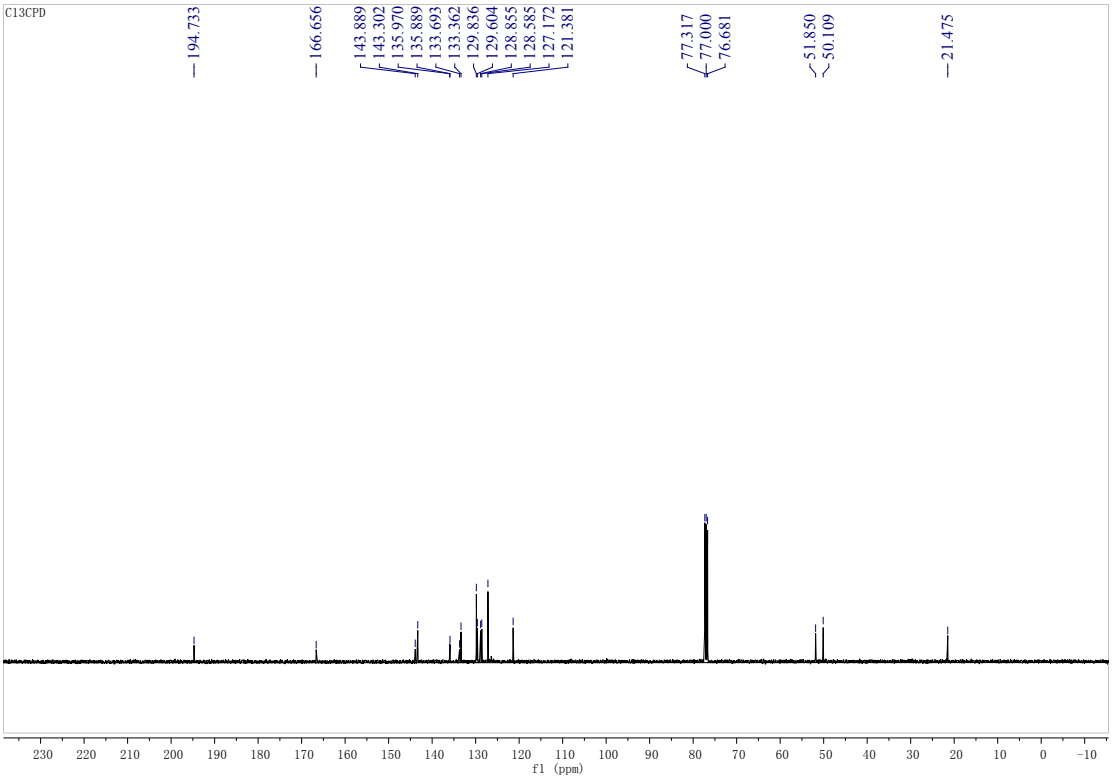
2v

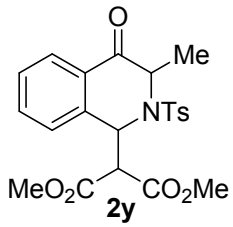

PROTON
7.566
7.546
7.366
7.350
7.293
7.278
7.259
7.244
7.216
7.205
7.197
7.186
7.120
7.102
6.919
6.899
5.995
5.971
5.291
5.261
5.166
5.019
4.474
4.313
4.463
4.294
4.244
3.977
3.953
2.211
1.11
13.11
2.00
1.96
1.00
1.07
1.17
2.23
1.08
1.04
1.05
3.08
f1 (ppm)


C13CPD
191.154
165.633
165.595
143.758
138.101
134.886
134.704
134.401
134.047
129.437
129.011
128.594
128.523
128.432
128.384
127.717
127.139
126.827
77.318
77.000
76.683
68.219
67.769
58.155
55.183
50.325
21.293
f1 (ppm)

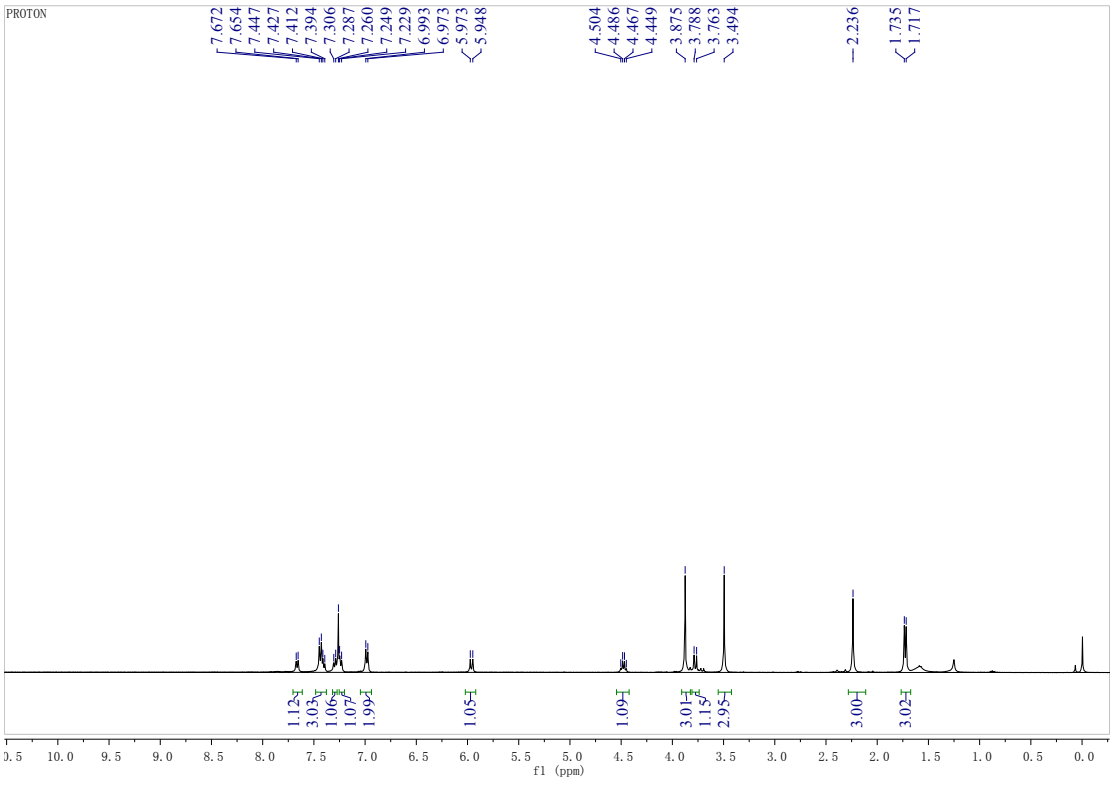

O
NHTs
3w
CO2Me

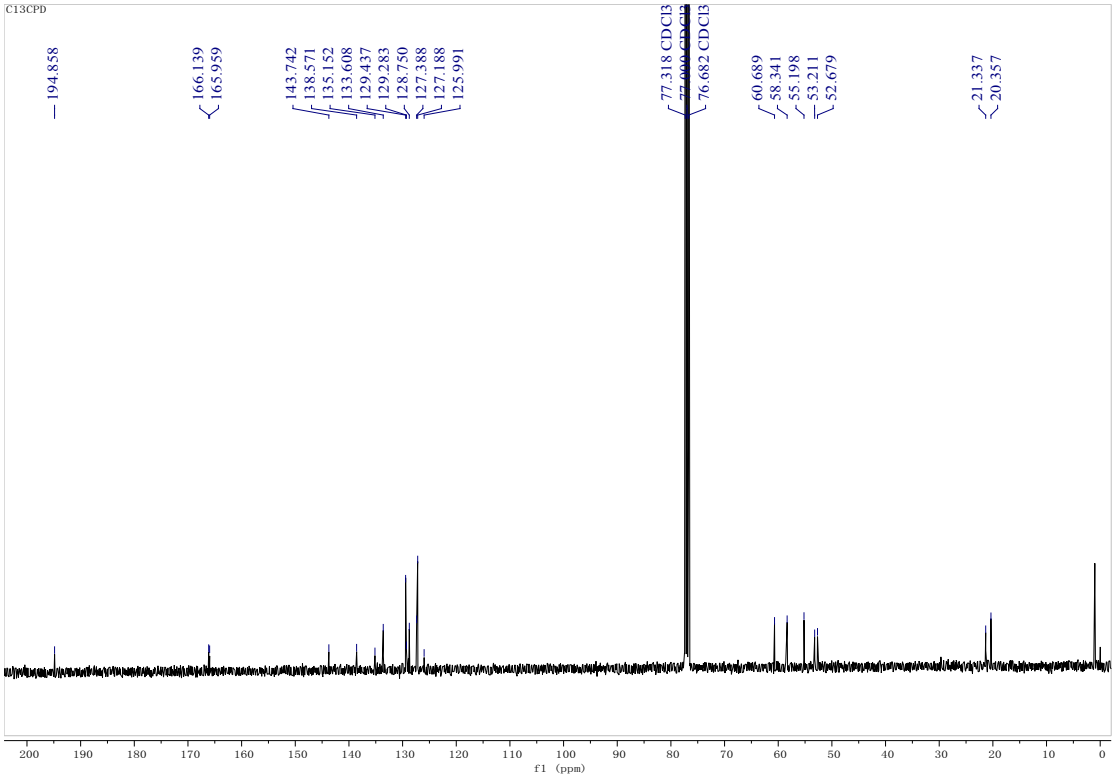

PROTON
8.069
8.029
7.916
7.895
7.873
7.853
7.742
7.723
7.676
7.666
7.583
7.572
7.563
7.553
7.542
7.398
7.378
7.356
6.362
6.322
5.726
5.716
5.705
4.507
4.495
3.904
2.484
0.94
1.95
0.97
1.93
1.05
2.21
0.96
1.00
2.00
2.99
3.16
f1 (ppm)

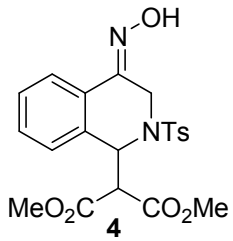

C13CPD
194.733
166.656
143.889
143.302
135.970
135.889
133.693
133.362
129.836
129.604
128.855
128.585
127.172
121.381
77.317
77.000
76.681
51.850
50.109
21.475
f1 (ppm)


O
Me
NTs
MeO2C
CO2Me

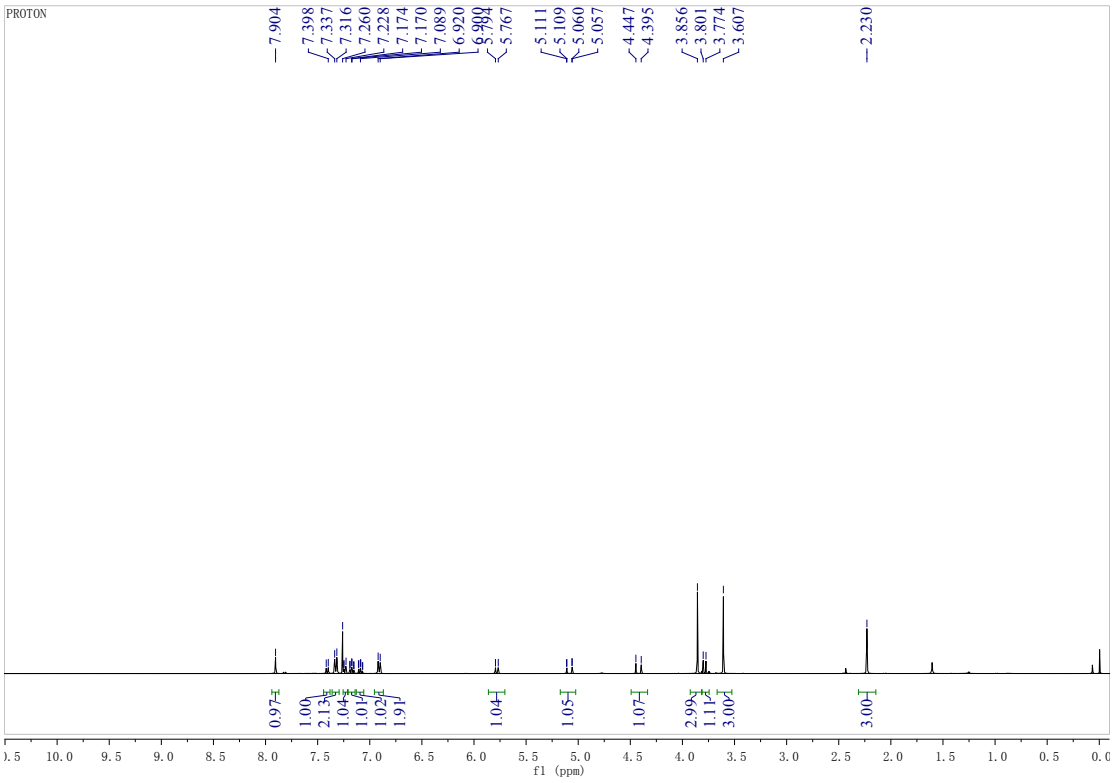
2y

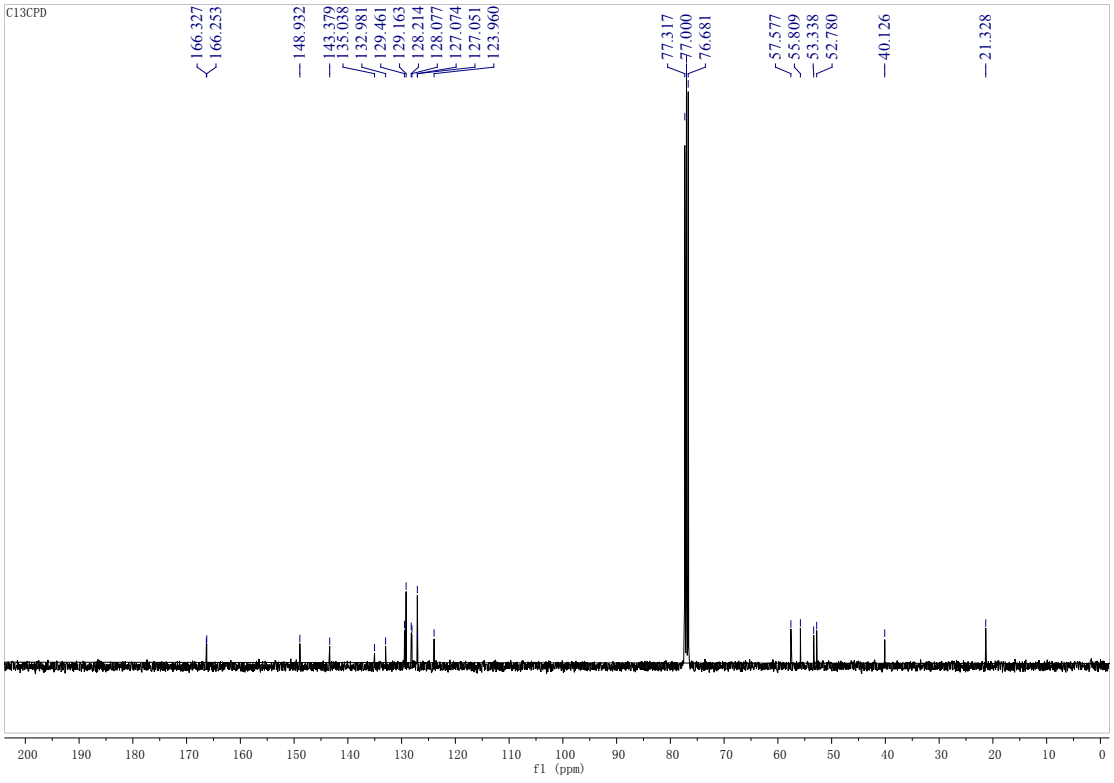

PROTON
7.672
7.654
7.447
7.427
7.412
7.394
7.306
7.287
7.260
7.249
7.229
6.993
6.973
5.973
5.948
4.504
4.486
4.467
4.449
3.875
3.788
3.763
3.494
2.236
1.735
1.717
1.12
3.03
1.06
1.07
1.99
1.05
1.09
3.01
1.15
2.95
3.00
3.02
f1 (ppm)

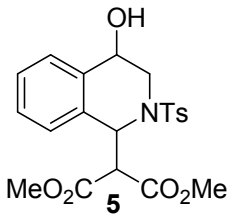

C13CPD
194.858
166.139
165.959
143.742
138.571
135.152
133.608
129.437
129.283
128.750
127.388
127.188
125.991
77.318 CDCl3
77.000 CDCl3
76.682 CDCl3
60.689
58.341
55.198
53.211
52.679
21.337
20.357
f1 (ppm)


N
OH
NTs
MeO2C
CO2Me

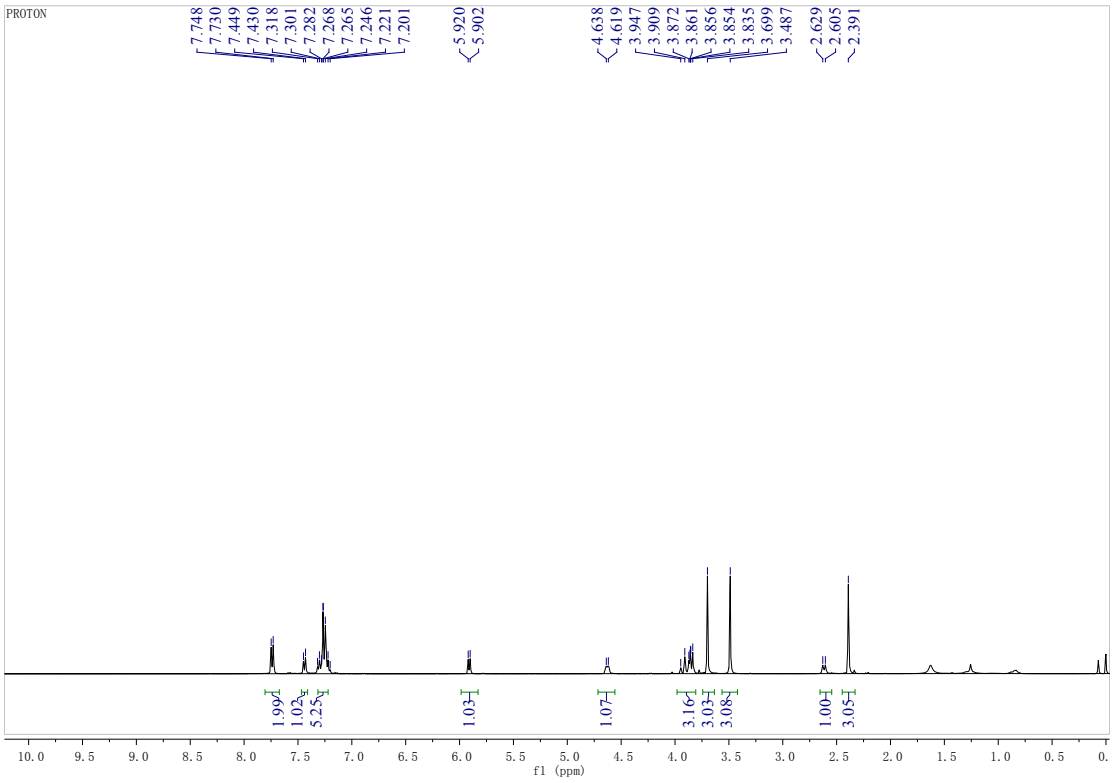
4

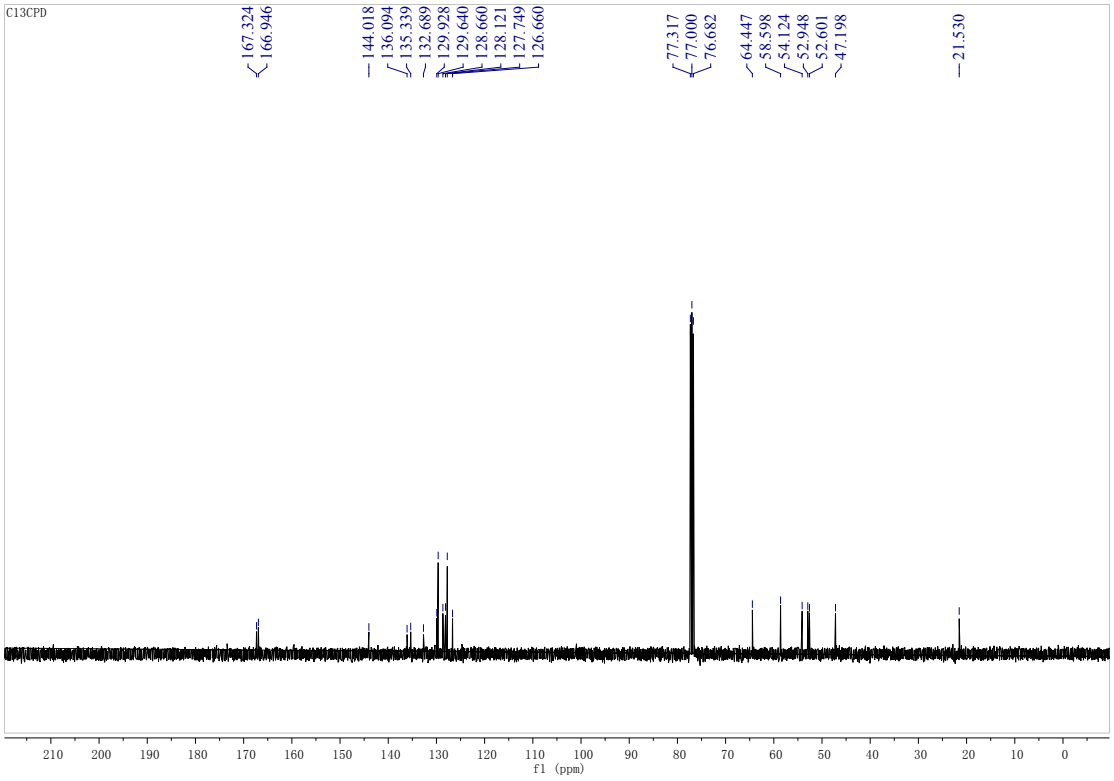

PROTON
7.904
7.398
7.337
7.316
7.260
7.228
7.174
7.170
7.089
6.920
6.900
5.767
5.111
5.109
5.060
5.057
4.447
4.395
3.856
3.801
3.774
3.607
2.230
0.97
1.00
2.13
1.04
1.01
1.02
1.91
1.04
1.05
1.07
2.99
1.11
3.00
3.00
f1 (ppm)


C13CPD
166.327
166.253
148.932
143.379
135.038
132.981
129.461
129.163
128.214
128.077
127.074
127.051
123.960
77.317
77.000
76.681
57.577
55.809
53.338
52.780
40.126
21.328
f1 (ppm)


OH
NTs
MeO2C
CO2Me

5


PROTON
7.748
7.730
7.449
7.430
7.318
7.301
7.282
7.268
7.265
7.246
7.221
7.201
5.920
5.902
4.638
4.619
3.947
3.909
3.872
3.861
3.856
3.854
3.835
3.699
3.487
2.629
2.605
2.391
1.99
1.02
5.25
1.03
1.07
3.16
3.03
3.08
1.00
3.05
f1 (ppm)


C13CPD
167.324
166.946
144.018
136.094
135.339
132.689
129.928
129.640
128.660
128.121
127.749
126.660
77.317
77.000
76.682
64.447
58.598
54.124
52.948
52.601
47.198
21.530
f1 (ppm)