Electronic Supplementary Material (ESI) for Chemical Communications

Metal-Free Cascade Radical Cyclization of 1, 6-Enynes with Aldehydes

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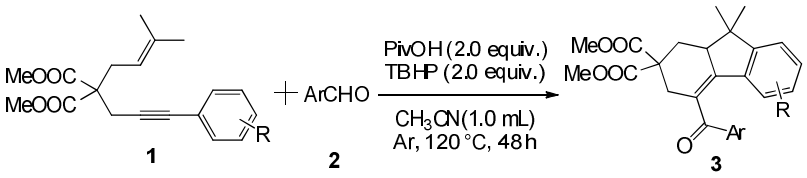
Experimental Section

1. General Remarks:

For product purification by flash column chromatography, silica gel (200~300 mesh). Reagents and solvents were purified using standard means.[1]H NMR spectra were recorded on 400 MHz in $CDCl_3$ and ^{13}C NMR spectra were recorded on 100 MHz in $CDCl_3$ using TMS as internal standard. All products were further characterized by HRMS (high resolution mass spectra). Melting points were determined on a microscopic apparatus and were uncorrected. Copies of their ^1H NMR and ^{13}C NMR spectra were provided. The parent ions $[M+H]^+$ or $[M+Na]^+$ are quoted.

2. General Procedure for cross coupling/cyclization of 1,6-enynes with aldehydes:

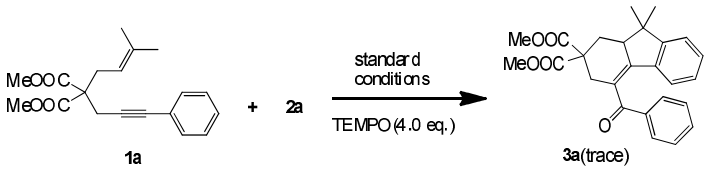


To a 10mL dried Schlenk-tube were added 1,6-enynes **1** (0.2 mmol, 1.0 equiv.) and aldehydes **2** (1.0 mmol, 5.0 equiv.) and PivOH (0.4 mmol, 2.0 equiv.) under an argon atmosphere. TBHP (0.4 mmol, 2.0 equiv.) in 1.0 mL of CH_3CN were introduced by syringe. The mixture was then stirred at 120 ℃ for 48 h. After completion of the reaction, the mixture was diluted with EtOAc. The combined organic layers were washed with saturated $NaHCO_3$ solution and saturated brine, dried over Na_2SO_4, concentrated in *vacuo* and purified by flash column chromatography on silica gel (gradient eluent of EtOAc/petroleum ether: 1/8 to 1/6) to give the corresponding products in Table 2 and Table 3.

3. General procedure for the preparation of 1,6-enynes 1a-1p.

All of 1,6-enynes **1** were synthesized according to the previous literature[1], CuI (0.1 mmol) and $[PdCl_2(PPh_3)_2]$ (0.05 mmol) were suspended in *i*-Pr_2NH, and the resulting mixture was stirred for 5 min. The corresponding arylbromide (1.3 mmo l) and the 1,6-enyne (1 mmol) in *i*-Pr_2NH were added sequentially. The reaction was stirred at room temperature until TLC showed total conversion. The crude mixture was diluted with Et_2O, filtered through Celite, and purified by chromatography (EtOAc-hexane mixtures).

4. Study on the reaction mechanism:[3]



When the TEMPO (2, 2, 6, 6-tetramethylpiperidine 1-oxyl) was added to the reaction of **1a** and **2a** in standard conditions, we could not detect the corresponding product **3**. It indicates that a SET (single-electron-transfer) process triggered by a free radical should be involved in the transformation.

5. Isotope Labeling Experiment[2]

a) Intramolecular Kinetic Isotope Effect (KIE) Experiment:

[D_1]-1a was synthesized according the literature procedure[1] using D_1-bromobenzene[3] as starting material. To a 10 mL dried Schlenk-tube were added [D_1]-1a (0.2mmol, 1.0 equiv.) and aldehyde **2a** (1.0mmol, 5.0 equiv.) and PivOH (0.4mmol, 2.0 equiv.) under an argon atmosphere. TBHP (0.4mmol, 2.0 equiv.) in 1.0 mL of CH_3CN were introduced by syringe. The mixture was then stirred at 120℃ for 48 h. After completion of the reaction, the mixture was diluted with EtOAc. The combined organic layers were washed with saturated $NaHCO_3$ solution and saturated brine, dried over Na_2SO_4, concentrated in *vacuo* and purified by flash column chromatography on silica gel. The product was analysis by ^{1}H NMR (Figure 1).

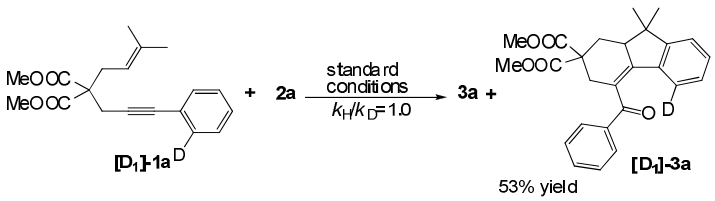


Figure 1. ^{1}H NMR spectra of the mixture of the product **3a** and [D_1]-**3a**.

b) Intermolecular Kinetic Isotope Effect (KIE) Experiment:

[D_5]-**1a** was synthesized according to the literature procedure[1] using D_5-bromobenzene[4] as starting material. To a 10 mL dried Schlenk-tube were added [D_5]-**1a** (0.1 mmol), **1a** (0.1 mmol), aldehyde **2a** (1.0 mmol, 5.0 equiv.) and PivOH (0.4 mmol, 2.0 equiv.) under an argon atmosphere. TBHP (0.4 mmol, 2.0 equiv.) in 1.0 mL of CH_3CN were introduced by syringe. The mixture was then stirred at 120℃ for 48 h. After completion of the reaction, the mixture was diluted with EtOAc. The combined organic layers were washed with saturated $NaHCO_3$ solution and saturated brine, dried over Na_2SO_4, concentrated in *vacuo* and purified by flash column chromatography on silica gel. The product was analysis by ^{1}H NMR (Figure 2).

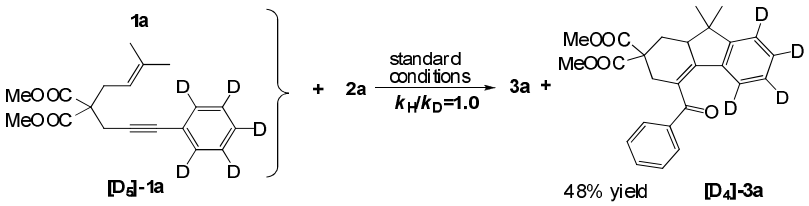
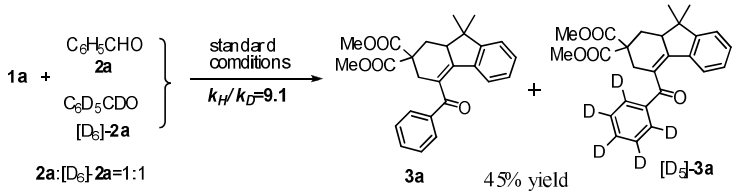


Figure 2. ^{1}H NMR spectra of the mixture of the product **3a** and [D_4]-**3a**.

c) Intermolecular Kinetic Isotope Effect (KIE) Experiment:

[D_6]-**2a** was synthesized according to the literature procedure[5] using D_5-bromobenzene[4] as starting material. To a 10 mL dried Schlenk-tube were added **1a** (0.2 mmol), aldehyde/ [D_6]-aldehyde (1:1) (1.0 mmol, 5.0 equiv.) and PivOH (0.4 mmol, 2.0 equiv.) under an argon atmosphere. TBHP (0.4 mmol, 2.0 equiv.) in 1.0 mL of CH_3CN were introduced by syringe. The mixture was then stirred at 120℃ for 48 h. After completion of the reaction, the mixture was diluted with EtOAc. The combined organic layers were washed with saturated $NaHCO_3$ solution and saturated brine, dried over Na_2SO_4, concentrated in *vacuo* and purified by flash column chromatography on silica gel. The product was analysis by ^{1}H NMR (Figure 3).



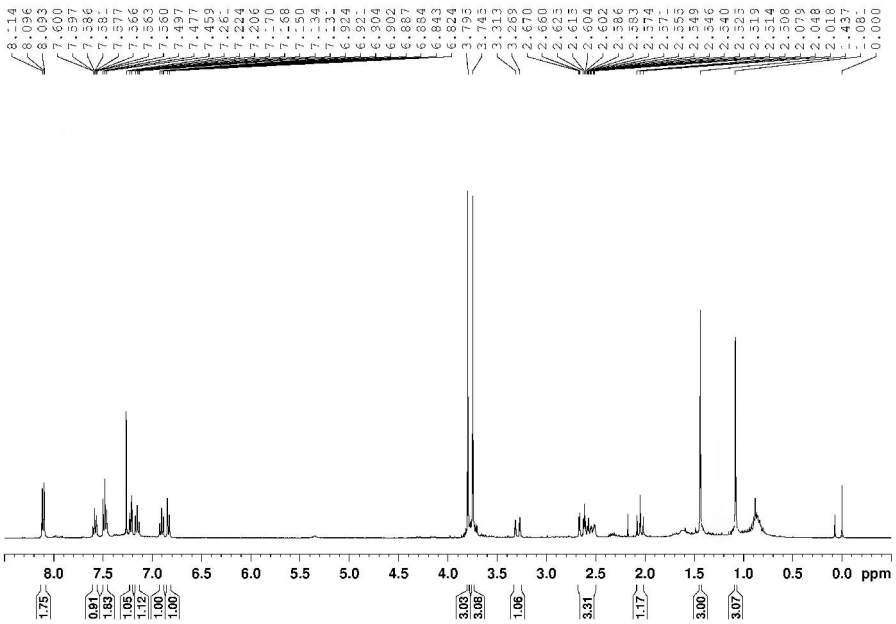
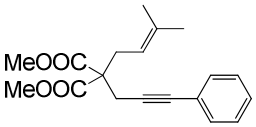


Figure 3. ^{1}H NMR spectra of the mixture of the product **3a** and [D_5]-**3a**.

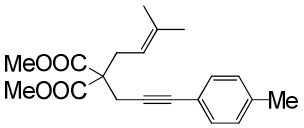
6. Characterization data of 1,6-enynes 1a-1p:

Enynes **1e**, **1j**, **1o**, **1p** were synthesized according to the previous literature[1], and the NMR spectroscopy and GC-MS data were in full accordance with the data in the literature[1b].



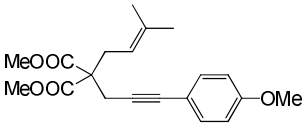
1a

Dimethyl 2-(3-methylbut-2-enyl)-2-(3-phenylprop-2-ynyl)malonate (1a): ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.37-7.35 (m, 2 H), 7.27-7.26 (m, 3 H), 4.98-4.94 (m, 1 H), 3.75 (s, 6 H), 2.99 (s, 2 H), 2.86-2.84 (d, *J* = 7.6 Hz, 2 H), 1.71 (s, 3 H), 1.68 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 170.6, 136.7, 131.6, 128.1, 127.9, 123.2, 117.1, 84.6, 83.3, 57.5, 52.5, 30.9, 26.0, 23.4, 17.9.



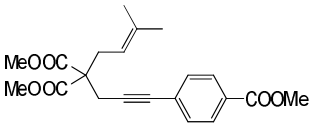
1b

Dimethyl 2-(3-methylbut-2-enyl)-2-(3-p-tolylprop-2-ynyl)malonate (1b): ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.29-7.27 (d, *J* = 8.0 Hz, 2 H), 7.11-7.09 (d, *J* = 7.6 Hz, 2 H), 4.99-4.95 (m, 1 H), 3.77 (s, 6 H), 3.60 (s, 2 H), 2.87-2.86 (d, *J* = 7.6 Hz, 2 H), 2.35 (s, 3 H), 1.74 (s, 3 H), 1.70 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 170.7, 137.9, 136.8, 131.5, 128.9, 120.2, 127.2, 83.9, 83.4, 57.5, 52.6, 30.9, 26.0, 23.5, 21.4, 17.9.



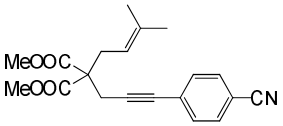
1c

Dimethyl 2-(3-(4-methoxyphenyl)prop-2-ynyl)-2-(3-methylbut-2-enyl)malonate (1c): ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.31-7.29 (d, *J* = 8.4 Hz, 2 H), 6.81-6.79 (d, *J* = 8.8 Hz, 2 H), 4.99-4.95 (m, 1 H), 3.78 (s, 3 H), 3.75 (s, 6 H), 2.98 (s, 2 H), 2.86-2.84 (d, *J* = 8.0 Hz, 2 H), 1.72 (s, 3 H), 1.69 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 170.6, 159.3, 136.6, 132.9, 117.2, 115.4, 113.7, 83.1, 83.0, 57.5, 55.1, 52.5, 30.9, 25.9, 23.4, 17.8.



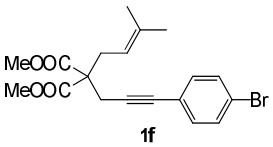
1d

Dimethyl 2-(3-(4-(methoxycarbonyl)phenyl)prop-2-ynyl)-2-(3-methylbut-2-enyl) malonate (1d): ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.31-7.29 (d, *J*=8.8 Hz, 2 H), 6.81-6.79 (d, *J* = 8.8 Hz, 2 H), 4.99-4.95 (m, 1 H), 3.78 (s, 3 H), 3.75 (s, 6 H), 2.98 (s, 2 H), 2.86-2.84 (d, *J* = 8.0 Hz, 2 H), 1.72 (s, 3 H), 1.69 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 170.6, 159.3, 136.6, 132.9, 117.2, 115.4, 113.7, 83.1, 83.0, 57.5, 55.1, 52.5, 30.9, 25.9, 23.4, 17.8.



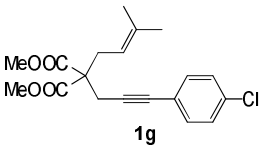
1e

Dimethyl 2-(3-(4-cyanophenyl)prop-2-ynyl)-2-(3-metylhbut-2-enyl)malonate (1e).



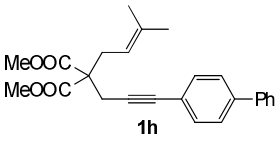
1f

Dimethyl 2-(3-(4-bromophenyl)prop-2-ynyl)-2-(3-methylbut-2-enyl)malonate (1f): ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.41-7.39 (d, *J* = 8.4 Hz, 2 H), 7.23-7.21 (d, *J* = 8.4 Hz, 2 H), 4.96-4.92 (m, 1 H), 3.75 (s, 6 H), 2.97 (s, 2 H), 2.83-2.81 (d, *J* = 7.6 Hz, 2 H), 1.71 (s, 3 H), 1.66 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 170.5, 136.9, 133.0, 31.4, 122.2, 122.1, 117.0, 86.1, 82.3, 57.4, 52.7, 31.0, 26.1, 23.5, 17.9.



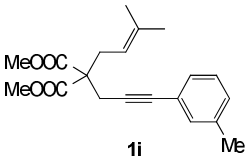
1g

Dimethyl 2-(3-(4-chlorophenyl)prop-2-ynyl)-2-(3-methylbut-2-enyl)malonate (1g): ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.31-7.29 (m, 2 H), 7.28-7.25 (m, 2 H), 4.99-4.95 (m, 1 H), 3.77 (s, 6 H), 3.00 (s, 2 H), 2.86-2.84 (d, *J* = 7.6 Hz, 2 H), 1.73 (s, 3 H), 1.69 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 170.5, 136.8, 133.9, 132.8, 128.5, 121.8, 117.1, 85.9, 82.3, 57.4, 52.7, 31.0, 26.0, 23.5, 17.9.



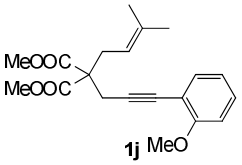
1h

Dimethyl 2-(3-(biphenyl-4-yl)prop-2-ynyl)-2-(3-methylbut-2-enyl)malonate (1h): ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.61-7.58 (m, 2 H), 7.56-7.54 (d, *J* = 8.0 Hz, 2 H), 7.49-7.45 (m, 4 H), 7.39-7.36 (m, 1 H), 5.04-5.00 (m, 1 H), 3.80 (s, 6 H), 3.07 (s, 2 H), 2.93-2.91 (d, *J* = 7.6 Hz, 2 H), 1.77 (s, 3 H), 1.74 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 170.6, 140.7, 140.4, 136.8, 132.0, 128.8, 127.5, 126.9, 126.8, 122.2, 117.1, 85.4, 83.2, 57.5, 52.6, 31.0, 26.0, 23.5, 17.9.



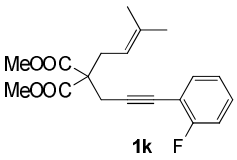
1i

Dimethyl 2-(3-methylbut-2-enyl)-2-(3-m-tolylprop-2-ynyl)malonate (1i): ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.26-7.17 (m, 3 H), 7.12-7.10 (d, *J* = 4.4 Hz, 1 H), 5.01-4.97 (m, 1 H), 3.77 (s, 6 H), 3.01 (s, 2 H), 2.88-2.86 (d, *J* = 7.6 Hz, 2 H), 2.33 (s, 3 H), 1.74 (s, 3 H), 1.70 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 170.6, 137.8, 136.7, 132.1, 128.8, 128.7, 128.0, 123.1, 117.2, 84.3, 83.6, 57.5, 52.6, 31.0, 26.0, 23.5, 21.1, 17.9.



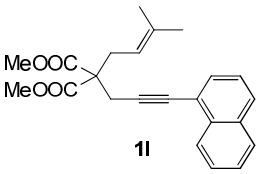
1j

Dimethyl 2-(3-(2-methoxyphenyl)prop-2-ynyl)-2-(3-methylbut-2-enyl)malonate (1j).



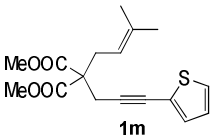
1k

Dimethyl 2-(3-(2-fluorophenyl)prop-2-ynyl)-2-(3-methylbut-2-enyl)malonate (1k): ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.37-7.23 (m, 1 H), 7.28-7.22 (m, 1 H), 7.07-7.00 (m, 2 H), 4.98-4.95 (m, 1 H), 3.76 (s, 6 H), 3.04 (s, 2 H), 2.87-2.85 (d, *J* = 7.6 Hz, 2 H), 1.72 (s, 3 H), 1.68 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 170.4, 164.1, 161.6, 136.8, 133.5, 129.6, 129.5, 123.7, 123.6, 117.1, 115.4, 115.2, 111.8, 111.6, 90.3, 90.2, 76.5, 57.4, 52.6, 30.9, 26.0, 23.6, 17.8.



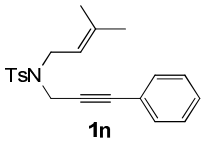
1l

Dimethyl 2-(3-methylbut-2-enyl)-2-(3-(naphthalen-1-yl)prop-2-ynyl)malonate (1m): ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.32-8.30 (d, *J* = 8.4 Hz, 1 H), 7.86-7.81 (m, 2 H), 7.64-7.51 (m, 2 H), 7.44-7.40 (m, 1 H), 7.28 (m, 1 H), 5.07-5.03 (m, 1 H), 3.81 (s, 6 H), 3.20 (s, 2 H), 2.98-2.97 (d, *J* = 7.6 Hz, 2 H), 1.77 (s, 3 H), 1.72 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 170.7, 136.9, 133.4, 133.1, 130.4, 128.3, 128.2, 126.6, 126.3, 126.1, 125.1, 121.0, 117.1, 89.7, 81.4, 57.6, 52.7, 31.1, 26.1, 23.9, 18.0.



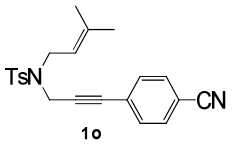
1m

Dimethyl 2-(3-methylbut-2-enyl)-2-(3-(thiophen-2-yl)prop-2-ynyl)malonate (1m): ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.20-7.19 (d, *J* = 4.4 Hz, 1 H), 3.77 (s, 6 H), 3.03 (s, 2 H), 2.85-2.83 (d, *J* = 7.6 Hz, 2 H), 1.73 (s, 3 H), 1.70 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 170.5, 136.9, 131.5, 126.7, 126.4, 123.3, 117.0, 88.8, 76.4, 57.4, 52.7, 31.0, 26.0, 23.7, 17.9.



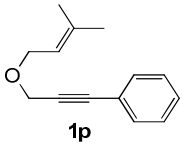
1n

4-methyl-N-(3-methylbut-2-enyl)-N-(3-phenylprop-2-ynyl)benzenesulfonamide (1n).



1o

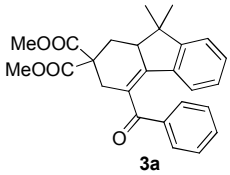
N-(3-(4-cyanophenyl)prop-2-ynyl)-4-methyl-N-(3-methylbut-2-enyl)benzenesulfonamide (1o): ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.77-7.76 (d, *J*=7.6 Hz, 2 H), 7.54-7.52 (d, *J* = 8.0 Hz, 2 H), 7.26-7.24 (d, *J* = 7.6 Hz, 2 H), 7.15-7.13 (d, *J* = 8.0 Hz, 2 H), 5.16 (s, 1 H), 4.29 (s, 2 H), 3.88-3.86 (d, *J* = 6.4 Hz, 2 H), 2.34 (s, 3 H), 1.75 (s, 3 H), 1.68 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 143.4, 139.3, 136.0, 131.9, 131.8, 129.4, 127.8, 127.1, 118.2, 117.7, 111.7, 87.2, 83.6, 44.3, 36.2, 25.9, 21.4, 17.9.



1p

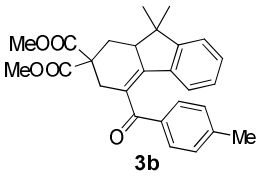
(3-(3-methylbut-2-enyloxy)prop-1-ynyl)benzene (1p).

7. Characterization data of Products 3a-3p:



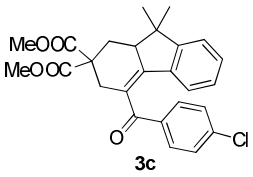
3a

Dimethyl 4-benzoyl-9,9-dimethyl-9,9a-dihydro-1*H*-fluorene-2,2(3*H*)-dicarboxylate (3a): Yellow oil; R_f (20% EtOAc/hexane) = 0.42; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.11-8.09 (d, *J* = 7.6 Hz, 2 H), 7.57 (t, *J* = 7.2 Hz, 1 H), 7.47 (t, *J* = 7.6 Hz, 2 H), 7.22-7.20 (d, *J* = 7.6 Hz, 1 H), 7.14 (t, *J* = 6.8 Hz, 1 H), 6.92-6.88 (m, 1 H), 6.85-6.83 (d, *J* = 7.6 Hz, 1 H), 3.79 (s, 3 H), 3.74 (s, 3 H), 3.32-3.28 (d, *J* = 18.0 Hz, 1 H), 2.68-2.52 (m, 3 H), 2.05 (t, *J* = 12.4 Hz, 1 H), 1.44 (s, 3 H), 1.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 198.8, 172.0, 171.1, 155.1, 139.4, 136.0, 135.9, 133.6, 129.7, 128.9, 128.6, 127.8, 126.6, 124.0, 122.2, 53.7, 52.9, 52.8, 49.5, 44.2, 33.5, 28.2, 26.4, 25.9; IR (KBr, cm^{-1}) 2956, 2926, 2857, 1738, 1650, 1666, 1456, 1264, 738; HRMS (ESI) m/z: calcd for $C_{26}H_{26}O_5$: $[M+H]^+$=419.1853; found: 419.1855.



3b

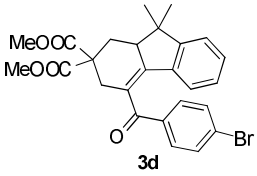
Dimethyl 9,9-dimethyl-4-(4-methylbenzoyl)-9,9a-dihydro-1*H*-fluorene-2,2(3*H*)-dicarboxylate (3b): Yellow solid; m.p. = 161-163 ℃; R_f (20% EtOAc/hexane) = 0.38; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.01-7.99 (d, *J* = 8.0 Hz, 2 H),7.28-7.26 (m, 2 H), 7.22-7.20 (d, *J* = 7.6 Hz, 1 H), 7.14 (t, *J* = 7.2 Hz, 1 H), 6.90 (t, *J* = 7.2 Hz, 1 H), 6.86-6.84 (d, *J* = 7.6 Hz, 1 H), 3.79 (s, 3 H), 3.74 (s, 3 H), 3.29-3.24 (d, *J* = 18.0 Hz, 1 H), 2.67-2.51 (m, 3 H), 2.41 (s, 3H), 2.04 (t, *J* = 12.4 Hz, 1 H), 1.43 (s,3 H), 1.07 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 198.6, 172.0, 171.2, 155.0, 144.6, 138.8, 136.0, 133.5, 129.9, 129.6, 128.5, 128.0, 126.6, 124.0, 122.2, 53.8, 52.9, 52.8, 49.4, 44.2, 33.6, 28.2, 26.4, 25.9, 21.8; IR (KBr, cm^{-1}) 2955, 2926, 1736, 1655, 1604, 1454, 1270, 1178, 738; HRMS (ESI) m/z: calcd for $C_{27}H_{28}O_5$: $[M+H]^+$ = 432.2010; found: 432.2015.



3c

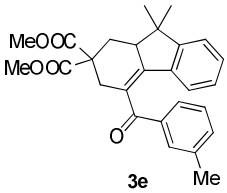
Dimethyl 4-(4-chlorobenzoyl)-9,9-dimethyl-9,9a-dihydro-1*H*-fluorene-2,2(3*H*)-dicarboxylate (3c): Yellow solid; m.p. = 169-171 ℃; R_f (20% EtOAc/hexane) = 0.47; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.07-8.05 (d, *J* = 8.4 Hz, 2 H), 7.46-7.44 (d, *J* = 8.4 Hz, 2 H), 7.23-7.21 (d, *J* = 7.6 Hz, 1 H), 7.16 (t, *J* = 7.2 Hz, 1 H), 6.92 (t, *J* = 7.6 Hz, 1 H), 6.80-6.78 (d, *J*=8.0 Hz, 1 H), 3.79(s, 3

H), 3.75 (s, 3 H), 3.28-3.23 (d, *J* = 18.0 Hz, 1 H), 2.64-2.49 (m, 3 H), 2.04 (t, *J* = 12.4 Hz, 1 H), 1.43 (s, 3 H), 1.07(s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 197.7, 171.9, 171.1, 155.2, 140.2, 139.8, 135.7, 134.4, 131.2, 129.3, 128.8, 127.2, 126.7, 123.9, 122.3, 53.7, 53.0, 52.9, 49.5, 44.2, 33.4, 28.1, 26.4, 25.9; IR (KBr, cm^{-1}) 2956, 2927, 2863, 1735, 1666, 1586, 1454, 1267, 1092, 738; HRMS (ESI) m/z: calcd for $C_{26}H_{25}ClO_5$: $[M+H]^+$ = 453.1463; found: 453.1468, 455.1463.



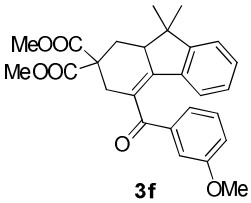
3d

Dimethyl 4-(4-bromobenzoyl)-9,9-dimethyl-9,9a-dihydro-1*H*-fluorene-2,2(3*H*)-dicarboxylate (3d): Yellow oil; R_f (20% EtOAc/hexane) = 0.44; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.00-7.97 (d, *J* = 8.4 Hz, 2 H), 7.63-7.61 (d, *J* = 8.4 Hz, 2 H), 7.23-7.21 (d, *J* = 7.2 Hz, 1 H), 7.17 (t, *J* = 7.2 Hz, 1 H), 6.92 (t, *J* = 7.2 Hz, 1 H), 6.80-6.79 (d, *J* = 7.6 Hz, 1 H), 3.79 (s, 3 H), 3.75 (s, 3 H), 3.27-3.23 (d, *J* = 18.0 Hz, 1 H), 2.64-2.49 (m, 3 H), 2.04 (t, *J* = 12.4 Hz, 1 H), 1.43 (s, 3 H), 1.07 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 197.9, 171.9, 171.1, 155.2, 139.9, 135.7, 134.7, 132.3, 131.3, 129.0, 128.8, 127.2, 126.7, 123.9, 122.3, 53.7, 53.0, 52.9, 49.5, 44.2, 33.4, 28.1, 26.4, 25.9; IR (KBr, cm^{-1}) 2957, 2927, 2864, 1737, 1669, 1466, 1241, 1047, 759; HRMS (ESI) m/z: calcd for $C_{26}H_{25}BrO_5$: $[M+H]^+$ = 497.0958; found: 497.0963, 499.0933.



3e

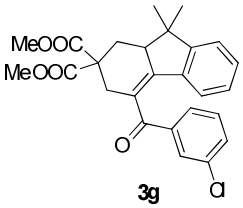
Dimethyl 9,9-dimethyl-4-(3-methylbenzoyl)-9,9a-dihydro-1*H*-fluorene-2,2(3*H*)-dicarboxylate (3e): Yellow oil; R_f (20% EtOAc/hexane) = 0.40; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.93-7.89 (m, 2 H), 7.40-7.33 (m, 2 H), 7.22-7.20 (d, *J* = 7.6 Hz, 1 H), 7.17-7.13 (m, 1 H), 6.93-6.89 (m, 1 H), 6.86-6.84 (d, *J* = 8.0 Hz, 1 H), 3.79 (s, 3 H), 3.74 (s, 3 H), 3.31-3.26 (d, *J* = 18.0 Hz, 1 H), 2.66-2.51 (m, 3 H), 2.40 (s, 3 H), 2.04 (t, *J* = 12.0 Hz, 1 H), 1.44 (s, 3 H), 1.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 199.1, 172.0, 171.1, 155.0, 139.2, 138.7, 136.0, 135.9, 134.5, 130.1, 128.7, 128.5, 128.0, 127.1, 126.6, 124.0, 122.2, 53.7, 52.9, 49.4, 44.2, 33.5, 28.2, 26.4, 25.9, 21.3; IR (KBr, cm^{-1}) 2956, 2926, 2862, 1736, 1663, 1454, 1270, 737; HRMS (ESI) m/z: calcd for $C_{27}H_{28}O_5$: $[M+H]^+$ = 432.2010; found: 432.2019.



3f

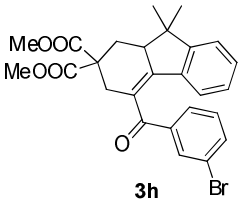
Dimethyl 4-(3-methoxybenzoyl)-9,9-dimethyl-9,9a-dihydro-1*H*-fluorene-2,2(3*H*)-dicarboxylate (3f): Yellow oil; R_f (20% EtOAc/hexane) = 0.34; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.71-7.66 (m, 2 H), 7.37 (t, *J* = 7.6 Hz, 1 H), 7.22-7.21 (d, *J* = 7.2 Hz, 1 H), 7.17-7.11 (m, 2 H), 6.94-6.90 (m, 1 H), 6.86-6.84 (d, *J* = 7.6 Hz, 1 H), 3.86 (s, 3 H), 3.79 (s, 3 H), 3.74 (s, 3 H), 3.32-3.27 (d, *J* = 18.0 Hz, 1 H), 2.66-2.50 (m, 3 H), 2.04 (t, *J* = 12.4 Hz, 1 H), 1.44 (s, 3 H), 1.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 198.7, 172.0, 171.1, 160.1, 155.0, 139.3, 137.3,

135.9, 129.9, 128.6, 127.9, 126.6, 124.0, 122.5, 122.2, 120.6, 113.4, 55.5, 53.7, 53.0, 52.9, 49.4, 44.2, 33.5, 28.1, 26.4, 25.9; IR (KBr, cm^{-1}) 2956, 2863, 1735, 1663, 1583, 1432, 1272, 1046, 735; HRMS (ESI) m/z: calcd for $C_{27}H_{28}O_6$: $[M+H]^+$ = 449.1959; found: 449.1965.



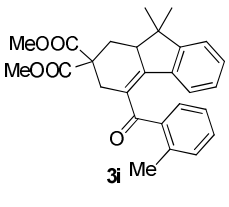
3g

Dimethyl 4-(3-chlorobenzoyl)-9,9-dimethyl-9,9a-dihydro-1*H*-fluorene-2,2(3*H*)-dicarboxylate (3g): Yellow oil; R_f (20% EtOAc/hexane) = 0.21; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.08 (s, 1 H), 8.00-7.98 (d, *J* = 8.0 Hz, 1 H), 7.56-7.53 (m, 1 H), 7.42 (t, *J* = 7.6 Hz, 1 H), 7.24-7.22 (d, *J* = 7.6 Hz, 1 H), 7.17 (t, *J* = 7.2 Hz, 1 H), 6.93 (t, *J* = 7.2 Hz, 1 H), 6.81-6.79 (d, *J* = 7.6 Hz, 1 H), 3.81 (s, 3 H), 3.75 (s, 3 H), 3.30-3.25 (d, *J* = 18.0 Hz, 1 H), 2.65-2.58 (m, 2 H), 2.56-2.52 (m, 1 H), 2.04 (t, *J* = 12.4 Hz, 1 H), 1.44 (s, 3 H), 1.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 197.5, 171.9, 171.1, 155.2, 140.4, 137.6, 135.7, 135.2, 133.6, 130.3, 129.6, 128.9, 127.9, 127.1, 126.6, 123.9, 123.3, 53.7, 53.0, 52.9, 49.6, 44.3, 33.3, 28.2, 26.4, 25.9; IR (KBr, cm^{-1}) 2957, 2928, 2866, 1735, 1669, 1571, 1434, 1264, 738; HRMS (ESI) m/z: calcd for $C_{26}H_{25}ClO_5$: $[M+H]^+$ = 453.1463; found: 453.1468, 455.1365.



3h

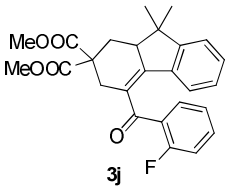
Dimethyl 4-(3-bromobenzoyl)-9,9-dimethyl-9,9a-dihydro-1*H*-fluorene-2,2(3*H*)-dicarboxylate (3h): Yellow solid; m.p. = 170-172 ℃; R_f (20% EtOAc/hexane) = 0.24; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.23 (s, 1 H), 8.04-8.02 (d, *J* = 8.0 Hz, 1 H), 7.71-7.69 (d, *J* = 8.0 Hz, 1 H), 7.35 (t, *J* = 7.6 Hz, 1 H), 7.24-7.21 (d, *J* = 7.6 Hz, 1 H), 7.17 (t, *J* = 7.2 Hz, 1 H), 6.93 (t, *J* = 7.2 Hz, 1 H), 6.81-6.79 (d, *J* = 7.6 Hz, 1 H), 3.81 (s, 3 H), 3.75 (s, 3 H), 3.30-3.25 (d, *J* = 18.4 Hz, 1 H), 2.64-2.51 (m, 3 H), 2.03 (t, *J* = 12.4 Hz, 1 H), 1.44 (s, 3 H), 1.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$):δ ppm 197.4, 171.9, 171.1 155.2, 140.5, 137.8, 136.5, 135.7, 132.5, 130.5, 128.9, 128.4, 127.0, 126.6, 123.9, 123.2, 122.3, 53.7, 53.1, 53.0, 49.6, 44.3, 33.3, 28.1, 26.4, 25.9; IR (KBr, cm^{-1}) 2956, 2927, 2865, 1735, 1666, 1584, 1454, 1267, 738; HRMS (ESI) m/z: calcd for $C_{26}H_{25}BrO_5$: $[M+H]^+$ = 497.0958; found: 497.0963, 499.0949.



3i

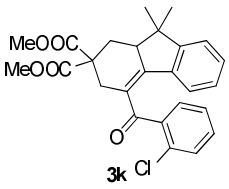
Dimethyl 9,9-dimethyl-4-(2-methylbenzoyl)-9,9a-dihydro-1*H*-fluorene-2,2(3*H*)-dicarboxylate (3i): White solid; m.p. = 128-130 ℃; R_f (20% EtOAc/hexane) = 0.40; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.84-7.83 (d, *J* = 7.6 Hz, 1 H), 7.48 (t, *J* = 6.8 Hz, 1 H), 7.29 (d, *J* = 7.2 Hz, 1 H), 7.22-7.15 (m, 3 H), 7.03-7.01 (d, *J* = 7.6 Hz, 1 H), 6.96-6.92 (m, 1 H), 3.77 (s, 3 H), 3.73 (s, 3 H), 3.28-3.24 (d, *J* = 18.0 Hz, 1 H), 2.65 (s, 3 H), 2.59-2.51 (m,3 H), 2.01 (t, *J* = 12.0 Hz, 1 H), 1.43 (s, 3 H), 1.07 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 200.4, 172.1, 171.1, 155.3, 140.9, 139.8,

136.1, 135.9, 132.1, 132.0, 131.7, 129.3, 128.8, 126.5, 125.9, 124.3, 122.1, 53.7, 52.9, 49.9, 44.3, 33.6, 28.1, 26.4, 25.8, 21.4; IR (KBr, cm^{-1}) 2957, 2927, 2854, 1741, 1664, 1456, 1373, 1241, 1047, 760, 738; HRMS (ESI) m/z: calcd for $C_{27}H_{28}O_5$: $[M+H]^+$ = 432.2010; found: 432.2015.



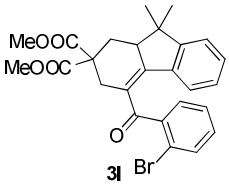
3j

Dimethyl 4-(2-fluorobenzoyl)-9,9-dimethyl-9,9a-dihydro-1*H*-fluorene-2,2(3*H*)-dicarboxylate (3j): White solid; m.p. = 151-153 ℃; R_f (20% EtOAc/hexane) = 0.36; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.90-7.86 (m, 1 H), 7.48-7.42 (m, 1 H), 7.21-7.14 (m, 3 H), 7.11-7.09 (d, J = 7.6 Hz, 1 H), 7.03-6.98 (m, 1 H), 6.94-6.90 (m, 1 H), 3.75(s, 6 H), 3.37-3.33 (d, J = 18.4 Hz, 1 H), 2.69 (dd, J_1 = 3.2 Hz, J_2 = 18.0 Hz, 1 H), 2.60-2.54 (m, 2 H), 2.04-1.99 (m, 1 H), 1.42 (s, 3 H), 1.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 194.9, 172.2, 171.0, 155.5, 142.1, 135.9, 134.6, 134.5, 131.8, 128.9, 128.8, 126.3, 124.4, 124.3, 122.1, 116.8, 116.6, 53.6, 52.9, 52.8, 50.2, 44.5, 32.8, 27.9, 26.3, 25.9; IR (KBr, cm^{-1}) 2956, 2926, 1739, 1664, 1608, 1453, 1241, 1047, 760; HRMS (ESI) m/z: calcd for $C_{26}H_{25}FO_5$: $[M+H]^+$ = 437.1759; found: 437.1761.



3k

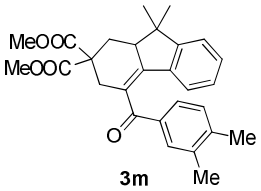
Dimethyl 4-(2-chlorobenzoyl)-9,9-dimethyl-9,9a-dihydro-1*H*-fluorene-2,2(3*H*)-dicarboxylate (3k): White solid; m.p. = 140-142 ℃; R_f (20% EtOAc/hexane) = 0.36; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.64 (dd, J_1 = 1.2 Hz, J_2 = 7.6 Hz, 1 H), 7.63-7.32 (m, 3 H), 7.29-7.28 (d, J = 1.2 Hz, 1 H), 7.26-7.18 (m, 2 H), 7.00-6.96 (m, 1 H), 3.74-3.73 (d, J = 2.8 Hz, 6 H), 3.33-3.29 (d, J = 17.6 Hz, 1 H), 2.64-2.54 (m, 3 H), 1.97 (t, J = 13.6 Hz, 1 H), 1.42 (s, 3 H), 1.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 196.4, 172.2, 170.9, 155.9, 145.8, 137.7, 135.9, 132.5, 132.2, 131.1, 130.8, 129.4, 127.9, 126.8, 126.3, 125.5, 122.0, 53.7, 52.9, 52.8, 50.9, 44.6, 33.2, 27.9, 26.6, 25.9; IR (KBr, cm^{-1}) 2957, 2927, 2858, 1737, 1672, 1435, 1242, 1046, 762; HRMS (ESI) m/z: calcd for $C_{26}H_{25}ClO_5$: $[M+H]^+$ = 453.1463; found: 453.1464, 455.1456.



3l

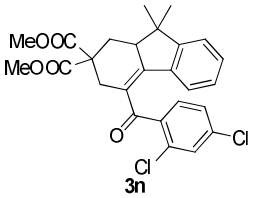
Dimethyl 4-(2-bromobenzoyl)-9,9-dimethyl-9,9a-dihydro-1*H*-fluorene-2,2(3*H*)-dicarboxylate (3l) : White solid; m.p. = 129-131 ℃; R_f (20% EtOAc/hexane) = 0.33; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.62-7.58 (m, 2 H), 7.45-7.43 (d, J = 8.0 Hz, 1 H), 7.32 (dd, J_1 = 1.2 Hz, J_2 = 7.2 Hz, 1 H), 7.30-7.26 (m, 1 H), 7.23-7.22 (d, J = 3.6 Hz, 2 H), 7.03-6.99 (d, J = 2.8 Hz, 1 H), 3.74-3.73 (d, J = 1.6 Hz, 6 H), 3.31-3.27 (m, 1 H), 2.62-2.54 (m, 3 H), 2.04-1.94 (m, 1 H), 1.42 (s, 3 H), 1.09 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 196.8, 172.2, 171.0, 156.0, 146.6, 139.6, 135.9, 134.1, 132.2, 131.0, 129.5, 127.3, 126.4, 125.7, 122.0, 120.7, 53.7, 53.0, 52.9, 51.0, 44.6, 33.3, 27.8, 26.7, 25.9; IR (KBr, cm^{-1}) 2956, 2926, 2855, 1735, 1672, 1432, 1262, 738; HRMS (ESI) m/z:

calcd for $C_{26}H_{25}BrO_5$: $[M+H]^+$ = 497.0958; found: 497.0965. 499.0956.



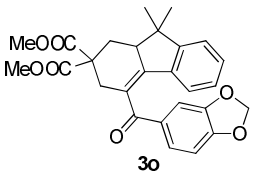
3m

Dimethyl 4-(3,4-dimethylbenzoyl)-9,9-dimethyl-9,9a-dihydro-1*H*-fluorene-2,2(3-*H*)-dicarboxylate (3m) : Yellow oil; R_f (20% EtOAc/hexane) = 0.40; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.90 (s, 1 H), 7.85-7.83 (d, *J* = 8.0 Hz, 1 H), 7.21 (t, *J* = 7.6 Hz, 1 H), 7.16-7.12 (m, 1 H), 6.93-6.86 (m, 2 H), 3.79 (s, 3 H), 3.73 (s, 3 H), 3.29-3.25 (d, *J* = 18.4 Hz, 1 H), 2.66-2.51 (m, 3 H), 2.31 (s, 3 H), 2.30 (s, 3 H), 2.04 (t, *J* = 12.0 Hz, 1 H), 1.44 (s, 3 H), 1.07 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 198.8, 172.1, 171.1, 155.0, 143.4, 138.6, 137.2, 136.1, 133.8, 130.8, 130.2, 128.4, 128.3, 127.7, 126.6, 123.9, 122.1, 53.8, 52.9, 52.8, 49.3, 44.2, 33.6, 28.2, 26.4, 25.9, 20.1, 19.7; IR (KBr, cm^{-1}) 2956, 2926, 2865, 1736, 1659, 1604, 1453, 1265, 737; HRMS (ESI) m/z: calcd for $C_{28}H_{30}O_5$: $[M+H]^+$ = 447.2166; found: 447.2170.



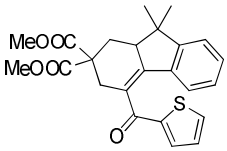
3n

Dimethyl 4-(2,4-dichlorobenzoyl)-9,9-dimethyl-9,9a-dihydro-1*H*-fluorene-2,2(3*H*)-dicarboxylate (3n): Yellow oil; R_f (20% EtOAc/hexane) = 0.47; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.63-7.61 (d, *J* = 8.4 Hz, 1 H), 7.42-7.41 (d, *J* = 1.6 Hz, 1 H), 7.31-7.29 (d, *J* = 8.0 Hz, 1 H), 7.27 (dd, J_1 = 2.0 Hz, J_2 = 6.4 Hz, 1 H), 7. 23-7.22 (d, *J* = 4.0 Hz, 2 H), 7.03-6.99 (m, 1 H), 3.75 (s, 3 H), 3.74 (s, 3 H), 3.31-3.27 (d, *J* = 17.6 Hz, 1 H), 2.61-2.53 (m, 3 H), 2.00-1.93 (m, 1 H), 1.42 (s, 3 H), 1.07 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 195.3, 172.0, 170.9, 156.0, 146.0, 137.9, 135.9, 135.7, 133.6, 132.2, 130.8, 129.6, 127.4, 127.2, 126.4, 125.3, 122.1, 53.6, 53.0, 52.9, 50.9, 44.6, 33.1, 27.8, 27.0, 26.6, 25.9; IR (KBr, cm^{-1}) 2957, 2926, 2855, 1736, 1583, 1463, 1262, 1102, 738; HRMS (ESI) m/z: calcd for $C_{26}H_{24}Cl_2O_5$: $[M+H]^+$ = 487.1074; found: 487.1080, 489.1037.



3o

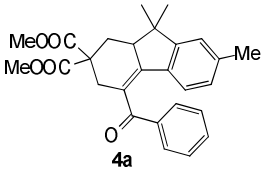
Dimethyl 4-(benzo[d][1,3]dioxole-5-carbonyl)-9,9-dimethyl-9,9a-dihydro-1*H*-fluorene-2,2(-3*H*)-dicarboxylate (3o): White solid; m.p. = 147-149 ℃; R_f (20% EtOAc/hexane) = 0.09; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.76 (dd, J_1 = 1.4 Hz, J_2 = 8.4 Hz, 1 H), 7.61-7.60 (d, *J*=1.6 Hz, 1 H), 7.22-7.20 (d, *J* =7.2 Hz, 1 H), 7.16 (t, *J* = 7.2 Hz, 1 H), 6.96-6.92 (m, 1 H), 6.87-6.85 (d, *J* = 8.0 Hz, 2 H), 6.06-6.05 (d, *J* = 1.6 Hz, 2 H), 3.79 (s, 3 H), 3.75 (s, 3 H), 3.26-3.22 (d, *J* = 18.0 Hz, 1 H), 2.67-2.48 (m, 3 H), 2.07-2.00 (m, 1 H), 1.43 (s, 3 H), 1.06 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 197.0, 172.0, 171.2, 155.0, 152.4, 148.4, 138.4, 135.9, 130.8, 128.5, 127.9, 127.0, 126.6, 123.8, 122.2, 108.7, 108.3, 101.9, 53.7, 52.9, 52.8, 49.2, 44.1, 33.6, 28.1, 26.4, 25.9; IR (KBr, cm^{-1}) 2956, 2926, 2865, 1735, 1654, 1441, 1259, 1039, 758, 737; HRMS (ESI) m/z: calcd for $C_{27}H_{26}O_7$: $[M+H]^+$ = 463.1751; found: 463.1757.



3p

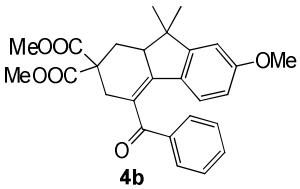
Dimethyl 9,9-dimethyl-4-(thiophene-2-carbonyl)-9,9a-dihydro-1*H*-fluorene-2,2(3*H*)-dicarboxylate (3p): Yellow oil; R_f (20% EtOAc/hexane) = 0.16; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.91-7.90 (d, J = 3.2 Hz, 1 H), 7.70-7.69 (d, J = 4.8 Hz, 1 H), 7.23-7.19 (m, 1 H), 7.18-7.15 (m, 1 H), 7.11 (t, J = 4.4 Hz, 1 H), 6.97 (t, J = 2.4 Hz, 2 H), 3.79 (s, 3 H), 3.76 (s, 3 H), 3.39-3.34 (d, J = 17.6 Hz, 1 H), 2.70 (dd, J_1 = 3.6 Hz, J_2 = 18.0 Hz, 1 H), 2.58 (dd, J_1 = 4.0 Hz, J_2 = 12.4 Hz, 1 H), 2.52-2.48 (m, 1 H), 2.05-1.99 (m, 1 H), 1.43 (s, 3 H), 1.07 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 191.1, 172.0, 171.2, 155.1, 143.4, 139.3, 135.8, 135.3, 135.0, 128.7, 128.6, 127.6, 126.7, 124.1, 122.2, 53.7, 53.0, 52.9, 49.5, 44.2, 33.6, 28.1, 26.3, 25.9; IR (KBr, cm^{-1}) 2957, 2927, 2855, 1735, 1639, 1411, 1265, 737; HRMS (ESI) m/z: calcd for $C_{24}H_{24}O_5S$: $[M+H]^+$ = 425.1417; found: 425.1422.

8. Characterization Data of Products 4a-4n:



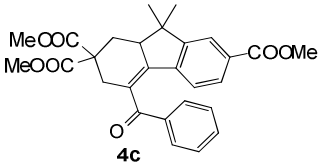
4a

Dimethyl 4-benzoyl-7,9,9-trimethyl-9,9a-dihydro-1*H*-fluorene-2,2(3*H*)-dicarboxylate (4a): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.09-8.07 (m, 2 H), 7.56 (t, J = 7.2 Hz, 1 H), 7.46 (t, J = 7.2 Hz, 2 H), 7.01 (s, 1 H), 6.71 (s, 2 H), 3.78 (s, 3 H), 3.74 (s, 3 H), 3.31-3.26 (d, J = 17.6 Hz, 1 H), 2.67-2.50 (m, 3 H), 2.26 (s, 3 H), 2.04 (t, J = 12.4 Hz, 1 H), 1.42 (s, 3 H), 1.07 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 199.0, 172.1, 171.2, 155.3, 139.5, 138.7, 136.1, 133.5, 133.2, 129.7, 128.8, 127.5, 126.6, 123.8, 122.8, 53.8, 52.9, 49.7, 44.1, 33.4, 28.2, 26.4, 25.8, 21.5. HRMS (ESI) m/z: calcd for $C_{27}H_{28}O_5$: $[M+H]^+$ = 433.2010; found: 433.2019.



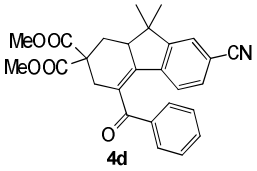
4b

Dimethyl 4-benzoyl-7-methoxy-9,9-dimethyl-9,9a-dihydro-1*H*-fluorene-2,2(3*H*)-dicarboxylate (4b): Yellow oil; ^{1}HNMR (400 MHz, $CDCl_3$): δ ppm 8.07-8.05 (m, 2 H), 7.56 (t, J = 7.2 Hz, 1 H), 7.45 (t, J = 7.6 Hz, 2 H), 6.77-6.72 (m, 2 H), 6.44 (dd, J_1 = 2.4 Hz, J_2 = 8.4 Hz, 1 H), 3.79 (s, 3 H), 3.74-3.73 (d, J = 2.4 Hz, 6 H), 3.31-3.27 (d, J = 18.0 Hz, 1 H), 2.66-2.51 (m, 2 H), 2.04 (t, J = 11.6 Hz, 1 H), 1.41 (s, 3 H), 1.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 199.0, 172.1, 171.2, 160.4, 157.3, 139.5, 136.3, 133.5, 129.7, 128.8, 125.4, 125.2, 112.4, 107.6, 55.3, 53.8, 52.9, 52.8, 50.0, 44.3, 33.4, 28.2, 26.3, 25.8. HRMS (ESI) m/z: calcd for $C_{27}H_{28}O_6$: $[M+H]^+$=449.1959; found: 449.1964.



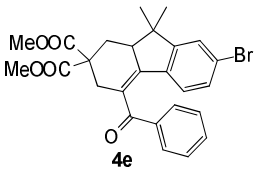
4c

Trimethyl 4-benzoyl-9,9-dimethyl-1*H*-fluorene-2,2,7(3*H*,9*H*,9a*H*)-tricarboxylate (4c): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.10-8.08 (m, 2 H), 7.88-7.87 (d, *J* = 1.2 Hz, 1 H), 7.61-7.58 (m, 2 H), 7.48 (t, *J* = 7.6 Hz, 2 H), 6.88-6.86 (d, *J* = 8.0 Hz, 1 H), 3.86 (s, 3 H), 3.81 (s, 3 H), 3.75 (s, 3 H), 3.35-3.30 (d, *J* = 18.4 Hz, 1 H), 2.70-2.55 (m, 3 H), 2.05 (t, *J* = 11.6 Hz, 1 H), 1.47 (s, 3 H), 1.10 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 198.4, 171.8, 171.0, 166.9, 155.2, 140.4, 138.3, 135.6, 133.9, 130.6, 130.0, 129.7, 129.0, 128.3, 123.7, 123.6, 53.6, 53.0, 52.9, 52.1, 49.5, 44.3, 33.6, 28.1, 26.3, 25.9. HRMS (ESI) m/z: calcd for $C_{28}H_{28}O_7$: $[M+H]^+$=477.1908; found: 477.1914.



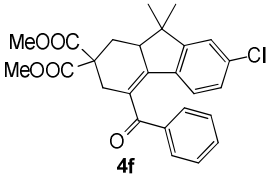
4d

Dimethyl 4-benzoyl-7-cyano-9,9-dimethyl-9,9a-dihydro-1H-fluorene-2,2(3H)-dicarboxylate (4d): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.10-8.08 (d, *J* = 7.2 Hz, 2 H), 7.62 (t, *J* = 7.2 Hz, 1 H), 7.53-7.47 (m, 3 H), 7.19 (dd, J_1 = 1.2 Hz, J_2 = 8.0 Hz, 1 H), 6.92-6.90 (d, *J* = 8.0 Hz, 1 H), 3.81 (s, 3 H), 3.75 (s, 3 H), 3.34-3.30 (d, *J* = 18.4 Hz, 1 H), 2.70-2.54 (m, 3 H), 2.06-2.00 (m, 1 H), 1.46 (s, 3 H), 1.09 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 198.0, 171.6, 170.9, 155.7, 140.4, 137.5, 135.4, 134.2, 132.2, 130.7, 129.7, 129.1, 126.2, 124.4, 119.0, 111.7, 53.5, 53.1, 53.0, 49.2, 44.5, 33.7, 27.9, 26.2, 25.7. HRMS (ESI) m/z: calcd for $C_{27}H_{25}NO_5$: $[M+H]^+$=444.1805; found: 444.1811.



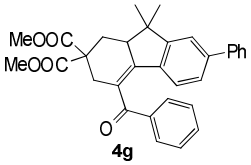
4e

Dimethyl 4-benzoyl-7-bromo-9,9-dimethyl-9,9a-dihydro-1*H*-fluorene-2,2(3*H*)-dicarboxylate (4e): Yellow oil;^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.07-8.05 (m, 2 H), 7.59 (t, *J* = 7.2 Hz, 1 H), 7.48 (t, *J* = 7.6 Hz, 2 H), 7.33-7.32 (d, *J* = 1.6 Hz, 1 H), 7.02 (dd, J_1 = 1.6 Hz, J_2 = 8.4 Hz, 1 H), 6.70-6.68 (d, *J* = 8.4 Hz, 1 H), 3.80 (s, 3 H), 3.74 (s, 3 H), 3.31-3.26 (d, *J* = 18.4 Hz, 1 H), 2.66-2.52 (m, 3 H), 2.02 (t, *J* = 11.6 Hz, 1 H), 1.42 (s, 3 H), 1.68 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 198.5, 171.8, 171.0, 157.2, 138.3, 135.8, 134.9, 133.8, 129.8, 129.7, 129.0, 128.7, 125.8, 125.4, 122.7, 53.6, 53.0, 52.9, 49.5, 44.5, 33.5, 28.1, 26.3, 25.7. HRMS (ESI) m/z: calcd for $C_{26}H_{25}BrO_5$: $[M+H]^+$=497.0958; found: 497.0964, 499.0956.



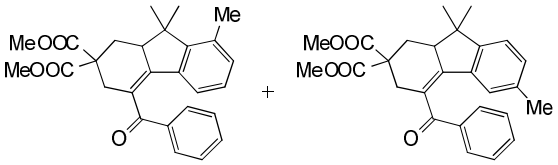
4f

Dimethyl 4-benzoyl-7-chloro-9,9-dimethyl-9,9a-dihydro-1*H*-fluorene-2,2(3*H*)-dicarboxylate (4f): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.07-8.05 (m, 2 H), 7.59 (t, *J* = 7.2 Hz, 1 H), 7.48 (t, *J* = 7.6 Hz, 2 H), 7.17-7.16 (d, *J* = 1.6 Hz, 1 H), 6.87 (dd, J_1 = 2.0 Hz, J_2 = 8.0 Hz, 1 H), 6.76-6.74 (d, *J* = 8.4 Hz, 1 H), 3.80 (s, 3 H), 3.74 (s, 3 H), 3.32-3.27 (d, *J* = 18.0 Hz, 1 H), 2.67-2.52(m, 3 H), 2.03 (t, *J* = 11.6 Hz, 1 H), 1.42 (s, 3 H), 1.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 198.5, 171.8, 171.0, 156.9, 138.3, 135.8, 134.5, 134.4, 133.8, 129.7, 129.0, 128.5, 126.9, 125.1, 122.7, 53.6, 53.0, 52.9, 49.6, 44.5, 33.5, 28.1, 26.2, 25.7. HRMS (ESI) m/z: calcd for $C_{26}H_{25}ClO_5$: $[M+H]^+$=453.1463; found: 453.1469, 455.1480.



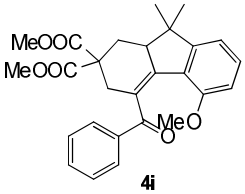
4g

Dimethyl 4-benzoyl-9,9-dimethyl-7-phenyl-9,9a-dihydro-1*H*-fluorene-2,2(3*H*)-dicarboxylate (4g): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.13-8.11 (d, *J* = 7.6 Hz, 2 H), 7.58 (t, *J* = 7.2 Hz, 1 H), 7.49 (t, *J* = 8.0 Hz, 4 H), 7.41-7.36 (m, 3 H), 7.32-7.25 (m, 1 H), 7.16-7.14 (d, *J* = 8.0 Hz, 1 H), 6.91-6.89 (d, *J* = 8.4 Hz, 1 H), 3.80 (s, 3 H), 3.75 (s, 3 H), 3.34-3.30 (d, *J* = 17.6 Hz, 1 H), 2.70-2.57 (m, 3 H), 2.11-2.04 (m, 1 H), 1.49 (s, 3 H), 1.13 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 198.8, 172.0, 171.2, 155.8, 141.7, 141.0, 139.1, 136.0, 135.1, 133.7, 129.8, 128.9, 128.7, 127.9, 127.3, 127.1, 125.8, 124.3, 120.9, 53.8, 53.0, 52.9, 49.7, 44.3, 33.5, 28.2, 26.5, 25.9. HRMS (ESI) m/z: calcd for $C_{32}H_{30}O_5$: $[M+ Na]^+$ =517.1985; found: 517.1987.



4h:4h'

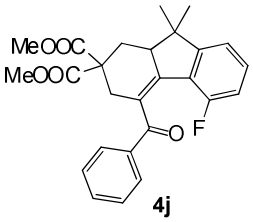
Dimethyl 4-benzoyl-8,9,9-trimethyl-9,9a-dihydro-1*H*-fluorene-2,2(3*H*)-dicarbo-xylate (4h); Dimethyl 4-benzoyl-6,9,9-trimethyl-9,9a-dihydro-1*H*-fluorene-2,2(3H)-dicarboxylate (4h′): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.07-8.06, (d, *J* = 2.0 Hz, 2 H), 7.58-7.54 (m, 1 H), 7.48-7.44 (m, 2 H), 7.10-7.08 (d, *J* = 8.0 Hz, 0.5 H), 6.97-6.95 (d, *J* = 7.6 Hz, 0.5 H), 6.90-6.88 (d, *J* = 7.6 Hz, 0.5 H), 6.81-6.77 (m, 0.5 H), 6.72-6.70 (d, *J* = 7.6 Hz, 0.5 H), 6.64 (s, 0.5 H), 3.79 (s, 1.5 H), 3.78 (s, 1.5 H), 3.74 (s, 3 H), 3.32-3.27 (d, *J* = 18.0 Hz, 1 H), 2.70-2.50 (m, 3 H), 2.39 (s, 1.5 H), 2.07-2.00 (m, 2.5 H), 1.54 (s, 1.5 H), 1.41 (s, 1.5 H), 1.15 (s, 1.5 H), 1.06 (s, 1.5 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 199.1, 198.9, 172.1, 171.1, 152.4, 151.4, 139.8, 139.3, 136.5, 136.2, 136.1, 136.0, 135.9, 133.8, 133.6, 133.5, 131.5, 129.7, 129.6, 129.5, 128.9, 128.8, 127.5, 127.2, 126.6, 124.7, 122.1, 121.9, 53.7, 52.9, 49.8, 49.7, 45.4, 43.8, 33.6, 33.5, 28.2, 27.7, 26.4, 26.2, 26.0, 23.1, 21.1, 19.5. HRMS (ESI) m/z: calcd for $C_{27}H_{28}ClO_5$: $[M+H]^+$=433.2010; found: 433.2019.



4i

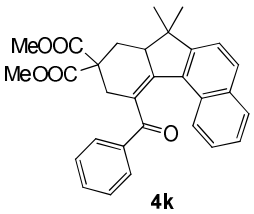
Dimethyl 4-benzoyl-5-methoxy-9,9-dimethyl-9,9a-dihydro-1*H*-fluorene-2,2(3*H*)-dicarboxyl-ate (4i): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.08 (s, 2 H), 7.50-7.48 (d, *J* = 7.2 Hz, 1

H), 7.45-7.35 (d, *J* = 7.2 Hz, 2 H), 7.15 (t, *J* = 7.6 Hz, 1 H), 6.84-6.82 (d, *J* = 7.2 Hz, 1 H), 6.46-6.44 (d, *J*=8.4 Hz, 1 H), 3.79 (s, 3 H), 3.72 (s, 3 H), 3.40-3.36 (d, *J* = 17.6 Hz, 1 H), 3.08 (s, 3 H), 2.57-2.50 (m, 3 H), 2.01 (t, *J* = 13.6 Hz, 4 H), 1.41 (s, 3 H), 1.12 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$):δ ppm 197.7, 172.2, 171.2, 156.9, 154.5, 136.8, 132.3, 130.2, 129.5, 128.1, 125.1, 114.3, 108.6, 53.6, 53.2, 52.8, 50.3, 44.7, 33.6, 28.1, 26.0, 25.9. HRMS (ESI) m/z: calcd for $C_{27}H_{28}O_6$: $[M+H]^+$=449.1959; found: 449.1965.



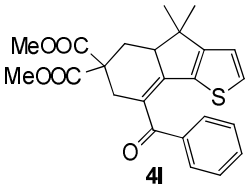
4j

Dimethyl 4-benzoyl-5-fluoro-9,9-dimethyl-9,9a-dihydro-1*H*-fluorene-2,2(3*H*)-dicarboxylate (4j): Yellow solid; m.p. = 166-168 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.08-8.06 (m, 2 H), 7.54 (t, *J* = 7.2 Hz, 1 H), 7.45 (t, *J* = 7.6 Hz, 2 H), 7.18-7.13 (m, 1 H), 7.02-7.00 (d, *J* = 7.6 Hz, 1 H), 6.64 (dd, J_1 = 8.0 Hz, J_2 = 9.6 Hz, 1 H), 3.81 (s, 3 H), 3.73 (s, 3 H), 3.45-3.39 (m, 1 H), 2.58-2.53 (m, 3 H), 2.02 (t, *J* = 13.2 Hz, 1 H), 1.44 (s, 3 H), 1.12 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 198.0, 171.9, 171.0, 158.6, 157.7, 156.1, 136.2, 135.9, 133.0, 130.5, 130.4, 129.7, 128.4, 123.8, 117.8, 53.5, 53.0, 52.9, 50.2, 45.1, 45.0, 33.5, 28.0, 25.9. HRMS (ESI) m/z: calcd for $C_{26}H_{25}FO_5$: $[M+H]^+$=437.1759; found: 437.1754.



4k

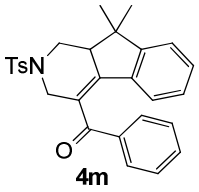
Dimethyl 11-benzoyl-7,7-dimethyl-7a,8-dihydro-7*H*-benzo[c]fluorene-9,9(10*H*)-dicarboxylate (4k): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.86-7.84 (d, *J* = 7.6 Hz, 2H), 7.62-7.54 (m, 3H), 7.43 (t, *J* = 7.6 Hz, 1 H), 7.35 (t, *J* = 7.2 Hz, 1 H), 7.23 (t, *J* = 7.6 Hz, 3 H), 7.04 (t, *J* = 7.6 Hz, 1 H), 3.79 (s, 3H), 3.76 (s, 3H), 3.60-3.56 (d, *J* = 16.8 Hz, 1H), 3.08 (t, *J* = 7.6 Hz, 1 H), 2.80-2.75 (m, 2H), 2.11 (dd, J_1 = 10.8 Hz, J_2 = 13.2 Hz, 1 H), 1.63 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 200.7, 172.3, 170.6, 144.6, 139.2, 137.4, 133.5, 132.7, 132.6, 131.6, 129.1, 129.0, 128.3, 127.7, 126.5, 126.3, 125.9, 124.7, 121.6, 53.6, 53.0, 52.7, 43.3, 40.5, 34.9, 30.4, 25.7, 25.6. HRMS (ESI) m/z: calcd for $C_{30}H_{28}O_5$: M+H=469.2010; found: 469.2015.



4l

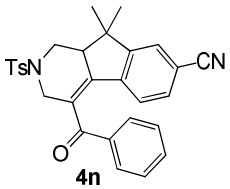
Dimethyl 8-benzoyl-4,4-dimethyl-4a,5-dihydro-4H-indeno[1,2-b]thiophene-6,6(-7H)-dicarb-oxylate (4l): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.86-7.84 (m, 2 H), 7.55 (t, *J* = 7.2 Hz, 1 H), 7.47 (t, *J* = 7.2 Hz, 2 H), 7.23-7.22 (d, *J* = 5.2 Hz, 1H), 6.80-6.79 (d, *J* = 5.2 Hz, 1 H), 3.78 (s, 3 H), 3.75 (s, 3 H), 3.20-3.15 (m, 1 H), 2.94-2.89 (m, 1 H), 2.11-2.04 (m, 1 H), 1.39 (s, 3 H), 1.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 197.4, 172.0, 171.2, 164.4, 138.6, 137.2,

133.6, 132.5, 129.4, 129.1, 128.7, 122.2, 120.0, 55.0, 54.1, 52.9, 42.4, 33.1, 28.3, 26.3, 25.9. HRMS (ESI) m/z: calcd for $C_{24}H_{24}O_5S$: $[M+H]^+$=425.1417; found: 425.1430.



4m

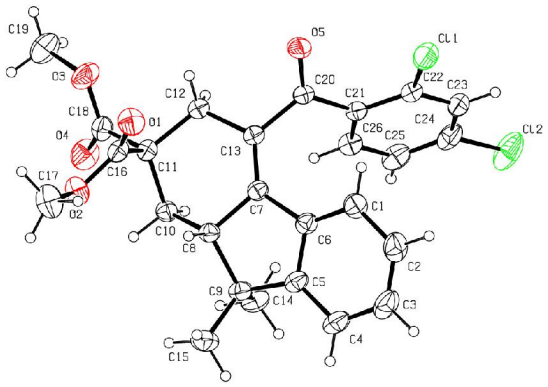
(9,9-dimethyl-2-tosyl-2,3,9,9a-tetrahydro-1*H*-indeno[2,1-c]pyridin-4-yl)(phenyl)methanone (4m): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.90-7.88 (m, 2 H), 7.73-7.71 (d, *J* = 8.4 Hz, 2 H), 7.55 (t, *J* = 7.2 Hz, 1 H), 7.40 (t, *J* = 8.0 Hz, 2 H), 7.34-7.32 (d, *J* = 8.0 Hz, 2 H), 7.21-7.14 (m, 2 H), 6.89-6.85 (m, 1 H), 6.77-6.76 (d, *J* = 7.6 Hz, 1 H), 4.49 (dd, J_1 = 2.4 Hz, J_2 = 16.8 Hz, 1 H), 4.21 (dd, J_1 = 5.2 Hz, J_2 = 11.2 Hz, 1 H), 3.50 (dd, J_1 = 3.6 Hz, J_2 = 17.2 Hz, 1 H), 3.01-2.95 (m, 1 H), 2.65 (t, *J* = 10.8 Hz, 1 H), 2.42 (s, 3 H), 1.49 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 196.8, 155.0, 143.8, 140.8, 135.8, 135.2, 133.9, 133.7, 129.9, 129.5, 129.3, 129.0, 127.6, 126.7, 125.5, 124.6, 122.3, 51.5, 46.4, 43.9, 43.8, 26.5, 21.5. HRMS (ESI) m/z: calcd for $C_{28}H_{27}NO_5S$: $[M+H]^+$=458.1784; found: 458.1779.

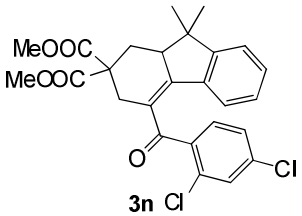


4n

4-benzoyl-9,9-dimethyl-2-tosyl-2,3,9,9a-tetrahydro-1*H*-indeno[2,1-c]pyridine-7-carbonitrile (4n): White solid; m.p. = 164-166 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.90-7.88 (d, *J* = 7.2 Hz, 2H), 7.22-7.20 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 1 H), 7.47-7.43 (m, 3H), 7.35-7.32 (d, *J* = 8.0 Hz, 2H), 7.18 (dd, J_1 = 1.2 Hz, J_2 = 8.0 Hz, 1 H), 6.87-6.85 (d, *J* = 8.0 Hz, 1H), 4.50 (dd, J_1 = 2.8 Hz, J_2 = 17.6 Hz, 1 H), 4.23 (dd, J_1 = 5.6 Hz, J_2 = 11.2 Hz, 1 H), 3.52 (dd, J_1 = 4.0 Hz, J_2 = 17.6 Hz, 1 H), 3.05-3.00 (m, 1H), 2.64 (t, *J* = 10.8 Hz, 1 H), 2.43 (s, 3H), 1.54 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 195.9, 155.5, 144.1, 139.6, 135.3, 134.5, 133.6, 130.8, 129.9, 129.8, 129.4, 129.2, 127.6, 126.3, 124.9, 118.7, 112.5, 51.2, 46.5, 44.1, 43.5, 26.2, 21.5. HRMS (ESI) m/z: calcd for $C_{29}H_{26}N_2O_5S$: $[M+H]^+$=483.1736; found: 483.1739.

9. The crystal structure of product 3n:





3n

Datablock:

Bond precision: C-C = 0.0033 A Wavelength=1.54180

Cell: a=7.9958(3) b=15.4197(5) c=19.3202(6)

alpha=90 beta=91.490(3) gamma=90

Temperature: 294K

	Calculated	Reported
Volume	2381.24(14)	2381.25(14)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2bc
Moiety formula	C26 H24 Cl2 O5	C26 H24 Cl2 O5
Sum formula	C26 H24 Cl2 O5	C26 H24 Cl2 O5
Mr	487.35	487.35
Dx,g cm-3	1.359	1.359
Z	4	4
Mu (mm-1)	2.747	2.747
F000	1016.0	1016.0
F000'	1021.71	
h,k,lmax	9,18,23	9,18,23
Nref	4573	4548
Tmin,Tmax	0.461,0.517	0.862,1.000
Tmin'	0.406	

Correction method= MULTI-SCAN

Data completeness= 0.995 Theta(max)= 70.702

R(reflections)= 0.0546(3747) wR2(reflections)= 0.1670(4548)

S = 1.042 Npar= 302

10. References

1. (a) C. J. Forsyth, J. Clardy, *J. Am. Chem. Soc.* 1990, **112**, 3497. (b) C. Nieto-Oberhuber, P. Pérez-Galán, E. Herrero-Gómez, T. Lauterbach, C. Rodríguez, S. López, C. Bour, A. Rosellón, D. J. Cárdenas, A. M. Echavarren, *J. Am. Chem. Soc.* 2008, **130**, 269.

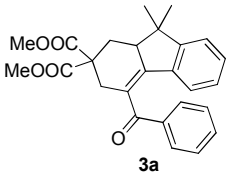
2. (a) W. D. Jones, *Acc. Chem. Res.* 2003, **36**, 140; (b) G.-B. Deng, Z.-Q. Wang, J.-D. Xia, P.-C. Qian, R.-J. Song, M. Hu, L.-B. Gong, J.-H. Li, *Angew. Chem. Int. Ed.* 2013, **52**, 1535.; (c) Y. Meng, L.-N. Guo, H. Wang, X.-H. Duan, *Chem. Commun.* 2013, **49**, 7540.

3. J. Karthikeyan, R. Haridharan, C.-H. Cheng, *Angew. Chem. Int. Ed.* 2012, **51**, 12343.

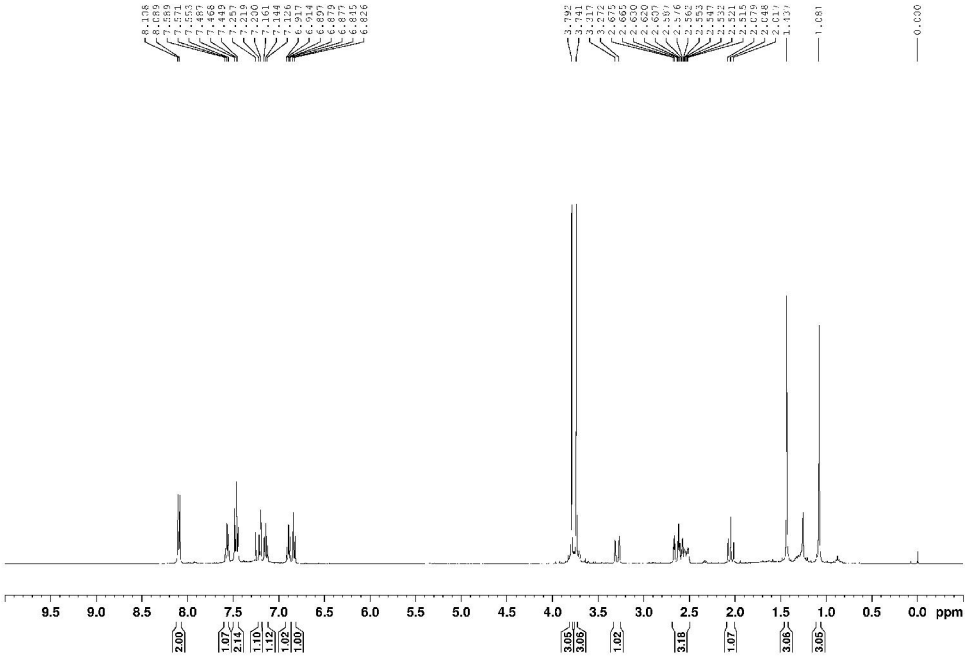
4. D_5-bromobenzene were purchased from Aldrich.

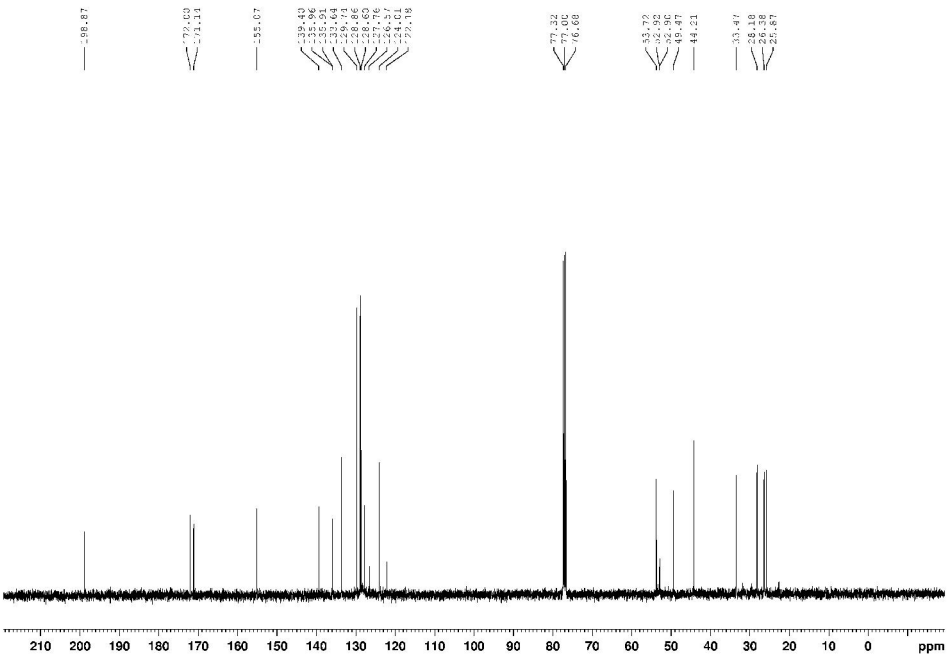
5. C. Pétrier, A. L. Gemal, J.-L. Luche, *Tetrahedron Letters*, **23**, 3361.

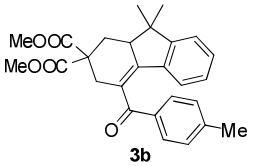
10. ^{1}H NMR and ^{13}C NMR Spectra of the Products 3a-3p:



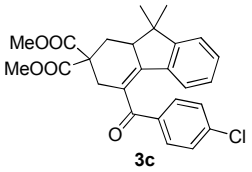
3a



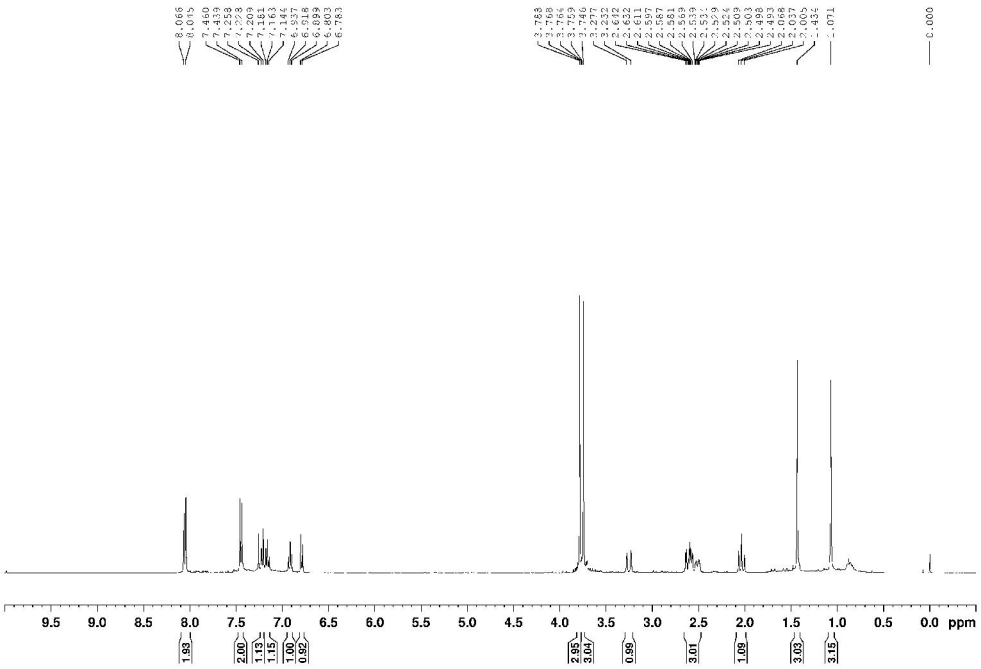


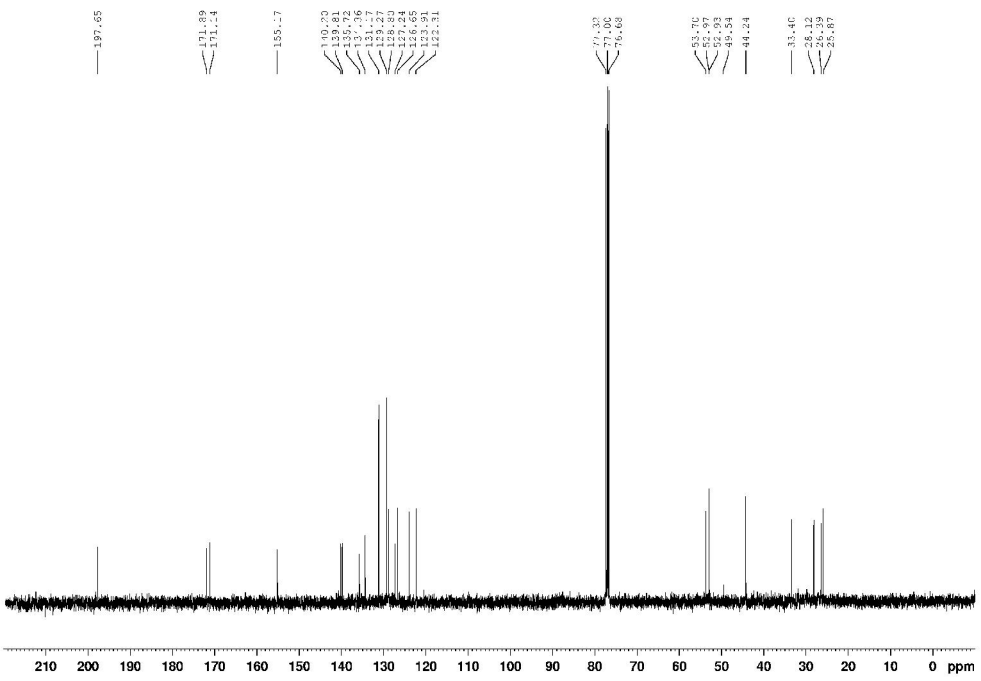


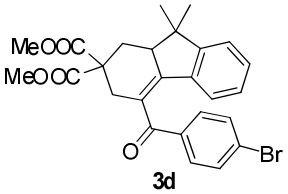
3b



3c



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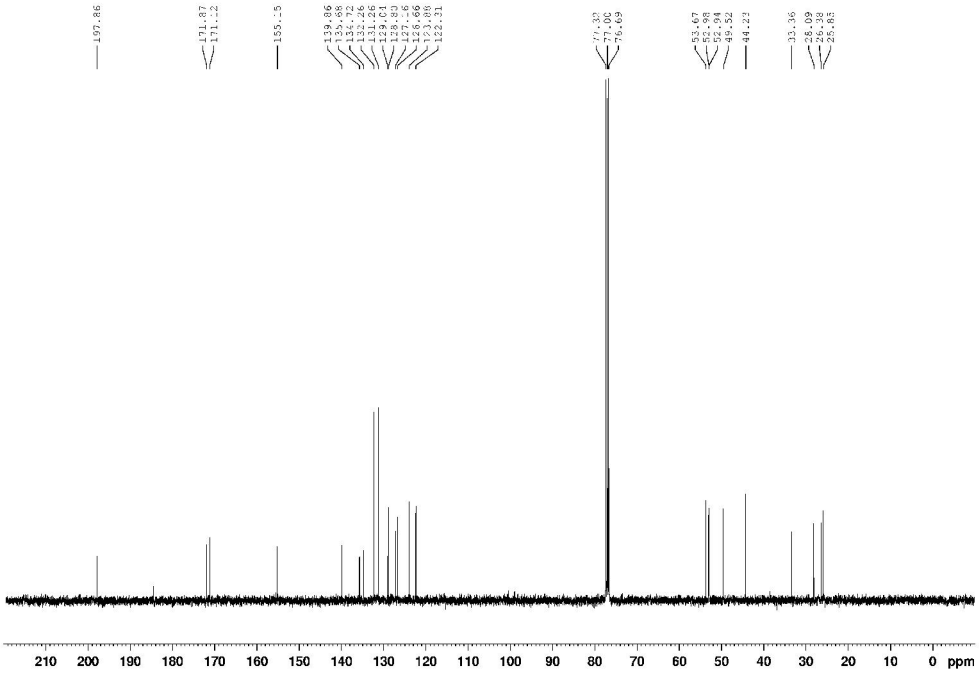
MeOOC
O
Br

3d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171.22
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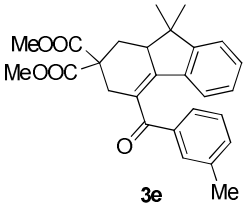
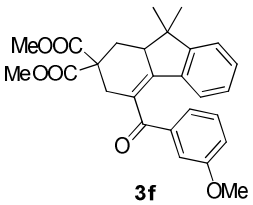
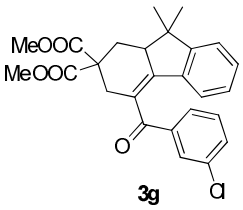
139.06
132.72
132.26
131.26
129.01
128.83
127.16
126.66
123.00
122.31
77.32
77.00
76.69
53.67
52.98
52.80
49.52
44.22
33.36
28.09
26.39
25.88
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



3e



3f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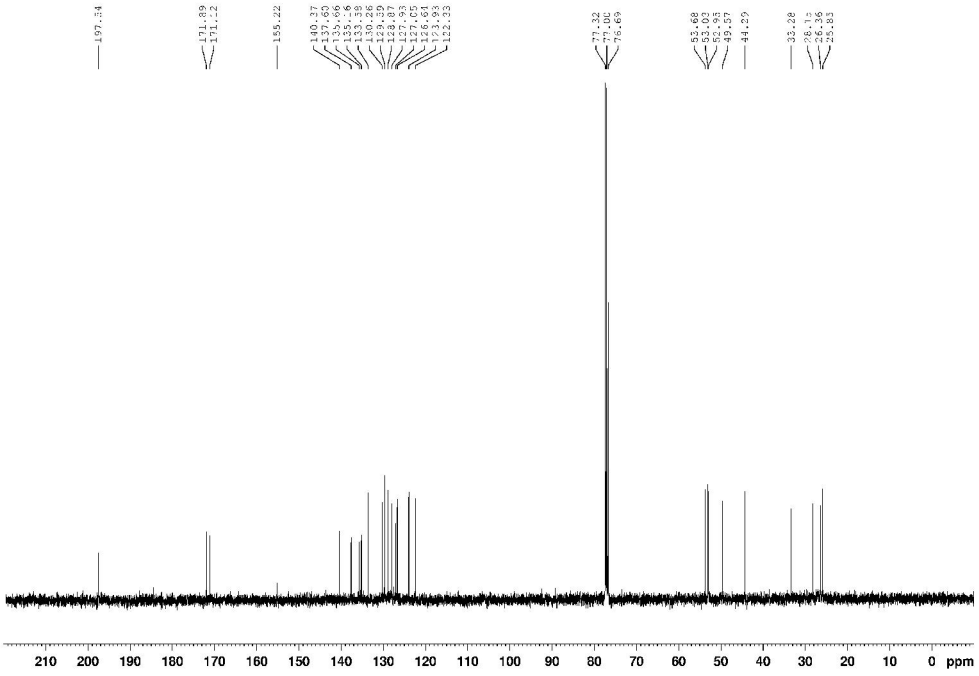
MeOOC
O
Cl

3g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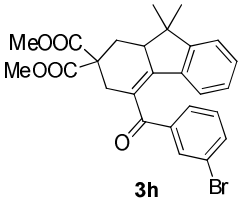
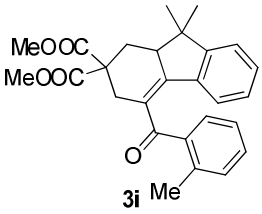
130.26
129.39
128.87
127.93
127.65
127.04
125.93
122.33
77.32
77.00
76.68
63.68
63.02
62.86
49.57
44.29
33.28
26.13
25.36
25.03
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



3h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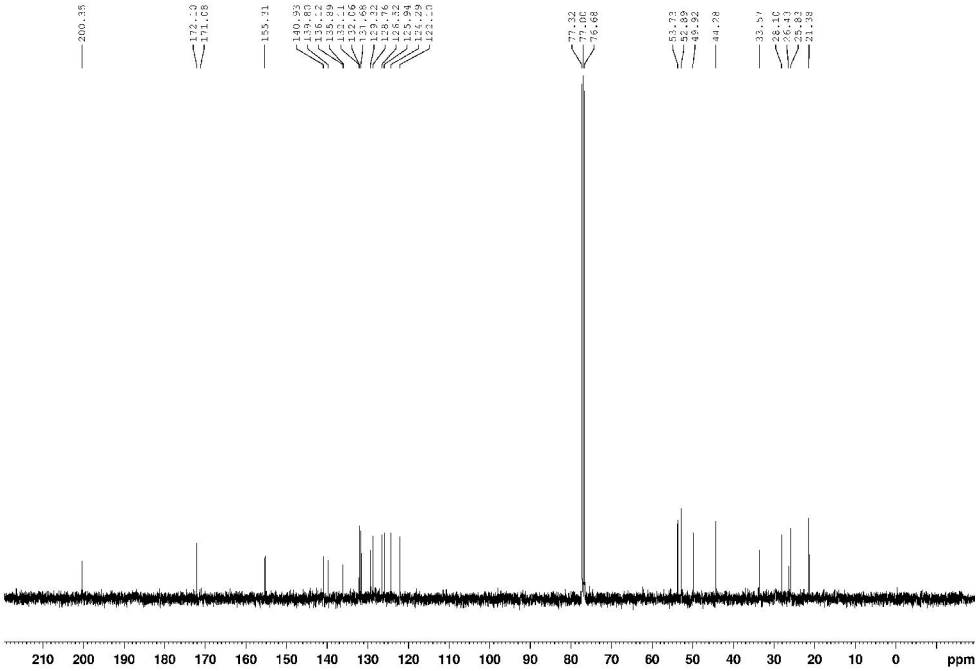
O
Me

3i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126.52
125.94
124.29
122.10
77.32
77.00
76.68
53.73
52.89
49.92
44.29
33.57
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26.10
25.83
21.38
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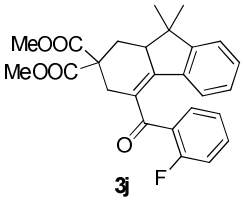
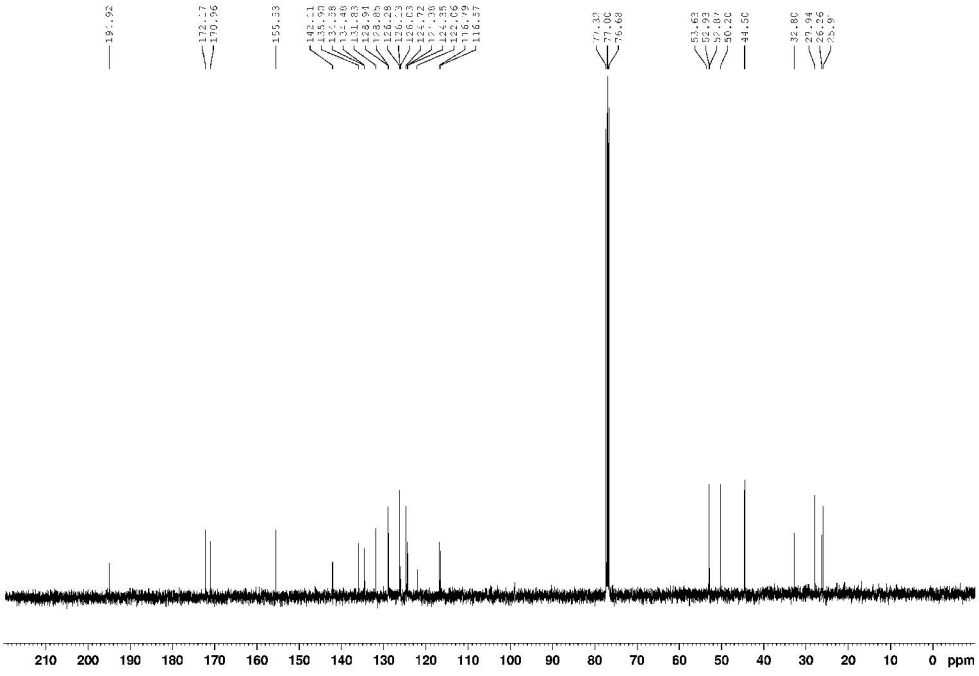

MeOOC
MeOOC
O
F

3j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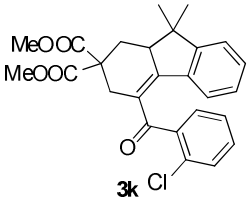
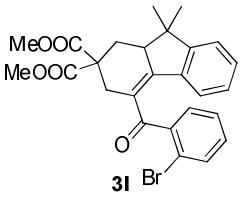
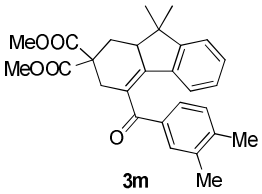
90.20
44.56
32.80
27.94
26.26
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



3k



3l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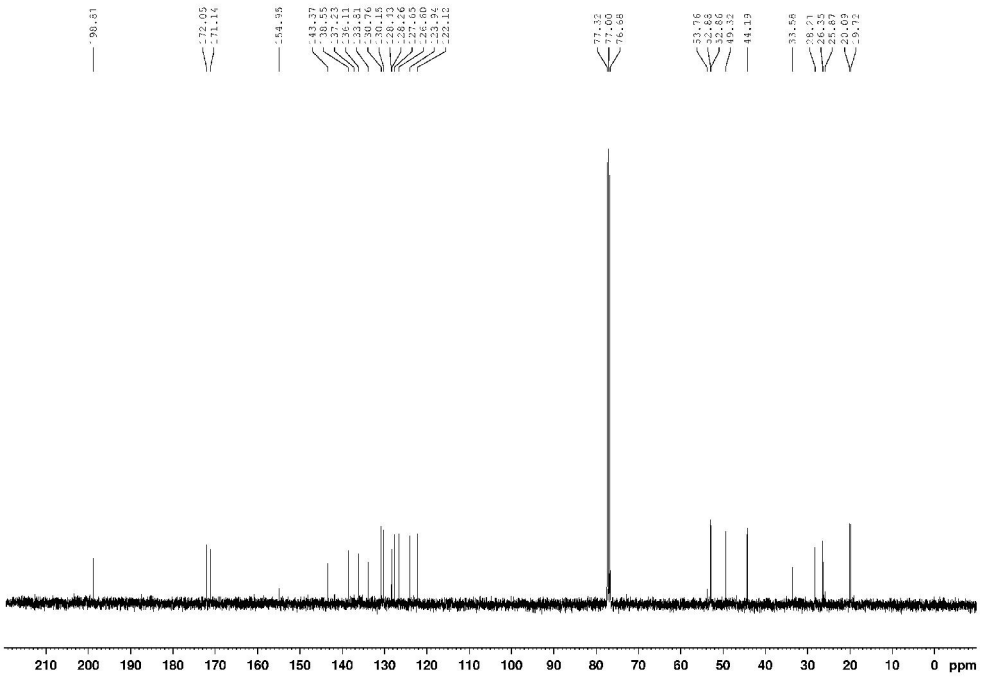
MeOOC
O
Me
Me

3m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76.68
53.76
52.88
52.86
46.32
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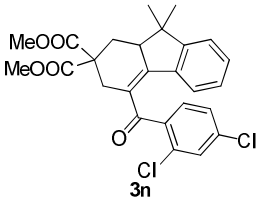

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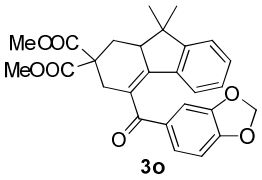
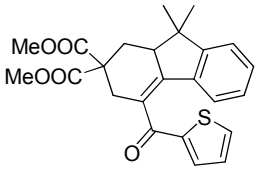
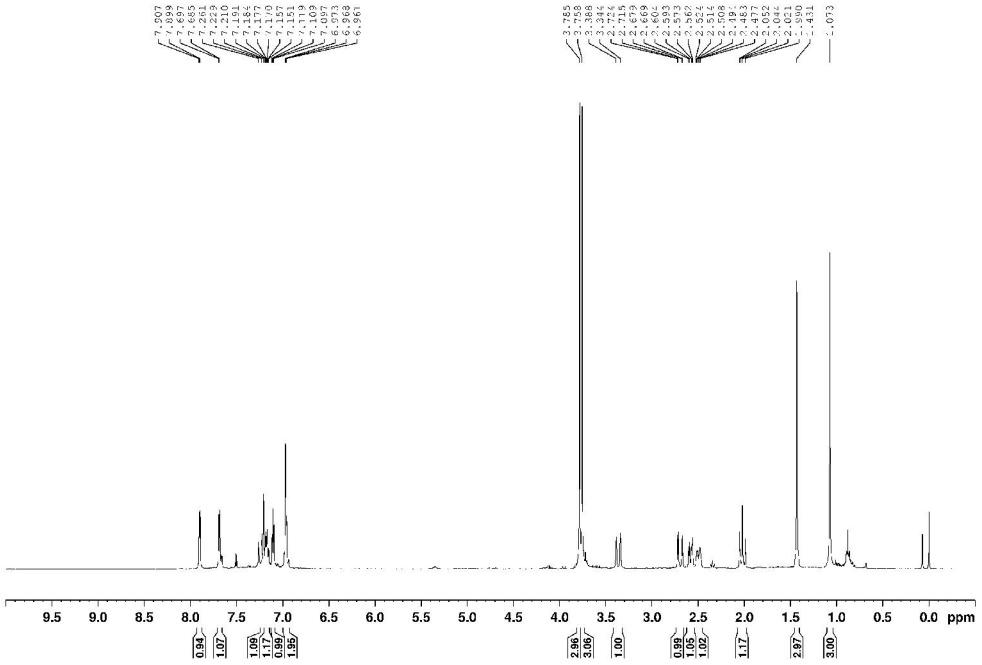
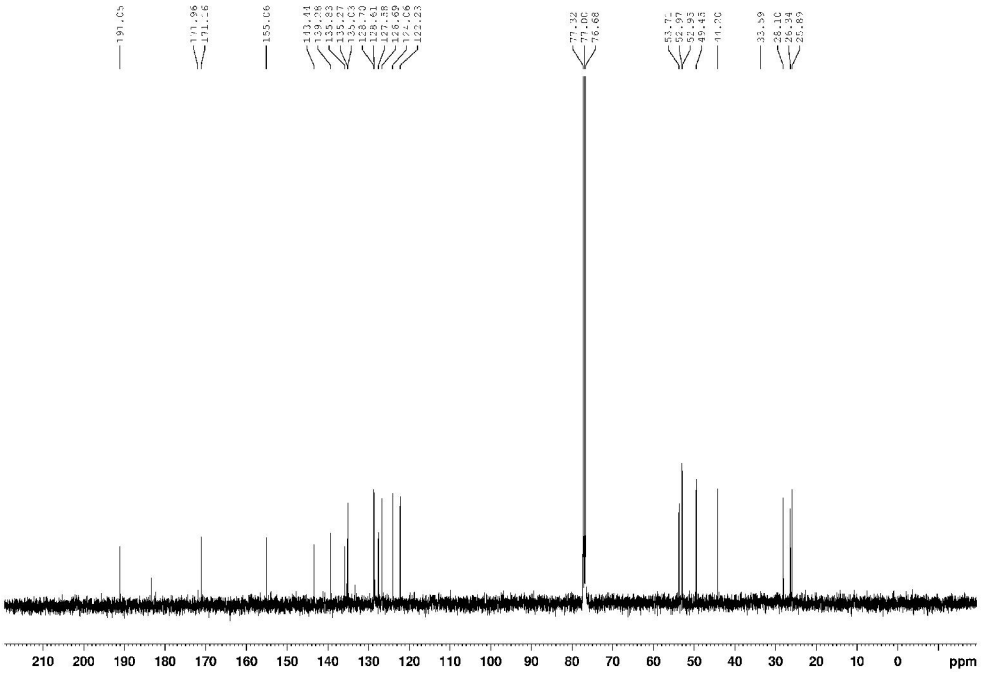


3o

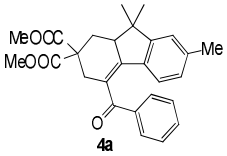


3p

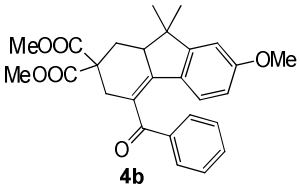




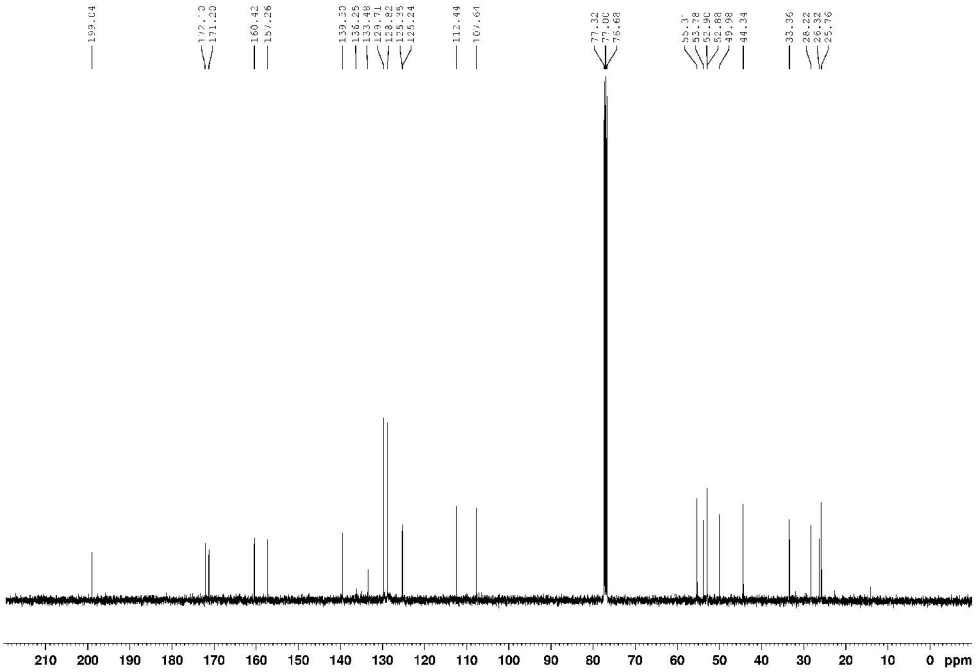
11. ^{1}H NMR and ^{13}C NMR Spectra of the Products 4a-4n:

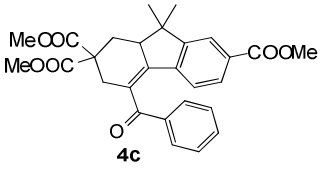


4a

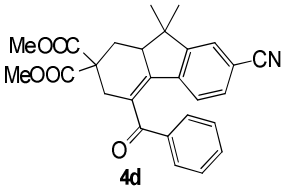

MeOOC
MeOOC
OMe
O

4b

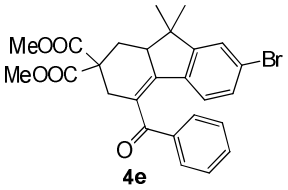

199.04
170.10
171.20
160.42
157.26
139.39
138.25
133.48
129.71
128.82
125.35
125.24
112.44
107.61
77.32
77.00
76.68
55.31
53.78
52.90
52.68
49.98
44.34
33.36
28.22
26.32
25.76
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



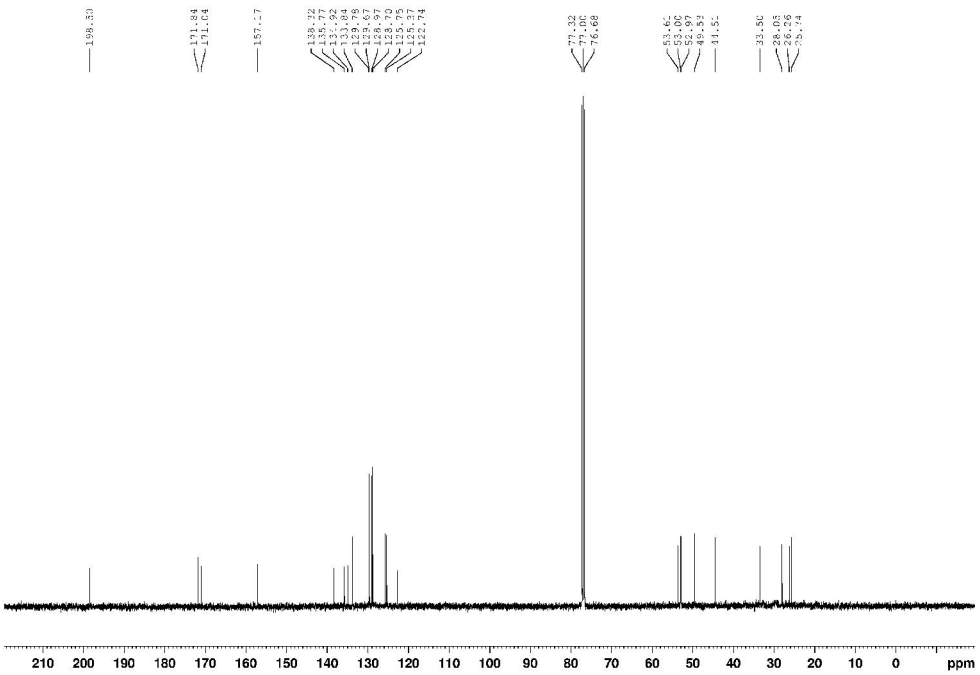
4c

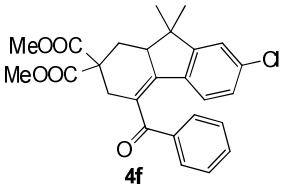


4d

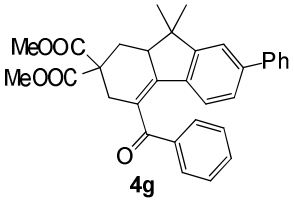

MeOOC
MeOOC
Br
O

4e

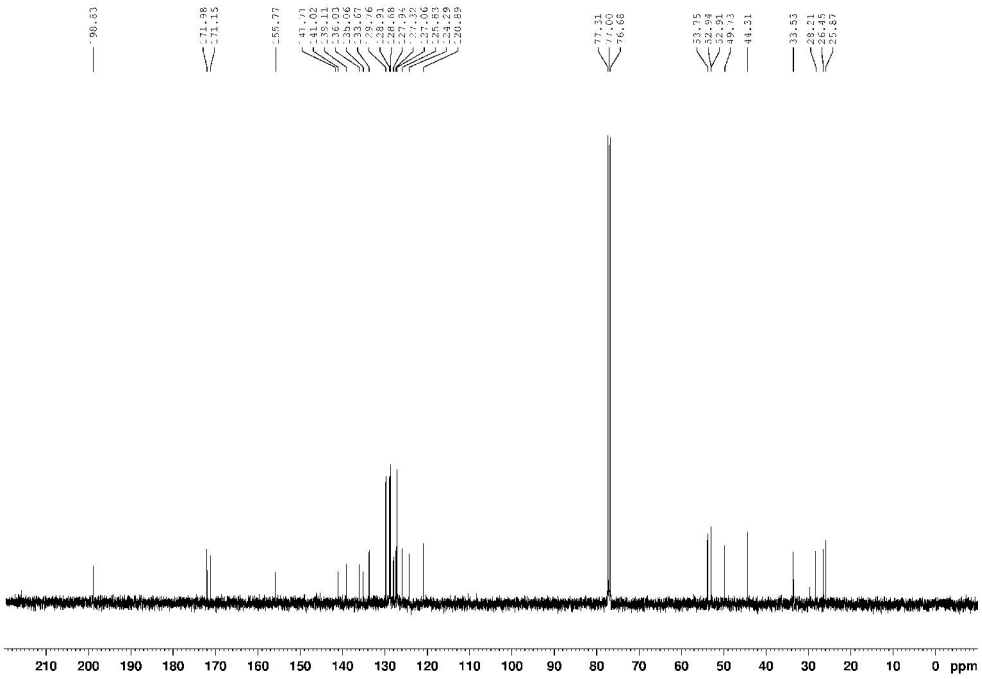

198.83
171.84
171.04
157.17
138.32
135.77
133.92
133.84
133.78
129.67
128.97
128.70
125.75
125.37
122.74
77.32
77.00
76.68
53.62
52.96
52.69
49.53
44.52
33.50
28.02
26.36
25.74
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

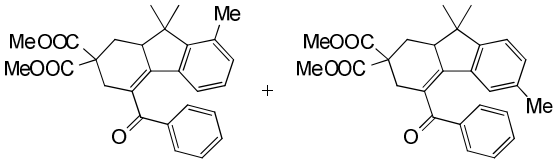


4f

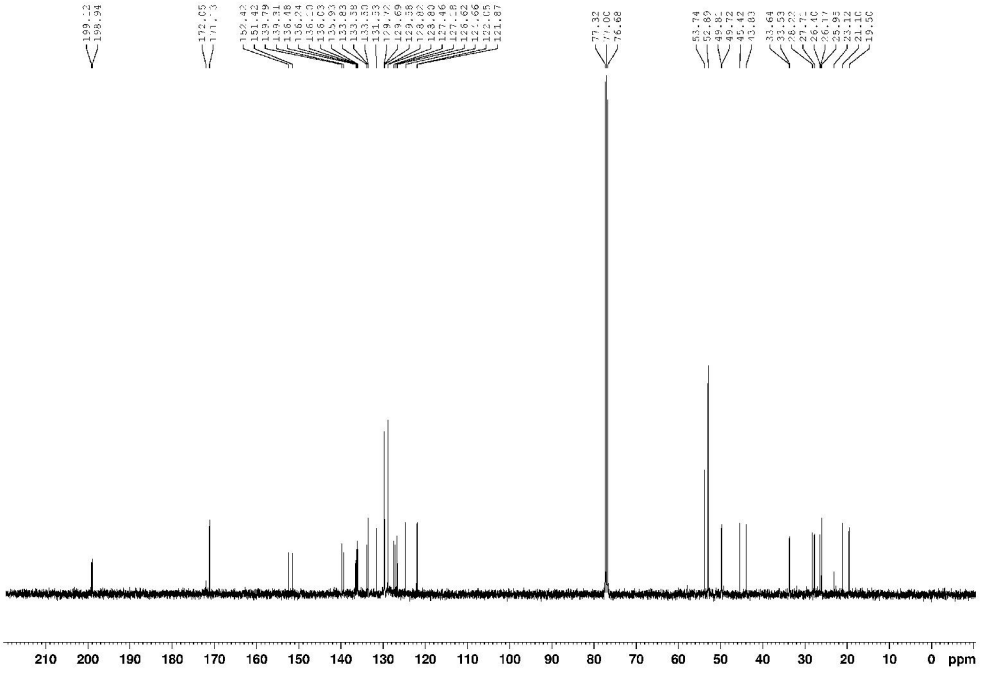

MeOOC
MeOOC
Ph
O

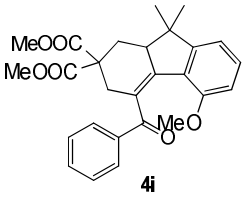
4g


90.83
71.98
71.15
55.77
41.71
41.02
38.11
36.03
35.06
33.67
29.16
28.93
28.68
27.94
27.32
27.06
25.85
24.29
20.89
77.31
77.00
76.68
53.75
52.94
52.91
50.73
44.31
33.53
28.21
26.45
25.87
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

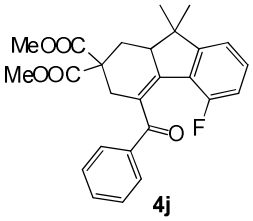

MeOOC
MeOOC
Me
O
+
MeOOC
MeOOC
Me
O

4h:4h'

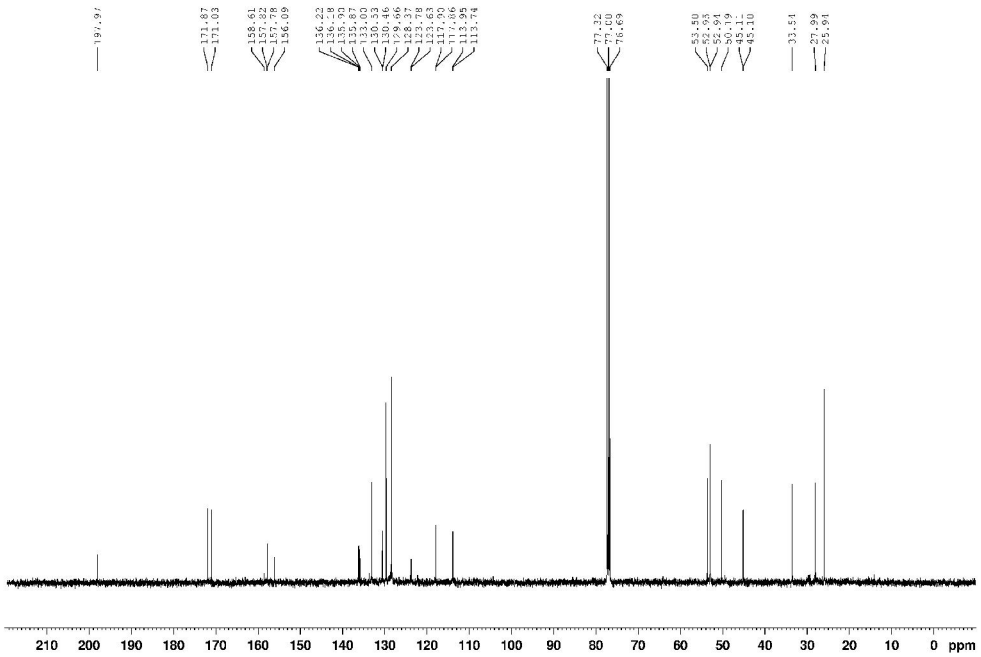

199.12
198.94
172.05
171.73
150.43
139.79
139.31
136.48
135.93
133.83
133.39
133.30
131.33
77.32
77.00
76.68
63.74
52.85
49.52
45.42
33.64
33.53
25.95
23.12
19.66
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

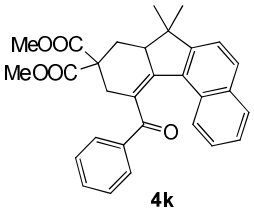


4i

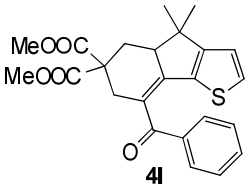

MeOOC
MeOOC
O
F

4j

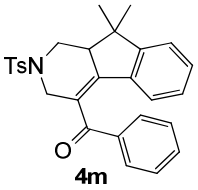

197.97
171.87
171.03
158.61
157.82
157.78
156.09
136.22
136.18
135.80
135.87
133.00
130.33
130.46
129.66
128.37
123.78
123.63
123.60
117.06
113.95
113.74
77.32
77.00
76.69
53.50
53.35
52.94
50.19
45.11
45.10
33.51
27.99
25.91
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



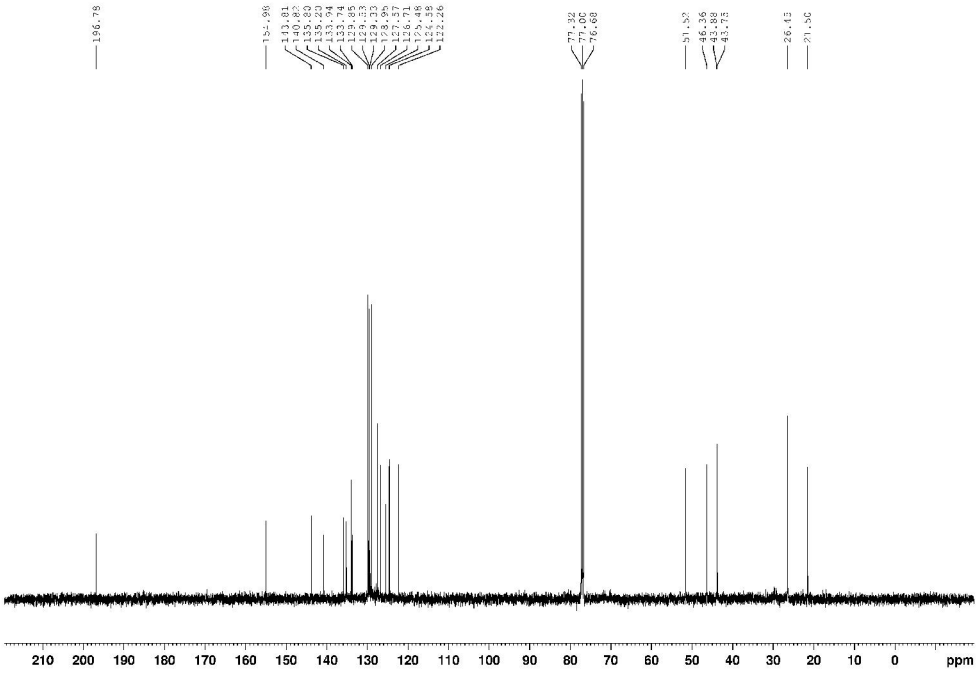
4k

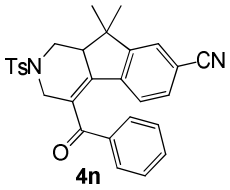


4l


TsN
O

4m


196.79
135.96
143.81
140.85
135.80
135.20
133.74
133.34
129.85
129.33
129.09
128.95
128.37
126.71
125.48
124.98
122.26
77.32
77.06
76.68
51.53
46.36
43.89
43.75
26.43
21.56
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



4n