# Suppplementary Information

## Convenient One-Step Construction of Yne-Functionalized Aryl Halides through Domino Cyclization from Tetraynes

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# Contents

## 1. General experimental procedures

All the catalytic reactions were performed under an argon atmosphere using the oven-dried Schlenk flask. The chemicals were purchased from Alfa Aesar and Acros Chemicals. All solvents and materials were pre-dried, redistilled or recrystallized before use. $^1$H NMR (300 MHz or 500 MHz) and $^{13}$C NMR (75 0r 125 MHz) spectra were recorded on a Bruker Avance 300 (500) spectrometer with $CDCl_3$ as the solvent. Chemical shifts are reported in ppm by assigning TMS resonance in the $^1$H NMR spectra as 0.00 ppm and $CDCl_3$ resonance in the $^{13}$C spectra as 77.0 ppm. All coupling constants (*J* values) were reported in Hertz (Hz). Column chromatography was performed on silica gel 300–400 mesh. Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. The FT-IR spectra were recorded from KBr pellets or thin film from $CHCl_3$ on the NaCl window in the 4000-400 $cm^{-1}$ ranges on a Nicolet 5DX spectrometer. All HRMS spectra were record using EI or APCI at 70 eV. X-ray Crystallography diffraction data of **ba**, **bb**, and **hb** were collected at room temperature with a Bruker SMART Apex CCD diffractometer with Mo-K$\alpha$ radiation ($\lambda$ = 0.71073 Å ) with a graphite monochromator using the $\omega$-scan mode. Data reductions and absorption corrections were performed with SAINT and SADABS software, respectively. The structure was solved by direct methods and refined on $F^2$ by full-matrix least squares using SHELXTL. All non-hydrogen atoms were treated anisotropically. The positions of hydrogen atoms were generated geometrically.

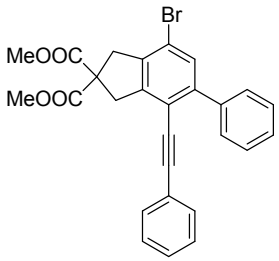
## General procedures:

**Preparation of tetrayne:** To a stirred mixture of 8.69 g (48.0 mmol) of (bromoethynyl)benzene, 380 mg (2.0 mmol) of CuI, and 700 mg (1.0 mmol) of $Pd(PPh_3)_2Cl_2$ in 50 mL of THF was added 10.1 g (75.0 mmol) of triethylamine. A solution of 4.16 g (20.0 mmol) of dimethyl 2,2-di(prop-2-yn-1-yl)malonate in 10 mL of THF was then added over 12 h. The solvent was evaporated, and the residue was treated with pentane. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 6:1) to give dimethyl 2,2-bis(5-phenylpenta-2,4-diyn-1-yl)malonate **(a).** Yellow solid; 3.06 g (75 % yield); m.p. 96-97℃; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.48-7.46 (m, 4H), 7.33-7.25 (m, 6H), 3.81 (s, 6H), 3.21 (s, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 168.7, 132.6, 129.2, 128.4, 121.5, 77.6, 76.0, 73.8, 68.5, 56.7, 53.5, 52.9, 50.6, 24.2, 19.6 ppm; FT-IR (KBr): $\nu$ 3462, 1744, 1491, 1300, 1207, 1069, 758, 691, 527 $cm^{-1}$; HRMS (APCI): *m/z* $[M + H]^+$ calcd for $C_{27}H_{20}O_4$: 409.1434; found: 409.1435.

**Preparation of aryl halides:** Tetrayne **a-l** (1.0 equiv), allyl halides (1.2 equiv), $H_2O$ (1.2 equiv), $Pd(OAc)_2$ (2 mol %), and $PPh_3$ (4 mol %), were added to the degassed solution of $n$Bu$_3$N (2 equiv ) in DMF (10 mL), and the mixture was stirred at room temperature for half an hour and then heated at 100 °C for 12 h. The reaction mixture was then cooled, quenched with water, and extracted with ethyl acetate

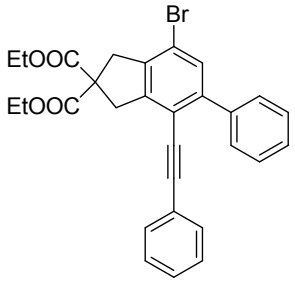
(30 mL). The combined organic layers were washed with hydrochloric acid (5 %), sodium carbonate (5 %), and saturated sodium chloride solution, dried over $MgSO_4$, and concentrated. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 6:1) to give **aa-lb**.

## 2. Characterization Data for the New Compounds



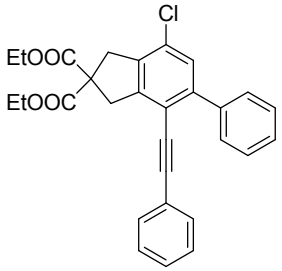

**Dimethyl 7-bromo-5-phenyl-4-(phenylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (aa)**

White crystal; 410 mg (84 % yield); m.p. 148-149 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.62-7.60 (d, 2H), 7.47-7.25 (m, 9H), 3.91 (s, 2H), 3.81 (s, 6H), 3.71 (s, 2H); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ 171.74, 144.47, 144.41, 139.11, 131.42, 131.37, 129.25, 128.47, 128.33, 128.01, 127.86, 123.08, 119.11, 117.13, 96.85, 86.38, 58.51, 53.29, 42.26, 41.99 ppm; FT-IR (KBr): *v* 3480, 2930, 1732, 1491, 1433, 1285, 1250, 1198, 1076, 871, 761, 694, 594, 527 cm$^{-1}$; HRMS (APCI): *m/z* $[M + H]^+$ calcd for $C_{27}H_{21}BrO_4$: 489.0696; found: 489.0689.



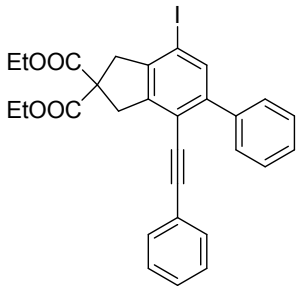

**Diethyl 7-bromo-5-phenyl-4-(phenylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (ba)**

White crystal, 464 mg (90 % yield); m.p. 120-121 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.62-7.60 (d, 2H), 7.44-7.26 (m, 9H), 4.30-4.23 (q, $J$ = 6 Hz, 4H), 3.90 (s, 2H), 3.70 (s, 2H), 1.33-1.28 (t, $J$ = 6 Hz, 6H); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ 171.31, 144.65, 144.37, 139.27, 139.15, 131.42, 131.32, 129.27, 128.44, 128.33, 128.01, 127.85, 123.12, 119.14, 117.16, 96.77, 86.44, 62.10, 58.61, 42.18, 41.88, 14.10; FT-IR (KBr): *v* 3450, 2990, 1728, 1443, 1273, 1244, 1155, 1049, 1013, 860, 756,691, 524 cm$^{-1}$; HRMS (APCI): *m/z* $[M + H]^+$ calcd for $C_{29}H_{25}BrO_4$: 518.1015; found: 518.1014.



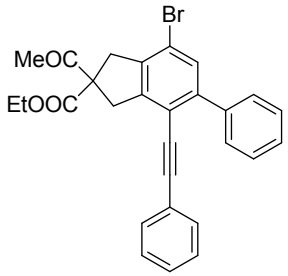

**Diethyl 7-chloro-5-phenyl-4-(phenylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (bb)**

White crystal, 420 mg (89 % yield); m.p. 120-121 °C; $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.63-7.60 (d, 2H), 7.47-7.26 (m, 9H), 4.30-4.23 (q, $J$ = 6 Hz, 4H), 3.87 (s, 2H), 3.73 (s, 2H), 1.33-1.28 (t, $J$ = 6 Hz, 6H); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ 171.30, 145.06, 144.37, 139.28, 137.14, 131.42, 130.15, 129.24, 128.40, 128.38, 128.31, 128.01, 127.82, 123.16, 116.52, 96.57, 86.39, 62.08, 58.92, 41.68, 40.20, 14.09; FT-IR (KBr): $\nu$ 3460, 2980, 1726, 1439, 1269, 1240, 1186, 1049, 761, 642, 523 cm$^{-1}$; HRMS (APCI): *m/z* $[M + H]^+$ calcd for $C_{29}H_{25}ClO_4$: 473.1514; found: 473.1508.



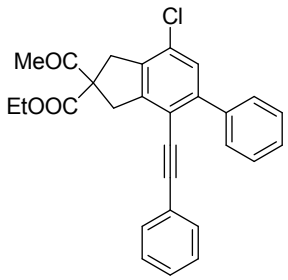

**Diethyl 7-iodo-5-phenyl-4-(phenylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (bc)**

White crystal, 439 mg (77 % yield); m.p. 123-124 °C; $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.68-7.60 (m, 2H), 7.47-7.30 (m, 9H), 4.31-4.24 (q, $J$ = 6 Hz, 4H), 3.95 (s, 2H), 3.67 (s, 2H), 1.33-1.28 (t, $J$ = 6 Hz, 6H); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ 171.31, 144.12, 143.37, 143.30, 138.97, 137.38, 131.43, 129.26, 128.47, 128.32, 127.99, 127.81, 123.11, 118.01, 97.00, 92.63, 86.51, 62.10, 58.12, 45.85, 42.19, 14.10; FT-IR (KBr): $\nu$ 3440, 2982, 1730, 1454, 1364, 1279, 1240, 1155, 1062, 860, 756, 691, 519 cm$^{-1}$; HRMS (APCI): *m/z* $[M + H]^+$ calcd for $C_{29}H_{25}IO_4$: 565.0870; found: 565.0856.



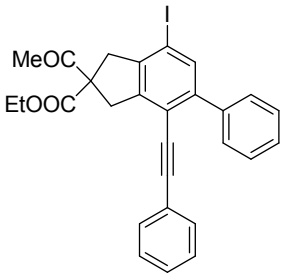

**Ethyl 2-acetyl-7-bromo-5-phenyl-4-(phenylethynyl)-2,3-dihydro-1*H*-indene-2-carboxylate (ca)**

Yellow solid, 369 mg (76 % yield); m.p. 102-103 °C; $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.61-7.59 (d, 2H), 7.43-7.25 (m, 9H), 4.31-4.24 (q, $J$ = 6 Hz, 2H), 3.82 (s, 2H), 3.62 (s, 2H), 2.30 (s, 3H), 1.33-1.27 (t, $J$ = 6 Hz, 3H); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ 201.80, 172.04, 144.44, 139.10, 139.07, 131.41, 131.35, 129.25, 128.48, 128.33, 128.02, 127.86, 123.08, 119.22, 117.24, 96.86, 86.39, 65.01, 62.25, 40.63, 40.27, 26.13, 14.11; FT-IR (KBr): $\nu$ 3410, 2999, 1715, 1489, 1442, 1267, 1229, 1098, 1017, 876, 756, 690, 525 cm$^{-1}$; HRMS (APCI): *m/z* $[M + H]^+$ calcd for $C_{28}H_{23}BrO_3$: 487.0903; found: 487.0898.



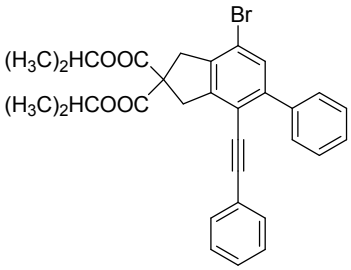

**Ethyl 2-acetyl-7-chloro-5-phenyl-4-(phenylethynyl)-2,3-dihydro-1*H*-indene-2-carboxylate (cb)**

Yellow solid, 376 mg (85 % yield); m.p. 97-98 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.62-7.60 (d, 2H), 7.46-7.26 (m, 9H), 4.32-4.25 (q, $J$ = 6 Hz, 2H), 3.80 (s, 2H), 3.65 (s, 2H), 2.30 (s, 3H), 1.34-1.29 (t, $J$ = 6 Hz, 3H,); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ 201.77, 172.04, 144.86, 144.46, 139.23, 136.96, 131.42, 130.21, 129.24, 128.45, 128.42, 128.03, 127.86, 123.11, 116.66, 96.65, 86.36, 65.34, 62.24, 40.09, 38.64, 26.12, 14.10; FT-IR (KBr): $v$ 3430, 2990, 1715, 1489, 1443, 1267, 1231, 1155, 1098, 918, 756, 691 cm$^{-1}$; HRMS (APCI): $m/z$ $[M + H]^+$ calcd for $C_{28}H_{23}ClO_3$: 443.1409; found: 443.1404.



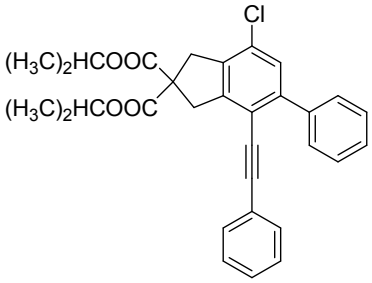

**Ethyl 2-acetyl-7-iodo-5-phenyl-4-(phenylethynyl)-2,3-dihydro-1*H*-indene-2-carboxylate (cc)**

White crystal, 428 mg (80 % yield); m.p. 111-112 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.66-7.58 (m, 2H), 7.46-7.26 (m, 9H), 4.32-4.25 (q, $J$ = 6 Hz, 2H), 3.86 (s, 2H), 3.57 (s, 2H), 2.30 (s, 3H), 1.34-1.29 (t, $J$ = 6 Hz, 3H); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ 201.81, 171.96, 144.21, 143.16, 143.09, 138.93, 137.42, 131.42, 129.24, 128.50, 128.32, 128.03, 128.00, 127.82, 123.08, 118.00, 97.24, 92.74, 86.42, 64.53, 62.24, 44.34, 40.63, 26.13, 14.10; FT-IR (KBr): $v$ 3462, 2980, 1715, 1442, 1263, 1224, 1150, 877, 752, 685, 523 cm$^{-1}$; HRMS (APCI): $m/z$ $[M + H]^+$ calcd for $C_{28}H_{23}IO_3$: 535.0765; found: 535.0765.




**Diisopropyl 7-bromo-5-phenyl-4-(phenylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (da)**

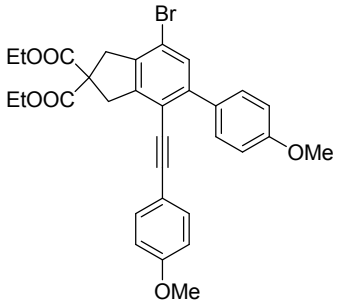
White crystal, 479 mg (88 % yield); m.p. 134-135 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.62-7.59 (d, 2H), 7.42-7.25 (m, 9H), 5.11-5.07 (m, 2H), 3.86 (s, 2H), 3.65 (s, 2H), 1.29-1.26(d, $J$ = 6 Hz, 12H); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ 170.83, 144.75, 144.34, 139.37, 131.40, 131.25, 129.27, 128.38, 128.30, 127.98, 127.79, 123.18, 119.09, 117.08, 96.69, 86.50, 69.57, 58.66, 42.14, 41.79, 21.57; FT-IR (KBr): $v$ 3435, 2976, 1722, 1456, 1273, 1105, 1063, 775, 752, 700, 637 cm$^{-1}$; HRMS (APCI): $m/z$ $[M + H]^+$ calcd for $C_{31}H_{29}BrO_4$: 545.1322; found: 545.1323.




**Diisopropyl 7-chloro-5-phenyl-4-(phenylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (db)**

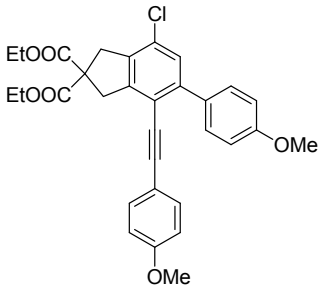
White crystal, 420 mg (84 % yield); m.p. 126-127 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.62-7.60 (d, 2H), 7.44-7.26 (m, 9H), 5.11-5.07 (m, 2H), 3.83 (s, 2H), 3.68 (s, 2H), 1.29-1.27 (d, $J$ = 6 Hz, 12H); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ 170.85, 145.29,

139.32, 137.24, 131.40, 130.07, 129.25, 128.36, 128.32, 128.30, 127.98, 127.79, 123.01, 116.64, 96.54, 86.39, 69.55, 58.96, 41.60, 40.16, 21.57; FT-IR (KBr): *v* 3450, 2990, 1724, 1456, 1373, 1275, 1188, 1105, 910, 772, 687, 607 $cm^{-1}$; HRMS (APCI): *m/z* $[M + H]^+$ calcd for $C_{31}H_{29}ClO_4$: 501.1827; found: 501.1826.



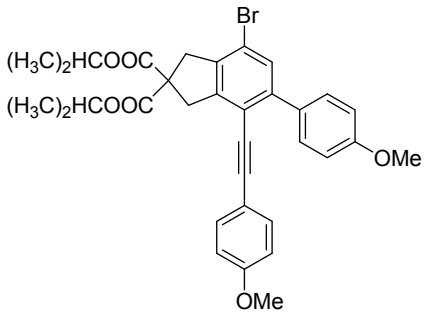

**Diethyl 7-bromo-5-(4-methoxyphenyl)-4-((4-methoxyphenyl)ethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (ea)**

White crystal, 478 mg (83 % yield); m.p. 149-150 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.57-7.55 (d, 2H), 7.38-7.25 (m, 3H), 6.97-6.81 (m, 4H), 4.28-4.22 (q, $J$ = 6 Hz, 4H), 3.86 (s, 2H), 3.80(s, 6H), 3.67(s, 2H), 1.31-1.27 (t, $J$ = 6 Hz, 6H); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ 171.35, 159.72, 159.30, 144.38, 144.36, 143.66, 138.68, 132.89, 131.73, 131.07, 130.42, 118.66, 117.31, 117.30, 115.33, 113.98, 113.37, 113.33, 96.83, 85.41, 62.05, 58.62, 55.36, 55.34, 42.14, 41.90, 14.09; FT-IR (KBr): *v* 3462, 2974, 1728, 1607, 1510, 1292, 1246, 1066, 1031, 829, 532 $cm^{-1}$; HRMS (APCI): *m/z* $[M + H]^+$ calcd for $C_{31}H_{29}BrO_6$: 577.1220; found: 577.1217.



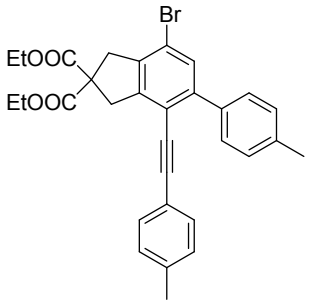

**Diethyl 7-chloro-5-(4-methoxyphenyl)-4-((4-methoxyphenyl)ethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (eb)**

White crystal, 458 mg (86 % yield); m.p. 133-134 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.58-7.55 (d, 2H), 7.32-7.22 (m, 3H), 6.98-6.82 (m, 4H), 4.29-4.22 (q, $J$ = 6 Hz, 4H), 3.86 (s, 3H), 3.84 (s, 2H), 3.81 (s, 3H), 3.70(s, 2H), 1.32-1.27(t, $J$ = 6 Hz, 6H); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ 171.37, 159.70, 159.29, 144.77, 143.63, 136.56, 132.88, 131.86, 130.40, 129.67, 128.14, 116.71, 115.36, 113.97, 113.37, 96.60, 85.34, 62.04, 58.91, 55.35, 41.70, 40.16, 14.08; FT-IR (KBr): *v* 3440, 2972, 1730, 1607, 1292, 1244, 1179, 1030, 829, 633, 532 $cm^{-1}$; HRMS (APCI): *m/z* $[M + H]^+$ calcd for $C_{31}H_{29}ClO_6$: 533.1725; found: 533.1724.



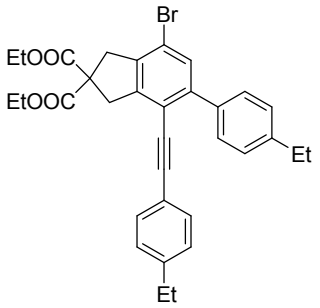

**Diisopropyl 7-bromo-5-(4-methoxyphenyl)-4-((4-methoxyphenyl)ethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (fa)**

White crystal, 484 mg (80 % yield); m.p. 160-161 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.58-7.55 (d, 2H), 7.38-6,82 (m, 7H), 5.11-5.07 (m, 2H), 3.86 (s, 2H), 3.84 (s, 3H), 3.81 (s, 3H) 3.64 (s, 2H), 1.29-1.27 (d, $J$ = 6 Hz, 12H); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ 170.88, 159.75, 159.27, 144.49, 138.78, 132.89, 131.02, 130.43, 118.63, 117.24, 115.38, 113.97, 113.35, 96.68, 85.42, 69.51, 58.66, 55.32, 42.11, 41.82, 21.57; FT-IR (KBr): $v$ 3422, 2980, 1724, 1605, 1510, 1290, 1247, 1099, 829, 667, 532 cm$^{-1}$; HRMS (APCI): $m/z$ $[M + H]^+$ calcd for $C_{33}H_{33}BrO_6$: 605.1533; found: 605.1519.



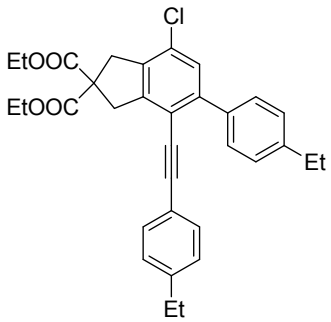

**Diethyl 7-bromo-5-(*p*-tolyl)-4-(*p*-tolylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (ga)**

Yellow solid, 462 mg (85 % yield); m.p. 145-146 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.53-7.50 (m, 2H), 7.41-7.10 (m, 7H), 4.29-4.23 (q, $J$ = 6 Hz, 4H), 3.88 (s, 2H), 3.68 (s, 2H), 2.41 (s, 3H), 2.35 (s, 3H), 1.32-1.27 (t, $J$ = 6 Hz, 6H); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ 171.35, 144.60, 138.60, 137.57, 136.28, 131.32, 131.22, 129.18, 129.08, 128.80, 128.71, 120.14, 118.89, 117.24, 96.96, 85.96, 62.06, 58.61, 42.16, 41.92, 21.58, 21.31, 14.09; FT-IR (KBr): $v$ 3460, 2974, 1732, 1510, 1267, 1242, 1184, 1070, 814, 667, 525 cm$^{-1}$; HRMS (APCI): $m/z$ $[M + H]^+$ calcd for $C_{31}H_{29}BrO_4$: 545.1322; found: 545.1319.



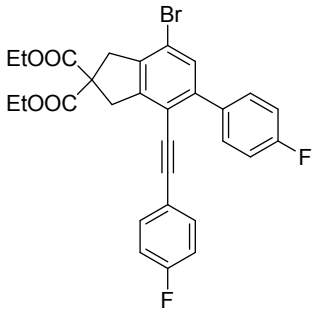

**Diethyl 7-bromo-5-(4-ethylphenyl)-4-((4-ethylphenyl)ethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (ha)**

White crystal, 486 mg (85 % yield); m.p. 140-141 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.55-7.53 (d, 2H), 7.42 (s, 1H), 7.28-7.25 (m, 4H), 7.14-7.12 (d, 2H), 4.29-4.22 (q, $J$ = 6 Hz, 4H), 3.88 (s, 2H), 3.68(s, 2H), 2.72-2.62 (m,4H) 1.31-1.19 (m, 12H); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ 171.34, 144.89, 144.54, 144.22, 143.89, 138.90, 136.52, 131.41, 131.21, 129.17, 127.87, 127.49, 120.42, 118.86, 117.29, 96.99, 86.00, 62.04, 58.60, 42.16, 41.90, 28.88, 28.66, 15.62, 15.41, 14.08; FT-IR (KBr): $v$ 3465, 2965, 1736, 1510, 1454, 1238, 1184, 1070, 829, 623, 556 cm$^{-1}$; HRMS (APCI): $m/z$ $[M + H]^+$ calcd for $C_{33}H_{33}BrO_4$: 573.1635; found: 573.1628.



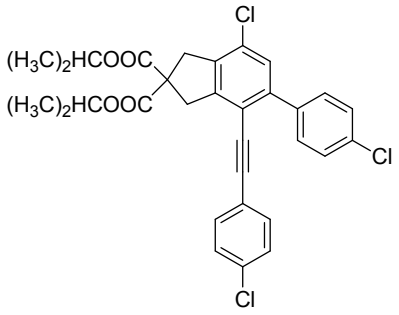
**Diethyl 7-chloro-5-(4-ethylphenyl)-4-((4-ethylphenyl)ethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (hb)**

White crystal, 386 mg (73 % yield); m.p. 138-139 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.56-7.53 (m, 2H), 7.28-7.26 (m, 5H), 7.14-7.12 (m, 2H), 4.29-4.22 (q, $J$ = 6 Hz, 4H), 3.85 (s, 2H), 3.71 (s, 2H), 2.72-2.62 (m,4H) 1.31-1.19 (m, 12H); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ 171.36, 144.94, 144.85, 144.20, 143.88, 136.79, 136.64, 131.41, 129.87, 129.17, 128.28, 127.88, 127.51, 120.44, 116.69, 96.77, 85.95, 62.04, 58.90, 41.71, 40.20, 28.87, 28.66, 15.63, 15.43, 14.08; FT-IR (KBr): $v$ 3460, 2967, 1736, 1510, 1454, 1269, 1244, 1184, 1155, 1070, 829, 627, 557 cm$^{-1}$; HRMS (APCI): $m/z$ [M + H]$^+$ calcd for $C_{33}H_{33}ClO_4$: 529.2140; found: 529.2139.



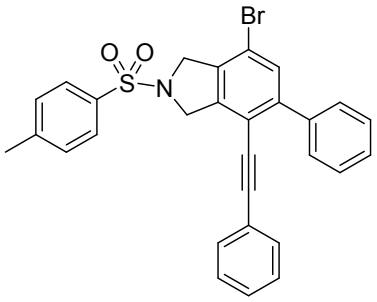

**Diethyl 7-bromo-5-(4-fluorophenyl)-4-((4-fluorophenyl)ethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (ia)**

White crystal, 425 mg (77 % yield); m.p. 128-129 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.57-7.53 (m, 2H), 7.38-7.6.97 (m, 7H), 4.29-4.22 (q, $J$ = 6 Hz, 4H), 3.87 (s, 2H), 3.68(s, 2H), 1.31-1.27(t, $J$ = 6 Hz, 6H); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ 171.22, 164.28, 164.21, 160.97, 144.64, 143.25, 139.49, 135.19, 133.34, 133.22, 131.21, 130.97, 130.86, 119.21, 115.87, 115.57, 115.09, 114.80, 95.83, 85.90, 62.10, 58.61, 42.15, 41.82, 14.06; FT-IR (KBr): $v$ 3456, 2961, 1724, 1601, 1508, 1279, 1186, 1155, 1091, 837, 511 cm$^{-1}$; HRMS (APCI): $m/z$ [M + H]$^+$ calcd for $C_{29}H_{23}BrF_2O_4$: 553.0821; found: 553.0821.



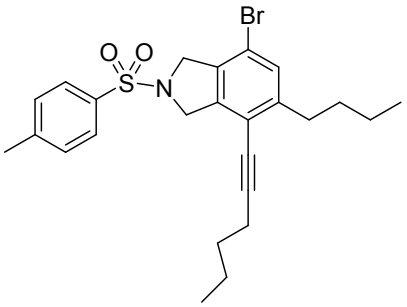

**Diisopropyl 7-chloro-5-(4-chlorophenyl)-4-((4-chlorophenyl)ethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (ja)**

White crystal, 426 mg (75 % yield); m.p. 156-157 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.58-7.55 (d, 2H), 7.45-7.25 (m, 7H), 5.14-5.11 (m, 2H), 3.84 (s, 2H), 3.71 (s, 2H), 1.32-1.31(d, $J$ = 6 Hz, 12H); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ 170.73, 145.51, 143.10, 137.78, 134.70, 134.03, 132.93, 132.57, 130.51, 128.75, 128.22, 128.08, 121.47, 116.15, 95.64, 86.83, 69.63, 58.81, 41.53, 40.14, 21.55; FT-IR (KBr): $v$ 3460, 2980, 1728, 1491, 1253, 1190, 1101, 1012, 827, 525 cm$^{-1}$; HRMS (APCI): $m/z$ [M + H]$^+$ calcd for $C_{31}H_{27}Cl_3O_4$: 569.1048; found: 569.1049.



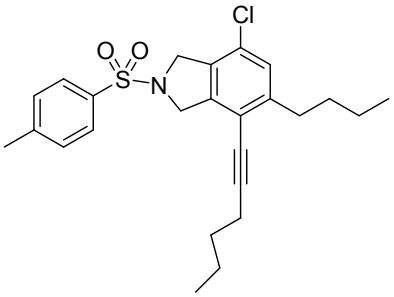

**7-Bromo-5-phenyl-4-(phenylethynyl)-2-tosylisoindoline (ka)**

White solid; 458 mg (87 % yield); m.p. 198-199 °C; $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.85-7.82 (d, 2H), 7.57-7.55 (d, 2H), 7.46-7.26 (m, 11H), 4.89 (s, 2H), 4.67 (s, 2H), 2.42 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 145.12, 144.02, 143.94, 141.05, 140.708, 138.41, 135.71, 133.65, 131.88, 131.48, 130.10, 129.95, 129.15, 129.00, 128.91, 128.46, 128.28, 128.20, 128.07, 127.86, 127.65, 127.47, 116.94, 115.93, 97.76, 85.01, 55.58, 55.28, 21.62 ppm; FT-IR (KBr): $\nu$ 3472, 1640, 1491, 1348, 1163, 1103, 756, 679, 578, 544 cm$^{-1}$; HRMS (APCI): *m/z* $[M + H]^+$ calcd for $C_{29}H_{22}BrNO_2S$: 528.0627; found: 528.0624.




**7-Bromo-5-butyl-4-(hex-1-yn-1-yl)-2-tosylisoindoline (la)**

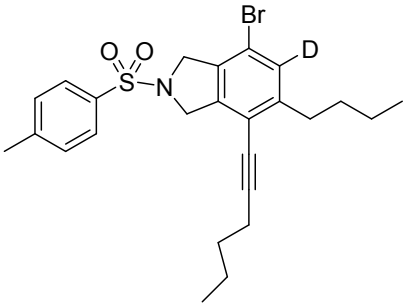
White solid; 410 mg (84 % yield); m.p. 110-111 °C; $^{1}$H NMR (500 MHz, $CDCl_3$): $\delta$ 7.78-7.76 (d, 2H), 7.33-7.31 (d, 2H), 7.16 (s, 1H), 4.68 (s, 2H), 4.54 (s, 2H), 2.65-2.62 (t, 2H), 2.44-2.43 (t, 2H), 2.42 (s, 3H), 1.59-1.57 (m, 2H), 1.56-1.51 (m, 2H), 1.49-1.46 (m, 4H), 0.96-0.93 (t, 3H), 0.91-0.88 (t, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 146.75, 144.20, 140.55, 134.24, 134.02, 130.33, 127.97, 118.08, 115.92, 100.19, 97.76, 55.82, 55.54, 34.05, 33.10, 31.12, 22.86, 22.38, 21.95, 19.75, 14.31, 14.02 ppm; FT-IR (KBr): $\nu$ 2951, 1637, 1458, 1346, 1154, 1101, 808, 677, 590, 543 cm$^{-1}$; HRMS (APCI): *m/z* $[M + H]^+$ calcd for $C_{25}H_{31}BrNO_2S$: 488.1271; found: 488.1270.




**5-Butyl-7-chloro-4-(hex-1-yn-1-yl)-2-tosylisoindoline (lb)**

White solid; 364 mg (82 % yield); m.p. 95-96 °C; $^{1}$H NMR (500 MHz, $CDCl_3$): $\delta$ 7.77-7.76 (d, 2H), 7.32-7.30 (d, 2H), 6.99 (s, 1H), 4.64 (s, 2H), 4.57 (s, 2H), 2.65-2.62 (t, 2H), 2.45-2.43 (t, 2H), 2.42 (s, 3H), 1.60-1.58 (m, 2H), 1.55-1.52 (m, 2H), 1.50-1.47 (m, 4H), 0.96-0.94 (t, 3H), 0.91-0.89 (t, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 146.76, 144.12, 140.82, 134.07, 132.13, 130.28, 128.36, 127.65, 117.48, 99.89, 55.32, 54.30, 34.14, 33.06, 29.60, 22.82, 22.35, 21.89, 19.68, 14.51, 14.25 ppm; FT-IR

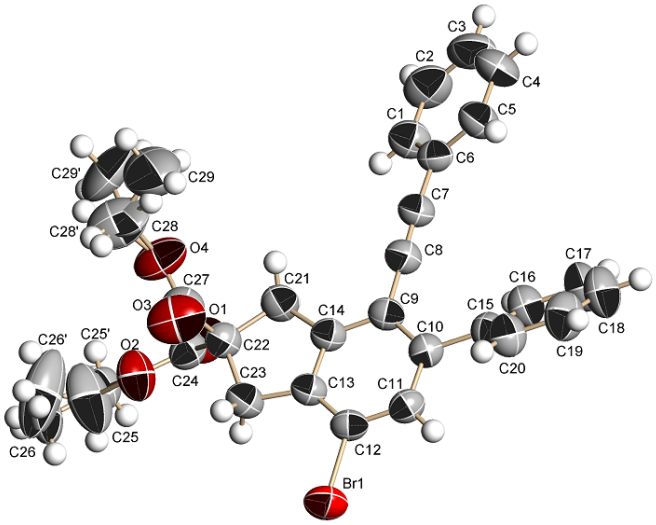
(KBr): *v* 3448, 2870, 1637, 1458, 1344, 1151, 1099, 817, 667, 551 $cm^{-1}$; HRMS (APCI): *m/z* $[M + H]^+$ calcd for $C_{25}H_{31}BrNO_2S$: 444.1776; found: 444.1773.

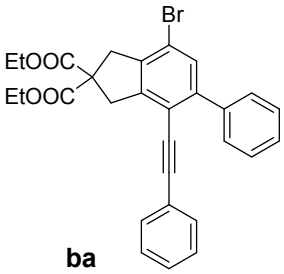



**7-Bromo-5-butyl-4-(hex-1-yn-1-yl)-2-tosylisoindoline-6-d (lc)**

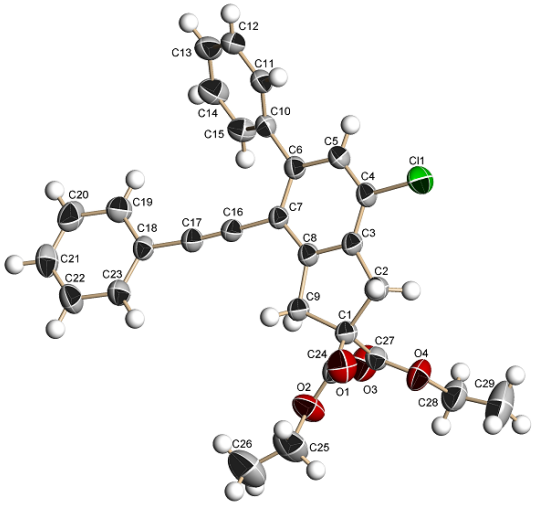
White solid; 397 mg (81 % yield); m.p. 112-113 °C; $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 7.78-7.67 (d, 2H), 7.33-7.31 (d, 2H), 4.68 (s, 2H), 4.54 (s, 2H), 2.65-2.62 (t, 2H), 2.44-2.43 (t, 2H), 2.42 (s, 3H), 1.59-1.57 (m, 2H), 1.56-1.51 (m, 2H), 1.49-1.46 (m, 4H), 0.96-0.93 (t, 3H), 0.91-0.88 (t, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 146.84, 144.17, 140.59, 134.27, 134.12, 131.29, 130.32, 127.97, 118.09, 116.02, 100.18, 97.76, 55.82, 55.54, 34.10, 33.10, 31.11, 22.85, 22.37, 21.94, 19.73, 14.28, 14.00 ppm; FT-IR (KBr): *v* 3032, 2951, 1903, 1637, 1598, 1431, 1344, 1159, 1101, 808, 675, 648, 547, 540 $cm^{-1}$; HRMS (APCI): *m/z* $[M + H]^+$ calcd for $C_{25}H_{30}DBrNO_2S$: 489.1333; found: 489.1331.

## 4. X-Ray Structure for ba, bb and hb




**ba**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C13
C11
C14
C10
C15
C6
C5
Cl1
C4
C20
C19
C7
C16
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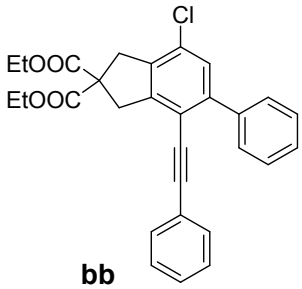
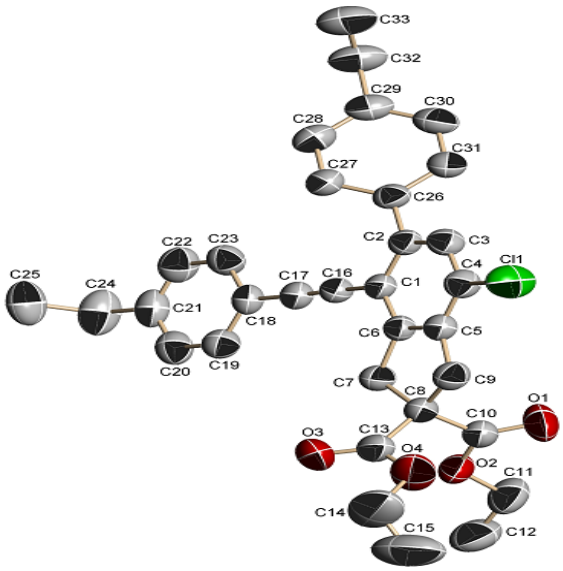
C17
C8
C3
C21
C22
C23
C2
C9
C1
C27
C24
O4
O2
O1
O3
C29
C28
C26
C25


Cl
EtOOC
EtOOC

**bb**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C29
C30
C28
C31
C27
C26
C2
C3
C22
C23
C4
Cl1
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C17
C16
C1
C21
C18
C6
C5
C20
C19
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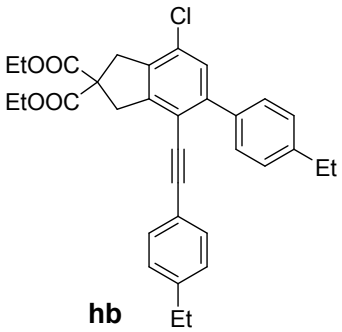
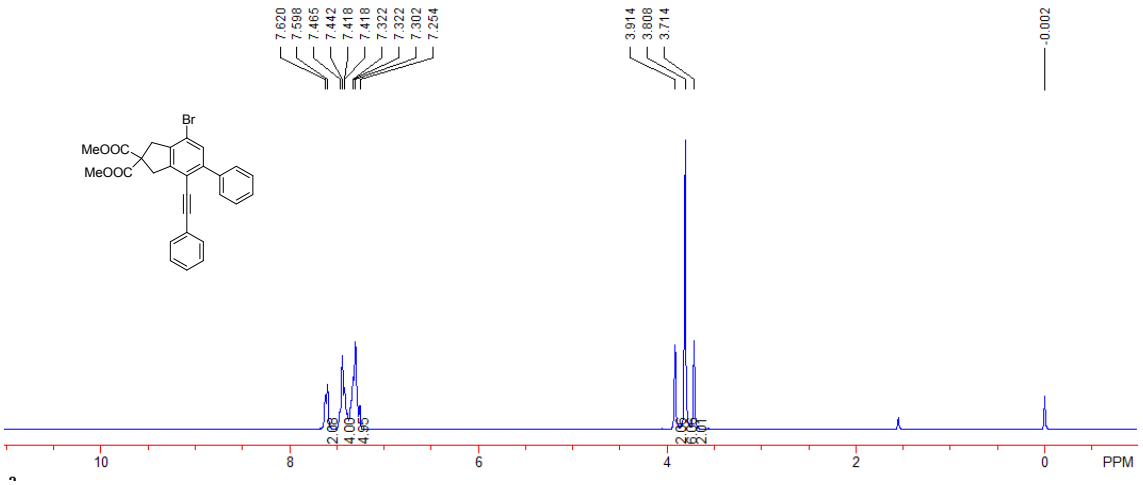
C8
C9
O1
C10
O3
C13
O4
O2
C11
C14
C15
C12

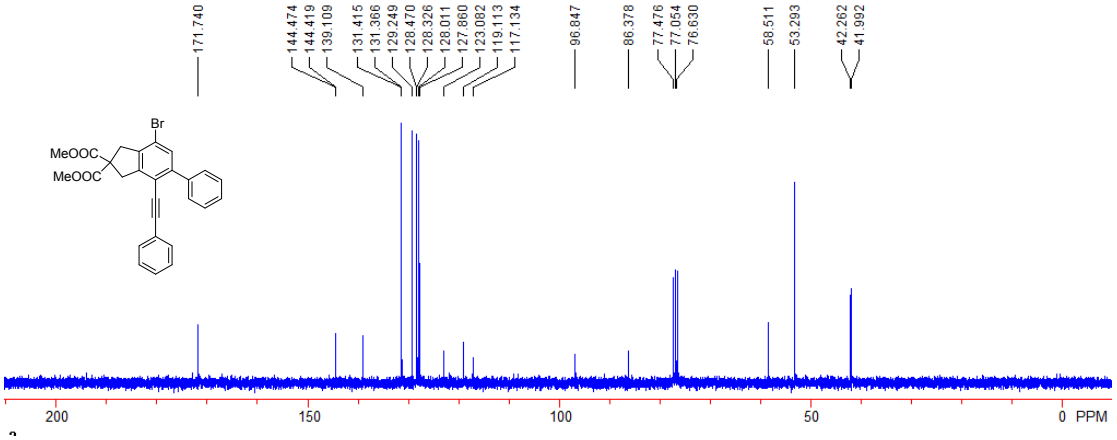

Cl
EtOOC
EtOOC
Et
Et

**hb**

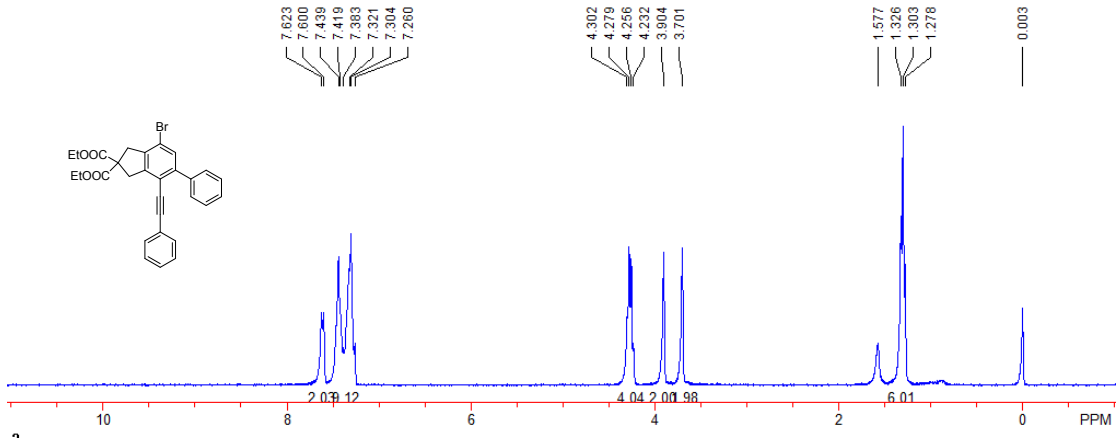
## 4. $^{1}$H NMR & $^{13}$C NMR Spectra for New Compounds



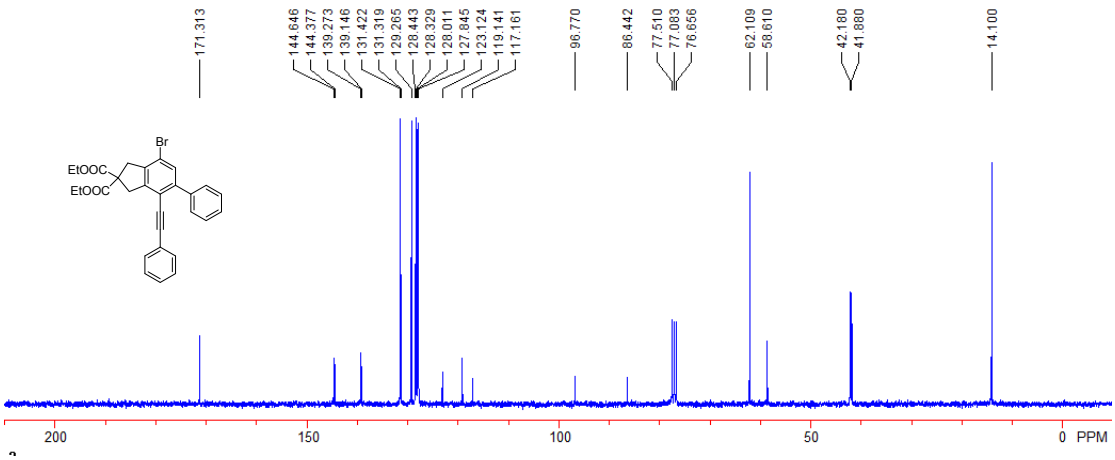

**aa**




**aa**




**ba**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119.141
117.161
96.770
86.442
77.510
77.083
76.656
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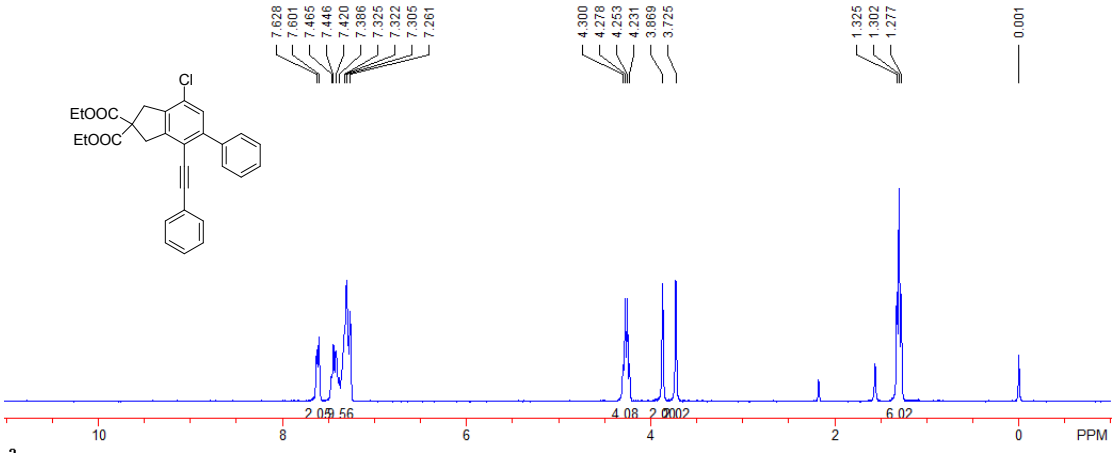
EtOOC
EtOOC
200
150
100
50
0
PPM

**ba**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4.253
4.231
3.869
3.725
1.325
1.302
1.277
0.001
Cl
EtOOC
EtOOC
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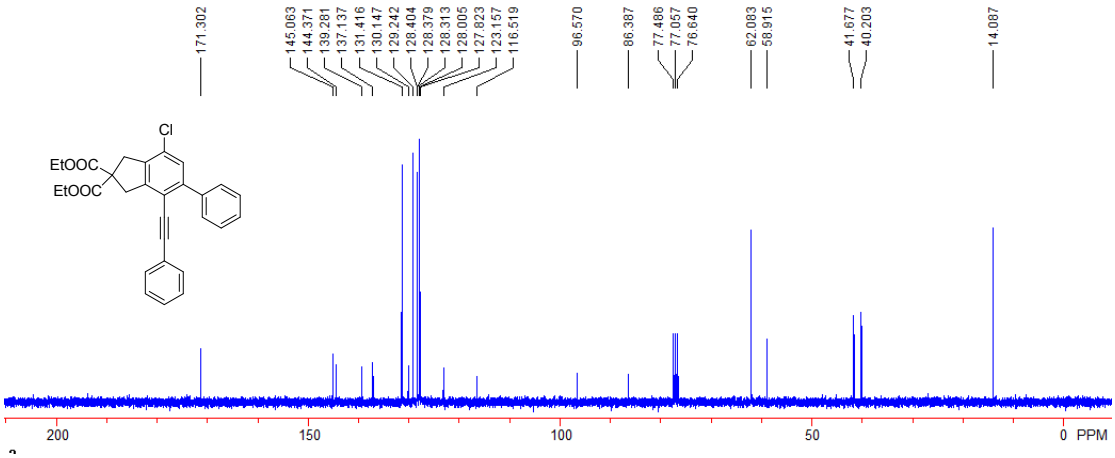
4.08
2.00
6.02
10
8
6
4
2
0
PPM

**bb**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Cl
EtOOC
EtOOC
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150
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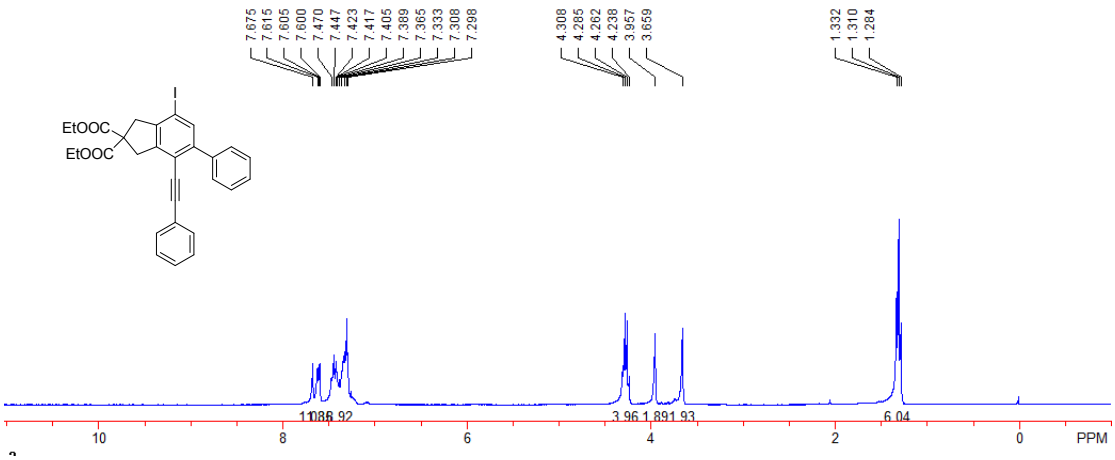
0
PPM

**bb**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7.298
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4.285
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4.238
3.957
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1.284
EtOOC
EtOOC
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1.93
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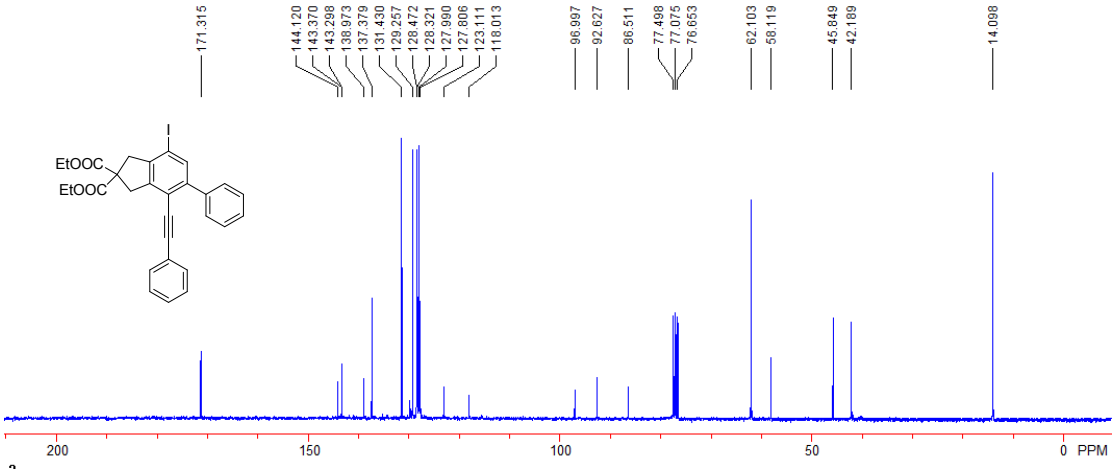
0
PPM

**bc**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77.075
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EtOOC
EtOOC
I
200
150
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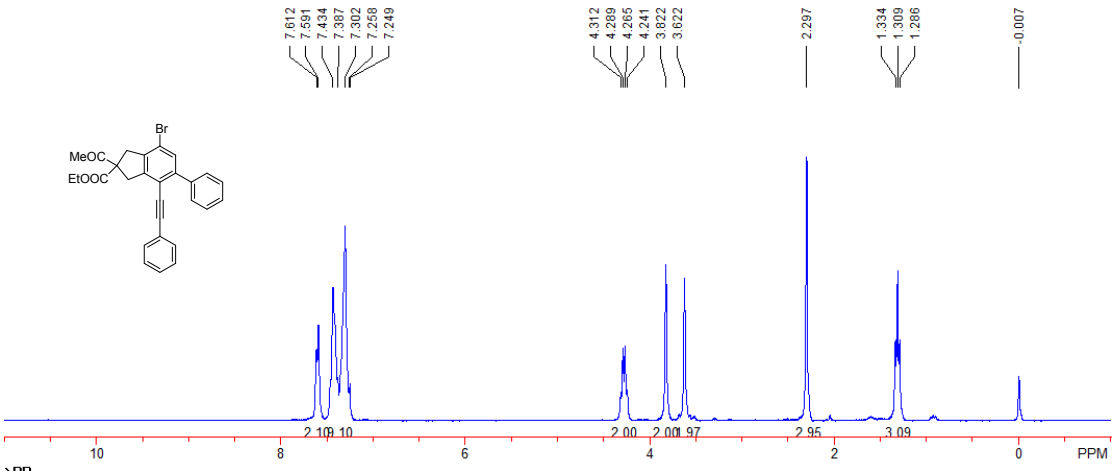
0
PPM

**bc**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2.297
1.334
1.309
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MeOC
EtOOC
Br
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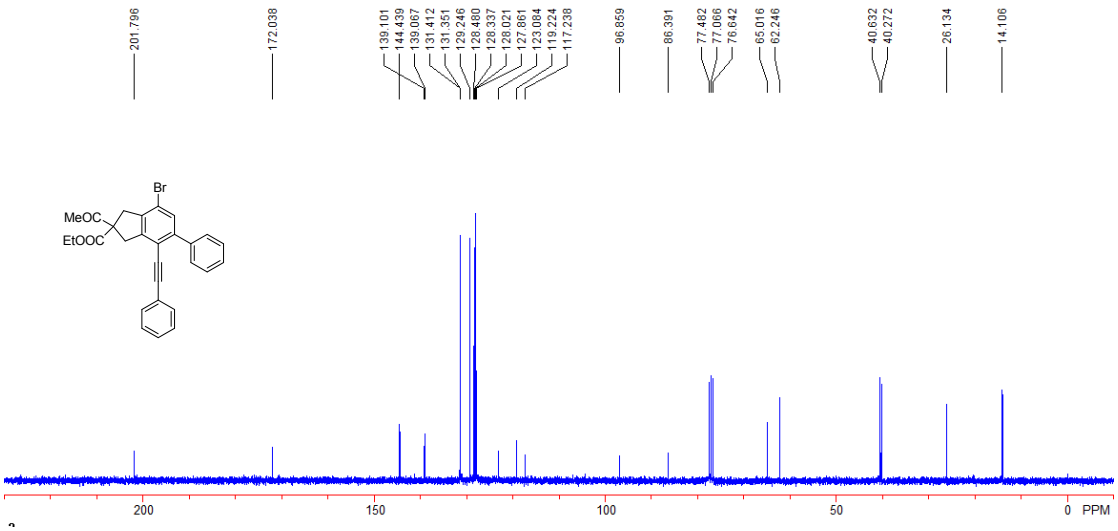
2.00
1.97
2.95
3.09
10
8
6
4
2
0
PPM

**ca**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65.016
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Br
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200
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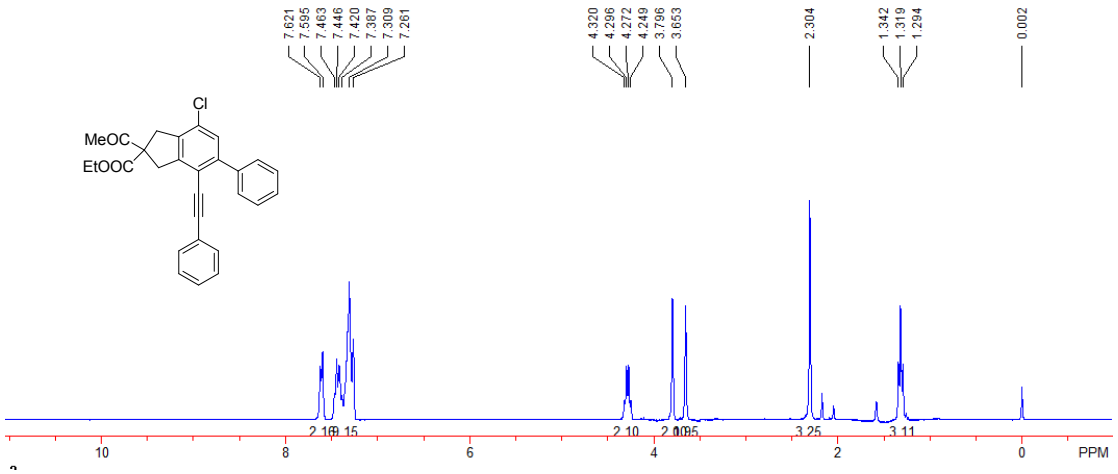
PPM

**ca**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1.294
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Cl
MeOC
EtOOC
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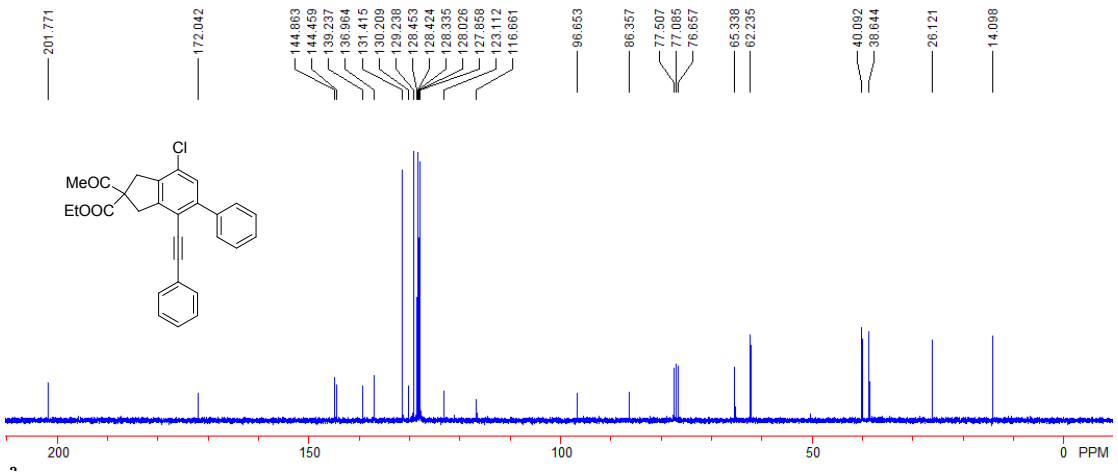
2.10
2.00
3.25
3.11
10
8
6
4
2
0
PPM

**cb**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128.335
128.026
127.858
123.112
116.661
96.653
86.357
77.507
77.085
76.657
65.338
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Cl
MeOC
EtOOC
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0
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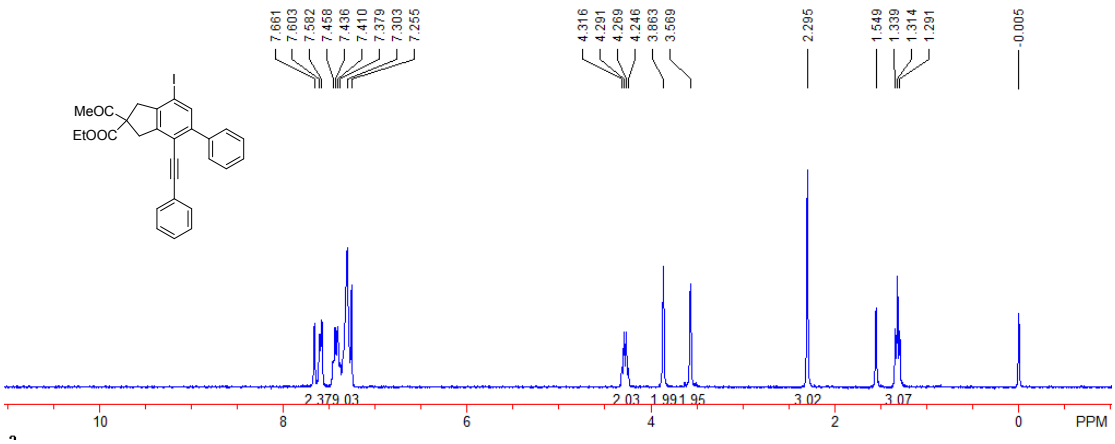
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7.303
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4.316
4.291
4.269
4.246
3.863
3.589
2.295
1.549
1.339
1.314
1.291
-0.005
I
MeOC
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3.02
3.07
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8
6
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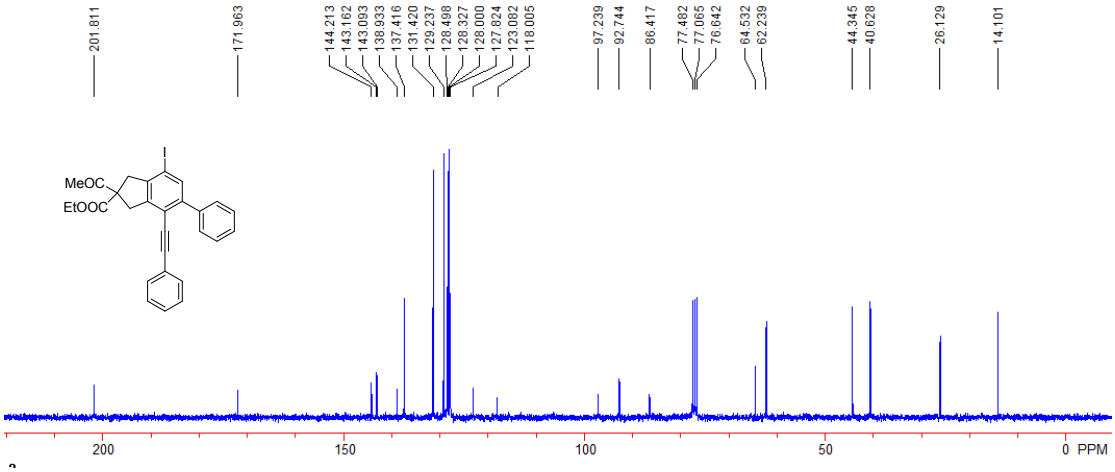
2
0
PPM

**cc**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127.824
123.082
118.005
97.239
92.744
86.417
77.482
77.065
76.642
64.532
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26.129
14.101
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MeOC
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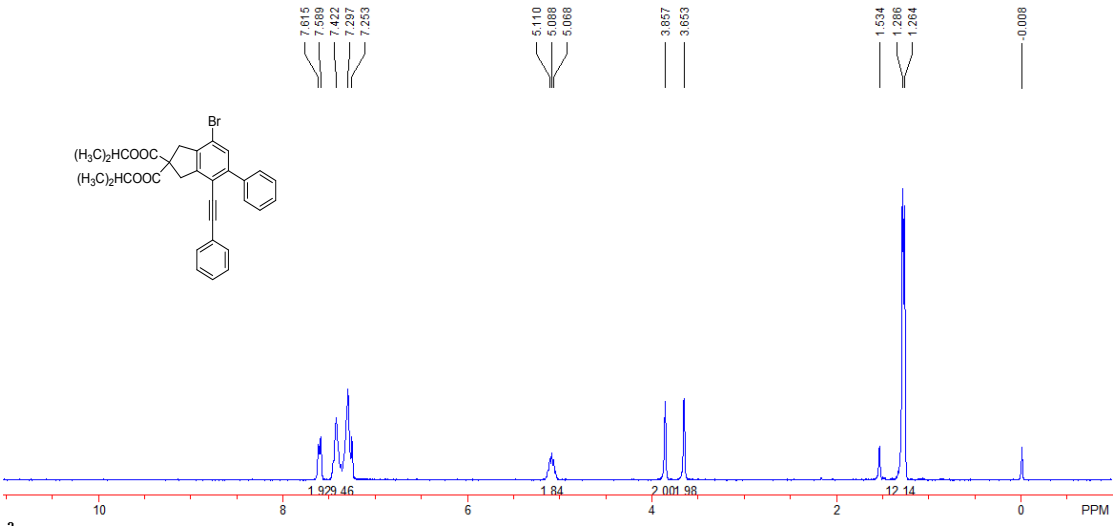
200
150
100
50
0 PPM

**cc**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5.088
5.068
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3.653
1.534
1.286
1.264
-0.008
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(H3C)2HCOOC
(H3C)2HCOOC
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1.84
2.001.98
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10
8
6
4
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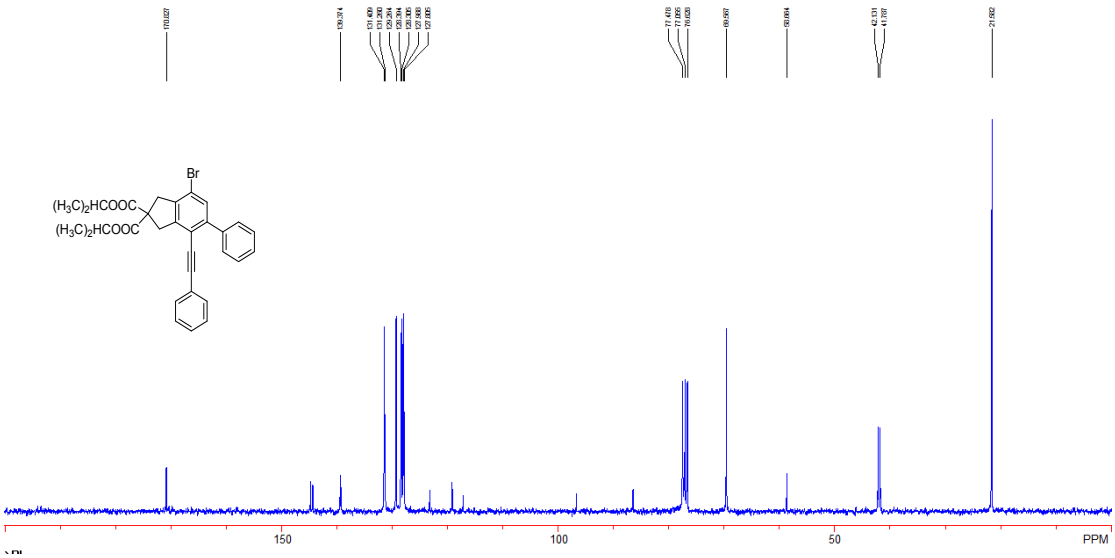
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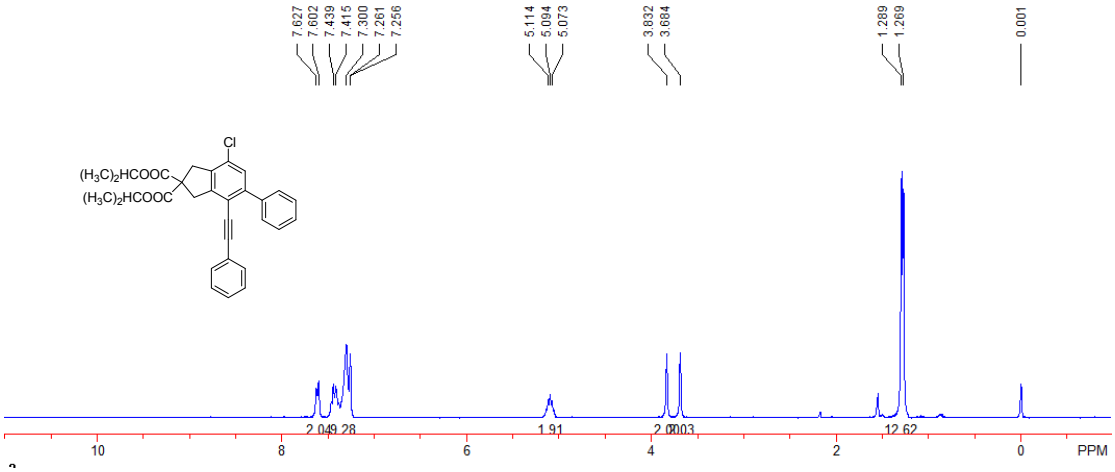
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7.261
7.256
5.114
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5.073
3.832
3.684
1.289
1.269
0.001
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8
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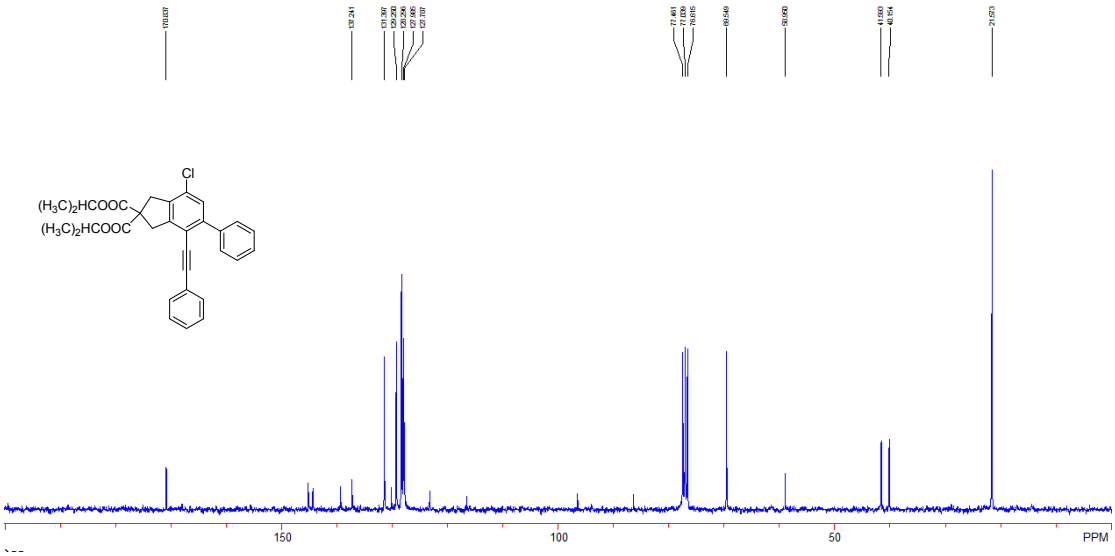
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(H3C)2HCOOC
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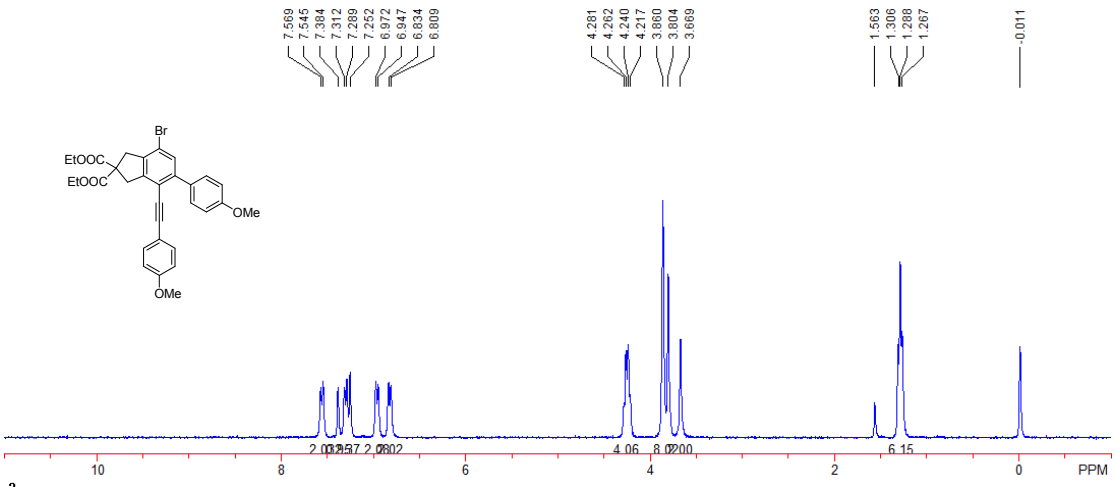
100
50
PPM

**db**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7.312
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7.252
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6.947
6.834
6.809
4.281
4.262
4.240
4.217
3.860
3.804
3.669
1.563
1.306
1.288
1.267
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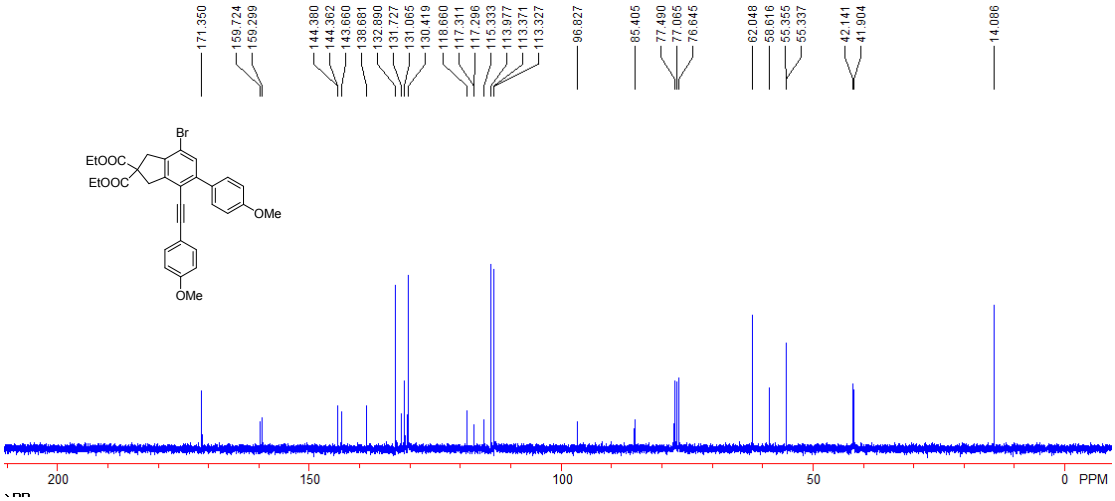
Br
EtOOC
EtOOC
OMe
OMe
10
8
6
4
2
0
PPM

**ea**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131.065
130.419
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117.311
117.296
115.333
113.977
113.371
113.327
96.827
85.405
77.490
77.065
76.645
62.048
58.616
55.355
55.337
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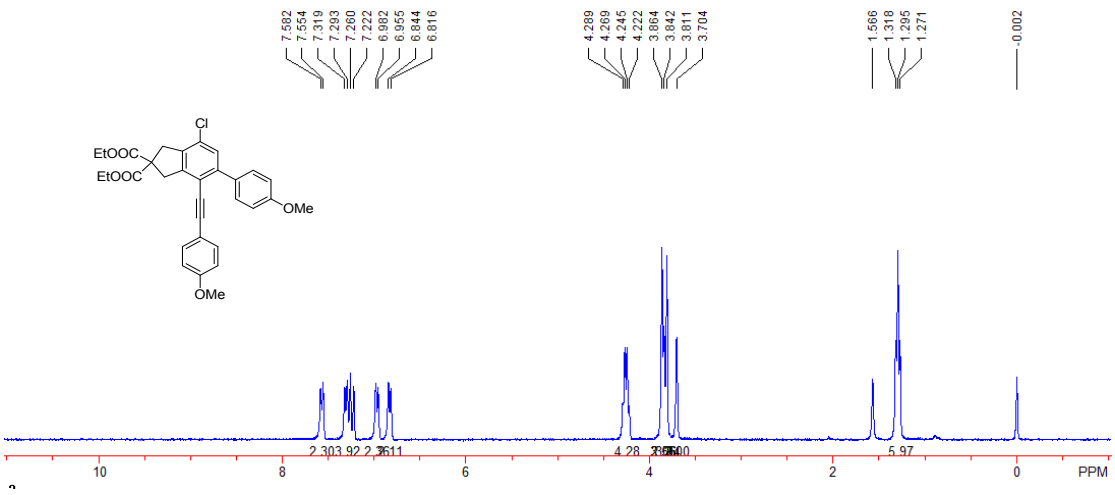
14.086
Br
EtOOC
EtOOC
OMe
OMe
200
150
100
50
0
PPM

**ea**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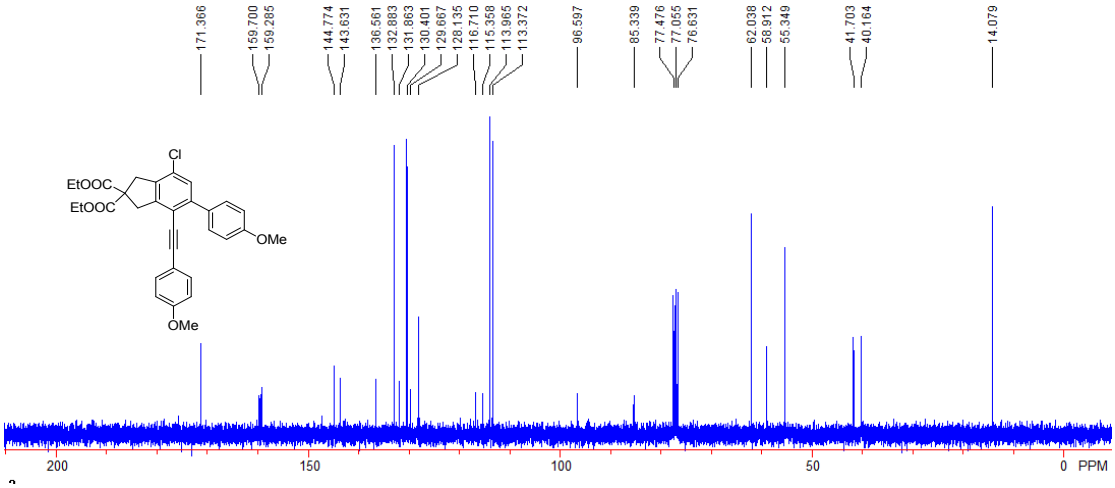
7.319
7.293
7.260
7.222
6.982
6.955
6.844
6.816
4.289
4.269
4.245
4.222
3.864
3.842
3.811
3.704
1.566
1.318
1.295
1.271
-0.002
Cl
EtOOC
EtOOC
OMe
OMe
10
8
6
4
2
0
PPM

**eb**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113.372
96.597
85.339
77.476
77.055
76.631
62.038
58.912
55.349
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Cl
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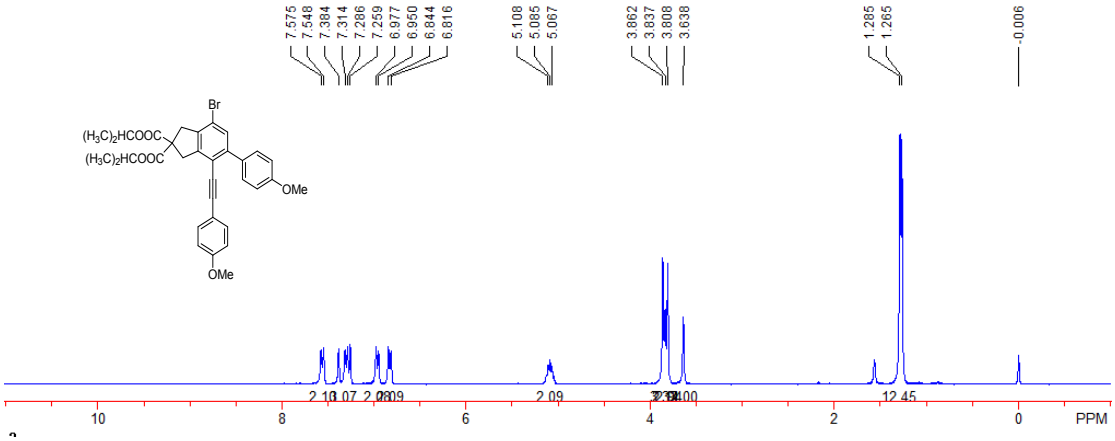
EtOOC
OMe
OMe
200
150
100
50
0
PPM

**eb**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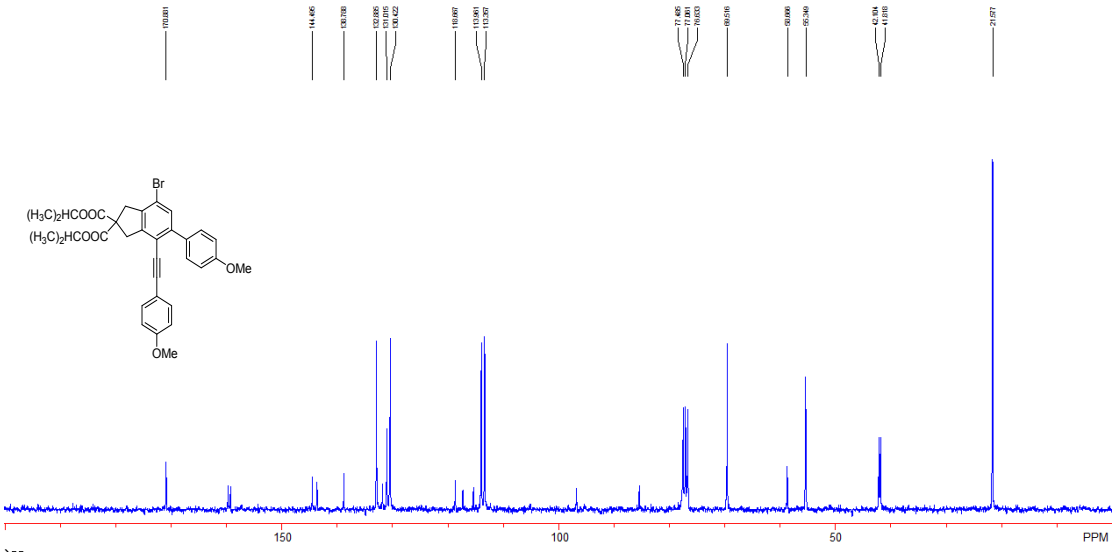
7.286
7.259
6.977
6.950
6.844
6.816
5.108
5.085
5.067
3.862
3.837
3.808
3.638
1.285
1.265
-0.006
Br
(H3C)2HCOOC
(H3C)2HCOOC
OMe
OMe
2.10
3.07
2.09
12.45
10
8
6
4
2
0
PPM

**fa**


Br
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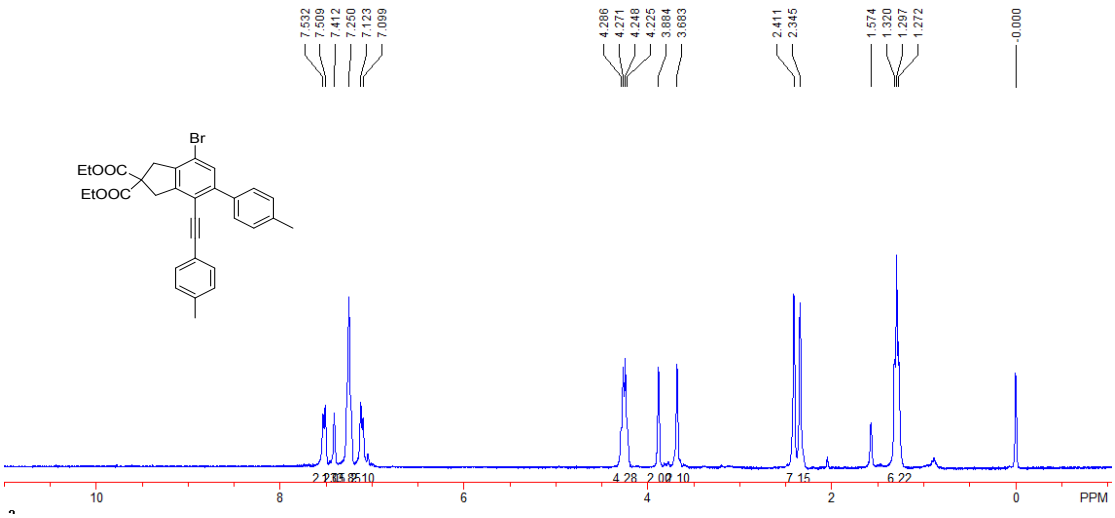
(H3C)2HCOOC
OMe
OMe
150
100
50
PPM

**fa**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7.250
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7.099
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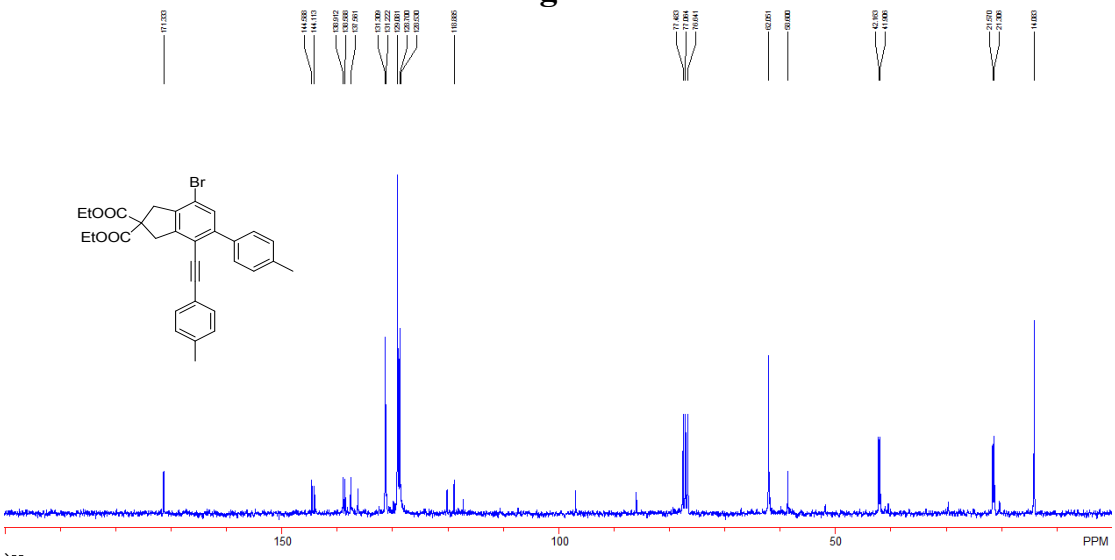
4.271
4.248
4.225
3.884
3.683
2.411
2.345
1.574
1.320
1.297
1.272
0.000
Br
EtOOC
EtOOC
10
8
6
4
2
0
PPM

**ga**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EtOOC
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100
50
PPM

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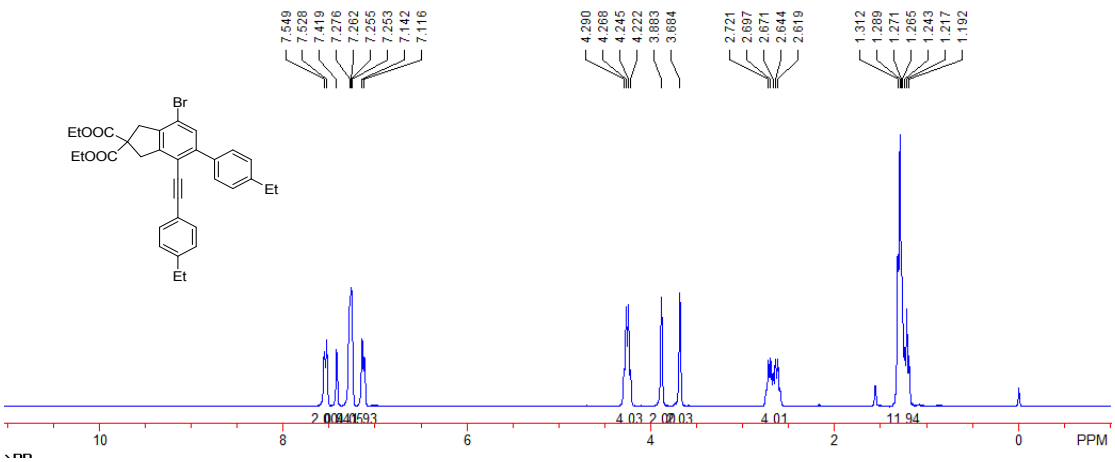
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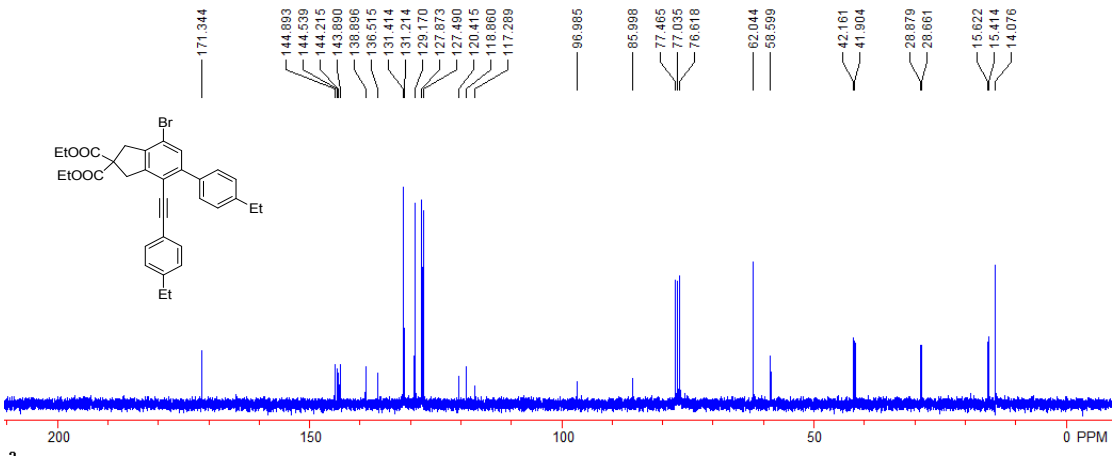
7.419
7.276
7.262
7.255
7.253
7.142
7.116
4.290
4.268
4.245
4.222
3.883
3.684
2.721
2.697
2.671
2.644
2.619
1.312
1.289
1.271
1.265
1.243
1.217
1.192
Br
EtOOC
EtOOC
Et
Et
10
8
6
4
2
0
PPM

**ha**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120.415
118.860
117.289
96.985
85.998
77.465
77.035
76.618
62.044
58.599
42.161
41.904
28.879
28.861
15.622
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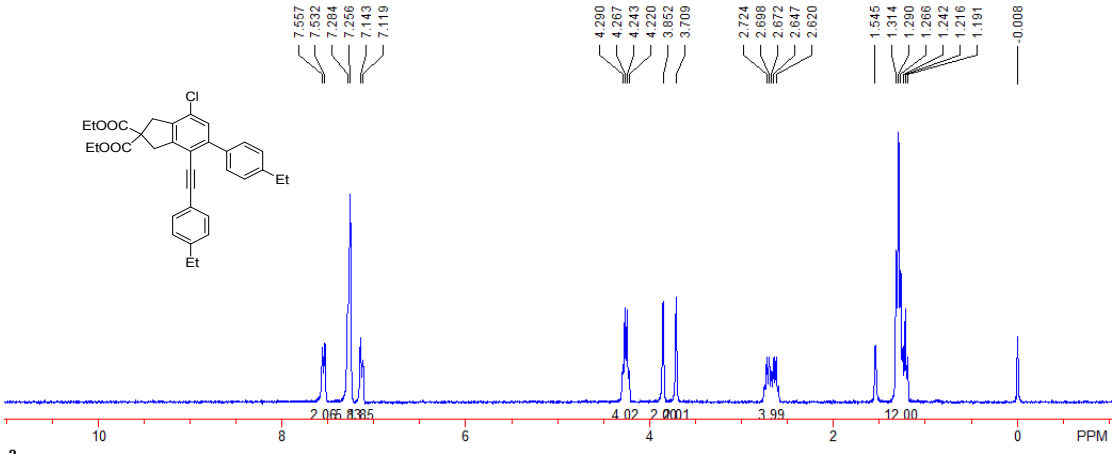
14.076
Br
EtOOC
EtOOC
Et
Et
200
150
100
50
0 PPM

**ha**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4.267
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2.620
1.545
1.314
1.290
1.266
1.242
1.216
1.191
-0.008
Cl
EtOOC
EtOOC
Et
Et
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2.00
3.99
12.00
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4
2
0
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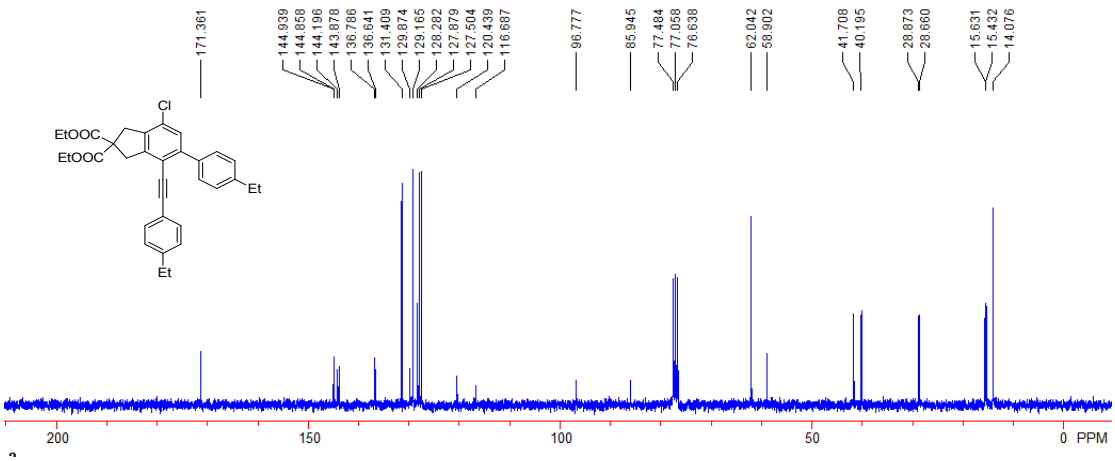
**hb**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127.504
120.439
116.687
96.777
85.945
77.484
77.058
76.638
62.042
58.902
41.708
40.195
28.873
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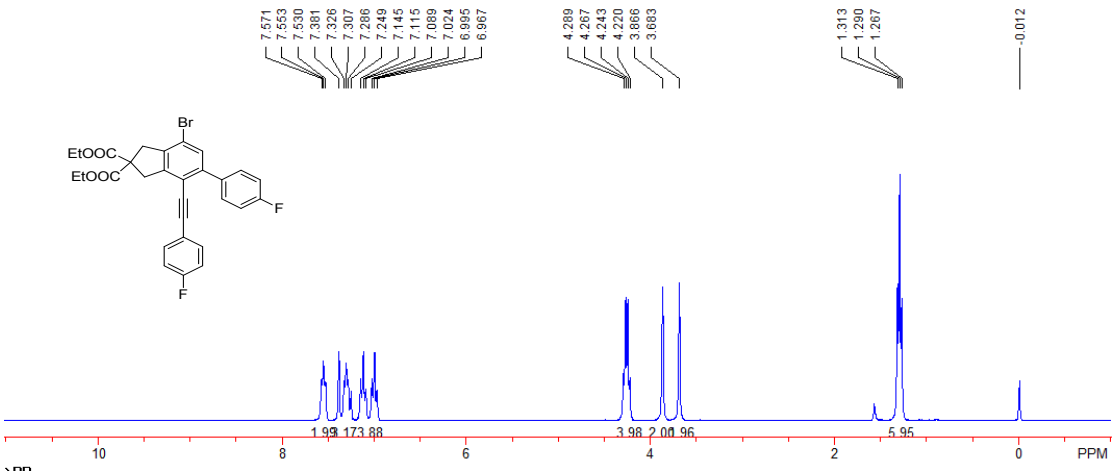
14.076
Cl
EtOOC
EtOOC
Et
Et
200
150
100
50
0 PPM

**hb**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7.115
7.089
7.024
6.995
6.967
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4.267
4.243
4.220
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3.683
1.313
1.290
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Br
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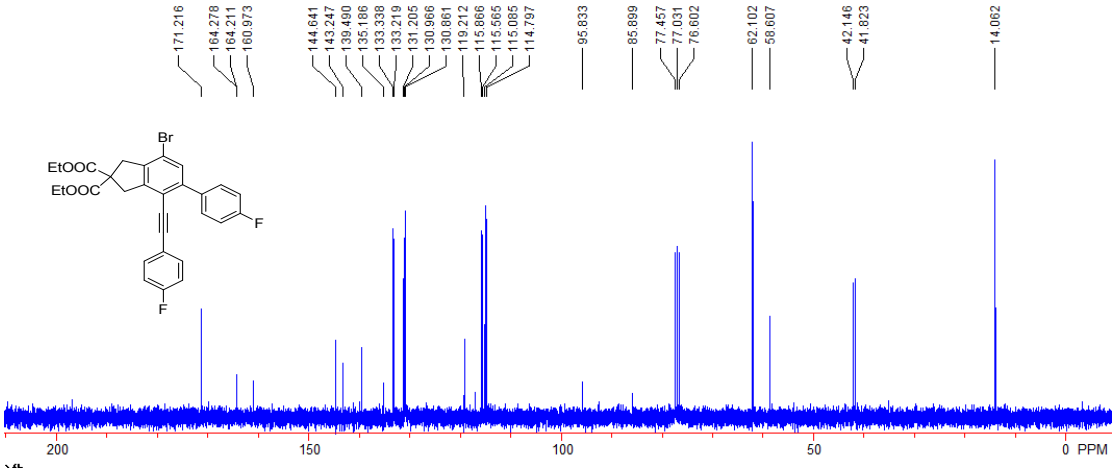
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95.833
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77.031
76.602
62.102
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Br
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EtOOC
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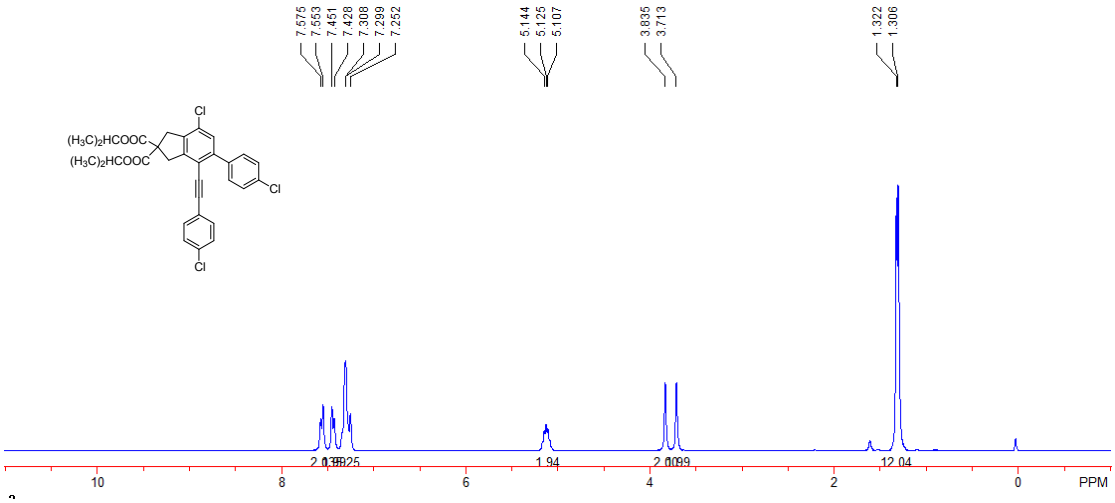
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7.428
7.308
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5.125
5.107
3.835
3.713
1.322
1.306
Cl
(H3C)2HCOOC
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Cl
Cl
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8
6
4
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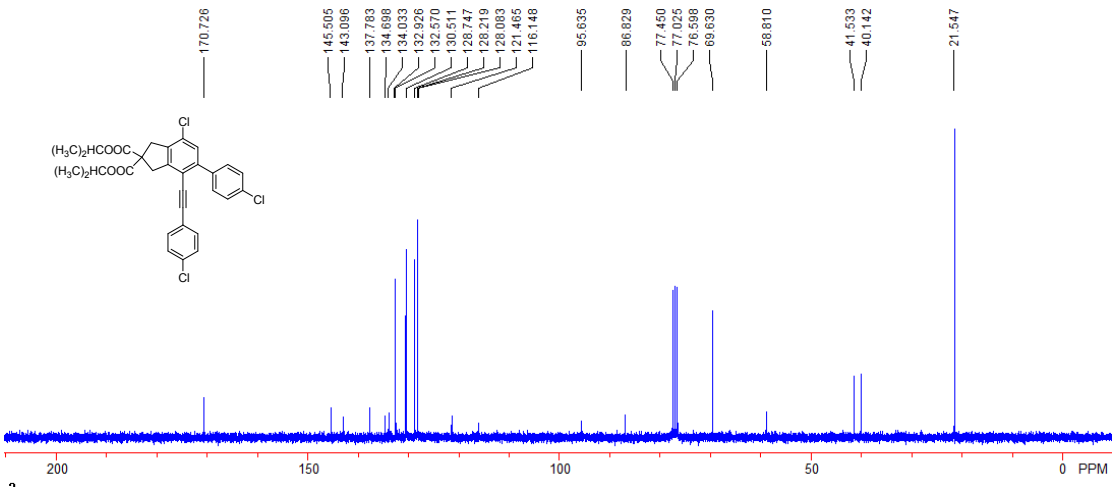
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121.465
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77.450
77.025
76.598
69.630
58.810
41.533
40.142
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(H3C)2HCOOC
Cl
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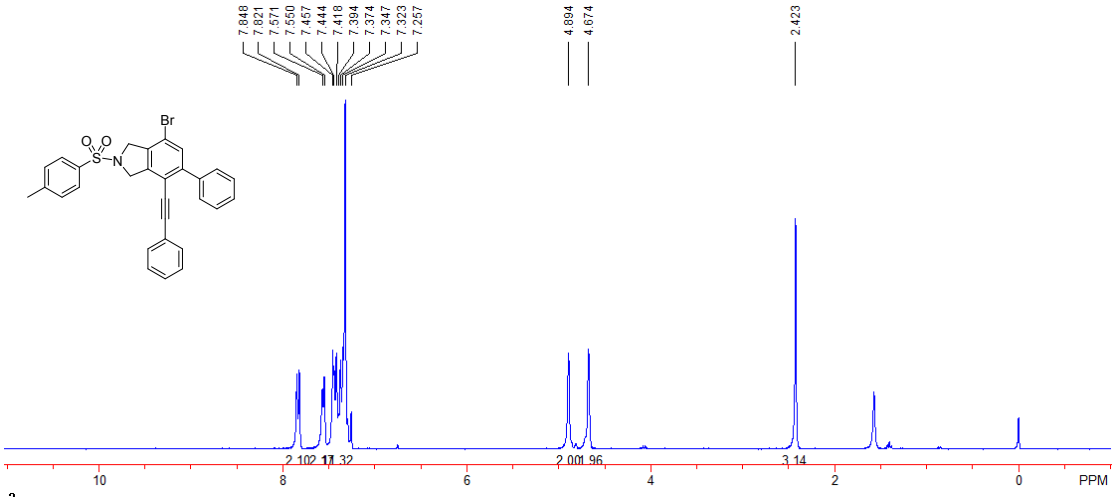
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4.674
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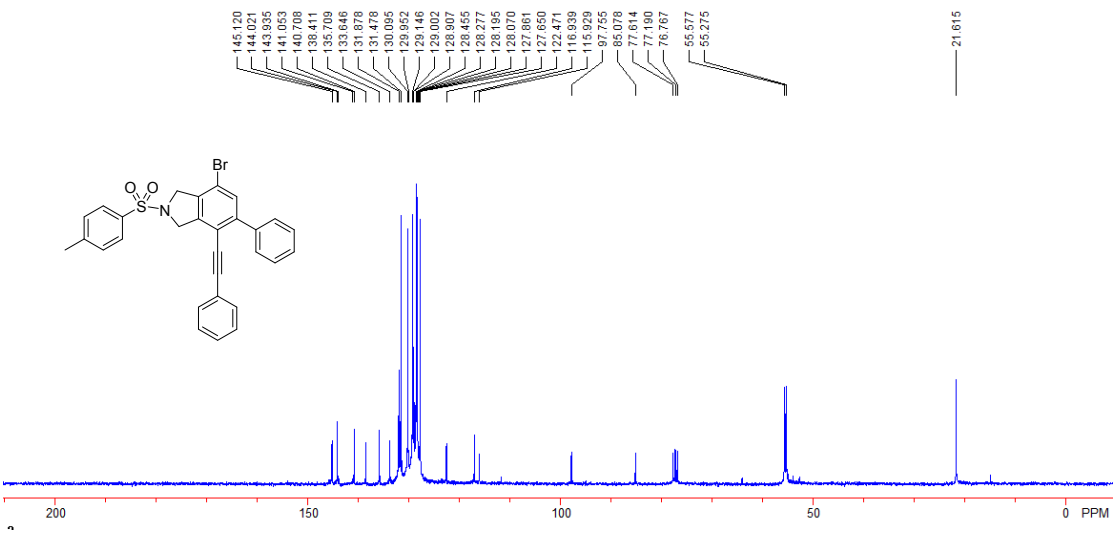
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PPM

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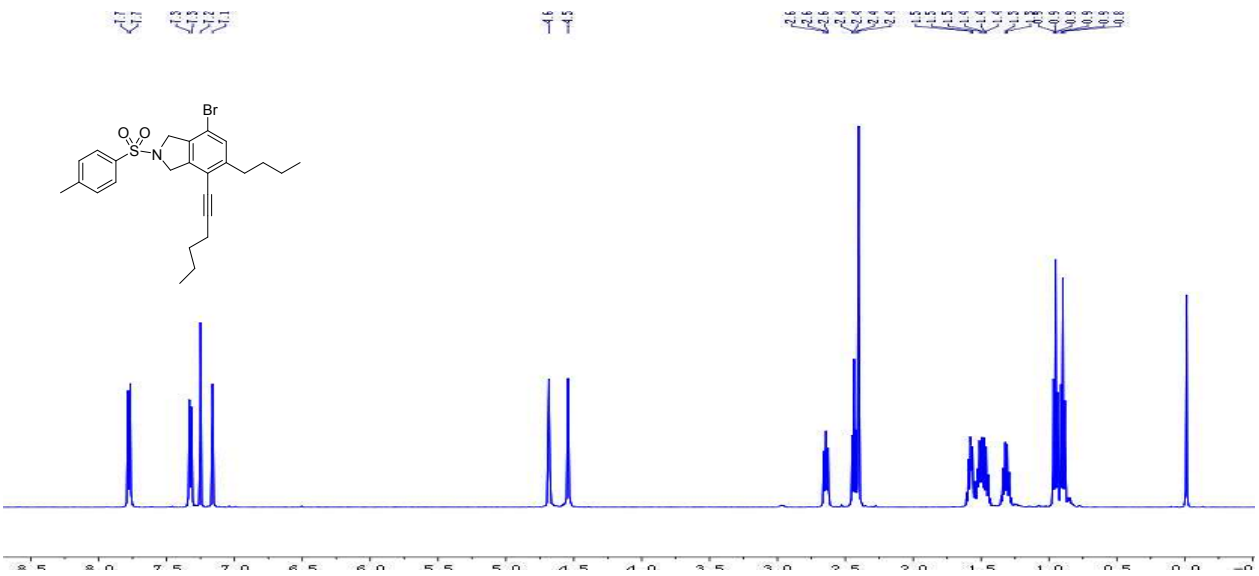
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S
N

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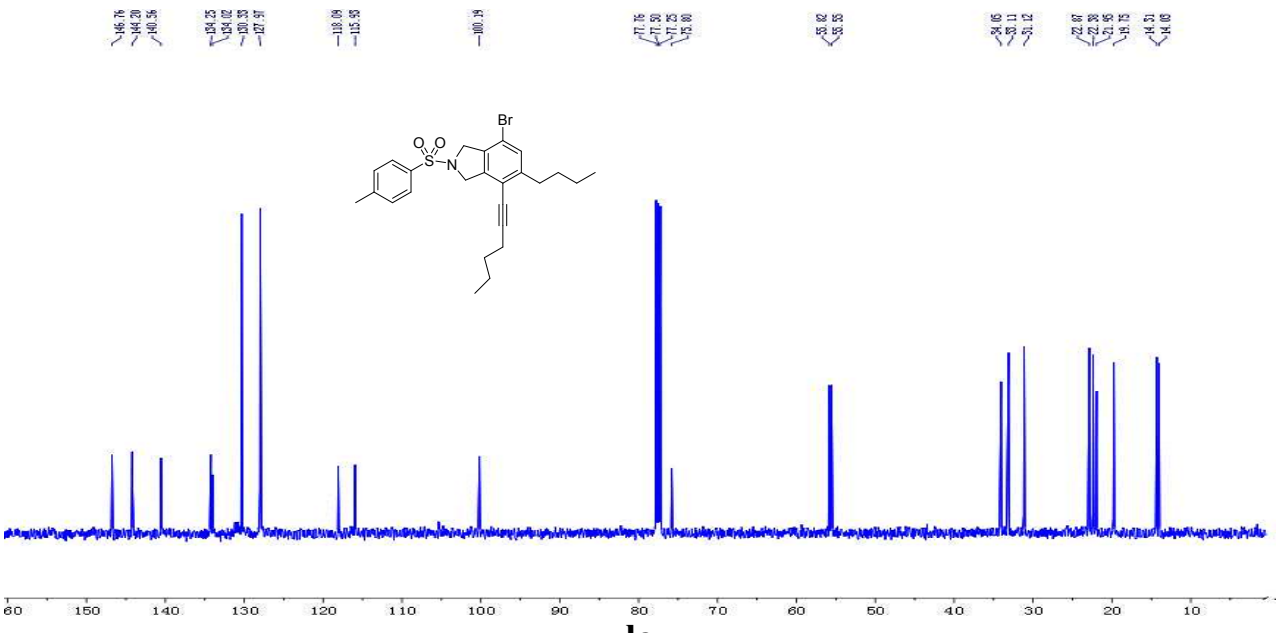
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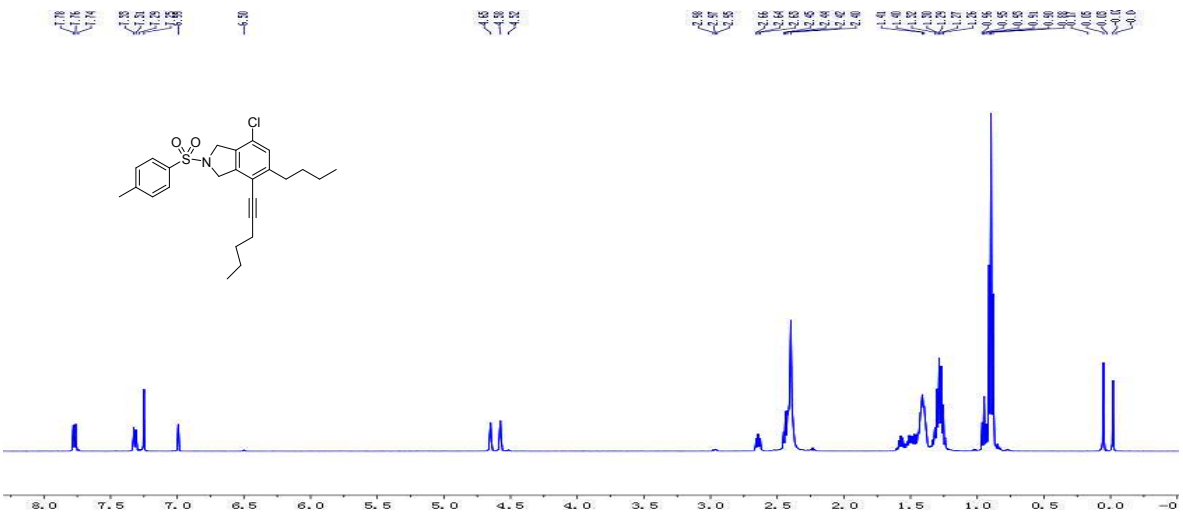
20
10

**1a**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1.5
1.0
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0.0

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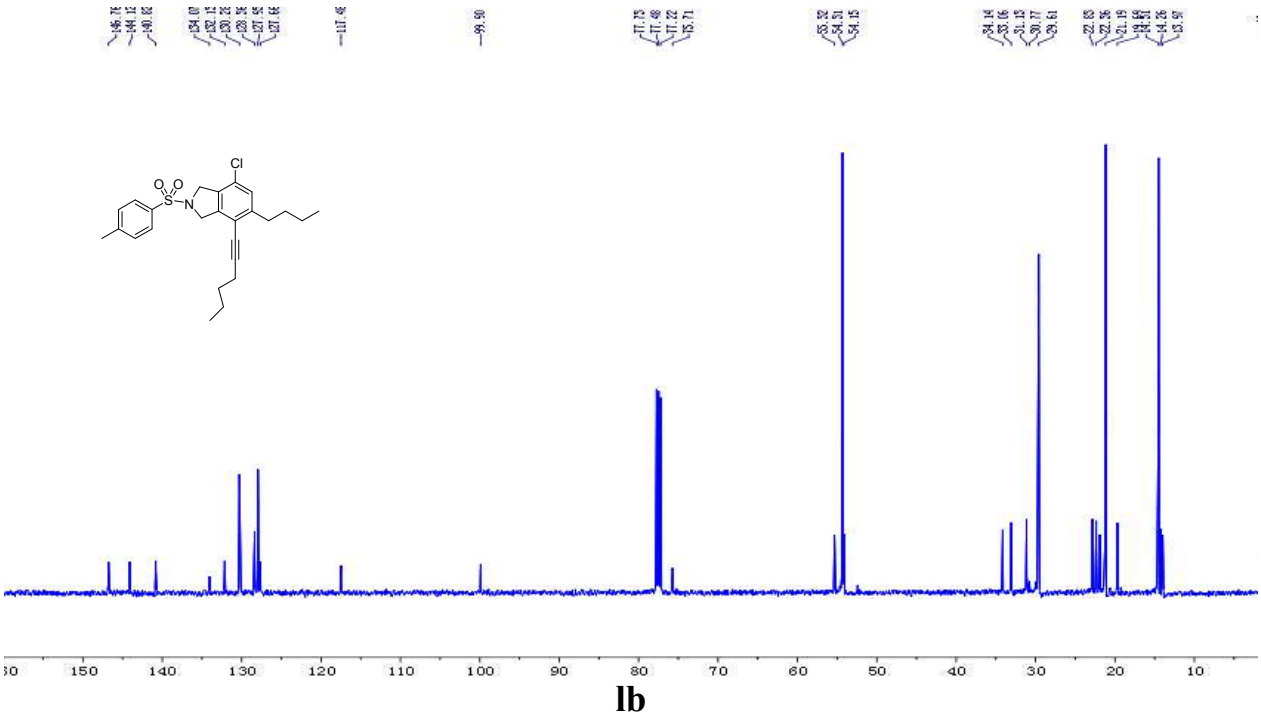
Cl
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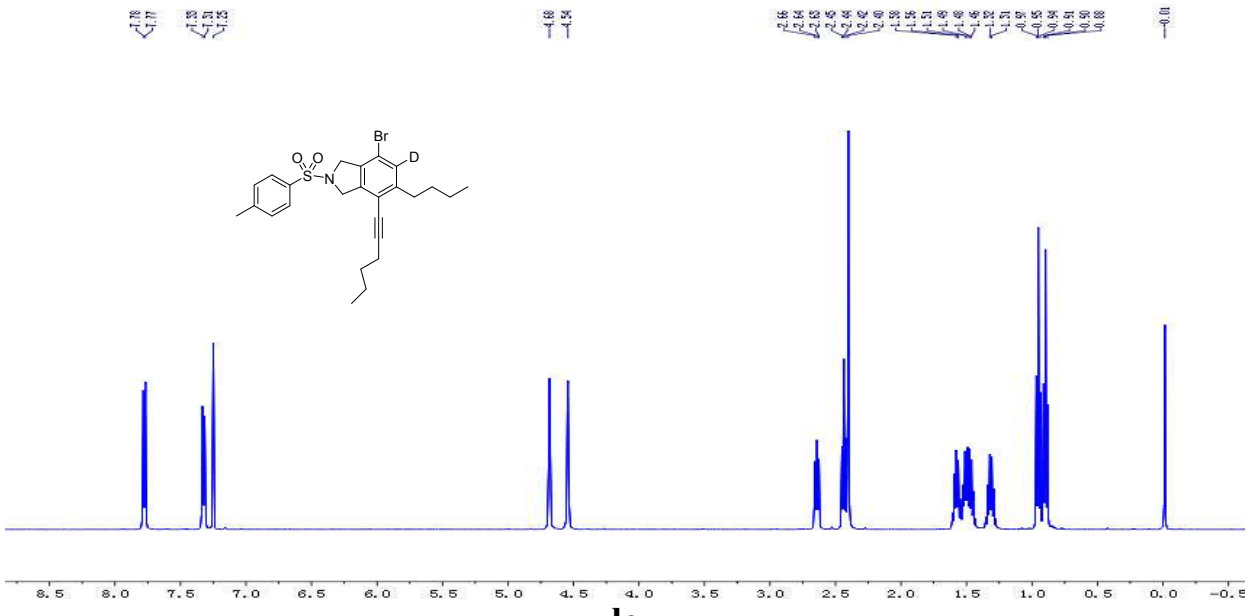
40
30
20
10

**lb**

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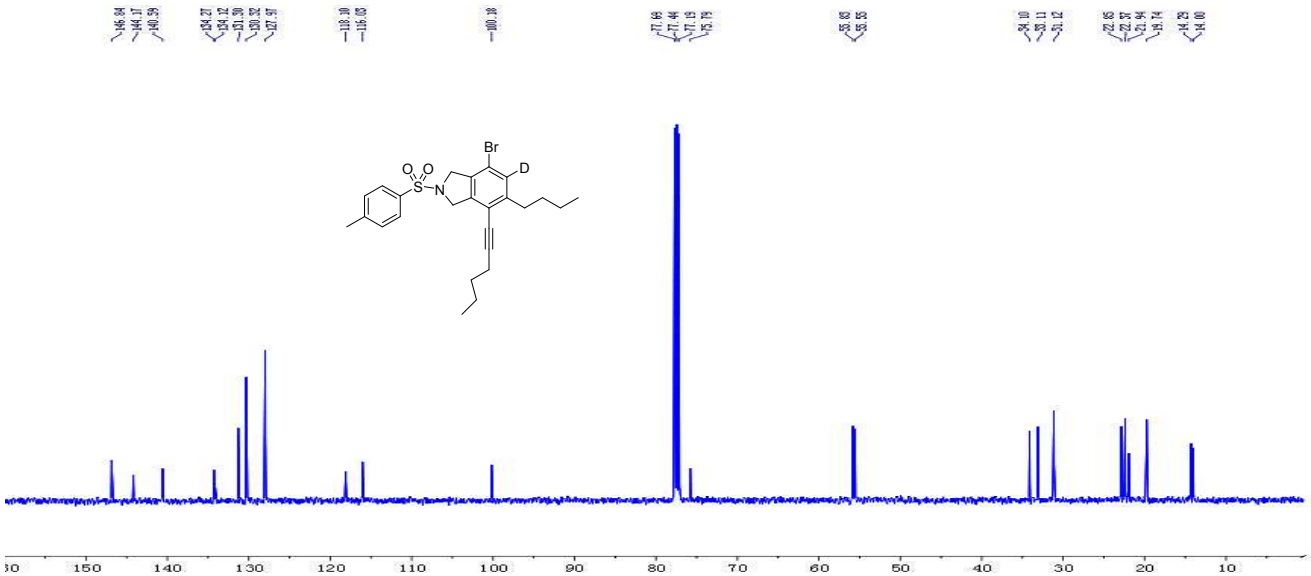


**lc**