

Supporting Information

Metal-free homo/cross anion-cation coupling of cyclic diaryl λ^3 -bromanes

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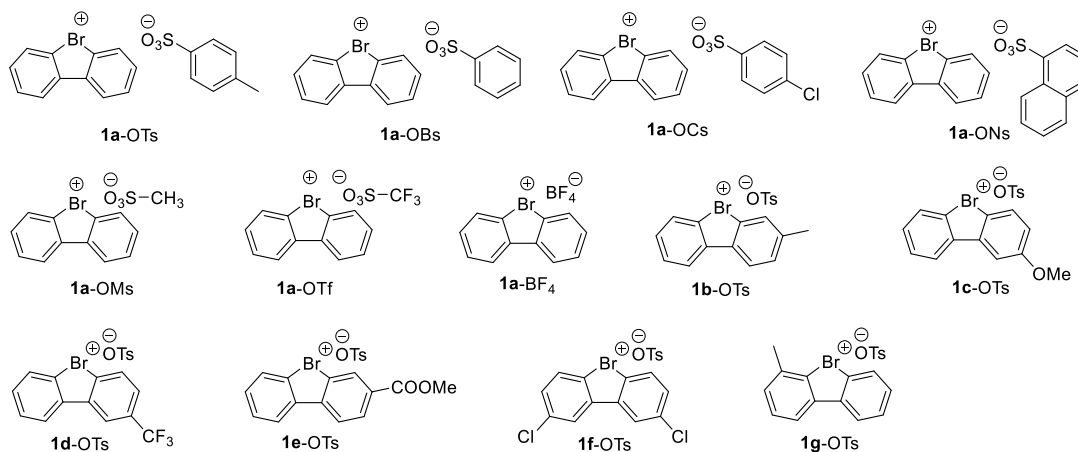
1. General remarks

NMR spectra were obtained on a BRUKER Ascend500. The ^1H NMR (500 MHz) chemical shifts were measured relative to CDCl_3 or $\text{DMSO}-d_6$ as the internal reference (CDCl_3 : $\delta = 7.26$ ppm; $\text{DMSO}-d_6$: $\delta = 2.50$ ppm). The ^{13}C NMR (125 MHz) chemical shifts were given using CDCl_3 or $\text{DMSO}-d_6$ the internal standard (CDCl_3 : $\delta = 77.16$ ppm; $\text{DMSO}-d_6$: $\delta = 39.52$ ppm). High-resolution mass spectra (HRMS) were recorded on an Agilent QTOF 6550 or Shimadzu LCMS-9030 instruments under ESI in positive ionization mode detection. Melting points were determined with SGW[®] X-4 and are uncorrected.

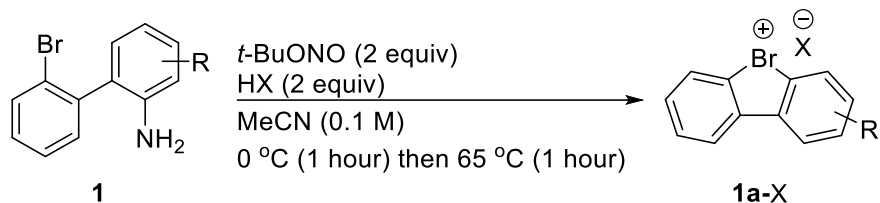
Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. 2-iodoanilines, 2-bromophenylboronic acids, Cs_2CO_3 were purchased from Beijing Innochem Chemical Engineering Reagent (China) Co., Ltd and Energy Chemical.

2. General procedures

2.1 General procedure for the synthesis of cyclic diaryl λ^3 -bromanones

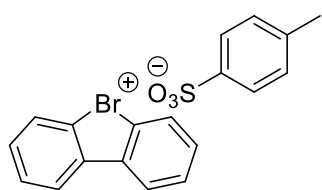


Compounds **1a-OTs**, **1a-OMs**, **1a-OTf** and **1a-BF₄** were prepared according to the modified literature procedures.¹ Compounds **1a-OBs**, **1a-OCs**, **1a-ONs**, **1b-OTs**, **1c-OTs**, **1d-OTs**, **1e-OTs**, **1f-OTs**, and **1g-OTs** were prepared as follows:



To a dry round bottom flask was added 2'-bromo-[1,1'-biphenyl]-2-amine **1** (1 mmol) and MeCN (10 mL). The solution was cooled to 0 °C before *t*-BuONO (2 equiv) was added dropwise. After that, acid HX (2 equiv) was added in portions. The mixture was stirred at 0 °C for 1 hour and then heated to 65 °C for 1 hour. The cooled mixture was purged in Et₂O where a solid precipitate. The product was collected through filtration, washed with Et₂O and dried under high vacuum.

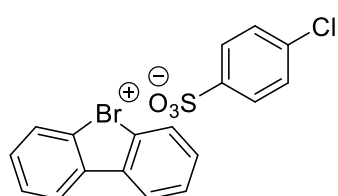
dibenzo[*b,d*]bromol-5-ium 4-methylbenzenesulfonate (**1a-OTs**)



White solid (371 mg, 92% yield). ¹H NMR (500MHz, DMSO-*d*₆): δ = 8.60 (d, *J* = 8 Hz, 2H), 8.50 (d, *J* = 8.5 Hz, 2H), 7.94 (t, *J* = 7.3 Hz, 2H), 7.84 (t, *J* = 7.3 Hz, 2H), 7.50 (d, *J* = 8 Hz, 2H), 7.11 (d, *J* = 8 Hz, 2H), 2.28 (s, 3H) ppm.

¹³C NMR (125 MHz, DMSO-*d*₆): δ = 145.47, 137.84, 136.61, 135.39, 131.84, 131.25, 128.14, 126.35, 125.70, 125.56, 20.83 ppm. Data in accordance with the literature.¹

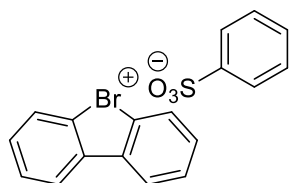
dibenzo[*b,d*]bromol-5-ium 4-chlorobenzenesulfonate (**1a-OCs**)



White solid (381 mg, 90% yield). M.p.: 217–219 °C. ¹H NMR (500MHz, DMSO-*d*₆): δ = 8.59–8.56 (m, 2H), 8.50 (d, *J* = 8.5 Hz, 2H), 7.95–7.90 (m, 2H), 7.84–7.81 (m, 2H), 7.64–7.61 (m, 2H), 7.38 (d, *J* = 8.5 Hz, 2H) ppm. ¹³C

NMR (125 MHz, DMSO-*d*₆): δ = 147.18, 136.54, 135.32, 133.00, 131.80, 131.20, 127.72, 127.49, 126.30, 125.60 ppm. HRMS (ESI) *m/z*: calcd for C₁₂H₈Br⁺ (M-OCs⁻) 230.9804, found 230.9808.

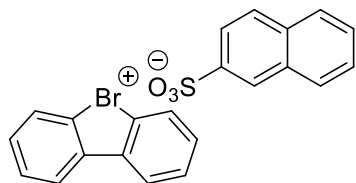
dibenzo[*b,d*]bromol-5-ium benzenesulfonate (1a-OBs)



Yellow solid (331 mg, 85% yield). M.p.: 195–197 °C. **¹H NMR (500MHz, DMSO-*d*₆)**: δ = 8.58 (d, *J* = 7.5 Hz, 2H), 8.51 (d, *J* = 8.5 Hz, 2H), 7.93 (t, *J* = 7.3 Hz, 2H), 7.83 (t, *J* = 7.8 Hz, 2H), 7.64 (d, *J* = 6.5 Hz, 2H), 7.34–7.30 (m, 3H) ppm.

¹³C NMR (125 MHz, DMSO-*d*₆): δ = 148.24, 136.56, 135.34, 131.81, 131.22, 128.49, 127.70, 126.31, 125.64, 125.51 ppm. **HRMS (ESI) *m/z***: calcd for C₁₂H₈Br⁺ (M-OBs⁻) 230.9804, found 230.9805.

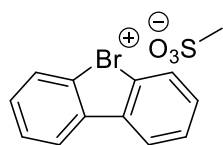
dibenzo[*b,d*]bromol-5-ium naphthalene-2-sulfonate (1a-ONs)



White solid (308 mg, 70% yield). M.p.: 200–202 °C. **¹H NMR (500MHz, DMSO-*d*₆)**: δ = 8.58 (d, *J* = 7.0 Hz, 2H), 8.50 (d, *J* = 8.0 Hz, 2H), 8.17 (s, 1H), 7.95–7.84 (m, 7H), 7.74–7.73 (m, 1H), 7.52 (s, 2H) ppm. **¹³C NMR (125 MHz, DMSO-*d*₆)**: δ = 145.58, 136.56, 135.34, 132.73, 132.15, 131.81, 131.21, 128.45, 127.46, 127.33, 126.44, 126.30, 125.61, 124.07, 123.99 ppm.

HRMS (ESI) *m/z*: calcd for C₁₂H₈Br⁺ (M-ONs⁻) 230.9804, found 230.9805.

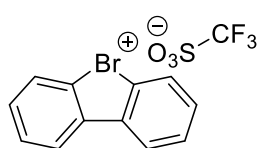
dibenzo[*b,d*]bromol-5-ium methanesulfonate (1a-OMs)



White solid (294 mg, 90% yield). **¹H NMR (500MHz, DMSO-*d*₆)**: δ = 8.60 (d, *J* = 8 Hz, 2H), 8.53 (d, *J* = 8.5 Hz, 2H), 7.95 (t, *J* = 7.3 Hz, 2H), 7.85 (t, *J* = 7.3 Hz, 2H), 2.33 (s, 3H) ppm. **¹³C NMR (125 MHz, DMSO-*d*₆)**: δ = 136.65, 135.39, 131.82, 131.23, 126.31, 125.71, 39.77 ppm.

Data in accordance with the literature.¹

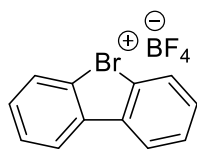
dibenzo[*b,d*]bromol-5-ium trifluoromethanesulfonate (1a-OTf)



White solid (228 mg, 60% yield). **¹H NMR (500MHz, DMSO-*d*₆)**: δ = 8.59 (d, *J* = 7.5 Hz, 2H), 8.47 (d, *J* = 8.5 Hz, 2H), 7.94 (t, *J* = 7.5 Hz, 2H), 7.85 (t, *J* = 8.0 Hz, 2H) ppm. **¹³C NMR (125 MHz, DMSO-*d*₆)**: δ = 136.65, 135.39, 131.82, 131.23, 126.31, 125.71, 39.77 ppm.

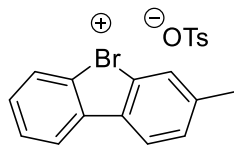
MHz, DMSO-*d*₆): δ = 136.61, 135.40, 131.89, 131.27, 126.35, 125.62 ppm. **¹⁹F NMR (471 MHz, DMSO-*d*₆):** δ = -78.18 (s) ppm. Data in accordance with the literature.¹

dibenzo[*b,d*]bromol-5-ium tetrafluoroborate (1a-BF₄)



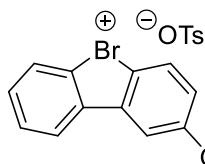
White solid (239 mg, 75% yield). **¹H NMR (500MHz, DMSO-*d*₆):** δ = 8.66 (d, *J* = 8.5 Hz, 4H), 8.00 (t, *J* = 7.3 Hz, 2H), 7.95 (t, *J* = 8.0 Hz, 2H) ppm. **¹³C NMR (125 MHz, DMSO-*d*₆):** δ = 140.04, 132.03, 131.75, 125.51, 122.95 ppm. **¹⁹F NMR (471 MHz, DMSO-*d*₆):** δ = -148.88 (s), -148.14 (s) ppm. Data in accordance with the literature.¹

3-methyldibenzo[*b,d*]bromol-5-ium 4-methylbenzenesulfonate (1b-OTs)



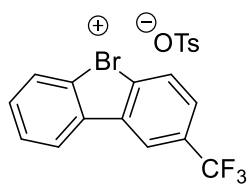
Orange solid (376 mg, 90% yield). M.p.: 174–176 °C. **¹H NMR (500MHz, DMSO-*d*₆):** δ = 8.51–8.43 (m, 3H), 8.29 (s, 1H), 7.90 (t, *J* = 7.5 Hz, 1H), 7.79 (t, *J* = 7.3 Hz, 1H), 7.73 (d, *J* = 8 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 2H), 7.12 (d, *J* = 7.5 Hz, 2H), 2.51 (s, 3H), 2.28 (s, 3H) ppm. **¹³C NMR (125 MHz, DMSO-*d*₆):** δ = 145.58, 142.54, 137.78, 136.60, 136.41, 135.33, 132.68, 132.09, 131.33, 131.19, 128.14, 125.98, 125.80, 125.63, 125.53, 125.28, 21.43, 20.81 ppm. **HRMS (ESI) *m/z*:** calcd for C₁₃H₁₀Br⁺ (M-OTs⁻) 244.9961, found 244.9960.

2-methoxydibenzo[*b,d*]bromol-5-ium 4-methylbenzenesulfonate (1c-OTs)



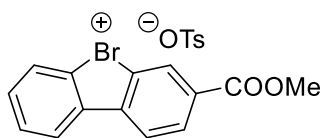
Yellow solid (443 mg, 92% yield). M.p.: 218–220 °C. **¹H NMR (500MHz, DMSO-*d*₆):** δ = 8.64 (d, *J* = 7.5, 1H), 8.48 (d, *J* = 8.5 Hz, 1H), 8.34 (d, *J* = 9.5 Hz, 1H), 8.15 (d, *J* = 1.5 Hz, 1H), 7.92 (t, *J* = 7.3 Hz, 1H), 7.83 (t, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.40 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.11 (d, *J* = 7.5 Hz, 2H), 3.95 (s, 3H), 2.28 (s, 3H) ppm. **¹³C NMR (125 MHz, DMSO-*d*₆):** δ = 162.02, 146.15, 138.13, 137.43, 137.31, 135.75, 132.32, 131.58, 128.55, 127.33, 127.05, 126.77, 126.14, 125.97, 119.23, 110.83, 56.93, 21.25 ppm. **HRMS (ESI) *m/z*:** calcd for C₁₃H₁₀BrO⁺ (M-OTs⁻) 260.9910, found 260.9907.

2-(trifluoromethyl)dibenzo[*b,d*]bromol-5-ium 4-methylbenzenesulfonate (1d-OTs)



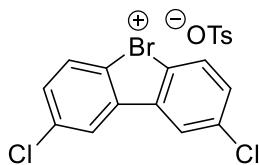
White solid (188 mg, 40% yield). M.p.: 223–225 °C. **¹H NMR (500MHz, DMSO-*d*₆)**: δ = 9.08 (s, 1H), 8.82 (d, *J* = 8.0 Hz, 1H), 8.73 (d, *J* = 8.5 Hz, 1H), 8.54 (d, *J* = 8.5 Hz, 1H), 8.22 (d, *J* = 9.0 Hz, 1H), 7.98 (t, *J* = 6.0 Hz, 1H), 7.90 (t, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 2.28 (s, 3H) ppm. **¹³C NMR (125 MHz, DMSO-*d*₆)**: 145.67, 139.43, 137.71 (d, *J*_{C-F} = 3.3 Hz), 137.51, 136.84, 134.48, 132.65, 131.79 (q, *J*_{C-F} = 32.6 Hz), 131.33, 128.11, 128.04 (d, *J*_{C-F} = 3.4 Hz), 127.12, 127.02, 125.62, 125.53, 123.50 (q, *J*_{C-F} = 271.8 Hz), 123.49, 20.80 ppm. **¹⁹F NMR (471 MHz, DMSO-*d*₆)**: δ = -60.80 (s) ppm. **HRMS (ESI) *m/z***: calcd for C₁₃H₇BrF₃⁺ (M-OTs⁻) 298.9678, found 298.9678.

3-(methoxycarbonyl)dibenzo[*b,d*]bromol-5-ium 4-methylbenzenesulfonate (1e-OTs)



Yellow solid (281 mg, 61% yield). M.p.: > 240 °C. **¹H NMR (500MHz, DMSO-*d*₆)**: δ = 9.07 (s, 1H), 8.69 (d, *J* = 8.5 Hz, 1H), 8.65 (d, *J* = 7.5 Hz, 1H), 8.53 (d, *J* = 8.5 Hz, 1H), 8.38 (d, *J* = 8.0 Hz, 1H), 7.96 (t, *J* = 7.0 Hz, 1H), 7.90 (t, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 3.95 (s, 3H), 2.28 (s, 3H) ppm. **¹³C NMR (125 MHz, DMSO-*d*₆)**: δ = 164.29, 145.67, 139.50, 137.79, 137.69, 136.29, 134.34, 132.90, 131.82, 131.54, 131.42, 128.10, 127.19, 126.58, 126.29, 125.77, 125.52, 53.06, 20.80 ppm. **HRMS (ESI) *m/z***: C₁₄H₁₀BrO₂⁺ (M-OTs⁻) 288.9859, found 288.9860.

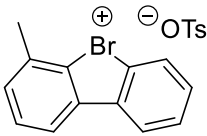
2,8-dichlorodibenzo[*b,d*]bromol-5-ium 4-methylbenzenesulfonate (1f-OTs)



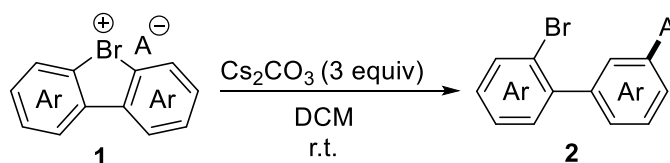
White solid (283 mg, 60% yield). M.p.: 185–187 °C. **¹H NMR (500MHz, DMSO-*d*₆)**: δ = 8.84 (s, 2H), 8.67 (d, *J* = 9.0 Hz, 2H), 7.93 (d, *J* = 9.0 Hz, 2H), 7.48 (d, *J* = 7.5 Hz, 2H), 7.11 (d, *J* = 7.5 Hz, 2H), 2.28 (s, 3H) ppm. **¹³C NMR (125 MHz, DMSO-*d*₆)**: δ = 145.74, 137.63, 136.45, 136.34, 135.67, 131.66, 128.07, 127.42, 126.22, 125.51,

20.80 ppm. **HRMS (ESI) m/z :** calcd for $C_{12}H_6BrCl_2^+$ ($M-OTs^-$) 298.9025, found 298.9025.

4-methyldibenzo[*b,d*]bromol-5-ium 4-methylbenzenesulfonate (**1g-OTs**)

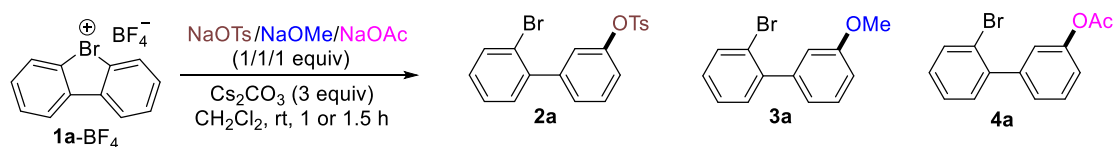
 White solid (355 mg, 85% yield). M.p.: 226–228. **1H NMR (500MHz, DMSO- d_6):** δ = 8.61 (d, J = 8.0 Hz, 2H), 8.44 (d, J = 7.5 Hz, 1H), 7.97 (t, J = 7.3 Hz, 1H), 7.87 (t, J = 7.8 Hz, 2H), 7.72 (d, J = 7.5 Hz, 1H), 7.48 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 7.5 Hz, 2H), 2.75 (s, 3H), 2.27 (s, 3H) ppm. **^{13}C NMR (125 MHz, DMSO- d_6):** δ = 145.72, 138.46, 137.65, 135.85, 135.09, 134.51, 132.65, 132.19, 131.57, 128.08, 127.14, 125.84, 125.50, 124.06, 21.45, 20.80 ppm. **HRMS (ESI) m/z :** calcd for $C_{13}H_{10}Br^+$ ($M-OTs^-$) 244.9960, found 244.9964.

2.2 General procedure for the homo anion-cation coupling



To a dry Schlenk tube was added **1** (0.1 mmol), Cs_2CO_3 (3 equiv), and dichloromethane (DCM, 1 mL). The mixture was stirred at room temperature under air for 12 hours. After the reaction was completed, the mixture was passed through a silica gel column (200–300 mesh), eluting with petroleum ether/EtOAc (40/1, v/v) to afford products **2**.

2.3 General procedure for competition experiments



The mixture of **1a-BF₄** (0.1 mmol), NaOMe (1 equiv), NaOAc (1 equiv), NaOTs (1 equiv), Cs_2CO_3 (3 equiv) and CH_2Cl_2 (1 mL) was stirred at room temperature for 1 or

1.5 hours, then the mixture was passed through a silica gel column (200–300 mesh), eluting with petroleum ether/EtOAc (40/1 to 10/1, v/v) to afford the mixture of **2a**, **3a** and **4a**. The mixture and DMAP (12.2 mg, 0.1 mmol) were added to a NMR tube for ^1H NMR analysis.

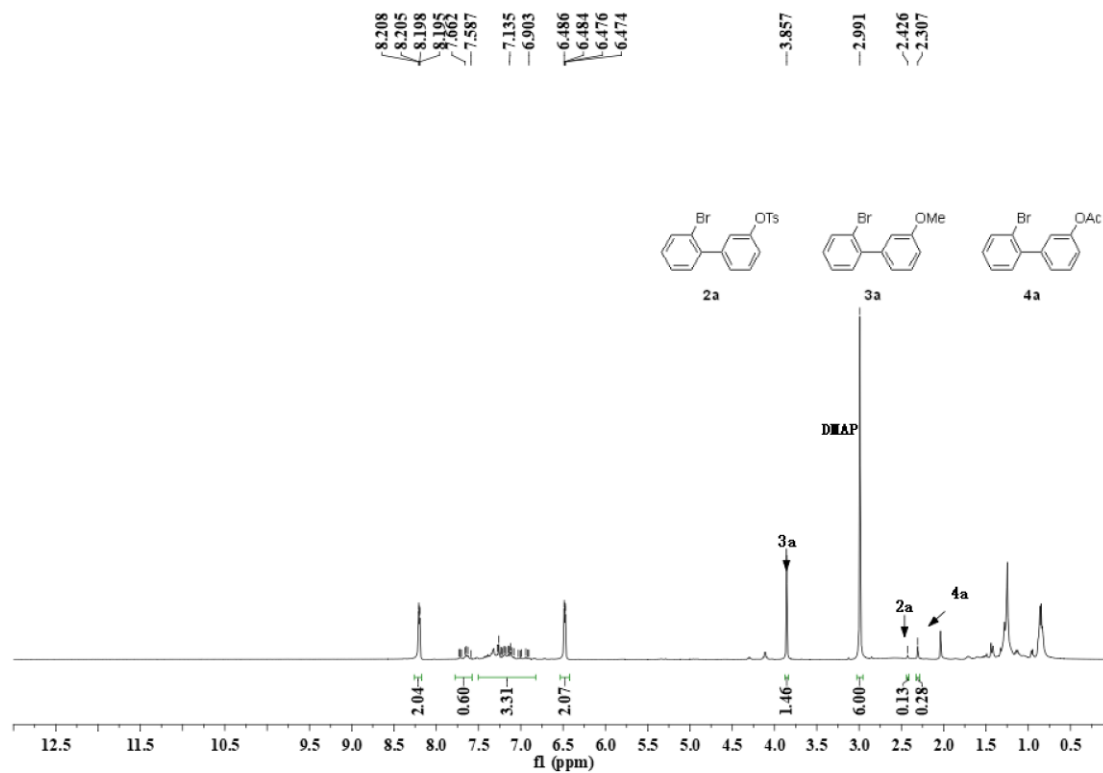


Figure S1. ^1H NMR (500 MHz, CDCl_3) of the mixture of **2a/3a/4a** after 1 h

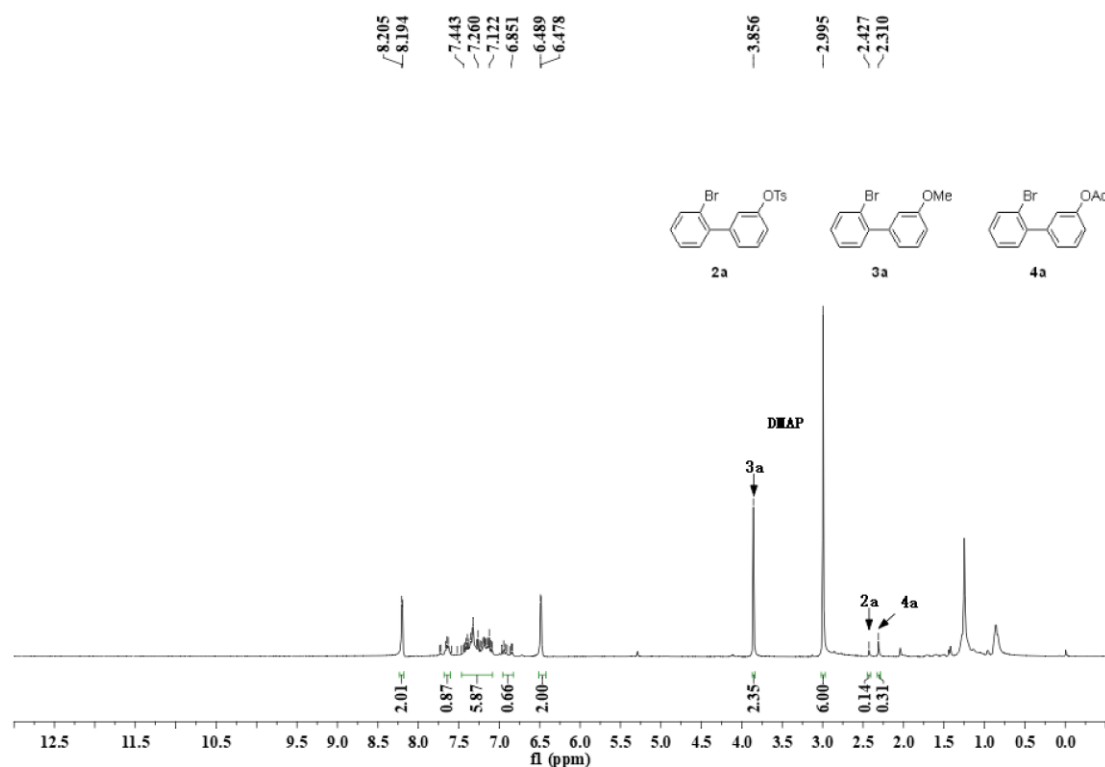
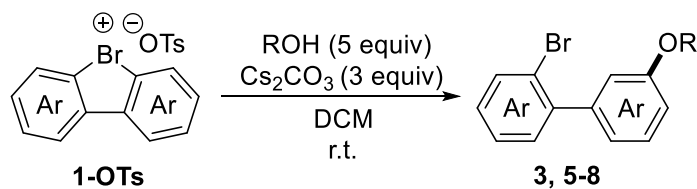


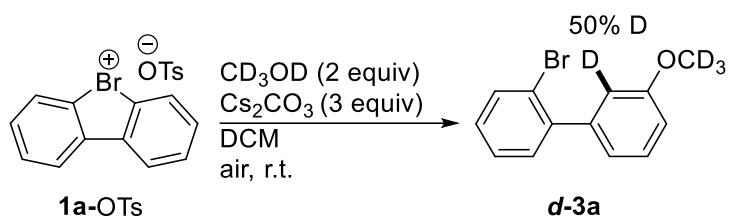
Figure S2. ^1H NMR (500 MHz, CDCl_3) of the mixture of **2a/3a/4a** after 1.5 h

2.4 General procedure for the cross anion-cation coupling

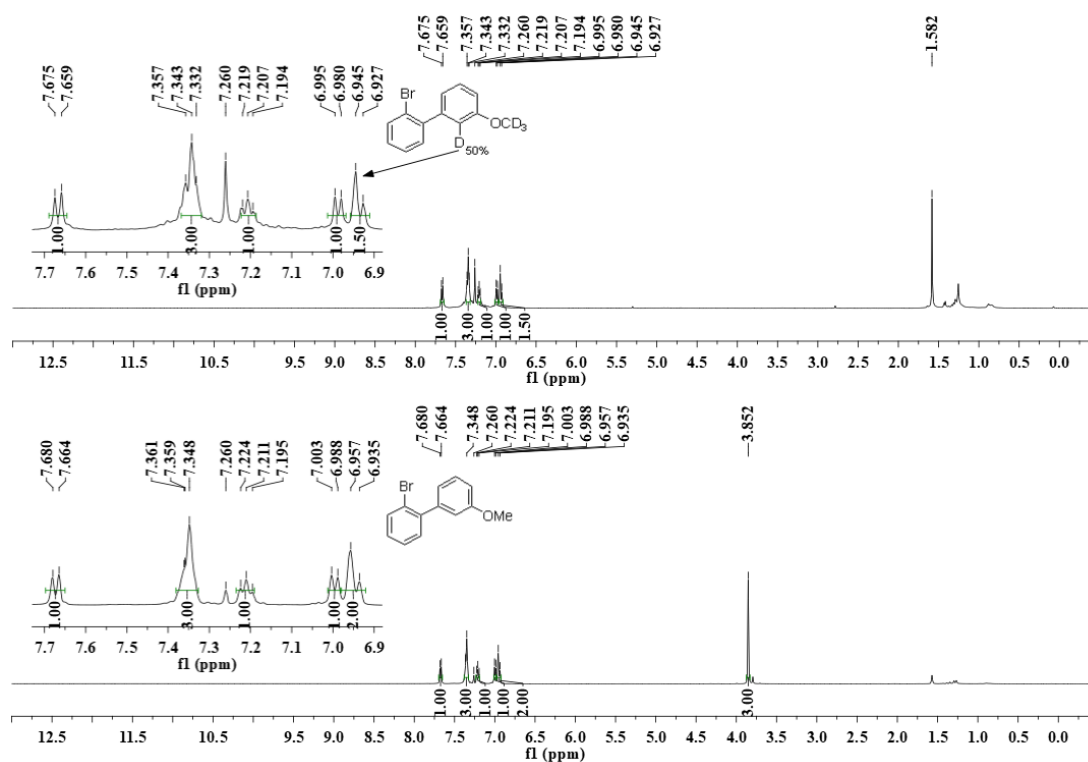


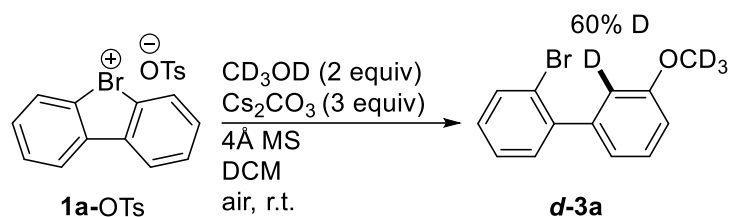
To a dry Schlenk tube was added **1-OTs** (0.1 mmol), alcohol/phenol/water (ROH, 5 equiv), Cs_2CO_3 (3 equiv) and DCM (1 mL). The mixture was stirred at room temperature for 12 hours. After the reaction was completed, the mixture was passed through a silica gel column (200–300 mesh), eluting with petroleum ether/EtOAc (40/1→5/1, v/v) to afford products **3**, and **5-8**.

3. Isotope labeling experiments

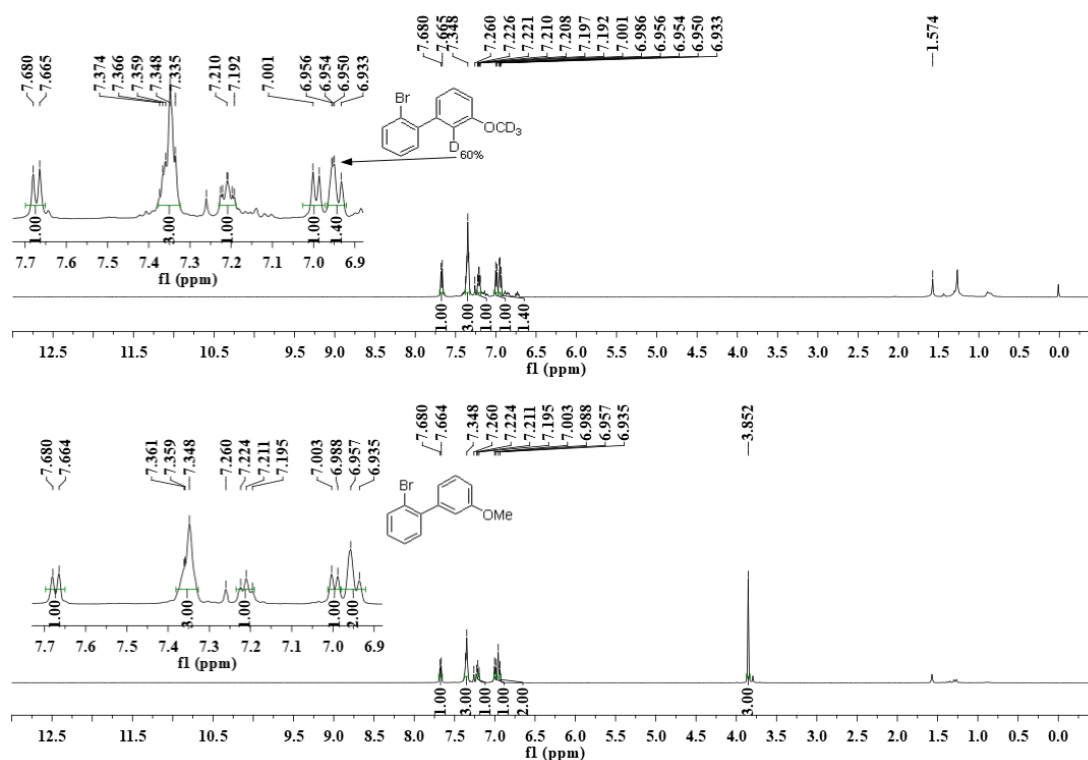


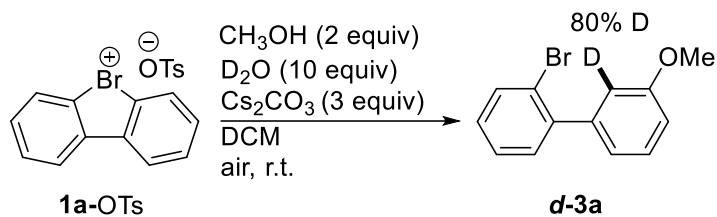
The mixture of **1a-OTs** (0.1 mmol), methanol-*d*₄ (2 equiv), Cs₂CO₃ (3 equiv) and DCM (1 mL) was stirred at room temperature for 12 hours. After the reaction was completed, the mixture was passed through a silica gel column (200–300 mesh), eluting with petroleum ether/EtOAc (40/1, v/v) to afford deuterium **d-3a**. ¹H NMR analysis showed that 50% hydrogen at the *ortho* position of the biphenyl was deuterated.



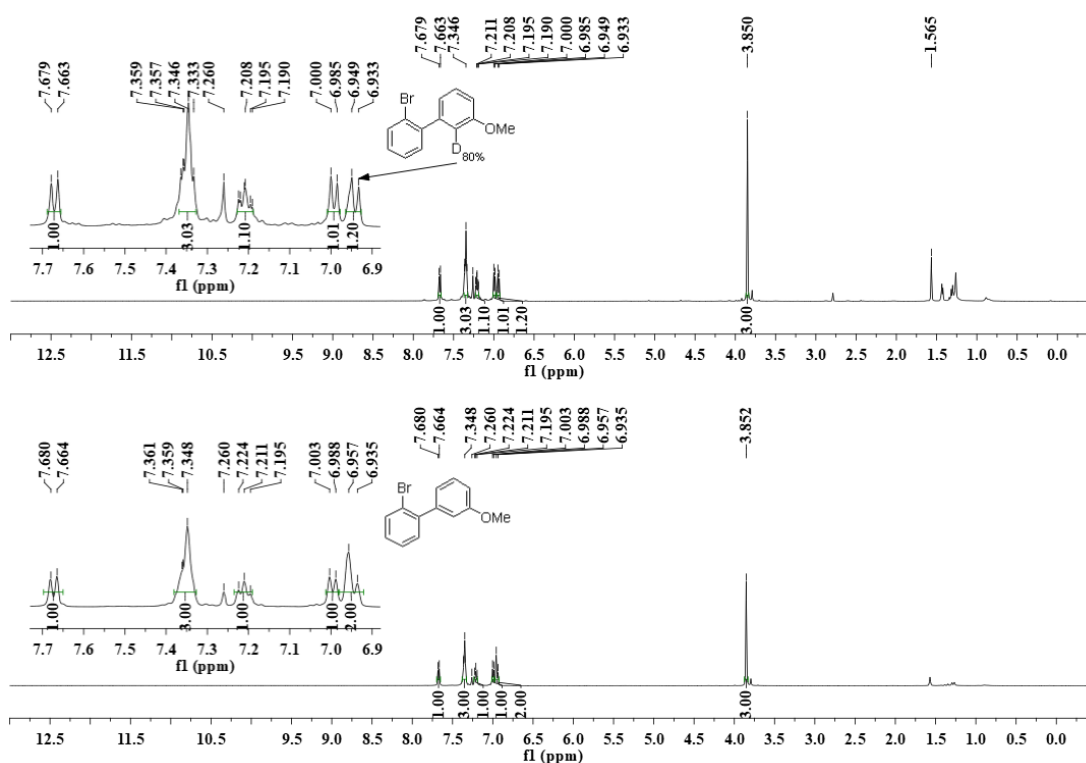


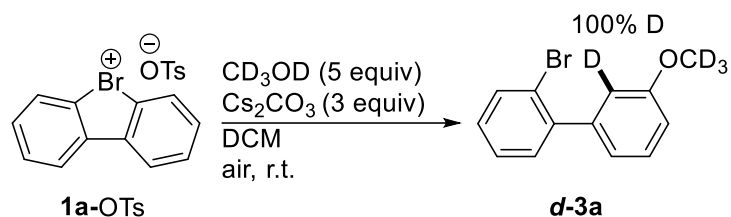
The mixture of **1a-OTs** (0.1 mmol), methanol-*d*₄ (2 equiv), Cs₂CO₃ (3 equiv), 4Å MS (30 mg) and DCM (1 mL) was stirred at room temperature for 12 hours. After the reaction was completed, the mixture was passed through a silica gel column (200–300 mesh), eluting with petroleum ether/EtOAc (40/1, v/v) to afford corresponding deuterium **d-3a**. ¹H NMR analysis showed that 60% hydrogen at the *ortho* position of the biphenyl was deuterated.



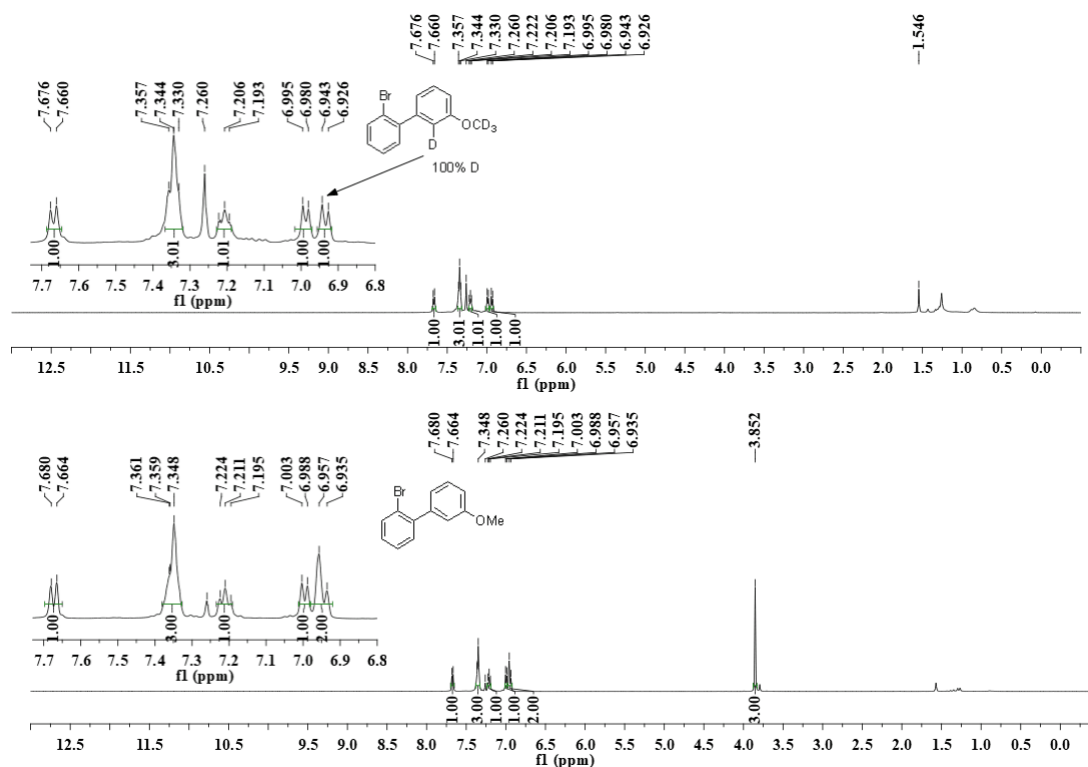


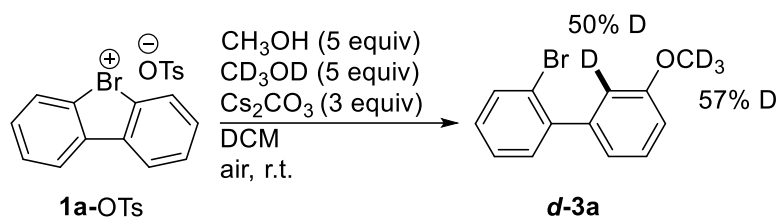
The mixture of **1a-OTs** (0.1 mmol), methanol (2 equiv), D₂O (10 equiv), Cs₂CO₃ (3 equiv) and DCM (0.1 mL) was stirred at room temperature for 12 hours. After the reaction was completed, the mixture was passed through a silica gel column (200–300 mesh), eluting with petroleum ether/EtOAc (40/1, v/v) to afford corresponding deuterium **d-3a**. ¹H NMR analysis showed that 80% hydrogen at the *ortho* position of the biphenyl was deuterated.



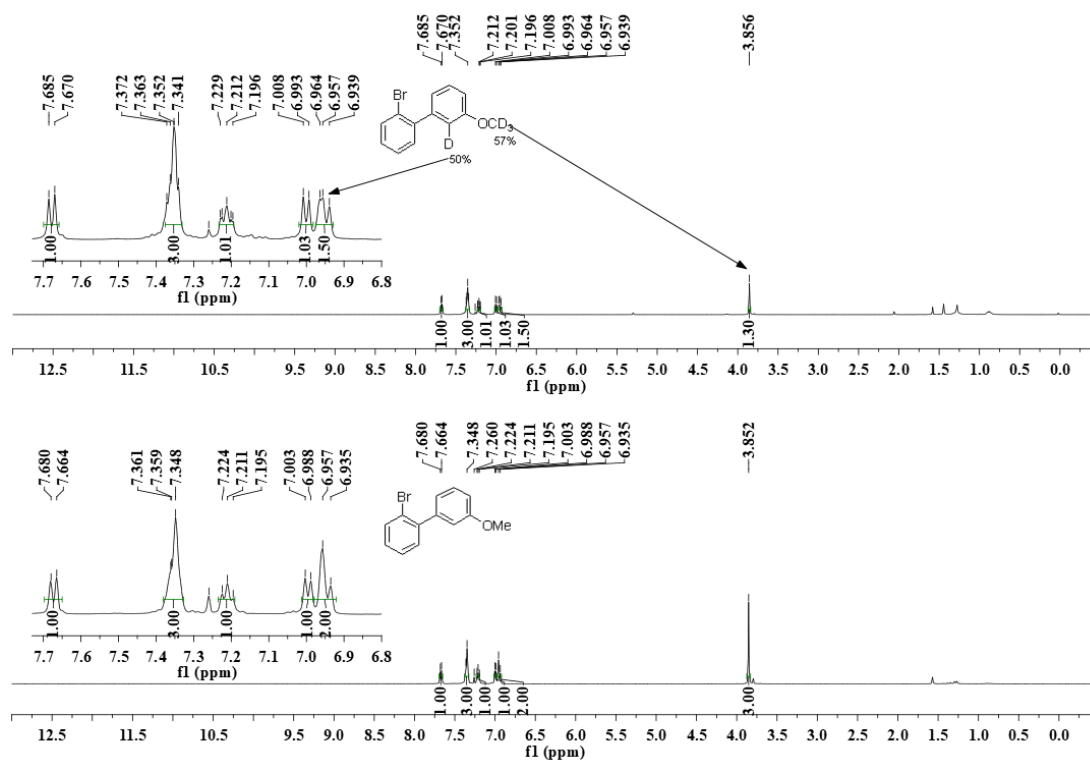


The mixture of **1a-OTs** (0.1 mmol), methanol-*d*4 (5 equiv), Cs₂CO₃ (3 equiv) and DCM (1 mL) was stirred at room temperature for 12 hours. After the reaction was completed, the mixture was passed through a silica gel column (200–300 mesh), eluting with petroleum ether/EtOAc (40/1, v/v) to afford corresponding deuterium **d-3a**. ¹H NMR analysis showed that 100% (> 95%) hydrogen at the *ortho* position of the biphenyl was deuterated.



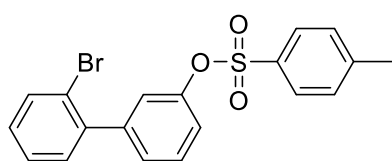


The mixture of **1a-OTs** (0.1 mmol), methanol-*d*4 (5 equiv), methanol (5 equiv), Cs₂CO₃ (3 equiv) and DCM (1 mL) was stirred at room temperature for 12 hours. After the reaction was completed, the mixture was passed through a silica gel column (200–300 mesh), eluting with petroleum ether/EtOAc (40/1, v/v) to afford deuterium **d-3a**. ¹H NMR analysis showed that 50% hydrogen at the *ortho* position of the biphenyl was deuterated and 57% hydrogen of the methoxy group was deuterated.



4. Experimental data for the described substances

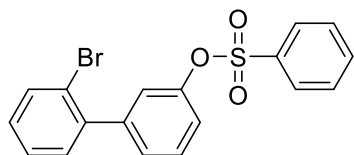
2'-bromo-[1,1'-biphenyl]-3-yl 4-methylbenzenesulfonate (**2a**)



Yellow oil (29 mg, 72% yield, *m:o* = 15:1). ¹H NMR (500MHz, CDCl₃): δ = 7.74 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.37–7.30 (m, 5H), 7.22–7.18 (m, 2H), 7.08 (dd, *J* = 8.5 Hz, 1.5 Hz, 1H), 7.00 (s, 1H), 2.44 (s, 3H) ppm. ¹³C NMR (125

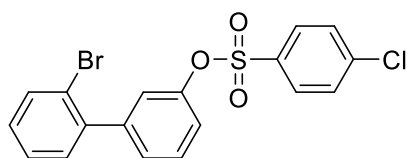
MHz, CDCl₃): δ = 149.30, 145.51, 142.72, 141.08, 133.29, 132.45, 131.21, 129.96, 129.37, 129.35, 128.78, 128.26, 127.57, 123.62, 122.46, 121.80, 21.84 ppm. **HRMS (ESI) *m/z*:** calcd for C₁₉H₁₆BrO₃S (M+H) 403.0004, found 403.0006.

2'-bromo-[1,1'-biphenyl]-3-yl benzenesulfonate (2b)



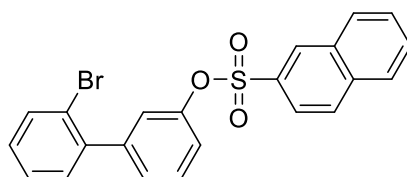
Yellow oil (27 mg, 69% yield, *m:o* > 20:1). **¹H NMR (500MHz, CDCl₃):** δ = 7.87 (d, *J* = 7.5 Hz, 2H), 7.67–7.61 (m, 2H), 7.53 (t, *J* = 7.3 Hz, 2H), 7.37–7.31 (m, 2H), 7.27 (d, *J* = 8.5 Hz, 1H, cover the solvent), 7.20 (t, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.00 (s, 1H) ppm. **¹³C NMR (125 MHz, CDCl₃):** δ = 149.23, 142.80, 141.01, 135.47, 134.35, 133.30, 131.18, 129.39, 129.35, 128.75, 128.37, 127.59, 123.55, 122.46, 121.75 ppm. **HRMS (ESI) *m/z*:** calcd for C₁₈H₁₄BrO₃S (M+H) 388.9847, found 388.9843.

2'-bromo-[1,1'-biphenyl]-3-yl 4-chlorobenzenesulfonate (2c)



Yellow oil (28 mg, 66% yield, *m:o* > 20:1). **¹H NMR (500MHz, CDCl₃):** δ = 7.80 (d, *J* = 8.5 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 9.0 Hz, 2H), 7.38–7.33 (m, 2H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.22–7.19 (m, 2H), 7.08 (d, *J* = 8.5 Hz, 1H), 7.02 (s, 1H) ppm. **¹³C NMR (125 MHz, CDCl₃):** δ = 149.08, 142.96, 141.21, 140.90, 133.85, 133.35, 131.18, 130.17, 129.73, 129.55, 129.50, 128.55, 127.66, 123.49, 122.42, 121.65. **HRMS (ESI) *m/z*:** calcd for C₁₈H₁₃BrClO₃S (M+H) 422.9457, found 422.9459.

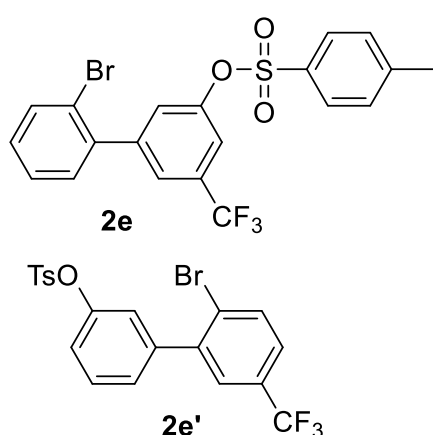
2'-bromo-[1,1'-biphenyl]-3-yl naphthalene-2-sulfonate (2d)



Yellow oil (28 mg, 60% yield, *m:o* > 20:1). **¹H NMR (500MHz, CDCl₃):** δ = 8.38 (s, 1H), 7.99 (d, *J* = 9.0 Hz, 1H), 7.93 (t, *J* = 7.3 Hz, 2H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.63 (d, *J* = 7.3 Hz,

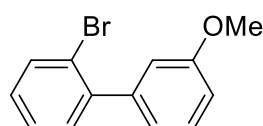
1H), 7.54 (d, $J = 8.0$ Hz, 1H), 7.34 (t, $J = 7.8$ Hz, 1H), 7.25–7.23 (m, 2H), 7.16–7.12 (m, 2H), 7.06 (d, $J = 7.5$ Hz, 1H), 6.97 (s, 1H) ppm. **^{13}C NMR (125 MHz, CDCl_3):** $\delta = 149.27, 142.73, 140.92, 135.61, 133.21, 132.17, 131.99, 131.14, 130.84, 129.77, 129.74, 129.59, 129.43, 129.30, 128.34, 128.13, 128.00, 127.50, 123.53, 123.08, 122.33, 121.84$ ppm. **HRMS (ESI) m/z :** calcd for $\text{C}_{22}\text{H}_{16}\text{BrO}_3\text{S}$ ($\text{M}+\text{H}$) 439.0004, found 439.0005.

2'-bromo-5-(trifluoromethyl)-[1,1'-biphenyl]-3-yl 4-methylbenzenesulfonate (2e)
and 2'-bromo-5'-(trifluoromethyl)-[1,1'-biphenyl]-3-yl 4-methylbenzenesulfonate (2e')



Yellow oil (38 mg, 75% yield, **2e:2e'** = 15:1, $m:o > 20:1$). **^1H NMR (500 MHz, CDCl_3 , major):** $\delta = 7.75$ (d, $J = 8.0$ Hz, 2H), 7.66 (dd, $J = 8.0$ Hz, 1.0 Hz, 1H), 7.55 (s, 1H), 7.37–7.34 (m, 3H), 7.27–7.26 (m, 3H, cover the solvent), 7.24–7.21 (m, 1H), 2.54 (s, 3H) ppm. **^{13}C NMR (125 MHz, CDCl_3 , major):** $\delta = 149.27, 146.10, 143.60, 139.66, 133.49, 131.99$ (q, $J_{\text{C-F}} = 33.0$ Hz), 131.92, 131.09, 130.14, 130.07, 128.77, 127.85, 127.21, 125.09 (q, $J_{\text{C-F}} = 3.4$ Hz), 123.22 (q, $J_{\text{C-F}} = 271.3$ Hz), 122.25, 119.03 (q, $J_{\text{C-F}} = 3.5$ Hz), 21.83 ppm. **^{19}F NMR (471 MHz, CDCl_3 , major):** $\delta = -62.69$ (s) ppm. **HRMS (ESI) m/z :** calcd for $\text{C}_{20}\text{H}_{15}\text{BrF}_3\text{O}_3\text{S}$ ($\text{M}+\text{H}$) 470.9877, found 470.9878.

2-bromo-3'-methoxy-1,1'-biphenyl (3a)²

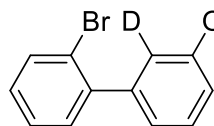


Yellow oil (25 mg, 97% yield, $m:o = 15:1$), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 40/1, v/v). **^1H NMR (500 MHz, CDCl_3):** $\delta = 7.67$ (d, $J = 8.0$ Hz, 1H), 7.36–7.35 (m, 3H), 7.22–7.20 (m, 1H), 7.00 (d, $J = 7.5$ Hz, 1H), 6.96–6.94 (m, 2H), 3.85 (s, 3H) ppm. **^{13}C NMR (125 MHz, CDCl_3):** $\delta = 159.24, 142.57, 142.55,$

133.25, 131.33, 129.14, 128.91, 127.46, 122.67, 121.95, 115.18, 113.35, 55.43 ppm.

HRMS (ESI) m/z : calcd for $C_{13}H_{12}BrO$ ($M+H$) 263.0072, found 263.0074. The NMR data are consistent with the reference.²

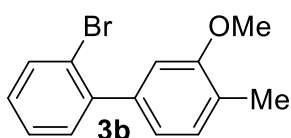
2-bromo-3'-(methoxy- d_3)-1,1'-biphenyl-2'- d (d-3a**)**



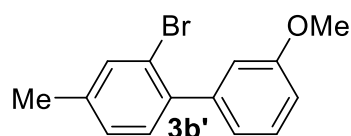
Yellow oil (26 mg, 97% yield), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 40/1, v/v).

1H NMR (500 MHz, $CDCl_3$): δ = 7.67 (d, J = 8.0 Hz, 1H), 7.36–7.33 (m, 3H), 7.22–7.20 (m, 1H), 6.99 (d, J = 7.5 Hz, 1H), 6.93 (d, J = 8.5 Hz, 1H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 159.22 (d, J_{C-D} = 5.6 Hz), 142.52 (J_{C-D} = 9.3 Hz), 142.48, 133.26, 131.34, 129.14, 128.92, 127.47, 122.69, 121.92, 115.20 (J_{C-D} = 3.8 Hz), 113.41, 55.31 ppm. **HRMS (ESI) m/z :** calcd for $C_{13}H_8D_4BrO_3$ ($M+H$) 267.0323, found 267.0325.

2-bromo-3'-methoxy-4'-methyl-1,1'-biphenyl (3b**) and 2-bromo-3'-methoxy-4-methyl-1,1'-biphenyl (**3b'**)**



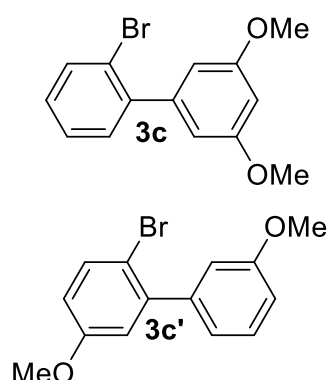
Yellow oil (29 mg, 70% yield, **3b:3b'** = 3:2, $m:o>20:1$), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 40/1, v/v). **1H NMR (500**



MHz, $CDCl_3$, isomers): δ = 7.67 (d, J = 8.0 Hz, 1H), 7.50 (s, 0.67H), 7.35–7.33 (m, 2.67H), 7.23–7.17 (m, 3.33H), 6.98 (d, J = 8.0 Hz, 0.67H), 6.95–6.89 (m, 3.33H), 3.86

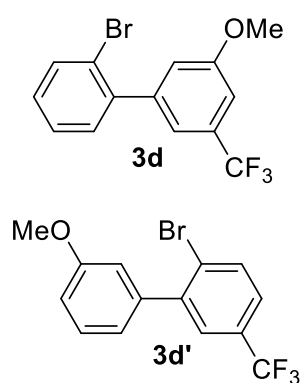
(s, 3H), 3.85 (s, 2H), 2.38 (s, 2H), 2.28 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$, isomers):** δ = 159.21, 157.27, 142.85, 142.50, 139.94, 139.61, 139.08, 133.68, 133.25, 131.44, 131.04, 130.29, 129.07, 128.71, 128.29, 127.45, 126.18, 122.81, 122.34, 122.07, 121.32, 115.29, 113.17, 111.49, 55.51, 55.42, 20.85, 16.23 ppm. **HRMS (ESI) m/z :** calcd for $C_{14}H_{14}BrO$ ($M+H$) 277.0228, found 277.0226.

2-bromo-3',5'-dimethoxy-1,1'-biphenyl (3c) and 2-bromo-3',5-dimethoxy-1,1'-biphenyl (3c')



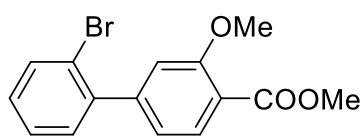
Yellow oil (18 mg, 61% yield, **3c:3c'** = 1:2), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 20/1, v/v). **¹H NMR (500 MHz, CDCl₃, isomers):** δ = 7.67 (d, J = 8.0 Hz, 0.5H), 7.54 (d, J = 8.5 Hz, 1H), 7.37–7.34 (m, 2.5H), 7.21–7.19 (m, 0.5H), 7.00 (d, J = 7.0 Hz, 1H), 6.96–6.93 (m, 1.5H), 6.89 (d, J = 3.0 Hz, 1H), 6.80–6.77 (m, 1H), 6.55 (d, J = 2.5 Hz, 1H), 6.55 (t, J = 2.0 Hz, 0.5H), 3.85 (s, 3H), 3.83 (s, 3H), 3.81 (s, 4.2H) ppm. **¹³C NMR (125 MHz, CDCl₃, isomers):** δ = 160.29, 159.12, 158.77, 143.24, 143.00, 142.53, 142.46, 133.72, 133.14, 131.11, 129.05, 128.84, 127.31, 122.45, 121.73, 116.58, 114.99, 114.83, 113.30, 112.98, 107.62, 99.77, 55.56, 55.44, 55.32 ppm. **HRMS (ESI) m/z :** calcd for C₁₄H₁₄BrO₂ (M+H) 293.0177, found 293.0177.

2-bromo-3'-methoxy-5'-(trifluoromethyl)-1,1'-biphenyl (3d) and 2-bromo-3'-methoxy-5-(trifluoromethyl)-1,1'-biphenyl (3d')



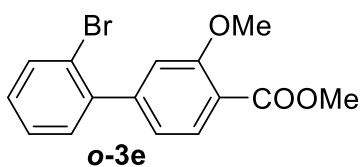
Yellow oil (32 mg, 96% yield, **3d:3d'** = 10:1), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 40/1, v/v). **¹H NMR (500 MHz, CDCl₃, major):** δ = 7.69 (d, J = 8.0 Hz, 1H), 7.40–7.37 (m, 1H), 7.34–7.32 (m, 1H), 7.26–7.23 (m, 2H, cover the solvent), 7.16 (s, 1H), 7.14 (s, 1H), 3.89 (s, 3H) ppm. **¹³C NMR (125 MHz, CDCl₃, major):** δ = 159.46, 143.19, 141.18, 133.43, 131.67 (q, J_{C-F} = 32.1 Hz), 131.21, 129.55, 127.68, 124.04 (q, J_{C-F} = 270.9 Hz), 122.45, 118.82, 118.73 (q, J_{C-F} = 3.8 Hz), 110.11 (q, J_{C-F} = 3.6 Hz), 55.77 ppm. **¹⁹F NMR (471 MHz, CDCl₃, major):** δ = -62.56 (s) ppm. **HRMS (ESI) m/z :** calcd for C₁₄H₁₁BrF₃O (M+H) 330.9945, found 330.9947.

methyl 2'-bromo-3-methoxy-[1,1'-biphenyl]-4-carboxylate (*m*-3e)

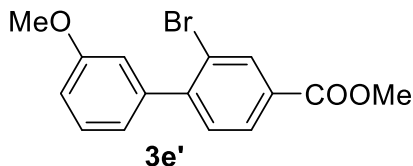


Yellow oil (23.7 mg, 74% yield), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 20/1, v/v). ¹H NMR (500 MHz, CDCl₃): δ = 7.86 (d, *J* = 7.5 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.34–7.32 (m, 1H), 7.24 (t, *J* = 7.5 Hz, 1H, cover the solvent), 7.03 (s, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 3.94 (s, 3H), 3.92 (s, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 166.53, 158.69, 146.35, 141.60, 133.31, 131.48, 130.96, 129.35, 127.49, 122.20, 121.25, 119.02, 113.48, 56.14, 52.11 ppm. HRMS (ESI) *m/z*: calcd for C₁₅H₁₄BrO₂ (M+H) 321.0121, found 321.0122.

methyl 2'-bromo-2-methoxy-[1,1'-biphenyl]-4-carboxylate (*o*-3e) and methyl 2-bromo-3'-methoxy-[1,1'-biphenyl]-4-carboxylate (*3e'*)



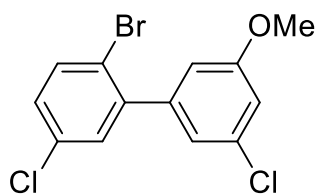
***o*-3e**



3e'

Yellow oil (7.8 mg, 25% yield, *o*-3e:*3e'* = 5:1), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 40/1, v/v). ¹H NMR (500 MHz, CDCl₃, major): δ = 7.72 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.67–7.65 (m, 2H), 7.37 (td, *J* = 7.5, 1.0 Hz, 1H), 7.28–7.23 (m, 3H, cover the solvent), 3.95 (s, 3H), 3.85 (s, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃, major): δ = 167.01, 156.71, 139.05, 135.03, 132.70, 131.32, 131.26, 130.98, 129.25, 127.24, 123.85, 121.91, 111.90, 55.94, 52.39 ppm. HRMS (ESI) *m/z*: calcd for C₁₅H₁₄BrO₃ (M+H) 321.0126, found 321.0125.

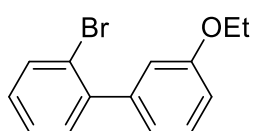
2-bromo-3',5-dichloro-5'-methoxy-1,1'-biphenyl (*3f*)



Yellow oil (19.3 mg, 58% yield, *m*:*o* > 20:1), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 40/1, v/v). ¹H NMR (500 MHz, CDCl₃): δ = 7.58 (d, *J* = 8.5 Hz, 1H), 7.30 (d, *J* = 2.5 Hz, 1H), 7.20 (dd, *J* = 2.5 Hz, 8.5 Hz, 1H), 6.96–6.93 (m, 2H), 6.81–6.80 (m, 1H), 3.84 (s, 3H) ppm. ¹³C

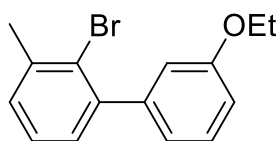
NMR (125 MHz, CDCl₃): δ = 159.81, 143.65, 141.07, 133.22, 131.04, 129.26, 127.45, 124.77, 122.33, 122.27, 116.38, 114.45, 55.62 ppm. **HRMS (ESI) *m/z*:** calcd for C₁₃H₁₀BrCl₂O (M+H) 330.9287, found 330.9285.

2-bromo-3'-ethoxy-1,1'-biphenyl (3g)



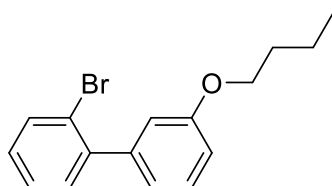
Yellow oil (27 mg, 97% yield, *m:o* > 20:1), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 40/1, v/v). **¹H NMR (500 MHz, CDCl₃):** δ = 7.67 (d, *J* = 8.5 Hz, 1H), 7.37–7.32 (m, 3H), 7.22–7.19 (m, 1H), 6.99–6.92 (m, 3H), 4.08 (q, *J* = 7.0 Hz, 2H), 1.44 (t, *J* = 7.0 Hz, 3H) ppm. **¹³C NMR (125 MHz, CDCl₃):** δ = 158.60, 142.64, 142.51, 133.23, 131.34, 129.11, 128.87, 127.44, 122.68, 121.80, 115.67, 113.99, 63.60, 15.01 ppm. **HRMS (ESI) *m/z*:** calcd for C₁₄H₁₄BrO (M+H) 277.0228, found 277.0226.

2-bromo-3'-ethoxy-3-methyl-1,1'-biphenyl (3h)



Colourless oil (20.5 mg, 70% yield, *m:o* = 5:1), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 40/1, v/v). **¹H NMR (500 MHz, CDCl₃):** δ = 7.33 (t, *J* = 8.0 Hz, 1H), 7.25–7.24 (m, 2H), 7.15 (t, *J* = 4.5 Hz, 1H), 6.96–6.92 (m, 3H), 4.08 (q, *J* = 7.0 Hz, 1H), 2.50 (s, 1H), 1.44 (t, *J* = 7.0 Hz, 3H) ppm. **¹³C NMR (125 MHz, CDCl₃):** δ = 158.54, 143.49, 143.38, 138.94, 129.82, 129.00, 128.70, 126.83, 125.37, 121.83, 115.68, 113.80, 63.55, 24.38, 15.01 ppm. **HRMS (ESI) *m/z*:** calcd for C₁₅H₁₆BrO (M+H) 291.0385, found 291.0383.

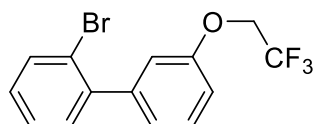
2-bromo-3'-butoxy-1,1'-biphenyl (3i)



Yellow oil (20 mg, 66% yield, *m:o* = 13:1), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 40/1, v/v). **¹H NMR (500 MHz, CDCl₃):** δ = 7.66 (d, *J* = 8.5 Hz, 1H), 7.37–7.31 (m, 3H), 7.21–7.19 (m, 1H), 6.98–6.92 (m, 3H), 4.00 (t, *J* = 6.3 Hz, 2H), 1.82–1.76 (m, 2H), 1.53–1.47 (m,

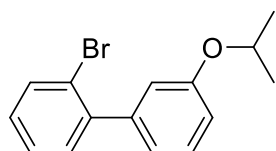
2H), 0.98 (t, $J = 7.5$ Hz, 3H) ppm. **^{13}C NMR (125 MHz, CDCl_3):** $\delta = 158.84, 142.67, 142.51, 133.23, 131.35, 129.08, 128.86, 127.44, 122.69, 121.74, 115.70, 114.03, 67.88, 31.50, 19.41, 14.03$ ppm. **HRMS (ESI) m/z :** calcd for $\text{C}_{16}\text{H}_{18}\text{BrO}$ ($\text{M}+\text{H}$) 305.0541, found 305.0544.

2-bromo-3'-(2,2,2-trifluoroethoxy)-1,1'-biphenyl (3j)



Yellow oil (28 mg, 85% yield, $m:o > 20:1$), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 40/1, v/v). **^1H NMR (500 MHz, CDCl_3):** $\delta = 7.67$ (d, $J = 8.0$ Hz, 1H), 7.40–7.35 (m, 2H), 7.33–7.31 (m, 1H), 7.24–7.21 (m, 1H), 7.09 (d, $J = 7.5$ Hz, 1H), 6.99–6.97 (m, 2H), 4.41–4.37 (m, 2H) ppm. **^{13}C NMR (125 MHz, CDCl_3):** $\delta = 157.05, 142.89, 141.95, 133.32, 131.27, 129.48, 129.19, 127.57, 123.79, 123.47$ (q, $J_{\text{C-F}} = 276.1$ Hz), 122.56, 116.10, 114.38, 66.02 (q, $J_{\text{C-F}} = 35.3$ Hz) ppm. **^{19}F NMR (471 MHz, CDCl_3):** $\delta = -73.91$ (s) ppm. **HRMS (ESI) m/z :** calcd for $\text{C}_{14}\text{H}_{11}\text{BrF}_3\text{O}$ ($\text{M}+\text{H}$) 330.9945, found 330.9946.

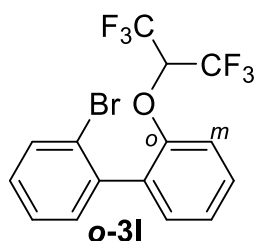
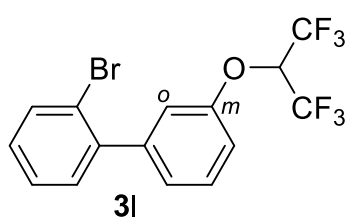
2-bromo-3'-isopropoxy-1,1'-biphenyl (3k)



Yellow oil (28 mg, 99% yield, $m:o > 20:1$), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 40/1, v/v). **^1H NMR (500 MHz, CDCl_3):** $\delta = 7.67$ (d, $J = 7.5$ Hz, 1H), 7.35–7.32 (m, 3H), 7.22–7.19 (m, 1H), 6.97–6.92 (m, 3H), 4.62–4.57 (m, 1H), 1.38 (d, $J = 6.0$ Hz, 6H) ppm. **^{13}C NMR (125 MHz, CDCl_3):** $\delta = 157.56, 142.67, 142.51, 133.23, 131.35, 129.15, 128.84, 127.44, 122.67, 121.68, 116.91, 115.53, 70.06, 22.24$ ppm. **HRMS (ESI) m/z :** calcd for $\text{C}_{15}\text{H}_{16}\text{BrO}$ ($\text{M}+\text{H}$) 291.0385, found 291.0388.

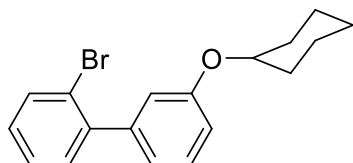
2-bromo-3'-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-1,1'-biphenyl (3l) and 2-bromo-2'-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-1,1'-biphenyl (o-3l)

Yellow oil (34 mg, 85% yield, $m:o = 3:1$), purification via a silica (200–300 meshes)



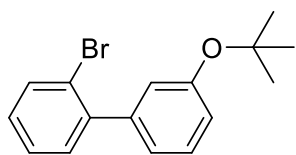
gel column (petroleum ether/EtOAc = 40/1, v/v). **¹H NMR (500 MHz, CDCl₃, isomers):** δ = 7.68 (d, J = 7.0 Hz, 1.33 H), 7.42 (t, J = 8.0 Hz, 1H), 7.39–7.36 (m, 1.66H), 7.32–7.29 (m, 1.33H), 7.26–7.20 (m, 2.66H), 7.15 (s, 1H), 7.11 (dd, J = 8.5 Hz, 1.5Hz, 1H), 7.04–7.01 (m, 0.66H), 5.01–4.96 (m, 0.33H), 4.87–4.83 (m, 1H) ppm. **¹³C NMR (125 MHz, CDCl₃, isomers):** δ = 157.27, 143.23, 142.97, 141.70, 141.39, 133.42, 133.36, 131.25, 131.22, 129.84, 129.54, 129.40, 129.25, 127.67, 125.94, 123.80 (q, J_{C-F} = 311.5 Hz), 122.38, 118.64, 116.67, 116.32, 114.54, 76.69 (heptet, J_{C-F} = 33.0 Hz, cover the solvent) ppm. **¹⁹F NMR (471 MHz, CDCl₃, isomers):** δ = -64.58 (d), -73.48 (t) ppm. **HRMS (ESI) m/z :** calcd for C₁₅H₁₀BrF₆O (M+H) 398.9819, found 398.9818.

2-bromo-3'-(cyclohexyloxy)-1,1'-biphenyl (3m)



Yellow oil (20 mg, 60% yield, $m:o$ > 20:1), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 40/1, v/v). **¹H NMR (500 MHz, CDCl₃):** δ = 7.66 (d, J = 8.0 Hz, 1H), 7.34–7.30 (m, 3H), 7.21–7.19 (m, 1H), 7.15–7.10 (m, 1H), 6.94–6.92 (m, 2H), 4.30–4.25 (m, 1H), 2.04–2.02 (m, 2H), 1.83–1.80 (m, 2H), 1.37–1.34 (m, 4H), 1.29 (s, 1H), 1.26 (s, 1H) ppm. **¹³C NMR (125 MHz, CDCl₃):** δ = 157.46, 142.68, 142.47, 133.23, 131.38, 129.12, 128.84, 127.45, 122.70, 121.67, 117.04, 115.68, 32.00, 25.78, 23.95 ppm. **HRMS (ESI) m/z :** calcd for C₁₈H₂₀BrO (M+H) 331.0698, found 331.0696.

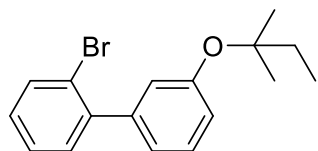
2-bromo-3'-(*tert*-butoxy)-1,1'-biphenyl (3n)



Yellow oil (30 mg, 77% yield, $m:o$ > 20:1), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 40/1, v/v). **¹H NMR (500 MHz, CDCl₃):** δ = 7.66 (d, J =

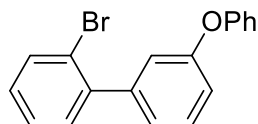
8.0 Hz, 1H), 7.33–7.30 (m, 3H), 7.21–7.20 (m, 1H), 7.10–7.07 (m, 2H), 7.02–7.01 (m, 1H), 1.38 (s, 9H) ppm. **¹³C NMR (125 MHz, CDCl₃):** δ = 155.04, 142.47, 141.99, 133.21, 131.34, 128.85, 128.57, 127.46, 125.43, 124.42, 123.56, 122.76, 78.96, 29.07 ppm. **HRMS (ESI) *m/z*:** calcd for C₁₆H₁₈BrO (M+H) 305.0541, found 305.0544.

2-bromo-3'-(*tert*-pentyloxy)-1,1'-biphenyl (3o)



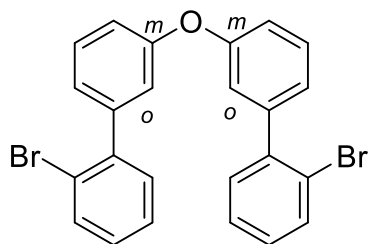
Yellow oil (23 mg, 70% yield, *m:o* > 20:1), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 40/1, v/v). **¹H NMR (500 MHz, CDCl₃):** δ = 7.66 (d, *J* = 8.0 Hz, 1H), 7.35–7.29 (m, 3H), 7.21–7.18 (m, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.05 (s, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 1.71 (q, *J* = 7.3 Hz, 2H), 1.30 (s, 6H), 1.02 (t, *J* = 7.3 Hz, 3H) ppm. **¹³C NMR (125 MHz, CDCl₃):** δ = 155.13, 142.49, 141.98, 133.21, 131.35, 128.85, 128.58, 127.46, 125.25, 124.22, 123.40, 122.77, 81.38, 34.68, 26.35, 8.85 ppm. **HRMS (ESI) *m/z*:** calcd for C₁₇H₂₀BrO (M+H) 319.0698, found 319.0700.

2-bromo-3'-phenoxy-1,1'-biphenyl (3p)



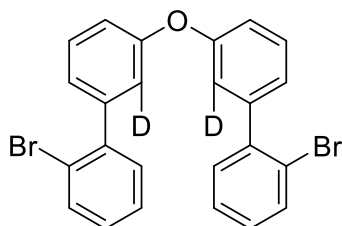
Yellow oil (29 mg, 90% yield, *m:o* = 10:1), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 40/1, v/v). **¹H NMR (500 MHz, CDCl₃):** δ = 7.65 (d, *J* = 7.5 Hz, 1H), 7.41–7.33 (m, 5H), 7.21–7.18 (m, 1H), 7.13 (t, *J* = 8.5 Hz, 2H), 7.09–7.04 (m, 4H) ppm. **¹³C NMR (125 MHz, CDCl₃):** δ = 157.16, 156.94, 142.83, 142.00, 133.27, 131.27, 129.91, 129.47, 129.06, 127.51, 124.36, 123.50, 122.62, 120.01, 119.16, 118.13 ppm. **HRMS (ESI) *m/z*:** calcd for C₁₈H₁₄BrO (M+H) 325.0228, found 325.0224.

3',3'''-oxybis(2-bromo-1,1'-biphenyl) (di-3q)



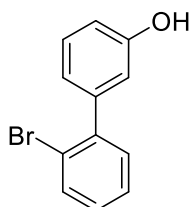
Yellow oil (23 mg, 96% yield, *m,m:others* = 5:1), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 40/1, v/v). **¹H NMR (500 MHz, CDCl₃, major):** δ = 7.64 (d, *J* = 8.0 Hz, 2H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.34–7.33 (m, 4H), 7.20–7.18 (m, 2H), 7.15–7.09 (m, 6H) ppm. **¹³C NMR (125 MHz, CDCl₃, major):** δ = 156.77, 142.88, 141.98, 133.26, 131.30, 129.51, 129.07, 127.50, 124.51, 122.64, 120.19, 118.27 ppm. **C₁₈H₁₄BrO (M+H)** 325.0228, found 325.0224. **HRMS (ESI) *m/z*:** calcd for C₂₄H₁₇Br₂O (M+H) 480.9626, found 480.9636.

3',3'''-oxybis(2-bromo-1,1'-biphenyl-2'-d) (*d*-di-3q)



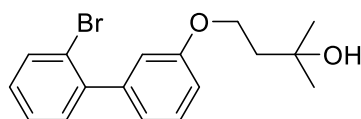
Yellow oil (24 mg, 95% yield), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 40/1, v/v). **¹H NMR (500 MHz, CDCl₃):** δ = 7.64 (d, *J* = 8.0 Hz, 2H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.36–7.33 (m, 4H), 7.21–7.18 (m, 2H), 7.14–7.13 (m, 2H), 7.10 (d, *J* = 8.5 Hz, 2H) ppm. **¹³C NMR (125 MHz, CDCl₃):** δ = 156.78 (d, *J*_{C-D} = 6.3 Hz), 142.86 (d, *J*_{C-D} = 11.0 Hz), 142.00 (d, *J*_{C-D} = 3.8 Hz), 133.28, 131.30, 129.51, 129.07, 127.51, 124.52, 122.66, 120.21, 118.28 ppm. **HRMS (ESI) *m/z*:** calcd for C₂₄H₁₅D₂Br₂O (M+H) 482.9746, found 482.9744.

2'-bromo-[1,1'-biphenyl]-3-ol (mono-3q)



Colourless oil (12 mg, 48% yield). **¹H NMR (500MHz, CDCl₃):** δ = 7.66 (d, *J* = 8.0 Hz, 1H), 7.37–7.29 (m, 3H), 7.20 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 2H), 6.88–6.86 (m, 2H), 4.99 (s, 1H) ppm. **¹³C NMR (125 MHz, CDCl₃):** δ = 155.16, 142.79, 142.23, 133.24, 131.29, 129.40, 128.97, 127.47, 122.59, 122.15, 116.58, 114.72 ppm. **HRMS (ESI) *m/z*:** calcd for C₁₂H₁₀BrO (M+H) 248.9915, found 248.9910.

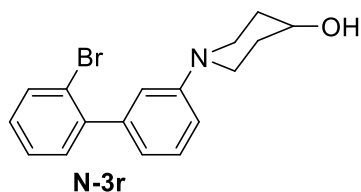
4-((2'-bromo-[1,1'-biphenyl]-3-yl)oxy)-2-methylbutan-2-ol (3r)



Yellow oil (30 mg, 90% yield, *m:o* = 15:1), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 10/1, v/v). **¹H NMR (500 MHz, CDCl₃):**

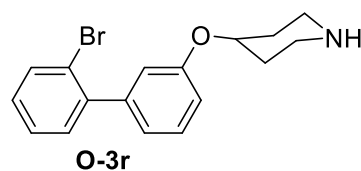
δ = 7.66 (d, *J* = 8.0 Hz, 1H), 7.35–7.34 (m, 3H), 7.22–7.19 (m, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.97–6.94 (m, 2H), 4.23 (t, *J* = 5.8 Hz, 2H), 2.35 (s, 1H), 2.02 (t, *J* = 6.0 Hz, 2H), 1.32 (s, 6H) ppm. **¹³C NMR (125 MHz, CDCl₃):** δ = 158.11, 142.50, 142.34, 133.14, 131.21, 129.08, 128.84, 127.37, 122.52, 122.18, 115.61, 113.92, 70.45, 65.24, 41.69, 29.63 ppm. **HRMS (ESI) *m/z*:** calcd for C₁₇H₂₀BrO (M+H) 335.0647, found 335.0645.

1-(2'-bromo-[1,1'-biphenyl]-3-yl)piperidin-4-ol (N-3s) and 4-((2'-bromo-[1,1'-biphenyl]-3-yl)oxy)piperidine (O-3s)



N-3r

Yellow oil (20 mg, 60% yield, **N-3r:O-3r** = 10:1), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 10/1, v/v). **¹H NMR (500 MHz, CDCl₃, major):** δ = 7.66 (d, *J* = 8.0 Hz, 1H),



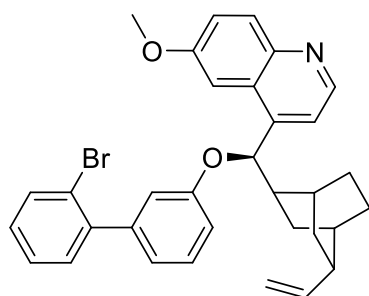
O-3r

7.34–7.29 (m, 3H), 7.21–7.17 (m, 1H), 6.97–6.96 (m, 2H), 6.86 (d, *J* = 7.5 Hz, 1H), 3.89–3.83 (m, 1H), 3.63–3.60 (m, 2H), 2.99–2.94 (m, 2H), 2.03–2.01 (m, 2H),

1.72–1.67 (m, 3H) ppm. **¹³C NMR (125 MHz, CDCl₃, major):** δ = 150.85, 143.15, 142.05, 133.18, 131.35, 128.83, 128.73, 127.41, 122.76, 120.55, 117.93, 115.70, 68.08, 65.72, 47.37, 34.30, 19.32, 13.88 ppm. **HRMS (ESI) *m/z*:** calcd for C₁₇H₁₉BrNO (M+H) 332.0650, found 332.0653.

4-((1R)-((2'-bromo-[1,1'-biphenyl]-3-yl)oxy)(5-vinylbicyclo[2.2.2]octan-2-yl)methyl)-6-methoxyquinoline (5)

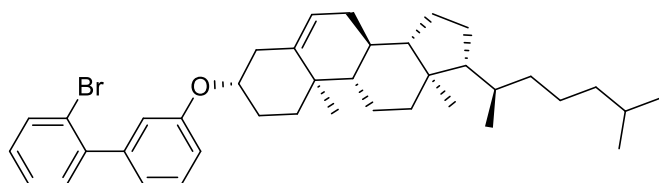
Yellow oil (50 mg, 91% yield, *m:o* > 20:1), purification via a silica (200–300 meshes)



gel column (petroleum ether/EtOAc = 5/1, v/v). **¹H NMR (500 MHz, CDCl₃):** δ = 8.75 (d, J = 4.0 Hz, 1H), 8.07 (d, J = 9.0 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.42 (dd, J = 9.3 Hz, 2.3 Hz, 1H), 7.34 (d, J = 4.0 Hz, 2H), 7.31 (d, J = 4.5 Hz, 2H), 7.20–7.17 (m, 1H), 6.95 (s, 2H),

6.86 (d, J = 7.5 Hz, 1H), 6.23–6.15 (m, 1H), 5.30 (s, 1H), 5.19–5.16 (m, 2H), 4.17 (s, 1H), 3.97 (s, 3H), 3.68–3.63 (m, 2H), 3.09 (d, J = 12.0 Hz, 1H), 3.05–3.04 (m, 1H), 2.93–2.88 (m, 1H), 2.60 (d, J = 5.0 Hz, 1H), 2.05–2.00 (m, 2H), 1.83–1.81 (m, 2H), 1.65–1.60 (m, 2H) ppm. **¹³C NMR (125 MHz, CDCl₃):** δ = 158.15, 151.76, 148.11, 144.05, 143.17, 142.02, 141.93, 137.49, 133.21, 131.90, 131.37, 128.77, 128.73, 127.56, 127.42, 122.78, 121.75, 120.59, 118.08, 117.26, 117.00, 115.93, 101.18, 61.43, 55.88, 55.77, 55.57, 49.15, 43.54, 37.02, 35.84, 29.84, 28.60 ppm. **HRMS (ESI) m/z :** calcd for C₃₃H₃₃BrNO₂ (M+H) 554.1695, found 554.1699.

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-3-((2'-bromo-[1,1'-biphenyl]-3-yl)oxy)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthrene (6)

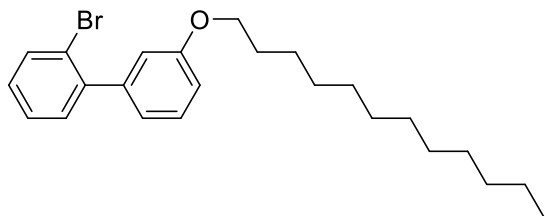


Yellow oil (23 mg, 38% yield, $m:o$ > 20:1), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc

= 10/1, v/v). **¹H NMR (500 MHz, CDCl₃):** δ = 7.66 (d, J = 7.0 Hz, 1H), 7.42–7.30 (m, 3H), 7.21–7.18 (m, 1H), 7.14–7.09 (m, 1H), 6.95–6.91 (m, 2H), 5.40–5.38 (m, 1H), 4.62–4.60 (m, 1H), 2.31 (d, J = 7.0 Hz, 2H), 2.66 (t, J = 7.5 Hz, 2H), 2.02–1.95 (m, 3H), 1.86–1.84 (m, 3H), 1.61–1.54 (m, 8H), 1.16–1.06 (m, 12H), 1.02 (s, 1H), 0.91 (d, J = 6.5 Hz, 3H), 0.86 (d, J = 4.5 Hz, 6H), 0.68 (s, 3H) ppm. **¹³C NMR (125 MHz, CDCl₃):** δ = 173.50, 157.38, 131.36, 129.19, 128.85, 127.45, 124.51, 122.73, 121.76, 120.20, 118.27, 116.88, 115.58, 73.81, 56.82, 56.26, 50.15, 42.45, 39.87, 39.66, 38.80, 37.14, 36.74, 36.32, 35.94, 32.08, 32.05, 32.00, 28.38, 28.16, 27.96, 24.43, 23.97, 22.98,

22.71, 21.17, 19.47, 18.86, 12.00 ppm. **HRMS (ESI) m/z :** calcd for $C_{39}H_{54}BrO$ ($M+H$) 617.3358, found 617.3355.

2-bromo-3'-(dodecyloxy)-1,1'-biphenyl (7)

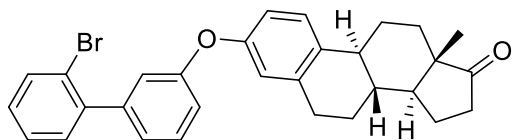


Colorless oil (23 mg, 40% yield, $m:o$ = 15:1), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 40/1, v/v). **1H NMR (500**

MHz, $CDCl_3$): δ = 7.66 (d, J = 8.0 Hz, 1H), 7.37–7.31 (m, 3H), 7.22–7.18 (m, 1H), 6.97 (d, J = 7.5 Hz, 1H), 6.94–6.92 (m, 2H), 3.99 (d, J = 6.5 Hz, 2H), 1.82–1.77 (m, 2H), 1.49–1.43 (m, 1H), 1.26 (s, 8H), 0.88 (t, J = 6.8 Hz, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 158.84, 142.69, 142.50, 133.23, 131.35, 129.08, 128.85, 127.43, 122.70, 121.73, 115.71, 114.05, 68.21, 32.07, 29.81, 29.79, 29.75, 29.74, 29.56, 29.50, 29.44, 26.21, 22.84, 14.27 ppm. **HRMS (ESI) m/z :** calcd for $C_{24}H_{34}BrO$ ($M+H$) 417.1793, found 417.1795.

(8R,9S,13S,14S)-3-((2'-bromo-[1,1'-biphenyl]-3-yl)oxy)-13-methyl-

6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (8)



Yellow oil (40 mg, 80% yield, $m:o$ > 20:1).

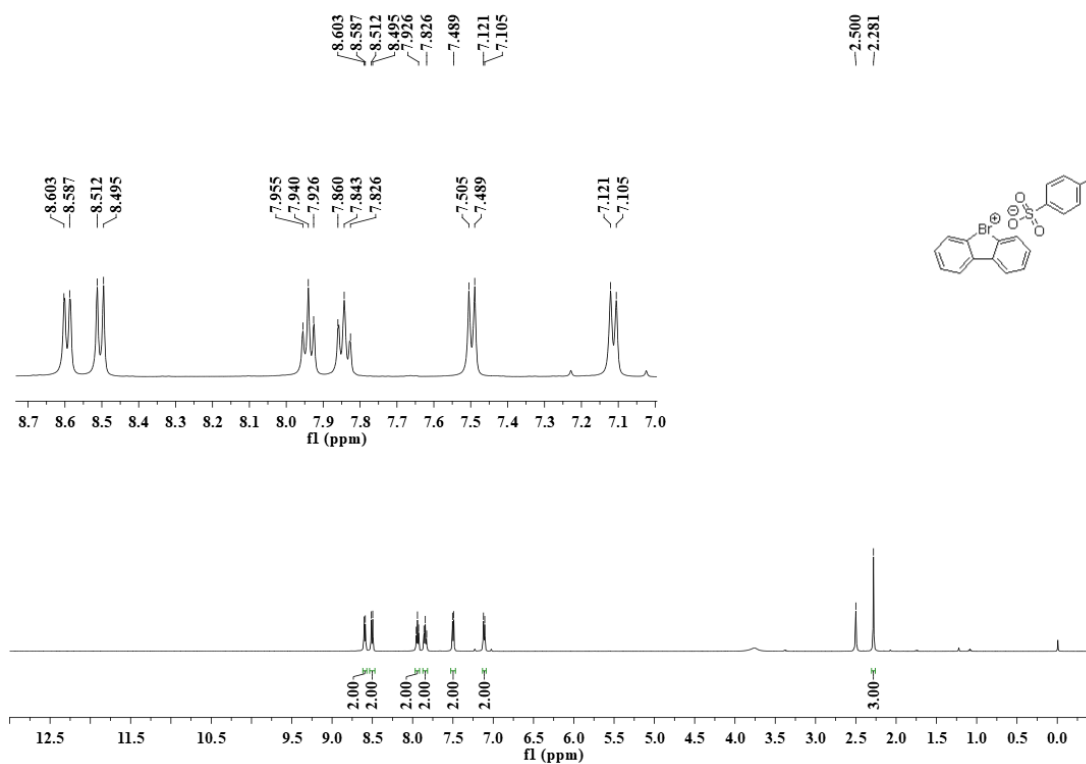
1H NMR (500 MHz, $CDCl_3$): δ = 7.65 (d, J = 7.5 Hz, 1H), 7.38 (t, J = 7.8 Hz, 1H), 7.34–7.31 (m, 2H), 7.25 (s, 1H), 7.21–7.18 (m, 1H), 7.11 (d, J = 7.5 Hz, 1H), 7.05–7.03 (m, 2H), 6.84 (d, J = 8.0 Hz, 1H), 6.82 (s, 1H), 2.90–2.87 (m, 2H), 2.54–2.48 (m, 1H), 2.42–2.39 (m, 1H), 2.31–2.26 (m, 1H), 2.19–2.11 (m, 1H), 2.08–1.96 (m, 4H), 1.54–1.42 (m, 5H), 0.93 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 157.03, 154.79, 142.60, 141.98, 138.24, 134.88, 133.11, 131.14, 129.28, 128.89, 127.35, 126.65, 123.91, 122.54, 119.62, 119.12, 117.83, 116.52, 53.43, 50.44, 47.99, 44.11, 38.19, 35.87, 31.57, 29.52, 26.45, 25.85, 21.59, 13.86 ppm. **HRMS (ESI) m/z :** calcd for $C_{30}H_{30}BrO_2$ ($M+H$) 501.1429, found 501.1425.

5. References

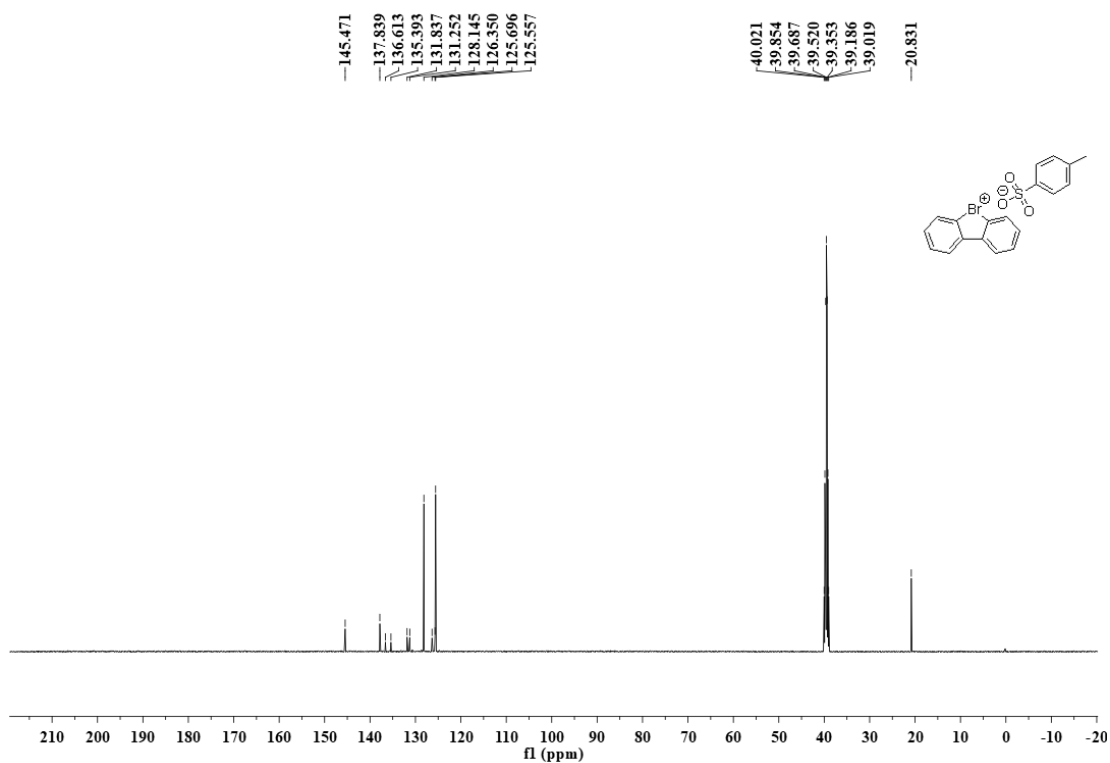
- [1] M. Lanzi, Q. Dherbassy, J. Wencel-Delord, Cyclic Diaryl λ^3 -Bromanes as Original Aryne Precursors, *Angew. Chem., Int. Ed.*, **2021**, *60*, 14852–14857.
- [2] Z. Jiang, K. Sekine, Y. Kuninobu, Synthesis of Fluorenes and Their Related Compounds from Biaryls and Meldrum's Acid Derivatives, *Chem. Commun.*, **2022**, *58*, 843–846.

6. Copies of ^1H and ^{13}C spectra

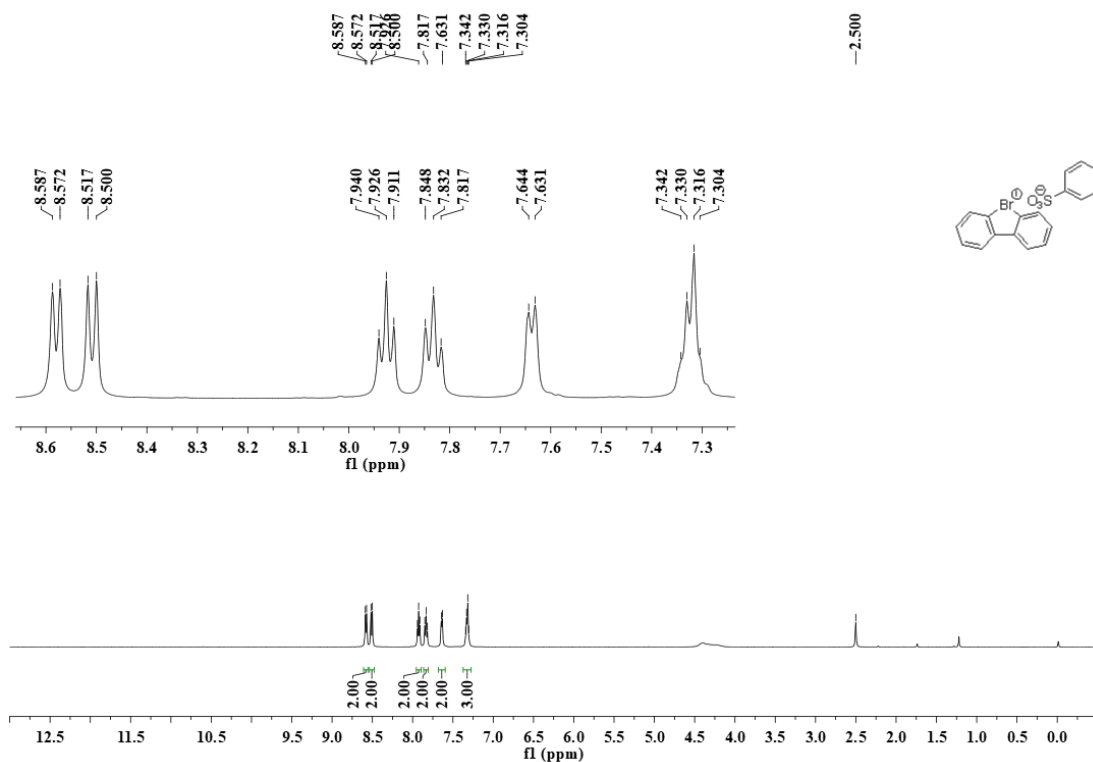
^1H NMR (500 MHz, $\text{DMSO}-d_6$) of **1a-OTs**



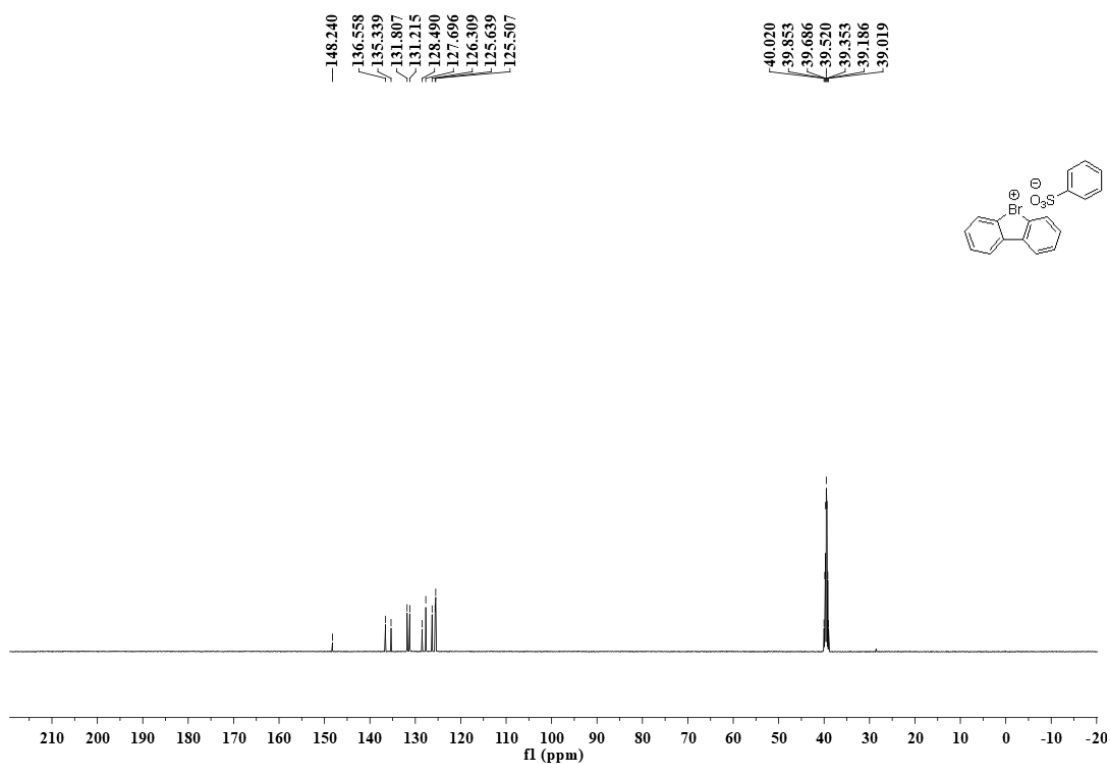
^{13}C NMR (125 MHz, $\text{DMSO}-d_6$) of **1a-OTs**



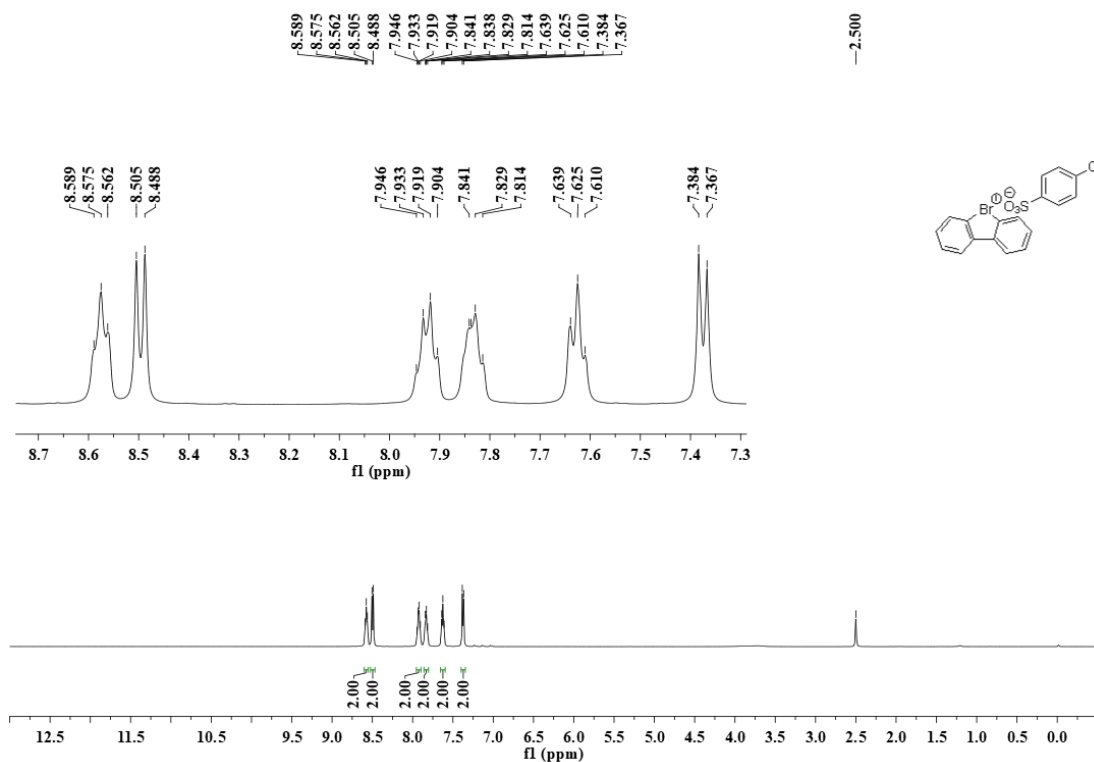
^1H NMR (500 MHz, $\text{DMSO-}d_6$) of **1a**-OBs



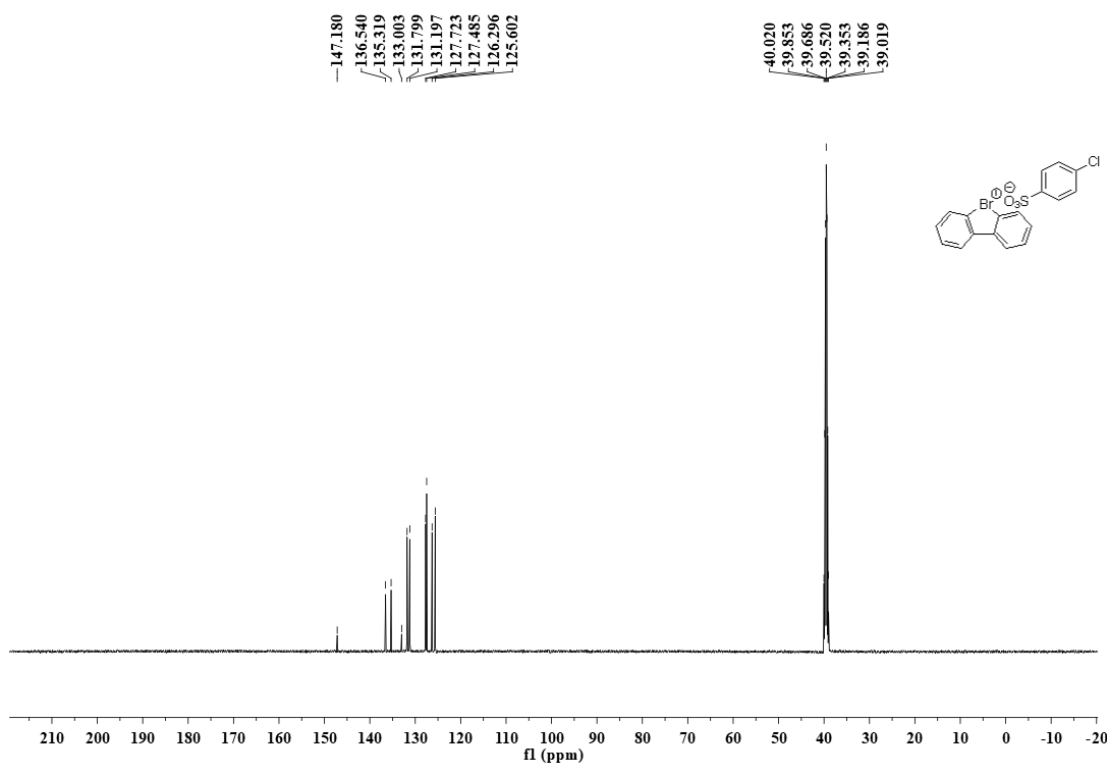
^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) of **1a**-OBs



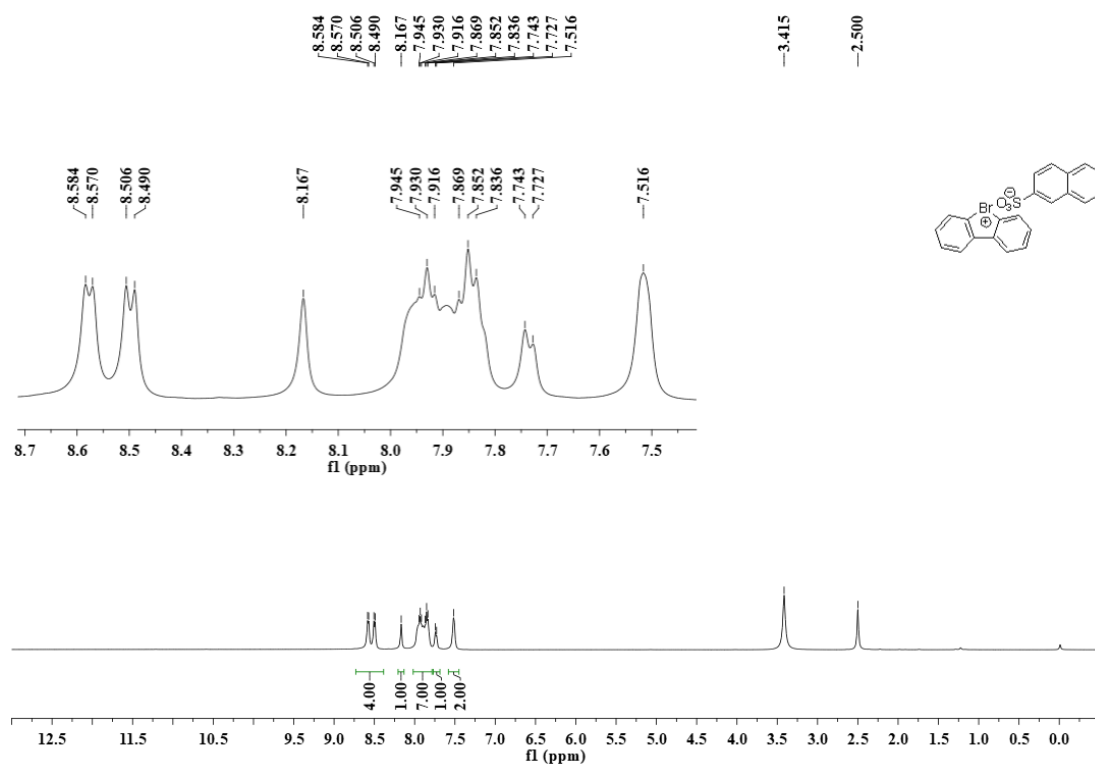
^1H NMR (500 MHz, $\text{DMSO-}d_6$) of **1a-OCs**



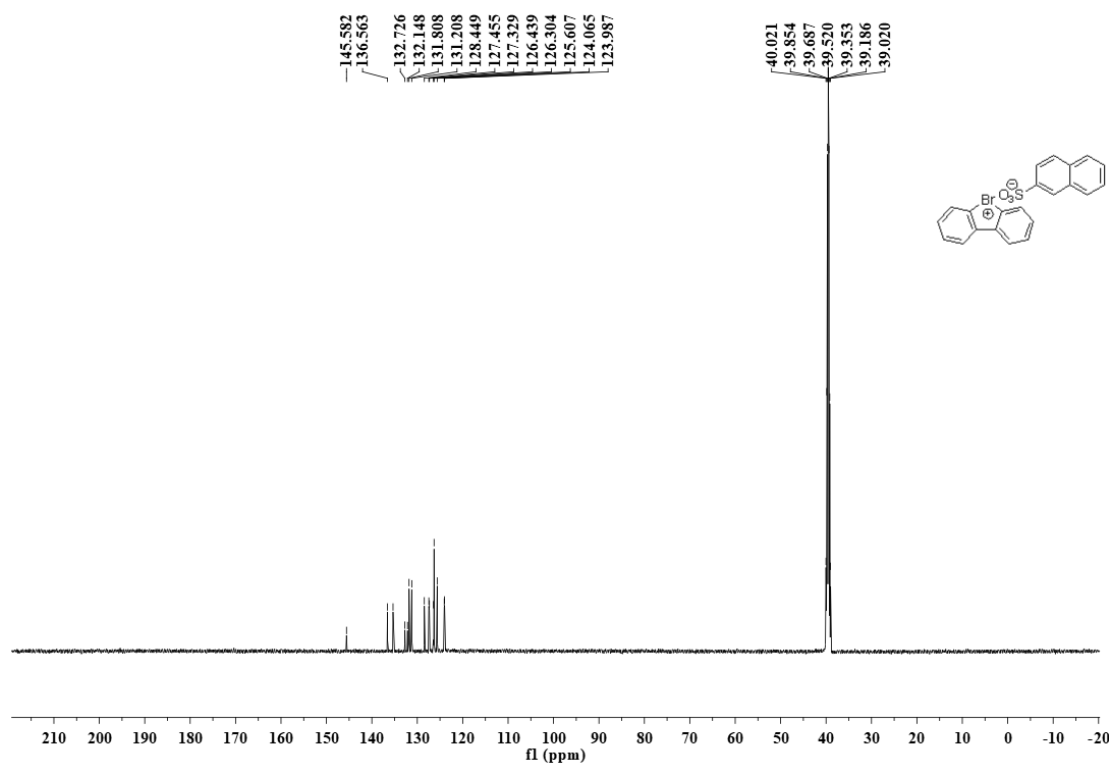
^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) of **1a-OCs**



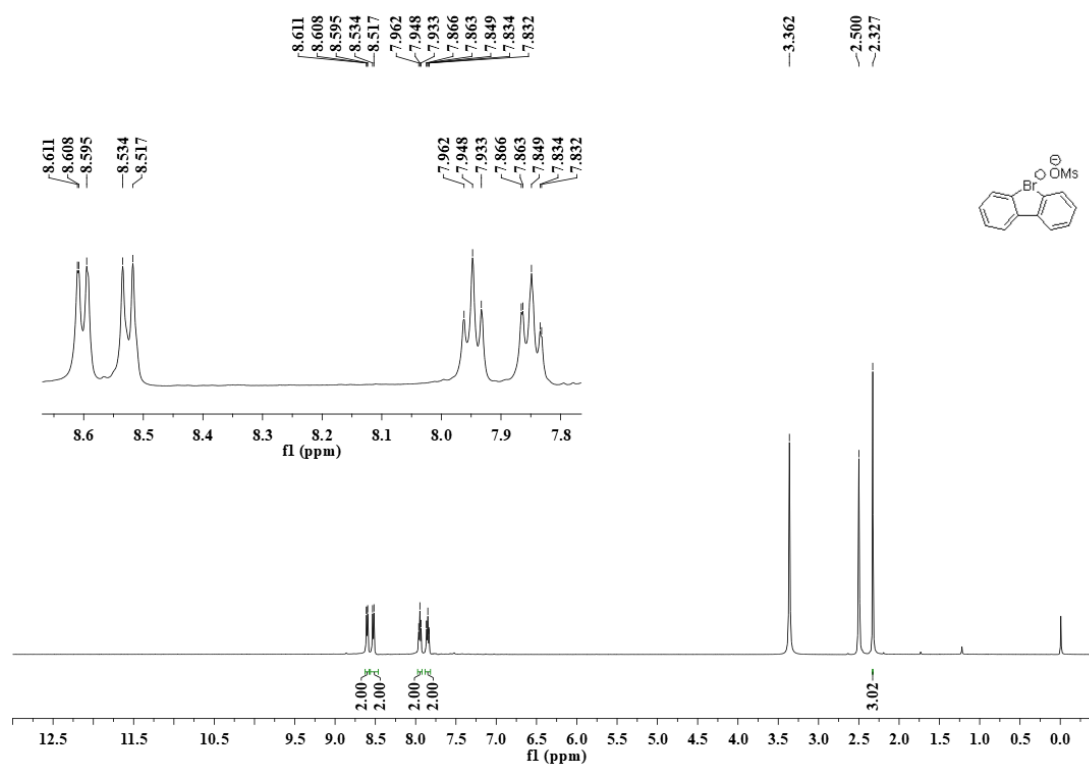
^1H NMR (500 MHz, $\text{DMSO-}d_6$) of **1a-ONs**



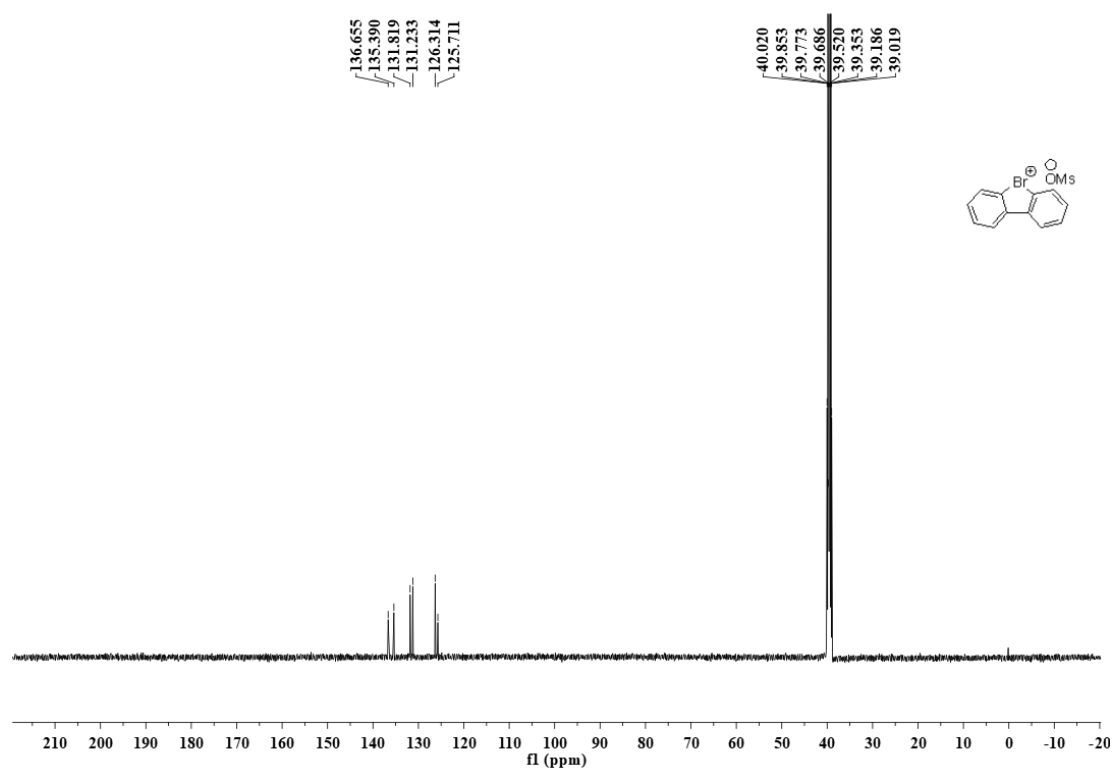
^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) of **1a-ONs**



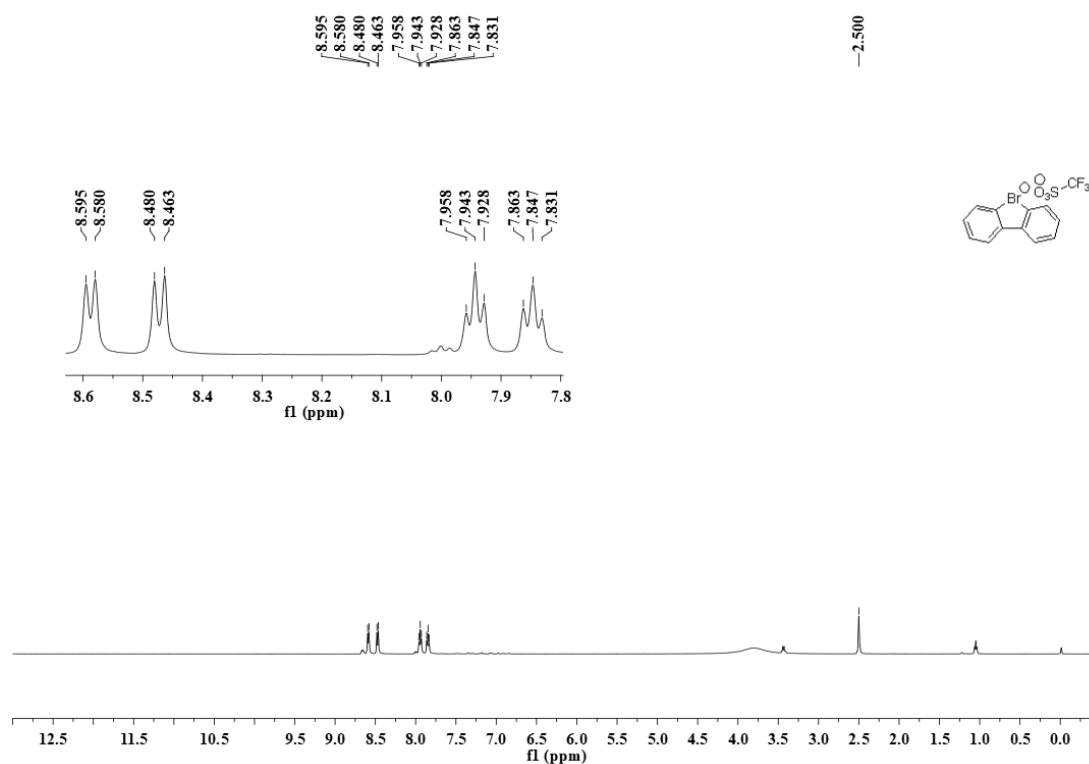
^1H NMR (500 MHz, $\text{DMSO-}d_6$) of **1a-OMs**



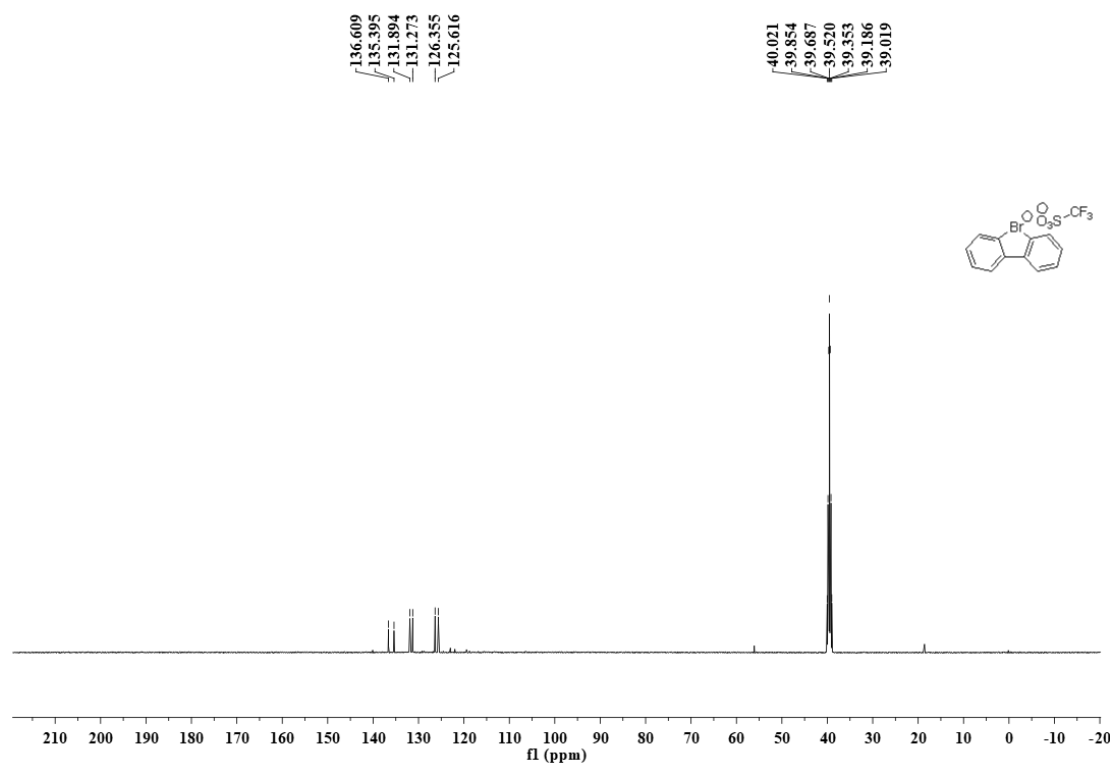
^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) of **1a-OMs**



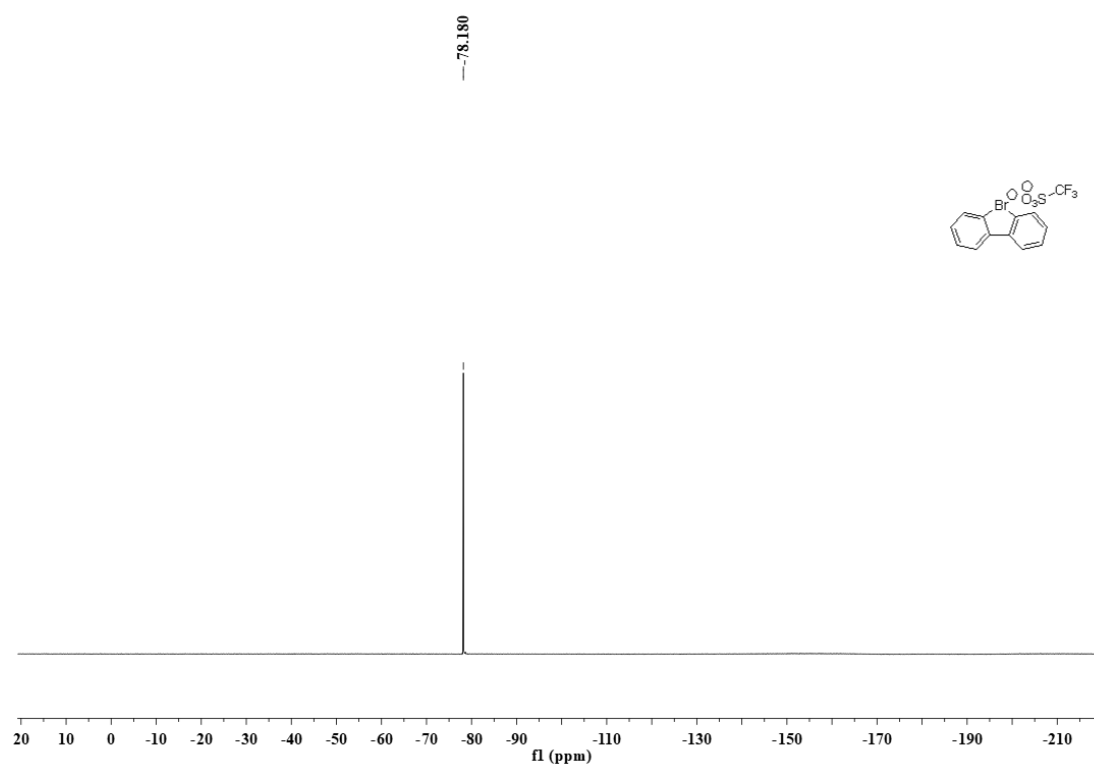
^1H NMR (500 MHz, $\text{DMSO-}d_6$) of **1a-OTf**



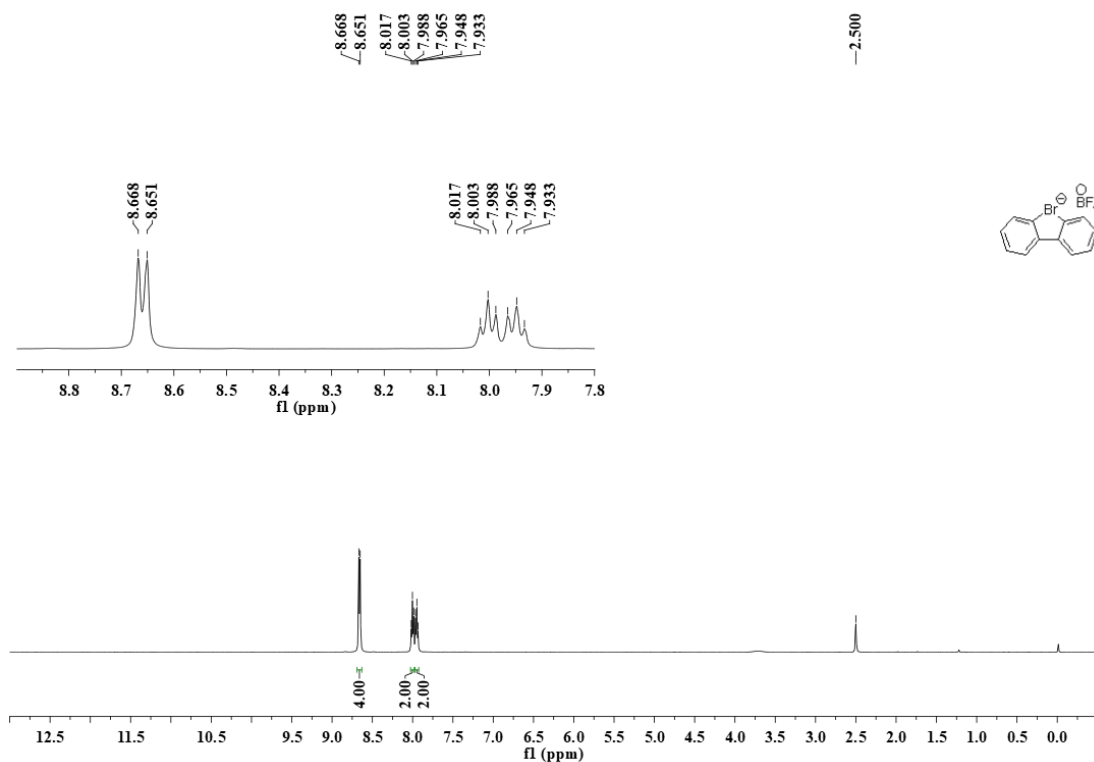
^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) of **1a-OTf**



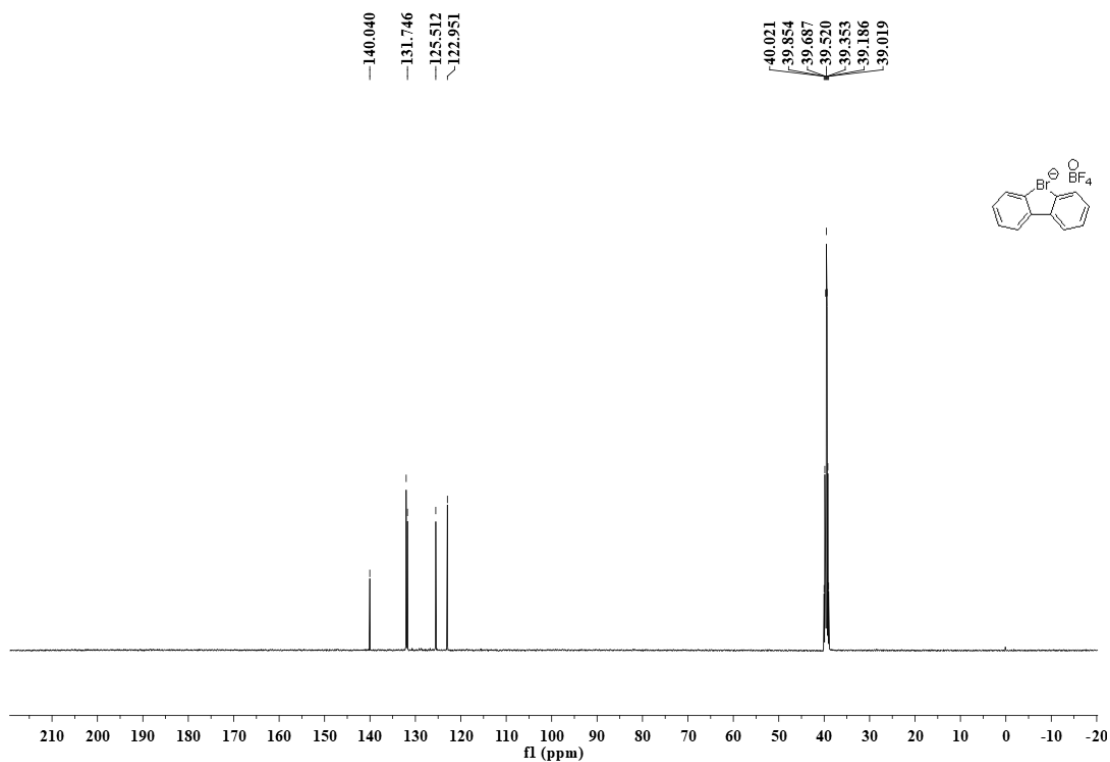
^{19}F NMR (471 MHz, $\text{DMSO-}d_6$) of **1a**-OTf



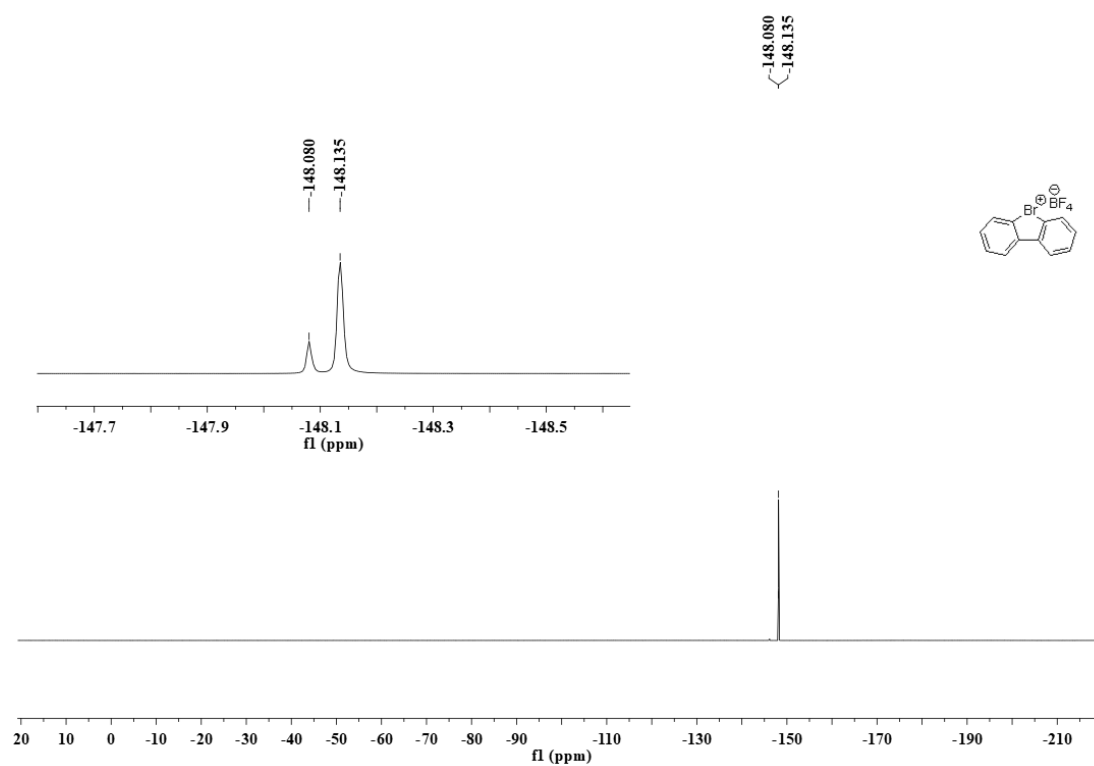
^1H NMR (500 MHz, $\text{DMSO-}d_6$) of **1a**- BF_4



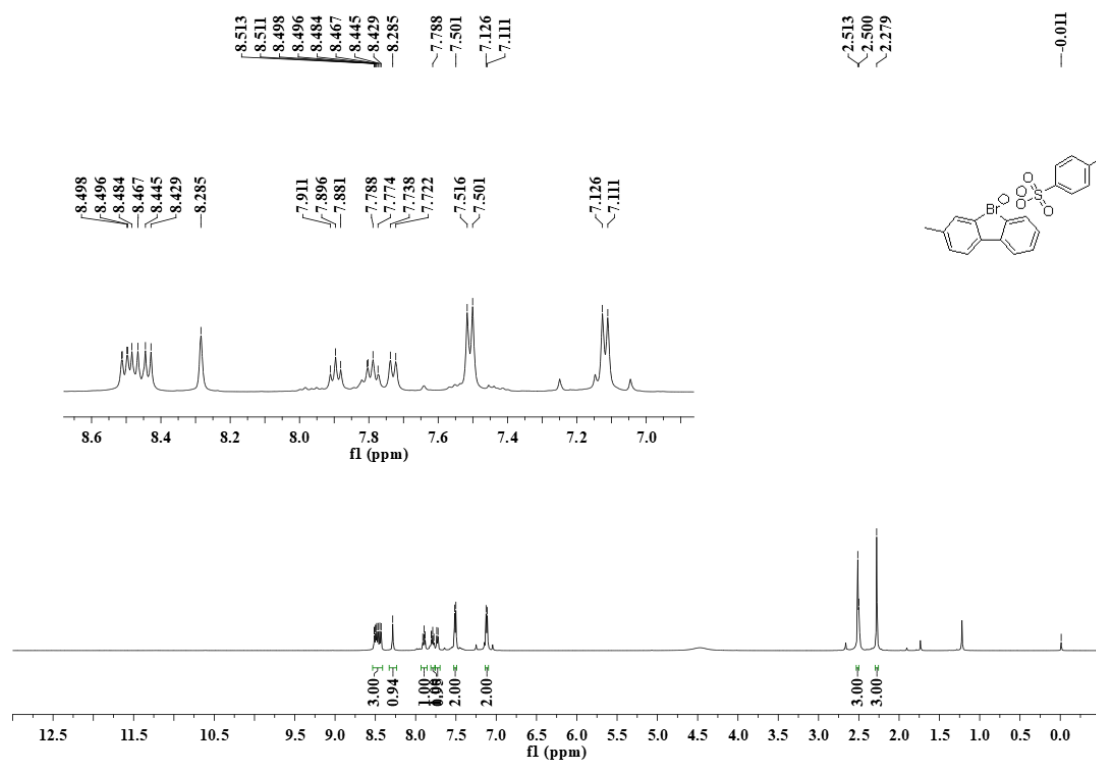
^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) of **1a**- BF_4



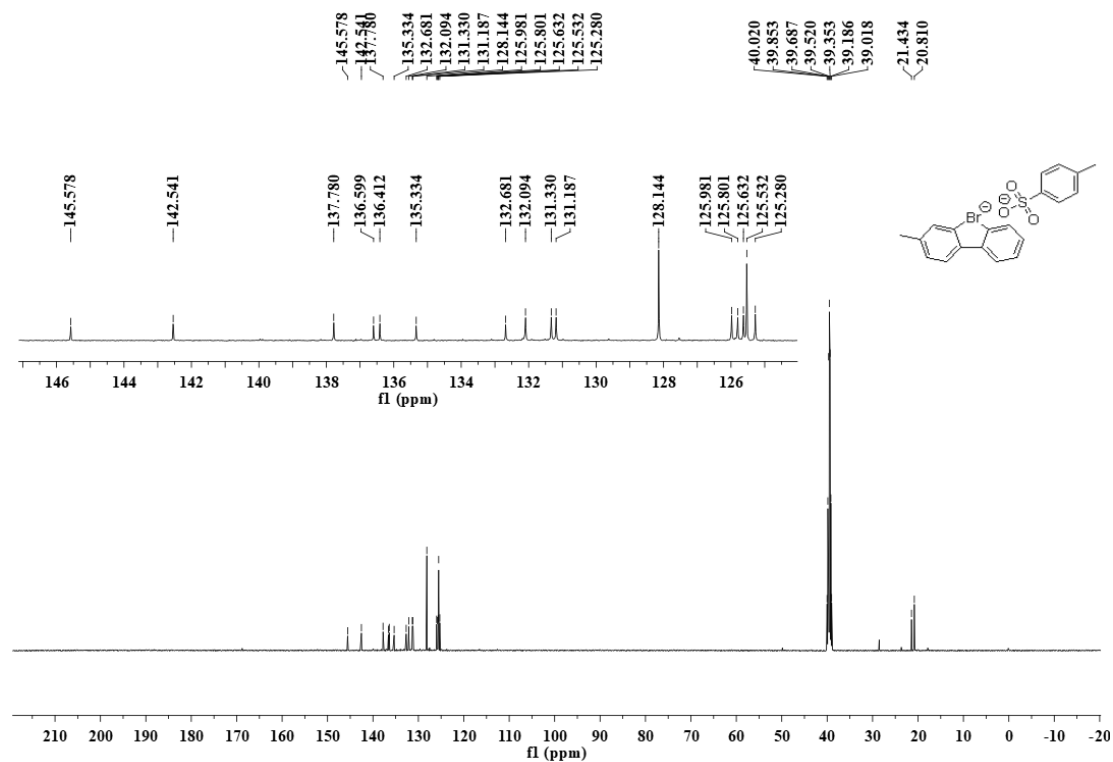
^{19}F NMR (471 MHz, $\text{DMSO-}d_6$) of **1a**- BF_4



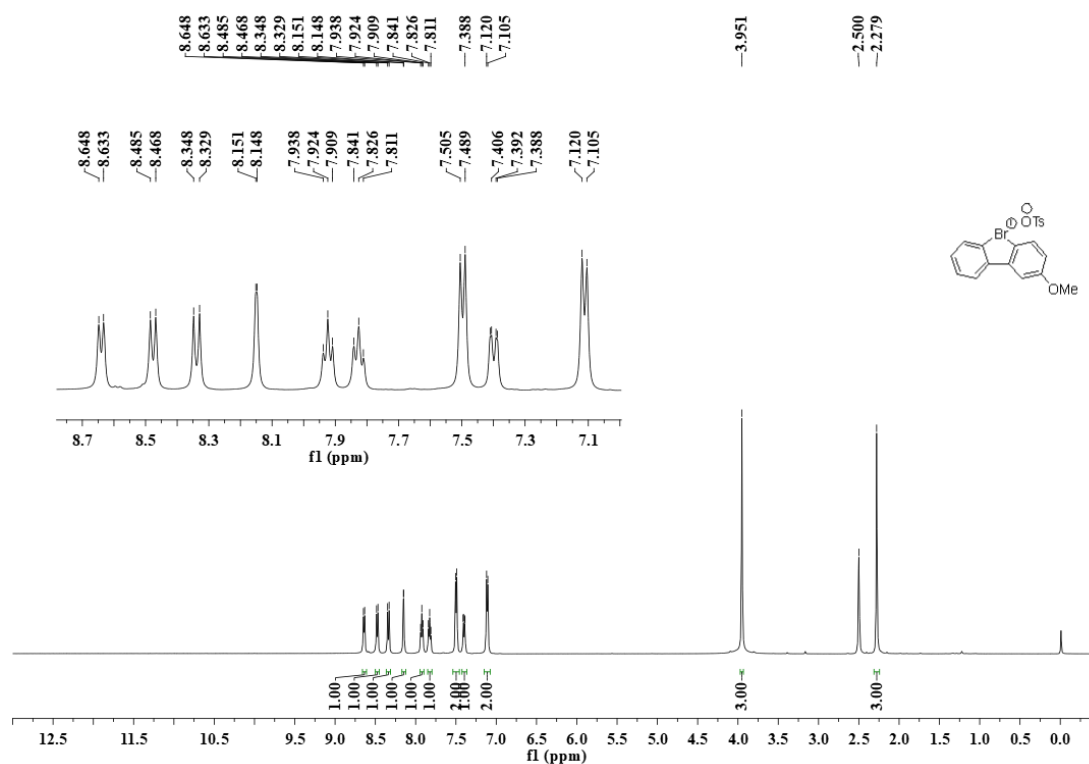
^1H NMR (500 MHz, $\text{DMSO}-d_6$) of **1b**-OTs



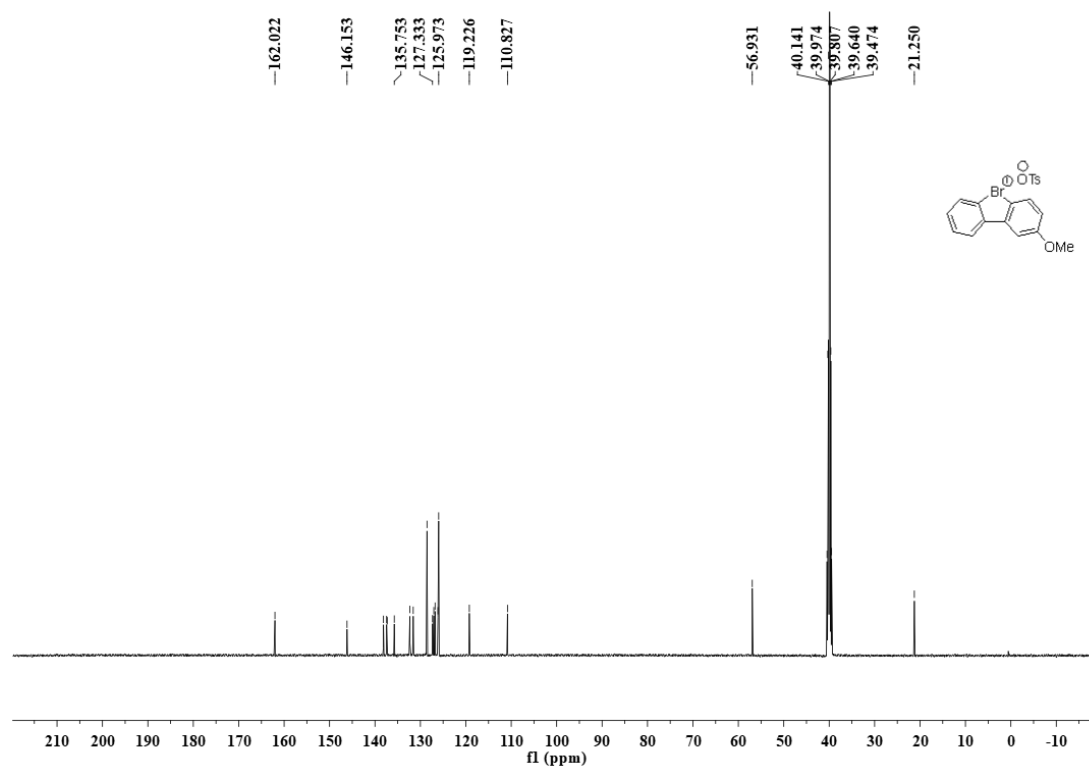
^{13}C NMR (125 MHz, $\text{DMSO}-d_6$) of **1b**-OTs



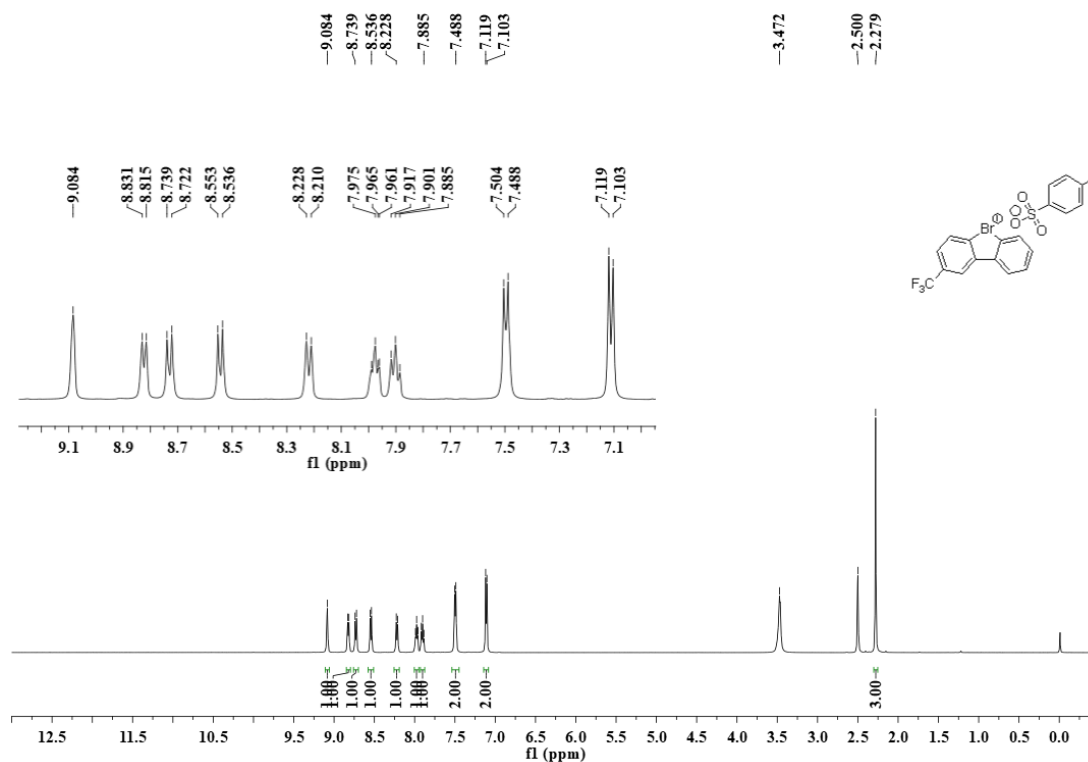
^1H NMR (500 MHz, $\text{DMSO}-d_6$) of **1c-OTs**



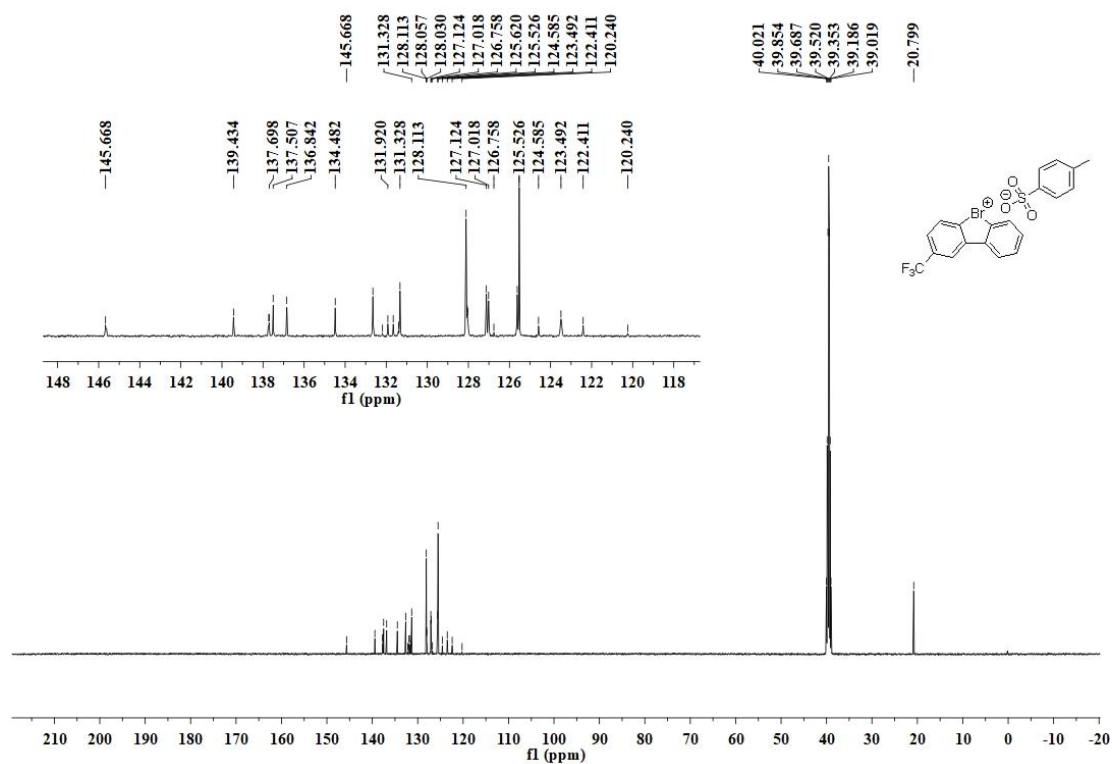
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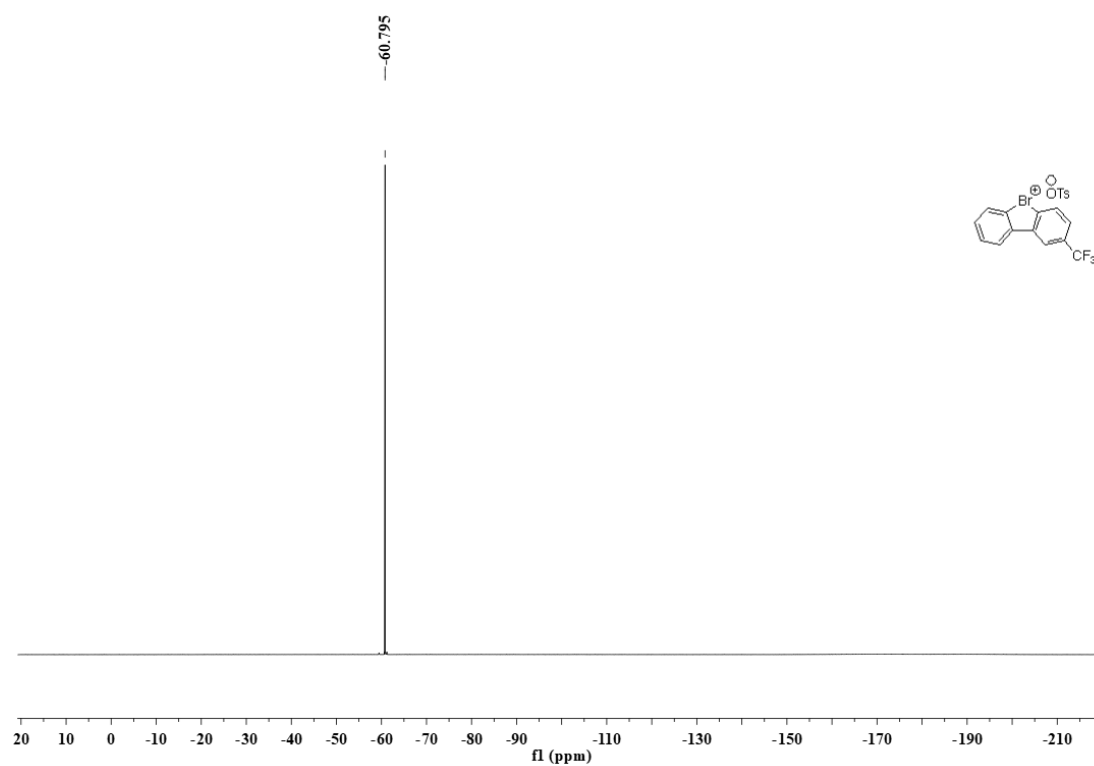
^1H NMR (500 MHz, $\text{DMSO-}d_6$) of **1d**-OTs



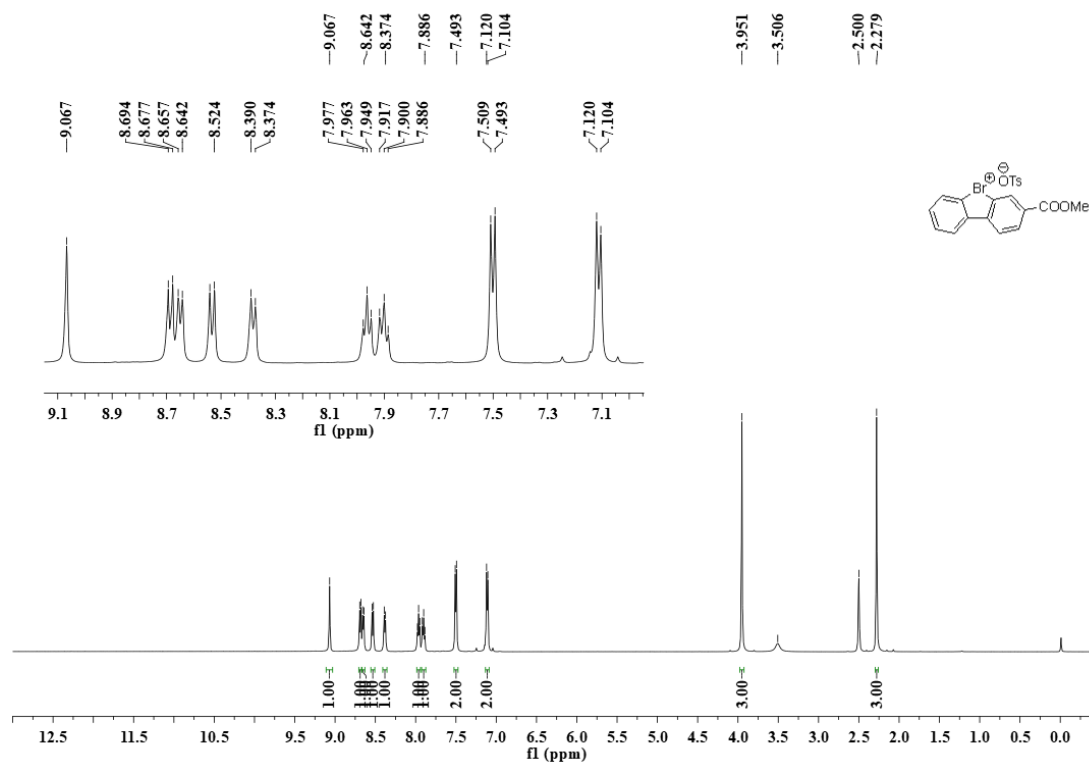
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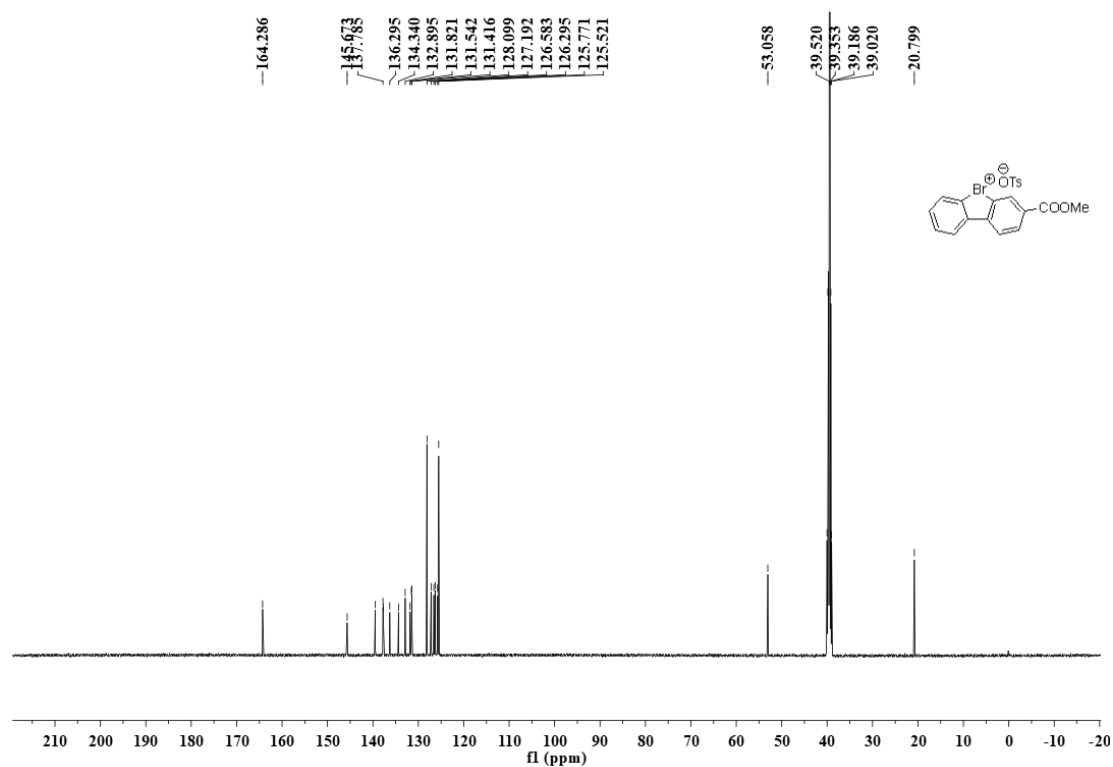
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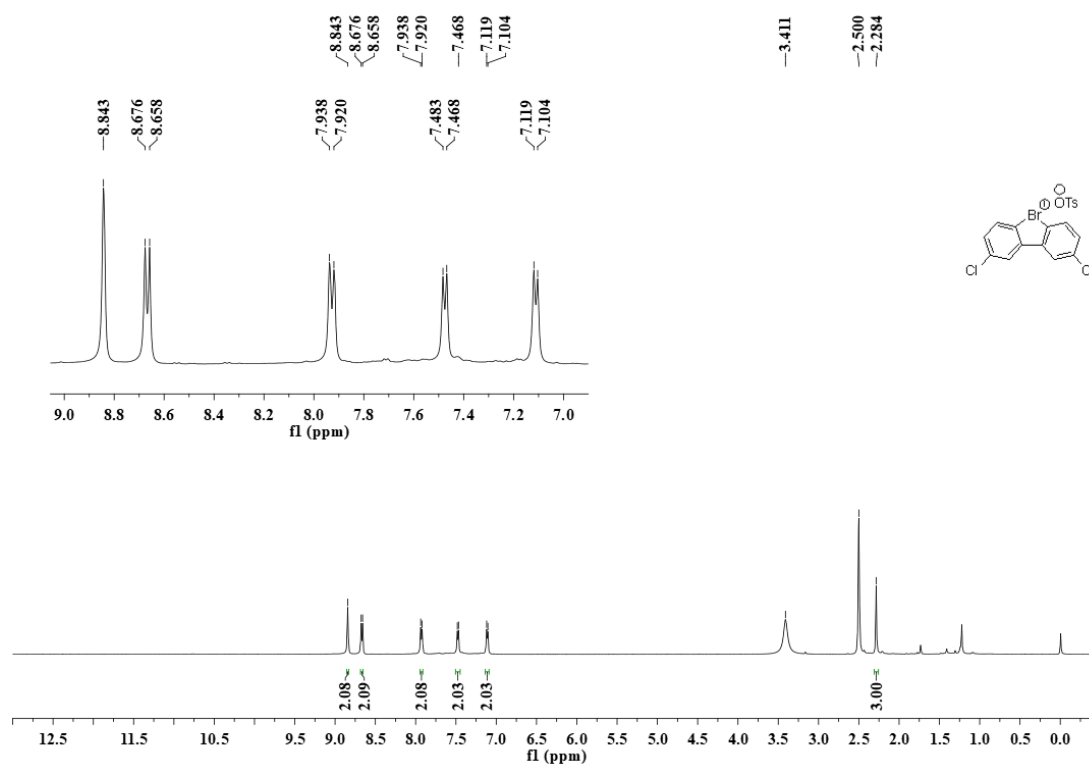
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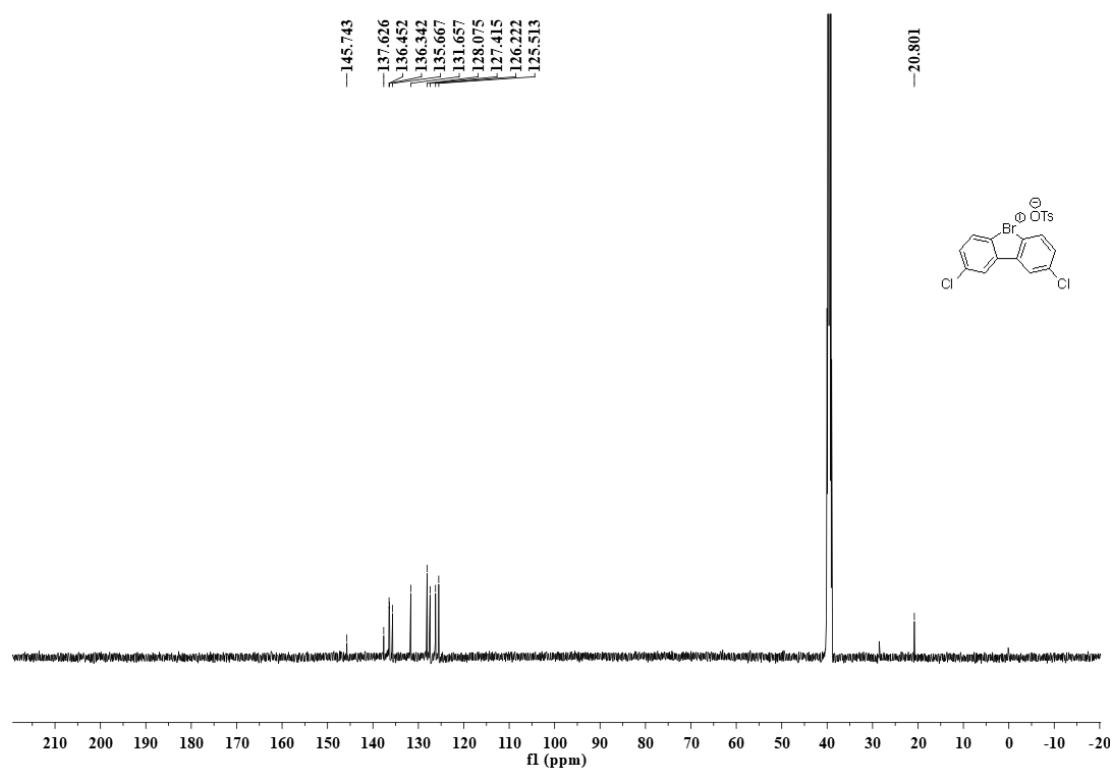
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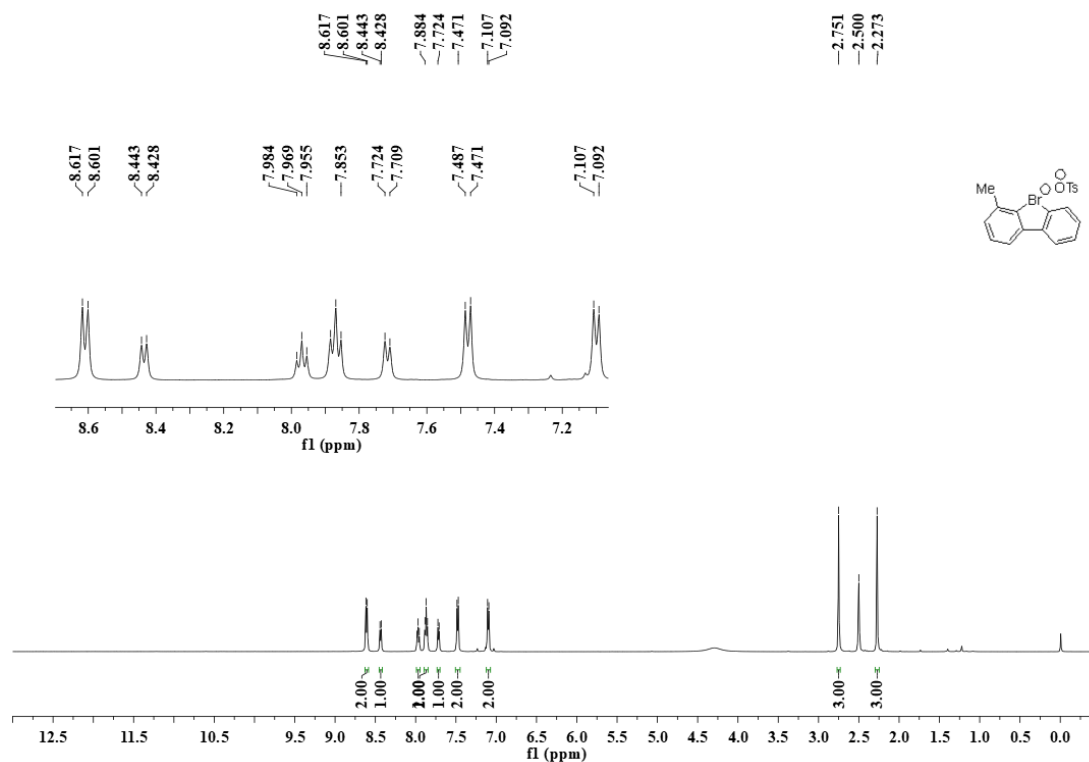
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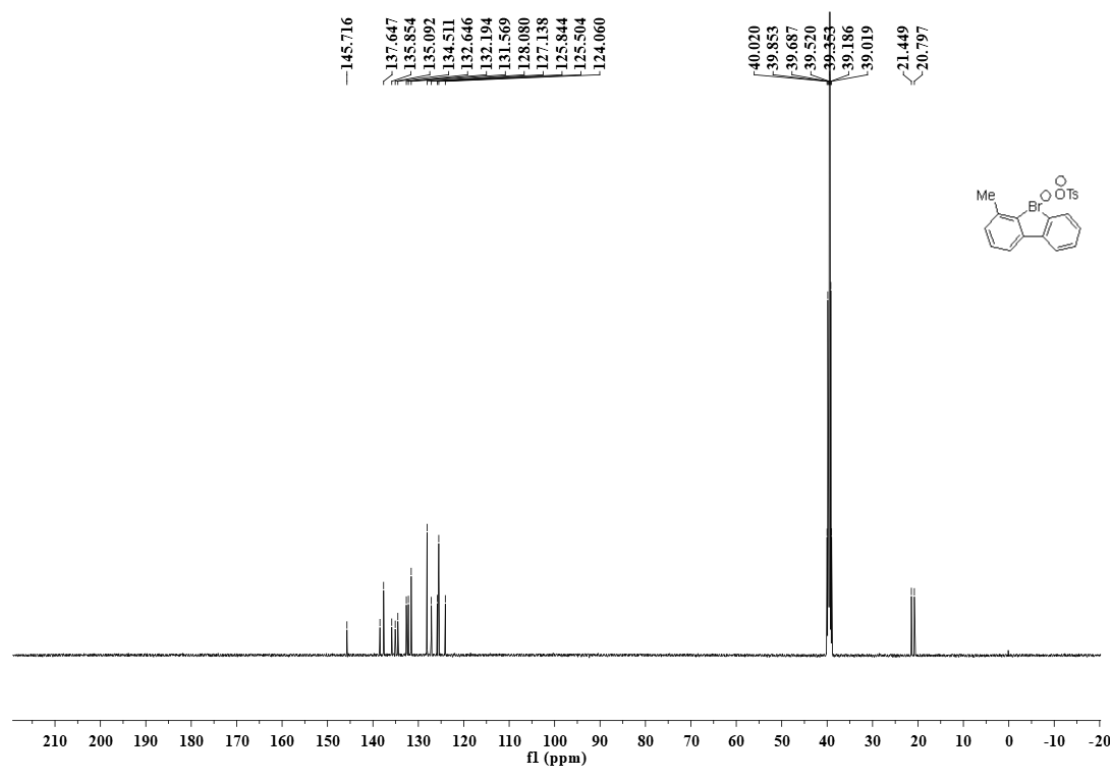
^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) of **1f-OTs**



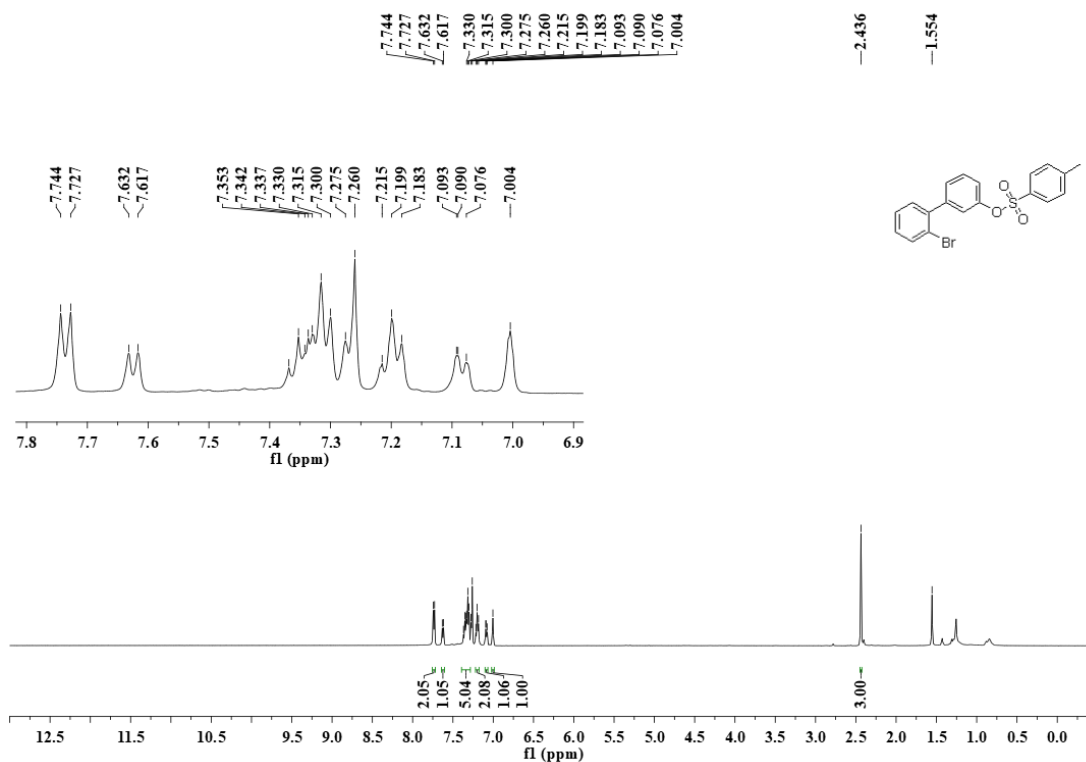
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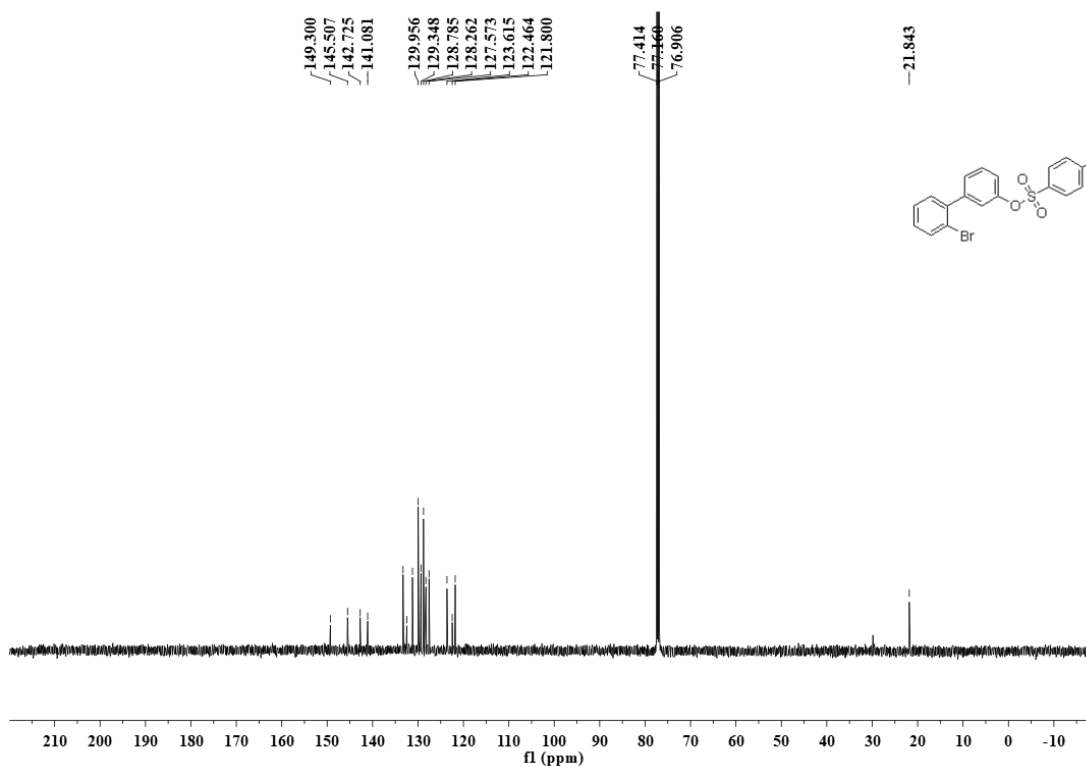
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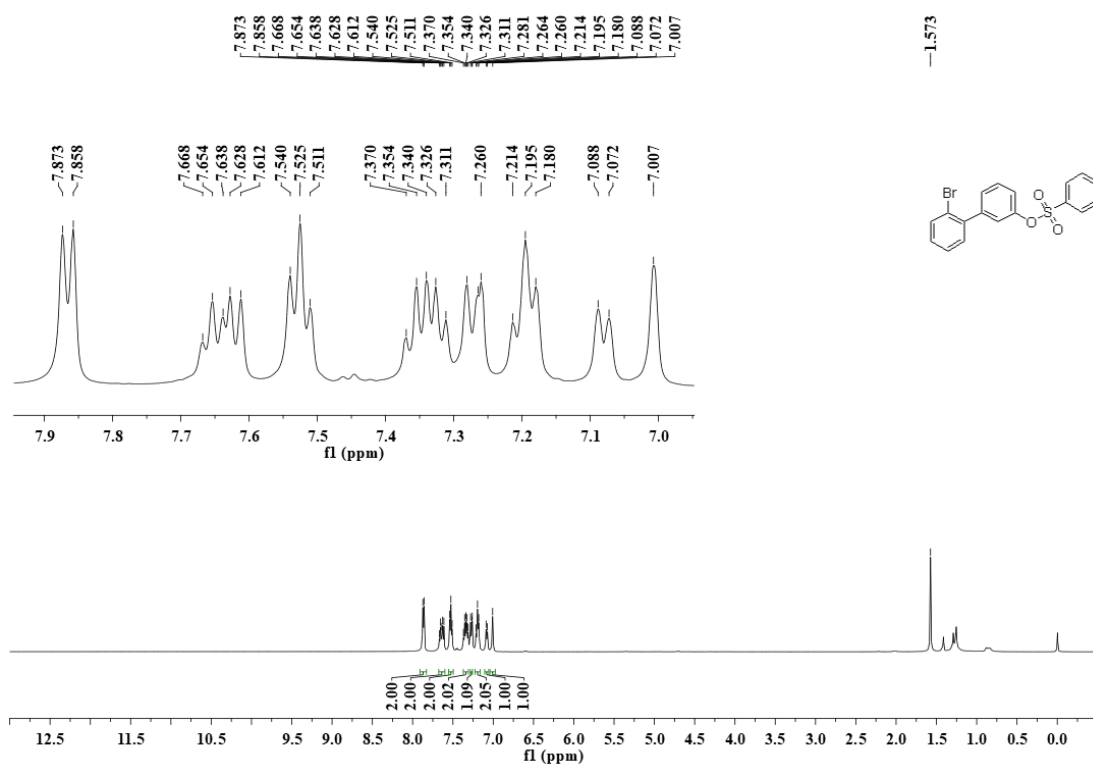
^1H NMR (500 MHz, CDCl_3) of **2a**



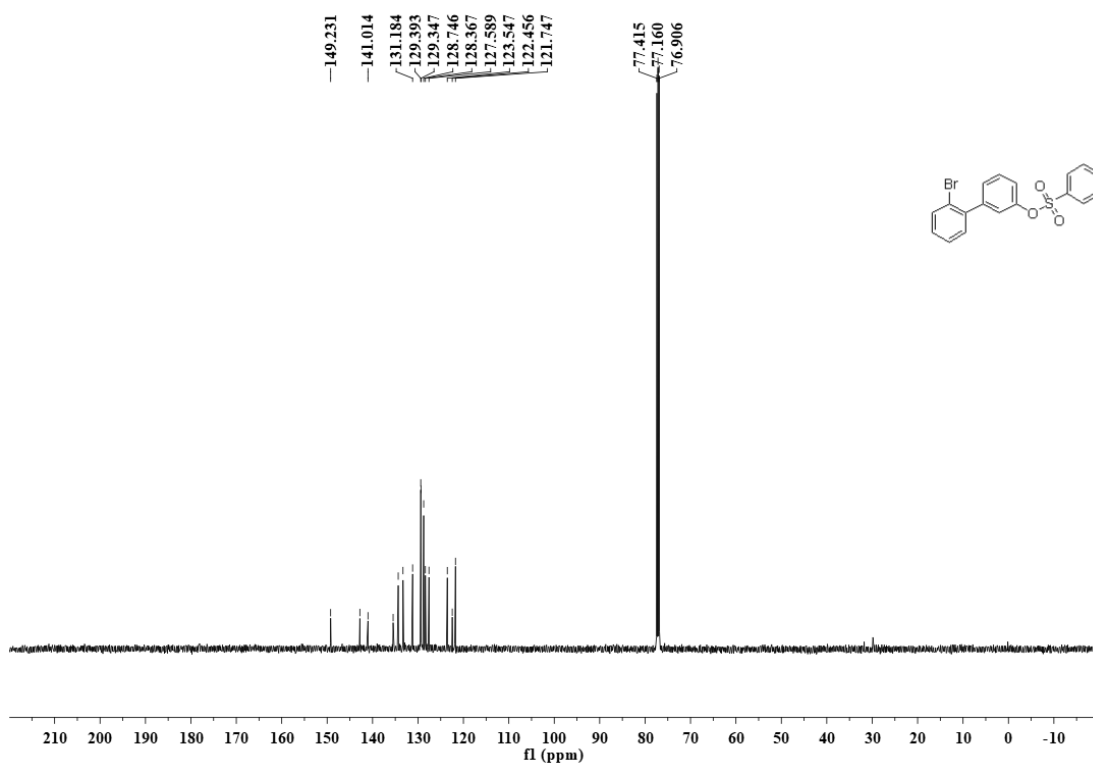
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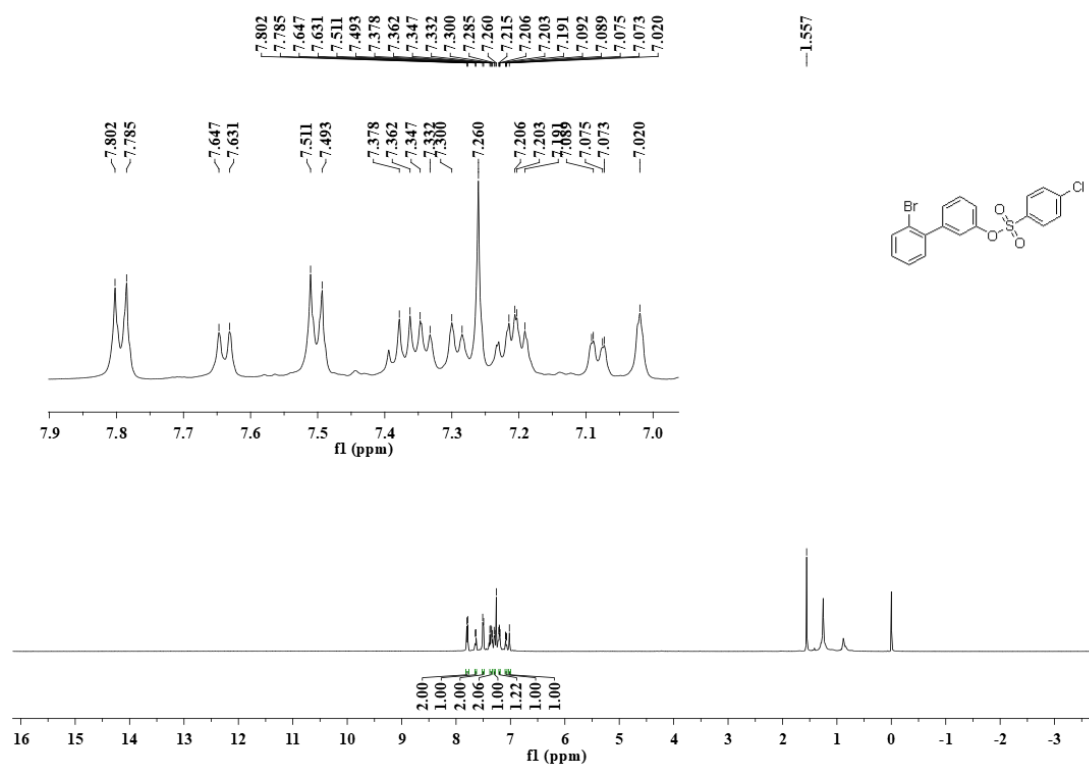
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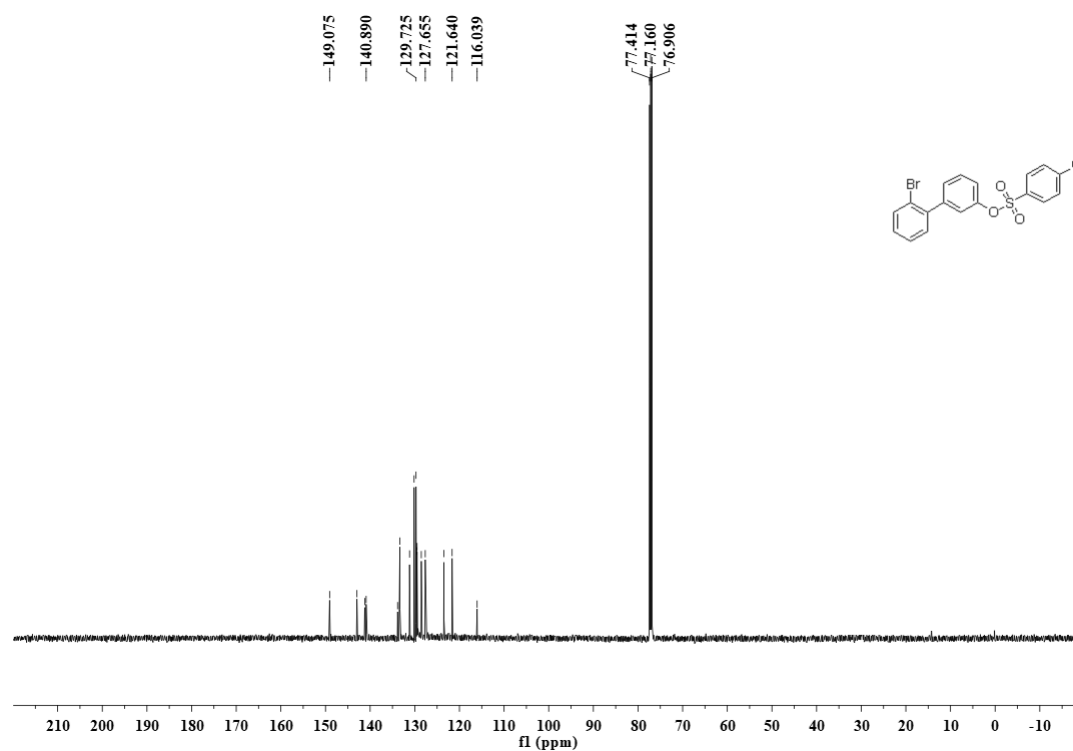
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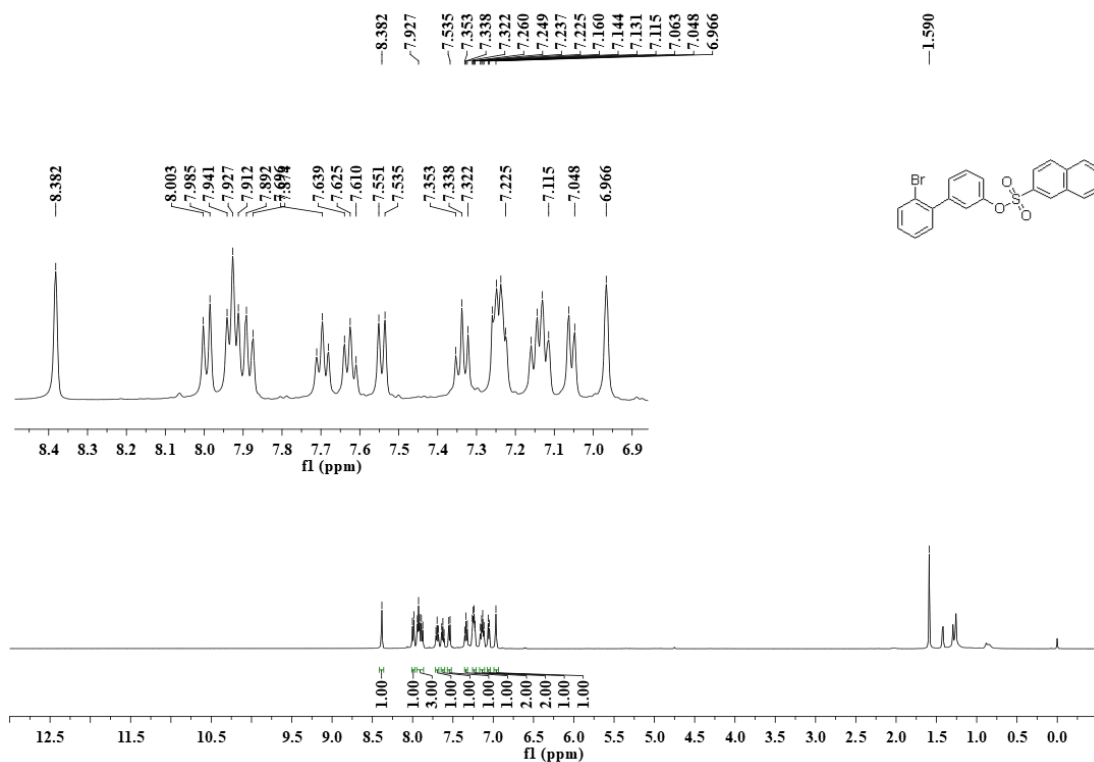
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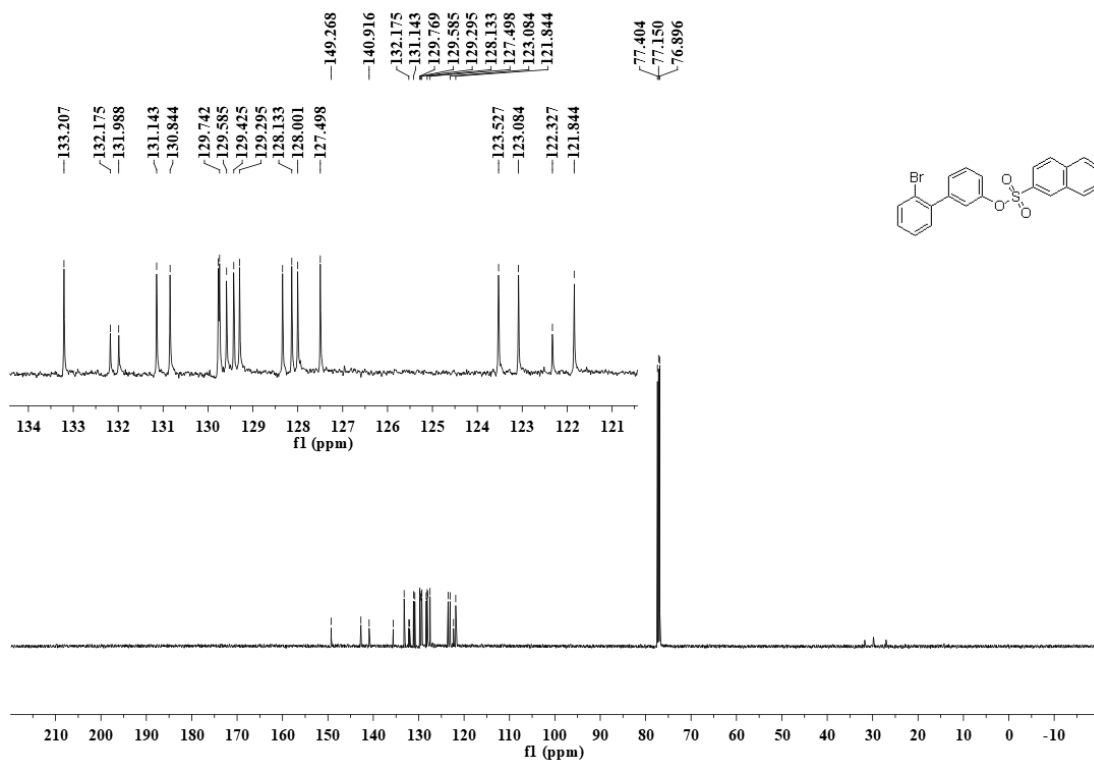
^{13}C NMR (125 MHz, CDCl_3) of **2c**



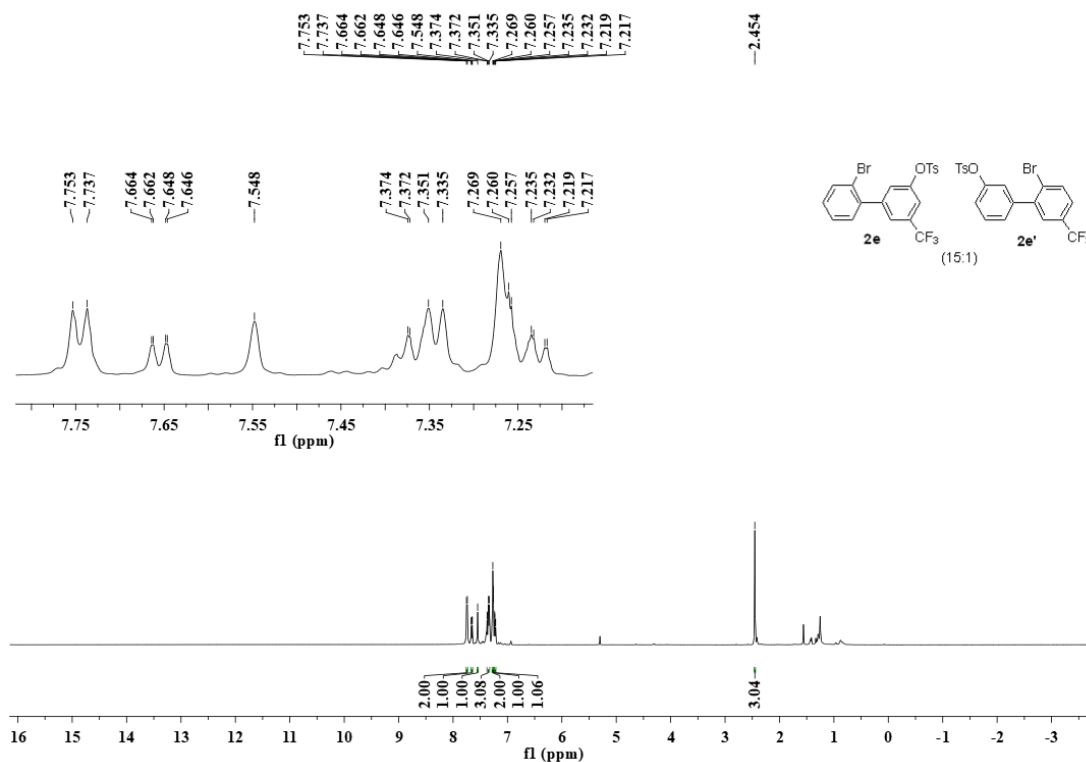
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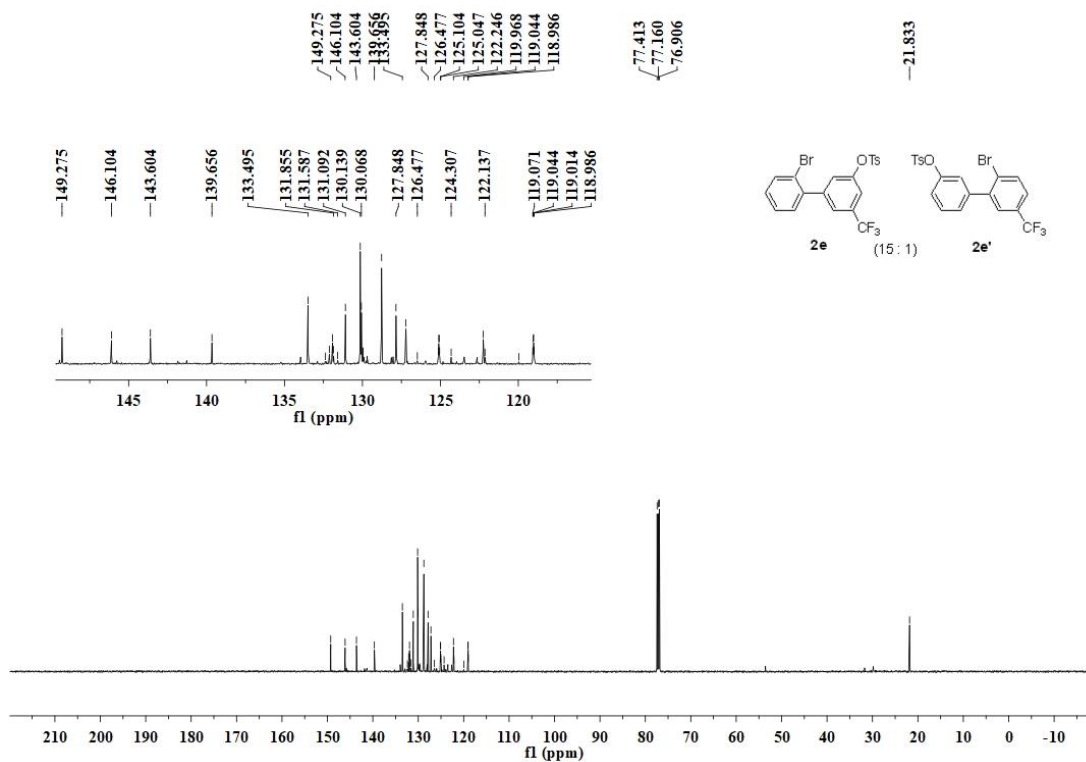
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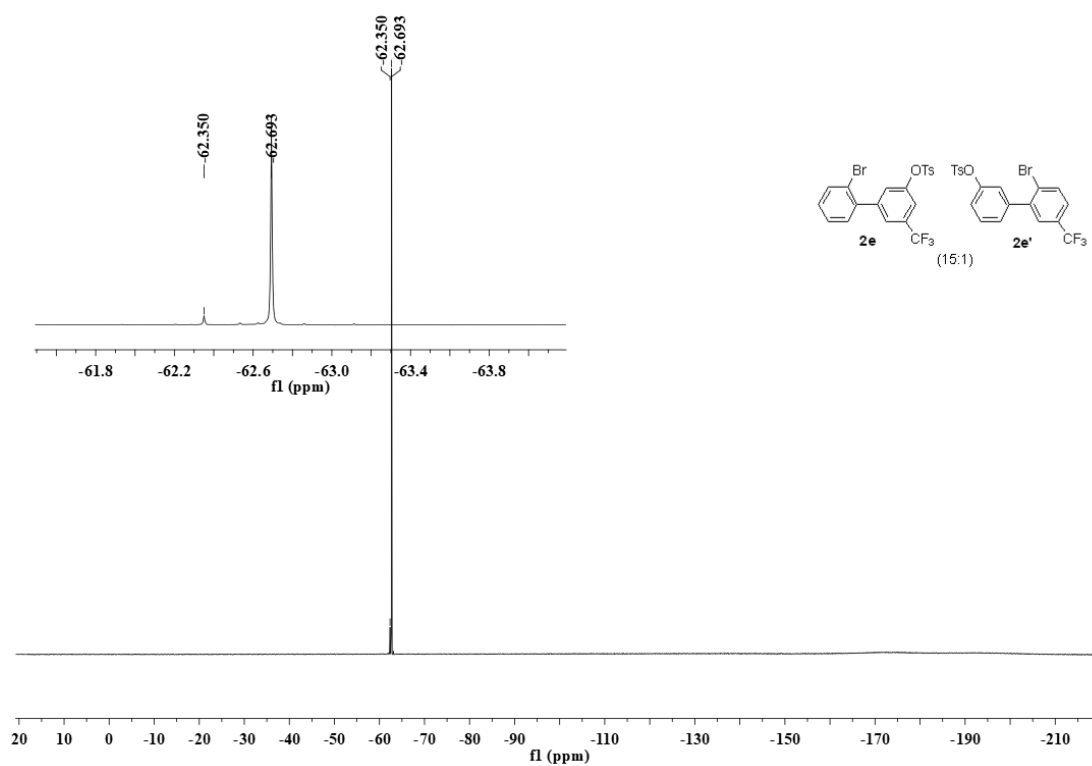
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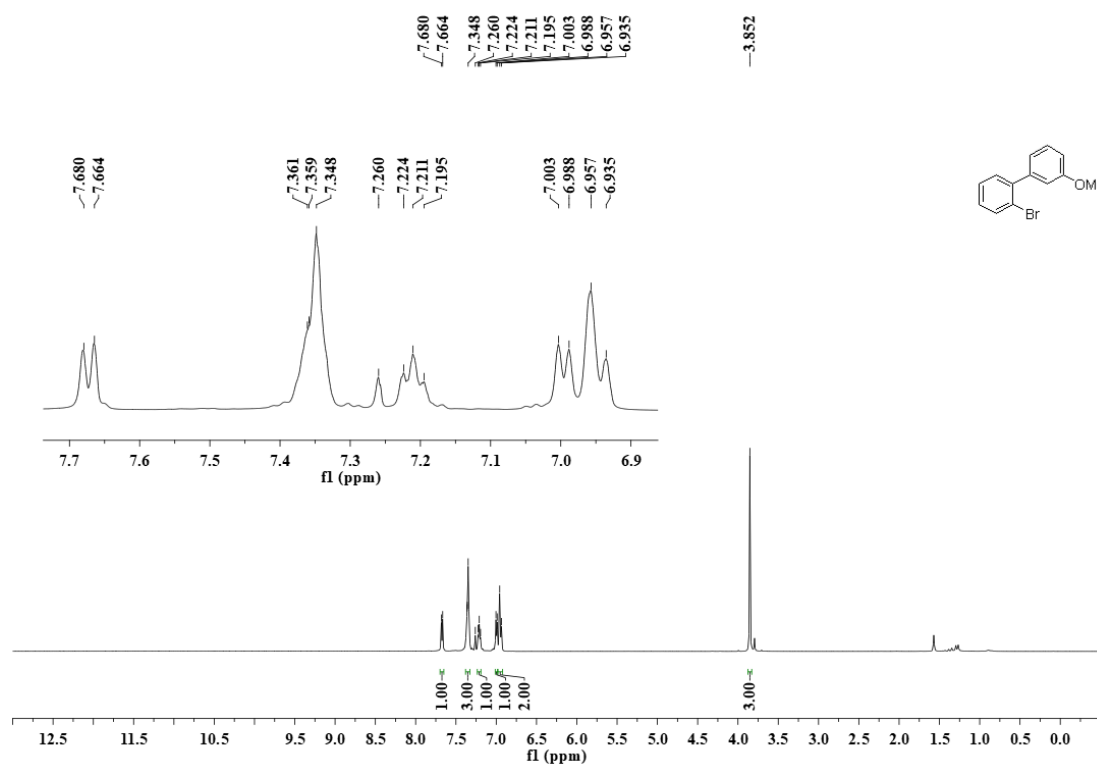
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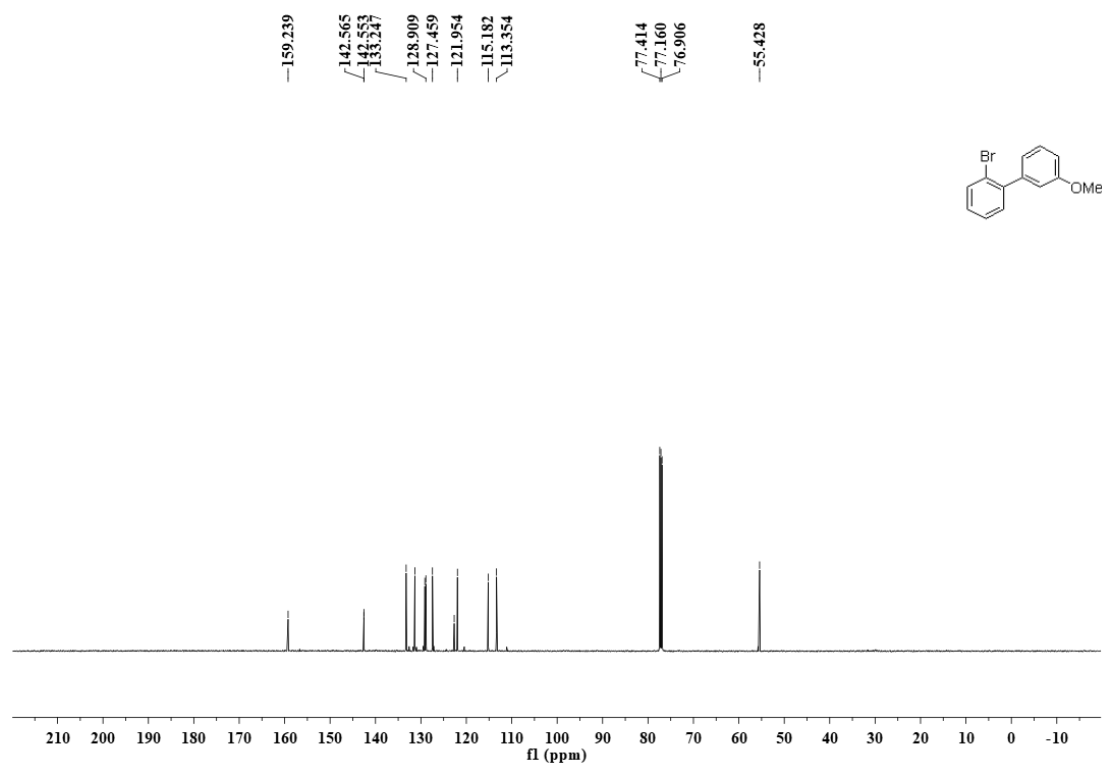
^{19}F NMR (471 MHz, CDCl_3) of **2e**



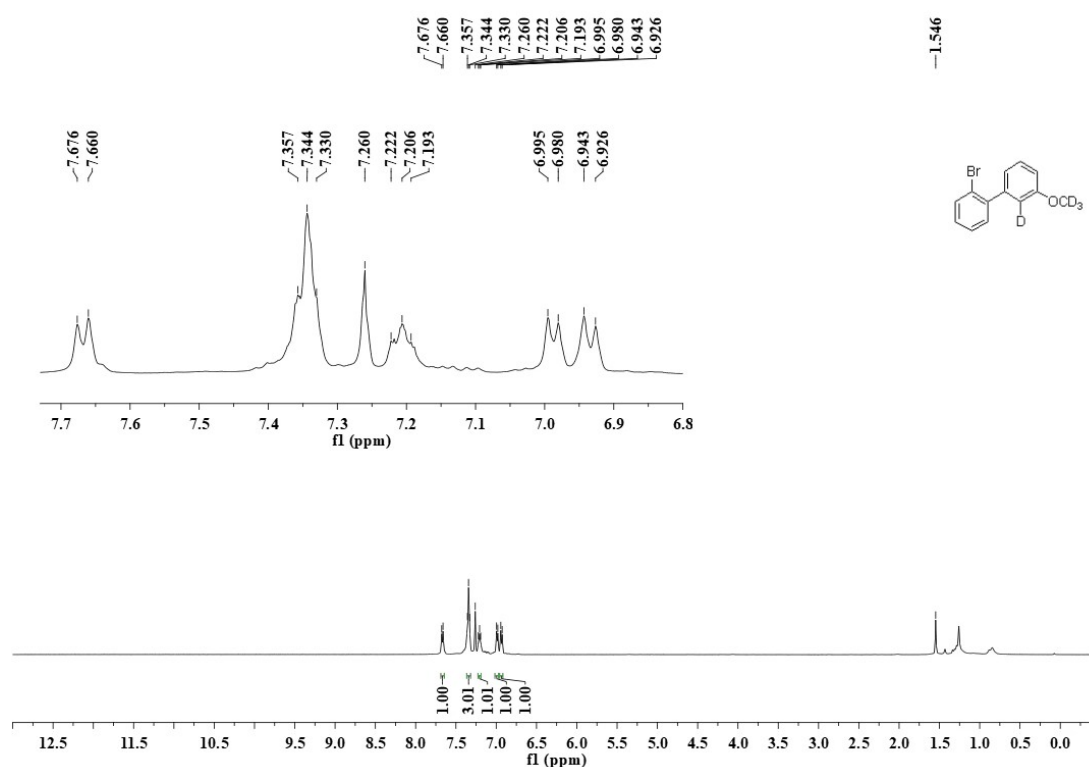
^1H NMR (500 MHz, CDCl_3) of **3a**



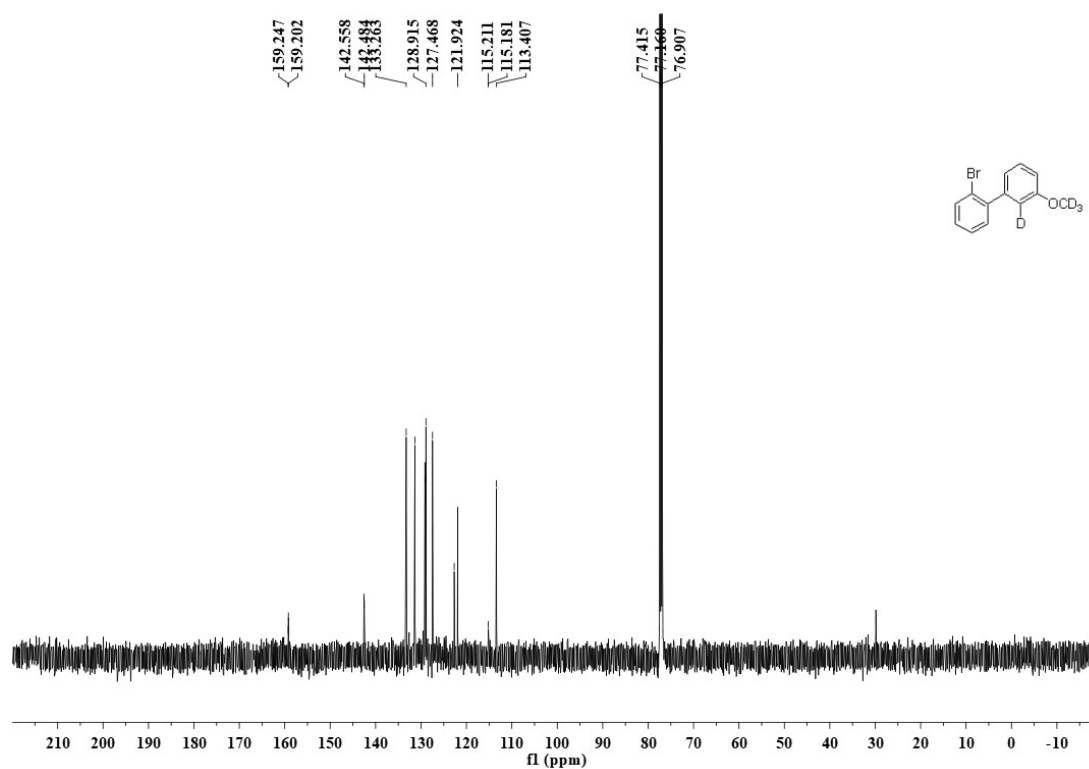
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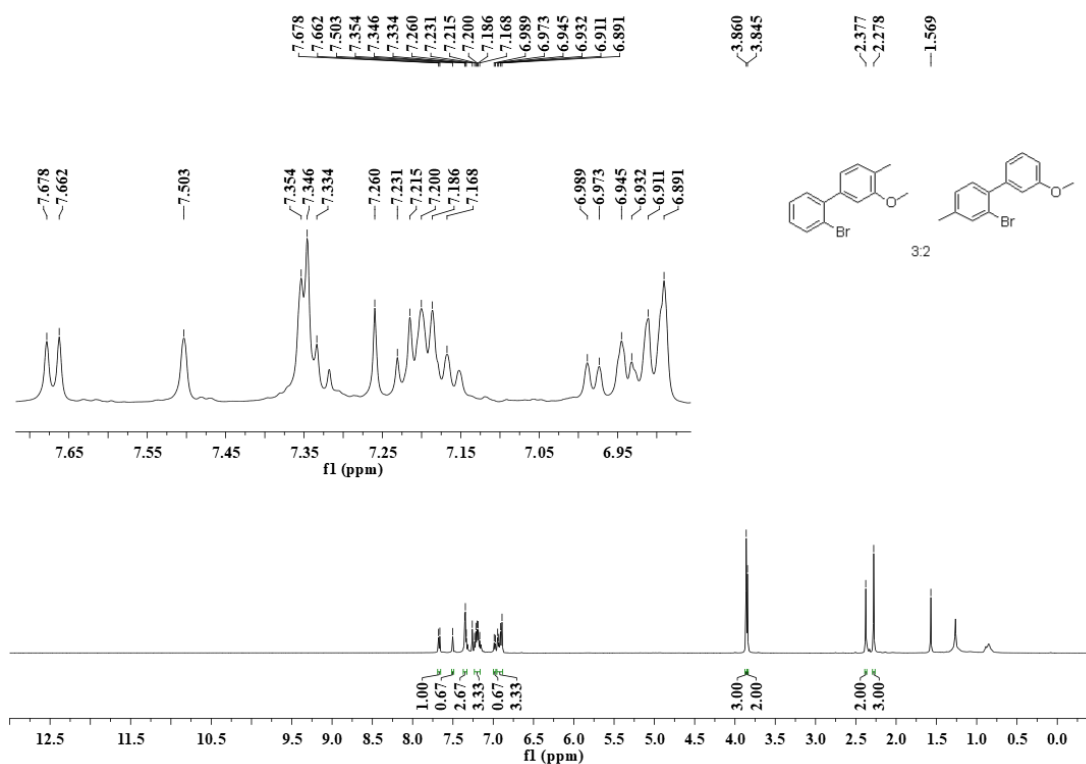
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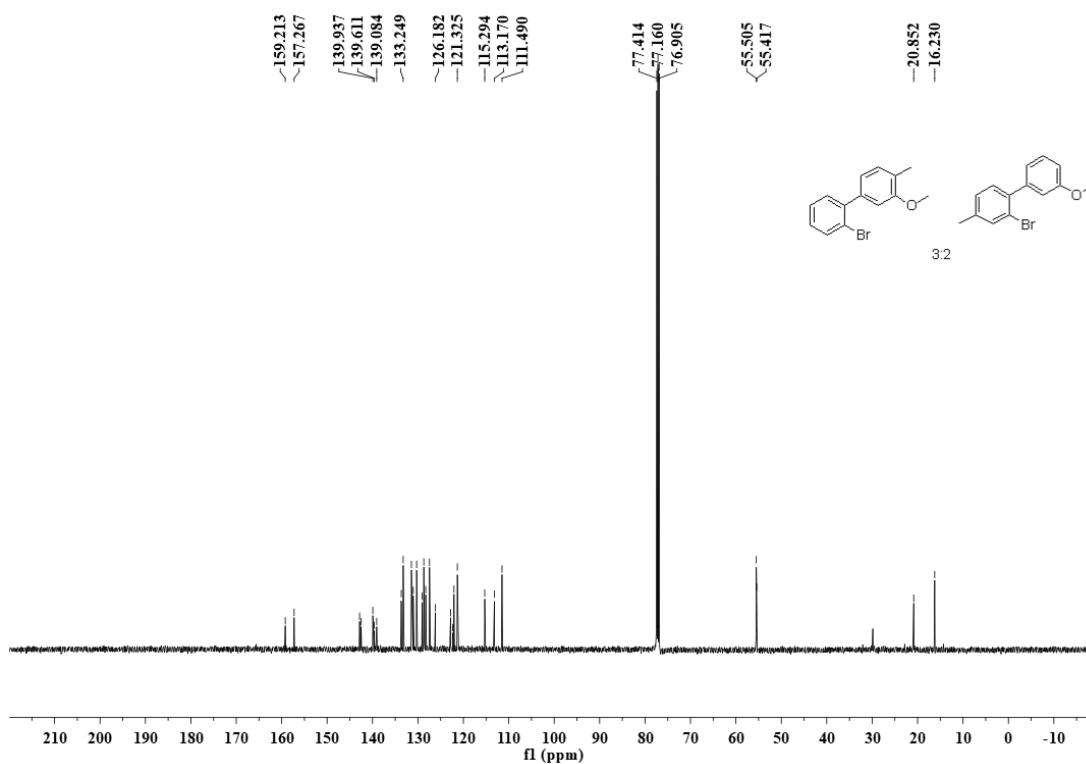
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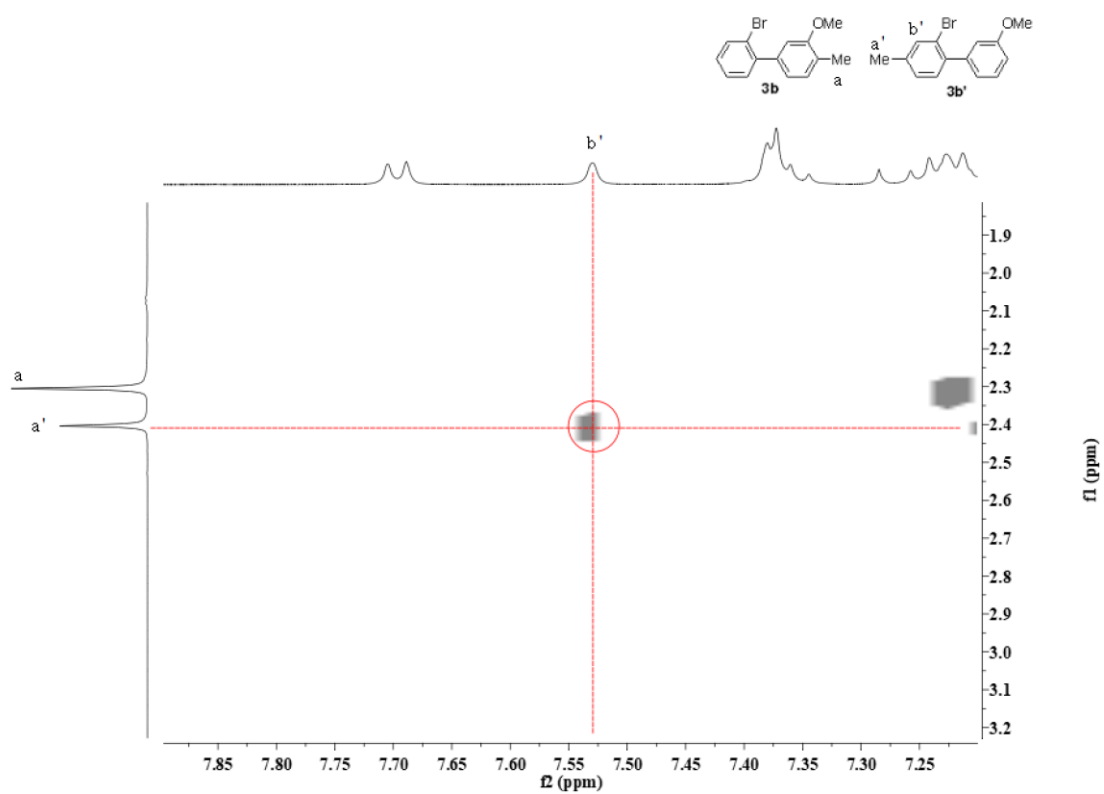
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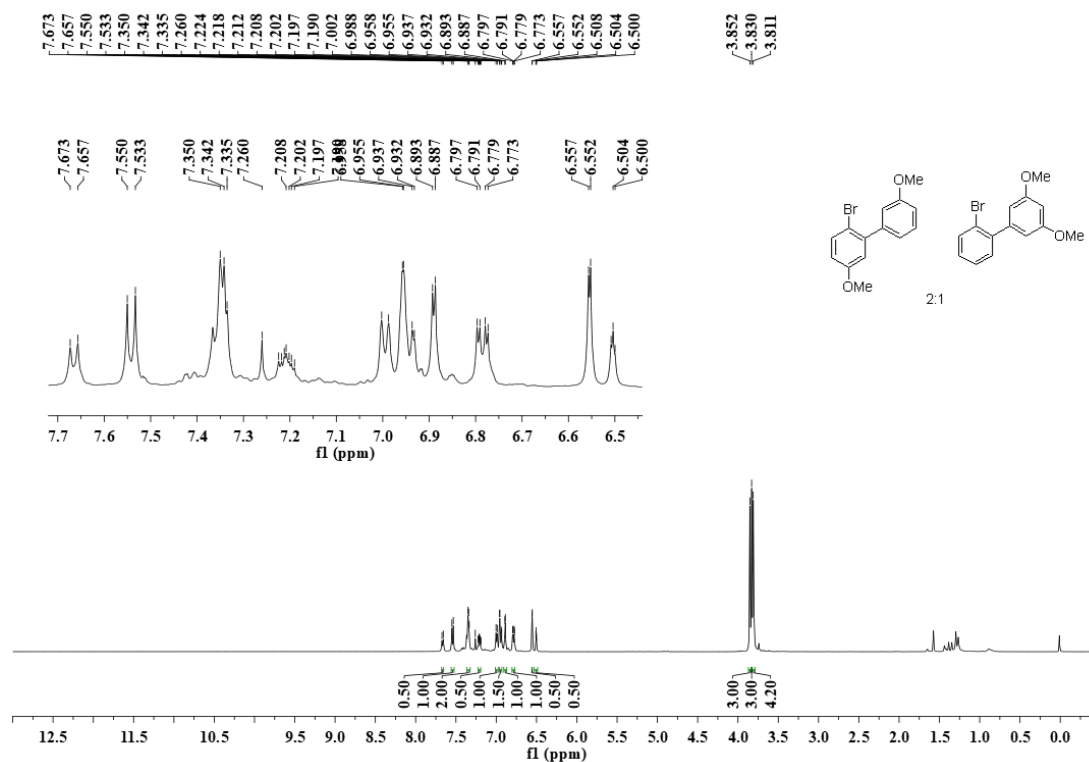
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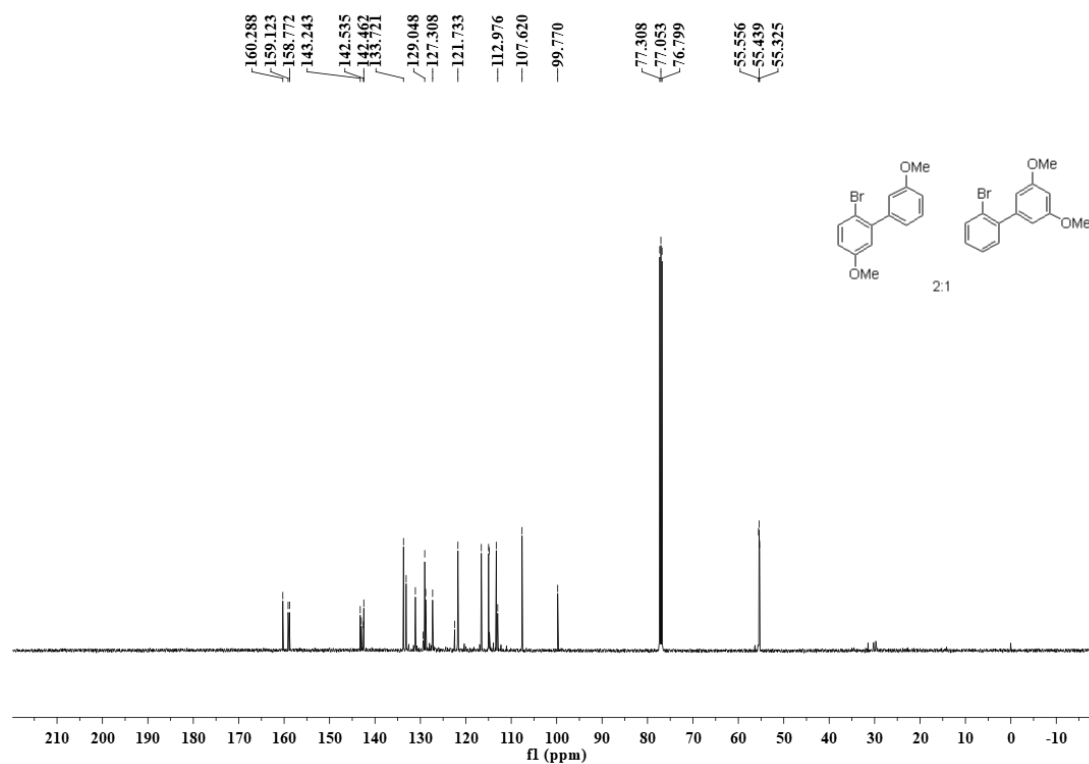
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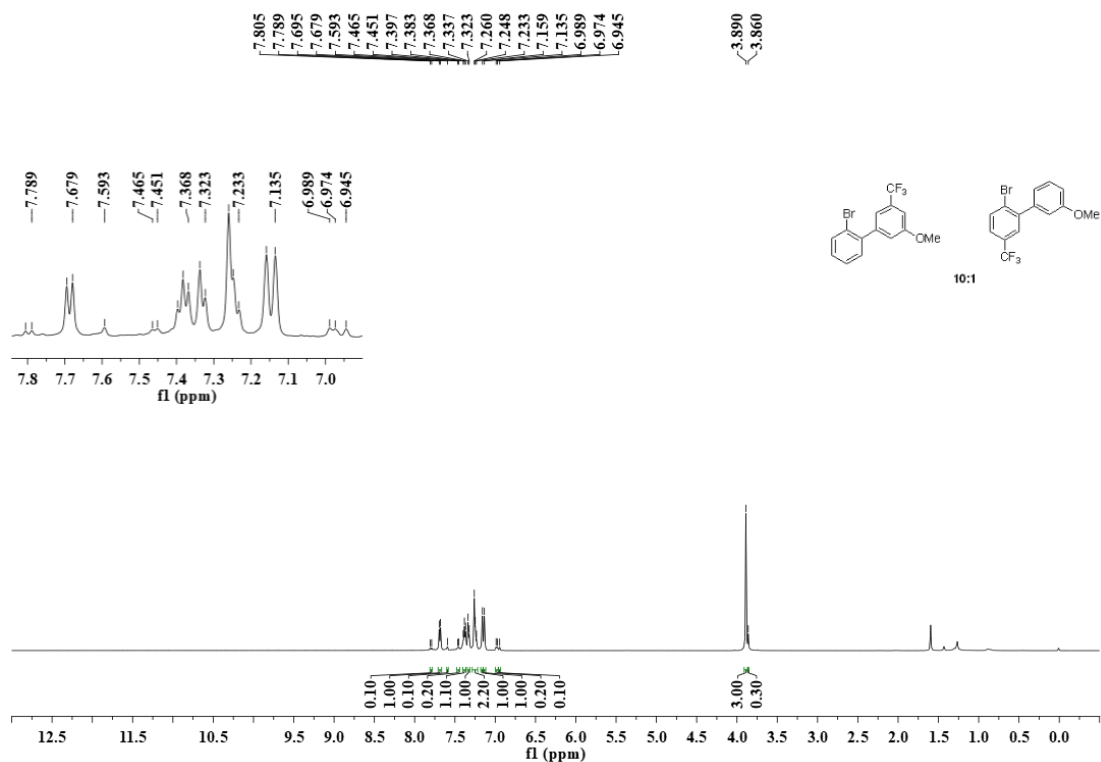
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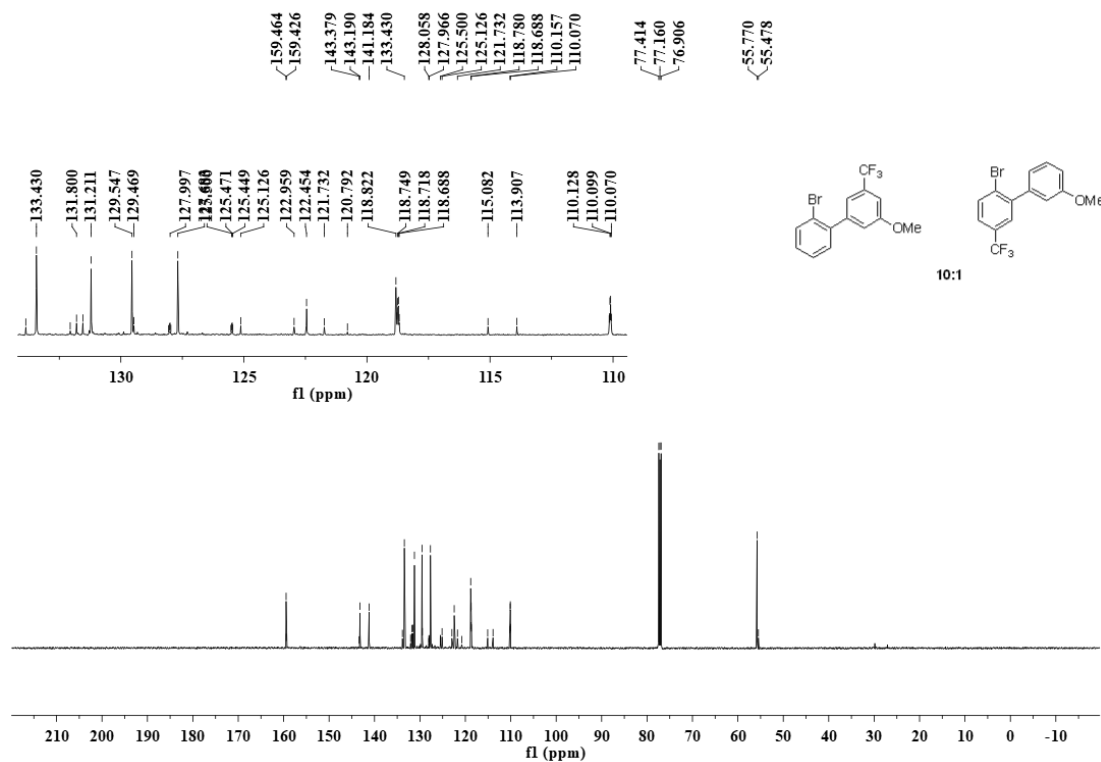
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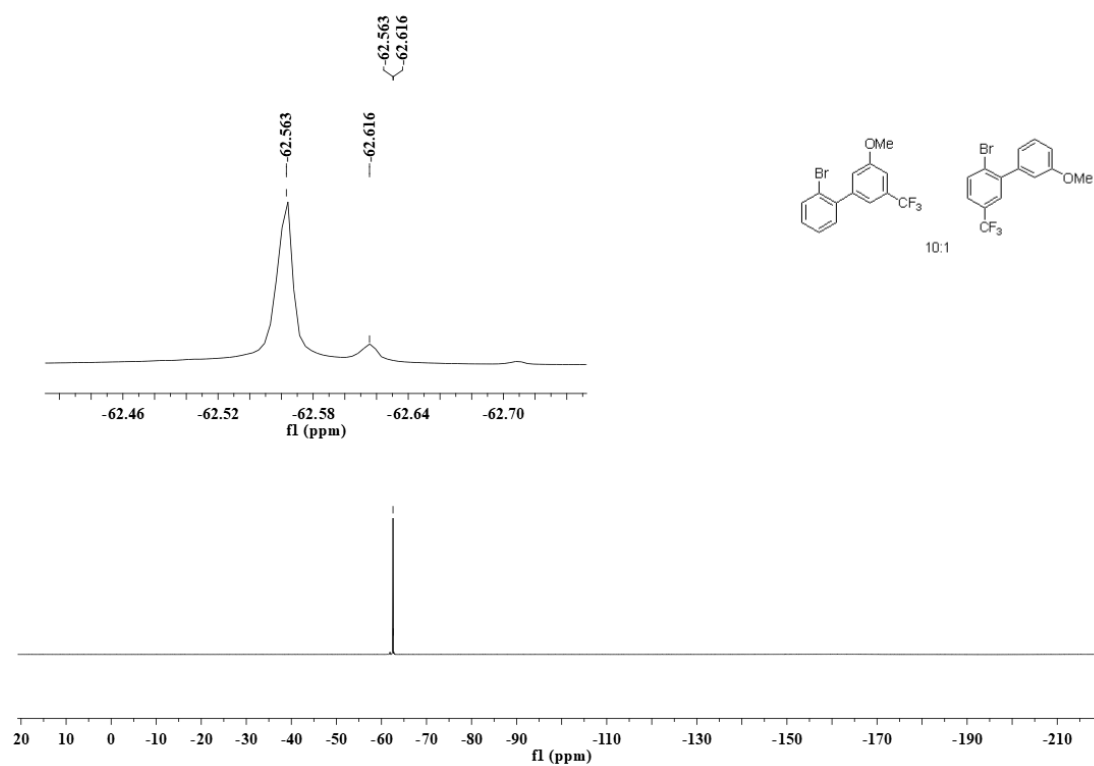
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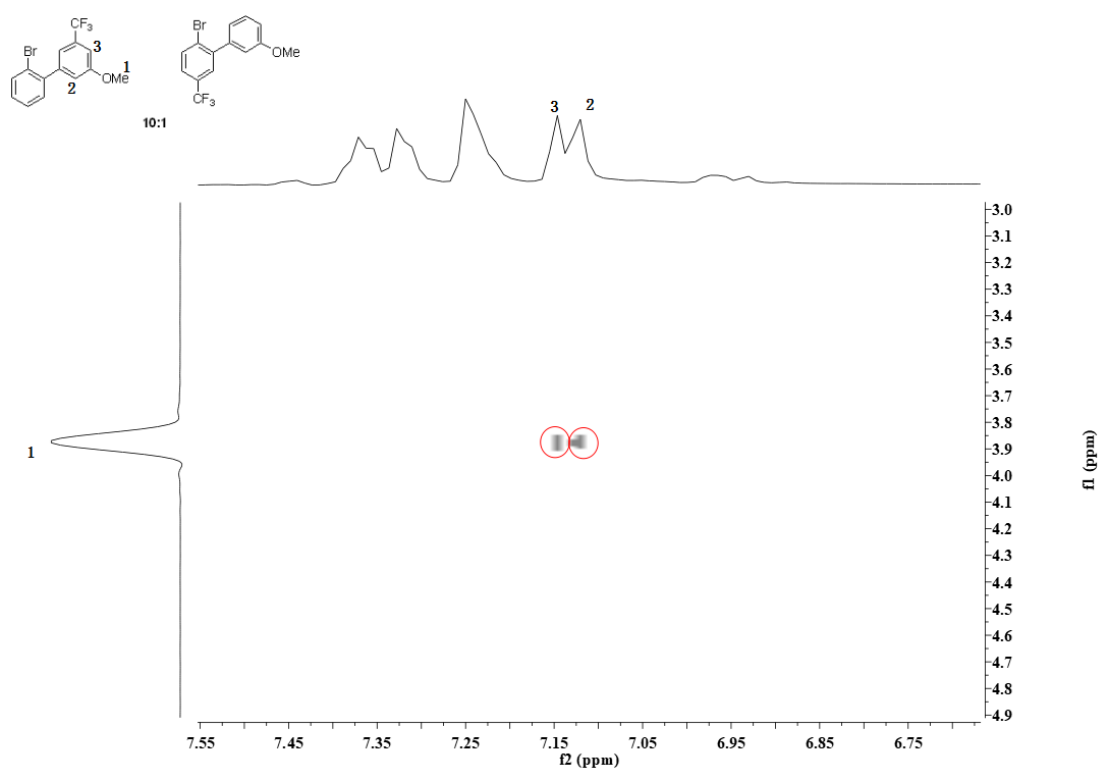
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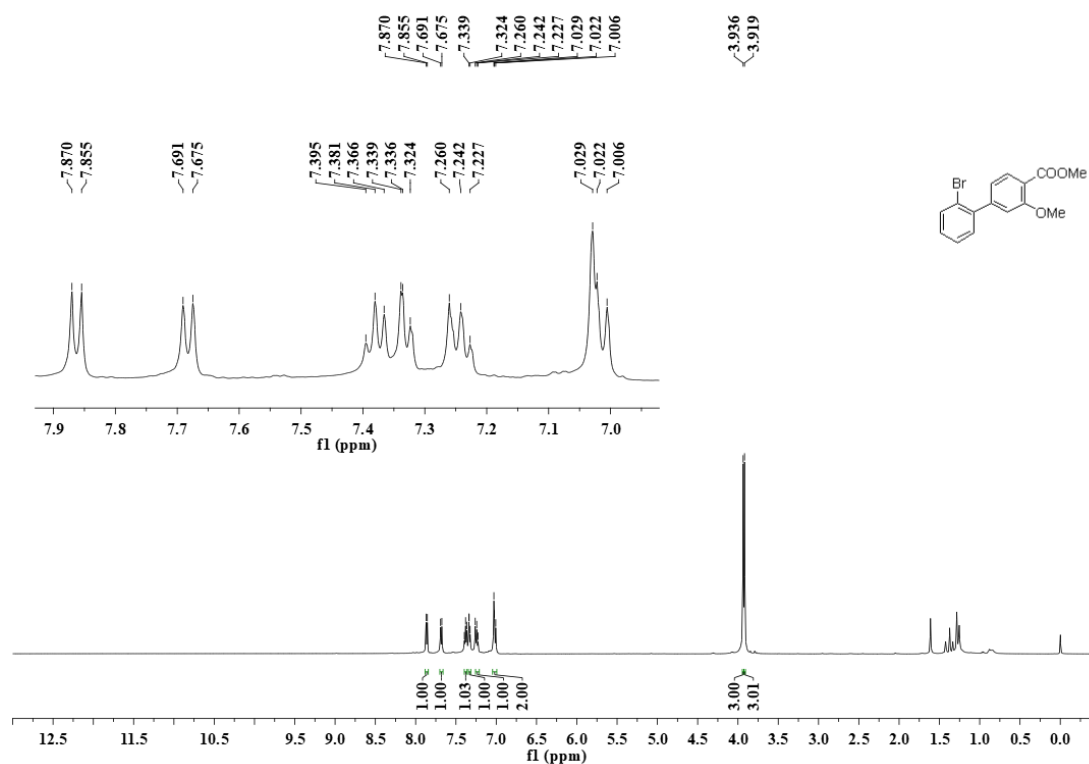
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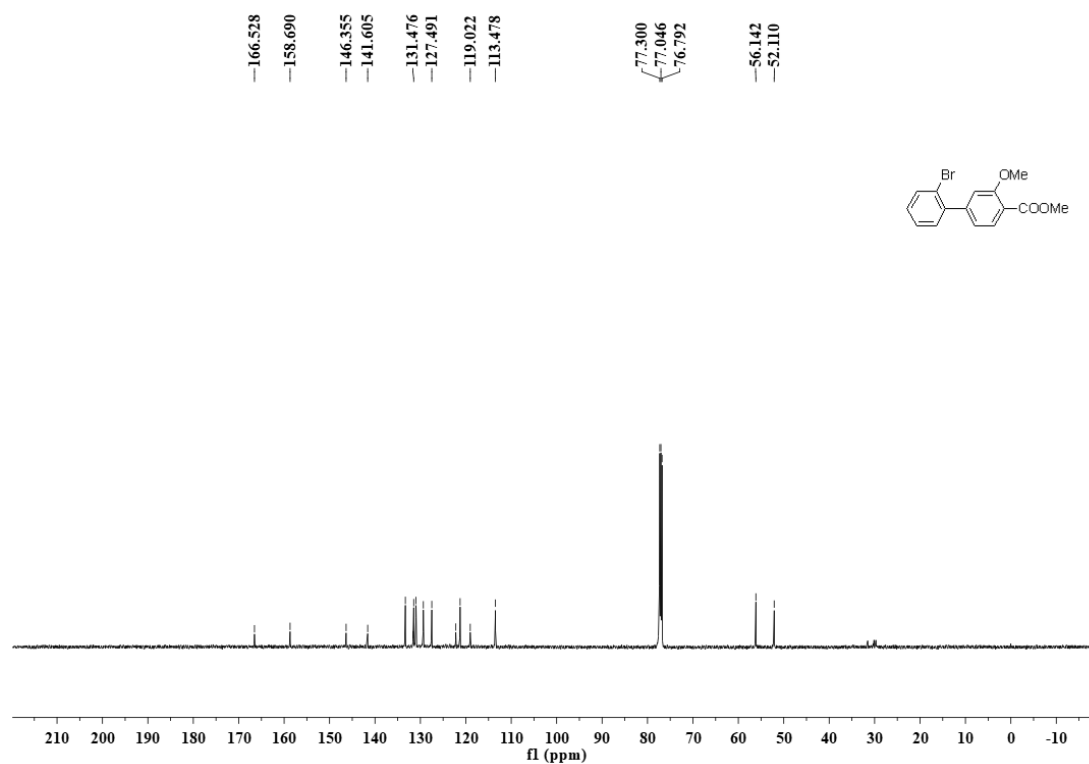
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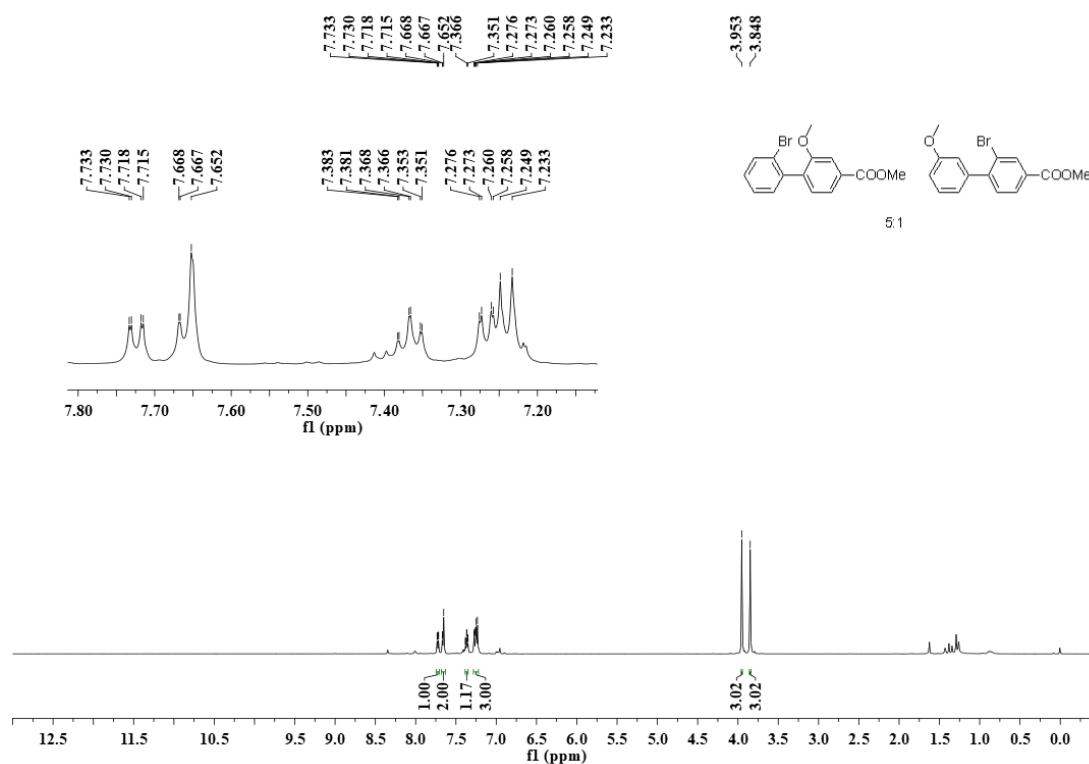
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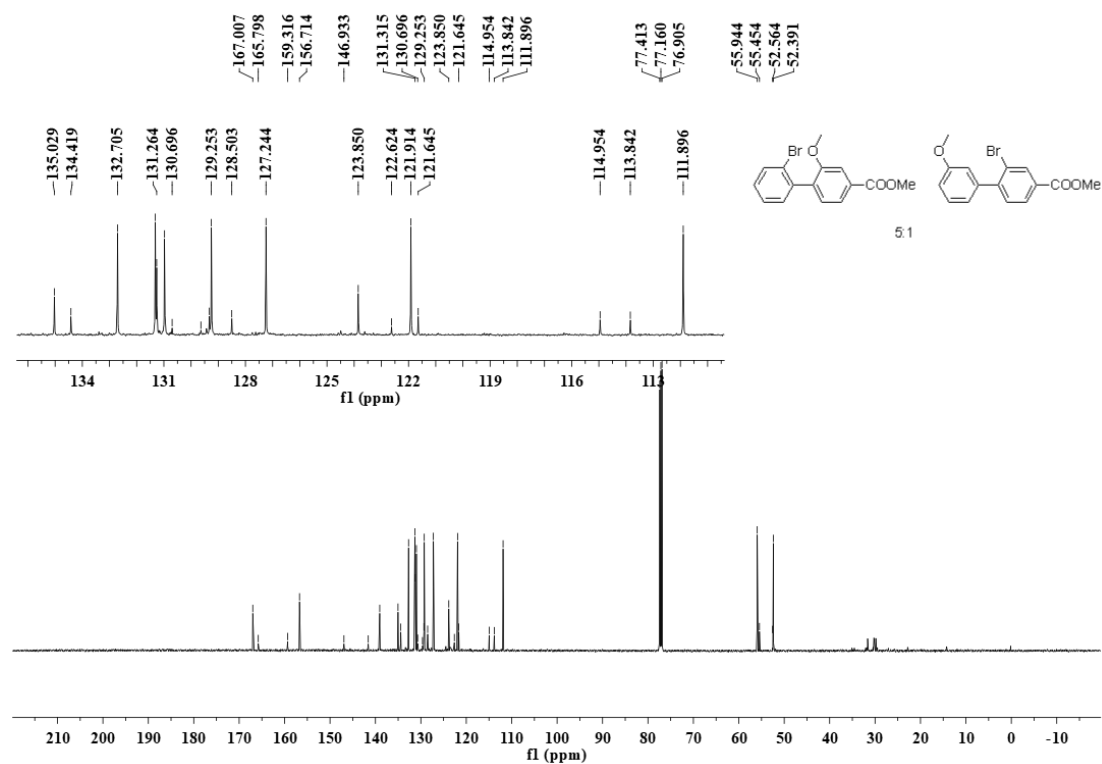
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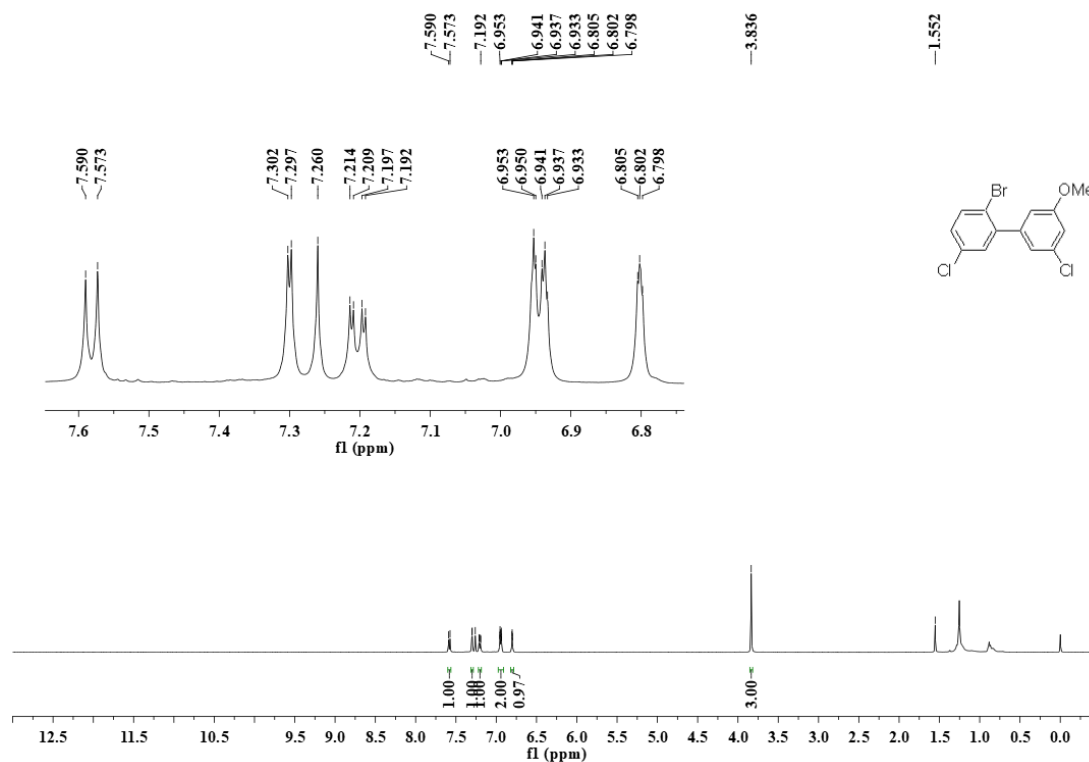
^1H NMR (500 MHz, CDCl_3) of *o*-**3e** and **3e'**



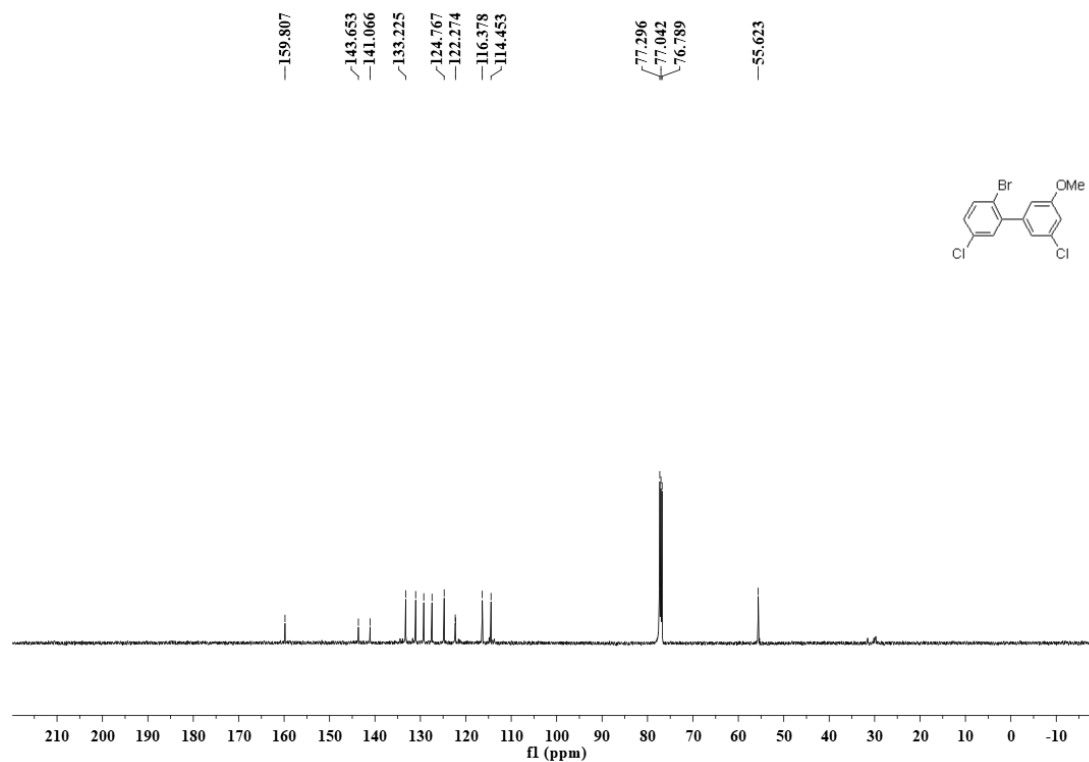
^{13}C NMR (125 MHz, CDCl_3) of *o*-**3e** and **3e'**



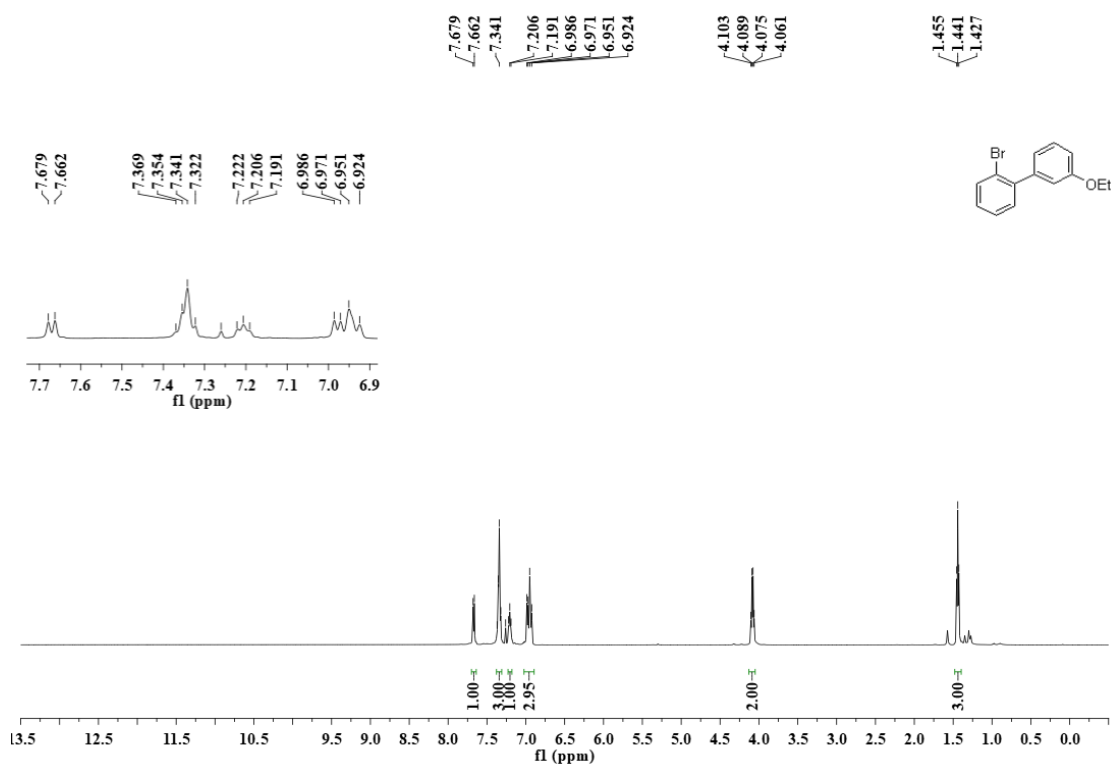
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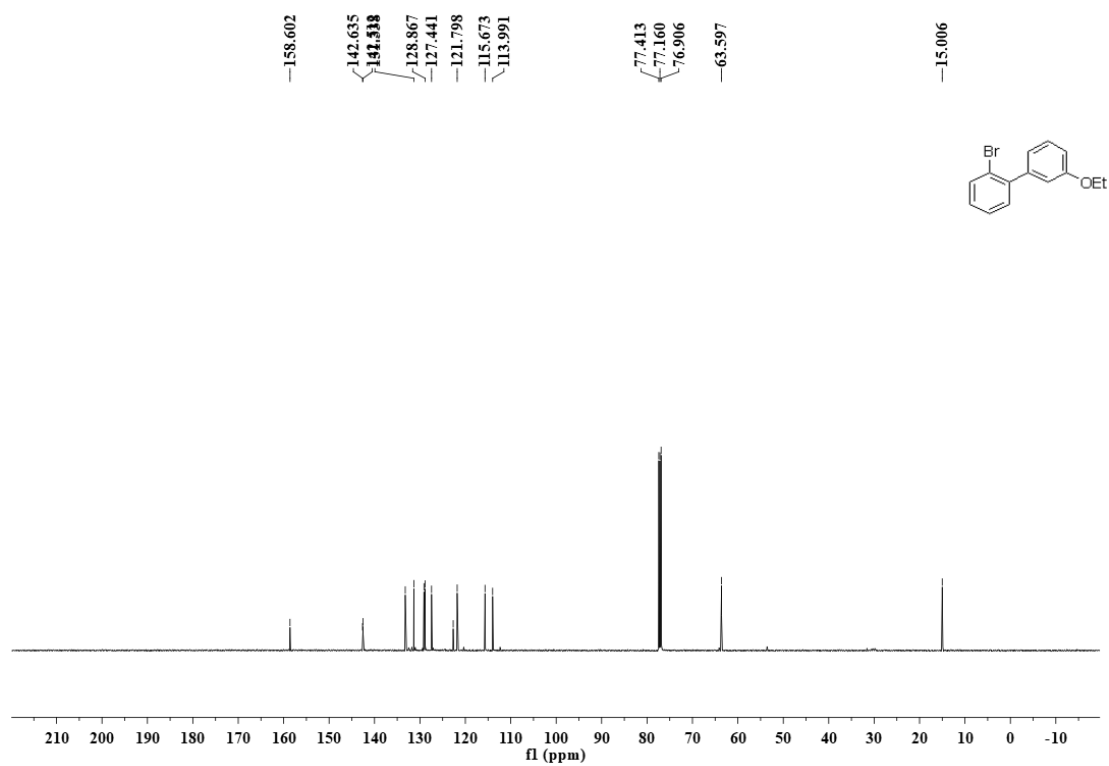
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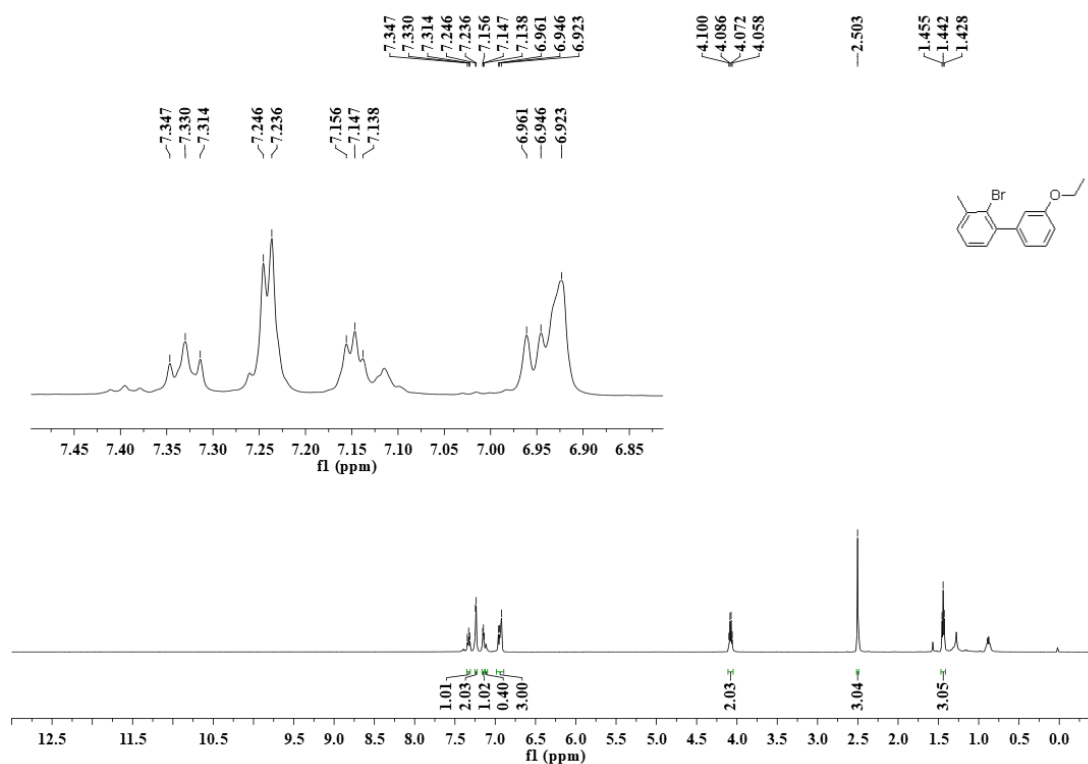
^1H NMR (500 MHz, CDCl_3) of **3g**



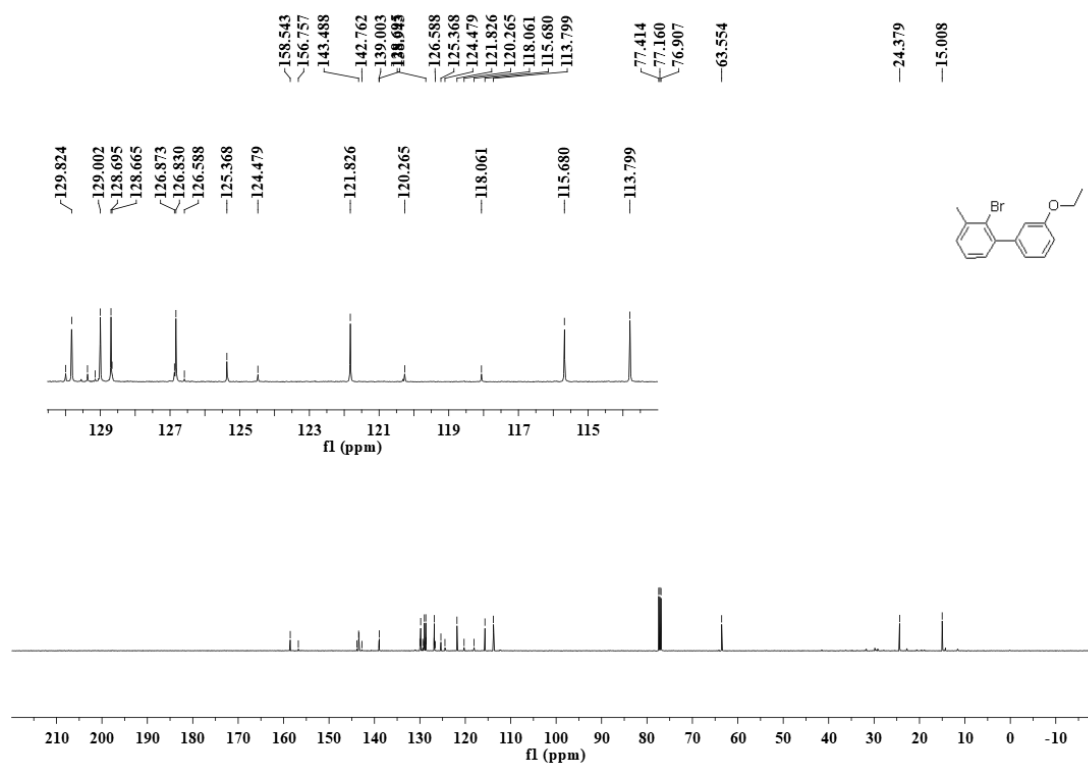
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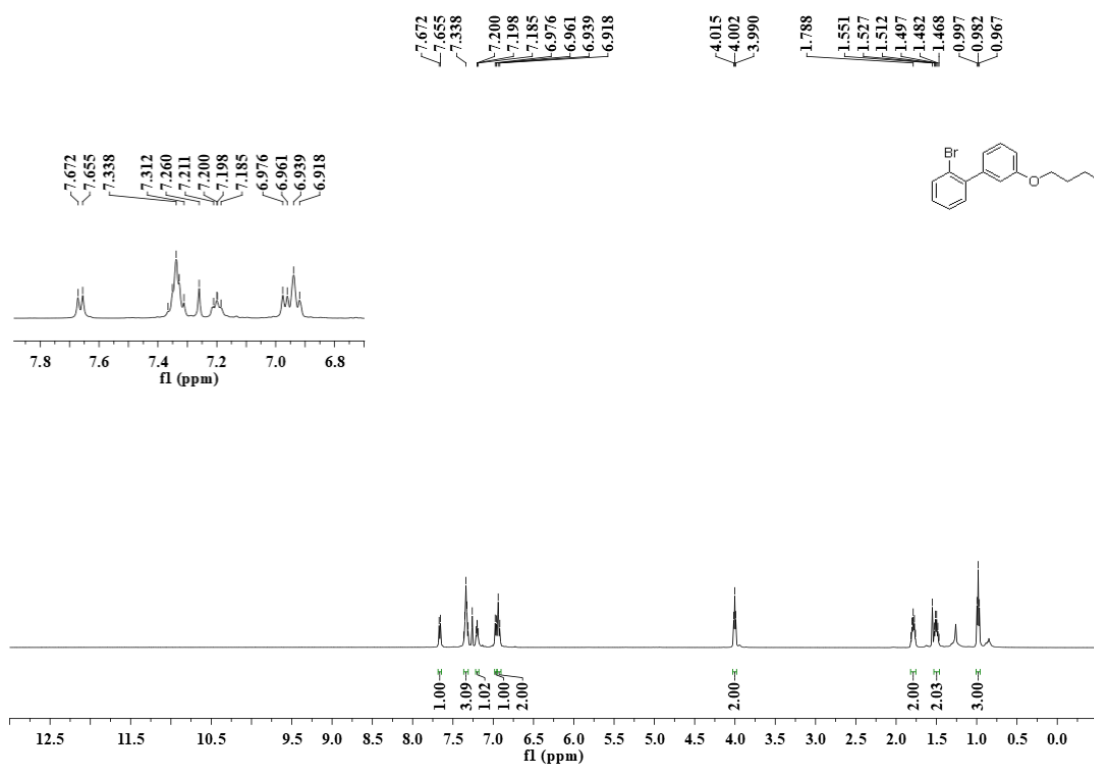
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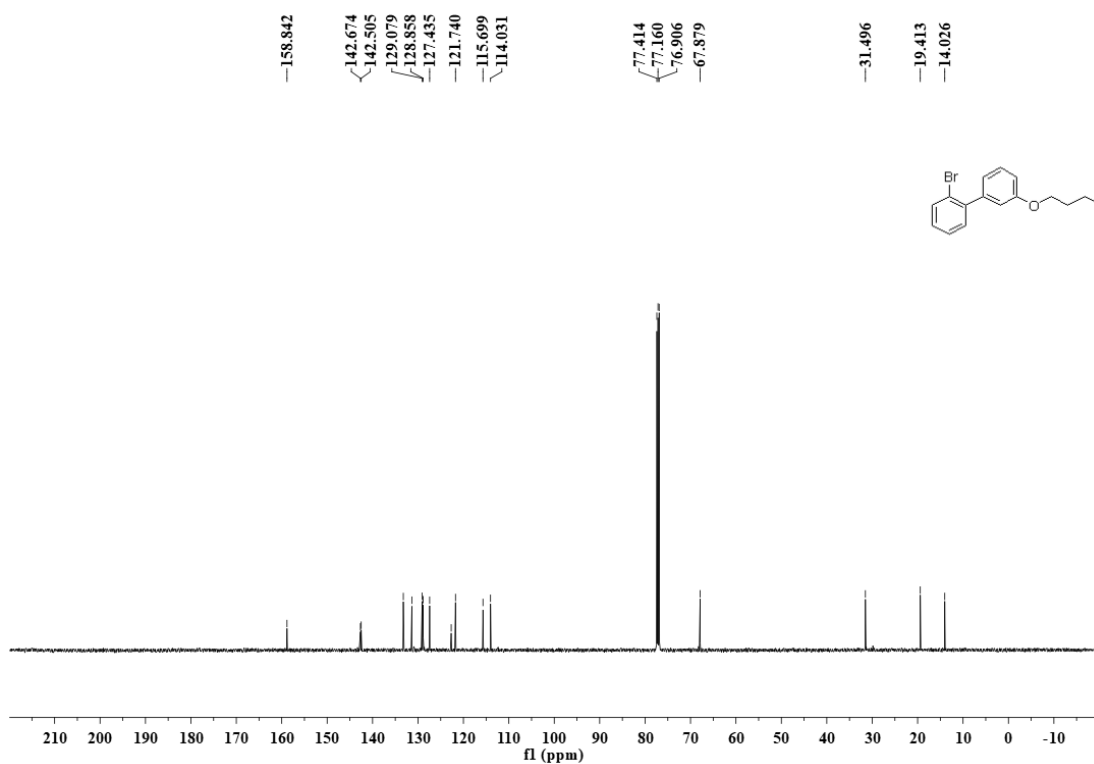
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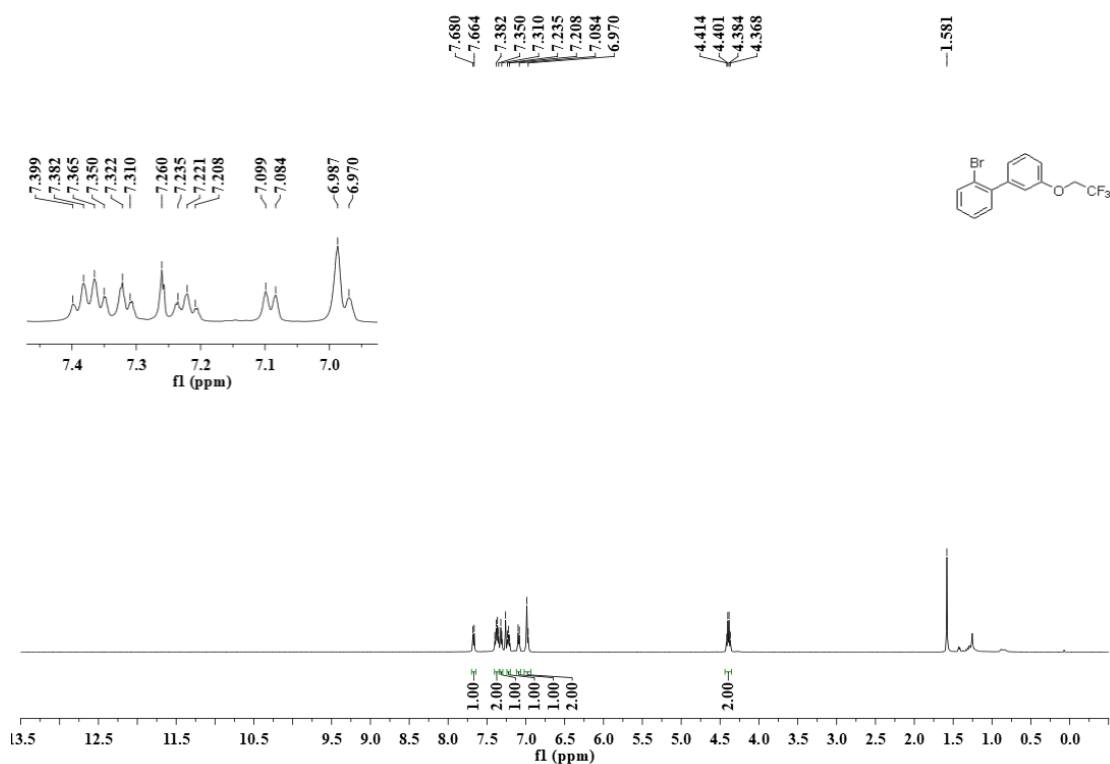
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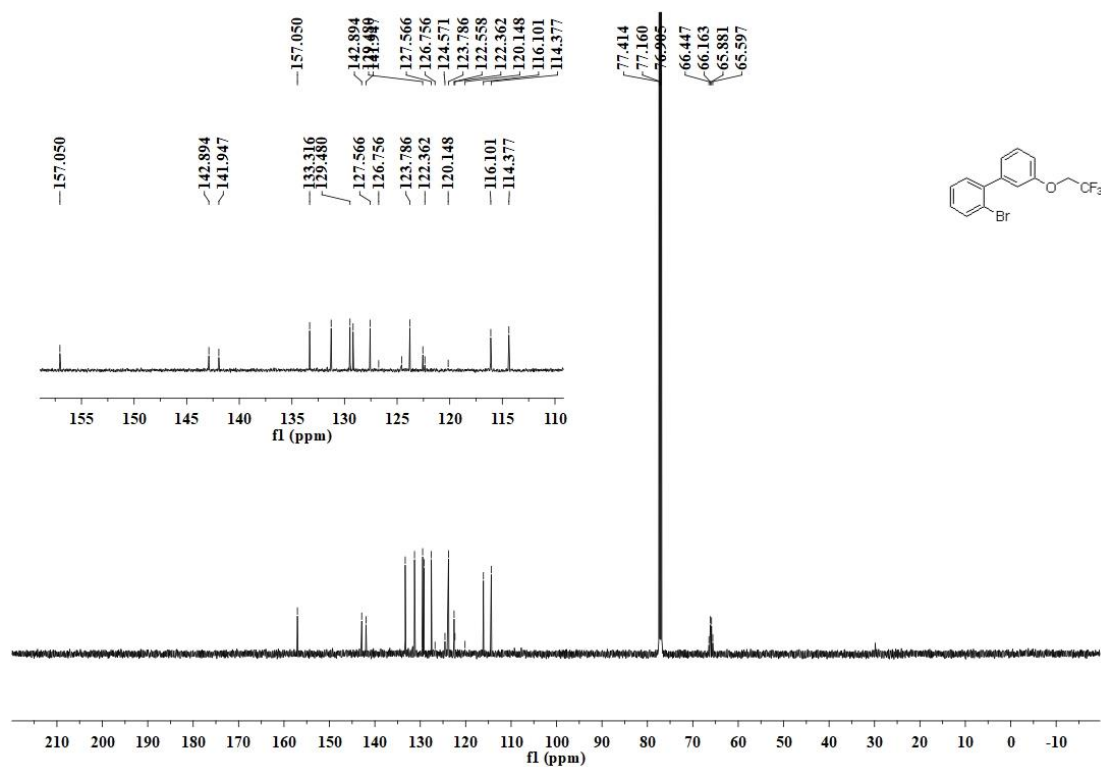
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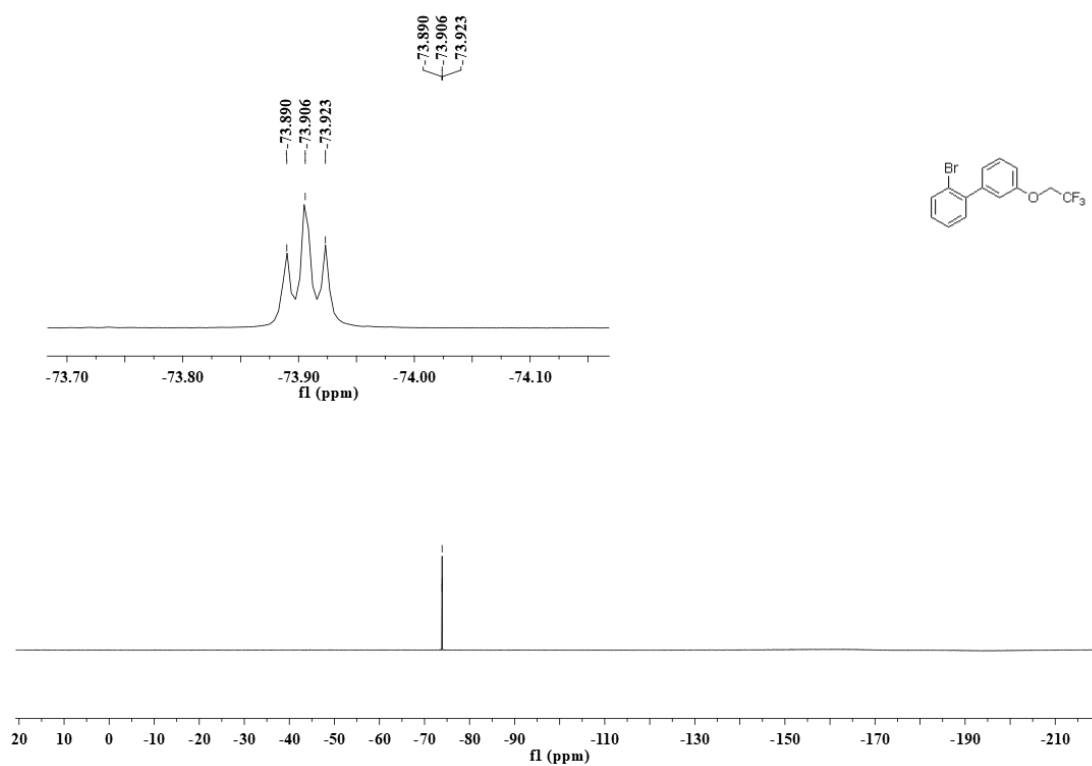
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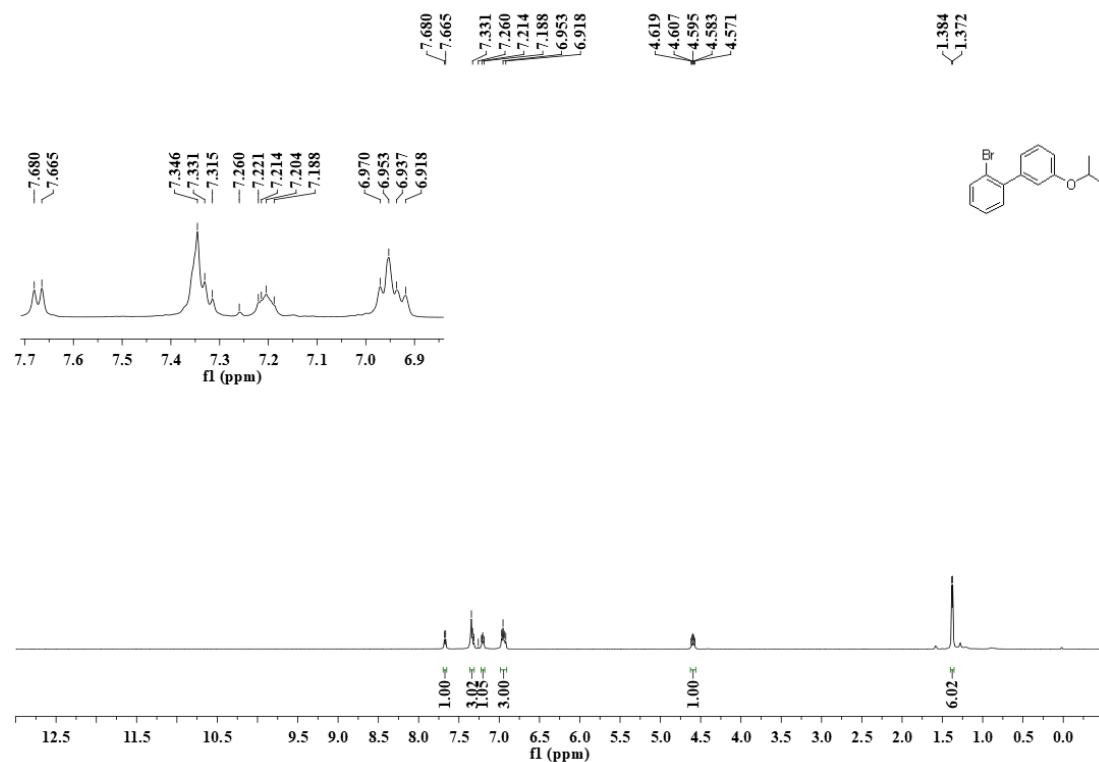
^{13}C NMR (125 MHz, CDCl_3) of **3j**



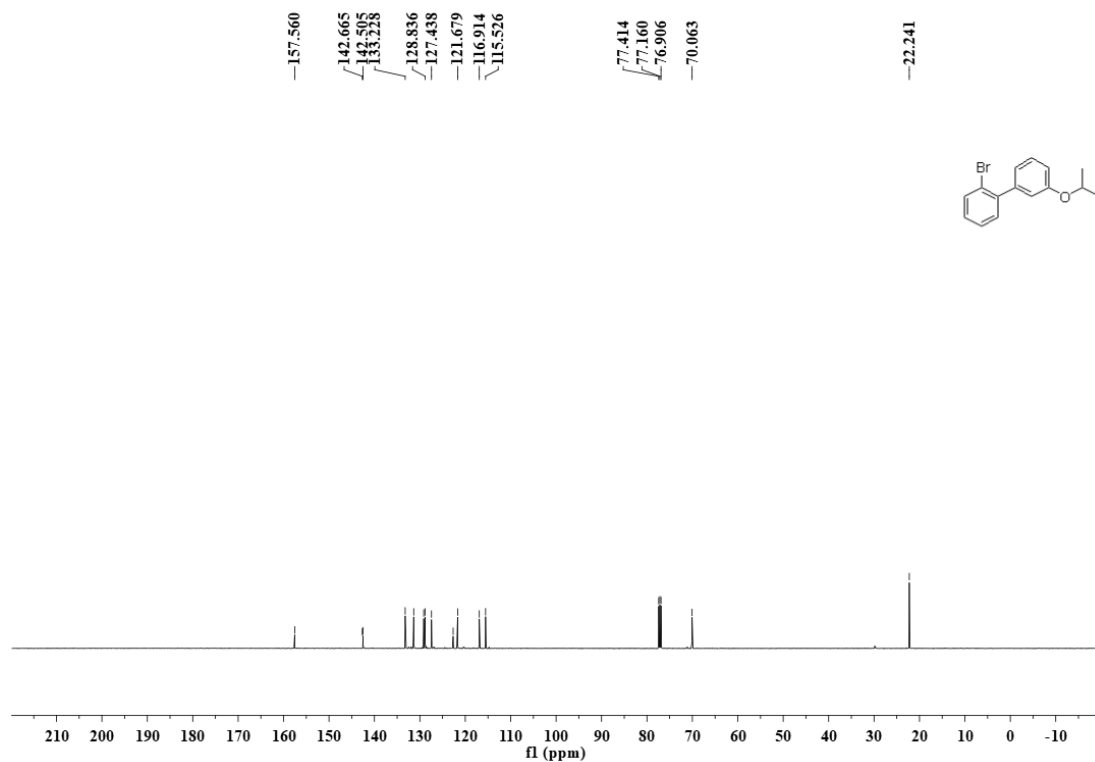
^{19}F NMR (471 MHz, CDCl_3) of **3j**



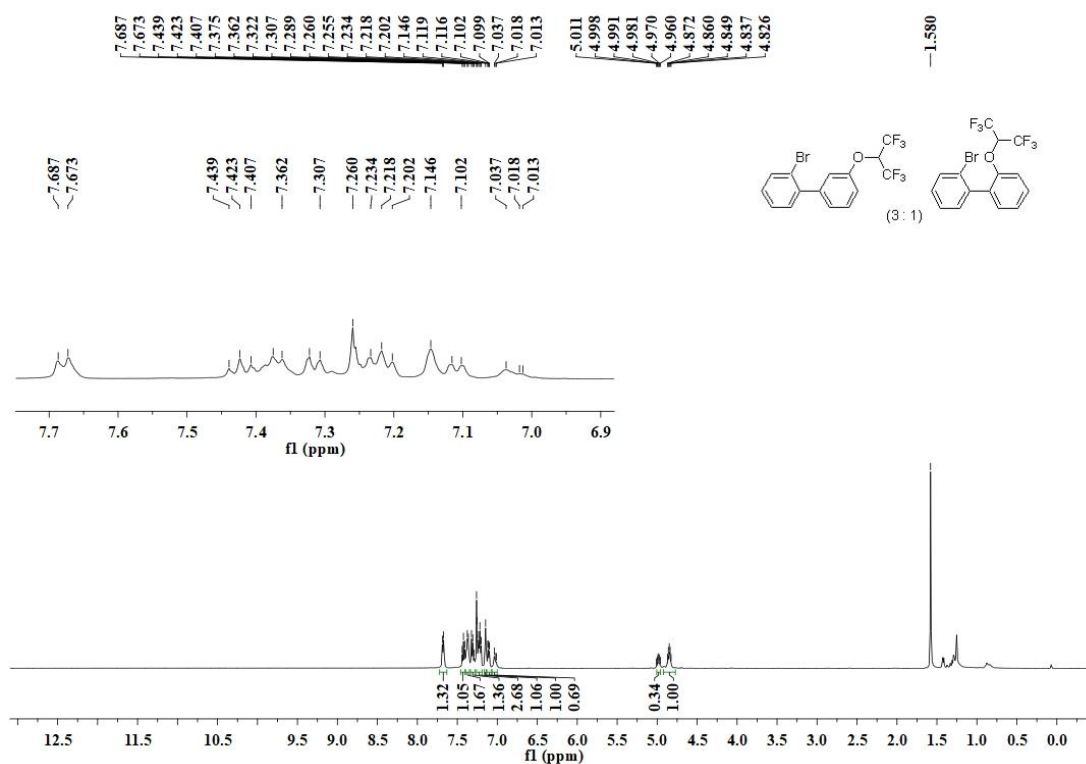
^1H NMR (500 MHz, CDCl_3) of **3k**



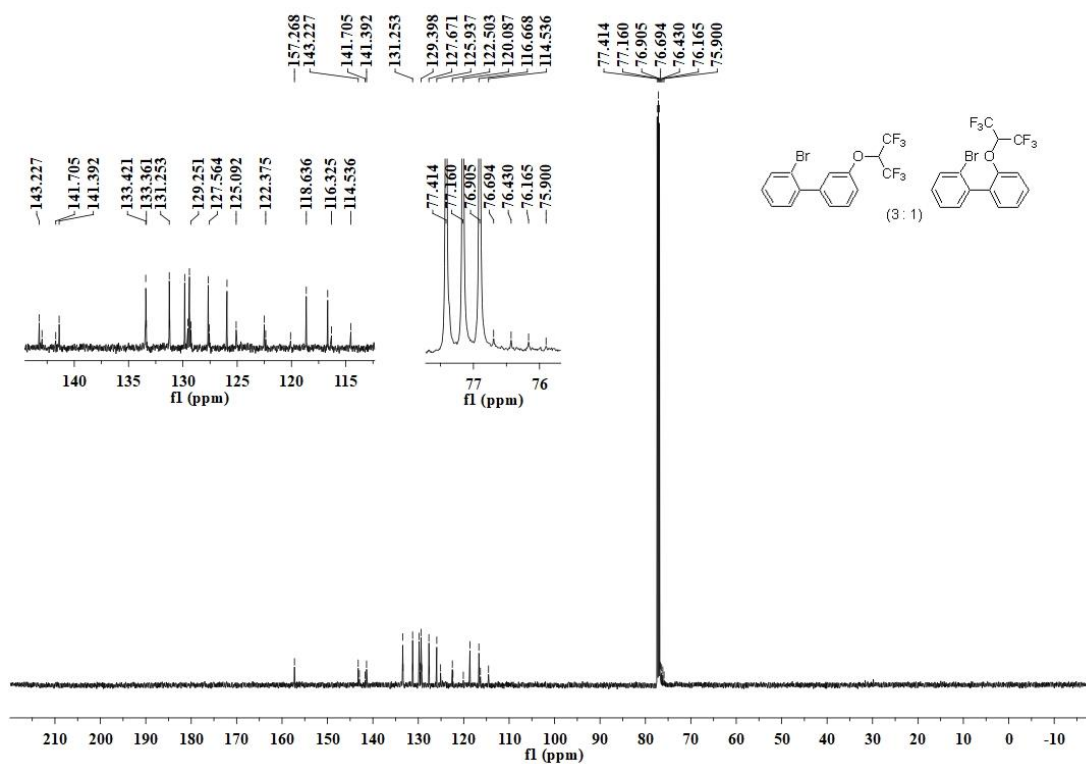
^{13}C NMR (125 MHz, CDCl_3) of **3k**



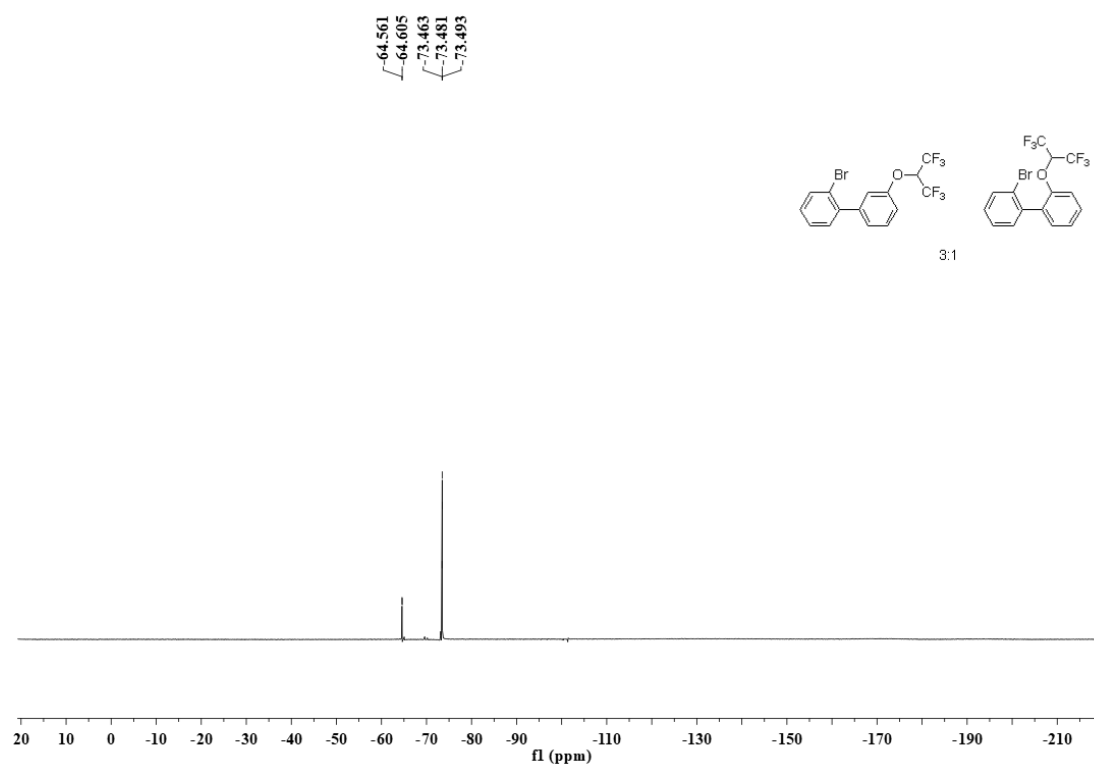
^1H NMR (500 MHz, CDCl_3) of **3I**



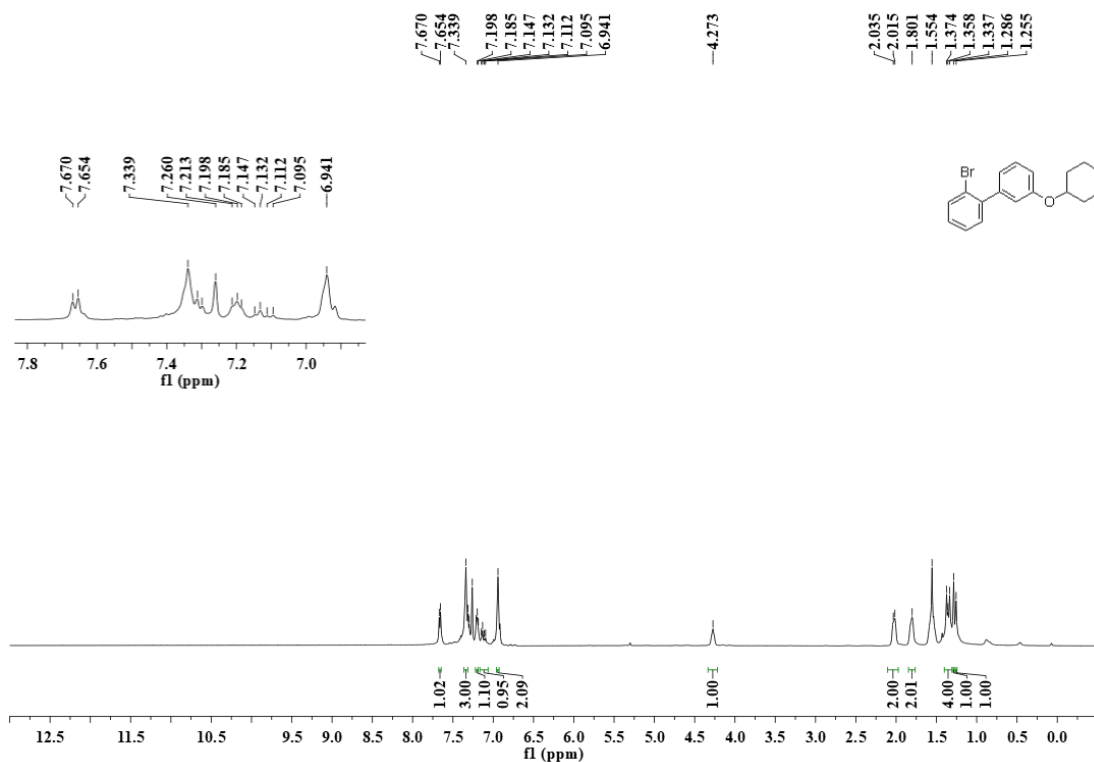
^{13}C NMR (125 MHz, CDCl_3) of **3I**



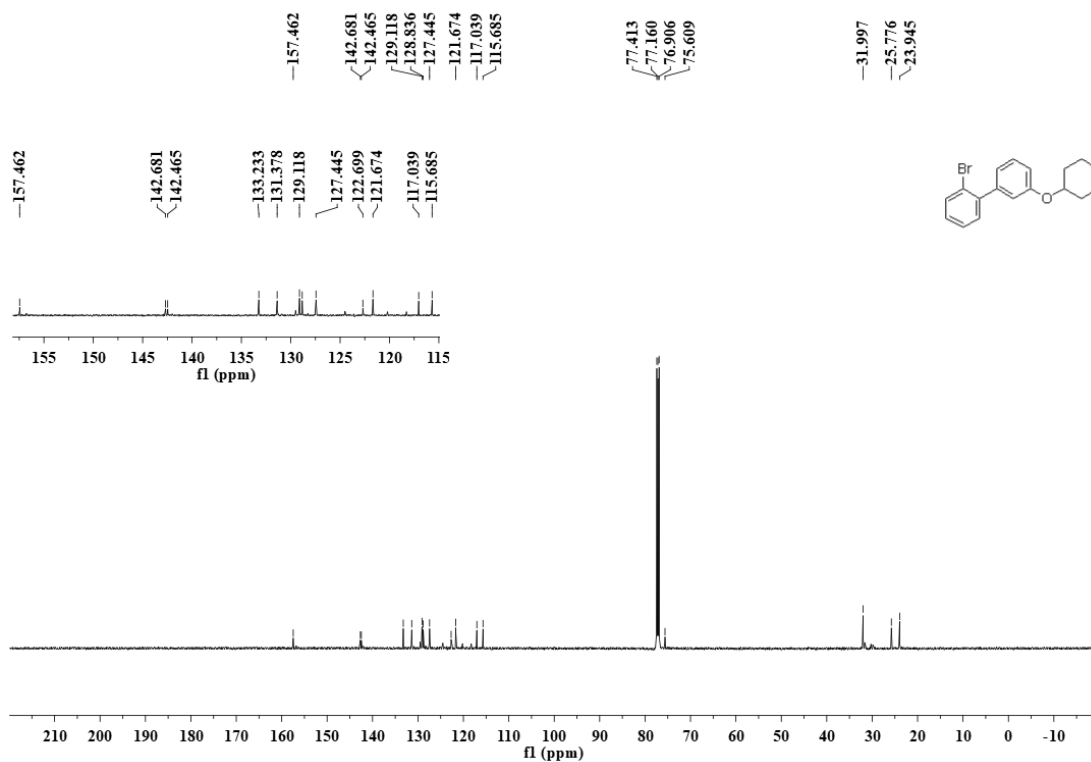
^{19}F NMR (471 MHz, CDCl_3) of **3I**



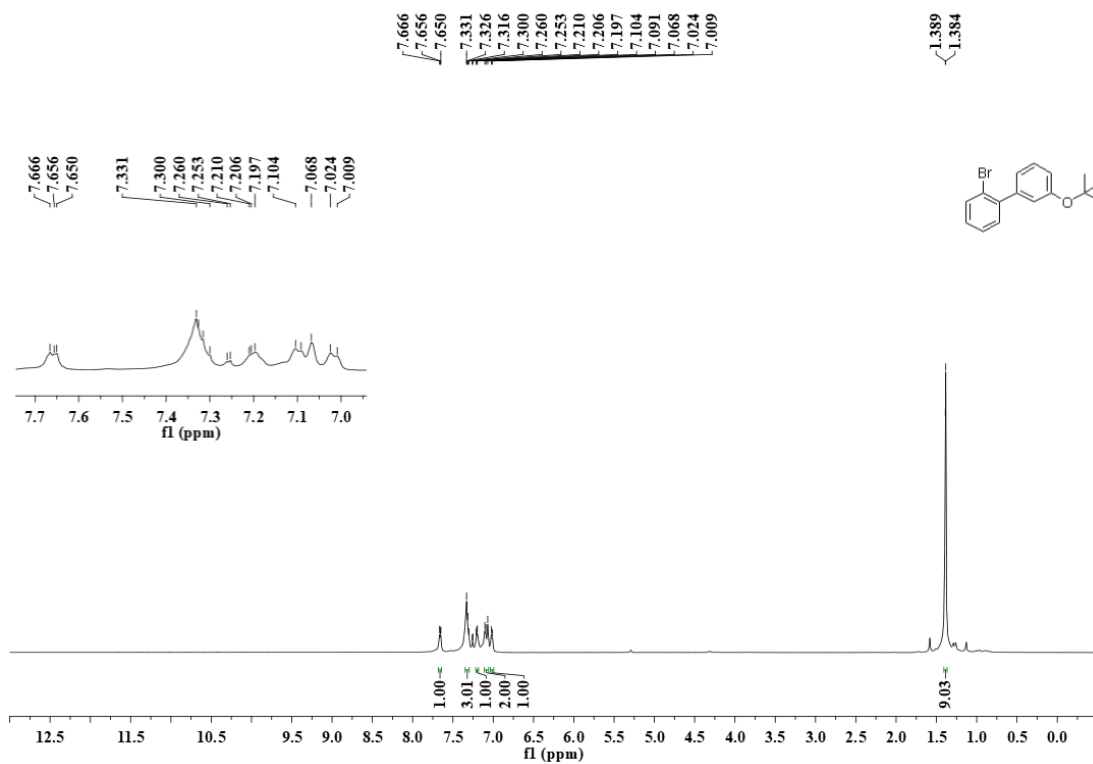
^1H NMR (500 MHz, CDCl_3) of **3m**



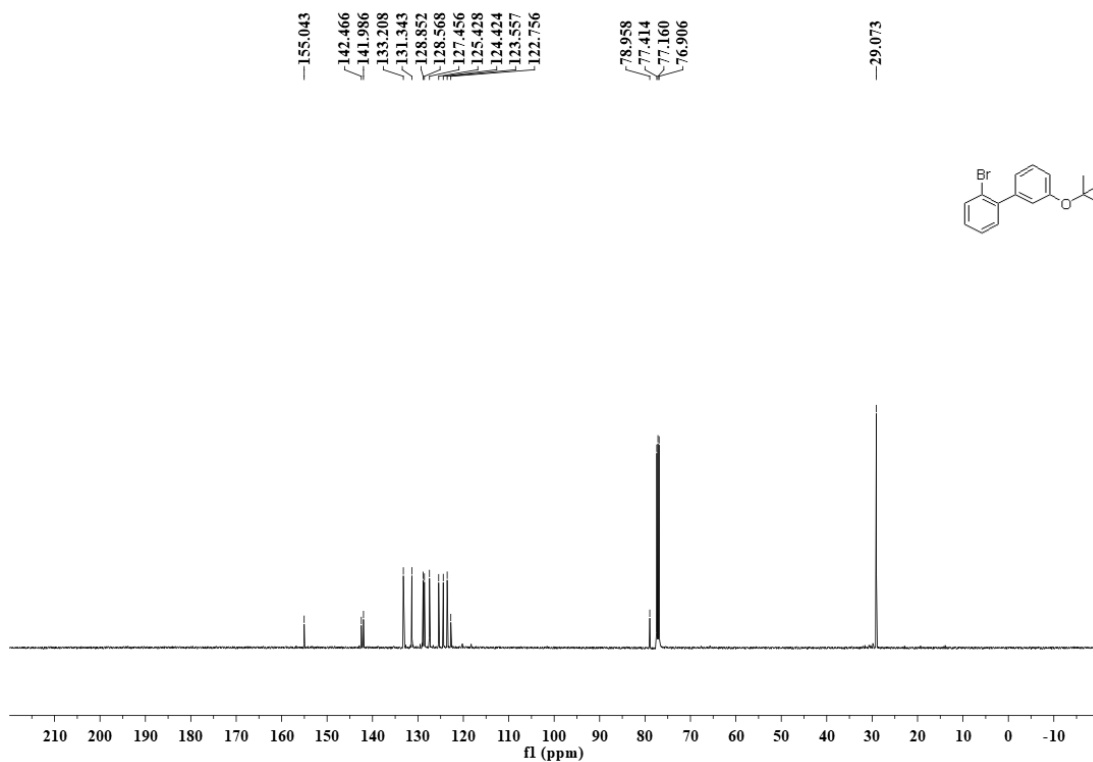
^{13}C NMR (125 MHz, CDCl_3) of **3m**



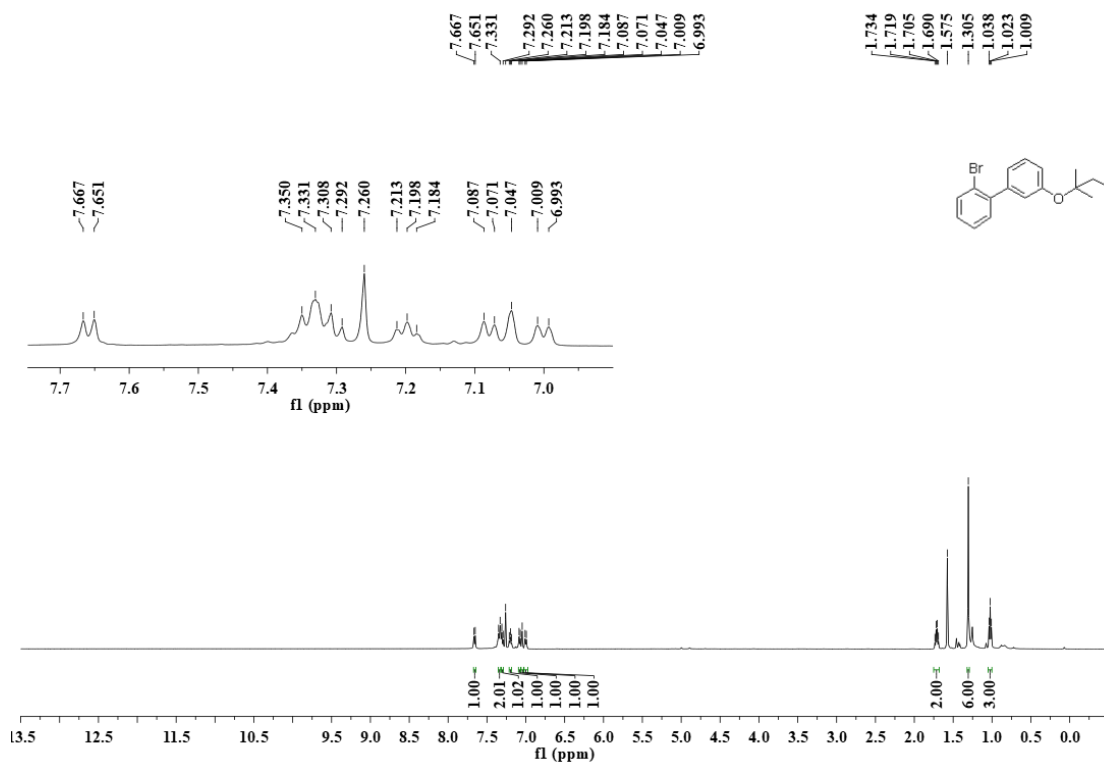
^1H NMR (500 MHz, CDCl_3) of **3n**



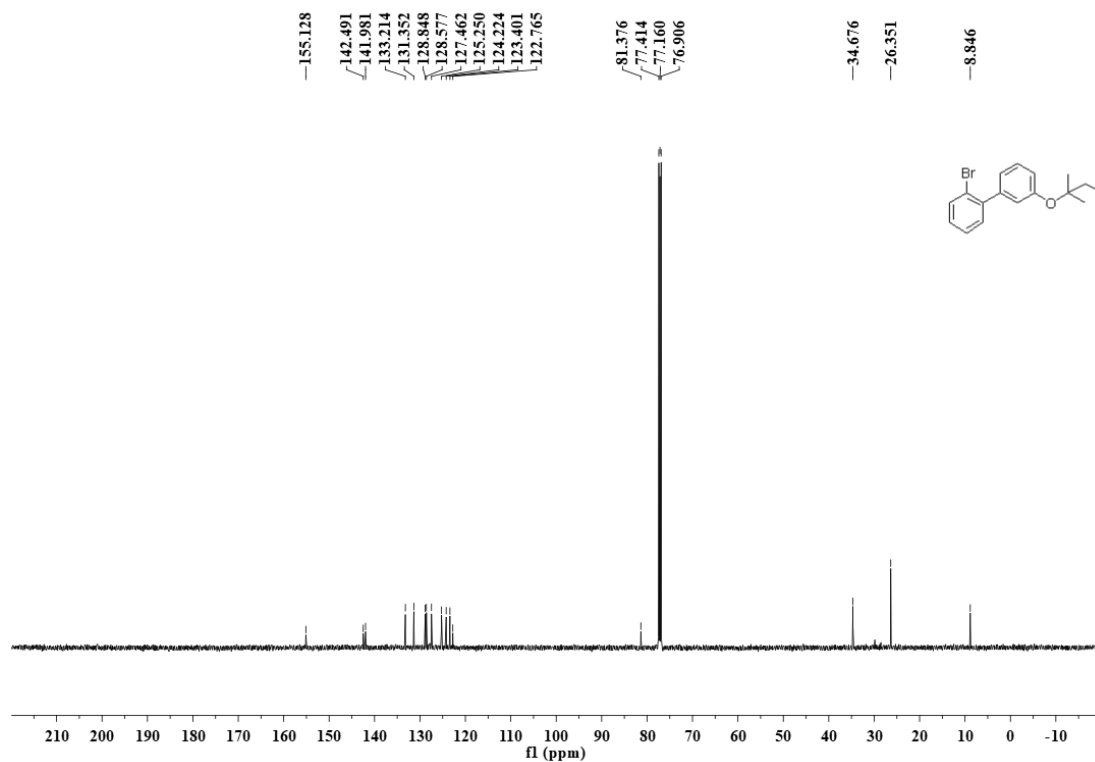
^{13}C NMR (125 MHz, CDCl_3) of **3n**



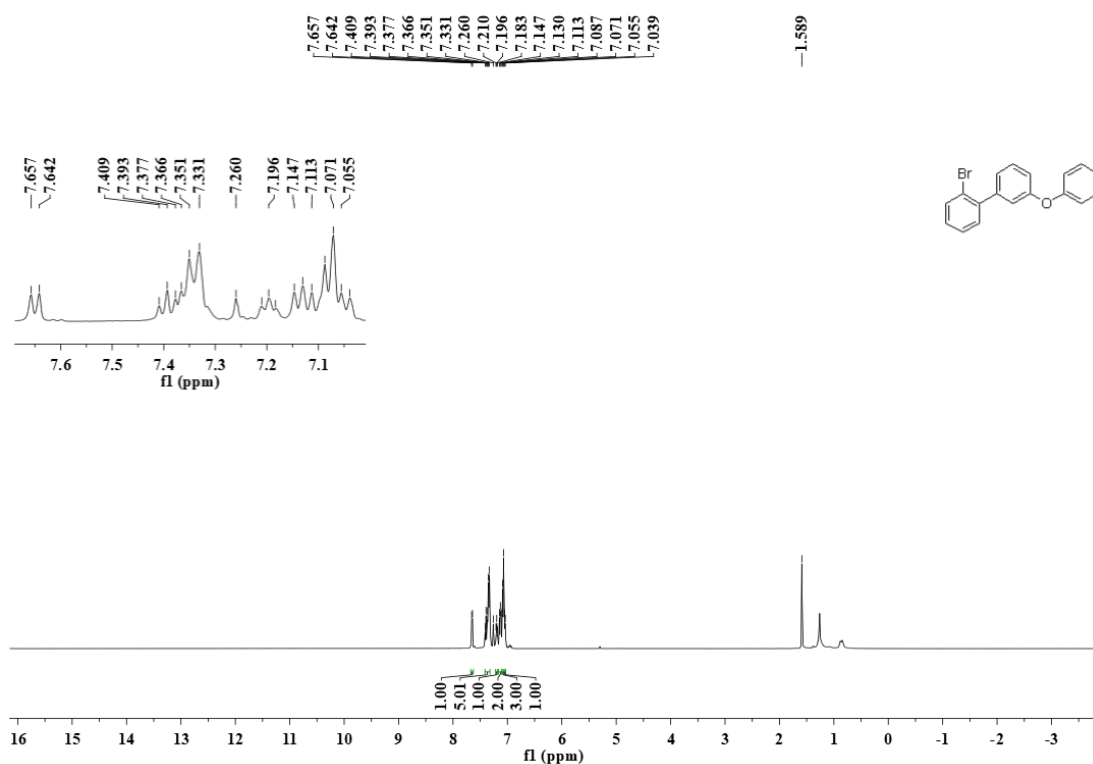
^1H NMR (500 MHz, CDCl_3) of **3o**



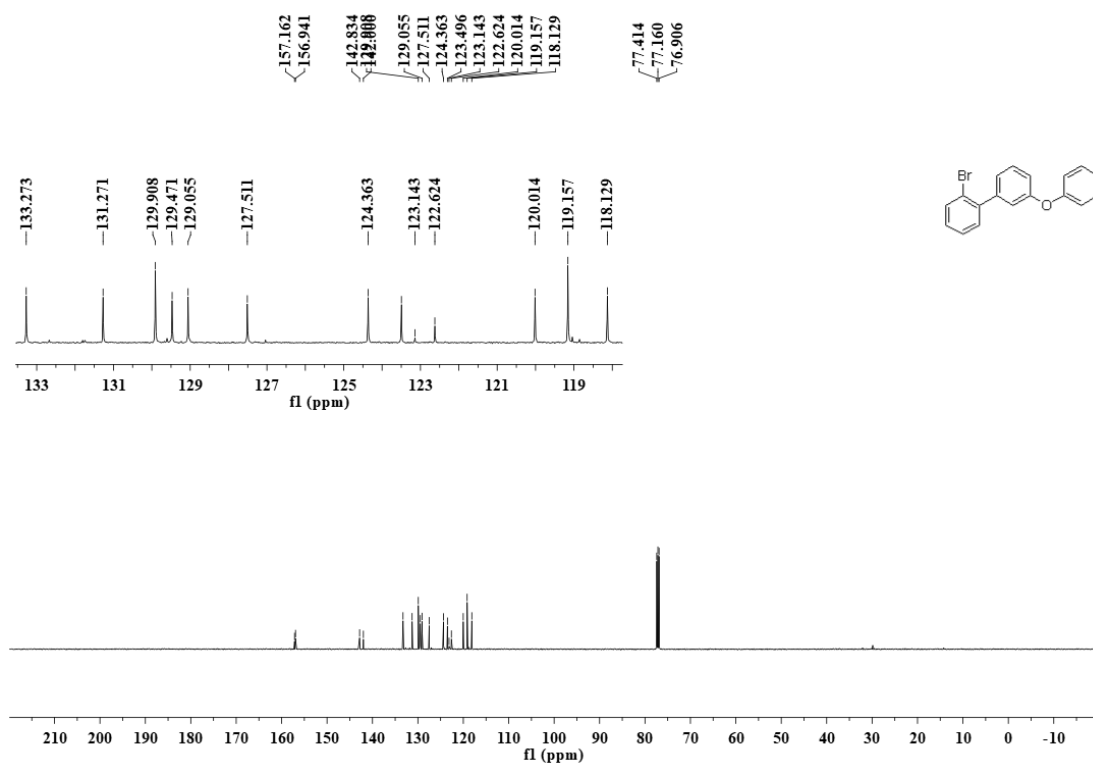
^{13}C NMR (125 MHz, CDCl_3) of **3o**



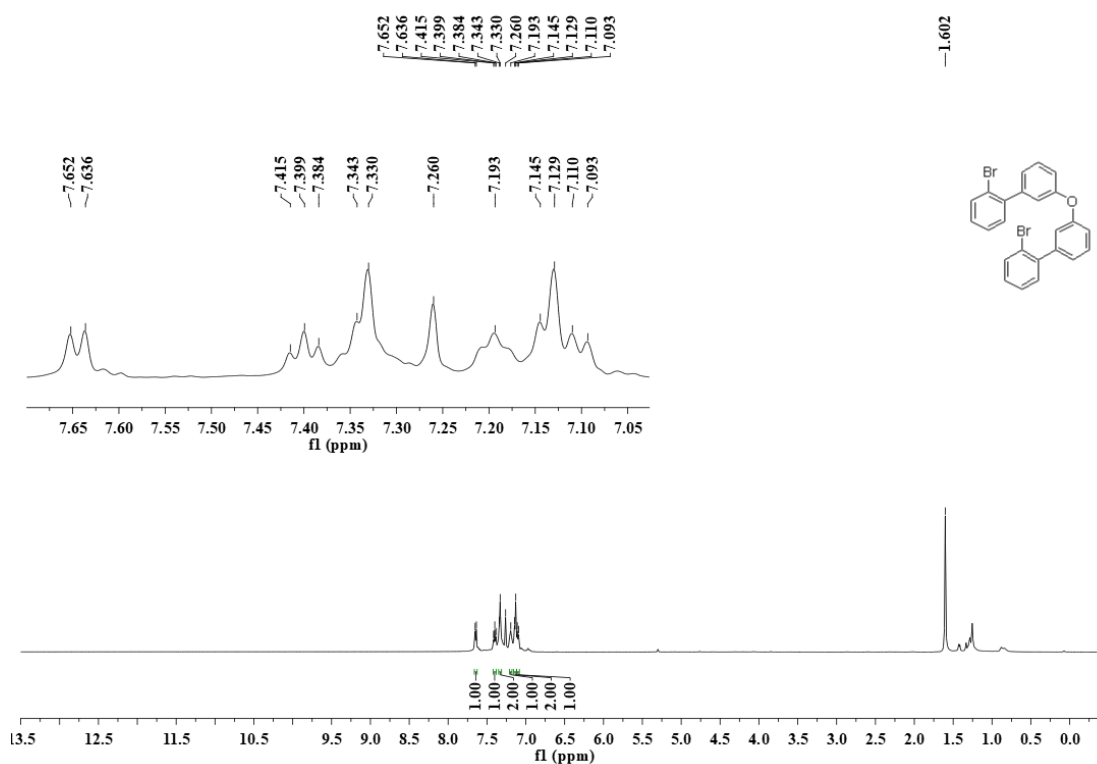
^1H NMR (500 MHz, CDCl_3) of **3p**



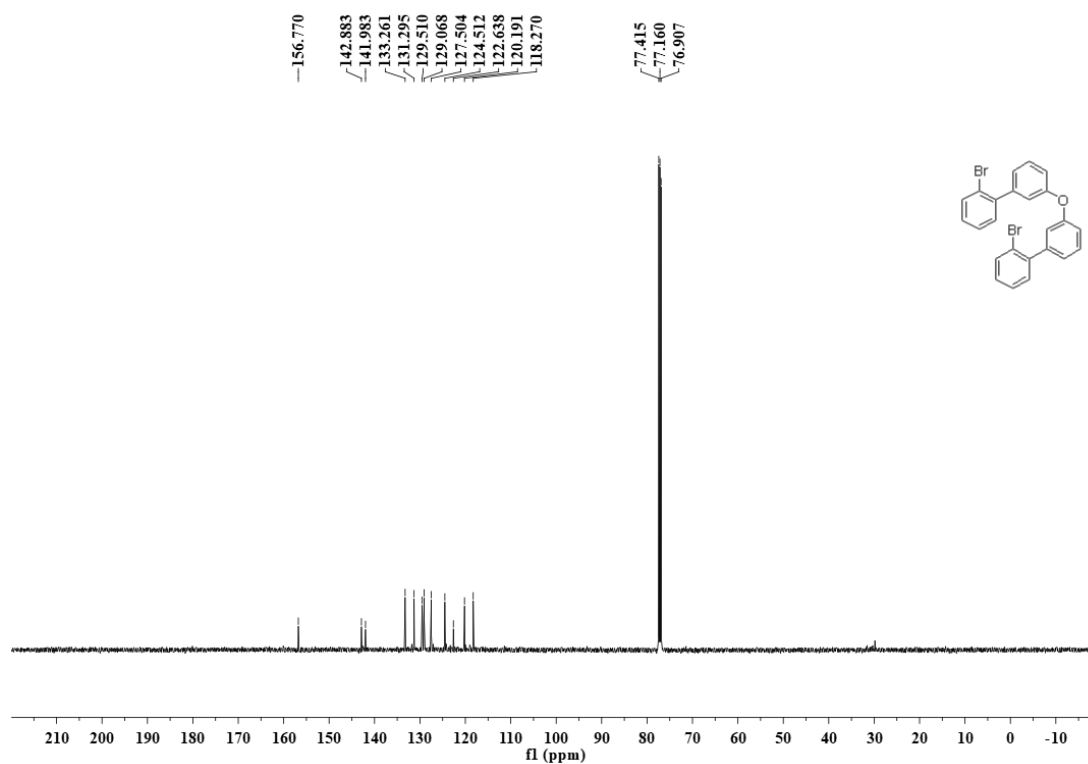
^{13}C NMR (125 MHz, CDCl_3) of **3p**



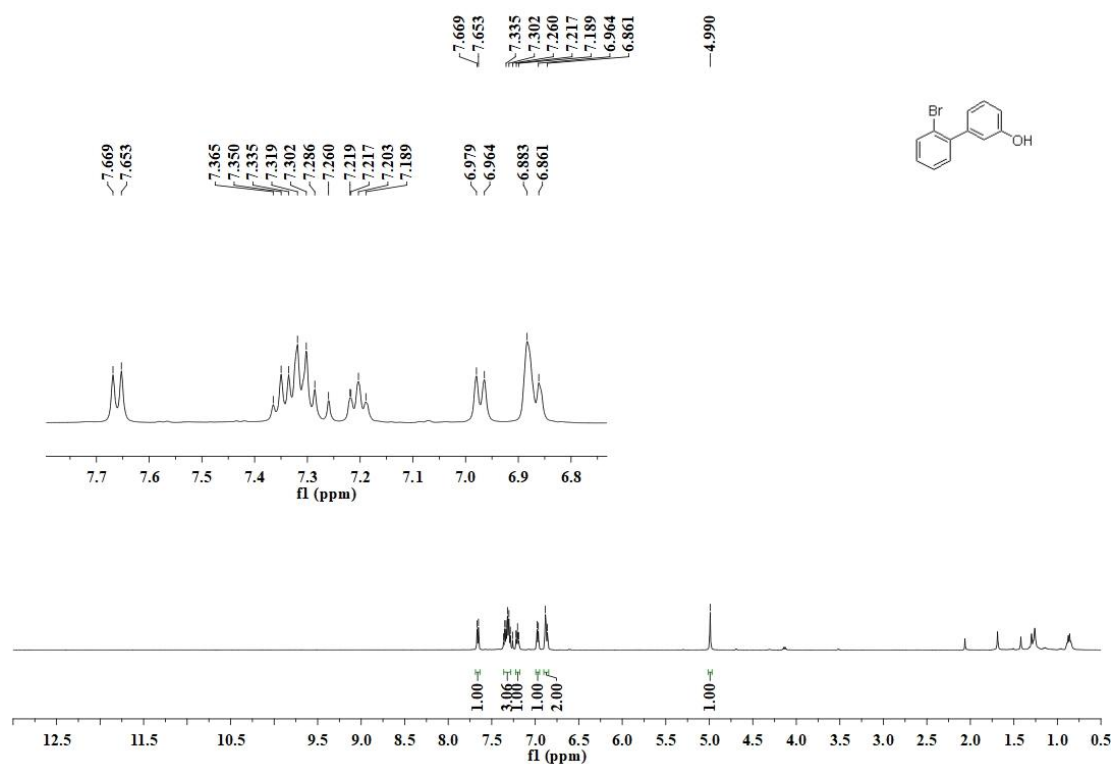
^1H NMR (500 MHz, CDCl_3) of **di-3q**



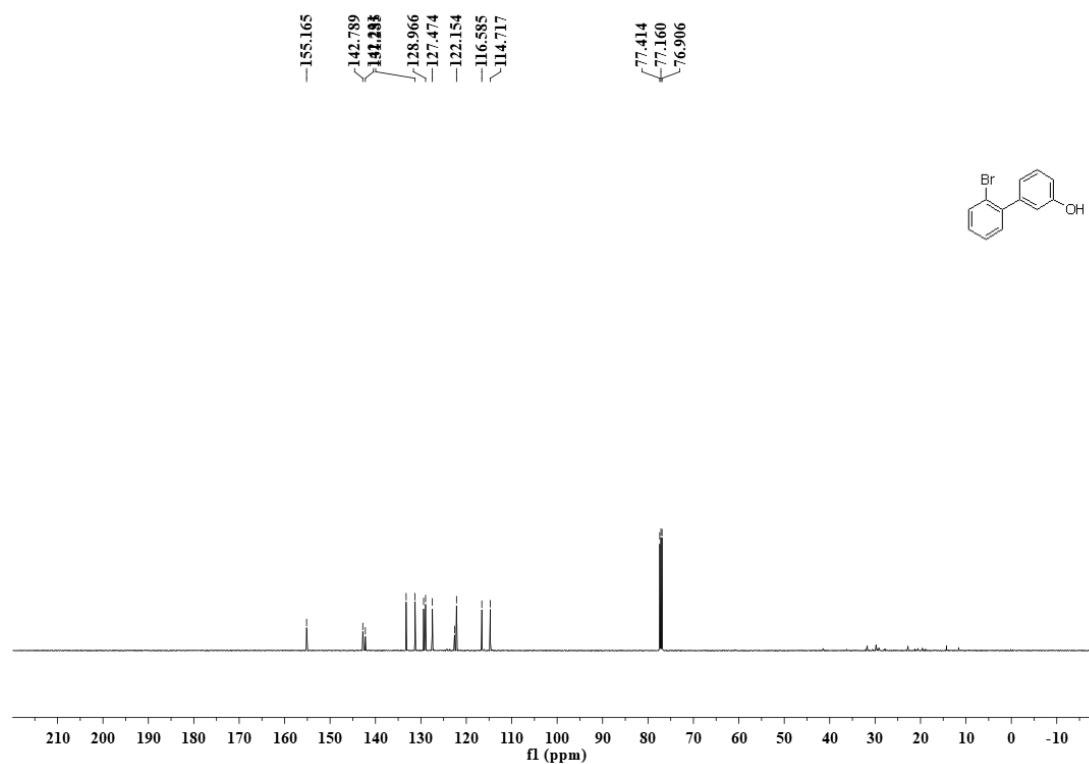
^{13}C NMR (125 MHz, CDCl_3) of **di-3q**



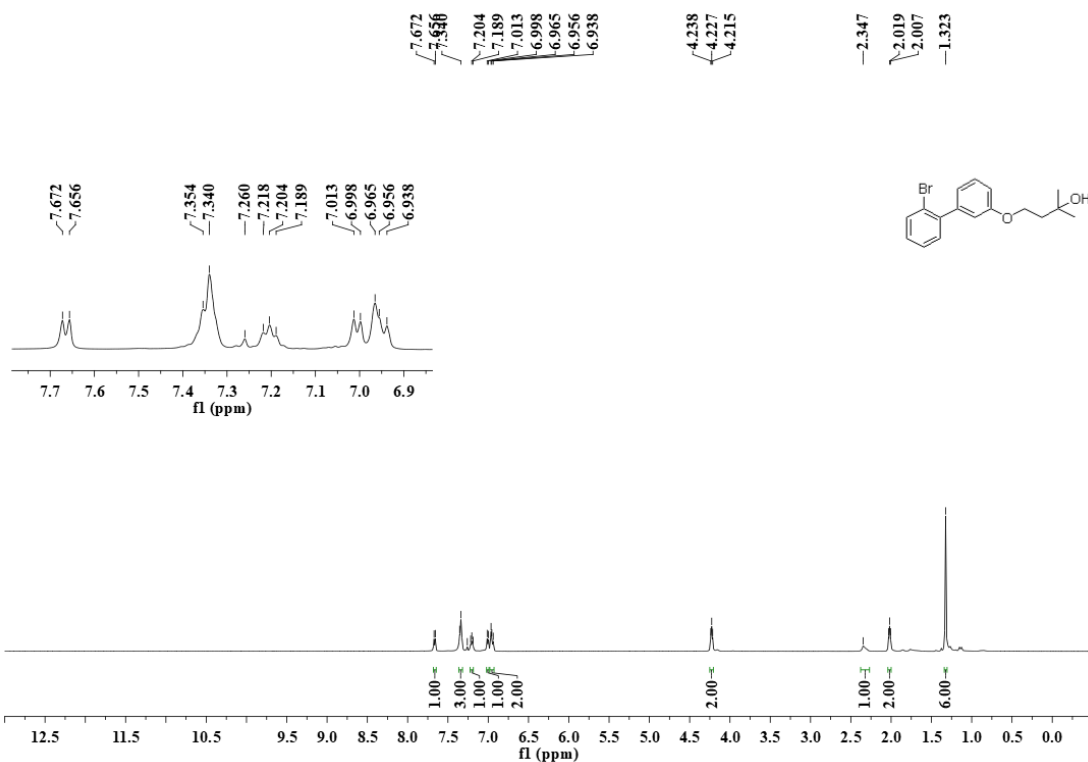
^1H NMR (500 MHz, CDCl_3) of **mono-3q**



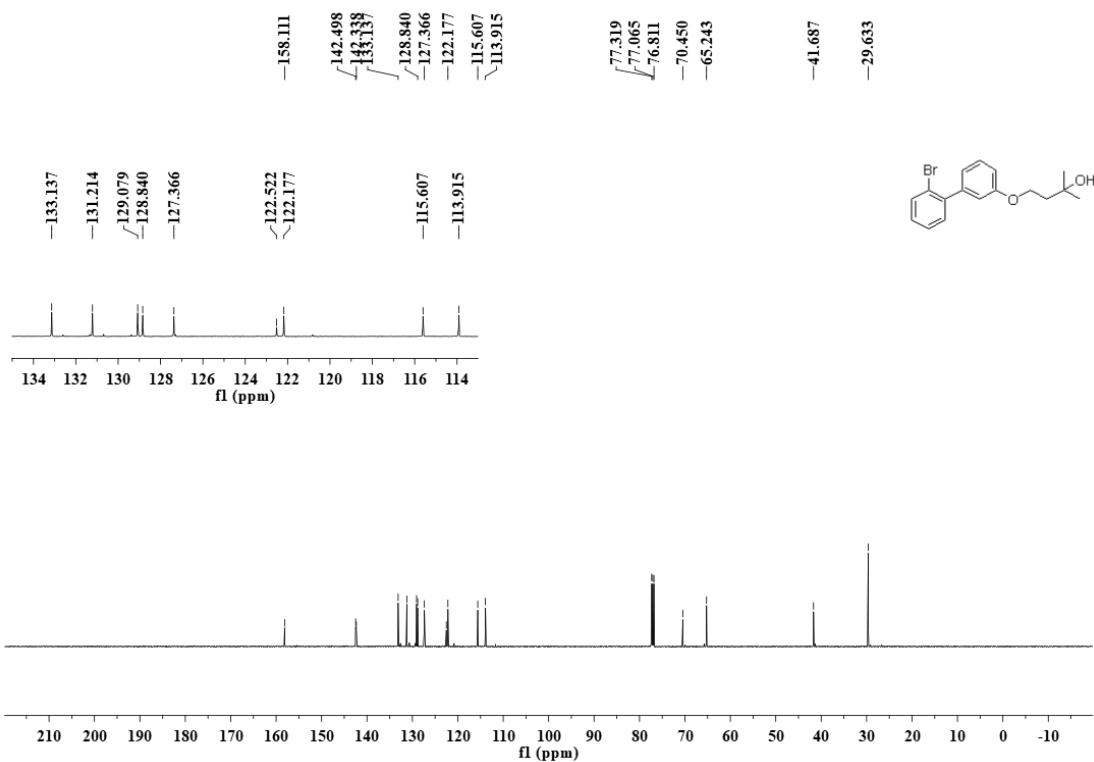
^{13}C NMR (125 MHz, CDCl_3) of **mono-3q**



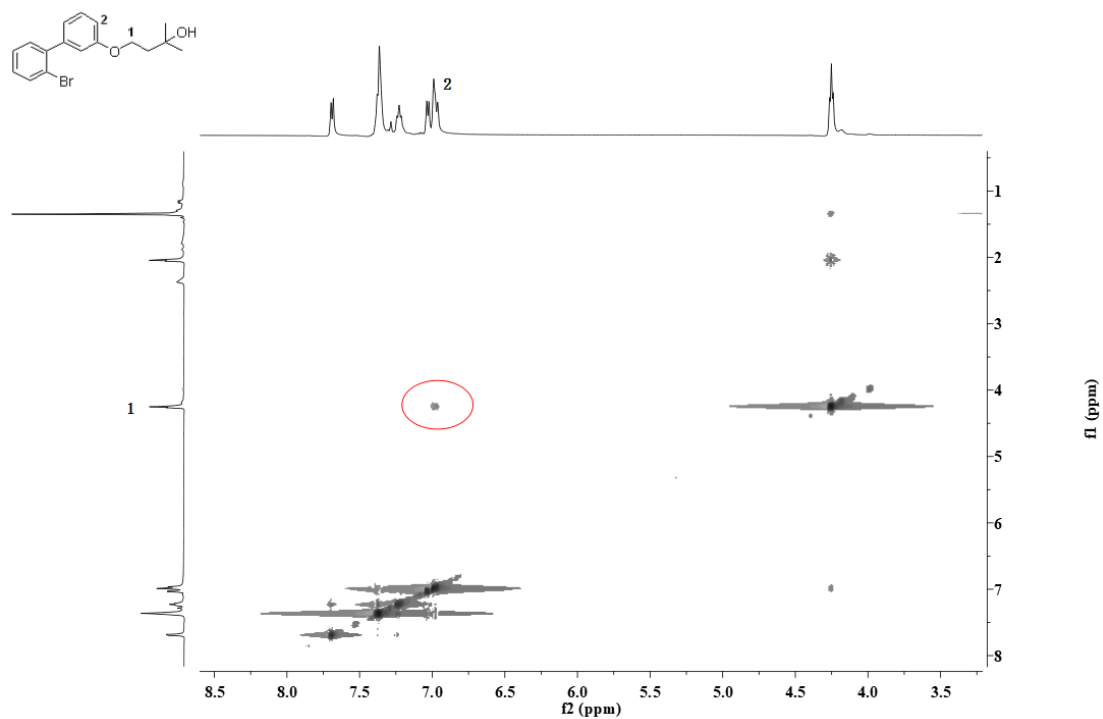
^1H NMR (500 MHz, CDCl_3) of **3r**



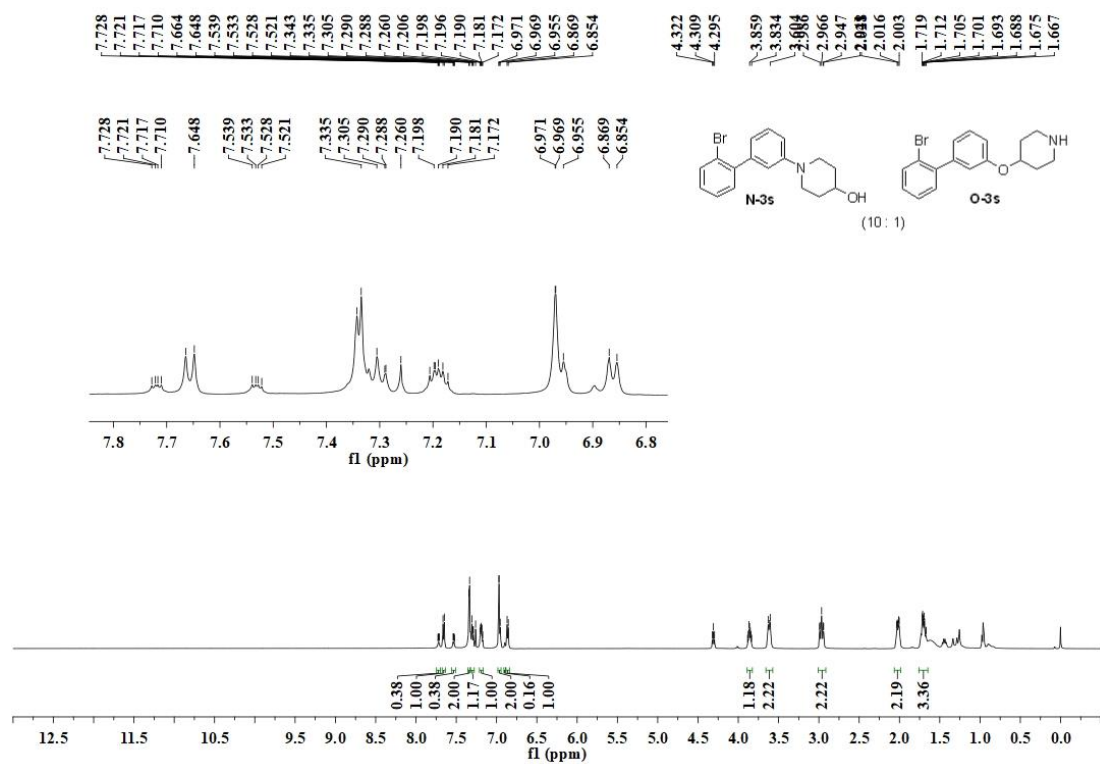
^{13}C NMR (125 MHz, CDCl_3) of **3r**



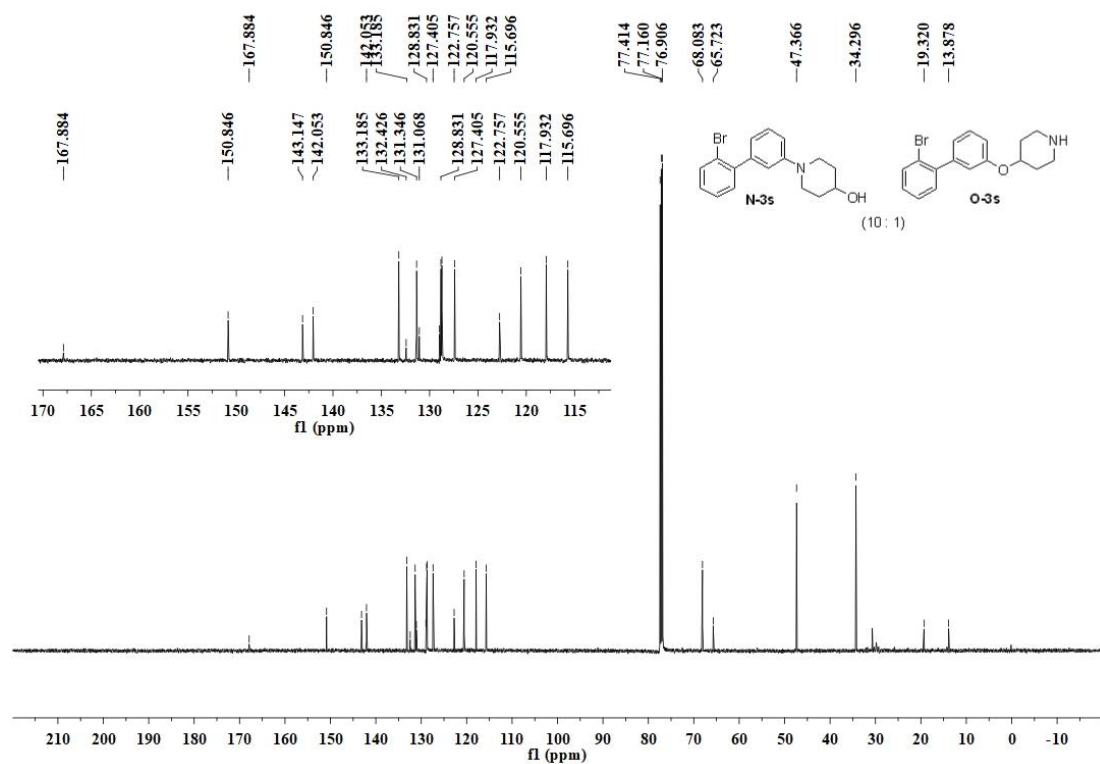
^1H - ^1H NOESY of **3r**



^1H NMR (500 MHz, CDCl_3) of N-3s



^{13}C NMR (125 MHz, CDCl_3) of N-3s



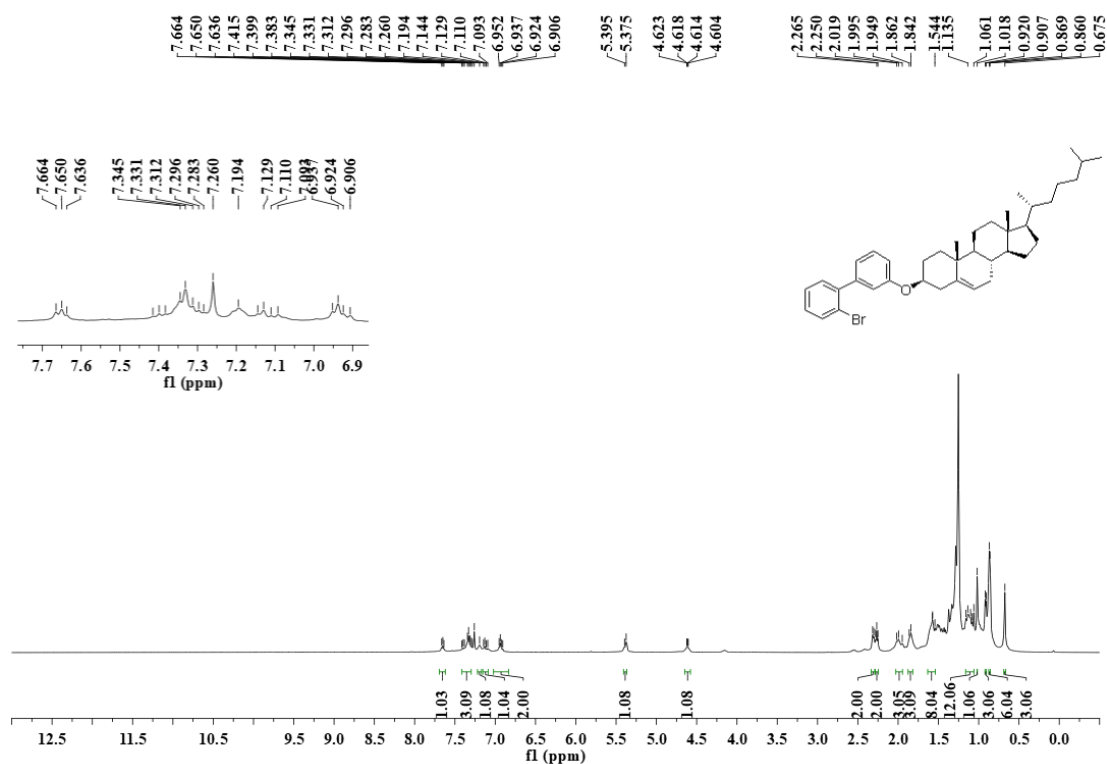
Chemical structure of 10: COc1ccc2c(c1)c(c3ccccc3OC2C4C5C6C7C8C9C10C11C12C13C14C15C16C17C18C19C20C21C22C23C24C25C26C27C28C29C30C31C32C33C34C35C36C37C38C39C40C41C42C43C44C45C46C47C48C49C50C51C52C53C54C55C56C57C58C59C60C61C62C63C64C65C66C67C68C69C70C71C72C73C74C75C76C77C78C79C80C81C82C83C84C85C86C87C88C89C90C91C92C93C94C95C96C97C98C99C100C101C102C103C104C105C106C107C108C109C110C111C112C113C114C115C116C117C118C119C120C121C122C123C124C125C126C127C128C129C130C131C132C133C134C135C136C137C138C139C140C141C142C143C144C145C146C147C148C149C150C151C152C153C154C155C156C157C158C159C160C161C162C163C164C165C166C167C168C169C170C171C172C173C174C175C176C177C178C179C180C181C182C183C184C185C186C187C188C189C190C191C192C193C194C195C196C197C198C199C200C201C202C203C204C205C206C207C208C209C210C211C212C213C214C215C216C217C218C219C220C221C222C223C224C225C226C227C228C229C230C231C232C233C234C235C236C237C238C239C240C241C242C243C244C245C246C247C248C249C250C251C252C253C254C255C256C257C258C259C260C261C262C263C264C265C266C267C268C269C270C271C272C273C274C275C276C277C278C279C280C281C282C283C284C285C286C287C288C289C290C291C292C293C294C295C296C297C298C299C300C301C302C303C304C305C306C307C308C309C310C311C312C313C314C315C316C317C318C319C320C321C322C323C324C325C326C327C328C329C330C331C332C333C334C335C336C337C338C339C340C341C342C343C344C345C346C347C348C349C350C351C352C353C354C355C356C357C358C359C360C361C362C363C364C365C366C367C368C369C370C371C372C373C374C375C376C377C378C379C380C381C382C383C384C385C386C387C388C389C390C391C392C393C394C395C396C397C398C399C400C401C402C403C404C405C406C407C408C409C410C411C412C413C414C415C416C417C418C419C420C421C422C423C424C425C426C427C428C429C430C431C432C433C434C435C436C437C438C439C440C441C442C443C444C445C446C447C448C449C450C451C452C453C454C455C456C457C458C459C460C461C462C463C464C465C466C467C468C469C470C471C472C473C474C475C476C477C478C479C480C481C482C483C484C485C486C487C488C489C490C491C492C493C494C495C496C497C498C499C500C501C502C503C504C505C506C507C508C509C510C511C512C513C514C515C516C517C518C519C520C521C522C523C524C525C526C527C528C529C530C531C532C533C534C535C536C537C538C539C540C541C542C543C544C545C546C547C548C549C550C551C552C553C554C555C556C557C558C559C560C561C562C563C564C565C566C567C568C569C570C571C572C573C574C575C576C577C578C579C580C581C582C583C584C585C586C587C588C589C590C591C592C593C594C595C596C597C598C599C600C601C602C603C604C605C606C607C608C609C610C611C612C613C614C615C616C617C618C619C620C621C622C623C624C625C626C627C628C629C630C631C632C633C634C635C636C637C638C639C640C641C642C643C644C645C646C647C648C649C650C651C652C653C654C655C656C657C658C659C660C661C662C663C664C665C666C667C668C669C670C671C672C673C674C675C676C677C678C679C680C681C682C683C684C685C686C687C688C689C690C691C692C693C694C695C696C697C698C699C700C701C702C703C704C705C706C707C708C709C710C711C712C713C714C715C716C717C718C719C720C721C722C723C724C725C726C727C728C729C730C731C732C733C734C735C736C737C738C739C740C741C742C743C744C745C746C747C748C749C750C751C752C753C754C755C756C757C758C759C760C761C762C763C764C765C766C767C768C769C770C771C772C773C774C775C776C777C778C779C780C781C782C783C784C785C786C787C788C789C790C791C792C793C794C795C796C797C798C799C800C801C802C803C804C805C806C807C808C809C810C811C812C813C814C815C816C817C818C819C820C821C822C823C824C825C826C827C828C829C830C831C832C833C834C835C836C837C838C839C840C841C842C843C844C845C846C847C848C849C850C851C852C853C854C855C856C857C858C859C860C861C862C863C864C865C866C867C868C869C870C871C872C873C874C875C876C877C878C879C880C881C882C883C884C885C886C887C888C889C890C891C892C893C894C895C896C897C898C899C900C901C902C903C904C905C906C907C908C909C910C911C912C913C914C915C916C917C918C919C920C921C922C923C924C925C926C927C928C929C930C931C932C933C934C935C936C937C938C939C940C941C942C943C944C945C946C947C948C949C950C951C952C953C954C955C956C957C958C959C960C961C962C963C964C965C966C967C968C969C970C971C972C973C974C975C976C977C978C979C980C981C982C983C984C985C986C987C988C989C990C991C992C993C994C995C996C997C998C999C1000C1001C1002C1003C1004C1005C1006C1007C1008C1009C1010C1011C1012C1013C1014C1015C

Chemical structure of compound 10 is shown in the top right corner. The structure is a complex molecule with a central carbon atom bonded to a phenyl ring, a 4-methoxyphenyl ring, a 4-bromophenyl ring, and a 4-allyloxyphenyl ring. The central carbon is also bonded to a methyl group and a methoxy group.

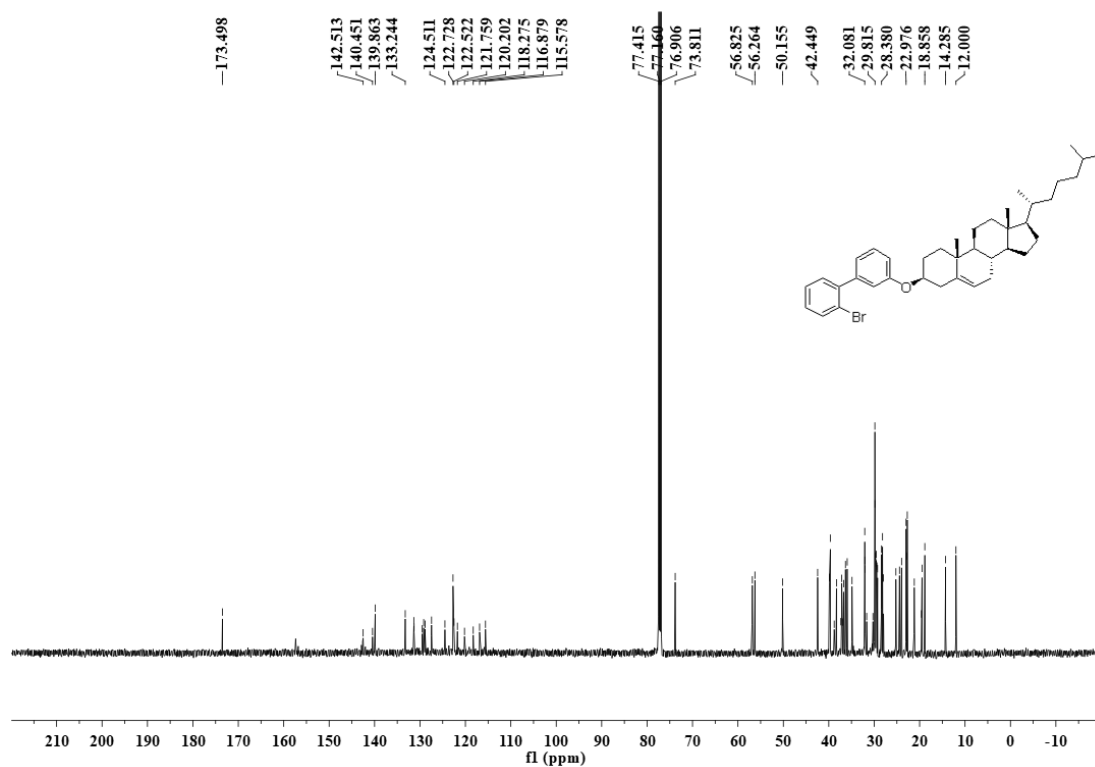
¹³C NMR spectrum (CDCl₃) of compound 10. The spectrum shows peaks from 28 to 158 ppm. The chemical shift values (ppm) are listed below the spectrum:

158.148, 148.106, 143.168, 141.931, 137.494, 133.209, 131.373, 128.765, 127.558, 127.418, 118.084, 117.262, 116.998, 115.928, 110.176, 77.413, 77.160, 76.906, 61.434, 55.567, 49.147, 43.536, 35.837, 29.841, 28.600.

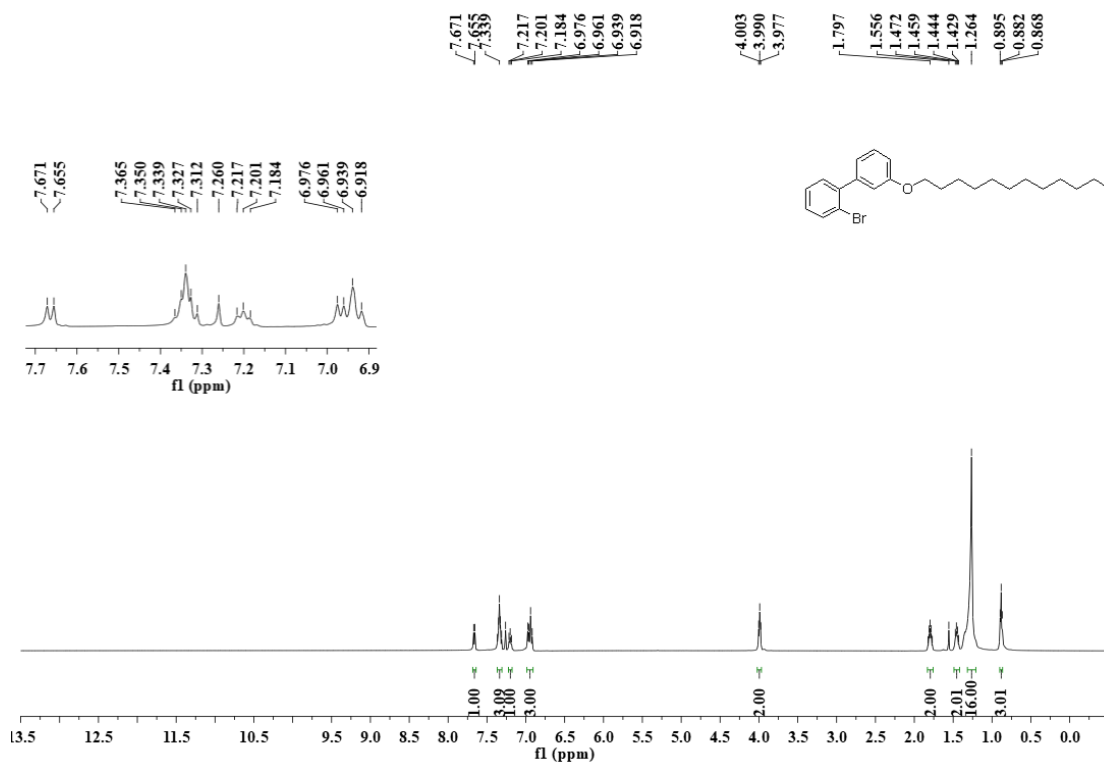
^1H NMR (500 MHz, CDCl_3) of **6**



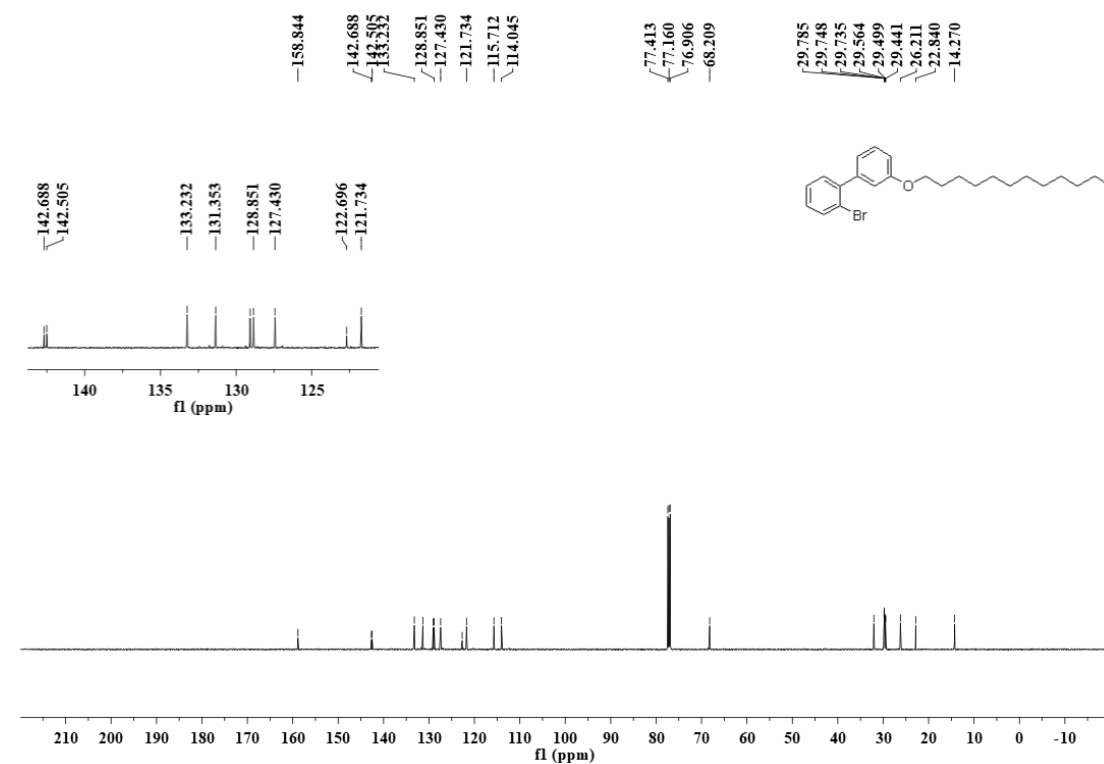
^{13}C NMR (125 MHz, CDCl_3) of **6**



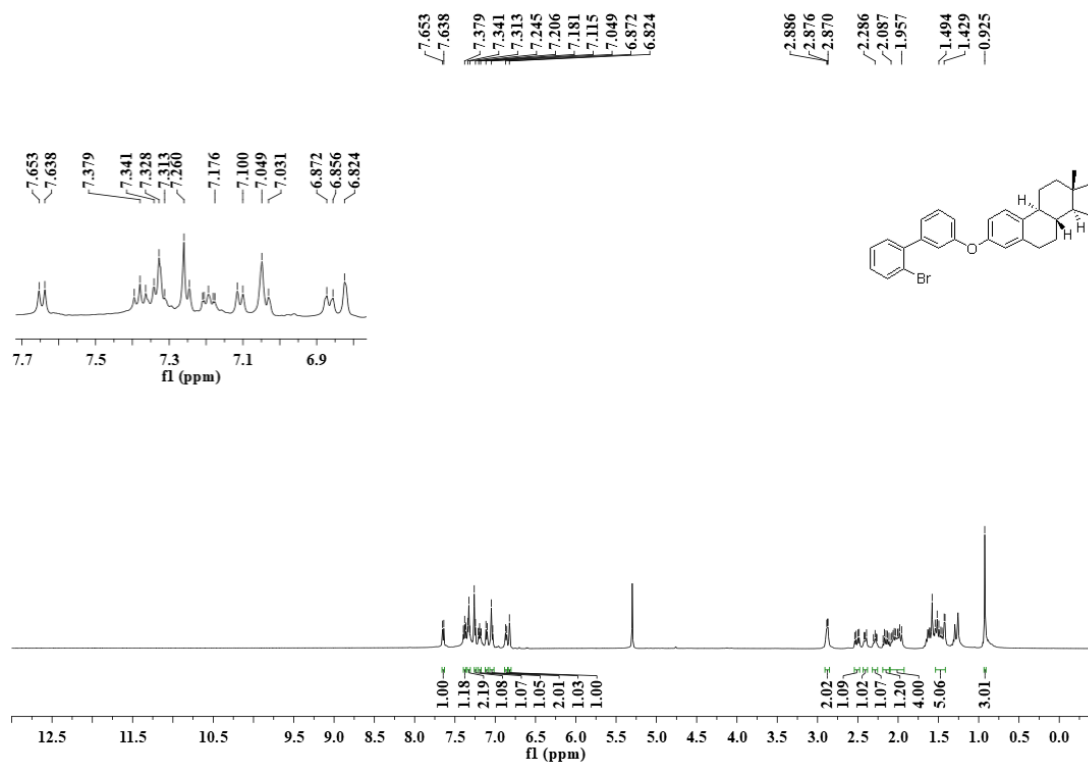
^1H NMR (500 MHz, CDCl_3) of 7



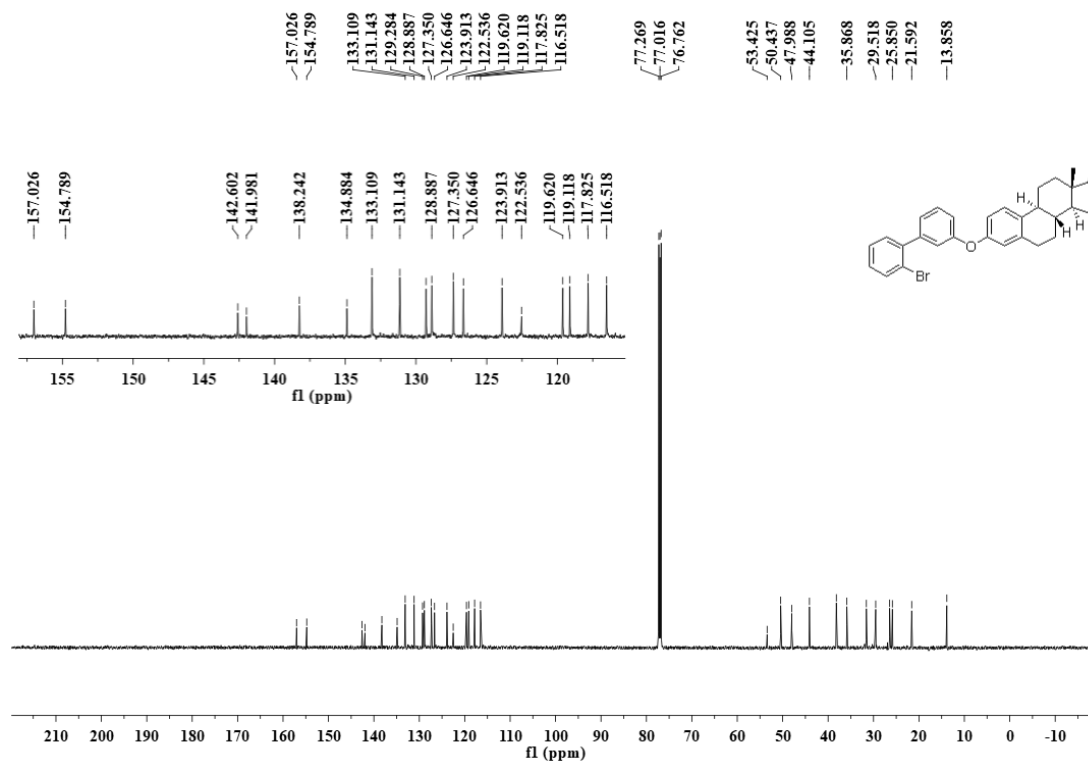
^{13}C NMR (125 MHz, CDCl_3) of 7



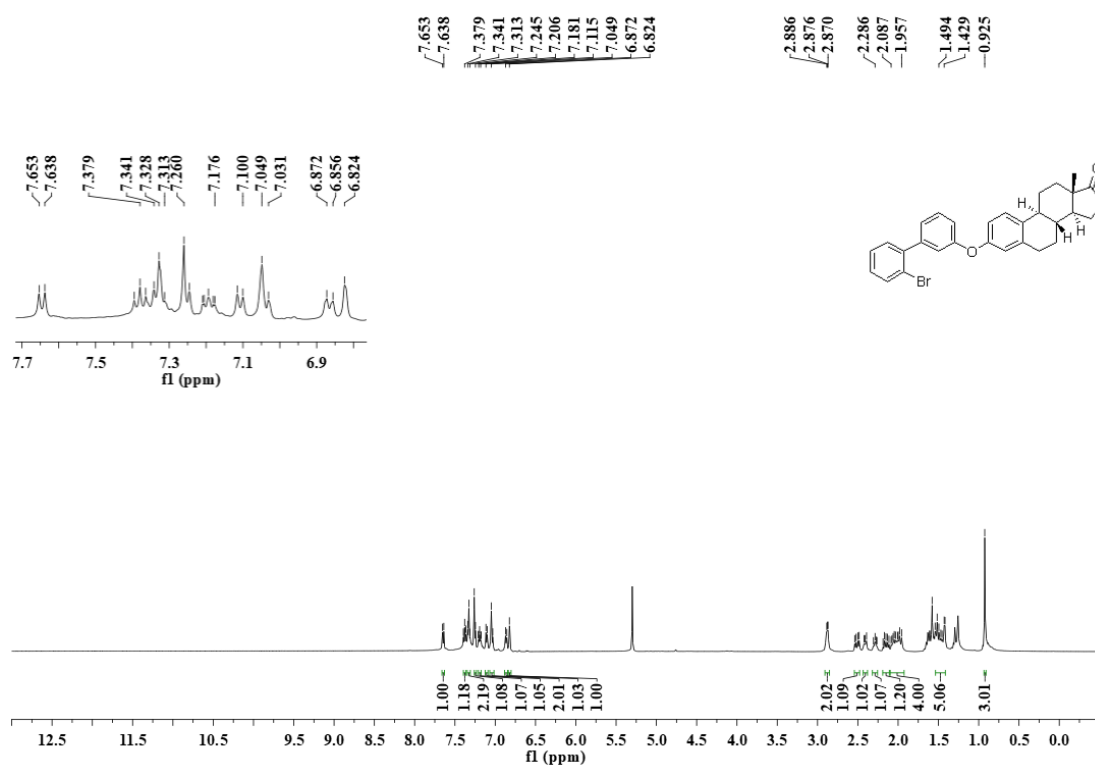
^1H NMR (500 MHz, CDCl_3) of **8**



^{13}C NMR (125 MHz, CDCl_3) of **8**



^1H NMR (500 MHz, CDCl_3) of **8**



^{13}C NMR (125 MHz, CDCl_3) of **8**

