Supporting Information

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

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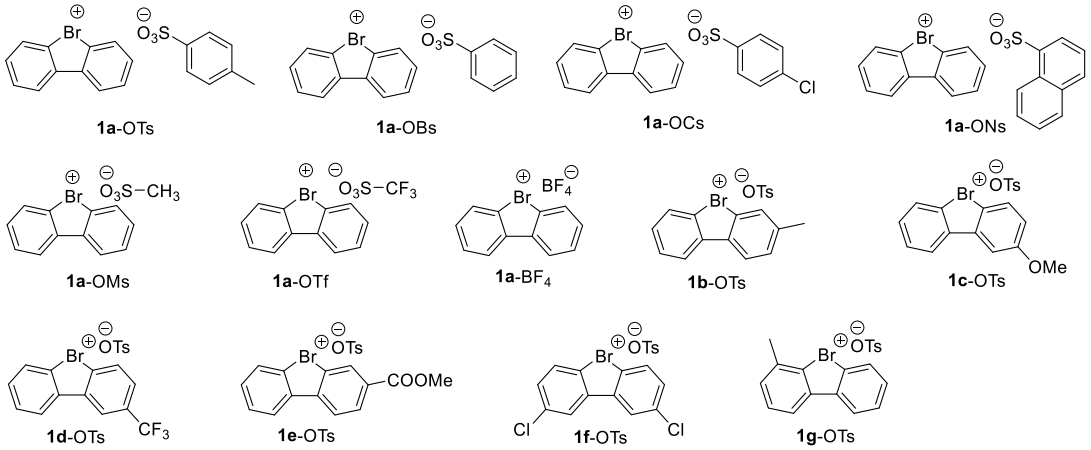
1. General remarks

NMR spectra were obtained on a BRUKER Ascend500. The ^{1}H NMR (500 MHz) chemical shifts were measured relative to $CDCl_3$ or DMSO-d_6 as the internal reference ($CDCl_3$: δ = 7.26 ppm; DMSO-d_6: δ = 2.50 ppm). The ^{13}C NMR (125 MHz) chemical shifts were given using $CDCl_3$ or DMSO-d_6 the internal standard ($CDCl_3$: δ = 77.16 ppm; DMSO-d_6: δ = 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.

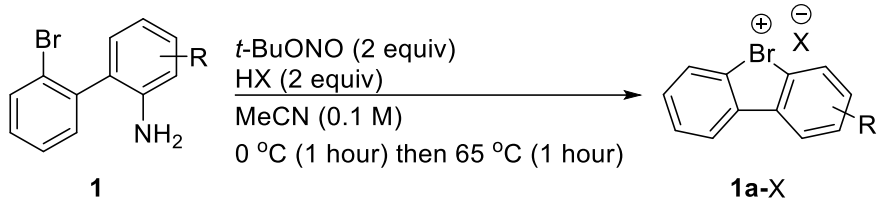
Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. 2-iodoanilines, 2-bromophenylboronic acids, Cs_2CO_3 were purchased from Beijing Innochem Chemical Engineering Reagent (China) Co., Ltd and Energy Chemical.

2. General procedures

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



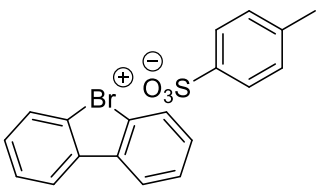
Compounds **1a**-OTs, **1a**-OMs, **1a**-OTf and **1a**-BF_4 were prepared according to the modified literature procedures.[1] Compounds **1a**-OBs, **1a**-OCs, **1a**-ONs, **1b**-OTs, **1c**-OTs, **1d**-OTs, **1e**-OTs, **1f**-OTs, and **1g**-OTs were prepared as follows:



1 **1a-X**

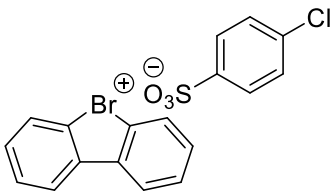
To a dry round bottom flask was added 2'-bromo-[1,1'-biphenyl]-2-amine **1** (1 mmol) and MeCN (10 mL). The solution was cooled to 0 ℃ before *t*-BuONO (2 equiv) was added dropwise. After that, acid HX (2 equiv) was added in portions. The mixture was stirred at 0 ℃ for 1 hour and then heated to 65 ℃ for 1 hour. The cooled mixture was purged in Et_2O where a solid precipitate. The product was collected through filtration, washed with Et_2O and dried under high vacuum.

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



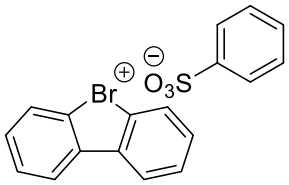
White solid (371 mg, 92% yield). **^{1}H NMR (500MHz, DMSO-*d*$_6$):** δ = 8.60 (d, *J* = 8 Hz, 2H), 8.50 (d, *J* = 8.5 Hz, 2H), 7.94 (t, *J* = 7.3 Hz, 2H), 7.84 (t, *J* = 7.3 Hz, 2H), 7.50 (d, *J* = 8 Hz, 2H), 7.11 (d, *J* = 8 Hz, 2H), 2.28 (s, 3H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 145.47, 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**)**



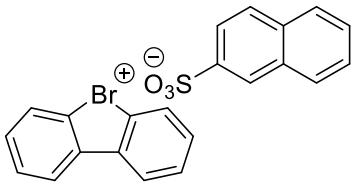
White solid (381 mg, 90% yield). M.p.: 217–219 ºC. **^{1}H NMR (500MHz, DMSO-*d*$_6$):** δ = 8.59–8.56 (m, 2H), 8.50 (d, *J* = 8.5 Hz, 2H), 7.95–7.90 (m, 2H), 7.84–7.81 (m, 2H), 7.64–7.61 (m, 2H), 7.38 (d, *J* = 8.5 Hz, 2H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 147.18, 136.54, 135.32, 133.00, 131.80, 131.20, 127.72, 127.49, 126.30, 125.60 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{12}H_8Br^+$ ($M-OCs^-$) 230.9804, found 230.9808.

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



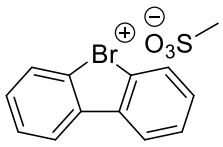
Yellow solid (331 mg, 85% yield). M.p.: 195–197 ºC. **^{1}H NMR (500MHz, DMSO-*d*$_6$):** δ = 8.58 (d, *J* = 7.5 Hz, 2H), 8.51 (d, *J* = 8.5 Hz, 2H), 7.93 (t, *J* = 7.3 Hz, 2H), 7.83 (t, *J* = 7.8 Hz, 2H), 7.64 (d, *J* = 6.5 Hz, 2H), 7.34–7.30 (m, 3H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 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 $C_{12}H_8Br^+$ (M−OBs$^-$) 230.9804, found 230.9805.

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



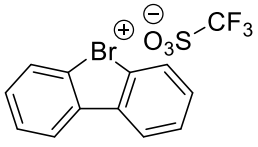
White solid (308 mg, 70% yield). M.p.: 200–202 ºC. **^{1}H NMR (500MHz, DMSO-*d*$_6$):** δ = 8.58 (d, *J* = 7.0 Hz, 2H), 8.50 (d, *J* = 8.0 Hz, 2H), 8.17 (s, 1H), 7.95–7.84 (m, 7H), 7.74–7.73 (m, 1H), 7.52 (s, 2H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 145.58, 136.56, 135.34, 132.73, 132.15, 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 $C_{12}H_8Br^+$ (M−ONs$^-$) 230.9804, found 230.9805.

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



White solid (294 mg, 90% yield). **^{1}H 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. **^{13}C 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]

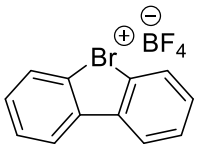
dibenzo[*b,d*]bromol-5-ium trifluoromethanesulfonate (1a-OTf**)**



White solid (228 mg, 60% yield). **^{1}H 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. **^{13}C NMR (125**

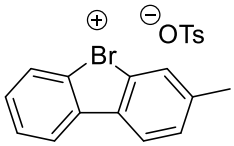
MHz, DMSO-*d*$_6$): δ = 136.61, 135.40, 131.89, 131.27, 126.35, 125.62 ppm. **^{19}F NMR (471 MHz, DMSO-*d*$_6$)**: δ = -78.18 (s) ppm. Data in accordance with the literature.[1]

dibenzo[*b,d*]bromol-5-ium tetrafluoroborate (1a-BF_4**)**



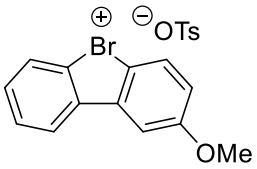
White solid (239 mg, 75% yield). **^{1}H NMR (500MHz, DMSO-*d*$_6$):** δ = 8.66 (d, *J* = 8.5 Hz, 4H), 8.00 (t, *J* = 7.3 Hz, 2H), 7.95 (t, *J* = 8.0 Hz, 2H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$)**: δ = 140.04, 132.03, 131.75, 125.51, 122.95 ppm. **^{19}F NMR (471 MHz, DMSO-*d*$_6$)**: δ = -148.88 (s), -148.14 (s) ppm. Data in accordance with the literature.[1]

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



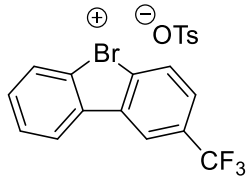
Orange solid (376 mg, 90% yield). M.p.: 174–176 ºC. **^{1}H NMR (500MHz, DMSO-*d*$_6$):** δ = 8.51–8.43 (m, 3H), 8.29 (s, 1H), 7.90 (t, *J* = 7.5 Hz, 1H), 7.79 (t, *J* = 7.3 Hz, 1H), 7.73 (d, *J* = 8 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 2H), 7.12 (d, *J* = 7.5 Hz, 2H), 2.51 (s, 3H), 2.28 (s, 3H) ppm. **^{13}C 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 $C_{13}H_{10}Br^+$ (M−OTs$^-$) 244.9961, found 244.9960.

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



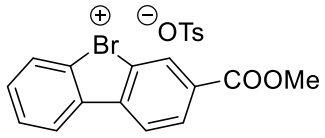
Yellow solid (443 mg, 92% yield). M.p.: 218–220 ºC. **^{1}H NMR (500MHz, DMSO-*d*$_6$):** δ = 8.64 (d, *J* = 7.5, 1H), 8.48 (d, *J* = 8.5 Hz, 1H), 8.34 (d, *J* = 9.5 Hz, 1H), 8.15 (d, *J* = 1.5 Hz, 1H), 7.92 (t, *J* = 7.3 Hz, 1H), 7.83 (t, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.40 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.11 (d, *J* = 7.5 Hz, 2H), 3.95 (s, 3H), 2.28 (s, 3H) ppm. **^{13}C 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 $C_{13}H_{10}BrO^+$ (M−OTs$^-$) 260.9910, found 260.9907.

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



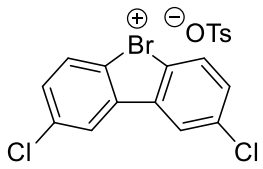
White solid (188 mg, 40% yield). M.p.: 223–225 ºC. **^{1}H NMR (500MHz, DMSO-*d*$_6$):** δ = 9.08 (s, 1H), 8.82 (d, *J* = 8.0 Hz, 1H), 8.73 (d, *J* = 8.5 Hz, 1H), 8.54 (d, *J* = 8.5 Hz, 1H), 8.22 (d, *J* = 9.0 Hz, 1H), 7.98 (t, *J* = 6.0 Hz, 1H), 7.90 (t, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 2.28 (s, 3H) ppm. **^{13}C 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. **^{19}F NMR (471 MHz, DMSO-*d*$_6$)**: δ = -60.80 (s) ppm. **HRMS (ESI) *m/z*:** calcd for $C_{13}H_7BrF_3^+$ (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 ºC. **^{1}H 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. **^{13}C 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*:** $C_{14}H_{10}BrO_2^+$ (M−OTs$^-$) 288.9859, found 288.9860.

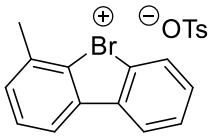
2,8-dichlorodibenzo[*b,d*]bromol-5-ium 4-methylbenzenesulfonate (1f-OTs**)**



White solid (283 mg, 60% yield). M.p.: 185–187 ºC. **^{1}H 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. **^{13}C 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,

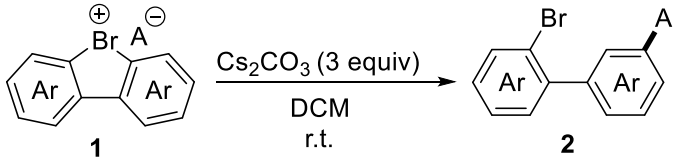
20.80 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{12}H_6BrCl_2^+$ ($M-OTs^-$) 298.9025, found 298.9025.

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



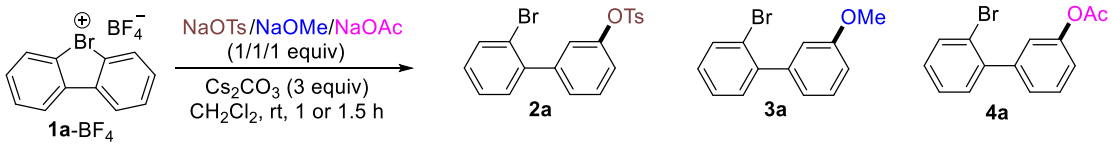
White solid (355 mg, 85% yield). M.p.: 226–228. **^{1}H NMR (500MHz, DMSO-*d*$_6$):** δ = 8.61 (d, *J* = 8.0 Hz, 2H), 8.44 (d, *J* = 7.5 Hz, 1H), 7.97 (t, *J* = 7.3 Hz, 1H), 7.87 (t, *J* = 7.8 Hz, 2H), 7.72 (d, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 7.5 Hz, 2H), 2.75 (s, 3H), 2.27 (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-**BF_4 (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 ^{1}H NMR analysis.

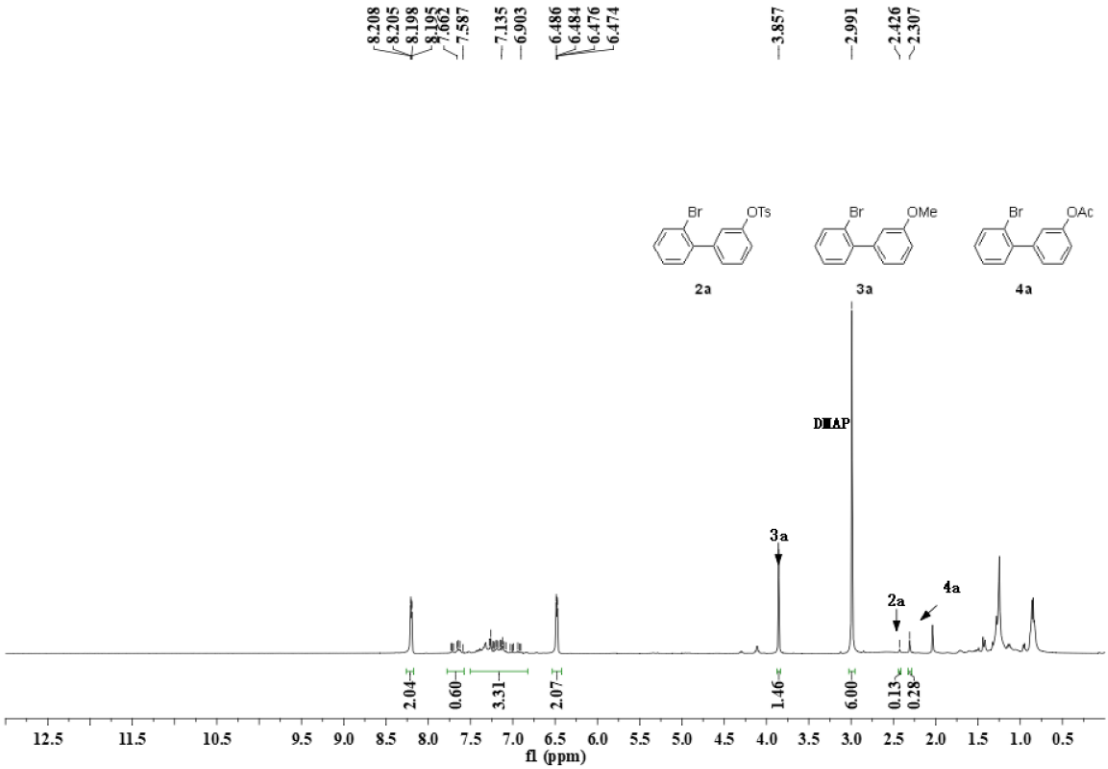


Figure S1. *^{1}H NMR (500 MHz, $CDCl_3$) of the mixture of **2a**/**3a**/**4a** after 1 h*

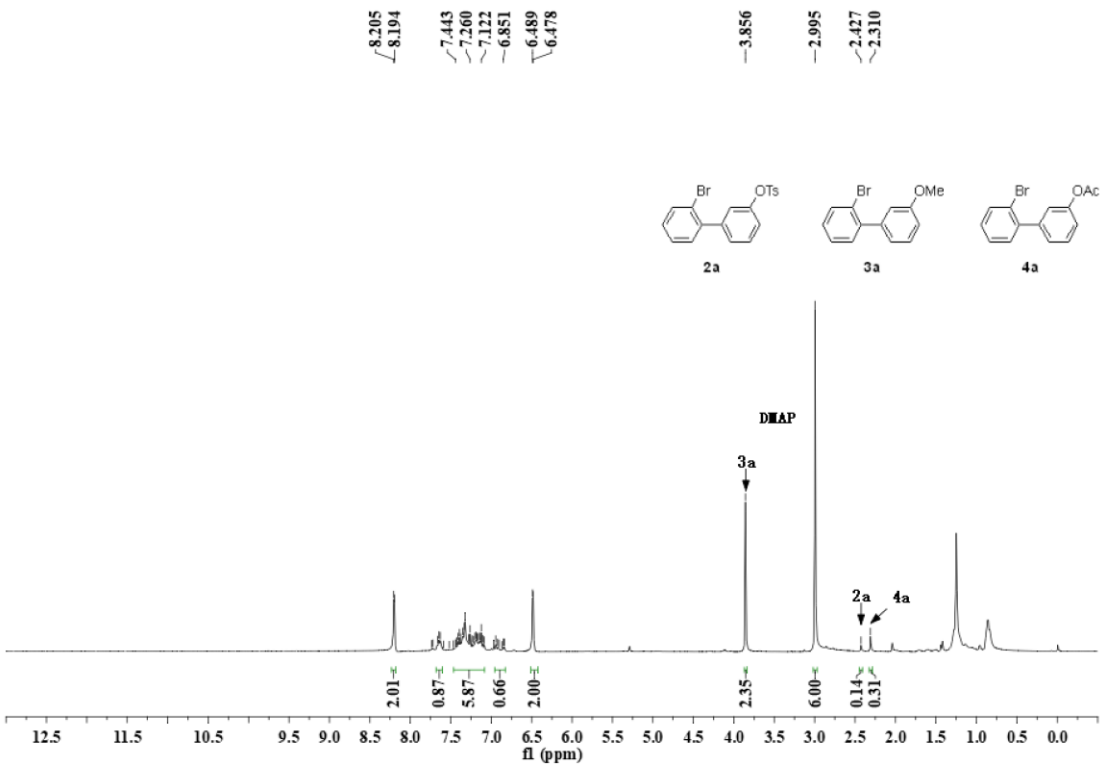
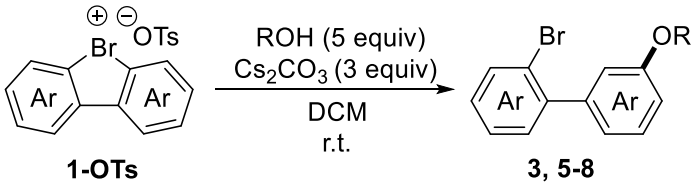


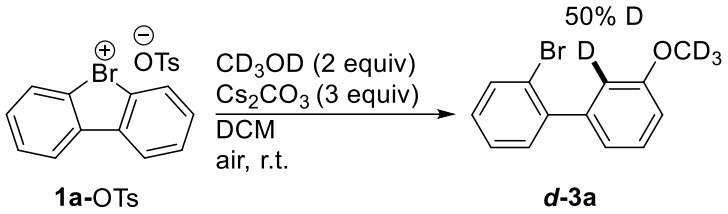
Figure S2*. [1]H NMR (500 MHz, $CDCl_3$) of the mixture of* ***2a/3a/4a*** *after 1.5 h*

2.4 General procedure for the cross anion-cation coupling



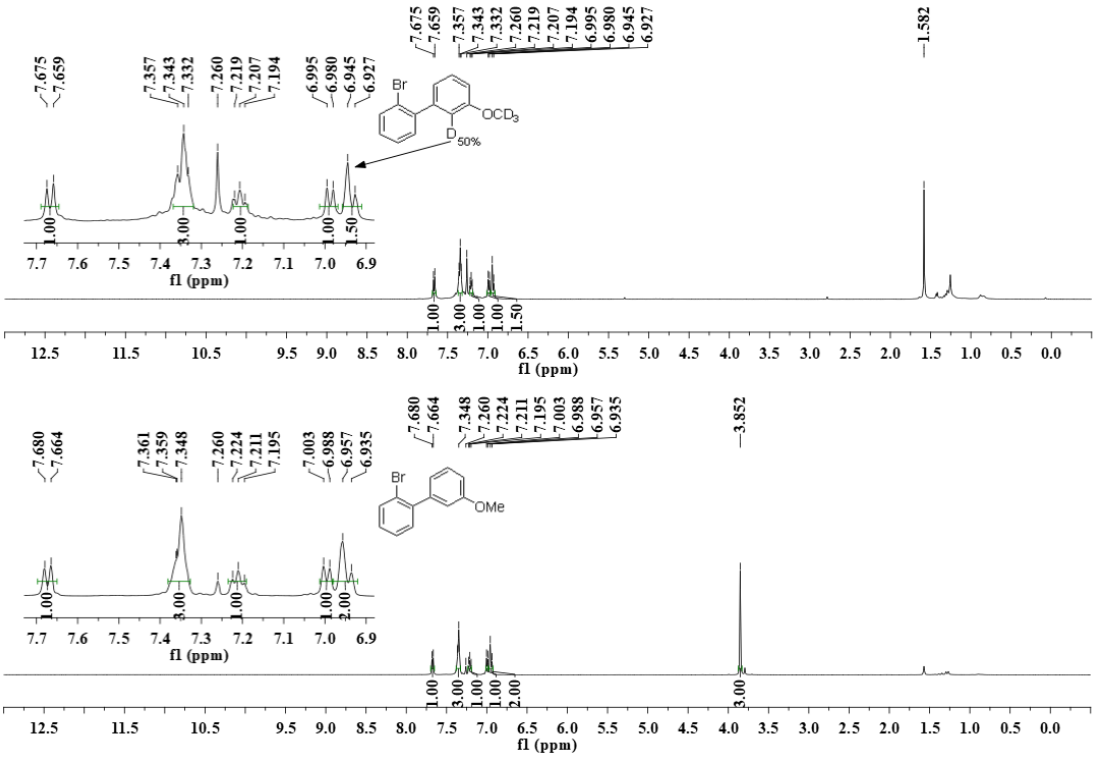
To a dry Schlenk tube was added **1-OTs** (0.1 mmol), alcohol/phenol/water (ROH, 5 equiv), Cs_2CO_3 (3 equiv) and DCM (1 mL). The mixture was stirred at room temperature for 12 hours. After the reaction was completed, the mixture was passed through a silica gel column (200–300 mesh), eluting with petroleum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

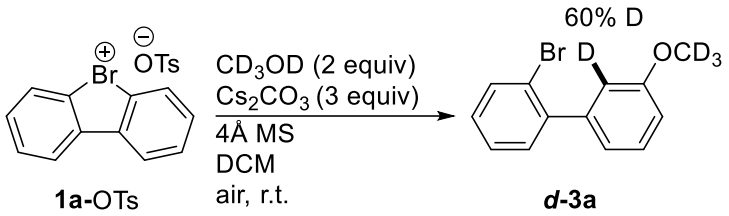
3. Isotope labeling experiments



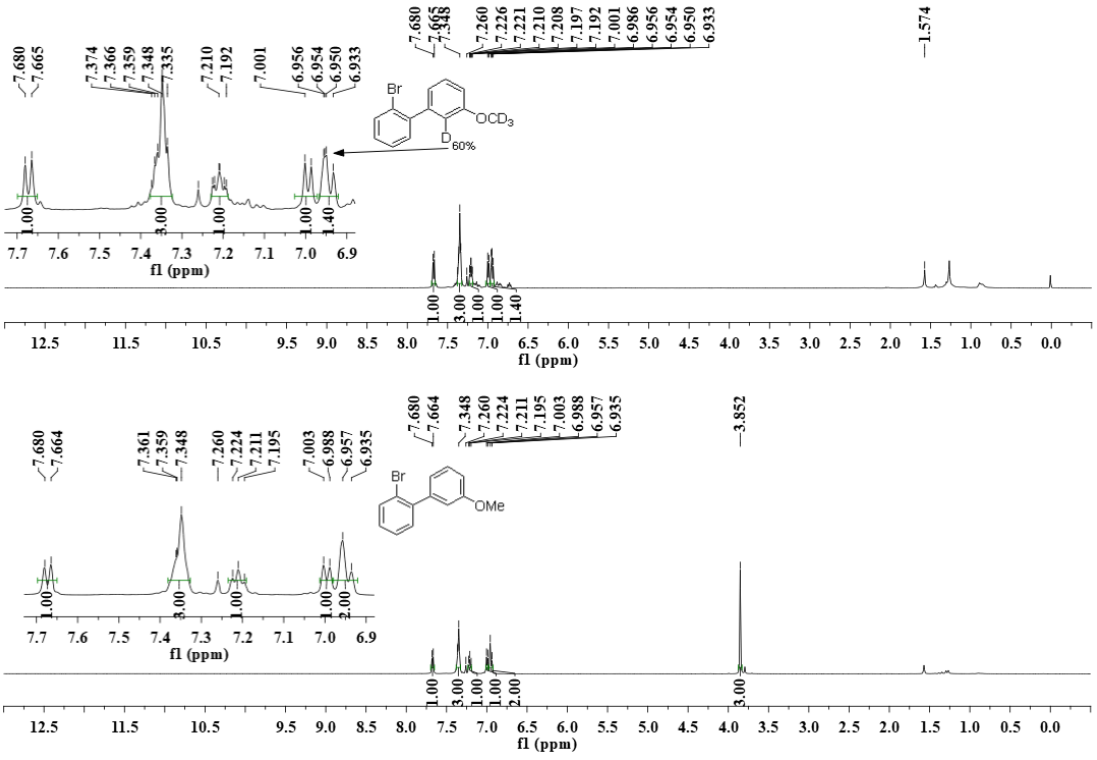
1a-OTs ***d*-3a**

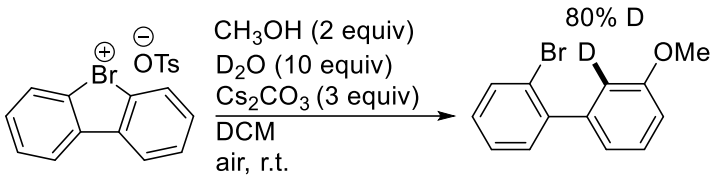
The mixture of **1a**-OTs (0.1 mmol), methanol-d_4 (2 equiv), Cs_2CO_3 (3 equiv) and DCM (1 mL) was stirred at room temperature for 12 hours. After the reaction was completed, the mixture was passed through a silica gel column (200–300 mesh), eluting with petroleum ether/EtOAc (40/1, v/v) to afford deuterium ***d*-3a**. ^{1}H NMR analysis showed that 50% hydrogen at the *ortho* position of the biphenyl was deuterated.





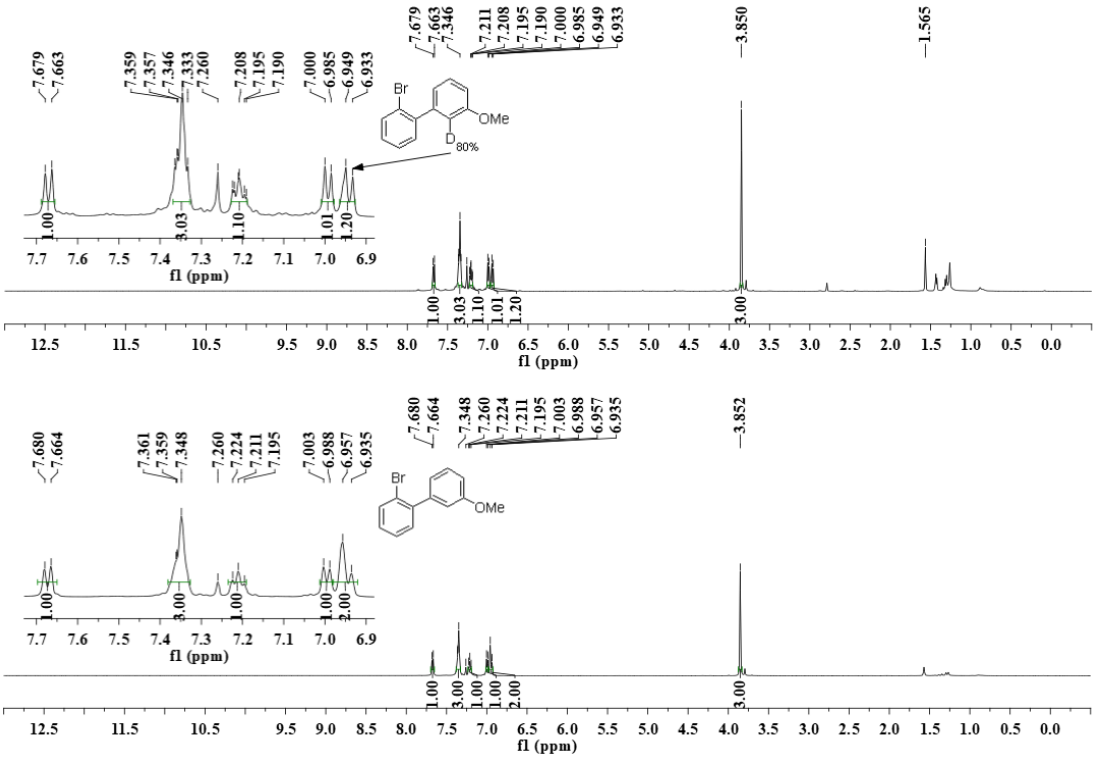
The mixture of **1a**-OTs (0.1 mmol), methanol-d_4 (2 equiv), Cs_2CO_3 (3 equiv), 4Å MS (30 mg) and DCM (1 mL) was stirred at room temperature for 12 hours. After the reaction was completed, the mixture was passed through a silica gel column (200–300 mesh), eluting with petroleum ether/EtOAc (40/1, v/v) to afford corresponding deuterium ***d*-3a**. ^{1}H NMR analysis showed that 60% hydrogen at the *ortho* position of the biphenyl was deuterated.

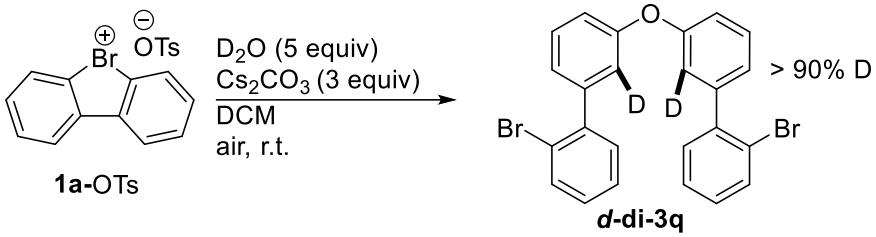




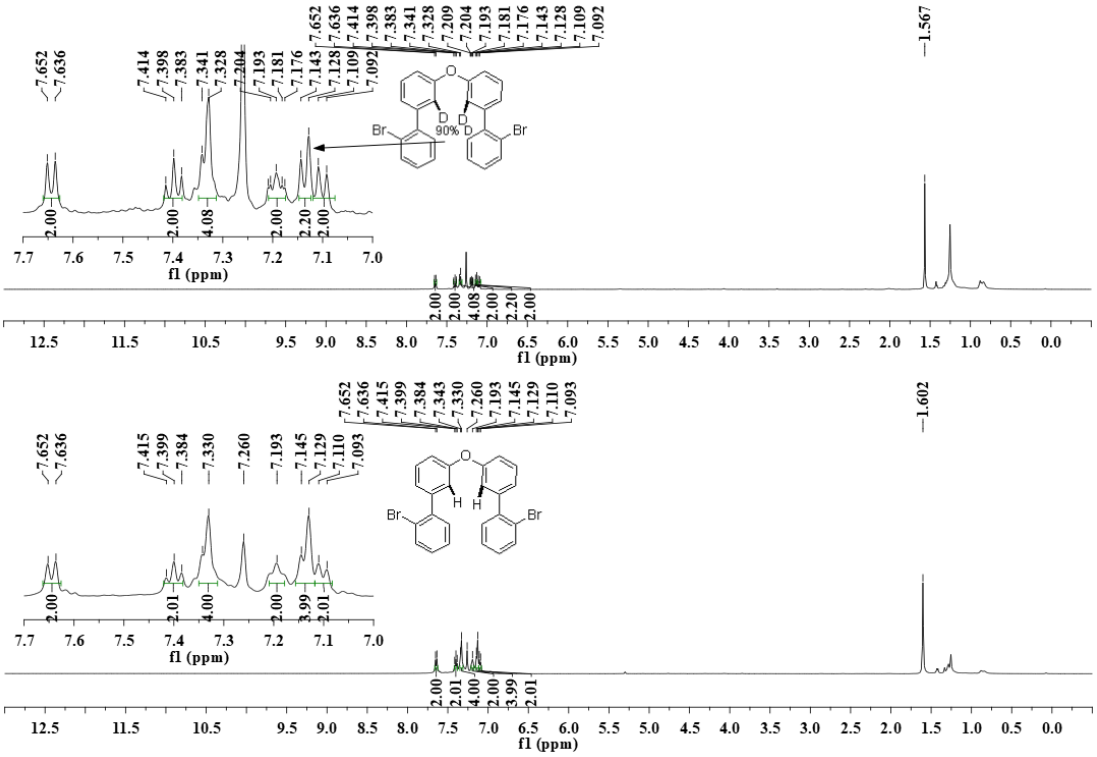
1a-OTs ***d*-3a**

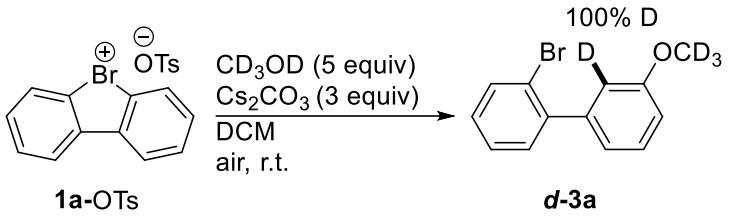
The mixture of **1a**-OTs (0.1 mmol), methanol (2 equiv), D_2O (10 equiv), Cs_2CO_3 (3 equiv) and DCM (0.1 mL) was stirred at room temperature for 12 hours. After the reaction was completed, the mixture was passed through a silica gel column (200–300 mesh), eluting with petroleum ether/EtOAc (40/1, v/v) to afford corresponding deuterium ***d*-3a**. ^{1}H NMR analysis showed that 80% hydrogen at the *ortho* position of the biphenyl was deuterated.





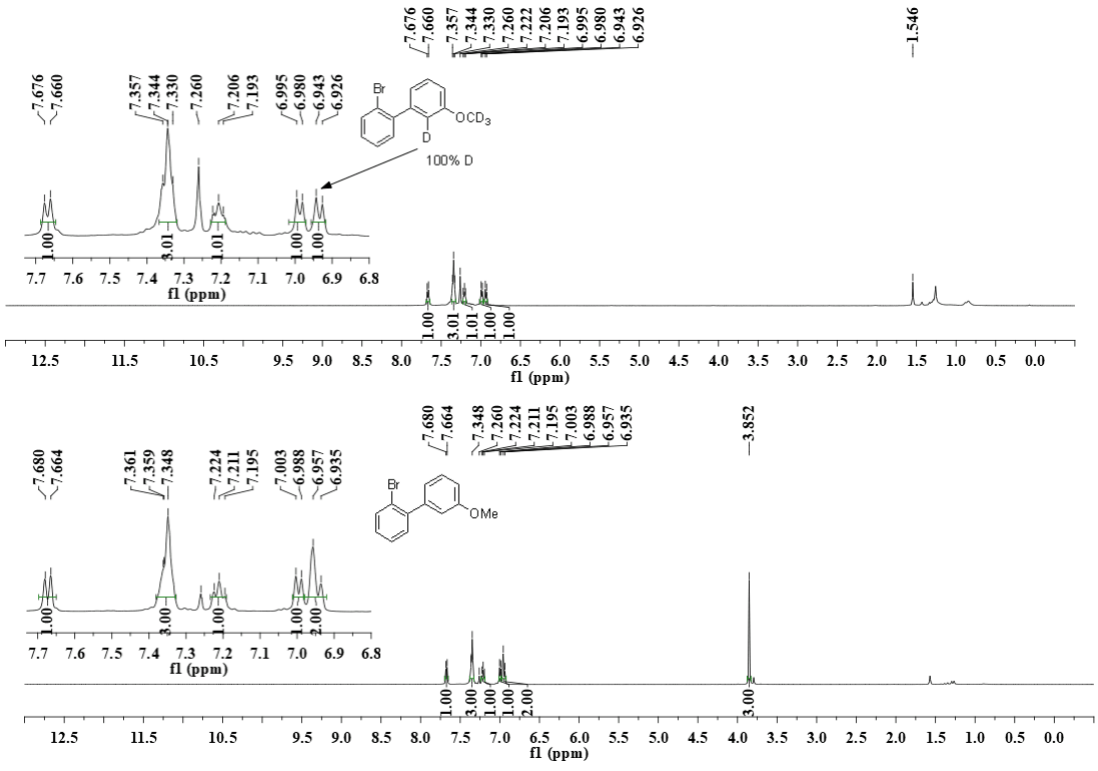
The mixture of **1a-**OTs (0.1 mmol), D_2O (5 equiv), Cs_2CO_3 (3 equiv) and DCM (1 mL) was stirred at room temperature for 12 hours. After the reaction was completed, the mixture was passed through a silica gel column (200–300 mesh), eluting with petroleum ether/EtOAc (40/1, v/v) to afford deuterium ***d*-di-3q** (23 mg, 95% yield). ^{1}H NMR analysis showed that > 90% hydrogen at the *ortho* position of the biphenyl was deuterated.

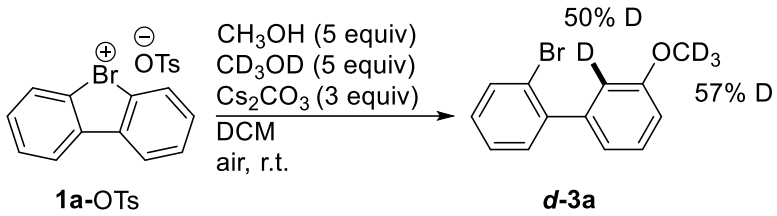




1a-OTs ***d*-3a**

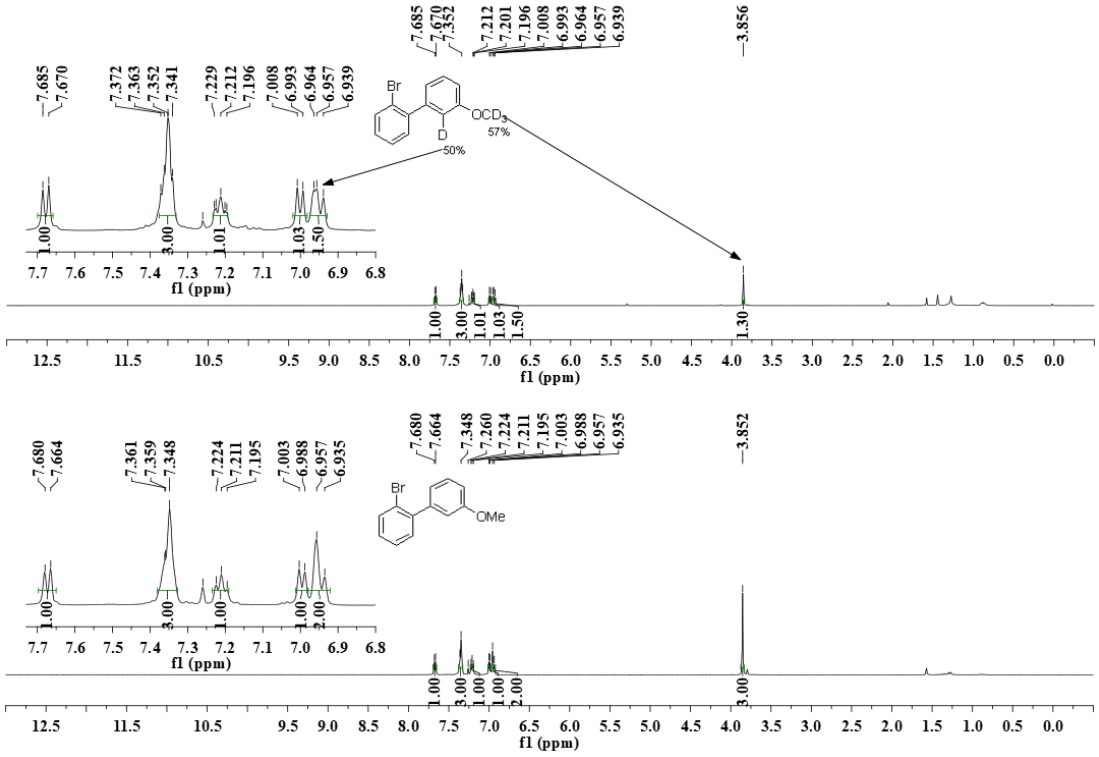
The mixture of **1a**-OTs (0.1 mmol), methanol-*d*4 (5 equiv), Cs_2CO_3 (3 equiv) and DCM (1 mL) was stirred at room temperature for 12 hours. After the reaction was completed, the mixture was passed through a silica gel column (200–300 mesh), eluting with petroleum ether/EtOAc (40/1, v/v) to afford corresponding deuterium ***d*-3a**. ^{1}H NMR analysis showed that 100% (> 95%) hydrogen at the *ortho* position of the biphenyl was deuterated.





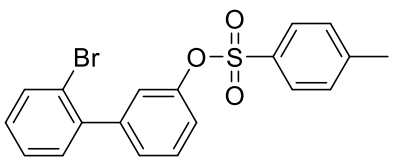
1a-OTs ***d*-3a**

The mixture of **1a-**OTs (0.1 mmol), methanol-*d*4 (5 equiv), methanol (5 equiv), Cs_2CO_3 (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**. ^{1}H 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

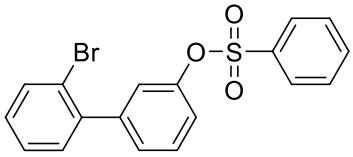
2'-bromo-[1,1'-biphenyl]-3-yl 4-methylbenzenesulfonate (2a)



Yellow oil (29 mg, 72% yield, *m:o* = 15:1). **^{1}H NMR (500MHz, $CDCl_3$):** 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. **^{13}C NMR (125**

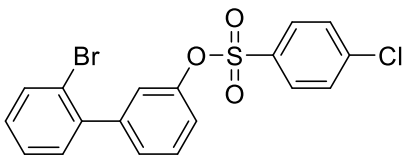
MHz, $CDCl_3$): δ = 149.30, 145.51, 142.72, 141.08, 133.29, 132.45, 131.21, 129.96, 129.37, 129.35, 128.78, 128.26, 127.57, 123.62, 122.46, 121.80, 21.84 ppm. **HRMS (ESI)** ***m/z*:** calcd for $C_{19}H_{16}BrO_3S$ (M+H) 403.0004, found 403.0006.

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



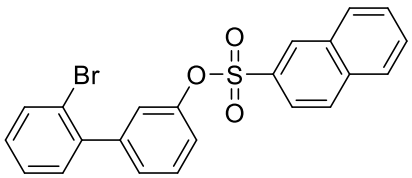
Yellow oil (27 mg, 69% yield, *m:o* > 20:1). **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.87 (d, *J* = 7.5 Hz, 2H), 7.67–7.61 (m, 2H), 7.53 (t, *J* = 7.3 Hz, 2H), 7.37–7.31 (m, 2H), 7.27 (d, *J* = 8.5 Hz, 1H, cover the solvent), 7.20 (t, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.00 (s, 1H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** 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 $C_{18}H_{14}BrO_3S$ (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). **^{1}H NMR (500MHz, $CDCl_3$):** 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. **^{13}C NMR (125 MHz, $CDCl_3$):** 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 $C_{18}H_{13}BrClO_3S$ (M+H) 422.9457, found 422.9459.

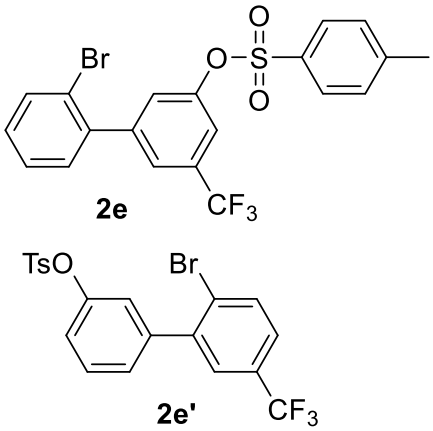
2'-bromo-[1,1'-biphenyl]-3-yl naphthalene-2-sulfonate (2d)



Yellow oil (28 mg, 60% yield, *m:o* > 20:1). **^{1}H NMR (500MHz, $CDCl_3$):** 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,

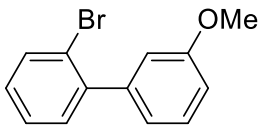
1H), 7.54 (d, J = 8.0 Hz, 1H), 7.34 (t, J = 7.8 Hz, 1H), 7.25–7.23 (m, 2H), 7.16–7.12 (m, 2H), 7.06 (d, J = 7.5 Hz, 1H), 6.97 (s, 1H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 149.27, 142.73, 140.92, 135.61, 133.21, 132.17, 131.99, 131.14, 130.84, 129.77, 129.74, 129.59, 129.43, 129.30, 128.34, 128.13, 128.00, 127.50, 123.53, 123.08, 122.33, 121.84 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{22}H_{16}BrO_3S$ (M+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). **^{1}H NMR (500MHz, $CDCl_3$, major):** δ = 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):** δ = 149.27, 146.10, 143.60, 139.66, 133.49, 131.99 (q, $J_{C\text{-}F}$ = 33.0 Hz), 131.92, 131.09, 130.14, 130.07, 128.77, 127.85, 127.21, 125.09 (q, $J_{C\text{-}F}$ = 3.4 Hz), 123.22 (q, $J_{C\text{-}F}$ = 271.3 Hz), 122.25, 119.03 (q, $J_{C\text{-}F}$ = 3.5 Hz), 21.83 ppm. **^{19}F NMR (471 MHz, $CDCl_3$, major):** δ = -62.69 (s) ppm. **HRMS (ESI) *m/z*:** calcd for $C_{20}H_{15}BrF_3O_3S$ (M+H) 470.9877, found 470.9878.

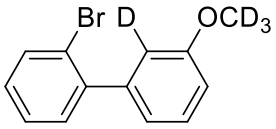
2-bromo-3'-methoxy-1,1'-biphenyl (3a)[2]



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). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 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, $CDCl_3$):** δ = 159.24, 142.57, 142.55,

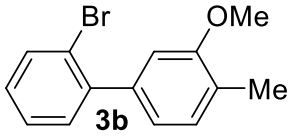
133.25, 131.33, 129.14, 128.91, 127.46, 122.67, 121.95, 115.18, 113.35, 55.43 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{13}H_{12}BrO$ (M+H) 263.0072, found 263.0074. The NMR data are consistent with the reference.[2]

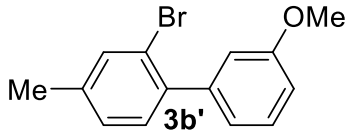
2-bromo-3'-(methoxy-*d*$_3$)-1,1'-biphenyl-2'-*d* (*d*-3a)



Yellow oil (26 mg, 97% yield), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 40/1, v/v). **^{1}H 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, $J_{C\text{-}D}$ = 5.6 Hz), 142.52 ($J_{C\text{-}D}$ = 9.3 Hz), 142.48, 133.26, 131.34, 129.14, 128.92, 127.47, 122.69, 121.92, 115.20 ($J_{C\text{-}D}$ = 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.

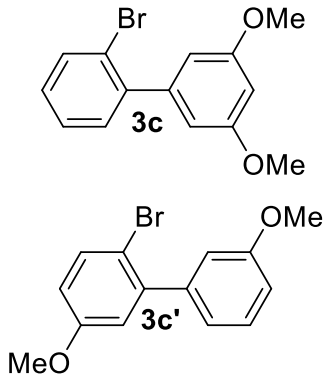
2-bromo-3'-methoxy-4'-methyl-1,1'-biphenyl (3b) and 2-bromo-3'-methoxy-4-methyl-1,1'-biphenyl (3b')





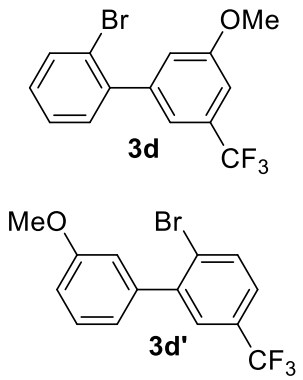
Yellow oil (29 mg, 70% yield, **3b**:**3b′** = 3:2, *m:o*>20:1), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 40/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$, isomers):** δ = 7.67 (d, J = 8.0 Hz, 1H), 7.50 (s, 0.67H), 7.35–7.33 (m, 2.67H), 7.23–7.17 (m, 3.33H), 6.98 (d, J = 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')



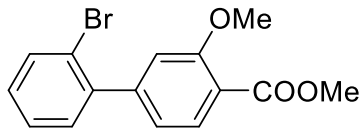
Yellow oil (18 mg, 61% yield, **3c**:**3c′** = 1:2), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 20/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$, isomers):** δ = 7.67 (d, J = 8.0 Hz, 0.5H), 7.54 (d, J = 8.5 Hz, 1H), 7.37–7.34 (m, 2.5H), 7.21–7.19 (m, 0.5H), 7.00 (d, J = 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. **^{13}C NMR (125 MHz, $CDCl_3$, 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 $C_{14}H_{14}BrO_2$ (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′)



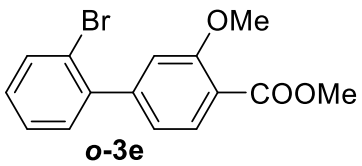
Yellow oil (32 mg, 96% yield, **3d**:**3d′** = 10:1), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 40/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$, major):** δ = 7.69 (d, J = 8.0 Hz, 1H), 7.40–7.37 (m, 1H), 7.34–7.32 (m, 1H), 7.26–7.23 (m, 2H, cover the solvent), 7.16 (s, 1H), 7.14 (s, 1H), 3.89 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$, major):** δ = 159.46, 143.19, 141.18, 133.43, 131.67 (q, $J_{C\text{-}F}$ = 32.1 Hz), 131.21, 129.55, 127.68, 124.04 (q, $J_{C\text{-}F}$ = 270.9 Hz), 122.45, 118.82, 118.73 (q, $J_{C\text{-}F}$ = 3.8 Hz), 110.11 (q, $J_{C\text{-}F}$ = 3.6 Hz), 55.77 ppm. **^{19}F NMR (471 MHz, $CDCl_3$, major):** δ = -62.56 (s) ppm. **HRMS (ESI) *m/z*:** calcd for $C_{14}H_{11}BrF_3O$ (M+H) 330.9945, found 330.9947.

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

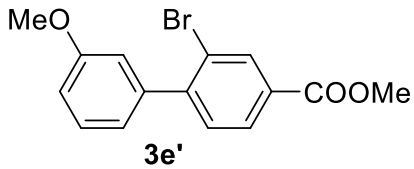


Yellow oil (23.7 mg, 74% yield), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 20/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.86 (d, *J* = 7.5 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.34–7.32 (m, 1H), 7.24 (t, *J* = 7.5 Hz, 1H, cover the solvent), 7.03 (s, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 3.94 (s, 3H), 3.92 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** 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 $C_{15}H_{14}BrO_2$ (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′)



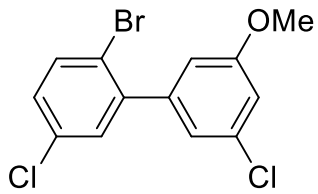
***o*-3e**



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). **^{1}H NMR (500 MHz, $CDCl_3$, 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. **^{13}C NMR (125 MHz, $CDCl_3$, 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 $C_{15}H_{14}BrO_3$ (M+H) 321.0126, found 321.0125.

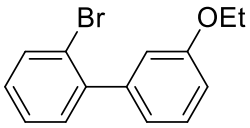
2-bromo-3',5-dichloro-5'-methoxy-1,1'-biphenyl (3f)



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). **^{1}H NMR (500 MHz, $CDCl_3$):** 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. **^{13}C**

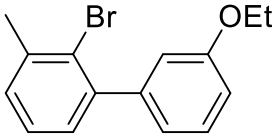
NMR (125 MHz, $CDCl_3$): δ = 159.81, 143.65, 141.07, 133.22, 131.04, 129.26, 127.45, 124.77, 122.33, 122.27, 116.38, 114.45, 55.62 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{13}H_{10}BrCl_2O$ (M+H) 330.9287, found 330.9285.

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



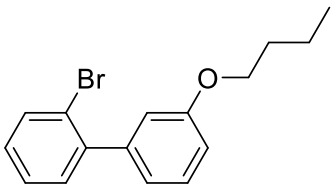
Yellow oil (27 mg, 97% yield, *m:o* > 20:1), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 40/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.67 (d, *J* = 8.5 Hz, 1H), 7.37–7.32 (m, 3H), 7.22–7.19 (m, 1H), 6.99–6.92 (m, 3H), 4.08 (q, *J* =7.0 Hz, 2H), 1.44 (t, *J* =7.0 Hz, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** 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 $C_{14}H_{14}BrO$ (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) **^{1}H NMR (500 MHz, $CDCl_3$):** 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. **^{13}C NMR (125 MHz, $CDCl_3$):** 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 $C_{15}H_{16}BrO$ (M+H) 291.0385, found 291.0383.

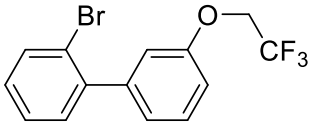
2-bromo-3'-butoxy-1,1'-biphenyl (3i)



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). **^{1}H NMR (500 MHz, $CDCl_3$):** 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,

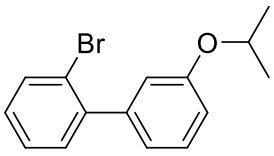
2H), 0.98 (t, *J* = 7.5 Hz, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 158.84, 142.67, 142.51, 133.23, 131.35, 129.08, 128.86, 127.44, 122.69, 121.74, 115.70, 114.03, 67.88, 31.50, 19.41, 14.03 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{16}H_{18}BrO$ (M+H) 305.0541, found 305.0544.

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). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 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, $CDCl_3$):** δ = 157.05, 142.89, 141.95, 133.32, 131.27, 129.48, 129.19, 127.57, 123.79, 123.47 (q, $J_{C\text{-}F}$ = 276.1 Hz), 122.56, 116.10, 114.38, 66.02 (q, $J_{C\text{-}F}$ = 35.3 Hz) ppm. **^{19}F NMR (471 MHz, $CDCl_3$):** δ = -73.91 (s) ppm. **HRMS (ESI) *m/z*:** calcd for $C_{14}H_{11}BrF_3O$ (M+H) 330.9945, found 330.9946.

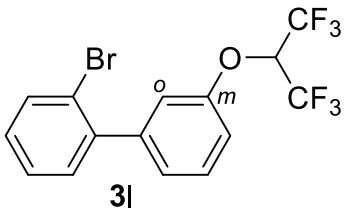
2-bromo-3'-isopropoxy-1,1'-biphenyl (3k)



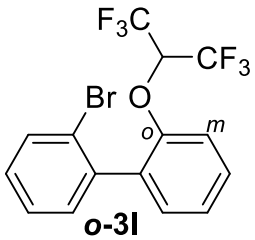
Yellow oil (28 mg, 99% yield, *m:o* > 20:1), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 40/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.67 (d, *J* = 7.5 Hz, 1H), 7.35–7.32 (m, 3H), 7.22–7.19 (m, 1H), 6.97–6.92 (m, 3H), 4.62–4.57 (m, 1H), 1.38 (d, *J* = 6.0 Hz, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 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 $C_{15}H_{16}BrO$ (M+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)



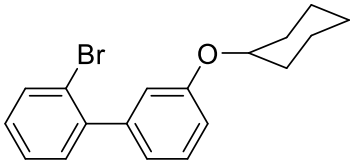
3l



***o*-3l**

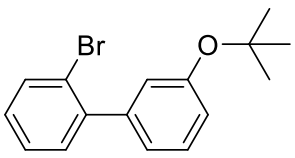
gel column (petroleum ether/EtOAc = 40/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$, isomers):** δ = 7.68 (d, J = 7.0 Hz, 1.33 H), 7.42 (t, J = 8.0 Hz, 1H), 7.39–7.36 (m, 1.66H), 7.32–7.29 (m, 1.33H), 7.26–7.20 (m, 2.66H), 7.15 (s, 1H), 7.11 (dd, J = 8.5 Hz, 1.5Hz, 1H), 7.04–7.01 (m, 0.66H), 5.01–4.96 (m, 0.33H), 4.87–4.83 (m, 1H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$, 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, $J_{C\text{-}F}$ = 311.5 Hz), 122.38, 118.64, 116.67, 116.32, 114.54, 76.69 (heptet, $J_{C\text{-}F}$ = 33.0 Hz, cover the solvent) ppm. **^{19}F NMR (471 MHz, $CDCl_3$, isomers):** δ = -64.58 (d), -73.48 (t) ppm. **HRMS (ESI) *m/z*:** calcd for $C_{15}H_{10}BrF_6O$ (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). **^{1}H NMR (500 MHz, $CDCl_3$):** 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. **^{13}C NMR (125 MHz, $CDCl_3$):** 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 $C_{18}H_{20}BrO$ (M+H) 331.0698, found 331.0696.

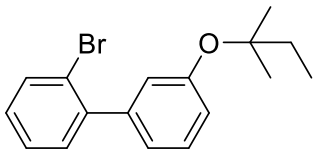
2-bromo-3'-(*tert*-butoxy)-1,1'-biphenyl (3n)



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). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.66 (d, J =

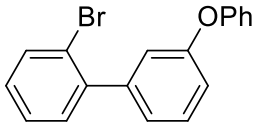
8.0 Hz, 1H), 7.33–7.30 (m, 3H), 7.21–7.20 (m, 1H), 7.10–7.07 (m, 2H), 7.02–7.01 (m, 1H), 1.38 (s, 9H) ppm. **^{13}C NMR (125 MHz, CDCl$_3$):** δ = 155.04, 142.47, 141.99, 133.21, 131.34, 128.85, 128.57, 127.46, 125.43, 124.42, 123.56, 122.76, 78.96, 29.07 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{16}H_{18}BrO$ (M+H) 305.0541, found 305.0544.

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



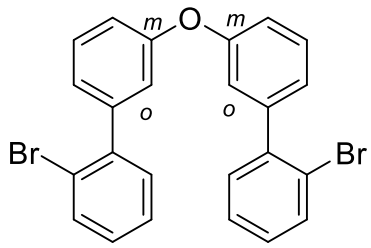
Yellow oil (23 mg, 70% yield, *m:o* > 20:1), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 40/1, v/v). **^{1}H NMR (500 MHz, CDCl$_3$):** δ = 7.66 (d, *J* = 8.0 Hz, 1H), 7.35–7.29 (m, 3H), 7.21–7.18 (m, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.05 (s, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 1.71 (q, *J* = 7.3 Hz, 2H), 1.30 (s, 6H), 1.02 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR (125 MHz, CDCl$_3$):** 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 $C_{17}H_{20}BrO$ (M+H) 319.0698, found 319.0700.

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



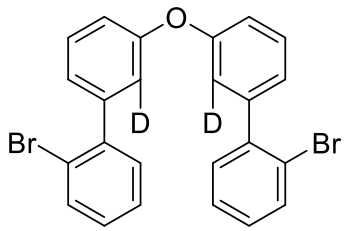
Yellow oil (29 mg, 90% yield, *m:o* = 10:1), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 40/1, v/v). **^{1}H NMR (500 MHz, CDCl$_3$):** δ = 7.65 (d, *J* = 7.5 Hz, 1H), 7.41–7.33 (m, 5H), 7.21–7.18 (m, 1H), 7.13 (t, *J* = 8.5 Hz, 2H), 7.09–7.04 (m, 4H) ppm. **^{13}C NMR (125 MHz, CDCl$_3$):** 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 $C_{18}H_{14}BrO$ (M+H) 325.0228, found 325.0224.

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



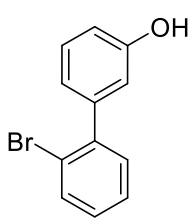
Yellow oil (23 mg, 96% yield, *m,m:others* = 5:1), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 40/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$, major):** δ = 7.64 (d, J = 8.0 Hz, 2H), 7.40 (t, J = 7.8 Hz, 2H), 7.34–7.33 (m, 4H), 7.20–7.18 (m, 2H), 7.15–7.09 (m, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$, 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. $C_{18}H_{14}BrO$ (M+H) 325.0228, found 325.0224. **HRMS (ESI) *m/z*:** calcd for $C_{24}H_{17}Br_2O$ (M+H) 480.9626, found 480.9636 .

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



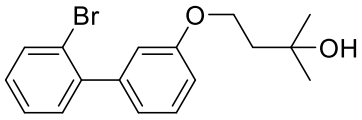
Yellow oil (24 mg, 95% yield), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 40/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.64 (d, J = 8.0 Hz, 2H), 7.40 (t, J = 7.8 Hz, 2H), 7.36–7.33 (m, 4H), 7.21–7.18 (m, 2H), 7.14–7.13 (m, 2H), 7.10 (d, J = 8.5 Hz, 2H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 156.78 (d, $J_{C\text{-}D}$ = 6.3 Hz), 142.86 (d, $J_{C\text{-}D}$ = 11.0 Hz), 142.00 (d, $J_{C\text{-}D}$ = 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 $C_{24}H_{15}D_2Br_2O$ (M+H) 482.9746, found 482.9744.

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



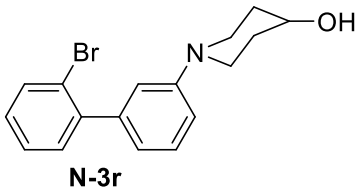
Colourless oil (12 mg, 48% yield). **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.66 (d, J = 8.0 Hz, 1H), 7.37–7.29 (m, 3H), 7.20 (t, J = 7.5 Hz, 1H), 6.97 (d, J = 7.5 Hz, 2H), 6.88–6.86 (m, 2H), 4.99 (s, 1H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 155.16, 142.79, 142.23, 133.24, 131.29, 129.40, 128.97, 127.47, 122.59, 122.15, 116.58, 114.72 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{12}H_{10}BrO$ (M+H) 248.9915, found 248.9910.

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

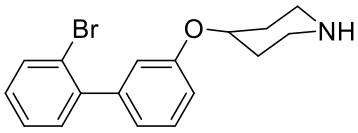


Yellow oil (30 mg, 90% yield, *m:o* = 15:1), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 10/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.66 (d, *J* =8.0 Hz, 1H), 7.35–7.34 (m, 3H), 7.22–7.19 (m, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.97–6.94 (m, 2H), 4.23 (t, *J* = 5.8 Hz, 2H), 2.35 (s, 1H), 2.02 (t, *J* = 6.0 Hz, 2H), 1.32 (s, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** 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 $C_{17}H_{20}BrO$ (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

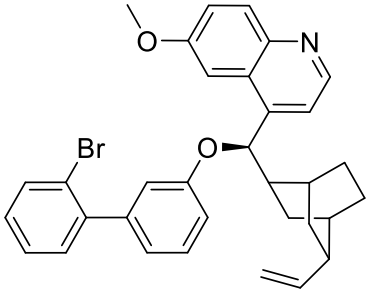


O-3r

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). **^{1}H NMR (500 MHz, $CDCl_3$, major):** δ = 7.66 (d, *J* = 8.0 Hz, 1H), 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. **^{13}C NMR (125 MHz, $CDCl_3$, 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 $C_{17}H_{19}BrNO$ (M+H) 332.0650, found 332.0653.

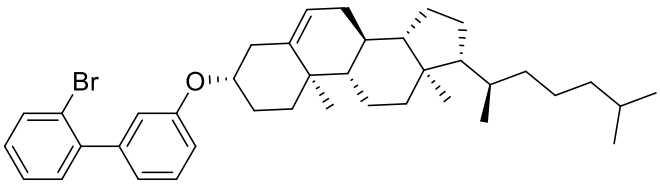
4-((1*R*)-((2'-bromo-[1,1'-biphenyl]-3-yl)oxy)(5-vinylbicyclo[2.2.2]octan-2-yl)methyl)-6-methoxyquinoline (5)

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). **^{1}H NMR (500 MHz, $CDCl_3$):** 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. **^{13}C NMR (125 MHz, $CDCl_3$):** 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 $C_{33}H_{33}BrNO_2$ (M+H) 554.1695, found 554.1699.

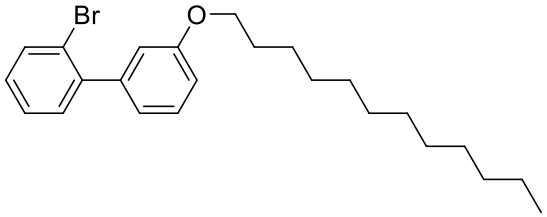
(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-3-((2'-bromo-[1,1'-biphenyl]-3-yl)oxy)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthrene (6)



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). **^{1}H NMR (500 MHz, $CDCl_3$):** 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. **^{13}C NMR (125 MHz, $CDCl_3$):** 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,

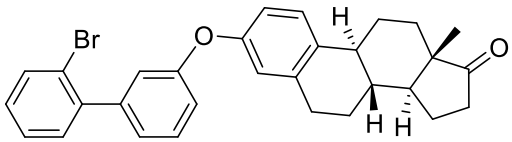
22.71, 21.17, 19.47, 18.86, 12.00 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{39}H_{54}BrO$ (M+H) 617.3358, found 617.3355.

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). **^{1}H 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.

(8*R*,9*S*,13*S*,14*S*)-3-((2'-bromo-[1,1'-biphenyl]-3-yl)oxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (8)



Yellow oil (40 mg, 80% yield, *m:o* > 20:1). **^{1}H 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.

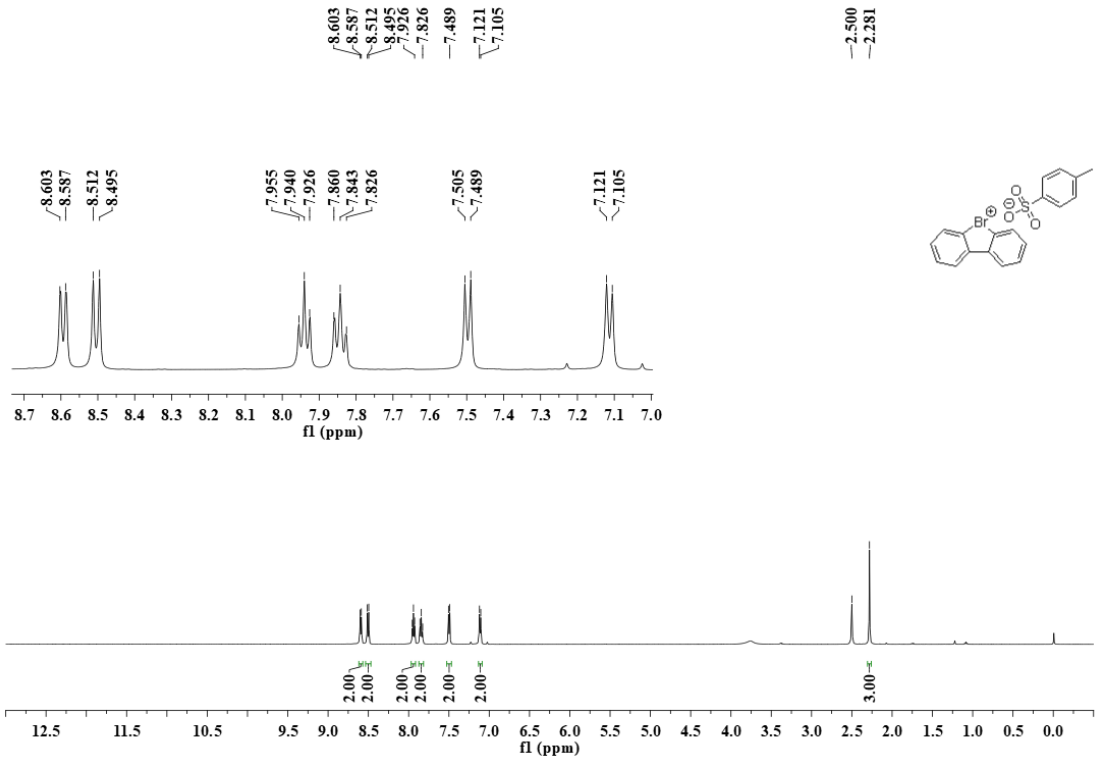
5. References

[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.

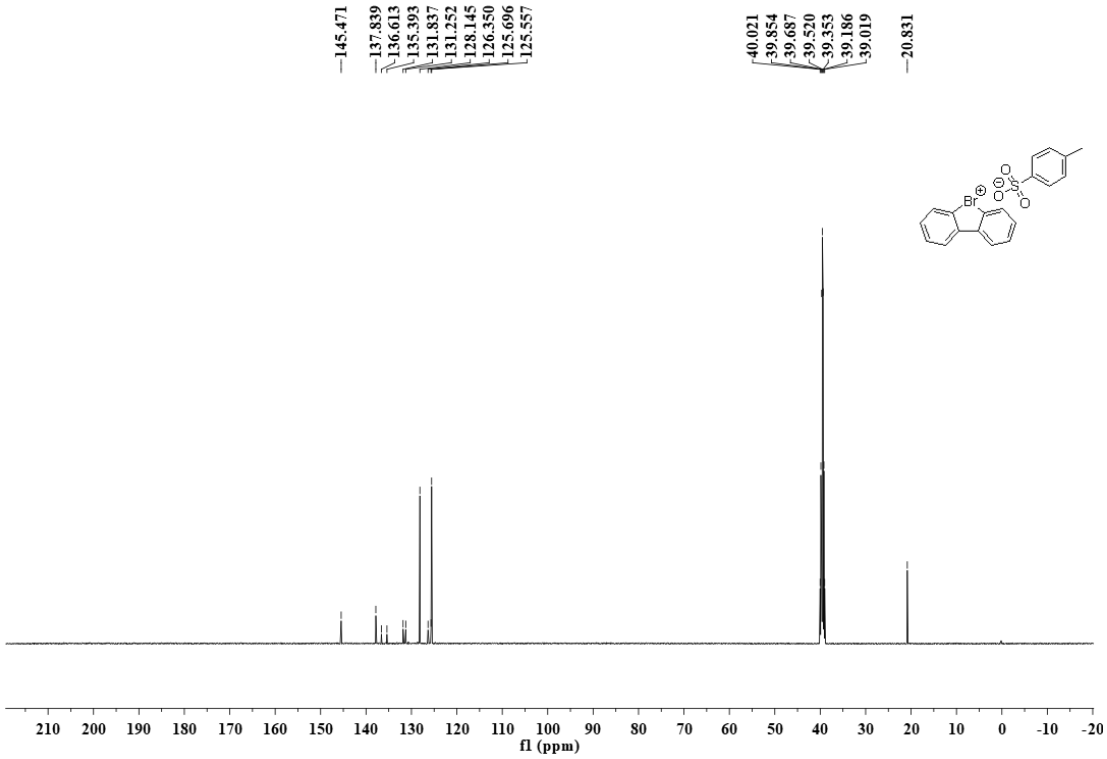
[2] Z. Jiang, K. Sekine, Y. Kuninobu, Synthesis of Fluorenes and Their Related Compounds from Biaryls and Meldrum's Acid Derivatives, *Chem. Commun.*, **2022**, *58*, 843–846.

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

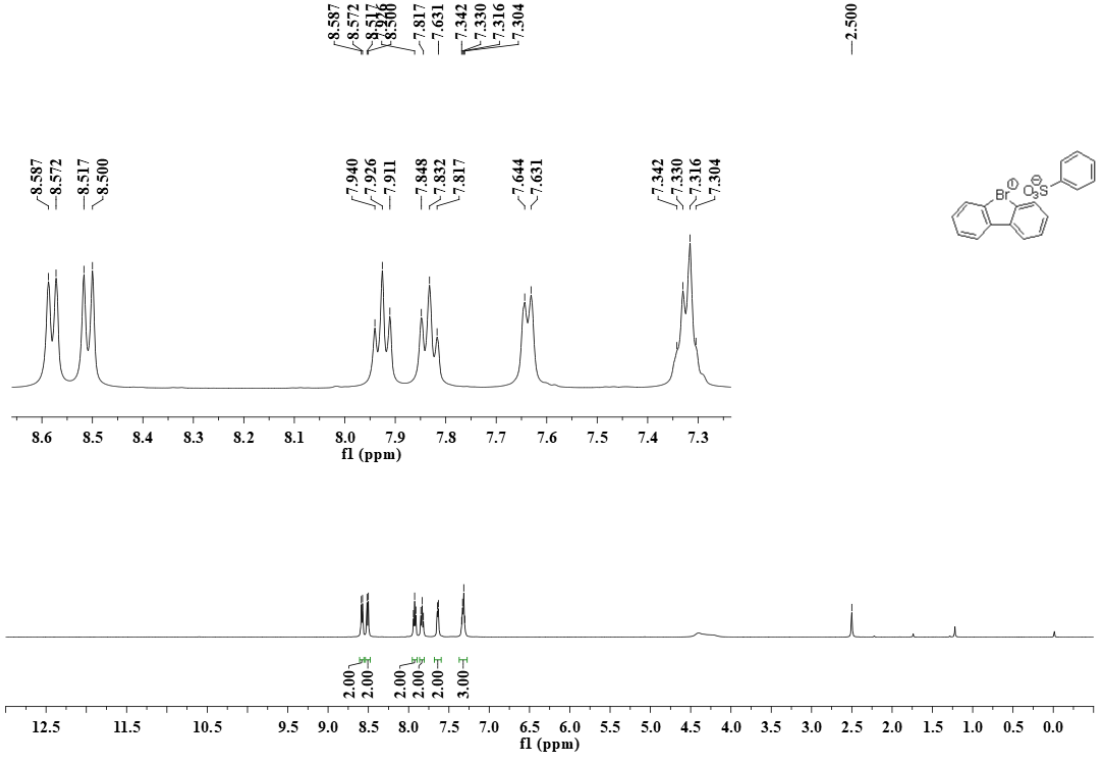
^{1}H NMR (500 MHz, DMSO-d_6) of **1a**-OTs



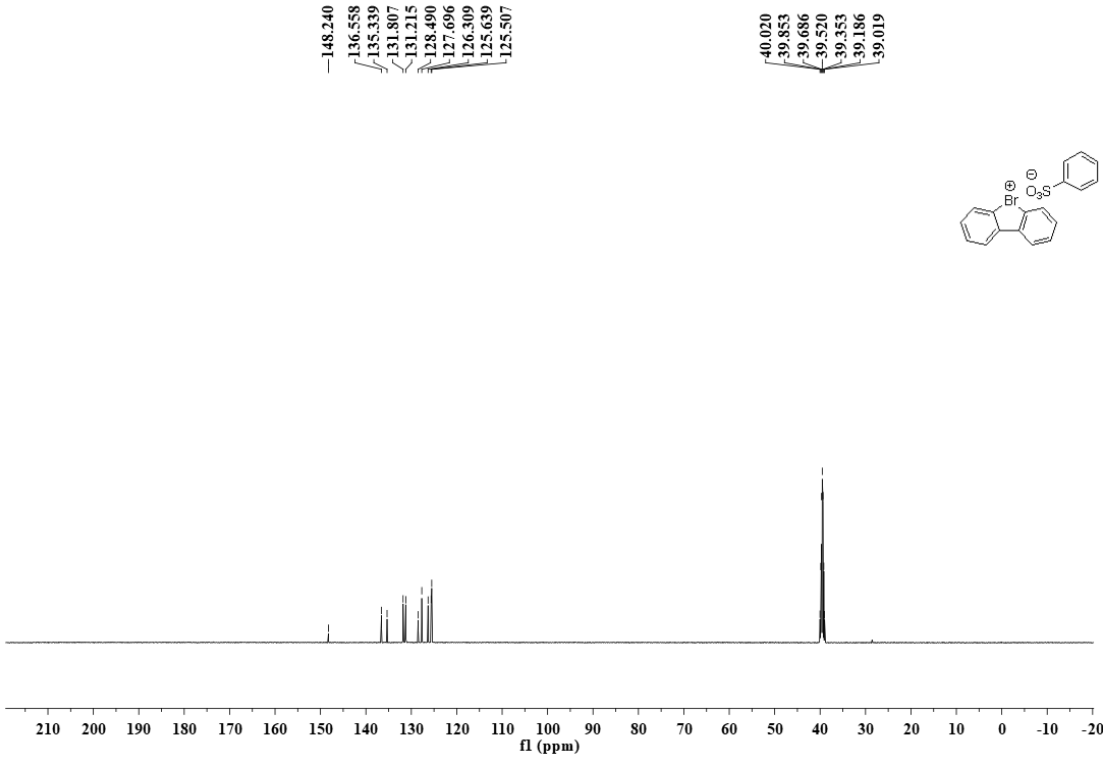
^{13}C NMR (125 MHz, DMSO-d_6) of **1a**-OTs



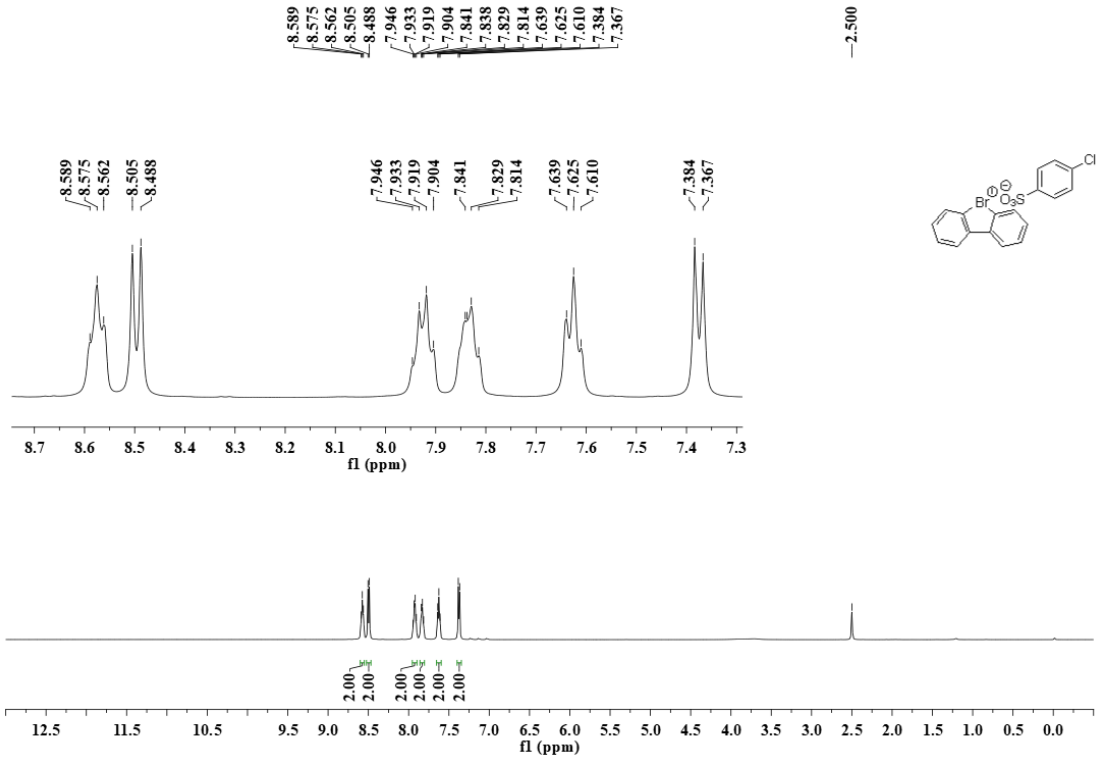
^{1}H NMR (500 MHz, DMSO-d_6) of **1a**-OBs



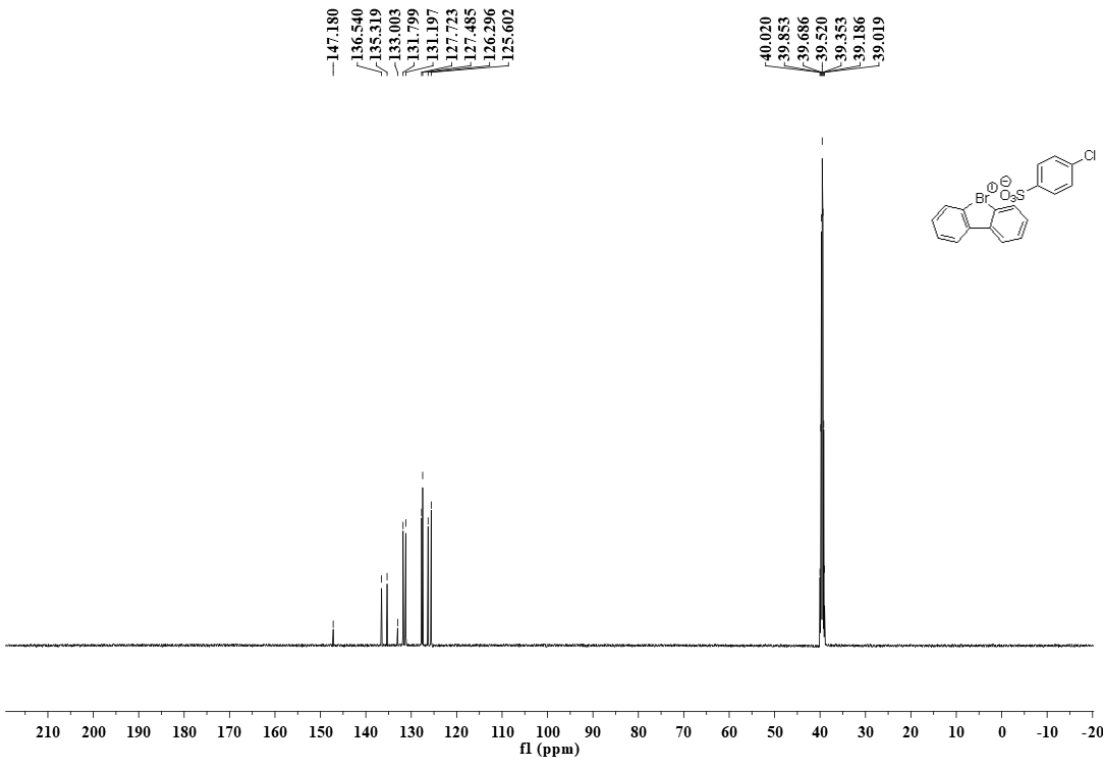
^{13}C NMR (125 MHz, DMSO-d_6) of **1a**-OBs



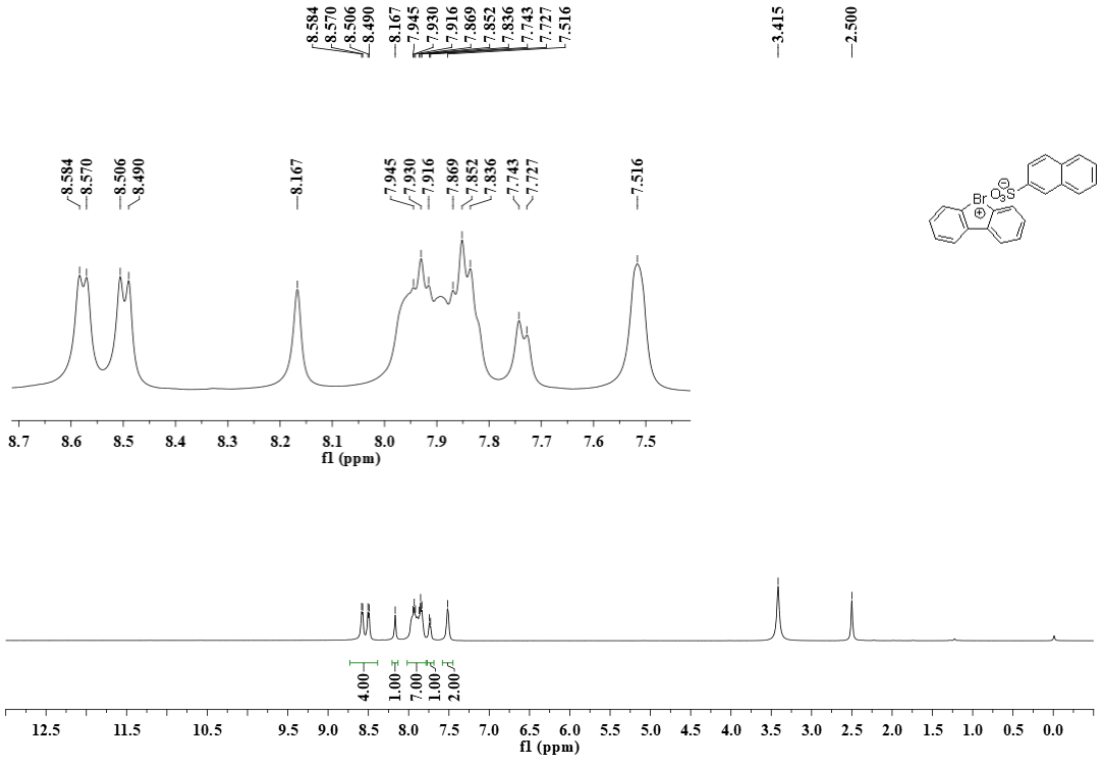
^{1}H NMR (500 MHz, DMSO-d_6) of **1a**-OCs



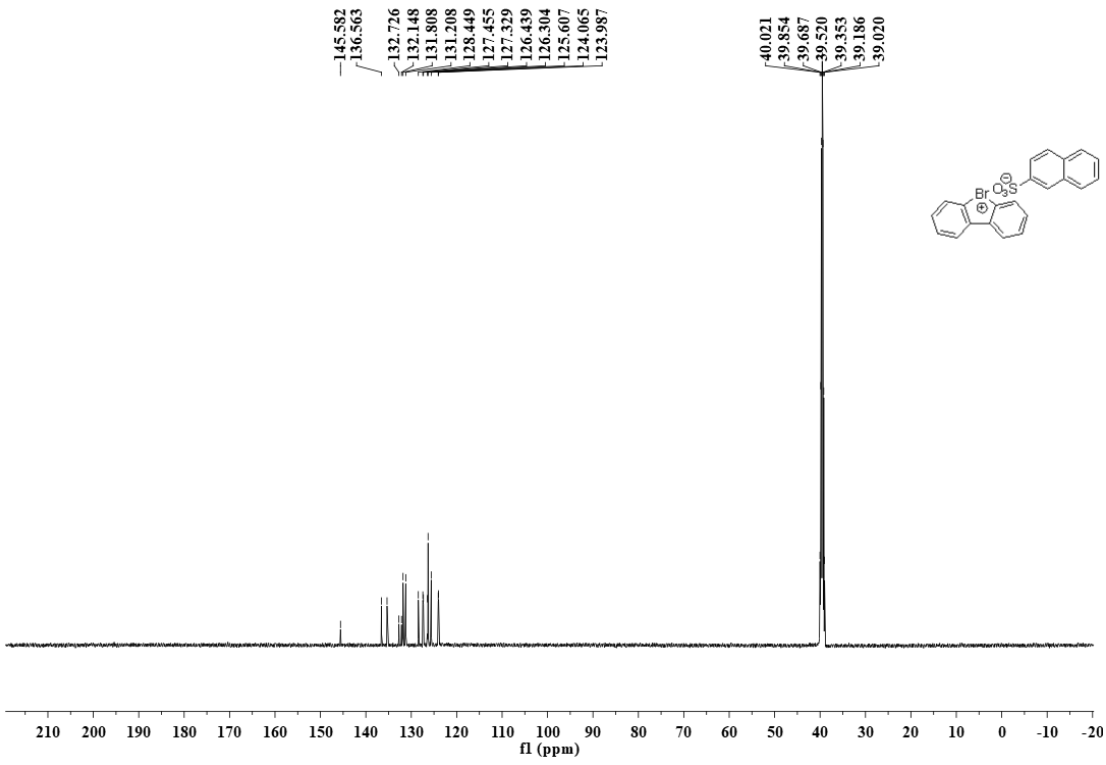
^{13}C NMR (125 MHz, DMSO-d_6) of **1a**-OCs



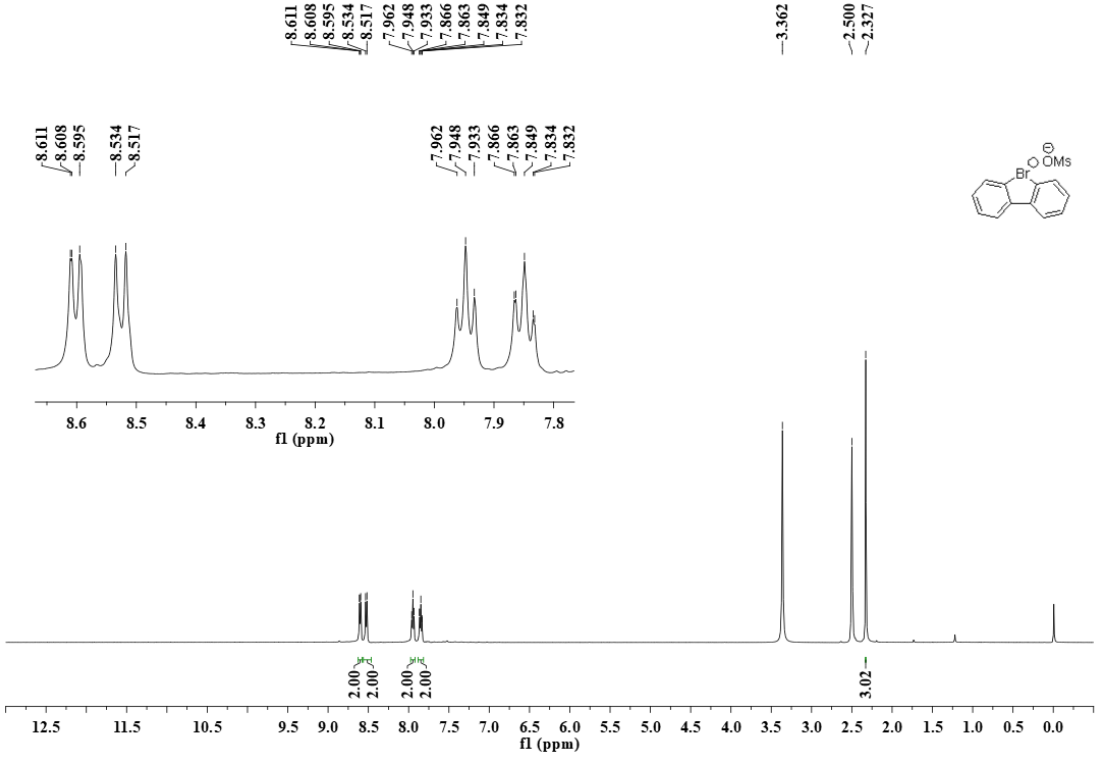
^{1}H NMR (500 MHz, DMSO-d_6) of **1a**-ONs



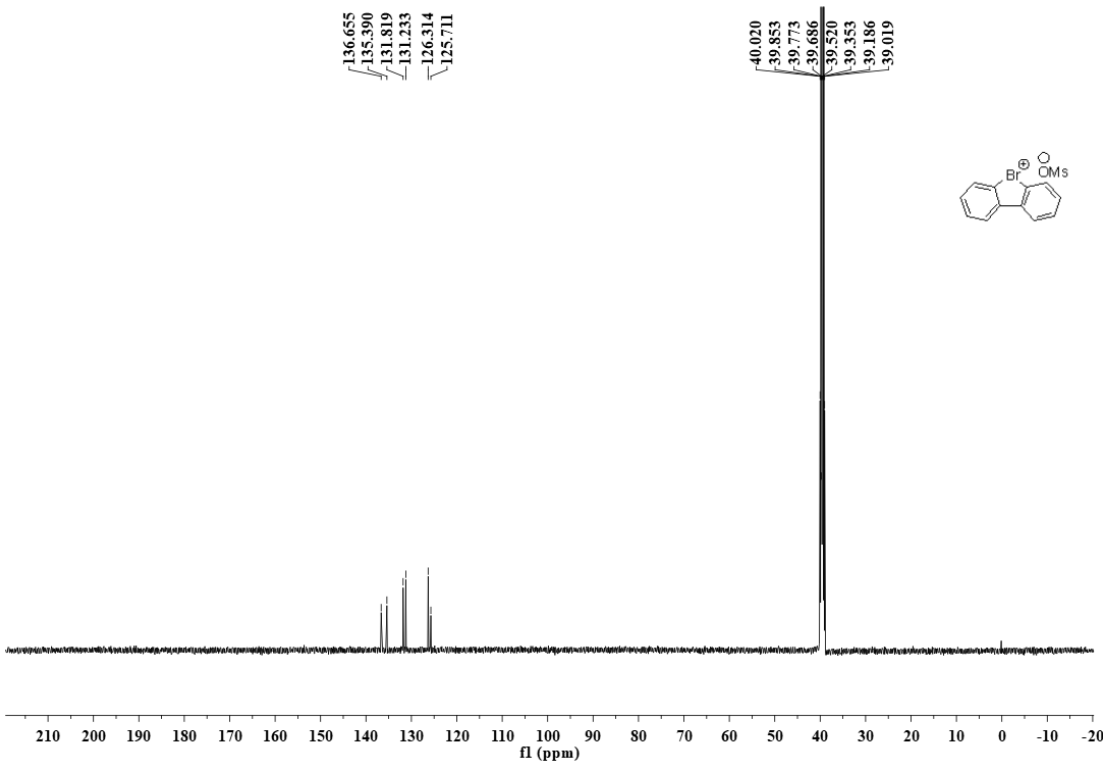
^{13}C NMR (125 MHz, DMSO-d_6) of **1a**-ONs



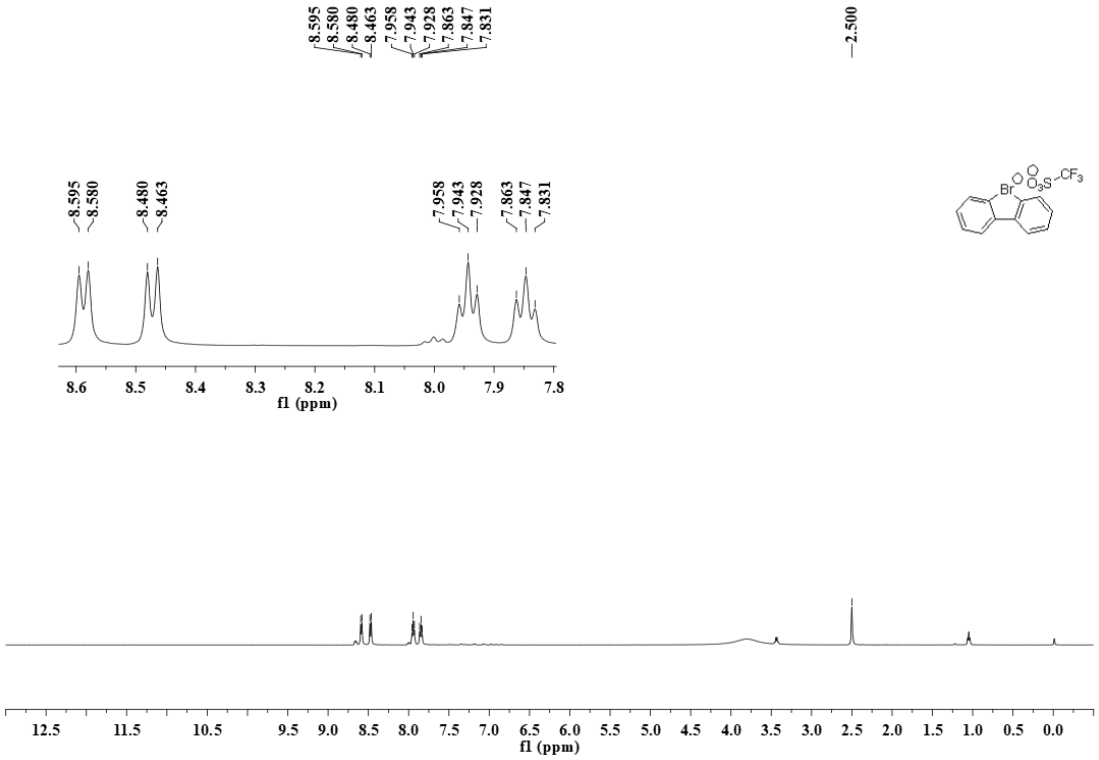
^{1}H NMR (500 MHz, DMSO-d_6) of **1a**-OMs



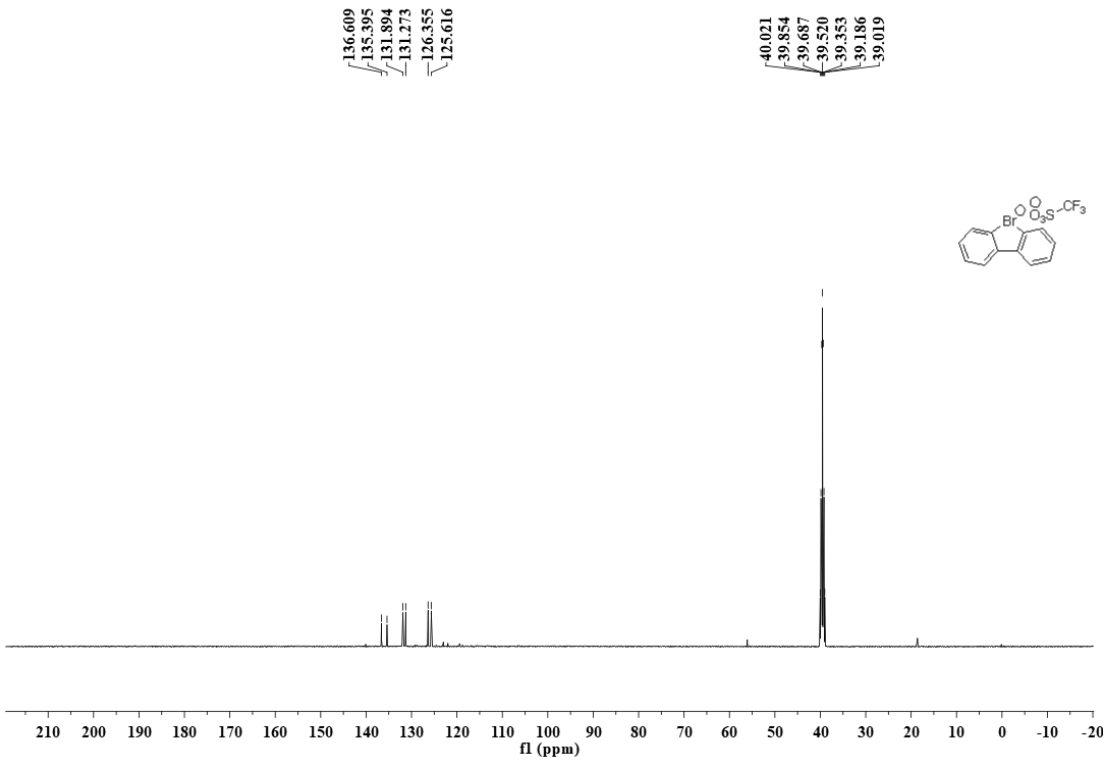
^{13}C NMR (125 MHz, DMSO-d_6) of **1a**-OMs



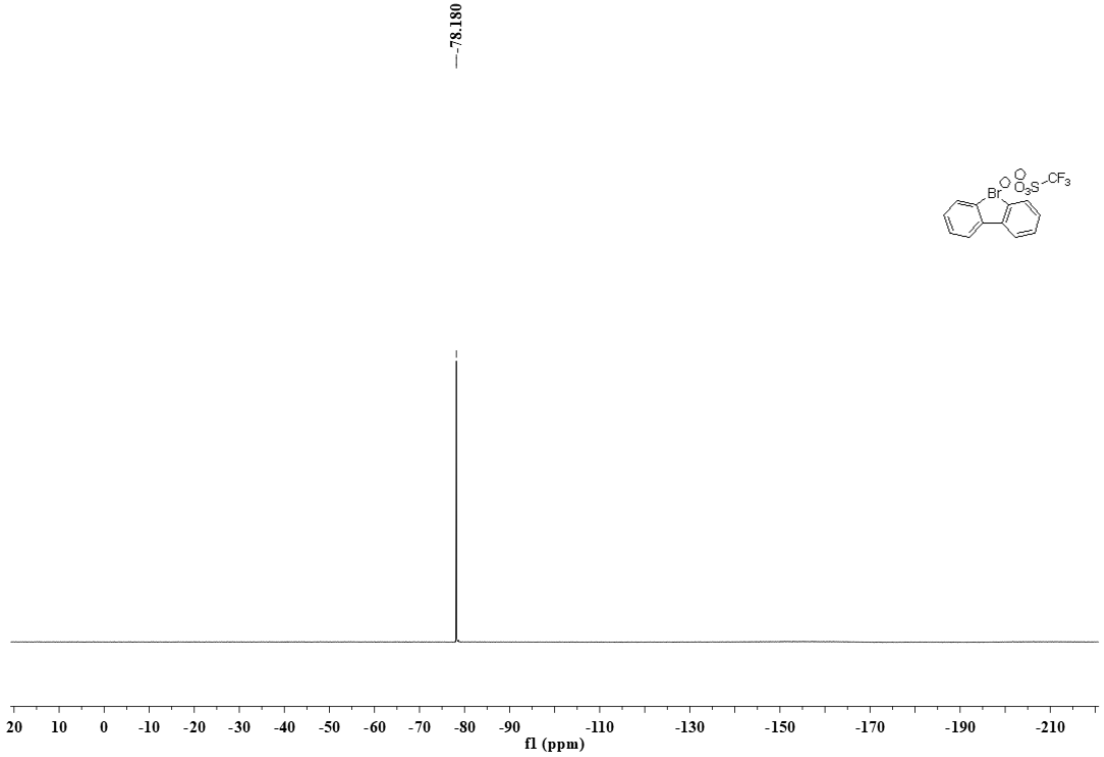
^{1}H NMR (500 MHz, DMSO-d_6) of **1a**-OTf



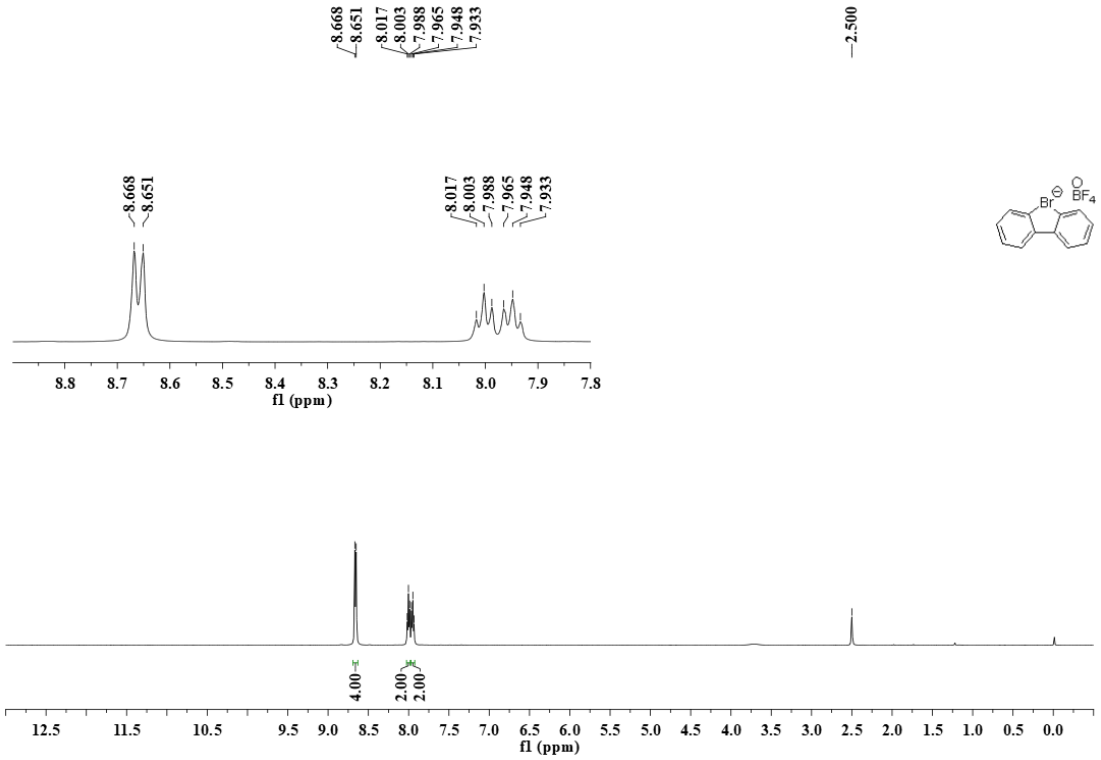
^{13}C NMR (125 MHz, DMSO-d_6) of **1a**-OTf



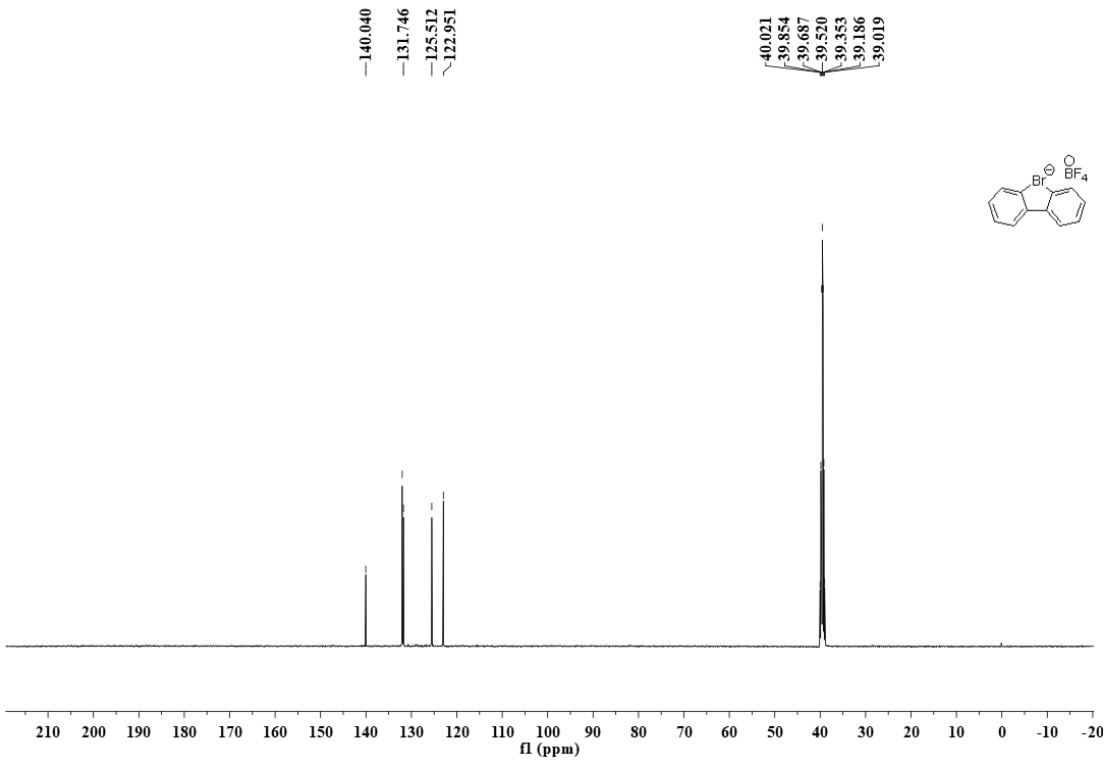
^{19}F NMR (471 MHz, DMSO-d_6) of **1a**-OTf



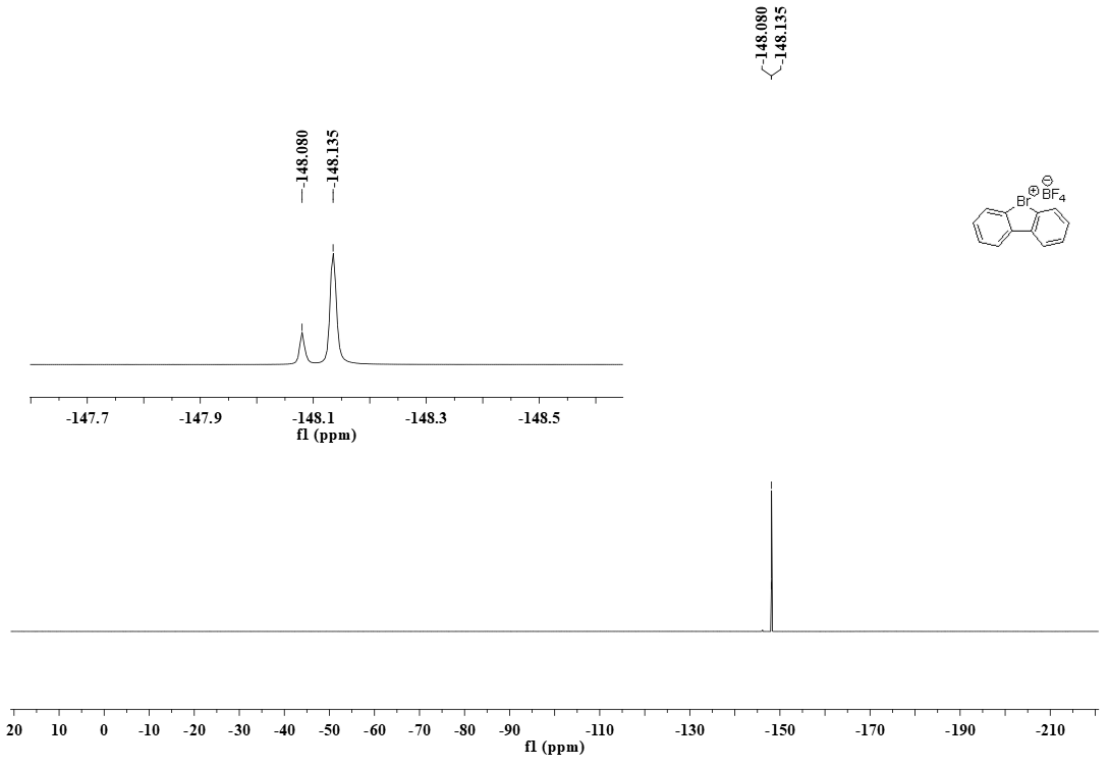
^{1}H NMR (500 MHz, DMSO-d_6) of **1a**-BF_4



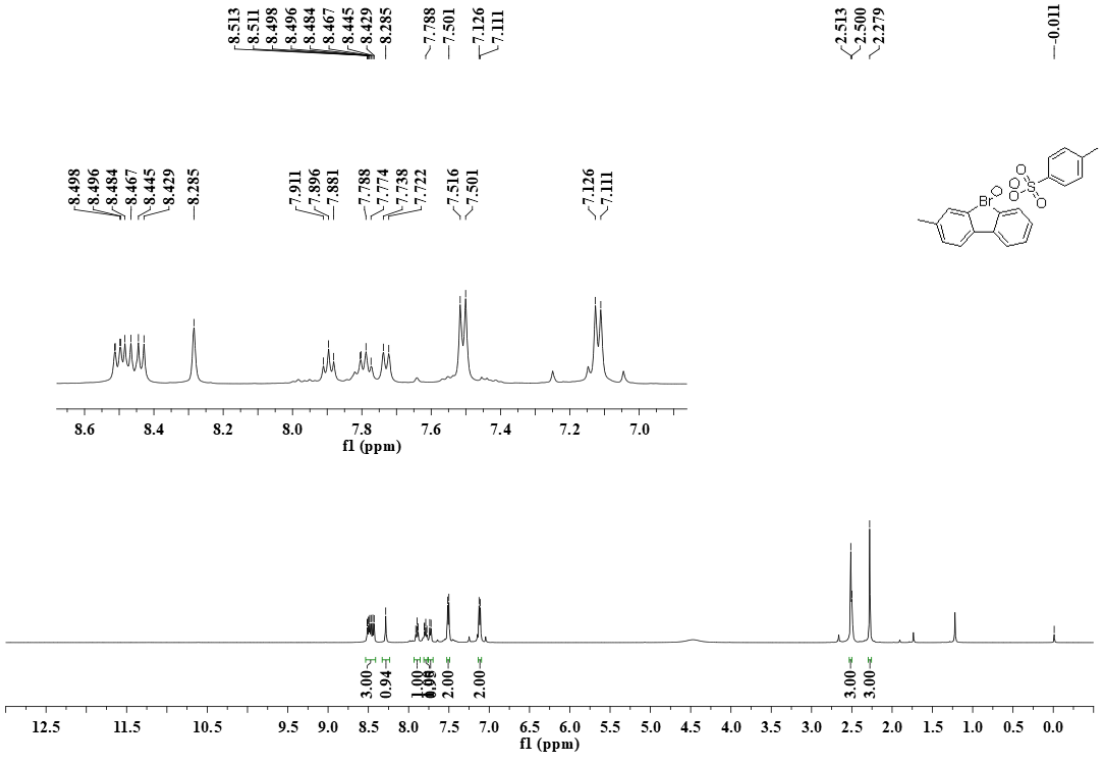
^{13}C NMR (125 MHz, DMSO-d_6) of **1a**-BF_4



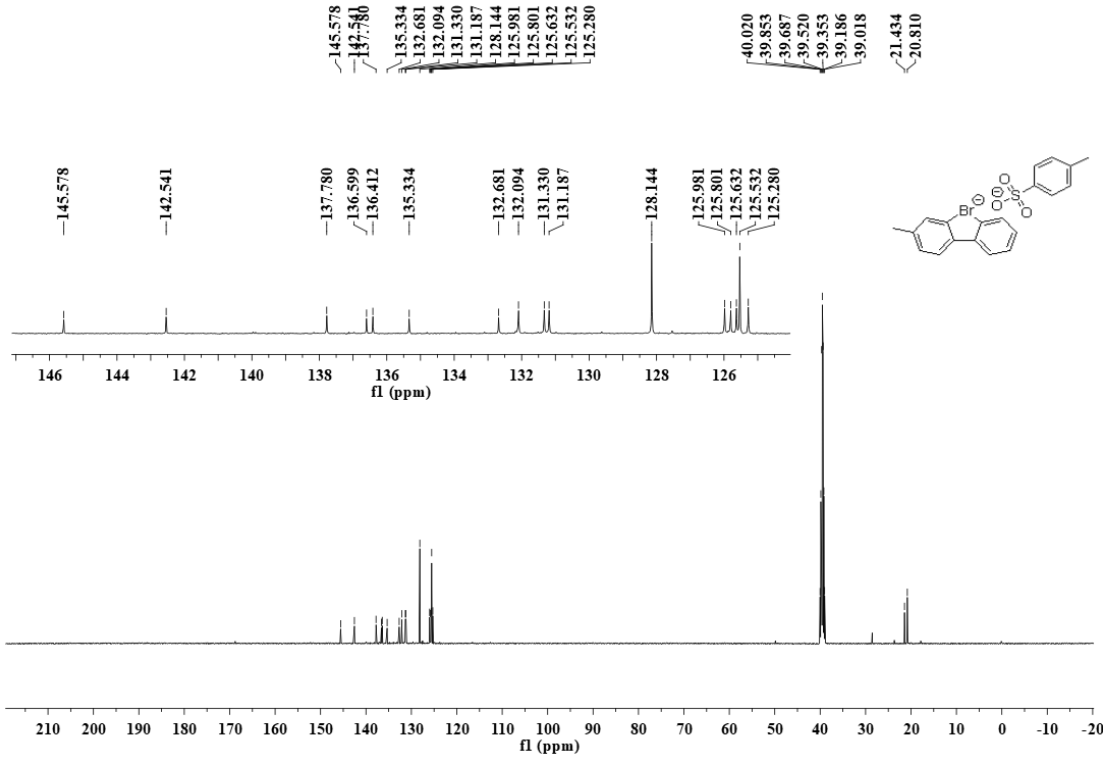
^{19}F NMR (471 MHz, DMSO-d_6) of **1a**-BF_4



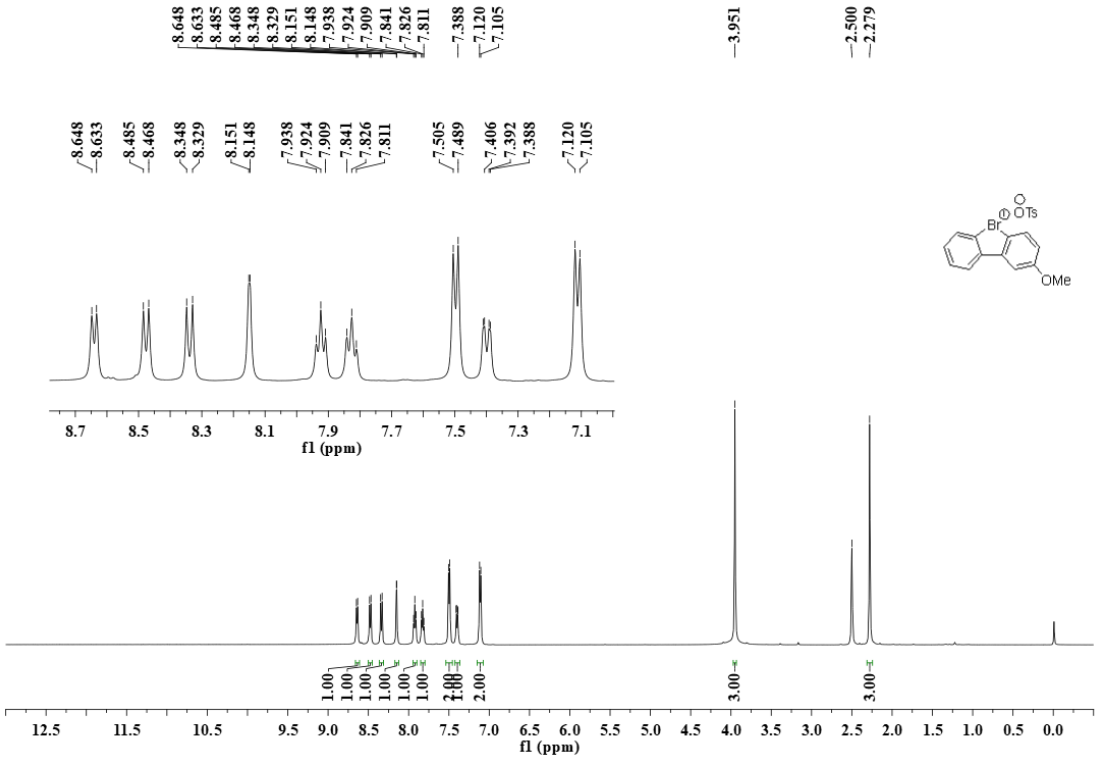
^{1}H NMR (500 MHz, DMSO-d_6) of **1b**-OTs



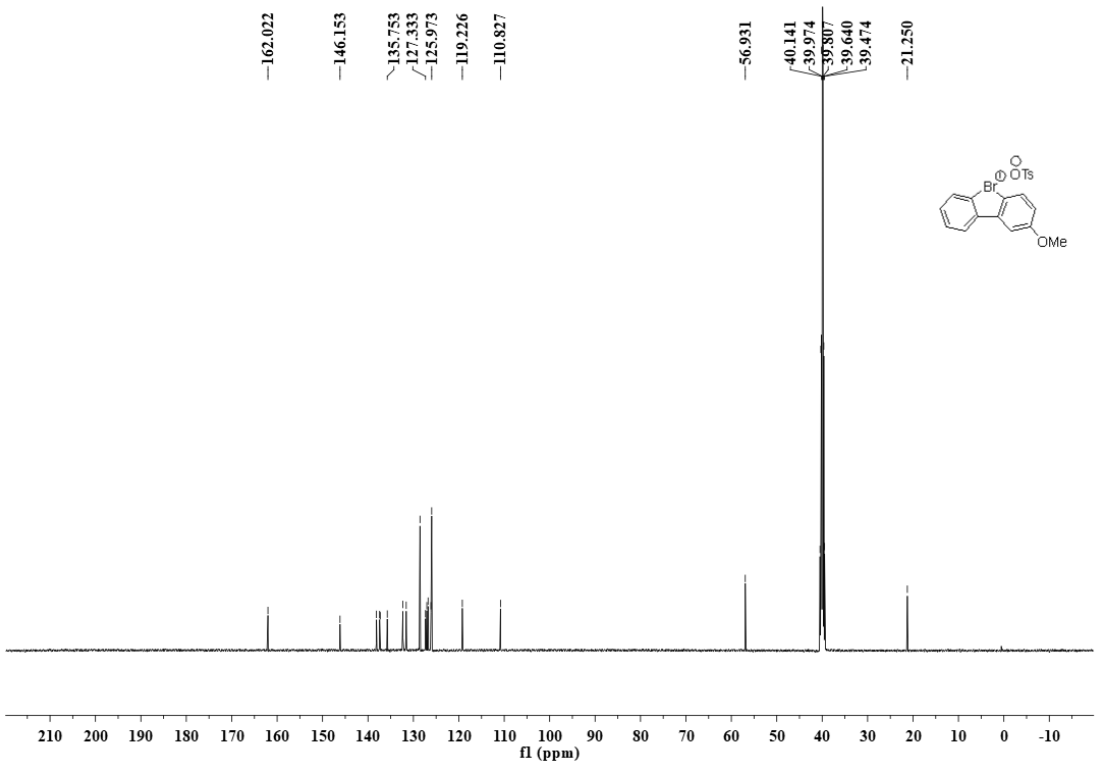
^{13}C NMR (125 MHz, DMSO-d_6) of **1b**-OTs



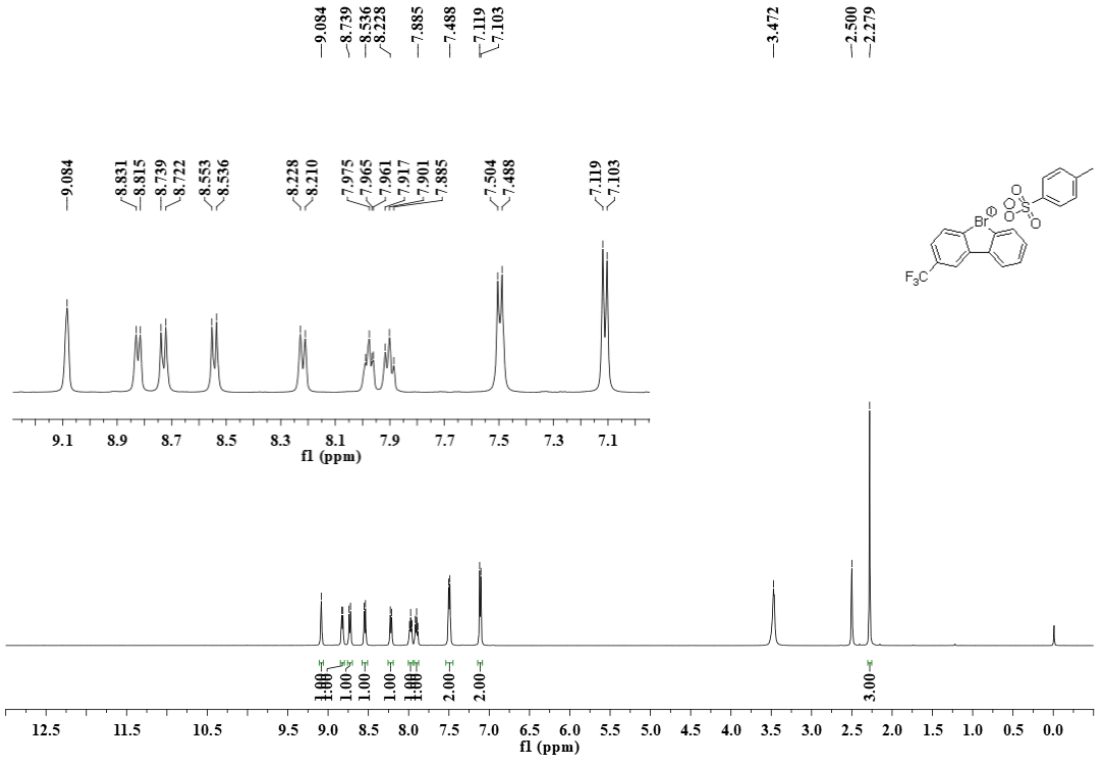
^{1}H NMR (500 MHz, DMSO-d_6) of **1c**-OTs



^{13}C NMR (125 MHz, DMSO-d_6) of **1c**-OTs



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



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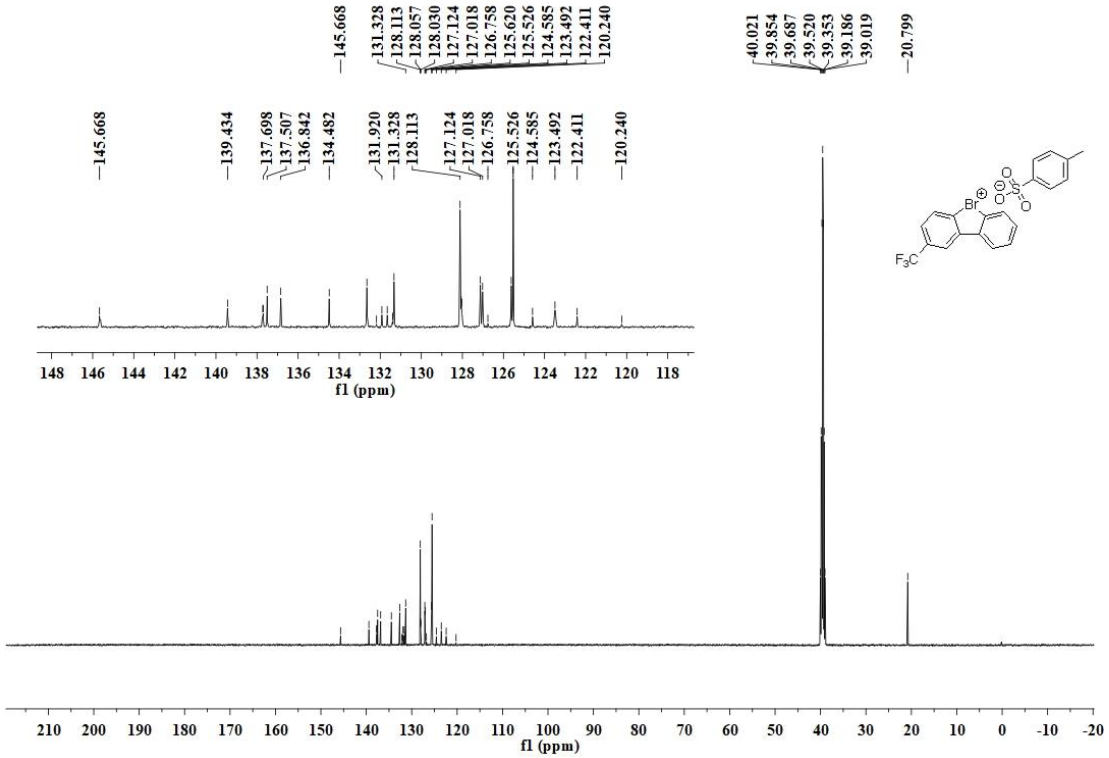
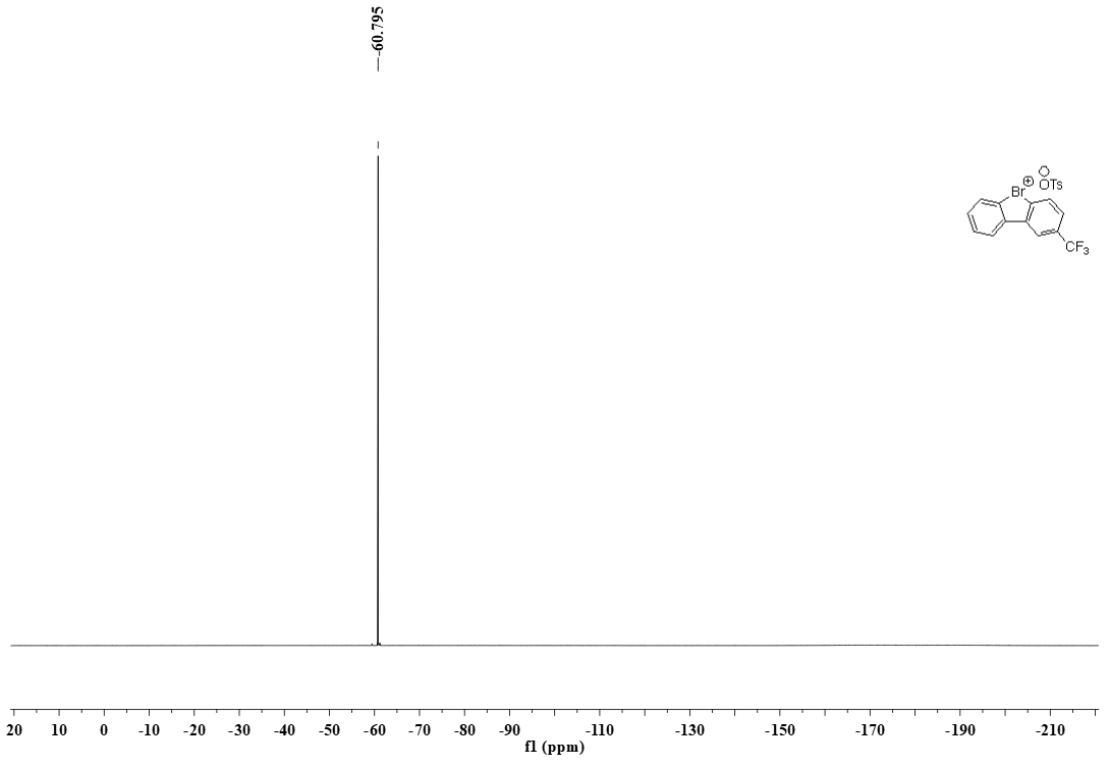


^{19}F NMR (471 MHz, DMSO-d_6) of **1d**-OTs



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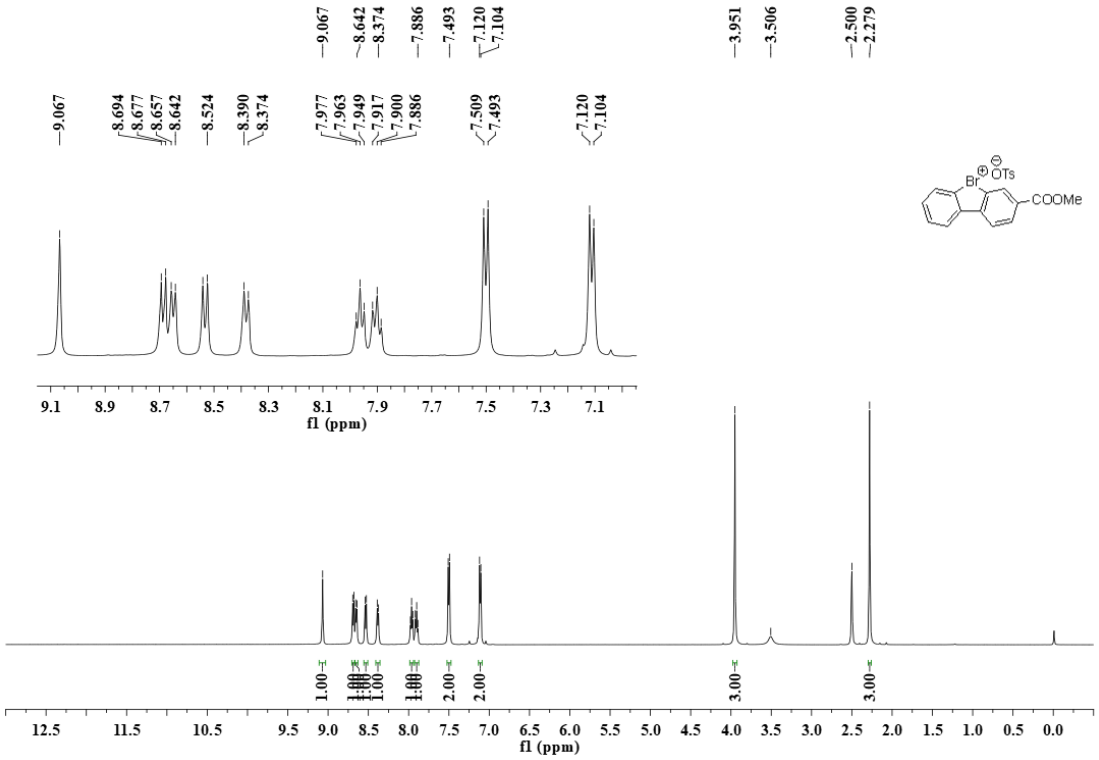

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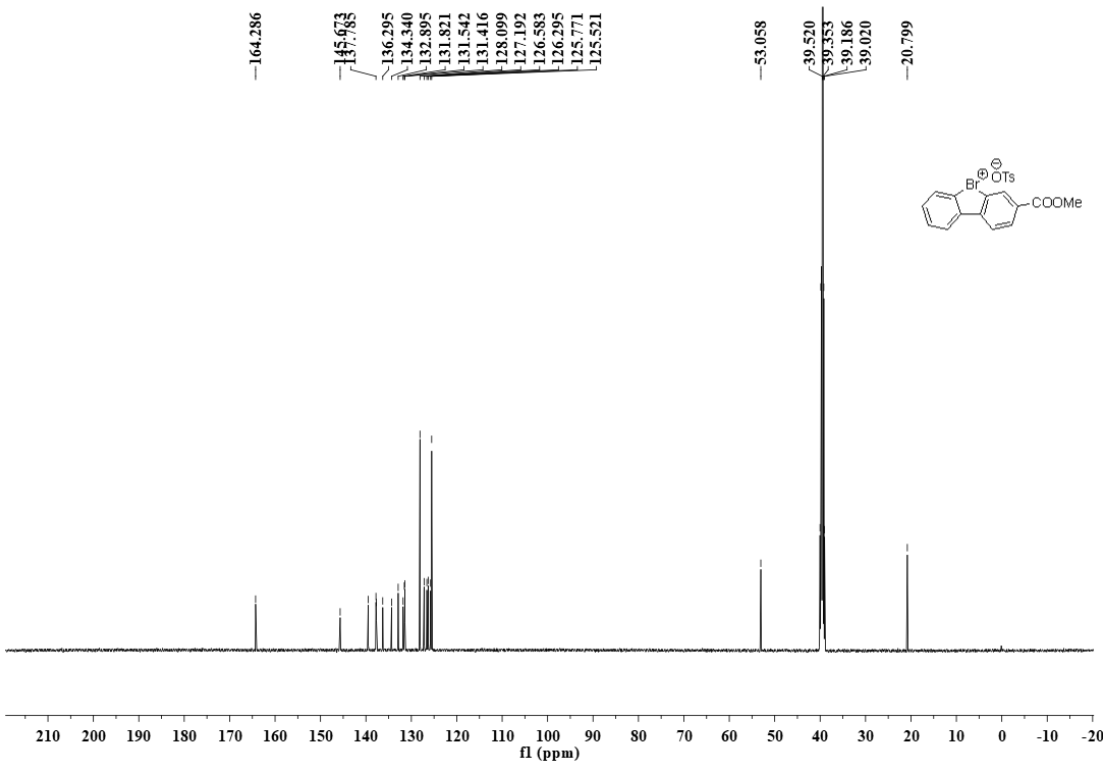
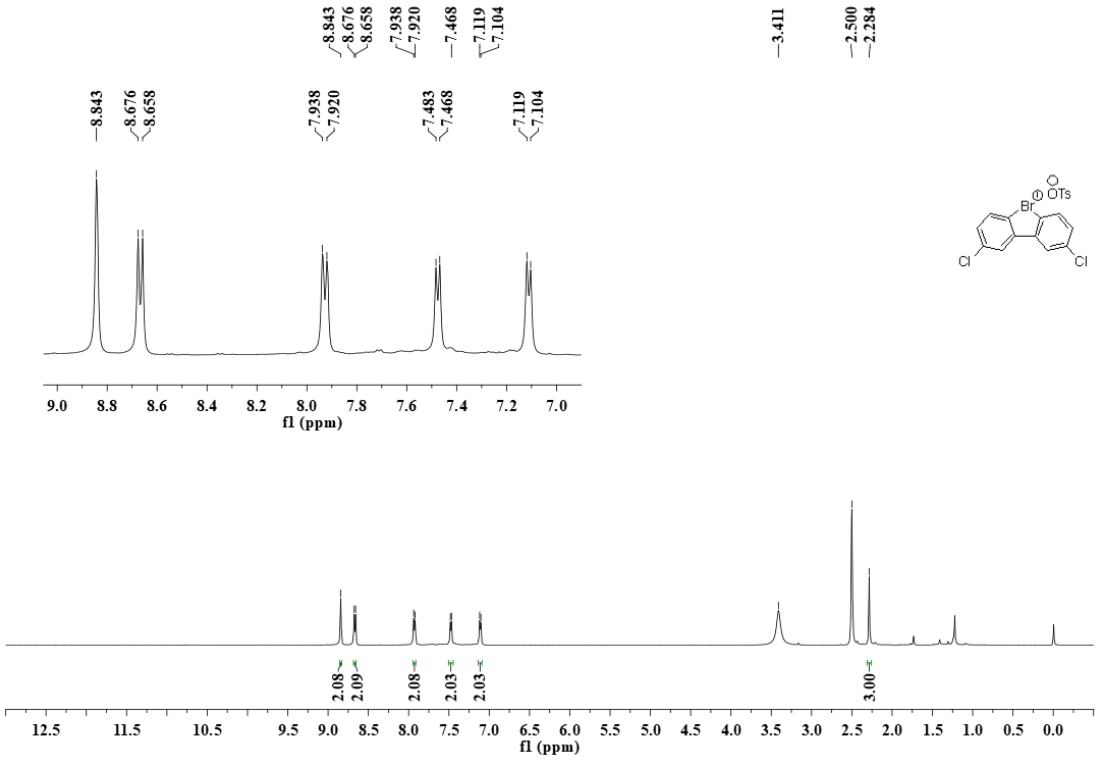
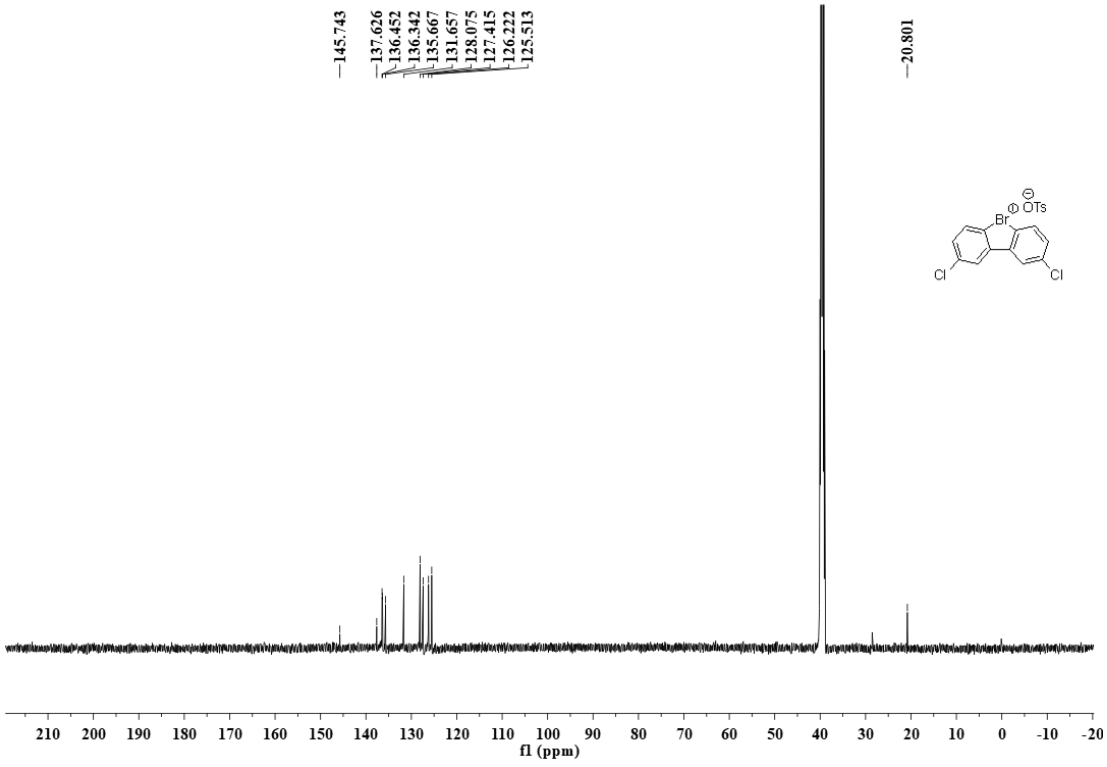


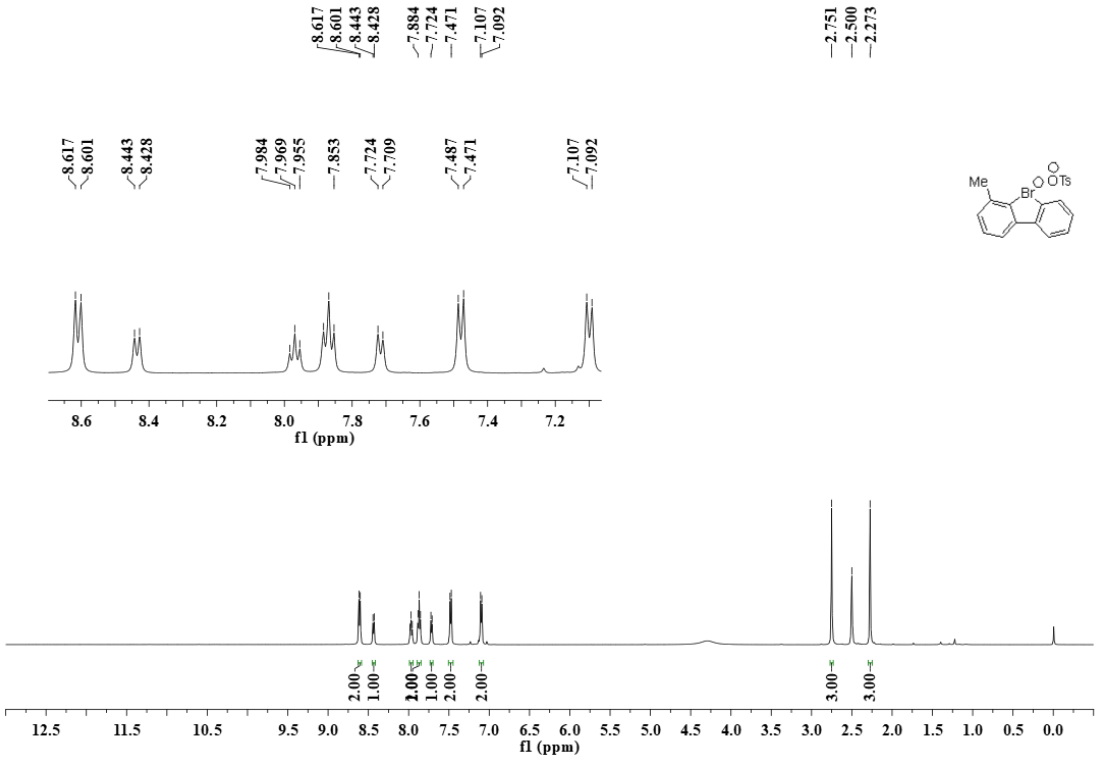
^{1}H NMR (500 MHz, DMSO-d_6) of **1f**-OTs



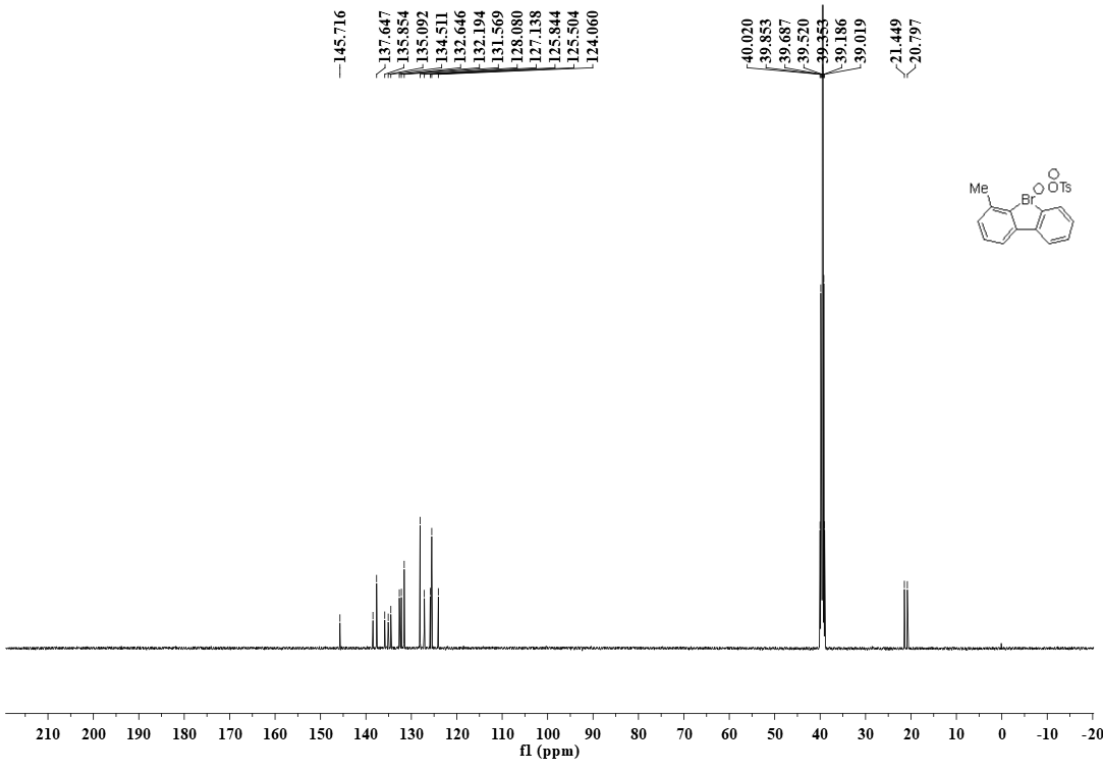
^{13}C NMR (125 MHz, DMSO-d_6) of **1f**-OTs



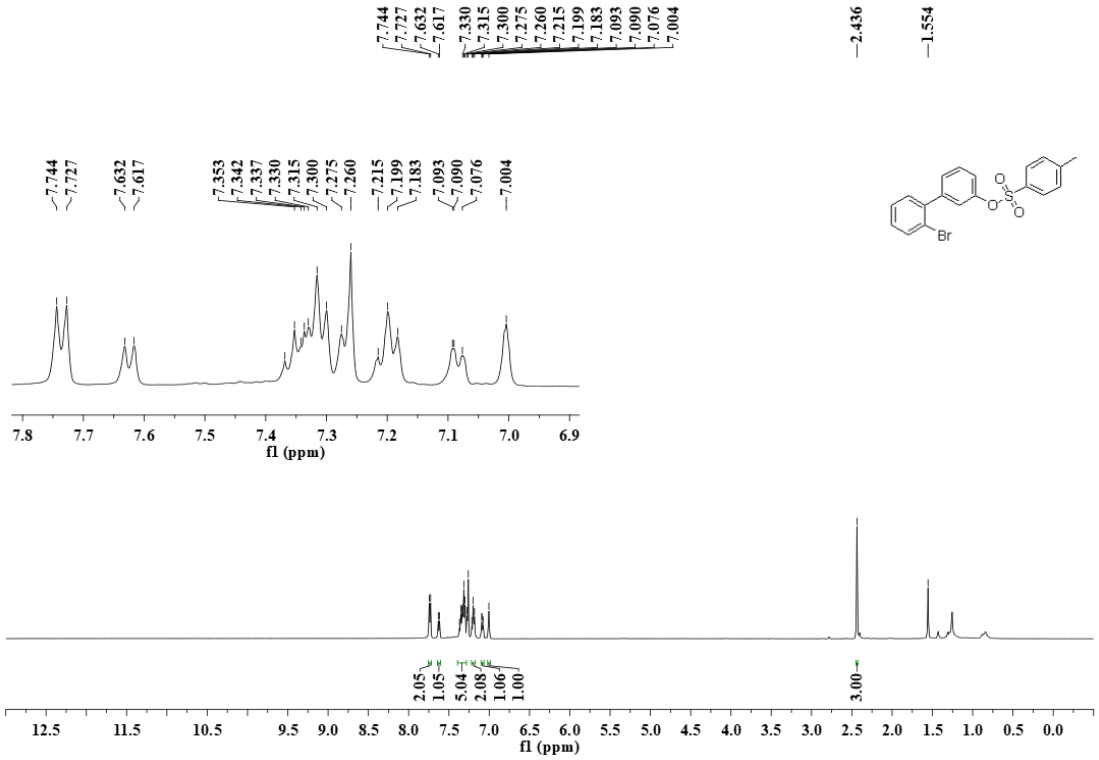
^{1}H NMR (500 MHz, DMSO-d_6) of **1g**-OTs



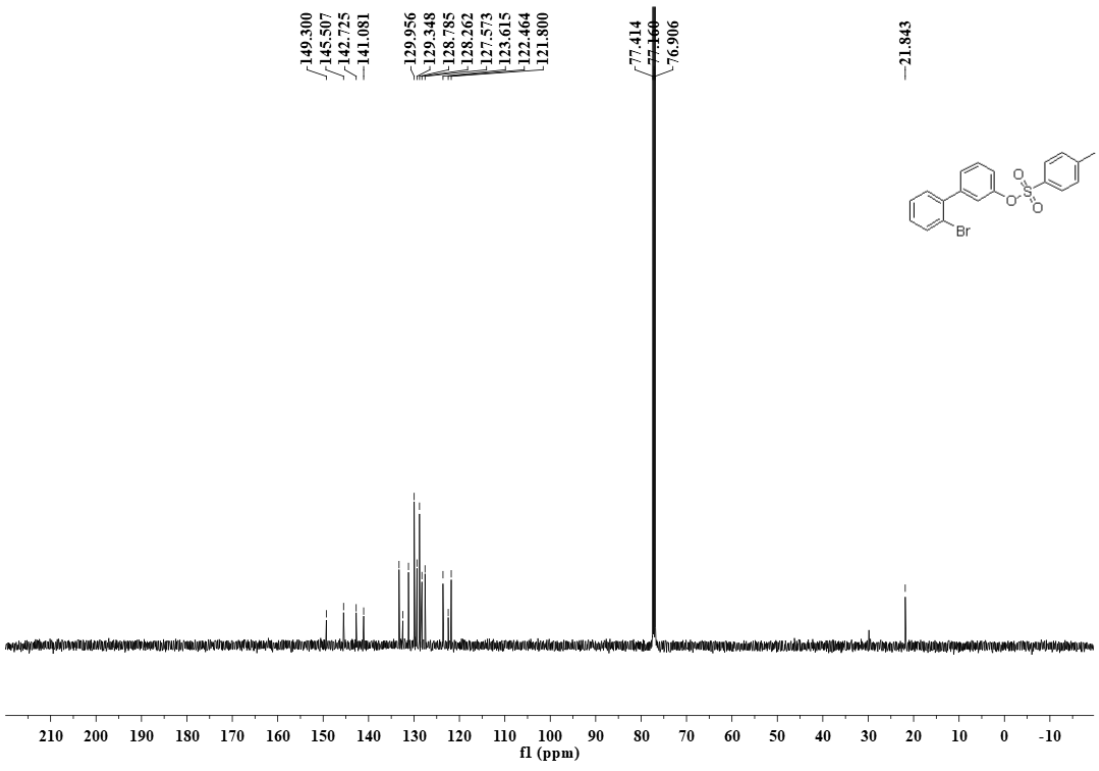
^{13}C NMR (125 MHz, DMSO-d_6) of **1g**-OTs



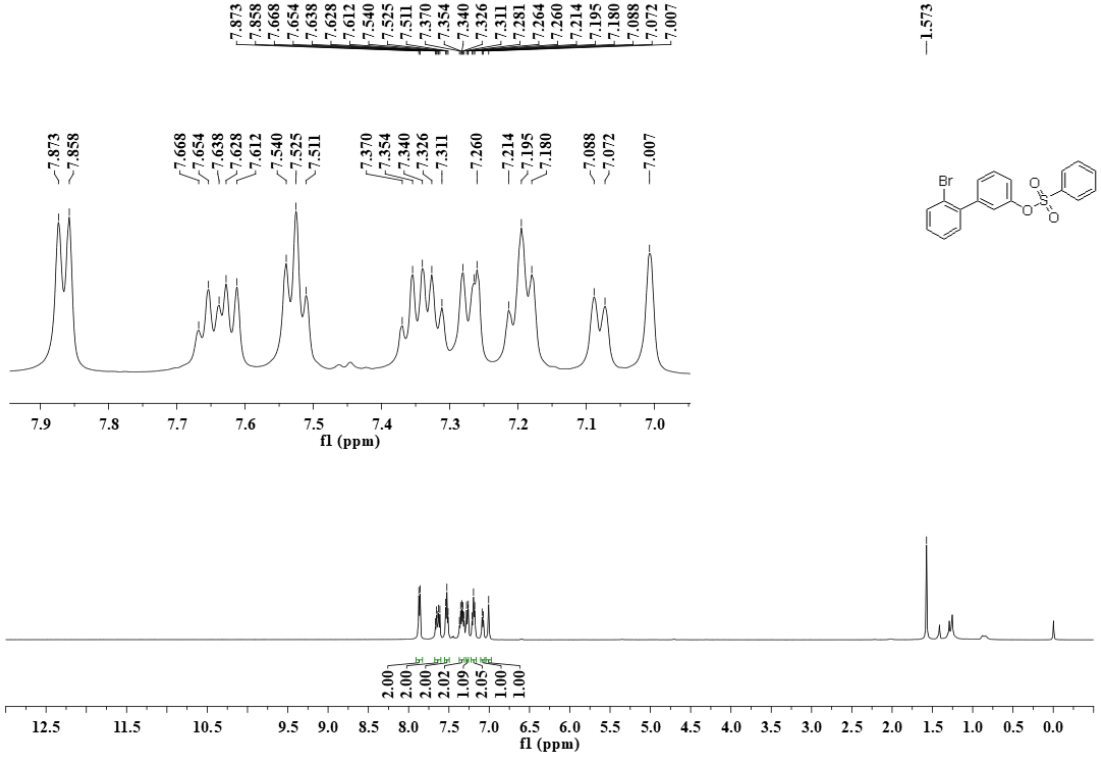
^{1}H NMR (500 MHz, $CDCl_3$) of **2a**



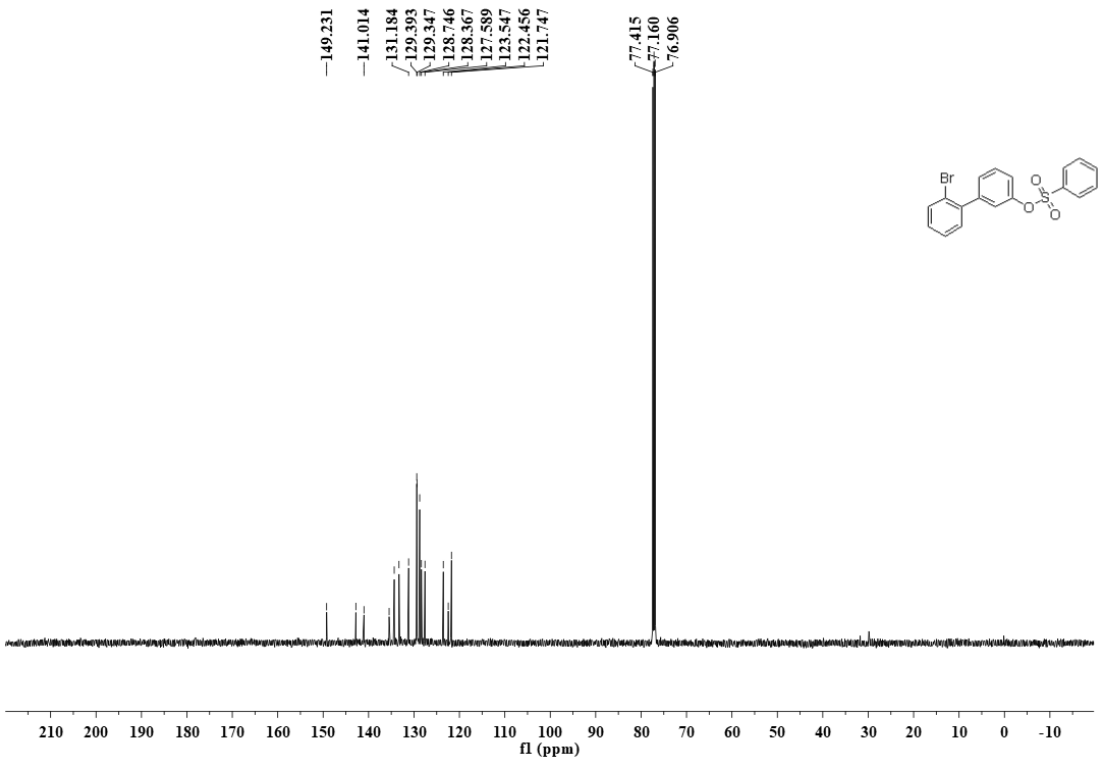
^{13}C NMR (125 MHz, $CDCl_3$) of **2a**



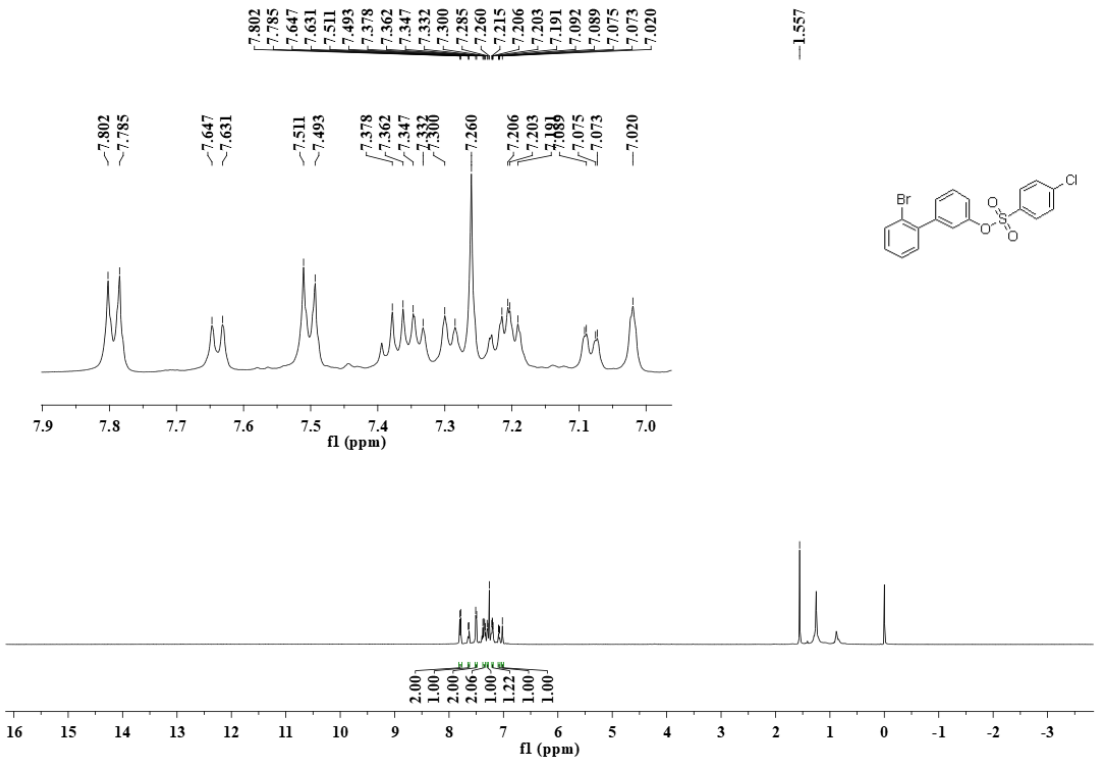
^{1}H NMR (500 MHz, $CDCl_3$) of **2b**



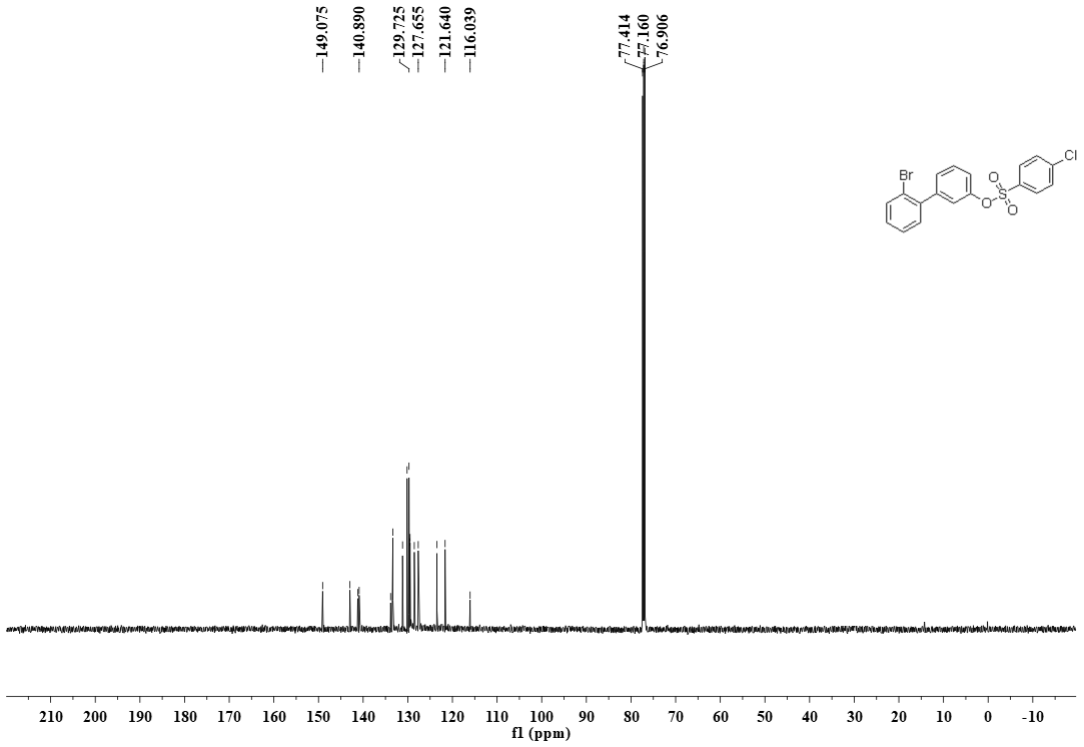
^{13}C NMR (125 MHz, $CDCl_3$) of **2b**



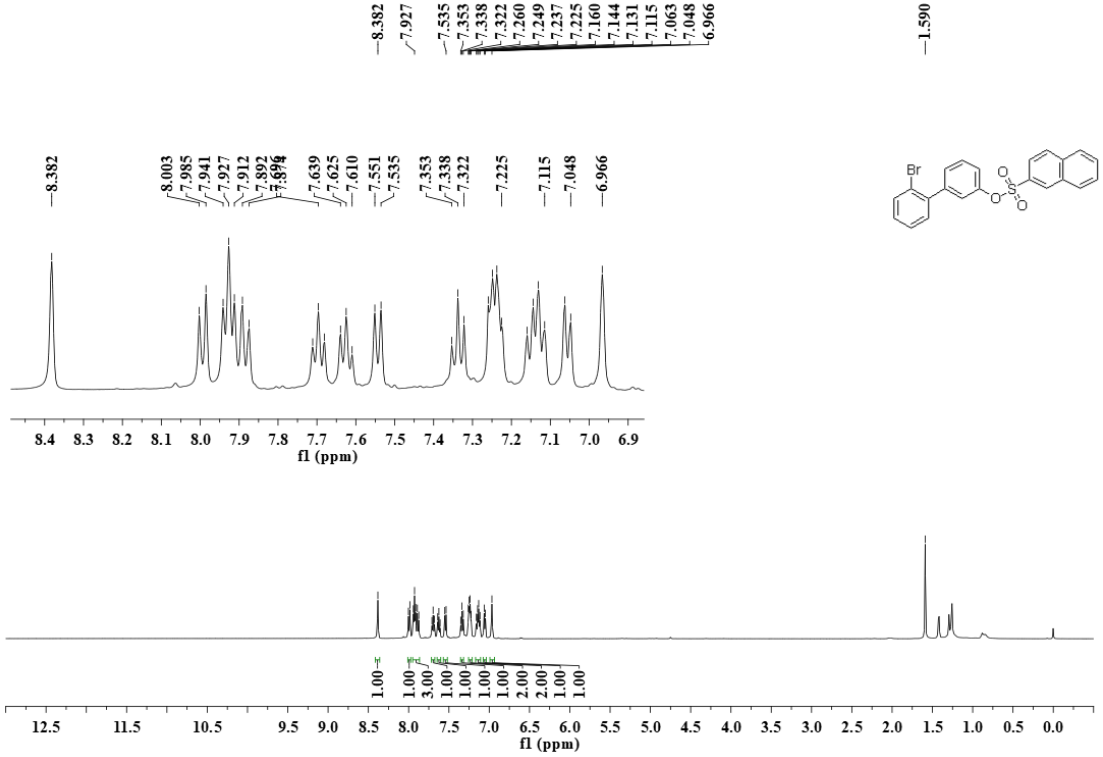
^{1}H NMR (500 MHz, $CDCl_3$) of **2c**



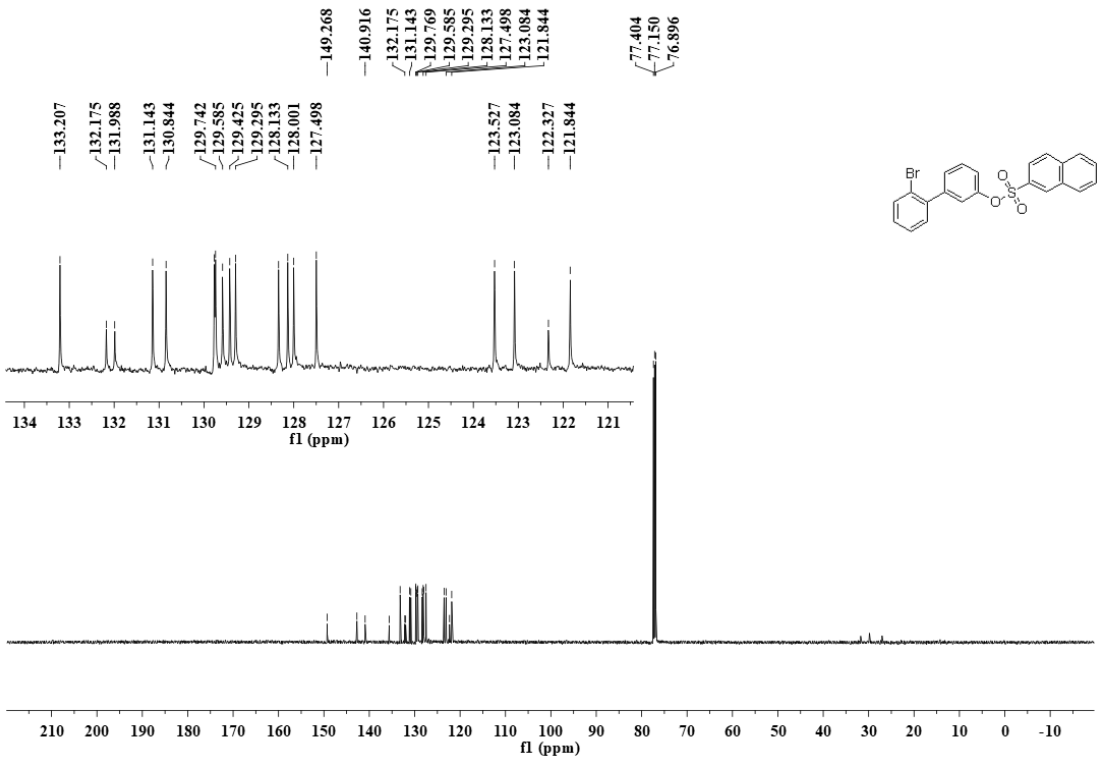
^{13}C NMR (125 MHz, $CDCl_3$) of **2c**



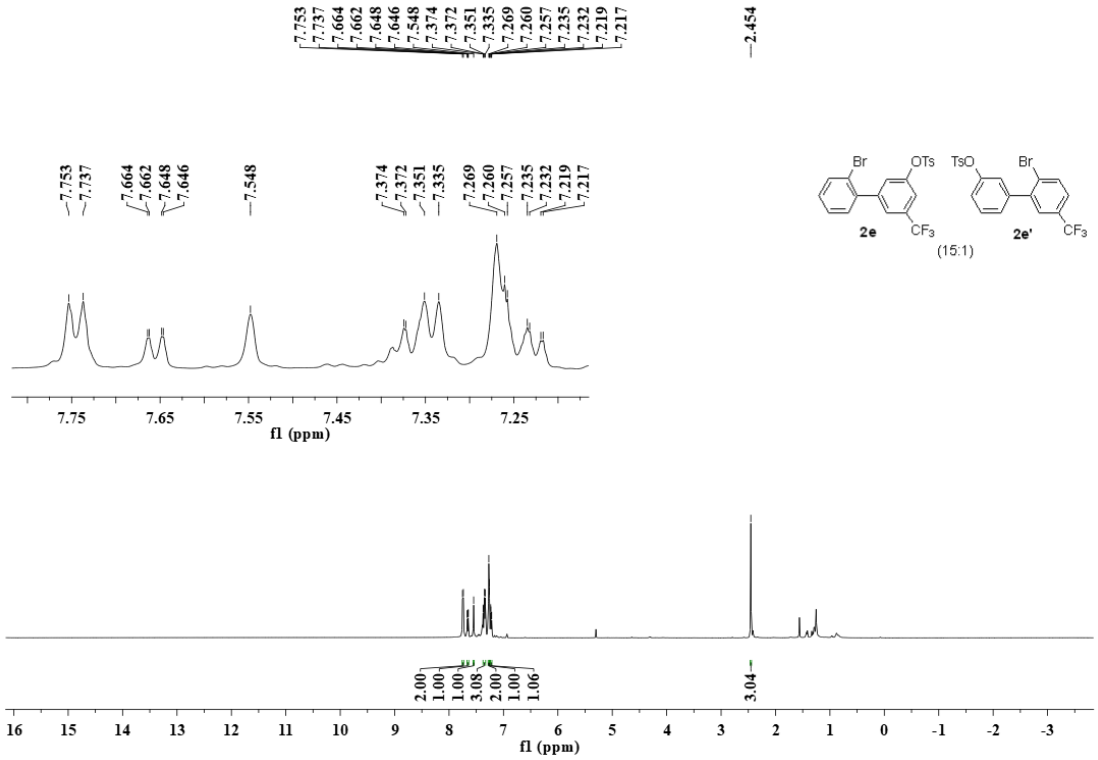
^{1}H NMR (500 MHz, $CDCl_3$) of **2d**



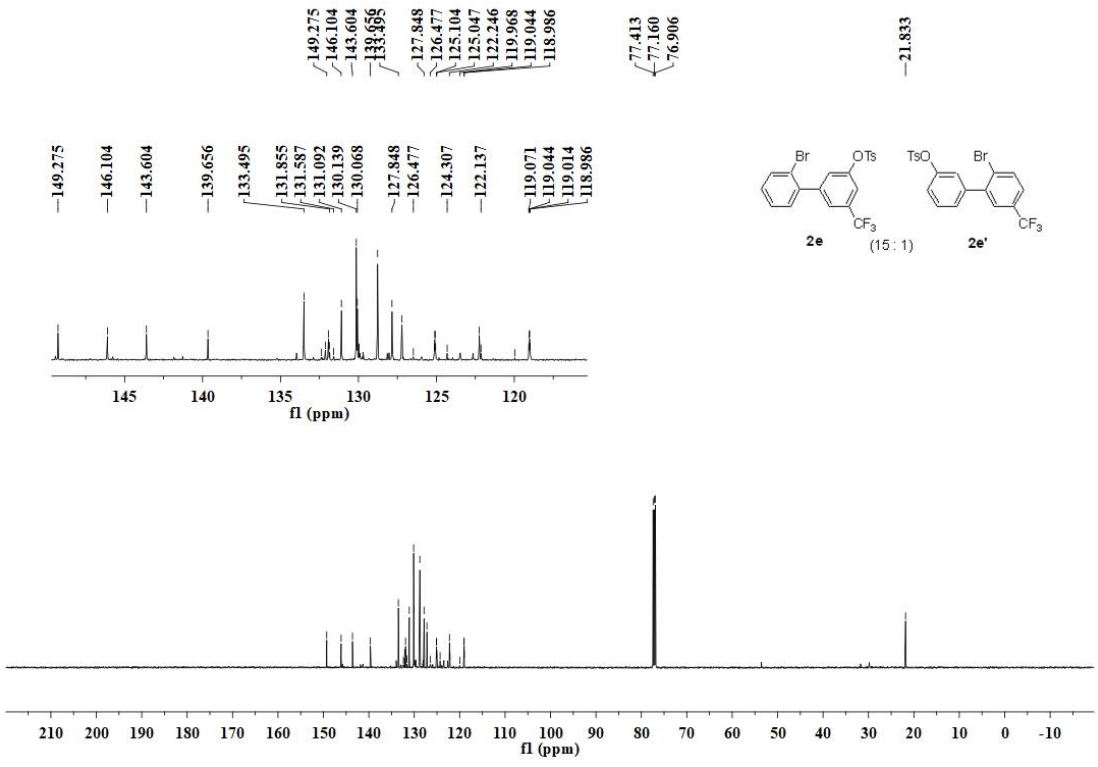
^{13}C NMR (125 MHz, $CDCl_3$) of **2d**



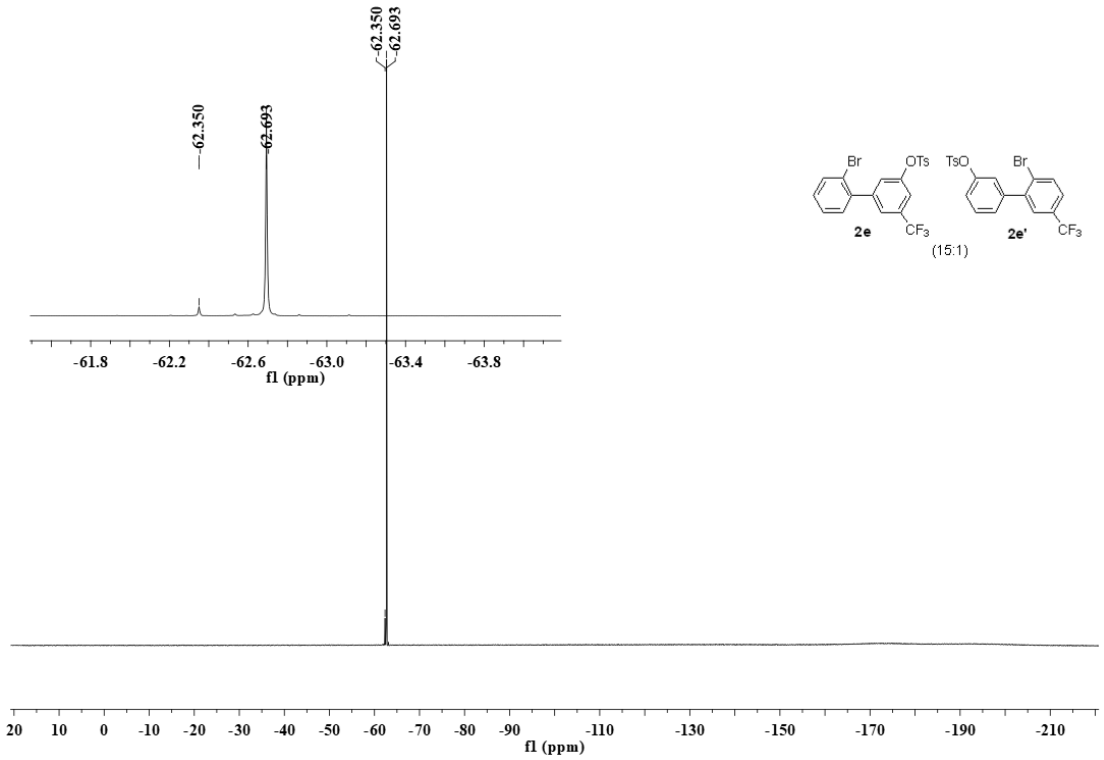
^{1}H NMR (500 MHz, $CDCl_3$) of **2e**



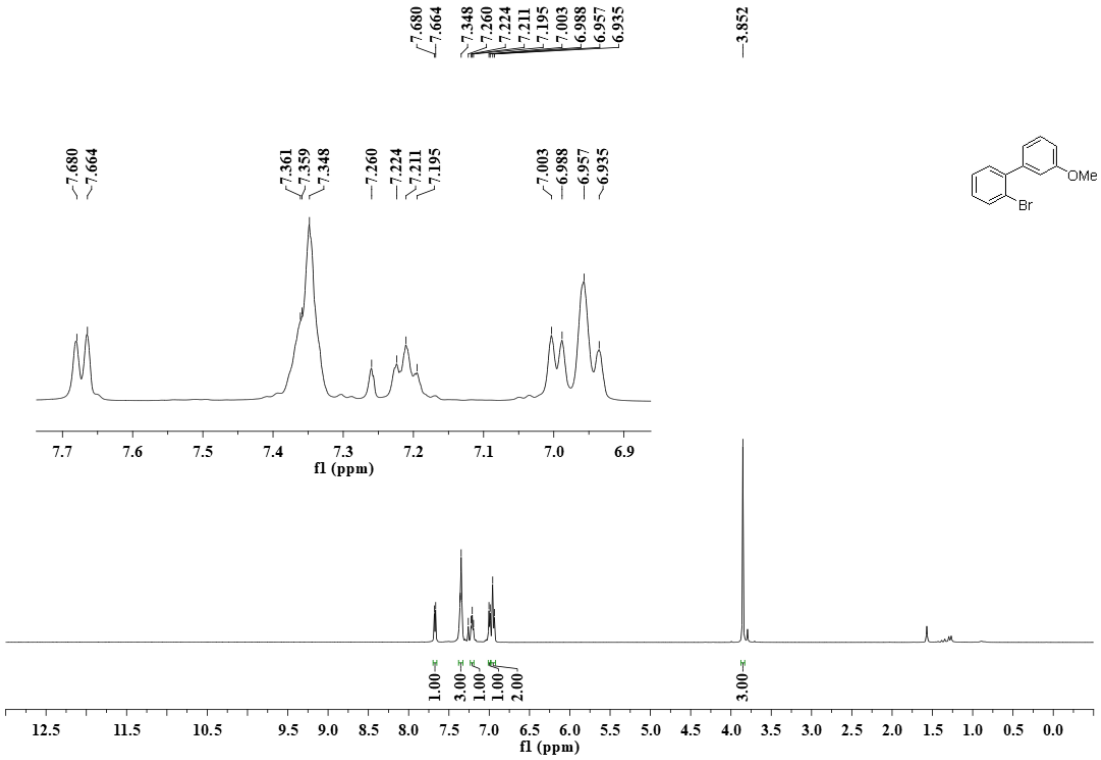
^{13}C NMR (125 MHz, $CDCl_3$) of **2e**



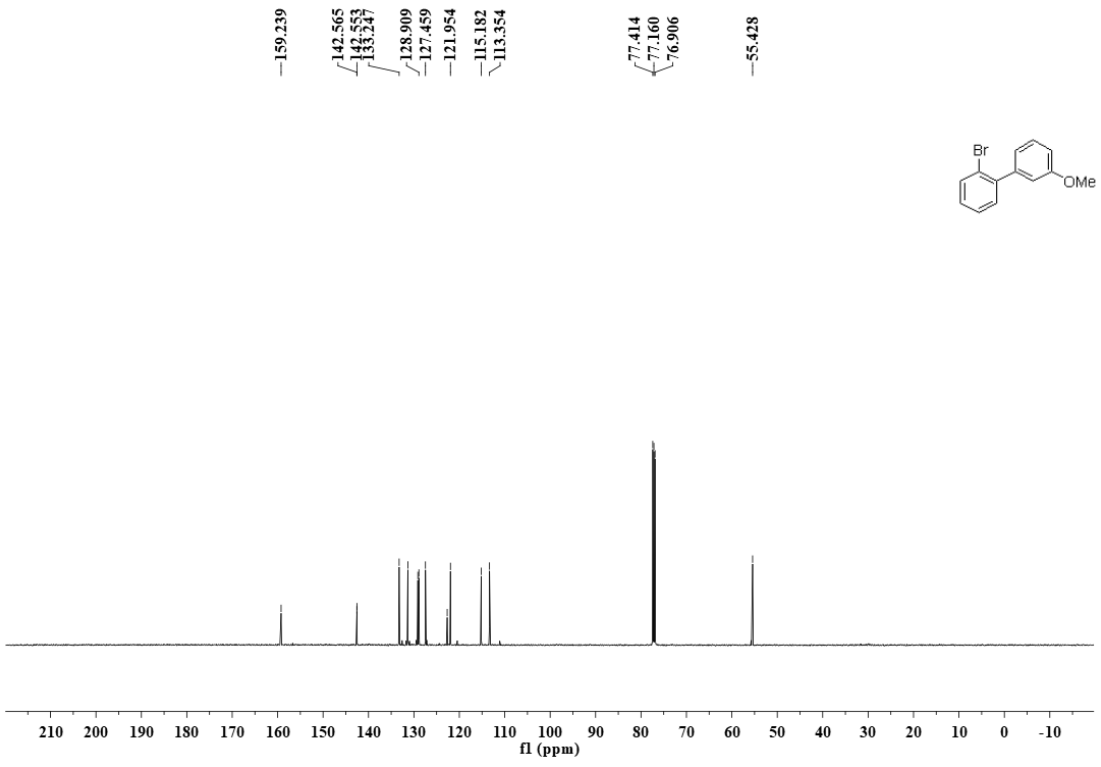
^{19}F NMR (471 MHz, $CDCl_3$) of **2e**



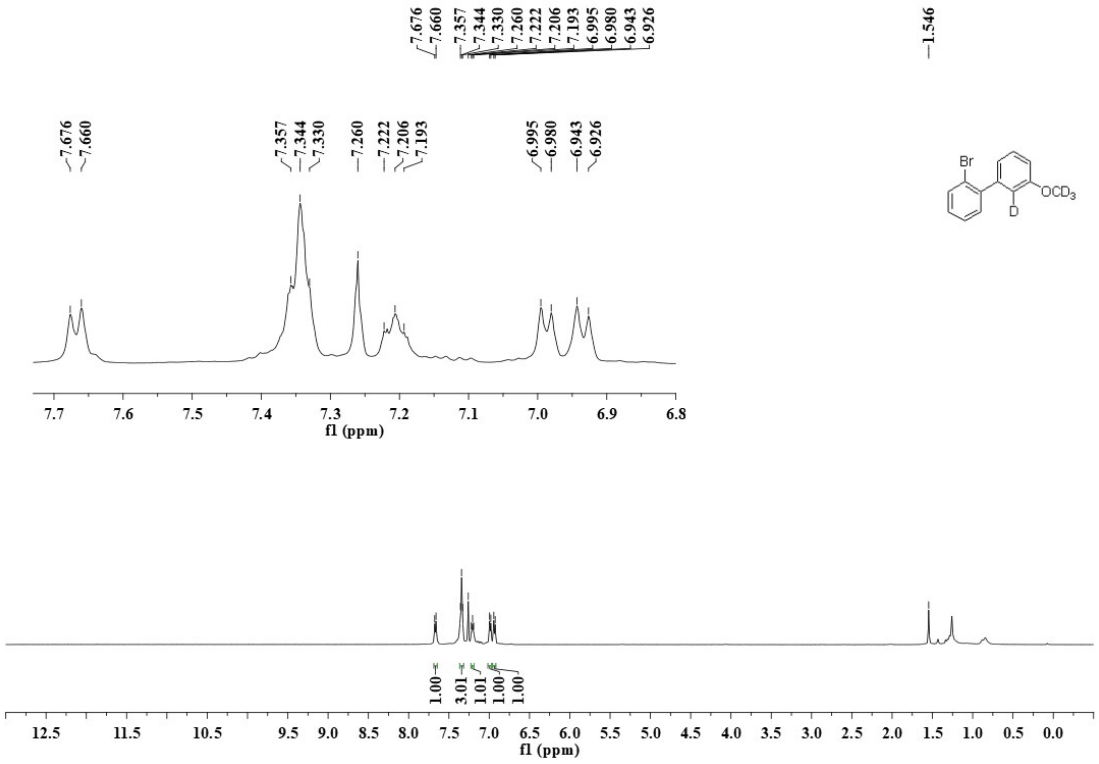
^{1}H NMR (500 MHz, $CDCl_3$) of **3a**



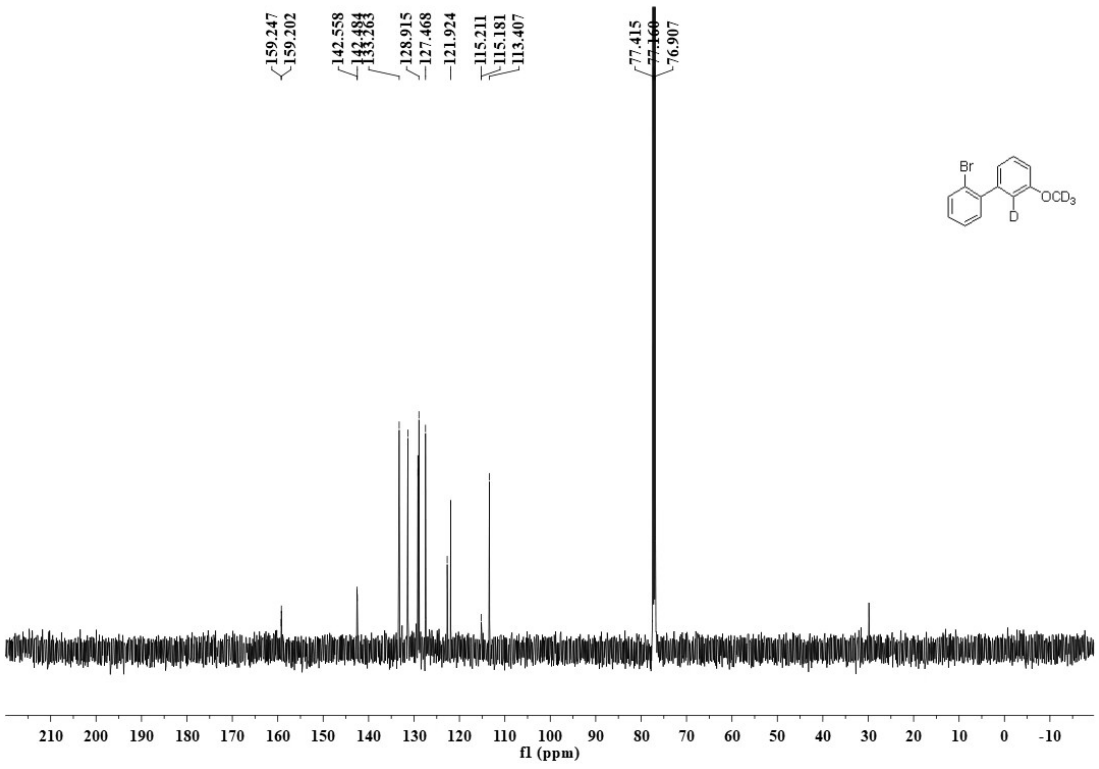
^{13}C NMR (125 MHz, $CDCl_3$) of **3a**



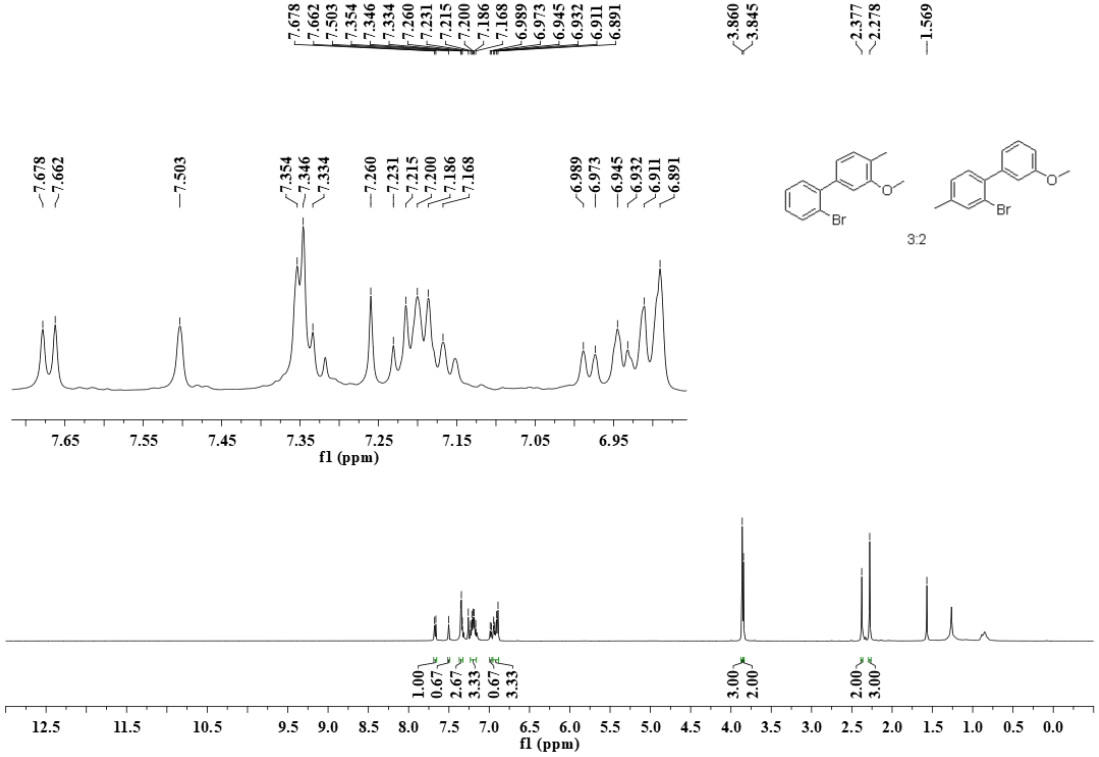
^{1}H NMR (500 MHz, $CDCl_3$) of ***d*-3a**



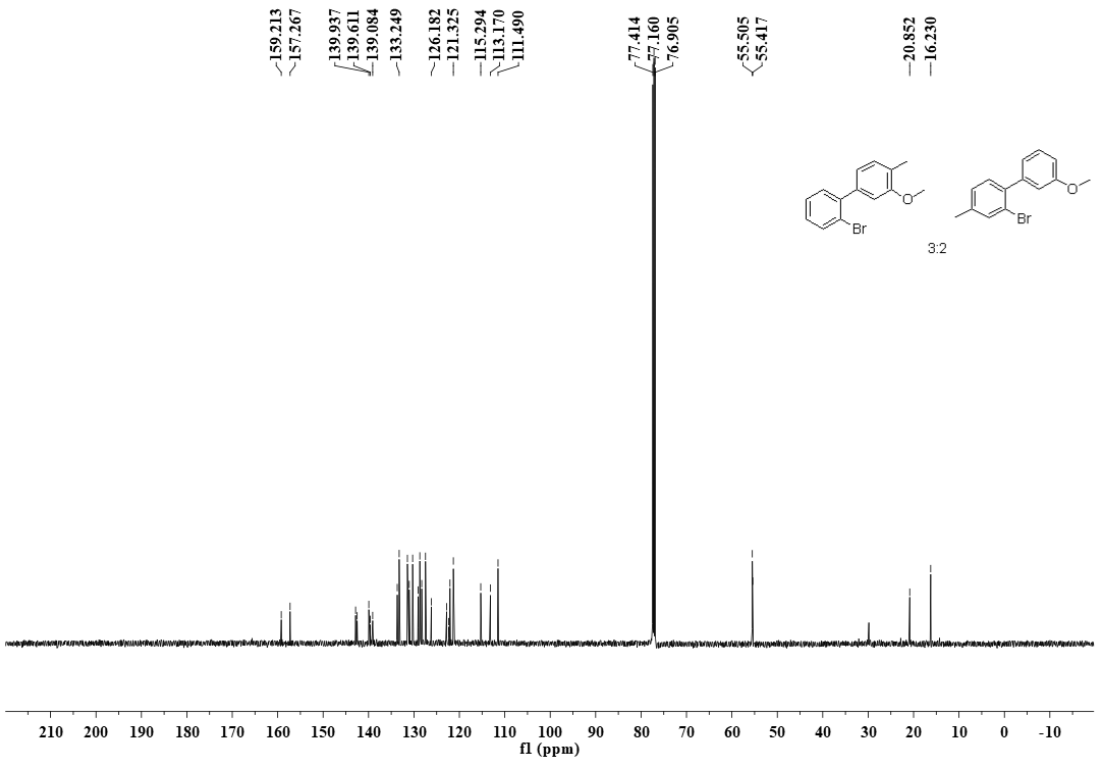
^{13}C NMR (125 MHz, $CDCl_3$) of ***d*-3a**



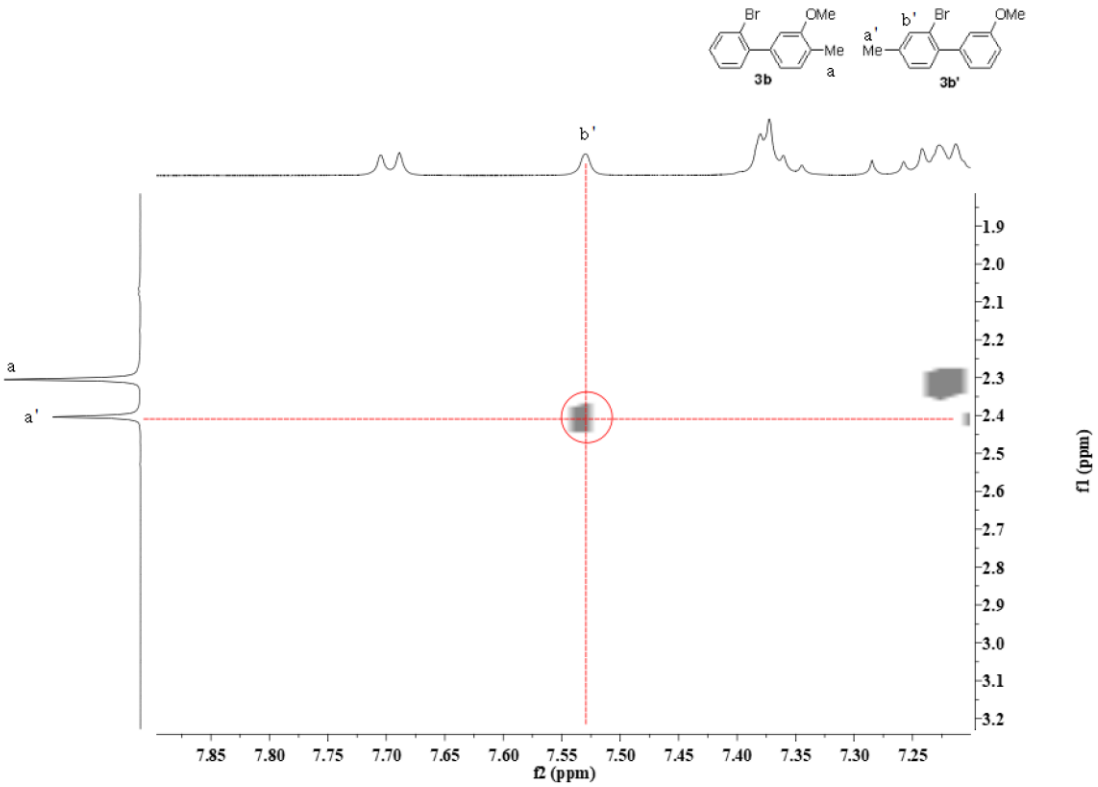
^{1}H NMR (500 MHz, $CDCl_3$) of **3b and 3b'**



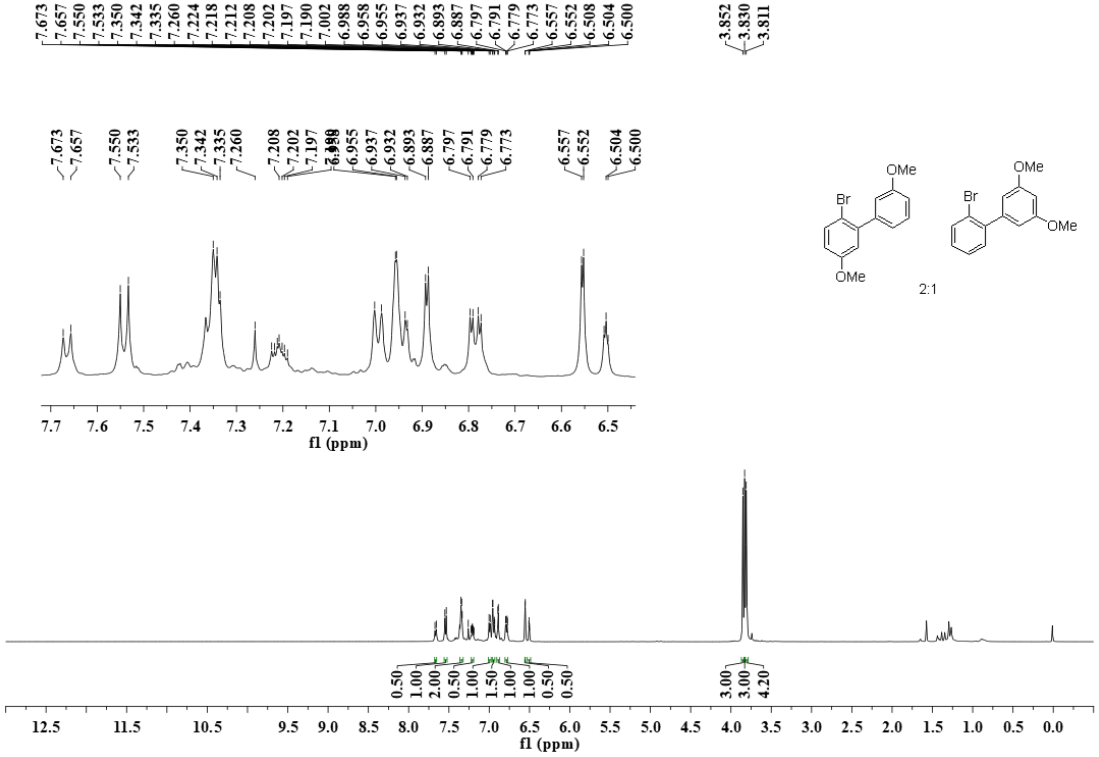
^{13}C NMR (125 MHz, $CDCl_3$) of **3b and 3b'**



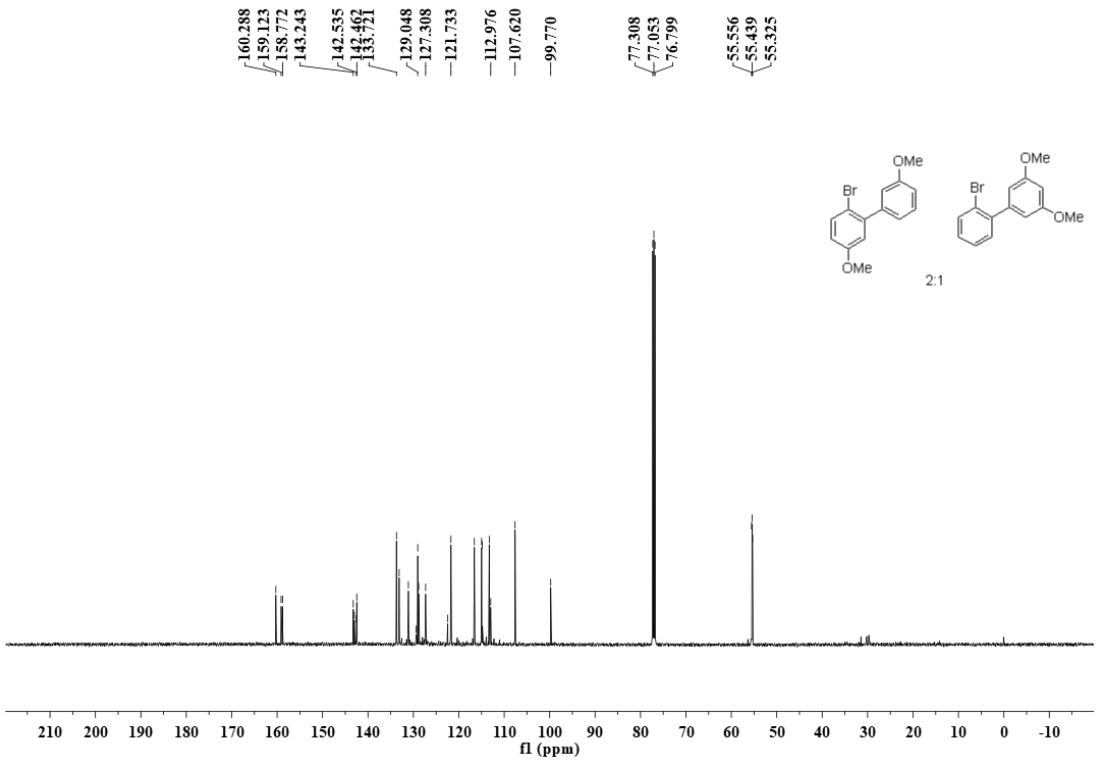
^{1}H-^{1}H NOESY of **3b and 3b'**



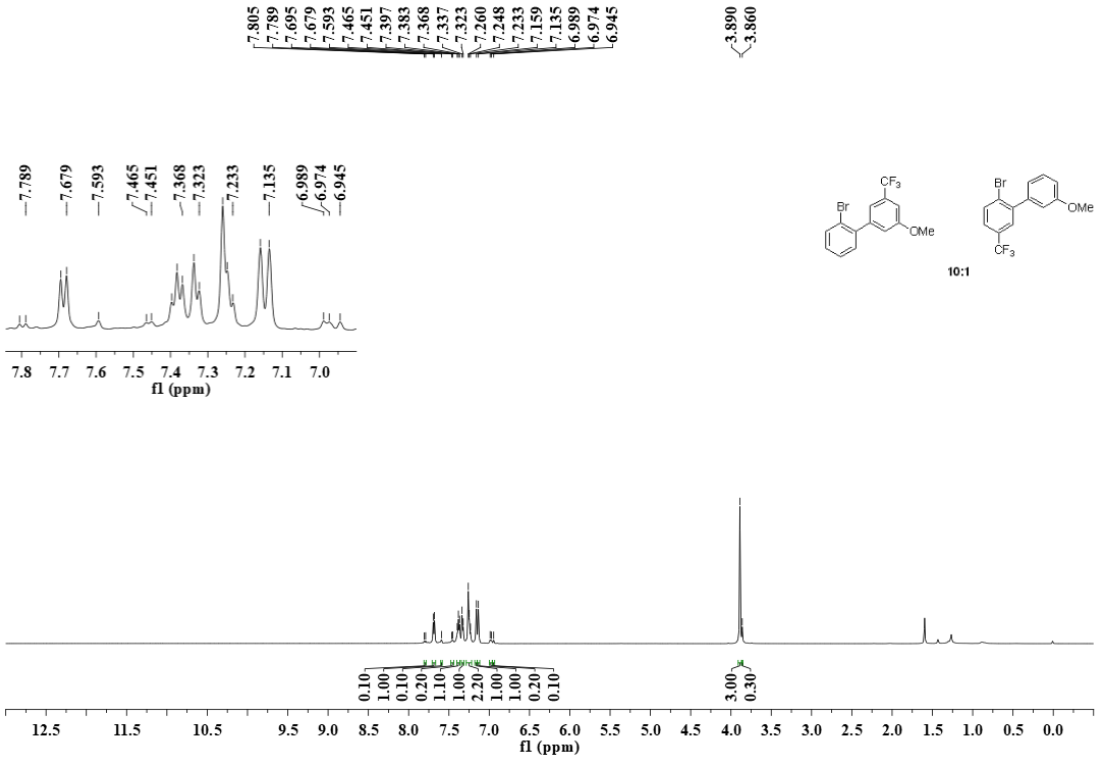
^{1}H NMR (500 MHz, $CDCl_3$) of **3c and 3c'**



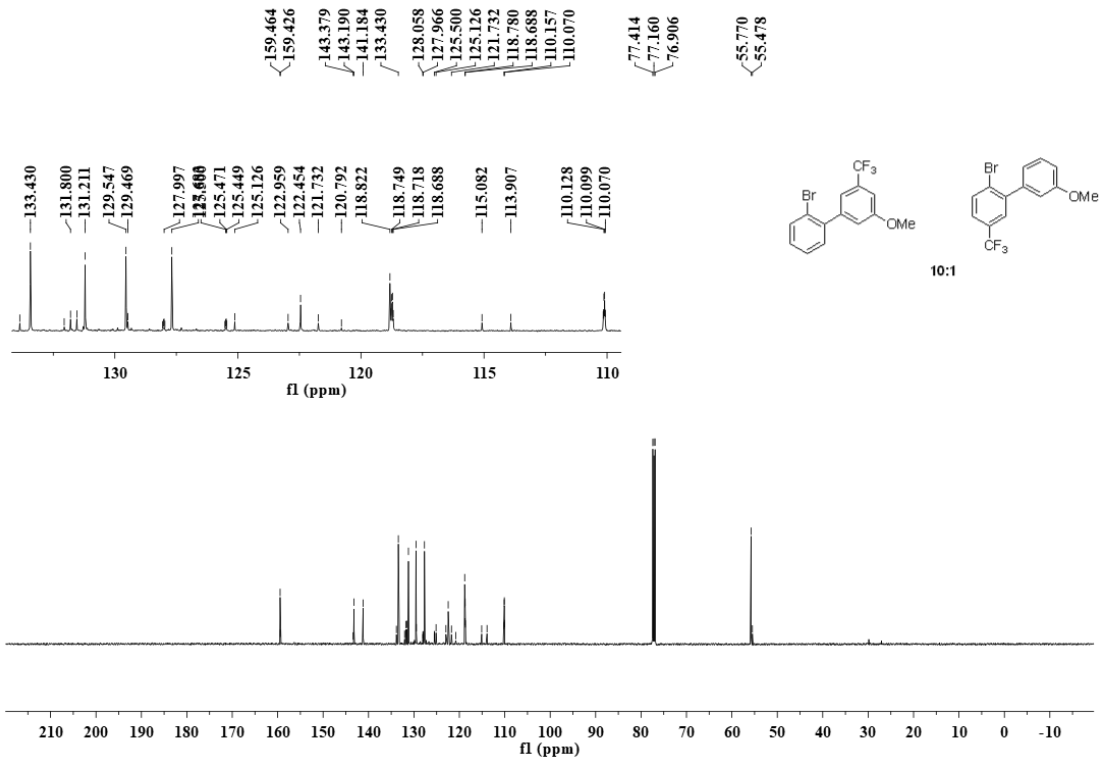
^{13}C NMR (125 MHz, $CDCl_3$) of **3c and 3c'**



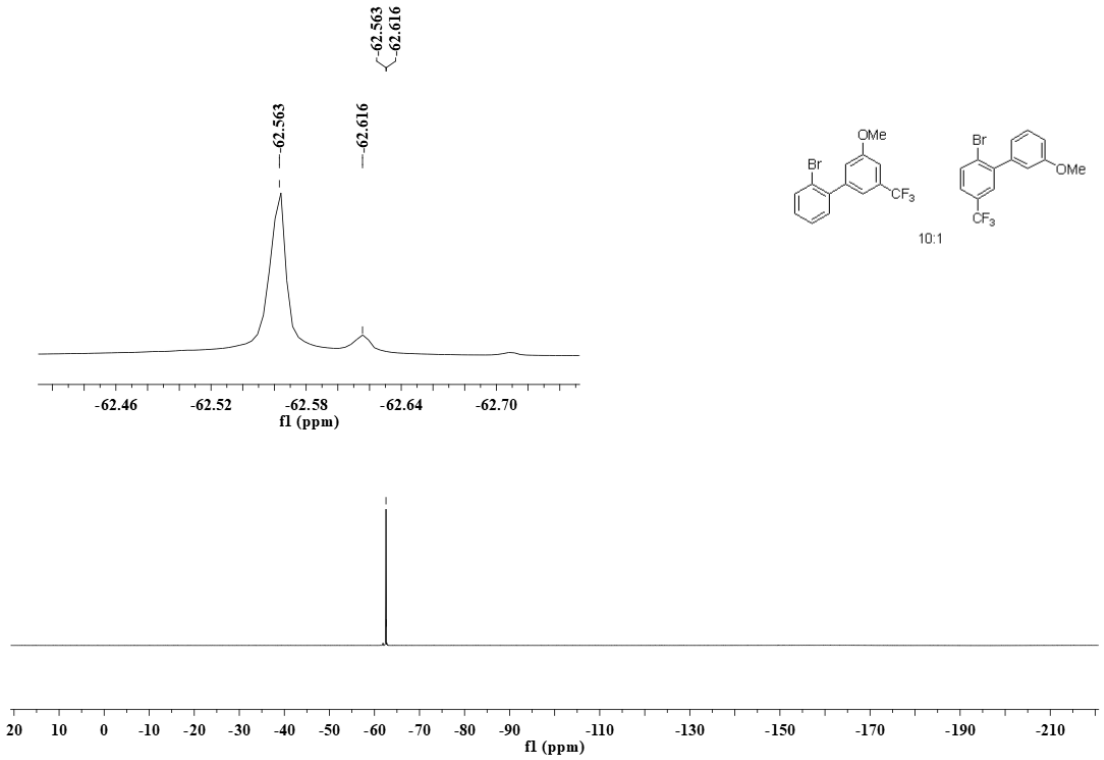
^{1}H NMR (500 MHz, $CDCl_3$) of **3d**



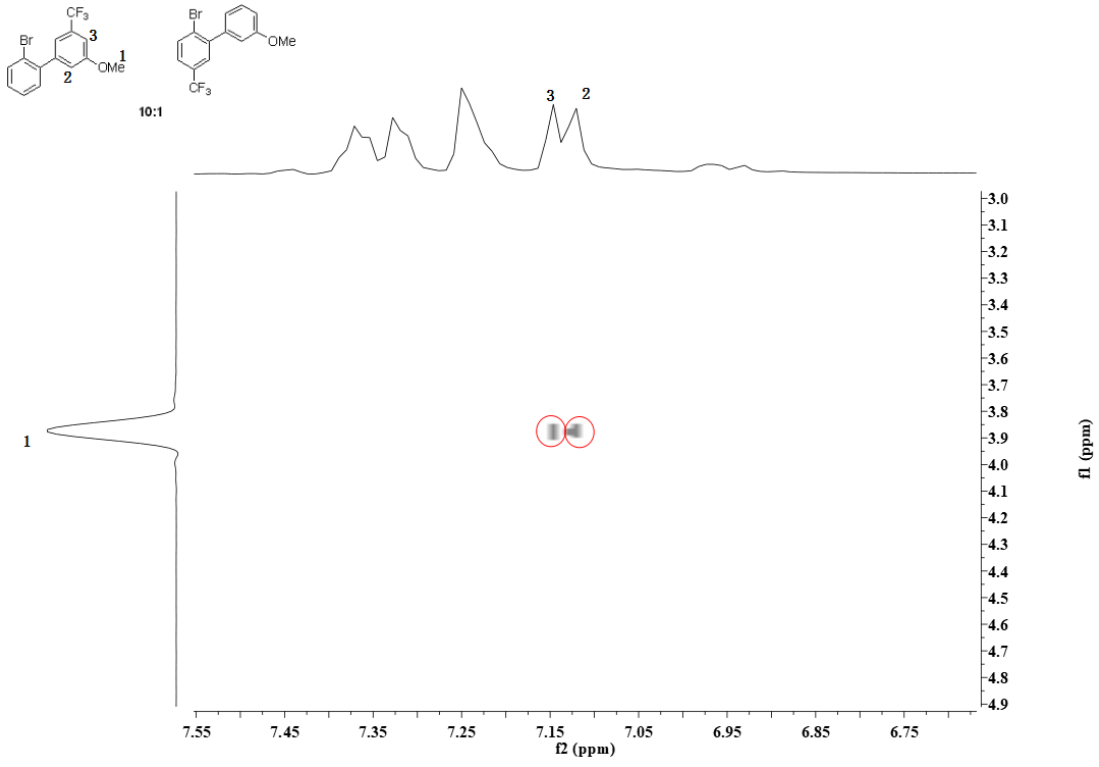
^{13}C NMR (125 MHz, $CDCl_3$) of **3d**



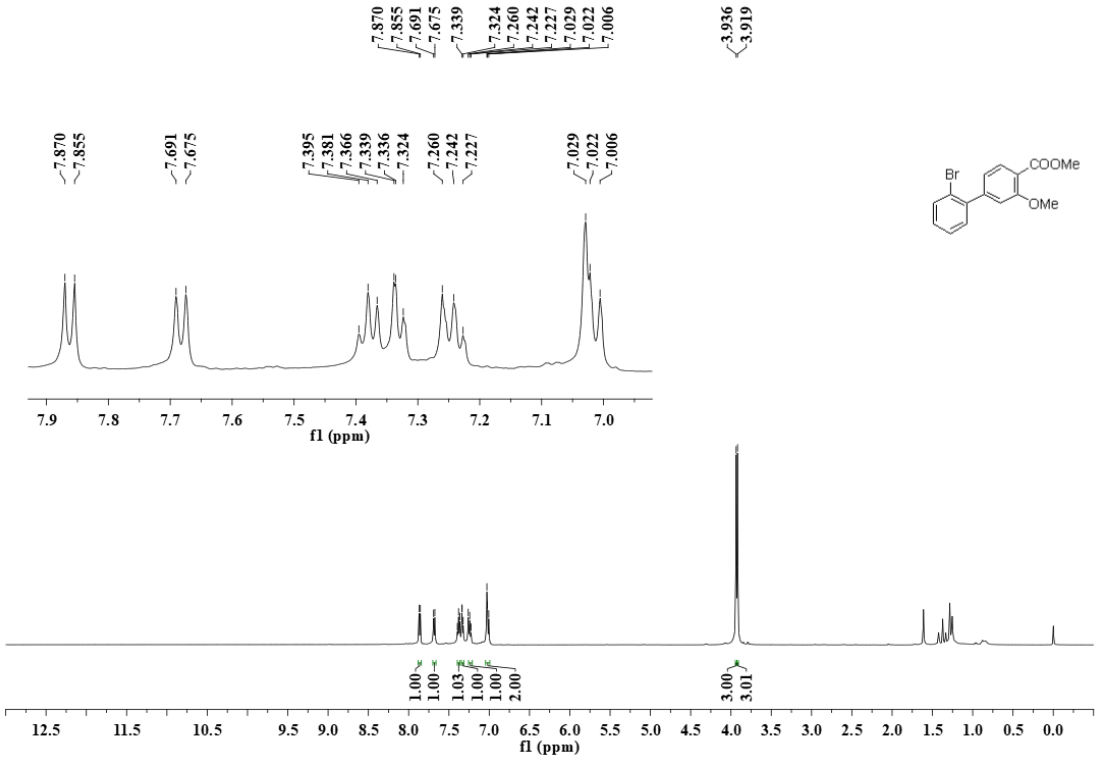
^{19}F NMR (471 MHz, $CDCl_3$) of **3d**



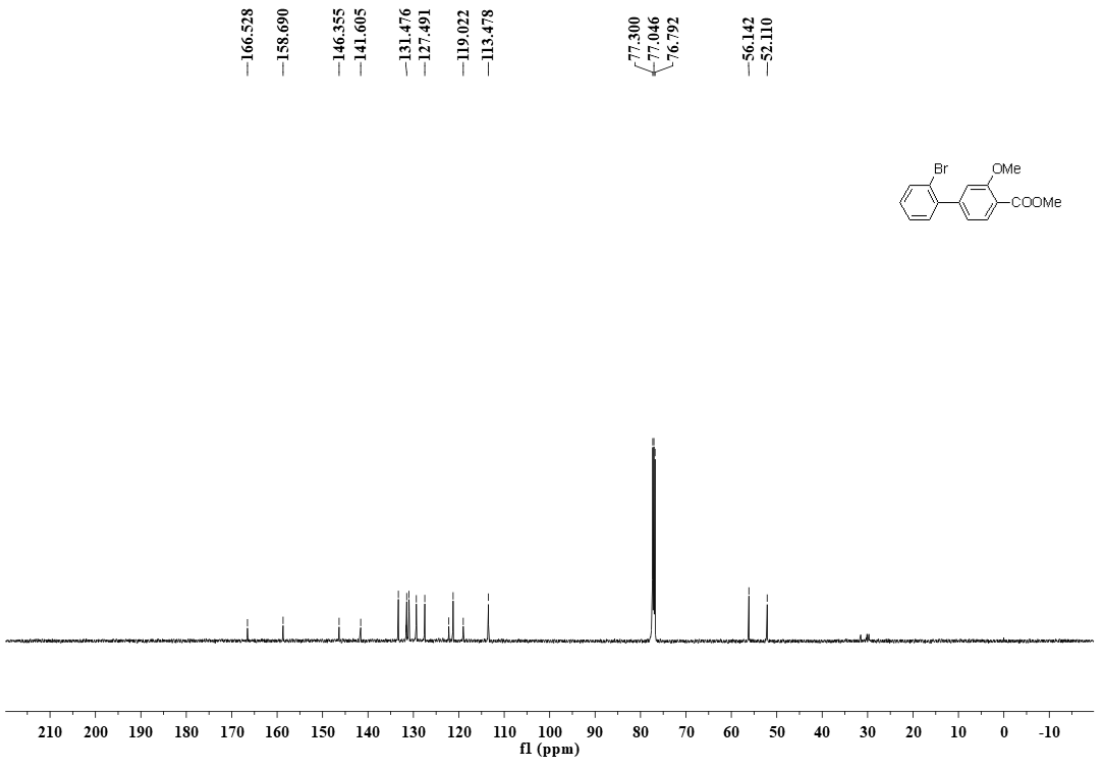
^{1}H-^{1}H NOESY of **3d**



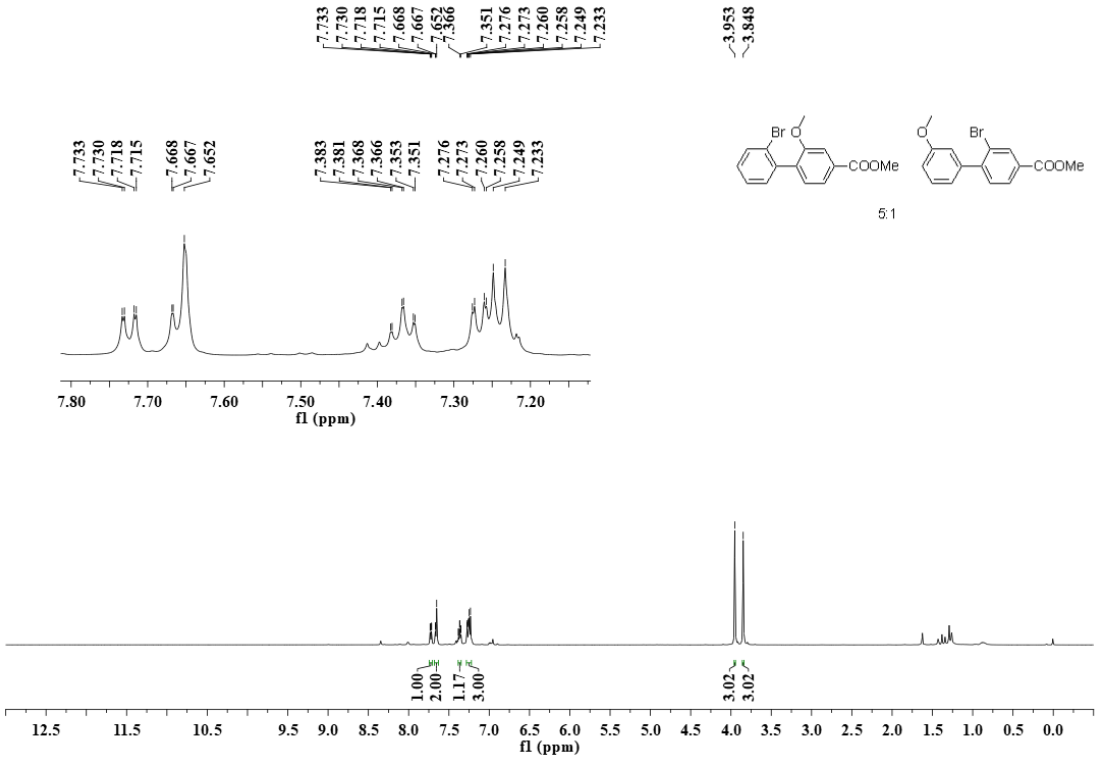
^{1}H NMR (500 MHz, $CDCl_3$) of ***m*-3e**



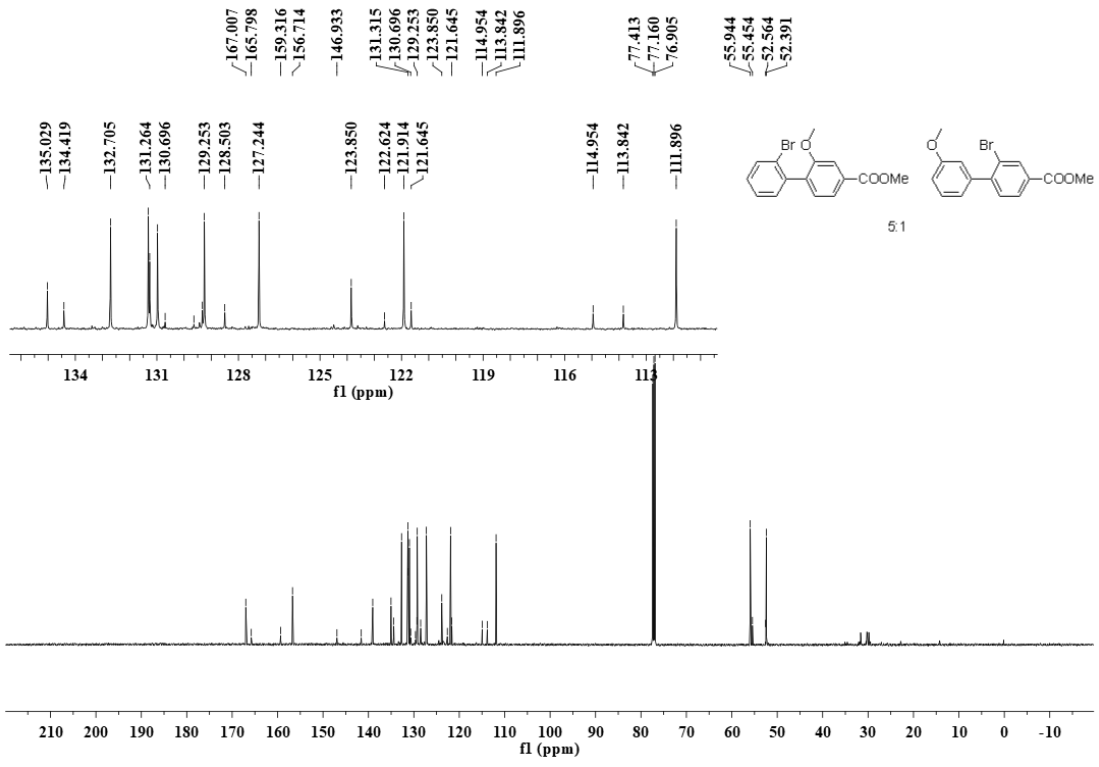
^{13}C NMR (125 MHz, $CDCl_3$) of ***m*-3e**



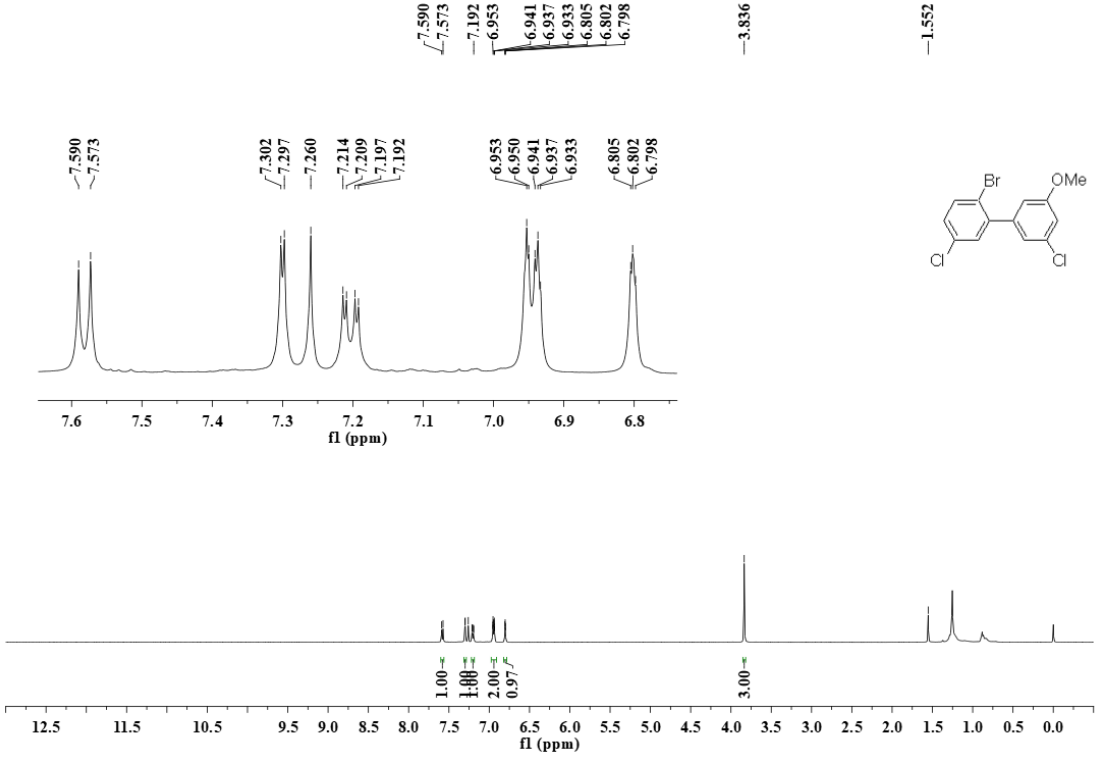
^{1}H NMR (500 MHz, $CDCl_3$) of ***o*-3e and 3e'**



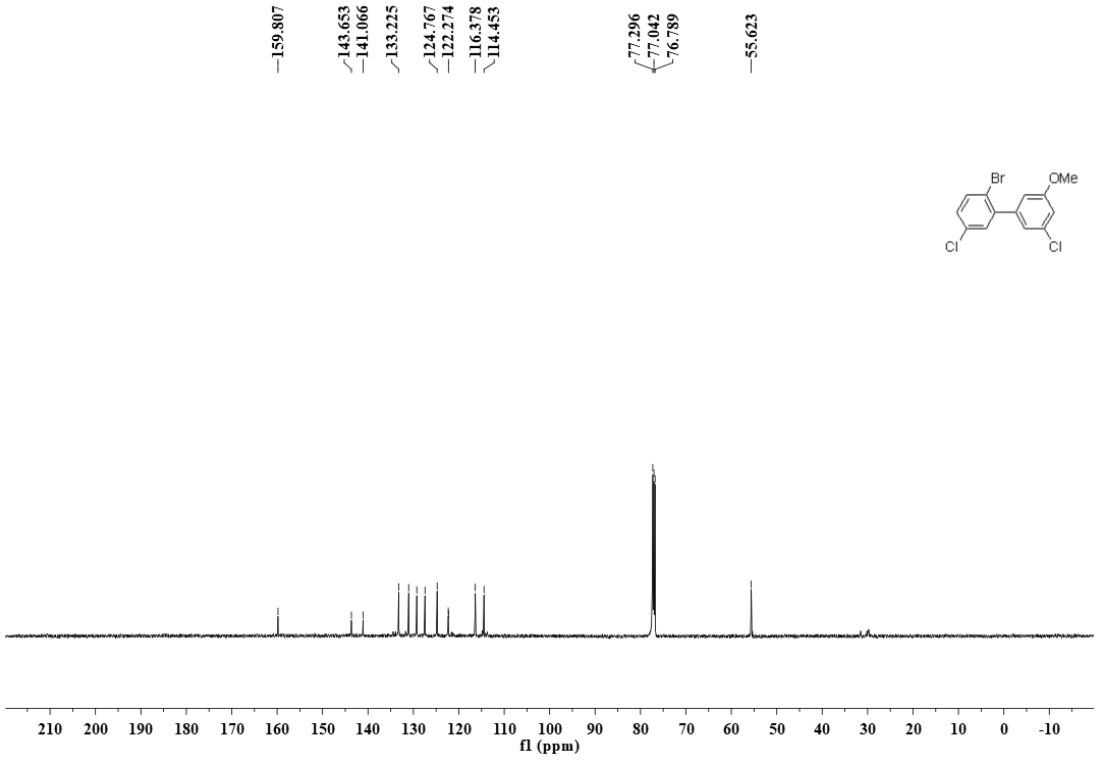
^{13}C NMR (125 MHz, $CDCl_3$) of ***o*-3e and 3e'**



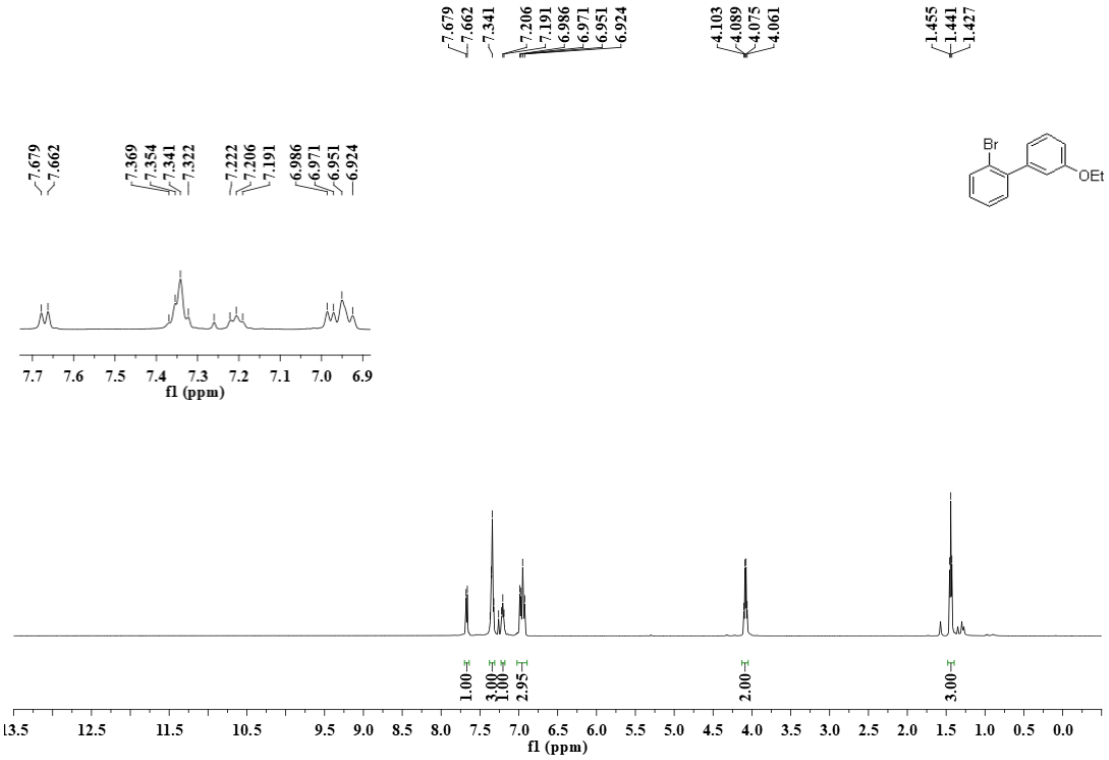
^{1}H NMR (500 MHz, $CDCl_3$) of **3f**



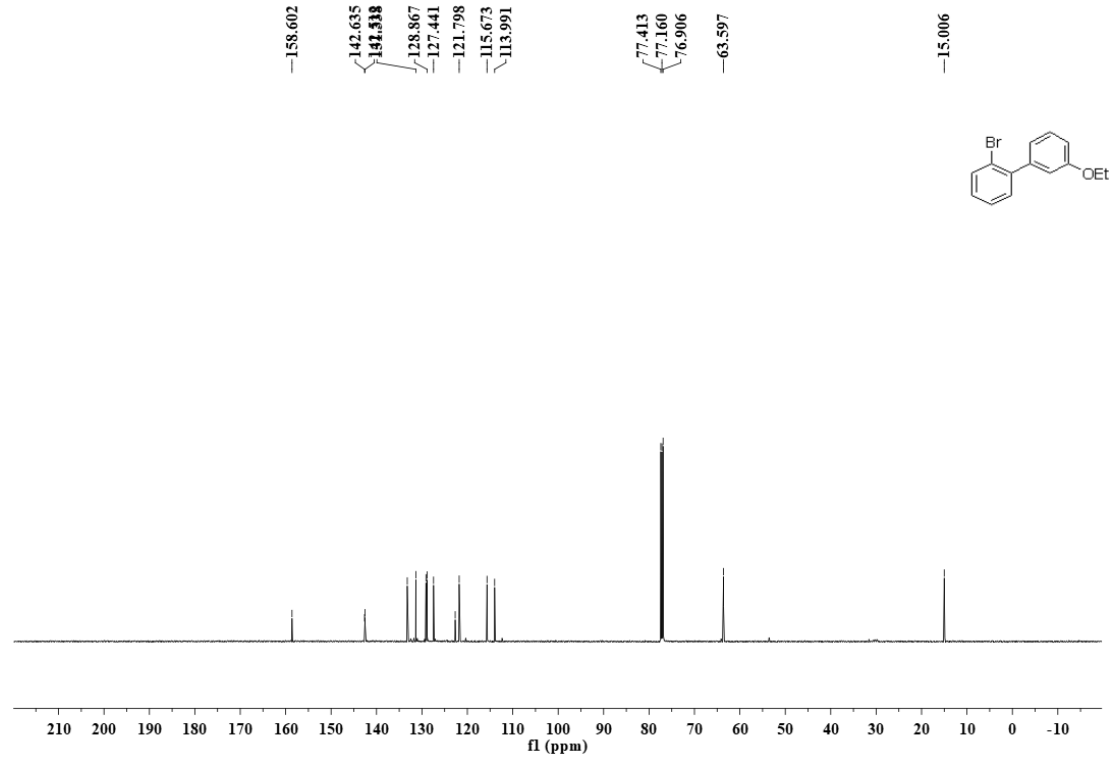
^{13}C NMR (125 MHz, $CDCl_3$) of **3f**



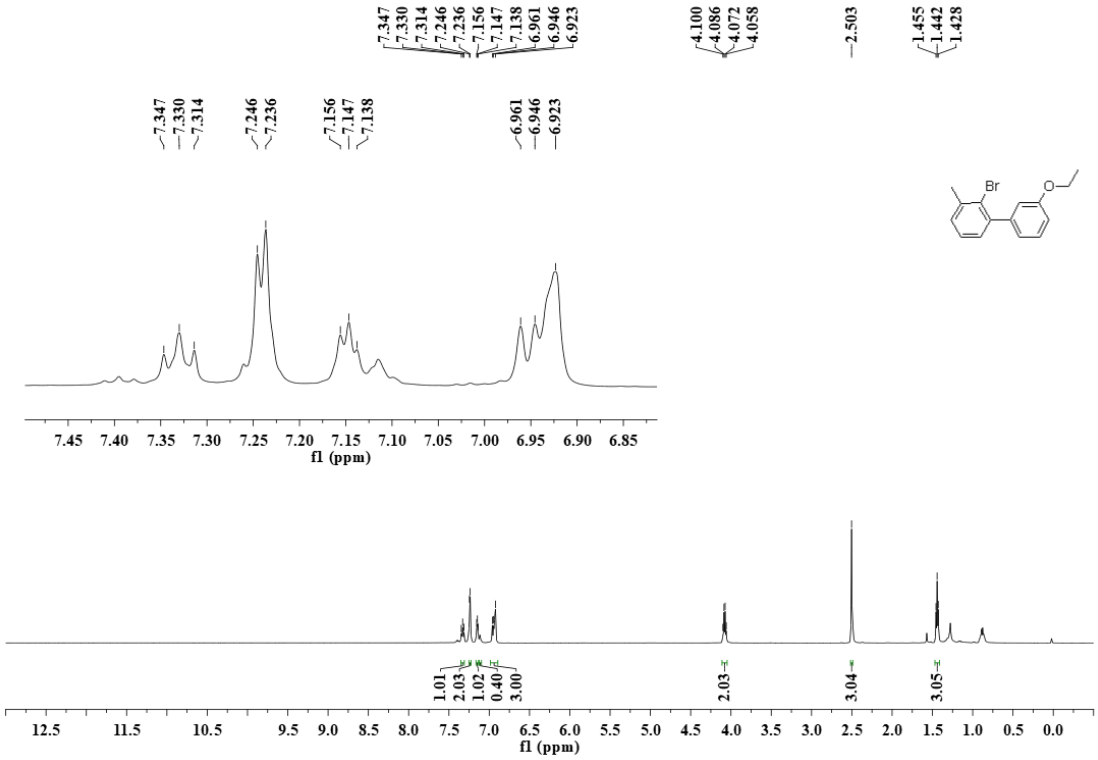
^{1}H NMR (500 MHz, $CDCl_3$) of **3g**



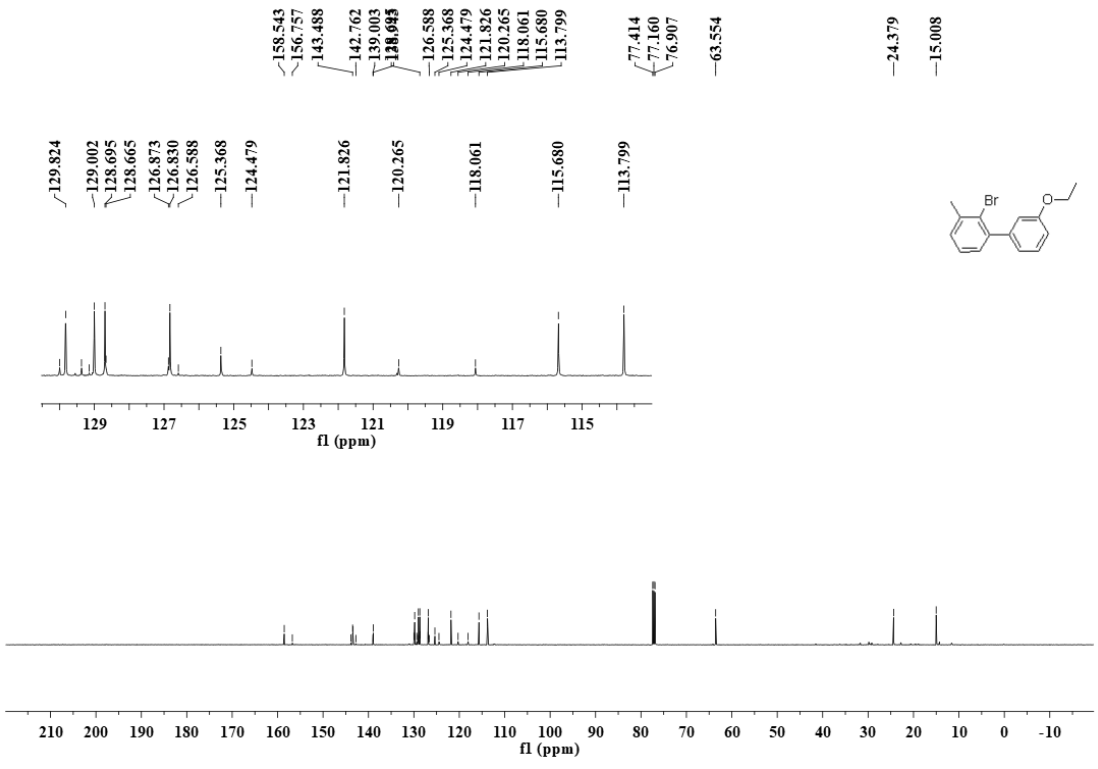
^{13}C NMR (125 MHz, $CDCl_3$) of **3g**



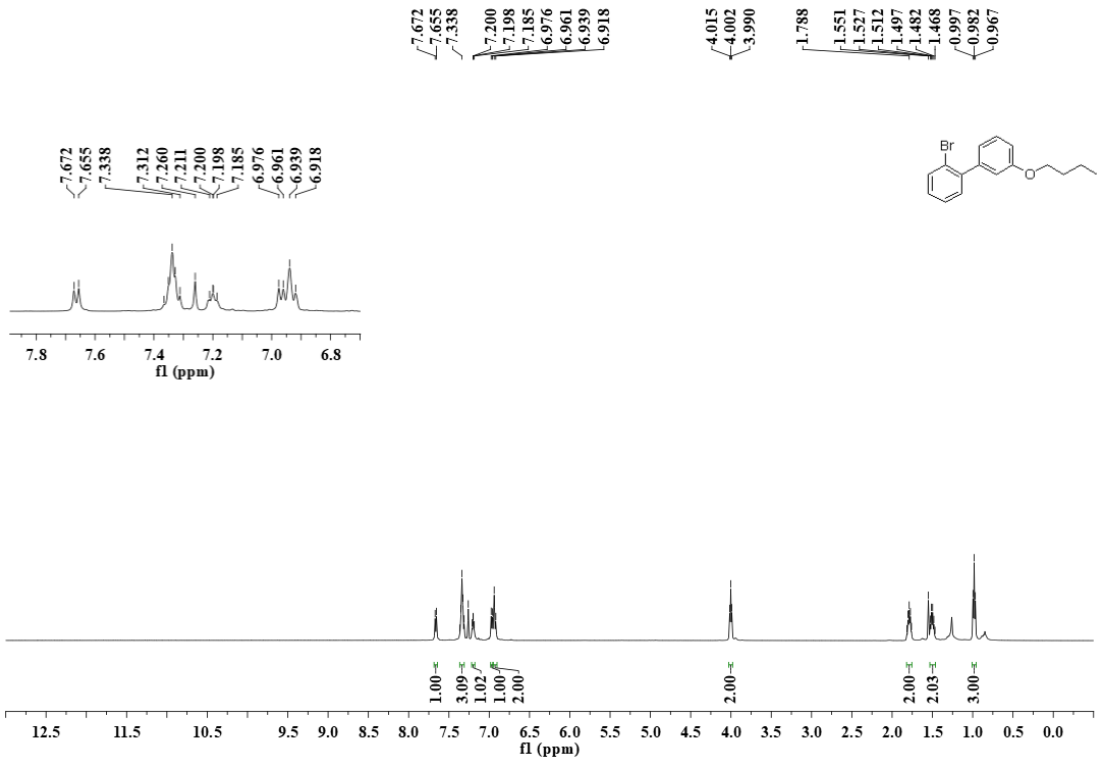
^{1}H NMR (500 MHz, $CDCl_3$) of **3h**



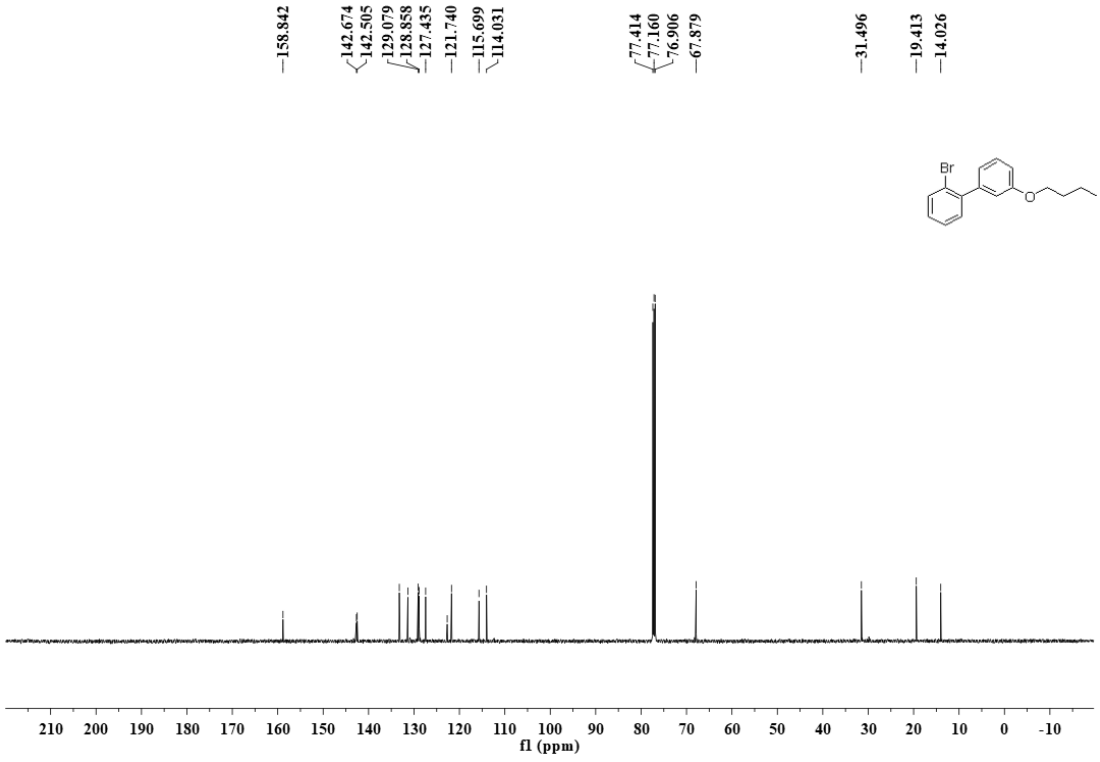
^{13}C NMR (125 MHz, $CDCl_3$) of **3h**



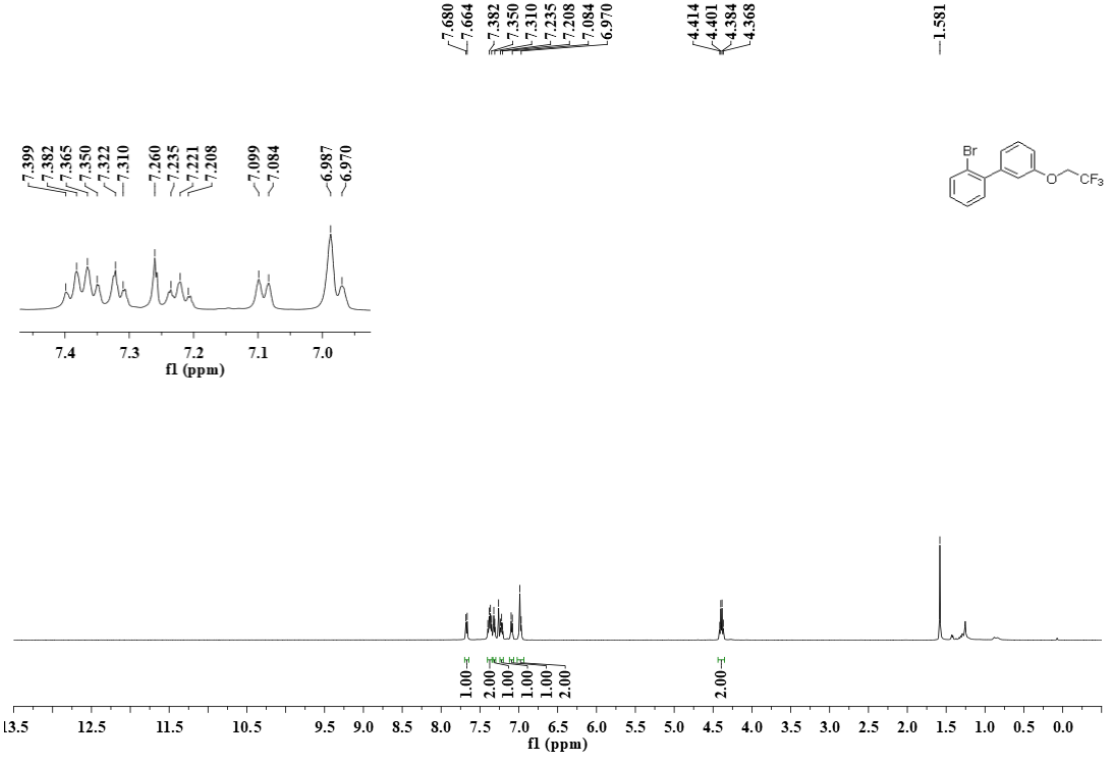
^{1}H NMR (500 MHz, $CDCl_3$) of **3i**



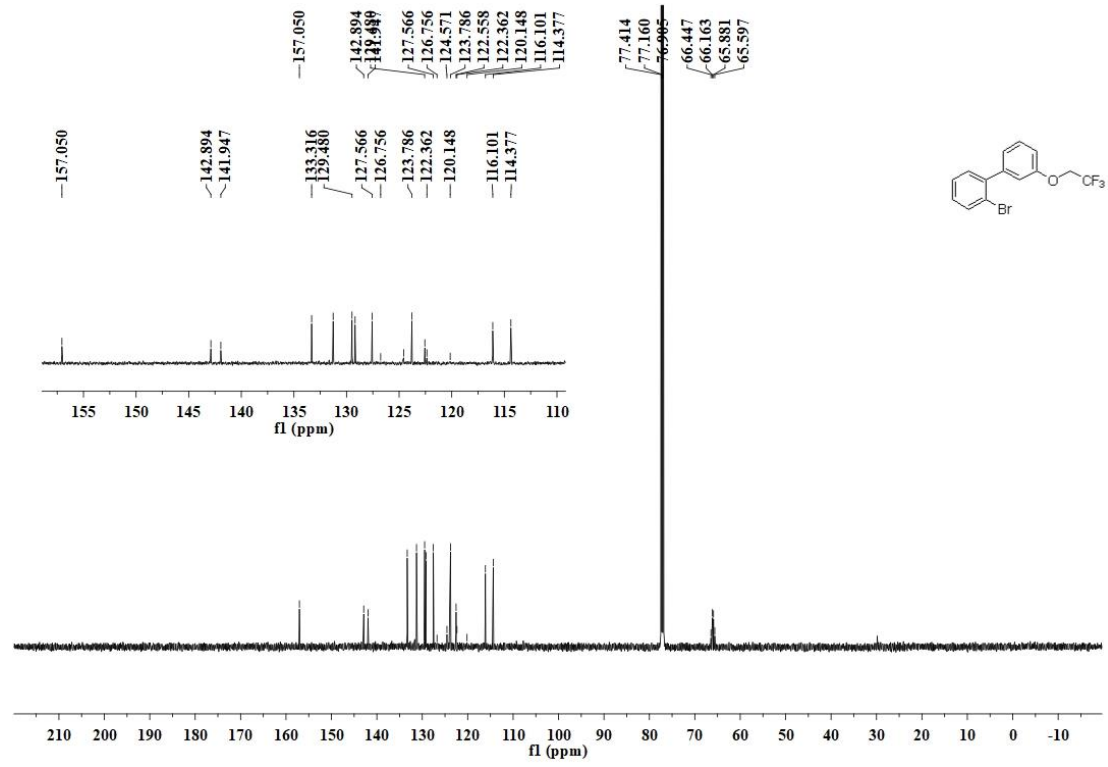
^{13}C NMR (125 MHz, $CDCl_3$) of **3i**



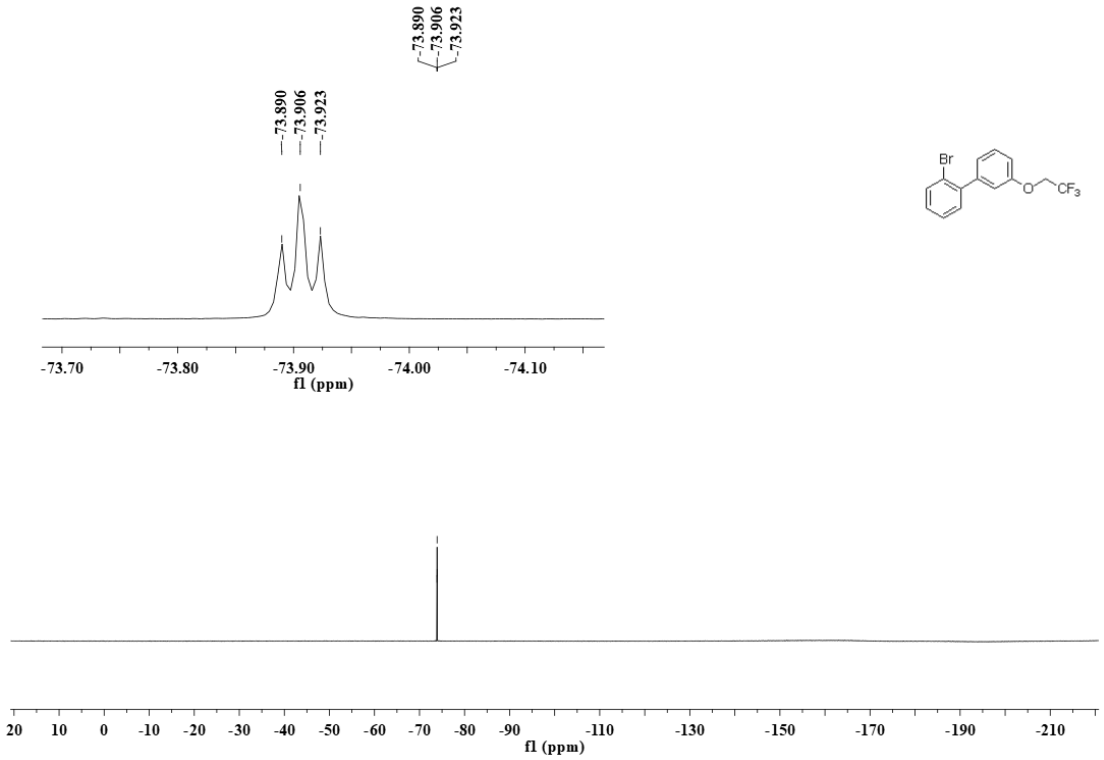
^{1}H NMR (500 MHz, $CDCl_3$) of **3j**



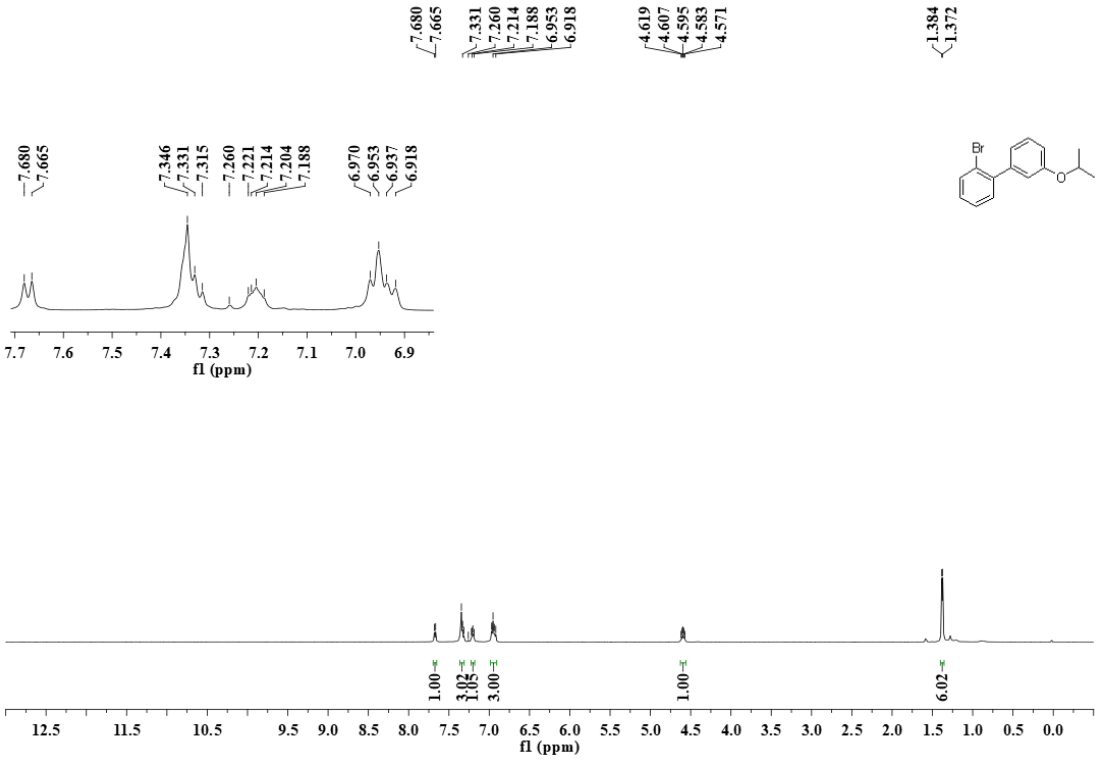
^{13}C NMR (125 MHz, $CDCl_3$) of **3j**



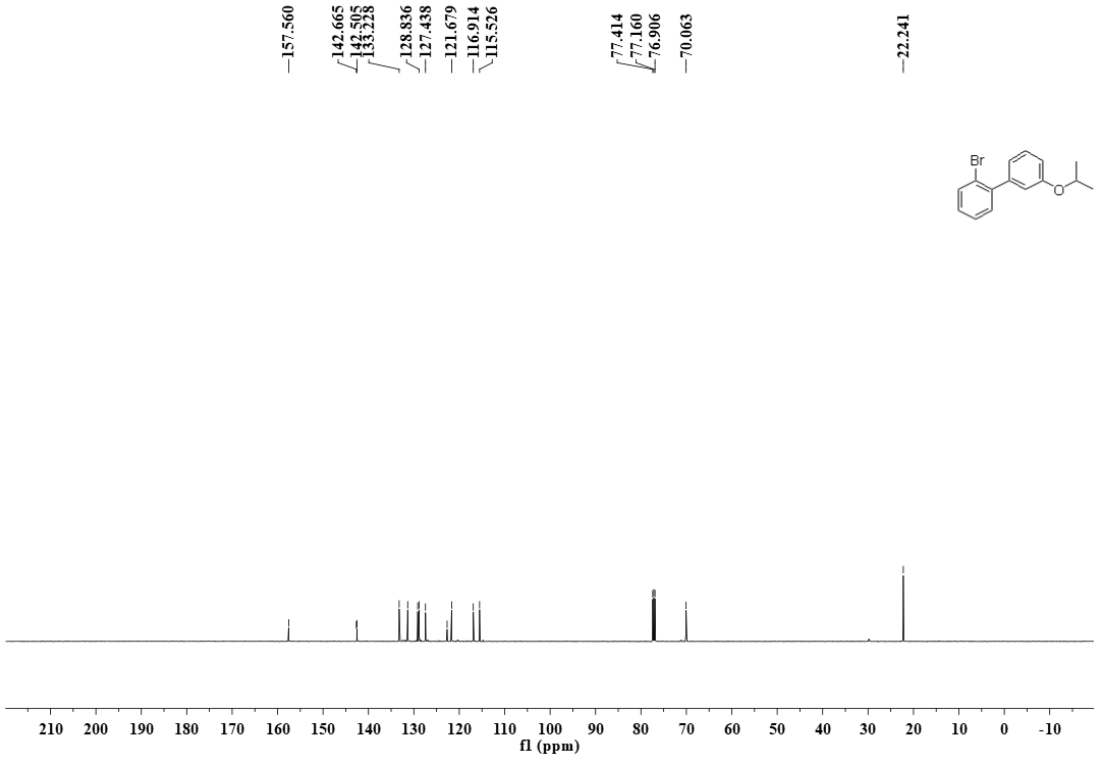
^{19}F NMR (471 MHz, $CDCl_3$) of **3j**



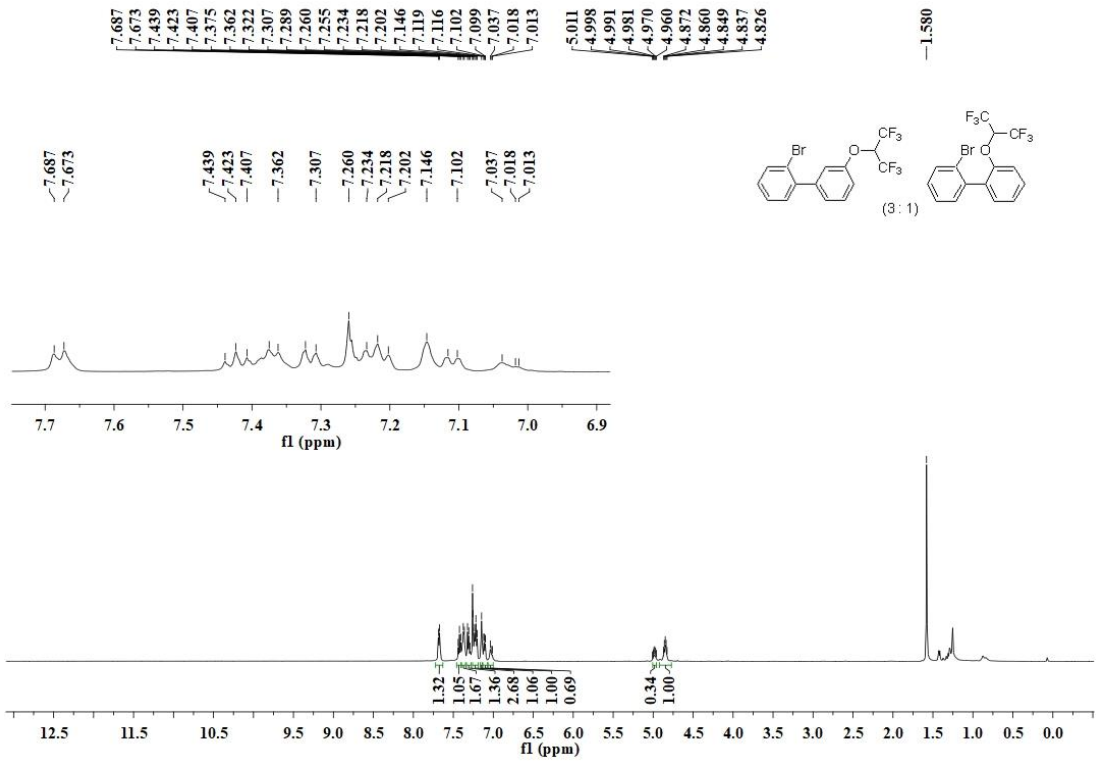
^{1}H NMR (500 MHz, $CDCl_3$) of **3k**



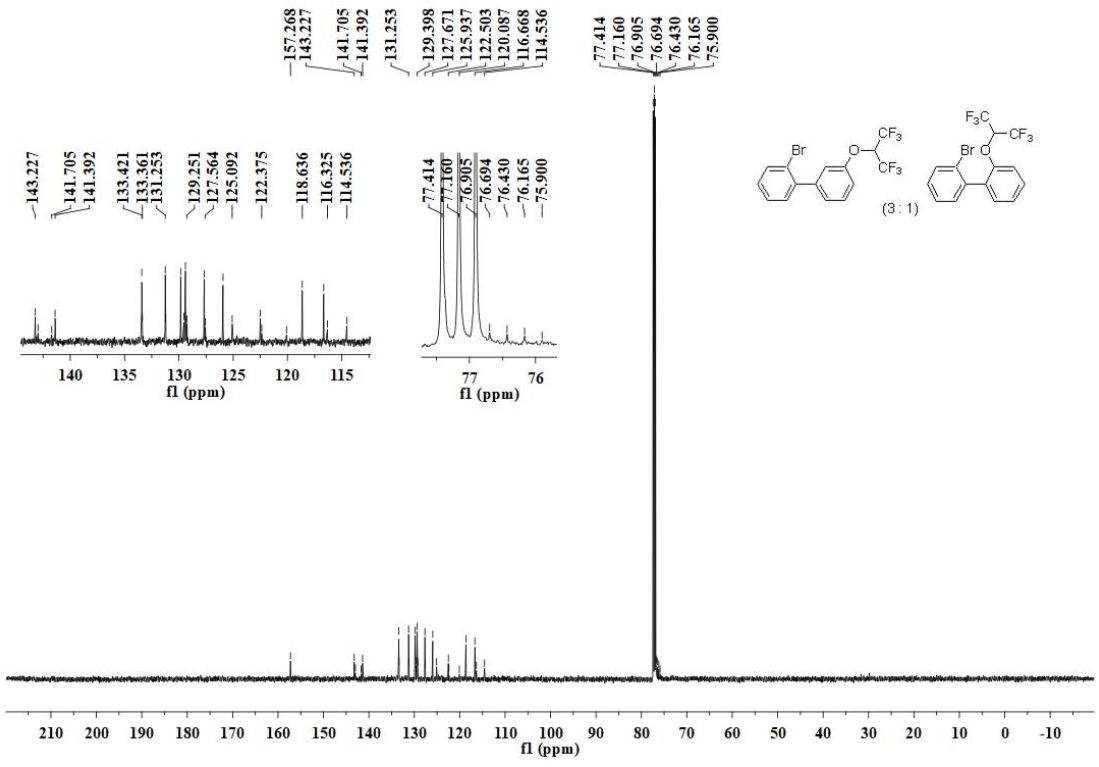
^{13}C NMR (125 MHz, $CDCl_3$) of **3k**



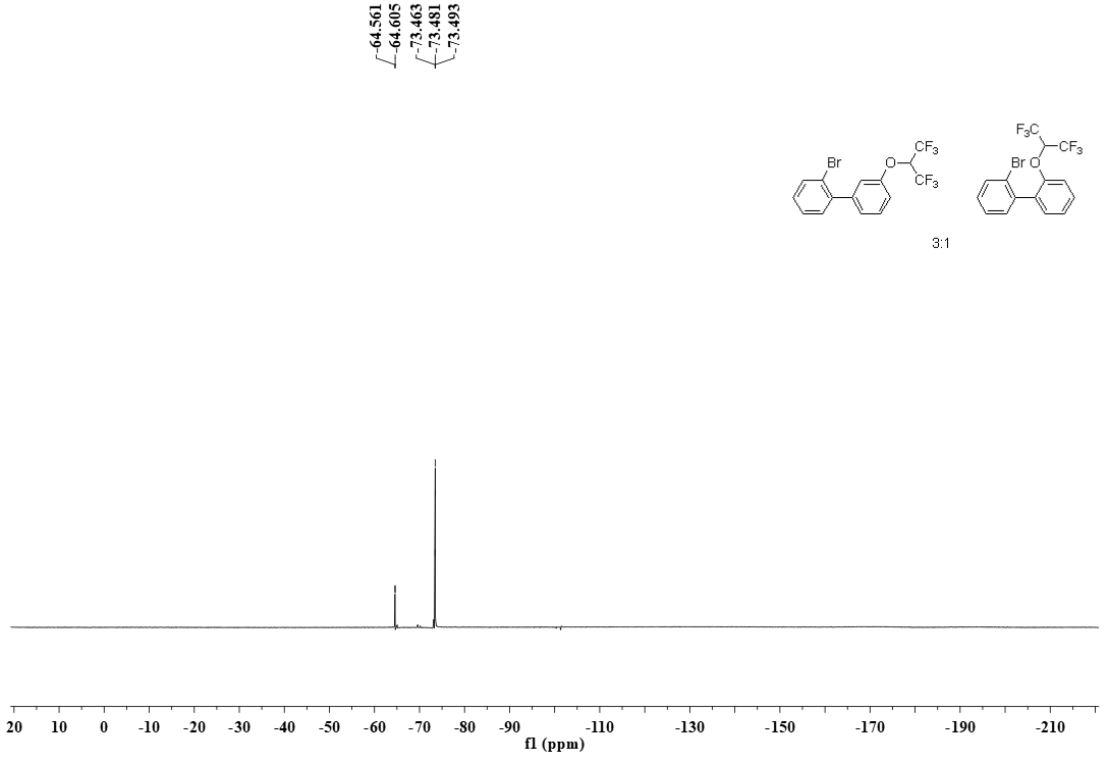
^{1}H NMR (500 MHz, $CDCl_3$) of **3l**



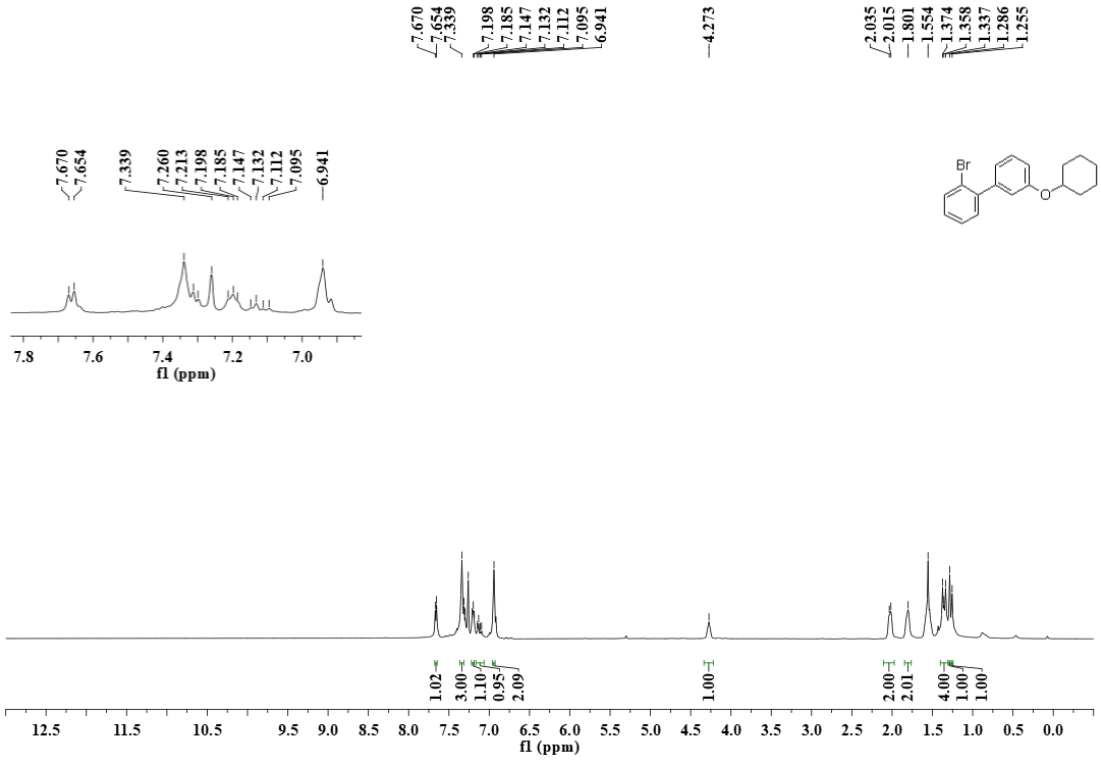
^{13}C NMR (125 MHz, $CDCl_3$) of **3l**



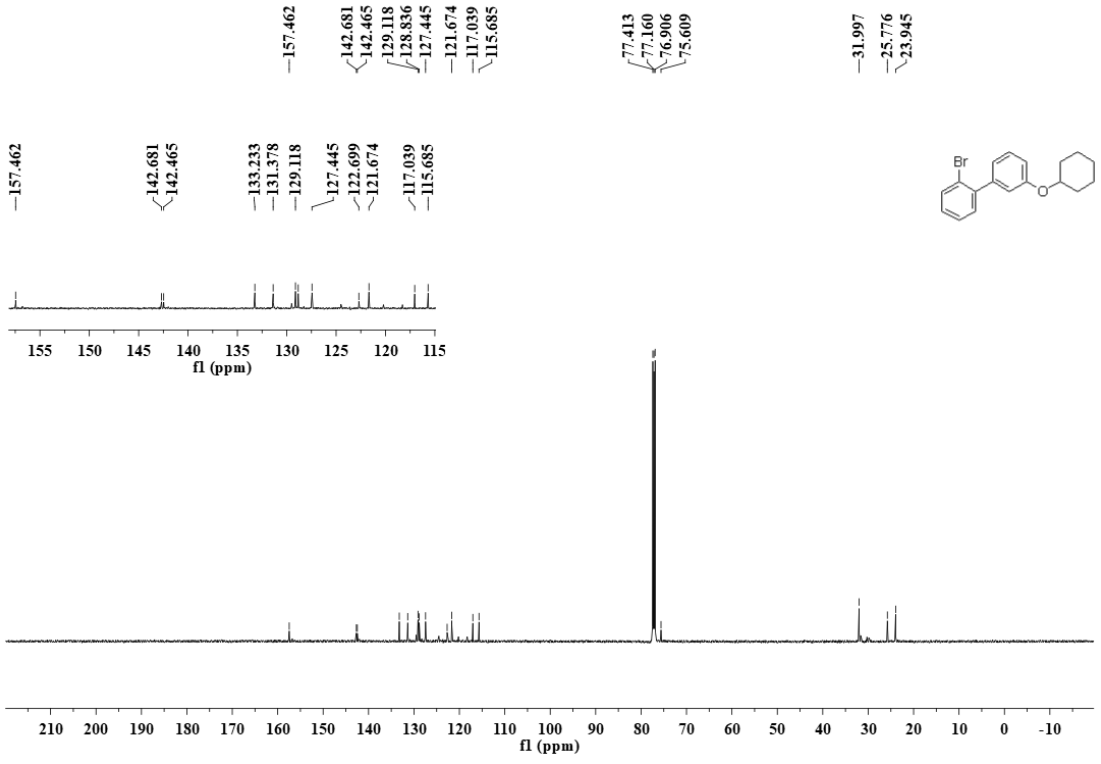
^{19}F NMR (471 MHz, $CDCl_3$) of **3l**



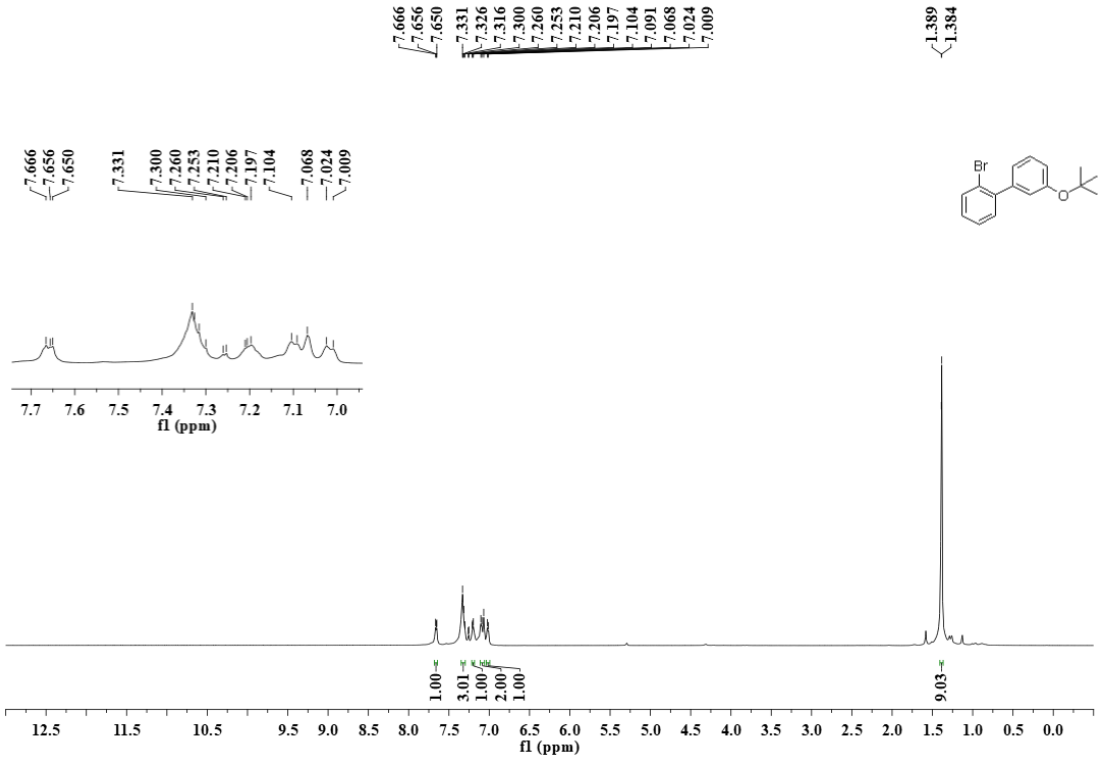
^{1}H NMR (500 MHz, $CDCl_3$) of **3m**



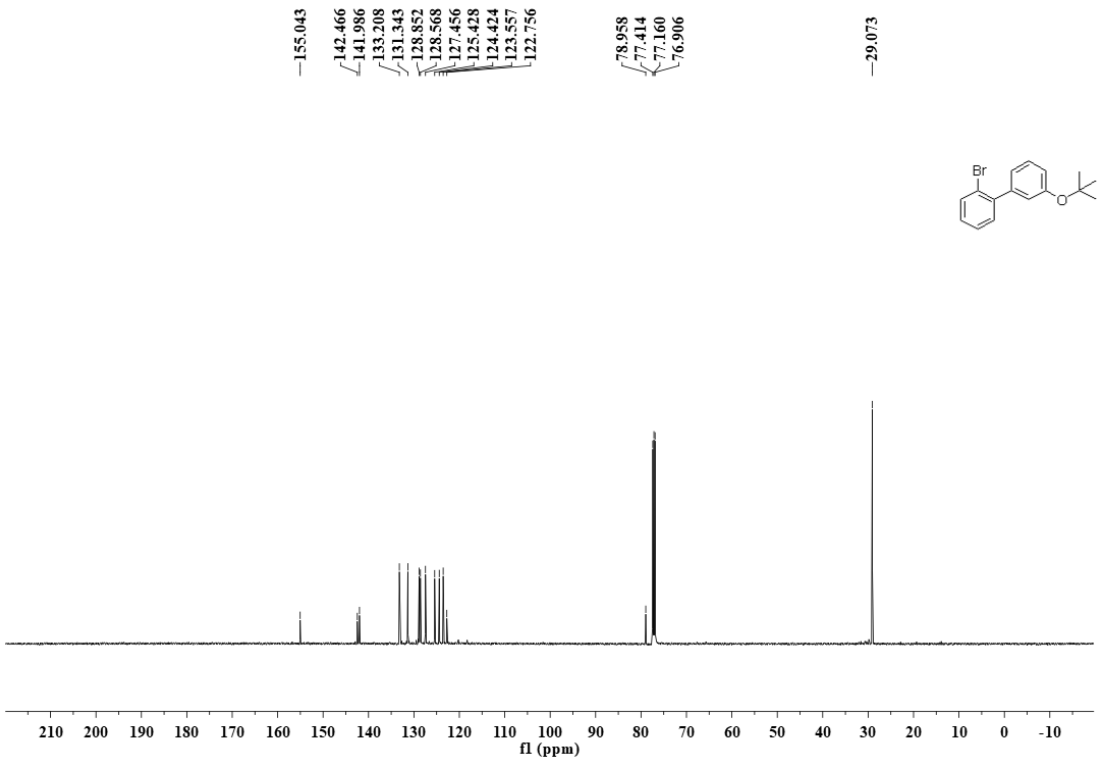
^{13}C NMR (125 MHz, $CDCl_3$) of **3m**



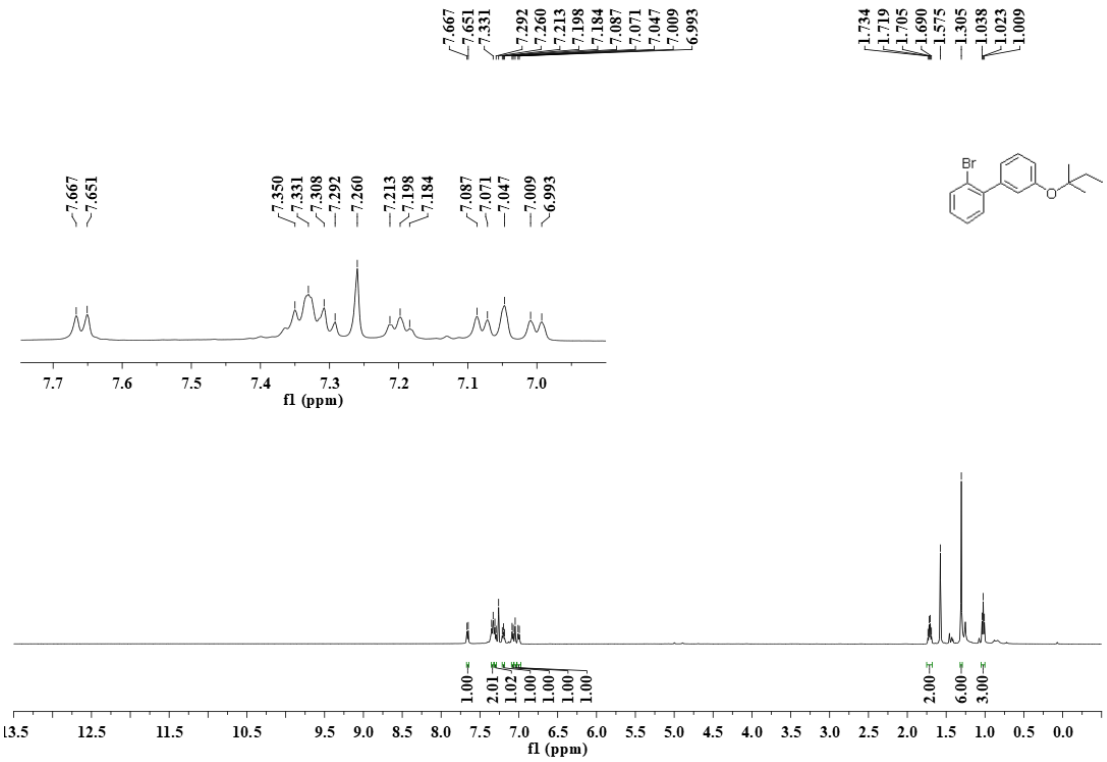
^{1}H NMR (500 MHz, $CDCl_3$) of **3n**



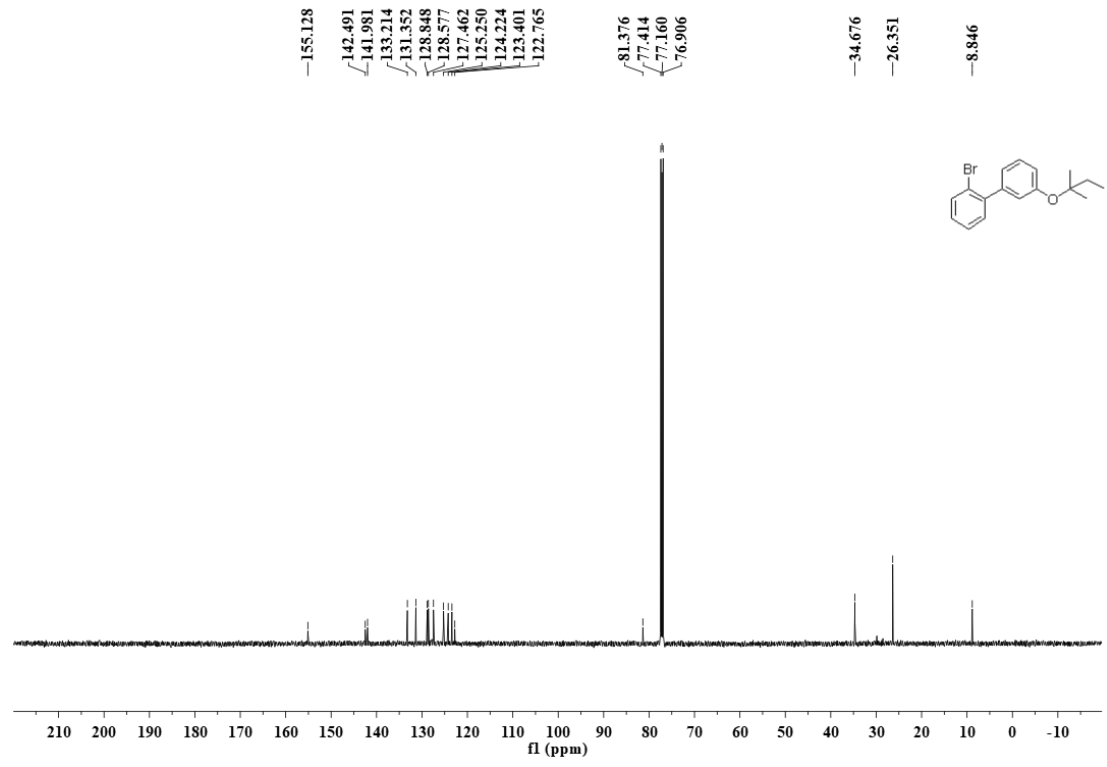
^{13}C NMR (125 MHz, $CDCl_3$) of **3n**



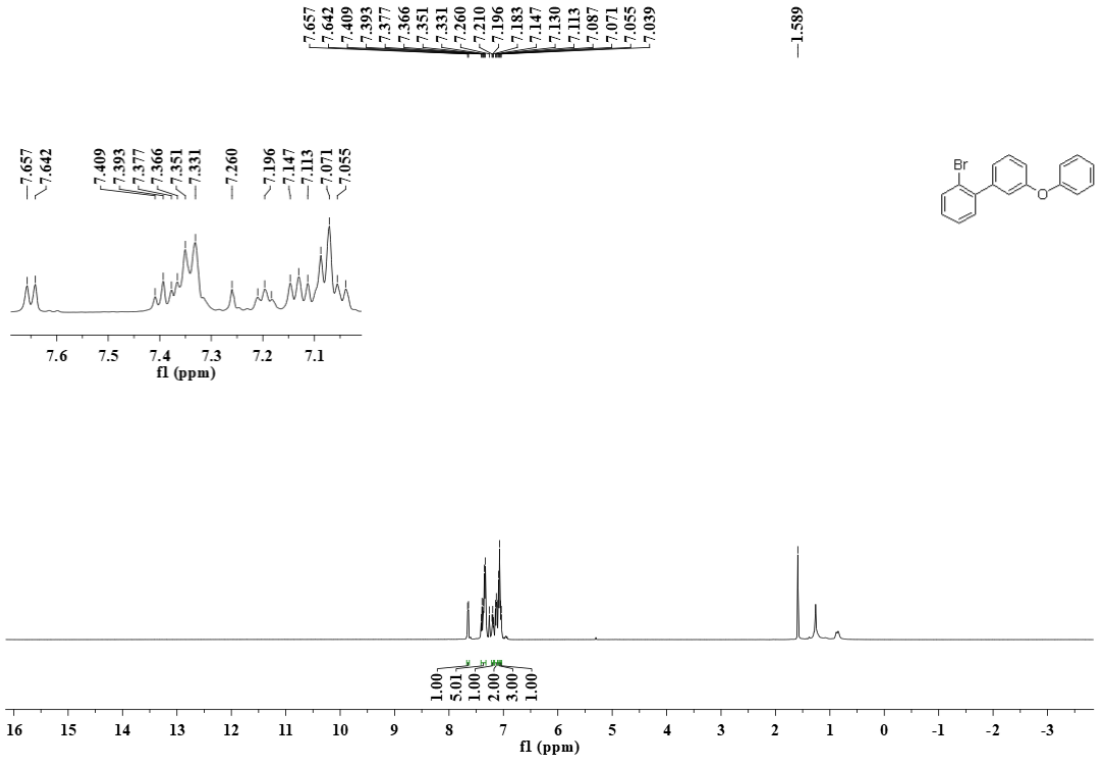
^{1}H NMR (500 MHz, $CDCl_3$) of **3o**



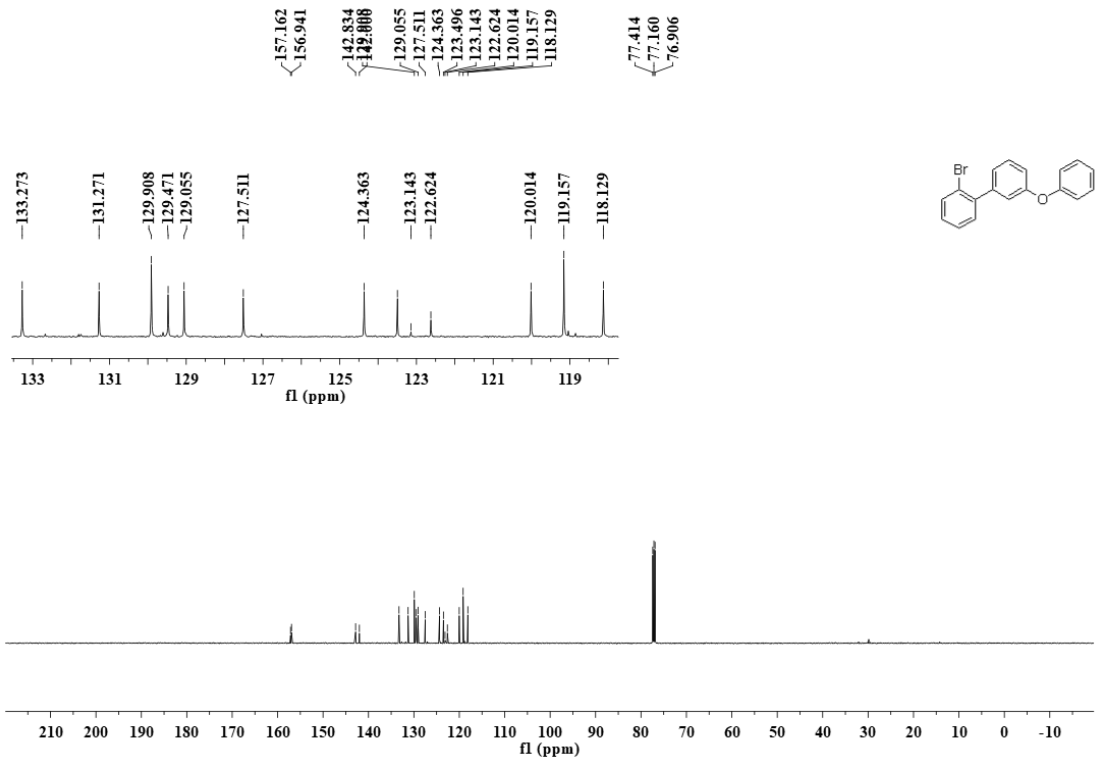
^{13}C NMR (125 MHz, $CDCl_3$) of **3o**



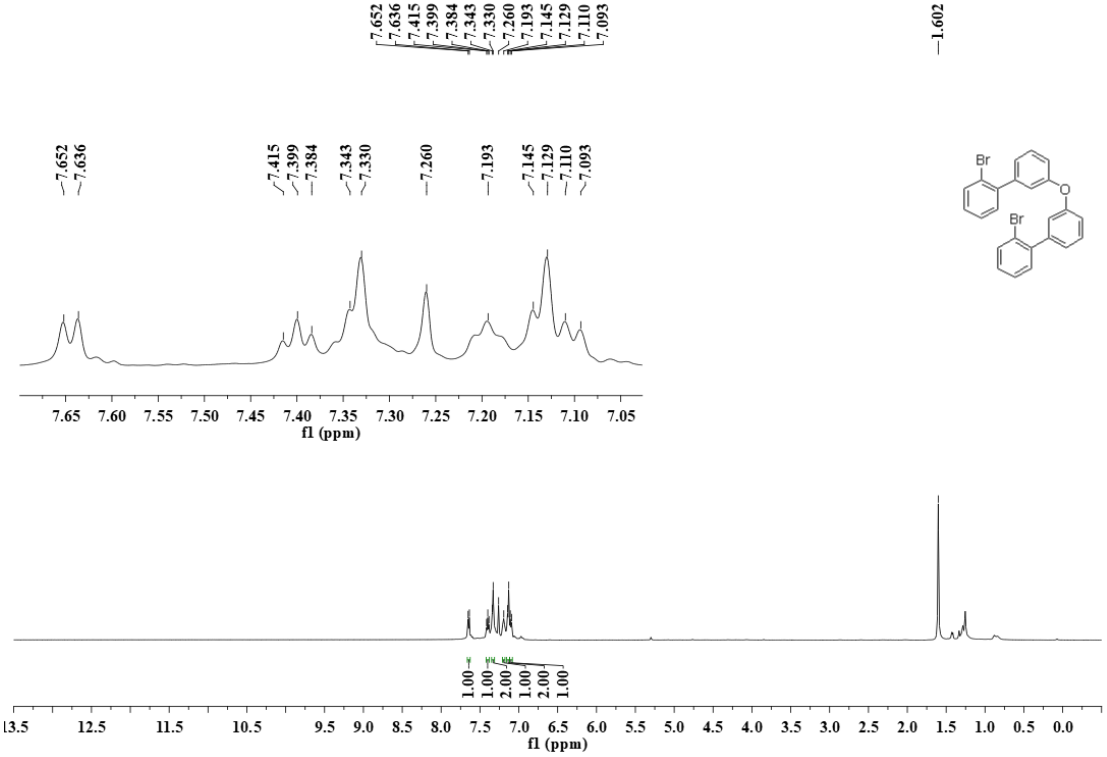
^{1}H NMR (500 MHz, $CDCl_3$) of **3p**



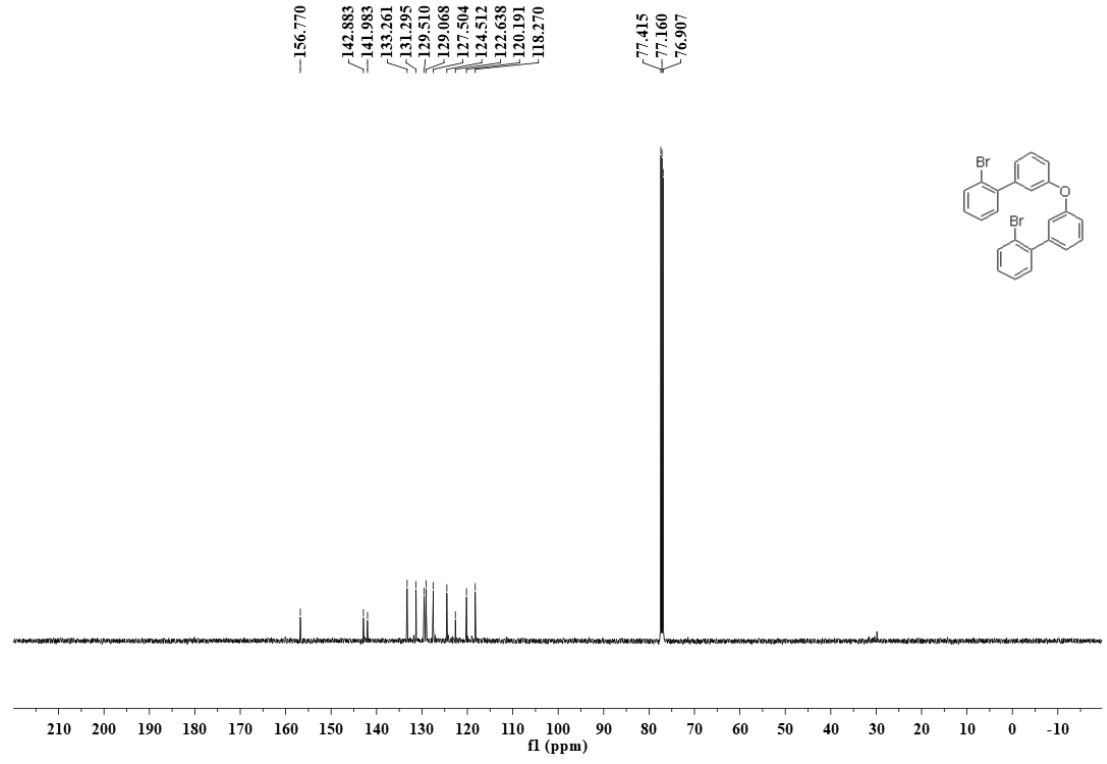
^{13}C NMR (125 MHz, $CDCl_3$) of **3p**



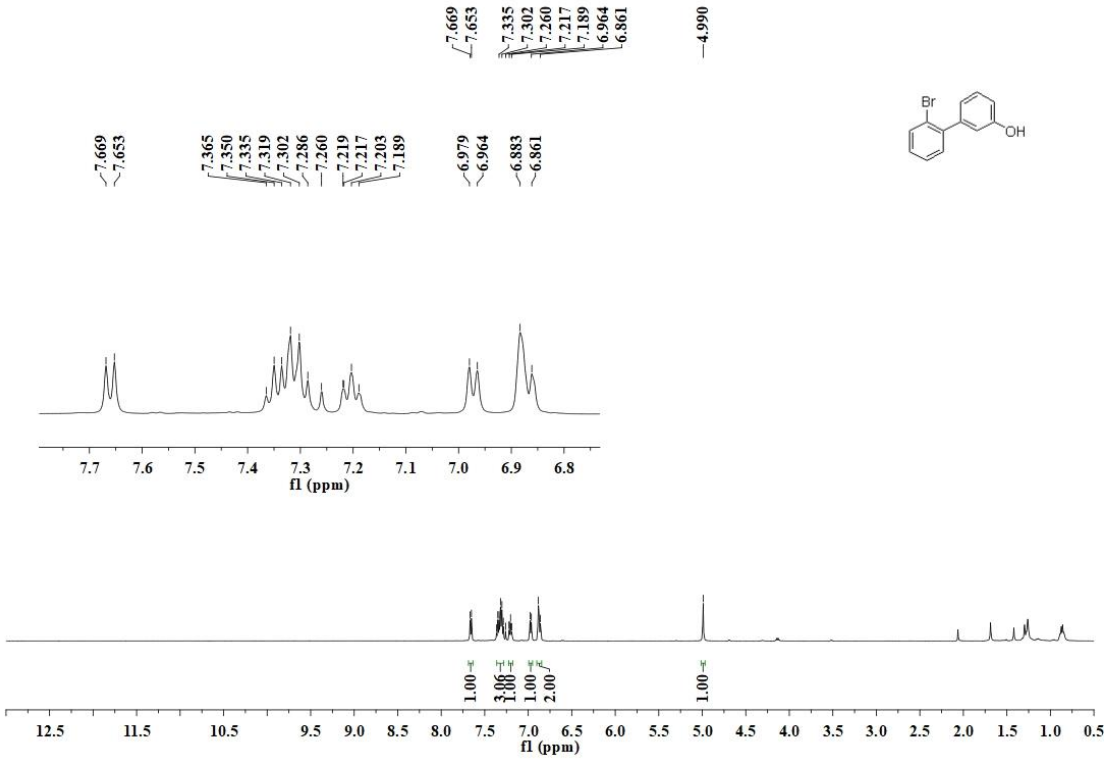
^{1}H NMR (500 MHz, $CDCl_3$) of **di-3q**



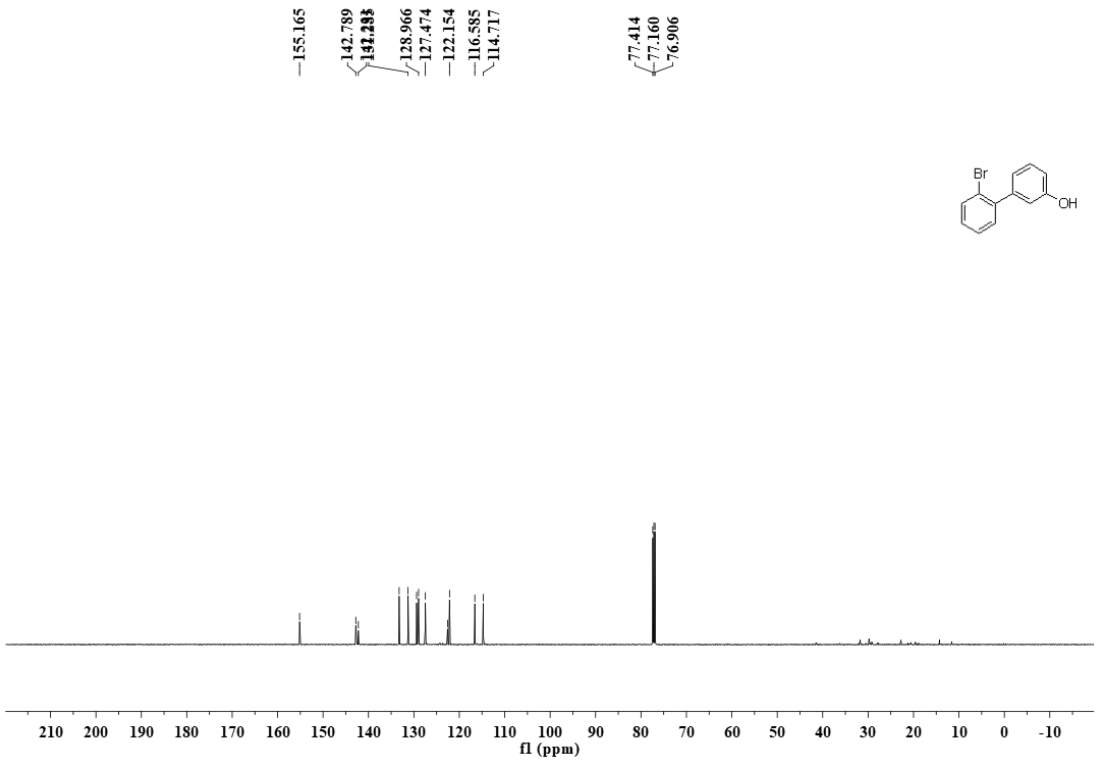
^{13}C NMR (125 MHz, $CDCl_3$) of **di-3q**



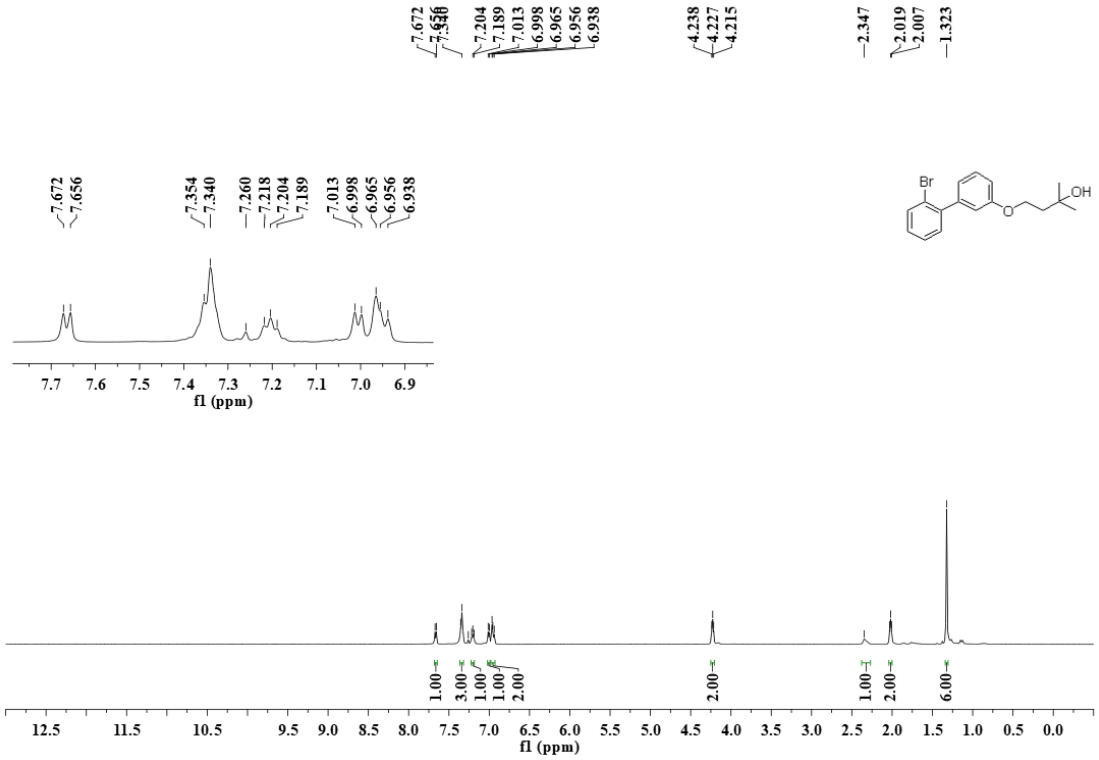
^{1}H NMR (500 MHz, $CDCl_3$) of **mono-3q**



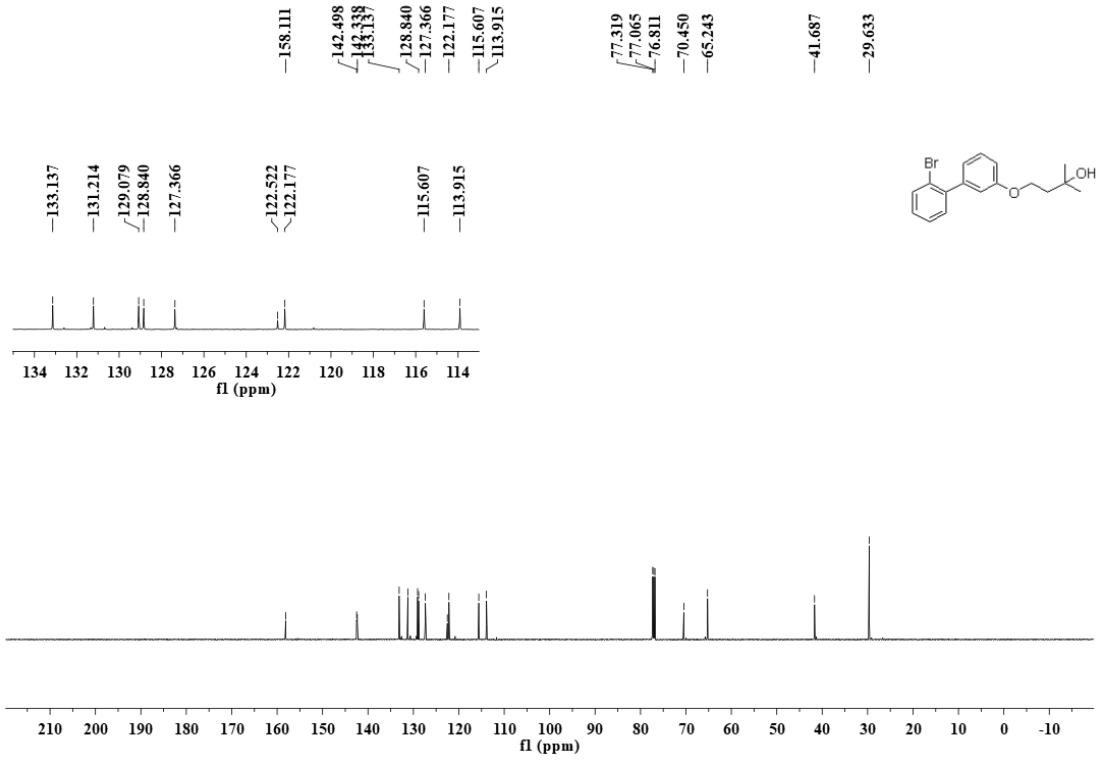
^{13}C NMR (125 MHz, $CDCl_3$) of **mono-3q**



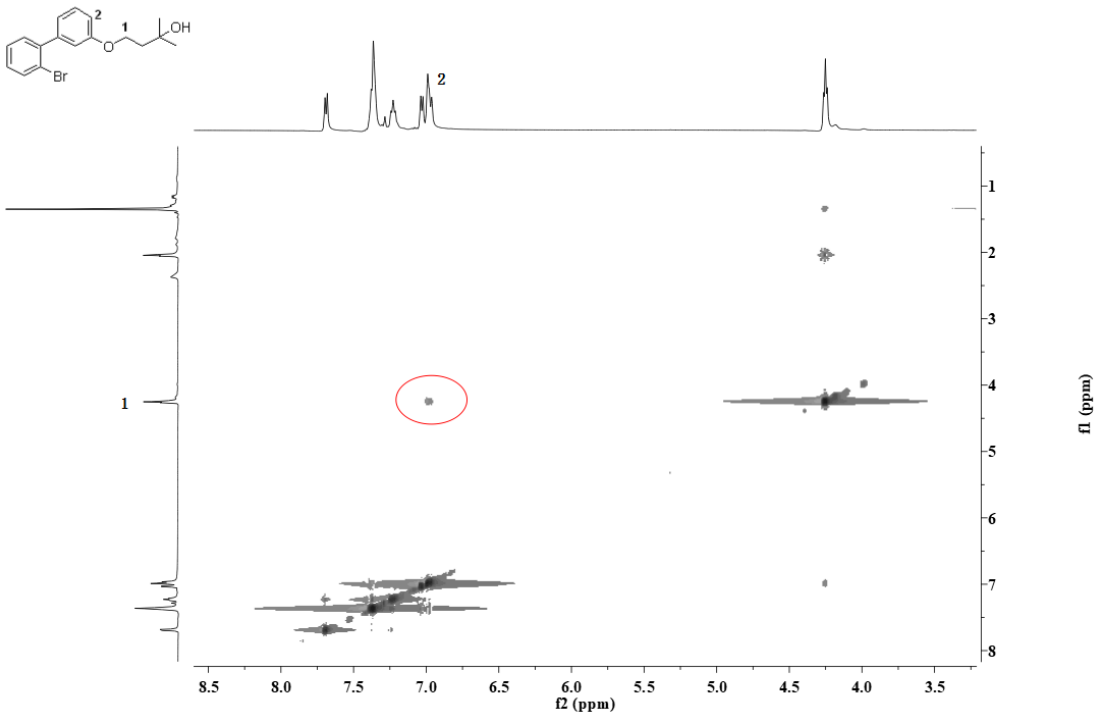
^{1}H NMR (500 MHz, $CDCl_3$) of **3r**



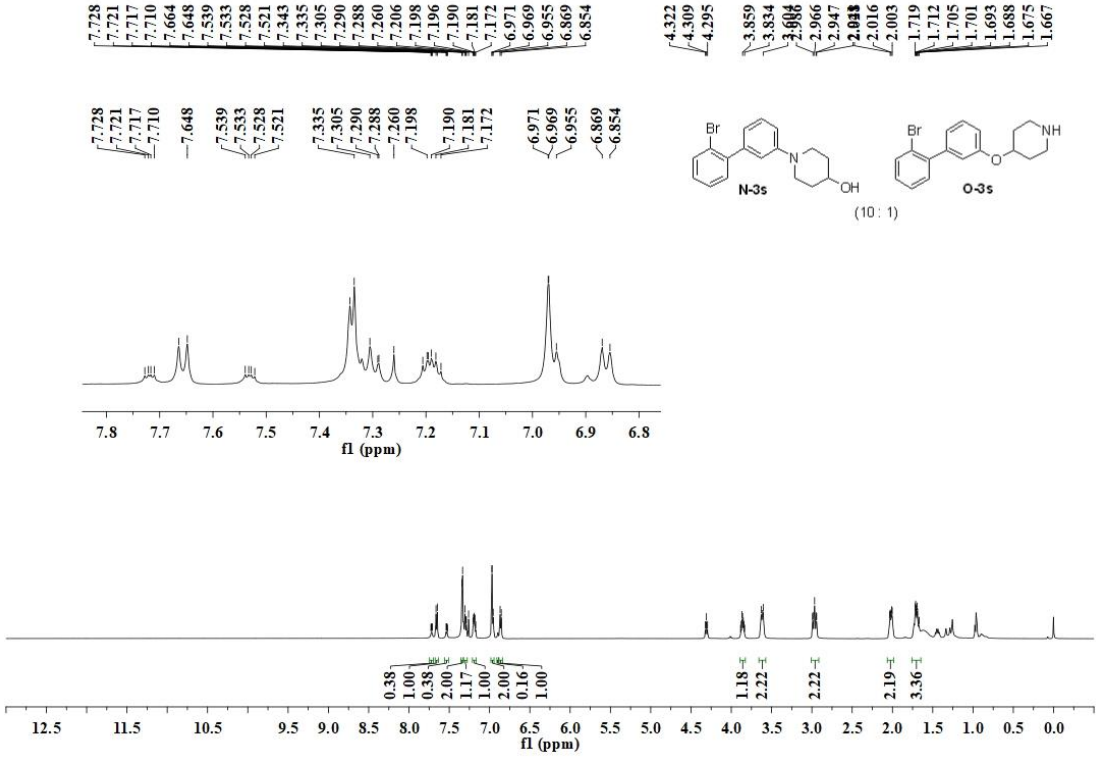
^{13}C NMR (125 MHz, $CDCl_3$) of **3r**



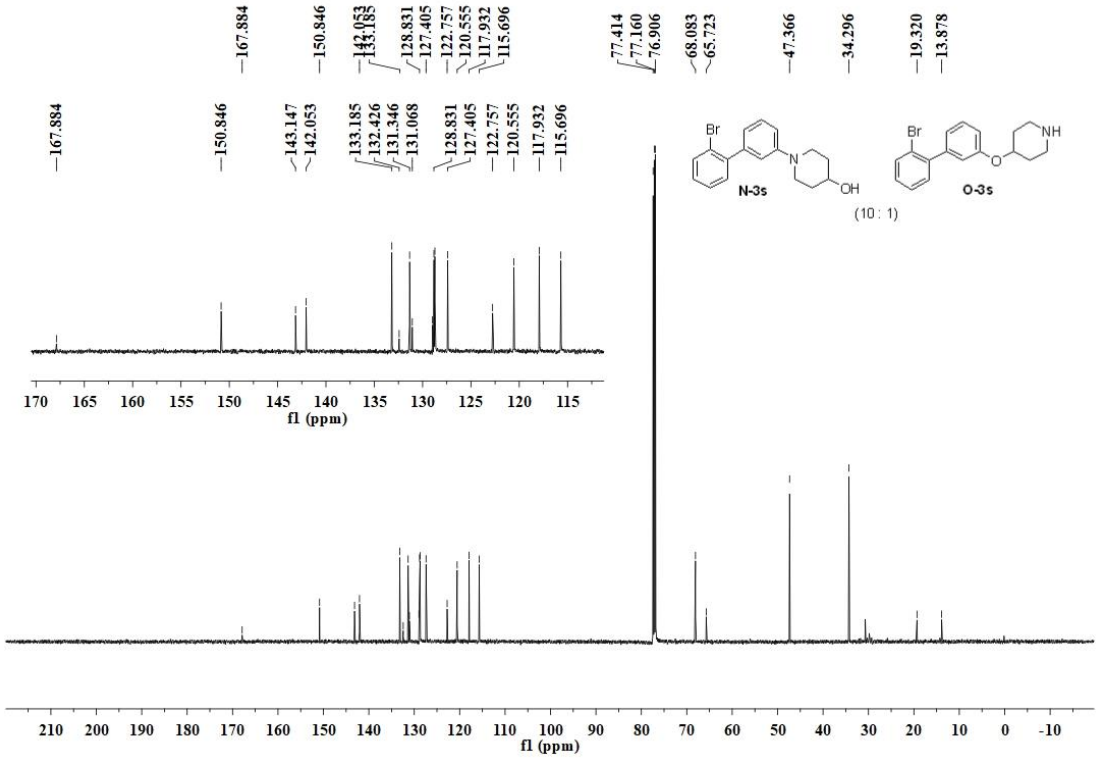
^{1}H-^{1}H NOESY of **3r**



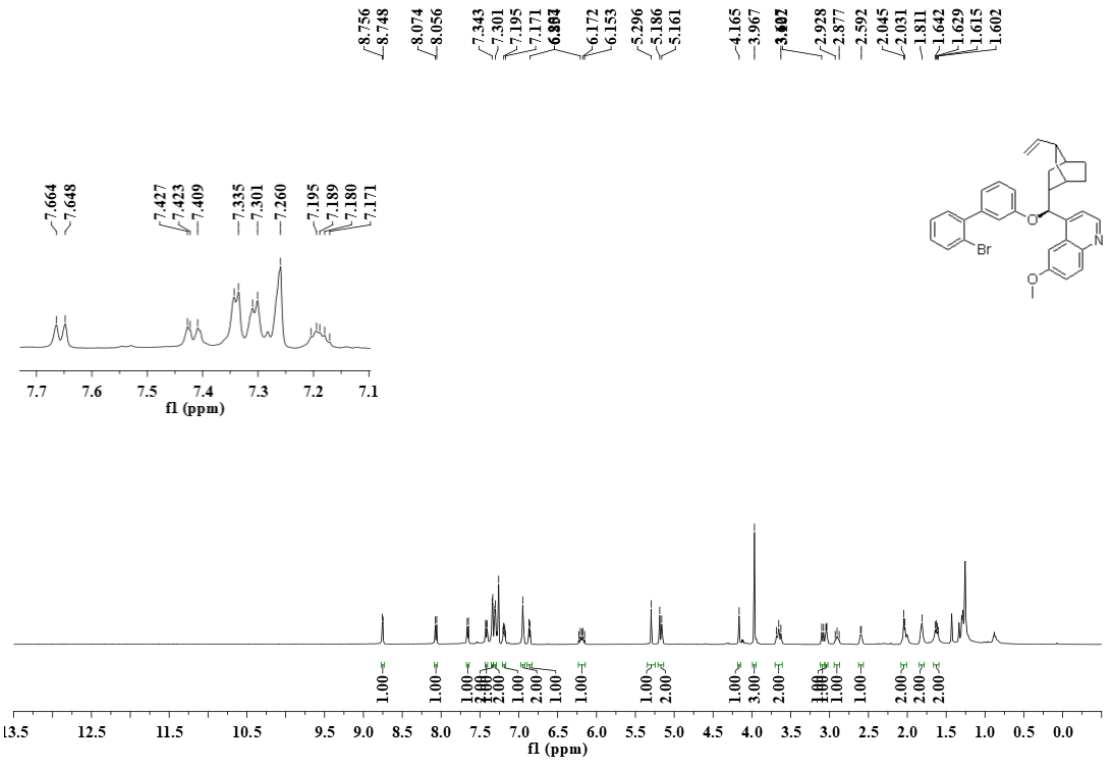
^{1}H NMR (500 MHz, $CDCl_3$) of **N-3s**



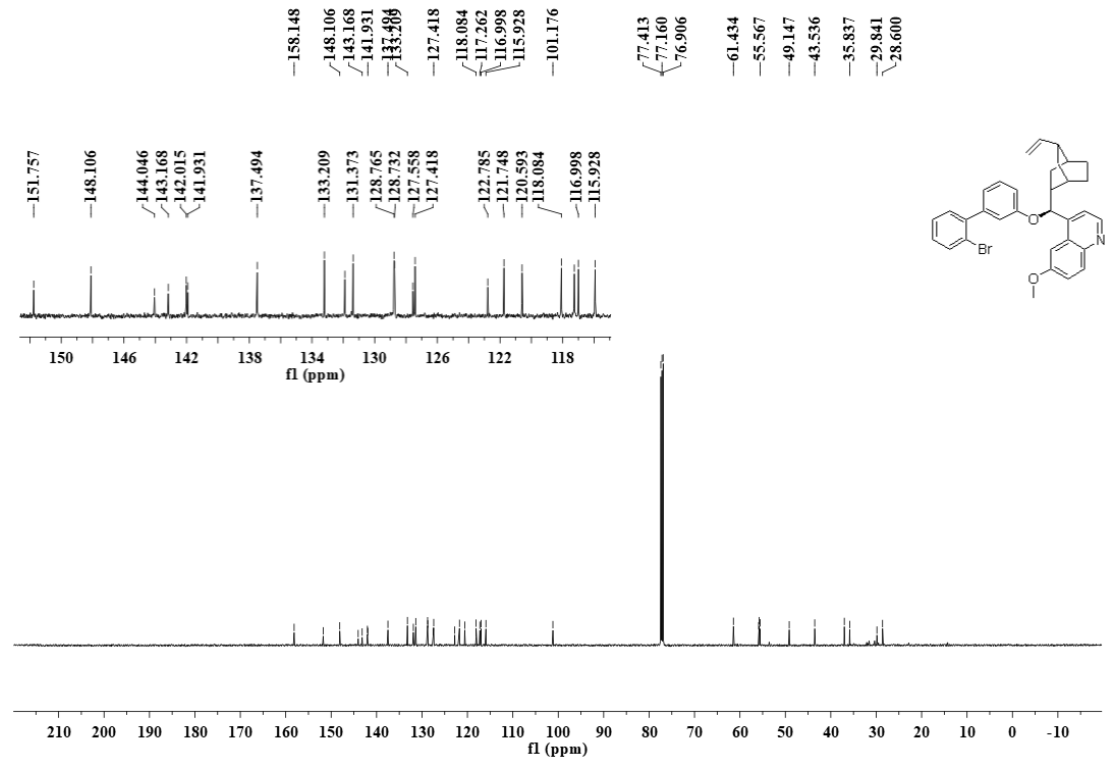
^{13}C NMR (125 MHz, $CDCl_3$) of **N-3s**



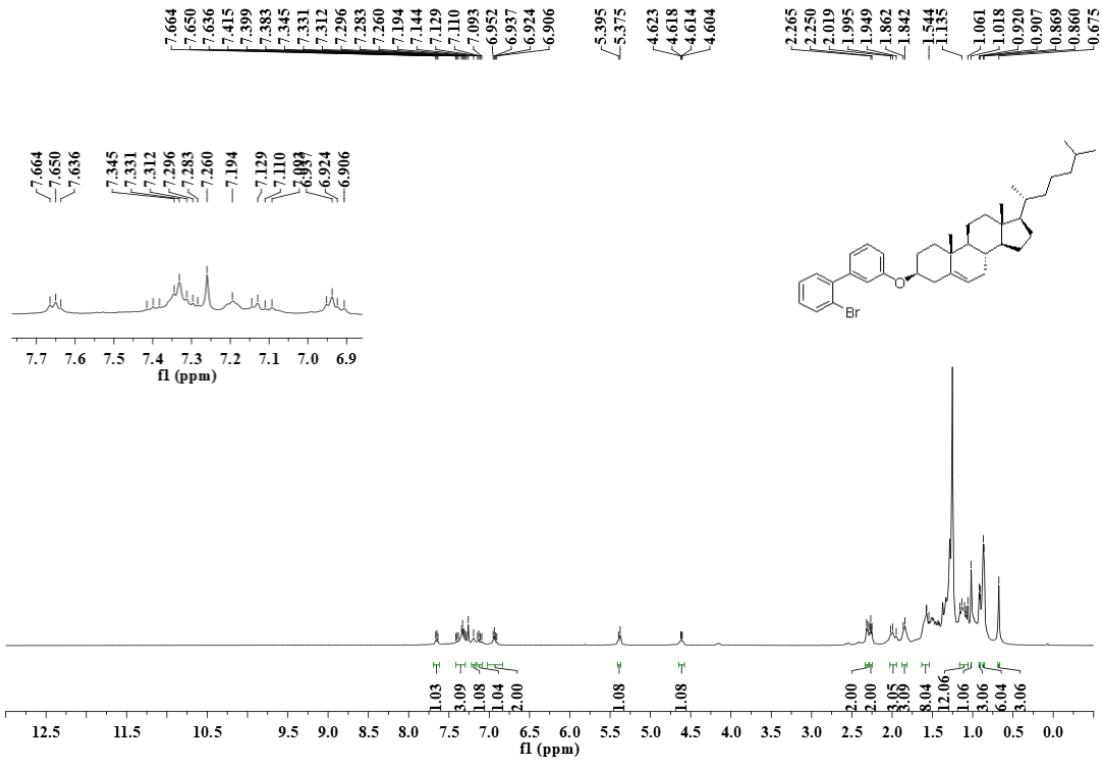
^{1}H NMR (500 MHz, $CDCl_3$) of **5**



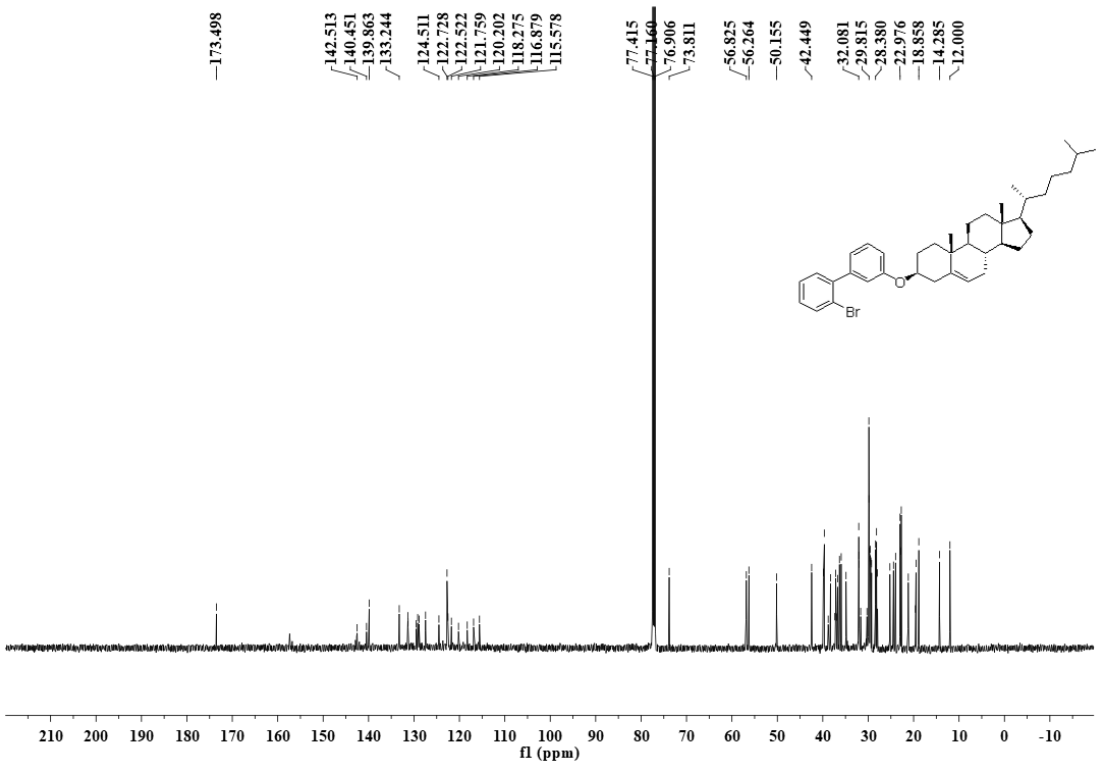
^{13}C NMR (125 MHz, $CDCl_3$) of **5**



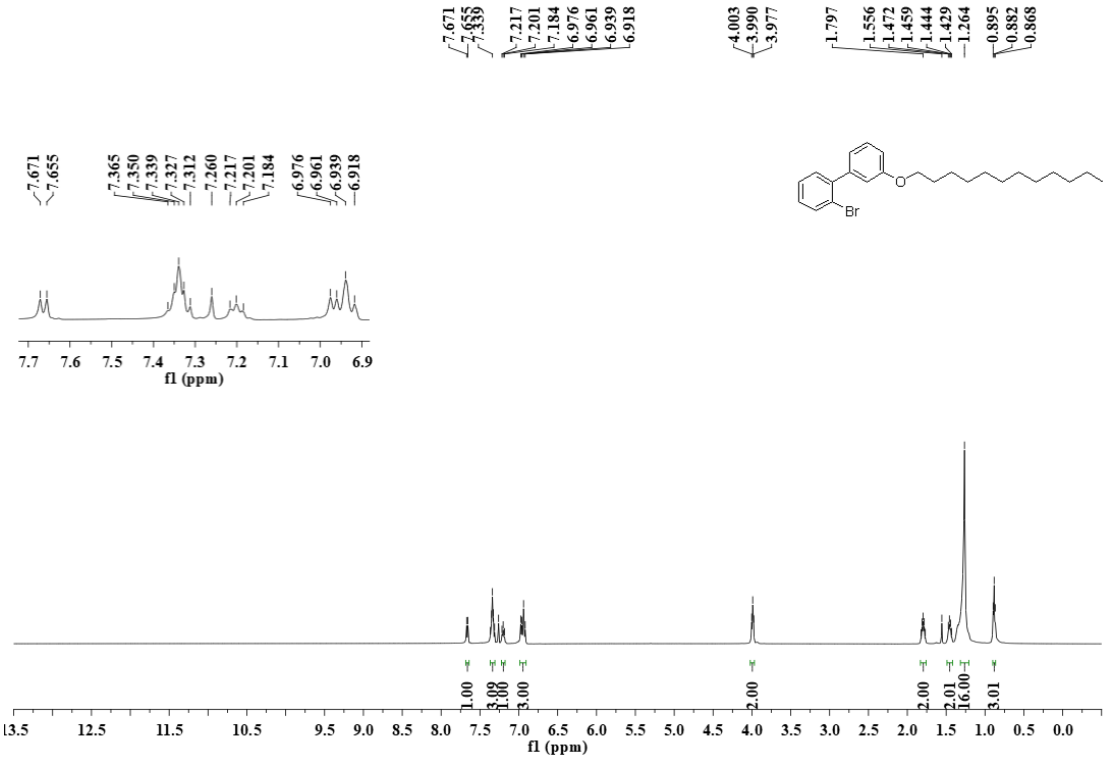
^{1}H NMR (500 MHz, $CDCl_3$) of **6**



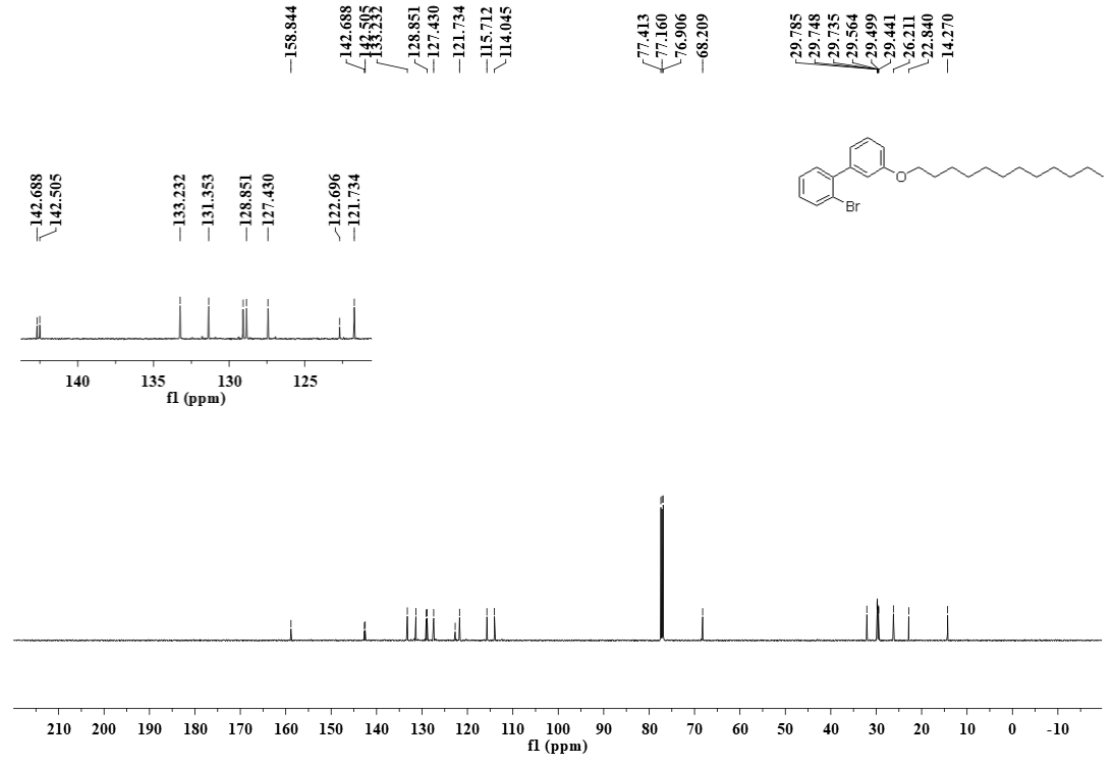
^{13}C NMR (125 MHz, $CDCl_3$) of **6**



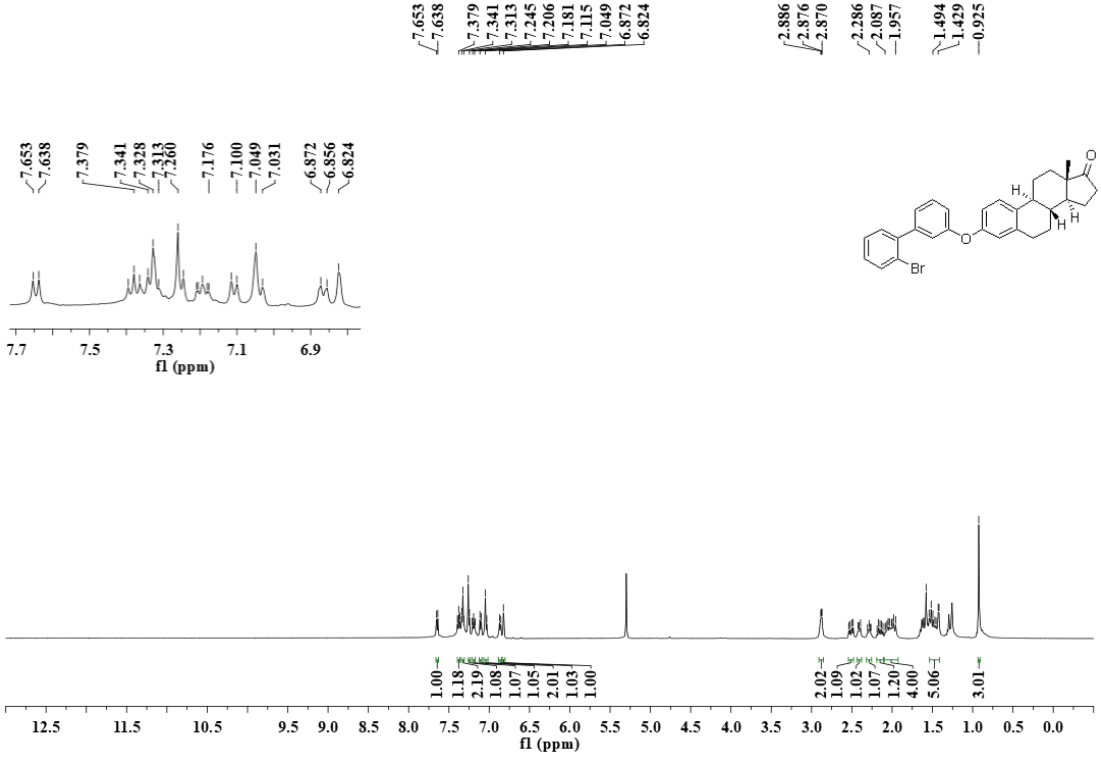
^{1}H NMR (500 MHz, $CDCl_3$) of **7**



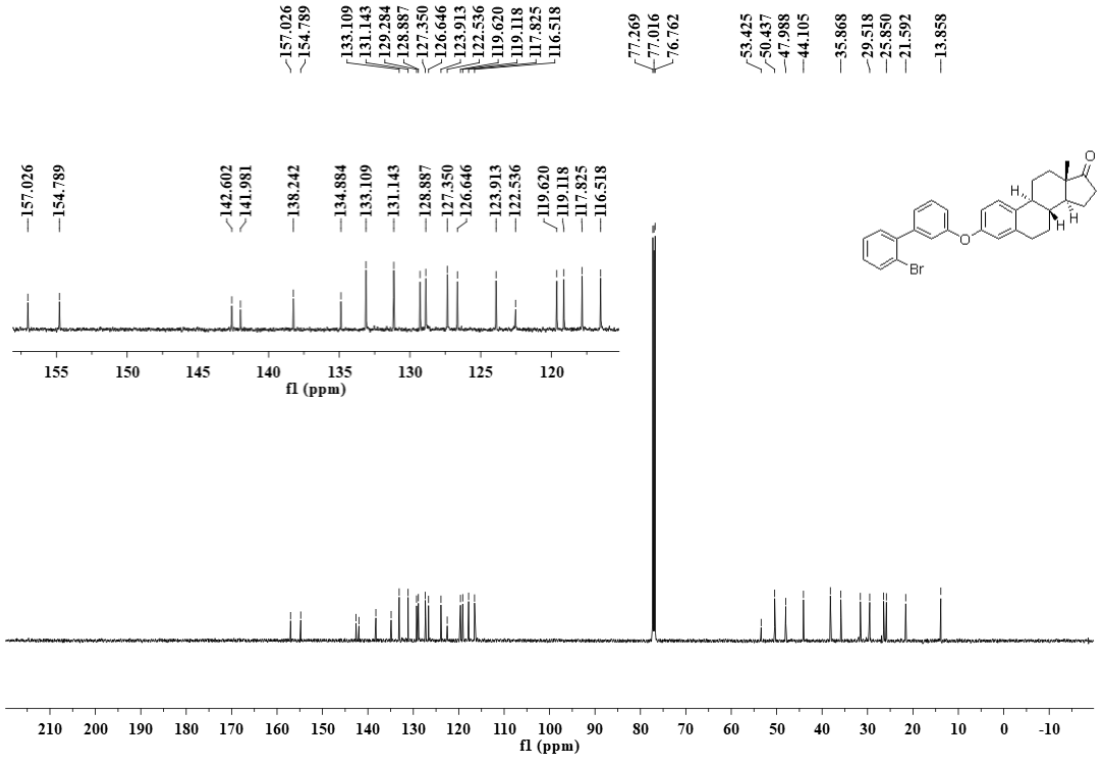
^{13}C NMR (125 MHz, $CDCl_3$) of **7**



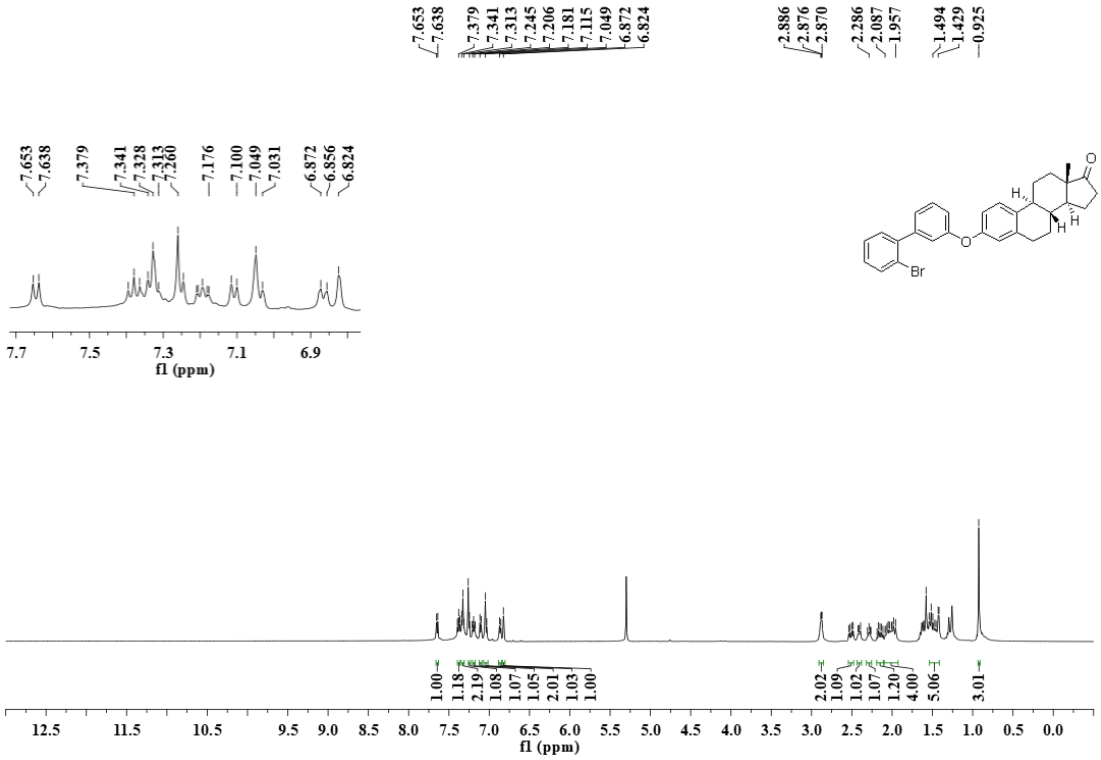
^{1}H NMR (500 MHz, $CDCl_3$) of **8**



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



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



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