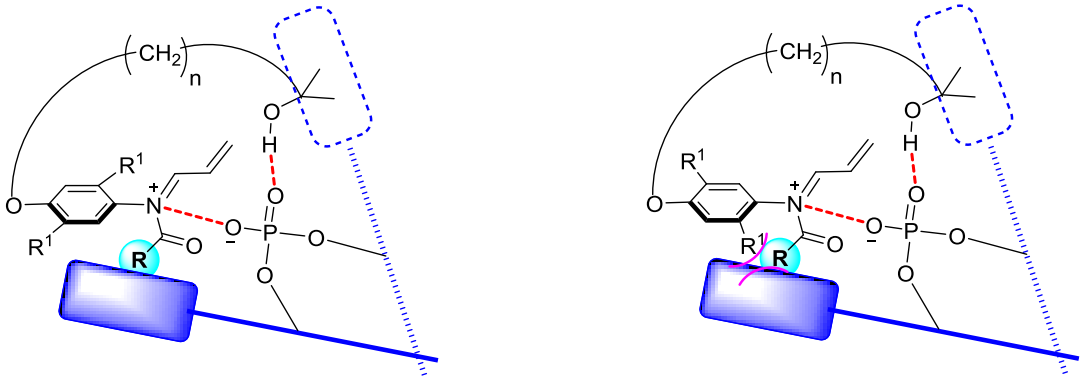
Electronic Supplementary Material (ESI) for ChemComm.

Table of Contents

General Information

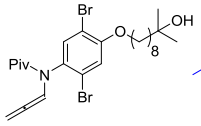
Unless otherwise noted, all commercial reagents were used without further purification. Dichloromethane, toluene, ether, THF were purified by passage through an activated alumina column under argon. Thin-layer chromatography (TLC) analysis of reaction mixtures were performed using Huanghai silica gel HSGF254 TLC plates, and visualized under UV or by staining with ceric ammonium molybdate or potassium permanganate. Flash column chromatography was carried out on Huanghai Silica Gel HHGJ-300, 300-400 mesh. Nuclear magnetic resonance (NMR) spectra were recorded using Bruker Avance III HD spectrometer (FT, 500 MHz or 400 MHz for ^{1}H, 126 MHz or 101 MHz for ^{13}C, 471 MHz for ^{19}F, 202 MHz for ^{31}P). Data for ^{1}H NMR were reported as follows: chemical shift (δ ppm downfield from tetramethylsilane and referenced to residual solvent peaks), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad resonance), integration, coupling constant (Hz). Data for ^{13}C NMR were reported in terms of chemical shift. Mass spectral data were obtained from the Agilent Technologies 6230 TOF LC/MS spectrometer in electrospray ionization (ESI^{+}) mode. Optical rotations were measured with an Autopol V Plus/VI digital polarimeter. X-Ray structure analyses were performed using a Bruker D8 Venture X-ray single crystal diffractometer. Enantiomeric excesses were determined on an Agilent 1260 Chiral HPLC using IA, IB, IC, ID and IG columns.

Scheme S1. Plausible enantiomeric determining model

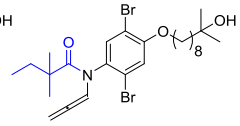


A plausible enantiomeric determining model was proposed based on previous studies (Scheme S1). Activation of the allenamide moiety would generate the α,β-unsaturated iminium group, which could form close ion-pair with the chiral phosphate anion. On the other hand, the P=O moiety of the phosphate would activate the hydroxy group through the hydrogen bonding interaction. Through this bifunctional activation model, the intramolecular conjugate addition of the hydroxy group with the α,β-unsaturated iminium group through an asymmetric manner would give access to the enantioenriched planar-chiral macrocycles. We proposed that the bulky size of the N-acyl groups may increase the energy difference between the favored transition state and the unflavored transition state by steric repulsion, and therefore afforded the products with better enantioselectivities.

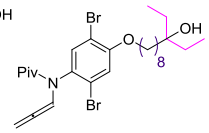
Synthesis of substrates 5



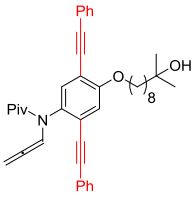
5a



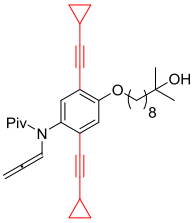
5b



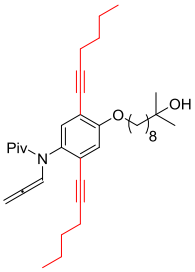
5c



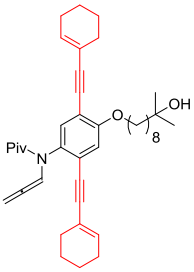
5d



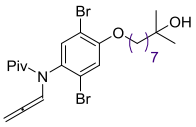
5e



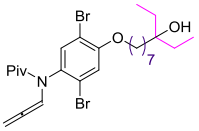
5f



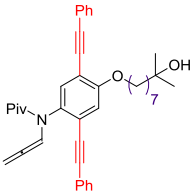
5g



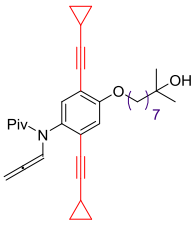
5h



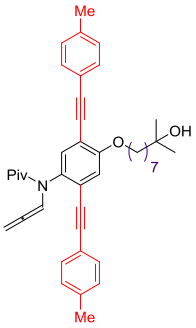
5i



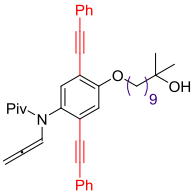
5j



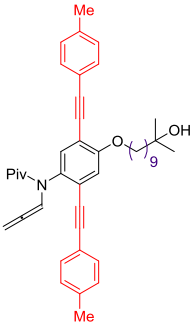
5k



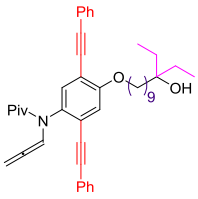
5l



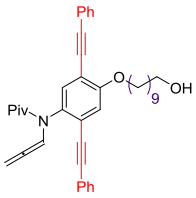
5m



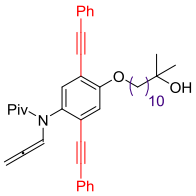
5n



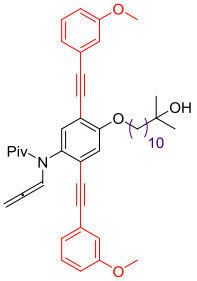
5o



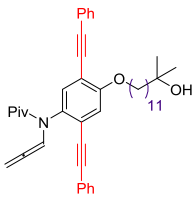
5p



5q

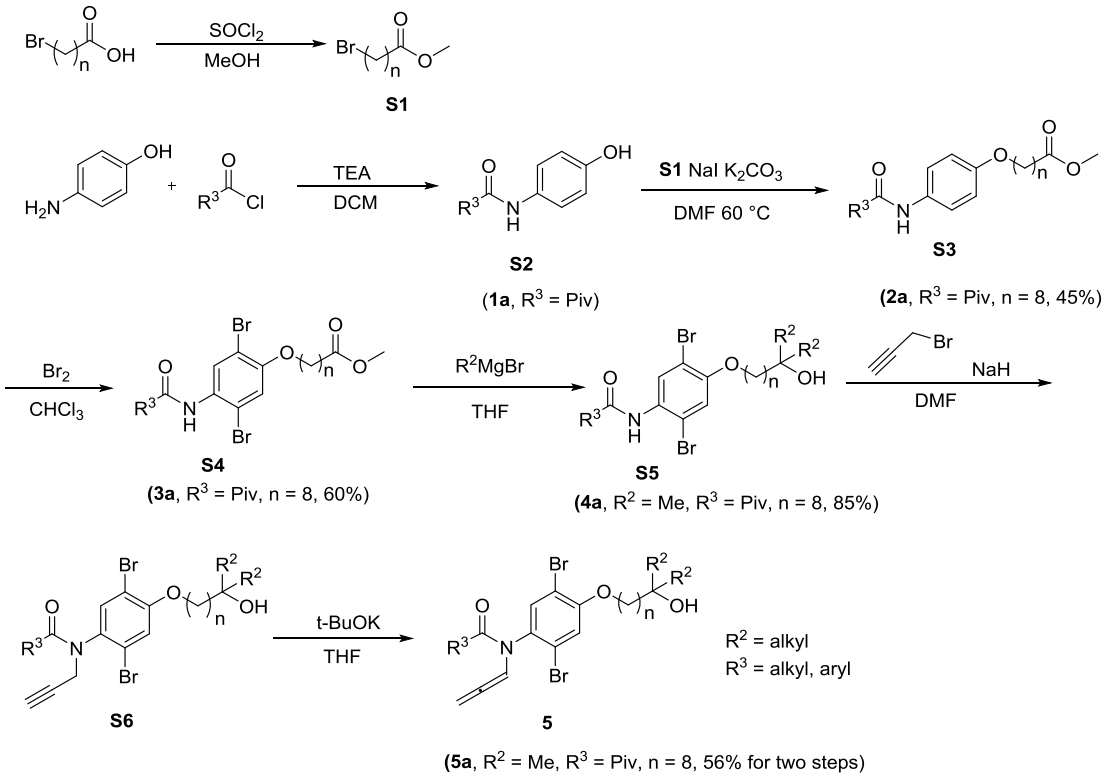


5r



5s

Method A:



General procedure of **method A**:

Synthesis of S1 (if **S1** is not commercial available): To a solution of carboxylic acid (1.0 equiv.) in MeOH was added $SOCl_2$ (1.5 equiv.) at 0 ^oC. The mixture was stirred at room temperature overnight. As the TLC analysis showed the completion of the reaction, the reaction mixture was concentrated under vacuum to give a residue, which was purified by column chromatography (petroleum ether:EtOAc = 20:1) to afford the corresponding ester **S1**.

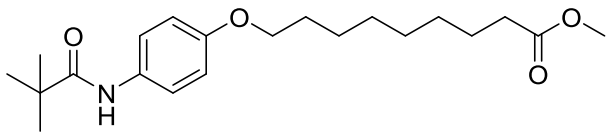
Allenamide **1** was synthesized by following steps.

Step 1: To a solution of 4-aminophenol (1.0 equiv.), TEA (2.0 equiv.) in DCM was added acyl chloride (1.1 equiv.) at 0 ^oC. After stirring at 0 ^oC for 0.5 h, the reaction mixture was quenched with H_2O and then extracted with DCM for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated to afford a residue, which was triturated with PE:EtOAc = 10:1. The precipitate was filtered to afford **S2** as white solid.

Step 2: To a solution of phenol **S2** (1.0 equiv.), K_2CO_3 (2.0 equiv.), NaI (0.5 equiv)

in DMF was added ester **S1** (1.2 equiv.) at rt. After stirring at 60 ^{o}C overnight, the reaction mixture was poured into H_2O and then extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated to give a residue, which was purified by column chromatography (petroleum ether:EtOAc = 6:1) to afford **S3** as a white solid.

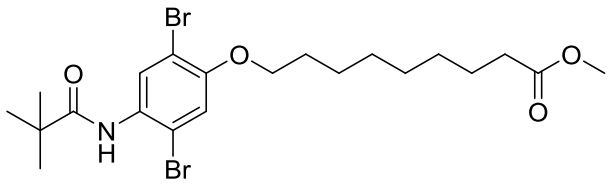
Methyl 9-(4-pivalamidophenoxy)nonanoate **(2a)**



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43-7.36 (m, 2H), 7.22 (s, 1H), 6.87-6.81 (m, 2H), 3.92 (t, *J* = 6.6 Hz, 2H), 3.66 (s, 3H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.80-1.71 (m, 2H), 1.67 -1.60 (m, 2H), 1.48-1.32 (m, 8H), 1.30 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.5, 174.4, 155.9, 131.1, 122.0, 114.8, 68.3, 51.5, 39.5, 34.2, 29.3, 29.2, 29.1, 27.7, 26.0, 25.0. m/z HRMS (ESI) found $[M+H]^+$ 364.2482, $C_{21}H_{34}NO_4^+$ requires 364.2482.

Step 3: To a solution of **S3** (1.0 equiv.) in $CHCl_3$ was added Br_2 (3.0 equiv.) at rt. After stirring overnight, the reaction mixture was quenched with Na_2SO_3 at 0 ^{o}C, and extracted with DCM for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated to give a residue, which was purified by column chromatography (petroleum ether:EtOAc = 15:1) to afford **S4** as colorless oil.

Methyl 9-(2,5-dibromo-4-pivalamidophenoxy)nonanoate **(3a)**

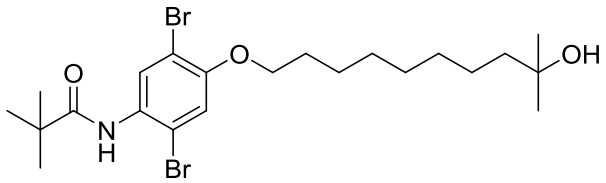


^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.57 (s, 1H), 7.73 (s, 1H), 7.03 (s, 1H), 3.96 (t, *J* = 6.4 Hz, 2H), 3.66 (s, 3H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.84-1.77 (m, 2H), 1.66-1.58 (s, 2H), 1.51-1.44 (s, 2H), 1.37-1.32 (s, 15H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ

176.6, 174.4, 152.4, 129.9, 126.5, 116.5, 112.8, 112.0, 70.0, 51.6, 40.1, 34.2, 29.2, 29.2, 29.0, 27.7, 26.0, 25.0. m/z HRMS (ESI) found $[M+H]^+$ 520.0698, $C_{21}H_{32}Br_2NO_4^+$ requires 520.0693.

Step 4: To a solution of **S4** (1.0 equiv.) in anhydrous THF was added MeMgBr (1.0 M in THF, 3.5 equiv.) under N_2 atmosphere at 0 ^oC. After stirring at rt for 3 h, the reaction mixture was quenched with saturated NH_4Cl solution at 0 ^oC and then extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated to afford **S5** as yellow oil.

N-(2,5-dibromo-4-((9-hydroxy-9-methyldecyl)oxy)phenyl)pivalamide **(4a)**

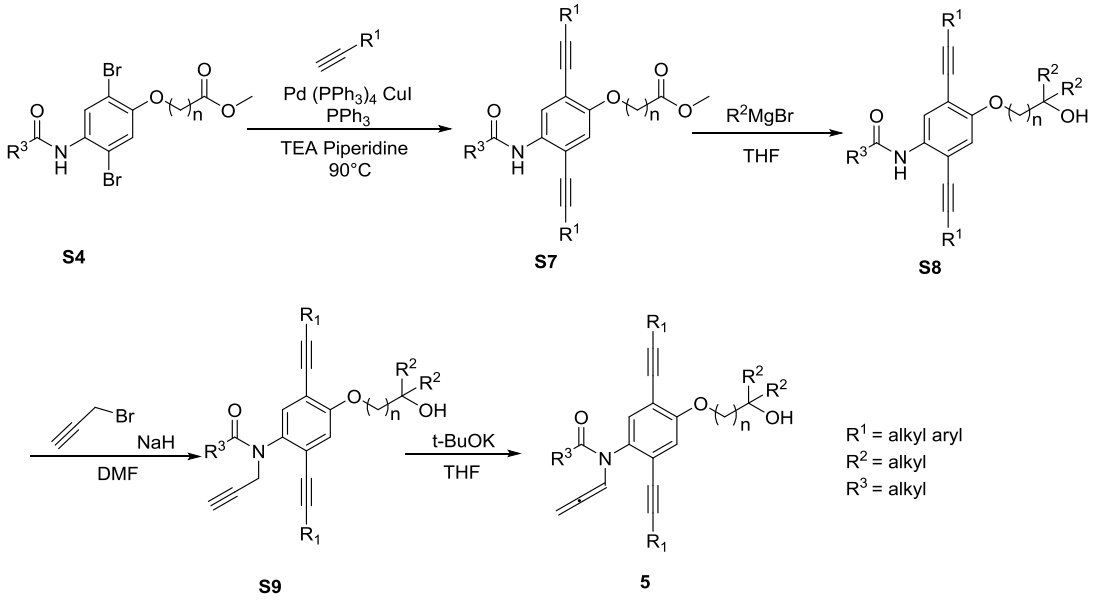


^1H NMR (400 MHz, Chloroform-*d*) δ 8.58 (s, 1H), 7.73 (s, 1H), 7.03 (s, 1H), 3.97 (t, *J* = 6.4 Hz, 2H), 1.85-1.78 (m, 2H), 1.52-1.42 (m, 4H), 1.36-1.32 (m, 17H), 1.21-1.20 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.6, 152.4, 129.9, 126.5, 116.5, 112.8, 111.9, 71.1, 70.0, 44.1, 40.1, 30.2, 29.6, 29.4, 29.3, 29.1, 27.7, 26.0, 24.4. m/z HRMS (ESI) found $[M-H_2O]^+$ 502.0956, $C_{22}H_{36}Br_2NO_3^+$requires 520.1056.

Step 5: To a solution of **S5** (1.0 equiv.) in anhydrous DMF was added NaH (60% dispersion in mineral oil, 2.2 equiv.) at 0 ^oC. After stirring at rt for 1 h, 3-bromopropyne (1.2 equiv.) was added in one portion. After stirring at RT for another 2 h, the reaction mixture was quenched with saturated NH_4Cl solution at 0 ^oC, and extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated to give a residue, which was purified by column chromatography (petroleum ether:EtOAc = 5:1) to afford **S6** as brown oil.

Step 6: To a solution of **S6** (1.0 equiv.) in THF was added t-BuOK (0.4 equiv.) at 0 ^oC. After stirring at rt for 1 h, the reaction mixture was concentrated under vacuum to give a residue, which was purified by column chromatography (petroleum ether:EtOAc = 5:1) to afford **6** as yellow oil.

Method B:



General procedure of **method B**:

Step 1: To a solution of **S4** (1.0 equiv.), alkyne (4.0 equiv.), PPh_3 (0.2 equiv.) and piperidine in TEA was added CuI (0.2 equiv.), $Pd(PPh_3)_4$ (0.1 equiv.) under N_2 atmosphere. After stirring at 90 ^oC overnight, the reaction mixture was cooled to rt, poured into H_2O and then extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated to give a residue, which was purified by column chromatography (petroleum ether:EtOAc = 20:1) to afford **S7** as brown oil.

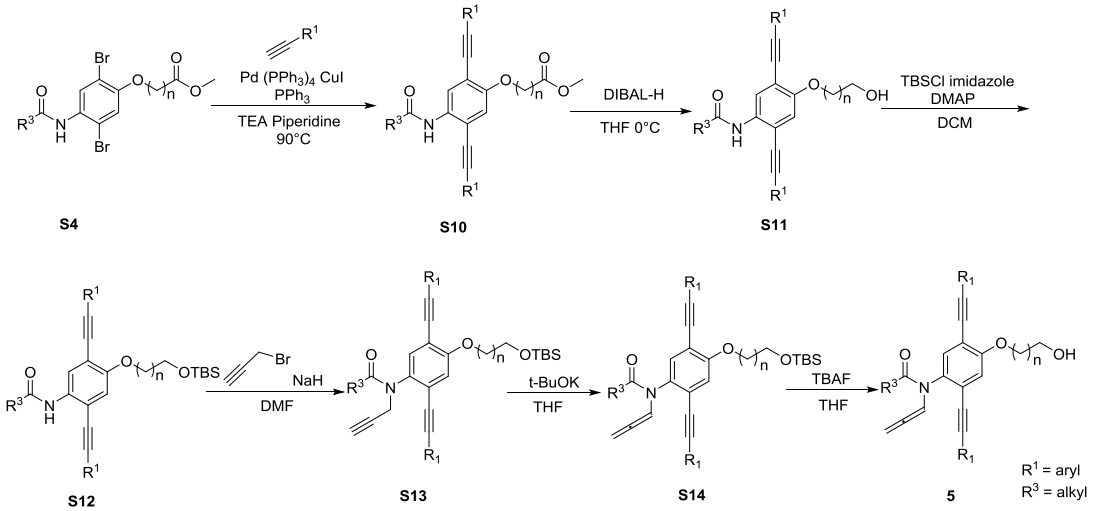
Step 2: To a solution of **S7** (1.0 equiv.) in anhydrous THF was added MeMgBr (1.0 M in THF, 3.5 equiv.) under N_2 atmosphere. After stirring at rt for 3 h, the reaction mixture was quenched with saturated NH_4Cl solution at 0 ^oC and then extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated to afford **S8** as brown oil.

Step 3: To a solution of **S8** (1.0 equiv.) in anhydrous DMF was added NaH (60% dispersion in mineral oil, 2.2 equiv.) at 0 ^oC. After stirring at rt for 1 h, 3-bromopropyne (1.2 equiv.) was added at rt. After stirring at rt for another 2 h, the reaction mixture was quenched with saturated NH_4Cl solution at 0 ^oC and then

extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated to give a residue, which was purified by column chromatography (petroleum ether:EtOAc = 5:1) to afford **S9** as brown oil.

Step 4: To a solution of **S9** (1.0 equiv.) in THF was added t-BuOK (0.4 equiv.) at 0 ^oC. After stirring at rt for 1 h, the reaction mixture was concentrated to give a residue, which was purified by column chromatography (petroleum ether:EtOAc = 5:1) to afford **6** as yellow solid.

Method C:



General procedure of **method C**:

Step 1: To a solution of **S4** (1.0 equiv.), alkyne (4.0 equiv.), PPh_3 (0.2 equiv.), piperidine in TEA was added CuI (0.2 equiv.) and $Pd(PPh_3)_4$ (0.1 equiv.) under N_2 atmosphere. After stirring at 90 ^oC overnight, the reaction mixture was poured into H_2O and then extracted with EtOAc for three times. The combined organic layers were then washed with brine, dried over Na_2SO_4, filtered and concentrated to give a residue, which was purified by column chromatography (petroleum ether:EtOAc = 20:1) to afford **S10** as brown oil.

Step 2: To a solution of **S10** (1.0 equiv.) in anhydrous THF was added DIBAL-H (1.0 M in hexane, 4.0 equiv.) under N_2 atmosphere at 0 ^oC. After stirring at this

temperature for 0.5 h, the reaction mixture was quenched with adding seignette salt solution and then extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated to afford **S11** as yellow oil.

Step 3: To a solution of **S11** (1.0 equiv.), imidazole (1.3 equiv.) and DMAP (0.2 equiv.) in DCM was added TBSCl (1.2 equiv.) at rt. After stirring at rt for 2 h, the reaction mixture was poured into H_2O, and then extracted with DCM for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under vacuum to give a residue, which was purified by column chromatography (petroleum ether:EtOAc = 20:1) to afford **S12** as brown oil.

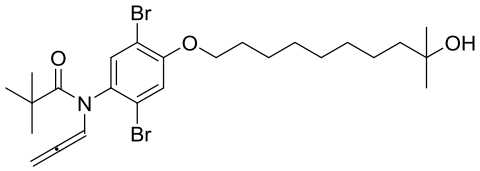
Step 4: To a solution of **S12** (1.0 equiv.) in anhydrous DMF was added NaH (60% dispersion in mineral oil, 1.2 equiv.) at 0 ^oC. After stirring at rt for 1 h, 3-bromopropyne (1.2 equiv.) was added. After stirring at rt for another 2 h, the reaction mixture was quenched with adding saturated NH_4Cl solution at 0 ^oC, and then extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under vacuum to give a residue, which was purified by column chromatography (petroleum ether:EtOAc = 20:1) to afford **S13** as brown oil.

Step 5: To a solution of **S13** (1.0 equiv.) in THF was added t-BuOK (0.4 equiv.) at 0 ^oC. After stirring at rt for 1 h, the reaction mixture was concentrated under vacuum to give a residue, which was purified by column chromatography (petroleum ether:EtOAc = 40:1) to afford **S14** as yellow oil.

Step 6: To a solution of **S14** (1.0 equiv.) in THF was added TBAF (1.0 M in THF, 5.0 equiv) at rt. After stirring at rt for 3 h, the reaction mixture was quenched with saturated NH_4Cl solution and then extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under vacuum to give a residue, which was purified by column chromatography (petroleum ether:EtOAc = 5:1) to afford **1** as yellow oil.

N-(2,5-dibromo-4-((9-hydroxy-9-methyldecyl)oxy)phenyl)-*N*-(propa-1,2-dien-1-yl)pi

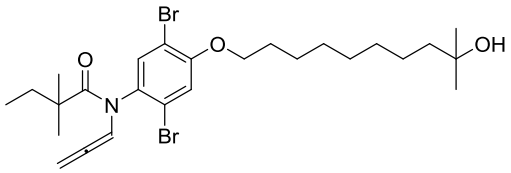
valamide **(5a)**



This reaction was performed on 3.19 mmol scale of **S1** according to **method A**, which gave the product **5a** (230 mg, 12.9% yield for 5 steps) as yellow oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.53 (t, *J* = 6.3, 1H), 7.44 (s, 1H), 7.07 (s, 1H), 5.04-4.95 (m, 2H), 4.03 - 4.00 (m, 2H), 1.87-1.84 (m, 2H), 1.55-1.43 (m, 4H), 1.41-1.28 (m, 9H), 1.21 (s, 6H), 1.16 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 202.2, 175.8, 155.8, 135.3, 133.3, 124.3, 116.8, 110.4, 102.8, 77.4, 71.2, 70.0, 44.1, 41.1, 30.2, 29.6, 29.4, 29.4, 29.0, 28.9, 26.1, 24.5. m/z HRMS (ESI) found $[M+H]^+$ 560.1191, $C_{25}H_{38}Br_2NO_3^+$ requires 560.1192

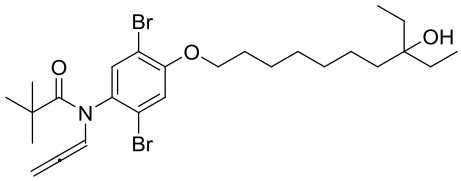
N-(2,5-dibromo-4-((9-hydroxy-9-methyldecyl)oxy)phenyl)-2,2-dimethyl-N-(propa-1, 2-dien-1-yl)butanamide **(5b)**



This reaction was performed on 3.19 mmol scale of **S1** according to **method A**, which gave the product **5b** (300 mg, 16.4% yield for 5 steps) as yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (t, 1H), 7.40 (s, 1H), 7.07 (s, 1H), 5.01-4.97 (m, 2H), 4.01 (t, *J* = 6.6 Hz, 2H), 1.89-1.82 (m, 2H), 1.71-1.62 (m, 1H), 1.51–1.44 (m, 4H), 1.36-1.33 (m, 9H), 1.21 (s, 6H), 1.10 (s, 3H), 1.05 (s, 3H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.2, 175.0, 155.7, 135.0, 133.3, 124.2, 116.7, 110.4, 102.6, 86.6, 71.2, 69.8, 45.1, 44.1, 35.0, 30.2, 29.6, 29.3, 29.0, 26.5, 26.2, 26.0, 24.4, 9.7. m/z HRMS (ESI) found $[M+H]^+$ 574.1344, $C_{26}H_{40}Br_2NO_3^+$ requires 574.1349

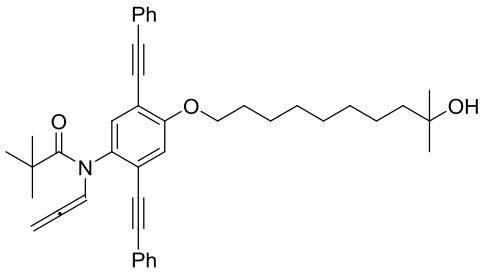
N-(2,5-dibromo-4-((8-ethyl-8-hydroxydecyl)oxy)phenyl)-*N*-(propa-1,2-dien-1-yl)piva lamide **(5c)**



This reaction was performed on 3.0 mmol scale of **S1** according to **method A**. Give the product **5c** (259 mg, 15.1% yield for 5 steps) as yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (t, *J* = 6.4 Hz, 1H)， 7.43 (s, 1H), 7.07 (s, 1H), 5.04-4.95 (m, 2H), 4.02 (t, *J* = 6.1 Hz, 2H), 1.90-1.81 (m, 2H), 1.56–1.49 (m, 2H), 1.46 (q, *J* = 7.5 Hz, 4H), 1.42-1.38 (m, 4H), 1.37-1.30 (m, 4H), 1.16 (s, 9H), 0.86 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.2, 175.8, 155.8, 135.2, 133.2, 124.3, 116.7, 110.4, 102.8, 86.6, 74.7, 69.9, 41.1, 38.3, 31.2, 30.3, 29.4, 29.0, 28.8, 26.1, 23.4, 7.9. m/z HRMS (ESI) found $[M+H]^+$ 574.1353, $C_{26}H_{40}Br_2NO_3^+$ requires 574.1349.

N-(4-((9-hydroxy-9-methyldecyl)oxy)-2,5-bis(phenylethynyl)phenyl)-*N*-(propa-1,2-di en-1-yl)pivalamide **(5d)**

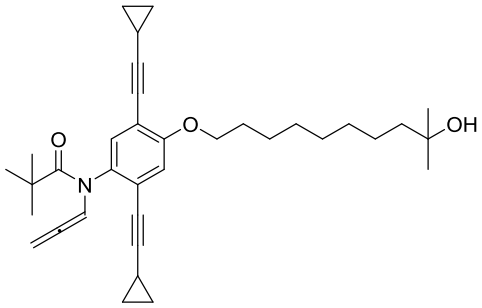


This reaction was performed on 1.07 mmol scale of **S4** according to **method B**, which gave the product **5d** (300 mg, 46.7% yield for 4 steps) as yellow solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (t, *J* = 6.3 Hz, 1H), 7.55-7.50 (m, 2H), 7.50-7.48 (m, 2H), 7.39-7.34 (m, 7H), 7.03 (s, 1H), 5.00 (d, *J* = 6.3 Hz, 2H), 4.10 (t, *J* = 6.4 Hz, 2H), 1.93-1.87 (m, 2H), 1.61-1.55 (m, 2H), 1.44-1.40 (m, 4H), 1.38-1.32 (m, 6H), 1.20 (s, 6H), 1.16 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 202.9, 176.4, 159.1, 135.1, 134.7, 131.9, 131.7, 129.0, 128.6, 128.6, 128.5, 125.6, 123.3, 122.7,

114.7, 113.4, 103.7, 95.9, 95.8, 86.4, 86.2, 85.0, 77.4, 71.1, 69.1, 44.1, 41.5, 30.3, 29.7, 29.5, 29.4, 29.3, 29.3, 26.2, 24.5. m/z HRMS (ESI) found $[M+H]^+$ 602.3628, $C_{41}H_{48}NO_3^+$ requires 602.3629.

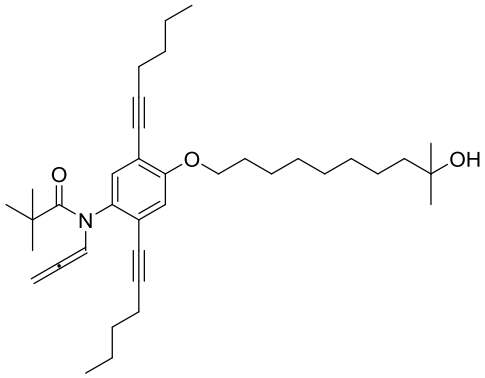
N-(2,5-bis(cyclopropylethynyl)-4-((9-hydroxy-9-methyldecyl)oxy)phenyl)-*N*-(propa-1,2-dien-1-yl)pivalamide **(5e)**



This reaction was performed on 0.87 mmol scale of **S4** according to **method B**. Give the product **5e** (228 mg, 43% yield for 4 steps) as yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (t, *J* = 6.3 Hz, 1H), 7.11 (s, 1H), 6.80 (s, 1H), 4.97-4.88 (m, 2H), 3.96 (t, *J* = 6.5 Hz, 2H), 1.84-1.79 (m, 2H), 1.53-1.43 (m, 5H), 1.42-1.30 (m, 9H), 1.21 (s, 6H), 1.09 (s, 9H), 0.91-0.79 (m, 6H), 0.75-0.73 (m, 2H).^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.8, 176.2, 159.0, 134.9, 134.65, 125.4, 114.7, 113.0, 103.4, 100.2, 99.8, 86.1, 72.4, 71.2, 71.0, 68.9, 44.1, 41.3, 30.2, 29.7, 29.5, 29.4, 29.2, 29.1, 26.1, 24.5, 9.00, 0.7, 0.5. m/z HRMS (ESI) found $[M+H]^+$ 530.3619, $C_{35}H_{48}NO_3^+$ requires 530.3629.

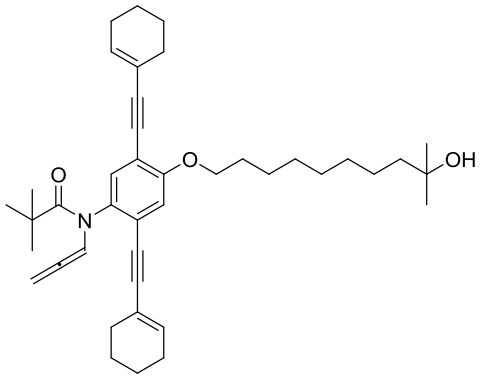
N-(2,5-di(hex-1-yn-1-yl)-4-((9-hydroxy-9-methyldecyl)oxy)phenyl)-N-(propa-1,2-dien-1-yl)pivalamide **(5f)**



This reaction was performed on 1 mmol scale of **S4** according to **method B**. Give the product **5f** (180 mg, 32% yield for 4 steps) as yellow oil.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.61 (t, *J* = 6.4 Hz, 1H), 7.13 (s, 1H), 6.83 (s, 1H), 4.95-4.93 (m, 2H), 3.98 (t, *J* = 6.6 Hz, 2H), 2.45 (t, *J* = 6.8 Hz, 2H), 2.37 (t, *J* = 7.0 Hz, 2H), 1.86-1.80 (m, 2H), 1.40-1.55 (m, 11H), 1.39-1.31 (m, 9H), 1.21 (s, 6H), 1.10 (s, 9H), 0.93 (m, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.9, 176.1, 158.9, 134.7, 134.6, 125.5, 114.8, 113.3, 103.5, 96.7, 86.0, 75.9, 71.2, 68.9, 44.1, 41.3, 30.8, 30.7, 30.3, 29.7, 29.5, 29.4, 29.3, 29.1, 26.1, 24.5, 22.0, 22.0, 19.6, 19.3, 13.8, 13.7. m/z HRMS (ESI) found $[M+H]^+$ 562.4243, $C_{37}H_{56}NO_3^+$ requires 562.4255.

N-(2,5-bis(cyclohex-1-en-1-ylethynyl)-4-((9-hydroxy-9-methyldecyl)oxy)phenyl)-*N*-(propa-1,2-dien-1-yl)pivalamide **(5g)**

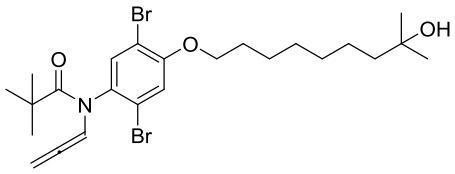


This reaction was performed on 1.72 mmol scale of **S4** according to **method B**. Give the product **5g** (320 mg, 30.9% yield for 4 steps) as yellow solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (t, *J* = 6.3 Hz, 1H), 7.17 (s, 1H), 6.86 (s, 1H), 6.27-6.14 (m, 2H), 5.01-4.90 (m, 2H), 4.00 (t, *J* = 6.5 Hz, 2H), 2.27-2.20 (m,

2H), 2.14 (q, *J* = 7.4, 6.3 Hz, 6H), 1.84 (t, *J* = 7.4 Hz, 2H), 1.72-1.60 (m, 7H), 1.53-1.43 (m, 4H), 1.41-1.27 (m, 9H), 1.21 (s, 6H), 1.11 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.9, 176.2, 158.7, 136.6, 135.8, 134.7, 134.4, 125.5, 120.9, 120.6, 114.5, 113.3, 103.6, 97.7, 97.6, 86.2, 83.7, 82.4, 71.2, 68.9, 44.1, 41.4, 30.2, 29.8, 29.7, 29.5, 29.3, 29.3, 29.2, 29.2, 29.0, 26.1, 25.9, 24.5, 22.4, 22.3, 21.6, 21.5. m/z HRMS (ESI) found $[M+H]^+$ 610.4247, $C_{41}H_{56}NO_3^+$ requires 610.4255.

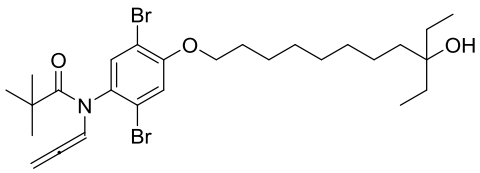
N-(2,5-dibromo-4-((8-hydroxy-8-methylnonyl)oxy)phenyl)-*N*-(propa-1,2-dien-1-yl)pivalamide **(5h)**



This reaction was performed on 3.19 mmol scale of **S1** according to **method A**. Give the product **5h** (300 mg, 17.2% yield for 5 steps) as yellow oil.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.53 (t, *J* = 6.3 Hz, 1H), 7.43 (s, 1H), 7.07 (s, 1H), 5.02-4.99 (m, 2H), 4.01 (t, *J* = 6.0 Hz, 2H), 1.88-1.83 (m, 2H), 1.53-1.49 (m, 2H), 1.49-1.45 (m, 2H), 1.42-1.33 (m, 6H), 1.21 (s, 6H), 1.16 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.2, 175.8, 155.8, 135.2, 133.2, 124.3, 116.7, 110.4, 102.7, 96.2, 71.1, 69.8, 44.0, 41.1, 30.1, 29.4, 29.0, 28.8, 26.0, 24.4. m/z HRMS (ESI) found $[M+H]^+$ 546.1025, $C_{24}H_{36}Br_2NO_3^+$ requires 546.1036.

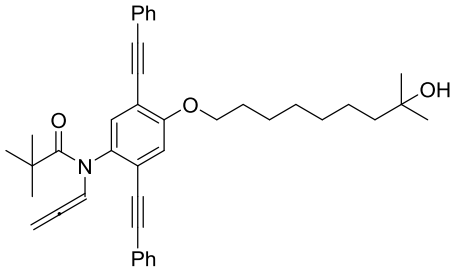
N-(2,5-dibromo-4-((9-ethyl-9-hydroxyundecyl)oxy)phenyl)-*N*-(propa-1,2-dien-1-yl)pivalamide **(5i)**



This reaction was performed on 3.94 mmol scale of **S1** according to **method A**. Give the product **5i** (300 mg, 12.9% yield for 5 steps) as yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (t, *J* = 6.4 Hz, 1H), 7.44 (s, 1H), 7.07 (s, 1H), 5.04-4.95 (m, 2H), 4.02(t, *J* = 6.1 Hz, 2H), 1.89-1.82 (m, 2H), 1.49-1.43 (m, 6H), 1.41-1.30 (m, 10H), 1.16 (s, 9H), 0.86 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 202.2, 175.8, 155.8, 135.3, 133.3, 124.3, 116.7, 110.4, 102.8, 86.6, 74.8, 70.0, 41.1, 38.3, 31.2, 30.3, 29.6, 29.4, 29.1, 28.9, 26.1, 23.5, 7.9. m/z HRMS (ESI) found $[M+H]^+$ 588.1500, $C_{27}H_{42}Br_2NO_3^+$ requires 588.1505.

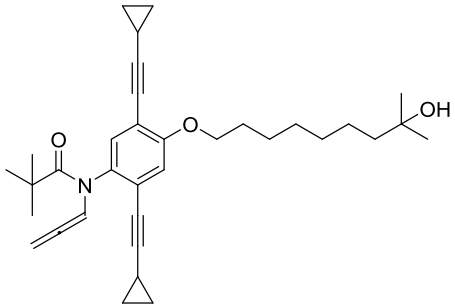
N-(4-((8-hydroxy-8-methylnonyl)oxy)-2,5-bis(phenylethynyl)phenyl)-*N*-(propa-1,2-dien-1-yl)pivalamide **(5j)**



This reaction was performed on 1.72 mmol scale of **S4** according to **method B**. Give the product **5j** (302 mg, 29.8% yield for 4 steps) as yellow solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (t, *J* = 6.3 Hz, 1H), 7.55-7.52 (m, 2H), 7.50-7.48 (m, 2H), 7.37-7.34 (m, 7H), 7.03 (s, 1H), 5.00 (d, *J* = 6.3 Hz, 2H), 4.10 (t, *J* = 6.4 Hz, 2H), 1.95-1.88 (m, 2H), 1.61-1.57 (s, 2H), 1.46-1.44 (m, 4H), 1.37-1.34 (m, 4H), 1.19 (s, 6H), 1.16 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 202.9, 176.4, 159.0, 135.2, 134.7, 131.9, 131.7, 129.0, 128.6, 128.6, 128.5, 125.6, 123.3, 122.7, 114.7, 113.4, 103.7, 95.9, 95.9, 86.4, 86.2, 85.0, 71.1, 69.1, 44.1, 41.5, 30.3, 29.6, 29.4, 29.3, 29.2, 26.2, 24.4. m/z HRMS (ESI) found $[M+H]^+$ 588.3465, $C_{40}H_{46}NO_3^+$ requires 588.3472.

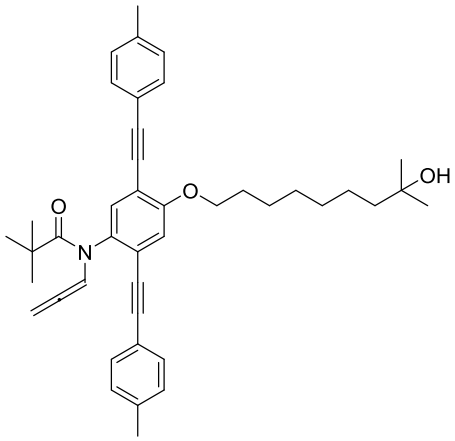
N-(2,5-bis(cyclopropylethynyl)-4-((8-hydroxy-8-methylnonyl)oxy)phenyl)-*N*-(propa-1,2-dien-1-yl)pivalamide **(5k)**



This reaction was performed on 1.8 mmol scale of **S4** according to **method B**. Give the product **5k** (400 mg, 43.1% yield for 4 steps) as yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (t, *J* = 6.3 Hz, 1H), 7.11 (s, 1H), 6.80 (s, 1H), 4.98-4.89 (m, 2H), 3.96 (t, *J* = 6.5 Hz, 2H), 1.84-1.81 (m, 2H), 1.52-1.45 (m, 5H), 1.42-1.35 (m, 7H), 1.21 (s, 6H), 1.09 (s, 9H), 0.92-0.79 (m, 6H), 0.78-0.71 (m, 2H).^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.8, 176.2, 134.9, 134.6, 125.4, 114.7, 113.0, 103.4, 100.2, 99.8, 86.1, 72.4, 71.1, 71.0, 68.8, 66.0, 44.1, 41.3, 30.3, 29.5, 29.4, 29.2, 29.1, 26.1, 24.4, 15.4, 9.0. m/z HRMS (ESI) found $[M+H]^+$ 516.3481, $C_{34}H_{46}NO_3^+$ requires 516.3472.

N-(4-((8-hydroxy-8-methylnonyl)oxy)-2,5-bis(p-tolylethynyl)phenyl)-*N*-(propa-1,2-dien-1-yl)pivalamide **(5l)**

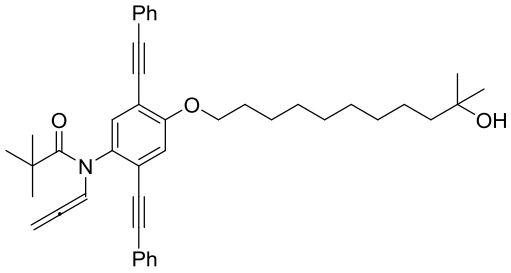


This reaction was performed on 1.8 mmol scale of **S4** according to **method B**. Give the product **5l** (360 mg, 32.5% yield for 4 steps) as yellow solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (t, *J* = 6.3 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.33 (s, 1H), 7.17-7.14 (m, 4H), 7.01 (s, 1H), 4.98 (d, *J*

= 6.3 Hz, 2H), 4.08 (t, *J* = 6.4 Hz, 2H), 2.37 (d, *J* = 3.7 Hz, 6H), 1.94-1.87 (m, 2H), 1.60-1.58 (m, 2H), 1.47-1.42 (m, 4H), 1.37-1.33 (m, 4H), 1.19 (s, 6H), 1.15 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.9, 176.4, 159.0, 139.3, 138.8, 135.0, 134.6, 131.8, 131.6, 129.4, 129.3, 125.6, 120.3, 119.7, 114.6, 113.4, 103.7, 96.2, 96.0, 86.3, 85.7, 84.4, 71.1, 69.1, 44.1, 41.5, 30.3, 29.6, 29.4, 29.3, 29.3, 26.2, 24.5, 21.7. m/z HRMS (ESI) found $[M+H]^+$ 616.3753, $C_{42}H_{50}NO_3^+$ requires 616.3785.

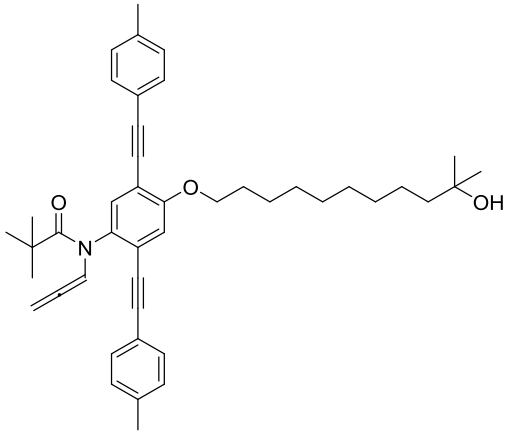
N-(4-((10-hydroxy-10-methylundecyl)oxy)-2,5-bis(phenylethynyl)phenyl)-*N*-(propa-1,2-dien-1-yl)pivalamide **(5m)**



This reaction was performed on 1.8 mmol scale of **S4** according to **method B**. Give the product **5m** (430 mg, 41.3% yield for 4 steps) as yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 (t, *J* = 6.5 Hz, 1H), 7.55-7.53 (m, 2H), 7.50-7.48 (m, 2H), 7.37-7.34 (m, 7H), 7.03 (s, 1H), 5.00 (d, *J* = 6.3 Hz, 2H), 4.09 (t, *J* = 6.5 Hz, 2H), 1.92-1.89 (m, 2H), 1.45-1.39 (m, 5H), 1.36-1.30 (m, 9H), 1.20 (s, 6H), 1.16 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.8, 176.4, 159.0, 135.1, 134.7, 131.8, 131.7, 129.0, 128.6, 128.6, 128.5, 125.6, 123.3, 122.7, 114.6, 113.4, 103.7, 95.9, 86.4, 86.2, 85.0, 71.2, 69.1, 44.1, 41.5, 30.3, 29.7, 29.6, 29.4, 29.3, 29.2, 26.2, 24.5. m/z HRMS (ESI) found $[M+H]^+$ 616.3774, $C_{42}H_{50}NO_3^+$ requires 616.3785.

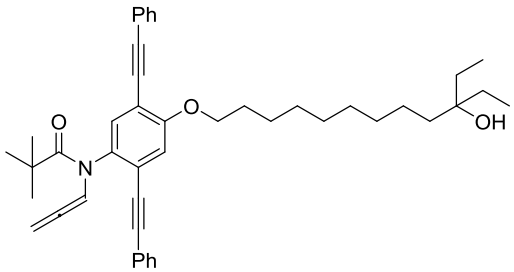
N-(4-((10-hydroxy-10-methylundecyl)oxy)-2,5-bis(p-tolylethynyl)phenyl)-*N*-(propa-1,2-dien-1-yl)pivalamide **(5n)**



This reaction was performed on 1.8 mmol scale of **S4** according to **method B**. Give the product **5n** (350 mg, 30.2% yield for 4 steps) as yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.71 (t, *J* = 6.3 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.33 (s, 1H), 7.17-7.15 (m, 4H), 7.01 (s, 1H), 4.98 (d, *J* = 6.3 Hz, 2H), 4.08 (t, *J* = 6.4 Hz, 2H), 2.38 (s, 3H), 2.37 (s, 3H), 1.95-1.85 (m, 2H), 1.45-1.41 (m, 4H), 1.35-1.30 (m, 10H), 1.20 (s, 6H), 1.15 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.9, 176.3, 158.9, 139.2, 138.7, 135.0, 134.5, 131.7, 131.6, 129.3, 129.2, 125.6, 120.2, 119.6, 114.5, 113.4, 103.7, 96.1, 96.0, 86.3, 85.7, 84.3, 71.1, 69.1, 44.1, 41., 30.30, 30.3, 29.7, 29.5, 29.3, 29.3, 29.2, 26.1, 24.4, 21.7, 21.6. m/z HRMS (ESI) found $[M+H]^+$ 644.4067, $C_{44}H_{54}NO_3^+$ requires 644.4098.

N-(4-((10-ethyl-10-hydroxydodecyl)oxy)-2,5-bis(phenylethynyl)phenyl)-*N*-(propa-1,2-dien-1-yl)pivalamide **(5o)**

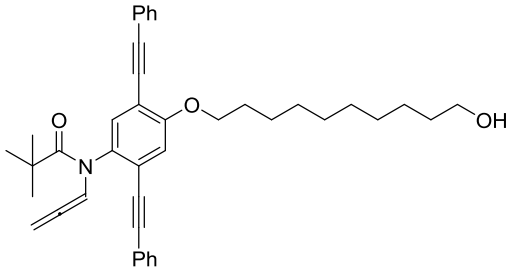


This reaction was performed on 1.8 mmol scale of **S4** according to **method B**. Give the product **5o** (400 mg, 34.5% yield for 4 steps) as yellow solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (t, *J* = 6.3 Hz, 1H), 7.57-7.52 (m, 2H), 7.52-7.48 (m, 2H), 7.35-7.34 (m, 7H), 7.03 (s, 1H), 5.00 (d, *J* = 6.4 Hz, 2H), 4.10 (t, *J*

= 6.5 Hz, 2H), 1.95-1.87 (m, 2H), 1.49-1.37 (m, 9H), 1.35-1.24 (m, 9H), 1.16 (s, 9H), 0.85 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.8, 176.3, 159.0, 135.1, 134.7, 131.8, 131.7, 129.0, 128.6, 128.6, 128.5, 128.4, 125.6, 123.3, 122.7, 114.6, 113.4, 103.7, 95.9, 86.4, 86.2, 84.9, 74.7, 69.1, 41.4, 38.3, 31.1, 30.4, 29.7, 29.5, 29.3, 29.2, 27.1, 26.2, 23.5, 7.9. m/z HRMS (ESI) found $[M+H]^+$ 644.4105, $C_{44}H_{54}NO_3^+$ requires 644.4098.

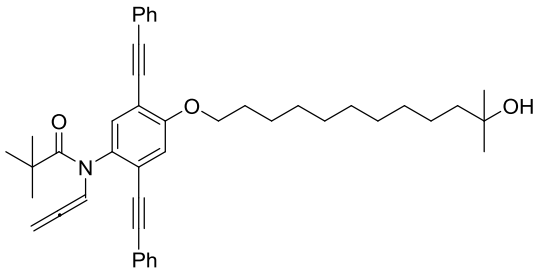
N-(4-((10-hydroxydecyl)oxy)-2,5-bis(phenylethynyl)phenyl)-*N*-(propa-1,2-dien-1-yl) pivalamide **(5p)**



This reaction was performed on 1.8 mmol scale of **S4** according to **method C**. Give the product **5p** (280 mg, 26.5% yield for 6 steps) as yellow solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (t, *J* = 6.4 Hz, 1H), 7.55-7.48 (m, 4H), 7.36 -7.34 (m, 7H), 7.03 (s, 1H), 5.00 (d, *J* = 6.3 Hz, 2H), 4.10 (t, *J* = 6.4 Hz, 2H), 3.63 (t, *J* = 6.7 Hz, 2H), 1.92-1.89 (m, 2H), 1.59-1.52 (m, 4H), 1.43-1.39 (m, 2H), 1.39-1.25 (m, 8H), 1.16 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.8, 176.4, 159.0, 135.1, 134.7, 131.8, 131.7, 129.0, 128.6, 128.6, 128.5, 125.6, 123.3, 122.7, 114.6, 113.4, 103.7, 95.9, 86., 86.21, 85.0, 69.1, 63.2, 41.5, 32.9, 29.7, 29.7, 29.6, 29.5, 29.3, 29.2, 26.2, 25.9. m/z HRMS (ESI) found $[M+H]^+$ 588.3477, $C_{40}H_{46}NO_3^+$ requires 588.3472.

N-(4-((11-hydroxy-11-methyldodecyl)oxy)-2,5-bis(phenylethynyl)phenyl)-*N*-(propa-1 ,2-dien-1-yl)pivalamide **(5q)**



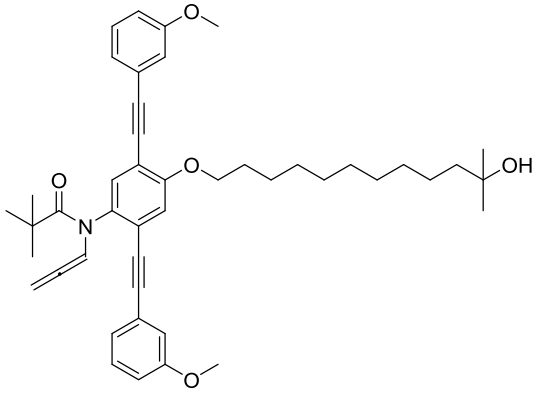
This reaction was performed on 1.3 mmol scale of **S4** according to **method B**. Give the product **5q** (200 mg, 24.4% yield for 4 steps) as yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 (t, *J* = 6.3 Hz, 1H), 7.55-7.48 (m, 4H), 7.40-7.32 (m, 7H), 7.03 (s, 1H), 5.00 (d, *J* = 6.3 Hz, 2H), 4.09 (t, *J* = 6.4 Hz, 2H), 1.96-1.87 (m, 2H), 1.46-1.36 (m, 4H), 1.36-1.24 (m, 12H), 1.20 (s, 6H), 1.16 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.8, 176.4, 159.0, 135.1, 134.7, 131.8, 131.7, 129.0, 128.6, 128.6, 128.5, 125.6, 123.3, 122.7, 114.7, 113.4, 103.7, 95.9, 86.4, 86.2, 85.0, 71.1, 69.1, 44.1, 41.4, 30.3, 29.8, 29.7, 29.7, 29.5, 29.3, 29.3, 29.2, 26.2, 24.5.

m/z HRMS (ESI) found $[M+H]^+$ 630.3931, $C_{43}H_{52}NO_3^+$ requires 630.3942.

N-(4-((11-hydroxy-11-methyldodecyl)oxy)-2,5-bis((3-methoxyphenyl)ethynyl)-*N*-(propa-1,2-dien-1-yl)pivalamide **(5r)**



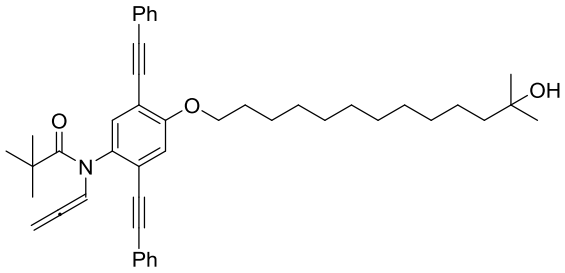
This reaction was performed on 1.8 mmol scale of **S4** according to **method B**. Give the product **5r** (380 mg, 30.6% yield for 4 steps) as yellow solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (t, *J* = 6.3 Hz, 1H), 7.36 (s, 1H), 7.28-7.27 (m, 1H), 7.24-7.24 (m, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.10-7.05 (m, 2H), 7.03-7.02 (m, 2H), 6.92-6.89 (m, 2H), 4.99 (d, *J* = 6.3 Hz, 2H), 4.09 (t, *J* = 6.4 Hz, 2H), 3.83 (s, 6H), 1.94-1.87 (m, 2H), 1.48-1.39 (m, 4H), 1.39-1.25 (s, 12H), 1.20 (s, 6H), 1.16 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 201.8, 175.4, 158.5, 158.5, 158.1, 134.2, 133.7, 128.7, 128.6, 124.6, 123.4, 123.3, 123.3, 122.7, 115.5, 114.7, 114.2, 113.7, 112.4, 102.7, 94.9, 94.8, 85.4, 85.1, 83.8, 70.2, 68.2, 54.5, 54.4, 43.1, 40.5, 29.3, 28.8, 28.8, 28.7, 28.6, 28.4, 28.3, 28.2, 25.2, 23.5.

m/z HRMS (ESI) found $[M+H]^+$ 690.4144, $C_{45}H_{56}NO_5^+$ requires 690.4153.

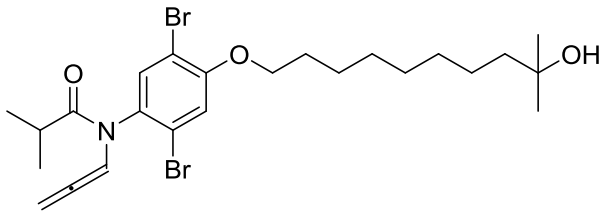
N-(4-((12-hydroxy-12-methyltridecyl)oxy)-2,5-bis(phenylethynyl)phenyl)-*N*-(propa-1,2-dien-1-yl)pivalamide **(5s)**



This reaction was performed on 1.8 mmol scale of **S4** according to **method B**. Give the product **5s** (360 mg, 31% yield for 4 steps) as yellow solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (t, *J* = 6.3 Hz, 1H), 7.55-7.53 (m, 2H), 7.49-7.48 (m, 2H), 7.40-7.30 (m, 7H), 7.03 (s, 1H), 5.00 (d, *J* = 6.3 Hz, 2H), 4.09 (t, *J* = 6.4 Hz, 2H), 1.97-1.85 (m, 2H), 1.47-1.41 (m, 5H), 1.36-1.25 (m, 13H), 1.20 (s, 6H), 1.16 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.8, 176.4, 159.0, 135.1, 134.7, 131.8, 131.2, 129.0, 128.6, 128.6, 128.5, 125.6, 123.3, 122.7, 114.6, 113.4, 103.7, 95.9, 86.49, 86.2, 85.0, 71.2, 69.1, 44.1, 41.5, 30.3, 29.8, 29.8, 29.7, 29.6, 29.3, 29.3, 29.2, 27.8, 26.2, 24.5. m/z HRMS (ESI) found $[M+H]^+$ 644.4113, $C_{44}H_{54}NO_3^+$ requires 644.4098.

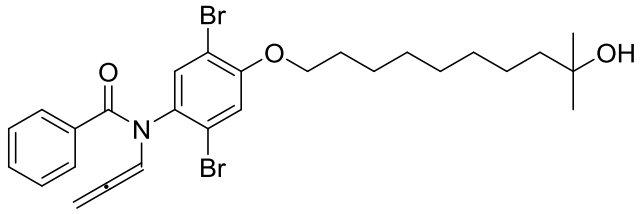
N-(2,5-dibromo-4-((9-hydroxy-9-methyldecyl)oxy)phenyl)-*N*-(propa-1,2-dien-1-yl)isobutyramide **(5t)**



This reaction was performed on 3.2 mmol scale of **S1** according to **method A**, which gave the product **5t** (197 mg, 11% yield for 5 steps) as yellow oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.60 (t, *J* = 6.4 Hz, 1H), 7.44 (s, 1H), 7.12 (s, 1H), 5.05-5.03 (m, 2H), 4.05-4.01 (m, 2H), 2.31 (hept, *J* = 6.7 Hz, 1H), 1.90-1.83 (m , 2H), 1.54-1.44 (m, 4H), 1.42-1.30 (m, 8H), 1.21 (s, 6H), 1.12 (d, *J* = 6.6 Hz, 3H), 1.04 (d, *J* = 6.8 Hz, 3H).^{13}C NMR (101 MHz, Chloroform-d) δ 202.6, 175.6, 156.1, 134.3, 132.0, 123.5, 116.9, 111.1, 100.2, 86.9, 71.2, 69.9, 44.1, 32.4, 30.2, 29.6, 29.4, 29.3, 29.0, 26.1, 24.45, 20.2, 19.4. m/z HRMS (ESI) found $[M+H]^+$ 544.1051, $C_{24}H_{36}Br_2NO_3^+$ requires 544.1056

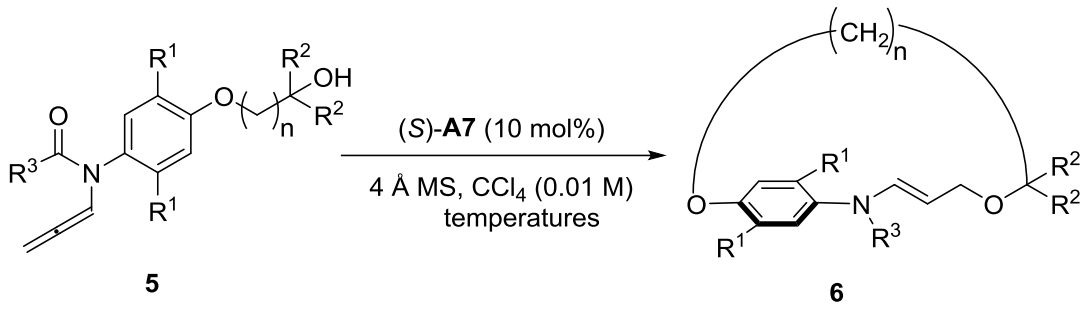
N-(2,5-dibromo-4-((9-hydroxy-9-methyldecyl)oxy)phenyl)-*N*-(propa-1,2-dien-1-yl)benzamide **(5u)**



This reaction was performed on 3.2 mmol scale of **S1** according to **method A**, which gave the product **5u** (310 mg, 17% yield for 5 steps) as yellow oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.69-7.26 (m, 5H), 7.26-6.93 (m, 3H), 5.13-5.10 (m, 2H), 3.94-3.91 (m, 2H), 1.83-1.79 (m, 2H), 1.53-1.42 (m, 4H), 1.40-1.29 (m, 8H), 1.21 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 202.6, 168.6, 155.6, 134.96, 132.7, 130.4, 128.3, 128.0, 123.0, 116.6, 110.7, 101.0, 87.4, 71.2, 69.8, 44.1, 30.2, 29.6, 29.36, 29.3, 29.0, 26.0, 24.4. m/z HRMS (ESI) found $[M+H]^+$ 578.0921, $C_{27}H_{34}Br_2NO_3^+$ requires 578.0900

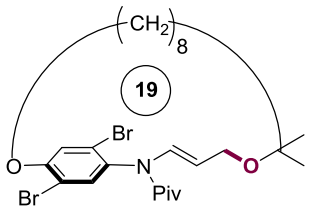
Asymmetric synthesis of products 6



General procedure for the asymmetric synthesis of products 2:

A flask containing a magnetic stir bar was added (*S*)-**A7** (18.2 mg, 0.02 mmol, 0.1 equiv.) and activated 4 Å MS (250 mg) under N_2 atmosphere. Then a solution of **5** (0.2 mmol, 1.0 equiv.) in dry CCl_4 (20 mL) was added using a syringe. After stirring at 20 ^oC for 18 h, the reaction mixture was filtered and concentrated to give a residue, which was purified by Preparative Thin-Layer Chromatography (petroleum ether/EtOAc = 10:1) to afford the product **6**.

(R_p,*E*)-1-(1^2,1^5-dibromo-7,7-dimethyl-6,16-dioxa-2-aza-1(1,4)-benzenacyclohexadeca p- pan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6a)**

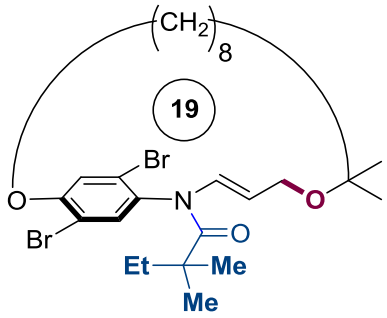


The reaction was performed on 0.2 mmol scale under the standard conditions at 20 ^oC for 17 h. Purification by Preparative Thin-Layer Chromatography (petroleum ether/EtOAc=10:1) afforded **6a** as a white solid (40 mg, 35.7% yield.)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (s, 1H), 7.41 (d, *J* = 14.0 Hz, 1H), 7.22 (s, 1H), 4.36-4.30 (m, 2H), 4.17-4,10 (m, 1H), 3.93-3.84 (m, 2H), 1.79-1.72 (m, 2H), 1.55-1.51 (m, 1H), 1.47-1.39 (m, 1H), 1.36-1.25 (m, 3H), 1.21 (s, 9H), 1.17-1.12 (m, 3H), 1.10 (s, 3H), 1.09 (s, 3H), 1.07-0.99 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.9, 155.6, 135.8, 133.2, 131.5, 119.3, 112.3, 111.7, 77.4, 75.8,

70.0, 61.2, 41.0, 39.1, 30.0, 29.5, 28.7, 27.9, 27.0, 26.3, 24.6, 24.1. $[\alpha]^{25}_{D}$ = -31.4 (c = 1.0, CH_2Cl_2). m/z HRMS (ESI) found $[M+H]^+$ 560.1210, $C_{25}H_{38}Br_2NO_3^+$ requires 560.1192. HPLC: Chiralpak IC column, 95:5 hexanes/isopropanol, 1 ml/min; t_R = 16.82 min (major), 23.49 min (minor); 92:8 er.

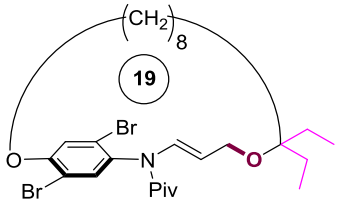
(*R*$_p$,*E*)-(1-(1^2,1^5-dibromo-7,7-dimethyl-6,16-dioxa-2-aza-1(1,4)-benzenacyclohexadecap- han-3-en-2-yl)-2,2- dimethylbutan-1-one **(6b)**



The reaction was performed on 0.2 mmol scale under the standard conditions at 20 ℃ for 36 h. Purification by Preparative Thin-Layer Chromatography (petroleum ether/EtOAc=10:1) to afford **6b** as a white solid (40 mg, 34.8% yield.)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.46 (s, 1H), 7.40 (d, *J* = 14.1 Hz, 1H), 7.20 (s, 1H), 4.33-4.30 (m, 2H), 4.14-4.08 (m, 1H), 3.88-3.61 (m, 2H), 1.76-1.71 (m, 2H), 1.69-1.65 (m, 2H), 1.56-1.50 (m, 2H), 1.45-1.41 (m, 1H), 1.35-1.18 (m, 4H), 1.18-1.11 (m, 4H), 1.10-1,02 (m, 12H), 1.05-0.99 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 175.2, 155.5, 135.6, 133.2, 131.4, 123.9, 119.2, 112.2, 111.7, 75.7, 69.9, 61.2, 45.0, 39.0, 34.7, 29.9, 29.5, 27.8, 27.0, 26.9, 26.5, 26.2, 26.2, 24.6, 24.1, 9.6. $[\alpha]^{25}_{D}$ = -28 (c = 1.0, CH_2Cl_2). m/z HRMS (ESI) found $[M+H]^+$ 574.1344, $C_{26}H_{40}Br_2NO_3^+$ requires 574.1349. HPLC: Chiralpak IC column, 95:5 hexanes/isopropanol, 1 ml/min; t_R = 13.81 min (major), 19.18 min (minor); 92:8 er.

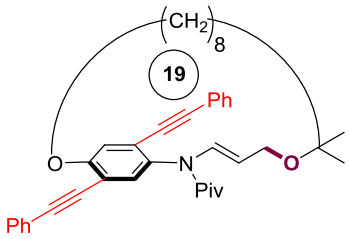
(*R*$_p$,*E*)-1-(1^2,1^5-dibromo-7,7-diethyl-6,15-dioxa-2-aza-1(1,4)-benzenacyclopentadecaph- an-3-en-2-yl)-2,2-dimethylpropan-1-one **(6c)**



The reaction was performed on 0.2 mmol scale under the standard conditions at 10 ℃ for 27 h. Purification by Preparative Thin-Layer Chromatography (petroleum ether/EtOAc=10:1) afforded **6c** as white solid (35 mg, 30.5% yield.).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50 (s, 1H), 7.40 (d, *J* = 13.7 Hz, 1H), 7.31 (s, 1H), 4.51-4.46 (m, 1H), 4.43-4.38 (m, 1H), 4.01-3.95 (m, 1H), 3.85-3.82 (m, 1H), 3.79-3.74 (m, 1H), 1.81-1.71 (m, 2H), 1.45-1.39 (m, 2H), 1.35-1.25 (m, 5H), 1.22 (s, 9H), 1.18-1.10 (m, 3H), 1.02-0.97 (m, 4H), 0.76 (t, *J* = 7.5 Hz, 3H), 0.73 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 175.8, 156.0, 135.9, 133.1, 131.3, 123.8, 120.0, 112.7, 111.2, 80.5, 70.8, 59.9, 41.0, 34.3, 30.5, 29.5, 28.9, 28.7, 26.7, 26.6, 26.5, 22.8, 8.2, 7.8. $[\alpha]^{25}_{D}$ = -17.4 (c = 1.0, CH_2Cl_2). m/z HRMS (ESI) found $[M+H]^+$ 574.1357, $C_{26}H_{40}Br_2NO_3^+$ requires 574.1349. HPLC: Chiralpak IC column, 95:5 hexanes/isopropanol, 1 ml/min; t_R = 15.95 min (major), 18.20 min (minor); 80:20 er.

(*R*$_p$,*E*)-1-(7,7-dimethyl-1^2,1^5-bis(phenylethynyl)-6,16-dioxa-2-aza-1(1,4)-benzenacyclo- hexadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6d)**

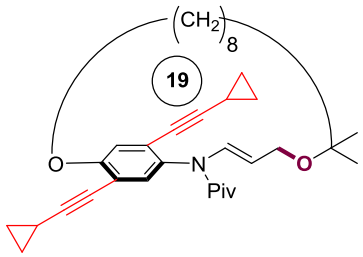


The reaction was performed on 0.2 mmol scale under the standard conditions at 20 ℃ for 21 h. Purification by Preparative Thin-Layer Chromatography (petroleum ether/EtOAc=10:1) afforded **6d** as white solid (40 mg, 33.3% yield.)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 14.2 Hz, 1H), 7.56-7.54 (m, 2H), 7.50-7.43 (m, 3H), 7.40 -7.31 (m, 6H), 7.16 (s, 1H), 4.40-4.37 (m, 2H), 4.28- 4.21 (m, 1H), 3.93-3.82 (m, 2H), 1.89-1.75 (m, 2H), 1.72-1.65 (m, 1H), 1.51-1.44 (m, 1H),

1.39 -1.24 (m, 3H), 1.19 (s, 9H), 1.17-1.10 (m, 5H), 1.07 (s, 3H), 1.06 (s, 3H), 1.05-0.95 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.5, 158.9, 135.6, 135.0, 132.9, 131.9, 131.8, 129.0, 128.6, 128.6, 128.5, 125.5, 123.3, 122.6, 118.0, 115.5, 111.8, 96.0, 95.9, 86.1, 84.9, 75.6, 69.5, 61.4, 41.4, 39.2, 30.0, 29.6, 29.1, 27.8, 27.4, 27.2, 26.1, 24.7, 24.1. $[\alpha]^{25}_{D}$ = 8.4 (c = 1.0, CH_2Cl_2). m/z HRMS (ESI) found $[M+H]^+$ 602.3614, $C_{41}H_{48}NO_3^+$ requires 602.3629. HPLC: Chiralpak IC column, 95:5 hexanes/isopropanol, 1 ml/min; t_R = 12.74 min (minor), 19.05 min (major); 92:8 er.

(*R*$_p$,*E*)-1-(1^2,1^5-bis(cyclopropylethynyl)-7,7-dimethyl-6,16-dioxa-2-aza-1(1,4)-benzen ac- yclohexadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6e)**

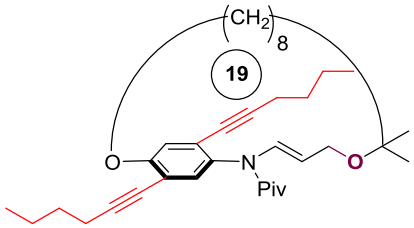


The reaction was performed on 0.2 mmol scale under the standard conditions at 20 ℃ for 21 h. Purification by Preparative Thin-Layer Chromatography (petroleum ether/EtOAc=10:1) to afford **6e** as white solid (30 mg, 28.3% yield.)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 14.1 Hz, 1H), 7.19 (s, 1H), 6.93 (s, 1H), 4.32-4.19 (m, 2H), 4.14-4.08 (m, 1H), 3.90-3.79 (m, 2H), 1.75-1.67 (m, 2H), 1.62 -1.52 (m, 1H), 1.49-1.46 (m, 1H), 1.42-1.36 (m, 3H), 1.28-1.15 (m, 3H), 1.13-1.04 (m, 19H), 1.03-0.94 (m, 2H), 0.91-0.76 (m, 6H), 0.76- -0.69 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 176.3, 158.8, 135.5, 134.8, 132.7, 125.2, 118.1, 115.4, 111.4, 100.0, 75.6, 72.4, 71.1, 69.3, 61.5, 41.3, 39.2, 30.0, 29.4, 29.0, 27.8, 27.2, 27.2, 26.2, 24.6, 24.1, 9.0, 8.9, 0.7, 0.5. $[\alpha]^{25}_{D}$ = -1.6 (c = 1.0, CH_2Cl_2). m/z HRMS (ESI) found $[M+H]^+$ 530.3621, $C_{35}H_{48}NO_3^+$ requires 530.3629. HPLC: Chiralpak IC column, 95:5 hexanes/isopropanol, 1 ml/min; t_R = 19.19 min (minor), 27.43 min (major); 85:15 er.

(R_p,*E*)-1-(1^2,1^5-di(hex-1-yn-1-yl)-7,7-dimethyl-6,16-dioxa-2-aza-1(1,4)-benzenacyclo he-

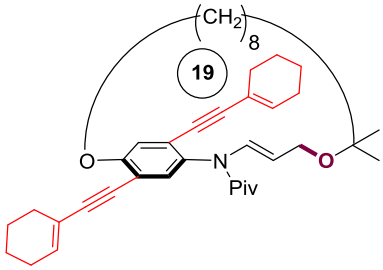
xadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6f)**



The reaction was performed on 0.2 mmol scale under the standard conditions at 20 ℃ for 12 h. Purification by Preparative Thin-Layer Chromatography (petroleum ether/EtOAc=10:1) afforded **6f** as colorless oil (34 mg, 30.2% yield.)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 14.1 Hz, 1H), 7.23 (s, 1H), 6.97 (s, 1H), 4.30-427 (m, 2H), 4.17-4.12 (m, 1H), 3.89-3.85 (m, 2H), 2.45 (t, *J* = 6.9 Hz, 2H), 2.34 (t, *J* = 7.0 Hz, 2H), 1.75-1.67 (m, 2H), 1.63-1.58 (m, 2H), 1.55-1.47 (m, 4H), 1.42-1.36(m, 3H), 1.34-1.20 (m, 4H), 1.18-1.11 (m, 13H), 1.09 (s, 3H), 1.08 (s, 3H), 1.05-0.95 (m, 3H), 0.95-0.89 (m, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 176.2, 158.6, 135.5, 134.6, 132.7, 125.4, 118.2, 115.6, 111.4, 97.0, 77.3, 76.0, 75.6, 69.3, 61.5, 41.3, 39.2, 30.8, 30.6, 29.9, 29.4, 29.0, 27.8, 27.3, 27.1, 26.2, 24.6, 24.1, 22.1, 22.0, 19.6, 19.3, 13.8, 13.69. $[\alpha]^{25}_D$ = -7 (c = 1.0, CH_2Cl_2). m/z HRMS (ESI) found $[M+H]^+$ 562.4247, $C_{37}H_{56}NO_3^+$ requires 562.4255. HPLC: Chiralpak IC column, 95:5 hexanes/isopropanol, 1 ml/min; t_R = 9.56 min (minor), 10.92 min (major); 82:18 er.

(R_p,*E*)-1-(1^2,1^5-bis(cyclohex-1-en-1-ylethynyl)-7,7-dimethyl-6,16-dioxa-2-aza-1(1,4)-benzenacyclohexadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6g)**

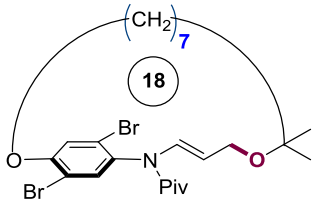


The reaction was performed on 0.25 mmol scale under the standard conditions at 30 ℃

for 5 h. Purification by Preparative Thin-Layer Chromatography (petroleum ether/EtOAc=5:1) to afford **6g** as a white solid (25 mg, 16% yield.) and recovered **5g** as yellow oil (45 mg, 30% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 14.1 Hz, 1H), 6.99 (s, 1H), 6.28-6.09 (m, 2H), 4.33-4.24 (m, 2H), 4.19-4.13 (m, 1H), 3.91-3.76 (m, 2H), 2.23-2.20 (m, 2H), 2.17-2.11 (m, 6H), 1.78-1.62 (m, 8H), 1.44-1.40 (m, 2H), 1.37-1.30 (m, 2H), 1.29-1.21 (m, 3H), 1.19-1.11 (m, 14H), 1.08 (s, 3H), 1.07 (s, 3H), 1.04-0.99 (m, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 176.3, 158.6, 136.7, 135.7, 135.3, 134.6, 132.8 125.4, 121.0, 120.6, 117.9, 115.5, 111.6, 97.7, 83.7, 82.3, 75.6, 69.4, 61.5, 41.4, 39.2, 30.0, 29.5, 29.2, 29.1, 29.0, 27.8, 27.4, 27.2, 26.2, 26.0, 25.9, 24.6, 24.1, 22.5, 22.3, 21.6, 21.5. $[\alpha]^{25}_{D}$ = -3.2 (c = 1.0, CH_2Cl_2). m/z HRMS (ESI) found $[M+H]^+$ 610.4246, $C_{41}H_{56}NO_3^+$ requires 610.4255. HPLC: Chiralpak IC column, 95:5 hexanes/isopropanol, 1 ml/min; t_R = 11.71 min (minor), 23.10 min (major); 91:9 er.

(*R*$_p$,*E*)-1-(1^2,1^5-dibromo-7,7-dimethyl-6,15-dioxa-2-aza-1(1,4)-benzenacyclopentadecap- han-3-en-2-yl)-2,2-dimethylpropan-1-one **(6h)**

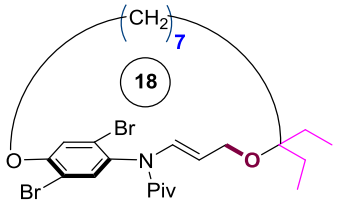


The reaction was performed on 0.2 mmol scale under the standard conditions at 20 ℃ for 22 h. Purification by Preparative Thin-Layer Chromatography (petroleum ether/EtOAc=10:1) afforded **6h** as a white solid (33 mg, 30.2% yield.).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50 (s, 1H), 7.40 (d, *J* = 14.0 Hz, 1H), 7.31 (s, 1H), 4.50-4.46 (m, 1H), 4.43-4.38 (m, 1H), 4.02-3.97 (m, 1H), 3.88-3.78 (m, 2H), 1.76-1.73 (m, 2H), 1.40-1.32 (m, 1H), 1.30-1.24 (m, 3H), 1.22 (s, 9H), 1.20-1.16 (m, 2H), 1.10 (s, 3H), 1.08 (s, 3H), 1.06-0.97 (m, 4H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 175.8, 156.0, 135.9, 133.2, 131.2, 123.9, 120.1, 112.8, 111.5, 75.6, 70.8, 60.8, 38.5, 41.0, 30.2, 29.5, 29.0, 28.7, 27.0, 26.7, 26.4, 23.5. $[\alpha]^{25}_{D}$ = -27.8 (c =

1.0, CH_2Cl_2). m/z HRMS (ESI) found $[M+H]^+$ 546.1028, $C_{24}H_{36}Br_2NO_3^+$ requires 546.1036. HPLC: Chiralpak IC column, 95:5 hexanes/isopropanol, 1 ml/min; t_R = 19.16 min (major), 22.86 min (minor); 88:12 er.

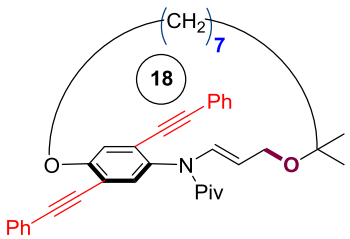
(*R*$_p$,*E*)-1-(1^2,1^5-dibromo-7,7-diethyl-6,16-dioxa-2-aza-1(1,4)-benzenacyclohexadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6i)**



The reaction was performed on 0.2 mmol scale under the standard conditions at 10 ℃ for 21 h. Purification by Preparative Thin-Layer (petroleum ether/EtOAc=10:1) to afford **6i** as white solid (45 mg, 38.4% yield.).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (s, 1H), 7.41 (d, *J* = 13.9 Hz, 1H), 7.21 (s, 1H), 4.33 (t, *J* = 5.6 Hz, 2H), 4.14-4.09 (m, 1H), 3.89-3.75 (m, 2H), 1.81-1.71 (m, 2H), 1.61-1.54 (m, 1H), 1.46-1.40 (m, 3H), 1.36-1.30 (m, 2H), 1.30-1.25 (m, 2H), 1.21 (s, 9H), 1.15-0.91 (m, 8H), 0.77 (t, *J* = 5.9 Hz, 3H), 0.73 (t, *J* = 5.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.9, 155.5, 135.7, 133.1, 131.8, 123.9, 119.2, 112.2, 111.2, 80.4, 69.9, 60.2, 41.0, 34.3, 30.2, 29.8, 29.7, 28.7, 27.8, 26.8, 26.8, 24.5, 23.4, 8.1, 7.8. $[\alpha]^{25}_D$ = -26.2 (c = 1.0, CH_2Cl_2). m/z HRMS (ESI) found $[M+H]^+$ 588.1499, $C_{27}H_{42}Br_2NO_3^+$ requires 588.1505. HPLC: Chiralpak IC column, 95:5 hexanes/isopropanol, 1 ml/min; t_R = 14.81 min (major), 19.30 min (minor); 84:16 er.

(*R*$_p$,*E*)-1-(7,7-dimethyl-1^2,1^5-bis(phenylethynyl)-6,15-dioxa-2-aza-1(1,4)-benzenacyclop- entadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6j)**

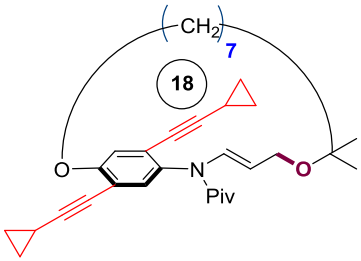


The reaction was performed on 0.2 mmol scale under the standard conditions at 20 ℃

for 21 h. Purification by Preparative Thin-Layer (petroleum ether/EtOAc=10:1) afforded **6j** as a white solid (32 mg, 27% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.61-7.54 (m, 3H), 7.49-7.46 (m, 2H), 7.44 (s, 1H), 7.39-7.32 (m, 6H), 7.24 (s, 1H), 4.56-4.51 (m, 1H), 4.49-4.44 (m, 1H), 4.13-4.11 (m, 1H), 3.89-3.78 (m, 2H), 1.81-1.75 (m, 2H), 1.43-1.32 (m, 3H), 1.26-1.23 (m, 1H), 1.21-1.14 (m, 10H), 1.18-1.12 (m, 1H), 1.08-1.06 (m, 10H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 176.4, 159.2, 135.8, 135.1, 132.6, 131.9, 131.8, 129.0, 128.7, 128.59, 128.5, 123.3, 122.6, 118.9, 115.9, 111.7, 96.2, 86.1, 85.0, 75.6, 70.5, 61.1, 41.4, 38.7, 30.3, 29.4, 29.1, 29.1, 27.1, 26.5, 26.4, 23.6. $[\alpha]^{25}_{D}$ = 18.2 (c = 1.0, CH_2Cl_2). m/z HRMS (ESI) found $[M+H]^+$ 588.3464, $C_{40}H_{46}NO_3^+$ requires 588.3472. HPLC: Chiralpak IC column, 95:5 hexanes/isopropanol, 1 ml/min; t_R = 15.02 min (minor), 25.01 min (major); 93:7 er.

(*R*$_p$,*E*)-1-(1^2,1^5-bis(cyclopropylethynyl)-7,7-dimethyl-6,15-dioxa-2-aza-1(1,4)-benzen ac- cyclopentadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6k)**

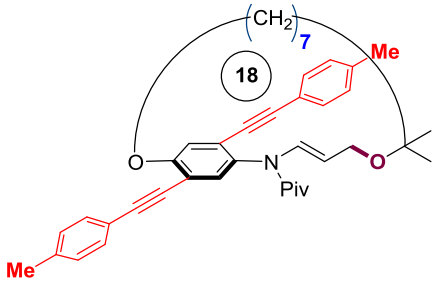


The reaction was performed on 0.2 mmol scale under the standard conditions at 20 ℃ for 23 h. Purification by Preparative Thin-Layer (petroleum ether/EtOAc=10:1) afforded **6k** as a white solid (26 mg, 25.2% yield.).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 14.1 Hz, 1H), 7.18 (s, 1H), 7.01 (s, 1H), 4.43-4.32 (m, 2H), 4.00-3.95 (m, 1H), 3.85-3.77 (m, 2H), 1.72-1.63 (m, 2H), 1.50-1.47 (m, 1H), 1.38-1.32 (m, 2H), 1.32-1.25 (m, 3H), 1.18-1.08 (s, 11H), 1.08 (s, 3H), 1.07 (s, 3H), 1.05-0.99 (m, 4H), 0.89-0.85 (m, 2H), 0.86-0.78 (m, 4H), 0.76-0.70 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 176.3, 159.2, 135.7, 134.9, 132.3, 119.1, 115.8, 111.4, 100.2, 75.5, 72.4, 71.2, 61.1, 41.3, 38.7, 30.3, 29.8, 29.4, 29.1,

29.0, 27.1, 26.6, 26.2, 23.6, 9.1, 9.0, 9.0, 0.7, 0.5. $[\alpha]^{25}_{D}$ = 5 (c = 1.0, CH_2Cl_2). m/z HRMS (ESI) found $[M+H]^+$ 516.3483, $C_{34}H_{46}NO_3^+$ requires 516.3472. HPLC: Chiralpak IC column, 80:20 hexanes/isopropanol, 1 ml/min; t_R = 7.76 min (minor), 19.04 min (major); 86:14 er.

(*R*$_p$,*E*)-1-(7,7-dimethyl-1^2,1^5-bis(p-tolylethynyl)-6,15-dioxa-2-aza-1(1,4)-benzenacyclop-entadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6l)**

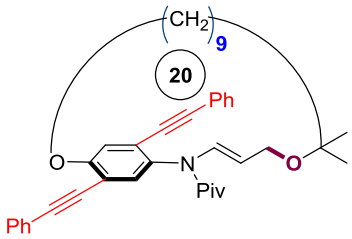


The reaction was performed on 0.4 mmol scale under the standard conditions at 40 ℃ for 9 h. Purification by Preparative Thin-Layer (petroleum ether/EtOAc=5:1) afforded **6l** as a white solid (45 mg, 18% yield.) and recovered **5l** as yellow oil (50 mg, 20% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 14.1 Hz, 1H), 7.48-7.40 (m, 3H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.22 (s, 1H), 7.18-7.13 (m, 4H), 4.57-4.40 (m, 2H), 4.14-4.07 (m, 1H), 3.86-3.80 (m, 2H), 2.38 (s, 3H), 2.36 (s, 3H), 1.40-1.32 (m, 5H), 1.28-1.16 (m, 13H), 1.06 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 176.4, 159.2, 139.3, 138.8, 135.6, 135.0, 132.5, 131.8, 131.7, 129.3, 129.3, 125.5, 120.2, 119.6, 118.9, 115.9, 111.7, 96.4, 96.1, 85.6, 84.4, 75.5, 70.5, 61.1, 41.4, 38.7, 30.2, 29.4, 29.2, 29.1, 27.1, 26.5, 26.3, 23.6, 21.7, 21.7. $[\alpha]^{25}_{D}$ = 21.6 (c = 1.0, CH_2Cl_2). m/z HRMS (ESI) found $[M+H]^+$ 616.3770, $C_{42}H_{50}NO_3^+$ requires 616.3785. HPLC: Chiralpak IC column, 90:10hexanes/isopropanol, 1 ml/min; t_R = 10.58 min (minor), 19.63 min (major); 91:9 er.

(*R*$_p$,*E*)-1-(7,7-dimethyl-1^2,1^5-bis(phenylethynyl)-6,17-dioxa-2-aza-1(1,4)-benzenacycl

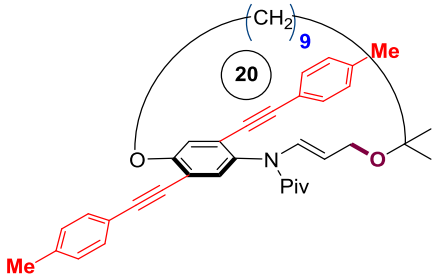
oh- eptadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6m)**



The reaction was performed on 0.2 mmol scale under the standard conditions at 20 ℃ for 24 h. Purification by Preparative Thin-Layer (petroleum ether/EtOAc=10:1) afforded **6m** as a yellow solid (47 mg, 38.1% yield.).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 14.2 Hz, 1H), 7.57-7.55 (m, 2H), 7.48-.46 (m, 3H), 7.40-7.32 (m, 6H), 7.15 (s, 1H), 4.49-4.45 (m, 1H), 4.35-4.24 (m, 2H), 3.84-3.76 (m, 2H), 1.91-1.84 (m, 1H), 1.71-1.59 (m, 2H), 1.47-1.36 (m, 3H), 1.26-1.22 (m, 2H), 1.17-1.13 (s, 17H), 1.09 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 176.5, 157.8, 135.7, 134.5, 133.1, 131.9, 131.8, 129.0, 128.6, 128.59, 128.5, 125.3, 123.3, 122.6, 116.9, 115.3, 110.2, 96.0, 86.2, 84.9, 75.1, 68.8, 61.2, 41.5, 38.7, 30.3, 29.4, 29.1, 28.3, 28.2, 27.2, 26.8, 26.4, 24.9, 23.3. $[\alpha]^{25}_{D}$ = -8.2 (c = 1.0, CH_2Cl_2). m/z HRMS (ESI) found $[M+H]^+$ 616.3778, $C_{42}H_{50}NO_3^+$ requires 616.3785. HPLC: Chiralpak IC column, 95:5 hexanes/isopropanol, 1 ml/min; t_R = 11.70 min (minor), 15.58 min (major); 88:12 er.

(*R*$_p$,*E*)-1-(7,7-dimethyl-1^2,1^5-bis(p-tolylethynyl)-6,17-dioxa-2-aza-1(1,4)-benzenacycl oh- eptadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6n)**

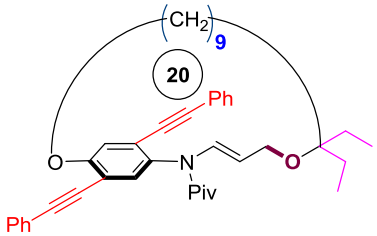


The reaction was performed on 0.3 mmol scale under the standard conditions at 20 ℃ for 12 h. Purification by Preparative Thin-Layer (petroleum ether/EtOAc=5:1) afforded **6n** as a yellow solid (45 mg, 23% yield.) and recovered **5n** as yellow oil (70

mg, 36% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 14.2 Hz, 1H), 7.45-7.44 (m, 3H), 7.38-7.34 (m, 2H), 7.19-7.10 (m, 5H), 4.46-4.43 (m, 1H), 4.35-4.22 (m, 2H), 3.81-3.79 (m, 2H), 2.38 (s, 3H), 2.36 (s, 3H), 1.93-1.81 (m, 1H), 1.71-1.64 (m, 1H), 1.45-1.35 (m, 3H), 1.30-1.21 (m, 2H), 1.20-1.10 (m, 16H), 1.09-1.03 (s, 8H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 176.5, 157.8, 139.3, 138.7, 135.5, 134.5, 133.0, 131.7, 131.7, 129.3, 129.2, 125.3, 120.3, 119.6, 116.9, 115.3, 110.3, 96.1, 85.7，84.4, 75.0, 68.8, 61.2, 41.5, 38.7, 30.2, 29.4, 29.1, 28.2, 28.2, 27.2, 26.9, 26.3, 24.9, 23.3, 21.7, 21.6. $[\alpha]^{25}_{D}$ = -4.4 (c = 1.0, CH_2Cl_2). m/z HRMS (ESI) found $[M+H]^+$ 644.4109, $C_{44}H_{54}NO_3^+$ requires 644.4098. HPLC: Chiralpak IC column, 90:10 hexanes/isopropanol, 1 ml/min; t_R = 8.41 min (minor), 12.09 min (major); 88:12 er.

(R_p,*E*)-1-(7,7-diethyl-1^2,1^5-bis(phenylethynyl)-6,17-dioxa-2-aza-1(1,4)-benzenacyclo he- ptadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6o)**

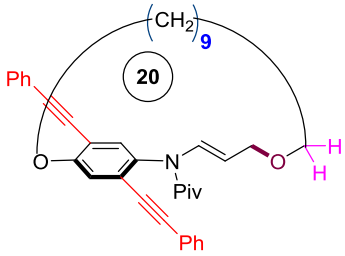


The reaction was performed on 0.2 mmol scale under the standard conditions at 20 ℃ for 24 h. Purification by Preparative Thin-Layer (petroleum ether/EtOAc=10:1) afforded **6o** as a yellow solid (55 mg, 43% yield.).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 14.1 Hz, 1H), 7.57-7.54 (m, 2H), 7.51-7.44 (m, 3H), 7.39-7.32 (m, 6H), 7.26 (s, 1H), 4.54-4.43 (m, 1H), 4.35-4.24 (m, 2H), 3.86-3.67 (m, 2H), 1.98-1.84 (m, 1H), 1.73-1.65 (m, 1H), 1.49-1.32 (m, 5H), 1.30-1.20 (m, 5H), 1.20-0.93 (m, 17H), 0.76 (t, *J* = 7.3 Hz, 3H), 0.72 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.5, 157.8, 135.6, 134.5, 133.3, 131.8, 131.8, 129.0, 128.6, 128.5, 125.2, 123.4, 122.6, 116.8, 115.2, 110.1, 95.9, 95.8, 86.2, 84.9, 79.8, 68.7, 60.2, 41.5, 33.9, 30.5, 29.4, 29.1, 28.2, 26.8, 26.7, 26.7, 24.8, 22.6, 8.4, 7.6. $[\alpha]^{25}_{D}$ = -11.8 (c = 1.0, CH_2Cl_2). m/z HRMS (ESI) found $[M+H]^+$ 644.4106,

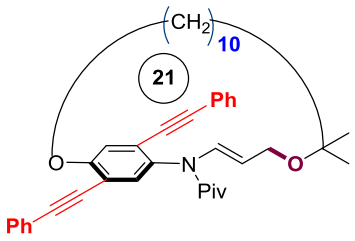
$C_{44}H_{54}NO_3^+$ requires 644.4098. HPLC: Chiralpak IC column, 95:5 hexanes/isopropanol, 1 ml/min; t_R = 9.20 min (minor), 11.50 min (major); 84:16 er.

(*S*$_p$,*E*)-1-(1^2,1^5-bis(phenylethynyl)-6,17-dioxa-2-aza-1(1,4)-benzenacycloheptadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6p)**



The reaction was performed on 0.2 mmol scale under the standard conditions using catalyst (*R*)-**A4** (0.1 equiv.) at 40 ℃ for 12 h. Purification by Preparative Thin-Layer (petroleum ether/EtOAc=10:1) afforded **6p** as a yellow solid (40 mg, 34% yield.). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 14.3 Hz, 1H), 7.50-7.46 (m, 2H), 7.40-7.37 (m, 2H), 7.35 (s, 1H), 7.32-7.27 (m, 6H), 7.08 (s, 1H), 4.32-4.25 (m, 3H), 4.03-3.98 (m, 1H), 3.86-3.81 (m, 1H), 3.28-3.155 (m, 2H), 1.83-1.57 (m, 3H), 1.41-1.28 (m, 4H), 1.24-1.04 (m, 18H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 176.6, 158.3, 135.4, 134.6, 133.6, 131.8, 131.7, 129.1, 128.7, 128.6, 128.5, 125.5, 123.2, 122.5, 116.7, 115.2, 111.3, 96.0, 86.3, 84.8, 69.4, 68.6, 67.9, 41.4, 30.0, 29.1, 29.1, 29.0, 27.9, 27.6, 26.6, 26.2, 24.3. $[\alpha]^{25}_D$ = -5 (c = 1.0, CH_2Cl_2). m/z HRMS (ESI) found $[M+H]^+$ 588.3479, $C_{40}H_{46}NO_3^+$ requires 588.3479. HPLC: Chiralpak IC column, 95:5 hexanes/isopropanol, 1 ml/min; t_R = 11.88 min (major), 16.04 min (minor); 80:20 er.

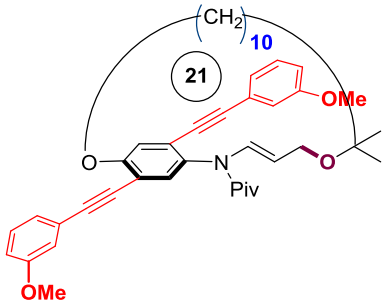
(*R*$_p$,*E*)-1-(7,7-dimethyl-12,15-bis(phenylethynyl)-6,18-dioxa-2-aza-1(1,4)-benzenacyclo- octadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6q)**



The reaction was performed on 0.2 mmol scale under the standard conditions at 40 ℃ for 11 h. Purification by Preparative Thin-Layer (petroleum ether/EtOAc=5:1) to afford **6q** as a white solid (44 mg, 35% yield.) and recovered **5q** as yellow oil (38 mg, 30% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 14.2 Hz, 1H), 7.57-7.51 (m, 2H), 7.49 -7.43 (m, 3H), 7.38-7.32 (m, 6H), 7.11 (s, 1H), 4.40-4.27 (m, 2H), 4.22-4.19 (m, 1H), 3.86-3.80 (m, 2H), 2.05-2.03 (m, 1H), 1.85-1.70 (m, 2H), 1.46-1.32 (m, 5H), 1.25 (s, 3H), 1.17 (s, 13H), 1.13-1.07 (m, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 176.6, 159.1, 135.4, 134.5, 133.345, 131.9, 131.7, 129.0, 128.6, 128.5, 125.4, 123.4, 122.6, 115.6, 114.4, 110.7, 95.9, 86.2, 84.9, 75.2, 68.6, 61.3, 41.5, 39.2, 29.9, 29.4, 29.2, 28.9, 28.4, 28.3, 27.3, 27.2, 26.2, 25.1, 24.1. $[\alpha]^{25}_{D}$ = -3.8 (c = 1.0, CH_2Cl_2). m/z HRMS (ESI) found $[M+H]^+$ 630.3933, $C_{43}H_{52}NO_3^+$ requires 630.3942. HPLC: Chiralpak IC column, 95:5 hexanes/isopropanol, 1 ml/min; t_R = 11.32 min (minor), 13.62 min (major); 90:10 er.

(R_p,*E*)-1-(1^2,1^5-bis((3-methoxyphenyl)ethynyl)-7,7-dimethyl-6,18-dioxa-2-aza-1(1,4)-benzenacyclooctadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6r)**

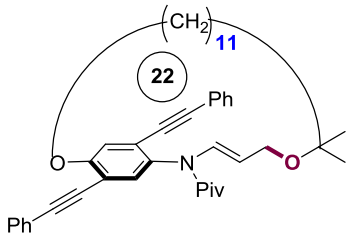


The reaction was performed on 0.2 mmol scale under the standard conditions at 40 ℃ for 11 h. Purification by Preparative Thin-Layer (petroleum ether/EtOAc=5:1)

afforded **6r** as a yellow solid (35 mg, 25% yield.) and recovered **5r** as yellow oil (45 mg, 33% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 14.1 Hz, 1H), 7.48 (s, 1H), 7.29-7.26 (m, 1H), 7.24-7.23 (m, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.10 (s, 1H), 7.08-7.04 (m, 2H), 7.03-6.97 (m, 1H), 6.92-6.89 (m, 2H), 4.37-4.29 (m, 2H), 4.21-4.16 (m, 1H), 3.88-3.79 (m, 8H), 2.05-2.02 (m, 1H), 1.80-1.75 (m, 2H), 1.45-1.36 (m, 3H), 1.35-1.21 (m, 8H), 1.17-1.12 (s, 13H), 1.10 (s, 3H), 1.09 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 176.6, 159.5, 159.5, 159.1, 135.4, 134.6, 133.4, 129.7, 129.6, 125.4, 124.4, 124.3, 123.6, 116.5, 116.4, 115.8, 115.5, 115.3, 114.4, 110.6, 95.9, 86.0, 84.7, 75.2, 68.6, 61.3, 55.5, 55.4, 41.5, 39.2, 29.9, 29.4, 29.2, 28.9, 28.4, 28.3, 27.3, 27.2, 26.2, 25.1, 24.1. $[\alpha]^{25}_D$ = -11.2 (c = 1.0, CH_2Cl_2). m/z HRMS (ESI) found $[M+H]^+$ 690.4143, $C_{45}H_{56}NO_5^+$ requires 690.4153. HPLC: Chiralpak IC column, 90:10 hexanes/isopropanol, 1 ml/min; t_R = 11.43 min (major), 15.63 min (minor); 91:9 er.

(*R*$_p$,*E*)-1-(7,7-dimethyl-1^2,1^5-bis(phenylethynyl)-6,19-dioxa-2-aza-1(1,4)-benzenacyclo- nonadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6s)**



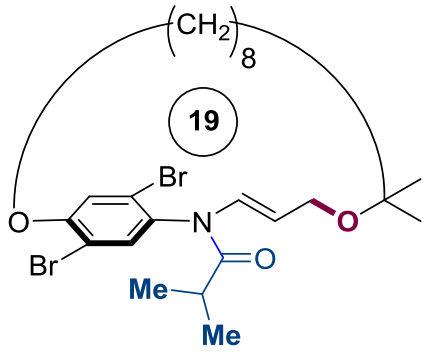
The reaction was performed on 0.2 mmol scale under the standard conditions at 20 ℃ for 16 h. Purification by Preparative Thin-Layer (petroleum ether/EtOAc=5:1) afforded **6s** as a white solid (45 mg, 35% yield.) and recovered **5s** as yellow oil (40 mg, 31% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 14.2 Hz, 1H), 7.56-7.54 (m, 2H), 7.48-7.44 (m, 3H), 7.39-7.31 (m, 6H), 7.11 (s, 1H), 4.38-4.32 (m, 1H), 4.29-4.25 (m, 1H), 4.18-4.13 (m, 1H), 3.83-3.80 (m, 2H), 2.06-2.03 (m, 1H), 1.92-1.82 (m, 1H),

1.76-1.73 (m, 1H), 1.50-1.36 (m, 3H), 1.36-1.19 (m, 8H), 1.16-1.13 (m, 15H), 1.11 (s, 3H), 1.10 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 176.6, 158.9, 135.3, 134.3, 133.1, 131.8, 131.7, 129.0, 128.6 128.6, 128.5, 125.3, 123.3, 122.6, 115.6, 114.4, 110.2, 96.0, 86.2, 84.9, 75.0, 67.8, 61.4, 41.5, 39.2, 30.3, 29.9, 29.1, 28.7, 28.6, 28.2, 27.9, 27.0, 26.5, 26.1, 24.5, 23.5. $[\alpha]^{25}_{D}$ = -8.4 (c = 1.0, CH_2Cl_2).m/z HRMS (ESI) found $[M+H]^+$ 644.4105, $C_{44}H_{54}NO_3^+$ requires 644.4098. HPLC: Chiralpak IA column, 95:5 hexanes/isopropanol, 1 ml/min; t_R = 4.48 min (major), 4.85 min (minor); 85:15 er.

Control Experiments

(*R*$_p$,E)-1-(1^2,1^5-dibromo-7,7-dimethyl-6,16-dioxa-2-aza-1(1,4)-benzenacyclohexadecaphan-3-en-2-yl)-2-methylpropan-1-one **(6t)**

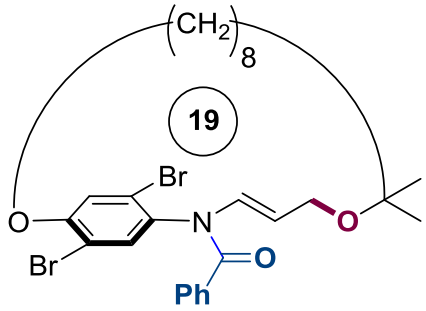


The reaction was performed on 0.1 mmol scale under the standard conditions at 20 ℃ for 43 h. Purification by Preparative Thin-Layer Chromatography (petroleum ether/EtOAc=10:1) to afford **6t** as a white solid (17 mg, 31% yield.)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55-7.45 (m, 2H), 7.28 (s, 1H), 4.36 (t, *J* = 5.6 Hz, 2H), 4.21-4.15 (m, 1H), 3.92-3.85 (m, 2H), 2.38 (hept, *J* =6.8 Hz, 1H), 1.78-1.73(m, 2H), 1.58-1.49 (m, 1H), 1.47-1.43 (m, 1H), 1.35-1.16 (m, 6H), 1.14 (d, *J* = 6.8 Hz, 3H), 1.09 (s, 9H), 1.05 (d, *J* = 6.9 Hz, 3H), 1.01-0.99 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 175.5, 155.8, 134.9, 131.8, 129.2, 123.5, 119.6, 112.9, 112.2, 75.8, 70.2, 61.1, 39.0, 32.7, 30.0, 29.6, 27.9, 27.0, 26.9, 26.3, 24.7, 24.1, 20.2, 19.2. $[\alpha]^{25}_{D}$ = -28.2 (c = 1.0, CH_2Cl_2). m/z HRMS (ESI) found $[M+H]^+$ 544.1079,

$C_{24}H_{36}Br_2NO_3^+$ requires 544.1056. HPLC: Chiralpak IC column, 95:5 hexanes/isopropanol, 1 ml/min; t_R = 19.04 min (major), 21.94 min (minor); 69:31 er.

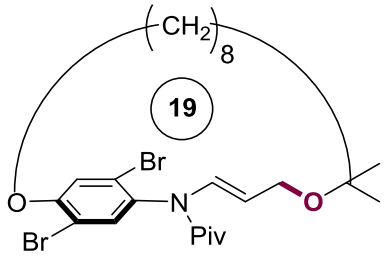
(*R*$_p$,E)-(12,15-dibromo-7,7-dimethyl-6,16-dioxa-2-aza-1(1,4)-benzenacyclohexadecaphan-3-en-2-yl)(phenyl)methanone (**6u**)



The reaction was performed on 0.2 mmol scale under the standard conditions at 20 ℃ for 69 h. Purification by Preparative Thin-Layer Chromatography (petroleum ether/EtOAc=10:1) to afford **6u** as a white solid (50 mg, 43% yield.)

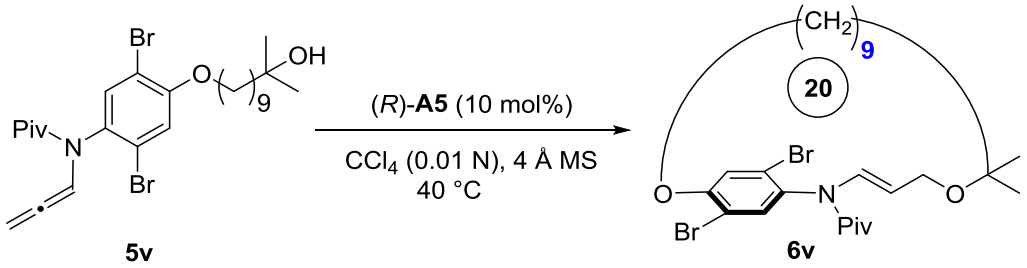
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77-7.33 (m, 5H), 7.26-6.47 (m, 3H), 4.52-4.19 (m, 3H), 4.05-3.64 (m, 2H), 1.89-1.59 (m, 3H), 1.53-1.36 (m, 3H), 1.27 (m, 4H), 1.10-0.98 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 135.7, 134.9, 130.4, 130.0, 129.4, 129.2, 128.2, 127.9, 127.4, 119.2, 113.7, 75.8, 69.9, 60.8, 39.0, 29.9, 29.4, 27.9, 26.8, 26.6, 26.3, 24.6, 24.1. $[\alpha]^{25}_D$ = 6.6 (c = 1.0, CH_2Cl_2). m/z HRMS (ESI) found $[M+H]^+$ 578.0921, $C_{27}H_{34}Br_2NO_3^+$ requires 578.0900. HPLC: Chiralpak IA column, 90:10 hexanes/isopropanol, 1 ml/min; t_R = 9.09 min (major), 14.82 min (minor); 75:25 er.

Study of the configurational stability of the planar-chiral macrocycles



6a

Dissolve 2.0 mg of **6a** (92:8 er) in toluene (2 mL) and then heated the solution to 100 ^{o}C. The er value were then determined to be 92:8 by chiral HPLC analysis after 24 h.

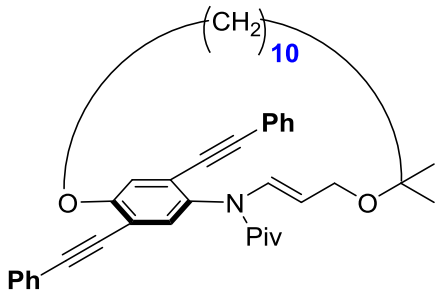


5v **6v**

monitoring the er values at different reaction time

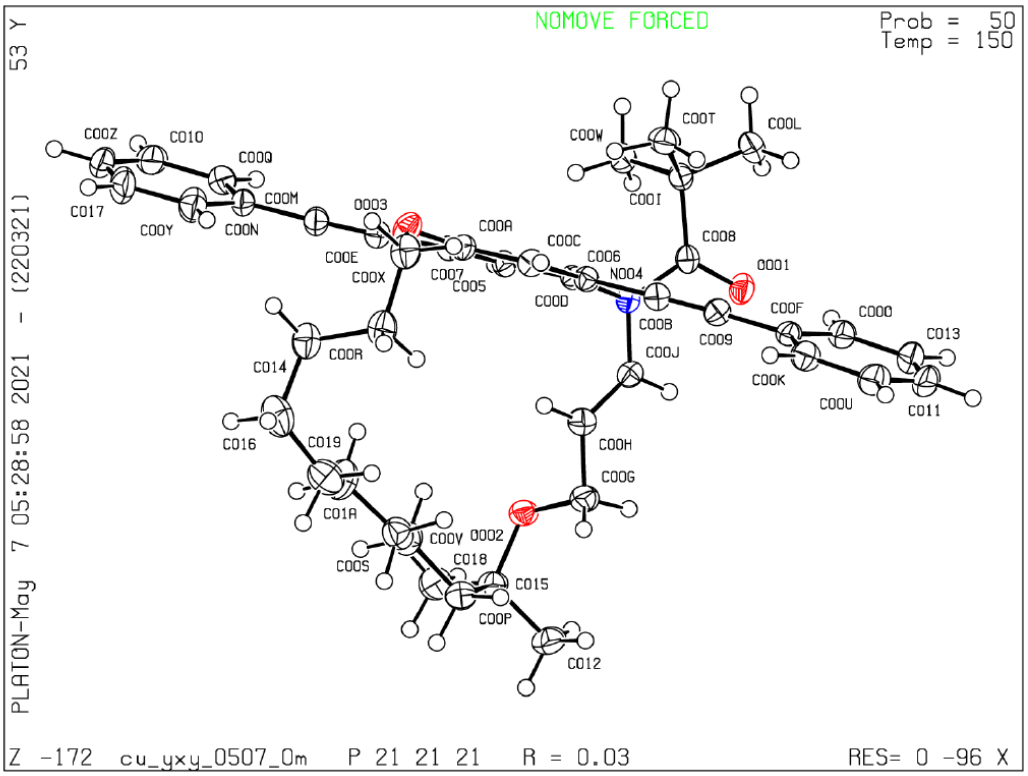
2 h, 80:20 er
3.5 h, 75:25 er
6.5 h, 66:34 er
after purification, 50:50 er

A flask containing a magnetic stir bar was added (*R*)-**A5** (0.005 mmol) and activated 4 Å MS (25 mg) under N_2 atmosphere. Then a solution of **5v** (0.05 mmol, 1.0 equiv.) in dry CCl_4 (2 mL) was added using a syringe. After stirring at 40 ^{o}C for 18 h, the reaction mixture was filtered and concentrated to give a residue, which was purified by Preparative Thin-Layer Chromatography (petroleum ether/EtOAc = 10:1) to afford the product **6v** as a racemic mixture (50:50 er). Interestingly, monitoring the er values of 6v in the reaction mixture suggested the rapid diminishment of the er values overtime (2 h, 80:20 er; 3.5 h, 75:25 er; 6.5 h, 66:34 er).



Dissolve 2.0 mg of **6q** (90:10 er) in toluene (2 mL) and then heated the solution to 80 ^{o}C. The er value were then determined to be 90:10 by chiral HPLC analysis after 48 h. Heating of **6q** at 100 ^{o}C (in toluene) led to the partial decomposition of **6q**.

X-Ray structures



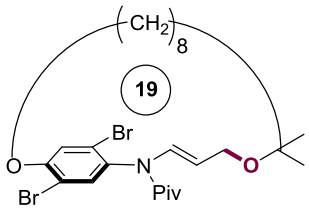
X-ray structure of **6m** (CCDC number 2160358)

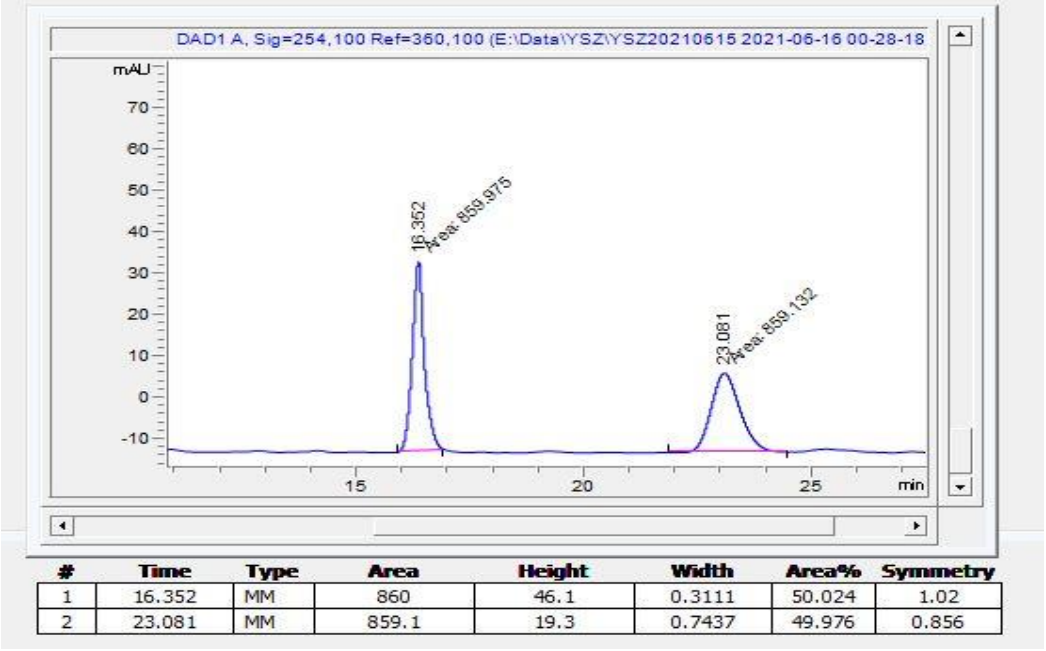
Single crystal data of **6m**

Identification code	
Empirical formula	C42H49NO3
Formula weight	615.82
Temperature/K	150.0
Crystal system	orthorhombic
Space group	P212121
a/Å	10.9530(2)
b/Å	11.3417(2)
c/Å	28.7781(5)
α/°	90
β/°	90
γ/°	90
Volume/Å3	3574.98(11)
Z	4
ρcalcg/cm3	1.144
μ/mm-1	0.547
F(000)	1328.0
Crystal size/mm3	0.25 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.142 to 158.926
Index ranges	-13 ≤ h ≤ 13, -13 ≤ k ≤ 14, -35 ≤ l ≤ 36
Reflections collected	72241
Independent reflections	7699 [Rint = 0.0319, Rsigma = 0.0185]
Data/restraints/parameters	7699/0/420
Goodness-of-fit on F2	1.059
Final R indexes [I>=2σ (I)]	R1 = 0.0283, wR2 = 0.0738
Final R indexes [all data]	R1 = 0.0286, wR2 = 0.0740
Largest diff. peak/hole / e Å-3	0.22/-0.14
Flack parameter	0.03(3)

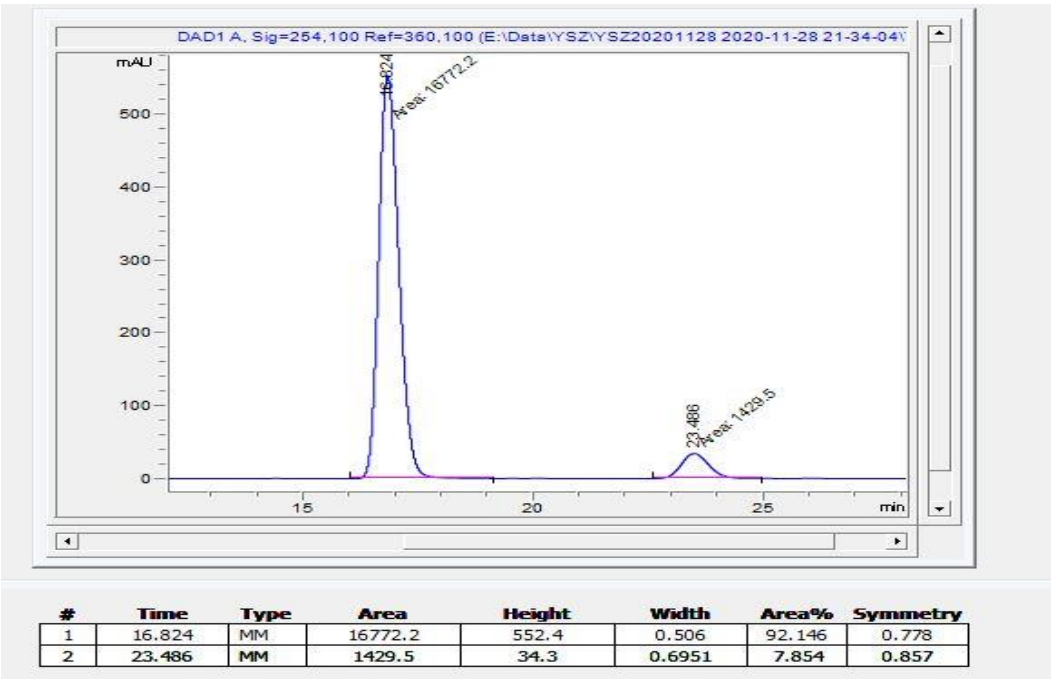
HPLC traces

(R_p,*E*)-1-(1^2,1^5-dibromo-7,7-dimethyl-6,16-dioxa-2-aza-1(1,4)-benzenacyclohexadecap- pan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6a)**



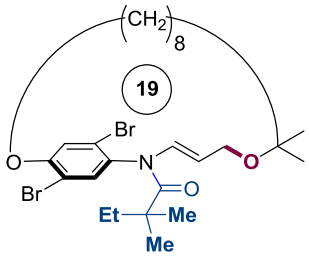


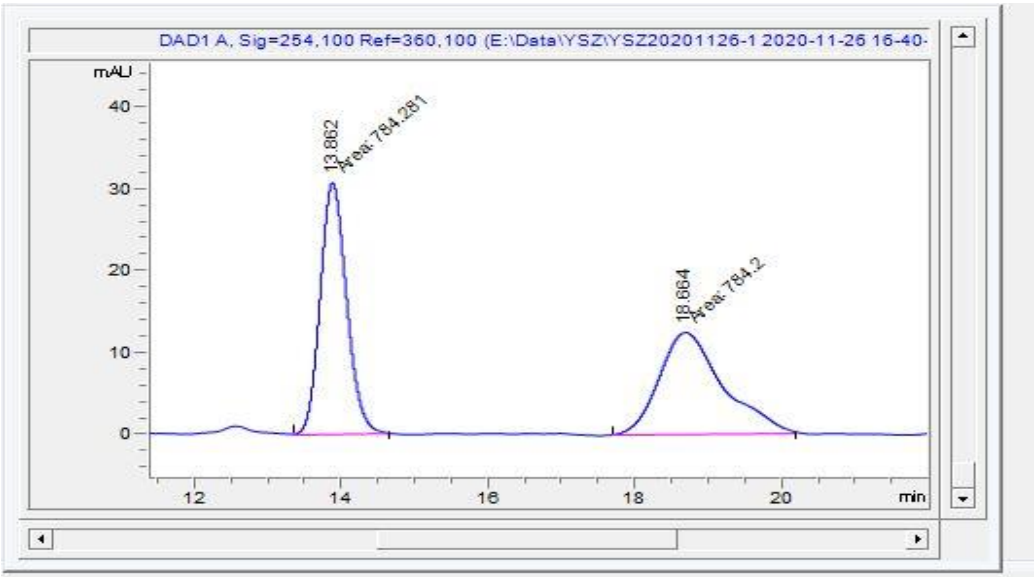
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	16.352	MM	860	46.1	0.3111	50.024	1.02
2	23.081	MM	859.1	19.3	0.7437	49.976	0.856



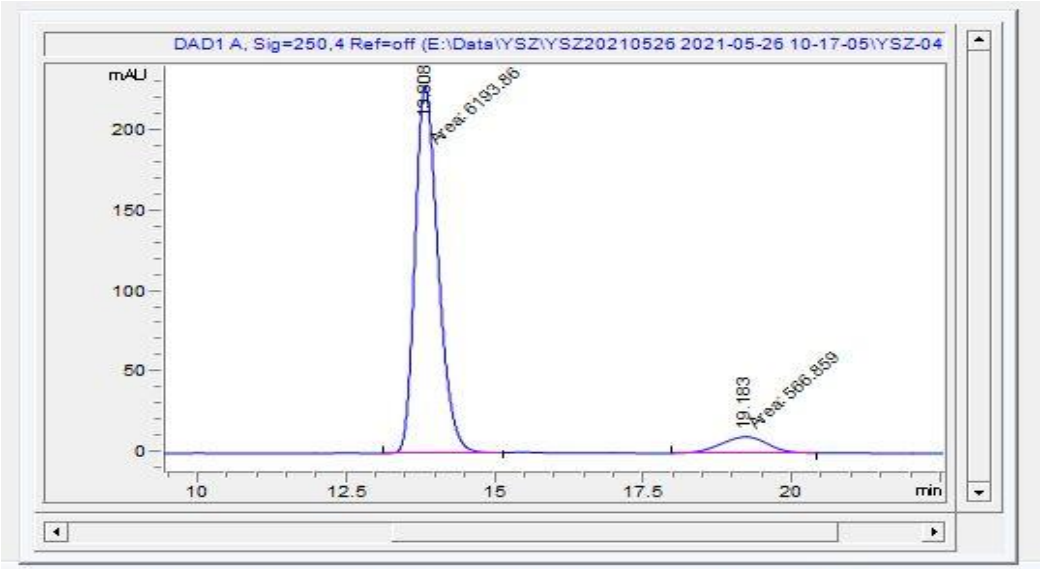
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	16.824	MM	16772.2	552.4	0.506	92.146	0.778
2	23.486	MM	1429.5	34.3	0.6951	7.854	0.857

(R_p,*E*)-(1-(1^2,1^5-dibromo-7,7-dimethyl-6,16-dioxa-2-aza-1(1,4)-benzenacyclohexadec ap- han-3-en-2-yl)-2,2- dimethylbutan-1-one **(6b)**



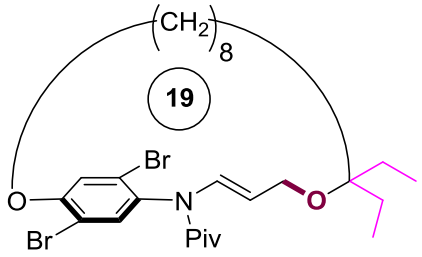


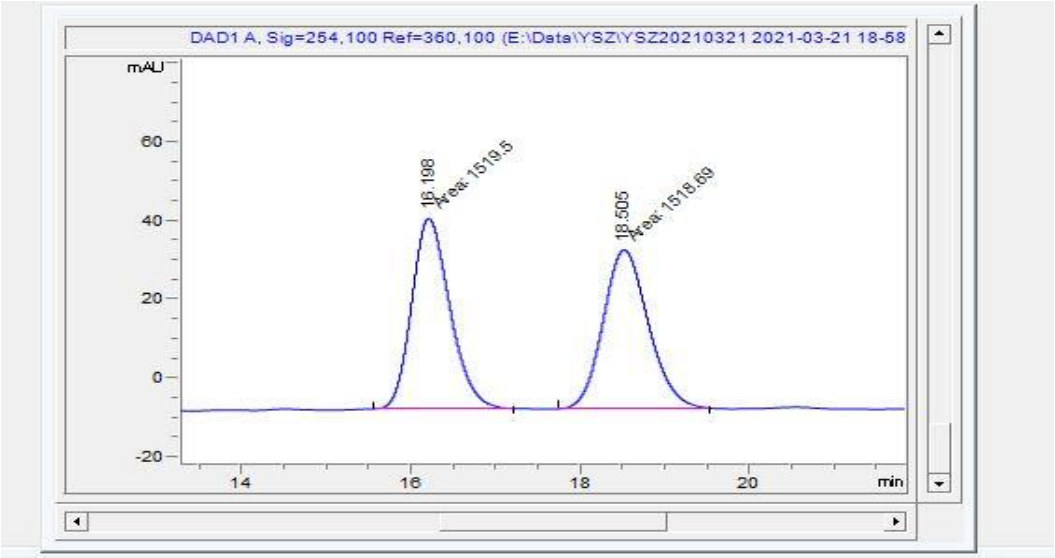
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	13.862	MM	784.3	31.1	0.4202	50.003	0.812
2	18.664	MM	784.2	12.7	1.0281	49.997	0.68



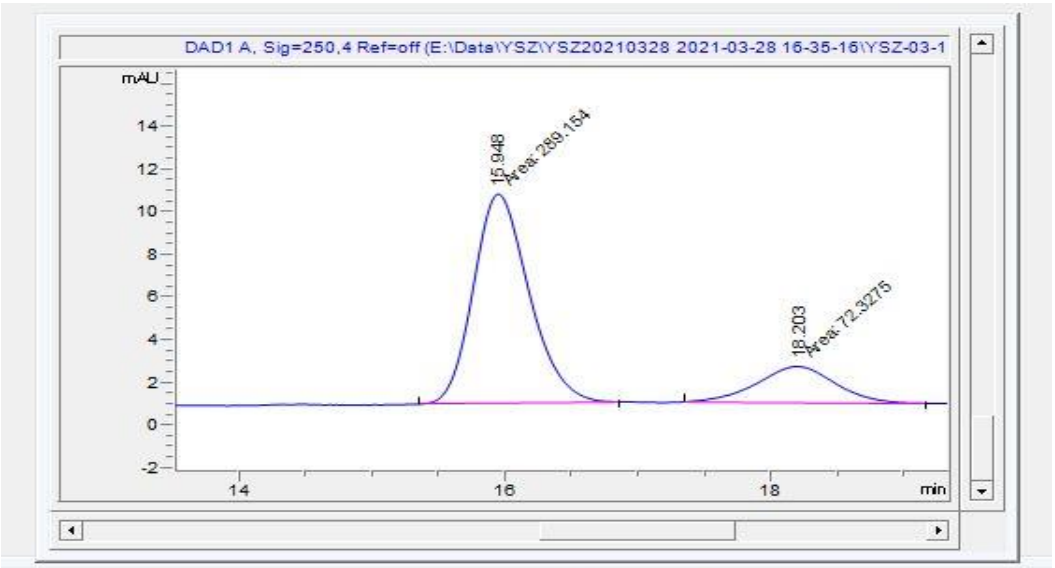
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	13.808	MM	6193.9	229.1	0.4507	91.615	0.733
2	19.183	MM	566.9	10.2	0.9244	8.385	1.088

(R_p,*E*)-1-(1^2,1^5-dibromo-7,7-diethyl-6,15-dioxa-2-aza-1(1,4)-benzenacyclopentadecaph- an-3-en-2-yl)-2,2-dimethylpropan-1-one **(6c)**



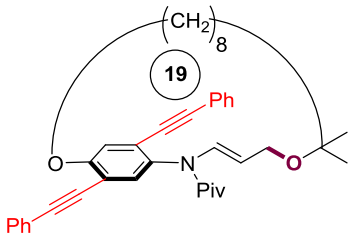


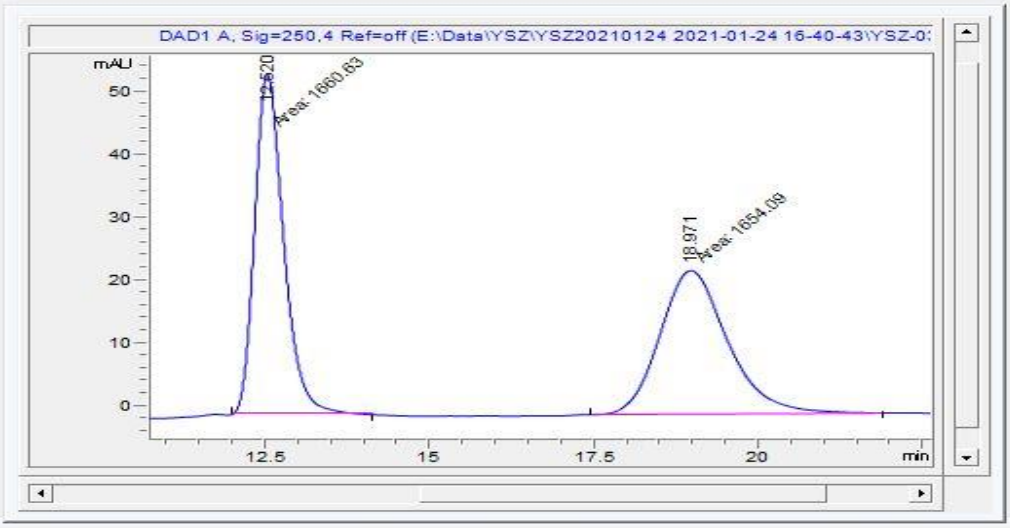
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	16.198	MM	1519.5	48.6	0.5214	50.013	0.782
2	18.505	MM	1518.7	40.7	0.622	49.987	0.853



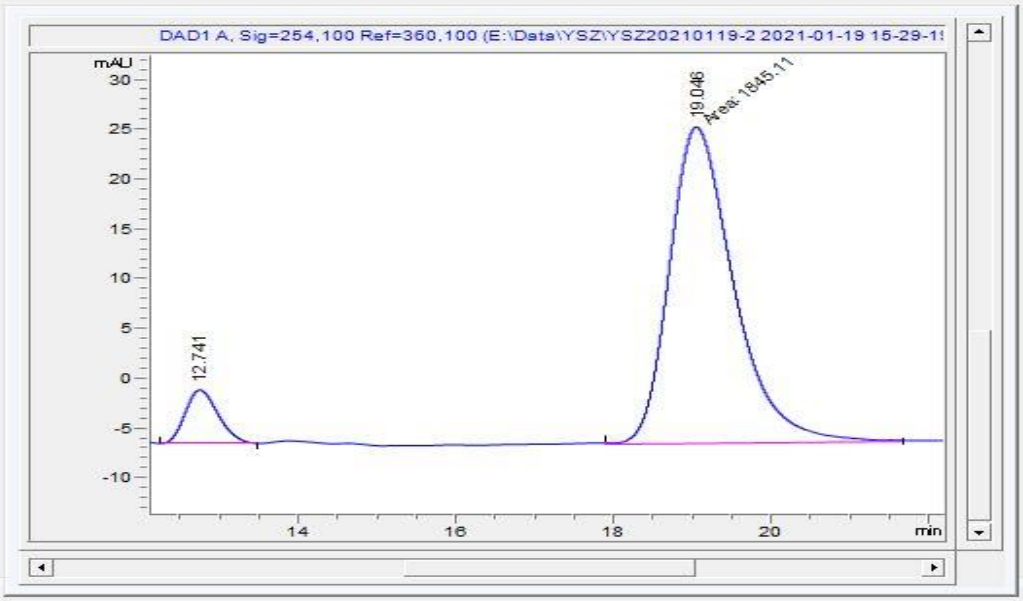
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	15.948	MM	289.2	9.8	0.4905	79.991	0.788
2	18.203	MM	72.3	1.7	0.7008	20.009	1.025

(R_p,*E*)-1-(7,7-dimethyl-1^2,1^5-bis(phenylethynyl)-6,16-dioxa-2-aza-1(1,4)-benzenacyclo- hexadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6d)**



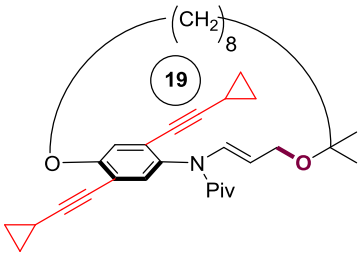


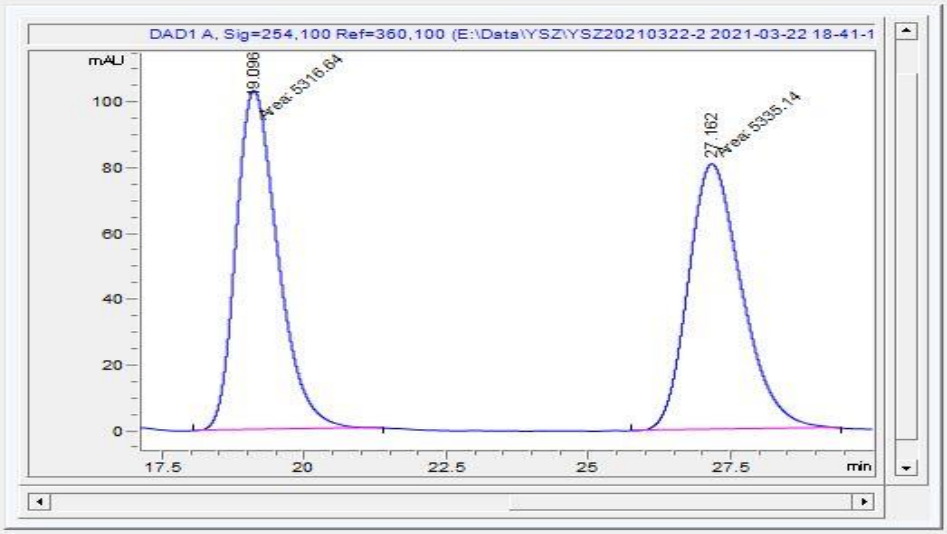
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	12.52	MM	1660.6	54.2	0.5109	50.099	0.736
2	18.971	MM	1654.1	22.9	1.2015	49.901	0.807



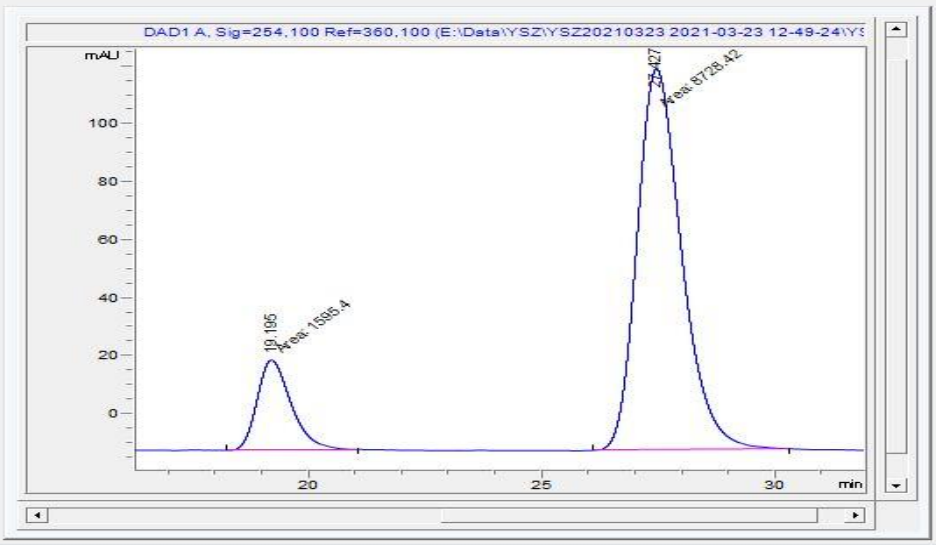
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	12.741	BB	157.7	5.4	0.3439	7.876	0.82
2	19.046	MM	1845.1	32.1	0.9595	92.124	0.686

(R_p,*E*)-1-(1^2,1^5-bis(cyclopropylethynyl)-7,7-dimethyl-6,16-dioxa-2-aza-1(1,4)-benzen ac- yclohexadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6e)**



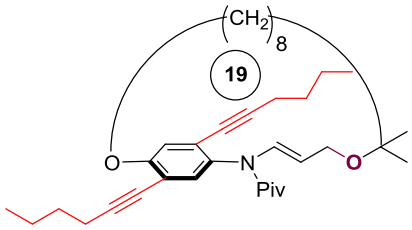


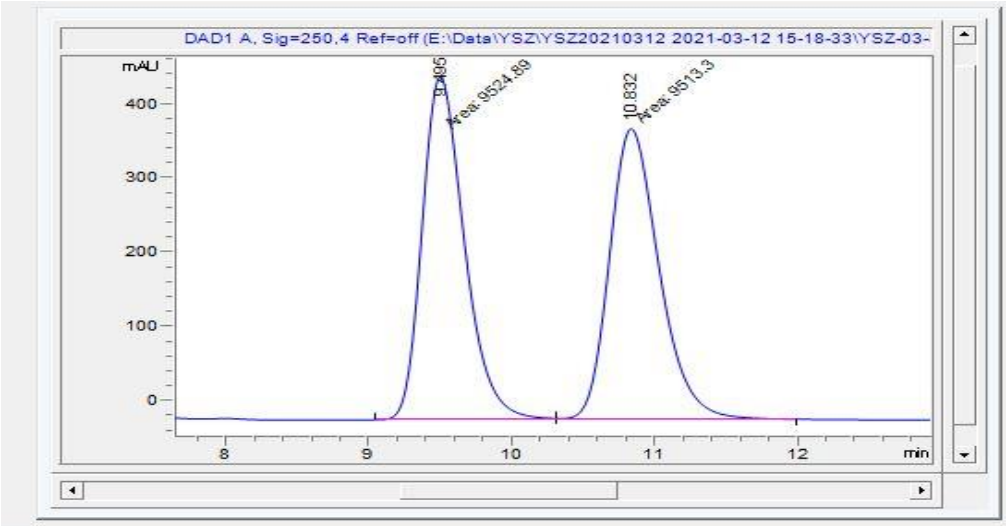
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	19.096	MM	5316.6	103.1	0.8591	49.913	0.711
2	27.162	MM	5335.1	80.9	1.0991	50.087	0.746



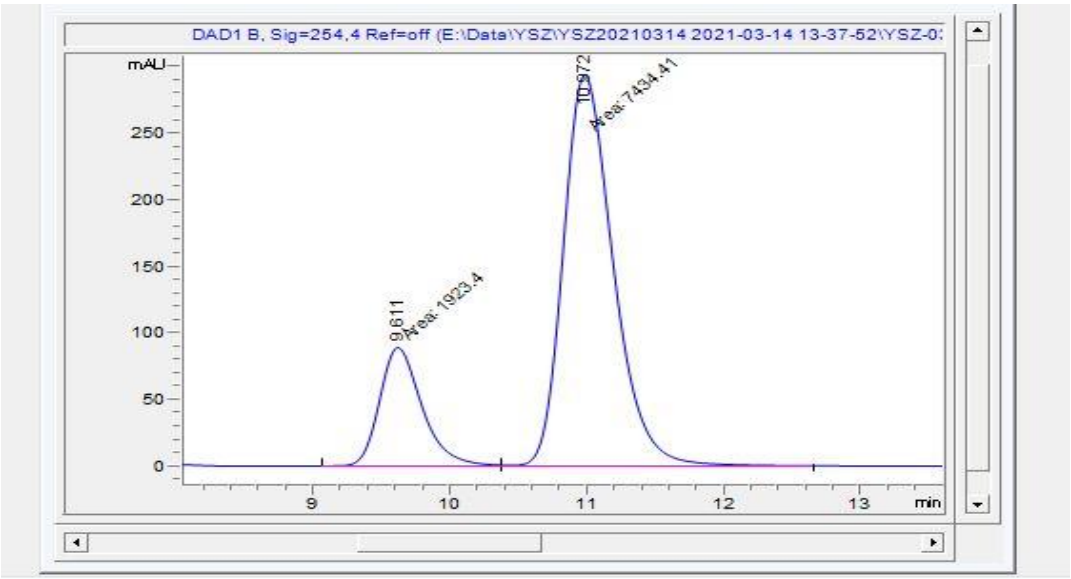
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	19.195	MM	1595.4	31.2	0.8518	15.454	0.713
2	27.427	MM	8728.4	131.7	1.1047	84.546	0.737

(R_p,*E*)-1-(1^2,1^5-di(hex-1-yn-1-yl)-7,7-dimethyl-6,16-dioxa-2-aza-1(1,4)-benzenacyclohexadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6f)**



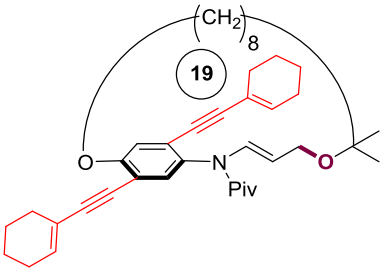


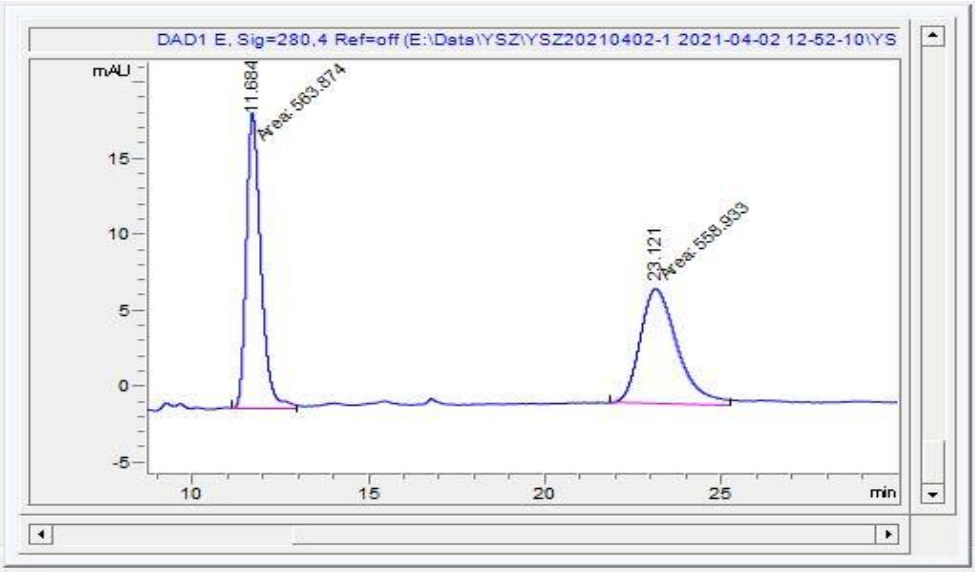
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.495	MF	9524.9	462.9	0.343	50.030	0.726
2	10.832	FM	9513.3	392.6	0.4038	49.970	0.752



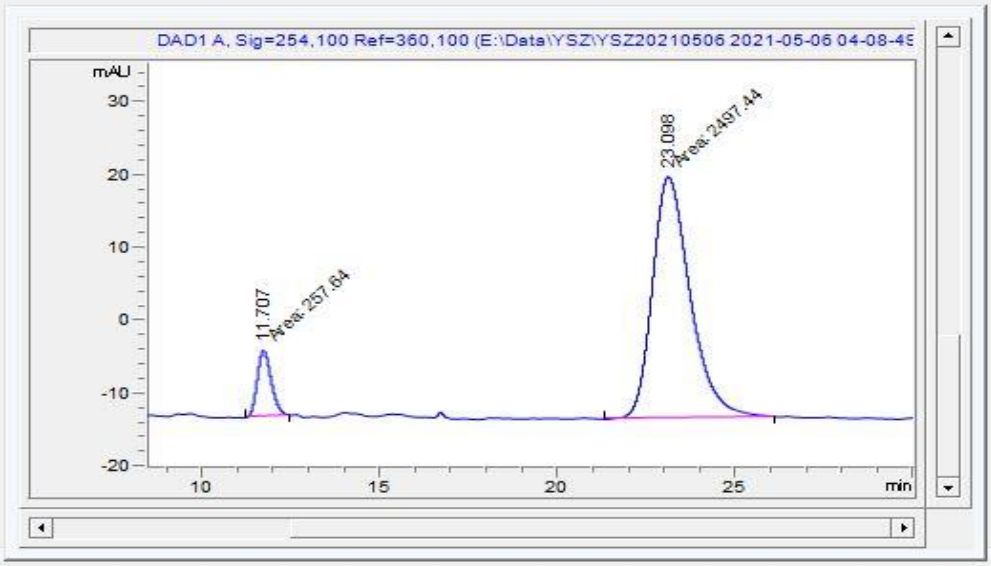
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.611	MF	1923.4	88.9	0.3605	20.554	0.736
2	10.972	FM	7434.4	293.4	0.4223	79.446	0.725

(R_p,*E*)-1-(1^2,1^5-bis(cyclohex-1-en-1-ylethynyl)-7,7-dimethyl-6,16-dioxa-2-aza-1(1,4)-benzenacyclohexadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6g)**



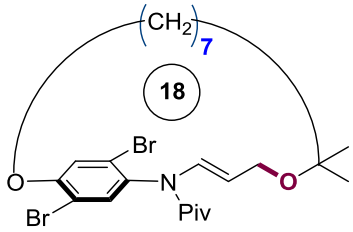


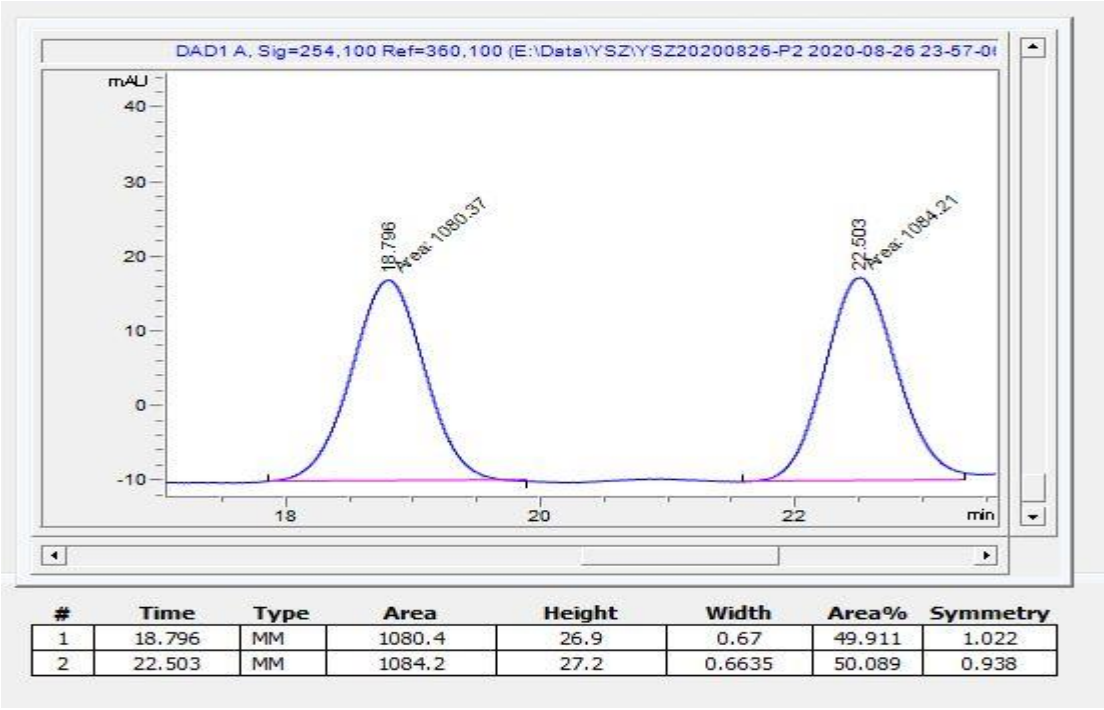
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.684	MM	563.9	19.4	0.4834	50.220	0.697
2	23.121	MM	558.9	7.6	1.2278	49.780	0.699



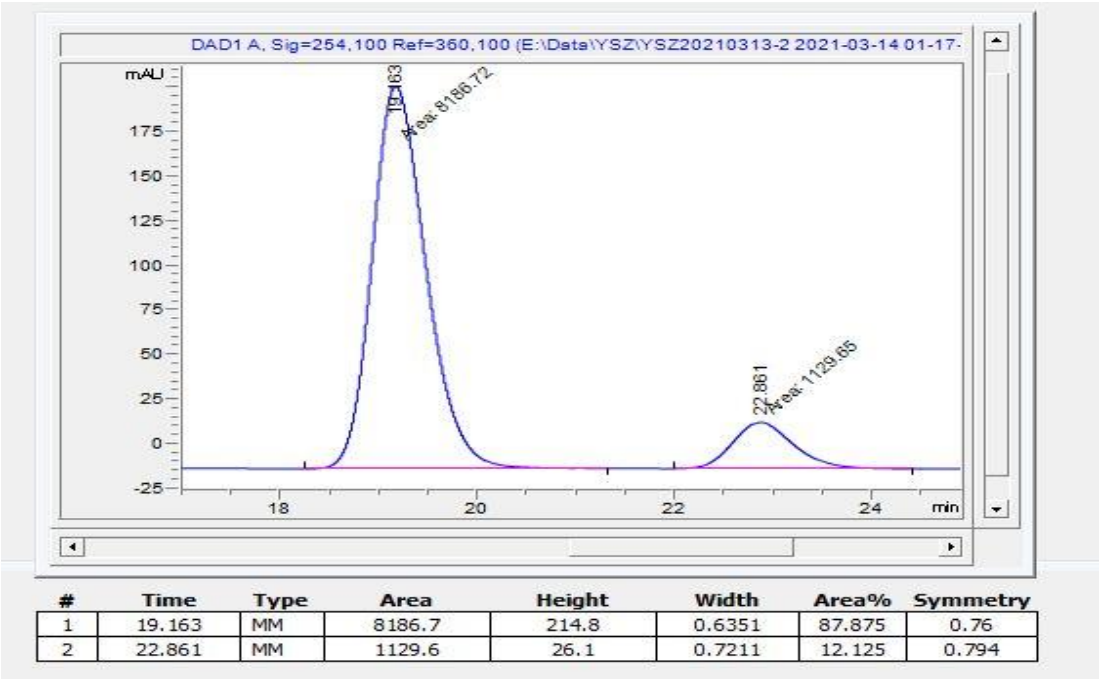
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.707	MM	257.6	9.2	0.4665	9.351	0.783
2	23.098	MM	2497.4	33.4	1.2464	90.649	0.695

(R_p,*E*)-1-(1^2,1^5-dibromo-7,7-dimethyl-6,15-dioxa-2-aza-1(1,4)-benzenacyclopentadecap- han-3-en-2-yl)-2,2-dimethylpropan-1-one **(6h)**



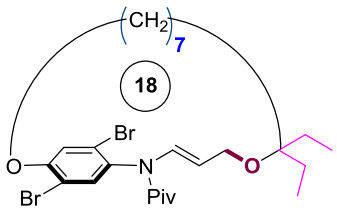


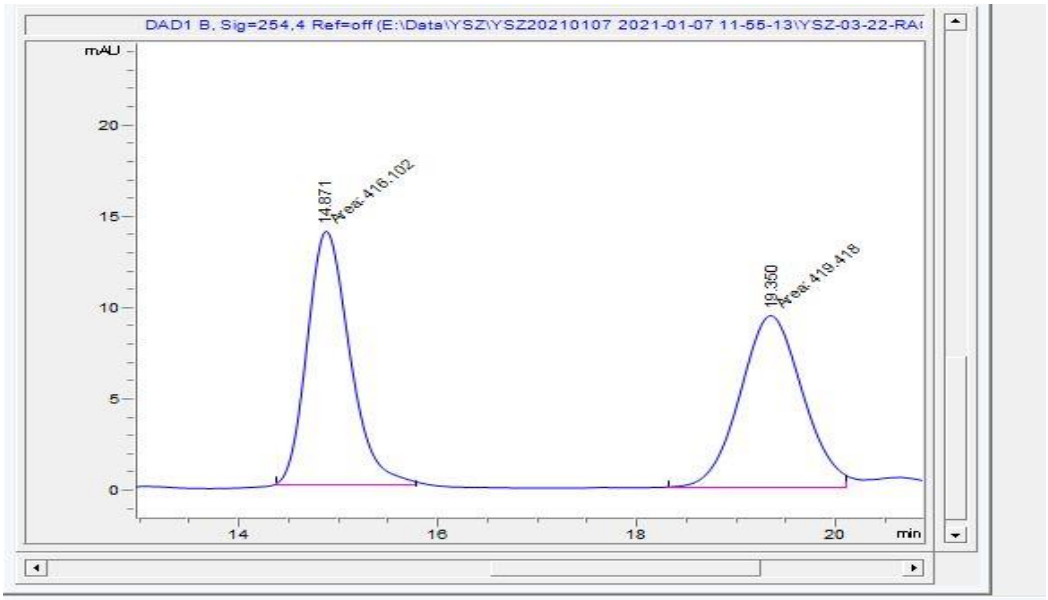
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	18.796	MM	1080.4	26.9	0.67	49.911	1.022
2	22.503	MM	1084.2	27.2	0.6635	50.089	0.938



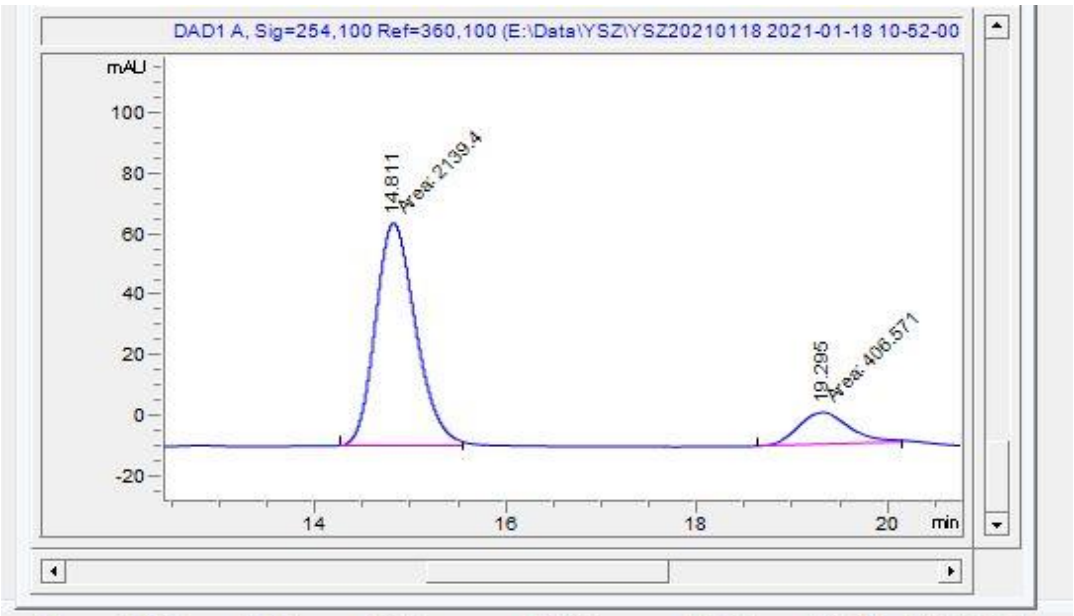
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	19.163	MM	8186.7	214.8	0.6351	87.875	0.76
2	22.861	MM	1129.6	26.1	0.7211	12.125	0.794

(R_p,*E*)-1-(1^2,1^5-dibromo-7,7-diethyl-6,16-dioxa-2-aza-1(1,4)-benzenacyclohexadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6i)**



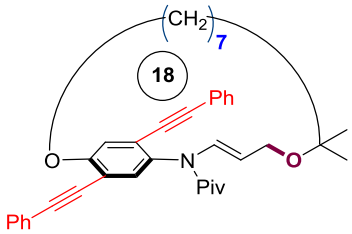


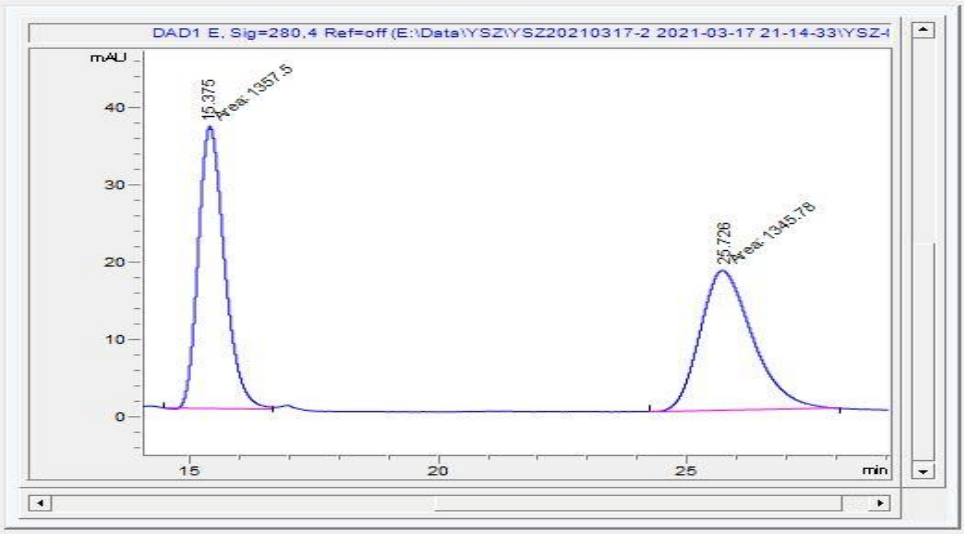
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	14.871	MM	416.1	13.9	0.4974	49.802	0.781
2	19.35	MF	419.4	9.5	0.7369	50.198	0.957



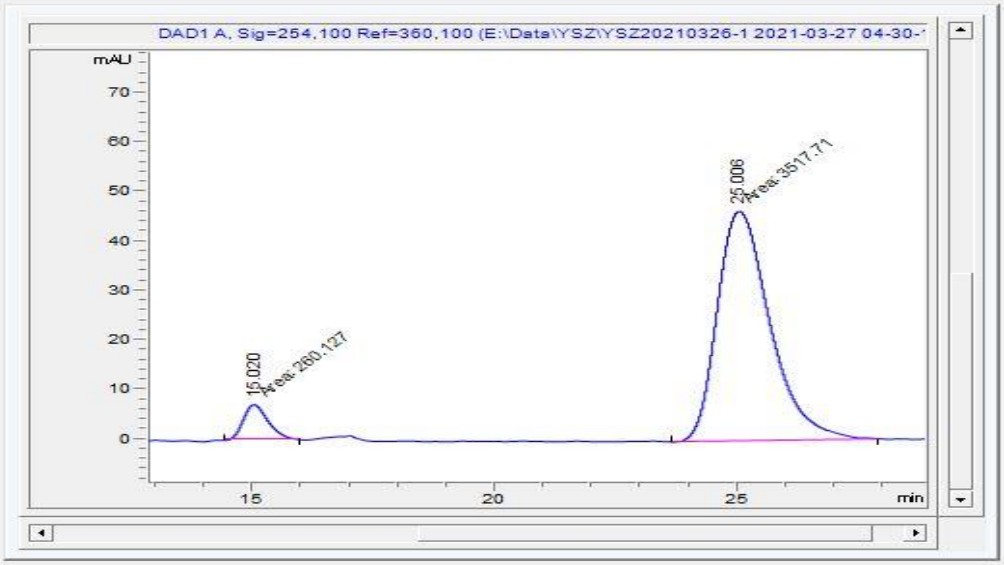
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	14.811	MM	2139.4	73.1	0.4877	84.031	0.797
2	19.295	MM	406.6	10.7	0.633	15.969	0.896

(R_p,*E*)-1-(7,7-dimethyl-1^2,1^5-bis(phenylethynyl)-6,15-dioxa-2-aza-1(1,4)-benzenacycl op- entadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6j)**



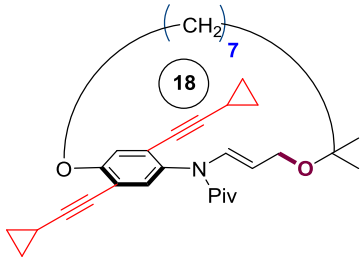


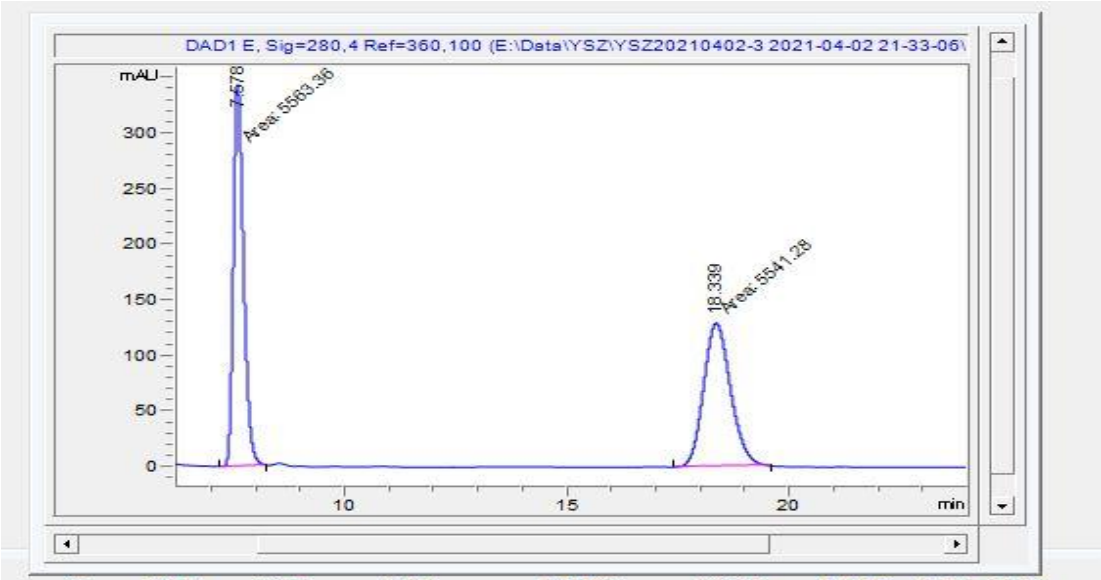
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	15.375	MM	1357.5	36.5	0.6197	50.217	0.747
2	25.726	MM	1345.8	18.1	1.2398	49.783	0.721



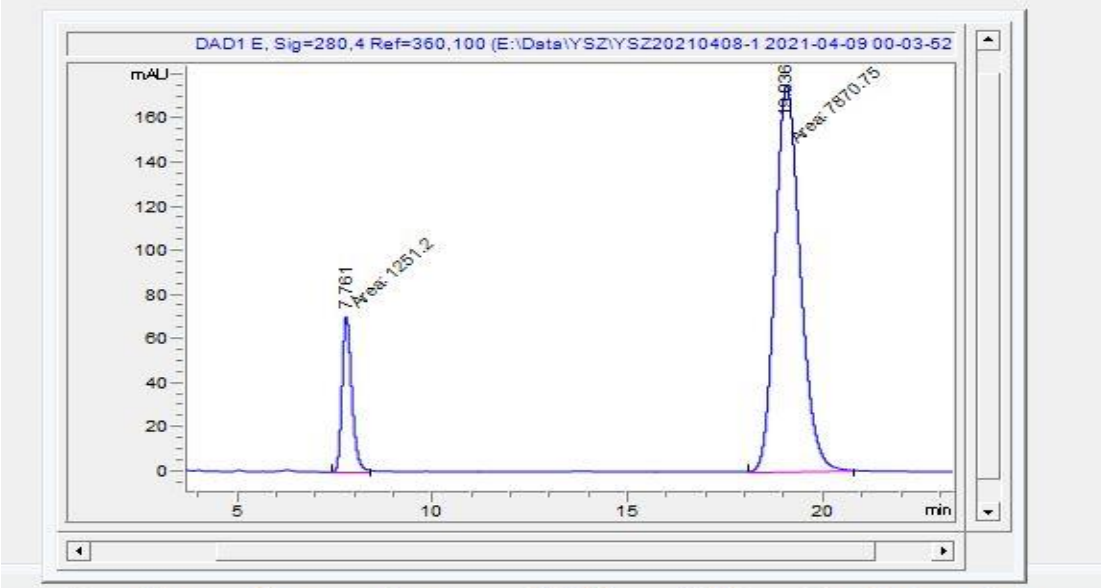
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	15.02	MM	260.1	7.2	0.6018	6.886	0.718
2	25.006	MM	3517.7	46.6	1.2584	93.114	0.681

(R_p,*E*)-1-(1^2,1^5-bis(cyclopropylethynyl)-7,7-dimethyl-6,15-dioxa-2-aza-1(1,4)-benzen ac- cyclopentadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6k)**



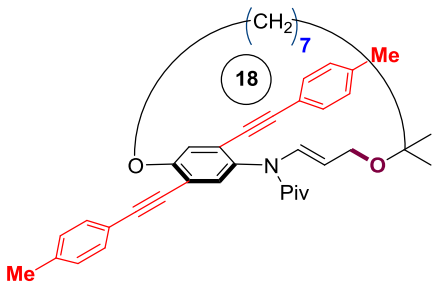


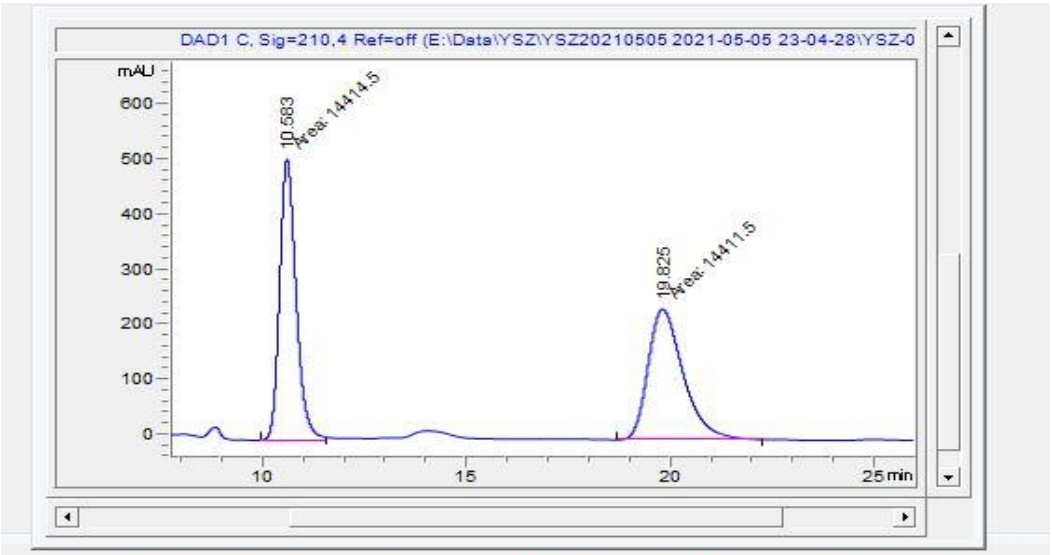
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.578	MM	5563.4	344.3	0.2693	50.099	0.72
2	18.339	MM	5541.3	129.8	0.7113	49.901	0.823



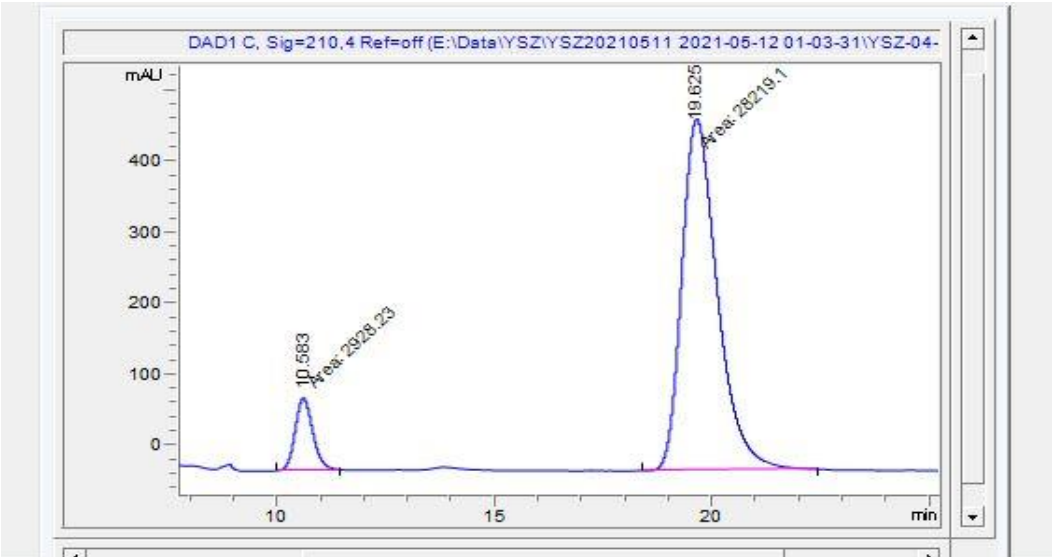
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.761	MM	1251.2	71	0.2939	13.716	0.729
2	19.036	MM	7870.8	175.6	0.747	86.284	0.82

(R_p,*E*)-1-(7,7-dimethyl-1^2,1^5-bis(p-tolylethynyl)-6,15-dioxa-2-aza-1(1,4)-benzenacyclop-entadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6l)**



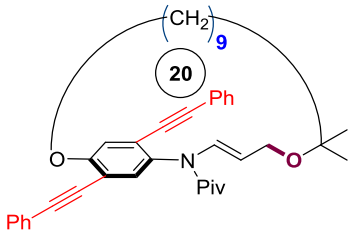


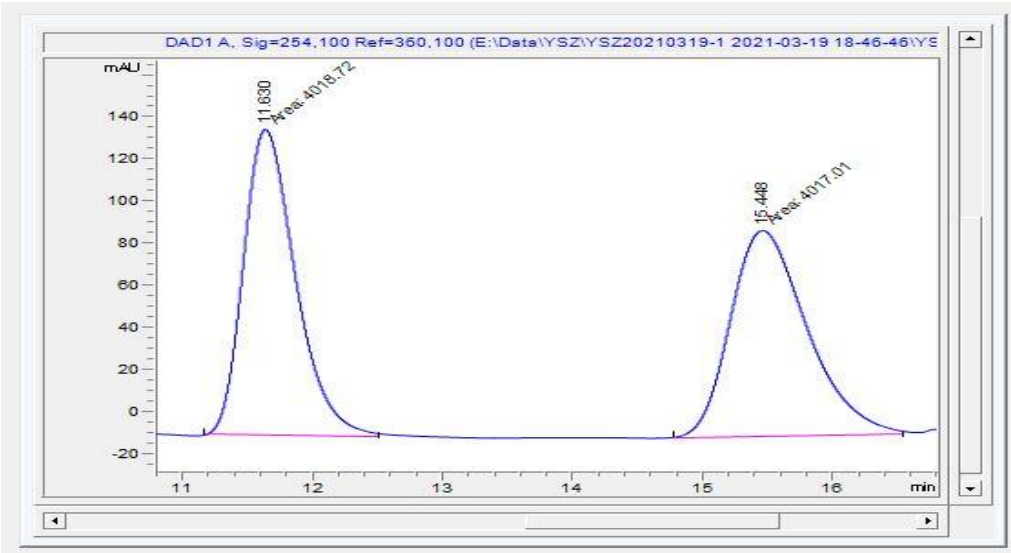
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.583	MM	14414.5	514.8	0.4667	50.005	0.768
2	19.825	MM	14411.5	239.3	1.0038	49.995	0.689



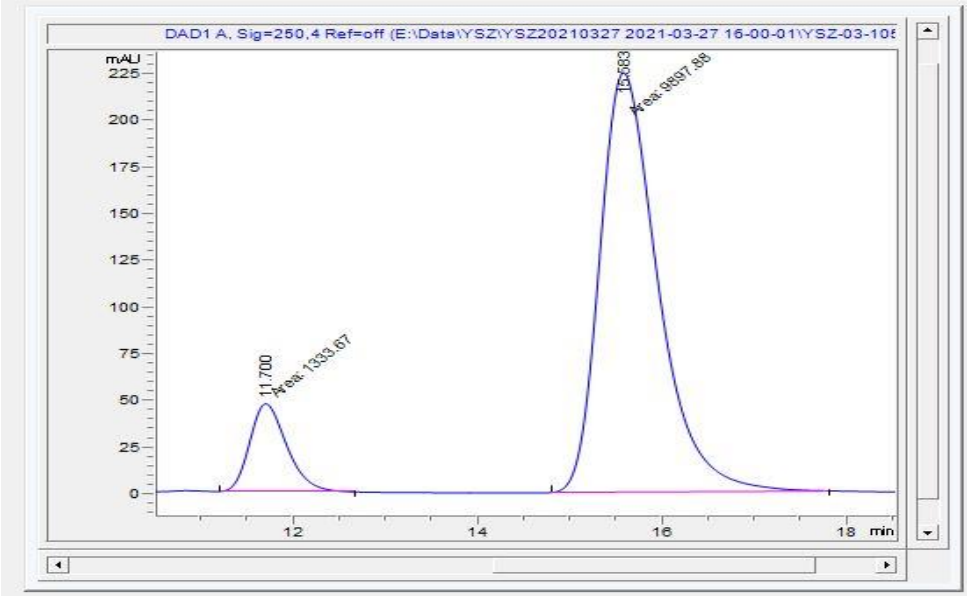
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.583	MM	2928.2	102.4	0.4766	9.401	0.843
2	19.625	MM	28219.1	494.4	0.9514	90.599	0.674

(R_p,*E*)-1-(7,7-dimethyl-1^2,1^5-bis(phenylethynyl)-6,17-dioxa-2-aza-1(1,4)-benzenacycl oh- eptadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6m)**



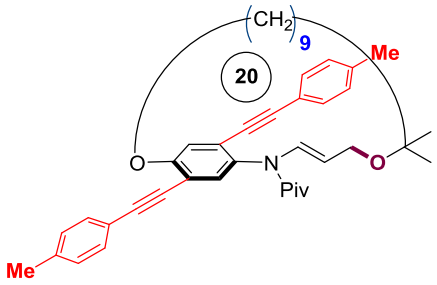


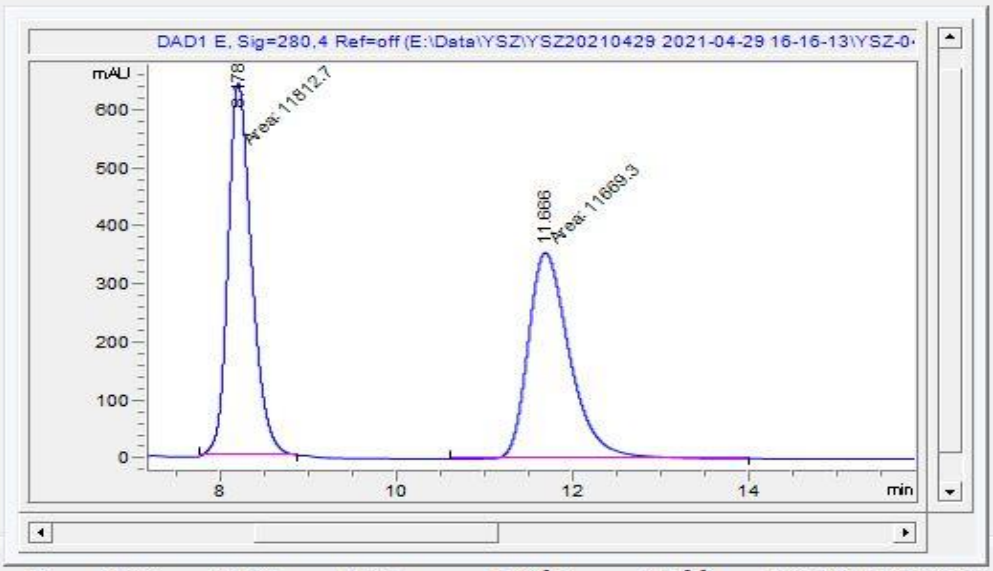
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.63	MM	4018.7	144.8	0.4626	50.011	0.694
2	15.448	MM	4017	97.8	0.6842	49.989	0.697



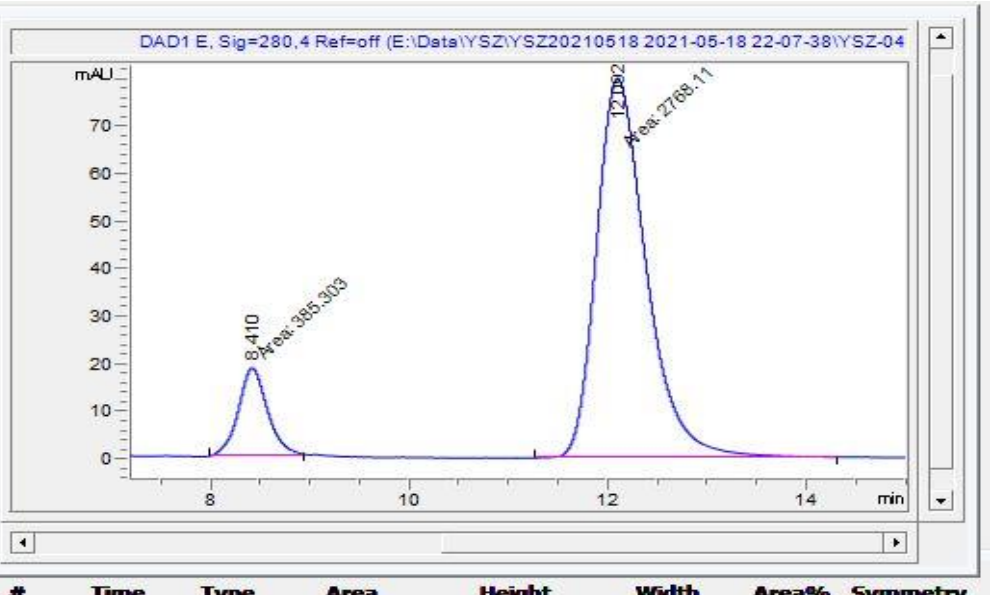
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.7	MM	1333.7	47.2	0.4711	11.874	0.742
2	15.583	MM	9897.9	224.6	0.7345	88.126	0.666

(R_p,*E*)-1-(7,7-dimethyl-1^2,1^5-bis(p-tolylethynyl)-6,17-dioxa-2-aza-1(1,4)-benzenacycl oh- eptadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6n)**



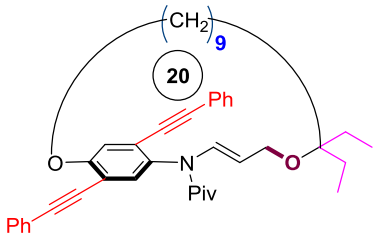


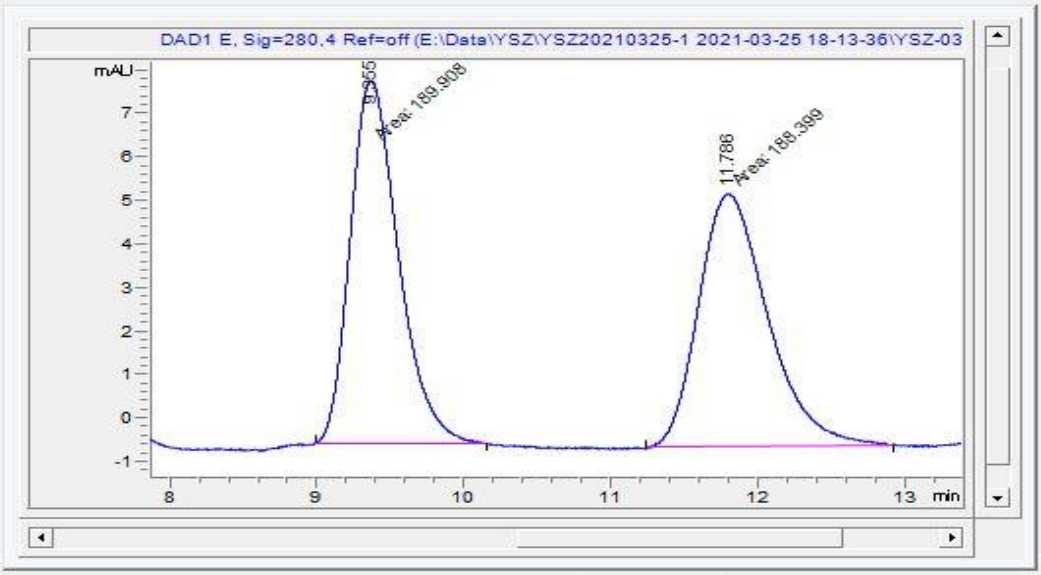
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.178	MM	11812.7	638.8	0.3082	50.305	0.74
2	11.666	MM	11669.3	354.6	0.5485	49.695	0.669



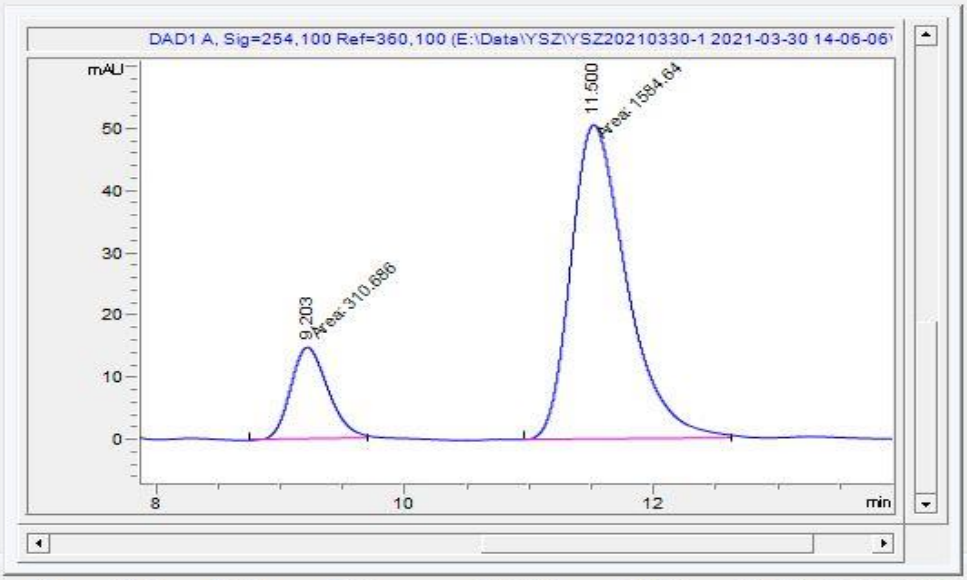
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.41	MM	385.3	18.5	0.3465	12.219	0.873
2	12.092	MM	2768.1	79.3	0.5818	87.781	0.714

(R_p,*E*)-1-(7,7-diethyl-1^2,1^5-bis(phenylethynyl)-6,17-dioxa-2-aza-1(1,4)-benzenacyclo he- ptadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6o)**



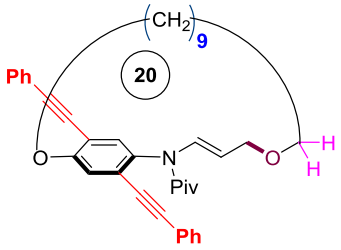


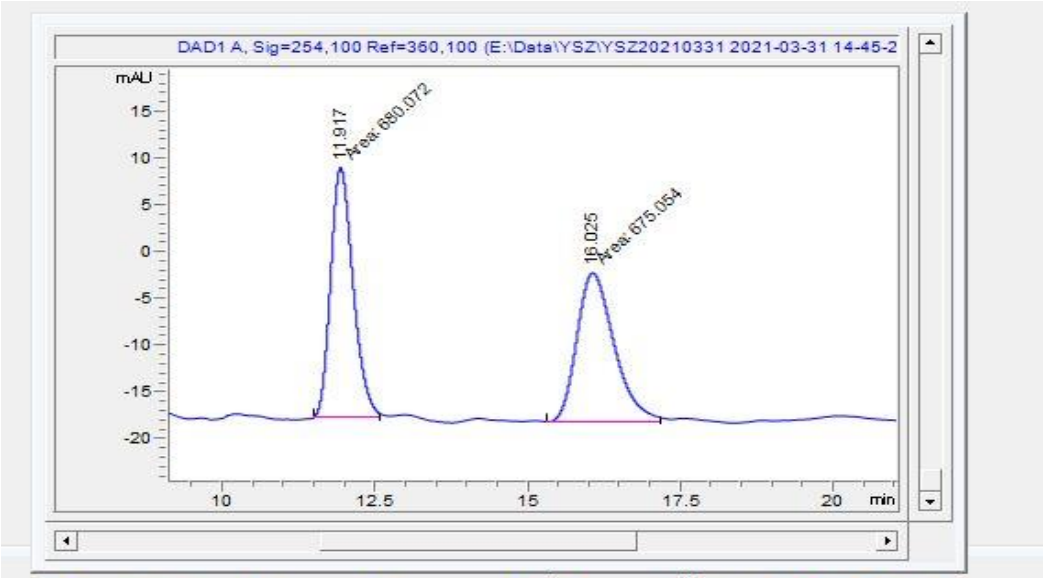
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.355	MM	189.9	8.3	0.3795	50.199	0.703
2	11.786	MM	188.4	5.8	0.5416	49.801	0.739



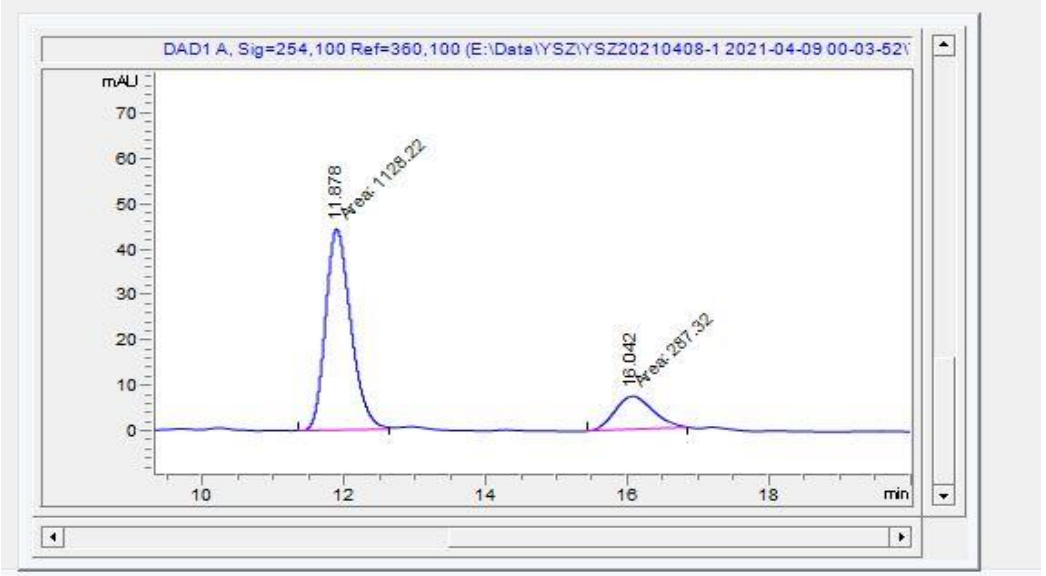
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.203	MM	310.7	14.8	0.3494	16.392	0.779
2	11.5	MM	1584.6	50.7	0.5205	83.608	0.667

(S_p,*E*)-1-(1^2,1^5-bis(phenylethynyl)-6,17-dioxa-2-aza-1(1,4)-benzenacycloheptadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6p)**



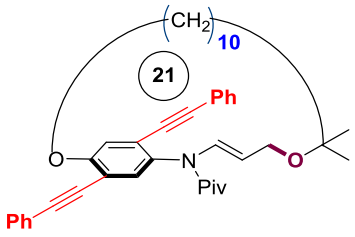


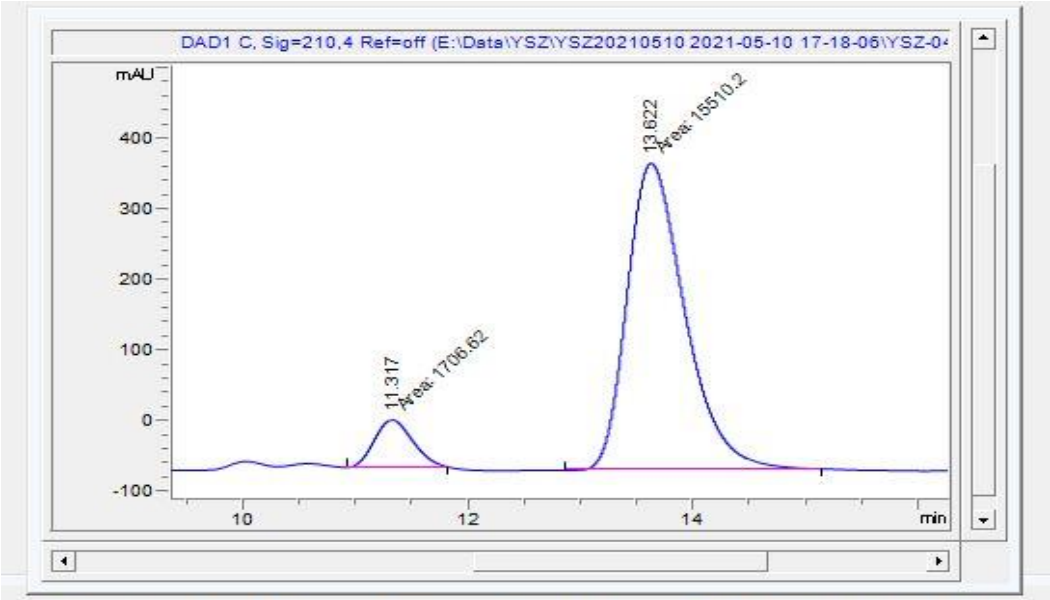
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.917	MM	680.1	26.7	0.4252	50.185	0.738
2	16.025	MM	675.1	15.9	0.7077	49.815	0.677



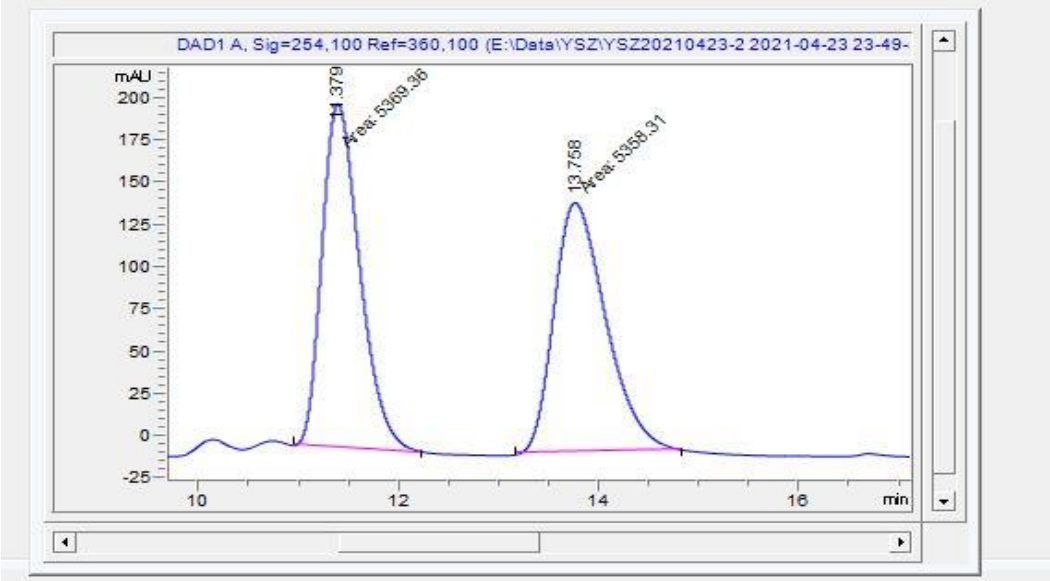
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.878	MM	1128.2	44.6	0.4218	79.702	0.763
2	16.042	MM	287.3	7.5	0.6414	20.298	0.802

(R_p,*E*)-1-(7,7-dimethyl-12,15-bis(phenylethynyl)-6,18-dioxa-2-aza-1(1,4)-benzenacyclo- octadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6q)**



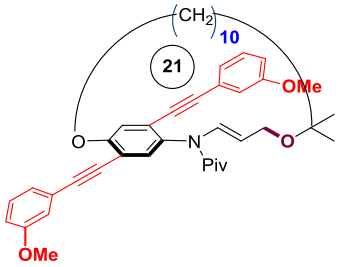


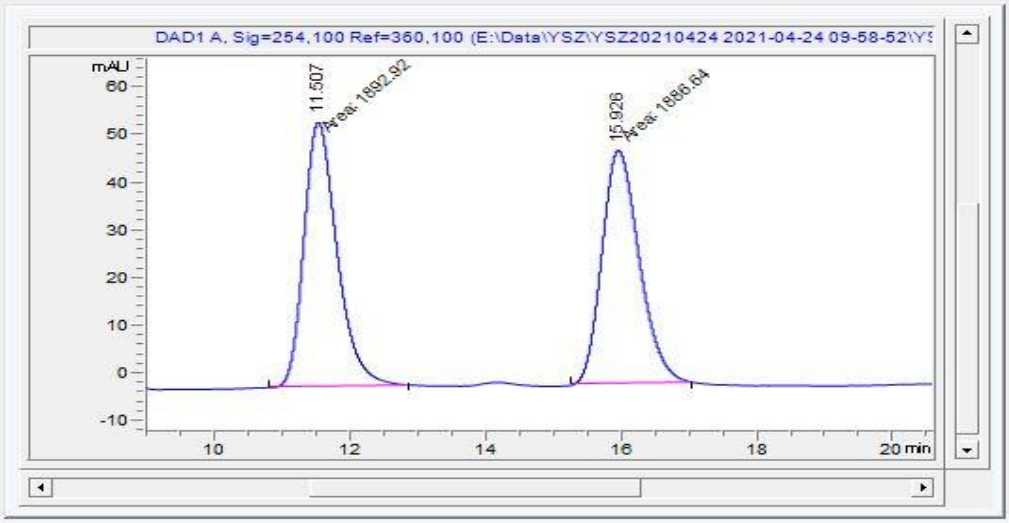
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.317	MM	1706.6	69.4	0.41	9.913	0.83
2	13.622	MM	15510.2	434.5	0.595	90.087	0.693



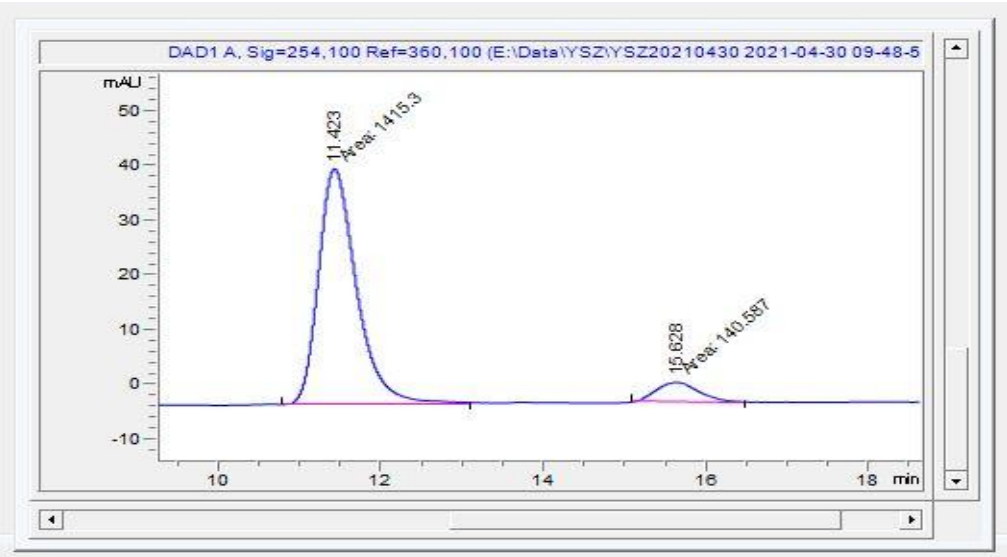
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.379	MM	5369.4	204.1	0.4385	50.051	0.667
2	13.758	MM	5358.3	148.3	0.6023	49.949	0.654

(R_p,*E*)-1-(1^2,1^5-bis((3-methoxyphenyl)ethynyl)-7,7-dimethyl-6,18-dioxa-2-aza-1(1,4)-benzenacyclooctadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6r)**



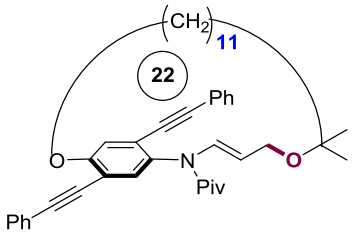


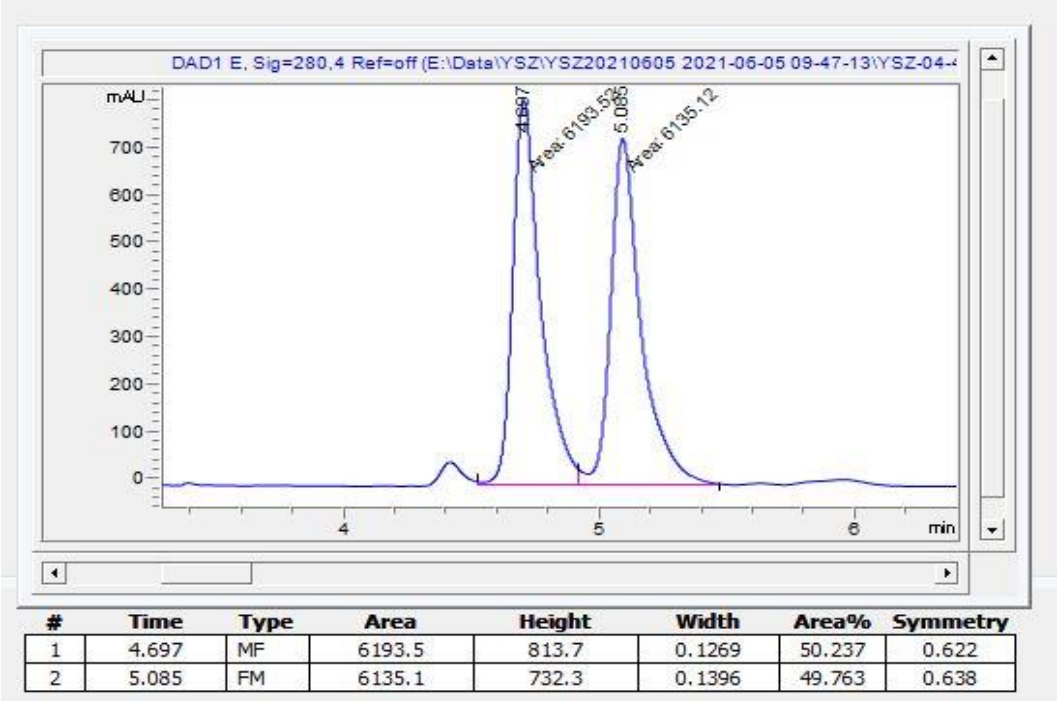
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.507	MM	1892.9	55.7	0.5661	50.083	0.723
2	15.926	MM	1886.6	49.2	0.6395	49.917	0.787



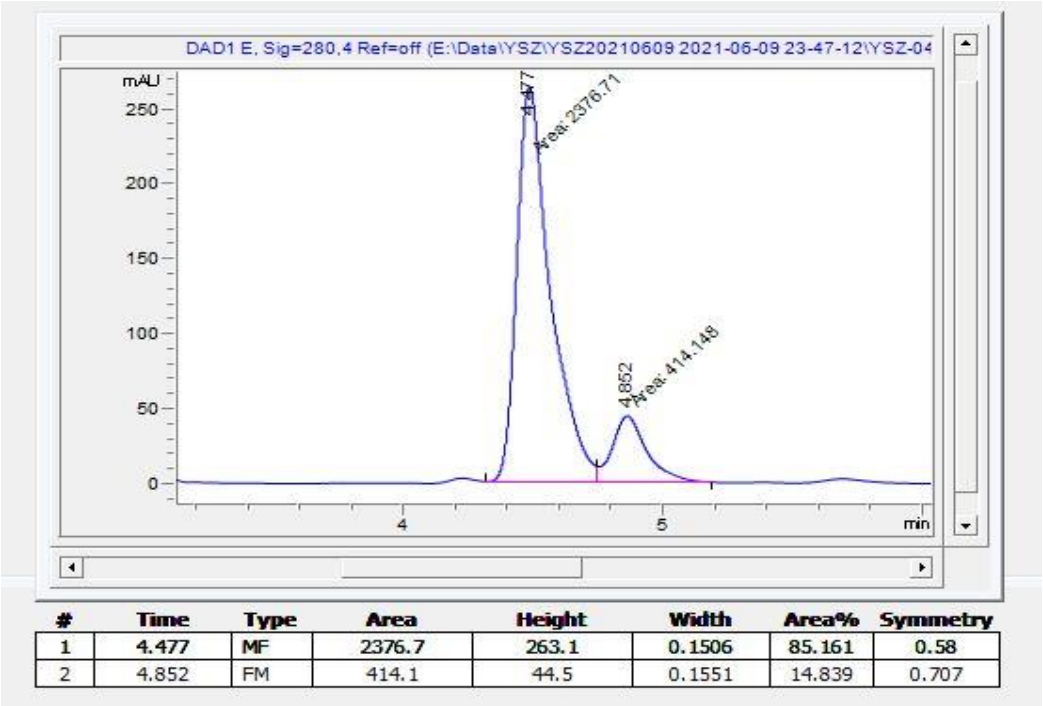
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.423	MM	1415.3	43	0.5484	90.964	0.662
2	15.628	MM	140.6	3.7	0.6339	9.036	0.782

(R_p,*E*)-1-(7,7-dimethyl-1^2,1^5-bis(phenylethynyl)-6,19-dioxa-2-aza-1(1,4)-benzenacyclo- nonadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6s)**



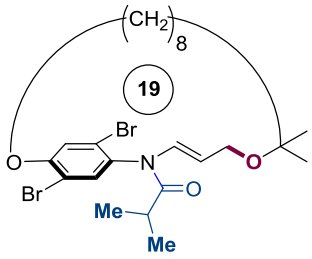


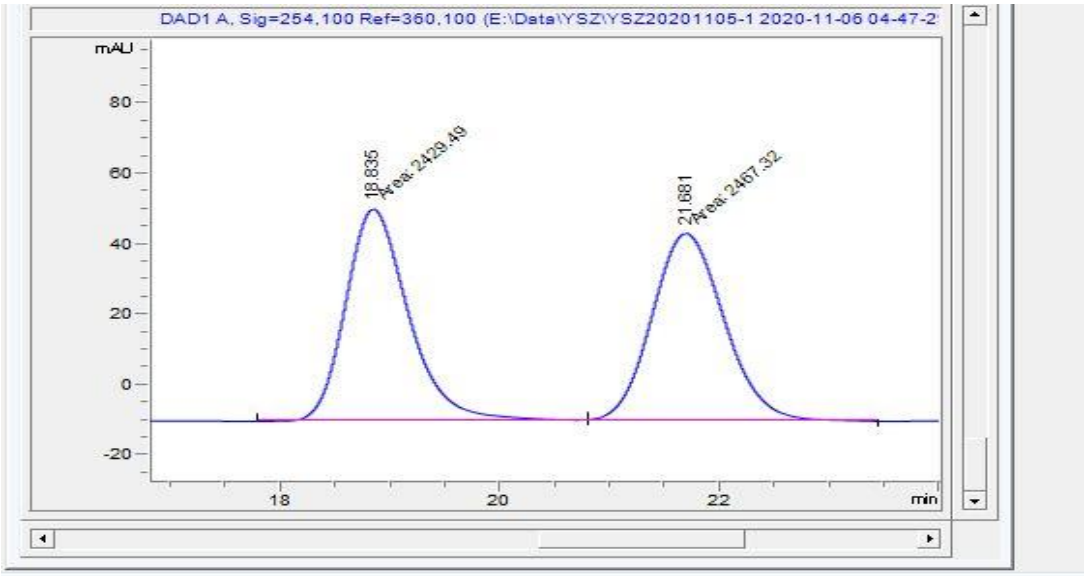
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.697	MF	6193.5	813.7	0.1269	50.237	0.622
2	5.085	FM	6135.1	732.3	0.1396	49.763	0.638



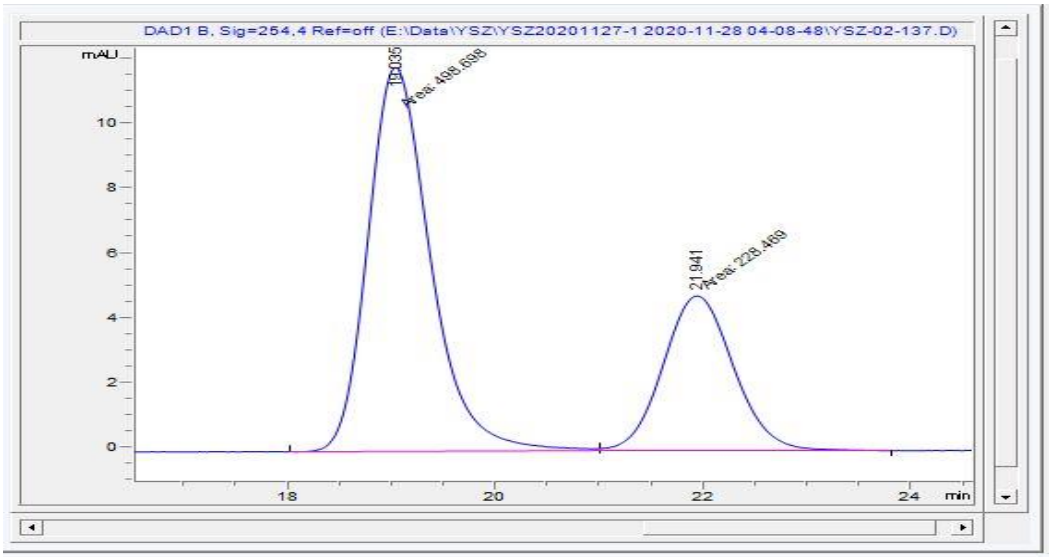
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.477	MF	2376.7	263.1	0.1506	85.161	0.58
2	4.852	FM	414.1	44.5	0.1551	14.839	0.707

(R_p,E)-1-(1^2,1^5-dibromo-7,7-dimethyl-6,16-dioxa-2-aza-1(1,4)-benzenacyclohexadecaphan-3-en-2-yl)-2-methylpropan-1-one **(6t)**



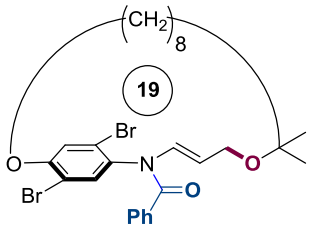


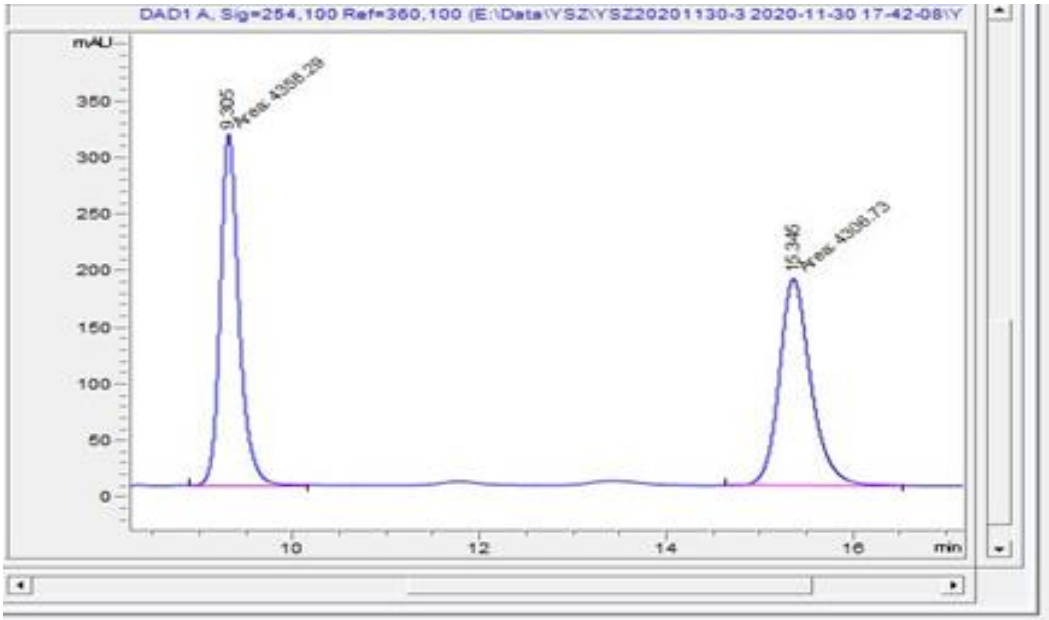
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	18.835	MF	2429.5	60.5	0.6695	49.614	0
2	21.681	FM	2467.3	53.6	0.7671	50.386	0.869



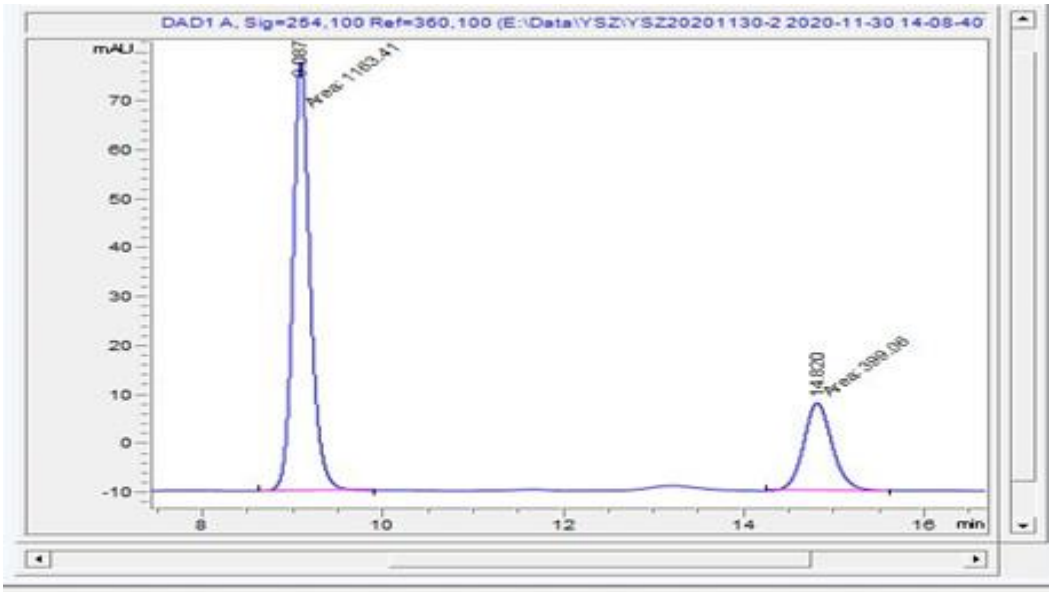
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	19.035	MF	498.7	11.9	0.7011	68.581	0
2	21.941	FM	228.5	4.8	0.7942	31.419	0.906

(R_p,E)-(12,15-dibromo-7,7-dimethyl-6,16-dioxa-2-aza-1(1,4)-benzenacyclohexadecaphan-3-en-2-yl)(phenyl)methanone (**6u**)





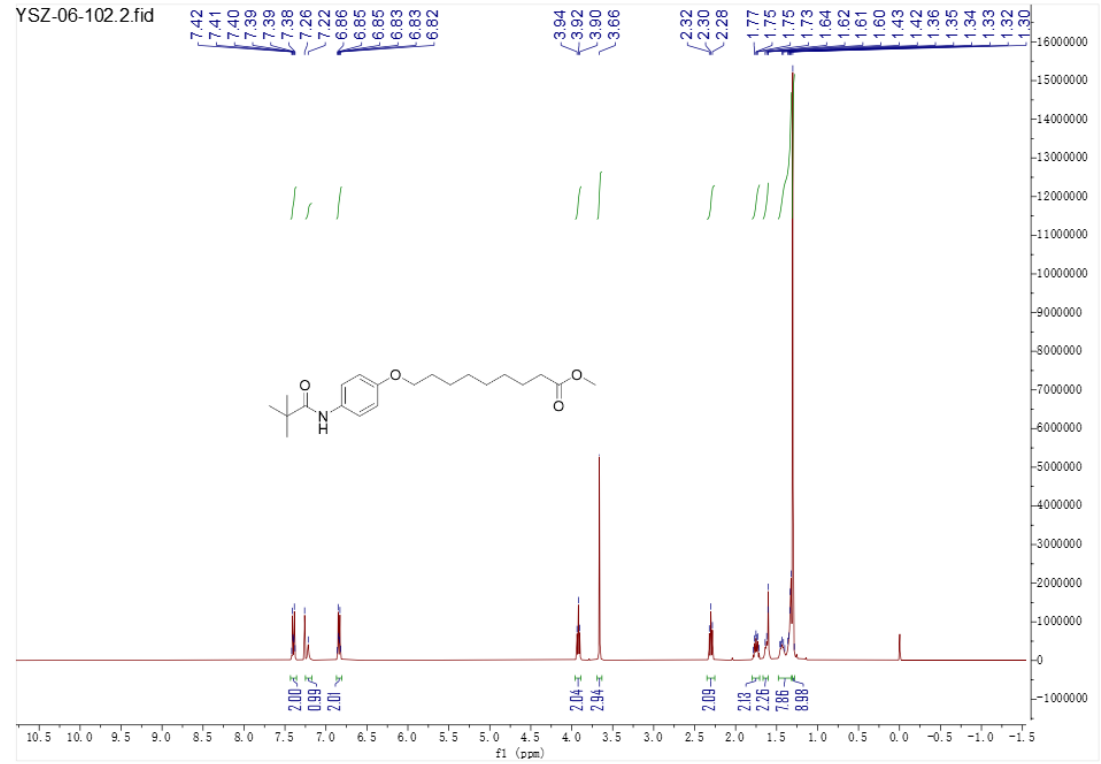
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.305	MM	4358.3	309.4	0.2348	50.298	0.775
2	15.345	MM	4306.7	182.1	0.3942	49.702	0.783

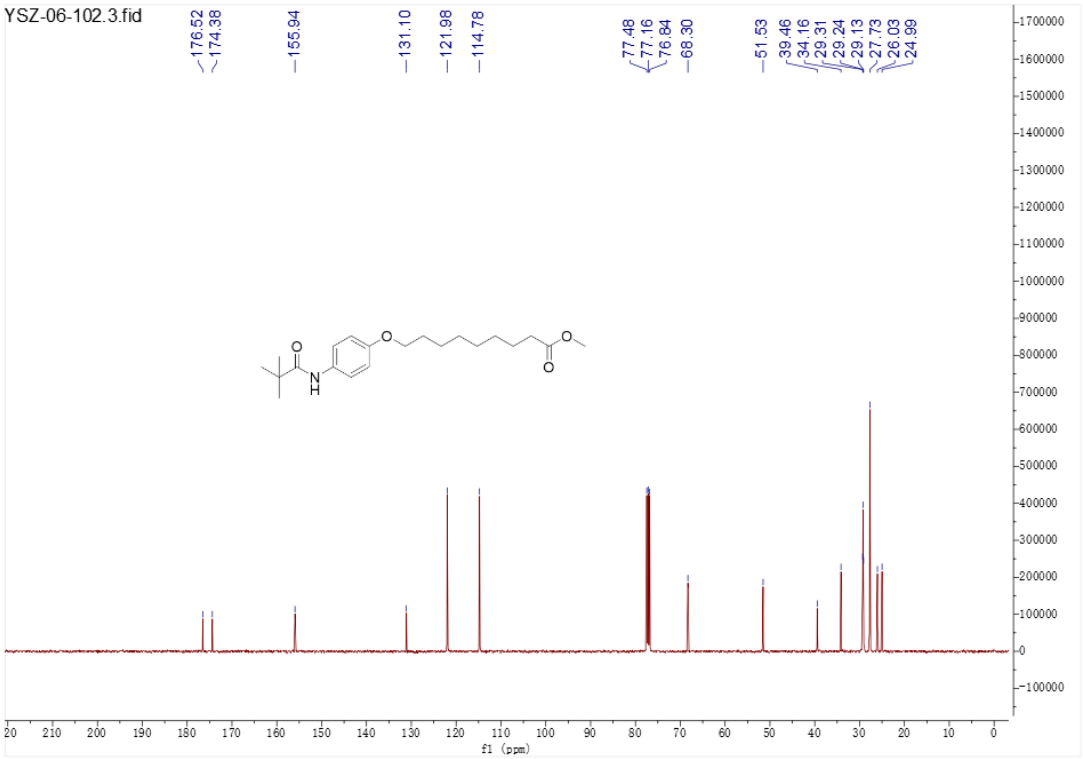


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.087	MM	1163.4	87.3	0.2221	74.460	0.837
2	14.82	MM	399.1	17.9	0.3707	25.540	0.86

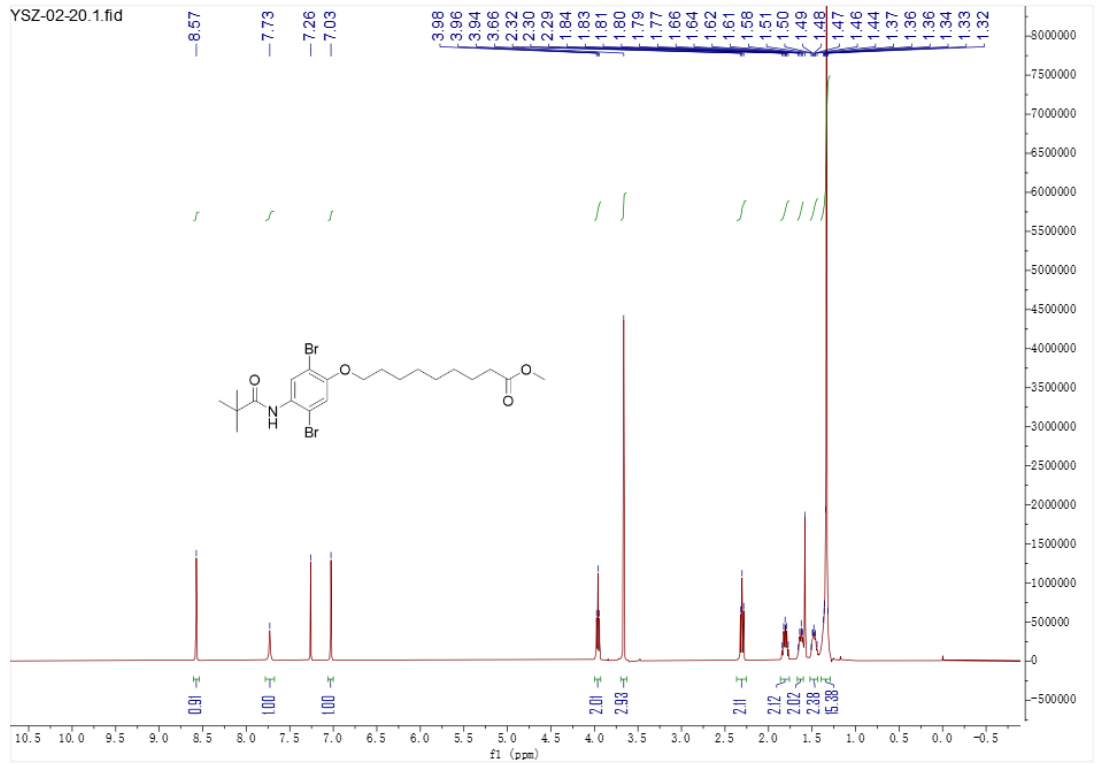
NMR spectrum

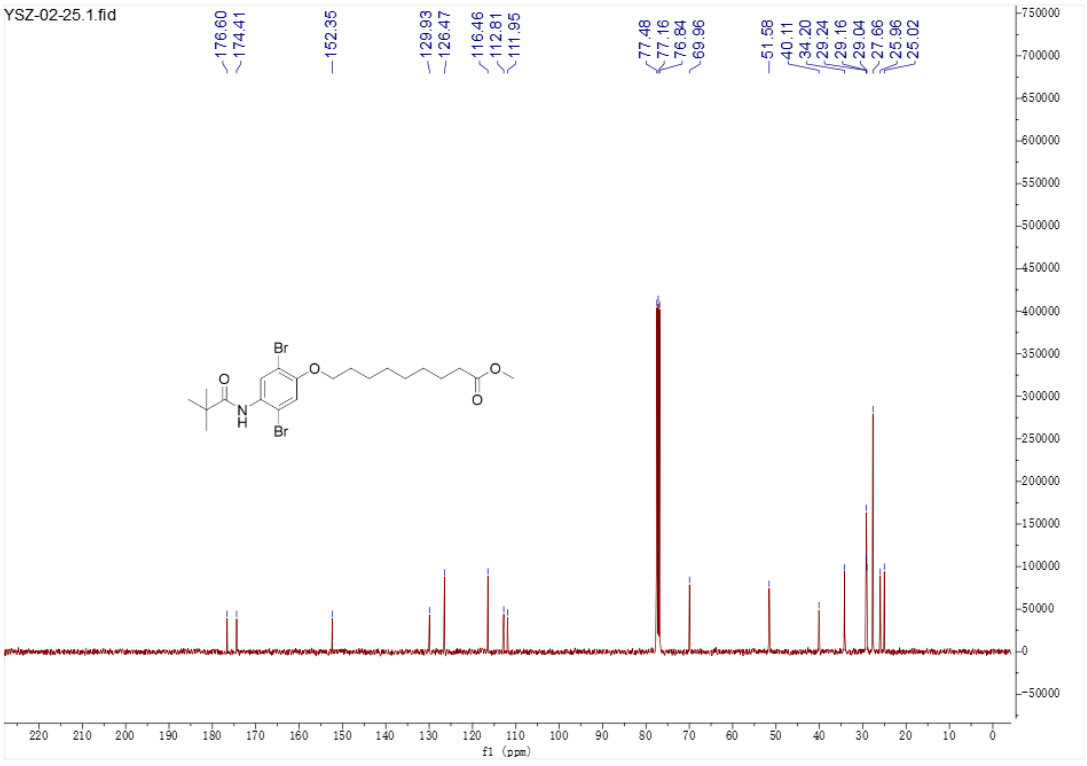
Methyl 9-(4-pivalamidophenoxy)nonanoate **(2a)**



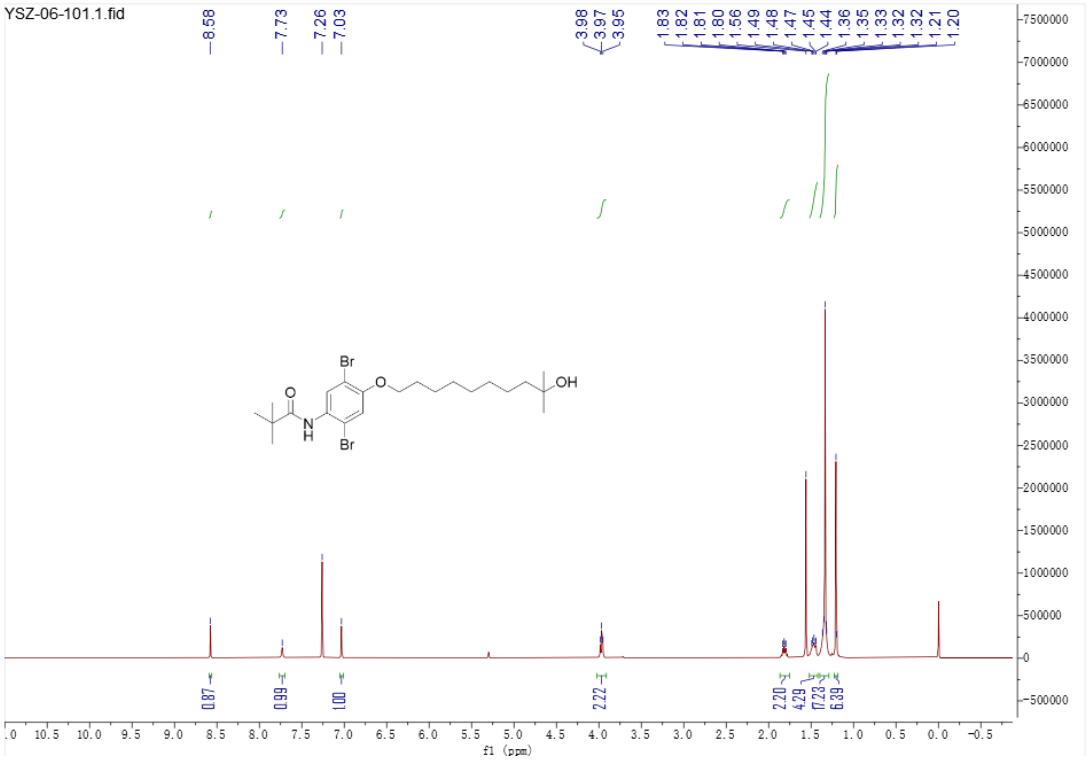


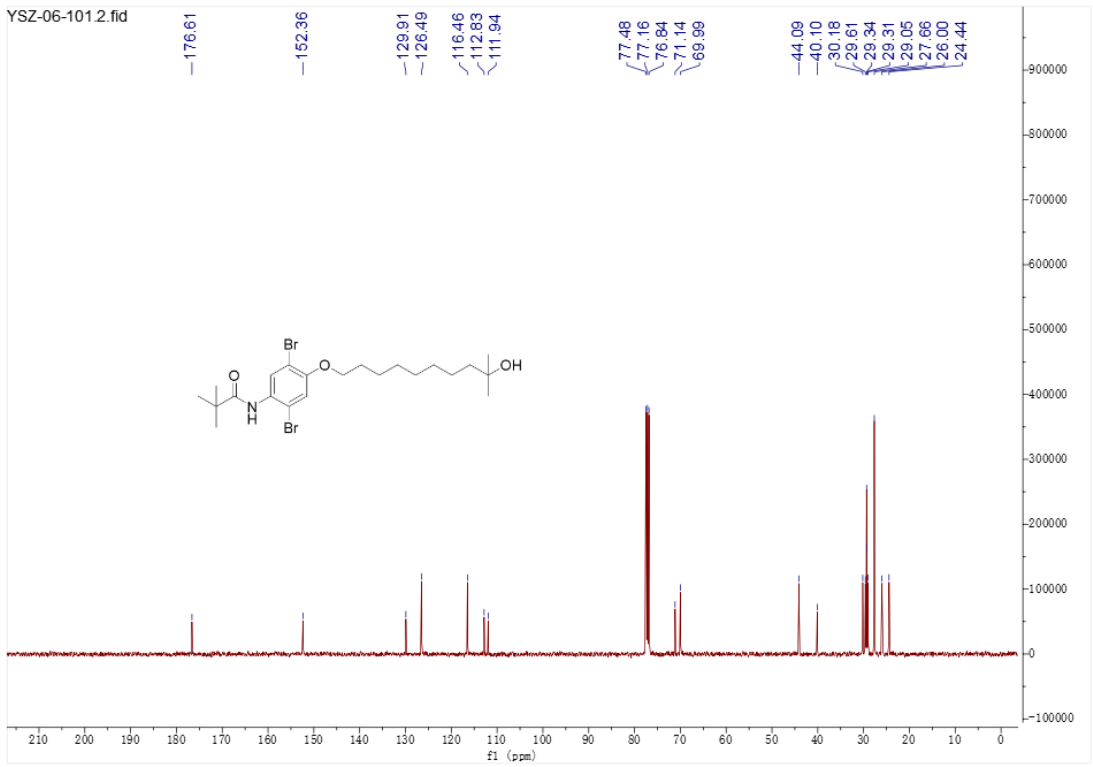
Methyl 9-(2,5-dibromo-4-pivalamidophenoxy)nonanoate **(3a)**



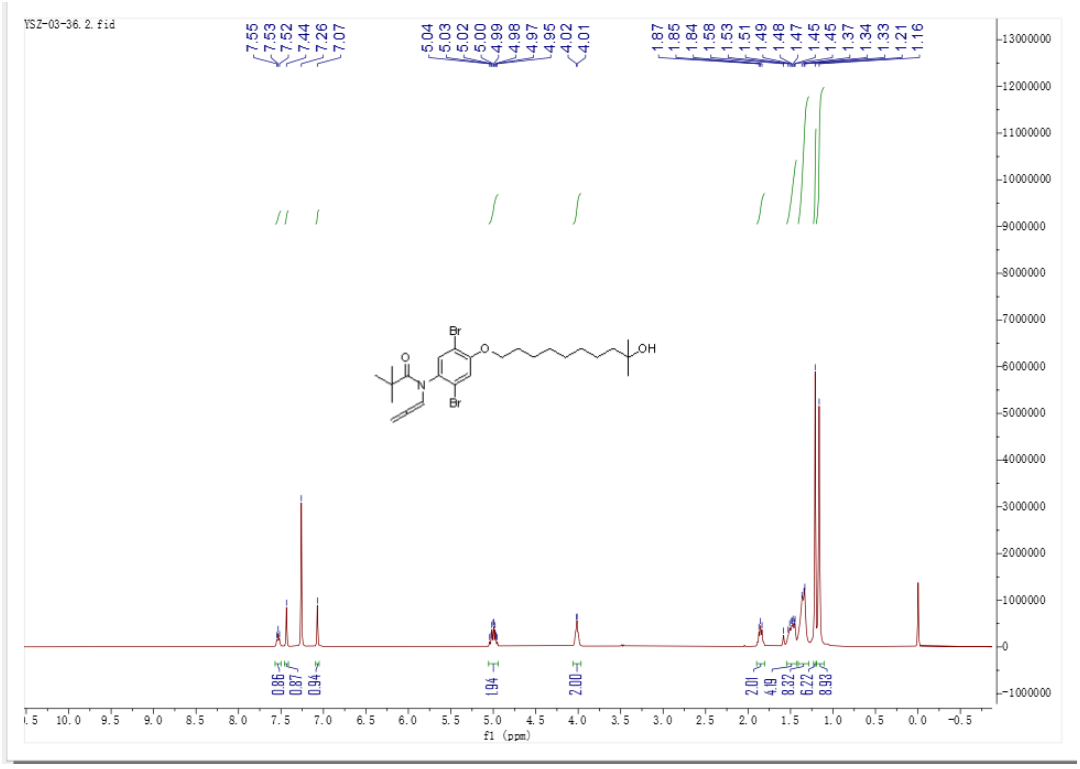


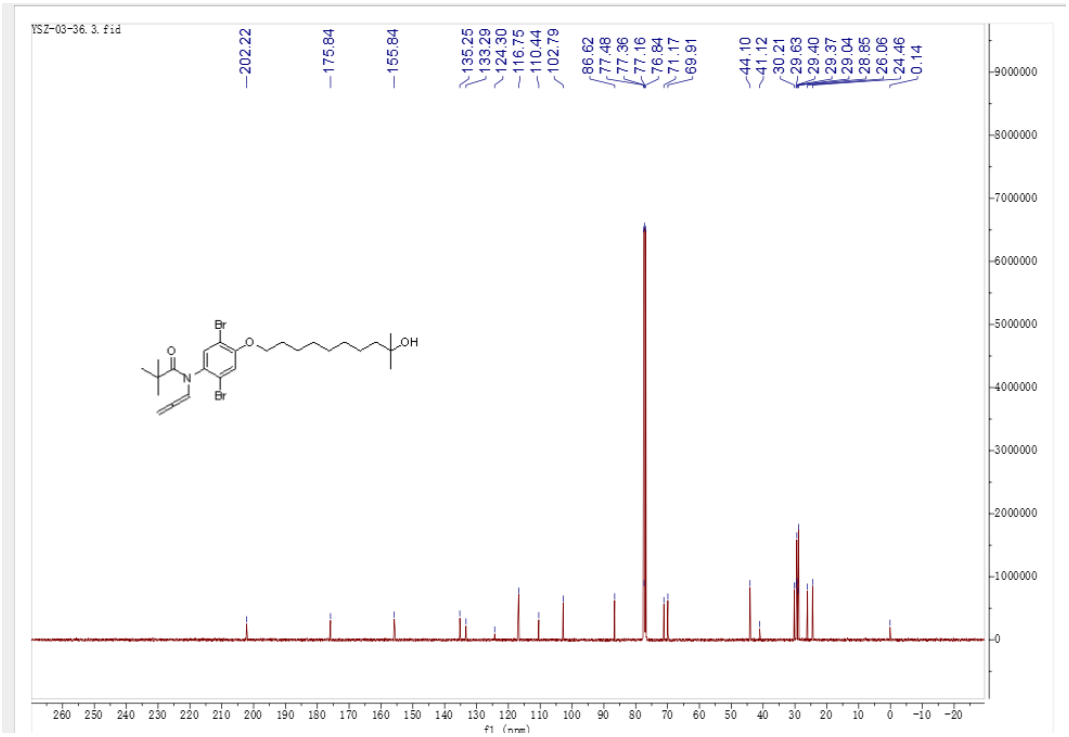
N-(2,5-dibromo-4-((9-hydroxy-9-methyldecyl)oxy)phenyl)pivalamide **(4a)**



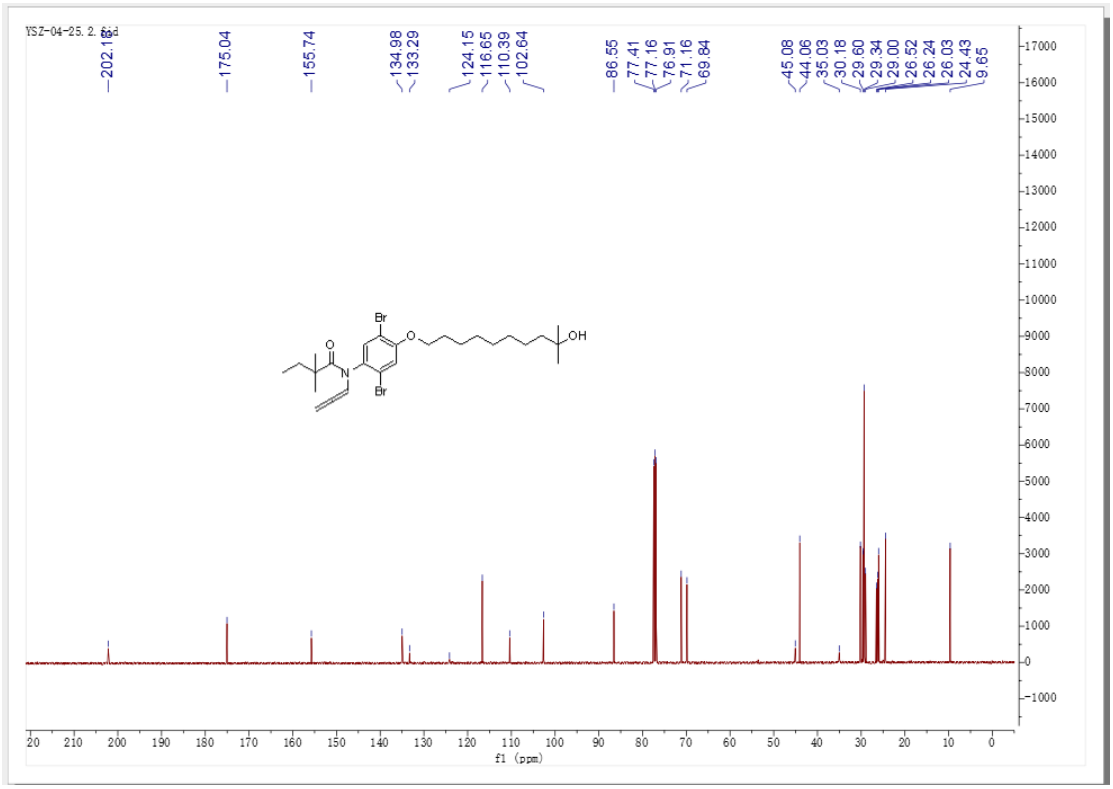


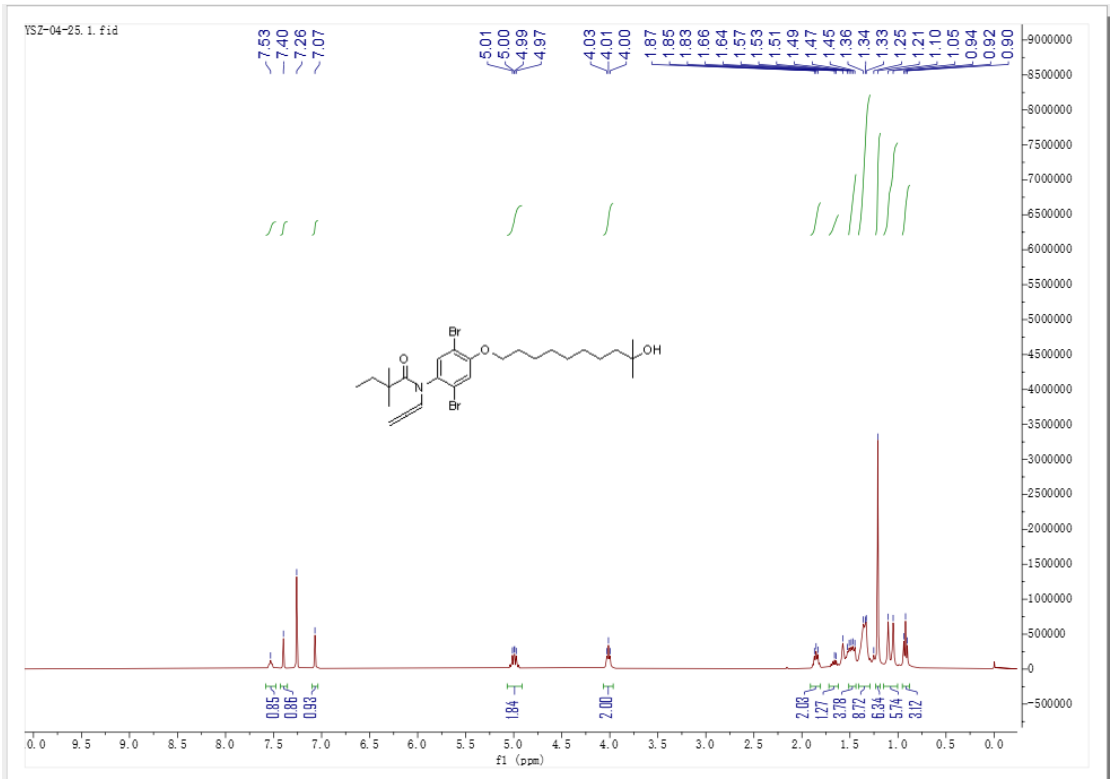
N-(2,5-dibromo-4-((9-hydroxy-9-methyldecyl)oxy)phenyl)-*N*-(propa-1,2-dien-1-yl)pivalamide **(5a)**



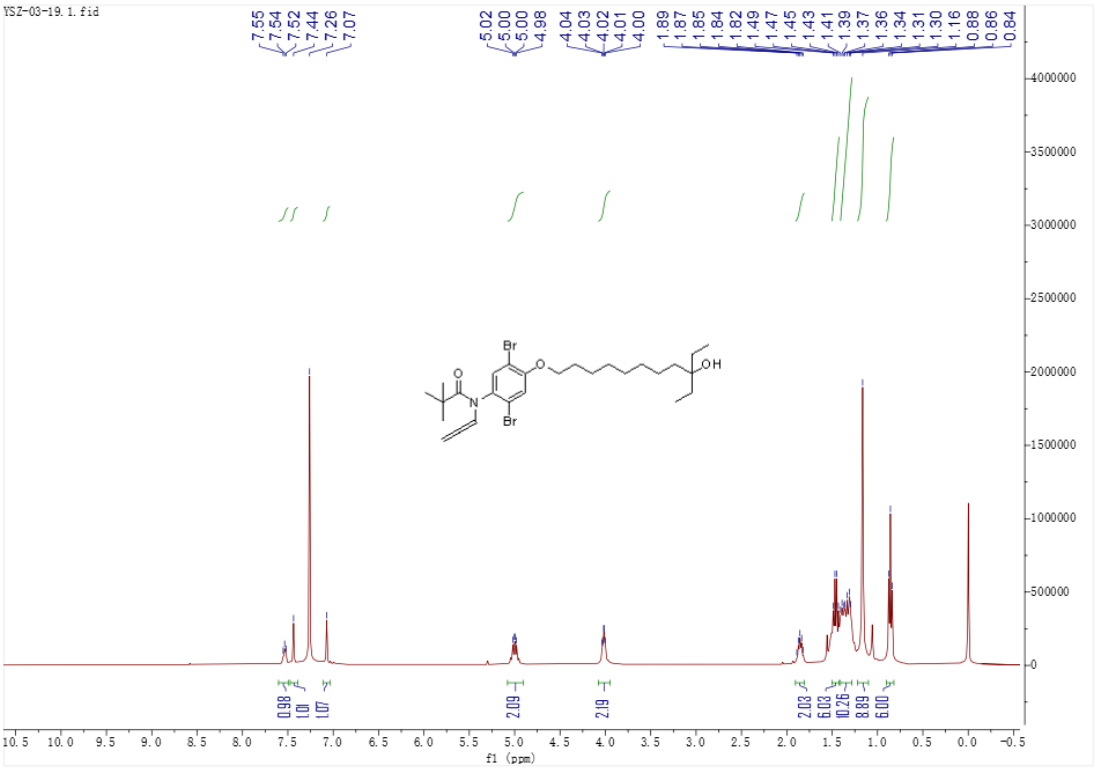


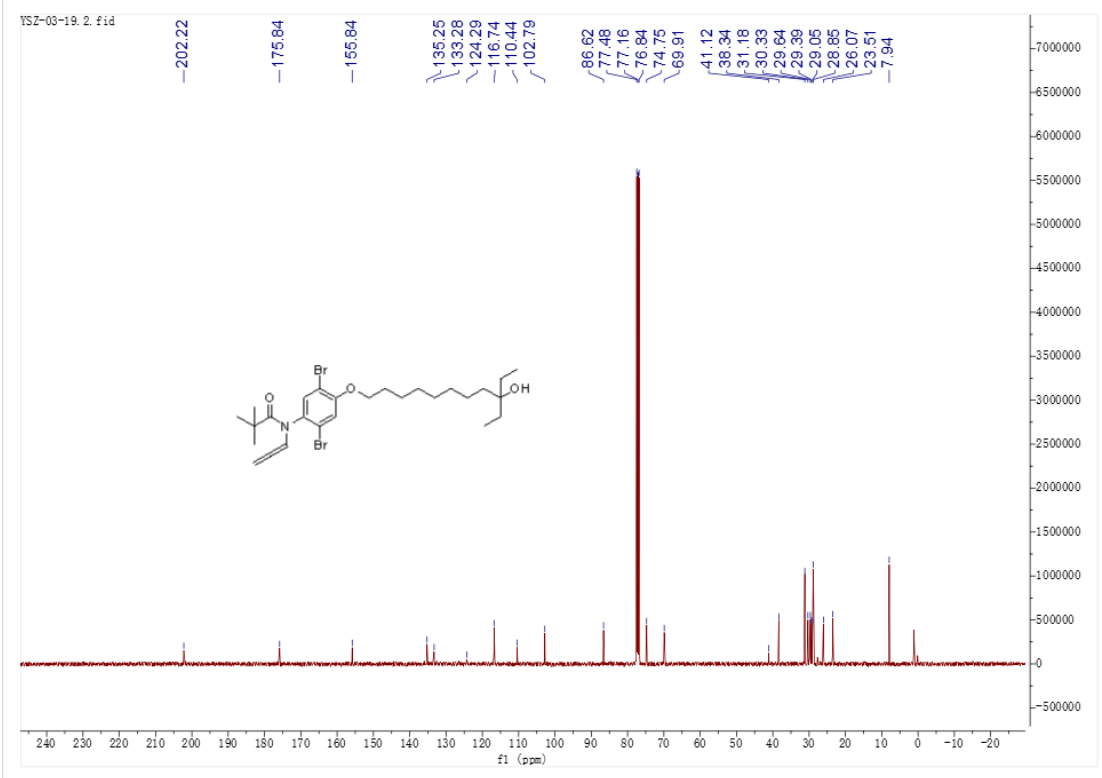
N-(2,5-dibromo-4-((9-hydroxy-9-methyldecyl)oxy)phenyl)-2,2-dimethyl-N-(propa-1, 2-dien-1-yl)butanamide **(5b)**



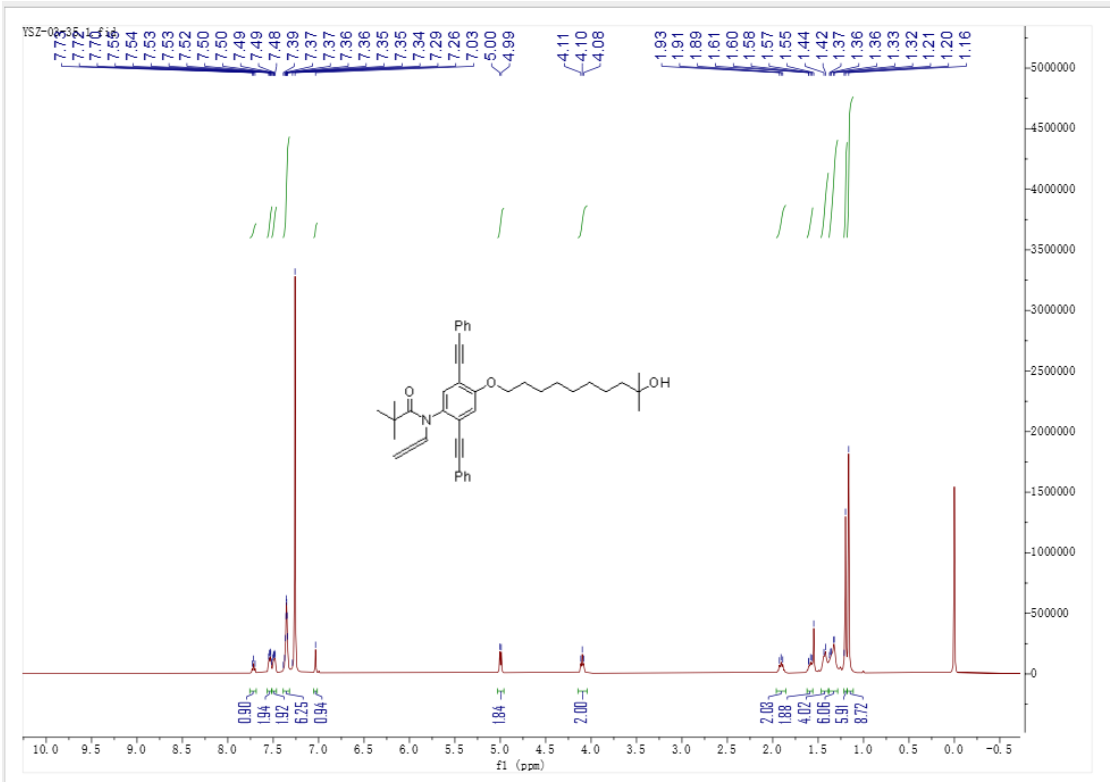


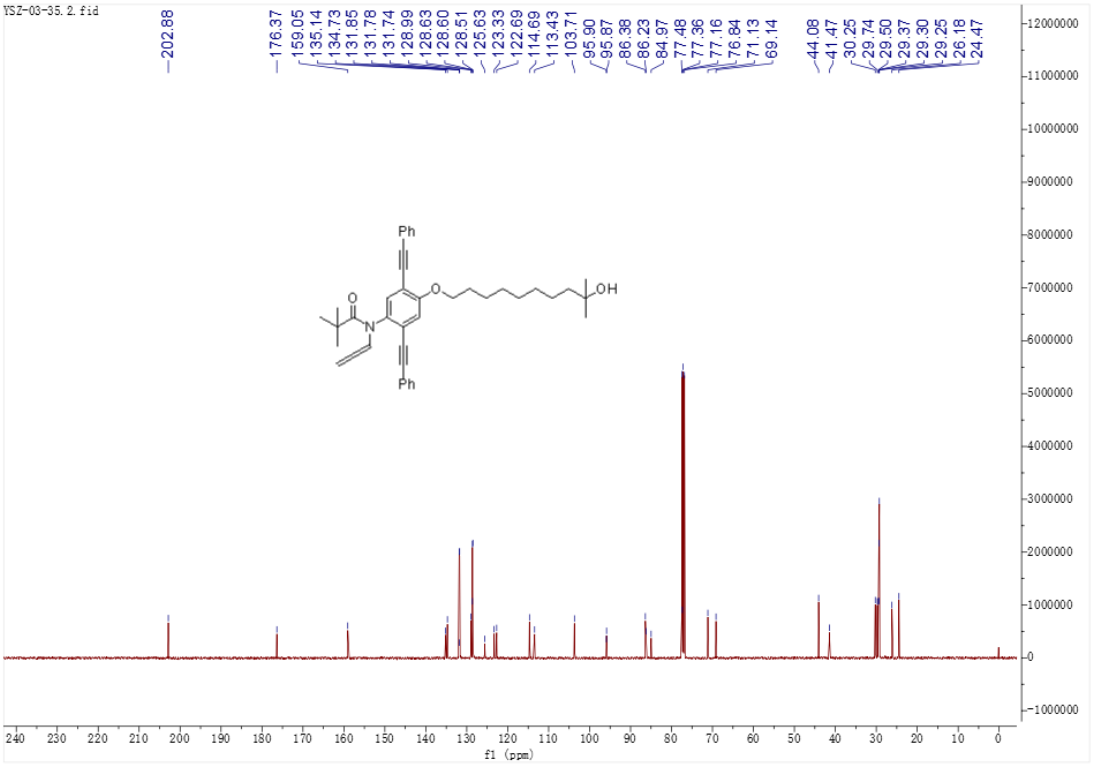
N-(2,5-dibromo-4-((9-ethyl-9-hydroxyundecyl)oxy)phenyl)-*N*-(propa-1,2-dien-1-yl)pivalamide **(5c)**



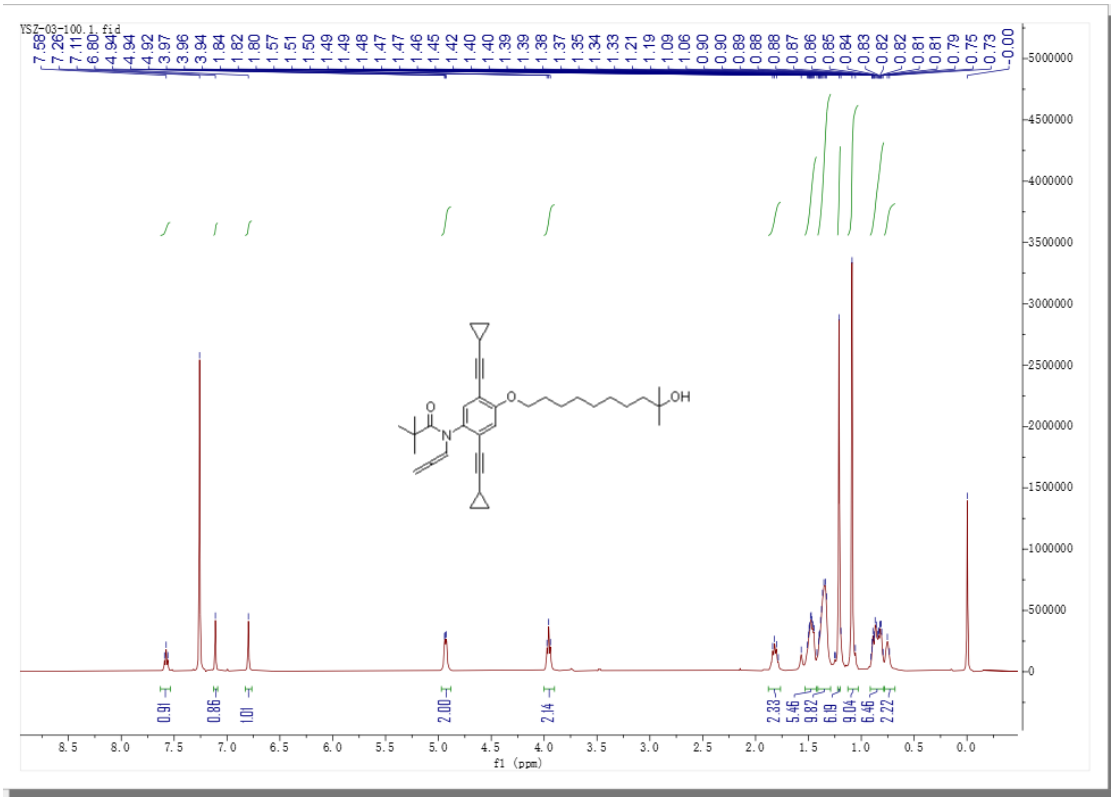


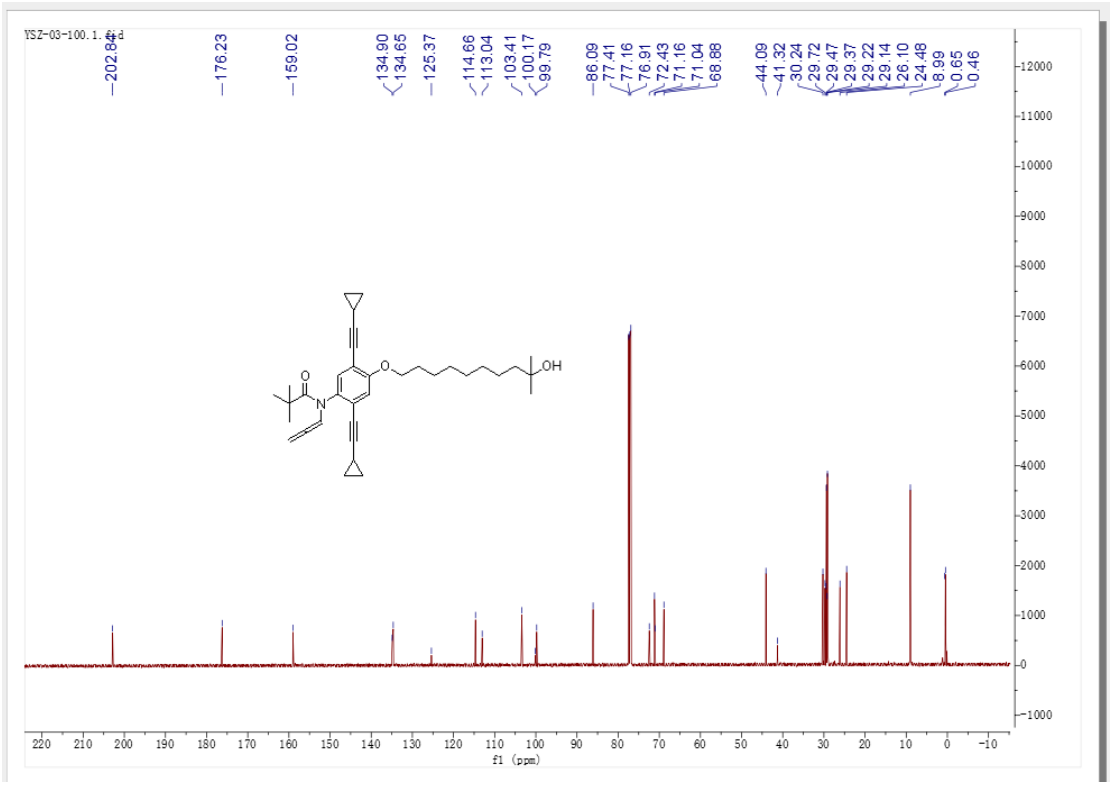
N-(4-((9-hydroxy-9-methyldecyl)oxy)-2,5-bis(phenylethynyl)phenyl)-*N*-(propa-1,2-dien-1-yl)pivalamide **(5d)**



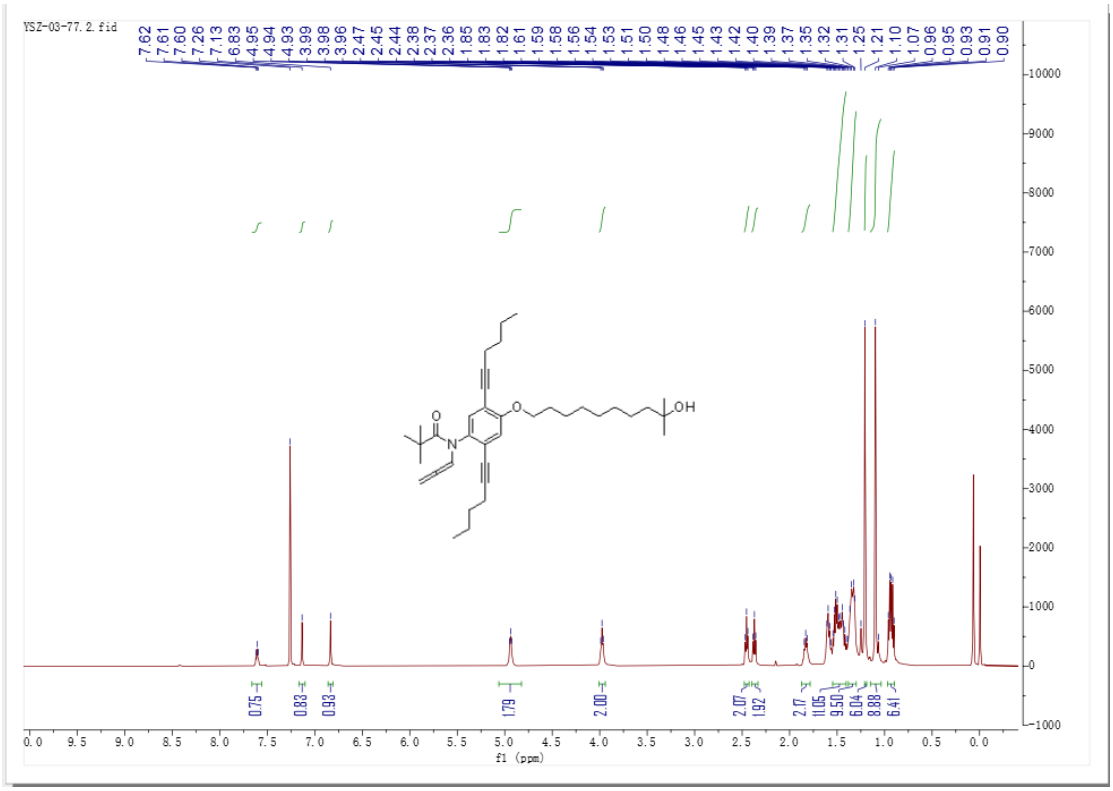


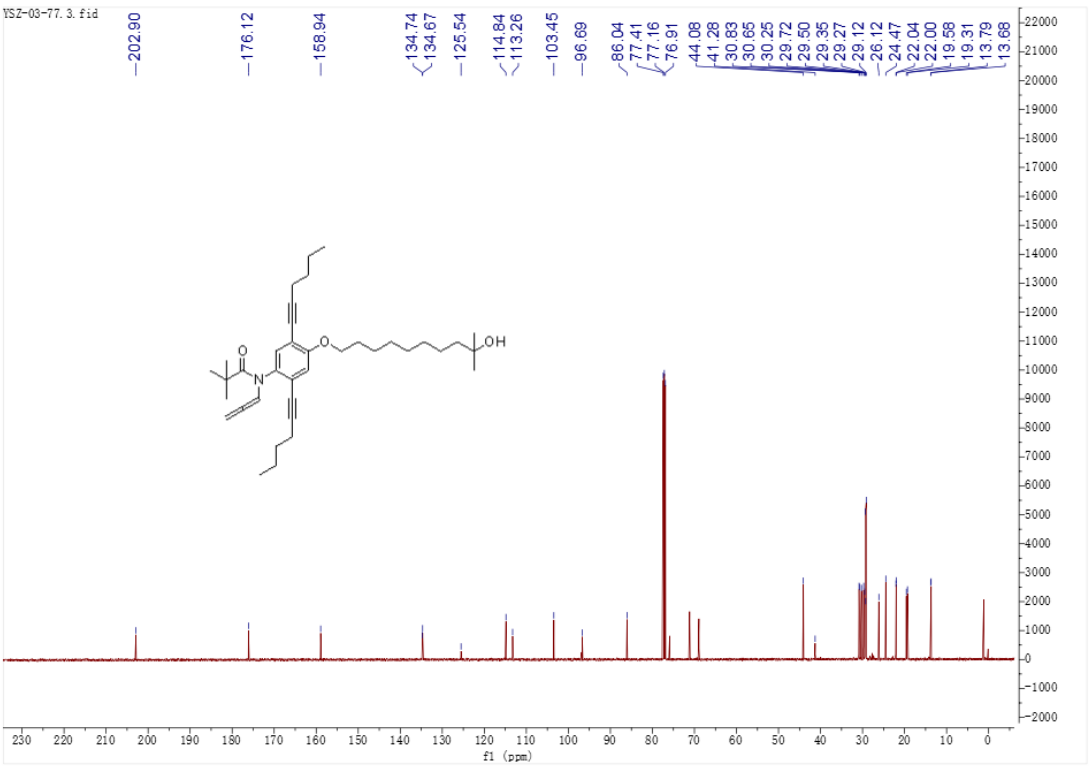
N-(2,5-bis(cyclopropylethynyl)-4-((9-hydroxy-9-methyldecyl)oxy)phenyl)-*N*-(propa-1,2-dien-1-yl)pivalamide **(5e)**



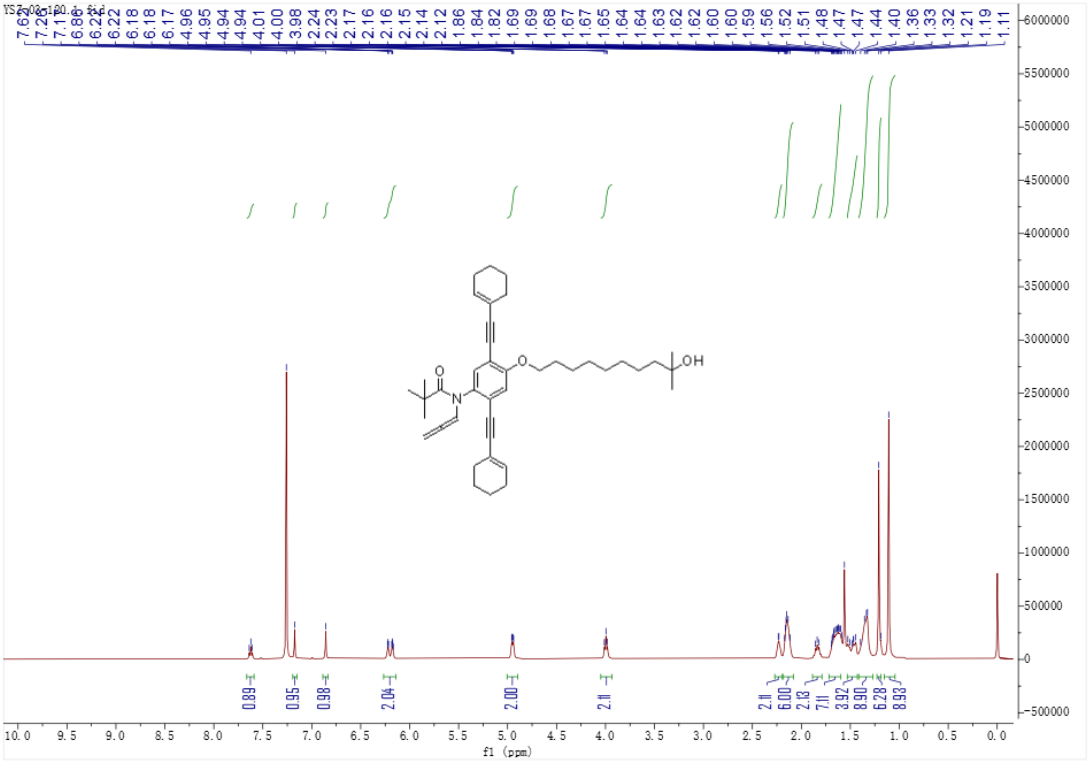


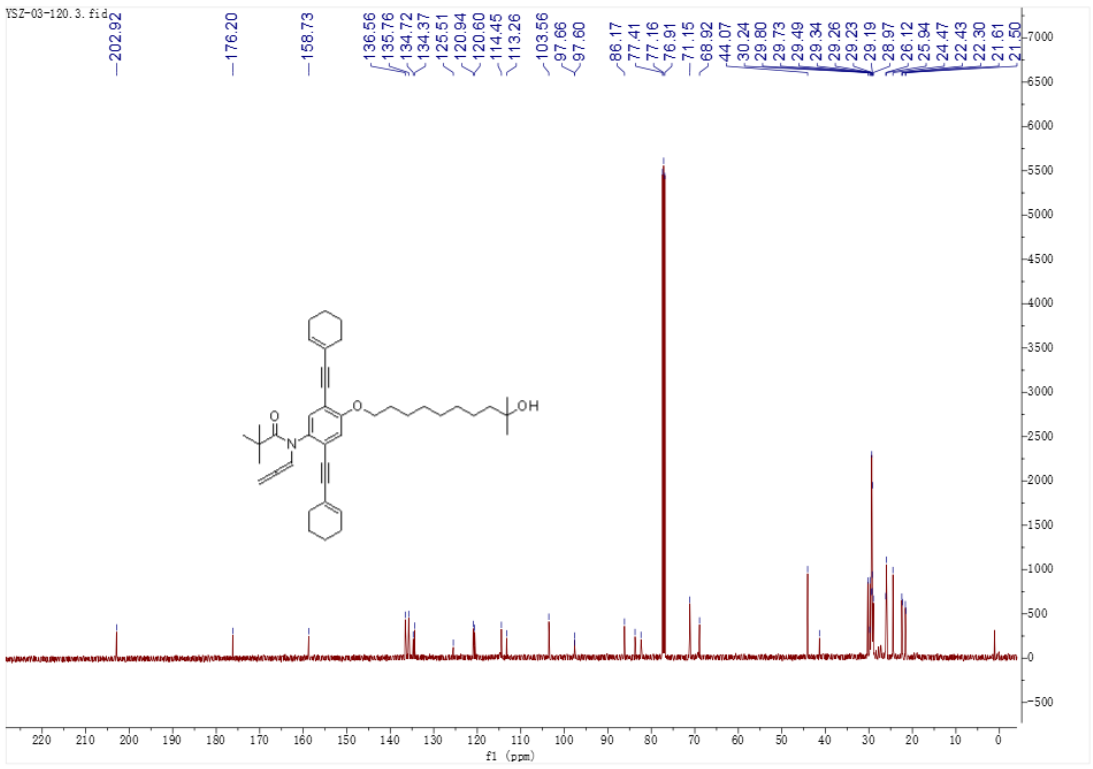
N-(2,5-di(hex-1-yn-1-yl)-4-((9-hydroxy-9-methyldecyl)oxy)phenyl)-N-(propa-1,2-dien-1-yl)pivalamide **(5f)**



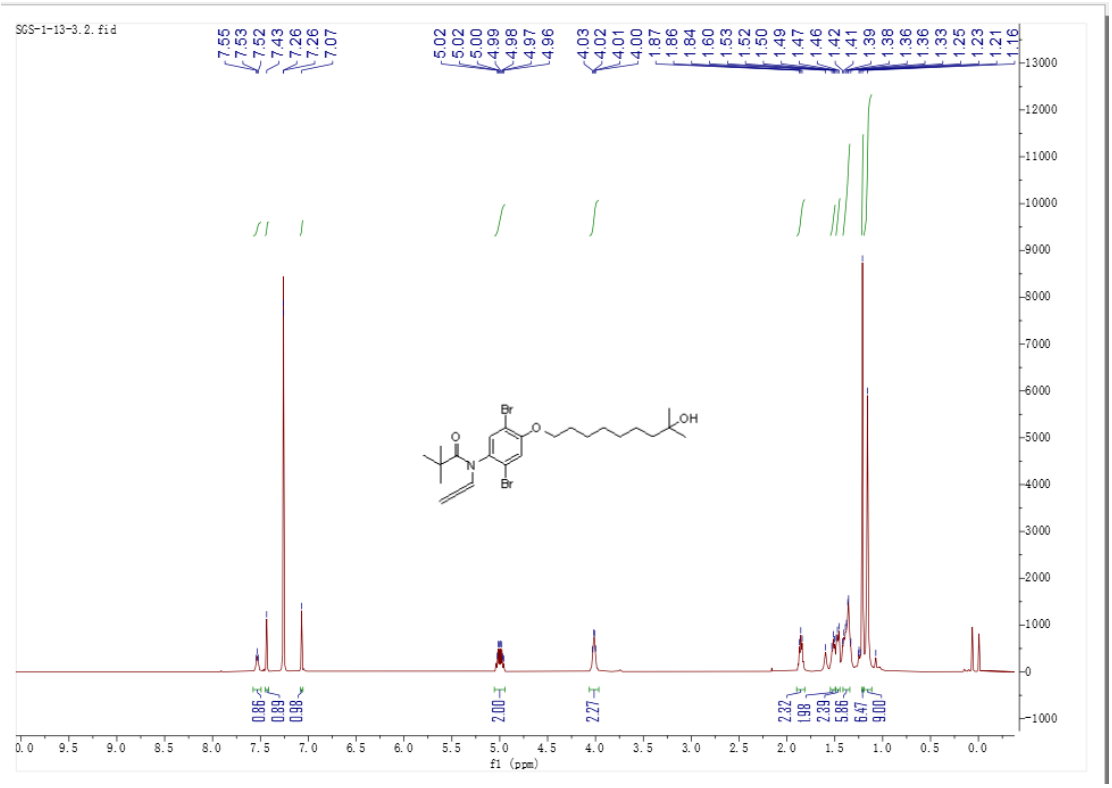


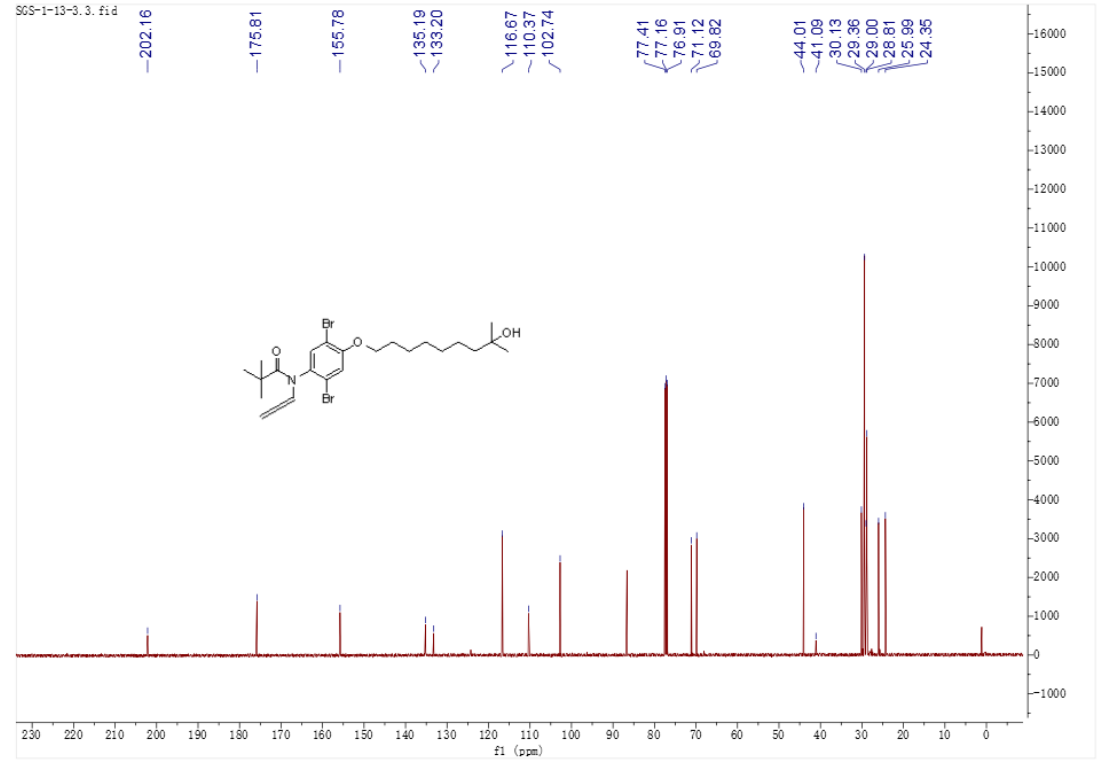
N-(2,5-bis(cyclohex-1-en-1-ylethynyl)-4-((9-hydroxy-9-methyldecyl)oxy)phenyl)-*N*-(propa-1,2-dien-1-yl)pivalamide **(5g)**





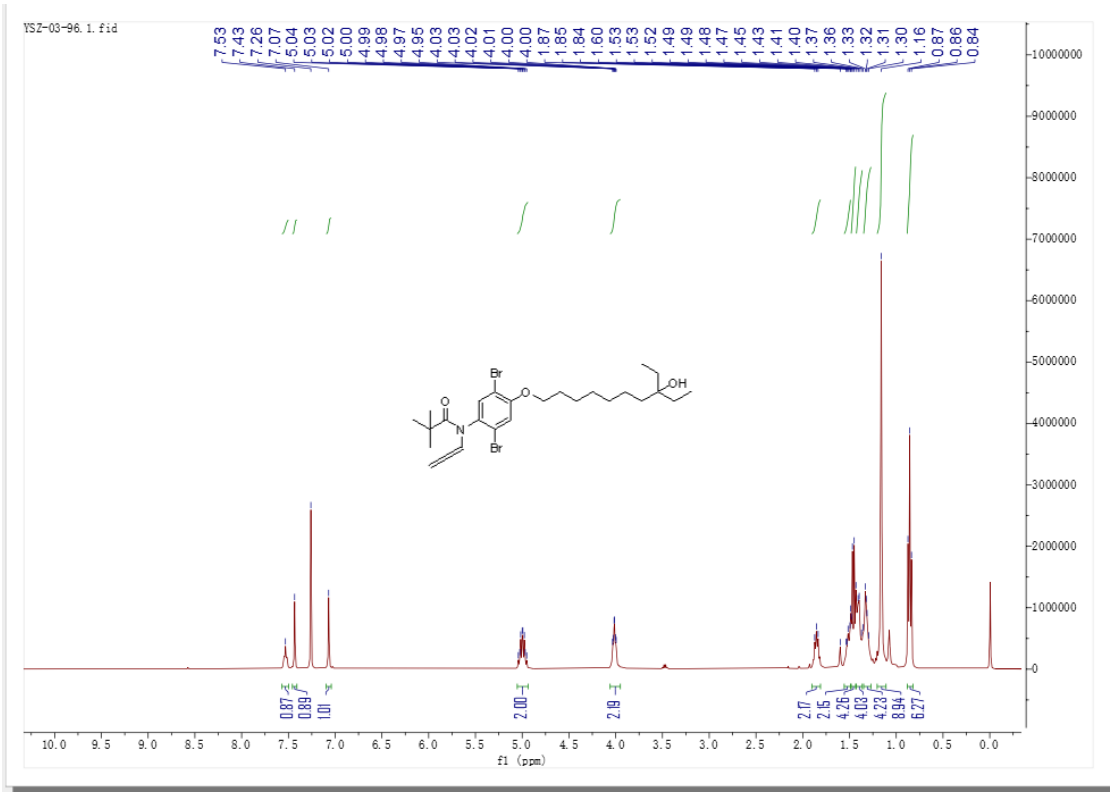
N-(2,5-dibromo-4-((8-hydroxy-8-methylnonyl)oxy)phenyl)-*N*-(propa-1,2-dien-1-yl)pivalamide **(5h)**

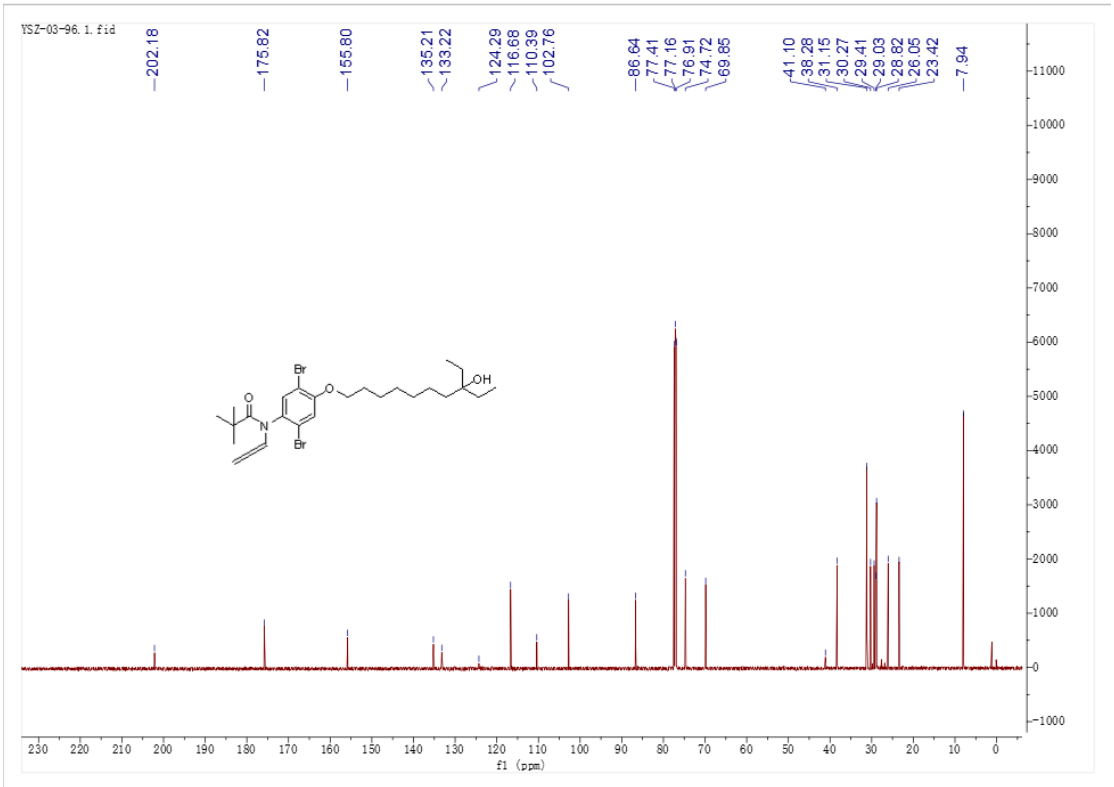




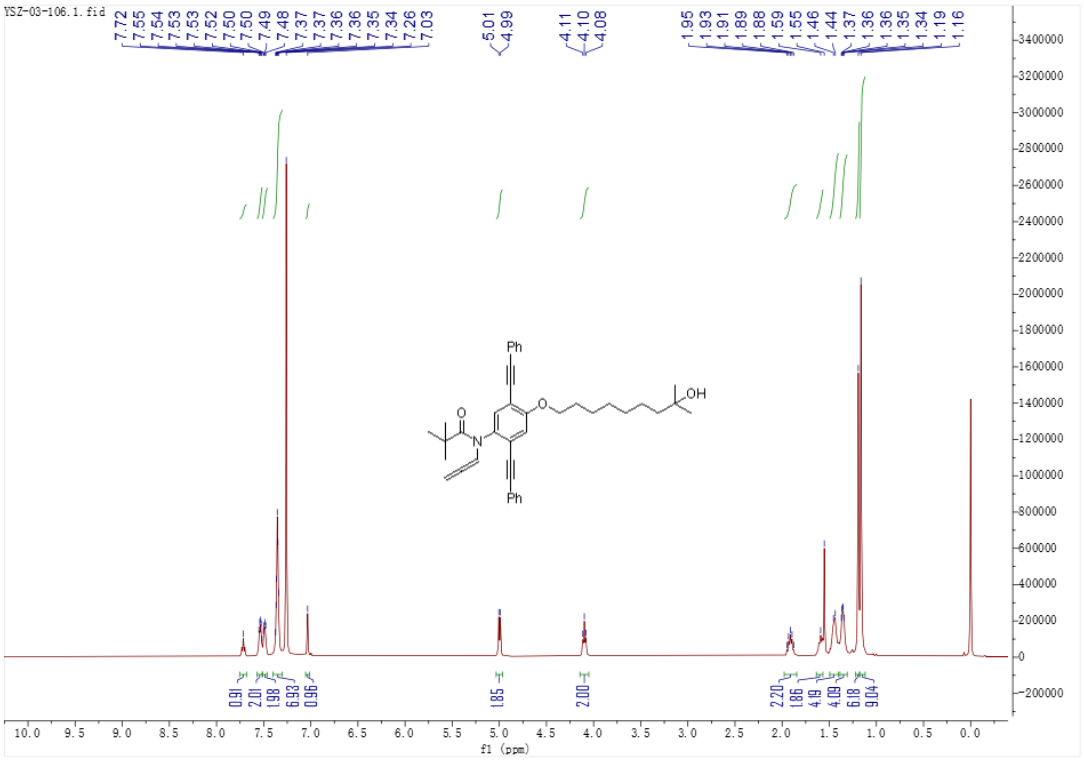
N-(2,5-dibromo-4-((8-ethyl-8-hydroxydecyl)oxy)phenyl)-*N*-(propa-1,2-dien-1-yl)piva

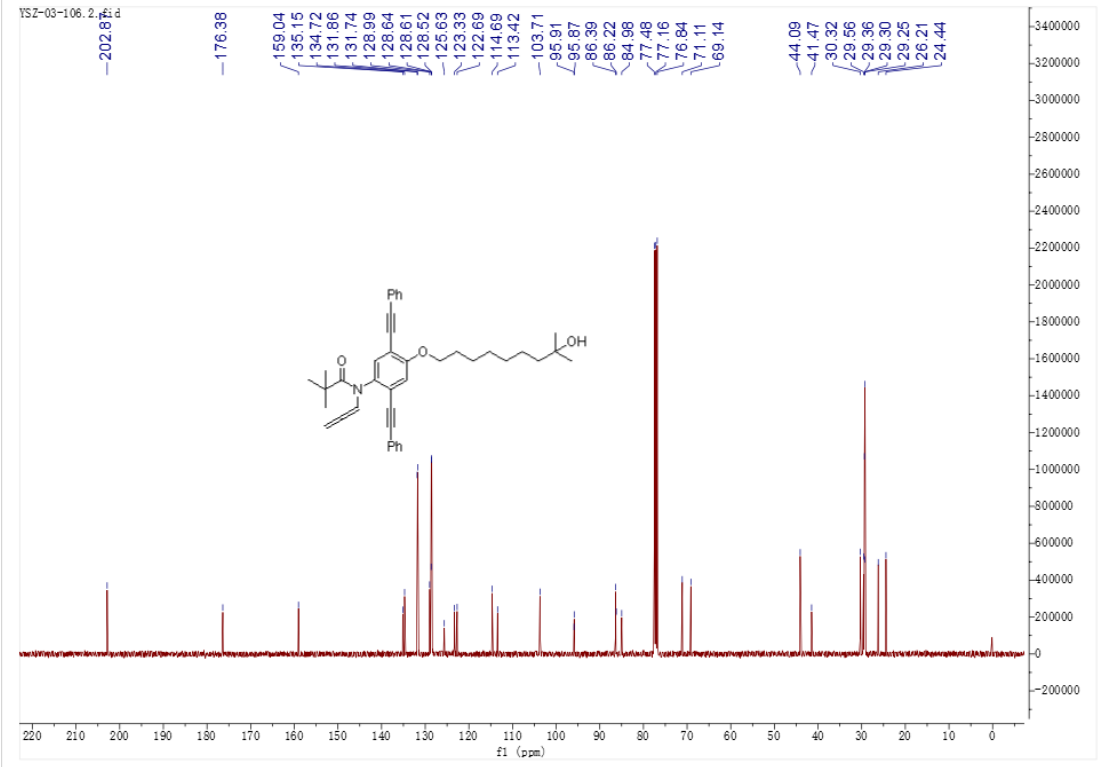
lamide **(5i)**



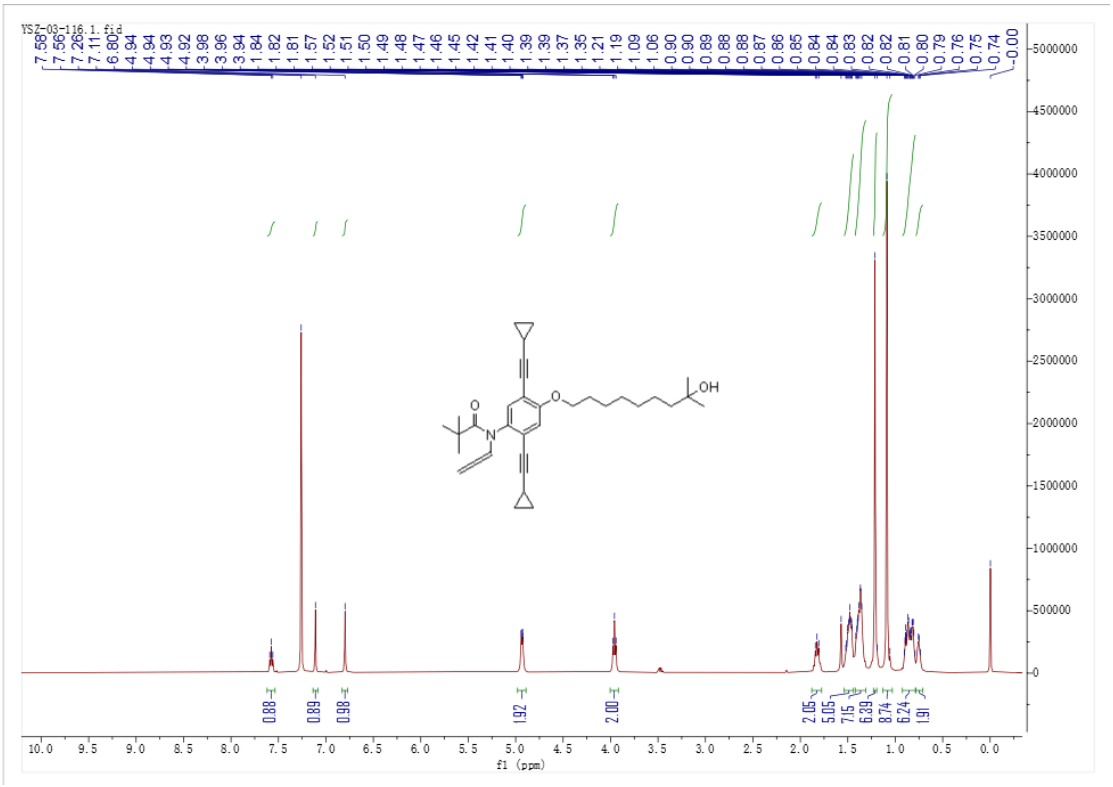


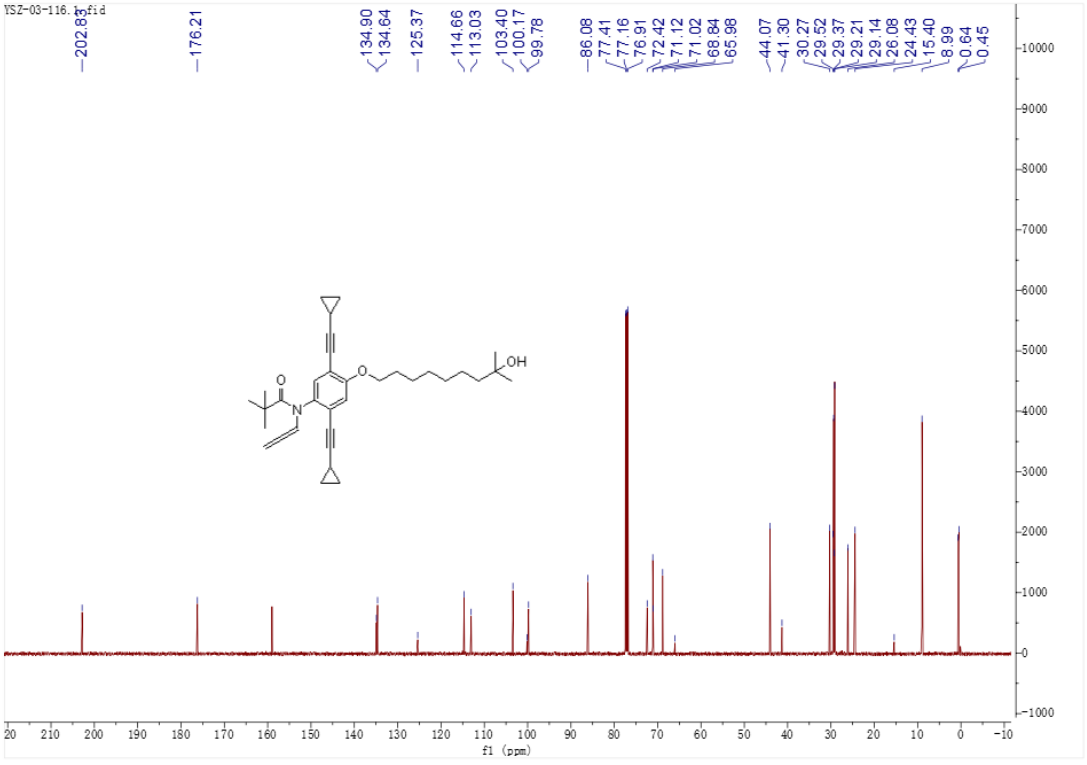
N-(4-((8-hydroxy-8-methylnonyl)oxy)-2,5-bis(phenylethynyl)phenyl)-*N*-(propa-1,2-dien-1-yl)pivalamide **(5j)**



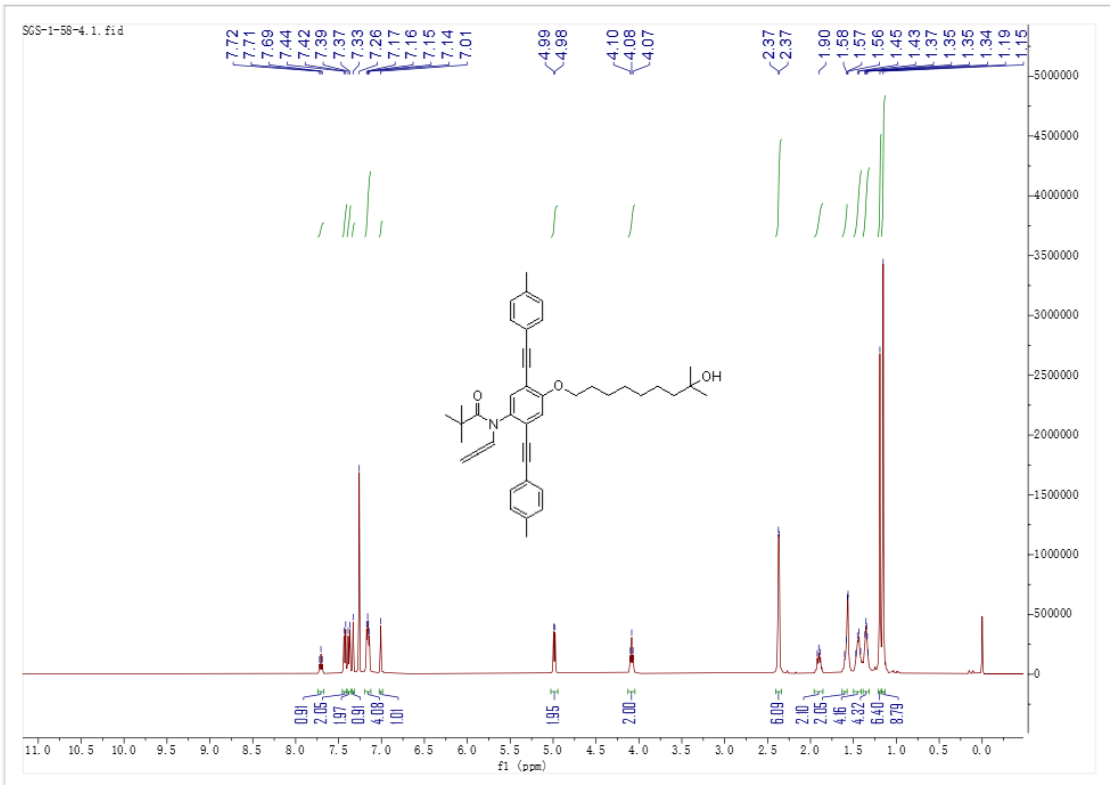


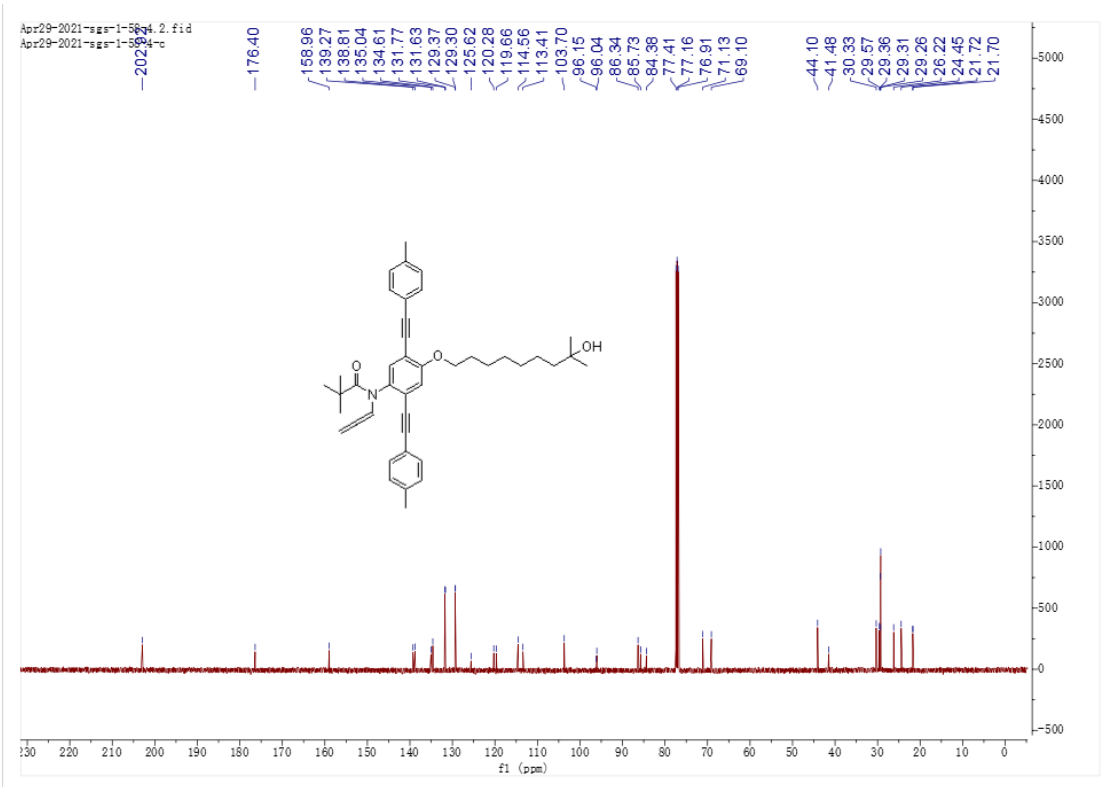
N-(2,5-bis(cyclopropylethynyl)-4-((8-hydroxy-8-methylnonyl)oxy)phenyl)-*N*-(propa-1,2-dien-1-yl)pivalamide **(5k)**



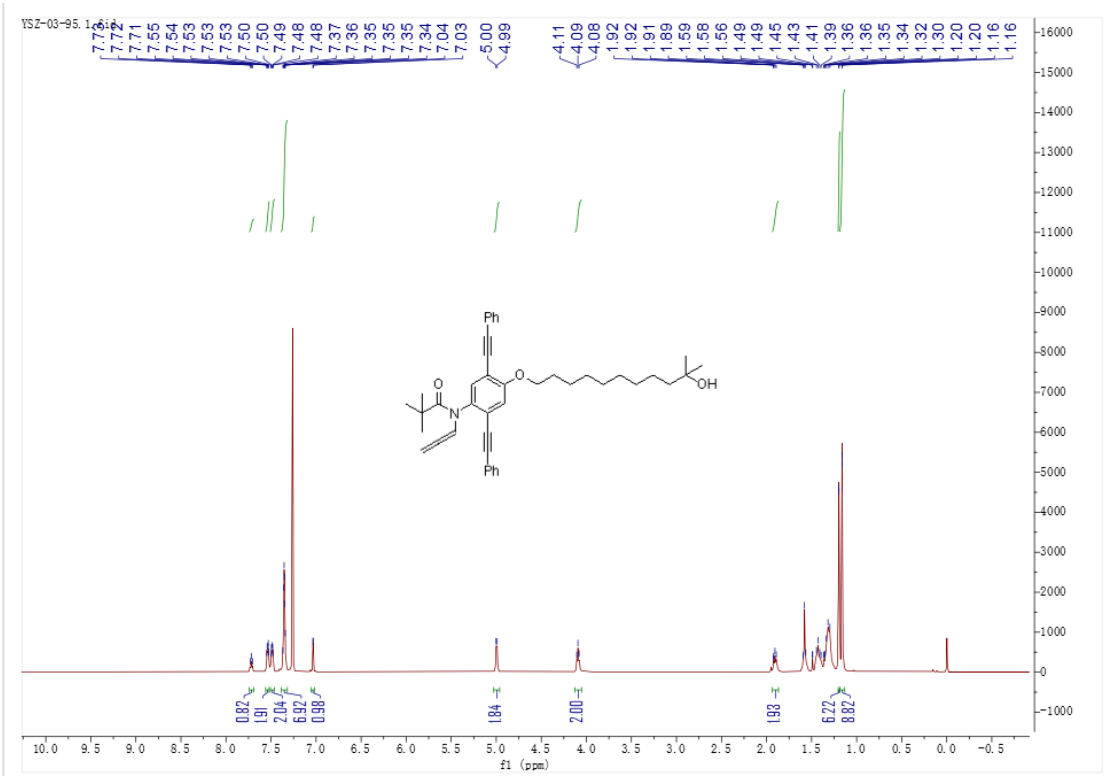


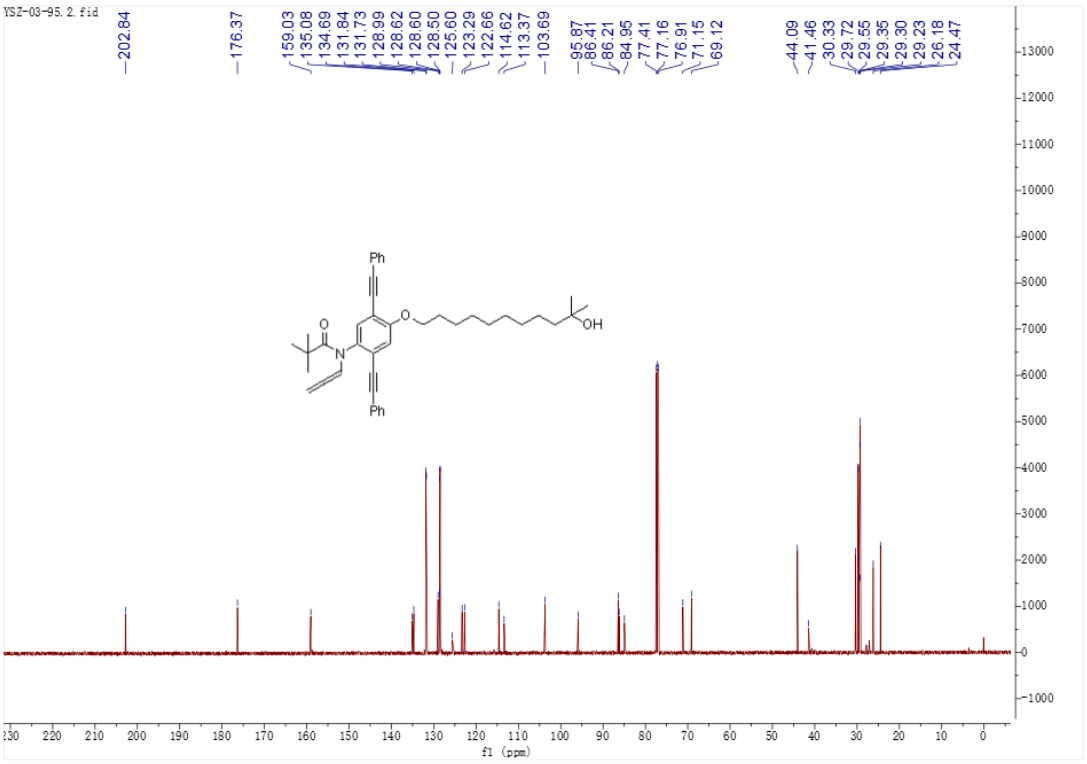
N-(4-((8-hydroxy-8-methylnonyl)oxy)-2,5-bis(p-tolylethynyl)phenyl)-*N*-(propa-1,2-dien-1-yl)pivalamide **(5l)**



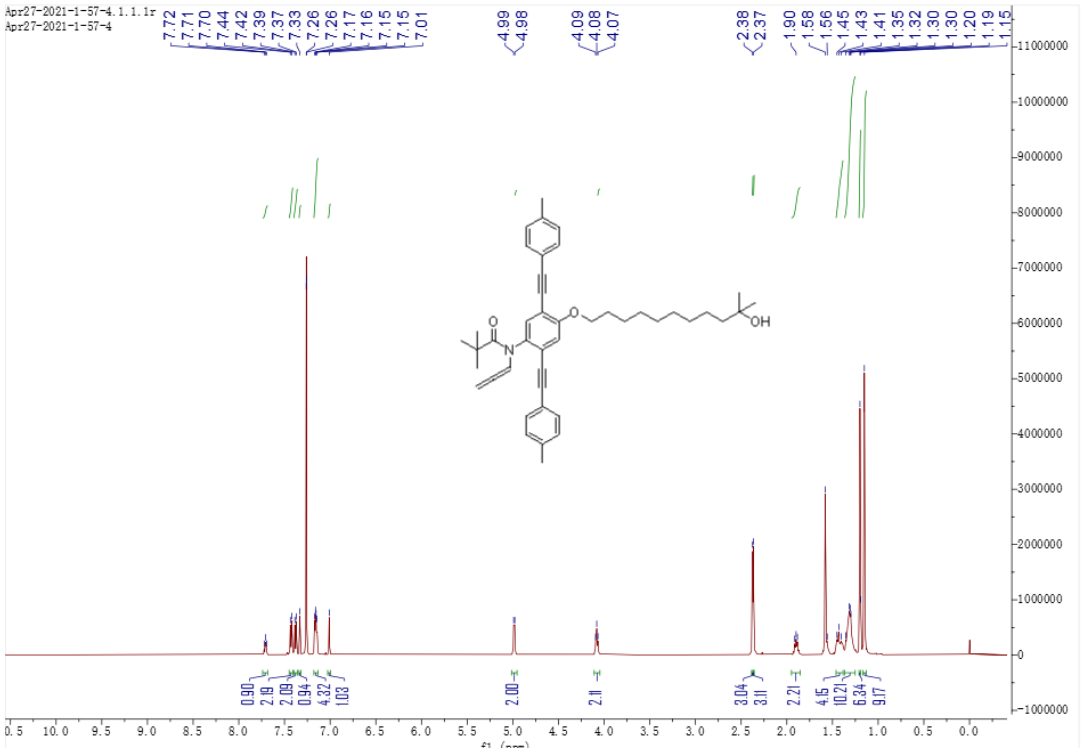


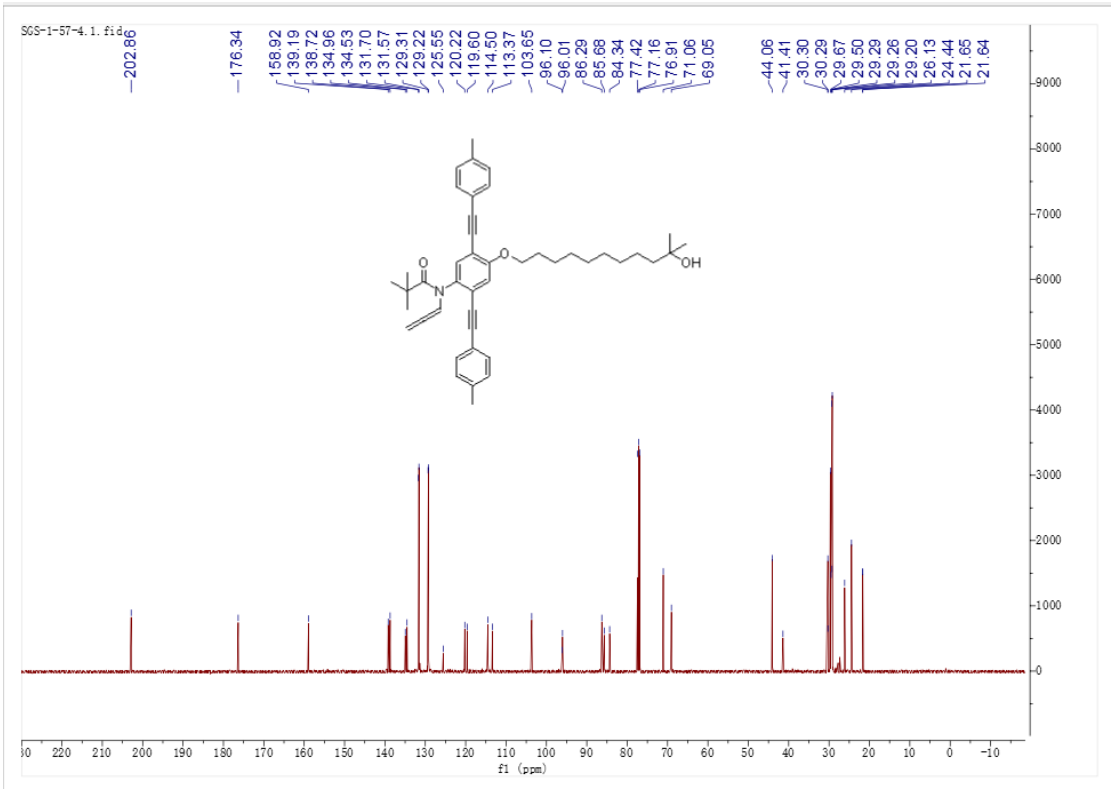
N-(4-((10-hydroxy-10-methylundecyl)oxy)-2,5-bis(phenylethynyl)phenyl)-*N*-(propa-1,2-dien-1-yl)pivalamide **(5m)**



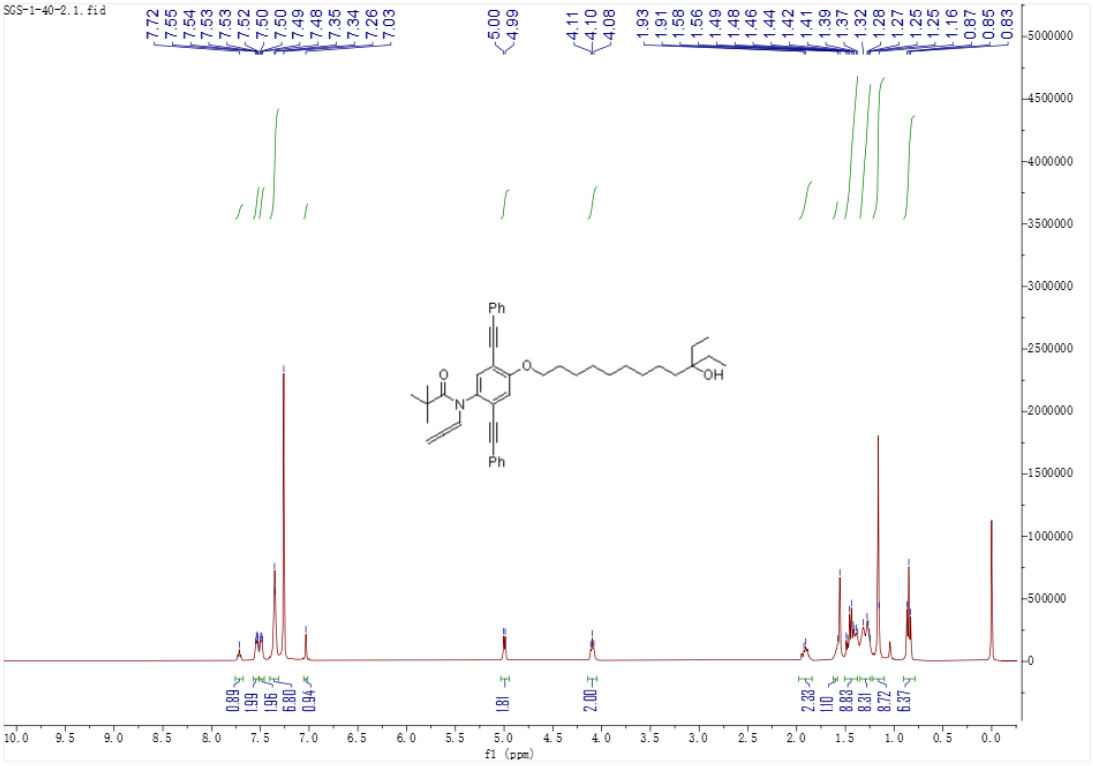


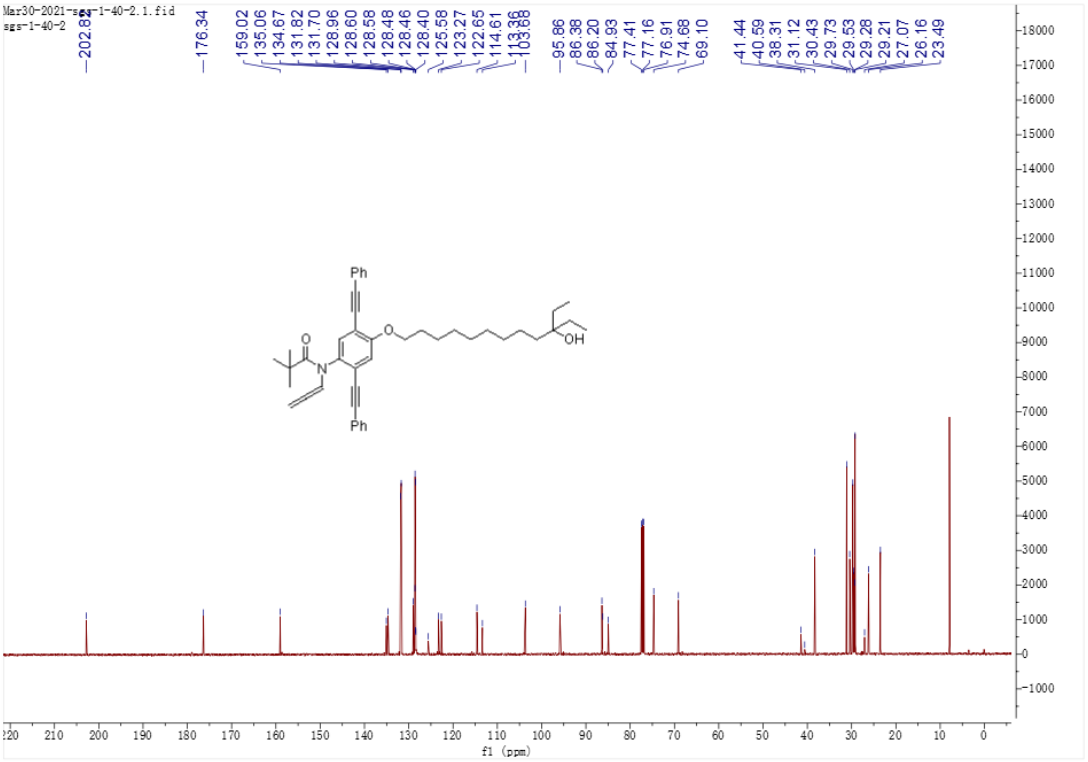
N-(4-((10-hydroxy-10-methylundecyl)oxy)-2,5-bis(p-tolylethynyl)phenyl)-*N*-(propa-1,2-dien-1-yl)pivalamide **(5n)**



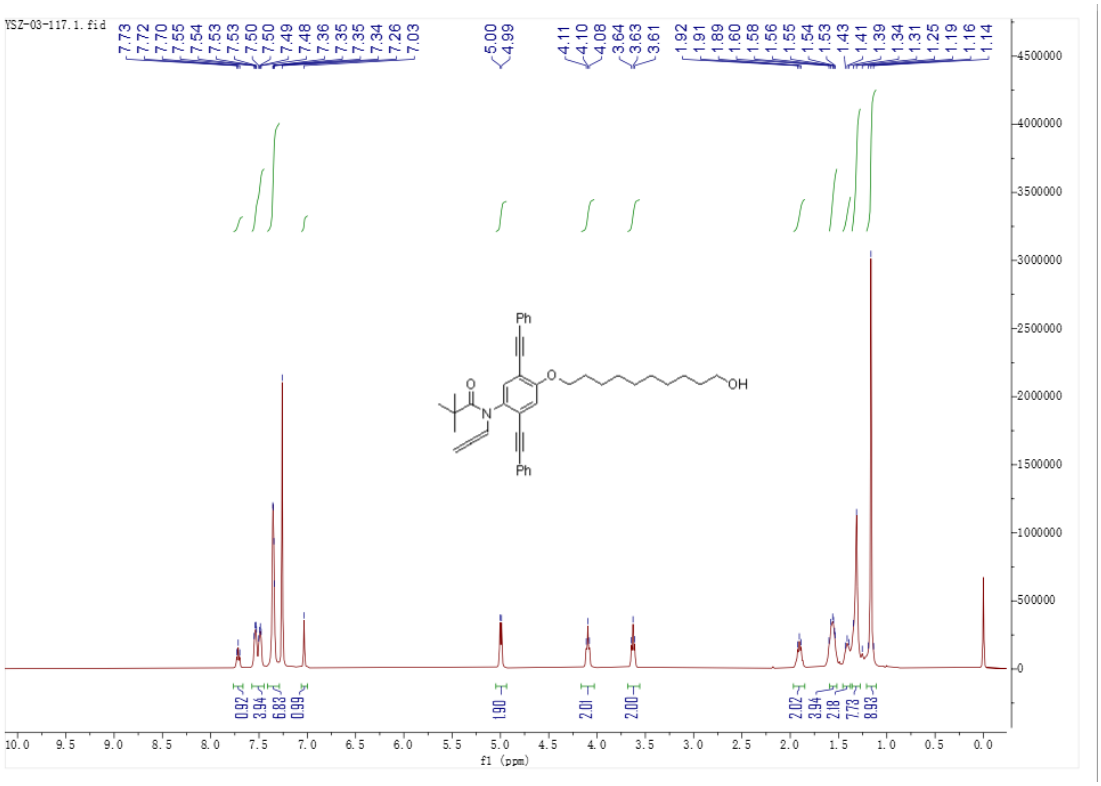


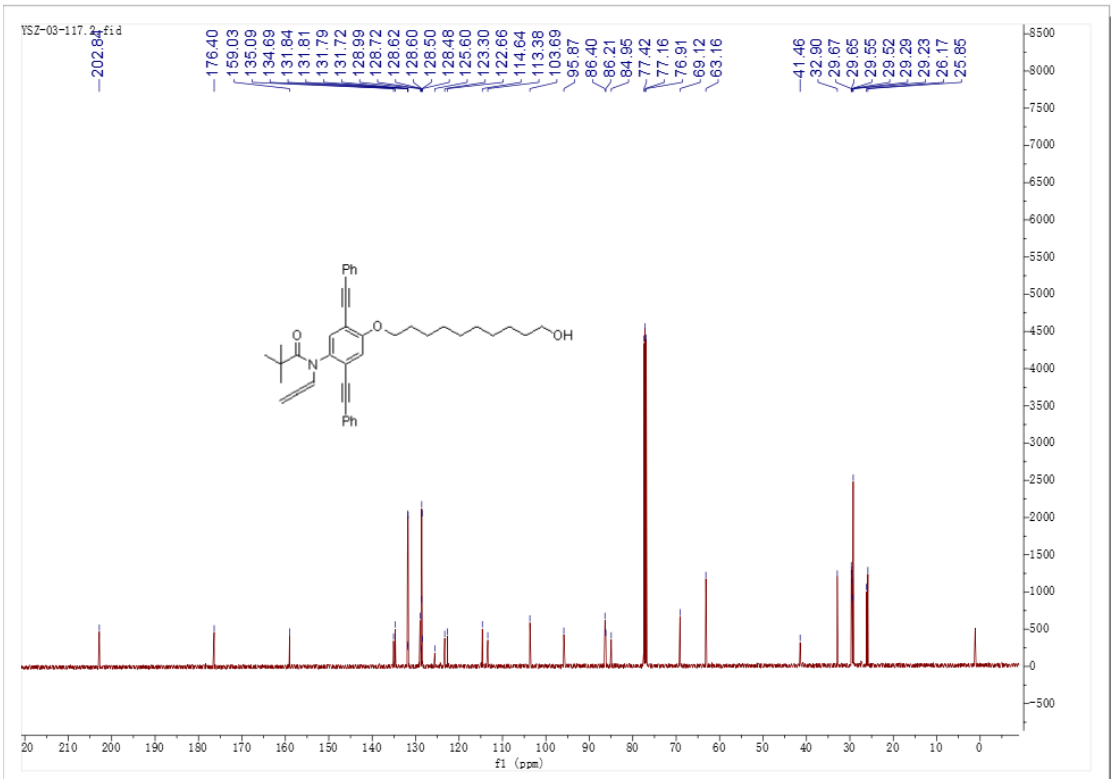
N-(4-((10-ethyl-10-hydroxydodecyl)oxy)-2,5-bis(phenylethynyl)phenyl)-*N*-(propa-1,2-dien-1-yl)pivalamide **(5o)**



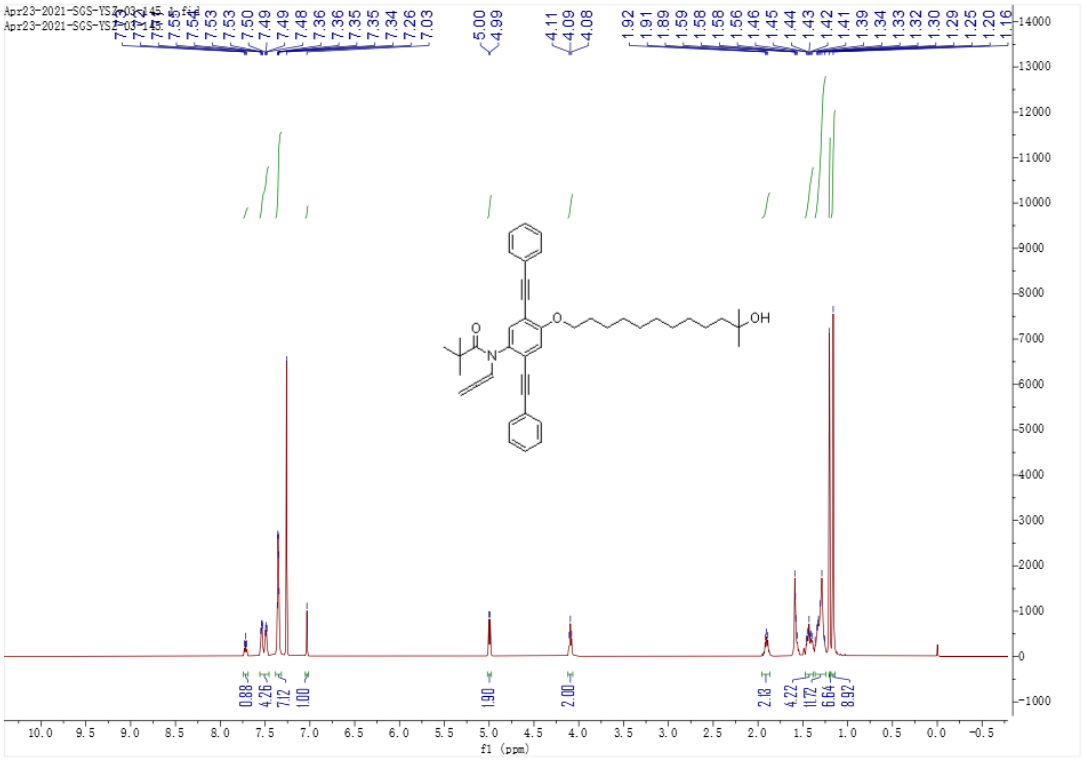


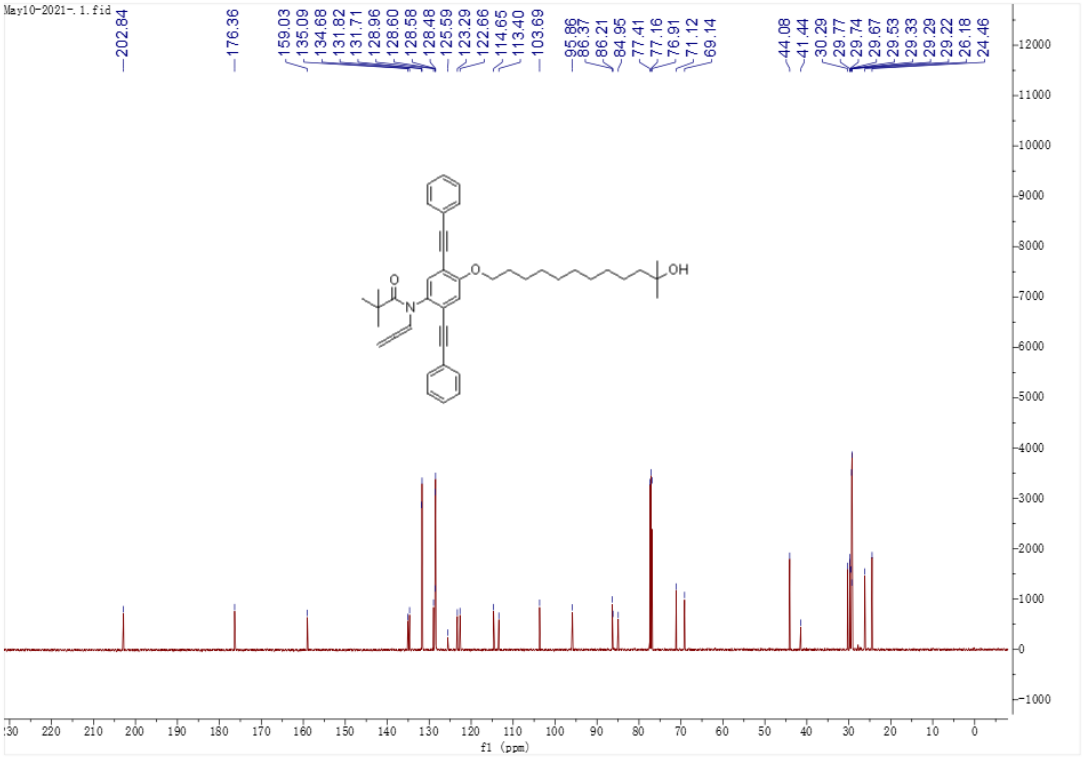
N-(4-((10-hydroxydecyl)oxy)-2,5-bis(phenylethynyl)phenyl)-*N*-(propa-1,2-dien-1-yl) pivalamide **(5p)**



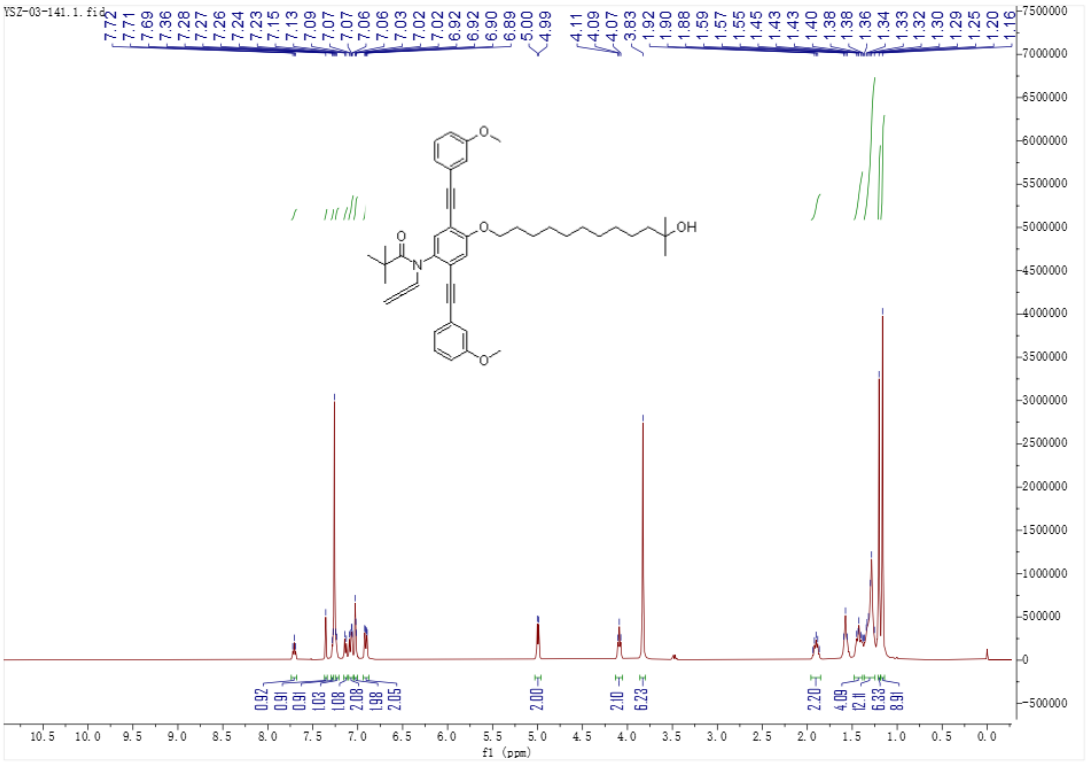


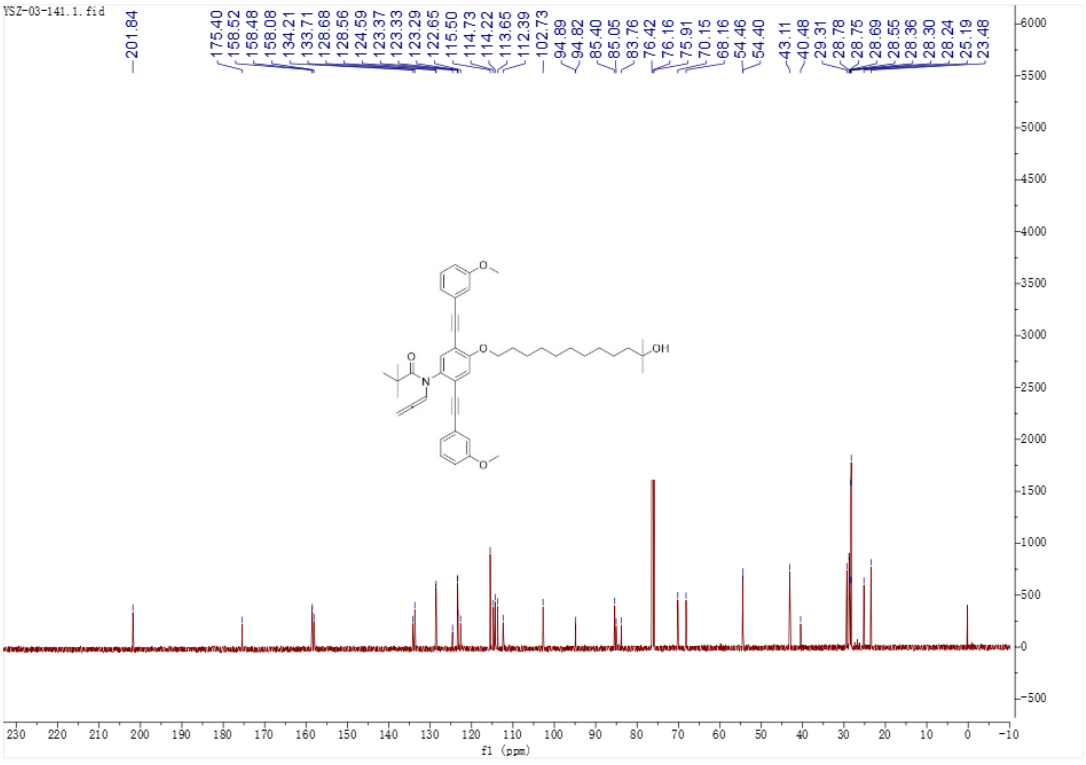
N-(4-((11-hydroxy-11-methyldodecyl)oxy)-2,5-bis(phenylethynyl)phenyl)-*N*-(propa-1,2-dien-1-yl)pivalamide **(5q)**



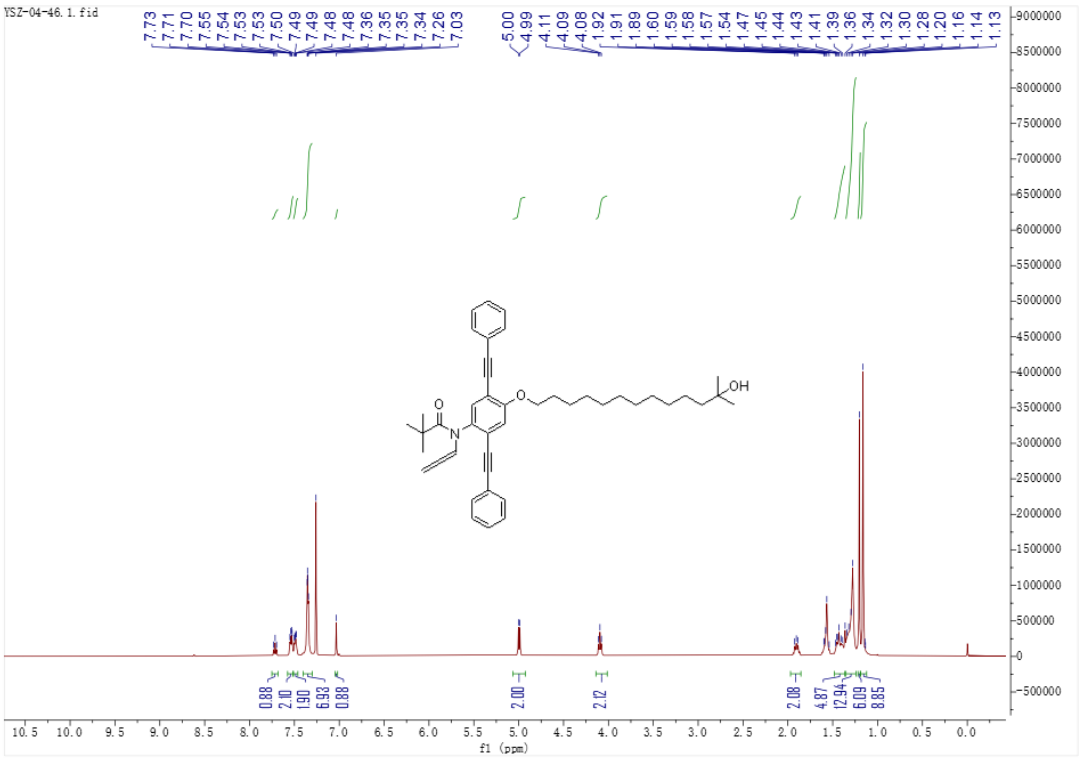


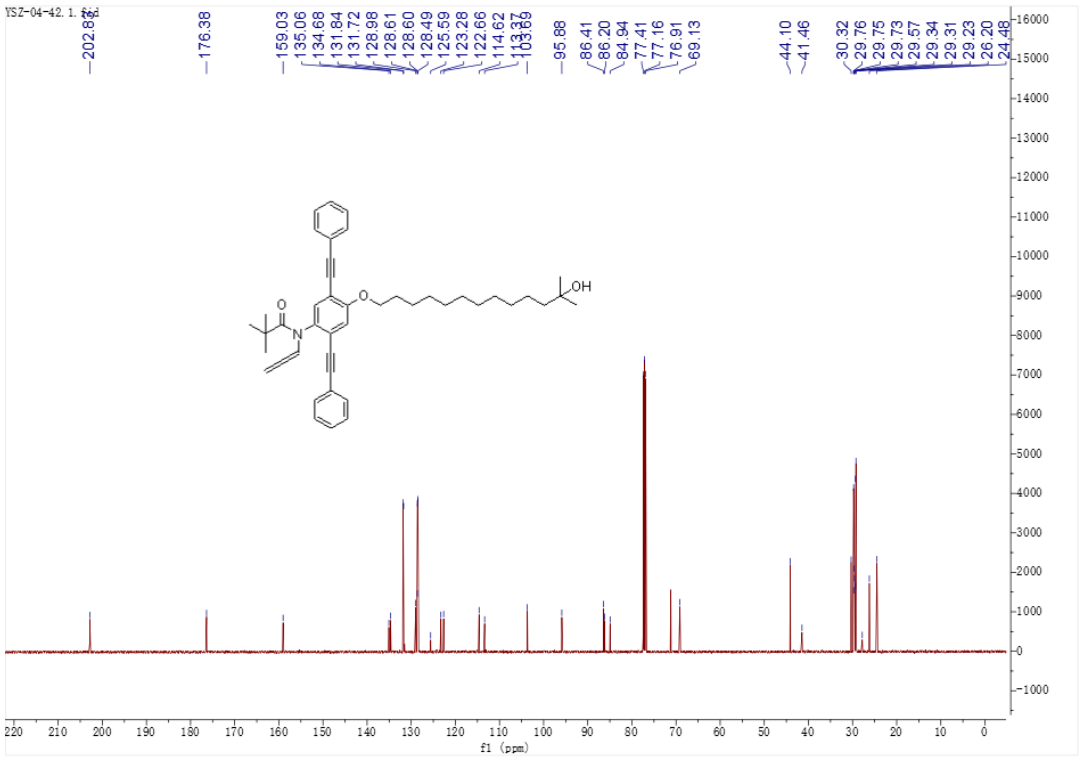
N-(4-((11-hydroxy-11-methyldodecyl)oxy)-2,5-bis((3-methoxyphenyl)ethynyl)-*N*-(propa-1,2-dien-1-yl)pivalamide **(5r)**



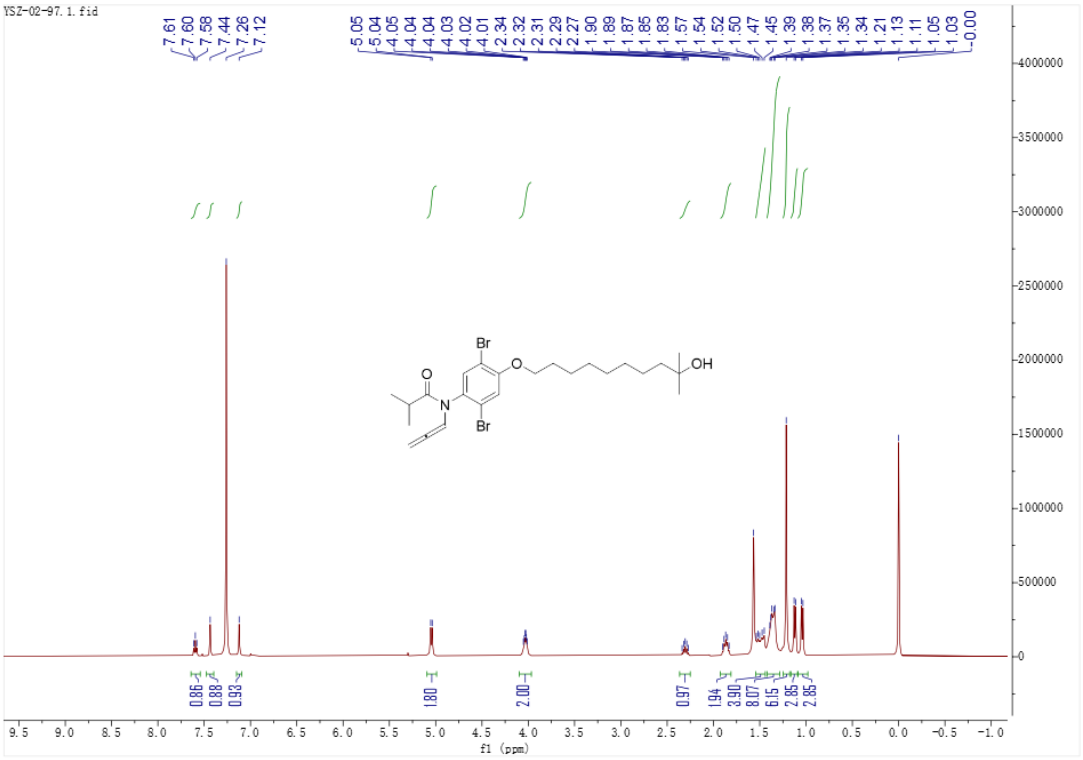


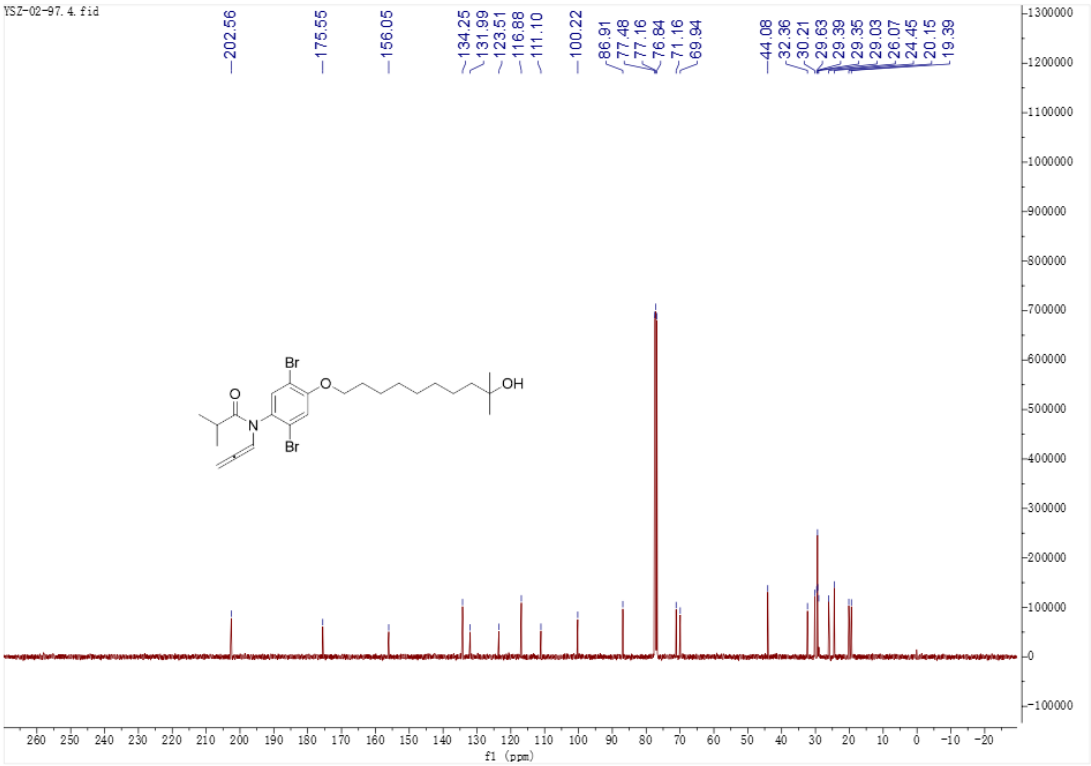
N-(4-((12-hydroxy-12-methyltridecyl)oxy)-2,5-bis(phenylethynyl)phenyl)-*N*-(propa-1,2-dien-1-yl)pivalamide **(5s)**



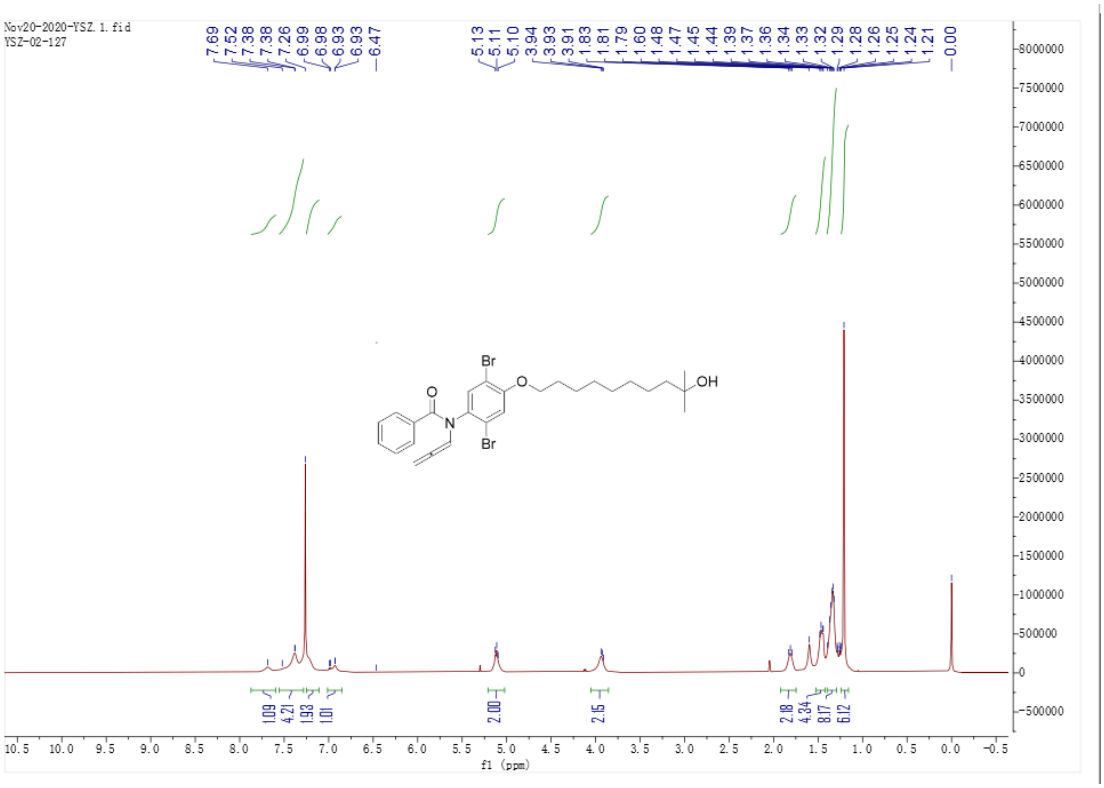


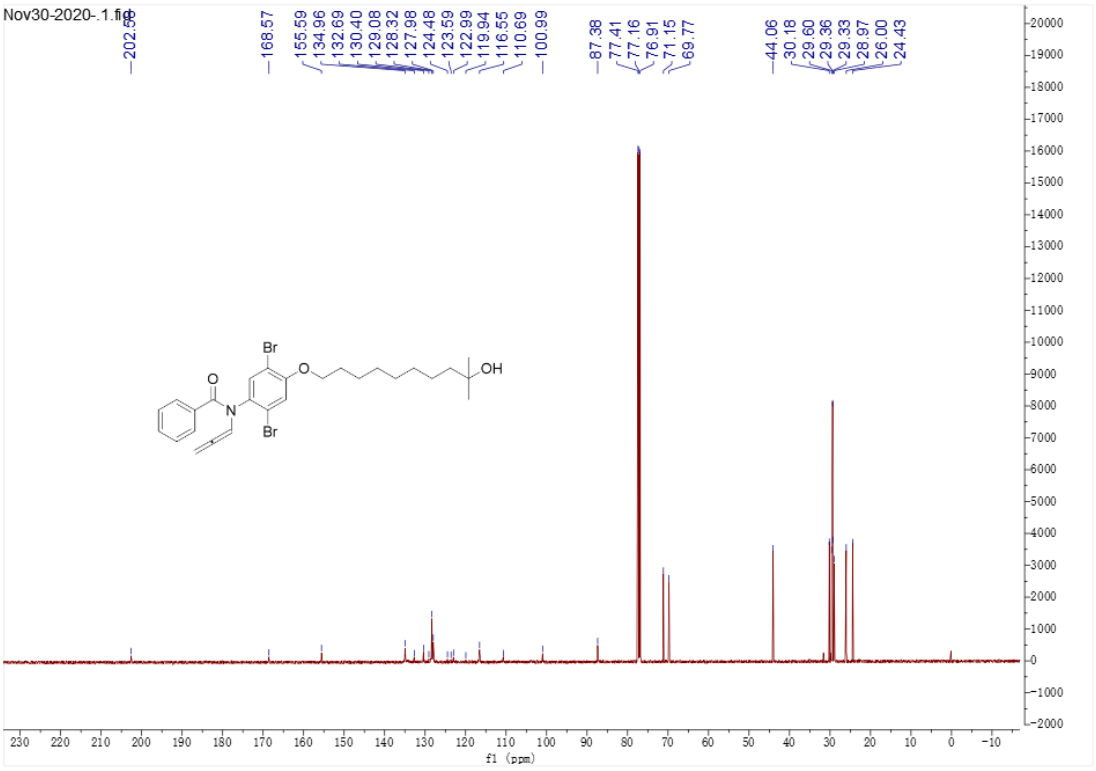
N-(2,5-dibromo-4-((9-hydroxy-9-methyldecyl)oxy)phenyl)-*N*-(propa-1,2-dien-1-yl)isobutyramide **(5t)**



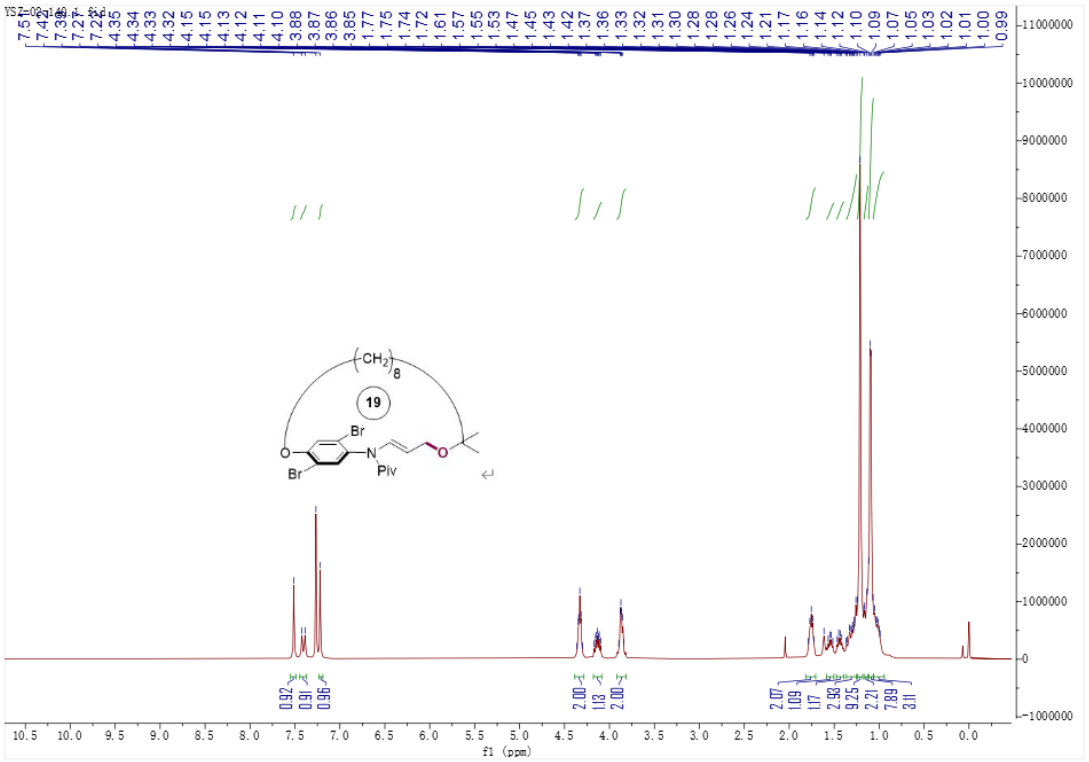


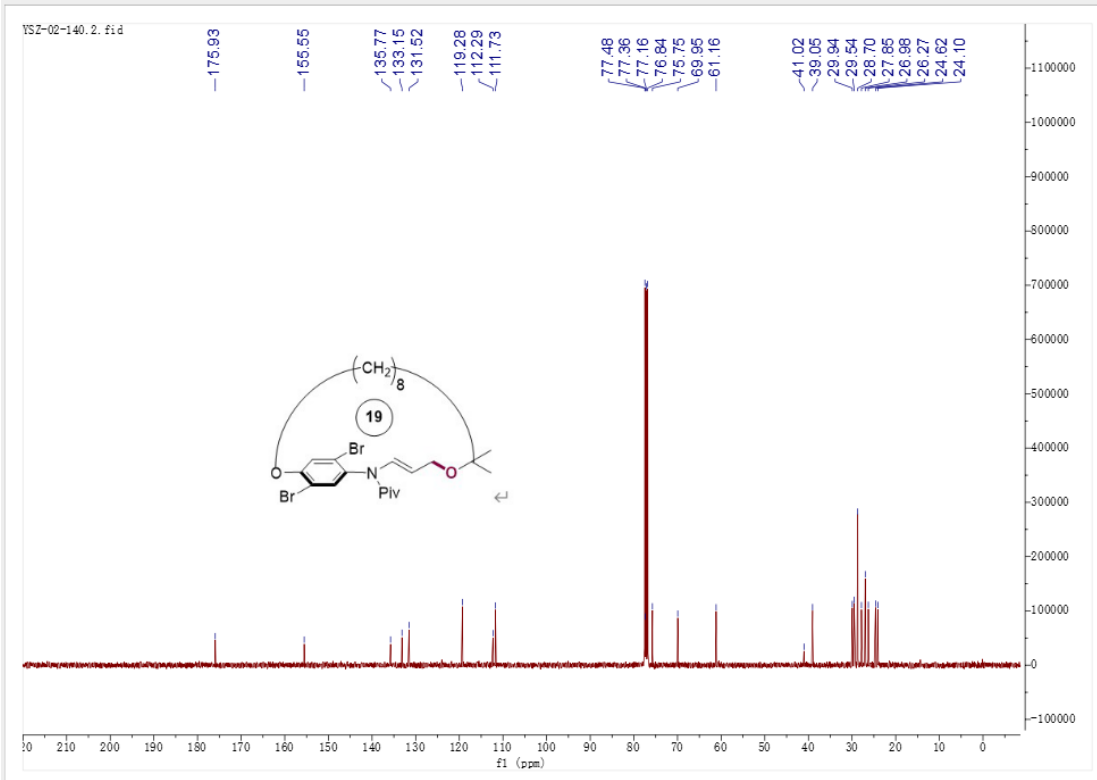
N-(2,5-dibromo-4-((9-hydroxy-9-methyldecyl)oxy)phenyl)-*N*-(propa-1,2-dien-1-yl)benzamide **(5u)**



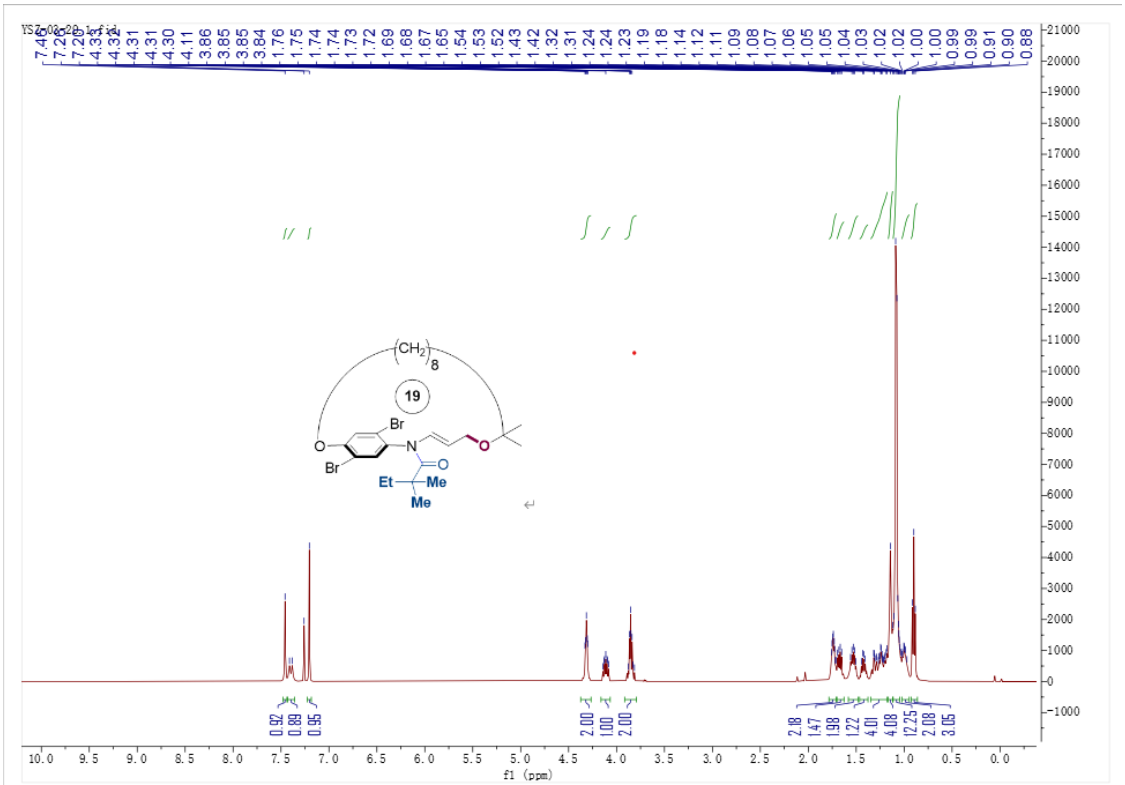


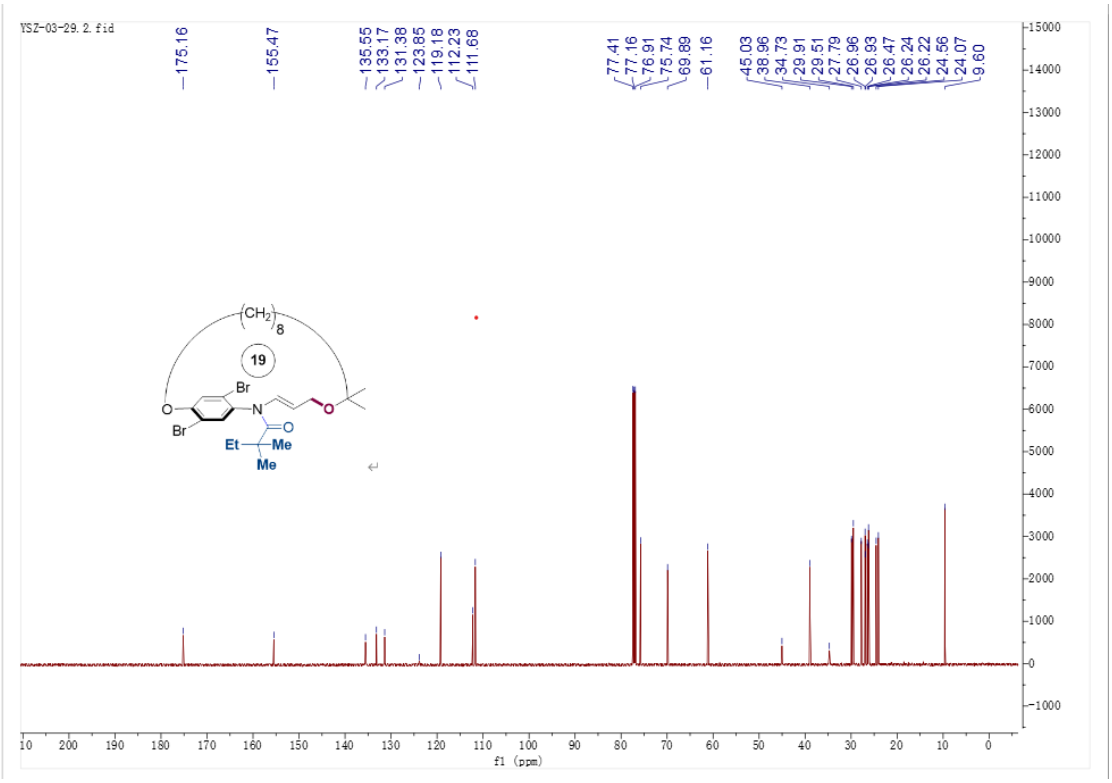
(R_p,*E*)-1-(1^2,1^5-dibromo-7,7-dimethyl-6,16-dioxa-2-aza-1(1,4)-benzenacyclohexadeca p- pan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6a)**



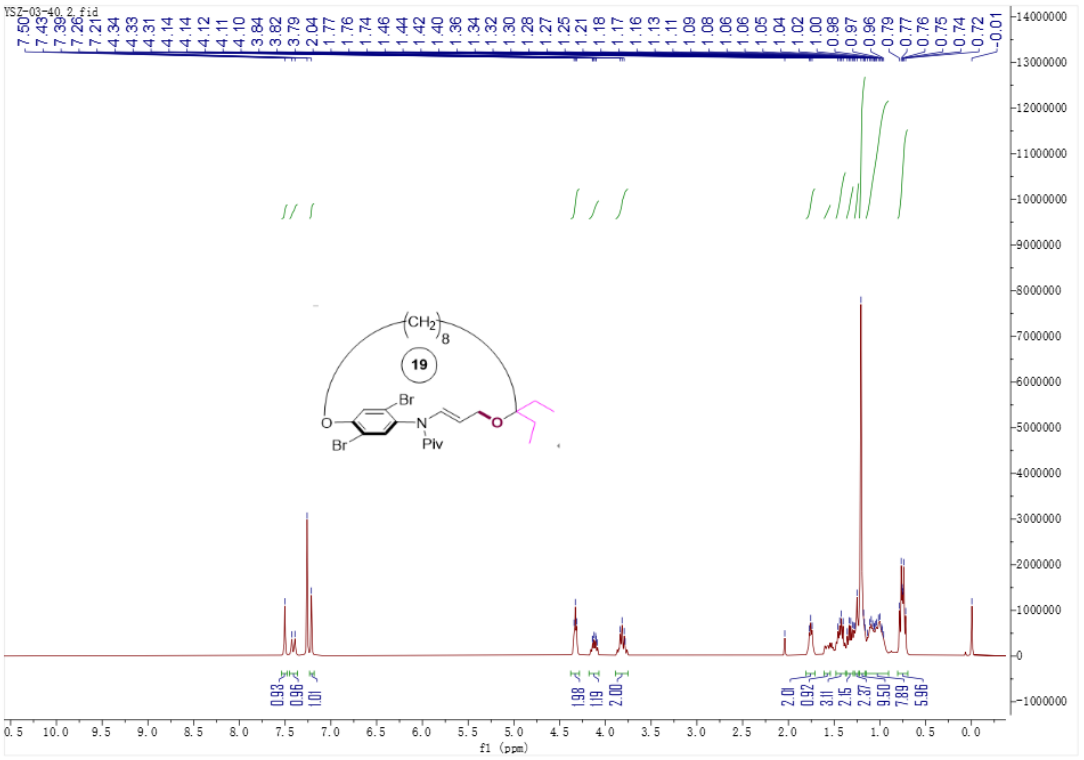


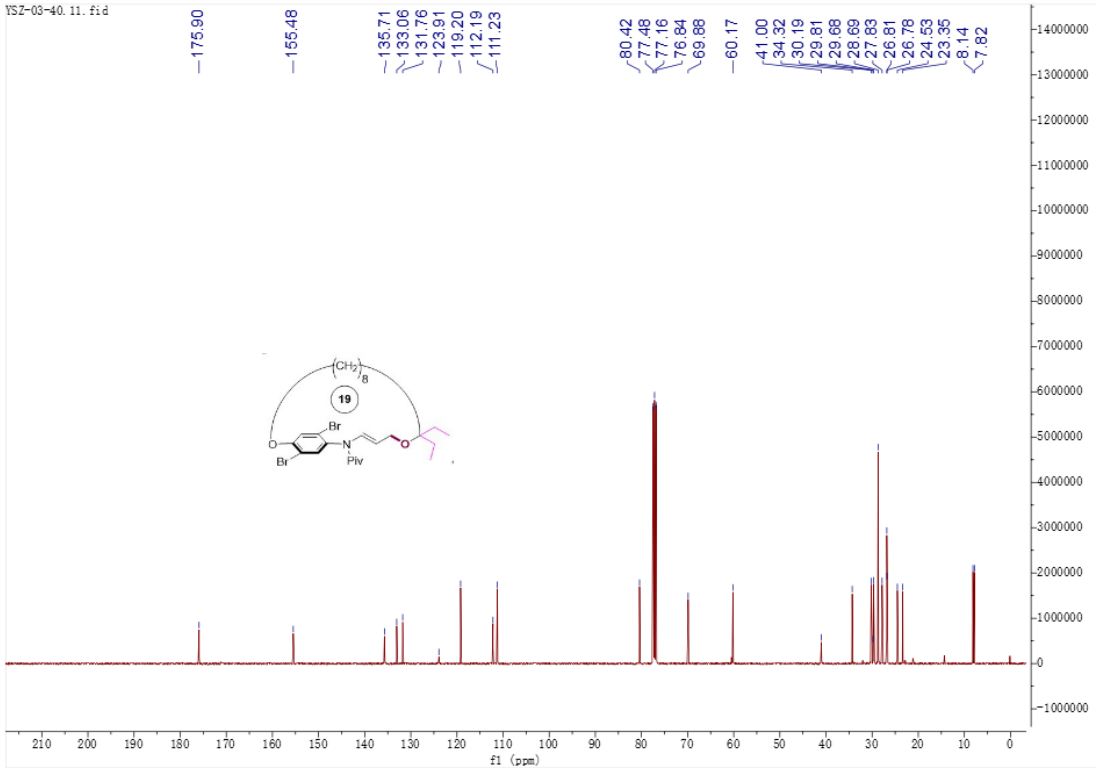
(R_p,*E*)-(1-(1^2,1^5-dibromo-7,7-dimethyl-6,16-dioxa-2-aza-1(1,4)-benzenacyclohexadecap- han-3-en-2-yl)-2,2- dimethylbutan-1-one **(6b)**



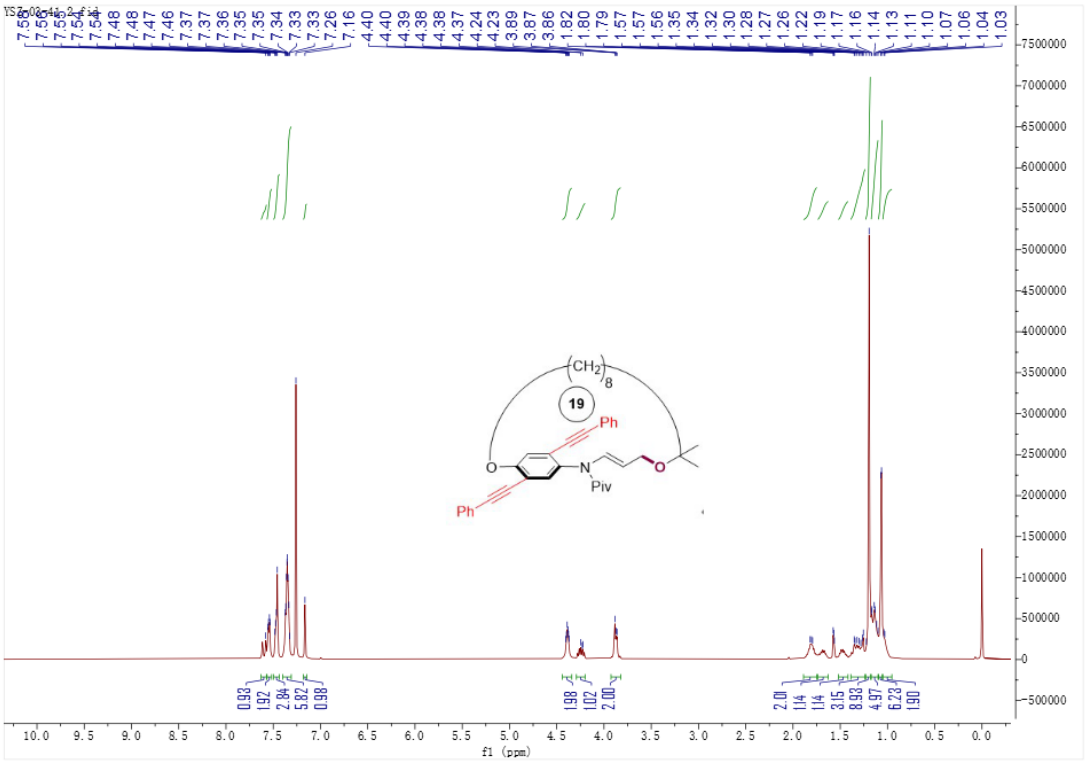


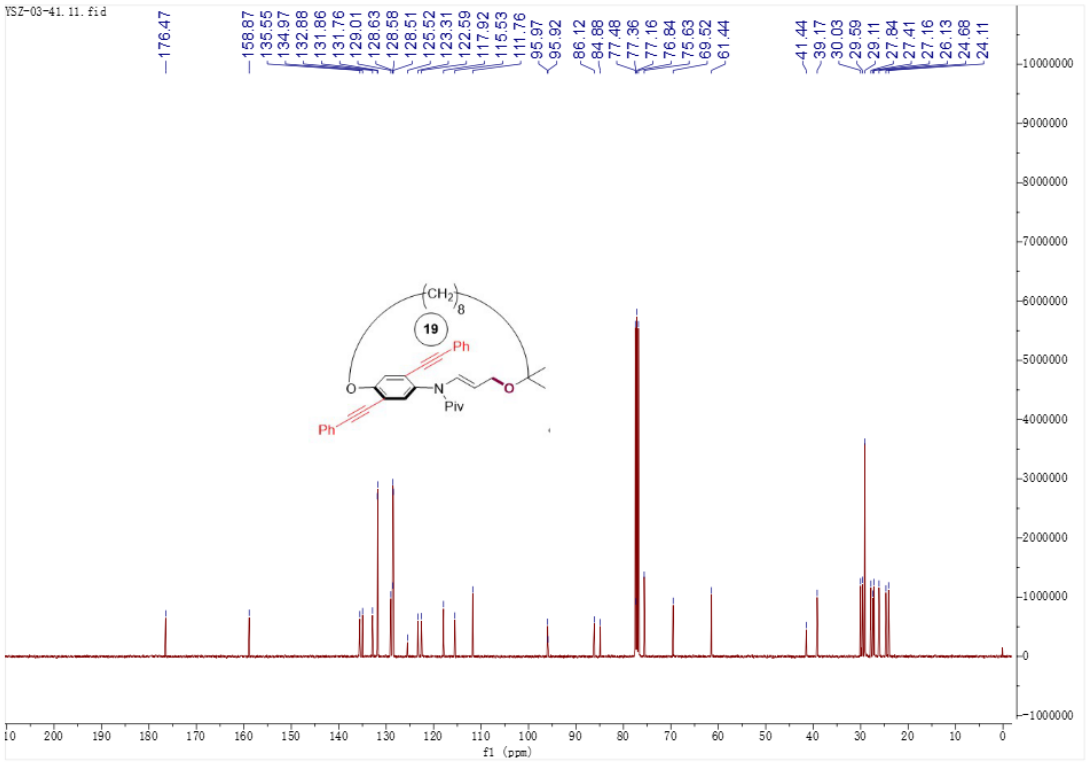
(R_p,*E*)-1-(1^2,1^5-dibromo-7,7-diethyl-6,15-dioxa-2-aza-1(1,4)-enzenacyclopentadecaph- an-3-en-2-yl)-2,2-dimethylpropan-1-one **(6c)**



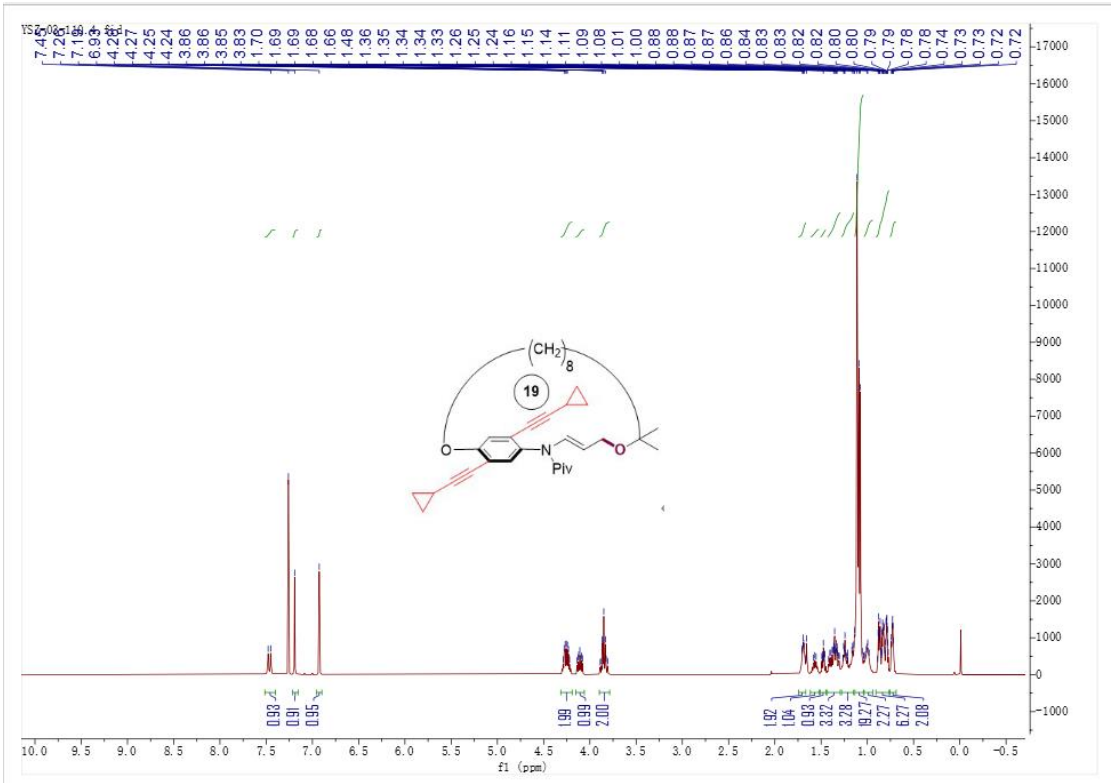


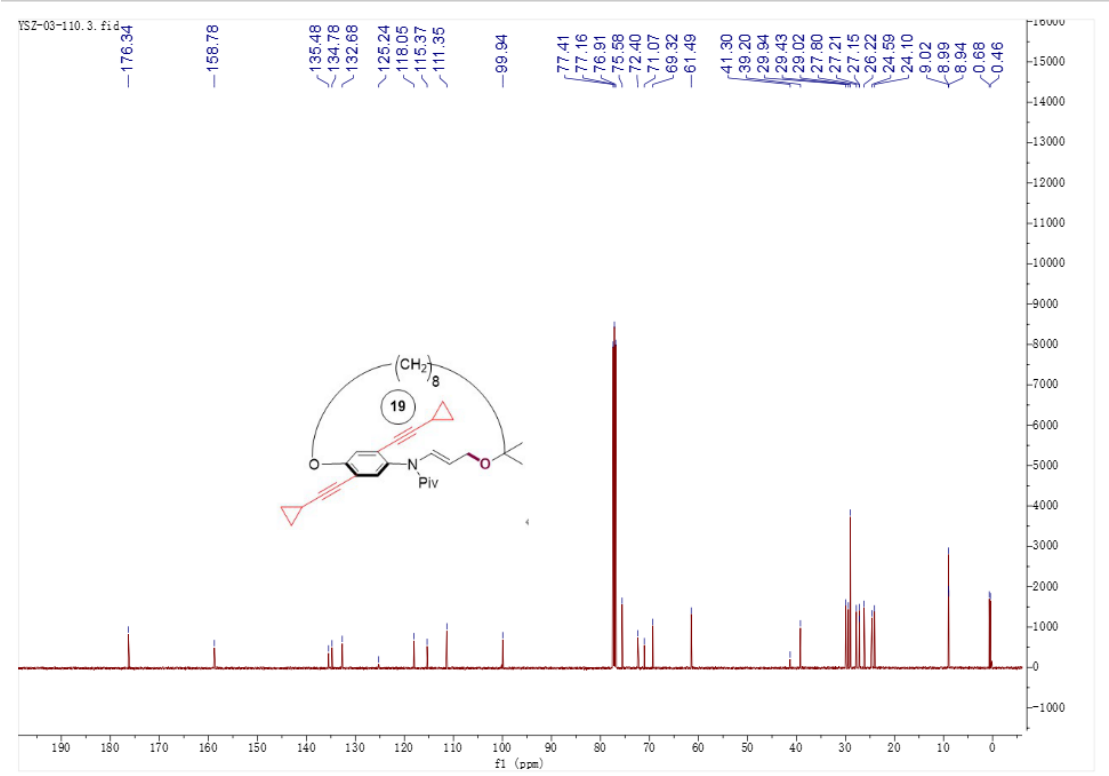
(R_p,*E*)-1-(7,7-dimethyl-1^2,1^5-bis(phenylethynyl)-6,16-dioxa-2-aza-1(1,4)-benzenacyclo- hexadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6d)**



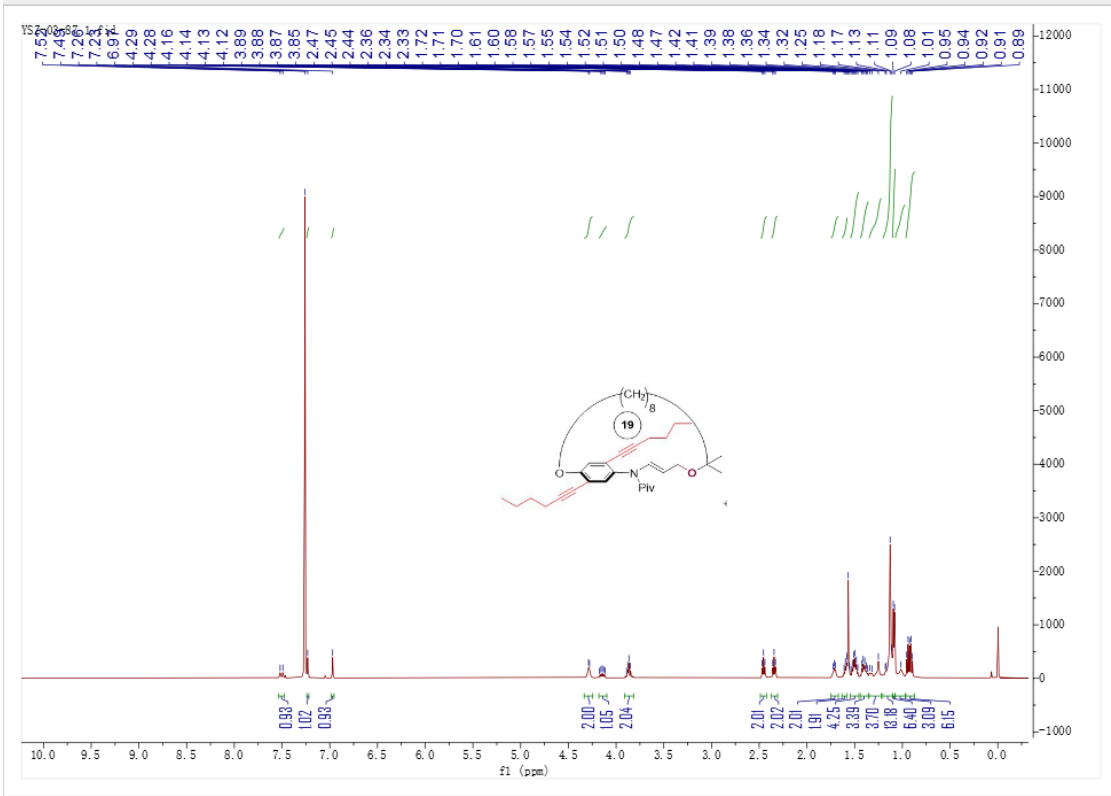


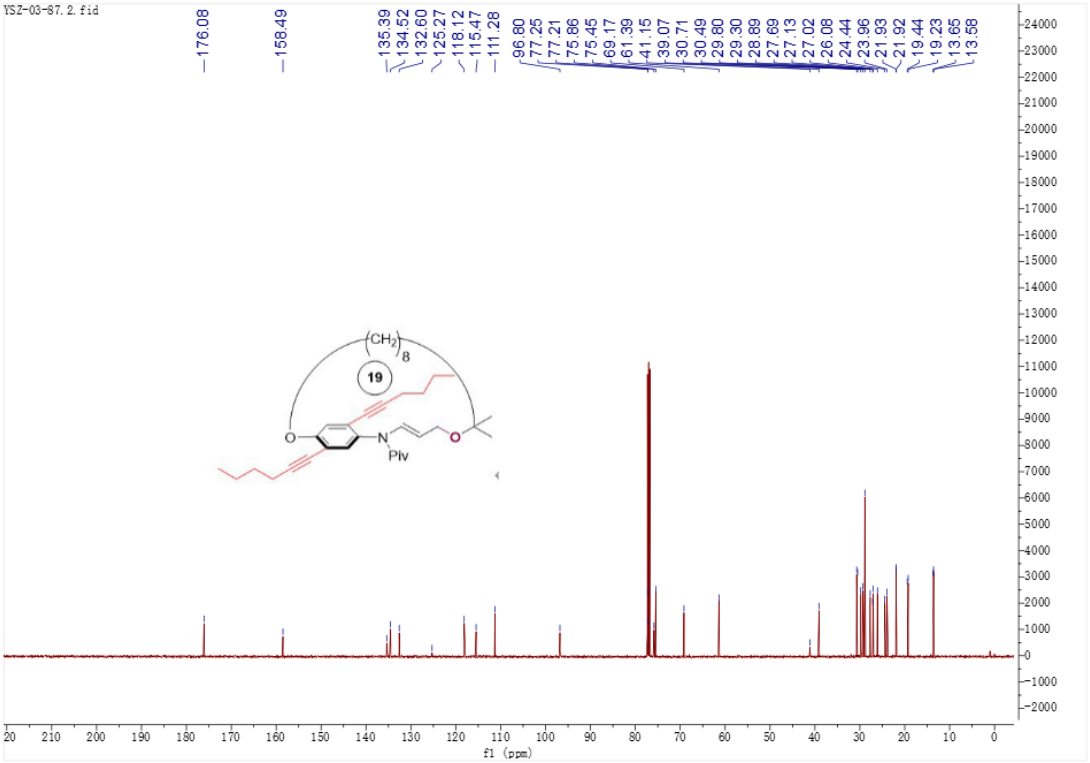
(R_p,*E*)-1-(1^2,1^5-bis(cyclopropylethynyl)-7,7-dimethyl-6,16-dioxa-2-aza-1(1,4)-benzen ac- yclohexadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6e)**



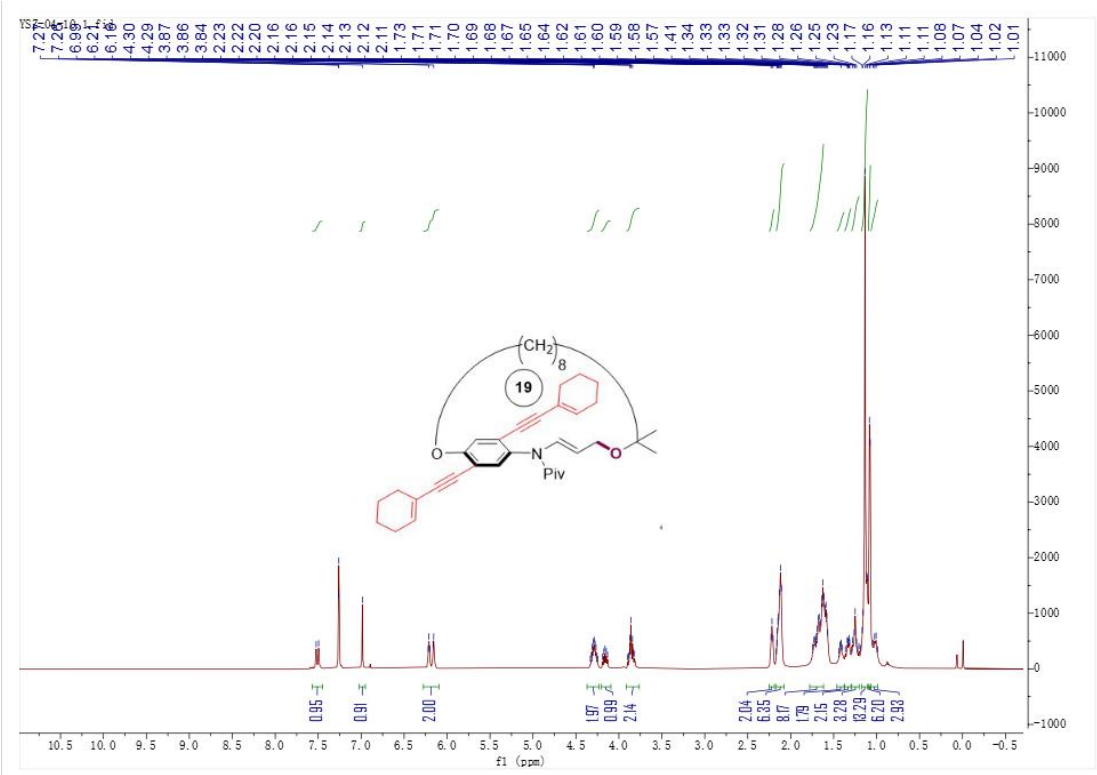


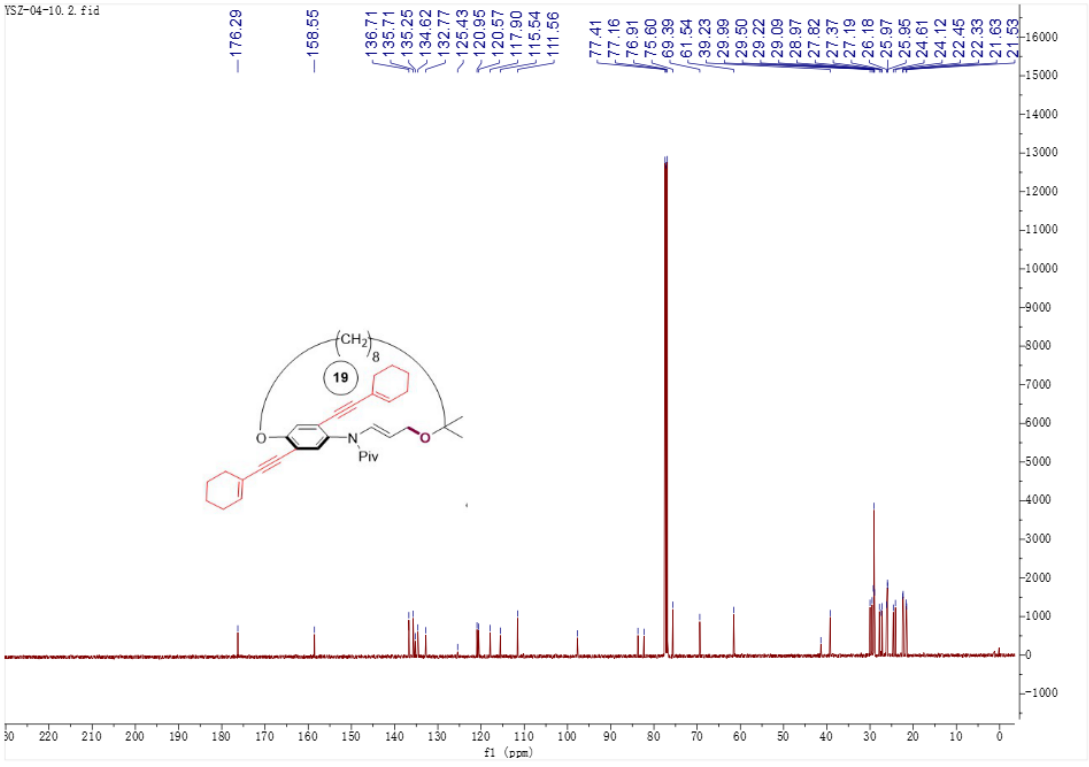
(R_p,*E*)-1-(1^2,1^5-di(hex-1-yn-1-yl)-7,7-dimethyl-6,16-dioxa-2-aza-1(1,4)-benzenacyclohe-xadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6f)**



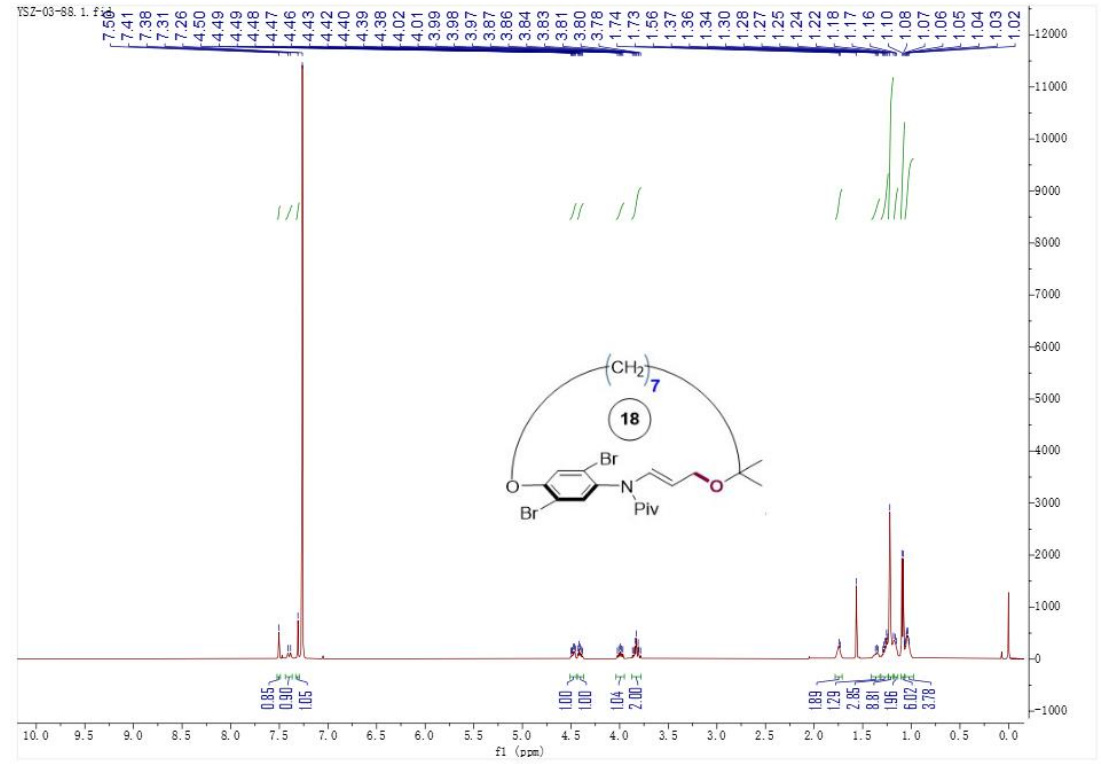


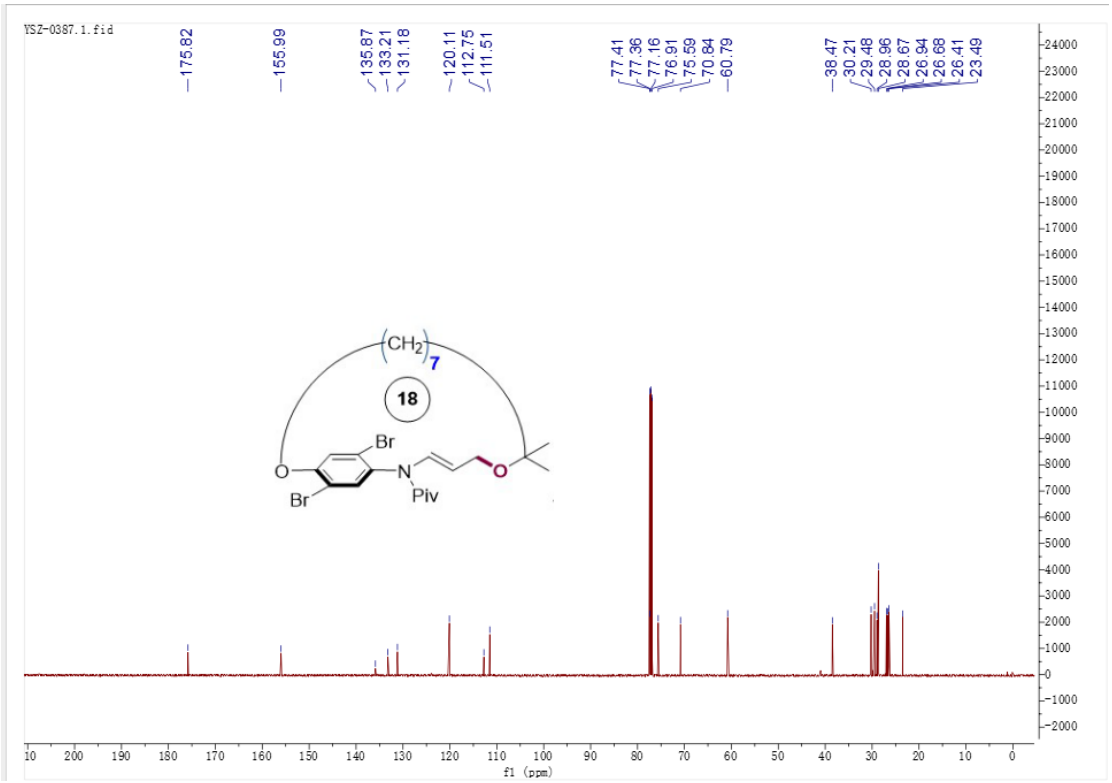
(R_p,*E*)-1-(1^2,1^5-bis(cyclohex-1-en-1-ylethynyl)-7,7-dimethyl-6,16-dioxa-2-aza-1(1,4)-benzenacyclohexadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6g)**



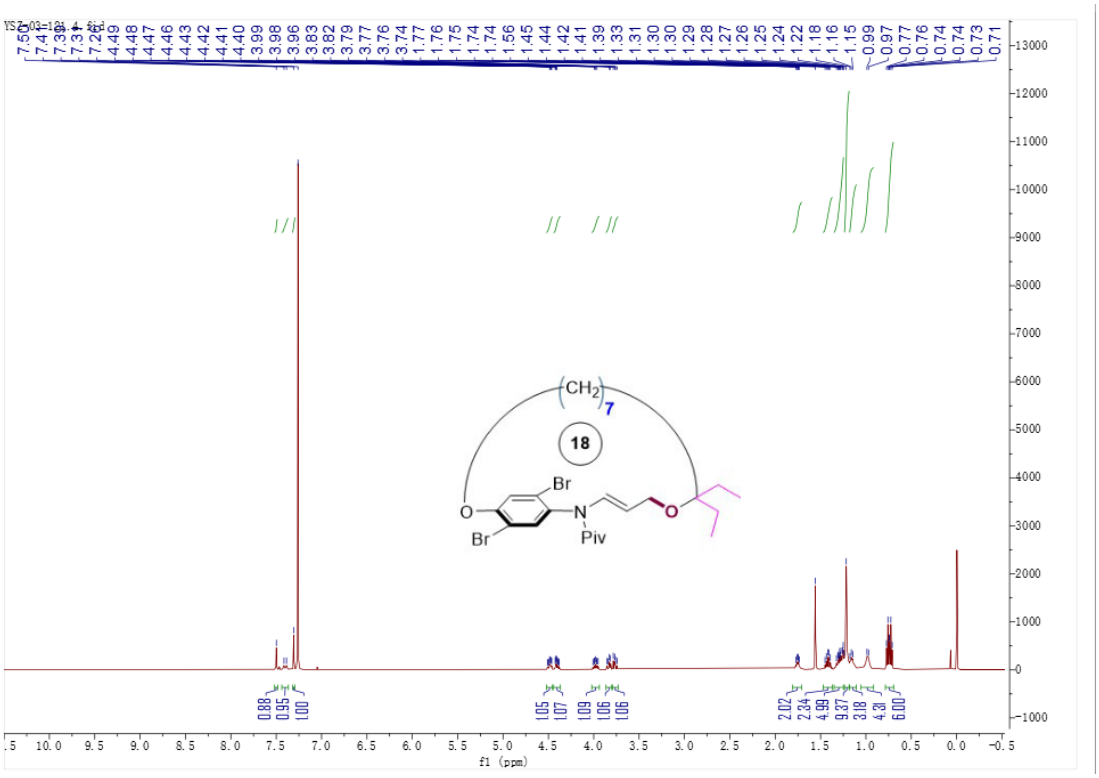


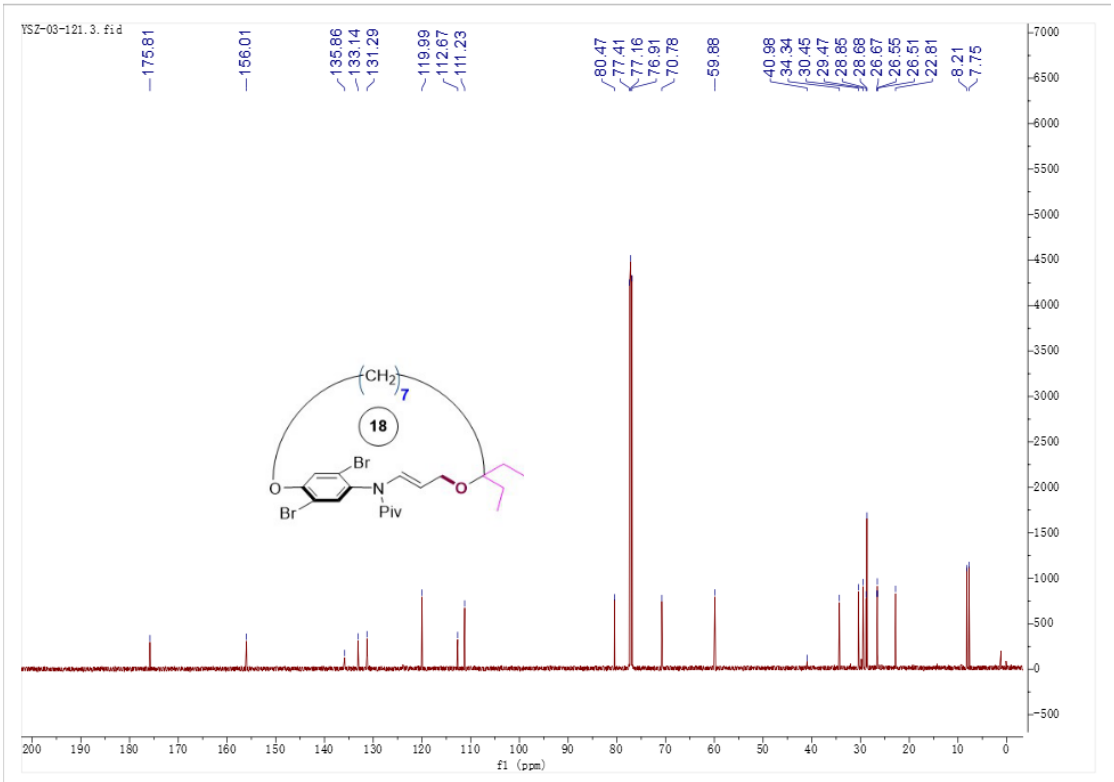
(R_p,*E*)-1-(1^2,1^5-dibromo-7,7-dimethyl-6,15-dioxa-2-aza-1(1,4)-benzenacyclopentadecap- han-3-en-2-yl)-2,2-dimethylpropan-1-one **(6h)**



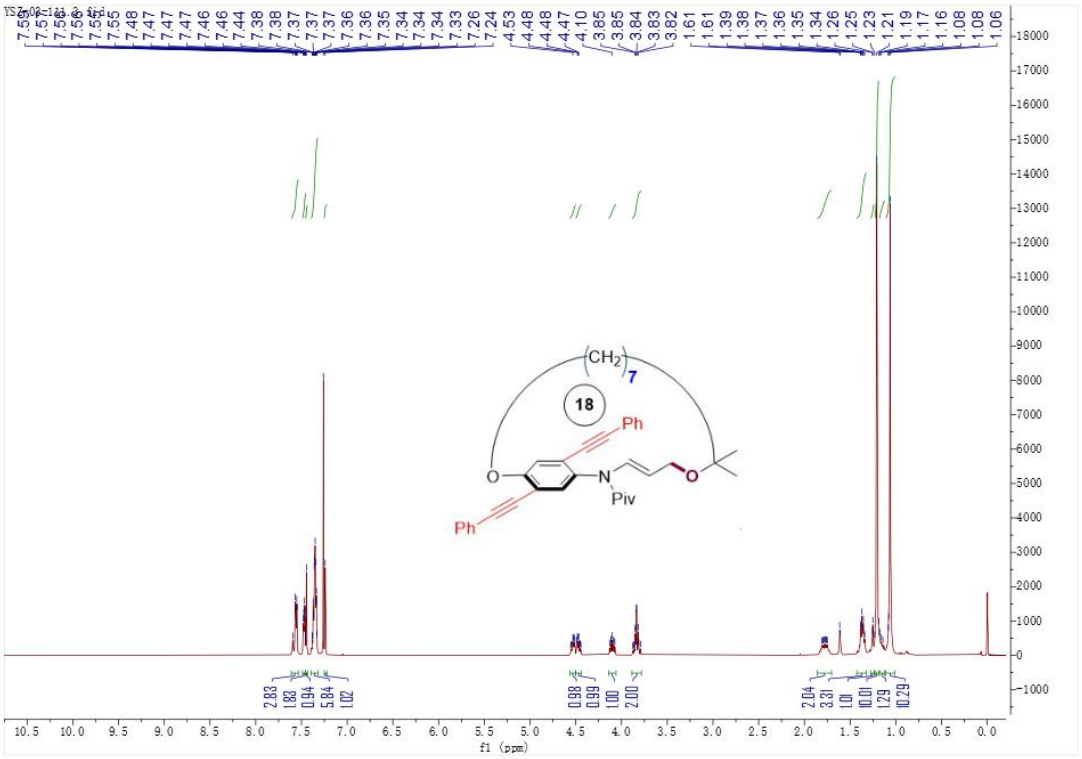


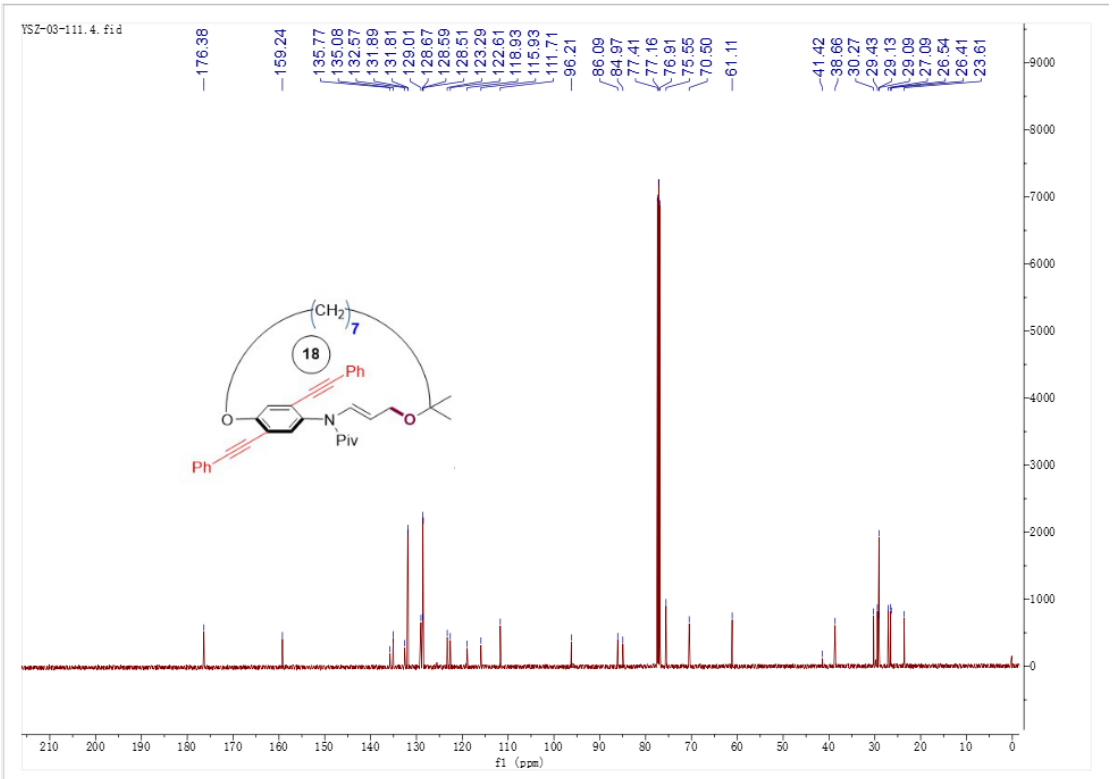
(R_p,*E*)-1-(1^2,1^5-dibromo-7,7-diethyl-6,16-dioxa-2-aza-1(1,4)-benzenacyclohexadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6i)**



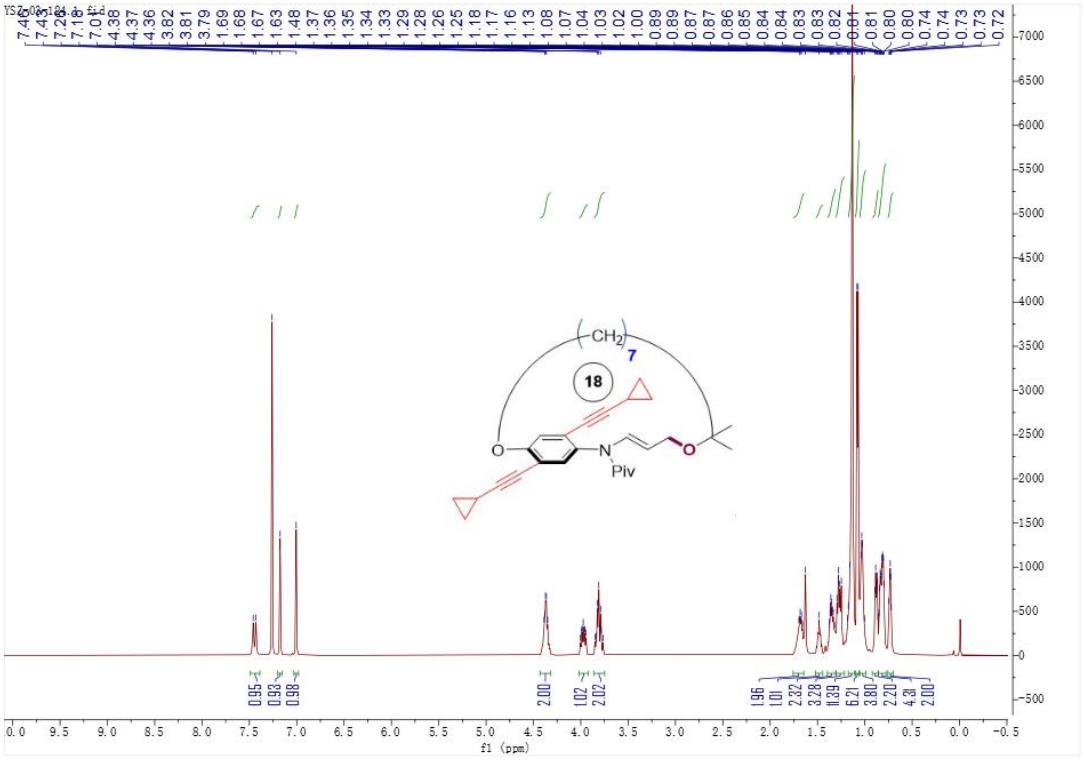


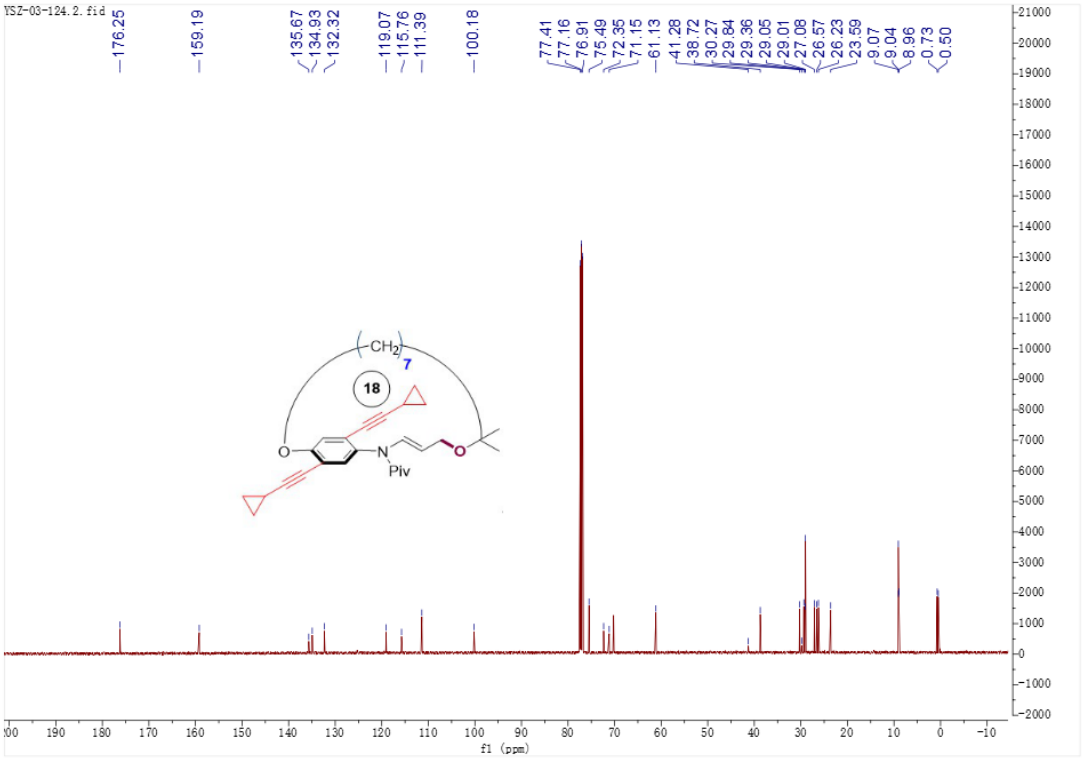
(R_p,*E*)-1-(7,7-dimethyl-1^2,1^5-bis(phenylethynyl)-6,15-dioxa-2-aza-1(1,4)-benzenacycl op- entadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6j)**



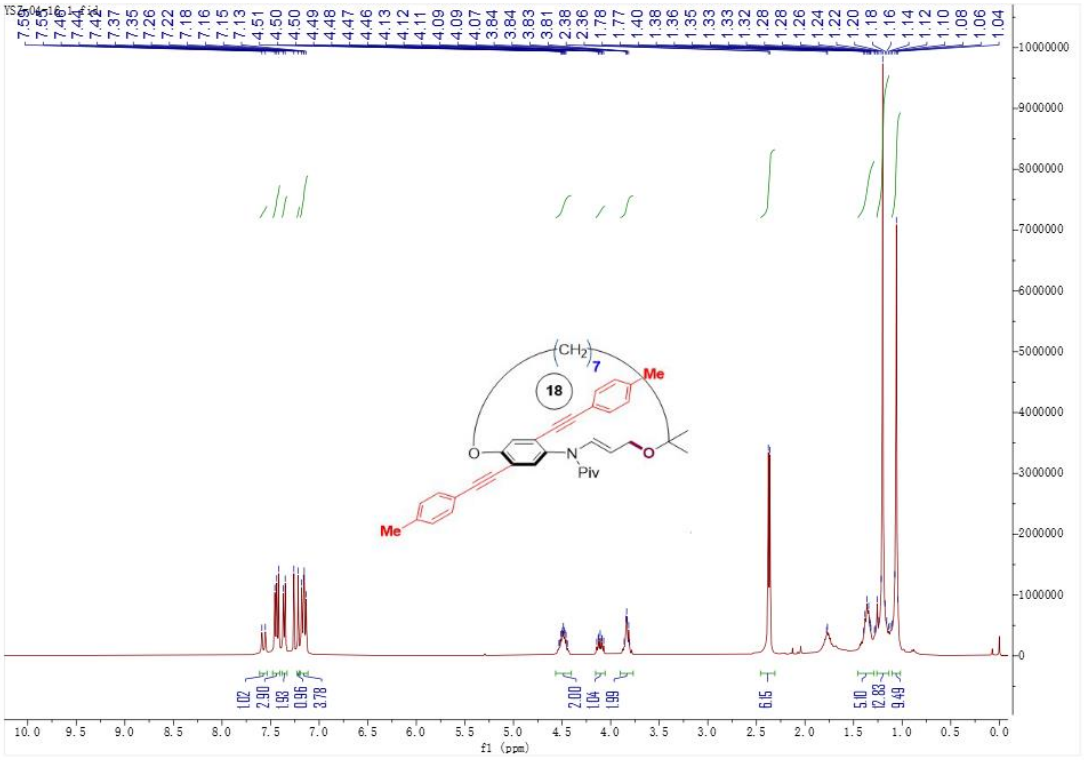


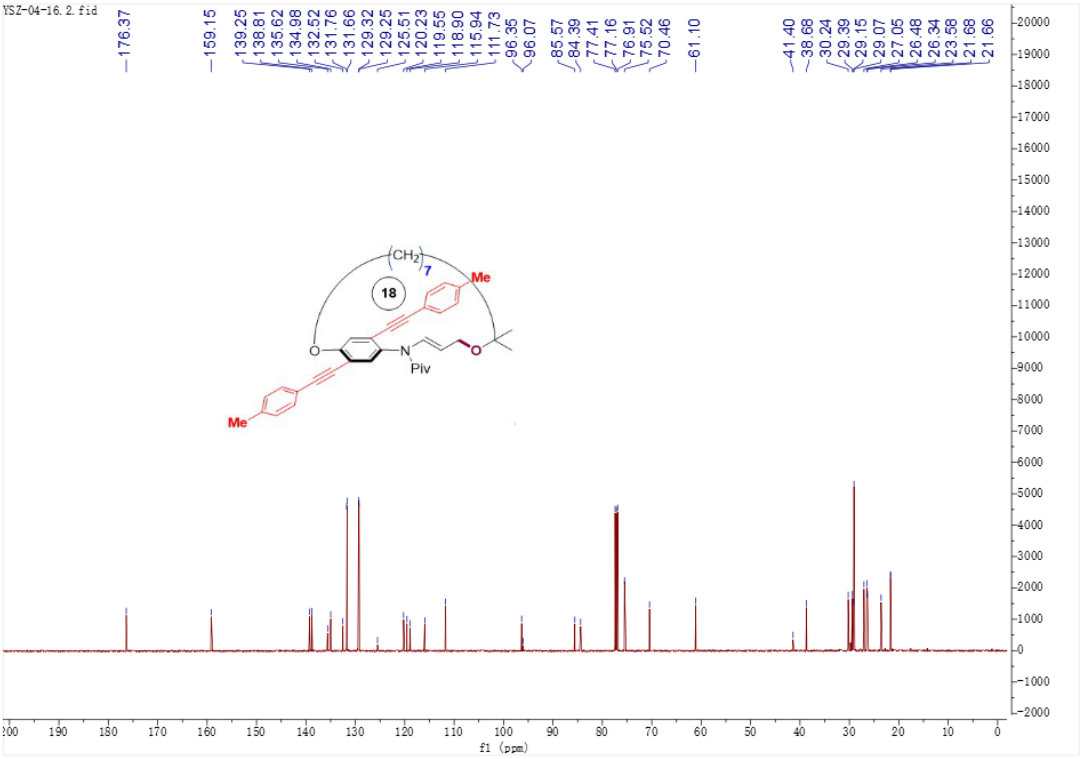
(R_p,*E*)-1-(1^2,1^5-bis(cyclopropylethynyl)-7,7-dimethyl-6,15-dioxa-2-aza-1(1,4)-benzen ac- cyclopentadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6k)**



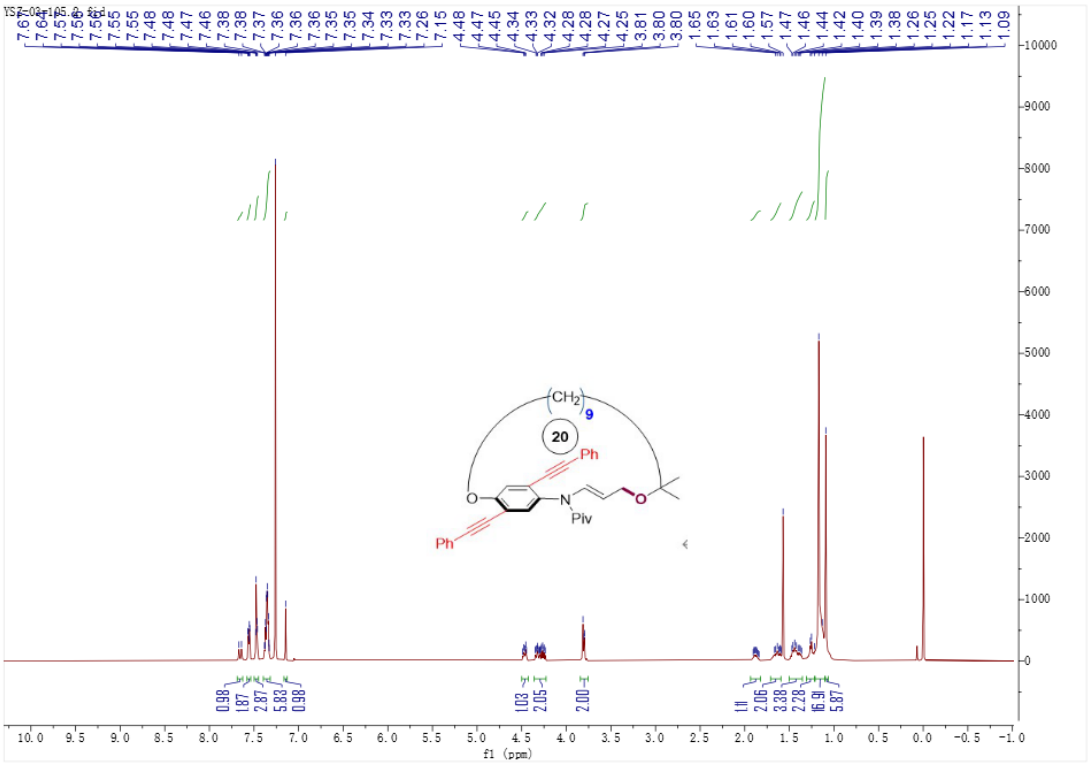


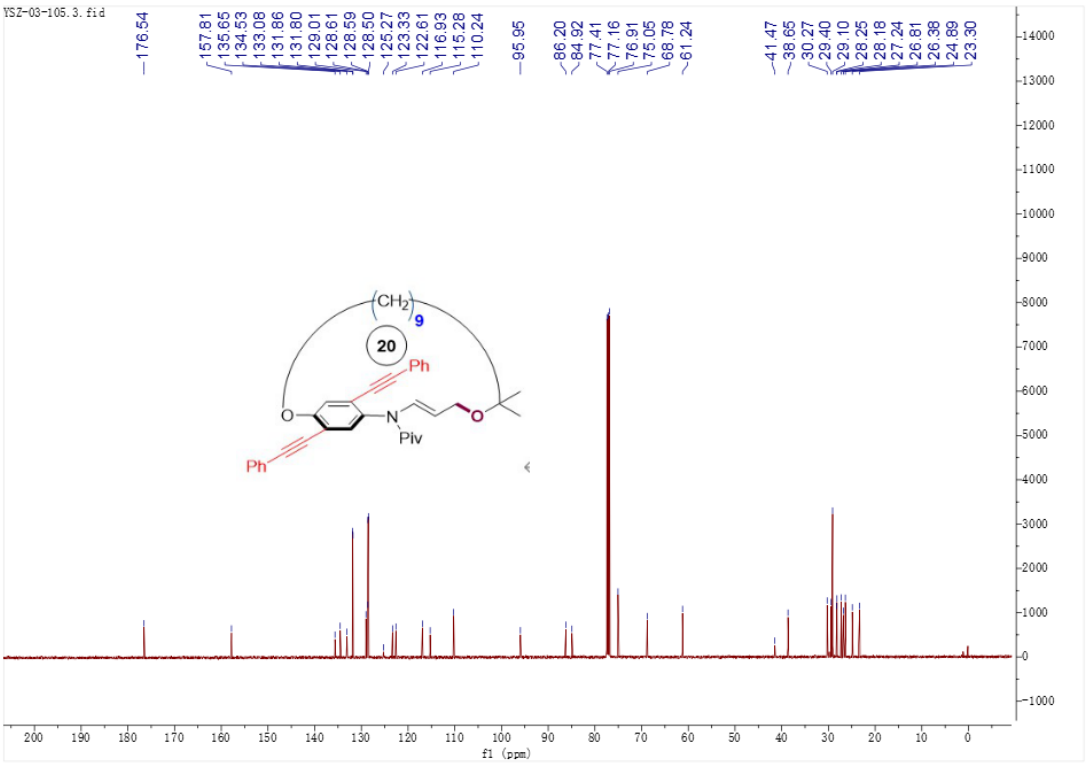
(R_p,*E*)-1-(7,7-dimethyl-1^2,1^5-bis(p-tolylethynyl)-6,15-dioxa-2-aza-1(1,4)-benzenacyclop-entadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6l)**



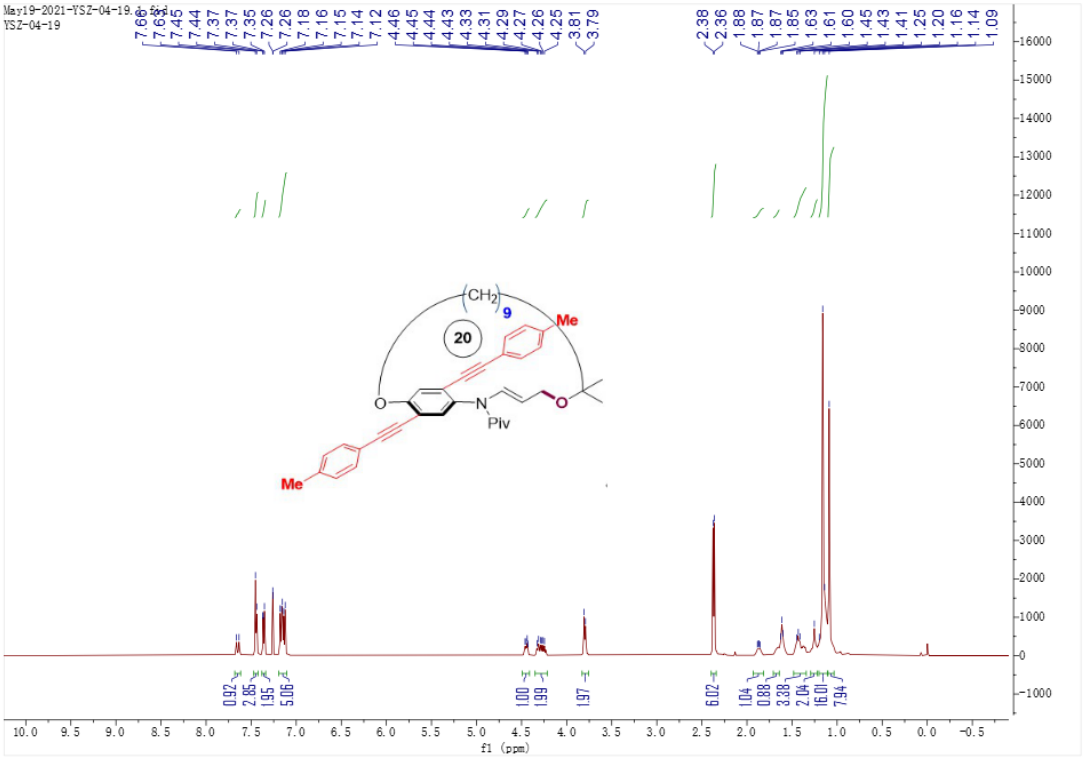


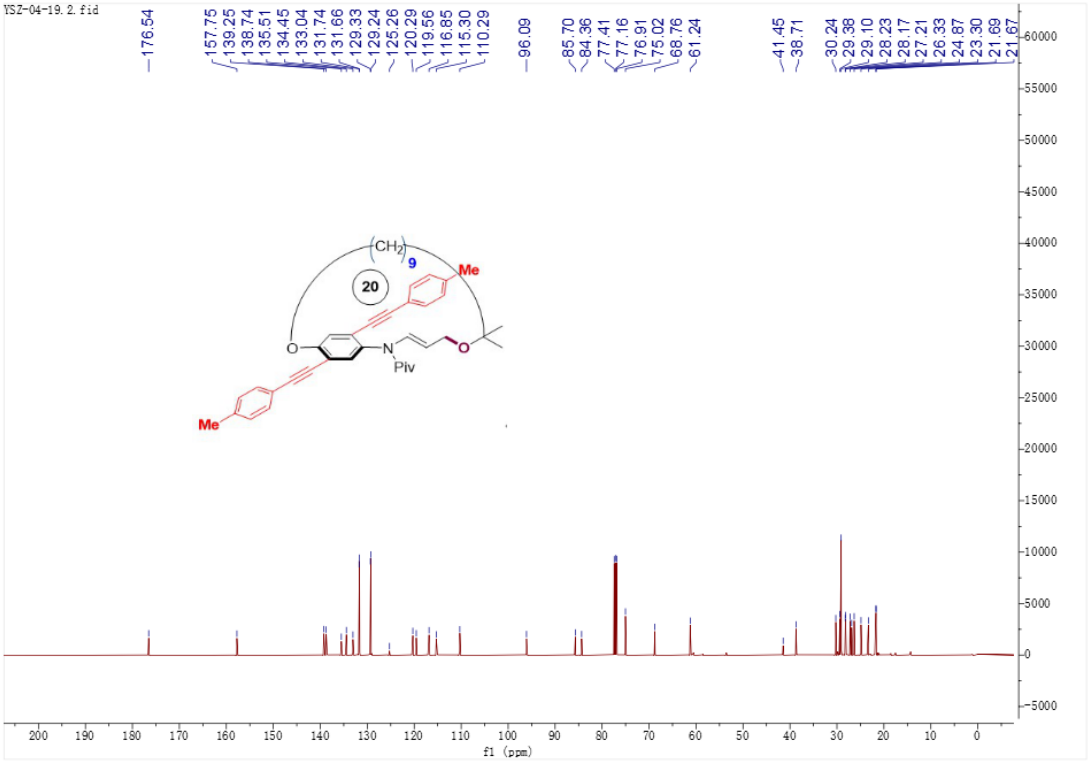
(R_p,*E*)-1-(7,7-dimethyl-1^2,1^5-bis(phenylethynyl)-6,17-dioxa-2-aza-1(1,4)-benzenacycloh- eptadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6m)**



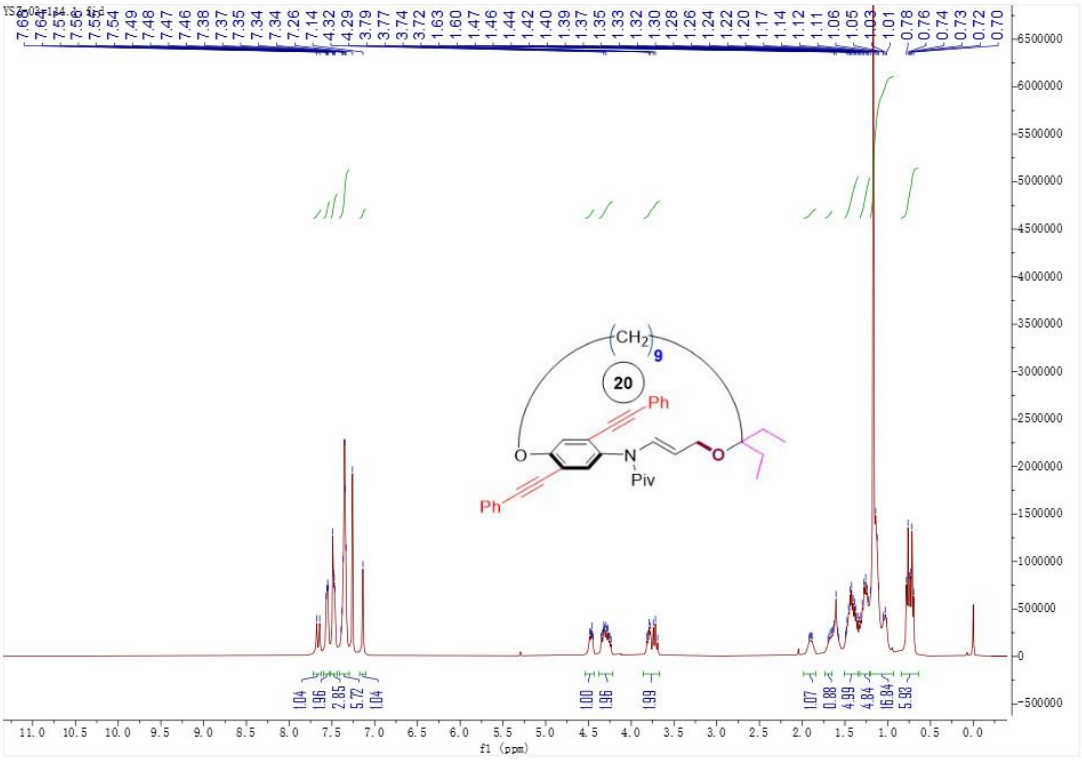


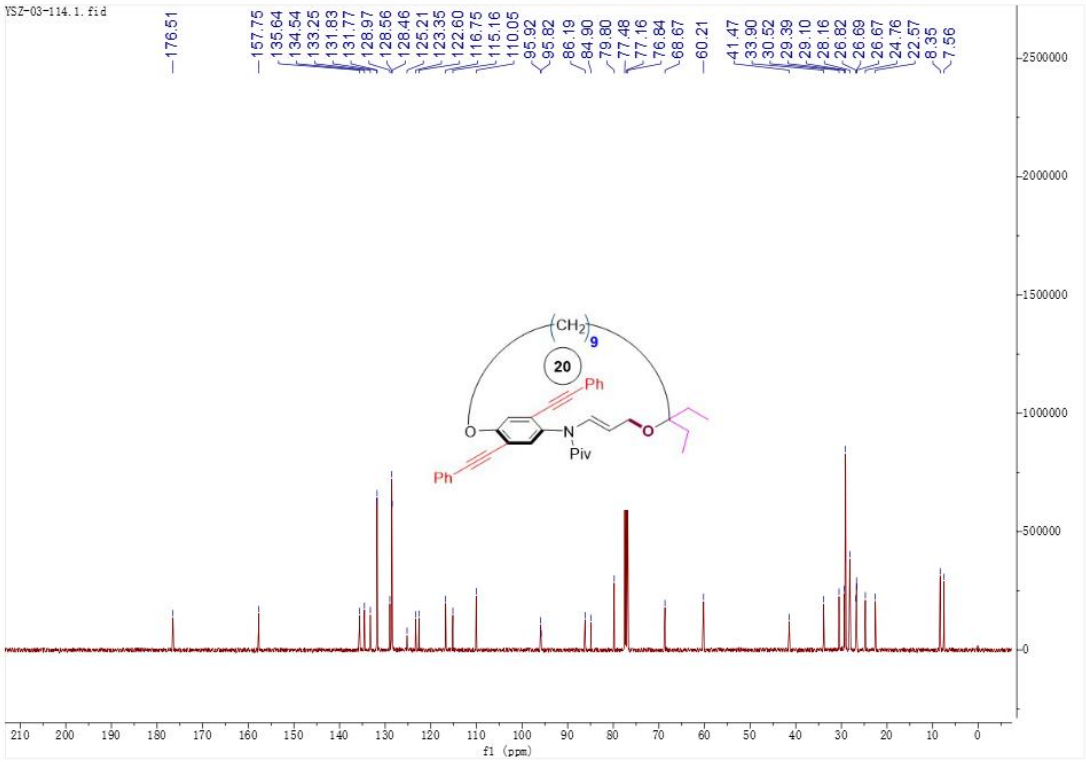
(R_p,*E*)-1-(7,7-dimethyl-1^2,1^5-bis(p-tolylethynyl)-6,17-dioxa-2-aza-1(1,4)-benzenacycl oh- eptadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6n)**



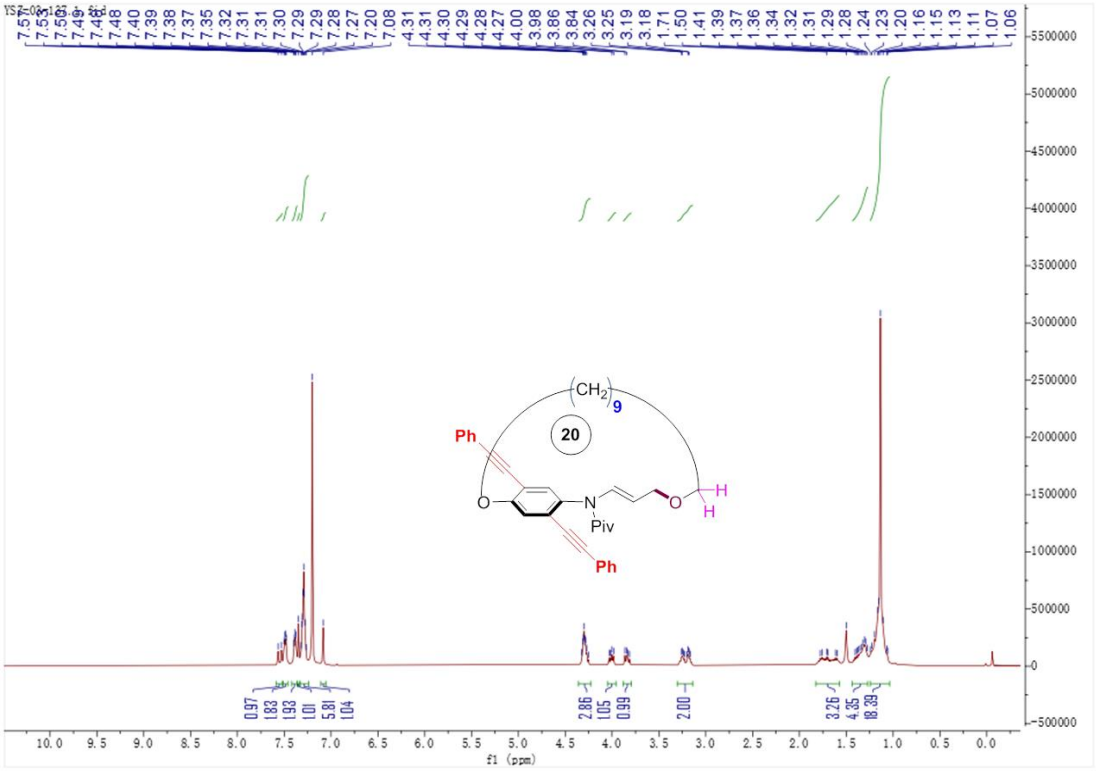


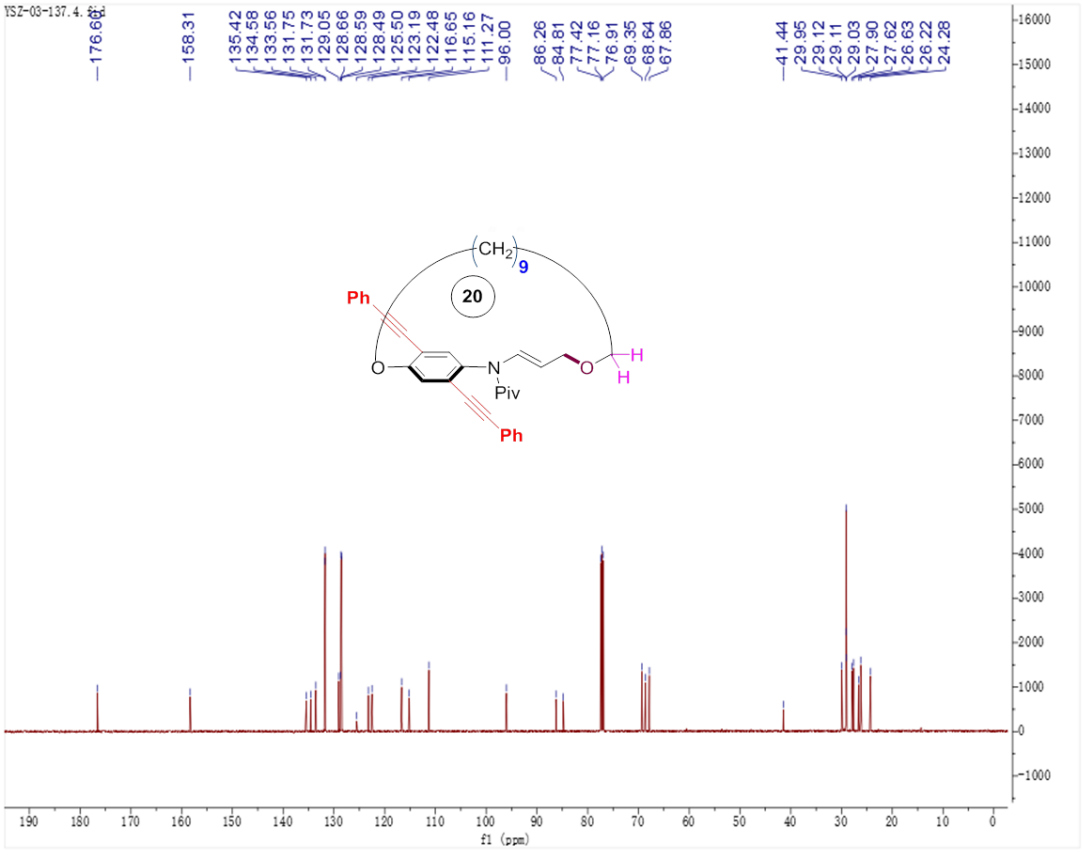
(R_p,*E*)-1-(7,7-diethyl-1^2,1^5-bis(phenylethynyl)-6,17-dioxa-2-aza-1(1,4)-benzenacyclo he- ptadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6o)**



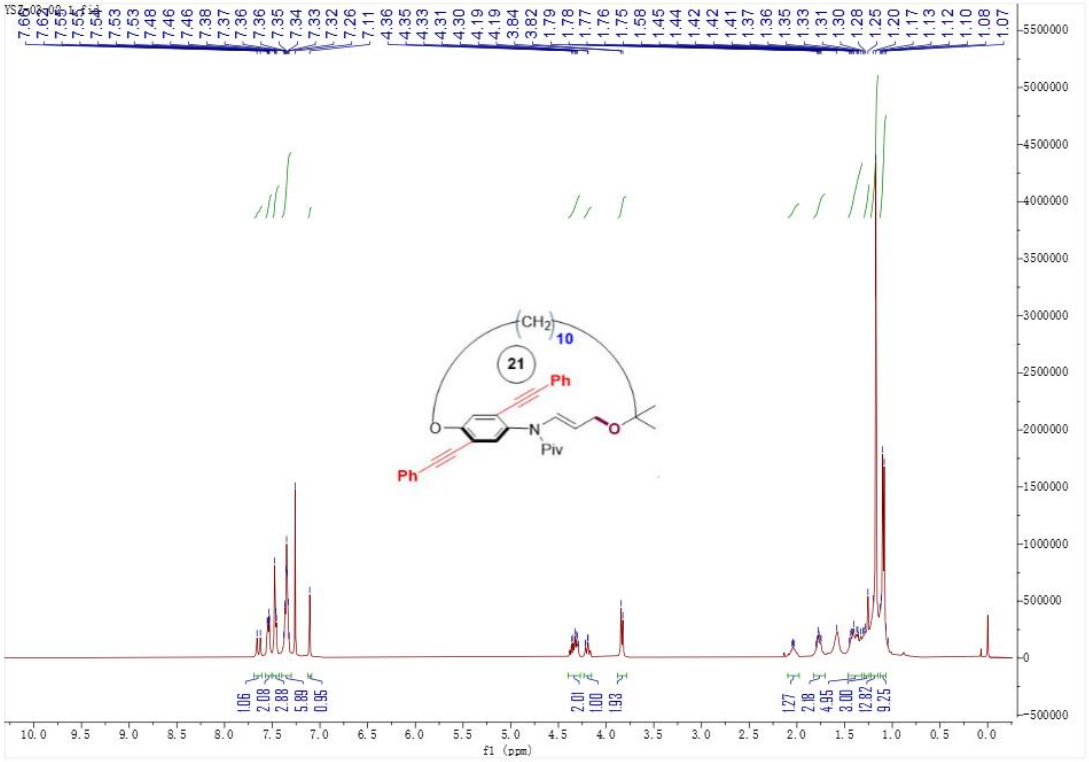


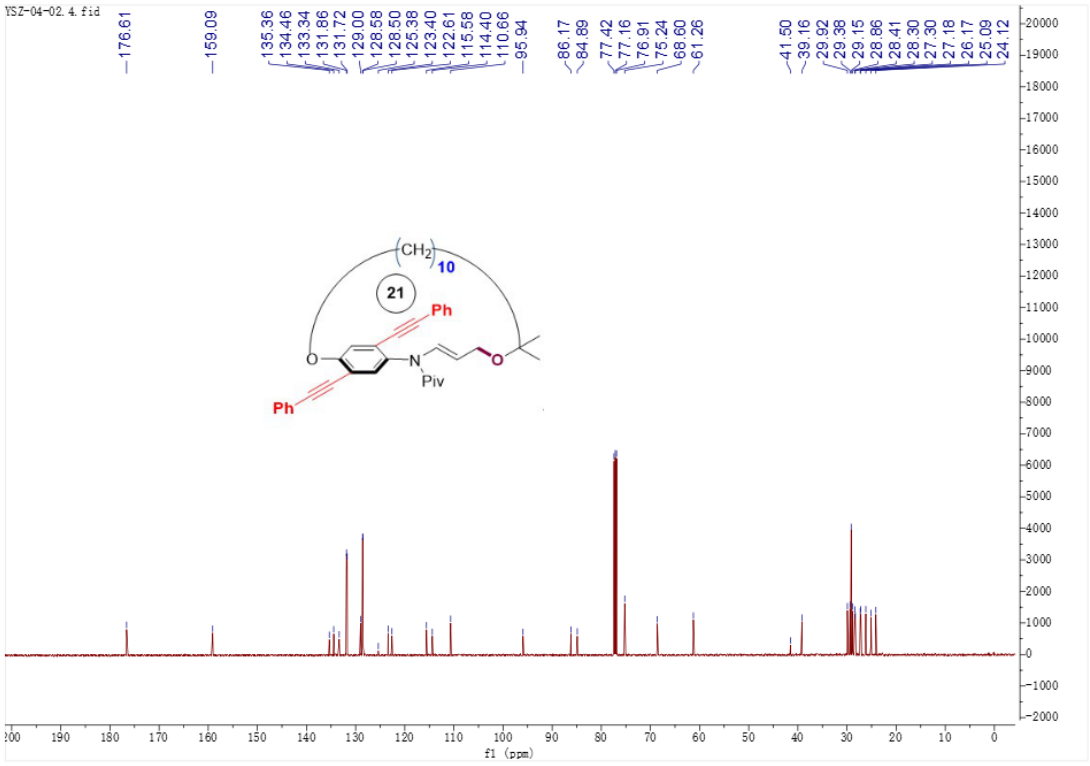
(S_p,*E*)-1-(1^2,1^5-bis(phenylethynyl)-6,17-dioxa-2-aza-1(1,4)-benzenacycloheptadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6p)**



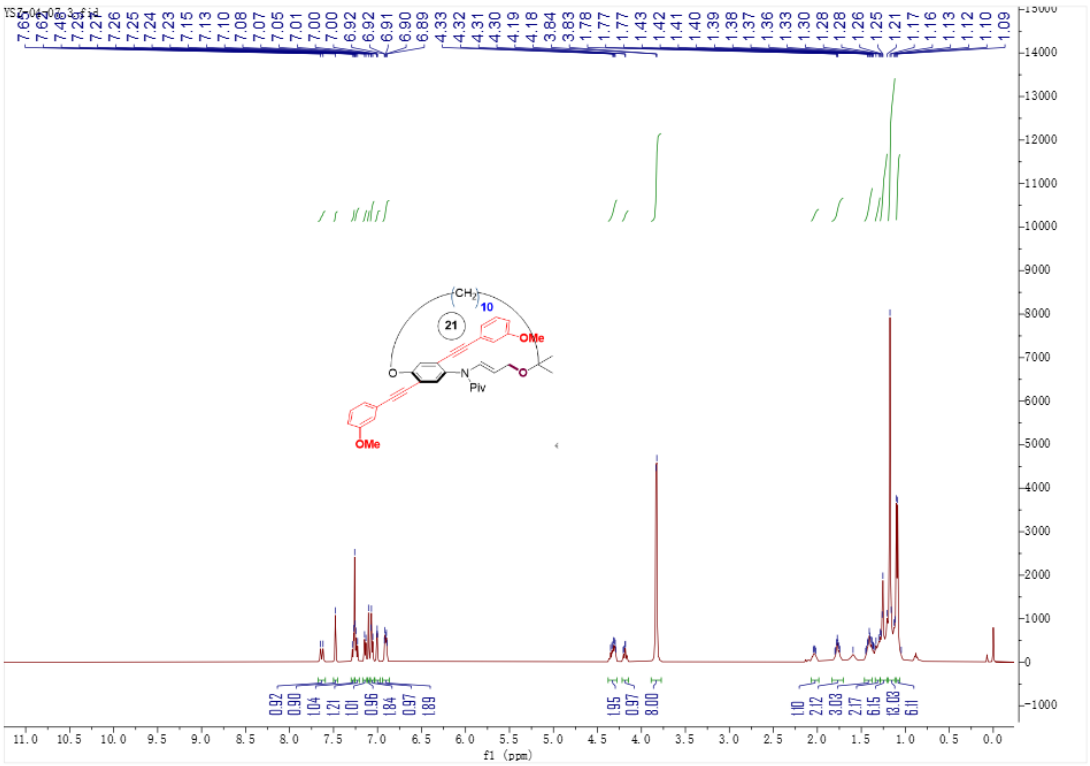


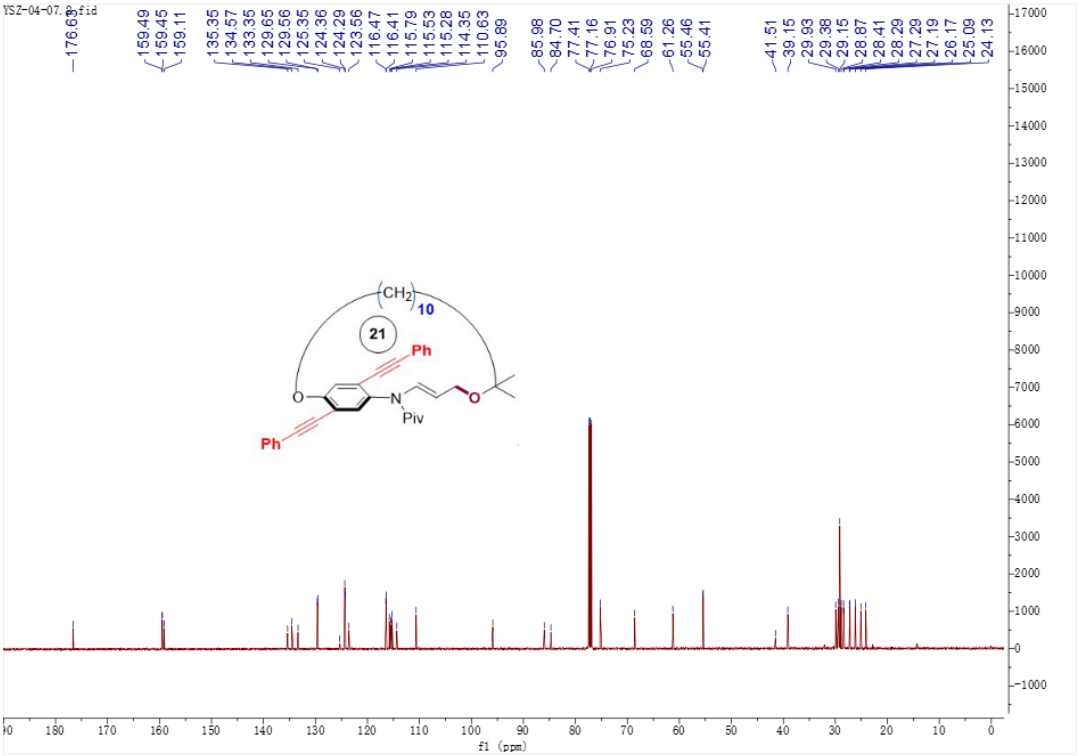
(R_p,*E*)-1-(7,7-dimethyl-12,15-bis(phenylethynyl)-6,18-dioxa-2-aza-1(1,4)-benzenacyclo- octadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6q)**



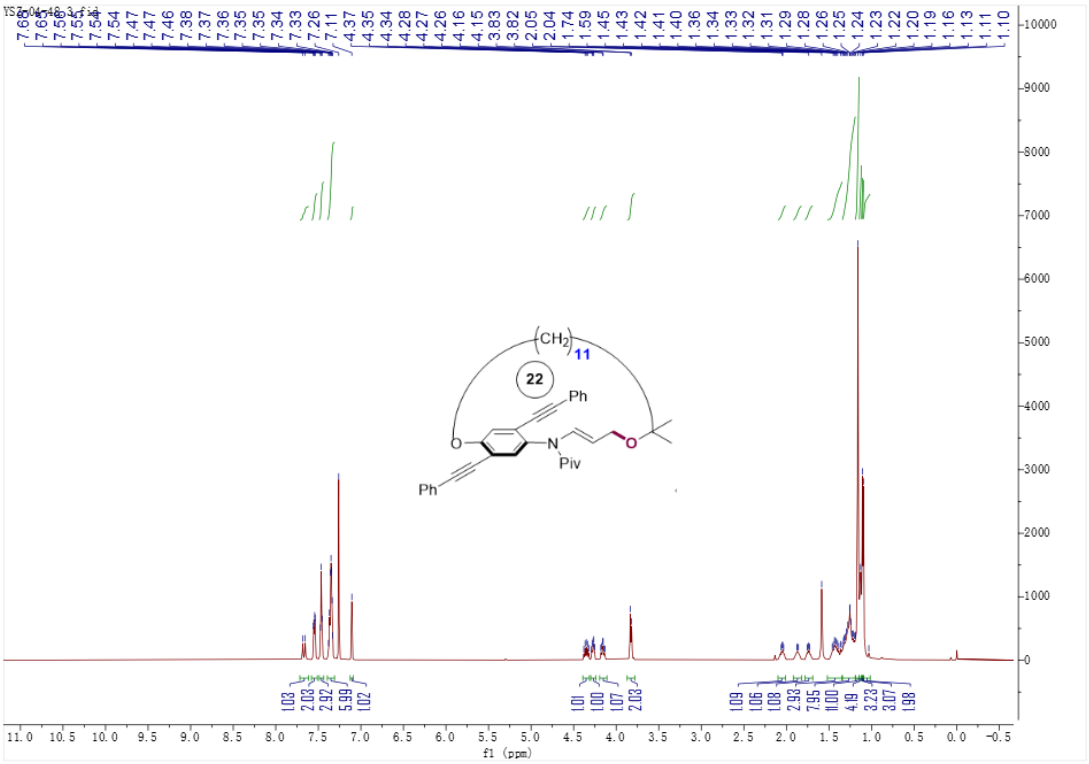


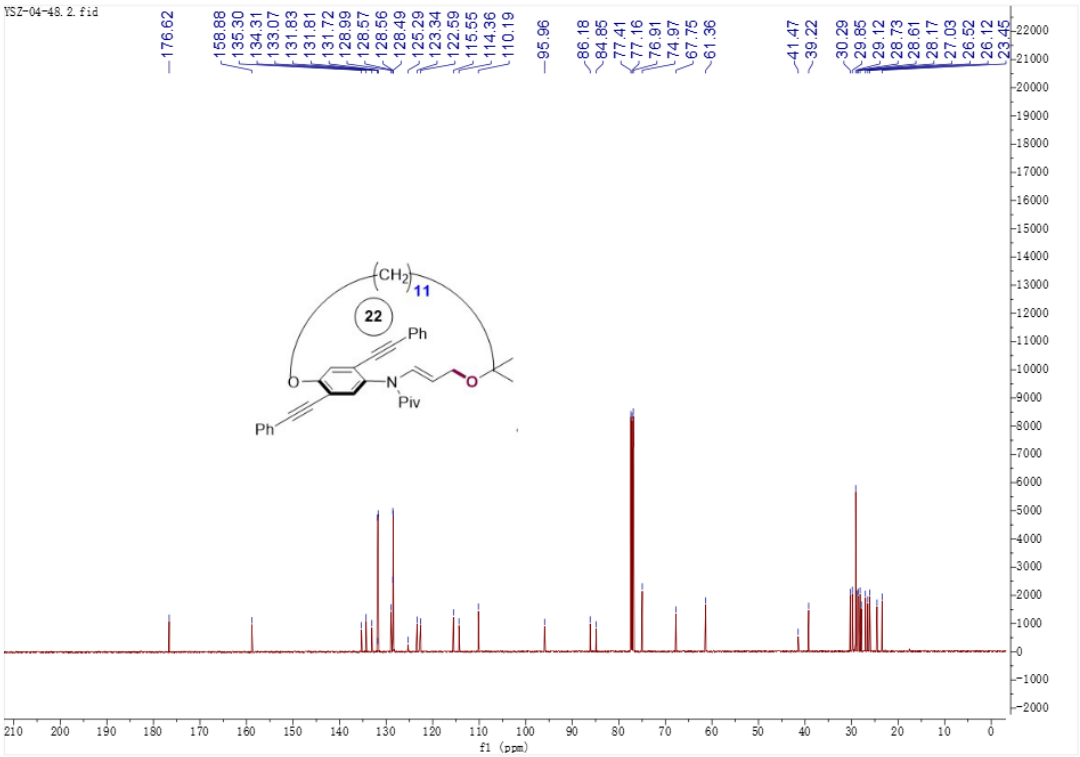
(R_p,*E*)-1-(1^2,1^5-bis((3-methoxyphenyl)ethynyl)-7,7-dimethyl-6,18-dioxa-2-aza-1(1,4)-benzenacyclooctadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6r)**



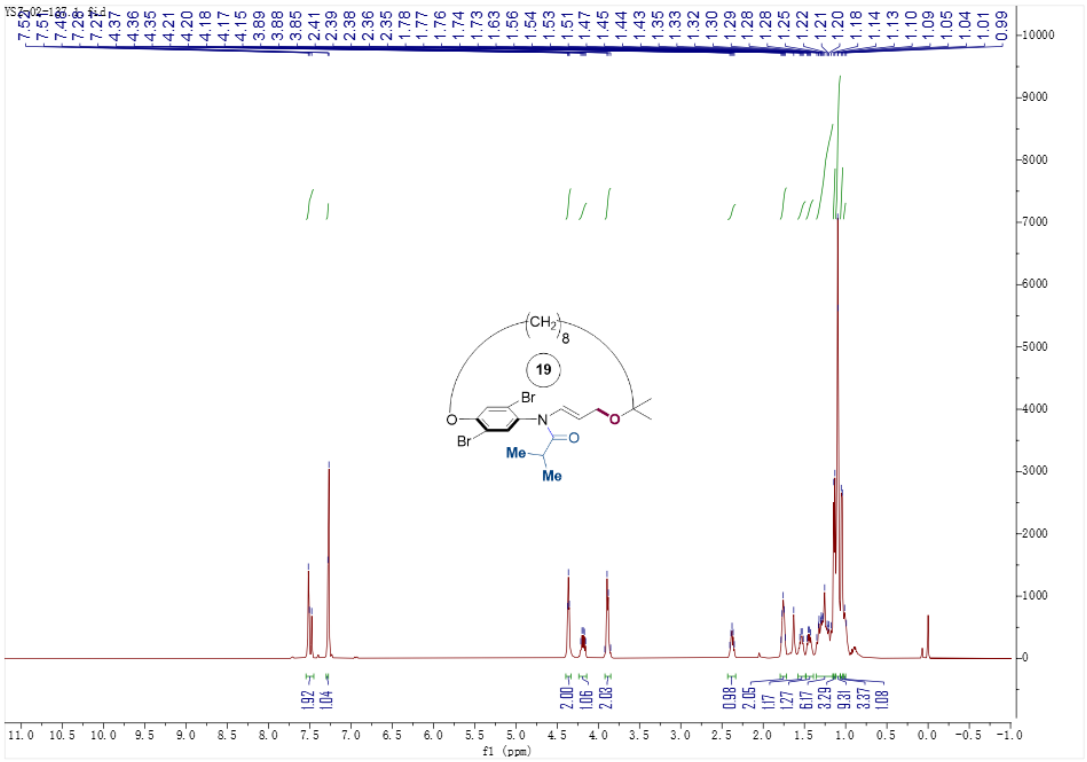


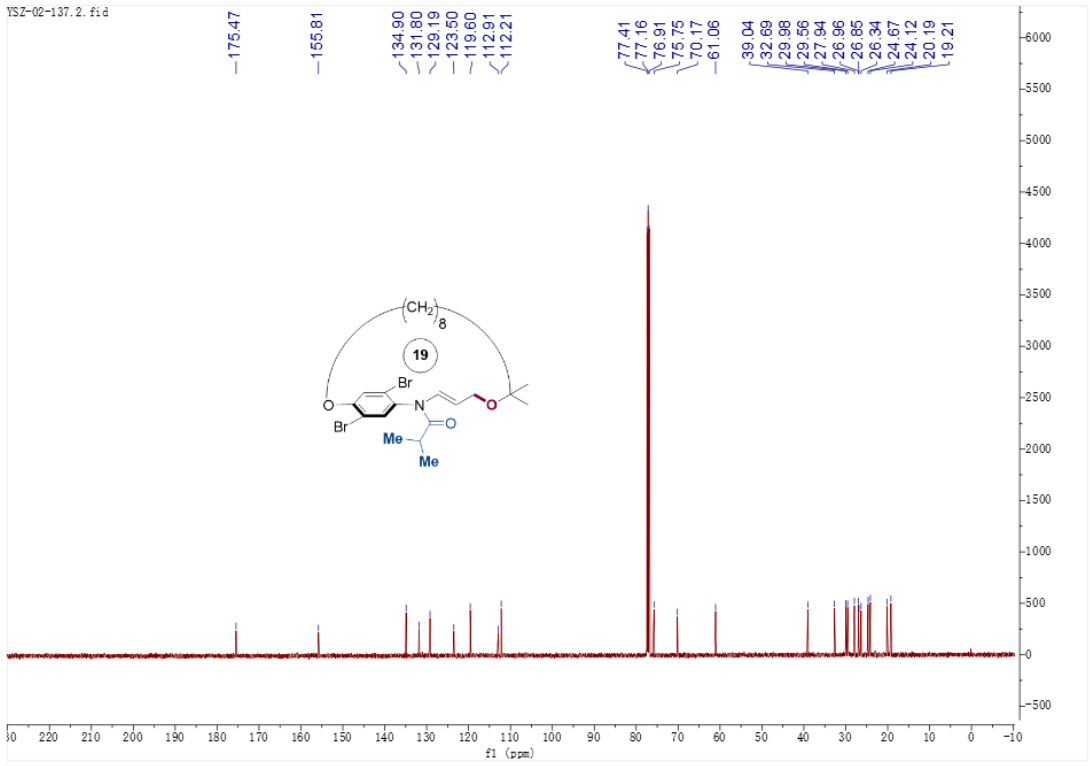
(R_p,*E*)-1-(7,7-dimethyl-1^2,1^5-bis(phenylethynyl)-6,19-dioxa-2-aza-1(1,4)-benzenacyclo- nonadecaphan-3-en-2-yl)-2,2-dimethylpropan-1-one **(6s)**





(R_p,E)-(12,15-dibromo-7,7-dimethyl-6,16-dioxa-2-aza-1(1,4)-benzenacyclohexadecaphan-3-en-2-yl)(phenyl)methanone (**6t**)





(R_p,E)-(12,15-dibromo-7,7-dimethyl-6,16-dioxa-2-aza-1(1,4)-benzenacyclohexadecaphan-3-en-2-yl)(phenyl)methanone (**6u**)