

Supporting Information

Organocatalyzed Asymmetric 1,6-Conjugate Addition of *para*-Quinone Methides with Dicyanoolefins

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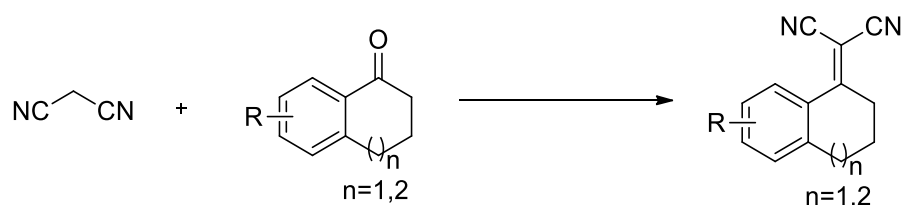
1. General Information

Reagents and Solvents: PE refers to petroleum ether (b.p. 60-90 °C) and EA refers to ethyl acetate. All other starting materials and solvents were commercially available and were used without further purification unless otherwise stated.

Chromatography: Flash column chromatography was carried out using commercially available 200-300 mesh under pressure unless otherwise indicated. Gradient flash chromatography was conducted eluting with PE/EA, they are listed as volume/volume ratios.

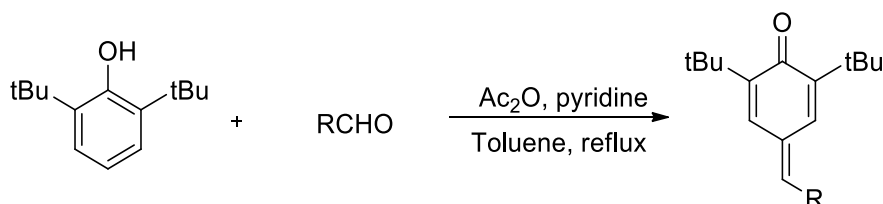
Data collection: ^1H and ^{13}C NMR spectra were collected on BRUKER AV-300 (300 MHz) spectrometer using CDCl_3 or DMSO as solvent. Chemical shifts of ^1H NMR were recorded in parts per million (ppm, δ) relative to tetramethylsilane ($\delta = 0.00$ ppm) with the solvent resonance as an internal standard (CDCl_3 : $\delta = 7.26$ ppm). Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, m = multiplet), coupling constant (Hz), and integration. Chemical shifts of ^{13}C NMR were reported in ppm with the solvent as the internal standard (CDCl_3 : $\delta = 77.0$ ppm). High Resolution Mass measurement was performed on Agilent QTOF 6520 mass spectrometer with electron spray ionization (ESI) as the ion source. Melting point (m.p.) was measured on a microscopic melting point apparatus.

2. General procedure for preparation of dicyanoolefin¹



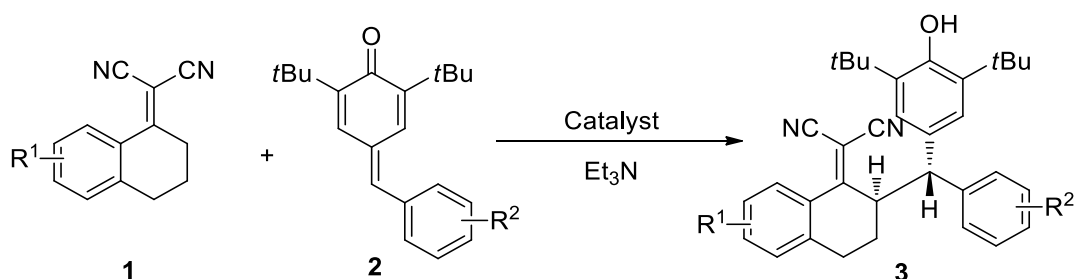
Malononitrile (32 mmol) and the ketone (28 mmol) were dissolved in 20 mL of toluene containing ammonium acetate (500 mg, 6.5 mmol) and glacial acetic acid (2 mL) in a 50 mL flask. By refluxing vigorously, the water formed in the reaction was removed by a Dean and Stark trap placed under the reflux condenser. Evaporation of the toluene left a residue that was recrystallized from alcohol or distilled under vacuum to give pure products (**1a-1l**)

3. Preparation of *p*-QMs²



Aldehydes (10 mmol) were added to a solution of phenols (10 mmol) in toluene (40 mL). The reaction mixture was heated in a Dean-Stark apparatus to reflux. Piperidine (20 mmol) was added dropwise over 1 h, and the reaction mixture continued to reflux for 3 h. After the mixture had cooled just below the boiling point of toluene, acetic anhydride (20 mmol) was added, and then the solution was stirred for 15 min. The residue was extracted three times with dichloromethane. The combined organic layers were washed with water and brine sequentially, dried over Na₂SO₄, filtered, and concentrated. The crude product was purified by flash column chromatography on silica gel to afford the corresponding product **2a-2q**.

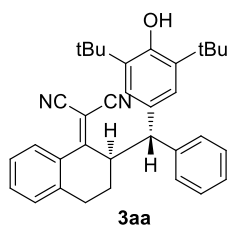
4. General Procedure for the asymmetric 1,6-conjugate Addition of Dicyanoolefins to *para*-Quinone Methides



In a 10 mL test tube was sequentially added dicyanoolefin **1** (0.1 mmol, 1 equiv), *p*-QMs **2** (0.1 mmol, 1 equiv), catalyst (0.02 mmol, 20 mol %) and solvent (1 mL). Then, the temperature was decreased to -40 °C. Finally, Et₃N (0.15 mmol, 1.5 equiv) was added. The tube was sealed and stirred at -40 °C. After the reaction was completed (detected by TLC), solvent was directly removed under reduce pressure and the crude mixture was purified by flash column chromatography on silica gel to afford the pure product.

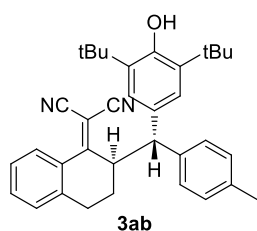
a) Characterization of the Products

2-((R)-2-((S)-(3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)-3,4-dihydronaphthalen-1(2H)-ylidene)malononitrile (3aa)



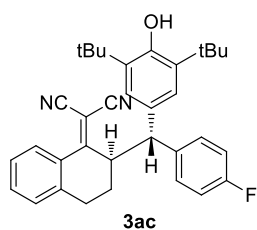
yield 76% (39.4 mg); white solid, m.p. 214-216 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.63-7.57 (m, 1H), 7.54-7.50(m, 1H), 7.47-7.40 (m, 2H), 7.39-7.28 (m, 4H), 7.33-7.24 (m, 1H), 6.74 (s, 2H), 5.12 (s, 1H), 4.19-4.12 (m, 1H), 3.73-3.68 (m, 1H), 3.15-2.89 (m, 2H), 2.14-1.92 (m, 2H), 1.36 (s, 18H) ppm; ^{13}C NMR (75 MHz, CDCl_3) δ 177.3, 152.9, 141.2, 139.7, 135.8, 133.4, 131.7, 129.9, 129.4, 129.0, 128.8, 128.0, 127.1, 126.5, 124.3, 113.7, 113.5, 80.5, 52.6, 47.4, 34.4, 30.1, 25.5, 24.3 ppm; $[\alpha]_{\text{D}}^{25} = -37.3$ (c = 0.3, EA); the dr value was evaluated by HPLC of the mixture and was found to be >20:1; the er value was determined by HPLC, using CHIRALCEL OD-H, *i*-PrOH: Hexane =1:99, $\nu = 0.5$ mL/min, $\lambda = 254$ nm, t (major) = 13.86 min, t (minor) = 18.22 min; er = 98:2; HRMS (ESI) calcd for $[\text{C}_{34}\text{H}_{36}\text{N}_2\text{NaO}]^+$ 511.2720, found 511.2713.

2-((R)-2-((S)-(3,5-di-tert-butyl-4-hydroxyphenyl)(*p*-tolyl)methyl)-3,4-dihydronaphthalen-1(2H)-ylidene)malononitrile (3ab)



yield 84% (42.2 mg); white solid, m.p. 187-189 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.63 (d, $J = 7.9$ Hz, 1H), 7.57-7.53 (m, 1H), 7.36-7.31 (m, 4H), 7.16 (d, $J = 7.9$ Hz, 2H), 6.72 (s, 2H), 5.10 (s, 1H), 4.12-4.06 (m, 1H), 3.63 (d, $J = 11.6$ Hz, 1H), 3.24-2.69 (m, 2H), 2.32 (s, 3H), 2.17-1.87 (m, 2H), 1.36 (s, 18H) ppm; ^{13}C NMR (75 MHz, CDCl_3) δ 177.5, 152.8, 139.6, 138.1, 136.7, 135.7, 133.4, 131.9, 129.8, 129.6, 129.4, 128.8, 128.1, 127.7, 126.5, 124.2, 113.7, 113.5, 52.2, 47.4, 34.3, 30.1, 25.5, 24.2, 21.0 ppm; $[\alpha]_{\text{D}}^{25} = -34.3$ (c = 0.3, EA); the dr value was evaluated by HPLC of the mixture and was found to be >20:1; the er value was determined by HPLC, using CHIRALCEL OD-H, *i*-PrOH: Hexane =1:99, $\nu = 0.5$ mL/min, $\lambda = 254$ nm, t (major) = 10.90 min, t (minor) = 14.56 min; er = 91:9; HRMS (ESI) calcd for $[\text{C}_{35}\text{H}_{38}\text{KN}_2\text{O}]^+$ 541.2616, found 541.2614.

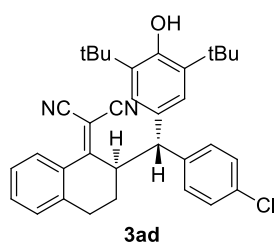
2-((R)-2-((S)-(3,5-di-tert-butyl-4-hydroxyphenyl)(4-fluorophenyl)methyl)-3,4-dihydronaphthalen-1(2H)-ylidene)malononitrile (3ac)



yield 81% (41.0 mg); white solid, m.p. 162-164 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.65 (d, $J = 7.8$ Hz, 1H), 7.56 (t, $J = 7.5$ Hz, 1H), 7.47-7.28 (m, 4H), 7.06 (t, $J = 8.0$ Hz, 2H), 6.70 (s, 2H), 5.15 (s, 1H), 4.07 (d, $J = 11.7$ Hz, 1H), 3.68 (d, $J = 11.6$ Hz, 1H), 3.01-2.87 (m, 2H), 2.08-2.07 (m, 2H), 1.36 (s, 18H) ppm; ^{13}C NMR (75 MHz, CDCl_3) δ 176.9, 163.5, 160.2, 152.9, 139.5, 137.0, 136.9, 136.0, 133.7, 133.5, 131.4, 129.8, 129.4, 129.3, 128.8, 126.9, 126.6,

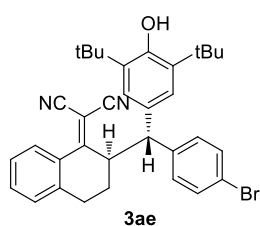
124.2, 116.0, 115.7, 113.6, 113.4, 80.6, 51.8, 47.5, 34.4, 30.1, 25.4, 24.2 ppm; $[\alpha]_D^{25} = -39.7$ ($c = 0.3$, EA); the dr value was evaluated by HPLC of the mixture and was found to be >20:1; the er value was determined by HPLC, using CHIRALCEL OD-H, *i*-PrOH: Hexane =1:99, $\nu = 0.5$ mL/min, $\lambda = 254$ nm, t (major) = 11.16 min, t (minor) = 14.47 min; er = 92:8; HRMS (ESI) calcd for $[C_{34}H_{35}FN_2NaO]^+$ 529.2626, found 529.2625.

2-((*R*)-2-((*S*)-(4-chlorophenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl)-3,4-dihydronaphthalen-1(2*H*)-ylidene)malononitrile (3ad)



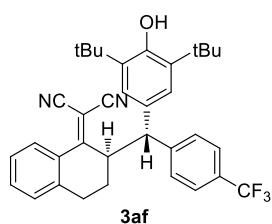
yield 82% (42.9 mg); white solid, m.p. 179-181 °C; 1H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, $J = 8.0$ Hz, 1H), 7.56-7.53 (m, 1H), 7.40-7.26 (m, 6H), 6.68 (s, 2H), 5.14 (s, 1H), 4.11-4.05 (m, 1H), 3.66 (d, $J = 11.7$ Hz, 1H), 3.24-2.68 (m, 2H), 2.20-1.90 (m, 2H), 1.36 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.7, 153.0, 139.7, 139.4, 136.0, 133.5, 132.9, 131.1, 129.8, 129.2, 129.1, 128.8, 126.9, 126.6, 124.2, 113.5, 113.4, 80.7, 51.9, 47.2, 34.4, 30.1, 25.4, 24.2 ppm; $[\alpha]_D^{25} = -31.3$ ($c = 0.3$, EA); the dr value was evaluated by HPLC of the mixture and was found to be >20:1; the er value was determined by HPLC, using CHIRALCEL OD-H, *i*-PrOH: Hexane =1:99, $\nu = 0.5$ mL/min, $\lambda = 254$ nm, t (major) = 11.58 min, t (minor) = 18.57 min; er = 95:5; HRMS (ESI) calcd for $[C_{34}H_{35}ClKN_2O]^+$ 561.2069, found 561.2059.

2-((*R*)-2-((*S*)-(4-bromophenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl)-3,4-dihydronaphthalen-1(2*H*)-ylidene)malononitrile (3ae)



yield 99% (56.1 mg); white solid, m.p. 163-165 °C; 1H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, $J = 8.0$ Hz, 1H), 7.60-7.53 (m, 1H), 7.50 (d, $J = 8.4$ Hz, 2H), 7.41-7.28 (m, 4H), 6.69 (s, 2H), 5.15 (s, 1H), 4.11-4.05 (m, 1H), 3.66 (d, $J = 11.7$ Hz, 1H), 3.06-2.87 (m, 2H), 2.27-1.79 (m, 2H), 1.37 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.7, 153.0, 140.2, 139.4, 136.0, 133.5, 132.1, 131.0, 129.8, 129.6, 129.2, 128.8, 126.6, 124.2, 120.9, 113.5, 113.4, 80.7, 52.0, 47.1, 34.4, 30.1, 25.4, 24.2 ppm; $[\alpha]_D^{25} = -36.7$ ($c = 0.3$, EA); the dr value was evaluated by HPLC of the mixture and was found to be >20:1; the er value was determined by HPLC, using CHIRALCEL OD-H, *i*-PrOH: Hexane =1:99, $\nu = 0.5$ mL/min, $\lambda = 254$ nm, t (major) = 12.04 min, t (minor) = 22.50 min; er = 99.5:0.5; HRMS (ESI) calcd for $[C_{34}H_{35}BrKN_2O]^+$ 605.1564, found 605.1549.

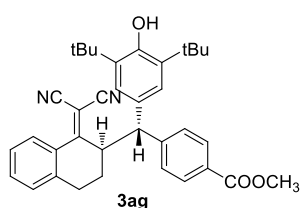
2-((R)-2-((S)-(3,5-di-tert-butyl-4-hydroxyphenyl)(4-(trifluoromethyl)phenyl)methyl)-3,4-dihydronaphthalen-1(2H)-ylidene)malononitrile (3af)



yield 91% (50.6 mg); white solid, m.p. 181-183 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.66-7.54 (m, 6H), 7.40 (t, J = 7.9 Hz, 2H), 6.76 (s, 2H), 5.21 (s, 1H), 4.19-4.12 (m, 1H), 3.80 (d, J = 11.7 Hz, 1H), 3.19-2.82 (m, 2H), 2.24-1.97 (m, 2H), 1.41 (s, 18H) ppm; ^{13}C NMR (75 MHz, CDCl_3) δ 175.9, 152.6, 144.8, 138.8, 135.6, 133.1, 130.1, 129.4, 128.7, 128.3, 127.8, 126.4, 126.2, 125.6, 125.5, 125.4, 125.4, 123.8, 113.0, 112.9, 80.3, 51.9, 46.5, 33.9, 29.6, 24.9, 23.7 ppm; $[\alpha]_{\text{D}}^{25}$ = -34.0 (c = 0.3, EA); the dr value was evaluated by HPLC of the mixture and was found to be >20:1; the er value was determined by HPLC, using CHIRALCEL OD-H, *i*-PrOH: Hexane = 1:99, ν = 0.5 mL/min, λ = 254 nm, t (major) = 10.70 min, t (minor) = 14.98 min; er = 93:7; HRMS (ESI) calcd for $[\text{C}_{35}\text{H}_{35}\text{F}_3\text{N}_2\text{NaO}]^+$ 579.2594, found 579.2587.

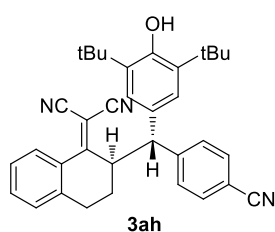
Methyl

4-((S)-(3,5-di-tert-butyl-4-hydroxyphenyl)((R)-1-(dicyanomethylene)-1,2,3,4-tetrahydronaphthalen-2-yl)methyl)benzoate (3ag)



yield 78% (42.6 mg); white solid, m.p. 185-187 °C; ^1H NMR (300 MHz, CDCl_3) δ 8.04 (d, J = 8.3 Hz, 2H), 7.66 (d, J = 7.9 Hz, 1H), 7.62-7.46 (m, 3H), 7.43-7.27 (m, 2H), 6.71 (s, 2H), 5.16 (s, 1H), 4.15 (d, J = 11.7 Hz, 1H), 3.90 (s, 3H), 3.75 (d, J = 11.7 Hz, 1H), 3.03-2.91 (m, 2H), 2.26-1.80 (m, 2H), 1.36 (s, 18H) ppm; ^{13}C NMR (75 MHz, CDCl_3) δ 176.6, 166.8, 153.1, 146.3, 139.4, 136.0, 133.5, 130.7, 130.3, 129.9, 129.2, 129.0, 128.8, 128.0, 126.6, 124.3, 113.5, 113.4, 80.7, 52.5, 52.1, 47.0, 34.4, 30.3, 30.0, 25.4, 24.2 ppm; $[\alpha]_{\text{D}}^{25}$ = -44.3 (c = 0.3, EA); the dr value was evaluated by HPLC of the mixture and was found to be >20:1; the er value was determined by HPLC, using CHIRALCEL OD-H, *i*-PrOH: Hexane = 1:99, ν = 0.5 mL/min, λ = 254 nm, t (major) = 24.09 min, t (minor) = 33.69 min; er = 96:4; HRMS (ESI) calcd for $[\text{C}_{36}\text{H}_{38}\text{N}_2\text{NaO}_3]^+$ 569.2775, found 569.2768.

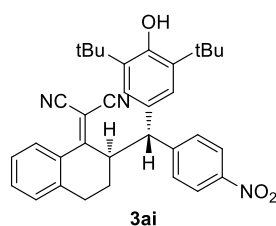
2-((R)-2-((S)-(4-cyanophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)-3,4-dihydronaphthalen-1(2H)-ylidene)malononitrile (3ah)



yield 78% (40.0 mg); white solid, m.p. 192-194 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.75-7.49 (m, 6H), 7.36 (t, J = 8.6 Hz, 2H), 6.66 (s, 2H), 5.19 (s, 1H), 4.17-4.10 (m, 1H), 3.74 (d, J = 11.7 Hz, 1H), 2.99-2.94 (m, 2H), 2.35-1.84 (m, 2H), 1.36 (s, 18H) ppm; ^{13}C NMR (75 MHz, CDCl_3) δ 176.0, 153.2, 146.6, 139.2, 136.2, 133.6, 132.8, 130.1, 129.9, 129.1, 128.8, 128.7, 126.7, 124.3, 118.5, 113.4, 113.3, 111.1, 80.9, 52.5, 46.6, 34.4, 30.0, 25.3, 24.2 ppm; $[\alpha]_{\text{D}}^{25}$ = -35.3

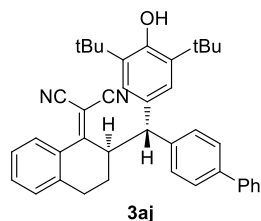
(*c* = 0.3, EA); the *dr* value was evaluated by HPLC of the mixture and was found to be 93:7; the *er* value was determined by HPLC, using CHIRALCEL OD-H, *i*-PrOH: Hexane = 1:99, ν = 0.5 mL/min, λ = 254 nm, *t* (major) = 36.02 min, *t* (minor) = 46.09 min; *er* = 99.5:0.5; HRMS (ESI) calcd for $[C_{35}H_{35}N_3NaO]^+$ 536.2672, found 536.2658.

2-((*R*)-2-((*S*)-(3,5-di-*tert*-butyl-4-hydroxyphenyl)(4-nitrophenyl)methyl)-3,4-dihydronaphthalen-1(2*H*)-ylidene)malononitrile (3ai)



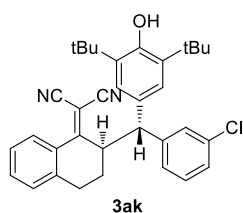
yield 90% (48.0 mg); white solid, m.p. 122-124 °C; 1H NMR (300 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.6 Hz, 2H), 7.76-7.48 (m, 4H), 7.40-7.25 (m, 2H), 6.68 (s, 2H), 5.20 (s, 1H), 4.36-4.02 (m, 1H), 3.81 (d, *J* = 11.7 Hz, 1H), 3.06-2.75 (m, 2H), 2.21-1.99 (m, 2H), 1.36 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.0, 153.4, 148.7, 147.1, 139.2, 136.3, 133.8, 130.0, 129.1, 128.9, 128.8, 128.7, 126.9, 124.4, 124.2, 124.1, 113.5, 81.1, 52.4, 46.8, 34.5, 30.1, 25.5, 24.3 ppm; $[\alpha]_D^{25}$ = -41.0 (*c* = 0.3, EA); the *dr* value was evaluated by HPLC of the mixture and was found to be >20:1; the *er* value was determined by HPLC, using CHIRALCEL OD-H, *i*-PrOH: Hexane = 1:99, ν = 0.5 mL/min, λ = 254 nm, *t* (major) = 31.25 min, *t* (minor) = 42.26 min; *er* = 99.5:0.5; HRMS (ESI) calcd for $[C_{34}H_{35}KN_3O_3]^+$ 572.2310, found 572.2296.

2-((*R*)-2-((*S*)-[1,1'-biphenyl]-4-yl(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl)-3,4-dihydronaphthalen-1(2*H*)-ylidene)malononitrile (3aj)



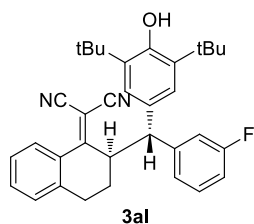
yield 94% (53.0 mg); white solid, m.p. 115-118 °C; 1H NMR (300 MHz, $CDCl_3$) δ 7.68-7.21 (m, 13H), 6.76 (s, 2H), 5.13 (s, 1H), 4.28-4.01 (m, 1H), 3.72 (d, *J* = 11.7 Hz, 1H), 3.28-2.71 (m, 2H), 2.35-1.90 (m, 2H), 1.40 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.3, 152.9, 140.6, 140.2, 140.0, 139.6, 135.8, 133.4, 131.6, 129.8, 129.3, 128.8, 128.3, 127.7, 127.3, 127.0, 126.5, 124.3, 113.7, 113.5, 80.5, 52.3, 47.4, 34.4, 30.1, 25.6, 24.3 ppm; $[\alpha]_D^{25}$ = -36.5 (*c* = 0.3, EA); the *dr* value was evaluated by HPLC of the mixture and was found to be >20:1; the *er* value was determined by HPLC, using CHIRALCEL OD-H, *i*-PrOH: Hexane = 1:99, ν = 0.5 mL/min, λ = 254 nm, *t* (major) = 19.77 min, *t* (minor) = 24.95 min; *er* = 90:10; HRMS (ESI) calcd for $[C_{40}H_{40}KN_2O]^+$ 603.2772, found 603.2762.

2-((R)-2-((R)-(3-chlorophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)-3,4-dihydronaphthalen-1(2H)-ylidene)malononitrile (3ak)



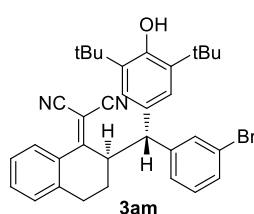
yield 84% (43.9 mg); white solid, m.p. 235-238 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.64 (d, $J = 7.9$ Hz, 1H), 7.55-7.52 (m, 1H), 7.43-7.19 (m, 6H), 6.70 (s, 2H), 5.15 (s, 1H), 4.11-4.04 (m, 1H), 3.64 (d, $J = 11.7$ Hz, 1H), 3.10-2.81 (m, 2H), 2.14-1.97 (m, 2H), 1.36 (s, 18H) ppm; ^{13}C NMR (75 MHz, CDCl_3) δ 176.6, 153.1, 143.2, 139.4, 136.0, 134.8, 133.5, 130.9, 130.2, 129.9, 129.2, 128.8, 128.6, 127.3, 126.6, 125.5, 124.3, 113.5, 113.4, 80.7, 52.3, 47.1, 34.4, 30.1, 25.4, 24.2 ppm; $[\alpha]_{\text{D}}^{25} = -32.7$ ($c = 0.3$, EA); the dr value was evaluated by HPLC of the mixture and was found to be >20:1; the er value was determined by HPLC, using CHIRALCEL OD-H, *i*-PrOH: Hexane =1:99, $\nu = 0.5$ mL/min, $\lambda = 254$ nm, t (major) = 11.35 min, t (minor) = 15.75 min; er = 97:3; HRMS (ESI) calcd for $[\text{C}_{34}\text{H}_{35}\text{ClN}_2\text{NaO}]^+$ 545.2330, found 545.2331.

2-((R)-2-((R)-(3,5-di-tert-butyl-4-hydroxyphenyl)(3-fluorophenyl)methyl)-3,4-dihydronaphthalen-1(2H)-ylidene)malononitrile (3al)



yield 89% (45.0 mg); white solid, m.p. 178-180 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.63 (d, $J = 7.8$ Hz, 1H), 7.60-7.52 (m, 1H), 7.39-7.30 (m, 3H), 7.26-7.25 (m, 1H), 7.12 (d, $J = 10.0$ Hz, 1H), 6.97-6.94 (m, 1H), 6.71 (s, 2H), 5.16 (s, 1H), 4.12-4.06 (m, 1H), 3.67 (d, $J = 11.7$ Hz, 1H), 3.20-2.65 (m, 2H), 2.21-1.95 (m, 2H), 1.36 (s, 18H) ppm; ^{13}C NMR (75 MHz, CDCl_3) δ 176.8, 153.0, 143.7, 139.5, 135.9, 133.5, 131.0, 130.6, 130.5, 129.9, 129.2, 128.8, 126.6, 124.3, 123.3, 115.3, 115.0, 114.2, 113.9, 113.4, 52.2, 47.2, 34.4, 30.1, 25.4, 24.2 ppm; $[\alpha]_{\text{D}}^{25} = -23.7$ ($c = 0.3$, EA); the dr value was evaluated by HPLC of the mixture and was found to be >20:1; the er value was determined by HPLC, using CHIRALCEL OD-H, *i*-PrOH: Hexane =1:99, $\nu = 0.5$ mL/min, $\lambda = 254$ nm, t (major) = 11.36 min, t (minor) = 14.38 min; er = 98:2; HRMS (ESI) calcd for $[\text{C}_{34}\text{H}_{35}\text{FN}_2\text{NaO}]^+$ 529.2626, found 529.2621.

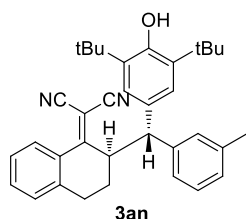
2-((R)-2-((R)-(3-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)-3,4-dihydronaphthalen-1(2H)-ylidene)malononitrile (3am)



yield 92% (52.2 mg); white solid, m.p. 189-191 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.64 (d, $J = 7.7$ Hz, 1H), 7.60-7.53 (m, 1H), 7.47 (m, 1H), 7.37-7.32 (m, 4H), 7.28-7.25 (m, 1H), 6.70 (s, 2H), 5.16 (s, 1H), 4.12-4.06 (m, 1H), 3.63 (d, $J = 11.7$ Hz, 1H), 3.17-2.80 (m, 2H), 2.12-2.05 (m, 2H), 1.37 (s, 18H) ppm; ^{13}C NMR (75 MHz, CDCl_3) δ 176.6, 153.1, 143.5, 139.4, 136.0, 131.6, 130.5, 130.2, 129.9, 129.2, 128.8, 128.0, 126.9, 126.6, 125.9, 124.3, 123.1, 113.6, 113.4, 80.7, 52.2, 47.1, 34.4, 30.1, 25.4, 24.2 ppm; $[\alpha]_{\text{D}}^{25} = -16.0$ ($c = 0.3$, EA); the dr value was evaluated by HPLC of the mixture and was found to be >20:1; the er

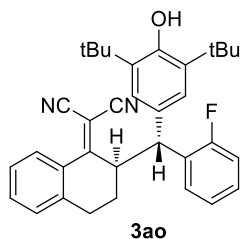
valure was determined by HPLC, using CHIRALCEL OD-H, *i*-PrOH: Hexane =1:99, $\nu = 0.5$ mL/min, $\lambda = 254$ nm, t (major) = 11.58 min, t (minor) = 14.66 min; er = 99:1; HRMS (ESI) calcd for $[C_{34}H_{35}BrN_2NaO]^+$ 589.1825, found 589.1818.

2-((*R*)-2-((*S*)-(3,5-di-*tert*-butyl-4-hydroxyphenyl)(*m*-tolyl)methyl)-3,4-dihydronaphthalen-1(2*H*)-ylidene)malononitrile (3an)



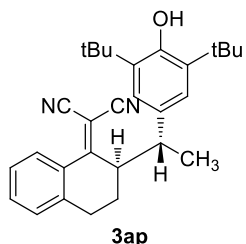
yield 84% (42.2 mg); white solid, m.p. 196-198 °C; 1H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, $J = 7.9$ Hz, 1H), 7.59-7.49 (m, 1H), 7.37-7.20 (m, 5H), 7.06 (d, $J = 6.7$ Hz, 1H), 6.74 (s, 2H), 5.11 (s, 1H), 4.15-4.08 (m, 1H), 3.64 (d, $J = 11.7$ Hz, 1H), 3.11-2.94 (m, 2H), 2.31 (s, 3H), 2.18-1.94 (m, 2H), 1.36 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.5, 152.8, 141.0, 139.7, 138.6, 135.7, 133.4, 131.8, 129.8, 129.4, 129.1, 128.9, 128.8, 127.9, 126.5, 124.5, 124.3, 113.7, 113.5, 80.4, 52.6, 47.4, 34.4, 30.1, 25.6, 24.3, 21.5 ppm; $[\alpha]_D^{25} = -40.3$ ($c = 0.3$, EA); the dr value was evaluated by HPLC of the mixture and was found to be >20:1; the er valure was determined by HPLC, using CHIRALCEL OD-H, *i*-PrOH: Hexane =1:99, $\nu = 0.5$ mL/min, $\lambda = 254$ nm, t (major) = 9.84 min, t (minor) = 11.99 min; er = 96:4; HRMS (ESI) calcd for $[C_{35}H_{38}KN_2O]^+$ 541.2616, found 541.2613.

2-((*R*)-2-((*R*)-(3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-fluorophenyl)methyl)-3,4-dihydronaphthalen-1(2*H*)-ylidene)malononitrile (3ao)



yield 99% (50.1 mg); white solid, m.p. 180°C decomposed; 1H NMR (300 MHz, $CDCl_3$) δ 7.71-7.50 (m, 3H), 7.35 (t, $J = 7.4$ Hz, 2H), 7.25-7.17 (m, 2H), 7.06-7.01 (m, 1H), 6.77 (s, 2H), 5.16 (s, 1H), 4.20-4.06 (m, 2H), 3.09-2.85 (m, 2H), 2.08-2.04 (m, 2H), 1.39 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.0, 162.5, 159.2, 153.0, 133.5, 130.5, 129.9, 129.1, 128.8, 128.6, 128.5, 128.4, 128.3, 126.6, 124.7, 124.6, 116.4, 116.0, 113.7, 113.4, 80.7, 46.6, 44.6, 34.3, 30.1, 25.7, 24.3 ppm; $[\alpha]_D^{25} = -3.0$ ($c = 0.3$, EA); the dr value was evaluated by HPLC of the mixture and was found to be >20:1; the er valure was determined by HPLC, using CHIRALCEL OD-H, *i*-PrOH: Hexane =1:99, $\nu = 0.5$ mL/min, $\lambda = 254$ nm, t (major) = 12.04 min, t (minor) = 15.07 min; er = 60:40; HRMS (ESI) calcd for $[C_{34}H_{35}FN_2NaO]^+$ 529.2626, found 529.2628.

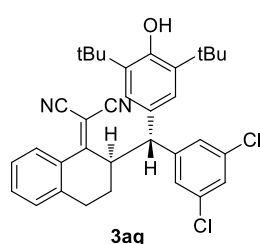
2-((*R*)-2-((*R*)-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)ethyl)-3,4-dihydronaphthalen-1(2*H*)-ylidene)malononitrile (3ap)



yield 47% (20.0 mg); white solid, m.p. 156-158 °C; 1H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, $J = 7.6$ Hz, 1H), 7.38-7.25 (m, 2H), 7.17 (d, $J = 7.1$ Hz, 1H), 6.75 (s, 2H), 6.41 (s, 1H), 5.18 (s, 1H), 3.85 (q, $J = 7.0$ Hz, 1H), 2.62-2.39 (m, 1H), 2.31-1.94 (m, 3H), 1.74 (d, $J = 7.0$ Hz, 3H), 1.30 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.7, 137.7, 135.5, 133.2, 130.2, 128.4, 128.1, 127.7,

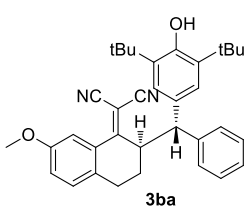
127.5, 126.6, 124.8, 123.4, 115.5, 114.4, 48.7, 44.8, 34.2, 30.0, 27.7, 23.1, 17.7 ppm; $[\alpha]_D^{25} = -1.2$ ($c = 0.3$, EA); the dr value was evaluated by HPLC of the mixture and was found to be >20:1; the er value was determined by HPLC, using CHIRALCEL IA, *i*-PrOH: Hexane =5:95, $v = 0.5$ mL/min, $\lambda = 254$ nm, t (major) = 8.59 min, t (minor) = 8.17 min; er = 53:47; HRMS (ESI) calcd for $[C_{29}H_{34}KN_2O]^+$ 465.2303, found 465.2306.

2-((*R*)-2-((*R*)-(3,5-di-*tert*-butyl-4-hydroxyphenyl)(3,5-dichlorophenyl)methyl)-3,4-dihydronaphthalen-1(2*H*)-ylidene)malononitrile (3aq)



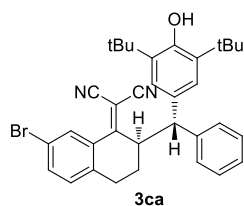
yield 54% (30.1 mg); white solid, m.p. 242-244 °C; 1H NMR (300 MHz, $CDCl_3$) δ 7.68-7.50 (m, 2H), 7.42-7.22 (m, 5H), 6.67 (s, 2H), 5.20 (s, 1H), 4.04 (d, $J = 11.7$ Hz, 1H), 3.62 (d, $J = 11.6$ Hz, 1H), 3.01-2.97 (m, 2H), 2.15-2.09 (m, 2H), 1.37 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.0, 153.3, 144.6, 139.2, 136.2, 135.5, 133.6, 130.1, 129.9, 129.1, 128.8, 127.4, 126.7, 126.4, 124.2, 113.4, 113.3, 80.9, 52.0, 46.8, 34.4, 30.0, 25.4, 24.2 ppm; $[\alpha]_D^{25} = -51.5$ ($c = 0.3$, EA); the dr value was evaluated by HPLC of the mixture and was found to be >20:1; the er value was determined by HPLC, using CHIRALCEL OD-H, *i*-PrOH: Hexane =1:99, $v = 0.5$ mL/min, $\lambda = 254$ nm, t (major) = 10.39 min, t (minor) = 12.86 min; er = 96:4; HRMS (ESI) calcd for $[C_{34}H_{34}Cl_2N_2NaO]^+$ 579.1940, found 579.1930.

2-((*R*)-2-((*S*)-(3,5-di-*tert*-butyl-4-hydroxyphenyl)(phenyl)methyl)-7-methoxy-3,4-dihydronaphthalen-1(2*H*)-ylidene)malononitrile (3ba)



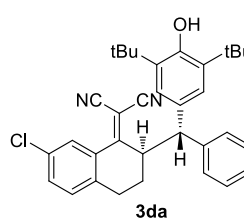
yield 85% (44.0 mg); white solid, m.p. 203-205 °C; 1H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, $J = 7.2$ Hz, 2H), 7.36 (t, $J = 7.5$ Hz, 2H), 7.30-7.16 (m, 3H), 7.15-7.12 (m, 1H), 6.77 (s, 2H), 5.12 (s, 1H), 4.14-4.08 (m, 1H), 3.84 (s, 3H), 3.75 (d, $J = 11.6$ Hz, 1H), 3.01-2.76 (m, 2H), 2.21-1.87 (m, 2H), 1.37 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.3, 157.7, 152.8, 141.3, 135.8, 131.8, 131.7, 130.9, 129.8, 129.0, 128.0, 127.0, 124.4, 121.6, 113.9, 113.5, 111.7, 80.4, 55.6, 52.6, 47.4, 34.4, 30.1, 26.0, 23.5 ppm; $[\alpha]_D^{25} = -63.7$ ($c = 0.3$, EA); the dr value was evaluated by HPLC of the mixture and was found to be >20:1; the er value was determined by HPLC, using CHIRALCEL OD-H, *i*-PrOH: Hexane =1:99, $v = 0.5$ mL/min, $\lambda = 254$ nm, t (major) = 11.31 min, t (minor) = 20.83 min; er = 90:10; HRMS (ESI) calcd for $[C_{35}H_{38}KN_2O_2]^+$ 557.2565, found 557.2571.

2-((R)-7-bromo-2-((S)-(3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)-3,4-dihydronaphthalen-1(2H)-ylidene)malononitrile (3ca)



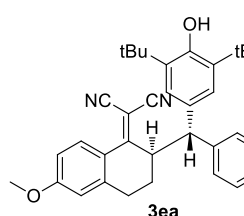
yield 77% (43.7 mg); white solid, m.p. 192-194 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.76-7.59 (m, 2H), 7.48-7.31 (m, 4H), 7.28-7.21 (m, 2H), 6.74 (s, 2H), 5.15 (s, 1H), 4.17-4.11 (m, 1H), 3.63 (d, *J* = 11.7 Hz, 1H), 3.09-2.73 (m, 2H), 2.22-1.91 (m, 2H), 1.40 (s, 18H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 175.6, 153.0, 140.9, 138.4, 136.1, 136.0, 131.5, 131.4, 131.1, 129.1, 127.8, 127.2, 124.2, 120.0, 113.1, 113.0, 81.7, 52.6, 47.2, 34.4, 30.1, 25.3, 23.9 ppm; [α]_D²⁵ = -69.7 (c = 0.3, EA); the dr value was evaluated by HPLC of the mixture and was found to be >20:1; the er value was determined by HPLC, using CHIRALCEL OD-H, *i*-PrOH: Hexane = 1:99, *v* = 0.5 mL/min, λ = 254 nm, *t* (major) = 9.23 min, *t* (minor) = 11.15 min; er = 93:7; HRMS (ESI) calcd for [C₃₄H₃₅BrN₂NaO]⁺ 589.1825, found 589.1819.

2-((R)-7-chloro-2-((S)-(3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)-3,4-dihydronaphthalen-1(2H)-ylidene)malononitrile (3da)



yield 98% (51.3 mg); white solid, m.p. 176-178 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.59-7.48 (m, 2H), 7.43 (d, *J* = 7.3 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.31-7.21 (m, 2H), 6.74 (s, 2H), 5.16 (s, 1H), 4.19-4.05 (m, 1H), 3.63 (d, *J* = 11.7 Hz, 1H), 3.10-2.77 (m, 2H), 2.02-1.95 (m, 2H), 1.38 (s, 18H); ¹³C NMR (75 MHz, CDCl₃) δ 175.8, 153.0, 140.9, 137.8, 135.9, 133.2, 132.4, 131.5, 131.2, 130.7, 129.1, 128.2, 127.8, 127.2, 124.2, 113.1, 113.0, 52.6, 47.2, 34.4, 30.1, 25.3, 23.9 ppm; [α]_D²⁵ = -58.7 (c = 0.3, EA); the dr value was evaluated by HPLC of the mixture and was found to be >20:1; the er value was determined by HPLC, using CHIRALCEL OD-H, *i*-PrOH: Hexane = 1:99, *v* = 0.5 mL/min, λ = 254 nm, *t* (major) = 13.04 min, *t* (minor) = 18.41 min; er = 86:14; HRMS (ESI) calcd for [C₃₄H₃₅ClKN₂O]⁺ 561.2069, found 561.2056.

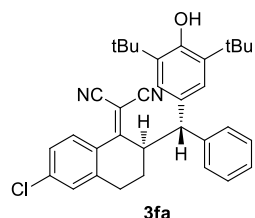
2-((R)-2-((S)-(3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)-6-methoxy-3,4-dihydronaphthalen-1(2H)-ylidene)malononitrile (3ea)



yield 87% (45.1 mg); white solid, m.p. 174-176 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.72 (d, *J* = 8.8 Hz, 1H), 7.44 (d, *J* = 7.1 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.29-7.20 (m, 1H), 6.87-6.91 (m, 1H), 6.81 (d, *J* = 2.3 Hz, 1H), 6.75 (s, 2H), 5.12 (s, 1H), 4.08-4.03 (m, 1H), 3.88 (s, 3H), 3.70 (d, *J* = 11.6 Hz, 1H), 3.01-2.96 (m, 1H), 2.86-2.79 (m, 1H), 2.11-1.92 (m, 2H), 1.36 (s, 18H); ¹³C NMR (75 MHz, CDCl₃) δ 176.2, 163.6, 152.8, 142.2, 141.2, 135.7, 131.6, 130.8, 129.0, 128.8, 128.0, 127.0, 124.4, 122.2, 114.4, 114.0, 112.8, 78.0, 55.6, 52.6, 47.2, 34.4, 30.1, 25.4, 24.6 ppm; [α]_D²⁵ = +14.7 (c = 0.3, EA); the dr value was evaluated by HPLC of the mixture and was found to be >20:1; the er value was

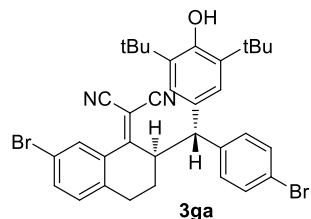
determined by HPLC, using CHIRALCEL OD-H, *i*-PrOH: Hexane =1:99, ν = 0.5 mL/min, λ = 254 nm, *t* (major) = 14.72 min, *t* (minor) = 23.78 min; er = 96:4; HRMS (ESI) calcd for $[\text{C}_{35}\text{H}_{38}\text{KN}_2\text{O}_2]^+$ 557.2565, found 557.2560.

2-((*R*)-6-chloro-2-((*S*)-(3,5-di-*tert*-butyl-4-hydroxyphenyl)(phenyl)methyl)-3,4-dihydronaphthalen-1(2*H*)-ylidene)malononitrile (3fa)



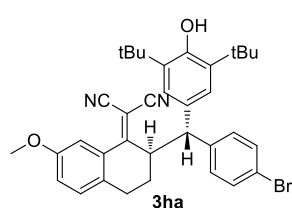
yield 99% (51.8 mg); white solid, m.p. 192-194 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.63-7.57 (m, 1H), 7.46-7.26 (m, 7H), 6.74 (s, 2H), 5.14 (s, 1H), 4.17-4.10 (m, 1H), 3.64 (d, J = 11.7 Hz, 1H), 3.14-2.75 (m, 2H), 2.18-1.85 (m, 2H), 1.36 (s, 18H) ppm; ^{13}C NMR (75 MHz, CDCl_3) δ 175.8, 152.9, 141.5, 140.9, 139.6, 135.9, 131.5, 130.0, 129.9, 129.1, 128.7, 127.9, 127.8, 127.2, 127.0, 124.2, 113.4, 113.2, 52.6, 47.2, 34.4, 30.1, 25.3, 24.3 ppm; $[\alpha]_{\text{D}}^{25}$ = -30.3 (c = 0.3, EA); the dr value was evaluated by HPLC of the mixture and was found to be >20:1; the er value was determined by HPLC, using CHIRALCEL OD-H, *i*-PrOH: Hexane =1:99, ν = 0.5 mL/min, λ = 254 nm, *t* (major) = 10.85 min, *t* (minor) = 13.42 min; er = 93:7; HRMS (ESI) calcd for $[\text{C}_{34}\text{H}_{35}\text{ClN}_2\text{NaO}]^+$ 545.2330, found 545.2328.

2-((*R*)-7-bromo-2-((*S*)-(4-bromophenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl)-3,4-dihydronaphthalen-1(2*H*)-ylidene)malononitrile (3ga)



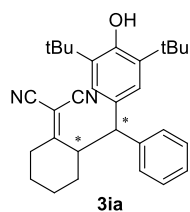
yield 90% (58.1 mg); white solid, m.p. 202-204 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.73-7.63 (m, 2H), 7.49 (d, J = 8.4 Hz, 2H), 7.36-7.18 (m, 4H), 6.69 (s, 2H), 5.18 (s, 1H), 4.13-4.09 (m, 1H), 3.60 (d, J = 11.7 Hz, 1H), 2.93-2.89 (m, 2H), 2.17-1.97 (m, 2H), 1.38 (s, 18H) ppm; ^{13}C NMR (75 MHz, CDCl_3) δ 175.0, 153.1, 140.0, 138.1, 136.2, 132.2, 131.4, 131.1, 130.9, 130.8, 129.5, 124.0, 121.1, 120.1, 113.0, 112.8, 81.9, 52.0, 46.9, 34.4, 30.0, 25.2, 23.9 ppm; $[\alpha]_{\text{D}}^{25}$ = -46.3 (c = 0.3, EA); the dr value was evaluated by HPLC of the mixture and was found to be >20:1; the er value was determined by HPLC, using CHIRALCEL OD-H, *i*-PrOH: Hexane =1:99, ν = 0.5 mL/min, λ = 254 nm, *t* (major) = 9.50 min, *t* (minor) = 15.77 min; er = 87:13; HRMS (ESI) calcd for $[\text{C}_{34}\text{H}_{34}\text{Br}_2\text{N}_2\text{NaO}]^+$ 667.0930, found 667.0919.

2-((R)-2-((S)-(4-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)-7-methoxy-3,4-dihydronaphthalen-1(2H)-ylidene)malononitrile (3ha)



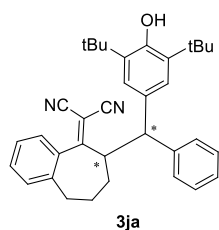
yield 99% (59.1 mg); white solid, m.p. 174-176 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.49 (d, $J = 8.4$ Hz, 2H), 7.34 (d, $J = 8.4$ Hz, 2H), 7.17-7.03 (m, 3H), 6.72 (s, 2H), 5.15 (s, 1H), 4.15-3.96 (m, 1H), 3.81 (s, 3H), 3.72 (d, $J = 11.7$ Hz, 1H), 3.00-2.70 (m, 2H), 2.12-1.98 (m, 2H), 1.29 (s, 18H) ppm; ^{13}C NMR (75 MHz, CDCl_3) δ 176.7, 157.8, 153.0, 140.3, 135.9, 132.1, 131.5, 131.1, 130.9, 129.6, 124.3, 121.7, 120.9, 113.8, 113.5, 111.7, 80.6, 55.6, 52.0, 47.2, 34.4, 30.1, 25.9, 23.5 ppm; $[\alpha]_{\text{D}}^{25} = -43.7$ ($c = 0.3$, EA); the dr value was evaluated by HPLC of the mixture and was found to be >20:1; the er value was determined by HPLC, using CHIRALCEL OD-H, i -PrOH: Hexane =1:99, $v = 0.5$ mL/min, $\lambda = 254$ nm, t (major) = 11.96 min, t (minor) = 25.84 min; er = 93:7; HRMS (ESI) calcd for $[\text{C}_{35}\text{H}_{37}\text{BrKN}_2\text{O}_2]^+$ 635.1670, found 635.1659.

2-((R)-2-((S)-(3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)cyclohexylidene)malononitrile (3ia)



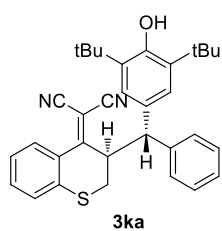
yield 99% (43.6 mg); white solid, m.p. 187-189 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.46-7.12 (m, 5H), 7.03 (s, 2H), 5.11 (s, 1H), 4.21-4.17 (m, 1H), 3.97-3.76 (m, 1H), 2.86-2.82 (m, 1H), 2.63-2.52 (m, 1H), 2.19-2.15 (m, 1H), 1.89-1.79 (m, 2H), 1.56-1.41 (m, 3H), 1.37 (s, 18H) ppm; ^{13}C NMR (75 MHz, CDCl_3) δ 187.2, 152.9, 141.4, 136.2, 131.3, 129.1, 128.0, 127.0, 124.0, 112.1, 111.6, 83.9, 52.9, 48.3, 34.4, 31.4, 30.6, 30.2, 28.9, 19.6 ppm; $[\alpha]_{\text{D}}^{25} = -58.3$ ($c = 0.3$, EA); the dr value was evaluated by HPLC of the mixture and was found to be >20:1; the er value was determined by HPLC, using CHIRALCEL OD-H, i -PrOH: Hexane =1:99, $v = 0.5$ mL/min, $\lambda = 254$ nm, t (major) = 8.58 min, t (minor) = 8.21 min; er = 56:44; HRMS (ESI) calcd for $[\text{C}_{30}\text{H}_{36}\text{N}_2\text{NaO}]^+$ 463.2720, found 463.2718.

2-((R)-6-((S)-(3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)-6,7,8,9-tetrahydro-5H-benzo[7]jannulen-5-ylidene)malononitrile (3ja)



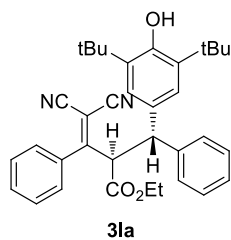
yield 75% (37.7 mg); white solid, m.p. 190-192 °C; ^1H NMR (300 MHz, DMSO) δ 7.49-7.04 (m, 9H), 6.82 (s, 2H), 5.75 (d, $J = 7.2$ Hz, 1H), 4.15 (d, $J = 11.8$ Hz, 1H), 3.67 (d, $J = 12.0$ Hz, 1H), 2.83 (s, 2H), 2.08-1.68 (m, 4H), 1.42 (s, 18H) ppm; ^{13}C NMR (75 MHz, CDCl_3) δ 187.3, 152.8, 142.2, 138.5, 136.0, 134.4, 131.5, 130.8, 129.8, 129.6, 129.0, 127.6, 126.9, 125.9, 124.8, 112.4, 112.0, 87.1, 52.0, 48.8, 36.2, 34.4, 33.9, 30.4, 21.8 ppm; $[\alpha]_{\text{D}}^{25} = +157.7$ ($c = 0.3$, EA); the dr value was evaluated by HPLC of the mixture and was found to be >20:1; the er value was determined by HPLC, using CHIRALCEL OD-H, i -PrOH: Hexane =1:99, $v = 0.5$ mL/min, $\lambda = 254$ nm, t (major) = 19.30 min, t (minor) = 18.46 min; er = 91:9; HRMS (ESI) calcd for $[\text{C}_{35}\text{H}_{38}\text{KN}_2\text{O}]^+$ 541.2616, found 541.2620.

2-((R)-3-((S)-(3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)thiochroman-4-ylidene)malononitrile (3ka)



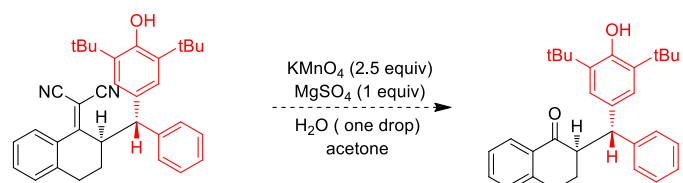
yield 98% (49.6 mg); yellow solid, m.p. 248-250 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.52 (d, *J* = 7.4 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.31-7.25 (m, 3H), 7.13 (d, *J* = 7.3 Hz, 1H), 6.77 (s, 2H), 5.14 (s, 1H), 4.29-4.24 (m, 1H), 4.03 (d, *J* = 11.4 Hz, 1H), 3.41-3.36 (m, 1H), 3.00-2.94 (m, 1H), 1.36 (s, 18H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 173.7, 153.0, 140.7, 137.7, 135.8, 133.4, 130.8, 130.7, 129.1, 127.9, 127.4, 126.8, 126.0, 124.6, 124.3, 113.1, 113.0, 82.8, 51.6, 43.9, 34.3, 30.1, 29.2 ppm; [α]_D²⁵ = +74.3 (c = 0.3, EA); the dr value was evaluated by HPLC of the mixture and was found to be >20:1; the er value was determined by HPLC, using CHIRALCEL IB, *i*-PrOH: Hexane = 0.5:99.5, *v* = 0.5 mL/min, λ = 254 nm, *t* (major) = 11.69 min, *t* (minor) = 17.41 min; er = 99:1; HRMS (ESI) calcd for [C₃₃H₃₄N₂NaOS]⁺ 529.2284, found 529.2279.

(R)-ethyl 4,4-dicyano-2-((S)-(3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)-3-phenylbut-3-enoate (3la)



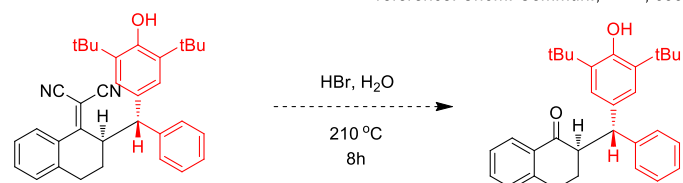
yield 56% (30 mg); white solid, m.p. 148-150 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.50-7.45 (m, 1H), 7.39-7.26 (m, 6H), 7.19 (d, *J* = 7.1 Hz, 1H), 6.97 (d, *J* = 7.3 Hz, 2H), 6.70 (s, 2H), 5.14-5.08 (m, 2H), 4.25 (d, *J* = 12.2 Hz, 1H), 4.14 (q, *J* = 7.0 Hz, 2H), 1.36 (s, 18H), 1.15 (t, *J* = 7.1 Hz, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 174.6, 168.1, 152.9, 141.8, 136.2, 133.5, 131.4, 130.0, 128.8, 128.5, 127.9, 127.4, 127.0, 124.6, 124.2, 112.4, 112.2, 62.5, 57.4, 51.6, 34.3, 30.2, 13.9 ppm; [α]_D²⁵ = +3.7 (c = 0.3, EA); the dr value was evaluated by HPLC of the mixture and was found to be >20:1; the er value was determined by HPLC, using CHIRALCEL IB, *i*-PrOH: Hexane = 0.5:99.5, *v* = 0.5 mL/min, λ = 254 nm, *t* (major) = 10.95 min, *t* (minor) = 10.59 min; er = 67:33; HRMS (ESI) calcd for [C₃₅H₃₈N₂NaO₃]⁺ 557.2775, found 557.2777.

5. Removal or functionalization of the tert-butyl groups and dicyanoolefin



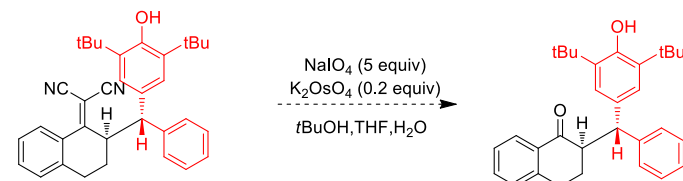
the product was not observed

reference: *Chem. Commun.*, **2009**, 6994



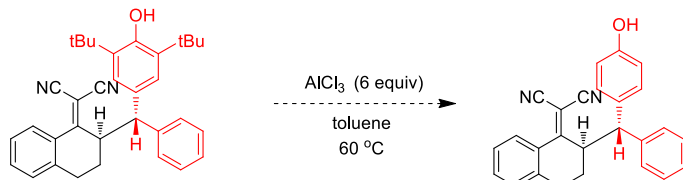
the product was not observed

reference: *Eur. J. Org. Chem.* **2015**, 4119



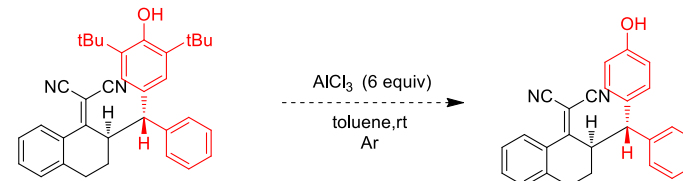
the product was not observed

reference: *Chem. Commun.*, **2015**, 51, 1070



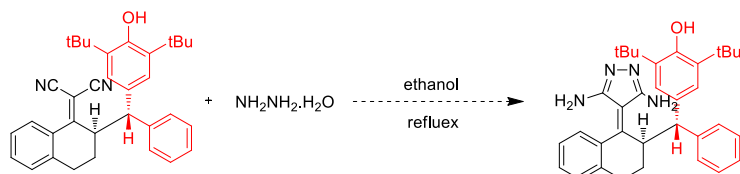
the product was not observed

reference: *J. Am. Chem. Soc.* **2014**, 136, 15929
Angew. Chem., Int. Ed. **2015**, 54, 12134



the product was not observed

reference: *Angew. Chem., Int. Ed.* **2015**, 54, 1-6
 DOI:10.1002/anie.201509110

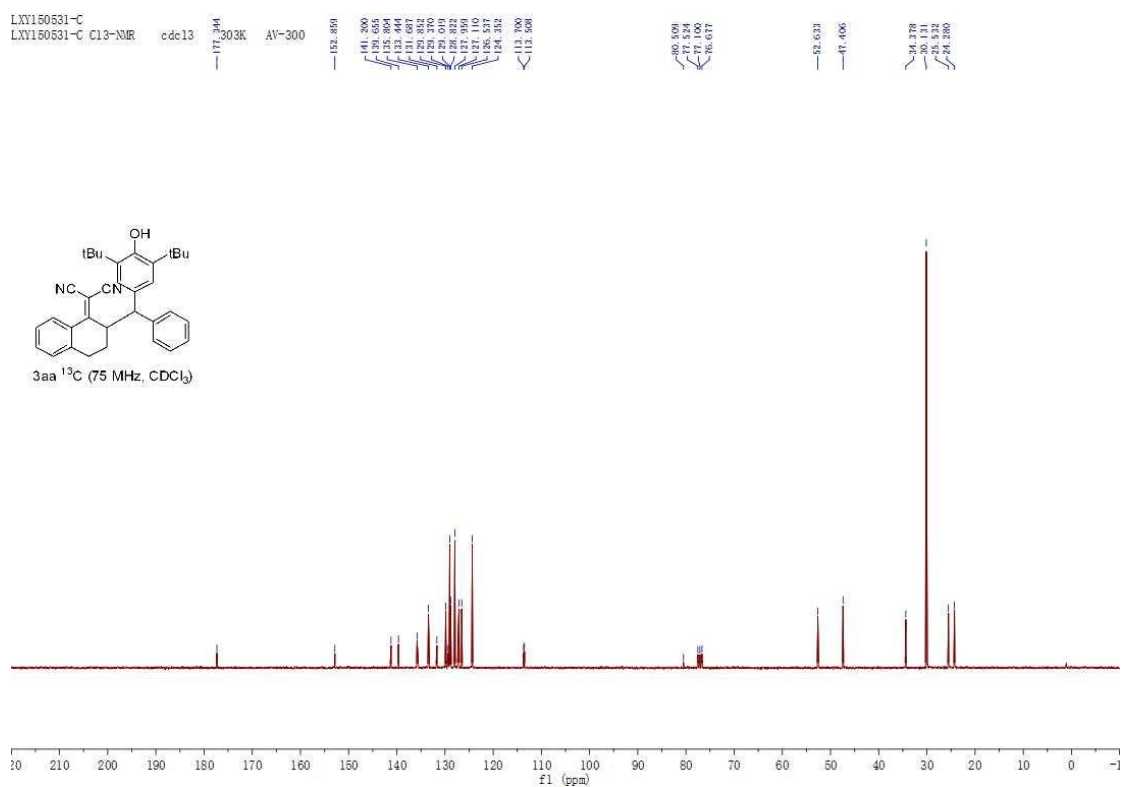
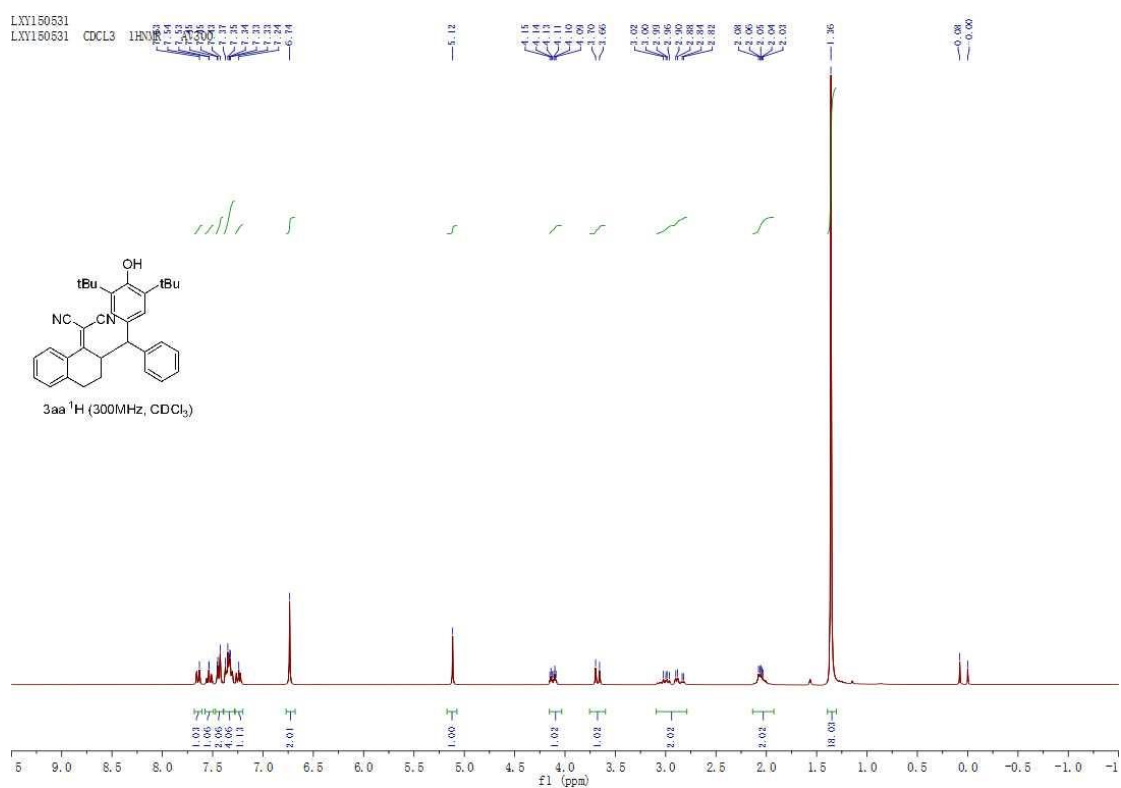


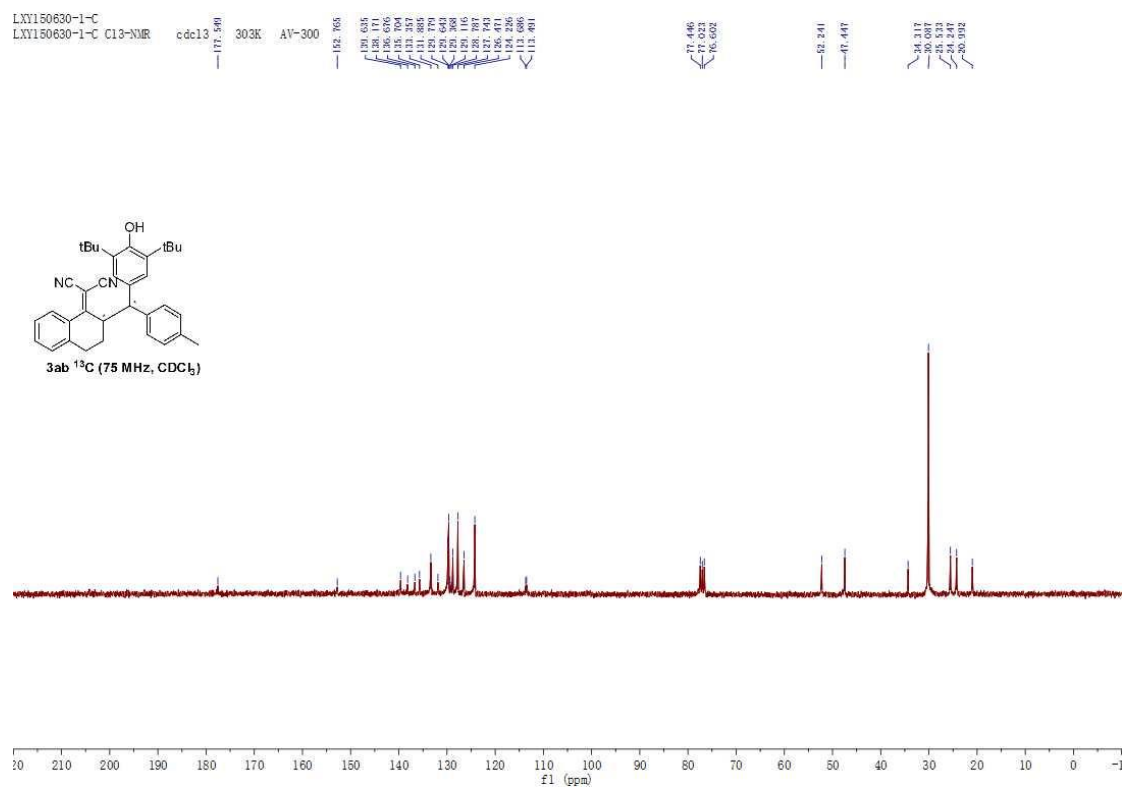
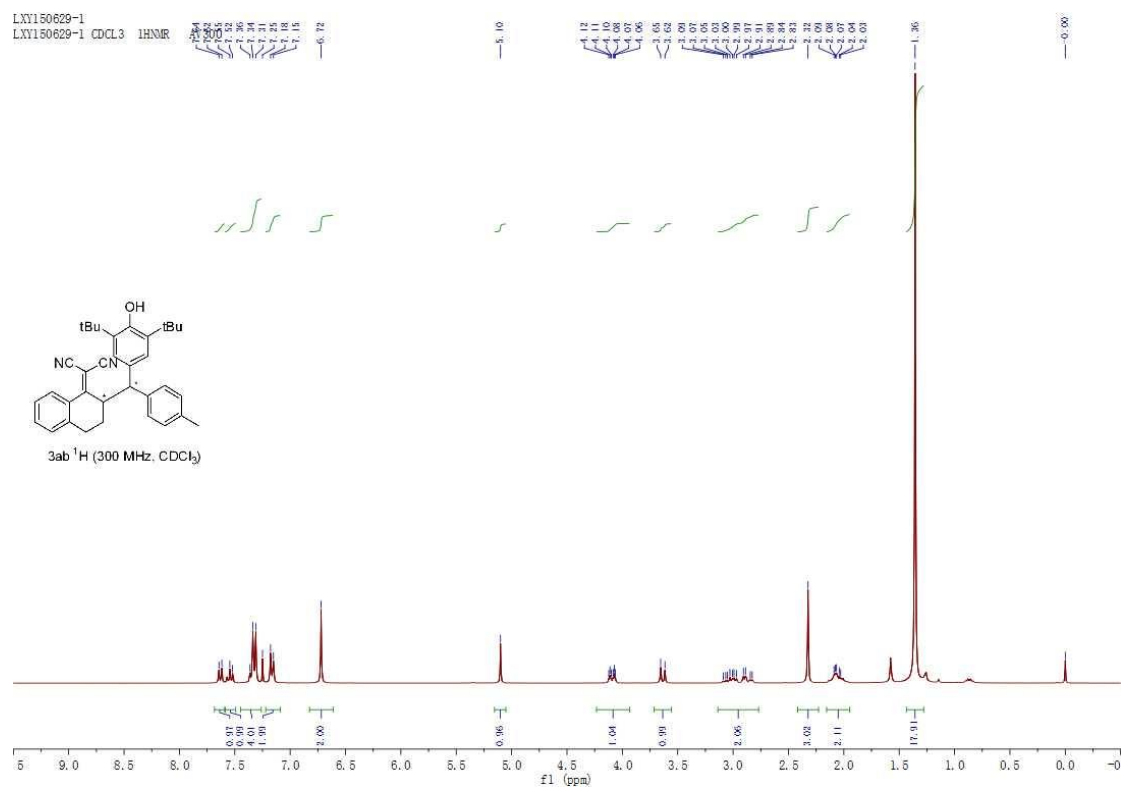
the product was not observed

reference: *Adv. Synth. Catal.* **2012**, 354, 2965

6. References

- (1) D. Xue, Y.-C. Chen, X. Cui, Q.-W. Wang, J. Zhu, and J.-G. Deng, *J. Org. Chem.*, **2015**, *70*, 3584.
- (2) (a) W.-D. Chu, L.-F. Zhang, X. Bao, X.-H. Zhao, C. Zeng, J.-Y. Du, G.-B. Zhang, F.-X. Wang, X. -Y. Ma, C.-A. Fan, *Angew. Chem., Int. Ed.*, **2013**, *52*, 9229. (b) L. Caruana, F. Kniep, T. K.Johansen, P. H. Poulsen, K. A. Jørgensen, *J. Am. Chem. Soc.*, **2014**, *136*, 15929. (c) D. Richter, N.Hampel, T. Singer, A. R. Ofial, H. Mayr, *Eur. J. Org. Chem.*, **2009**, *19*, 3203.





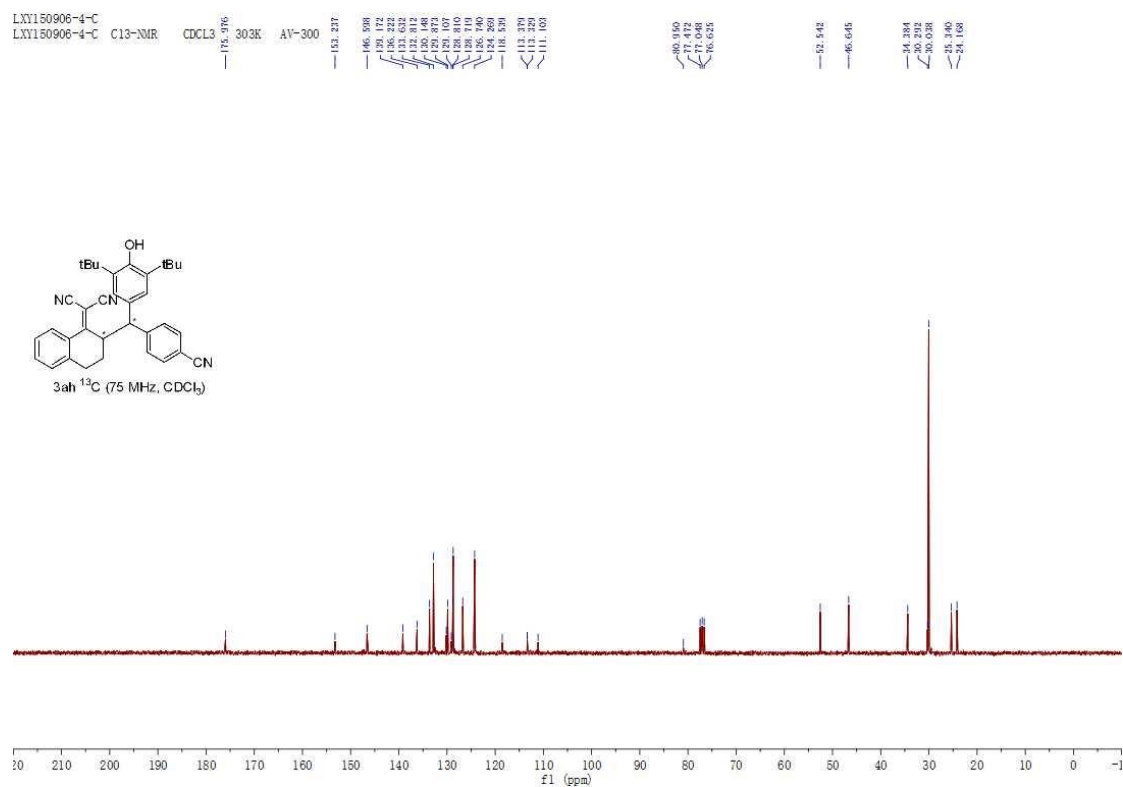
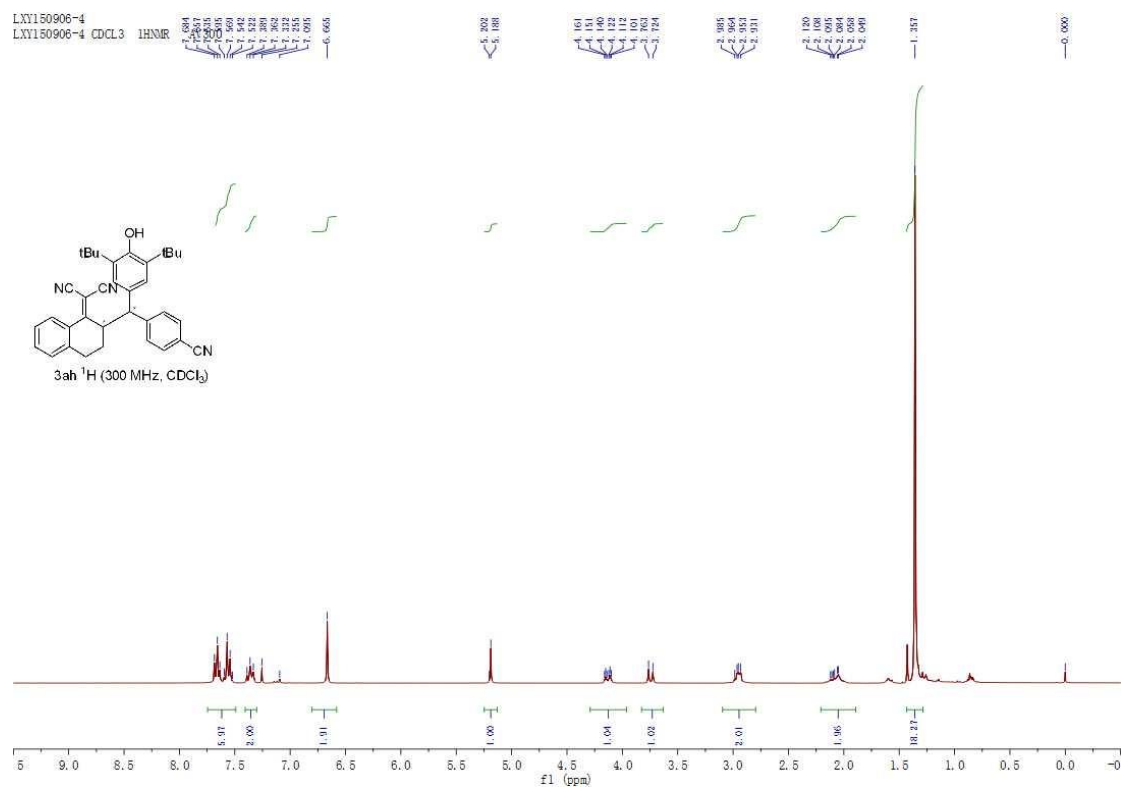
LXY20150612
LXY20150612 CDCl₃ 1H NMR

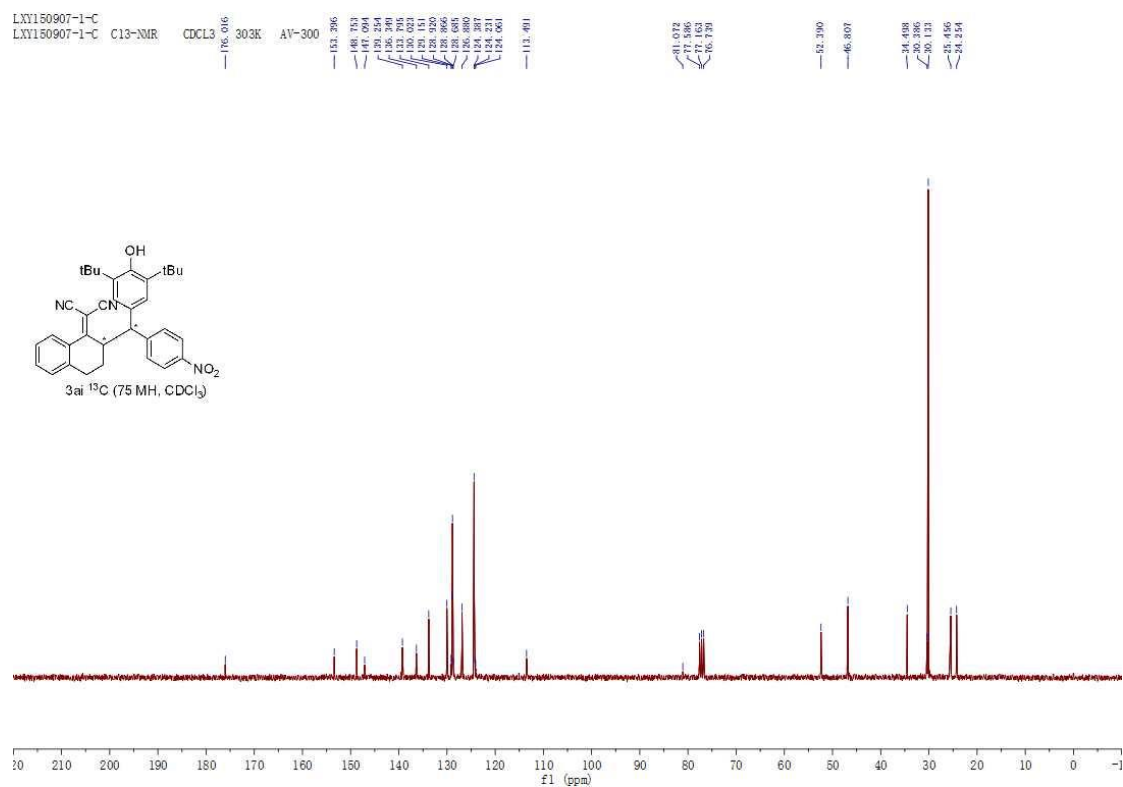
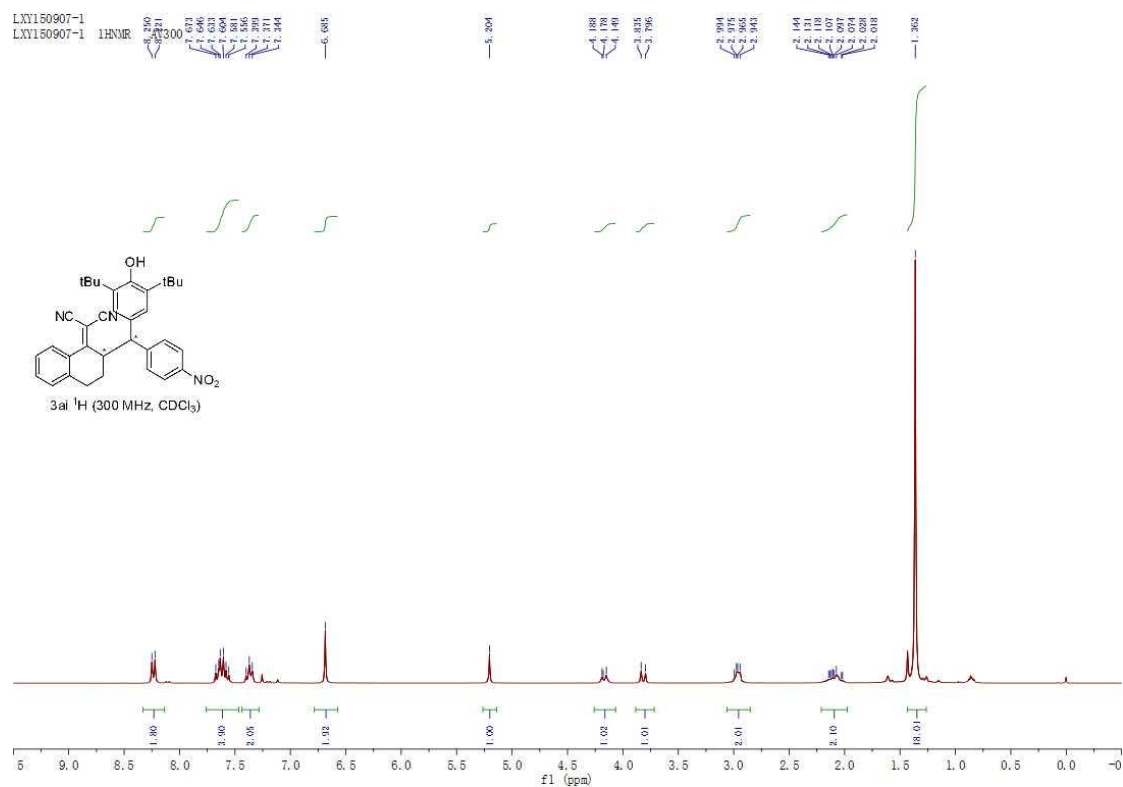
3a ¹H (300 MHz, CDCl₃)

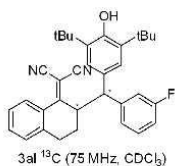
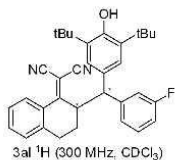
Chemical structure of 3a: CC(C)(C)c1cc(O)c(C(C)(C)C)c1C2=C(C#N)C3=CC=CC=C3CC2c4ccc(C(F)(F)F)cc4

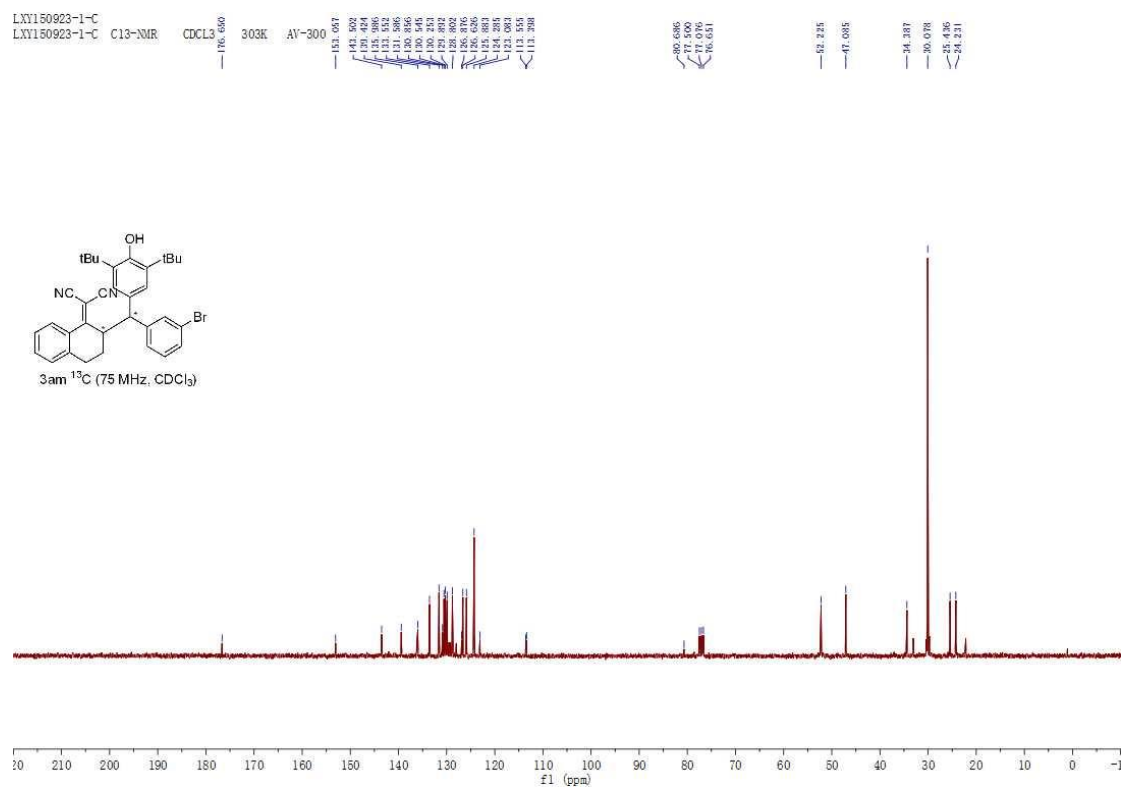
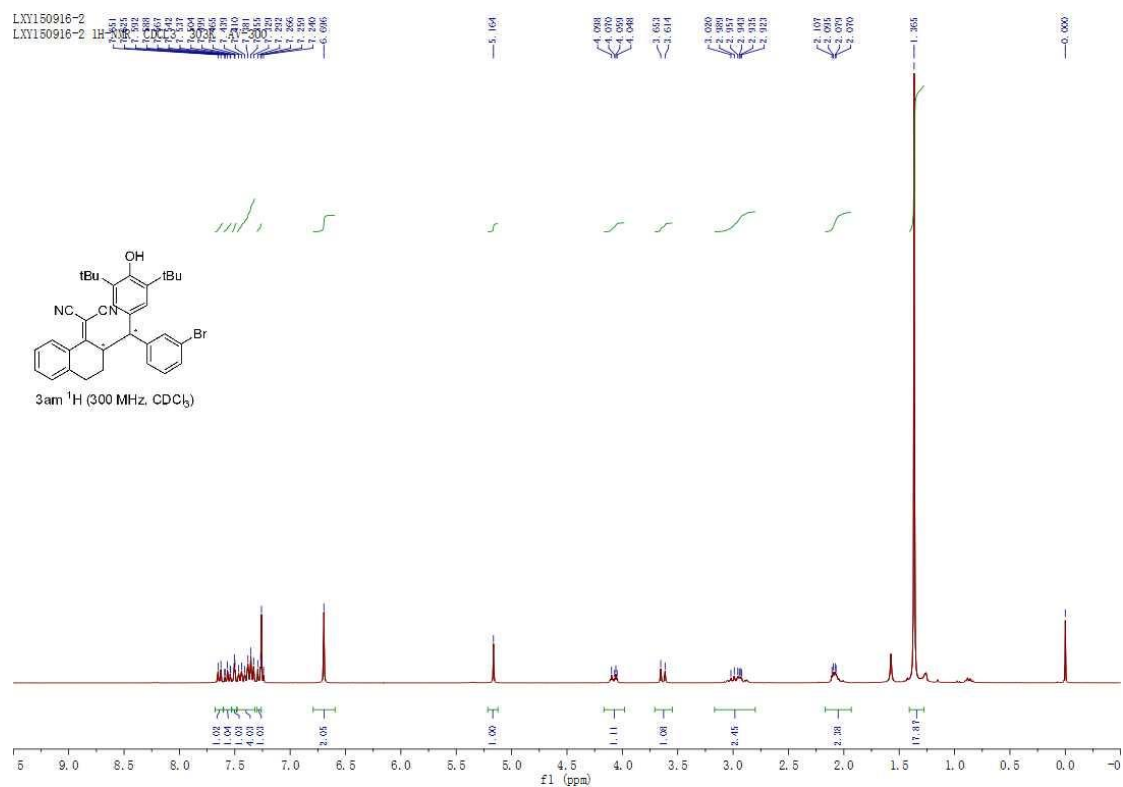
Integration values (from left to right): 2.90, 2.80, 1.98, 1.00, 1.12, 1.01, 2.28, 2.14, 18.15.

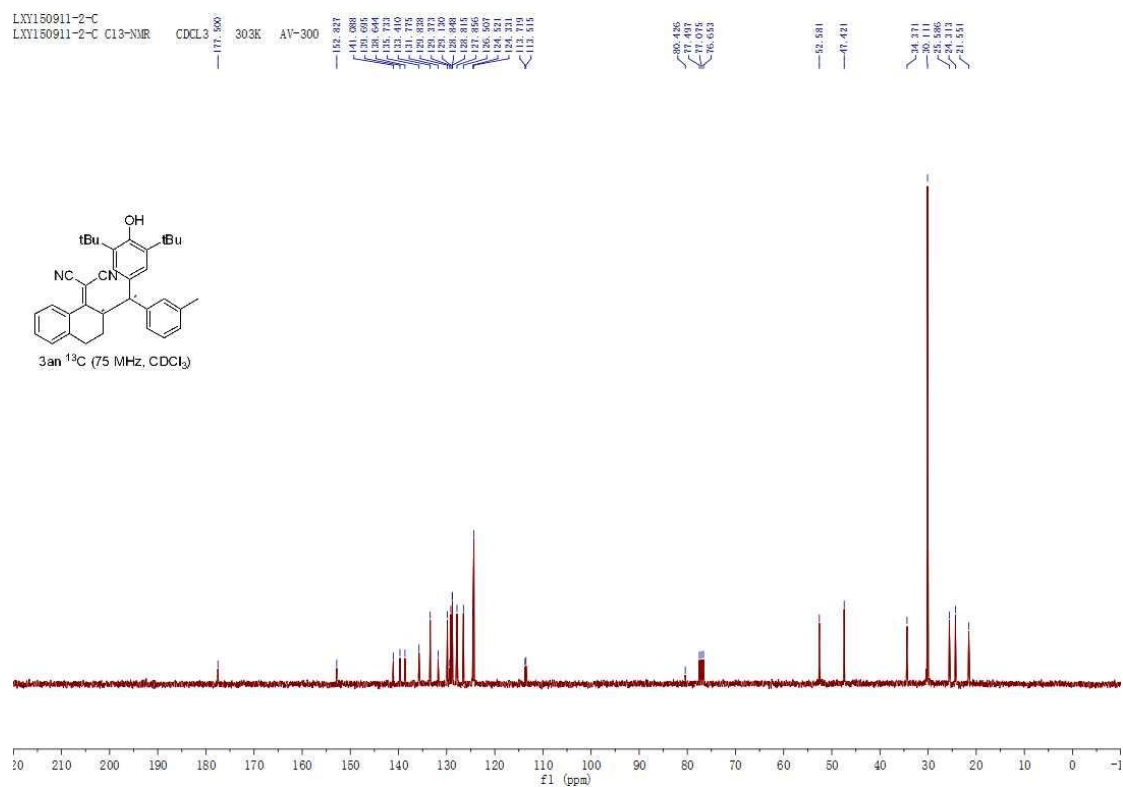
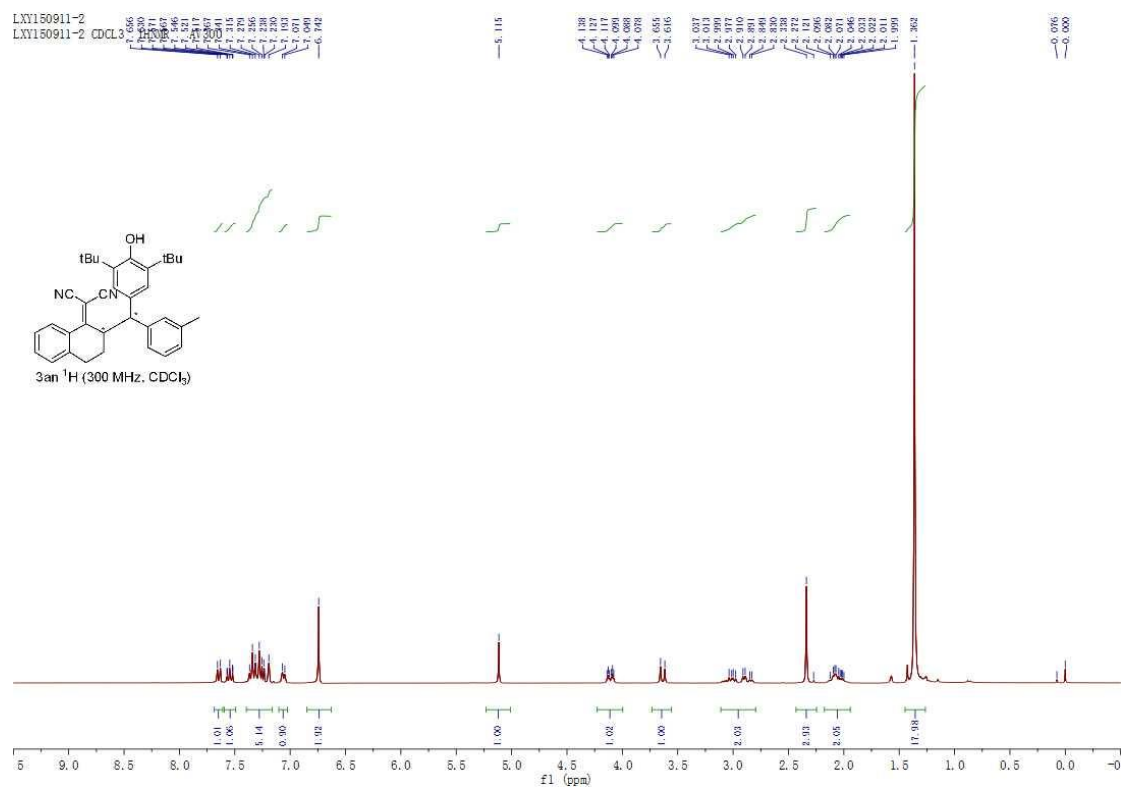
[illegible]

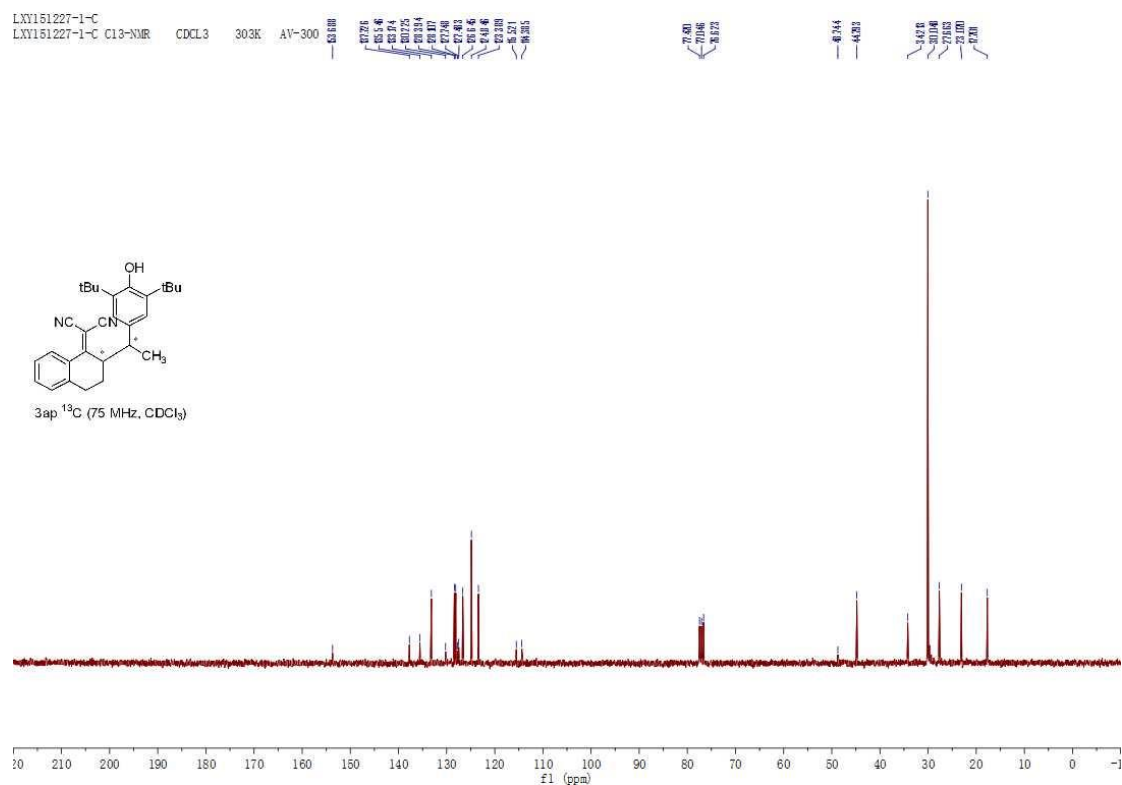
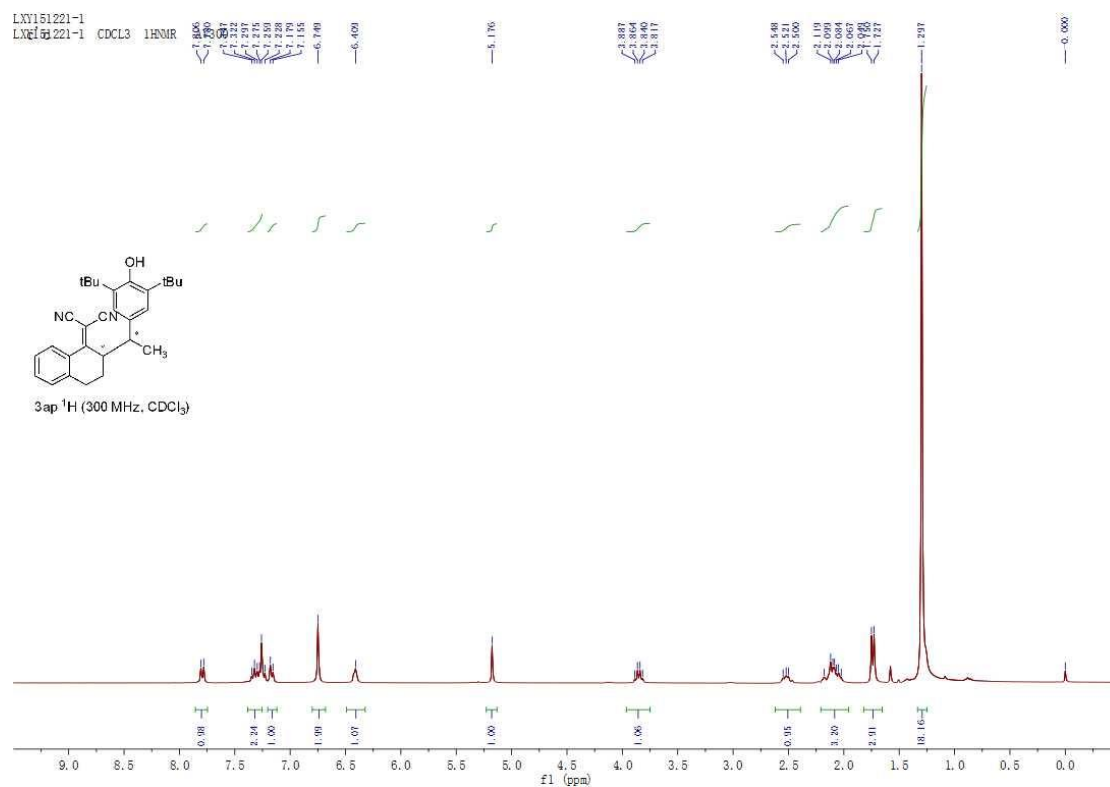


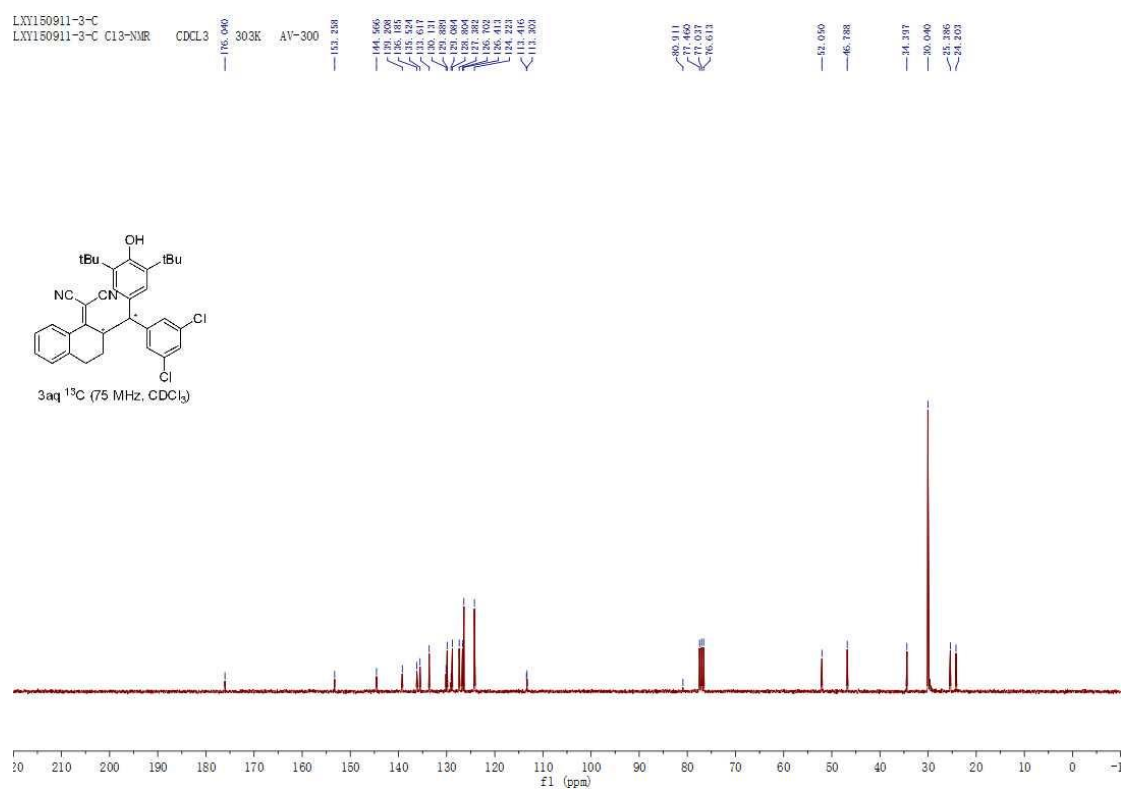
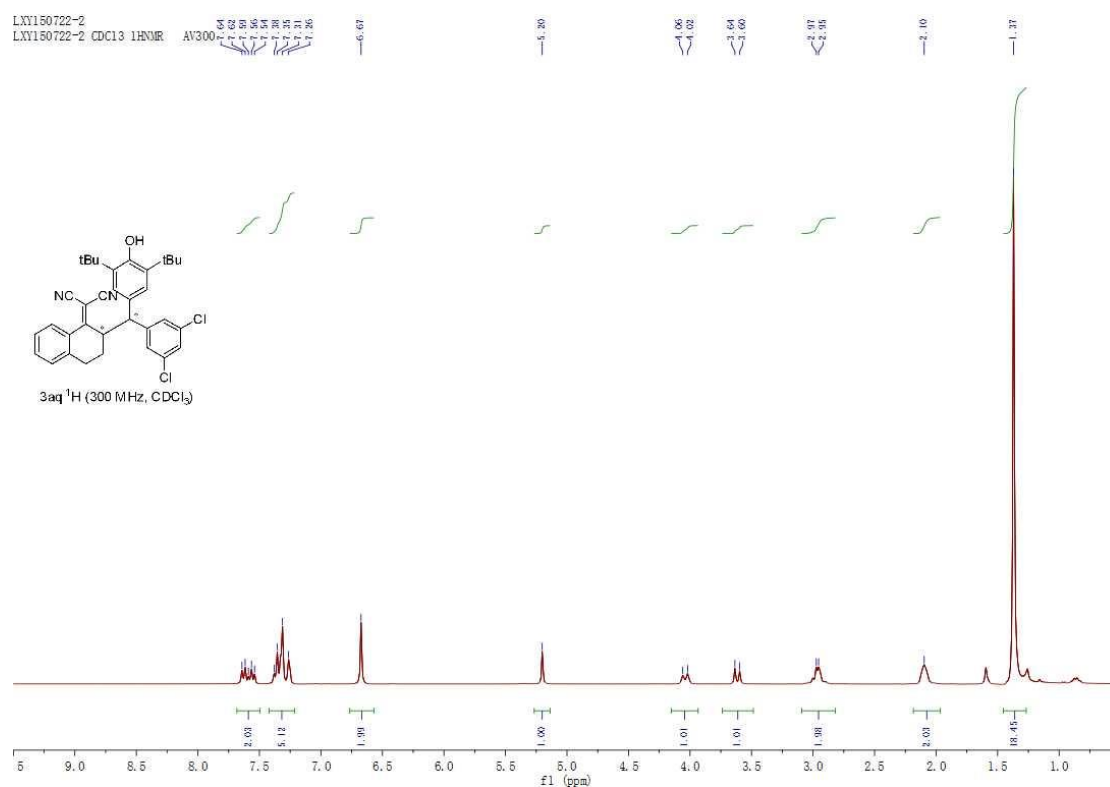












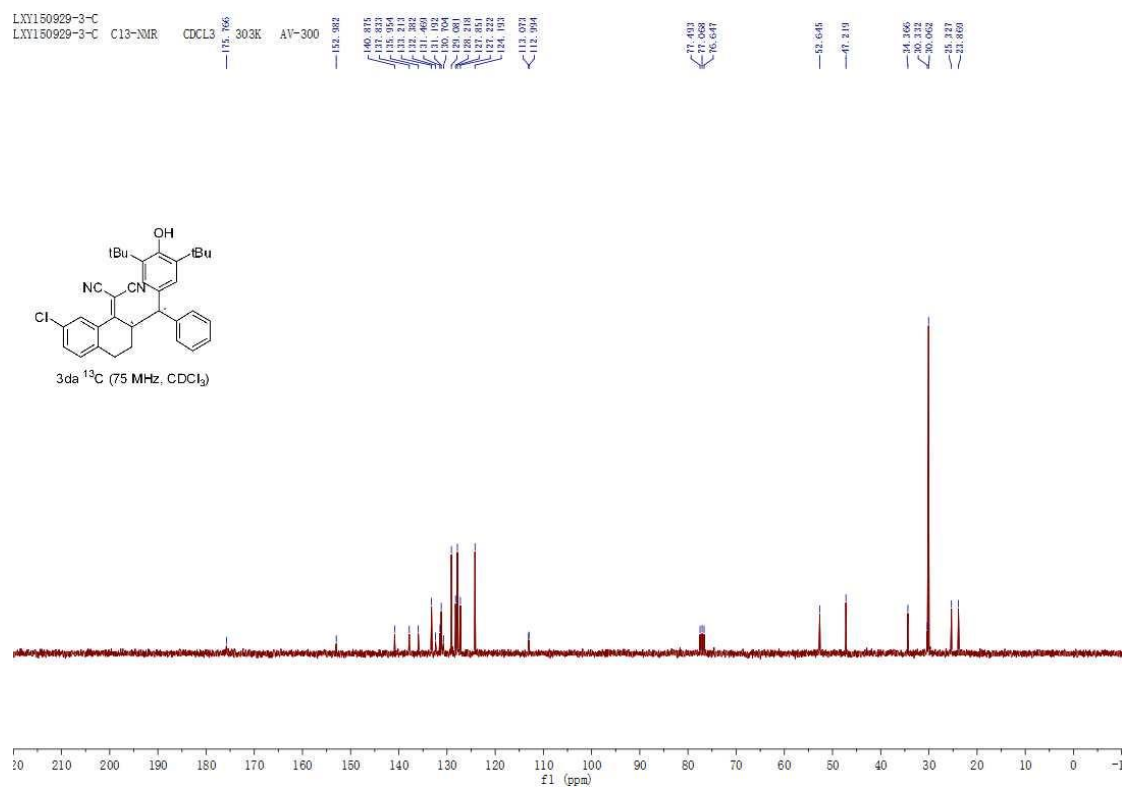
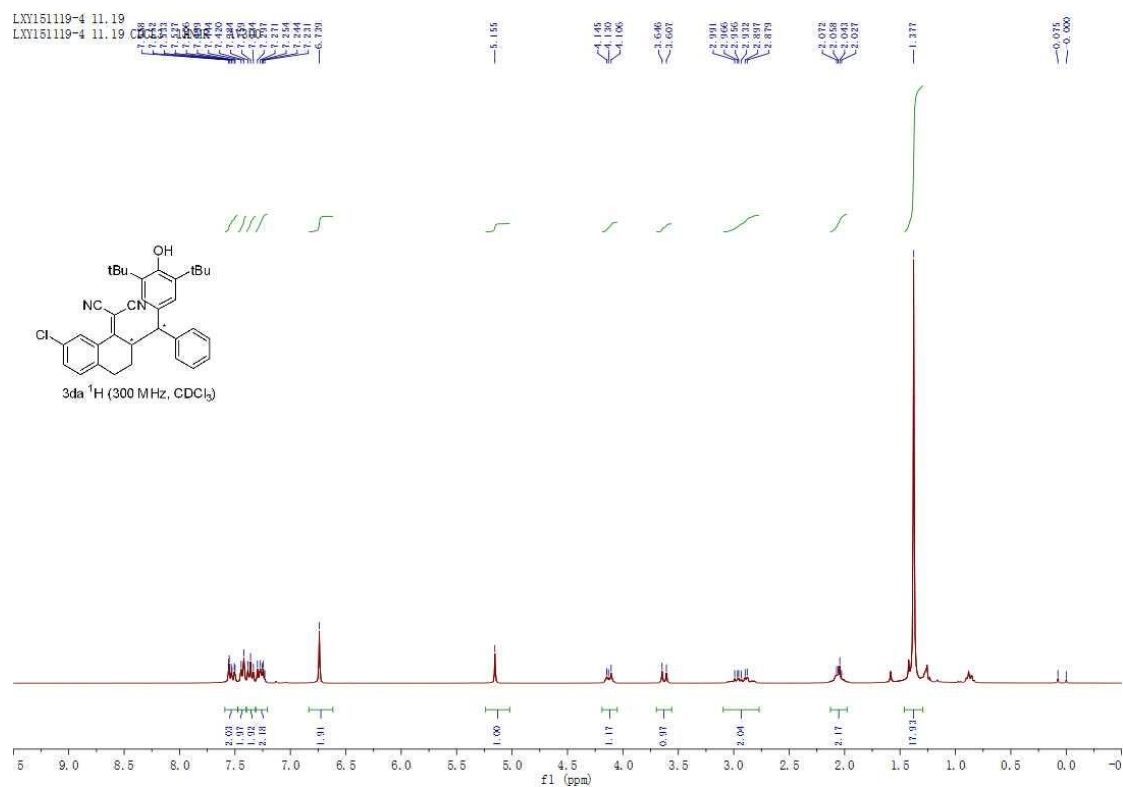
LXY130815-1
LXY130815-1 CDCl₃ 1H NMR

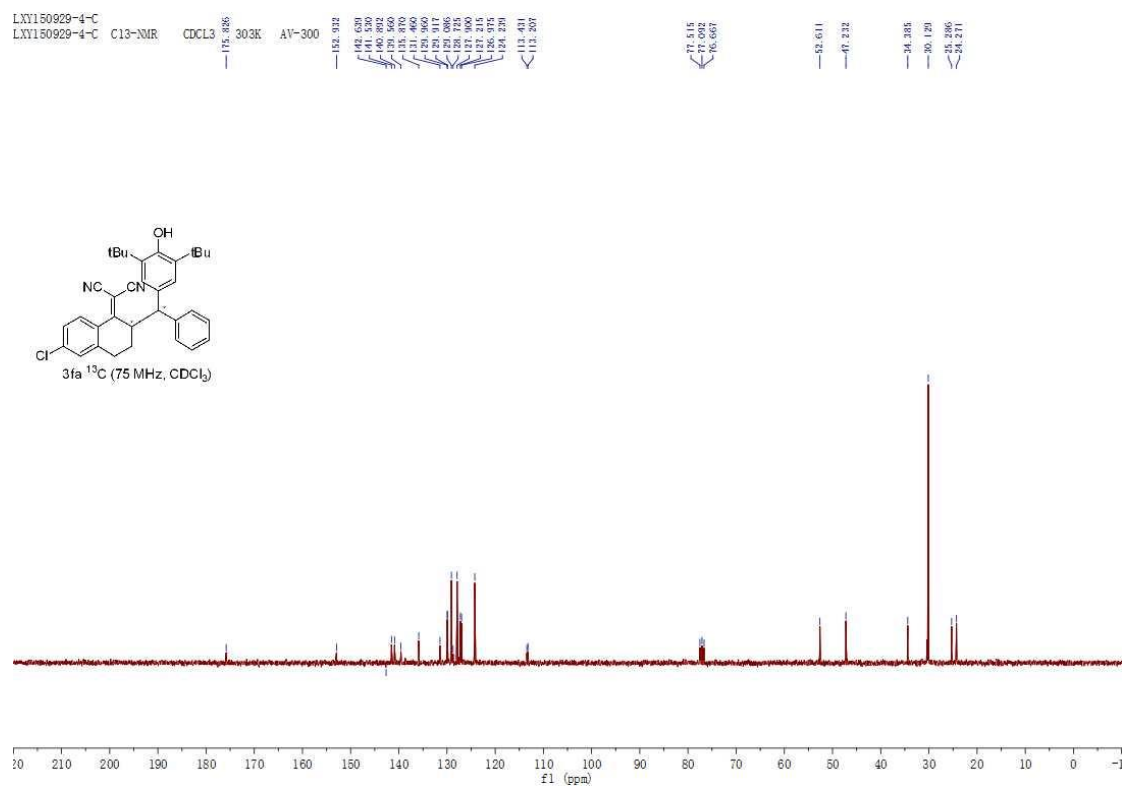
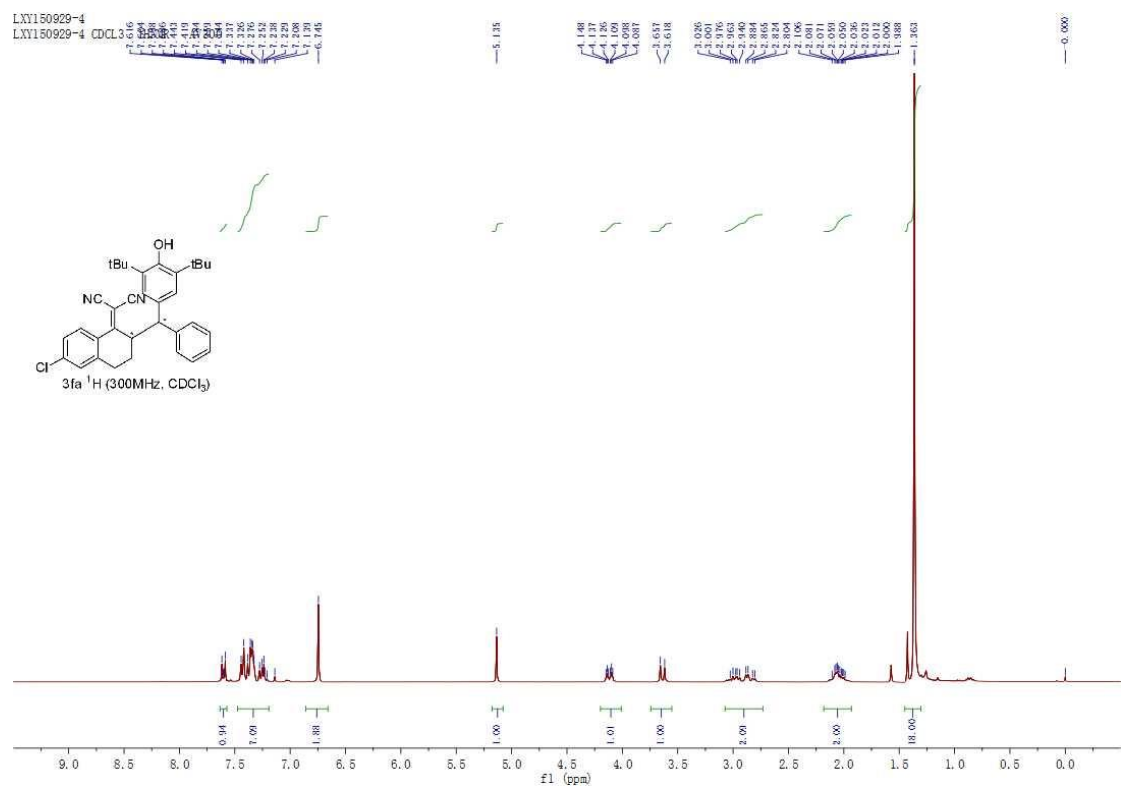
CC(C)(C)c1cc(O)c(C(C#N)C2=C(C#N)C(=C(C2)C3=CC=CC=C3C4=CC=CC=C4Br)C5=CC=CC=C5)c1

3ca ¹H (300MHz, CDCl₃)

CC(C)(C)c1cc(O)c(C#N)c(C#N)c1C2=C(C#N)C(=C3C=CC(=C(C=C3)Br)CC2)c4ccccc4
 LX1150924-3-C
 LX150924-3-C
 C13-NMR
 CDCl3
 303K
 AV-300
 175.804
 152.988
 140.872
 138.354
 136.585
 135.985
 131.463
 130.527
 129.087
 128.522
 127.252
 124.184
 120.011
 112.066
 112.390
 77.669
 77.511
 77.007
 76.864
 52.643
 47.204
 34.287
 30.698
 25.301
 23.351

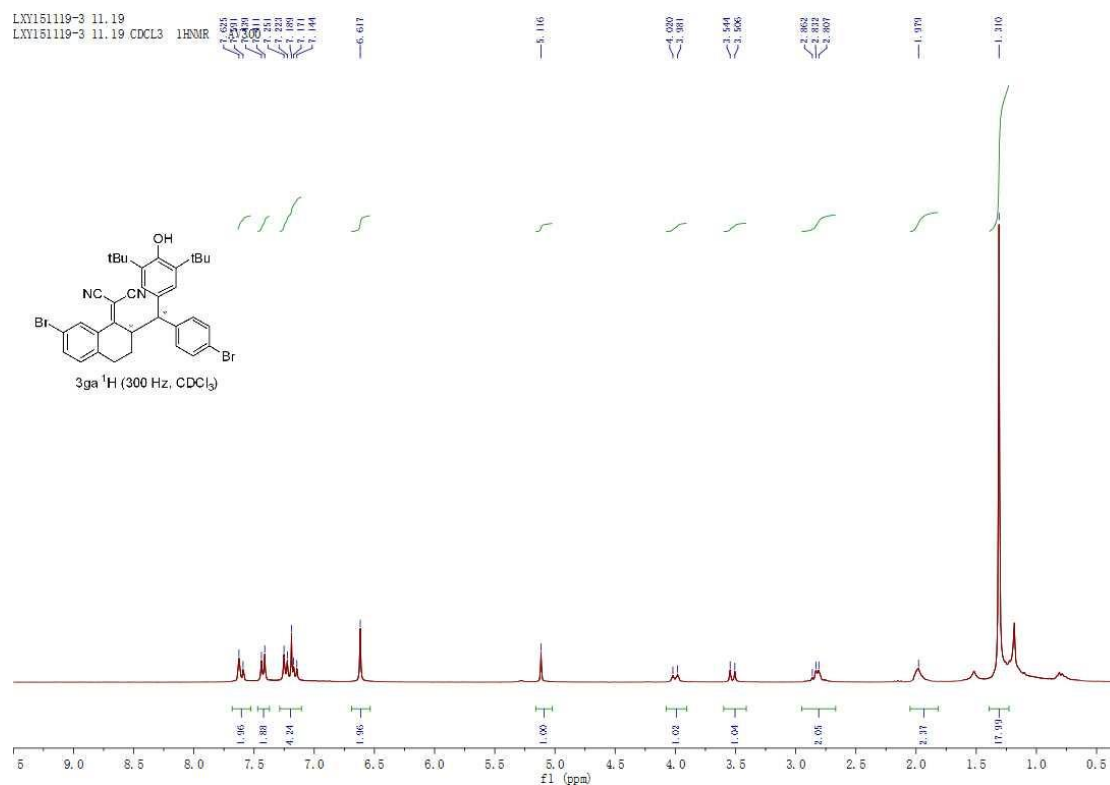
3ca ¹³C (75 MHz, CDCl₃)





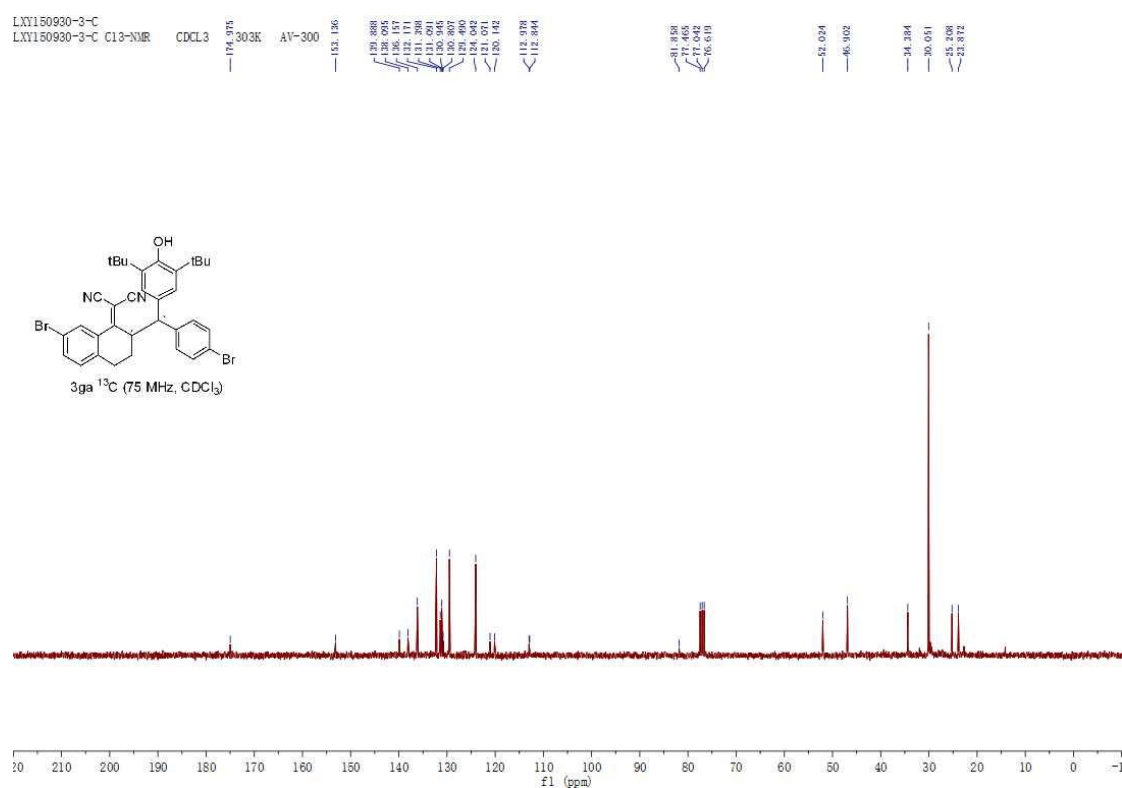
LXY151119-3 11.19

LXY151119-3 11.19 CDCL₃ 1HMR



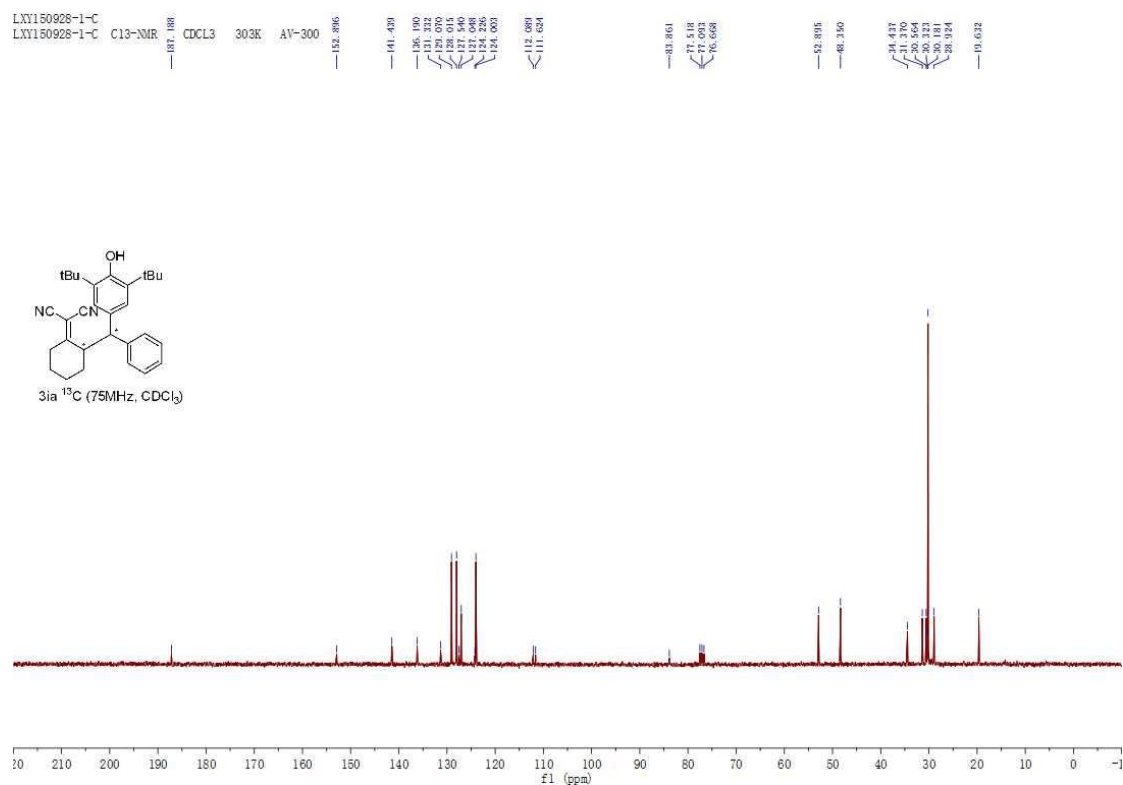
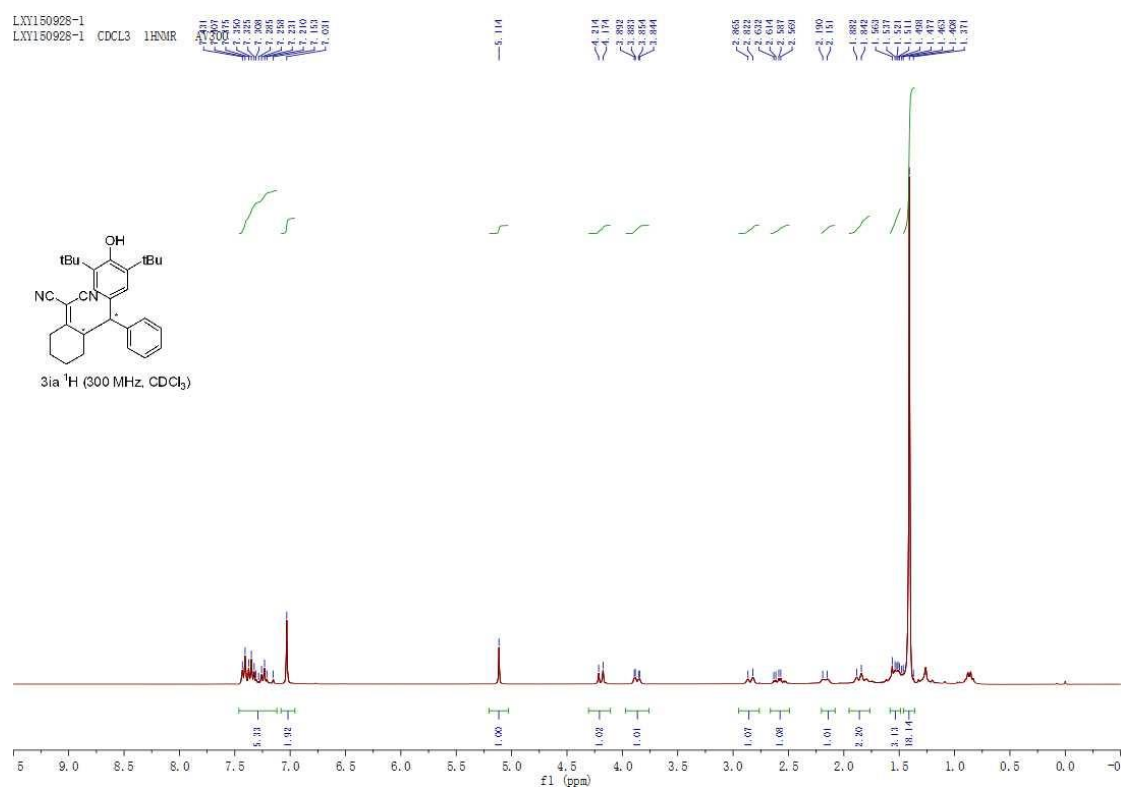
LXY150930-3-C

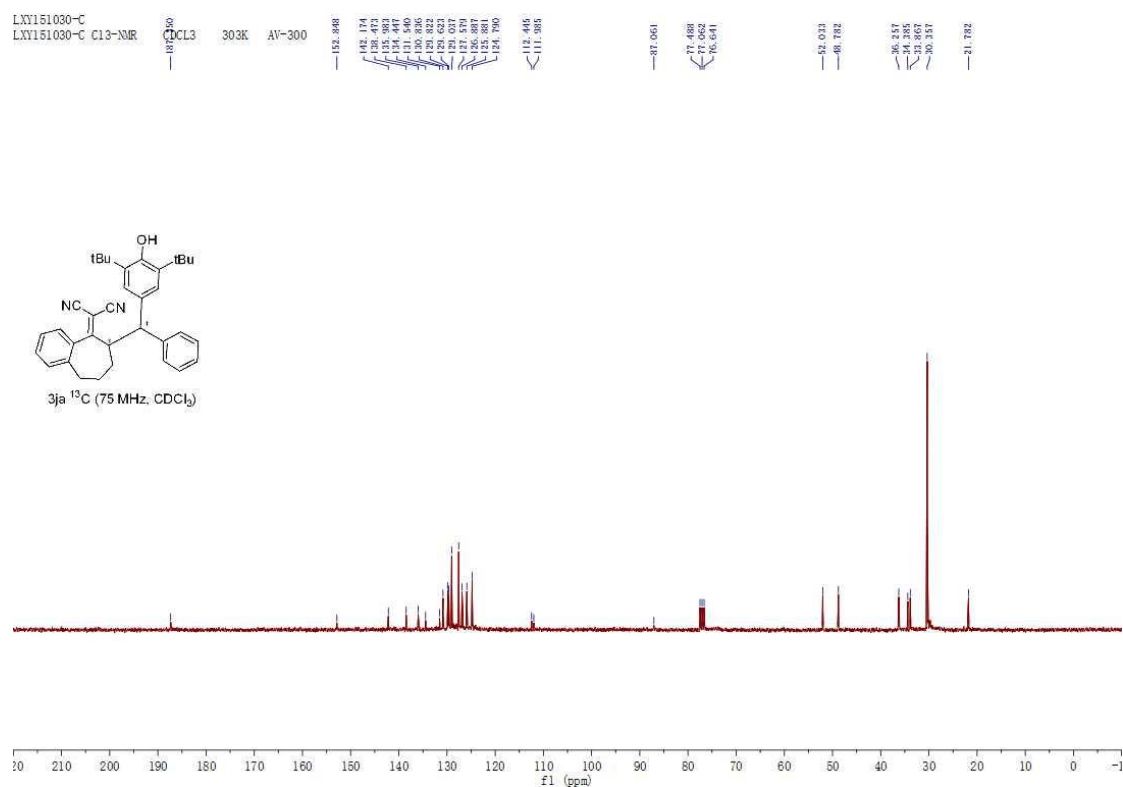
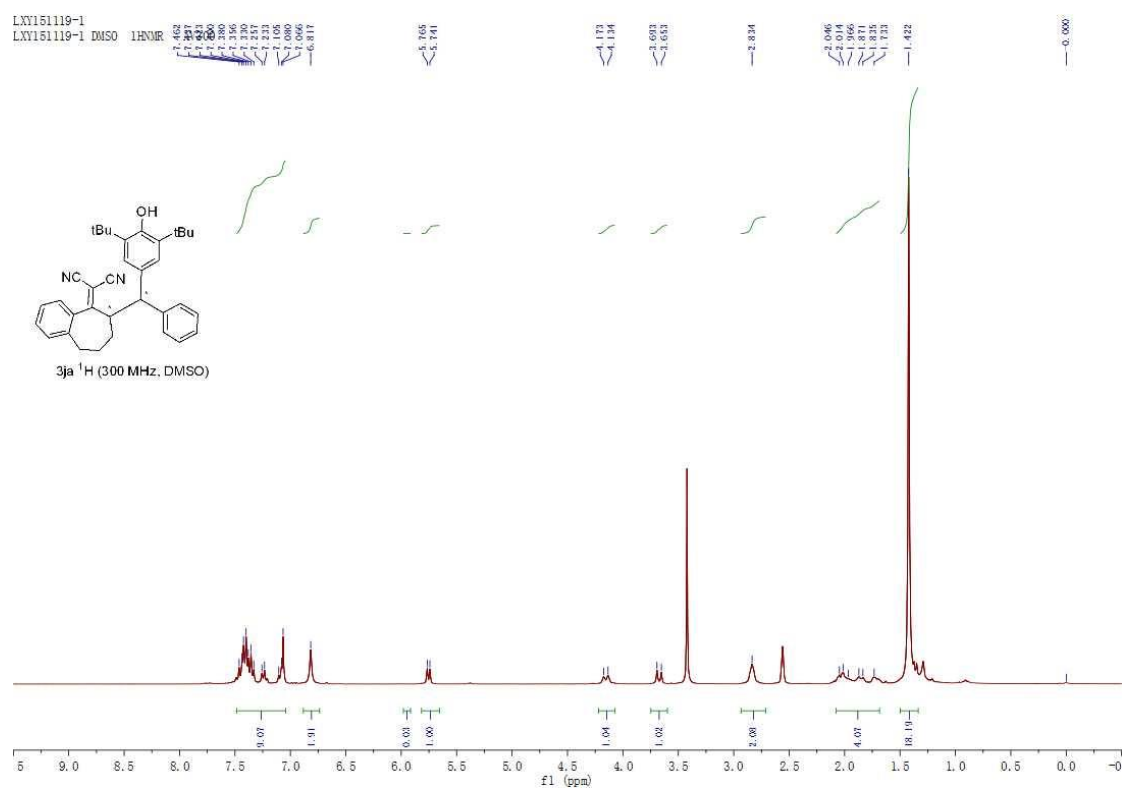
LXY150930-3-C C13-NMR



LXY151119-2 11.19
LXY151119-2 11.19 CDCl₃ 1H-NMR

7.387, 7.380, 7.373, 7.366, 7.359, 7.352, 7.345, 7.338, 7.331, 7.324, 7.317, 7.310, 7.303, 7.296, 7.289, 7.282, 7.275, 7.268, 7.261, 7.254, 7.247, 7.240, 7.233, 7.226, 7.219, 7.212, 7.205, 7.198, 7.191, 7.184, 7.177, 7.170, 7.163, 7.156, 7.149, 7.142, 7.135, 7.128, 7.121, 7.114, 7.107, 7.100, 7.093, 7.086, 7.079, 7.072, 7.065, 7.058, 7.051, 7.044, 7.037, 7.030, 7.023, 7.016, 7.009, 7.002, 6.995, 6.988, 6.981, 6.974, 6.967, 6.960, 6.953, 6.946, 6.939, 6.932, 6.925, 6.918, 6.911, 6.904, 6.897, 6.890, 6.883, 6.876, 6.869, 6.862, 6.855, 6.848, 6.841, 6.834, 6.827, 6.820, 6.813, 6.806, 6.799, 6.792, 6.785, 6.778, 6.771, 6.764, 6.757, 6.750, 6.743, 6.736, 6.729, 6.722, 6.715, 6.708, 6.701, 6.694, 6.687, 6.680, 6.673, 6.666, 6.659, 6.652, 6.645, 6.638, 6.631, 6.624, 6.617, 6.610, 6.603, 6.596, 6.589, 6.582, 6.575, 6.568, 6.561, 6.554, 6.547, 6.540, 6.533, 6.526, 6.519, 6.512, 6.505, 6.498, 6.491, 6.484, 6.477, 6.470, 6.463, 6.456, 6.449, 6.442, 6.435, 6.428, 6.421, 6.414, 6.407, 6.400, 6.393, 6.386, 6.379, 6.372, 6.365, 6.358, 6.351, 6.344, 6.337, 6.330, 6.323, 6.316, 6.309, 6.302, 6.295, 6.288, 6.281, 6.274, 6.267, 6.260, 6.253, 6.246, 6.239, 6.232, 6.225, 6.218, 6.211, 6.204, 6.197, 6.190, 6.183, 6.176, 6.169, 6.162, 6.155, 6.148, 6.141, 6.134, 6.127, 6.120, 6.113, 6.106, 6.099, 6.092, 6.085, 6.078, 6.071, 6.064, 6.057, 6.050, 6.043, 6.036, 6.029, 6.022, 6.015, 6.008, 6.001, 5.994, 5.987, 5.980, 5.973, 5.966, 5.959, 5.952, 5.945, 5.938, 5.931, 5.924, 5.917, 5.910, 5.903, 5.896, 5.889, 5.882, 5.875, 5.868, 5.861, 5.854, 5.847, 5.840, 5.833, 5.826, 5.819, 5.812, 5.805, 5.798, 5.791, 5.784, 5.777, 5.770, 5.763, 5.756, 5.749, 5.742, 5.735, 5.728, 5.721, 5.714, 5.707, 5.700, 5.693, 5.686, 5.679, 5.672, 5.665, 5.658, 5.651, 5.644, 5.637, 5.630, 5.623, 5.616, 5.609, 5.602, 5.595, 5.588, 5.581, 5.574, 5.567, 5.560, 5.553, 5.546, 5.539, 5.532, 5.525, 5.518, 5.511, 5.504, 5.497, 5.490, 5.483, 5.476, 5.469, 5.462, 5.455, 5.448, 5.441, 5.434, 5.427, 5.420, 5.413, 5.406, 5.399, 5.392, 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3.382, 3.375, 3.368, 3.361, 3.354, 3.347, 3.340, 3.333, 3.326, 3.319, 3.312, 3.305, 3.298, 3.291, 3.284, 3.277, 3.270, 3.263, 3.256, 3.249, 3.242, 3.235, 3.228, 3.221, 3.214, 3.207, 3.200, 3.193, 3.186, 3.179, 3.172, 3.165, 3.158, 3.151, 3.144, 3.137, 3.130, 3.123, 3.116, 3.109, 3.102, 3.095, 3.088, 3.081, 3.074, 3.067, 3.060, 3.053, 3.046, 3.039, 3.032, 3.025, 3.018, 3.011, 3.004, 2.997, 2.990, 2.983, 2.976, 2.969, 2.962, 2.955, 2.948, 2.941, 2.934, 2.927, 2.920, 2.913, 2.906, 2.899, 2.892, 2.885, 2.878, 2.871, 2.864, 2.857, 2.850, 2.843, 2.836, 2.829, 2.822, 2.815, 2.808, 2.801, 2.794, 2.787, 2.780, 2.773, 2.766, 2.759, 2.752, 2.745, 2.738, 2.731, 2.724, 2.717, 2.710, 2.703, 2.696, 2.689, 2.682, 2.675, 2.668, 2.661, 2.654, 2.647, 2.640, 2.633, 2.626, 2.619, 2.612, 2.605, 2.598, 2.591, 2.584, 2.577, 2.570, 2.563, 2.556, 2.549, 2.542, 2.535, 2.528, 2.521, 2.514, 2.507, 2.500, 2.493, 2.486, 2.479, 2.472, 2.465, 2.458, 2.451, 2.444, 2.437, 2.430, 2.423, 2.416, 2.409, 2.402, 2.395, 2.388, 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1.380, 1.373, 1.366, 1.359, 1.352, 1.345, 1.338, 1.331, 1.324, 1.317, 1.310, 1.303, 1.296, 1.289, 1.282, 1.275, 1.268, 1.261, 1.254, 1.247, 1.240, 1.233, 1.226, 1.219, 1.212, 1.205, 1.198, 1.191, 1.184, 1.177, 1.170, 1.163, 1.156, 1.149, 1.142, 1.135, 1.128, 1.121, 1.114, 1.107, 1.100, 1.093, 1.086, 1.079, 1.072, 1.065, 1.058, 1.051, 1.044, 1.037, 1.030, 1.023, 1.016, 1.009, 1.002, 9.995, 9.988, 9.981, 9.974, 9.967, 9.960, 9.953, 9.946, 9.939, 9.932, 9.925, 9.918, 9.911, 9.904, 9.897, 9.890, 9.883, 9.876, 9.869, 9.862, 9.855, 9.848, 9.841, 9.834, 9.827, 9.820, 9.813, 9.806, 9.799, 9.792, 9.785, 9.778, 9.771, 9.764, 9.757, 9.750, 9.743, 9.736, 9.729, 9.722, 9.715, 9.708, 9.701, 9.694, 9.687, 9.680, 9.673, 9.666, 9.659, 9.652, 9.645, 9.638, 9.631, 9.624, 9.617, 9.610, 9.603, 9.596, 9.589, 9.582, 9.575, 9.568, 9.561, 9.554, 9.547, 9.540, 9.533, 9.526, 9.519, 9.512, 9.505, 9.498, 9.491, 9.484, 9.477, 9.470, 9.463, 9.456, 9.449, 9.442, 9.435, 9.428, 9.421, 9.414, 9.407, 9.400, 9.393, 9.386, 9.379, 9.372, 9.365, 9.358, 9.351, 9.344, 9.337, 9.330, 9.323, 9.316, 9.309, 9.302, 9.295, 9.288, 9.281, 9.274, 9.267, 9.260, 9.253, 9.246, 9.239, 9.232, 9.225, 9.218, 9.211, 9.204, 9.197, 9.190, 9.183, 9.176, 9.169, 9.162, 9.155, 9.148, 9.141, 9.134, 9.127, 9.120, 9.113, 9.106, 9.099, 9.092, 9.085, 9.078, 9.071, 9.064, 9.057, 9.050, 9.043, 9.036, 9.029, 9.022, 9.015, 9.008, 8.999, 8.992, 8.985, 8.978, 8.971, 8.964, 8.957, 8.950, 8.943, 8.936, 8.929, 8.922, 8.915, 8.908, 8.901, 8.894, 8.887, 8.880, 8.873, 8.866, 8.859, 8.852, 8.845, 8.838, 8.831, 8.824, 8.817, 8.810, 8.803, 8.796, 8.789, 8.782, 8.775, 8.768, 8.761, 8.754, 8.747, 8.740, 8.733, 8.726, 8.719, 8.712, 8.705, 8.698, 8.691, 8.684, 8.677, 8.670, 8.663, 8.656, 8.649, 8.642, 8.635, 8.628, 8.621, 8.614, 8.607, 8.600, 8.593, 8.586, 8.579, 8.572, 8.565, 8.558, 8.551, 8.544, 8.537, 8.530, 8.523, 8.516, 8.509, 8.502, 8.495, 8.488, 8.481, 8.474, 8.467, 8.460, 8.453, 8.446, 8.439, 8.432, 8.425, 8.418, 8.411, 8.404, 8.397, 8.390, 8.383, 8.376, 8.369, 8.362, 8.355, 8.348, 8.341, 8.334, 8.327, 8.320, 8.313, 8.306, 8.299, 8.292, 8.285, 8.278, 8.271, 8.264, 8.257, 8.250, 8.243, 8.236, 8.229, 8.222, 8.215, 8.208, 8.201, 8.194, 8.187, 8.180, 8.173, 8.166, 8.159, 8.152, 8.145, 8.138, 8.131, 8.124, 8.117, 8.110, 8.103, 8.096, 8.089, 8.082, 8.075, 8.068, 8.061, 8.054, 8.047, 8.040, 8.033, 8.026, 8.019, 8.012, 8.005, 7.998, 7.991, 7.984, 7.977, 7.970, 7.963, 7.956, 7.949, 7.942, 7.935, 7.928, 7.921, 7.914, 7.907, 7.900, 7.893, 7.886, 7.879, 7.872, 7.865, 7.858, 7.851, 7.844, 7.837, 7.830, 7.823, 7.816, 7.809, 7.802, 7.795, 7.788, 7.781, 7.774, 7.767, 7.760, 7.753, 7.746, 7.739, 7.732, 7.725, 7.718, 7.711, 7.704, 7.697, 7.690, 7.683, 7.676, 7.669, 7.662, 7.655, 7.648, 7.641, 7.634, 7.627, 7.620, 7.613, 7.606, 7.599, 7.592, 7.585, 7.578, 7.571, 7.564, 7.557, 7.550, 7.543, 7.536, 7.529, 7.522, 7.515, 7.508, 7.501, 7.494, 7.487, 7.480, 7.473, 7.466, 7.459, 7.452, 7.445, 7.438, 7.431, 7.424, 7.417, 7.410, 7.403, 7.396, 7.389, 7.382, 7.375, 7.368, 7.361, 7.354, 7.347, 7.340, 7.333, 7.326, 7.319, 7.312, 7.305, 7.298, 7.291, 7.284, 7.277, 7.270, 7.263, 7.256, 7.249, 7.242, 7.235, 7.228, 7.221, 7.214, 7.207, 7.200, 7.193, 7.186, 7.179, 7.172, 7.165, 7.158, 7.151, 7.144, 7.137, 7.130, 7.123, 7.116, 7.109, 7.102, 7.095, 7.088, 7.081, 7.074, 7.067, 7.060, 7.053, 7.046, 7.039, 7.032, 7.025, 7.018, 7.011, 7.004, 6.997, 6.990, 6.983, 6.976, 6.969, 6.962, 6.955, 6.948, 6.941, 6.934, 6.927, 6.920, 6.913, 6.906, 6.899, 6.892, 6.885, 6.878, 6.871, 6.864, 6.857, 6.850, 6.843, 6.836, 6.829, 6.822, 6.815, 6.808, 6.801, 6.794, 6.787, 6.780, 6.773, 6.766, 6.759, 6.752, 6.745, 6.738, 6.731, 6.724, 6.717, 6.710, 6.703, 6.696, 6.689, 6.682, 6.675, 6.668, 6.661, 6.654, 6.647, 6.640, 6.633, 6.626, 6.619, 6.612, 6.605, 6.598, 6.591, 6.584, 6.577, 6.570, 6.563, 6.556, 6.549, 6.542, 6.535, 6.528, 6.521, 6.514, 6.507, 6.500, 6.493, 6.486, 6.479, 6.472, 6.465, 6.458, 6.451, 6.444, 6.437, 6.430, 6.423, 6.416, 6.409, 6.402, 6.395, 6.388, 6.381, 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5.373, 5.366, 5.359, 5.352, 5.345, 5.338, 5.331, 5.324, 5.317, 5.310, 5.303, 5.296, 5.289, 5.282, 5.275, 5.268, 5.261, 5.254, 5.247, 5.240, 5.233, 5.226, 5.219, 5.212, 5.205, 5.198, 5.191, 5.184, 5.177, 5.170, 5.163, 5.156, 5.149, 5.142, 5.135, 5.128, 5.121, 5.114, 5.107, 5.100, 5.093, 5.086, 5.079, 5.072, 5.065, 5.058, 5.051, 5.044, 5.037, 5.030, 5.023, 5.016, 5.009, 4.999, 4.992, 4.985, 4.978, 4.971, 4.964, 4.957, 4.950, 4.943, 4.936, 4.929, 4.922, 4.915, 4.908, 4.901, 4.894, 4.887, 4.880, 4.873, 4.866, 4.859, 4.852, 4.845, 4.838, 4.831, 4.824, 4.817, 4.810, 4.803, 4.796, 4.789, 4.782, 4.775, 4.768, 4.761, 4.754, 4.747, 4.740, 4.733, 4.726, 4.719, 4.712, 4.705, 4.698, 4.691, 4.684, 4.677, 4.670, 4.663, 4.656, 4.649, 4.642, 4.635, 4.628, 4.621, 4.614, 4.607, 4.600, 4.593, 4.586, 4.579, 4.572, 4.565, 4.558, 4.551, 4.544, 4.537, 4.530, 4.523, 4.516, 4.509, 4.502, 4.495, 4.488, 4.481, 4.474, 4.467, 4.460, 4.453, 4.446, 4.439, 4.432, 4.425, 4.418, 4.411, 4.404, 4.397, 4.390, 4.383, 4.376, 4.369, 4.362, 4.355, 4.348, 4.341, 4.334, 4.327, 4.320, 4.313, 4.306, 4.299, 4.292, 4.285, 4.278, 4.271, 4.264, 4.257, 4.250, 4.243, 4.236, 4.229, 4.222, 4.215, 4.208, 4.201, 4.194, 4.187, 4.180, 4.173, 4.166, 4.159, 4.152, 4.145, 4.138, 4.131, 4.124, 4.117,





CC1(C)C(C#N)C(C#N)C(C1Cc2ccccc2)C3=CC=CC=C3

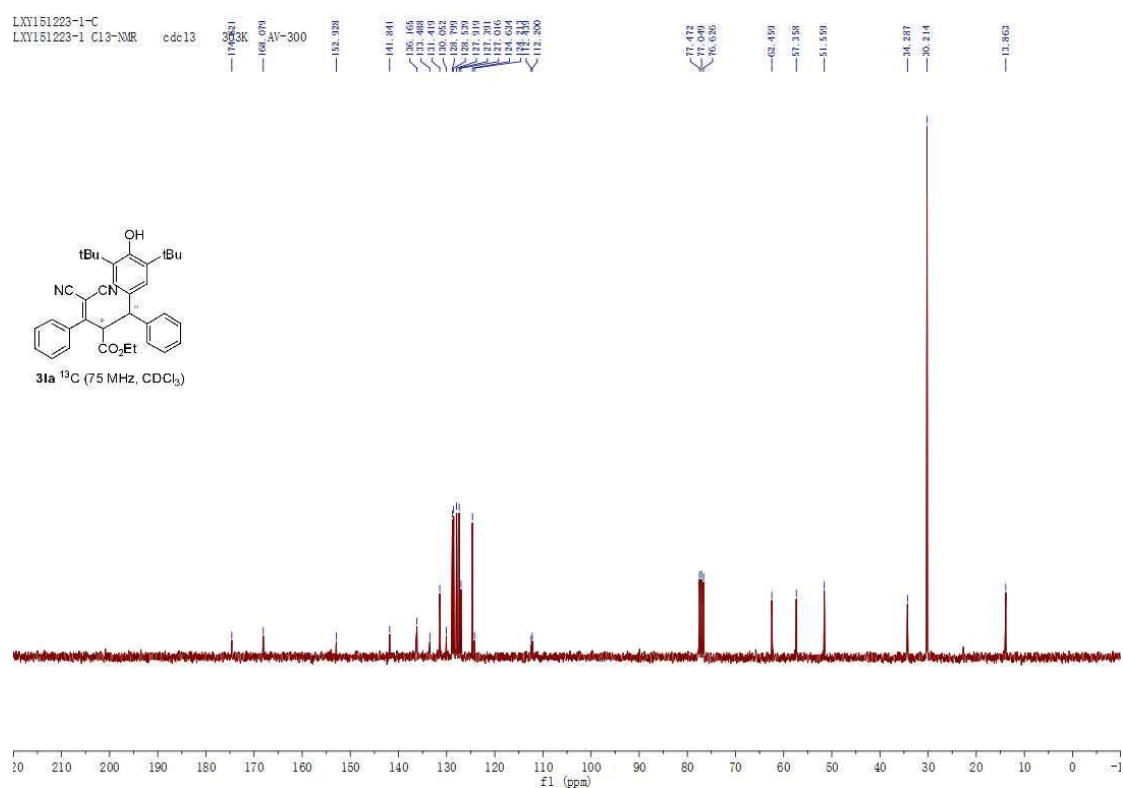
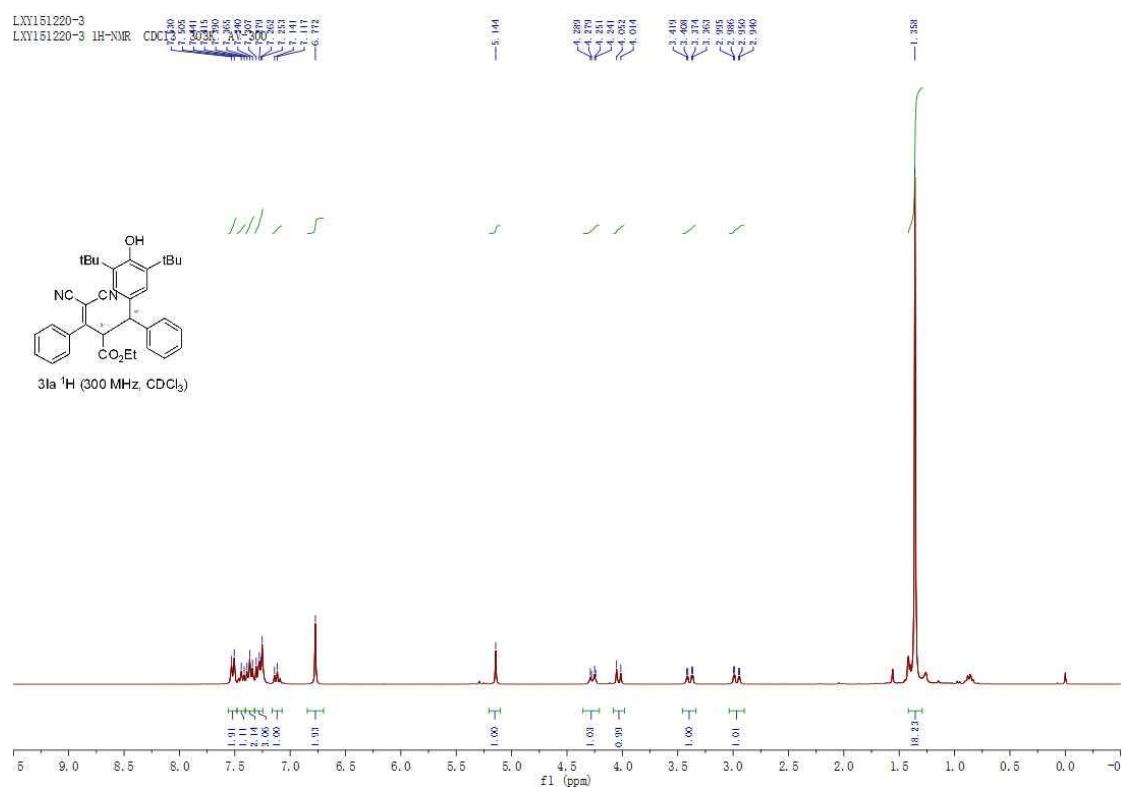
3ka ^1H (300 MHz, CDCl_3)

10
9
8
7
6
5
4
3
2
1
0

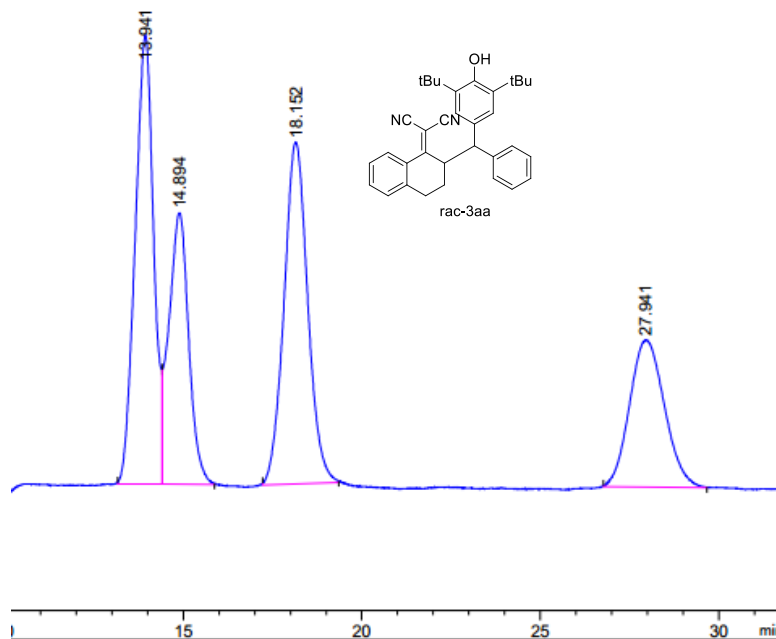
1.91
1.14
1.08
1.00
1.91
1.00
1.03
0.99
1.00
1.01
18.23

f1 (ppm)

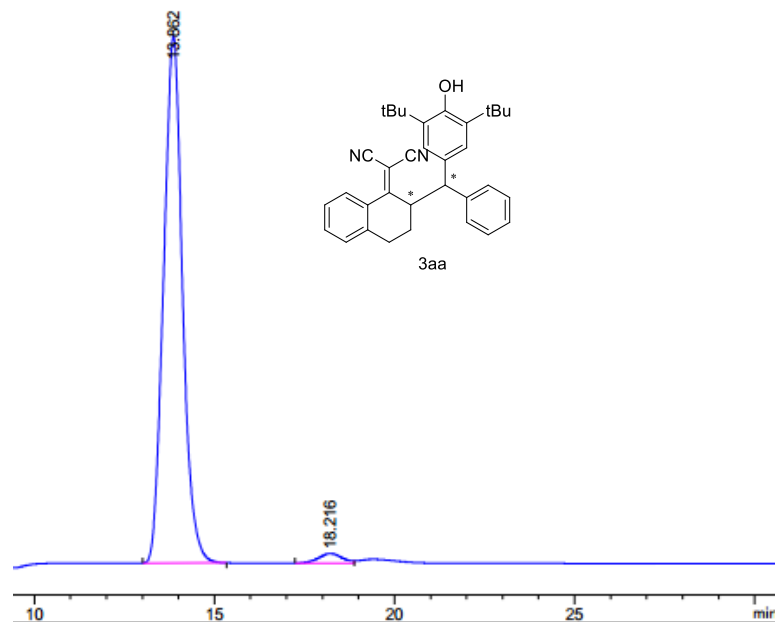
¹³C NMR spectrum (75 MHz, CDCl₃) of compound 3ka. The chemical structure of 3ka is shown above the spectrum. The spectrum displays peaks corresponding to the following chemical shifts (ppm): 172.036, 153.009, 140.721, 137.735, 135.711, 133.281, 130.818, 130.724, 129.714, 127.427, 127.417, 125.965, 124.606, 124.266, 113.151, 112.077, 77.469, 77.046, 76.622, 51.396, 41.898, 34.235, 33.135, 30.136, 29.184.



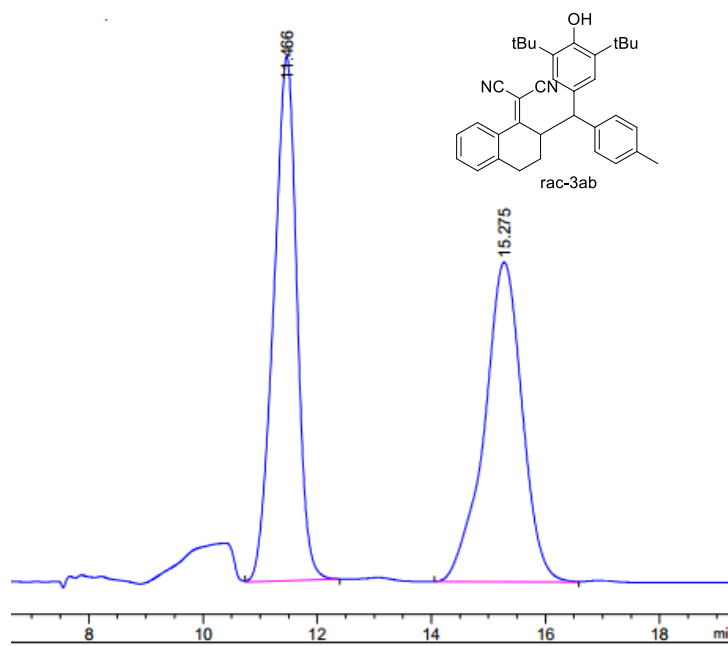
8. HPLC analysis



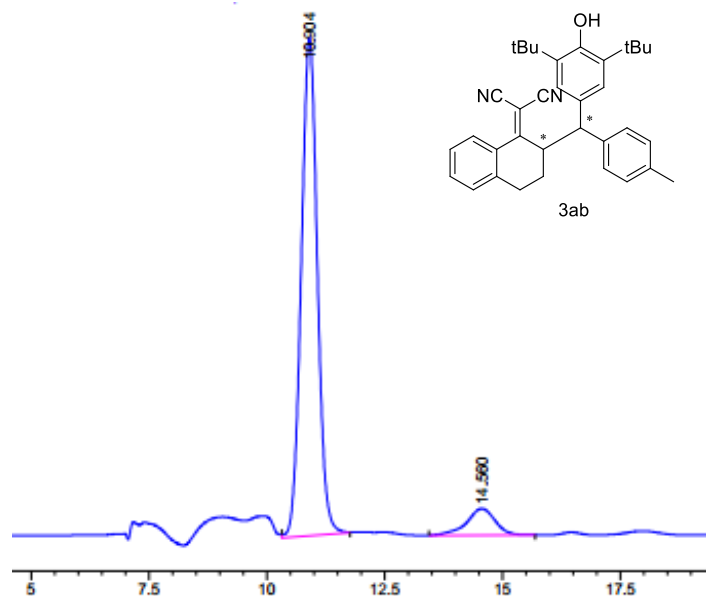
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.941	BV	0.5284	401.57260	11.19847	30.7488
2	14.894	VB	0.5435	263.29697	6.77319	20.1609
3	18.152	BB	0.6645	392.17157	8.52834	30.0290
4	27.941	BB	0.8034	248.93552	3.66955	19.0613



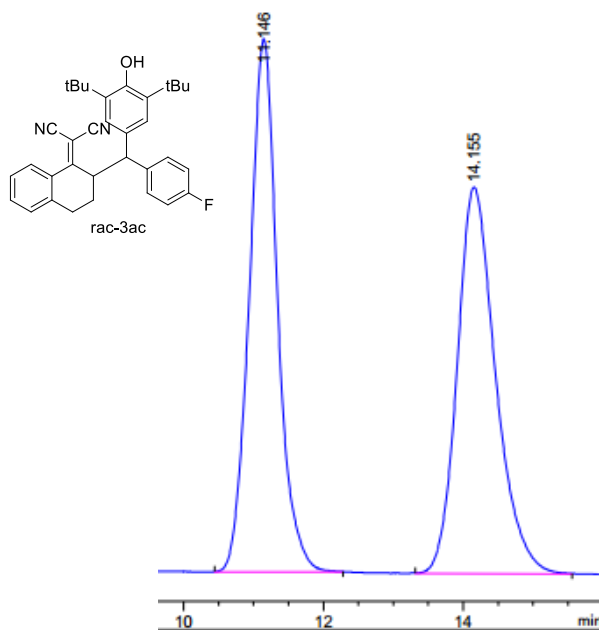
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.862	BB	0.5569	1.08073e4	296.70984	97.7350
2	18.216	BV	0.6300	250.46124	5.45147	2.2650



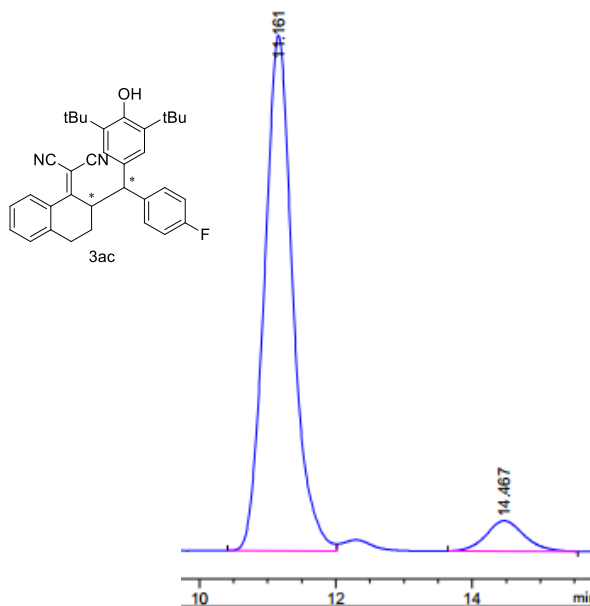
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.466	VB	0.4275	7474.76611	264.64288	50.1067
2	15.275	BB	0.6984	7442.92090	161.27902	49.8933



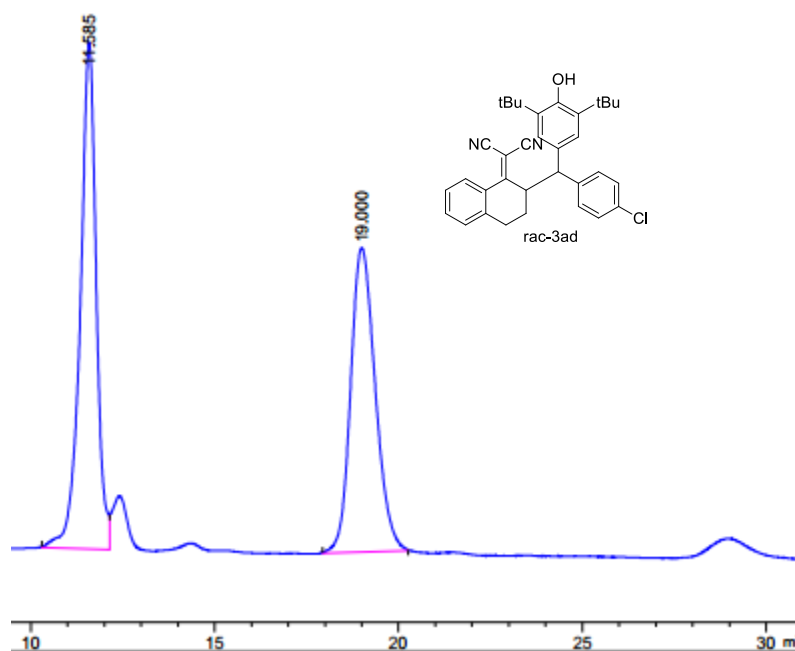
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.904	VB	0.3685	4295.97803	181.23276	91.3798
2	14.560	BB	0.6200	405.25546	9.64920	8.6202



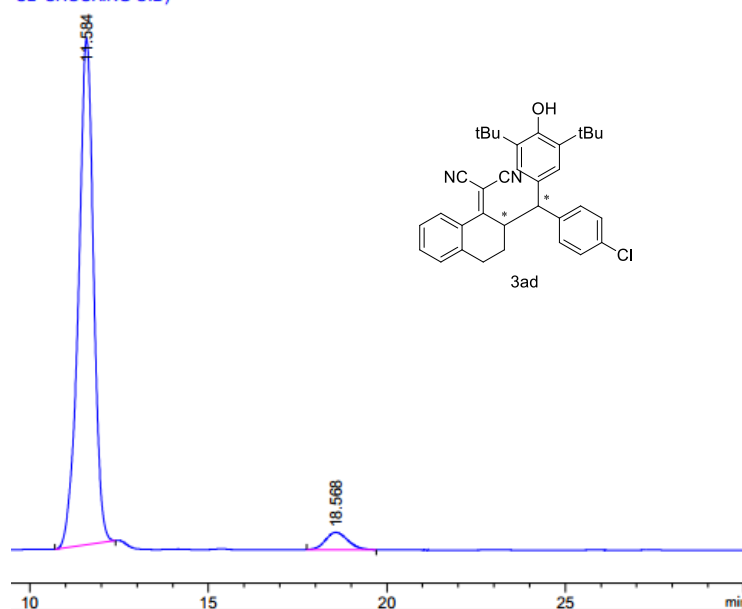
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.146	BB	0.4200	3654.24683	130.75867	50.2630
2	14.155	BB	0.5754	3616.00854	94.72015	49.7370



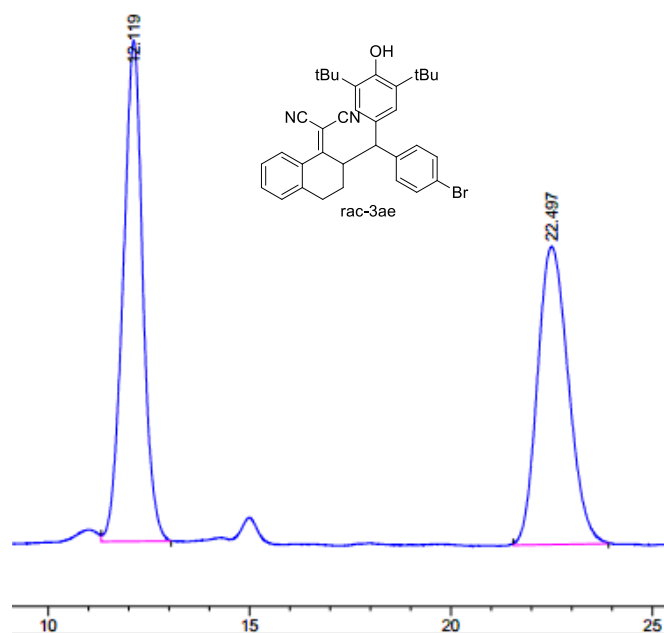
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.161	BV	0.4314	7993.67725	278.02841	92.6087
2	14.467	BB	0.5815	637.99084	16.41267	7.3913



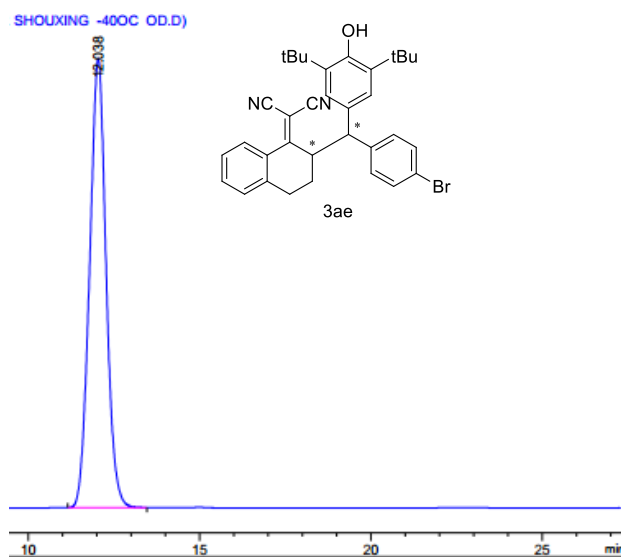
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.585	BV	0.4467	869.62250	28.76390	51.9305
2	19.000	BB	0.7092	804.96796	17.28789	48.0695



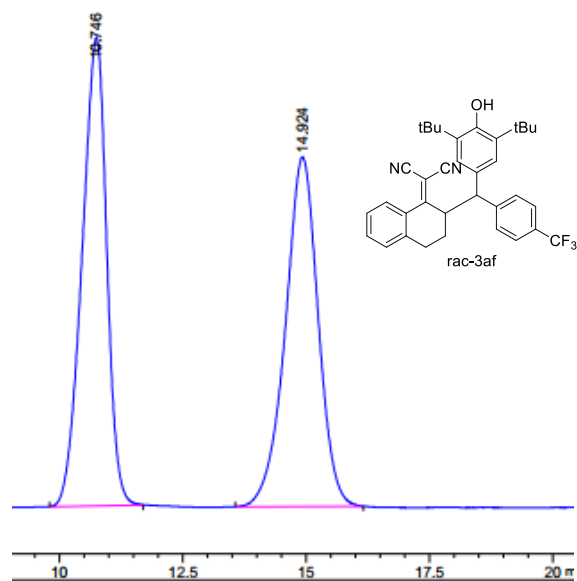
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.584	BB	0.4432	5272.53320	179.22054	95.1853
2	18.568	BB	0.6030	266.69827	6.13718	4.8147



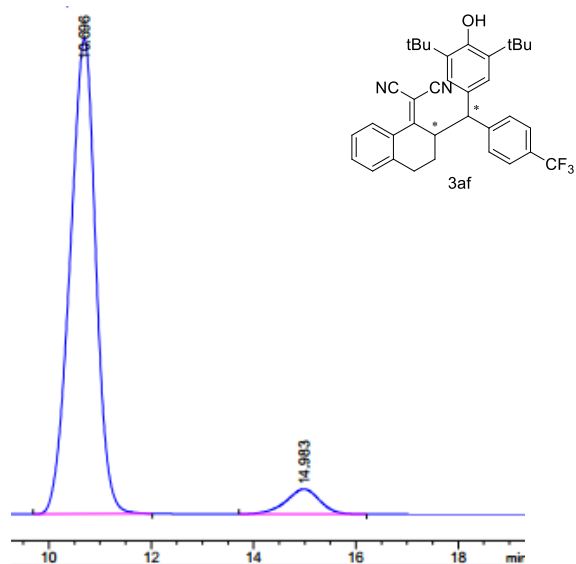
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.119	VB	0.5040	749.22723	21.96227	51.9176
2	22.497	BB	0.7523	693.88245	13.05101	48.0824



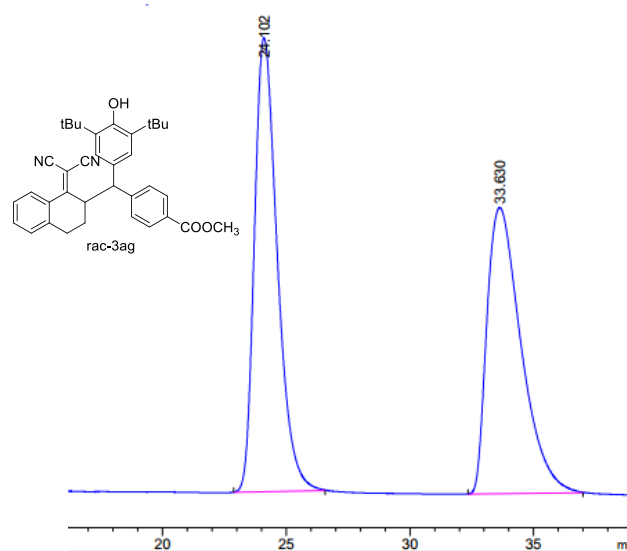
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.038	BB	0.5056	2.21775e4	664.13660	100.0000



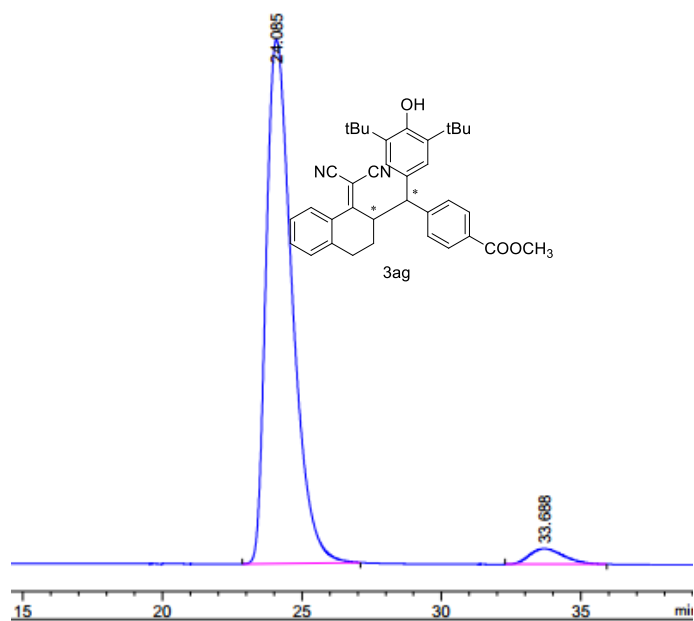
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.746	BB	0.5303	2329.23804	67.21255	50.0434
2	14.924	BB	0.7027	2325.19507	50.17455	49.9566



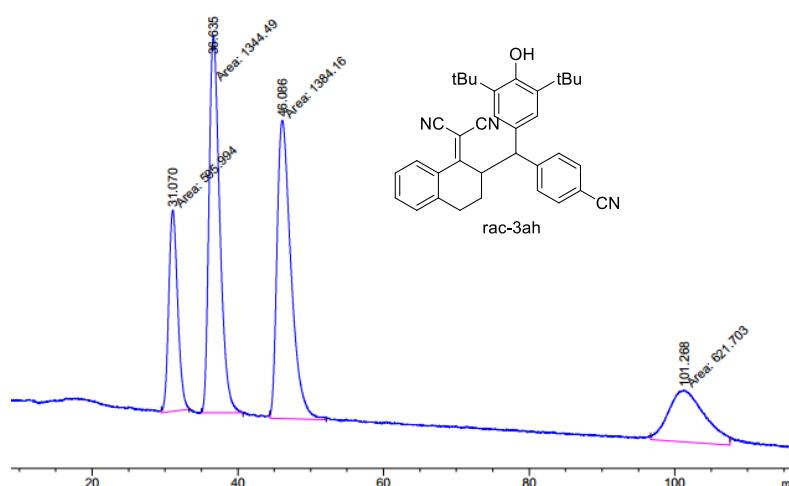
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.696	BB	0.5412	2.02676e4	580.63324	93.4526
2	14.983	BB	0.6894	1419.96655	30.71255	6.5474



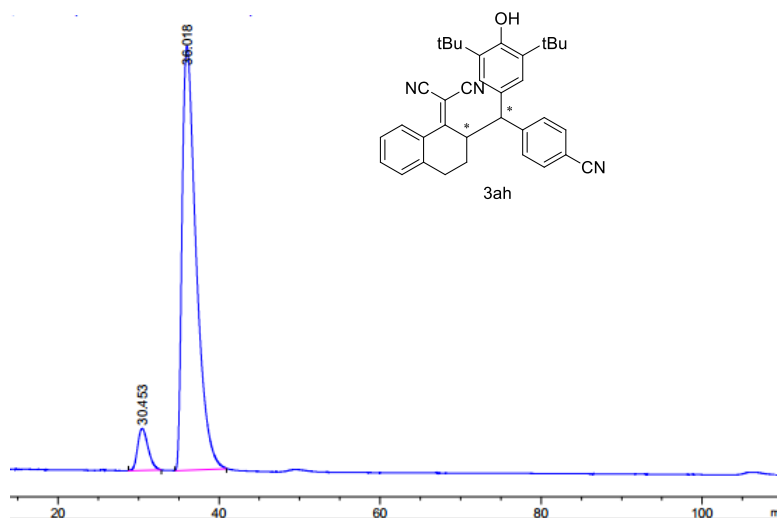
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.102	BB	0.9777	6055.70020	94.23968	51.5379
2	33.630	BB	1.4039	5694.29639	59.42558	48.4621



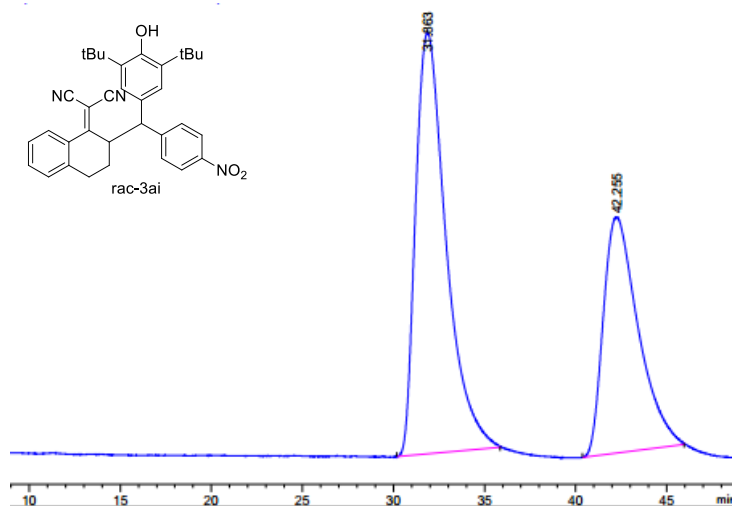
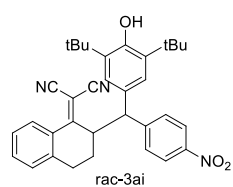
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.085	BB	0.9966	2.04761e4	315.74185	96.2082
2	33.688	BB	1.0155	807.01331	9.40099	3.7918



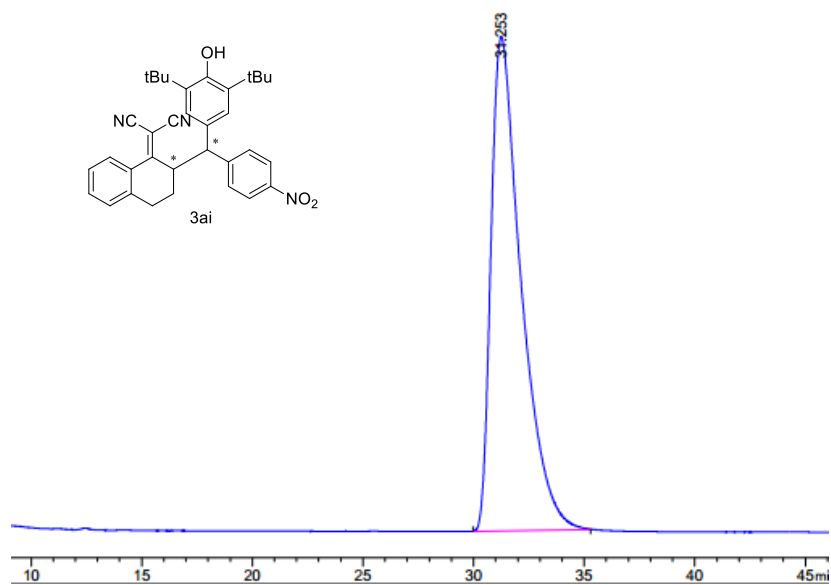
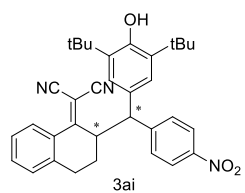
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.070	BB	1.0003	586.17096	6.94793	15.6592
2	36.635	BB	1.1733	1288.61316	12.94515	34.4245
3	46.086	BB	1.4745	1272.71106	10.15278	33.9997
4	101.271	MM T	5.5981	595.81067	1.77386	15.9167



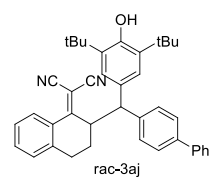
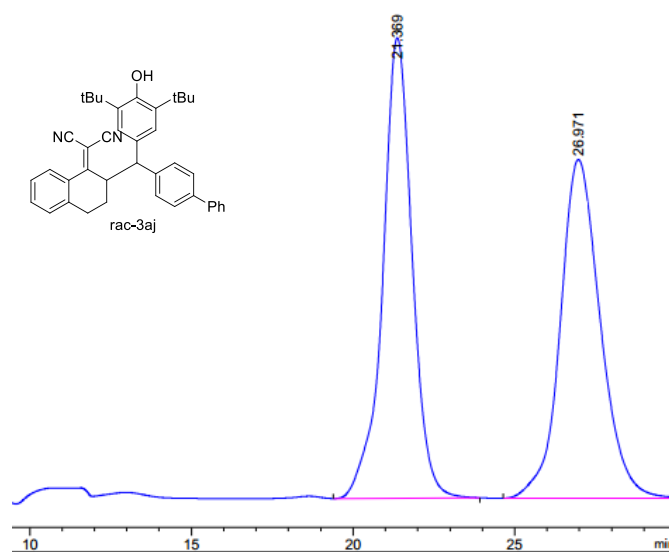
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.453	BB	1.0704	1181.38611	13.04736	6.8608
2	36.018	BB	1.7411	1.60379e4	132.22672	93.1392



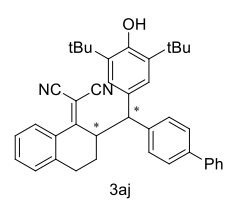
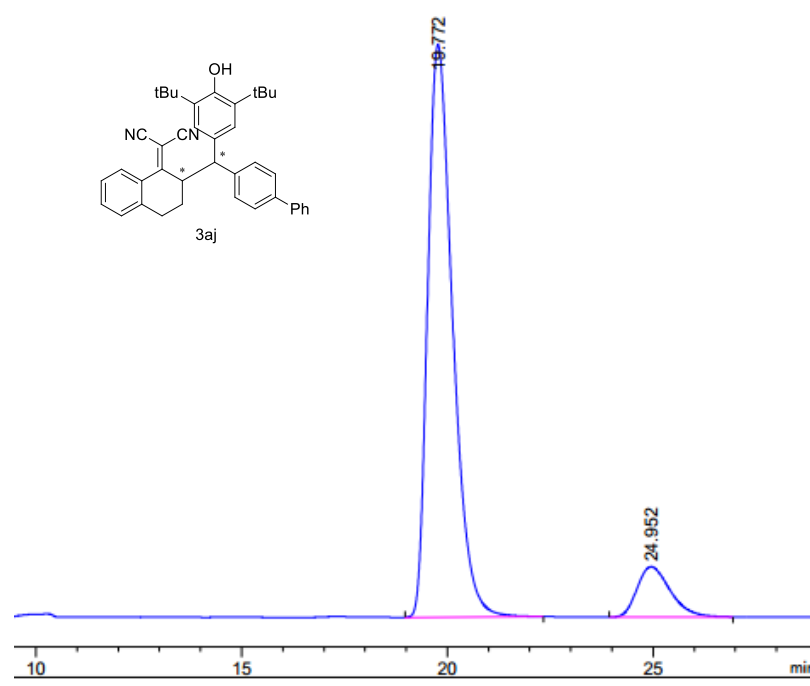
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.863	BB	1.6080	5099.86914	43.74910	60.9614
2	42.255	BB	1.5669	3265.86377	24.53552	39.0386



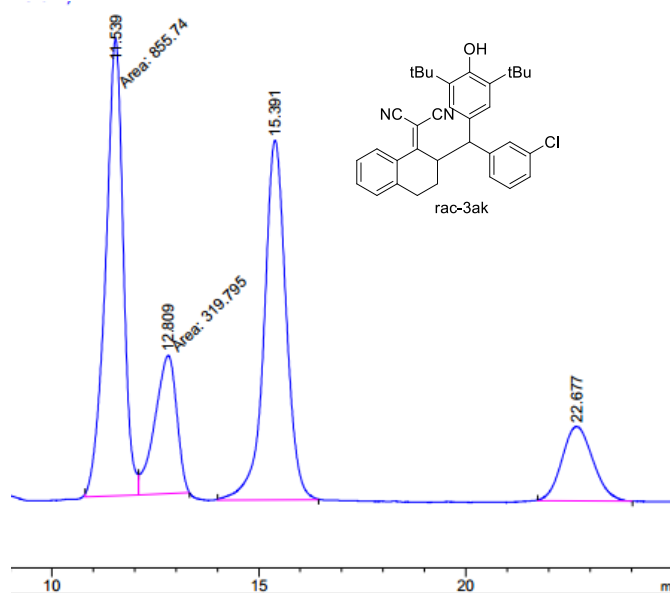
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.253	BB	1.3934	1.56185e4	164.54762	100.0000



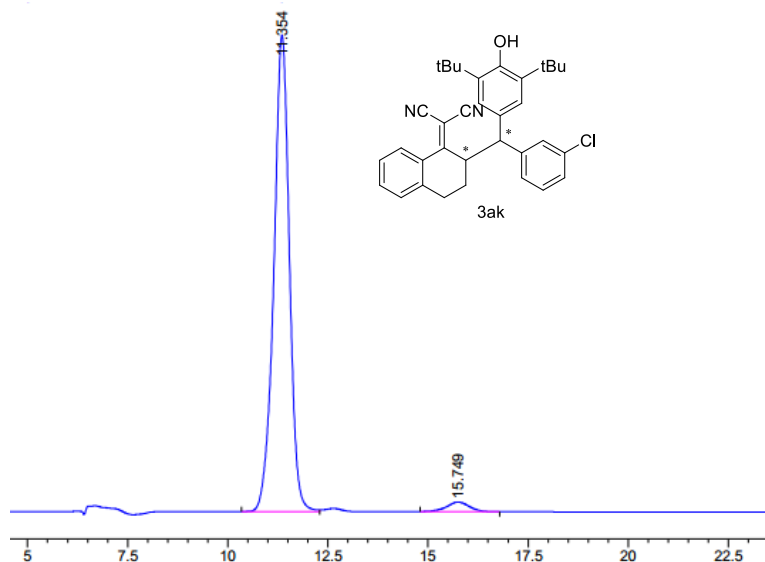
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.369	VB	0.9639	1.94542e4	306.74078	50.0520
2	26.971	BBA	1.3080	1.94137e4	225.60011	49.9480



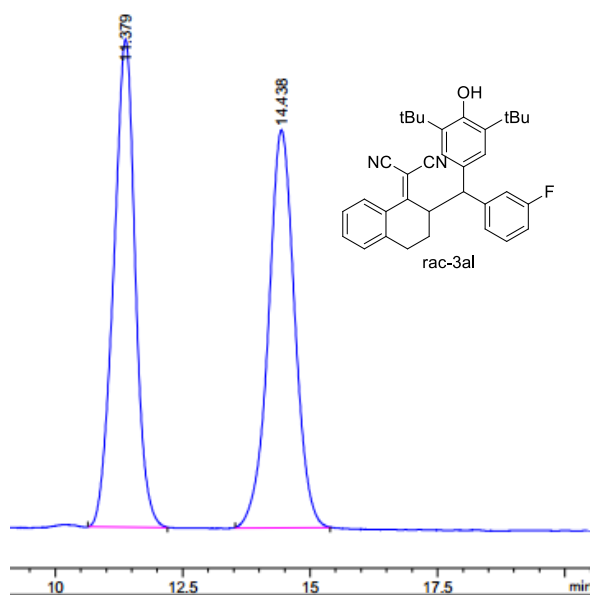
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.772	BB	0.6512	3.16288e4	751.25262	89.5198
2	24.952	BB	0.8604	3702.84326	66.01476	10.4802



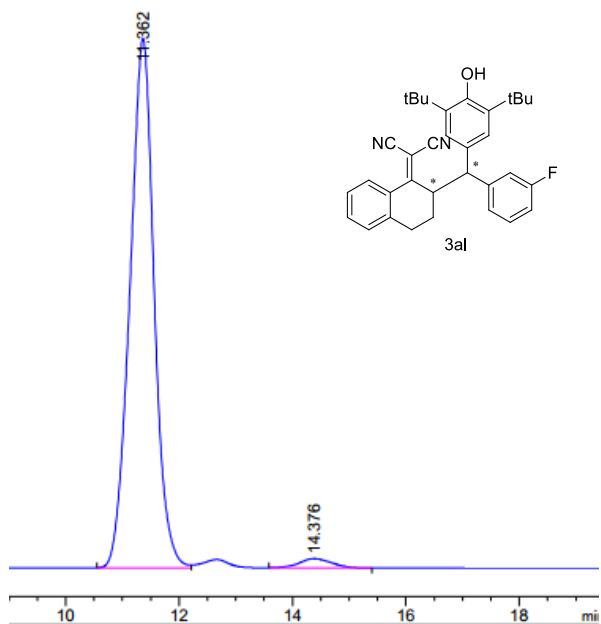
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.539	MF	0.4952	855.74017	28.80072	37.9221
2	12.809	FM	0.6126	319.79453	8.70103	14.1717
3	15.391	BB	0.5546	836.95258	22.67617	37.0896
4	22.677	BB	0.6432	244.08440	4.68955	10.8166



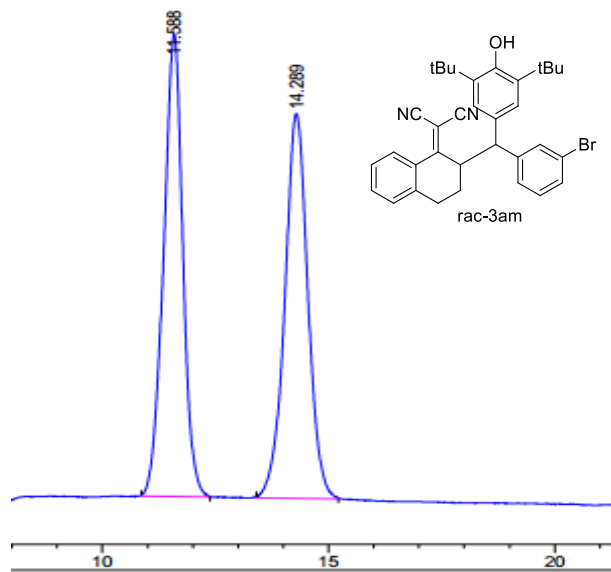
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.354	BB	0.4084	8527.61328	316.43628	97.1143
2	15.749	BB	0.5563	253.39124	6.36742	2.8857



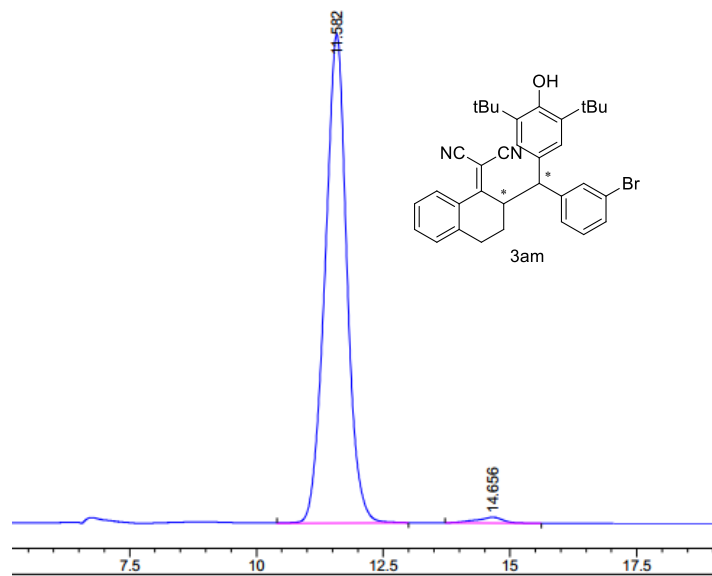
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.379	BB	0.4372	892.90454	30.34986	50.1185
2	14.438	BB	0.5472	888.68347	24.73130	49.8815



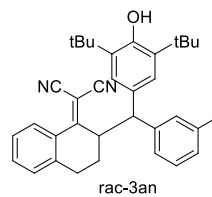
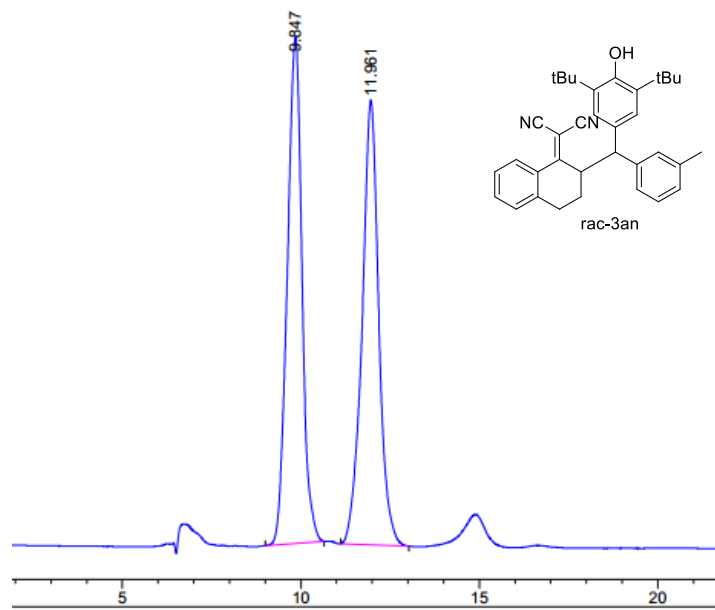
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.362	BV	0.4445	8020.31592	271.59613	97.7224
2	14.376	BB	0.5148	186.92627	4.77371	2.2776



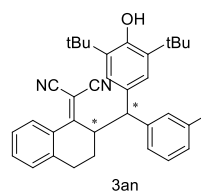
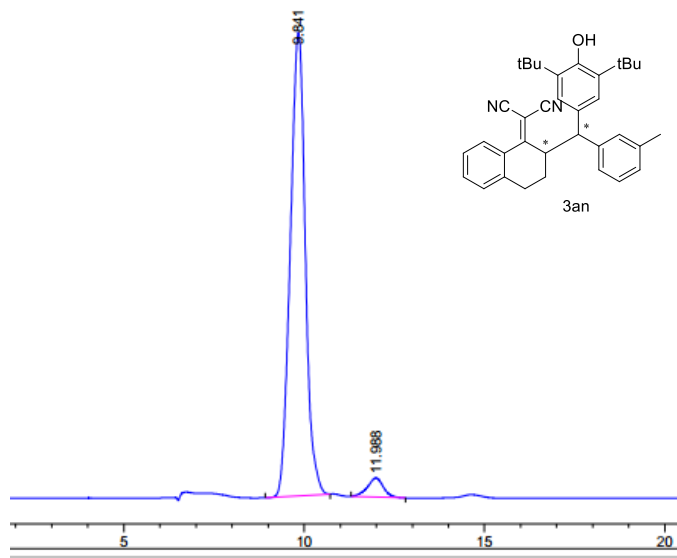
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.588	BB	0.4411	576.74896	19.49867	50.0995
2	14.289	BB	0.5271	574.45917	16.22481	49.9005



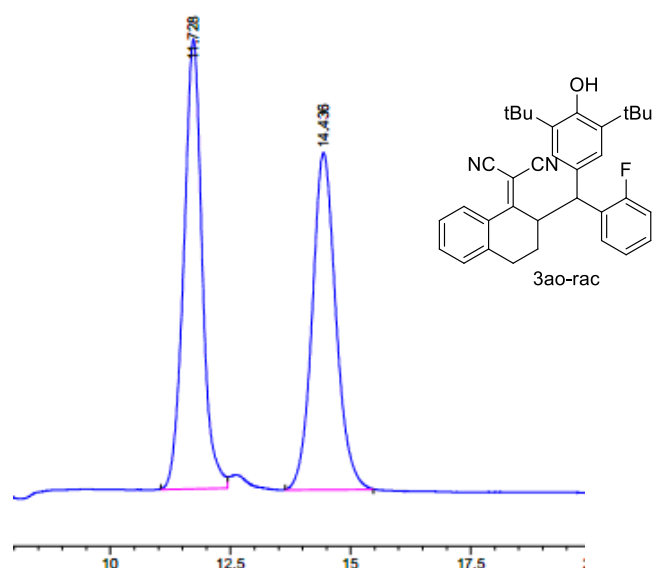
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.582	VB	0.4481	1.03567e4	347.10953	98.5551
2	14.656	BB	0.5045	151.83305	4.11517	1.4449



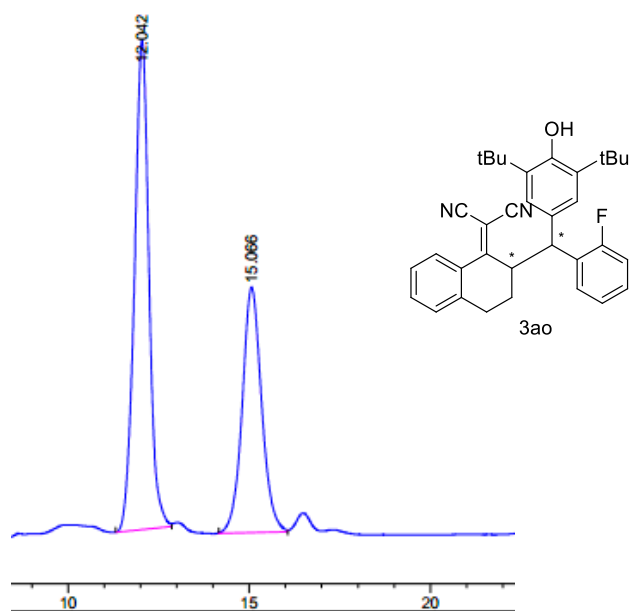
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.847	BB	0.4393	2056.07593	71.97681	50.1132
2	11.961	BB	0.4799	2046.78784	63.19711	49.8868



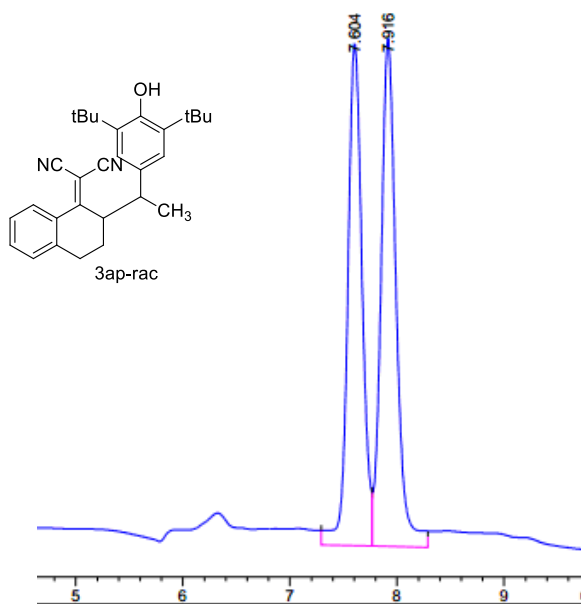
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.841	BB	0.4483	7368.78857	255.66217	95.7761
2	11.988	BB	0.4535	324.97989	10.54687	4.2239



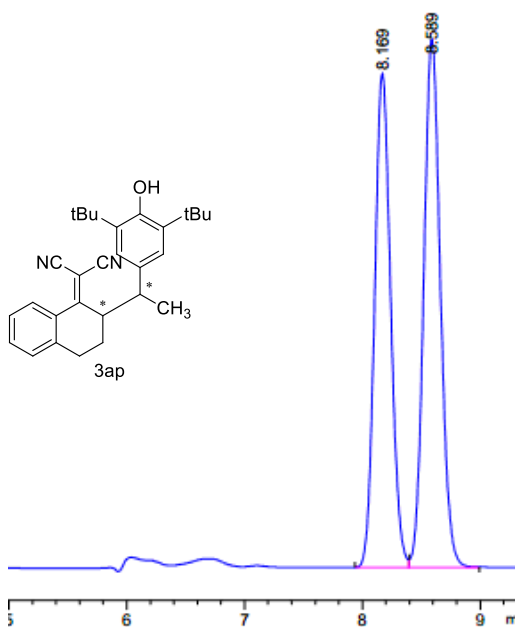
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.728	BB	0.4002	909.35266	34.20288	50.8068
2	14.436	BB	0.5246	880.47046	25.64507	49.1932



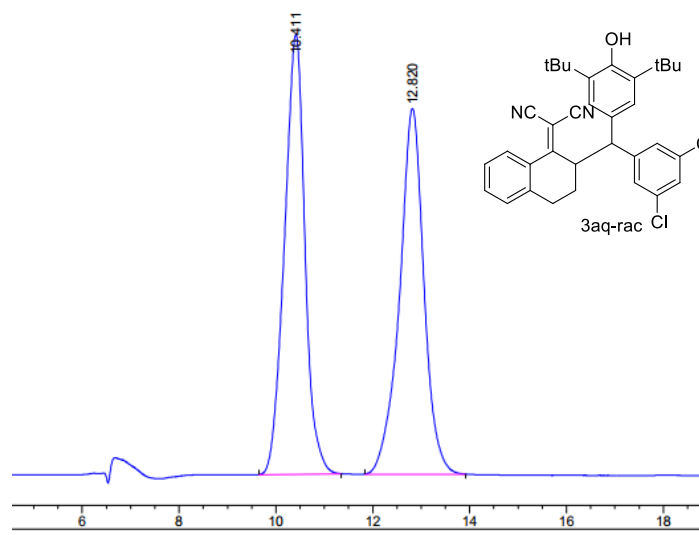
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.042	BB	0.4192	1103.68005	39.59580	59.8452
2	15.066	BB	0.5584	740.54517	19.88861	40.1548



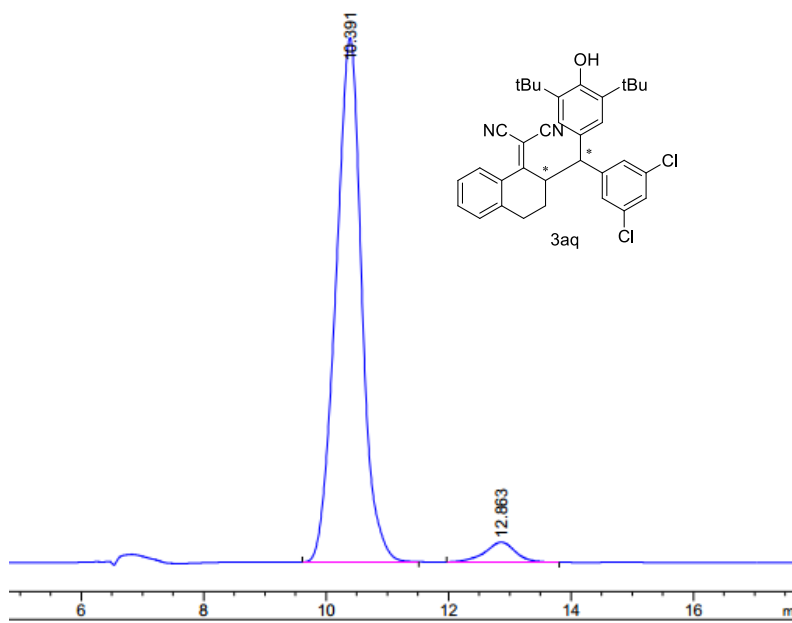
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.604	VV	0.1410	1316.05505	140.82602	48.4184
2	7.916	VB	0.1489	1402.03162	142.33968	51.5816



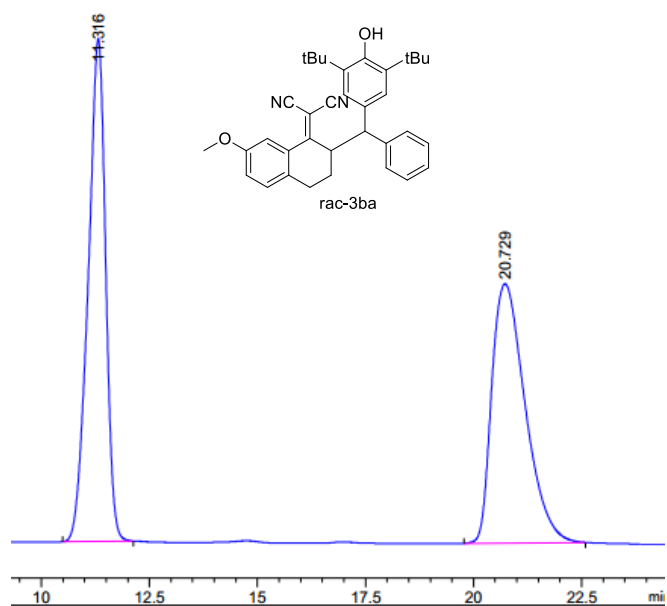
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.169	EV	0.1461	926.89667	98.23972	47.3741
2	8.589	VB	0.1524	1029.65063	105.04683	52.6259



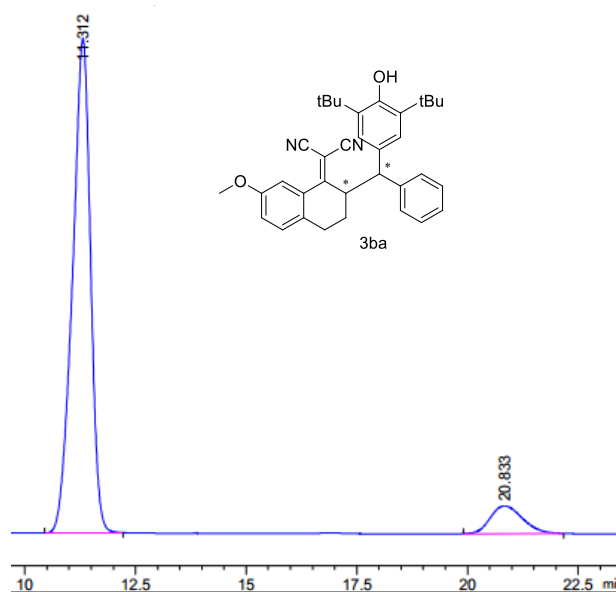
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.411	BB	0.4423	2202.16357	75.06171	50.1259
2	12.820	BB	0.5175	2191.10474	62.42304	49.8741



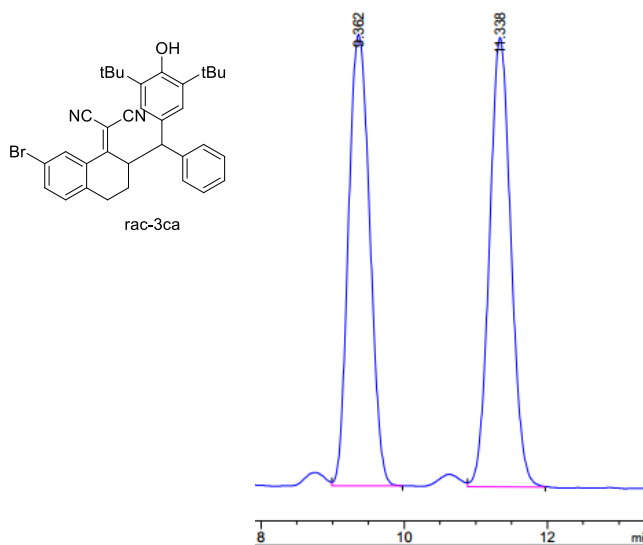
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.391	BB	0.4422	7640.63574	260.51291	95.6456
2	12.863	BB	0.5150	347.84738	9.97002	4.3544



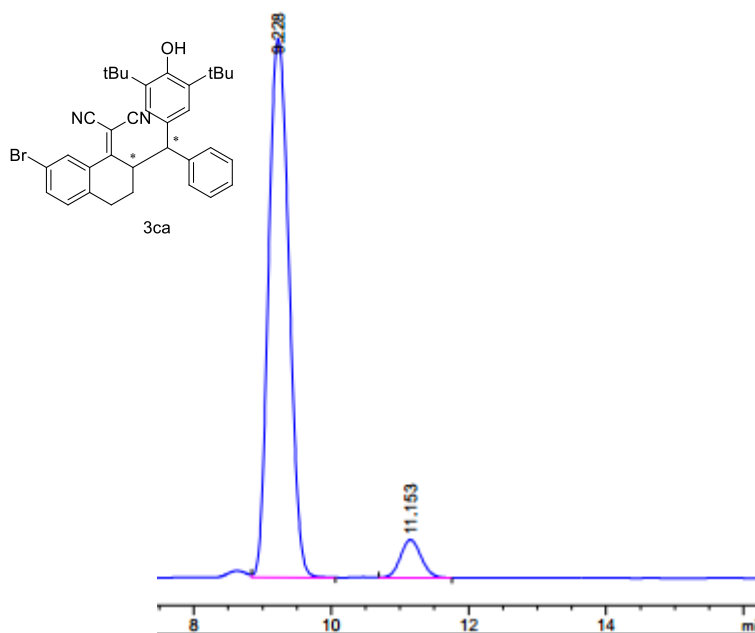
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.316	BB	0.4176	3217.39966	114.57600	50.3040
2	20.729	BB	0.8233	3178.51489	59.11327	49.6960



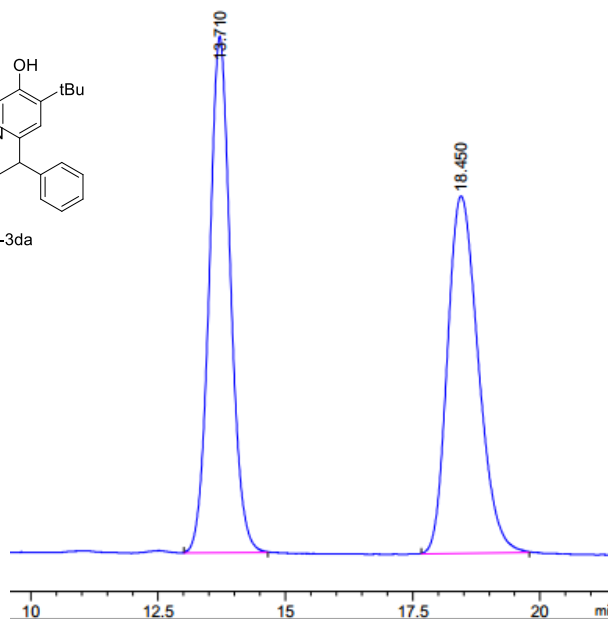
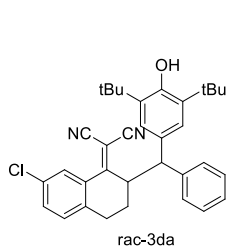
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.312	BB	0.4195	5359.28125	189.72858	90.8169
2	20.833	BB	0.7234	541.91138	10.65501	9.1831



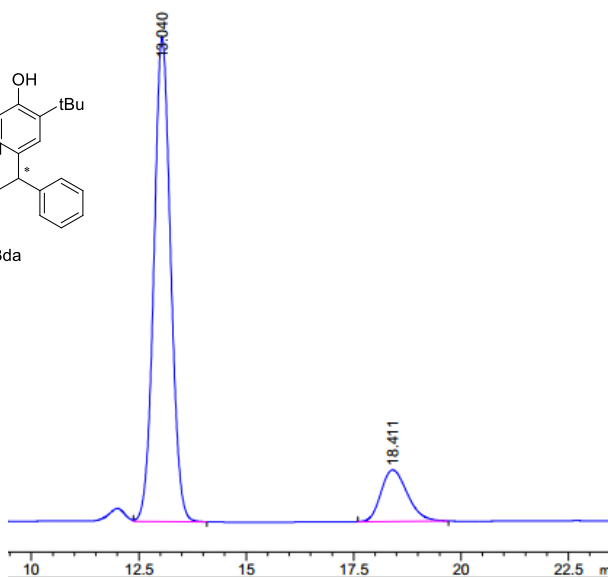
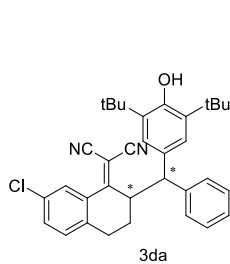
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.362	VB	0.3333	802.09442	38.77528	49.8702
2	11.338	VB	0.3236	806.27026	38.61765	50.1298



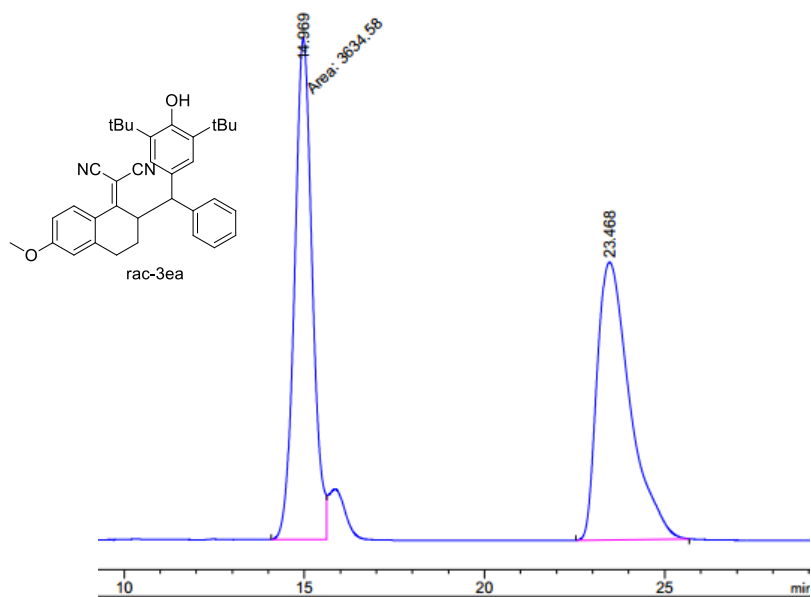
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.228	VB	0.3331	5473.47119	264.82690	93.3172
2	11.153	VB	0.3264	391.97430	18.71007	6.6828



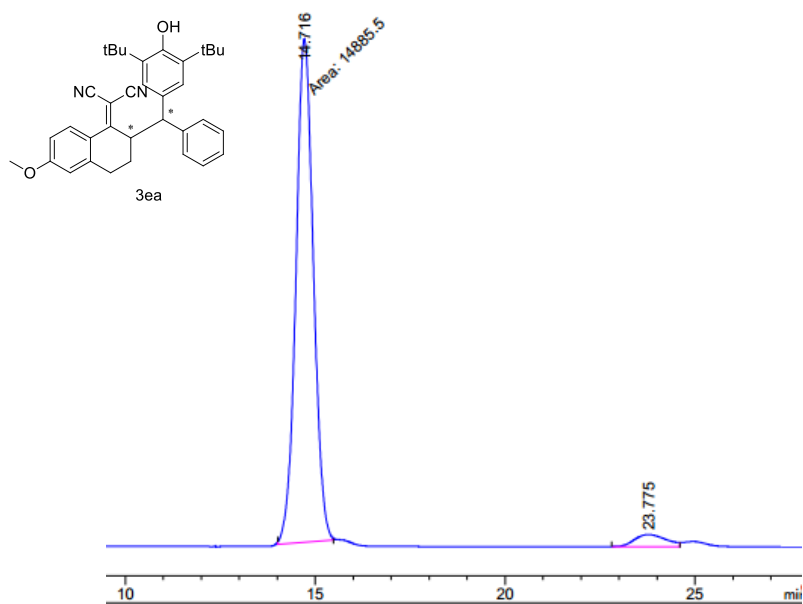
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.710	BB	0.4435	1335.07690	45.88496	49.9995
2	18.450	BB	0.6559	1335.10364	31.79351	50.0005



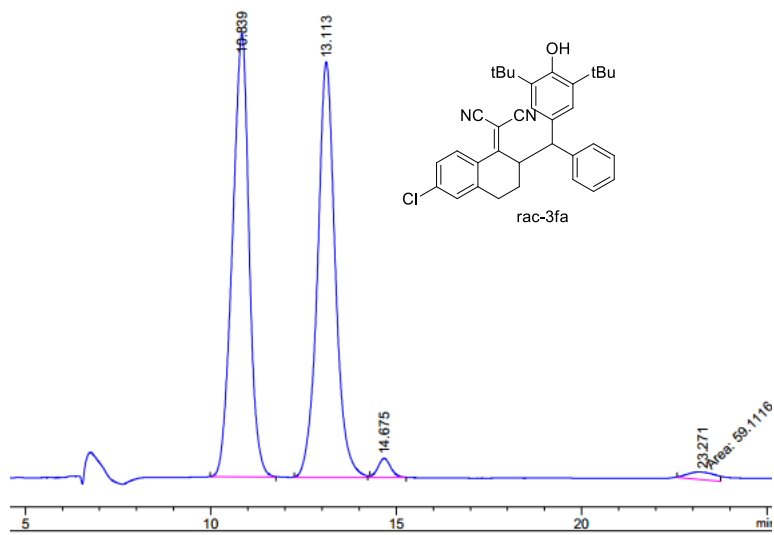
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.040	VB	0.4188	7261.20752	267.39682	85.6473
2	18.411	BB	0.6608	1216.82886	28.45995	14.3527



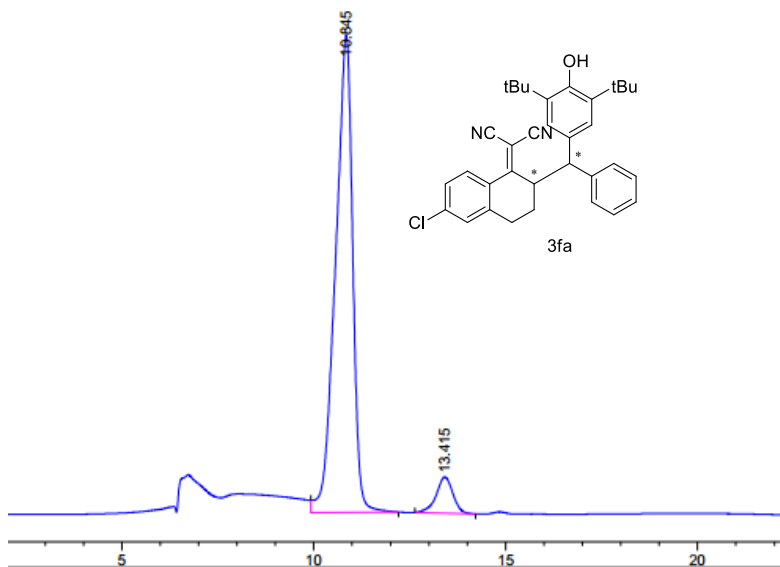
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.969	MF	0.5701	3634.57520	106.26124	49.2982
2	23.468	BB	0.9664	3738.06055	58.90547	50.7018



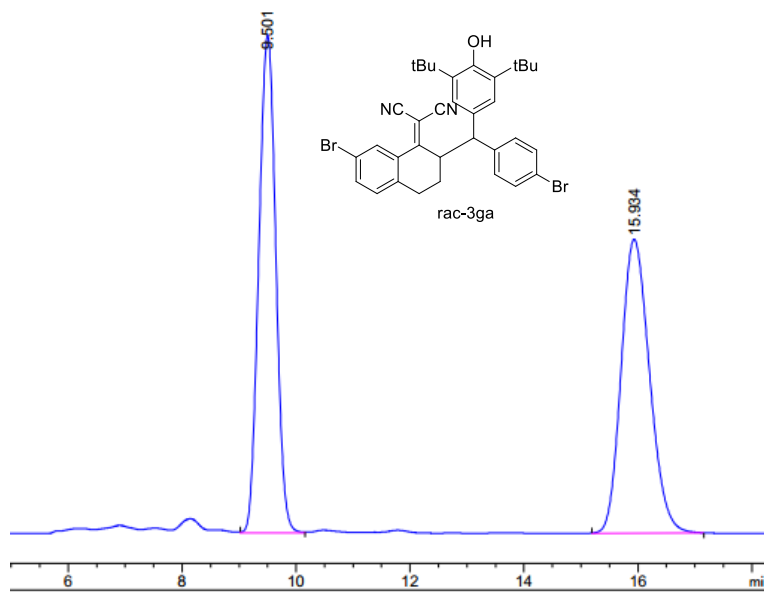
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.716	MM T	0.5318	1.48855e4	466.49179	95.8884
2	23.775	BV	0.8254	638.27435	11.09132	4.1116



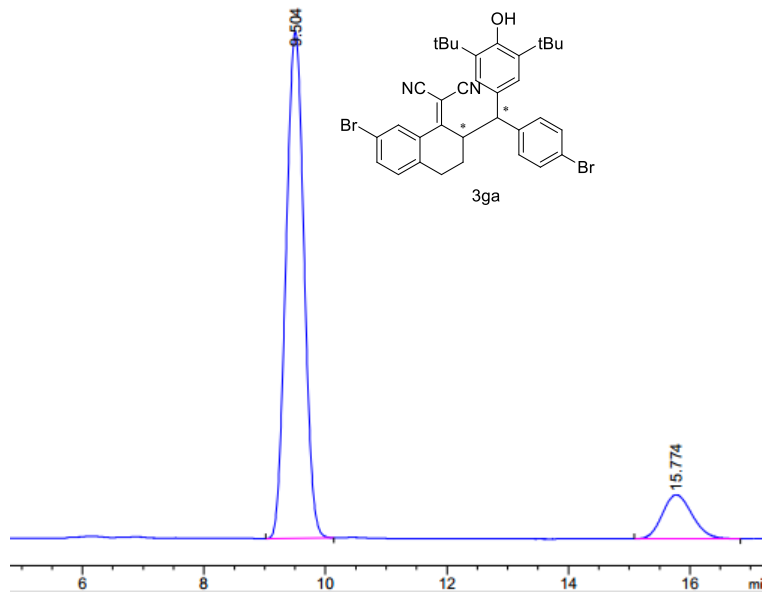
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.839	BB	0.4702	2173.25342	69.60928	48.5928
2	13.113	BB	0.4979	2168.46143	65.21452	48.4856
3	14.675	BB	0.3507	71.55264	2.99480	1.5999
4	23.271	MM T	0.8427	59.11160	1.16916	1.3217



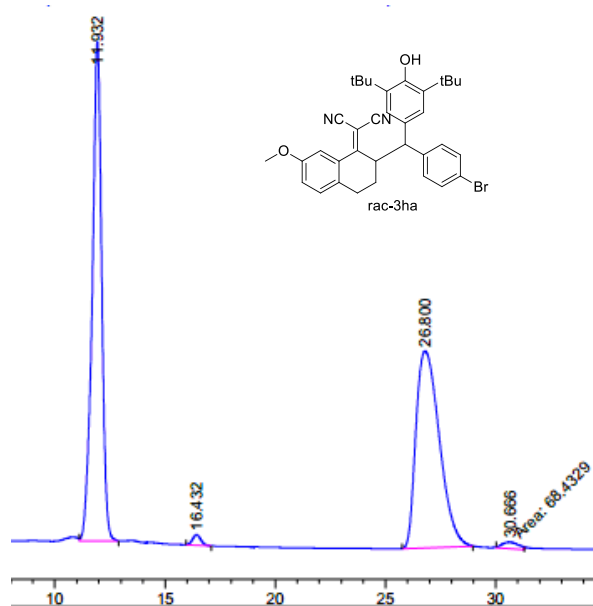
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.845	VB	0.4476	4369.84912	140.21834	93.1127
2	13.415	BB	0.4572	323.22437	10.61732	6.8873



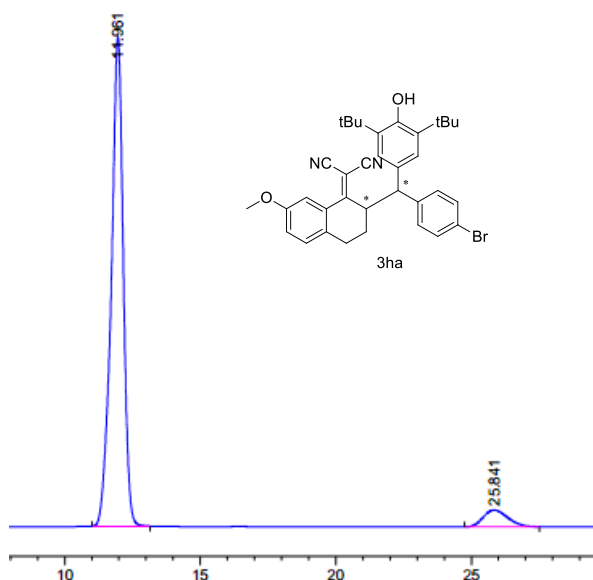
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.501	BB	0.3317	2782.28760	134.29787	50.3042
2	15.934	BB	0.5420	2748.63965	79.36874	49.6958



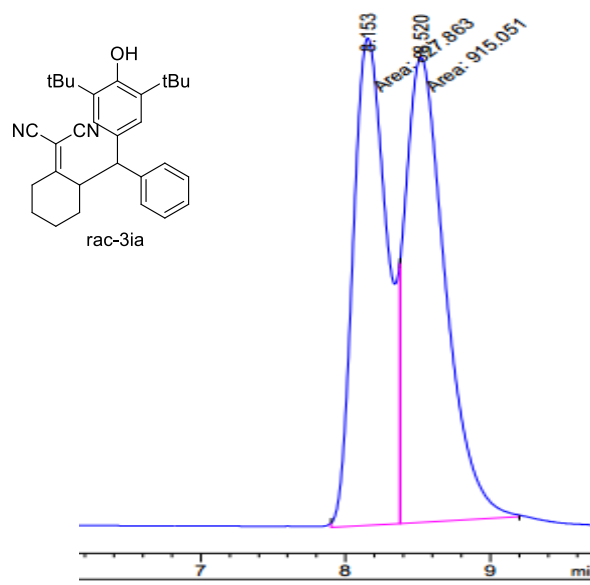
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.504	BB	0.3292	7260.87744	354.17154	87.3030
2	15.774	BB	0.5353	1055.99182	30.85729	12.6970



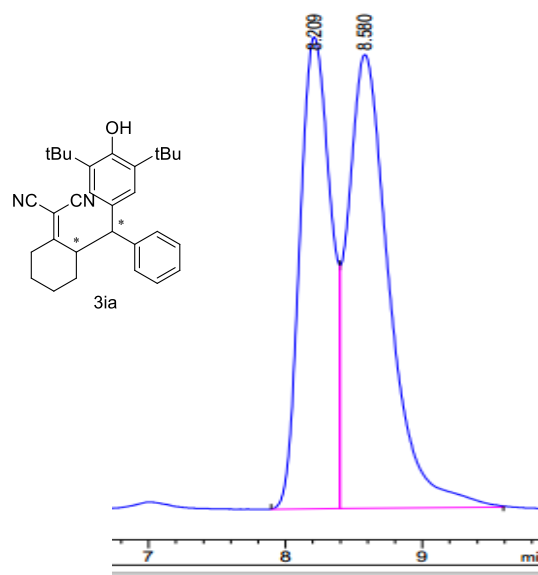
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.932	VB	0.4448	2962.60913	99.10355	49.5502
2	16.432	BB	0.3879	54.32132	2.09906	0.9085
3	26.800	BB	1.1662	2893.64185	39.06584	48.3967
4	30.666	MM	0.8721	68.43294	1.30786	1.1446



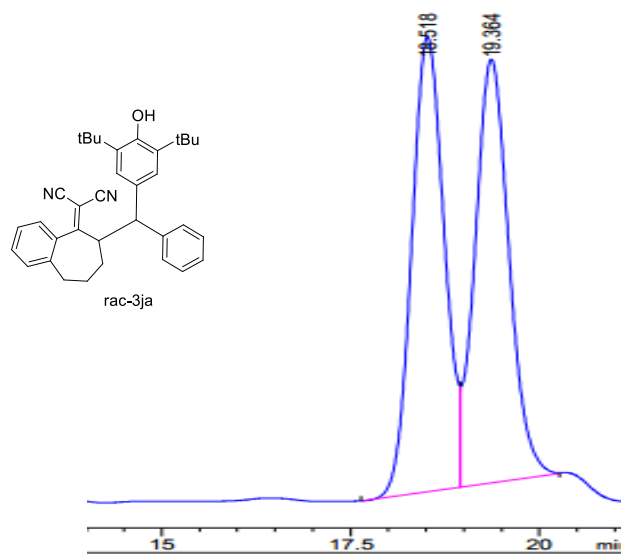
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.961	BB	0.4564	1.00903e4	328.49875	93.4003
2	25.841	BB	0.8857	712.98718	11.24463	6.5997



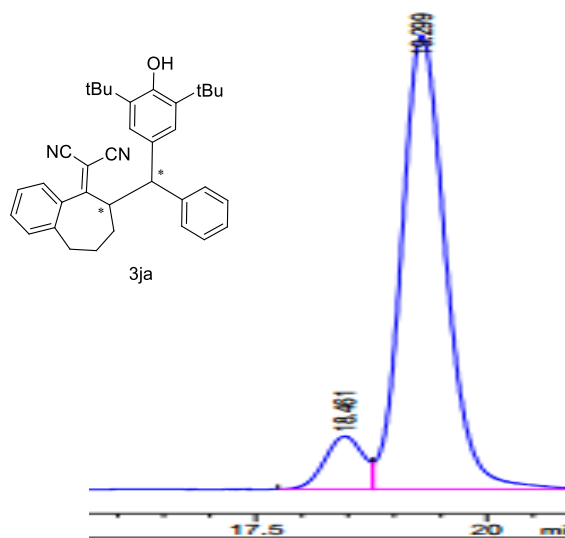
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.153	MF	0.2729	827.86285	50.56288	47.4988
2	8.520	FM	0.3159	915.05072	48.28263	52.5012



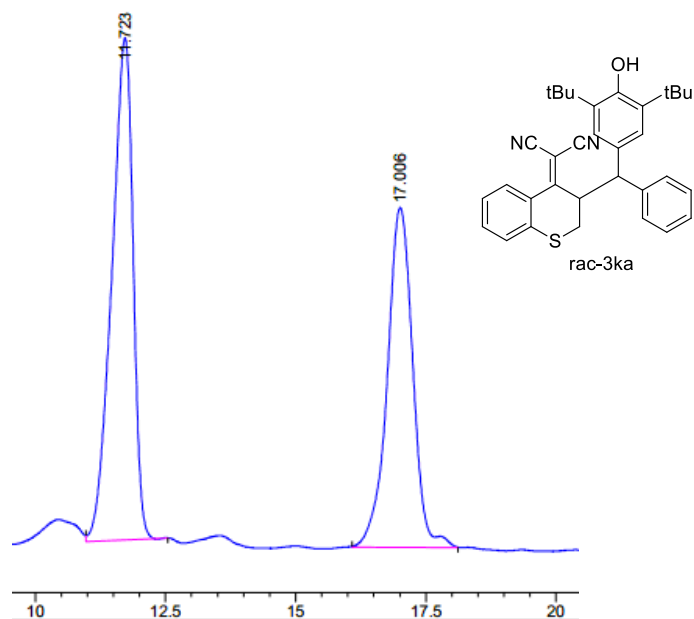
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.209	BV	0.2433	365.99634	23.29137	43.5918
2	8.580	VB	0.3126	473.60355	22.40889	56.4082



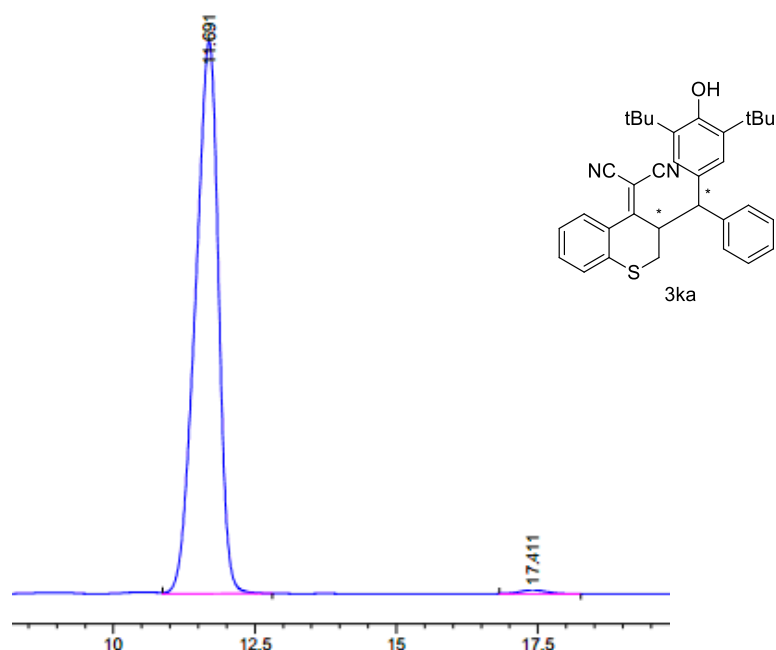
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.518	BV	0.4628	3807.95068	127.36438	50.5616
2	19.364	VB	0.4842	3723.35693	118.62897	49.4384



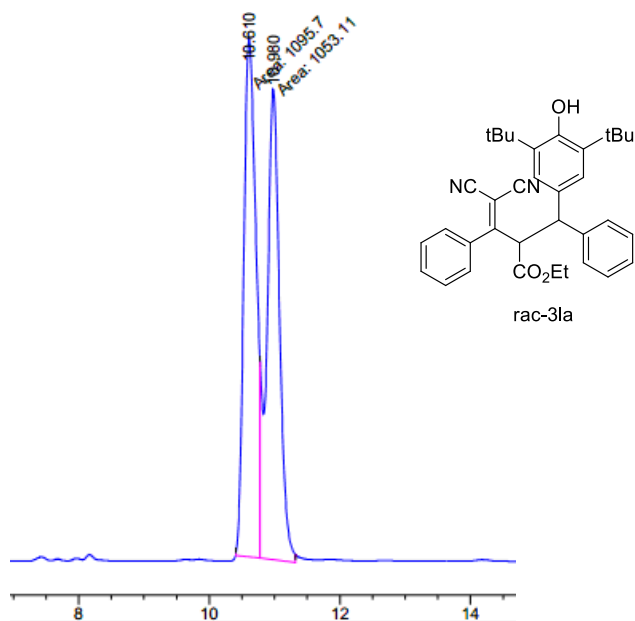
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.461	BV	0.4453	1000.85339	34.82912	9.2063
2	19.299	VBA	0.5101	9870.58887	298.23688	90.7937



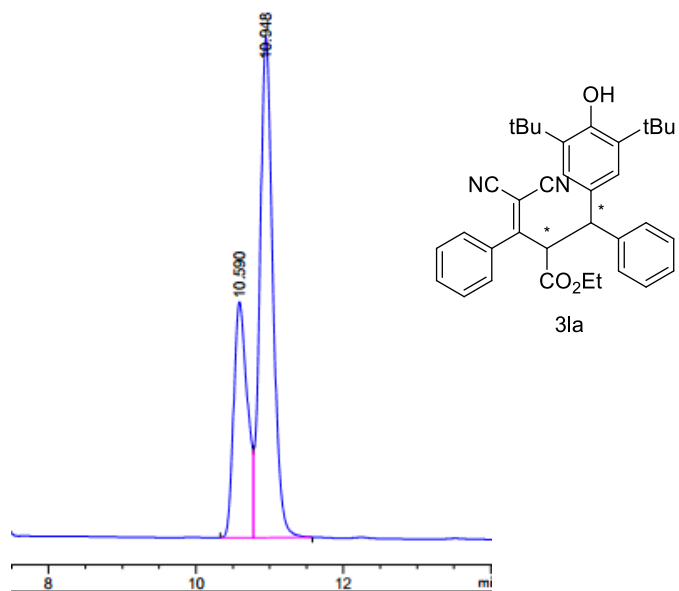
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.723	VB	0.4253	719.79681	25.34511	55.2285
2	17.006	BB	0.5272	583.50928	17.13687	44.7715



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.691	VB	0.4256	9994.12012	353.78693	99.1641
2	17.411	BB	0.4701	84.24352	2.55853	0.8359

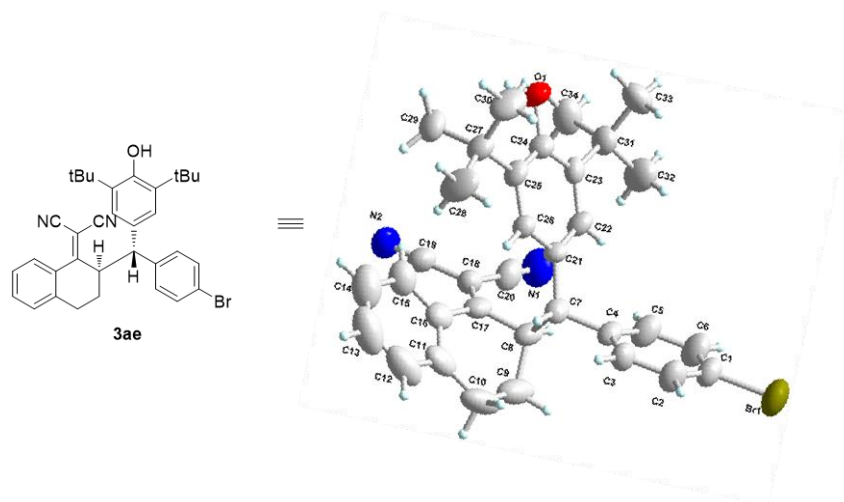


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.610	MF	0.2131	1095.70142	85.68573	50.9910
2	10.980	FM	0.2258	1053.11096	77.72159	49.0090



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.590	BV	0.1954	766.28302	59.05068	33.2902
2	10.948	VB	0.1869	1535.54175	125.35744	66.7098

9. X-ray crystal structure of 3ae



Bond precision:	C-C = 0.0131 Å	Wavelength=0.71073	
Cell:	a=10.839(5) alpha=90	b=23.282(10) beta=90	c=24.360(11) gamma=90
Temperature:	296 K		
	Calculated	Reported	
Volume	6147(5)	6147(5)	
Space group	P 21 21 21	P 21 21 21	
Hall group	P 2ac 2ab	P 2ac 2ab	
Moiety formula	C34 H35 Br N2 O	?	
Sum formula	C34 H35 Br N2 O	C34 H35 Br N2 O	
Mr	567.54	567.55	
Dx, g cm-3	1.227	1.226	
Z	8	8	
Mu (mm-1)	1.365	1.364	
F000	2368.0	2368.0	
F000'	2366.47		
h, k, lmax	12, 27, 28	12, 27, 28	
Nref	10822[5994]	10820	
Tmin, Tmax	0.689, 0.741		
Tmin'	0.676		
Correction method= Not given			
Data completeness=	1.81/1.00	Theta(max)= 25.005	
R(reflections)=	0.0547(4970)	wR2(reflections)= 0.1408(10820)	
S =	0.958	Npar= 701	