Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Phosphine-Catalyzed Asymmetric [4+1] Annulation of Morita-Baylis-Hillman Carbonates with Dicyano-2-methylenebut-3-enoates

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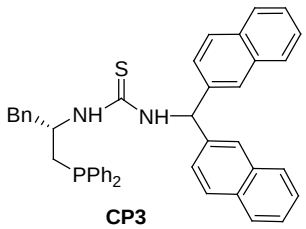
General Remarks:

Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer-341 MC digital polarimeter; $[\alpha]_D$-values are given in unit of 10 deg^{-1} cm^2 g^{-1}. ^1H NMR spectra were recorded on a Bruker AM-300 and AM-400 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; coupling constants *J* are given in Hz. ^{13}C NMR spectra were recorded on a Bruker AM-300 and AM-400 spectrophotometers (75 or 100 MHz) with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Flash column chromatography was performed using 300-400 mesh silica gel. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF254) were used. Chiral HPLC was performed on a Waters 2487 series with chiral columns (Chiralpak AD-H and Phenomenex Lux 5μ Cellulose-2 column 4.6x250 mm (PC-2, (Phenomenex Ind., Ltd.))). Mass spectra were recorded by ESI and HRMS was measured on a HP-5989 instrument.

1. Synthesis of Chiral Bifunctional Organophosphane Catalysts

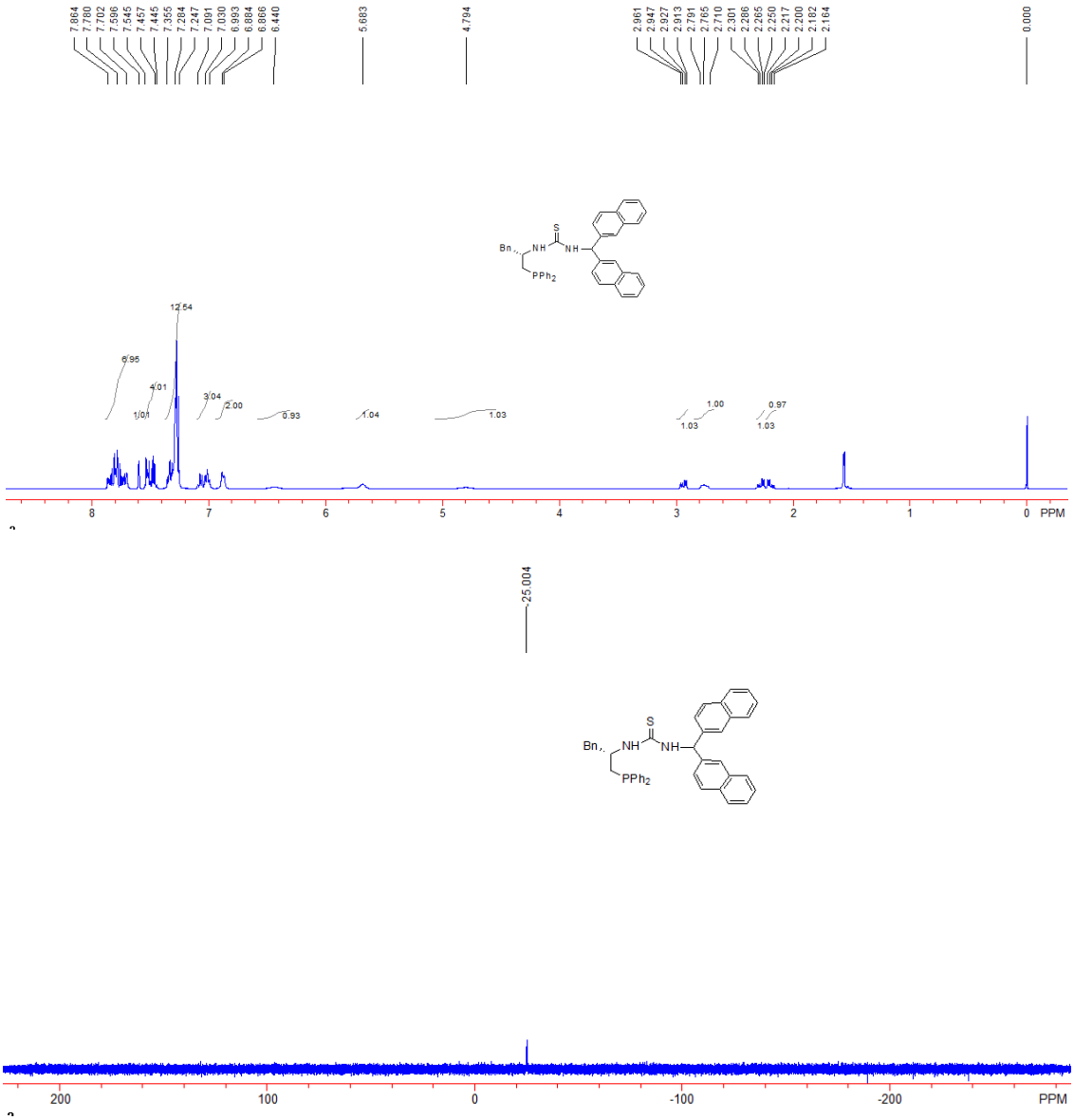
Chiral Bifunctional Organophosphane Catalysts **CP3** were prepared according to a procedure in the literature.[1] Chiral Bifunctional Organophosphane Catalysts **CP8** and **CP9** were prepared according to a procedure in the literature.[2]



CP3

Compound (*R*)-**CP3**. A white solid; m. p. 79-80 ^oC; IR (KBr): ν 3726, 3261, 3052, 2924, 2360, 2342, 1526, 1453, 1434, 1349, 1272, 1216, 1125, 1027, 896, 859, 820, 741, 696, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 2.19 (dd, 1H, *J* = 7.2, 14.0 Hz, CH), 2.28 (dd, 1H, *J* = 6.0, 14.0 Hz, CH), 2.71-2.79 (m, 1H, CH), 2.94 (dd, 1H, *J* = 5.6, 13.6 Hz, CH), 4.79 (br, 1H, CH), 5.68 (br, 1H, NH), 6.44 (br, 1H, CH), 6.87-6.88 (m, 2H, ArH), 6.99-7.09 (m, 3H, ArH), 7.25-7.36 (m, 12H, ArH), 7.45-7.55 (m, 4H, ArH), 7.60 (s, 1H, ArH), 7.70-7.86 (m, 7H, ArH); ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4): δ

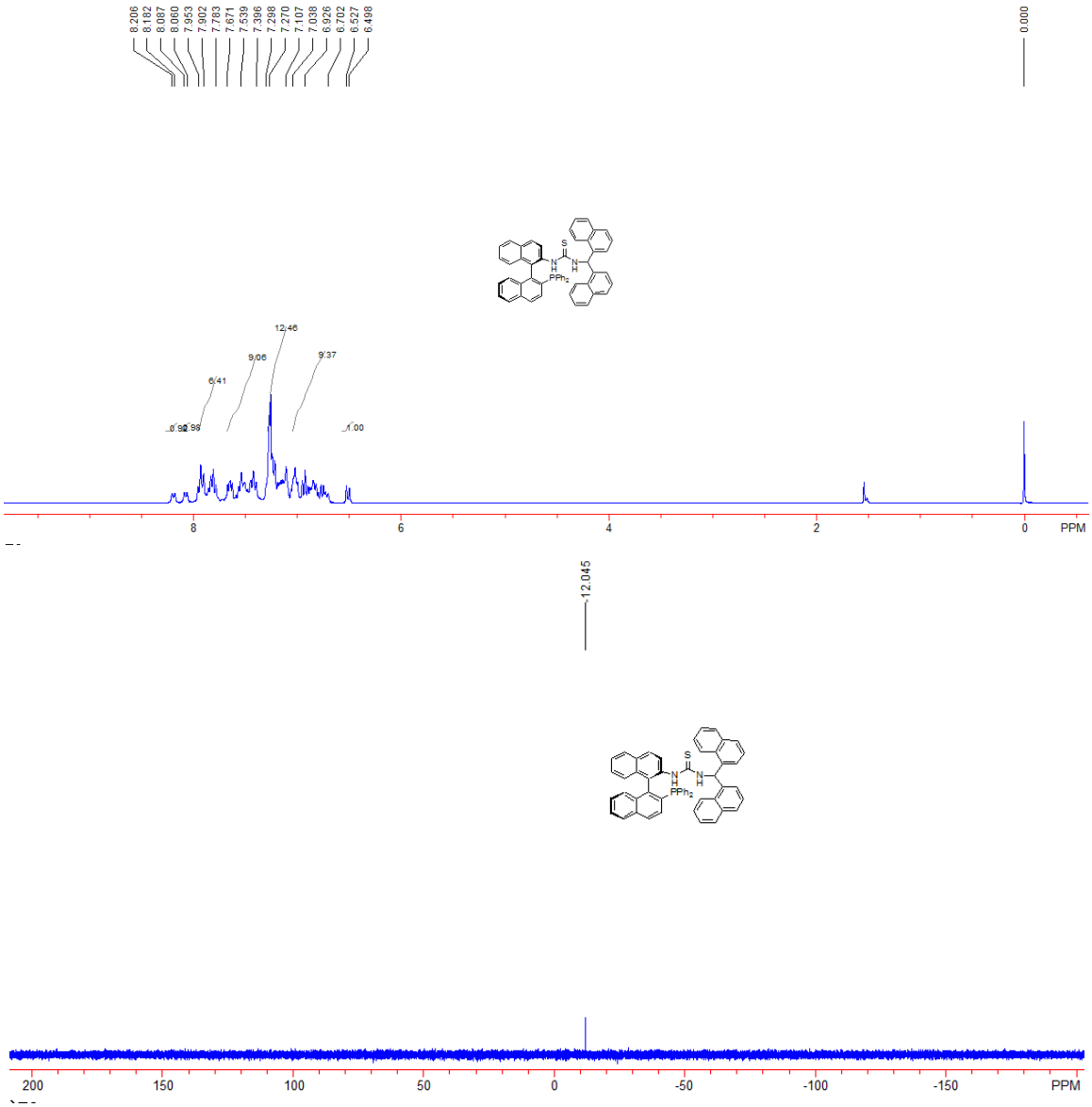
-25.00; HRMS (ESI) Calcd. For $C_{43}H_{38}N_2OPS^{+1}$ $(M+OH)^+$ requires 661.2442, Found: 661.2433; $[\alpha]^{20}_D$ = -5.8 (c 1.00, $CHCl_3$).

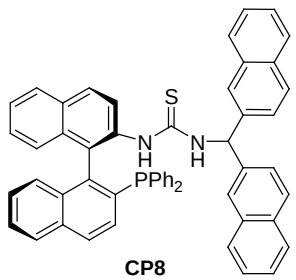


CP7

Compound (*R*)-**CP7**. A white solid; m. p. 138-139 ^oC; IR (KBr): ν 3385, 3053, 2926, 2855, 1776, 1727, 1506, 1434, 1328, 1216, 1105,1027, 759, 697 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 6.51 (d, 1H, *J* = 8.7 Hz), 6.70-7.04 (m, 9H), 7.11-7.30 (m, 12H), 7.40-7.67 (m, 9H), 7.78-7.95 (m, 6H), 8.07 (d, 1H, *J* = 8.1 Hz), 8.19 (d, 1H, *J* = 7.2 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz, 85% H_3PO_4): δ -12.05; HRMS

(ESI) Calcd. For $C_{54}H_{40}N_2PS^{+1}$ $(M+H)^+$ requires 779.2650, Found: 779.2649; $[\alpha]^{20}_D$ = +109.4 (c 1.00, $CHCl_3$).

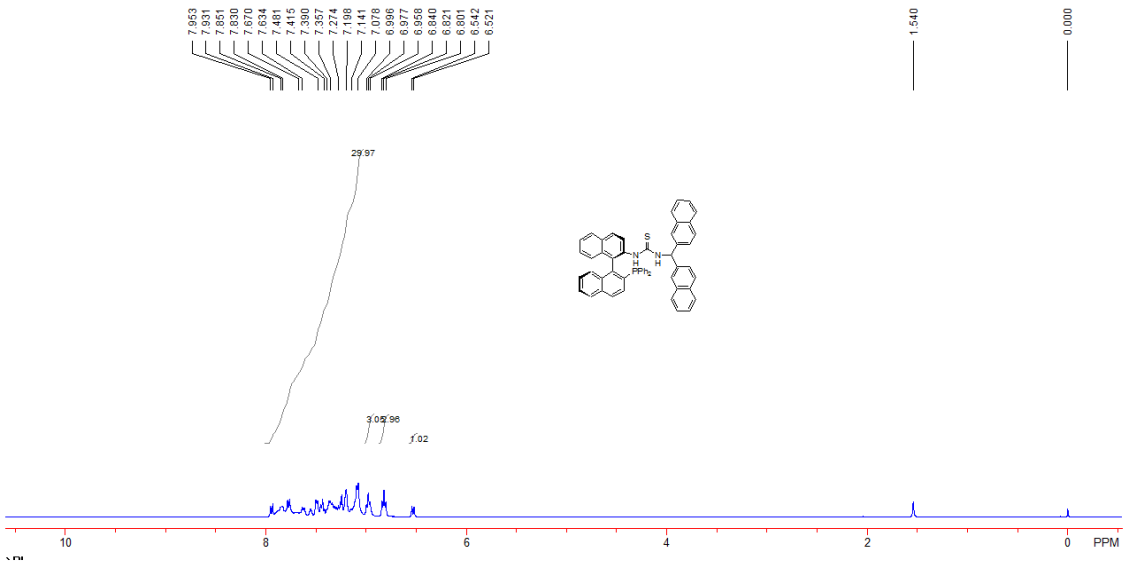


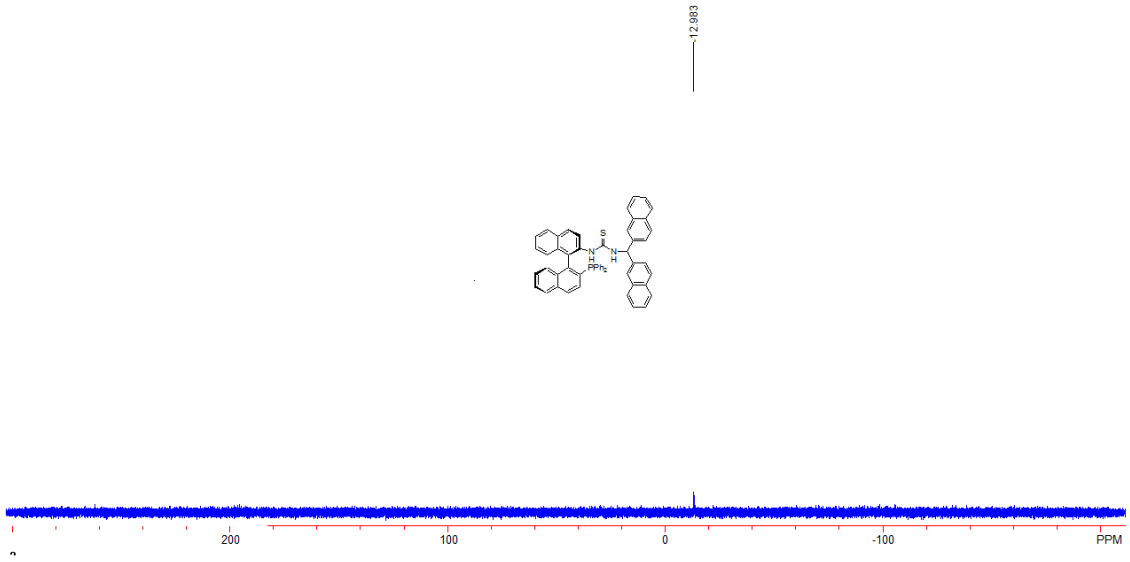


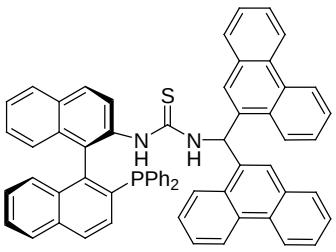
CP8

Compound (*R*)-**CP8**. A white solid; m. p. 142-143 ^oC; IR (KBr): ν 3381, 3052, 1591, 1505, 1480, 1433, 1327, 1264, 1192, 818, 741, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 6.53 (d, 1H, *J* = 8.4 Hz), 6.82 (t, 3H, *J* = 8.0 Hz), 6.98 (t, 3H, *J* = 7.6 Hz), 7.08-7.95 (m, 30H); ^{31}P NMR ($CDCl_3$, 161.95 MHz,

85% H_3PO_4): δ -12.98; HRMS (ESI) Calcd. For $C_{54}H_{40}N_2PS^{+1}$ $(M+H)^+$ requires 779.2650, Found: 779.2637; $[\alpha]^{20}_D$ = +122.4 (c 1.5, $CHCl_3$).



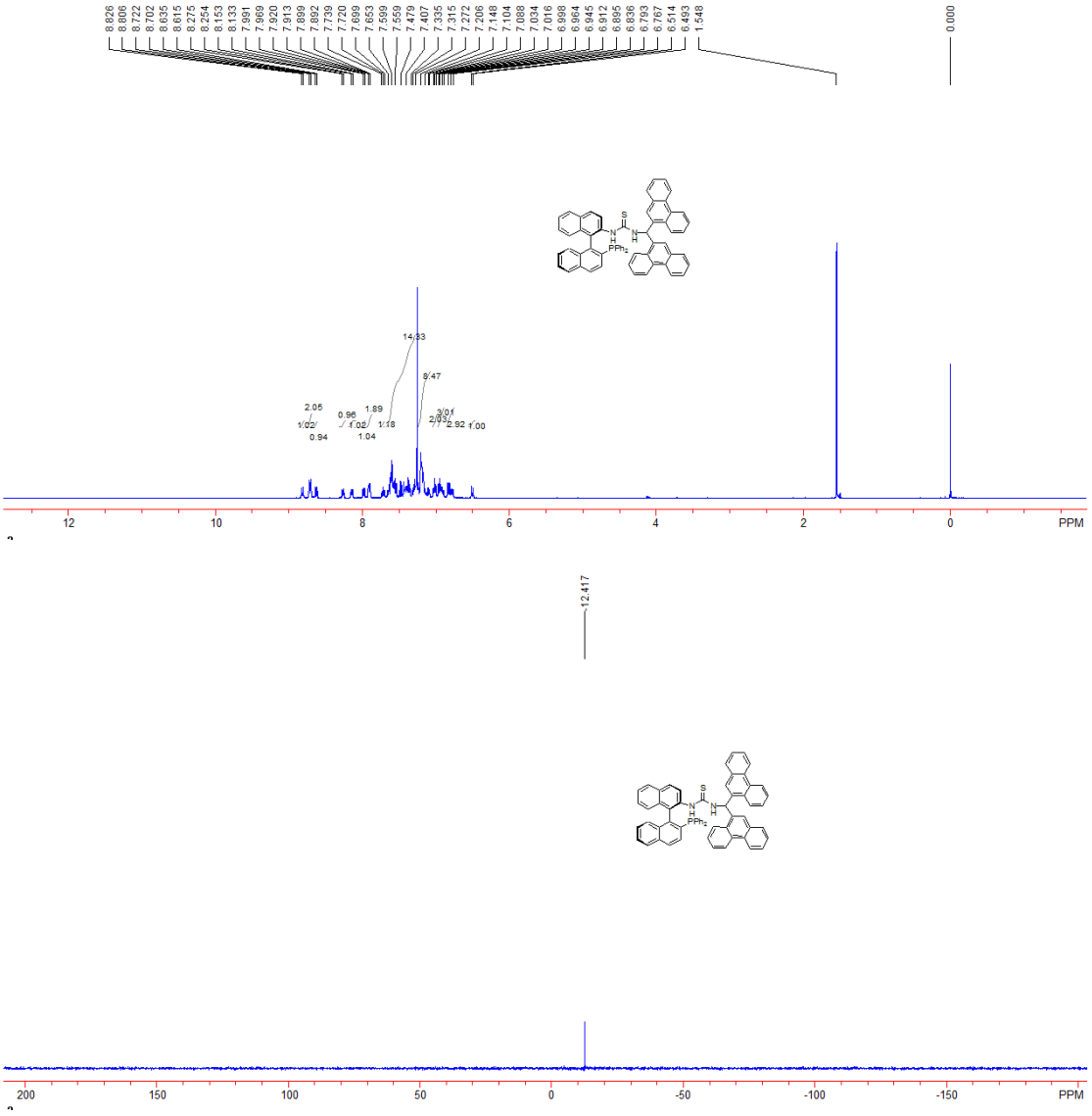




CP9

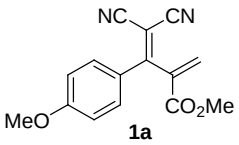
Compound (*R*)-**CP9**. A white solid; m. p. 197-198 ^oC; IR (KBr): ν 3382, 3052, 1497, 1450, 1433, 1250, 747,727, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 6.50 (d, 1H, *J* = 8.4 Hz, ArH), 6.77-6.84 (m,

3H), 6.90-6.96 (m, 3H), 7.02 (t, 2H, *J* = 7.2 Hz), 7.09-7.21 (m, 8H), 7.27-7.74 (m, 14H), 7.70-7.74 (m, 1H), 7.89-7.92 (m, 1H), 7.98 (d, 1H, *J* = 8.4 Hz, ArH), 8.14 (d, 1H, *J* = 8.0 Hz, ArH), 8.26 (d, 1H, *J* = 8.4 Hz, ArH), 8.63 (d, 1H, *J* = 8.0 Hz, ArH), 8.71 (d, 2H, *J* = 8.0 Hz, ArH), 8.82 (d, 1H, *J* = 8.0 Hz, ArH); ^{31}P NMR ($CDCl_3$, 121.5 MHz, 85% H_3PO_4): δ -12.42; HRMS (ESI) Calcd. For $C_{62}H_{44}N_2PS^{+1}$ $(M+H)^+$ requires 879.2963, Found: 879.2965; $[\alpha]^{20}_D$ = +39.0 (c 1.00, $CHCl_3$).



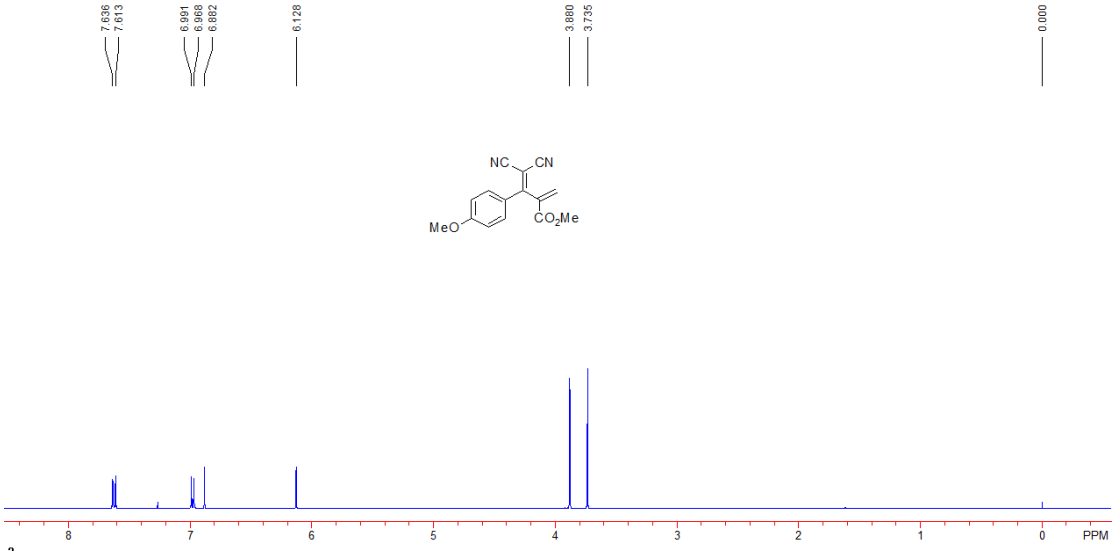
2. General Procedure for the Synthesis of Dicyano-2-methylenebut-3-enoates and Spectroscopic Data of the Products

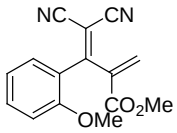
Dicyano-2-methylenebut-3-enoates **1** were prepared according to a procedure in the literature.[3]



1a

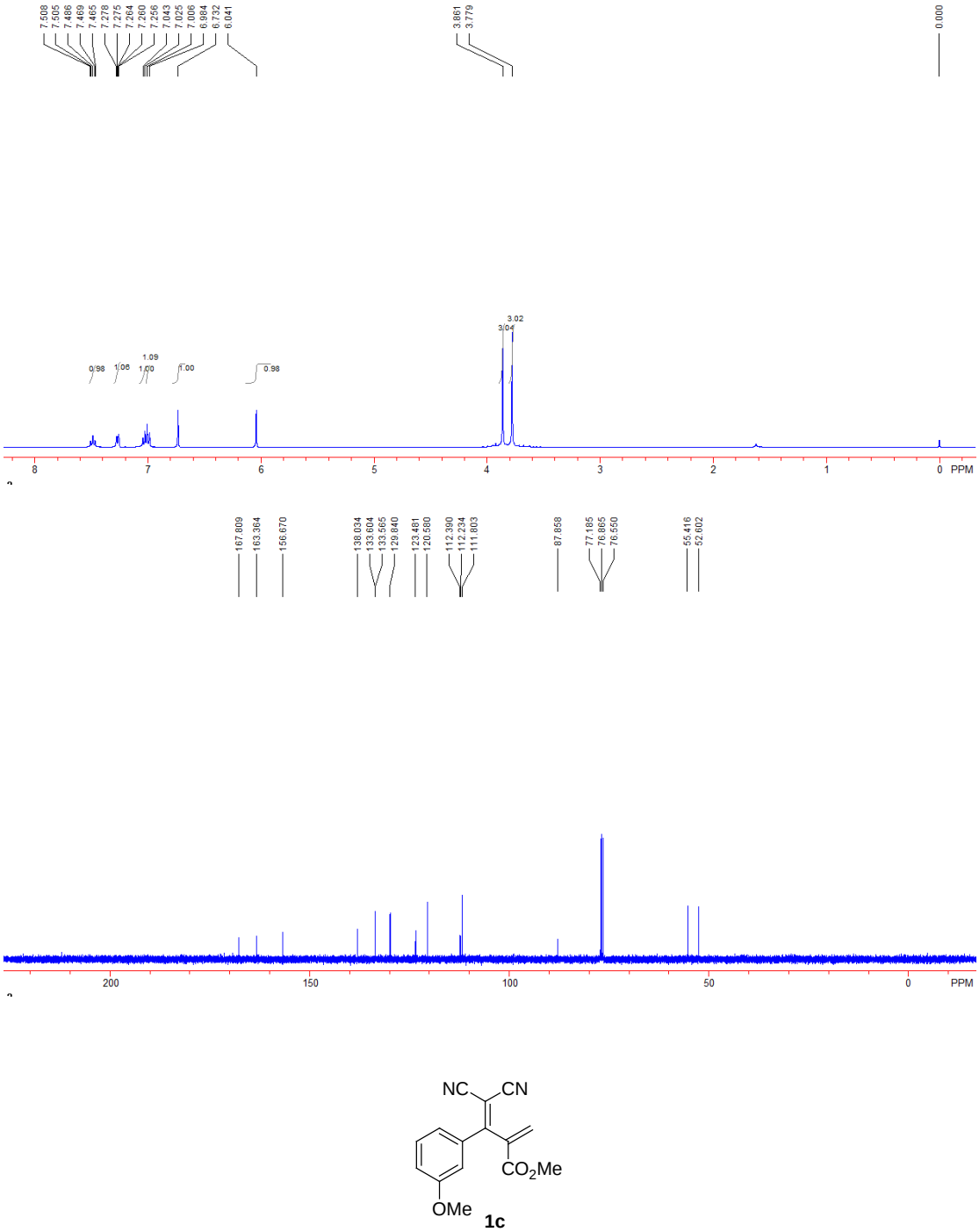
methyl 4,4-dicyano-3-(4-methoxyphenyl)-2-methylenebut-3-enoate (1a). This is a known compound.[3] ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.74 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 6.13 (s, 1H, $=CH_2$), 6.88 (s, 1H, $=CH_2$), 6.98 (d, 2H, *J* = 9.2 Hz, ArH), 7.62 (d, 2H, *J* = 9.2 Hz, ArH).





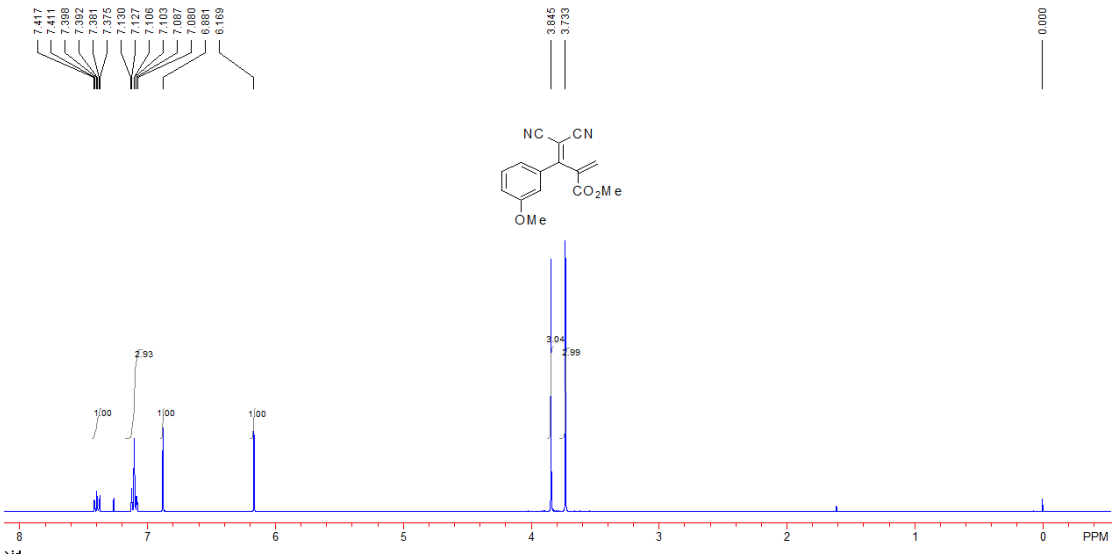
1b

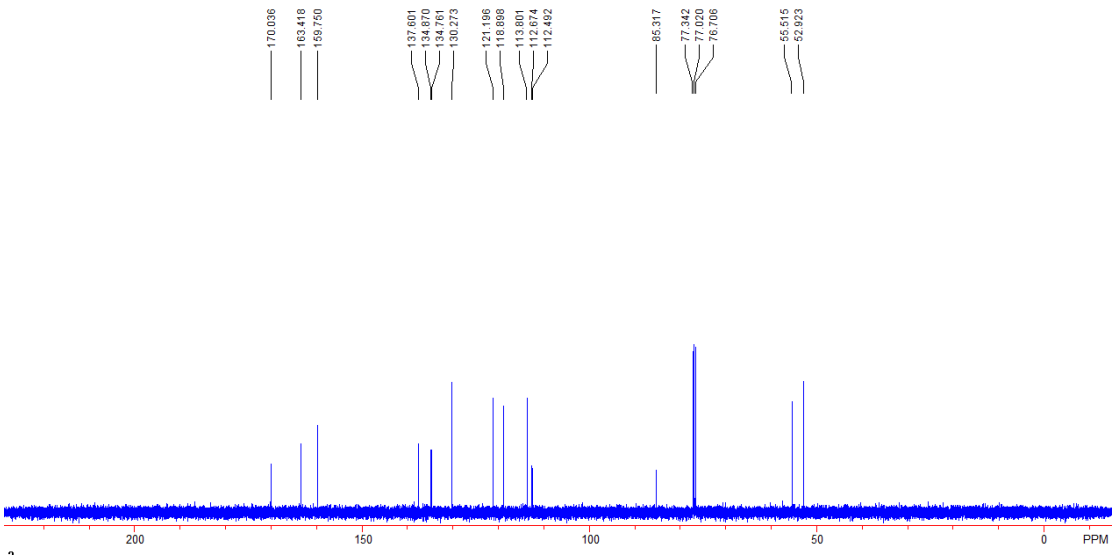
methyl 4,4-dicyano-3-(2-methoxyphenyl)-2-methylenebut-3-enoate (1b). A colorless oil, 36% yield; IR (KBr): ν 2960, 2923, 2853, 2227, 1729, 1597, 1488, 1463, 1435, 1284, 1260, 1153, 1118, 1020, 981, 797, 754 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.78 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 6.04 (s, 1H, $=CH_2$), 6.73 (s, 1H, $=CH_2$), 7.00 (d, 1H, *J* = 8.8 Hz, ArH), 7.03 (d, 1H, *J* = 7.2 Hz, ArH), 7.26-7.28 (m, 1H, ArH), 7.47-7.51 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 52.6, 55.4, 87.9, 111.8, 112.2, 112.4, 120.6, 123.5, 129.8, 133.57, 133.60, 138.0, 156.7, 163.4, 167.8; MS (ESI) *m/z* (%): 301.1 (100) $[M+CH_3OH+H^+]$; HRMS (ESI) Calcd. For $C_{16}H_{17}N_2O_4^{+1}$ $(M+CH_3OH+H)^+$ requires 301.1188, Found: 301.1178.

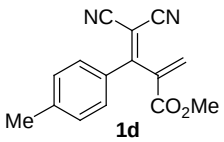


1c

methyl 4,4-dicyano-3-(3-methoxyphenyl)-2-methylenebut-3-enoate (1c). A colorless oil, 45% yield; IR (KBr): ν 2951, 2838, 2229, 1726, 1597, 1578, 1560, 1489, 1432, 1331, 1289, 1269, 1234, 1151, 1048, 981, 857, 787, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.73 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 6.17 (s, 1H, $=CH_2$), 6.88 (s, 1H, $=CH_2$), 7.08-7.13 (m, 3H, ArH), 7.38-7.42 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 52.9, 55.5, 85.3, 112.5, 112.7, 113.8, 118.9, 121.2, 130.3, 134.8, 134.9, 137.6, 159.8, 163.4, 170.0; MS (ESI) *m/z* (%): 301.1 (100) $[M+CH_3OH+H]^+$; HRMS (ESI) Calcd. For $C_{16}H_{17}N_2O_4^{+1}$ $(M+CH_3OH+H)^+$ requires 301.1188, Found: 301.1183.

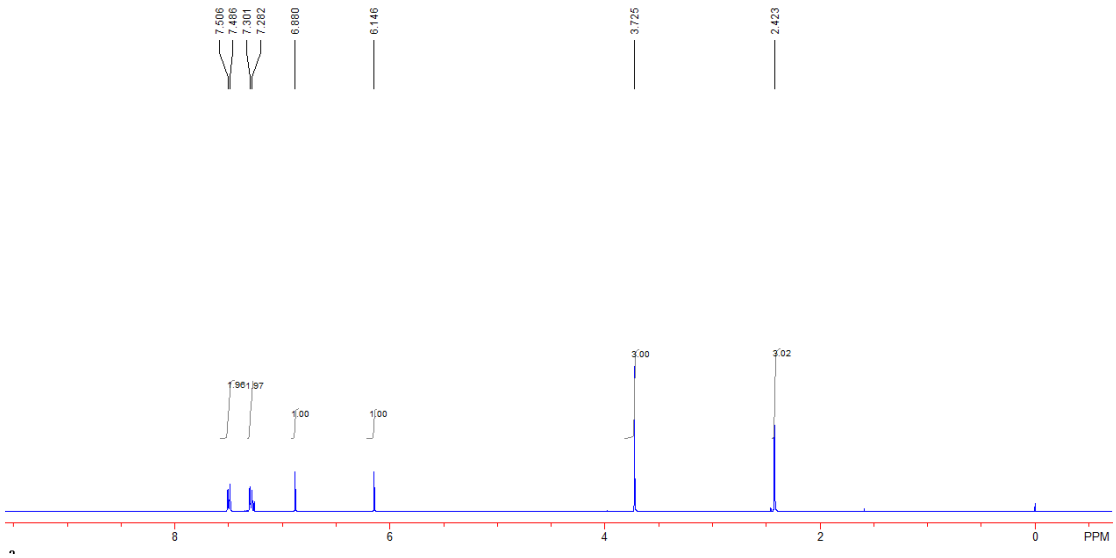


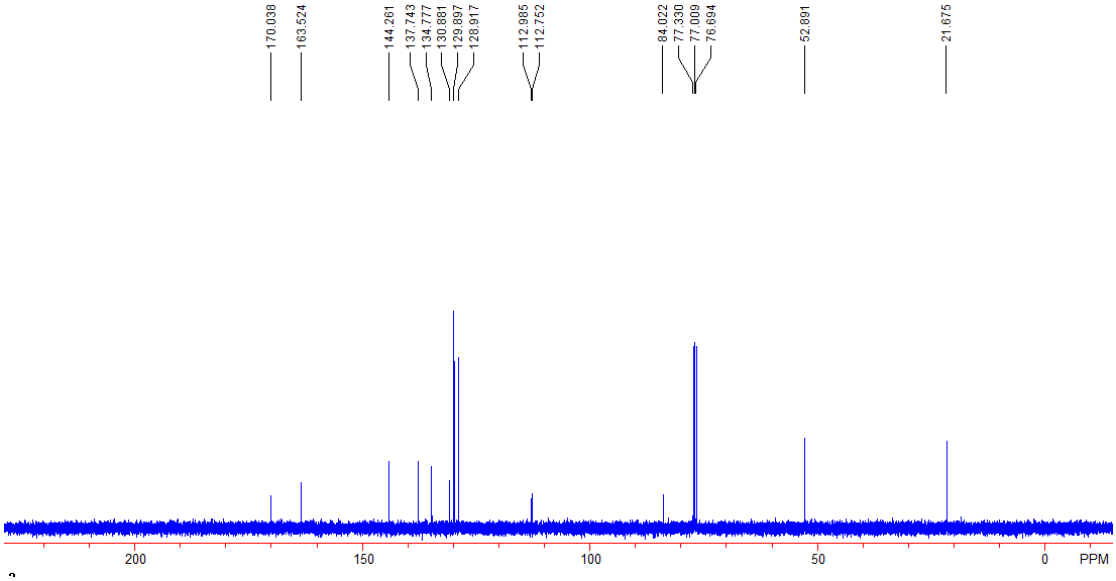


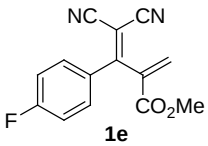


1d

methyl 4,4-dicyano-2-methylene-3-p-tolylbut-3-enoate (1d). A colorless solid, 62% yield; m.p. 63-64 ^{o}C; IR (KBr): ν 2954, 2919, 2228, 1727, 1607, 1572, 1544, 1436, 1339, 1253, 1196, 1153, 978, 856, 821, 743 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.42 (s, 3H, CH_3), 3.73 (s, 3H, OCH_3), 6.15 (s, 1H, $=CH_2$), 6.88 (s, 1H, $=CH_2$), 7.29 (d, 2H, J = 8.0 Hz, ArH), 7.50 (d, 2H, J = 8.0 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 21.7, 52.9, 84.0, 112.8, 113.0, 128.9, 129.9, 130.9, 134.8, 137.7, 144.3, 163.5, 170.0; MS (ESI) *m/z* (%): 285.1 (100) $[M+CH_3OH+H]^+$; HRMS (ESI) Calcd. For $C_{16}H_{17}N_2O_3^{+1}$ $(M+CH_3OH+H)^+$ requires 285.1239, Found: 285.1234.



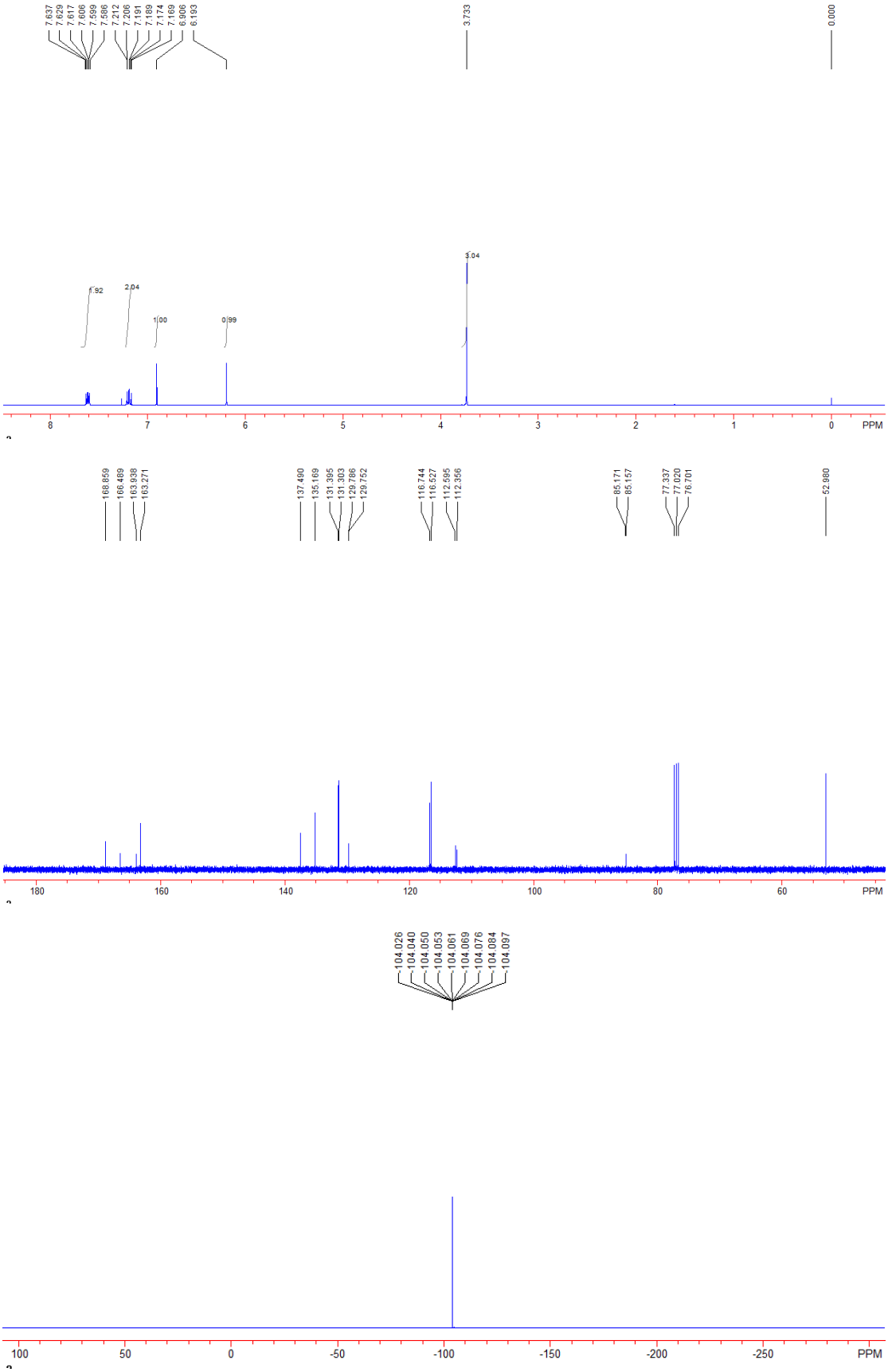


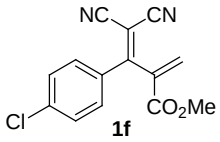


1e

methyl 4,4-dicyano-3-(4-fluorophenyl)-2-methylenebut-3-enoate (1e). A colorless oil, 56% yield; IR (KBr): ν 2915, 2854, 2227, 1729, 1600, 1555, 1508, 1438, 1340, 1241, 1196, 1160, 980, 840, 809 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): 3.73 (s, 3H, OCH_3), 6.19 (s, 1H, $=CH_2$), 6.91 (s, 1H, $=CH_2$), 7.17-7.21 (m, 2H, ArH), 7.59-7.64 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 53.0, 85.2 (d, *J* = 1.4 Hz), 112.4, 112.6, 116.6 (d, *J* = 21.7 Hz), 129.8 (d, *J* = 3.4 Hz), 131.3 (d, *J* = 9.2 Hz), 135.2, 137.5, 163.3, 165.2 (d, *J* = 255.2 Hz), 168.9; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -104.06; MS (ESI) *m/z* (%): 289.1 (100) $[M+CH_3OH+H]^+$; HRMS (ESI) Calcd. For $C_{15}H_{14}FN_2O_3^{+1}$ $(M+CH_3OH+H)^+$

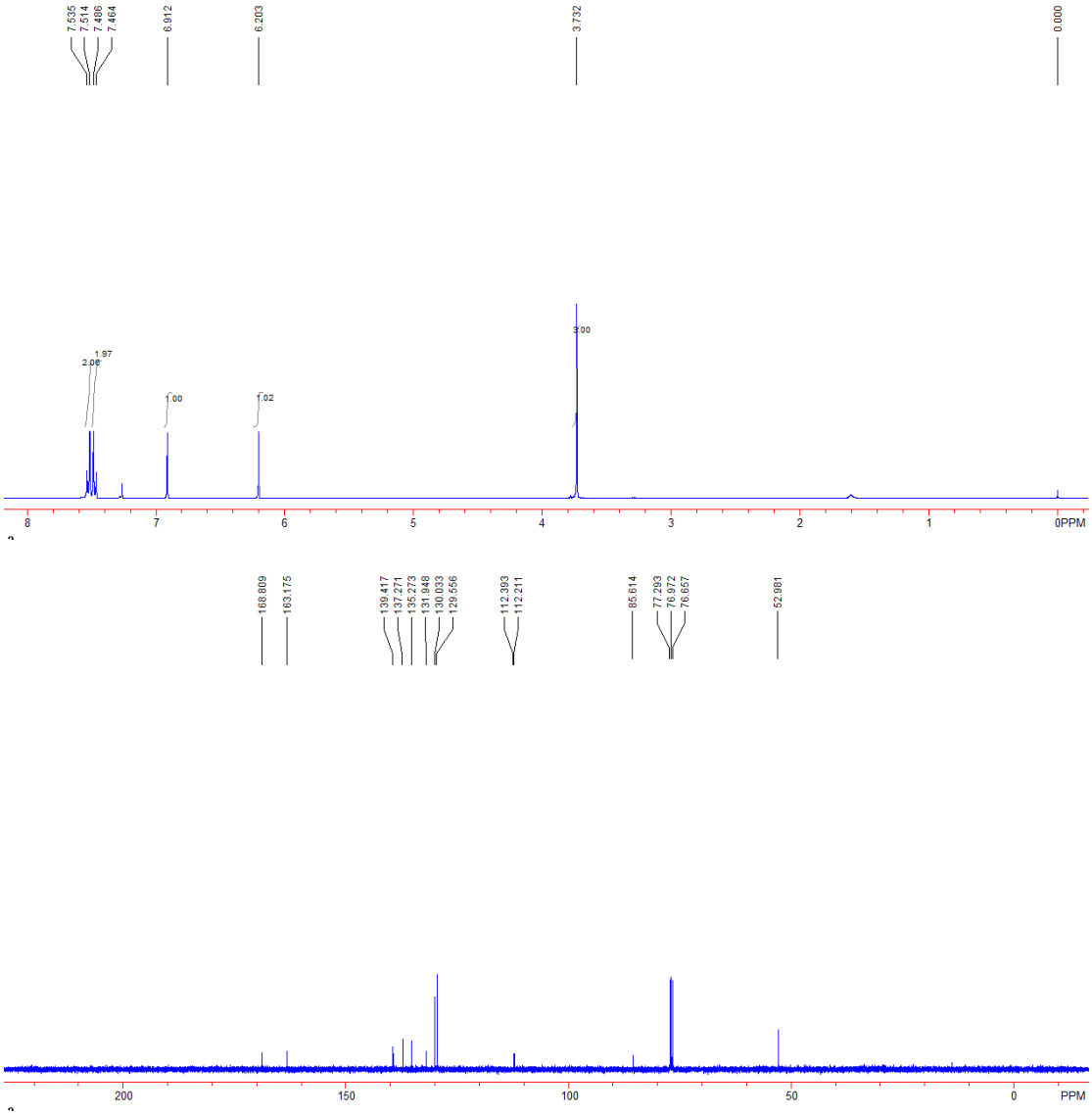
requires 289.0988, Found: 289.0982.

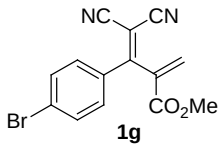




1f

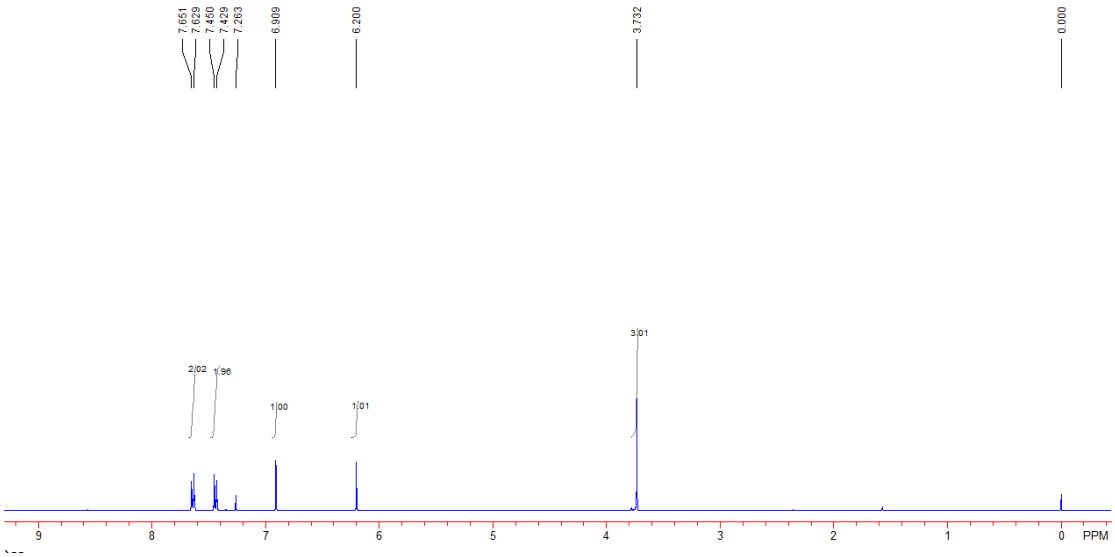
methyl 3-(4-chlorophenyl)-4,4-dicyano-2-methylenebut-3-enoate (1f). A colorless oil, 60% yield; IR (KBr): ν 2954, 2230, 1725, 1590, 1549, 1436, 1402, 1338, 1251, 1155, 1093, 979, 831, 735 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.73 (s, 3H, OCH_3), 6.20 (s, 1H, $=CH_2$), 6.91 (s, 1H, $=CH_2$), 7.48 (d, 2H, *J* = 8.4 Hz, ArH), 7.53 (d, 2H, *J* = 8.4 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 53.0, 85.6, 112.2, 112.4, 129.6, 130.0, 131.9, 135.3, 137.3, 139.4, 163.2, 168.8; MS (ESI) *m/z* (%): 305.1 (100) $[M+CH_3OH+H]^+$; HRMS (ESI) Calcd. For $C_{15}H_{14}ClN_2O_3^{+1}$ $(M+CH_3OH+H)^+$ requires 305.0693, Found: 305.0683.

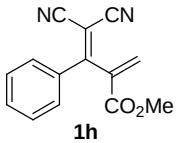




1g

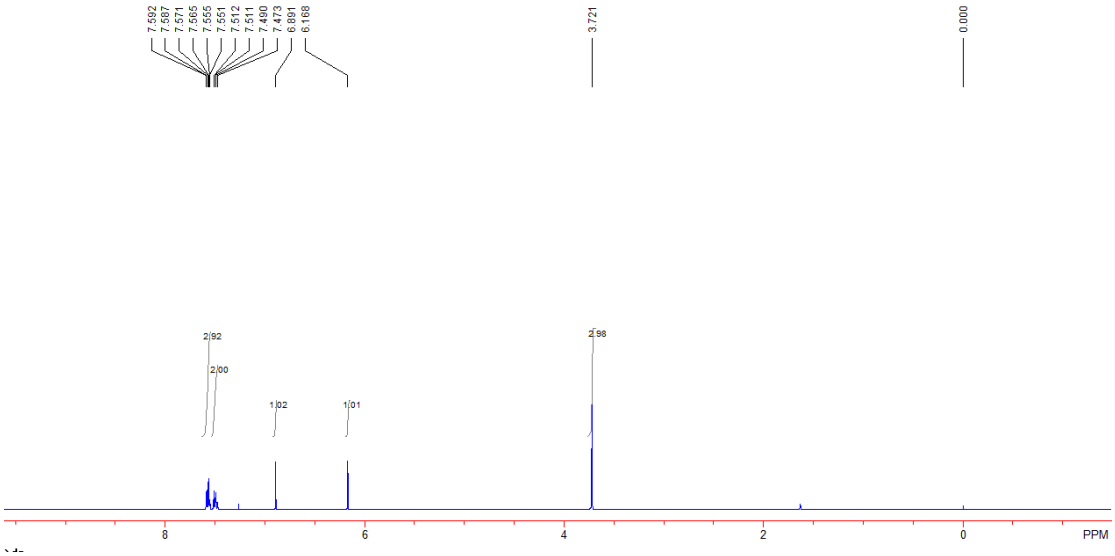
methyl 3-(4-bromophenyl)-4,4-dicyano-2-methylenebut-3-enoate (1g). This is a known compound.[3] ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.73 (s, 3H, OCH_3), 6.20 (s, 1H, $=CH_2$), 6.91 (s, 1H, $=CH_2$), 7.44 (d, 2H, J = 8.4 Hz, ArH), 7.64 (d, 2H, J = 8.4 Hz, ArH).

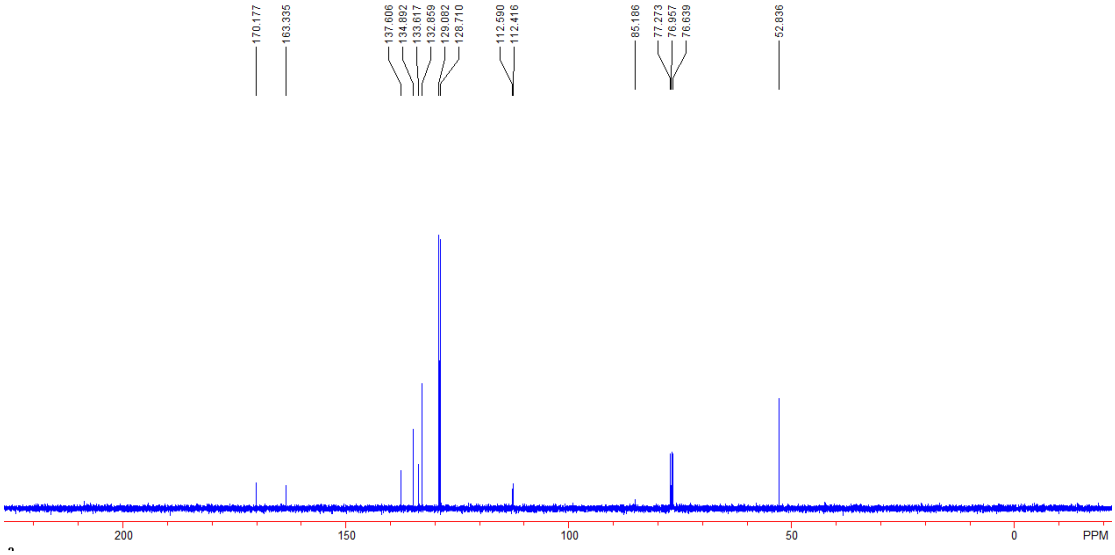


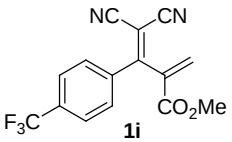


1h

methyl 4,4-dicyano-2-methylene-3-phenylbut-3-enoate (1h). A colorless oil, 48% yield; IR (KBr): ν 2960, 2927, 2230, 1727, 1553, 1436, 1339, 1252, 1196, 1154, 1001, 977, 774, 734, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.72 (s, 3H, OCH_3), 6.17 (s, 1H, $=CH_2$), 6.89 (s, 1H, $=CH_2$), 7.47-7.51 (m, 2H, ArH), 7.55-7.59 (m, 3H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 52.8, 85.2, 112.4, 112.6, 128.7, 129.1, 132.9, 133.6, 134.9, 137.6, 163.3, 170.2; MS (ESI) *m/z* (%): 271.1 (100) $[M+CH_3OH+H]^+$; HRMS (ESI) Calcd. For $C_{15}H_{15}N_2O_3^{+1}$ $(M+CH_3OH+H)^+$ requires 271.1083, Found: 271.1073.



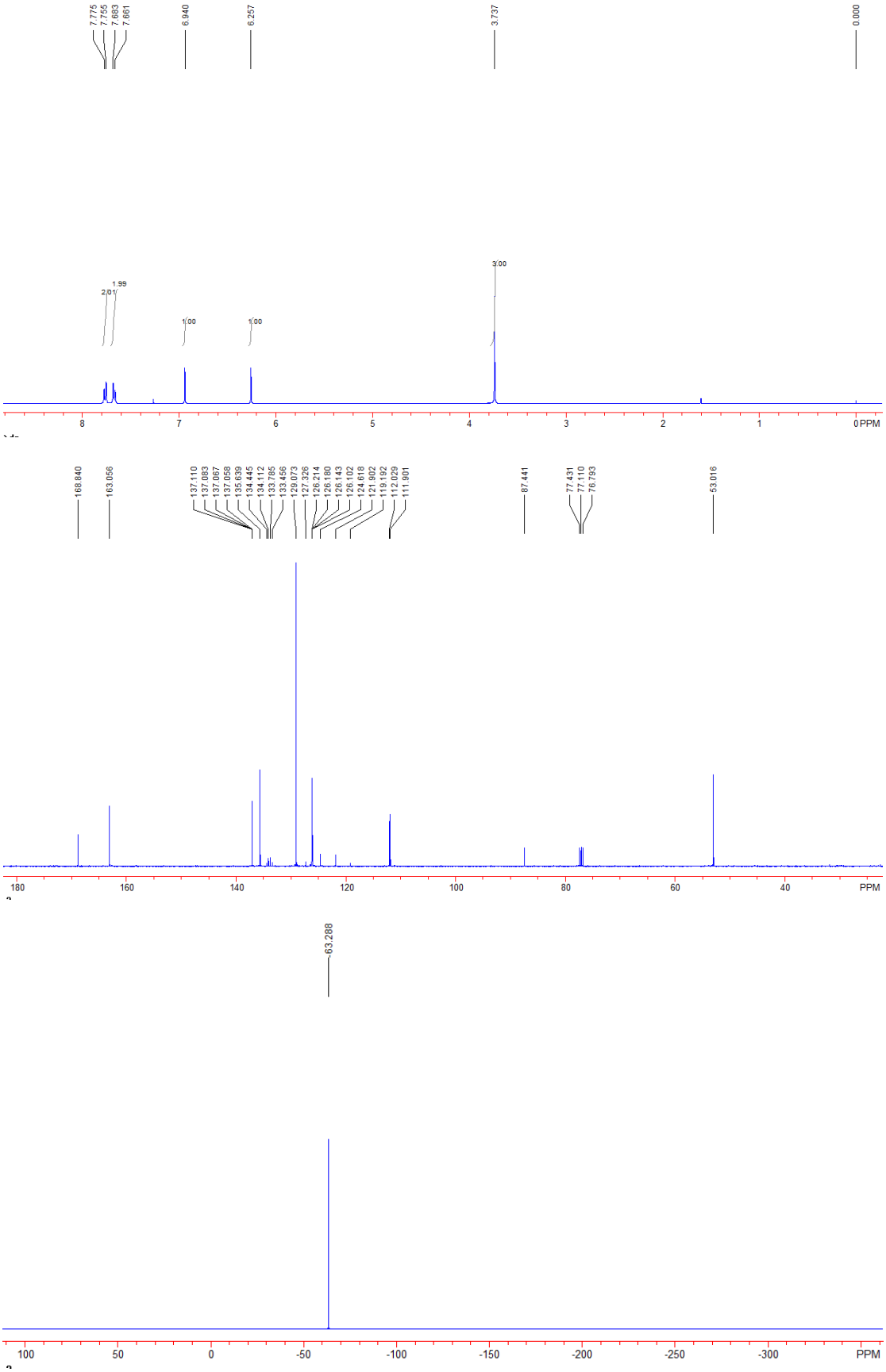


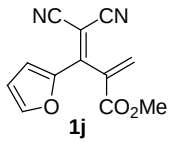


1i

methyl 4,4-dicyano-3-(4-(trifluoromethyl)phenyl)-2-methylenebut-3-enoate (1i). A white solid, 44% yield; m.p. 79-80 ^{o}C; IR (KBr): ν 2957, 2931, 2233, 1731, 1560, 1438, 1410, 1323, 1266, 1167, 1129, 1069, 1017, 981, 842 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.74 (s, 3H, OCH_3), 6.26 (s, 1H, $=CH_2$), 6.94 (s, 1H, $=CH_2$), 7.67 (d, 2H, *J* = 8.4 Hz, ArH), 7.77 (d, 2H, *J* = 8.4 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 53.0, 87.4, 111.9, 112.0, 123.3 (q, *J* = 271.0 Hz), 126.2 (q, *J* = 3.7 Hz), 129.1, 133.9 (q, *J* = 32.9 Hz), 135.6, 137.07 (q, *J* = 0.9 Hz), 137.1, 163.1, 168.8; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -63.29; MS (ESI) *m/z* (%): 339.1 (100) $[M+CH_3OH+H]^+$; HRMS (ESI) Calcd.

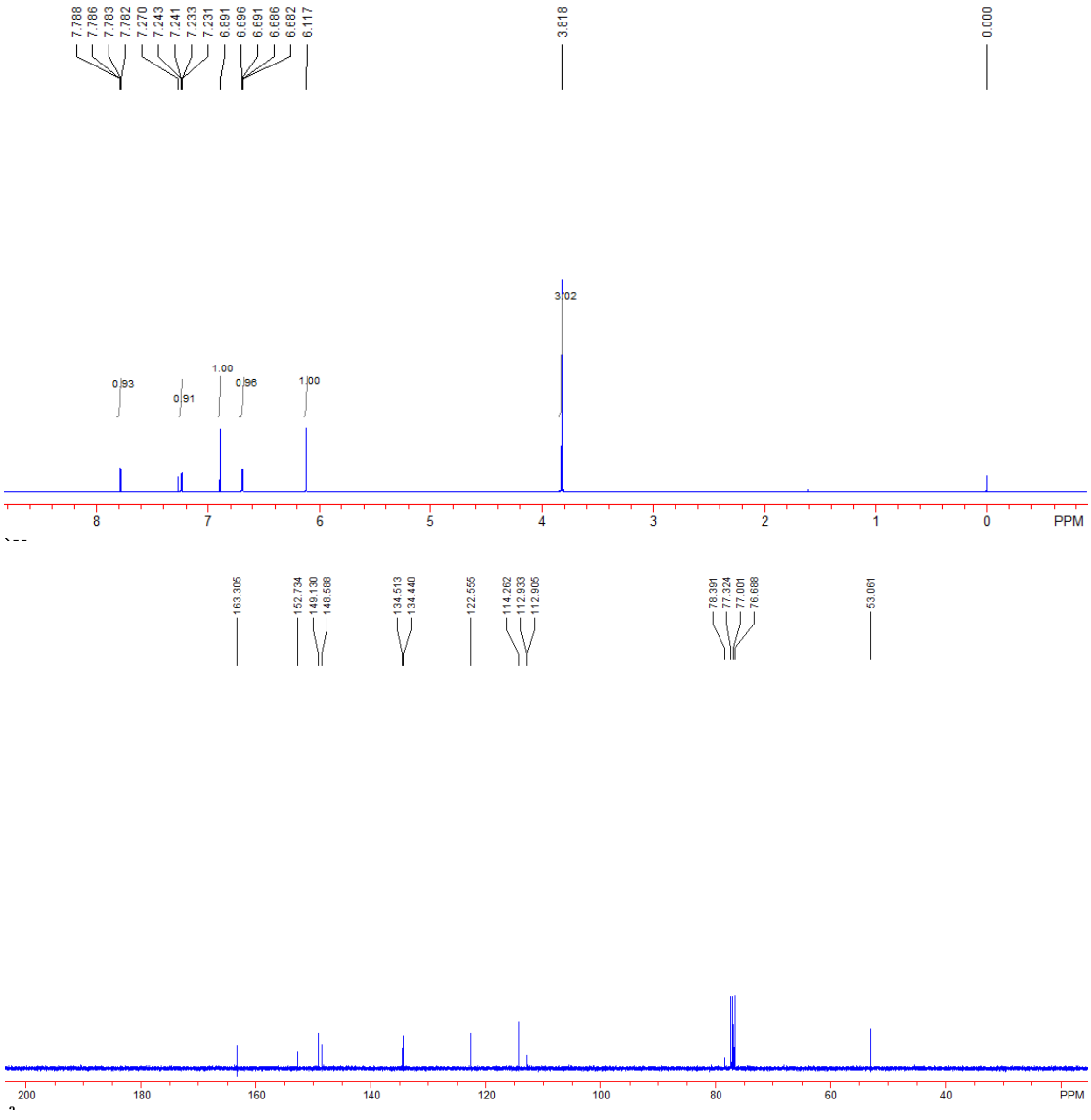
For $C_{16}H_{14}F_3N_2O_3^{+1}$ $(M+CH_3OH+H)^+$ requires 339.0957, Found: 339.0948.

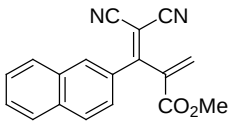




1j

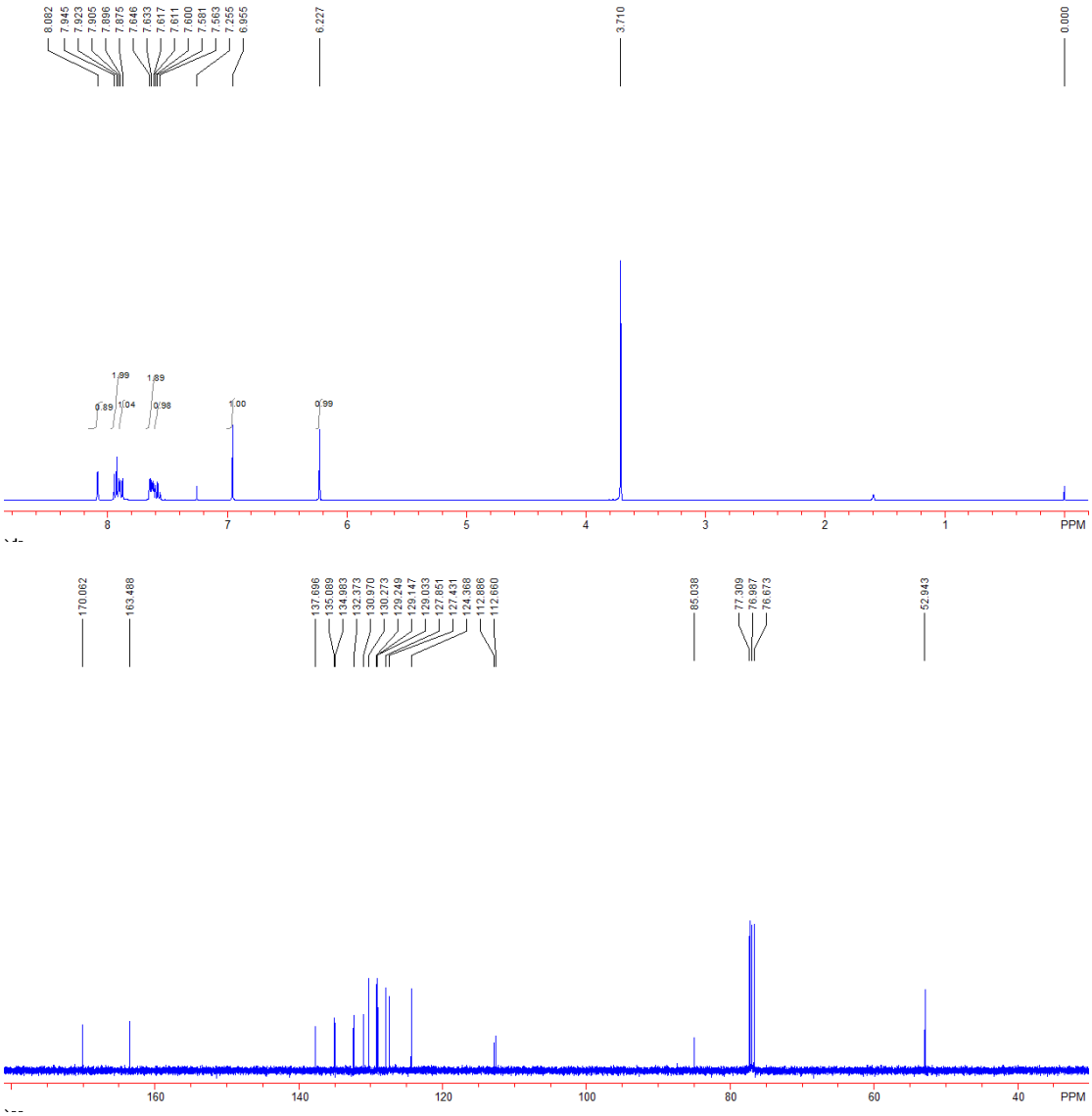
methyl 4,4-dicyano-3-(furan-2-yl)-2-methylenebut-3-enoate (1j). A yellowish solid, 70% yield; m.p. 118-120 ^{o}C; IR (KBr): ν 2955, 2923, 2224, 1725, 1570, 1523, 1454, 1296, 1263, 1203, 1164, 1033, 980, 884, 850, 765, 695 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.82 (s, 3H, OCH_3), 6.12 (s, 1H, $=CH_2$), 6.69 (dd, 1H, *J* = 4.0, 2.0 Hz, ArH), 6.89 (s, 1H, =CH), 7.24 (dd, 1H, *J* = 4.0, 0.8 Hz, ArH), 7.78 (dd, 1H, *J* = 2.0, 0.8 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 53.1, 78.4, 112.91, 112.93, 114.3, 122.6, 134.4, 134.5, 148.6, 149.1, 152.7, 163.3; MS (ESI) *m/z* (%): 246.1 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{12}H_{12}N_3O_3^{+1}$ $(M+NH_4)^+$ requires 246.0879, Found: 246.0877.

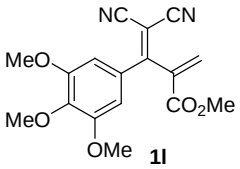




1k

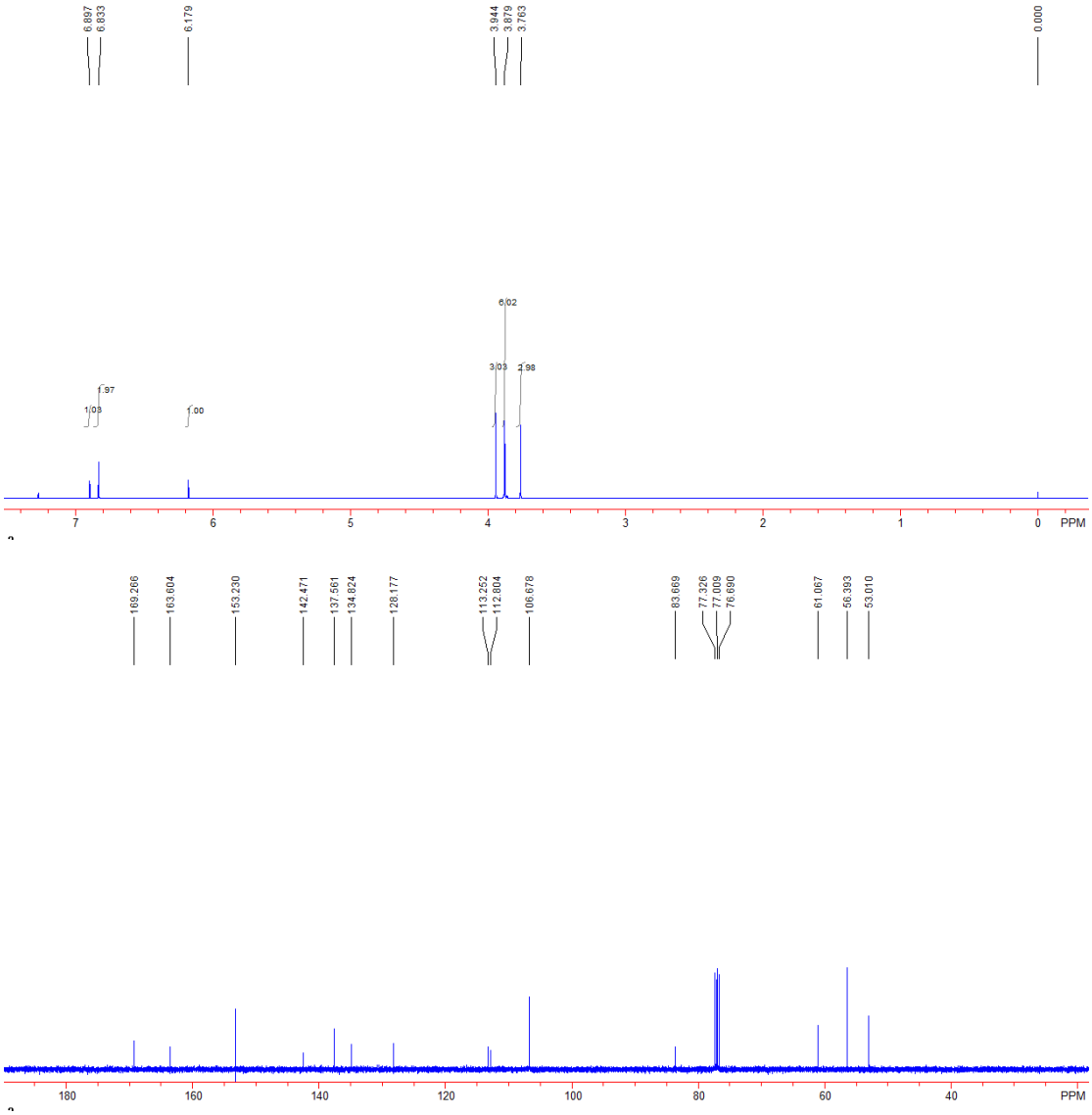
methyl 4,4-dicyano-2-methylene-3-(naphthalen-3-yl)but-3-enoate (1k). A colorless oil, 55% yield; IR (KBr): ν 2955, 2927, 2858, 2228, 1728, 1548, 1436, 1330, 1263, 1236, 1154, 1127, 981, 865, 816, 755, 734 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.71 (s, 3H, OCH_3), 6.23 (s, 1H, $=CH_2$), 6.96 (s, 1H, $=CH_2$), 7.58 (t, 1H, *J* = 7.6 Hz, ArH), 7.61-7.65 (m, 2H, ArH), 7.89 (d, 1H, *J* = 8.4 Hz, ArH), 7.91-7.95 (m, 2H, ArH), 8.08 (s, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 52.9, 85.0, 112.7, 112.9, 124.4, 127.4, 127.9, 129.0, 129.1, 129.2, 130.3, 131.0, 132.4, 135.0, 135.1, 137.7, 163.5, 170.1; MS (ESI) *m/z* (%): 321.1 (100) $[M+CH_3OH+H]^+$; HRMS (ESI) Calcd. For $C_{19}H_{17}N_2O_3^{+1}$ $(M+CH_3OH+H)^+$ requires 321.1239, Found: 321.1232.





1l

methyl 4,4-dicyano-3-(3,4,5-trimethoxyphenyl)-2-methylenebut-3-enoate (1l). A yellowish solid, 43% yield; m.p. 101-102 ^{o}C; IR (KBr): ν 2939, 2842, 2227, 1727, 1581, 1502, 1415, 1343, 1263, 1232, 1124, 995, 843, 820,735, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.76 (s, 3H, OCH_3), 3.88 (s, 6H, $2OCH_3$), 3.94 (s, 3H, OCH_3), 6.18 (s, 1H, $=CH_2$), 6.83 (s, 2H, ArH), 6.90 (s, 1H, $=CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 53.0, 56.4, 61.1, 83.7, 106.7, 112.8, 113.3, 128.2, 134.8, 137.6, 142.5, 153.2, 163.6, 169.3; MS (ESI) *m/z* (%): 361.1 (100) $[M+CH_3OH+H]^+$; HRMS (ESI) Calcd. For $C_{18}H_{21}N_2O_6^{+1}$ $(M+CH_3OH+H)^+$ requires 361.1400, Found: 361.1400.

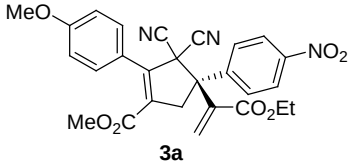


3. Optimization of the Reaction Conditions

Table SI-1: Optimization of the reaction conditions.[a]

4. General Procedure for Phosphine Catalyzed [4+1] Annulation of Dicyano-2-methylenebut-3-enoates with Morita-Baylis-Hilmann Carbonates and Spectroscopic Data of the Products

General procedure: To a solution of Morita-Baylis-Hilmann carbonates (**2**) (0.15 mmol) in toluene (0.5 mL) was added the corresponding dicyano-2-methylenebut-3-enoates (**1**) (0.1 mmol). The reaction mixture was stirred at room temperature. To this resulting reaction mixture a toluene solution (0.5 mL) of **CP9** (0.02 mmol) was slowly added. The reaction mixture was stirred at room temperature until the reaction complete (monitoring by TLC). Then the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography to afford the desired cyclic products **3a-3y**.

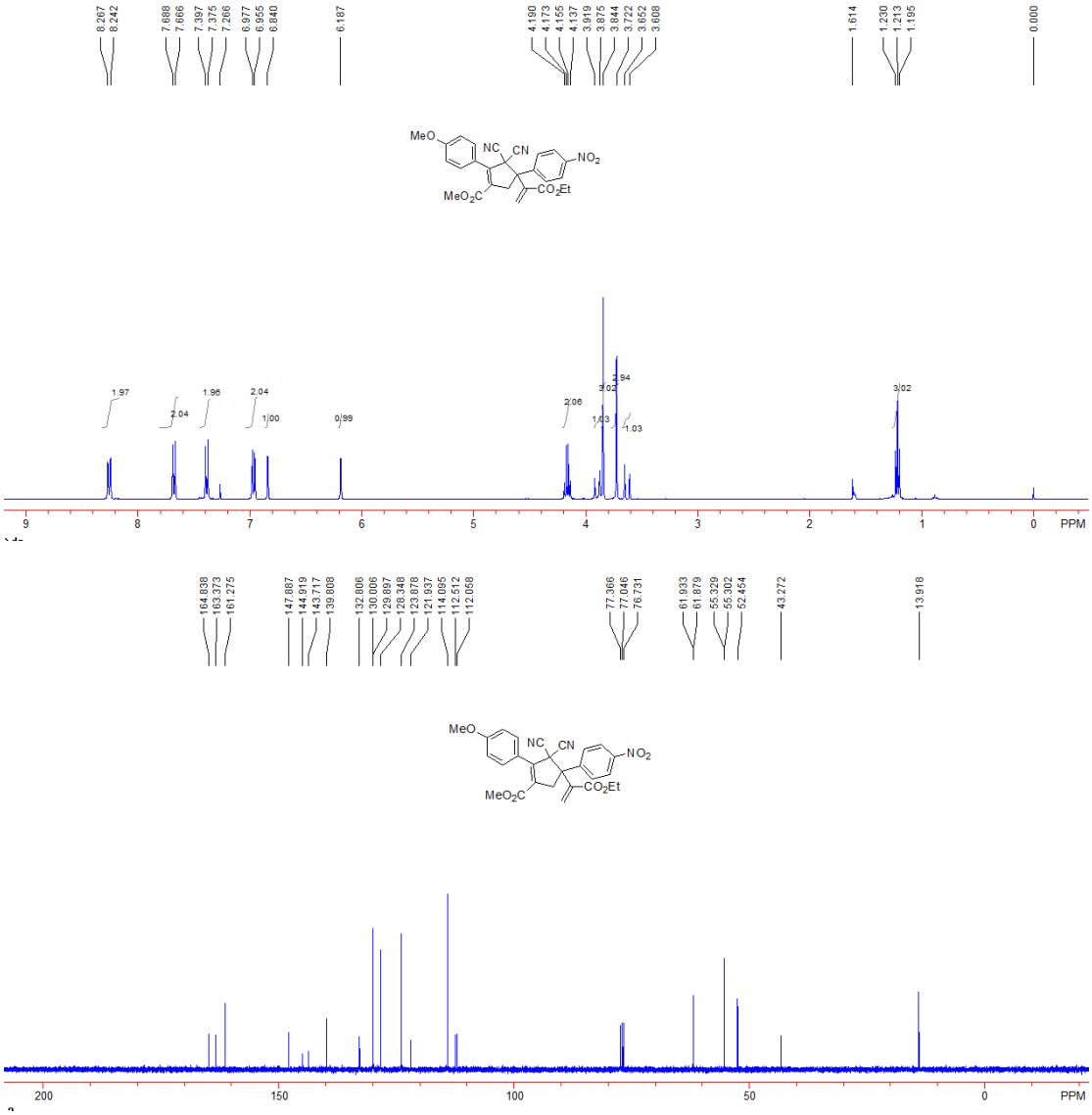


3a

(*R*)-methyl

4-(1-(ethoxycarbonyl)vinyl)-3,3-dicyano-2-(4-methoxyphenyl)-4-(4-nitrophenyl)cyclopent-1-enec

arboxylate (3a). A colorless solid, 42 mg, 84% yield; m. p. 65-66 ^{o}C; IR (KBr): ν 2955, 2841, 1716, 1606, 1522, 1512, 1349, 1256, 1232, 1180, 1133, 1022, 966, 839, 735, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.21 (t, 3H, *J* = 7.2 Hz, CH_3), 3.63 (d, 1H, *J* = 17.6 Hz, CH_2), 3.72 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 3.90 (d, 1H, *J* = 17.6 Hz, CH_2), 4.16 (q, 2H, *J* = 7.2 Hz, CH_2), 6.19 (s, 1H, =CH_2), 6.84 (s, 1H, =CH_2), 6.97 (d, 2H, *J* = 8.8 Hz, ArH), 7.39 (d, 2H, *J* = 8.8 Hz, ArH), 7.68 (d, 2H, *J* = 8.8 Hz, ArH), 8.25 (d, 2H, *J* = 8.8 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 13.9, 43.3, 52.5, 55.30, 55.33, 61.88, 61.93, 112.1, 112.5, 114.1, 121.9, 123.9, 128.3, 129.9, 130.0, 132.8, 139.8, 143.7, 144.9, 147.9, 161.3, 163.4, 164.8; HRMS (ESI) Calcd. For $C_{27}H_{27}N_4O_7^{+1}$ $(M+NH_4)^+$ requires 519.1880, Found: 519.1864.

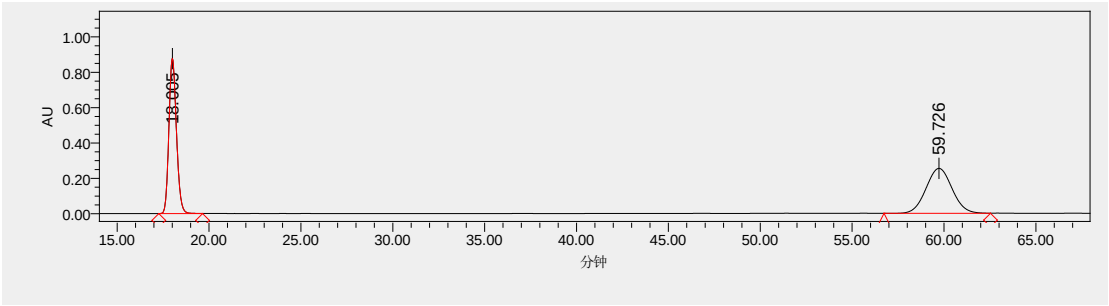


HPLC REPORT

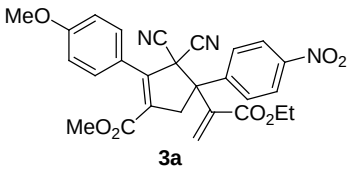
Sample Name: zhxn-9-18 Date: ####

Column: AD-H Mobile Phase: hex/ipr =60/40

Velocity (mL/min): 0.75 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	18.005	24941661	49.86	876782
2	59.726	25083549	50.14	254044



3a

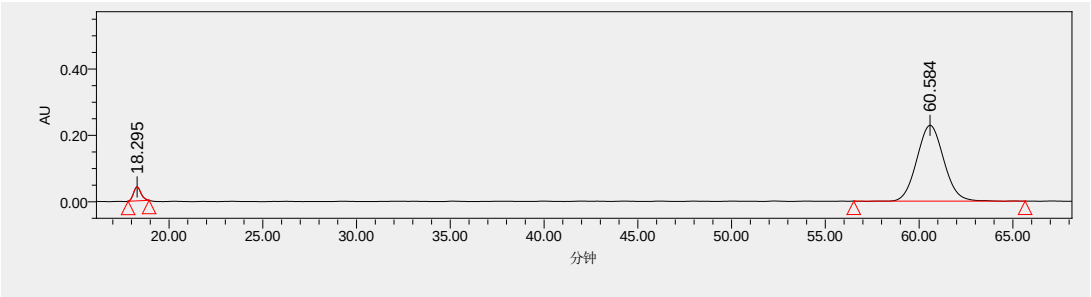
Chiral HPLC report: racemate (**3a)**

HPLC REPORT

Sample Name: zhxn-9-18 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 60/40

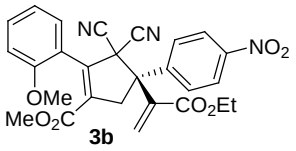
Velocity (mL/min): 0.75 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	18.295	1171626	4.87	42127

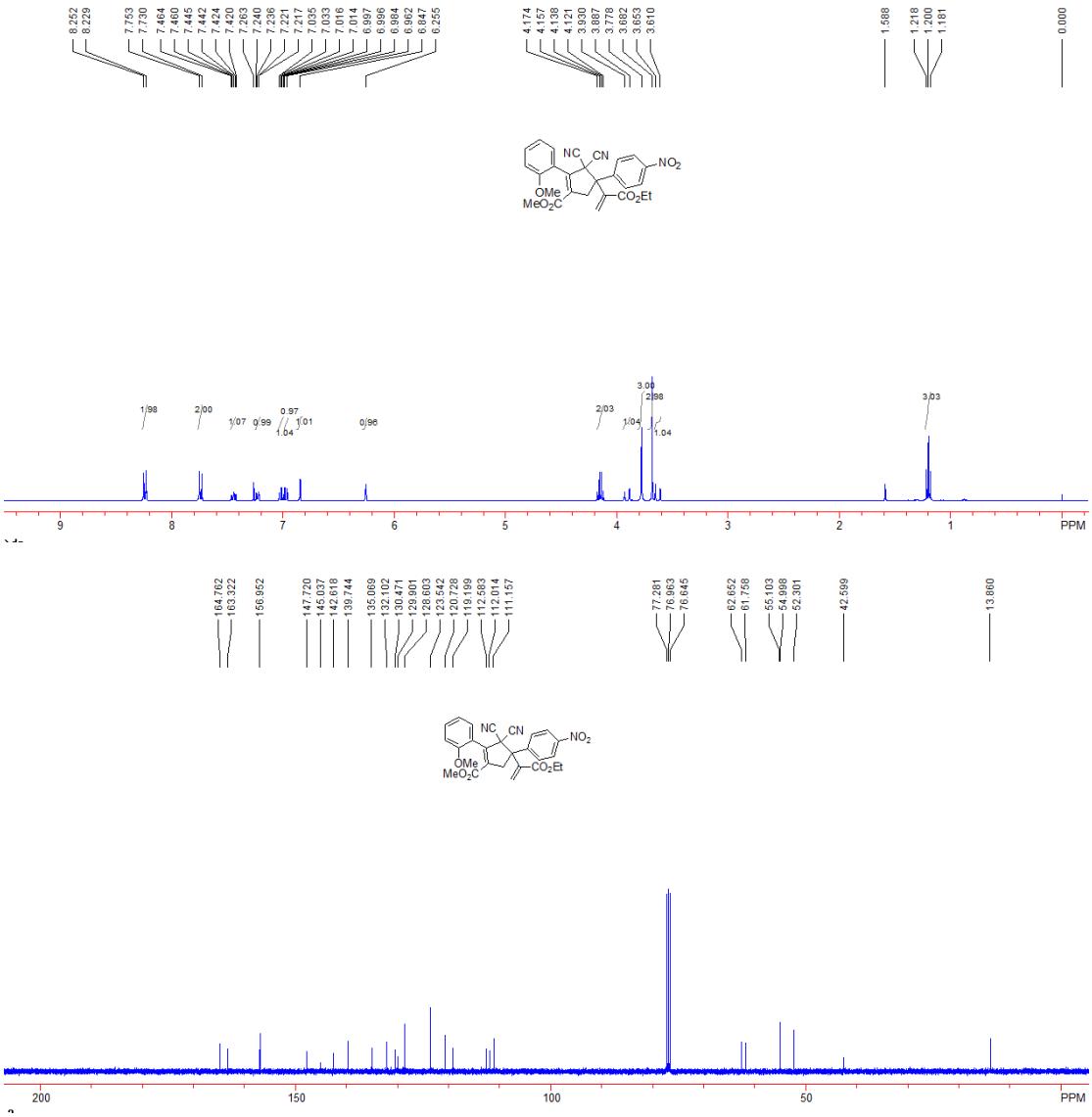
2	60.584	22906978	95.13	228564

Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 214 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.75 mL/min; t_{minor} = 18.30 min, t_{major} = 60.58 min; ee% =90; $[\alpha]^{20}_{D}$ = +52.3 (c1.80, $CHCl_3$).



3b

(*R*)-methyl 4-(1-(ethoxycarbonyl)vinyl)-3,3-dicyano-2-(2-methoxyphenyl)-4-(4-nitrophenyl)cyclopent-1-enec arboxylate (3b). A colorless solid, 40 mg, 80% yield; m. p. 60-61 ^{o}C; IR (KBr): ν 2988, 2954, 1717, 1599, 1522, 1491, 1436, 1350, 1255, 1182, 1022, 967, 855, 755 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.20 (t, 3H, *J* = 7.2 Hz, CH_3), 3.63 (d, 1H, *J* = 17.2 Hz, CH_2), 3.68 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 3.91 (d, 1H, *J* = 17.2 Hz, CH_2), 4.15 (q, 2H, *J* = 7.2 Hz, CH_2), 6.26 (s, 1H, $=CH_2$), 6.85 (s, 1H, $=CH_2$), 6.97 (d, 1H, *J* = 8.8 Hz, ArH), 7.02 (td, 1H, *J* = 7.6, 0.8 Hz, ArH), 7.23 (dd, 1H, *J* = 7.6, 1.6 Hz, ArH), 7.42-7.46 (m, 1H, ArH), 7.74 (d, 2H, *J* = 9.2 Hz, ArH), 8.24 (d, 2H, *J* = 9.2 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 13.9, 42.6, 52.3, 55.0, 55.1, 61.8, 62.7, 111.2, 112.0, 112.6, 119.2, 120.7, 123.5, 128.6, 129.9, 130.5, 132.1, 135.1, 139.7, 142.6, 145.0, 147.7, 157.0, 163.3, 164.8; HRMS (ESI) Calcd. For $C_{27}H_{27}N_4O_7^{+1}$ $(M+NH_4)^+$ requires 519.1880, Found: 519.1866; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.75 mL/min; t_{minor} = 36.25 min, t_{major} = 77.53 min; ee% = 77%; $[\alpha]^{20}_{D}$ = +42.0 (c1.50, $CHCl_3$)].


8.252
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7.730
7.464
7.460
7.445
7.442
7.424
7.420
7.263
7.240
7.236
7.221
7.217
7.035
7.033
7.016
7.014
6.997
6.996
6.984
6.962
6.847
6.255
4.174
4.157
4.138
4.121
3.930
3.887
3.778
3.682
3.653
3.610
1.588
1.218
1.200
1.181
0.000
NC
CN
NO2
OMe
MeO2C
CO2Et
1.98
2.00
1.07
0.99
0.97
1.04
1.01
0.96
2.03
3.00
2.98
1.04
3.03
9
8
7
6
5
4
3
2
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PPM
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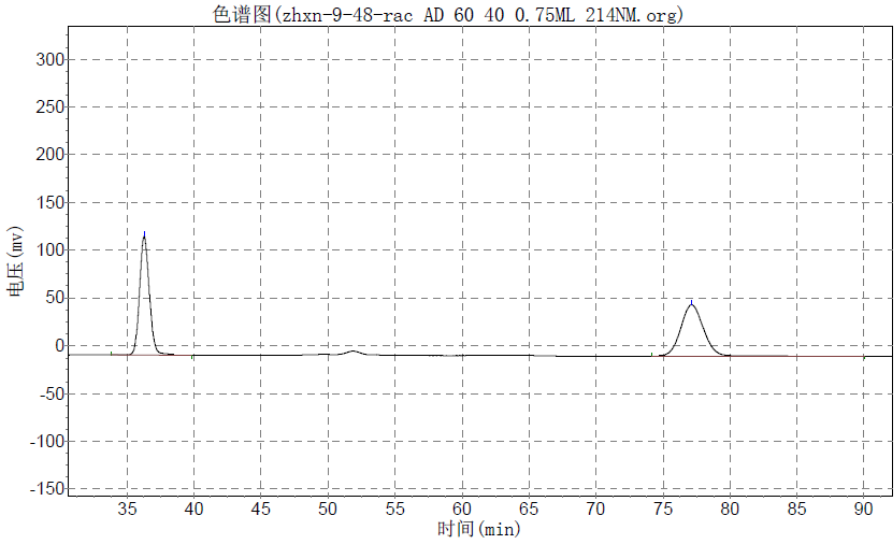
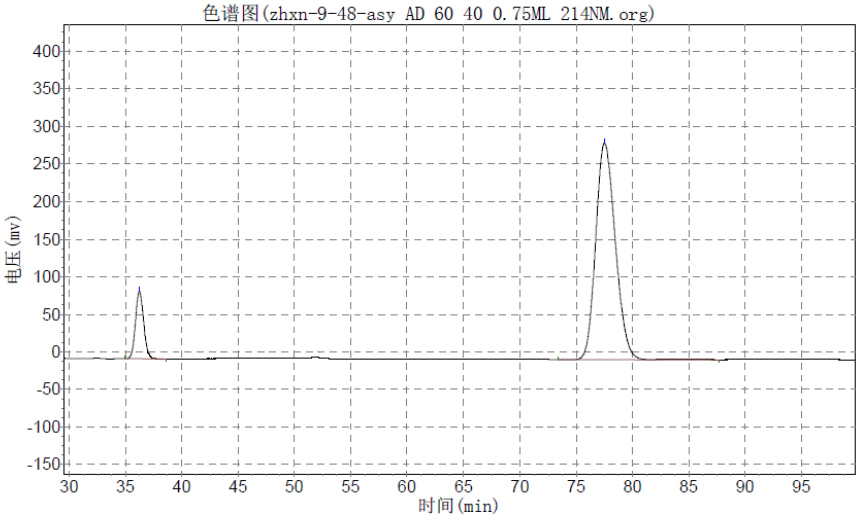
50
PPM



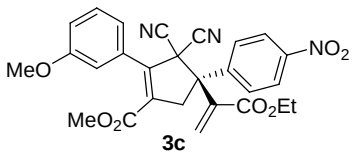
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		36.277	124057.141	6346915.500	50.7324
2		77.135	53258.074	6163667.000	49.2676
总计			177315.215	12510582.500	100.0000



分析结果表

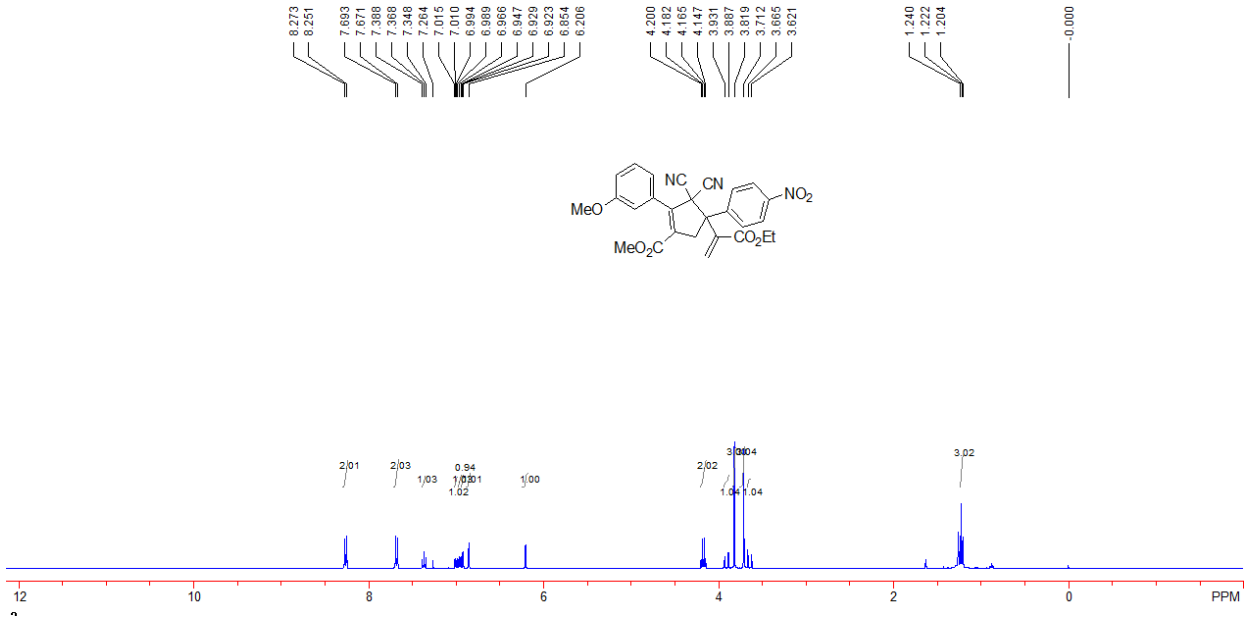
峰号	峰名	保留时间	峰高	峰面积	含量
1		36.253	89750.703	4512836.000	11.4673
2		77.527	288062.063	34841088.000	88.5327
总计			377812.766	39353924.000	100.0000

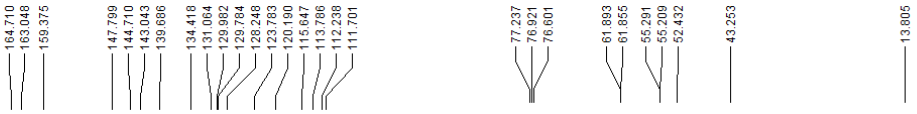


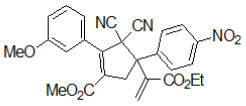
3c

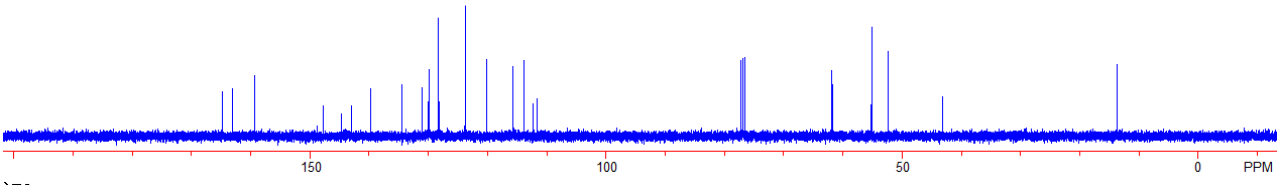
(*R*)-methyl

4-(1-(ethoxycarbonyl)vinyl)-3,3-dicyano-2-(3-methoxyphenyl)-4-(4-nitrophenyl)cyclopent-1-enec arboxylate (3c). A colorless solid, 41 mg, 82% yield; m. p. 71-72 ^{o}C; IR (KBr): ν 2964, 2838, 1717, 1605, 1578, 1523, 1434, 1350, 1289, 1254, 1181, 1027, 856, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.22 (t, 3H, *J* = 7.2 Hz, CH_3), 3.64 (d, 1H, *J* = 17.6 Hz, CH_2), 3.71 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 3.91 (d, 1H, *J* = 17.6 Hz, CH_2), 4.17 (q, 2H, *J* = 7.2 Hz, CH_2), 6.21 (s, 1H, =CH_2), 6.85 (s, 1H, =CH_2), 6.92-6.93 (m, 1H, ArH), 6.96 (d, 1H, *J* = 7.6 Hz, ArH), 7.00 (dd, 1H, *J* = 8.4, 2.0 Hz, ArH), 7.37 (t, 1H, *J* = 8.0 Hz, ArH), 7.68 (d, 2H, *J* = 8.8 Hz, ArH), 8.26 (d, 2H, *J* = 8.8 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 13.8, 43.3, 52.4, 55.2, 55.3, 61.86, 61.89, 111.7, 112.2, 113.8, 115.6, 120.2, 123.8, 128.2, 129.8, 130.0, 131.1, 134.4, 139.7, 143.0, 144.7, 147.8, 159.4, 163.0, 164.7; HRMS (ESI) Calcd. For $C_{27}H_{27}N_4O_7^{+1}$ $(M+NH_4)^+$ requires 519.1880, Found: 519.1865.







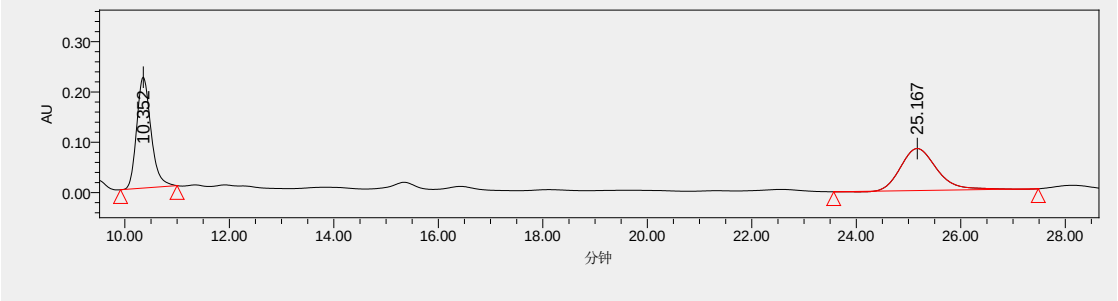


HPLC REPORT

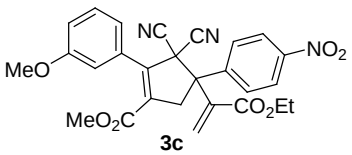
Sample Name: zhxn-9-52 Date: ####

Column: AD-H Mobile Phase: hex/ipr =60/40

Velocity (mL/min): 0.75 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	10.352	4204498	50.88	220492
2	25.167	4058374	49.12	83572



3c

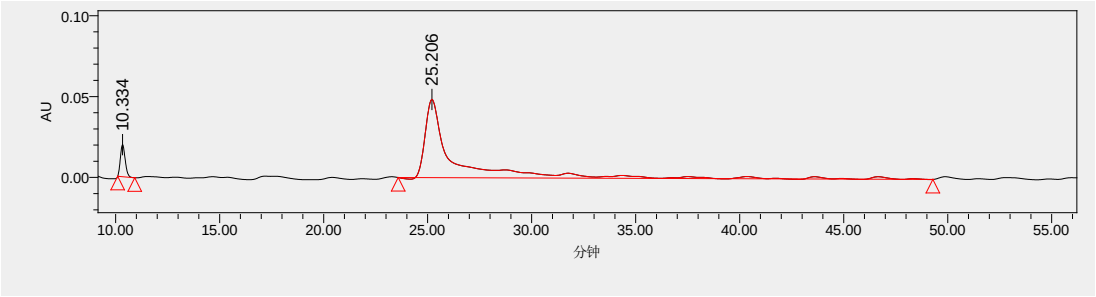
Chiral HPLC report: racemate (**3c**)

HPLC REPORT

Sample Name: zhxn-9-52 Date: ###

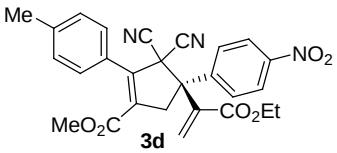
Column: AD-H Mobile Phase: hex/ipr = 60/40

Velocity (mL/min): 0.75 Detection Wavelength (nm): 214



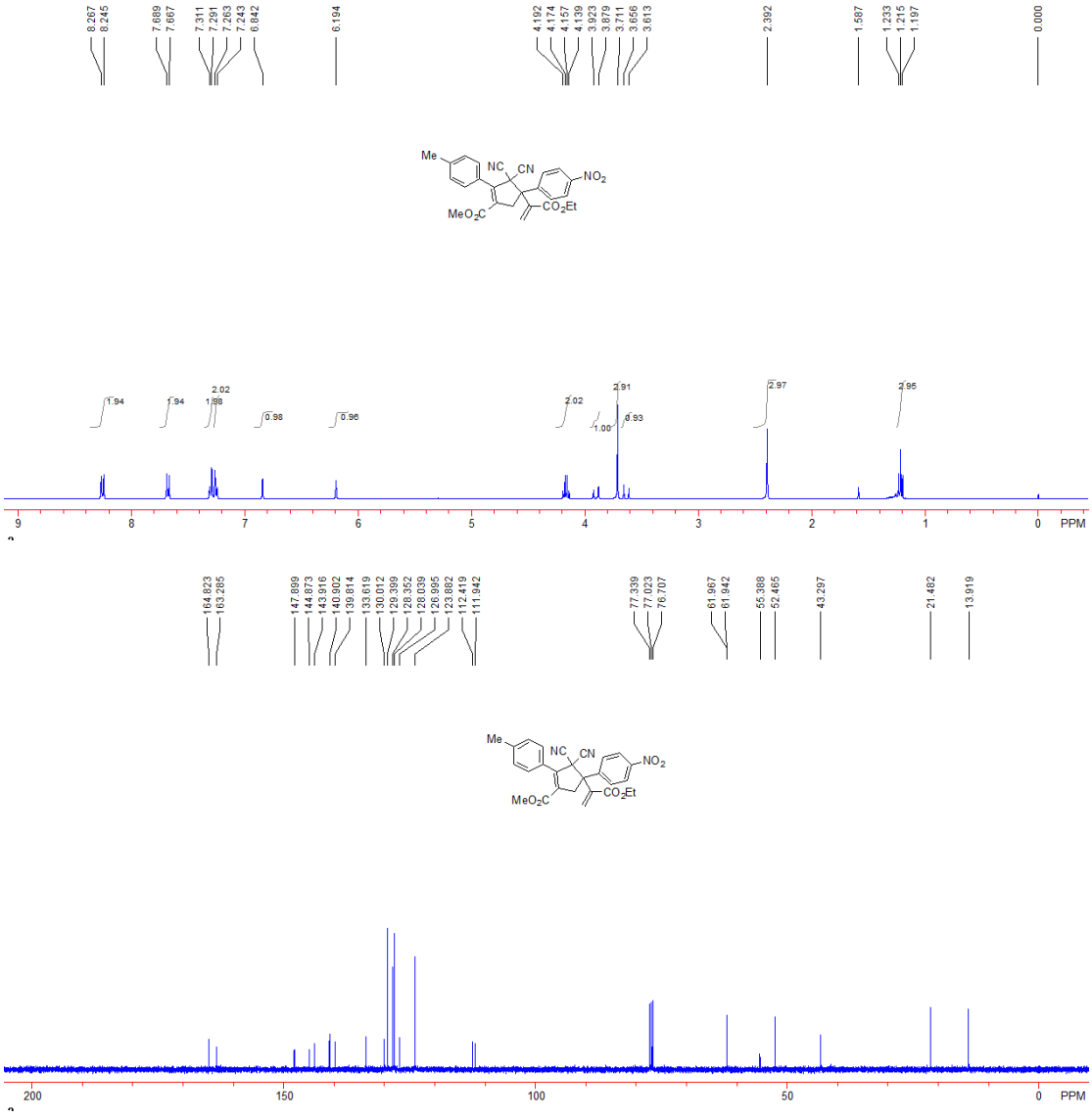
NO	R. Time	Peak Area	Percent	Peak Height
1	10.334	317429	6.32	19838
2	25.206	4704619	93.68	48341

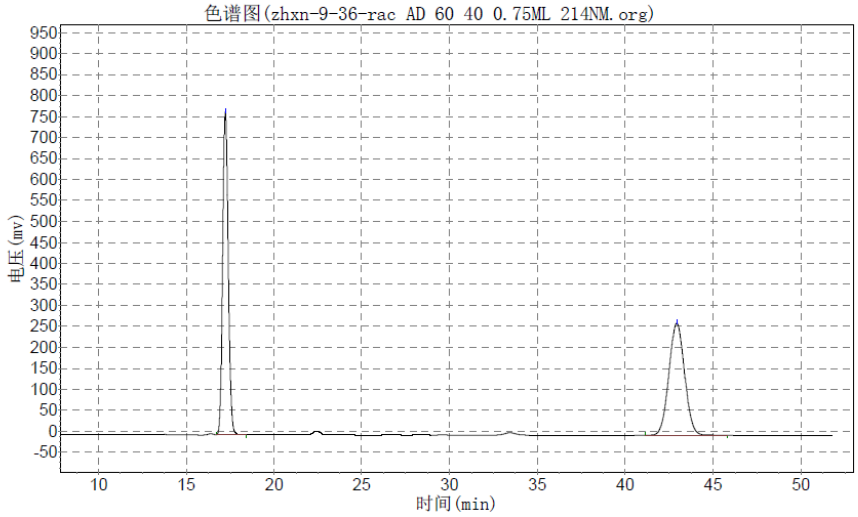
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 214 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.75 mL/min; t_{minor} = 10.33 min, t_{major} = 25.21 min; ee% =87; $[\alpha]^{20}_{D}$ = +78.6 (c2.00, $CHCl_3$)



(*R*)-methyl 4-(1-(ethoxycarbonyl)vinyl)-3,3-dicyano-4-(4-nitrophenyl)-2-p-tolylcyclopent-1-enecarboxylate (3d). A colorless solid, 42 mg, 86% yield; m. p. 79-80 ^{o}C; IR (KBr): ν 2984, 2954, 1717, 1606, 1523, 1436, 1350, 1275, 1231, 1184, 1018, 855, 816, 733, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.22 (t, 3H, *J* = 7.2 Hz, CH_3), 2.39 (s, 3H, CH_3), 3.63 (d, 1H, *J* = 17.6 Hz, CH_2), 3.71 (s, 3H, OCH_3), 3.90 (d, 1H, *J* = 17.6 Hz, CH_2), 4.16 (q, 2H, *J* = 7.2 Hz, CH_2), 6.19 (s, 1H, =CH_2), 6.84 (s, 1H, =CH_2), 7.25 (d, 2H, *J* = 8.0 Hz, ArH), 7.30 (d, 2H, *J* = 8.0 Hz, ArH), 7.68 (d, 2H, *J* = 8.8 Hz, ArH), 8.26 (d, 2H, *J* = 8.8 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 13.9, 21.5, 43.3, 52.5, 55.4, 61.94, 61.97, 111.9, 112.4, 123.9, 127.0, 128.0, 128.4, 129.4, 130.0, 133.6, 139.8, 140.9, 143.9, 144.9, 147.9, 163.3, 164.8; HRMS (ESI) Calcd. For $C_{27}H_{27}N_4O_6^{+1}$ $(M+NH_4)^+$ requires 503.1931, Found: 503.1914;

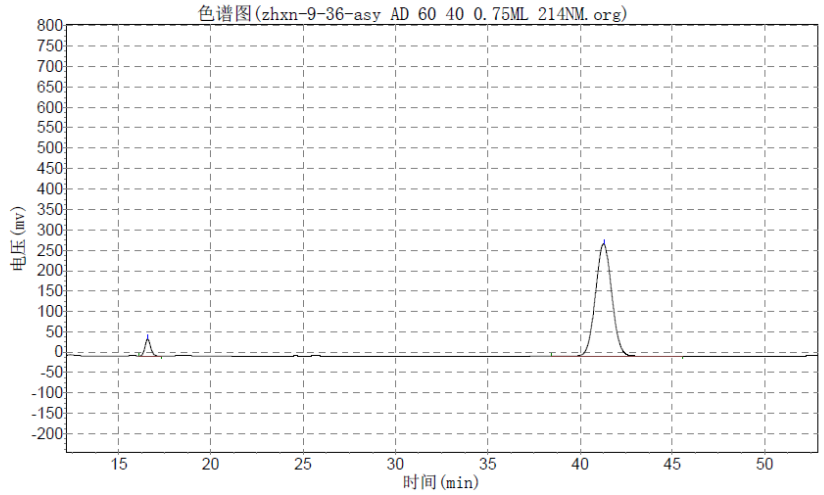
Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.75 mL/min; t_{minor} = 16.58 min, t_{major} = 41.28 min; ee% = 90%; $[\alpha]^{20}_{D}$ = +93.3 (c 2.05, $CHCl_3$)].





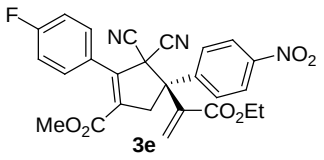
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		17.232	766402.938	16974820.000	50.5328
2		42.965	266586.500	16616860.000	49.4672
总计			1032989.438	33591680.000	100.0000



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		16.575	41102.113	885295.938	4.9947
2		41.275	274780.875	16839342.000	95.0053
总计			315882.988	17724637.938	100.0000

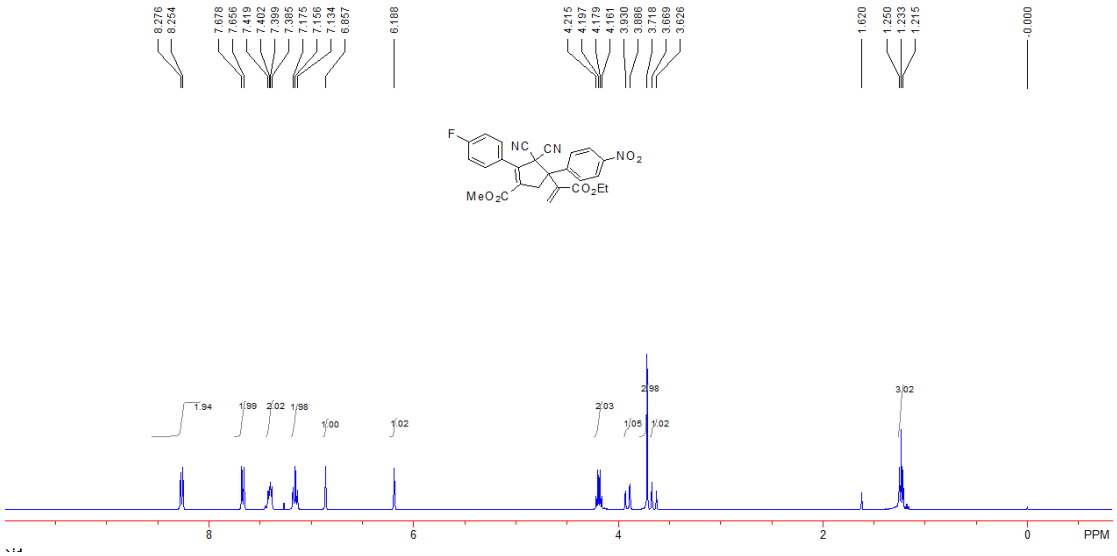


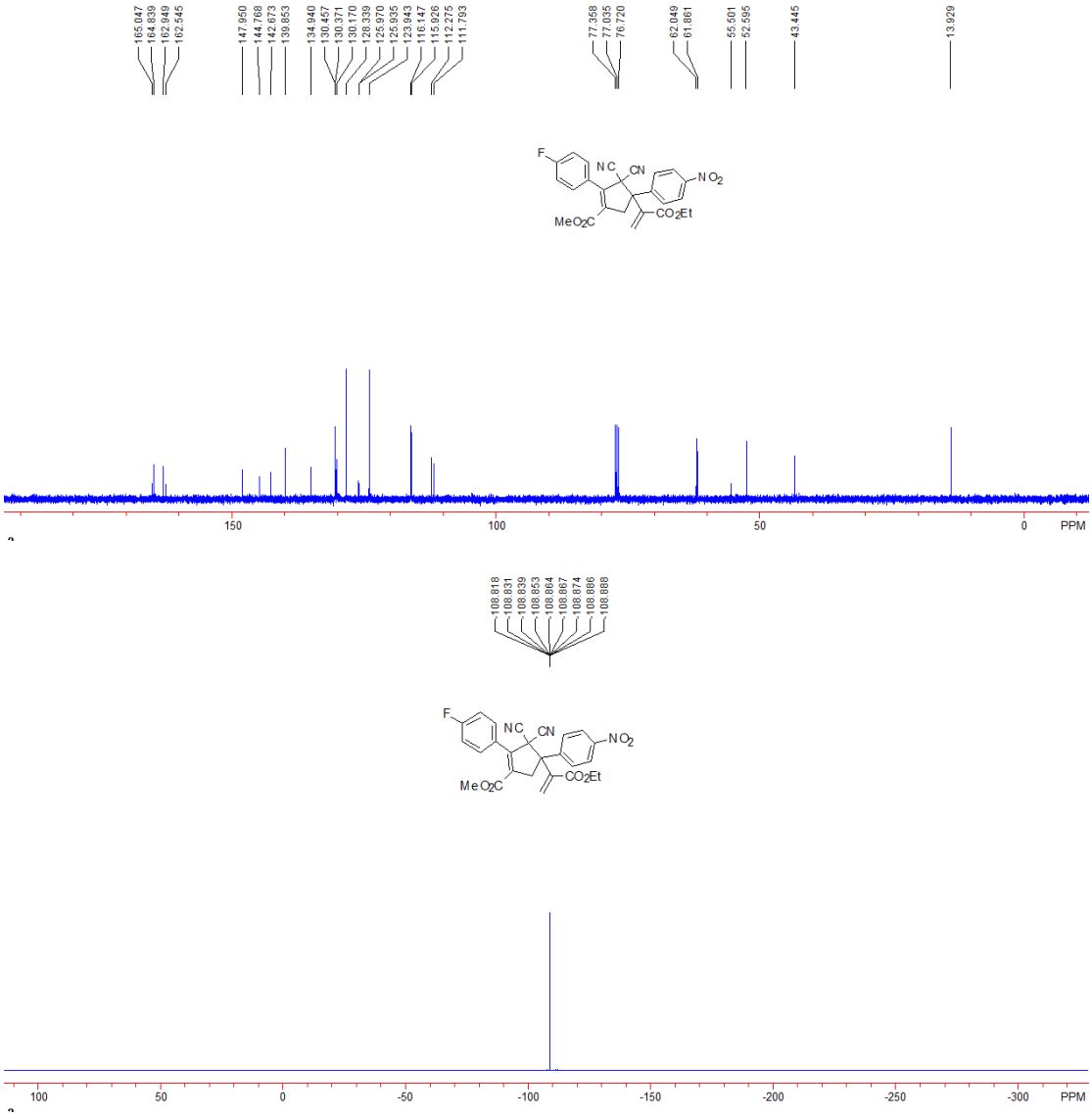
3e

(*R*)-methyl

4-(1-(ethoxycarbonyl)vinyl)-3,3-dicyano-2-(4-fluorophenyl)-4-(4-nitrophenyl)cyclopent-1-enecar

boxylate (3e). A colorless solid, 39 mg, 80% yield; m. p. 86-87 ^{o}C; IR (KBr): ν 2984, 2955, 1715, 1602, 1522, 1508, 1436, 1349, 1269, 1230, 1182, 1162, 1014, 967, 846, 736, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.23 (t, 3H, *J* = 7.2 Hz, CH_3), 3.65 (d, 1H, *J* = 17.6 Hz, CH_2), 3.72 (s, 3H, OCH_3), 3.91 (d, 1H, *J* = 17.6 Hz, CH_2), 4.19 (q, 2H, *J* = 7.2 Hz, CH_2), 6.19 (s, 1H, =CH_2), 6.86 (s, 1H, =CH_2), 7.16 (t, 2H, *J* = 8.8 Hz, ArH), 7.39-7.42 (m, 2H, ArH), 7.67 (d, 2H, *J* = 8.8 Hz, ArH), 8.26 (d, 2H, *J* = 8.8 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 13.9, 43.4, 52.6, 55.5, 61.9, 62.0, 111.8, 112.3, 116.0 (d, *J* = 22.1 Hz), 123.9, 126.0 (d, *J* = 3.5 Hz), 128.3, 130.2, 130.4 (d, *J* = 8.6 Hz), 134.9, 139.9, 142.7, 144.8, 148.0, 162.9, 163.8 (d, *J* = 250.2 Hz), 164.8; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -108.85; HRMS (ESI) Calcd. For $C_{26}H_{24}FN_4O_6^{+1}$ $(M+NH_4)^+$ requires 507.1680, Found: 507.1665; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.75 mL/min; t_{minor} = 15.95 min, t_{major} = 32.68 min; ee% = 89%; $[\alpha]^{20}_D$ = +53.8 (c 2.00, $CHCl_3$)].

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162.545
147.950
144.768
142.673
139.853
134.940
130.457
130.371
130.170
128.339
125.970
125.935
123.943
116.147
115.926
112.275
111.793
77.358
77.035
76.720
62.049
61.861
55.501
52.595
43.445
13.929
F
NC
CN
NO2
MeO2C
CO2Et
150
100
50
0
PPM
108.818
108.831
108.839
108.853
108.864
108.867
108.874
108.886
108.888
F
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CN
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MeO2C
CO2Et
100
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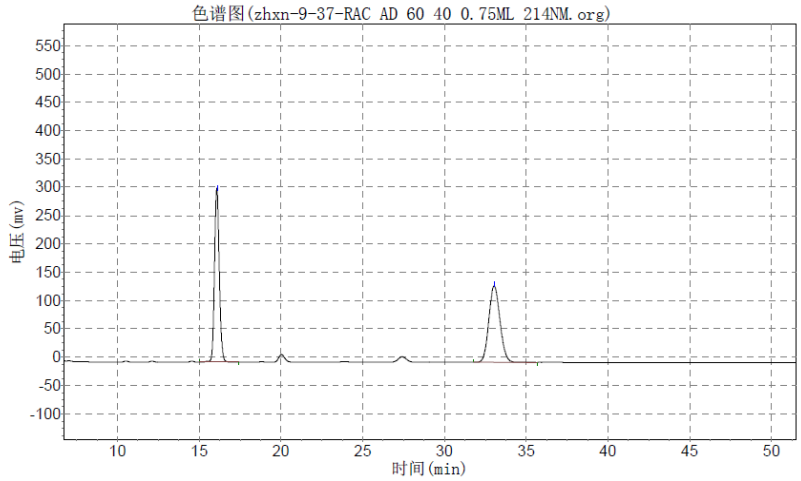
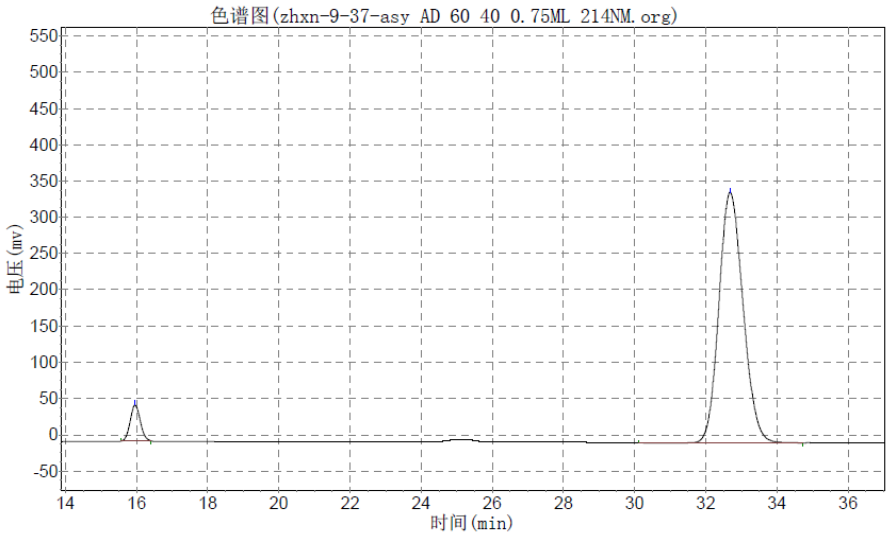
0
-50
-100
-150
-200
-250
-300
PPM



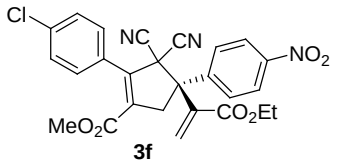
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		16.090	306727.969	6388364.500	50.0203
2		33.057	134353.953	6383180.000	49.9797
总计			441081.922	12771544.500	100.0000



分析结果表

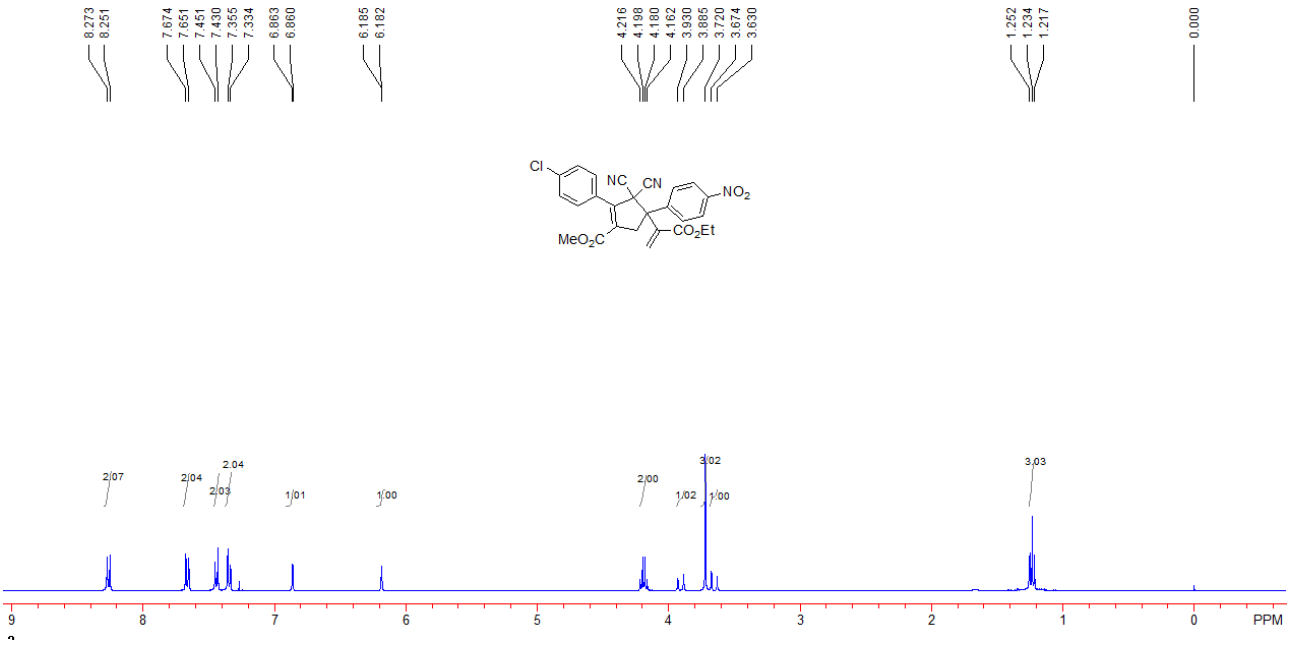
峰号	峰名	保留时间	峰高	峰面积	含量
1		15.952	49004.320	970516.813	5.6140
2		32.680	345491.094	16317036.000	94.3860
总计			394495.414	17287552.813	100.0000

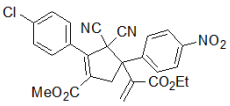


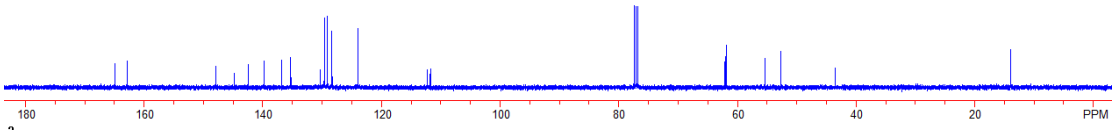
3f

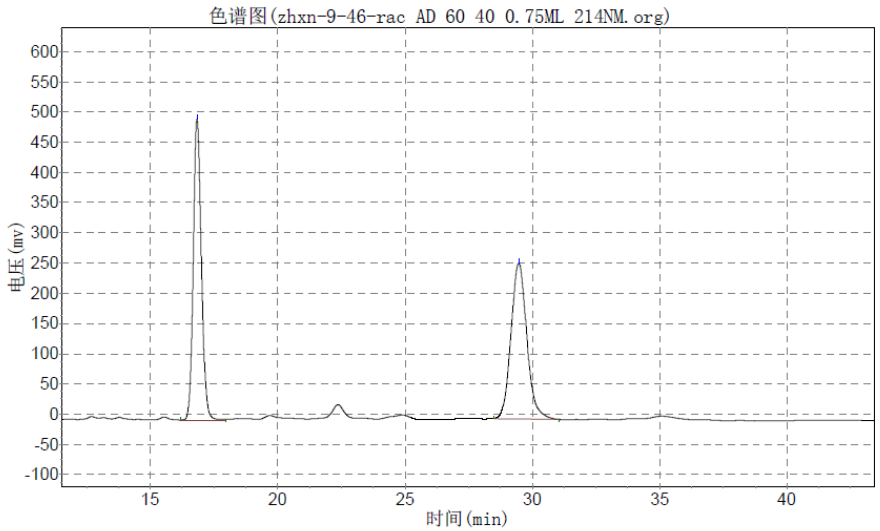
(*R*)-methyl

4-(1-(ethoxycarbonyl)vinyl)-2-(4-chlorophenyl)-3,3-dicyano-4-(4-nitrophenyl)cyclopent-1-enecarboxylate (3f). A colorless solid, 40 mg, 79% yield; m. p. 52-53 ^{o}C; IR (KBr): ν 2955, 2928, 1716, 1594, 1522, 1492, 1348, 1269, 1233, 1183, 1093, 1014, 854, 840, 736, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.23 (t, 3H, *J* = 7.2 Hz, CH_3), 3.65 (d, 1H, *J* = 17.6 Hz, CH_2), 3.72 (s, 3H, OCH_3), 3.91 (d, 1H, *J* = 17.6 Hz, CH_2), 4.19 (q, 2H, *J* = 7.2 Hz, CH_2), 6.18 (d, 1H, *J* = 1.2 Hz, $=CH_2$), 6.86 (d, 1H, *J* = 1.2 Hz, $=CH_2$), 7.34 (d, 2H, *J* = 8.4 Hz, ArH), 7.44 (d, 2H, *J* = 8.4 Hz, ArH), 7.66 (d, 2H, *J* = 8.8 Hz, ArH), 8.26 (d, 2H, *J* = 8.8 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 13.9, 43.5, 52.7, 55.4, 61.9, 62.1, 111.8, 112.2, 124.0, 128.3, 128.4, 129.1, 129.6, 130.3, 135.3, 136.8, 139.8, 142.5, 144.8, 147.9, 162.9, 164.9; HRMS (ESI) Calcd. For $C_{26}H_{24}ClN_4O_6^{+1}$ $(M+NH_4)^+$ requires 523.1384, Found: 523.1379; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.75 mL/min; t_{minor} = 17.06 min, t_{major} = 29.96 min; ee% = 90%; $[\alpha]^{20}_{D}$ = +72.0 (c 1.80, $CHCl_3$)].



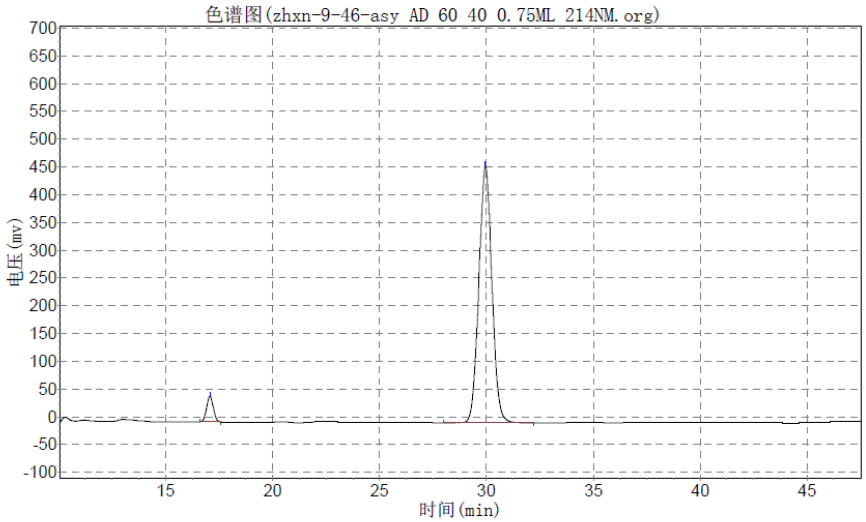






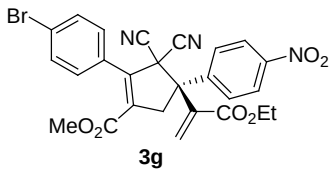
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		16.833	497984.219	11041899.000	49.8284
2		29.473	257217.500	11117968.000	50.1716
总计			755201.719	22159867.000	100.0000



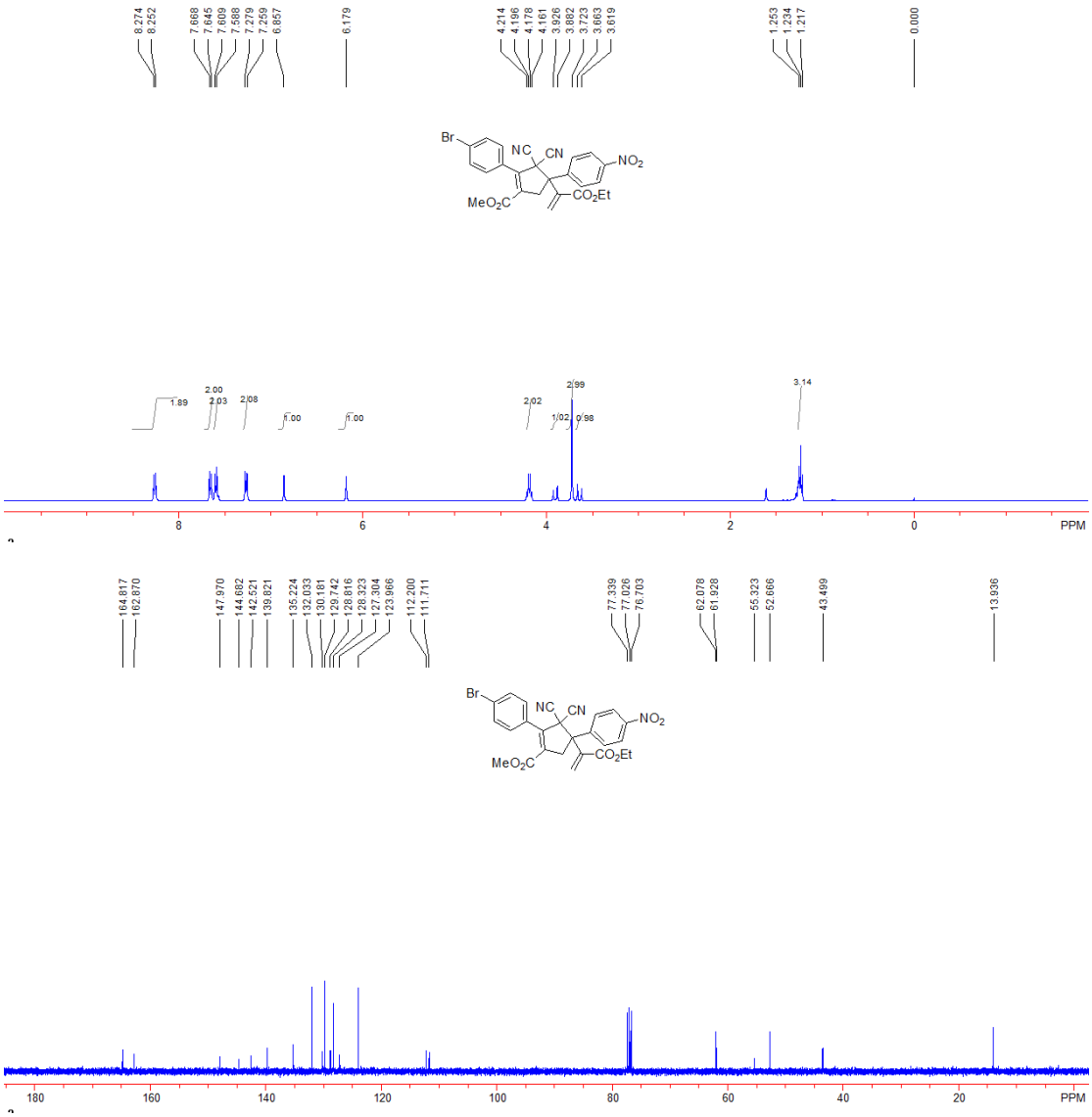
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		17.063	46008.609	1003573.813	4.8312
2		29.955	462456.219	19769072.000	95.1688
总计			508464.828	20772645.813	100.0000



3g

(*R*)-methyl 4-(1-(ethoxycarbonyl)vinyl)-2-(4-bromophenyl)-3,3-dicyano-4-(4-nitrophenyl)cyclopent-1-enecarboxylate (3g). A colorless solid, 38 mg, 70% yield; m. p. 67-68 ^{o}C; IR (KBr): ν 2988, 2960, 1715, 1522, 1488, 1349, 1269, 1234, 1183, 1073, 1010, 854 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.23 (t, 3H, *J* = 7.2 Hz, CH_3), 3.64 (d, 1H, *J* = 17.6 Hz, CH_2), 3.72 (s, 3H, OCH_3), 3.90 (d, 1H, *J* = 17.6 Hz, CH_2), 4.19 (q, 2H, *J* = 7.2 Hz, CH_2), 6.18 (s, 1H, =CH_2), 6.86 (s, 1H, =CH_2), 7.27 (d, 2H, *J* = 8.4 Hz, ArH), 7.60 (d, 2H, *J* = 8.4 Hz, ArH), 7.66 (d, 2H, *J* = 8.8 Hz, ArH), 8.26 (d, 2H, *J* = 8.8 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 13.9, 43.5, 52.7, 55.3, 61.9, 62.1, 111.7, 112.2, 124.0, 127.3, 128.3, 128.8, 129.7, 130.2, 132.0, 135.2, 139.8, 142.5, 144.7, 148.0, 162.9, 164.8; HRMS (ESI) Calcd. For $C_{26}H_{24}BrN_4O_6^{+1}$ $(M+NH_4)^+$ requires 567.0879, Found: 567.0871; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.75 mL/min; t_{minor} = 18.05 min, t_{major} = 30.83 min; ee% = 90%; $[\alpha]^{20}_{D}$ = +60.3 (c 1.60, $CHCl_3$)].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7.588
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7.259
6.857
6.179
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4.178
4.161
3.926
3.882
3.723
3.663
3.619
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1.234
1.217
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NC
CN
NO2
MeO2C
CO2Et
1.89
2.00
2.03
2.08
1.00
1.00
2.02
2.99
1.02
0.98
3.14
8
6
4
2
0
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139.821
135.224
132.033
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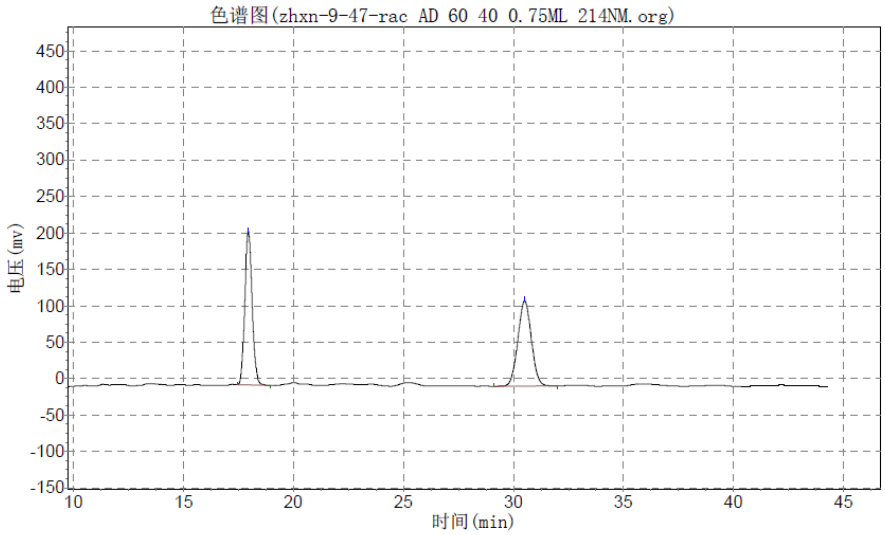
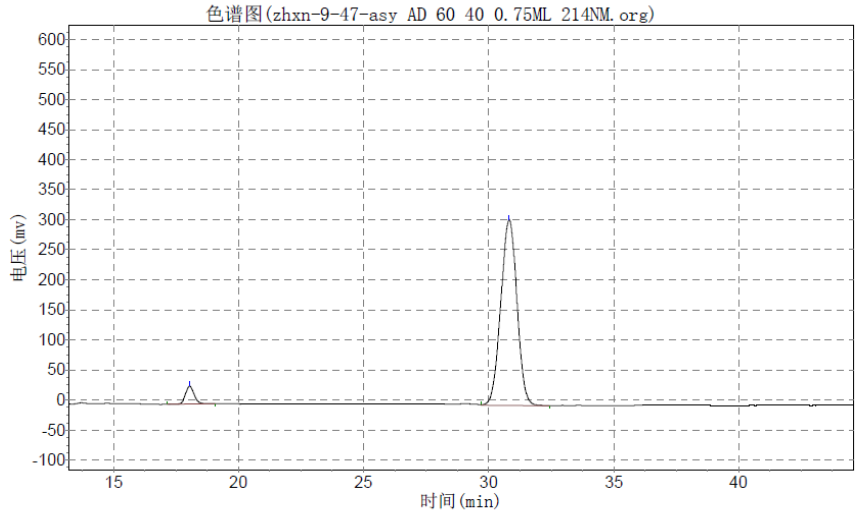


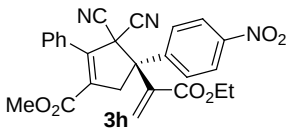
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		17.965	213043.938	5115417.500	50.0006
2		30.532	117109.836	5115304.500	49.9994
总计			330153.773	10230722.000	100.0000



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		18.047	30025.318	732183.250	4.9961
2		30.825	309135.625	13922871.000	95.0039
总计			339160.943	14655054.250	100.0000

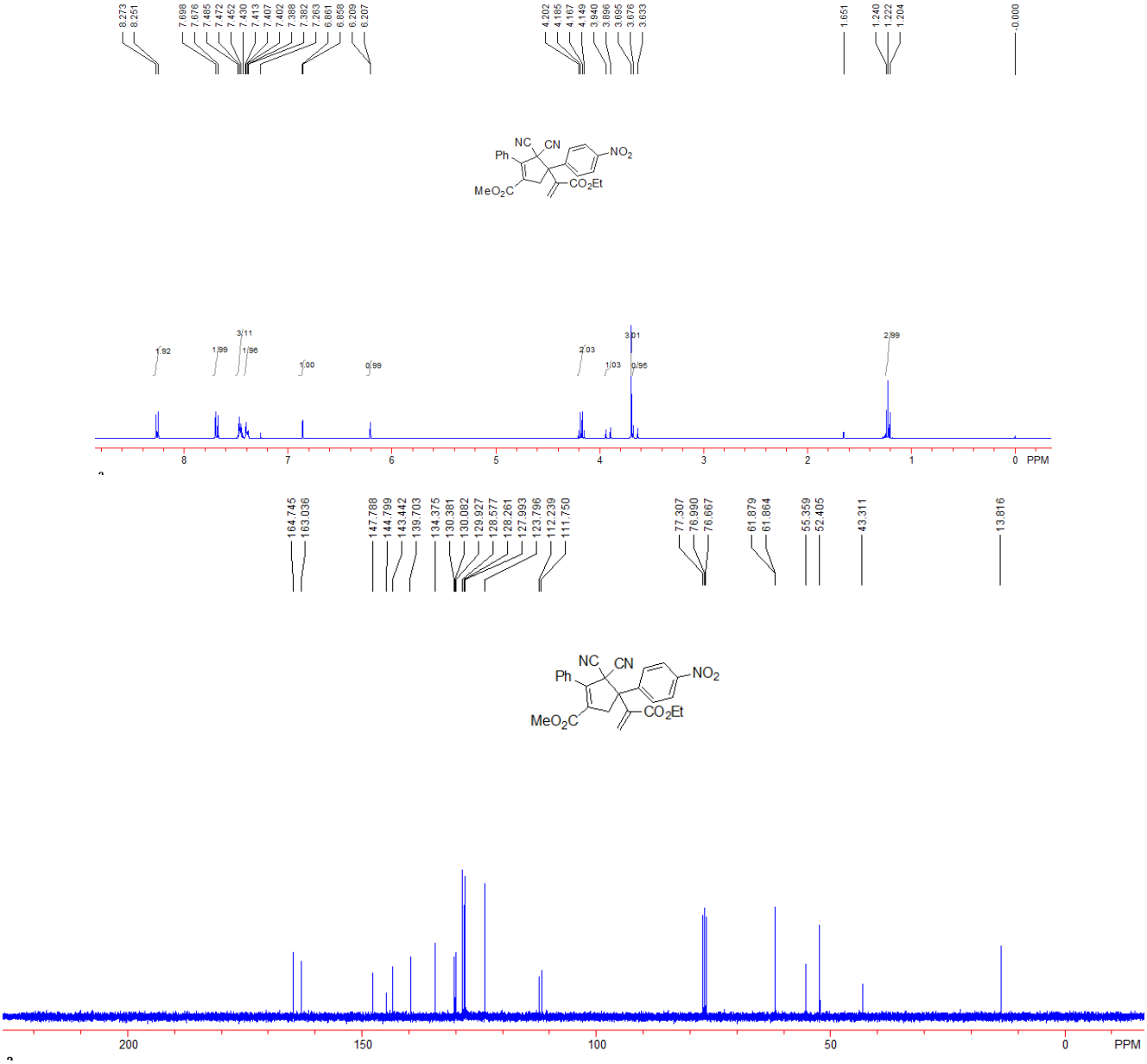


3h

(R)-methyl

4-(1-(ethoxycarbonyl)vinyl)-3,3-dicyano-4-(4-nitrophenyl)-2-phenylcyclopent-1-enecarboxylate

(3h). A colorless solid, 40 mg, 85% yield; m. p. 70-71 ^{o}C; IR (KBr): ν 2982, 2954, 1713, 1605, 1520, 1436, 1347, 1267, 1229, 1180, 1014, 853, 819, 734, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.22 (t, 3H, *J* = 7.2 Hz, CH_3), 3.65 (d, 1H, *J* = 17.2 Hz, CH_2), 3.70 (s, 3H, OCH_3), 3.92 (d, 1H, *J* = 17.2 Hz, CH_2), 4.18 (q, 2H, *J* = 7.2 Hz, CH_2), 6.21 (d, 1H, *J* = 0.8 Hz, $=CH_2$), 6.86 (d, 1H, *J* = 0.8 Hz, $=CH_2$), 7.38-7.43 (m, 2H, ArH), 7.47-7.49 (m, 3H, ArH), 7.69 (d, 2H, *J* = 8.8 Hz, ArH), 8.26 (d, 2H, *J* = 8.8 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 13.8, 43.3, 52.4, 55.4, 61.86, 61.88, 111.8, 112.2, 123.8, 128.0, 128.3, 128.6, 129.9, 130.1, 130.4, 134.4, 139.7, 143.4, 144.8, 147.8, 163.0, 164.7; HRMS (ESI) Calcd. For $C_{26}H_{25}N_4O_6^{+1}$ $(M+NH_4)^+$ requires 489.1774, Found: 489.1754.

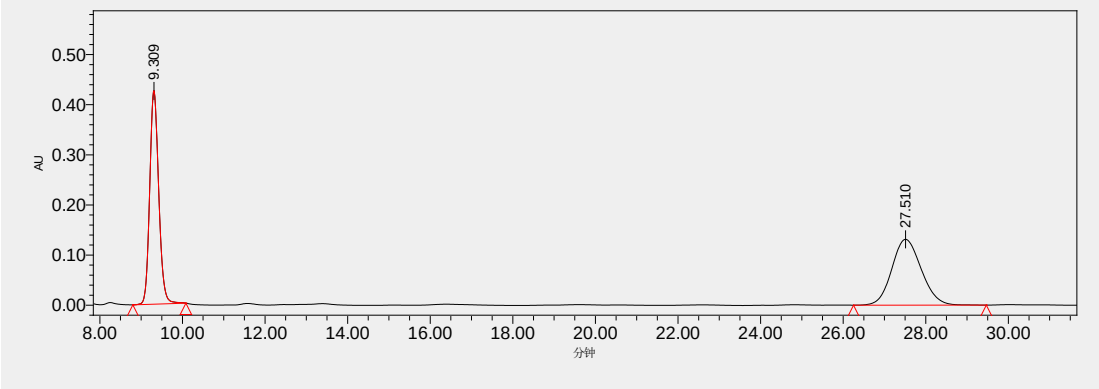


HPLC REPORT

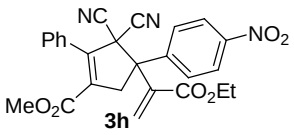
Sample Name: zhxn-9-53 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 60/40

Velocity (mL/min): 0.75 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	9.309	6445536	49.74	426683
2	27.510	6513566	50.26	131286



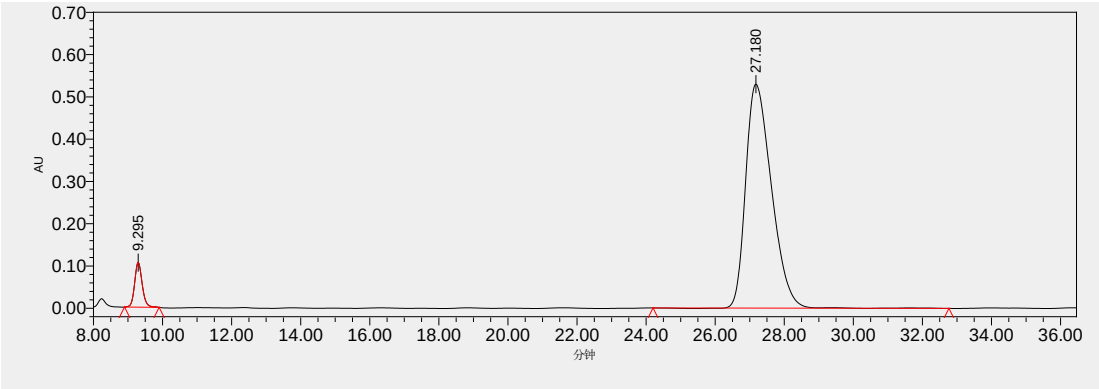
Chiral HPLC report: racemate (**3h**)

HPLC REPORT

Sample Name: zhxn-9-53 Date: ####

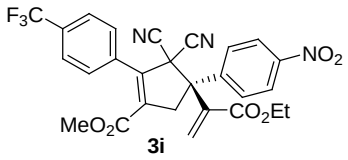
Column: AD-H Mobile Phase: hex/ipr = 60/40

Velocity (mL/min): 0.75 Detection Wavelength (nm): 214



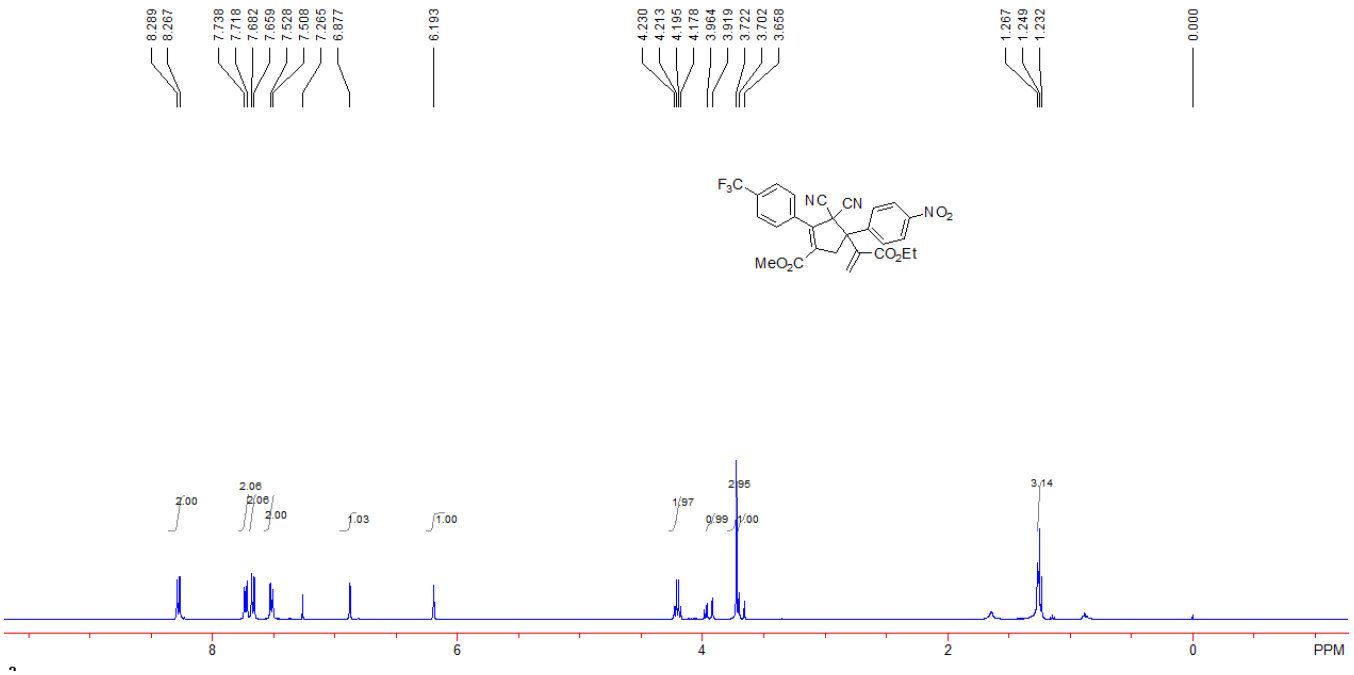
NO	R. Time	Peak Area	Percent	Peak Height
1	9.295	1607645	5.50	105704
2	27.180	27612930	94.50	529803

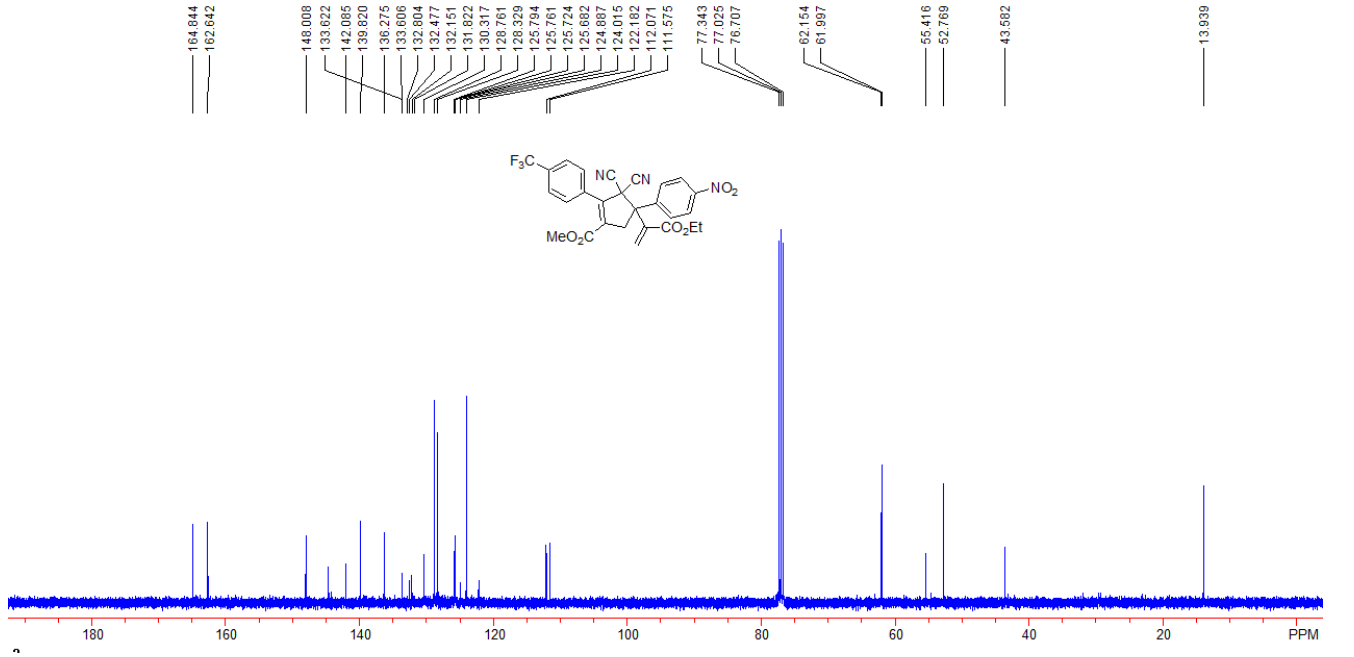
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 214 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.75 mL/min; t_{minor} = 9.30 min, t_{major} = 27.18 min; ee% = 89%; $[\alpha]^{20}_{D}$ = +54.6 (c 1.90, $CHCl_3$).

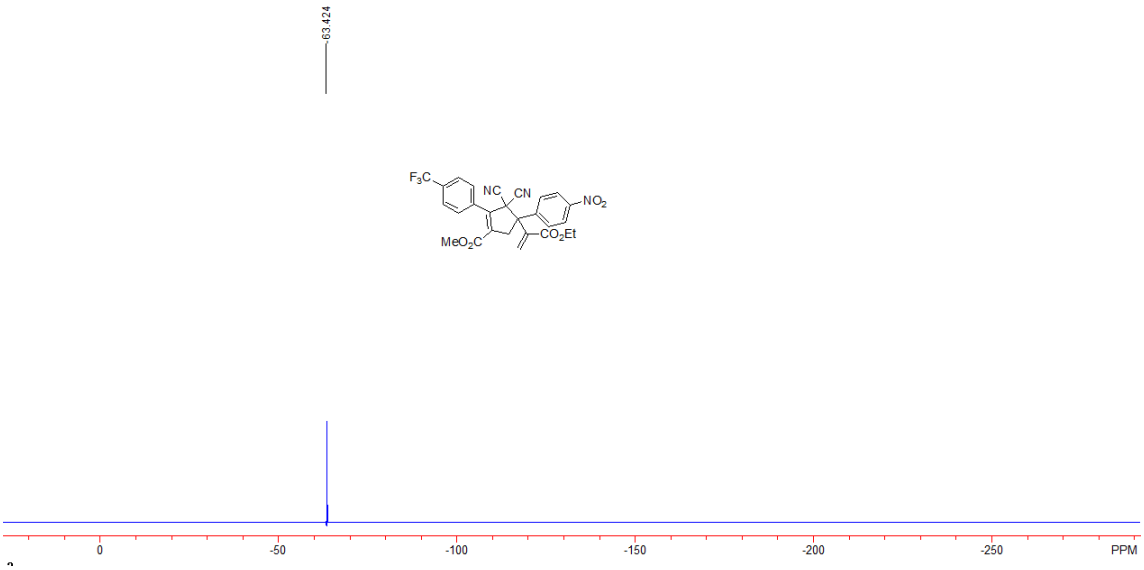


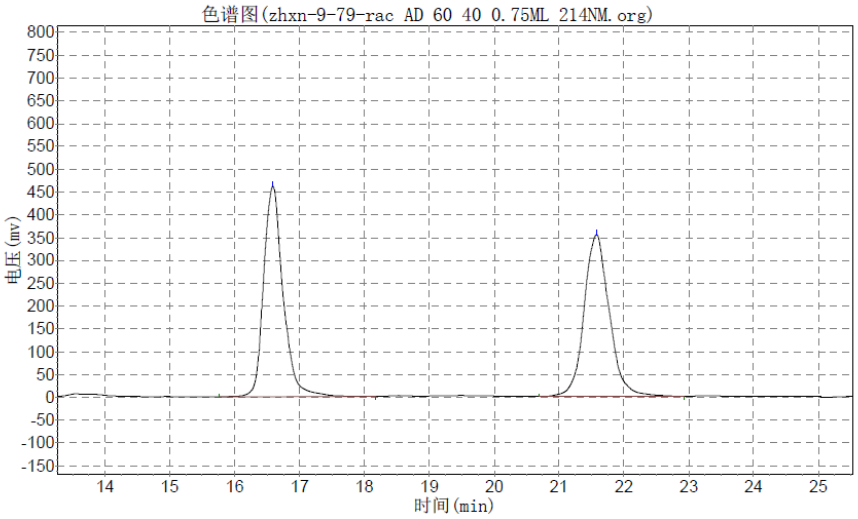
3i

(*R*)-methyl 4-(1-(ethoxycarbonyl)vinyl)-3,3-dicyano-2-(4-(trifluoromethyl)phenyl)-4-(4-nitrophenyl)cyclopent-1-enecarboxylate (3i). A colorless solid, 40 mg, 75% yield; m. p. 64-65 ^{o}C; IR (KBr): ν 2988, 2956, 1719, 1606, 1523, 1437, 1350, 1323, 1270, 1169, 1129, 1069, 1016, 851, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.25 (t, 3H, *J* = 7.2 Hz, CH_3), 3.68 (d, 1H, *J* = 17.6 Hz, CH_2), 3.72 (s, 3H, OCH_3), 3.94 (d, 1H, *J* = 17.6 Hz, CH_2), 4.20 (q, 2H, *J* = 7.2 Hz, CH_2), 6.19 (s, 1H, =CH_2), 6.88 (s, 1H, =CH_2), 7.52 (d, 2H, *J* = 8.0 Hz, ArH), 7.67 (d, 2H, *J* = 8.8 Hz, ArH), 7.73 (d, 2H, *J* = 8.0 Hz, ArH), 8.28 (d, 2H, *J* = 8.8 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 13.9, 43.6, 52.8, 55.4, 62.0, 62.2, 111.6, 112.1, 123.5 (q, *J* = 270.5 Hz), 124.0, 125.7 (q, *J* = 3.7 Hz), 128.3, 128.8, 130.3, 132.3 (q, *J* = 32.6 Hz), 133.6 (q, J = 1.6 Hz), 136.3, 139.8, 142.1, 148.0, 162.6, 164.8; ^{19}F NMR (282.27 MHz, $CDCl_3$, $CFCl_3$): δ -63.42; HRMS (ESI) Calcd. For $C_{27}H_{24}F_3N_4O_6^{+1}$ $(M+NH_4)^+$ requires 557.1648, Found: 557.1637; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.75 mL/min; t_{minor} = 16.44 min, t_{major} = 21.40 min; ee% = 87%; $[\alpha]^{20}_{D}$ = +43.5 (c 1.80, $CHCl_3$)].


8.289
8.267
7.738
7.718
7.682
7.659
7.528
7.508
7.265
6.877
6.193
4.230
4.213
4.195
4.178
3.964
3.919
3.722
3.702
3.658
1.267
1.249
1.232
0.000
F3C
NC
CN
NO2
MeO2C
CO2Et
2.00
2.06
2.06
2.00
1.03
1.00
1.97
0.99
2.95
1.00
3.14
8
6
4
2
0
PPM

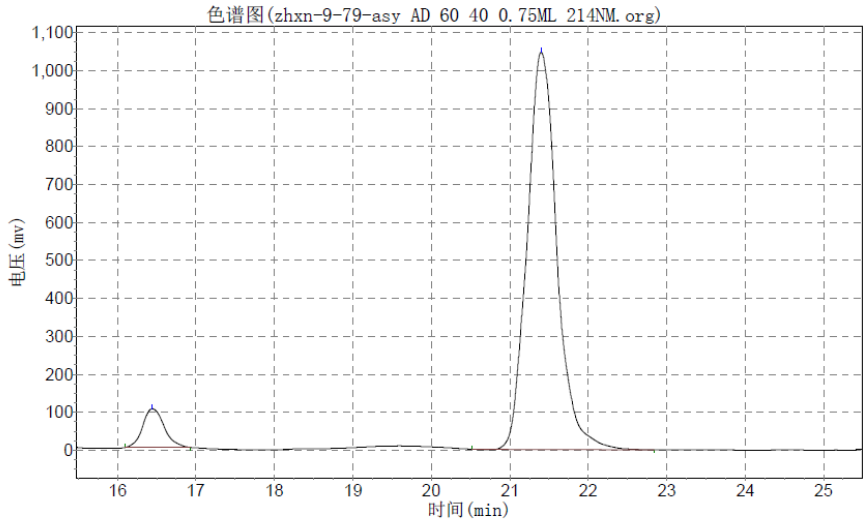

164.844
162.642
148.008
133.622
142.085
139.820
136.275
133.606
132.804
132.477
132.151
131.822
130.317
128.761
128.329
125.794
125.761
125.724
125.682
124.887
124.015
122.182
112.071
111.575
77.343
77.025
76.707
62.154
61.997
55.416
52.769
43.582
13.939
F3C
NC
CN
NO2
MeO2C
CO2Et
180
160
140
120
100
80
60
40
20
PPM





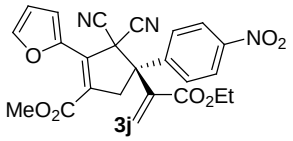
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		16.590	461611.031	9645768.000	50.1555
2		21.578	355051.625	9585972.000	49.8445
总计			816662.656	19231740.000	100.0000



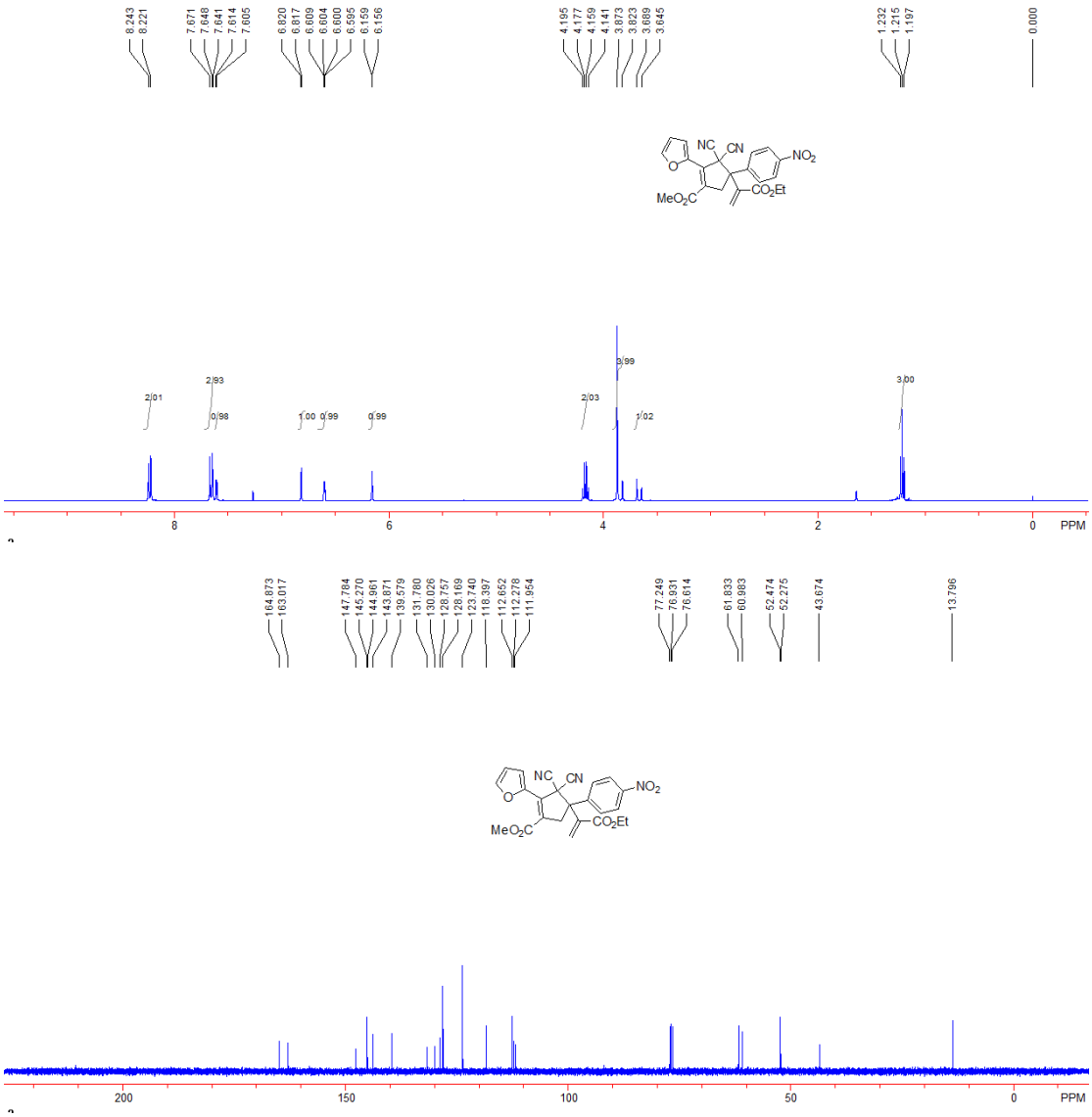
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		16.443	101342.273	1930366.125	6.5602
2		21.397	1046201.500	27495086.000	93.4398
总计			1147543.773	29425452.125	100.0000



3j

(*R*)-methyl 4-(1-(ethoxycarbonyl)vinyl)-3,3-dicyano-2-(furan-2-yl)-4-(4-nitrophenyl)cyclopent-1-enecarboxylate (3j). A colorless solid, 37 mg, 81% yield; m. p. 57-58 ^{o}C; IR (KBr): ν 2955, 2925, 2853, 1717, 1606, 1523, 1435, 1350, 1321, 1268, 1239, 1181, 1133, 1062, 1016, 854, 754, 737, 712 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.22 (t, 3H, *J* = 7.2 Hz, CH_3), 3.67 (d, 1H, *J* = 17.6 Hz, CH_2), 3.82-3.87 (m, 4H, OCH_3+CH_2), 4.17 (q, 2H, *J* = 7.2 Hz, CH_2), 6.16 (d, 1H, *J* = 1.2 Hz, =CH_2), 6.60 (dd, 1H, *J* = 3.6, 2.0 Hz, ArH), 6.82 (d, 1H, *J* = 1.2 Hz, =CH_2), 7.61 (d, 1H, *J* = 3.6 Hz, ArH), 7.64-7.67 (m, 3H, ArH), 8.23 (d, 2H, *J* = 8.8 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 13.8, 43.7, 52.3, 52.5, 61.0, 61.8, 112.0, 112.3, 112.7, 118.4, 123.7, 128.2, 128.8, 130.0, 131.8, 139.6, 143.9, 145.0, 145.3, 147.8, 163.0, 164.9; HRMS (ESI) Calcd. For $C_{24}H_{23}N_4O_7^{+1}$ $(M+NH_4)^+$ requires 479.1567, Found: 479.1551.

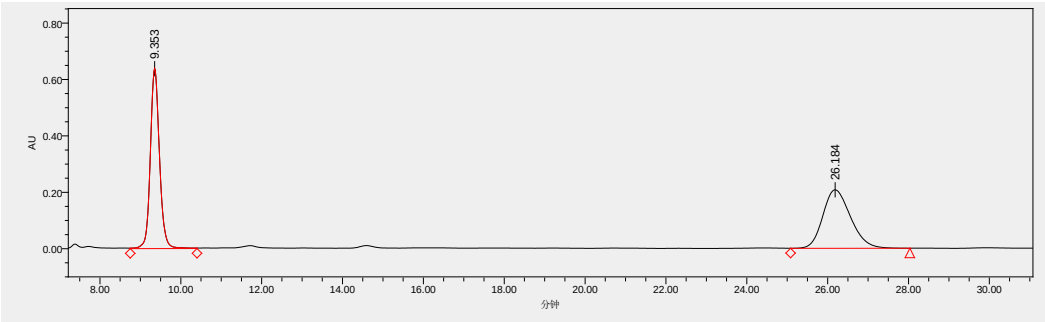


HPLC REPORT

Sample Name: zhxn-9-55 Date: ####

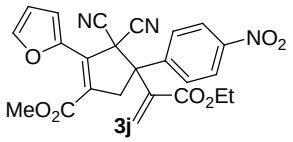
Column: AD-H Mobile Phase: hex/ipr = 60/40

Velocity (mL/min): 0.75 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height

1	9.353	10076136	50.54	639156
2	26.184	9859178	49.46	207337



3j

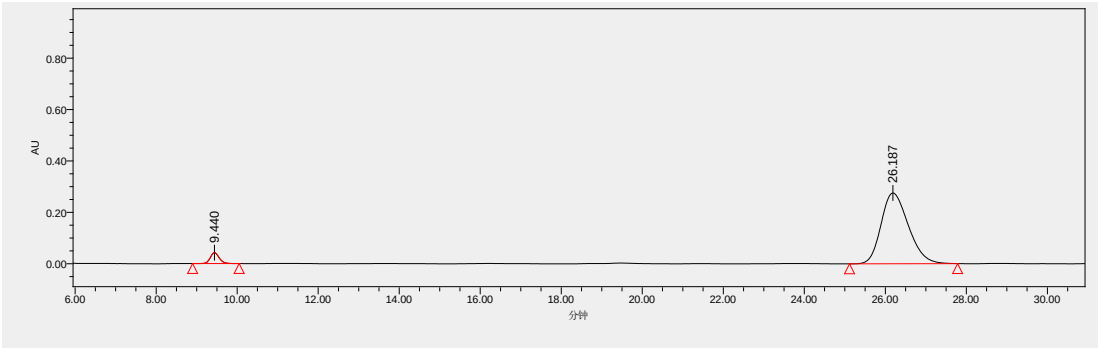
Chiral HPLC report: racemate (**3j**)

HPLC REPORT

Sample Name: zhxn-9-55 Date: ####

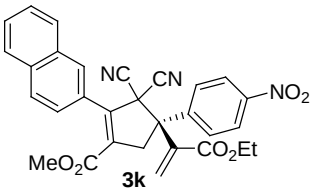
Column: AD-H Mobile Phase: hex/ipr = 60/40

Velocity (mL/min): 0.75 Detection Wavelength (nm): 214



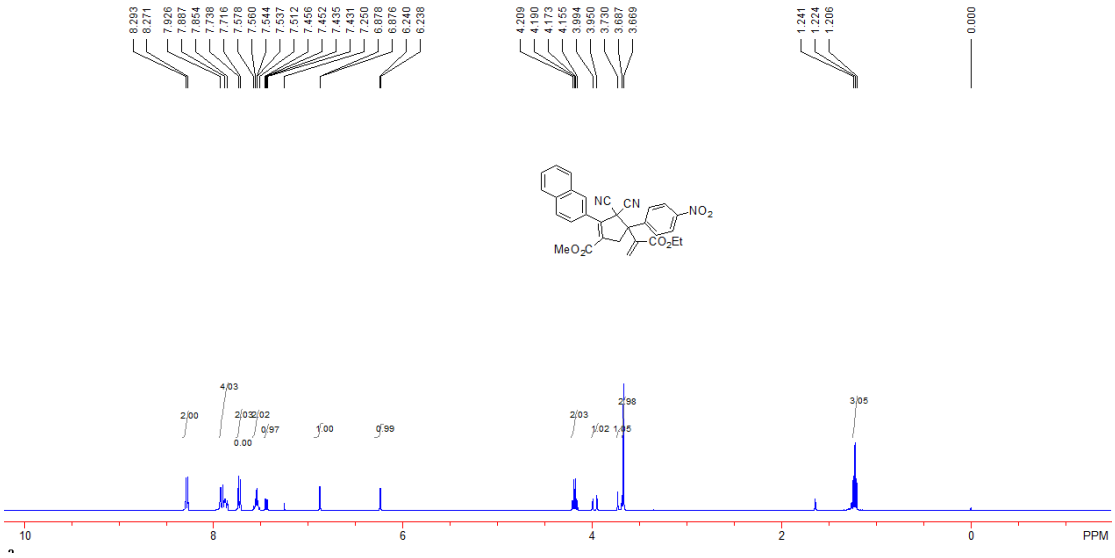
NO	R. Time	Peak Area	Percent	Peak Height
1	9.440	645114	4.77	42421
2	26.187	12887046	95.23	275419

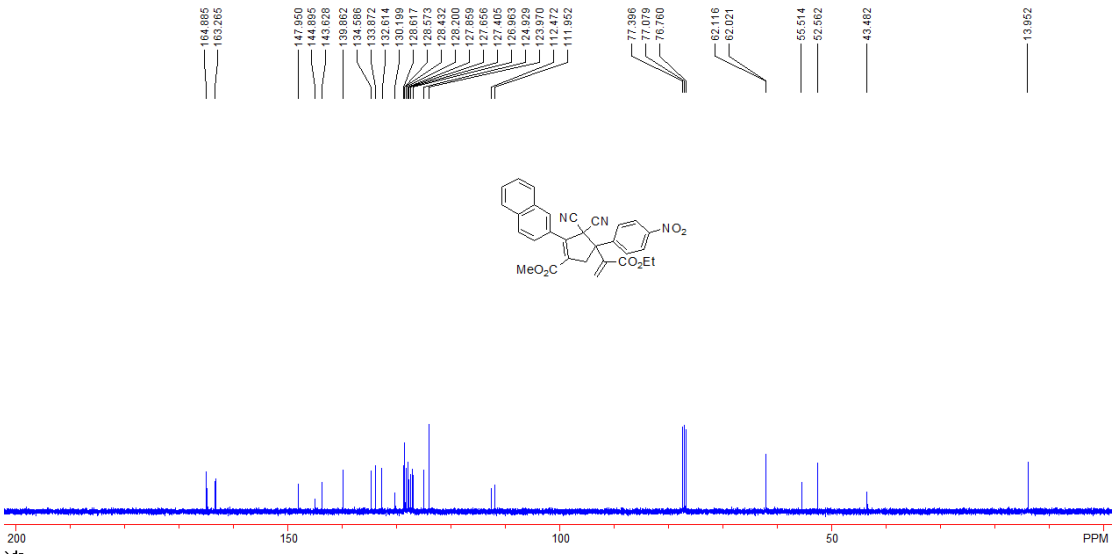
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 214 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.75 mL/min; t_{minor} = 9.44 min, t_{major} = 26.19 min; ee% = 91%; $[\alpha]^{20}_{D}$ = +90.6 (c 1.8, $CHCl_3$).



3k

(*R*)-methyl 4-(1-(ethoxycarbonyl)vinyl)-3,3-dicyano-2-(naphthalen-2-yl)-4-(4-nitrophenyl)cyclopent-1-enecarboxylate (3k). A colorless solid, 44 mg, 84% yield; m. p. 72-73 ^{o}C; IR (KBr): ν 2955, 2927, 2854, 1716, 1603, 1523, 1436, 1350, 1268, 1184, 1131, 1015, 859, 820, 751, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.22 (t, 3H, *J* = 7.2 Hz, CH_3), 3.67 (s, 3H, OCH_3), 3.71 (d, 1H, *J* = 17.6 Hz, CH_2), 3.97 (d, 1H, *J* = 17.6 Hz, CH_2), 4.18 (q, 2H, *J* = 7.2 Hz, CH_2), 6.24 (d, 1H, *J* = 0.8 Hz, =CH_2), 6.88 (d, 1H, *J* = 0.8 Hz, =CH_2), 7.44 (dd, 1H, *J* = 8.4, 1.6 Hz, ArH), 7.51-7.58 (m, 2H, ArH), 7.73 (d, 2H, *J* = 8.8 Hz, ArH), 7.85-7.93 (m, 4H, ArH), 8.28 (d, 2H, *J* = 8.8 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.0, 43.5, 52.6, 55.5, 62.0, 62.1, 112.0, 112.5, 124.0, 124.9, 127.0, 127.4, 127.7, 127.9, 128.2, 128.4, 128.57, 128.62, 130.2, 132.6, 133.9, 134.6, 139.9, 143.6, 144.9, 148.0, 163.3, 164.9; HRMS (ESI) Calcd. For $C_{30}H_{27}N_4O_6^{+1}$ $(M+NH_4)^+$ requires 539.1931, Found: 539.1914.



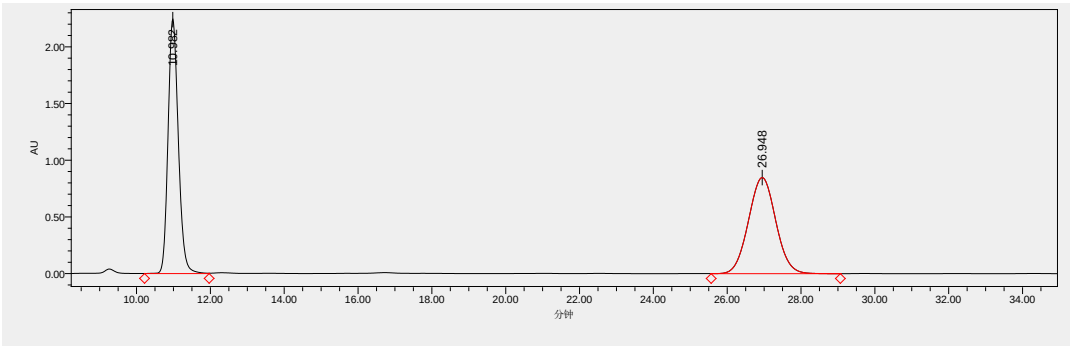


HPLC REPORT

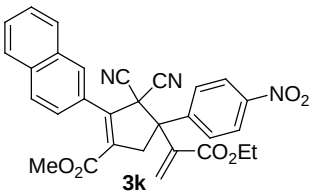
Sample Name: zhxn-9-54 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 60/40

Velocity (mL/min): 0.75 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	10.982	43465561	49.93	2241633
2	26.948	43578893	50.07	847673



3k

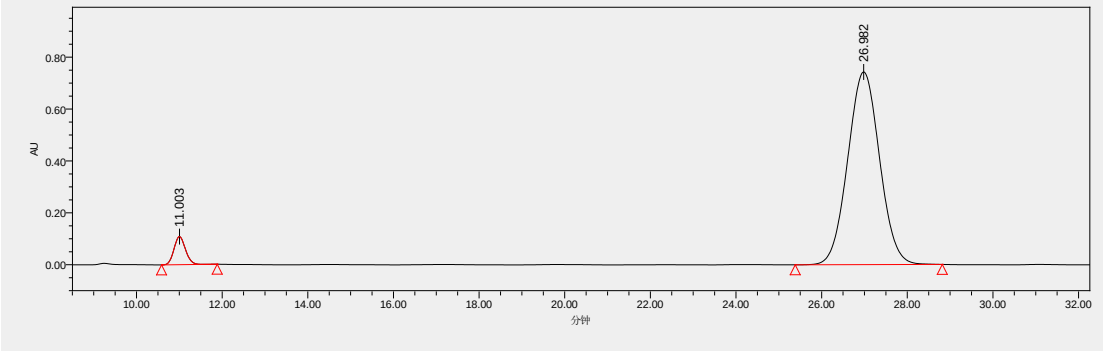
Chiral HPLC report: racemate (**3k**)

HPLC REPORT

ample Name: zhxn-9-54 Date: ####

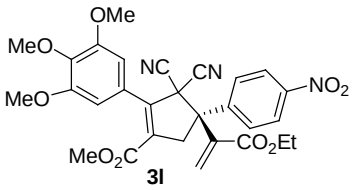
Column: AD-H Mobile Phase: hex/ipr = 60/40

Velocity (mL/min): 0.75 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	11.003	2030087	5.02	108431
2	26.982	38402366	94.98	742804

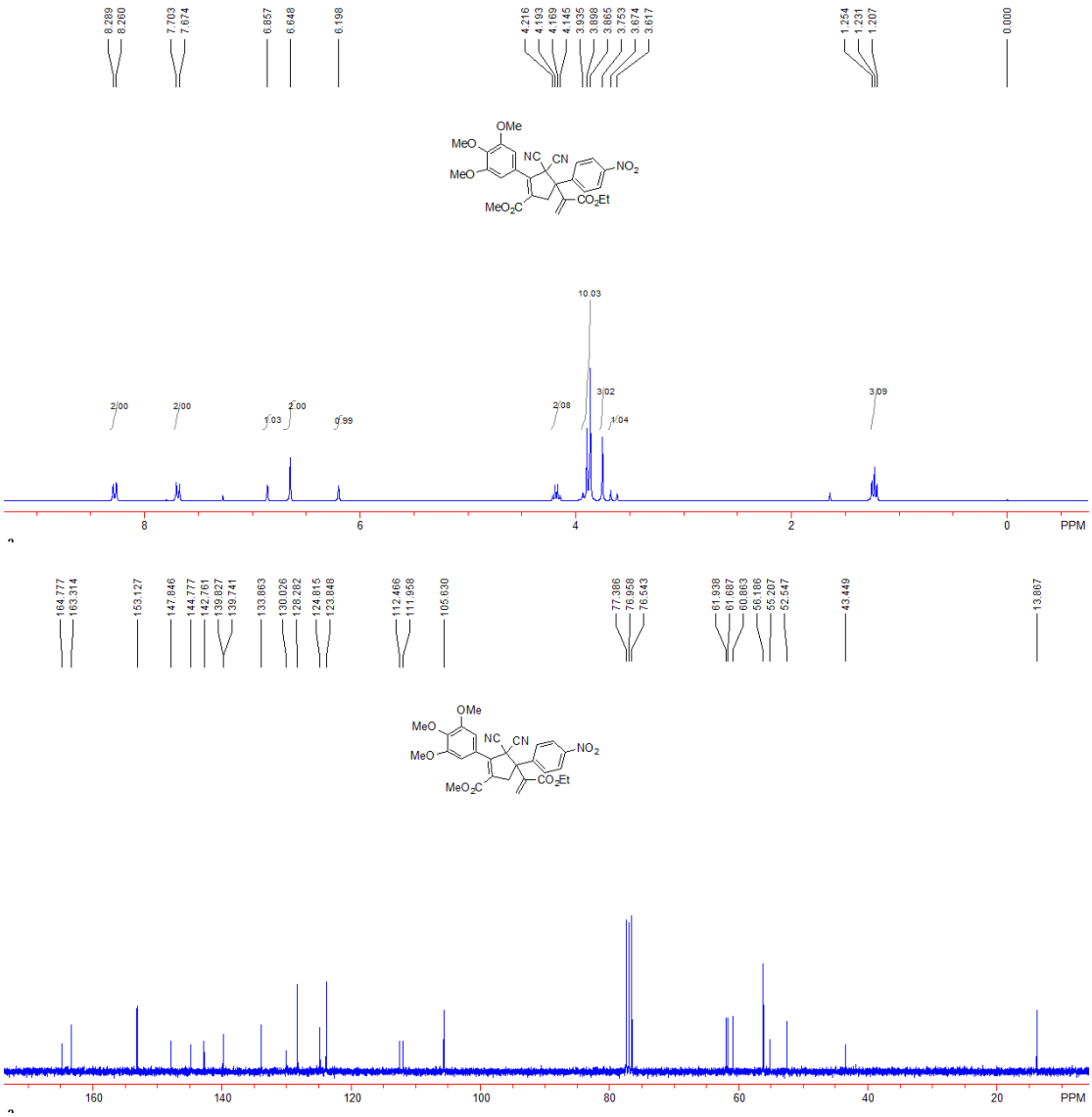
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 214 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.75 mL/min; t_{minor} = 11.00 min, t_{major} = 26.98 min; ee% = 90%; $[\alpha]^{20}_{D}$ = +81.8 (c 2.40, $CHCl_3$).

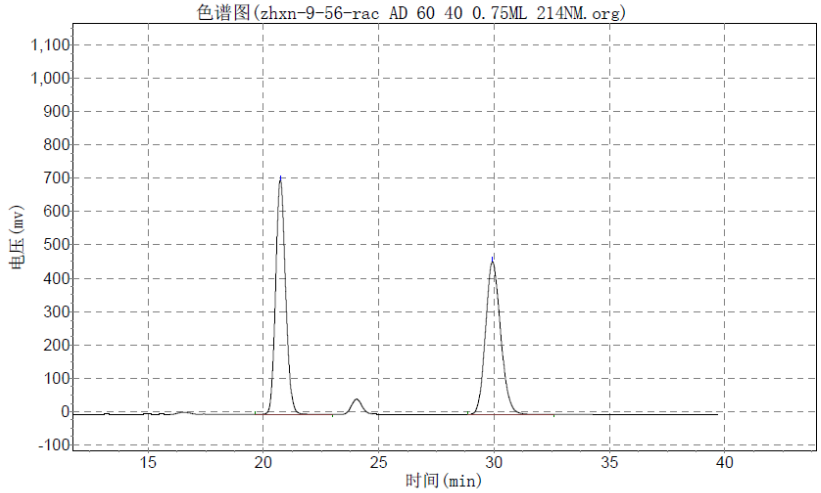


3l

(*R*)-methyl 4-(1-(ethoxycarbonyl)vinyl)-3,3-dicyano-2-(3,4,5-trimethoxyphenyl)-4-(4-nitrophenyl)cyclopent-1-enecarboxylate (3l). A colorless solid, 45 mg, 70% yield; m. p. 78-79 ^{o}C; IR (KBr): ν 2943, 1717, 1582, 1524, 1506, 1455, 1415, 1351, 1319, 1246, 1183, 1128, 1003, 859, 835, 699 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.23 (t, 3H, *J* = 7.2 Hz, CH_3), 3.65 (d, 1H, *J* = 17.1 Hz, CH_2), 3.75 (s, 3H, OCH_3), 3.87-3.94 (m, 10H, $3OCH_3$+CH_2), 4.18 (q, 2H, *J* = 7.2 Hz, CH_2), 6.20 (s, 1H, =CH_2), 6.65 (s, 2H, ArH), 6.86 (s, 1H, =CH_2), 7.69 (d, 2H, *J* = 8.7 Hz, ArH), 8.27 (d, 2H, *J* = 8.7 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 13.9, 43.4, 52.5, 55.2, 56.2, 60.9, 61.7, 61.9, 105.6, 112.0, 112.5, 123.8,

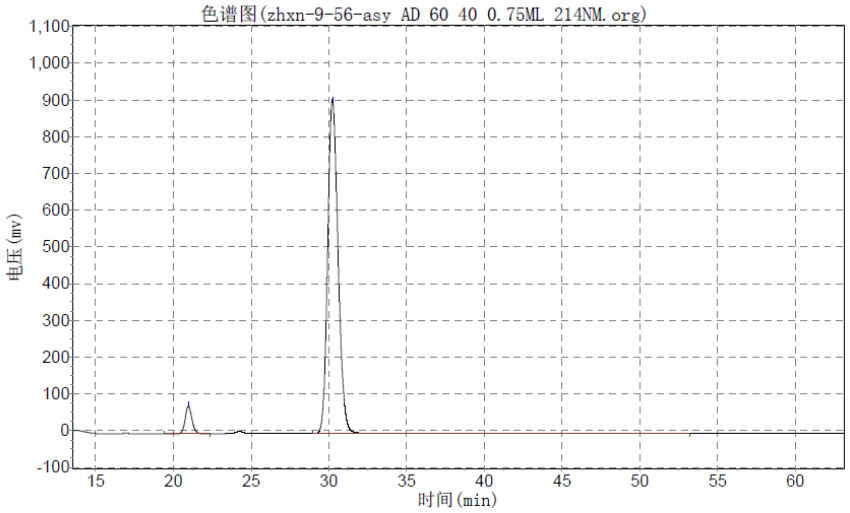
124.8, 128.3, 130.0, 133.9, 139.7, 139.8, 142.8, 144.8, 147.8, 153.1, 163.3, 164.8; HRMS (ESI) Calcd. For $C_{29}H_{31}N_4O_9^{+1}$ $(M+NH_4)^+$ requires 579.2091, Found: 579.2077; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.75 mL/min; t_{minor} = 20.99 min, t_{major} = 30.26 min; ee% =90%; $[\alpha]^{20}_D$ = +71.4 (c 1.50, $CHCl_3$)].





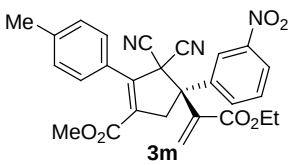
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		20.733	703710.813	21157886.000	50.3475
2		29.927	458488.000	20865846.000	49.6525
总计			1162198.813	42023732.000	100.0000



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		20.990	74772.023	2274761.500	5.0854
2		30.257	909169.063	42456264.000	94.9146
总计			983941.086	44731025.500	100.0000

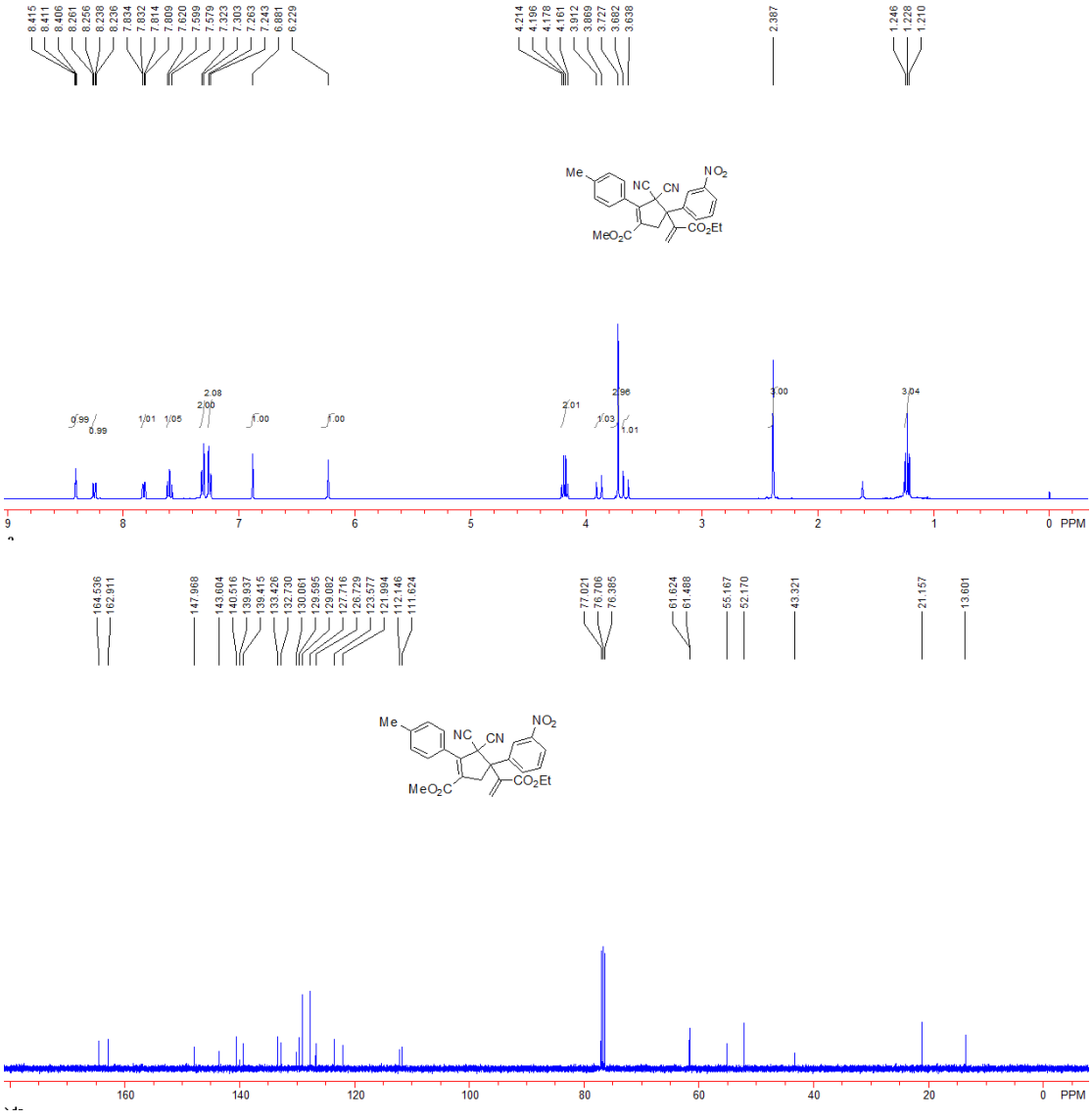


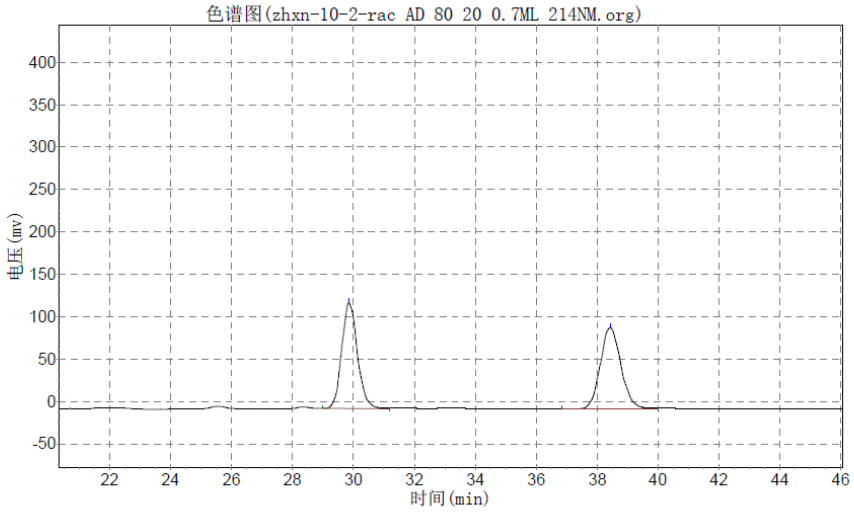
3m

(*R*)-methyl

4-(1-(ethoxycarbonyl)vinyl)-3,3-dicyano-4-(3-nitrophenyl)-2-p-tolylcyclopent-1-enecarboxylate

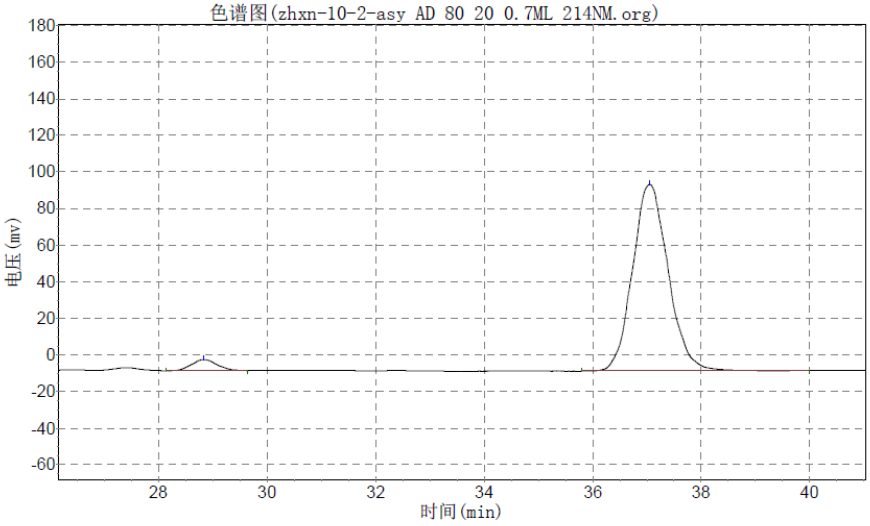
(3m). A colorless solid, 37 mg, 76% yield; m. p. 52-53 ^{o}C; IR (KBr): ν 2980, 2954, 2870, 1713, 1611, 1530, 1435, 1348, 1316, 1267, 1229, 1180, 1136, 1019, 966, 808, 735, 690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.23 (t, 3H, *J* = 7.2 Hz, CH_3), 2.39 (s, 3H, CH_3), 3.66 (d, 1H, *J* = 17.6 Hz, CH_2), 3.73 (s, 3H, OCH_3), 3.89 (d, 1H, *J* = 17.6 Hz, CH_2), 4.19 (q, 2H, *J* = 7.2 Hz, CH_2), 6.23 (s, 1H, $=CH_2$), 6.88 (s, 1H, $=CH_2$), 7.25 (d, 2H, *J* = 8.0 Hz, ArH), 7.31 (d, 2H, *J* = 8.0 Hz, ArH), 7.58-7.62 (m, 1H, ArH), 7.81-7.83 (m, 1H, ArH), 8.24-8.26 (m, 1H, ArH), 8.41-8.42 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 13.6, 21.2, 43.3, 52.2, 55.2, 61.5, 61.6, 111.6, 112.1, 122.0, 123.6, 126.7, 127.7, 129.1, 129.6, 130.1, 132.7, 133.4, 139.4, 139.9, 140.5, 143.6, 148.0, 162.9, 164.5; HRMS (ESI) Calcd. For $C_{27}H_{27}N_4O_6^{+1}$ $(M+NH_4)^+$ requires 503.1931, Found: 503.1921; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.75 mL/min; t_{minor} = 28.83 min, t_{major} = 37.05 min; ee% = 92%; $[\alpha]^{20}_{D}$ = +118.6 (c1.50, $CHCl_3$)].





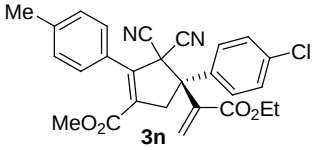
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		29.848	124814.148	4457704.500	49.9248
2		38.435	95341.727	4471140.000	50.0752
总计			220155.875	8928844.500	100.0000



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		28.828	6031.460	201840.563	4.1553
2		37.052	101956.898	4655564.500	95.8447
总计			107988.358	4857405.063	100.0000

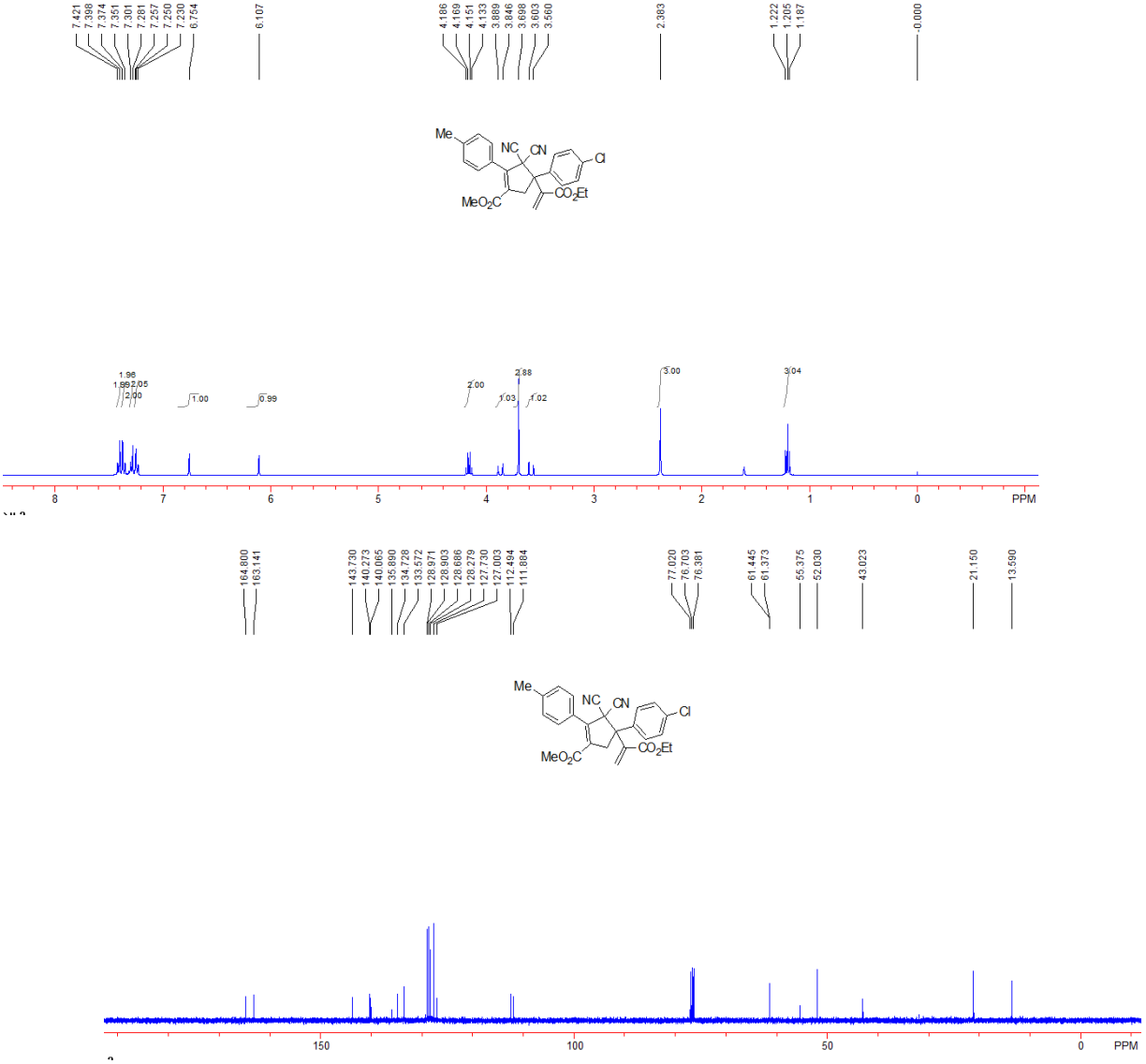


3n

(*R*)-methyl

4-(1-(ethoxycarbonyl)vinyl)-4-(4-chlorophenyl)-3,3-dicyano-2-p-tolylcyclopent-1-enecarboxylate

(3n). A colorless solid, 20 mg, 42% yield; m. p. 58-59 ^{o}C; IR (KBr): ν 2980, 2953, 2927, 1714, 1622, 1493, 1435, 1264, 1226, 1179, 1097, 1014, 965, 833, 815, 735 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.21 (t, 3H, *J* = 7.2 Hz, CH_3), 2.38 (s, 3H, CH_3), 3.58 (d, 1H, *J* = 17.2 Hz, CH_2), 3.70 (s, 3H, OCH_3), 3.87 (d, 1H, *J* = 17.2 Hz, CH_2), 4.16 (q, 2H, *J* = 7.2 Hz, CH_2), 6.11 (s, 1H, =CH_2), 6.75 (s, 1H, =CH_2), 7.24 (d, 2H, *J* = 8.0 Hz, ArH), 7.29 (d, 2H, *J* = 8.0 Hz, ArH), 7.36 (d, 2H, *J* = 9.2 Hz, ArH), 7.41 (d, 2H, *J* = 9.2 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 13.6, 21.1, 43.0, 52.0, 55.4, 61.37, 61.44, 111.9, 112.5, 127.0, 127.7, 128.3, 128.7, 128.9, 129.0, 133.6, 134.7, 135.9, 140.1, 140.3, 143.7, 163.1, 164.8; HRMS (ESI) Calcd. For $C_{27}H_{27}ClN_3O_4^{+1}$ $(M+NH_4)^+$ requires 492.1690, Found:492.1676.

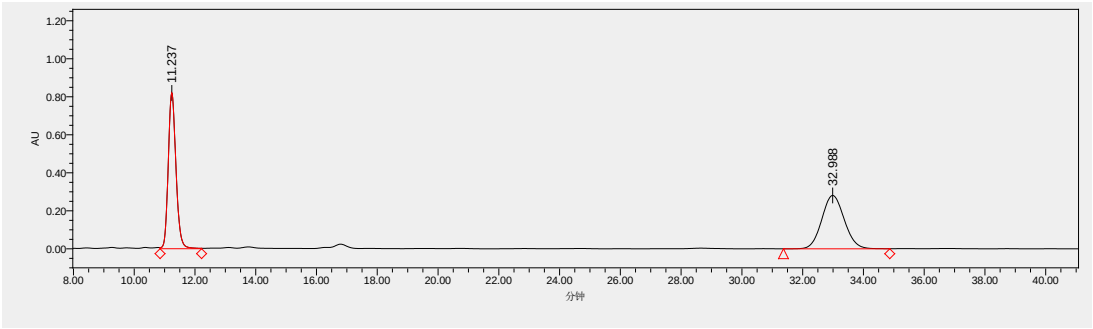


HPLC REPORT

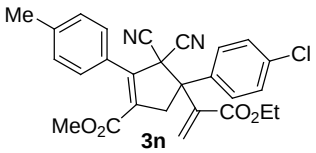
Sample Name: zhxn-9-98 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 90/10

Velocity (mL/min): 0.75 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	11.237	14500524	50.09	821460
2	32.988	14449921	49.91	280856



3n

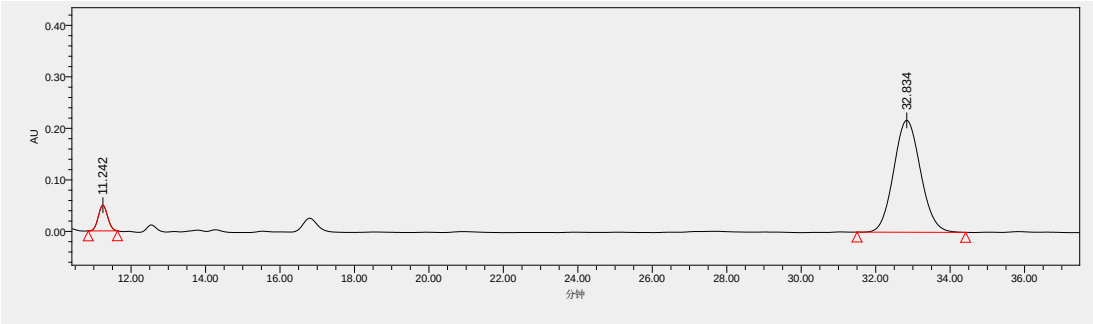
Chiral HPLC report: racemate (**3n**)

HPLC REPORT

Sample Name: zhxn-9-98 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 90/10

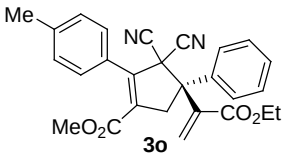
Velocity (mL/min): 0.75 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	11.242	870212	7.39	49977

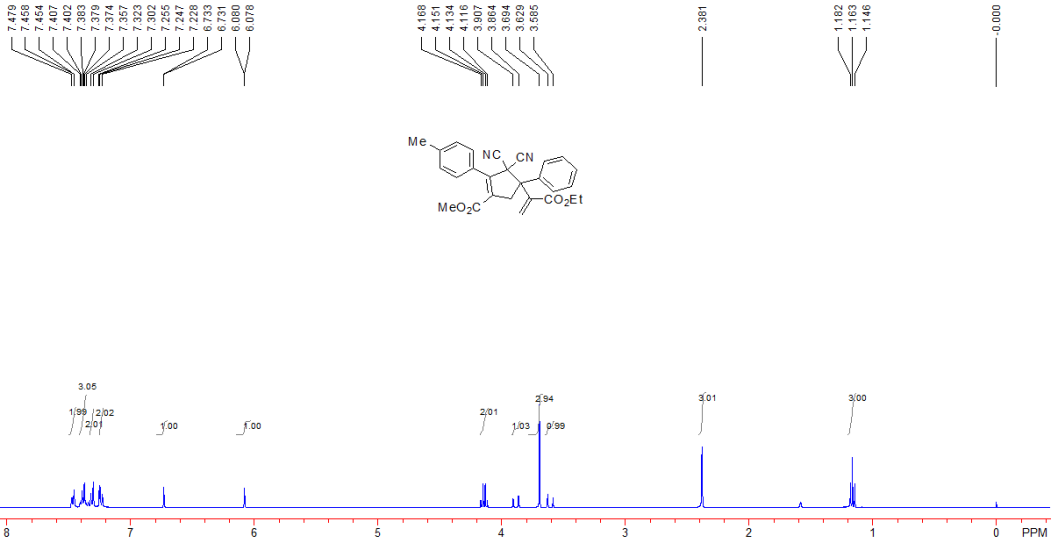
2	32.834	10897469	92.61	217307

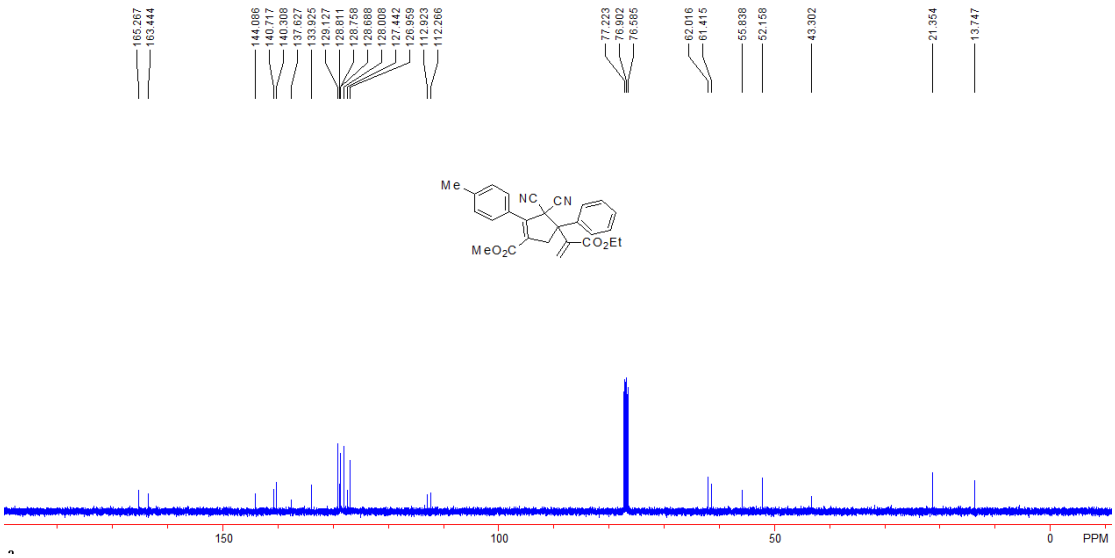
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 214 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.75 mL/min; t_{minor} = 11.24 min, t_{major} = 32.83 min; ee% = 85%; $[\alpha]^{20}_{D}$ = +50.5 (c 1.80, $CHCl_3$).



3o

(*R*)-methyl 4-(1-(ethoxycarbonyl)vinyl)-3,3-dicyano-4-phenyl-2-p-tolylcyclopent-1-enecarboxylate (3o). A colorless solid, 17 mg, 39% yield; m. p. 39-40 ^{o}C; IR (KBr): ν 2954, 2924, 1720, 1447, 1307, 1266, 1230, 1187, 1097, 1020, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.16 (t, 3H, *J* = 6.8 Hz, CH_3), 2.38 (s, 3H, CH_3), 3.61 (d, 1H, *J* = 17.2 Hz, CH_2), 3.69 (s, 3H, OCH_3), 3.89 (d, 1H, *J* = 17.2 Hz, CH_2), 4.14 (q, 2H, *J* = 6.8 Hz, CH_2), 6.08 (d, 1H, *J* = 0.8 Hz, =CH_2), 6.73 (d, 1H, *J* = 0.8 Hz, =CH_2), 7.24 (d, 2H, *J* = 8.0 Hz, ArH), 7.31 (d, 2H, *J* = 8.0 Hz, ArH), 7.36-7.41 (m, 3H, ArH), 7.45-7.48 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 13.7, 21.4, 43.3, 52.2, 55.8, 61.4, 62.0, 112.3, 112.9, 127.0, 127.4, 128.0, 128.69, 128.76, 128.8, 129.1, 133.9, 137.6, 140.3, 140.7, 144.1, 163.4, 165.3; HRMS (ESI) Calcd. For $C_{27}H_{28}N_3O_4^{+1}$ $(M+NH_4)^+$ requires 458.2080, Found: 458.2070.



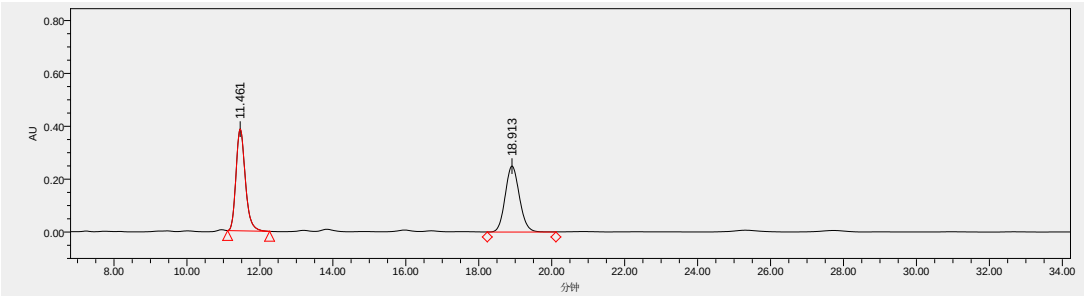


HPLC REPORT

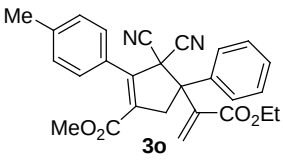
Sample Name: zhxn-10-30 Date: ####

Column: AD-H Mobile Phase: hex/ipr =90/10

Velocity (mL/min): 0.75 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	11.461	6834263	50.15	385281
2	18.913	6792730	49.85	249762



3o

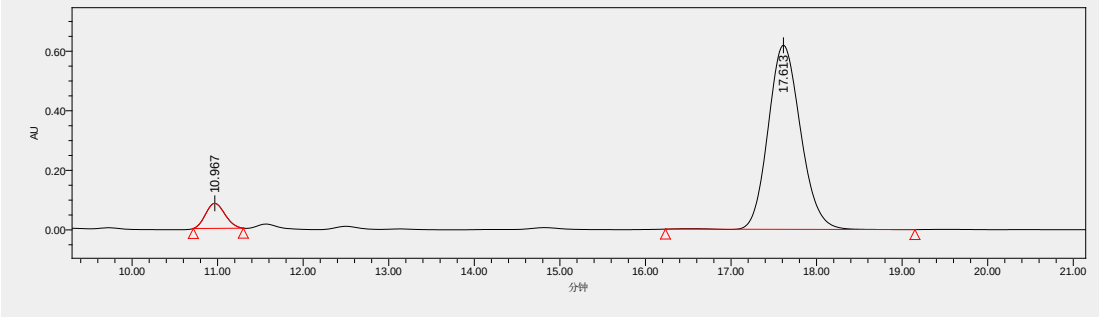
Chiral HPLC report: racemate (**3o**)

HPLC REPORT

Sample Name: zhxn-10-30 Date: ###

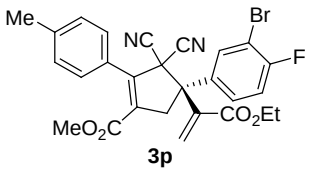
Column: AD-H Mobile Phase: hex/ipr = 90/10

Velocity (mL/min): 0.75 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	10.967	1319146	7.49	84271
2	17.613	16294961	92.51	618855

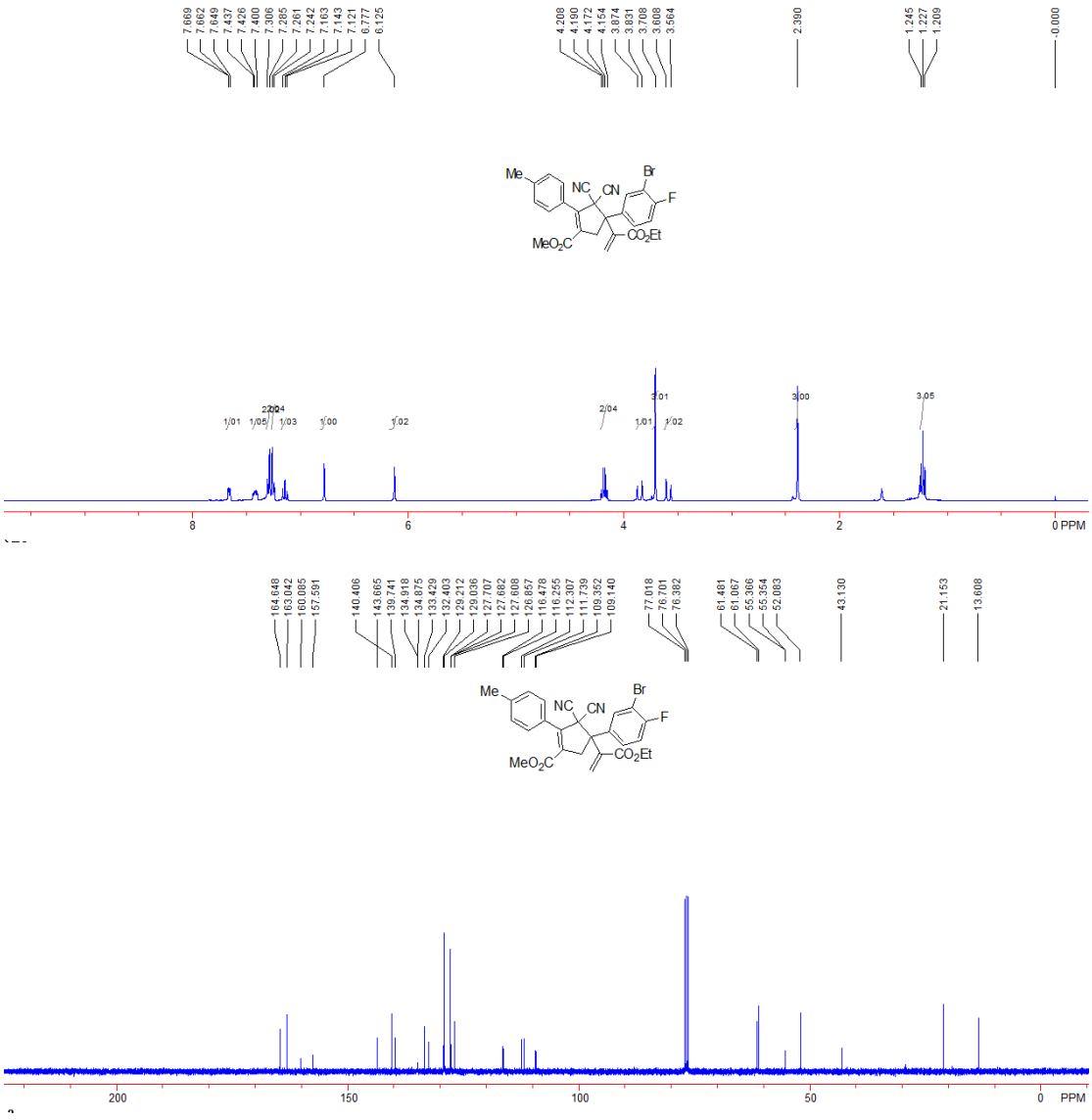
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 214 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.75 mL/min; t_{minor} = 10.97 min, t_{major} = 17.61 min; ee% = 85%; $[\alpha]^{20}_{D}$ = +50.1 (c 1.80, $CHCl_3$).

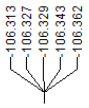


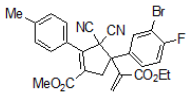
3p

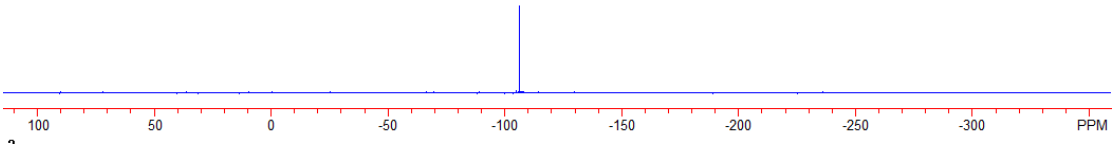
(*R*)-methyl 4-(1-(ethoxycarbonyl)vinyl)-4-(3-bromo-4-fluorophenyl)-3,3-dicyano-2-p-tolylcyclopent-1-enecarboxylate (3p). A colorless solid, 39 mg, 69% yield; m. p. 46-47 ^{o}C; IR (KBr): ν 2984, 2951, 1714, 1496, 1436, 1312, 1266, 1229, 1180, 1158, 1049, 1020, 966, 816, 735, 695 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.23 (t, 3H, *J* = 7.2 Hz, CH_3), 2.39 (s, 3H, CH_3), 3.59 (d, 1H, *J* = 17.6 Hz, CH_2), 3.71 (s, 3H, OCH_3), 3.85 (d, 1H, *J* = 17.6 Hz, CH_2), 4.18 (q, 2H, *J* = 7.2 Hz, CH_2), 6.13 (s, 1H, $=CH_2$), 6.78 (s, 1H, $=CH_2$), 7.12-7.16 (m, 1H, ArH), 7.25 (d, 2H, *J* = 8.0 Hz, ArH), 7.30 (d, 2H, *J* = 8.0 Hz, ArH), 7.40-7.44 (m, 1H, ArH), 7.65-7.67 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 13.6, 21.2, 43.1, 52.1, 55.4 (d, *J* = 1.2 Hz), 61.1, 61.5, 109.2 (d, *J* = 21.2 Hz), 111.7, 112.3, 116.4 (d, *J* = 22.3 Hz), 126.9, 127.6 (d, *J* = 7.4 Hz), 127.7, 129.0, 129.2, 132.4, 133.4, 134.9 (d, *J* = 4.3 Hz), 139.7, 140.4,

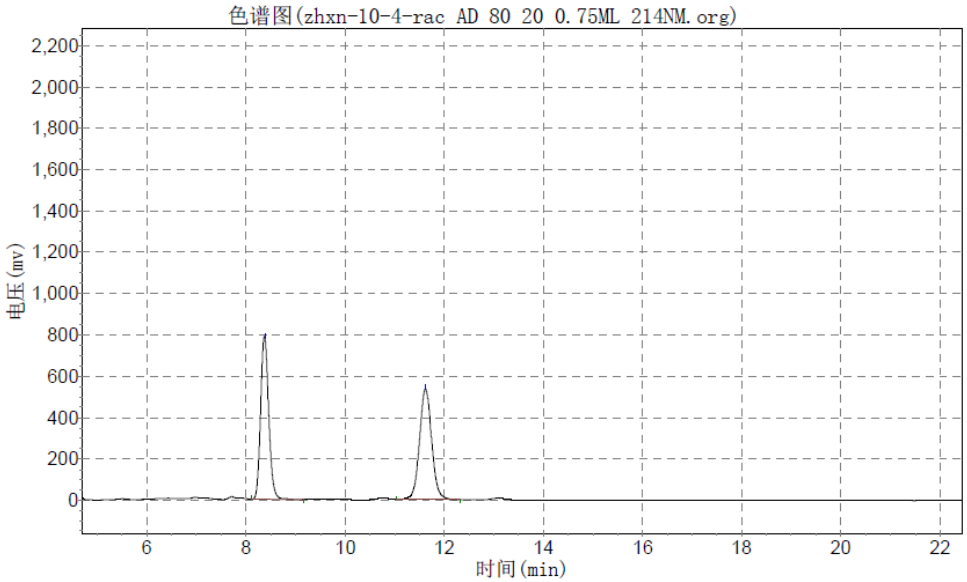
143.7, 158.8 (d, J = 249.4 Hz), 163.0, 164.6; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -106.33; HRMS (ESI) Calcd. For $C_{27}H_{26}BrFN_3O_4^{+1}$ $(M+NH_4)^+$ requires 554.1091, Found: 554.1071; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.75 mL/min; t_{minor} = 8.36 min, t_{major} = 11.53 min; ee% = 89%; $[\alpha]^{20}_D$ = +98.7 (c 1.80, $CHCl_3$)].





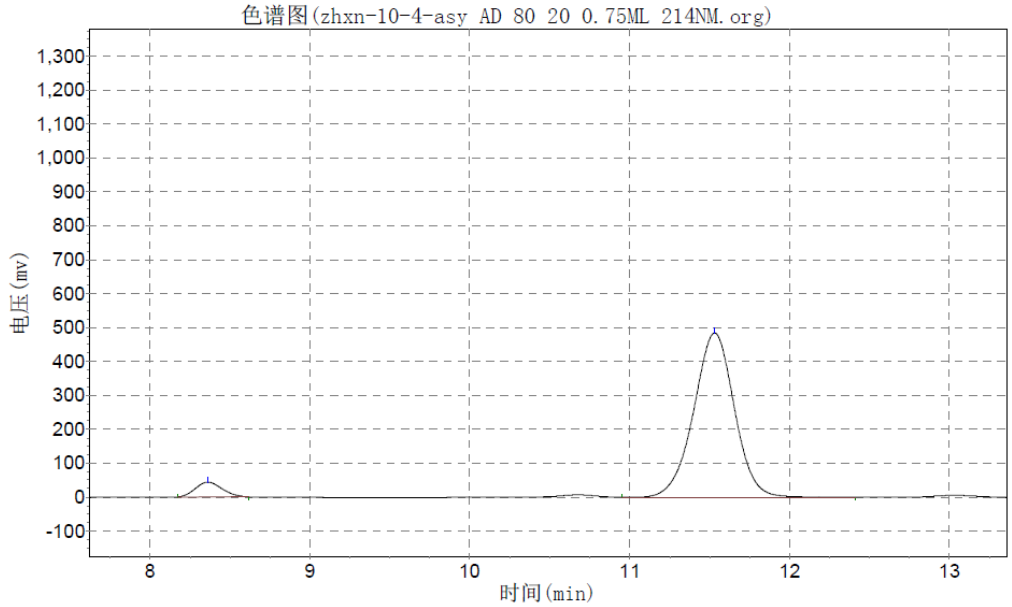






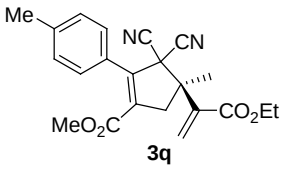
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		8.382	790807.750	9231935.000	49.3391
2		11.632	539391.688	9479259.000	50.6609
总计			1330199.438	18711194.000	100.0000



分析结果表

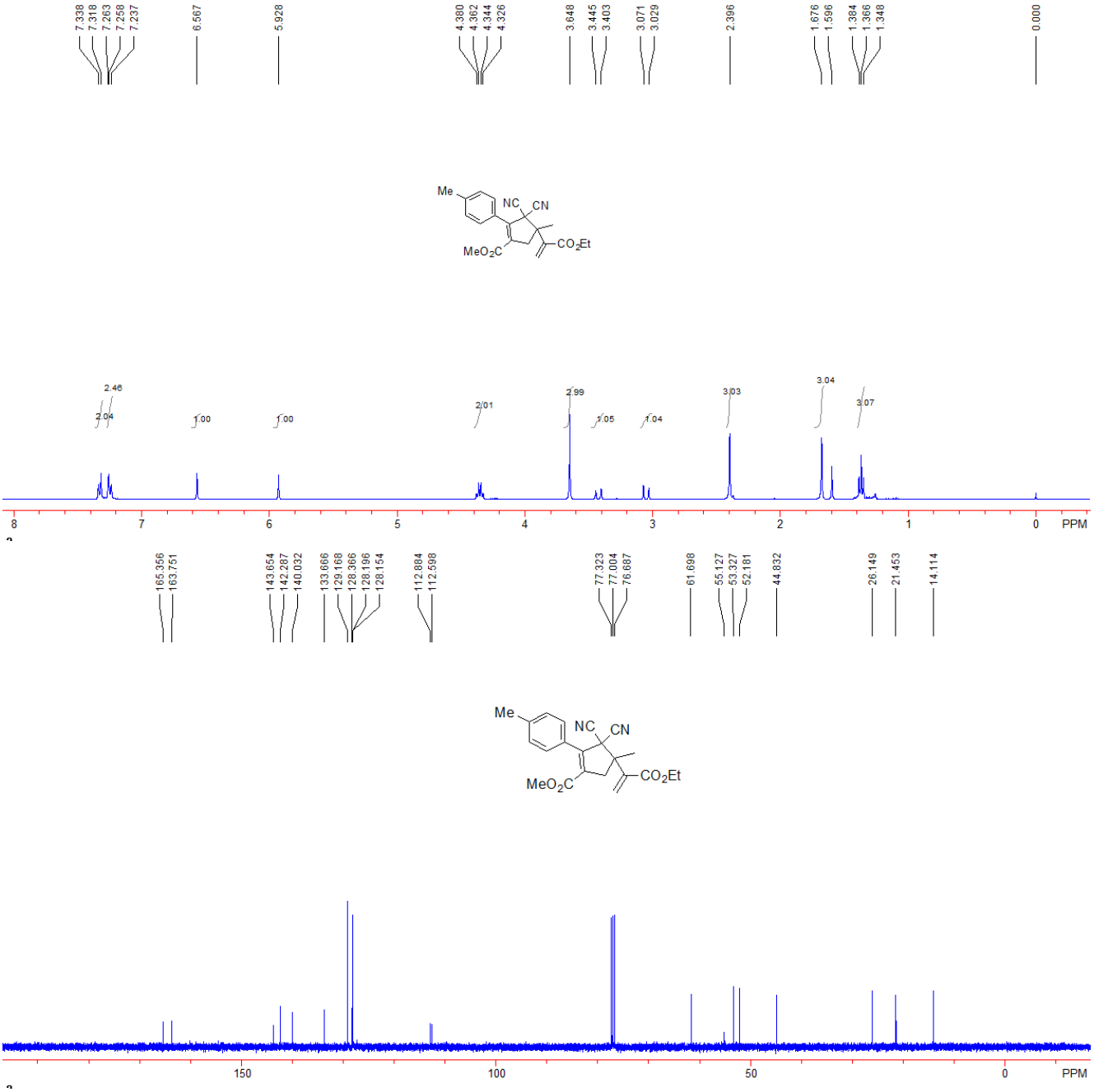
峰号	峰名	保留时间	峰高	峰面积	含量
1		8.360	43219.309	497740.188	5.4945
2		11.532	483856.656	8561094.000	94.5055
总计			527075.965	9058834.188	100.0000

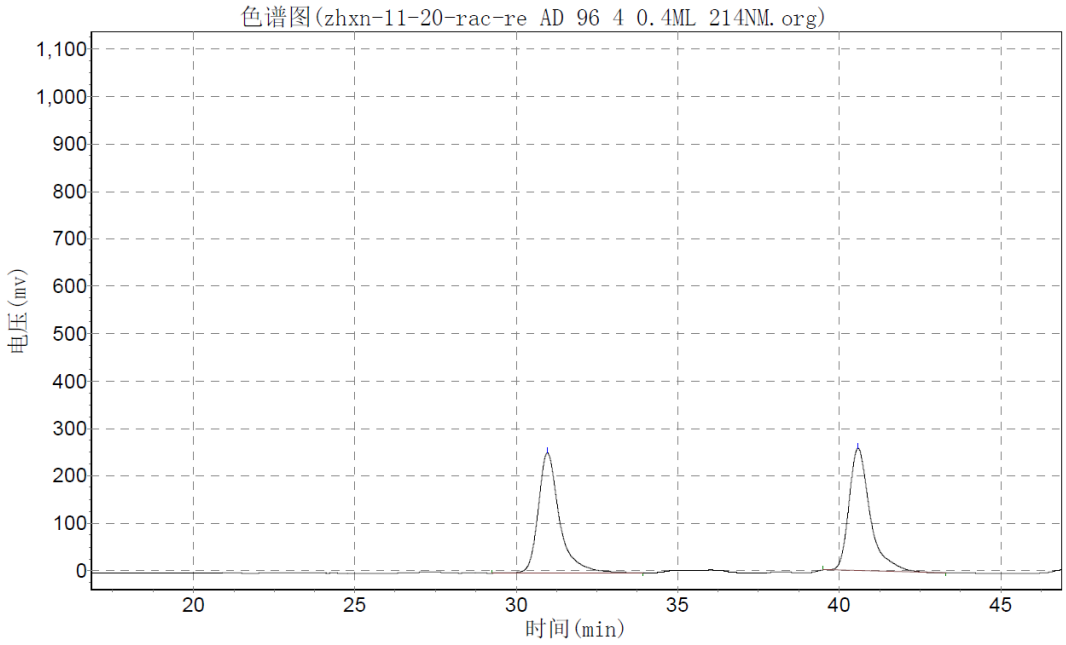


3q

(S)-methyl 4-(1-(ethoxycarbonyl)vinyl)-3,3-dicyano-4-methyl-2-p-tolylcyclopent-1-enecarboxylate (3q). A colorless oil, 11 mg, 29% yield; IR (KBr): ν 3726, 2922, 2851, 2360, 2342, 1716, 1440, 1322, 1226, 1198, 1106, 1025, 676, 668 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.37 (t, 3H, *J* = 7.2 Hz, CH_3), 1.68 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 3.05 (d, 1H, *J* = 16.8 Hz, CH_2), 3.42 (d, 1H, *J* = 16.8 Hz, CH_2), 3.65 (s, 3H, OCH_3), 4.35 (q, 2H, *J* = 7.2 Hz, CH_2), 5.93 (s, 1H, $=CH_2$), 6.57 (s, 1H, $=CH_2$), 7.25 (d, 2H, *J* = 8.0 Hz, ArH), 7.33 (d, 2H, *J* = 8.0 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.1, 21.5, 26.1, 44.8, 52.2, 53.3, 55.1, 61.7, 112.6, 112.9, 128.15, 128.2, 128.4, 129.2, 133.7, 140.0, 142.3, 143.7, 163.8, 165.4; HRMS (ESI) Calcd. For $C_{22}H_{26}N_3O_4^{+1}$ $(M+NH_4)^+$ requires 396.1923, Found: 396.1913; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent:

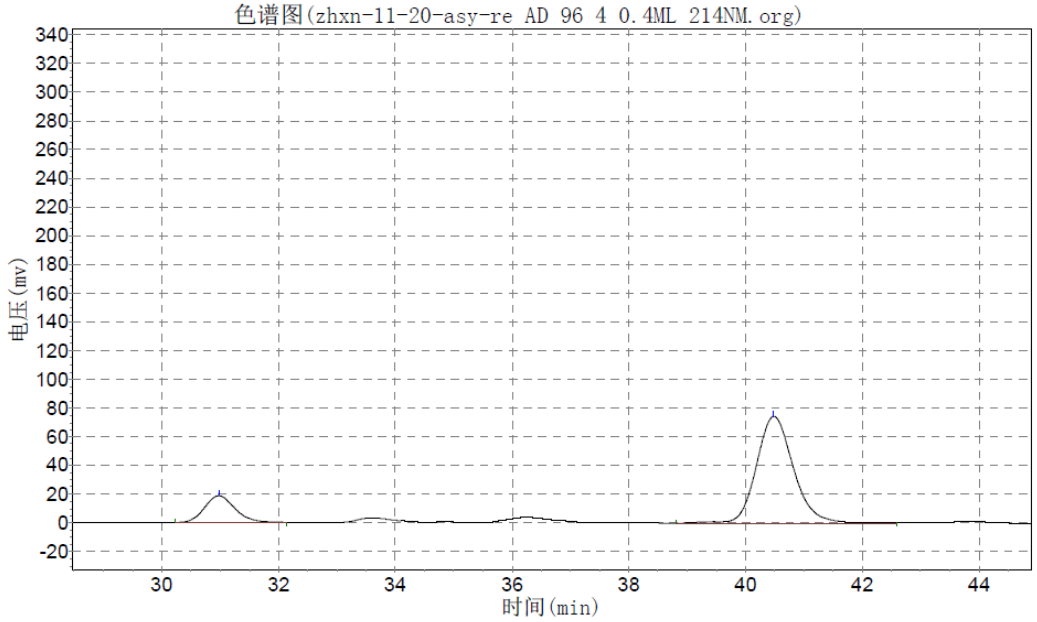
Hexane/Isopropanol = 96/4; Flow rate: 0.40 mL/min; t_{minor} = 30.97 min, t_{major} = 40.48 min; ee% = 66%; $[\alpha]^{20}_{D}$ = +39.0 (c 0.60, $CHCl_3$)].





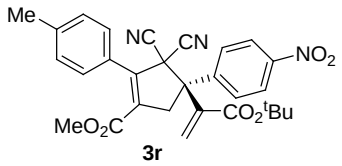
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		30.965	253785.922	11688483.000	49.8600
2		40.585	258201.719	11754104.000	50.1400
总计			511987.641	23442587.000	100.0000



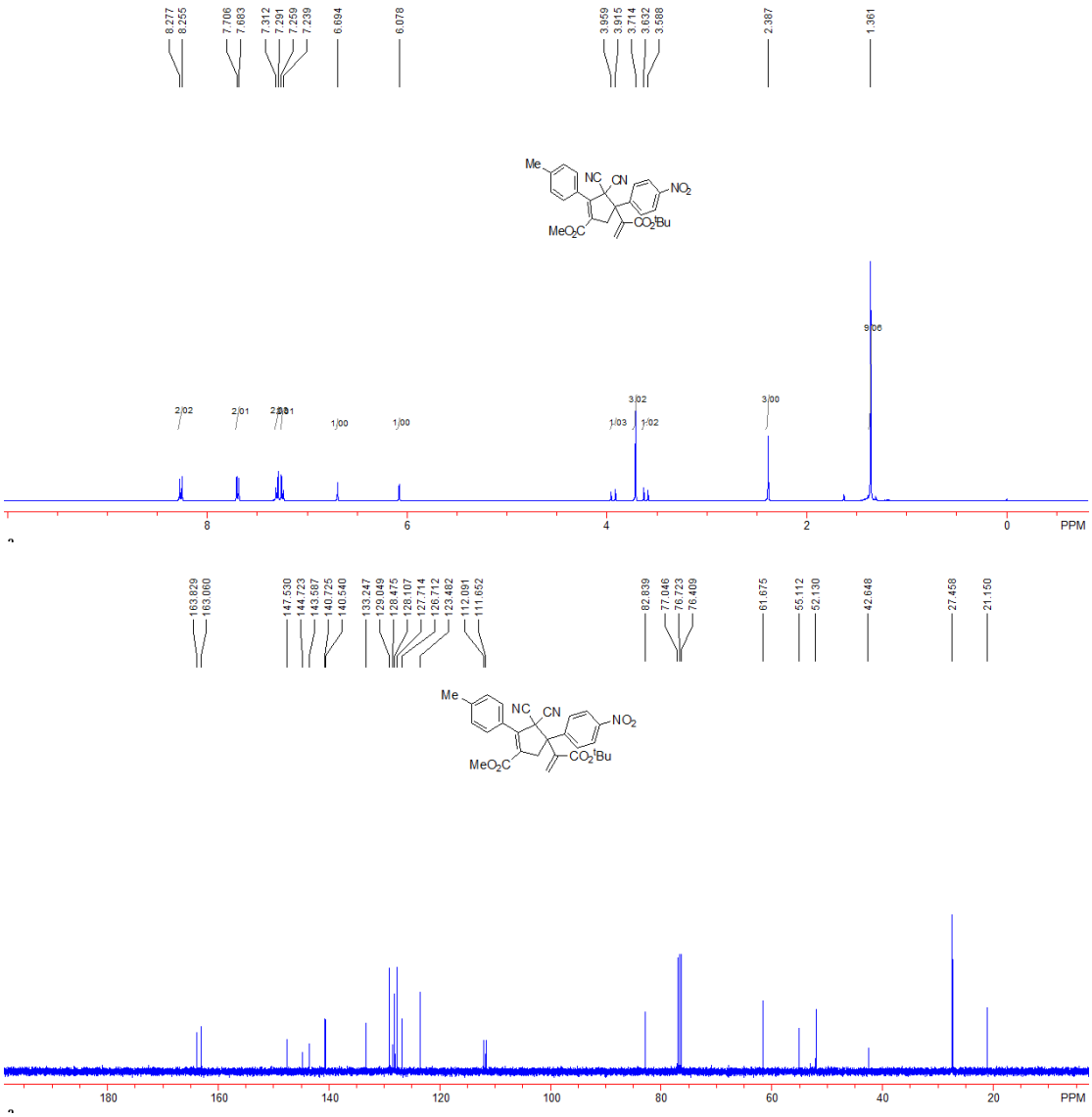
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		30.973	18663.189	680521.000	17.1479
2		40.482	74436.500	3288009.000	82.8521
总计			93099.689	3968530.000	100.0000



3r

(*R*)-methyl 4-(1-(tert-butoxycarbonyl)vinyl)-3,3-dicyano-4-(4-nitrophenyl)-2-p-tolylcyclopent-1-enecarboxylate (3r). A colorless solid, 36 mg, 70% yield; m. p. 44-45 ^{o}C; IR (KBr): ν 2979, 2927, 1712, 1606, 1522, 1436, 1349, 1268, 1228, 1147, 965, 853, 736, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.36 (s, 9H, $3CH_3$), 2.39 (s, 3H, CH_3), 3.61 (d, 1H, *J* = 17.6 Hz, CH_2), 3.71 (s, 3H, OCH_3), 3.94 (d, 1H, *J* = 17.6 Hz, CH_2), 6.08 (s, 1H, $=CH_2$), 6.69 (s, 1H, $=CH_2$), 7.25 (d, 2H, *J* = 8.0 Hz, ArH), 7.30 (d, 2H, *J* = 8.0 Hz, ArH), 7.69 (d, 2H, *J* = 8.8 Hz, ArH), 8.27 (d, 2H, *J* = 8.8 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 21.2, 27.5, 42.6, 52.1, 55.1, 61.7, 82.8, 111.7, 112.1, 123.5, 126.7, 127.7, 128.1, 128.5, 129.0, 133.2, 140.5, 140.7, 143.6, 144.7, 147.5, 163.1, 163.8; HRMS (ESI) Calcd. For $C_{29}H_{31}N_4O_6^{+1}$ $(M+NH_4)^+$ requires 531.2244, Found: 531.2225.

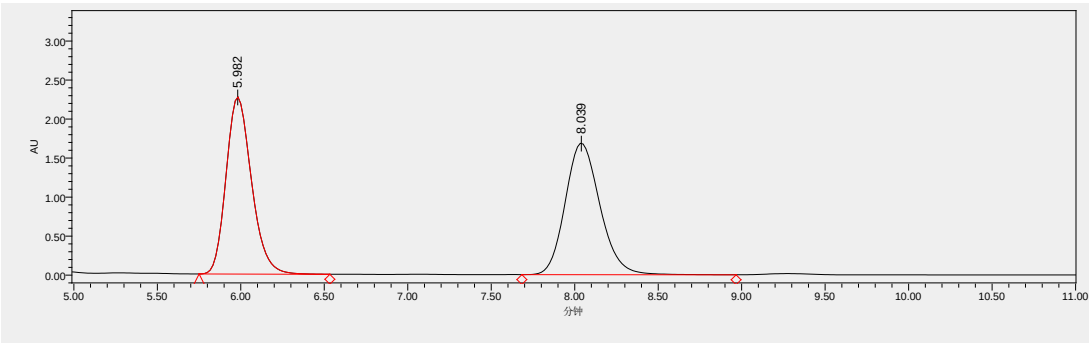


HPLC REPORT

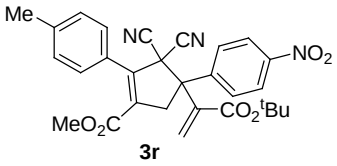
Sample Name: zhxn-10-12 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 60/40

Velocity (mL/min): 0.75 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	5.982	24038951	49.64	2266592
2	8.039	24385683	50.36	1686304



3r

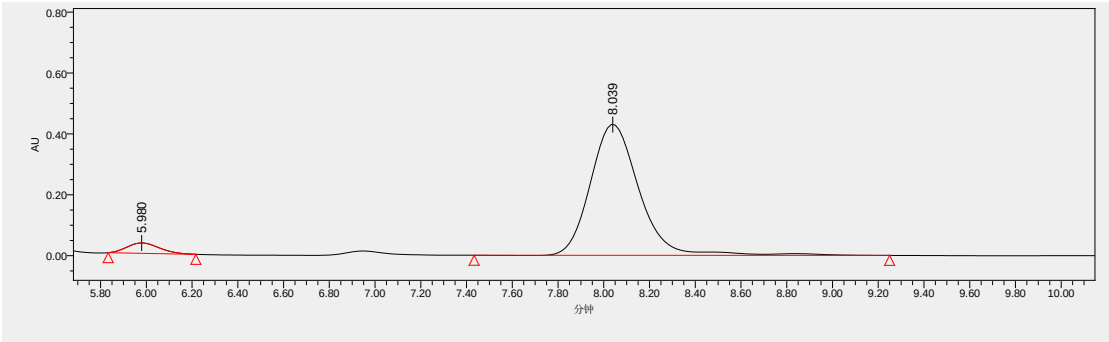
Chiral HPLC report: racemate (**3r**)

HPLC REPORT

Sample Name: zhxn-10-12 Date: ###

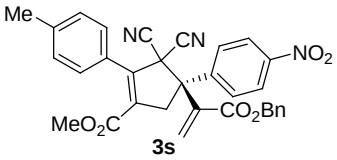
Column: AD-H Mobile Phase: hex/ipr = 60/40

Velocity (mL/min): 0.75 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	5.980	336170	4.98	34260
2	8.039	6415209	95.02	430700

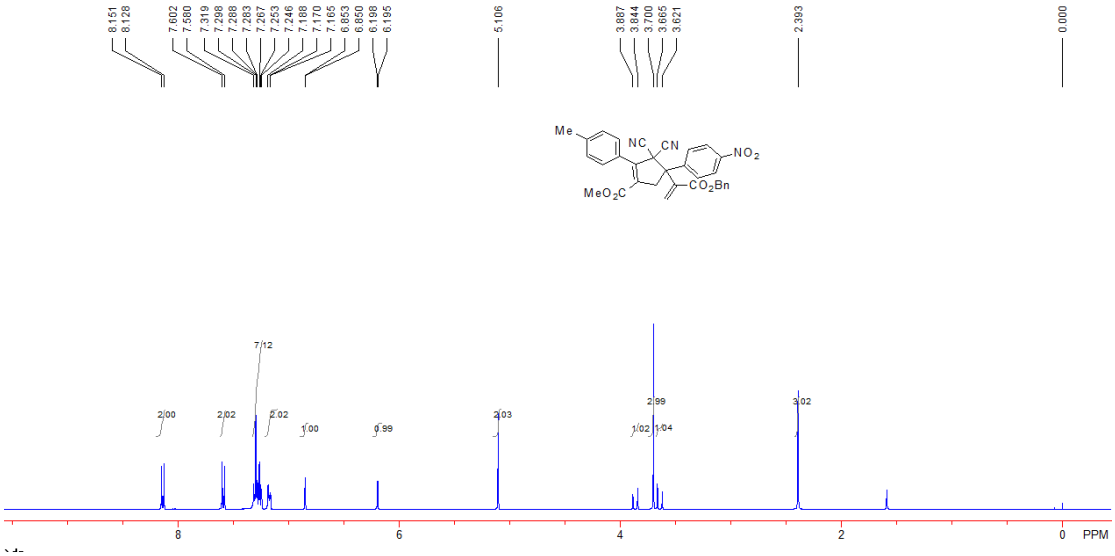
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 214 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.75 mL/min; t_{minor} = 5.98 min, t_{major} = 8.04 min; ee% = 90%; $[\alpha]^{20}_{D}$ = +59.6 (c 0.80, $CHCl_3$).

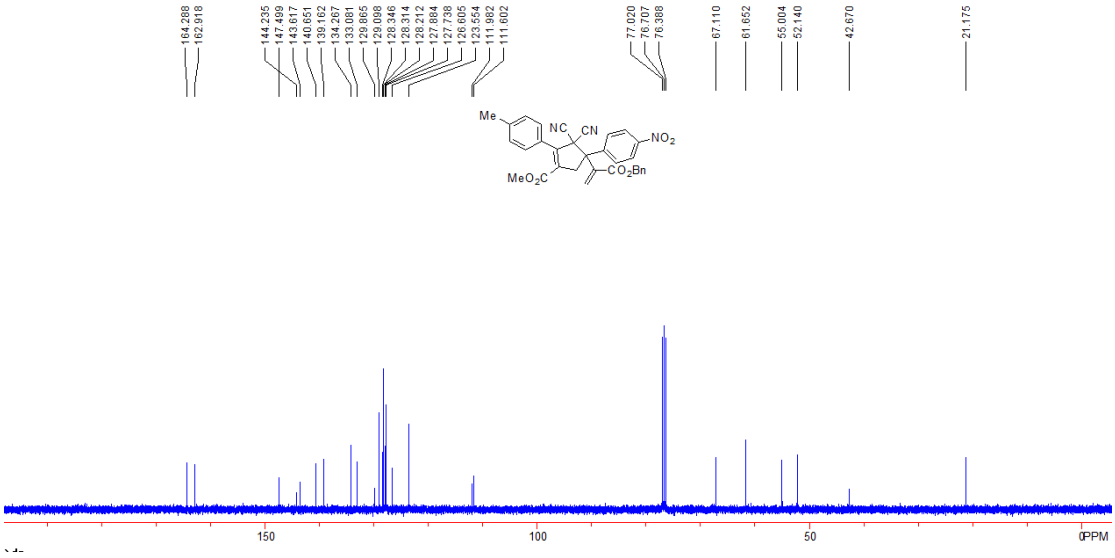


3s

(*R*)-methyl

4-(1-((benzyloxy)carbonyl)vinyl)-3,3-dicyano-4-(4-nitrophenyl)-2-p-tolylcyclopent-1-enecarboxyl ate (3s). A colorless solid, 44 mg, 80% yield; m. p. 42-43 ^{o}C; IR (KBr): ν 3036, 2953, 2858, 1716, 1606, 1522, 1436, 1348, 1266, 1227, 1169, 963, 854, 816, 733, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.39 (s, 3H, CH_3), 3.64 (d, 1H, *J* = 17.6 Hz, CH_2), 3.70 (s, 3H, OCH_3), 3.87 (d, 1H, *J* = 17.6 Hz, CH_2), 5.11 (s, 2H, CH_2), 6.20 (d, *J* = 1.2 Hz, 1H, =CH_2), 6.85 (d, 1H, *J* = 1.2 Hz, =CH_2), 7.17-7.19 (m, 2H, ArH), 7.25-7.32 (m, 7H, ArH), 7.59 (d, 2H, *J* = 8.8 Hz, ArH), 8.14 (d, 2H, *J* = 8.8 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 21.1, 42.7, 52.1, 55.0, 61.7, 67.1, 111.6, 112.0, 123.6, 126.6, 127.7, 127.9, 128.2, 128.31, 128.34, 129.1, 129.9, 133.1, 134.3, 139.2, 140.7, 143.6, 144.2, 147.5, 162.9, 164.3; HRMS (ESI) Calcd. For $C_{32}H_{29}N_4O_6^{+1}$ $(M+NH_4)^+$ requires 565.2087, Found: 565.2070.



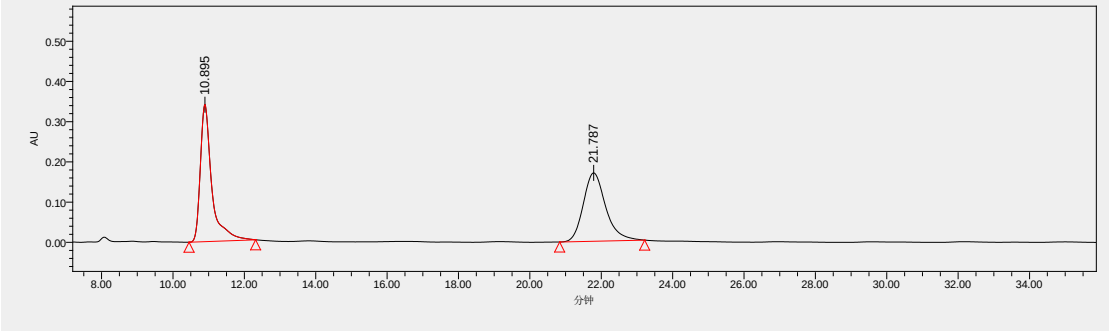


HPLC REPORT

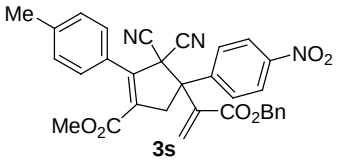
Sample Name: zhxn-10-13 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 60/40

Velocity (mL/min): 0.75 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	10.895	7619102	50.75	341055
2	21.787	7391583	49.24	169973



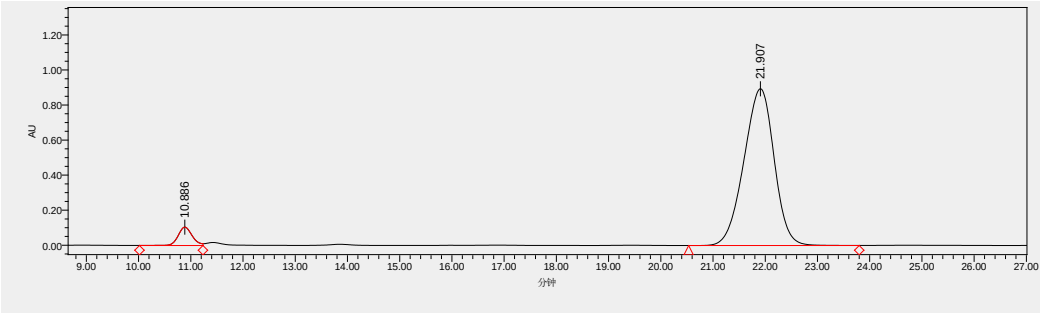
Chiral HPLC report: racemate (**3s**)

HPLC REPORT

Sample Name: zhxn-10-13 Date: ###

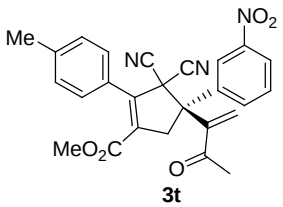
Column: AD-H Mobile Phase: hex/ipr = 60/40

Velocity (mL/min): 0.75 Detection Wavelength (nm): 214



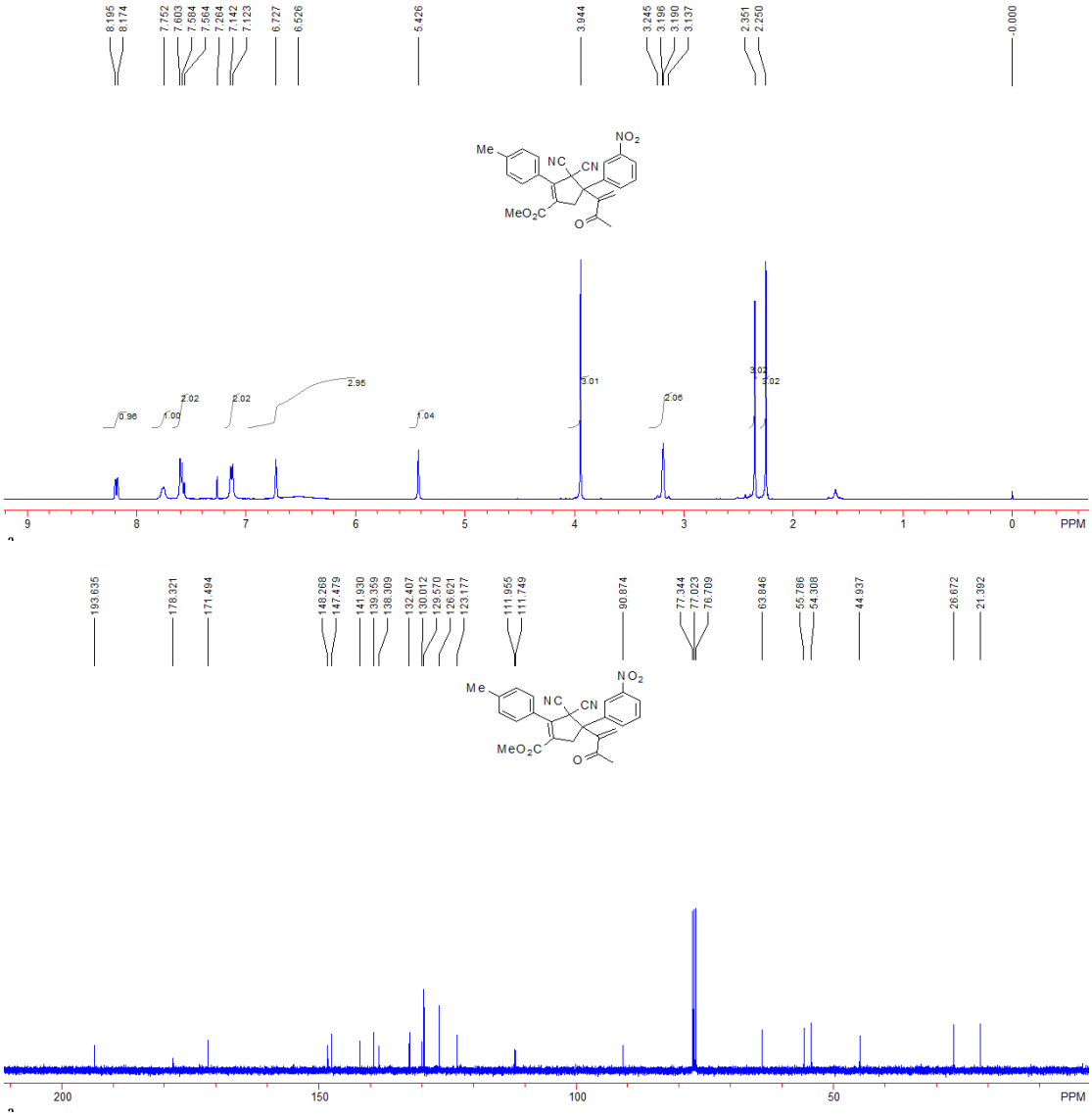
NO	R. Time	Peak Area	Percent	Peak Height
1	10.886	1959850	5.16	104959
2	21.907	36029562	94.84	894825

Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 214 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.75 mL/min; t_{minor} = 10.89 min, t_{major} = 21.91 min; ee% = 90%; $[\alpha]^{20}_{D}$ = +88.8 (c 2.00, $CHCl_3$).



3t

compound 3t. A colorless solid, 41 mg, 90% yield; m. p. 160-161 ^{o}C; IR (KBr): ν 2955, 2925, 2854, 2360, 1744, 1673, 1625, 1529, 1439, 1350, 1221, 1169, 1087, 959, 811, 737 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.25 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 3.14-3.25 (m, 2H, CH_2), 3.94 (s, 3H, OCH_3), 5.43 (s, 1H, =CH), 6.53 (brs, 2H, ArH), 6.73 (s, 1H, =CH), 7.13 (d, 2H, *J* = 7.6 Hz, ArH), 7.56-7.60 (m, 2H, ArH), 7.75 (s, 1H, ArH), 8.18 (d, 1H, *J* = 8.4 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 21.4, 26.7, 44.9, 54.3, 55.8, 63.8, 90.9, 111.7, 112.0, 123.2, 126.6, 129.6, 130.0, 132.4, 138.3, 139.4, 141.9, 147.5, 148.3, 171.5, 178.3, 193.6; HRMS (ESI) Calcd. For $C_{26}H_{25}N_4O_5^{+1}$ $(M+NH_4)^+$ requires 473.1825, Found: 473.1813.

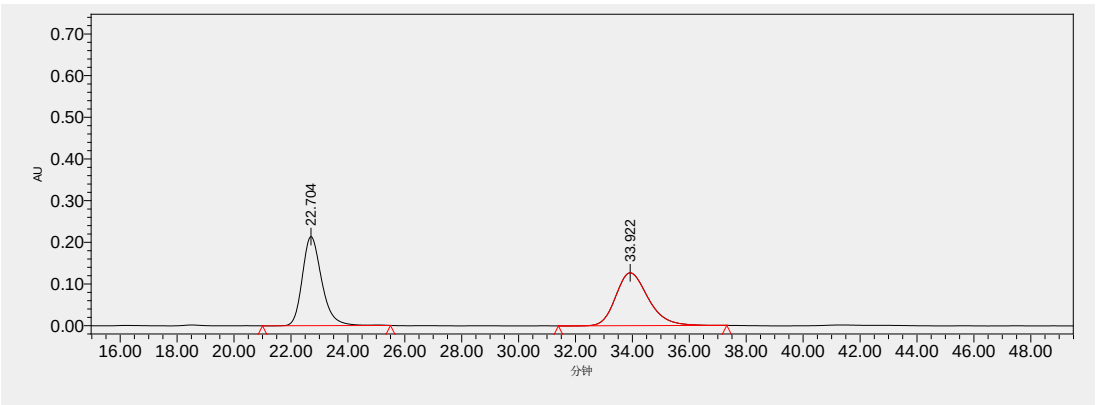


HPLC REPORT

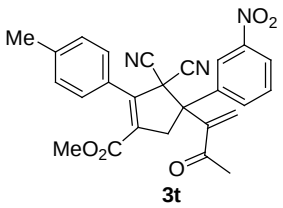
Sample Name: zhxn-10-31 Date: ####

Column: pc-2 Mobile Phase: hex/ipr = 60/40

Velocity (mL/min): 0.5 Detection Wavelength (nm): 230



NO	R. Time	Peak Area	Percent	Peak Height
1	22.704	10131770	50.16	213861
2	33.922	10065505	49.84	126897



3t

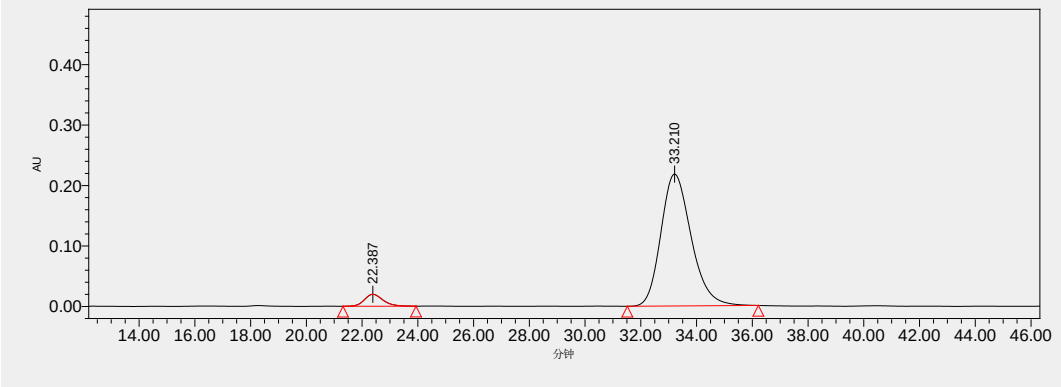
Chiral HPLC report: racemate (**3t**)

HPLC REPORT

Sample Name: zhxn-10-31 Date: ###

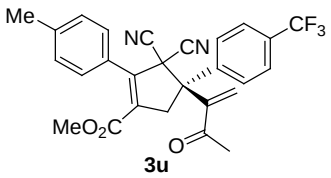
Column: pc-2 Mobile Phase: hex/ipr = 60/40

Velocity (mL/min): 0.5 Detection Wavelength (nm): 230



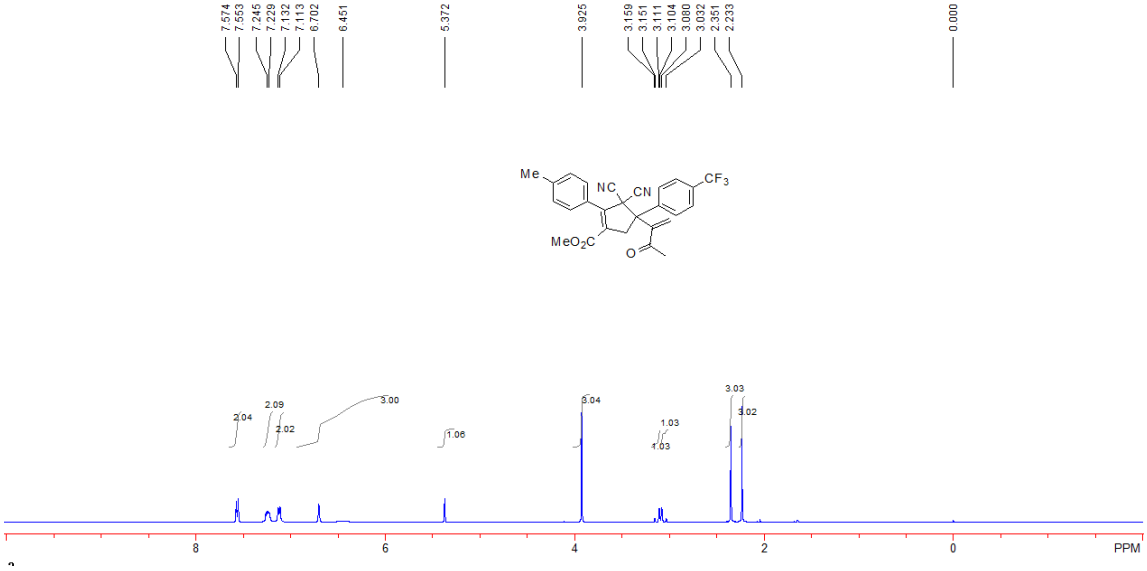
NO	R. Time	Peak Area	Percent	Peak Height
1	22.387	905968	5.21	19664
2	33.210	16471121	94.79	218114

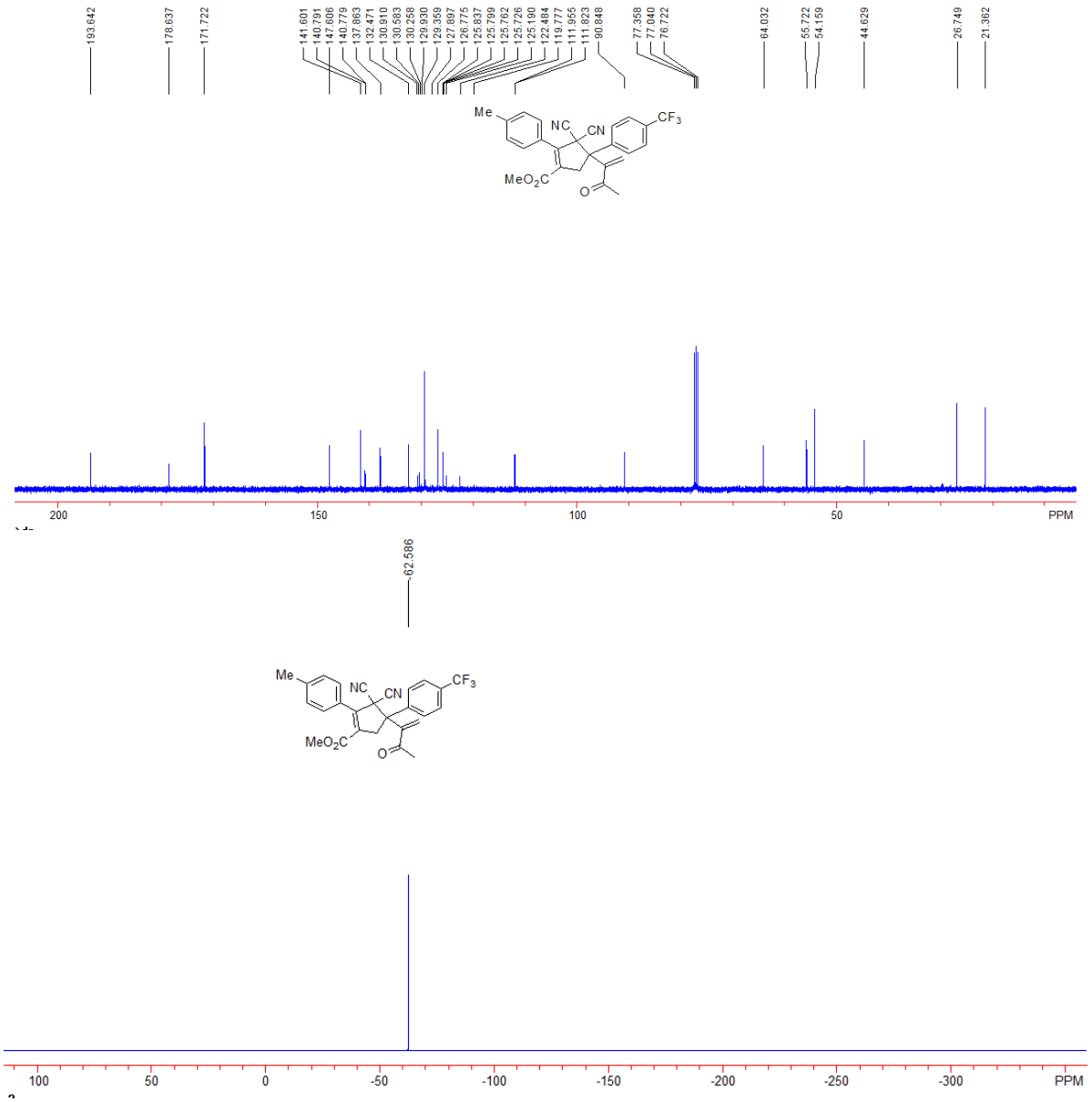
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak PC-2 column; λ = 230 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.5 mL/min; t_{minor} = 22.39 min, t_{major} = 33.21 min; ee% = 90%; $[\alpha]^{20}_{D}$ = -567.1 (c 2.10, $CHCl_3$).



3u

compound 3u. A colorless solid, 41 mg, 86% yield; m. p. 112-113 ^{o}C; IR (KBr): ν 2957, 2923, 2365, 2233, 1746, 1673, 1618, 1420, 1325, 1242, 1221, 1166, 1114, 1069, 1018, 812,738 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.23 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 3.07 (d, 1H, *J* = 19.2 Hz, CH_2), 3.13 (dd, 1H, *J* = 19.2, 3.2 Hz, CH_2), 3.93 (s, 3H, OCH_3), 5.37 (s, 1H, =CH), 6.45 (brs, 2H, ArH), 6.70 (s, 1H, =CH), 7.12 (d, 2H, *J* = 7.6 Hz, ArH), 7.23-7.25 (m, 2H, ArH), 7.56 (d, 1H, *J* = 8.4 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 21.4, 26.7, 44.6, 54.2, 55.7, 64.0, 90.8, 111.8, 112.0, 123.8 (q, *J* = 270.6 Hz), 125.8 (q, *J* = 3.7 Hz), 126.8, 129.4, 130.42 (q, *J* = 32.5 Hz), 132.5, 137.9, 140.78, 140.79, 141.6, 147.6, 171.7, 178.6, 193.6; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -62.59; HRMS (ESI) Calcd. For $C_{27}H_{25}F_3N_3O_3^{+1}$ $(M+NH_4)^+$ requires 496.1848, Found: 496.1849.



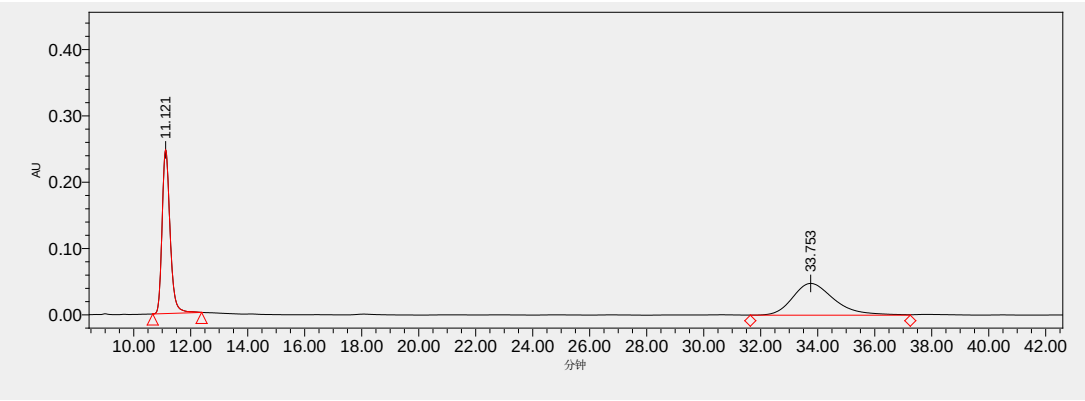


HPLC REPORT

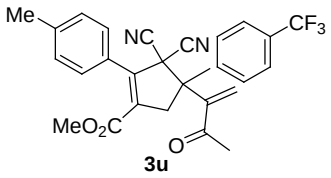
Sample Name: zhxn-10-32 Date: ####

Column: PC-2 Mobile Phase: hex/ipr = 60/40

Velocity (mL/min): 0.5 Detection Wavelength (nm): 230



NO	R. Time	Peak Area	Percent	Peak Height
1	11.121	4813878	49.72	247155
2	33.753	4868679	50.28	47879



3u

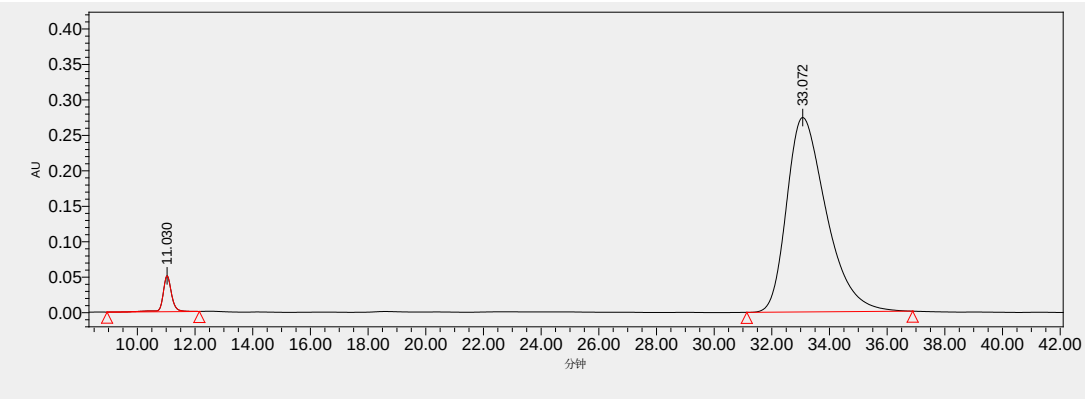
Chiral HPLC report: racemate (**3u**)

HPLC REPORT

Sample Name: zhxn-10-32 Date: ###

Column: PC-2 Mobile Phase: hex/ipr = 60/40

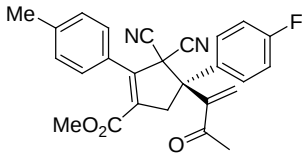
Velocity (mL/min): 0.5 Detection Wavelength (nm): 230



NO	R. Time	Peak Area	Percent	Peak Height
1	11.030	1040090	3.83	50534

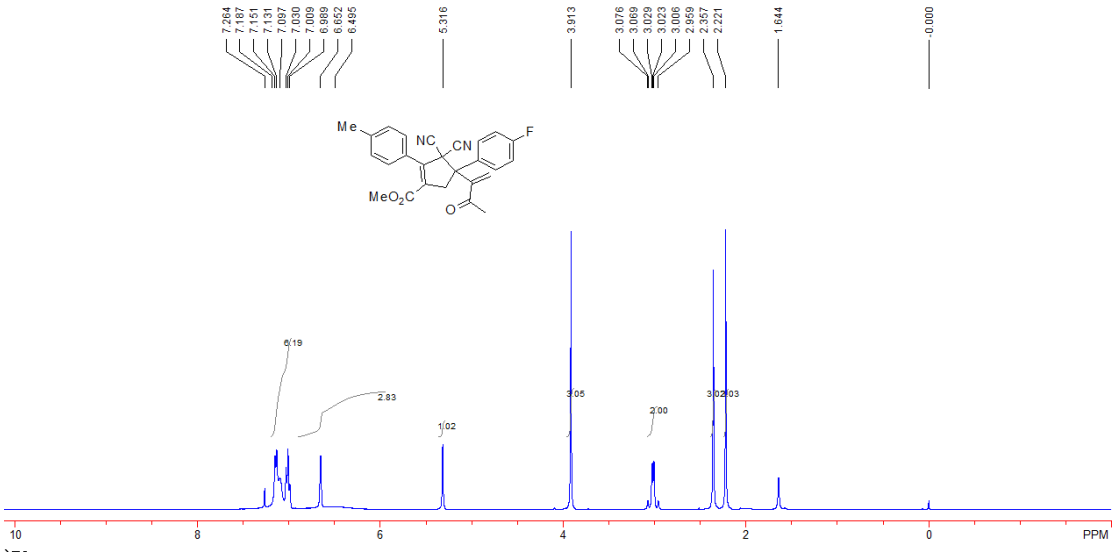
2	33.070	26108183	96.17	274174

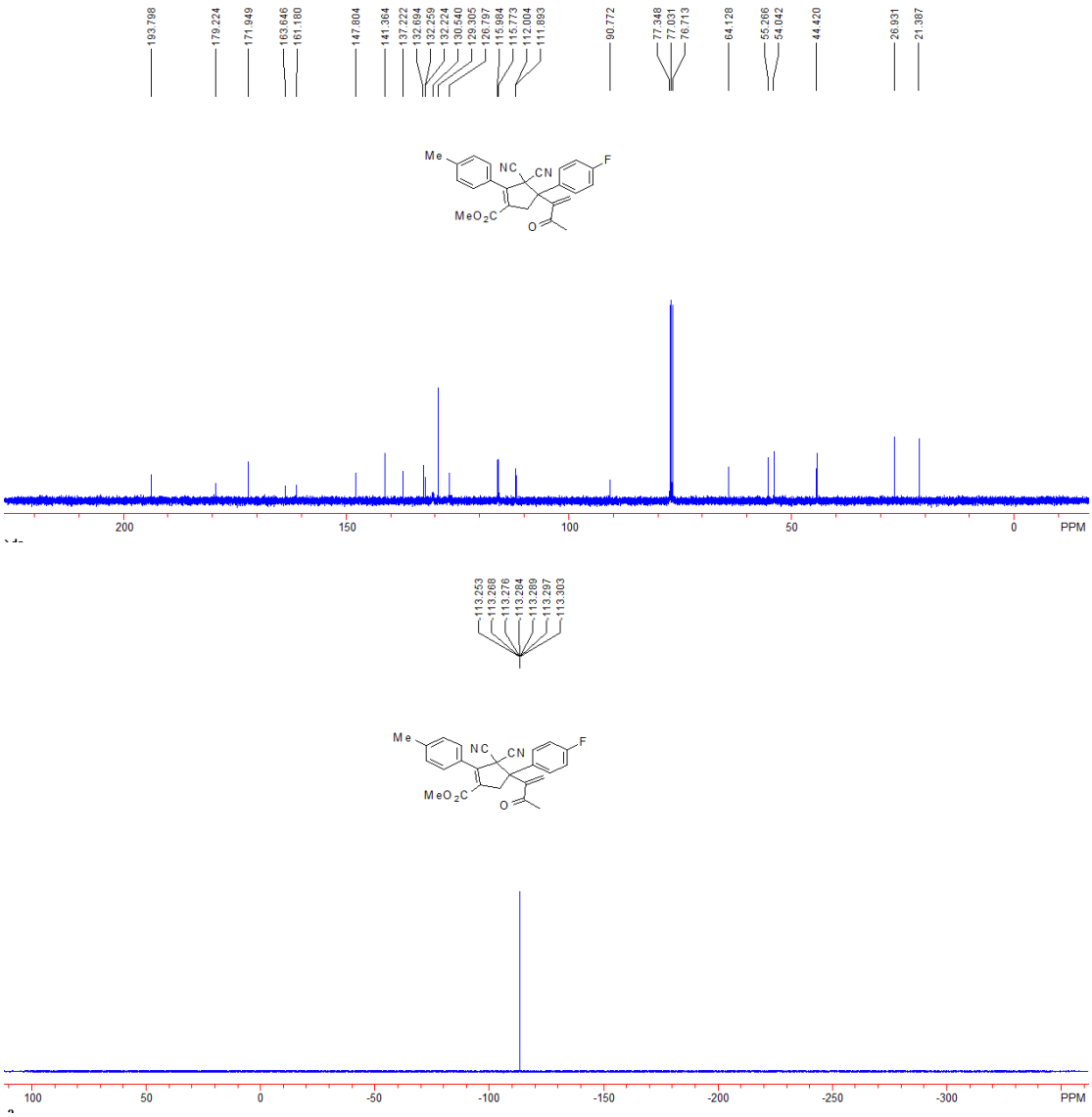
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak PC-2 column; λ = 230 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.5 mL/min; t_{minor} = 11.03 min, t_{major} = 33.07 min; ee% = 92%; $[\alpha]^{20}_{D}$ = -585.5 (c 1.70, $CHCl_3$).



3v

compound 3v. A colorless solid, 38 mg, 88% yield; m. p. 167-168 ^{o}C; IR (KBr): ν 2955, 2919, 2360, 2342, 2231, 1745, 1671, 1605, 1508, 1434, 1369, 1221, 1162, 842, 797, 736, 668 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.22 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 2.96-3.08 (m, 2H, CH_2), 3.91 (s, 3H, OCH_3), 5.32 (s, 1H, =CH), 6.50 (brs, 2H, ArH), 6.65 (s, 1H, =CH), 6.99-7.19 (m, 6H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 21.4, 26.9, 44.4, 54.0, 55.3, 64.1, 90.8, 111.9, 112.0, 115.9 (d, *J* = 21.1 Hz), 126.8, 129.3, 130.5, 132.2 (d, *J* = 3.5 Hz), 132.7, 137.2, 141.4, 147.8, 162.4 (d, *J* = 246.6 Hz), 171.9, 179.2, 193.8; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -113.28; HRMS (ESI) Calcd. For $C_{26}H_{22}FN_2O_3^{+1}$ $(M+H)^+$ requires 429.1614, Found: 429.1607.



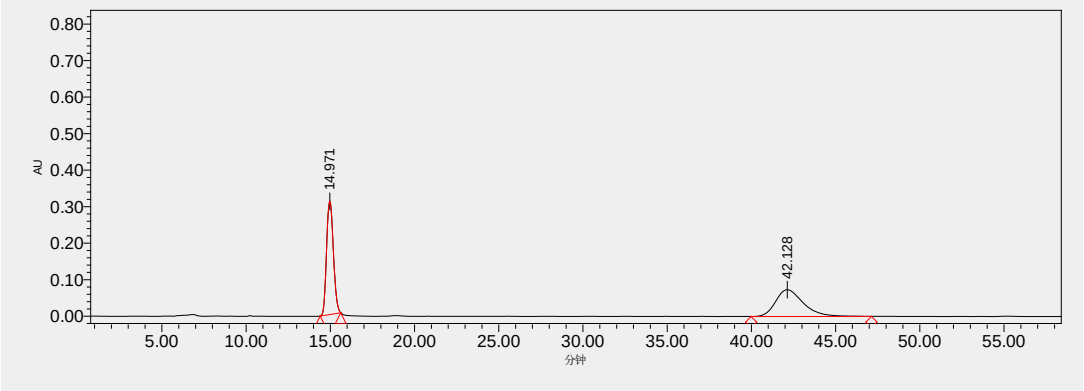


HPLC REPORT

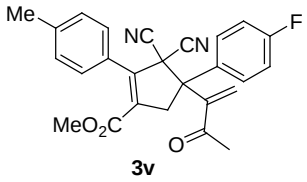
Sample Name: zhxn-10-33 Date: ####

Column: PC-2 Mobile Phase: hex/ipr = 60/40

Velocity (mL/min): 0.5 Detection Wavelength (nm): 230



NO	R. Time	Peak Area	Percent	Peak Height
1	14.971	8719090	50.82	310204
2	42.128	8438268	49.18	73349



3v

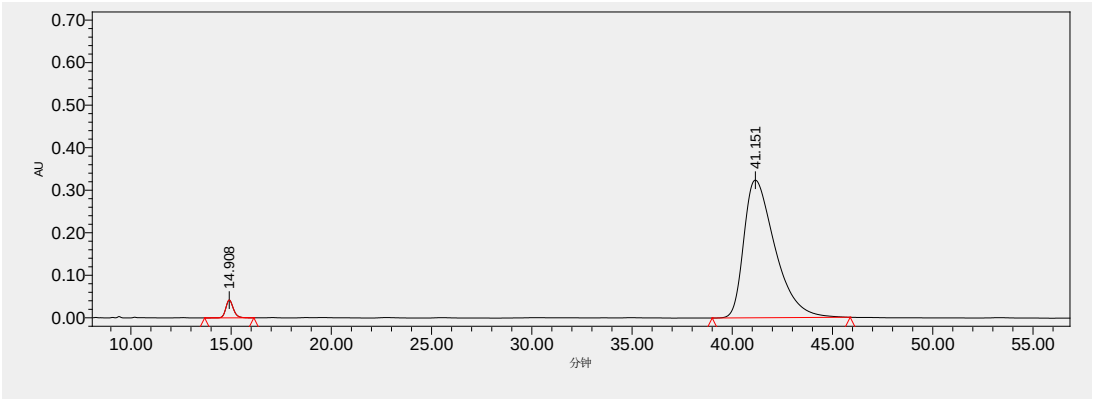
Chiral HPLC report: racemate (**3v**)

HPLC REPORT

Sample Name: zhxn-10-33 Date: ###

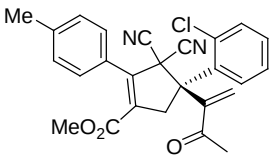
Column: PC-2 Mobile Phase: hex/ipr = 60/40

Velocity (mL/min): 0.5 Detection Wavelength (nm): 230



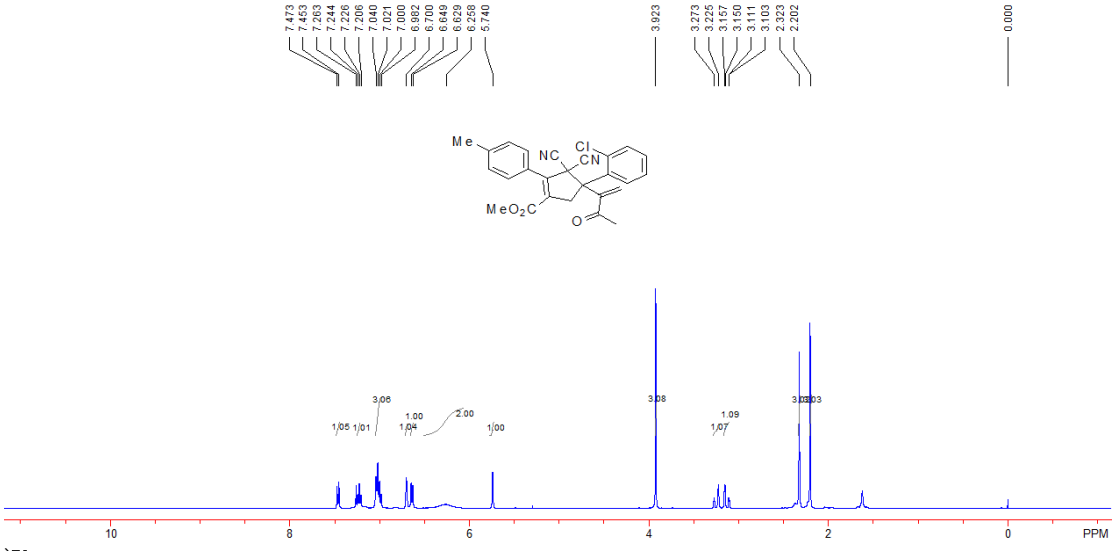
NO	R. Time	Peak Area	Percent	Peak Height
1	14.908	1099180	3.05	418739
2	41.151	34940982	96.95	323580

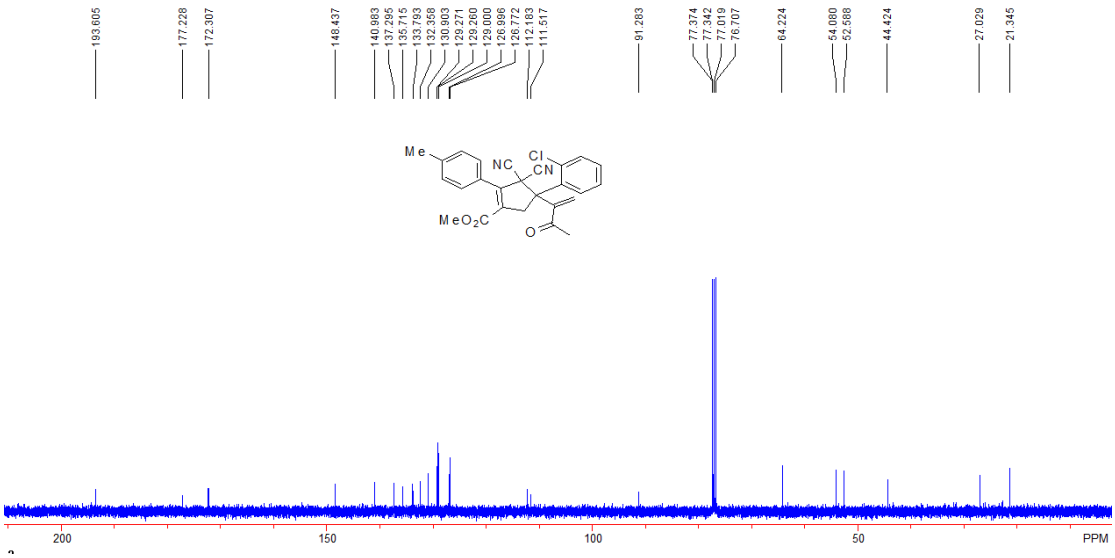
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak PC-2 column; λ = 230 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.5 mL/min; t_{minor} = 14.91 min, t_{major} = 41.15 min; ee% = 94%; $[\alpha]^{20}_{D}$ = -563.4 (c 1.90, $CHCl_3$).



3w

compound 3w. A colorless solid, 18 mg, 41% yield; m. p. 145-146 ^{o}C; IR (KBr): ν 2953, 2924, 2853, 2360, 2342, 2230, 1746, 1671, 1627, 1440, 1368, 1251, 1219, 1167, 1042, 961, 810, 733, 702 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.20 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 3.13 (dd, 1H, *J* = 18.8, 3.2 Hz, CH_2), 3.25 (d, 1H, *J* = 18.8 Hz, ArH), 3.92 (s, 3H, OCH_3), 5.74 (s, 1H, =CH), 6.26 (brs, 2H, ArH), 6.64 (d, 1H, *J* = 8.0 Hz, ArH), 6.70 (s, 1H, =CH), 6.98-7.04 (m, 3H, ArH), 7.21-7.24 (m, 1H, ArH), 7.46 (d, 1H, *J* = 8.0 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 21.3, 27.0, 44.4, 52.6, 54.1, 64.2, 91.3, 111.5, 112.2, 126.8, 127.0, 129.0, 129.26, 129.27, 130.9, 132.4, 133.8, 135.7, 137.3, 141.0, 148.4, 172.3, 177.2, 193.6; HRMS (ESI) Calcd. For $C_{26}H_{25}ClN_3O_3^{+1}$ $(M+NH_4)^+$ requires 462.1548, Found: 462.1575.



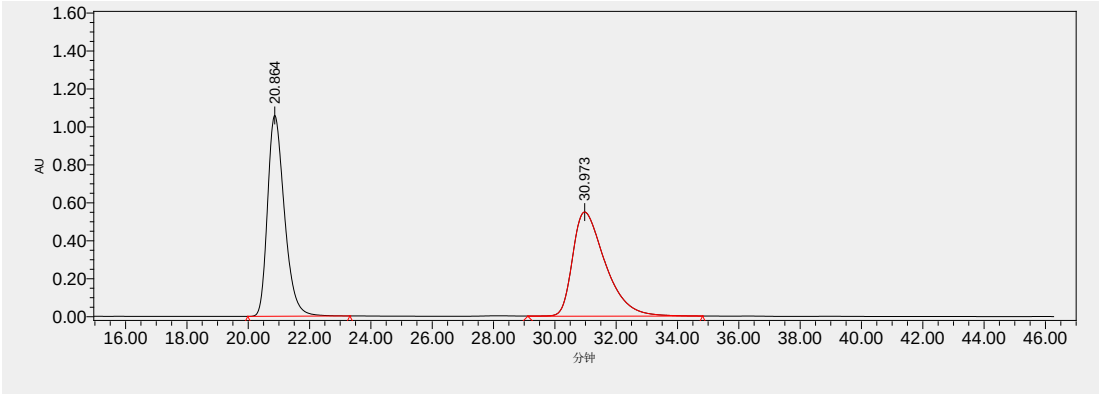


HPLC REPORT

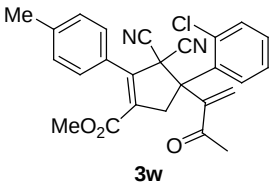
Sample Name: zhxn-10-39 Date: ####

Column: PC-2 Mobile Phase: hex/ipr = 60/40

Velocity (mL/min): 0.5 Detection Wavelength (nm): 230



NO	R. Time	Peak Area	Percent	Peak Height
1	20.864	40462528	49.88	1058277
2	30.973	40651813	50.12	548567



3w

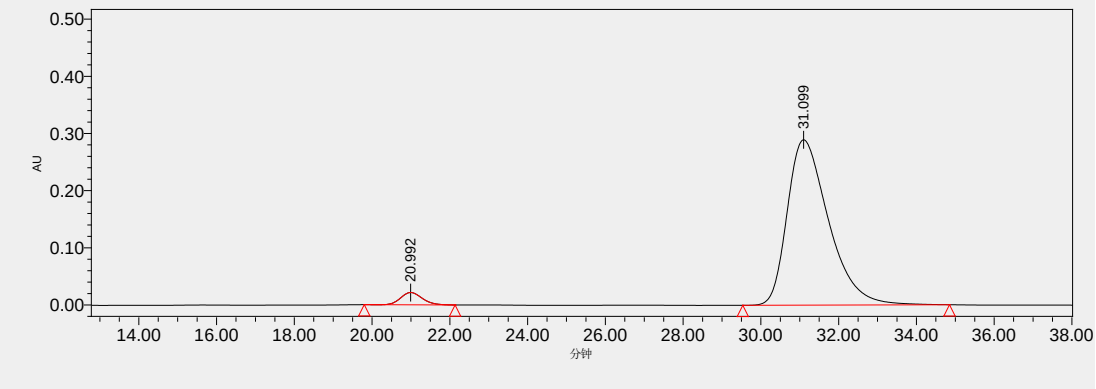
Chiral HPLC report: racemate (**3w**)

HPLC REPORT

Sample Name: zhxn-10-39 Date: ###

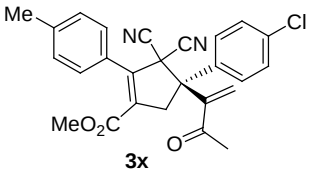
Column: PC-2 Mobile Phase: hex/ipr = 60/40

Velocity (mL/min): 0.5 Detection Wavelength (nm): 230



NO	R. Time	Peak Area	Percent	Peak Height
1	20.992	829436	3.74	21527
2	31.099	21360098	96.26	289185

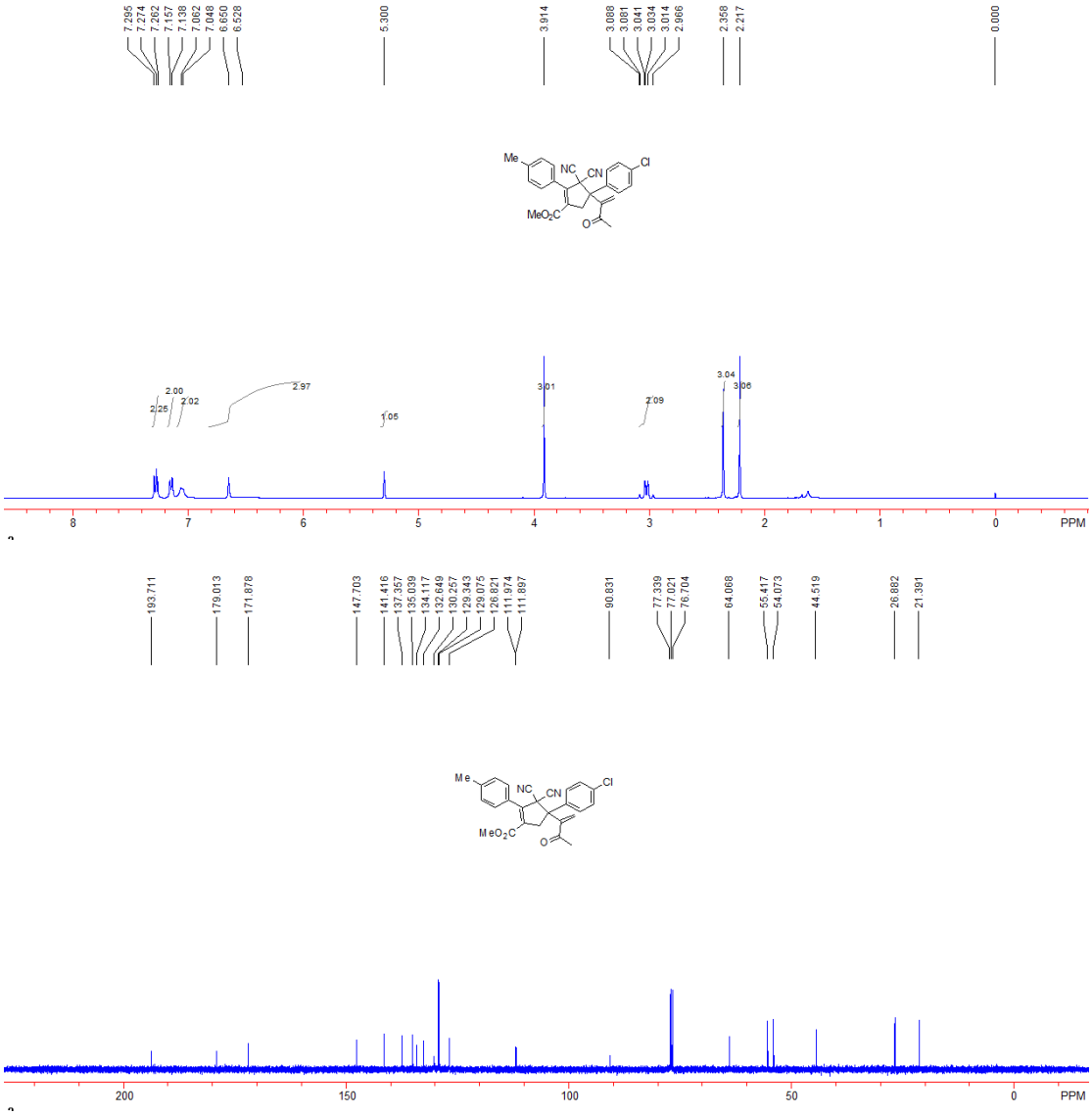
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak PC-2 column; λ = 230 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.5 mL/min; t_{minor} = 20.99 min, t_{major} = 31.10 min; ee% = 93%; $[\alpha]^{20}_{D}$ = -436.7 (c 0.80, $CHCl_3$).



3x

compound 3x. A colorless solid, 40 mg, 90% yield; m. p. 174-175 °C; IR (KBr): ν 2964, 2927, 2360, 2342, 1745, 1671, 1561, 1490, 1433, 1368, 1220, 1168, 1093, 1014, 811, 728, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 2.22 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 2.97-3.09 (m, 2H, CH_2), 3.91 (s, 3H, OCH_3), 5.30 (s, 1H, =CH), 6.53 (brs, 2H, ArH), 6.65 (s, 1H, =CH), 7.05-7.06 (m, 2H, ArH), 7.15 (d, 2H, *J* = 7.6 Hz, ArH), 7.28 (d, 1H, *J* = 8.4 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 21.4, 26.9, 44.5, 54.1, 55.4, 64.1, 90.8, 111.9, 112.0, 126.8, 129.1, 129.3, 130.3, 132.6, 134.1, 135.0, 137.4, 141.4, 147.7, 171.9, 179.0, 193.7; HRMS (ESI) Calcd. For $C_{26}H_{22}ClN_2O_3^{+1}$ $(M+H)^+$ requires 445.1319,

Found: 445.1309.

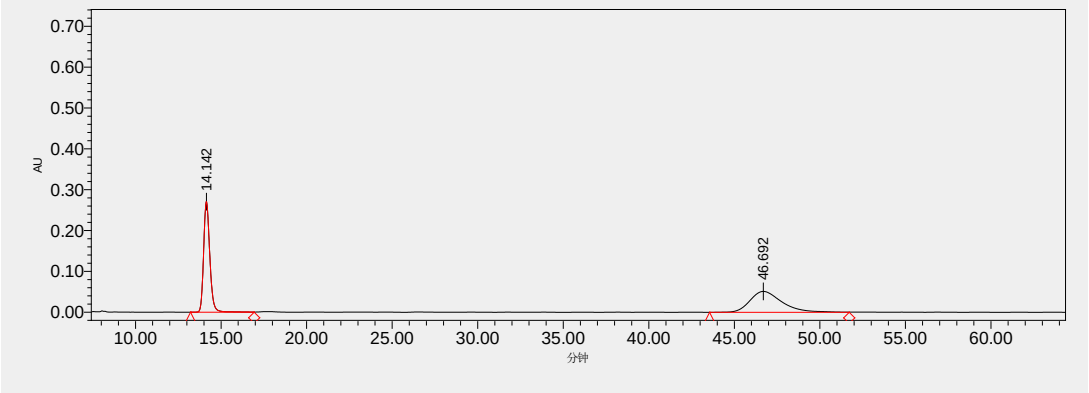


HPLC REPORT

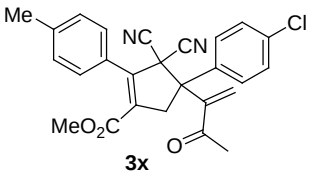
Sample Name: zhxn-10-34 Date: ####

Column: PC-2 Mobile Phase: hex/ipr = 60/40

Velocity (mL/min): 0.5 Detection Wavelength (nm): 230



NO	R. Time	Peak Area	Percent	Peak Height
1	14.142	683.4211	50.61	270854
2	46.692	6669096	49.39	51116



3x

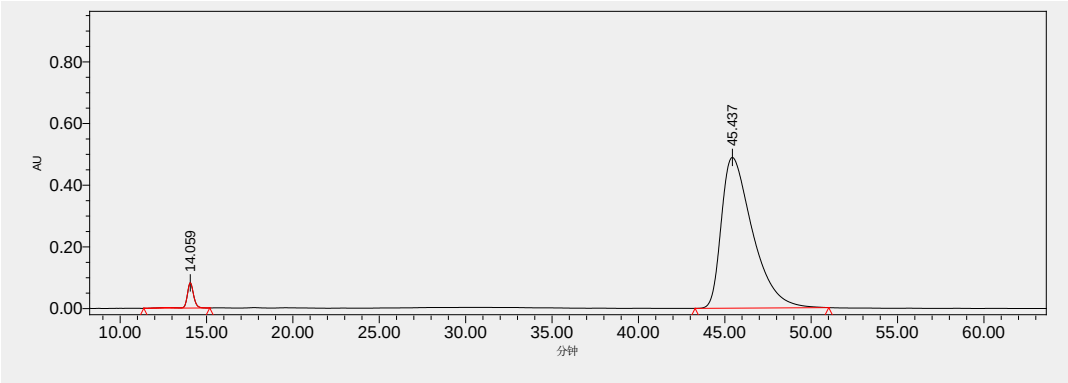
Chiral HPLC report: racemate (**3x**)

HPLC REPORT

Sample Name: zhxn-10-34 Date: ###

Column: PC-2 Mobile Phase: hex/ipr = 60/40

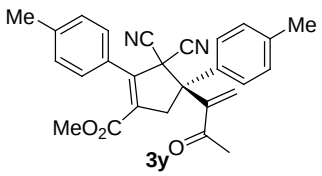
Velocity (mL/min): 0.5 Detection Wavelength (nm): 230



NO	R. Time	Peak Area	Percent	Peak Height

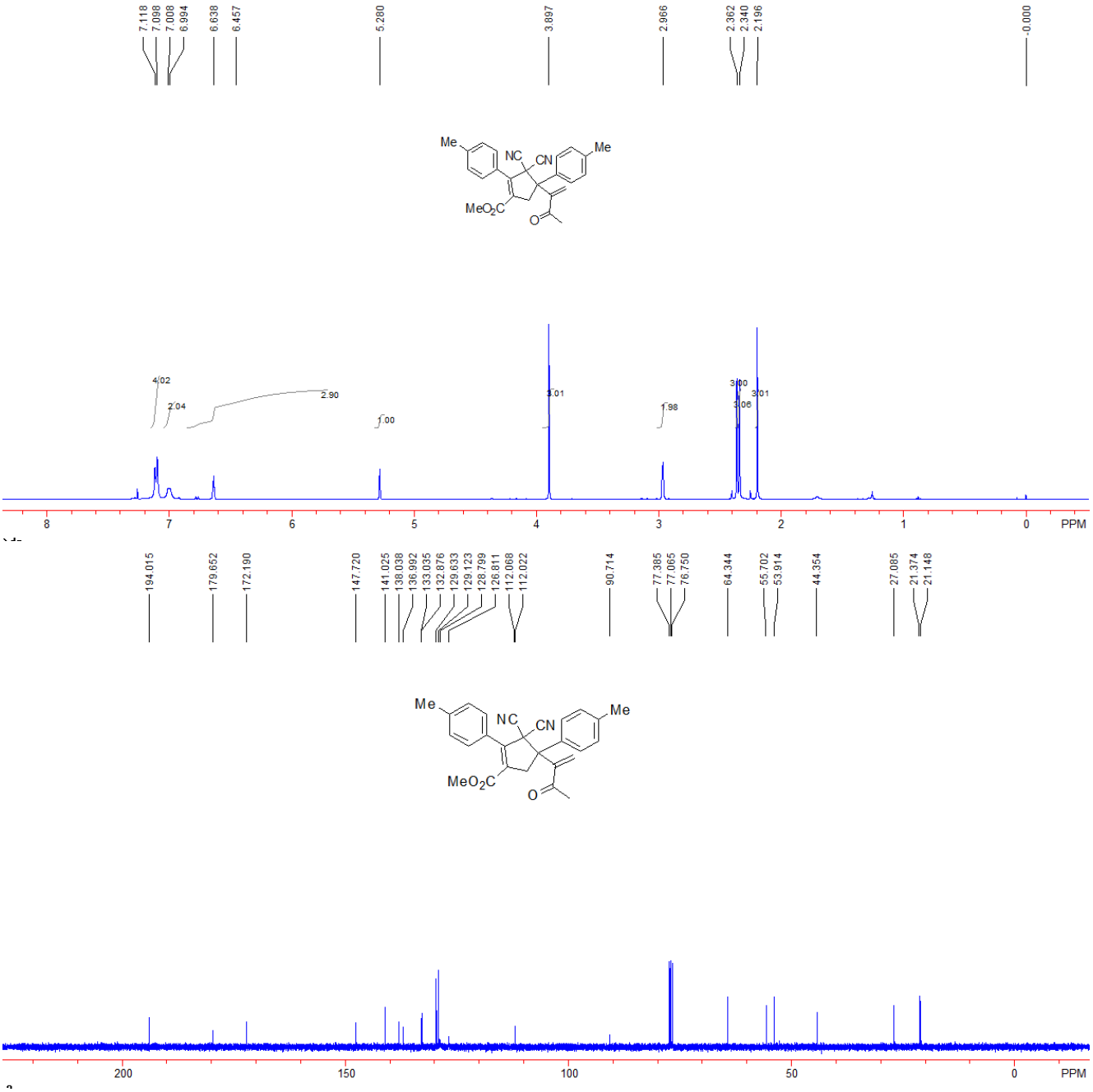
1	14.059	2192583	3.45	81889
2	45.437	61336067	96.55	488725

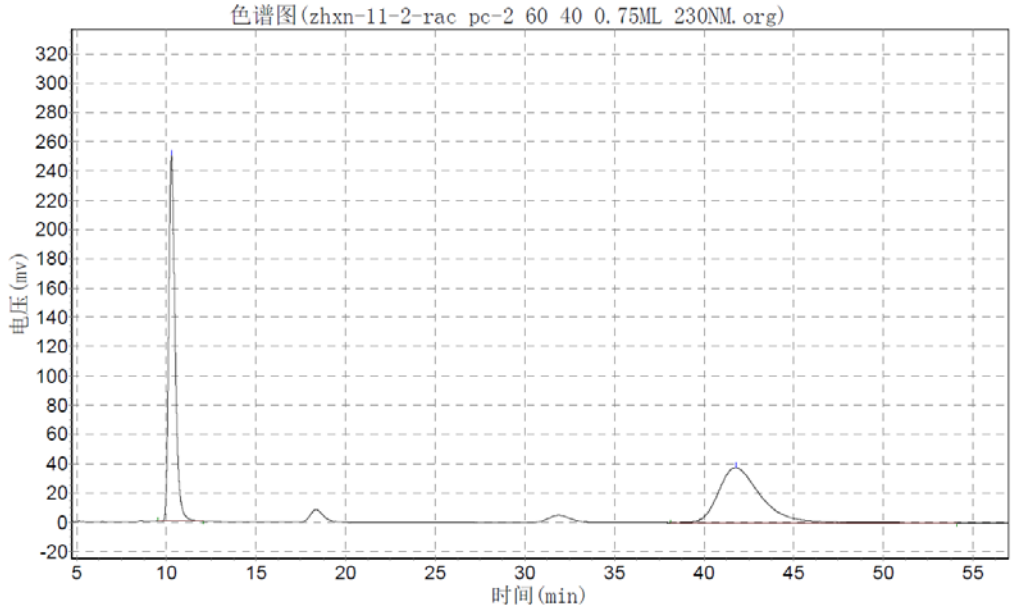
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak PC-2 column; λ = 230 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.5 mL/min; t_{minor} = 14.06 min, t_{major} = 45.44 min; ee% = 93%; $[\alpha]^{20}_{D}$ = -555.6 (c2.00, $CHCl_3$).



3y

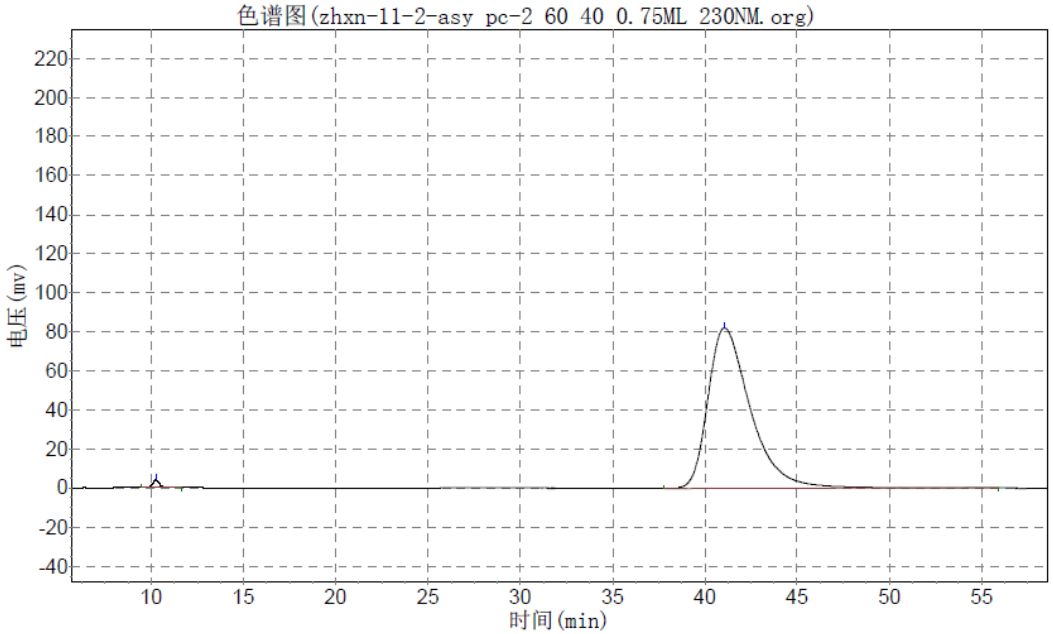
compound 3y. A colorless solid, 36 mg, 86% yield; m. p. 205-206 ^{o}C; IR (KBr): ν 2953, 2925, 2228, 1747, 1673, 1627, 1608, 1513, 1434, 1368, 1254, 1221, 1167, 1021, 961, 811, 793cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.20 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 2.95-2.98 (m, 2H, CH_2), 3.90 (s, 3H, OCH_3), 5.28 (s, 1H, =CH), 6.46 (brs, 2H, ArH), 6.64 (s, 1H, =CH), 6.99-7.01 (m, 2H, ArH), 7.10-7.12 (m, 4H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 21.1, 21.4, 27.1, 44.4, 53.9, 55.7, 64.3, 90.7, 112.0, 112.1, 126.8, 128.8, 129.1, 129.6, 132.9, 133.0, 137.0, 138.0, 141.0, 147.7, 172.2, 179.7, 194.0; HRMS (ESI) Calcd. For $C_{27}H_{28}N_3O_3^{+1}$ $(M+NH_4)^+$ requires 442.2131, Found: 442.2116; Enantiomeric excess was determined by HPLC with a Chiralcel PC-2 column [λ = 230 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.75 mL/min; t_{minor} = 10.25 min, t_{major} = 41.06 min; ee% = 98%; $[\alpha]^{20}_{D}$ = -630.6 (c 1.00, $CHCl_3$)].


7.118
7.098
7.008
6.994
6.638
6.457
5.280
3.897
2.966
2.362
2.340
2.196
0.000
Me
NC
CN
Me
MeO2C
O
4.02
2.04
2.90
1.00
3.01
1.98
3.00
3.06
3.01
PPM
194.015
179.652
172.190
147.720
141.025
138.038
136.992
133.035
132.876
129.633
129.123
128.799
126.811
112.068
112.022
90.714
77.385
77.065
76.750
64.344
55.702
53.914
44.354
27.085
21.374
21.148
Me
NC
CN
Me
MeO2C
O
200
150
100
50
0
PPM



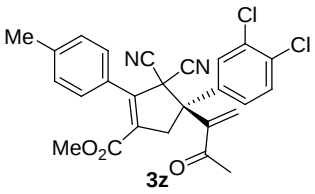
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		10.293	249560.141	6132745.000	49.8317
2		41.753	37720.449	6174158.000	50.1683
总计			287280.590	12306903.000	100.0000



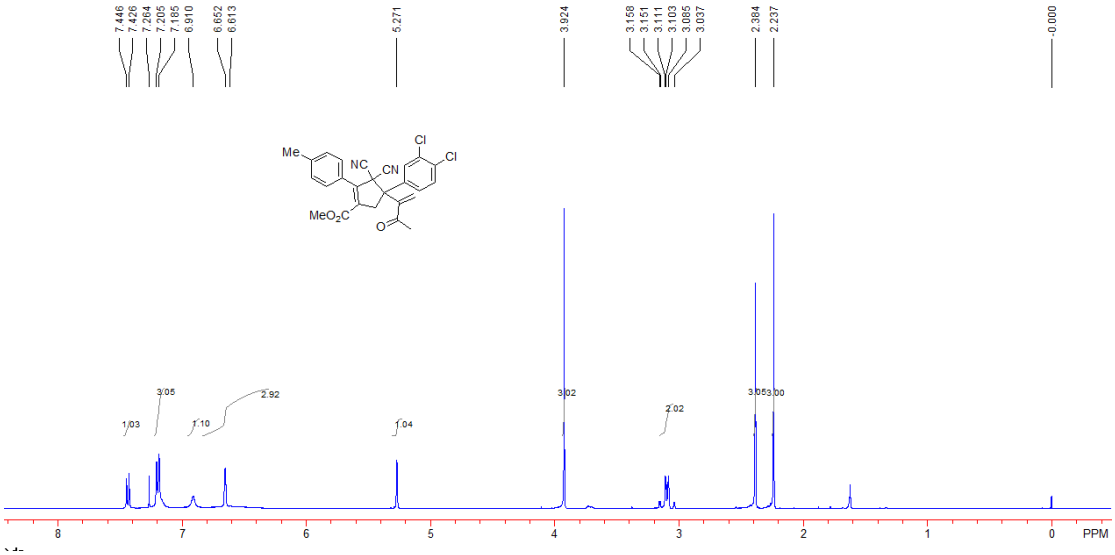
分析结果表

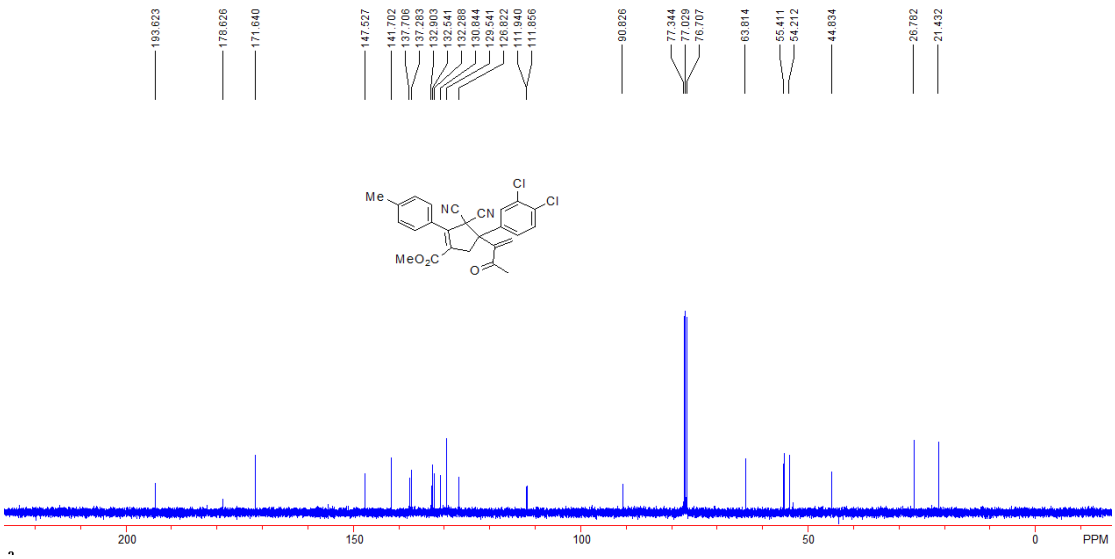
峰号	峰名	保留时间	峰高	峰面积	含量
1		10.245	3848.371	101368.539	0.7674
2		41.060	82029.586	13108800.000	99.2327
总计			85877.957	13210168.539	100.0000



3z

compound 3z. A colorless solid, 44 mg, 92% yield; m. p. 197-198 ^{o}C; IR (KBr): ν 2954, 2923, 2854, 2360, 2342, 2231, 1747, 1672, 1631, 1559, 1470, 1368, 1221, 1169, 1031, 813, 737, 668 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.24 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 3.04-3.16 (m, 2H, CH_2), 3.92 (s, 3H, OCH_3), 5.27 (s, 1H, =CH), 6.61 (brs, 2H, ArH), 6.65 (s, 1H, =CH), 6.91 (s, 1H, ArH), 7.19-7.21 (m, 3H, ArH), 7.44 (d, 1H, *J* = 8.0 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 21.4, 26.8, 44.8, 54.2, 55.4, 63.8, 90.8, 111.86, 111.9, 126.8, 129.5, 130.8, 132.3, 132.5, 132.9, 137.3, 137.7, 141.7, 147.5, 171.6, 178.6, 193.6; HRMS (ESI) Calcd. For $C_{26}H_{21}Cl_2N_2O_3^{+1}$ $(M+H)^+$ requires 479.0929, Found: 479.0916.



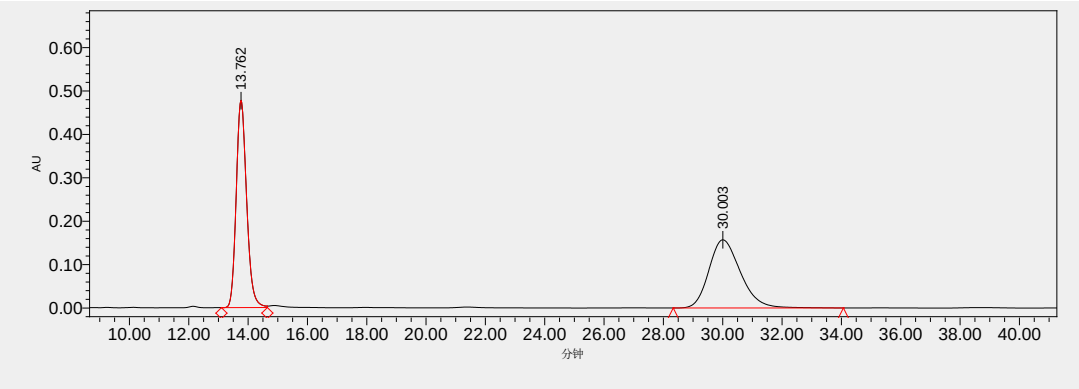


HPLC REPORT

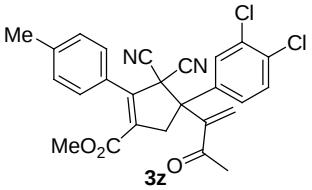
Sample Name: zhxn-10-35 Date: ####

Column: PC-2 Mobile Phase: hex/ipr = 60/40

Velocity (mL/min): 0.5 Detection Wavelength (nm): 230



NO	R. Time	Peak Area	Percent	Peak Height
1	13.762	11657947	50.08	477361
2	30.003	11622755	49.92	157063



3z

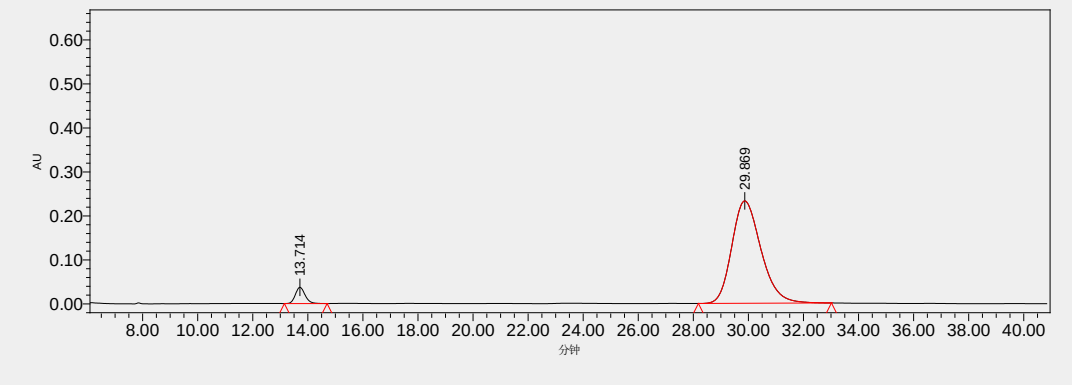
Chiral HPLC report: racemate (**3z**)

HPLC REPORT

Sample Name: zhxn-10-35 Date: ###

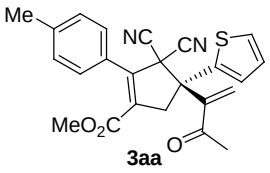
Column: PC-2 Mobile Phase: hex/ipr = 60/40

Velocity (mL/min): 0.5 Detection Wavelength (nm): 230



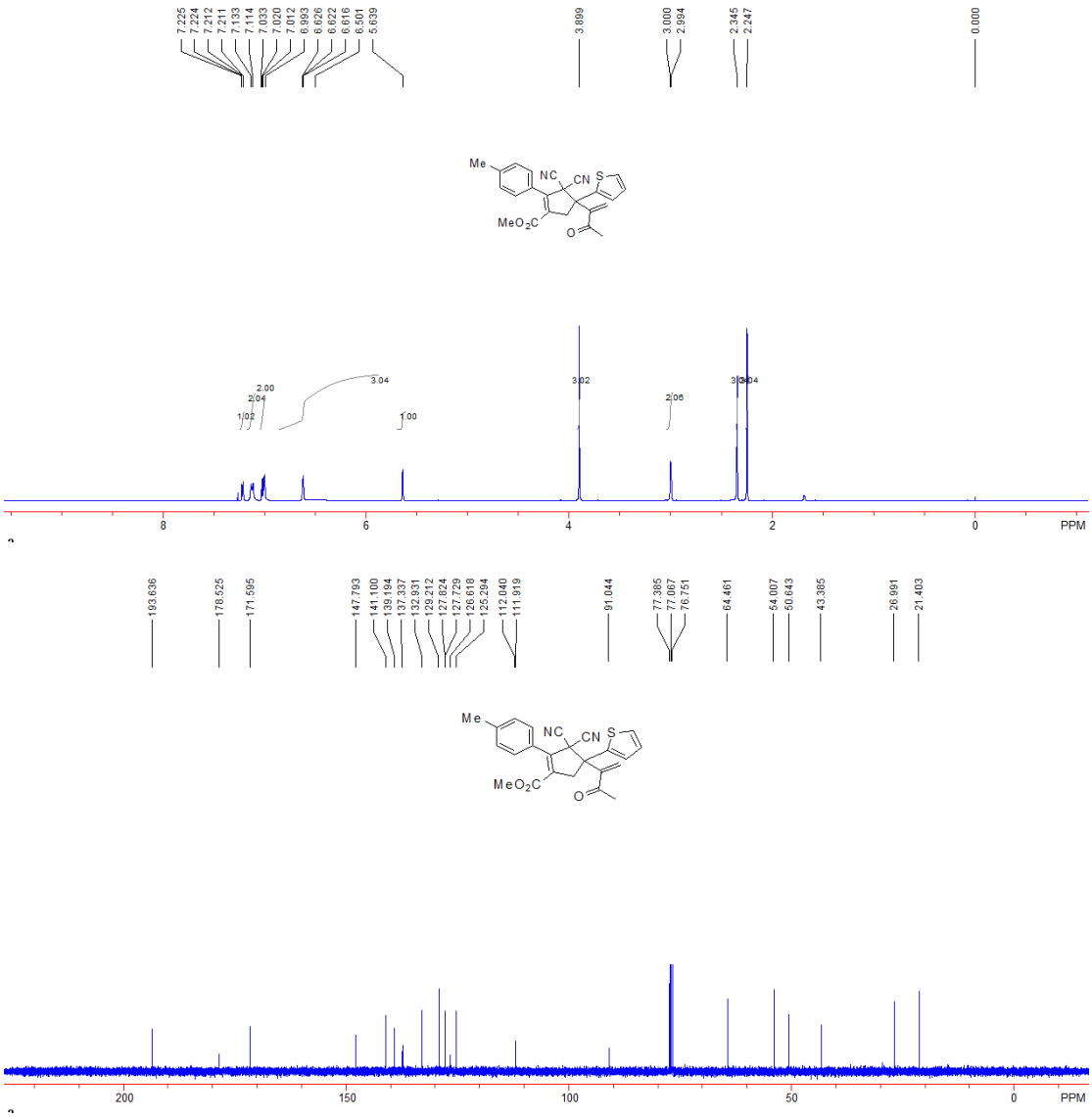
NO	R. Time	Peak Area	Percent	Peak Height
1	13.714	904111	5.0	36935
2	29.869	17174636	95.00	232696

Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak PC-2 column; λ = 230 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.5 mL/min; t_{minor} = 13.71 min, t_{major} = 29.87 min; ee% = 90%; $[\alpha]^{20}_{D}$ = -535.5 (c 2.20, $CHCl_3$).



3aa

compound 3aa. A colorless solid, 38 mg, 91% yield; m. p. 164-165 ^{o}C; IR (KBr): ν 2954, 2927, 2850, 2360, 2341, 2231, 1744, 1672, 1627, 1607, 1559, 1435, 1370, 1250, 1219, 1169, 1003, 811, 704 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.25 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.99-3.00 (m, 2H, CH_2), 3.90 (s, 3H, OCH_3), 5.64 (s, 1H, =CH), 6.50 (brs, 2H, ArH), 6.62-6.63 (m, 1H, =CH), 6.99-7.03 (m, 2H, ArH), 7.12 (d, 2H, *J* = 7.6 Hz, ArH), 7.21-7.23 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 21.4, 27.0, 43.4, 50.6, 54.0, 64.5, 91.0, 111.9, 112.0, 125.3, 126.6, 127.7, 127.8, 129.2, 132.9, 137.3, 139.2, 141.1, 147.8, 171.6, 178.5, 193.6; HRMS (ESI) Calcd. For $C_{24}H_{24}SN_3O_3^{+1}$ $(M+NH_4)^+$ requires 434.1538, Found: 434.1526.

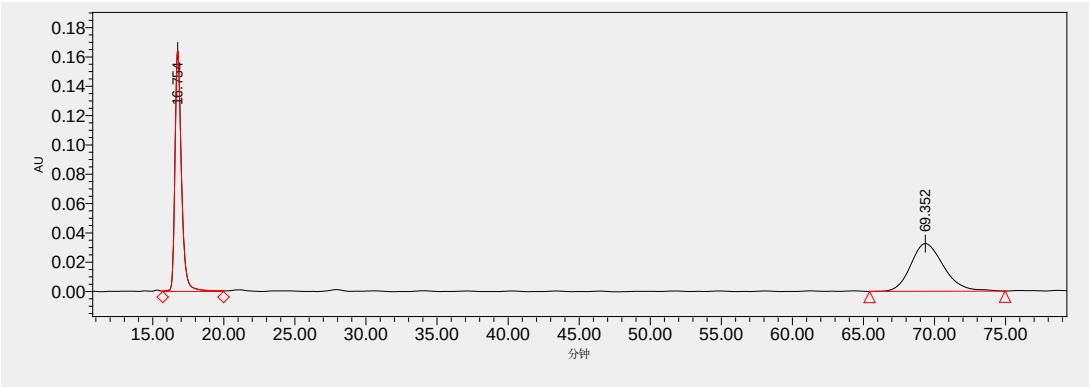


HPLC REPORT

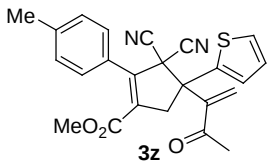
Sample Name: zhxn-10-40 Date: ####

Column: PC-2 Mobile Phase: hex/ipr = 60/40

Velocity (mL/min): 0.5 Detection Wavelength (nm): 230



NO	R. Time	Peak Area	Percent	Peak Height
1	16.754	5244951	49.97	164113
2	69.352	5251987	50.03	32531



3z

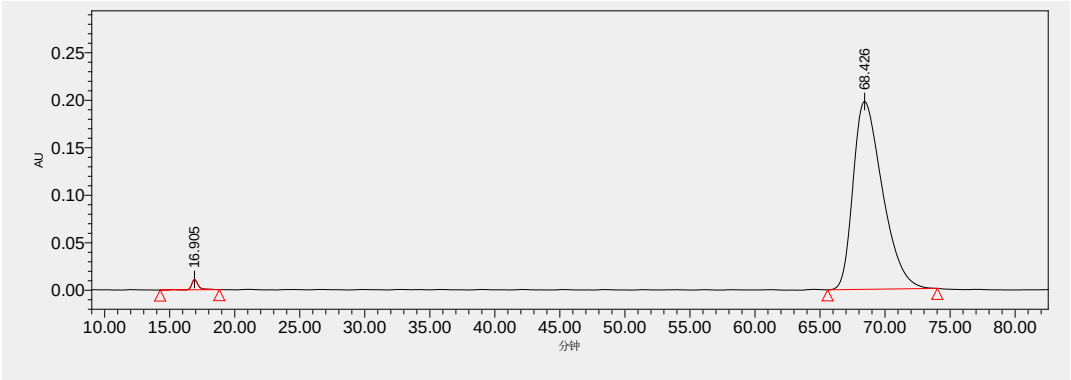
Chiral HPLC report: racemate (**3z**)

HPLC REPORT

Sample Name: zhxn-10-40 Date: ###

Column: PC-2 Mobile Phase: hex/ipr = 60/40

Velocity (mL/min): 0.5 Detection Wavelength (nm): 230

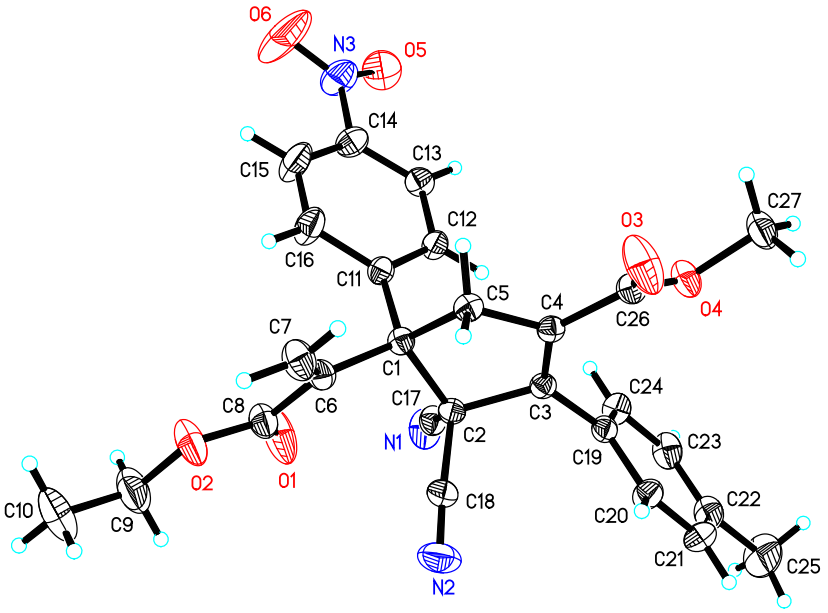


NO	R. Time	Peak Area	Percent	Peak Height
1	16.905	413192	1.32	10887
2	68.426	31002258	98.68	197693

Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak PC-2 column; λ = 230 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.5 mL/min; t_{minor} = 16.91 min, t_{major} = 68.43 min; ee% = 97%; $[\alpha]^{20}_{D}$ = -592.5 (c 1.75, $CHCl_3$).

5. X-ray Data of 3d

X-ray Data of **3d**



The crystal data of **3d** have been deposited in CCDC with number 872182. Empirical Formula: $C_{27}H_{23}N_3O_6$; Formula Weight: 485.48; Crystal Color, Habit: colorless; Crystal System: Orthorhombic; Crystal size: 0.35 x 0.30 x 0.28; Lattice Parameters: a = 10.2839(4)Å, b = 15.4819(6)Å, c = 15.8271(5)Å, $\alpha = 90^o$, $\beta = 90^o$, $\gamma = 90^o$, V = 2519.90(16)Å^3; Space group: P2(1)2(1)2(1); Z = 4; D_{calc} = 1.280 g/cm^3; F_{000} = 1016; Final R indices [I>2sigma(I)]: R1 = 0.0404; wR2 = 0.1134.

6. References

1) H.-P. Deng, Y. Wei, M. Shi, *Adv. Synth. Catal.* **2012**, *354*, 783-789.

2) H.-P. Deng, Y. Wei, M. Shi, *Eur. J. Org. Chem.* **2011**, 1956.

3) X. Jiang, D. Fu, X. Shi, S. Wang, R. Wang, *Chem. Commun.* **2011**, *47*, 8289-8291.