

Supporting Information

Construction of Spirooxindole-Fused Spiropyrazolones Containing Contiguous Three Stereocentres through [3+2] Annulation using Ferrocene Derived Bifunctional Phosphine-Catalyst

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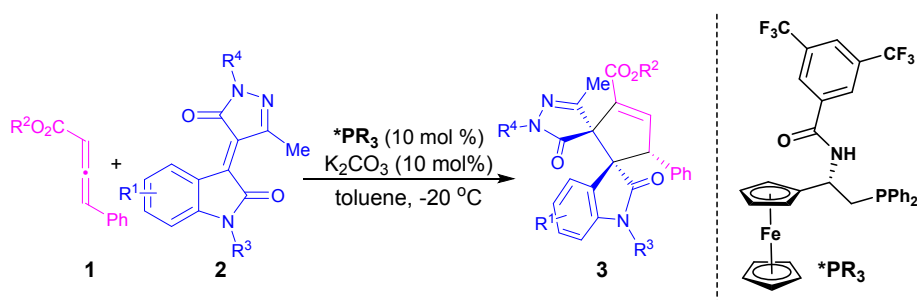
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1. General experimental information

Unless otherwise noted, all reactions were carried out under the nitrogen atmosphere, Anhydrous Et₂O and toluene were distilled from sodium benzophenone. Anhydrous acetonitrile and CH₂Cl₂ were distilled from CaH₂; materials obtained from commercial suppliers were used directly without further purification. The $[\alpha]_D$ was recorded using AUTOPOL V polarimeter. ¹H NMR spectra, ¹³C NMR spectra, ³¹P NMR spectra were recorded on a Bruker 400 MHz spectrometer in CDCl₃. Chemical shifts were reported in ppm from the solvent resonance as the internal standard (CDCl₃: 7.26 ppm, 77.0 ppm). HPLC analyses were performed using Agilent 1100 equipped with AD-H and OD-H column.

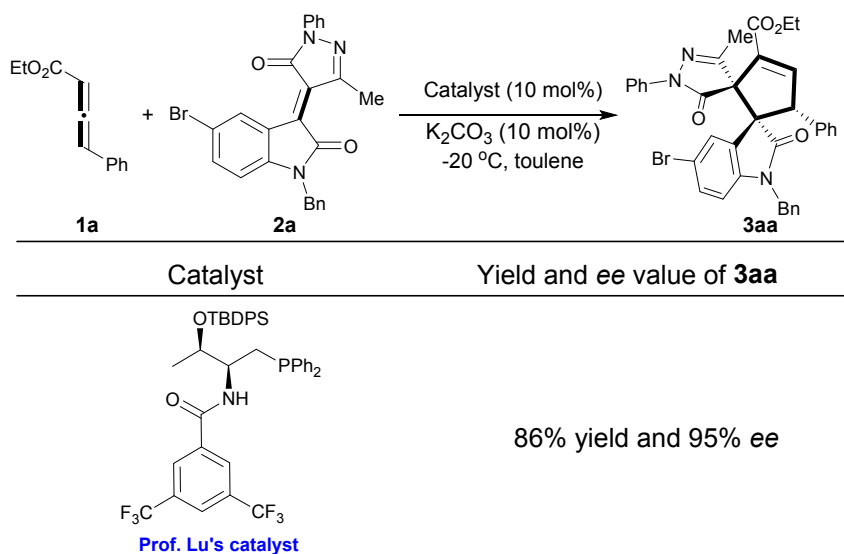
2. General procedure for the synthesis of Products 3



To a 10 mL dried Schlenk charged with γ -substituted allenates **1** (0.18 mmol), pyrazolone-oxindole components **2** (0.15 mmol), γ -substituted allenates **1** (0.30 mmol) and K_2CO_3 (10 mol%) and **P8** (10 mol%) was purged under N₂ atmosphere. Then, 3.0 mL toluene was added and the mixture was stirred at $-20\text{ }^\circ\text{C}$ for 4-6 h. After the reaction was complete, and directly purified by chromatography on silica gel with hexane/ethyl acetate = 6:1 affording spiro-cyclopentene-linked oxindole and pyrazolone compounds **3**.

3. The attempt of Lu's catalyst¹

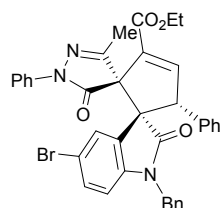
Lu's catalyst was performed on the allenolate **1a** and **2a** under standard conditions, the desired product **3aa** was obtained with 86% yield and 95% *ee*.



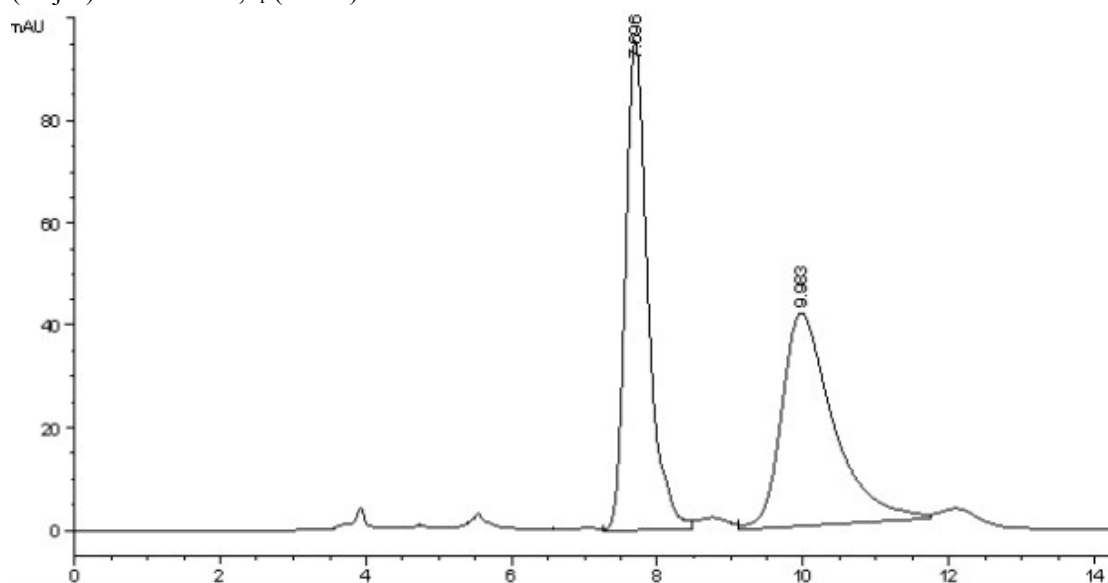
1. (a) W.-L. Chan, X. Tang, F. Zhang, G. Quek, G.-J. Mei and Y. Lu, Phosphine-catalyzed (3+2) annulation of isoindigos with allenes: enantioselective formation of two vicinal quaternary stereogenic centers, *Angew. Chem., Int. Ed.*, 2019, **58**, 6260; (b) X. Han, W.-L. Chan, W. Yao, Y. Wang, Y. Lu, PhosphineMediated Highly Enantioselective Spirocyclization with Ketimines as Substrates. *Angew. Chem., Int. Ed.*, 2016, **55**, 6492; (c) W. Yao, X. Dou, Y. Lu, Highly Enantioselective Synthesis of 3,4-Dihydropyrans through a Phosphine-Catalyzed [4+2] Annulation of Allenones and β,γ -Unsaturated α -Keto Esters, *J. Am. Chem. Soc.*, 2015, **137**, 54; (d) F. Zhong, X. Han, Y. Wang, Y. Lu, Highly Enantioselective [4+2] Annulations Catalyzed by Amino Acid-Based Phosphines: Synthesis of Functionalized Cyclohexenes and 3-Spirocyclohexene-2-oxindoles. *Chem. Sci.*, 2012, **3**, 1231.

4. General Datas and HPLC Spectra for 3

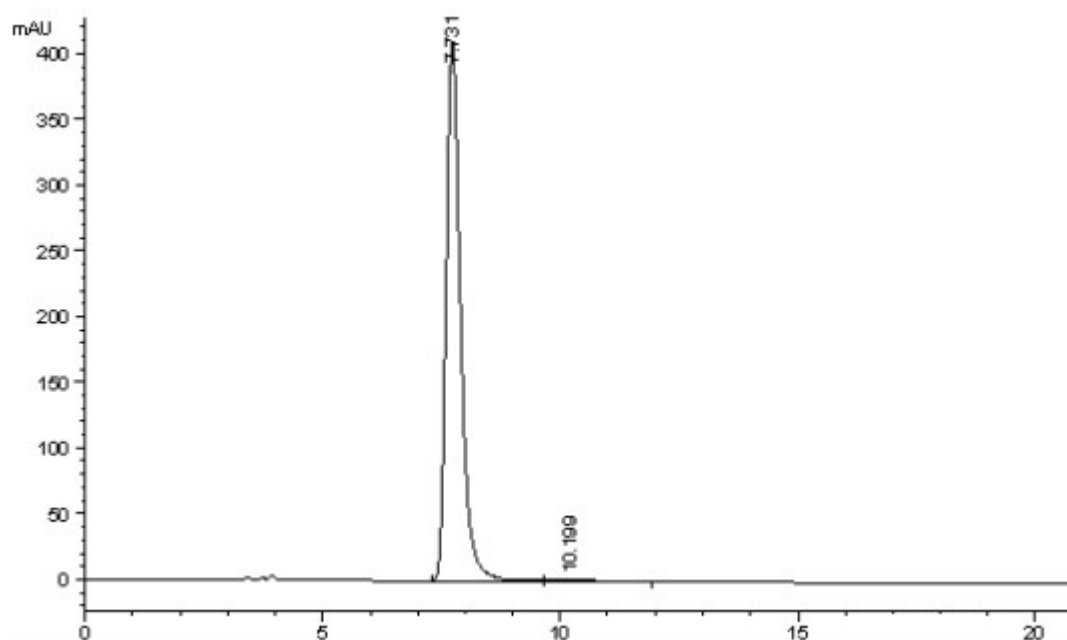
1) ethyl (2'*R*, 3*R*, 5'*R*)-1-benzyl-5-bromo-3''-methyl-2,5''-dioxo-1'',5'-diphenyl- 1'',5''-dihydrodispiro-[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-3'-carboxylate (3aa)



88% yield, 98% *ee*; m.p.: 106-107 °C; $[\alpha]_D^{25} = +141.0$ ($c = 1.0$, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ 8.01 (s, 1H), 7.77 (d, $J = 8.0$ Hz, 2H), 7.71 (s, 1H), 7.40 (t, $J = 8.0$ Hz, 2H), 7.31 (t, $J = 7.6$ Hz, 1H), 7.23-7.19 (m, 4H), 7.13 (t, $J = 7.2$ Hz, 1H), 7.07-7.0 (m, 4H), 6.31 (d, $J = 7.6$ Hz, 2H), 6.26 (d, $J = 8.4$ Hz, 1H), 5.40 (s, 1H), 5.01 (d, $J = 15.6$ Hz, 1H), 4.30-4.12 (m, 3H), 2.08 (s, 3H), 1.29 (t, $J = 7.2$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 171.9, 171.1, 162.3, 157.8, 150.6, 142.0, 137.1, 134.7, 134.3, 133.9, 132.7, 129.0 (2C), 128.8 (2C), 128.7 (2C), 128.4 (2C), 128.0, 127.9, 127.4, 126.3 (2C), 126.0, 125.6, 119.6, 115.8, 110.7, 70.8, 65.9, 61.3, 55.8, 43.2, 17.1, 14.0; HRMS (ESI) m/z calculated for C₃₇H₃₀BrN₃NaO₄ [M+H]⁺ = 682.1311, found = 682.1327; Enantiomeric excess: 98%, determined by HPLC (Chiralpak OD-H, hexane/*i*-PrOH = 70/30; flow rate 0.8 mL/min; 25 °C; 254 nm), t_r (major) = 7.731 min, t_r (minor) = 10.199 min.

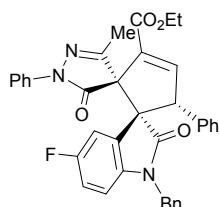


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	7.696	VV	0.3265	2053.88818	50.0299	95.53207	50.0299
2	9.983	MM R	0.9066	2051.43701	49.9701	41.57655	49.9701

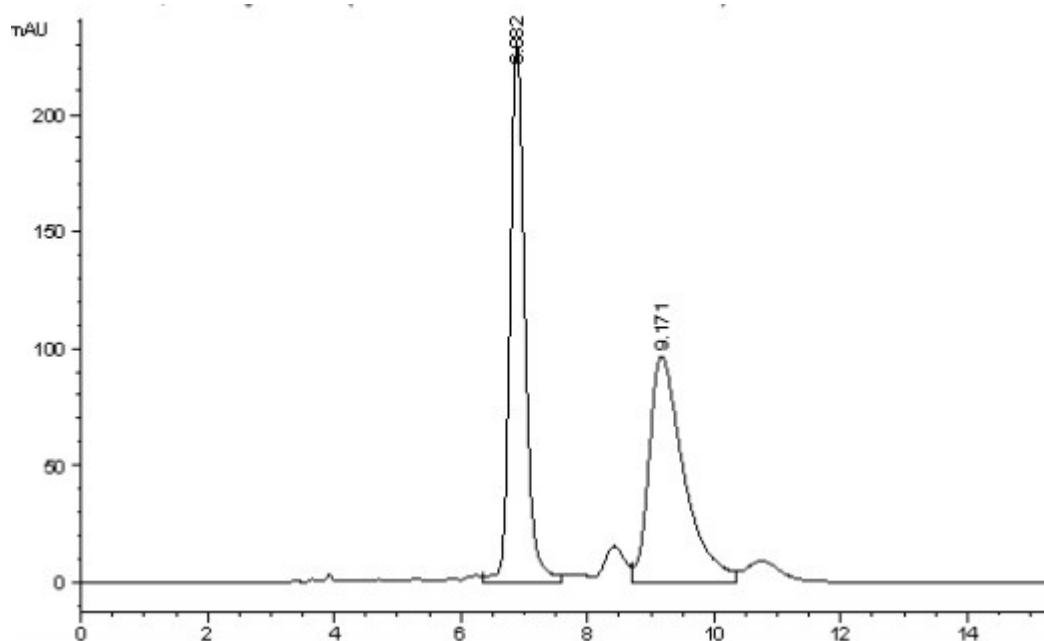


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.731	BV	0.3258	8762.47266	408.72659	98.8486
2	10.199	VV	0.8191	102.06433	1.76791	1.1514

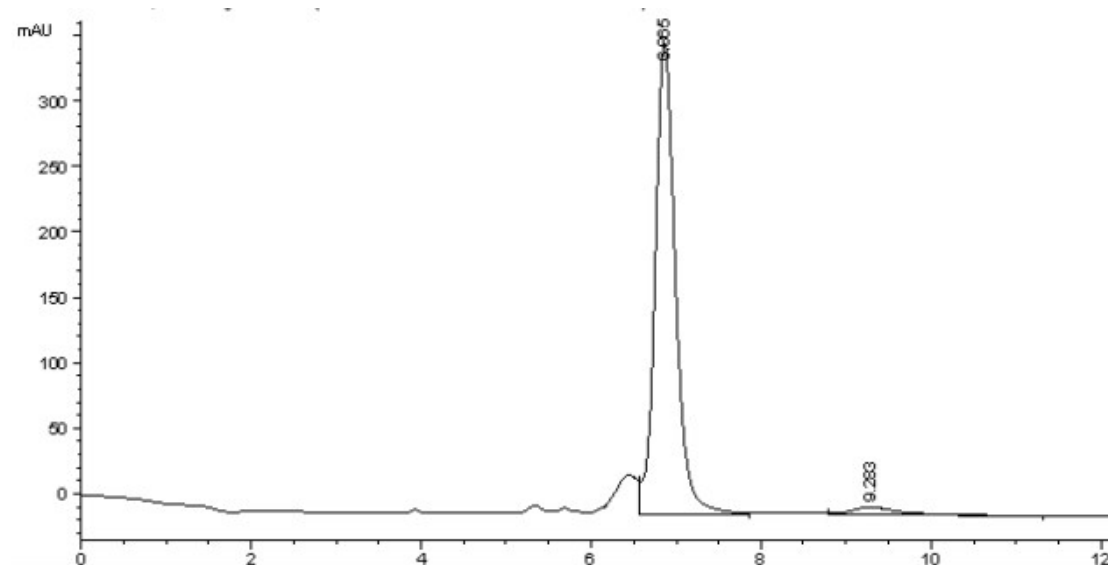
2) ethyl (2'*R*, 3*R*, 5'*R*)-1-benzyl-5-fluoro-3''-methyl-2,5''-dioxo-1'',5'-diphenyl- 1'',5''-dihydrodispiro[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-3'-carboxylate (3ab)



90% yield, 92% *ee*; white solid; m.p.: 96-97 °C; $[\alpha]_D^{25} = +32.0$ ($c = 1.0$, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, $J = 8.0$ Hz, 2H), 7.70 (d, $J = 1.2$ Hz, 1H), 7.64-7.2 (m, 1H), 7.39 (t, $J = 8.0$ Hz, 2H), 7.34-7.28 (m, 1H), 7.23-7.17 (m, 3H), 7.13 (t, $J = 7.2$ Hz, 1H), 7.05 (t, $J = 7.6$ Hz, 2H), 7.00 (d, $J = 7.6$ Hz, 2H), 6.82-6.77 (m, 1H), 6.33-6.30 (m, 3H), 5.40 (s, 1H), 5.01 (d, $J = 15.6$ Hz, 1H), 4.30-4.14 (m, 3H), 2.09 (s, 3H), 1.28 (t, $J = 7.2$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 172.3, 171.2, 162.3, 158.0, 150.6, 144.7 (d, $J_{C-F} = 251.0$ Hz), 139.0 (d, $J_{C-F} = 2.0$ Hz), 137.4, 134.8, 134.5, 134.1, 129.0 (2C), 128.9 (2C), 128.7 (2C), 128.4 (2C), 127.9, 127.4, 126.4 (2C), 125.7, 125.6, 119.4 (2C), 116.3 (d, $J_{C-F} = 21.0$ Hz), 112.9, 110.0 (d, $J_{C-F} = 8.0$ Hz), 70.9, 66.1, 61.3, 56.1, 43.3, 17.2, 14.0; HRMS (ESI) m/z calculated for C₃₇H₂₀FN₃NaO₄ [M+Na]⁺ = 622.2112, found = 622.2120; Enantiomeric excess: 92%, determined by HPLC (Chiralpak OD-H, hexane/*i*-PrOH = 70/30; flow rate 0.8 mL/min; 25 °C; 254 nm), t_r (major) = 6.865 min, t_r (minor) = 9.283 min.

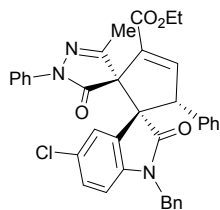


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	6.882	VV	0.2507	3794.17822	229.95364	50.5366
2	9.171	VV	0.5691	3713.60718	96.97685	49.4634

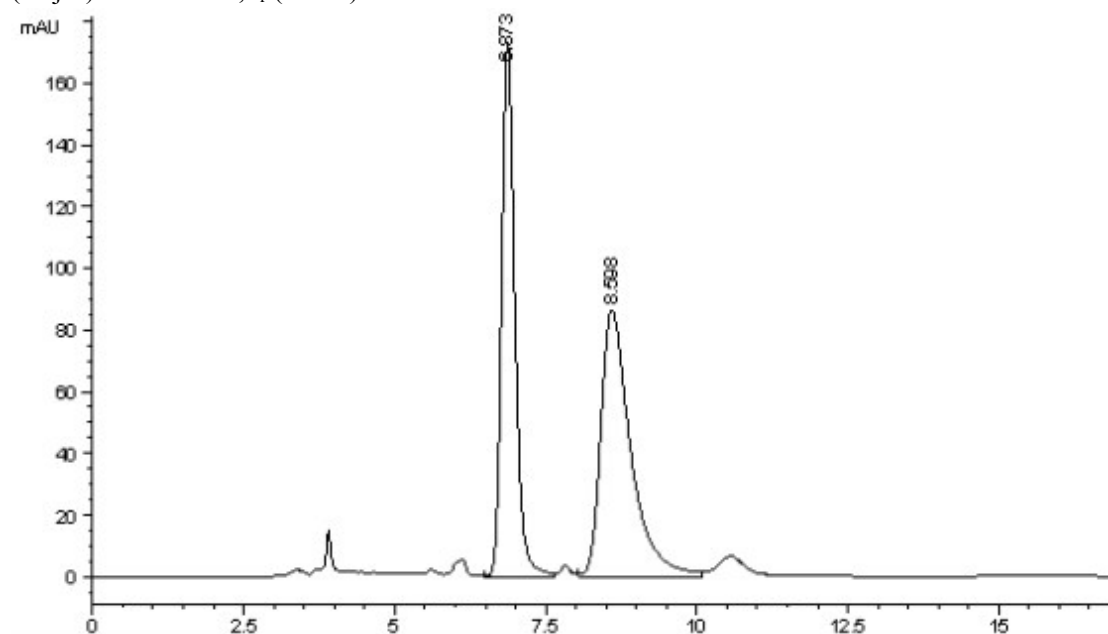


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	6.865	VV	0.2535	6018.46191	359.58517	95.9372
2	9.283	VB	0.6405	254.87610	5.80355	4.0628

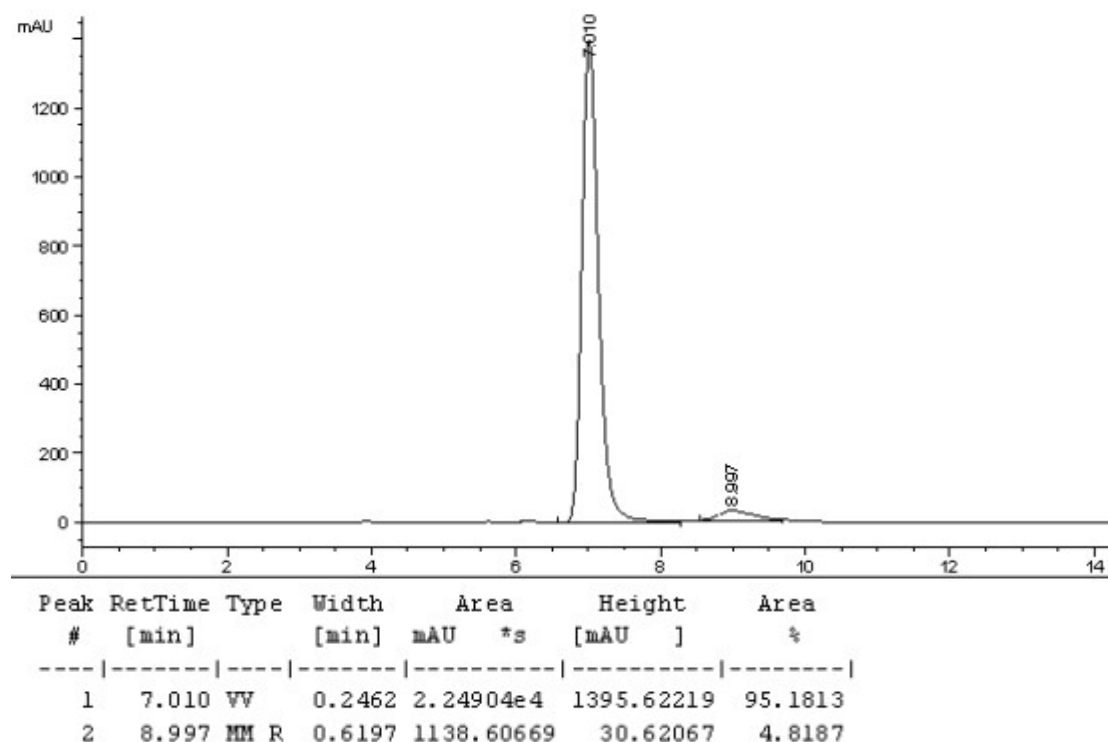
3) ethyl (2'*R*, 3*R*, 5'*R*)-1-benzyl-5-chloro-3''-methyl-2,5''-dioxo-1'',5'-diphenyl- 1'',5''-dihydrodispiro-[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-3'-carboxylate (3ac)



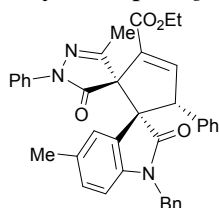
93 % yield, 90% *ee*; white solid; m.p.: 115-116 °C; $[\alpha]_D^{25} = +137.8$ ($c = 1.0$, CH_2Cl_2); **^1H NMR** (400 MHz, CDCl_3): δ 7.86-7.73 (m, 4H), 7.38 (t, $J = 8.0$ Hz, 2H), 7.32-7.27 (m, 1H), 7.19 (t, $J = 7.6$ Hz, 3H), 7.14-7.05 (m, 4H), 6.98 (t, $J = 7.6$ Hz, 3H), 6.42 (d, $J = 7.6$ Hz, 1H), 6.37 (d, $J = 7.6$ Hz, 2H), 5.45 (d, $J = 0.8$ Hz, 1H), 5.03 (d, $J = 15.6$ Hz, 1H), 4.32-4.18 (m, 3H), 2.10 (s, 3H), 1.30 (t, $J = 7.2$ Hz, 3H); **^{13}C NMR** (100 MHz, CDCl_3): δ 172.5, 171.4, 162.4, 158.1, 150.8, 143.0, 137.5, 135.1, 134.6, 134.5, 129.8, 129.0 (2C), 128.7 (2C), 128.6 (2C), 128.3 (2C), 127.7, 127.2, 126.4 (2C), 125.4, 124.9, 123.9, 123.0, 119.4 (2C), 109.3, 71.0, 66.1, 61.2, 55.8, 43.2, 17.2, 14.0; HRMS (ESI) m/z calculated for $\text{C}_{37}\text{H}_{31}\text{N}_3\text{NaO}_4$ $[\text{M}+\text{Na}]^+ = 604.2206$, found = 604.2210; Enantiomeric excess: 90%, determined by HPLC (Chiralpak OD-H, hexane/*i*-PrOH = 70/30; flow rate 0.8 mL/min; 25 °C; 254 nm), t_r (major) = 7.010 min, t_r (minor) = 8.997 min.



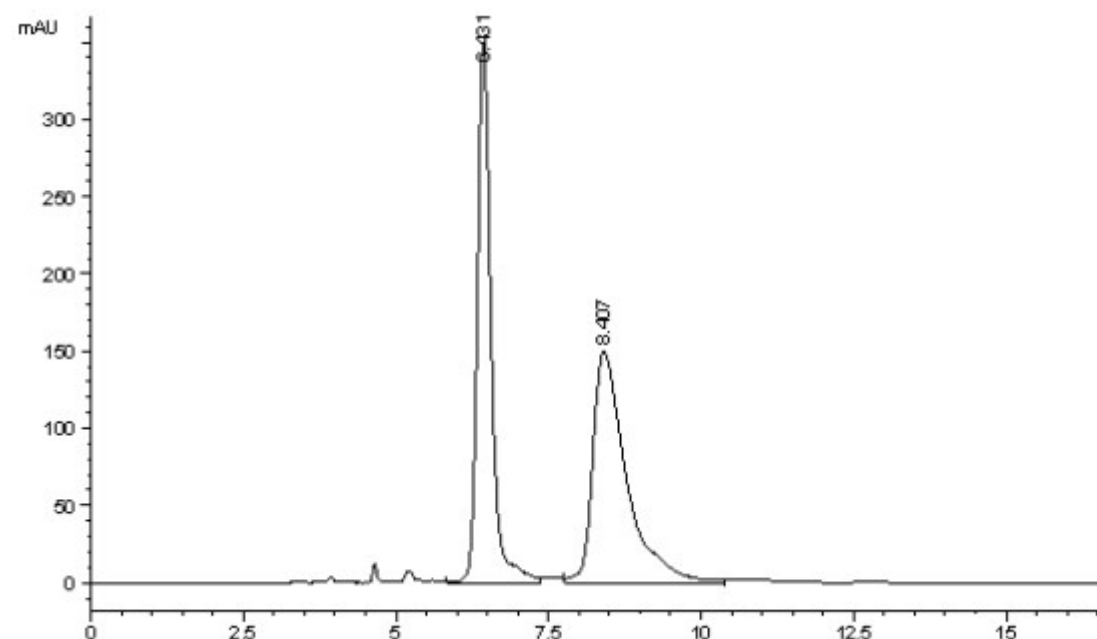
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	6.873	VV	0.2370	2648.02344	47.1552	172.80478	47.1552
2	8.598	VV	0.5117	2967.53052	52.8448	86.32154	52.8448



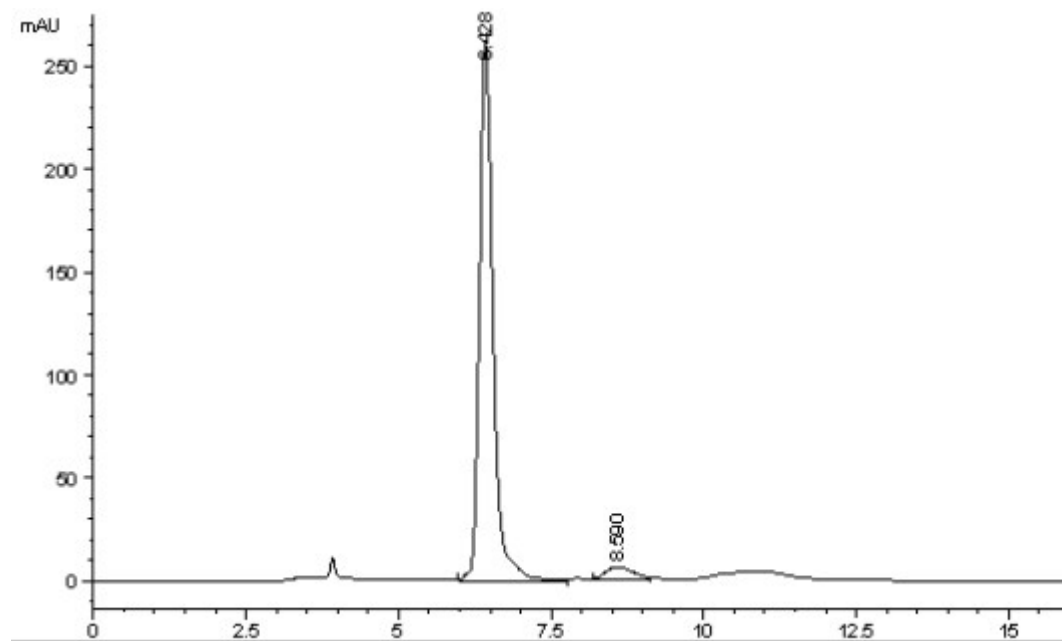
4) ethyl (2'*R*, 3*R*, 5'*R*)-1-benzyl-3'',5-dimethyl-2,5''-dioxo-1'',5'-diphenyl-1'',5''-dihydrodispiro-[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-3'-carboxylate (3ad)



85% yield, 90% *ee*; m.p.: 113-114 °C; $[\alpha]_D^{25} = +559.0$ ($c = 1.0$, CH_2Cl_2); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.76-7.73 (m, 3H), 7.62 (s, 1H), 7.37 (t, $J = 8.0$ Hz, 2H), 7.29 (d, $J = 7.2$ Hz, 1H), 7.20-7.16 (m, 3H), 7.11 (t, $J = 7.2$ Hz, 1H), 7.07-6.96 (m, 4H), 6.86 (d, $J = 7.8$ Hz, 1H), 6.34 (d, $J = 7.2$ Hz, 2H), 6.28 (d, $J = 8.0$ Hz, 1H), 5.39 (s, 1H), 4.99 (d, $J = 15.6$ Hz, 1H), 4.31-4.10 (m, 3H), 2.15 (s, 3H), 2.07 (s, 3H), 1.29 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 172.4, 171.5, 162.5, 158.2, 150.9, 140.5, 137.5, 135.2, 134.6, 134.3, 132.6, 130.1, 129.0 (2C), 128.7 (2C), 128.5 (2C), 128.3 (2C), 127.7, 127.1, 126.5 (2C), 125.5, 125.3, 123.8, 119.3 (2C), 109.0, 71.1, 66.3, 61.2, 55.5, 43.2, 20.9, 17.1, 14.0; HRMS (ESI) m/z calculated for $\text{C}_{38}\text{H}_{33}\text{N}_3\text{NaO}_4$ $[\text{M}+\text{H}]^+ = 618.2363$, found = 618.2380; Enantiomeric excess: 90%, determined by HPLC (Chiralpak OD-H, hexane/*i*-PrOH = 70/30; flow rate 0.8 mL/min; 25 °C; 254 nm), t_r (major) = 6.428 min, t_r (minor) = 8.509 min.

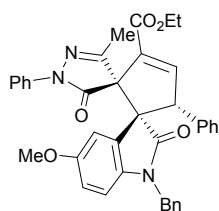


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.431	VV	0.2375	5538.91602	349.08047	48.8939
2	8.407	VV	0.5673	5789.51660	149.81111	51.1061

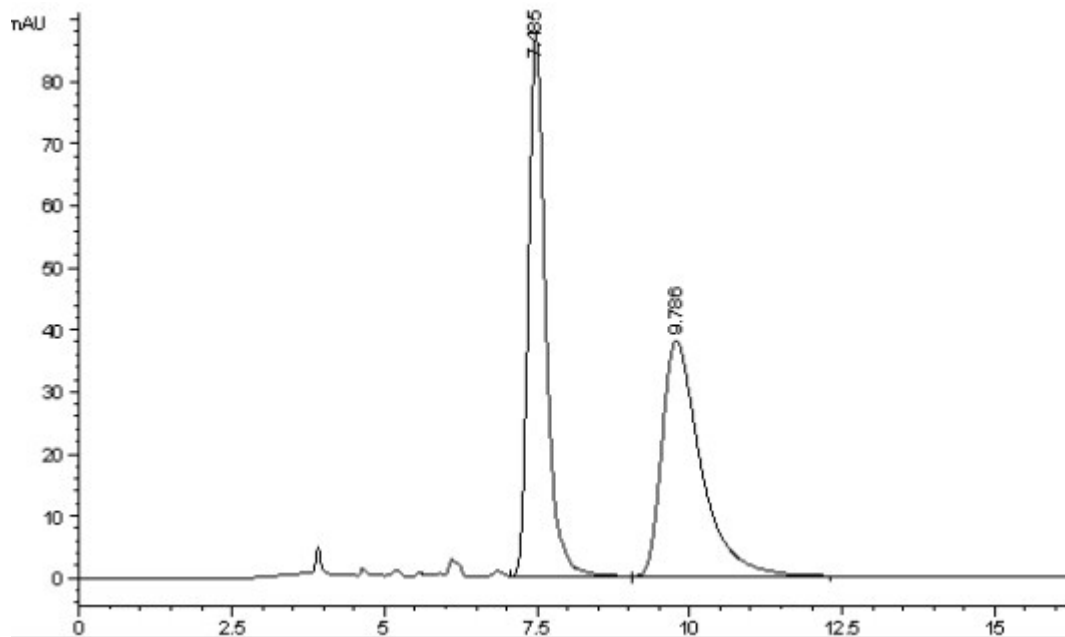


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.428	VV	0.2340	4078.79810	262.05545	95.1618
2	8.590	MM R	0.5433	207.37462	6.36165	4.8382

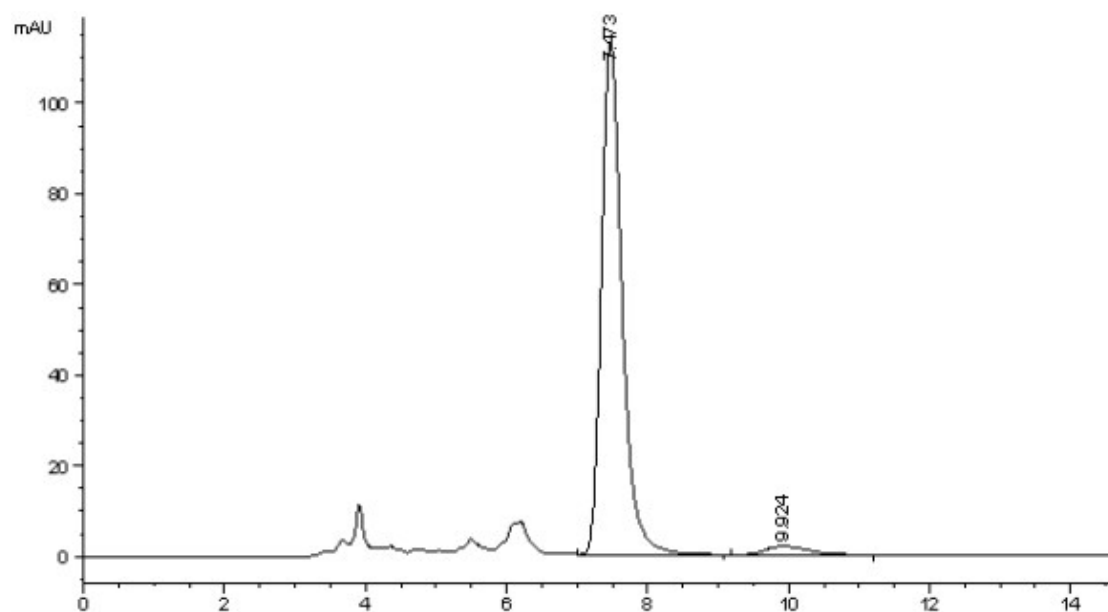
5) ethyl (2'*R*, 3*R*, 5'*R*)-1-benzyl-5-methoxy-3''-methyl-2,5''-dioxo-1'',5'-diphenyl- 1'',5''-dihydrodispiro- [indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-3'-carboxylate (3ae)



82% yield, 92% *ee*; m.p.: 115-116 °C; $[\alpha]_D^{25} = +204.4$ ($c = 1.0$, CH_2Cl_2); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.81 (d, $J = 8.0$ Hz, 2H), 7.72 (d, $J = 1.6$ Hz, 1H), 7.41 (d, $J = 2.4$ Hz, 1H), 7.36 (t, $J = 8.0$ Hz, 2H), 7.30 (d, $J = 7.2$ Hz, 1H), 7.22-7.09 (m, 4H), 7.08-6.97 (m, 4H), 6.63-6.6 (m, 1H), 6.34 (d, $J = 7.6$ Hz, 2H), 6.29 (d, $J = 8.8$ Hz, 1H), 5.40 (s, 1H), 4.99 (d, $J = 15.6$ Hz, 1H), 4.29-4.13 (m, 3H), 3.56 (s, 3H), 2.10 (s, 3H), 1.29 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 172.2, 171.4, 162.4, 158.3, 156.2, 150.7, 137.6, 136.4, 135.1, 134.5 (2C), 129.0 (2C), 128.7 (2C), 128.6 (2C), 128.3 (2C), 127.7, 127.2, 126.4 (2C), 125.3, 124.9, 119.1 (2C), 115.7, 111.0, 109.9, 71.1, 66.5, 61.2, 55.8 (2C), 43.2, 17.2, 14.0; HRMS (ESI) m/z calculated for $\text{C}_{38}\text{H}_{33}\text{N}_3\text{NaO}_5$ $[\text{M}+\text{H}]^+ = 634.2312$, found = 634.2328; Enantiomeric excess: 92%, determined by HPLC (Chiralpak OD-H, hexane/*i*-PrOH = 70/30; flow rate 0.8 mL/min; 25 °C; 254 nm), t_r (major) = 7.473 min, t_r (minor) = 9.924 min.

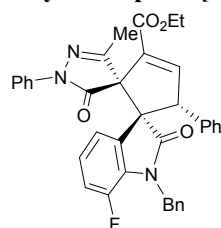


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	7.485	VV	0.3105	1745.54175	50.5718	86.73431	50.5718
2	9.786	VB	0.6677	1706.06689	49.4282	38.12176	49.4282

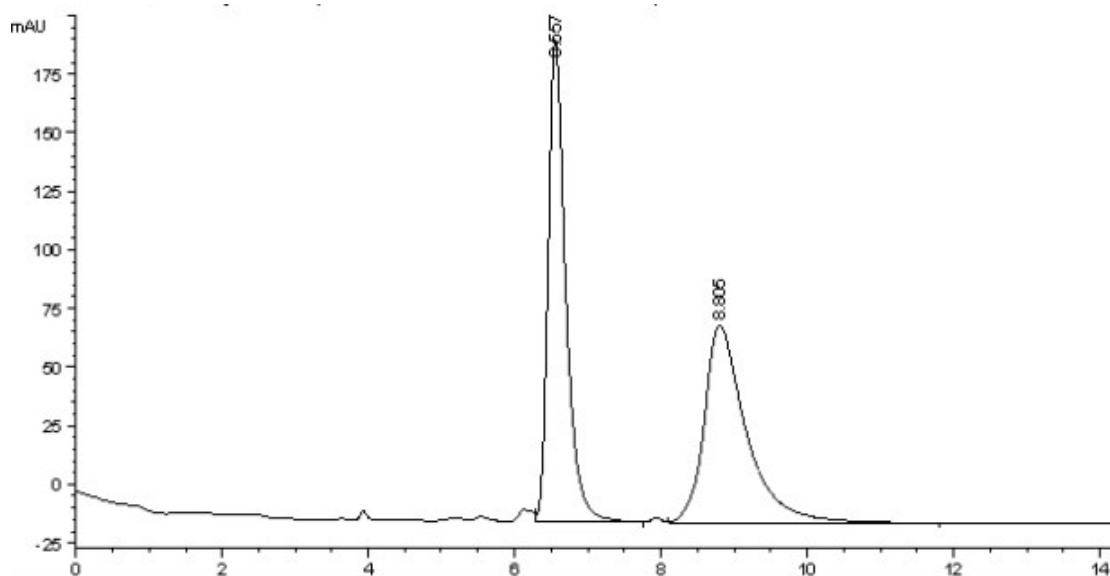


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	7.473	VB	0.3104	2333.04468	113.17308	95.7728
2	9.924	BB	0.7243	102.97643	2.09712	4.2272

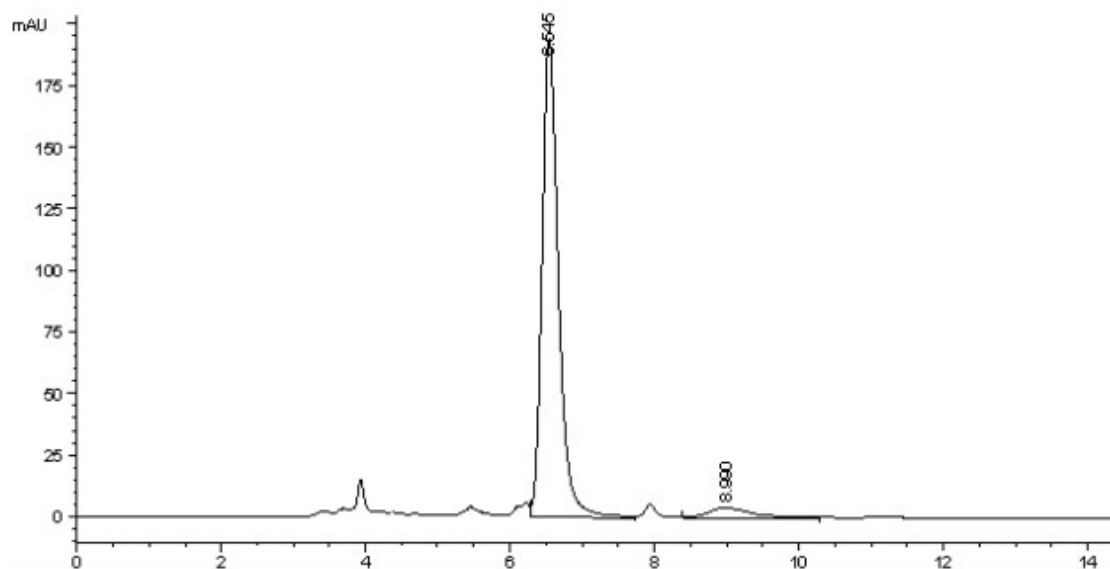
6) ethyl (2'*R*, 3*R*, 5'*R*)-1-benzyl-7-fluoro-3''-methyl-2,5''-dioxo-1'',5'-diphenyl- 1'',5''-dihydrodispiro- [indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-3'-carboxylate (3af)



86% yield, 93% *ee*; m.p.: 98-99 °C; $[\alpha]_D^{25} = +311.8$ ($c = 1.0$, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ 7.76 (d, $J = 8.0$ Hz, 2H), 7.72 (d, $J = 1.6$ Hz, 1H), 7.64 (d, $J = 7.6$ Hz, 1H), 7.37 (t, $J = 8.0$ Hz, 2H), 7.29 (t, $J = 7.2$ Hz, 1H), 7.21-7.17 (m, 3H), 7.12 (t, $J = 7.2$ Hz, 1H), 7.07-6.97 (m, 4H), 6.96-6.84 (m, 2H), 6.41 (d, $J = 7.6$ Hz, 2H), 5.43 (s, 1H), 5.05 (d, $J = 15.6$ Hz, 1H), 4.45 (d, $J = 15.6$ Hz, 1H), 4.29-4.15 (m, 2H), 2.06 (s, 3H), 1.28 (t, $J = 7.2$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 172.2, 171.2, 162.3, 157.9, 150.6, 146.9 (d, $J_{C-F} = 244.0$ Hz), 137.4, 135.6, 134.7, 134.3, 129.9 (d, $J_{C-F} = 9.0$ Hz), 128.9 (2C), 128.7 (2C), 128.4 (4C), 127.9, 127.0, 126.9, 126.4 (2C), 125.4, 123.6 (d, $J_{C-F} = 6.0$ Hz), 120.8, 119.3 (2C), 118.0 (d, $J_{C-F} = 19.0$ Hz), 71.2, 66.1, 61.3, 55.8, 44.8, 17.1, 14.0; HRMS (ESI) m/z calculated for C₃₇H₂₀FN₃NaO₄ $[M+Na]^+ = 622.2112$, found = 622.2134; Enantiomeric excess: 90%, determined by HPLC (Chiralpak OD-H, hexane/*i*-PrOH = 70/30; flow rate 0.8 mL/min; 25 °C; 254 nm), t_r (major) = 6.545 min, t_r (minor) = 8.990 min.

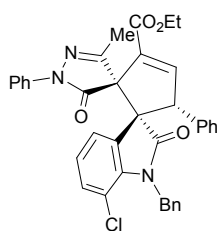


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	6.557	VV	0.2532	3440.21680	205.87083	50.6068
2	8.805	VB	0.5817	3357.71143	84.20139	49.3932

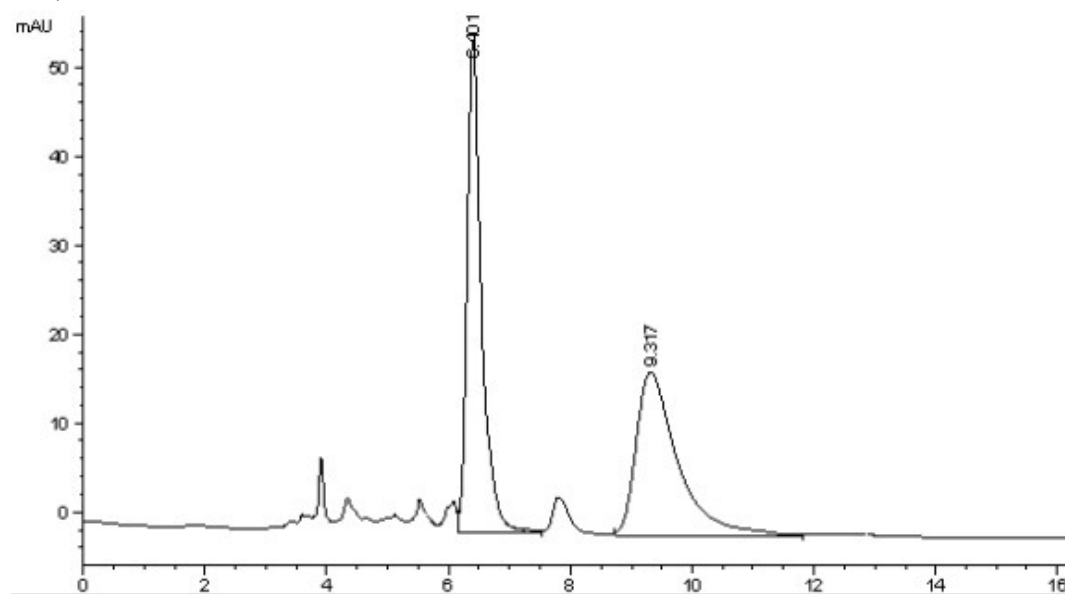


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	6.545	VV	0.2433	3075.92139	193.88670	94.8680
2	8.990	BB	0.6151	166.39619	3.98620	5.1320

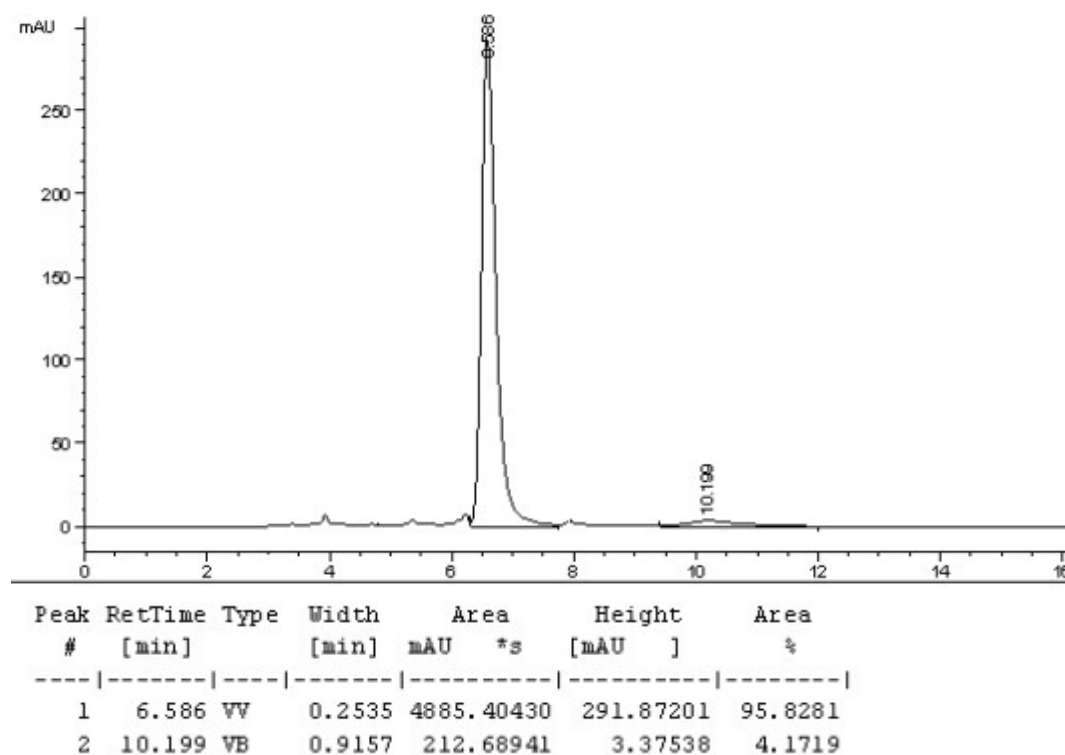
7) ethyl (2'*R*, 3*R*, 5'*R*)-1-benzyl-7-chloro-3''-methyl-2,5''-dioxo-1'',5'-diphenyl- 1'',5''-dihydrodispiro- [indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-3'-carboxylate (3ag)



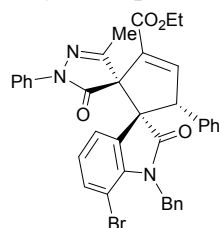
85% yield, 92% *ee*; m.p.: 91-92 °C; $[\alpha]_D^{25} = +363.6$ ($c = 1.0$, CH_2Cl_2); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.81 (d, $J = 7.2$ Hz, 1H), 7.75 (d, $J = 8.0$ Hz, 2H), 7.71 (d, $J = 2.0$ Hz, 1H), 7.37 (t, $J = 8.0$ Hz, 2H), 7.33-7.29 (m, 1H), 7.21 (t, $J = 8.0$ Hz, 3H), 7.12-7.07 (m, 2H), 7.04-7.01 (m, 4H), 6.93 (t, $J = 8.0$ Hz, 1H), 6.26 (d, $J = 7.6$ Hz, 2H), 5.43 (s, 1H), 5.20 (d, $J = 16.0$ Hz, 1H), 4.89 (d, $J = 16.0$ Hz, 1H), 4.27-4.16 (m, 2H), 2.05 (s, 3H), 1.27 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 173.0, 171.2, 162.3, 157.9, 150.7, 139.2, 137.3, 136.3, 134.7, 134.2, 132.5, 129.1 (2C), 128.8 (2C), 128.44 (2C), 128.40 (2C), 128.0, 126.8, 126.6, 125.55 (2C), 125.48, 123.7, 123.6, 119.4 (2C), 115.3, 71.41, 65.6, 61.3, 55.8, 44.5, 17.1, 14.0; HRMS (ESI) m/z calculated for $\text{C}_{37}\text{H}_{30}\text{ClN}_3\text{NaO}_4$ $[\text{M}+\text{H}]^+ = 638.1817$, found = 638.1826; Enantiomeric excess: 92%, determined by HPLC (Chiralpak OD-H, hexane/*i*-PrOH = 70/30; flow rate 0.8 mL/min; 25 °C; 254 nm), t_r (major) = 6.586 min, t_r (minor) = 10.199 min.



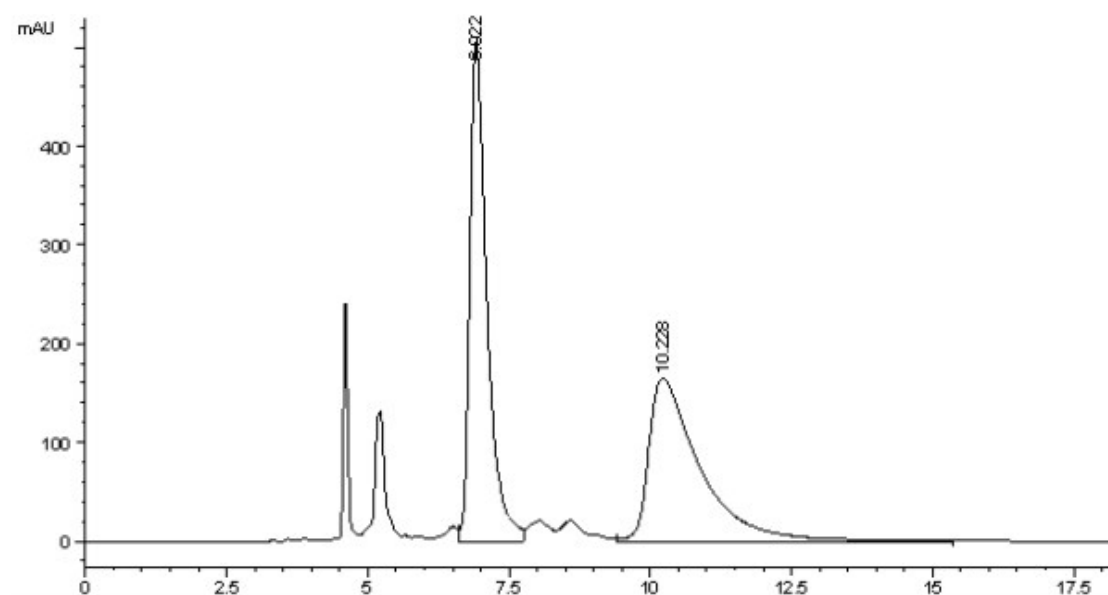
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	6.401	VV	0.2458	915.50110	55.22049	51.2308
2	9.317	MM R	0.7909	871.51086	18.36425	48.7692



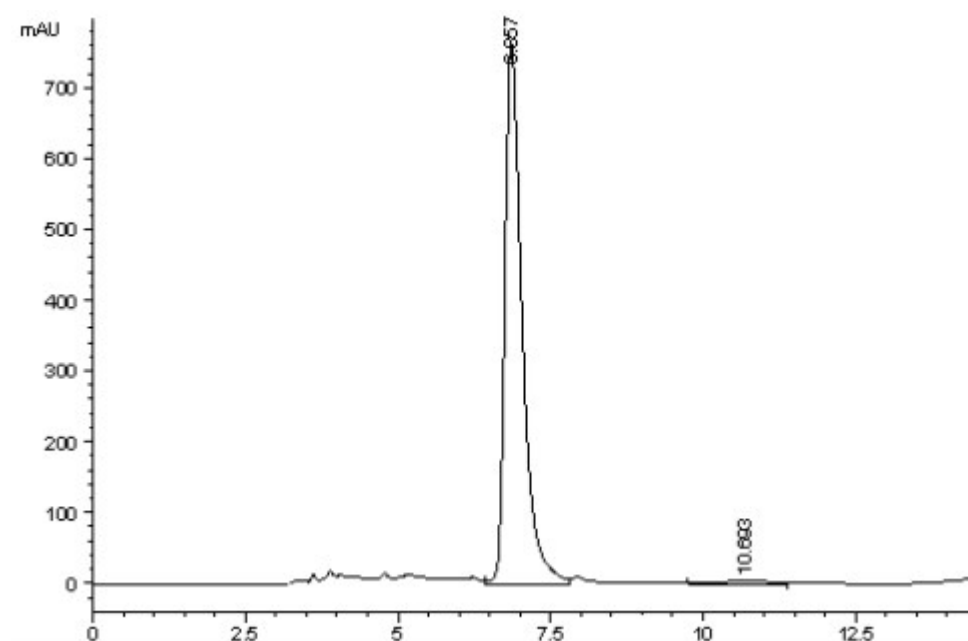
8) ethyl (2'*R*, 3*R*, 5'*R*)-1-benzyl-7-bromo-3''-methyl-2,5''-dioxo-1'',5'-diphenyl- 1'',5''-dihydrodispiro-[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-3'-carboxylate (3ah)



82% yield, 96% *ee*; m.p.: 110-111 °C; $[\alpha]_D^{25} = +19.0$ ($c = 1.0$, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ 7.86 (d, $J = 7.6$ Hz, 1H), 7.74 (d, $J = 8.0$ Hz, 2H), 7.69 (d, $J = 1.6$ Hz, 1H), 7.37 (t, $J = 8.0$ Hz, 2H), 7.33-7.28 (m, 2H), 7.22-7.17 (m, 3H), 7.09 (t, $J = 7.2$ Hz, 1H), 7.01 (t, $J = 6.8$ Hz, 4H), 6.87 (t, $J = 8.0$ Hz, 1H), 6.24 (d, $J = 7.6$ Hz, 2H), 5.42 (s, 1H), 5.17 (d, $J = 16.4$ Hz, 1H), 5.00 (d, $J = 16.4$ Hz, 1H), 4.26-4.16 (m, 2H), 2.04 (s, 3H), 1.27 (t, $J = 7.2$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 173.2, 171.2, 162.3, 157.9, 150.7, 139.0, 137.3, 136.2, 136.0, 134.7, 134.2, 129.1 (2C), 128.8 (2C), 128.5 (2C), 128.4 (2C), 128.1, 127.2, 126.6, 125.5 (3C), 124.1 (2C), 119.4 (2C), 102.4, 65.5, 61.3, 55.9, 44.2, 39.3, 17.1, 14.0; HRMS (ESI) m/z calculated for C₃₇H₃₀BrN₃NaO₄ [M+H]⁺ = 682.1311, found = 682.1340; Enantiomeric excess: 98%, determined by HPLC (Chiralpak OD-H, hexane/*i*-PrOH = 70/30; flow rate 0.8 mL/min; 25 °C; 254 nm), t_r (major) = 6.857 min, t_r (minor) = 10.693 min.

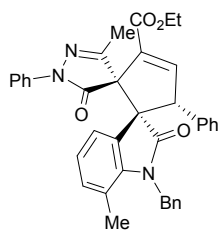


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.922	VV	0.3171	1.06992e4	504.94659	50.4945
2	10.228	VV	0.9175	1.04896e4	164.76158	49.5055

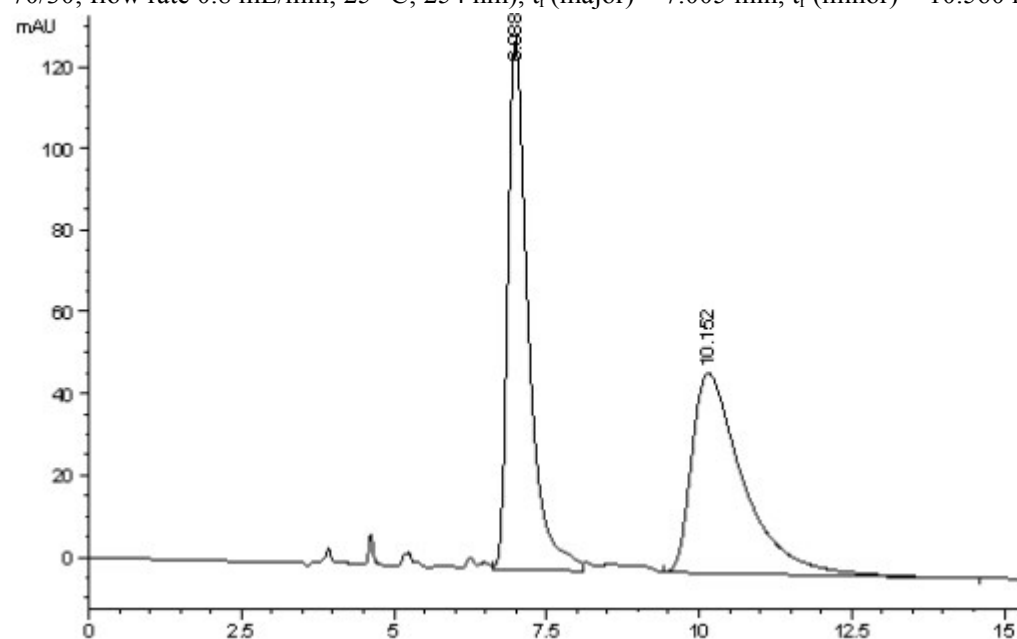


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.857	VV	0.2947	1.50505e4	761.30457	98.2315
2	10.693	VV	0.9084	270.96643	4.48669	1.7685

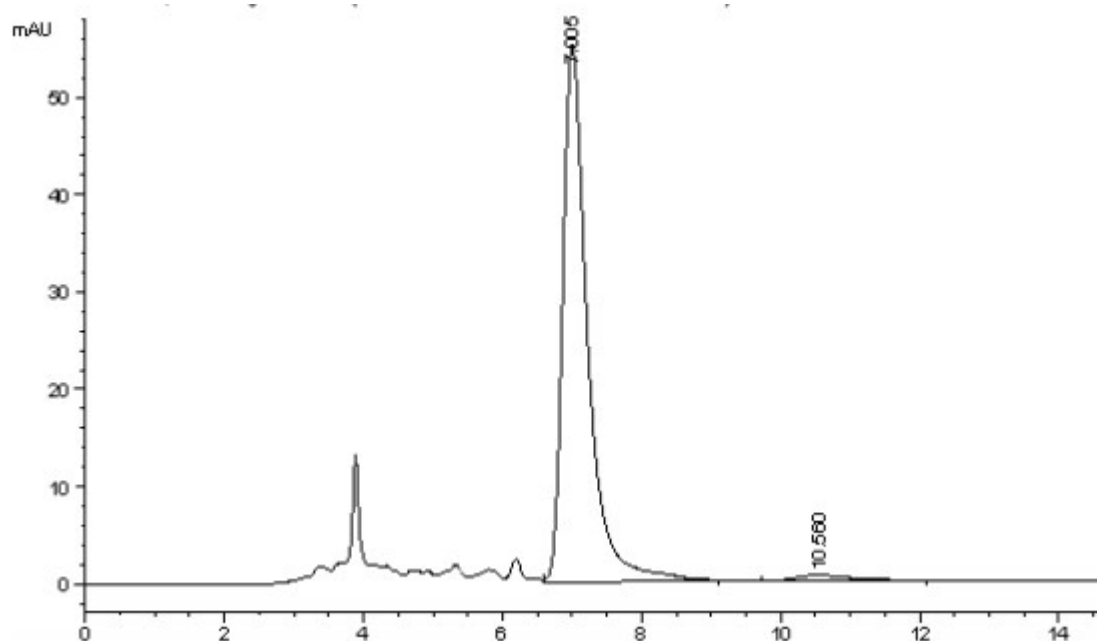
9) ethyl (2'*R*, 3*R*, 5'*R*)-1-benzyl-3'',7-dimethyl-2,5''-dioxo-1'',5'-diphenyl-1'',5''-dihydrodispiro-[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-3'-carboxylate (3ai)



79% yield, 95% *ee*; m.p.: 112-113 °C; $[\alpha]_D^{25} = +68.8$ ($c = 1.0$, CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3): δ 7.75 (d, $J = 7.8$ Hz, 3H), 7.72 (d, $J = 1.6$ Hz, 1H), 7.36 (t, $J = 8.0$ Hz, 2H), 7.30 (t, $J = 7.2$ Hz, 1H), 7.12-7.15 (m, 3H), 7.09 (t, $J = 7.2$ Hz, 1H), 7.02 (dd, $J = 13.6$, 7.1 Hz, 4H), 6.94-6.84 (m, 2H), 6.15 (d, $J = 7.6$ Hz, 2H), 5.44 (s, 1H), 5.21 (d, $J = 16.8$ Hz, 1H), 4.58 (d, $J = 16.8$ Hz, 1H), 4.26-4.16 (m, 2H), 2.09 (s, 3H), 2.02 (s, 3H), 1.27 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 173.4, 171.5, 162.5, 158.1, 151.0, 141.1, 137.5, 136.4, 135.2, 134.2, 134.0, 129.2 (2C), 128.7 (4C), 128.3 (2C), 127.8, 126.7, 125.3, 125.0 (2C), 124.4, 123.0, 122.8, 119.6, 119.5 (2C), 71.4, 65.6, 61.2, 55.8, 44.6, 18.6, 17.2, 14.0; HRMS (ESI) m/z calculated for $\text{C}_{38}\text{H}_{33}\text{N}_3\text{NaO}_4$ $[\text{M}+\text{H}]^+ = 618.2363$, found = 618.2391; Enantiomeric excess: 95%, determined by HPLC (Chiralpak OD-H, hexane/*i*-PrOH = 70/30; flow rate 0.8 mL/min; 25 °C; 254 nm), t_r (major) = 7.005 min, t_r (minor) = 10.560 min.

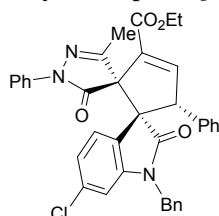


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.988	VV	0.3486	3016.23535	128.94060	51.3278
2	10.152	VB	0.8626	2860.17578	48.92555	48.6722

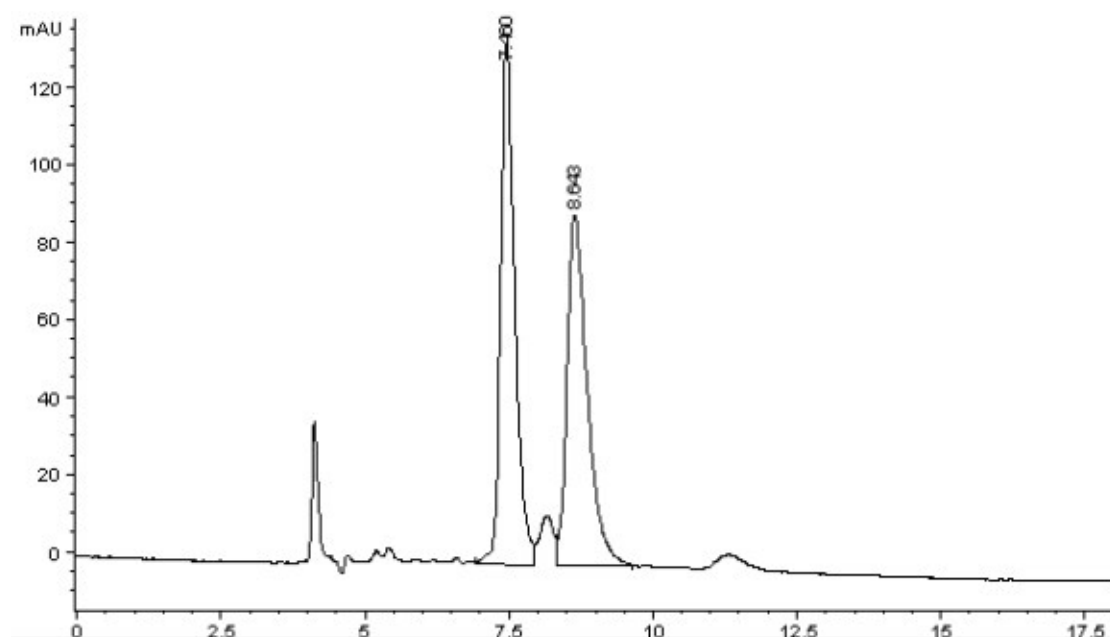


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	7.005	VB	0.3733	1381.09338	55.22447	97.8845
2	10.560	BB	0.6899	29.84779	5.22372e-1	2.1155

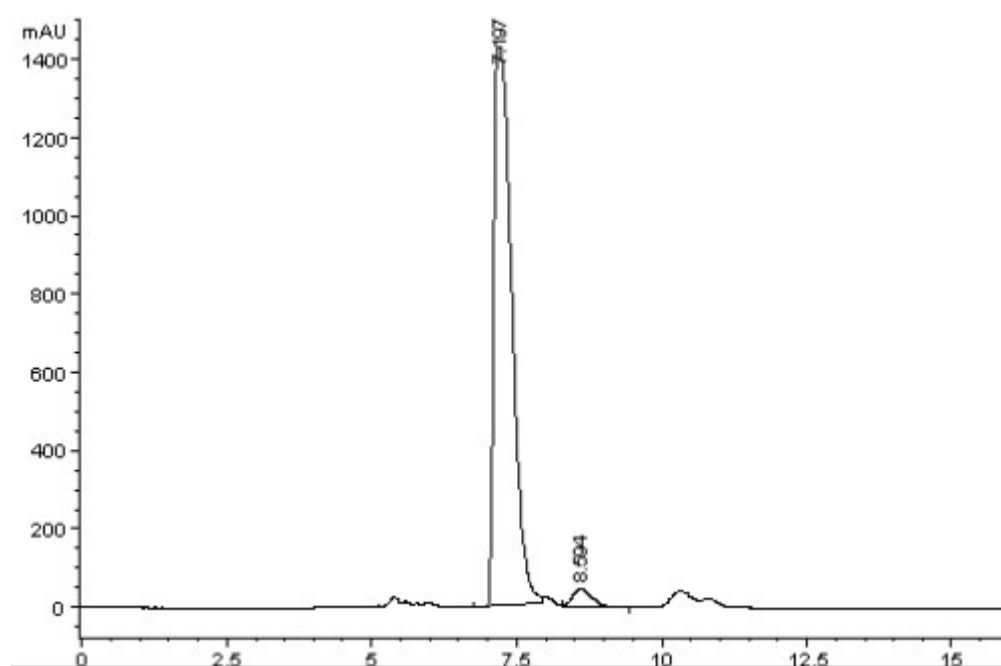
10) ethyl (2'*R*, 3*R*, 5'*R*)-1-benzyl-6-chloro-3''-methyl-2,5''-dioxo-1'',5'-diphenyl- 1'',5''-dihydrodispiro- [indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-3'-carboxylate (3aj)



86% yield, 93% *ee*; m.p.: 112-113 °C; $[\alpha]_D^{25} = +100.4$ ($c = 1.0$, CH₂Cl₂); **¹H NMR** (400 MHz, CDCl₃): δ 7.78 (d, $J = 8.0$ Hz, 2H), 7.74-7.70 (m, 2H), 7.38 (t, $J = 8.0$ Hz, 2H), 7.31 (t, $J = 7.6$ Hz, 1H), 7.22-7.13 (m, 5H), 7.07 (t, $J = 7.6$ Hz, 2H), 6.98-6.93 (m, 3H), 6.40 (d, $J = 1.2$ Hz, 1H), 6.34 (d, $J = 7.6$ Hz, 2H), 5.41 (s, 1H), 4.99 (d, $J = 15.6$ Hz, 1H), 4.28-4.12 (m, 3H), 2.06 (s, 3H), 1.28 (t, $J = 7.2$ Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 172.5, 171.3, 162.3, 158.0, 150.6, 144.2, 137.4, 135.7, 134.8, 134.6, 133.8, 129.0 (2C), 128.81 (2C), 128.76 (2C), 128.4 (2C), 127.9, 127.5, 126.3 (2C), 125.9, 125.5, 123.0, 122.4, 119.3 (2C), 109.9, 70.9, 65.7, 61.3, 55.8, 43.3, 17.2, 14.0; HRMS (ESI) m/z calculated for C₃₇H₃₀ClN₃NaO₄ $[M+H]^+ = 638.1817$, found = 638.1837; Enantiomeric excess: 93%, determined by HPLC (Chiralpak OD-H, hexane/EtOH = 70/30; flow rate 0.8 mL/min; 25 °C; 254 nm), t_r (major) = 7.197 min, t_r (minor) = 8.594 min.

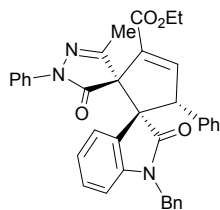


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.460	BV	0.2630	2343.65503	134.66046	51.4724
2	8.643	VB	0.3695	2209.56934	90.29736	48.5276

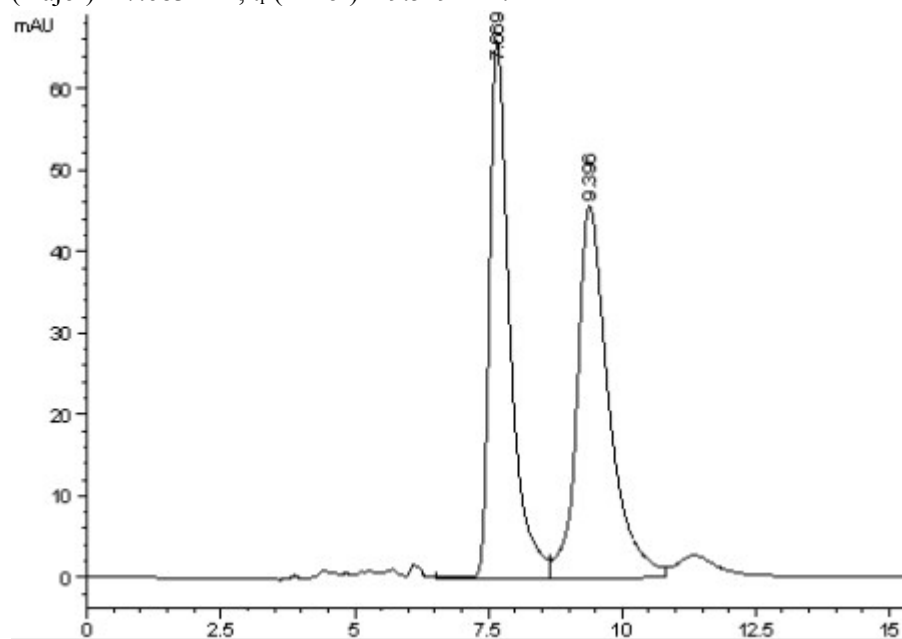


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.197	VB	0.3448	3.09124e4	1426.74512	96.9648
2	8.594	BP	0.3421	967.61224	43.39554	3.0352

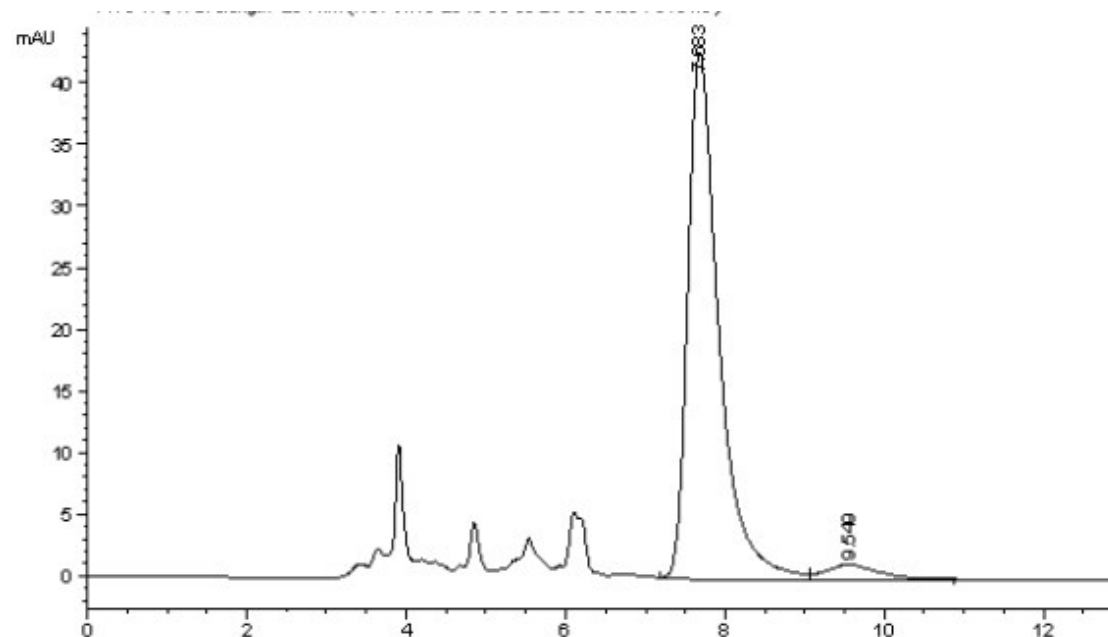
11) ethyl (2'*R*, 3*R*, 5'*R*)-1-benzyl-3''-methyl-2,5''-dioxo-1'',5'-diphenyl-1'',5''-dihydrodispiro[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-3'-carboxylate (3ak)



93 % yield, 90% *ee*; white solid; m.p.: 115-116 °C; $[\alpha]_D^{25} = +137.8$ ($c = 1.0$, CH_2Cl_2); **^1H NMR** (400 MHz, CDCl_3): δ 7.86-7.73 (m, 4H), 7.38 (t, $J = 8.0$ Hz, 2H), 7.32-7.27 (m, 1H), 7.19 (t, $J = 7.6$ Hz, 3H), 7.14-7.05 (m, 4H), 6.98 (t, $J = 7.6$ Hz, 3H), 6.42 (d, $J = 7.6$ Hz, 1H), 6.37 (d, $J = 7.6$ Hz, 2H), 5.45 (d, $J = 0.8$ Hz, 1H), 5.03 (d, $J = 15.6$ Hz, 1H), 4.32-4.18 (m, 3H), 2.10 (s, 3H), 1.30 (t, $J = 7.2$ Hz, 3H); **^{13}C NMR** (100 MHz, CDCl_3): δ 172.5, 171.4, 162.4, 158.1, 150.8, 143.0, 137.5, 135.1, 134.6, 134.5, 129.8, 129.0 (2C), 128.7 (2C), 128.6 (2C), 128.3 (2C), 127.7, 127.2, 126.4 (2C), 125.4, 124.9, 123.9, 123.0, 119.4 (2C), 109.3, 71.0, 66.1, 61.2, 55.8, 43.2, 17.2, 14.0; HRMS (ESI) m/z calculated for $\text{C}_{37}\text{H}_{31}\text{N}_3\text{NaO}_4$ $[\text{M}+\text{Na}]^+ = 604.2206$, found = 604.2210; Enantiomeric excess: 90%, determined by HPLC (Chiralpak OD-H, hexane/*i*-PrOH = 70/30; flow rate 0.8 mL/min; 25 °C; 254 nm), t_r (major) = 7.683 min, t_r (minor) = 9.549 min.

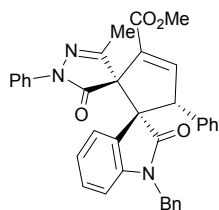


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	7.669	VV	0.3970	1750.04150	48.2989	65.94589	48.2989
2	9.396	VV	0.6012	1873.31641	51.7011	45.63738	51.7011

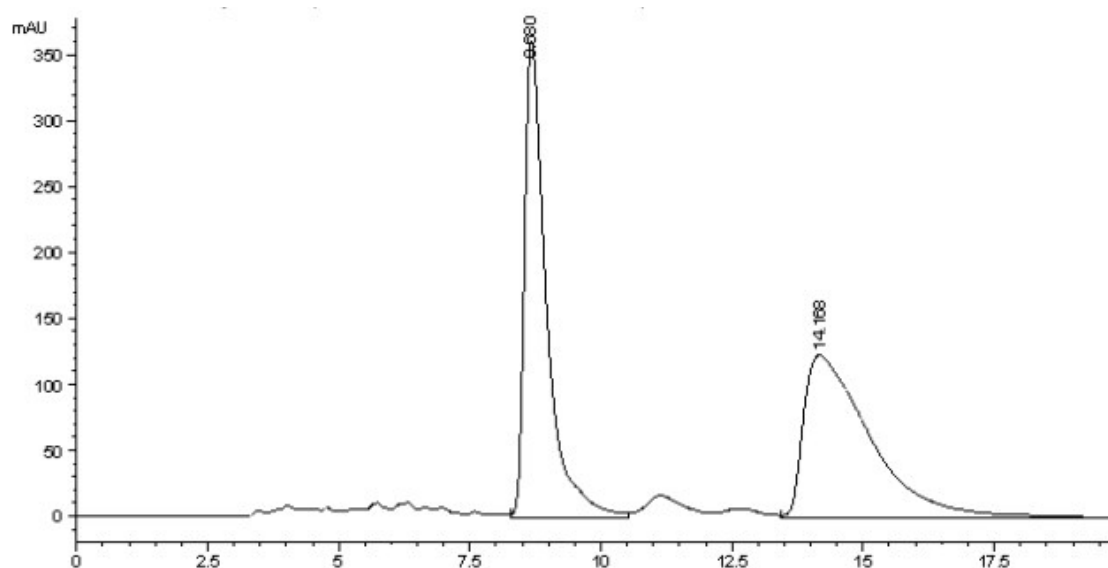


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	7.683	VV	0.4038	1157.19495	42.66236	95.2300
2	9.549	VB	0.6957	57.96245	1.19148	4.7700

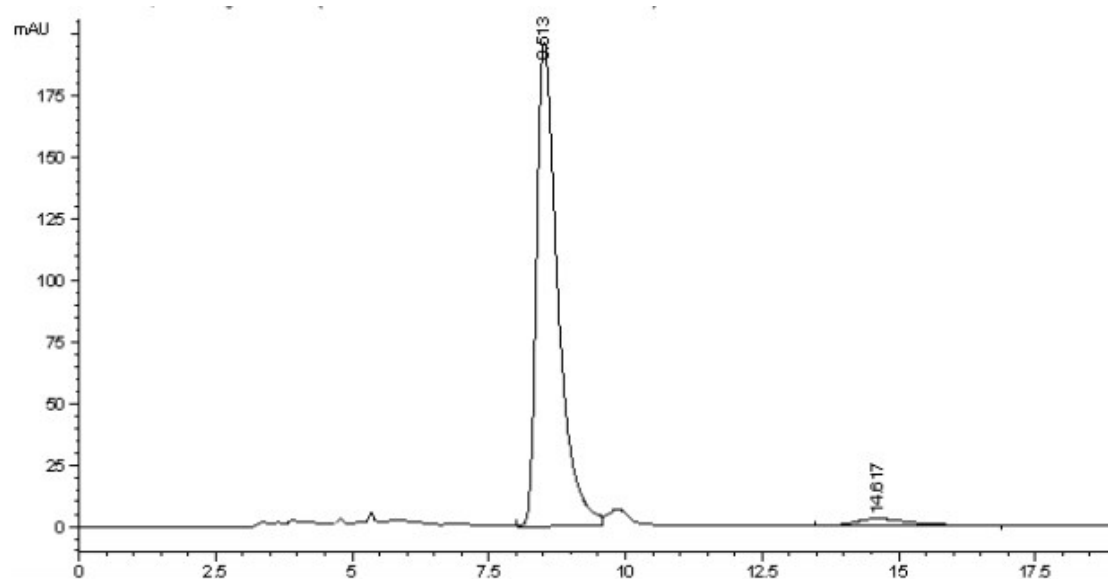
12) methyl (2'*R*, 3*R*, 5'*R*)-1-benzyl-3''-methyl-2,5''-dioxo-1'',5'-diphenyl-1'',5'-dihydrodispiro-[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-3'-carboxylate (3bk)



91 % yield, 92% *ee*; white solid; m.p.: 115-116 °C; $[\alpha]_D^{25} = +70.2$ ($c = 1.0$, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ 7.82-7.77 (m, 3H), 7.73 (s, 1H), 7.37 (t, $J = 8.0$ Hz, 2H), 7.30 (d, $J = 7.2$ Hz, 1H), 7.18 (t, $J = 7.2$ Hz, 3H), 7.13-7.03 (m, 4H), 7.00-6.94 (m, 3H), 6.41 (d, $J = 7.6$ Hz, 1H), 6.35 (d, $J = 7.2$ Hz, 2H), 5.45 (s, 1H), 5.02 (d, $J = 15.6$ Hz, 1H), 4.21 (d, $J = 15.6$ Hz, 1H), 3.78 (s, 3H), 2.09 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 172.4, 171.3, 162.9, 158.0, 151.0, 142.9, 137.4, 135.0, 134.4, 134.3, 129.8, 129.0 (2C), 128.7 (2C), 128.6 (2C), 128.3 (2C), 127.7, 127.2, 126.4 (2C), 125.3, 124.8, 123.8, 123.0, 119.4 (2C), 109.3, 70.9, 66.1, 55.8, 52.1, 43.1, 17.2; HRMS (ESI) m/z calculated for C₃₆H₂₉N₃NaO₄ [M+Na]⁺ = 590.2050, found = 590.2066; Enantiomeric excess: 92%, determined by HPLC (Chiralpak OD-H, hexane/*i*-PrOH = 70/30; flow rate 0.8 mL/min; 25 °C; 254 nm), t_r (major) = 8.513 min, t_r (minor) = 14.617 min.

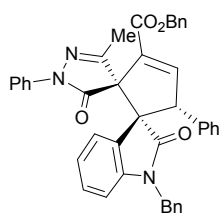


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]
1	8.680	VV	0.4280	1.05289e4	49.2881	360.55893
2	14.168	VB	1.3910	1.08331e4	50.7119	122.72023

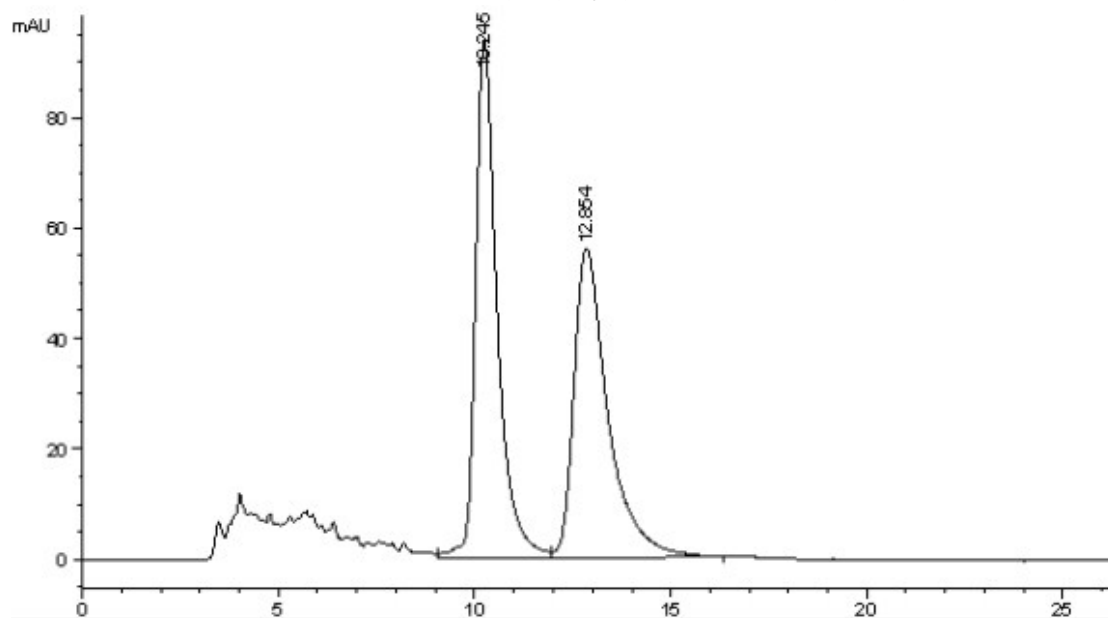


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]
1	8.513	VV	0.4040	5330.20850	95.9826	196.41400
2	14.617	VB	1.1457	223.09792	4.0174	2.83367

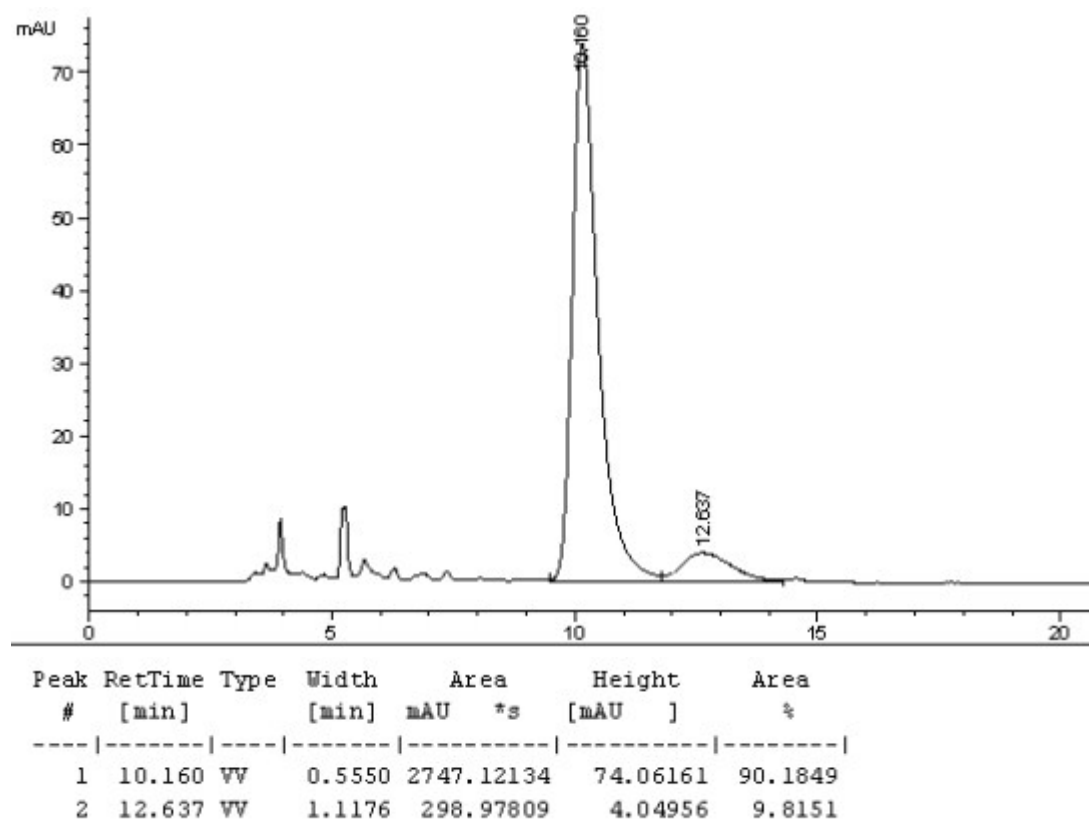
13) benzyl (2'*R*, 3*R*, 5'*R*)-1-benzyl-3''-methyl-2,5''-dioxo-1'',5''-diphenyl-1'',5''-dihydrodispiro-[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-3'-carboxylate (3ck)



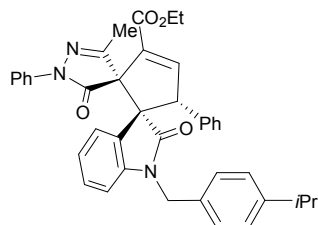
90 % yield, 80% *ee*; white solid; m.p.: 122-123 °C; $[\alpha]_D^{25} = +229.2$ ($c = 1.0$, CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3): δ 7.81 (d, $J = 7.6$ Hz, 1H), 7.78 (d, $J = 1.6$ Hz, 1H), 7.72 (d, $J = 8.0$ Hz, 2H), 7.39-7.27 (m, 8H), 7.20-7.15 (m, 3H), 7.12-7.03 (m, 4H), 6.99-6.96 (m, 3H), 6.40 (d, $J = 7.6$ Hz, 1H), 6.35 (d, $J = 7.2$ Hz, 2H), 5.44 (s, 1H), 5.20 (q, $J = 12.4$ Hz, 2H), 5.00 (d, $J = 15.6$ Hz, 1H), 4.20 (d, $J = 15.6$ Hz, 1H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.4, 171.4, 162.2, 158.0, 151.6, 143.0, 137.4, 135.1, 135.0, 134.4, 134.2, 129.8, 129.0 (2C), 128.7 (2C), 128.6 (2C), 128.5 (2C), 128.34 (2C), 128.27 (2C), 127.7, 127.2, 126.4 (2C), 125.3, 124.9, 123.8, 123.1, 119.4 (2C), 109.3, 70.9, 67.0, 66.2, 55.8, 43.2, 17.2; HRMS (ESI) m/z calculated for $\text{C}_{42}\text{H}_{33}\text{N}_3\text{NaO}_4$ $[\text{M}+\text{Na}]^+ = 666.2363$, found = 666.2402; Enantiomeric excess: 80%, determined by HPLC (Chiralpak OD-H, hexane/*i*-PrOH = 70/30; flow rate 0.8 mL/min; 25 °C; 254 nm), t_r (major) = 10.160 min, t_r (minor) = 12.637 min.



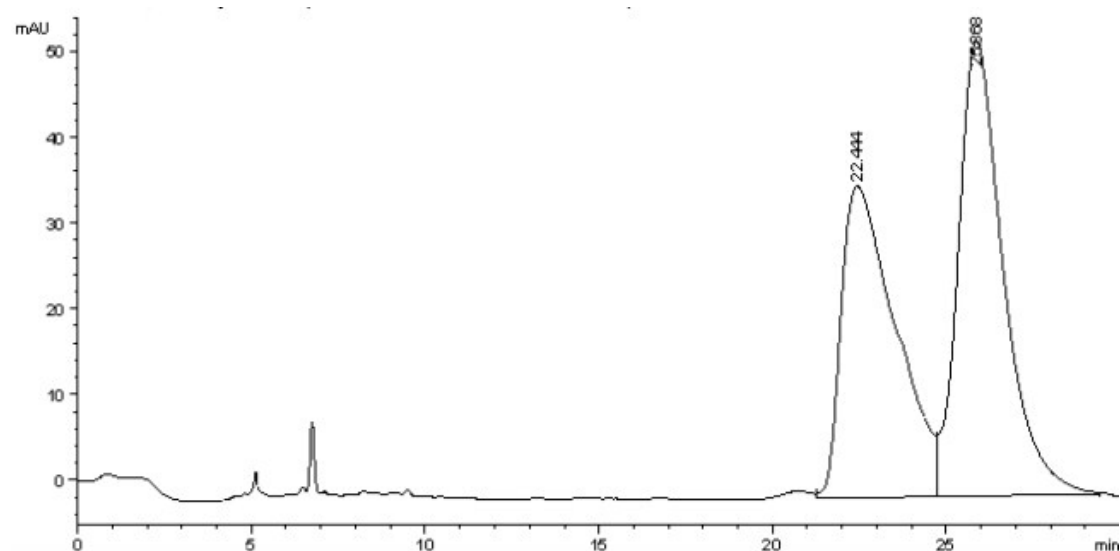
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	10.245	VV	0.5783	3617.84375	51.6790	93.76622	51.6790
2	12.854	VB	0.8972	3382.75903	48.3210	55.98137	48.3210



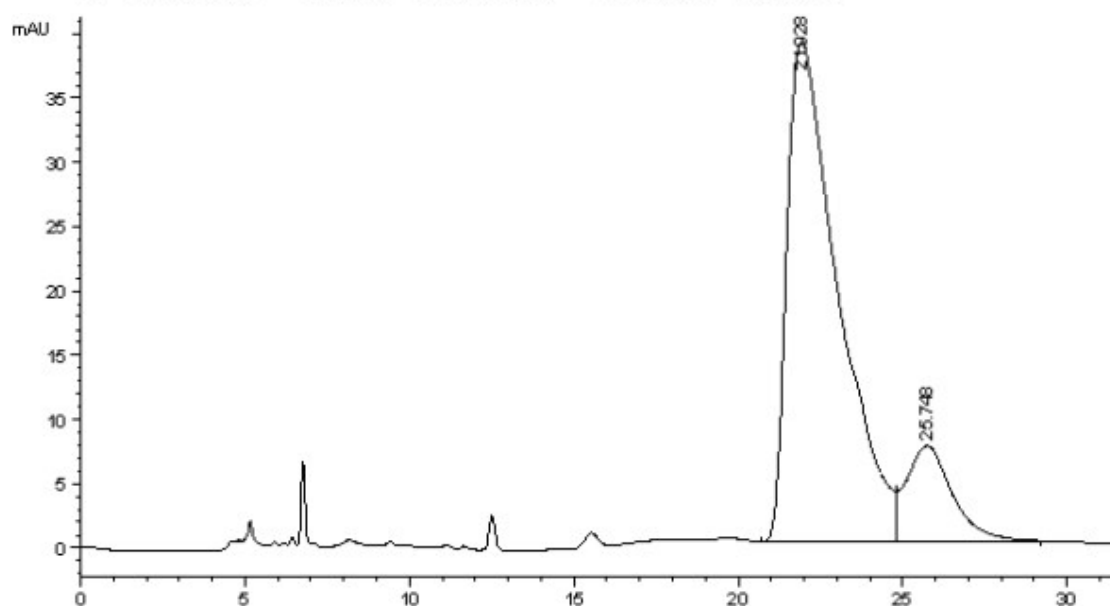
14) ethyl (2'*R*, 3*R*, 5'*R*)-1-(4-isopropylbenzyl)-3''-methyl-2,5''-dioxo-1'',5'-diphenyl- 1'',5''-dihydrodispiro- [indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-3'-carboxylate (3al)



95 % yield, 70% *ee*; white solid; m.p.: 122-123 °C; $[\alpha]_D^{25} = +479.4$ ($c = 1.0$, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ 7.81 (d, $J = 7.6$ Hz, 1H), 7.77 (d, $J = 7.6$ Hz, 2H), 7.73 (d, $J = 2.0$ Hz, 1H), 7.37 (t, $J = 8.0$ Hz, 2H), 7.28 (d, $J = 7.6$ Hz, 1H), 7.17 (t, $J = 7.6$ Hz, 3H), 7.10 (t, $J = 7.6$ Hz, 1H), 6.98-6.94 (m, 3H), 6.91 (d, $J = 8.0$ Hz, 2H), 6.45 (d, $J = 8.0$ Hz, 1H), 6.34 (d, $J = 8.0$ Hz, 2H), 5.43 (s, 1H), 4.91 (d, $J = 15.7$ Hz, 1H), 4.30-4.14 (m, 3H), 2.85-2.76 (m, 1H), 2.08 (s, 3H), 1.28 (t, $J = 7.2$ Hz, 3H), 1.19 (d, $J = 7.2$ Hz, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 172.4, 171.4, 162.4, 158.2, 150.8, 147.8, 143.1, 137.5, 135.0, 134.5, 131.7, 129.8, 128.9 (2C), 128.7 (2C), 128.2 (2C), 127.7, 126.6 (2C), 126.4 (2C), 125.3, 124.8, 123.9, 122.9, 119.4 (2C), 109.3, 71.0, 66.1, 61.2, 55.8, 42.9, 33.6, 23.8, 23.9, 17.2, 14.0; HRMS (ESI) m/z calculated for C₄₀H₃₇N₃NaO₄ $[M+H]^+ = 646.2676$, found = 646.2698; Enantiomeric excess: 70%, determined by HPLC (Chiralpak OD-H, hexane/*i*-PrOH = 95/5; flow rate 0.8 mL/min; 25 °C; 254 nm), t_r (major) = 21.928 min, t_r (minor) = 25.748 min.

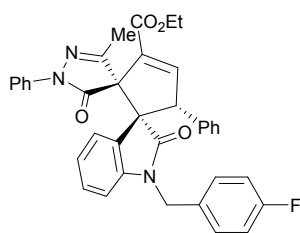


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]
1	22.444	VV	1.6011	3952.05615	45.1351	36.33108
2	25.868	VB	1.3571	4804.00635	54.8649	53.16403

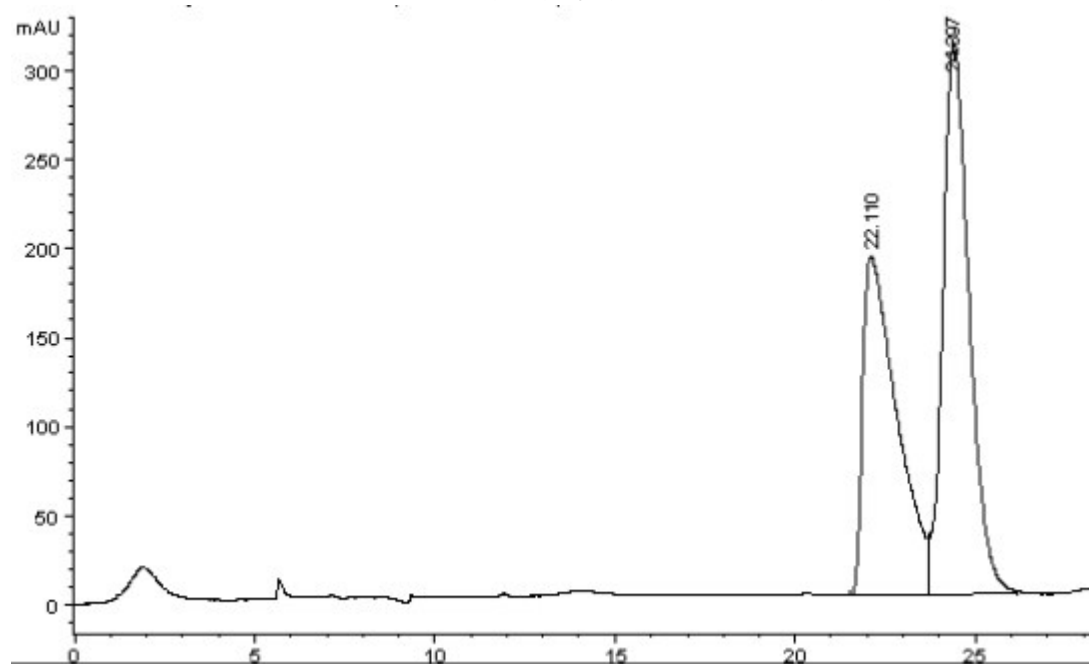


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]
1	21.928	BV	1.5860	4204.20410	85.1353	38.93354
2	25.748	VB	1.4106	734.05878	14.8647	7.45641

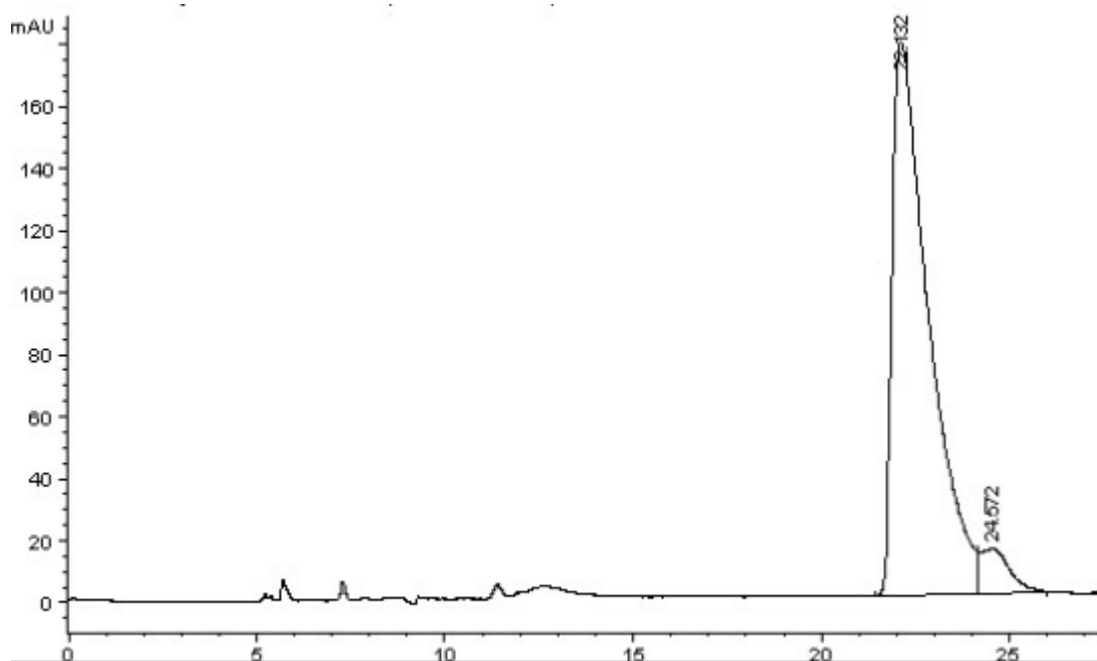
15) ethyl (2'*R*, 3*R*, 5'*R*)-1-(4-fluorobenzyl)-3'-methyl-2,5"-dioxo-1'',5"-diphenyl- 1'',5"-dihydrodispiro- [indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-3'-carboxylate (3am)



86 % yield, 88% *ee*; white solid; m.p.: 113-114 °C; $[\alpha]_D^{25} = +148.2$ ($c = 1.0$, CH_2Cl_2); **¹H NMR** (400 MHz, CDCl_3): δ 7.83 (d, $J = 7.6$ Hz, 1H), 7.77 (d, $J = 8.0$ Hz, 2H), 7.73 (s, 1H), 7.36 (t, $J = 7.6$ Hz, 2H), 7.29 (d, $J = 7.2$ Hz, 1H), 7.17 (t, $J = 7.2$ Hz, 3H), 7.10 (t, $J = 7.6$ Hz, 1H), 7.00-6.95 (m, 3H), 6.73 (t, $J = 8.4$ Hz, 2H), 6.40 (d, $J = 7.7$ Hz, 1H), 6.33-6.26 (m, 2H), 5.44 (s, 1H), 5.01 (d, $J = 15.6$ Hz, 1H), 4.29-4.12 (m, 3H), 2.09 (s, 3H), 1.28 (t, $J = 7.2$ Hz, 3H); **¹³C NMR** (100 MHz, CDCl_3): δ 172.5, 171.4, 162.4, 161.8 (d, $J_{\text{C-F}} = 244.0$ Hz), 158.0, 150.7, 142.7, 137.4, 135.1, 134.5, 130.13 (d, $J_{\text{C-F}} = 3.0$ Hz), 129.8, 129.0 (2C), 128.7 (2C Hz), 128.3 (2C), 128.1 (d, $J_{\text{C-F}} = 8.0$ Hz) (2C), 127.7, 125.4, 125.0, 123.9, 123.2, 119.3 (2C), 115.5 (d, $J_{\text{C-F}} = 22.0$ Hz) (2C), 109.1, 71.0, 66.0, 61.2, 55.7, 42.5, 17.2, 14.0; HRMS (ESI) m/z calculated for $\text{C}_{37}\text{H}_{20}\text{FN}_3\text{NaO}_4$ $[\text{M}+\text{Na}]^+ = 622.2112$, found = 622.2138; Enantiomeric excess: 88%, determined by HPLC (Chiralpak OD-H, hexane/EtOH = 95/5; flow rate 0.8 mL/min; 25 °C; 254 nm), t_r (major) = 22.132 min, t_r (minor) = 24.572 min.

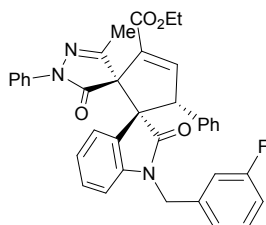


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.110	BV	0.8655	1.26140e4	190.26646	44.4753
2	24.397	VB	0.7256	1.57478e4	309.49762	55.5247

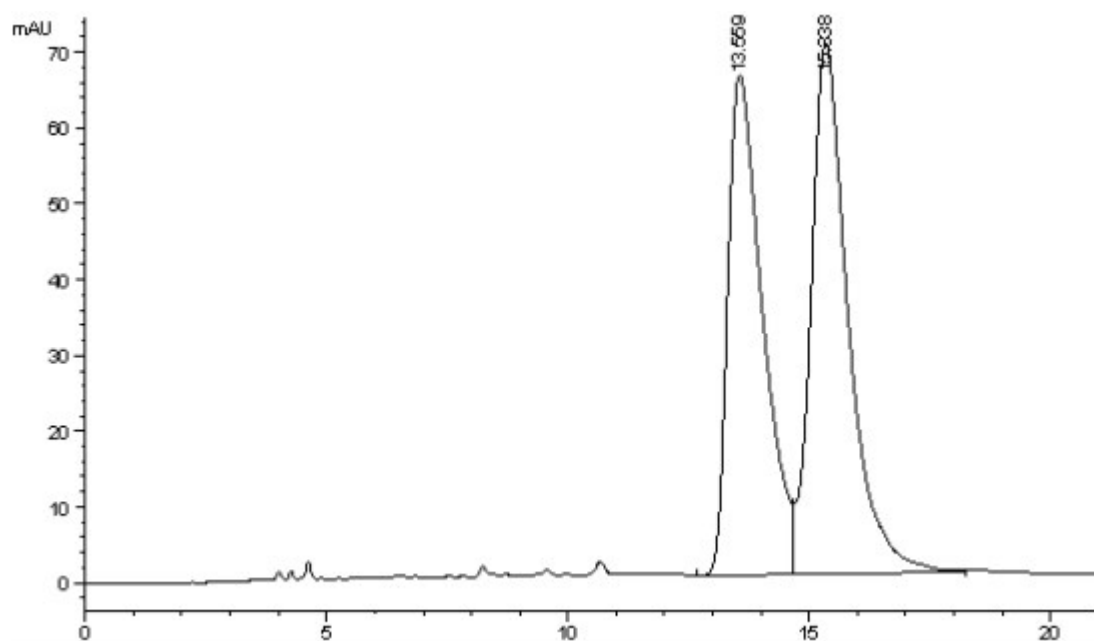


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.132	BB	0.8846	1.20452e4	178.65672	93.7868
2	24.572	BB	0.6392	797.97748	14.65699	6.2132

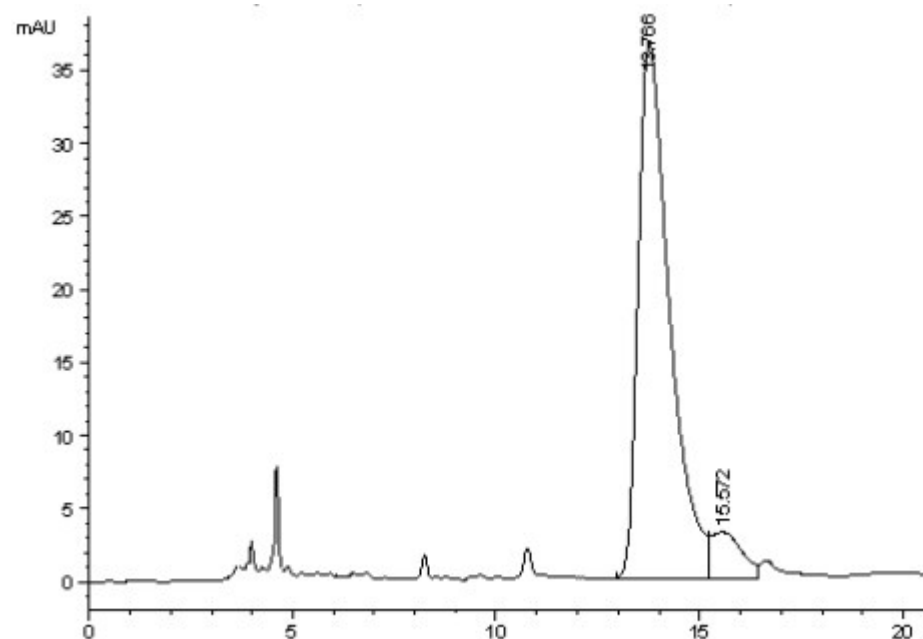
16) ethyl (2'*R*, 3*R*, 5'*R*)-1-(3-fluorobenzyl)-3''-methyl-2,5''-dioxo-1'',5'-diphenyl- 1'',5''-dihydrodispiro- [indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-3'-carboxylate (3an)



87 % yield, 86% *ee*; white solid; m.p.: 120-121 °C; $[\alpha]_D^{25} = +270.6$ ($c = 1.0$, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ 7.82 (d, $J = 7.6$ Hz, 1H), 7.76 (d, $J = 8.0$ Hz, 2H), 7.72 (d, $J = 1.6$ Hz, 1H), 7.36 (t, $J = 8.0$ Hz, 2H), 7.24 (d, $J = 7.2$ Hz, 1H), 7.20-.08 (m, 4H), 7.03-.92 (m, 4H), 6.82 (td, $J = 8.4$, 1.6Hz, 1H), 6.41 (d, $J = 7.6$ Hz, 1H), 6.18 (d, $J = 9.2$ Hz, 1H), 6.10 (d, $J = 7.6$ Hz, 1H), 5.43 (s, 1H), 5.00 (d, $J = 15.6$ Hz, 1H), 4.31-4.14 (m, 3H), 2.08 (s, 3H), 1.28 (t, $J = 7.2$ Hz, 3H); ¹³C NMR (100MHz, CDCl₃): 172.5, 171.4 162.8 (d, $J_{C-F} = 246.0$ Hz), 162.4, 161.5, 158.0, 150.7, 142.8, 137.5, 137.1 (d, $J_{C-F} = 7.0$ Hz), 134.9, 134.5, 130.2 (d, $J_{C-F} = 9.0$ Hz), 129.9, 128.8 (2C), 128.7 (2C), 128.3 (2C), 128.1, 125.4, 125.0, 123.9, 123.2, 122.0, 119.4 (2C), 117.2, 114.4 (d, $J_{C-F} = 22.0$ Hz), 113.6 (d, $J_{C-F} = 22.0$ Hz), 113.5, 109.1, 71.0, 66.1, 61.2, 55.8, 42.8, 17.2, 14.0; HRMS (ESI) m/z calculated for C₄₀H₃₇N₃NaO₄ [M+H]⁺ = 646.2676, found = 646.2696; Enantiomeric excess: 86%, determined by HPLC (Chiralpak OD-H, hexane/*i*-PrOH = 85/15; flow rate 0.8 mL/min; 25 °C; 254 nm), t_r (major) = 21.928 min, t_r (minor) = 25.748 min.

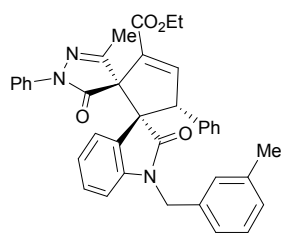


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.559	VV	0.7305	3300.79980	65.83984	46.7442
2	15.338	VB	0.8016	3760.60767	69.98473	53.2558

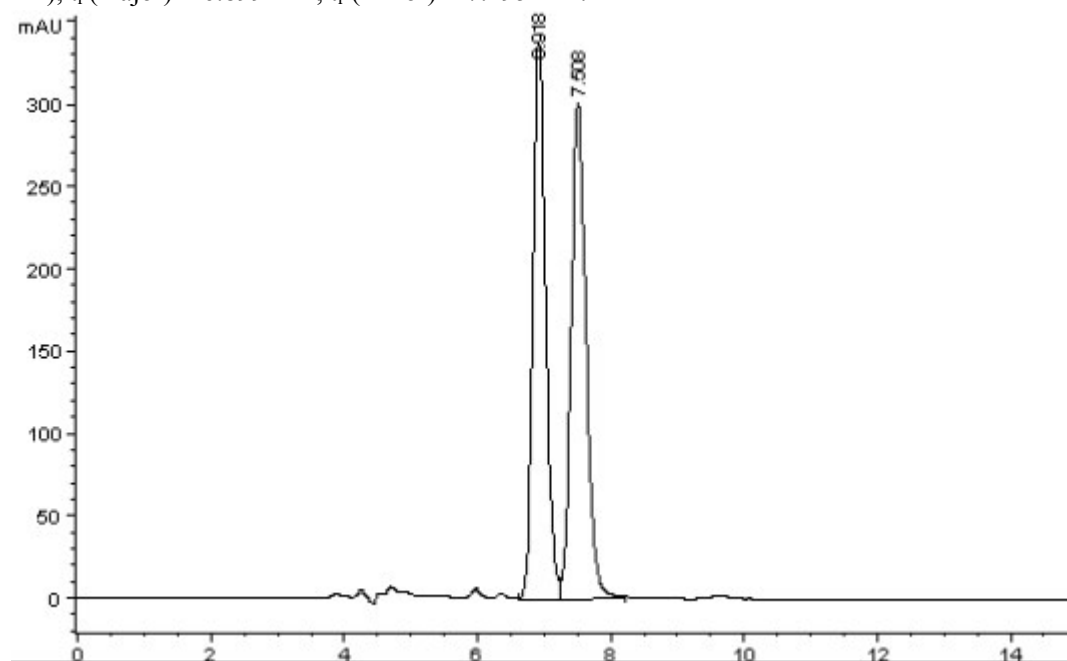


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.766	BV	0.8197	1969.92395	36.62339	92.3941
2	15.572	VV	0.7346	162.16539	3.14963	7.6059

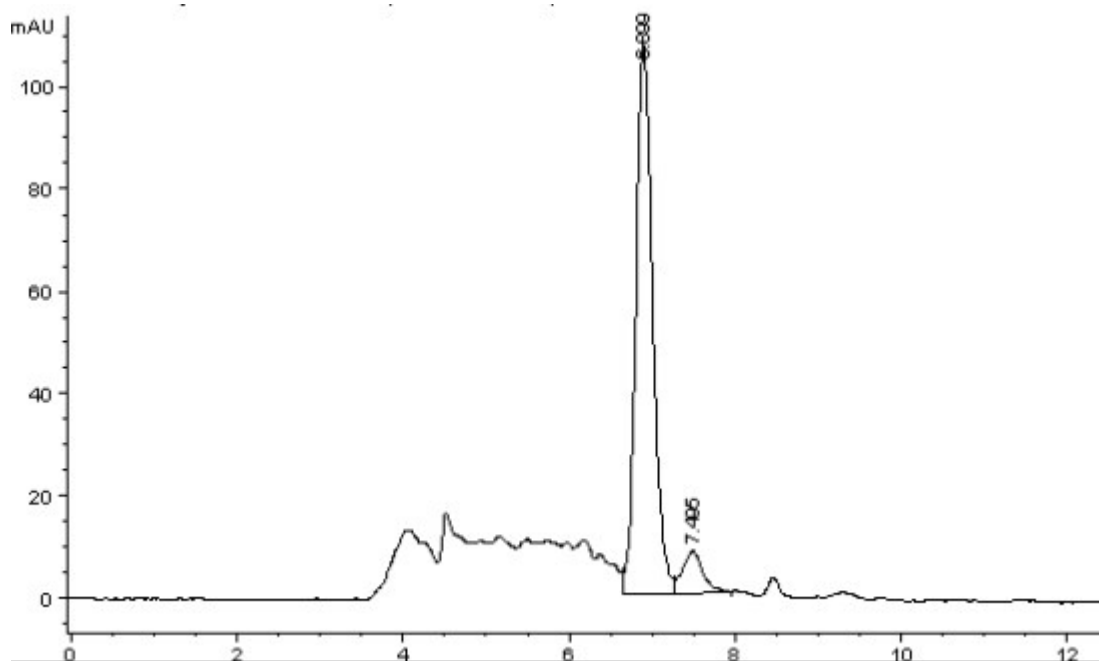
17) ethyl (2'*R*, 3*R*, 5'*R*)-3''-methyl-1-(3-methylbenzyl)-2,5''-dioxo-1'',5'-diphenyl- 1'',5'-dihydrodispiro- [indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-3'-carboxylate (3ao)



85 % yield, 84% *ee*; white solid; m.p.: 124-125 °C; $[\alpha]_D^{25} = +97.5$ ($c = 1.0$, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ 7.81 (d, $J = 7.6$ Hz, 1H), 7.77 (d, $J = 8.0$ Hz, 2H), 7.72 (d, $J = 1.6$ Hz, 1H), 7.36 (t, $J = 8.0$ Hz, 2H), 7.23 (d, $J = 7.2$ Hz, 1H), 7.19-7.13 (m, 3H), 7.10 (t, $J = 7.6$ Hz, 1H), 6.99-6.94 (m, 4H), 6.90 (t, $J = 7.6$ Hz, 1H), 6.66 (s, 1H), 6.44 (d, $J = 7.6$ Hz, 1H), 5.95 (d, $J = 7.2$ Hz, 1H), 5.42 (s, 1H), 4.88 (d, $J = 15.6$ Hz, 1H), 4.31-4.13 (m, 3H), 2.23 (s, 3H), 2.07 (s, 3H), 1.28 (t, $J = 7.2$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 172.5, 171.5, 162.4, 158.1, 150.8, 143.2, 138.1, 137.5, 135.1, 134.52, 134.49, 129.8, 128.9 (2C), 128.7 (2C), 128.6, 128.2 (2C), 128.1, 127.8, 127.5, 125.3, 124.8, 123.9, 123.4, 123.0, 119.4 (2C), 109.3, 71.0, 66.1, 61.2, 55.8, 43.3, 21.3, 17.2, 14.0; HRMS (ESI) m/z calculated for C₃₈H₃₃N₃NaO₄ [M+Na]⁺ = 618.2363, found = 618.2380; Enantiomeric excess: 84%, determined by HPLC (Chiralpak OD-H, hexane/EtOH = 70/30; flow rate 0.8 mL/min; 25 °C; 254 nm), t_r (major) = 6.899 min, t_r (minor) = 7.495 min.

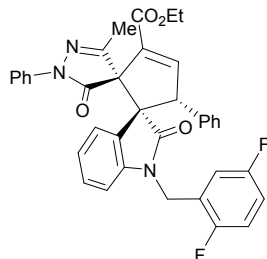


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.918	BV	0.2088	4557.22021	339.13263	49.3079
2	7.508	VB	0.2393	4685.15479	301.54431	50.6921

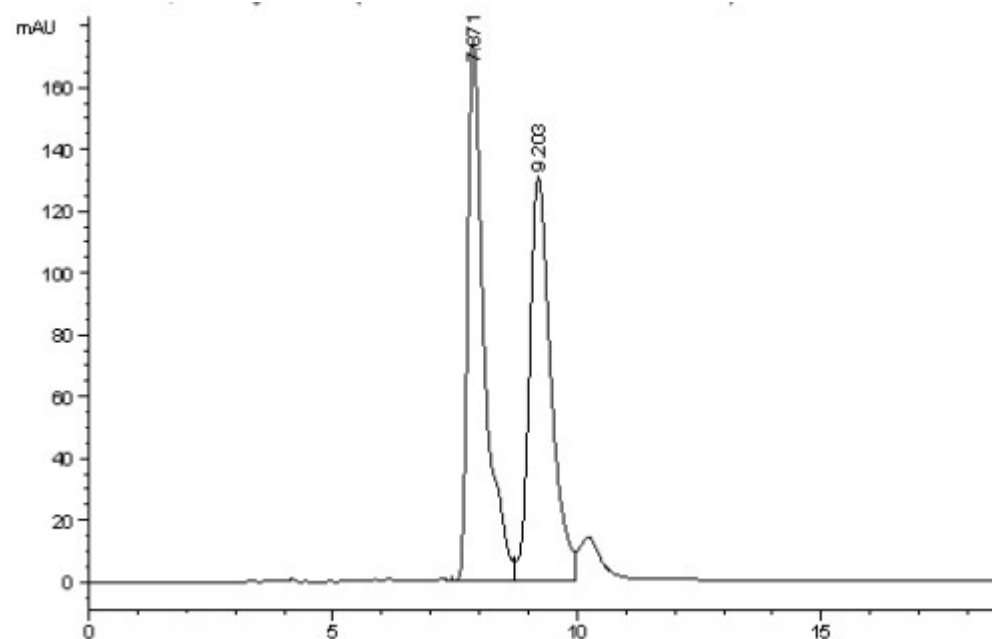


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.899	VV	0.2157	1515.90698	108.02499	91.8215
2	7.495	VB	0.2391	135.02110	8.15567	8.1785

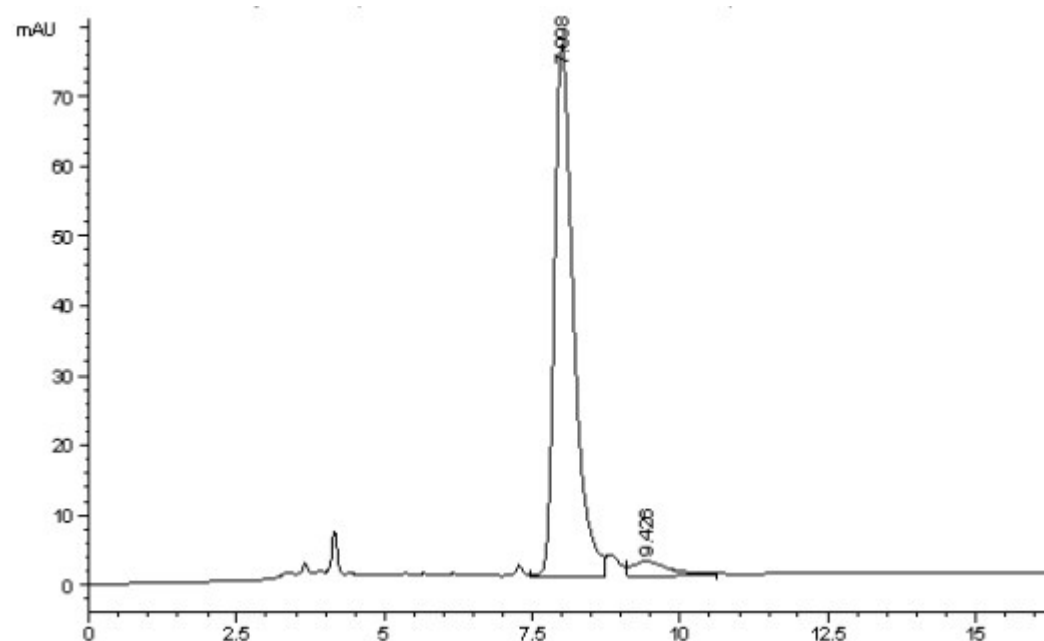
18) ethyl (2'*R*, 3*R*, 5'*R*)-1-(2,5-difluorobenzyl)-3''-methyl-2,5''-dioxo-1'',5'-diphenyl- 1'',5''-dihydrodispiro- [indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-3'-carboxylate (3ap)



86 % yield, 90% *ee*; white solid; m.p.: 124-125 °C; $[\alpha]_D^{25} = +136.8$ ($c = 1.0$, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ 7.83 (d, $J = 7.6$ Hz, 1H), 7.77 (d, $J = 8.4$ Hz, 2H), 7.72 (s, 1H), 7.36 (t, $J = 7.6$ Hz, 2H), 7.22-7.10 (m, 5H), 7.01 (t, $J = 7.6$ Hz, 1H), 6.93-6.89 (m, 3H), 6.83-6.75 (m, 1H), 6.51 (d, $J = 7.6$ Hz, 1H), 5.56-5.52 (m, 1H), 5.43 (s, 1H), 4.86 (d, $J = 16.0$ Hz, 1H), 4.41 (d, $J = 16.0$ Hz, 1H), 4.30-4.13 (m, 2H), 2.09 (s, 3H), 1.28 (t, $J = 7.2$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 172.7, 171.3, 162.3, 158.5 (d, $J_{C-F} = 242.0$ Hz), 157.9, 156.1 (d, $J_{C-F} = 242.0$ Hz), 150.6, 142.4, 137.4, 134.6, 134.5, 130.0, 128.7 (2C), 128.5 (2C), 128.4, 128.1 (2C), 125.3, 125.0, 123.8, 123.5 (d, $J_{C-F} = 7.0$ Hz), 123.3, 119.3 (2C), 116.2 (dd, $J_{C-F} = 24.0, 8.0$ Hz), 115.7 (dd, $J_{C-F} = 24.0, 8.0$ Hz), 114.9 (d, $J_{C-F} = 24.0$ Hz), 108.7, 70.94, 66.0, 61.2, 55.75, 36.4 (d, $J_{C-F} = 4.0$ Hz), 17.2, 14.0; HRMS (ESI) m/z calculated for C₃₇H₂₉F₂N₃NaO₄ [M+Na]⁺ = 640.2018, found = 640.2046; Enantiomeric excess: 90%, determined by HPLC (Chiralpak OD-H, hexane/EtOH = 85/15; flow rate 0.8 mL/min; 25 °C; 254 nm), t_r (major) = 7.998 min, t_r (minor) = 9.426 min.

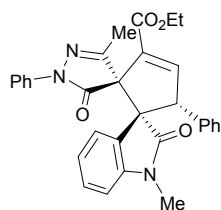


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	7.871	VV	0.3556	4177.07031	174.11523	51.1017
2	9.203	VV	0.4615	3996.96729	130.72844	48.8983

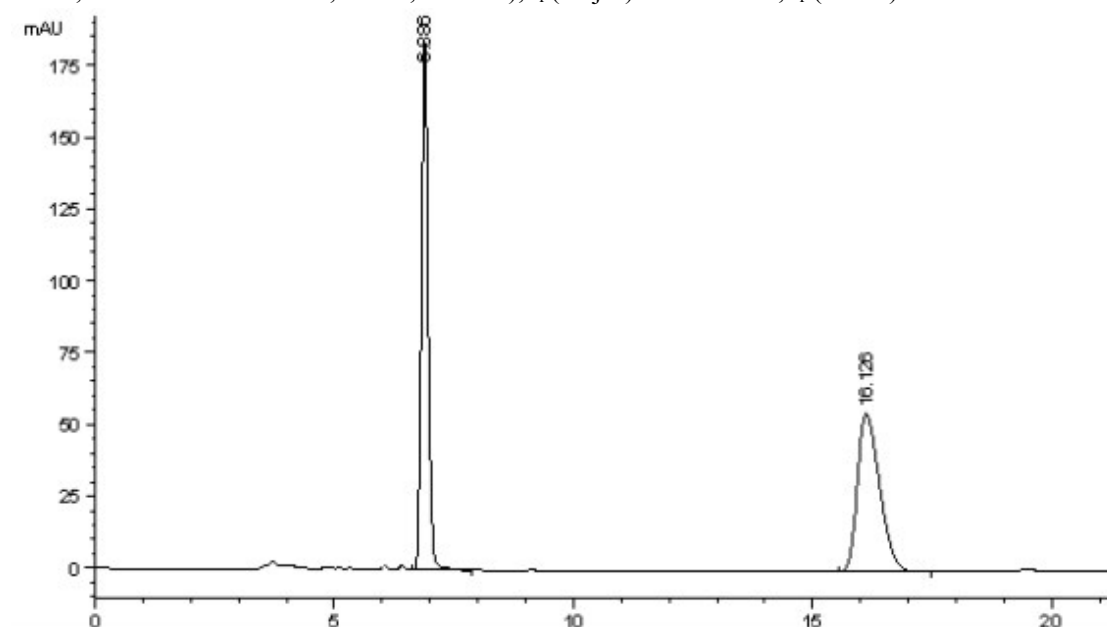


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	7.998	VV	0.3411	1735.40356	76.28513	94.9403
2	9.426	VB	0.6448	92.48574	2.06528	5.0597

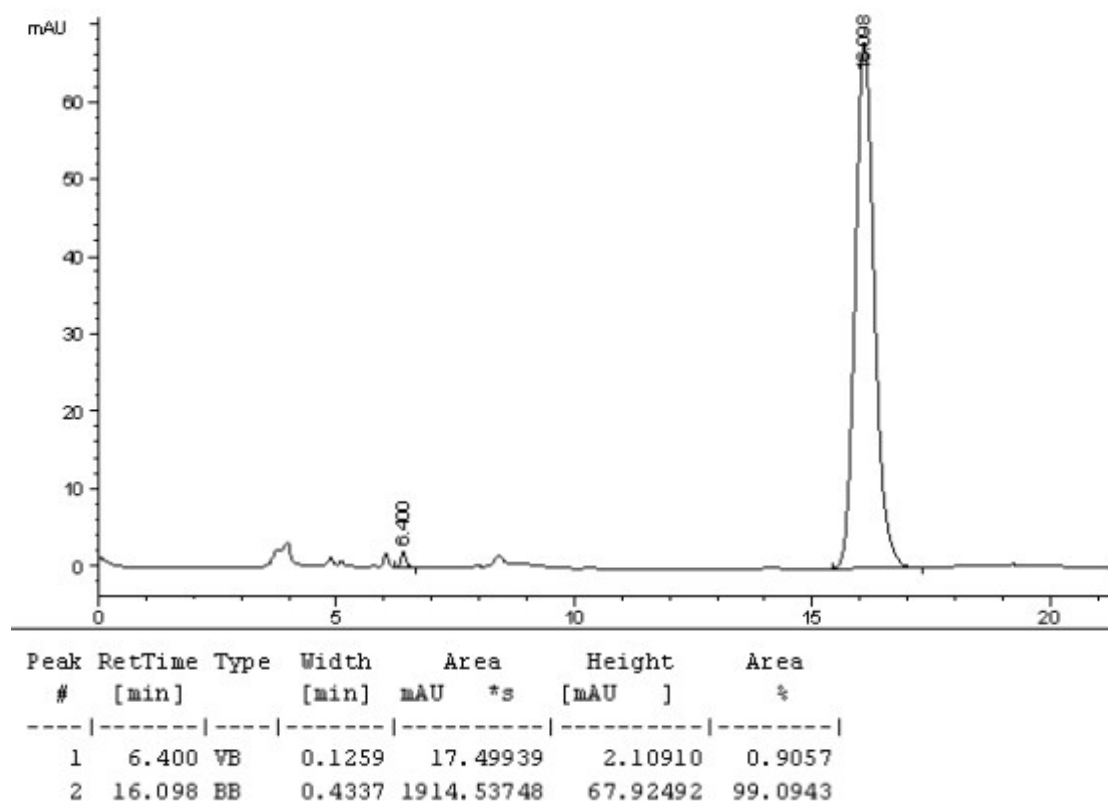
19) ethyl (2'*R*, 3*R*, 5'*R*)-1,3''-dimethyl-2,5''-dioxo-1'',5'-diphenyl-1'',5'-dihydrodispiro-[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-3'-carboxylate (3aq)



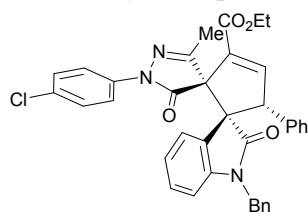
80 % yield, 98% *ee*; white solid; m.p.: 96-97 °C; $[\alpha]_D^{25} = +173.0$ ($c = 1.0$, CH_2Cl_2); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.77 (d, $J = 8.8$ Hz, 3H), 7.68 (d, $J = 2.0$ Hz, 1H), 7.36 (t, $J = 8.0$ Hz, 2H), 7.23 (d, $J = 8.0$ Hz, 1H), 7.20-7.08 (m, 4H), 7.00 (t, $J = 7.6$ Hz, 1H), 6.86 (d, $J = 6.8$ Hz, 2H), 6.60 (d, $J = 7.6$ Hz, 1H), 5.34 (s, 1H), 4.28-4.14 (m, 2H), 2.77 (s, 3H), 2.07 (s, 3H), 1.27 (t, $J = 7.0$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 172.3, 171.5, 162.4, 158.3, 150.5, 144.0, 137.5, 135.0, 134.6, 129.8, 128.7 (2C), 128.4 (2C), 127.9 (2C), 127.6, 125.3, 124.8, 124.1, 123.1, 119.4 (2C), 108.0, 70.6, 66.2, 61.2, 55.9, 25.6, 17.2, 14.0; HRMS (ESI) m/z calculated for $\text{C}_{31}\text{H}_{27}\text{F}_2\text{N}_3\text{NaO}_4$ $[\text{M}+\text{Na}]^+ = 528.1893$, found = 528.1911; Enantiomeric excess: 90%, determined by HPLC (Chiralpak AD-H, hexane/EtOH = 70/30; flow rate 0.8 mL/min; 25 °C; 254 nm), t_r (major) = 6.400 min, t_r (minor) = 16.098 min.



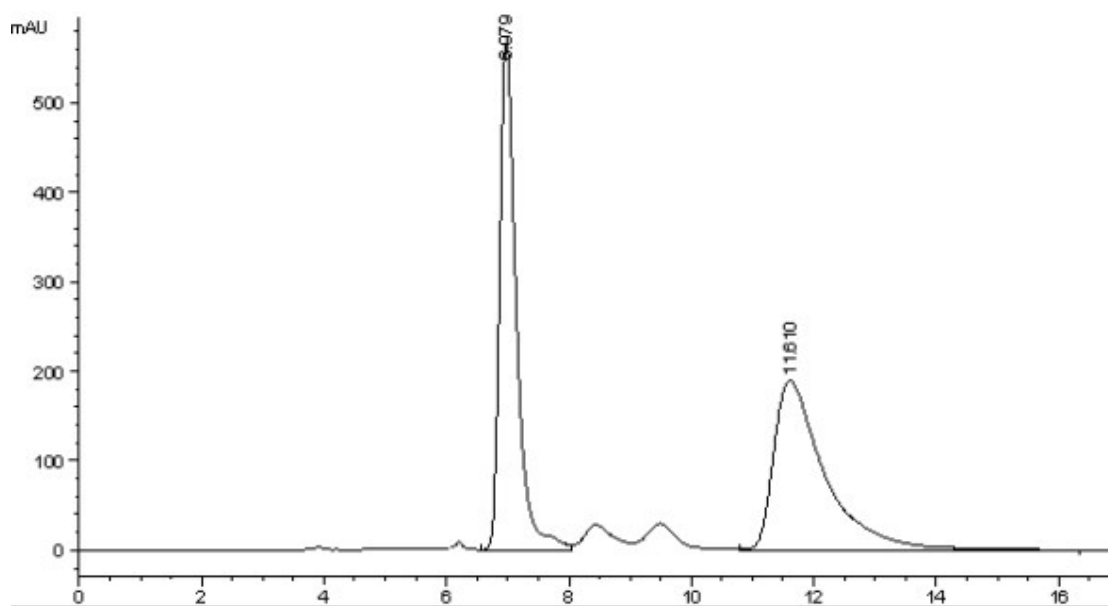
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.886	VB	0.1485	1782.28320	183.06154	50.0285
2	16.126	BB	0.5058	1780.25598	54.99347	49.9715



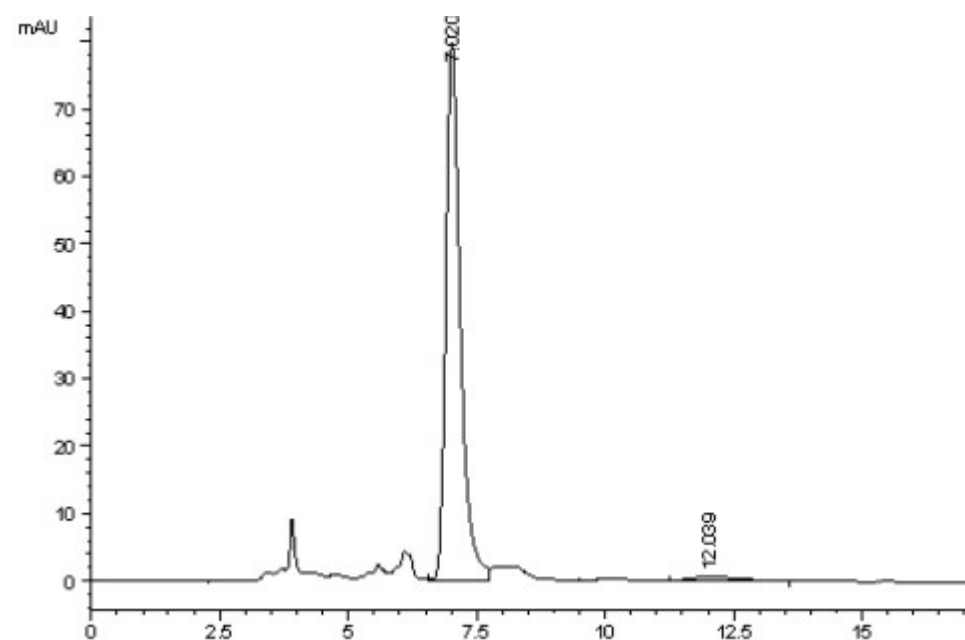
20) ethyl (2'*R*, 3*R*, 5'*R*)-1-benzyl-1''-(4-chlorophenyl)-3''-methyl-2,5''-dioxo-5'-phenyl-1'',5''- dihydrodispiro[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-3'-carboxylate (3ar)



92 % yield, 94% *ee*; white solid; m.p.: 113-114 °C; $[\alpha]_D^{25} = +131.2$ ($c = 1.0$, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ 7.77-7.74 (m, 3H), 7.72 (d, $J = 1.6$ Hz, 1H), 7.36-7.27 (m, 3H), 7.21-7.01 (m, 7H), 6.99-6.92 (m, 3H), 6.41 (d, $J = 7.6$ Hz, 1H), 6.35 (d, $J = 7.6$ Hz, 2H), 5.41 (s, 1H), 5.01 (d, $J = 15.6$ Hz, 1H), 4.28-4.15 (m, 3H), 2.08 (s, 3H), 1.28 (t, $J = 7.2$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 172.4, 171.4, 162.4, 158.5, 150.8, 143.0, 136.1, 135.0, 134.4 (2C), 130.4, 129.9, 129.0 (2C), 128.8 (2C), 128.6 (2C), 128.3 (2C), 127.8, 127.2, 126.4 (2C), 124.7, 123.8, 123.0, 120.2 (2C), 109.4, 71.1, 66.1, 61.3, 55.8, 43.2, 17.2, 14.0; HRMS (ESI) m/z calculated for C₃₇H₃₀ClN₃NaO₄ [M+H]⁺ = 638.1817, found = 638.1835; Enantiomeric excess: 94%, determined by HPLC (Chiralpak OD-H, hexane/*i*-PrOH = 70/30; flow rate 0.8 mL/min; 25 °C; 254 nm), t_r (major) = 7.020 min, t_r (minor) = 12.039 min.

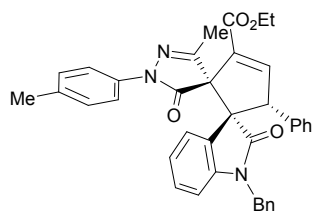


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	6.979	VV	0.2858	1.08001e4	568.13214	49.4818
2	11.610	VB	0.8546	1.10263e4	189.21490	50.5182

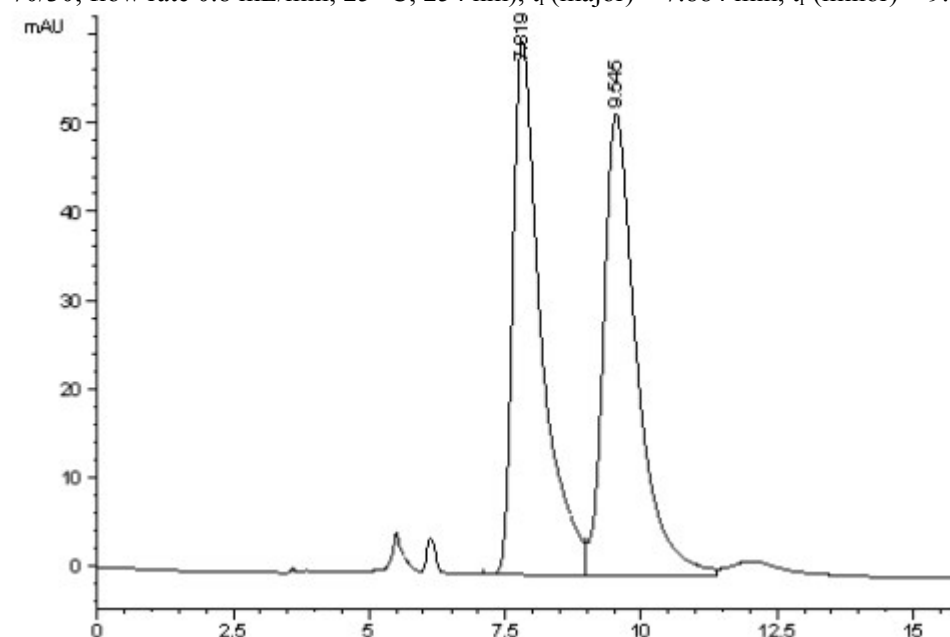


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	7.020	VV	0.3019	1588.51428	79.87417	96.9766
2	12.039	BB	0.8708	49.52470	7.43012e-1	3.0234

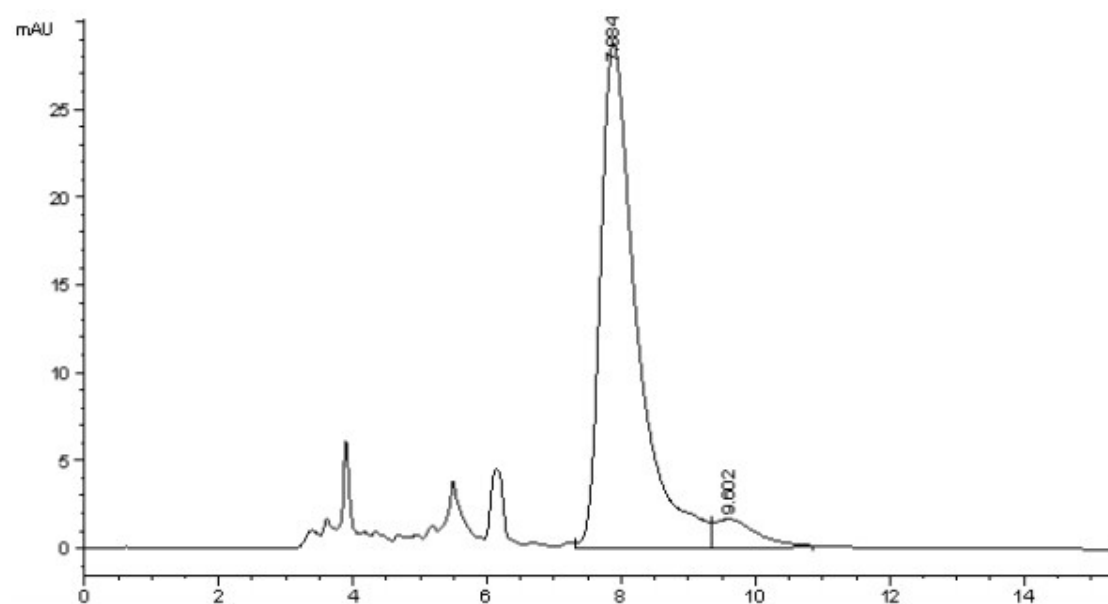
21) ethyl (2'*R*, 3*R*, 5'*R*)-1-benzyl-3''-methyl-2,5''-dioxo-5'-phenyl-1''-(*p*-tolyl)- 1'',5''-dihydrodispiro-[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-3'-carboxylate (3as)



85 % yield, 88% *ee*; white solid; m.p.: 113-114 °C; $[\alpha]_D^{25} = +114.6$ ($c = 1.0$, CH₂Cl₂); **¹H NMR** (400 MHz, CDCl₃): δ 7.82 (d, $J = 7.2$ Hz, 1H), 7.72 (d, $J = 2.0$ Hz, 1H), 7.62 (d, $J = 8.4$ Hz, 2H), 7.29 (d, $J = 6.8$ Hz, 1H), 7.19-7.15 (m, 4H), 7.12-7.02 (m, 4H), 7.00-6.94 (m, 3H), 6.40 (d, $J = 7.6$ Hz, 1H), 6.35 (d, $J = 7.2$ Hz, 2H), 5.43 (s, 1H), 5.01 (d, $J = 15.6$ Hz, 1H), 4.27-4.16 (m, 3H), 2.33 (s, 3H), 2.07 (s, 3H), 1.28 (t, $J = 7.2$ Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 172.5, 171.3, 162.4, 157.9, 150.7, 143.0, 135.13, 135.11, 135.06, 134.6, 134.5, 129.7, 129.3 (2C), 129.0 (2C), 128.6 (2C), 128.3 (2C), 127.7, 127.2, 126.4 (2C), 124.9, 123.9, 123.0, 119.5 (2C), 109.3, 70.9, 66.1, 61.2, 55.8, 43.2, 20.9, 17.2, 14.02; HRMS (ESI) m/z calculated for C₃₈H₃₃N₃NaO₄ $[M+Na]^+ = 618.2363$, found = 618.2376; Enantiomeric excess: 88%, determined by HPLC (Chiralpak OD-H, hexane/*i*-PrOH = 70/30; flow rate 0.8 mL/min; 25 °C; 254 nm), t_r (major) = 7.884 min, t_r (minor) = 9.602 min.



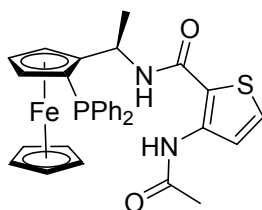
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	7.819	BV	0.5261	2173.71265	60.20446	49.6609
2	9.545	VV	0.6329	2203.39478	52.13342	50.3391



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.884	VV	0.5556	1080.67383	28.71486	93.7324
2	9.602	VB	0.6177	72.26117	1.60722	6.2676

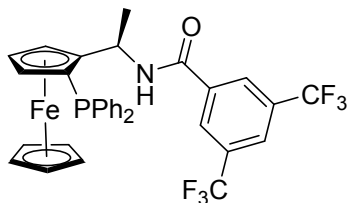
5. General Datas for P3-P5

(R)-3-acetamido-N-[1'-(S)-2'-(diphenylphosphanyl)ferrocenyl]ethyl]-thiophene-2-carboxamide (P3)



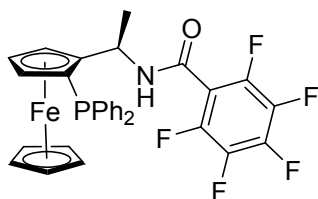
A yellow solid, m.p.:131.9-133.4 °C; $[\alpha]_D^{20} = -158.8$ ($c = 1.0$, CH_2Cl_2); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 11.96 (s, 1H), 7.54-7.50 (m, 2H), 7.38 (d, $J = 4.8$ Hz, 3H), 7.19-7.08 (m, 5H), 6.99 (t, $J = 7.2$ Hz, 1H), 6.76 (d, $J = 5.6$ Hz, 1H), 6.65 (d, $J = 5.6$ Hz, 1H), 5.74-5.30 (m, 1H), 4.51 (s, 1H), 4.34 (s, 1H), 4.01 (s, 5H), 3.83 (s, 1H), 2.26 (s, 3H), 1.41 (d, $J = 6.8$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.9, 163.3, 146.6, 138.2, 136.1, 136.0, 134.9, 134.7, 132.3, 132.2, 129.4, 128.3, 128.2, 128.14, 128.08, 128.0, 120.4, 117.2, 115.9, 114.2, 95.4, 95.3, 72.14, 72.11, 70.80, 70.76, 69.8, 69.4, 44.70, 44.67, 23.5, 22.6; $^{31}\text{P NMR}$ (162 MHz, CDCl_3): δ -23.87; HRMS (ESI) m/z calculated for $\text{C}_{31}\text{H}_{30}\text{FeN}_2\text{O}_2\text{PS}$ $[\text{M}+\text{H}]^+ = 581.1110$, found = 581.1158.

(R)-5-chloro-N-[1'-(S)-2'-(dicyclohexylphosphanyl)ferrocenyl]ethyl]-3,5-bis(trifluoromethyl)benzamide (P4)



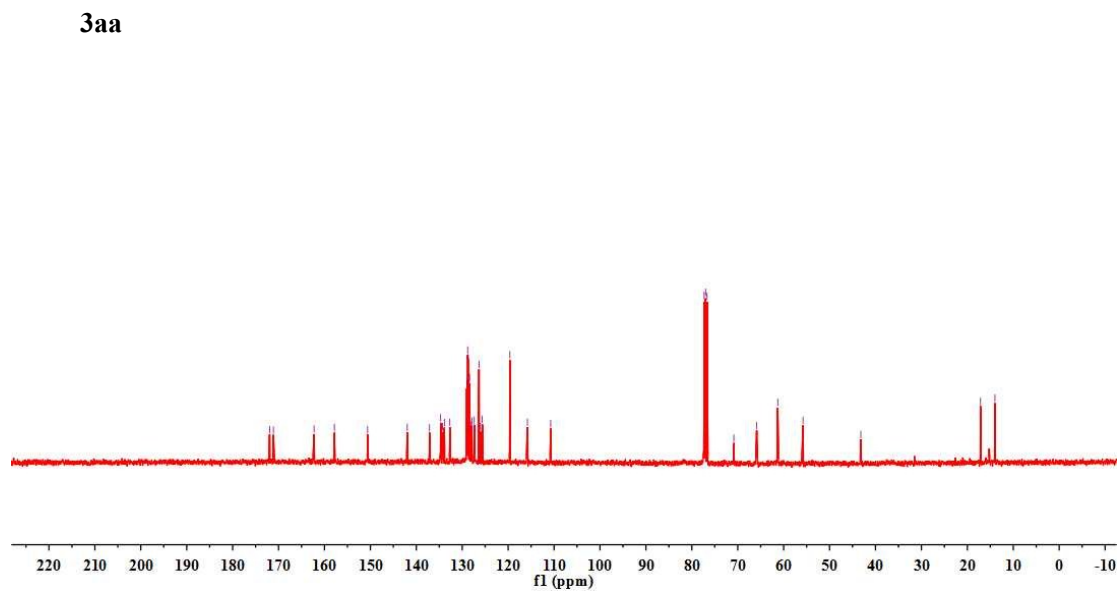
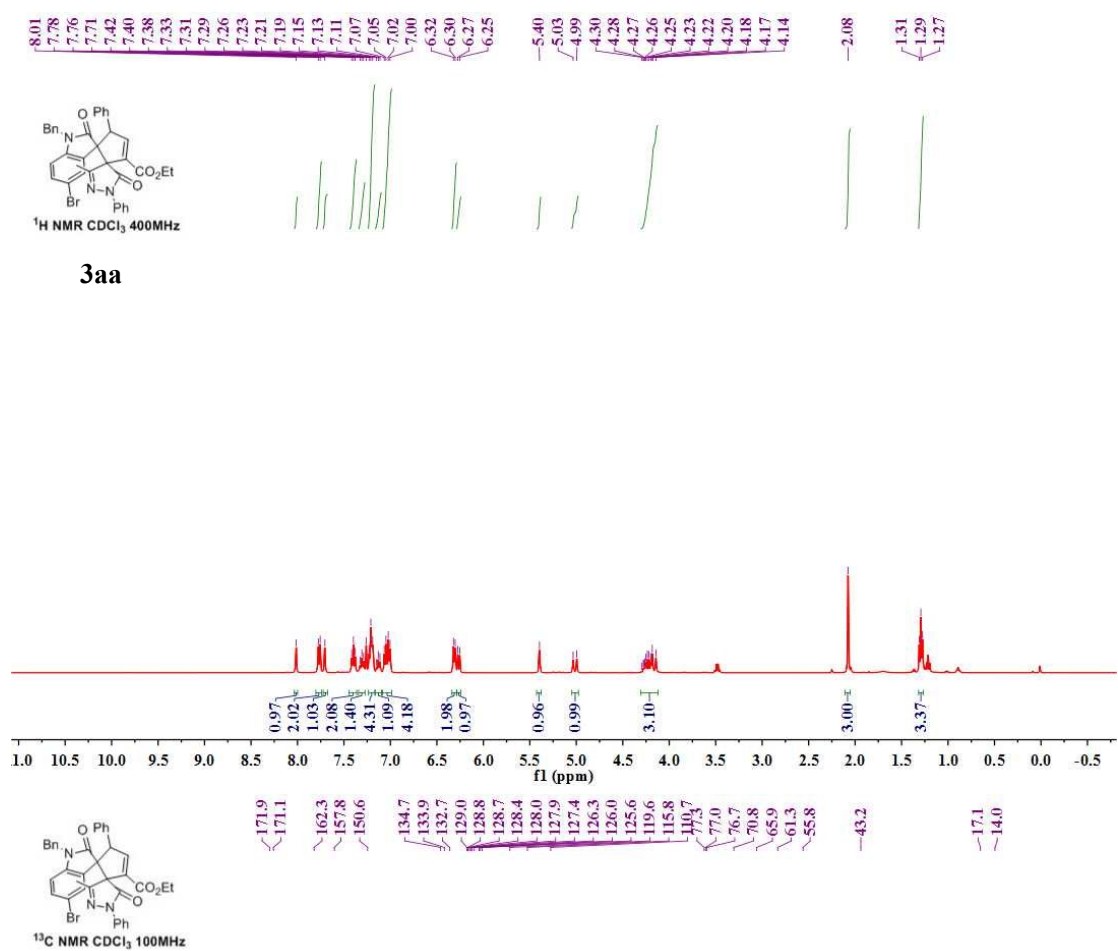
A yellow solid, m.p.:201.7-202.0 °C; $[\alpha]_D^{20} = -339.8$ ($c = 1.0$, CH_2Cl_2); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.05 (s, 2H), 7.93 (s, 1H), 7.52-7.48 (m, 2H), 7.38-7.37 (m, 3H), 7.13 (t, $J = 7.2$ Hz, 2H), 7.02 (t, $J = 7.2$ Hz, 2H), 6.97-6.89 (m, 2H), 5.44 (p, $J = 6.5$ Hz, 1H), 4.59 (s, 1H), 4.38 (s, 1H), 4.04 (s, 5H), 3.86 (s, 1H), 1.52 (d, $J = 6.8$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 162.0, 138.6, 138.6, 136.2, 135.93, 135.88, 134.9, 134.7, 132.3, 132.1, 131.9, 131.5, 128.3, 128.2, 128.13, 128.06, 127.1, 124.5, 124.3, 121.6, 94.6, 94.3, 72.24, 72.20, 70.66, 70.62, 69.9, 69.5, 46.0, 45.9, 21.7; $^{31}\text{P NMR}$ (162 MHz, CDCl_3): δ -24.34; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -62.70; HRMS (ESI) m/z calculated for $\text{C}_{33}\text{H}_{27}\text{F}_6\text{FeNOP}$ $[\text{M}+\text{H}]^+ = 654.1079$, found = 654.1112.

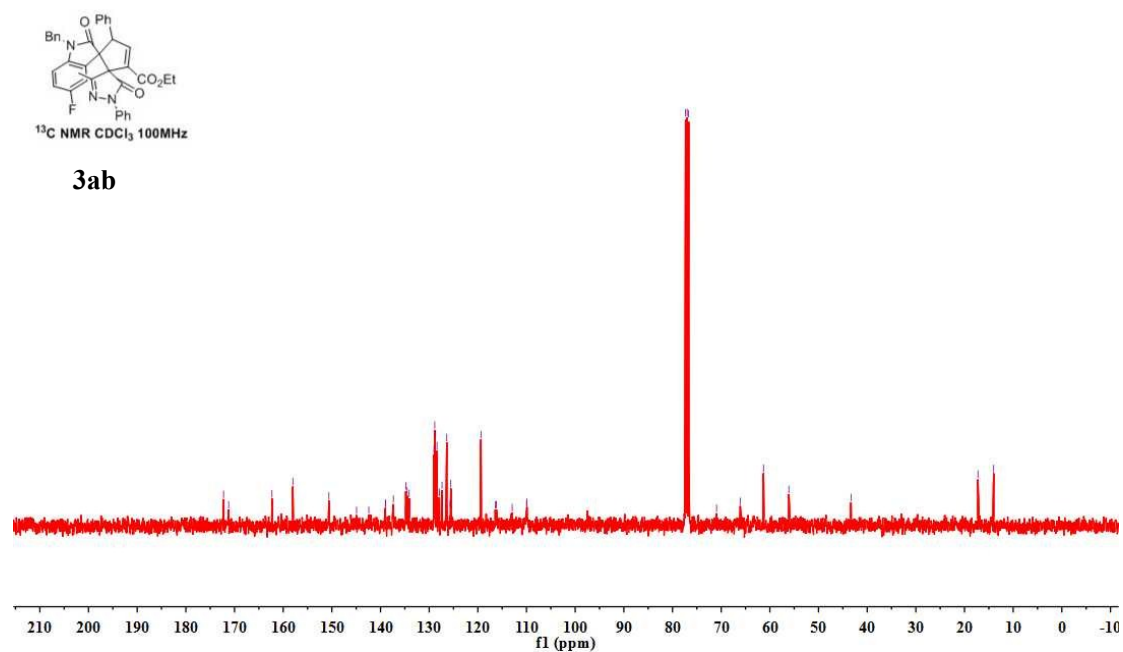
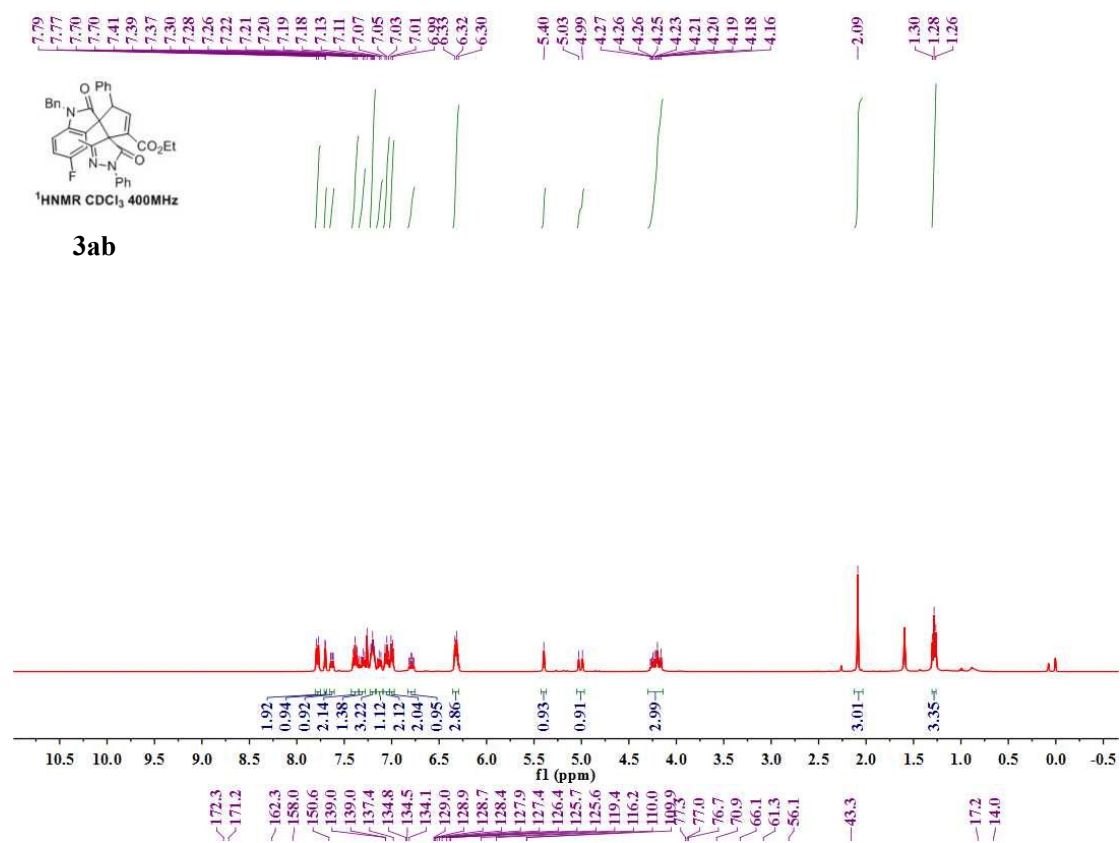
(R)-5-chloro-N-[1'-(S)-2'-(dicyclohexylphosphanyl)ferrocenyl]ethyl]-2,3,4,5,6-pentafluorobenzamide (P5)

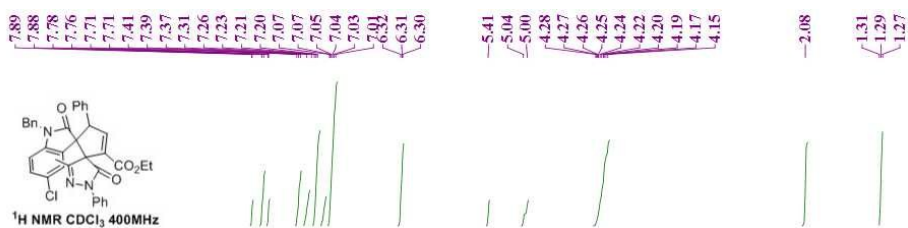


A yellow solid, m.p.:160.2-161.7 °C; $[\alpha]_D^{20} = -158.8$ ($c = 1.0$, CH_2Cl_2); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.50-7.45 (m, 2H), 7.38-7.36 (m, 3H), 7.14-7.09 (m, 4H), 7.06-7.03 (m, 1H), 6.42 (s, 1H), 5.38-5.31 (m, 1H), 4.53 (s, 1H), 4.35 (s, 1H), 4.06 (s, 5H), 3.80 (s, 1H), 1.52 (d, $J = 6.8$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 155.4, 145.3, 139.33, 139.25, 136.1, 136.0, 135.0, 134.8, 132.2, 132.1, 129.4, 128.23, 128.15, 128.0, 127.9, 127.8, 93.6, 93.4, 74.5, 74.4, 72.34, 72.30, 70.51, 70.47, 70.0, 69.5, 46.6, 46.5, 21.1; $^{31}\text{P NMR}$ (162 MHz, CDCl_3): δ -24.46; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -139.81 (d, $J = 15.5$ Hz), -151.75 (t, $J = 20.8$ Hz), -160.71 (qd, $J = 10.8, 4.3$ Hz); HRMS (ESI) m/z calculated for $\text{C}_{31}\text{H}_{24}\text{F}_6\text{FeNOP}$ $[\text{M}+\text{H}]^+ = 608.0860$, found = 608.0891.

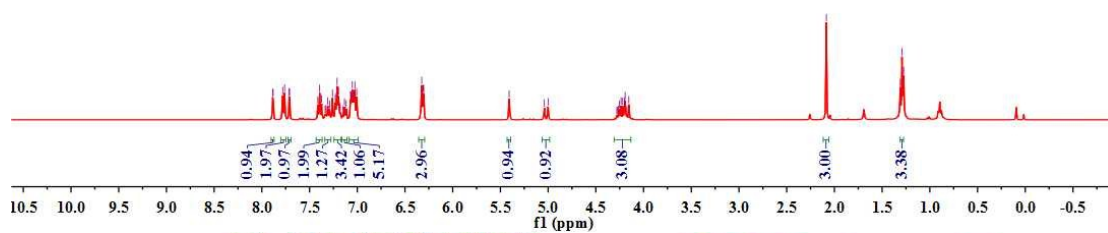
6. Copies of NMR Spectra



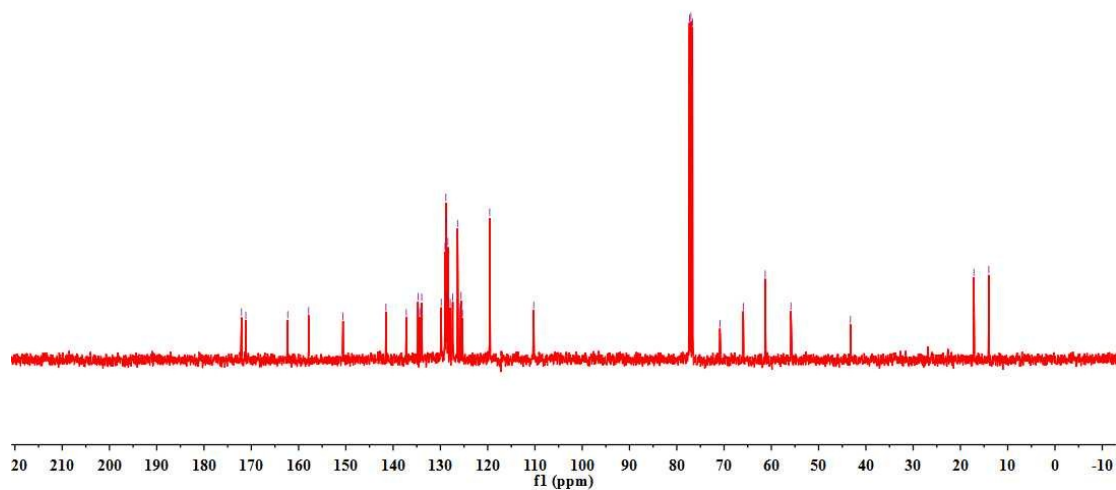


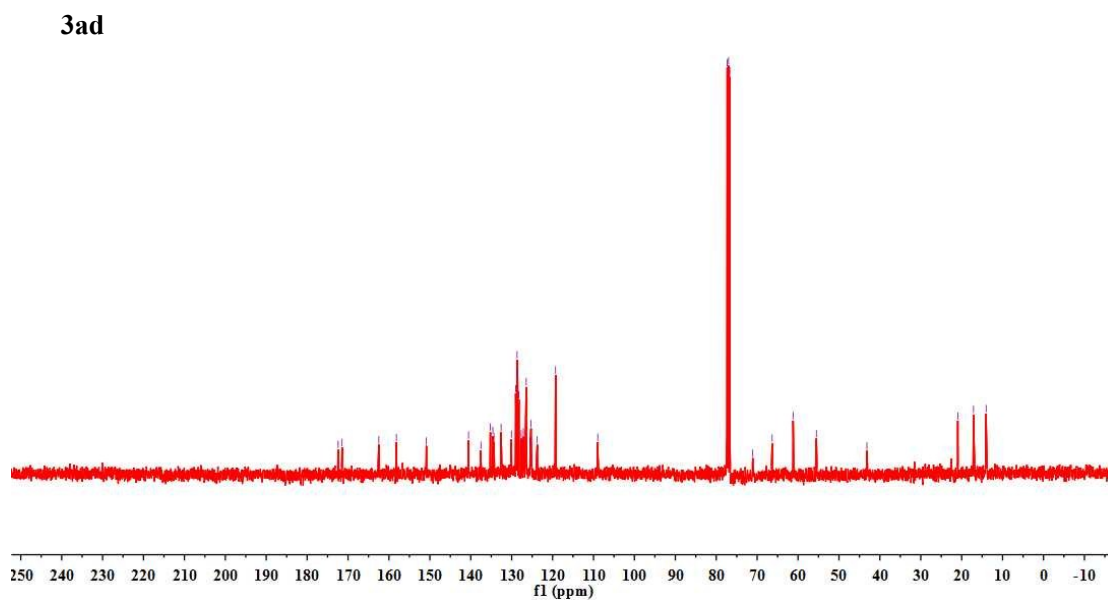
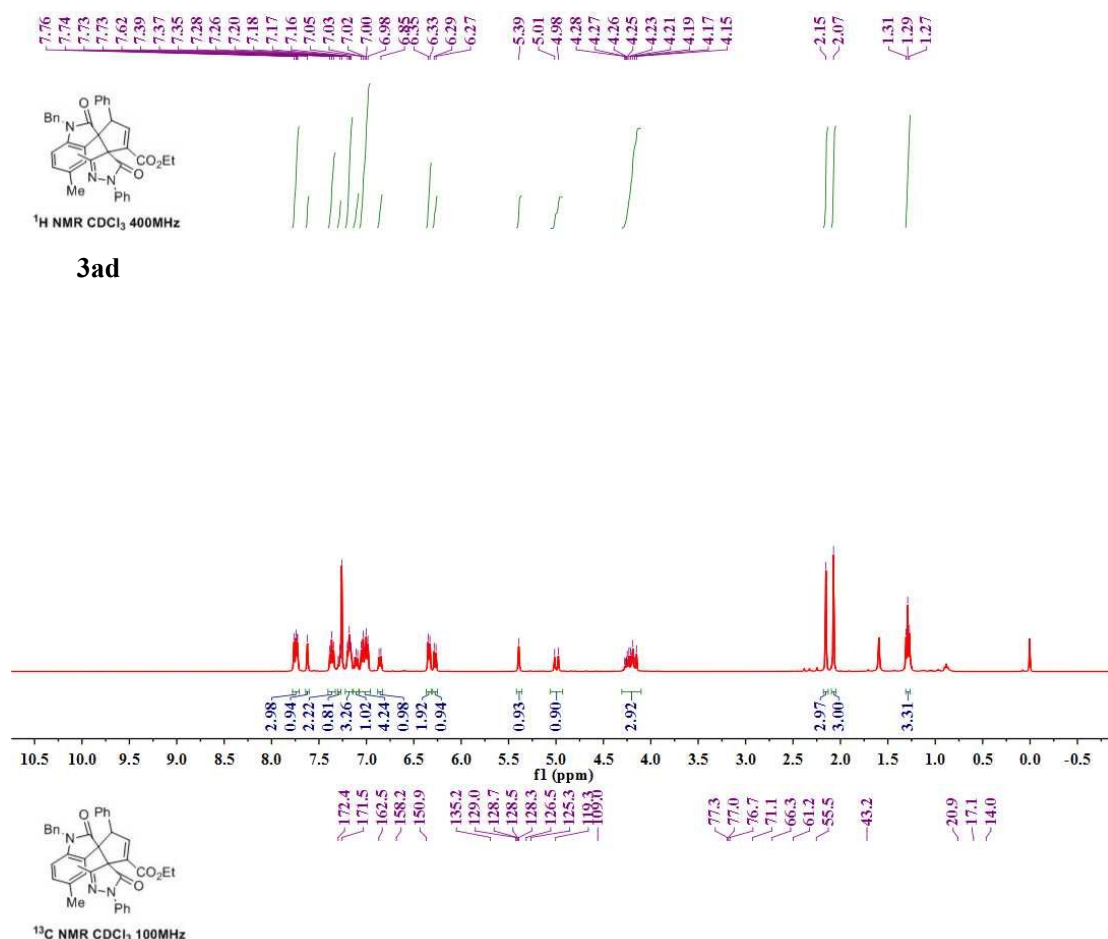


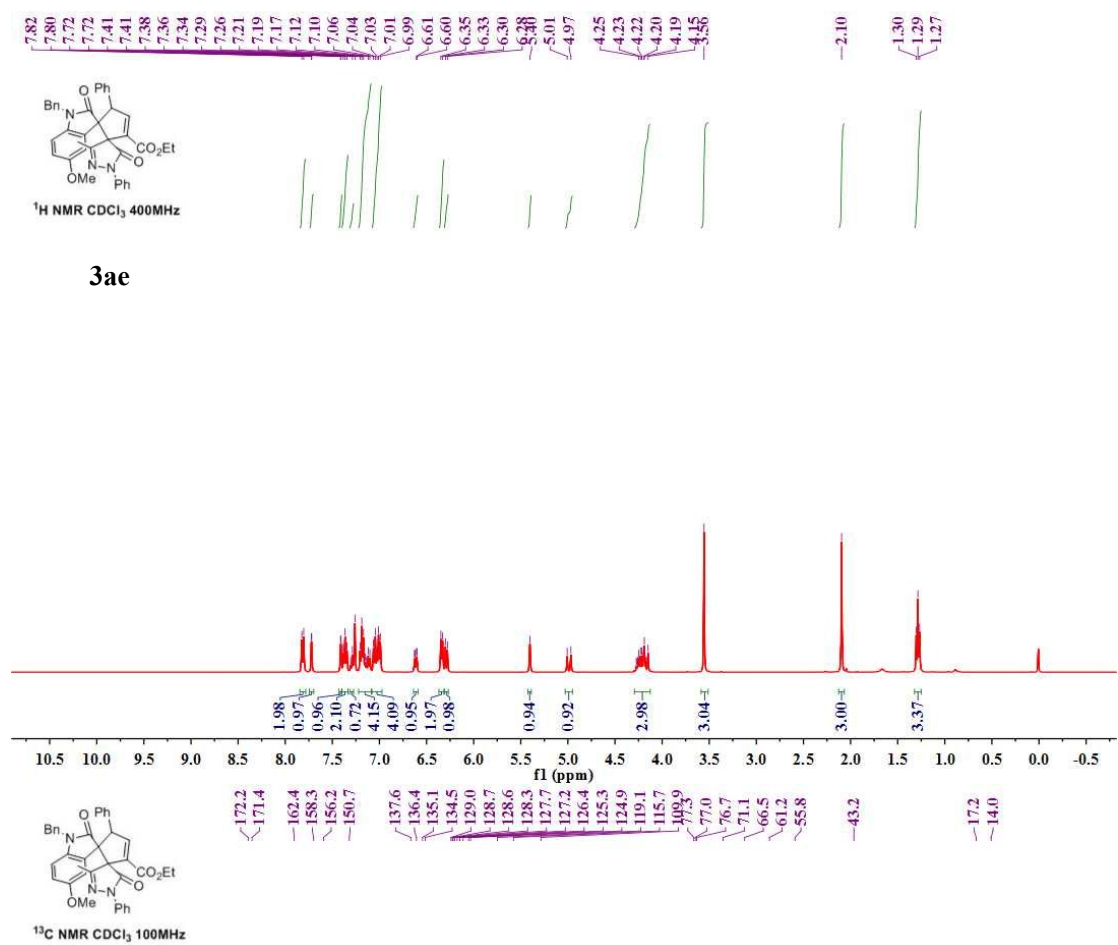
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3ac

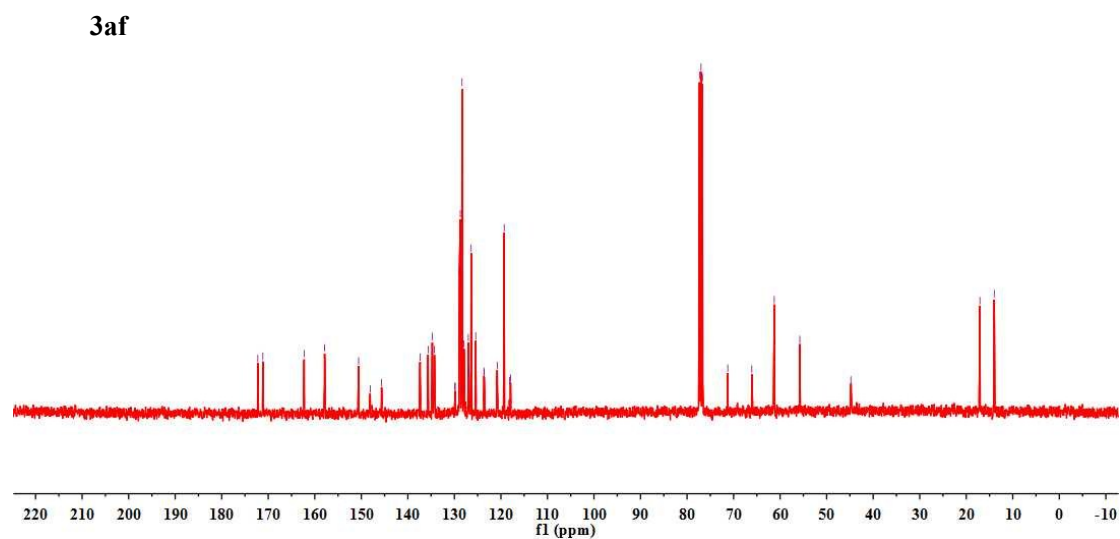
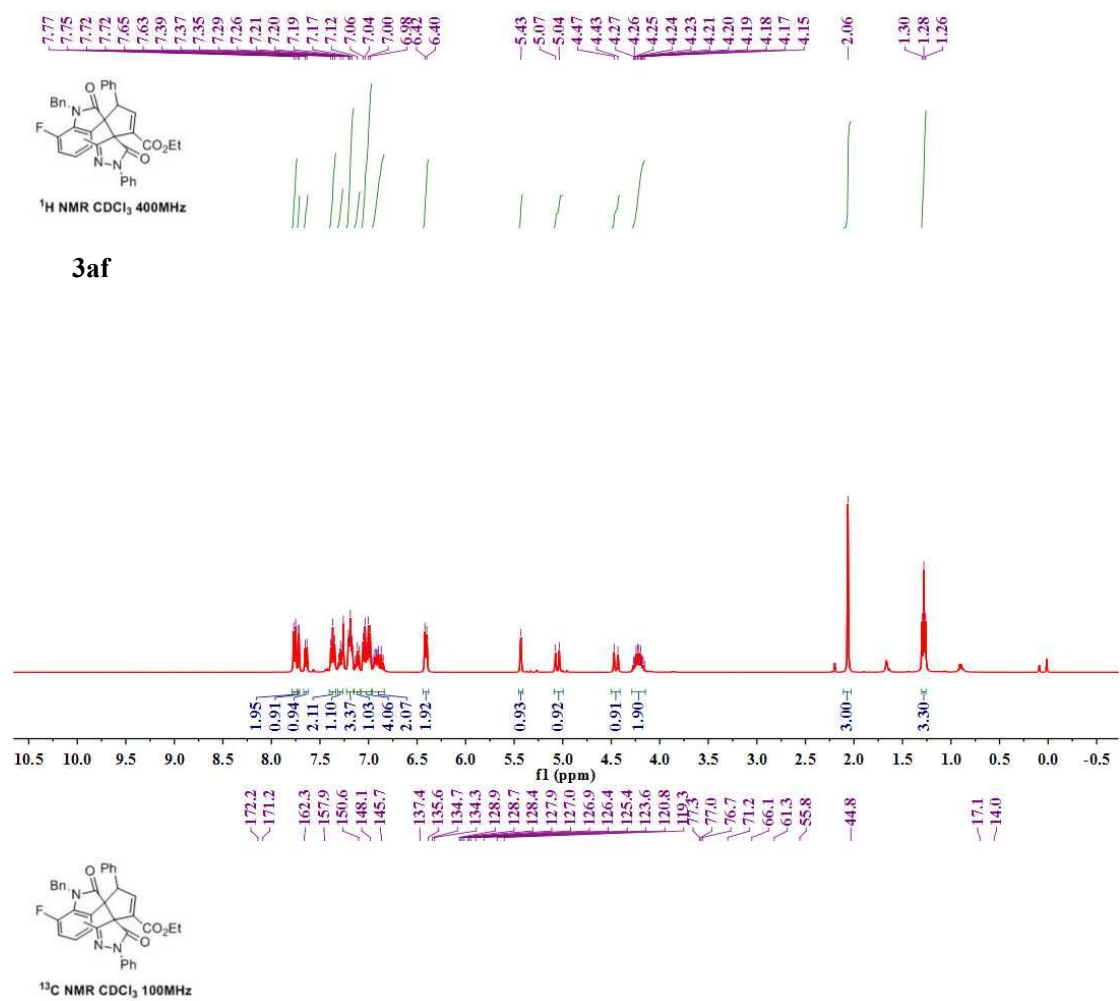


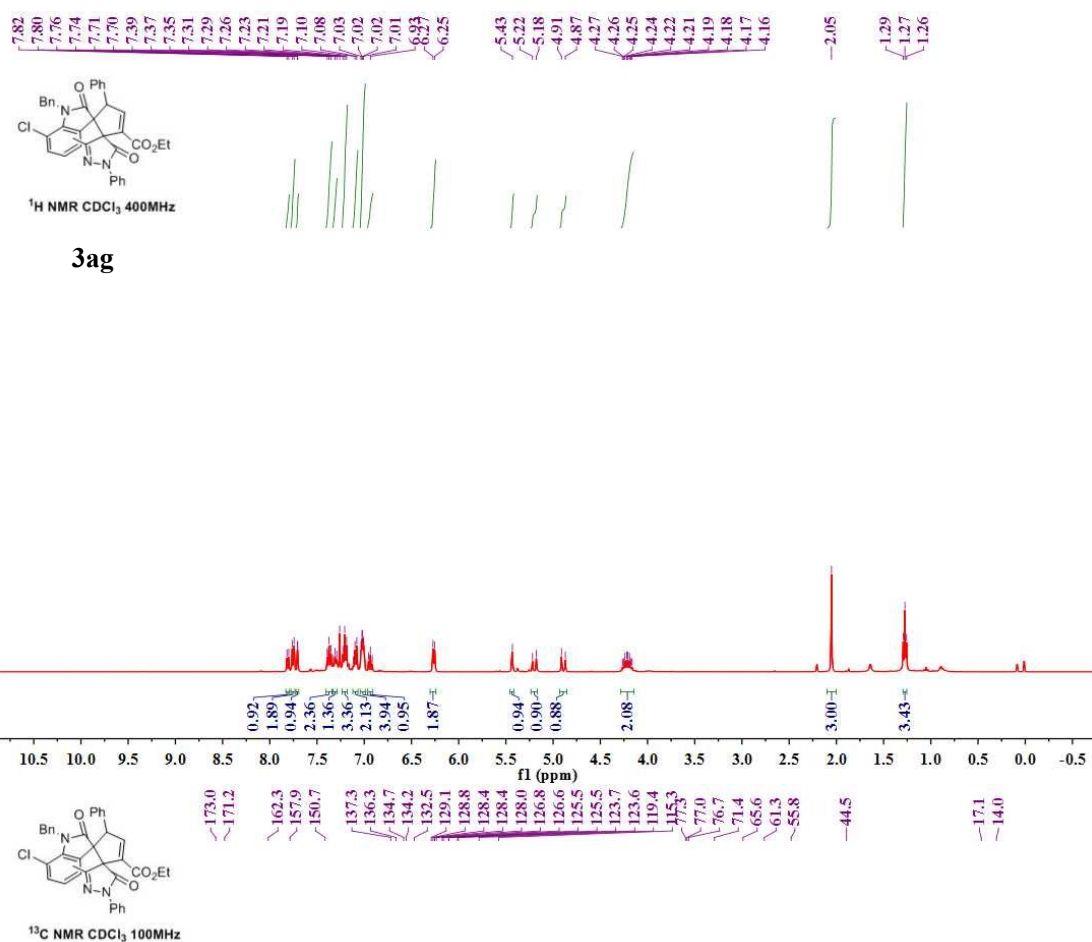


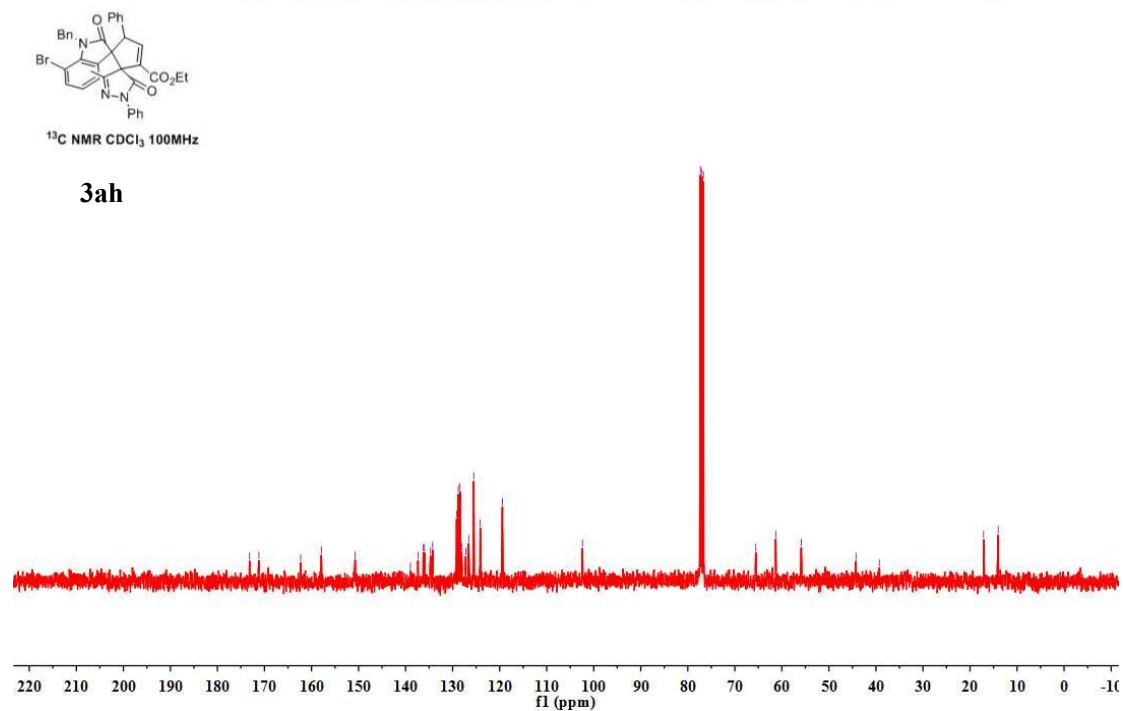
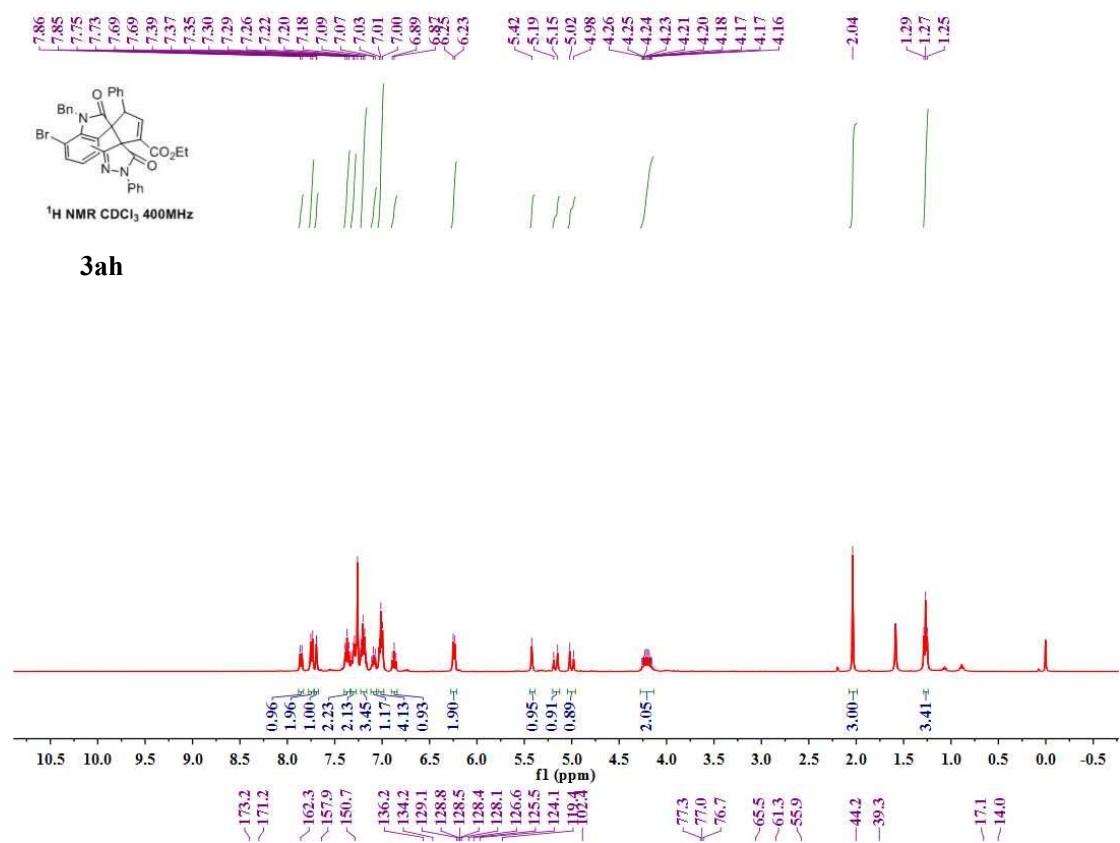


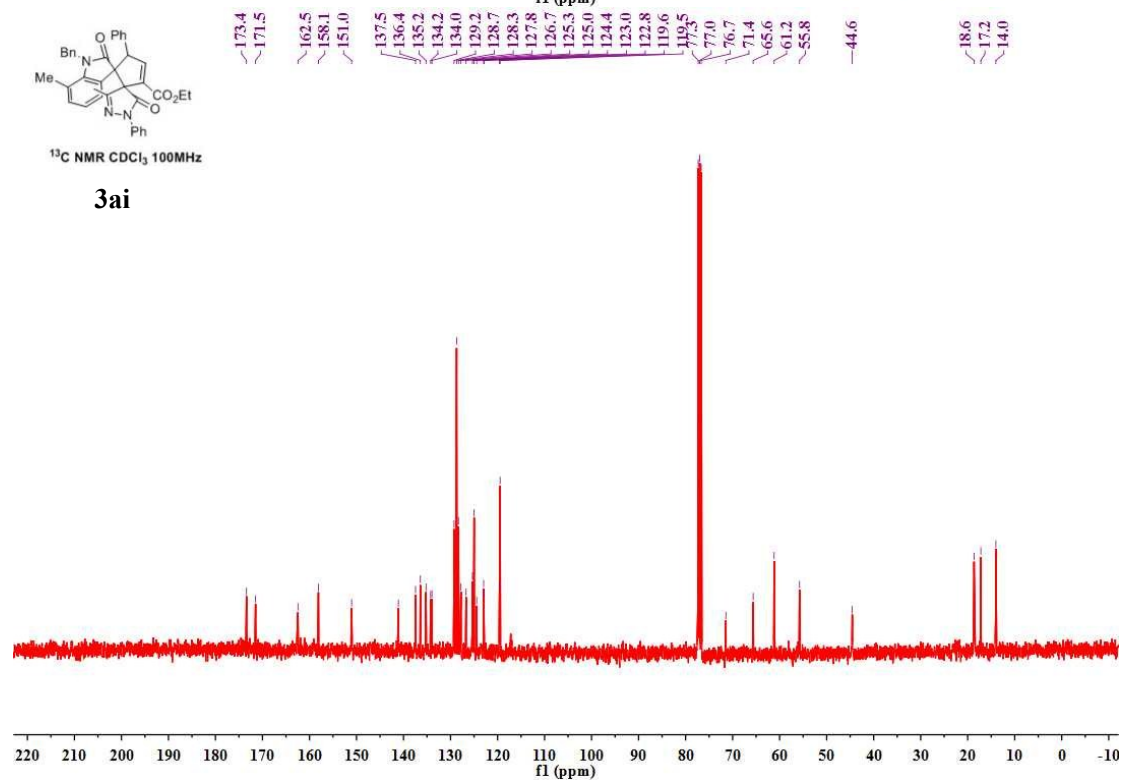
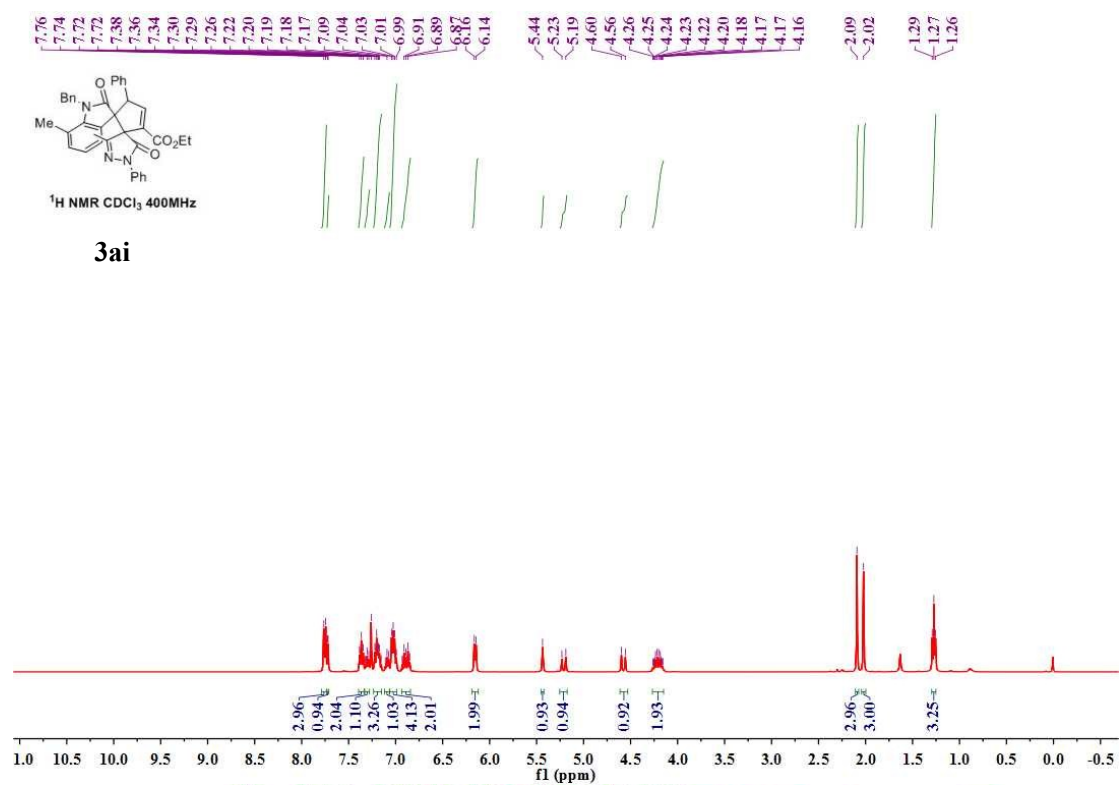
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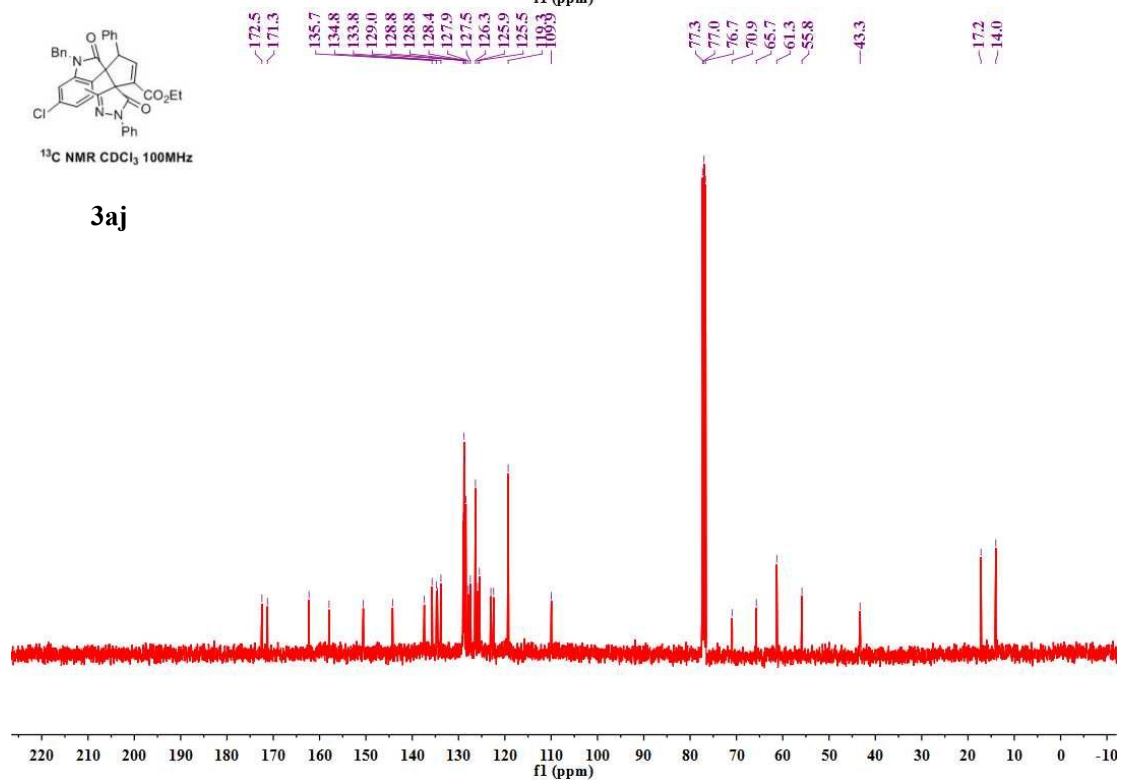
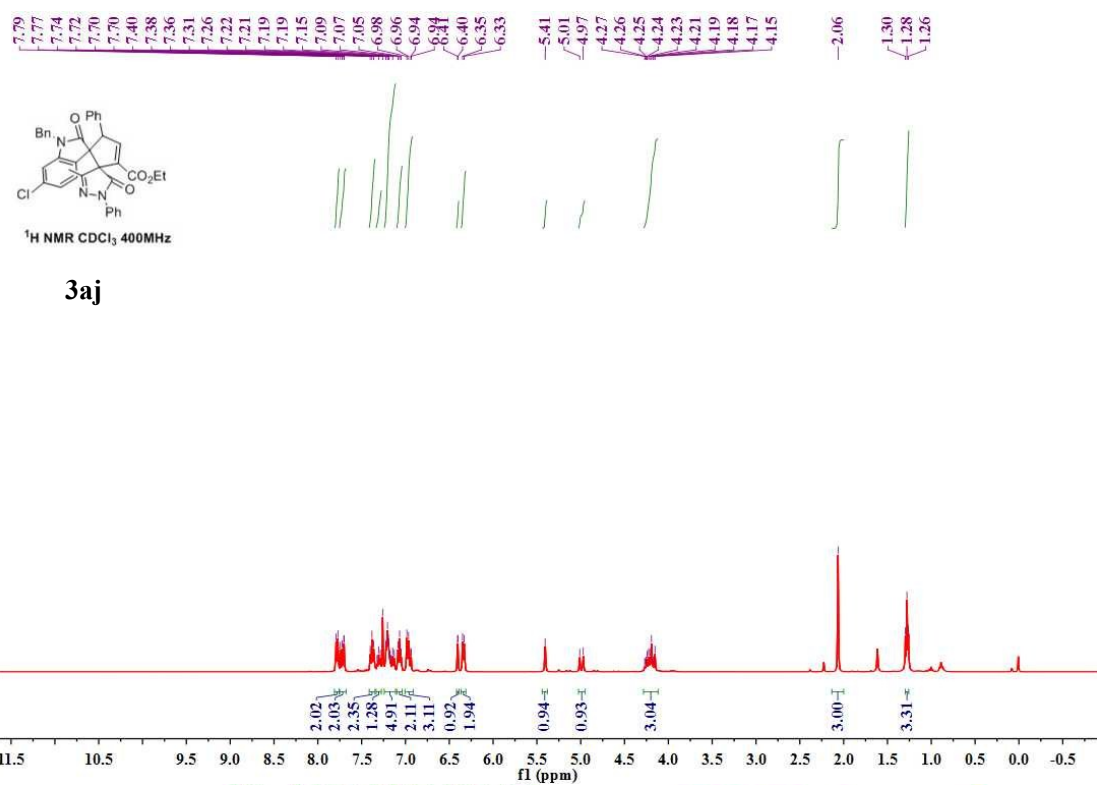


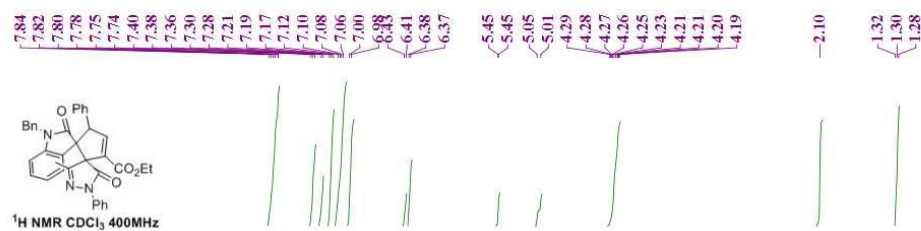




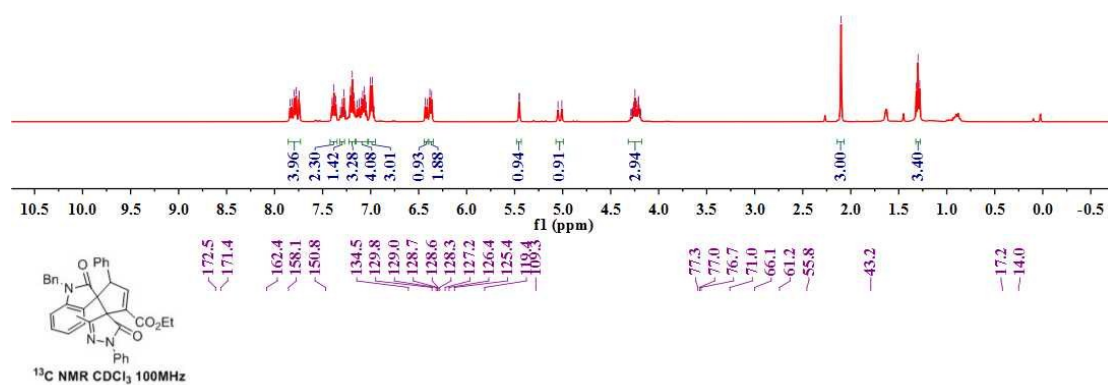


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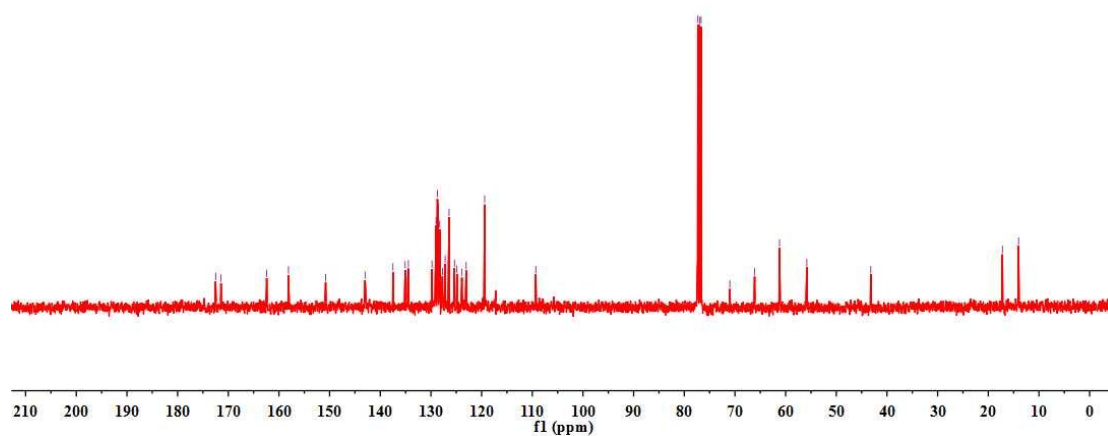


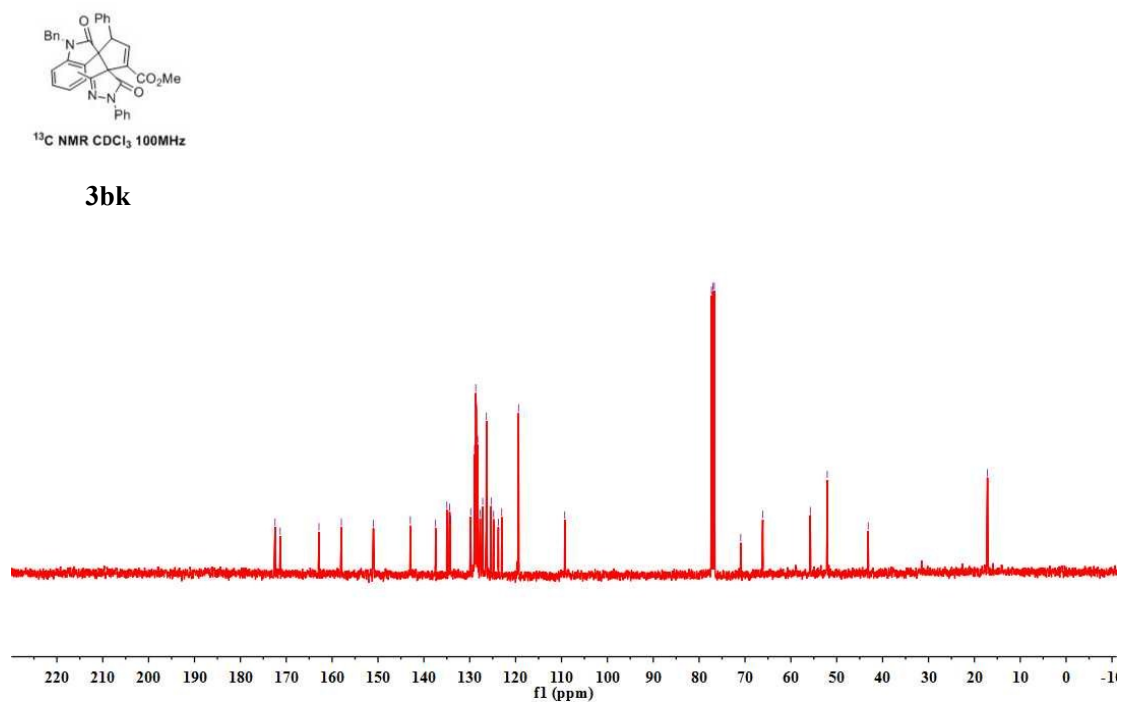
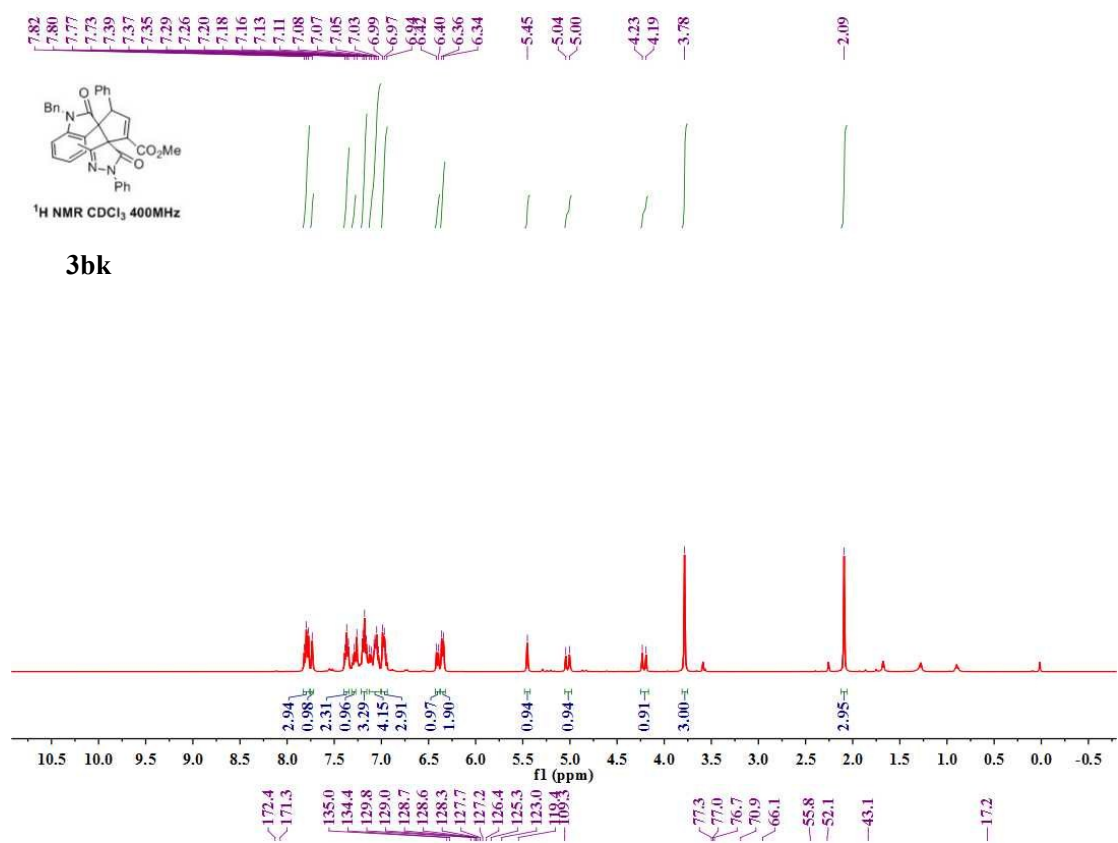


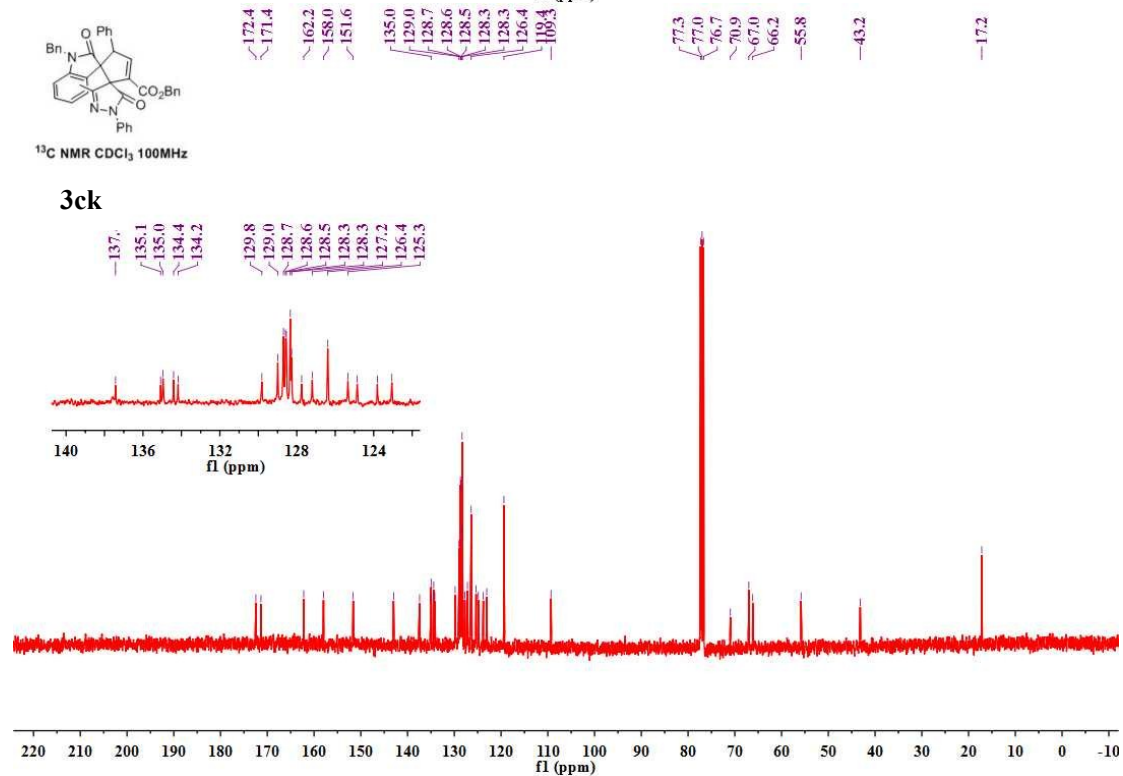
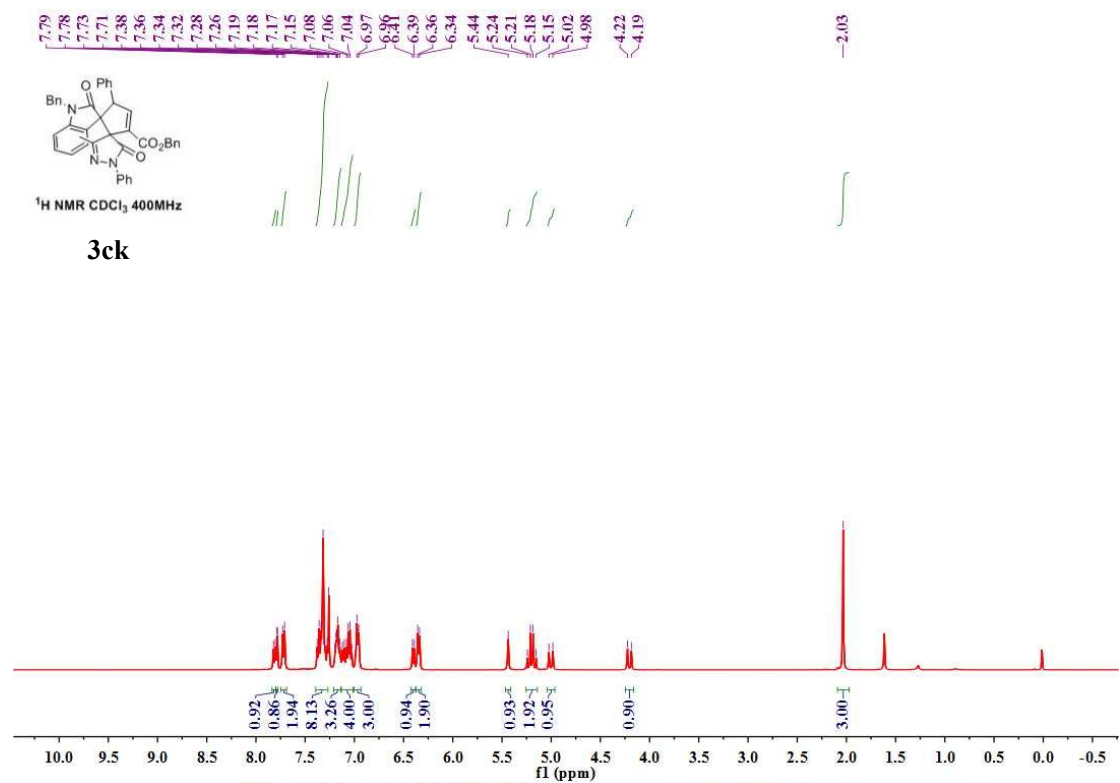
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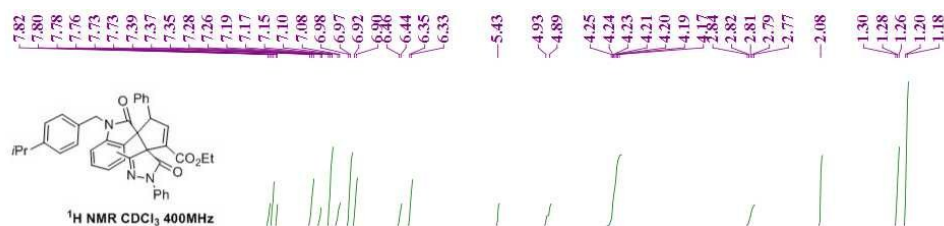


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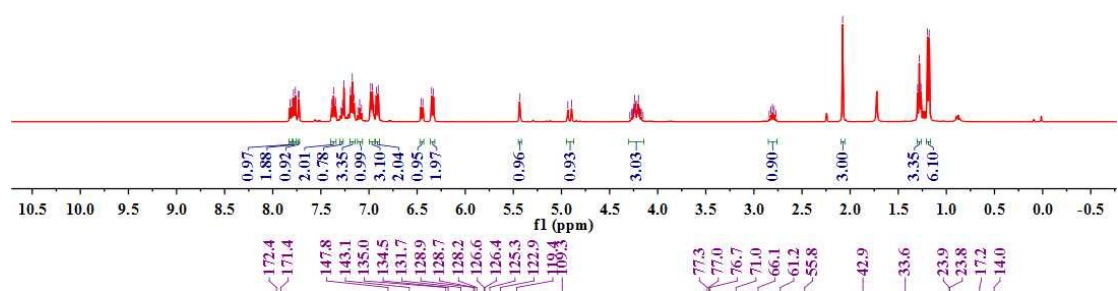




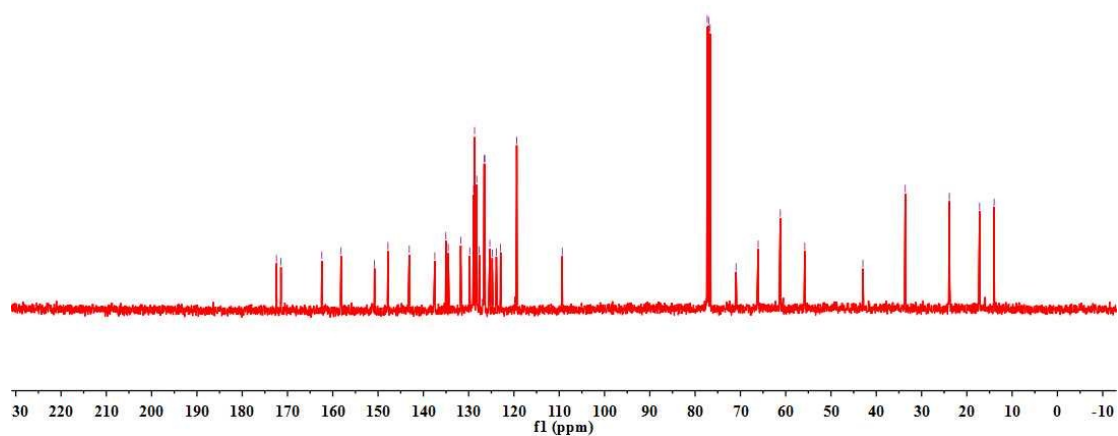


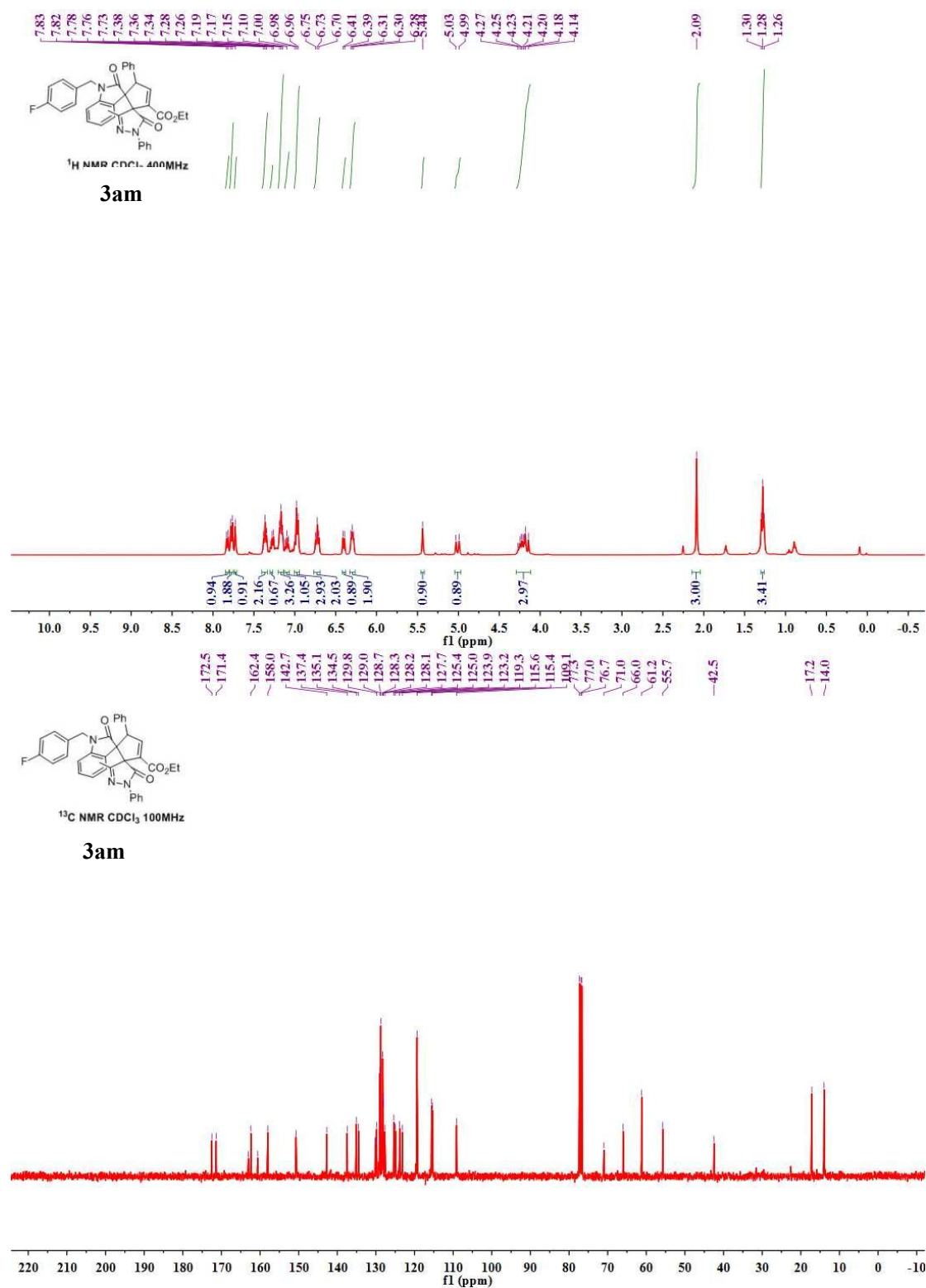


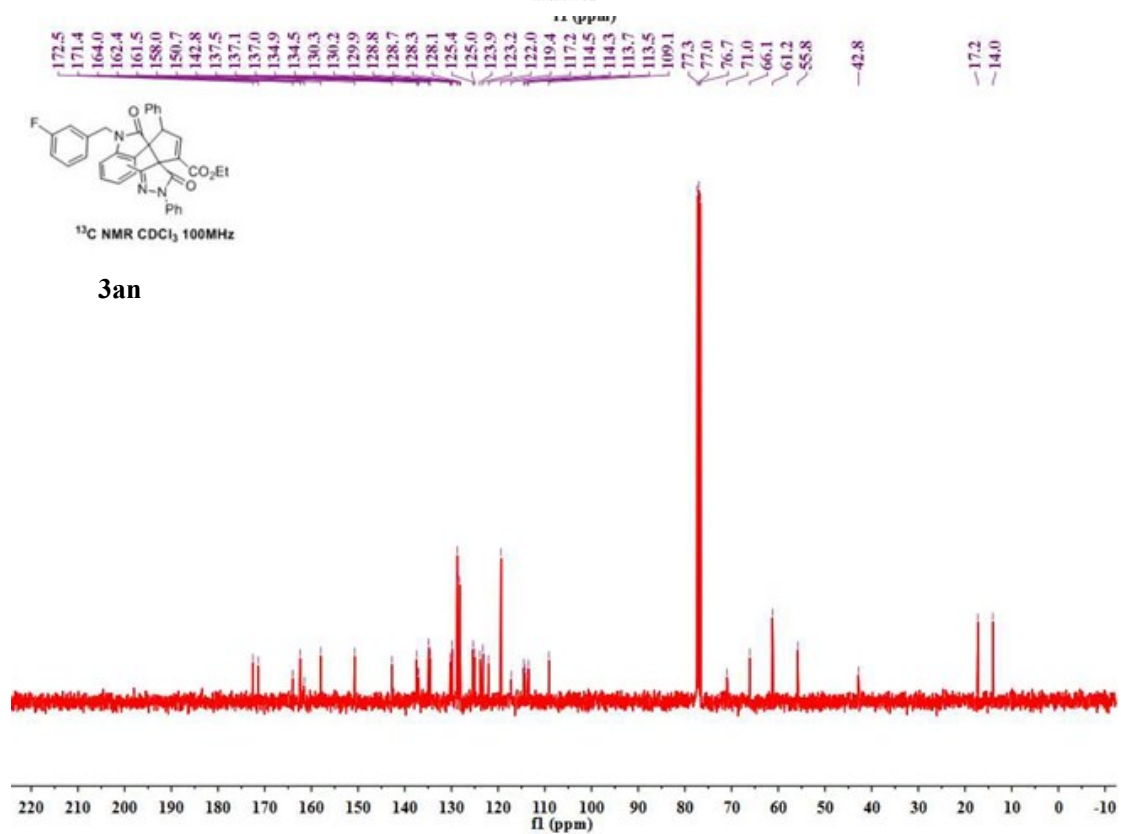
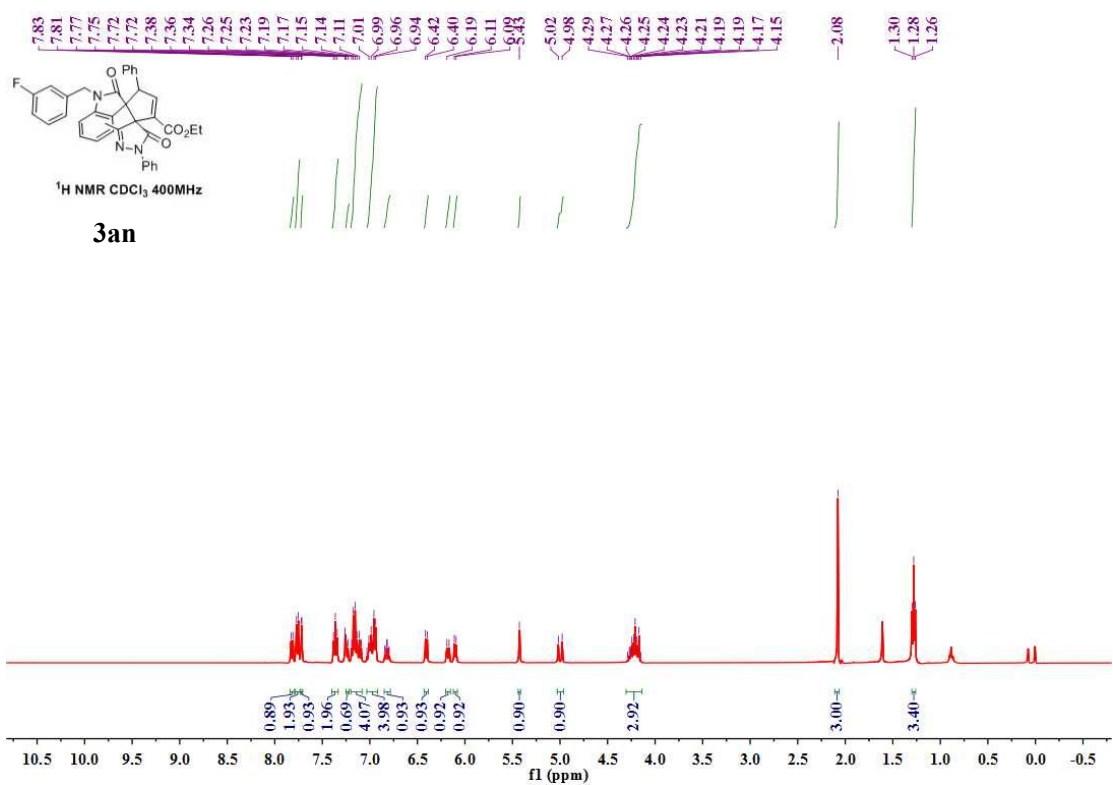
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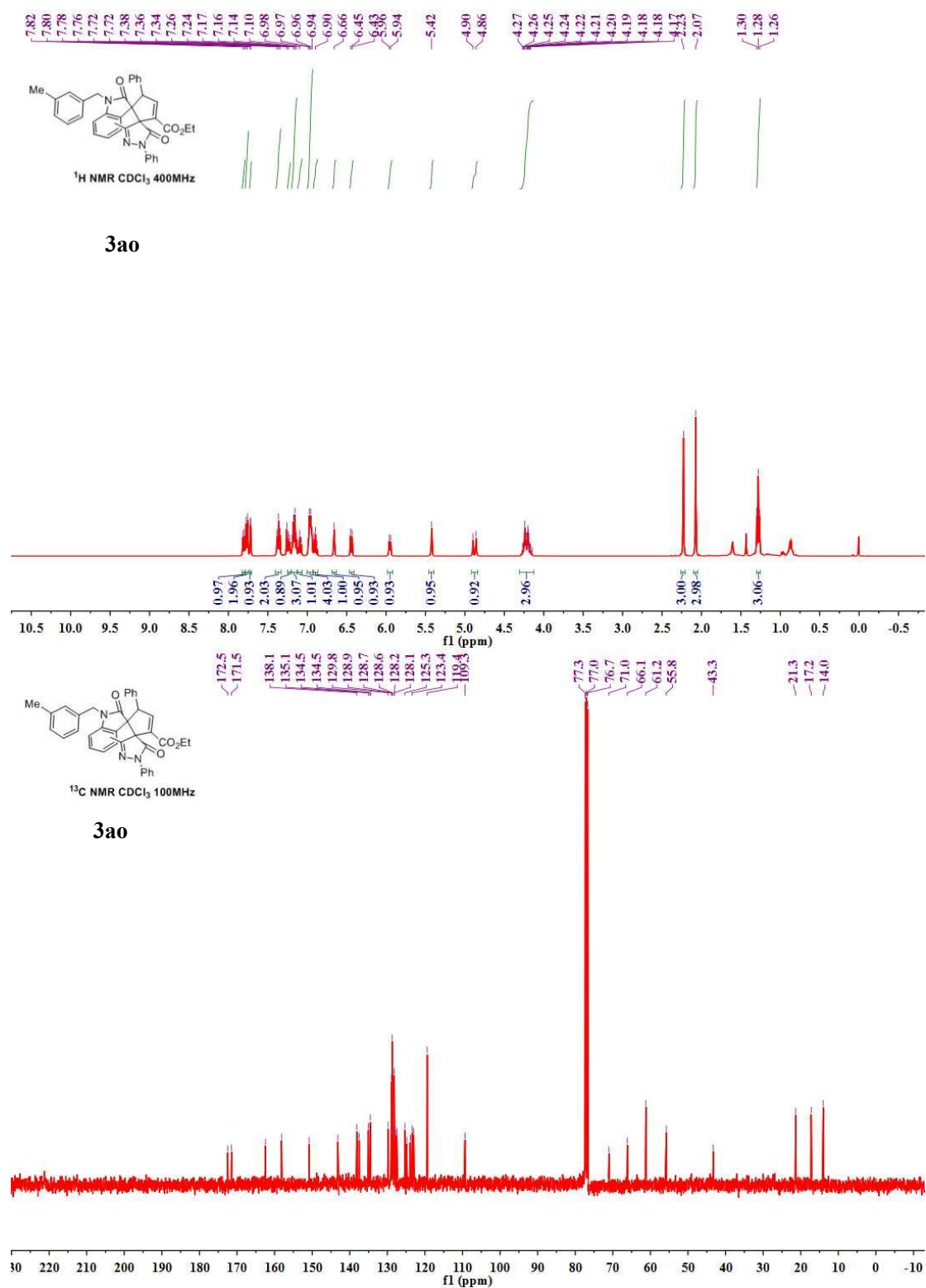


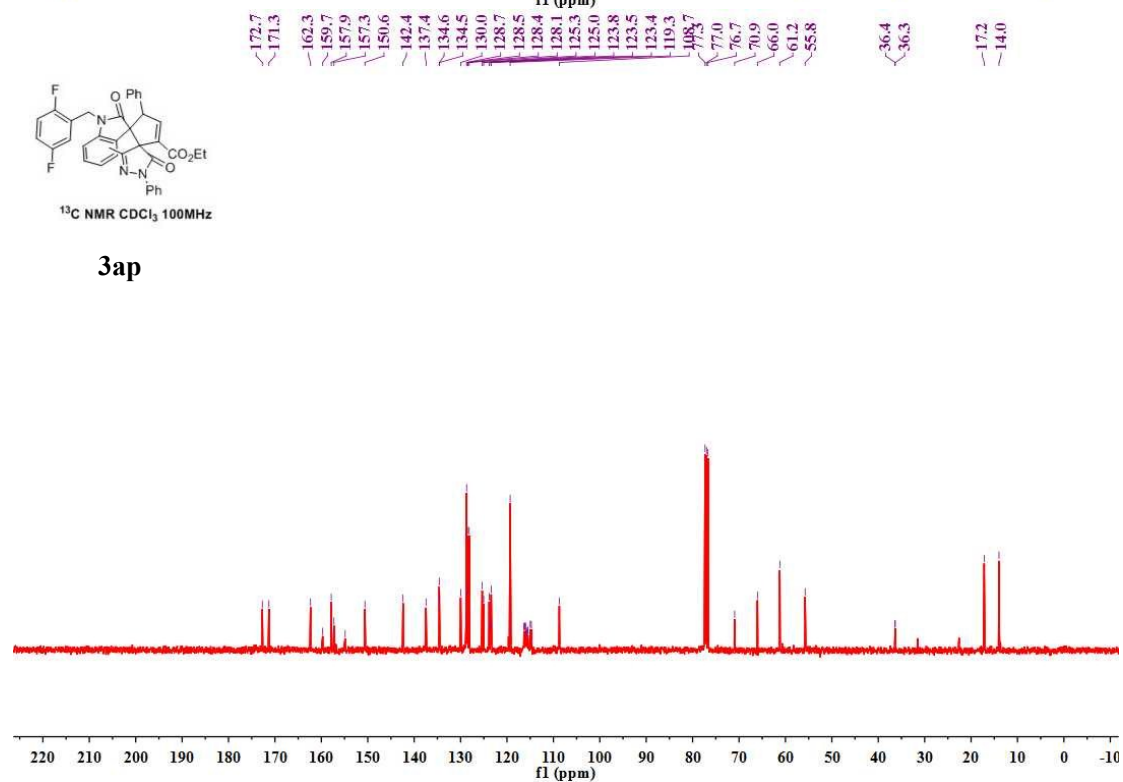
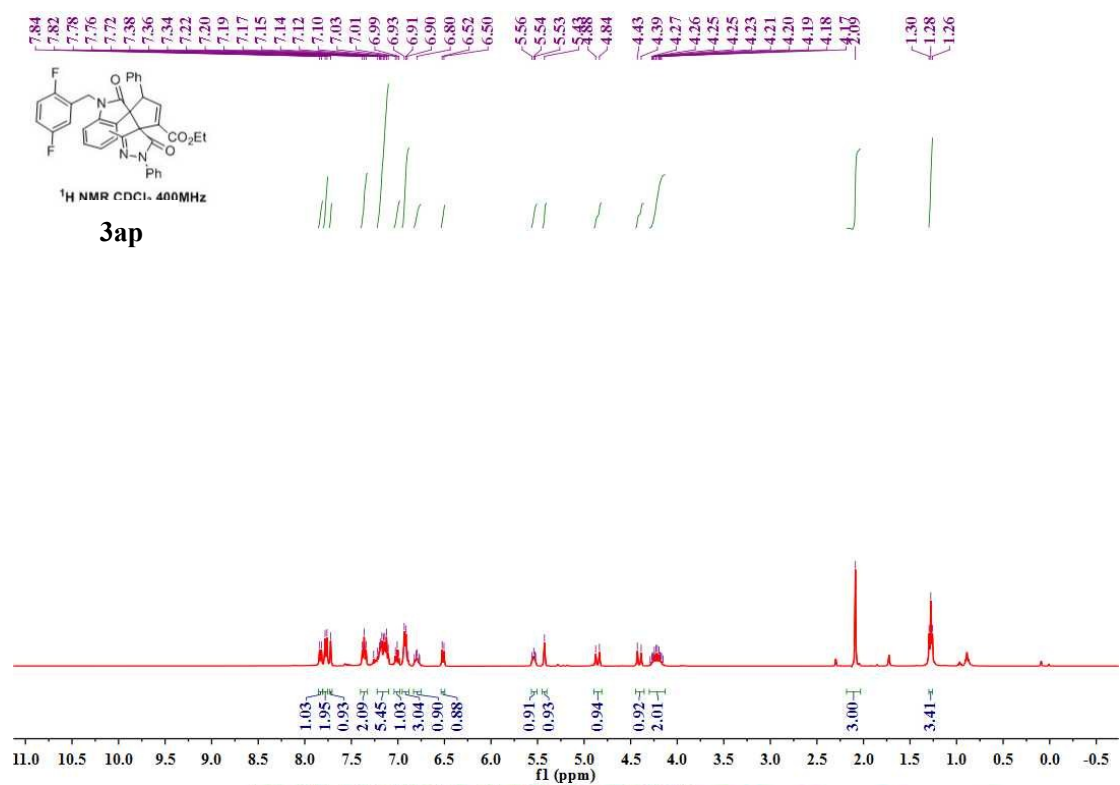
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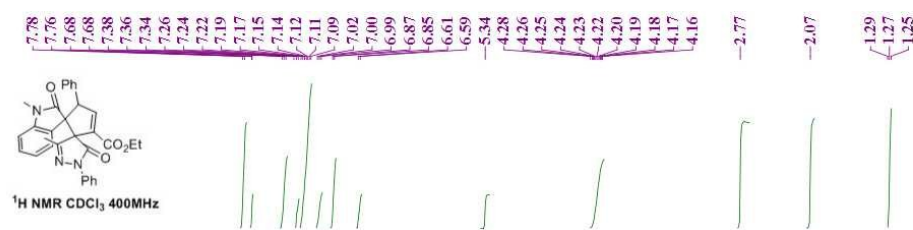




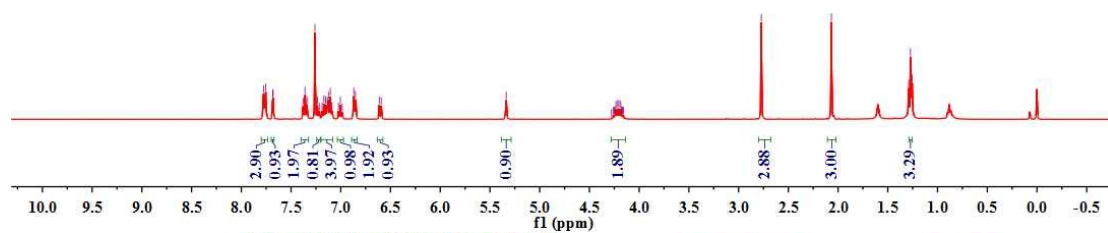








3aq



3aq

