

Creation of Bispiro[pyrazolone–3,3'–oxindoles] via a Phosphine-Catalyzed Enantioselective [3 + 2] Annulation of the Morita–Baylis–Hillman Carbonates with Pyrazoloneyldiene Oxindoles

Supporting Information

Table of contents

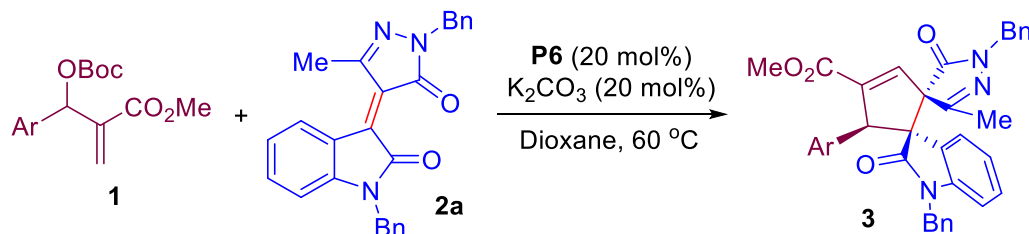
1. General Information	S2
2. Representative Procedure	S2
3. Analytical Data of the Products	S3
4. X-Ray Crystallographic Analysis and Determination of the Absolute Configurations of the Products	S21
5. References	S22
6. NMR Spectra of the Products	S23

1. General Information

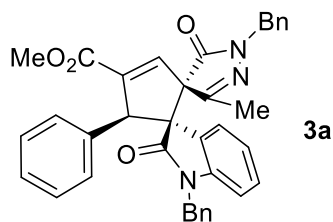
Unless otherwise specified, all reactions were carried out under a nitrogen atmosphere in anhydrous conditions. All the solvents were purified according to the standard procedures. All chemicals which are commercially available were used without further purification unless otherwise noted. Thin-layer chromatography (TLC) was performed on silica gel plates (60F-254) using UV-light (254 and 365 nm). Flash chromatography was conducted on silica gel (200–300 mesh). ^1H and ^{13}C NMR spectra were recorded at ambient temperature in CDCl_3 on a Bruker AMX400 MHz spectrometer. Chemical shifts were reported in parts per million (ppm). All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T spectrometer. Optical rotations were measured using a Jasco DIP-1000 polarimeter. Enantiomeric excesses were determined by HPLC analysis on a chiral stationary phase. MBH carbonates **1** were synthesized according to literature reported procedures ¹. pyrazoloneyldiene oxindoles **2** were synthesized according to literature reported procedures ².

2. Representative Procedure

To a dried round bottle flask with a magnetic stirring bar under N_2 at room temperature were added MBH carbonates **1** (0.1 mmol) and pyrazoloneyldiene oxindoles **2** (0.12 mmol), followed by the addition of anhydrous toluene (0.5 mL) and K_2CO_3 (0.02 mmol). Catalyst **P6** (0.02 mmol, 7.1 mg) was then introduced, and the reaction mixture was stirred for 2-12 hours at 60 °C. The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography (hexane/ ethyl acetate = 7:1) on silica gel to afford products

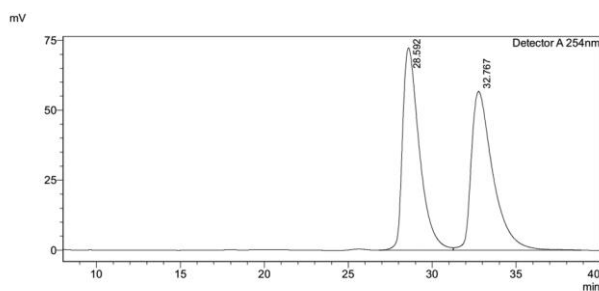


3. Analytical Data of the Products



methyl (2'S,3R,5'R)-1,1''-dibenzyl-3''-methyl-2,5''-dioxo-5'-phenyl-1'',5''-dihydrodispiro[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-4'-carboxylate (3a)

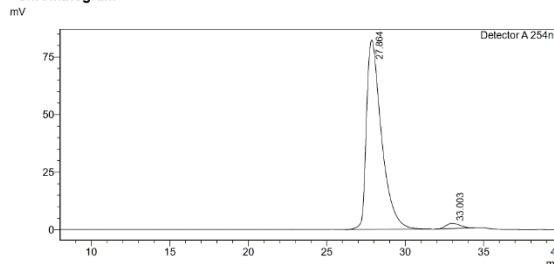
White solid, 55.2 mg, 95% yield, $[\alpha]_{D}^{25} = 396$ ($c = 1.0$ CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.79 (dd, $J = 7.6, 0.8$ Hz, 1H), 7.25 – 7.16 (m, 4H), 7.12 (t, $J = 7.7$ Hz, 4H), 7.04 (t, $J = 7.4$ Hz, 2H), 7.01 – 6.93 (m, 3H), 6.91 (s, 1H), 6.89 (s, 1H), 6.75 (d, $J = 2.6$ Hz, 1H), 6.36 (d, $J = 7.7$ Hz, 1H), 6.31 (s, 1H), 6.29 (s, 1H), 5.55 (d, $J = 2.6$ Hz, 1H), 4.99 (d, $J = 15.8$ Hz, 1H), 4.83 (d, $J = 15.2$ Hz, 1H), 4.61 (d, $J = 15.3$ Hz, 1H), 4.17 (d, $J = 15.9$ Hz, 1H), 3.70 (s, 3H), 2.01 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.6, 172.1, 164.2, 157.4, 143.6, 143.1, 138.7, 135.6, 135.1, 134.4, 129.6, 129.2, 128.6, 128.5, 127.9, 127.8, 127.6, 127.3, 127.2, 126.4, 125.5, 124.3, 123.1, 109.2, 69.7, 65.5, 56.4, 51.8, 47.9, 43.1, 17.6. HRMS (ESI-TOF) m/z [M + H]⁺ calcd for C₃₇H₃₂N₃O₄⁺ 582.2387, found 582.2398. HPLC (Chiralpak IA, *i*-PrOH /hexane = 80/20, flow rate = 1.0 mL/min, $\lambda = 254$ nm): $t_{\text{major}} = 27.8$ min, $t_{\text{minor}} = 33.0$ min, *ee* = 95%.



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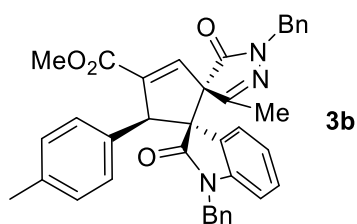
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1	28.592	5019819	72296	49.707			49.707
2	32.767	5078991	56726	50.293		V	50.293
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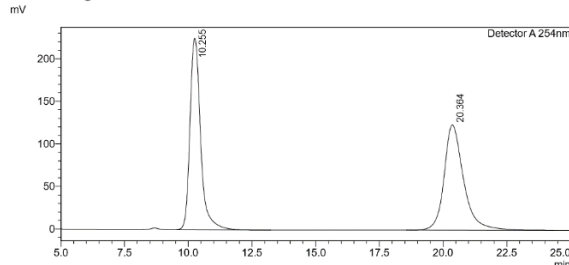
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1	27.864	5482019	82206	97.385			97.385
2	33.003	147221	2282	2.615			2.615
Total		5629240	84488				100.000



methyl (2'S,3R,5'R)-1,1''-dibenzyl-3''-methyl-2,5''-dioxo-5'-(p-tolyl)-1'',5''-dihydrodispiro[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-4'-carboxylate (3b)

White solid, 45.8 mg, 77% yield, $[\alpha]_D^{25} = 247$ ($c = 1.0$ CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.78 (dd, $J = 7.6, 0.7$ Hz, 1H), 7.23 – 7.16 (m, 3H), 7.15 – 7.06 (m, 2H), 7.03 (t, $J = 7.5$ Hz, 2H), 7.00 – 6.94 (m, 3H), 6.93 (s, 1H), 6.91 (s, 1H), 6.80 (s, 1H), 6.78 (s, 1H), 6.72 (d, $J = 2.6$ Hz, 1H), 6.34 (t, $J = 6.7$ Hz, 3H), 5.51 (d, $J = 2.6$ Hz, 1H), 5.04 (d, $J = 15.9$ Hz, 1H), 4.82 (d, $J = 15.3$ Hz, 1H), 4.60 (d, $J = 15.3$ Hz, 1H), 4.17 (d, $J = 15.9$ Hz, 1H), 3.71 (s, 3H), 2.30 (s, 3H), 2.01 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.7, 172.1, 164.2, 157.5, 143.8, 143.0, 138.5, 136.8, 135.7, 134.5, 131.9, 129.5, 129.1, 128.5, 128.5, 128.5, 127.9, 127.5, 127.2, 126.5, 125.5, 124.4, 123.1, 109.2, 69.7, 65.5, 56.1, 51.8, 47.9, 43.1, 21.3, 17.6. HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for C₃₈H₃₄N₃O₄⁺ 596.2544, found 596.2554. HPLC (Chiralpak IA, *i*-PrOH/hexane = 80/20, flow rate = 1.0 mL/min, $\lambda = 254$ nm): $t_{major} = 20.3$ min, $t_{minor} = 10.3$ min, $ee = 93\%$.

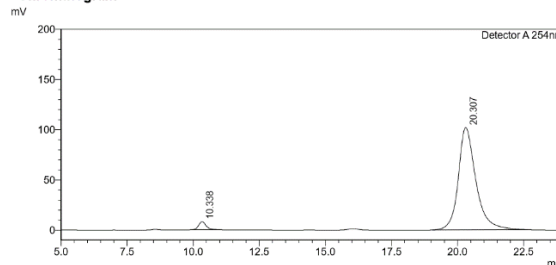
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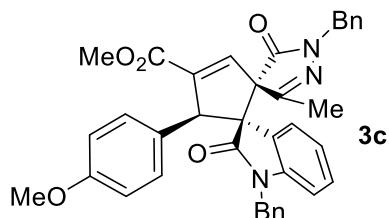
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1	10.255	6584879	225197	50.006			50.006
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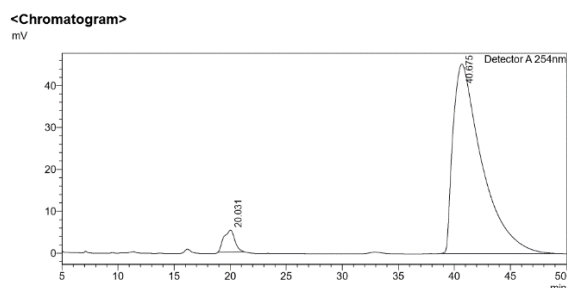
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1	10.338	159820	8075	3.270			3.270
2	20.307	4727451	101997	96.730		M	96.730
Total		4887271	110073				100.000



methyl (2'S,3R,5'R)-1,1''-dibenzyl-5'-(4-methoxyphenyl)-3''-methyl-2,5''-dioxo-1'',5''-dihydrodispiro[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-4'-carboxylate (3c)

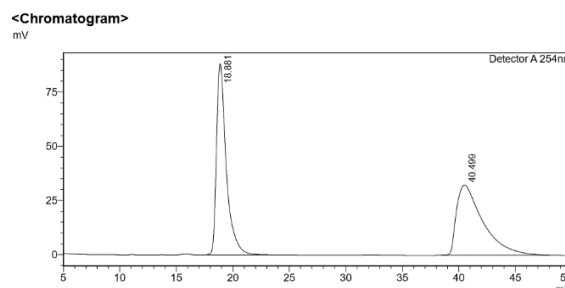
White solid, 46.4 mg, 76% yield, $[\alpha]_D^{25} = 483$ ($c = 1.0$ CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.78 (dd, $J = 7.6, 0.8$ Hz, 1H), 7.23 – 7.16 (m, 3H), 7.15 – 7.09 (m, 2H), 7.05 (t, $J = 7.4$ Hz, 2H), 7.01 – 6.92 (m, 3H), 6.82 (s, 1H), 6.80 (s, 1H), 6.72 (d, $J = 2.6$ Hz, 1H), 6.66 (s, 1H), 6.64 (s, 1H), 6.38 (d, $J = 7.7$ Hz, 1H), 6.33 (s, 1H), 6.32 (s, 1H), 5.50 (d, $J = 2.6$ Hz, 1H), 5.05 (d, $J = 15.9$ Hz, 1H), 4.82 (d, $J = 15.3$ Hz, 1H), 4.61 (d, $J = 15.3$ Hz, 1H), 4.18 (d, $J = 15.9$ Hz, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 2.01 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.8, 172.1, 164.2, 158.9, 157.5, 143.7, 143.1, 138.5, 135.7, 134.4, 130.3, 129.5, 128.5, 128.5, 127.9, 127.6, 127.3,

127.1, 126.4, 125.5, 124.4, 123.1, 113.2, 109.2, 69.6, 65.5, 55.8, 54.9, 51.8, 47.9, 43.1, 17.6. HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{38}H_{34}N_3O_5^+$ 612.2493, found 612.2502. HPLC (Chiralpak IF, *i*-PrOH/hexane = 80/20, flow rate = 1.0 mL/min, λ = 254 nm): t_{major} = 40.7 min, t_{minor} = 18.8 min, ee = 92%.



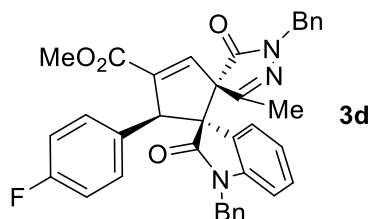
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Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	20.031	351074	5213	4.158		M	4.158
2	40.675	8092409	45247	95.842			95.842
Total		8443483	50460				100.000



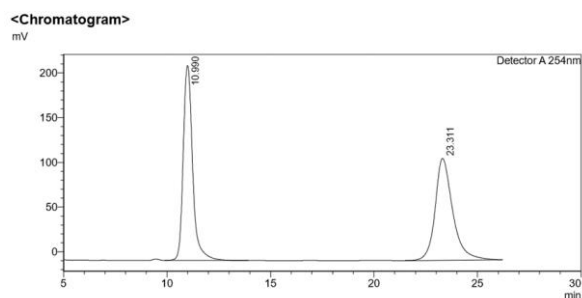
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Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	18.881	5303843	88164	50.367			50.367
2	40.499	5226654	32357	49.633			49.633
Total		10530497	120521				100.000



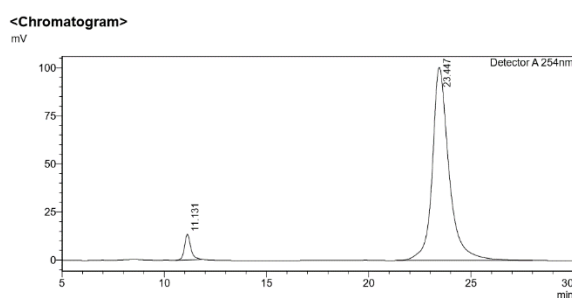
methyl (2'S,3R,5'R)-1,1''-dibenzyl-5'-(4-fluorophenyl)-3''-methyl-2,5''-dioxo-1',5''-dihydrodispiro[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-4'-carboxylate (3d)

White solid, 50.9 mg, 85% yield, $[\alpha]_D^{25} = 324$ ($c = 1.0$ $CHCl_3$). 1H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, $J = 7.6, 0.8$ Hz, 1H), 7.23 – 7.06 (m, 7H), 7.01 – 6.93 (m, 3H), 6.86 (dd, $J = 8.6, 5.5$ Hz, 2H), 6.79 (t, $J = 8.8$ Hz, 2H), 6.75 (d, $J = 2.6$ Hz, 1H), 6.42 (d, $J = 7.7$ Hz, 1H), 6.38 (s, 1H), 6.36 (s, 1H), 5.51 (d, $J = 2.6$ Hz, 1H), 5.01 (d, $J = 15.8$ Hz, 1H), 4.82 (d, $J = 15.2$ Hz, 1H), 4.61 (d, $J = 15.3$ Hz, 1H), 4.20 (d, $J = 15.8$ Hz, 1H), 3.72 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 171.9, 164.0, 157.3, 143.1, 143.1(d, $J = 10.5$ Hz), 139.0, 135.6, 134.3, 130.9, 130.8, 129.7, 128.6, 128.6, 127.9, 127.6, 127.5, 126.4, 125.5, 124.1, 123.2, 114.8, 114.6, 109.3, 69.6, 65.4, 55.7, 51.9, 48.0, 43.2, 17.5. HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{37}H_{31}FN_3O_4^+$ 600.2293, found 600.2302. HPLC (Chiralpak IF, *i*-PrOH/hexane = 80/20, flow rate = 1.0 mL/min, λ = 254 nm): t_{major} = 23.4 min, t_{minor} = 11.1 min, ee = 90%.



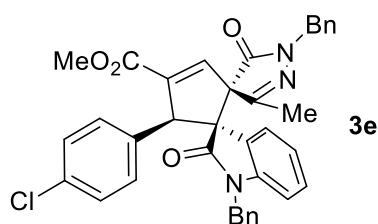
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Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	10.990	6882520	218005	50.546			50.546
2	23.311	6733902	113958	49.454			49.454
Total		13616421	331963				100.000



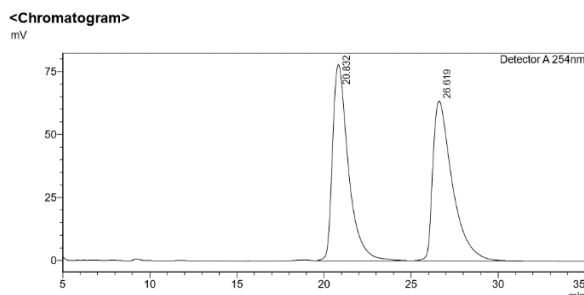
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Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	11.131	290377	13359	4.853		M	4.853
2	23.447	5692924	100378	95.147		S	95.147
Total		5983300	113737				100.000



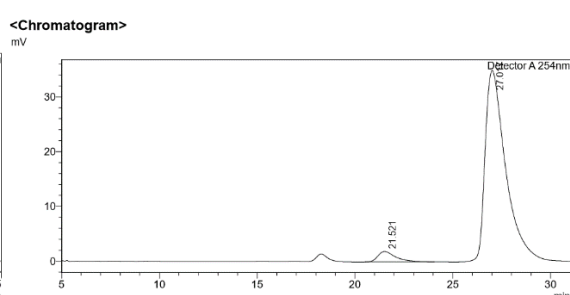
methyl (2'S,3R,5'R)-1,1''-dibenzyl-5'-(4-chlorophenyl)-3''-methyl-2,5''-dioxo-1'',5''-dihydrodispiro[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-4'-carboxylate (3e)

White solid, 59.7 mg, 97% yield, $[\alpha]_D^{25} = 302$ ($c = 1.0$ CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.77 (dd, $J = 7.6, 0.6$ Hz, 1H), 7.24 – 7.11 (m, 7H), 7.10 (s, 1H), 7.08 (s, 1H), 6.97 (dd, $J = 16.0, 7.5$ Hz, 3H), 6.85 (s, 1H), 6.83 (s, 1H), 6.76 (d, $J = 2.6$ Hz, 1H), 6.42 (d, $J = 7.8$ Hz, 1H), 6.39 – 6.33 (m, 2H), 5.51 (d, $J = 2.6$ Hz, 1H), 5.05 (d, $J = 15.8$ Hz, 1H), 4.82 (d, $J = 15.2$ Hz, 1H), 4.61 (d, $J = 15.2$ Hz, 1H), 4.19 (d, $J = 15.8$ Hz, 1H), 3.72 (s, 3H), 2.01 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.5, 171.9, 163.9, 157.2, 1423.0, 139.2, 135.6, 134.2, 133.69, 133.4, 130.6, 129.8, 128.7, 128.6, 128.0, 127.9, 127.6, 127.5, 126.3, 125.4, 123.9, 123.3, 109.3, 69.6, 65.3, 55.7, 51.9, 48.0, 43.3, 17.5. HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for C₃₇H₃₁ClN₃O₄⁺ 616.1998, found 616.1999. HPLC (Chiralpak IA, *i*-PrOH /hexane = 80/20, flow rate = 1.0 mL/min, $\lambda = 254$ nm): $t_{major} = 27.0$ min, $t_{minor} = 21.5$ min, $ee = 91\%$.



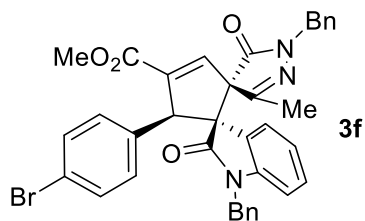
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Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	20.832	4932117	77898	50.043			50.043
2	26.619	4923683	63338	49.957			49.957
Total		9855700	141237				100.000



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Detector A 254nm

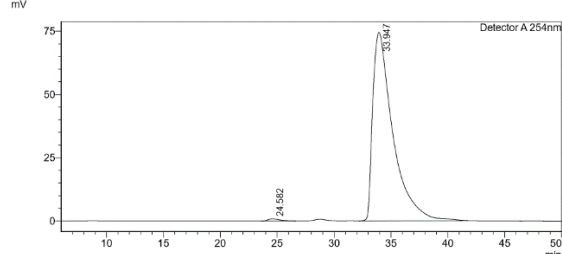
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	21.521	123037	1917	4.579		M	
2	27.017	2564162	34905	95.421			
Total		2687199	36822				



methyl (2'S,3R,5'R)-1,1''-dibenzyl-5'-(4-bromophenyl)-3''-methyl-2,5''-dioxo-1'',5''-dihydrodispiro[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-4'-carboxylate (3f)

White solid, 62 mg, 94% yield, $[\alpha]_D^{25} = 276$ ($c = 1.0$ CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.76 (dd, $J = 7.6, 0.7$ Hz, 1H), 7.26 – 7.10 (m, 9H), 7.01 – 6.91 (m, 3H), 6.79 (s, 1H), 6.77 (s, 1H), 6.76 (d, $J = 2.6$ Hz, 1H), 6.41 (d, $J = 7.8$ Hz, 1H), 6.37 (dd, $J = 6.6, 2.7$ Hz, 2H), 5.49 (d, $J = 2.6$ Hz, 1H), 5.05 (d, $J = 15.8$ Hz, 1H), 4.81 (d, $J = 15.2$ Hz, 1H), 4.60 (d, $J = 15.3$ Hz, 1H), 4.19 (d, $J = 15.8$ Hz, 1H), 3.72 (s, 3H), 2.00 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.5, 171.9, 163.9, 157.2, 143.0, 142.9, 139.3, 135.6, 134.3, 134.2, 130.9, 129.7, 128.8, 128.6, 127.9, 127.6, 127.5, 126.3, 125.4, 123.9, 123.3, 121.7, 109.4, 69.7, 65.2, 55.8, 51.9, 48.0, 43.3, 17.5. HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for C₃₇H₃₁BrN₃O₄⁺ 660.1492, found 660.1501. HPLC (Chiralpak IF, *i*-PrOH/hexane = 80/20, flow rate = 1.0 mL/min, $\lambda = 254$ nm): $t_{\text{major}} = 34.7$ min, $t_{\text{minor}} = 24.0$ min, $ee = 99\%$.

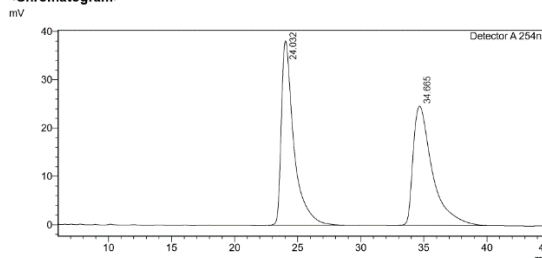
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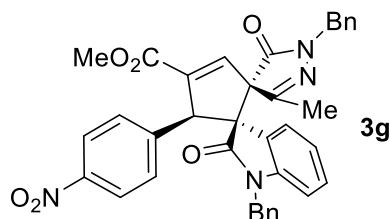
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	24.582	62663	882	0.677			0.877
2	33.947	9194215	74553	99.323			99.323
Total		9256879	75415				100.000

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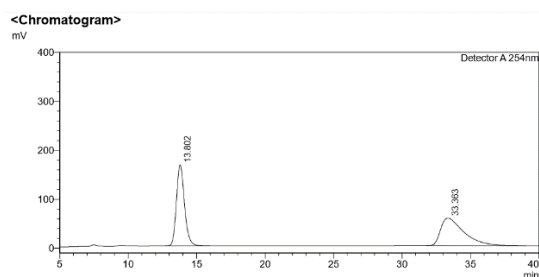
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	24.032	2629243	38223	50.133			50.133
2	34.865	2615292	24729	49.867			49.867
Total		5244536	62952				100.000



methyl (2'S,3R,5'R)-1,1''-dibenzyl-3''-methyl-5'-(4-nitrophenyl)-2,5''-dioxo-1'',5''-dihydrodispiro[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-4'-carboxylate (3g)

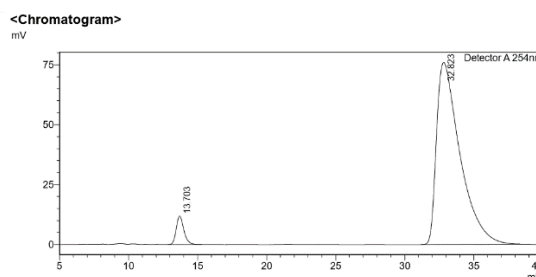
White solid, 62 mg, 99% yield, $[\alpha]_D^{25} = 343$ ($c = 1.0$ CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ

7.90 (s, 1H), 7.88 (s, 1H), 7.79 (d, $J = 7.6$ Hz, 1H), 7.24 – 7.17 (m, 4H), 7.09 (t, $J = 7.4$ Hz, 1H), 7.05 – 6.95 (m, 7H), 6.82 (d, $J = 2.5$ Hz, 1H), 6.53 (d, $J = 7.8$ Hz, 1H), 6.48 (s, 1H), 6.46 (s, 1H), 5.58 (d, $J = 2.5$ Hz, 1H), 4.88 (d, $J = 15.6$ Hz, 1H), 4.82 (d, $J = 15.2$ Hz, 1H), 4.62 (d, $J = 15.2$ Hz, 1H), 4.23 (d, $J = 15.6$ Hz, 1H), 3.72 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 172.2, 171.6, 163.6, 156.9, 147.3, 143.0, 142.7, 142.0, 140.1, 135.5, 134.3, 130.1, 130.0, 128.6, 128.4, 127.9, 127.7, 127.7, 126.6, 125.5, 123.5, 123.5, 122.9, 109.3, 69.6, 65.1, 56.0, 52.0, 48.1, 43.4, 17.5. HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{37}\text{H}_{31}\text{N}_4\text{O}_6^+$ 627.2238, found 627.2248. HPLC (Chiralpak AD, *i*-PrOH /hexane = 60/40, flow rate = 1.0 mL/min, $\lambda = 254$ nm): $t_{\text{major}} = 32.8$ min, $t_{\text{minor}} = 13.7$ min, $ee = 90\%$.



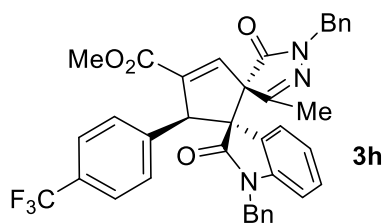
<Peak Table>

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	13.802	8754859	165269	50.451			50.451
2	33.363	8634063	56274	49.549			49.549
Total		13388922	221543				100.000



<Peak Table>

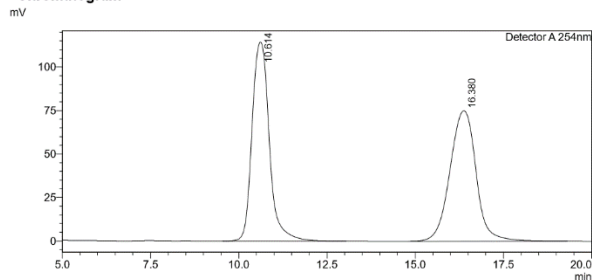
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	13.703	454322	11657	4.812			4.812
2	32.823	8987692	76985	95.188			95.188
Total		9441984	87845				100.000



methyl (2'*S*,3*R*,5'*R*)-1,1''-dibenzyl-3''-methyl-2,5''-dioxo-5'-(4-(trifluoromethyl)phenyl)-1'',5''-dihydrodispiro[indoline-3,1'-cyclopentane-2',4'-pyrazol]-3'-ene-4'-carboxylate (**3h**)

White solid, 57.1 mg, 88% yield, $[\alpha]_{\text{D}}^{25} = 400$ ($c = 1.0$ CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.79 (dd, $J = 7.6, 0.7$ Hz, 1H), 7.39 (s, 1H), 7.37 (s, 1H), 7.23 – 7.11 (m, 5H), 7.09 – 7.01 (m, 4H), 6.97 (td, $J = 7.6, 1.0$ Hz, 3H), 6.79 (d, $J = 2.6$ Hz, 1H), 6.44 – 6.36 (m, 3H), 5.58 (d, $J = 2.5$ Hz, 1H), 4.98 (d, $J = 15.8$ Hz, 1H), 4.82 (d, $J = 15.2$ Hz, 1H), 4.61 (d, $J = 15.2$ Hz, 1H), 4.20 (d, $J = 15.8$ Hz, 1H), 3.72 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 172.5, 171.8, 163.8, 157.1, 142.9, 142.8, 139.5, 139.3, 135.5, 134.3, 129.9, 129.7, 129.4, 128.6, 128.5, 127.9, 127.6, 127.5, 126.3, 125.5 (q, $J = 273$ Hz), 125.4, 124.7 (q, $J = 3.6$ Hz), 123.7, 123.4, 109.5, 69.8, 65.3, 55.9, 51.9, 48.0, 43.3, 17.5. HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{38}\text{H}_{31}\text{F}_3\text{N}_3\text{O}_4^+$ 650.2261, found 650.2264. HPLC (Chiralpak IA, *i*-PrOH /hexane = 80/20, flow rate = 1.0 mL/min, $\lambda = 254$ nm): $t_{\text{major}} = 16.5$ min, $t_{\text{minor}} = 10.7$ min, $ee = 92\%$.

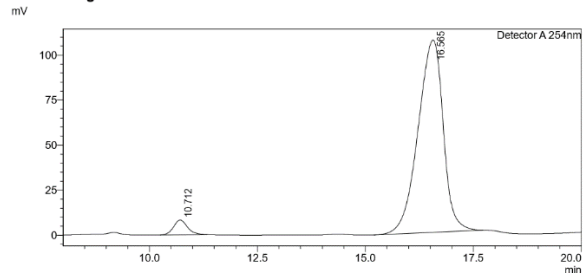
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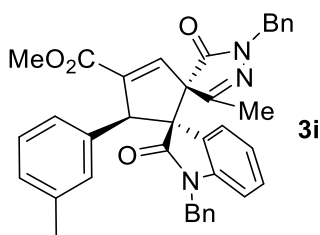
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	10.614	3910814	114451	50.256			50.256
2	16.380	3871031	75067	49.744			49.744
Total		7781845	189518				100.000

<Chromatogram>



<Peak Table>

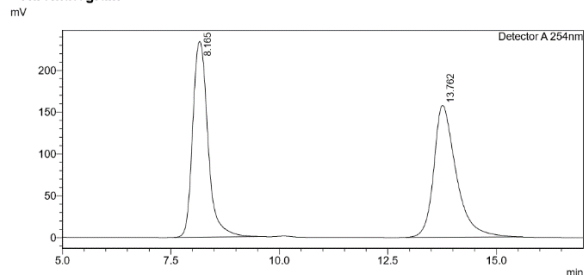
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	10.712	187226	8251	4.137		M	4.137
2	16.565	4338439	106758	95.863			95.863
Total		4525665	115010				100.000



methyl (2'S,3R,5'R)-1,1''-dibenzyl-3''-methyl-2,5''-dioxo-5'-(m-tolyl)-1'',5''-dihydrodispiro[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-4'-carboxylate (3i)

White solid, 52.9 mg, 89% yield, $[\alpha]_D^{25} = 388$ ($c = 1.0$ CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.79 (dd, $J = 7.6, 0.8$ Hz, 1H), 7.23 – 7.16 (m, 3H), 7.15 – 7.08 (m, 2H), 7.07 – 6.92 (m, 7H), 6.73 (d, $J = 2.6$ Hz, 1H), 6.69 (d, $J = 6.4$ Hz, 2H), 6.36 (d, $J = 7.7$ Hz, 1H), 6.31 (s, 1H), 6.29 (s, 1H), 5.51 (d, $J = 2.6$ Hz, 1H), 5.02 (d, $J = 15.8$ Hz, 1H), 4.83 (d, $J = 15.3$ Hz, 1H), 4.61 (d, $J = 15.3$ Hz, 1H), 4.16 (d, $J = 15.8$ Hz, 1H), 3.71 (s, 3H), 2.12 (s, 3H), 2.01 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.6, 172.1, 164.3, 157.5, 143.7, 143.1, 138.5, 137.2, 135.6, 134.8, 134.5, 129.7, 129.5, 128.6, 128.5, 128.1, 127.8, 127.7, 127.6, 127.2, 126.3, 126.3, 125.5, 124.4, 123.1, 109.1, 69.6, 65.5, 56.4, 51.8, 47.9, 43.2, 21.3, 17.6. HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for C₃₈H₃₄N₃O₄⁺ 596.2544, found 596.2554. HPLC (Chiralpak IA, *i*-PrOH /hexane = 80/20, flow rate = 1.0 mL/min, $\lambda = 254$ nm): $t_{major} = 13.2$ min, $t_{minor} = 8.0$ min, $ee = 95\%$.

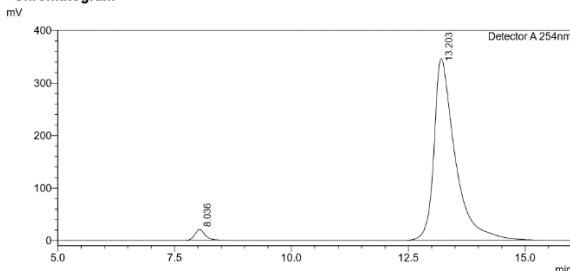
<Chromatogram>



<Peak Table>

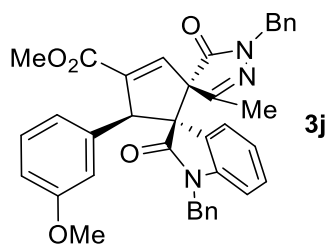
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	8.165	5723932	234022	50.285		M	50.285
2	13.762	5659067	157620	49.715		M	49.715
Total		11382999	391642				100.000

<Chromatogram>



<Peak Table>

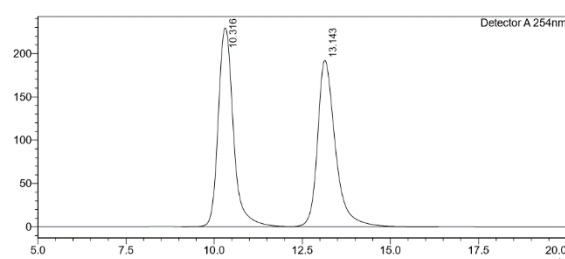
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	8.036	300409	20254	2.698		M	2.698
2	13.203	10833246	345767	97.302		M	97.302
Total		11133655	366021				100.000



methyl (2'S,3R,5'R)-1,1''-dibenzyl-5'-(3-methoxyphenyl)-3''-methyl-2,5''-dioxo-1'',5''-dihydrodispiro[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-4'-carboxylate (3j)

White solid, 58.6 mg, 96% yield, $[\alpha]_D^{25} = 398$ ($c = 1.0$ CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.79 (dd, $J = 7.6, 0.7$ Hz, 1H), 7.25 – 7.17 (m, 3H), 7.16 – 6.92 (m, 8H), 6.77 (dd, $J = 7.9, 2.9$ Hz, 1H), 6.73 (d, $J = 2.6$ Hz, 1H), 6.52 (d, $J = 7.6$ Hz, 1H), 6.37 (d, $J = 7.4$ Hz, 4H), 5.53 (d, $J = 2.6$ Hz, 1H), 5.00 (d, $J = 15.8$ Hz, 1H), 4.82 (d, $J = 15.2$ Hz, 1H), 4.61 (d, $J = 15.3$ Hz, 1H), 4.20 (d, $J = 15.9$ Hz, 1H), 3.71 (s, 3H), 3.48 (s, 3H), 2.01 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.6, 172.1, 164.3, 159.0, 157.4, 143.5, 143.2, 138.6, 136.4, 135.6, 134.5, 129.5, 128.7, 128.6, 128.5, 127.9, 127.6, 127.3, 126.4, 125.5, 124.4, 123.1, 121.6, 114.1, 113.7, 109.2, 69.6, 65.4, 56.5, 55.0, 51.8, 48.0, 43.2, 17.6. HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for C₃₈H₃₄N₃O₅⁺ 612.2493, found 612.2495. HPLC (Chiralpak IA, *i*-PrOH /hexane = 80/20, flow rate = 1.0 mL/min, $\lambda = 254$ nm): $t_{\text{major}} = 13.1$ min, $t_{\text{minor}} = 10.4$ min, $ee = 94\%$.

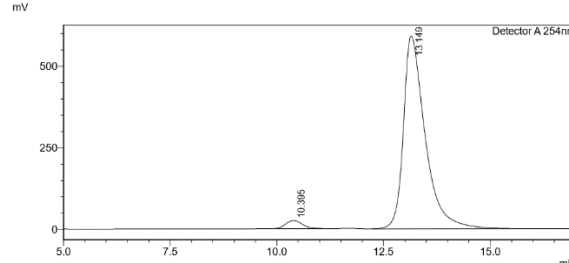
<Chromatogram>
mv



<Peak Table>

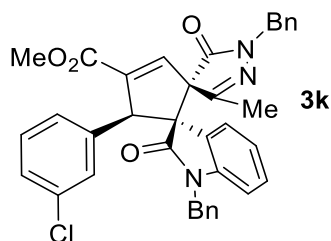
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	10.316	6884498	229458	50.290			50.290
2	13.143	6805083	192062	49.710		V	49.710
Total		13689581	421520				100.000

<Chromatogram>
mv



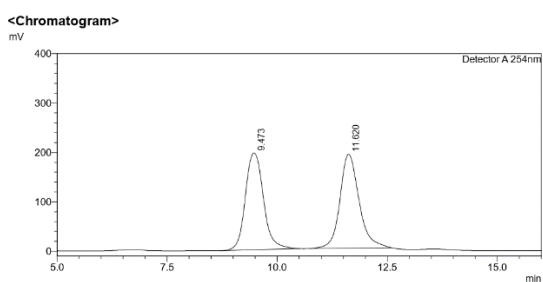
<Peak Table>

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	10.395	683335	24465	3.150		M	3.150
2	13.149	21012004	591139	96.850		M	96.850
Total		21695339	615604				100.000



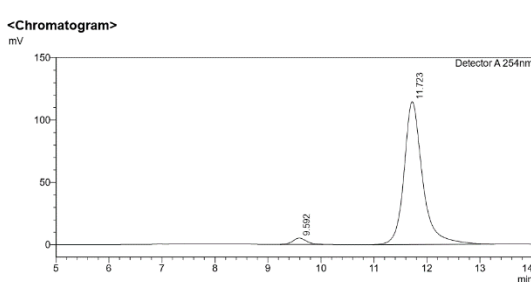
methyl (2'S,3R,5'R)-1,1''-dibenzyl-5'-(3-chlorophenyl)-3''-methyl-2,5''-dioxo-1'',5''-dihydrodispiro[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-4'-carboxylate (3k)

White solid, 56.6 mg, 92% yield, $[\alpha]_D^{25} = 401$ ($c = 1.0$ CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, $J = 7.5$ Hz, 1H), 7.23 – 7.07 (m, 8H), 7.06 – 6.93 (m, 4H), 6.86 (s, 1H), 6.80 (d, $J = 7.6$ Hz, 1H), 6.76 (d, $J = 2.6$ Hz, 1H), 6.43 (d, $J = 7.8$ Hz, 3H), 5.49 (d, $J = 2.5$ Hz, 1H), 4.99 (d, $J = 15.8$ Hz, 1H), 4.82 (d, $J = 15.2$ Hz, 1H), 4.61 (d, $J = 15.2$ Hz, 1H), 4.21 (d, $J = 15.8$ Hz, 1H), 3.72 (s, 3H), 2.00 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.5, 171.9, 163.9, 157.2, 143.0, 142.8, 139.3, 137.2, 135.6, 134.4, 133.6, 129.8, 129.2, 128.9, 128.7, 128.6, 127.7, 127.6, 127.5, 127.4, 126.4, 125.4, 123.9, 123.3, 109.3, 69.6, 65.3, 56.0, 51.9, 48.0, 43.2, 17.5. HRMS (ESI-TOF) m/z [M + H]⁺ calcd for C₃₇H₃₁ClN₃O₄⁺ 616.1998, found 616.2007. HPLC (Chiralpak IA, *i*-PrOH /hexane = 80/20, flow rate = 1.0 mL/min, $\lambda = 254$ nm): $t_{\text{major}} = 11.7$ min, $t_{\text{minor}} = 9.6$ min, $ee = 94\%$.



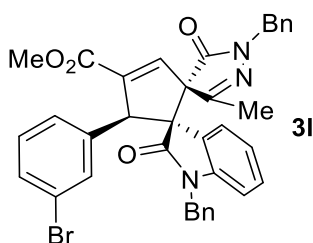
<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	9.473	5620345	196125	49.531		M	49.531
2	11.620	5726767	190216	50.469		M	50.469
Total		11347112	386341				100.000



<Peak Table>
Detector A 254nm

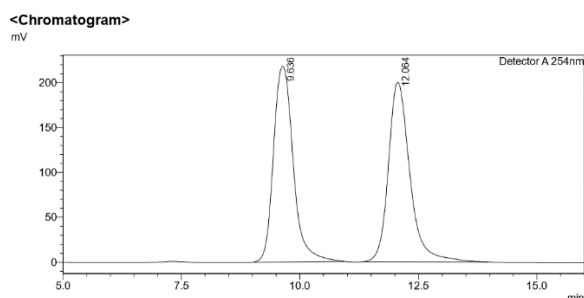
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	9.592	87639	5017	3.049		M	3.049
2	11.723	2769846	114519	96.951		M	96.951
Total		2857485	119536				100.000



methyl (2'S,3R,5'R)-1,1''-dibenzyl-5''-(3-bromophenyl)-3''-methyl-2,5''-dioxo-1',5''-dihydrodispiro[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-4'-carboxylate (31)

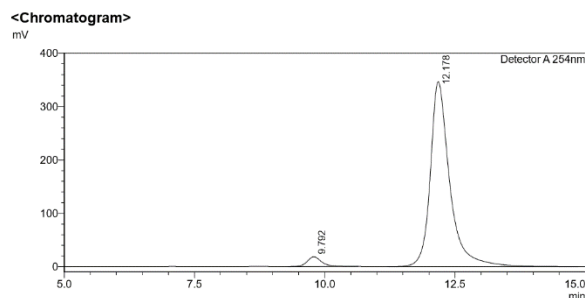
White solid, 63.9 mg, 97% yield, $[\alpha]_D^{25} = 395$ ($c = 1.0$ CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.77 (dd, $J = 7.6, 0.7$ Hz, 1H), 7.36 – 7.30 (m, 1H), 7.23 – 7.07 (m, 7H), 6.98 (dt, $J = 22.2, 7.1$ Hz, 5H), 6.84 (d, $J = 7.8$ Hz, 1H), 6.76 (d, $J = 2.6$ Hz, 1H), 6.43 (dd, $J = 7.4, 2.3$ Hz, 3H), 5.48 (d, $J = 2.5$ Hz, 1H), 5.00 (d, $J = 15.8$ Hz, 1H), 4.82 (d, $J = 15.2$ Hz, 1H), 4.61 (d, $J = 15.2$ Hz, 1H), 4.21 (d, $J = 15.8$ Hz, 1H), 3.72 (s, 3H), 2.00 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.5, 171.8, 163.8, 157.2, 143.0, 142.8, 139.3, 137.5, 135.6, 134.4, 132.0, 130.5, 129.8, 129.3, 128.7, 128.6, 127.9, 127.9, 127.6, 127.4, 126.4, 125.4, 123.8, 123.3, 121.7, 109.3, 69.6, 65.3, 55.9, 51.9, 48.0, 43.3, 17.5. HRMS (ESI-TOF) m/z [M + H]⁺ calcd for C₃₇H₃₁BrN₃O₄⁺ 660.1492,

found 660.1495. HPLC (Chiralpak IA, *i*-PrOH /hexane = 80/20, flow rate = 1.0 mL/min, $\lambda = 254$ nm): $t_{\text{major}} = 12.1$ min, $t_{\text{minor}} = 9.8$ min, $ee = 92\%$.



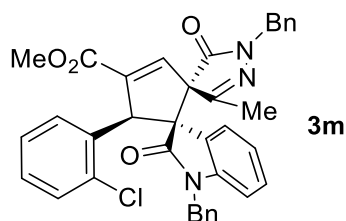
<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	9.836	6317579	218240	49.957		M	49.957
2	12.064	6328560	200276	50.043		M	50.043
Total		12646138	418517				100.000



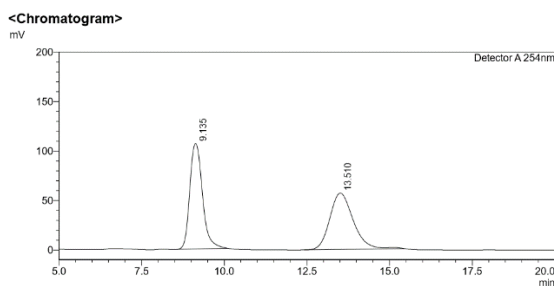
<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	9.792	356385	18414	3.796		M	3.796
2	12.178	9031348	346506	96.204			96.204
Total		9387733	364920				100.000



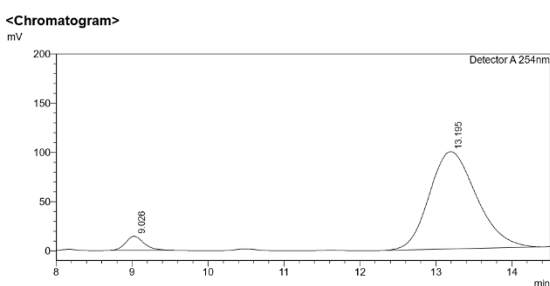
methyl (2'S,3R,5'R)-1,1''-dibenzyl-5'-(2-chlorophenyl)-3''-methyl-2,5''-dioxo-1',5''-dihydrodispiro[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-4'-carboxylate (3m)

White solid, 53.5 mg, 87% yield, $[\alpha]_{\text{D}}^{25} = 307$ ($c = 1.0$ CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, $J = 7.7$ Hz, 1H), 7.51 – 7.46 (m, 1H), 7.21 (dd, $J = 8.2, 3.1$ Hz, 3H), 7.11 (ddd, $J = 10.3, 9.0, 2.2$ Hz, 5H), 7.07 – 7.01 (m, 4H), 6.89 (td, $J = 7.7, 0.9$ Hz, 1H), 6.79 (d, $J = 2.6$ Hz, 1H), 6.44 (s, 1H), 6.42 (s, 1H), 6.40 (d, $J = 7.8$ Hz, 1H), 6.19 (d, $J = 2.6$ Hz, 1H), 5.05 (d, $J = 15.8$ Hz, 1H), 4.81 (d, $J = 15.2$ Hz, 1H), 4.63 (d, $J = 15.2$ Hz, 1H), 4.24 (d, $J = 15.8$ Hz, 1H), 3.65 (s, 3H), 2.01 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.4, 172.1, 163.8, 157.3, 143.7, 142.6, 139.2, 135.6, 134.6, 134.6, 133.3, 132.5, 129.5, 129.2, 128.65, 128.64, 128.5, 128.0, 127.6, 127.6, 127.3, 126.4, 126.1, 123.6, 122.7, 108.8, 69.9, 65.5, 51.9, 51.8, 48.1, 43.2, 17.7. HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for C₃₇H₃₁ClN₃O₄⁺ 616.1998, found 616.2004. HPLC (Chiralpak IA, *i*-PrOH /hexane = 80/20, flow rate = 1.0 mL/min, $\lambda = 254$ nm): $t_{\text{major}} = 13.2$ min, $t_{\text{minor}} = 9.0$ min, $ee = 90\%$.



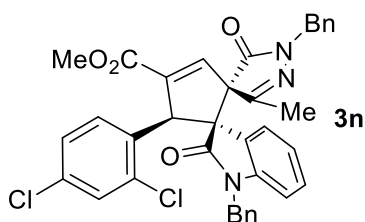
<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	9.135	2845098	106609	50.316		M	50.316
2	13.510	2809334	56949	49.684		M	49.684
Total		5654431	163558				100.000



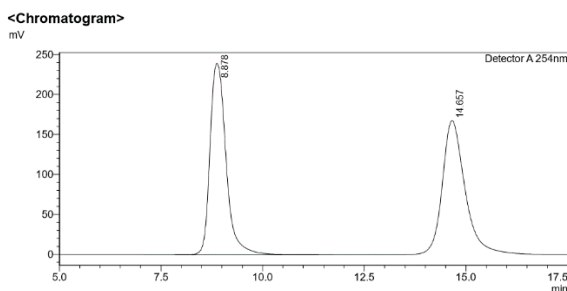
<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	9.026	238691	14224	5.292		M	5.292
2	13.195	4271405	98922	94.708		M	94.708
Total		4510095	113146				100.000



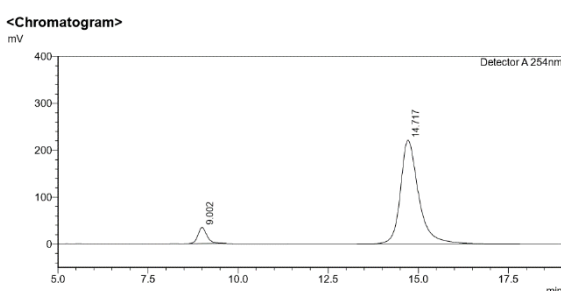
methyl (2'S,3R,5'R)-1,1''-dibenzyl-5'-(2,4-dichlorophenyl)-3''-methyl-2,5''-dioxo-1'',5''-dihydrodispiro[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-4'-carboxylate (3n)

White solid, 52.6 mg, 90% yield, $[\alpha]_D^{25} = 423$ ($c = 1.0$ CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.79 (dd, $J = 7.7, 0.7$ Hz, 1H), 7.40 (d, $J = 8.5$ Hz, 1H), 7.24 – 7.16 (m, 5H), 7.13 – 7.06 (m, 3H), 7.08 (dd, $J = 8.5, 2.2$ Hz, 1H), 7.03 (dd, $J = 7.3, 2.2$ Hz, 2H), 6.88 (td, $J = 7.7, 0.9$ Hz, 1H), 6.80 (d, $J = 2.6$ Hz, 1H), 6.49 (s, 1H), 6.48 – 6.44 (m, 2H), 6.13 (d, $J = 2.6$ Hz, 1H), 5.07 (d, $J = 15.8$ Hz, 1H), 4.81 (d, $J = 15.2$ Hz, 1H), 4.63 (d, $J = 15.2$ Hz, 1H), 4.25 (d, $J = 15.8$ Hz, 1H), 3.67 (s, 3H), 2.01 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.3, 171.9, 163.6, 157.0, 143.1, 142.6, 139.7, 135.6, 135.2, 134.5, 133.9, 133.4, 132.0, 129.7, 128.9, 128.7, 128.6, 128.0, 127.6, 127.5, 126.5, 126.3, 123.3, 122.9, 108.9, 69.8, 65.4, 51.9, 51.3, 48.1, 43.3, 17.7. HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for C₃₇H₃₀Cl₂N₃O₄⁺ 650.1608, found 650.1619. HPLC (Chiralpak IA, *i*-PrOH /hexane = 80/20, flow rate = 1.0 mL/min, $\lambda = 254$ nm): $t_{major} = 14.7$ min, $t_{minor} = 9.0$ min, $ee = 86\%$.



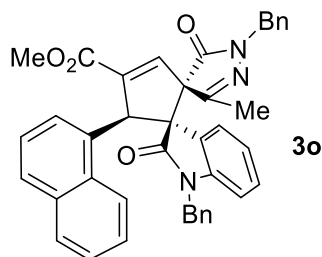
<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	8.878	6576052	239345	49.953			49.953
2	14.657	6588465	187887	50.047			50.047
Total		13164517	407232				100.000



<Peak Table>
Detector A 254nm

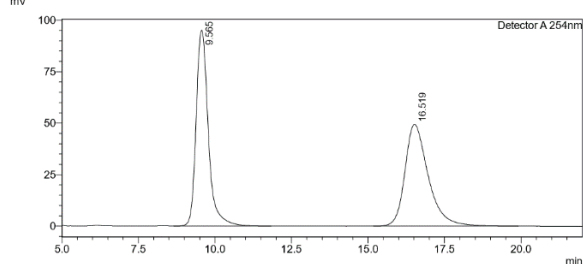
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	9.002	594097	34136	7.053		M	7.053
2	14.717	7829578	221366	92.947		M	92.947
Total		8423675	255502				100.000



methyl (2'S,3R,5'R)-1,1''-dibenzyl-3''-methyl-5'-(naphthalen-1-yl)-2,5''-dioxo-1'',5''-dihydrodispiro[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-4'-carboxylate (3o)

White solid, 50.5 mg, 80% yield, $[\alpha]_D^{25} = 250$ ($c = 1.0$ CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.97 (dd, $J = 7.5, 1.2$ Hz, 1H), 7.73 (t, $J = 7.8$ Hz, 2H), 7.55 (dd, $J = 7.3, 1.0$ Hz, 1H), 7.50 (d, $J = 8.6$ Hz, 1H), 7.40 – 7.35 (m, 1H), 7.26 – 7.19 (m, 4H), 7.10 (dd, $J = 6.7, 2.9$ Hz, 2H), 7.05 – 6.90 (m, 4H), 6.87 (t, $J = 7.7$ Hz, 2H), 6.83 (d, $J = 2.5$ Hz, 1H), 6.44 (d, $J = 2.4$ Hz, 1H), 6.09 (d, $J = 7.4$ Hz, 1H), 6.01 (d, $J = 7.5$ Hz, 2H), 4.86 (d, $J = 15.1$ Hz, 2H), 4.70 (d, $J = 15.2$ Hz, 1H), 4.04 (d, $J = 16.0$ Hz, 1H), 3.61 (s, 3H), 2.05 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.6, 172.3, 164.4, 157.8, 144.7, 142.9, 138.7, 135.7, 134.2, 133.5, 131.8, 131.4, 129.5, 128.6, 128.4, 128.2, 128.07, 128.05, 127.7, 127.1, 126.1, 125.9, 125.1, 125.0, 124.4, 123.7, 122.7, 109.2, 69.9, 65.5, 51.8, 51.77, 48.2, 42.9, 17.9. HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for C₄₁H₃₄N₃O₄⁺ 632.2544, found 632.2552. HPLC (Chiralpak IA, *i*-PrOH /hexane = 80/20, flow rate = 1.0 mL/min, $\lambda = 254$ nm): $t_{\text{major}} = 16.5$ min, $t_{\text{minor}} = 9.7$ min, *ee* = 96%.

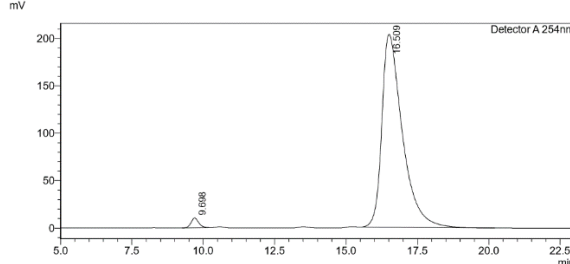
<Chromatogram>
mV



<Peak Table>

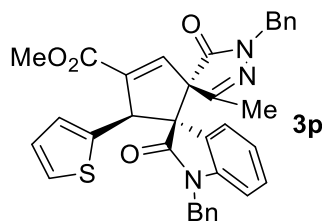
Peak#	Rel. Time	Area	Height	Conc.	Unit	Mark	Area%
1	9.565	2626609	95056	50.092			50.092
2	16.519	2617002	49435	49.908			49.908
Total		5243612	144492				100.000

<Chromatogram>
mV



<Peak Table>

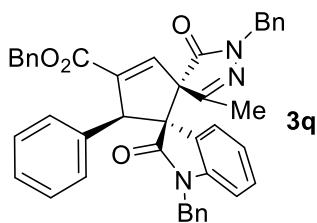
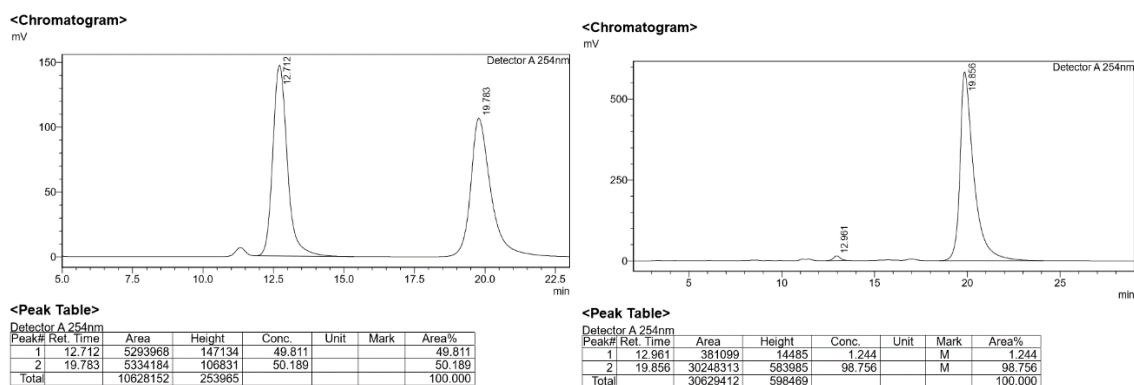
Peak#	Rel. Time	Area	Height	Conc.	Unit	Mark	Area%
1	9.698	192270	10276	1.852		M	1.852
2	16.509	10188444	203546	98.148			98.148
Total		10380714	213822				100.000



methyl (2'S,3R,5'R)-1,1''-dibenzyl-3''-methyl-2,5''-dioxo-5'-(thiophen-2-yl)-1'',5''-dihydrodispiro[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-4'-

carboxylate (**3p**)

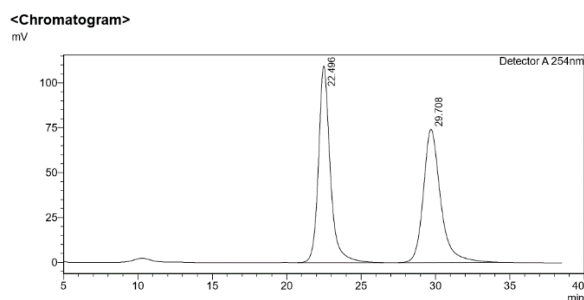
White solid, 55.8 mg, 95% yield, $[\alpha]_D^{25} = 365$ ($c = 1.0$ CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.73 (dd, $J = 7.6, 0.7$ Hz, 1H), 7.23 – 7.09 (m, 7H), 7.06 (dd, $J = 5.1, 1.1$ Hz, 1H), 6.96 (td, $J = 8.9, 1.2$ Hz, 3H), 6.85 (dd, $J = 5.1, 3.6$ Hz, 1H), 6.74 (d, $J = 3.5$ Hz, 1H), 6.71 (d, $J = 2.7$ Hz, 1H), 6.55 (d, $J = 6.5$ Hz, 2H), 6.45 (d, $J = 7.8$ Hz, 1H), 5.78 (d, $J = 2.6$ Hz, 1H), 5.04 (d, $J = 15.8$ Hz, 1H), 4.81 (d, $J = 15.2$ Hz, 1H), 4.60 (d, $J = 15.3$ Hz, 1H), 4.31 (d, $J = 15.8$ Hz, 1H), 3.73 (s, 3H), 2.00 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.8, 171.8, 163.8, 157.2, 143.3, 143.1, 138.3, 136.9, 135.6, 134.6, 129.7, 128.7, 128.5, 127.9, 127.6, 127.3, 127.2, 126.6, 125.4, 124.5, 124.0, 123.2, 109.2, 69.3, 65.4, 51.89, 51.88, 48.0, 44.3, 17.4. HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for C₃₅H₃₀N₃O₄S⁺ 588.1952, found 588.1951. HPLC (Chiralpak IA, *i*-PrOH/hexane = 80/20, flow rate = 1.0 mL/min, $\lambda = 254$ nm): $t_{major} = 19.8$ min, $t_{minor} = 12.9$ min, $ee = 97\%$.



benzyl (2'*S*,3*R*,5'*R*)-1,1''-dibenzyl-3''-methyl-2,5''-dioxo-5'-phenyl-1'',5''-dihydrodispiro[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-4'-carboxylate (**3q**)

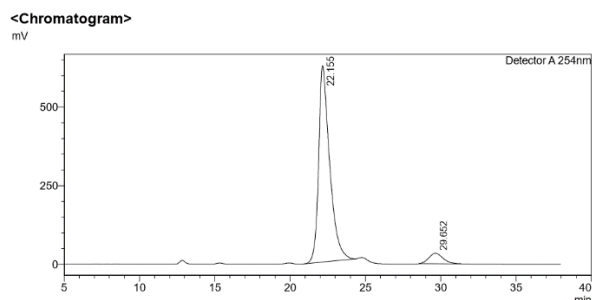
White solid, 59.1 mg, 90% yield, $[\alpha]_D^{25} = 346$ ($c = 1.0$ CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, $J = 7.6$ Hz, 1H), 7.26 – 7.16 (m, 7H), 7.11 (dd, $J = 12.6, 4.9$ Hz, 4H), 7.04 (t, $J = 7.3$ Hz, 4H), 7.00 – 6.95 (m, 3H), 6.92 (d, $J = 6.6$ Hz, 2H), 6.79 (d, $J = 2.6$ Hz, 1H), 6.36 (d, $J = 7.7$ Hz, 1H), 6.30 (d, $J = 7.4$ Hz, 2H), 5.56 (d, $J = 2.6$ Hz, 1H), 5.21 (d, $J = 12.5$ Hz, 1H), 5.05 (d, $J = 12.5$ Hz, 1H), 5.01 (d, $J = 15.9$ Hz, 1H), 4.83 (d, $J = 15.2$ Hz, 1H), 4.60 (d, $J = 15.3$ Hz, 1H), 4.18 (d, $J = 15.9$ Hz, 1H), 2.01 (s, 3H). ¹³C NMR (101 MHz,

CDCl₃) δ 172.6, 172.1, 163.6, 157.5, 143.6, 143.0, 139.1, 135.6, 135.4, 135.2, 134.4, 129.6, 129.4, 128.6, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.6, 127.3, 127.2, 126.3, 125.5, 124.3, 123.1, 109.2, 69.7, 66.6, 65.5, 56.6, 48.0, 43.1, 17.6. HRMS (ESI-TOF) m/z [M + H]⁺ calcd for C₄₃H₃₆N₃O₄⁺ 658.2700, found 658.2702. HPLC (Chiralpak IA, *i*-PrOH /hexane = 80/20, flow rate = 1.0 mL/min, λ = 254 nm): t_{major} = 22.1 min, t_{minor} = 29.6 min, *ee* = 87%.



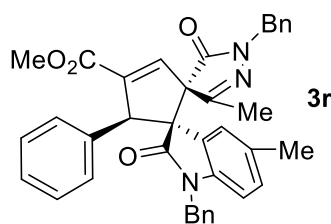
<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	22.496	6022555	109463	50.150			50.150
2	29.708	5986610	74208	49.850			49.850
Total		12009164	183671				100.000



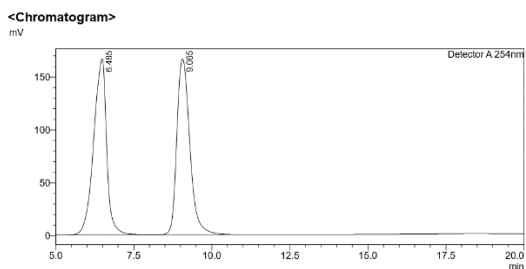
<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	22.155	31864070	624741	93.670			93.670
2	29.652	2153217	33334	6.330		M	6.330
Total		34017288	658074				100.000



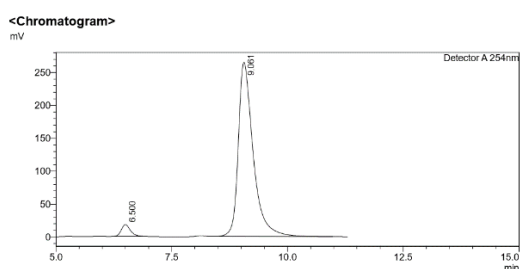
methyl (2'S,3R,5'R)-1,1''-dibenzyl-3'',5-dimethyl-2,5''-dioxo-5'-phenyl-1'',5''-dihydrodispiro[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-4'-carboxylate (3r)

White solid, 55.9 mg, 94% yield, $[\alpha]_{\text{D}}^{25} = 190$ ($c = 1.0$ CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.64 (d, $J = 8.5$ Hz, 1H), 7.21 (dd, $J = 6.9, 5.6$ Hz, 3H), 7.12 (dd, $J = 14.8, 7.5$ Hz, 3H), 7.07 – 6.97 (m, 4H), 6.91 (d, $J = 7.3$ Hz, 2H), 6.73 (d, $J = 2.6$ Hz, 1H), 6.40 (dd, $J = 8.5, 2.4$ Hz, 1H), 6.31 (s, 1H), 6.29 (s, 1H), 5.94 (s, 1H), 5.48 (d, $J = 2.6$ Hz, 1H), 4.96 (d, $J = 15.8$ Hz, 1H), 4.84 (d, $J = 15.3$ Hz, 1H), 4.61 (d, $J = 15.3$ Hz, 1H), 4.14 (d, $J = 15.8$ Hz, 1H), 3.70 (s, 3H), 3.66 (s, 3H), 2.00 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 173.1, 172.2, 164.2, 160.9, 157.5, 144.3, 143.6, 138.6, 135.7, 135.1, 134.4, 129.2, 128.6, 128.4, 127.8, 127.8, 127.5, 127.2, 127.2, 126.4, 126.3, 115.9, 106.7, 97.1, 69.8, 65.3, 56.2, 55.2, 51.8, 47.9, 43.1, 17.5. HRMS (ESI-TOF) m/z [M + H]⁺ calcd for C₃₈H₃₄N₃O₄⁺ 596.2544, found 596.2554. HPLC (Chiralpak IA, *i*-PrOH /hexane = 80/20, flow rate = 1.0 mL/min, λ = 254 nm): t_{major} = 9.0 min, t_{minor} = 6.5 min, *ee* = 92%.



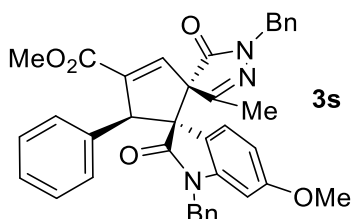
<Peak Table>

Peak#	Rel. Time	Area	Height	Conc.	Unit	Area%
1	6.485	4840885	186427	50.042		50.042
2	9.065	4832749	186121	49.958		49.958
Total		9673635	332548			100.000



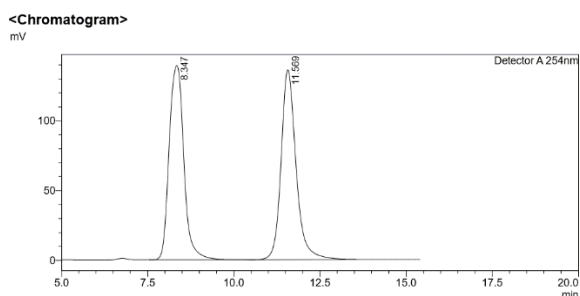
<Peak Table>

Peak#	Rel. Time	Area	Height	Conc.	Unit	Area%
1	6.500	246539	17893	4.006		4.006
2	9.061	5908115	284649	95.994		95.994
Total		6154655	282542			100.000



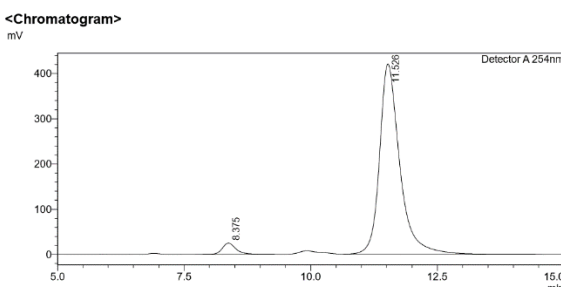
methyl (2'S,3R,5'R)-1,1''-dibenzyl-6-methoxy-3''-methyl-2,5''-dioxo-5'-phenyl-1'',5''-dihydrodispiro[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-4'-carboxylate (3s)

White solid, 58 mg, 95% yield, $[\alpha]_D^{25} = 133$ ($c = 1.0$ CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.64 (s, 1H), 7.25 – 7.07 (m, 7H), 7.03 (t, $J = 7.4$ Hz, 2H), 6.96 – 6.87 (m, 5H), 6.74 (d, $J = 2.6$ Hz, 1H), 6.30 (s, 1H), 6.28 (s, 1H), 6.25 (d, $J = 8.0$ Hz, 1H), 5.53 (d, $J = 2.6$ Hz, 1H), 4.98 (d, $J = 15.8$ Hz, 1H), 4.92 (d, $J = 15.4$ Hz, 1H), 4.56 (d, $J = 15.4$ Hz, 1H), 4.15 (d, $J = 15.8$ Hz, 1H), 3.70 (s, 3H), 2.22 (s, 3H), 2.01 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.6, 172.2, 164.2, 157.6, 143.6, 140.7, 138.8, 135.7, 135.1, 134.6, 132.7, 129.9, 129.2, 128.6, 128.5, 127.8, 127.5, 127.5, 127.3, 127.1, 126.4, 126.1, 124.4, 109.0, 69.7, 65.5, 56.4, 51.8, 47.8, 43.1, 21.2, 17.6. HRMS (ESI-TOF) m/z [M + H]⁺ calcd for C₃₈H₃₄N₃O₅⁺ 612.2493, found 612.2499. HPLC (Chiralpak IA, *i*-PrOH /hexane = 60/40, flow rate = 1.0 mL/min, $\lambda = 254$ nm): $t_{major} = 11.5$ min, $t_{minor} = 8.3$ min, $ee = 92\%$.



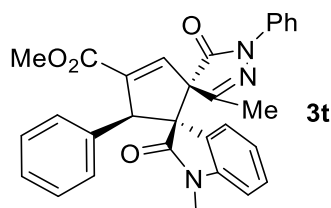
<Peak Table>

Peak#	Rel. Time	Area	Height	Conc.	Unit	Area%
1	8.347	4139713	139160	50.047		50.047
2	11.569	4131977	135931	49.953		49.953
Total		8271691	275091			100.000



<Peak Table>

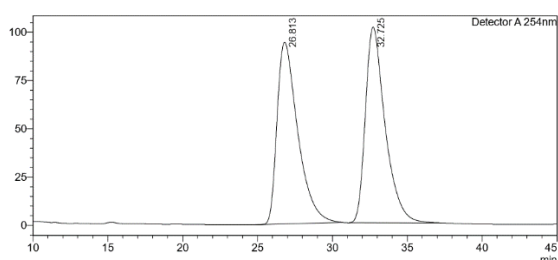
Peak#	Rel. Time	Area	Height	Conc.	Unit	Area%
1	8.375	475868	25036	3.916		3.916
2	11.526	11676139	420274	96.084		96.084
Total		12152007	445311			100.000



methyl (2'*S*,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-4'-carboxylate (3t)

White solid, 55.9 mg, 97% yield, $[\alpha]_{\text{D}}^{25} = 345$ ($c = 1.0$ CHCl₃). ¹H NMR (500 MHz, CDCl₃) δ 7.78 (d, $J = 7.8$ Hz, 3H), 7.37 (t, $J = 8.0$ Hz, 2H), 7.22 (t, $J = 7.5$ Hz, 1H), 7.18 (t, $J = 7.4$ Hz, 1H), 7.10 (t, $J = 7.2$ Hz, 1H), 7.05 (t, $J = 7.3$ Hz, 2H), 7.01 (t, $J = 7.7$ Hz, 1H), 6.82 (d, $J = 2.5$ Hz, 1H), 6.78 (s, 1H), 6.77 (s, 1H), 6.56 (d, $J = 7.8$ Hz, 1H), 5.48 (d, $J = 2.4$ Hz, 1H), 3.70 (s, 3H), 2.72 (s, 3H), 2.13 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 172.3, 170.6, 164.2, 158.1, 144.1, 143.4, 138.8, 137.37, 134.7, 129.8, 128.9, 128.7, 127.4, 127.2, 125.6, 125.0, 124.2, 123.2, 119.1, 107.9, 70.3, 66.1, 56.9, 51.8, 25.5, 17.6. HRMS (ESI-TOF) m/z [M + Na]⁺ C₃₀H₂₅N₃NaO₄⁺ 514.1737, found 514.1737. HPLC (Chiralpak Ic, *i*-PrOH /hexane = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm): $t_{\text{major}} = 27.1$ min, $t_{\text{minor}} = 33.4$ min, $ee = 97\%$.

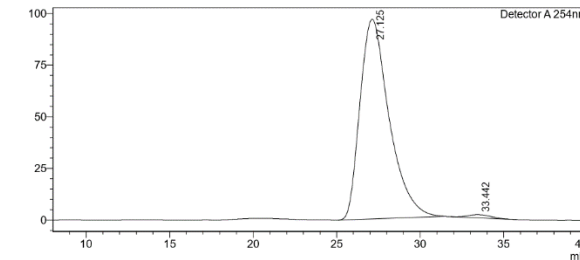
<Chromatogram>
mV



<Peak Table>

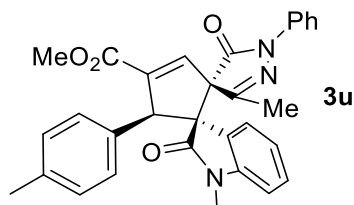
Peak#	Ret. Time	Area	Height	Unit	Mark	Name	Area%
1	26.813	9063585	94036		M		49.351
2	32.725	9302107	101384		M		50.649
Total		18365692	195419				100.000

<Chromatogram>
mV



<Peak Table>

Peak#	Ret. Time	Area	Height	Unit	Mark	Name	Area%
1	27.125	11732294	96635		M		98.698
2	33.442	154804	1600		M		1.302
Total		11887098	98235				100.000

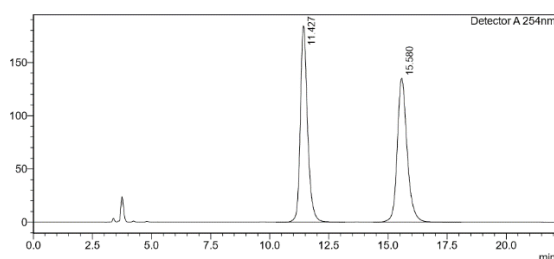


methyl (2'*S*,3*R*,5'*R*)-1,3''-dimethyl-2,5''-dioxo-1''-phenyl-5'-(*p*-tolyl)-1'',5''-dihydrodispiro[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-4'-carboxylate (3u)

White solid, 55.9 mg, 94% yield, $[\alpha]_{\text{D}}^{25} = 315$ ($c = 1.0$ CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, $J = 7.6$ Hz, 3H), 7.41 – 7.32 (m, 2H), 7.25 – 7.15 (m, 2H), 7.00 (td, $J = 7.7, 0.9$ Hz,

1H), 6.86 (s, 1H), 6.84 (s, 1H), 6.79 (d, $J = 2.6$ Hz, 1H), 6.68 (s, 1H), 6.66 (s, 1H), 6.57 (d, $J = 7.7$ Hz, 1H), 5.44 (d, $J = 2.6$ Hz, 1H), 3.71 (s, 3H), 2.76 (s, 3H), 2.20 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 172.5, 170.6, 164.2, 158.1, 144.1, 143.6, 138.5, 137.4, 136.7, 131.6, 129.7, 128.9, 128.5, 128.2, 125.5, 125.0, 124.3, 123.1, 119.1, 107.9, 70.3, 66.1, 56.6, 51.8, 25.6, 21.1, 17.6. HRMS (ESI-TOF) m/z $[\text{M} + \text{Na}]^+ \text{C}_{31}\text{H}_{27}\text{N}_3\text{NaO}_4^+ 528.1894$, found 528.1905. HPLC (Chiralpak IC, *i*-PrOH /hexane = 80/20, flow rate = 1.0 mL/min, $\lambda = 254$ nm): $t_{\text{major}} = 11.7$ min, $t_{\text{minor}} = 16.0$ min, $ee = 97\%$.

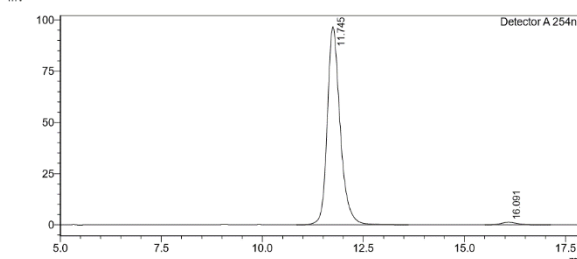
<Chromatogram>
mV



<Peak Table>

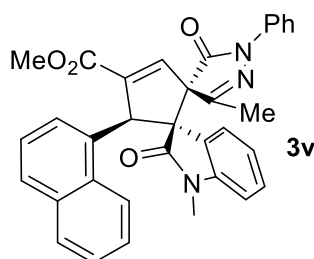
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.427	3929929	184380	50.013			
2	15.580	3927863	135185	49.987			
Total		7857792	319565				

<Chromatogram>
mV



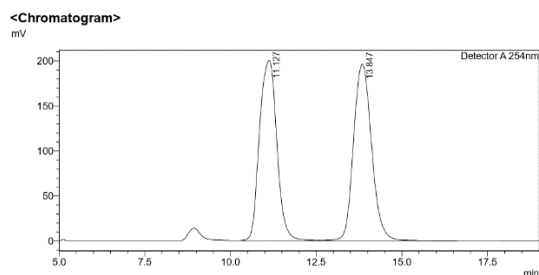
<Peak Table>

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	11.745	2143152	98655	98.338			98.338
2	16.091	36214	1246	1.662			1.662
Total		2179367	97901				100.000



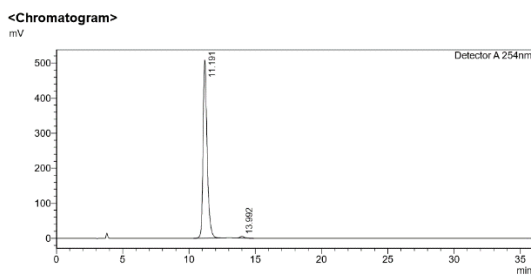
methyl (2'S,3R,5'R)-1,3''-dimethyl-5'-(naphthalen-1-yl)-2,5''-dioxo-1''-phenyl-1'',5''-dihydrodispiro[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-4'-carboxylate (3v)

White solid, 55.9 mg, 94% yield, $[\alpha]_{\text{D}}^{25} = 172$ ($c = 1.0$ CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.93 (dd, $J = 7.6, 0.9$ Hz, 1H), 7.84 (d, $J = 1.1$ Hz, 1H), 7.81 (d, $J = 1.0$ Hz, 1H), 7.66 (d, $J = 1.9$ Hz, 1H), 7.64 (d, $J = 2.4$ Hz, 1H), 7.47 (dd, $J = 7.3, 1.1$ Hz, 1H), 7.45 – 7.35 (m, 4H), 7.18 – 7.23 (m, 2H), 7.08 (td, $J = 7.7, 1.2$ Hz, 1H), 7.03 – 6.96 (m, 2H), 6.91 (d, $J = 2.4$ Hz, 1H), 6.38 (d, $J = 2.4$ Hz, 1H), 6.28 (d, $J = 7.8$ Hz, 1H), 3.62 (s, 3H), 2.56 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 172.1, 171.0, 164.3, 158.5, 144.4, 143.7, 138.8, 137.4, 133.2, 131.8, 131.1, 129.7, 128.9, 128.2, 128.0, 127.9, 125.6, 125.6, 124.9, 124.8, 124.6, 124.4, 123.3, 122.8, 119.1, 107.9, 70.6, 66.4, 52.1, 51.9, 25.4, 18.0. HRMS (ESI-TOF) m/z $[\text{M} + \text{Na}]^+ \text{C}_{34}\text{H}_{27}\text{N}_3\text{NaO}_4^+ 564.1894$, found 564.1892. HPLC (Chiralpak IA, *i*-PrOH /hexane = 80/20, flow rate = 1.0 mL/min, $\lambda = 254$ nm): $t_{\text{major}} = 11.2$ min, $t_{\text{minor}} = 14.0$ min, $ee = 98\%$.



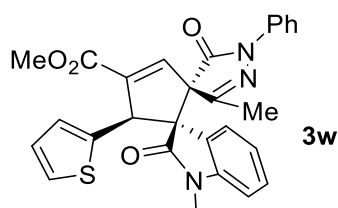
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Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	11.127	7038347	200065	49.356			49.356
2	13.847	7222047	196136	50.644		V	50.644
Total		14260394	396200				100.000



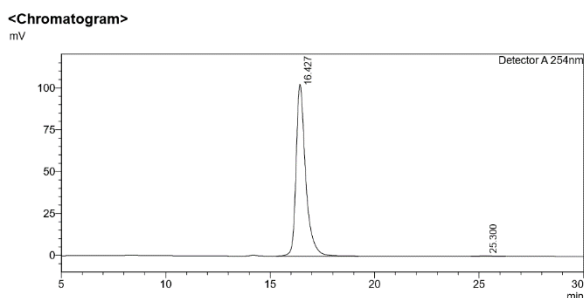
<Peak Table>

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.191	10950223	508633	98.905			
2	13.992	121226	4876	1.095			
Total		11071449	513509				



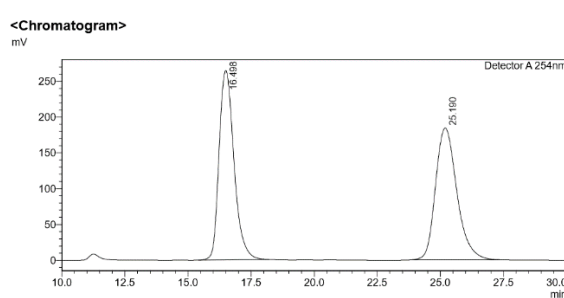
methyl (2'S,3R,5'R)-1,3''-dimethyl-2,5''-dioxo-1''-phenyl-5'-(thiophen-2-yl)-1',5''-dihydrodispiro[indoline-3,1'-cyclopentane-2',4''-pyrazol]-3'-ene-4'-carboxylate (3w)

White solid, 55.9 mg, 94% yield, $[\alpha]_D^{25} = 515$ ($c = 1.0$ CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, $J = 1.2$ Hz, 1H), 7.74 (d, $J = 1.0$ Hz, 1H), 7.72 (dd, $J = 7.6, 0.7$ Hz, 1H), 7.40 – 7.33 (m, 2H), 7.24 (dd, $J = 7.7, 1.2$ Hz, 1H), 7.22 – 7.15 (m, 1H), 7.03 – 6.97 (m, 2H), 6.80 – 6.75 (m, 2H), 6.67 (d, $J = 2.7$ Hz, 1H), 6.64 (d, $J = 7.7$ Hz, 1H), 5.74 (d, $J = 2.7$ Hz, 1H), 3.73 (s, 3H), 2.90 (s, 3H), 2.14 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.6, 170.3, 163.7, 157.7, 144.2, 143.1, 138.1, 137.2, 136.7, 129.9, 128.8, 126.9, 126.3, 125.6, 124.9, 124.4, 123.8, 123.2, 119.1, 108.0, 70.1, 65.9, 52.2, 51.9, 25.8, 17.4. HRMS (ESI-TOF) m/z $[M + Na]^+$ C₂₈H₂₃N₃NaO₄S⁺ 520.1301, found 520.1306. HPLC (Chiralpak Ic, *i*-PrOH /hexane = 80/20, flow rate = 1.0 mL/min, $\lambda = 254$ nm): $t_{major} = 16.5$ min, $t_{minor} = 25.2$ min, $ee = 99\%$.



<Peak Table>

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	16.427	3249586	102481	99.687			99.687
2	25.300	10200	239	0.313			0.313
Total		3259787	102720				100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	16.498	10846887	264553	49.997		M	49.997
2	25.190	10847988	184128	50.003		M	50.003
Total		21694876	448681				100.000

4. X-Ray Crystallographic Analysis and Determination of the Absolute Configurations of the Products

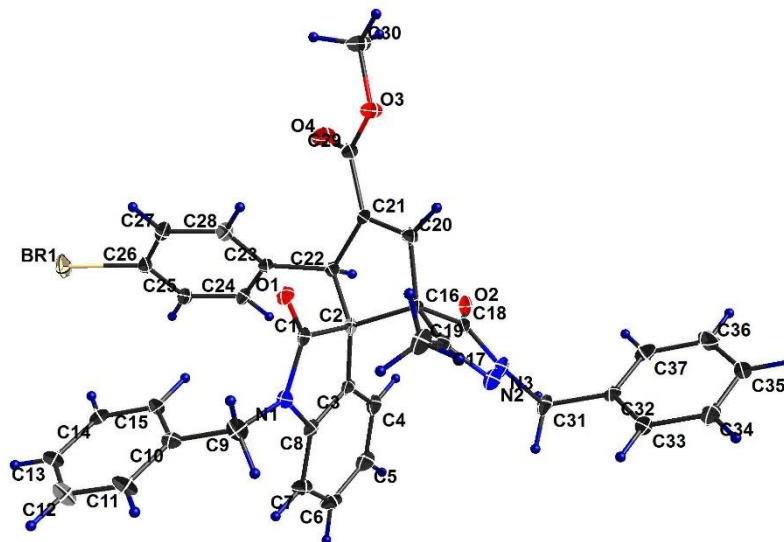


Figure 1 X-ray structure of **3f**

Identification code	I559	
Empirical formula	C ₃₈ H ₃₁ Br Cl ₃ N ₃ O ₄	
Formula weight	779.92	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	a = 9.1965(3) Å	α = 90°.
	b = 9.6940(4) Å	β = 90°.
	c = 38.3086(14) Å	γ = 90°.
Volume	3415.2(2) Å ³	
Z	4	
Density (calculated)	1.517 Mg/m ³	
Absorption coefficient	4.180 mm ⁻¹	
F (000)	1592	
Crystal size	0.294 x 0.225 x 0.158 mm ³	
Theta range for data collection	4.617 to 72.330°.	
Index ranges	-9 ≤ h ≤ 11, -11 ≤ k ≤ 11, -47 ≤ l ≤ 47	

Reflections collected	34770
Independent reflections	6745 [R (int) = 0.0446]
Completeness to theta = 67.679°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7536 and 0.5297
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6745 / 36 / 475
Goodness-of-fit on F ²	1.082
Final R indices [I > 2sigma (I)]	R1 = 0.0249, wR2 = 0.0597
R indices (all data)	R1 = 0.0252, wR2 = 0.0599
Absolute structure parameter	0.034(4)
Extinction coefficient	n/a
Largest diff. peak and hole	0.366 and -0.396 e.Å ⁻³

5. References

- 1 Correia, J. T. M.; Acconcia, L. V.; Coelho, F. *Eur. J. Org. Chem.* **2016**, *11*, 1972.
- 2 Wang, S.; Izquierdo, J.; Rodríguez-Esrich, C.; Pericàs, Miquel A. *ACS Catal.* **2017**, *7*, 2780.

6. NMR Spectra of the Products

