

## Supporting Information

### The catalytic asymmetric synthesis of Spiro- Oxindole- Pyrrolidine- Pyrazolone compounds

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## 1. General Information

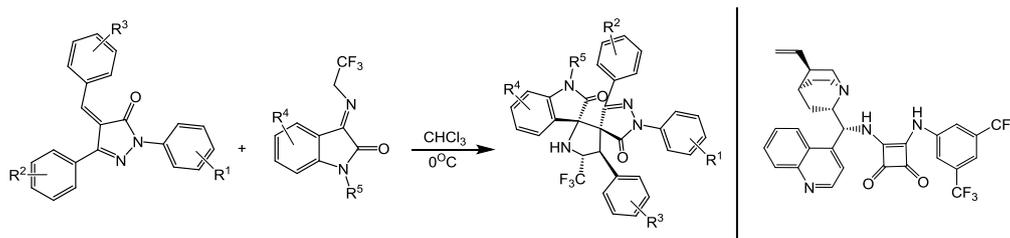
Reactions were monitored by thin layer chromatography (TLC), and compounds were visualized with a UV light at 254 nm. Column chromatography purifications were carried out using silica gel.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra were recorded on a Bruker (300 MHz and 400MHz) spectrometer in  $\text{CDCl}_3$  using tetramethylsilane (TMS) as internal standard. Data are presented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) and coupling constant in Hertz (Hz). Mass peaks are identified by the corresponding  $m/z$  values. The ee values determination was carried out using chiral high-performance liquid chromatography (HPLC) with Chiracel IA column, Chiracel IC column and Chiracel OD column. Optical rotations were measured on a digital polarimeter and are reported as follows:  $[\alpha]_{\text{D}}^{25}$  (1 g/100 mL,  $\text{CHCl}_3$ ).

All solvents were obtained from commercial sources and were purified according to standard procedures. 4-benzylidene-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one were synthesized by literature method. <sup>[1]</sup>

### Reference:

[1] Ramajayam, R.; Tan, K.-P.; Liu, H.-G.; Liang, P.-H. *Bio & Med Chem.* **2010**, 2010(18), 7849–7854.

## 2. Representative Procedure

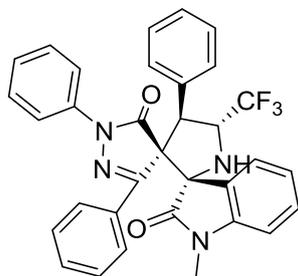


To a solution of cinchonine derived squaramide organocatalyst **C6** (12 mg, 0.02 mmol) and (Z)-1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one (0.2 mmol) in chloroform (2.0 mL) was added (E)-4-benzylidene-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (0.22 mmol) in chloroform (2.0 mL) at 0°C. The reaction mixture was monitored by TLC inspection. The solvent was evaporated under reduced pressure and the crude residue was purified on silica gel flash column chromatography using ethylacetate/hexanes (1/20) eluent to give the corresponding CF<sub>3</sub>- and Isatin-containing Pyrazolone **3aa-3xa** and **3ab-3am**.

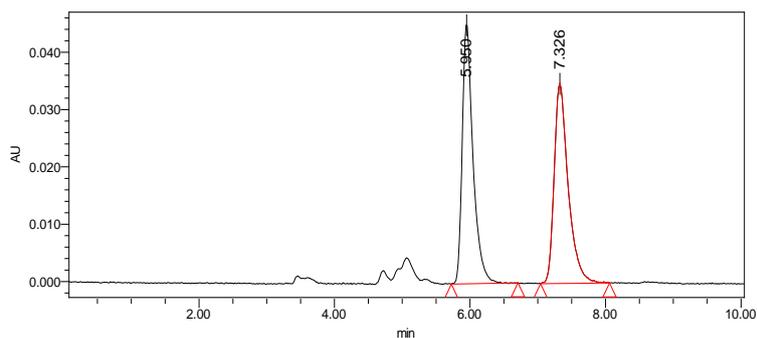
Racemates were prepared following the general procedure by triethylenediamine.

## 3. Analytical Data and HPLC Chromatogram of the Addition Products

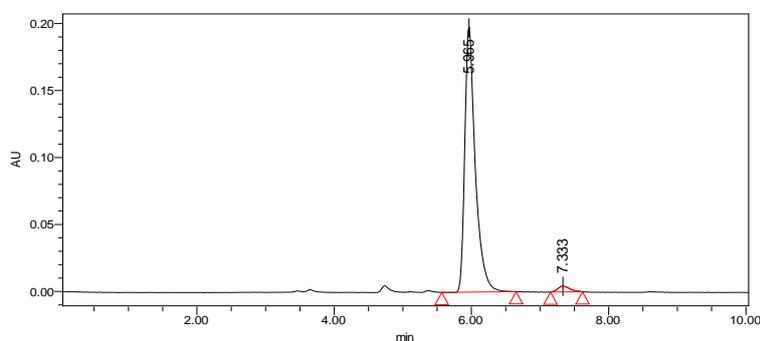
(3*S*,3'*S*,4'*R*,5'*R*)-1-methyl-1'',3'',4'-triphenyl-5'-(trifluoromethyl)dispiro[indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''H)-dione (**3aa**)



From 48.4 mg (0.20 mmol) 1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 71.28 mg (0.22 mmol, 1.1 equiv) 4-benzylidene-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one, 99.0 mg (88% yield) compound **3aa** was obtained as light yellow solid, mp = 98 - 99 °C.  $[\alpha]_D^{20} = +153$  ( $c = 1.0$ , CHCl<sub>3</sub>). Dr (>20:1) determined by <sup>1</sup>H and <sup>19</sup>F NMR analysis. 95% ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 7.3$  min and  $t_{\text{minor}} = 6.0$  min. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.64 – 7.41 (m, 10H), 7.31 (dd,  $J = 13.1, 4.9$  Hz, 3H), 7.26 – 7.14 (m, 4H), 6.91 (t,  $J = 7.6$  Hz, 1H), 6.60 (d,  $J = 7.8$  Hz, 1H), 5.80 (d,  $J = 10.1$  Hz, 1H), 5.62 – 5.40 (m, 1H), 3.54 (d,  $J = 9.8$  Hz, 1H), 2.35 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 173.9, 170.7, 154.9, 143.8, 136.7, 132.9, 131.1, 131.0, 130.4, 128.9, 128.9, 128.8, 128.5, 128.1, 126.3, 126.1 (q,  $J_{\text{C-F}} = 278.7$  Hz), 124.4, 123.0, 122.9, 120.2, 108.1, 72.9, 70.5, 61.6 (q,  $J_{\text{C-F}} = 30.7$  Hz), 48.0, 25.0. <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ -72.1; HRMS (ESI)  $m/z$  calcd for C<sub>33</sub>H<sub>25</sub>F<sub>3</sub>N<sub>4</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup>: 589.1822, found 589.1832.

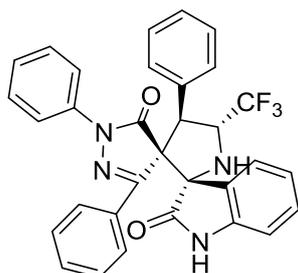


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	5.950	501114	49.97	45462	bb	Unknown
2	7.326	501701	50.03	34880	bb	Unknown



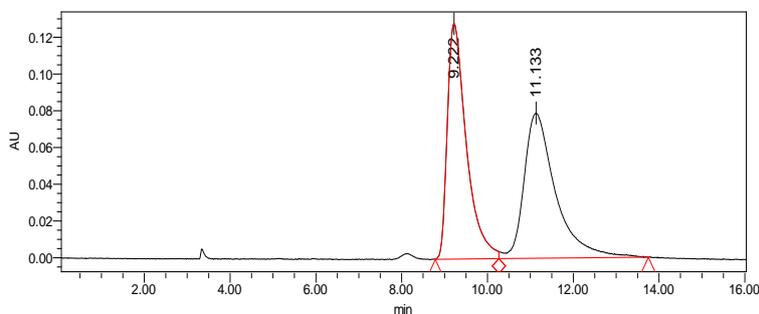
	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	5.965	2098272	97.54	197896	bb	Unknown
2	7.333	52854	2.46	4236	bb	Unknown

**(3*S*,3'*S*,4'*R*,5'*R*)-1''',3'',4'-triphenyl-5'-(trifluoromethyl)dispiro[indoline-3,2'-pyrrolidine-3',4'-pyrazole]-2,5''(1''H)-dione (3ab)**

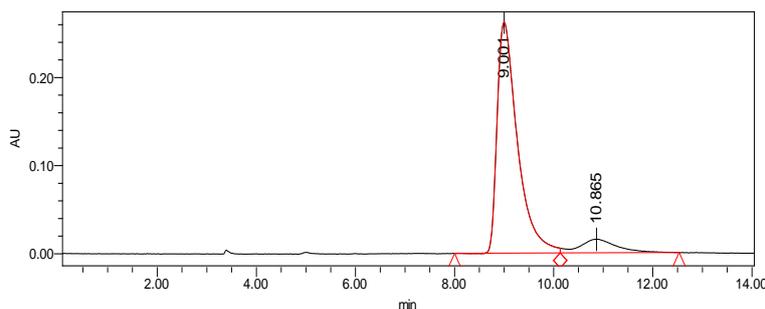


From 45.6 mg (0.20 mmol) 3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 71.28 mg (0.22 mmol, 1.1 equiv) 4-benzylidene-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one, 93.5 mg (77% yield) compound **3ab** was obtained as light yellow solid. mp = 139 - 140 °C.  $[\alpha]_D^{20} = +85$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis. 80% ee was determined by HPLC analysis (Daicel Chiralcel OD column, hexane/2-propanol 20:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 10.9$  min and  $t_{\text{minor}} = 9.0$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 – 7.47 (m, 8H), 7.43 – 7.15 (m, 12H), 6.89 (td,  $J = 7.7, 0.8$  Hz, 1H), 6.65 (d,  $J = 7.7$  Hz, 1H), 5.70 (dd,  $J = 15.3, 10.1$  Hz, 1H), 5.46 (td,  $J = 9.8, 4.9$  Hz, 1H), 3.47 (d,  $J = 9.8$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

$\delta$  176.1, 170.7, 155.0, 141.3, 136.7, 132.9, 131.1, 131.0, 130.5, 128.9, 128.9, 128.6, 128.5, 128.1, 126.3, 126.0 (q,  $J_{C-F} = 278.6$  Hz), 125.1, 123.6, 123.0, 120.2, 110.0, 72.7, 70.6, 61.6 (q,  $J_{C-F} = 30.3$  Hz), 48.1.  $^{19}\text{F}$  NMR (282MHz,  $\text{CDCl}_3$ )  $\delta$  -72.0; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{32}\text{H}_{23}\text{F}_3\text{N}_4\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 575.1665, found 575.1665.

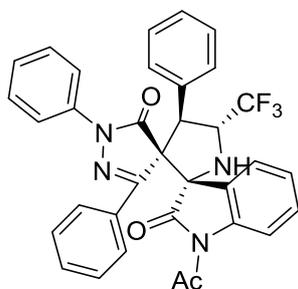


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	9.222	3955584	49.53	128199	bv	Unknown
2	11.133	4031039	50.47	78962	vb	Unknown



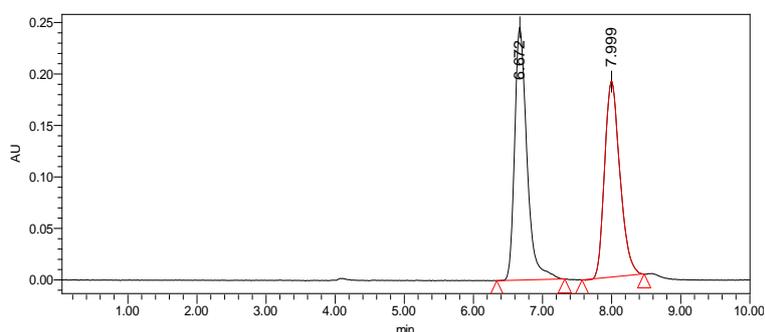
	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	9.001	7474264	90.18	262339	bv	Unknown
2	10.865	814051	9.82	15424	vb	Unknown

**(3*S*,3'*S*,4'*R*,5'*R*)-1-acetyl-1'',3'',4'-triphenyl-5'-(trifluoromethyl)dispiro[indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''H)-dione (3ac)**

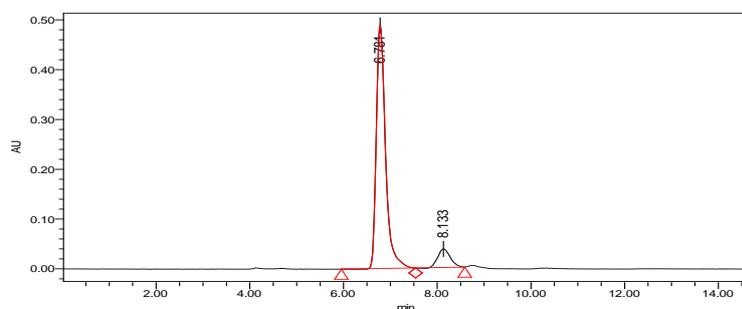


From 54 mg (0.20 mmol) 1-acetyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 71.28 mg (0.22 mmol, 1.1 equiv) 4-benzylidene-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one, 103.4 mg (87 % yield) compound **3ac** was obtained as red solid. mp =

110 - 111 °C.  $[\alpha]_D^{20} = + 182$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis. 81% ee was determined by HPLC analysis (Daicel Chiralcel IC column, hexane/2-propanol 20:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 8.1$  min and  $t_{\text{minor}} = 6.8$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 (d,  $J = 8.1$  Hz, 1H), 7.67 – 7.58 (m, 5H), 7.48 (ddd,  $J = 9.1, 4.7, 1.4$  Hz, 5H), 7.37 – 7.24 (m, 6H), 7.20 (dd,  $J = 11.6, 4.2$  Hz, 1H), 7.10 (td,  $J = 7.7, 0.8$  Hz, 1H), 5.56 (ddd,  $J = 17.4, 17.0, 6.3$  Hz, 2H), 3.44 (d,  $J = 9.1$  Hz, 1H), 1.85 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  175.2, 170.4, 170.0, 154.2, 140.2, 136.5, 132.4, 131.6, 131.2, 130.9, 129.1, 128.9, 128.7, 128.7, 128.6, 126.5, 126.0 (q,  $J_{\text{C-F}} = 278.3$  Hz), 125.6, 124.2, 122.3, 120.1, 116.7, 73.6, 70.9, 61.8 (q,  $J_{\text{C-F}} = 30.7$  Hz), 47.9, 25.7.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.4; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{34}\text{H}_{25}\text{F}_3\text{N}_4\text{NaO}_3$   $[\text{M}+\text{Na}]^+$ : 617.1771, found 617.1775.

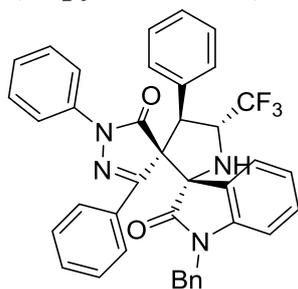


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	6.672	3036874	50.90	245310	bb	Unknown
2	7.999	2928898	49.10	190516	bb	Unknown



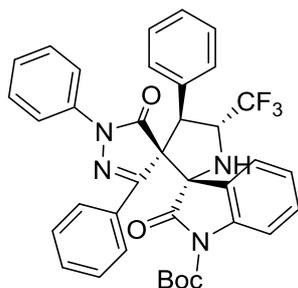
	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	6.781	6687139	90.43	489262	bv	Unknown
2	8.133	707449	9.57	37307	vb	Unknown

**(3*S*,3'*S*,4'*R*,5'*R*)-1-benzyl-1'',3'',4'-triphenyl-5'-(trifluoromethyl)dispiro[indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''H)-dione (3ad)**



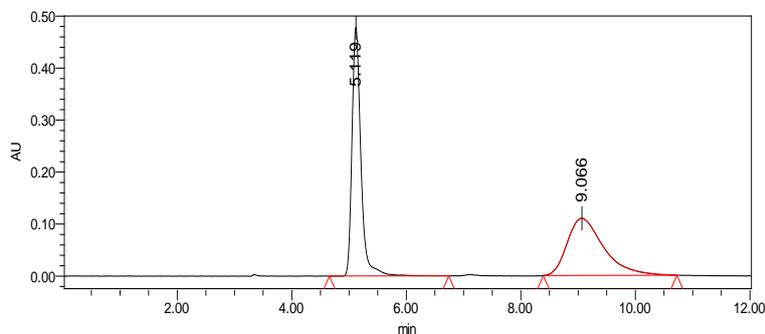
From 63.6 mg (0.20 mmol) 1-benzyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 71.28 mg (0.22 mmol, 1.1 equiv) 4-benzylidene-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one, 101.4 mg (79 % yield) compound **3ad** was obtained as light yellow solid, mp = 120 - 121 °C.  $[\alpha]_D^{20} = +99$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 – 7.61 (m, 2H), 7.42 (ddd,  $J = 13.2, 9.3, 5.0$  Hz, 8H), 7.24 – 6.93 (m, 11H), 6.85 – 6.68 (m, 3H), 6.36 (d,  $J = 7.8$  Hz, 1H), 5.81 (d,  $J = 10.0$  Hz, 1H), 5.45 (dd,  $J = 15.6, 7.9$  Hz, 1H), 4.01 (d,  $J = 15.8$  Hz, 1H), 3.75 (d,  $J = 15.8$  Hz, 1H), 3.47 (d,  $J = 9.4$  Hz, 1H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  173.1, 169.6, 153.4, 142.0, 135.5, 133.7, 131.7, 130.0, 129.8, 129.5, 127.8, 127.8, 127.8, 127.6, 127.4, 127.3 (q,  $J_{\text{C-F}} = 277.8$  Hz), 127.1, 126.5, 126.2, 125.2, 123.5, 122.0, 121.9, 119.0, 108.4, 72.0, 69.5, 60.4 (q,  $J_{\text{C-F}} = 30.7$  Hz), 47.3, 42.2, -0.00.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -71.9; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{39}\text{H}_{29}\text{F}_3\text{N}_4\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 665.2135, found 665.2126.

**tert-butyl(3*S*,3'*S*,4'*R*,5'*R*)-2,5''-dioxo-1'',3'',4'-triphenyl-5'-(trifluoromethyl)-1'',5''-dihydrodispiro[indoline-3,2'-pyrrolidine-3',4''-pyrazole]-1-carboxylate (3ae)**

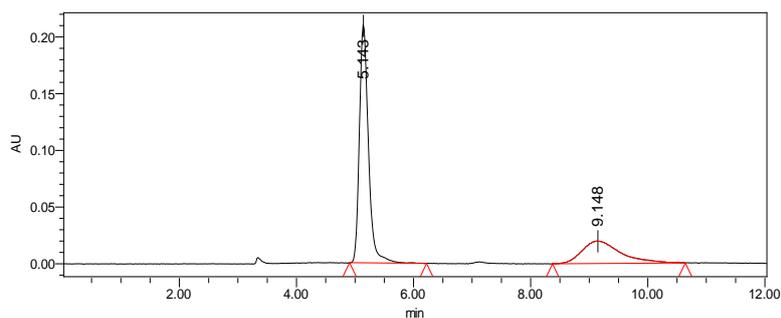


From 65.6 mg (0.20 mmol) tert-butyl 2-oxo-3-((2,2,2-trifluoroethyl)imino)indoline-1-carboxylate and 71.28 mg (0.22 mmol, 1.1 equiv) 4-benzylidene-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one, 78.2 mg (66% yield) compound **3ae** was obtained as light yellow solid. mp = 119 - 120°C.  $[\alpha]_D^{20} = +172$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis. 42% ee was determined by HPLC analysis (Daicel Chiralcel OD column, hexane/2-propanol 20:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 9.1$  min and  $t_{\text{minor}} = 5.1$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 (d,  $J = 8.1$  Hz, 1H), 7.62 (ddd,  $J = 11.9, 7.8, 3.4$  Hz, 5H), 7.52 – 7.43 (m, 5H), 7.35 – 7.14 (m, 8H), 7.09 – 6.94 (m, 1H), 5.71 (d,  $J = 10.1$  Hz, 1H), 5.63 – 5.46 (m, 1H), 3.42 (d,  $J = 9.4$  Hz, 1H), 1.41 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.4, 170.2, 154.4, 148.3,

140.2, 136.6, 132.6, 131.3, 130.9, 130.8, 128.9, 128.9, 128.9, 128.6, 128.6, 128.5, 126.3, 126.0 (q,  $J_{C-F} = 278.7$  Hz), 124.7, 124.3, 122.1, 120.2, 115.2, 84.2, 77.3, 73.6, 70.6, 61.5 (q,  $J_{C-F} = 30.7$ Hz), 48.0, 27.9.  $^{19}\text{F}$  NMR (282MHz,  $\text{CDCl}_3$ )  $\delta$ -72.1; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{37}\text{H}_{31}\text{F}_3\text{N}_4\text{NaO}_4$   $[\text{M}+\text{Na}]^+$ : 675.2190, found 675.2196.

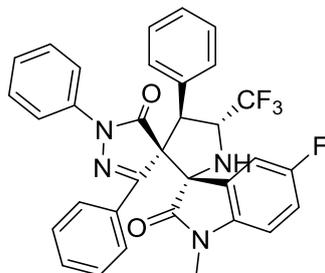


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	5.119	5178143	51.67	479484	bb	Unknown
2	9.066	4844002	48.33	109958	bb	Unknown



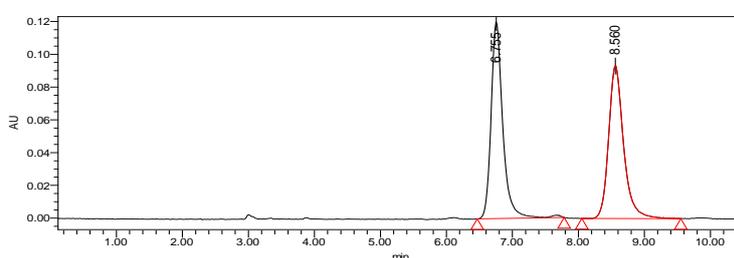
	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	5.143	2252032	71.23	210036	bb	Unknown
2	9.148	909390	28.77	19652	bb	Unknown

**(3*S*,3'*S*,4'*R*,5'*R*)-5-fluoro-1-methyl-1'',3'',4'-triphenyl-5'-(trifluoromethyl)dispiro [indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''H)-dione (3af)**

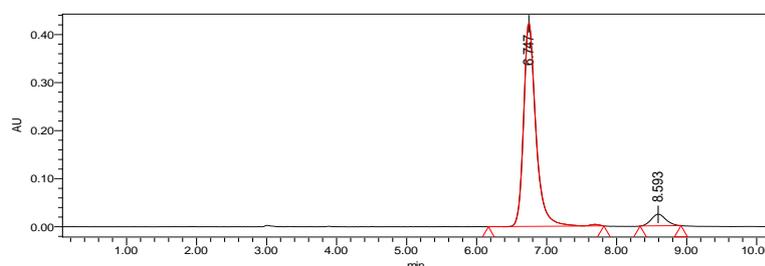


From 52 mg (0.20mmol) 5-fluoro-1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 71.28 mg (0.22 mmol, 1.1 equiv) 4-benzylidene-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one, 94.6 mg (81% yield) compound **3af** was obtained as light yellow

solid, mp = 105 - 106 °C.  $[\alpha]_D^{20} = +82$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis. 87% ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 8.6$  min and  $t_{\text{minor}} = 6.7$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 – 7.41 (m, 6H), 7.42 – 7.31 (m, 3H), 7.31 – 7.23 (m, 3H), 7.23 – 7.10 (m, 5H), 6.90 (td,  $J = 8.7, 2.6$  Hz, 1H), 6.46 (dd,  $J = 8.6, 4.1$  Hz, 1H), 5.69 (d,  $J = 10.1$  Hz, 1H), 5.39 (ddd,  $J = 17.2, 7.4, 2.5$  Hz, 1H), 3.40 (d,  $J = 9.7$  Hz, 1H), 2.28 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.7, 169.4, 159.2, 156.7, 153.8, 138.8, 138.8, 135.5, 131.5, 129.8, 129.4, 127.9, 127.9, 127.7, 127.6, 127.4, 127.1, 125.4, 124.9 (q,  $J_{\text{C-F}} = 278.3$  Hz), 119.1, 116.3 (d,  $J_{\text{C-F}} = 18$  Hz), 112.1 (d,  $J_{\text{C-F}} = 19.5$  Hz), 107.7, 107.6, 71.7, 69.3, 69.3, 60.5 (q,  $J_{\text{C-F}} = 30.7$  Hz), 47.0, 24.1.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.2, -118.9; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{33}\text{H}_{24}\text{F}_4\text{N}_4\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 607.1728, found 607.1735.

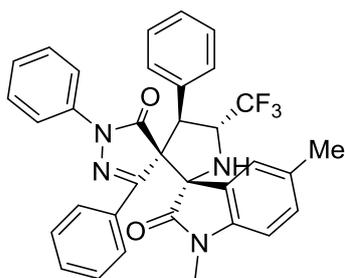


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	6.755	1481361	50.21	120333	bb	Unknown
2	8.560	1468974	49.79	93366	bb	Unknown

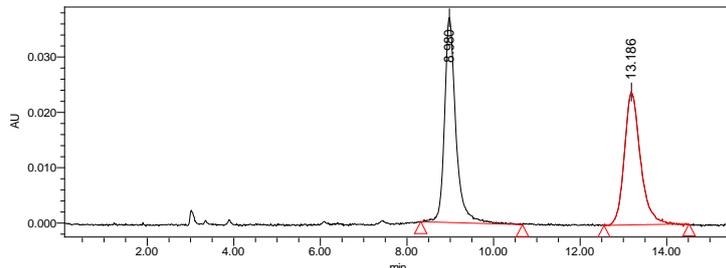


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	6.747	5174202	93.61	423338	bb	Unknown
2	8.593	353157	6.39	24233	bb	Unknown

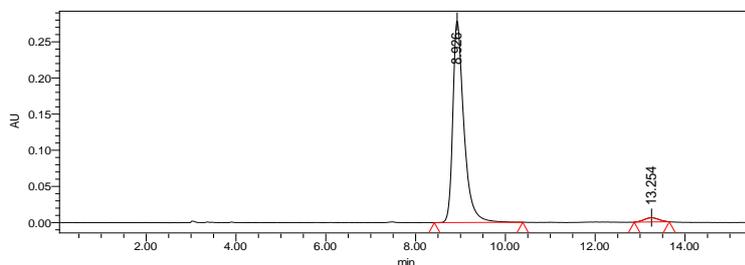
**(3S,3'S,4'R,5'R)-1,5-dimethyl-1'',3'',4'-triphenyl-5'-(trifluoromethyl)dispiro[indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''H)-dione (3ag)**



From 51.2 mg (0.20 mmol) 1,5-dimethyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 71.28 mg (0.22 mmol, 1.1 equiv) 4-benzylidene-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one, 98.8 mg (85% yield) compound **3ag** was obtained as light yellow solid, mp = 158 - 159 °C.  $[\alpha]_D^{20} = +99$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis. 95% ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 13.3$  min and  $t_{\text{minor}} = 9.0$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 – 7.49 (m, 6H), 7.47 – 7.40 (m, 3H), 7.36 – 7.15 (m, 7H), 7.02 (d,  $J = 7.9$  Hz, 1H), 6.48 (d,  $J = 7.9$  Hz, 1H), 5.81 (d,  $J = 10.1$  Hz, 1H), 5.60 – 5.42 (m, 1H), 3.51 (d,  $J = 9.8$  Hz, 1H), 2.33 (s, 3H), 2.11 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.7, 169.8, 153.8, 140.3, 135.7, 132.0, 131.4, 130.2, 130.0, 129.3, 127.9, 127.8, 127.6, 127.5, 127.4, 127.0, 125.2, 125.0 (q,  $J_{\text{C-F}} = 278.7$  Hz), 124.1, 121.8, 119.0, 106.8, 71.9, 69.8, 60.8 (q,  $J_{\text{C-F}} = 30.3$  Hz), 46.7, 24.0, 19.8.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.0; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{34}\text{H}_{28}\text{F}_3\text{N}_4\text{O}_2$   $[\text{M}+\text{H}]^+$ : 581.2159, found 581.2159.



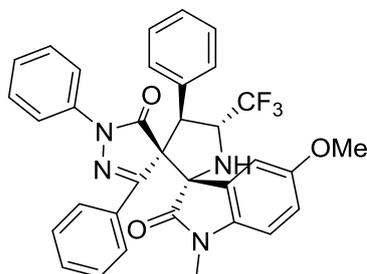
	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	8.980	675856	52.06	36988	bb	Unknown
2	13.186	622381	47.94	23968	bb	Unknown



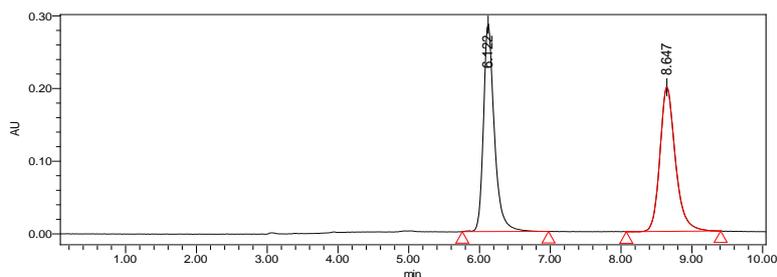
	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	8.926	4756063	97.25	279156	bb	Unknown

2	13.254	134715	2.75	6105	bb	Unknown
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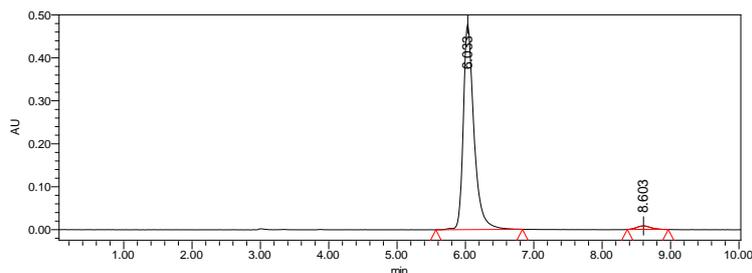
**(3*S*,3'*S*,4'*R*,5'*R*)-1-benzyl-1'',3'',4'-triphenyl-5'-(trifluoromethyl)dispiro[indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''*H*)-dione (3ah)**



From 54.4 mg (0.20 mmol) 5-methoxy-1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 71.28 mg (0.22 mmol, 1.1 equiv) 4-benzylidene-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one, 103.9 mg (87% yield) compound **3ah** was obtained as light yellow solid, mp = 126 - 127 °C.  $[\alpha]_D^{20} = +71$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis. 96% ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 8.6$  min and  $t_{\text{minor}} = 6.0$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (dt,  $J = 7.4, 3.0$  Hz, 4H), 7.43 – 7.32 (m, 4H), 7.28 – 7.06 (m, 7H), 6.82 (t,  $J = 7.4$  Hz, 1H), 6.72 – 6.63 (m, 1H), 6.52 (d,  $J = 7.8$  Hz, 1H), 5.69 (d,  $J = 10.1$  Hz, 1H), 5.38 (td,  $J = 9.8, 4.9$  Hz, 1H), 3.55 (s, 3H), 3.45 (d,  $J = 9.8$  Hz, 1H), 2.27 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.6, 170.7, 156.0, 155.0, 137.1, 136.7, 132.9, 131.0, 130.4, 130.2, 129.0, 128.8, 128.7, 128.5, 128.0, 126.2, 126.1 (q,  $J_{\text{C-F}} = 278.7$  Hz), 123.9, 119.9, 116.4, 111.1, 108.7, 73.0, 70.8, 61.7 (q,  $J_{\text{C-F}} = 30.3$  Hz), 55.7, 47.9, 25.1.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.0; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{34}\text{H}_{27}\text{F}_3\text{N}_4\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 619.1927, found 619.1931.

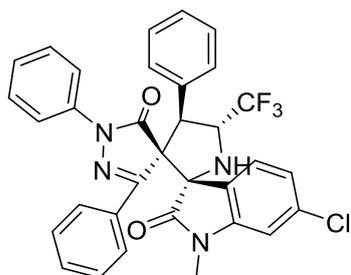


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	6.122	3056342	50.28	285414	bb	Unknown
2	8.647	3022094	49.72	198897	bb	Unknown

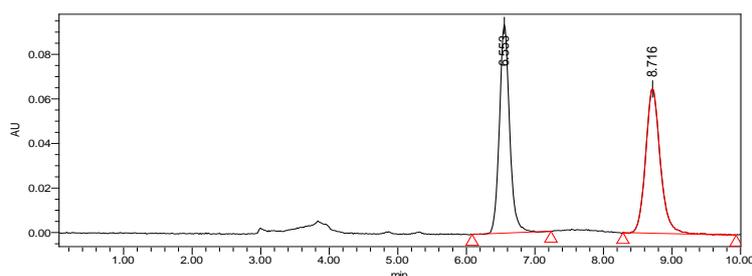


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	6.033	5194723	97.83	478192	bb	Unknown
2	8.603	115172	2.17	8186	bb	Unknown

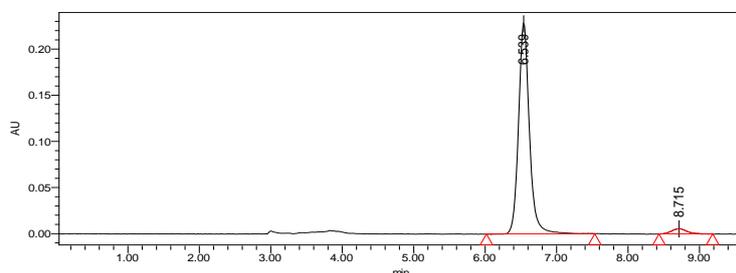
**(3*S*,3'*S*,4'*R*,5'*R*)-6-chloro-1-methyl-1'',3'',4'-triphenyl-5'-(trifluoromethyl)dispiro [indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''H)-dione (**3ai**)**



From 55.4 mg (0.20 mmol) 6-chloro-1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 71.28 mg (0.22 mmol, 1.1 equiv) 4-benzylidene-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one, 103.4 mg (86% yield) compound **3ai** was obtained as light yellow solid, mp = 123 - 124 °C.  $[\alpha]_D^{20} = +103$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis. 93% ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 8.7$  min and  $t_{\text{minor}} = 6.5$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 – 7.50 (m, 6H), 7.50 – 7.31 (m, 6H), 7.30 – 7.16 (m, 4H), 6.89 (d,  $J = 8.1$  Hz, 1H), 6.61 (s, 1H), 5.75 (d,  $J = 9.9$  Hz, 1H), 5.47 (dt,  $J = 15.6, 7.9$  Hz, 1H), 3.48 (d,  $J = 9.5$  Hz, 1H), 2.34 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.9, 170.6, 154.8, 145.1, 137.0, 136.6, 132.6, 130.8, 130.5, 129.0, 128.9, 128.8, 128.6, 128.4, 128.1, 126.4, 125.9 (q,  $J_{\text{C-F}} = 278.7$  Hz), 125.6, 122.7, 121.5, 120.0, 108.9, 72.8, 70.0, 61.4 (q,  $J_{\text{C-F}} = 30.7$  Hz), 48.0, 25.2, 0.01.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.2; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{33}\text{H}_{24}\text{ClF}_3\text{N}_4 \text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 623.1432, found 623.1436.

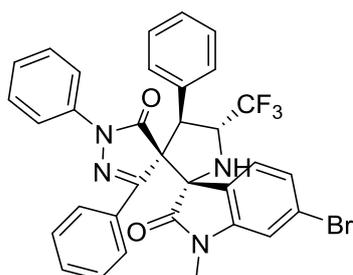


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	6.553	965608	49.87	93634	bb	Unknown
2	8.716	970508	50.13	65021	bb	Unknown

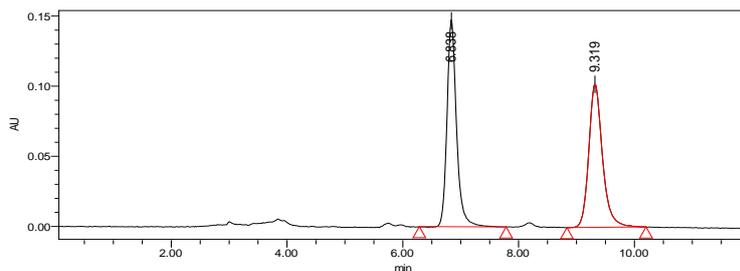


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	6.539	2418892	96.70	228693	bb	Unknown
2	8.715	82668	3.30	5560	bb	Unknown

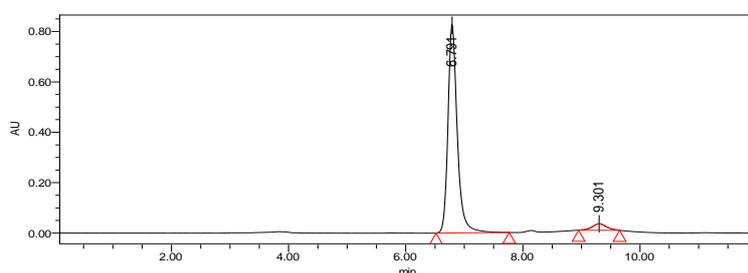
**(3*S*,3'*S*,4'*R*,5'*R*)-6-bromo-1-methyl-1'',3'',4'-triphenyl-5'-(trifluoromethyl)dispiro[indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''H)-dione (3aj)**



From 64.2 mg (0.20 mmol) 6-bromo-1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 71.28 mg (0.22 mmol, 1.1 equiv) 4-benzylidene-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one, 105.8 mg (82% yield) compound **3aj** was obtained as light yellow solid, mp = 96 - 97 °C.  $[\alpha]_D^{20} = +100$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis. 91% ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 9.3$  min and  $t_{\text{minor}} = 6.8$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (ddd,  $J = 10.5, 7.5, 4.8$  Hz, 6H), 7.49 – 7.41 (m, 3H), 7.39 – 7.16 (m, 7H), 7.04 (dd,  $J = 8.1, 1.6$  Hz, 1H), 6.75 (d,  $J = 1.5$  Hz, 1H), 5.75 (d,  $J = 10.1$  Hz, 1H), 5.57 – 5.38 (m, 1H), 3.49 (d,  $J = 9.8$  Hz, 1H), 2.34 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.7, 169.5, 153.7, 144.1, 135.5, 131.4, 129.8, 129.5, 127.9, 127.9, 127.8, 127.6, 127.4, 127.1, 125.3, 125.0 (q,  $J_{\text{C-F}} = 278.3$  Hz), 124.8, 124.6, 124.0, 121.0, 119.0, 110.6, 71.7, 69.0, 60.4 (q,  $J_{\text{C-F}} = 30.7$  Hz), 47.0, 24.1.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.1; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{33}\text{H}_{25}\text{BrF}_3\text{N}_4\text{O}_2$   $[\text{M}+\text{H}]^+$ : 645.1107, found 645.1103.

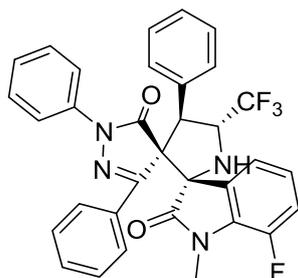


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	6.838	1689636	50.17	147392	bb	Unknown
2	9.319	1678142	49.83	102341	bb	Unknown



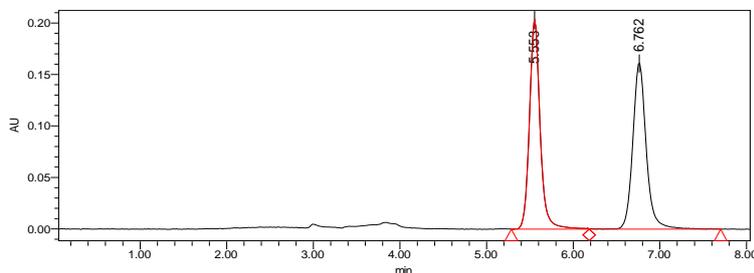
	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	6.791	9152712	95.46	829679	bb	Unknown
2	9.301	434873	4.54	25683	bb	Unknown

**(3*S*,3'*S*,4'*R*,5'*R*)-7-fluoro-1-methyl-1'',3'',4'-triphenyl-5'-(trifluoromethyl)dispiro [indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''H)-dione (**3ak**)**

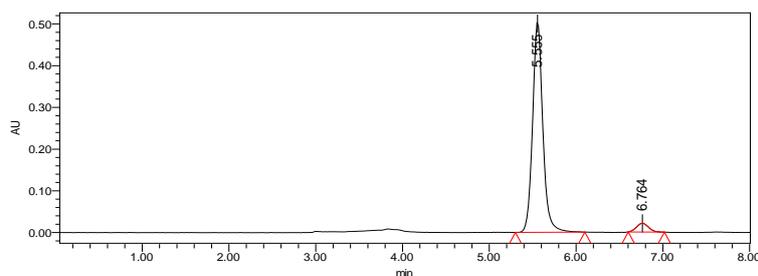


From 52 mg (0.20 mmol) 7-fluoro-1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 71.28 mg (0.22 mmol, 1.1 equiv) 4-benzylidene-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one, 97.1 mg (83% yield) compound **3ak** was obtained as light yellow solid, mp = 89 - 90 °C.  $[\alpha]_D^{20} = +119$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis. 91% ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 6.8$  min and  $t_{\text{minor}} = 5.6$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 – 7.46 (m, 10H), 7.37 – 7.28 (m, 3H), 7.21 (dt,  $J = 14.8, 4.7$  Hz, 3H), 6.74 (t,  $J = 7.9$  Hz, 1H), 5.76 (d,  $J = 10.1$  Hz, 1H), 5.62 – 5.38 (m, 1H), 3.46 (d,  $J = 9.7$  Hz, 1H), 3.22 (dd,  $J = 9.8, 3.8$  Hz, 1H), 2.72 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.7, 170.5, 154.7, 148.6, 146.1, 136.6, 132.6,

130.9, 130.6, 130.5, 129.0, 128.9, 128.8, 128.6, 128.5, 128.2, 126.3, 126.0, 126.0 (q,  $J_{C-F} = 278.7$  Hz), 126.0, 123.4 (d,  $J_{C-F} = 4.5$  Hz), 120.4, 120.4, 120.1, 119.1 (d,  $J_{C-F} = 14.3$  Hz), 73.0, 70.5, 61.6 (q,  $J_{C-F} = 30.7$  Hz). 47.9, 27.6, 27.6.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.1, 136.0; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{33}\text{H}_{24}\text{F}_4\text{N}_4\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 607.1728, found 607.1731.

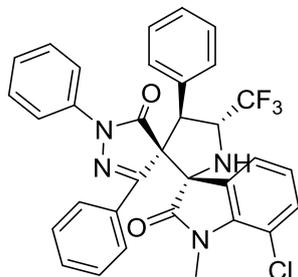


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	5.553	1745888	50.01	203561	bv	Unknown
2	6.762	1745299	49.99	161728	vb	Unknown



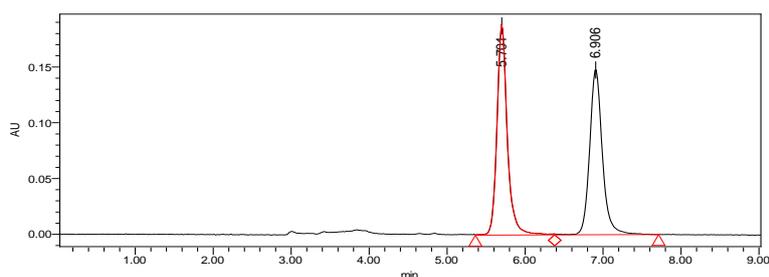
	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	5.555	4136089	95.36	503981	bb	Unknown
2	6.764	201380	4.64	21065	bb	Unknown

**(3*S*,3'*S*,4'*R*,5'*R*)-7-chloro-1-methyl-1'',3'',4'-triphenyl-5'-(trifluoromethyl)dispiro [indoline-3,2'-pyrrolidine-3',4'-pyrazole]-2,5''(1''H)-dione (3a)**

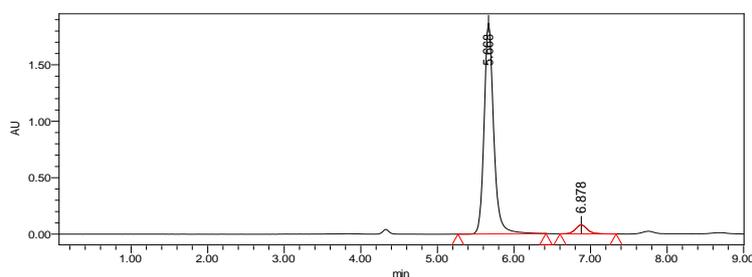


From 55.4 mg (0.20 mmol) 7-chloro-1-methyl-3-((2,2,2-trifluoroethyl) imino)indolin-2-one and 71.28 mg (0.22 mmol, 1.1 equiv) 4-benzylidene-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one, 99.8 mg (83% yield) compound **3a** was obtained as light yellow solid, mp = 105 - 106 °C.  $[\alpha]_{\text{D}}^{20} = +74$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis. 90% ee was determined by HPLC

analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 6.9$  min and  $t_{\text{minor}} = 5.7$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (dtd,  $J = 10.6, 7.5, 4.0$  Hz, 10H), 7.33 (t,  $J = 7.9$  Hz, 2H), 7.27 – 7.14 (m, 4H), 6.89 (t,  $J = 7.4$  Hz, 1H), 6.59 (d,  $J = 7.7$  Hz, 1H), 5.79 (d,  $J = 10.1$  Hz, 1H), 5.46 (dd,  $J = 15.8, 8.2$  Hz, 1H), 3.54 (d,  $J = 9.4$  Hz, 1H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.3, 170.4, 154.7, 139.6, 136.5, 133.3, 132.5, 130.8, 130.6, 128.9, 128.9, 128.8, 128.6, 128.5, 128.2, 126.3, 126.0, 126.0 (q,  $J_{\text{C-F}} = 278.3$  Hz), 123.4, 122.9, 120.1, 115.6, 73.0, 70.1, 61.5 (q,  $J_{\text{C-F}} = 30.7$  Hz), 47.9, 28.5.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.1; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{33}\text{H}_{24}\text{ClF}_3\text{N}_4\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 623.1432, found 623.1441.

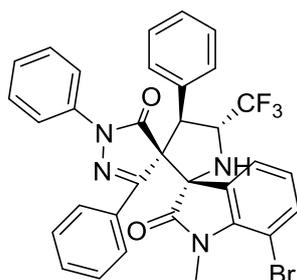


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	5.701	1742745	50.94	188590	bv	Unknown
2	6.906	1678381	49.06	148490	vb	Unknown

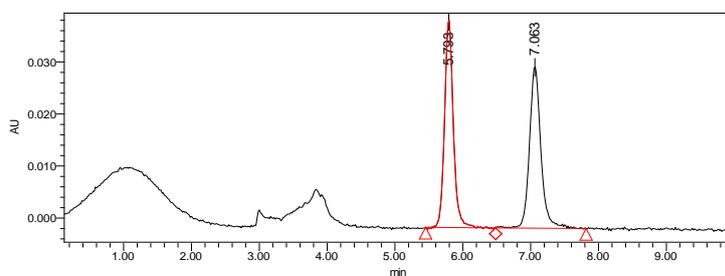


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	5.668	16214718	95.00	1867369	bb	Unknown
2	6.878	853404	5.00	79877	bb	Unknown

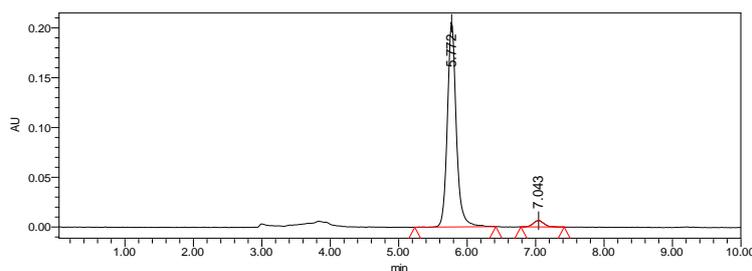
**(3*S*,3'*S*,4'*R*,5'*R*)-7-bromo-1-methyl-1'',3'',4'-triphenyl-5'-(trifluoromethyl)dispiro[indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''H)-dione (3am)**



From 64.2 mg (0.20 mmol) 7-bromo-1-methyl-3-((2,2,2-trifluoroethyl) imino)indolin-2-one and 71.28 mg (0.22 mmol, 1.1 equiv) 4-benzylidene-2,5-diphenyl-2,4-dihydro-3H-pyrazol -3-one, 109.6 mg (85% yield) compound **3am** was obtained as light yellow solid, mp = 108 - 109 °C.  $[\alpha]_D^{20} = +168$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis. 93% ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane /2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 7.0$  min and  $t_{\text{minor}} = 5.8$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (dddd,  $J = 12.9, 8.8, 5.5, 2.6$  Hz, 11H), 7.37 – 7.28 (m, 3H), 7.25 – 7.15 (m, 3H), 6.74 (t,  $J = 7.9$  Hz, 1H), 5.76 (d,  $J = 10.1$  Hz, 1H), 5.59 – 5.42 (m, 1H), 3.51 – 3.41 (m, 1H), 3.22 (dd,  $J = 9.8, 3.8$  Hz, 1H), 2.72 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.4, 170.4, 154.7, 141.1, 136.7, 136.5, 132.5, 130.9, 130.6, 129.0, 128.9, 128.9, 128.6, 128.5, 128.3, 126.4, 126.0 (q,  $J_{\text{C-F}} = 278.3$ Hz), 126.3, 123.8, 123.4, 120.1, 102.4, 73.1, 70.1, 61.5 (q,  $J_{\text{C-F}} = 30.7$  Hz), 48.0, 28.7.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.1; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{33}\text{H}_{24}\text{BrF}_3\text{N}_4\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 667.0927, found 667.0930.

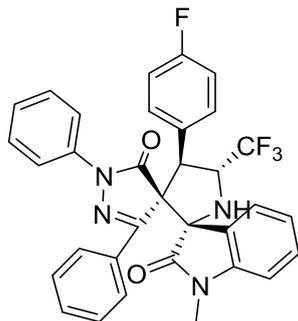


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	5.793	360379	49.69	39777	bv	Unknown
2	7.063	364833	50.31	31086	vb	Unknown

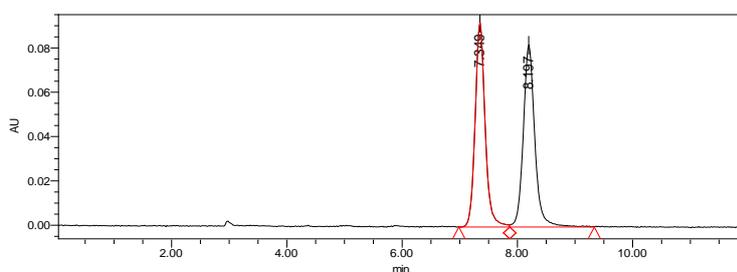


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	5.772	1866741	96.41	205914	bb	Unknown
2	7.043	69596	3.59	6442	bb	Unknown

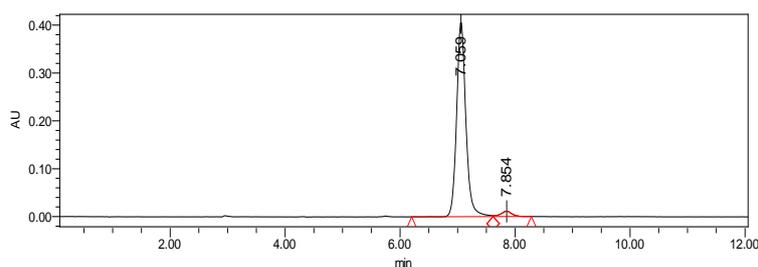
**(3*S*,3'*S*,4*R*,5'*R*)-4'-(4-fluorophenyl)-1-methyl-1'',3''-diphenyl-5'-(trifluoromethyl)dispiro[indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''*H*)-dione (3*ba*)**



From 48.2 mg (0.20 mmol) 1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-on and 75.24 mg (0.22 mmol, 1.1 equiv) 4-(4-fluorobenzylidene)-2,5-diphenyl-2,4-dihydro-3*H*-pyrazol-3-one, 99.5 mg (85% yield) compound **3ba** was obtained as light yellow solid, mp = 112 - 114 °C.  $[\alpha]_D^{20} = +146$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis. 94% ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 7.9$  min and  $t_{\text{minor}} = 7.1$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 – 7.51 (m, 6H), 7.51 – 7.38 (m, 4H), 7.32 (dd,  $J = 10.7, 5.0$  Hz, 2H), 7.20 (dt,  $J = 14.8, 4.2$  Hz, 2H), 6.91 (dt,  $J = 15.4, 8.1$  Hz, 3H), 6.58 (d,  $J = 7.7$  Hz, 1H), 5.81 (d,  $J = 10.0$  Hz, 1H), 5.47 (d,  $J = 7.1$  Hz, 1H), 3.55 (d,  $J = 8.7$  Hz, 1H), 2.34 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  173.9, 170.6, 164.2, 160.9, 154.8, 143.8, 136.6, 131.2, 130.9, 130.5, 130.4, 130.3, 128.9, 128.7, 128.1, 126.4, 126.1 (q,  $J_{\text{C-F}} = 278.3$  Hz), 124.4, 122.9 (d,  $J_{\text{C-F}} = 6$  Hz), 120.0, 116.0 (d,  $J_{\text{C-F}} = 21.8$  Hz), 108.2, 72.9, 70.5, 62.3 (q,  $J_{\text{C-F}} = 30.8$  Hz), 47.2, 25.0.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.0, 113.1; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{33}\text{H}_{24}\text{F}_4\text{N}_4\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 607.1728, found 607.1730.

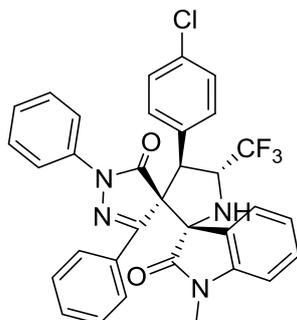


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	7.349	1114070	49.41	92109	bv	Unknown
2	8.197	1140827	50.59	82001	vb	Unknown

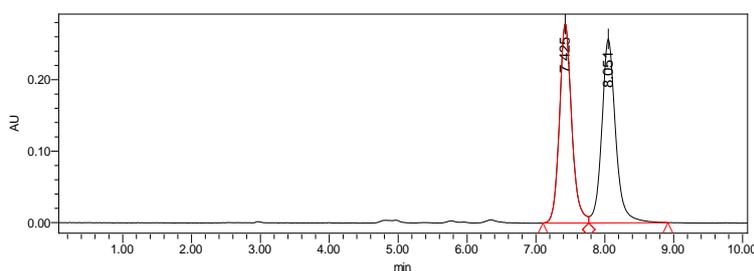


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	7.059	4548931	96.81	406860	bv	Unknown
2	7.854	149719	3.19	11097	vb	Unknown

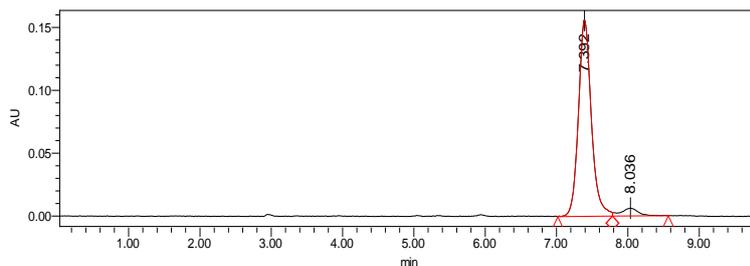
**(3*S*,3'*S*,4'*R*,5'*R*)-4'-(4-chlorophenyl)-1-methyl-1'',3''-diphenyl-5'-(trifluoromethyl)dispiro[indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''*H*)-dione (3ca)**



From 48.2 mg (0.20 mmol) 1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 78.98 mg (0.22 mmol, 1.1 equiv) 4-(4-chlorobenzylidene)-2,5-diphenyl-2,4-dihydro-3*H*-pyrazol-3-one, 101.0 mg (84% yield) compound **3ca** was obtained as light yellow solid, mp = 216 - 217 °C.  $[\alpha]_D^{20} = +169$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis. 90% ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 8.0$  min and  $t_{\text{minor}} = 7.4$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (dtd,  $J = 10.6, 7.5, 4.0$  Hz, 10H), 7.33 (t,  $J = 7.9$  Hz, 2H), 7.27 - 7.14 (m, 4H), 6.89 (t,  $J = 7.4$  Hz, 1H), 6.59 (d,  $J = 7.7$  Hz, 1H), 5.79 (d,  $J = 10.1$  Hz, 1H), 5.46 (dd,  $J = 15.8, 8.2$  Hz, 1H), 3.54 (d,  $J = 9.4$  Hz, 1H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  173.8, 170.5, 154.6, 143.7, 136.5, 134.4, 131.5, 131.1, 130.8, 130.5, 129.9, 129.1, 128.9, 128.6, 128.1, 126.3, 125.9 (q,  $J_{\text{C-F}} = 278.5$  Hz), 124.3, 122.9, 122.7, 120.0, 108.2, 72.7, 70.5, 61.7 (q,  $J_{\text{C-F}} = 30.8$  Hz), 47.2, 25.0.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.0; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{33}\text{H}_{25}\text{ClF}_3\text{N}_4\text{O}_2$   $[\text{M}+\text{H}]^+$ : 601.1613, found 601.1609.

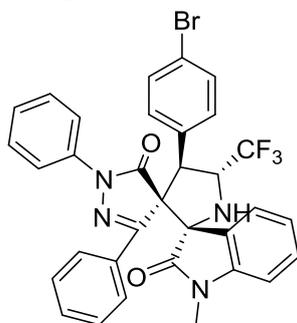


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	7.425	3449087	48.96	279994	bv	Unknown
2	8.051	3595732	51.04	257463	vb	Unknown

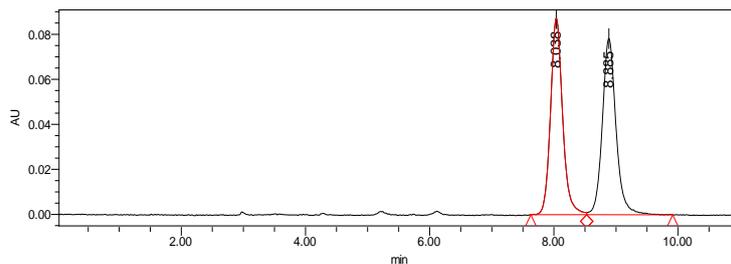


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	7.392	1961816	94.92	156590	bv	Unknown
2	8.036	105007	5.08	6186	vb	Unknown

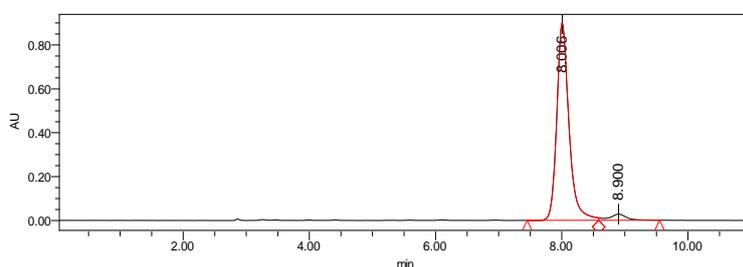
**(3*S*,3'*S*,4'*R*,5'*R*)-4'-(4-bromophenyl)-1-methyl-1'',3''-diphenyl-5'-(trifluoromethyl)dispiro[indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''*H*)-dione (3da)**



From 48.2 mg (0.20 mmol) 1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 88.66 mg (0.22 mmol, 1.1 equiv) 4-(4-bromobenzylidene)-2,5-diphenyl-2,4-dihydro-3*H*-pyrazol-3-one, 110.9 mg (86% yield) compound **3da** was obtained as light yellow solid, mp = 118 - 119 °C.  $[\alpha]_D^{20} = +130$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis. 92% ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 8.9$  min and  $t_{\text{minor}} = 8.0$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 – 7.51 (m, 4H), 7.51 – 7.29 (m, 10H), 7.28 – 7.13 (m, 2H), 6.89 (t,  $J = 7.6$  Hz, 1H), 6.60 (d,  $J = 7.8$  Hz, 1H), 5.77 (d,  $J = 10.1$  Hz, 1H), 5.45 (d,  $J = 7.5$  Hz, 1H), 3.53 (d,  $J = 8.6$  Hz, 1H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  173.8, 170.5, 154.7, 143.8, 136.5, 132.2, 132.1, 131.2, 130.8, 130.5, 130.3, 129.0, 128.7, 128.1, 126.4, 126.0 (q,  $J_{\text{C-F}} = 278.5$  Hz), 124.3, 123.0, 122.7, 122.7, 120.0, 108.2, 72.7, 70.6, 61.7 (q,  $J_{\text{C-F}} = 30.8$  Hz), 47.3, 25.0.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.0; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{33}\text{H}_{24}\text{BrF}_3\text{N}_4\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 667.0927, found 667.0926.

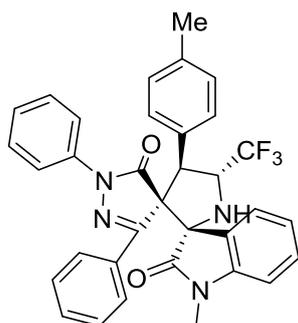


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	8.038	1176929	49.51	87442	bv	Unknown
2	8.885	1200443	50.49	78455	vb	Unknown



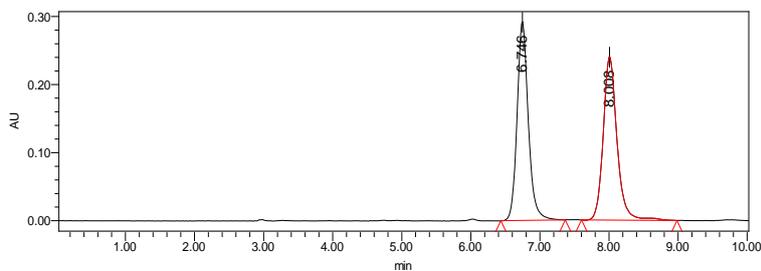
	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	8.006	12086575	95.75	900003	bv	Unknown
2	8.900	536523	4.25	28232	vb	Unknown

**(3*S*,3'*S*,4'*R*,5'*R*)-1-methyl-1'',3''-diphenyl-4'-(*p*-tolyl)-5'-(trifluoromethyl)dispiro [indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''H)-dione (**3ea**)**

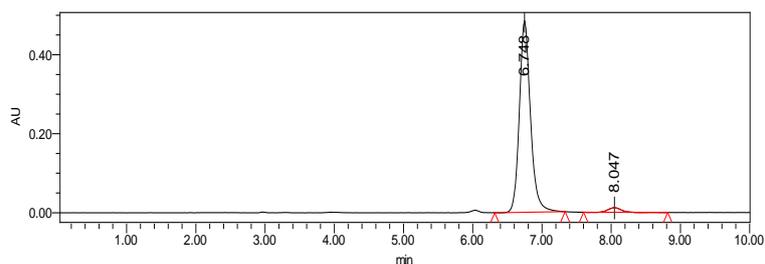


From 48.2 mg (0.20 mmol) 1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 74.36 mg (0.22 mmol, 1.1 equiv) 4-(4-methylbenzylidene)-2,5-diphenyl-2,4-dihydro-3*H*-pyrazol-3-one, 98.8 mg (85% yield) compound **3ea** was obtained as light yellow solid, mp = 126 - 127 °C.  $[\alpha]_D^{20} = +128$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis. 90% ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 8.0$  min and  $t_{\text{minor}} = 6.7$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (d,  $J = 7.6$  Hz, 4H), 7.49 (d,  $J = 8.2$  Hz, 3H), 7.45 – 7.39 (m, 3H), 7.30 (t,  $J = 7.8$  Hz, 2H), 7.25 – 7.12 (m, 2H), 7.04 (d,  $J = 8.0$  Hz, 2H), 6.86 (t,  $J = 7.6$  Hz, 1H), 6.57 (d,  $J = 7.8$  Hz, 1H), 5.79 (d,  $J = 10.1$

Hz, 1H), 5.48 (dd,  $J = 15.8, 8.1$  Hz, 1H), 3.54 (d,  $J = 9.2$  Hz, 1H), 2.33 (s, 3H), 2.19 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  174.0, 170.8, 155.1, 143.8, 138.3, 136.8, 131.1, 130.4, 129.8, 129.7, 128.9, 128.8, 128.4, 128.1, 128.1 (q,  $J_{\text{C-F}} = 185.7$  Hz), 126.2, 124.4, 123.0, 122.9, 120.1, 108.2, 73.0, 70.6, 61.8 (q,  $J_{\text{C-F}} = 30.2$  Hz), 47.7, 25.0, 21.0.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.0; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{34}\text{H}_{27}\text{F}_3\text{N}_4\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 603.1978, found 603.1972.

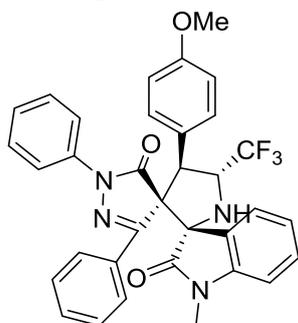


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	6.746	3290938	49.65	292239	bb	Unknown
2	8.008	3337091	50.35	240280	bb	Unknown



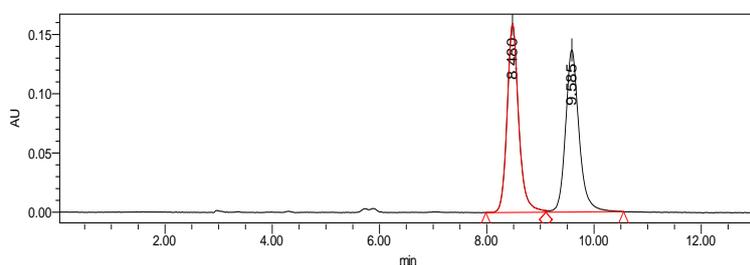
	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	6.748	5409362	97.14	484222	bb	Unknown
2	8.047	159137	2.86	11698	bb	Unknown

**(3S,3'S,4'R,5'R)-4'-(4-methoxyphenyl)-1-methyl-1'',3''-diphenyl-5'-(trifluoromethyl)dispiro[indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''H)-dione (3fa)**

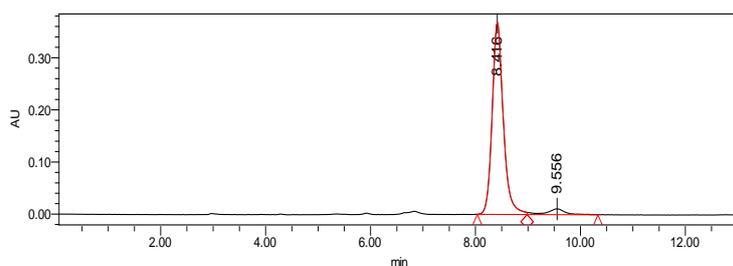


From 48.2 mg (0.20 mmol) 1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 77.88 mg (0.22 mmol, 1.1 equiv) 4-(4-methoxybenzylidene)-2,5-diphenyl-

2,4-dihydro-3H-pyrazol-3-one, 100.1 mg (84% yield) compound **3fa** was obtained as light yellow solid, mp = 109 - 110 °C.  $[\alpha]_D^{20} = +145$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis. 90% ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 9.6$  min and  $t_{\text{minor}} = 8.4$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 – 7.47 (m, 8H), 7.47 – 7.38 (m, 3H), 7.33 (dd,  $J = 10.7, 5.0$  Hz, 2H), 7.21 (dt,  $J = 14.9, 6.2$  Hz, 2H), 6.89 (t,  $J = 7.6$  Hz, 1H), 6.78 (d,  $J = 8.8$  Hz, 2H), 6.59 (d,  $J = 7.7$  Hz, 1H), 5.78 (dd,  $J = 9.7, 6.8$  Hz, 1H), 5.56 – 5.34 (m, 1H), 3.66 (d,  $J = 9.0$  Hz, 3H), 3.52 (d,  $J = 9.1$  Hz, 1H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  173.9, 170.7, 159.4, 150.0, 143.7, 136.6, 131.0, 131.0, 130.3, 129.6, 128.8, 128.7, 128.0, 126.2, 126.1 (q,  $J_{\text{C-F}} = 278.5$  Hz), 124.6, 124.3, 123.0, 122.8, 120.0, 114.2, 108.1, 72.9, 70.4, 61.7 (q,  $J_{\text{C-F}} = 30.2$  Hz), 55.1, 47.3, 25.0.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.0; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{34}\text{H}_{27}\text{F}_3\text{N}_4\text{NaO}_3$   $[\text{M}+\text{Na}]^+$ : 619.1927, found 619.1928.

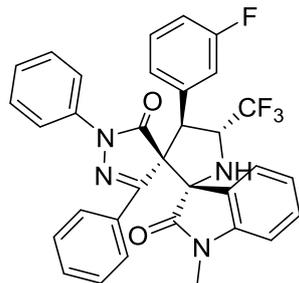


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	8.480	2388154	49.93	159377	bv	Unknown
2	9.585	2395011	50.07	137025	vb	Unknown

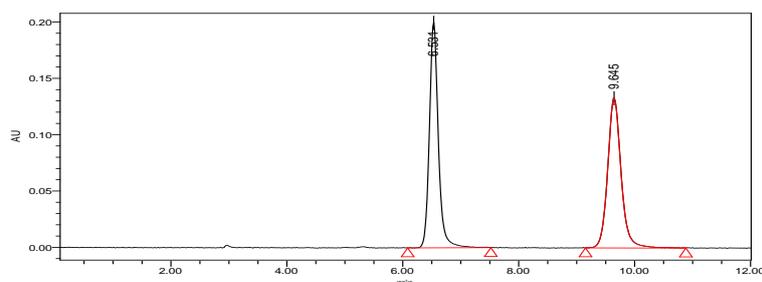


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	8.416	5420030	95.13	368805	bv	Unknown
2	9.556	277687	4.87	11045	vb	Unknown

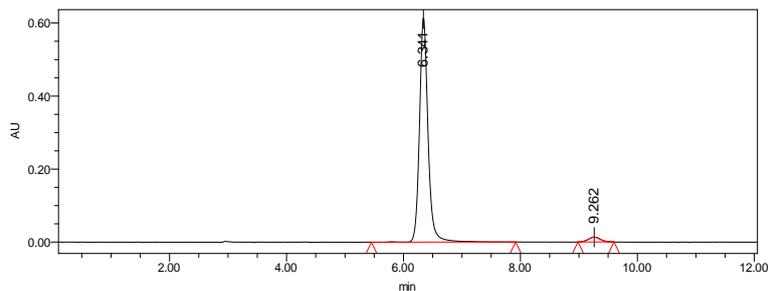
**(3*S*,3'*S*,4'*R*,5'*R*)-4'-(3-fluorophenyl)-1-methyl-1'',3''-diphenyl-5'-(trifluoromethyl) dispiro[indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''H)-dione (3ga)**



From 48.2 mg (0.20 mmol) 1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 75.24 mg (0.22 mmol, 1.1 equiv) 4-(3-fluorobenzylidene)-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one, 99.5 mg (85% yield) compound **3ga** was obtained as light yellow solid, mp = 108 - 109 °C.  $[\alpha]_D^{20} = +158$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis. 94% ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 9.3$  min and  $t_{\text{minor}} = 6.3$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 – 7.51 (m, 4H), 7.51 – 7.42 (m, 4H), 7.41 – 7.29 (m, 4H), 7.29 – 7.15 (m, 3H), 7.02 – 6.81 (m, 2H), 6.60 (d,  $J = 7.7$  Hz, 1H), 5.81 (dd,  $J = 10.0, 5.8$  Hz, 1H), 5.47 (s, 1H), 3.64 – 3.44 (m, 1H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  173.8, 170.5, 164.4, 161.1, 154.7, 143.8, 136.5, 135.6, 135.5, 131.2, 130.8, 130.6, 130.5, 130.5, 128.9, 128.7, 128.2, 126.4, 126.0 (q,  $J_{\text{C-F}} = 278.5$  Hz), 124.5, 124.5, 124.4, 122.8 (d,  $J_{\text{C-F}} = 18$  Hz), 120.1, 115.8, 115.6 (d,  $J_{\text{C-F}} = 19.5$  Hz), 108.2, 72.7, 70.6, 61.8 (q,  $J_{\text{C-F}} = 30.8$  Hz), 47.5, 25.0.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.0, 111.4; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{33}\text{H}_{24}\text{F}_4\text{N}_4\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 607.1728, found 607.1729.

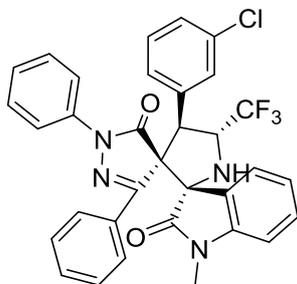


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	6.531	2148364	50.06	200245	bb	Unknown
2	9.645	2143620	49.94	133292	bb	Unknown

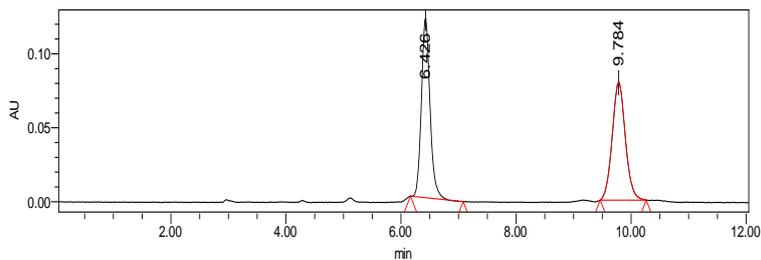


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	6.341	6225979	97.07	615824	bb	Unknown
2	9.262	187983	2.93	13292	bb	Unknown

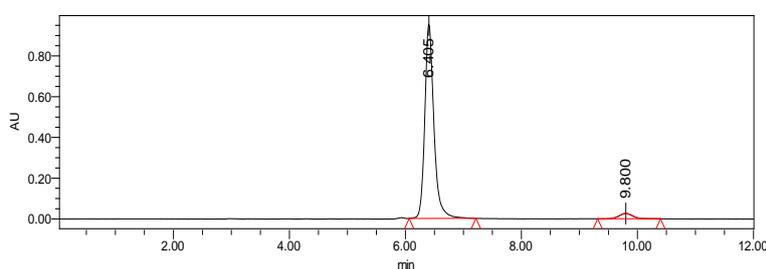
**(3*S*,3'*S*,4'*R*,5'*R*)-4'-(3-chlorophenyl)-1-methyl-1'',3''-diphenyl-5'-(trifluoromethyl)dispiro[indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''*H*)-dione (**3ha**)**



From 48.2 mg (0.20 mmol) 1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 78.98 mg (0.22 mmol, 1.1 equiv) 4-(3-chlorobenzylidene)-2,5-diphenyl-2,4-dihydro-3*H*-pyrazol-3-one, 101.0 mg (84% yield) compound **3ha** was obtained as light yellow solid, mp = 145 - 146 °C.  $[\alpha]_D^{20} = +108$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis. 92% ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 9.8$  min and  $t_{\text{minor}} = 6.4$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (s, 1H), 7.58 – 7.42 (m, 9H), 7.33 (t,  $J = 7.9$  Hz, 2H), 7.21 (pd,  $J = 7.9, 2.9$  Hz, 4H), 6.89 (dd,  $J = 11.2, 4.1$  Hz, 1H), 6.59 (d,  $J = 7.8$  Hz, 1H), 5.78 (d,  $J = 10.0$  Hz, 1H), 5.57 – 5.27 (m, 1H), 3.54 (d,  $J = 9.8$  Hz, 1H), 2.34 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  173.7, 170.4, 154.7, 143.7, 136.4, 135.1, 134.7, 131.1, 130.7, 130.5, 130.2, 128.9, 128.8, 128.6, 128.1, 126.9, 126.4, 125.9 (q,  $J_{\text{C-F}} = 278.7$  Hz), 124.4, 122.9, 122.7, 120.1, 108.2, 72.6, 70.5, 61.7 (q,  $J_{\text{C-F}} = 30.8$  Hz), 47.4, 25.0.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.0; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{33}\text{H}_{25}\text{ClF}_3\text{N}_4\text{NaO}_2$   $[\text{M}+\text{H}]^+$ : 601.1613, found 601.1604.

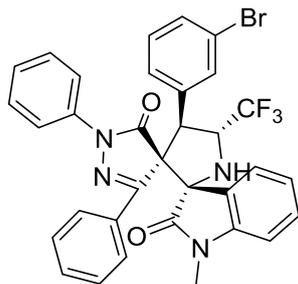


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	6.426	1267343	50.02	121611	bb	Unknown
2	9.784	1266150	49.98	79745	bb	Unknown



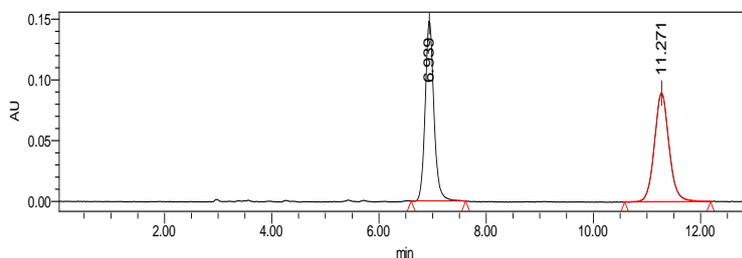
	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	6.405	10387998	96.03	955836	bb	Unknown
2	9.800	429778	3.97	26697	bb	Unknown

**(3*S*,3'*S*,4'*R*,5'*R*)-4'-(3-bromophenyl)-1-methyl-1'',3''-diphenyl-5'-(trifluoromethyl)dispiro[indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''H)-dione (3ia)**

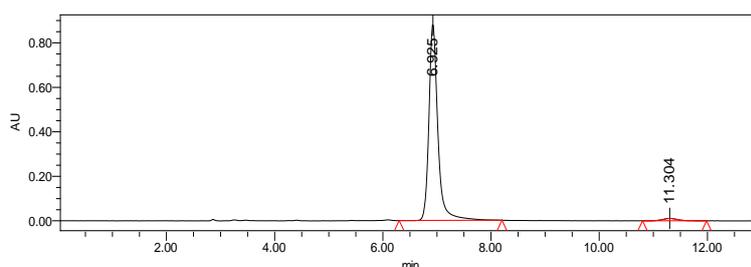


From 48.2 mg (0.20 mmol) 1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 88.66 mg (0.22 mmol, 1.1 equiv) 4-(3-bromobenzylidene)-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one, 117.3 mg (91% yield) compound **3ia** was obtained as light yellow solid, mp = 89 - 90 °C.  $[\alpha]_D^{20} = +6$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis. 96% ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 11.3$  min and  $t_{\text{minor}} = 6.9$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (s, 1H), 7.59 – 7.11 (m, 16H), 6.92 (t,  $J = 7.6$  Hz, 1H), 6.62 (d,  $J = 7.7$  Hz, 1H), 5.75 (d,  $J = 10.1$  Hz, 1H), 5.52 – 5.34 (m, 1H), 3.52 (d,  $J = 9.9$  Hz, 1H), 2.36 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$

173.8, 170.5, 154.7, 143.8, 136.5, 135.4, 131.8, 131.2, 130.8, 130.5, 128.9, 128.7, 128.2, 127.4, 126.5, 126.0 (q,  $J_{C-F} = 278.2$  Hz), 124.4, 123.0, 123.0, 122.7, 120.3, 108.2, 72.7, 70.5, 61.8 (q,  $J_{C-F} = 30.8$  Hz), 47.5, 25.0.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.0; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{33}\text{H}_{24}\text{BrF}_3\text{N}_4\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 667.0927, found 667.0927.

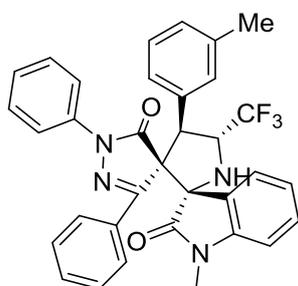


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	6.939	1669815	49.58	148097	bb	Unknown
2	11.271	1697910	50.42	89546	bb	Unknown



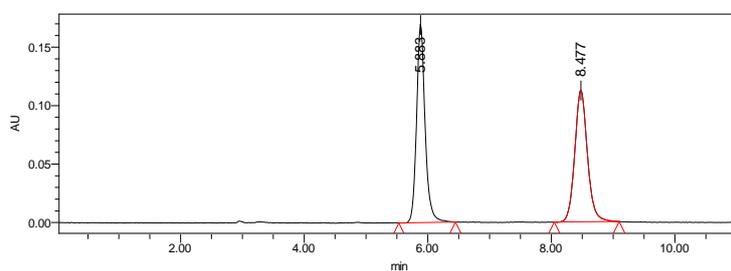
	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	6.925	10178994	98.00	884075	bb	Unknown
2	11.304	208157	2.00	10943	bb	Unknown

**(3*S*,3'*S*,4'*R*,5'*R*)-1-methyl-1'',3''-diphenyl-4'-(*m*-tolyl)-5'-(trifluoromethyl)dispiro [indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''*H*)-dione (3ja)**

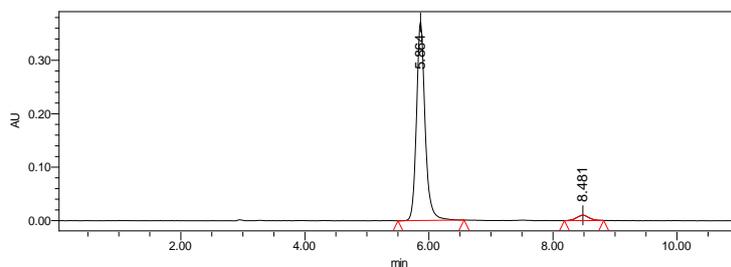


From 48.2 mg (0.20 mmol) 1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 74.36 mg (0.22 mmol, 1.1 equiv) 4-(3-methylbenzylidene)-2,5-diphenyl-2,4-dihydro-3*H*-pyrazol-3-one, 100.0 mg (86% yield) compound **3ja** was obtained as light

yellow solid, mp = 195 - 196 °C.  $[\alpha]_D^{20} = +178$  (c = 1.0, CHCl<sub>3</sub>). Dr (>20:1) determined by <sup>1</sup>H and <sup>19</sup>F NMR analysis. 93% ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 8.5$  min and  $t_{\text{minor}} = 5.9$  min. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.54 (dt,  $J = 8.7, 2.8$  Hz, 4H), 7.45 (dd,  $J = 7.9, 6.5$  Hz, 3H), 7.35 (dd,  $J = 16.3, 8.6$  Hz, 4H), 7.20 (ddd,  $J = 21.9, 15.2, 8.7$  Hz, 4H), 7.03 (d,  $J = 7.4$  Hz, 1H), 6.92 (t,  $J = 7.6$  Hz, 1H), 6.60 (d,  $J = 7.7$  Hz, 1H), 5.75 (d,  $J = 10.1$  Hz, 1H), 5.58 – 5.39 (m, 1H), 3.52 (d,  $J = 9.8$  Hz, 1H), 2.35 (s, 3H), 2.24 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 173.9, 170.7, 155.0, 143.7, 138.4, 136.6, 132.7, 131.0, 131.0, 130.3, 129.3, 129.1, 128.8, 128.7, 128.0, 126.2, 126.1 (q,  $J_{\text{C-F}} = 278.5$  Hz), 125.6, 124.4, 123.0, 122.8, 120.1, 108.1, 77.1 (q,  $J_{\text{C-F}} = 31.9$  Hz), 72.8, 70.3, 47.9, 24.9, 21.4. <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ -71.9; HRMS (ESI) m/z calcd for C<sub>34</sub>H<sub>27</sub>F<sub>3</sub>N<sub>4</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup>: 603.1978, found 603.1985.

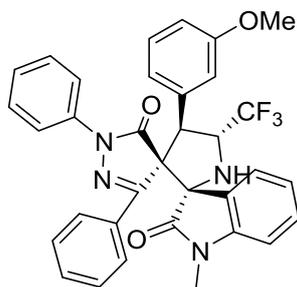


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	5.883	1631257	50.48	169642	bb	Unknown
2	8.477	1599940	49.52	112768	bb	Unknown

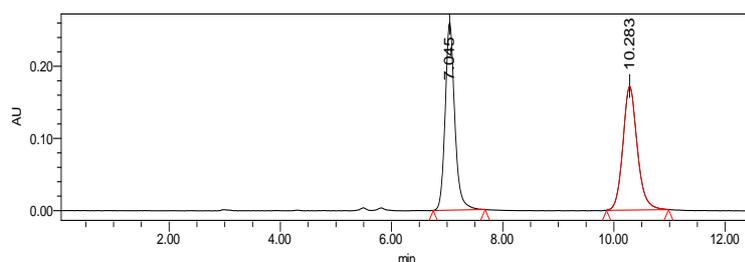


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	5.864	3576047	96.26	372003	bb	Unknown
2	8.481	138860	3.74	9955	bb	Unknown

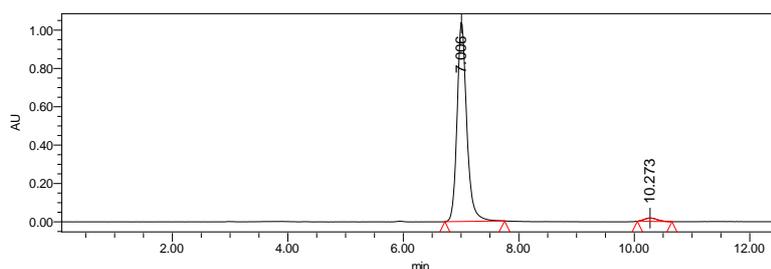
**(3*S*,3'*S*,4'*R*,5'*R*)-4'-(3-methoxyphenyl)-1-methyl-1'',3''-diphenyl-5'-(trifluoromethyl)dispiro[indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''*H*)-dione (3*ka*)**



From 48.2 mg (0.20 mmol) 1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 77.88 mg (0.22 mmol, 1.1 equiv) 4-(3-methoxybenzylidene)-2,5-diphenyl-2,4-dihydro-3*H*-pyrazol-3-one, 101.5 mg (85% yield) compound **3ka** was obtained as light yellow solid, mp = 138 - 139 °C.  $[\alpha]_D^{20} = +155$  ( $c = 1.0$ , CHCl<sub>3</sub>). Dr (>20:1) determined by <sup>1</sup>H and <sup>19</sup>F NMR analysis. 96% ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 10.3$  min and  $t_{\text{minor}} = 7.0$  min. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.52 (dt,  $J = 25.3$ , 6.7 Hz, 5H), 7.46 – 7.37 (m, 3H), 7.21 (ddt,  $J = 14.7$ , 7.8, 5.5 Hz, 7H), 6.87 (t,  $J = 7.6$  Hz, 1H), 6.80 – 6.66 (m, 1H), 6.57 (d,  $J = 7.8$  Hz, 1H), 5.79 (d,  $J = 10.1$  Hz, 1H), 5.47 (dd,  $J = 16.5$ , 8.9 Hz, 1H), 3.60 (s, 4H), 2.33 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 173.8, 170.7, 159.7, 154.9, 143.7, 136.6, 134.3, 131.0, 130.9, 130.3, 129.9, 128.8, 128.7, 128.0, 126.2, 126.0 61.8 (q,  $J_{\text{C-F}} = 278.5$  Hz), 124.3, 122.9, 120.9, 119.9, 114.1, 114.0, 108.1, 72.7, 70.4, 61.7 (q,  $J_{\text{C-F}} = 278.5$  Hz), 55.0, 47.9, 25.0. <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ -72.0; HRMS (ESI)  $m/z$  calcd for C<sub>34</sub>H<sub>27</sub>F<sub>3</sub>N<sub>4</sub>NaO<sub>3</sub> [M+Na]<sup>+</sup>: 619.1927, found 619.1927.

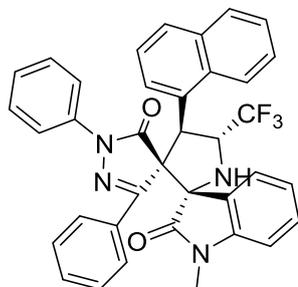


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	7.045	3097367	50.14	260497	bb	Unknown
2	10.283	3080343	49.86	171991	bb	Unknown

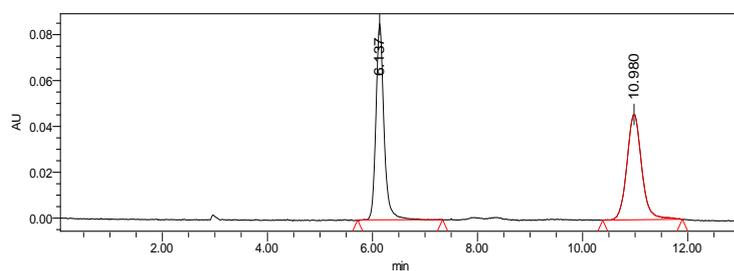


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	7.006	12034419	97.76	1040309	bb	Unknown
2	10.273	276089	2.24	17754	bb	Unknown

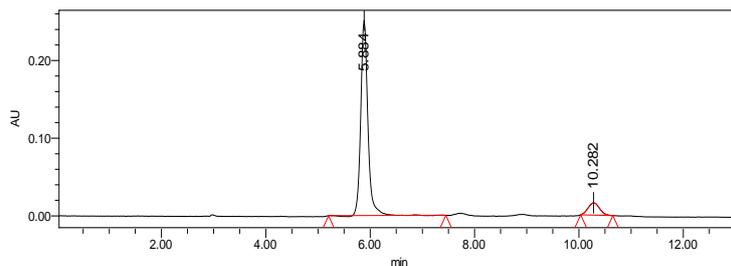
**(3*S*,3'*S*,4'*R*,5'*R*)-1-methyl-4'-(naphthalen-1-yl)-1'',3''-diphenyl-5'-(trifluoromethyl)dispiro[indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''H)-dione (3*la*)**



From 48.2 mg (0.20 mmol) 1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 82.28 mg (0.22 mmol, 1.1 equiv) 4-(naphthalen-1-ylmethylene)-2,5 -diphenyl- 2,4-dihydro-3*H*-pyrazol-3-one, 97.5 mg (79% yield) compound **3*la*** was obtained as light yellow solid, mp = 208 - 209 °C.  $[\alpha]_D^{20} = -141$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis. 82% ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 10.3$  min and  $t_{\text{minor}} = 5.9$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.66 (d,  $J = 8.7$  Hz, 1H), 8.05 (d,  $J = 7.4$  Hz, 1H), 7.85 (d,  $J = 7.9$  Hz, 1H), 7.75 (t,  $J = 9.0$  Hz, 4H), 7.64 (d,  $J = 7.6$  Hz, 1H), 7.58 – 7.50 (m, 1H), 7.42 (t,  $J = 7.9$  Hz, 2H), 7.27 (ddd,  $J = 22.4$ , 15.3, 7.7 Hz, 7H), 7.09 (d,  $J = 7.3$  Hz, 2H), 7.04 – 6.90 (m, 2H), 6.67 (d,  $J = 7.7$  Hz, 1H), 5.42 (d,  $J = 7.7$  Hz, 1H), 3.69 (d,  $J = 8.3$  Hz, 1H), 2.51 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  174.0, 171.7, 156.3, 143.9, 136.9, 134.4, 132.5, 131.2, 130.6, 130.1, 129.8, 129.3, 129.3, 129.0, 128.5, 127.8, 126.9, 126.4, 126.0, 126.0 (q,  $J_{\text{C-F}} = 278.2$  Hz), 125.4, 124.9, 124.6, 123.3, 123.0, 122.8, 120.1, 108.2, 72.4, 70.1, 63.4 (q,  $J_{\text{C-F}} = 31.0$ ), 40.6, 25.4.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.1; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{37}\text{H}_{27}\text{F}_3\text{N}_4\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 639.1978, found 639.1976.

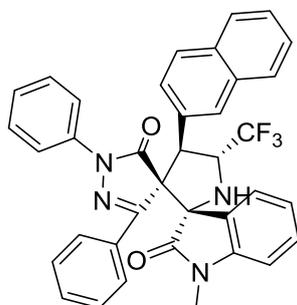


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	6.137	914186	50.38	85477	bb	Unknown
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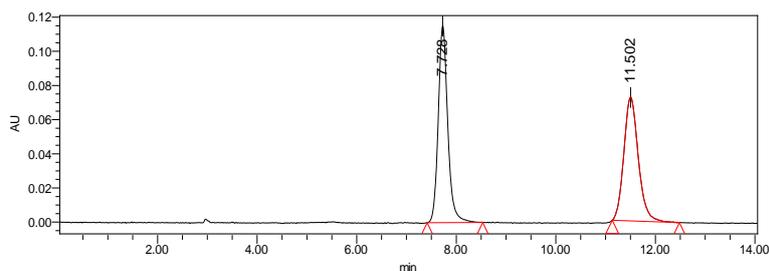


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	5.884	2394240	90.83	250753	bb	Unknown
2	10.282	241620	9.17	15859	bb	Unknown

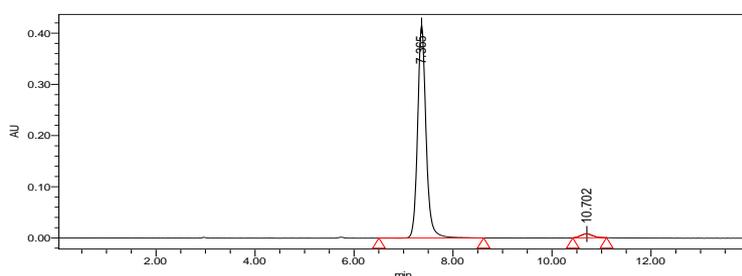
**(3*S*,3'*S*,4'*R*,5'*R*)-1-methyl-4'-(naphthalen-2-yl)-1'',3''-diphenyl-5'-(trifluoromethyl)dispiro[indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''*H*)-dione (3*ma*)**



From 48.2 mg (0.20 mmol) 1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 82.28 mg (0.22 mmol, 1.1 equiv) 4-(naphthalen-2-ylmethylene)-2,5-diphenyl-2,4-dihydro-3*H*-pyrazol-3-one, 107.4 mg (87% yield) compound **3ma** was obtained as light yellow solid, mp = 138 - 139°C.  $[\alpha]_D^{20} = +132$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis. 95% ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 10.7$  min and  $t_{\text{minor}} = 7.4$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (s, 1H), 7.69 – 7.58 (m, 4H), 7.51 (dd,  $J = 6.7, 3.0$  Hz, 2H), 7.43 (dd,  $J = 7.6, 1.1$  Hz, 3H), 7.35 (dd,  $J = 7.1, 3.0$  Hz, 3H), 7.33 – 7.25 (m, 2H), 7.21 – 7.11 (m, 3H), 7.04 (t,  $J = 7.4$  Hz, 1H), 6.88 – 6.68 (m, 1H), 6.49 (d,  $J = 7.7$  Hz, 1H), 5.90 (d,  $J = 10.1$  Hz, 1H), 5.53 (td,  $J = 9.8, 4.9$  Hz, 1H), 3.51 (d,  $J = 9.8$  Hz, 1H), 2.27 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  174.0, 171.7, 156.3, 143.9, 136.9, 134.4, 132.5, 131.2, 130.6, 130.1, 129.8, 129.3, 129.3, 129.0, 128.5, 127.8, 126.9, 126.4, 126.0, 126.0 (q,  $J_{\text{C-F}} = 278.3$  Hz), 125.4, 124.9, 124.6, 123.3, 123.0, 122.8, 120.1, 108.2, 72.4, 70.1, 63.4 (q,  $J_{\text{C-F}} = 30.2$  Hz), 40.6, 25.4.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -71.8; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{37}\text{H}_{27}\text{F}_3\text{N}_4\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 639.1978, found 639.1976.

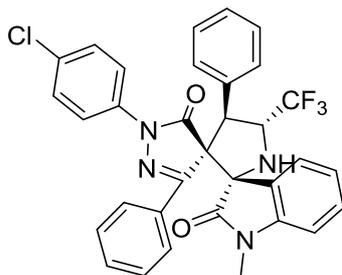


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	7.728	1534705	51.21	115487	bb	Unknown
2	11.502	1462219	48.79	72431	bb	Unknown



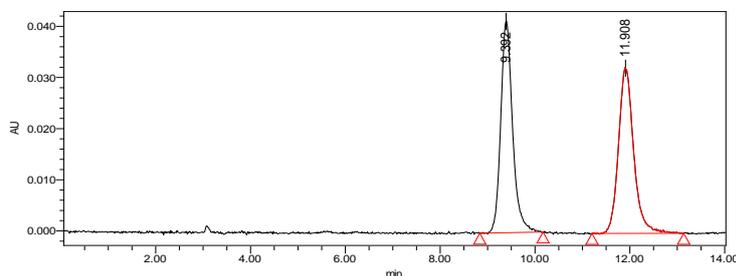
	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	7.365	4916437	97.43	415790	bb	Unknown
2	10.702	129844	2.57	7771	bb	Unknown

**(3*S*,3'*S*,4*R*,5'*R*)-1''-(4-chlorophenyl)-1-methyl-3'',4'-diphenyl-5'-(trifluoromethyl)dispiro[indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''H)-dione (3na)**

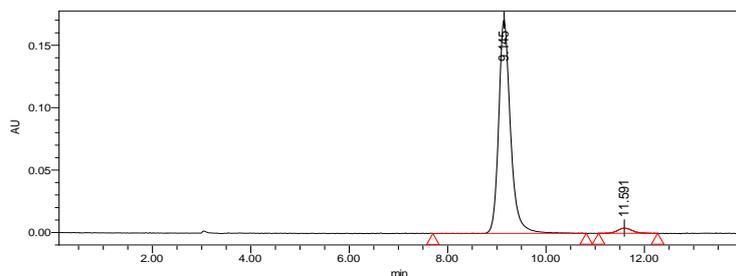


From 48.2 mg (0.20 mmol) 1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 78.98 mg (0.22 mmol, 1.1 equiv) 4-benzylidene-2-(4-chlorophenyl)-5-phenyl-2,4-dihydro-3H-pyrazol-3-one, 105.8 mg (88% yield) compound **3na** was obtained as light yellow solid, mp = 196 - 197 °C.  $[\alpha]_D^{20} = +174$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis. 94% ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 11.6$  min and  $t_{\text{minor}} = 9.1$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 – 7.43 (m, 10H), 7.30 – 7.22 (m, 6H), 6.90 (td,  $J = 7.7, 0.7$  Hz, 1H), 6.61 (d,  $J = 7.7$  Hz, 1H), 5.80 (d,  $J = 10.1$  Hz, 1H), 5.49 (dd,  $J = 15.3, 7.7$  Hz, 1H), 3.52 (d,  $J = 8.5$  Hz, 1H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.8, 170.6, 155.3, 143.8, 135.2, 132.7,

131.4, 131.1, 130.8, 130.5, 130.2, 129.0, 128.8, 128.6, 128.4, 128.1, 126.0 (q,  $J_{C-F} = 278.3$  Hz), 124.3, 122.9, 122.9, 120.9, 108.2, 73.0, 70.5, 61.6 (q,  $J_{C-F} = 30.7$  Hz), 48.0, 25.0.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.1; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{33}\text{H}_{24}\text{ClF}_3\text{N}_4\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 623.1432, found 623.1436.

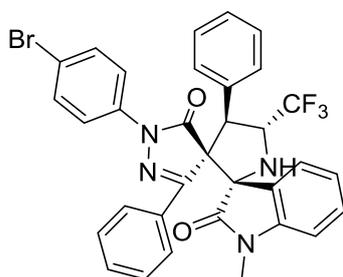


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	9.392	719199	49.86	41375	bb	Unknown
2	11.908	723304	50.14	32352	bb	Unknown



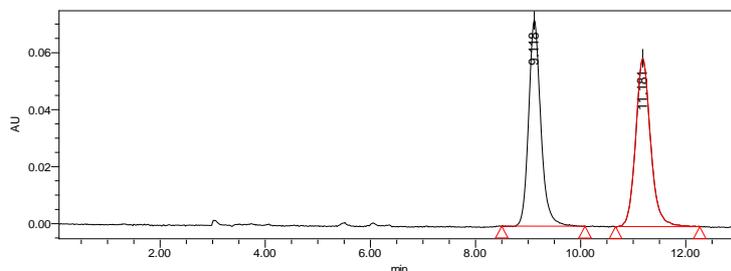
	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	9.145	2850817	97.04	171192	bb	Unknown
2	11.591	87030	2.96	4208	bb	Unknown

**(3*S*,3'*S*,4'*R*,5'*R*)-1'--(4-bromophenyl)-1-methyl-3'',4'-diphenyl-5'-(trifluoromethyl)dispiro[indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''*H*)-dione (3*o*a)**

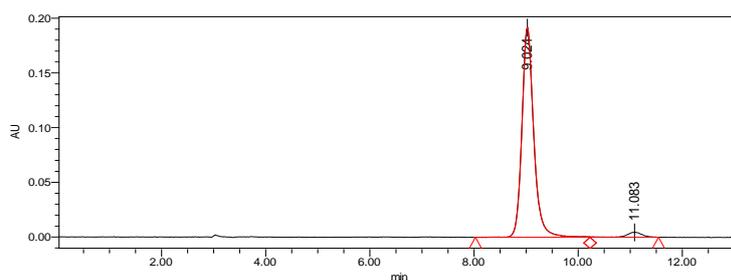


From 48.2 mg (0.20 mmol) 1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 88.66 mg (0.22 mmol, 1.1 equiv) 4-benzylidene-2-(4-bromophenyl)-5-phenyl-2,4-dihydro-3*H*-pyrazol-3-one, 112.2 mg (87% yield) compound **3o a** was obtained as light yellow solid, mp = 179 - 180°C.  $[\alpha]_D^{20} = +162$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis. 94% ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 11.1$  min and  $t_{\text{minor}} = 9.0$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 - 7.52 (m,

4H), 7.46 (dddd,  $J = 11.5, 9.1, 6.5, 2.2$  Hz, 8H), 7.31 – 7.17 (m, 4H), 6.89 (td,  $J = 7.7, 0.7$  Hz, 1H), 6.60 (d,  $J = 7.7$  Hz, 1H), 5.80 (d,  $J = 10.1$  Hz, 1H), 5.59 – 5.36 (m, 1H), 3.52 (d,  $J = 9.8$  Hz, 1H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  173.8, 170.6, 155.3, 143.8, 135.7, 132.7, 131.9, 131.1, 130.8, 130.6, 129.0, 128.8, 128.6, 128.4, 128.1, 126.0 (q,  $J_{\text{C-F}} = 278.2$  Hz), 124.2, 122.9, 121.1, 120.0, 119.2, 108.2, 73.1, 70.5, 61.6 (q,  $J_{\text{C-F}} = 30.8$  Hz), 48.0, 25.0.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.1; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{33}\text{H}_{24}\text{BrF}_3\text{N}_4\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 667.0927, found 667.0931.

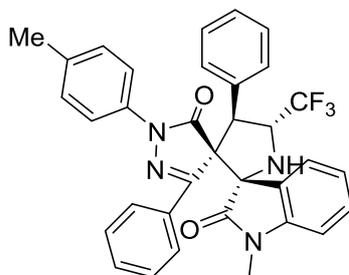


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	9.118	1162959	49.95	72328	bb	Unknown
2	11.181	1165065	50.05	58947	bb	Unknown



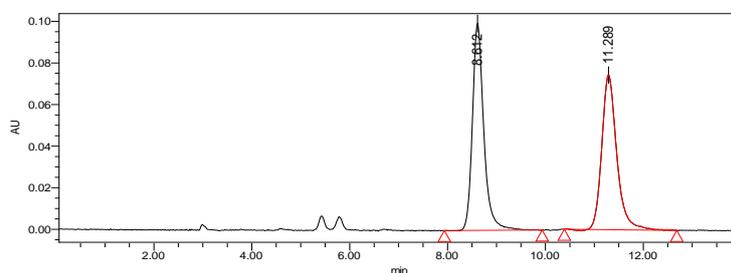
	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	9.024	3032687	97.09	191874	bv	Unknown
2	11.083	90868	2.91	4466	vb	Unknown

**(3*S*,3'*S*,4*R*,5'*R*)-1-methyl-3'',4'-diphenyl-1''-(*p*-tolyl)-5''-(trifluoromethyl)dispiro [indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''H)-dione (3pa)**

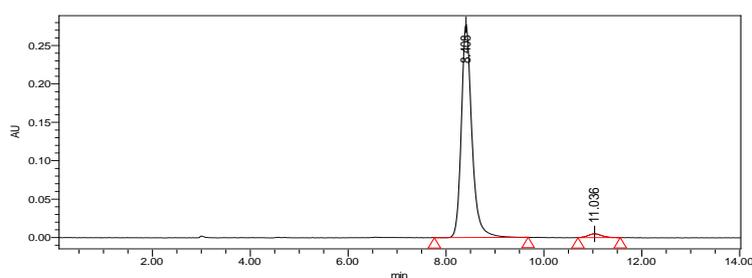


From 48.2 mg (0.20 mmol) 1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 74.36 mg (0.22 mmol, 1.1 equiv) 4-benzylidene-5-phenyl-2-(*p*-tolyl)-2,4-dihydro-3*H*-pyrazol-3-one, 103.4 mg (89% yield) compound **3pa** was obtained as light yellow

solid, mp = 180 - 181 °C.  $[\alpha]_D^{20} = + 162$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis. 96% ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 11.0$  min and  $t_{\text{minor}} = 8.4$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (dd,  $J = 11.0, 5.5$  Hz, 4H), 7.50 (d,  $J = 7.3$  Hz, 1H), 7.47 – 7.33 (m, 5H), 7.30 – 7.19 (m, 4H), 7.12 (d,  $J = 8.3$  Hz, 2H), 6.91 (t,  $J = 7.4$  Hz, 1H), 6.59 (d,  $J = 7.8$  Hz, 1H), 5.80 (d,  $J = 10.1$  Hz, 1H), 5.63 – 5.36 (m, 1H), 3.54 (d,  $J = 9.9$  Hz, 1H), 2.34 (s, 3H), 2.30 (s, 3H).  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ )  $\delta$  174.0, 170.6, 154.8, 143.8, 136.2, 134.2, 132.9, 131.07, 131.0, 130.3, 129.4, 128.9, 128.8, 128.5, 128.5, 128.1, 126.1 (q,  $J_{\text{C-F}} = 279.0$  Hz), 124.5, 123.1, 122.9, 120.4, 108.1, 72.8, 70.5, 61.6 (q,  $J_{\text{C-F}} = 30.7$  Hz), 48.0, 25.0, 21.0.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.0; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{34}\text{H}_{27}\text{F}_3\text{N}_4\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 603.1978, found 603.1983.

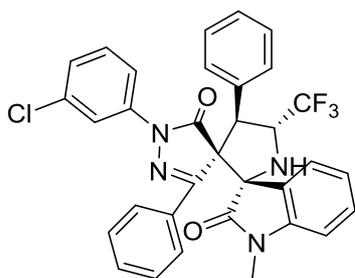


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	8.612	1607740	50.19	99613	bb	Unknown
2	11.289	1595477	49.81	74512	bb	Unknown

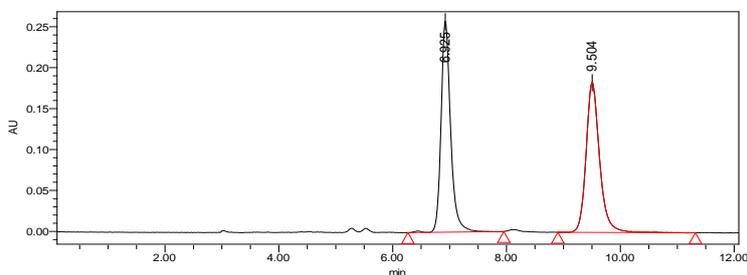


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	8.408	4166262	97.74	277532	bb	Unknown
2	11.036	96219	2.26	4980	bb	Unknown

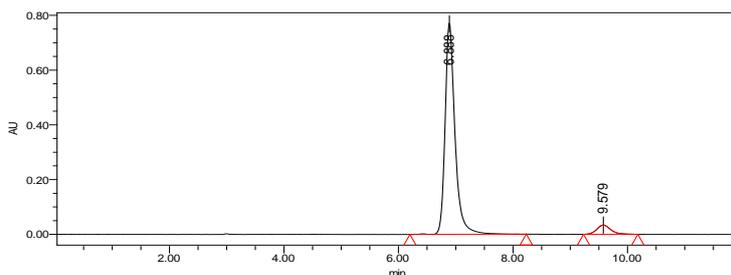
**(3S,3'S,4'R,5'R)-1''-(3-chlorophenyl)-1-methyl-3'',4'-diphenyl-5''-(trifluoromethyl)dispiro[indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''H)-dione (3qa)**



From 48.2 mg (0.20 mmol) 1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 78.98 mg (0.22 mmol, 1.1 equiv) 4-benzylidene-2-(3-chlorophenyl)- 5-phenyl-2,4-dihydro-3H-pyrazol-3-one, 99.8 mg (83% yield) compound **3qa** was obtained as light yellow solid, mp = 98 - 99 °C.  $[\alpha]_D^{20} = +186$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis. 88% ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 9.6$  min and  $t_{\text{minor}} = 6.9$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (dd,  $J = 9.7, 5.2$  Hz, 4H), 7.51 (d,  $J = 7.6$  Hz, 1H), 7.44 (dd,  $J = 5.1, 1.6$  Hz, 3H), 7.36 (d,  $J = 8.1$  Hz, 1H), 7.32 - 7.16 (m, 7H), 7.03 - 6.87 (m, 2H), 6.59 (d,  $J = 7.7$  Hz, 1H), 5.81 (dd,  $J = 10.1, 2.1$  Hz, 1H), 5.59 - 5.43 (m, 1H), 3.54 (dd,  $J = 9.8, 2.7$  Hz, 1H), 2.32 (d,  $J = 14.0$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.8, 170.7, 155.4, 143.8, 137.8, 132.7, 131.2, 130.8, 130.6, 130.2, 129.0, 128.9, 128.8, 128.6, 128.4, 128.1, 126.0 (q,  $J_{\text{C-F}} = 278.7$  Hz), 124.3, 122.9, 122.9, 122.5, 122.4, 117.9, 108.2, 73.2, 70.6, 61.6 (q,  $J_{\text{C-F}} = 30.7$  Hz), 48.0, 25.0.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.0; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{33}\text{H}_{24}\text{ClF}_3\text{N}_4\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 623.1432, found 623.1436.

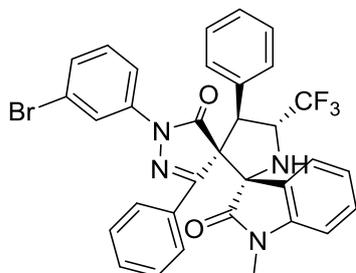


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	6.925	3014720	49.90	258763	bb	Unknown
2	9.504	3026999	50.10	183416	bb	Unknown

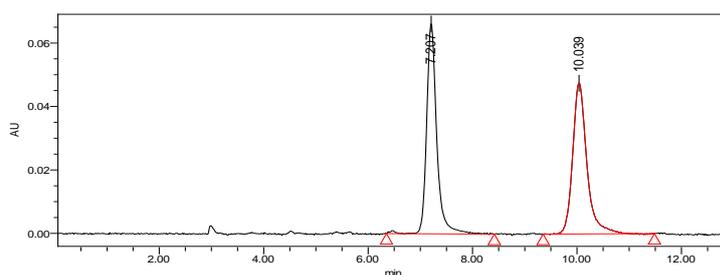


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	6.888	9258896	94.23	773920	bb	Unknown
2	9.579	567189	5.77	33817	bb	Unknown

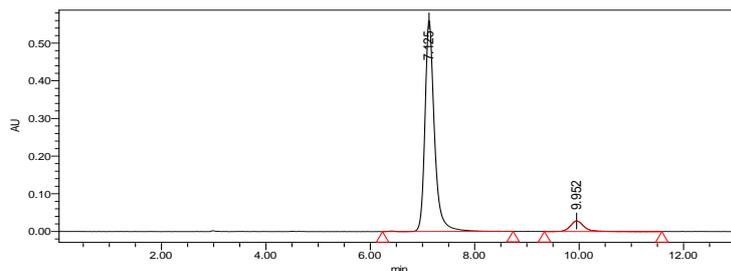
**(3*S*,3'*S*,4'*R*,5'*R*)-1''-(3-bromophenyl)-1-methyl-3'',4'-diphenyl-5'-(trifluoromethyl)dispiro[indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''*H*)-dione (3*ra*)**



From 48.2 mg (0.20 mmol) 1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 88.66 mg (0.22 mmol, 1.1 equiv) 4-benzylidene-2-(3-bromophenyl)-5-phenyl-2,4-dihydro-3*H*-pyrazol-3-one, 104.3 mg (81% yield) compound **3ra** was obtained as light yellow solid, mp = 109 - 110 °C.  $[\alpha]_D^{20} = +280$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis. 88% ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 10.0$  min and  $t_{\text{minor}} = 7.1$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (dd,  $J = 9.7, 5.2$  Hz, 4H), 7.51 (d,  $J = 7.6$  Hz, 1H), 7.44 (dd,  $J = 5.1, 1.6$  Hz, 3H), 7.36 (d,  $J = 8.1$  Hz, 1H), 7.32 – 7.16 (m, 7H), 7.03 – 6.87 (m, 2H), 6.59 (d,  $J = 7.7$  Hz, 1H), 5.81 (dd,  $J = 10.1, 2.1$  Hz, 1H), 5.59 – 5.43 (m, 1H), 3.54 (dd,  $J = 9.8, 2.7$  Hz, 1H), 2.32 (d,  $J = 14.0$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.8, 170.7, 155.4, 143.8, 137.7, 134.6, 132.7, 131.2, 130.8, 130.6, 129.9, 129.0, 128.8, 128.6, 128.4, 128.1, 126.0, 126.0 (q,  $J_{\text{C-F}} = 278.7$  Hz), 124.3, 122.9, 122.9, 119.5, 117.4, 108.2, 73.2, 70.6, 61.6 (q,  $J_{\text{C-F}} = 30.7$  Hz), 48.0, 25.0.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.0; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{33}\text{H}_{24}\text{BrF}_3\text{N}_4\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 667.0927, found 667.0931.

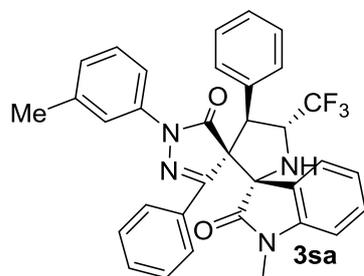


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	7.207	897300	49.99	66456	bb	Unknown
2	10.039	897813	50.01	47627	bb	Unknown

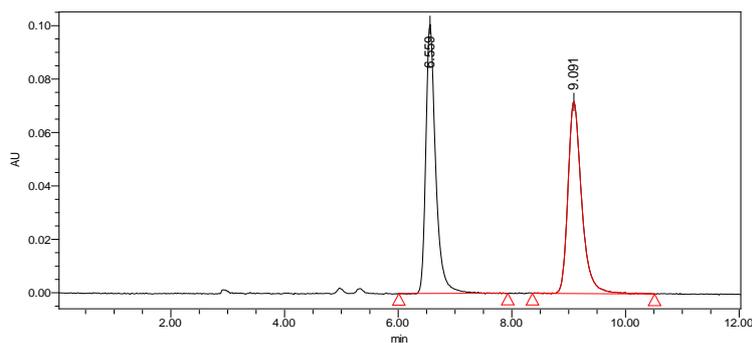


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	7.125	7044652	93.17	563053	bb	Unknown
2	9.952	516759	6.83	28052	bb	Unknown

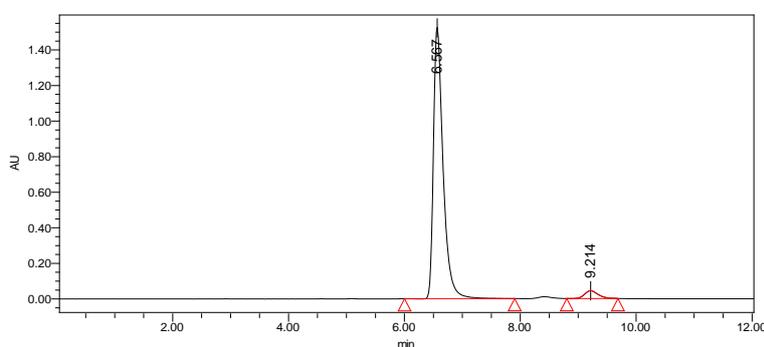
**(3*S*,3'*S*,4'*R*,5'*R*)-1-methyl-3'',4'-diphenyl-1''-(*m*-tolyl)-5'-(trifluoromethyl)dispiro [indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''H)-dione**



From 48.2 mg (0.20 mmol) 1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 74.36 mg (0.22 mmol, 1.1 equiv) 4-benzylidene-5-phenyl-2-(*m*-tolyl)-2,4-dihydro-3*H*-pyrazol-3-one, 101.1 mg (87% yield) compound **3sa** was obtained as light yellow solid, mp = 99 - 100 °C.  $[\alpha]_D^{20} = +129$  ( $c = 1.0$ , CHCl<sub>3</sub>). Dr (>20:1) determined by <sup>1</sup>H and <sup>19</sup>F NMR analysis. 92% ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 9.2$  min and  $t_{\text{minor}} = 6.6$  min. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.58 (dd,  $J = 9.7, 5.2$  Hz, 4H), 7.51 (d,  $J = 7.6$  Hz, 1H), 7.44 (dd,  $J = 5.1, 1.6$  Hz, 3H), 7.36 (d,  $J = 8.1$  Hz, 1H), 7.32 – 7.16 (m, 7H), 7.03 – 6.87 (m, 2H), 6.59 (d,  $J = 7.7$  Hz, 1H), 5.81 (dd,  $J = 10.1, 2.1$  Hz, 1H), 5.59 – 5.43 (m, 1H), 3.54 (dd,  $J = 9.8, 2.7$  Hz, 1H), 2.32 (d,  $J = 14.0$  Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  173.9, 170.7, 154.9, 143.8, 138.8, 136.6, 132.9, 131.0, 130.4, 128.9, 128.8, 128.7, 128.5, 128.5, 128.1, 127.1, 126.6 (q,  $J_{\text{C-F}} = 278.3$  Hz), 124.5, 123.1, 122.9, 120.8, 117.4, 108.1, 72.85, 70.48, 61.6 (q,  $J_{\text{C-F}} = 30.7$  Hz), 48.00, 25.02, 21.50. <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)  $\delta$  -72.0; HRMS (ESI)  $m/z$  calcd for C<sub>34</sub>H<sub>27</sub>F<sub>3</sub>N<sub>4</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup>: 603.1978, found 603.1981.

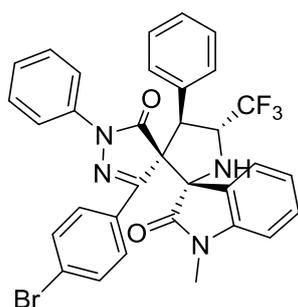


	Retention Time	Area	% Area	Height	Int Type	Peak Type
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2	9.091	1204475	49.86	71882	bb	Unknown



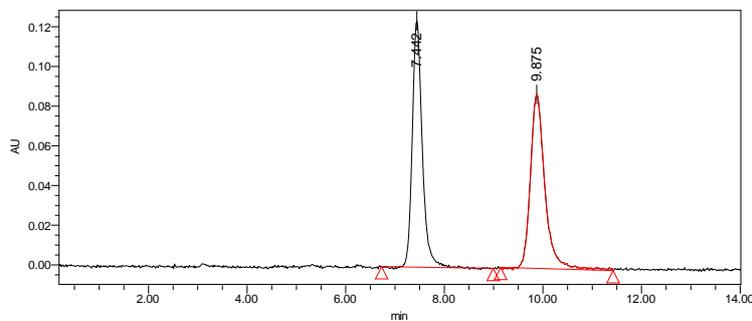
	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	6.567	17666723	96.13	1524854	bb	Unknown
2	9.214	711388	3.87	44091	bb	Unknown

**(3*S*,3'*S*,4'*R*,5'*R*)-3''-(4-bromophenyl)-1-methyl-1'',4'-diphenyl-5'-(trifluoromethyl)dispiro[indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''H)-dione (3ta)**

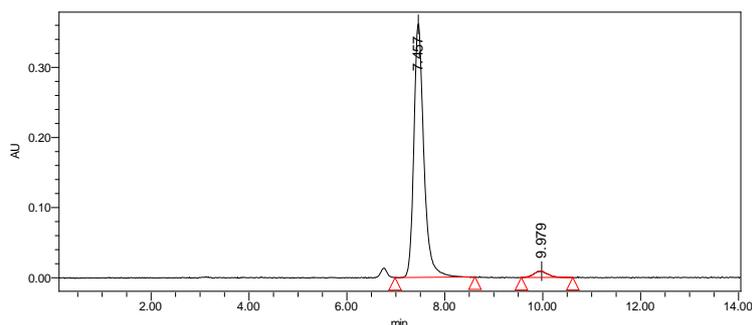


From 48.2 mg (0.20 mmol) 1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 88.66 mg (0.22 mmol, 1.1 equiv) 4-benzylidene-5-(4-bromophenyl)-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one, 110.9 mg (86% yield) compound **3ta** was obtained as light yellow solid, mp = 108 - 109 °C.  $[\alpha]_D^{20} = +130$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis. 93% ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 10.0$  min and  $t_{\text{minor}} = 7.5$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (ddd,  $J = 12.8, 11.4, 6.9$  Hz, 9H), 7.25 - 7.04 (m, 7H), 6.82 (t,  $J = 7.6$  Hz, 1H), 6.53 (d,  $J = 7.8$  Hz,

1H), 5.66 (d,  $J = 10.0$  Hz, 1H), 5.50 – 5.31 (m, 1H), 3.45 (d,  $J = 9.7$  Hz, 1H), 2.36 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.0, 169.5, 152.7, 142.6, 135.4, 131.6, 130.2, 130.1, 129.14, 128.8, 128.0, 127.8, 127.6, 127.4, 125.3, 125.0 (q,  $J_{\text{C-F}} = 278.7$  Hz), 123.9, 123.4, 122.0, 121.9, 119.1, 107.2, 71.7, 69.5, 60.5 (q,  $J_{\text{C-F}} = 30.3$  Hz), 47.0, 24.1.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.2; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{33}\text{H}_{24}\text{BrF}_3\text{N}_4\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 667.0927, found 667.0932.

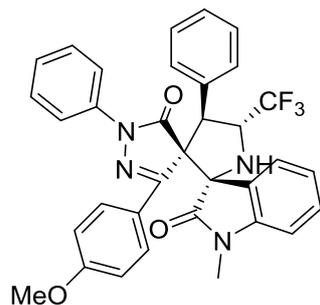


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	7.442	1762451	49.47	124305	bb	Unknown
2	9.875	1800124	50.53	87697	bb	Unknown

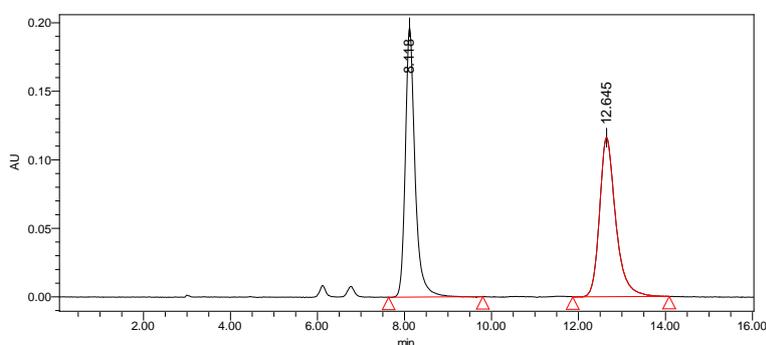


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	7.457	5120281	96.55	362633	bb	Unknown
2	9.979	182817	3.45	8980	bb	Unknown

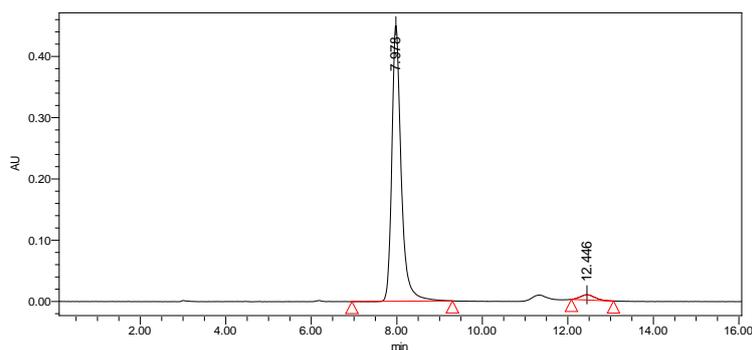
**(3*S*,3'*S*,4'*R*,5'*R*)-3''-(4-methoxyphenyl)-1-methyl-1'',4'-diphenyl-5'-(trifluoromethyl)dispiro[indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''H)-dione (3ua)**



From 48.2 mg (0.20 mmol) 1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 77.88 mg (0.22 mmol, 1.1 equiv) 4-benzylidene-5-(4-methoxyphenyl)-2-phenyl-2,4-dihydro-3H-pyrazol-3-one, 106.3 mg (89% yield) compound **3ua** was obtained as light yellow solid, mp = 209 - 210 °C.  $[\alpha]_D^{20} = +161$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis. 94% ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 12.4$  min and  $t_{\text{minor}} = 8.0$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 – 7.47 (m, 7H), 7.38 – 7.27 (m, 3H), 7.26 – 7.14 (m, 4H), 7.00 – 6.87 (m, 3H), 6.61 (d,  $J = 7.8$  Hz, 1H), 5.76 (d,  $J = 10.1$  Hz, 1H), 5.59 – 5.44 (m, 1H), 3.86 (s, 3H), 3.54 (d,  $J = 9.9$  Hz, 1H), 2.44 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.1, 169.5, 160.3, 153.4, 142.7, 135.7, 131.9, 129.9, 129.3, 127.8, 127.7, 127.4, 127.4, 127.4, 125.1 (q,  $J_{\text{C-F}} = 279.0$  Hz), 123.4, 122.4, 122.0, 121.8, 119.0, 112.4, 107.0, 71.9, 69.6, 60.5 (q,  $J_{\text{C-F}} = 30.3$  Hz), 54.4, 46.8, 24.2.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.1; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{34}\text{H}_{27}\text{F}_3\text{N}_4\text{NaO}_3$   $[\text{M}+\text{Na}]^+$ : 619.1927, found 619.1935.

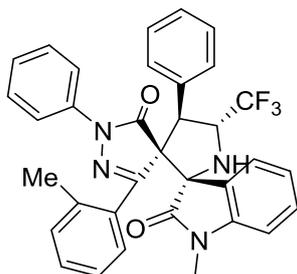


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	8.118	3046632	50.40	196838	bb	Unknown
2	12.645	2998435	49.60	116185	bb	Unknown

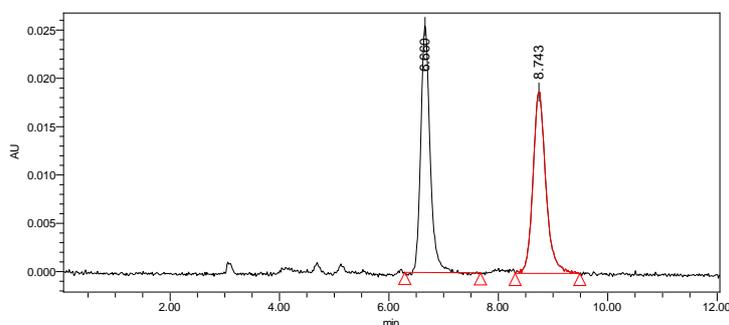


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	7.978	6836531	97.16	450847	bb	Unknown
2	12.446	199729	2.84	8603	bb	Unknown

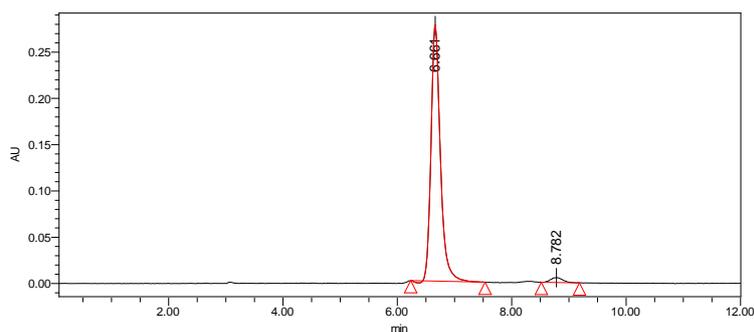
**(3*S*,3'*S*,4'*R*,5'*R*)-1-methyl-1'',4'-diphenyl-3''-(*o*-tolyl)-5''-(trifluoromethyl)dispiro[indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''*H*)-dione (3va)**



From 48.2 mg (0.20 mmol) 1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 74.36 mg (0.22 mmol, 1.1 equiv) 4-benzylidene-2-phenyl-5-(*o*-tolyl)-2,4-dihydro-3*H*-pyrazol-3-one, 102.1 mg (88% yield) compound **3va** was obtained as light yellow solid, mp = 186 - 188 °C.  $[\alpha]_D^{20} = +174$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis. 95% ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 8.8$  min and  $t_{\text{minor}} = 6.7$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (d,  $J = 7.5$  Hz, 1H), 7.65 (d,  $J = 7.4$  Hz, 2H), 7.57 (d,  $J = 7.9$  Hz, 3H), 7.33 (dt,  $J = 21.8, 7.2$  Hz, 8H), 7.26 - 7.16 (m, 4H), 6.93 (t,  $J = 7.6$  Hz, 1H), 6.63 (d,  $J = 7.8$  Hz, 1H), 5.85 (d,  $J = 10.1$  Hz, 1H), 5.52 - 5.26 (m, 1H), 3.51 (d,  $J = 9.9$  Hz, 1H), 2.46 (s, 3H), 1.74 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.5, 170.6, 154.3, 144.5, 137.8, 136.8, 132.9, 131.1, 130.5, 130.4, 129.7, 129.4, 128.9, 128.9, 128.7, 128.6, 126.2, 126.0 (q,  $J_{\text{C-F}} = 278.3$  Hz), 125.5, 124.9, 123.5, 123.1, 119.9, 108.2, 73.1, 69.3, 61.8 (q,  $J_{\text{C-F}} = 30.3$  Hz), 48.6, 25.3, 20.6.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.0; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{34}\text{H}_{27}\text{F}_3\text{N}_4\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 603.1978, found 603.1985.

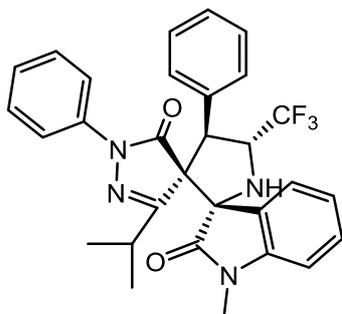


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	6.660	305212	49.73	25561	bb	Unknown
2	8.743	308533	50.27	18843	bb	Unknown

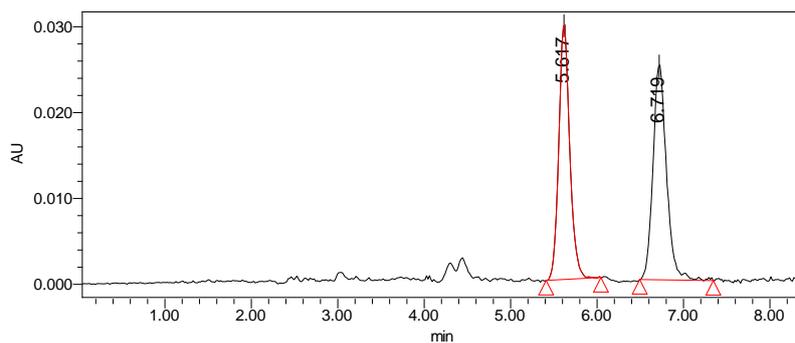


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	6.661	3170355	97.60	276819	bb	Unknown
2	8.782	78061	2.40	5289	bb	Unknown

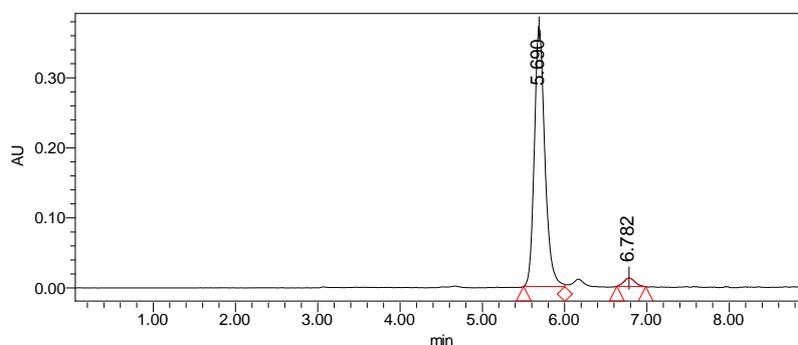
**(3*S*,3'*S*,4'*R*,5'*R*)-3''-isopropyl-1-methyl-1'',4'-diphenyl-5'-(trifluoromethyl)dispiro[indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''H)-dione (3wa)**



From 48.4 mg (0.20 mmol) 1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 58 mg (0.22 mmol, 1.1 equiv) 4-benzylidene-5-isopropyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one, 91.0 mg (86 % yield) compound **3wa** was obtained as light yellow solid, mp = 182 - 183 °C.  $[\alpha]_D^{20} = +69$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis. 92 % ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 6.8$  min and  $t_{\text{minor}} = 5.7$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 (d,  $J = 7.6$  Hz, 1H), 7.74 (d,  $J = 8.0$  Hz, 2H), 7.50 – 7.45 (m, 2H), 7.38 (dd,  $J = 14.6, 7.3$  Hz, 3H), 7.25 (d,  $J = 4.4$  Hz, 4H), 7.18 (t,  $J = 7.5$  Hz, 1H), 6.84 (d,  $J = 7.8$  Hz, 1H), 5.45 – 5.24 (m, 1H), 4.61 (d,  $J = 10.6$  Hz, 1H), 4.00 (d,  $J = 10.4$  Hz, 1H), 3.10 (s, 3H), 2.02 (dt,  $J = 13.3, 6.6$  Hz, 1H), 0.78 (d,  $J = 6.7$  Hz, 3H), 0.31 (d,  $J = 6.6$  Hz, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  172.8, 169.1, 162.7, 143.3, 137.4, 132.4, 130.5, 130.2, 129.5, 128.9, 128.8, 128.8, 126.0, 125.4, 124.6 (q,  $J_{\text{C-F}} = 243.8$  Hz), 123.2, 119.6, 109.1, 71.8, 62.6 (q,  $J_{\text{C-F}} = 30$  Hz), 50.9, 28.5, 27.0, 22.8, 20.8, -0.00.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.6; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{30}\text{H}_{27}\text{F}_3\text{N}_4\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 555.1978, found 555.1958.

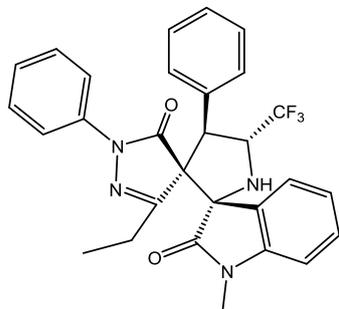


	保留时间	面积	% 面积	高度	积分类型	峰类型
1	5.616	416060	48.74	47595	bb	未知
2	6.719	437608	51.26	40655	bb	未知



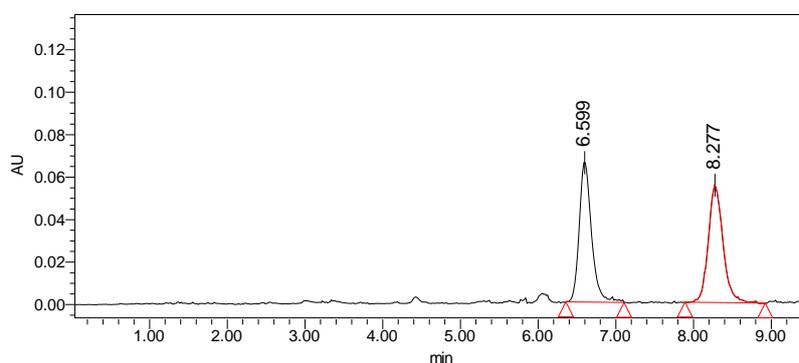
	保留时间	面积	% 面积	高度	积分类型	峰类型
1	5.690	3278862	96.70	372118	bv	未知
2	6.782	111859	3.30	12118	bb	未知

**(3*S*,3'*S*,4'*R*,5'*R*)-3''-ethyl-1-methyl-1'',4'-diphenyl-5'-(trifluoromethyl)dispiro[indoline-3,2'-pyrrolidine-3',4''-pyrazole]-2,5''(1''H)-dione (3xa)**

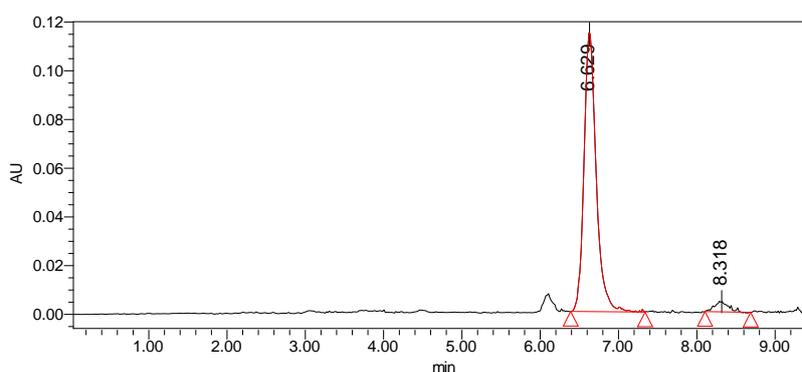


From 48.4 mg (0.20 mmol) 1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one and 55.2 mg (0.22 mmol, 1.1 equiv) 4-benzylidene-5-ethyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one, 97.0 mg (94% yield) compound **3xa** was obtained as light yellow solid, mp = 174 - 175 °C.  $[\alpha]_D^{20} = +97$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). Dr (>20:1) determined by  $^1\text{H}$

and  $^{19}\text{F}$  NMR analysis. 93 % ee was determined by HPLC analysis (Daicel Chiralcel IA column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time:  $t_{\text{major}} = 8.3$  min and  $t_{\text{minor}} = 6.6$  min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (d,  $J = 7.5$  Hz, 1H), 7.63 (d,  $J = 7.6$  Hz, 2H), 7.42 (d,  $J = 7.7$  Hz, 1H), 7.36 (dd,  $J=9.2, 4.9$  Hz, 3H), 7.31 (s, 1H), 7.28 (s, 1H), 7.26 – 7.22 (m, 3H), 7.12 (t,  $J = 7.4$  Hz, 1H), 6.82 (d,  $J = 7.8$  Hz, 1H), 5.57 – 5.37 (m, 1H), 4.53 (d,  $J = 10.8$  Hz, 1H), 3.96 (d,  $J = 10.2$  Hz, 1H), 3.06 (s, 3H), 2.04-1.88 (m, 1H), 0.92 (dd,  $J= 14.1, 6.9$  Hz, 1H), 0.88-0.79 (m, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  173.3, 168.7, 158.2, 142.8, 137.3, 131.6, 130.5, 130.4, 128.9, 128.8, 128.7, 128.6, 126.3 (q,  $J_{\text{C-F}} = 277.7$  Hz), 125.8, 125.4, 123.1, 119.4, 108.8, 72.4, 71.6, 61.1 (q,  $J_{\text{C-F}} = 30.2$  Hz), 50.7, 27.0, 22.5, 9.5.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -73.0; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{33}\text{H}_{25}\text{F}_3\text{N}_4\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 541.1822, found 541.1802.

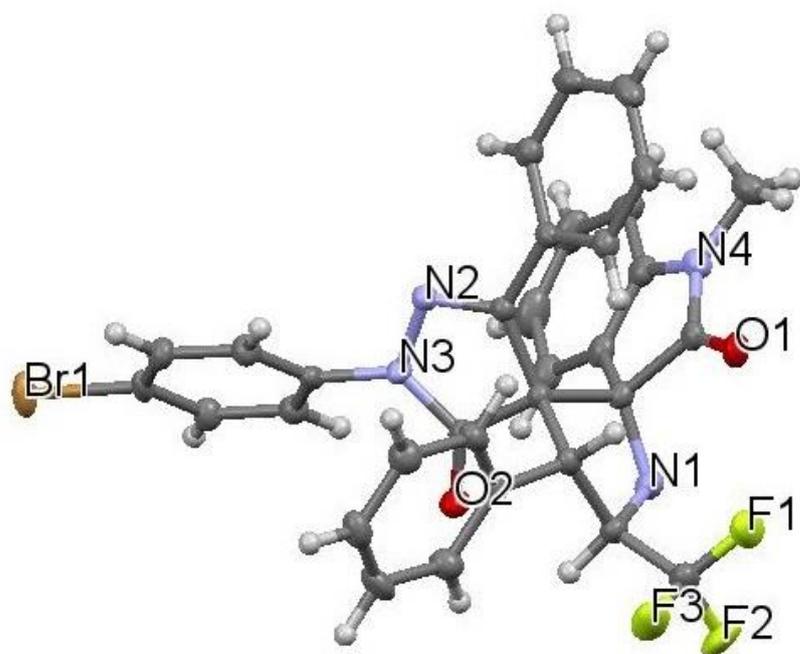


	保留时间	面积	% 面积	高度	积分类型	峰类型
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2	8.277	729444	50.04	55060	bb	未知

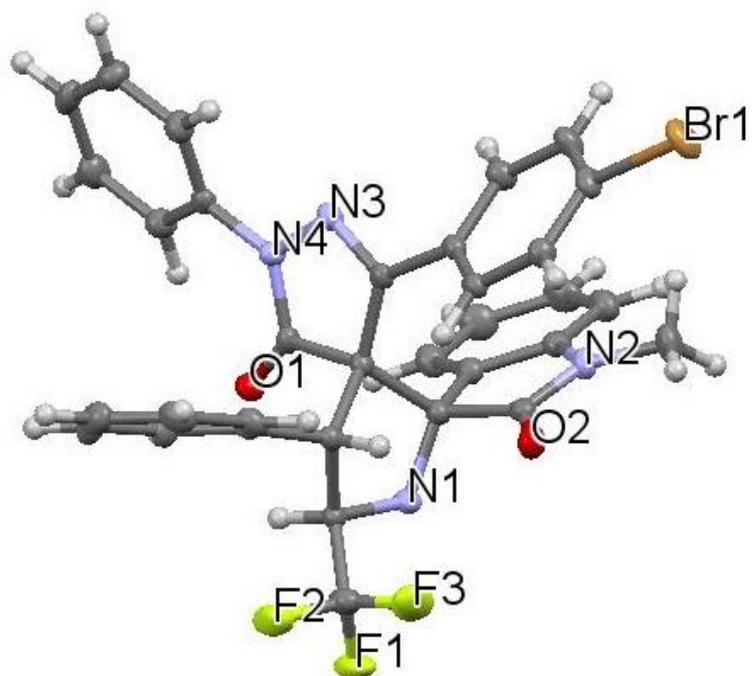


	保留时间	面积	% 面积	高度	积分类型	峰类型
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2	8.318	54580	4.21	4196	bb	未知

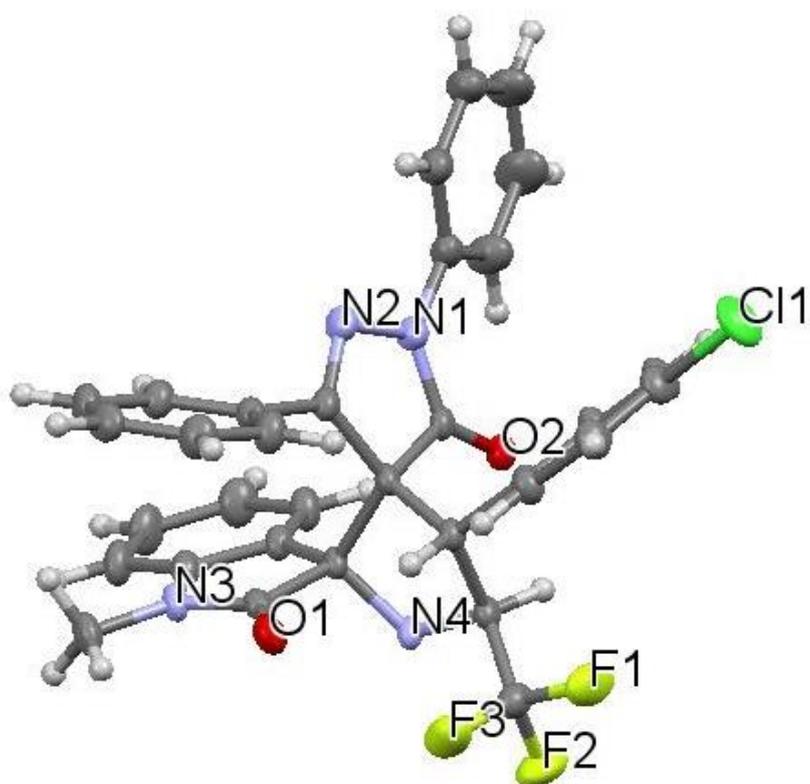
#### 4. X-ray Structure of Compound 3ca



## 5. X-ray Structure of Compound 30a



## 6. X-ray Structure of Compound 3ta

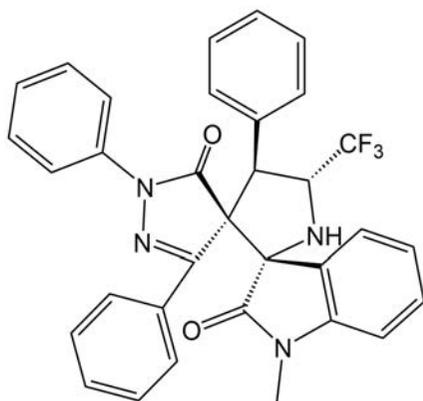


7.296  
7.288  
7.266  
7.242  
7.235  
7.222  
7.210  
7.206  
7.181  
7.157  
7.132  
7.106  
7.083  
7.051  
7.016  
6.992  
6.974  
6.947  
6.934  
6.909  
6.884  
6.857  
6.611  
6.585  
5.821  
5.787  
5.596  
5.575  
5.551  
5.519  
5.494  
5.468  
5.462  
5.436

3.560  
3.527

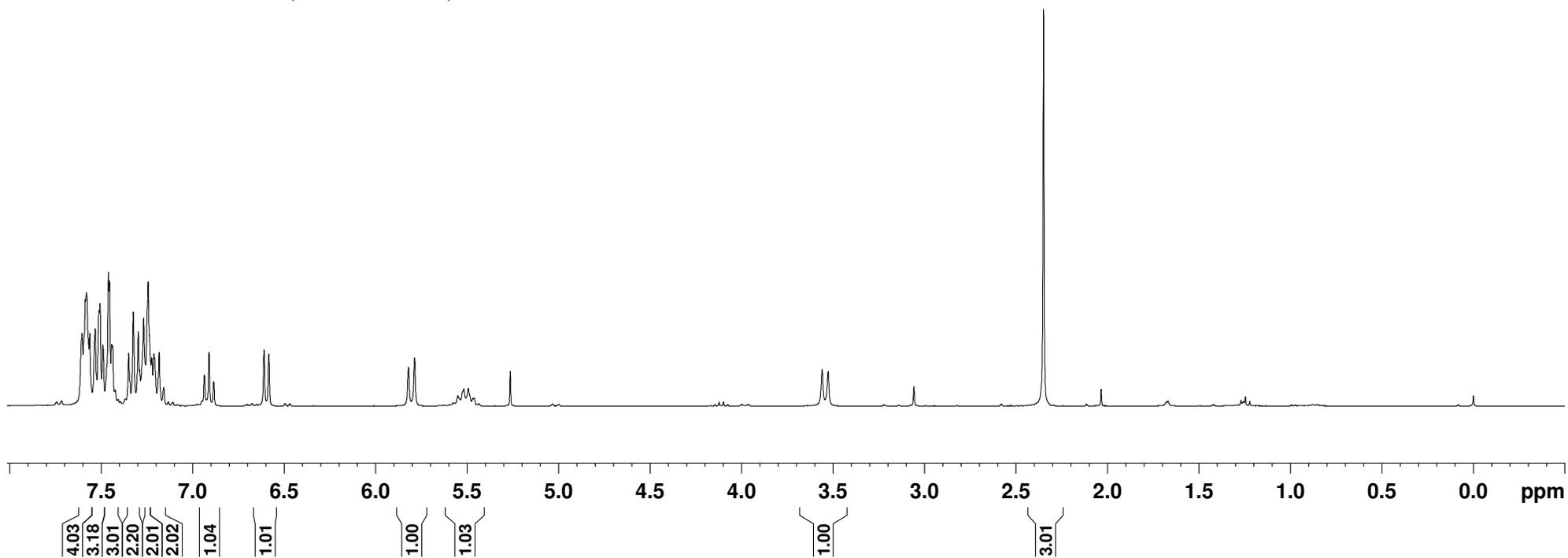
2.349

-0.000

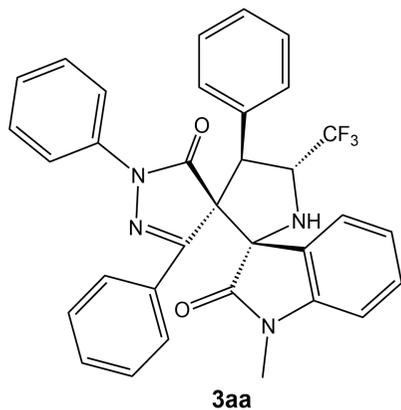


**3aa**

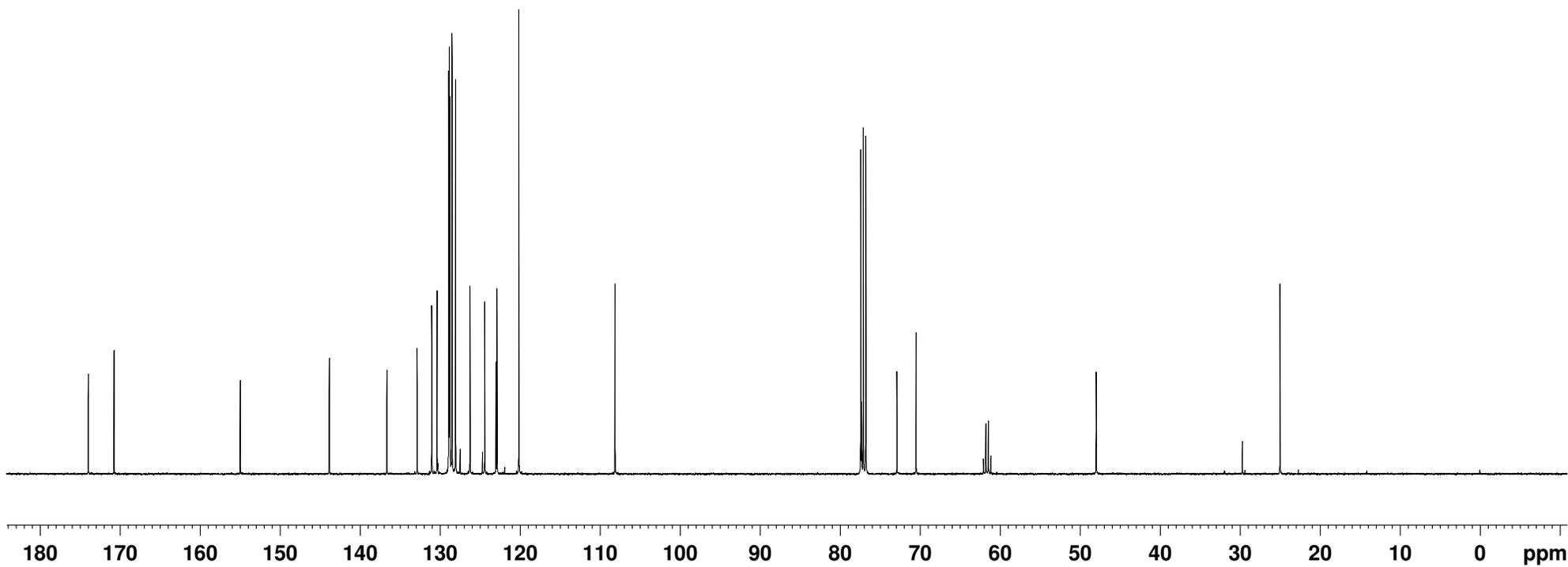
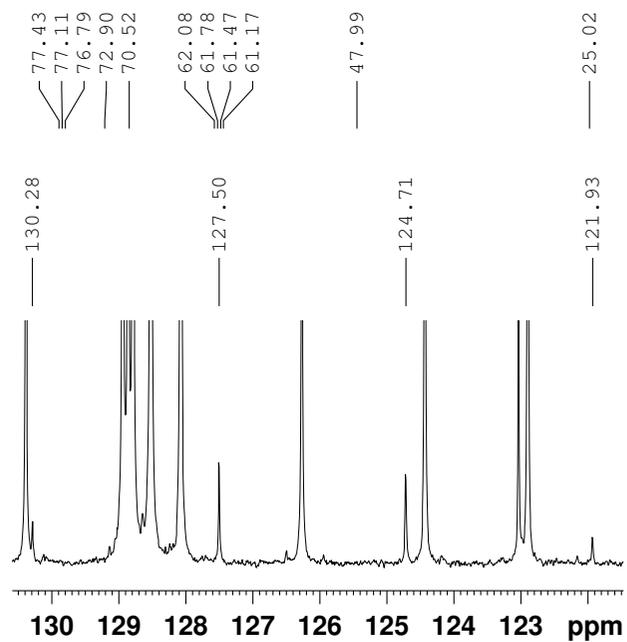
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

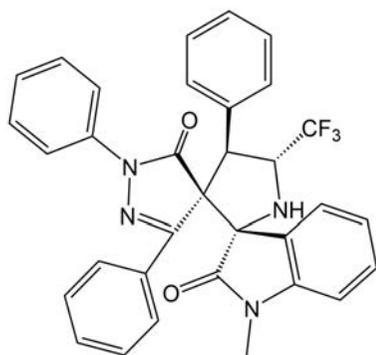


— 173.93  
 — 170.70  
 — 154.93  
 — 143.81  
 — 136.65  
 — 132.87  
 — 131.06  
 — 130.38  
 — 130.28  
 — 128.94  
 — 128.85  
 — 128.78  
 — 128.51  
 — 128.07  
 — 127.50  
 — 126.26  
 — 124.71  
 — 124.43  
 — 123.03  
 — 122.89  
 — 121.93  
 — 120.17  
 — 108.14



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

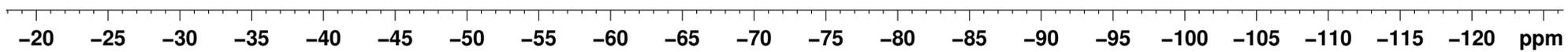




**3aa**

<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)

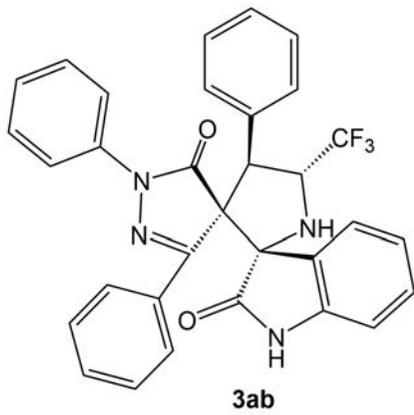
— -72.050



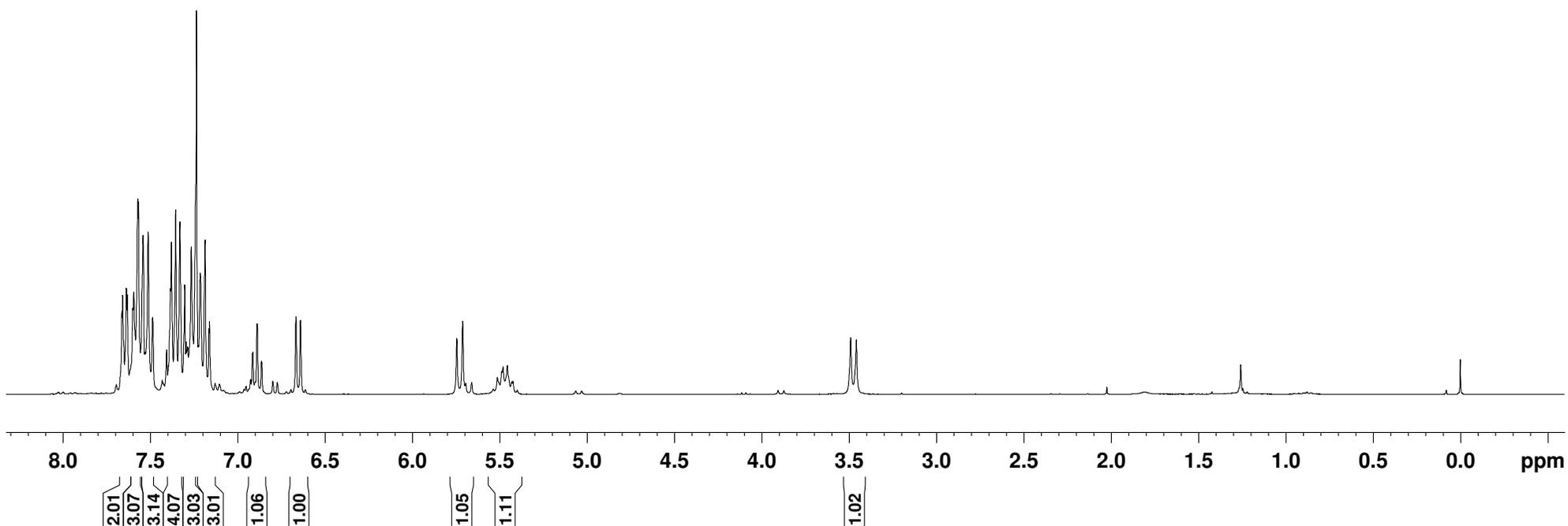
7.529  
7.525  
7.511  
7.486  
7.405  
7.383  
7.378  
7.354  
7.330  
7.302  
7.294  
7.285  
7.264  
7.235  
7.223  
7.213  
7.185  
7.163  
7.160  
6.914  
6.912  
6.888  
6.886  
6.863  
6.861  
6.665  
6.639  
5.744  
5.711  
5.512  
5.487  
5.480  
5.455  
5.430  
5.423

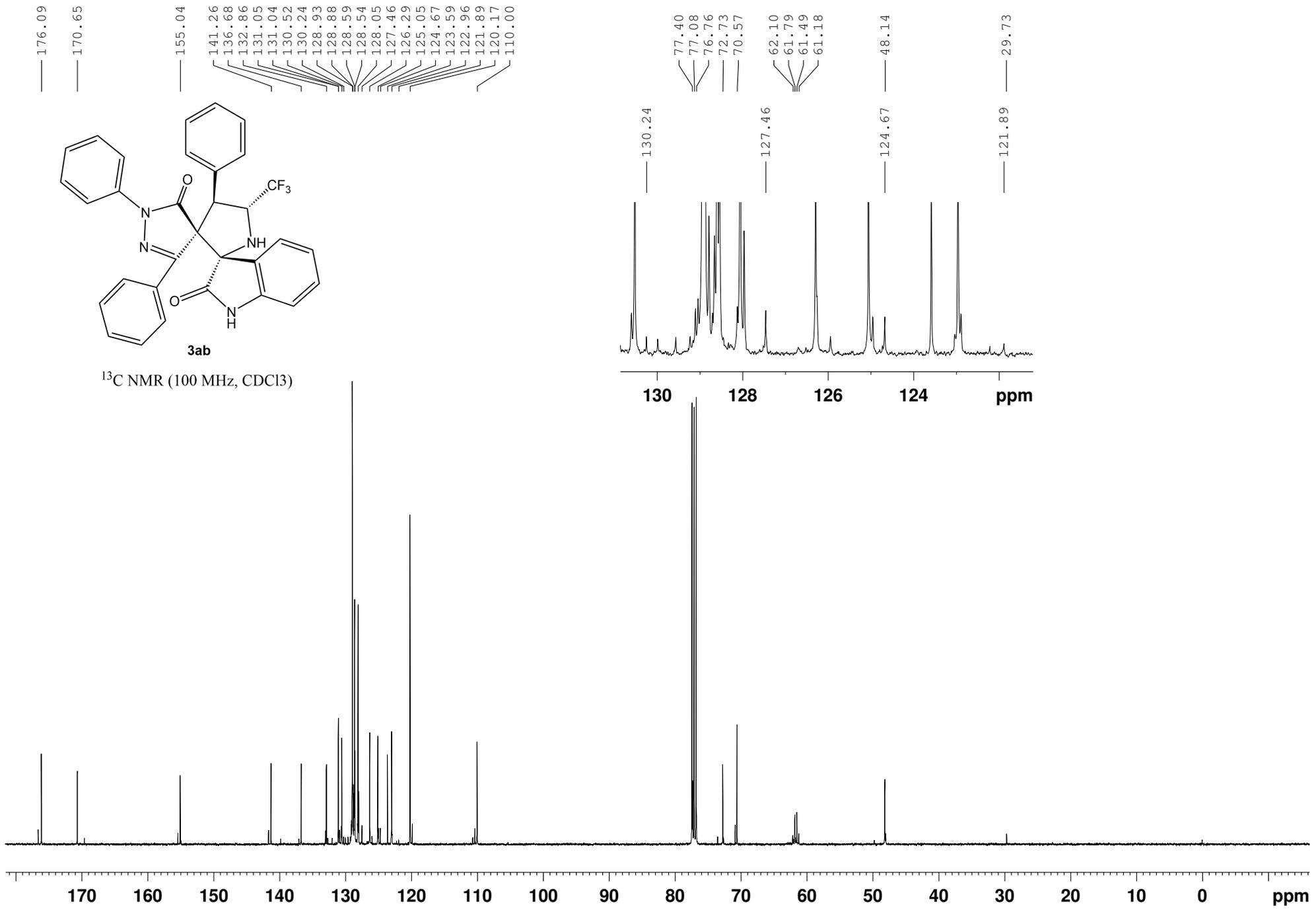
3.490  
3.457

— 0.000



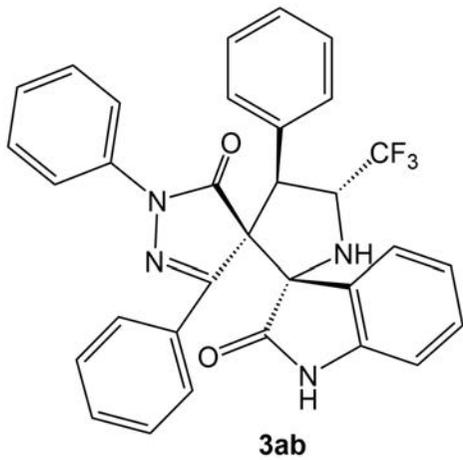
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)





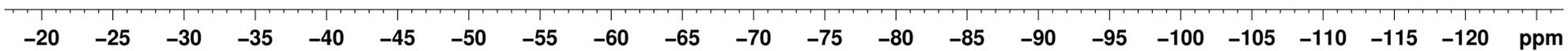
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

130 128 126 124 ppm

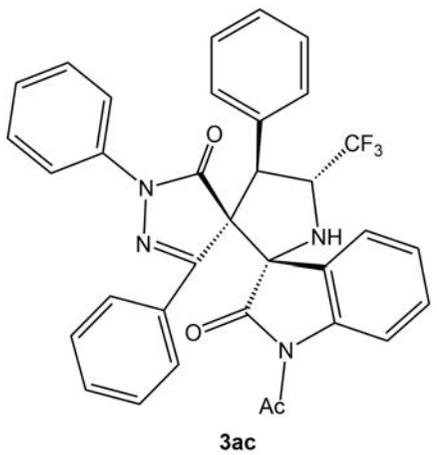


$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )

— -72.036



7.510  
7.506  
7.499  
7.481  
7.469  
7.459  
7.444  
7.439  
7.430  
7.360  
7.356  
7.350  
7.343  
7.325  
7.307  
7.303  
7.297  
7.271  
7.262  
7.255  
7.246  
7.220  
7.216  
7.192  
7.167  
7.125  
7.122  
7.099  
7.096  
7.073  
7.071  
5.664  
5.630  
5.603  
5.580  
5.557  
5.550  
5.526  
5.518  
5.502  
5.493  
5.470

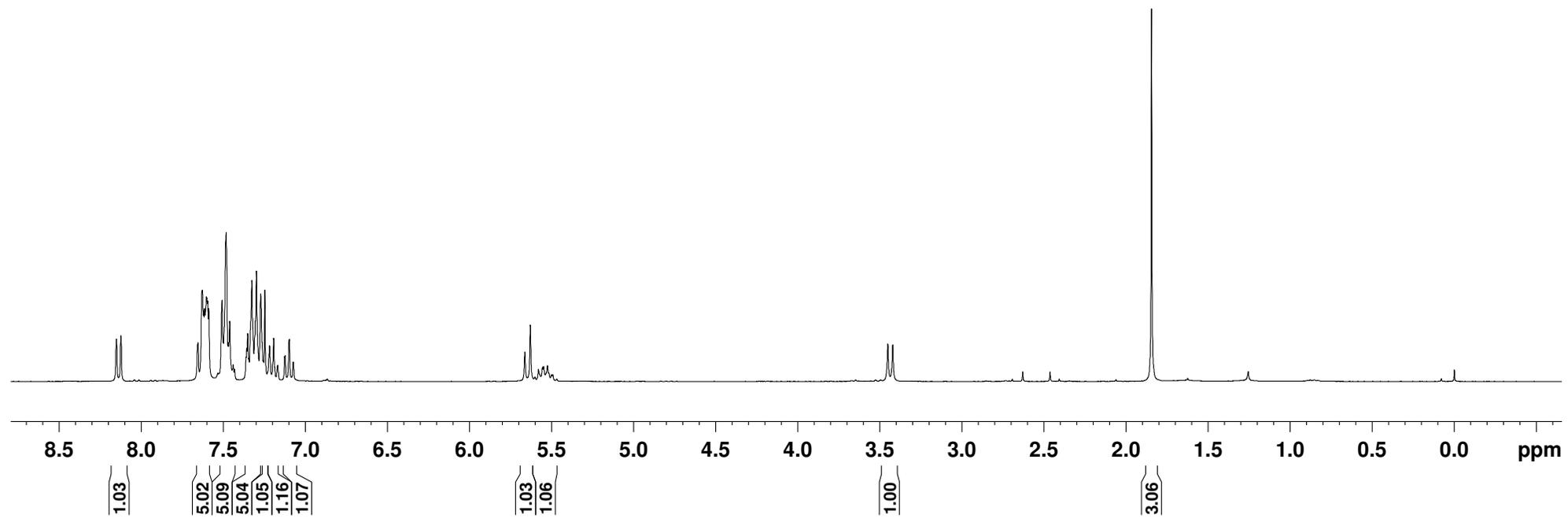


<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

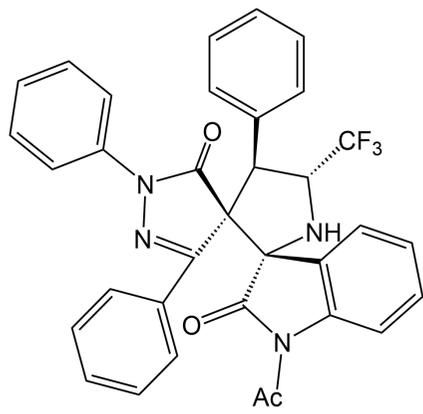
3.452  
3.422

1.845

-0.000

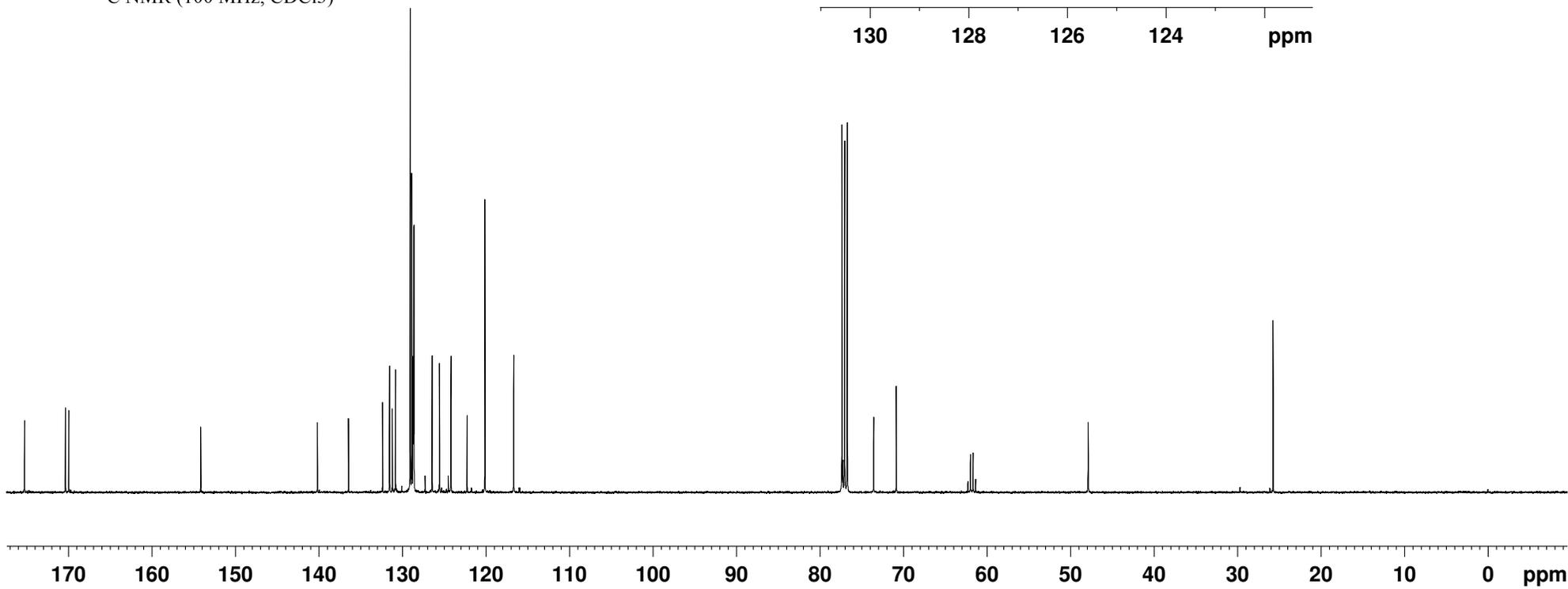
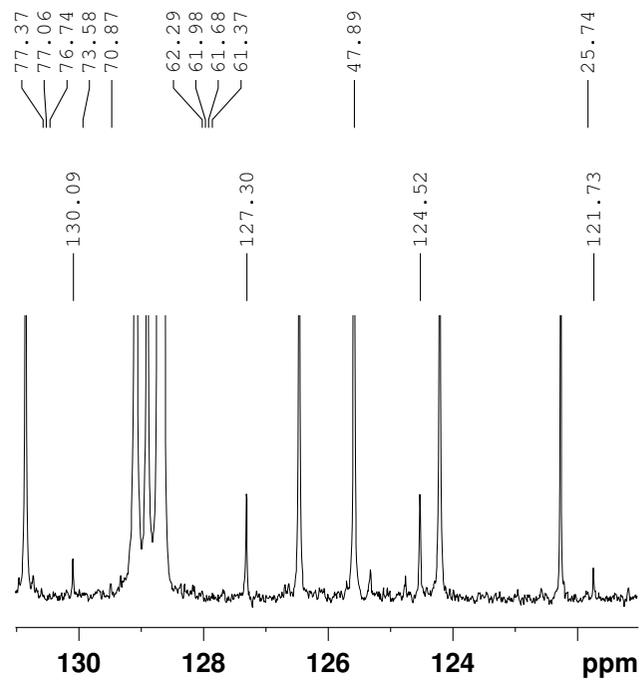


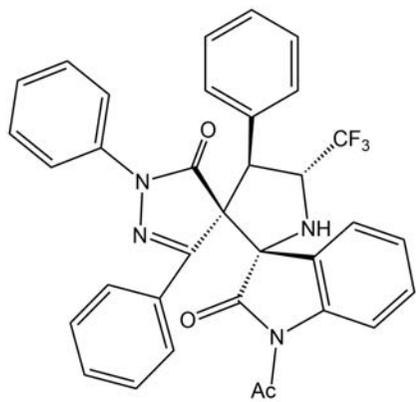
175.22  
 170.36  
 169.97  
 154.17  
 140.19  
 136.46  
 132.39  
 131.55  
 131.22  
 130.84  
 130.09  
 129.08  
 128.89  
 128.73  
 128.68  
 128.63  
 127.30  
 126.45  
 125.58  
 124.52  
 124.20  
 122.26  
 121.73  
 120.13  
 116.69



**3ac**

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

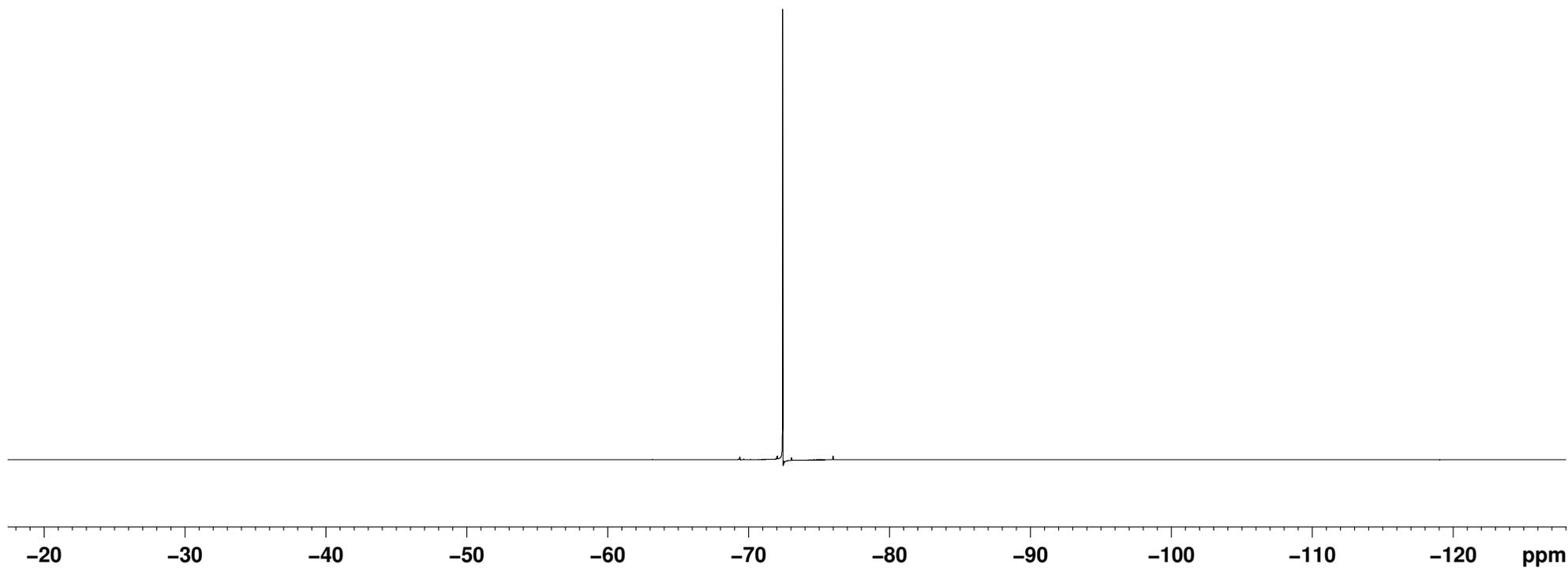




3ac

<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)

— -72.429

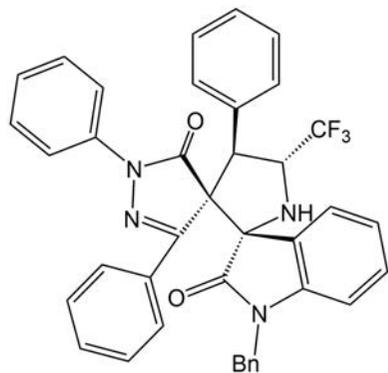


7.375  
7.365  
7.355  
7.305  
7.279  
7.231  
7.205  
7.178  
7.151  
7.129  
7.104  
7.095  
7.074  
7.055  
7.046  
7.038  
6.991  
6.967  
6.941  
6.827  
6.816  
6.803  
6.748  
6.723  
6.698  
6.698  
6.374  
6.348  
5.822  
5.789  
5.494  
5.466  
5.441  
5.415

4.032  
3.980  
3.780  
3.727  
3.490  
3.458

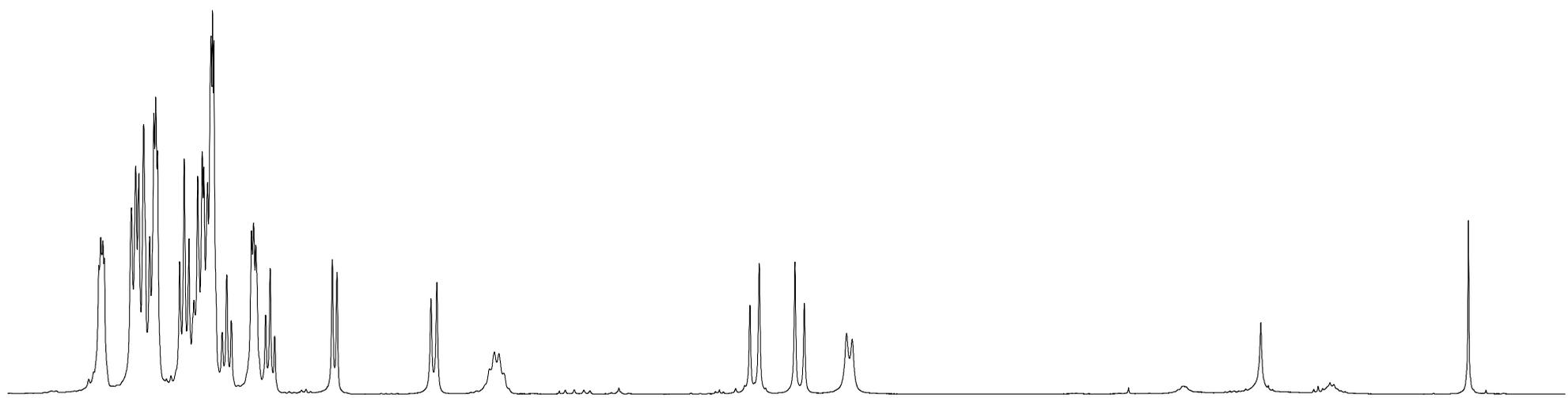
1.165

-0.000



**3ad**

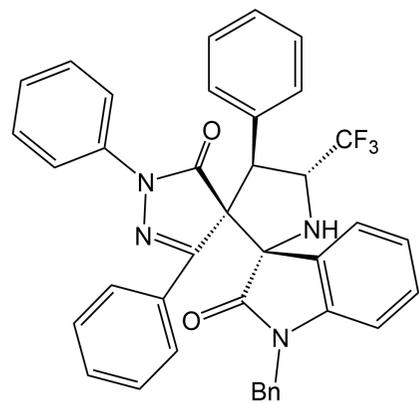
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)



8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

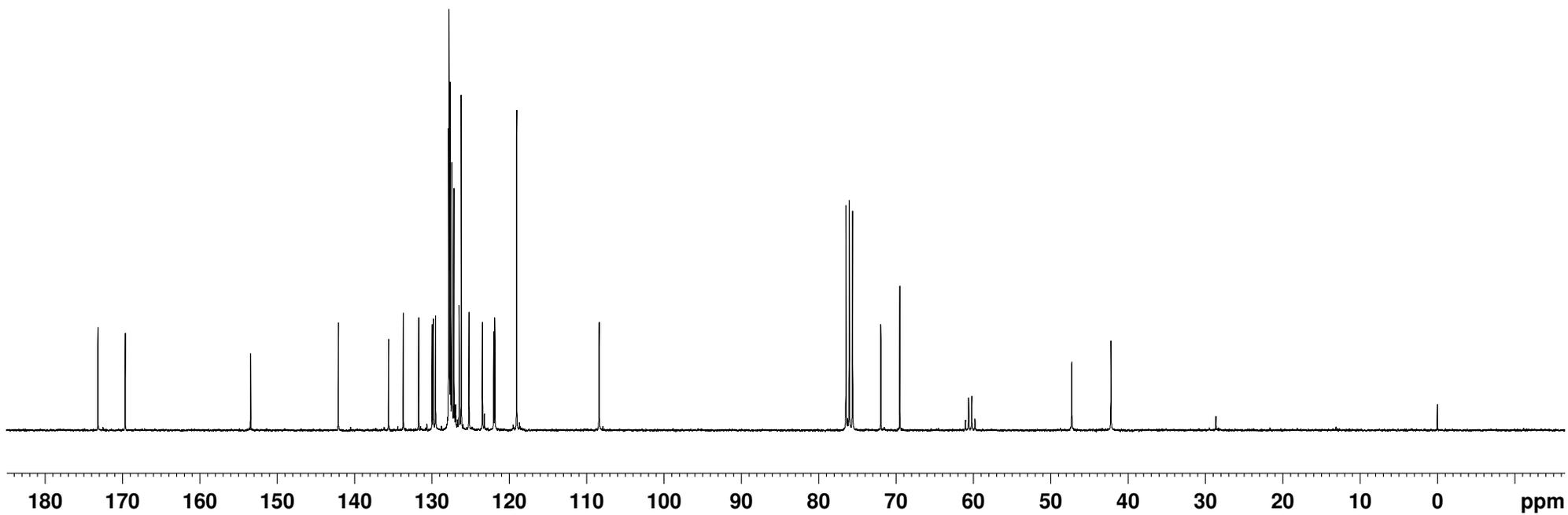
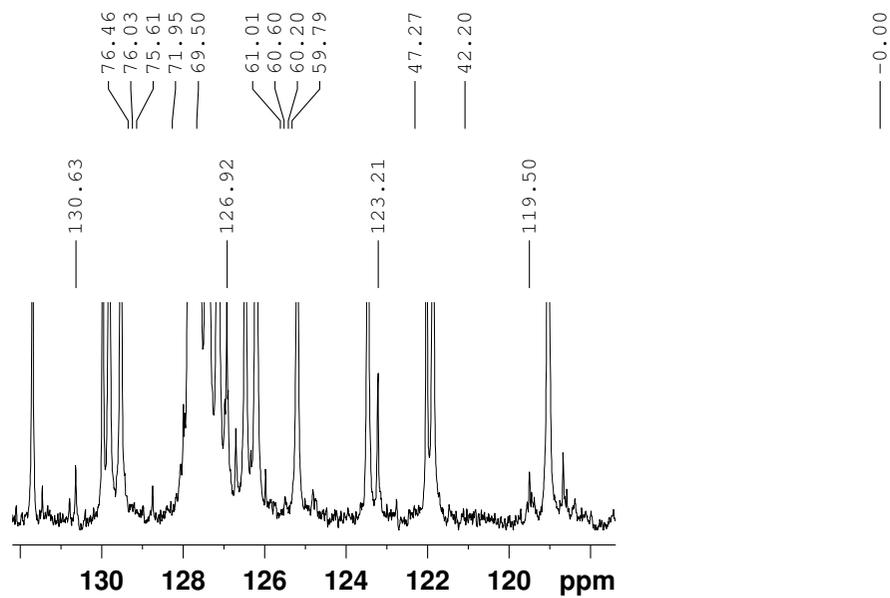
2.08  
3.07  
2.01  
3.12  
3.03  
3.06  
3.12  
1.10  
2.07  
1.09  
1.10  
1.05  
1.09  
1.09  
1.04  
1.00

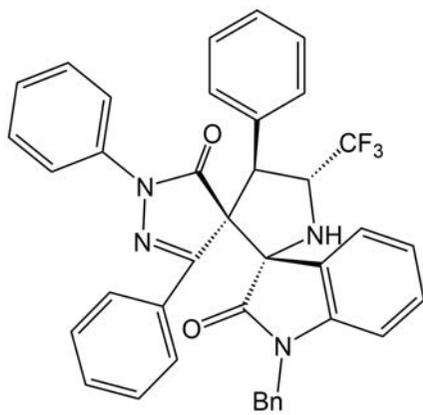
173.11  
169.59  
153.38  
142.04  
135.54  
133.69  
131.69  
130.63  
129.97  
129.81  
129.53  
127.82  
127.77  
127.62  
127.39  
127.14  
126.92  
126.46  
126.20  
125.19  
123.46  
123.21  
122.01  
121.86  
119.50  
119.04  
108.38



**3ad**

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )

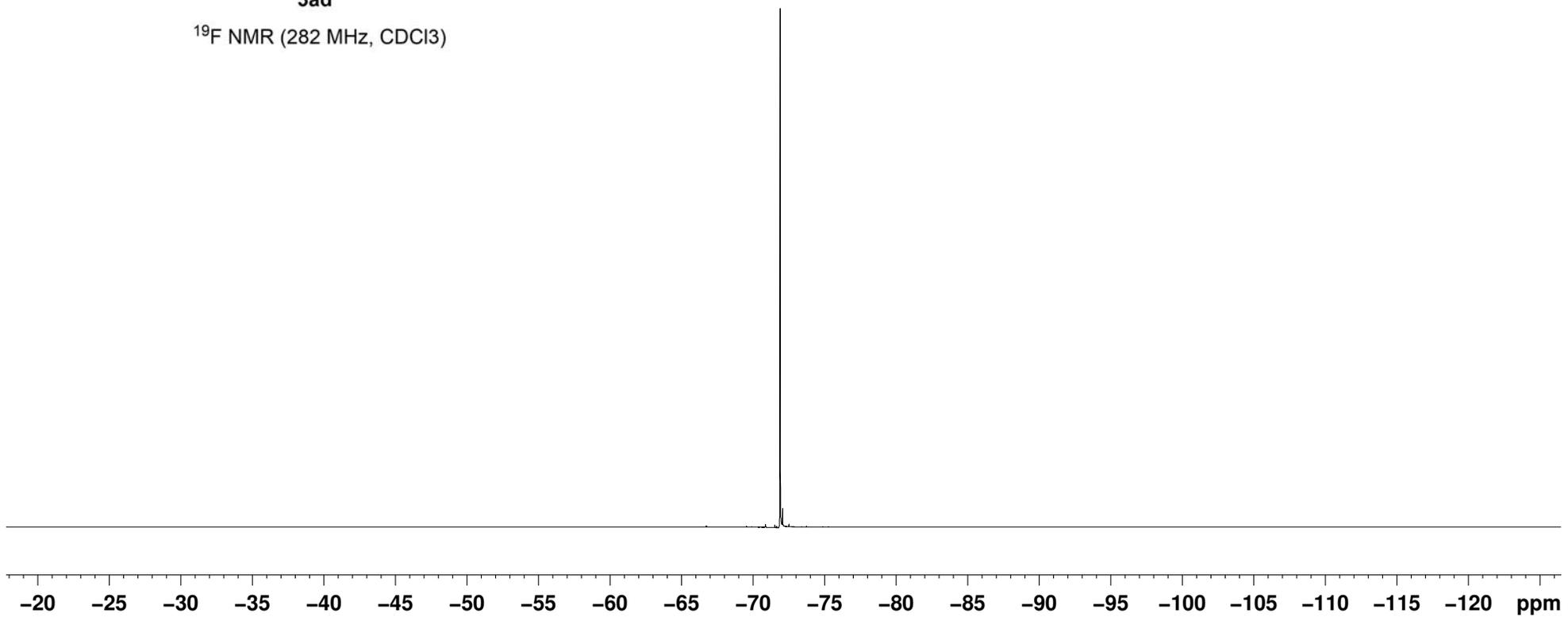




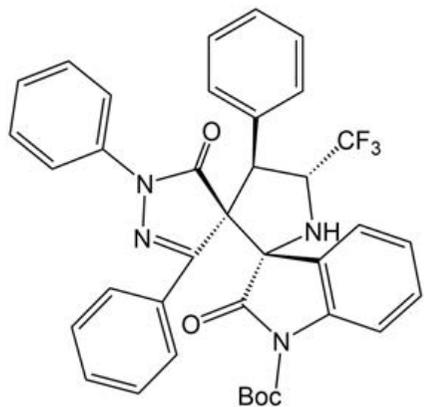
**3ad**

<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)

— -71.899



7.481  
7.479  
7.471  
7.464  
7.449  
7.438  
7.424  
7.418  
7.409  
7.337  
7.331  
7.313  
7.286  
7.258  
7.235  
7.206  
7.203  
7.199  
7.188  
7.174  
7.150  
7.045  
7.021  
7.020  
6.996  
6.994  
5.731  
5.697  
5.595  
5.571  
5.564  
5.539  
5.515  
5.507

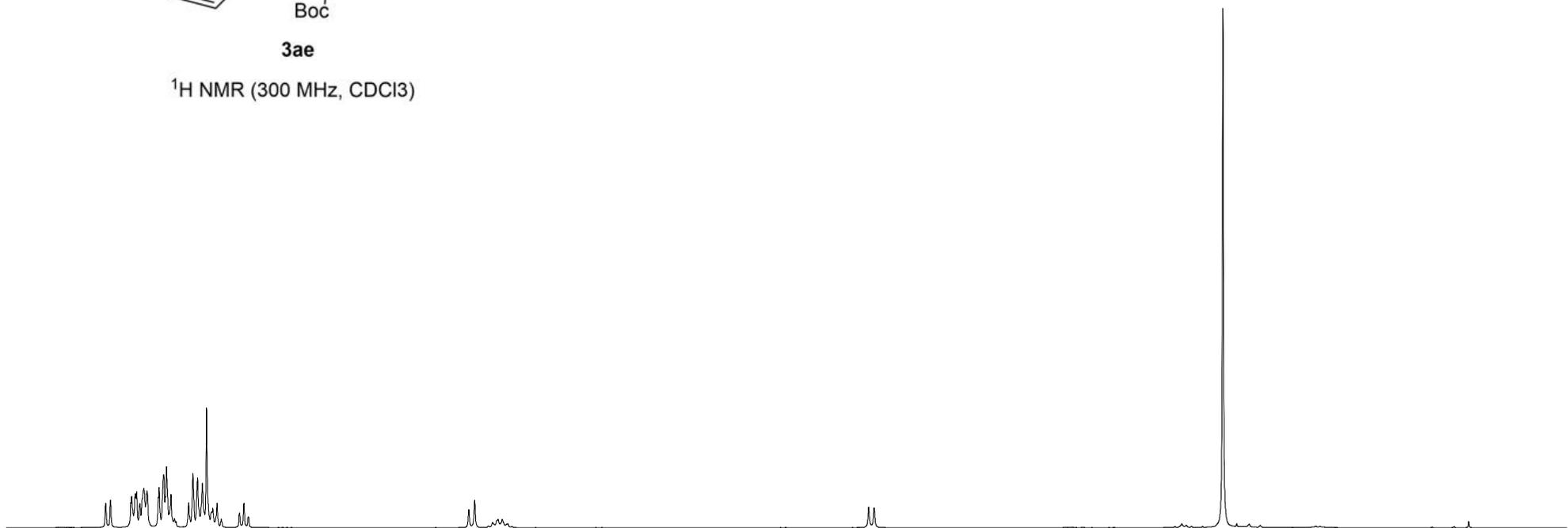


**3ae**

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

3.439  
3.408

1.409



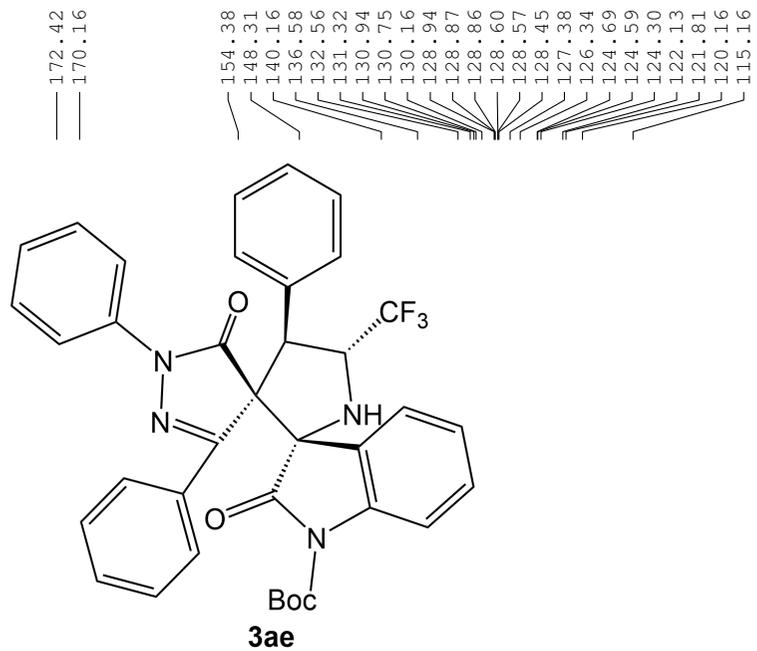
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

1.05  
2.02  
3.03  
2.13  
2.07  
3.03  
5.09  
1.06

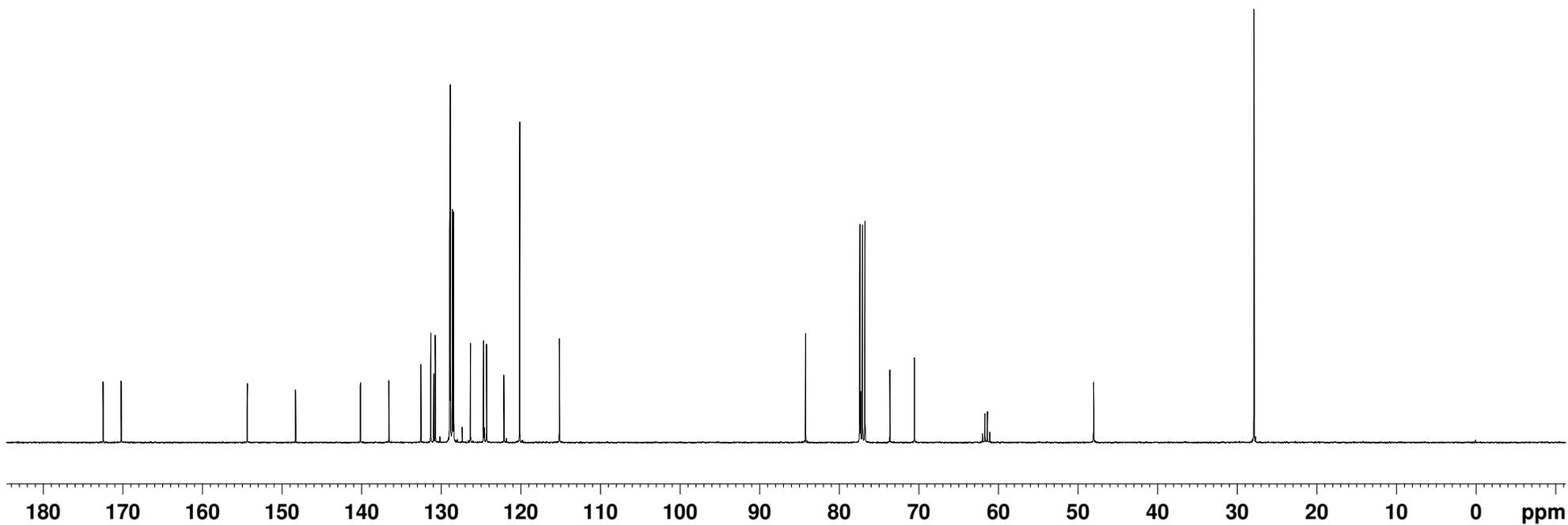
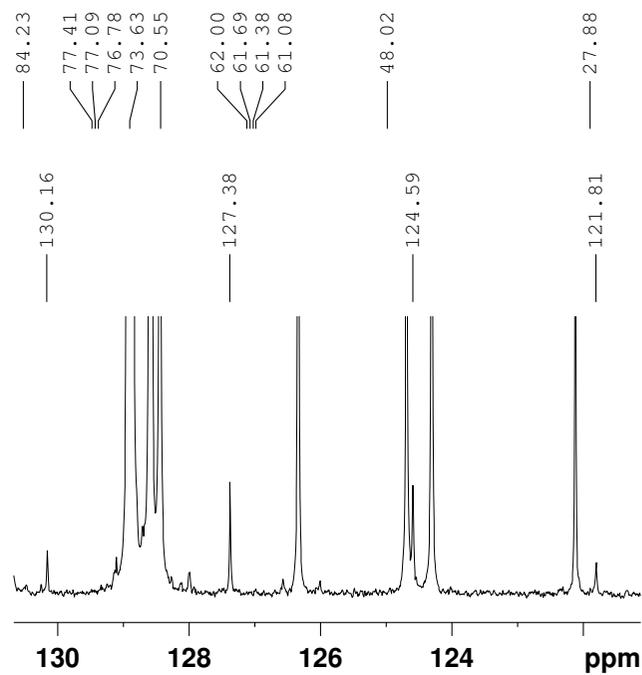
1.00  
1.02

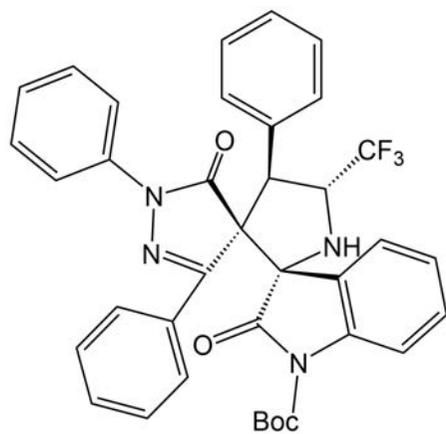
1.00

9.05



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

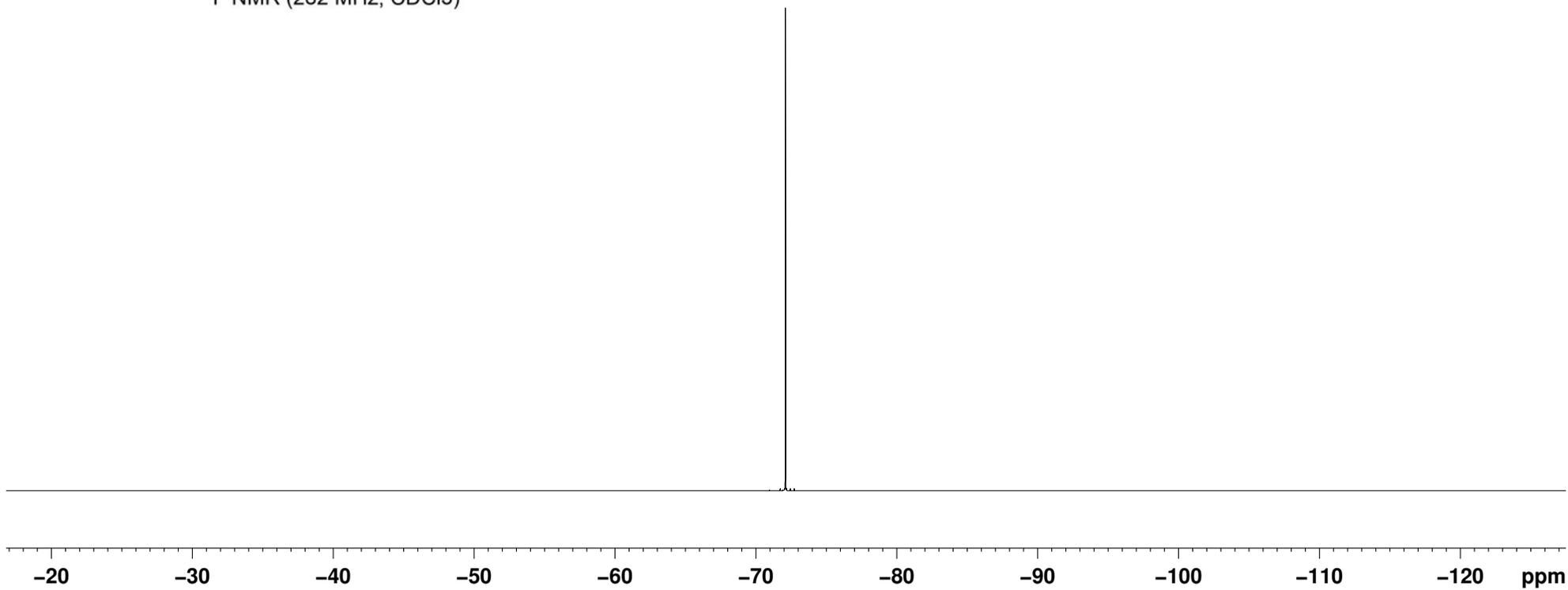




**3ae**

<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)

— -72.090

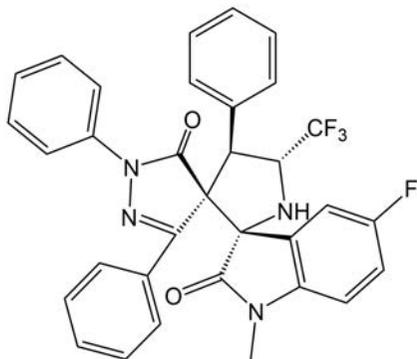


7.252  
7.242  
7.224  
7.214  
7.207  
7.194  
7.176  
7.169  
7.162  
7.158  
7.154  
7.150  
7.130  
7.105  
6.933  
6.924  
6.904  
6.896  
6.875  
6.867  
6.485  
6.471  
6.456  
6.443  
5.711  
5.678  
5.463  
5.439  
5.431  
5.415  
5.407  
5.382  
5.374  
5.358  
5.349  
5.325

3.413  
3.381

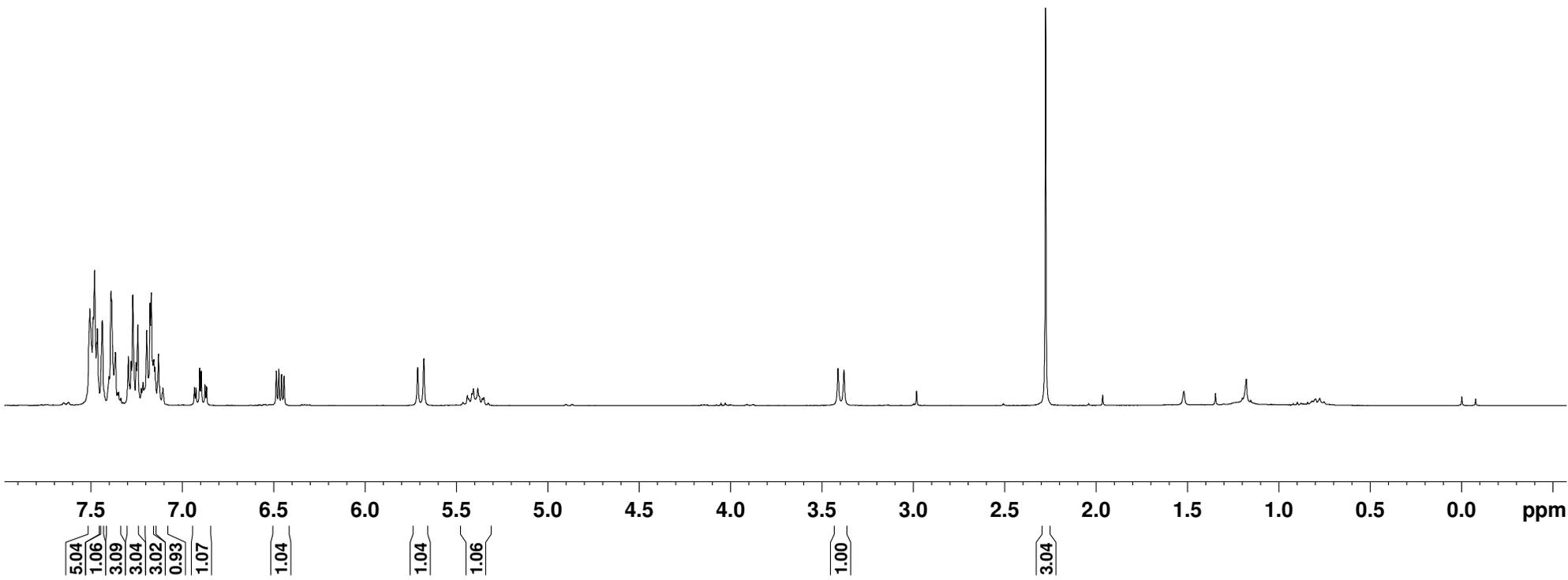
2.277

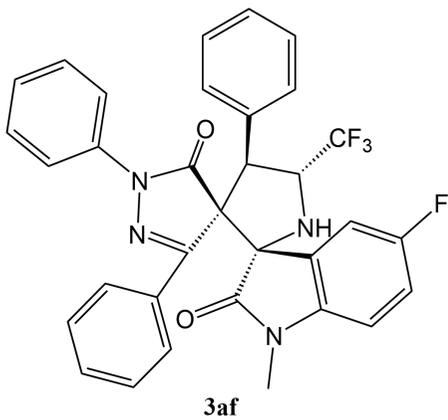
-0.000



3af

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)





**3af**

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

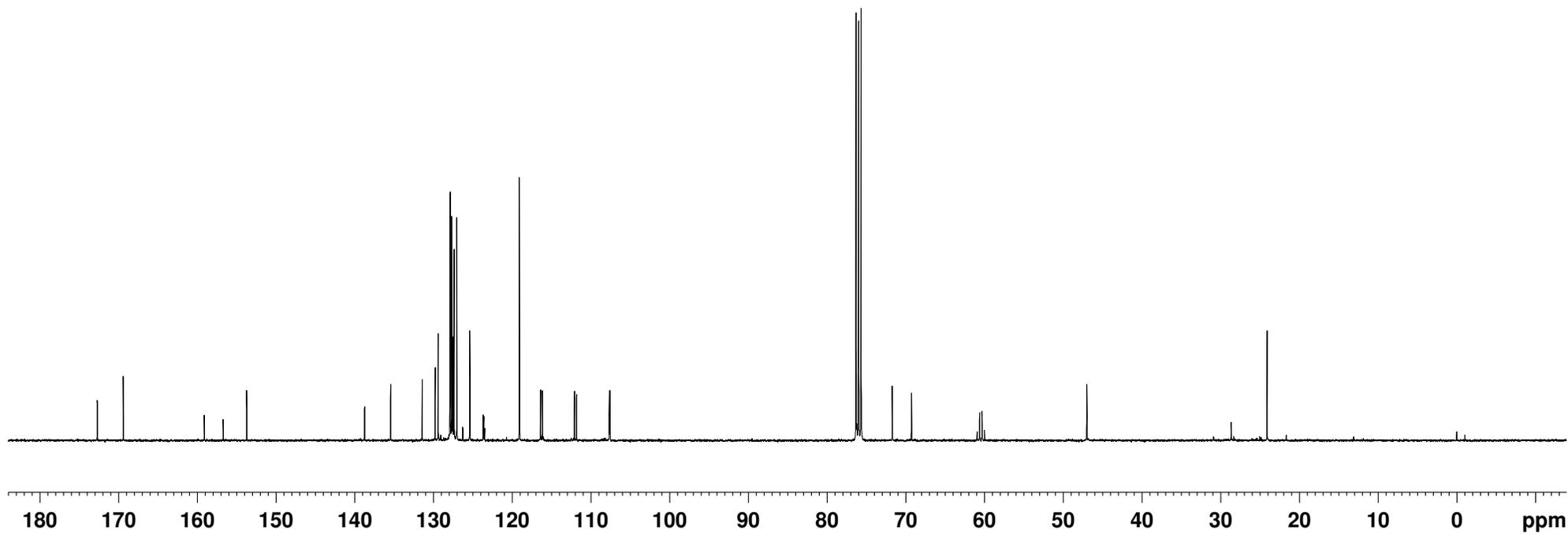
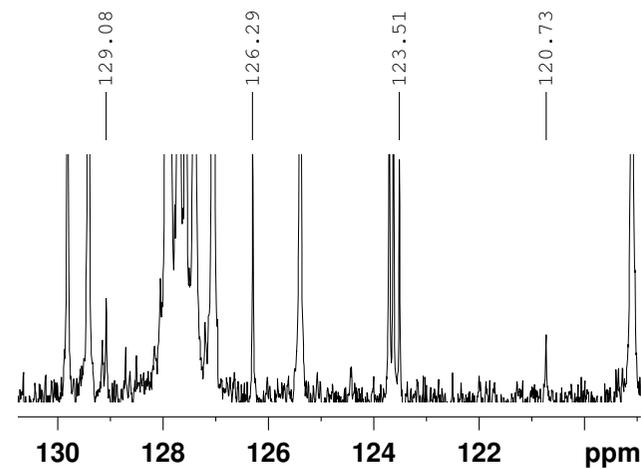
172.67  
169.42  
159.14  
156.73  
153.75  
138.78  
138.76  
135.46  
131.45  
129.81  
129.42  
129.08  
127.92  
127.89  
127.70  
127.57  
127.40  
127.05  
126.29  
125.39  
123.51  
120.73  
119.10  
116.42  
116.18  
112.11  
111.85  
107.69  
107.61

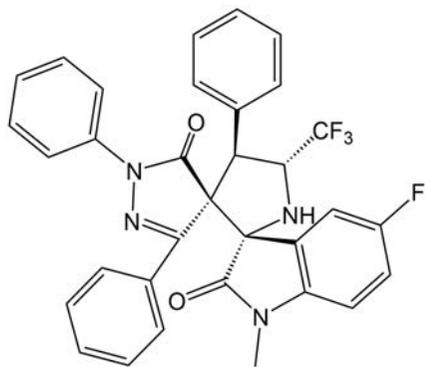
76.32  
76.01  
75.69  
71.73  
69.29  
69.28  
60.93  
60.62  
60.32  
60.01

47.01

24.10

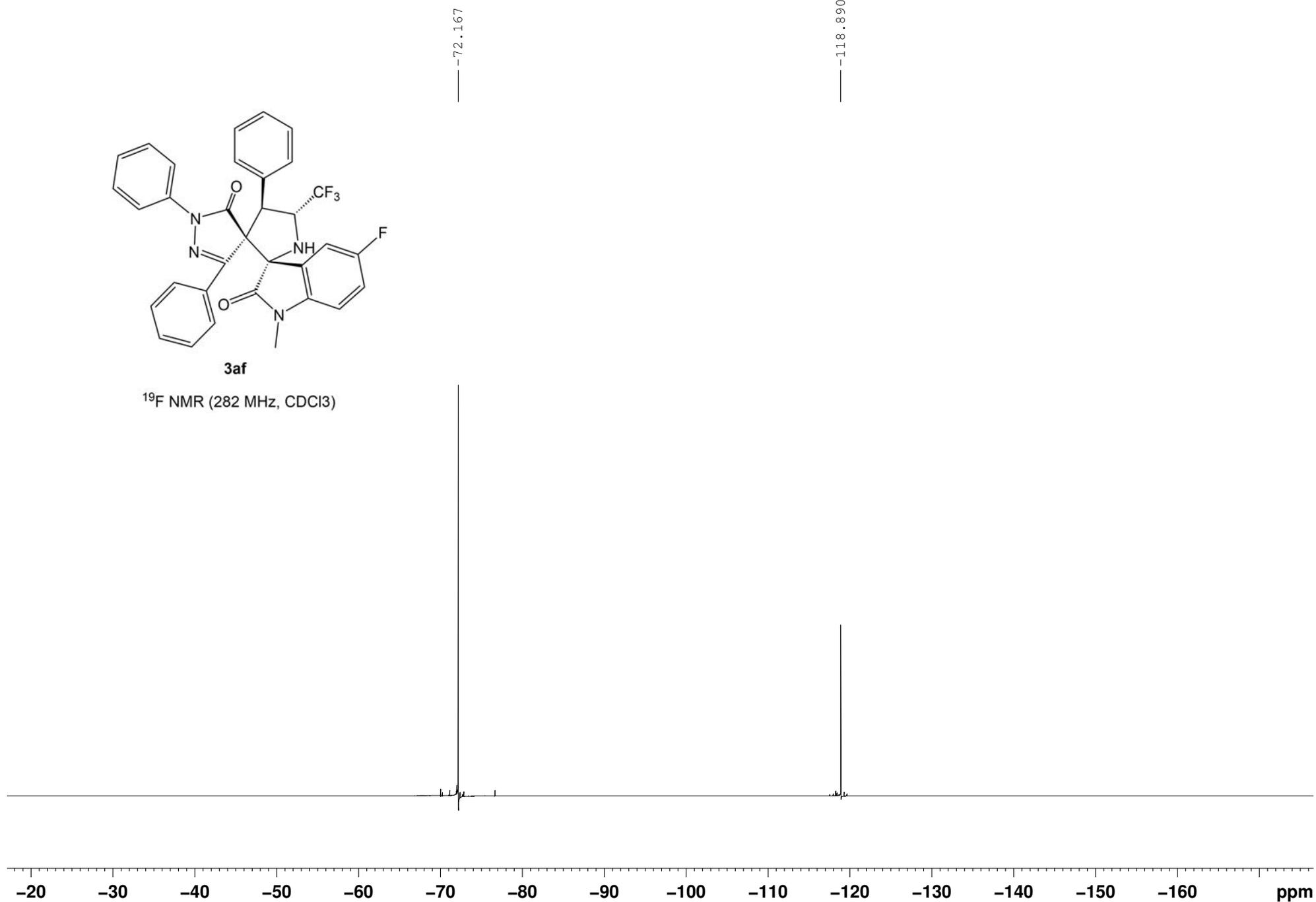
-0.00





3af

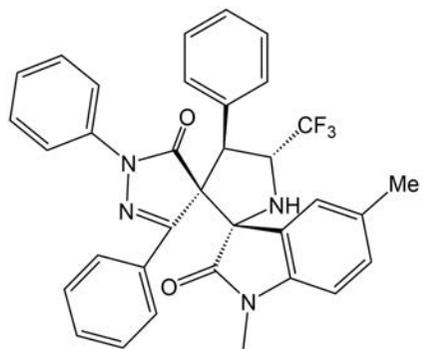
<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)



7.427  
7.422  
7.407  
7.396  
7.391  
7.355  
7.349  
7.329  
7.325  
7.303  
7.292  
7.284  
7.277  
7.262  
7.236  
7.230  
7.207  
7.183  
7.158  
7.033  
7.007  
6.490  
6.463  
5.824  
5.791  
5.552  
5.520  
5.495  
5.470  
5.463

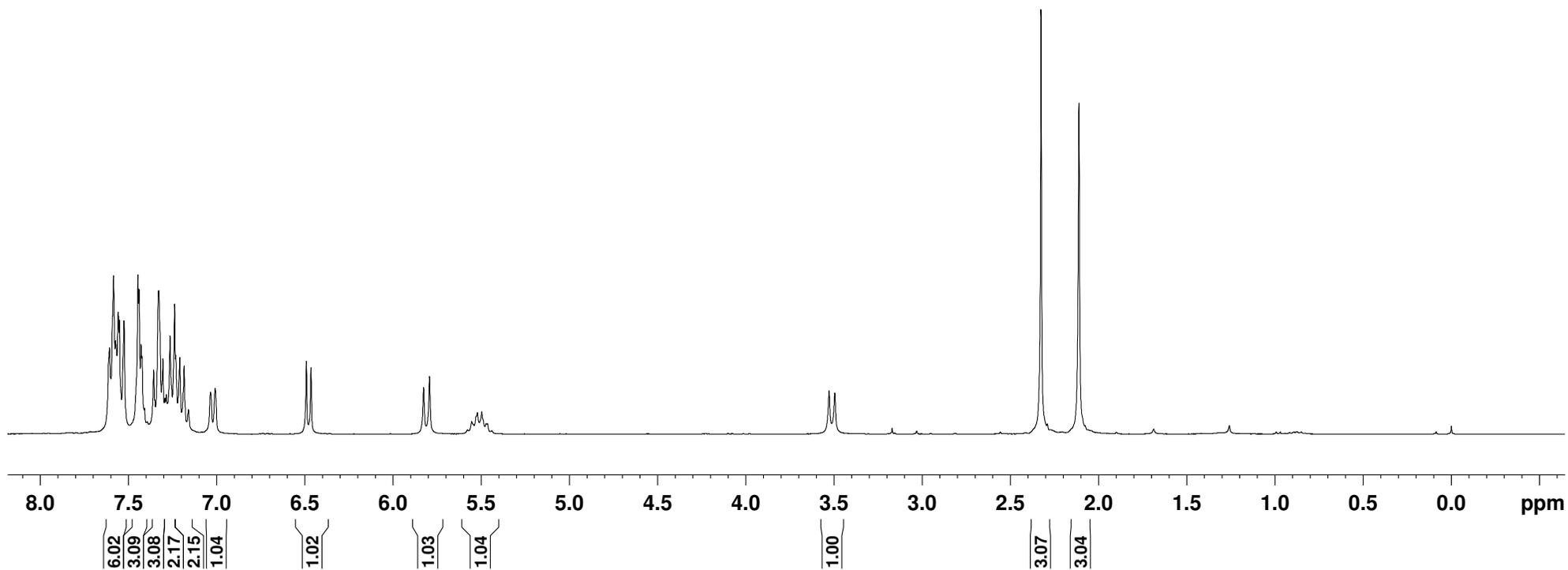
3.529  
3.496

2.326  
2.111

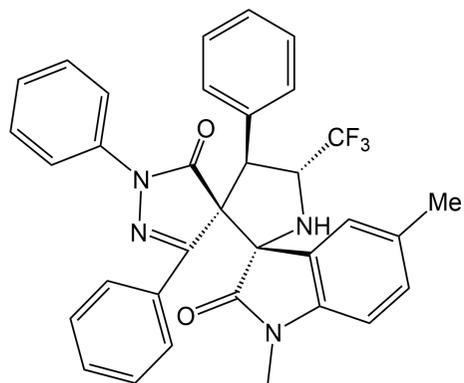


**3ag**

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

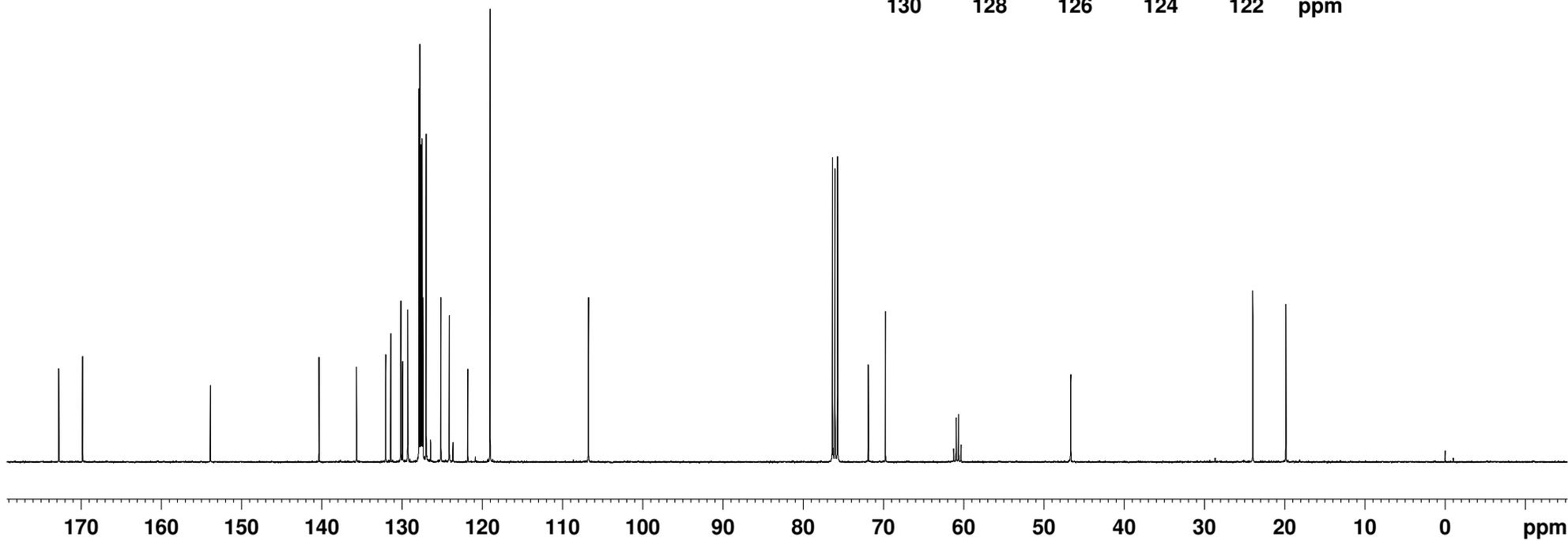
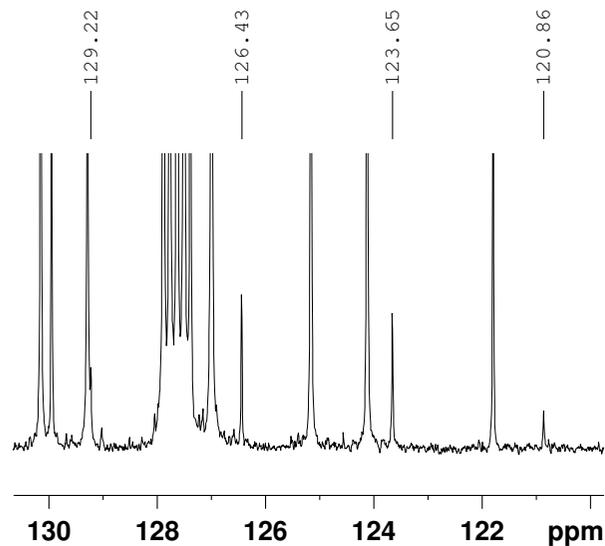


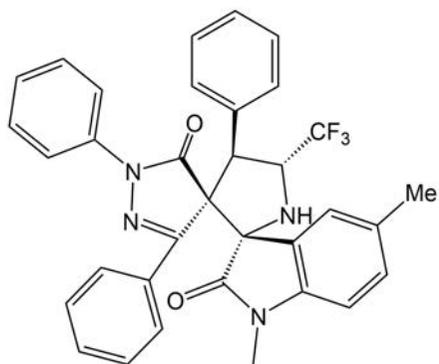
172.72  
169.75  
153.83  
140.29  
135.66  
132.03  
131.40  
130.14  
129.94  
129.28  
129.22  
127.88  
127.76  
127.63  
127.50  
127.38  
126.99  
126.43  
125.15  
124.11  
123.65  
121.79  
120.86  
119.02  
106.77



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

76.35  
76.03  
75.71  
71.89  
69.75  
61.24  
60.93  
60.63  
60.32  
46.65  
23.96  
19.84

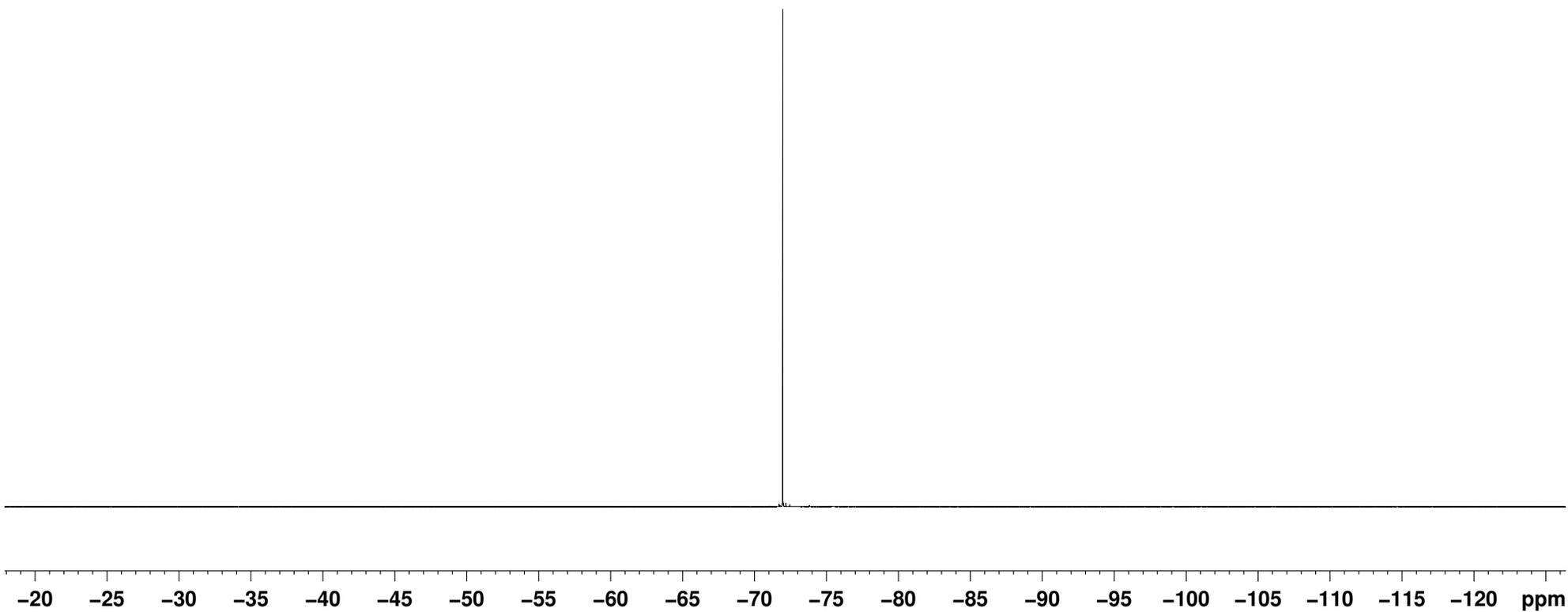




**3ag**

<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)

— -71.963

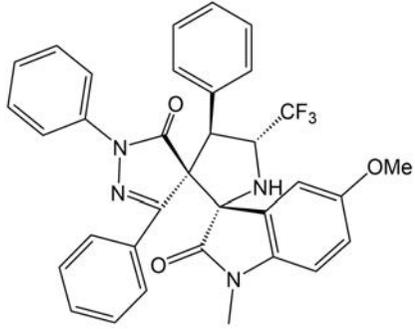


7.249  
7.222  
7.191  
7.188  
7.164  
7.139  
7.136  
7.127  
7.102  
7.085  
7.072  
7.065  
6.844  
6.820  
6.795  
6.706  
6.693  
6.685  
6.680  
6.676  
6.670  
6.663  
6.654  
6.529  
6.503  
5.708  
5.674  
5.448  
5.423  
5.416  
5.398  
5.390  
5.366  
5.341  
5.333  
5.308

3.580  
3.548  
3.519  
3.462  
3.430

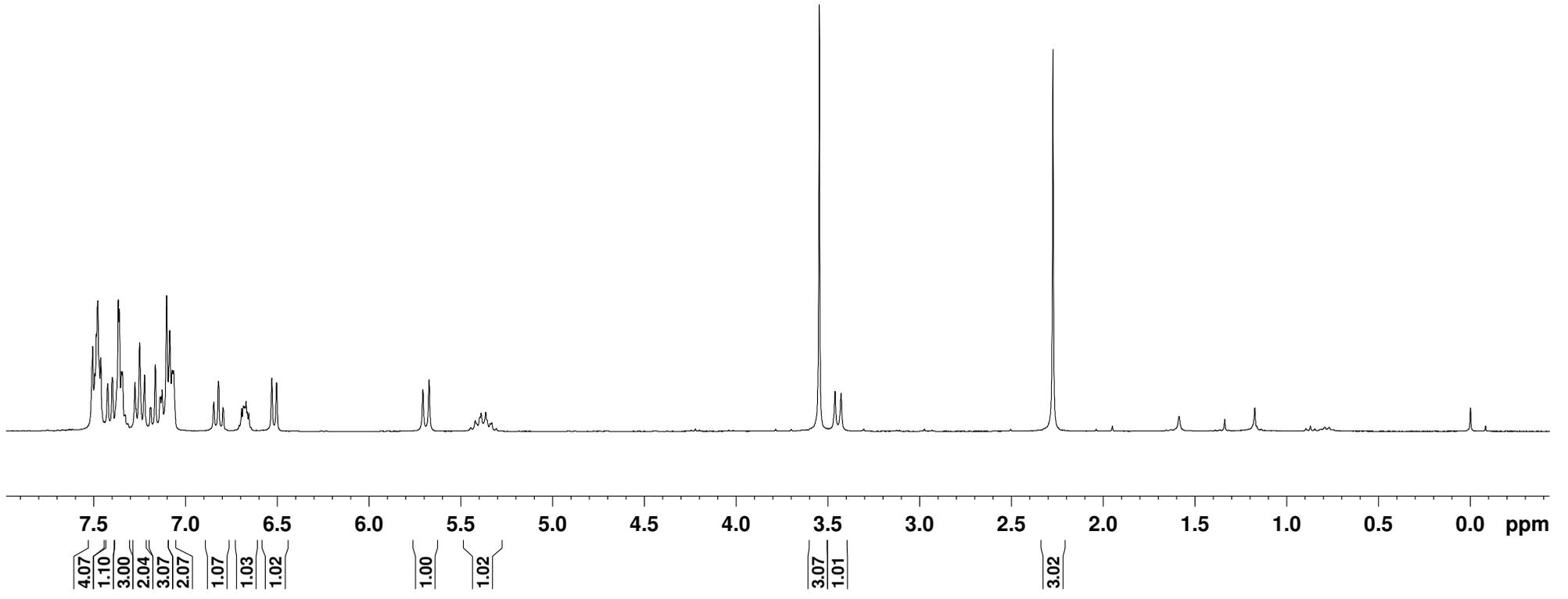
— 2.275

— -0.000

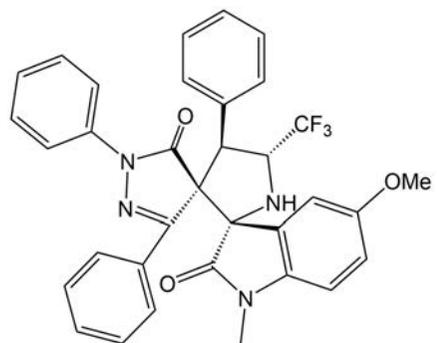


**3ah**

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)



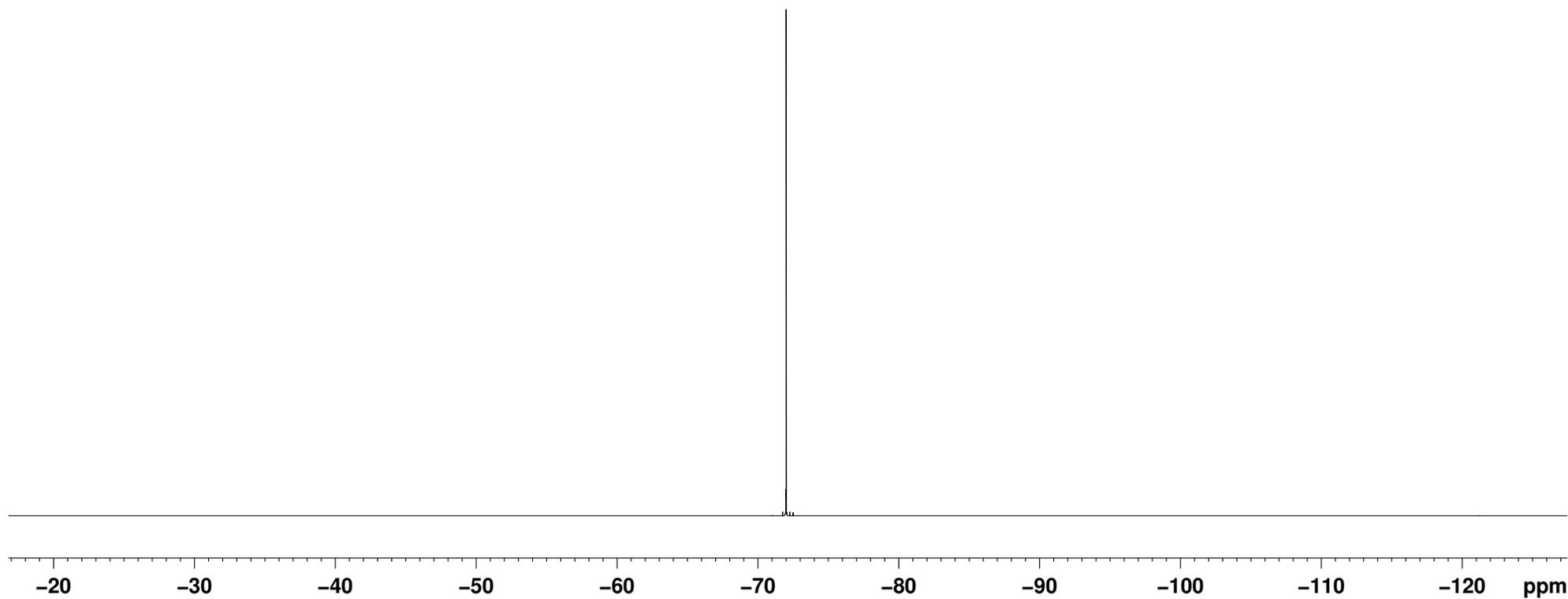




**3ah**

<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)

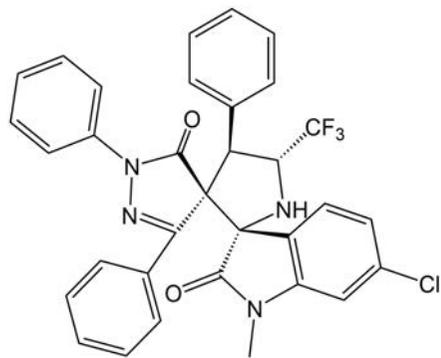
— -72.006



7.471  
7.453  
7.441  
7.436  
7.414  
7.408  
7.365  
7.341  
7.318  
7.297  
7.290  
7.271  
7.249  
7.228  
7.225  
7.205  
7.200  
7.178  
6.906  
6.900  
6.879  
6.873  
6.611  
5.768  
5.735  
5.544  
5.519  
5.493  
5.463  
5.437  
5.411

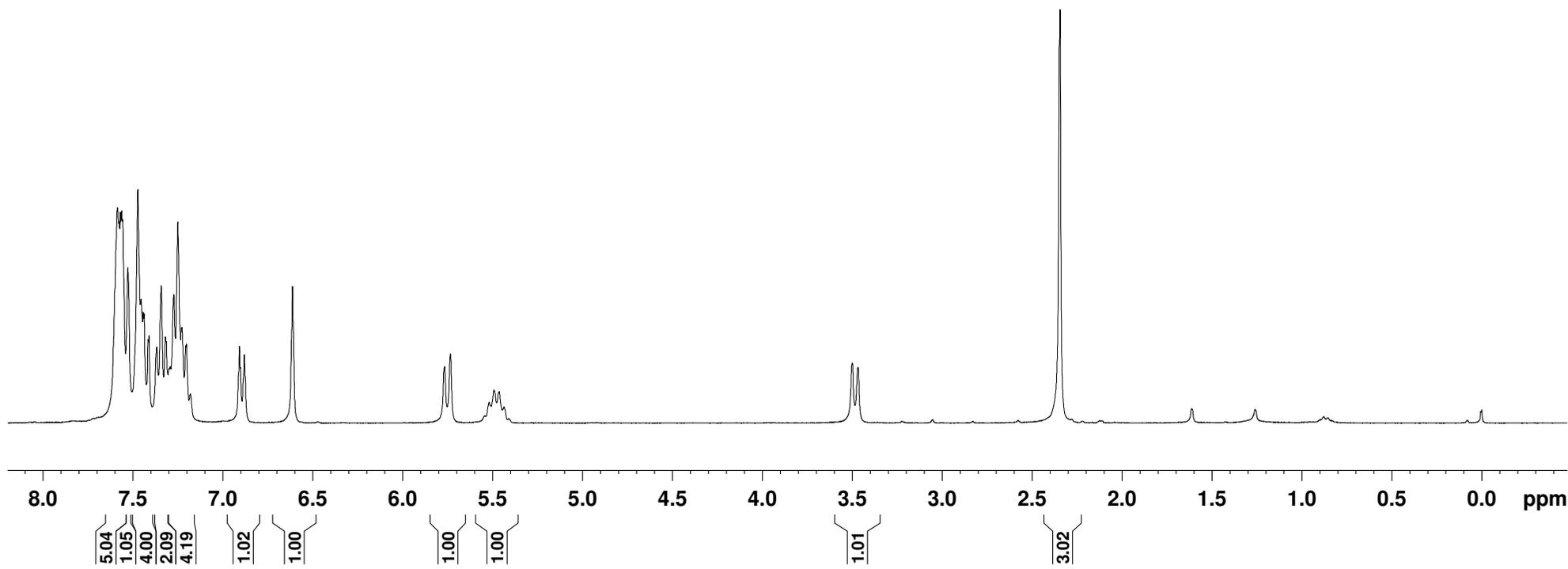
3.500  
3.469

2.344

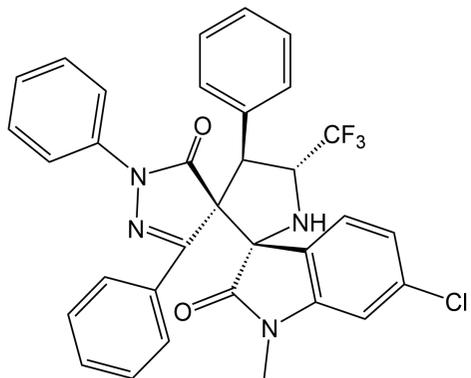


**3ai**

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

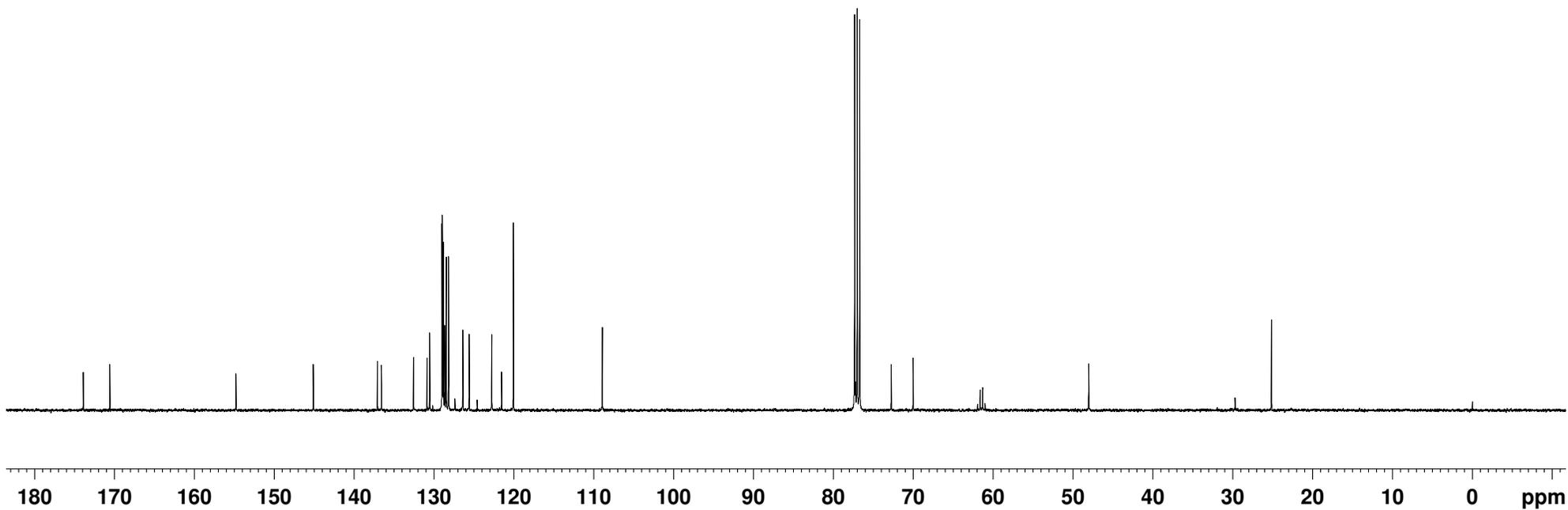
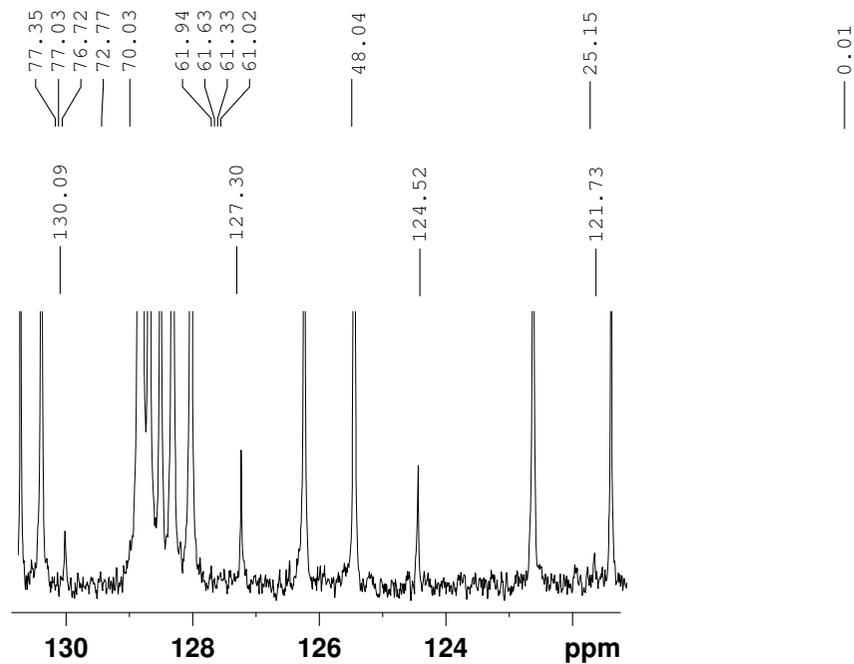


— 173.87  
 — 170.54  
 — 154.76  
 — 145.06  
 — 137.04  
 — 136.54  
 — 132.52  
 — 130.83  
 — 130.50  
 — 130.12  
 — 128.96  
 — 128.90  
 — 128.79  
 — 128.61  
 — 128.42  
 — 128.13  
 — 127.33  
 — 126.35  
 — 125.56  
 — 124.55  
 — 122.73  
 — 121.50  
 — 120.02  
 — 108.89



**3ai**

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

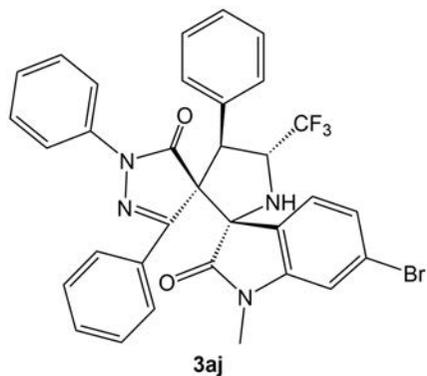




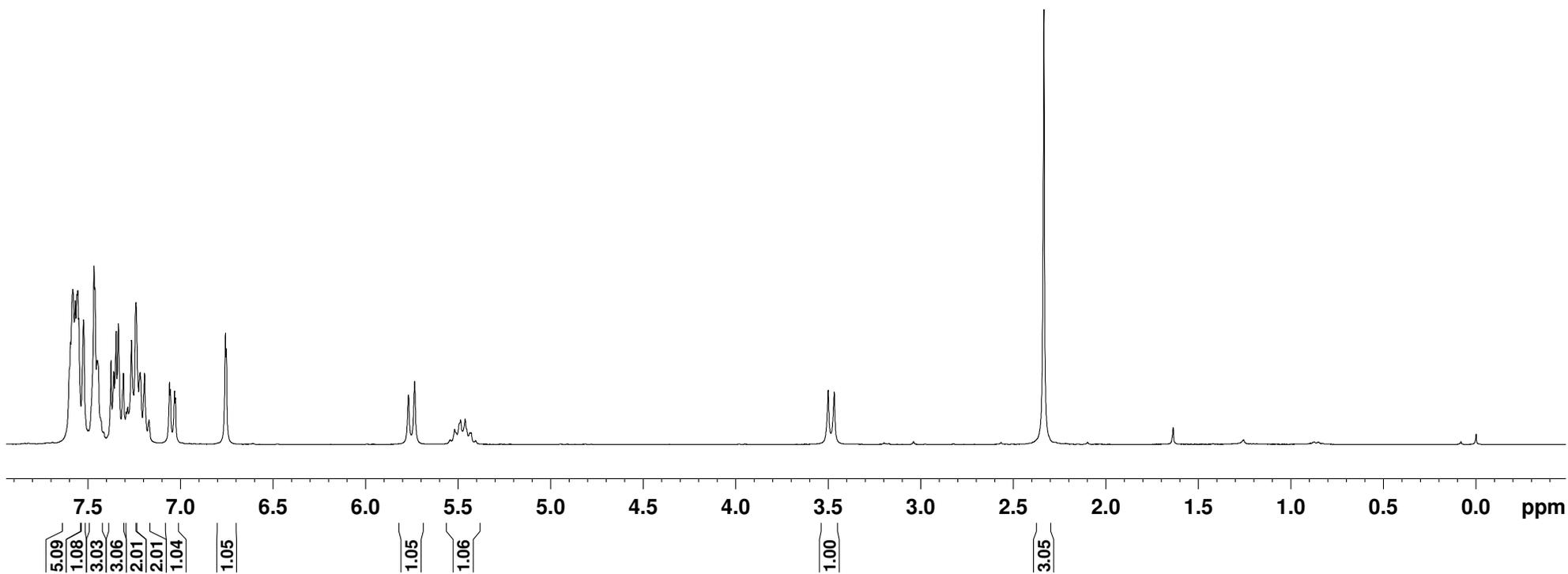
7.418  
7.414  
7.375  
7.360  
7.347  
7.335  
7.307  
7.293  
7.284  
7.264  
7.239  
7.218  
7.193  
7.169  
7.059  
7.053  
7.032  
7.026  
6.757  
6.751  
5.767  
5.734  
5.544  
5.520  
5.495  
5.488  
5.463  
5.438  
5.431  
5.406

3.501  
3.469

2.336

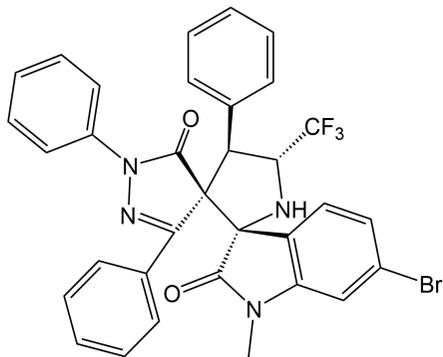


<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)



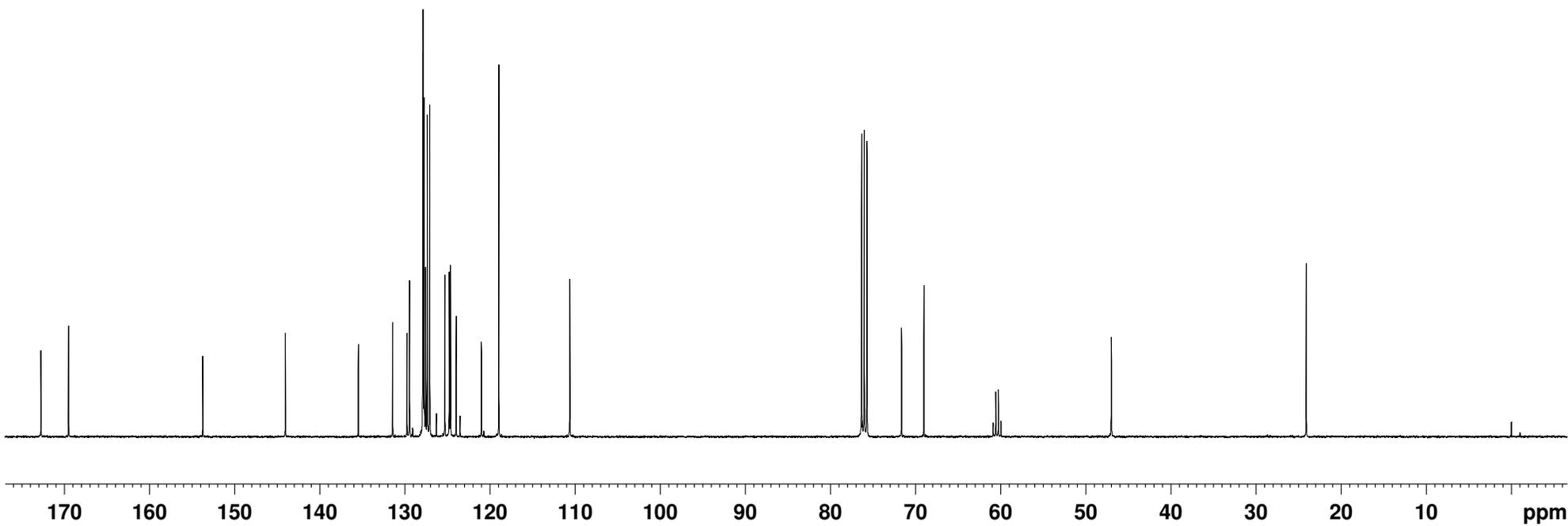
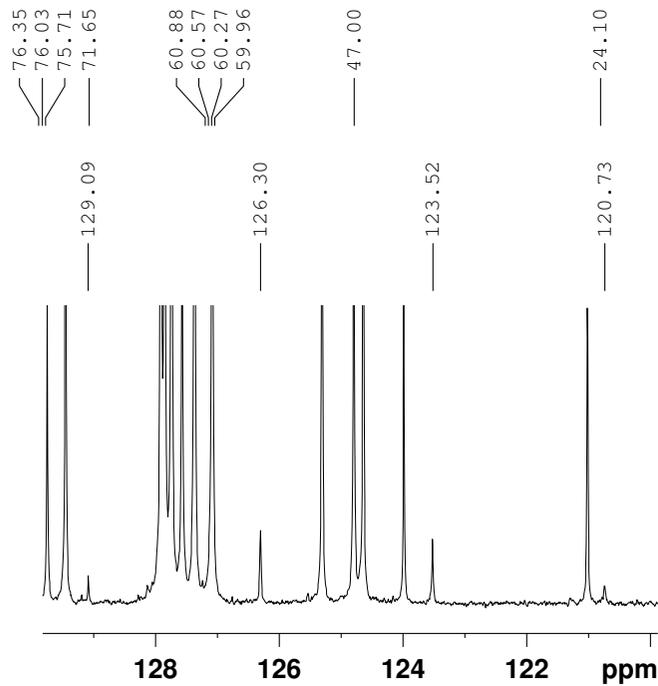
— 172.71  
— 169.46

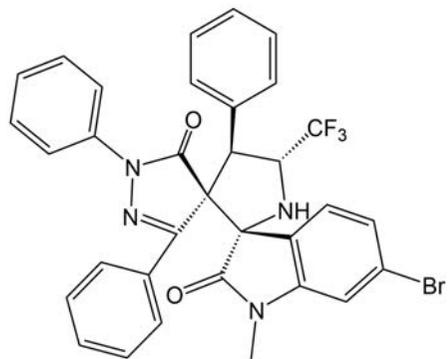
— 153.71  
— 144.05  
— 135.47  
— 131.44  
— 129.75  
— 129.46  
— 129.09  
— 127.91  
— 127.85  
— 127.74  
— 127.57  
— 127.37  
— 127.08  
— 126.30  
— 125.30  
— 124.79  
— 124.64  
— 123.98  
— 123.52  
— 121.01  
— 120.73  
— 118.96  
— 110.63



**3aj**

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

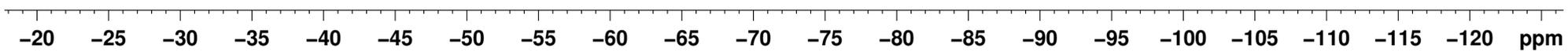




3aj

<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)

-72.113

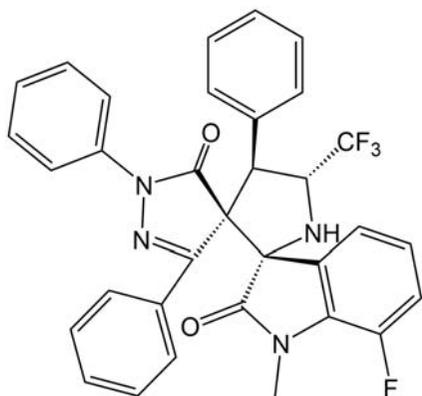


7.472  
7.463  
7.368  
7.365  
7.341  
7.318  
7.291  
7.283  
7.262  
7.244  
7.237  
7.221  
7.209  
7.205  
7.180  
7.166  
7.159  
7.156  
6.907  
6.901  
6.883  
6.878  
6.770  
6.743  
6.717  
5.779  
5.745  
5.613  
5.576  
5.551  
5.520  
5.495  
5.470  
5.463  
5.438

3.473  
3.441  
3.241  
3.231  
3.211  
3.196

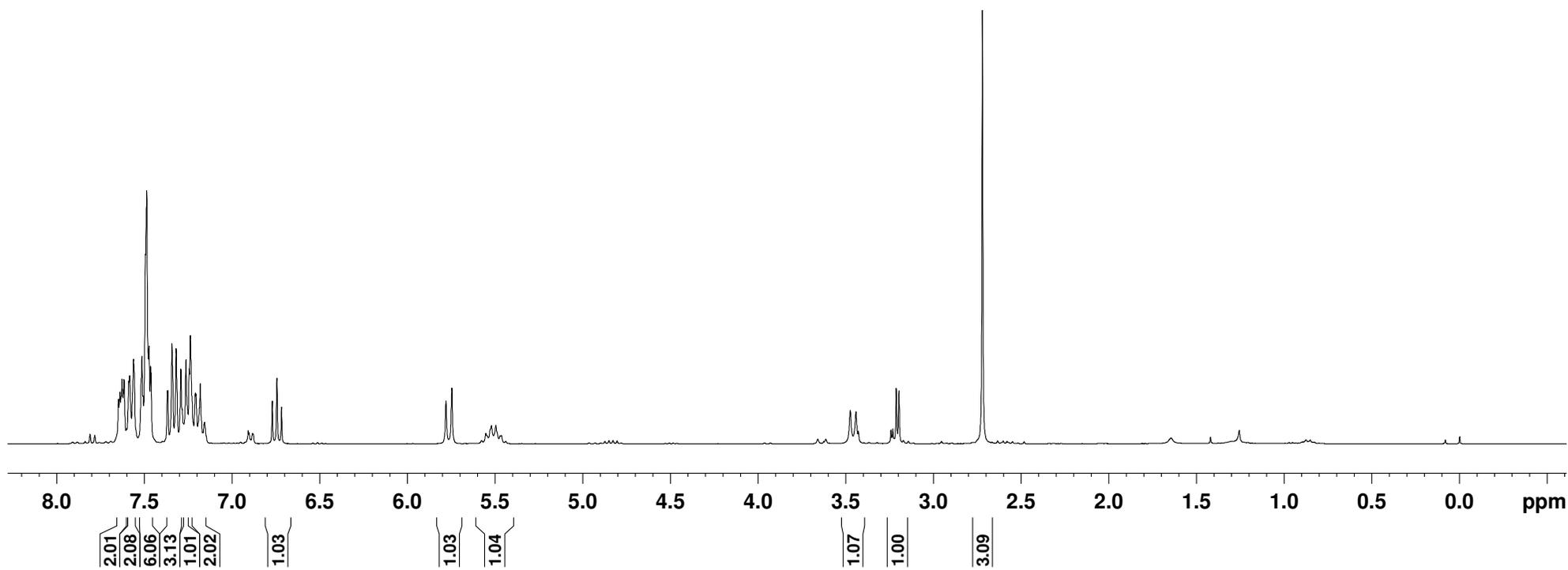
2.719

0.000

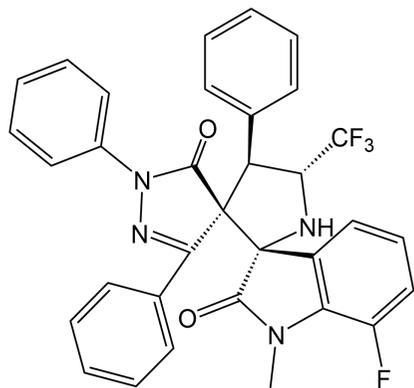


**3ak**

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

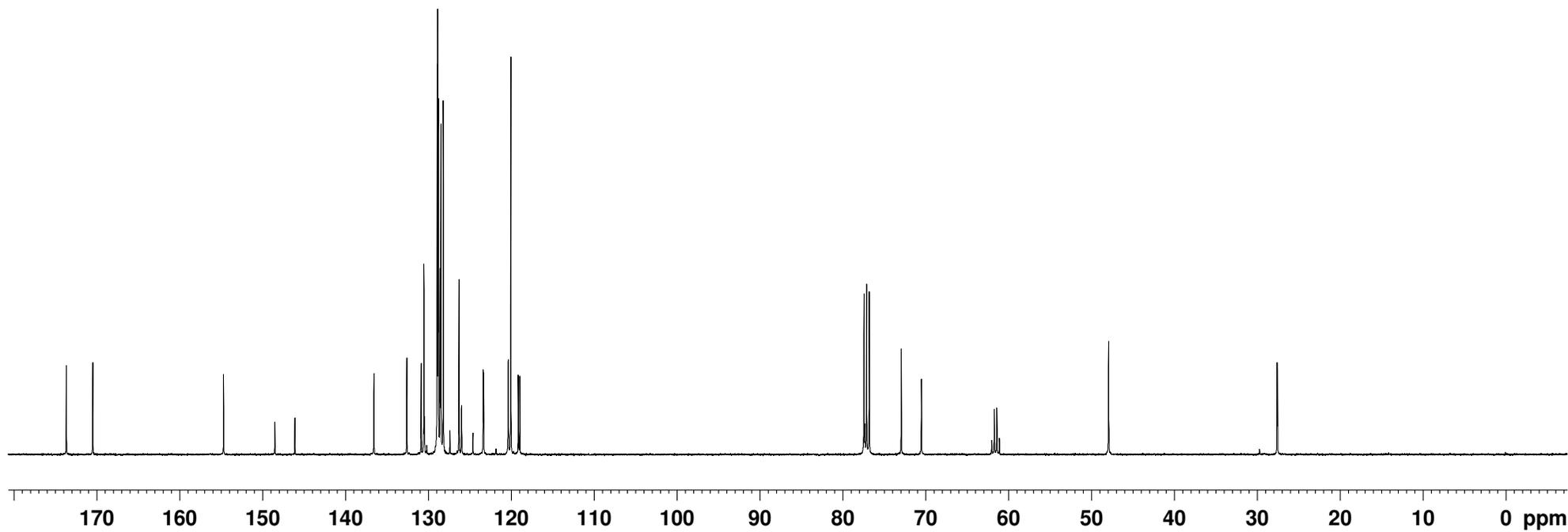
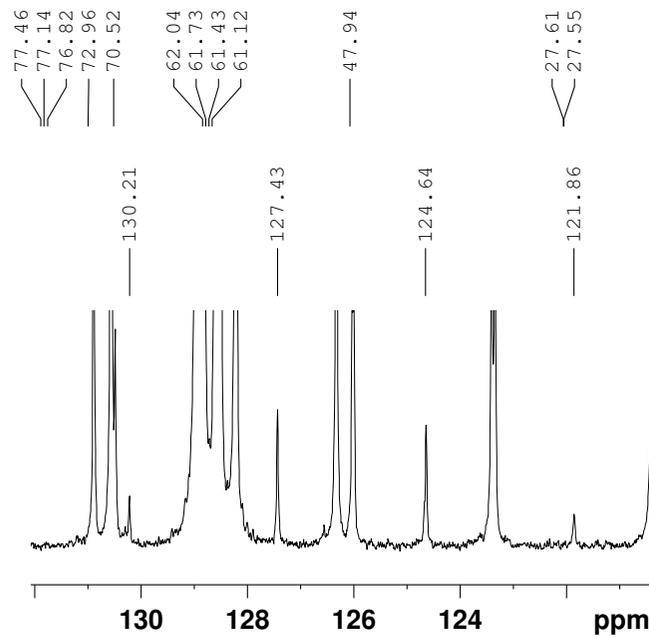


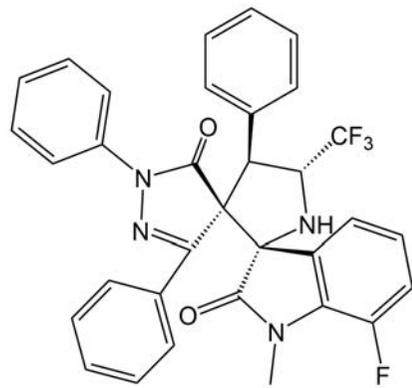
173.66  
170.47  
154.74  
148.55  
146.12  
136.59  
132.62  
130.89  
130.56  
130.21  
128.97  
128.88  
128.82  
128.60  
128.51  
128.22  
127.43  
126.32  
126.02  
126.00  
124.64  
123.41  
123.35  
121.86  
120.40  
120.37  
120.07  
119.18  
118.99



**3ak**

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)





3ak

<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)

— — -72.092

— — -135.985



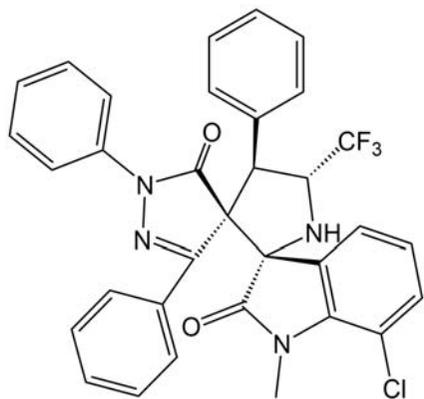
7.561  
7.517  
7.491  
7.482  
7.470  
7.444  
7.421  
7.419  
7.345  
7.319  
7.292  
7.284  
7.263  
7.238  
7.210  
7.207  
7.187  
7.182  
7.160  
6.837  
6.811  
6.785

5.784  
5.750  
5.541  
5.518  
5.492

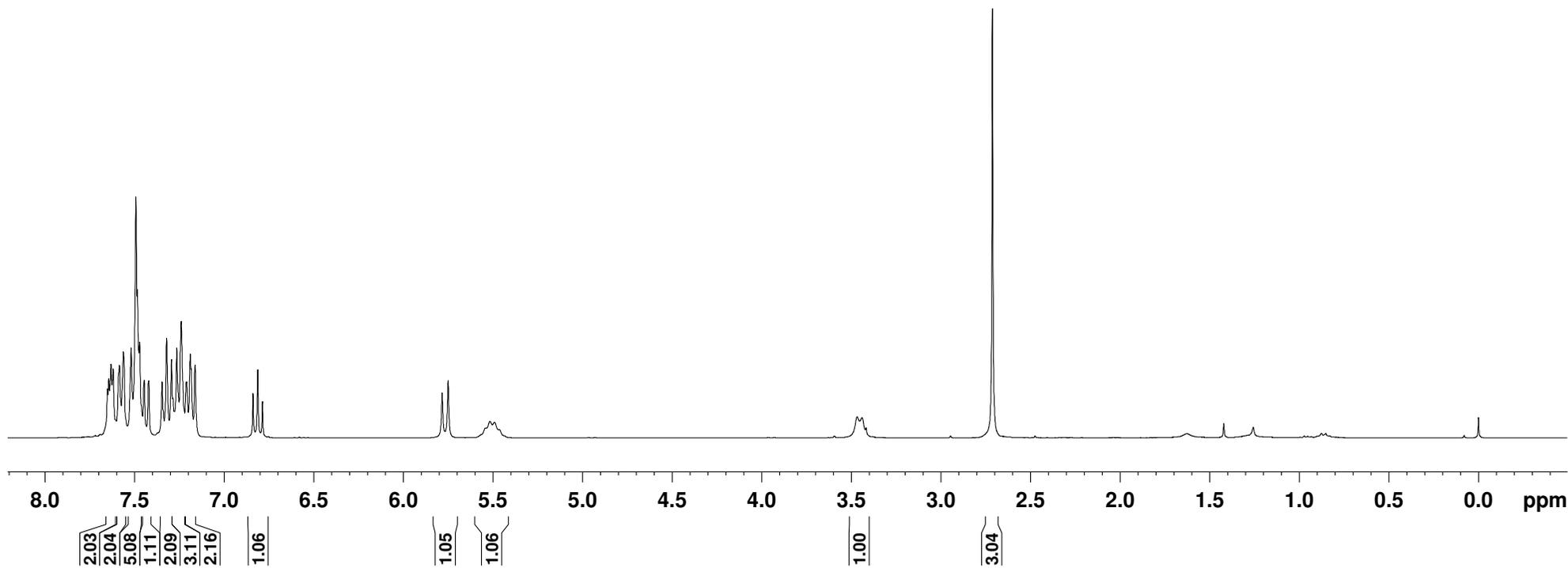
3.468  
3.441  
3.418  
3.381

2.712

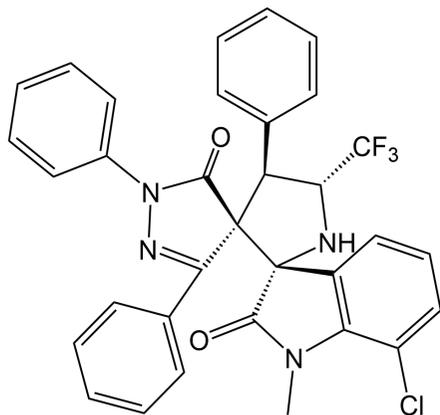
-0.000



<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

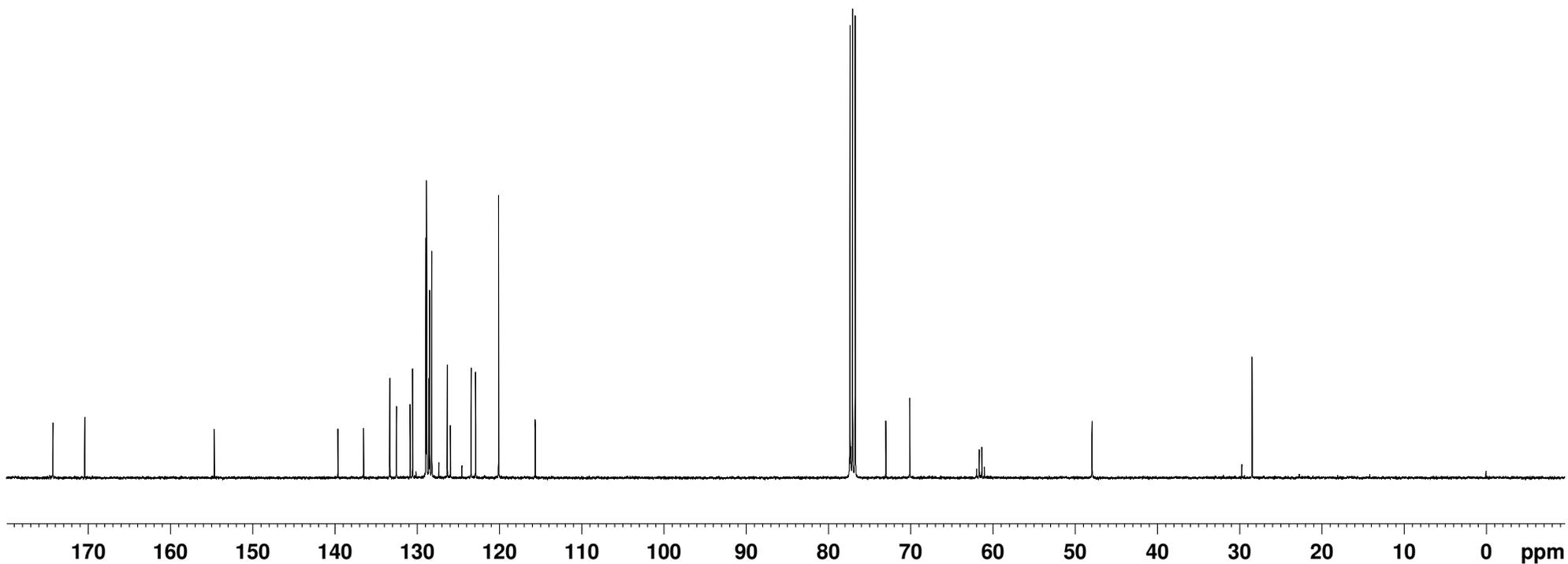
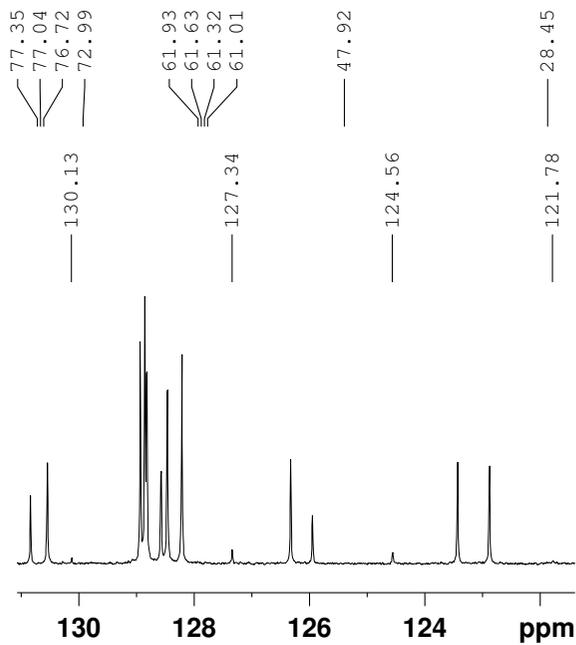


— 174.25  
 — 170.37  
 — 154.67  
 139.63  
 136.52  
 133.31  
 132.52  
 130.84  
 130.55  
 130.13  
 128.94  
 128.86  
 128.82  
 128.58  
 128.47  
 128.22  
 127.34  
 126.33  
 125.95  
 124.56  
 123.43  
 122.88  
 120.09  
 115.63



**3al**

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



— 0.01

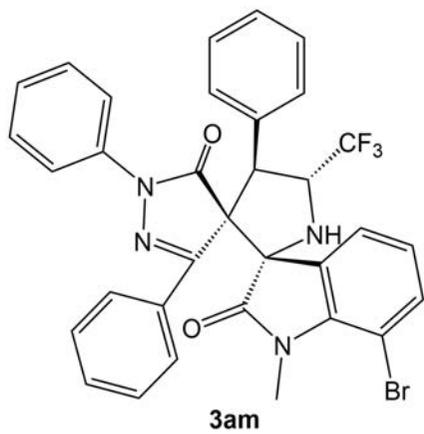


7.485  
7.472  
7.464  
7.368  
7.365  
7.341  
7.318  
7.291  
7.283  
7.276  
7.262  
7.244  
7.237  
7.221  
7.209  
7.205  
7.186  
7.180  
7.166  
7.159  
7.156  
7.146  
6.770  
6.744  
6.717  
5.779  
5.745  
5.576  
5.552  
5.520  
5.495  
5.470  
5.463  
5.438

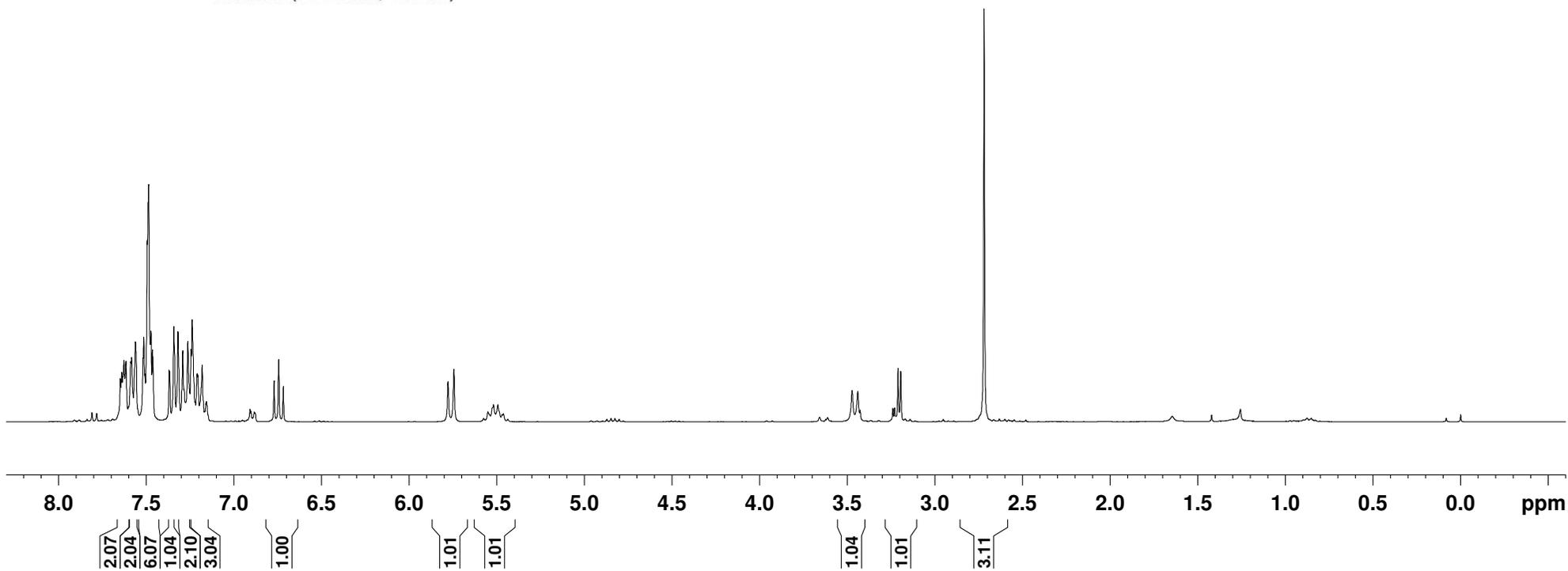
3.473  
3.441  
3.427  
3.241  
3.231  
3.211  
3.196

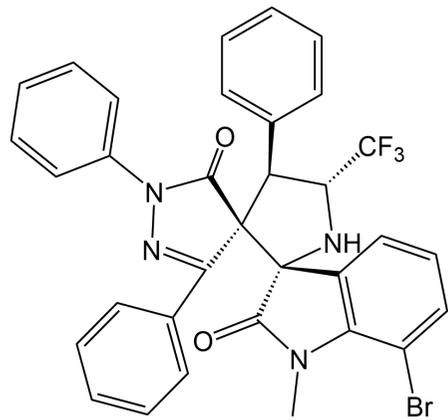
2.719

-0.000



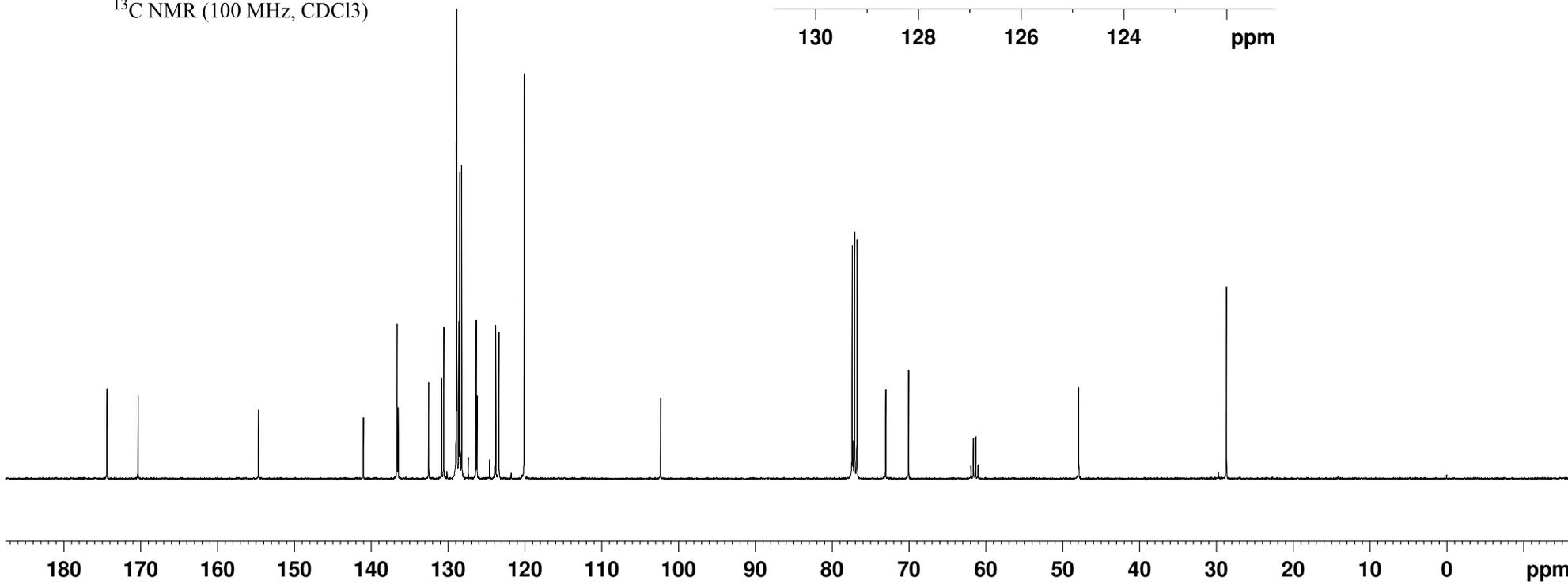
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)



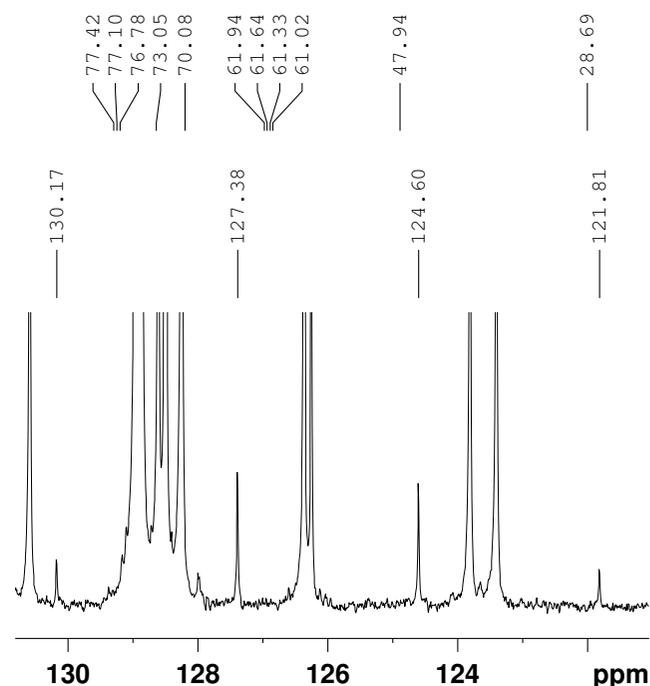


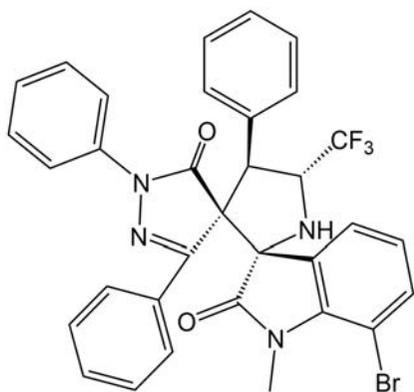
**3am**

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



174.43  
170.37  
154.68  
141.05  
136.65  
136.52  
132.54  
130.86  
130.58  
130.17  
128.96  
128.88  
128.86  
128.60  
128.49  
128.24  
127.38  
126.36  
126.25  
124.60  
123.80  
123.40  
121.81  
120.11  
102.36

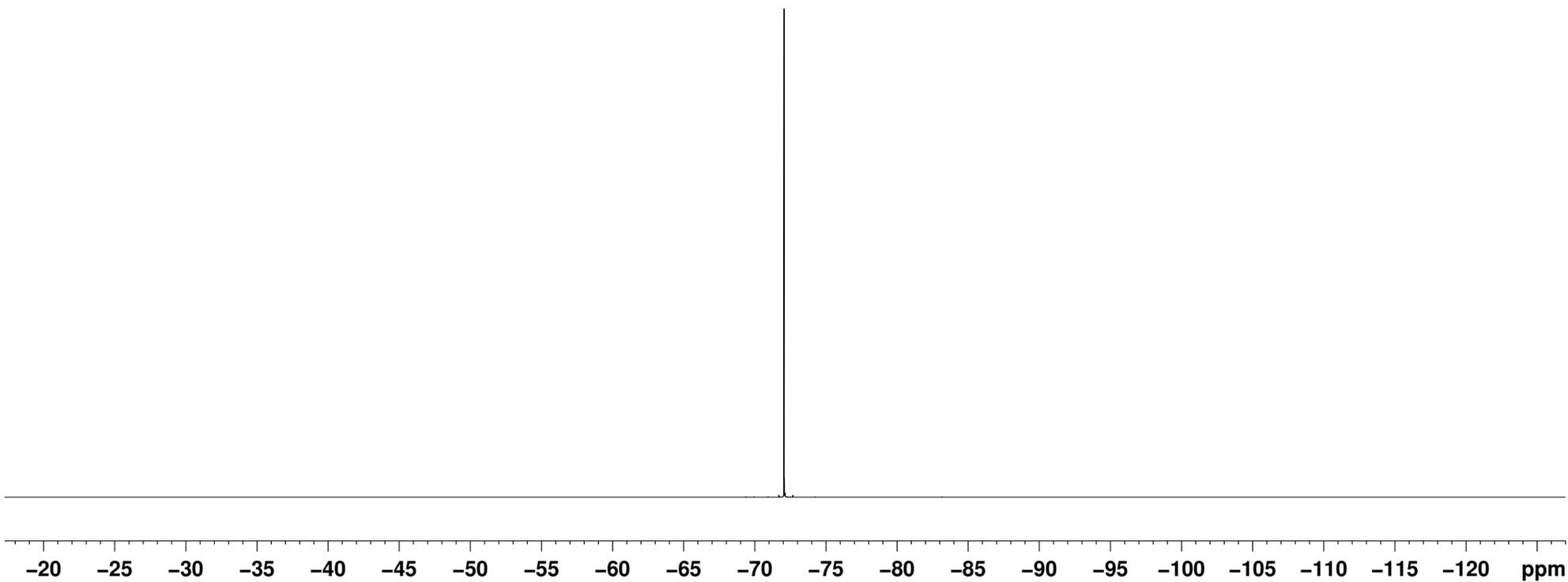




**3am**

<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)

— -72.065

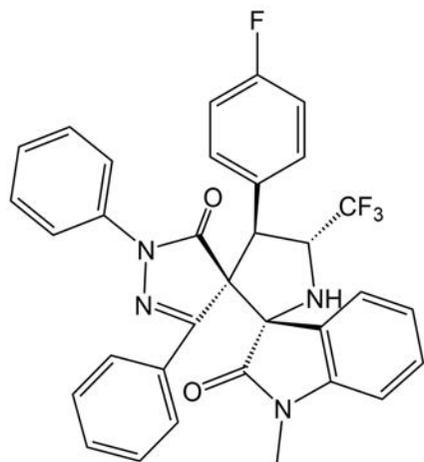


7.441  
7.429  
7.424  
7.409  
7.393  
7.341  
7.335  
7.316  
7.289  
7.247  
7.244  
7.221  
7.194  
7.170  
7.145  
6.973  
6.945  
6.916  
6.905  
6.879  
6.853  
6.596  
6.570  
5.827  
5.794  
5.479  
5.456

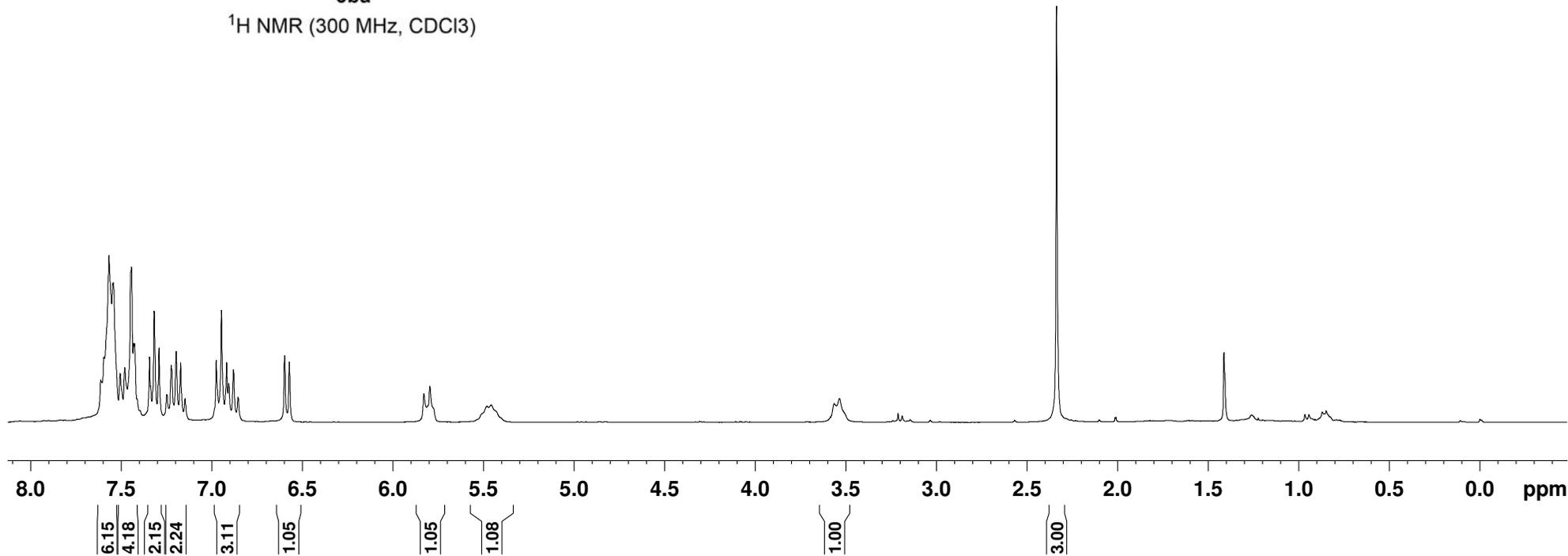
3.564  
3.535

2.337

-0.000  
-0.010

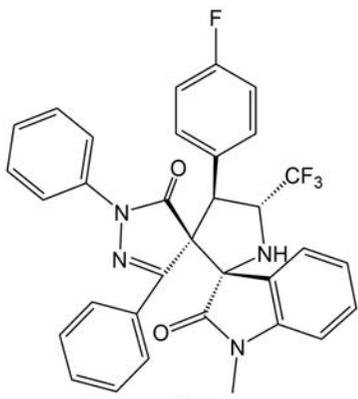


<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

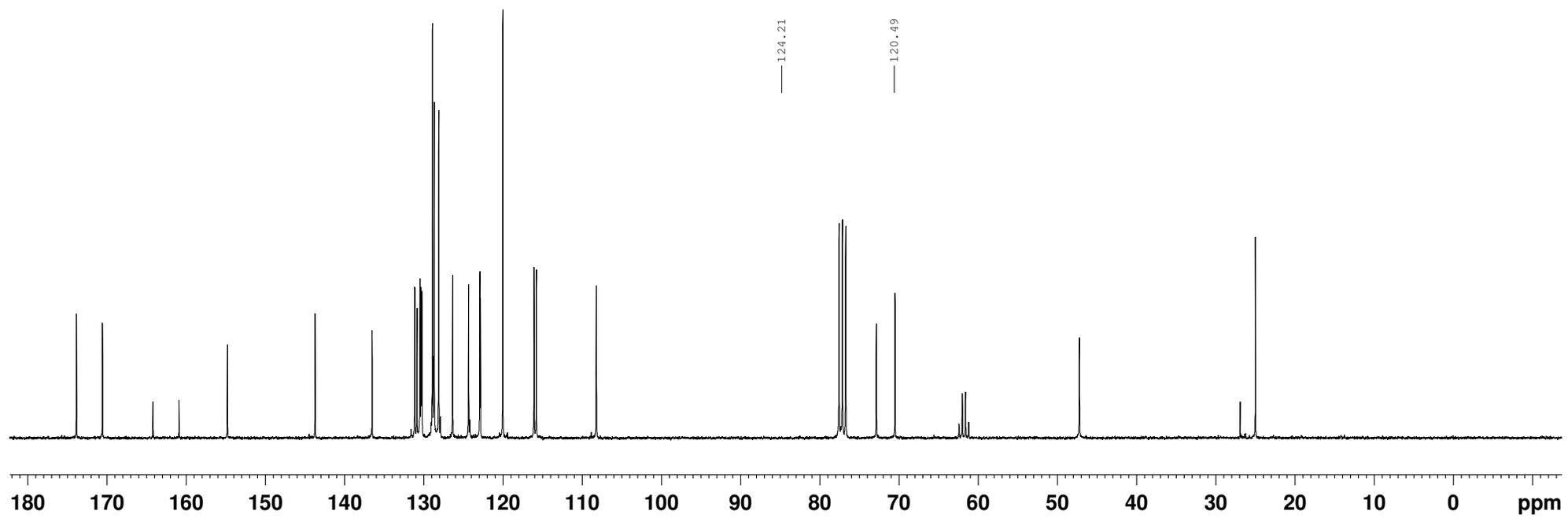
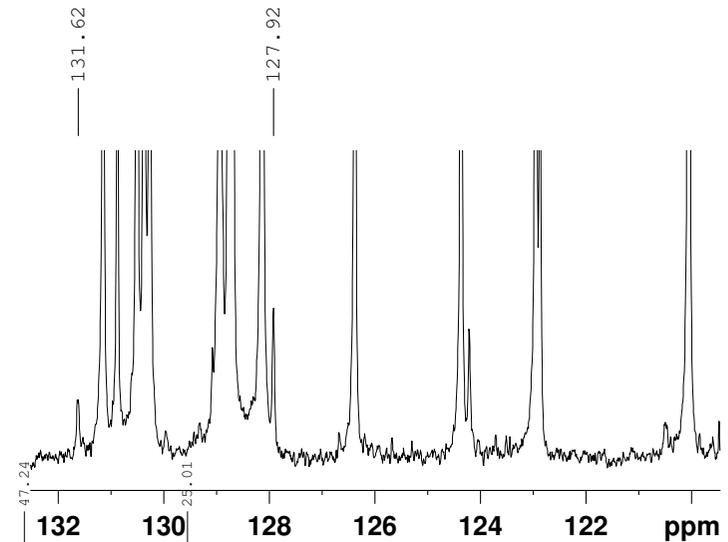


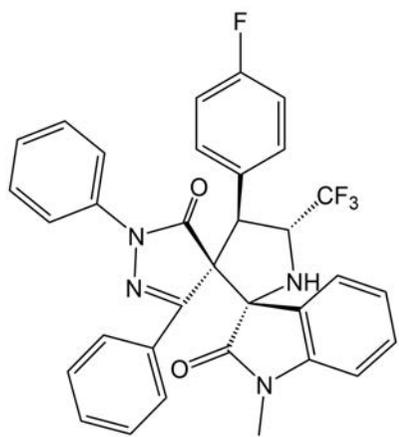
— 173.88  
 — 170.59  
 — 164.21  
 — 160.93  
 — 154.81  
 — 143.75  
 — 136.55  
 — 131.62  
 — 131.15  
 — 130.87  
 — 130.50  
 — 130.37  
 — 130.26  
 — 128.93  
 — 128.70  
 — 128.13  
 — 127.92  
 — 126.38  
 — 124.36  
 — 124.21  
 — 122.94  
 — 122.86  
 — 120.49  
 — 120.04  
 — 116.10  
 — 115.81  
 — 108.23

— 77.59  
 — 77.17  
 — 76.74  
 — 72.87  
 — 70.51  
 — 62.44  
 — 62.03  
 — 61.62  
 — 61.21



**3ba**  
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)

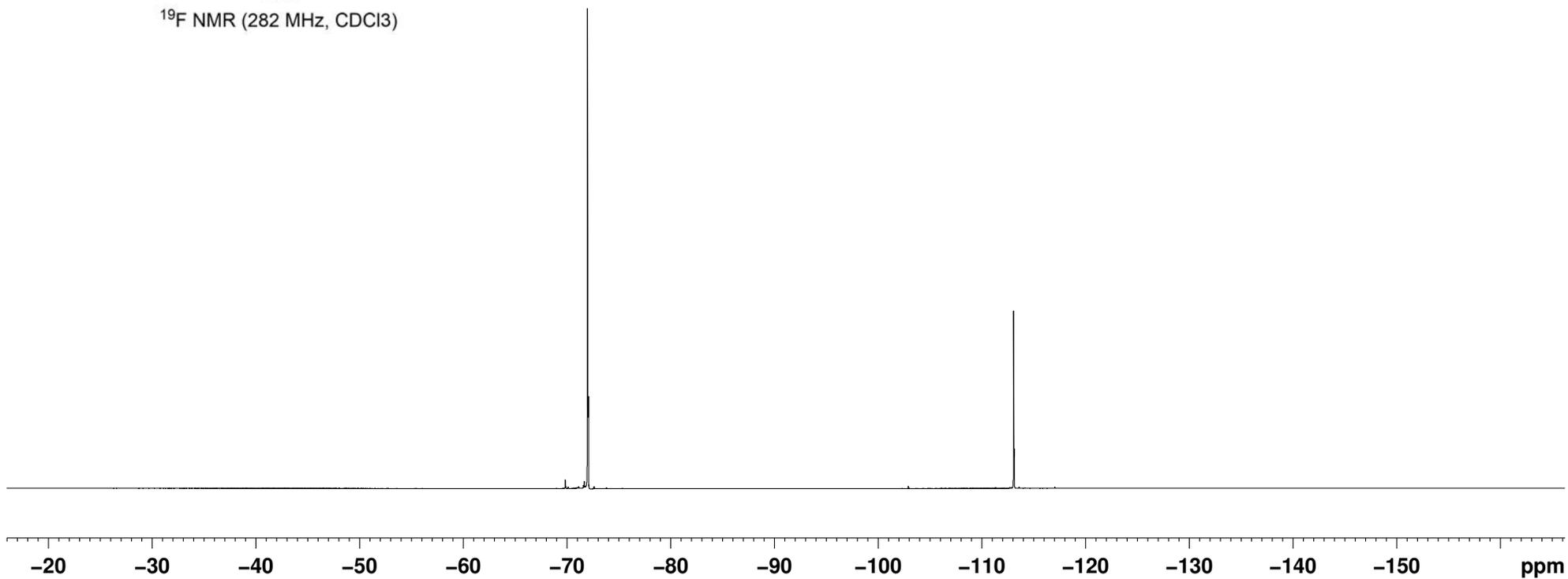




<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)

— -71.97

— -113.05

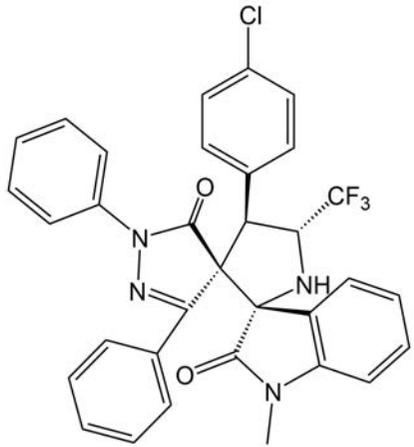


7.528  
7.492  
7.467  
7.452  
7.447  
7.437  
7.428  
7.412  
7.398  
7.356  
7.331  
7.304  
7.251  
7.233  
7.230  
7.223  
7.209  
7.185  
7.161  
6.911  
6.886  
6.862  
6.606  
6.580  
5.805  
5.771  
5.497  
5.469  
5.444  
5.417

3.553  
3.522

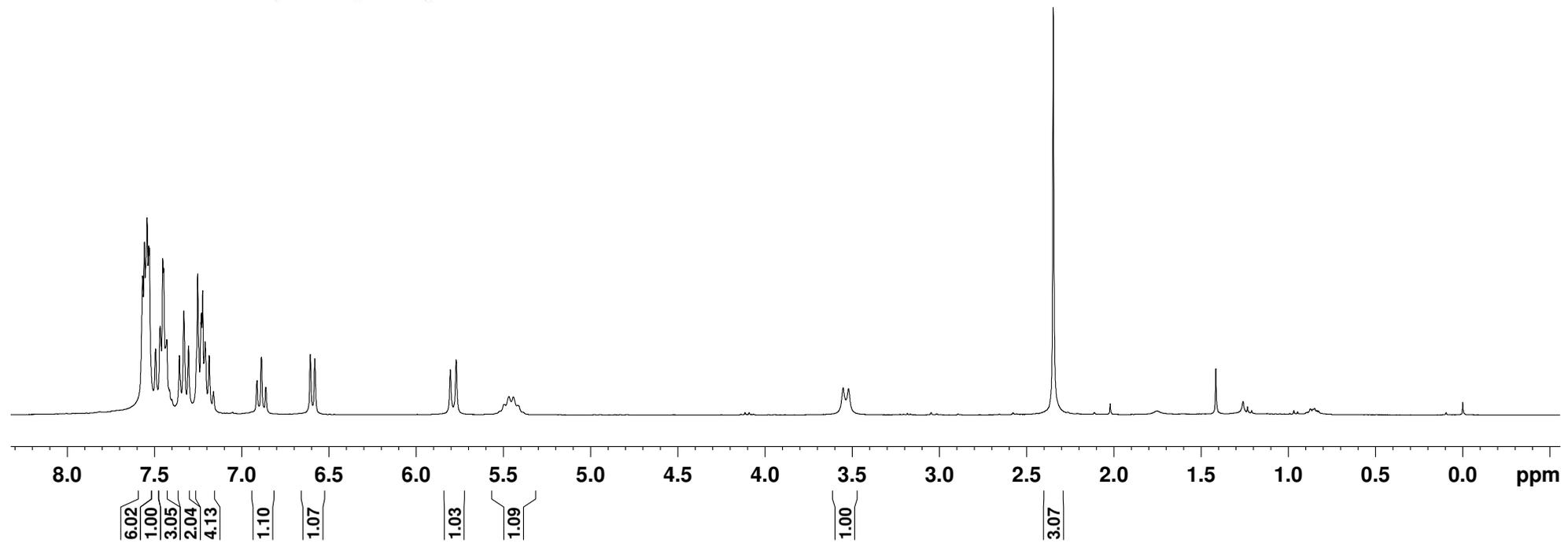
2.348

-0.000

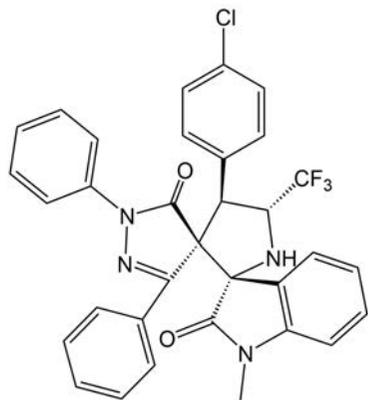


**3ca**

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

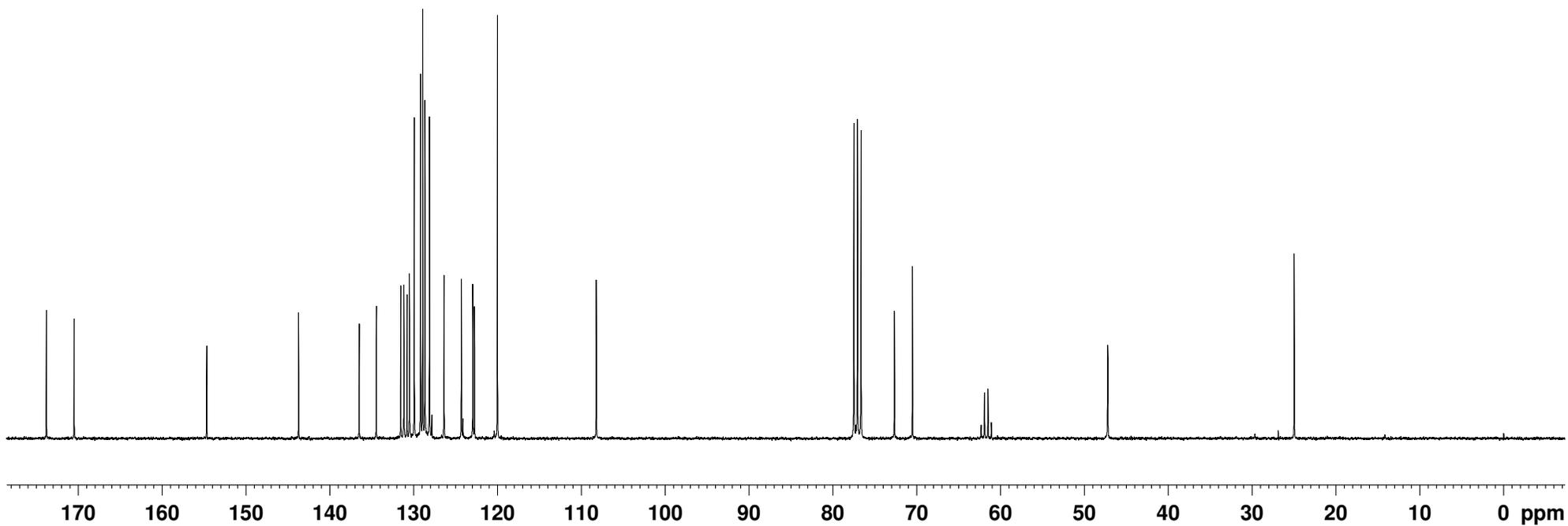
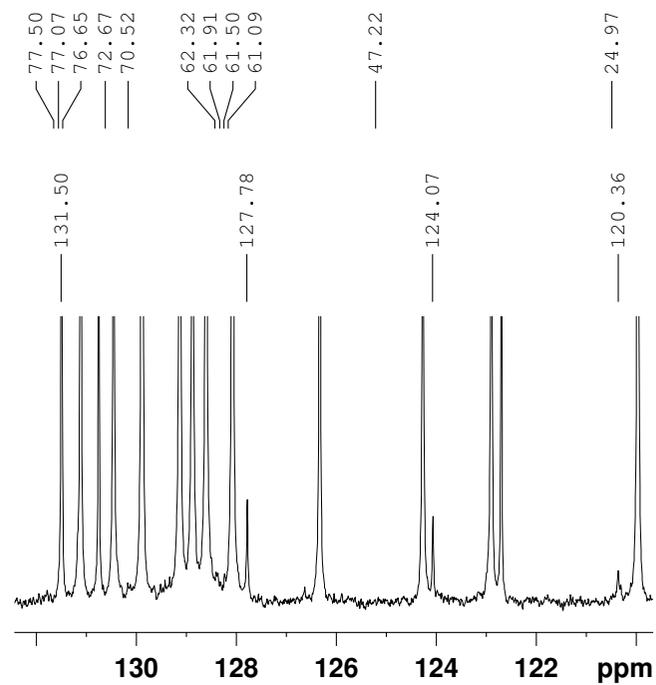


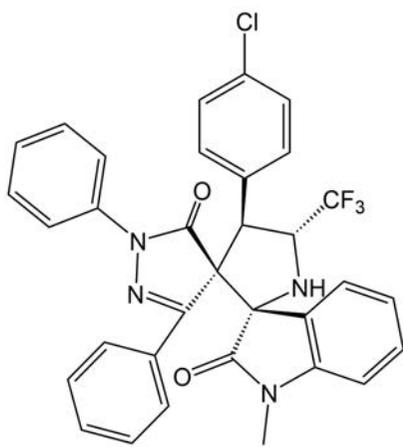
— 173.76  
— 170.45  
  
— 154.64  
143.68  
136.46  
134.41  
131.50  
131.12  
130.75  
130.46  
129.89  
129.13  
128.88  
128.60  
128.08  
127.78  
126.33  
124.27  
124.07  
122.90  
122.70  
120.36  
119.97  
108.17



**3ca**

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)





3ca

<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)

— -72.02



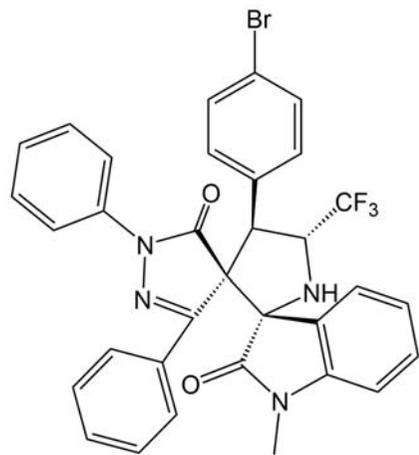
7.542  
7.528  
7.494  
7.466  
7.452  
7.429  
7.405  
7.377  
7.362  
7.336  
7.309  
7.263  
7.238  
7.213  
7.191  
7.167  
6.916  
6.891  
6.866  
6.609  
6.583

5.787  
5.753  
5.487  
5.462  
5.437

3.546  
3.517

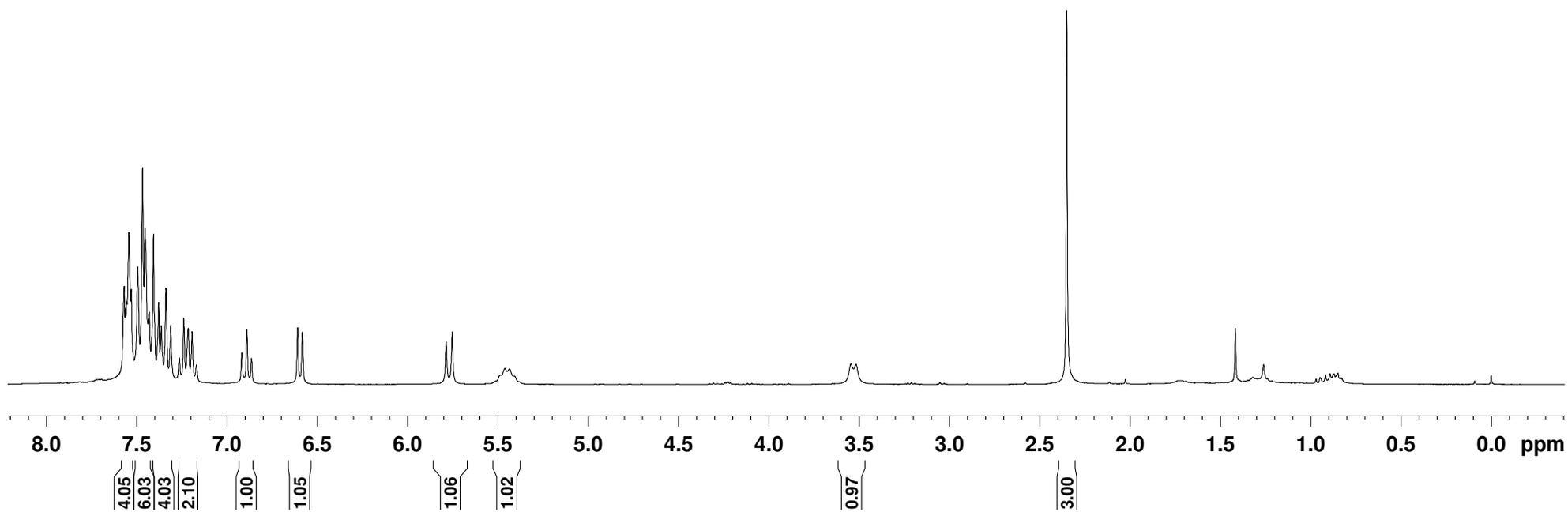
2.350

-0.000

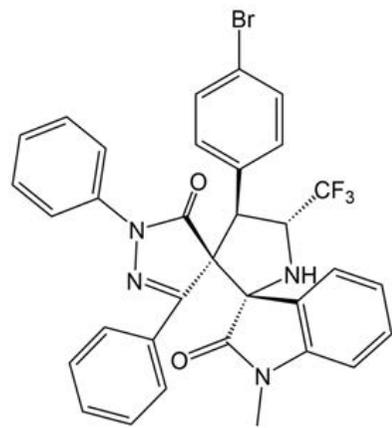


**3da**

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )

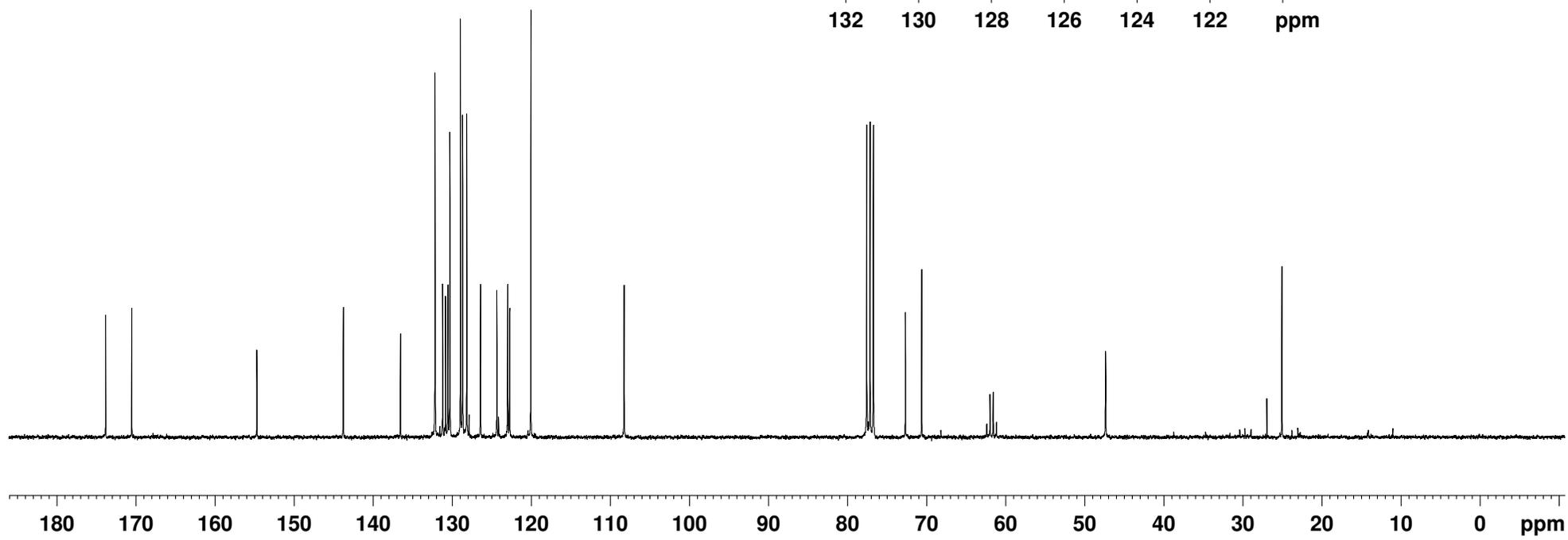
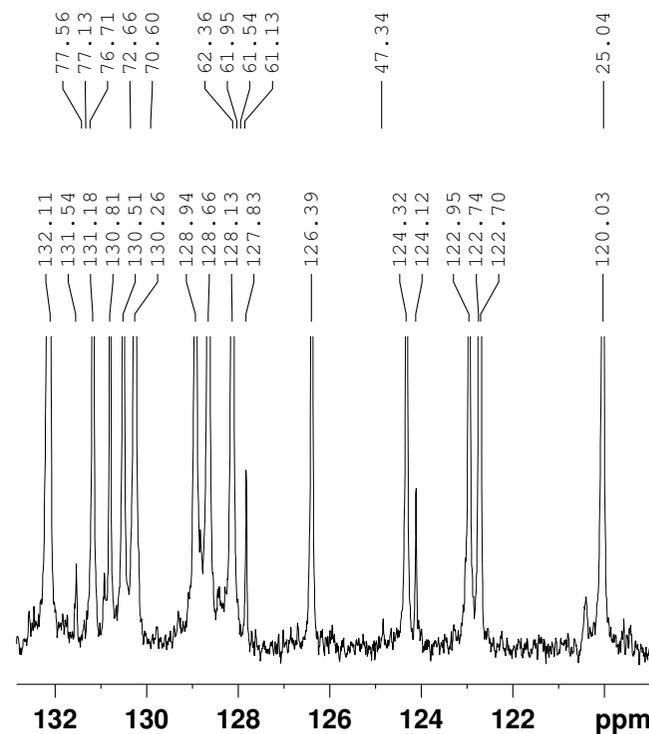


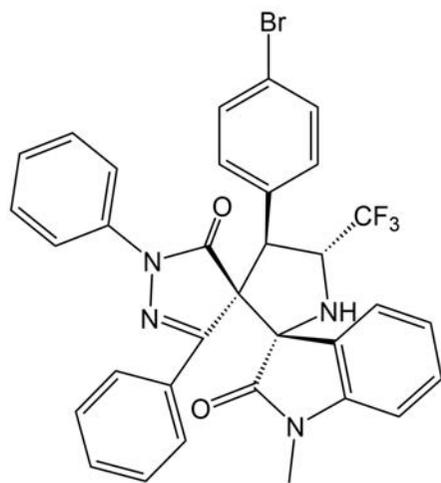
— 173.81  
 — 170.50  
 — 154.68  
 — 143.75  
 — 136.52  
 — 132.15  
 — 132.11  
 — 131.54  
 — 131.18  
 — 130.81  
 — 130.51  
 — 130.26  
 — 128.94  
 — 128.66  
 — 128.13  
 — 127.83  
 — 126.39  
 — 124.32  
 — 124.12  
 — 122.95  
 — 122.74  
 — 122.70  
 — 120.03  
 — 108.23



**3da**

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)





**3da**

<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)

— -72.04



-20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 ppm

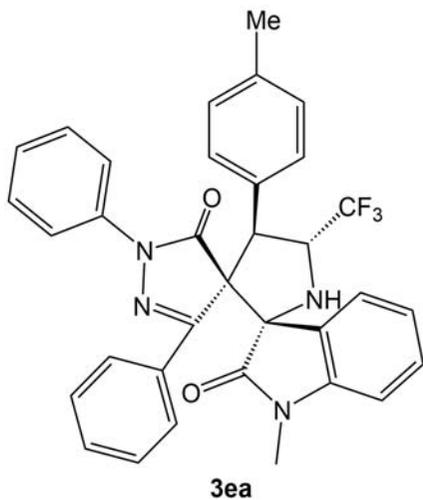
7.498  
7.471  
7.430  
7.424  
7.412  
7.328  
7.303  
7.276  
7.231  
7.206  
7.177  
7.150  
7.125  
7.056  
7.029  
6.888  
6.863  
6.838  
6.579  
6.553

5.804  
5.770  
5.521  
5.493  
5.467  
5.441

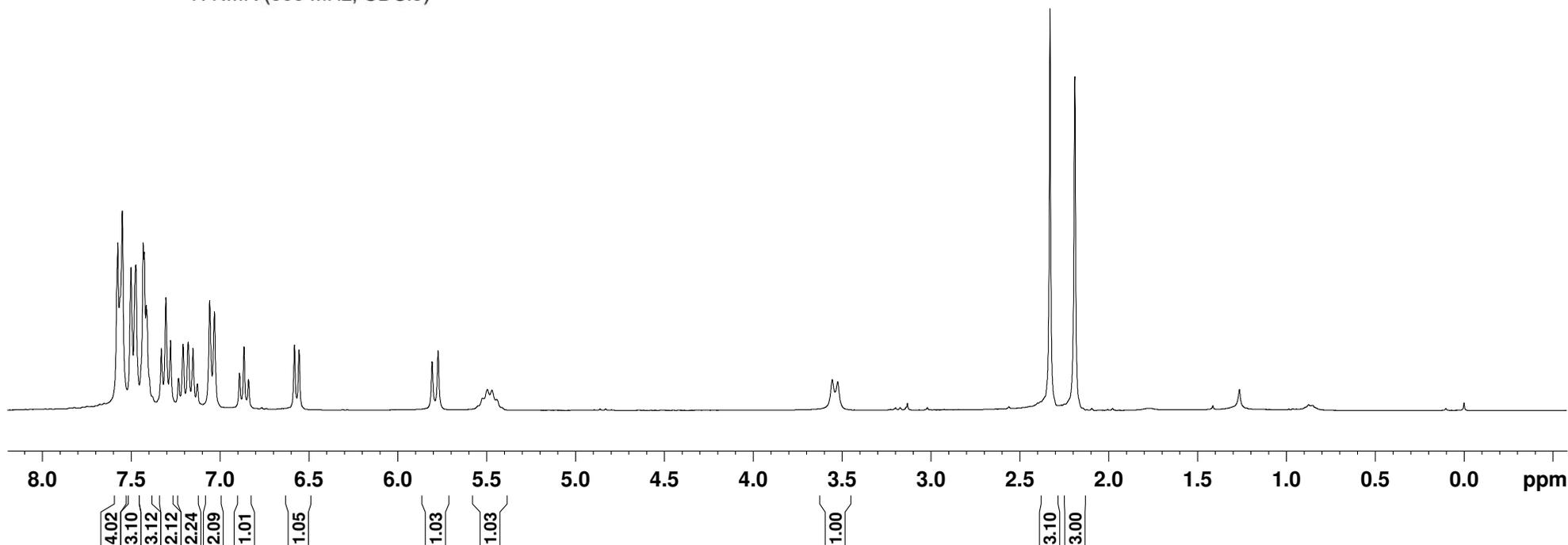
3.553  
3.522

2.329  
2.190

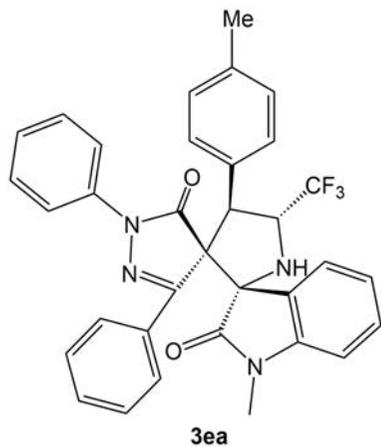
-0.000



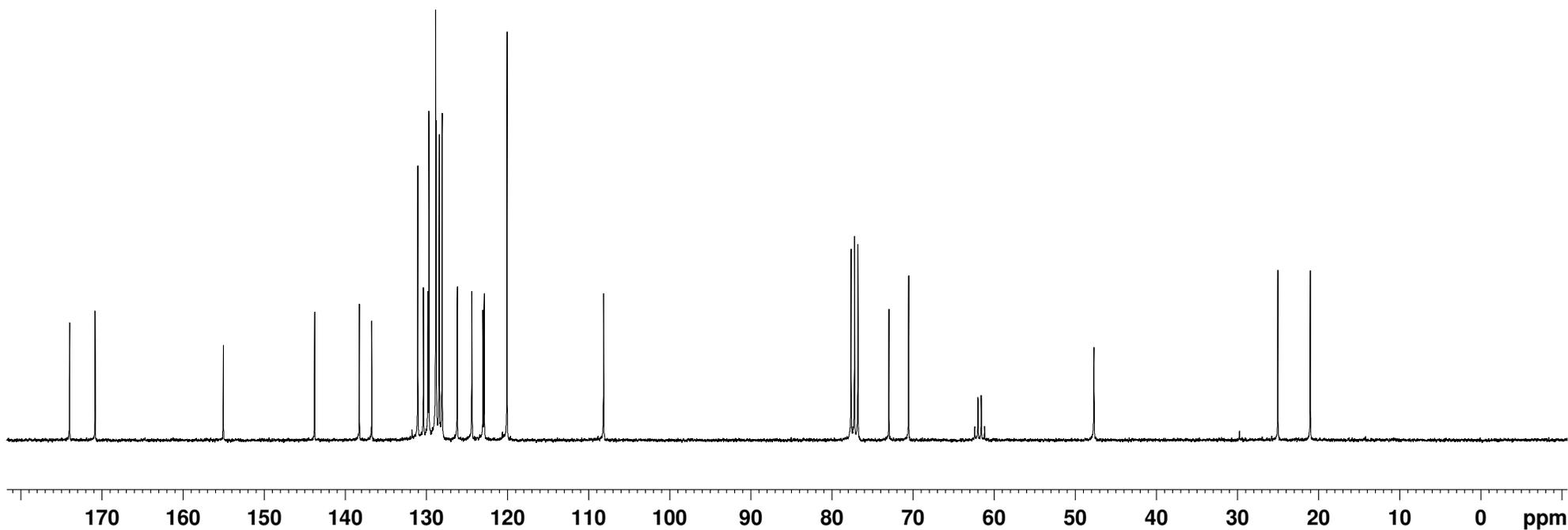
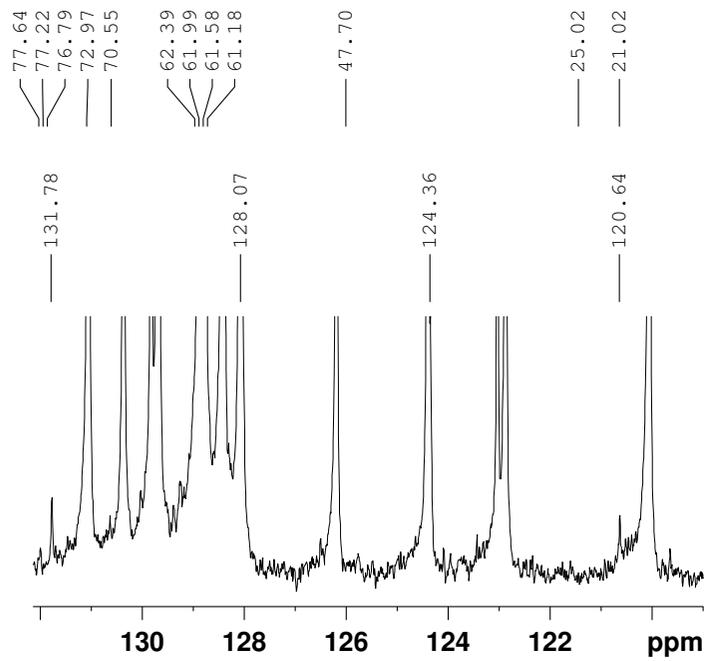
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

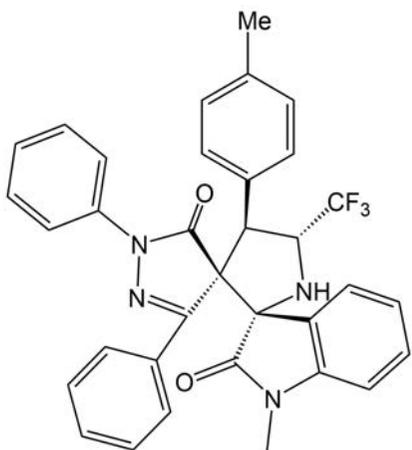


173.95  
170.81  
155.04  
143.79  
138.27  
136.74  
131.78  
131.06  
130.37  
129.83  
129.69  
128.86  
128.78  
128.42  
128.07  
126.20  
124.40  
123.04  
122.88  
120.64  
120.06  
108.16



<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)

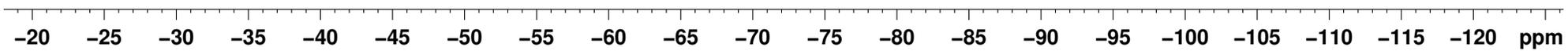




**3ea**

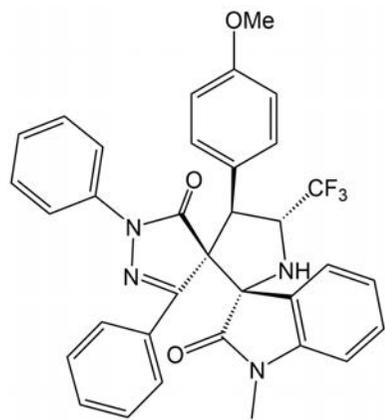
$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )

— -71.967

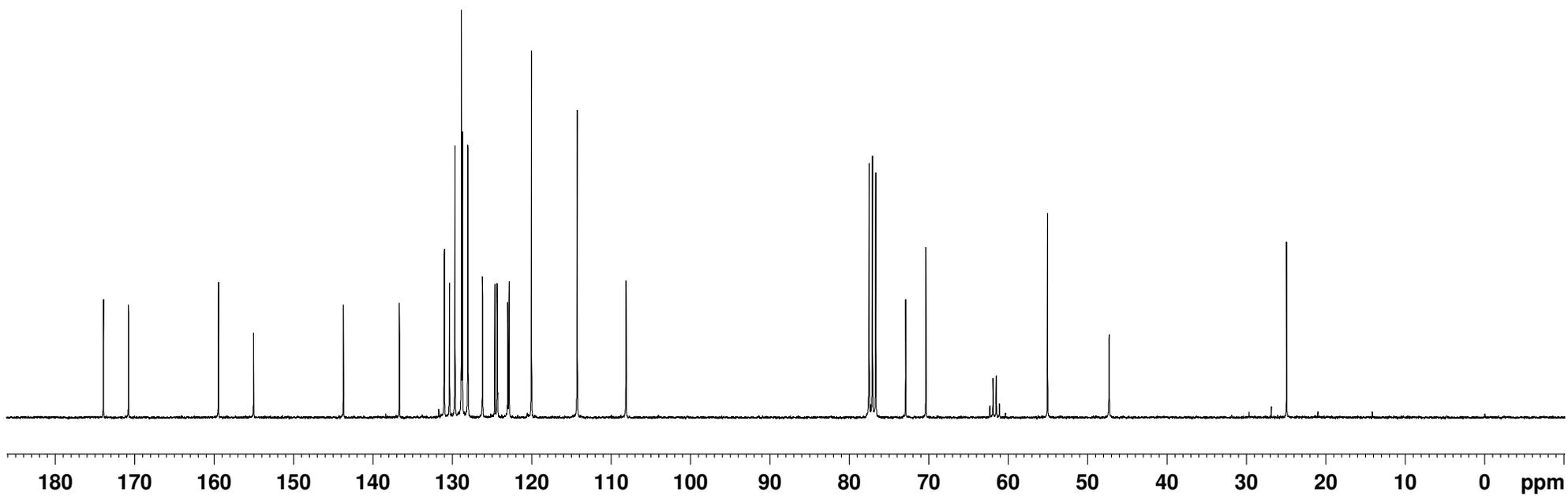
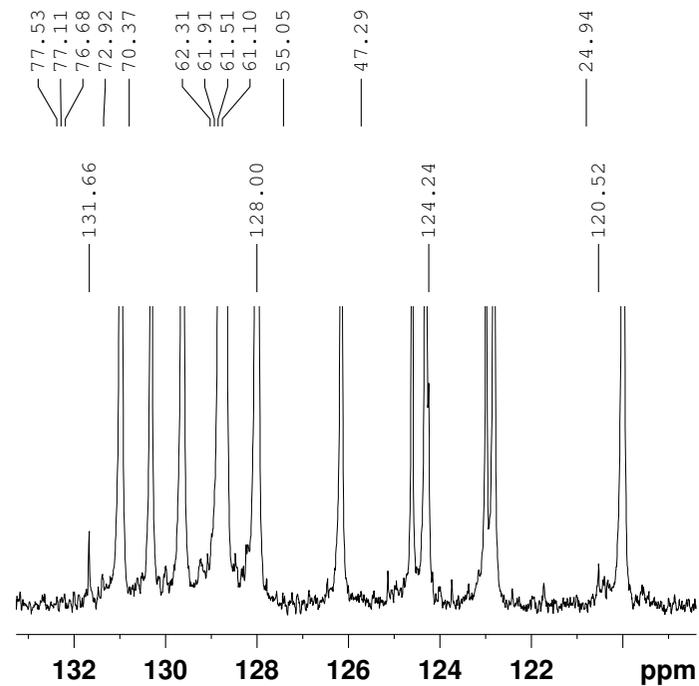


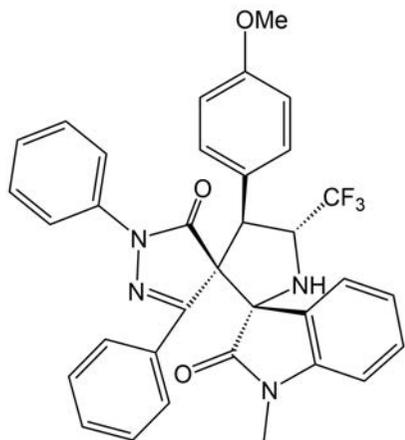


173.90  
170.73  
159.41  
154.99  
143.67  
136.62  
131.66  
130.97  
130.95  
130.30  
129.62  
128.80  
128.68  
128.00  
126.15  
124.60  
124.30  
124.24  
122.98  
122.81  
120.52  
119.99  
114.23  
108.08



**3fa**  
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)

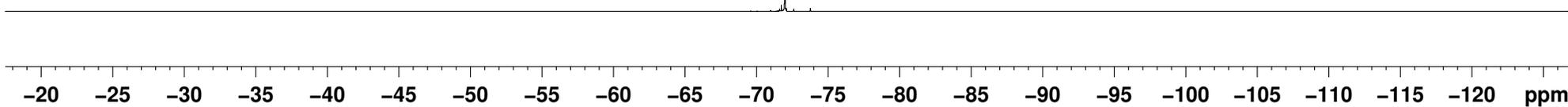




**3fa**

<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)

— -71.996

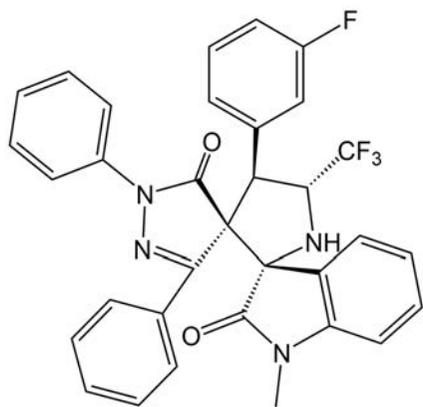


7.424  
7.399  
7.390  
7.383  
7.377  
7.372  
7.360  
7.335  
7.312  
7.307  
7.273  
7.268  
7.247  
7.243  
7.216  
7.213  
7.190  
7.166  
7.163  
6.958  
6.951  
6.923  
6.898  
6.872  
6.615  
6.589  
5.832  
5.813  
5.799  
5.780  
5.489  
5.469

3.568  
3.542  
3.517

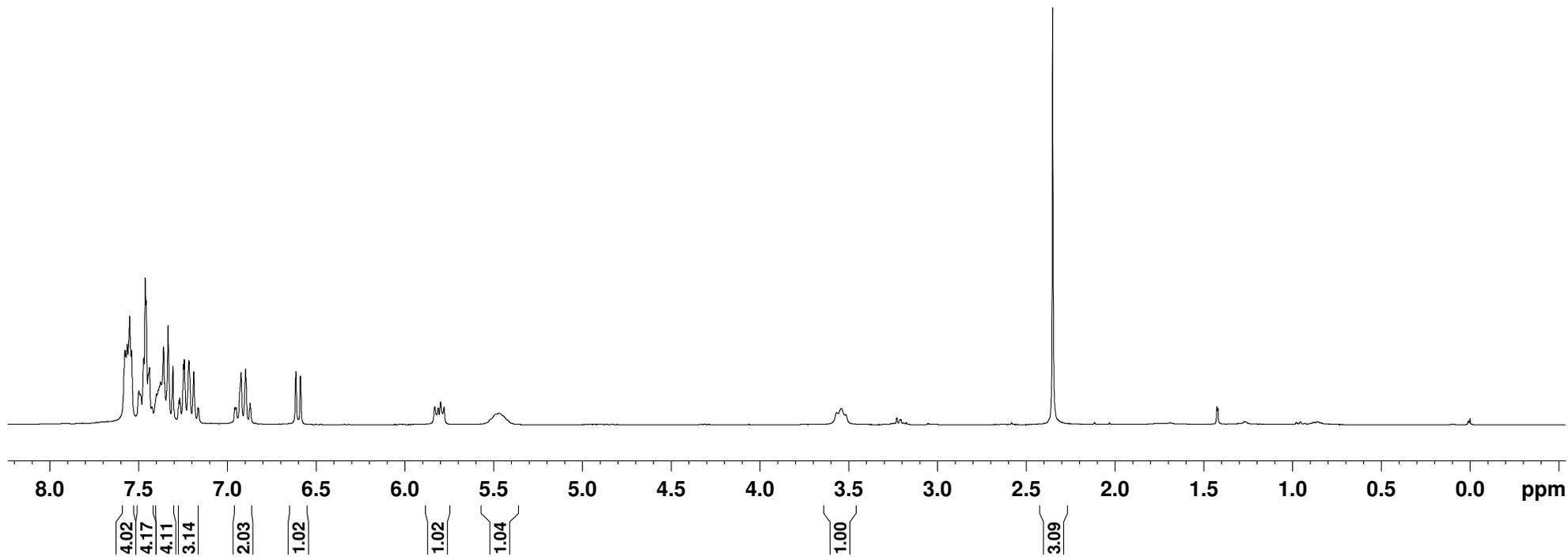
2.351

0.059  
0.010  
-0.000

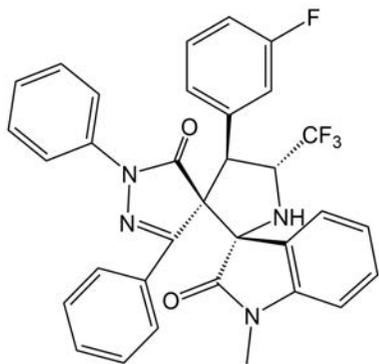


**3ga**

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

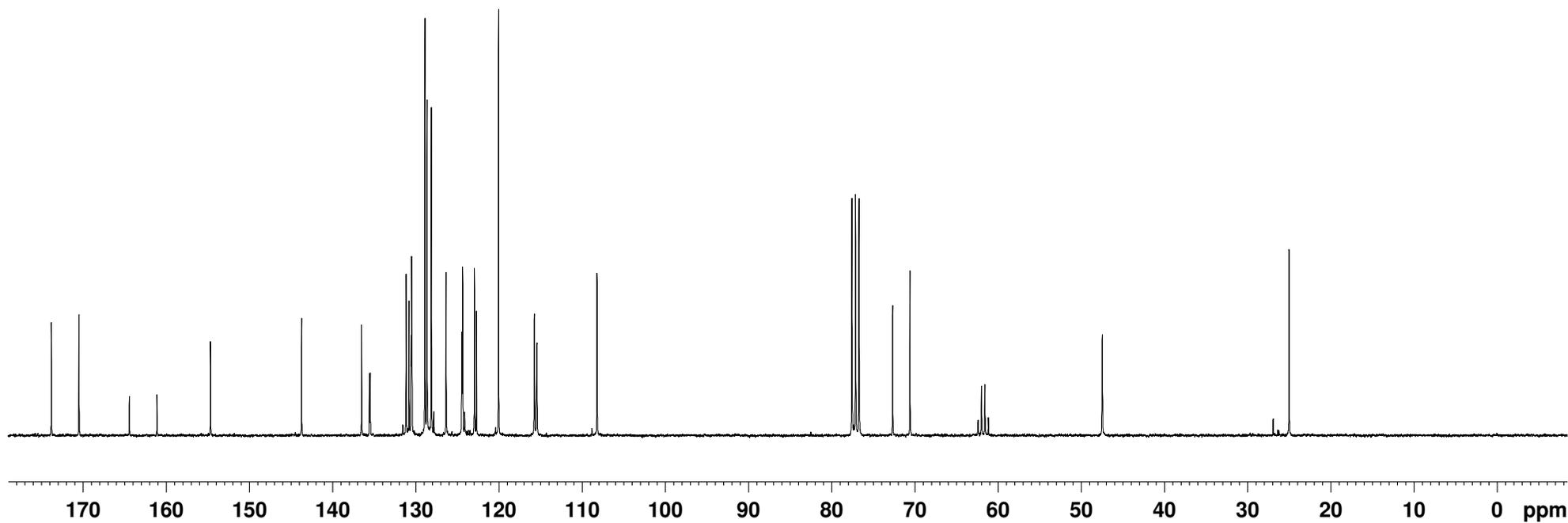
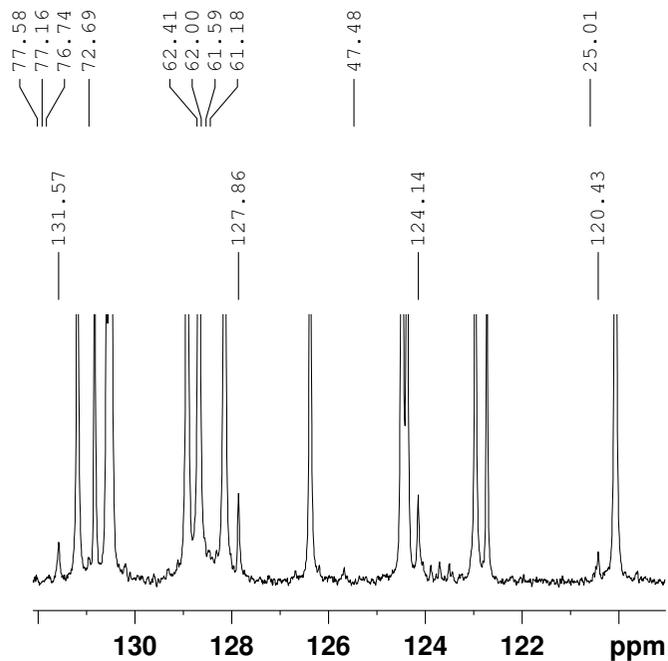


— 173.79  
 — 170.47  
 — 164.41  
 — 161.14  
 — 154.70  
 — 143.76  
 — 136.54  
 — 135.60  
 — 135.50  
 — 131.57  
 — 131.19  
 — 130.83  
 — 130.58  
 — 130.52  
 — 130.47  
 — 128.92  
 — 128.68  
 — 128.15  
 — 127.86  
 — 126.38  
 — 124.50  
 — 124.46  
 — 124.38  
 — 124.14  
 — 122.96  
 — 122.72  
 — 120.43  
 — 120.07  
 — 115.76  
 — 115.50  
 — 115.45  
 — 108.23



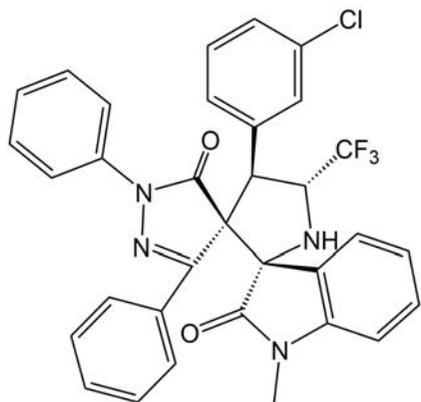
**3ga**

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)





7.470  
7.453  
7.447  
7.436  
7.429  
7.418  
7.413  
7.358  
7.333  
7.305  
7.264  
7.261  
7.239  
7.235  
7.211  
7.192  
7.186  
7.172  
7.162  
7.146  
6.913  
6.911  
6.887  
6.862  
6.604  
6.579  
5.793  
5.759  
5.520  
5.496  
5.464  
5.439  
5.414  
5.407  
5.382



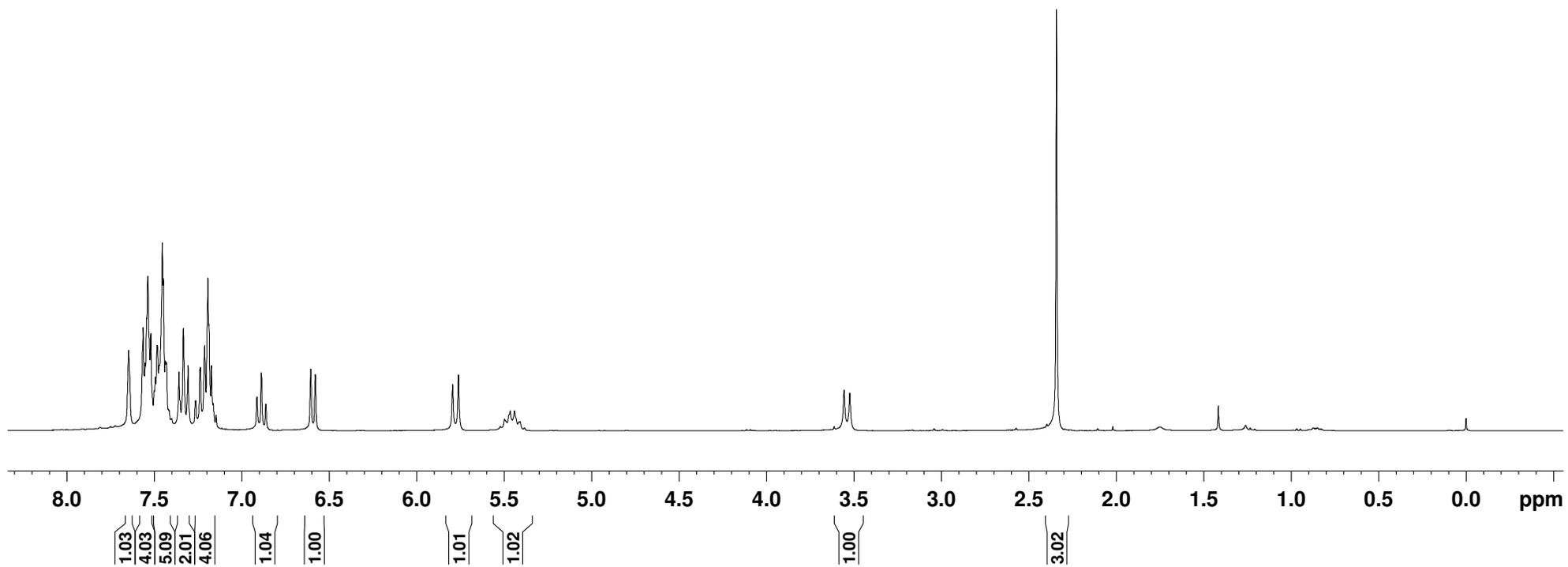
**3ha**

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

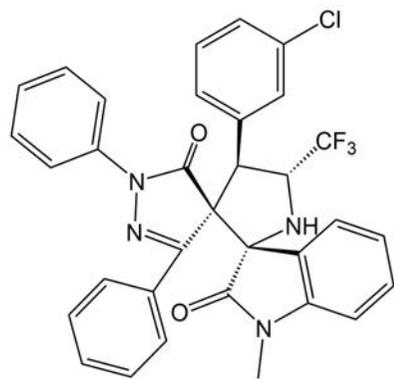
3.557  
3.524

2.342

-0.000

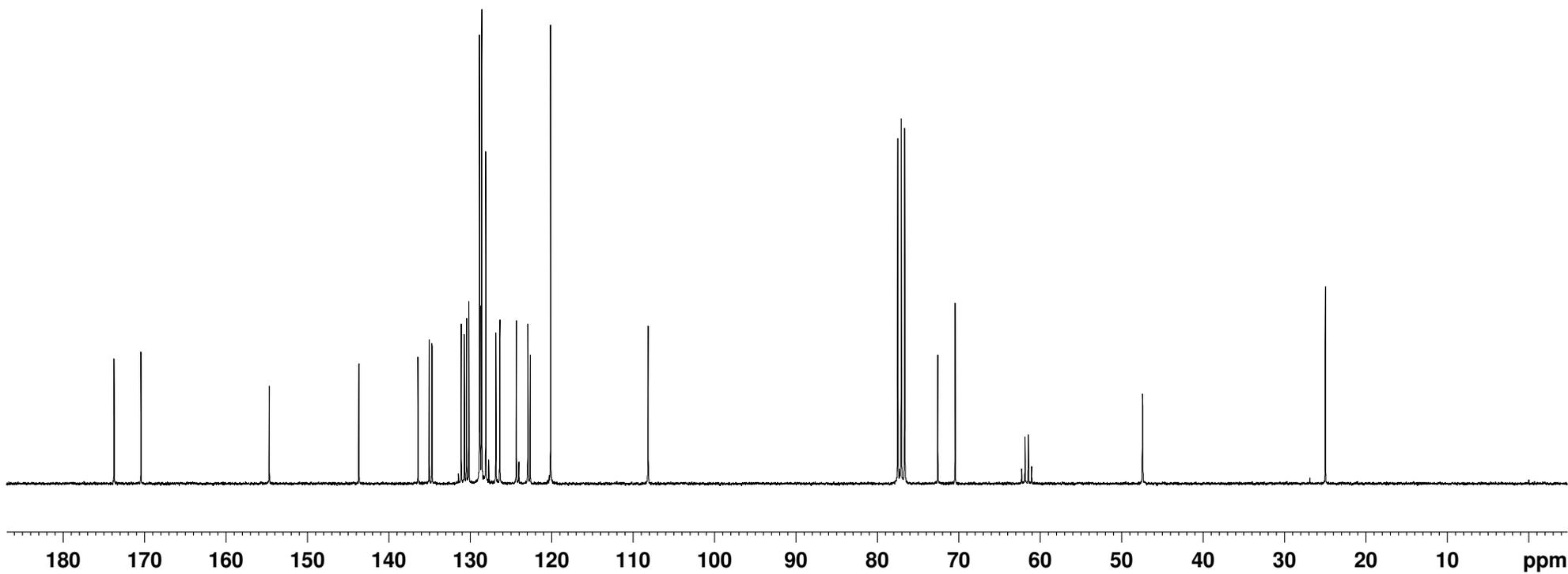
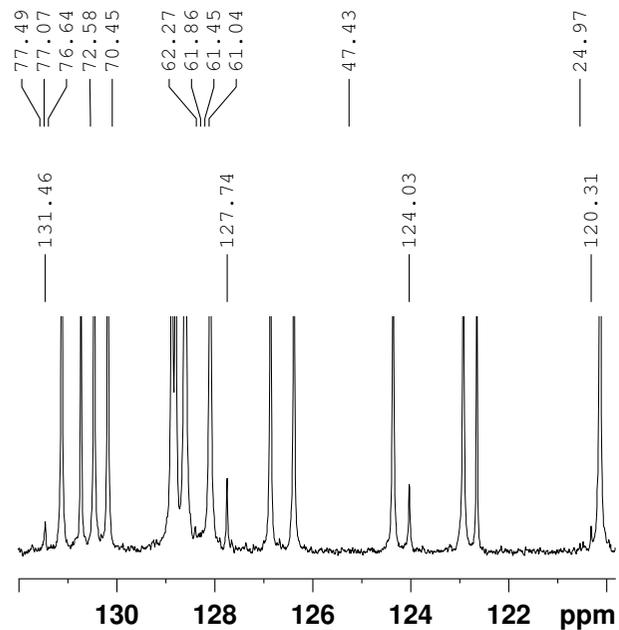


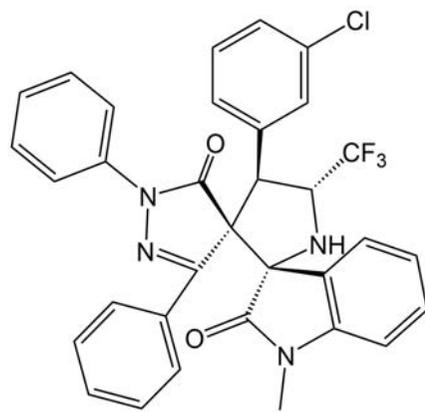
173.70  
170.39  
154.64  
143.68  
136.41  
135.04  
134.70  
131.46  
131.12  
130.73  
130.46  
130.18  
128.87  
128.79  
128.60  
128.09  
127.74  
126.86  
126.37  
124.35  
124.03  
122.93  
122.65  
120.31  
108.17



**3ha**

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)

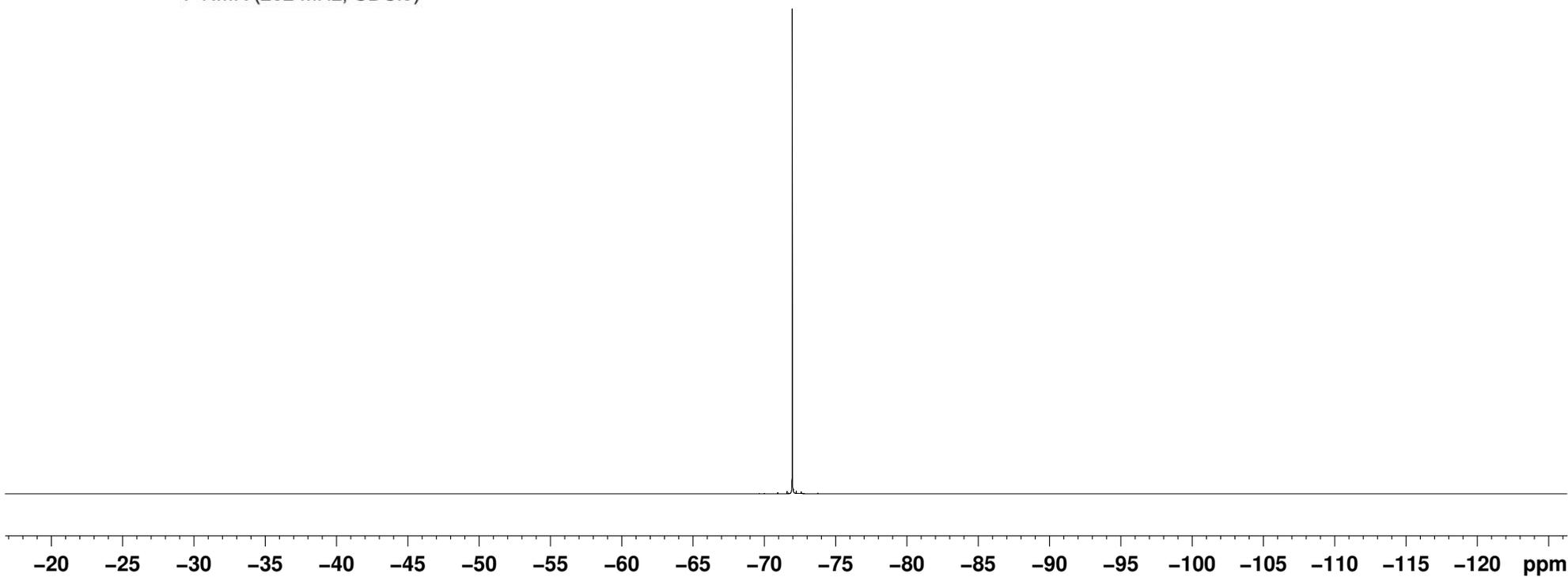




**3ha**

$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )

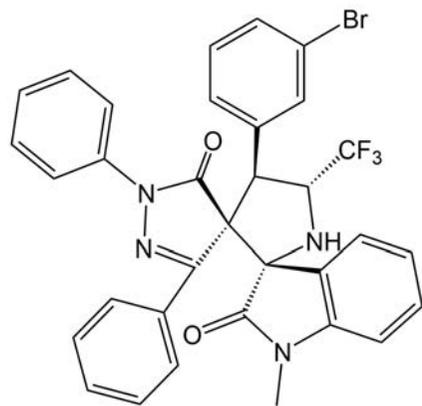
— -72.00



7.480  
7.467  
7.444  
7.427  
7.414  
7.383  
7.357  
7.329  
7.295  
7.272  
7.269  
7.256  
7.243  
7.215  
7.190  
7.169  
7.142  
7.116  
6.943  
6.918  
6.893  
6.628  
6.602  
5.765  
5.731  
5.478  
5.469  
5.453  
5.445  
5.420  
5.412  
5.396  
5.388

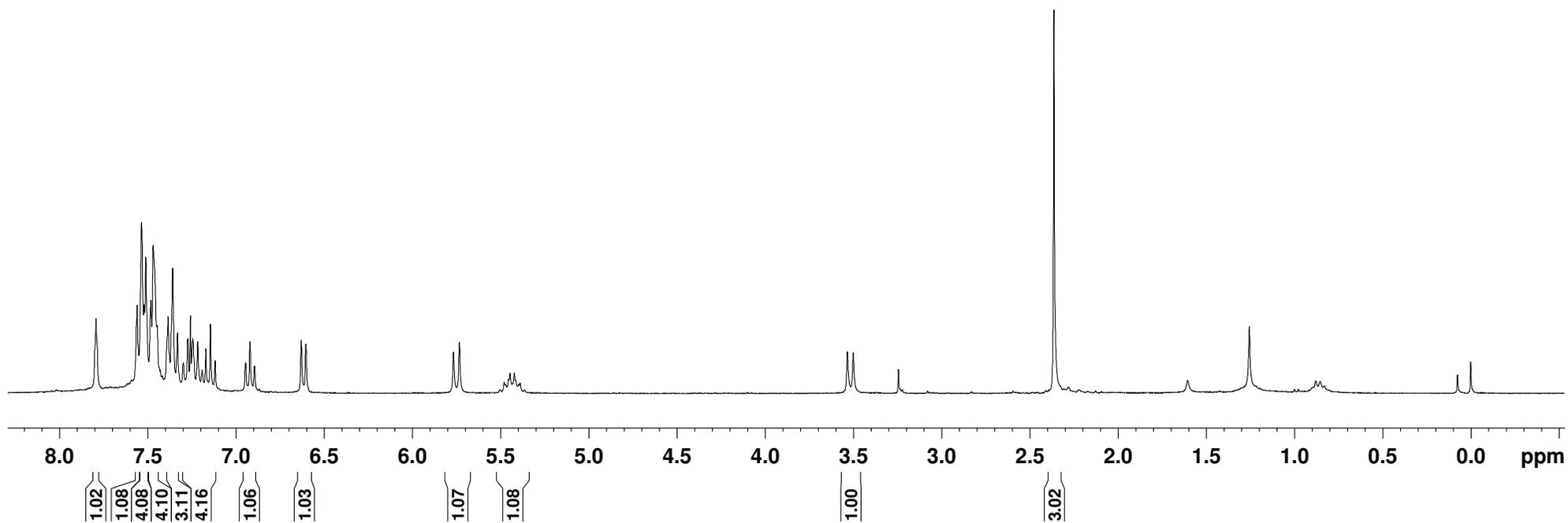
3.532  
3.499

2.362

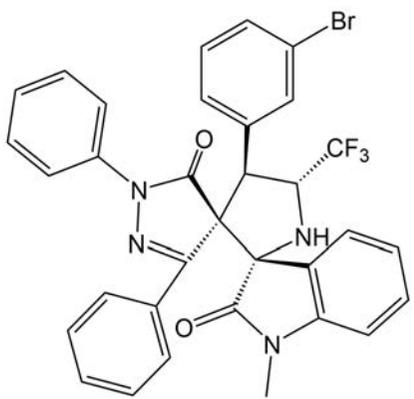


**3ia**

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

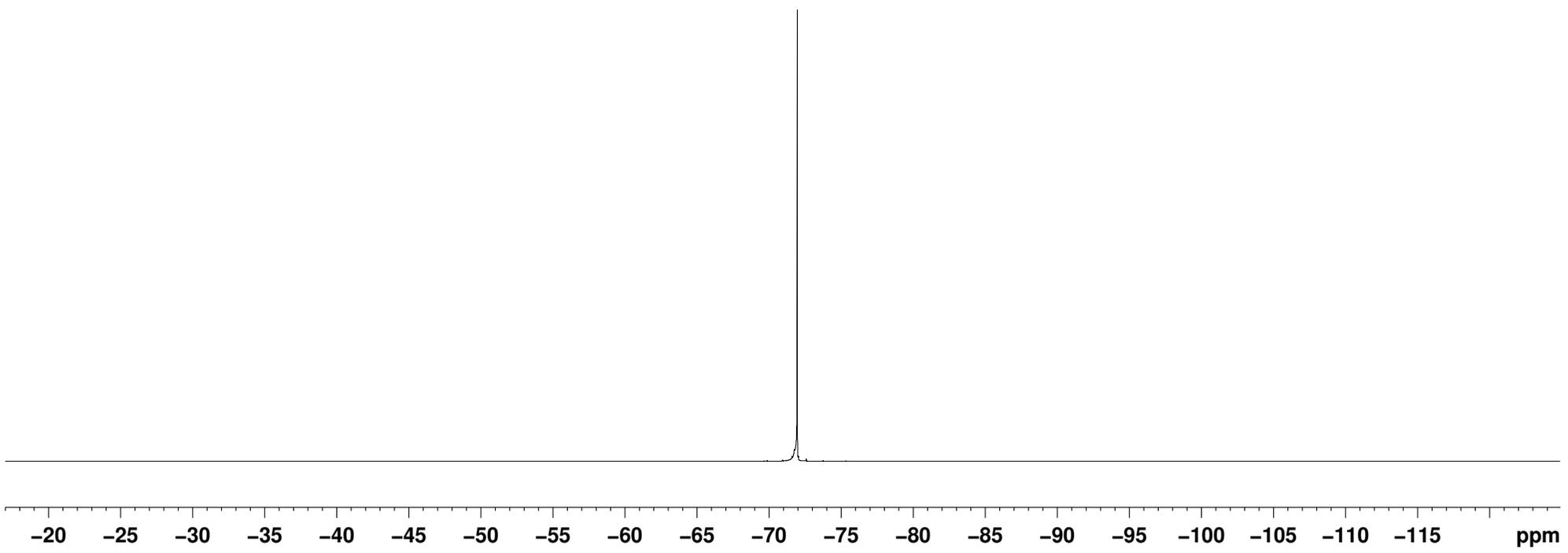






3ia  
<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)

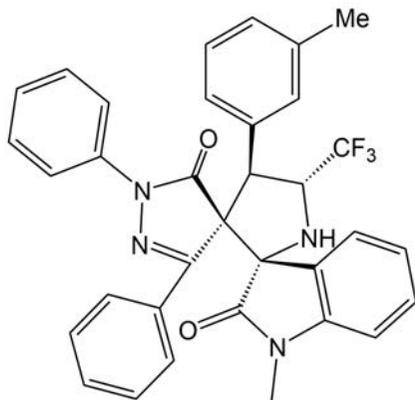
-71.946



7.431  
7.420  
7.415  
7.393  
7.363  
7.337  
7.310  
7.286  
7.254  
7.234  
7.219  
7.195  
7.171  
7.147  
7.122  
7.041  
7.017  
6.942  
6.917  
6.891  
6.616  
6.590  
5.767  
5.733  
5.530  
5.505  
5.473  
5.448  
5.423  
5.416  
5.391

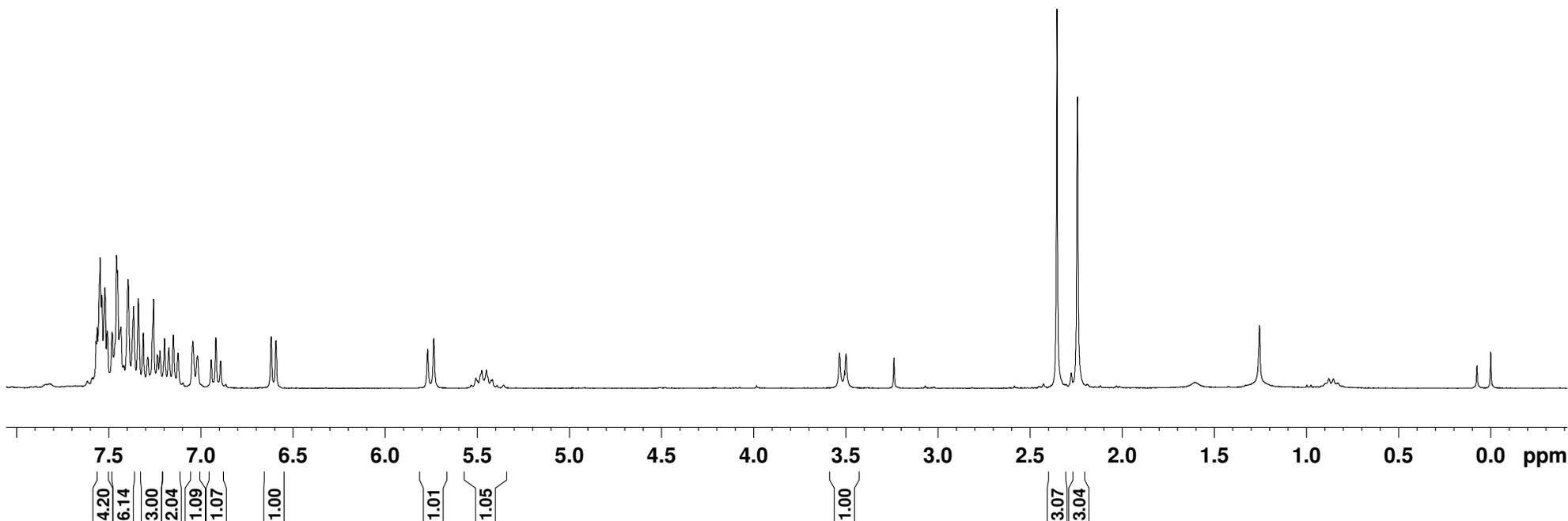
3.531  
3.499

2.353  
2.243

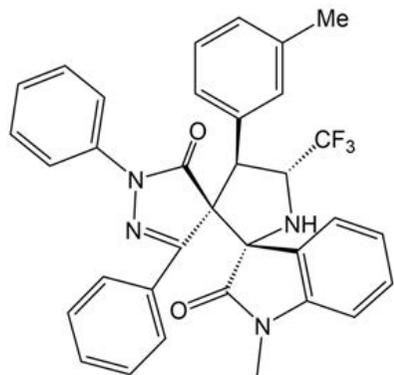


**3ja**

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)



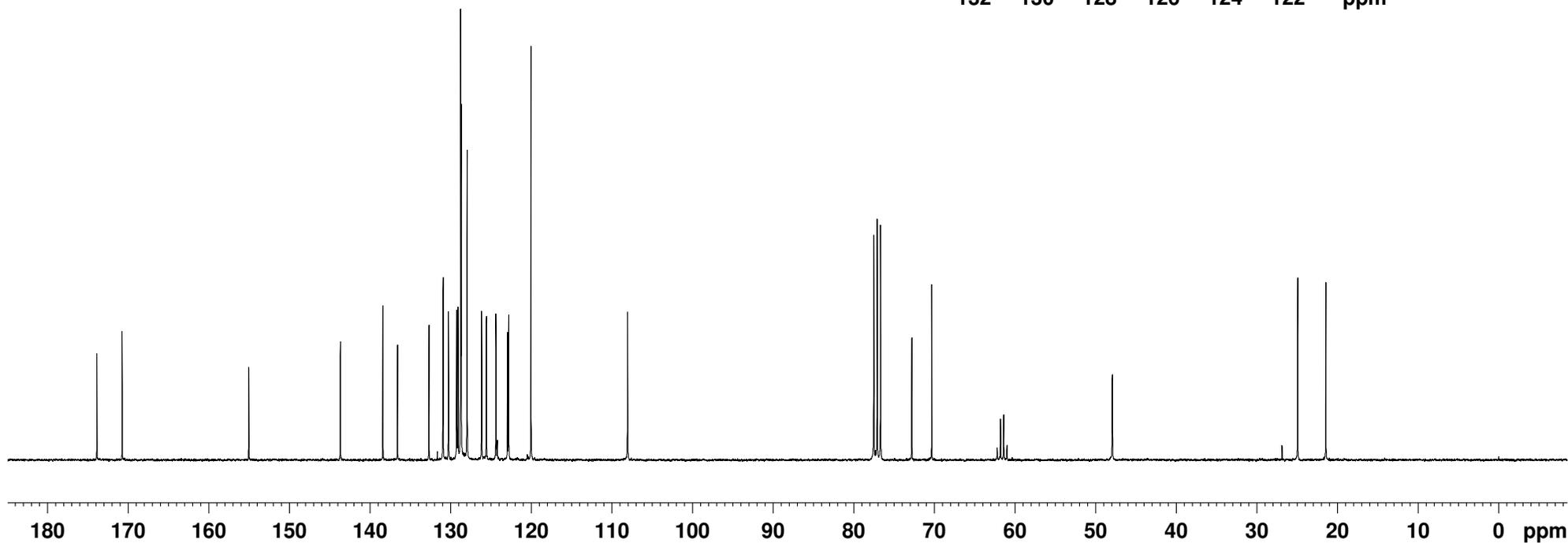
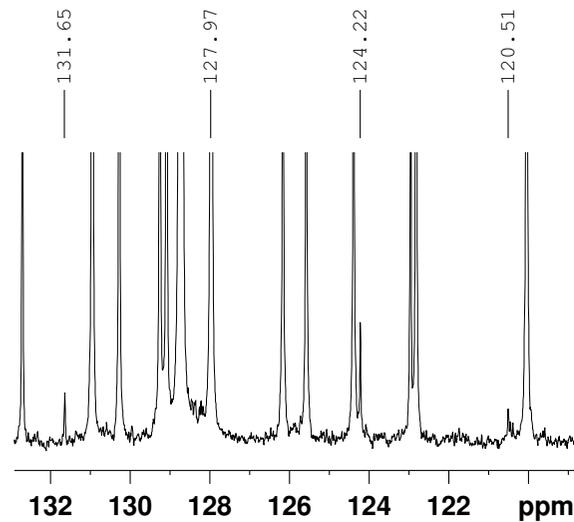
— 173.84  
 — 170.71  
 — 155.01  
 — 143.69  
 — 138.42  
 — 136.61  
 — 132.70  
 — 131.65  
 — 130.96  
 — 130.94  
 — 130.28  
 — 129.26  
 — 129.09  
 — 128.78  
 — 128.70  
 — 127.97  
 — 126.17  
 — 125.58  
 — 124.39  
 — 124.22  
 — 122.96  
 — 122.82  
 — 120.51  
 — 120.05  
 — 108.06

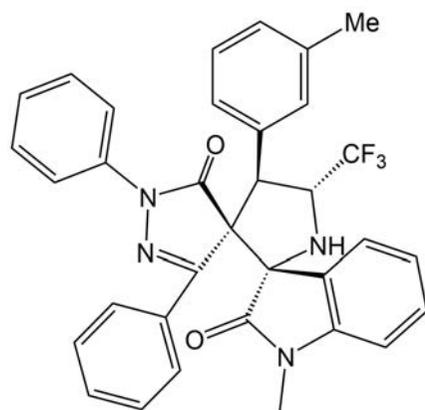


**3ja**

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)

77.52  
 77.10  
 76.67  
 72.80  
 70.33  
 62.21  
 61.80  
 61.40  
 60.99  
 47.93  
 24.93  
 21.43

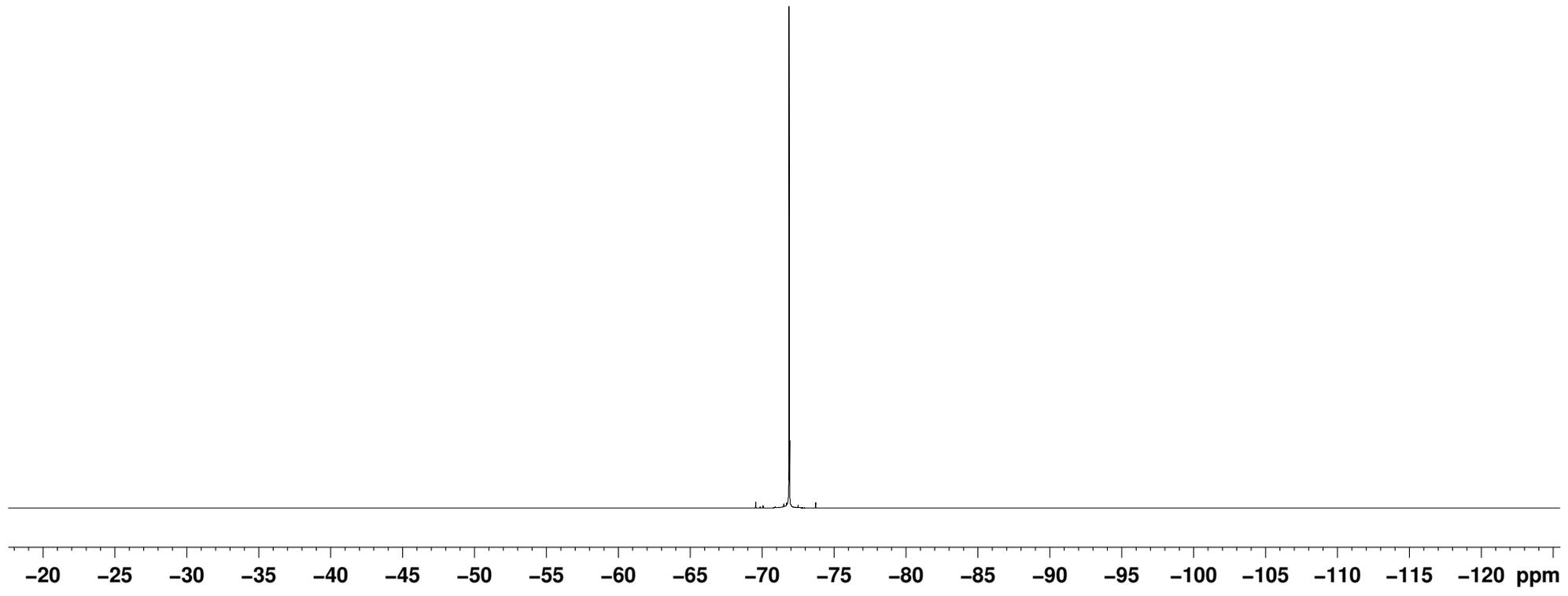




3ja

<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)

-71.879

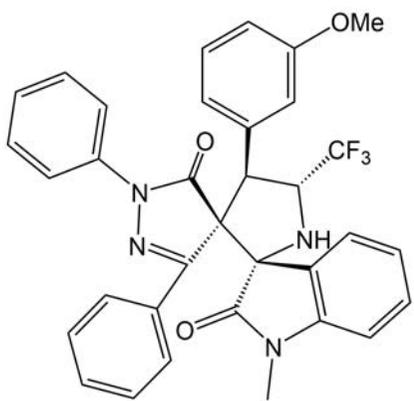


7.283  
7.236  
7.225  
7.210  
7.197  
7.171  
7.159  
7.149  
7.134  
7.123  
6.989  
6.896  
6.871  
6.845  
6.805  
6.781  
6.747  
6.740  
6.722  
6.653  
6.641  
6.584  
6.558  
6.469  
6.445  
6.381  
5.803  
5.770  
5.542  
5.517  
5.487  
5.462  
5.432  
5.406  
5.352

3.595  
3.565  
3.533

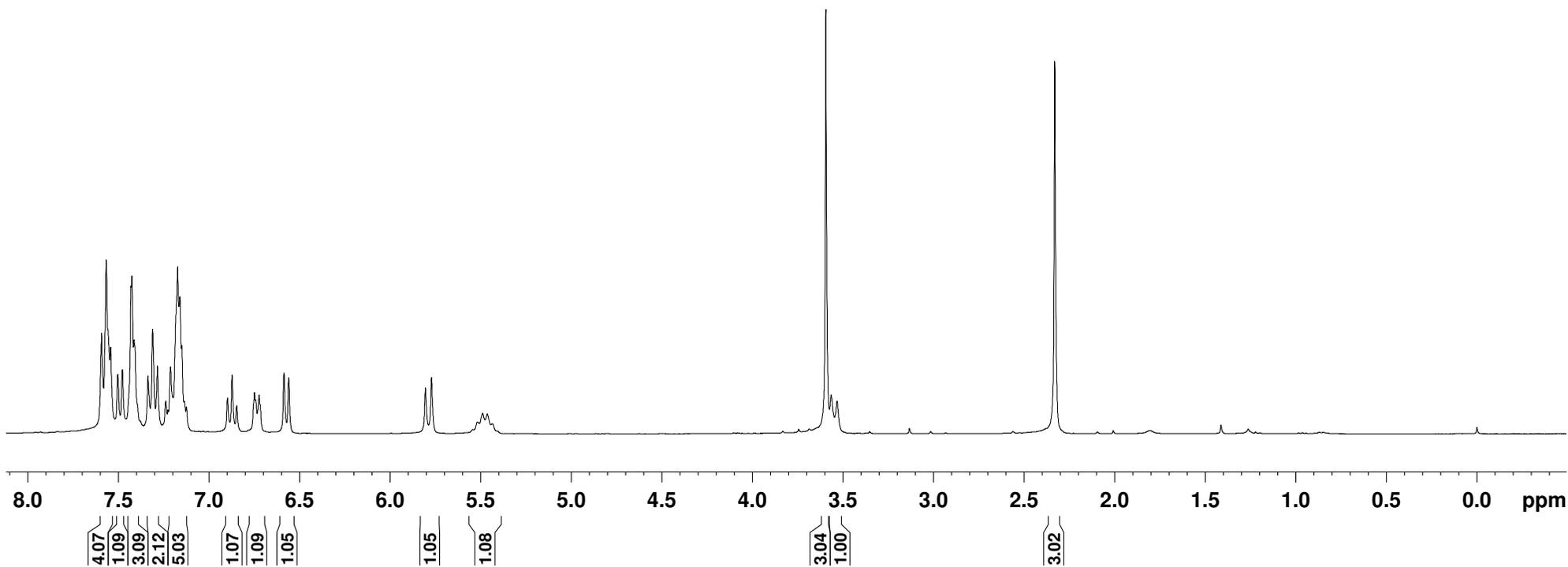
2.331

-0.000

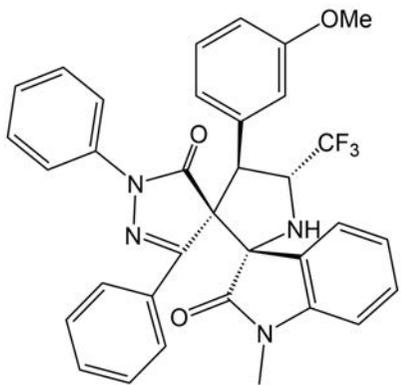


**3ka**

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

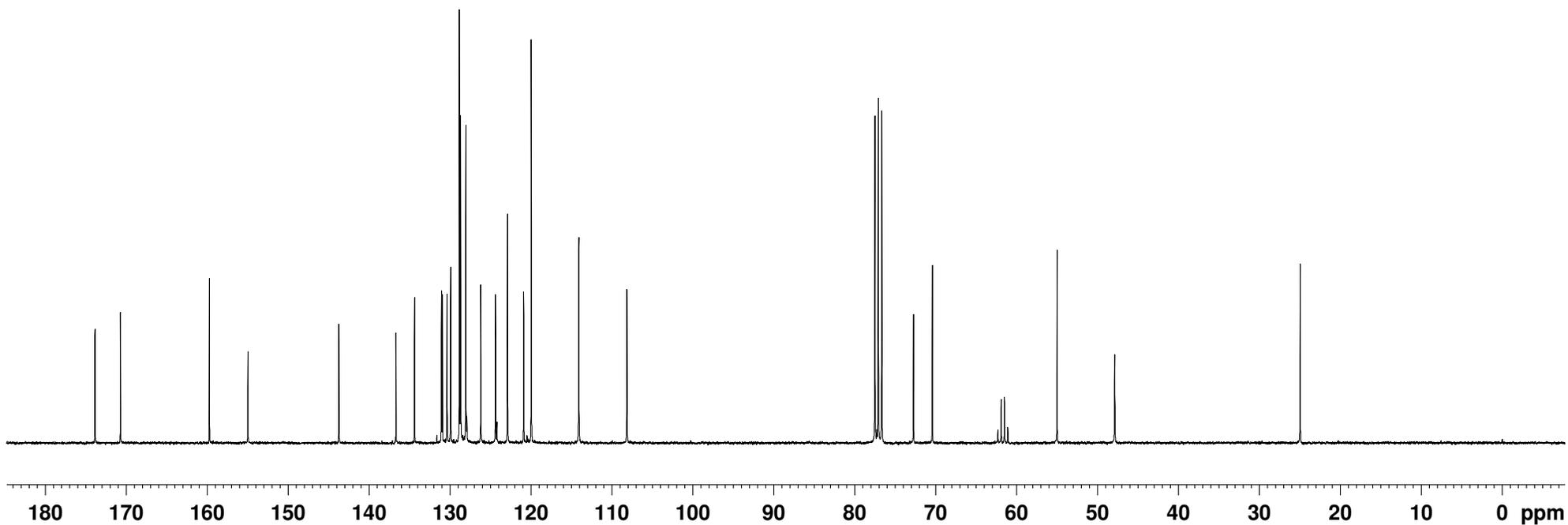
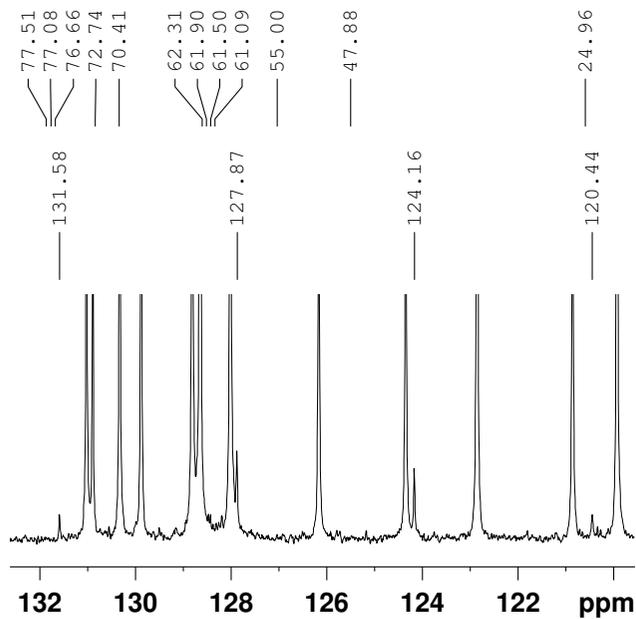


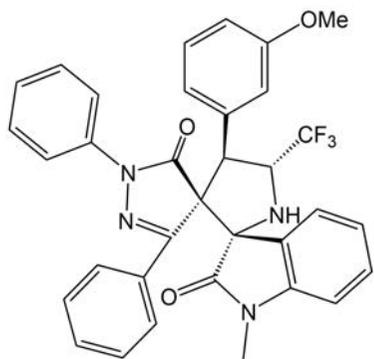
— 173.82  
 — 170.67  
  
 — 159.69  
 — 154.94  
  
 — 143.69  
 — 136.64  
 — 134.34  
 — 131.58  
 — 131.02  
 — 130.89  
 — 130.32  
 — 129.87  
 — 128.80  
 — 128.64  
 — 128.01  
 — 127.87  
 — 126.16  
 — 124.34  
 — 124.16  
 — 122.86  
 — 120.86  
 — 120.44  
 — 119.93  
 — 114.04  
 — 108.11



**3ka**

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)

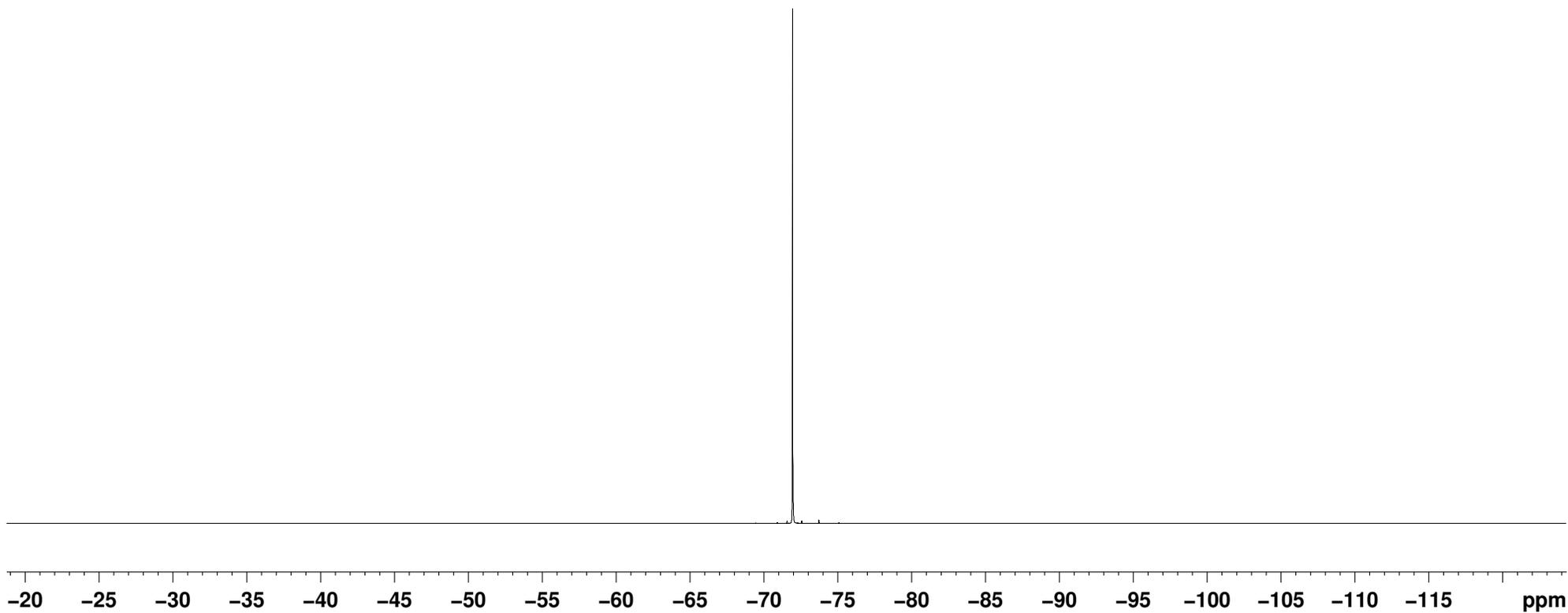




**3ka**

<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)

— -71.95

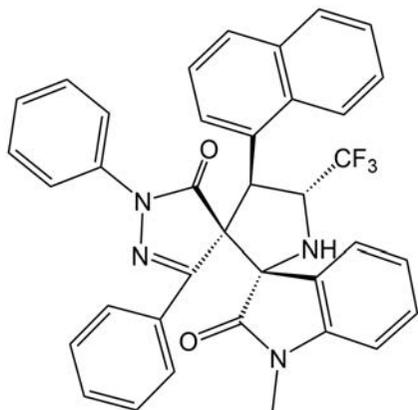


8.041  
7.863  
7.837  
7.776  
7.750  
7.716  
7.649  
7.624  
7.565  
7.540  
7.515  
7.441  
7.416  
7.389  
7.349  
7.323  
7.297  
7.280  
7.255  
7.230  
7.205  
7.181  
7.138  
7.106  
7.082  
7.029  
6.994  
6.970  
6.945  
6.919  
6.882  
6.656  
5.434  
5.409

3.700  
3.673

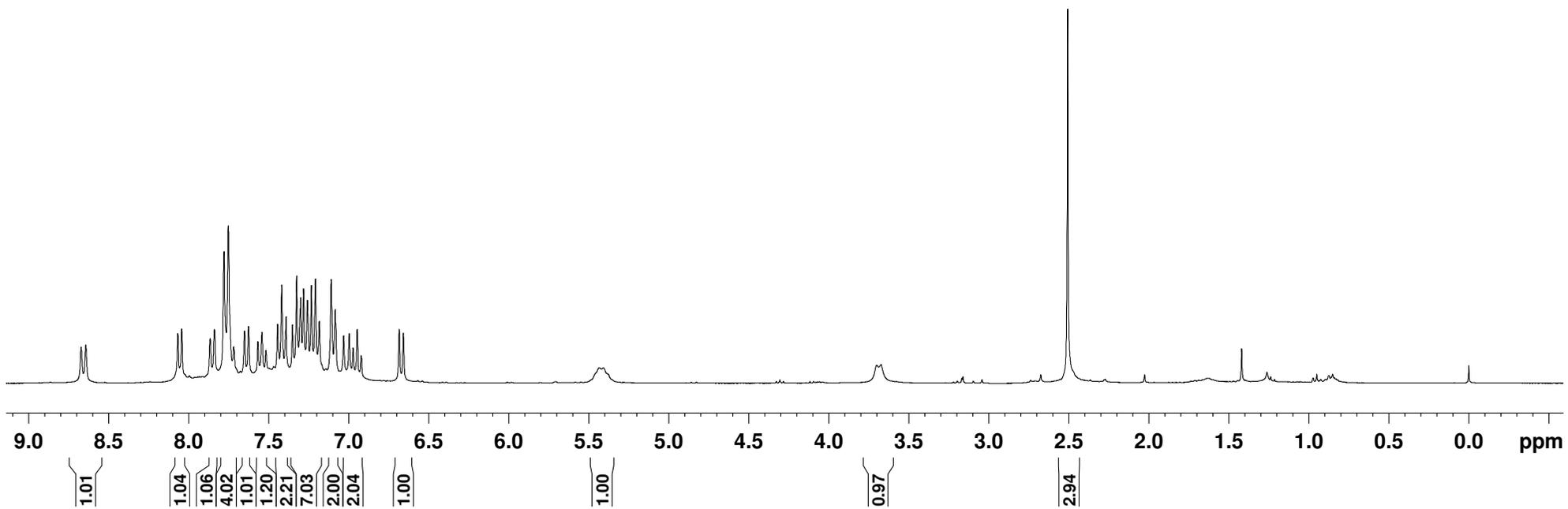
2.506

-0.000

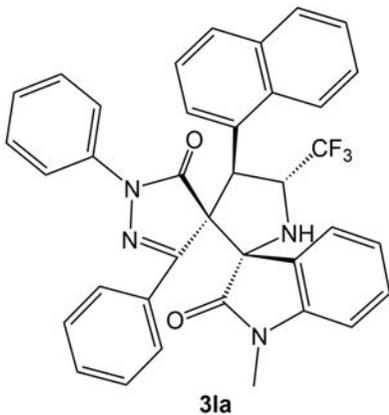


**3a**

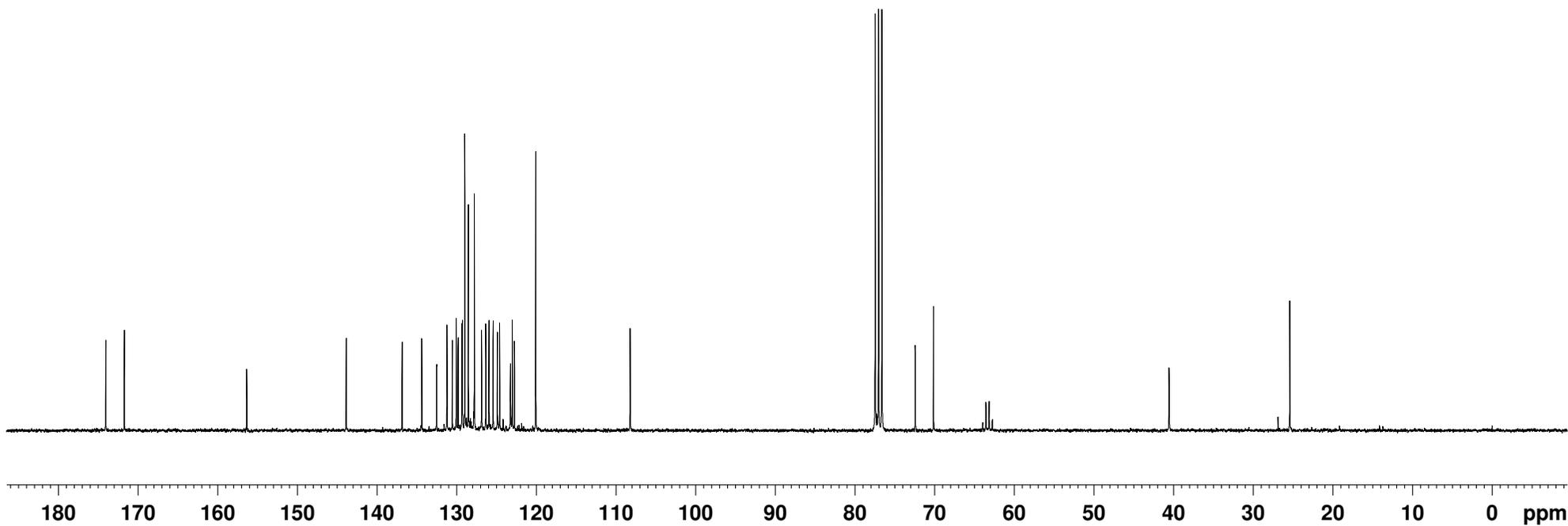
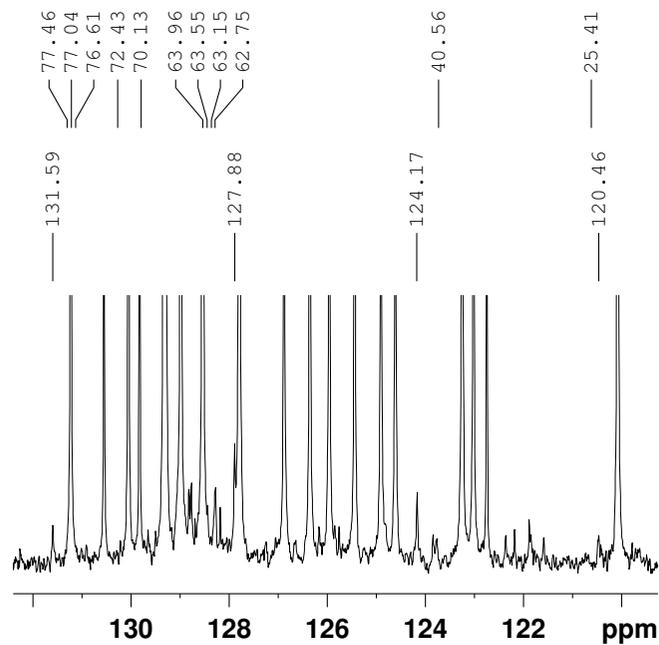
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )



174.00  
 171.68  
 156.31  
 143.87  
 136.85  
 134.38  
 132.52  
 131.59  
 131.22  
 130.54  
 130.05  
 129.82  
 129.33  
 129.28  
 128.98  
 128.53  
 127.88  
 127.79  
 126.87  
 126.34  
 125.95  
 125.43  
 124.89  
 124.60  
 124.17  
 123.25  
 123.02  
 122.75  
 120.46  
 120.08  
 108.22



<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)



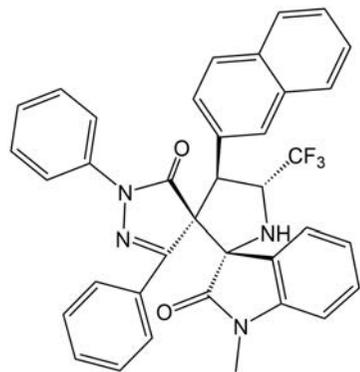


7.411  
7.363  
7.354  
7.341  
7.329  
7.314  
7.306  
7.301  
7.296  
7.291  
7.282  
7.268  
7.207  
7.202  
7.182  
7.160  
7.155  
7.138  
7.134  
7.124  
7.112  
7.109  
7.067  
7.042  
7.017  
6.824  
6.801  
6.798  
6.775  
6.773  
6.506  
6.480  
5.918  
5.885  
5.602  
5.577  
5.552  
5.545  
5.520  
5.495  
5.487  
5.463

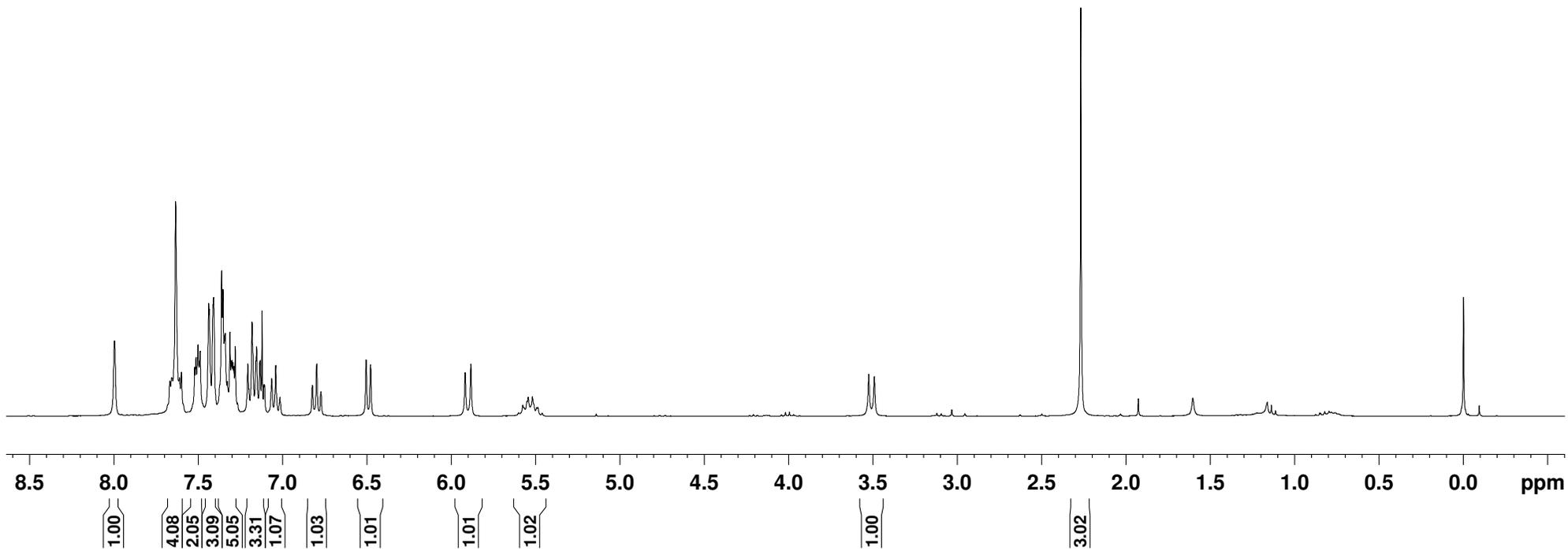
3.526  
3.493

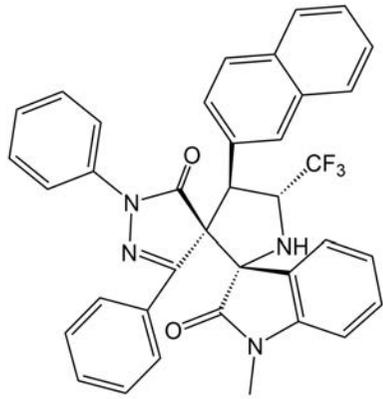
2.268

0.000

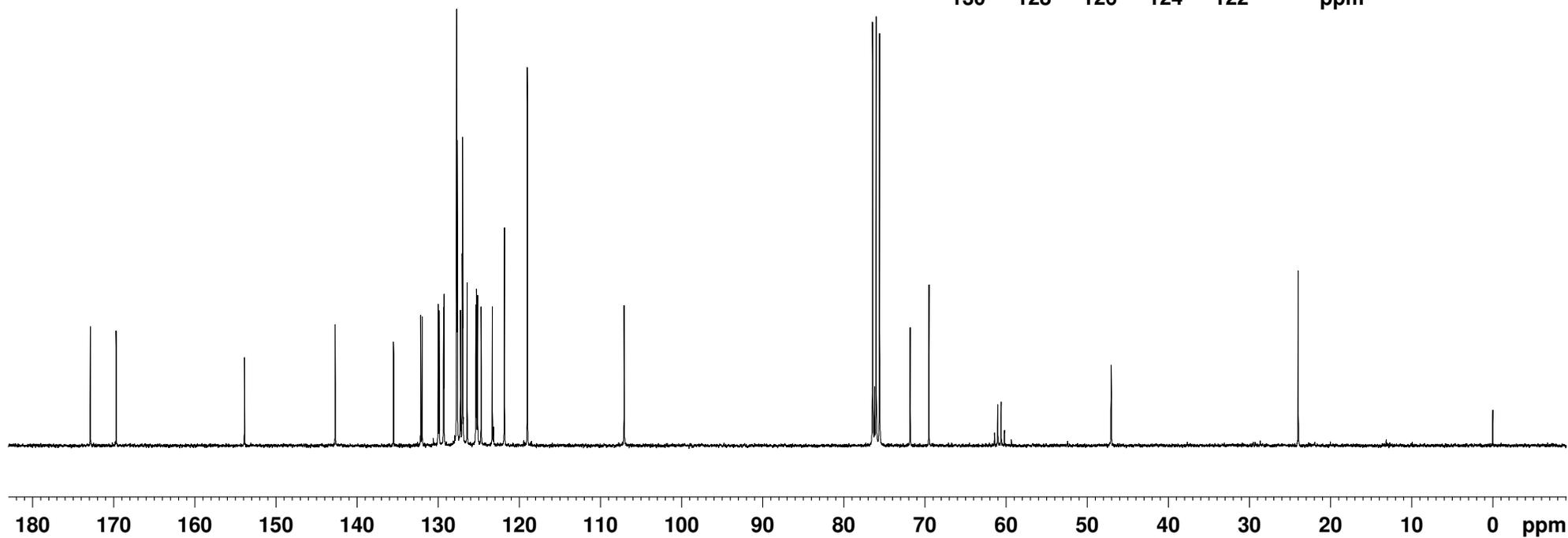


**3ma**  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)



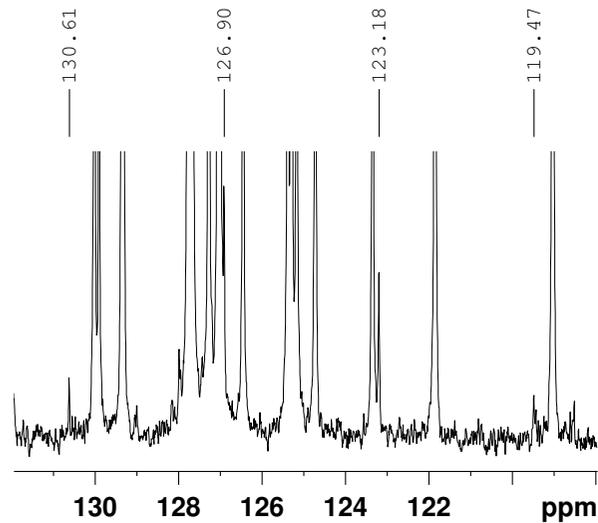


**3ma**  
 $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )



172.84  
 169.71  
 153.90  
 142.71  
 135.51  
 132.16  
 131.98  
 130.61  
 130.01  
 129.89  
 129.35  
 129.31  
 127.74  
 127.66  
 127.26  
 127.04  
 127.00  
 126.90  
 126.44  
 125.37  
 125.28  
 125.16  
 124.71  
 123.34  
 123.18  
 121.84  
 119.47  
 119.02  
 107.08

76.45  
 76.02  
 75.60  
 71.82  
 69.51  
 61.42  
 61.02  
 60.61  
 60.20  
 47.04  
 23.97  
 -0.00



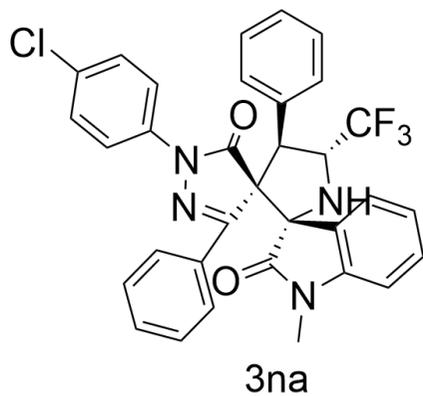


7.479  
7.468  
7.464  
7.443  
7.433  
7.414  
7.303  
7.294  
7.287  
7.282  
7.278  
7.264  
7.256  
7.252  
7.241  
7.231  
7.226  
7.217  
7.191  
6.923  
6.921  
6.898  
6.896  
6.872  
6.870  
6.618  
6.593  
5.813  
5.779  
5.527  
5.501  
5.476  
5.450

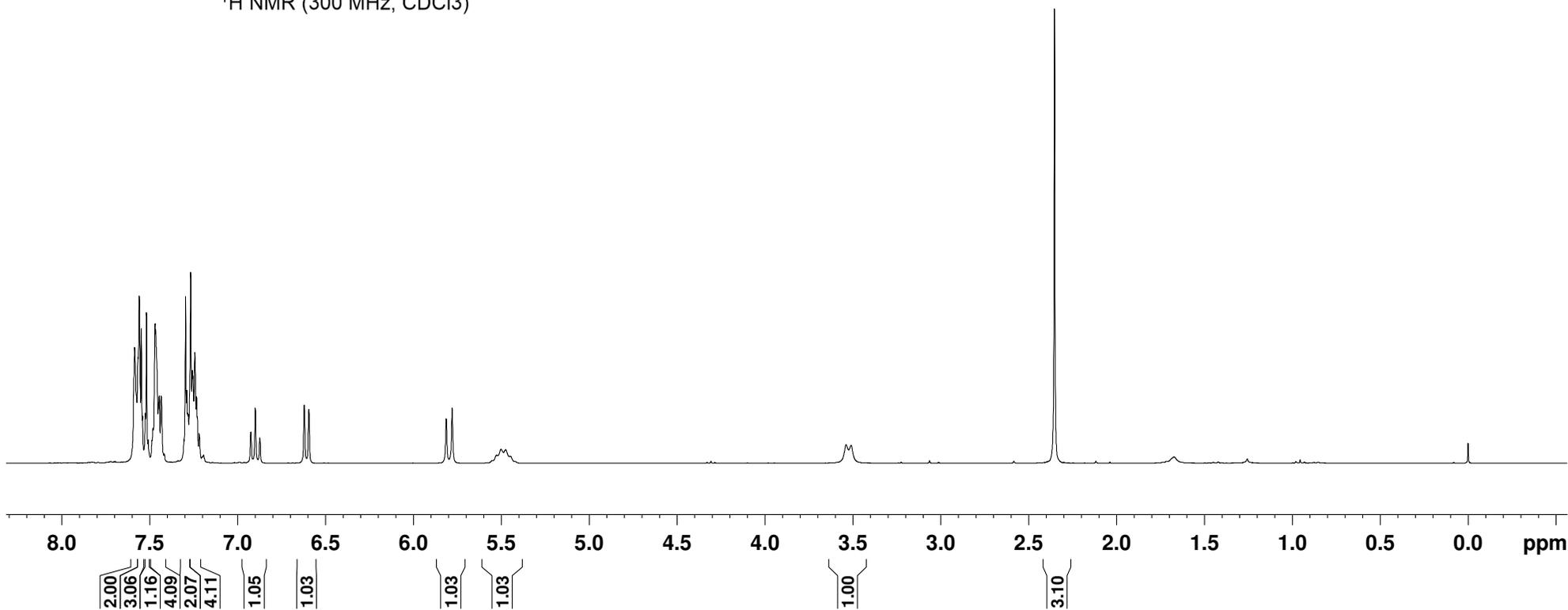
3.538  
3.510

2.352

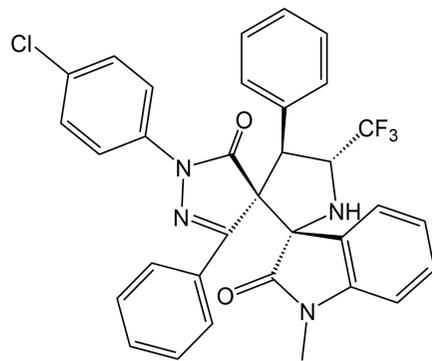
-0.000



<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)



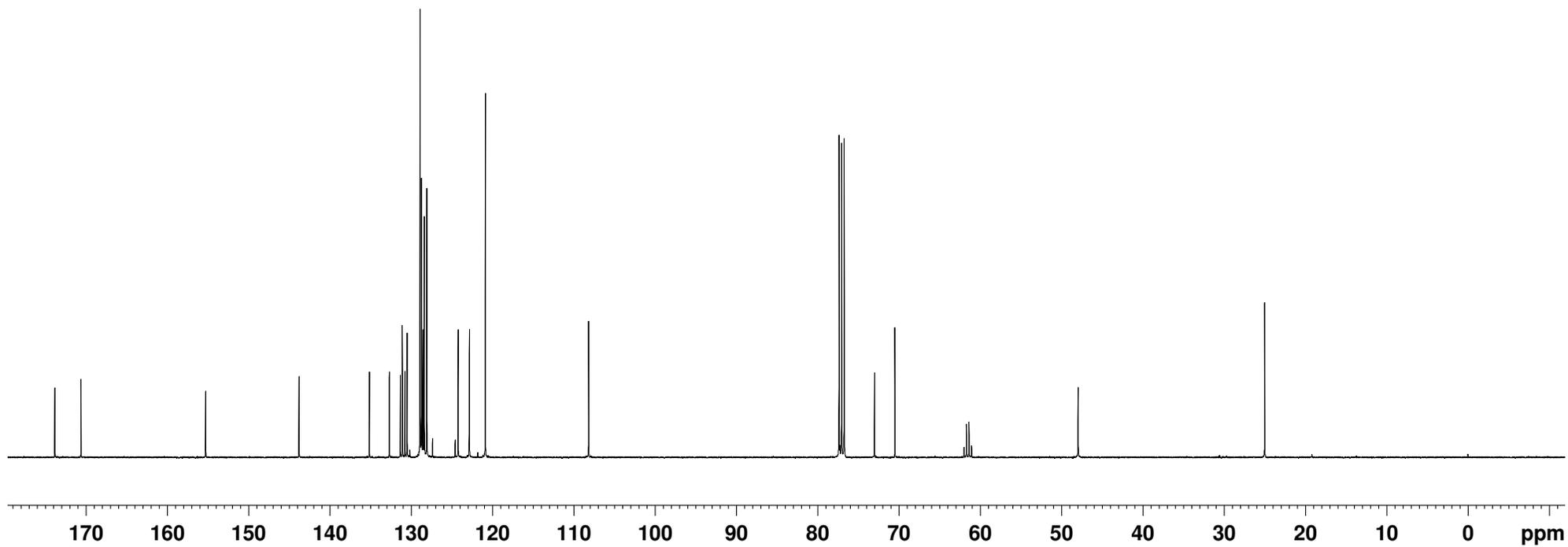
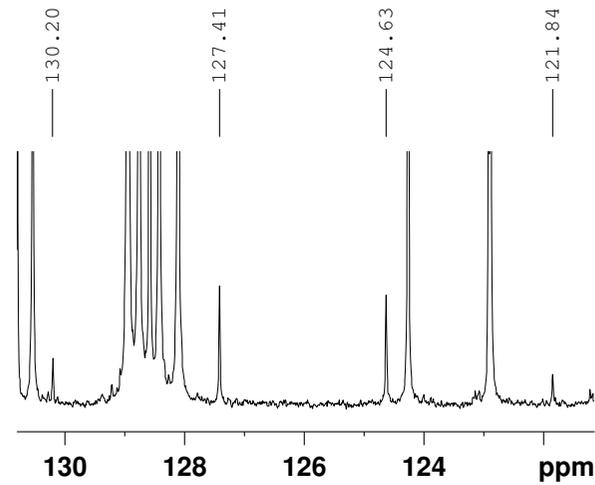
— 173.83  
 — 170.61  
 — 155.27  
 — 143.79  
 — 135.19  
 — 132.72  
 — 131.37  
 — 131.13  
 — 130.79  
 — 130.54  
 — 130.20  
 — 128.95  
 — 128.76  
 — 128.59  
 — 128.42  
 — 128.11  
 — 127.41  
 — 124.63  
 — 124.26  
 — 122.92  
 — 122.88  
 — 121.84  
 — 120.92  
 — 108.21

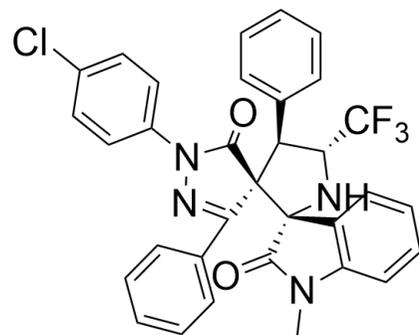


**3na**

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

— 77.40  
 — 77.09  
 — 76.77  
 — 73.04  
 — 70.53  
 — 62.02  
 — 61.72  
 — 61.41  
 — 61.10  
 — 47.99  
 — 25.03

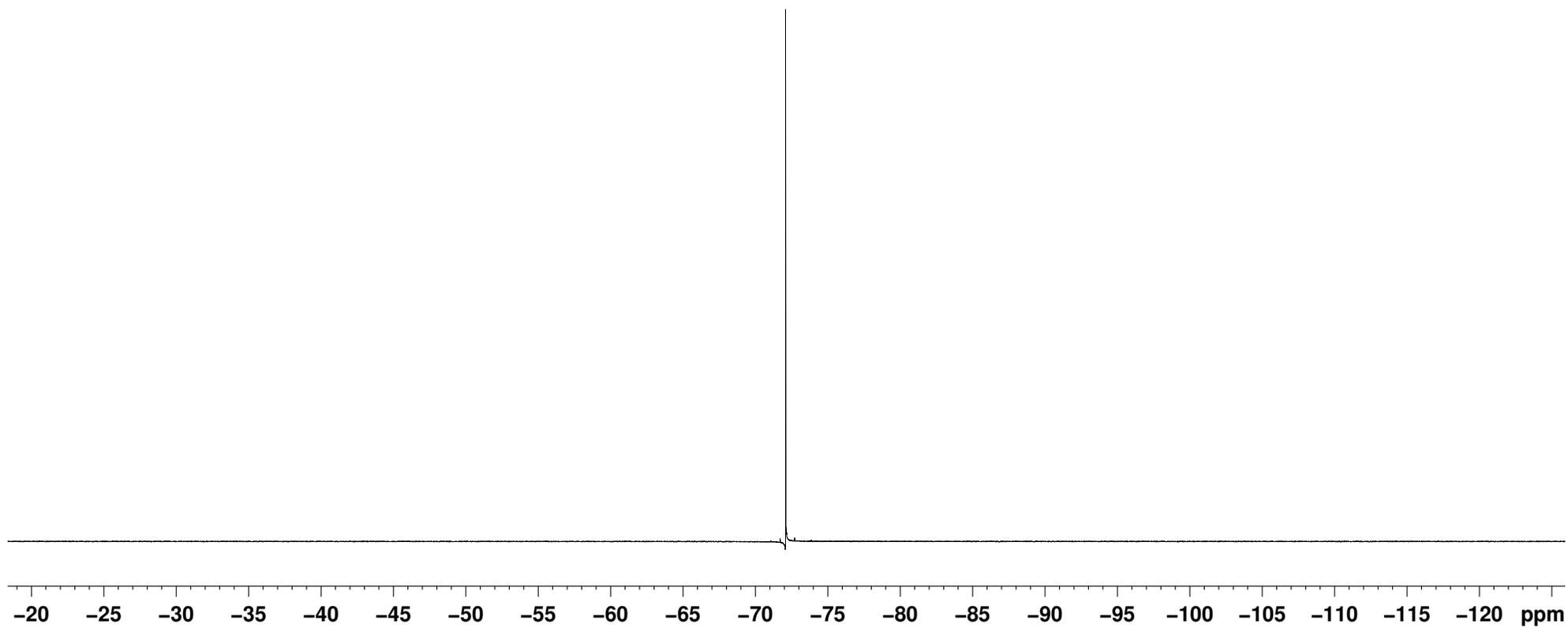




3na

<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)

— -72.085

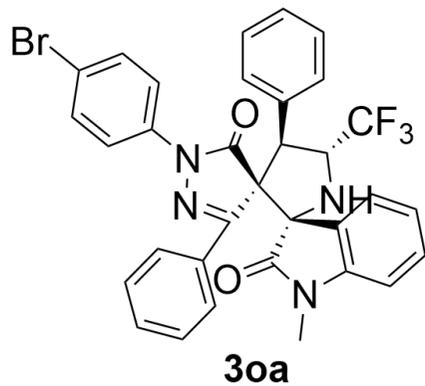


7.408  
7.290  
7.281  
7.275  
7.271  
7.261  
7.249  
7.246  
7.236  
7.226  
7.220  
7.211  
7.195  
7.190  
7.186  
6.915  
6.913  
6.890  
6.888  
6.864  
6.862  
6.613  
6.588  
5.813  
5.779  
5.604  
5.554  
5.530  
5.522  
5.505  
5.497  
5.473  
5.448  
5.440  
5.415

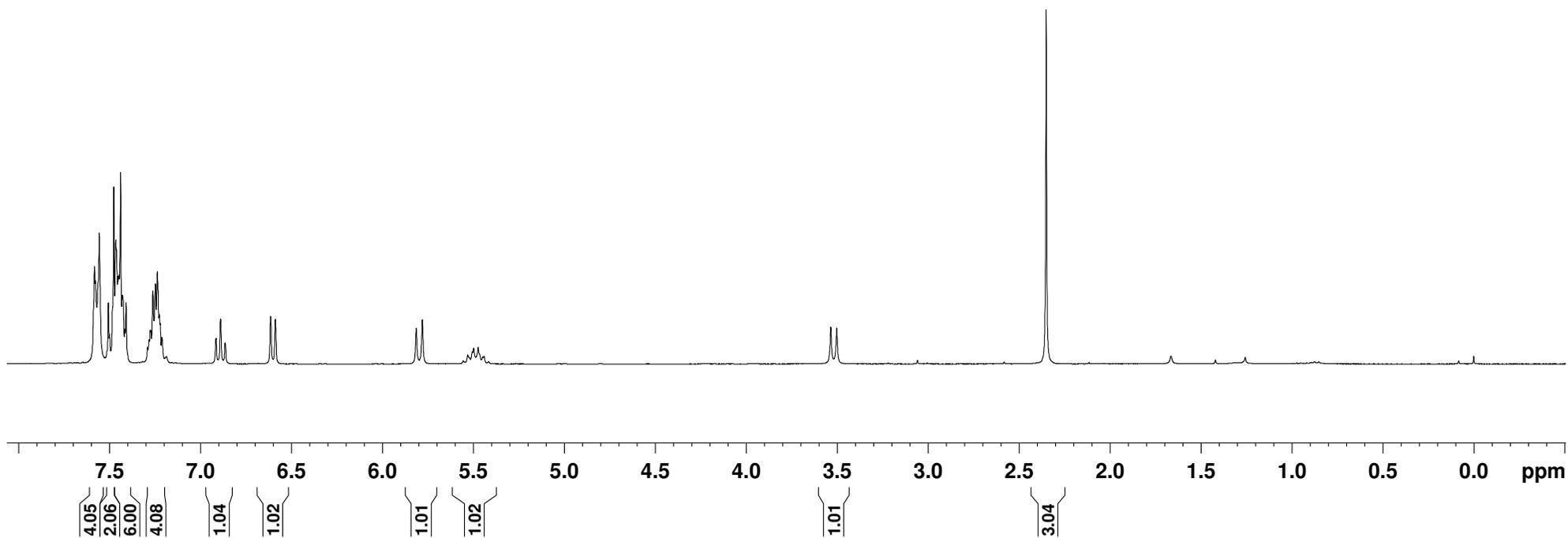
3.534  
3.502

2.350

-0.000

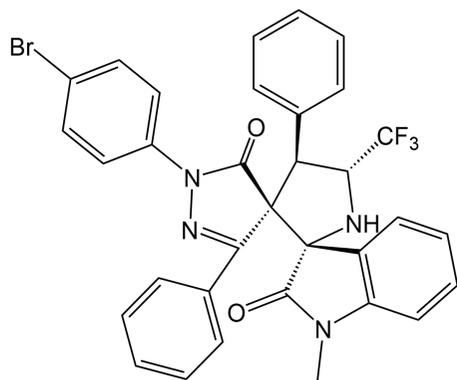


<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)



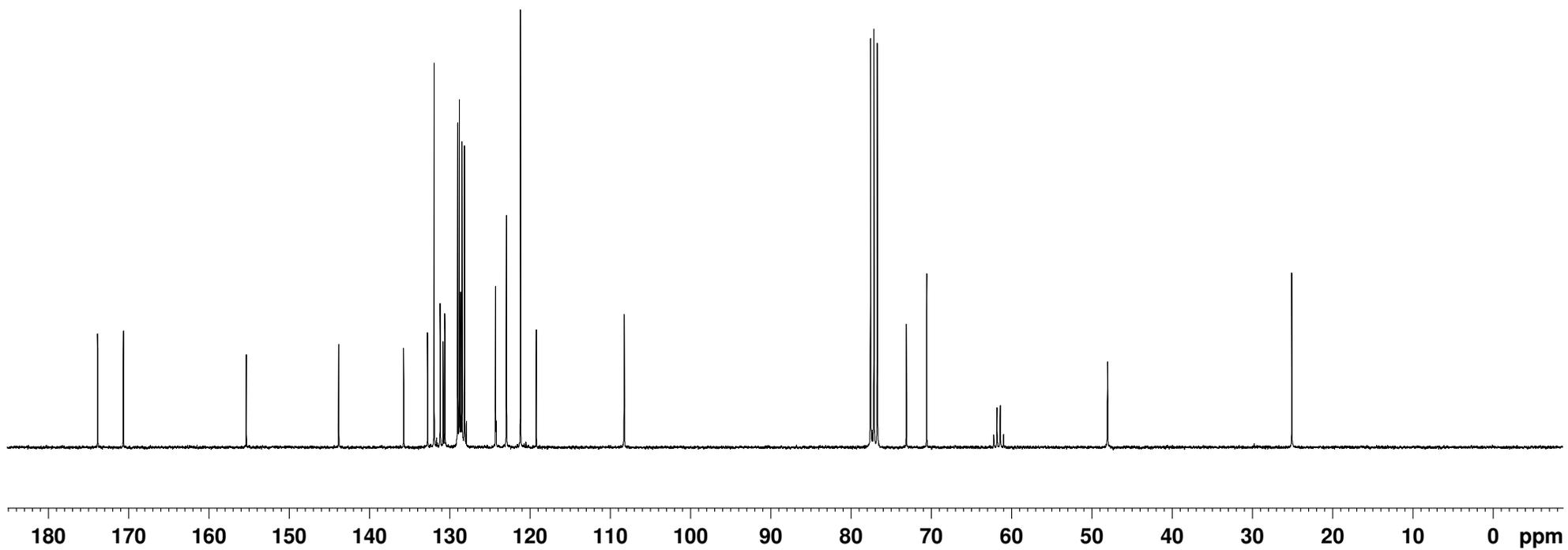
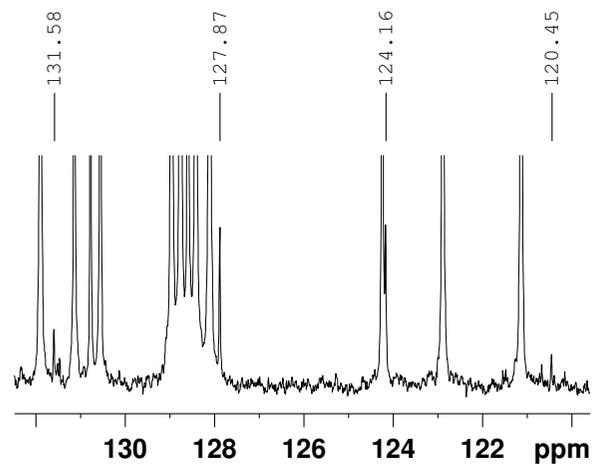
— 173.80  
 — 170.60  
 — 155.29  
 143.76  
 135.68  
 132.69  
 131.88  
 131.58  
 131.12  
 130.76  
 130.54  
 128.95  
 128.75  
 128.58  
 128.41  
 128.10  
 127.87  
 124.23  
 124.16  
 122.88  
 121.12  
 120.45  
 119.16  
 108.21

77.51  
 77.09  
 76.67  
 73.05  
 70.52  
 62.16  
 61.75  
 61.35  
 60.94  
 47.98  
 25.02



**30a**

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



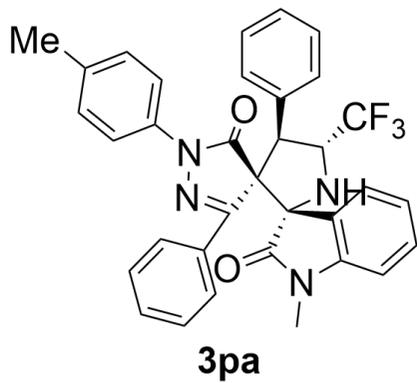


7.215  
7.211  
7.208  
7.192  
7.181  
7.129  
7.101  
7.053  
7.014  
6.991  
6.960  
6.931  
6.907  
6.881  
6.840  
6.814  
6.790  
6.762  
6.710  
6.691  
6.666  
6.599  
6.573  
6.506  
6.481  
6.455  
5.813  
5.779  
5.678  
5.619  
5.571  
5.547  
5.521  
5.514  
5.489  
5.464  
5.457  
5.432  
5.373

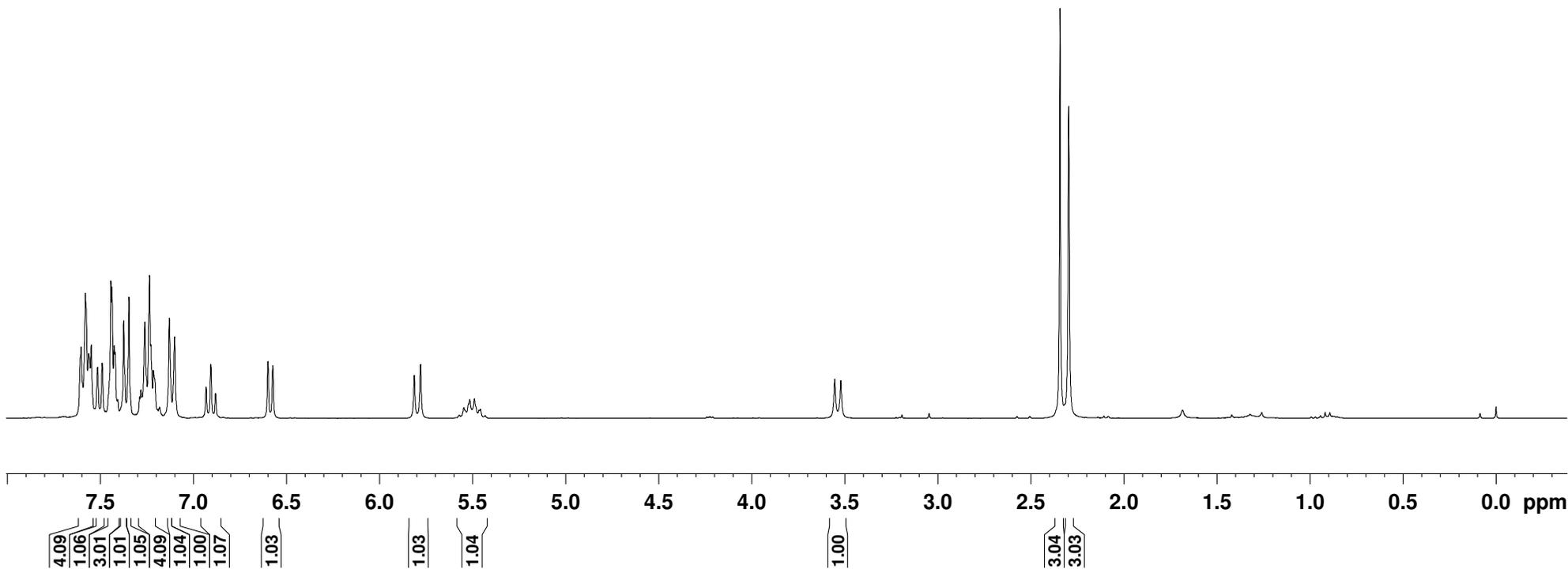
3.553  
3.521

2.343  
2.296

-0.000

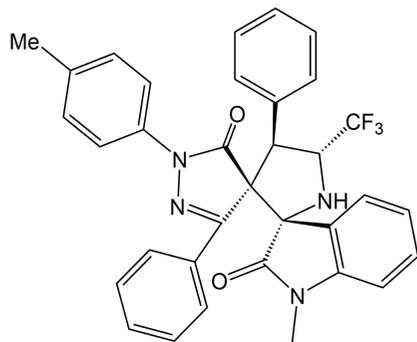


<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)



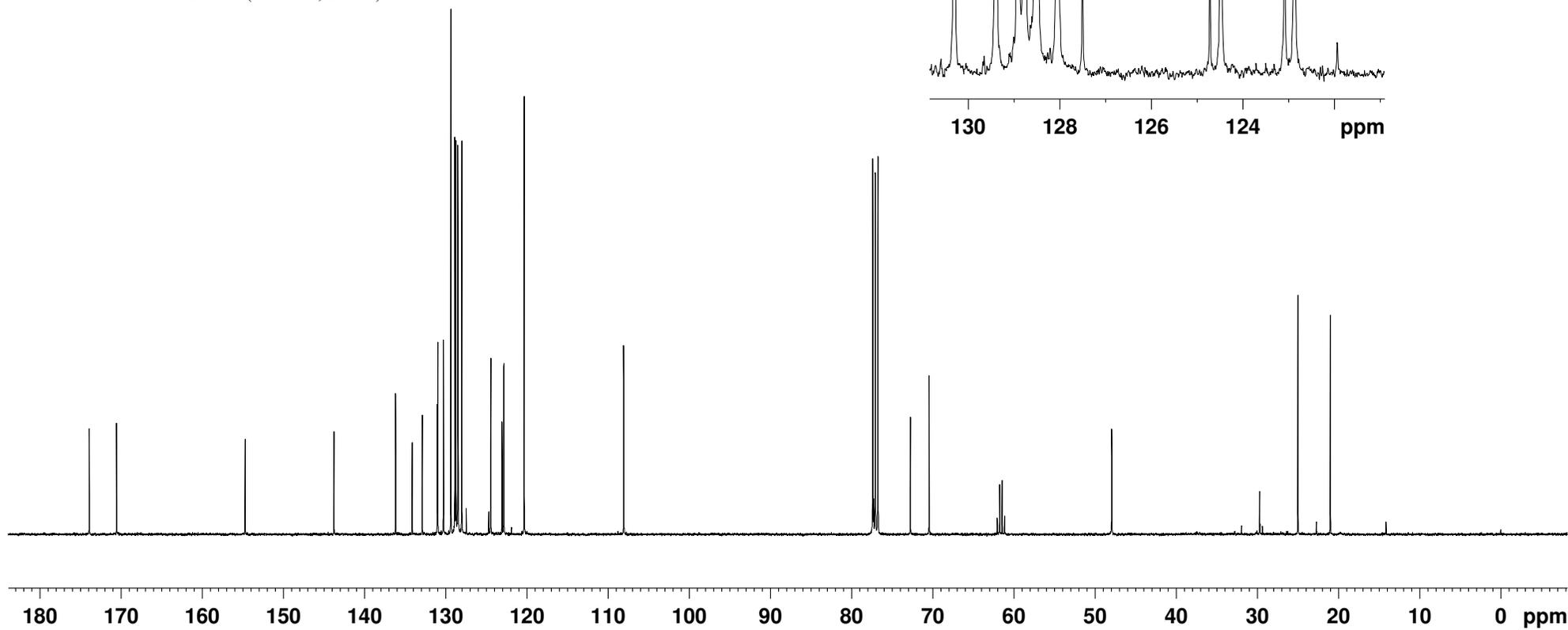
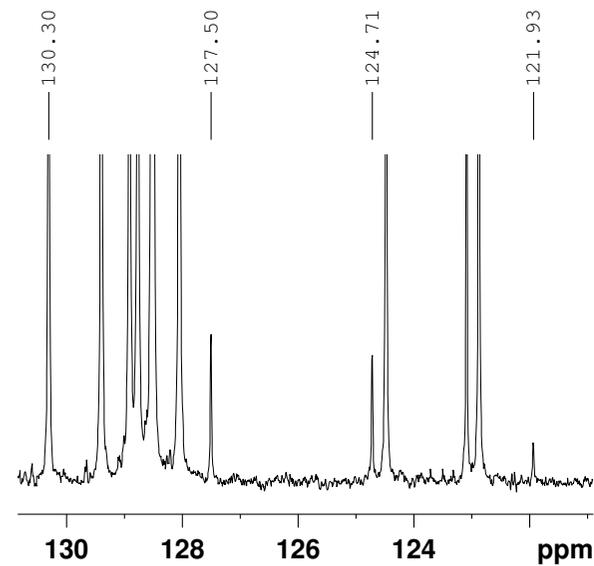
173.95  
170.58  
154.75  
143.80  
136.20  
134.16  
132.92  
131.07  
131.00  
130.30  
129.39  
128.90  
128.76  
128.52  
128.48  
128.04  
127.50  
124.71  
124.47  
123.08  
122.87  
121.93  
120.36  
108.09

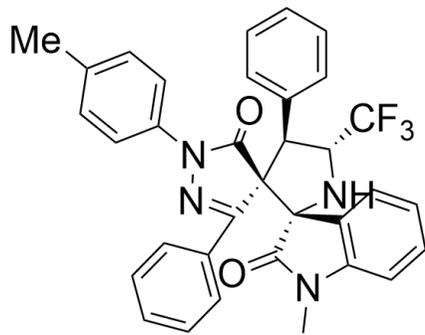
77.40  
77.09  
76.77  
72.77  
70.46  
62.07  
61.76  
61.46  
61.15  
47.95  
25.00  
21.01



**3pa**

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

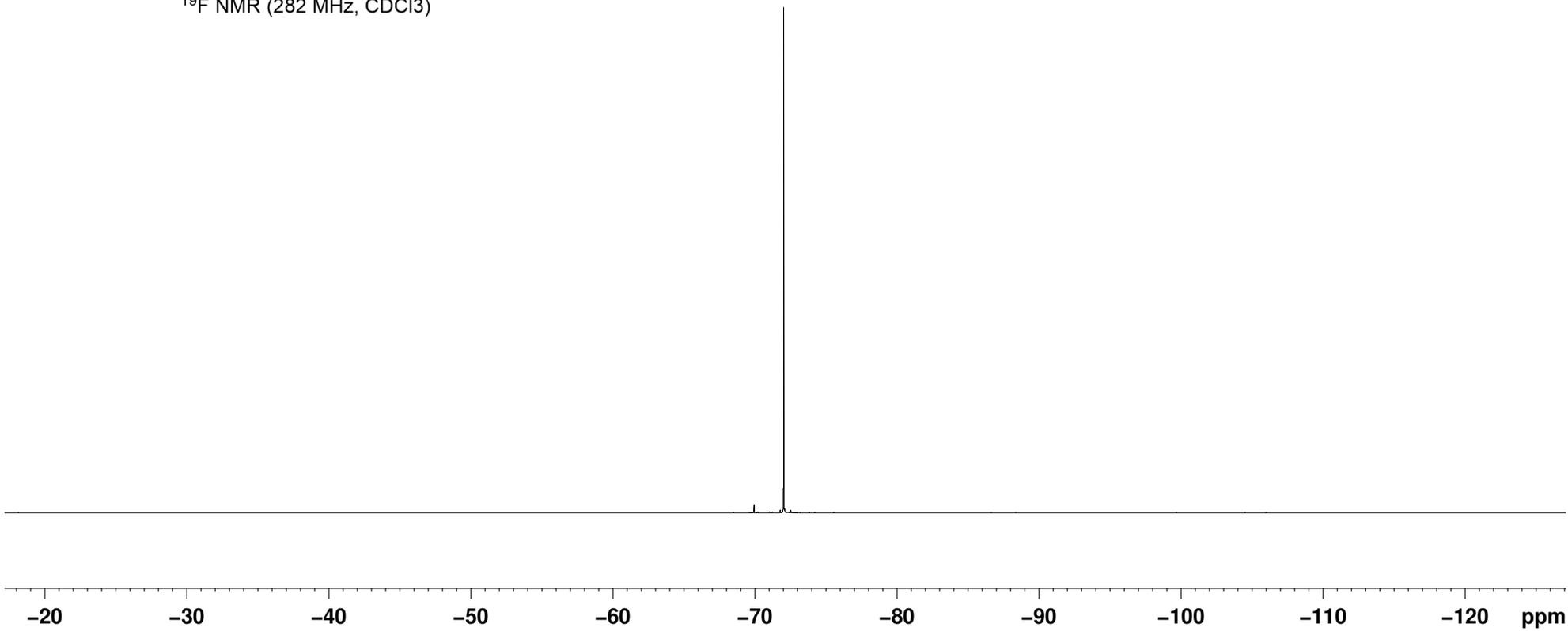




**3pa**

<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)

— -72.023

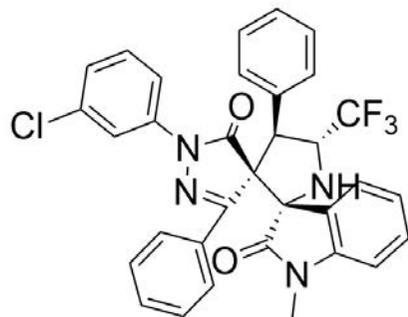


7.443  
7.433  
7.292  
7.285  
7.279  
7.264  
7.239  
7.231  
7.217  
7.208  
7.186  
7.145  
7.142  
7.139  
7.118  
7.115  
7.112  
6.917  
6.892  
6.866  
6.609  
6.584  
5.830  
5.823  
5.796  
5.790  
5.557  
5.532  
5.507  
5.481  
5.475  
5.450  
5.424

3.540  
3.531  
3.508  
3.499

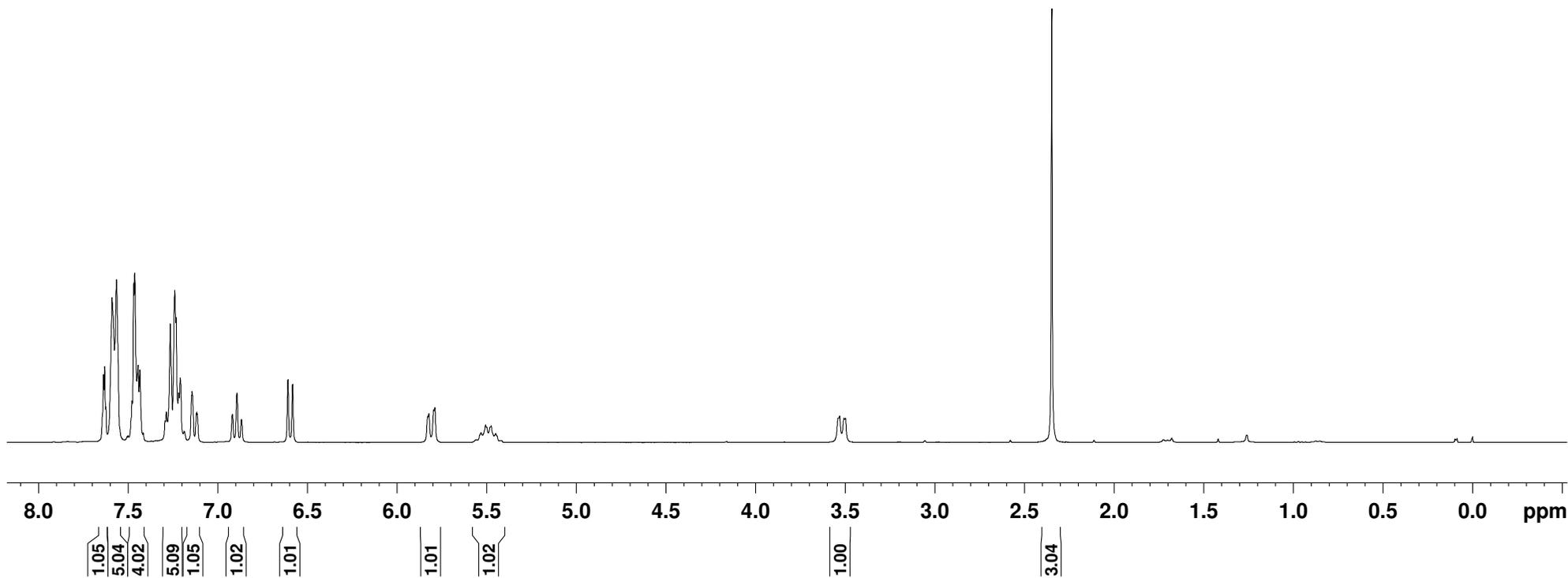
2.348

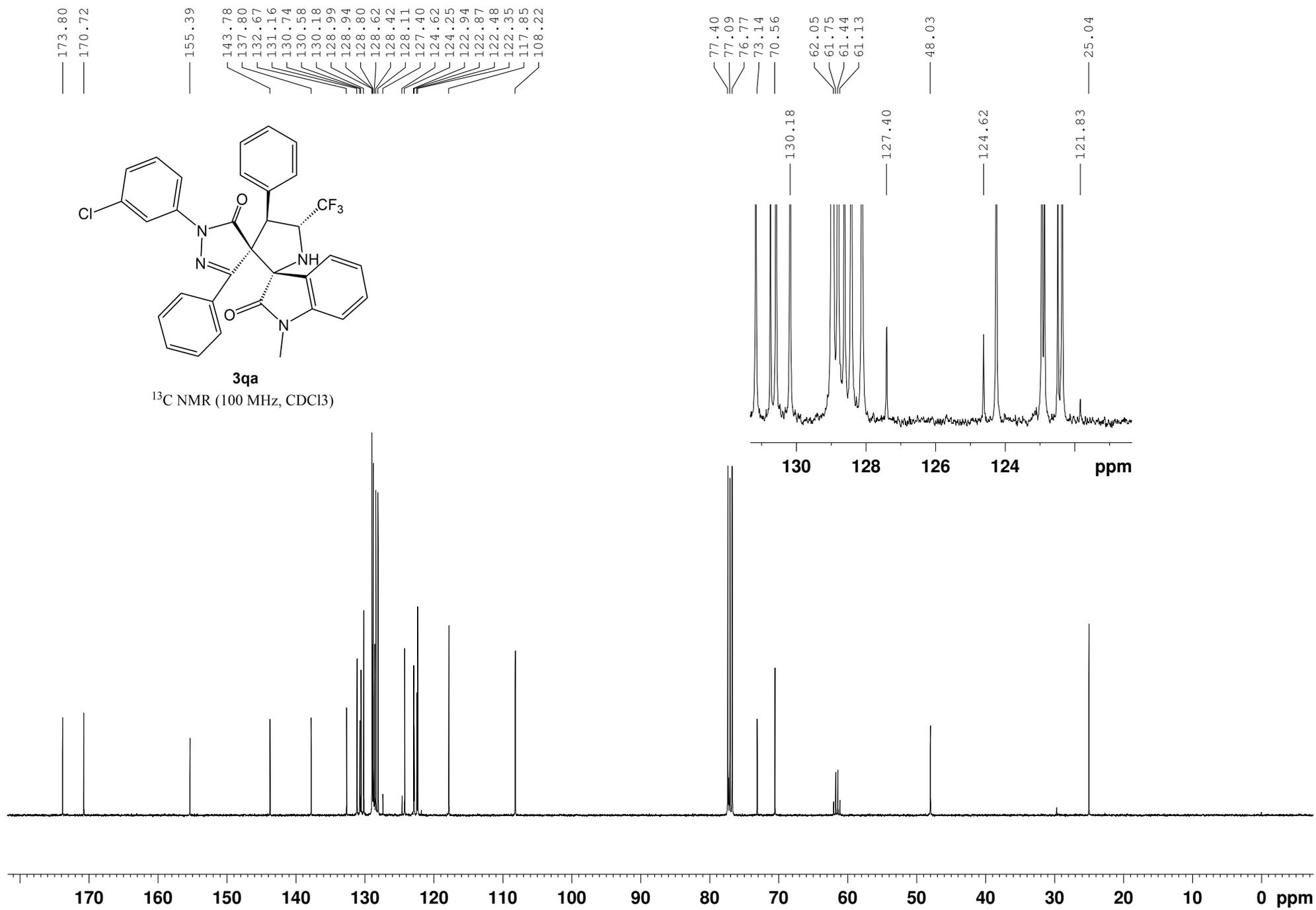
0.004  
-0.000

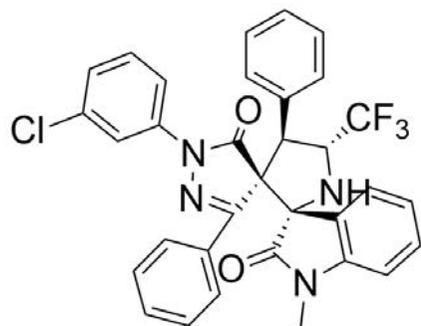


**3qa**

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)



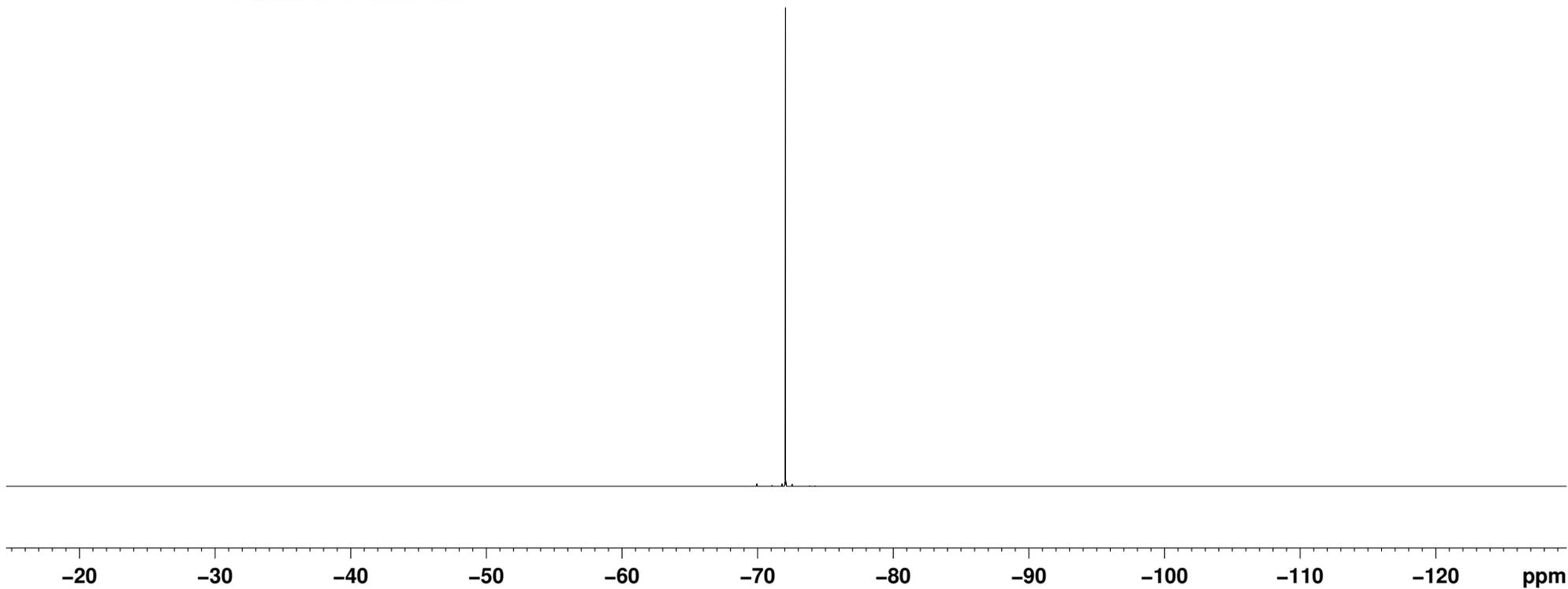




**3qa**

<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)

— -72.037

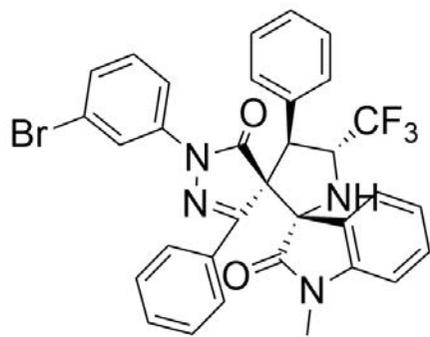


7.473  
7.464  
7.458  
7.440  
7.428  
7.290  
7.282  
7.261  
7.236  
7.227  
7.214  
7.210  
7.206  
7.191  
7.181  
7.164  
7.137  
6.912  
6.889  
6.887  
6.863  
6.605  
6.579  
6.026  
6.014  
5.930  
5.824  
5.790  
5.679  
5.646  
5.613  
5.598  
5.587  
5.556  
5.531  
5.506  
5.499  
5.474  
5.449  
5.442  
5.417  
5.356

3.534  
3.501

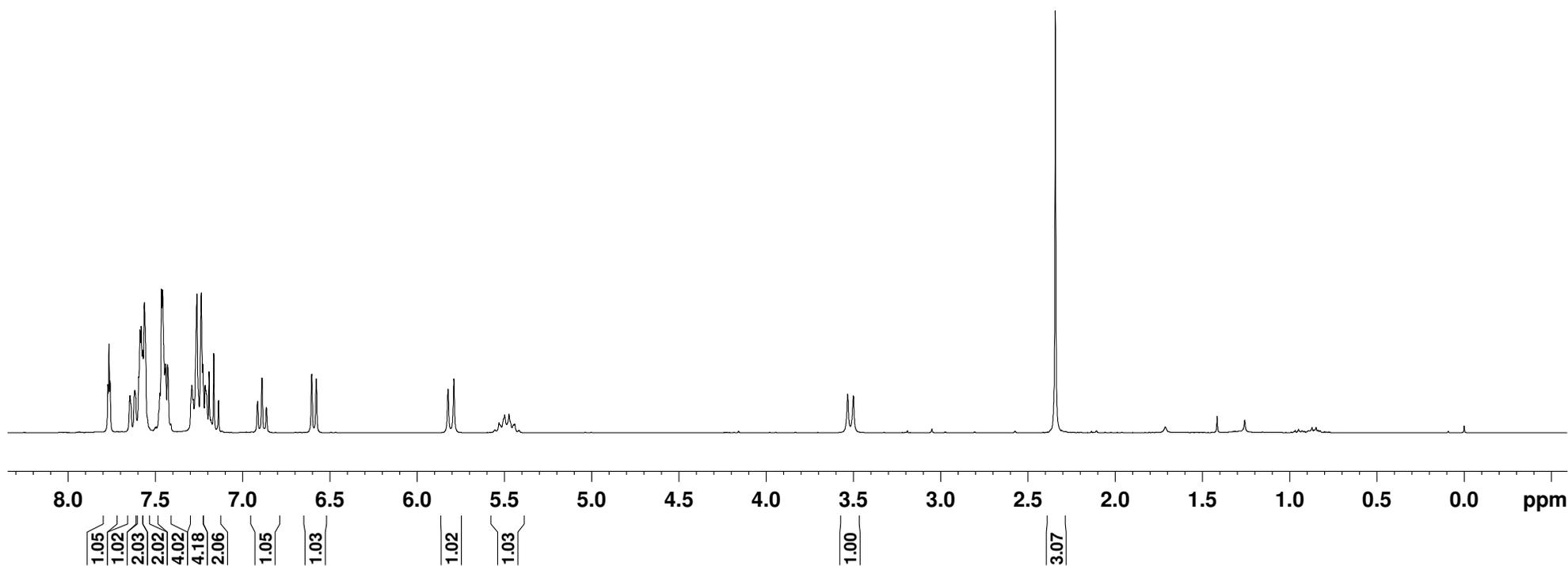
2.343

-0.000

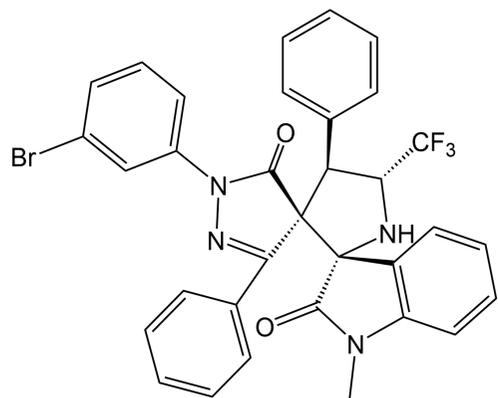


**3ra**

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)



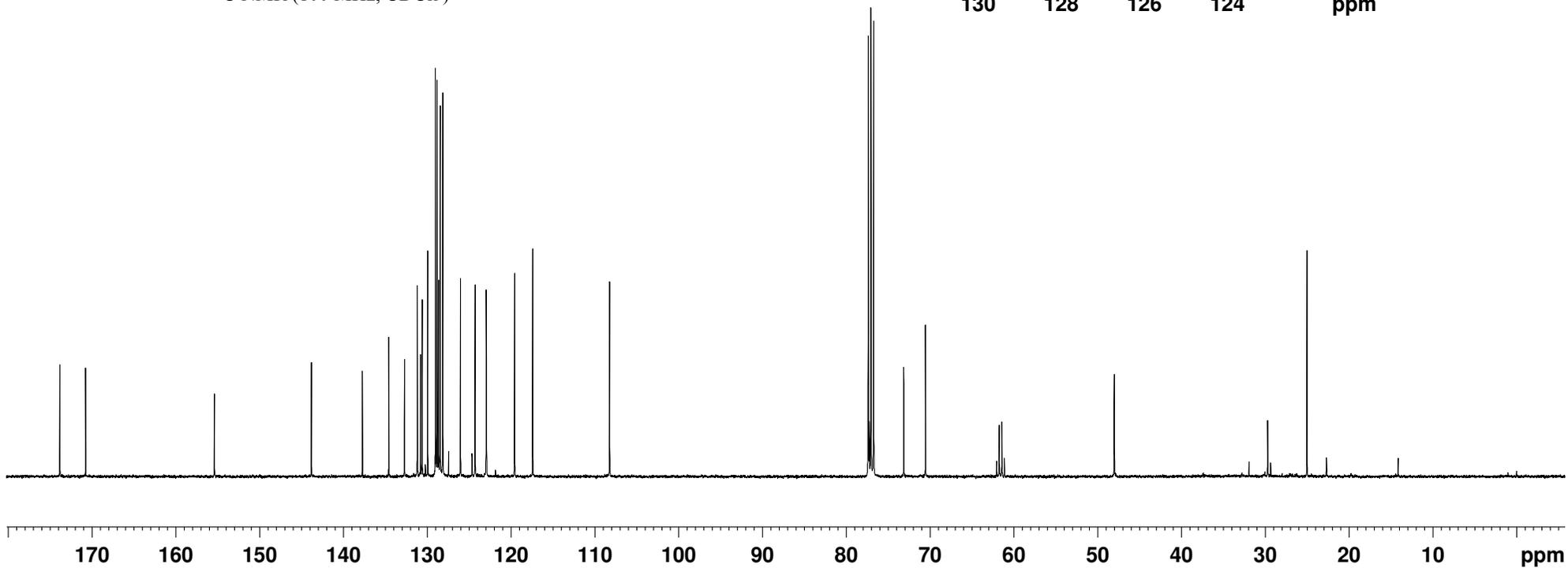
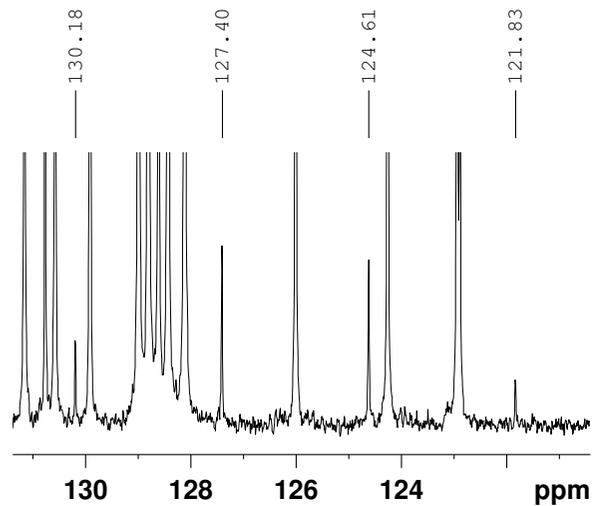
— 173.81  
 — 170.72  
 — 155.36  
 — 143.78  
 — 137.70  
 — 134.55  
 — 132.68  
 — 131.15  
 — 130.75  
 — 130.57  
 — 130.18  
 — 129.90  
 — 128.98  
 — 128.79  
 — 128.60  
 — 128.42  
 — 128.11  
 — 127.40  
 — 126.00  
 — 124.61  
 — 124.25  
 — 122.93  
 — 122.88  
 — 121.83  
 — 119.54  
 — 117.38  
 — 108.20



**3ra**

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

— 77.38  
 — 77.07  
 — 76.75  
 — 73.15  
 — 70.56  
 — 62.06  
 — 61.75  
 — 61.44  
 — 61.14  
 — 48.03  
 — 25.03



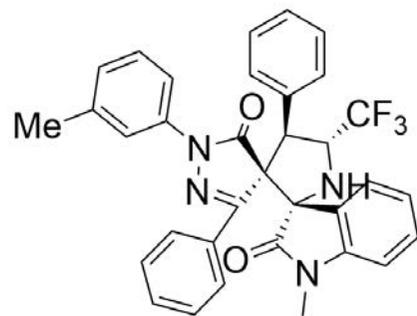


7.434  
7.429  
7.415  
7.398  
7.372  
7.345  
7.286  
7.264  
7.240  
7.230  
7.218  
7.204  
7.177  
7.004  
6.979  
6.937  
6.912  
6.886  
6.604  
6.578  
5.827  
5.820  
5.793  
5.787  
5.594  
5.571  
5.547  
5.522  
5.515  
5.497  
5.490  
5.473  
5.465  
5.440

3.561  
3.552  
3.529  
3.520

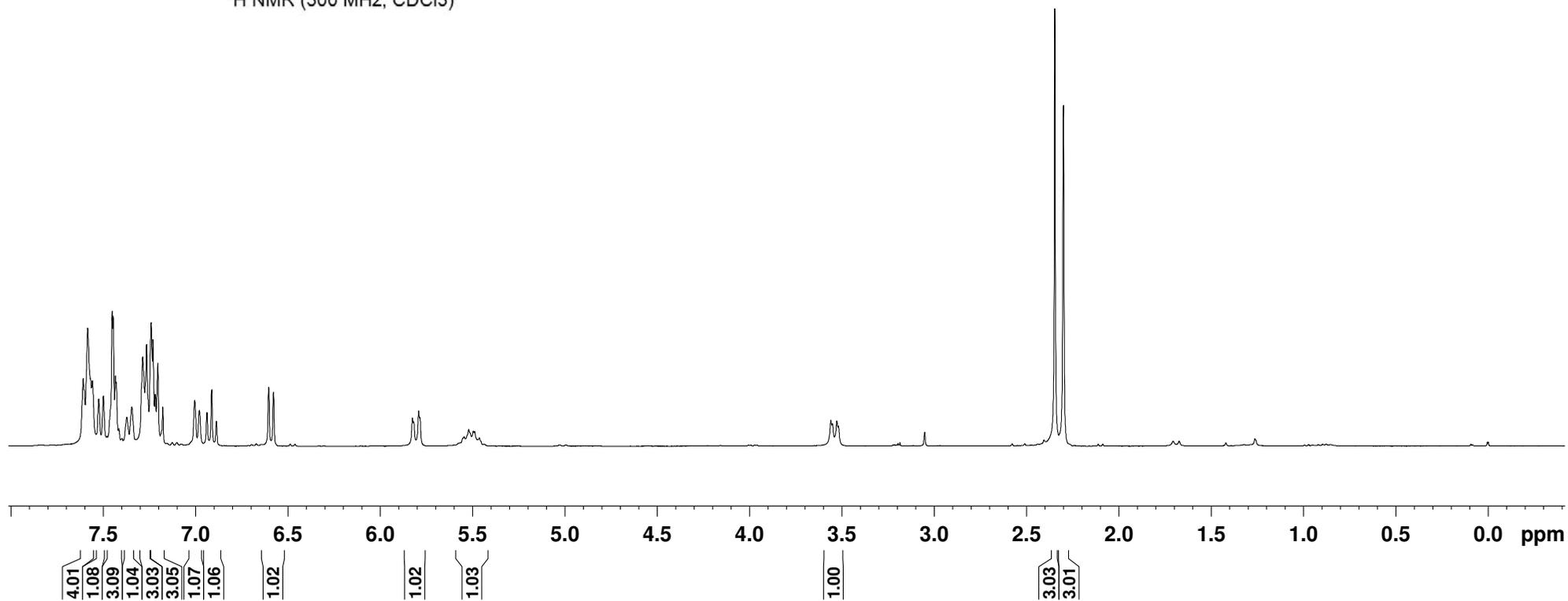
2.348  
2.301

0.005  
-0.000



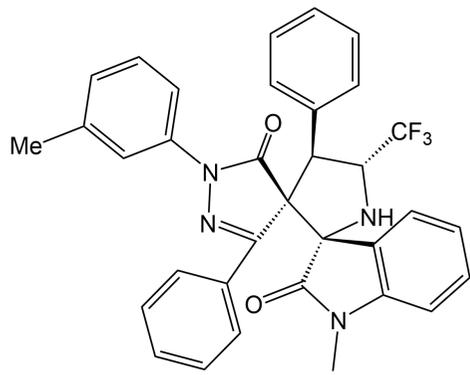
**3sa**

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)



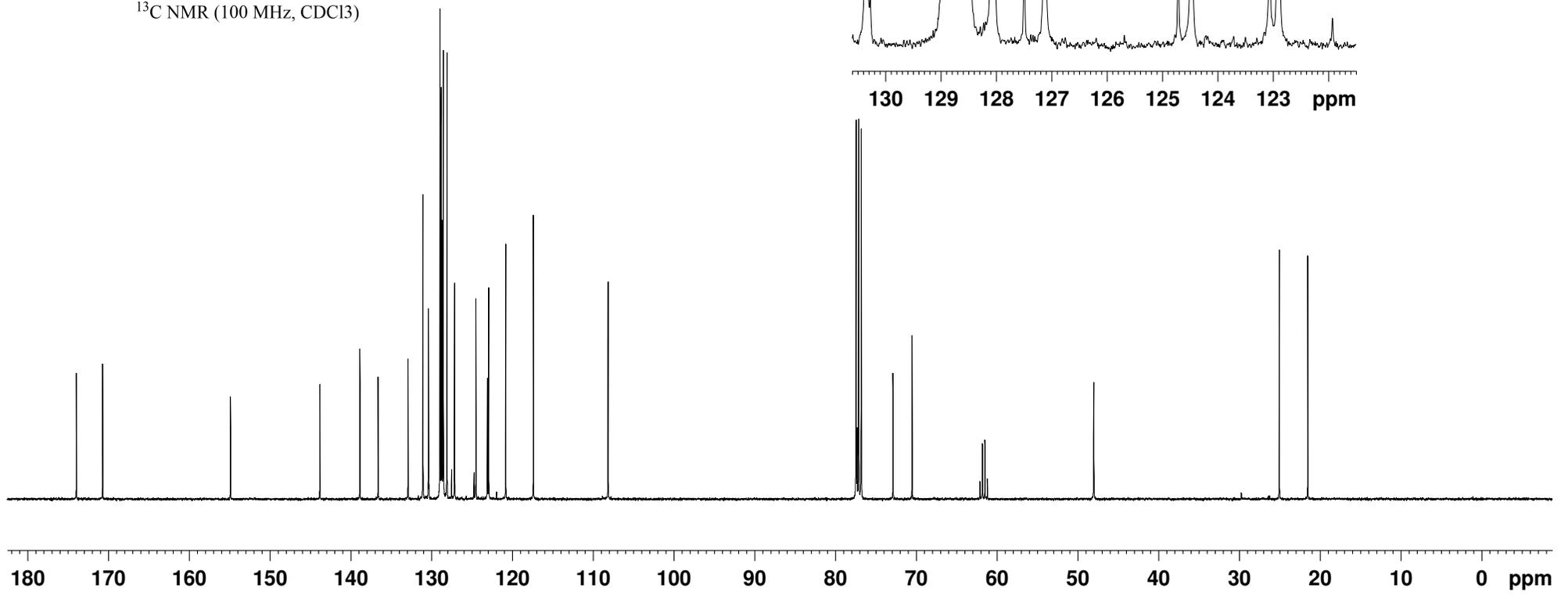
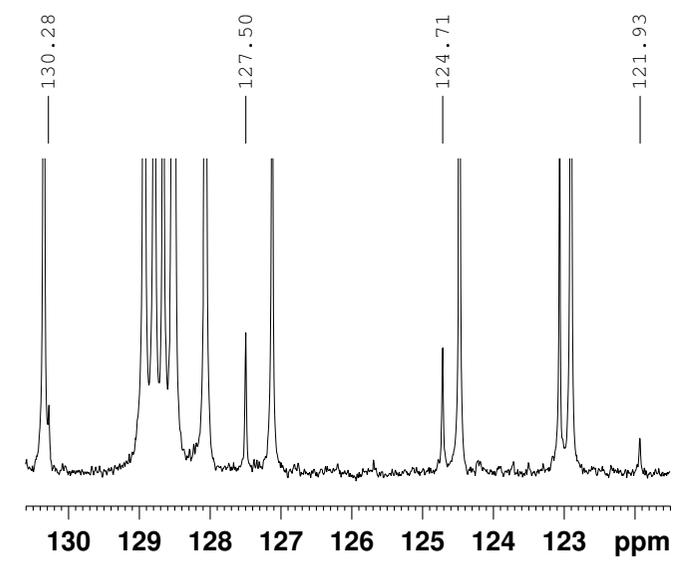
— 173.94  
 — 170.70  
 — 154.87  
 — 143.80  
 — 138.84  
 — 136.58  
 — 132.88  
 — 131.04  
 — 130.35  
 — 130.28  
 — 128.93  
 — 128.79  
 — 128.66  
 — 128.52  
 — 128.50  
 — 128.06  
 — 127.50  
 — 127.12  
 — 124.71  
 — 124.47  
 — 123.06  
 — 122.90  
 — 121.93  
 — 120.79  
 — 117.37  
 — 108.12

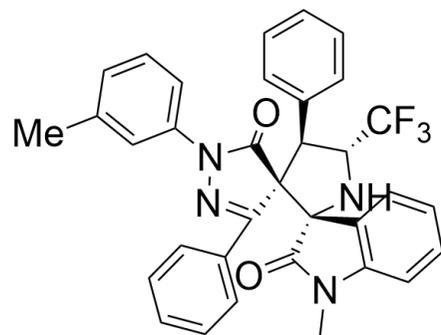
— 77.42  
 — 77.10  
 — 76.78  
 — 72.84  
 — 70.48  
 — 62.07  
 — 61.77  
 — 61.46  
 — 61.16  
 — 47.99  
 — 25.02  
 — 21.49



**3sa**

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

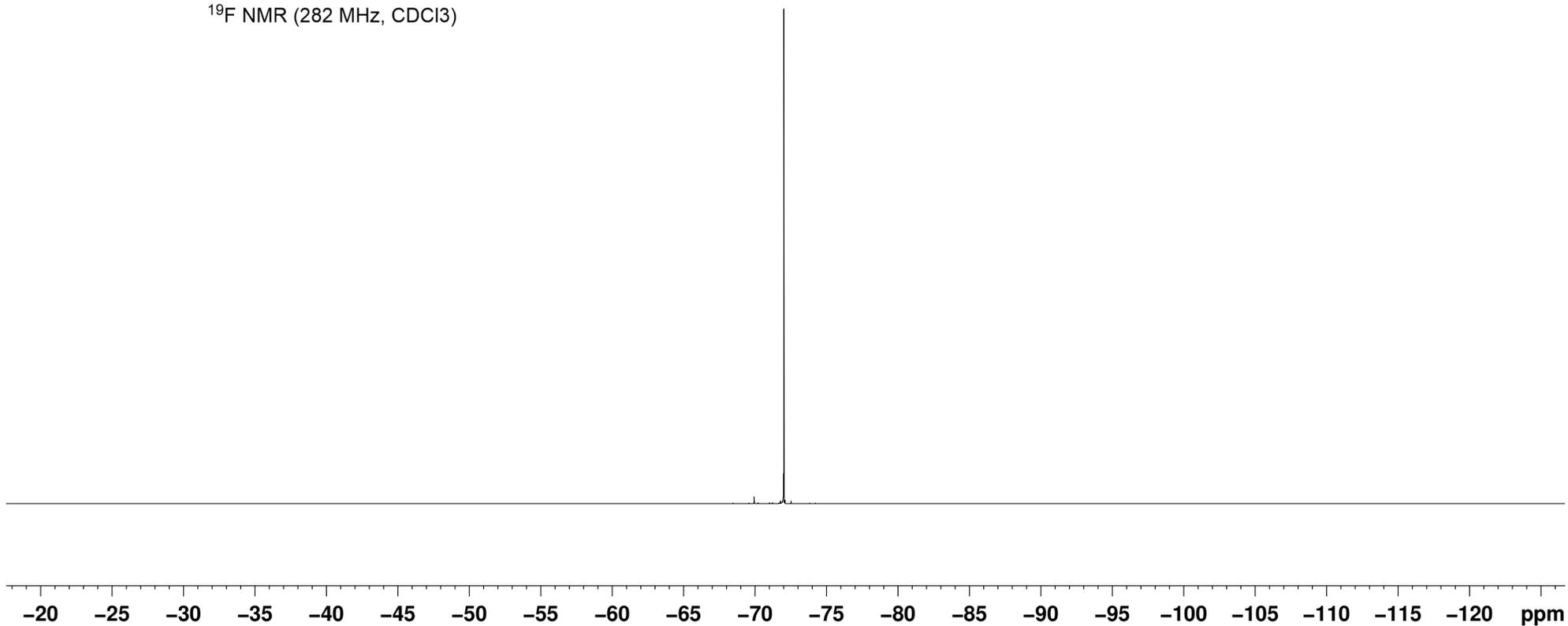




**3sa**

<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)

— -72.007

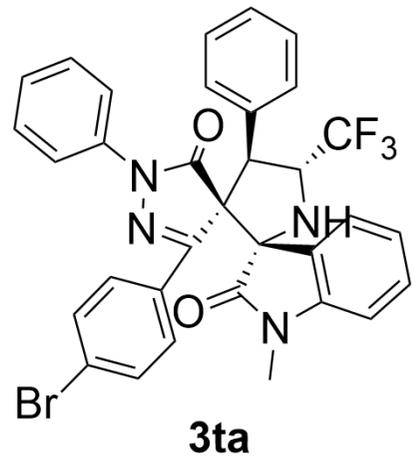


7.447  
7.418  
7.404  
7.393  
7.376  
7.261  
7.236  
7.208  
7.194  
7.175  
7.168  
7.150  
7.125  
7.099  
7.074  
6.850  
6.824  
6.799  
6.541  
6.515  
5.674  
5.641  
5.521  
5.481  
5.457  
5.425  
5.401  
5.375  
5.368  
5.343

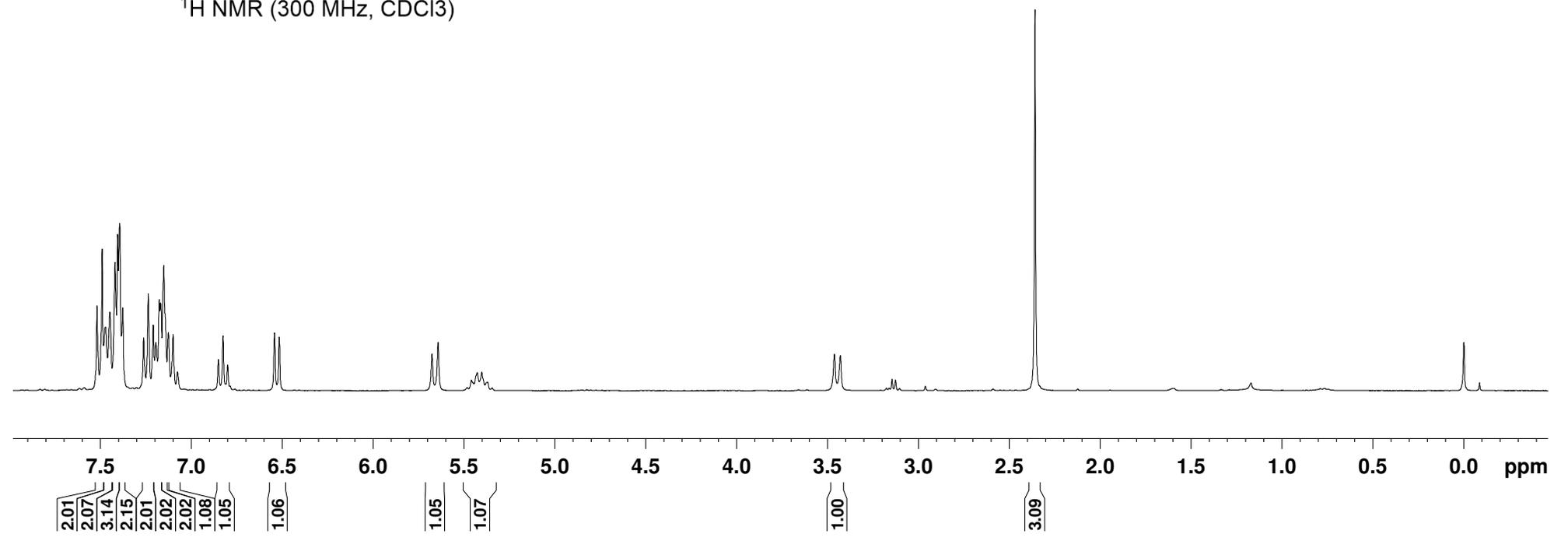
3.463  
3.430

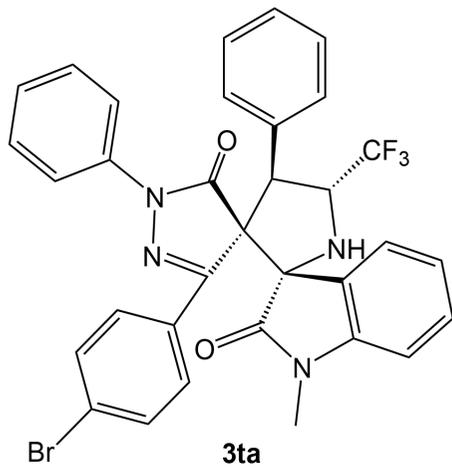
2.359

-0.000

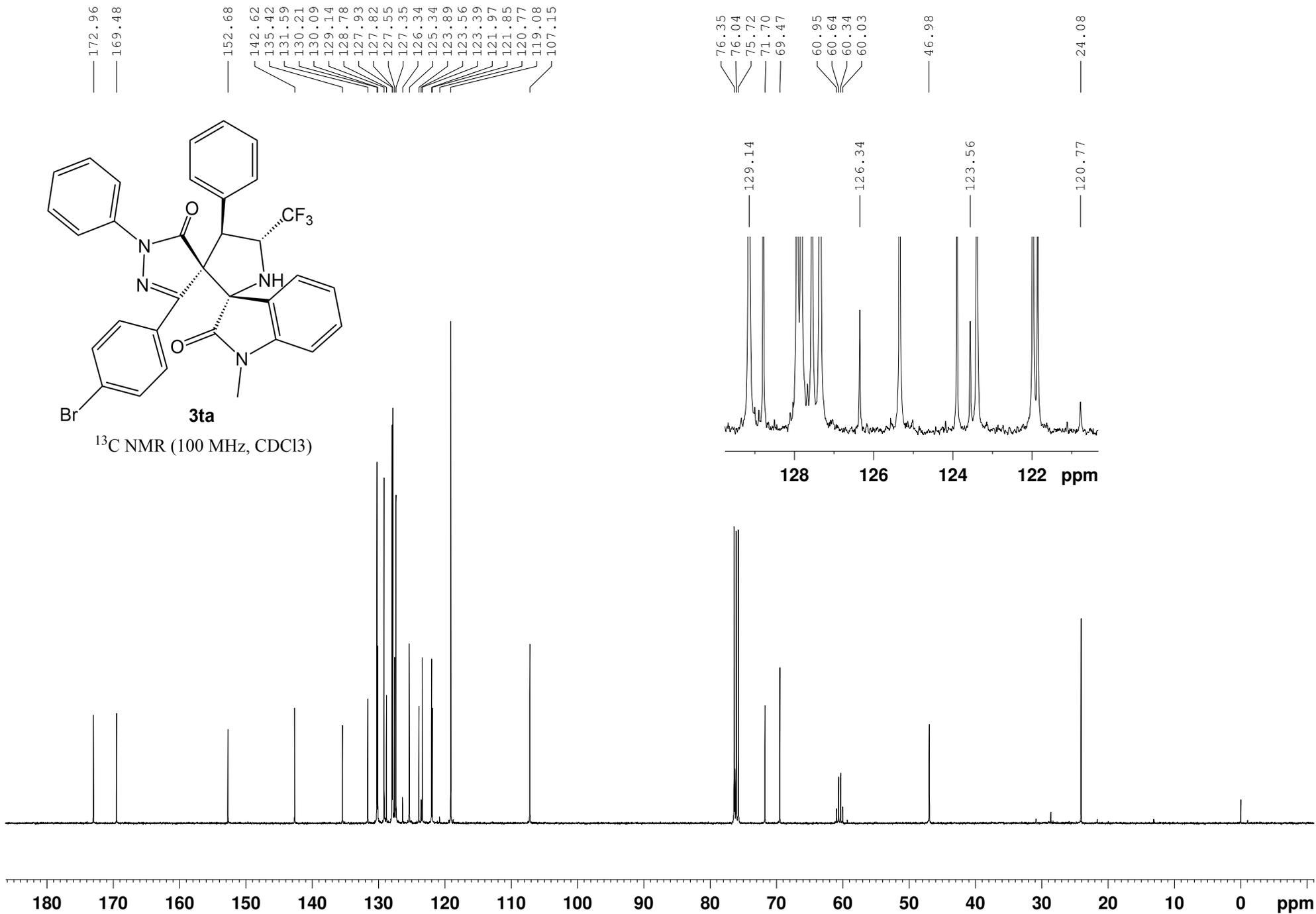


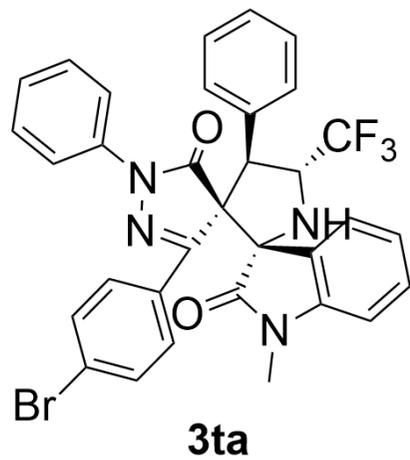
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)





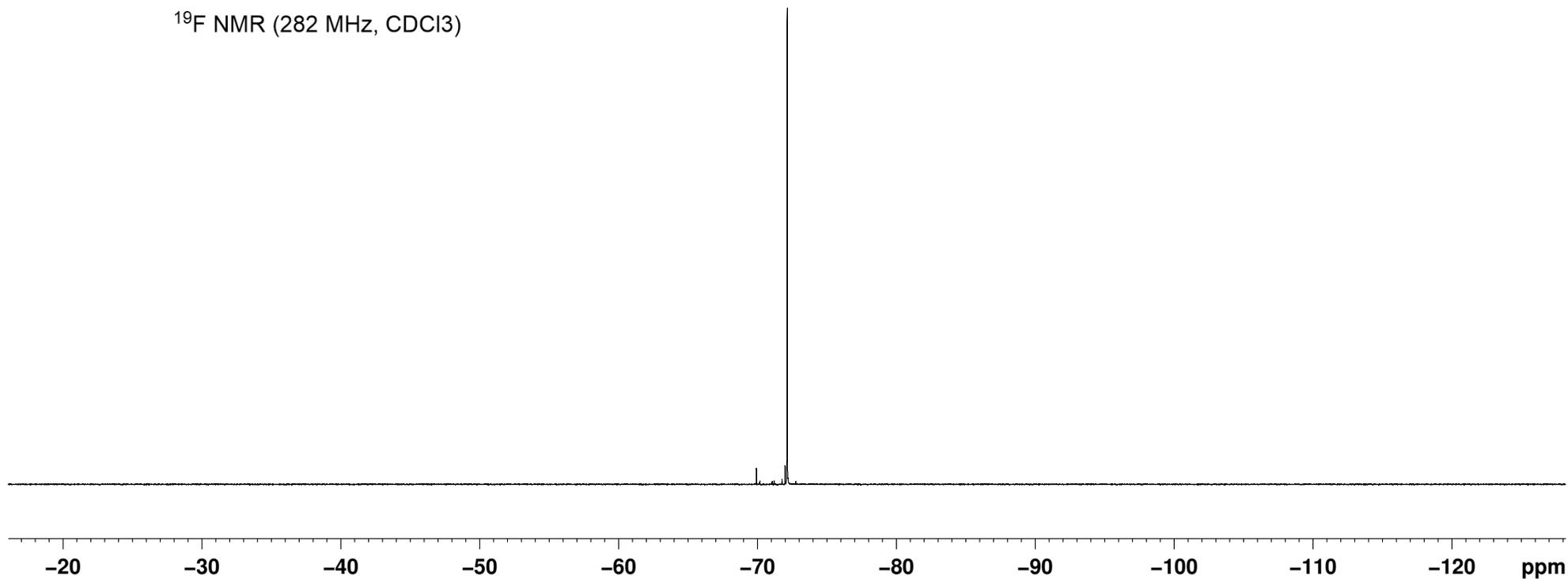
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )





<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)

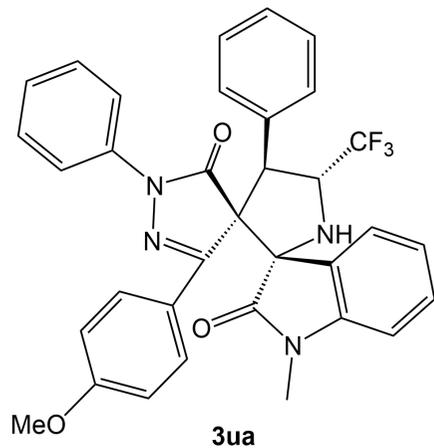
— -72.154



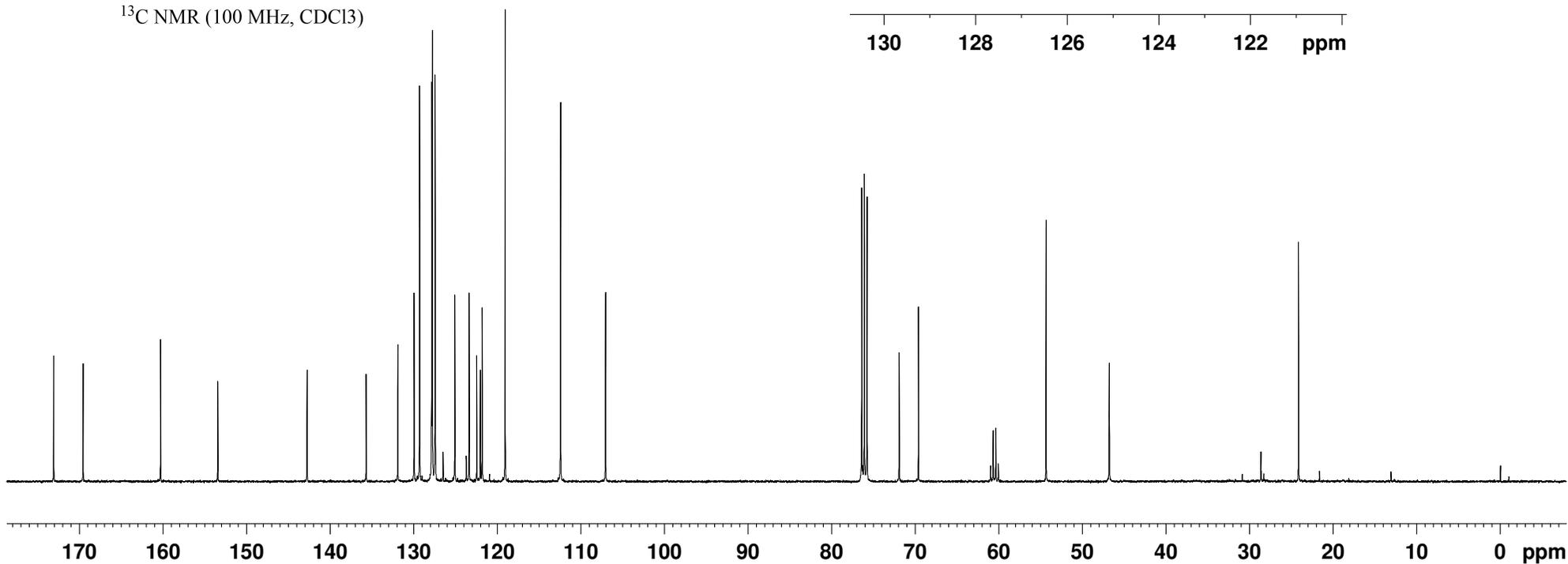
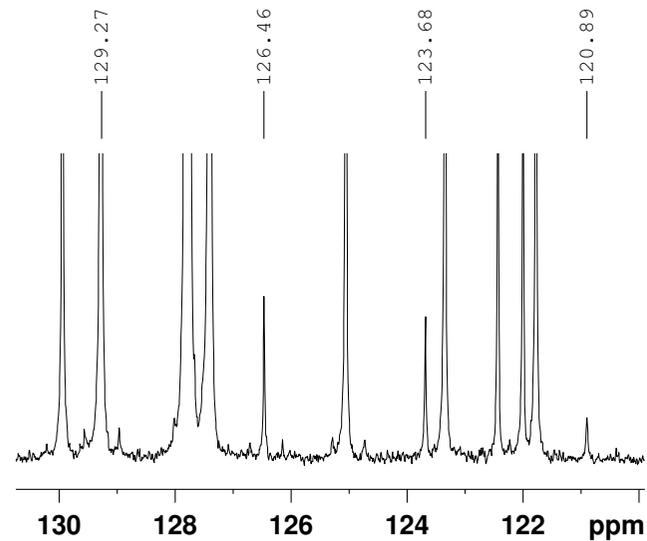


— 173.05  
 — 169.53  
 — 160.26  
 — 153.41  
 — 142.74  
 — 135.66  
 — 131.87  
 — 129.93  
 — 129.27  
 — 127.83  
 — 127.74  
 — 127.41  
 — 126.46  
 — 125.05  
 — 123.68  
 — 123.34  
 — 122.43  
 — 122.00  
 — 121.77  
 — 120.89  
 — 119.03  
 — 112.40  
 — 107.02

— 76.37  
 — 76.05  
 — 75.74  
 — 71.88  
 — 69.58  
 — 60.99  
 — 60.69  
 — 60.38  
 — 60.07  
 — 54.36  
 — 46.80  
 — 24.15  
 — 0.00



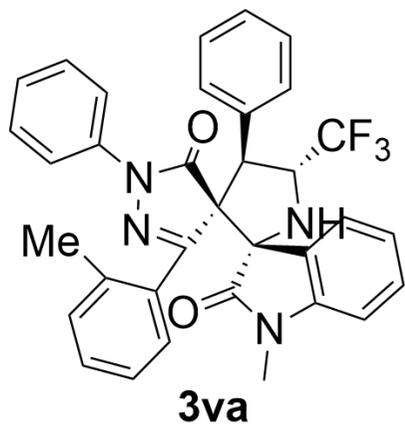
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



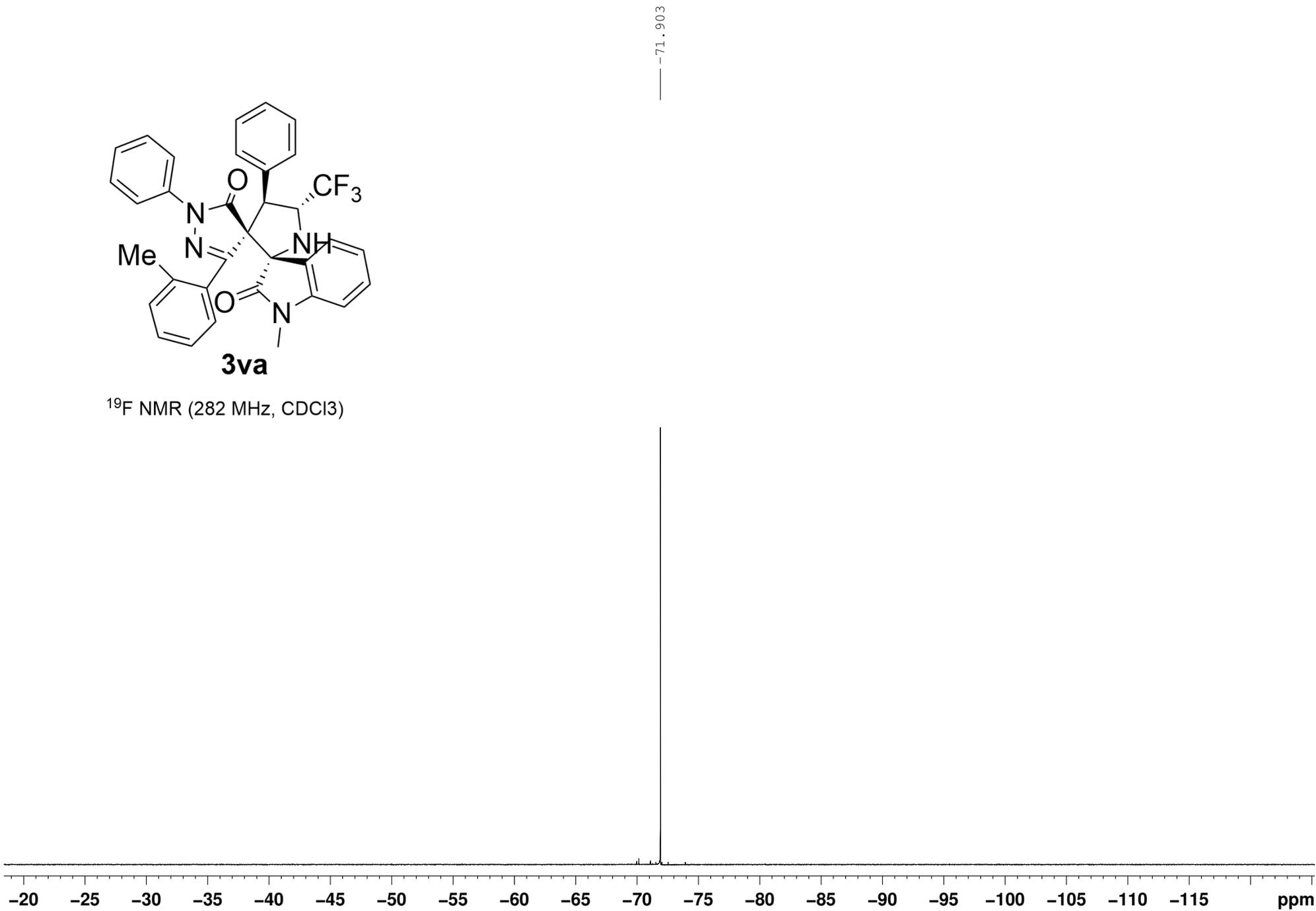




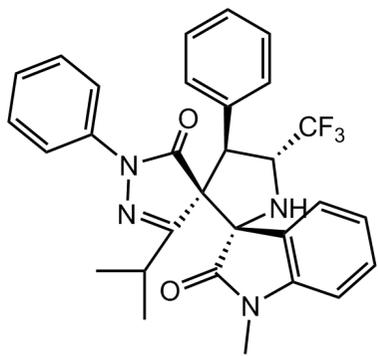




$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )

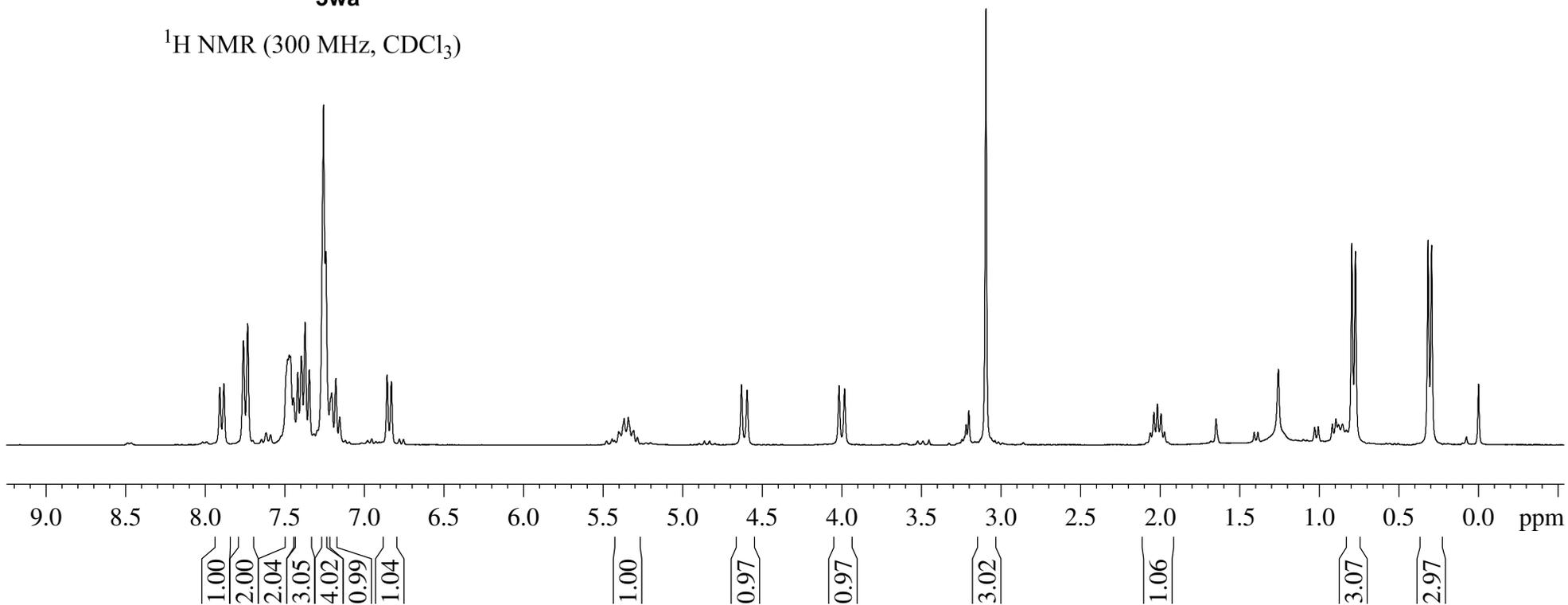


7.905  
7.880  
7.757  
7.730  
7.479  
7.470  
7.461  
7.443  
7.416  
7.394  
7.370  
7.343  
7.293  
7.254  
7.239  
7.202  
7.177  
7.152  
6.854  
6.828  
5.399  
5.365  
5.339  
5.305  
4.628  
4.592  
4.018  
3.983  
3.095  
2.062  
2.040  
2.018  
1.995  
1.973  
1.649  
1.258  
0.796  
0.773  
0.317  
0.295  
-0.000



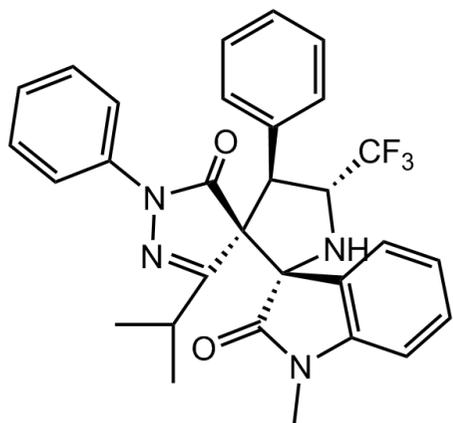
**3wa**

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)



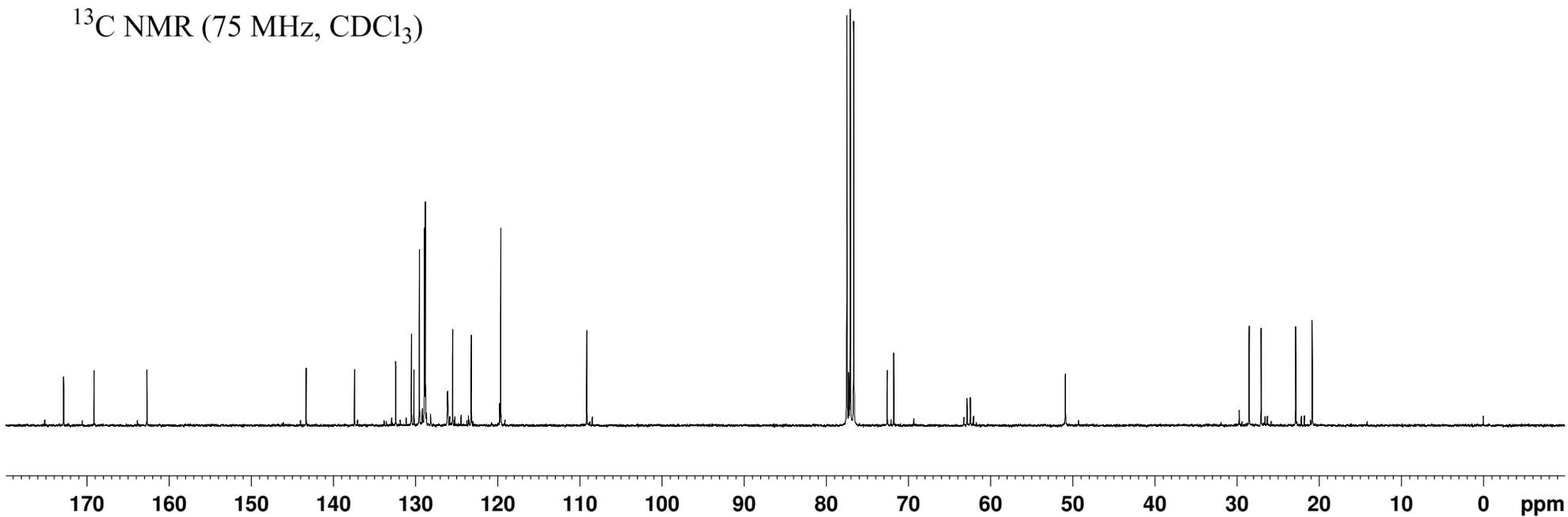
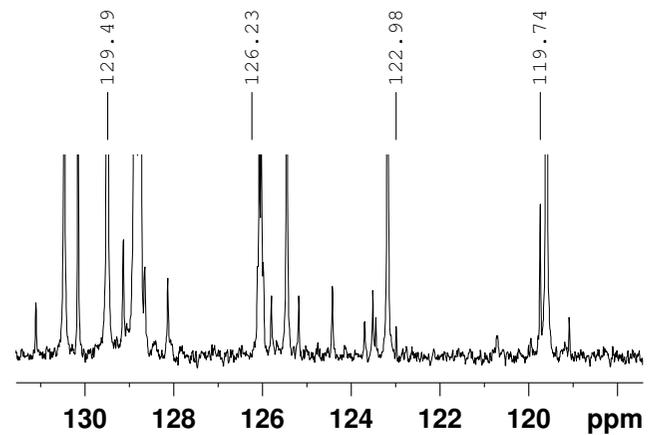
— 172.80  
 — 169.09  
 — 162.65  
 — 143.28  
 — 137.38  
 — 132.37  
 — 130.46  
 — 130.15  
 — 129.49  
 — 128.87  
 — 128.84  
 — 128.76  
 — 126.02  
 — 125.44  
 — 123.17  
 — 119.59  
 — 109.12

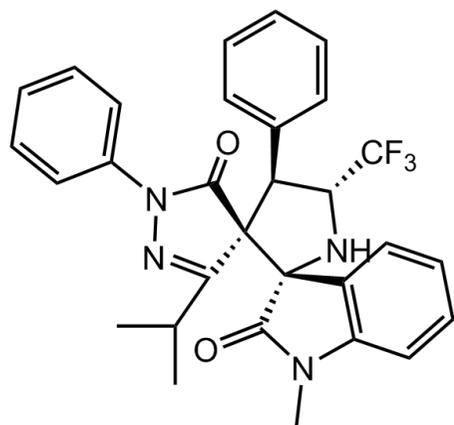
77.46  
 77.04  
 76.61  
 72.55  
 71.75  
 63.21  
 62.82  
 62.42  
 62.03  
 50.85  
 28.49  
 27.03  
 22.82  
 20.81



**3wa**

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )

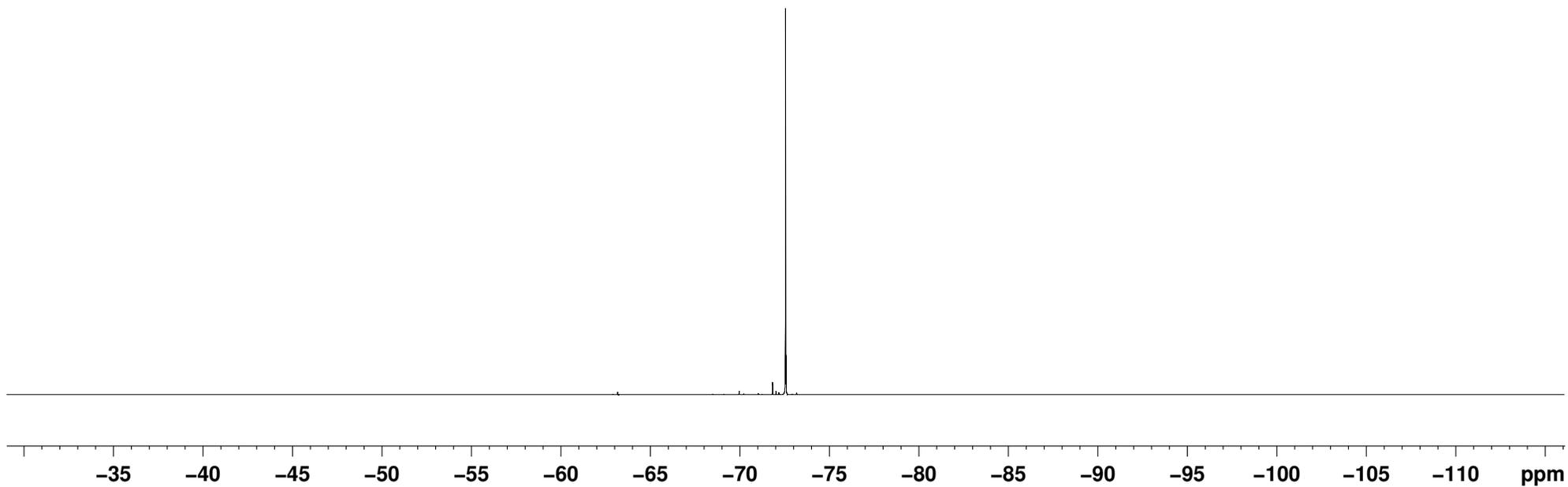




**3wa**

<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)

— -72.564



7.851  
7.826  
7.643  
7.618  
7.491  
7.465  
7.430  
7.404  
7.378  
7.363  
7.349  
7.332  
7.305  
7.279  
7.263  
7.245  
7.231  
7.223  
7.214  
7.192  
7.147  
7.122  
7.098  
6.833  
6.807

5.515  
5.508  
5.482  
5.457  
5.423  
5.398  
5.331

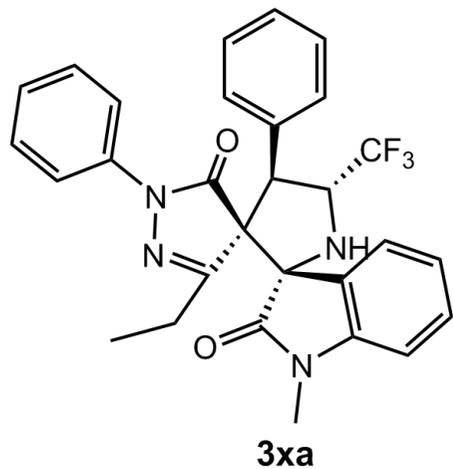
4.543  
4.507

3.978  
3.944

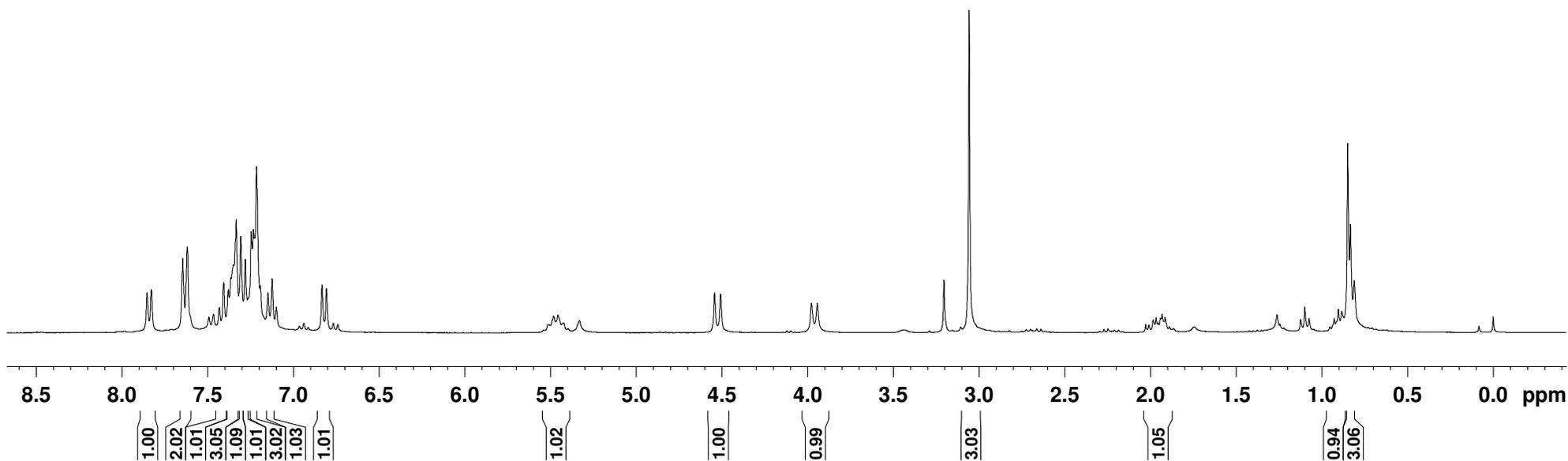
3.204  
3.058

2.028  
2.009  
1.984  
1.967  
1.955  
1.939  
1.931  
1.922  
1.914  
1.260  
1.122  
1.098  
1.074  
0.927  
0.913  
0.903  
0.883  
0.848  
0.832  
0.810

-0.000

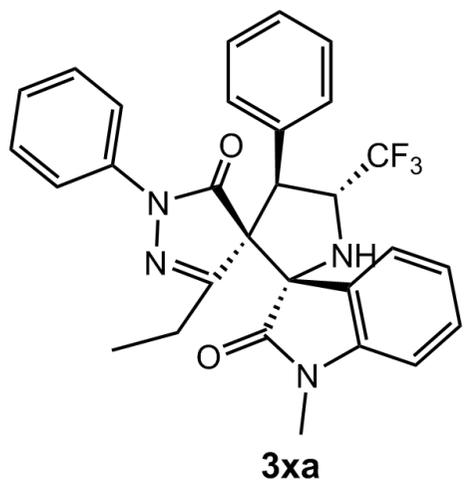


<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

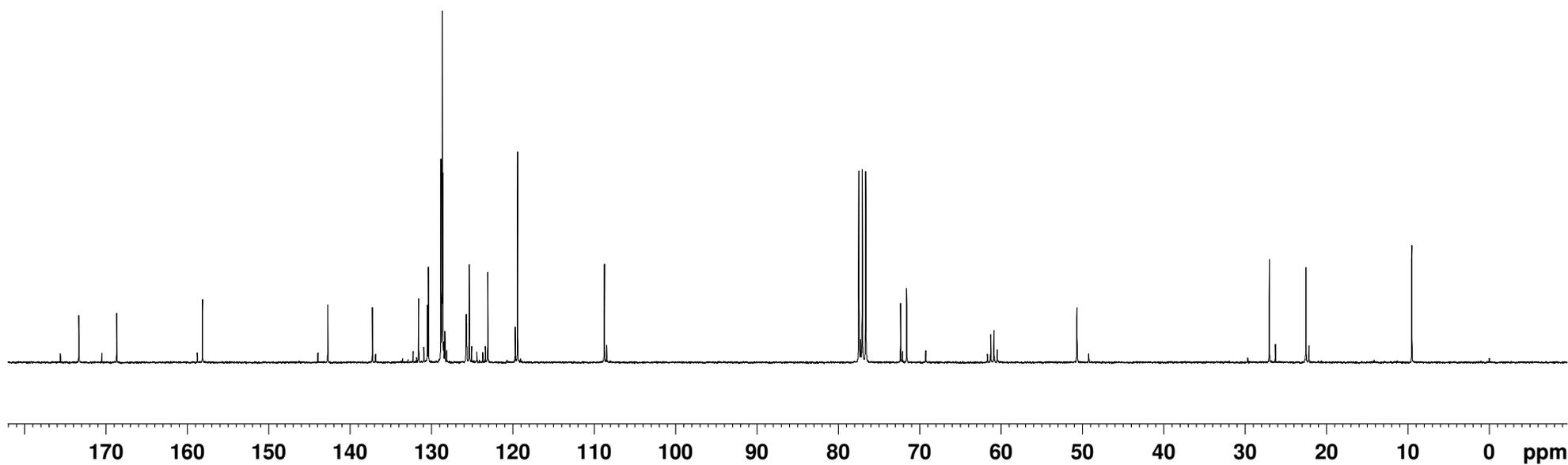
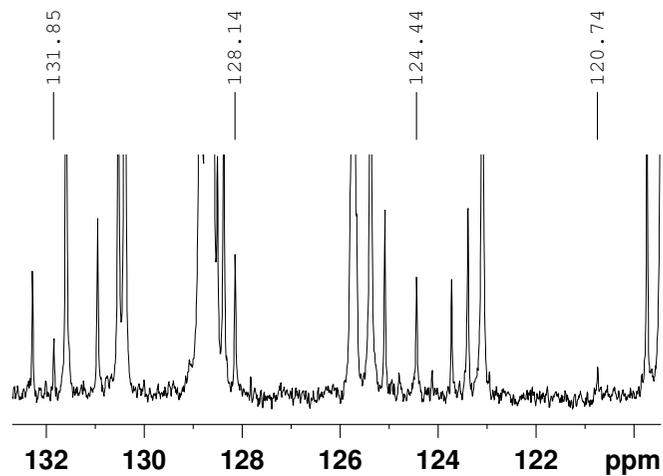


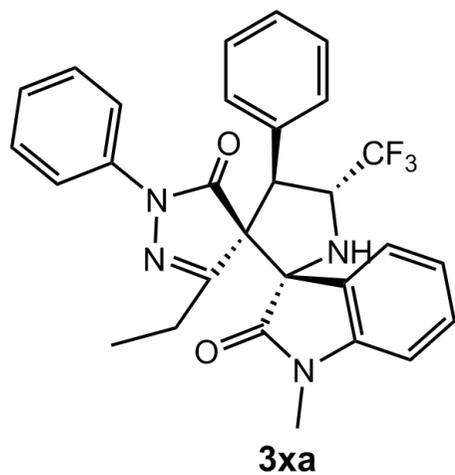
— 173.31  
 — 168.66  
 — 158.17  
 — 142.77  
 — 137.28  
 — 131.60  
 — 130.53  
 — 130.40  
 — 128.86  
 — 128.75  
 — 128.69  
 — 128.61  
 — 125.76  
 — 125.38  
 — 123.10  
 — 119.44  
 — 108.78

77.49  
 77.07  
 76.65  
 72.36  
 71.62  
 61.69  
 61.28  
 60.89  
 60.48  
 50.69  
 27.04  
 22.54  
 9.54



$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )





$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )

— -72.97

