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Supporting Information

Asymmetric Synthesis of Spiropyrazolones by Sequential Organo- and Silver Catalysis

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Inhalt

1.0 General Information

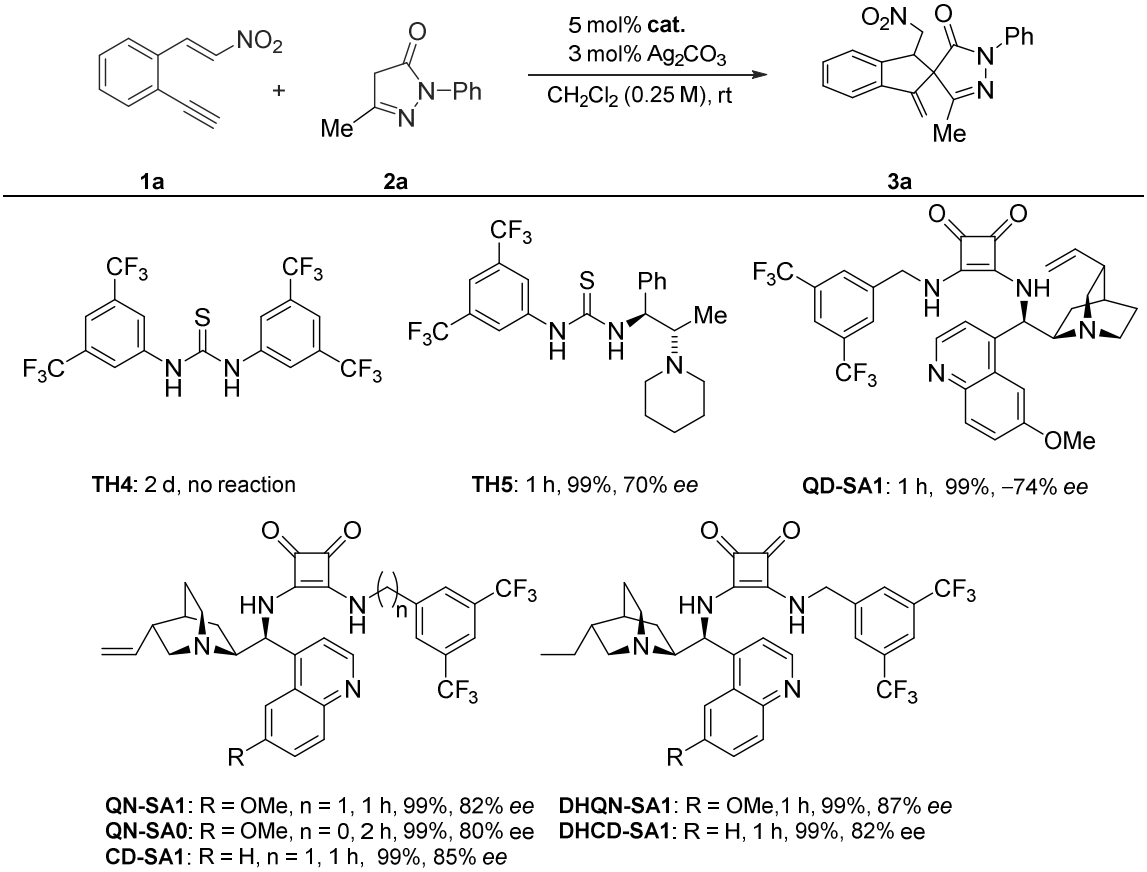
Unless otherwise noted, all commercially available compounds were used without further purification. For preparative column chromatography SIL G-25 UV252 from Macherey-Nagel, particle size 0.040-0.063 nm (230-240 mesh. flash) was used. Visualization of the developed TLC plates was performed with UV irradiation (254 nm) or by staining with $KMnO_4$. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. Mass spectra were recorded on a Finnigan SSQ7000 (EI 70 eV) spectrometer and high-resolution mass spectra on a Thermo Fisher Scientific Orbitrap XL spectrometer. IR spectra were recorded on a Perkin-Elmer FT-IR Spectrum 100 using ATR-Unit. ^{1}H, ^{13}C and ^{19}F spectra were recorded at ambient temperature on Varian Mercury 300, Inova 400, Varian VNMRS-400, or Varian VNMRS-600 spectrometers with TMS as an internal standard. Analytical HPLC was performed on a Hewlett-Packard 1100 Series instrument using chiral stationary phases (Daicel AD, Daicel AS, Daicel IA, Chiralpak IC, Chiralpak IB columns). Analytical SFC was performed on a THAR-SFC MethodStation II with a WATERS 2998 Photodiode Array Dectector using chiral stationary phases (Daicel Chiralpak IA, (*R*, *R*)-Whelk O1),

Abbreviations:

OR	optical rotation
EA	elemental analysis
CH_{Ar}	aromatic proton
CH_{ol}	olefinic proton
{^{19}F}	^{19}F decoupled spectra
{^{1}H}	^{1}H decoupled spectra

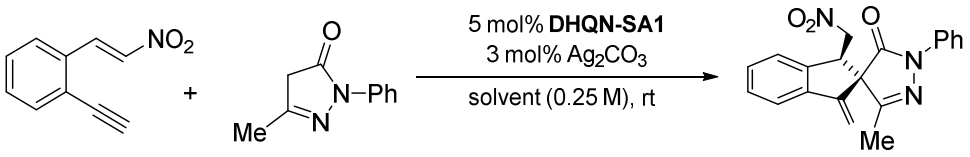
2.0 Additional Screening Tables

2.1 Catalyst screening



Scheme 1 Catalyst influence. [Reaction conditons: **1a** (0.33 mmol), **2a** (0.30 mmol), organocatalyst (5 mol%), Ag_2CO_3 (3 mol%), CH_2Cl_2 (1.3 mL), rt]

2.2 Solvent Screening

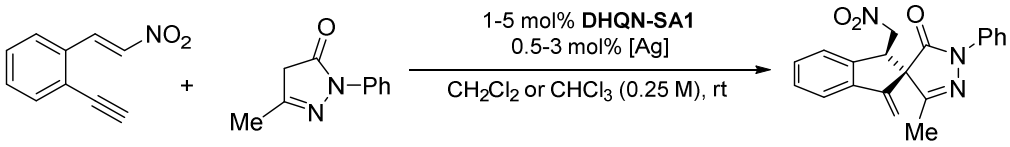


1a **2a** **3a**

№	solvent	*t* [h]	yield [%][b]	*ee* [%][c]
1	CH_2Cl_2	1	99	87
2	$CHCl_3$	1	99	89
3	CCl_4	24	traces	-
4	1,2-dichlorethane	5.5	67	84
5	PhCl	1	99	84
6	toluene	3	99	83
7[d]	ether	24+1	91	71

[a] Reaction conditions: **1a** (0.33 mmol), **2a** (0.30 mmol), **DHQN-SA1** (5 mol%), Ag_2CO_3 (3 mol%), solvent (1.2 mL), rt. [b] >Yield of **3a** after flash chromatography. [c] Determined by HPLC using a chiral stationary phase. [d] Cyclisation only occurred after the addition of CH_2Cl_2.

2.3 Influence of catalyst loading

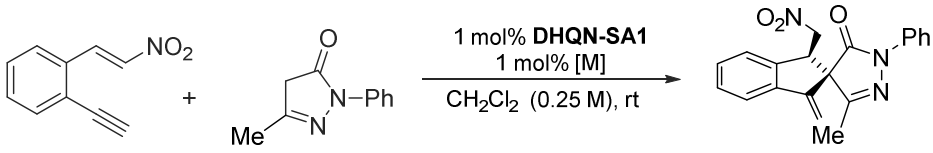


1a **2a** **3a**

№	**DHQN-SA1** [mol%]	metal salt	solvent	*t* [h]	yield [%]	*ee* [%]
1	5	3 mol% Ag_2CO_3	CH_2Cl_2	1	99	87
2	3	3 mol% Ag_2CO_3	CH_2Cl_2	1	99	87
3	1	3 mol% Ag_2CO_3	CH_2Cl_2	1	99	87
4	1	1 mol% Ag_2CO_3	CH_2Cl_2	1	99	82
5	1	0.5 mol% Ag_2CO_3	CH_2Cl_2	4	38	-
6	1	1 mol% Ag_2O	CH_2Cl_2	1	99	83
7	1	0.5 mol% Ag_2O	CH_2Cl_2	25	21	-
8	1	3 mol% Ag_2CO_3	$CHCl_3$	1	99	89
9	1	1 mol% Ag_2CO_3	$CHCl_3$	1.5	15	-

[a] Reaction conditions: **1a** (0.33 mmol), **2a** (0.30 mmol), **DHQN-SA1** (1-5 mol%), silver salt (0.5-3 mol%), solvent (1.2 mL), rt. [b] Yield of **3a** after flash chromatography. [c] Determined by HPLC using a chiral stationary phase.

2.4 Influence of the applied metal salt

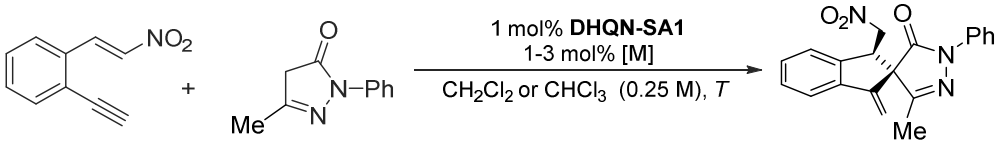


1a **2a** **3a**

№	catalyst	*t* [h]	yield [%][b]	*ee* [%][c]
1	Ag_2CO_3	1	99	82
2	Ag_2O	0.75	99	83
3	$AgBF_4$	2	99	84
4	Cu(I)I	24	39	87
5	$PtCl_2$	24	27	86
6	$PPh_3AuCl/AgNTf_2$	24	21	84

[a] Reaction conditions: **1a** (0.33 mmol), **2a** (0.30 mmol), **DHQN-SA1** (1-5 mol%), silver salt(0.5-3 mol%), CH_2Cl_2 (1.2 ml), rt. [b] Yield of **3a** after flash chromatography. [c] Determined by HPLC using a chiral stationary phase.

2.5 Temperature influence



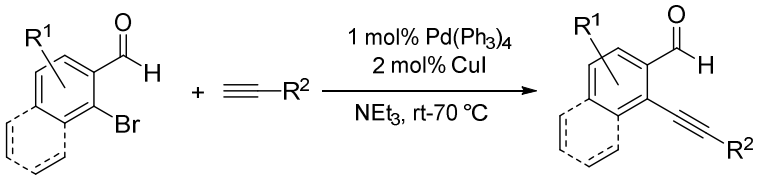
1a **2a** **3a**

№	Cat./loading	solvent	*T* [°C]	*t* [h][b]	yield [%][c]	*ee* [%][d]
1	1 mol% Ag_2CO_3	CH_2Cl_2	RT	1	99	82
2	1 mol% Ag_2CO_3	CH_2Cl_2	0	1 + 1	99	86
3	1 mol% Ag_2CO_3	CH_2Cl_2	−20	1 + 1	99	85
4	1 mol% Ag_2CO_3	CH_2Cl_2	−40	18 + 1,5	15	-
5	3 mol% Ag_2CO_3	CH_2Cl_2	−40	18 + 1	64	91
6	3 mol% Ag_2CO_3	$CHCl_3$	−40	18 + 1.5	82	94
7	3 mol% Ag_2O	$CHCl_3$	−40	20 + 0.75	99	94

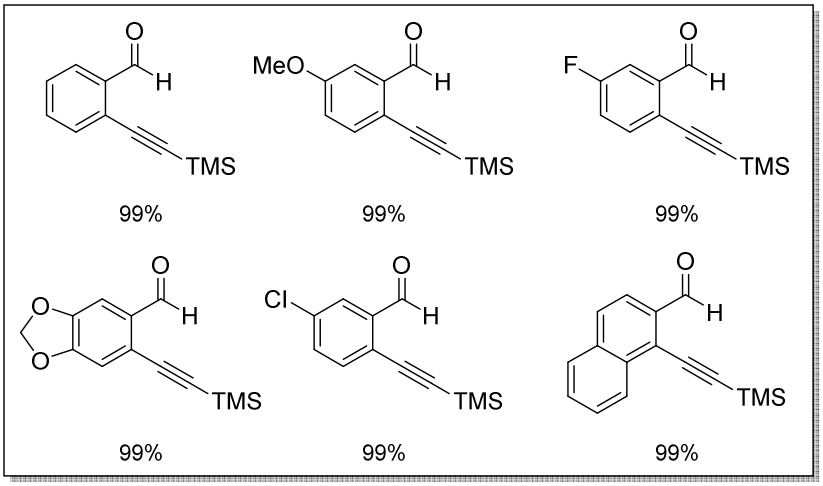
[a] Reaction conditions: **1a** (0.33 mmol), **2a** (0.3 mmol), **DHQN-SA1** (1 mol%), silver salt (1-3 mol%), solvent (1.2 mL), −40 °C-RT. [b] Combined reaction time (low temperatur + RT). [c] Yield of **3a** after flash chromatography. [d] Determined by HPLC using a chiral stationary phase.

3.0 General procedures

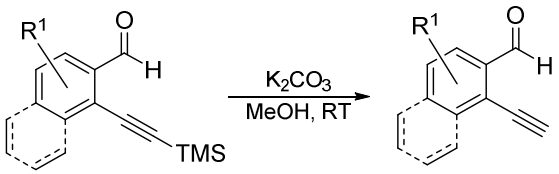
3.1 Sonogashira Cross-Coupling



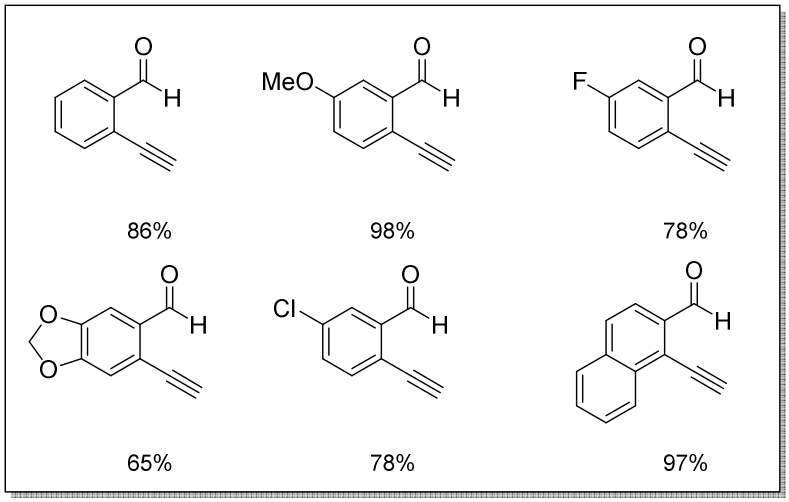
Under an atmosphere of argon, the alkyne (1.1 equiv.) was added to a suspension of arylbromide (1.0 equiv.), CuI (2 mol%) and $Pd(PPh_3)_4$ (1 mol%) in degassed NEt_3 (2 mL/mmol substrate) and the reaction mixture was stirred until complete conversion of the starting materials at room temperature. Water was added, the product was extracted with CH_2Cl_2 and the combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure and the corresponding alkynylated aldehydes was obtained after flash chromatography with silica (*n*-pentanee/Et_2O, dry loading).



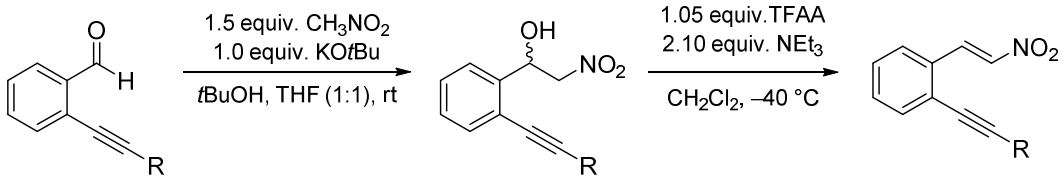
3.2 TMS-cleavage



A suspension of the aldehyde (1.0 equiv.) and K_2CO_3 (2.0 equiv.) in freshly distilled MeOH (0.05 M) was stirred at room temperature until complete conversion of the substrate was observed. The solvent was removed under reduced pressure, and the deprotected aldehyde was obtained after flash chromatography on silica (*n*-pentane/Et_2O).

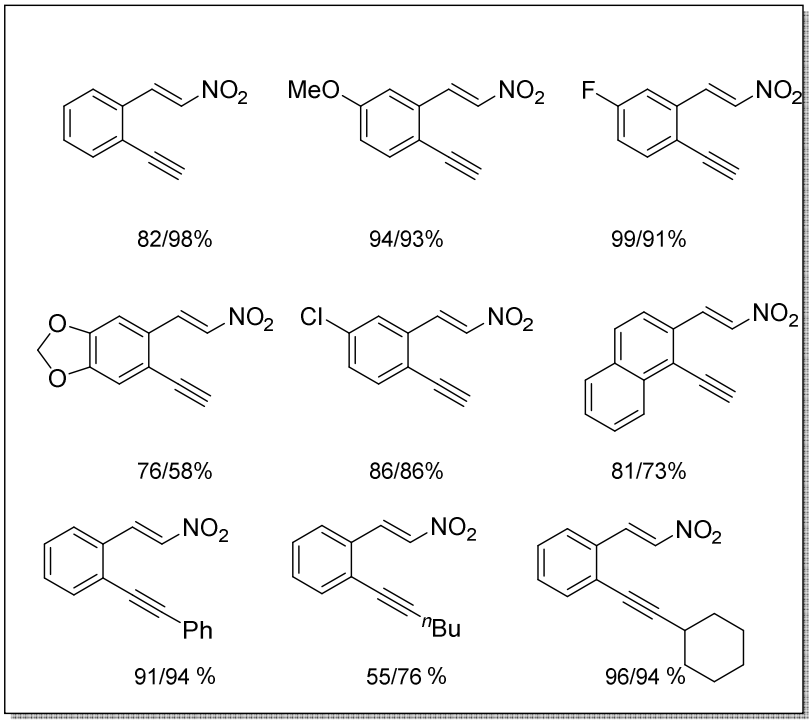


3.3 Synthesis of nitro olefines



Henry-reaction: Under an atmosphere of argon, nitromethane (1.5 eq.) and KO*t*Bu (1 eq.) were added to a solution of aldehyde (1 eq.) in a solution of THF and *t*BuOH (1:1, 0.5 M), and the mixture was stirred overnight. Then a solution of NH_4Cl was added, the product was extracted twice with Et_2O, the combined organic phases were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was subjected to flash chromatography on silica (*n*-pentanee/Et_2O 5:1 to 1:1).

TFA-mediated dehydration: Under an atmosphere of argon, TFAA (1.05 eq.) was added over a period of 30 min to a solution of nitroalcohol (1 eq.) in DCM (0.5 M) at −40 °C. Then triethylamine (2.1 eq.) was added, and the mixture was stirred at −0 °C for 45 min. The reaction was quenched with a solution of NH_4Cl was added, the liquid phases were separated, and the aqueous phase was extracted twice with DCM. The combined organic phases were washed with a saturated solution of $NaHCO_3$ and brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure and the product was purified by flash chromatography on silica (*n*-pentane/Et_2O 5:1).



3.4 Asymmetric synthesis of spiropyrazolones

Method A: R^4 = H

A suspension of nitro olefine **1** (0.33 mmol, 1.1 equiv.), pyrazolone **2** (0.3 mmol, 1.0 equiv.), **DHQN-SA1** (1 mol%) and Ag_2O (3 mol%) in chloroform (1.2 mL) was stirred at −40° C until complete conversion of the starting materials was observed as indicated by TLC. The reaction mixture was allowed to warm to room temperature and stirred for additional one to two hours, until the intermediate Michael-adduct was completely converted as indicated by TLC. The corresponding spiropyrazolone **3** was obtained after flash chromatography on silica with a mixture of *n*-pentane/Et_2O as eluent.

Method B: R^4 = Alkyl

A suspension of nitro olefine **1** (0.33 mmol, 1.1 equiv.), pyrazolone **2** (0.3 mmol, 1.0 equiv.), **DHQN-SA1** (1 mol%) and Ag_2O (10 mol%) in chloroform (1.2 mL) was stirred at −40° C until complete conversion of the starting materials was observed as indicated by TLC. The reaction mixture was allowed to warm to room temperature and stirred for additional one to two hours, until the intermediate Michael-adduct was completely converted as indicated by TLC. The corresponding

spiropyrazolone **3** was obtained after flash chromatography on silica with a mixture of *n*-pentane/Et_2O as eluent.

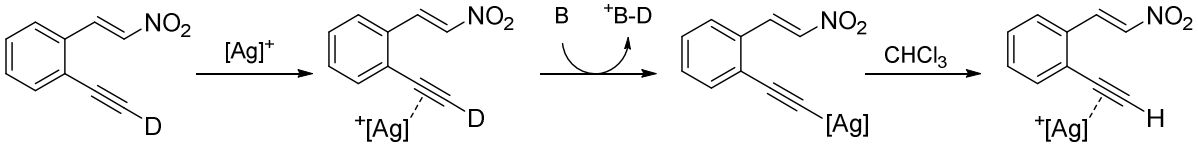
Method C: R^4 = Ph

A suspension of nitro olefine **1** (0.33 mmol, 1.1 equiv.), pyrazolone **2** (0.3 mmol, 1.0 equiv.), **DHQN-SA1** (3 mol%) in chloroform (1.2 mL) was stirred at room temperature until complete conversion of the starting materials was observed as indicated by TLC. The corresponding spiropyrazolone **4** was obtained after flash chromatography on silica with a mixture of *n*-pentane/Et_2O as eluent

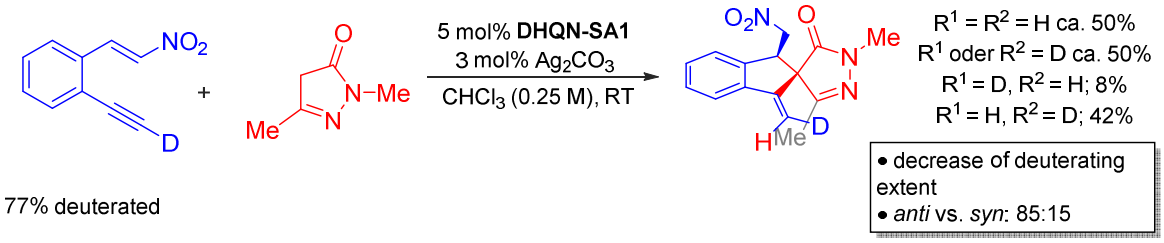
4.0 Experiments with deuterium-labeled substrates

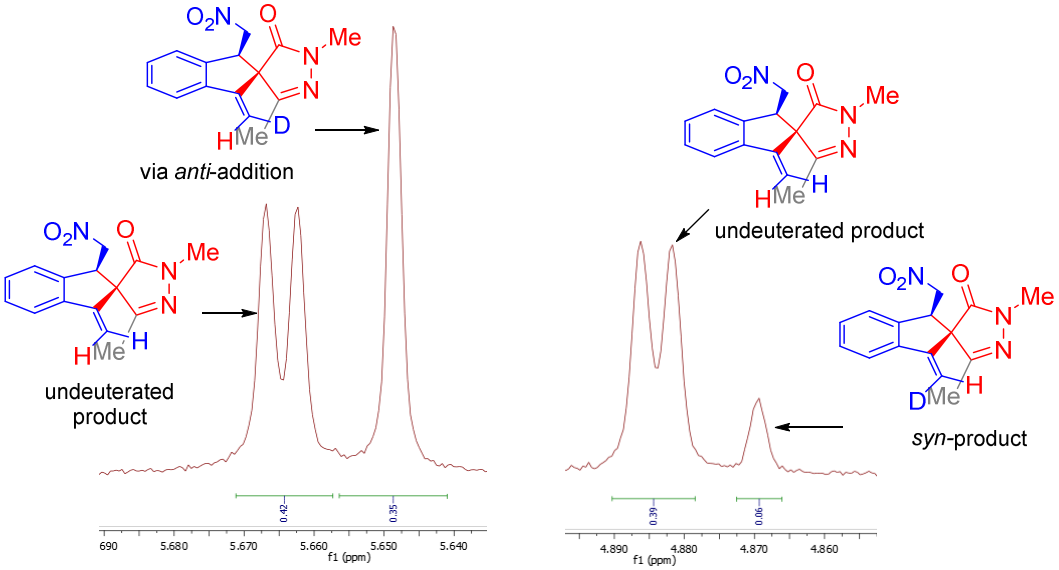
For the experiments in which deuterated-substrates were applied, the following observations were made:

- The extent of deuteration decreases from 77% to 50%. This can be rationalized considering that there is an easy H/D-exchange by coordination of Ag(I) to the alkyne in basic media is available.

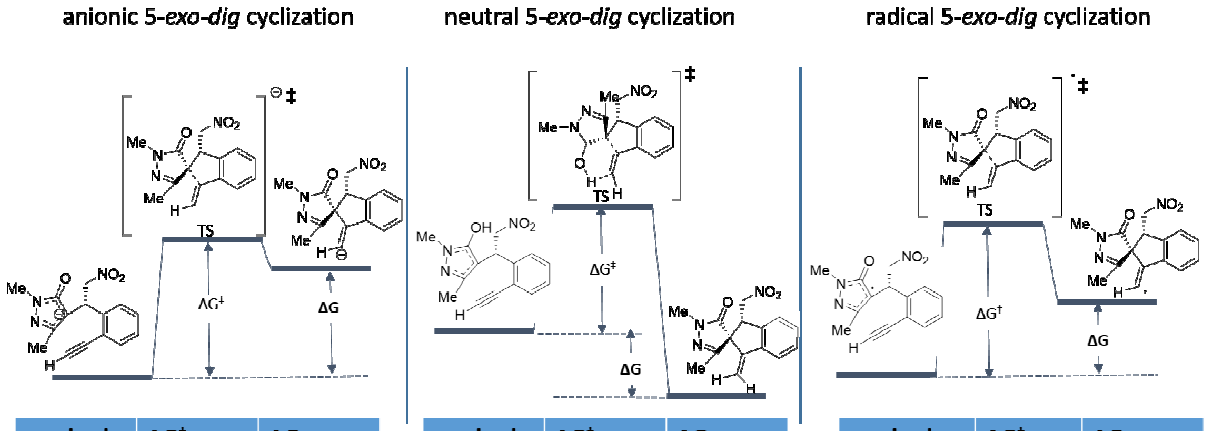


- For deuterated products, a strong bias towards the formation of the *anti*-product has been observed (85% *anti vs.* 15% *syn*).





5.0 Computational details

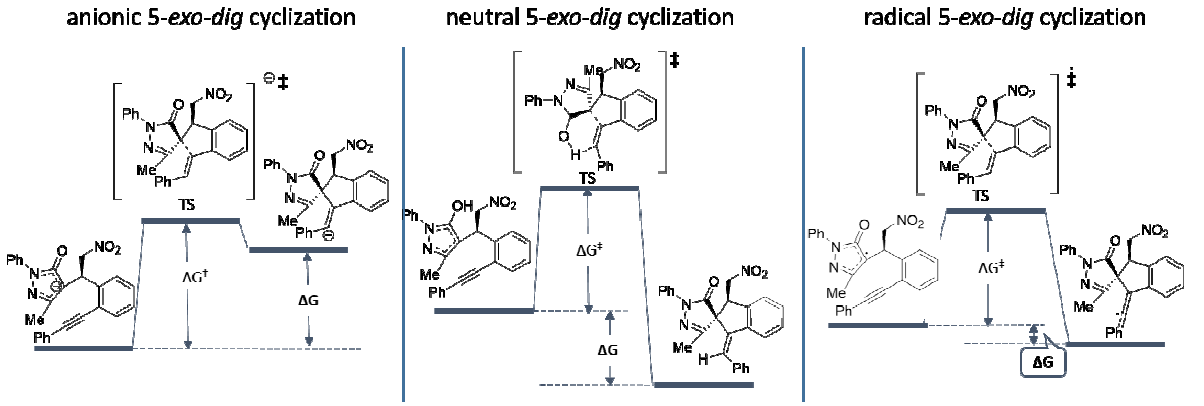


method	ΔG‡	ΔG
M06	21.7	.20.5
M06L	21.6	20.8
B3LYP	24.6	23.6
B3LYP-D3	22.6	21.5

method	ΔG‡	ΔG
M06	29.3	- 31.1
M06L	24.4	- 32.5
B3LYP	27.4	- 30.2
B3LYP-D3	26.3	- 31.9

method	ΔG‡	ΔG
M06	20.0	9.0
M06L	21.0	11.4
ROB3LYP	23.6	12.4
ROB3LYP-D3	21.7	10.5

Fig S1. Energetic comparison of computed pathways considered for substrate **5a** depending on the method employed, in kcal/mol.

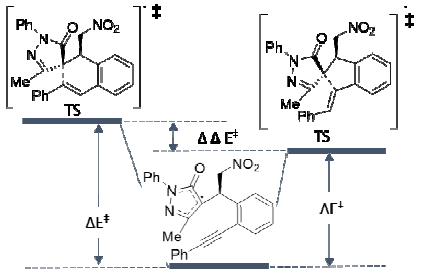


method	ΔG‡	ΔG
M06	26.7	19.7
M06L	25.9	20.2
B3LYP	27.2	25.7
B3LYP-D3	23.6	21.1

method	ΔG‡	ΔG
M06	32.6	-24.7
M06L	26.6	-25.0
B3LYP	31.2	20.4
B3LYP-D3	28.3	24.3

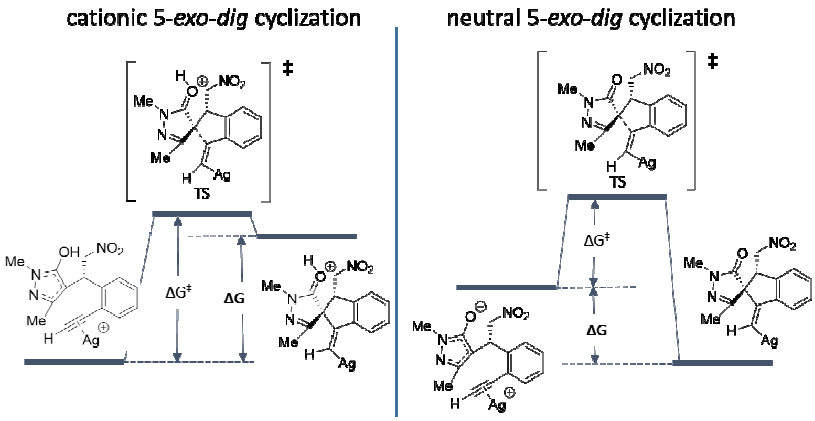
method	ΔG‡	ΔG
M06	11.1	-0.6
M06L	11.0	2.5
ROB3LYP	15.9	5.7
ROB3LYP-D3	11.8	2.4

Fig S2. Energetic comparison of computed pathways for substrate **5b** depending on the method employed, in kcal/mol.



method	ΔΔE‡
M06	13.9
M06L	14.6
ROB3LYP	16.5
ROB3LYP-D3	14.9

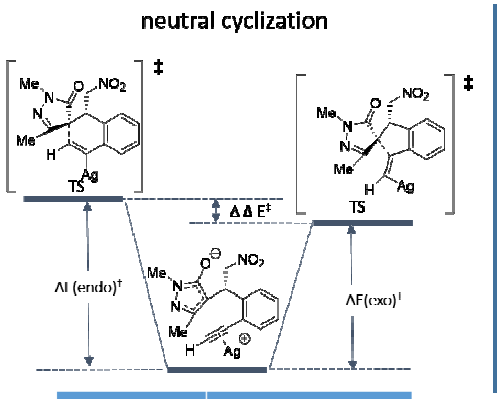
Fig S3. 6-endo-dig vs 5-endo-dig selectivity for **5b** considering the radical pathway. Differences of activation barriers are shown depending on the method employed. Electronic energies in kcal/mol shown.



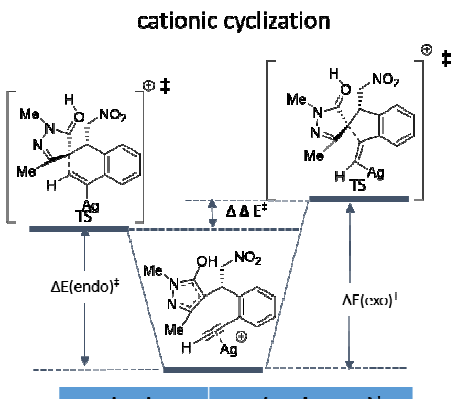
method	ΔG‡	ΔG
M06	14.0	6.8
M06L	13.1	8.7
B3LYP	10.0	3.7
B3LYP-D3	12.4	5.3

method	ΔG‡	ΔG
M06	17.3	-17.5
M06L	15.6	-15.4
B3LYP	13.4	-20.2
B3LYP-D3	15.6	-21.1

Fig S4. Energetic comparison of computed cationic pathways, in kcal/mol.



method	ΔΔE(endo-exo)‡
M06	2.3
M06L	4.4
B3LYP	3.4
B3LYP-D3	4.5



method	ΔΔE(endo-exo)‡
M06	-3.9
M06L	-3.4
B3LYP	-1.9
B3LYP-D3	-3.4

Fig S5. 6-endo-dig vs 5-endo-dig selectivity for **5a** considering both the neutral and the cationic system. Differences of activation barriers are shown depending on the method employed. Electronic energies in kcal/mol are shown.

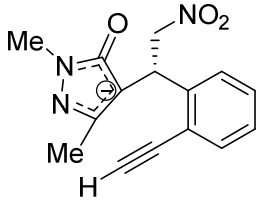
Full Gaussian Reference:

Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

General Information

All calculations were performed using Gaussian 09. Structural optimizations and frequency calculations were performed with the B3LYP functional along with the 6-31G(d) basis set and the LANL2DZ ECP on Ag atoms for closed shell molecules. For radicals, structural optimizations and frequency calculations were performed with the (RO)B3LYP functional along with the 6-31G(d) basis set. Single point energy calculations were done with the M06 functional and def2-TZVP basis set, unless otherwise stated. Solvent effects of dichloromethane were included in the single point calculations using the CPCM solvation model.

[(enolate-5a)]



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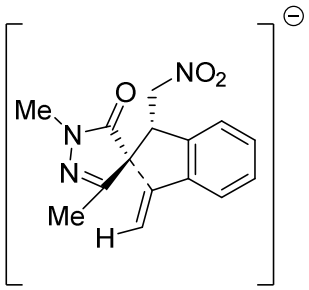
H	-0.894834000	-1.736886000	-2.740897000
H	3.765504000	1.183691000	-2.198108000
H	3.278831000	3.503242000	-1.448610000
H	-1.342917000	-2.996210000	-1.592369000
H	-4.418930000	1.683470000	1.060860000
H	0.455075000	-1.524934000	-0.275093000

Zero-point correction= 0.267962 (Hartree/Particle)
Thermal correction to Energy= 0.287819
Thermal correction to Enthalpy= 0.288763
Thermal correction to Gibbs Free Energy= 0.217887
Sum of electronic and zero-point Energies= -969.566331
Sum of electronic and thermal Energies= -969.546474
Sum of electronic and thermal Enthalpies= -969.545530
Sum of electronic and thermal Free Energies= -969.616406

CPCM (dichloromethane) M06/def2TZVP E = -969.6383318
CPCM (dichloromethane) M06L/def2TZVP E = - 970.1577064

CPCM (dichloromethane) B3LYP/def2TZVP E = - 970.2932131
CPCM (dichloromethane) B3LYP-d3/def2TZVP E = - 970.3308715

[(anionic-TS-6a)]



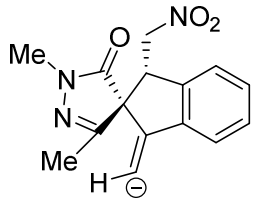
O	2.625473000	2.995202000	-0.846074000
O	1.966281000	2.866925000	1.222893000
O	-2.003112000	1.522077000	-1.468202000
N	-3.218960000	0.211679000	0.007675000
N	-3.013052000	-0.611094000	1.118926000
N	1.840957000	2.617959000	0.021371000
C	-1.720286000	-0.709671000	1.251557000
C	-2.054317000	0.689985000	-0.552337000
C	3.150955000	-2.504113000	-0.536317000
C	0.945073000	-1.507521000	-0.554654000
C	-0.482031000	-1.452827000	-0.876757000
C	2.771030000	-0.420333000	0.637208000
C	1.819731000	-2.536568000	-0.942936000
C	3.632432000	-1.454718000	0.259501000
C	1.439175000	-0.449184000	0.221874000
C	0.376710000	0.612781000	0.468691000
C	0.621733000	1.849686000	-0.419972000
C	-1.132891000	-1.527271000	2.357024000
C	-1.196405000	-2.260288000	-1.630989000
C	-0.974157000	-0.060920000	0.152666000
C	-4.550086000	0.593019000	-0.371905000
H	0.786872000	1.594461000	-1.463886000
H	3.137070000	0.399857000	1.251396000
H	4.671369000	-1.443115000	0.582382000
H	-1.933294000	-1.909457000	2.998003000
H	-4.455064000	1.249809000	-1.239906000
H	-0.204858000	2.560464000	-0.360166000
H	0.399274000	0.966634000	1.506186000
H	-5.061447000	1.129822000	0.439369000
H	-2.277733000	-2.075586000	-1.700431000
H	-0.564727000	-2.372889000	1.951589000
H	1.416289000	-3.342380000	-1.549828000
H	3.823630000	-3.308639000	-0.830418000
H	-0.439954000	-0.938349000	2.973198000
H	-5.149162000	-0.286417000	-0.638150000

Zero-point correction= 0.267224 (Hartree/Particle)
Thermal correction to Energy= 0.285787
Thermal correction to Enthalpy= 0.286731
Thermal correction to Gibbs Free Energy= 0.219464

Sum of electronic and zero-point Energies= -969.531629
Sum of electronic and thermal Energies= -969.513066
Sum of electronic and thermal Enthalpies= -969.512122
Sum of electronic and thermal Free Energies= -969.579388

CPCM (dichloromethane) M06/def2TZVP E = - 969.6052519
CPCM (dichloromethane) M06L/def2TZVP E = - 970.1247759
CPCM (dichloromethane) B3LYP/def2TZVP E = - 970.2556207
CPCM (dichloromethane) B3LYP-d3/def2TZVP E = - 970.2965116

[(anion-7a)]



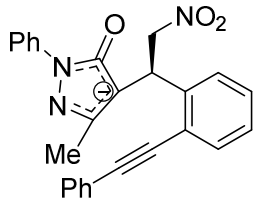
O	2.587131000	3.024401000	-0.829206000
O	1.905005000	2.885995000	1.231836000
O	-2.037373000	1.494414000	-1.467451000
N	-3.221700000	0.194297000	0.037803000
N	-2.991271000	-0.645976000	1.132800000
N	1.798208000	2.635560000	0.028881000
C	-1.699536000	-0.765634000	1.226970000
C	-2.071233000	0.659762000	-0.556376000
C	3.180502000	-2.462836000	-0.526081000
C	0.969191000	-1.484069000	-0.565280000
C	-0.457083000	-1.415539000	-0.900047000
C	2.768792000	-0.395362000	0.668041000
C	1.855972000	-2.501274000	-0.954501000
C	3.642751000	-1.419862000	0.290106000
C	1.444164000	-0.432382000	0.232691000
C	0.359894000	0.610907000	0.462209000
C	0.595994000	1.849116000	-0.426341000
C	-1.093202000	-1.606101000	2.304265000
C	-1.137769000	-2.224201000	-1.701585000
C	-0.967284000	-0.107633000	0.111944000
C	-4.561227000	0.583952000	-0.302803000
H	0.778314000	1.592444000	-1.467222000
H	3.120225000	0.421277000	1.295576000
H	4.676885000	-1.405260000	0.628017000
H	-1.881347000	-1.991858000	2.958114000
H	-4.487528000	1.247173000	-1.167888000
H	-0.240768000	2.548920000	-0.378628000
H	0.348453000	0.966839000	1.498772000
H	-5.047584000	1.115892000	0.526553000
H	-2.219819000	-2.021596000	-1.773686000
H	-0.542851000	-2.448601000	1.869542000
H	1.466847000	-3.300745000	-1.579106000
H	3.864546000	-3.258191000	-0.819379000
H	-0.379563000	-1.033619000	2.911825000
H	-5.170134000	-0.291397000	-0.559592000

Zero-point correction= 0.267728 (Hartree/Particle)

Thermal correction to Energy= 0.286806
Thermal correction to Enthalpy= 0.287750
Thermal correction to Gibbs Free Energy= 0.219355
Sum of electronic and zero-point Energies= -969.531156
Sum of electronic and thermal Energies= -969.512078
Sum of electronic and thermal Enthalpies= -969.511134
Sum of electronic and thermal Free Energies= -969.579529

CPCM (dichloromethane) M06/def2TZVP E = - 969.6070768
CPCM (dichloromethane) M06L/def2TZVP E = - 970.1260091
CPCM (dichloromethane) B3LYP/def2TZVP E = - 970.2570907
CPCM (dichloromethane) B3LYP-d3/def2TZVP E = - 970.2980678

[(enolate-5b)]



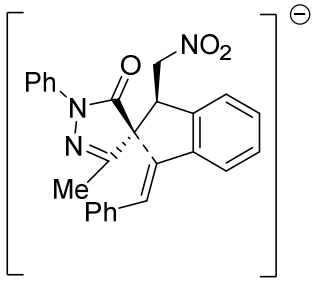
C	-1.938868000	2.973366000	-1.792653000
C	-6.844423000	-2.607735000	0.143413000
C	-3.703836000	0.108693000	-0.701066000
C	-4.812793000	-1.470935000	0.814169000
C	-4.763477000	-0.803759000	-0.428296000
C	-0.952920000	3.940145000	-1.930302000
C	-0.455172000	1.626251000	-0.383560000
C	-1.710918000	1.818228000	-1.013083000
C	1.153600000	-0.305832000	0.014759000
C	2.450243000	0.127633000	0.403339000
C	0.523546000	2.619224000	-0.534798000
C	-2.776124000	0.880934000	-0.856710000
C	5.376733000	-1.975904000	-0.761236000
C	-0.110949000	0.597124000	1.942681000
C	-0.143687000	0.352260000	0.404749000
C	0.278680000	3.763025000	-1.290745000
C	-6.805515000	-1.948882000	-1.087965000
C	-5.845118000	-2.363504000	1.089837000
C	4.708400000	-0.918217000	-0.111637000
C	-5.776505000	-1.055193000	-1.374997000
C	5.471236000	0.040419000	0.586925000
C	7.524034000	-1.119353000	-0.018922000
C	6.859815000	-0.071768000	0.624021000
C	6.764732000	-2.067350000	-0.710220000
O	2.823638000	1.119333000	1.089604000
O	-2.252212000	0.205051000	2.802198000
O	-1.643317000	2.278475000	2.511113000
N	-1.431020000	1.067714000	2.468879000
N	3.314731000	-0.843203000	-0.174075000
N	2.616138000	-1.821179000	-0.877087000
C	0.290532000	-2.340478000	-1.390200000
C	1.340274000	-1.482621000	-0.745613000
H	0.090364000	-0.346998000	2.446726000
H	-2.905267000	3.094897000	-2.274026000

H	1.485334000	2.471367000	-0.048256000
H	-0.957821000	-0.357490000	0.223524000
H	4.949206000	0.848645000	1.082247000
H	-5.871065000	-2.869812000	2.051648000
H	0.641321000	1.343471000	2.194351000
H	-1.142108000	4.828183000	-2.528972000
H	-7.648148000	-3.305882000	0.364256000
H	1.056629000	4.516657000	-1.388878000
H	-4.039658000	-1.265182000	1.548330000
H	-5.741850000	-0.543823000	-2.332539000
H	4.781734000	-2.706432000	-1.294815000
H	8.608570000	-1.195771000	0.017621000
H	7.430747000	0.678546000	1.168733000
H	-7.579461000	-2.133556000	-1.829334000
H	0.770329000	-3.175534000	-1.910113000
H	-0.411711000	-2.752471000	-0.652391000
H	-0.308523000	-1.776126000	-2.117112000
H	7.258440000	-2.893521000	-1.219678000

Zero-point correction= 0.402954 (Hartree/Particle)
Thermal correction to Energy= 0.430380
Thermal correction to Enthalpy= 0.431324
Thermal correction to Gibbs Free Energy= 0.340217
Sum of electronic and zero-point Energies= -1392.252812
Sum of electronic and thermal Energies= -1392.225385
Sum of electronic and thermal Enthalpies= -1392.224441
Sum of electronic and thermal Free Energies= -1392.315549

CPCM (dichloromethane) M06/def2TZVP E = - 1392.2602756
CPCM (dichloromethane) M06L/def2TZVP E = - 1393.0579796
CPCM (dichloromethane) B3LYP/def2TZVP E = - 1393.2533908
CPCM (dichloromethane) B3LYP-d3/def2TZVP E = - 1393.3080145

[(anionic-TS-6b)]



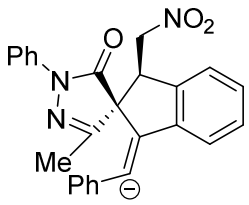
C	2.481275000	2.537305000	-1.793196000
C	-4.363751000	3.235186000	0.582426000
C	-0.306561000	2.344331000	-0.412779000
C	-2.736244000	2.166403000	-0.874680000
C	-1.649874000	2.585613000	-0.051375000
C	3.798952000	2.501267000	-2.244114000
C	2.921188000	0.595230000	-0.413374000
C	2.033855000	1.574490000	-0.878709000
C	0.745089000	-0.092092000	0.483410000
C	0.030240000	-1.032834000	-0.430810000
C	4.241432000	0.559912000	-0.863014000

C	0.675400000	1.501766000	-0.327113000
C	-3.464132000	-2.085266000	0.531682000
C	2.652231000	-1.784026000	0.564026000
C	2.264749000	-0.294591000	0.629657000
C	4.679504000	1.513823000	-1.786655000
C	-3.312357000	3.668560000	1.398662000
C	-4.050767000	2.481481000	-0.556343000
C	-2.306872000	-2.004322000	-0.263253000
C	-1.991344000	3.363719000	1.093651000
C	-2.276823000	-2.664343000	-1.505873000
C	-4.537444000	-3.480831000	-1.138285000
C	-3.389044000	-3.391541000	-1.926924000
C	-4.562168000	-2.819316000	0.091620000
O	0.409576000	-1.517558000	-1.498339000
O	4.859980000	-2.603855000	0.484582000
O	4.174281000	-1.703203000	2.345451000
N	4.007769000	-2.046037000	1.175377000
N	-1.203796000	-1.265563000	0.196410000
N	-1.249520000	-0.710713000	1.482468000
C	0.154929000	0.600974000	2.965556000
C	-0.118602000	-0.100465000	1.673916000
H	1.967776000	-2.377720000	1.175801000
H	1.777402000	3.291142000	-2.134296000
H	4.931547000	-0.204446000	-0.516279000
H	2.554455000	0.052262000	1.631108000
H	-1.385759000	-2.596420000	-2.114748000
H	-4.849681000	2.126693000	-1.206413000
H	2.680358000	-2.166835000	-0.453011000
H	4.143955000	3.242537000	-2.962585000
H	-5.395508000	3.478992000	0.824155000
H	5.705097000	1.484823000	-2.147744000
H	-2.517779000	1.578236000	-1.762113000
H	-1.189972000	3.723550000	1.735085000
H	-3.482670000	-1.562217000	1.479025000
H	-5.398840000	-4.051372000	-1.477198000
H	-3.350348000	-3.896003000	-2.890223000
H	-3.526521000	4.257199000	2.290517000
H	-0.708444000	0.504945000	3.629391000
H	1.037341000	0.187869000	3.473022000
H	0.348218000	1.664977000	2.785406000
H	-5.449674000	-2.867694000	0.719114000

Zero-point correction= 0.401037 (Hartree/Particle)
Thermal correction to Energy= 0.427458
Thermal correction to Enthalpy= 0.428403
Thermal correction to Gibbs Free Energy= 0.341052
Sum of electronic and zero-point Energies= -1392.216274
Sum of electronic and thermal Energies= -1392.189853
Sum of electronic and thermal Enthalpies= -1392.188909
Sum of electronic and thermal Free Energies= -1392.276259

CPCM (dichloromethane) M06/def2TZVP E = - 1392.2254648
CPCM (dichloromethane) M06L/def2TZVP E = - 1393.0223965
CPCM (dichloromethane) B3LYP/def2TZVP E = - 1393.210949
CPCM (dichloromethane) B3LYP-d3/def2TZVP E = - 1393.2712965

[(anion-7b)]



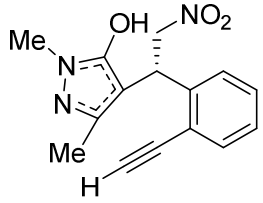
C	3.244606000	2.405940000	-1.379213000
C	-3.689416000	3.529906000	0.593674000
C	0.356262000	2.465700000	-0.311214000
C	-2.063110000	2.487917000	-0.884857000
C	-0.991611000	2.756234000	0.017938000
C	4.589474000	2.241352000	-1.702373000
C	3.267447000	0.248553000	-0.283916000
C	2.574824000	1.401470000	-0.667142000
C	0.930007000	-0.111421000	0.390048000
C	0.039561000	-0.843582000	-0.584491000
C	4.617512000	0.088877000	-0.592962000
C	1.174112000	1.437820000	-0.224242000
C	-3.554935000	-1.407523000	0.382691000
C	2.562742000	-2.133357000	0.117860000
C	2.376591000	-0.677237000	0.536289000
C	5.282086000	1.087534000	-1.311787000
C	-2.652057000	3.818101000	1.488852000
C	-3.369395000	2.861601000	-0.595139000
C	-2.408531000	-1.466349000	-0.428581000
C	-1.339875000	3.454325000	1.212136000
C	-2.500377000	-2.031117000	-1.713652000
C	-4.863674000	-2.476284000	-1.358554000
C	-3.723682000	-2.526821000	-2.162178000
C	-4.765517000	-1.910992000	-0.085251000
O	0.316069000	-1.262248000	-1.709255000
O	1.685684000	-2.770343000	2.230387000
O	2.147023000	-4.327978000	0.782114000
N	2.079362000	-3.150706000	1.130288000
N	-1.191372000	-0.958991000	0.061360000
N	-1.135175000	-0.504283000	1.388422000
C	0.458453000	0.463040000	2.936013000
C	0.066558000	-0.078272000	1.600771000
H	2.038285000	-2.366475000	-0.810646000
H	2.685717000	3.295082000	-1.657852000
H	5.165059000	-0.797886000	-0.276077000
H	2.665569000	-0.601005000	1.592279000
H	-1.617728000	-2.070547000	-2.336794000
H	-4.157021000	2.619097000	-1.307791000
H	3.617794000	-2.389337000	-0.012282000
H	5.108557000	3.016363000	-2.263546000
H	-4.714260000	3.819856000	0.813342000
H	6.333311000	0.967267000	-1.564267000
H	-1.841097000	1.968442000	-1.813704000
H	-0.549044000	3.705104000	1.915963000
H	-3.476672000	-0.959554000	1.364596000
H	-5.812549000	-2.866289000	-1.718980000

H	-3.779169000	-2.959859000	-3.158754000
H	-2.870832000	4.338769000	2.421280000
H	-0.416389000	0.504224000	3.590132000
H	1.220406000	-0.170975000	3.407432000
H	0.874736000	1.471149000	2.829556000
H	-5.642927000	-1.853504000	0.555327000

Zero-point correction= 0.401670 (Hartree/Particle)
Thermal correction to Energy= 0.428400
Thermal correction to Enthalpy= 0.429344
Thermal correction to Gibbs Free Energy= 0.340686
Sum of electronic and zero-point Energies= -1392.214854
Sum of electronic and thermal Energies= -1392.188125
Sum of electronic and thermal Enthalpies= -1392.187181
Sum of electronic and thermal Free Energies= -1392.275839

CPCM (dichloromethane) M06/def2TZVP E = - 1392.229994
CPCM (dichloromethane) M06L/def2TZVP E = - 1393.0266945
CPCM (dichloromethane) B3LYP/def2TZVP E = - 1393.2128538
CPCM (dichloromethane) B3LYP-d3/def2TZVP E = - 1393.27487

[(neutral-5a)]



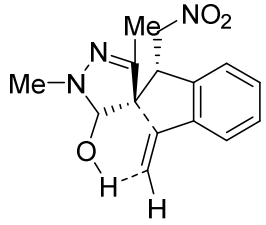
O	1.828694000	3.604109000	0.236566000
O	1.756140000	2.262370000	-1.470488000
O	2.353525000	-0.537394000	-1.549688000
N	2.515350000	-1.538333000	0.561456000
N	1.868610000	-1.610969000	1.759495000
N	1.306086000	2.710610000	-0.409720000
C	0.812120000	-0.808667000	1.641447000
C	1.870381000	-0.720045000	-0.300621000
C	-4.395154000	-0.516305000	0.245659000
C	-2.258922000	-0.717196000	-0.901522000
C	-1.473483000	-1.344004000	-1.918850000
C	-2.537985000	0.894454000	0.877782000
C	-3.595114000	-1.116338000	-0.722615000
C	-3.865394000	0.493652000	1.047044000
C	-1.712639000	0.305612000	-0.084128000
C	-0.256827000	0.721472000	-0.293045000
C	-0.022435000	2.186476000	0.099112000
C	-0.107145000	-0.651813000	2.816305000
C	-0.812426000	-1.864904000	-2.788371000
C	0.747219000	-0.213911000	0.346001000
C	3.709108000	-2.320208000	0.318672000
H	-0.764405000	2.856387000	-0.349890000
H	-2.145745000	1.677094000	1.520425000
H	-4.478982000	0.971129000	1.805864000

H	0.272814000	-1.254377000	3.645742000
H	4.215194000	-1.917663000	-0.560290000
H	0.013739000	2.361469000	1.173587000
H	3.460226000	-3.372842000	0.143653000
H	-0.217085000	-2.331396000	-3.540161000
H	-0.169068000	0.390572000	3.155252000
H	-3.994596000	-1.899508000	-1.359276000
H	-5.426024000	-0.834763000	0.371021000
H	-1.126982000	-0.978911000	2.586192000
H	4.362271000	-2.248462000	1.191260000
H	2.140115000	0.377814000	-1.816597000
H	-0.086491000	0.671996000	-1.373727000

Zero-point correction= 0.281681 (Hartree/Particle)
Thermal correction to Energy= 0.301718
Thermal correction to Enthalpy= 0.302662
Thermal correction to Gibbs Free Energy= 0.231813
Sum of electronic and zero-point Energies= -970.090453
Sum of electronic and thermal Energies= -970.070416
Sum of electronic and thermal Enthalpies= -970.069471
Sum of electronic and thermal Free Energies= -970.140321

CPCM (dichloromethane) M06/def2TZVP E = - 970.1112072
CPCM (dichloromethane) M06L/def2TZVP E = - 970.6334545
CPCM (dichloromethane) B3LYP/def2TZVP E = - 970.766019
CPCM (dichloromethane) B3LYP-d3/def2TZVP E = - 970.8058737

[(neutral-TS-6a)]



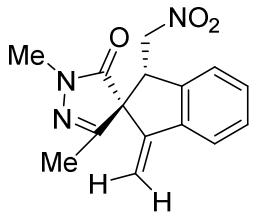
O	1.628710000	2.578335000	-1.324144000
O	1.625438000	3.685604000	0.554606000
O	2.154922000	0.076113000	1.462844000
N	2.417834000	-1.599932000	-0.142252000
N	1.781273000	-2.113191000	-1.227225000
N	1.193373000	2.826600000	-0.204382000
C	0.706806000	-1.363222000	-1.410103000
C	1.791075000	-0.484269000	0.357644000
C	-4.263669000	-0.734528000	0.469205000
C	-1.880508000	-0.562710000	0.860353000
C	-0.719411000	-0.810572000	1.663241000
C	-2.902928000	0.692968000	-0.935991000
C	-3.133540000	-1.096865000	1.202417000
C	-4.151290000	0.162077000	-0.593691000
C	-1.762300000	0.334454000	-0.223042000
C	-0.357506000	0.834903000	-0.563045000
C	-0.016221000	2.060051000	0.294854000

C	-0.216803000	-1.639269000	-2.556295000
C	0.081597000	-0.816407000	2.640224000
C	0.618837000	-0.311648000	-0.435750000
C	3.633071000	-2.202925000	0.359868000
H	-0.827852000	2.792772000	0.276898000
H	-2.815811000	1.373734000	-1.779400000
H	-5.030551000	0.437298000	-1.169093000
H	0.156546000	-2.495778000	-3.123643000
H	4.399778000	-2.216313000	-0.420785000
H	0.216062000	1.815438000	1.329456000
H	-0.363034000	1.174609000	-1.605408000
H	3.442680000	-3.228884000	0.690955000
H	-0.021482000	-0.938430000	3.712301000
H	-1.235147000	-1.862707000	-2.216355000
H	-3.214303000	-1.785550000	2.037468000
H	-5.229814000	-1.158240000	0.727483000
H	-0.283127000	-0.780645000	-3.237545000
H	3.974994000	-1.601100000	1.203060000
H	1.247884000	-0.413188000	2.265831000

Zero-point correction= 0.276078 (Hartree/Particle)
Thermal correction to Energy= 0.295043
Thermal correction to Enthalpy= 0.295987
Thermal correction to Gibbs Free Energy= 0.227990
Sum of electronic and zero-point Energies= -970.053019
Sum of electronic and thermal Energies= -970.034055
Sum of electronic and thermal Enthalpies= -970.033111
Sum of electronic and thermal Free Energies= -970.101108

CPCM (dichloromethane) M06/def2TZVP E = - 970.0596956
CPCM (dichloromethane) M06L/def2TZVP E = - 970.5907334
CPCM (dichloromethane) B3LYP/def2TZVP E = - 970.7185919
CPCM (dichloromethane) B3LYP-d3/def2TZVP E = - 970.76015

[(3h)]



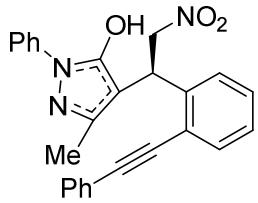
O	-1.761033000	3.632201000	-0.351950000
O	-2.118767000	1.862007000	0.870192000
O	-1.671208000	0.095124000	-1.912308000
N	-2.543237000	-1.166606000	-0.177451000
N	-2.146823000	-1.653076000	1.069743000
N	-1.439845000	2.541416000	0.101156000
C	-0.910507000	-1.341319000	1.246391000
C	-1.565183000	-0.469712000	-0.832579000
C	4.434836000	-0.248590000	-0.393107000
C	2.068111000	-0.692908000	-0.396596000
C	0.800919000	-1.404070000	-0.611786000
C	2.904869000	1.374276000	0.564902000

C	3.372288000	-1.089399000	-0.716746000
C	4.205043000	0.975987000	0.247693000
C	1.840455000	0.535481000	0.236786000
C	0.359016000	0.782548000	0.467620000
C	-0.095247000	2.005758000	-0.335144000
C	-0.167250000	-1.747016000	2.475878000
C	0.615527000	-2.567194000	-1.246693000
C	-0.316185000	-0.585812000	0.066692000
C	-3.933456000	-1.243434000	-0.566090000
H	0.591053000	2.845789000	-0.213734000
H	2.732852000	2.324766000	1.064912000
H	5.043499000	1.618512000	0.501363000
H	-0.835880000	-2.290325000	3.148005000
H	-4.558343000	-0.661507000	0.119961000
H	-0.212441000	1.787575000	-1.398221000
H	0.157004000	0.991560000	1.523390000
H	-4.270468000	-2.284374000	-0.566248000
H	1.443832000	-3.108593000	-1.694449000
H	0.683808000	-2.391202000	2.222791000
H	3.557205000	-2.041977000	-1.205560000
H	5.451141000	-0.547416000	-0.634445000
H	0.233552000	-0.876406000	3.010476000
H	-4.010116000	-0.827648000	-1.572236000
H	-0.368715000	-3.013111000	-1.350925000

Zero-point correction= 0.283865 (Hartree/Particle)
Thermal correction to Energy= 0.302552
Thermal correction to Enthalpy= 0.303497
Thermal correction to Gibbs Free Energy= 0.235864
Sum of electronic and zero-point Energies= -970.150738
Sum of electronic and thermal Energies= -970.132051
Sum of electronic and thermal Enthalpies= -970.131106
Sum of electronic and thermal Free Energies= -970.198739

CPCM (dichloromethane) M06/def2TZVP E = - 970.1647903
CPCM (dichloromethane) M06L/def2TZVP E = - 970.689328
CPCM (dichloromethane) B3LYP/def2TZVP E = - 970.8181263
CPCM (dichloromethane) B3LYP-d3/def2TZVP E = - 970.8607275

[(neutral-5b)]



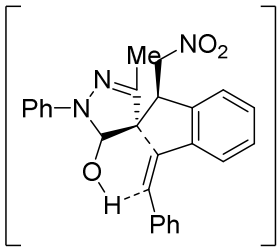
C	2.384440000	3.617317000	-0.181618000
C	7.032982000	-2.434268000	0.537932000
C	3.963137000	0.449199000	0.129416000
C	6.300949000	-0.131039000	0.635036000
C	4.998000000	-0.521775000	0.266781000
C	1.403045000	4.587853000	-0.350763000
C	0.685543000	1.863878000	-0.257763000
C	2.046636000	2.249855000	-0.138228000

C	-1.083746000	0.109976000	0.304860000
C	-2.277238000	-0.105696000	-0.369768000
C	-0.281331000	2.856520000	-0.430912000
C	3.079828000	1.279322000	0.014875000
C	-5.335206000	-1.162445000	1.432361000
C	0.569307000	-0.191237000	-1.636526000
C	0.304052000	0.378090000	-0.221920000
C	0.066375000	4.207145000	-0.479851000
C	5.744089000	-2.830027000	0.171087000
C	7.307022000	-1.083655000	0.768618000
C	-4.652457000	-0.513795000	0.395580000
C	4.729935000	-1.886107000	0.034823000
C	-5.333696000	-0.137263000	-0.768416000
C	-7.378812000	-1.079219000	0.134203000
C	-6.691636000	-0.431667000	-0.892673000
C	-6.693920000	-1.436767000	1.297540000
O	-2.550073000	-0.191480000	-1.695560000
O	1.252090000	-2.377586000	-1.152359000
O	-0.643808000	-2.141010000	-2.185980000
N	0.383689000	-1.686301000	-1.662584000
N	-3.268670000	-0.231418000	0.568639000
N	-2.761317000	-0.107908000	1.833225000
C	-0.578505000	0.284618000	2.875143000
C	-1.459034000	0.090524000	1.679166000
H	-0.106492000	0.224412000	-2.381458000
H	3.427753000	3.899726000	-0.080441000
H	-1.323615000	2.565174000	-0.514725000
H	1.023585000	-0.122526000	0.436722000
H	-4.809864000	0.375392000	-1.564187000
H	8.308032000	-0.771825000	1.054027000
H	1.610571000	-0.025471000	-1.913847000
H	1.680715000	5.637728000	-0.381016000
H	7.820838000	-3.175040000	0.643490000
H	-0.707282000	4.958097000	-0.612686000
H	6.508741000	0.919389000	0.814476000
H	3.727638000	-2.187576000	-0.253217000
H	-4.792810000	-1.432530000	2.330167000
H	-8.437475000	-1.300311000	0.031043000
H	-7.214543000	-0.139514000	-1.799417000
H	5.527245000	-3.879183000	-0.010080000
H	-0.107299000	1.275063000	2.872283000
H	-1.173348000	0.187387000	3.786931000
H	0.227711000	-0.459144000	2.907459000
H	-7.217147000	-1.939372000	2.106572000
H	-2.013099000	-0.925907000	-2.069749000

Zero-point correction= 0.417166 (Hartree/Particle)
Thermal correction to Energy= 0.444410
Thermal correction to Enthalpy= 0.445354
Thermal correction to Gibbs Free Energy= 0.356080
Sum of electronic and zero-point Energies= -1392.767947
Sum of electronic and thermal Energies= -1392.740704
Sum of electronic and thermal Enthalpies= -1392.739759
Sum of electronic and thermal Free Energies= -1392.829034

CPCM (dichloromethane) M06/def2TZVP E = - 1392.7232766
CPCM (dichloromethane) M06L/def2TZVP E = - 1393.5237496
CPCM (dichloromethane) B3LYP/def2TZVP E = - 1393.7178437
CPCM (dichloromethane) B3LYP-d3/def2TZVP E = - 1393.7743695

[(neutral-TS-6b)]



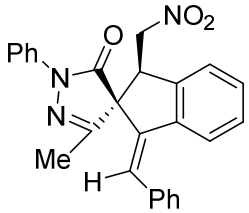
C	-2.802958000	1.144186000	-2.094776000
C	1.547299000	5.577484000	0.060687000
C	0.090546000	1.570218000	-0.107945000
C	1.693432000	3.260476000	0.734741000
C	0.581267000	2.946742000	-0.064613000
C	-4.101112000	0.764804000	-2.433739000
C	-2.707666000	-0.677778000	-0.471435000
C	-2.099532000	0.428572000	-1.108816000
C	-0.452348000	-1.565075000	0.046629000
C	0.793138000	-1.164670000	0.601896000
C	-4.008309000	-1.034483000	-0.816421000
C	-0.815272000	0.866251000	-0.661420000
C	3.956352000	-2.016098000	-1.197647000
C	-1.928198000	-0.772812000	1.948558000
C	-1.867299000	-1.430685000	0.559740000
C	-4.706330000	-0.316561000	-1.793381000
C	0.442157000	5.273901000	-0.740598000
C	2.170623000	4.567933000	0.796239000
C	3.180991000	-1.662445000	-0.084898000
C	-0.038155000	3.970172000	-0.806659000
C	3.802493000	-1.212372000	1.088322000
C	5.971523000	-1.457747000	0.026906000
C	5.192771000	-1.108335000	1.130549000
C	5.343938000	-1.915714000	-1.133329000
O	1.043786000	-0.246762000	1.467033000
O	-3.714449000	0.064185000	3.202209000
O	-3.915226000	-1.952130000	2.398774000
N	-3.307259000	-0.894157000	2.556539000
N	1.769397000	-1.785662000	-0.168301000
N	1.215310000	-2.584755000	-1.131048000
C	-1.001269000	-3.237943000	-1.918251000
C	-0.092456000	-2.459008000	-1.018507000
H	-1.256694000	-1.276069000	2.649281000
H	-2.329226000	1.984545000	-2.592315000
H	-4.476419000	-1.880516000	-0.321927000
H	-2.294218000	-2.432818000	0.677938000
H	3.204232000	-0.945649000	1.949185000
H	3.031471000	4.797530000	1.417832000
H	-1.699753000	0.290155000	1.945640000
H	-4.635153000	1.313903000	-3.203906000

H	1.920798000	6.596616000	0.108029000
H	-5.716907000	-0.611920000	-2.059930000
H	2.179774000	2.470689000	1.299998000
H	-0.897731000	3.735036000	-1.427295000
H	3.461272000	-2.372037000	-2.092785000
H	7.054053000	-1.377058000	0.070707000
H	5.667447000	-0.758462000	2.043558000
H	-0.045460000	6.056424000	-1.315566000
H	-0.403341000	-3.872329000	-2.577554000
H	-1.682436000	-3.881002000	-1.345916000
H	-1.622805000	-2.578637000	-2.535329000
H	5.936362000	-2.194015000	-2.000963000
H	0.675950000	0.831203000	0.715877000

Zero-point correction= 0.410874 (Hartree/Particle)
Thermal correction to Energy= 0.437449
Thermal correction to Enthalpy= 0.438393
Thermal correction to Gibbs Free Energy= 0.350892
Sum of electronic and zero-point Energies= -1392.722565
Sum of electronic and thermal Energies= -1392.695990
Sum of electronic and thermal Enthalpies= -1392.695046
Sum of electronic and thermal Free Energies= -1392.782547

CPCM (dichloromethane) M06/def2TZVP E = - 1392.6661572
CPCM (dichloromethane) M06L/def2TZVP E = - 1393.4762375
CPCM (dichloromethane) B3LYP/def2TZVP E = - 1393.6628567
CPCM (dichloromethane) B3LYP-d3/def2TZVP E = - 1393.7240126

[(neutral-7b)]



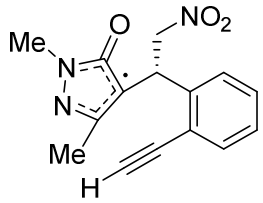
C	-3.212423000	1.166155000	-1.182759000
C	-1.567628000	-1.149325000	0.476035000
C	-3.718460000	2.336992000	-1.744040000
C	-1.308751000	2.425555000	-0.361109000
C	-2.004773000	1.210169000	-0.471355000
C	0.162066000	0.695695000	0.493995000
C	1.147746000	0.124597000	-0.548856000
C	-1.827214000	3.597861000	-0.905363000
C	-1.249968000	0.130027000	0.182515000
C	3.837037000	-2.225659000	0.615357000
C	1.133978000	3.038637000	-0.213531000
C	-0.013523000	2.253378000	0.416521000
C	-3.039153000	3.550726000	-1.597859000
C	3.043087000	-1.533822000	-0.311069000
C	3.298211000	-1.657889000	-1.685636000
C	5.140267000	-3.164486000	-1.200521000
C	4.345562000	-2.472316000	-2.114624000

C	4.877535000	-3.034419000	0.163979000
O	1.170692000	0.366892000	-1.745966000
O	2.324299000	2.666715000	1.795394000
O	3.320275000	3.730907000	0.173864000
N	2.362809000	3.145589000	0.662955000
N	1.981214000	-0.717840000	0.162277000
N	1.726154000	-0.681701000	1.545754000
C	0.253103000	0.389201000	3.145081000
C	0.749976000	0.126828000	1.763052000
H	1.474727000	2.605876000	-1.155355000
H	-3.744528000	0.231139000	-1.309802000
H	-1.302206000	4.544400000	-0.805206000
H	-0.150370000	2.627639000	1.438568000
H	2.689158000	-1.119206000	-2.398026000
H	0.853942000	4.078063000	-0.399724000
H	-4.649254000	2.303119000	-2.303399000
H	-3.447890000	4.458410000	-2.032836000
H	3.631958000	-2.122856000	1.672995000
H	5.954179000	-3.795508000	-1.546208000
H	4.537208000	-2.561630000	-3.180653000
H	0.784584000	-0.247109000	3.856706000
H	0.424748000	1.436334000	3.420976000
H	-0.822786000	0.191959000	3.218138000
H	5.487151000	-3.564843000	0.890725000
H	-0.759350000	-1.765608000	0.870634000
C	-2.852013000	-1.864952000	0.356180000
C	-4.075893000	-1.301835000	0.759005000
C	-2.849944000	-3.198342000	-0.091373000
C	-5.258435000	-2.035897000	0.684413000
H	-4.093589000	-0.288384000	1.148618000
C	-4.033548000	-3.929320000	-0.174350000
H	-1.908934000	-3.657335000	-0.384649000
C	-5.244125000	-3.349936000	0.210986000
H	-6.192421000	-1.583321000	1.007198000
H	-4.009201000	-4.954388000	-0.534343000
H	-6.166802000	-3.920929000	0.154363000

Zero-point correction= 0.418069 (Hartree/Particle)
Thermal correction to Energy= 0.444409
Thermal correction to Enthalpy= 0.445353
Thermal correction to Gibbs Free Energy= 0.358014
Sum of electronic and zero-point Energies= -1392.808425
Sum of electronic and thermal Energies= -1392.782085
Sum of electronic and thermal Enthalpies= -1392.781141
Sum of electronic and thermal Free Energies= -1392.868480

CPCM (dichloromethane) M06/def2TZVP E = - 1392.7637041
CPCM (dichloromethane) M06L/def2TZVP E = - 1393.5655819
CPCM (dichloromethane) B3LYP/def2TZVP E = - 1393.7522105
CPCM (dichloromethane) B3LYP-d3/def2TZVP E = - 1393.815107

[(radical-5a)]

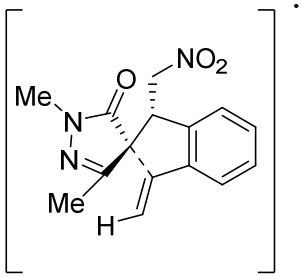


O	-1.586412000	2.635153000	-2.506621000
O	-1.114704000	2.947018000	-0.401312000
O	-1.733993000	-1.499512000	-1.506261000
N	-2.746706000	-1.422074000	0.601101000
N	-2.573541000	-0.802910000	1.765651000
N	-0.989841000	2.358439000	-1.472529000
C	-1.459159000	-0.008116000	1.626933000
C	-1.767056000	-1.063605000	-0.349755000
C	3.802951000	-1.978248000	-0.519597000
C	2.707083000	-0.020682000	0.422879000
C	2.793934000	1.123468000	1.279018000
C	1.516945000	-1.463409000	-1.116781000
C	3.834092000	-0.857066000	0.301673000
C	2.640635000	-2.281657000	-1.230642000
C	1.527274000	-0.327294000	-0.298974000
C	0.298420000	0.582245000	-0.194819000
C	0.013253000	1.224463000	-1.561506000
C	-1.028244000	0.846280000	2.777696000
C	2.897008000	2.083555000	2.009529000
C	-0.911931000	-0.120139000	0.363845000
C	-3.849480000	-2.334790000	0.375517000
H	0.915986000	1.684584000	-1.974073000
H	0.611882000	-1.715344000	-1.661267000
H	2.604679000	-3.156783000	-1.873495000
H	-1.641186000	0.623135000	3.654595000
H	-4.804192000	-1.814515000	0.496076000
H	-0.401505000	0.528421000	-2.289042000
H	-3.800573000	-3.169217000	1.081010000
H	2.988071000	2.934461000	2.646149000
H	0.024590000	0.680873000	3.030287000
H	4.729654000	-0.608990000	0.862655000
H	4.680700000	-2.612852000	-0.602798000
H	-1.143184000	1.908952000	2.532966000
H	-3.756121000	-2.705193000	-0.646567000
H	0.548323000	1.396975000	0.487391000

Zero-point correction= 0.268727 (Hartree/Particle)
Thermal correction to Energy= 0.288770
Thermal correction to Enthalpy= 0.289714
Thermal correction to Gibbs Free Energy= 0.216823
Sum of electronic and zero-point Energies= -969.489546
Sum of electronic and thermal Energies= -969.469503
Sum of electronic and thermal Enthalpies= -969.468559
Sum of electronic and thermal Free Energies= -969.541451

CPCM (dichloromethane) M06/def2TZVP E = - 969.4861822
CPCM (dichloromethane) M06L/def2TZVP E = - 970.0137265
CPCM (dichloromethane) ROB3LYP/def2TZVP E = - 970.1418038
CPCM (dichloromethane) ROB3LYP-d3/def2TZVP E = - 970.1795332

[(radical-TS-6a)]



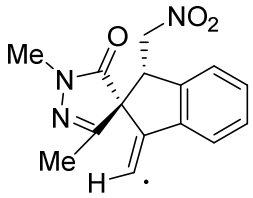
O	2.676284000	2.966360000	-0.891331000
O	2.162511000	2.701275000	1.210721000
O	-2.044246000	1.607951000	-1.359464000
N	-3.240148000	0.159421000	0.016003000
N	-2.999921000	-0.642578000	1.113259000
N	1.948773000	2.559959000	0.005622000
C	-1.703007000	-0.688579000	1.290589000
C	-2.091487000	0.751067000	-0.481678000
C	3.096826000	-2.565612000	-0.546557000
C	0.930872000	-1.502739000	-0.617117000
C	-0.461952000	-1.426869000	-1.024441000
C	2.724356000	-0.496477000	0.663581000
C	1.781031000	-2.550513000	-1.001597000
C	3.565923000	-1.545202000	0.287184000
C	1.406489000	-0.470311000	0.204782000
C	0.399267000	0.638067000	0.482020000
C	0.666937000	1.874252000	-0.400731000
C	-1.109318000	-1.489975000	2.404282000
C	-1.340895000	-1.910790000	-1.774152000
C	-0.992300000	0.066271000	0.266987000
C	-4.594863000	0.528964000	-0.331576000
H	0.770213000	1.637034000	-1.457270000
H	3.092210000	0.296037000	1.308164000
H	4.590675000	-1.566862000	0.646959000
H	-1.909915000	-1.914867000	3.014804000
H	-5.081818000	1.053069000	0.498223000
H	-0.114717000	2.627278000	-0.285048000
H	0.491135000	0.972180000	1.522399000
H	-5.180068000	-0.360754000	-0.582366000
H	-2.307088000	-2.046659000	-2.212746000
H	-0.487169000	-2.306893000	2.019791000
H	1.400978000	-3.341311000	-1.640633000
H	3.756871000	-3.378720000	-0.835125000
H	-0.469810000	-0.872213000	3.047209000
H	-4.536089000	1.191049000	-1.197415000

Zero-point correction= 0.267630 (Hartree/Particle)
Thermal correction to Energy= 0.286666
Thermal correction to Enthalpy= 0.287610
Thermal correction to Gibbs Free Energy= 0.218884
Sum of electronic and zero-point Energies= -969.454035
Sum of electronic and thermal Energies= -969.434999
Sum of electronic and thermal Enthalpies= -969.434055

Sum of electronic and thermal Free Energies= -969.502781

CPCM (dichloromethane) M06/def2TZVP E = - 969.4564493
CPCM (dichloromethane) M06L/def2TZVP E = - 969.982247
CPCM (dichloromethane) ROB3LYP/def2TZVP E = - 970.1063088
CPCM (dichloromethane) ROB3LYP-d3/def2TZVP E = - 970.147028

[(radical-7a)]



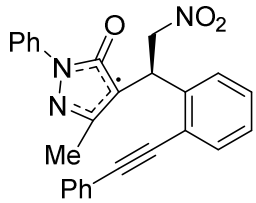
O	2.267893000	3.266136000	-0.776627000
O	1.679898000	2.851584000	1.281671000
O	-2.131571000	1.154920000	-1.647939000
N	-3.208250000	0.122252000	0.123455000
N	-2.898633000	-0.696380000	1.211918000
N	1.562944000	2.720915000	0.062575000
C	-1.635602000	-0.950058000	1.175858000
C	-2.128341000	0.439547000	-0.656372000
C	3.377764000	-2.250959000	-0.460337000
C	1.121945000	-1.435746000	-0.584173000
C	-0.309254000	-1.381508000	-0.938096000
C	2.764500000	-0.216184000	0.722298000
C	2.077173000	-2.390558000	-0.943206000
C	3.717896000	-1.175898000	0.370019000
C	1.464980000	-0.350993000	0.235298000
C	0.283535000	0.589437000	0.419719000
C	0.431821000	1.856645000	-0.442220000
C	-0.985903000	-1.817616000	2.202937000
C	-0.956091000	-2.100976000	-1.829246000
C	-0.940794000	-0.298260000	-0.012161000
C	-4.564052000	0.586273000	-0.065269000
H	0.652851000	1.645166000	-1.486483000
H	3.033569000	0.618284000	1.362761000
H	4.732959000	-1.086010000	0.746534000
H	-1.732410000	-2.141040000	2.932466000
H	-4.570683000	1.201621000	-0.966740000
H	-0.454568000	2.492755000	-0.394147000
H	0.170408000	0.915154000	1.457781000
H	-4.890548000	1.183419000	0.792672000
H	-1.952789000	-2.190858000	-2.236459000
H	-0.533164000	-2.701878000	1.739139000
H	1.802819000	-3.228735000	-1.577168000
H	4.131557000	-2.987932000	-0.723379000
H	-0.183545000	-1.286461000	2.729647000
H	-5.246106000	-0.261002000	-0.189377000

Zero-point correction= 0.270346 (Hartree/Particle)
Thermal correction to Energy= 0.289182
Thermal correction to Enthalpy= 0.290126
Thermal correction to Gibbs Free Energy= 0.221584

Sum of electronic and zero-point Energies= -969.475855
Sum of electronic and thermal Energies= -969.457020
Sum of electronic and thermal Enthalpies= -969.456076
Sum of electronic and thermal Free Energies= -969.524617

CPCM (dichloromethane) M06/def2TZVP E = - 969.4766711
CPCM (dichloromethane) M06L/def2TZVP E = - 970.0003548
CPCM (dichloromethane) ROB3LYP/def2TZVP E = - 970.1267942
CPCM (dichloromethane) ROB3LYP-d3/def2TZVP E = - 970.167595

[(radical-5b)]



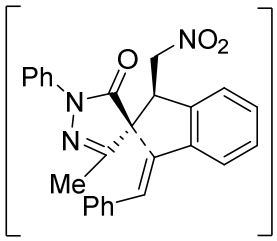
C	-2.192403000	3.718232000	-0.278380000
C	-6.923575000	-2.352420000	-0.465172000
C	-3.871900000	0.573408000	-0.288832000
C	-4.635258000	-1.740013000	0.030740000
C	-4.902626000	-0.409252000	-0.351395000
C	-1.184261000	4.665571000	-0.138259000
C	-0.594625000	1.927766000	0.183708000
C	-1.919136000	2.345811000	-0.114570000
C	1.012431000	-0.026030000	-0.206172000
C	2.318986000	0.122527000	0.416199000
C	0.397958000	2.898935000	0.337339000
C	-2.979347000	1.398923000	-0.226044000
C	5.358553000	-0.889848000	-1.585528000
C	-0.476494000	0.048760000	1.835177000
C	-0.306675000	0.432304000	0.354700000
C	0.111810000	4.255926000	0.178054000
C	-7.196744000	-1.035655000	-0.844501000
C	-5.642374000	-2.699254000	-0.028316000
C	4.631171000	-0.629080000	-0.415832000
C	-6.197483000	-0.068032000	-0.789931000
C	5.289795000	-0.492899000	0.813827000
C	7.411030000	-0.875185000	-0.300345000
C	6.678396000	-0.612600000	0.857580000
C	6.742991000	-1.015670000	-1.519276000
O	2.650715000	0.671797000	1.468575000
O	-0.064656000	-1.893339000	3.072216000
O	-1.073419000	-2.131124000	1.155759000
N	-0.533597000	-1.453078000	2.030514000
N	3.216397000	-0.520963000	-0.498558000
N	2.562799000	-0.998375000	-1.561035000
C	0.252687000	-1.160395000	-2.419471000
C	1.235716000	-0.707605000	-1.386395000
H	0.336750000	0.401167000	2.467002000
H	-3.207422000	4.023055000	-0.513571000
H	1.406150000	2.595282000	0.596984000
H	-1.088394000	-0.104924000	-0.187069000
H	4.724545000	-0.292536000	1.713632000

H	-5.426178000	-3.721670000	0.269120000
H	-1.434473000	0.414113000	2.216134000
H	-1.410935000	5.719995000	-0.268891000
H	-7.706253000	-3.104821000	-0.509086000
H	0.903420000	4.989503000	0.302119000
H	-3.639022000	-2.004144000	0.373179000
H	-6.404982000	0.956245000	-1.084234000
H	4.830981000	-0.994575000	-2.525883000
H	8.492161000	-0.970171000	-0.254628000
H	7.186457000	-0.506193000	1.811956000
H	-8.191978000	-0.761957000	-1.184143000
H	0.767546000	-1.729869000	-3.197020000
H	-0.517908000	-1.797176000	-1.970251000
H	-0.254554000	-0.309616000	-2.889157000
H	7.302044000	-1.218825000	-2.428476000

Zero-point correction= 0.403620 (Hartree/Particle)
Thermal correction to Energy= 0.431242
Thermal correction to Enthalpy= 0.432186
Thermal correction to Gibbs Free Energy= 0.338959
Sum of electronic and zero-point Energies= -1392.162798
Sum of electronic and thermal Energies= -1392.135176
Sum of electronic and thermal Enthalpies= -1392.134231
Sum of electronic and thermal Free Energies= -1392.227459

CPCM (dichloromethane) M06/def2TZVP E = - 1392.1021468
CPCM (dichloromethane) M06L/def2TZVP E = - 1392.9078568
CPCM (dichloromethane) ROB3LYP/def2TZVP E = - 1393.0959609
CPCM (dichloromethane) ROB3LYP-d3/def2TZVP E = - 1393.1505171

[(radical-TS-6b)]



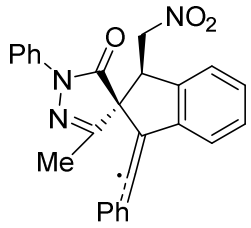
C	2.476168000	3.065205000	-1.210835000
C	-4.454254000	2.963423000	0.632041000
C	-0.392918000	2.041691000	-0.015785000
C	-2.732907000	1.974381000	-0.750275000
C	-1.748689000	2.337643000	0.203979000
C	3.795086000	3.295969000	-1.586047000
C	3.110213000	0.898523000	-0.301284000
C	2.129342000	1.866323000	-0.564143000
C	1.135659000	-0.388132000	0.536336000
C	0.280468000	-1.008446000	-0.509813000
C	4.434603000	1.149767000	-0.667870000
C	0.775217000	1.608759000	-0.126293000
C	-3.247345000	-1.912102000	0.474823000
C	3.219735000	-1.619446000	-0.209016000
C	2.648887000	-0.352252000	0.444703000
C	4.776916000	2.339936000	-1.309682000
C	-3.493190000	3.330693000	1.580939000
C	-4.068301000	2.284255000	-0.529012000

C	-2.152516000	-1.733797000	-0.384388000
C	-2.154467000	3.024871000	1.376295000
C	-2.278152000	-2.037220000	-1.749604000
C	-4.588296000	-2.695804000	-1.387541000
C	-3.495447000	-2.514658000	-2.235463000
C	-4.452760000	-2.391637000	-0.031592000
O	0.558042000	-1.258034000	-1.681851000
O	2.744204000	-2.718427000	1.834586000
O	3.469374000	-3.901270000	0.153591000
N	3.125606000	-2.846622000	0.672831000
N	-0.934942000	-1.236045000	0.143162000
N	-0.848904000	-0.954306000	1.499239000
C	0.769994000	-0.136327000	3.131112000
C	0.358747000	-0.510332000	1.743887000
H	2.697320000	-1.874016000	-1.131985000
H	1.704295000	3.801587000	-1.411333000
H	5.213207000	0.423638000	-0.449361000
H	3.045437000	-0.305023000	1.466081000
H	-1.430298000	-1.909322000	-2.408307000
H	-4.814847000	1.990755000	-1.261262000
H	4.286492000	-1.531877000	-0.423894000
H	4.059703000	4.221215000	-2.089892000
H	-5.500656000	3.203230000	0.798465000
H	5.809739000	2.521053000	-1.593462000
H	-2.429726000	1.439311000	-1.644074000
H	-1.404231000	3.305913000	2.108674000
H	-3.139503000	-1.673221000	1.525013000
H	-5.530864000	-3.071205000	-1.776179000
H	-3.581298000	-2.750504000	-3.293086000
H	-3.793335000	3.855646000	2.483550000
H	-0.062363000	-0.304740000	3.818944000
H	1.622924000	-0.740985000	3.460068000
H	1.064588000	0.919205000	3.187043000
H	-5.292609000	-2.527719000	0.644927000

Zero-point correction= 0.402499 (Hartree/Particle)
Thermal correction to Energy= 0.429221
Thermal correction to Enthalpy= 0.430165
Thermal correction to Gibbs Free Energy= 0.339663
Sum of electronic and zero-point Energies= -1392.137899
Sum of electronic and thermal Energies= -1392.111177
Sum of electronic and thermal Enthalpies= -1392.110233
Sum of electronic and thermal Free Energies= -1392.200735

CPCM (dichloromethane) M06/def2TZVP E = - 1392.0850771
CPCM (dichloromethane) M06L/def2TZVP E = - 1392.890299
CPCM (dichloromethane) ROB3LYP/def2TZVP E = - 1393.0713263
CPCM (dichloromethane) ROB3LYP-d3/def2TZVP E = - 1393.132382

[(radical-7b)]



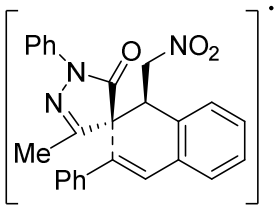
C	3.800498000	2.004889000	-0.015689000
C	-2.619397000	4.646308000	-0.824716000
C	0.635919000	2.081441000	-0.096603000
C	-1.063824000	2.964961000	-1.612852000
C	-0.451067000	2.907823000	-0.321417000
C	5.159776000	1.696271000	-0.023591000
C	3.299981000	-0.368764000	0.132604000
C	2.872717000	0.962055000	0.066083000
C	0.883297000	-0.404945000	0.429334000
C	-0.391926000	-0.728400000	-0.363501000
C	4.659914000	-0.675381000	0.126049000
C	1.399533000	1.035734000	0.101210000
C	-3.587290000	-1.339331000	1.514267000
C	2.081746000	-2.136909000	-1.136304000
C	2.126966000	-1.335281000	0.168080000
C	5.589409000	0.364890000	0.050467000
C	-2.031789000	4.604603000	0.447882000
C	-2.128202000	3.820229000	-1.845932000
C	-2.760080000	-1.193593000	0.391011000
C	-0.966130000	3.757955000	0.705674000
C	-3.294192000	-1.346025000	-0.897657000
C	-5.479195000	-1.787514000	0.066640000
C	-4.648853000	-1.641641000	-1.044733000
C	-4.937792000	-1.634652000	1.343827000
O	-0.498887000	-0.785381000	-1.580833000
O	0.523775000	-3.536058000	-0.046058000
O	1.256774000	-4.128218000	-2.013219000
N	1.208777000	-3.370011000	-1.053618000
N	-1.386095000	-0.889838000	0.580137000
N	-0.905949000	-0.744632000	1.890194000
C	1.149429000	-0.269086000	3.086634000
C	0.352890000	-0.488800000	1.842771000
H	1.678628000	-1.562280000	-1.971513000
H	3.460629000	3.035444000	-0.066729000
H	4.999027000	-1.707449000	0.183097000
H	2.224157000	-2.051948000	0.989599000
H	-2.654668000	-1.237347000	-1.762057000
H	-2.589104000	3.843740000	-2.829758000
H	3.069776000	-2.514637000	-1.406935000
H	5.893181000	2.495850000	-0.081741000
H	-3.454610000	5.313275000	-1.017417000
H	6.652106000	0.139381000	0.051680000
H	-0.691792000	2.309973000	-2.393857000
H	-0.510113000	3.725918000	1.690354000
H	-3.165664000	-1.222309000	2.504044000
H	-6.533041000	-2.018989000	-0.060213000
H	-5.053464000	-1.760188000	-2.046451000
H	-2.414816000	5.240166000	1.241838000
H	0.502974000	-0.369827000	3.961659000

H	1.968739000	-0.994138000	3.170853000
H	1.602234000	0.729719000	3.088443000
H	-5.568632000	-1.746757000	2.221758000

Zero-point correction= 0.404267 (Hartree/Particle)
Thermal correction to Energy= 0.430852
Thermal correction to Enthalpy= 0.431796
Thermal correction to Gibbs Free Energy= 0.342990
Sum of electronic and zero-point Energies= -1392.158959
Sum of electronic and thermal Energies= -1392.132374
Sum of electronic and thermal Enthalpies= -1392.131430
Sum of electronic and thermal Free Energies= -1392.220235

CPCM (dichloromethane) M06/def2TZVP E = - 1392.1072008
CPCM (dichloromethane) M06L/def2TZVP E = - 1392.9079583
CPCM (dichloromethane) ROB3LYP/def2TZVP E = - 1393.0909303
CPCM (dichloromethane) ROB3LYP-d3/def2TZVP E = - 1393.1507433

[(endo-radical-TS-6b)]



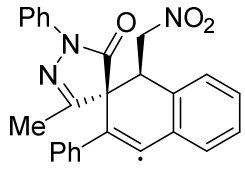
C	-0.792205000	1.666747000	-0.180390000
C	-1.948744000	1.667889000	-0.836605000
C	-2.845383000	0.602833000	-1.172651000
C	-2.635022000	-0.619682000	-0.486529000
C	-1.580281000	-0.635386000	0.616903000
C	-0.324962000	0.273947000	0.321729000
H	-3.993512000	1.655174000	-2.653653000
C	-3.855988000	0.710837000	-2.135773000
C	-3.452757000	-1.705493000	-0.791668000
C	-4.459871000	-1.592255000	-1.758602000
C	-4.662964000	-0.387608000	-2.428408000
H	-3.328646000	-2.655849000	-0.282118000
H	-5.083321000	-2.453529000	-1.980536000
H	-5.444957000	-0.302159000	-3.177386000
H	-2.042734000	-0.186686000	1.506585000
C	-1.144632000	-2.052424000	1.024229000
N	-2.095172000	-2.665932000	2.030962000
O	-2.481055000	-3.810982000	1.821875000
O	-2.383034000	-1.987796000	3.014278000
C	0.625837000	-0.409569000	-0.689450000
O	0.386036000	-0.687622000	-1.849546000
N	1.791588000	-0.668931000	0.024643000
N	1.716752000	-0.220250000	1.351998000
C	0.565116000	0.323250000	1.546295000
C	0.182839000	0.878865000	2.878847000
H	1.040026000	0.837386000	3.555195000
H	-0.150611000	1.918452000	2.785830000
H	-0.640880000	0.304082000	3.321252000

H	-1.088542000	-2.747584000	0.188381000
H	-0.187474000	-2.039501000	1.551819000
C	0.014048000	2.896188000	0.007102000
C	-0.646681000	4.124346000	0.200802000
C	1.418747000	2.896622000	-0.041038000
C	0.070889000	5.309595000	0.336920000
H	-1.731704000	4.133622000	0.251145000
C	2.134844000	4.085346000	0.098470000
H	1.962368000	1.974609000	-0.214763000
C	1.466946000	5.295477000	0.289036000
H	-0.460888000	6.245112000	0.488888000
H	3.220141000	4.062582000	0.050622000
H	2.028334000	6.218992000	0.400478000
C	2.986945000	-1.304167000	-0.411379000
C	4.035526000	-1.488642000	0.501886000
C	3.123214000	-1.745354000	-1.736666000
C	5.210331000	-2.111415000	0.086336000
H	3.921446000	-1.144218000	1.521603000
C	4.308249000	-2.366440000	-2.130071000
H	2.313672000	-1.602302000	-2.438697000
C	5.356397000	-2.554633000	-1.228994000
H	6.016324000	-2.249367000	0.802161000
H	4.405835000	-2.705084000	-3.158038000
H	6.274744000	-3.039989000	-1.546846000

Zero-point correction= 0.403190 (Hartree/Particle)
Thermal correction to Energy= 0.429514
Thermal correction to Enthalpy= 0.430458
Thermal correction to Gibbs Free Energy= 0.343482
Sum of electronic and zero-point Energies= -1392.111253
Sum of electronic and thermal Energies= -1392.084930
Sum of electronic and thermal Enthalpies= -1392.083986
Sum of electronic and thermal Free Energies= -1392.170962

CPCM (dichloromethane) M06/def2TZVP E = - 1392.0629294
CPCM (dichloromethane) M06L/def2TZVP E = - 1392.8670189
CPCM (dichloromethane) ROB3LYP/def2TZVP E = - 1393.0449851
CPCM (dichloromethane) ROB3LYP-d3/def2TZVP E = - 1393.1086793

[(endo-radical-7b)]



C	0.694934000	1.429461000	-0.197685000
C	1.984054000	1.700908000	-0.007039000
C	3.067199000	0.867020000	0.437487000
C	2.802730000	-0.525896000	0.471628000
C	1.486175000	-1.020602000	-0.114149000
C	0.298142000	-0.034198000	0.184834000
H	4.494450000	2.424444000	0.848959000
C	4.305243000	1.355514000	0.878422000
C	3.779076000	-1.392401000	0.960085000

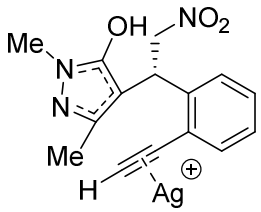
C	5.010188000	-0.895464000	1.403299000
C	5.273883000	0.473994000	1.356527000
H	3.584025000	-2.460785000	0.982763000
H	5.761254000	-1.583174000	1.781098000
H	6.231720000	0.856912000	1.696938000
C	-0.132053000	-0.067928000	1.651296000
N	-1.347135000	-0.457716000	1.808447000
N	-1.895200000	-0.758004000	0.554630000
C	-1.004268000	-0.549420000	-0.473085000
C	-0.291108000	2.496008000	-0.527321000
C	-0.229324000	3.705778000	0.189464000
C	-1.242626000	2.376233000	-1.555069000
C	-1.095153000	4.757476000	-0.101599000
H	0.501904000	3.807990000	0.986022000
C	-2.108637000	3.431568000	-1.842037000
H	-1.293672000	1.468625000	-2.143751000
C	-2.042252000	4.622713000	-1.118242000
H	-1.032914000	5.679770000	0.469886000
H	-2.834209000	3.321106000	-2.643433000
H	-2.721686000	5.439766000	-1.345298000
O	-1.200118000	-0.763329000	-1.664246000
C	0.686845000	0.314512000	2.842288000
H	0.056943000	0.281983000	3.734552000
H	1.533133000	-0.367867000	2.978810000
H	1.101192000	1.321533000	2.729384000
C	-3.237918000	-1.226376000	0.499084000
C	-3.970110000	-1.323399000	1.691555000
C	-3.830855000	-1.588415000	-0.720123000
C	-5.285631000	-1.779587000	1.658684000
H	-3.504194000	-1.042471000	2.626914000
C	-5.149478000	-2.042217000	-0.729258000
H	-3.266467000	-1.516014000	-1.638580000
C	-5.885079000	-2.141820000	0.451549000
H	-5.843164000	-1.850275000	2.588772000
H	-5.600619000	-2.321373000	-1.677655000
H	-6.911386000	-2.497227000	0.431958000
C	1.672011000	-1.243099000	-1.632244000
H	0.727834000	-1.489925000	-2.121249000
H	2.126772000	-0.389484000	-2.131799000
N	2.582765000	-2.414134000	-1.903388000
O	2.436447000	-3.424932000	-1.215956000
O	3.380906000	-2.297306000	-2.825100000
H	1.232264000	-1.992193000	0.320214000

Zero-point correction= 0.406138 (Hartree/Particle)
Thermal correction to Energy= 0.432146
Thermal correction to Enthalpy= 0.433090
Thermal correction to Gibbs Free Energy= 0.346223
Sum of electronic and zero-point Energies= -1392.137440
Sum of electronic and thermal Energies= -1392.111432
Sum of electronic and thermal Enthalpies= -1392.110487
Sum of electronic and thermal Free Energies= -1392.197355

CPCM (dichloromethane) M06/def2TZVP E = - 1392.0860012
CPCM (dichloromethane) M06L/def2TZVP E = - 1392.8866748

CPCM (dichloromethane) ROB3LYP/def2TZVP E = - 1393.0694862
CPCM (dichloromethane) ROB3LYP-d3/def2TZVP E = - 1393.1327463

[(cationic-8a)]



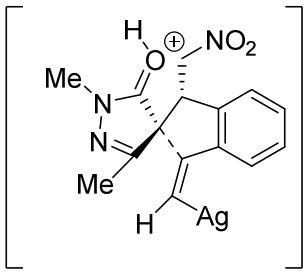
O	1.289029000	2.456402000	-1.608744000
O	3.371613000	1.939597000	-1.267483000
O	-0.931836000	2.980471000	-0.219087000
N	-2.321262000	1.310357000	0.569561000
N	-2.301144000	0.138167000	1.291578000
N	2.261662000	2.226420000	-0.868010000
C	-0.996028000	-0.066800000	1.591563000
C	-1.076210000	1.817925000	0.418475000
C	3.573221000	-2.550704000	-0.185002000
C	1.631697000	-1.092879000	-0.474621000
C	0.481412000	-0.866190000	-1.282095000
C	3.226410000	-0.661737000	1.285512000
C	2.403626000	-2.220340000	-0.854707000
C	3.985215000	-1.765959000	0.893203000
C	2.052793000	-0.290052000	0.624694000
C	1.333141000	0.967002000	1.143552000
C	2.033891000	2.255199000	0.621584000
C	-0.609135000	-1.227616000	2.462101000
C	-0.488400000	-0.861901000	-2.048861000
C	-0.172818000	0.937285000	1.033574000
C	-3.583554000	1.964673000	0.249239000
H	1.448369000	3.149304000	0.843291000
H	3.558427000	-0.074333000	2.138079000
H	4.891035000	-2.015325000	1.437442000
H	-0.114807000	-0.871589000	3.374253000
H	-4.282899000	1.224686000	-0.146155000
H	3.030777000	2.339875000	1.050044000
H	1.564080000	1.004103000	2.217642000
H	-3.390005000	2.733336000	-0.499068000
H	-1.503503000	-1.778327000	2.766747000
H	2.062807000	-2.821365000	-1.691401000
H	4.152251000	-3.414429000	-0.495045000
H	0.084570000	-1.917178000	1.969544000
H	-4.012838000	2.422306000	1.145053000
H	-0.927884000	-0.619954000	-3.000040000
Ag	-2.181276000	-1.384401000	-0.540118000
H	-0.117191000	2.941938000	-0.783490000

Zero-point correction= 0.283282 (Hartree/Particle)
Thermal correction to Energy= 0.304635
Thermal correction to Enthalpy= 0.305580
Thermal correction to Gibbs Free Energy= 0.231416
Sum of electronic and zero-point Energies= -1115.646024

Sum of electronic and thermal Energies= -1115.624670
Sum of electronic and thermal Enthalpies= -1115.623725
Sum of electronic and thermal Free Energies= -1115.697889

CPCM (dichloromethane) M06/def2TZVP E = - 1117.007912
CPCM (dichloromethane) M06L/def2TZVP E = - 1117.5991059
CPCM (dichloromethane) B3LYP/def2TZVP E = - 1117.6617265
CPCM (dichloromethane) B3LYP-d3/def2TZVP E = - 1117.7128399

[(cationic-9a)]



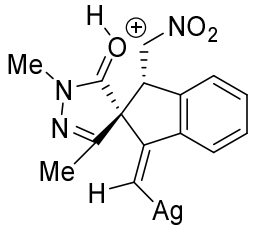
O	3.295982000	-1.436203000	-2.562830000
O	4.531579000	-0.387950000	-1.092600000
O	0.107714000	2.460351000	-1.831223000
N	-0.409173000	3.239314000	0.283310000
N	-0.191157000	3.012406000	1.617195000
N	3.497638000	-0.563222000	-1.731564000
C	0.666106000	2.007748000	1.672342000
C	0.298220000	2.400696000	-0.494015000
C	0.751881000	-3.411194000	1.594350000
C	0.211375000	-1.201079000	0.738807000
C	-0.790217000	-0.239575000	0.422113000
C	2.519687000	-1.895778000	0.916136000
C	-0.193342000	-2.443479000	1.279349000
C	2.109734000	-3.136028000	1.413341000
C	1.586453000	-0.919713000	0.565380000
C	2.024507000	0.452719000	0.046184000
C	2.369023000	0.403151000	-1.458791000
C	1.187181000	1.523686000	2.988797000
C	-1.927719000	0.259496000	0.189085000
C	0.994932000	1.517280000	0.353811000
C	-1.233302000	4.368403000	-0.128512000
H	1.537315000	0.072112000	-2.080415000
H	3.579185000	-1.684499000	0.812342000
H	2.855584000	-3.877930000	1.681403000
H	0.726325000	2.098810000	3.795015000
H	-2.225806000	4.280361000	0.319389000
H	2.756854000	1.371976000	-1.790683000
H	2.961119000	0.711672000	0.554582000
H	-1.309529000	4.369647000	-1.215571000
H	-2.334860000	1.257992000	0.276190000
H	0.975932000	0.460652000	3.149917000
H	-1.249733000	-2.632472000	1.445634000
H	0.433464000	-4.366021000	2.000468000
H	2.274795000	1.652870000	3.052965000
H	-0.770774000	5.297408000	0.214690000
H	0.925655000	2.269888000	-2.314445000

Ag	-3.369064000	-1.155522000	-0.591087000

Zero-point correction= 0.281362 (Hartree/Particle)
Thermal correction to Energy= 0.303107
Thermal correction to Enthalpy= 0.304051
Thermal correction to Gibbs Free Energy= 0.226679
Sum of electronic and zero-point Energies= -1115.606313
Sum of electronic and thermal Energies= -1115.584568
Sum of electronic and thermal Enthalpies= -1115.583624
Sum of electronic and thermal Free Energies= -1115.660996

CPCM (dichloromethane) M06/def2TZVP E = - 1116.9808214
CPCM (dichloromethane) M06L/def2TZVP E = - 1117.5734327
CPCM (dichloromethane) B3LYP/def2TZVP E = - 1117.6411274
CPCM (dichloromethane) B3LYP-d3/def2TZVP E = - 1117.6883673

[(cationic-10a)]



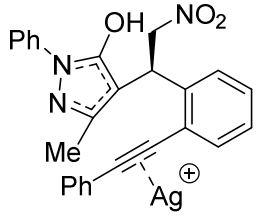
O	-4.060150000	0.949629000	-2.456603000
O	-3.879382000	0.032928000	-0.482119000
O	-1.513814000	-1.698342000	-1.422621000
N	-2.158839000	-2.109772000	0.737577000
N	-1.999367000	-1.602126000	2.053861000
N	-3.475536000	0.737738000	-1.410259000
C	-1.277176000	-0.536592000	1.956673000
C	-1.567738000	-1.364846000	-0.151597000
C	2.199163000	3.388087000	0.345831000
C	0.911388000	1.354124000	0.244120000
C	0.604237000	-0.090002000	0.207752000
C	-0.224799000	3.508745000	0.292735000
C	2.152985000	1.995254000	0.301633000
C	1.019067000	4.143020000	0.342197000
C	-0.265005000	2.116456000	0.245930000
C	-1.505096000	1.242833000	0.144025000
C	-2.124766000	1.406698000	-1.247035000
C	-0.868173000	0.240973000	3.159153000
C	1.384369000	-1.153904000	-0.044436000
C	-0.923937000	-0.191235000	0.514397000
C	-2.964275000	-3.309757000	0.545748000
H	-2.308360000	2.463340000	-1.453976000
H	-1.138925000	4.097292000	0.299793000
H	1.070281000	5.226385000	0.389514000
H	-1.276674000	-0.224438000	4.058321000
H	-4.013316000	-3.059625000	0.723709000
H	-1.503596000	1.028874000	-2.063557000
H	-2.270886000	1.518318000	0.874516000
H	-2.635528000	-4.062528000	1.263964000
H	0.224795000	0.275976000	3.233701000

H	3.071559000	1.415767000	0.334847000
H	3.159078000	3.892828000	0.399467000
H	-1.220870000	1.277229000	3.101127000
H	-2.830568000	-3.664617000	-0.476315000
H	0.936734000	-2.146259000	0.018530000
Ag	3.430922000	-1.207420000	-0.527270000
H	-0.755584000	-1.243542000	-1.842219000

Zero-point correction= 0.284794 (Hartree/Particle)
Thermal correction to Energy= 0.305538
Thermal correction to Enthalpy= 0.306482
Thermal correction to Gibbs Free Energy= 0.232981
Sum of electronic and zero-point Energies= -1115.638339
Sum of electronic and thermal Energies= -1115.617595
Sum of electronic and thermal Enthalpies= -1115.616651
Sum of electronic and thermal Free Energies= -1115.690152

CPCM (dichloromethane) M06/def2TZVP E = - 1116.9986335
CPCM (dichloromethane) M06L/def2TZVP E = - 1117.5867959
CPCM (dichloromethane) B3LYP/def2TZVP E = - 1117.6574334
CPCM (dichloromethane) B3LYP-d3/def2TZVP E = - 1117.7059973

[(cationic-8b)]



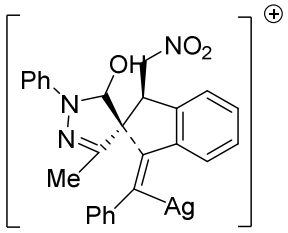
C	-1.438807000	-2.257898000	2.385617000
C	-5.899507000	3.529897000	0.413014000
C	-3.054798000	0.409835000	0.763954000
C	-5.094180000	1.552746000	1.552717000
C	-4.025682000	1.464887000	0.637859000
C	-0.508680000	-3.206395000	2.788398000
C	0.187479000	-1.286748000	0.824110000
C	-1.112326000	-1.300356000	1.398897000
C	1.953872000	0.396598000	0.062674000
C	3.219599000	-0.067975000	-0.253875000
C	1.098436000	-2.260832000	1.244420000
C	-2.142330000	-0.380472000	1.018052000
C	6.195653000	1.995818000	-0.377669000
C	0.594488000	-0.791885000	-1.672613000
C	0.612659000	-0.233362000	-0.206569000
C	0.760673000	-3.214169000	2.204952000
C	-4.842094000	3.446405000	-0.497649000
C	-6.021407000	2.584572000	1.435939000
C	5.537874000	0.825388000	0.015164000
C	-3.906896000	2.420473000	-0.392749000
C	6.255058000	-0.359071000	0.232701000
C	8.297202000	0.786542000	-0.382104000
C	7.635990000	-0.374225000	0.018165000
C	7.575609000	1.970630000	-0.565657000

O	3.541967000	-1.209585000	-0.909391000
O	-1.311182000	-2.161213000	-1.762274000
O	-1.513071000	-0.100695000	-2.417758000
N	-0.829870000	-1.051116000	-2.029458000
N	4.125982000	0.845587000	0.192257000
N	3.498214000	1.920339000	0.770533000
C	1.202373000	2.608962000	1.271664000
C	2.202561000	1.650212000	0.701967000
H	0.955043000	-0.039369000	-2.371938000
H	-2.430629000	-2.239898000	2.826676000
H	2.095160000	-2.272894000	0.816051000
H	-0.124877000	0.576221000	-0.188110000
H	5.754813000	-1.241080000	0.623513000
H	-6.839547000	2.653082000	2.146378000
H	1.136528000	-1.730418000	-1.769402000
H	-0.771112000	-3.934979000	3.548968000
H	-6.626095000	4.332203000	0.327578000
H	1.493934000	-3.956582000	2.505277000
H	-5.181568000	0.820311000	2.349210000
H	-3.078352000	2.356246000	-1.092313000
H	5.621295000	2.904359000	-0.518717000
H	9.371503000	0.774349000	-0.538426000
H	8.193353000	-1.290192000	0.190121000
H	-4.744222000	4.183664000	-1.288670000
H	0.625032000	2.154379000	2.085972000
H	1.722886000	3.483482000	1.669070000
H	0.489227000	2.952441000	0.511374000
H	8.089721000	2.879177000	-0.864814000
H	4.485438000	-1.190145000	-1.157680000
Ag	-3.515669000	-1.188586000	-1.050135000

Zero-point correction= 0.417012 (Hartree/Particle)
Thermal correction to Energy= 0.446901
Thermal correction to Enthalpy= 0.447845
Thermal correction to Gibbs Free Energy= 0.350766
Sum of electronic and zero-point Energies= -1538.311420
Sum of electronic and thermal Energies= -1538.281531
Sum of electronic and thermal Enthalpies= -1538.280586
Sum of electronic and thermal Free Energies= -1538.377666

CPCM (dichloromethane) M06/def2TZVP E = - 1539.6176797
CPCM (dichloromethane) M06L/def2TZVP E = - 1540.4872325
CPCM (dichloromethane) B3LYP/def2TZVP E = - 1540.6125072
CPCM (dichloromethane) B3LYP-d3/def2TZVP E = - 1540.6776084

[(cationic-TS-9b)]



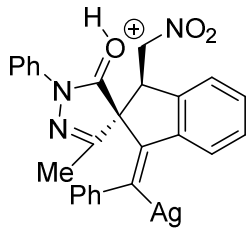
C	-2.782950000	1.255922000	-1.919104000
C	0.602521000	-4.604193000	1.462862000
C	-1.436263000	-1.123392000	0.090851000
C	0.262872000	-2.898874000	-0.222471000
C	-0.731012000	-2.304383000	0.576730000
C	-3.278855000	2.428576000	-2.482378000
C	-1.420467000	2.560373000	-0.369779000
C	-1.868470000	1.307644000	-0.849434000
C	0.484297000	1.301078000	0.613386000
C	1.360231000	1.087788000	-0.482544000
C	-1.927637000	3.726867000	-0.947550000
C	-1.371721000	0.103797000	-0.224896000
C	3.882623000	-1.620496000	-0.397317000
C	0.403332000	3.822903000	0.888595000
C	-0.407698000	2.514130000	0.774029000
C	-2.854890000	3.664718000	-1.992602000
C	-0.387017000	-4.020191000	2.258615000
C	0.922943000	-4.041633000	0.224427000
C	3.356224000	-0.407447000	-0.859966000
C	-1.059980000	-2.883255000	1.817014000
C	3.880848000	0.210185000	-2.002052000
C	5.451425000	-1.622401000	-2.243395000
C	4.924161000	-0.409675000	-2.689622000
C	4.929903000	-2.219627000	-1.093702000
O	1.344737000	1.621473000	-1.712093000
O	0.747874000	3.645238000	3.180909000
O	2.513541000	3.801644000	1.897459000
N	1.307700000	3.755890000	2.091743000
N	2.291091000	0.190044000	-0.115036000
N	2.099995000	-0.195879000	1.206863000
C	0.602591000	0.315279000	3.065960000
C	1.060163000	0.471285000	1.649867000
H	1.046315000	4.002748000	0.026910000
H	-3.086244000	0.289640000	-2.315040000
H	-1.606605000	4.700831000	-0.593816000
H	-0.955700000	2.407530000	1.719278000
H	3.497890000	1.161611000	-2.345592000
H	1.691269000	-4.491126000	-0.397470000
H	-0.246088000	4.681726000	1.068940000
H	-3.981333000	2.376813000	-3.308280000
H	1.118479000	-5.496079000	1.805202000
H	-3.232260000	4.583638000	-2.430303000
H	0.515163000	-2.461554000	-1.183402000
H	-1.831152000	-2.431901000	2.435918000
H	3.479756000	-2.067029000	0.502638000
H	6.268278000	-2.093281000	-2.781780000
H	5.333087000	0.070956000	-3.573278000
H	-0.638429000	-4.452814000	3.222286000

H	1.175982000	-0.480575000	3.546195000
H	0.747833000	1.241707000	3.631898000
H	-0.462388000	0.060775000	3.113245000
H	5.342243000	-3.156436000	-0.730557000
Ag	-3.553417000	-1.681749000	-0.354507000
H	0.510724000	2.107939000	-1.839500000

Zero-point correction= 0.416147 (Hartree/Particle)
Thermal correction to Energy= 0.445366
Thermal correction to Enthalpy= 0.446310
Thermal correction to Gibbs Free Energy= 0.350802
Sum of electronic and zero-point Energies= -1538.265866
Sum of electronic and thermal Energies= -1538.236647
Sum of electronic and thermal Enthalpies= -1538.235703
Sum of electronic and thermal Free Energies= -1538.331211

CPCM (dichloromethane) M06/def2TZVP E = - 1539.5930317
CPCM (dichloromethane) M06L/def2TZVP E = - 1540.462361
CPCM (dichloromethane) B3LYP/def2TZVP E = - 1540.5837117
CPCM (dichloromethane) B3LYP-d3/def2TZVP E = - 1540.6567148

[(cationic-10b)]



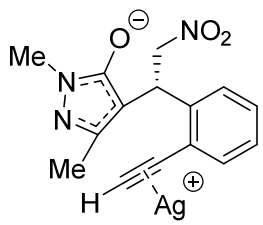
C	-3.008294000	1.780849000	-1.373637000
C	0.396963000	-4.453687000	0.950223000
C	-1.814993000	-0.886374000	0.051378000
C	-0.065799000	-2.575412000	-0.502288000
C	-1.053343000	-2.103036000	0.384938000
C	-3.417295000	3.071512000	-1.712266000
C	-1.207017000	2.735239000	-0.063722000
C	-1.908247000	1.605751000	-0.523486000
C	0.132231000	0.785322000	0.480073000
C	1.141146000	0.596874000	-0.610064000
C	-1.616768000	4.024997000	-0.395830000
C	-1.300262000	0.353654000	-0.015899000
C	4.536301000	-0.573328000	-0.037393000
C	1.169408000	3.221642000	0.717025000
C	-0.063286000	2.320018000	0.844029000
C	-2.732597000	4.188807000	-1.222394000
C	-0.595562000	-4.009078000	1.830205000
C	0.652073000	-3.737955000	-0.220610000
C	3.372591000	-0.497994000	-0.809050000
C	-1.324935000	-2.858101000	1.543682000
C	3.372709000	-0.812971000	-2.171911000
C	5.743941000	-1.279582000	-2.013593000
C	4.570835000	-1.203485000	-2.767908000
C	5.723101000	-0.965408000	-0.652418000

O	1.067368000	1.050770000	-1.844488000
O	1.927438000	2.813979000	2.885835000
O	3.355204000	2.571900000	1.246118000
N	2.249402000	2.835404000	1.701409000
N	2.164091000	-0.088348000	-0.157366000
N	1.986929000	-0.437599000	1.214478000
C	0.345223000	-0.140163000	2.978994000
C	0.831562000	0.009523000	1.576709000
H	1.630341000	3.207648000	-0.270466000
H	-3.525922000	0.920278000	-1.788192000
H	-1.090163000	4.899165000	-0.023361000
H	-0.387052000	2.356267000	1.891317000
H	2.463050000	-0.763164000	-2.757995000
H	1.405952000	-4.087822000	-0.920116000
H	0.900118000	4.247533000	0.979077000
H	-4.265754000	3.208440000	-2.376010000
H	0.953647000	-5.359878000	1.168980000
H	-3.058091000	5.187584000	-1.496088000
H	0.111669000	-2.042986000	-1.433448000
H	-2.111092000	-2.532263000	2.220649000
H	4.504107000	-0.322610000	1.015776000
H	6.672606000	-1.584811000	-2.485900000
H	4.582835000	-1.453811000	-3.824091000
H	-0.809005000	-4.569076000	2.736222000
H	0.871561000	-0.962551000	3.467532000
H	0.546836000	0.778893000	3.542592000
H	-0.730630000	-0.330057000	2.999518000
H	6.633468000	-1.022423000	-0.064170000
Ag	-3.880575000	-1.287677000	-0.336296000
H	0.207392000	1.501420000	-1.974014000

Zero-point correction= 0.418592 (Hartree/Particle)
Thermal correction to Energy= 0.447179
Thermal correction to Enthalpy= 0.448124
Thermal correction to Gibbs Free Energy= 0.356071
Sum of electronic and zero-point Energies= -1538.290008
Sum of electronic and thermal Energies= -1538.261420
Sum of electronic and thermal Enthalpies= -1538.260476
Sum of electronic and thermal Free Energies= -1538.352528

CPCM (dichloromethane) M06/def2TZVP E = - 1539.6055944
CPCM (dichloromethane) M06L/def2TZVP E = - 1540.4702875
CPCM (dichloromethane) B3LYP/def2TZVP E = - 1540.5910602
CPCM (dichloromethane) B3LYP-d3/def2TZVP E = - 1540.6690051

[(neutral-8a)]

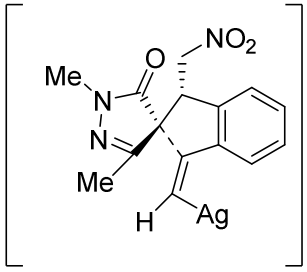


O	4.065058000	1.981467000	0.743951000
O	4.234448000	1.666269000	-1.406314000
O	-0.477668000	2.909546000	-0.910984000
N	-2.121600000	1.804777000	0.314110000
N	-2.242435000	0.768161000	1.222453000
N	3.584111000	1.799280000	-0.375362000
C	-0.943748000	0.362053000	1.445118000
C	-0.807965000	2.037971000	-0.088247000
C	2.821464000	-3.246287000	-0.151596000
C	1.186563000	-1.484635000	-0.589440000
C	0.005517000	-1.159541000	-1.323322000
C	3.009329000	-1.098174000	0.944194000
C	1.679958000	-2.793997000	-0.800635000
C	3.486811000	-2.392078000	0.728176000
C	1.866501000	-0.608884000	0.301774000
C	1.452871000	0.845057000	0.569433000
C	2.082140000	1.775951000	-0.493940000
C	-0.693546000	-0.694357000	2.484863000
C	-1.028033000	-1.101811000	-1.990706000
C	-0.036933000	1.061659000	0.662661000
C	-3.275959000	2.536552000	-0.135619000
H	1.864982000	1.474822000	-1.516365000
H	3.542191000	-0.441224000	1.624569000
H	4.376278000	-2.729964000	1.252426000
H	-1.642796000	-1.007753000	2.931009000
H	-3.818026000	2.974463000	0.709179000
H	1.743570000	2.803598000	-0.355217000
H	1.926919000	1.128768000	1.517576000
H	-3.966778000	1.888541000	-0.696810000
H	-0.184842000	-1.576511000	2.081079000
H	1.144725000	-3.443594000	-1.486170000
H	3.183309000	-4.254952000	-0.326711000
H	-0.058896000	-0.300218000	3.288730000
H	-2.909058000	3.326281000	-0.794545000
H	-1.595284000	-0.961347000	-2.889426000
Ag	-2.671305000	-0.982586000	-0.218239000

Zero-point correction= 0.269554 (Hartree/Particle)
Thermal correction to Energy= 0.291182
Thermal correction to Enthalpy= 0.292126
Thermal correction to Gibbs Free Energy= 0.216447
Sum of electronic and zero-point Energies= -1115.251577
Sum of electronic and thermal Energies= -1115.229949
Sum of electronic and thermal Enthalpies= -1115.229005
Sum of electronic and thermal Free Energies= -1115.304684

CPCM (dichloromethane) M06/def2TZVP E = - 1116.5592186
CPCM (dichloromethane) M06L/def2TZVP E = - 1117.1468242
CPCM (dichloromethane) B3LYP/def2TZVP E = - 1117.2120653
CPCM (dichloromethane) B3LYP-d3/def2TZVP E = - 1117.2606859

[(neutral-TS-9a)]

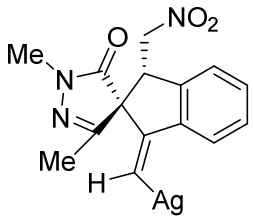


O	4.821885000	-1.034124000	0.091107000
O	4.092396000	-0.487378000	-1.891100000
O	1.382392000	-0.259555000	2.341312000
N	0.555148000	-2.206141000	1.325271000
N	0.452323000	-2.723282000	0.058914000
N	4.137871000	-0.359835000	-0.667296000
C	0.903862000	-1.785838000	-0.778897000
C	1.089255000	-0.917849000	1.337830000
C	-0.522133000	4.115781000	0.642362000
C	-0.345057000	1.733414000	0.126258000
C	-1.058408000	0.501604000	-0.028966000
C	1.589696000	3.165729000	-0.043400000
C	-1.101159000	2.857832000	0.527403000
C	0.830616000	4.270542000	0.345068000
C	1.037318000	1.886485000	-0.147683000
C	1.853381000	0.665855000	-0.574473000
C	3.308538000	0.747344000	-0.063597000
C	0.913645000	-2.041412000	-2.255160000
C	-1.685370000	-0.581023000	-0.165279000
C	1.209844000	-0.594565000	-0.089372000
C	0.302784000	-3.026087000	2.485881000
H	3.816611000	1.660774000	-0.381348000
H	2.642355000	3.316358000	-0.258184000
H	1.303544000	5.245104000	0.425622000
H	0.648465000	-3.084407000	-2.448862000
H	0.960358000	-3.902513000	2.498332000
H	3.359883000	0.630891000	1.017721000
H	1.900285000	0.647202000	-1.670932000
H	-0.739282000	-3.364612000	2.507035000
H	0.194361000	-1.398047000	-2.779963000
H	-2.156302000	2.724330000	0.748289000
H	-1.121070000	4.964013000	0.960157000
H	1.903828000	-1.846832000	-2.682147000
H	0.504376000	-2.405661000	3.361743000
H	-1.421558000	-1.641603000	-0.188345000
Ag	-3.832925000	-0.345928000	-0.390760000

Zero-point correction= 0.269105 (Hartree/Particle)
Thermal correction to Energy= 0.290012
Thermal correction to Enthalpy= 0.290957
Thermal correction to Gibbs Free Energy= 0.216254
Sum of electronic and zero-point Energies= -1115.220605
Sum of electronic and thermal Energies= -1115.199697
Sum of electronic and thermal Enthalpies= -1115.198753
Sum of electronic and thermal Free Energies= -1115.273456

CPCM (dichloromethane) M06/def2TZVP E = - 1116.5315079
CPCM (dichloromethane) M06L/def2TZVP E = - 1117.1217765
CPCM (dichloromethane) B3LYP/def2TZVP E = - 1117.1905045
CPCM (dichloromethane) B3LYP-d3/def2TZVP E = - 1117.2357831

[(neutral-10a)]



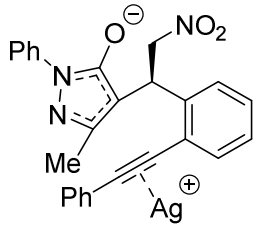
O	-4.446339000	1.064018000	-1.971187000
O	-4.049813000	0.100851000	-0.055383000
O	-1.624015000	-1.432644000	-1.656604000
N	-1.909259000	-2.355274000	0.447715000
N	-1.694630000	-2.013489000	1.783952000
N	-3.724114000	0.786800000	-1.022539000
C	-1.139312000	-0.851724000	1.814107000
C	-1.518413000	-1.387968000	-0.437776000
C	2.060752000	3.473187000	0.285417000
C	0.863778000	1.378279000	0.203830000
C	0.615219000	-0.075801000	0.151636000
C	-0.362163000	3.476675000	0.345306000
C	2.073721000	2.081251000	0.215358000
C	0.848714000	4.172296000	0.350798000
C	-0.345806000	2.084212000	0.273330000
C	-1.544401000	1.152712000	0.239155000
C	-2.322330000	1.354266000	-1.065459000
C	-0.748276000	-0.204534000	3.102005000
C	1.454310000	-1.095035000	-0.067596000
C	-0.904761000	-0.272502000	0.428562000
C	-2.639594000	-3.558744000	0.122783000
H	-2.459594000	2.413470000	-1.292248000
H	-1.303567000	4.018737000	0.403708000
H	0.850705000	5.256905000	0.413557000
H	-1.032716000	-0.847470000	3.938710000
H	-3.655684000	-3.514569000	0.529518000
H	-1.849275000	0.862598000	-1.917122000
H	-2.231234000	1.361795000	1.065597000
H	-2.128183000	-4.438046000	0.527262000
H	0.334133000	-0.030295000	3.137634000
H	3.018867000	1.544575000	0.184265000
H	2.999579000	4.020477000	0.299963000
H	-1.235976000	0.770711000	3.226882000
H	-2.684236000	-3.623054000	-0.965932000
H	1.060905000	-2.109438000	-0.062362000
Ag	3.494149000	-1.038934000	-0.516099000

Zero-point correction= 0.272594 (Hartree/Particle)
Thermal correction to Energy= 0.293109

Thermal correction to Enthalpy= 0.294054
Thermal correction to Gibbs Free Energy= 0.220185
Sum of electronic and zero-point Energies= -1115.288601
Sum of electronic and thermal Energies= -1115.268085
Sum of electronic and thermal Enthalpies= -1115.267141
Sum of electronic and thermal Free Energies= -1115.341010

CPCM (dichloromethane) M06/def2TZVP E = - 1116.5909064
CPCM (dichloromethane) M06L/def2TZVP E = - 1117.1750856
CPCM (dichloromethane) B3LYP/def2TZVP E = - 1117.2479789
CPCM (dichloromethane) B3LYP-d3/def2TZVP E = - 1117.294276

[(neutral -8b)]



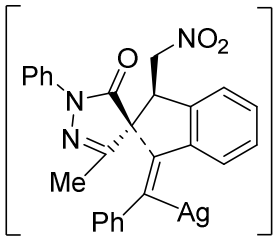
C	3.331041000	1.878234000	1.552023000
C	-3.762005000	3.719994000	0.588512000
C	0.067845000	1.911090000	0.627051000
C	-2.368849000	1.775535000	0.954040000
C	-1.226896000	2.528958000	0.614628000
C	4.648093000	1.596865000	1.889389000
C	2.954988000	-0.442855000	0.876538000
C	2.469101000	0.878667000	1.045469000
C	0.686833000	-1.722132000	0.651501000
C	-0.409867000	-1.611056000	-0.224913000
C	4.288797000	-0.693320000	1.232526000
C	1.135747000	1.314795000	0.744020000
C	-3.306751000	-1.792136000	-1.155280000
C	2.431050000	-1.951559000	-1.192172000
C	2.157843000	-1.646440000	0.336509000
C	5.132673000	0.298520000	1.726031000
C	-2.632132000	4.475221000	0.260072000
C	-3.626238000	2.373161000	0.935779000
C	-2.902070000	-1.844573000	0.189199000
C	-1.369754000	3.887897000	0.269545000
C	-3.874305000	-1.872625000	1.204289000
C	-5.636371000	-1.776206000	-0.460479000
C	-5.227533000	-1.839380000	0.874143000
C	-4.667124000	-1.755221000	-1.464281000
O	-0.464160000	-1.310292000	-1.491291000
O	4.431154000	-1.155890000	-2.106851000
O	2.714739000	0.163017000	-2.207446000
N	3.256625000	-0.910315000	-1.886739000
N	-1.535898000	-1.871975000	0.554299000
N	-1.199307000	-2.129758000	1.867926000
C	0.836601000	-2.301811000	3.207069000
C	0.121523000	-2.047050000	1.914309000
H	3.001082000	-2.870727000	-1.309509000
H	2.937042000	2.882046000	1.676071000

H	4.674232000	-1.703211000	1.115342000
H	2.623608000	-2.497379000	0.849500000
H	-3.548861000	-1.933074000	2.235236000
H	-4.499059000	1.778026000	1.187328000
H	1.485620000	-1.994173000	-1.737894000
H	5.287982000	2.382930000	2.279448000
H	-4.745584000	4.181211000	0.573225000
H	6.159432000	0.056394000	1.984919000
H	-2.259135000	0.732281000	1.228209000
H	-0.489052000	4.469769000	0.013498000
H	-2.557123000	-1.783591000	-1.934463000
H	-6.692930000	-1.750856000	-0.713065000
H	-5.967142000	-1.866909000	1.670751000
H	-2.735171000	5.523489000	-0.006070000
H	1.542036000	-3.139800000	3.120944000
H	1.414233000	-1.427753000	3.533323000
H	0.109560000	-2.547985000	3.985710000
H	-4.967019000	-1.717439000	-2.508731000
Ag	0.353383000	0.765553000	-1.653629000

Zero-point correction= 0.405249 (Hartree/Particle)
Thermal correction to Energy= 0.434273
Thermal correction to Enthalpy= 0.435217
Thermal correction to Gibbs Free Energy= 0.341662
Sum of electronic and zero-point Energies= -1537.927612
Sum of electronic and thermal Energies= -1537.898587
Sum of electronic and thermal Enthalpies= -1537.897643
Sum of electronic and thermal Free Energies= -1537.991199

CPCM (dichloromethane) M06/def2TZVP E = - 1539.1799649
CPCM (dichloromethane) M06L/def2TZVP E = - 1540.0475638
CPCM (dichloromethane) B3LYP/def2TZVP E = - 1540.1675198
CPCM (dichloromethane) B3LYP-d3/def2TZVP E = - 1540.2389857

[(neutral –TS-9b)]



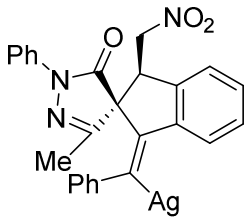
C	2.537695000	-1.665453000	-2.118402000
C	0.064481000	4.684990000	1.714161000
C	1.418319000	1.027641000	0.084414000
C	-0.247064000	2.818484000	0.206471000
C	0.976848000	2.268287000	0.637919000
C	2.597135000	-2.953536000	-2.637408000
C	1.076212000	-2.415448000	-0.301165000
C	1.793067000	-1.381972000	-0.959508000
C	-0.815188000	-1.095459000	0.747794000
C	-1.673871000	-1.108983000	-0.422204000
C	1.144511000	-3.697563000	-0.853438000

C	1.718466000	-0.031673000	-0.473824000
C	-4.563967000	1.346500000	-0.461512000
C	-0.263157000	-3.399897000	1.618420000
C	0.282988000	-2.101586000	0.973360000
C	1.892836000	-3.971951000	-1.999197000
C	1.280232000	4.144368000	2.146816000
C	-0.695742000	4.020345000	0.749813000
C	-3.670868000	0.391912000	-0.977260000
C	1.734558000	2.939946000	1.619679000
C	-3.843888000	-0.087967000	-2.286622000
C	-5.790372000	1.342481000	-2.553875000
C	-4.901819000	0.391639000	-3.058546000
C	-5.611658000	1.813827000	-1.250828000
O	-1.656152000	-1.844911000	-1.416474000
O	0.073913000	-2.716670000	3.818598000
O	-1.954531000	-3.274984000	3.235212000
N	-0.762673000	-3.111131000	3.005920000
N	-2.603581000	-0.059857000	-0.168109000
N	-2.398523000	0.505066000	1.057088000
C	-0.908486000	0.294450000	2.980241000
C	-1.349878000	-0.120526000	1.607815000
H	-1.103439000	-3.816637000	1.065141000
H	3.057670000	-0.851113000	-2.618395000
H	0.587402000	-4.511259000	-0.403752000
H	0.989240000	-1.687109000	1.704753000
H	-3.160202000	-0.830073000	-2.675498000
H	-1.644196000	4.433021000	0.419862000
H	0.527510000	-4.141552000	1.755866000
H	3.174211000	-3.153955000	-3.534971000
H	-0.289576000	5.623135000	2.132209000
H	1.911286000	-4.982989000	-2.395996000
H	-0.835324000	2.296655000	-0.539327000
H	2.670052000	2.506796000	1.962051000
H	-4.423981000	1.702067000	0.551639000
H	-6.611249000	1.708805000	-3.164265000
H	-5.027686000	0.012273000	-4.069559000
H	1.870021000	4.659989000	2.899100000
H	-1.377061000	1.248566000	3.235773000
H	-1.192816000	-0.442432000	3.739351000
H	0.179638000	0.412990000	3.036046000
H	-6.297142000	2.550285000	-0.838630000
Ag	3.841594000	1.231902000	-0.915385000

Zero-point correction= 0.403343 (Hartree/Particle)
Thermal correction to Energy= 0.432512
Thermal correction to Enthalpy= 0.433456
Thermal correction to Gibbs Free Energy= 0.337140
Sum of electronic and zero-point Energies= -1537.871091
Sum of electronic and thermal Energies= -1537.841922
Sum of electronic and thermal Enthalpies= -1537.840978
Sum of electronic and thermal Free Energies= -1537.937294

CPCM (dichloromethane) M06/def2TZVP E = - 1539.155532
CPCM (dichloromethane) M06L/def2TZVP E = - 1540.0209546
CPCM (dichloromethane) B3LYP/def2TZVP E = - 1540.1420325
CPCM (dichloromethane) B3LYP-d3/def2TZVP E = - 1540.2115123

[(neutral-10b)]



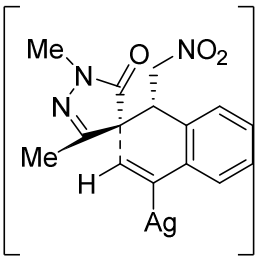
C	-3.376390000	1.398913000	-1.184966000
C	1.045934000	-4.309651000	0.732761000
C	-1.648043000	-1.035984000	0.042635000
C	0.284708000	-2.462983000	-0.635434000
C	-0.717652000	-2.148845000	0.304067000
C	-4.014109000	2.604476000	-1.477577000
C	-1.611655000	2.627761000	-0.082935000
C	-2.179622000	1.402217000	-0.459362000
C	0.028067000	0.894004000	0.418897000
C	1.098390000	0.721334000	-0.677226000
C	-2.248773000	3.833439000	-0.365958000
C	-1.333957000	0.270860000	-0.023158000
C	4.329140000	-0.980269000	0.212858000
C	0.763832000	3.426379000	0.287430000
C	-0.315484000	2.415943000	0.673325000
C	-3.460257000	3.819273000	-1.062543000
C	0.043879000	-4.021732000	1.665600000
C	1.157499000	-3.529777000	-0.419195000
C	3.406621000	-0.310265000	-0.605378000
C	-0.834998000	-2.964713000	1.447561000
C	3.711728000	-0.069011000	-1.954576000
C	5.857302000	-1.169880000	-1.660653000
C	4.934364000	-0.502907000	-2.466979000
C	5.544867000	-1.403167000	-0.319953000
O	1.016744000	1.073424000	-1.845289000
O	1.702557000	3.249240000	2.439135000
O	3.036401000	3.683537000	0.768438000
N	1.937295000	3.436430000	1.246512000
N	2.171920000	0.113889000	-0.049415000
N	1.920795000	-0.152050000	1.305067000
C	0.191012000	0.138707000	2.978395000
C	0.733833000	0.251228000	1.591413000
H	1.178510000	3.267415000	-0.706650000
H	-3.792977000	0.465143000	-1.553581000
H	-1.818337000	4.782462000	-0.056003000
H	-0.498651000	2.545408000	1.746357000
H	3.000816000	0.449600000	-2.582239000
H	1.928324000	-3.747399000	-1.153322000
H	0.369099000	4.444827000	0.349429000
H	-4.938348000	2.598765000	-2.049129000
H	1.726207000	-5.140106000	0.900069000
H	-3.960665000	4.754538000	-1.297127000
H	0.369579000	-1.867449000	-1.539691000
H	-1.624558000	-2.757147000	2.166192000
H	4.084367000	-1.158968000	1.251627000
H	6.807597000	-1.501207000	-2.069889000
H	5.162492000	-0.310722000	-3.512125000

H	-0.055186000	-4.627731000	2.562631000
H	0.835739000	-0.511376000	3.574482000
H	0.155979000	1.123520000	3.460667000
H	-0.824886000	-0.269438000	2.966700000
H	6.252404000	-1.919086000	0.323898000
Ag	-3.637332000	-1.741077000	-0.275532000

Zero-point correction= 0.406390 (Hartree/Particle)
Thermal correction to Energy= 0.434689
Thermal correction to Enthalpy= 0.435633
Thermal correction to Gibbs Free Energy= 0.342883
Sum of electronic and zero-point Energies= -1537.935862
Sum of electronic and thermal Energies= -1537.907563
Sum of electronic and thermal Enthalpies= -1537.906619
Sum of electronic and thermal Free Energies= -1537.999369

CPCM (dichloromethane) M06/def2TZVP E = - 1539.1997864
CPCM (dichloromethane) M06L/def2TZVP E = - 1540.0601275
CPCM (dichloromethane) B3LYP/def2TZVP E = - 1540.183928
CPCM (dichloromethane) B3LYP-d3/def2TZVP E = - 1540.2582085

[(endo-neutral-TS-9b)]



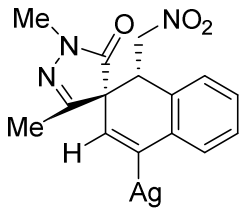
C	1.411023000	1.191239000	-0.405245000
C	1.293294000	0.059989000	0.061126000
C	0.678877000	-1.111125000	0.616244000
C	-0.719364000	-1.284799000	0.434102000
C	-1.507058000	-0.308109000	-0.449746000
C	-1.323639000	1.142758000	-0.089220000
H	2.492709000	-1.847603000	1.507944000
H	1.531916000	2.196984000	-0.746841000
C	1.427813000	-2.022433000	1.375634000
C	-1.305916000	-2.397151000	1.043577000
C	-0.555806000	-3.303709000	1.797244000
C	0.815180000	-3.121860000	1.966365000
H	-2.368357000	-2.582492000	0.939289000
H	-1.054496000	-4.154131000	2.253268000
H	1.399808000	-3.821556000	2.555630000
H	-1.151212000	-0.445485000	-1.480025000
C	-3.021877000	-0.595650000	-0.495710000
N	-3.370272000	-1.859390000	-1.256578000
O	-4.188036000	-2.621866000	-0.748104000
O	-2.833651000	-2.018506000	-2.348919000
C	-1.300815000	1.678584000	1.266872000
O	-1.325834000	1.121652000	2.371912000
N	-1.250767000	3.066928000	1.058936000
N	-1.331771000	3.413033000	-0.254281000

C	-1.390858000	2.267259000	-0.941949000
C	-1.274049000	4.067154000	2.099561000
H	-2.192918000	4.662626000	2.051892000
H	-1.232321000	3.534754000	3.052164000
H	-0.413343000	4.739620000	2.013970000
C	-1.472990000	2.302909000	-2.439730000
H	-1.493103000	3.342357000	-2.778770000
H	-0.615889000	1.801566000	-2.910199000
H	-2.374997000	1.804171000	-2.817789000
H	-3.475502000	-0.682325000	0.490628000
H	-3.519757000	0.198782000	-1.055739000
Ag	3.667966000	-0.092167000	-0.620124000

Zero-point correction= 0.268192 (Hartree/Particle)
Thermal correction to Energy= 0.289826
Thermal correction to Enthalpy= 0.290770
Thermal correction to Gibbs Free Energy= 0.213605
Sum of electronic and zero-point Energies= -1115.206153
Sum of electronic and thermal Energies= -1115.184520
Sum of electronic and thermal Enthalpies= -1115.183576
Sum of electronic and thermal Free Energies= -1115.260740

CPCM (dichloromethane) M06/def2TZVP E = - 1116.5278269
CPCM (dichloromethane) M06L/def2TZVP E = - 1117.1148129
CPCM (dichloromethane) B3LYP/def2TZVP E = - 1117.1835713
CPCM (dichloromethane) B3LYP-d3/def2TZVP E = - 1117.2285095

[(endo-10b)]



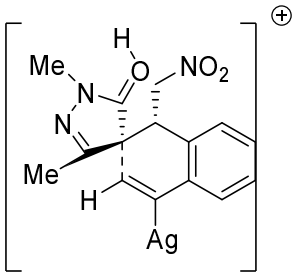
C	-0.640195000	-1.179011000	-0.334682000
C	-1.539922000	-0.201121000	-0.147382000
C	-1.131172000	1.144203000	0.286651000
C	0.237691000	1.509310000	0.221231000
C	1.221096000	0.525486000	-0.403907000
C	0.855922000	-0.955488000	-0.106680000
H	-3.099619000	1.787808000	0.843176000
H	-0.928503000	-2.191010000	-0.602534000
C	-2.050697000	2.073219000	0.789615000
C	0.627827000	2.778003000	0.651416000
C	-0.305756000	3.688958000	1.156646000
C	-1.650074000	3.334900000	1.227410000
H	1.668245000	3.082789000	0.598331000
H	0.025568000	4.669025000	1.487978000
H	-2.384753000	4.033837000	1.617560000
H	1.138292000	0.630278000	-1.494764000
C	2.694443000	0.791113000	-0.053596000
N	3.323711000	1.822508000	-0.964105000
O	3.943315000	2.742938000	-0.440773000

O	3.203477000	1.645265000	-2.174011000
C	1.241513000	-1.405643000	1.327742000
O	0.914517000	-0.920977000	2.397314000
N	2.057952000	-2.498640000	1.140967000
N	2.314323000	-2.790998000	-0.197898000
C	1.676586000	-1.937132000	-0.925504000
C	2.669632000	-3.292089000	2.182505000
H	3.762236000	-3.237777000	2.123983000
H	2.331727000	-2.881512000	3.135995000
H	2.361230000	-4.339702000	2.100759000
C	1.757108000	-1.961301000	-2.417733000
H	2.353548000	-2.817489000	-2.743081000
H	0.757858000	-2.028763000	-2.865870000
H	2.220561000	-1.043284000	-2.802307000
H	2.842163000	1.141364000	0.966478000
H	3.298830000	-0.104271000	-0.225801000
Ag	-3.589229000	-0.630843000	-0.446283000

Zero-point correction= 0.273450 (Hartree/Particle)
Thermal correction to Energy= 0.293802
Thermal correction to Enthalpy= 0.294747
Thermal correction to Gibbs Free Energy= 0.222123
Sum of electronic and zero-point Energies= -1115.286585
Sum of electronic and thermal Energies= -1115.266233
Sum of electronic and thermal Enthalpies= -1115.265289
Sum of electronic and thermal Free Energies= -1115.337912

CPCM (dichloromethane) M06/def2TZVP E = - 1116.589173
CPCM (dichloromethane) M06L/def2TZVP E = - 1117.1717061
CPCM (dichloromethane) B3LYP/def2TZVP E = - 1117.2463036
CPCM (dichloromethane) B3LYP-d3/def2TZVP E = - 1117.2917055

[(endo-cationic-TS-9b)]



C	1.180842000	1.291526000	-0.399426000
C	1.383115000	0.170716000	0.105049000
C	0.813926000	-0.993956000	0.744813000
C	-0.561707000	-1.277447000	0.507303000
C	-1.354348000	-0.441880000	-0.508208000
C	-1.436228000	1.024181000	-0.142248000
H	2.616874000	-1.532421000	1.796277000
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C	1.571202000	-1.778003000	1.627192000
C	-1.121465000	-2.350749000	1.211414000
C	-0.361861000	-3.123348000	2.099064000
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H	-0.833433000	-3.952624000	2.617169000
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H	-0.818304000	-0.513973000	-1.462670000
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C	-1.597862000	2.146870000	-1.024719000
C	-1.910479000	3.936845000	2.004178000
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H	-0.733819000	1.639054000	-2.946586000
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H	-3.401889000	-1.083621000	0.075003000
H	-3.260878000	-0.323488000	-1.522375000
Ag	3.541848000	0.222128000	-0.606321000
H	-1.416732000	0.116507000	2.323481000

Zero-point correction= 0.281442 (Hartree/Particle)
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Thermal correction to Enthalpy= 0.304114
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CPCM (dichloromethane) M06/def2TZVP E = - 1116.9870542
CPCM (dichloromethane) M06L/def2TZVP E = - 1117.5773392
CPCM (dichloromethane) B3LYP/def2TZVP E = - 1117.6449185
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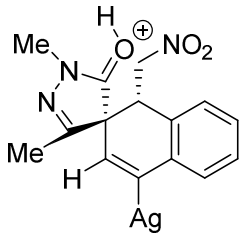
[(endo-cation-10b)]



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C	1.847837000	-1.880351000	-2.407301000
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H	3.356525000	-0.024172000	-0.252358000
Ag	-3.561615000	-0.577508000	-0.560358000
H	1.025504000	-1.404571000	3.176569000

Zero-point correction= 0.285315 (Hartree/Particle)
Thermal correction to Energy= 0.305979
Thermal correction to Enthalpy= 0.306923
Thermal correction to Gibbs Free Energy= 0.233588
Sum of electronic and zero-point Energies= -1115.629411
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Sum of electronic and thermal Free Energies= -1115.681138

CPCM (dichloromethane) M06/def2TZVP E = - 1116.9967476
CPCM (dichloromethane) M06L/def2TZVP E = - 1117.5838045
CPCM (dichloromethane) B3LYP/def2TZVP E = - 1117.6559747
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7.0 Crystal structures

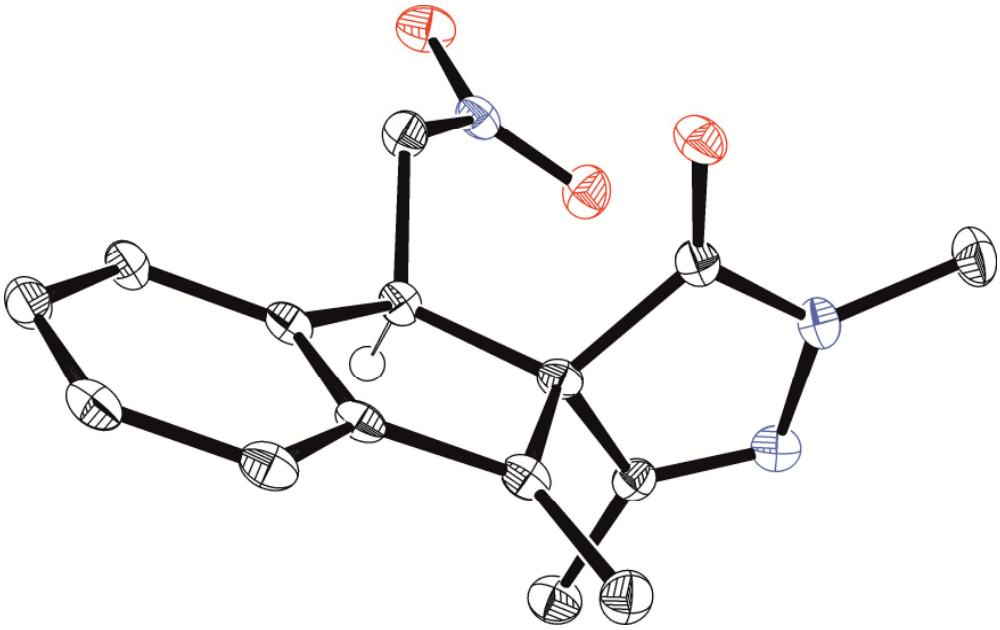


Fig 6 X-ray crystal structure of (*R*,*R*)-**3h**.

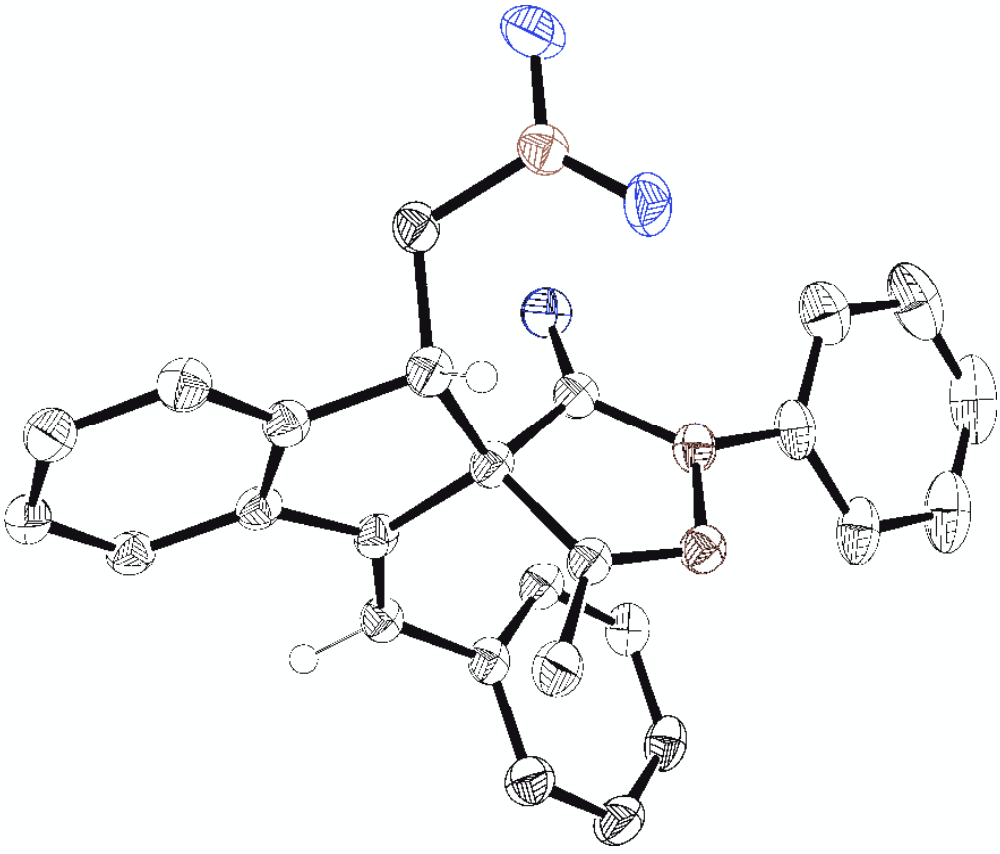
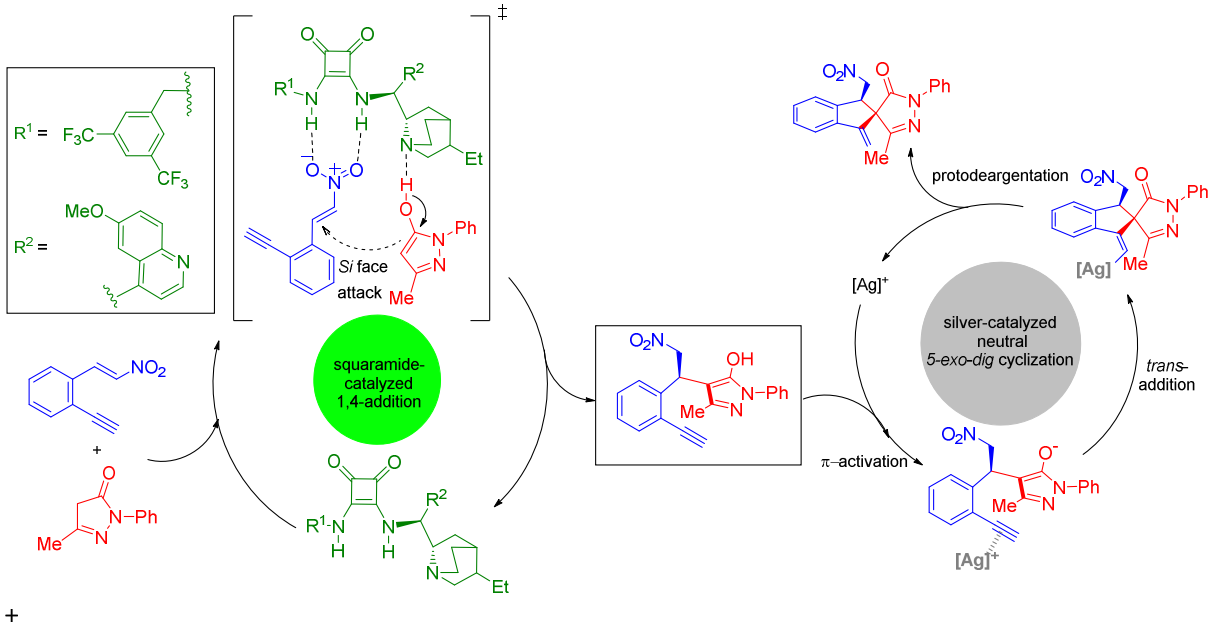


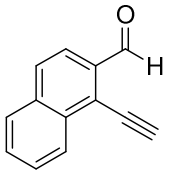
Fig 7 X-ray crystal structure of (*S*,*S*)-**4a**. (taken from a racemic crystal)

8.0 Mechanism



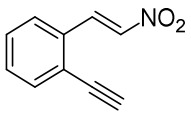
9.0 Analytical Data

1-Ethinyl-2-naphthaldehyde



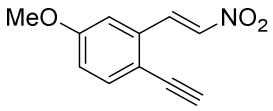
1-Ethynyl-2-naphthaldehyde was obtained after flash chromatography (SiO_2, *n*-pentane/EtOAc 10:1 to pure CH_2Cl_2) as colorless solid (560 mg, 97%). **Molecular formular:** $C_{13}H_8O$. **Molecular mass:** 180.21 g mol^{-1}. $\mathbf{R_f}$ (*n*-pentane/Et_2O 15:1) = 0.53. **Mp:** 135-138 °C. **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 3.92 (s, 1 H, C*H*), 7.63-7.71 (m, 2 H, CH_{Ar}), 7.87-7.91 (m, 2 H, CH_{Ar}), 7.97 (d, J = 8.6 Hz, 1 H, CH_{Ar}), 8.38-8.66 (m, 1 H, CH_{Ar}), 10.78 (s, 1 H, C*H*O) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 77.3 (s), 90.2 (d), 122.0 (d), 126.2 (s), 127.2 (d), 128.0 (d), 128.6 (d), 129.6 (d, 2C), 132.5 (s), 135.4 (s), 135.8 (s), 192.0 (d) ppm. **IR** (ATR): $\tilde{\nu}$ = 3965, 3884, 3421, 3344, 3242, 3056, 2846, 2740, 2462, 2316, 2094, 1994, 1918, 1823, 1670, 1575, 1436, 1370, 1320, 1222, 1143, 1020, 913, 867, 813, 761, 711, 679, 656 cm^{-1}. **MS (EI$^+$, 70 eV)** *m*/*z* (%): 180.9 (21), 179.8 (100) $[M]^+ = [C_{13}H_8O]^+$, 152.9 (13), 151.8 (98), 150.9 (23), 149.9 (23). **MS (CI$^+$, methane)** *m*/*z* (%): 208.9 (17) $[M+C_2H_5]^+ = [C_{15}H_{13}O]^+$, 180.9 (100) $[M+H]^+ = [C_{13}H_9O]^+$. **EA:** calc. for $C_{13}H_8O$: C 86.65%, H 4.47%; found: C 86.16%, H 4.47%.

(*E*)-1-Ethinyl-2-(2-nitrovinyl)benzene (1a)



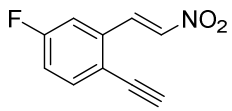
1a was obtained after flash chromatography (SiO_2, *n*-pentane/Et_2O 5:1 to pure Et_2O) as yellow solid (1.75 g, 98%). **Molecular formular:** $C_{10}H_7NO_2$. **Molecular mass:** 173.17 g mol^{-1}. $\mathbf{R_f}$ (*n*-pentane/Et_2O 10:1) = 0.42. **Mp:** 88-91 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 3.52 (s, 1 H, C*H*), 7.40-7.47 (m, 2 H, CH_{Ar}), 7.57-7.63 (m, 2 H, CH_{Ar}), 7.73 (d, J = 13.8 Hz, 1 H, CH_{ol}), 8.46 (d, J = 13.8 Hz, 1 H, CH_{ol}) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 80.7 (s), 85.0 (d), 124.2 (s), 127.6 (d), 129.6 (d), 131.6 (d), 132.1 (s), 134.3 (d), 136.9 (d), 138.7 (d) ppm. **IR** (ATR): $\tilde{\nu}$ = 3838, 3461, 3280, 3108, 2923, 2832, 2660, 2327, 2102, 1725, 1625, 1497, 1332, 1278, 1207, 962, 838, 753 cm^{-1}. **MS (EI$^+$, 70 eV)** *m*/*z* (%): 172.9 (14) $[M]^+ = [C_{10}H_7NO_2]^+$, 127.9 (15), 126.9 (100) $[M-NO_2]^+ = [C_{10}H_7]^+$, 125.9 (33), 114.9 (33), 100.9 (15), 88.9 (9), 76.9 (27), 74.9 (23), 73.9 (15), 63.0 (14), 51.1 (18). **MS (CI$^+$, methane)** *m*/*z* (%): 202.0 (28) $[M+C_2H_5]^+ = [C_{12}H_{12}NO_2]^+$, 173.9 (100) $[M+H]^+ = [C_{10}H_8NO_2]^+$. All analytical date is in accordance with the reported literature.[i]

(*E*)-1-Ethinyl-4-methoxy-2-(2-nitrovinyl)benzene (1b)



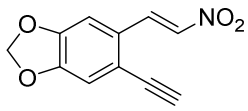
1b was obtained after flash chromatography (SiO_2, *n*-pentane/Et_2O 5:1 to pure Et_2O) as yellow solid (1.54 g, 93%). **Molecular formular:** $C_{11}H_9NO_3$. **Molecular mass:** 203.20 g mol^{-1}. $\mathbf{R_f}$ (*n*-pentane/Et_2O 6:1) = 0.49. **Mp:** 98-101 °C. **^{1}H NMR** (600 MHz, $CDCl_3$, major diastereomer): δ = 3.43 (s, 1 H, C*H*), 3.86 (s, 3 H, OCH_3), 6.98 (dd, *J* = 2.6 Hz, *J* = 8.6 Hz, 1 H, CH_{Ar}), 7.03 (d, *J* = 2.6 Hz, 1 H, CH_{Ar}), 7.53 (d, *J* = 8.6 Hz, 1 H, CH_{Ar}), 7.70 53 (d, *J* = 13.8 Hz, 1 H, CH_{ol}), 8.39 (dd, *J* = 1.4 Hz, *J* = 13.7 Hz, 1 H, CH_{ol}) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$, major diastereomer): δ = 55.7 (q), 80.7 (s), 83.3 (d), 112.4 (d), 116.5 (s), 118.6 (d), 133.4 (s), 135.3 (d), 136.9 (d), 138.8 (d), 160.1 (s) ppm. **IR** (ATR): $\tilde{\nu}$ = 3958, 3876, 3837, 3767, 3699, 3596, 3458, 3266, 3097, 3023, 2950, 2841, 2699, 2578, 2464, 2355, 2283, 2194, 2162, 2104, 1955, 1938, 1901, 1857, 1813, 1774, 1718, 1676, 1633, 1598, 1560, 1513, 1484, 1322, 1290, 1232, 1164, 1087, 1021, 958, 821, 692 cm^{-1}. **MS (EI$^+$, 70 eV)** *m*/*z* (%): 204.0 (10), 203.0 (81) $[M]^+ = [C_{11}H_9NO_3]^+$, 157.9 (17), 156.9 (100) $[M-NO_2]^+ = [C_{11}H_9O]^+$, 156.0 (18), 141.9 (36), 127.9 (13), 126.9 (15), 113.9 (52), 119.9 (27), 87.9 (15), 63.0 (12) ppm. **MS (CI$^+$, methane)** *m*/*z* (%): 232.1 (17) $[M+C_2H_5]^+ = [C_{13}H_{14}NO_3]^+$, 203.9 (100) $[M+H]^+ = [C_{11}H_{10}NO_3]^+$. **HR-MS (EI$^+$)**: calc. for $[M]^+ = [C_{22}H_{19}NO_3]^+$: 203.0577; found: 203.0578.

(*E*)-1-Ethinyl-4-fluoro-2-(2-nitrovinyl)benzene (1c)



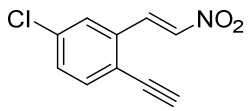
1c was obtained after flash chromatography (SiO_2, *n*-pentane/Et_2O 2:1 to pure Et_2O) as yellow solid (1.16 g, 91%). **Molecular formular:** $C_{10}H_6FNO_2$. **Molecular mass:** 191.16 g mol^{-1}. $\mathbf{R_f}$ (*n*-pentane/Et_2O 15:1) = 0.49. **Mp:** 127-131 °C. **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 3.50 (s, 1 H, C*H*), 7.15-7.20 (m, 1 H, CH_{Ar}), 7.27 (dd, *J* = 2.5 Hz, *J* = 9.1 Hz, 1 H, CH_{Ar}), 7.61 (dd, *J* = 5.6 Hz, *J* = 8.6 Hz, 1 H, CH_{Ar}), 7.67 (d, *J* = 13.8 Hz, 1 H, CH_{ol}), 8.40 (dd, *J* = 0.7 Hz, *J* = 13.8 Hz, 1 H, CH_{ol}) ppm. **^{13}C{^{19}F} NMR** (101 MHz, $CDCl_3$): δ = 79.7 (s), 84.5 (d), 114.2 (d), 119.1 (d), 120.4 (s), 134.3 (s), 135.7 (d), 136.1 (d), 139.5 (d), 162.6 (s) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = −108.24 (dd, *J* = 8.3 Hz, *J* = 14.1 Hz) ppm. **IR** (ATR): $\tilde{\nu}$ = 3780, 3700, 3291, 3124, 3045, 2965, 2844, 2666, 2498, 2347, 2107, 1997, 1900, 1742, 1684, 1632, 1605, 1569, 1511, 1477, 1424, 1343, 1277, 1220, 1185, 1158, 963, 870, 843, 823, 715, 681 cm^{-1}. **MS (EI$^+$, 70 eV)** *m*/*z* (%): 191.0 (30) $[M]^+ = [C_{10}H_6FNO_2]^+$, 145.9 (16), 144.9 (100) $[M-NO_2]^+ = [C_{10}H_6F]^+$, 143.9 (34), 132.9 (32), 124.9 (42), 98.9 (17), 74.9 (13). **MS (CI$^+$, methane)** *m*/*z* (%): 220.0 (19) $[M+C_2H_5]^+ = [C_{12}H_{11}FNO_2]^+$, 191.9 (100) $[M+H]^+ = [C_{10}H_7FNO_2]^+$. **HR-MS (EI$^+$)**: calc. for $[M]^+ = [C_{10}H_6FNO_2]^+$: 191.0377; found: 191.0376.

(*E*)-5-Ethinyl-6-(2-nitrovinyl)benzo[*d*][1,3]dioxole (1d)



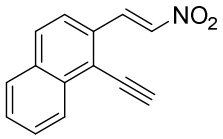
1d was obtained after flash chromatography (SiO_2, *n*-pentane/CH_2Cl_2 1:1 zu 1:2) as yellow solid (938 mg, 58%). **Molecular formular:** $C_{11}H_7NO_4$. **Molecular mass:** 217.18 g mol^{-1}. $\mathbf{R_f}$ (*n*-pentane/Et_2O 6:1) = 0.32. **Mp:** 178-183 °C. **^{1}H NMR** (600 MHz, $CDCl_3$, major diastereomer): δ = 3.46 (s, 1 H, C*H*), 6.08 (s, 2 H, CH_2), 7.00 (s, 1 H, CH_{Ar}), 7.01 (s, 1 H, CH_{Ar}), 7.55 (d, *J* = 13.6 Hz, 1 H, CH_{ol}), 8.46 (d, *J* = 13.6 Hz, 1 H, CH_{ol}) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$, major diastereomer): δ = 80.4 (s), 83.9 (d), 102.6 (t), 106.0 (d), 113.1 (d), 120.1 (s), 127.1 (s), 136.8 (d), 137.1 (d), 149.3 (s), 150.9 (s) ppm. **IR** (ATR): $\tilde{\nu}$ = 3946, 3400, 3267, 3114, 2928, 2647, 2304, 2098, 1935, 1819, 1709, 1608, 1483, 1259, 1161, 918, 837, 730, 697 cm^{-1}. **MS (EI$^+$, 70 eV)** *m*/*z* (%): 217.0 (49) $[M]^+ = [C_{11}H_7NO_4]^+$, 171.9 (17), 170.9 (100) $[M-NO_2]^+ = [C_{11}H_7O_2]^+$, 169.9 (17), 168.9 (13), 140.9 (69), 112.8 (52), 86.9 (16), 85.9 (13), 63.0 (23), 62.0 (10). **MS (CI$^+$, methane)** *m*/*z* (%): 246.1 (6) $[M+C_2H_5]^+ = [C_{13}H_{12}NO_4]^+$, 218.0 (100) $[M+H]^+ = [C_{11}H_8NO_4]^+$. **HR-MS (ESI$^+$)**: calc. for $[M+Na]^+ = [C_{11}H_7NaNO_3]^+$: 240.0267; found: 240.0263.

***(E)*-4-Chloro-1-ethinyl-2-(2-nitrovinyl)benzene (1e)**



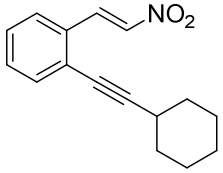
1e was obtained after flash chromatography (SiO_2, *n*-pentane/Et_2O 2:1 to pure Et_2O) as yellow solid (1.03 g, 86%). **Molecular formular:** $C_{10}H_6ClNO_2$. **Molecular mass:** 207.61 g mol^{-1}. $\mathbf{R_f}$ (*n*-pentane/Et_2O 15:1) = 0.54. **Mp:** 109-113 °C. **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 3.56 (s, 1 H, C*H*), 7.40-7.43 (m, 1 H, CH_{Ar}), 7.53-7.57 (m, 2 H, CH_{Ar}), 7.69 (d, *J* = 13.8 Hz, 1 H, CH_{ol}), 8.36 (dd, *J* = 0.9 Hz, *J* = 13.7 Hz, 1 H, CH_{ol}) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 79.8 (s), 85.8 (d), 122.4 (s), 127.5 (d), 131.6 (d), 133.7 (s), 135.2 (d), 135.4 (d), 135.7 (s), 139.5 (d) ppm. **IR** (ATR): $\tilde{\nu}$ = 3948, 3780, 3698, 3432, 3282, 3109, 3062, 2968, 2924, 2844, 2743, 2595, 2487, 2295, 2105, 1999, 1911, 1822, 1774, 1682, 1635, 1587, 1547, 1510, 1470, 1339, 1281, 1207, 1180, 1115, 1082, 1038, 963, 919, 889, 826, 717, 677 cm^{-1}. **MS (EI$^+$, 70 eV)** *m*/*z* (%): 209.0 (14) [M, ^{37}Cl]$^+ = [C_{10}H_6ClNO_2]^+$, 207.0 (41) [M, ^{35}Cl]$^+ = [C_{10}H_6ClNO_2]^+$, 162.9 (34) [M–NO_2, ^{37}Cl]$^+ = [C_{10}H_6Cl]^+$, 161.9 (22), 160.9 (100) [M–NO_2, ^{35}Cl]$^+ = [C_{10}H_6Cl]^+$, 159.9 (20), 150.9 (11), 148.9 (31), 126.9 (10), 125.9 (78), 124.9 (20), 98.9 (12), 74.9 (11). **MS (CI$^+$, methane)** *m*/*z* (%): 238.0 (6) [M+C_2H_5, ^{37}Cl]$^+ = [C_{12}H_{11}ClNO_2]^+$, 236.0 (18) [M+$C_2H_5$, ^{35}Cl]$^+ = [C_{12}H_{11}ClNO_2]^+$, 209.9 (32) [M+H, ^{37}Cl]$^+ = [C_{10}H_7ClNO_2]^+$, 207.9 (100) [M+H, ^{35}Cl]$^+ = [C_{10}H_7ClNO_2]^+$. **EA:** calc. for $C_{10}H_6ClNO_3$: C 57.85%, H 2.91%, N 6.75%; found: C 57.61%, H 3.35%, N 6.55%.

***(E)*-1-Ethinyl-2-(2-nitrovinyl)naphthaline (1f)**



1f was obtained after flash chromatography (SiO_2, *n*-pentane/CH_2Cl_2 5:1 zu 1:1) as yellow solid (368 mg, 73%). **Molecular formular:** $C_{14}H_9NO_2$. **Molecular mass:** 223.23 g mol^{-1}. $\mathbf{R_f}$ (*n*-pentane/Et_2O 10:1) = 0.36. **Mp:** 143-145 °C. **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 3.99 (s, 1 H, C*H*), 7.59 (d, *J* = 8.7 Hz, 1 H, CH_{Ar}), 7.60-7.67 (m, 2 H, CH_{Ar}), 7.74 (d, *J* = 13.7 Hz, 1 H, CH_{ol}), 7.83-7.89 (m, 2 H, CH_{Ar}), 8.44 (d, *J* = 8.1 Hz, 1 H, CH_{Ar}), 8.76 (d, *J* = 13.7 Hz, 1 H, CH_{ol}) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 78.6 (s), 90.8 (d), 122.4 (d), 123.8 (s), 127.5 (d), 128.3 (d), 128.5 (d), 128.8 (d), 129.9 (d), 130.8 (s), 133.9 (s), 134.3 (s), 137.3 (d), 138.8 (d) ppm. **IR** (ATR): $\tilde{\nu}$ = 3897, 3428, 3282, 3103, 2932, 2812, 2296, 2090, 1986, 1924, 1690, 1615, 1499, 1324, 1242, 965, 812, 754, 724, 667 cm^{-1}. **MS (EI$^+$, 70 eV)** *m*/*z* (%): 222.9 (45) $[M]^+ = [C_{14}H_9NO_2]^+$, 177.9 (20), 176.9 (100) $[M-NO_2]^+ = [C_{14}H_9]^+$, 175.9 (76), 164.9 (14), 150.9 (18), 149.9 (14), **MS (CI$^+$, methane)** *m*/*z* (%): 447.5 (100) = $[2M+H]^+ = [C_{28}H_{19}N_2O_4]^+$. **EA:** calc. for $C_{14}H_9NO_{23}$: C 75.33%, H 4.06%, N 6.27%; found: C 75.03%, H 4.16%, N 6.25%.

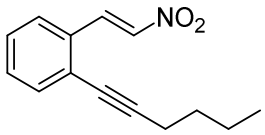
(*E*)-1-(Cyclohexylethinyl)-2-(2-nitrovinyl)benzene (1g)



1g was obtained after flash chromatography (SiO_2, *n*-pentane/Et_2O 20:1 zu 10:1) as yellow solid (2.08 g, 94%). **Molecular formular:** $C_{16}H_{17}NO_2$. **Molecular mass:** 255.32 g mol^{-1}. $\mathbf{R_f}$ (*n*-pentane/Et_2O 20:1) = 0.57. **Mp:** 81-83 °C. **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 1.40 (t, *J* = 7.1 Hz, 3 H, CH_2), 1.53-1.66 (m, 3 H, CH_2), 1.75-1.83 (m, 2 H, CH_2), 1.88-1.98 (m, 2 H, CH_2), 2.67-2.74 (m, 1 H, C*H*), 7.32 (td, *J* = 1.1 Hz, *J* = 7.6 Hz, 1 H, CH_{Ar}), 7.39 (td, *J* = 1.2 Hz, *J* = 7.6 Hz, 1 H, CH_{Ar}), 7.47-7.55 (m, 2 H, CH_{Ar}), 7.77 (d, *J* = 13.8 Hz, 1 H, CH_{ol}), 8.47 (d, *J* = 13.8 Hz, 1 H, CH_{ol}) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 25.0 (t), 26.0 (t, 2 C), 30.0 (d), 32.6 (t, 2 C) 78.2 (s), 103.0 (s), 126.4 (s), 127.8 (d), 128.2 (d), 131.3 (s), 131.5 (d), 133.5 (d), 137.7 (d), 138.1 (d) ppm. **IR** (ATR): $\tilde{\nu}$ = 3831, 3111, 2927, 2858, 2662, 2488, 2310, 2221, 2098, 1934, 1822, 1731, 1632, 1501, 1338, 1198, 1097, 1028, 964, 847, 752 cm^{-1}. **MS (EI$^+$, 70 eV)** *m*/*z* (%): 255.1 (17) $[M]^+ = [C_{16}H_{17}NO_2]^+$, 210.1 (7), 209.1 (40) $[M-NO_2]^+ = [C_{16}H_{17}]^+$, 208.1 (9), 194.0 (5), 181.0 (20), 180.0 (11), 179.0 (17), 178.0 (14), 169.0 (6), 168.0 (14), 167.0 (53) $[M-C_3H_6NO_2]^+ = [C_{13}H_{11}]^+$, 164.9 (46) $[M-C_3H_8NO_2]^+ = [C_{13}H_9]^+$, 153.0 (24), 151.9 (45) $[M-C_4H_9NO_2]^+ = [C_{12}H_8]^+$, 150.9 (14), 142.9 (10), 141.9 (22), 140.9 (100) $[M-C_5H_8NO_2]^+ = [C_{11}H_9]^+$, 138.9 (19), 128.9 (23), 127.9 (15), 126.9 (10), 125.9 (7), 116.9 (9), 114.9 (53), 80.9 (17). **MS (CI$^+$,**

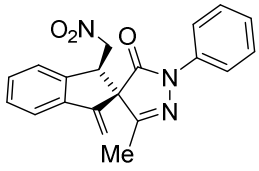
methane) *m/z* (%): 284.1 (27) $[M+C_2H_5]^+ = [C_{18}H_{22}NO_2]^+$, 256.0 (100) $[M+H]^+ = [C_{16}H_{18}NO_2]^+$. **HR-MS (ESI$^+$):** calc. for $[M+H]^+ = [C_{16}H_{18}NO_2]^+$: 256.1336, found: 256.1332.

(*E*)-1-(Hex-1-yn-1-yl)-2-(2-nitrovinyl)benzene [1h]



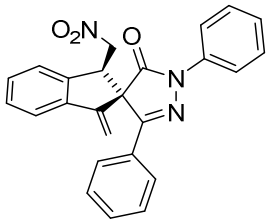
1h was isolated after flash chromatography (SiO_2, *n*-pentane/Et_2O 20:1) as yellow solid (920 mg, 76%). **Molecular formula:** $C_{14}H_{15}NO_2$. **Molecular mass:** 229.28 g mol^{-1}. **R_f**(*n*-pentane/ether 20:1) = 0.57. **Mp:** 153-155 °C. **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 7.4 Hz, 3 H, C*H*$_3$), 1.45-1.51 (m, 2 H, C*H*$_2$), 1.57-1.63 (m, 2 H, C*H*$_2$), 2.43 (t, *J* = 7.1 Hz, 2 H, C*H*$_2$), 7.42 (m, 4 H, C*H*$_{Ar}$), 7.56 (d, *J* = 13.6 Hz, 1 H, C*H*$_{ol}$), 7.96 (dd, *J* = 0.9 Hz, *J* = 13.7 Hz, 1 H, C*H*$_{ol}$) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 13.8 (q), 19.4 (t), 22.2 (t), 30.8 (t), 80.2 (s), 94.9 (s), 128.5 (s), 129.0 (s), 129.1 (d, 2 C), 132.5 (d, 2 C), 137.2 (d), 138.5 (d) ppm. **IR** (ATR): $\tilde{\nu}$ = 3734, 3112, 3045, 2932, 2865, 2652, 2298, 2222, 2108, 1995, 1925, 1800, 1701, 1630, 1598, 1549, 1499, 1413, 1334, 1256, 1203, 1178, 1107, 1053, 1008, 969, 825, 738, 687 cm^{-1}. **MS (EI$^+$, 70 eV)** *m/z* (%): 229.1 (100) $[M]^+ = [C_{14}H_{15}NO_2]^+$, 214.0 (28), 213.1 (7), 212.0 (6), 195.0 (9), 186.0 (9), 183.0 (10), 182.0 (18) $[M-HNO_2]^+ = [C_{14}H_{14}]^+$, 181.0 (5), 171.0 (6), 169.0 (6), 168.0 (12), 167.0 (39) $[M-CH_4NO_2]^+ = [C_{13}H_{12}]^+$, 164.9 (10), 155.0 (9), 154.0 (16), 153.0 (35) $[M-C_2H_5NO_2]^+ = [C_{12}H_{10}]^+$, 151.9 (29), 150.9 (6), 142.0 (11), 141.0 (19), 140.0 (21), 138.9 (94) $[M-C_3H_8NO_2]^+ = [C_{11}H_7]^+$, 127.9 (22), 114.9 (35). **MS (CI$^+$, methane)** *m/z* (%): 258.1 (16) $[M+C_2H_5]^+ = [C_{16}H_{20}NO_2]^+$, 230.1 (100) $[M+H, {}^{35}Cl]^+ = [C_{14}H_{16}NO_2]^+$. **HRMS (ESI):** calcd. for $C_{14}H_{16}NO_2$: 230.1177, found: 230.1176.

(2*R*,3*R*)-3'-Methyl-1-methylene-3-(nitromethyl)-1'-phenyl-1,3-dihydrospiro[indene-2,4'-pyrazole]-5'(1'*H*)-one (3a)



3a was obtained after flash chromatography (SiO_2, *n*-pentane/EtOAc 6:1) as off-white solid (104 mg, 99%, d.r. 10:1). **Molecular formular:** $C_{20}H_{17}N_3O_3$. **Molecular mass:** 347.37 g mol^{-1}. $\mathbf{R_f}$ (*n*-pentane/EtOAc 6:1) = 0.34. **Mp:** 83-84 °C. **HPLC:** AS, 7/3 *n*-heptane/*i*-PrOH, 0.5 mL/min, λ = 254 nm, τ_{Neben} = 17.1 min, $\tau Major$ = 14.2 min. **OR:** $[\alpha]_D^{20}$ = −86.8 (*c* = 0.5, $CHCl_3$, 94% *ee*). **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 1.94 (s, 0.3 H, CH_3, b), 2.04 (s, 3.0 H, CH_3, a), 4.31 (dd, *J* = 4.2 Hz, *J* = 10.2 Hz, 1.0 H, C*H*, a), 4.37 (dd, *J* = 9.2 Hz, *J* = 14.5 Hz, 0.2 H, CH_2, b), 4.66 (dd, *J* = 6.3 Hz, *J* = 8.8 Hz, 0.2 H, C*H*, b), 4.81 (dd, *J* = 4.3 Hz, *J* = 15.2 Hz, 1.0 H, CH_2, a), 4.93 (dd, *J* = 6.0 Hz, *J* = 14.5 Hz, 0.2 H, CH_2, b), 4.98 (d, *J* = 1.3 Hz, 1.0 H, CH_{ol}, a), 5.00 (d, *J* = 1.2 Hz, 0.2 H, CH_{ol}, b), 5.27 (dd, *J* = 10.3 Hz, *J* = 15.2 Hz, 1.0 H, CH_2, a), 5.70-5.73 (m, 1.2 H, CH_{ol}, a+b), 7.18-7.24 (m, 1.2 H, CH_{Ar}), 7.26-7.30 (m, 1.0 H, CH_{Ar}), 7.37-7.45 (m, 4.3 H, CH_{Ar}), 7.57-7.63 (m, 1.1 H, CH_{Ar}), 7.85 (dd, *J* = 1.1 Hz, *J* = 7.7 Hz, 2.0 H, CH_{Ar}), 7.94 (dd, *J* = 0.9 Hz, *J* = 8.6 Hz, 1.0 H, CH_{Ar}) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$, major diastereomer): δ = 13.7 (q), 45.2 (d), 65.8 (s), 73.7 (t), 107.1 (t), 119.6 (d, 2 C), 122.3 (d), 124.5 (d), 125.6 (d), 129.0 (d, 2 C), 129.5 (d), 130.4 (d), 137.8 (s), 138.9 (s), 140.6 (s), 146.0 (s), 161.6 (s), 172.4 (s) ppm. **IR** (ATR): $\tilde{\nu}$ = 3743, 3392, 3060, 2916, 2650, 2243, 2192, 2157, 2106, 2030, 1951, 1777, 1702, 1637, 1619, 1594, 1543, 1492, 1461, 1397, 1365, 1329, 1287, 1238, 1204, 1181, 1129, 1097, 1068, 914, 886, 838, 760, 731, 695, 672 cm^{-1}. **MS (EI$^+$, 70 eV)** *m*/*z* (%): 348.1 (23), 347.1 (100) $[M]^+$ = $[C_{20}H_{17}N_3O_3]^+$, 300.1 (10) $[M-HNO_2]^+$ = $[C_{20}H_{16}N_2O]^+$. **MS (CI$^+$, methane)** *m*/*z* (%): 376.0 (13) $[M+C_2H_5]^+$ = $[C_{22}H_{22}N_3O_3]^+$, 348.0 (100) $[M+H]^+$ = $[C_{20}H_{18}N_3O_3]^+$. **HR-MS (ESI$^+$)**: calc. for $[M+Na]^+$ = $[C_{20}H_{17}NaN_3O_3]^+$: 370.1162; found: 370.1166.

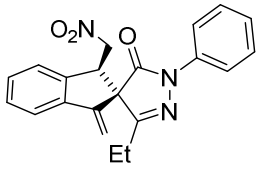
(2*R*,3*R*)-1-methylene-3-(nitromethyl)-1',3'-diphenyl-1,3-dihydrospiro[indene-2,4'-pyrazole]-5'(1'*H*)-on (3b)



3b was obtained after flash chromatography (SiO_2, *n*-pentane/EtOAc 6:1) as colorless solid (91 mg, 99%, d.r. 10:1). **Molecular formular:** $C_{25}H_{19}N_3O_3$. **Molecular mass:** 409.45 g mol^{-1}. $\mathbf{R_f}$ (*n*-pentane/EtOAc 6:1) = 0.30. **Mp:** 70-73 °C. **HPLC:** IA, 7/3 *n*-heptane/EtOH, 1.0 mL/min, λ = 254 nm, $\tau Minor$ = 13.1 min, $\tau Major$ = 15.5 min. **OR:** $[\alpha]_D^{20}$ = +5.2 (*c* = 0.5, $CHCl_3$, 95% *ee*). **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 4.48 (dd, *J* = 11.8 Hz, *J* = 16.6 Hz, 0.2 H, CH_2, b), 4.54 (dd, *J* = 3.8 Hz, *J* = 10.7 Hz, 1.0 H, C*H*, a), 4.72-4.78 (m, 0.3 H, C*H*, CH_2, b), 4.88 (dd, *J* = 4.0 Hz, *J* = 15.0 Hz, 1.0 H, CH_2, a),

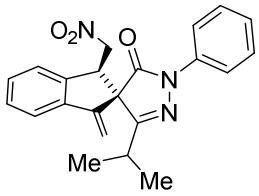
5.08 (s, 1.0 H, CH_{ol}, a), 5.10 (d, 0.2 H, CH_{ol}, b), 5.34 (dd, J = 10.7 Hz, J = 15.0 Hz, 1.0 H, CH_2, a), 5.75 (s, 1.0 H, CH_{ol}, a), 5.79 (s, 0.2 H, CH_{ol}, b), 7.20-7.31 (m, 2.7 H, CH_{Ar}), 7.31-7.38 (m, 2.1 H, CH_{Ar}), 7.38-7.51 (m, 5.1 H, CH_{Ar}), 7.61 (d, J = 7.6 Hz, 1.8 H, CH_{Ar}), 7.68-7.72 (m, 1.0 H, CH_{Ar}), 7.95-7.98 (m, 1.8 H, CH_{Ar}), 8.04-8.07 (m, 0.2 H, CH_{Ar}) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$, major diastereomer): δ = 46.5 (d), 64.6 (s), 73.4 (t), 106.9 (t), 119.9 (d, 2 C), 122.6 (d), 124.6 (d), 125.9 (d), 127.0 (d, 2 C), 129.1 (d, 4 C), 129.4 (s), 129.5 (d), 130.5 (d), 130.8 (d), 137.9 (s), 139.0 (s), 140.8 (s), 147.2 (s), 160.3 (s), 173.0 (s) ppm. **IR** (ATR): $\tilde{\nu}$ = 3349, 3228, 2856, 2758, 2324, 2096, 1934, 1834, 1679, 1589, 1455, 1354, 1271, 1201, 1093, 956, 892, 834, 738, 675 cm^{-1}. **MS (EI, 70 eV)** *m/z* (%): 409.0 (100) $[M]^+ = [C_{25}H_{19}N_3O_3]^+$, 362.1 (22) $[M-HNO_2]^+ = [C_{25}H_{18}N_2O]^+$. **MS (CI$^+$, methane)** *m/z* (%): 410.0 (48) $[M+H]^+ = [C_{25}H_{20}N_3O_3]^+$. **HR-MS (EI$^+$)**: calc. for $[M]^+ = [C_{25}H_{19}N_3O_3]$: 409.1421; found: 409.1423.

(2*R*,3*R*)-3'-Ethyl-1-methylene-3-(nitromethyl)-1'-phenyl-1,3-dihydrospiro[indene-2,4'-pyrazole]-5'(1'*H*)-on (3c)



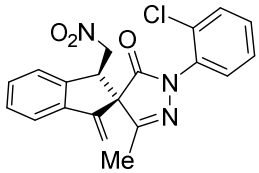
3c was obtained after flash chromatography (SiO_2, *n*-pentane/EtOAc 4:1) as colorless solid (55 mg, 51%, d.r. >20:1). **Molecular formular:** $C_{21}H_{19}N_3O_3$. **Molecular mass:** 361.40 g mol^{-1}. **R_f** (*n*-pentane/EtOAc 6:1) = 0.30. **Mp:** 149-151 °C. **HPLC:** IA, 7/3 *n*-heptane/EtOH, 0.7 mL/min, λ = 254 nm, τ*Minor* = 12.3 min, τ*Major* = 10.7 min. **OR:** $[\alpha]_D^{20}$ = +86.4 (c = 0.7, $CHCl_3$, 91% *ee*). **^{1}H NMR** (600 MHz, $CDCl_3$, major diastereomer): δ = 1.28 (t, J = 7.3 Hz, 3 H, CH_3), 2.23-2.32 (m, 1 H, CH_2), 2.34-2.43 (m, 1 H, CH_2), 4.33 (dd, J = 4.3 Hz, J = 10.2 Hz, 1 H, C*H*), 4.79 (dd, J = 4.3 Hz, J = 15.1 Hz, 1 H, CH_2), 4.97 (d, J = 1.2 Hz, 1 H, CH_{ol}), 5.27 (dd, J = 10.2 Hz, J = 15.2 Hz, 1 H, CH_2), 5.70 (d, J = 1.2 Hz, 1 H, CH_{ol},), 7.18-7.23 (m, 1 H, CH_{Ar}), 7.24-7.30 (m, 1 H, CH_{Ar}), 7.36-7.45 (m, 4 H, CH_{Ar}), 7.57-7.63 (m, 1 H, CH_{Ar}), 7.86-7.94 (m, 2 H, CH_{Ar}) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$, major diastereomer): δ = 9.5 (q), 21.1 (t), 45.2 (d), 65.7 (s), 73.7 (t), 106.9 (d), 119.4 (d, 2 C), 122.1 (d), 124.3 (d), 125.4 (d), 128.8 (d, 2 C), 129.3 (d), 130.2 (d), 137.8 (s), 138.8 (s), 140.7 (s), 146.2 (s), 165.3 (s), 172.8 (s) ppm. **IR** (ATR): $\tilde{\nu}$ = 3925, 3876, 3838, 3769, 3701, 3595, 3391, 3275, 3025, 2984, 2913, 2641, 2340, 2271, 2224, 2071, 1992, 1943, 1889, 1826, 1779, 1700, 1637, 1594, 1542, 1491, 1400, 1350, 1244, 1221, 1181, 1131, 1100, 1035, 957, 911, 885, 760, 736, 688 cm^{-1}. **MS (EI$^+$, 70 eV)** *m/z* (%): 361.0 (100) $[M]^+ = [C_{21}H_{19}N_3O_3]^+$, 315.1 (12) $[M-NO_2]^+ = [C_{21}H_{19}N_2O]^+$. **MS (CI$^+$, methane)** *m/z* (%): 390.0 (16) $[M+C_2H_5]^+ = [C_{23}H_{23}N_3O_3]^+$, 362.0 (100) $[M+H]^+ = [C_{21}H_{20}N_3O_3]^+$. **EA**: calc. for $C_{21}H_{19}N_3O_3$: C 69.79%, H 5.30%, N 11.63%; found: C 69.73%, H 5.63%, N 11.28%.

(2*R*,3*R*)-3'-Isopropyl-1-methylene-3-(nitromethyl)-1'-phenyl-1,3-dihydrospiro[indene-2,4'-pyrazole]-5'(1'*H*)-on (3d)



3d was obtained after flash chromatography (SiO_2, *n*-pentane/EtOAc 4:1) as off-white solid (56 mg, 50%, d.r. 7:1). **Molecular formular:** $C_{22}H_{21}N_3O_3$. **Molecular mass:** 375.43 g mol^{-1}. $\mathbf{R_f}$ (*n*-pentane/EtOAc 6:1) = 0.27. **Mp:** 114-116 °C. **HPLC:** IC, 7/3 *n*-heptane/EtOH, 1.0 mL/min, λ = 254 nm, $\tau Minor$ = 7.5 min, $\tau Major$ = 9.2 min. **OR:** $[\alpha]_D^{20} = -48.8$ (c = 0.5, $CHCl_3$, 76% *ee*). **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 1.14 (d, J = 6.7 H, 0.4 H, CH_3, b), 1.18 (d, J = 6.9 H, 3.0 H, CH_3, a), 1.24 (d, J = 6.8 H, 0.5 H, CH_3, b), 1.32 (d, J = 6.8 H, 3.0 H, CH_3, a), 2.15 (sept, J = 6.8 H, 0.2 H, CH, b), 2.55 (sept, J = 6.9 H, 1.0 H, CH, a), 4.40 (dd, J = 4.3 Hz, J = 10.2 Hz, 1.0 H, CH, a), 4.51 (dd, J = 9.0 Hz, J = 14.7 Hz, 0.2 H, CH_2, b), 4.66 (dd, J = 6.6 Hz, J = 8.5 Hz, 0.2 H, CH, b), 4.79 (dd, J = 4.3 Hz, J = 15.0 Hz, 1.0 H, CH_2, a), 4.94 (dd, J = 6.1 Hz, J = 14.7 Hz, 0.2 H, CH_2, b), 4.99 (d, J = 1.1 Hz, 1.0 H, CH_{ol}, a), 5.05 (d, J = 1.0 Hz, 0.2 H, CH_{ol}, b), 5.31 (dd, J = 10.2 Hz, J = 15.1 Hz, 1.0 H, CH_2, a), 5.70 (d, J = 1.1 Hz, 0.2 H, CH_{ol}, b), 5.71 (d, J = 1.3 Hz, 1.0 H, CH_{ol}, a), 7.16-7.24 (m, 1.2 H, CH_{Ar}), 7.24-7.30 (m, 1.2 H, CH_{Ar}), 7.36-7.46 (m, 4.3 H, CH_{Ar}), 7.56-7.63 (m, 1.1 H, CH_{Ar}), 7.88 (d, J = 7.8 Hz, 1.8 H, CH_{Ar}), 7.94 (d, J = 7.8 Hz, 0.3 H, CH_{Ar}) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$, major diastereomer): δ = 21.0 (q), 22.5 (q), 28.8 (d), 45.0 (d), 65.7 (s), 73.7 (t), 107.1 (t), 119.6 (d, 2 C), 122.2 (d), 124.5 (d), 125.4 (d), 129.0 (d, 2 C), 129.4 (d), 130.3 (d), 138.0 (s), 139.1 (s), 141.0 (s), 146.2 (s), 169.7 (s), 172.6 (s) ppm. **IR** (ATR): $\tilde{\nu}$ = 3839, 3386, 3080, 2976, 2927, 2693, 2472, 2321, 2197, 2172, 2092, 2054, 1987, 1957, 1697, 1636, 1595, 1542, 1491, 1460, 1401, 1371, 1349, 1223, 1152, 1134, 1086, 1054, 1024, 977, 909, 885, 817, 759, 693, 661 cm^{-1}. **MS (EI$^+$, 70 eV)** *m/z* (%): 375.1 (100) $[M]^+ = [C_{22}H_{21}N_3O_3]^+$, 329.1 (14) $[M-NO_2]^+ = [C_{22}H_{21}N_2O]^+$. **MS (CI$^+$, methane)** *m/z* (%): 404.1 (14) $[M+C_2H_5]^+ = [C_{24}H_{26}N_3O_3]^+$, 376.1 (100) $[M+H]^+ = [C_{22}H_{22}N_3O_3]^+$. **HR-MS (EI$^+$)**: calc. for $[M]^+ = [C_{22}H_{21}N_3O_3]^+$: 375.1575; found: 375.1577.

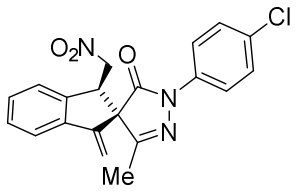
(2*R*,3*R*)-1'-(2-Chlorophenyl)-3'-methyl-1-methylene-3-(nitromethyl)-1,3-dihydrospiro[indene-2,4'-pyrazole]-5'(1'*H*)-on [3e]



3e was obtained after flash chromatography (SiO_2, *n*-pentane/EtOAc 4:1) as off-white solid (90 mg, 78%, d.r. 20:1). **Molecular formular:** $C_{20}H_{16}ClN_3O_3$. **Molecular mass:** 381.82 g mol^{-1}. $\mathbf{R_f}$ (*n*-pentane/EtOAc 5:1) = 0.32. **Mp:** 124-127 °C. **HPLC:** IC, 7/3 *n*-heptane/EtOH, 0.5 mL/min, λ = 254

nm, *τMinor* = 7.6 min, *τMajor* = 10.4 min. **OR:** $[\alpha]_D^{20}$ = −101.0 (*c* = 0.5, $CHCl_3$, 92% *ee*). **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 1.93 (s, 0.2 H, CH_3, b), 2.03 (s, 3.0 H, CH_3, a), 4.34 (dd, *J* = 3.7 Hz, *J* = 10.7 Hz, 1.0 H, C*H*, a), 4.63-4.70 (m, 0.2 H, CH_2, b), 4.81 (dd, *J* = 3.8 Hz, *J* = 18.9 Hz, 1.1 H, CH_2(a), C*H*(b)), 5.02 (dd, *J* = 9.8 Hz, *J* = 18.9 Hz, 0.1 H, CH_2, b), 5.28 (s, 1.0 H, CH_{ol}, a), 5.30 (s, 0.1 H, CH_{ol}, b), 5.36 (dd, *J* = 10.8 Hz, *J* = 15.4 Hz, 1.0 H, CH_2, a), 5.76 (s, 0.1 H, CH_{ol}, b), 5.78 (s, 1.0 H, CH_{ol}, a), 7.22-7.31 (m, 1.4 H, CH_{Ar}), 7.31-7.46 (m, 5.0 H, CH_{Ar}), 7.47-7.58 (m, 1.1 H, CH_{Ar}), 7.59-7.64 (m, 1.0 H, CH_{Ar}) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$, major diastereomer): δ = 13.6 (q), 45.1 (d), 64.1 (s), 73.5 (t), 107.5 (t), 122.3 (d), 124.4 (d), 127.9 (d), 129.1 (d), 129.5 (d), 130.1 (d), 130.3 (d), 130.5 (d), 132.0 (s), 134.2 (s), 139.1 (s), 140.5 (s), 145.7 (s), 162.0 (s), 173.0 (s) ppm. **IR** (ATR): $\tilde{\nu}$ = 3856, 3746, 3301, 3013, 2916, 2668, 2460, 2289, 2080, 1992, 1934, 1809, 1705, 1638, 1611, 1548, 1485, 1438, 1408, 1373, 1288, 1205, 1132, 1100, 1054, 1003, 945, 888, 848, 763, 739, 670 cm^{-1}. **MS (EI$^+$)** *m*/*z* (%): 383.0 (32) $[M, ^{37}Cl]^+ = [C_{20}H_{16}ClN_3O_3]^+$, 382.1 (25), 381.0 (100) $[M, ^{35}Cl]^+ = [C_{20}H_{16}ClN_3O_3]^+$, 346.0 (17) $[M–Cl]^+ = [C_{20}H_{16}N_3O_3]^+$, 333.5 (15), 334.0 (24), 305.0 (11), 300.0 (13), 299.0 (56), 195.0 (18), 180.0 (11), 167.0 (12), 166.0 (10), 164.9 (11), 152.9 (14), 151.9 (15), 140.9 (17), 138.9 (21), 126.9 (12), 124.8 (12), 114.8 (22), 110.8 (18). **MS (CI$^+$, methane)** *m*/*z* (%): 410.1 (14) $[M+C_2H_5, ^{35}Cl]^+ = [C_{22}H_{21}ClN_3O_3]^+$, 384.1 (29) $[M+H, ^{37}Cl]^+ = [C_{20}H_{17}ClN_3O_3]^+$, $[M+H, ^{35}Cl]^+ = [C_{20}H_{17}ClN_3O_3]^+$. **HR-MS (ESI$^+$)**: calc. for $[M+Na, ^{35}Cl]^+ = [C_{20}H_{16}ClNaN_3O_3]^+$: 404.0772; found: 404.0767.

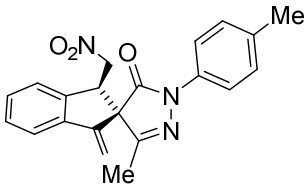
(2*R*,3*R*)-1'-(4-Chlorophenyl)-3'-methyl-1-methylene-3-(nitromethyl)-1,3-dihydrospiro[indene-2,4'-pyrazole]-5'(1'*H*)-on (3f)



3f was obtained after flash chromatography (SiO_2, *n*-pentane/EtOAc 6:1) as colorless solid (36 mg, 38%, d.r. >20:1). **Molecular formular:** $C_{20}H_{16}ClN_3O_3$. **Molecular mass:** 381.82 g mol^{-1}. **R_f** (*n*-pentane/EtOAc 6:1) = 0.34. **Mp:** 127-130 °C. **HPLC:** IC, 9/1 *n*-heptane/EtOH, 1.0 mL/min, λ = 254 nm, *τMinor* = 4.1 min, *τMajor* = 4.7 min. **OR:** $[\alpha]_D^{20}$ = −106.1 (*c* = 0.5, $CHCl_3$, 99% *ee*). **^{1}H NMR** (600 MHz, $CDCl_3$, major diastereomer): δ = 2.04 (s, 3 H, CH_3), 4.30 (dd, *J* = 4.0 Hz, *J* = 10.5 Hz, 1 H, C*H*), 4.80 (dd, *J* = 4.1 Hz, *J* = 15.2 Hz, 1 H, CH_2), 4.06 (s, 1 H, CH_{ol}), 5.25 (dd, *J* = 10.6 Hz, *J* = 15.2 Hz, 1 H, CH_2), 5.72 (d, *J* = 0.6 Hz, 1 H, CH_{ol}), 7.26-7.31 (m, 1 H, CH_{Ar}), 7.35 (d, *J* = 8.9 Hz, 2 H, CH_{Ar}), 7.37-7.44 (m, 2 H, CH_{Ar}), 7.58-7.63 (m, 1 H, CH_{Ar}), 7.83 (d, *J* = 8.9 Hz, 2 H, CH_{Ar}) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$, major diastereomer): δ = 13.7 (q), 45.3 (d), 65.8 (s), 73.6 (t), 107.3 (t), 120.5 (d, 2 C), 122.3 (d), 124.5 (d), 129.1 (d, 2 C), 129.5 (d), 130.5 (d), 130.7 (s), 136.4 (s), 138.9 (s), 140.5 (s), 145.9 (s), 161.9 (s), 172.4 (s) ppm. **IR** (ATR): $\tilde{\nu}$ = 3859, 3742, 3617, 3566, 3379, 3091, 3036, 2919, 2852, 2656, 2324, 2223, 2194, 2056, 2017, 1964, 1934, 1901, 1798, 1698, 1629, 1594, 1545, 1490, 1438, 1361, 1296, 1216, 1186, 1129, 1090, 1009, 951, 895, 825, 777, 739 cm^{-1}. **MS (EI$^+$)** *m*/*z*

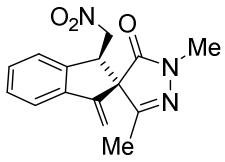
(%): 383.1 (32) [M, $^{37}Cl]^+$ = $[C_{20}H_{16}ClN_3O_3]^+$, 382.1 (25), 381.0 (100) [M, $^{35}Cl]^+$ = $[C_{20}H_{16}ClN_3O_3]^+$, 333.1 (11), 334.1 (10), 305.0 (12), 194.9 (15), 180.0 (12), 169.0 (10), 168.0 (11), 167.0 (22), 166.0 (12), 164.9 (14), 152.9 (19), 151.9 (20), 140.9 (21), 139.9 (10), 138.9 (21), 127.9 (11), 126.9 (16), 124.8 (20), 114.8 (27), 112.9 (11), 110.8 (30), 74.9 (10), 71.0 (10). **MS (CI$^+$, methane)** *m/z* (%): 410.1 (2) $[M+C_2H_5, ^{35}Cl]^+$ = $[C_{22}H_{21}ClN_3O_3]^+$, 382.0 (15) $[M+H, ^{35}Cl]^+$ = $[C_{20}H_{17}ClN_3O_3]^+$. **HR-MS (ESI$^+$)**: calc. for $[M+Na]^+$ = $[C_{20}H_{16}ClNaN_3O_3]^+$: 404.0772; found: 404.0769.

(2*R*,3*R*)-3'-Methyl-1-methylene-3-(nitromethyl)-1'-(*p*-tolyl)-1,3-dihydrospiro[indene-2,4'-pyrazole]-5'(1'*H*)-on (3g)



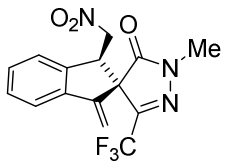
3g was obtained after flash chromatography (SiO_2, *n*-pentane/EtOAc 6:1) as colorless solid(102 mg, 94%, d.r. 10:1). **Molecular formular:** $C_{21}H_{19}N_3O_3$. **Molecular mass:** 361.40 g mol^{-1}. **R_f** (*n*-pentane/EtOAc 6:1) = 0.34. **Mp:** 127-130 °C. **HPLC:** AS, 7/3 *n*-heptane/*i*-PrOH, 1.0 mL/min, λ = 254 nm, τ*Minor* = 9.3 min, τ*Major* = 6.5 min. **OR:** $[\alpha]_D^{20} = -87.4$ (*c* = 0.5, $CHCl_3$, 94% *ee*). **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 1.93 (s, 0.3 H, CH_3, b), 2.03 (s, 3.0 H, CH_3, a), 2.35 (s, 3.0 H, CH_3, a), 2.36 (s, 3.0 H, CH_3, b), 4.30 (dd, *J* = 4.3 Hz, *J* = 10.2 Hz, 1.0 H, C*H*, a), 4.56 (dd, *J* = 9.1 Hz, *J* = 14.5 Hz, 0.2 H, CH_2, b), 4.61-4.69 (m, 0.2 H, C*H*, b), 4.80 (dd, *J* = 4.3 Hz, *J* = 15.2 Hz, 1.0 H, CH_2, a), 4.92 (dd, *J* = 6.0 Hz, *J* = 14.5 Hz, 0.2 H, CH_2, b), 4.97 (d, *J* = 1.3 Hz, 1.0 H, CH_{ol}, a), 4.99 (d, *J* = 1.2 Hz, 0.2 H, CH_{ol}, b), 5.26 (dd, *J* = 10.2 Hz, *J* = 15.2 Hz, 1.0 H, CH_2, a), 5.70 (d, *J* = 1.4 Hz, 0.2 H, CH_{ol}, b), 5.71 (d, *J* = 1.3 Hz, 1.0 H, CH_{ol}, a), 7.18-7.25 (m, 2.3 H, CH_{Ar}), 7.25-7.31 (m, 1.3 H, CH_{Ar}), 7.36-7.43 (m, 2.1 H, CH_{Ar}), 7.57-7.64 (m, 1.1 H, CH_{Ar}), 7.69-7.72 (m, 1.9 H, CH_{Ar}), 7.78-7.81 (m, 0.2 H, CH_{Ar}) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$, major diastereomer): δ = 13.6 (q), 21.1 (q), 45.2 (d), 65.8 (s), 73.8 (t), 107.1 (t), 119.7 (d, 2 C), 122.3 (d), 124.4 (d), 129.4 (d), 129.5 (d, 2 C), 130.3 (d), 135.3 (s), 135.4 (s), 139.0 (s), 140.7 (s), 146.0 (s), 161.5 (s), 172.3 (s) ppm. **IR** (ATR): $\tilde{\nu}$ = 3375, 3095, 3004, 2918, 2857, 2317, 2125, 1904, 1794, 1693, 1645, 1615, 1553, 1508, 1462, 1404, 1364, 1285, 1200, 1129, 1067, 1017, 936, 894, 818, 782, 724, 709, 676 cm^{-1}. **MS (EI$^+$)** *m/z* (%): 361.2 (13) $[M]^+$ = $[C_{21}H_{19}N_3O_3]^+$, 152.1 (14), 141.2 (19), 139.1 (13), 128.1 (12), 127.1 (11), 115.1 (34), 106.2 (14), 105.1 (22), 104.1 (18), 91.2 (100), 65.3 (52). **MS (CI$^+$, methane)** *m/z* (%): 390.1 (7) $[M+C_2H_5]^+$ = $[C_{23}H_{24}N_3O_3]^+$, 362.1 (100) $[M+H]^+$ = $[C_{21}H_{20}N_3O_3]^+$. **HR-MS (ESI$^+$)**: calc. for $[M+Na]^+$ = $[C_{21}H_{19}NaN_3O_3]^+$: 384.1319; found: 384.1301.

(2*R*,3*R*)-1',3'-Dimethyl-1-methylene-3-(nitromethyl)-1,3-dihydrospiro[indene-2,4'-pyrazole]-5'(1'*H*)-on (3h)



3h was obtained after flash chromatography (SiO_2, *n*-pentane/EtOAc 5:1) as off-white solid (77 mg, 90%, d.r. >20:1). **Molecular formular:** $C_{15}H_{15}N_3O_3$. **Molecular mass:** 285.30 g mol^{-1}. $\mathbf{R_f}$ (*n*-pentane/EtOAc 5:1) = 0.23. **Mp:** 101-104 °C. **HPLC:** IA, 7/3 *n*-heptane/EtOH, 0.7 mL/min, λ = 254 nm, *τMinor* = 13.4 min, *τMajor* = 10.1 min. **OR:** $[\alpha]_D^{20}$ = −118.6 (*c* = 0.5, $CHCl_3$, 93% *ee*). **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 1.93 (s, 3 H, CH_3), 3.30 (s, 3 H, CH_3), 4.22 (dd, *J* = 4.2 Hz, *J* = 10.3 Hz, 1 H, C*H*), 4.75 (dd, *J* = 4.2 Hz, *J* = 15.1 Hz, 1 H, CH_2), 4.88 (d, *J* = 1.1 Hz, 1 H, CH_{ol}), 5.22 (dd, *J* = 10.3 Hz, *J* = 15.1 Hz, 1 H, CH_2), 5.67 (d, *J* = 1.3 Hz, 1 H, CH_{ol}), 7.24-7.28 (m, 1 H, CH_{Ar}), 7.35-7.40 (m, 1 H, CH_{Ar}), 7.56-7.60 (m, 2 H, CH_{Ar}) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 13.4 (q), 31.4 (q), 44.9 (d), 64.3 (s), 74.8 (t), 106.7 (t), 122.2 (d), 124.4 (d), 129.3 (d), 130.2 (d), 139.1 (s), 140.7 (s), 145.8 (s), 161.1 (s), 174.1 (s) ppm. **IR** (ATR): $\tilde{\nu}$ = 3744, 3305, 3119, 3033, 2989, 2920, 2472, 2324, 2170, 2059, 1989, 1958, 1809, 1677, 1639, 1551, 1469, 1422, 1377, 1304, 1263, 1230, 1169, 1111, 1084, 1041, 1013, 958, 895, 787, 731, 679, 658 cm^{-1}. **MS (EI$^+$)** *m/z* (%): 286.1 (22), 285.0 (100) $[M]^+$ = $[C_{15}H_{15}N_3O_3]^+$, 239.1 (32) $[M-HNO_2]^+$ = $[C_{15}H_{14}N_2O]^+$, 238.1 (60), 237.1 (23), 210.1 (21), 209.0 (43), 197.0 (22), 196.0 (79), 195.0 (44), 182.0 (15), 181.0 (13), 180.0 (13), 169.0 (17), 168.0 (20), 167.0 (33), 166.0 (23), 164.9 (23), 153.0 (21), 151.9 (30), 141.0 (28), 140.0 (15), 138.9 (26), 128.0 (15), 127.0 (15), 114.9 (42). **MS (CI$^+$, methane)** *m/z* (%): 314.1 (12) $[M+C_2H_5]^+$ = $[C_{17}H_{20}N_3O_3]^+$, 286.1 (100) $[M+H]^+$ = $[C_{15}H_{16}N_3O_3]^+$. **HR-MS (ESI$^+$)**: calc. for $[M+Na]^+$ = $[C_{15}H_{15}NaN_3O_3]^+$: 308.1006; found: 308.1000.

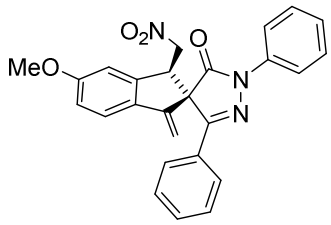
(2*R*,3*R*)-1'-Methyl-1-methylene-3-(nitromethyl)-3'-(trifluoromethyl)-1,3-dihydrospiro[indene-2,4'-pyrazole]-5'(1'*H*)-on (3i)



3i was obtained after flash chromatography (SiO_2, *n*-pentane/EtOAc 6:1) as off-white solid (99 mg, 97%, d.r. 10:1). **Molecular formular:** $C_{15}H_{12}F_3N_3O_3$. **Molecular mass:** 339.27 g mol^{-1}. $\mathbf{R_f}$ (*n*-pentane/EtOAc 6:1) = 0.46. **Mp:** 126-130°C. **SFC:** R-Whelk, CO_2/EtOH 97:3, 4.0 mL/min, λ = 254 nm, *τMinor* = 3.4 min, *τMajor* = 3.8 min. **OR:** $[\alpha]_D^{20}$ = −64.2 (*c* = 0.5, $CHCl_3$, 42% *ee*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 3.41 (s, 3 H, CH_3, a), 3.53 (s, 0.3 H, CH_3, b), 4.50 (dd, *J* = 3.4 Hz, *J* = 11.2 Hz, 1.0 H, C*H*, a), 4.54-4.57 (m, 0.1 H, C*H*, b), 4.64 (dd, *J* = 11.0 Hz, *J* = 15.2 Hz, 0.1 H, CH_2, b), 4.79 (dd, *J* = 3.5 Hz, *J* = 15.4 Hz, 1 H, CH_2, a), 4.93 (d, *J* = 1.9 Hz, 1 H, CH_{ol}, a), 4.94 (d, *J* = 1.9 Hz, 0.1 H,

CH_{ol}, b), 5.00 (dd, J = 4.1 Hz, J = 15.3 Hz, 0.1 H, CH_2, b), 5.27 (dd, J = 11.3 Hz, J = 15.5 Hz, 1.0 H, CH_2, a), 5.72 (d, J = 1.9 Hz, 1.1 H, CH_{ol}, a+b), 7.17-7.31 (m, 1.5 H, CH_{Ar}), 7.35-7.45 (m, 2.2 H, CH_{Ar}), 7.53-7.64 (m, 2 H, CH_{Ar}) ppm. **^{13}C{^{19}F} NMR** (101 MHz, $CDCl_3$, major diastereomer): δ = 32.1 (q), 44.8 (d), 61.7 (s), 72.8 (t), 107.1 (t), 119.3 (s), 122.4 (d), 124.4 (d), 129.6 (d), 130.5 (d), 138.4 (s), 139.9 (s), 144.3 (s), 149.5 (s), 173.7 (s) ppm. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ = −63.6 (s) ppm. **IR** (ATR): $\tilde{\nu}$ = 3013, 2925, 2662, 2333, 2090, 2013, 1811, 1719, 1638, 1550, 1472, 1409, 1472, 1409, 1340, 1247, 1170, 1133, 1026, 970, 903, 861, 781, 744, 714 cm^{-1}. **MS (EI$^+$)** *m/z* (%): 339.0 (24) $[M]^+ = [C_{15}H_{12}F_3N_3O_3]^+$, 293.1 (23), 292.0 (100) $[M-HNO_2]^+ = [C_{15}H_{11}F_3N_2O]^+$, 263.0 (14), 250.0 (40), 249.0 (22), 200.9 (11). **MS (CI$^+$, methane)** *m/z* (%): 286.1 (100) $[M+H]^+ = [C_{15}H_{13}F_3N_3O_3]^+$. **HR-MS (ESI$^+$)**: calc. for $[M+Na]^+ = [C_{15}H_{12}F_3NaN_3O_3]^+$: 362.0723; found: 362.0705.

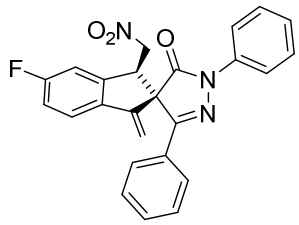
(2*R*,3*R*)-5-Methoxy-1-methylene-3-(nitromethyl)-1',3'-diphenyl-1,3-dihydrospiro[indene-2,4'-pyrazole]-5'(1'*H*)-on (3j)



3j was obtained after flash chromatography (SiO_2, *n*-pentane/EtOAc 6:1) as off-white solid (120 mg, 91%, d.r. 10:1). **Molecular formular:** $C_{26}H_{21}N_3O_4$. **Molecular mass:** 439.47 g mol^{-1}. **R_f** (*n*-pentane/EtOAc 6:1) = 0.27. **Mp:** 146-150 °C. **HPLC:** IB, 7/3 *n*-heptane/EtOH, 1.0 mL/min, λ = 254 nm, τ*Minor* = 5.6 min, τ*Major* = 9.6 min. **OR:** $[\alpha]_D^{20}$ = +3.33 (c = 0.5, $CHCl_3$, 92% *ee*). **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 3.87 (s, 3.2 H, CH_3, a+b), 4.46-4.50 (m, 0.1 H, CH_2, b), 4.49 (dd, J = 4.0 Hz, J = 10.6 Hz, 1.0 H, CH, a), 4.74-4.69 (m, 0.2 H, CH, CH_2, b), 4.86 (dd, J = 4.0 Hz, J = 15.0 Hz, 1.0 H, CH_2, a), 4.94 (d, J = 1.6 Hz, 1.0 H, CH_{ol}, a), 4.95 (d, J = 1.6 Hz, 0.1 H, CH_{ol}, b), 5.35 (dd, J = 10.7 Hz, J = 15.0 Hz, 1.0 H, CH_2, a), 5.56 (d, J = 1.6 Hz, 1.0 H, CH_{ol}, a), 5.59 (d, J = 1.6 Hz, 0.2 H, CH_{ol}, b), 6.72-6.74 (m, 0.1 H, CH_{Ar}), 6.75 (d, J = 1.4 Hz, 1.0, CH_{Ar}), 7.02 (dd, J = 1.8 Hz, J = 8.6 Hz, 1.0 H, CH_{Ar}), 7.22-7.30 (m, 1.6 H, CH_{Ar}), 7.32-7.38 (m, 2.0 H, CH_{Ar}), 7.57-7.65 (m, 3.0 H, CH_{Ar}), 7.94-8.00 (m, 1.9 H, CH_{Ar}), 8.05 (d, J = 7.8 Hz, 0.2 H, CH_{Ar}) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$, major diastereomer): δ = 46.3 (d), 55.9 (q), 65.0 (s), 73.4 (t), 104.2 (t), 109.1 (d), 116.4 (d), 119.8 (d, 2 C), 123.7 (d), 125.8 (d), 127.0 (d, 2 C), 129.1 (d, 4 C), 129.4 (s), 130.8 (d), 131.7 (s), 137.9 (s), 142.7 (s), 146.5 (s), 160.4 (s), 161.8 (s), 173.1 (s) ppm. **IR** (ATR): $\tilde{\nu}$ = 3843, 3641, 3453, 3317, 2940, 2701, 2492, 2294, 2051, 1988, 1910, 1736, 1596, 1549, 1489, 1367, 1218, 1138, 1085, 1023, 846, 757, 686 cm^{-1}. **MS (EI$^+$)** *m/z* (%): 440.1 (16), 439.1 (49) $[M]^+ = [C_{26}H_{21}N_3O_4]^+$, 394.2 (10), 393.2 (35) $[M-HNO_2]^+ = [C_{26}H_{20}N_2O_2]^+$, 392.2 (38), 391.2 (12), 288.1 (10), 287.1 (29), 273.1 (18), 260.1 (21), 259.1 (19), 258.1 (13), 245.2 (12), 231.1(13), 230.2 (15), 215.2 (24), 202.1 (18), 199.2 (25), 189.1 (11), 171.1 (14), 128.1 (26), 127.1 (13), 119.1 (18), 115.1 (11), 105.2 (13), 91.2 (43), 77.2 (100). **MS**

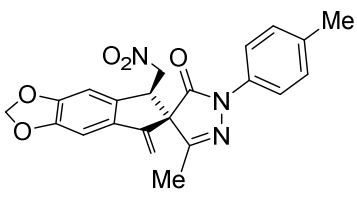
(CI$^+$, methane) *m/z* (%): 468.1 (10) $[M+C_2H_5]^+$ = $[C_{28}H_{26}N_3O_4]^+$, 440.1 (100) $[M+H]^+$ = $[C_{26}H_{22}N_3O_4]^+$. **HR-MS (ESI$^+$)**: calc. for $[M+Na]^+$ = $[C_{26}H_{21}NaN_3O_4]^+$: 462.1424; found: 462.1421.

(2*R*,3*R*)-5-Fluoro-1-methylene-3-(nitromethyl)-1',3'-diphenyl-1,3-dihydrospiro[indene-2,4'-pyrazole]-5'(1'*H*)-on (3k)



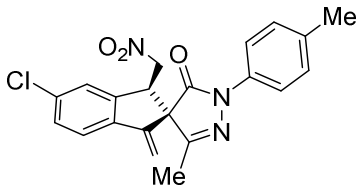
3k was obtained after flash chromatography (SiO_2, *n*-pentane/EtOAc 6:1) as off-white solid (127 mg, 99%, d.r. 10:1). **Molecular formular:** $C_{25}H_{18}FN_3O_3$. **Molecular mass:** 427.44 g mol^{-1}. **R_f** (*n*-pentane/EtOAc 6:1) = 0.54. **Mp:** 142-146 °C. **HPLC:** IA, 7/3 *n*-heptane/EtOH, 0.7 mL/min, λ = 254 nm, τ*Minor* = 13.2 min, τ*Major* = 10.0 min. **OR:** $[\alpha]_D^{20}$ = +12.9 (*c* = 0.5, $CHCl_3$, 96% *ee*). **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 4.50-4.43 (m, 0.1 H, CH_2, b), 4.52 (dd, *J* = 3.8 Hz, *J* = 10.6 Hz, 1.0 H, C*H*, a), 4.73 (dd, *J* = 4.8 Hz, *J* = 15.4 Hz, 0.3 H, CH_2, b), 4.73 (dd, *J* = 5.1 Hz, *J* = 10.1 Hz, 0.1 H, C*H*, b), 5.05 (d, *J* = 1.5 Hz, 1.0 H, CH_{ol}, a), 5.08 (d, *J* = 1.6 Hz, 0.1 H, CH_{ol}, b), 5.32 (dd, *J* = 10.5 Hz, *J* = 15.0 Hz, 1.0 H, CH_2, a), 5.66 (d, *J* = 1.7 Hz, 1.0 H, CH_{ol}, a), 5.71 (d, *J* = 1.7 H, 0.1 H, CH_{ol}, b), 6.95-7.01 (m, 1.1 H, CH_{Ar}), 7.18 (dt, *J* = 2.3 Hz, *J* = 8.6 Hz, 1.1 H, CH_{Ar}), 7.22-7.32 (m, 1.7 H, CH_{Ar}), 7.32-7.39 (m, 2.0 H, CH_{Ar}), 7.39-7.55 (m, 3.3 H, CH_{Ar}), 7.55-7.63 (m, 1.9 H, CH_{Ar}), 7.67 (d, *J* = 5.1 Hz, *J* = 8.6 Hz, 1.0 H, CH_{Ar}) ppm. **^{13}C{^{19}F} NMR** (101 MHz, $CDCl_3$, major diastereomer): δ = 46.1 (d), 65.0 (s), 73.1 (t), 106.4 (t), 111.8 (d), 117.4 (d), 119.9 (d, 2 C), 124.1 (d), 126.6 (d), 127.0 (d, 2 C), 129.1 (d, 4 C), 129.3 (s), 130.9 (d), 135.0 (s), 137.8 (s), 143.0 (s), 145.9 (s), 160.0 (s), 164.2 (s), 172.7 (s) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = −109.37 (dd, *J* = 8.3 Hz, *J* = 13.5 Hz) ppm. **IR** (ATR): $\tilde{\nu}$ = 3846, 3646, 3393, 3064, 2925, 2695, 2467, 2301, 2106, 1898, 1711, 1550, 1488, 1374, 1305, 1232, 1134, 892, 758, 683 cm^{-1}. **MS (EI$^+$)** *m/z* (%): 428.0 (49), 427.0 (100) $[M]^+$ = $[C_{25}H_{18}FN_3O_3]^+$, 381.1 (31), 380.0 (26), 379.0 (14), 351.1 (18), 275.1 (18), 262.1 (31), 261.1 (24), 260.0 (11), 248.1 (30), 247.0 (12), 246.0 (14), 233.1 (17), 187.0 (10), 159.1 (22), 133.1 (13), 105.1 (18), 91.1 (28), 77.2 (29). **MS (CI$^+$, methane)** *m/z* (%): 456.1 (3) $[M+C_2H_5]^+$ = $[C_{27}H_{23}FN_3O]^+$, 428.1 (34) $[M+H]^+$ = $[C_{25}H_{19}FN_3O]^+$. **HR-MS (ESI$^+$)**: calc. for $[M+H]^+$ = $[C_{25}H_{19}FN_3O_3]^+$: 428.1405; found: 428.1398.

(6*R*, 7*R*)-3'-Ethyl-5-methylene-7-(nitromethyl)-1'-(*p*-tolyl)-5,7-dihydrospiro[indeneo[5,6*d*][1,3]dioxole-6,4'-pyrazole]-5'(1'*H*)-on (3l)



3l was obtained after flash chromatography (SiO_2, *n*-pentane/EtOAc 6:1) as colorless solid (33 mg, 27%, d.r. 15:1). **Molecular formular:** $C_{22}H_{19}N_3O_5$. **Molecular mass:** 405.41 g mol^{-1}. $\mathbf{R_f}$ (*n*-pentane/EtOAc 6:1) = 0.19. **Mp:** 141-144 °C. **HPLC:** AD, 6/4 *n*-heptane/*i*-PrOH, 1.0 mL/min, λ = 254 nm, τ*Minor* = 15.5 min, τ*Major* = 9.3 min. **OR:** $[\alpha]_D^{20}$ = −80.9 (*c* = 0.4, $CHCl_3$, 93% *ee*). **^{1}H NMR** (600 MHz, $CDCl_3$, major diastereomer): δ = 2.02 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 4.16 (dd, *J* = 4.4 Hz, *J* = 10.0 Hz, 1 H, C*H*), 4.69 (dd, *J* = 4.4 Hz, *J* = 15.1 Hz, 1 H, CH_2), 4.81 (d, *J* = 1.4 Hz, 1 H, CH_{ol}), 5.22 (dd, *J* = 10.0 Hz, *J* = 15.1 Hz, 1 H, CH_2), 5.44 (d, *J* = 1.5 H, 1 H, CH_{ol}), 6.04 (dd, *J* = 0.8 Hz, *J* = 6.5 Hz, 2 H, CH_2), 6.67 (s, 1 H, CH_{Ar}), 6.96 (s, 1 H, CH_{Ar}), 7.20 (d, *J* = 8.3 Hz, 2 H, CH_{Ar}), 7.70 (d, *J* = 8.5 Hz, 2 H, CH_{Ar}), ppm. **^{13}C NMR** (151 MHz, $CDCl_3$, major diastereomer): δ = 13.6 (q), 21.1 (q), 44.8 (d), 66.1 (s), 73.8 (t), 101.7 (d), 102.3 (t), 104.1 (d), 104.6 (t), 119.7 (d, 2 C), 129.6 (d, 2 C), 133.3 (s), 134.8 (s), 135.3 (s), 135.4 (s), 145.5 (s), 149.6 (s), 150.4 (s), 161.5 (s), 172.2 (s) ppm. **IR** (ATR): $\tilde{\nu}$ = 3852, 3643, 3380, 2918, 2714, 2471, 2264, 2062, 1901, 1697, 1624, 1500, 1292, 1112, 1032, 935, 860, 668 cm^{-1}. **MS (EI$^+$)** *m*/*z* (%): 405.1 (8) $[M]^+ = [C_{22}H_{19}N_3O_5]^+$, 211.0 (15), 185.0 (13), 153.0 (22), 152.0 (25), 141.0 (10), 139.0 (19), 133.0 (12), 132.0 (12), 128.1 (16), 127.0 (31), 126.0 (18), 115.1 (20), 106.1 (12), 105.1 (23), 104.0 (20), 91.1 (100), 78.2 (15), 77.2 (23), 65.2 (41), 63.2 (12). **MS (CI$^+$, methane)** *m*/*z* (%): 434.2 (8) $[M+C_2H_5]^+ = [C_{24}H_{24}N_3O_5]^+$, 406.1 (100) $[M+H]^+ = [C_{22}H_{20}N_3O_5]^+$. **HR-MS (ESI$^+$)**: calc. for $[M+Na]^+ = [C_{22}H_{19}NaN_3O_5]^+$: 428.1217; found: 428.1214.

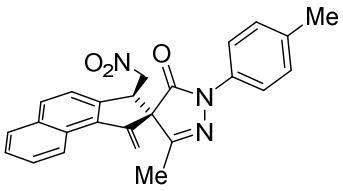
(2*R*,3*R*)-5-Chloro-3'-methyl-1-methylene-3-(nitromethyl)-1'-(*p*-tolyl)-1,3-dihydrospiro[indene-2,4'-pyrazole]-5'(1'*H*)-on (3m)



3m was obtained after flash chromatography (SiO_2, *n*-pentane/EtOAc 6:1) as colorless solid (104 mg, 87%, d.r. 10:1). **Molecular formular:** $C_{21}H_{18}ClN_3O_3$. **Molecular mass:** 395.84 g mol^{-1}. $\mathbf{R_f}$ (*n*-pentane/EtOAc 6:1) = 0.51. **Mp:** 61-65 °C. **HPLC:** IC, 7/3 *n*-heptane/*i*-PrOH, 1.0 mL/min, λ = 254 nm, τ*Minor* = 7.7 min, τ*Major* = 21.9 min. **OR:** $[\alpha]_D^{20}$ = −41.6 (*c* = 0.5, $CHCl_3$, 99% *ee*). **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 1.94 (s, 0.3 H, CH_3, b), 2.04 (s, 3.0 H, CH_3, a), 2.35 (s, 3.0 H, CH_3, a), 2.36 (s, 3.0 H, CH_3, b), 4.28 (dd, *J* = 4.3 Hz, *J* = 10.1 Hz, 1.0 H, C*H*, a), 4.55 (dd, *J* = 8.8 Hz, *J* = 14.5 Hz, 0.1 H, CH_2, b), 4.65-4.68 (m, 0.1 H, C*H*, b), 4.77 (dd, *J* = 4.3 Hz, *J* = 15.2 Hz, 1.0 H, CH_2, a), 4.87 (dd, *J* = 6.1 Hz, *J* = 14.5 Hz, 0.1 H, CH_2, b), 4.99 (d, *J* = 1.5 Hz, 1.0 H, CH_{ol}, a), 5.01 (d, *J* = 1.2 Hz, 0.1 H, CH_{ol}, b), 5.25 (dd, *J* = 10.2 Hz, *J* = 15.2 Hz, 1.0 H, CH_2, a), 5.68 (d, *J* = 1.5 Hz, 1.2 H, CH_{ol}, a+b), 7.20 (d, *J* = 8.4 Hz, 2.0 H, CH_{Ar}), 7.22-7.25 (m, 0.4 H, CH_{Ar}), 7.25-7.27 (m, 1.3 H, CH_{Ar}), 7.37 (dd, *J* = 1.1 Hz, *J* = 8.3 Hz, 1.1 H, CH_{Ar}), 7.49-7.54 (m, 1.2 H, CH_{Ar}), 7.70 (d, *J* = 8.5 Hz, 2.0 H, CH_{Ar}), 7.78 (d, *J* = 8.5 Hz, 0.2 H, CH_{Ar}) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$, major diastereomer): δ = 13.7 (q), 21.1 (q), 44.8 (d), 65.9 (s), 73.4 (t), 107.7 (t), 119.7 (d, 2 C), 123.3 (d), 124.8 (d), 129.6 (d), 129.9 (d, 2 C),

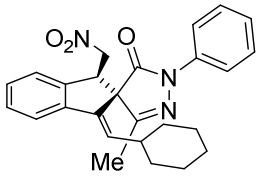
135.2 (s), 135.5 (s), 136.2 (s), 137.6 (s), 142.3 (s), 144.8 (s), 161.1 (s), 171.9 (s) ppm. **IR** (ATR): $\tilde{\nu}$ = 3863, 3652, 3437, 2927, 2716, 2488, 2297, 2092, 1902, 1700, 1543, 1367, 1295, 1212, 1089, 1000, 892, 821, 685 cm^{-1}. **MS (EI$^+$)** *m/z* (%): 395.1 (10) [M, $^{35}Cl]^+$ = $[C_{21}H_{18}ClN_3O_3]^+$, 181.0 (12), 174.9 (24), 166.0 (18), 165.0 (40), 152.0 (27), 150.9 (13), 148.9 (16), 140.0 (16), 139.0 (44), 132.0 (12), 128.0 (13), 127.0 (12), 126.0 (13), 106.1 (24), 105.0 (37), 104.0 (20), 91.1 (100), 78.2 (15), 77.1 (17), 65.2 (40). **MS (CI$^+$, methane)** *m/z* (%): 424.1 (11) [M+C_2H_5, $^{35}Cl]^+$ = $[C_{23}H_{23}ClN_3O_3]^+$, 398.1 (41) [M+H, $^{37}Cl]^+$ = $[C_{22}H_{19}ClN_3O_3]^+$, 396.1 (100) [M+H, $^{35}Cl]^+$ = $[C_{22}H_{19}ClN_3O_3]^+$. **HR-MS (ESI$^+$)**: calc. for [M+Na, $^{35}Cl]^+$ = $[C_{21}H_{18}ClNaN_3O_3]^+$: 418.0929; found: 418.0914.

(2*R*,3*R*)-3'-Methyl-1-methylene-3-(nitromethyl)-1'-(*p*-tolyl)-1,3-dihydrospiro[cyclopenta-[*a*]naphthalen-2,4'-pyrazole]-5'(1'*H*)-on (3n)



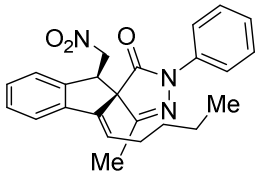
3n was obtained after flash chromatography (SiO_2, *n*-pentane/EtOAc 6:1) as colorless solid (66 mg, 54%, d.r. 10:1). **Molecular formular:** $C_{25}H_{21}N_3O_3$. **Molecular mass:** 411.46 g mol^{-1}. **R_f** (*n*-pentane/EtOAc 6:1) = 0.32. **Mp:** 165-170 °C. **HPLC:** AS, 9/1 *n*-heptane/EtOH, 0.7 mL/min, λ = 254 nm, *τMinor* = 20.4 min, *τMajor* = 13.8 min. **OR:** $[\alpha]_D^{20}$ = −167.7 (*c* = 0.5, $CHCl_3$, 99% *ee*). **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 1.91 (s, 0.3 H, C*H*$_3$, b), 2.01 (s, 3.0 H, C*H*$_3$, b), 2.36 (s, 3.0 H, C*H*$_3$, a), 2.37 (s, 3.0 H, C*H*$_3$, a), 4.39 (dd, *J* = 4.1 Hz, *J* = 10.1 Hz, 1.0 H, C*H*, a), 4.57 (dd, *J* = 8.7 Hz, *J* = 14.5 Hz, 0.1 H, C*H*$_2$, b), 4.79-4.83 (m, 0.1 H, C*H*, b), 4.84 (dd, *J* = 4.1 Hz, *J* = 15.2 Hz, 1.0 H, C*H*$_2$, a), 4.98 (dd, *J* = 6.2 Hz, *J* = 14.6 Hz, 0.1 H, C*H*$_2$, b), 5.23 (s, 1.0 H, C*H*$_{ol}$, a), 5.27 (s, 0.1 H, C*H*$_{ol}$, b), 5.31 (dd, *J* = 10.1 Hz, *J* = 15.1 Hz, 1.0 H, C*H*$_2$, a), 6.09 (s, 0.1 H, C*H*$_{ol}$, b), 6.13 (s, 1.0 H, C*H*$_{ol}$, a), 7.18-7.25 (m, 2.2 H, C*H*$_{Ar}$), 7.29-7.34 (m, 0.2 H, C*H*$_{Ar}$), 7.36 (d, *J* = 8.4 Hz, 1.0 H, C*H*$_{Ar}$), 7.59 (t, *J* = 7.5 Hz, 1.0 H, C*H*$_{Ar}$), 7.65 (t, *J* = 7.6 Hz, 1.1 H, C*H*$_{Ar}$), 7.74 (d, *J* = 8.3 Hz, 1.9 H, C*H*$_{Ar}$), 7.84 (d, *J* = 8.3 Hz, 0.2 H, C*H*$_{Ar}$), 7.90 (d, *J* = 8.4 Hz, 1.1 H, C*H*$_{Ar}$), 7.95 (d, *J* = 8.2 Hz, 1.1 H, C*H*$_{Ar}$) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$, major diastereomer): δ = 13.9 (q), 21.2 (q), 45.4 (d), 66.9 (s), 73.9 (t), 111.3 (t), 119.7 (d, 2 C), 121.3 (d), 124.9 (d), 126.8 (d), 128.4 (d), 129.6 (d, 3 C), 129.6 (s), 131.9 (d), 134.0 (s), 134.4 (s), 135.4 (s, 2 C), 140.2 (s), 146.5 (s), 161.2 (s), 172.2 (s) ppm. **IR** (ATR): $\tilde{\nu}$ = 3865, 3656, 3385, 2925, 2724, 2465, 2297, 2059, 1912, 1781, 1699, 1614, 1541, 1364, 1307, 1212, 1132, 1013, 964, 822, 751 cm^{-1}. **MS (EI$^+$)** *m/z* (%): 411.1 (17) $[M]^+$ = $[C_{25}H_{21}N_3O_3]^+$, 217.1 (14), 202.1 (19), 191.1 (11), 190.0 (17), 189.0 (32), 165.0 (10), 119.0 (14), 106.1 (14), 105.1 (24), 104.1 (16), 91.1 (100), 78.2 (12), 77.1 (13), 65.3 (33). **MS (CI$^+$, methane)** *m/z* (%): 439.5 (12) $[M+C_2H_5]^+$ = $[C_{27}H_{26}N_3O_3]^+$, 411.6 (100) $[M+H]^+$ = $[C_{25}H_{22}N_3O_3]^+$. **HR-MS (ESI$^+$)**: calc. for $[M+Na]^+$ = $[C_{25}H_{21}NaN_3O_3]^+$: 434.1475; found: 434.1472.

(2*R*,3*R*,*Z*)-1-(Cyclohexylmethylene)-3'-methyl-3-(nitromethyl)-1'-phenyl-1,3-dihydrospiro-[indene-2,4'-pyrazole]-5'(1'*H*)-one (3o)



3o was obtained after flash chromatography (SiO_2, *n*-pentane/EtOAc 4:1) as off-white solid (105 mg, 81%, d.r. 7:1). **Molecular formular:** $C_{26}H_{27}N_3O_3$. **Molecular mass:** 429.52 g mol^{-1}. **R_f** (*n*-pentane/EtOAc 6:1) = 0.55. **Mp:** 133-139 °C. **HPLC:** AD, 6/4 *n*-heptane/*i*-PrOH, 1.0 mL/min, λ = 254 nm, τ*Minor* = 13.5 min, τ*Major* = 10.9 min. **OR:** $[\alpha]_D^{20}$ = −113.0 (*c* = 0.5, $CHCl_3$, 91% *ee*). **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 0.78-0.92 (m, 2.2 H, CH_2), 0.98-1.12 (m, 5.1 H, CH_2), 1.47-1.68 (m, 7.2 H, CH_2), 1.80-1.88 (m, 1.3 H, C*H*), 1.95 (s, 0.4 H, CH_3, b), 2.01 (s, 3.0 H, CH_3, a), 4.26 (dd, *J* = 4.3 Hz, *J* = 9.8 Hz, 1.0 H, C*H*, a), 4.49 (dd, *J* = 8.0 Hz, *J* = 14.5 Hz, 0.2 H, CH_2, b), 4.64 (dd, *J* = 4.3 Hz, *J* = 15.5 Hz, 1.0 H, CH_2, a), 4.69 (t, *J* = 7.3 Hz, 0.2 H, C*H*, b), 4.86 (dd, *J* = 6.7 Hz, *J* = 14.5 Hz, 0.2 H, CH_2, b), 5.23 (dd, *J* = 9.8 Hz, *J* = 15.5 Hz, 1.0 H, CH_2, a), 6.03 (d, *J* = 10.6 Hz, 0.2 H, CH_{ol}, b), 6.07 (d, *J* = 10.8 Hz, 1.0 H, CH_{ol}, a), 7.14 (d, *J* = 7.6 Hz, 0.3 H, CH_{Ar}), 7.19-7.25 (m, 2.2 H, CH_{Ar}), 7.29 (dt, *J* = 0.6 Hz, *J* = 7.6 Hz, 1.2 H, CH_{Ar}), 7.35 (t, *J* = 7.5 Hz, 1.2 H, CH_{Ar}), 7.38-7.47 (m, 2.3 H, CH_{Ar}), 7.48-7.54 (m, 1.1 H, CH_{Ar}) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$, major diastereomer): δ = 13.5 (q), 25.4 (t), 25.8 (t), 25.9 (t), 32.1 (t), 32.9 (t), 37.9 (d), 46.8 (d), 63.6 (s), 74.8 (t), 119.7 (d, 2 C), 121.1 (d), 124.6 (d), 125.7 (d), 129.1 (d, 3 C), 129.3 (d), 132.7 (d), 134.8 (s), 137.7 (s), 138.7 (s), 139.0 (s), 140.9 (s), 161.5 (s), 172.8 (s) ppm. **IR** (ATR): $\tilde{\nu}$ = 3863, 3654, 3401, 2925, 2476, 2273, 2080, 1908, 1704, 1547, 1367, 1294, 1215, 1113, 999, 896, 827, 754 cm^{-1}. **MS (EI$^+$)** *m*/*z* (%): 429.1 (4) $[M]^+ = [C_{26}H_{27}N_3O_3]^+$, 287.1 (23), 211.1 (24), 187.0 (33), 181.1 (12), 180.0 (12), 179.0 (19), 178.0 (24), 167.0 (22), 166.0 (16), 165.0 (41), 155.1 (10), 153.0 (20), 152.0 (24), 141.1 (31), 129.1 (11), 128.0 (17), 127.0 (10), 119.0 (17), 107.1 (10), 105.1 (27), 93.2 (13), 92.1 (23), 91.1 (60), 83.2 (14), 82.2 (14), 81.2 (27), 79.2 (15), 78.2 (11), 77.1 (100), 67.2 (39), 65.2 (14), 55.2 (40). **MS (CI$^+$, methane)** *m*/*z* (%): 458.2 (9) $[M+C_2H_5]^+ = [C_{28}H_{32}N_3O_3]^+$, 430.2 (100) $[M+H]^+ = [C_{26}H_{28}N_3O_3]^+$. **HR-MS (ESI$^+$)**: calc. for $[M+Na]^+ = [C_{26}H_{27}NaN_3O_3]^+$: 452.1945; found: 452.1943.

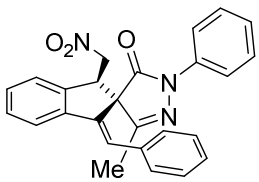
(1*R*,2*R*,*Z*)-3'-Methyl-1-(nitromethyl)-3-pentylidene-1'-phenyl-1,3-dihydrospiro[indene-2,4'-pyrazole]-5'(1'*H*)-one (3p)



3p was obtained after flash chromatography (SiO_2, *n*-pentane/EtOAc 4:1) as yellow oil (72 mg, 60%, d.r. 6:1). **Molecular formular:** $C_{24}H_{25}N_3O_3$. **Molecular mass:** 403.48 g mol^{-1}. **R_f** (*n*-pentane/EtOAc

6:1) = 0.56**. SFC:** R-Whelk, CO_2/MeOH 99:1 zu 70:30, 4.0 mL/min, λ = 214.9 nm, *τMinor* = 17.0 min, *τMajor* = 17.2 min. **OR:** $[\alpha]_D^{20} = -129.9$ (*c* = 0.4, $CHCl_3$, 92% *ee*). **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 0.80 (t, *J* = 7.4 Hz, 3 H, C*H*$_3$), 1.16-1.25 (m, 2 H, C*H*$_2$), 1.32-1.42 (m, 2 H, C*H*$_2$), 1.83-1.92 (m, 1 H, C*H*$_2$), 1.93-1.99 (m, 1 H, C*H*$_2$), 2.01 (s, 3 H, C*H*$_3$), 4.28 (dd, *J* = 4.3 Hz, *J* = 9.9 Hz, 1 H, C*H*), 4.65 (dd, *J* = 4.3 Hz, *J* = 15.5 Hz, 1 H, C*H*$_2$), 5.21 (dd, *J* = 9.8 Hz, *J* = 15.4 Hz, 1 H, C*H*$_2$), 6.25 (t, *J* = 7.6 Hz, 1 H, C*H*$_{ol}$), 7.21-7.24 (m, 2 H, C*H*$_{Ar}$), 7.30 (t, *J* = 7.4 Hz, 1 H, C*H*$_{Ar}$), 7.35 (t, *J* = 7.6 Hz, 1 H, C*H*$_{Ar}$), 7.42 (t, *J* = 7.9 Hz, 2 H, C*H*$_{Ar}$), 7.51 (d, *J* = 7.8 Hz, 1 H, C*H*$_{Ar}$), 7.79-7.84 (m, 2 H, C*H*$_{Ar}$). **^{13}C NMR** (151 MHz, $CDCl_3$, major diastereomer): δ = 13.6 (q), 13.9 (q), 22.5 (t), 27.5 (t), 31.3 (t), 46.9 (d), 63.8 (s), 74.8 (t), 119.6 (d, 2 C), 121.0 (d), 124.6 (d), 125.7 (d), 127.6 (d), 129.1 (d, 3 C), 129.4 (d), 136.4 (s), 137.7 (s), 138.9 (s), 140.8 (s), 160.8 (s), 172.4 (s) ppm. **IR** (ATR): $\tilde{\nu}$ = 3074, 2924, 2856, 2324, 2094, 1999, 1954, 1708, 1595, 1546, 1495, 1460.1411, 1360, 1284, 1234, 1203, 1119, 1061, 1027, 993, 970, 910, 878, 857, 757, 694, 656 cm^{-1}. **MS (EI$^+$)** *m*/*z* (%): 403.1 (18) $[M]^+ = [C_{24}H_{25}N_3O_3]^+$, 357.1 (21), 355.1 (10), 313.1 (17), 299.0 (13), 287.0 (19), 272.0 (23), 271.0 (21), 259.1 (11), 195.1 (11), 194.0 (23), 187.0 (64), 181.0 (26), 180.0 (17), 179.0 (16), 178.0 (23), 168.0 (12), 167.0 (21), 166.0 (23), 165.0 (54), 155.1 (15), 154.0 (17), 153.0 (45), 152.0 (51), 151.0 (0), 141.0 (32), 139.0 (14), 129.1 (12), 128.0 (24), 127.0 (19), 119.0 (18), 115.0 (30), 92.1 (16), 91.1 (46), 85.2 (10), 77.2 (100), 65.3 (10), 57.3 (24), 56.2 (12), 55.2 (24), 51.2 (13). **MS (CI$^+$, methane)** *m*/*z* (%): 432.2 (16) $[M+C_2H_5]^+ = [C_{26}H_{30}N_3O_3]^+$, 404.2 (100) $[M+H]^+ = [C_{24}H_{26}N_3O_3]^+$. **HR-MS (ESI$^+$)**: calc. for $[M+Na]^+ = [C_{24}H_{25}NaN_3O_3]^+$: 426.1788; found: 426.1788.

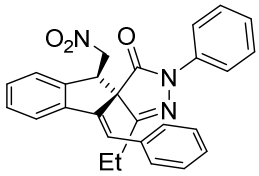
(2*R*,3*R*)-1-((*Z*)-Benzylidene)-3'-methyl-3-(nitromethyl)-1'-phenyl-1,3-dihydrospiro[indene-2,4'-pyrazole]-5'(1'*H*)-one (4a)



4a was obtained after flash chromatography (SiO_2, *n*-pentane/EtOAc 4:1) as off-white solid (127 mg, 99%, d.r. 10:1). **Molecular formular:** $C_{26}H_{21}N_3O_3$. **Molecular mass:** 423.47 g mol^{-1}. **Mp:** 156-158 °C. **R$_f$** (*n*-pentane/EtOAc 6:1) = 0.34. **HPLC:** IC, 7/3 *n*-heptane/EtOH, 1.0 mL/min, λ = 214 nm, *τMinor* = 44.6 min, *τMajor* = 31.9 min. **OR:** $[\alpha]_D^{20} = -168.5$ (*c* = 0.6, $CHCl_3$, 90% *ee*). **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 1.95 (s, 3 H, C*H*$_3$), 4.30 (dd, *J* = 5.3 Hz, *J* = 8.7 Hz, 1 H, C*H*), 4.66 (dd, *J* = 5.3 Hz, *J* = 15.1 Hz, 1 H, C*H*$_2$), 5.03 (dd, *J* = 8.8 Hz *J* = 15.1 Hz, 1 H, C*H*$_2$), 7.01-7.04 (m, 2 H, C*H*$_{Ar,}$ CH$_{ol}$), 7.06-7.10 (m, 3 H, C*H*$_{Ar}$), 7.17 (t, *J* = 7.4 Hz, 1 H, C*H*$_{Ar}$), 7.25-7.27 (m, 1 H, C*H*$_{Ar}$), 7.33 (t, *J* = 7.9 Hz, 2 H, C*H*$_{Ar}$), 7.37-7.40 (m, 2 H, C*H*$_{Ar}$), 7.44 (t, *J* = 7.6 Hz, 1 H, C*H*$_{Ar}$), 7.52 (d, *J* = 7.8 Hz, 2 H, C*H*$_{Ar}$), 7.68 (d, *J* = 7.7 Hz, 1 H, C*H*$_{Ar}$) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 14.1 (q), 47.6 (d), 64.9 (s), 75.0 (t), 119.5 (d, 2 C), 121.6 (d), 124.6 (d), 125.5 (d), 126.4 (d), 128.1 (d), 128.2 (d, 2 C), 128.3 (d, 2 C), 128.7 (d, 2 C), 129.6 (d), 130.0 (d), 135.3 (s), 137.5 (s), 138.2 (s), 139.7 (s), 141.1 (s), 160.2 (s),

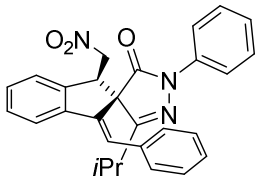
171.2 (s) ppm. **IR** (ATR): $\tilde{\nu}$ = 3852, 3391, 3019, 2948, 2669, 2323, 2101, 1946, 1701, 1596, 1548, 1491, 1368, 1292, 1195, 1122, 1005, 912, 836, 755, 695 cm^{-1}. **MS (EI$^+$, 70 eV)** *m/z* (%): 423.2 (100) $[M]^+ = [C_{26}H_{21}N_3O_3]^+$, 377.1 (17) $[M-NO_2]^+ = [C_{26}H_{21}N_2O]^+$, 367.1 (26), 334.1 (7), 284.1 (6), 272.1 (14), 271.1 (57), 258.1 (15), 243.1 (20), 229.1 (14), 228.1 (24), 217.1 (9), 216.1 (16), 215.1 (48), 203.0 (15), 202.0 (34), 189.0 (7), 165.0 (7), 119.0 (12), 105.0 (41). **MS (CI$^+$, methane)** *m/z* (%): 452.4 (17) $[M+C_2H_5]^+ = [C_{28}H_{26}N_3O_3]^+$, 424.3 (100) $[M+H]^+ = [C_{26}H_{22}N_3O_3]^+$. **EA:** calc. for $C_{26}H_{21}N_3O_3$: C 73.74%, H 5.00%, N 9.92%; found: C 74.04%, H 4.75%, N 10.16%.

(2*R*,3*R*)-1-((*Z*)-benzyliden)-3'-ethyl-3-(nitromethyl)-1'-phenyl-1,3-dihydrospiro[indene-2,4'-pyrazole]-5'(1'*H*)-one (4b)



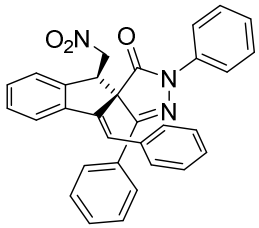
4b was obtained after flash chromatography (SiO_2, *n*-pentane/EtOAc 4:1) as off-white solid (109 mg, 83%, d.r. >20:1). **Molecular formular:** $C_{27}H_{23}N_3O_3$. **Molecular mass:** 437.50 g mol^{-1}. **Mp:** 142-147 °C. **R$_f$** (*n*-pentane/EtOAc 6:1) = 0.46. **HPLC:** AD, 6/4 *n*-heptane/*i*-PrOH, 1.0 mL/min, λ = 254 nm, τ*Minor* = 35.3 min, τ*Major* = 7.4 min. **OR:** $[\alpha]_D^{20} = -159.6$ (*c* = 0.5, $CHCl_3$, 93% *ee*). **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 1.11 (t, *J* = 7.3 Hz, 3 H, C*H*$_3$), 2.16-2.24 (m, 1 H, C*H*$_2$), 2.25-2.33 (m, 1 H, C*H*$_2$), 4.32 (dd, *J* = 5.5 Hz, *J* = 8.6 Hz, 1 H, C*H*), 4.66 (dd, *J* = 5.5 Hz, *J* = 15.0 Hz, 1 H, C*H*$_2$), 5.00 (dd, *J* = 8.8 Hz *J* = 15.0 Hz, 1 H, C*H*$_2$), 6.98-7.04 (m, 2 H, C*H*$_{Ar}$), 7.04-7.12 (m, 3 H, C*H*$_{Ar}$), 7.14-7.20 (m, 1 H, C*H*$_{Ar}$), 7.24-7.28 (m, 1 H, C*H*$_{Ar}$), 7.31-7.40 (m, 4 H, C*H*$_{Ar}$, C*H*$_{ol}$), 7.40-7.48 (m, 1 H, C*H*$_{Ar}$), 7.58 (t, *J* = 7.8 Hz, 2 H, C*H*$_{Ar}$), 7.67 (d, *J* = 7.7 Hz, 1 H, C*H*$_{Ar}$) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 9.3 (q), 21.6 (t), 47.9 (d), 65.0 (s), 75.1 (t), 119.4 (d, 2 C), 121.2 (d), 124.5 (d), 125.4 (d), 126.7 (d), 128.0 (d), 128.1 (d, 2 C), 128.2 (d, 2 C), 128.7 (d, 2 C), 129.6 (d), 130.5 (d), 135.3 (s), 137.7 (s), 138.4 (s), 139.8 (s), 141.2 (s), 164.0 (s), 171.4 (s) ppm. **IR** (ATR): $\tilde{\nu}$ = 3847, 3456, 2971, 2693, 2470, 2301, 2100, 1957, 1728, 1550, 1487, 1438, 1362, 1217, 1123, 1043, 913, 847, 754, 698 cm^{-1}. **MS (EI$^+$, 70 eV)** *m/z* (%): 438.1 (22), 437.0 (81) $[M]^+ = [C_{27}H_{23}N_3O_3]^+$, 391.2 (17) $[M-NO_2]^+ = [C_{27}H_{23}N_2O]^+$, 390.1 (27), 299.1 (12), 298.1 (13), 285.1 (60), 273.1 (13), 272.1 (17), 271.0 (16), 270.0 (21), 258.0 (11), 257.0 (28), 256.0 (27), 245.0 (20), 244.0 (25), 243.0 (36), 242.0 (28), 241.0 (21), 240.0 (16), 239.0 (16), 231.0 (15), 230.0 (22), 229.0 (20), 228.0 (43), 227.0 (24), 226.0 (21), 217.0 (20), 216.0 (32), 215.0 (100), 213.0 (16), 204.0 (16), 203.0 (32), 202.0 (70), 201.0 (10), 195.0 (11), 189.0 (19), 180.0 (12), 178.0 (11), 166.0 (14), 165.0 (21), 152.0 (13), 128.0 (10), 127.0 (11), 119.0 (24), 115.0 (14), 105.0 (46), 92.1 (12), 91.1 (77), 77.1 (93), 65.1 (10), 64.1 (10), 51.2 (15). **MS (CI$^+$, methane)** *m/z* (%): 466.1 (7) $[M+C_2H_5]^+ = [C_{29}H_{28}N_3O_3]^+$, 438.1 (100) $[M+H]^+ = [C_{27}H_{24}N_3O_3]^+$. **HR-MS (ESI$^+$):** calc. for $C_{27}H_{23}NaN_3O_3$: 460.1632, found: 460.1632.

(2*R*,3*R*)-1-((*Z*)-Benzyliden)-3'-isopropyl-3-(nitromethyl)-1'-phenyl-1,3-dihydrospiro[indene-2,4'-pyrazole]-5'(1'*H*)-one (4c)



4c was obtained after flash chromatography (SiO_2, *n*-pentane/EtOAc 4:1) as off-white solid (100 mg, 74%, d.r. >20:1). **Molecular formular:** $C_{28}H_{25}N_3O_3$. **Molecular mass:** 451.53 g mol^{-1}. **Mp:** 140-144 °C. **R_f** (*n*-pentane/EtOAc 6:1) = 0.47. **HPLC:** IA, 7/3 *n*-heptane/EtOH, 0.7 mL/min, λ = 254 nm, τ*Minor* = 28.0 min, τ*Major* = 14.7 min. **OR:** $[\alpha]_D^{20} = -59.6$ (*c* = 0.5, $CHCl_3$, 92% *ee*). **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 1.15 (d, *J* = 8.4 Hz, 3 H, CH_3), 1.28 (d, *J* = 6.8 Hz, 3 H, CH_3), 2.40-2.48 (m, 1 H, C*H*), 4.31 (dd, *J* = 5.6 Hz, *J* = 8.5 Hz, 1 H, C*H*), 4.55 (dd, *J* = 5.5 Hz, *J* = 15.1 Hz, 1 H, CH_2), 5.05 (dd, *J* = 8.6 Hz *J* = 15.1 Hz, 1 H, CH_2), 7.00-7.04 (m, 2 H, CH_{Ar}), 7.04-7.10 (m, 3 H, CH_{Ar}), 7.15 (t, *J* = 7.4 Hz, 1 H, CH_{Ar}), 7.25-7.29 (m, 1 H, CH_{Ar}), 7.32 (t, *J* = 8.0 Hz, 2 H, CH_{Ar}), 7.35 (s, 1 H, CH_{ol}), 7.38 (t, *J* = 7.5 Hz, 1 H, CH_{Ar}), 7.44 (t, *J* = 7.5 Hz, 1 H, CH_{Ar}), 7.52 (d, *J* = 8.5 Hz, 2 H, CH_{Ar}), 7.68 (d, *J* = 7.7 Hz, 1 H, CH_{Ar}) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 21.0 (q), 22.1 (q), 28.9 (d), 48,1 (d), 64.6 (s), 75.4 (t), 119.5 (d, 2 C), 121.5 (d), 124.8 (d), 125.3 (d), 126.7 (d), 127.9 (d), 128.1 (d, 2 C), 128.3 (d, 2 C), 128.7 (d, 2 C), 129.7 (d), 130.0 (d), 135.6 (s), 137.7 (s), 138.1 (s), 139.9 (s), 141.8 (s), 167.3 (s), 170.7 (s) ppm. **IR** (ATR): $\tilde{\nu}$ = 3846, 3453, 2931, 2666, 2309, 2095, 1705, 1554, 1487, 1362, 1218, 1084, 912, 867, 753, 693 cm^{-1}. **MS (EI$^+$, 70 eV)** *m/z* (%): 451.1 (27) $[M]^+ = [C_{28}H_{25}N_3O_3]^+$, 405.2 (15) $[M-NO_2]^+ = [C_{28}H_{25}N_2O]^+$, 313.1 (13), 299.1 (16), 271.1 (17), 270.1 (13), 245.0 (18), 244.0 (22), 243.0 (25), 242.0 (32), 241.0 (22), 240.0 (22), 239.0 (19), 231.1 (14), 230.0 (24), 229.0 (19), 228.0 (39), 227.0 (26), 226.0 (20), 217.1 (18), 216.0 (29), 215.0 (100), 213.0 (15), 203.0 (27), 202.0 (70), 201.0 (13), 189.0 (16), 180.0 (12), 178.0 (15), 166.0 (14), 165.0 (21), 128.0 (11), 127.0 (12), 119.0 (20), 115.0 (15), 105.0 (33), 92.1 (15), 91.1 (89), 78.1 (11), 77.1 (99), 65.1 (14), 64.1 (13), 51.1 (15). **MS (CI$^+$, methane)** *m/z* (%): 480.21 (7) $[M+C_2H_5]^+ = [C_{30}H_{30}N_3O_3]^+$, 452.0 (100) $[M+H]^+ = [C_{28}H_{26}N_3O_3]^+$. **HR-MS (ESI$^+$):** calc. for $C_{28}H_{26}N_3O_3$: 452.1969, found: 459.1953.

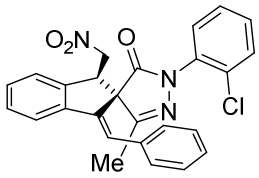
(2*R*,3*R*)-1-((*Z*)-Benzyliden)-3-(nitromethyl)-1',3'-diphenyl-1,3-dihydrospiro[indene-2,4'-pyrazole]-5'(1'H)-one (4d)



4d was obtained after flash chromatography (SiO_2, *n*-pentane/EtOAc 4:1) as off-white solid (139 mg, 95%, d.r. 6:1). **Molecular formular:** $C_{31}H_{23}N_3O_3$. **Molecular mass:** 485.54 g mol^{-1}. **Mp:** 75-79 °C.

R_f (*n*-pentane/EtOAc 6:1) = 0.39. **HPLC:** AD, 6/4 *n*-heptane/*i*-PrOH, 1.0 mL/min, λ = 230 nm, *τMinor* = 46.6 min, *τMajor* = 16.6 min. **OR:** $[\alpha]_D^{20}$ = −109.7 (*c* = 0.5, $CHCl_3$, 91% *ee*). **^{1}H NMR** (600 MHz, $CDCl_3$, major diastereomer): δ = 4.62 (dd, *J* = 4.9 Hz, *J* = 9.2 Hz, 1 H, C*H*), 4.81 (dd, *J* = 4.9 Hz, *J* = 14.9 Hz, 1 H, CH_2), 5.08 (dd, *J* = 9.3 Hz *J* = 14.9 Hz, 1 H, CH_2), 6.82 (d, *J* = 7.4 Hz, 2 H, CH_{Ar}), 6.92 (t, *J* = 7.7 Hz, 2 H, CH_{Ar}), 7.03 (t, *J* = 7.4 Hz, 1 H, CH_{Ar}), 7.19-7.26 (m, 2 H, C$H_{Ar,}$), 7.26-7.33 (m, 2 H, CH_{Ar}), 7.33-7.45 (m, 5 H, CH_{Ar}, CH_{ol}), 7.47 -7.53 (m, 1 H, CH_{Ar}), 7.58 (d, *J* = 7.9 Hz, 2 H, CH_{Ar}), 7.64 (d, *J* = 7.9 Hz, 2 H, CH_{Ar}), 7.77 (d, *J* = 7.7 Hz, 1 H, CH_{Ar}) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 48.2 (d), 63.5 (s), 74.5 (t), 119.6 (d, 2 C), 121.6 (d), 124.4 (d), 125.6 (d, 2 C), 126.3 (d, 2 C), 127.7 (d, 2 C), 128.1 (d, 2 C), 128.6 (d, 2 C), 128.7 (d, 3 C), 129.4 (d), 129.7 (s), 130.0 (d), 130.5 (d), 134.8 (s), 137.3 (s), 139.8 (s), 140.7 (s), 141.0 (s), 158.5 (s), 172.2 (s) ppm. **IR** (ATR): $\tilde{\nu}$ = 3882, 3396, 3043, 2924, 2654, 2311, 2095, 1890, 1700, 1550, 1491, 1374, 1305, 1132, 1011, 912, 848, 752, 689 cm^{-1}. **MS (EI$^+$, 70 eV)** *m*/*z* (%): 485.1 (1) $[M]^+ = [C_{31}H_{23}N_3O_3]^+$, 289.0 (11), 228.0 (16), 227.0 (10), 227.0 (12), 216.0 (13), 215.0 (46), 202.0 (31), 119.0 (24), 105.1 (11), 91.1 (40), 78.2 (11), 77.1 (100), 51.3 (20). **HR-MS (ESI$^+$):** calc. for $C_{31}H_{24}N_3O_3$: 486.1812, found: 486.1809.

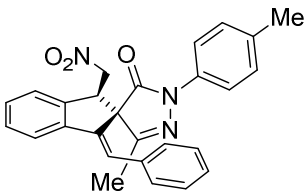
(2*R*,3*R*)-1-((*Z*)-Benzyliden)-1'-(2-chlorophenyl)-3'-methyl-3-(nitromethyl)-1,3-dihydrospiro-[indene-2,4'-pyrazole]-5'(1'*H*)-one (4e)



4e was obtained after flash chromatography (SiO_2, *n*-pentane/EtOAc 4:1) as off-white solid (100 mg, 73%, d.r. 10:1). **Molecular formular:** $C_{26}H_{20}ClN_3O_3$. **Molecular mass:** 457.91 g mol^{-1}. **Mp:** 148-152 °C. **R_f** (*n*-pentane/EtOAc 6:1) = 0.27. **HPLC:** IC, 7/3 *n*-heptane/EtOH, 0.7 mL/min, λ = 214 nm, *τMinor* = 36.0 min, *τMajor* = 19.3 min. **OR:** $[\alpha]_D^{20}$ = −201.7 (*c* = 0.5, $CHCl_3$, 82% *ee*). **^{1}H NMR** (600 MHz, $CDCl_3$, major diastereomer): δ = 1.93 (s, 3 H, CH_3), 4.37 (dd, *J* = 6.7 Hz, *J* = 7.7 Hz, 1 H, C*H*), 4.71 (dd, *J* = 7.7 Hz, *J* = 14.5 Hz, 1 H, CH_2), 4.94 (dd, *J* = 6.4 Hz, *J* = 14.5 Hz, 1 H, CH_2), 6.87-6.94 (m, 1 H, CH_{Ar}), 7.13-7.18 (m, 2 H, CH_{Ar}), 7.22 (d, *J* = 7.5 Hz, 1 H, CH_{Ar}), 7.24-7.28 (m, 2 H, CH_{Ar}), 7.28-7.33 (m, 4 H, CH_{Ar}), 7.36 (t, *J* = 7.4 Hz, 1 H, CH_{Ar}), 7.40 (s, 1 H, CH_{ol}), 7.41-7.47 (m, 2 H, CH_{Ar}) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 14.3 (q), 47.9 (d), 64.3 (s), 76.1 (t), 121.6 (d), 124.5 (d), 126.2 (d), 127.3 (d), 127.8 (d), 128.3 (d), 128.4 (d, 2 C), 128.7 (d, 2 C), 129.5 (d), 129.6 (d), 130.1 (d), 130.5 (s), 130.7 (d), 134.0 (s), 135.7 (s), 137.2 (s), 140.0 (s), 141.0 (s), 160.8 (s), 171.1 (s) ppm. **IR** (ATR): $\tilde{\nu}$ = 3880, 3431, 3006, 2650, 2313, 2087, 1902, 1717, 1552, 1479, 1365, 1289, 1193, 1096, 947, 846, 754, 697, 572 cm^{-1}. **MS (EI$^+$, 70 eV)** *m*/*z* (%): 459.2 (29) [M, $^{37}Cl]^+ = [C_{26}H_{20}ClN_3O_3]^+$, 457.2 (100) [M, $^{35}Cl]^+ = [C_{26}H_{20}ClN_3O_3]^+$, 412.2 (12), 411.2 (14), 410.2 (27) [M−HNO_2, $^{35}Cl]^+ = [C_{26}H_{19}ClO]^+$, 375.2 (8), 215.1 (8), 202.1 (6), 111.0 (5). **MS (CI$^+$, methane)** *m*/*z* (%): 468.1 (30) [M+C_2H_5, $^{35}Cl]^+$ =

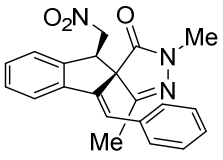
$[C_{28}H_{25}ClN_3O_3]^+$, 458.3 (100) [M+H, $^{35}Cl]^+$ = $[C_{26}H_{21}ClN_3O_3]^+$. **HR-MS (ESI$^+$):** calc. for $C_{26}H_{20}ClNaN_3O_3$: 480.1084, found: 480.1085.

(2*R*,3*R*)-1-((*Z*)-Benzyliden)-3'-methyl-3-(nitromethyl)-1'-(p-tolyl)-1,3-dihydrospiro[indene-2,4'-pyrazole]-5'(1'*H*) on (4f)



4f wurde nach säulenchromatographischer Aufarbeitung (SiO_2, *n*-pentane/EtOAc 4:1) as off-white solid(105 mg, 89%, d.r. 10:1). **Molecular formular:** $C_{27}H_{23}N_3O_3$. **Molecular mass:** 437.50 g mol^{-1}. **R$_f$** (*n*-pentane/EtOAc 6:1) = 0.36. **Mp:** 148-152 °C. **HPLC:** IC, 7/3 *n*-heptane/EtOH, 1.0 mL/min, λ = 214 nm, *τMinor* = 36.3 min, *τMajor* = 25.6 min. **OR:** $[\alpha]_D^{20}$ = −179.2 (*c* = 0.5, $CHCl_3$, 99% *ee*). **^{1}H NMR** (600 MHz, $CDCl_3$, major diastereomer): δ = 1.93 (s, 3 H, C*H*$_3$), 2.34 (s, 3 H, C*H*$_3$), 4.30 (dd, *J* = 5.4 Hz, *J* = 8.6 Hz, 1 H, C*H*), 4.65 (dd, *J* = 5.4 Hz, *J* = 15.0 Hz, 1 H, C*H*$_2$), 5.00 (dd, *J* = 8.7 Hz, *J* = 15.0 Hz, 1 H, C*H*$_2$), 7.01-7.05 (m, 2 H, C*H*$_{Ar}$), 7.07-7.15 (m, 5 H, C*H*$_{Ar}$), 7.26 (s, 1 H, C*H*$_{ol}$), 7.35-7.40 (m, 4 H, C*H*$_{Ar}$), 7.43 (d, *J* = 7.5 Hz, 1 H, C*H*$_{Ar}$), 7.67 (d, *J* = 7.7 Hz, 1 H, C*H*$_{Ar}$) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 13.9 (q), 21.0 (q), 47.4 (d), 64.7 (s), 74.9 (t), 119.3 (d, 2 C), 121.4 (d), 124.4 (d), 126.1 (d), 127.9 (d), 128.0 (d, 2 C), 128.2 (d, 2 C), 129.1 (d, 2 C), 129.4 (d), 129.8 (d), 134.9 (s), 135.0 (s), 135.1 (s), 138.0 (s), 139.6 (s), 141.0 (s), 159.9 (s), 170.8 (s) ppm. **IR** (ATR): $\tilde{\nu}$ = 3021, 2921, 2644, 2310, 2060, 1893, 1705, 1613, 1552, 1511, 1366, 1288, 1202, 1119, 1024, 932, 820, 757, 698, 622, 561 cm^{-1}. **MS (EI$^+$, 70 eV)** *m/z* (%): 437.3 (100) $[M]^+$ = $[C_{27}H_{23}N_3O_3]^+$, 391.2 (5), 390.2 (6) $[M-HNO_2]^+$ = $[C_{27}H_{22}N_2O]$. **MS (CI$^+$, methane)** *m/z* (%): 466.1 (11) $[M+C_2H_5]^+$ = $[C_{29}H_{28}N_3O_3]^+$, 438.0 (100) $[M+H]^+$ = $[C_{27}H_{24}N_3O_3]^+$. **HR-MS (ESI$^+$):** calc. for $C_{27}H_{24}N_3O_3$: 438.1813, found: 438.1812.

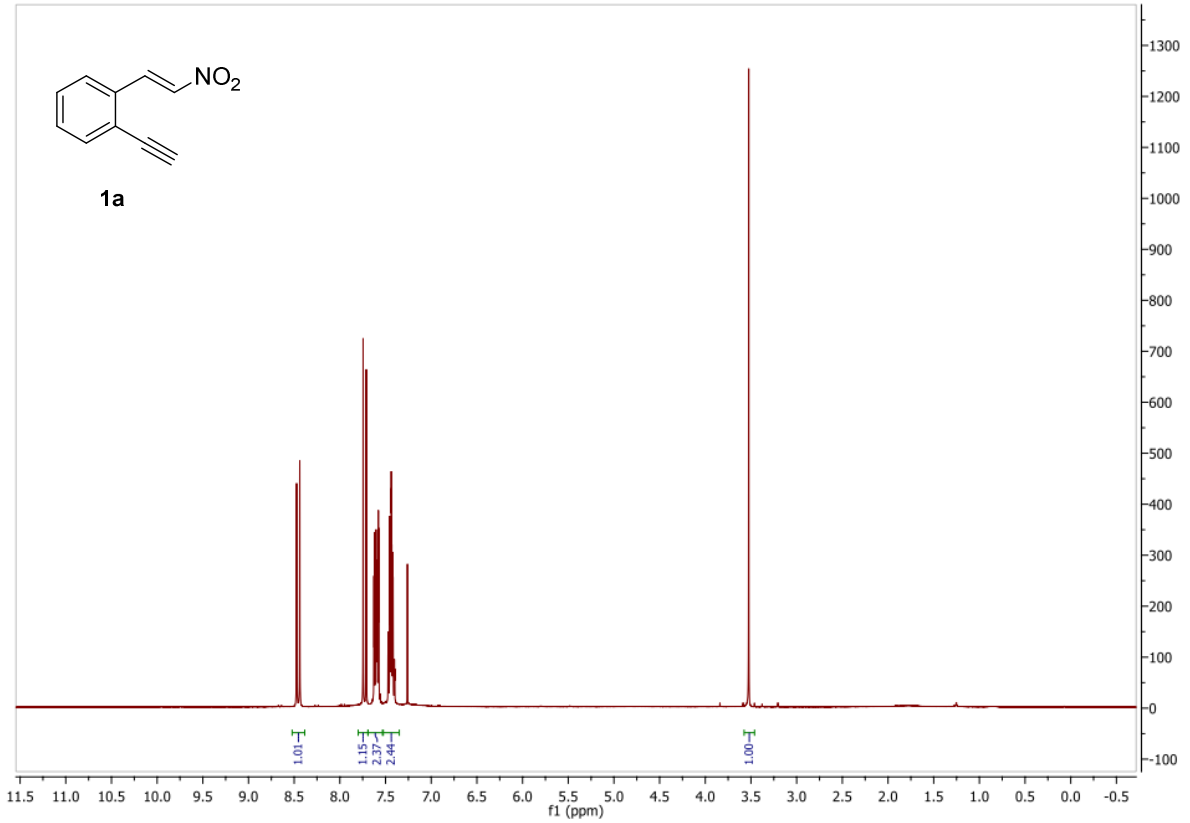
(2*R*,3*R*)-1-((*Z*)-benzyliden)-1',3'-dimethyl-3-(nitromethyl)-1,3-dihydrospiro[indee-2,4'-pyrazole]-5'(1'*H*)-one (4g)

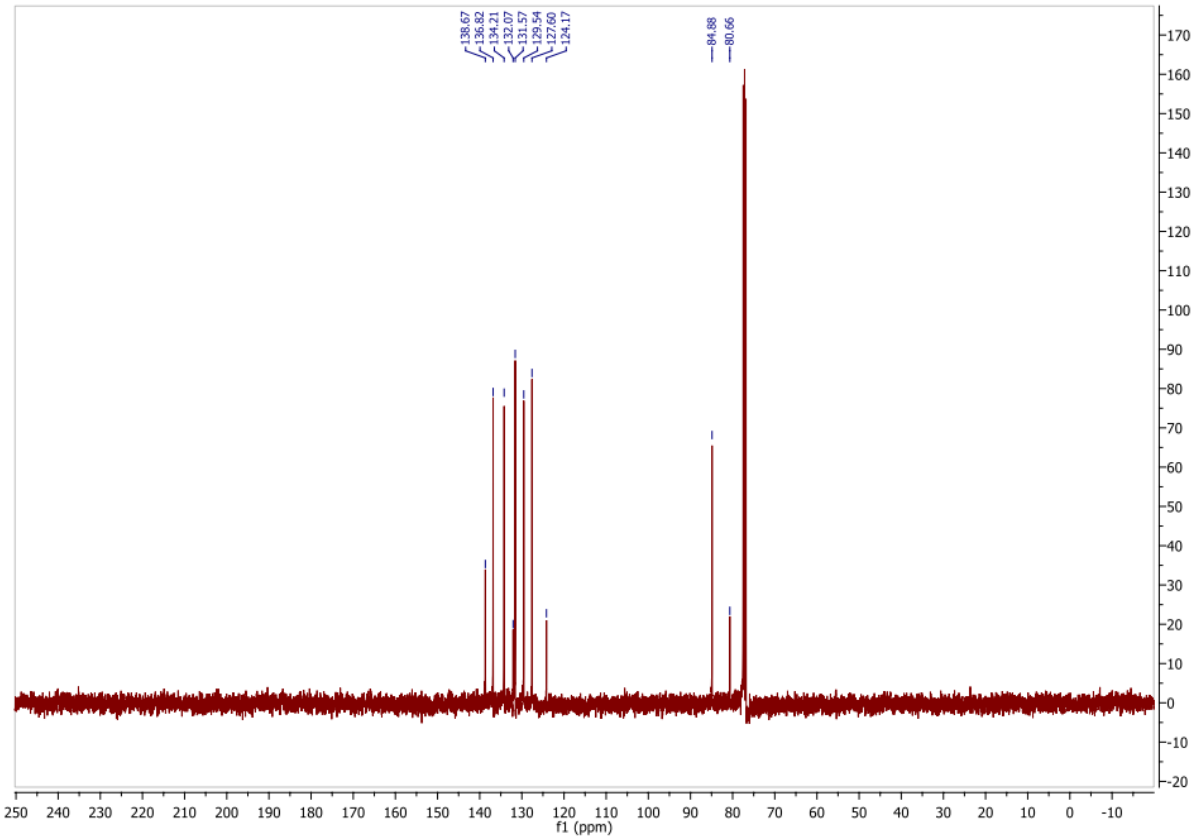


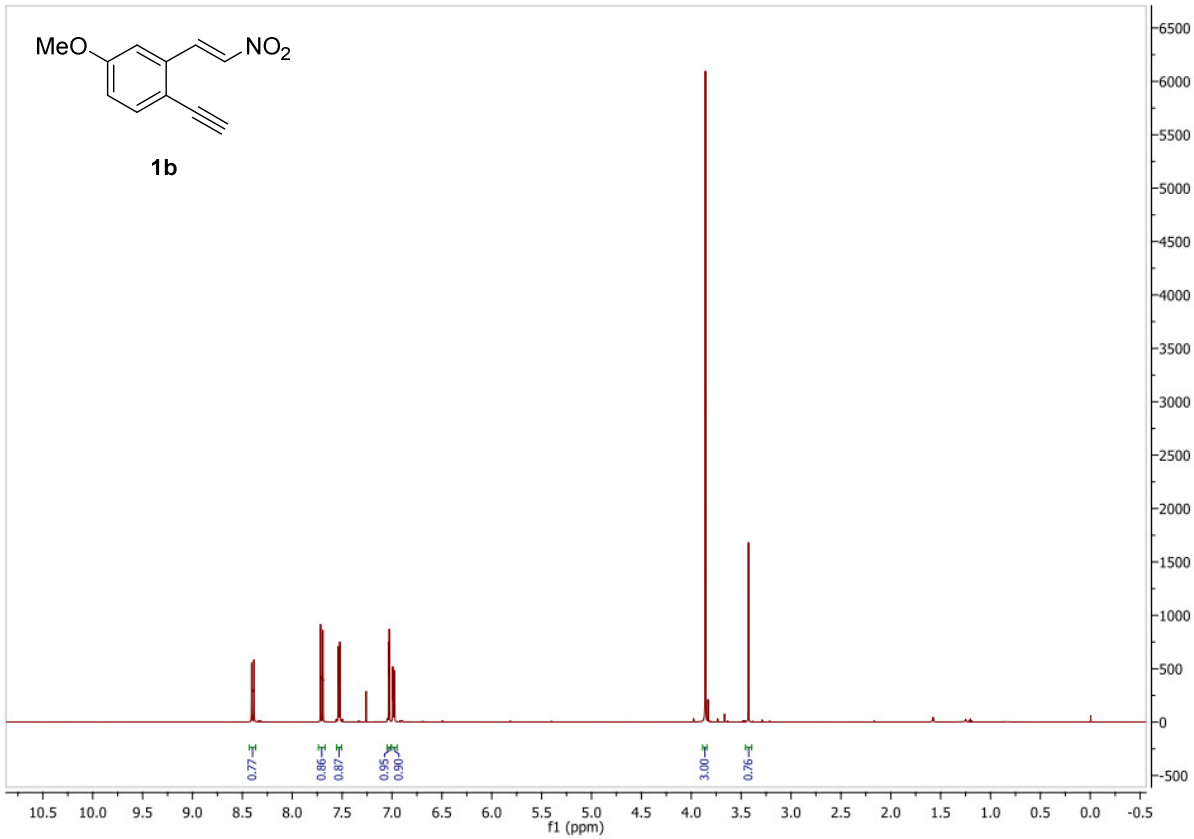
4g was obtained after flash chromatography (SiO_2, *n*-pentane/EtOAc 3:1) as off-white solid (64 mg, 59%, d.r. 20:3:1). **Molecular formular:** $C_{21}H_{19}N_3O_3$. **Molecular mass:** 361.40 g mol^{-1}. **R$_f$** (*n*-pentane/EtOAc 6:1) = 0.15. **Mp:** 142-145 °C. **HPLC:** AD, 7/3 *n*-heptane/*i*-PrOH, 0.5 mL/min, λ = 214 nm, *τMinor* = 24.0 min, *τMajor* = 20.5 min. **OR:** $[\alpha]_D^{20}$ = −120.5 (*c* = 0.5, $CHCl_3$, 86% *ee*). **^{1}H NMR** (600 MHz, $CDCl_3$, major diastereomer): δ = 1.85 (s, 3 H, C*H*$_3$), 2.93 (s, 3 H, C*H*$_3$), 4.17 (dd, *J* =

5.2 Hz, *J* = 9.0 Hz, 1 H, C*H*), 4.59 (dd, *J* = 5.2 Hz, *J* = 15.0 Hz, 1 H, CH_2), 5.00 (dd, *J* = 9.0 Hz, *J* = 15.0 Hz, 1 H, CH_2), 7.02 (dd, *J* = 0.8 Hz, *J* = 7.2, 2 H, CH_{Ar}), 7.23 (d, *J* = 7.7 Hz, 1 H, CH_{Ar}), 7.26-7.30 (m, 4 H, CH_{Ar}), 7.41 (d, *J* = 7.5 Hz, 1 H, CH_{ol}), 7.36 (dd, *J* = 3.8 Hz, *J* = 11.1 Hz, 1 H, CH_{Ar}), 7.41 (d, *J* = 7.5 Hz, 1 H, CH_{Ar}) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 13.8 (q), 31.0 (q), 46.9 (d), 63.1 (s), 75.1 (t), 121.5 (d), 124.6 (d), 126.0 (d), 128.0 (d, 2 C), 128.1 (d), 128.4 (d, 2 C), 129.5 (d), 129.9 (d), 135.3 (s), 138.3 (s), 139.9 (s), 141.6 (s), 159.5 (s), 172.7 (s) ppm. **IR** (ATR): $\tilde{\nu}$ = 3371, 3066, 2913, 2322, 2202, 1927, 1690, 1601, 1548, 1461, 1409, 1375, 1289, 1223, 1183, 1158, 1113, 1032, 994, 951, 919, 865, 761, 727, 698, 670 cm^{-1}. **MS (EI$^+$, 70 eV)** *m*/*z* (%): 362.0 (34), 361.0 (100) $[M]^+ = [C_{21}H_{19}N_3O_3]^+$, 315.0 (33), 314.0 (64) $[M-NO_2]^+ = [C_{21}H_{19}N_2O]$, 313.0 (10), 284.9 (12), 272.0 (17), 270.9 (18), 227.9 (13), 215.0 (21), 209. (12), 202.0 (14). **MS (CI$^+$, methane)** *m*/*z* (%): 390.1 (7) $[M+C_2H_5]^+ = [C_{23}H_{24}N_3O_3]^+$, 362.0 (100) $[M+H]^+ = [C_{21}H_{20}N_3O_3]^+$. **HR-MS (ESI$^+$):** calc. for $[M+H]^+ = [C_{21}H_{19}NaN_3O_3]^+$: 384.1319, found: 384.1323.

10.0 NMR Spectra






MeO
NO2
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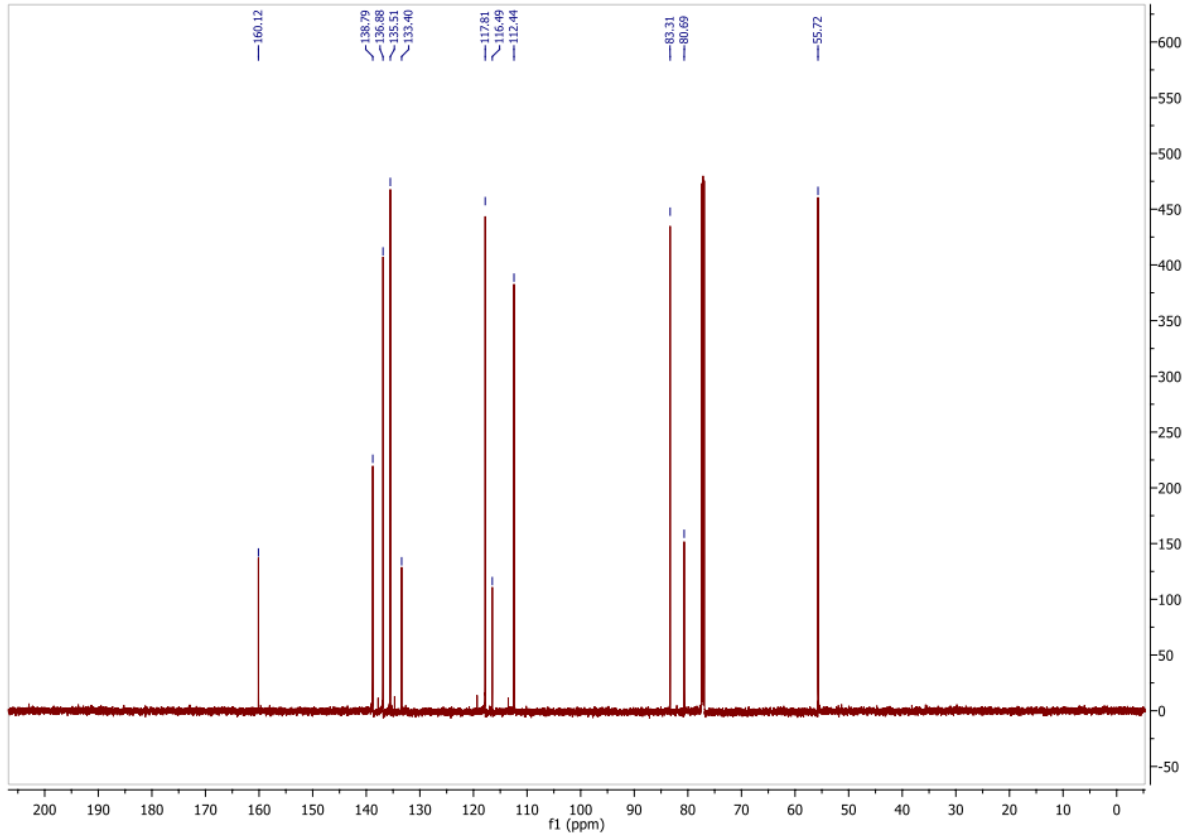
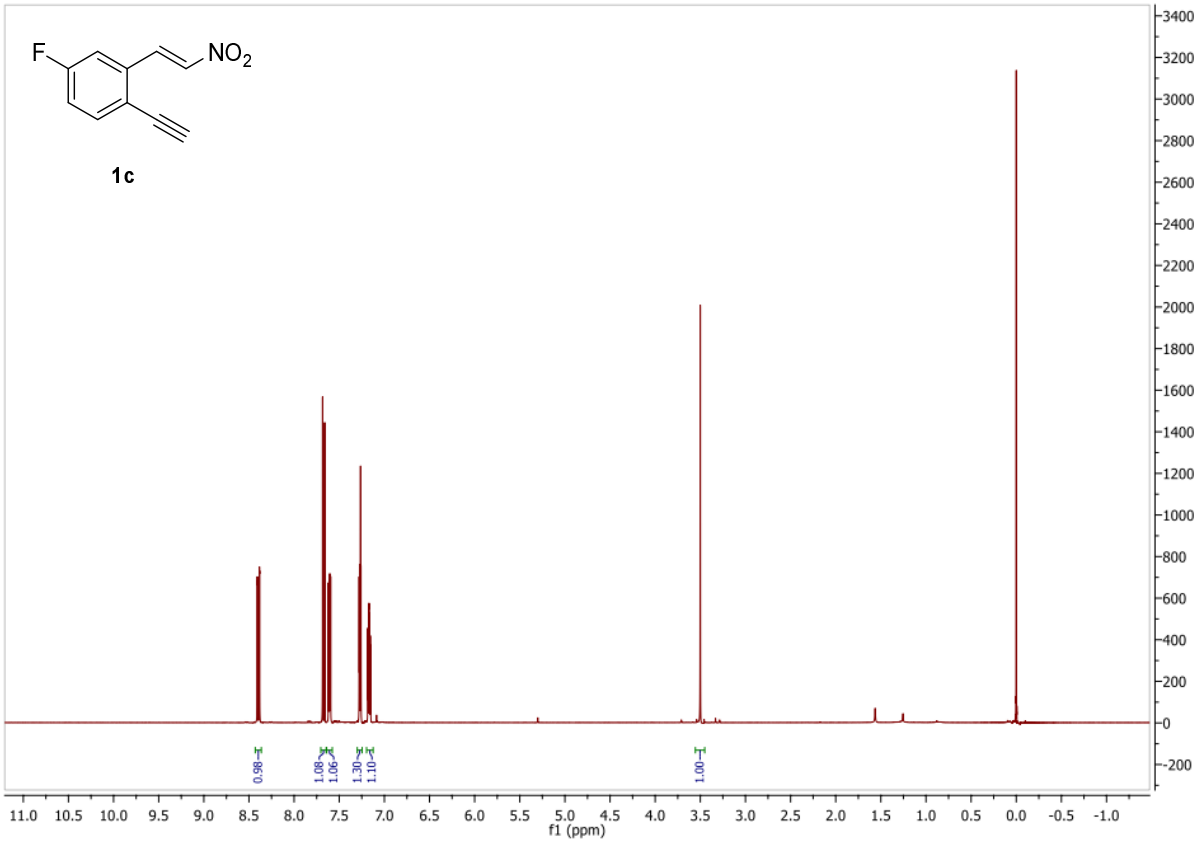
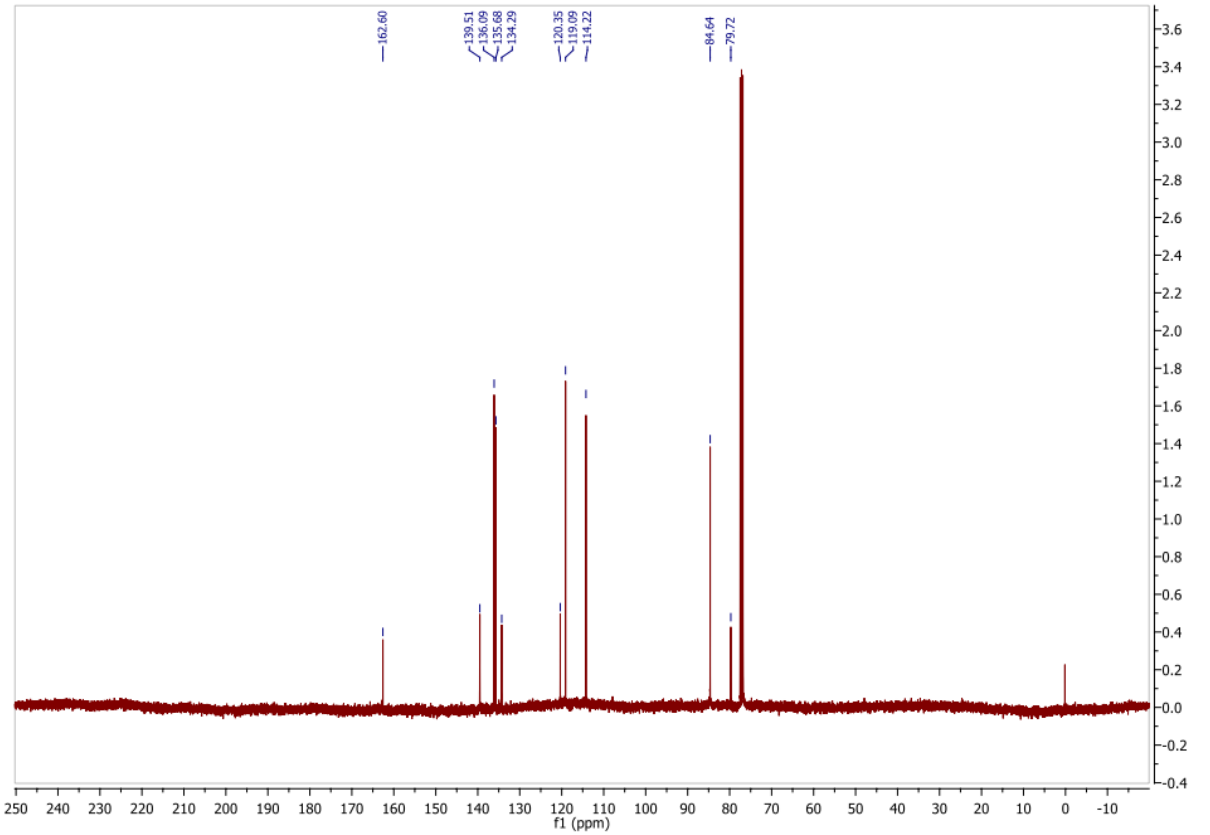
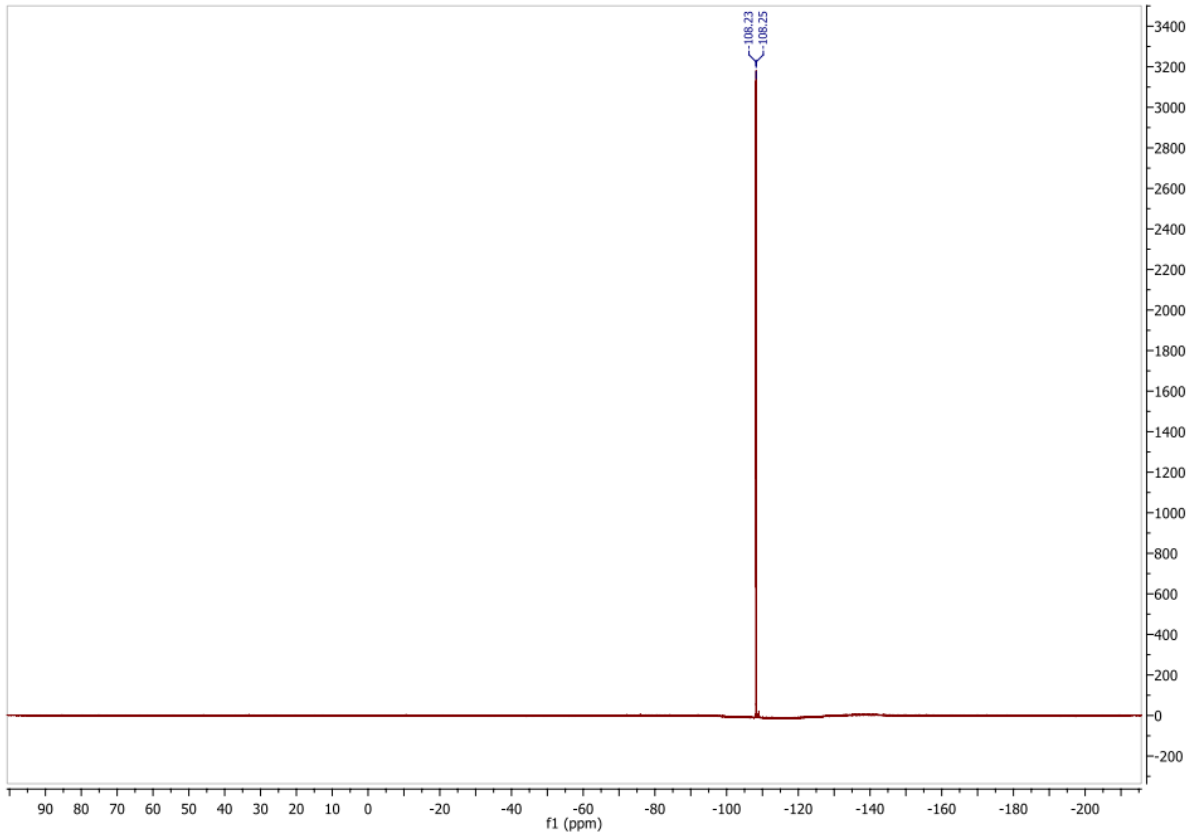
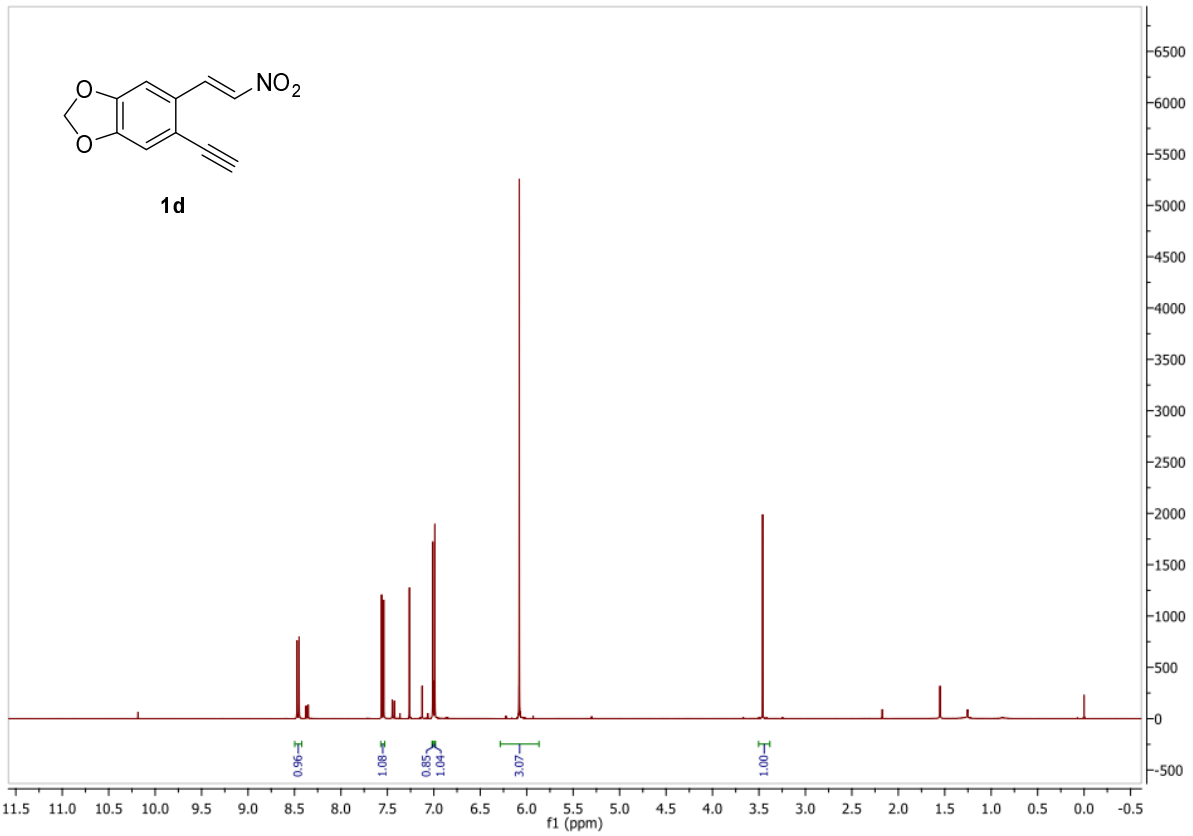
0.77
0.86
0.87
0.95
0.90
3.00
0.76
f1 (ppm)


160.12
138.79
136.88
135.51
133.40
117.81
116.49
112.44
83.31
80.69
55.72
f1 (ppm)


F
NO2
1c
0.98
1.08
1.06
1.30
1.10
1.00
f1 (ppm)


162.60
139.51
136.09
135.68
134.29
120.35
119.09
114.22
84.64
79.72
f1 (ppm)


-106.23
-106.25
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)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O
NO2
1d
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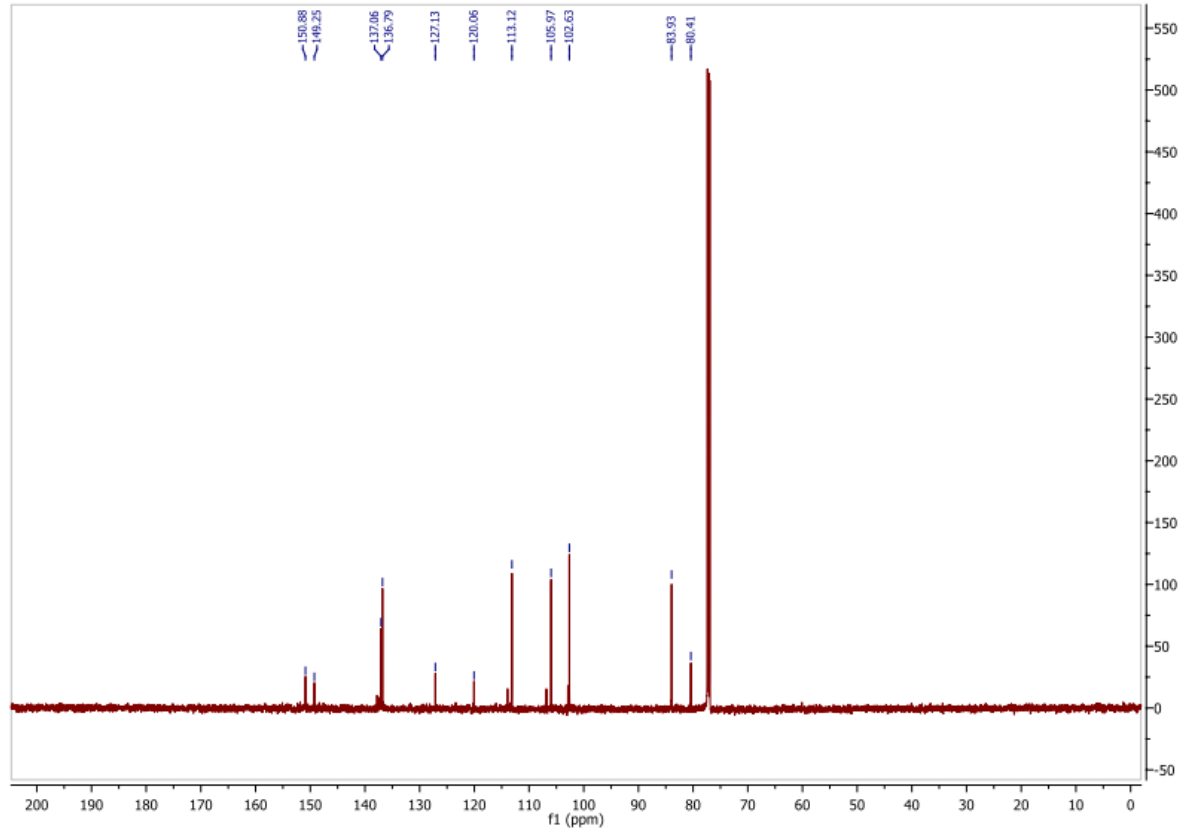
1.08
0.85
1.04
3.07
1.00
f1 (ppm)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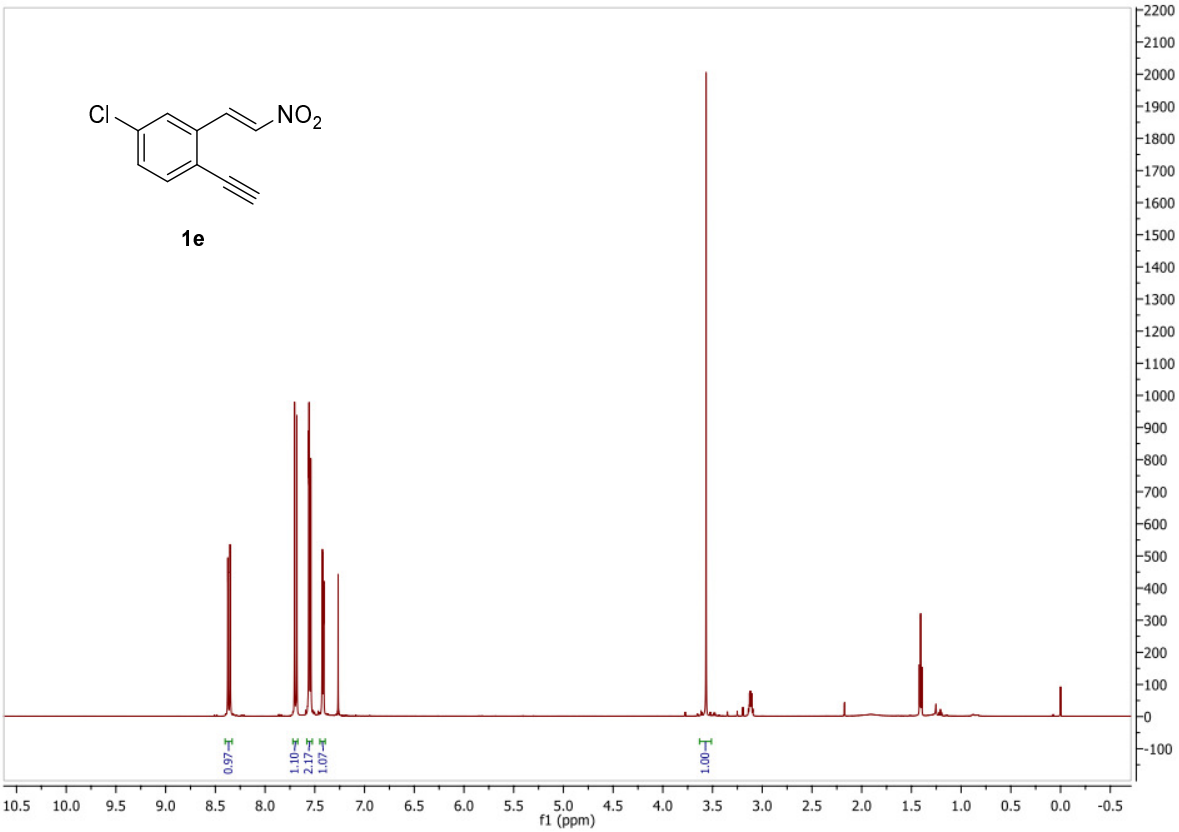
149.25
137.06
136.79
127.13
120.06
113.12
105.97
102.63
83.93
80.41
f1 (ppm)


Cl
NO2
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0.97
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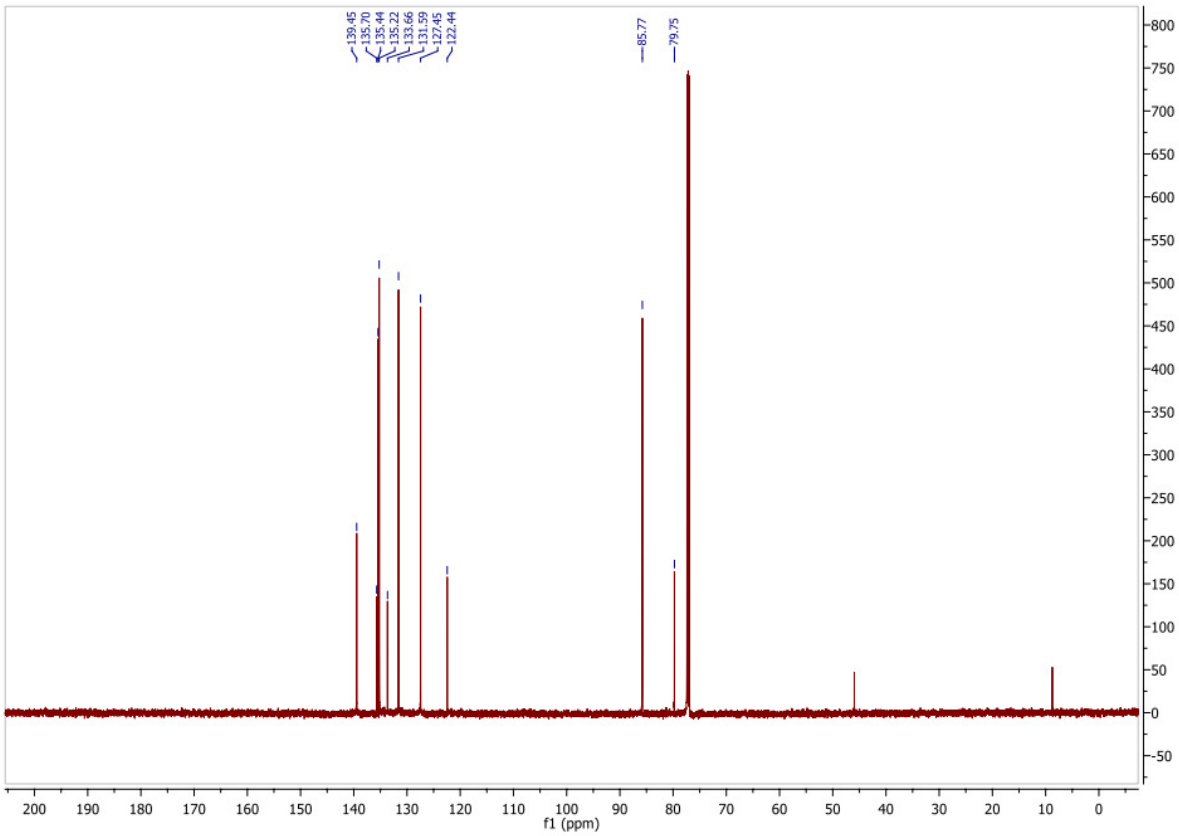
2.17
1.07
1.00
f1 (ppm)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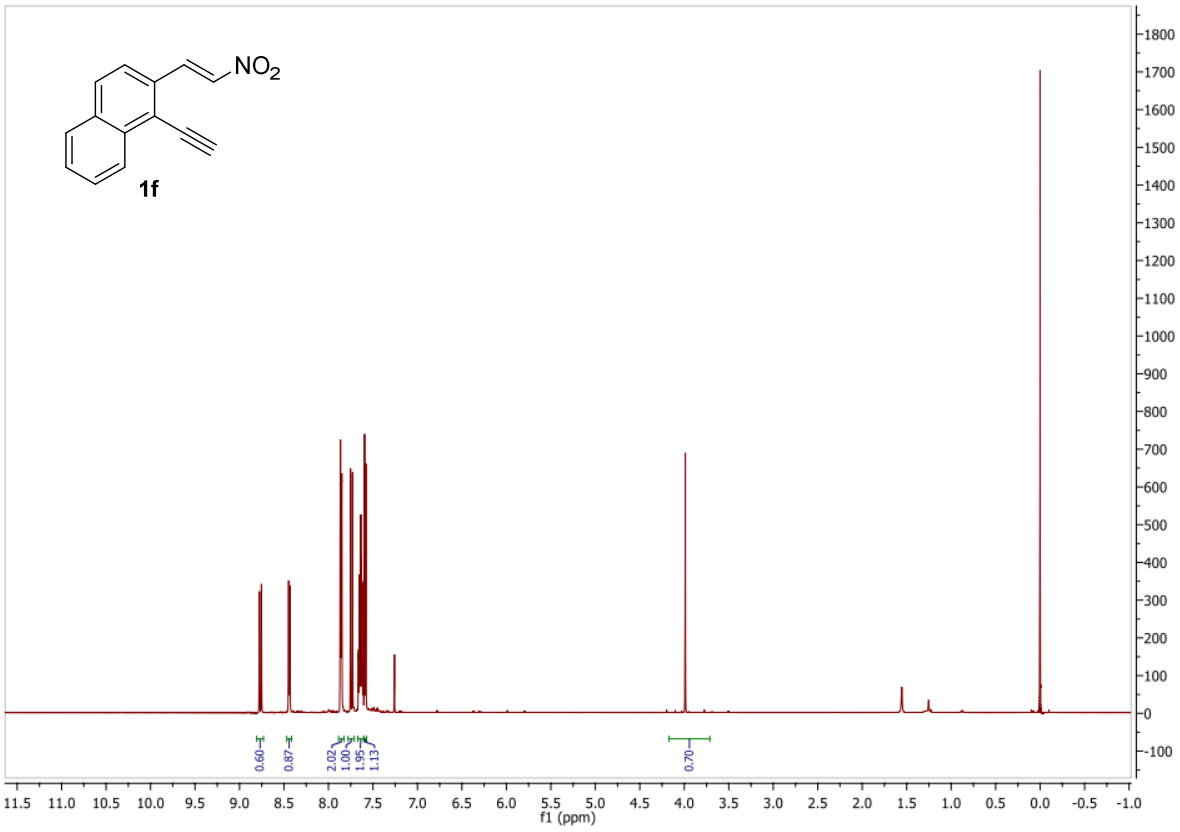
135.70
135.44
135.22
133.66
131.59
127.45
122.44
85.77
79.75
f1 (ppm)


NO2
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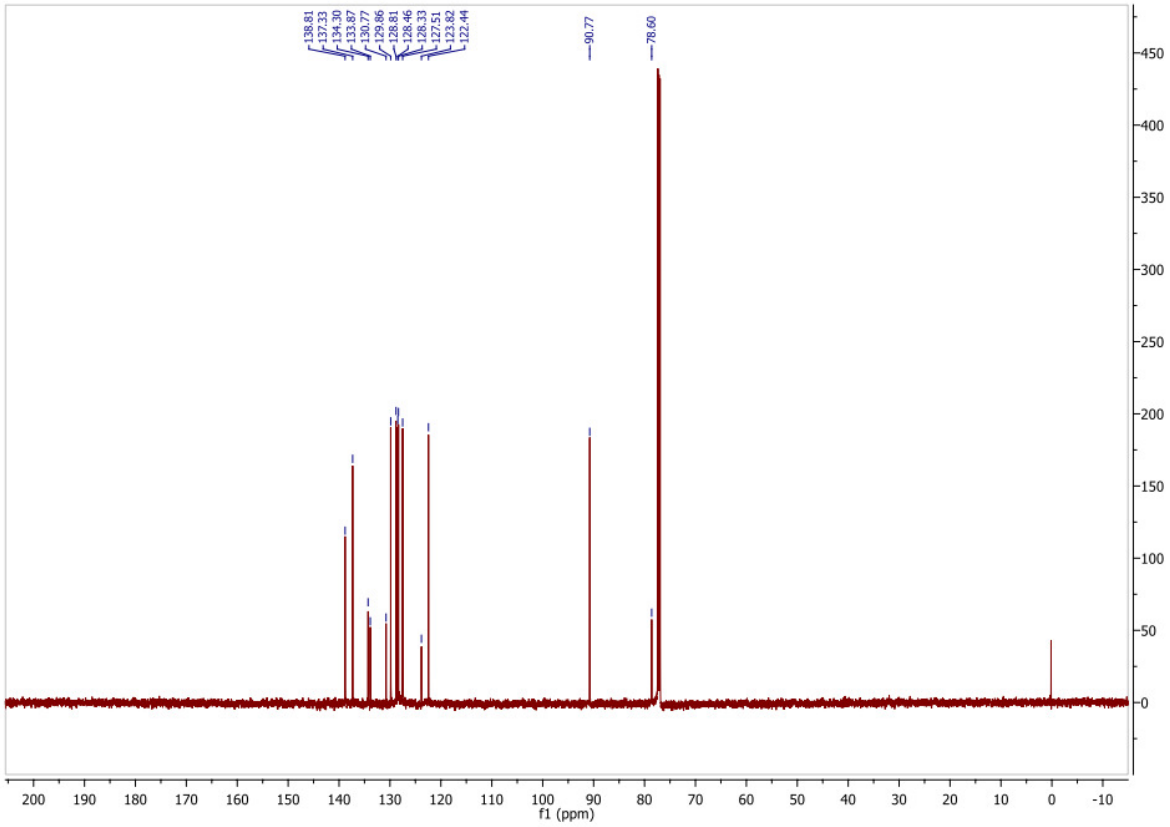
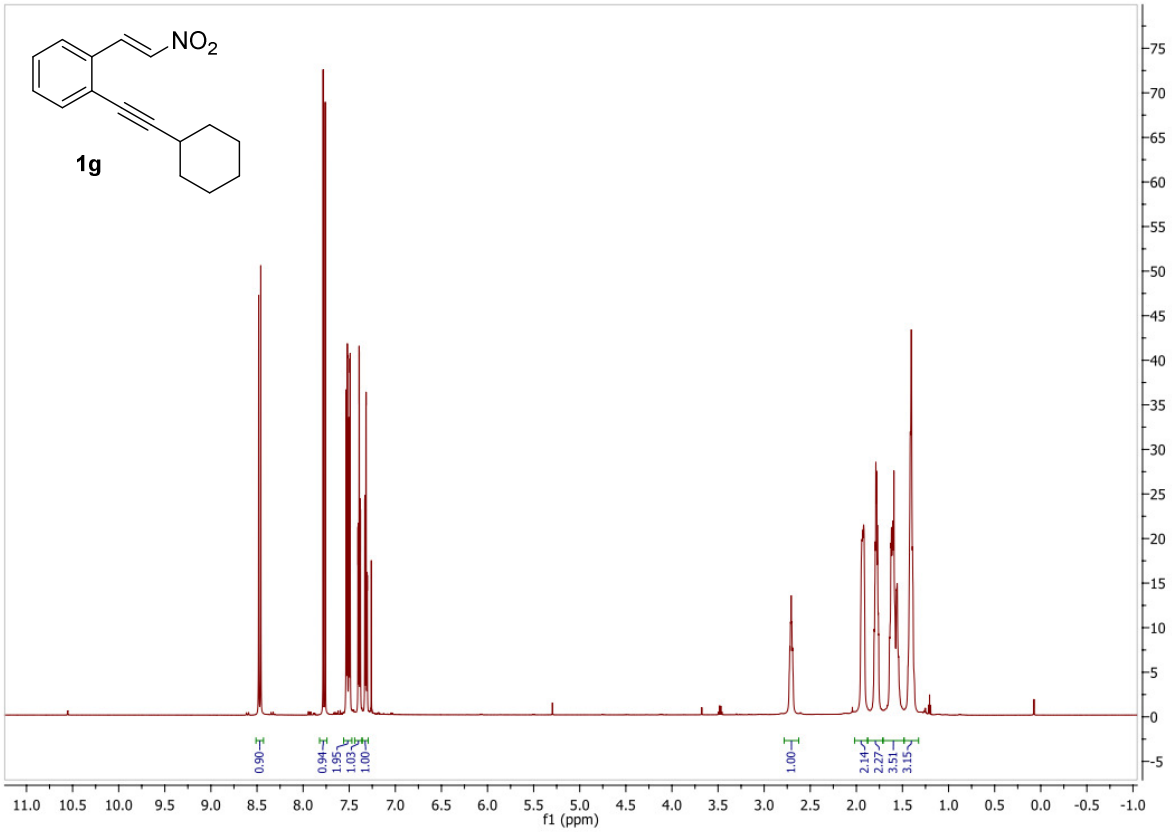
0.87
2.02
1.00
1.95
1.13
0.70
f1 (ppm)


138.81
137.33
134.30
133.87
130.77
129.86
128.81
128.46
128.33
127.51
123.82
122.44
90.77
78.60
f1 (ppm)


NO2
1g
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1.03
1.00
1.00
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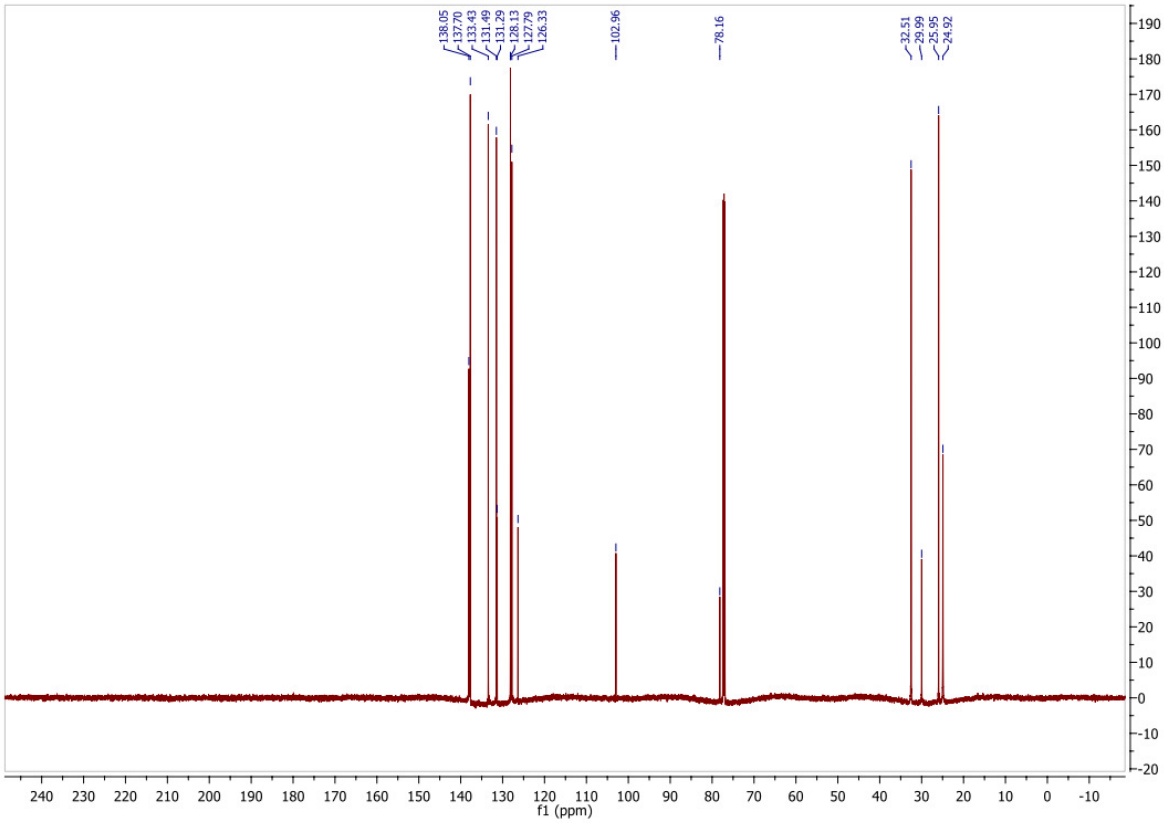
2.27
3.51
3.15
f1 (ppm)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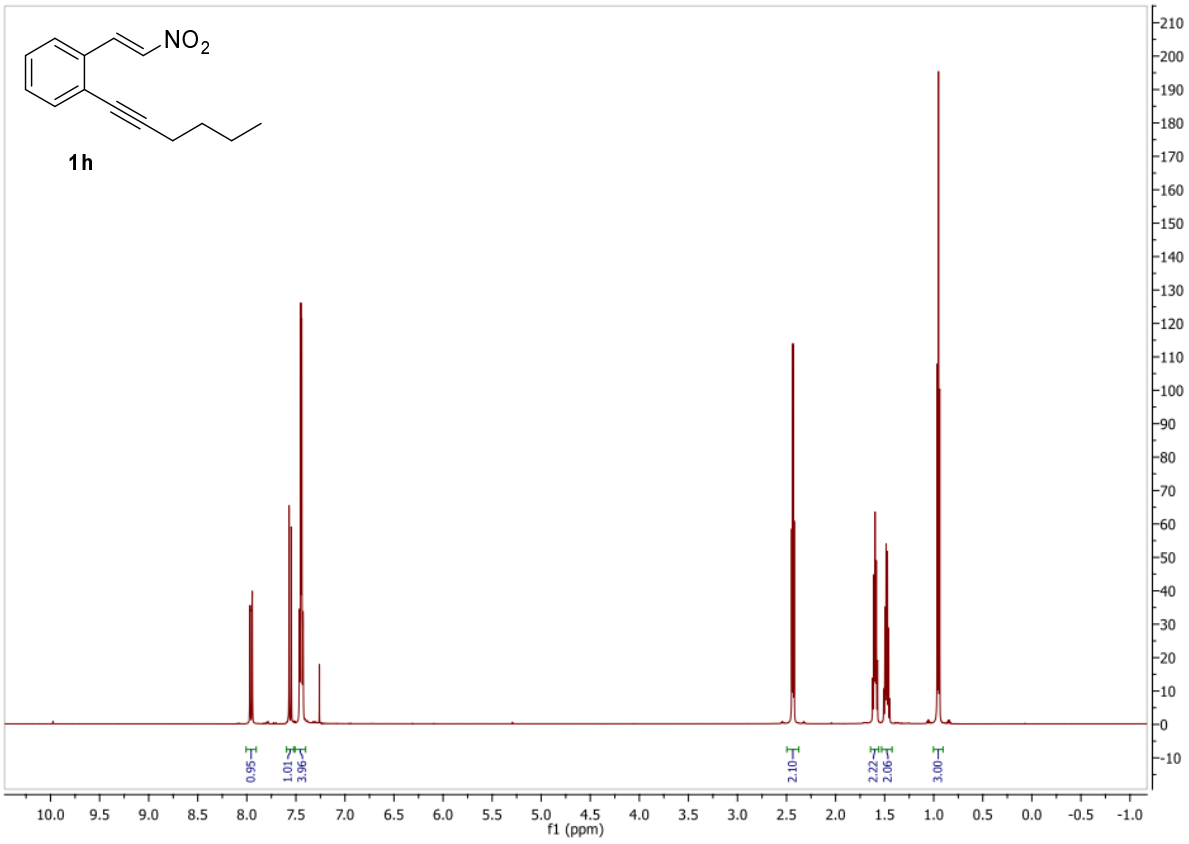
137.70
133.43
131.49
131.29
128.13
127.79
126.33
102.96
78.16
32.51
29.99
25.95
24.92
f1 (ppm)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3.96
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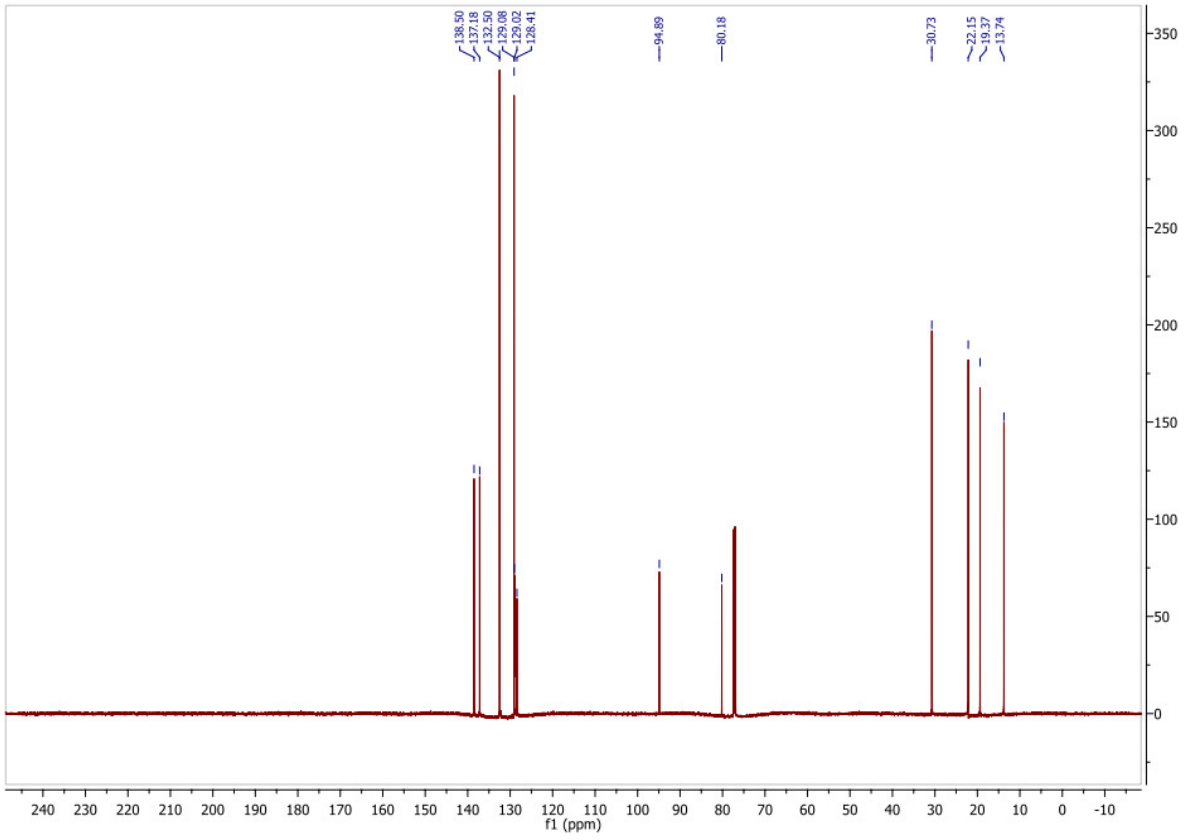
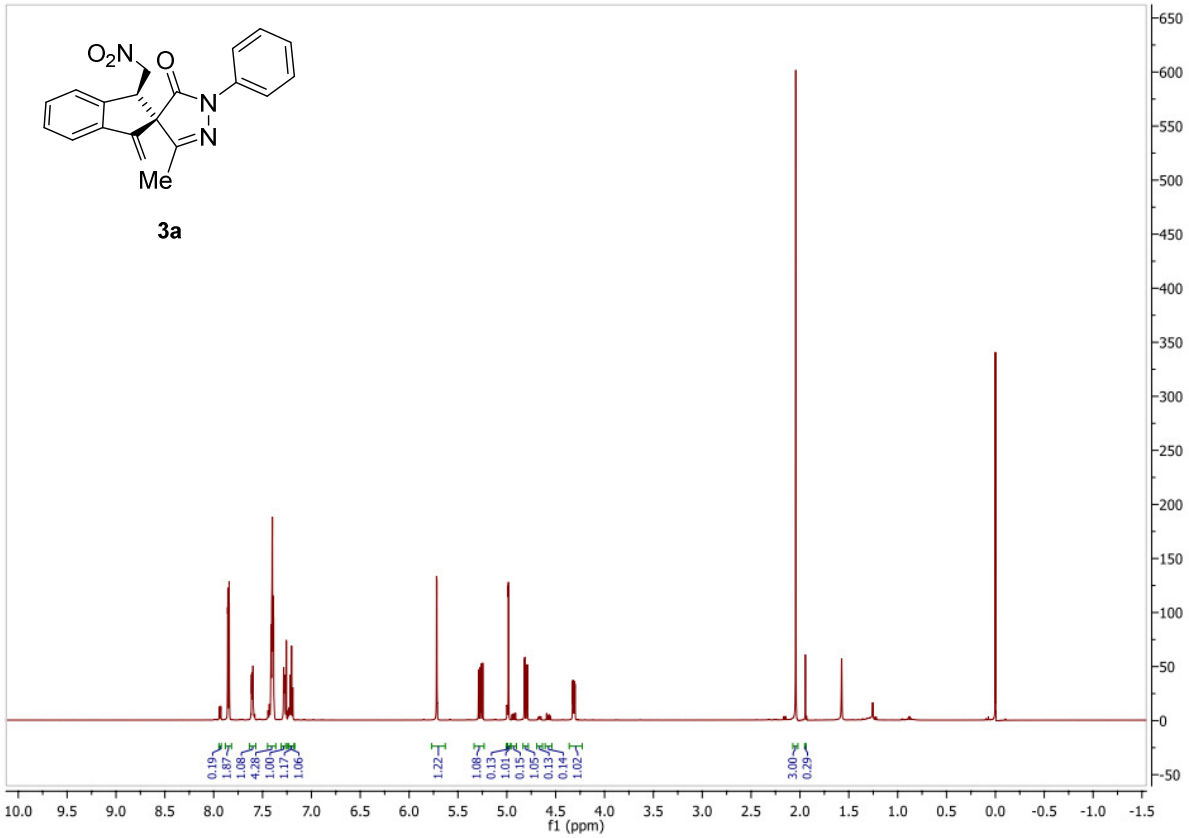
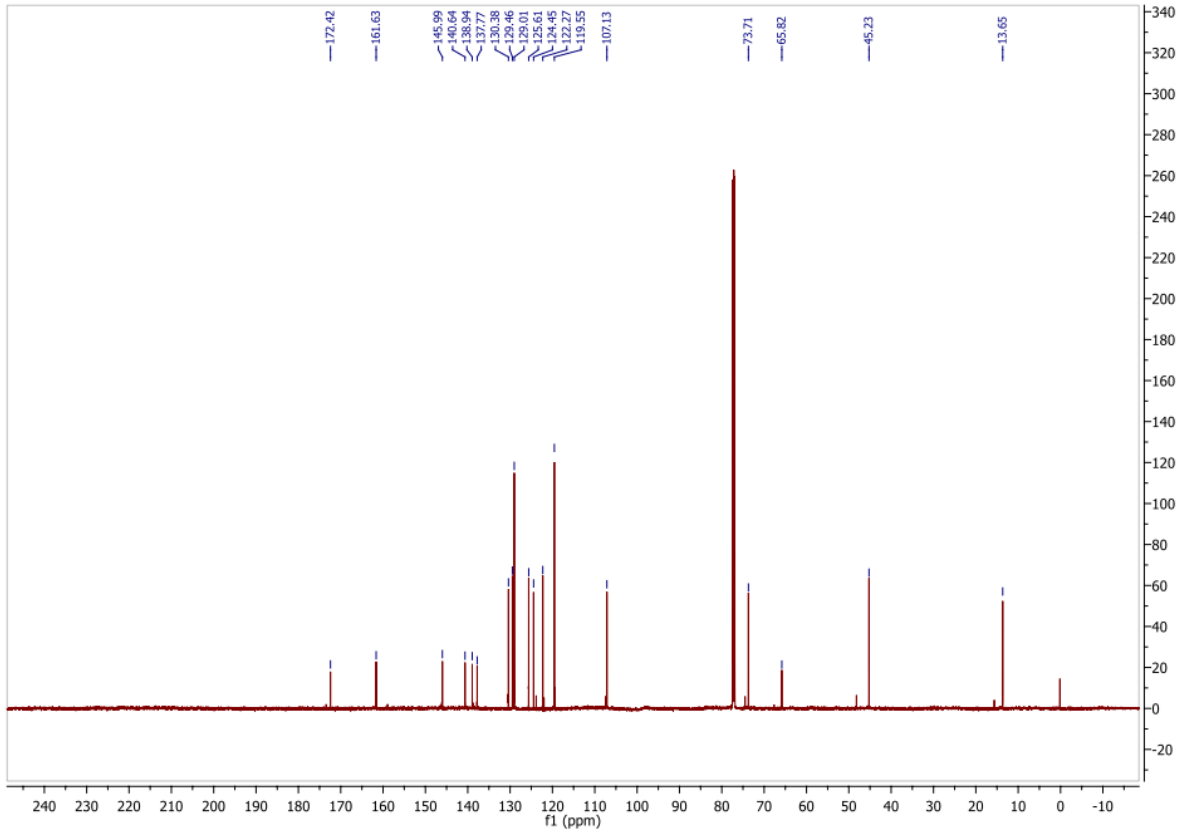
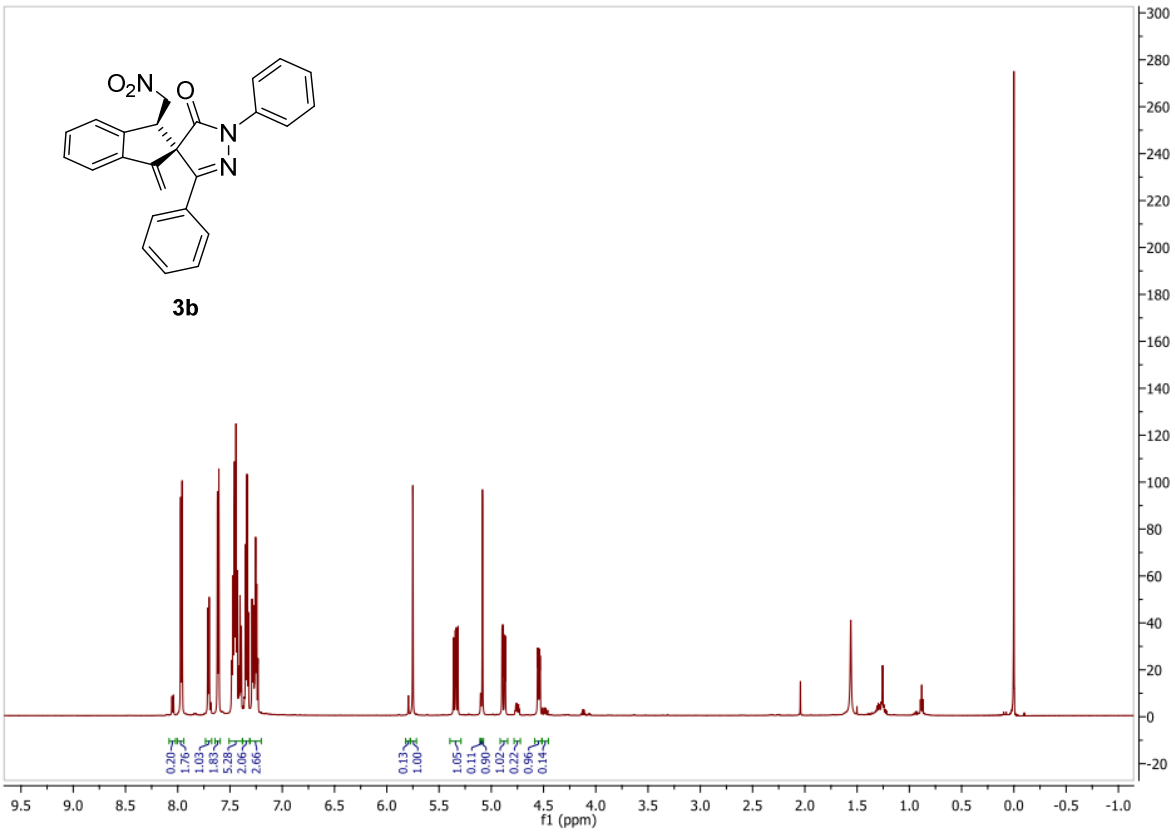
2.06
3.00
f1 (ppm)

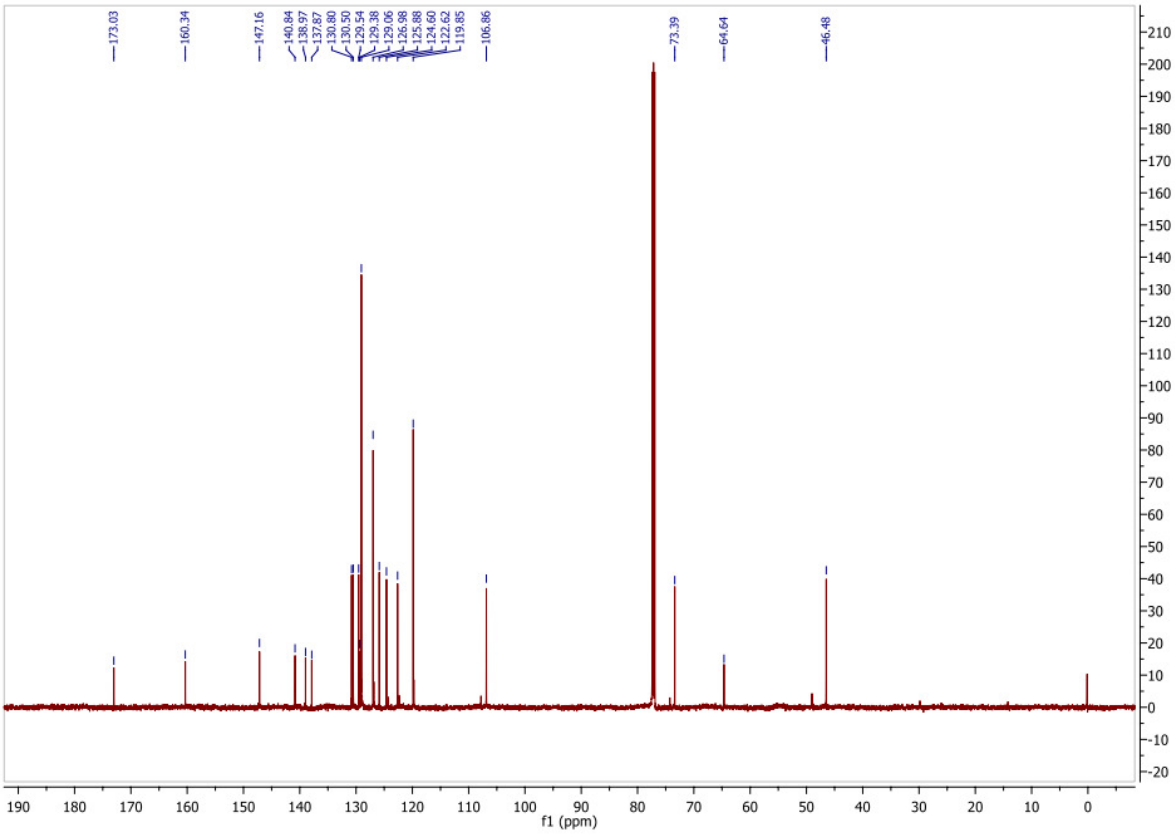

138.50
137.18
132.50
129.08
129.02
128.41
94.89
80.18
30.73
22.15
19.37
13.74
f1 (ppm)

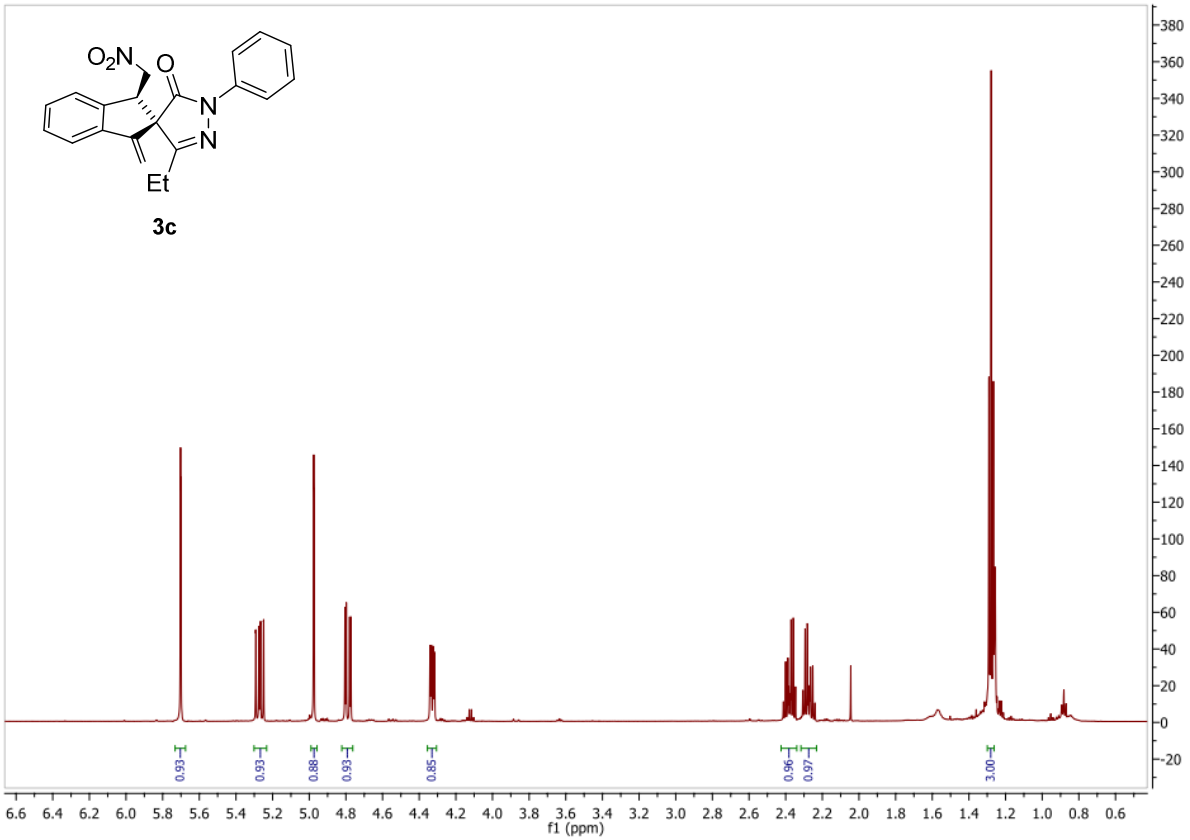

O2N
O
N
N
Me
0.19
1.87
1.08
4.28
1.00
1.17
1.06
1.22
1.08
0.13
1.01
0.15
1.05
0.13
0.14
1.02
3.00
0.29
f1 (ppm)

3a

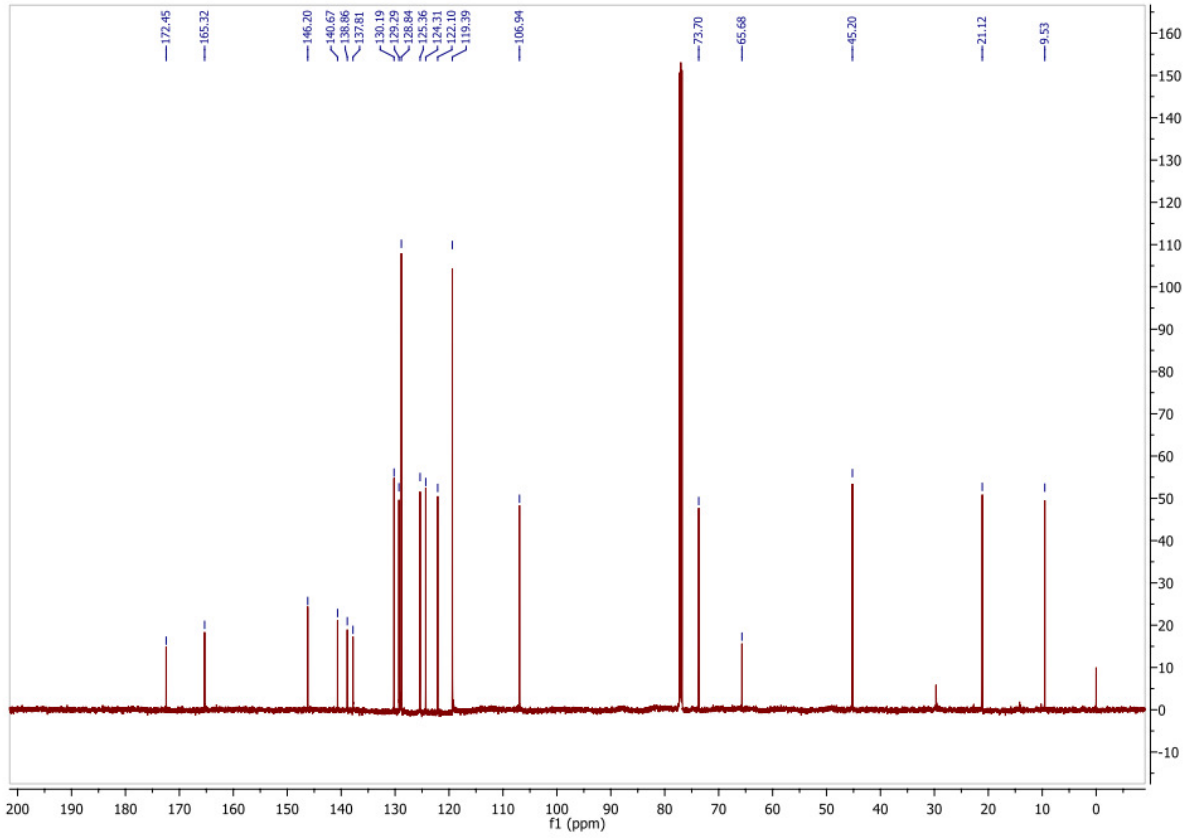

172.42
161.63
145.99
140.64
138.94
137.77
130.38
129.46
129.01
125.61
124.45
122.27
119.55
107.13
73.71
65.82
45.23
13.65
f1 (ppm)

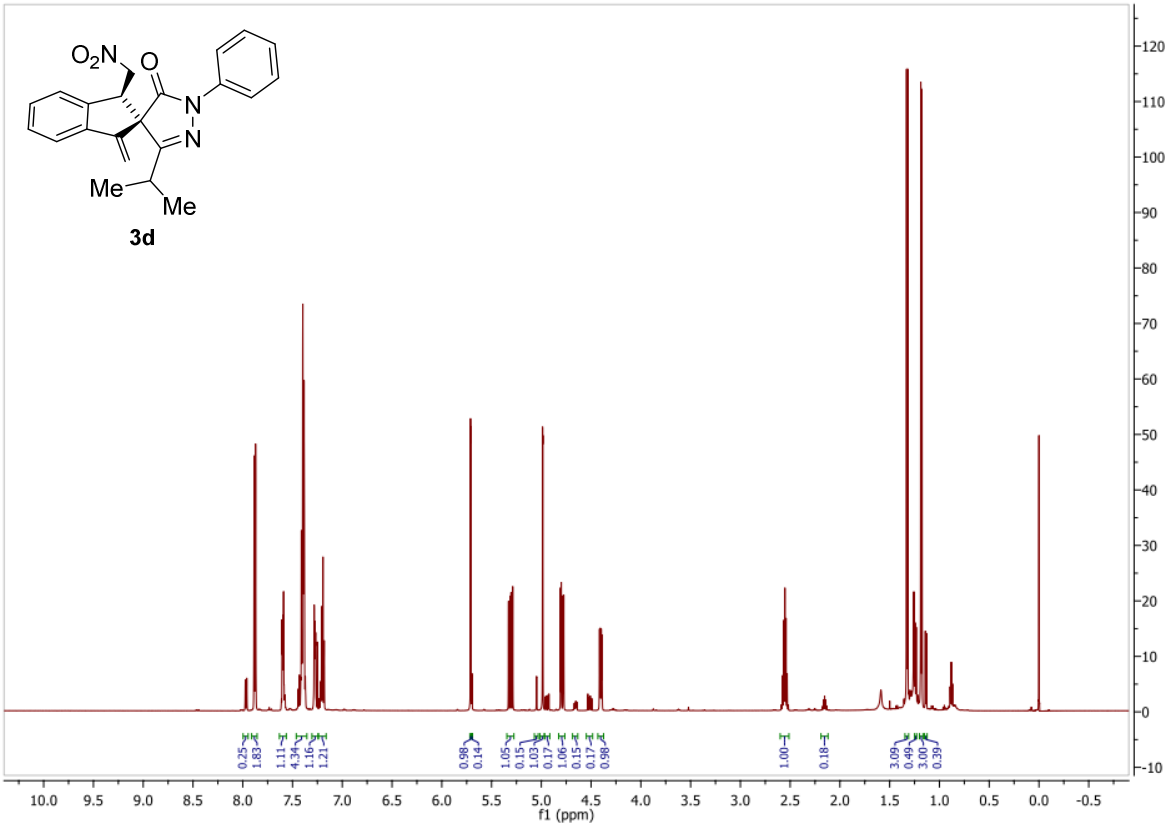

O2N
O
N
N
3b
0.20
1.76
1.03
1.83
5.28
2.06
2.66
0.13
1.00
1.05
0.11
0.90
1.02
0.22
0.96
0.14
f1 (ppm)

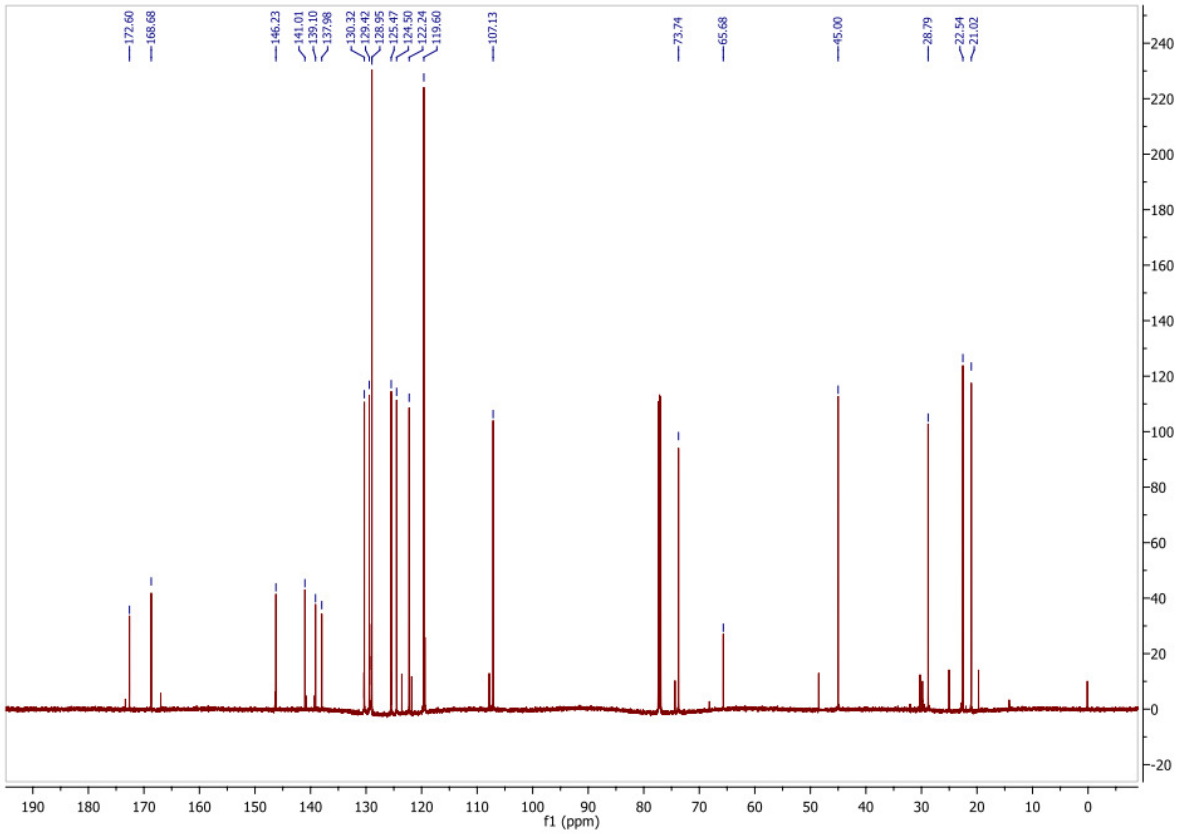

173.03
160.34
147.16
140.84
138.97
137.87
130.80
130.50
129.54
129.38
129.06
126.98
125.88
124.60
122.62
119.85
106.86
73.39
64.64
46.48
f1 (ppm)

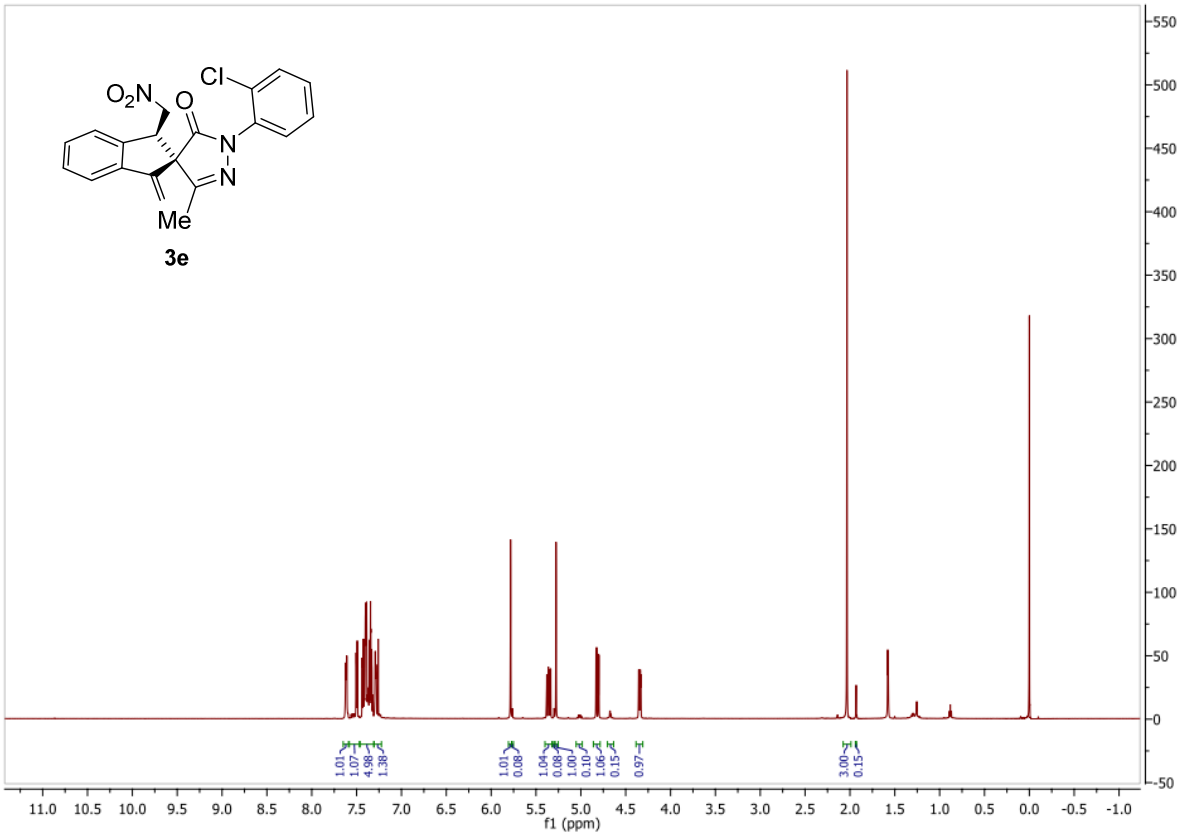

O2N
O
N
N
Et
0.93
0.93
0.88
0.93
0.85
0.96
0.97
3.00
f1 (ppm)

3c

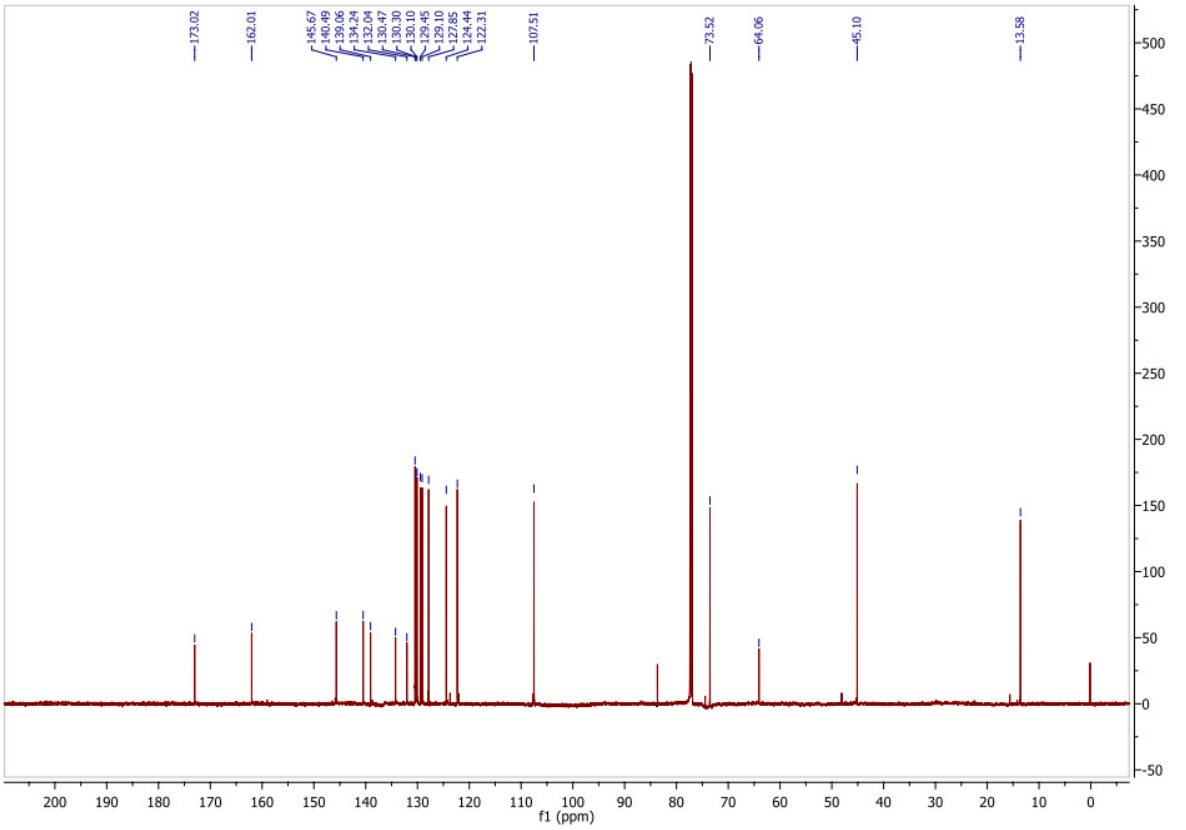

172.45
165.32
146.20
140.67
138.86
137.81
130.19
129.29
128.84
125.36
124.31
122.10
119.39
106.94
73.70
65.68
45.20
21.12
9.53
f1 (ppm)

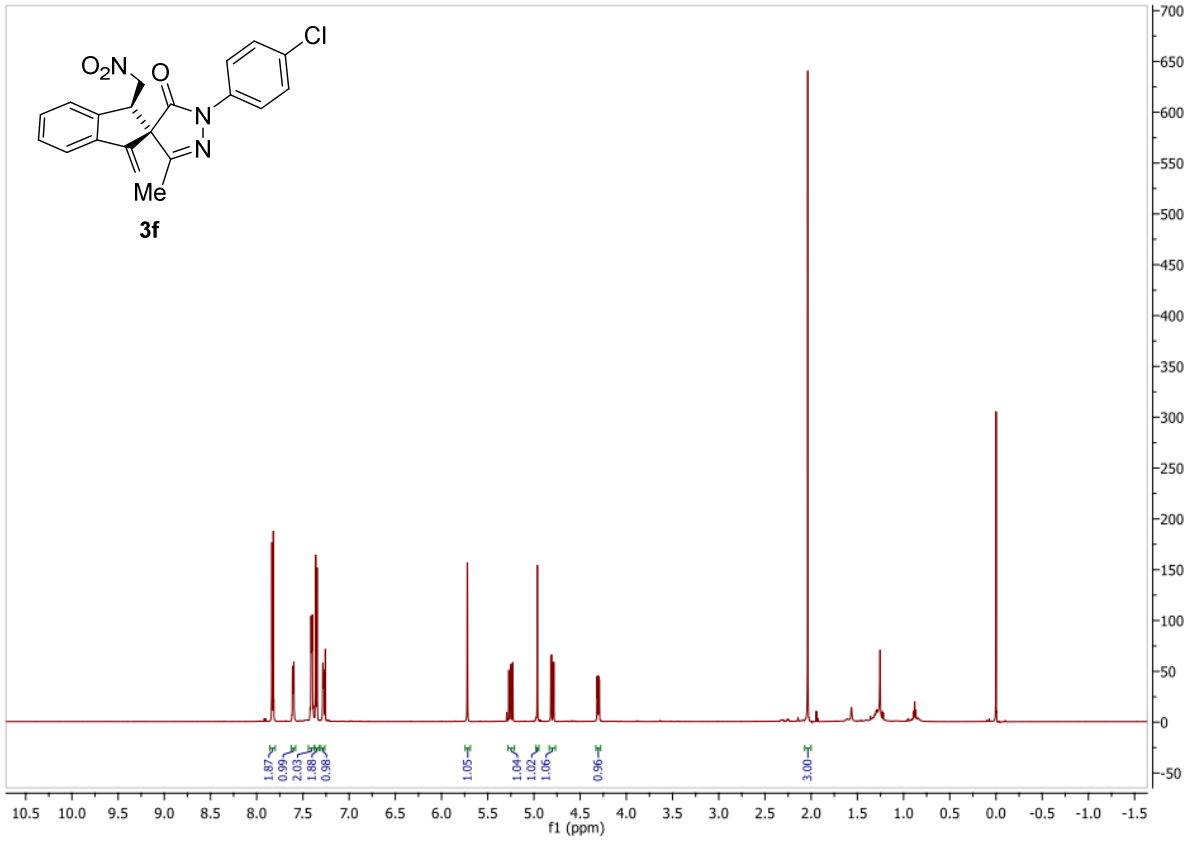

O2N
O
N
N
Me
Me
3d
0.25
1.83
1.11
4.34
1.16
1.21
0.98
0.14
1.05
0.15
1.03
0.17
1.06
0.15
0.17
0.98
1.00
0.18
3.09
0.49
3.00
0.39
f1 (ppm)


172.60
168.68
146.23
141.01
139.10
137.98
130.32
129.42
128.95
125.47
124.50
122.24
119.60
107.13
73.74
65.68
45.00
28.79
22.54
21.02
f1 (ppm)

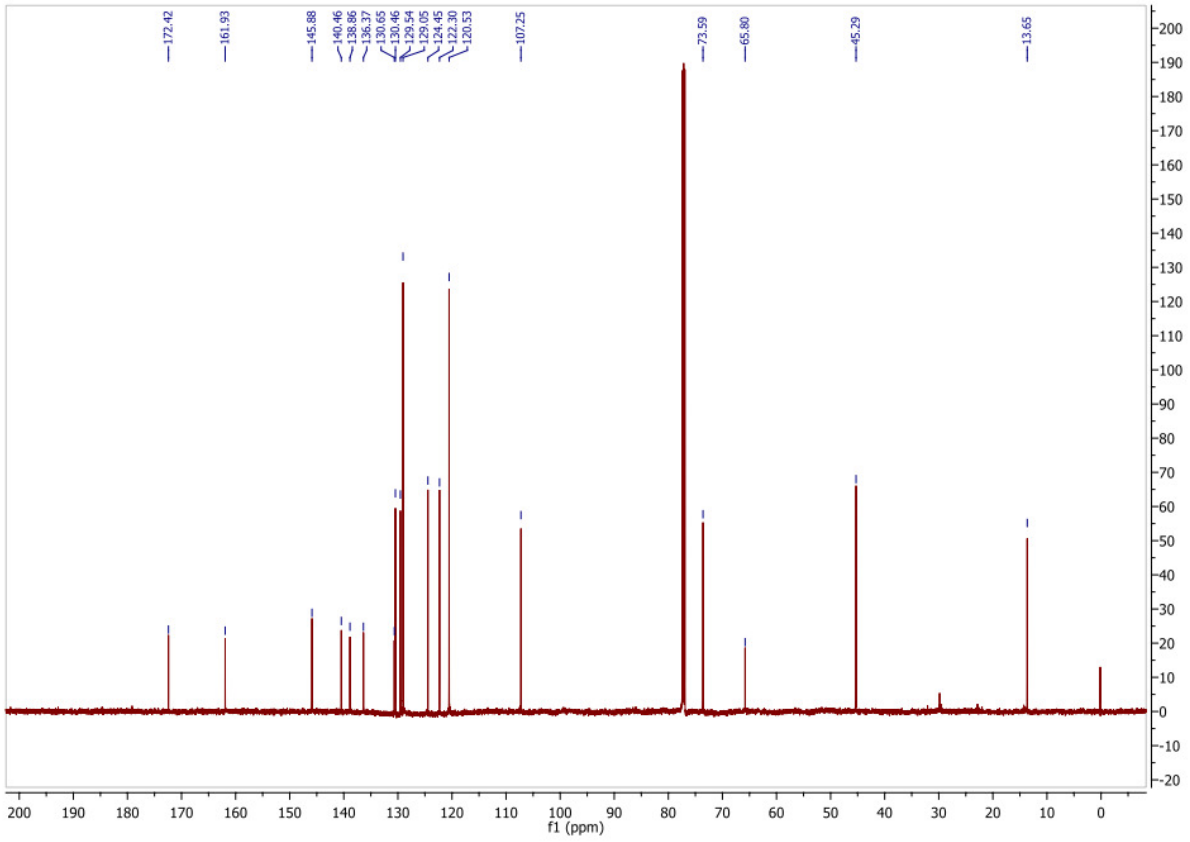

O2N
O
Cl
N
N
Me
1.01
1.07
4.98
1.38
1.01
0.08
1.04
0.08
1.00
0.10
1.06
0.15
0.97
3.00
0.15
f1 (ppm)

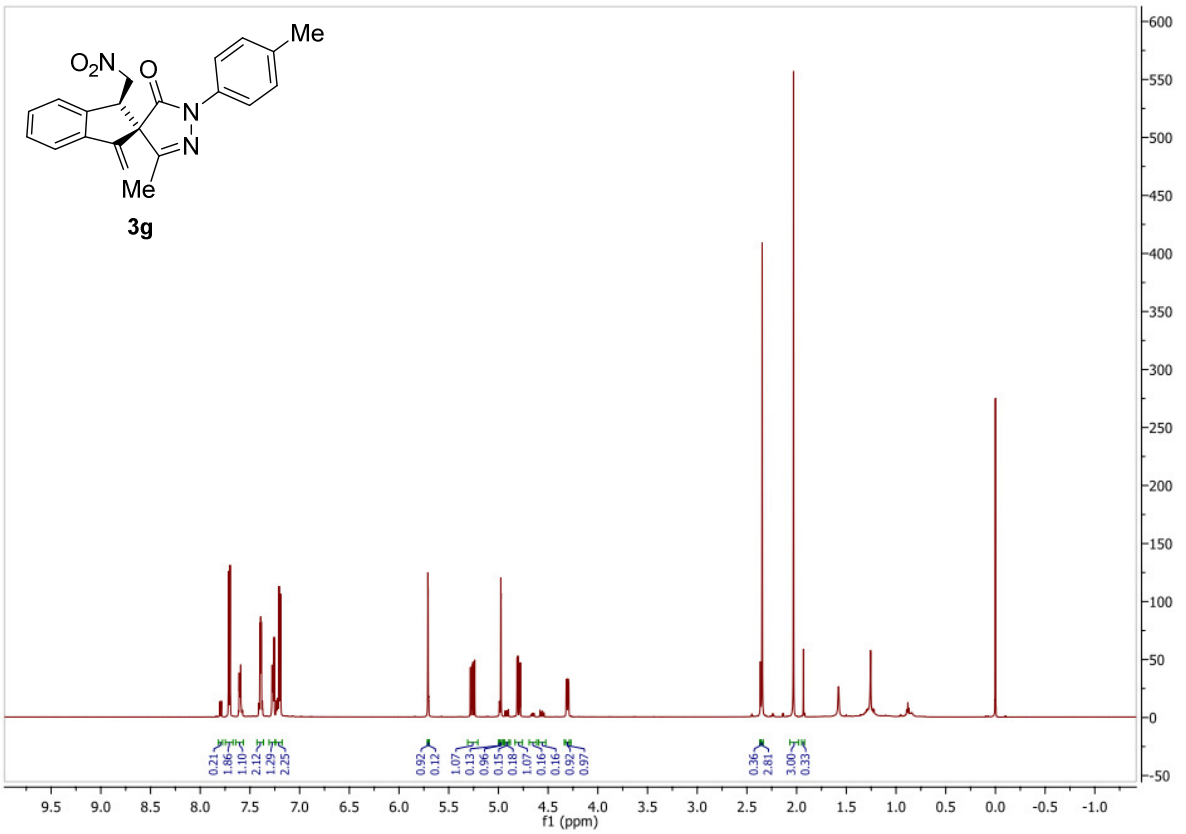
3e

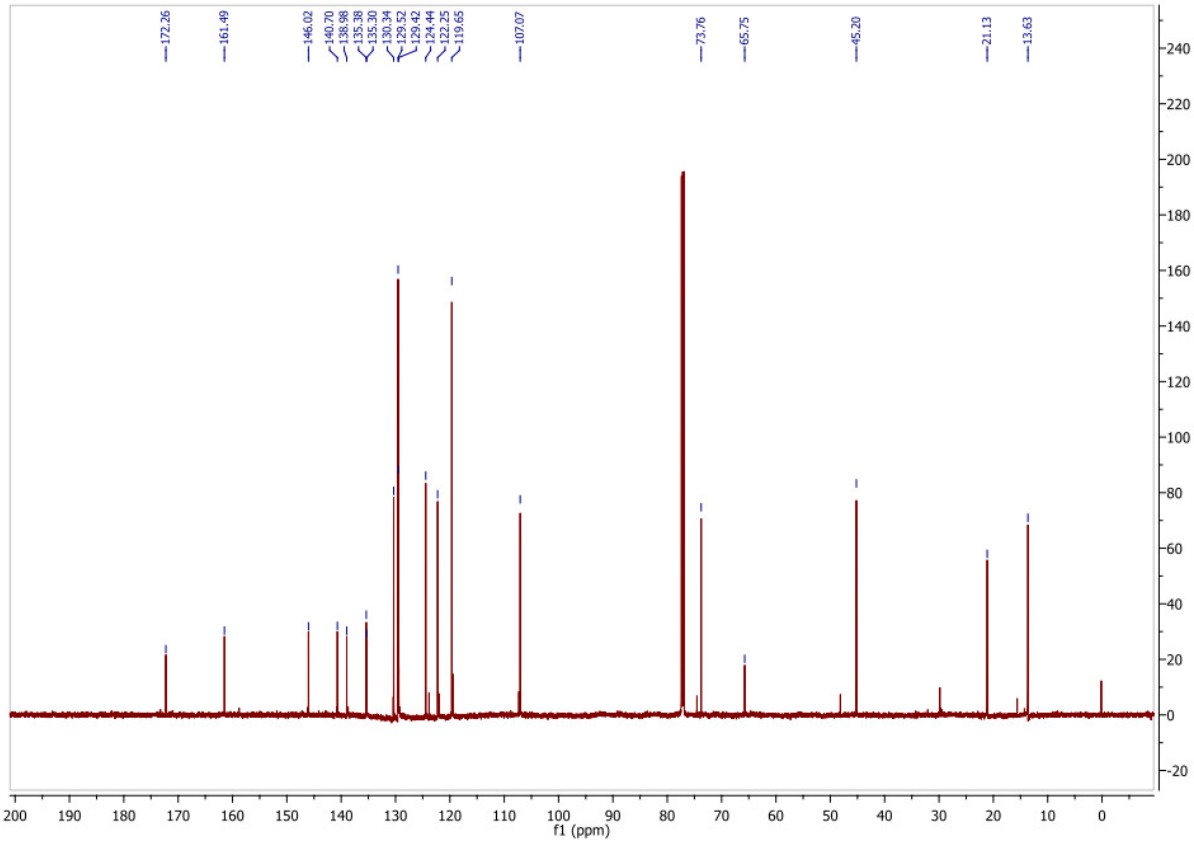

173.02
162.01
145.67
140.49
139.06
134.24
132.04
130.47
130.30
130.10
129.45
129.10
127.85
124.44
122.31
107.51
73.52
64.06
45.10
13.58
f1 (ppm)

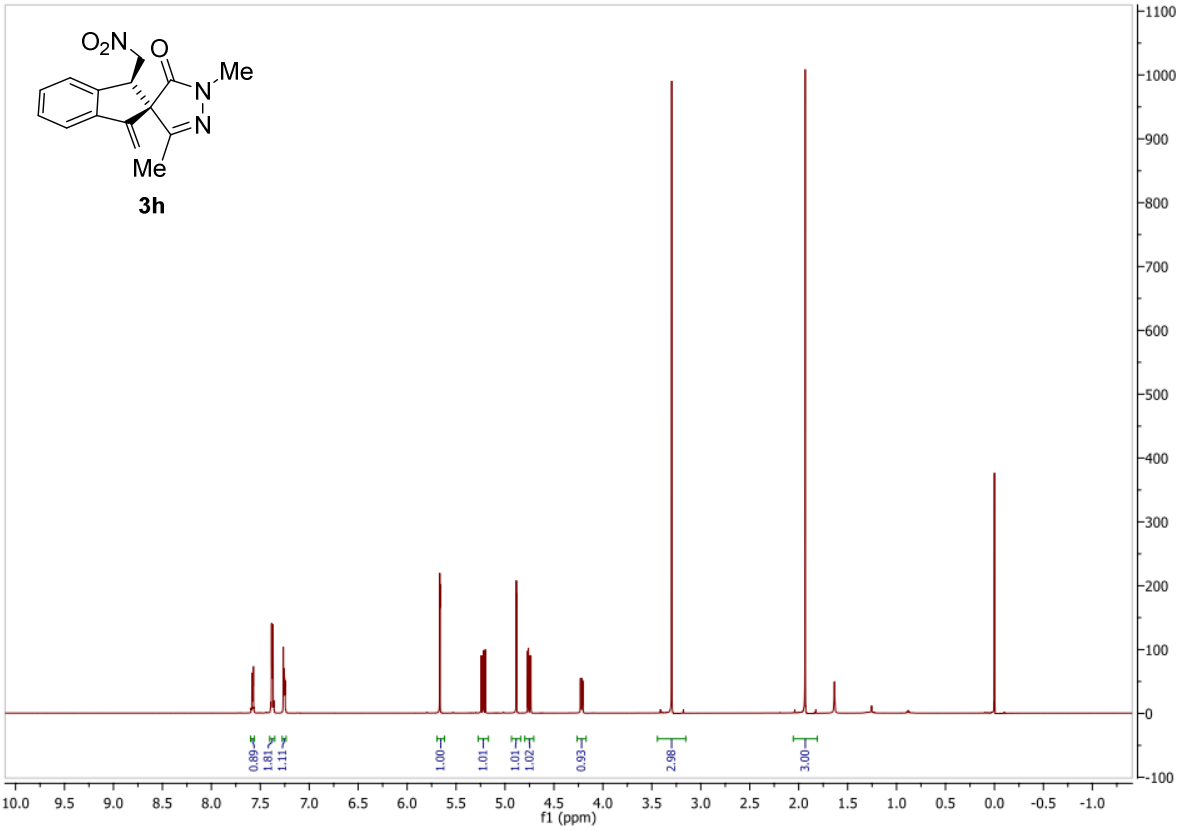

O2N
O
Cl
N
N
Me
1.87
0.99
2.03
1.88
0.98
1.05
1.04
1.02
1.06
0.96
3.00
f1 (ppm)

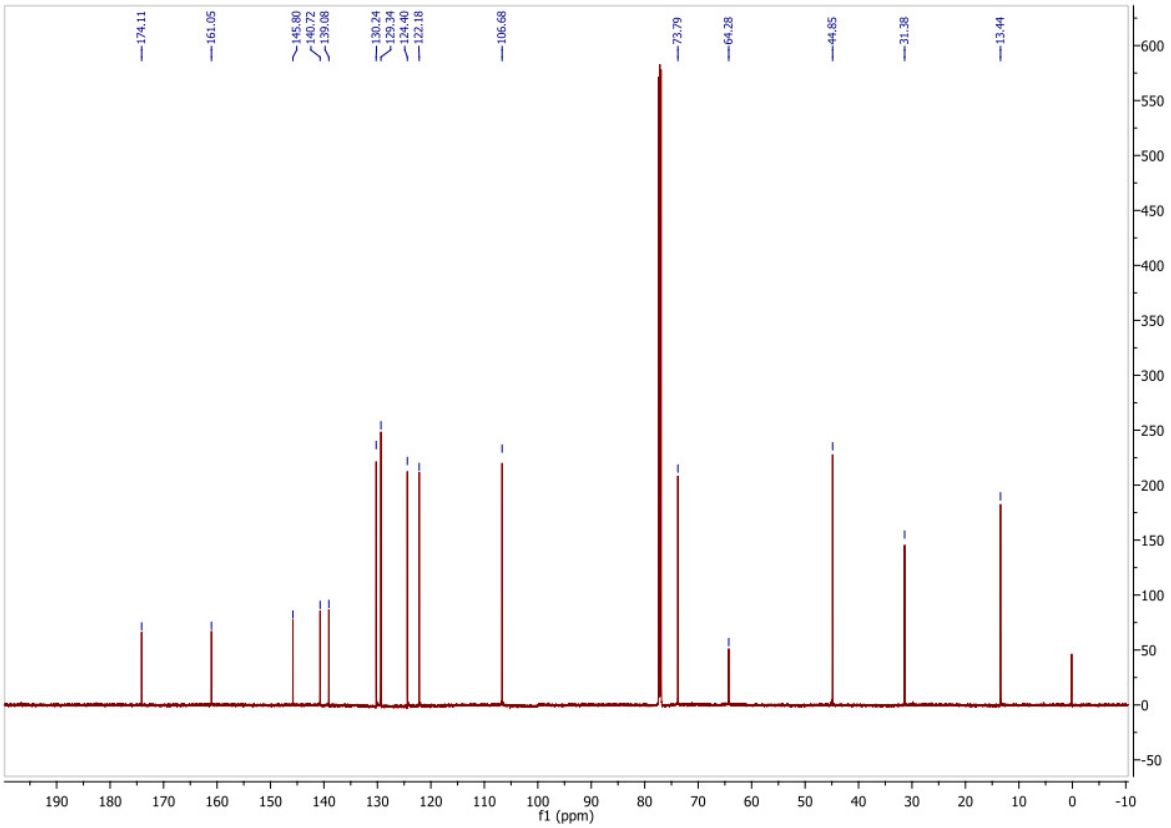
3f

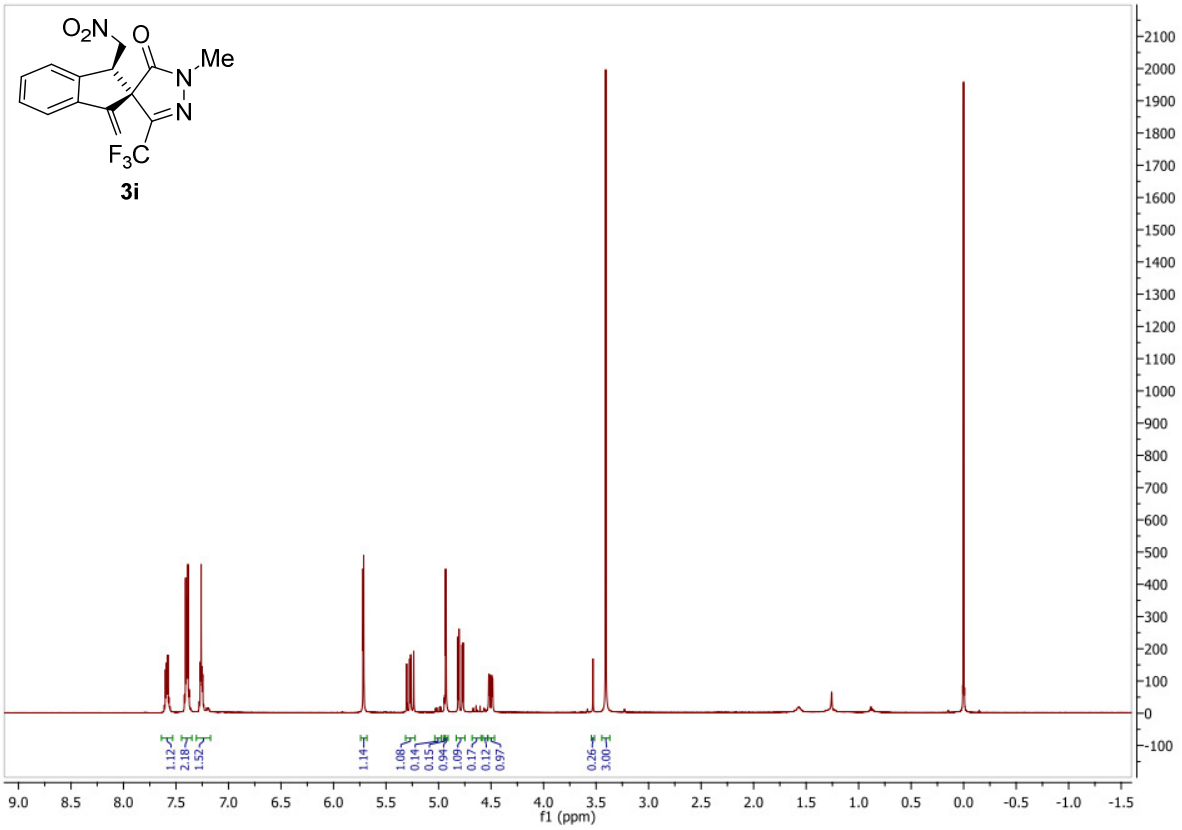

172.42
161.93
145.88
140.46
138.86
136.37
130.65
130.46
129.54
129.05
124.45
122.30
120.53
107.25
73.59
65.80
45.29
13.65
f1 (ppm)

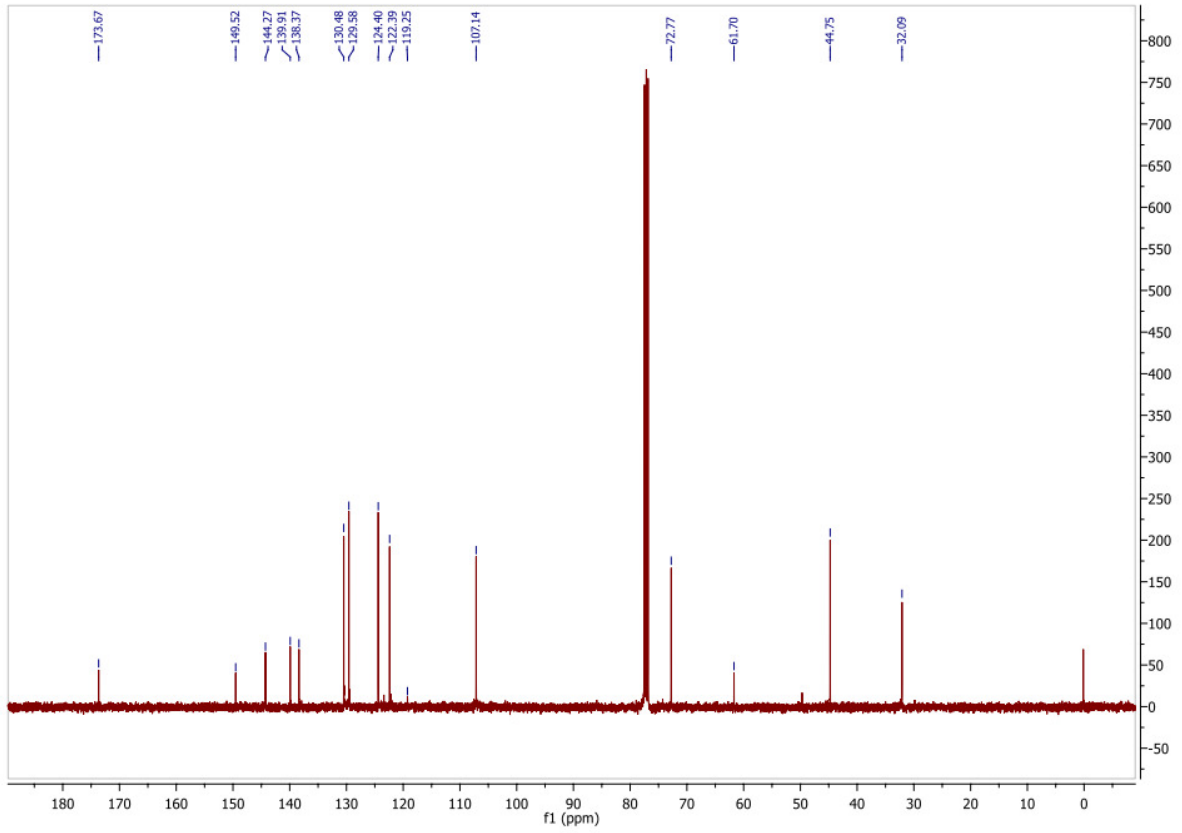

O2N
O
N
N
Me
Me
3g
f1 (ppm)

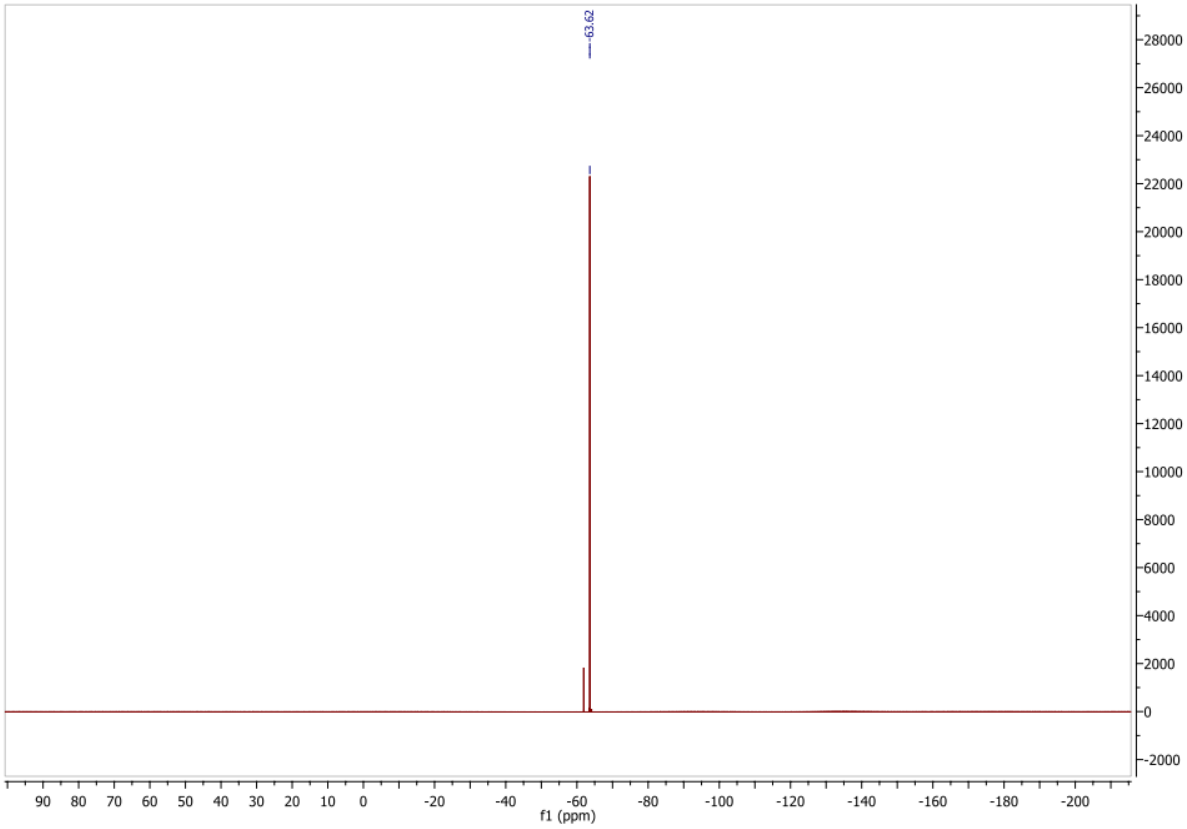

172.26
161.49
146.02
140.70
138.98
135.38
135.30
130.34
129.52
129.42
124.44
122.25
119.65
107.07
73.76
65.75
45.20
21.13
13.63
f1 (ppm)

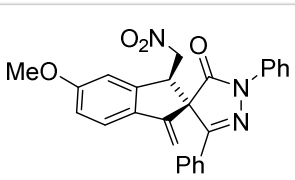

O2N
O
N
Me
N
Me
3h
0.89
1.81
1.11
1.00
1.01
1.01
1.02
0.93
2.98
3.00
f1 (ppm)


174.11
161.05
145.80
140.72
139.08
130.24
129.34
124.40
122.18
106.68
73.79
64.28
44.85
31.38
13.44
f1 (ppm)


O2N
O
N
Me
N
F3C
3i
1.12
2.18
1.52
1.14
1.08
0.14
0.15
0.94
1.09
0.17
0.12
0.97
0.26
3.00
f1 (ppm)

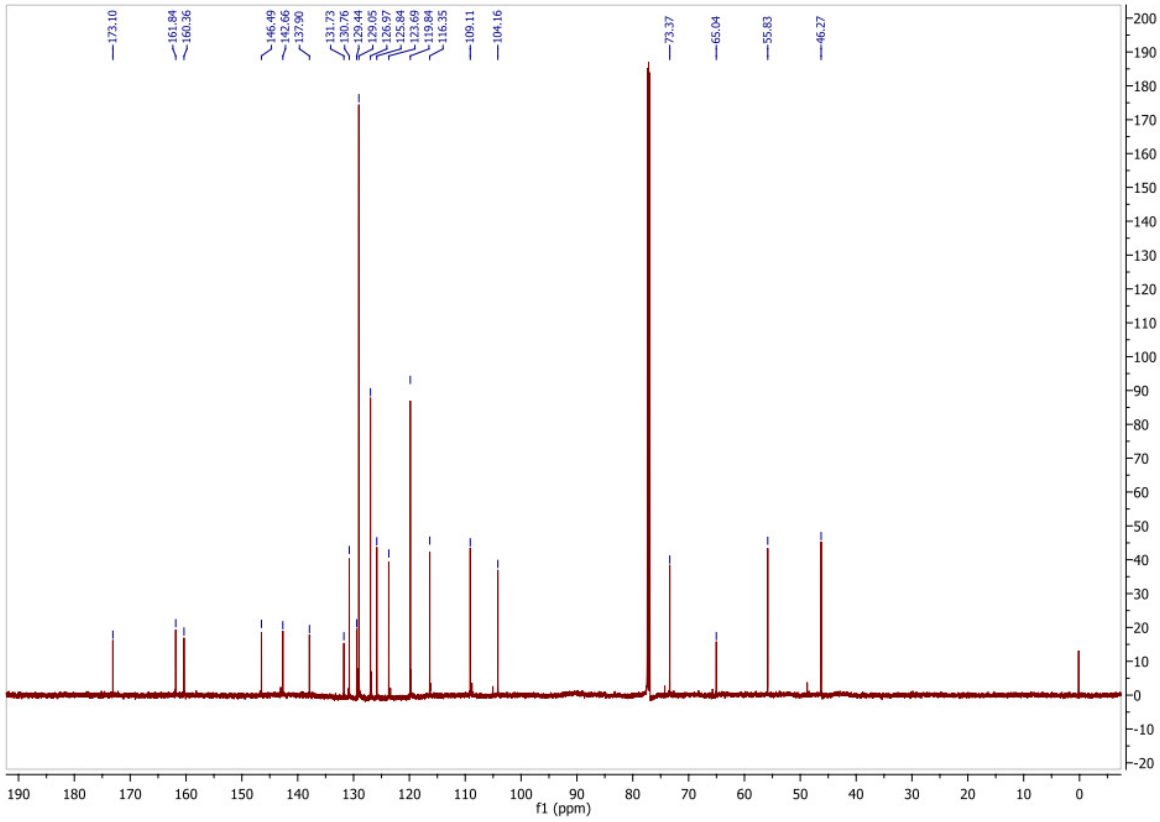

173.67
149.52
144.27
139.91
138.37
130.48
129.58
124.40
122.39
119.25
107.14
72.77
61.70
44.75
32.09
f1 (ppm)

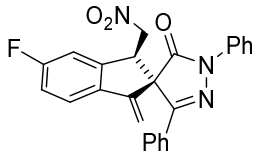

-63.62
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)


O2N
O
MeO
Ph
N
N
Ph

3j

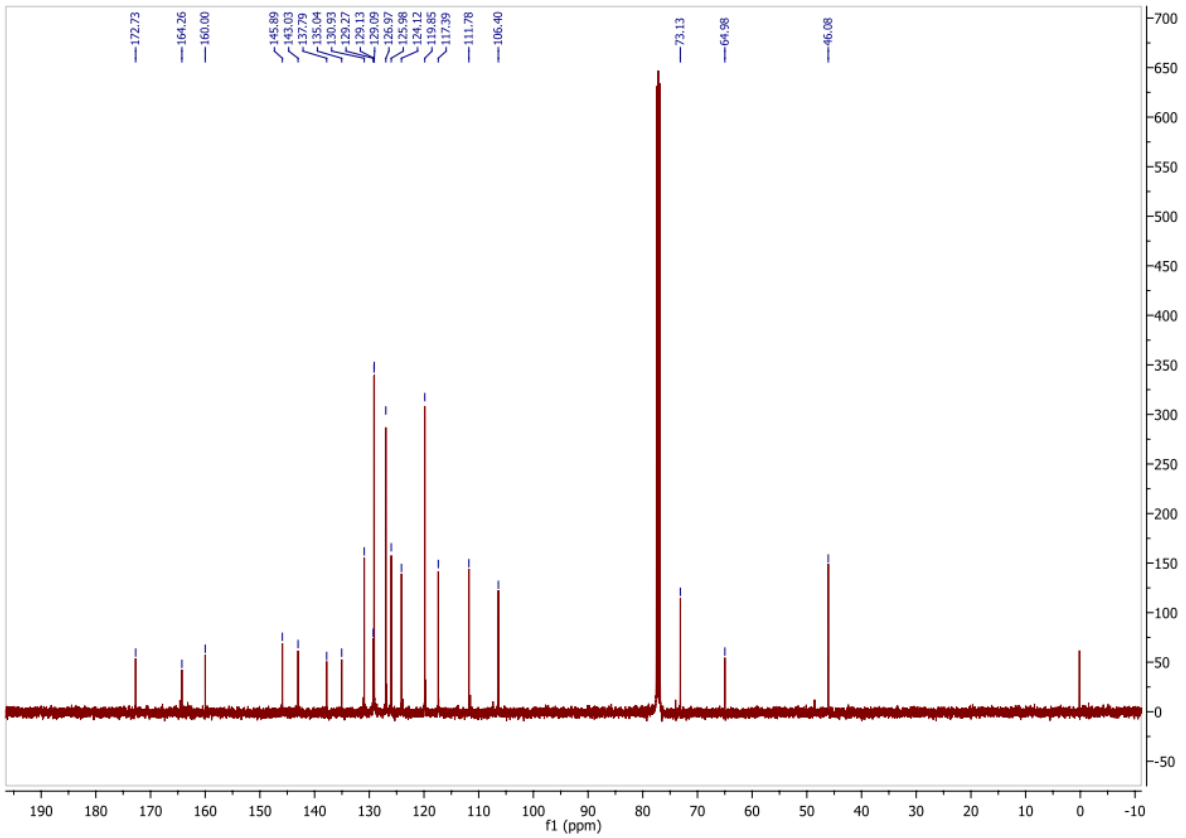
0.19
1.85
2.97
3.32
2.04
1.57
1.05
0.95
0.09
0.09
1.00
1.04
0.12
0.97
1.04
0.20
1.05
0.07
3.22
f1 (ppm)

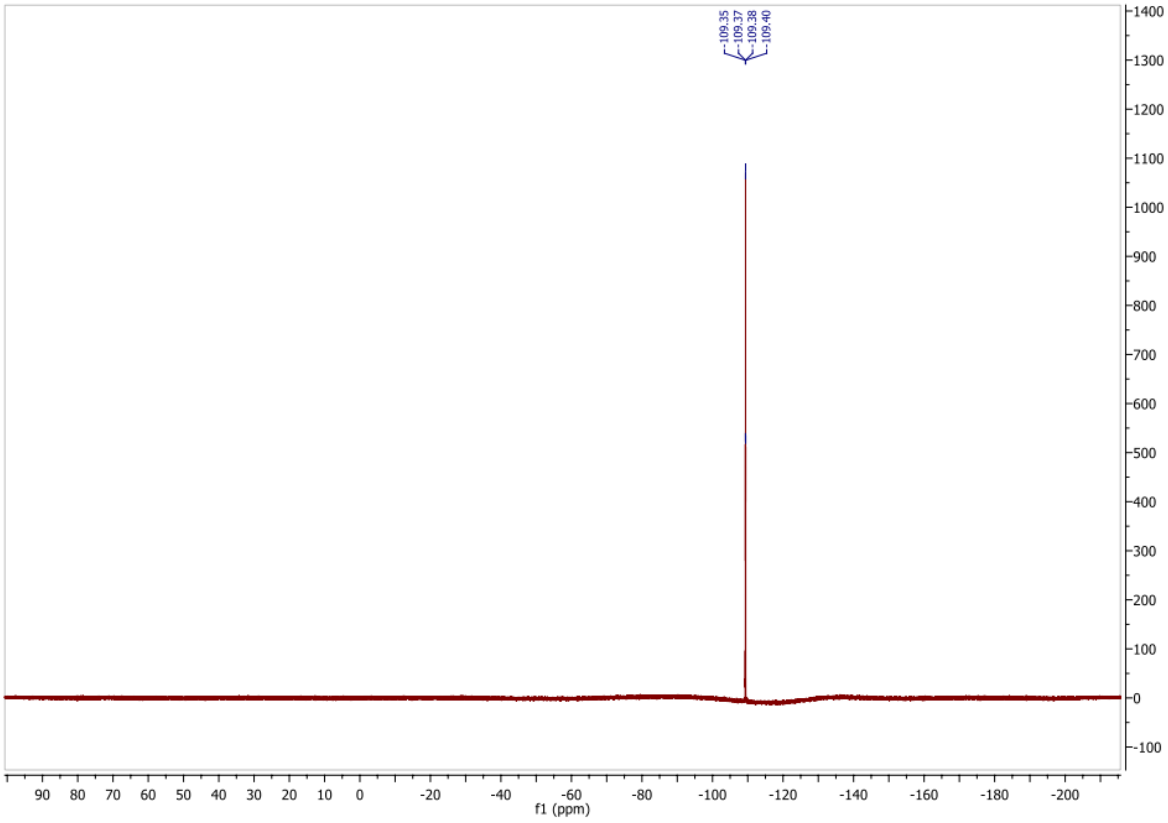

173.10
161.84
160.36
146.49
142.66
137.90
131.73
130.76
129.44
129.05
126.97
125.84
123.69
119.84
116.35
109.11
104.16
73.37
65.04
55.83
46.27
f1 (ppm)

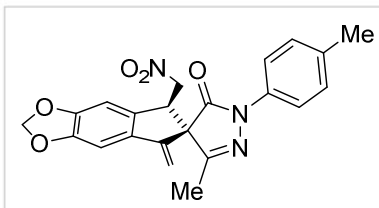

O_2N
O
F
N
Ph
N
Ph

3k

0.21
1.83
1.05
1.93
3.30
2.02
1.69
1.11
1.08
0.12
0.98
1.03
0.12
0.95
1.02
0.14
0.16
1.00
0.18
f1 (ppm)

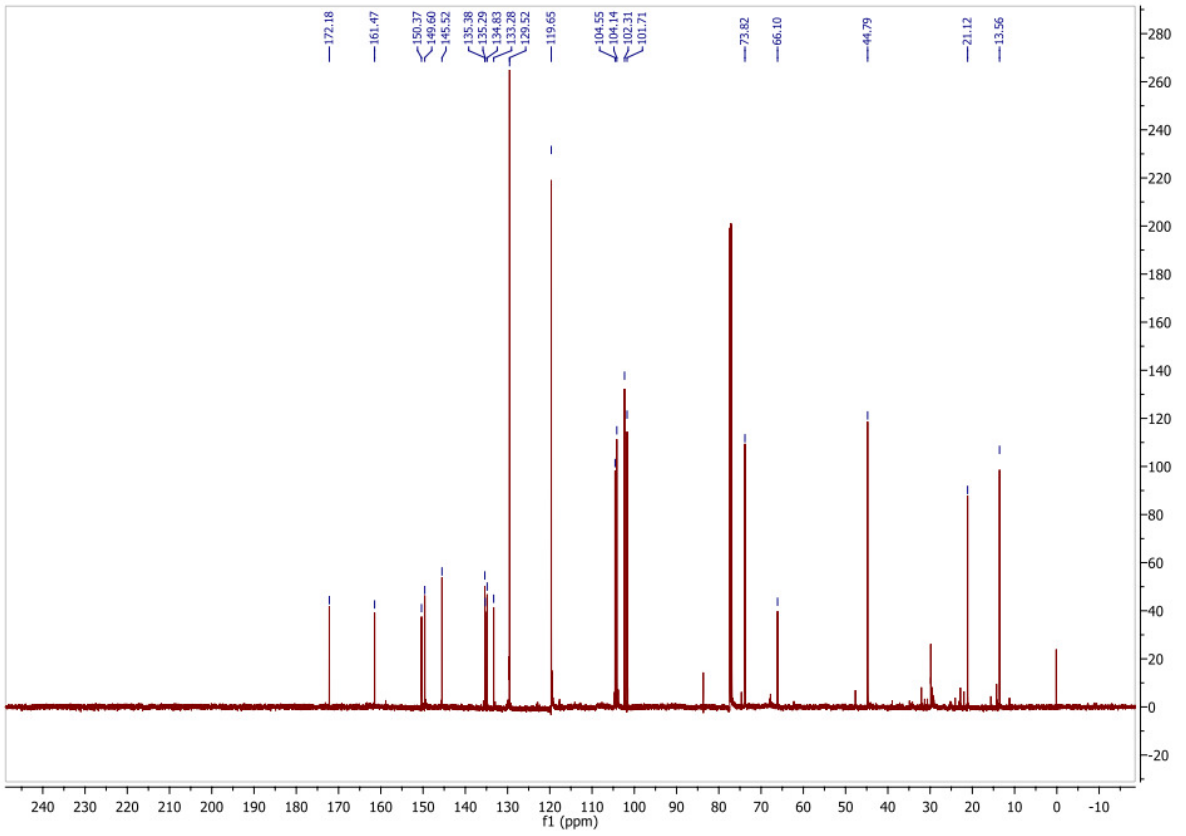

172.73
164.26
160.00
145.89
143.03
137.79
135.04
130.93
129.27
129.13
129.09
126.97
125.98
124.12
119.85
117.39
111.78
106.40
73.13
64.98
46.08
f1 (ppm)

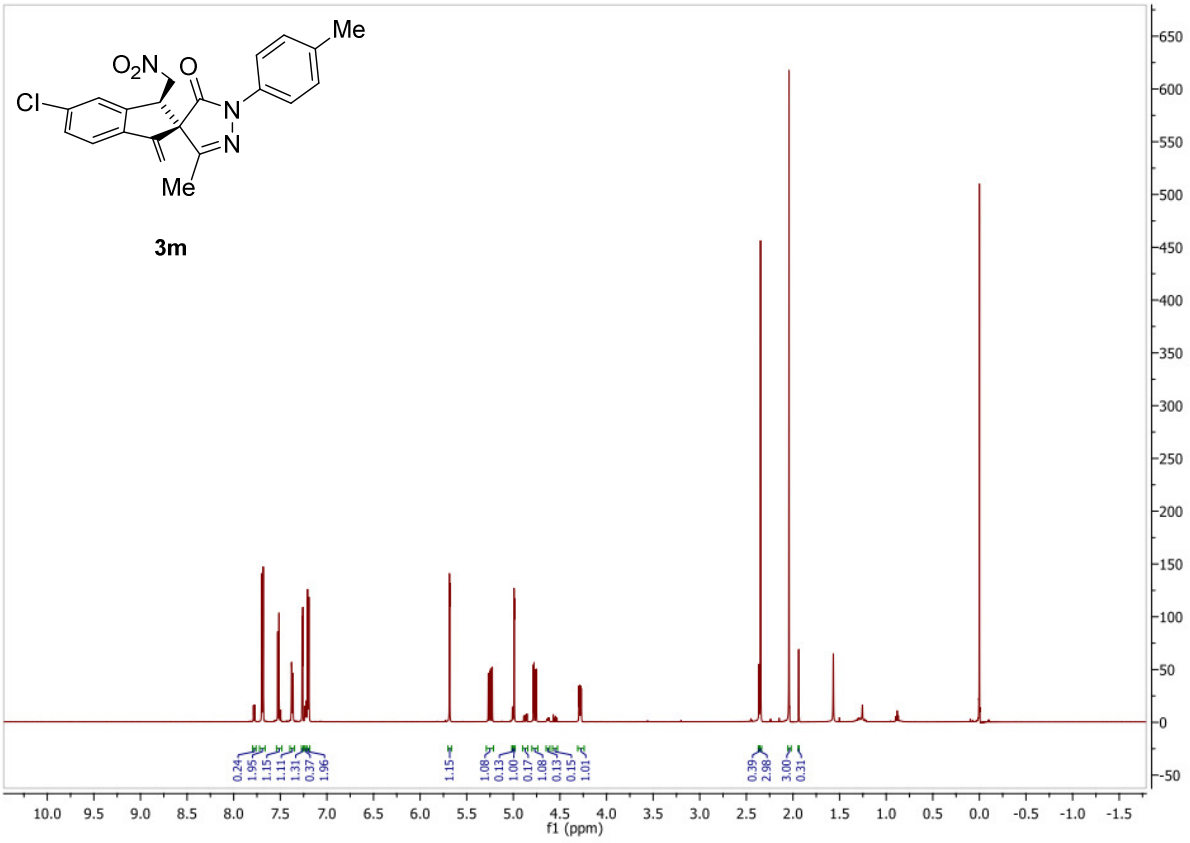

-109.35
-109.37
-109.38
-109.40
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

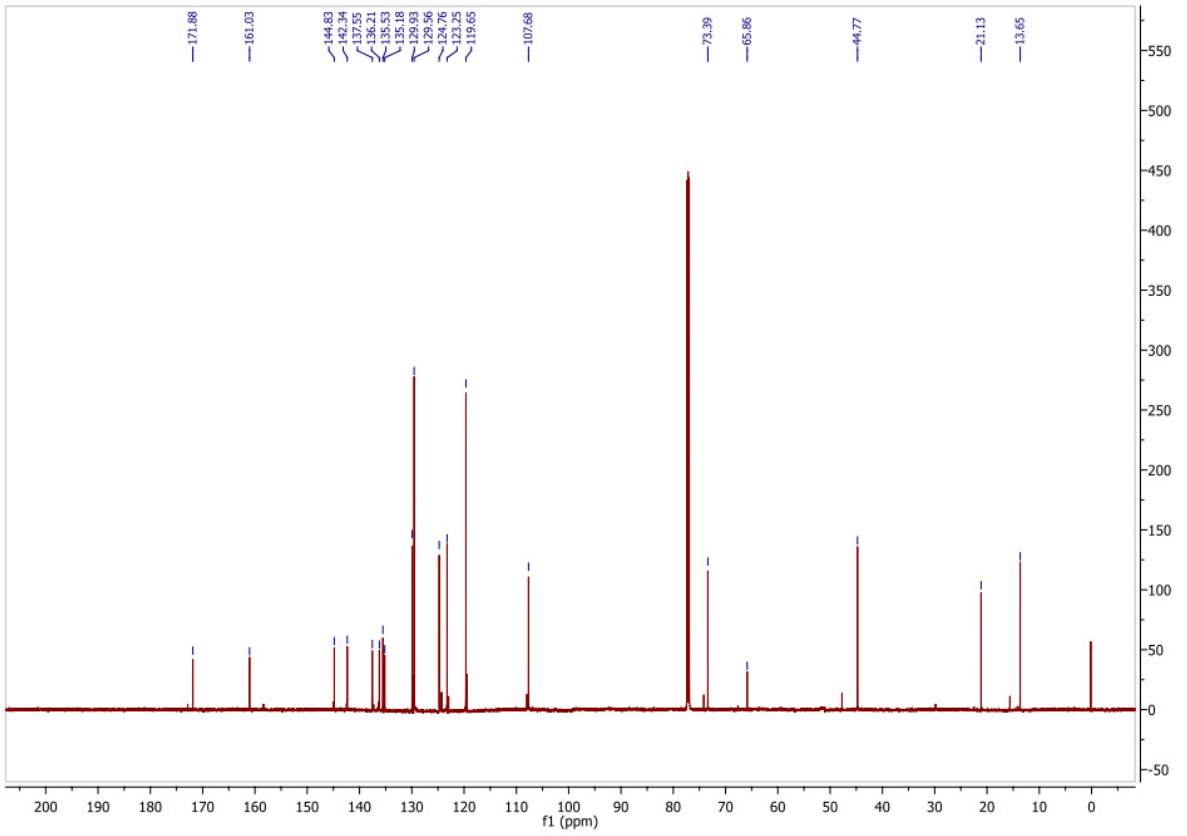

Me
O_2N
O
O
O
N
N
Me

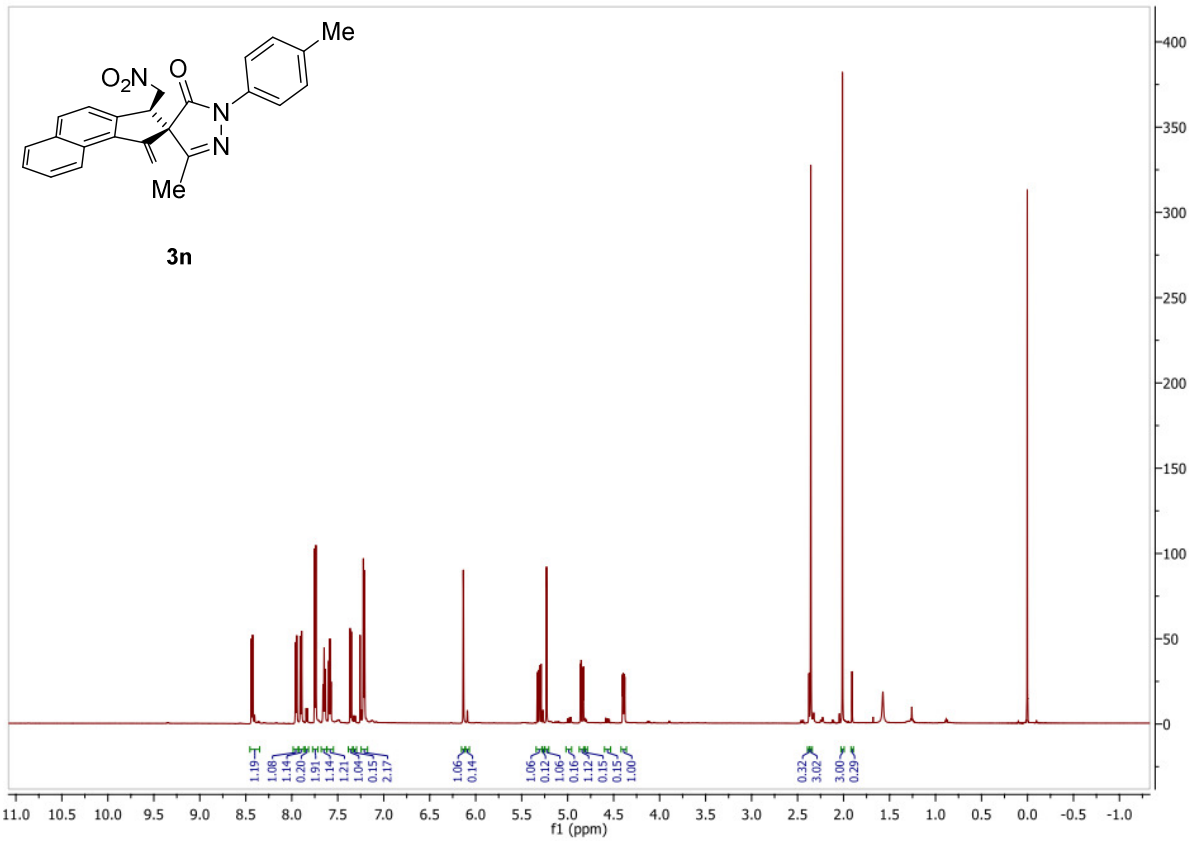
3l

1.84
2.01
0.87
0.91
2.17
1.08
1.10
1.20
1.13
1.00
3.07
3.00
0.18
f1 (ppm)

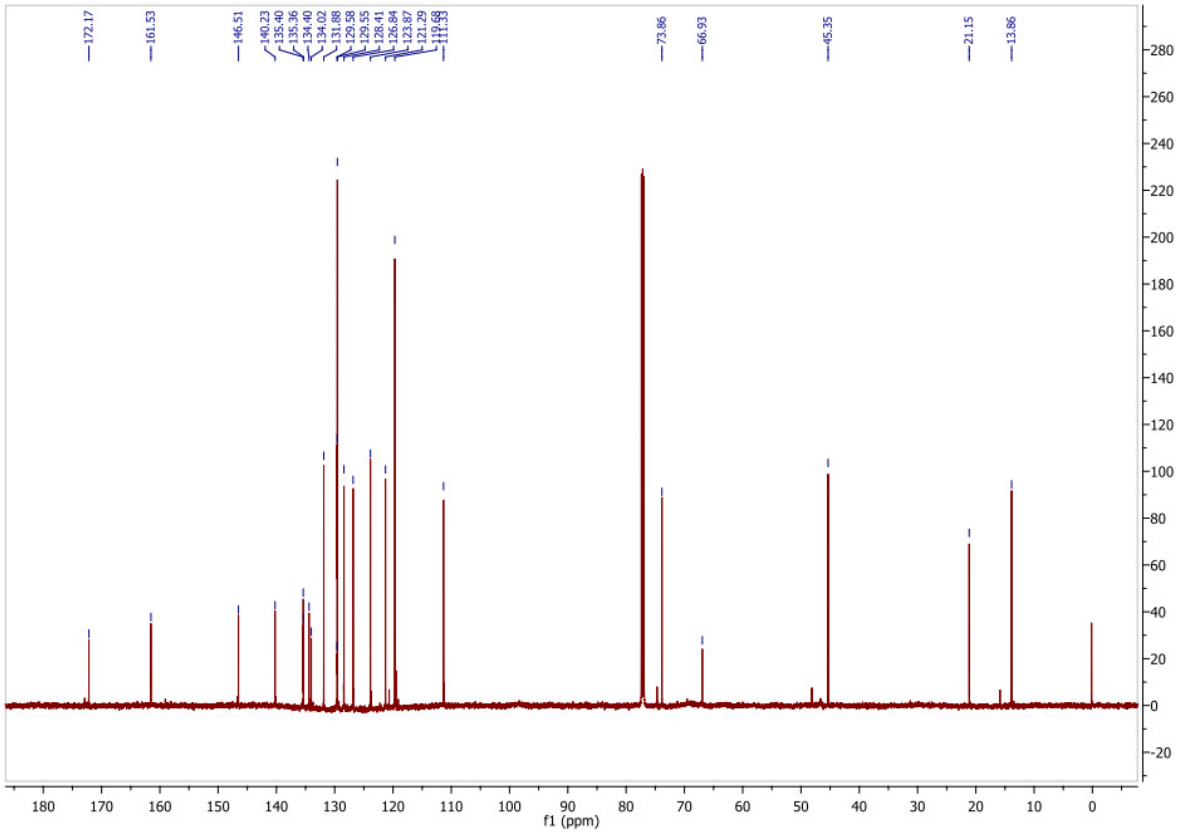

172.18
161.47
150.37
149.60
145.52
135.38
135.29
134.83
133.28
129.52
119.65
104.55
104.14
102.31
101.71
73.82
66.10
44.79
21.12
13.56
f1 (ppm)

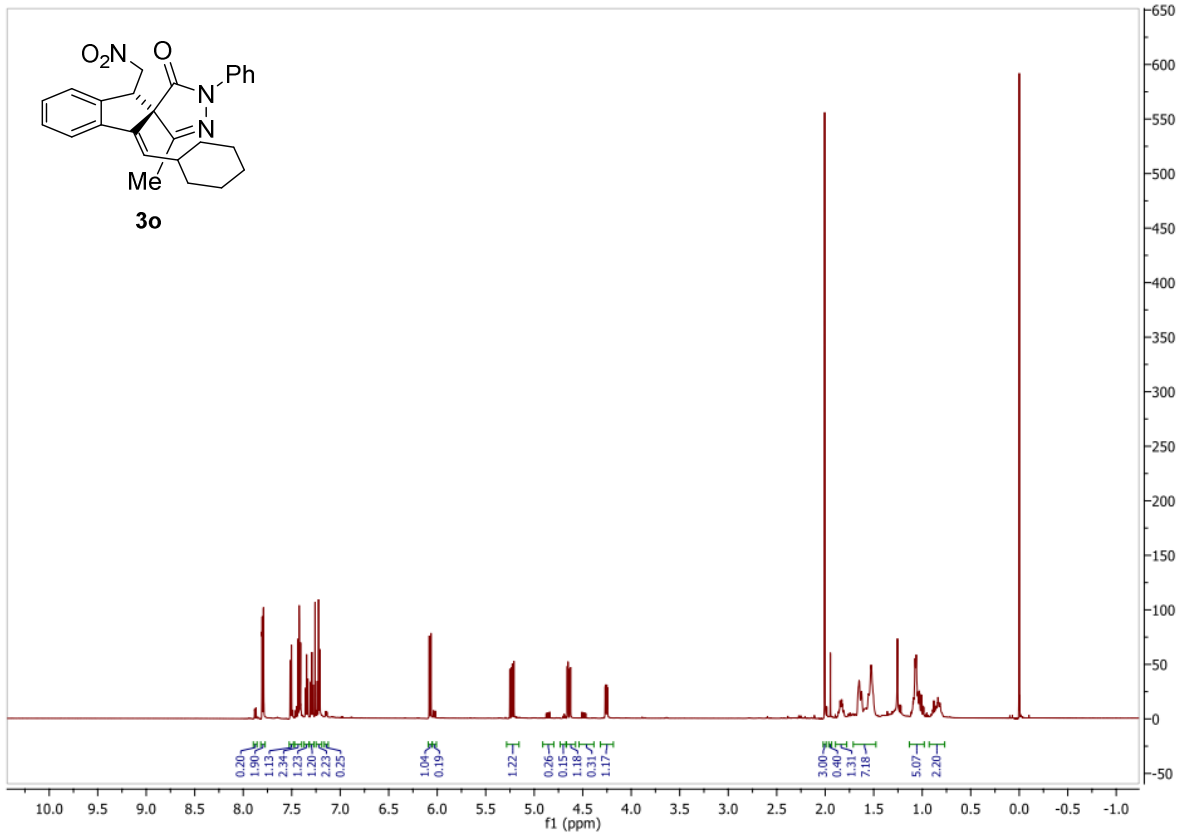

Me
O2N
O
Cl
N
N
Me
3m
0.24
1.95
1.15
1.11
1.31
0.37
1.96
1.15
1.08
0.13
1.00
0.17
1.08
0.13
0.15
1.01
0.39
2.98
3.00
0.31
f1 (ppm)

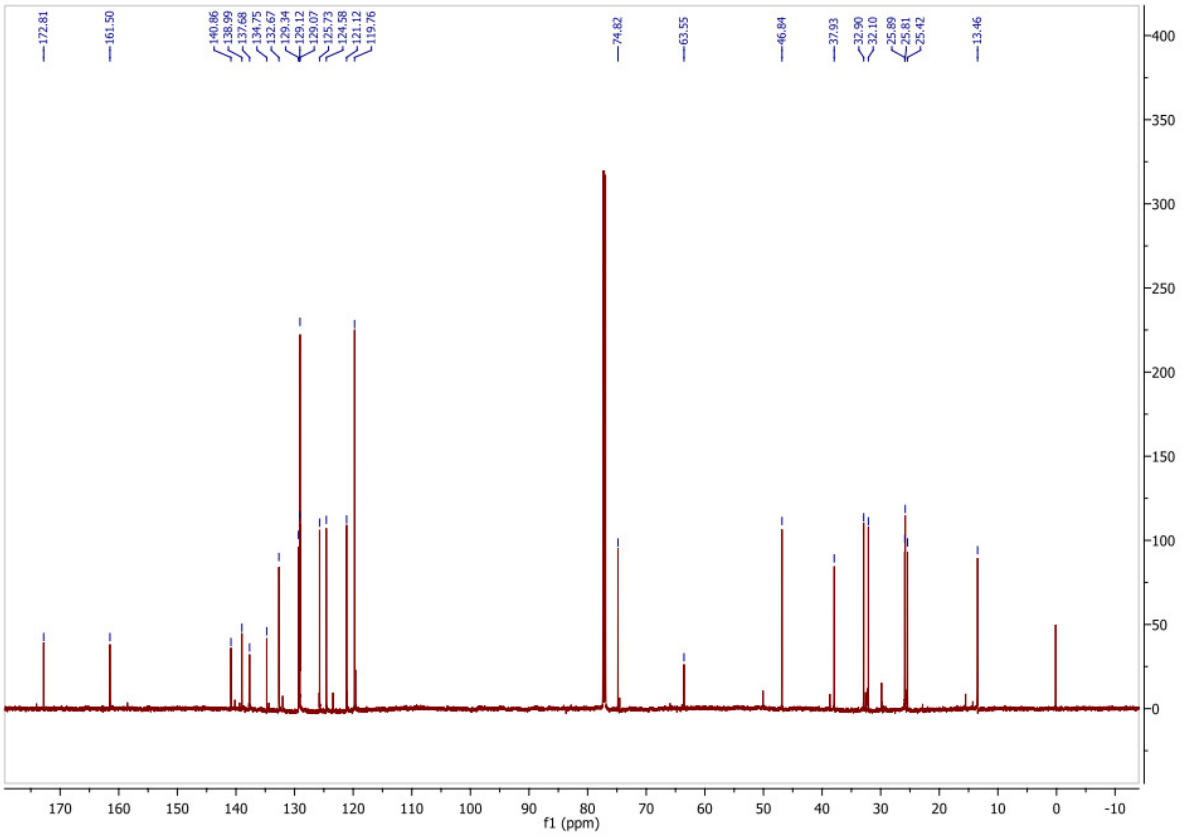

171.88
161.03
144.83
142.34
137.55
136.21
135.53
135.18
129.93
129.56
124.76
123.25
119.65
107.68
73.39
65.86
44.77
21.13
13.65
f1 (ppm)

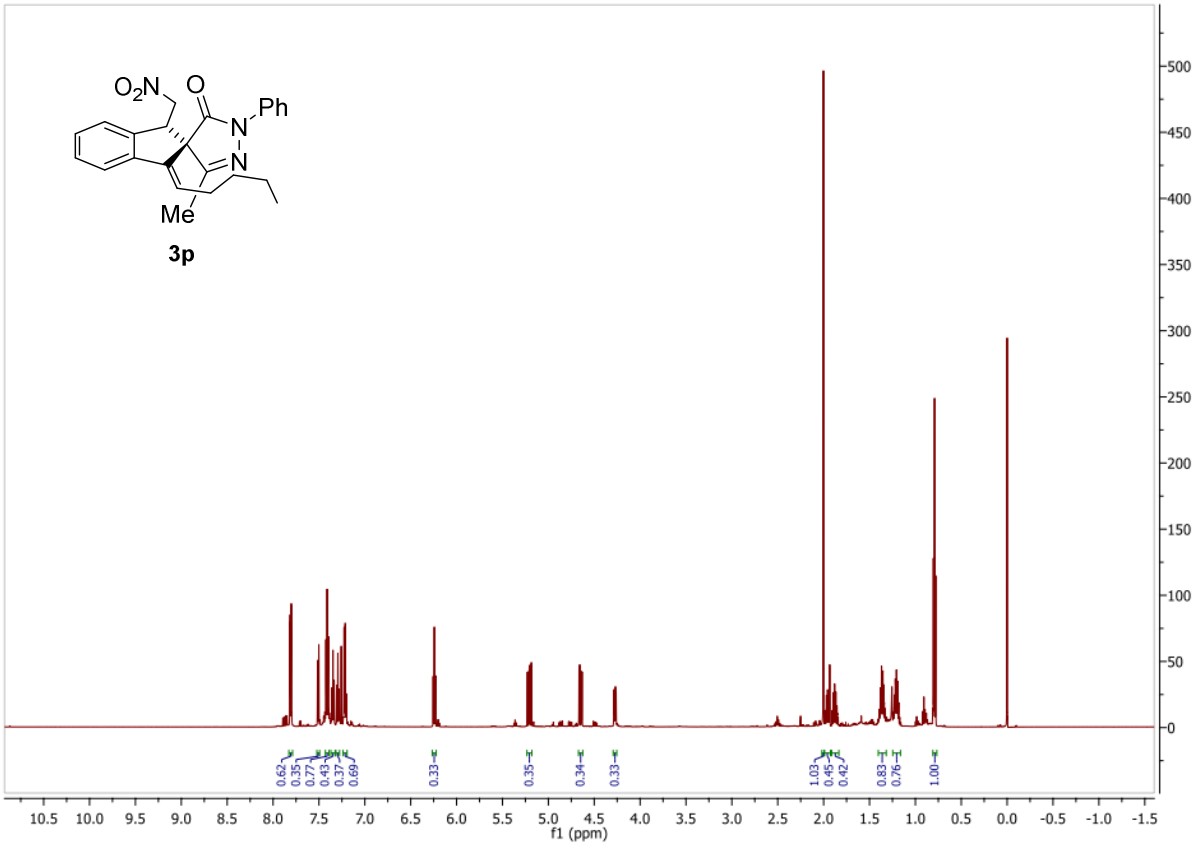

Me
O2N
O
N
N
Me
1.19
1.08
1.14
0.20
1.91
1.14
1.21
1.04
0.15
2.17
1.06
0.14
1.06
0.12
1.06
0.16
1.12
0.15
0.15
1.00
0.32
3.02
3.00
0.29
f1 (ppm)

3n

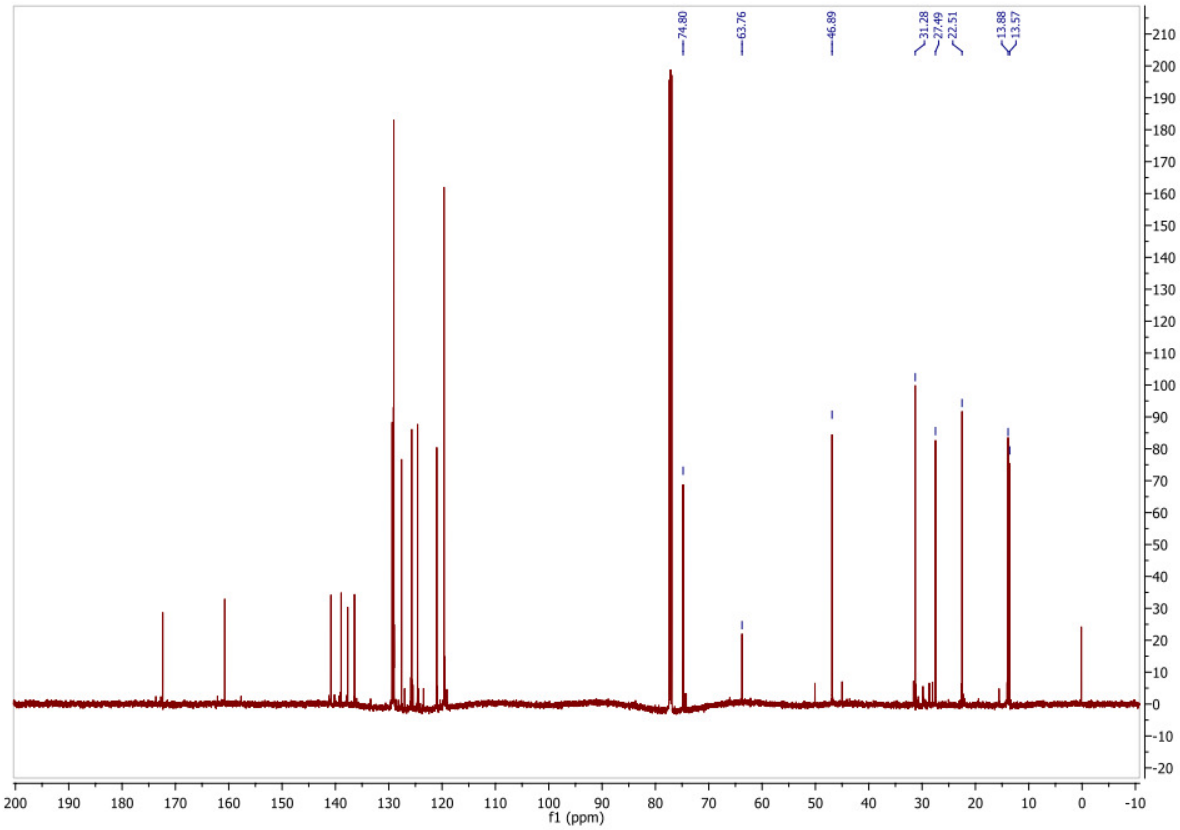

172.17
161.53
146.51
140.23
135.40
135.36
134.40
134.02
131.88
129.58
129.55
128.41
126.84
123.87
121.29
119.68
111.33
73.86
66.93
45.35
21.15
13.86
f1 (ppm)

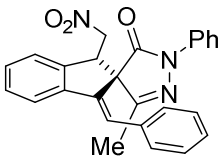

O2N
O
Ph
N
N
Me
3o
f1 (ppm)


172.81
161.50
140.86
138.99
137.68
134.75
132.67
129.34
129.12
129.07
125.73
124.58
121.12
119.76
74.82
63.55
46.84
37.93
32.90
32.10
25.89
25.81
25.42
13.46
f1 (ppm)


O2N
O
Ph
N
N
Me
0.62
0.35
0.77
0.43
0.37
0.69
0.33
0.35
0.34
0.33
1.03
0.45
0.42
0.83
0.76
1.00
f1 (ppm)

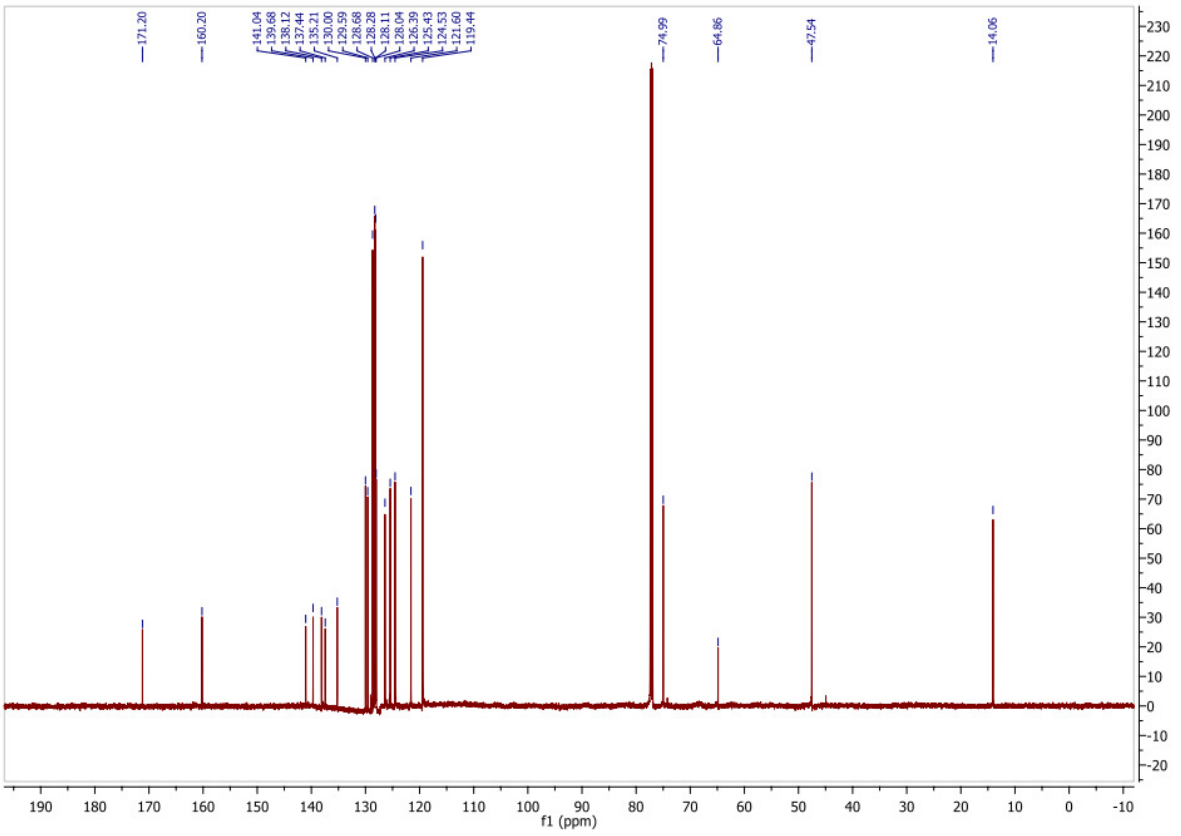
3p

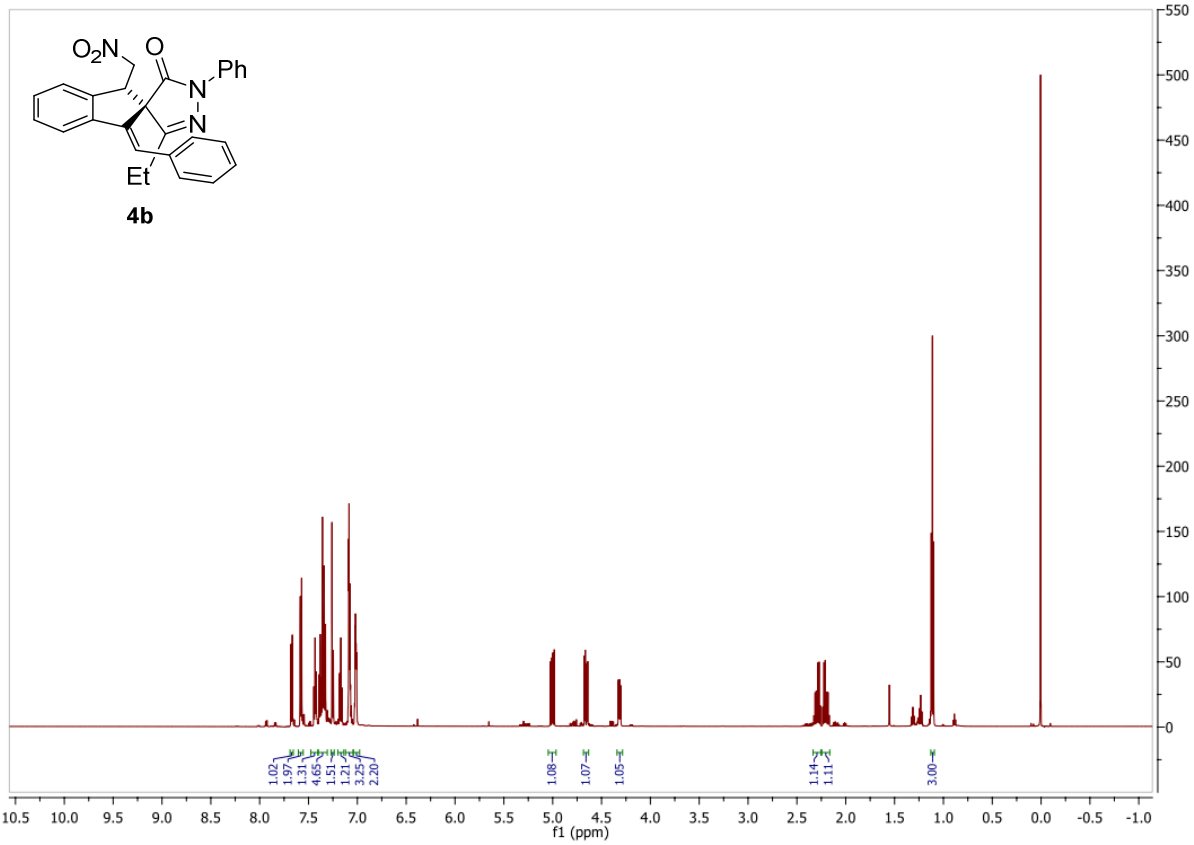

74.80
63.76
46.89
31.28
27.49
22.51
13.88
13.57
f1 (ppm)


O2N
O
Ph
N
N
Me

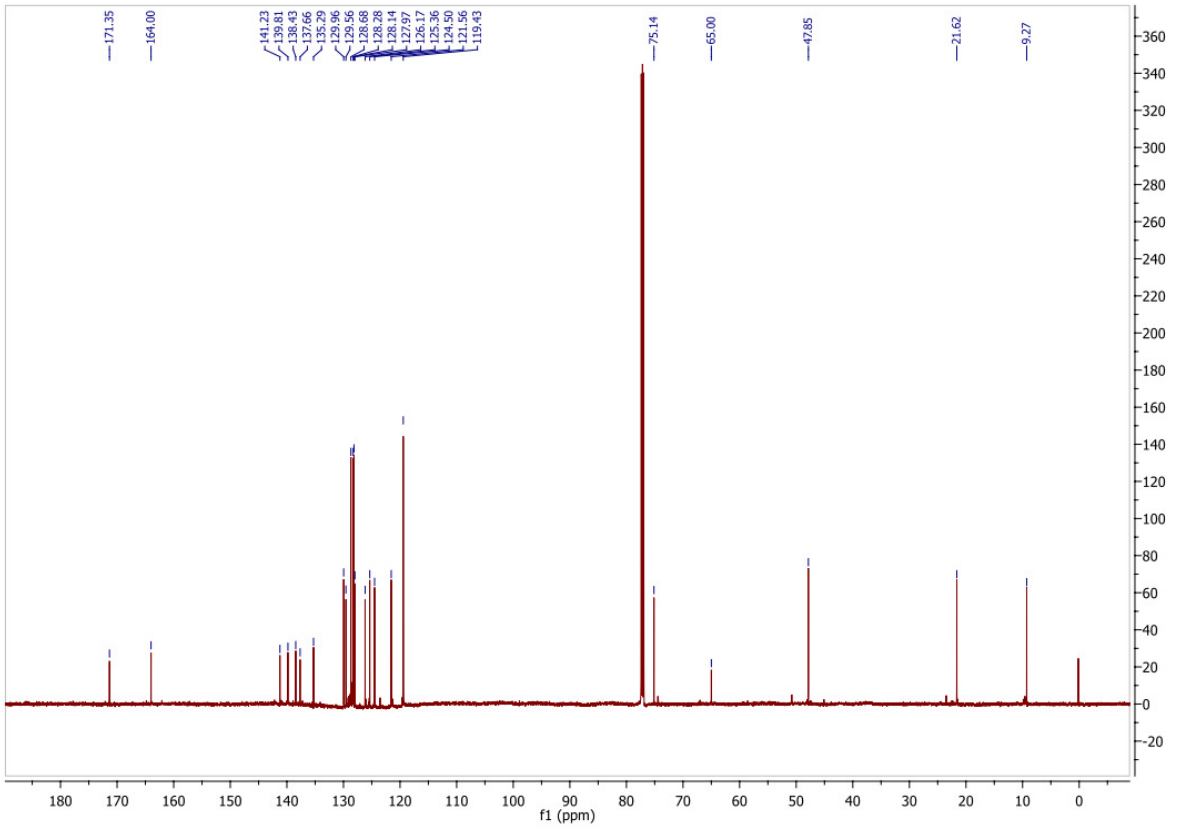
4a

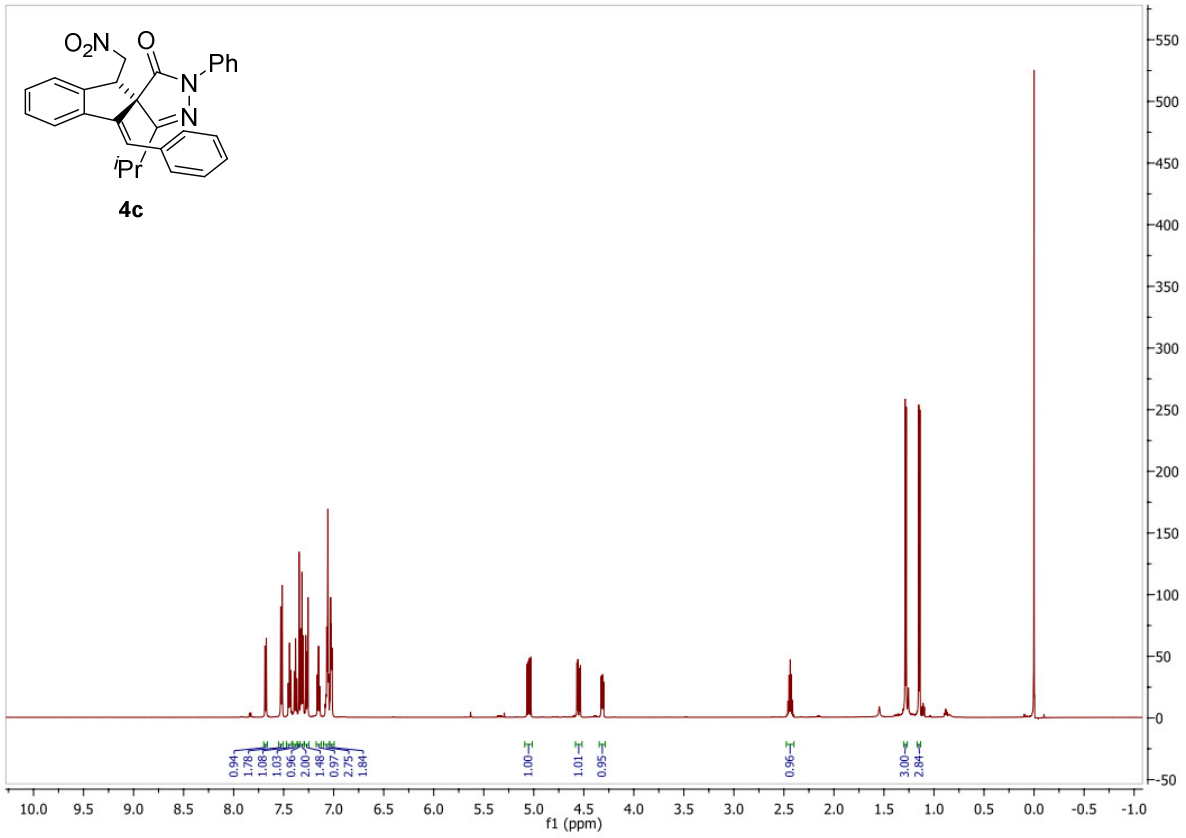
1.00
1.85
1.07
2.00
1.93
1.31
0.99
2.79
1.85
1.03
1.04
1.00
3.00
f1 (ppm)

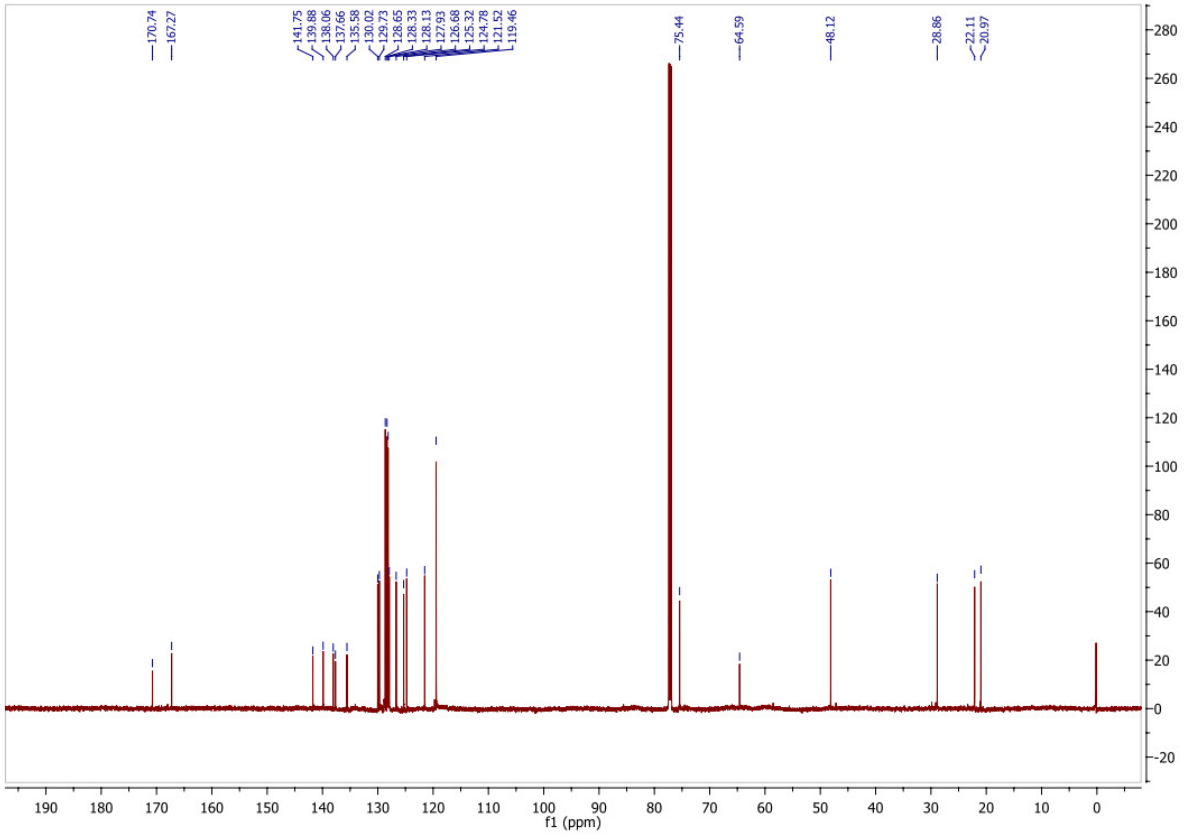

171.20
160.20
141.04
139.68
138.12
137.44
135.21
130.00
129.99
128.68
128.28
128.11
128.04
126.39
125.43
124.53
121.60
119.44
74.99
64.86
47.54
14.06
f1 (ppm)

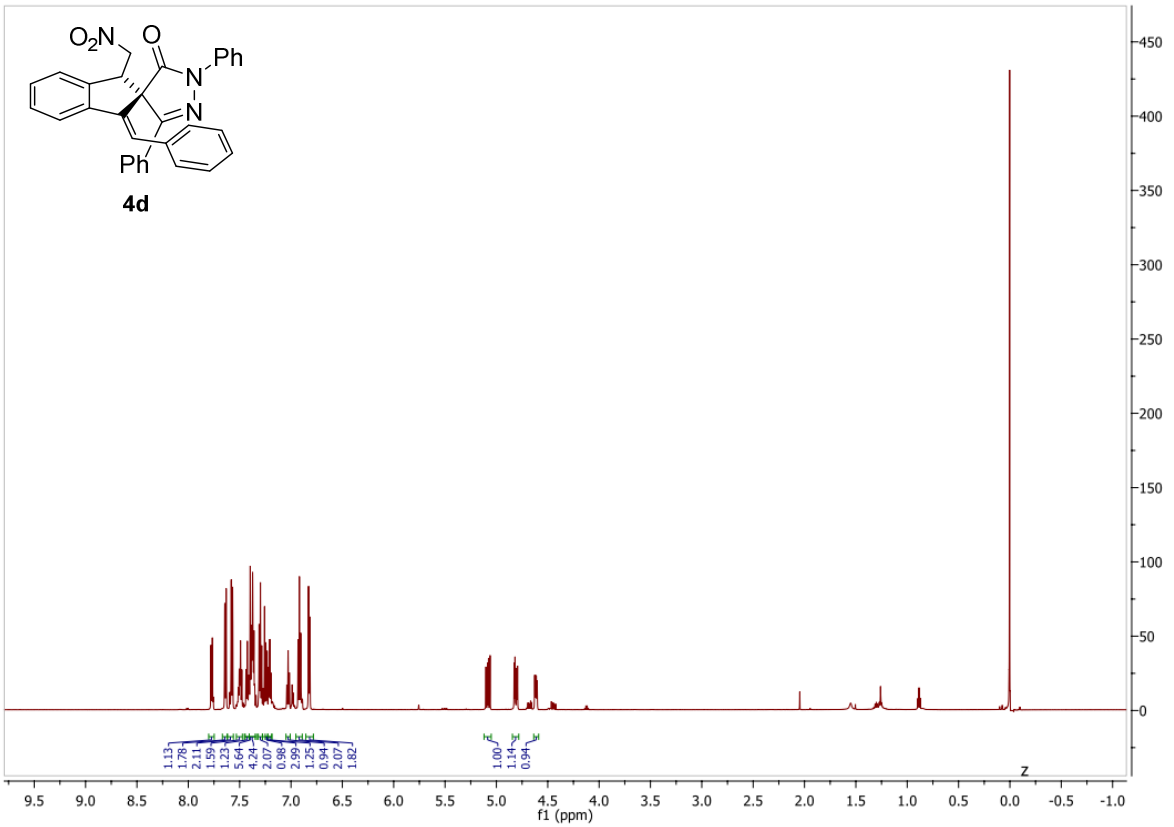

O2N
O
N
Ph
N
Et
1.02
1.97
1.31
4.65
1.51
1.21
3.25
2.20
1.08
1.07
1.05
1.14
1.11
3.00
f1 (ppm)

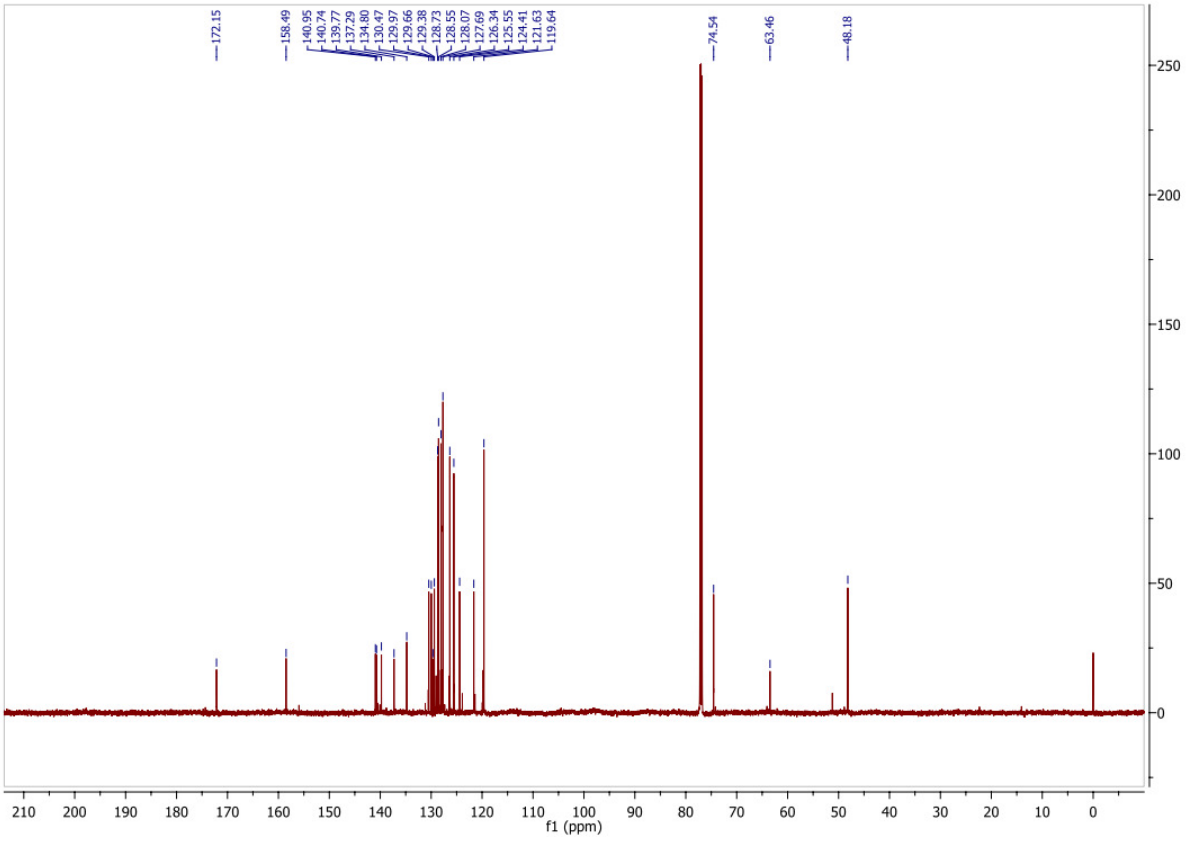
4b

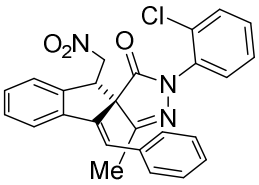

171.35
164.00
141.23
139.81
138.43
137.66
135.29
129.96
129.56
128.68
128.28
128.14
127.97
126.17
125.36
124.50
121.56
119.43
75.14
65.00
47.85
21.62
9.27
f1 (ppm)


O2N
O
Ph
N
N
iPr
4c
0.94
1.78
1.08
1.03
0.96
2.00
1.48
0.97
2.75
1.84
1.00
1.01
0.95
0.96
3.00
2.84
f1 (ppm)


170.74
167.27
141.75
139.88
138.06
137.66
135.58
130.02
129.73
128.65
128.33
128.13
127.93
126.68
125.32
124.78
121.52
119.46
75.44
64.59
48.12
28.86
22.11
20.97
f1 (ppm)

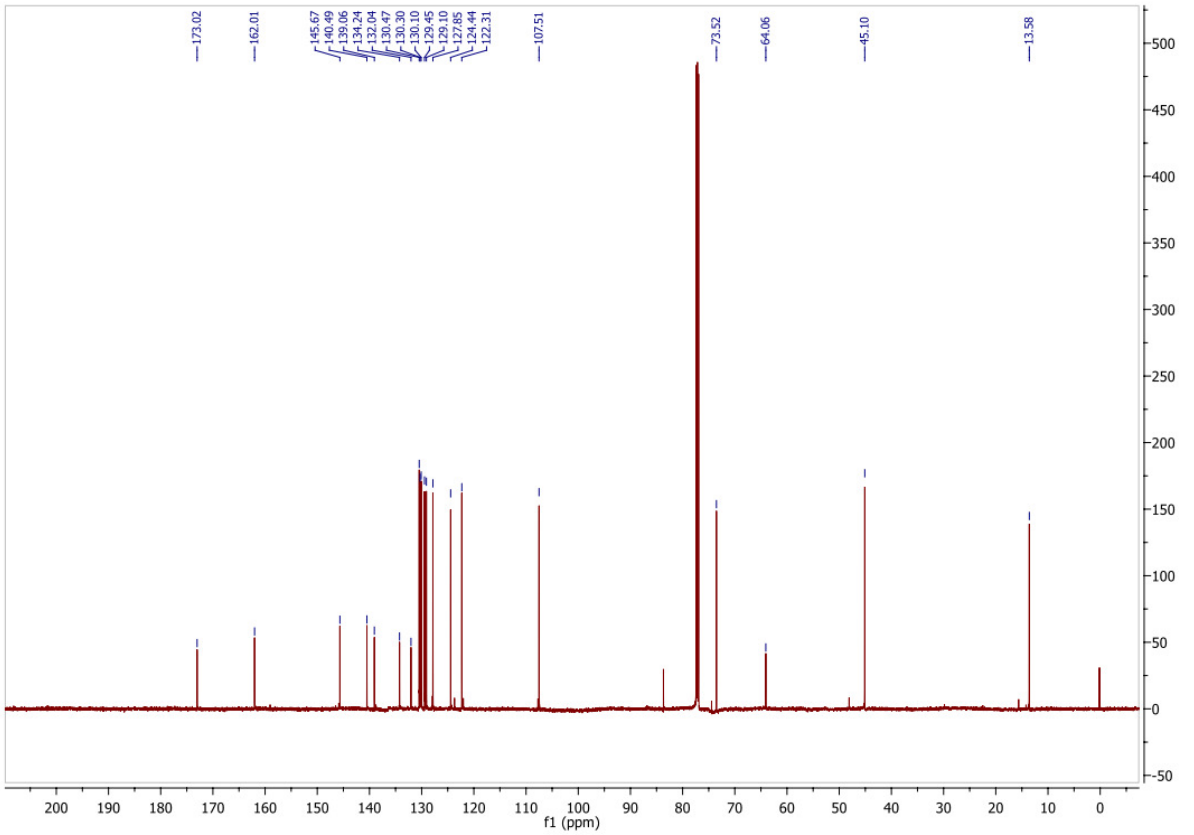

O2N
O
Ph
N
N
Ph
4d
1.13
1.78
2.11
1.59
1.23
5.64
4.24
2.07
0.98
2.99
1.25
0.94
2.07
1.82
1.00
1.14
0.94
z
f1 (ppm)

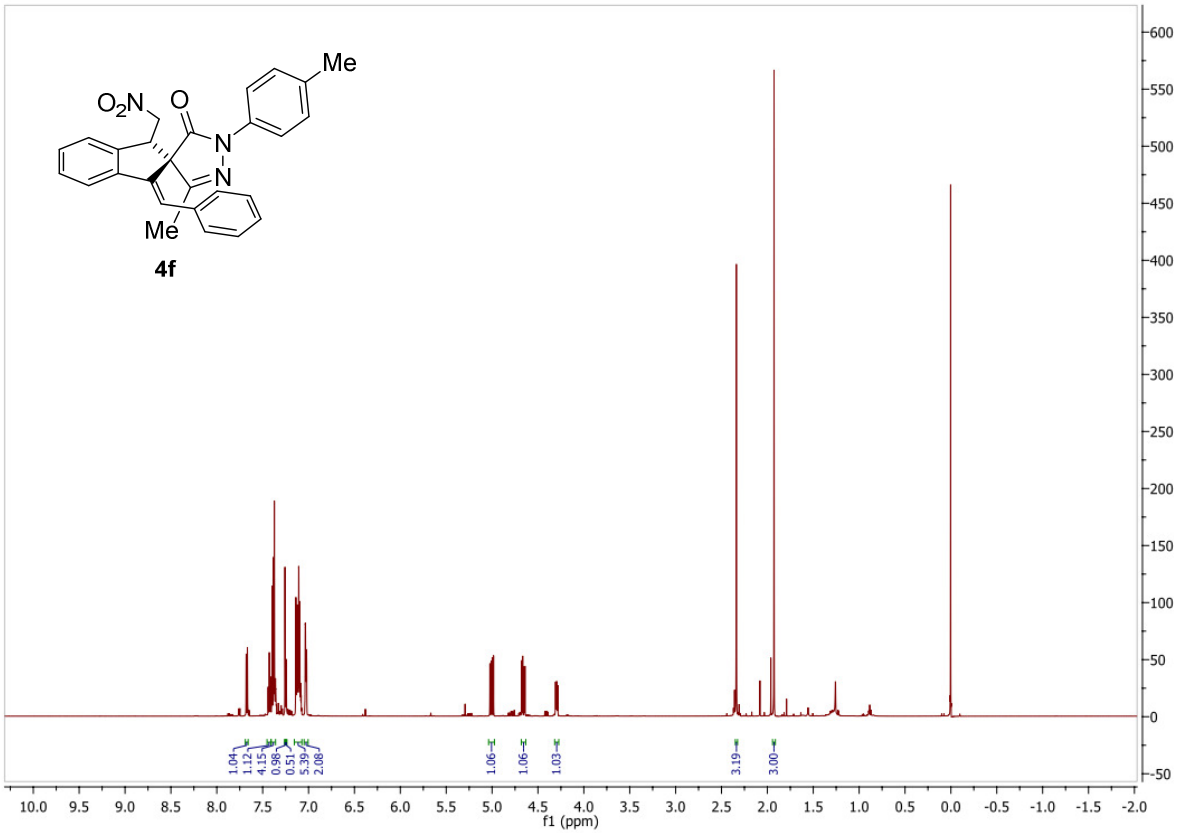

172.15
158.49
140.95
140.74
139.77
137.29
134.80
130.47
129.97
129.66
129.38
128.73
128.55
128.07
127.69
126.34
125.55
124.41
121.63
119.64
74.54
63.46
48.18
f1 (ppm)

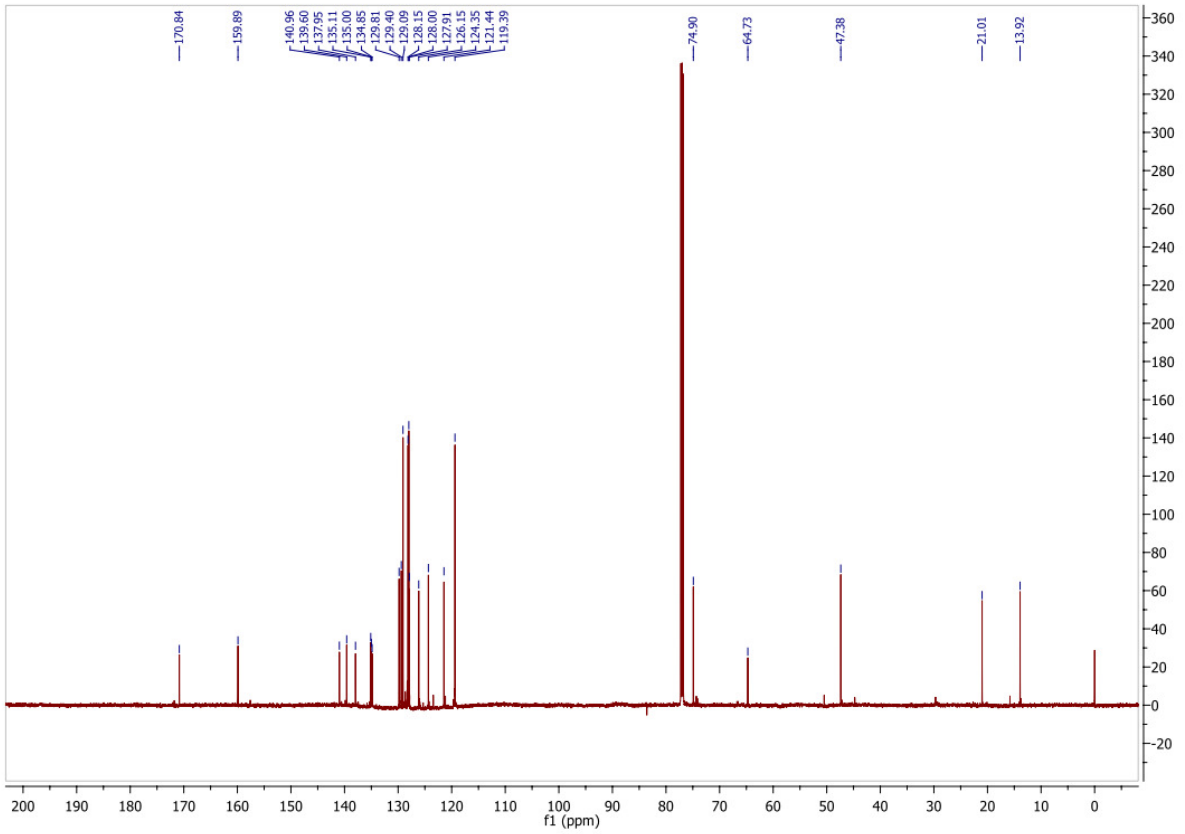

Cl
O2N
O
N
N
Me

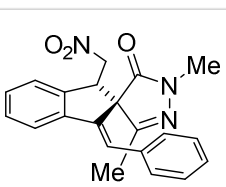
4e

1.01
1.07
4.98
1.38
1.01
0.08
1.04
0.08
1.00
0.10
1.06
0.15
0.97
3.00
0.15
f1 (ppm)


173.02
162.01
145.67
140.49
139.06
134.24
132.04
130.47
130.30
130.10
129.45
129.10
127.85
124.44
122.31
107.51
73.52
64.06
45.10
13.58
f1 (ppm)

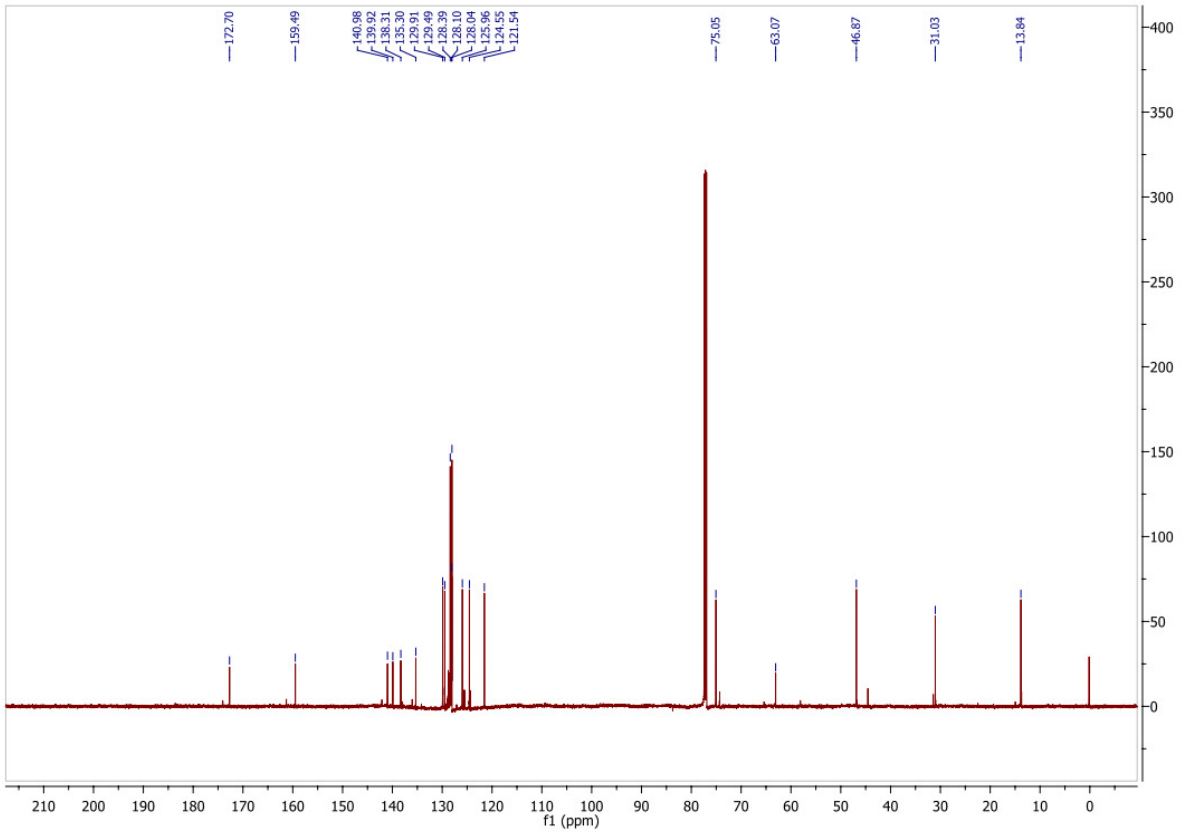

Me
O2N
O
N
N
Me
4f
1.04
1.12
4.15
0.98
0.51
5.39
2.08
1.06
1.06
1.03
3.19
3.00
f1 (ppm)


170.84
159.89
140.96
139.60
137.95
135.11
135.00
134.85
129.81
129.40
129.09
128.15
128.00
127.91
126.15
124.35
121.44
119.39
74.90
64.73
47.38
21.01
13.92
f1 (ppm)


O2N
O
Me
N
N
Me

4g

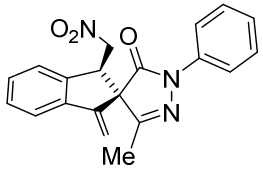
1.04
1.07
1.59
1.07
2.88
0.68
1.09
1.94
1.09
1.11
0.98
2.96
3.00
f1 (ppm)


172.70
159.49
140.98
139.92
138.31
135.30
129.91
129.49
128.39
128.10
128.04
125.96
124.55
121.54
75.05
63.07
46.87
31.03
13.84
f1 (ppm)

11.0 HPLC data

Sample Name: KD 1008 A rac
Data file: D:\ERNIE\KD\1008AYAS.D
Sample Info: Laufmittel: n-Heptan/iPrOH 7:3;
Die Probe ist in DCM/LM gelöst

Agilent Technologies



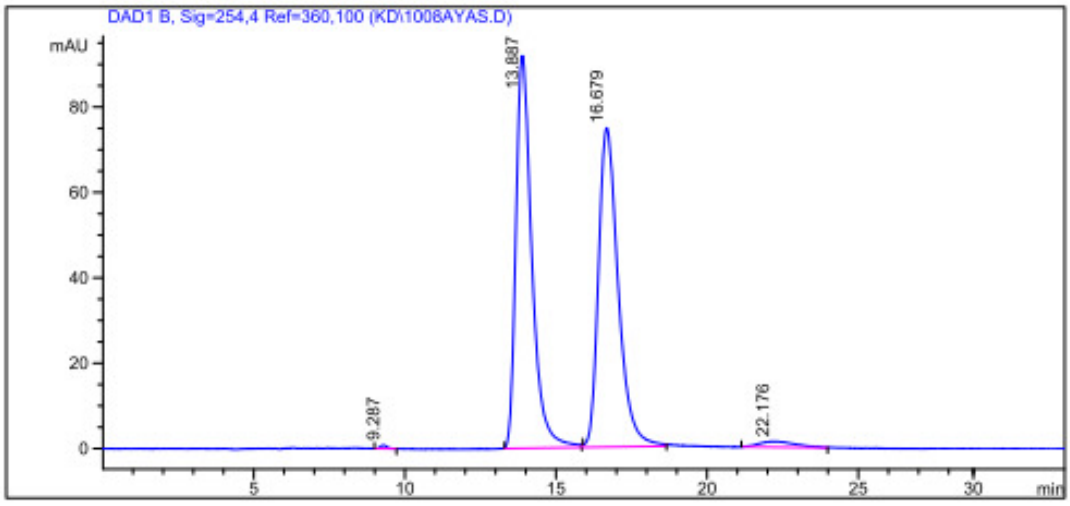
3a

Säule: DAICELAS.M
Säuleninfo: Chiralpak AS (250 x 4.6)mm 10µ

Operator: Analytik Labor AKEN

Injektion Time: 10:59:46
Injektion Date: 04.12.2014

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	20.6	19.5
Flow in ml/min:	0.5	0.5



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	9.29	0.24	0.80	12.54	0.18
2	13.89	0.56	91.94	3379.78	48.99
3	16.68	0.70	74.74	3392.58	49.17
4	22.18	1.05	1.34	114.65	1.66
Total				6899.55	100.00

Sample Name: KD 1062 J
Data file: D:\ERNIE\KD\1062JAS.D
Sample Info: Laufmittel: n-Heptan/iPrOH 7:3;
Die Probe ist in DCM/LM gelöst

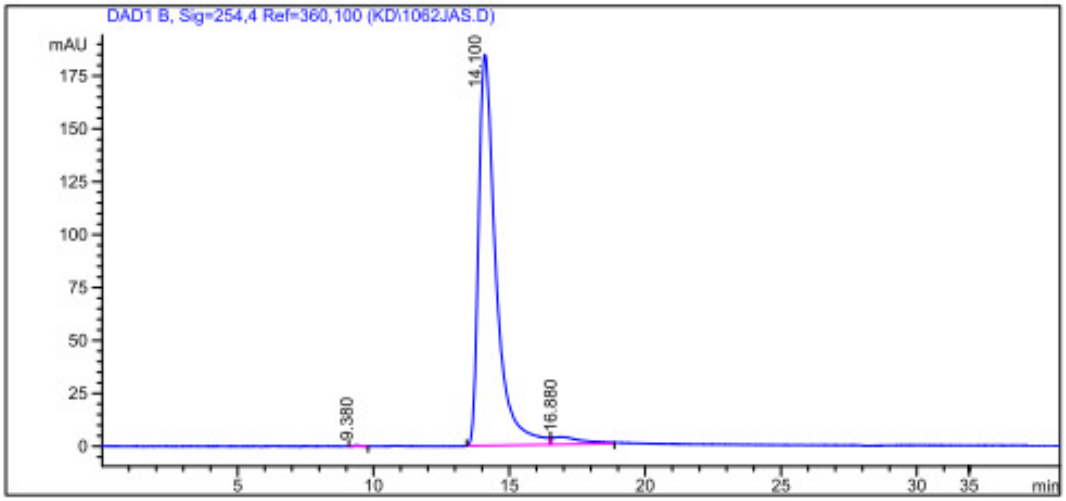
Agilent Technologies

Säule: DAICELAS.M
Säuleninfo: Chiralpak AS (250 x 4.6)mm 10µ

Operator: Analytik Labor AKEN

Injektion Time: 13:13:27
Injektion Date: 25.03.2015

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	19.5	19.5
Flow in ml/min:	0.5	0.5



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	9.38	0.23	0.49	7.33	0.09
2	14.10	0.65	184.72	8149.16	96.68
3	16.88	0.92	3.56	272.92	3.24
Total				8429.40	100.00

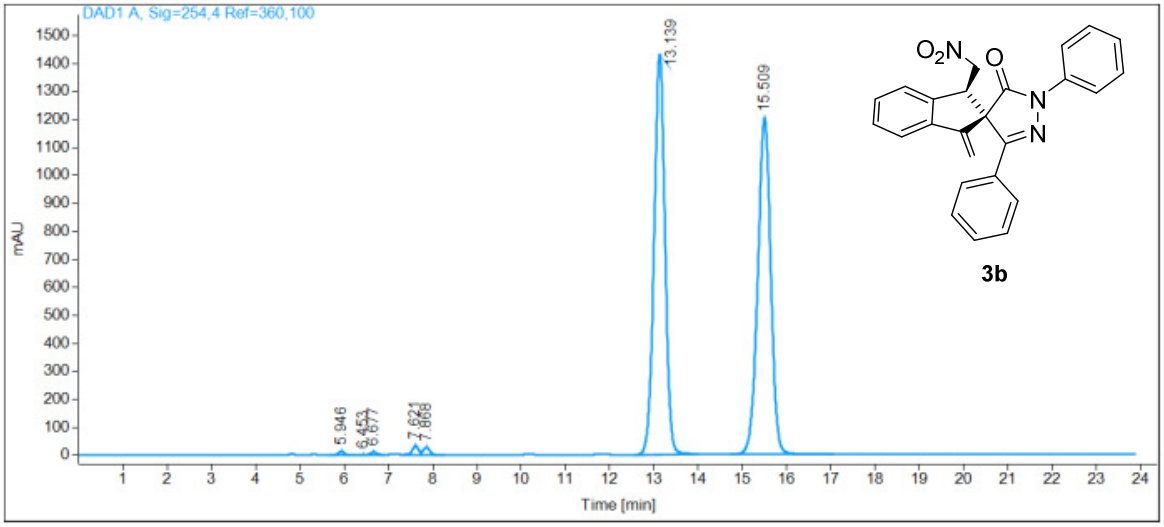
Sample name: **DH LR 21 rac**

Data file: C:\SNOOPY\KD\DH LR 21 RAC NIA.D
Description: Laufmittel: n-Heptan/EtOH 7:3 ; Die Probe ist DCM/LM gelöst.

Injection date: 3/27/2015 12:17:59 PM
Acq. Analysis method: CHIRALPAKIARNP.M

Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

Pressure at start: 42 bar **Start flow:** 0.700 ml/min **Column oven:** 29.99 °C



3b

Name DH LR 21 rac

RT [min]	Type	Area%	Area	Height	Width [min]
5.95	VB	0.21	107.20	12.99	0.13
6.45	BV	0.01	6.34	1.00	0.10
6.68	VB	0.19	96.32	10.23	0.15
7.62	BV	0.64	318.11	31.85	0.15
7.87	VB	0.56	278.37	26.90	0.16
13.14	BB	49.21	24554.32	1429.01	0.26
15.51	BB	49.17	24533.71	1201.76	0.31
	Sum	100.00	49894.37		

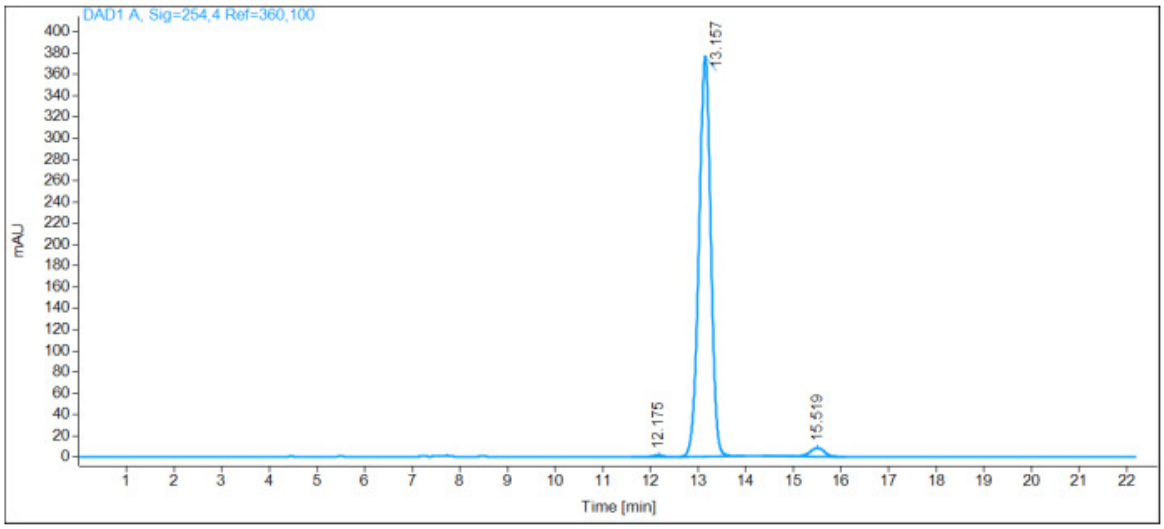
Sample name: **KD 1068 A**

Data file: C:\SNOOPY\KD\KD 1068 A IA.D
Description: Laufmittel: n-Heptan/EtOH 7:3 ; Die Probe ist DCM/LM gelöst.

Injection date: 3/27/2015 11:48:15 AM
Acq. Analysis method: CHIRALPAKIARNP.M

Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

Pressure at start: 42 bar **Start flow:** 0.700 ml/min **Column oven:** 29.97 °C



Name KD 1068 A

RT [min]	Type	Area%	Area	Height	Width [min]
12.18	BB	0.39	26.00	1.76	0.23
13.16	BB	97.04	6457.11	376.63	0.26
15.52	BB	2.57	170.75	8.04	0.32
	Sum	100.00	6653.86		

Sample name: DH LR 30 rac

Data file: C:\SNOOPY\DH\LR30RIA.D

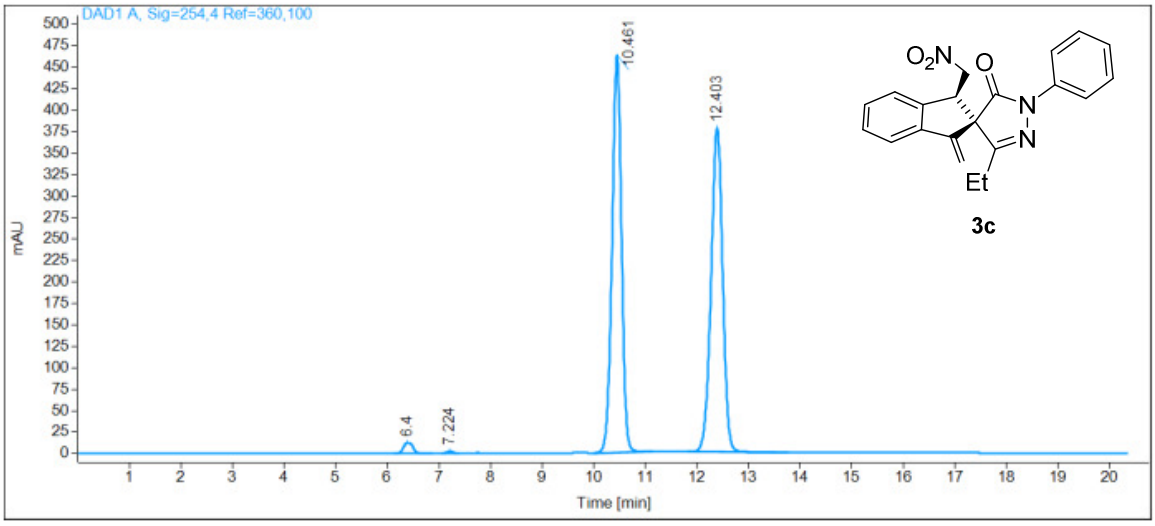
Description: Laufmittel: n-Heptan/EtOH 7:3;
Probe ist in DCM/LM gelöst.

Injection date: 1/8/2015 3:21:58 PM

Acq. Analysis method: CHIRALPAKIARNP.M

Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

Pressure at start: 41 bar **Start flow:** 0.700 ml/min **Column oven:** 29.98 °C



3c

Name DH LR 30 rac

RT [min]	Type	Area%	Area	Height	Width [min]
6.40	BB	1.26	150.71	11.87	0.20
7.22	BB	0.15	18.52	2.51	0.12
10.46	BB	49.32	5896.54	463.37	0.20
12.40	BB	49.26	5889.45	377.74	0.24
	Sum	100.00	11955.22		

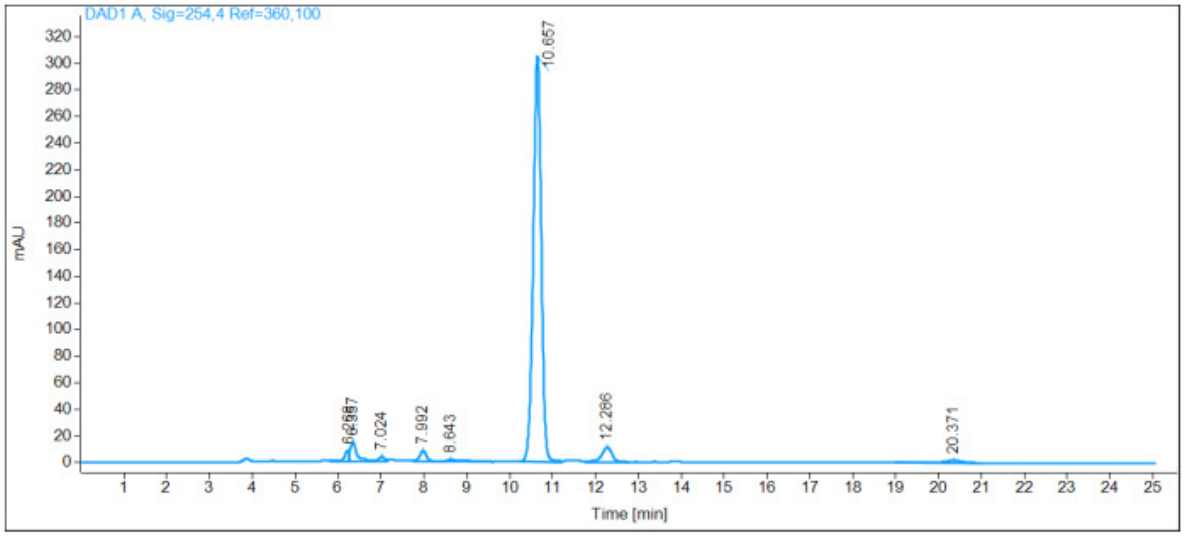
Sample name: **KD 1067 A**

Data file: C:\SNOOPY\KD\KD 1067 A IA.D
Description: Laufmittel: n-Heptan/EtOH 7:3 ; Die Probe ist DCM/LM gelöst.

Injection date: 4/1/2015 1:59:54 PM
Acq. Analysis method: CHIRALPAKIARNP.M

Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

Pressure at start: 41 bar **Start flow:** 0.700 ml/min **Column oven:** 30 °C



Name KD 1067 A

RT [min]	Type	Area%	Area	Height	Width [min]
6.27	MF	1.57	72.08	8.28	0.14
6.36	FM	3.27	149.77	14.47	0.17
7.02	VV	0.68	31.32	3.14	0.15
7.99	VB	1.82	83.53	8.01	0.16
8.64	BB	0.86	39.54	1.53	0.34
10.66	BV	86.38	3955.41	304.87	0.20
12.29	VB	4.03	184.44	11.08	0.25
20.37	BB	1.38	63.26	1.81	0.52
	Sum	100.00	4579.33		

Sample name: DH LR 32 rac

Data file: C:\SNOOPY\DH LR 32 RAC IC.D

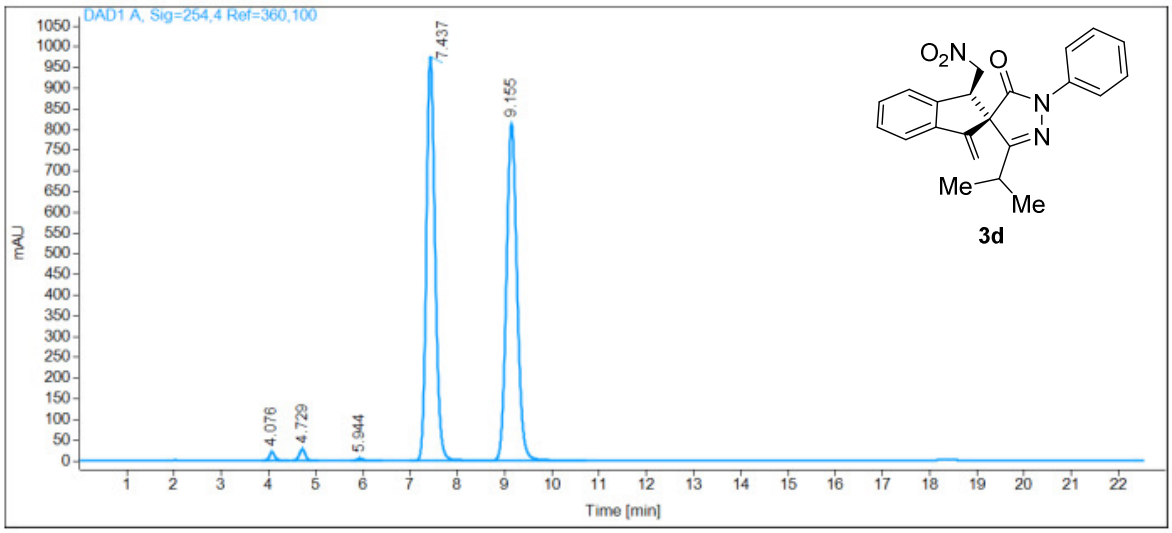
Description: Laufmittel: n-Heptan/EtOH 97:3; Die Probe ist DCM/LM gelöst.

Injection date: 1/8/2015 8:55:16 AM

Acq. Analysis method: CHIRALPAKIC1-6LNP.M

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Pressure at start: 31 bar **Start flow:** 1.000 ml/min **Column oven:** 29.98 °C



Name DH LR 32 rac

RT [min]	Type	Area%	Area	Height	Width [min]
4.08	BB	0.62	159.66	21.17	0.11
4.73	BB	0.91	233.72	26.74	0.14
5.94	BB	0.17	44.78	5.41	0.13
7.44	BB	49.08	12594.48	974.89	0.20
9.15	BB	49.22	12630.33	813.79	0.24
	Sum	100.00	25662.98		

Sample name: **KD 1116 A**

Data file: C:\SNOOPY\KD\1116AIC.D

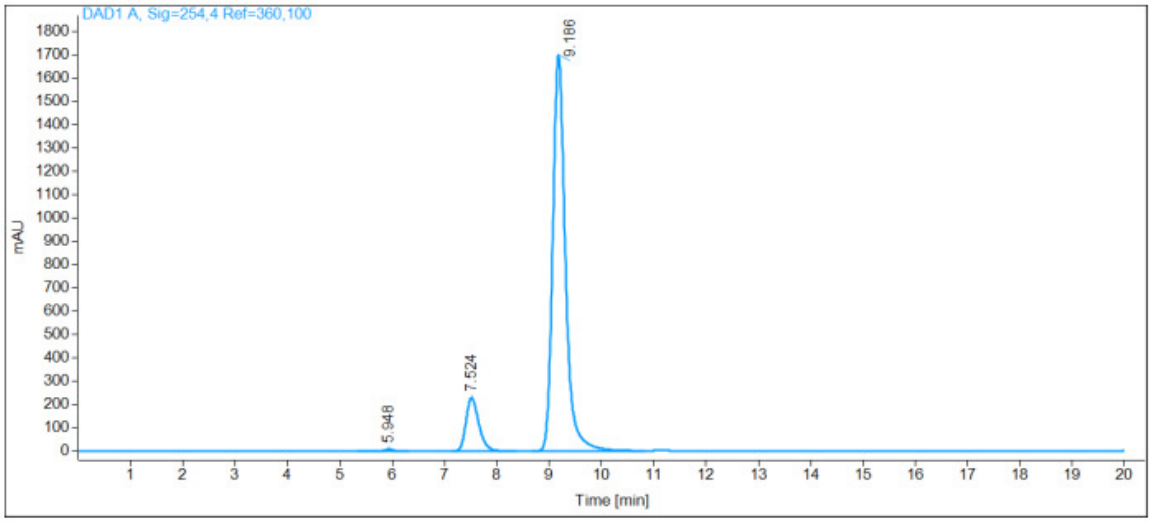
Description: Laufmittel: n-Heptan/EtOH 97:3;
Probe ist in LM/DCM gelöst

Injection date: 5/8/2015 1:54:08 PM

Acq. Analysis method: CHIRALPAKIC1-6LNP.M

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Pressure at start: 35 bar **Start flow:** 1.000 ml/min **Column oven:** 29.99 °C



Name KD 1116 A

RT [min]	Type	Area%	Area	Height	Width [min]
5.95	BV	0.29	95.67	9.24	0.15
7.52	BB	11.84	3866.95	228.17	0.26
9.19	BV	87.87	28706.98	1697.70	0.26
	Sum	100.00	32669.61		

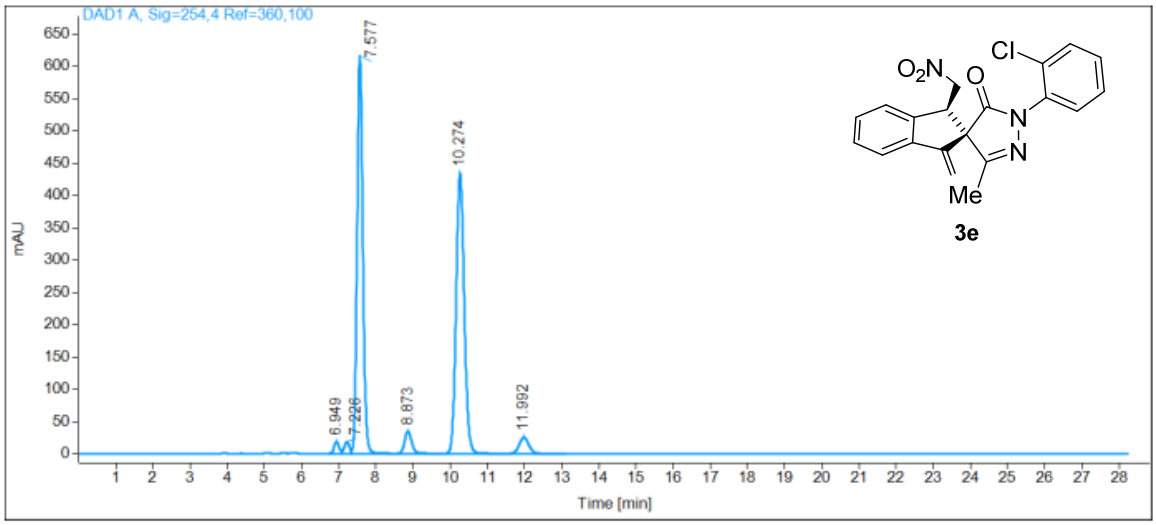
Sample name: **KD 1031 A rac**

Data file: C:\SNOOPY\KD\KD 1031 A RAC IC.D
Description: Laufmittel: n-Heptan/EtOH 7:3; Die Probe ist DCM/LM gelöst.

Injection date: 1/7/2015 9:14:35 AM
Acq. Analysis method: CHIRALPAKIC1-6LNP.M

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Pressure at start: 21 bar **Start flow:** 0.500 ml/min **Column oven:** 29.99 °C



3e

Name KD 1031 A rac

RT [min]	Type	Area%	Area	Height	Width [min]
6.95	BV	1.19	171.69	18.89	0.15
7.23	VV	1.19	171.10	18.40	0.14
7.58	VB	45.69	6577.14	614.28	0.16
8.87	BB	3.17	457.02	34.44	0.21
10.27	BV	45.59	6562.28	433.79	0.24
11.99	VB	3.16	454.97	25.11	0.28
	Sum	100.00	14394.19		

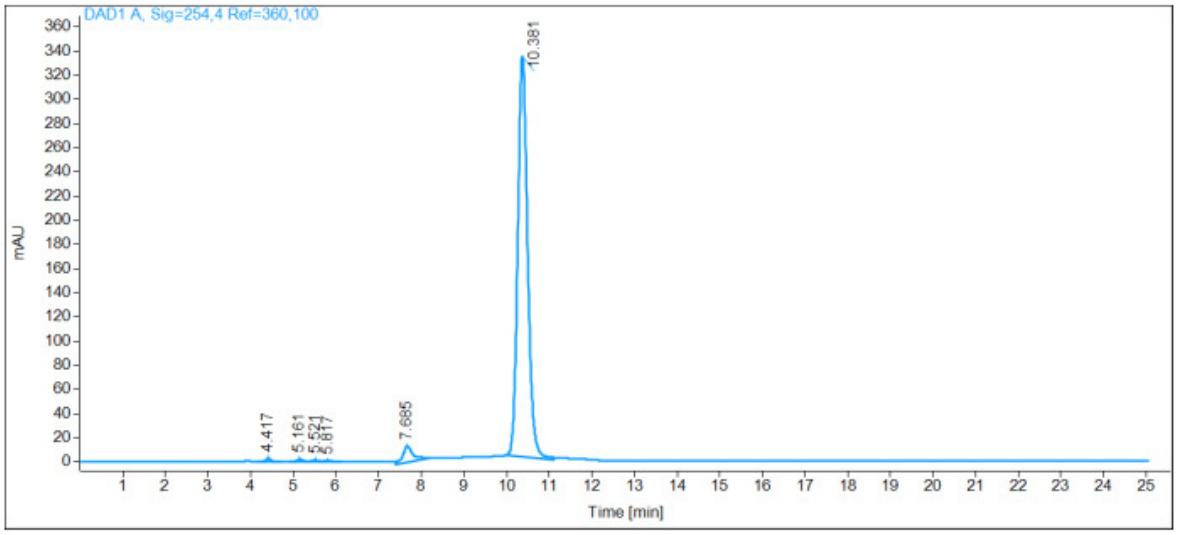
Sample name: **KD 1096 A**

Data file: C:\SNOOPY\KD\KD 1096 A IC.D
Description: Laufmittel: n-Heptan/EtOH 7:3 ; Die Probe ist DCM/LM gelöst.

Injection date: 4/20/2015 2:15:29 PM
Acq. Analysis method: CHIRALPAKIC1-6LNP.M

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Pressure at start: 23 bar **Start flow:** 0.500 ml/min **Column oven:** 29.99 °C



Name KD 1096 A

RT [min]	Type	Area%	Area	Height	Width [min]
4.42	VV	0.37	20.87	2.79	0.11
5.16	VV	0.29	16.42	1.95	0.12
5.52	VV	0.18	10.07	1.08	0.14
5.82	VB	0.13	7.17	0.75	0.14
7.68	MM	4.09	229.56	13.53	0.28
10.38	MM	94.94	5328.09	331.41	0.27
	Sum	100.00	5612.18		

Sample name: KD 1038 A rac

Data file: C:\SNOOPY\KD\1038AR1IC.D

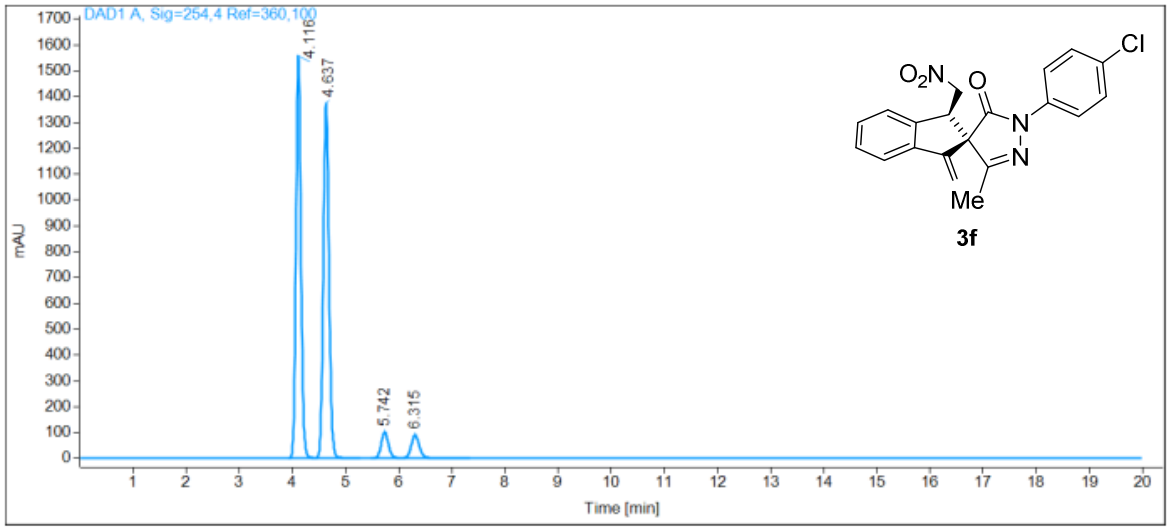
Description: Laufmittel: n-Heptan/EtOH 9:1;
Probe ist in LM/DCM gelöst

Injection date: 1/7/2015 11:06:20 AM

Acq. Analysis method: CHIRALPAKIC1-6LNP.M

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Pressure at start: 33 bar **Start flow:** 1.000 ml/min **Column oven:** 30.01 °C



3f

Name KD 1038 A rac

RT [min]	Type	Area%	Area	Height	Width [min]
4.12	VB	45.69	10092.69	1556.43	0.10
4.64	BB	45.81	10119.11	1374.11	0.11
5.74	BV	4.24	936.74	99.91	0.15
6.32	VB	4.27	943.05	88.22	0.16
	Sum	100.00	22091.59		

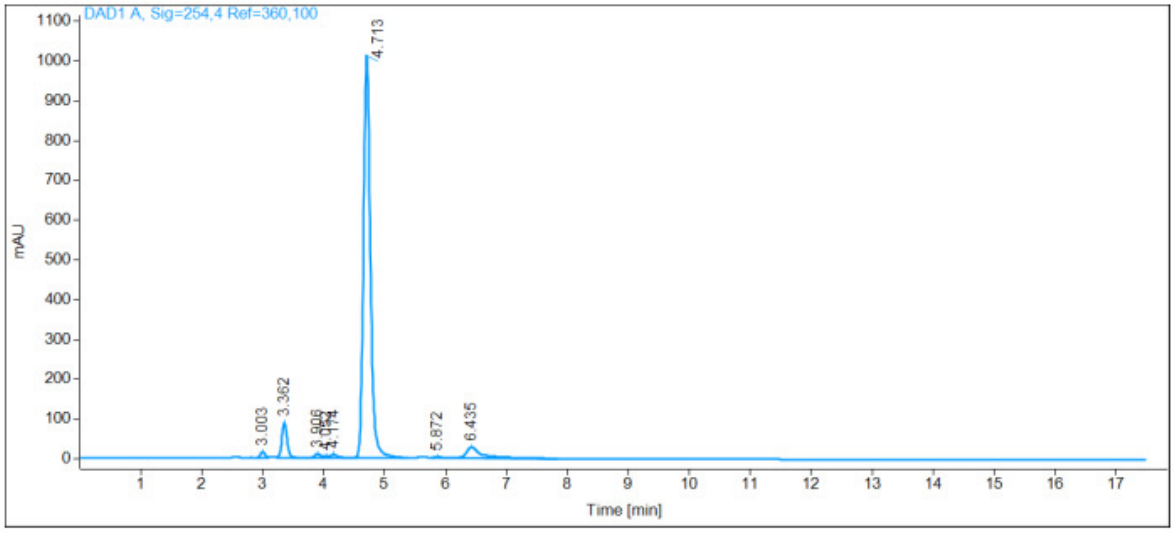
Sample name: **KD 1100 A2**

Data file: C:\SNOOPY\KD\KD 1100 A2 IC.D
Description: Laufmittel: n-Heptan/EtOH 9:1 ; Die Probe ist DCM/LM gelöst.

Injection date: 5/4/2015 3:35:48 PM
Acq. Analysis method: CHIRALPAKIC1-6LNP.M

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Pressure at start: 38 bar **Start flow:** 1.000 ml/min **Column oven:** 30 °C



Name KD 1100 A2

RT [min]	Type	Area%	Area	Height	Width [min]
3.00	BV	0.84	78.32	15.18	0.08
3.36	VB	5.68	527.07	88.62	0.09
3.91	BV	0.71	65.57	9.54	0.10
4.05	VV	0.35	32.62	5.37	0.09
4.17	VB	0.71	65.81	8.19	0.12
4.71	BB	86.21	7995.97	1012.13	0.12
5.87	VB	0.13	12.44	1.34	0.14
6.43	BB	5.36	496.73	27.56	0.25
	Sum	100.00	9274.53		

Sample Name: KD 1092 A rac
Data file: D:\ERNIE\KD\1092ARAS.D
Sample Info: Laufmittel: n-Heptan/iPrOH 7:3;
Die Probe ist in DCM/LM gelöst

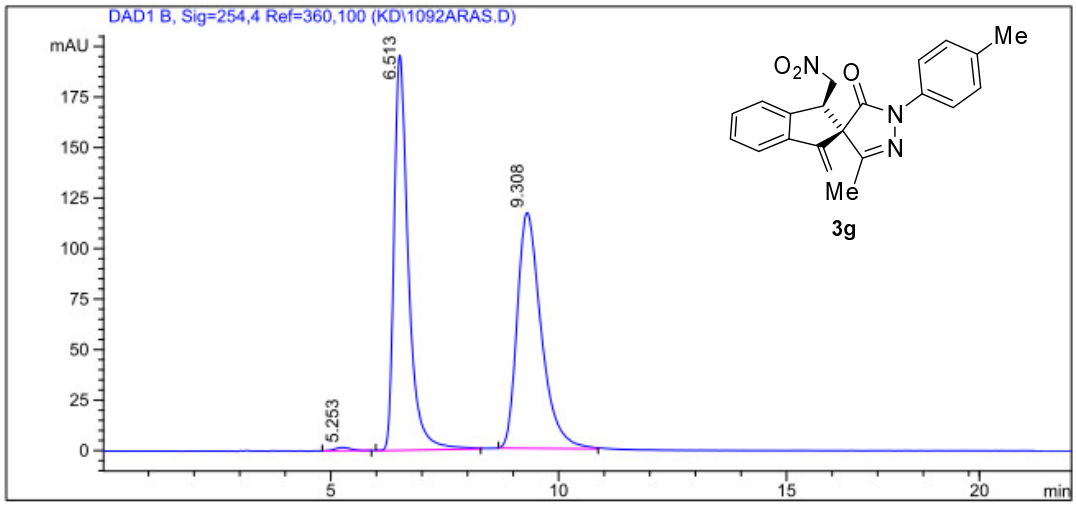
Agilent Technologies

Säule: DAICELAS.M
Säuleninfo: Chiralpak AS (250 x 4.6)mm 10µ

Operator: Analytik Labor AKEN

Injektion Time: 10:01:36
Injektion Date: 22.04.2015

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	41.0	41.1
Flow in ml/min:	1.0	1.0



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	5.25	0.33	1.58	37.86	0.44
2	6.51	0.36	195.71	4258.81	49.61
3	9.31	0.56	116.67	4288.29	49.95
Total				8584.95	100.00

Sample Name: KD 1095 A
Data file: D:\ERNIE\KD\1095AAS.D
Sample Info: Laufmittel: n-Heptan/iPrOH 7:3;
Die Probe ist in DCM/LM gelöst

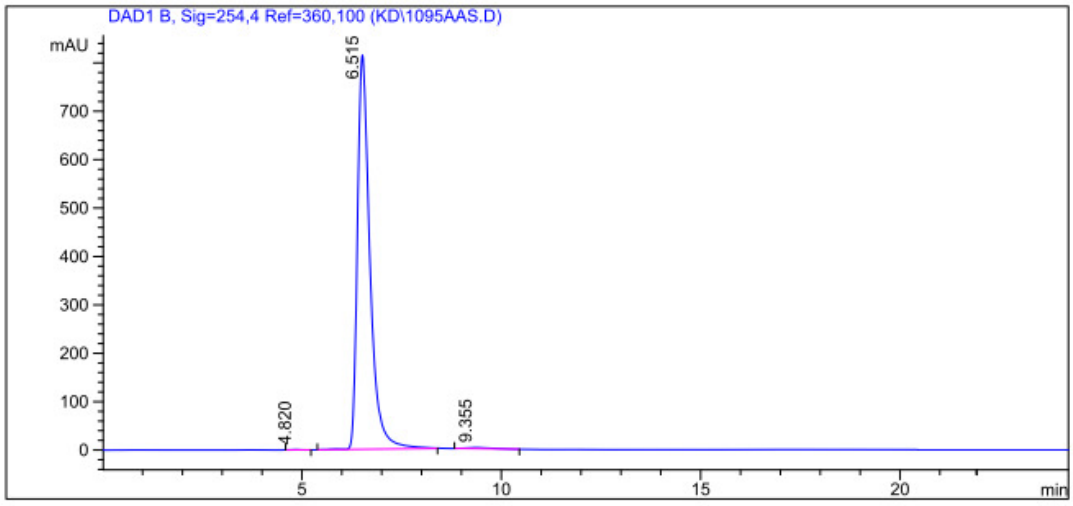
Agilent Technologies

Säule: DAICELAS.M
Säuleninfo: Chiralpak AS (250 x 4.6)mm 10µ

Operator: Analytik Labor AKEN

Injektion Time: 10:27:42
Injektion Date: 22.04.2015

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	41.2	41.2
Flow in ml/min:	1.0	1.0



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.82	0.18	1.15	14.39	0.08
2	6.51	0.33	814.67	17795.78	99.34
3	9.36	0.50	2.50	103.38	0.58
Total				17913.54	100.00

Sample name: KD 1037 A rac

Data file: C:\SNOOPY\KD\1037AR1IA.D

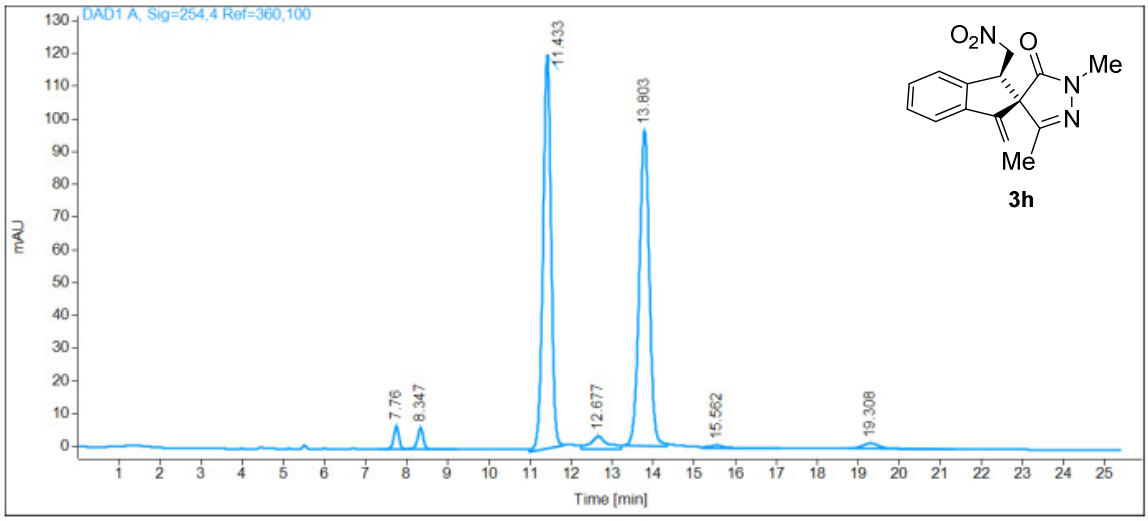
Description: Laufmittel: n-Heptan/EtOH 7:3;
Probe ist in DCM/LM gelöst.

Injection date: 1/8/2015 2:19:23 PM

Acq. Analysis method: CHIRALPAKIARNP.M

Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

Pressure at start: 41 bar **Start flow:** 0.700 ml/min **Column oven:** 30 °C



3h

Name KD 1037 A rac

RT [min]	Type	Area%	Area	Height	Width [min]
7.76	BV	1.70	61.54	6.96	0.14
8.35	VB	1.82	65.58	6.50	0.15
11.43	MM	45.29	1635.55	120.07	0.23
12.68	VV	3.11	112.36	3.82	0.41
13.80	MM	45.74	1651.83	96.35	0.29
15.56	VB	0.96	34.49	0.93	0.52
19.31	BB	1.38	49.93	1.69	0.45
	Sum	100.00	3611.28		

Sample name: **KD 1101 A**

Data file: C:\SNOOPY\KD\1101AIA.D

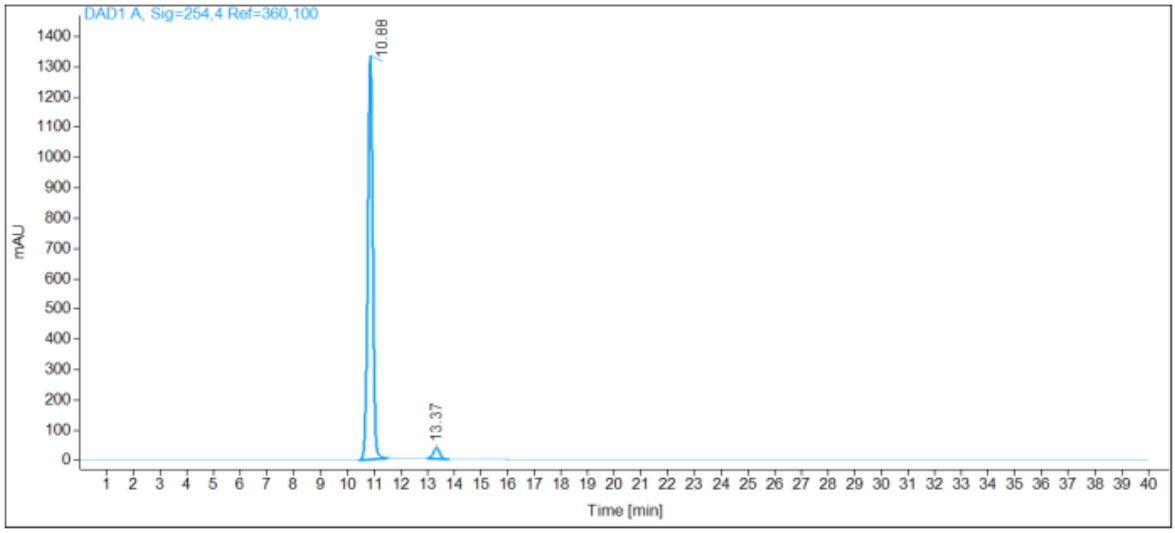
Description: Laufmittel: n-Heptan/EtOH 7:3;
Probe ist in DCM/LM gelöst

Injection date: 4/22/2015 11:37:59 AM

Acq. Analysis method: CHIRALPAKIARNP.M

Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

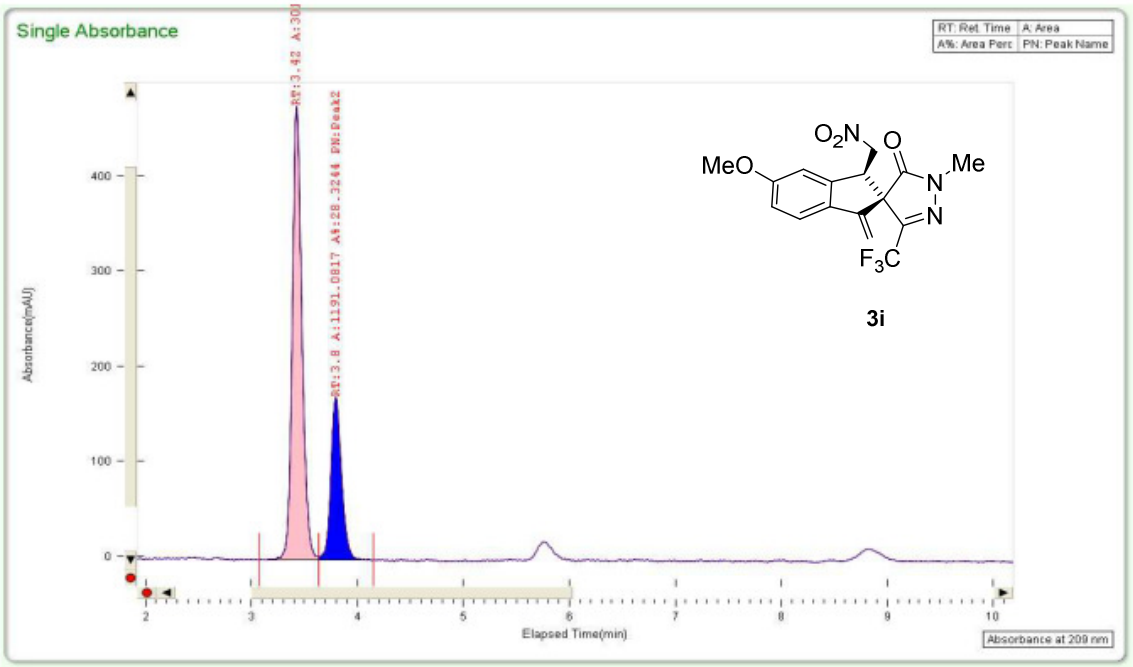
Pressure at start: 42 bar **Start flow:** 0.700 ml/min **Column oven:** 29.99 °C



Name KD 1101 A

RT [min]	Type	Area%	Area	Height	Width [min]
10.88	MM	96.58	17299.20	1333.67	0.22
13.37	MM	3.42	612.36	35.98	0.28
	Sum	100.00	17911.55		

ThárSFC



3i

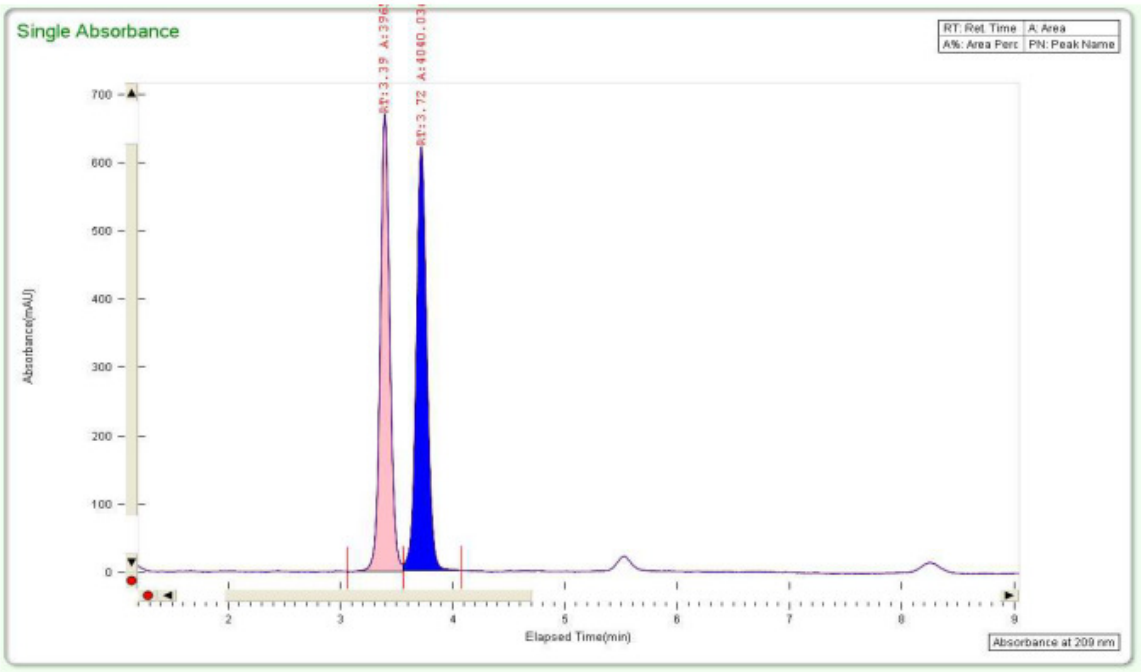
General Info		**Report Date**	9/30/2015
Log Author		**Method Name**	4ml_3.met
Log Date	4/22/2015 5:08:35 PM	**Notes**	
Report By	current_User		

Injection Info		**Temp**	37.9
Inj Vol	5	**Flow**	4
Solvent	Ethanol	**% Modifier**	3
Column	R(R)-Whelk-01	**Pressure**	151
Sample	AKEn-KD-1098-A		
Well location	P1: 5A		

Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	71.6756	3014.064	3.42	477.2136	0.0033
2	28.3244	1191.0817	3.8	170.8121	0.0037
Total:	100	4205.1457			

ThарSFC



General Info		**Report Date**	9/30/2015
Log Author		**Method Name**	4ml_3.met
Log Date	3/30/2015 10:56:53 AM	**Notes**	
Report By	current_User		

Injection Info		**Temp**	38
Inj Vol	5	**Flow**	4
Solvent	Methanol	**% Modifier**	3
Column	R(R)-Whelk-01	**Pressure**	149
Sample	AKEn-KD-1036		
Well location	P2: 2A		

Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	49.5365	3965.8295	3.39	670.5	0.0052
2	50.4635	4040.0365	3.72	621.4785	0.0057
Total:	100	8005.866			

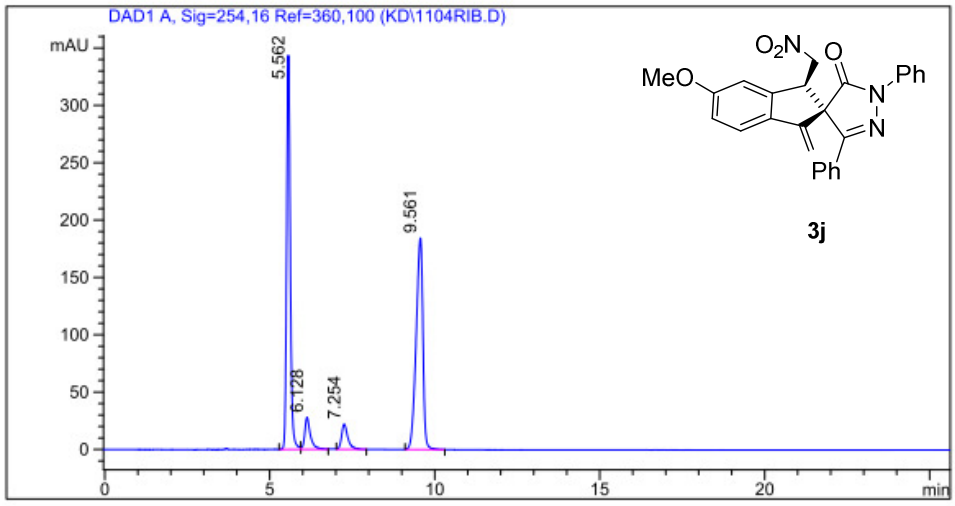
Sample Name: KD 1104 A rac
Data file: D:\GONZO\KD\1104RIB.D
Sample Info: Laufmittel: n-Heptan/EtOH 7:3;
Die Probe ist in DCM/LM gelöst.

->

Säule: DAICELIB.M
Säuleninfo: Chiralcel OD (250x4,6)mm Chiralpak IB
Operator: Analytik Labor AKEN

Injektion Time: 08:36:11
Injektion Date: 05.05.2015

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	59.6	60.9
Flow in ml/min:	1.00	1.00



3j

#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	5.56	0.12	344.39	2635.23	44.69
2	6.13	0.18	27.93	339.06	5.75
3	7.25	0.20	22.07	294.53	4.99
4	9.56	0.22	184.51	2628.24	44.57
Total				5897.05	100.00

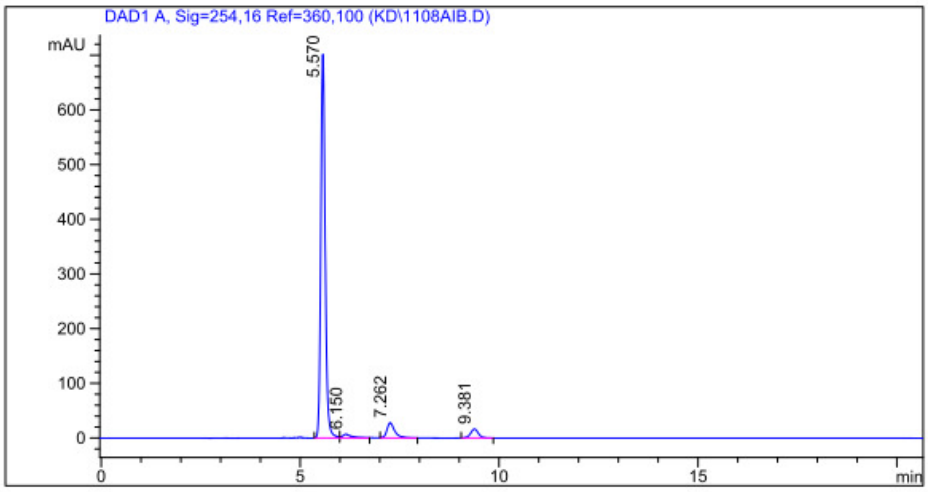
Sample Name: KD 1108 A
Data file: D:\GONZO\KD\1108AIB.D
Sample Info: Laufmittel: n-Heptan/EtOH 7:3;
Die Probe ist in DCM/LM gelöst.

->

Säule: DAICELIB.M
Säuleninfo: Chiralpak IB (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 11:00:00
Injektion Date: 05.05.2015

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	60.1	60.8
Flow in ml/min:	1.00	1.00



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	5.57	0.12	701.75	5376.00	88.22
2	6.15	0.23	6.94	116.37	1.91
3	7.26	0.20	27.87	380.90	6.25
4	9.38	0.21	16.45	220.51	3.62
Total				6093.77	100.00

Sample name: **KD 1106 A rac**

Data file: C:\SNOOPY\KD\1106ARIA.D

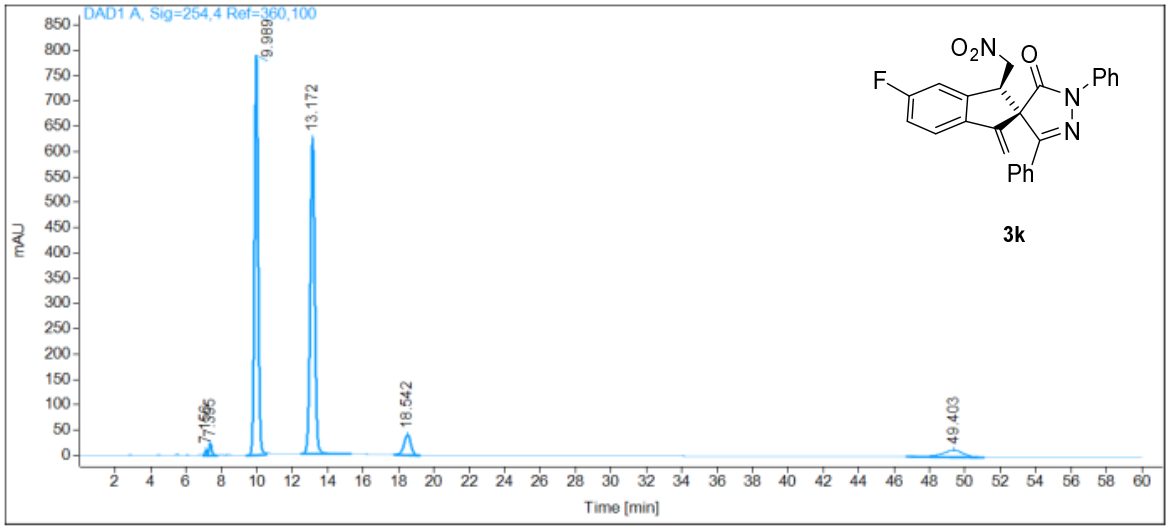
Description: Laufmittel: n-Heptan/EtOH 7:3;
Probe ist in DCM/LM gelöst

Injection date: 5/4/2015 6:40:36 PM

Acq. Analysis method: CHIRALPAKIARNP.M

Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

Pressure at start: 42 bar **Start flow:** 0.700 ml/min **Column oven:** 30 °C



3k

Name KD 1106 A rac

RT [min]	Type	Area%	Area	Height	Width [min]
7.16	VV	0.33	81.40	10.28	0.12
7.40	VB	0.95	234.84	24.35	0.15
9.99	BV	45.14	11125.46	789.58	0.22
13.17	VB	45.02	11097.71	625.42	0.27
18.54	VB	4.39	1083.29	40.07	0.42
49.40	BBA	4.16	1026.45	13.02	1.20
	Sum	100.00	24649.15		

Sample name: **KD 1109 A**

Data file: C:\SNOOPY\KD\1109AIA.D

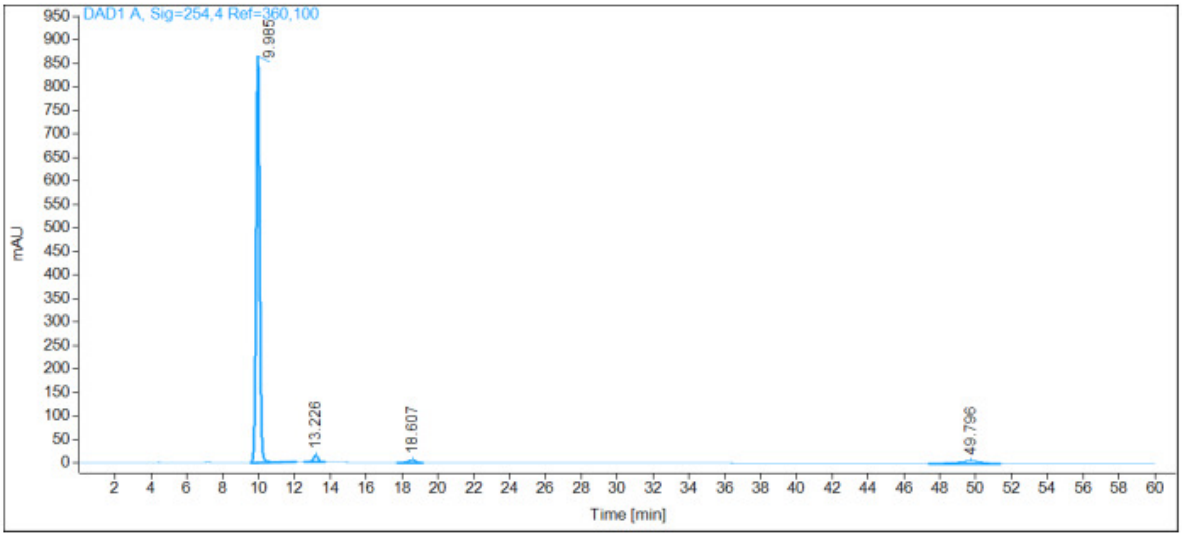
Description: Laufmittel: n-Heptan/EtOH 7:3;
Probe ist in DCM/LM gelöst

Injection date: 5/5/2015 1:25:16 PM

Acq. Analysis method: CHIRALPAKIARNP.M

Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

Pressure at start: 41 bar **Start flow:** 0.700 ml/min **Column oven:** 30 °C



Name KD 1109 A

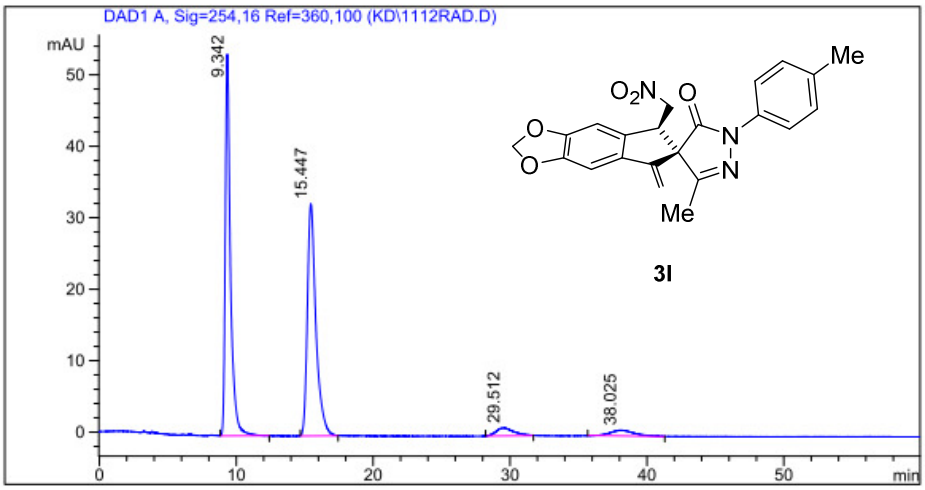
RT [min]	Type	Area%	Area	Height	Width [min]
9.99	BB	93.19	11873.19	865.45	0.21
13.23	BB	1.99	252.92	14.11	0.28
18.61	BB	1.31	167.44	6.17	0.42
49.80	BB	3.52	447.94	5.56	1.23
	Sum	100.00	12741.49		

Sample Name: KD 1112 A rac
Data file: D:\GONZO\KD\1112RAD.D
Sample Info: Laufmittel: n-Heptan/iPrOH 6:4
Die Probe ist in LM/DCM gelöst

Säule: DAICELAD.M
Säuleninfo: Chiralpak AD (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 16:23:36
Injektion Date: 06.05.2015

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	47.5	47.4
Flow in ml/min:	1.00	1.00



3l

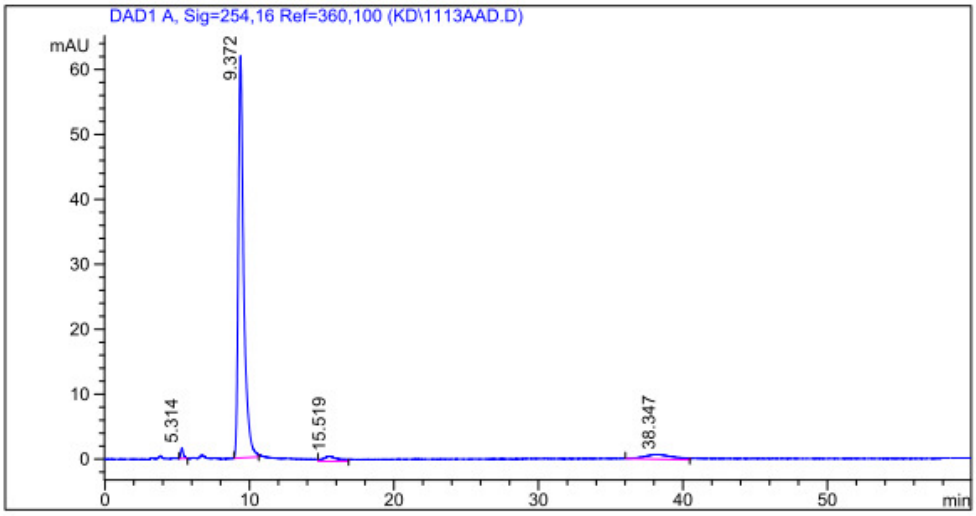
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	9.34	0.44	53.45	1413.17	46.72
2	15.45	0.65	32.47	1410.59	46.64
3	29.51	1.10	1.13	103.27	3.41
4	38.03	2.02	0.81	97.71	3.23
Total				3024.75	100.00

Sample Name: KD 1113 A
Data file: D:\GONZO\KD\1113AAD.D
Sample Info: Laufmittel: n-Heptan/iPrOH 6:4
Die Probe ist in LM/DCM gelöst

Säule: DAICELAD.M
Säuleninfo: Chiralpak AD (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 08:15:32
Injektion Date: 07.05.2015

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	47.7	48.8
Flow in ml/min:	1.00	1.00



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	5.31	0.19	1.62	20.18	1.13
2	9.37	0.38	61.89	1598.69	89.72
3	15.52	1.23	0.77	56.74	3.18
4	38.35	2.40	0.74	106.27	5.96
Total				1781.88	100.00

Sample name: KD 1105 A rac

Data file: C:\SNOOPY\KD\1105ARIC.D

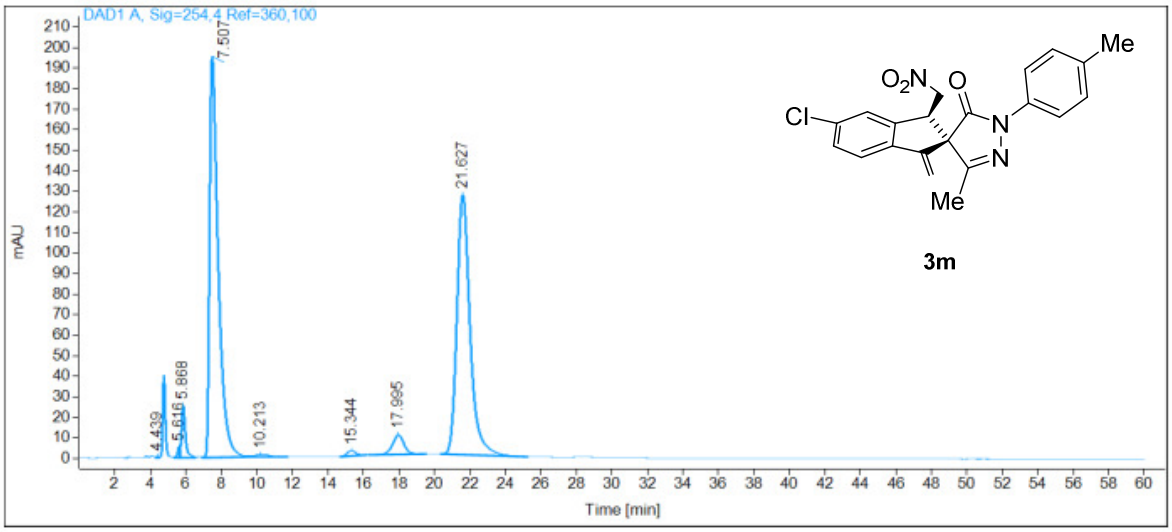
Description: Laufmittel: n-Heptan/iPrOH 7:3; Probe ist in LM/DCM gelöst

Injection date: 4/30/2015 5:23:30 PM

Acq. Analysis method: CHIRALPAKIC1-6LNP.M

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Pressure at start: 33 bar **Start flow:** 0.700 ml/min **Column oven:** 30.01 °C



3m

Name KD 1105 A rac

RT [min]	Type	Area%	Area	Height	Width [min]
4.44	VB	0.02	3.28	0.34	0.13
5.62	BV	0.26	37.11	4.97	0.11
5.87	VB	2.67	376.58	25.20	0.22
7.51	VV	46.66	6586.09	195.02	0.50
10.21	VV	0.53	75.32	1.20	0.80
15.34	BB	0.59	83.82	2.41	0.54
18.00	BB	3.02	426.10	9.41	0.69
21.63	BB	46.24	6528.08	126.39	0.78
	Sum	100.00	14116.38		

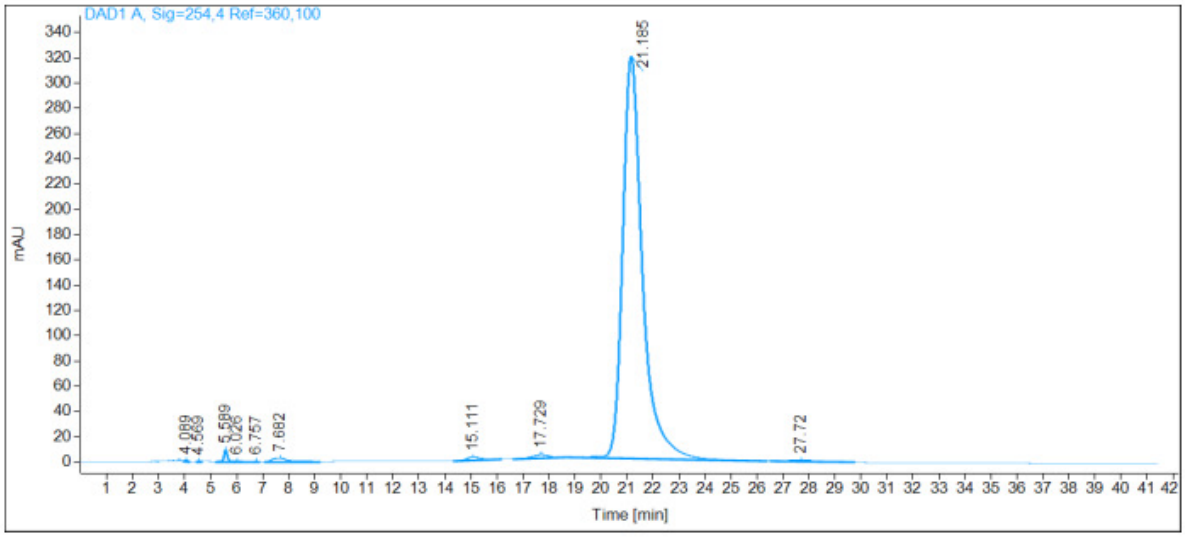
Sample name: **KD 1110 A**

Data file: C:\SNOOPY\KD\KD 1110 A IC.D
Description: Laufmittel: n-Heptan/iPrOH 7:3 ; Die Probe ist DCM/LM gelöst.

Injection date: 5/12/2015 9:56:46 AM
Acq. Analysis method: CHIRALPAKIC1-6LNP.M

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Pressure at start: 32 bar **Start flow:** 0.700 ml/min **Column oven:** 29.99 °C



Name KD 1110 A

RT [min]	Type	Area%	Area	Height	Width [min]
4.09	VB	0.05	9.58	0.96	0.14
4.57	BV	0.01	2.22	0.28	0.12
5.59	BV	0.48	83.27	9.50	0.13
6.03	VV	0.06	9.86	0.81	0.17
6.76	VB	0.02	2.93	0.22	0.19
7.68	BB	0.68	118.29	3.00	0.52
15.11	BB	0.56	96.90	2.54	0.56
17.73	BB	0.71	124.46	2.79	0.65
21.18	BB	96.91	16883.94	318.53	0.80
27.72	BB	0.52	90.88	1.49	0.80
	Sum	100.00	17422.34		

Sample Name: KD 1107 A rac
Data file: D:\ERNIE\KD\1107RXAS.D
Sample Info: Laufmittel: n-Heptan/EtOH 9:1;
Die Probe ist in DCM/LM gelöst

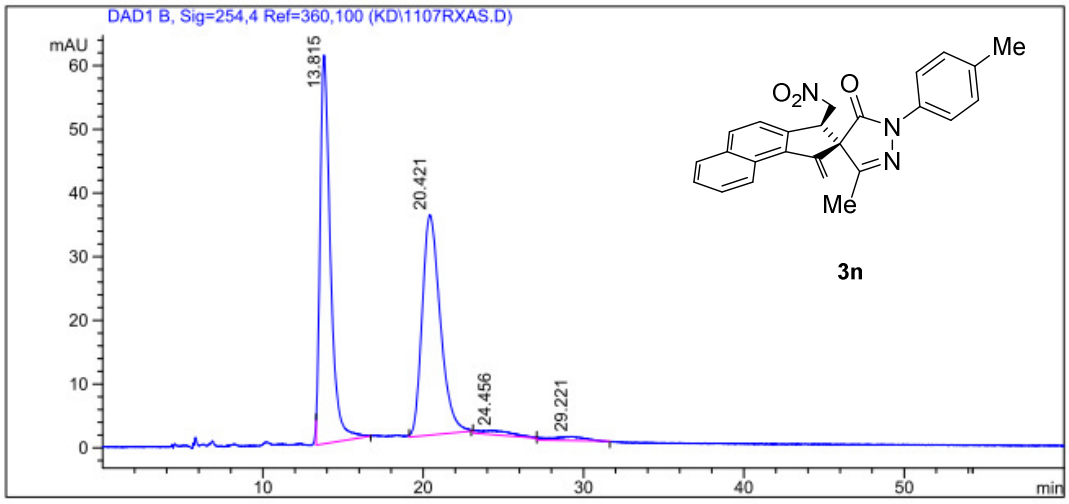
Agilent Technologies

Säule: DAICELAS.M
Säuleninfo: Chiralpak AS (250 x 4.6)mm 10µ

Operator: Analytik Labor AKEN

Injektion Time: 11:33:37
Injektion Date: 18.05.2015

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	23.4	23.6
Flow in ml/min:	0.7	0.7



3n

#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	13.81	0.75	61.04	2740.97	48.54
2	20.42	1.31	34.58	2714.12	48.07
3	24.46	2.46	0.67	99.36	1.76
4	29.22	2.39	0.64	92.05	1.63
Total				5646.50	100.00

Sample Name: KD 1111 A
Data file: D:\ERNIE\KD\1111AXAS.D
Sample Info: Laufmittel: n-Heptan/EtOH 9:1;
Die Probe ist in DCM/LM gelöst

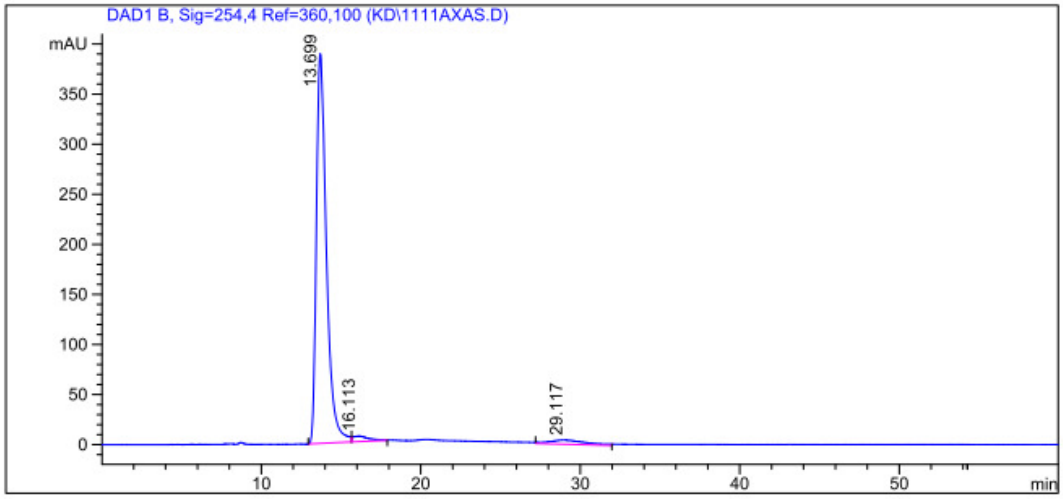
Agilent Technologies

Säule: DAICELAS.M
Säuleninfo: Chiralpak AS (250 x 4.6)mm 10µ

Operator: Analytik Labor AKEN

Injektion Time: 12:59:02
Injektion Date: 18.05.2015

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	24.1	23.7
Flow in ml/min:	0.7	0.7



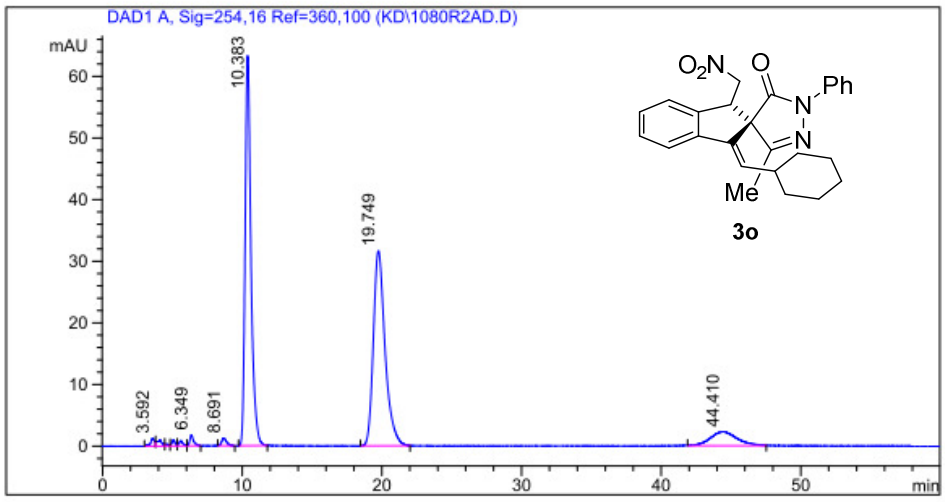
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	13.70	0.67	389.12	16990.23	93.99
2	16.11	0.83	5.61	392.27	2.17
3	29.12	2.75	4.20	694.88	3.84
Total				18077.38	100.00

Sample Name: KD 1080 A rac
Data file: D:\GONZO\KD\1080R2AD.D
Sample Info: Laufmittel: n-Heptan/iPrOH 6:4
Die Probe ist in LM/DCM gelöst

Säule: DAICELAD.M
Säuleninfo: Chiralpak AD (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 09:44:07
Injektion Date: 13.04.2015

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	48.3	48.6
Flow in ml/min:	1.00	1.00



3o

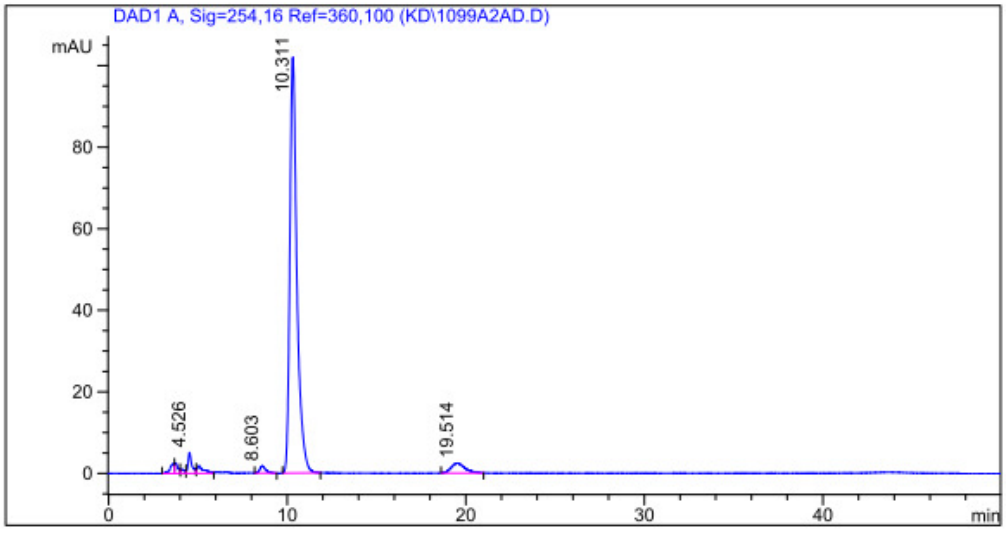
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.59	0.30	1.28	26.40	0.64
2	4.10	0.31	1.04	25.55	0.62
3	4.59	0.26	0.32	6.05	0.15
4	5.06	0.24	1.00	16.77	0.40
5	5.61	0.28	0.84	16.77	0.40
6	6.35	0.27	1.78	33.29	0.80
7	8.69	0.35	1.25	30.81	0.74
8	10.38	0.44	63.29	1841.86	44.36
9	19.75	0.88	31.65	1844.92	44.43
10	44.41	1.60	2.28	309.92	7.46
Total				4152.33	100.00

Sample Name: KD 1099 A2
Data file: D:\GONZO\KD\1099A2AD.D
Sample Info: Laufmittel: n-Heptan/iPrOH 6:4
Die Probe ist in LM/DCM gelöst

Säule: DAICELAD.M
Säuleninfo: Chiralpak AD (250x4,6)mm
Operator: Analytik Labor AKEN

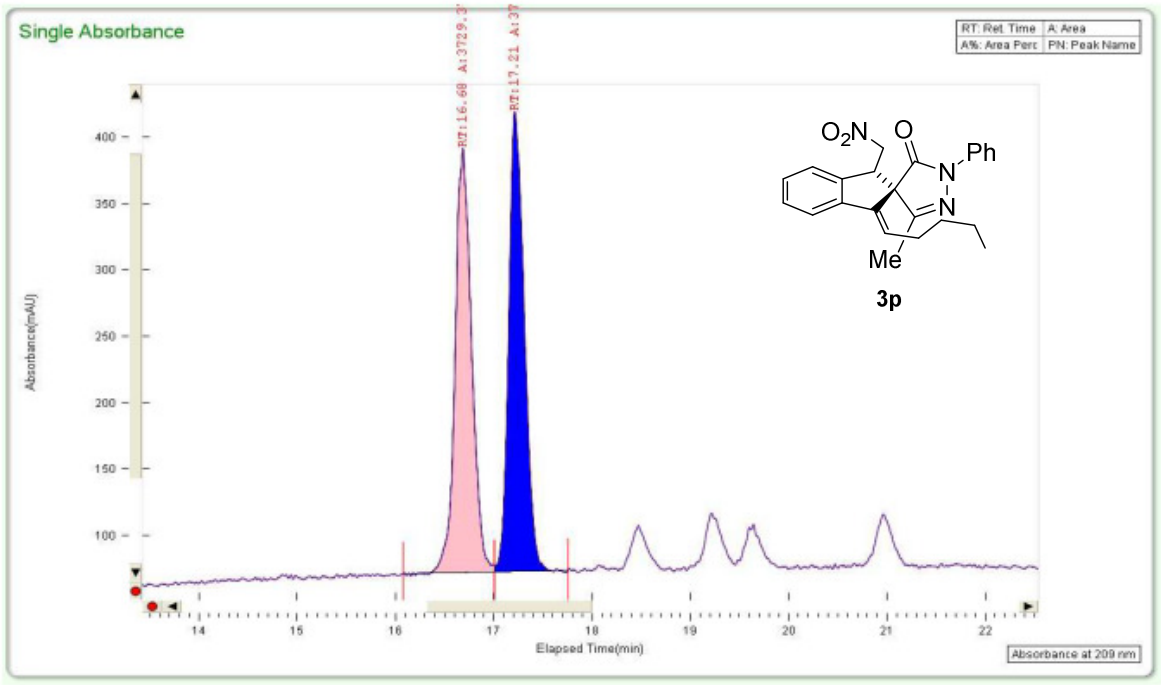
Injektion Time: 14:31:12
Injektion Date: 06.05.2015

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	47.2	48.0
Flow in ml/min:	1.00	1.00



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.62	0.21	2.44	39.63	1.24
2	3.76	0.18	2.57	32.77	1.03
3	4.11	0.19	1.09	15.73	0.49
4	4.53	0.20	5.14	74.23	2.33
5	5.06	0.35	1.86	48.39	1.52
6	8.60	0.34	1.74	40.67	1.28
7	10.31	0.41	101.95	2805.66	87.96
8	19.51	0.77	2.44	132.53	4.16
Total				3189.60	100.00

TharSFC



3p

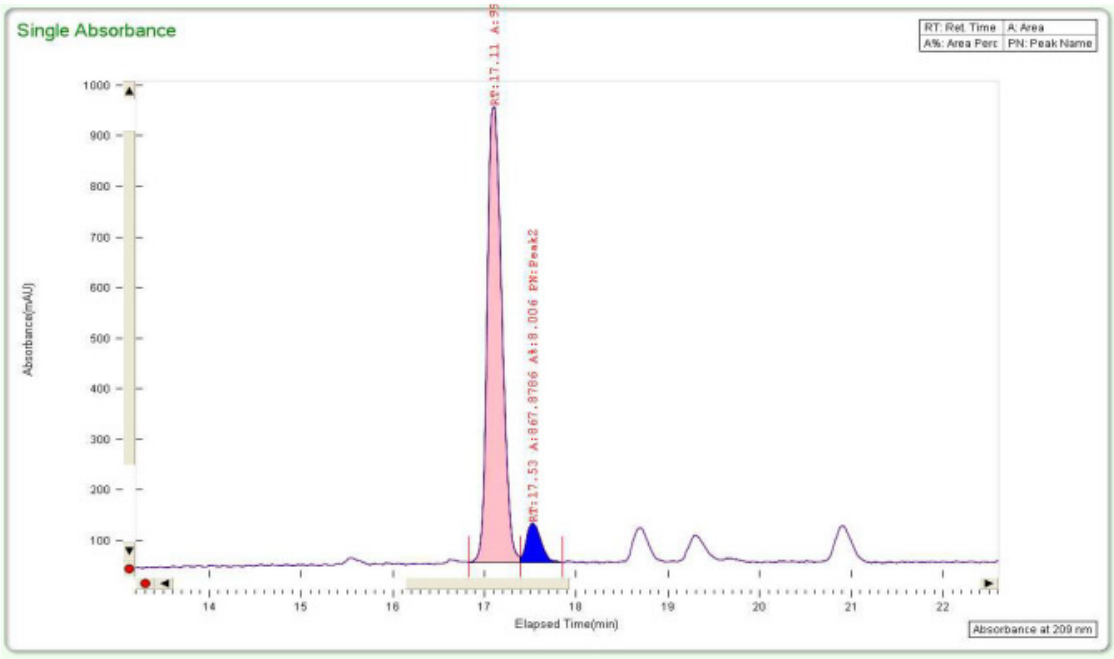
General Info	
Log Author	
Log Date	6/19/2015 10:13:43 AM
Report By	current_User
Report Date	9/30/2015
Method Name	4ml_1_30_grad_langsam.met
Notes	

Injection Info		**Temp**	37.8
Inj Vol	5	**Flow**	4
Solvent	Methanol	**% Modifier**	1
Column	R(R)-Whelk-01	**Pressure**	148
Sample	AKEn_KD-1114a		
Well location	P2: 1D		

Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	49.7068	3729.3761	16.68	319.4947	0.0272
2	50.2932	3773.3767	17.21	346.6515	0.028
Total:	100	7502.7528			

ThарSFC



General Info	
Log Author	
Log Date	6/19/2015 11:51:20 AM
Report By	current_User
Report Date	9/30/2015
Method Name	4ml_1_30_grad_langsam.met
Notes	

Injection Info		**Temp**	38
Inj Vol	5	**Flow**	4
Solvent	Methanol	**% Modifier**	1
Column	R(R)-Whelk-01	**Pressure**	150
Sample	AKEn_KD-1115-A2		
Well location	P2: 1F		

Peak Info

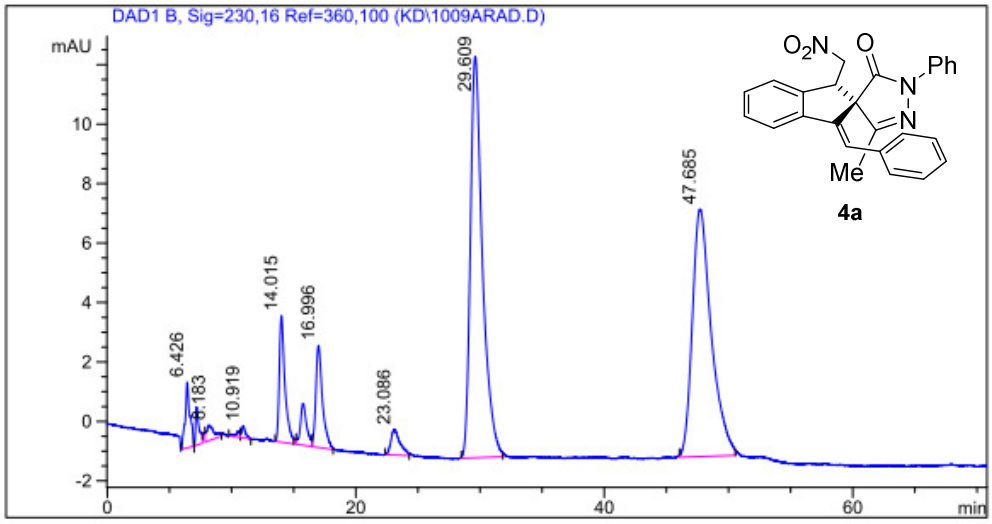
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	91.994	9972.4814	17.11	901.5144	0.024
2	8.006	867.8786	17.53	77.9865	0.0246
Total:	100	10840.36			

Sample Name: KD 1009 A rac
Data file: D:\GONZO\KD\1009ARAD.D
Sample Info: Laufmittel: n-Heptan/EtOH 7:3;
Die Probe ist in DCM/LM gelöst.

Säule: DAICELAD.M
Säuleninfo: Chiralpak AD (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 08:40:58
Injektion Date: 31.03.2015

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	21.4	21.8
Flow in ml/min:	0.50	0.50



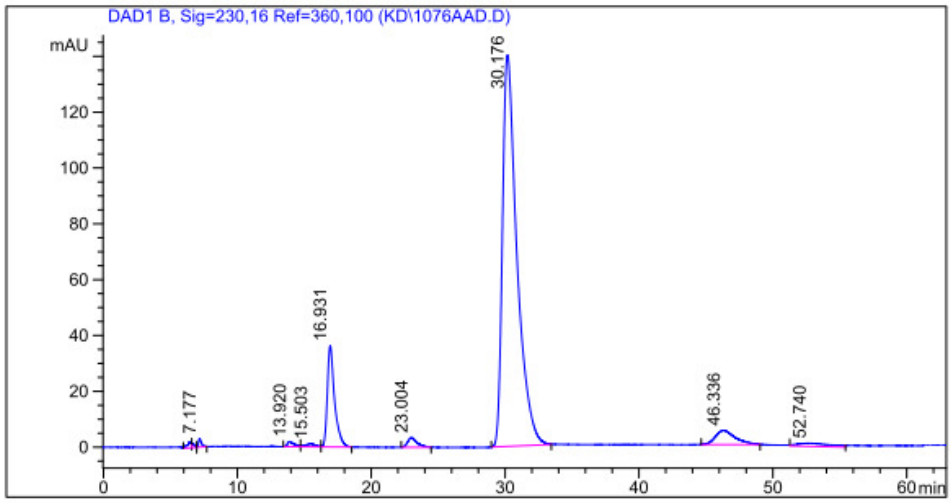
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	6.43	0.36	2.21	57.88	2.55
2	7.19	0.27	1.29	24.48	1.08
3	8.18	0.52	0.52	22.27	0.98
4	10.51	0.30	0.19	4.70	0.21
5	10.92	0.26	0.39	8.06	0.36
6	14.01	0.46	4.25	133.72	5.89
7	15.76	0.49	1.40	48.86	2.15
8	17.00	0.54	3.43	127.42	5.62
9	23.09	0.61	0.86	44.10	1.94
10	29.61	0.99	13.49	913.12	40.25
11	47.69	1.31	8.32	883.94	38.97
Total				2268.54	100.00

Sample Name: KD 1076 A
Data file: D:\GONZO\KD\1076AAD.D
Sample Info: Laufmittel: n-Heptan/EtOH 7:3
Die Probe ist in LM/DCM gelöst

Säule: DAICELAD.M
Säuleninfo: Chiralpak AD (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 09:21:03
Injektion Date: 07.04.2015

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	20.7	21.0
Flow in ml/min:	0.50	0.50



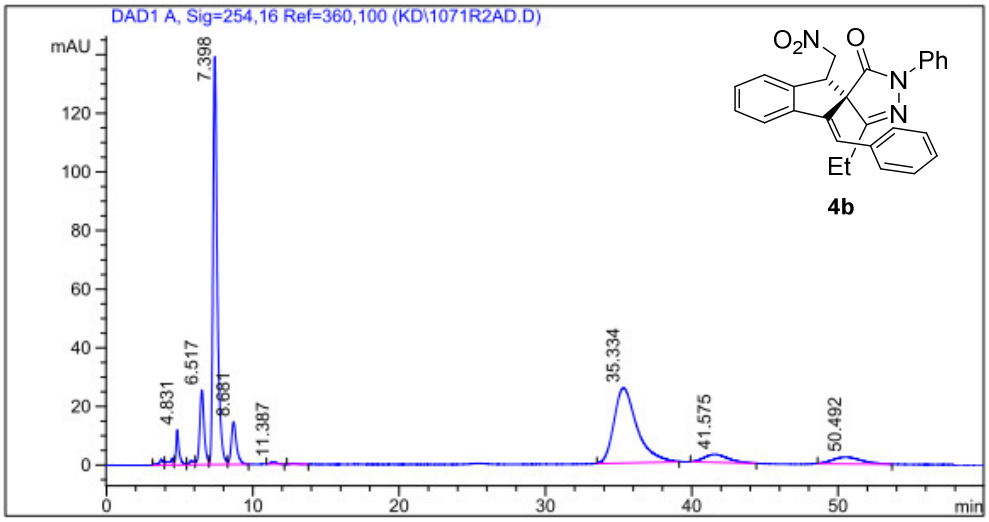
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	6.43	0.28	2.24	43.82	0.34
2	6.68	0.20	1.40	20.11	0.15
3	7.18	0.22	3.07	47.40	0.36
4	13.92	0.51	1.84	68.63	0.53
5	15.50	0.67	1.10	62.38	0.48
6	16.93	0.55	36.21	1355.40	10.41
7	23.00	0.67	3.45	171.96	1.32
8	30.18	1.10	140.15	10505.87	80.72
9	46.34	1.25	5.07	530.56	4.08
10	52.74	2.98	1.17	208.27	1.60
Total				13014.42	100.00

Sample Name: KD 1071 A rac
Data file: D:\GONZO\KD\1071R2AD.D
Sample Info: Laufmittel: n-Heptan/iPrOH 6:4
Die Probe ist in LM/DCM gelöst

Säule: DAICELAD.M
Säuleninfo: Chiralpak AD (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 08:42:54
Injektion Date: 13.04.2015

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	48.2	49.3
Flow in ml/min:	1.00	1.00



4b

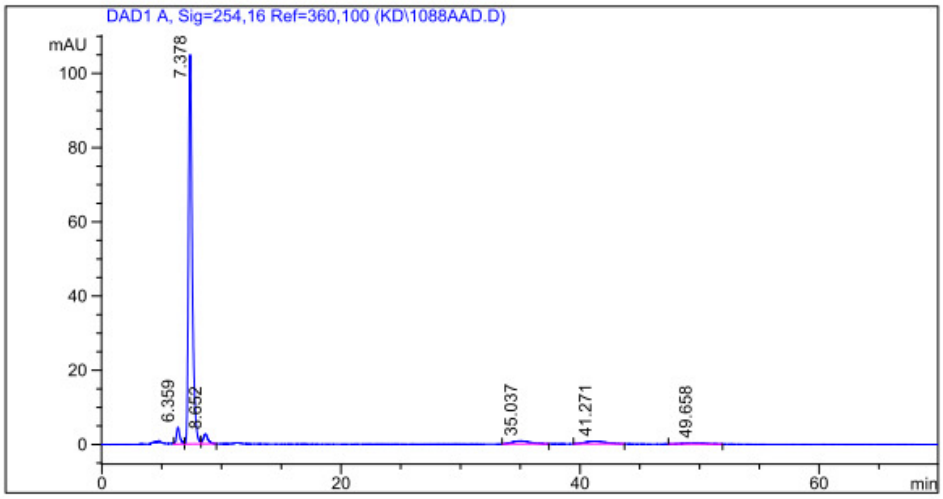
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.73	0.25	2.05	37.10	0.49
2	4.49	0.31	2.22	50.65	0.67
3	4.83	0.21	11.93	173.21	2.30
4	5.79	0.34	1.33	32.46	0.43
5	6.52	0.31	25.52	536.95	7.14
6	7.40	0.31	139.07	2830.78	37.63
7	8.68	0.37	14.57	361.80	4.81
8	11.39	0.46	0.72	22.71	0.30
9	12.77	0.47	0.30	11.05	0.15
10	35.33	1.63	25.68	2815.87	37.43
11	41.58	1.42	2.74	322.19	4.28
12	50.49	1.66	2.35	328.30	4.36
Total				7523.07	100.00

Sample Name: KD 1088 A
Data file: D:\GONZO\KD\1088AAD.D
Sample Info: Laufmittel: n-Heptan/iPrOH 6:4
Die Probe ist in LM/DCM gelöst

Säule: DAICELAD.M
Säuleninfo: Chiralpak AD (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 15:23:24
Injektion Date: 16.04.2015

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	46.7	47.4
Flow in ml/min:	1.00	1.00



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	6.36	0.30	4.54	90.38	3.42
2	7.38	0.32	104.91	2263.49	85.57
3	8.65	0.42	2.65	75.42	2.85
4	35.04	1.24	0.83	86.89	3.28
5	41.27	1.42	0.73	87.41	3.30
6	49.66	2.18	0.32	41.69	1.58
Total				2645.28	100.00

Sample name: **KD 1072 A rac**

Data file: C:\SNOOPY\KD\1072ARIA.D

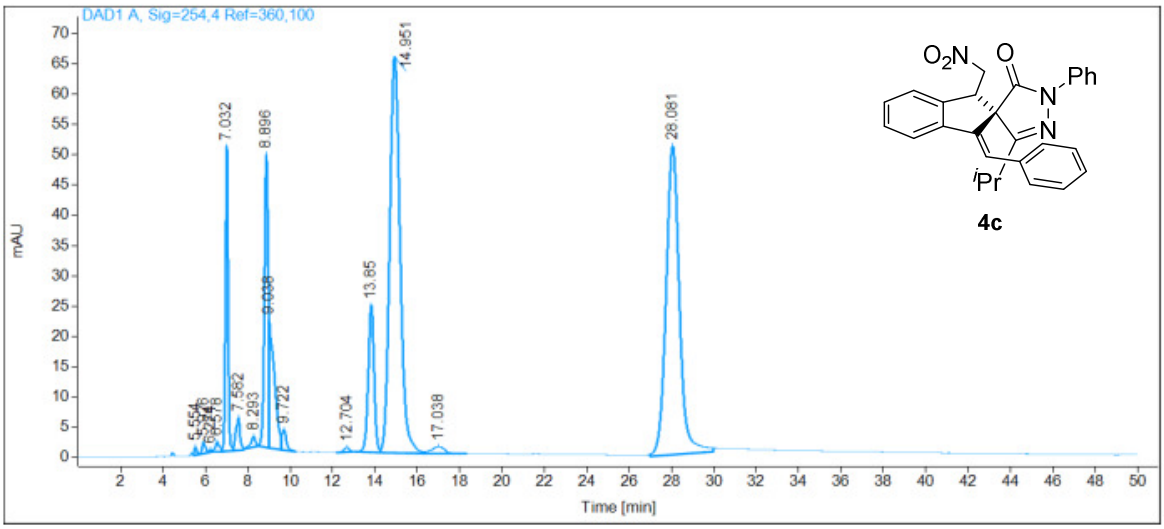
Description: Laufmittel: n-Heptan/EtOH 7:3;
Probe ist in DCM/LM gelöst

Injection date: 4/22/2015 12:19:04 PM

Acq. Analysis method: CHIRALPAKIARNP.M

Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

Pressure at start: 42 bar **Start flow:** 0.700 ml/min **Column oven:** 29.98 °C



4c

Name KD 1072 A rac

RT [min]	Type	Area%	Area	Height	Width [min]
5.55	VB	0.15	9.94	1.27	0.12
5.93	BB	0.28	18.18	1.80	0.14
6.27	BV	0.05	3.14	0.44	0.11
6.58	VV	0.32	20.89	1.53	0.19
7.03	VV	6.55	429.12	50.29	0.13
7.58	VB	1.09	71.28	5.27	0.19
8.29	BB	0.41	26.89	1.79	0.22
8.90	MF	9.30	609.80	48.45	0.21
9.04	FM	5.18	339.79	20.99	0.27
9.72	VB	0.77	50.31	3.35	0.22
12.70	BB	0.19	12.67	0.76	0.26
13.85	BV	7.07	463.38	24.18	0.30
14.95	VV	34.00	2228.68	65.40	0.53
17.04	VB	0.69	45.45	1.12	0.62
28.08	MM	33.95	2225.02	51.00	0.73
	Sum	100.00	6554.54		

Sample name: **KD 1089 A**

Data file: C:\SNOOPY\KD\1089AIA.D

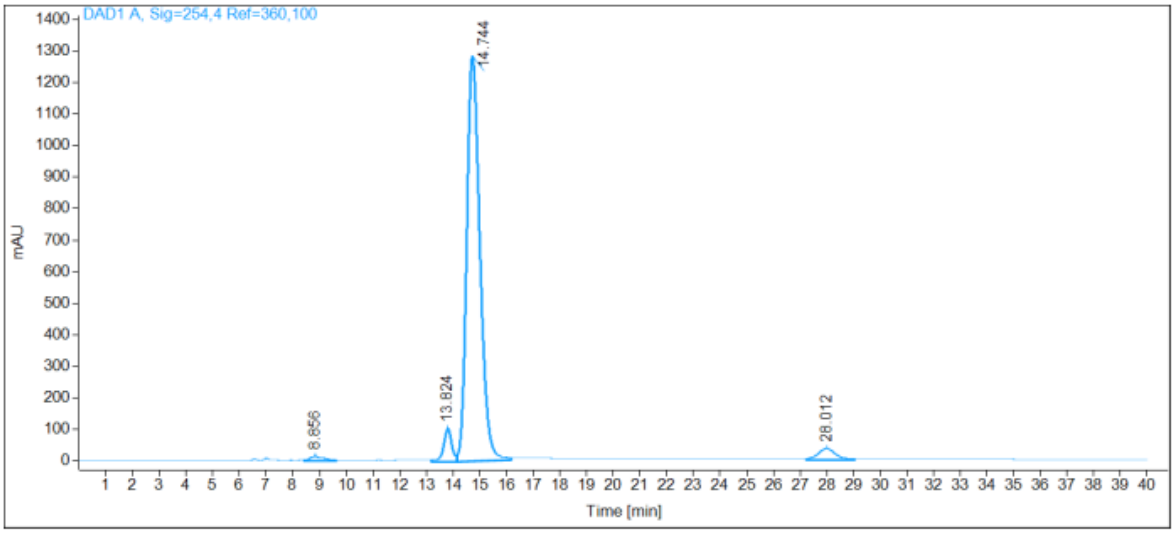
Description: Laufmittel: n-Heptan/EtOH 7:3;
Probe ist in DCM/LM gelöst

Injection date: 4/22/2015 1:41:17 PM

Acq. Analysis method: CHIRALPAKIARNP.M

Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

Pressure at start: 41 bar **Start flow:** 0.700 ml/min **Column oven:** 29.99 °C



Name KD 1089 A

RT [min]	Type	Area%	Area	Height	Width [min]
8.86	VV	0.83	399.27	12.59	0.46
13.82	MF	4.68	2264.96	104.49	0.36
14.74	FM	90.72	43866.96	1284.27	0.57
28.01	MM	3.77	1821.40	37.09	0.82
	Sum	100.00	48352.60		

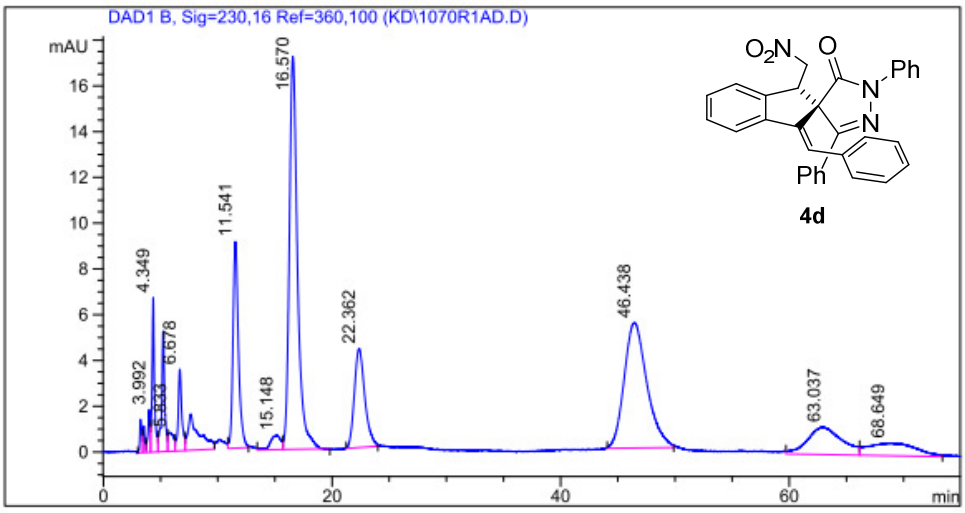
Sample Name: KD 1070 A rac
Data file: D:\GONZO\KD\1070R1AD.D
Sample Info: Laufmittel: n-Heptan/iPrOH 6:4;
Die Probe ist in DCM/LM gelöst.

->

Säule: DAICELAD.M
Säuleninfo: Chiralpak AD (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 14:53:42
Injektion Date: 21.04.2015

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	47.5	47.7
Flow in ml/min:	1.00	1.00



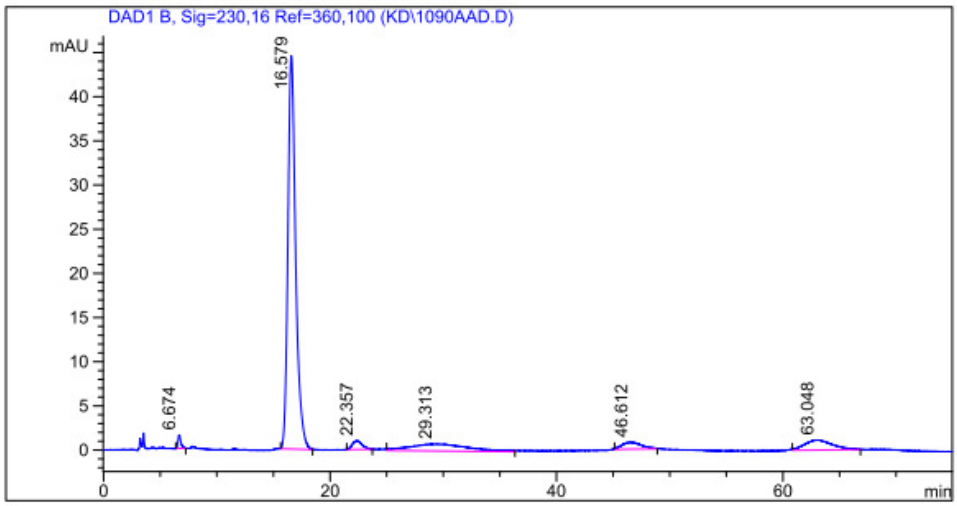
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.24	0.18	1.46	19.67	0.63
2	3.53	0.15	1.16	12.74	0.41
3	3.99	0.19	1.87	25.16	0.81
4	4.35	0.21	6.76	99.46	3.20
5	5.22	0.26	5.27	97.73	3.14
6	5.83	0.41	0.83	27.54	0.89
7	6.68	0.32	3.56	79.22	2.55
8	7.64	0.86	1.59	108.14	3.48
9	11.54	0.50	9.03	300.96	9.68
10	15.15	1.06	0.63	39.82	1.28
11	16.57	0.83	17.16	854.32	27.48
12	22.36	0.82	4.32	275.32	8.86
13	46.44	1.64	5.47	757.50	24.37
14	63.04	3.48	1.20	250.73	8.07
15	68.65	4.83	0.55	160.03	5.15
Total				3108.34	100.00

Sample Name: KD 1090 A
Data file: D:\GONZO\KD\1090AAD.D
Sample Info: Laufmittel: n-Heptan/iPrOH 6:4
Die Probe ist in LM/DCM gelöst

Säule: DAICELAD.M
Säuleninfo: Chiralpak AD (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 16:12:30
Injektion Date: 21.04.2015

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	46.8	48.1
Flow in ml/min:	1.00	1.00



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	6.67	0.26	1.53	27.01	0.97
2	16.58	0.71	44.49	2105.91	75.82
3	22.36	0.72	0.99	59.55	2.14
4	29.31	6.12	0.80	293.10	10.55
5	46.61	1.42	0.79	95.74	3.45
6	63.05	2.02	1.14	196.17	7.06
Total				2777.48	100.00

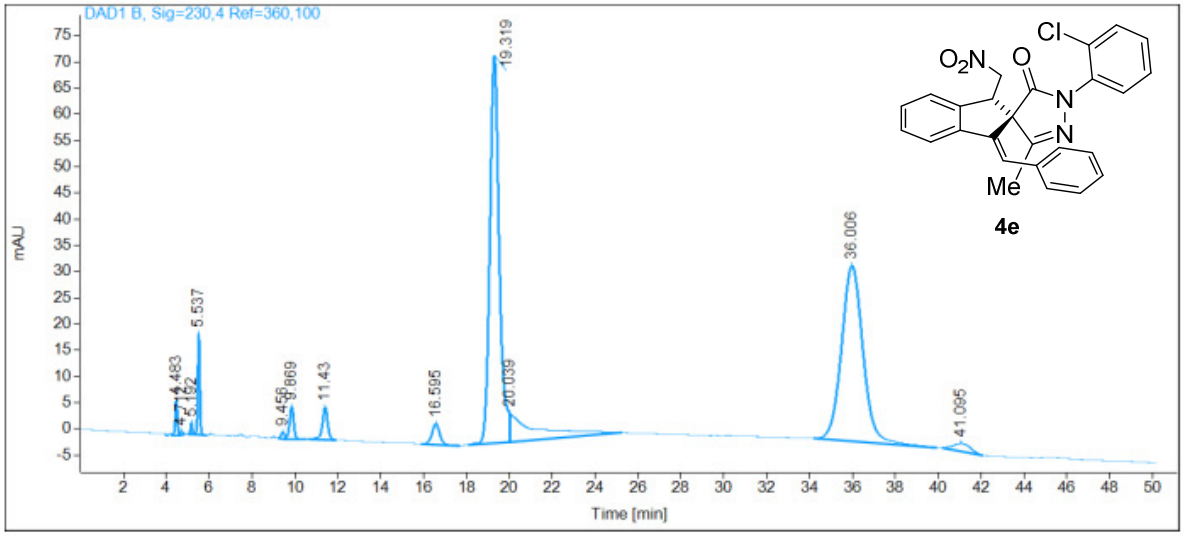
Sample name: **DH NS 17 rac**

Data file: C:\SNOOPY\DH\DH NS 17 RAC IA.D
Description: Laufmittel: n-Heptan/EtOH 7:3 Die Probe ist DCM/LM gelöst.

Injection date: 10/1/2014 12:52:52 PM
Acq. Analysis method: CHIRALPAKIARNP.M

Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

Pressure at start: 42 bar **Start flow:** 0.700 ml/min **Column oven:** 30 °C



4e

Name DH NS 17 rac

RT [min]	Type	Area%	Area	Height	Width [min]
4.48	VV	0.82	45.90	6.58	0.11
4.71	VV	0.13	7.16	0.67	0.17
5.19	BV	0.24	13.69	2.32	0.09
5.54	VB	2.20	123.69	19.33	0.10
9.46	BV	0.24	13.63	1.22	0.17
9.87	VB	1.44	80.99	6.16	0.20
11.43	BB	1.88	106.02	6.16	0.26
16.59	BB	1.77	99.67	3.97	0.38
19.32	MF	40.09	2257.32	73.92	0.51
20.04	FM	8.36	470.93	5.39	1.46
36.01	BB	41.34	2327.37	33.46	1.06
41.10	BB	1.49	84.02	1.52	0.85
	Sum	100.00	5630.40		

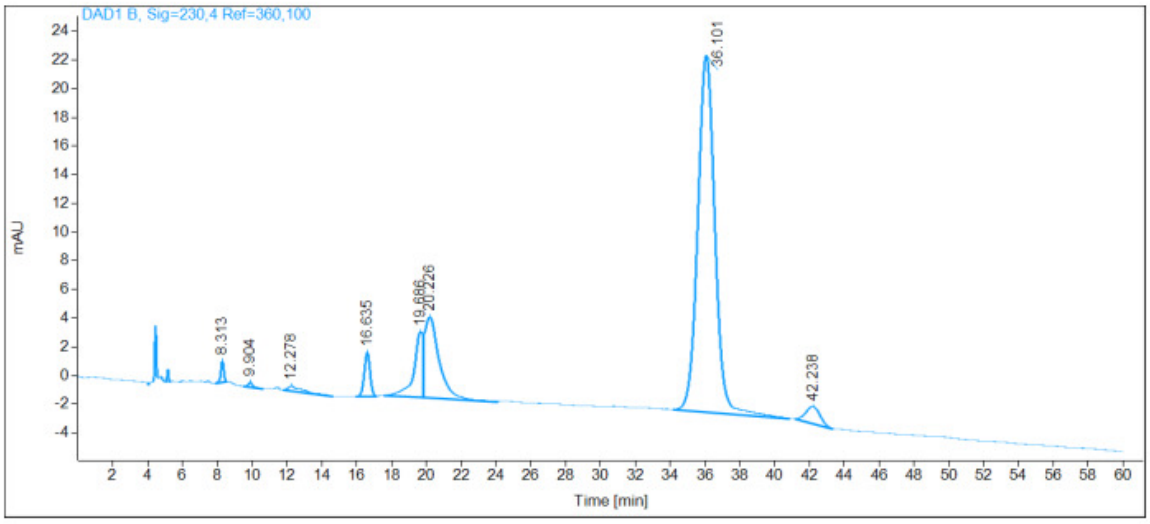
Sample name: **KD 1086 A**

Data file: C:\SNOOPY\KD\KD 1086 A IA.D
Description: Laufmittel: n-Heptan/EtOH 7:3 ; Die Probe ist DCM/LM gelöst.

Injection date: 4/15/2015 11:39:33 AM
Acq. Analysis method: CHIRALPAKIARNP.M

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Pressure at start: 41 bar **Start flow:** 0.700 ml/min **Column oven:** 29.99 °C



Name KD 1086 A

RT [min]	Type	Area%	Area	Height	Width [min]
8.31	BB	0.77	18.27	1.52	0.18
9.90	BB	0.27	6.36	0.35	0.26
12.28	BB	0.85	20.23	0.35	0.72
16.63	BB	2.95	70.13	3.04	0.35
19.69	BV	6.90	164.17	4.59	0.51
20.23	VB	13.95	331.98	5.67	0.84
36.10	BB	71.47	1701.37	24.89	1.05
42.24	BB	2.85	67.90	1.20	0.74
	Sum	100.00	2380.42		

Sample name: **DH NS 18 rac**

Data file: C:\SNOOPY\DH\NS18RIC1.D

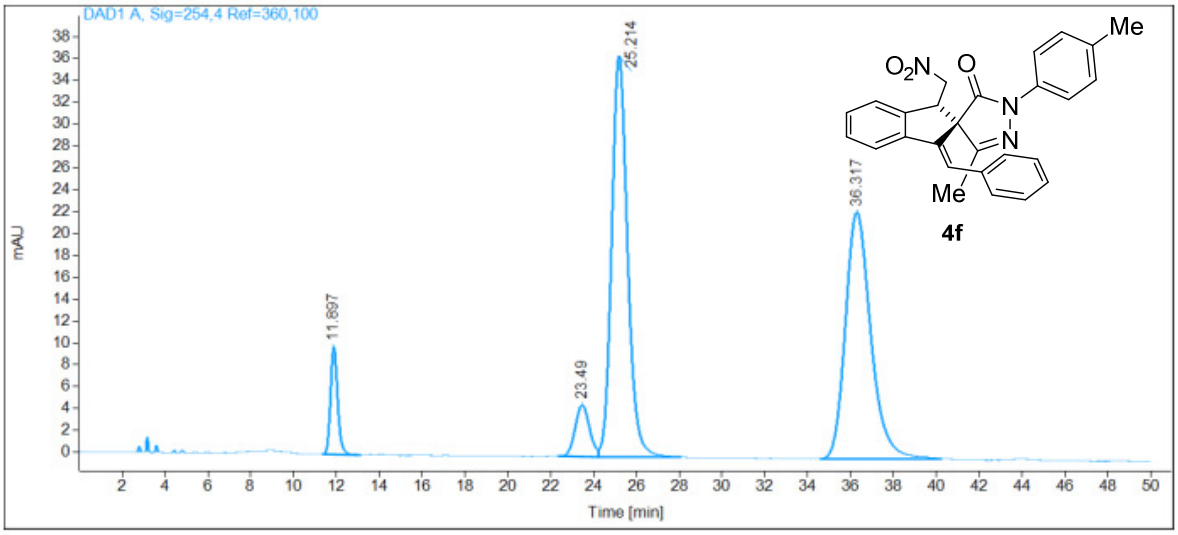
Description: Laufmittel: n-Heptan/iPrOH 9:1;
Probe ist in LM/DCM gelöst

Injection date: 9/29/2014 2:51:29 PM

Acq. Analysis method: CHIRALPAKIC1-6LNP.M

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Pressure at start: 23 bar **Start flow:** 0.700 ml/min **Column oven:** 30.01 °C



Name DH NS 18 rac

RT [min]	Type	Area%	Area	Height	Width [min]
11.90	BB	5.46	228.30	9.80	0.36
23.49	BV	5.22	218.59	4.71	0.70
25.21	VB	45.03	1884.33	36.62	0.79
36.32	BB	44.29	1853.06	22.53	1.25
	Sum	100.00	4184.28		

Sample name: **KD 1085 A**

Data file: C:\SNOOPY\KD\1085ARIC.D

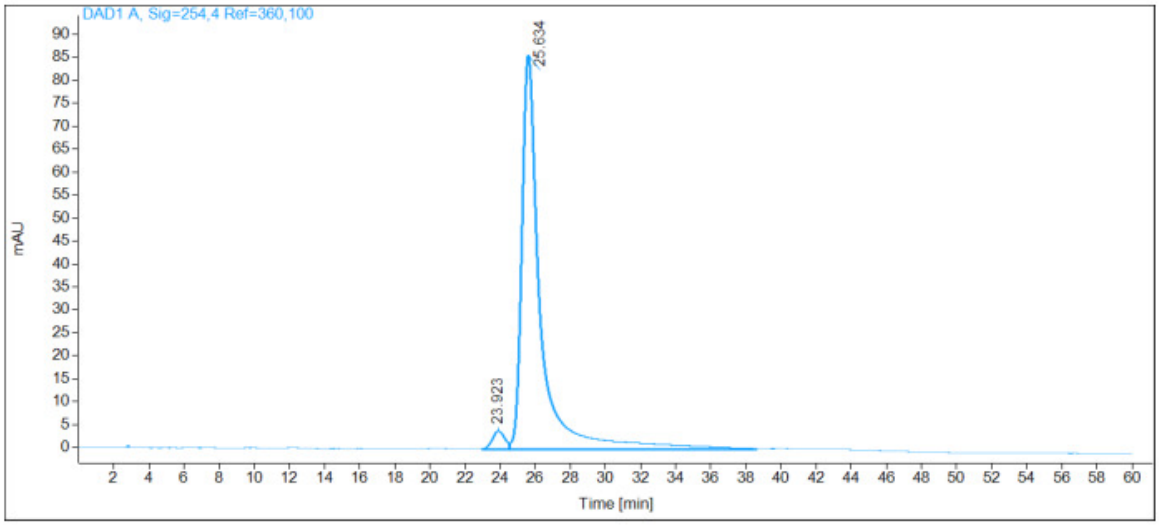
Description: Laufmittel: n-Heptan/iPrOH 9:1;
Probe ist in LM/DCM gelöst

Injection date: 4/14/2015 4:43:50 PM

Acq. Analysis method: CHIRALPAKIC1-6LNP.M

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Pressure at start: 26 bar **Start flow:** 0.700 ml/min **Column oven:** 29.98 °C



Name KD 1085 A

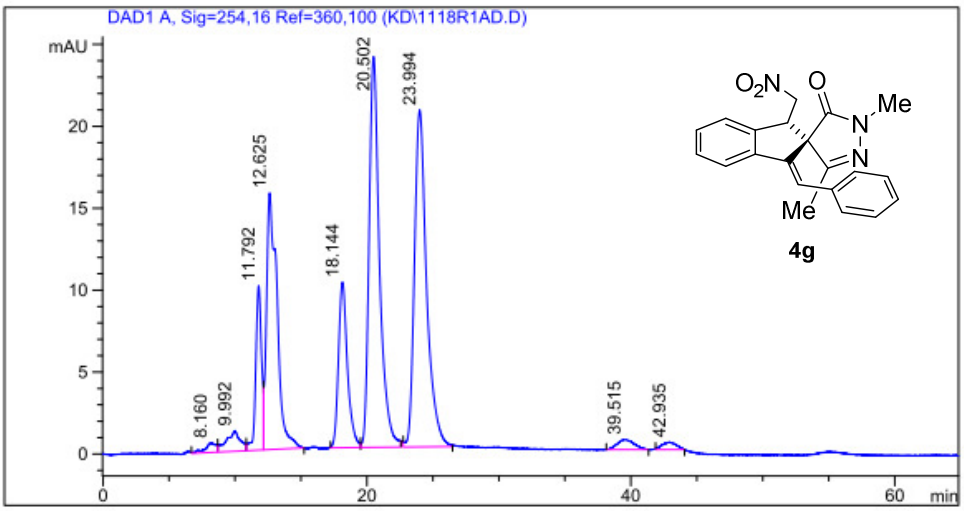
RT [min]	Type	Area%	Area	Height	Width [min]
23.92	BV	3.00	194.63	3.97	0.73
25.63	VB	97.00	6295.50	85.80	1.05
	Sum	100.00	6490.12		

Sample Name: KD 1118 A rac
Data file: D:\GONZO\KD\1118R1AD.D
Sample Info: Laufmittel: n-Heptan/iPrOH 7:3
Die Probe ist in LM/DCM gelöst

Säule: DAICELAD.M
Säuleninfo: Chiralpak AD (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 12:26:21
Injektion Date: 22.05.2015

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	20.2	21.2
Flow in ml/min:	0.50	0.50

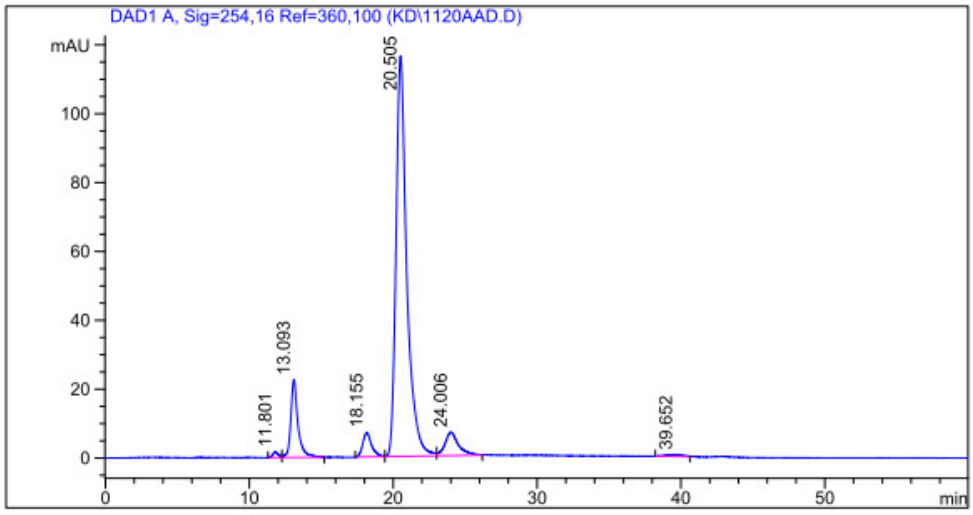


4g

#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	8.16	0.71	0.58	34.41	0.76
2	9.99	0.91	1.26	91.52	2.03
3	11.79	0.47	10.02	306.54	6.81
4	12.62	0.75	15.65	872.11	19.39
5	18.14	0.71	10.09	476.93	10.60
6	20.50	0.92	23.83	1311.77	29.16
7	23.99	0.96	20.55	1317.14	29.28
8	39.51	1.08	0.60	54.89	1.22
9	42.93	0.90	0.45	33.53	0.75
Total				4498.84	100.00

Sample Name:	KD 1120 A
Data file:	D:\GONZO\KD\1120AAD.D
Sample Info:	Laufmittel: n-Heptan/iPrOH 7:3 Die Probe ist in LM/DCM gelöst
Säule:	DAICELAD.M
Säuleninfo:	Chiralpak AD (250x4,6)mm
Operator:	Analytik Labor AKEN
Injektion Time:	13:32:28
Injektion Date:	22.05.2015

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	21.1	21.4
Flow in ml/min:	0.50	0.50



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	11.80	0.40	1.70	47.25	0.62
2	13.09	0.50	22.53	778.83	10.18
3	18.15	0.65	7.09	302.38	3.95
4	20.51	0.86	116.22	6024.90	78.75
5	24.01	1.10	6.80	448.29	5.86
6	39.65	1.05	0.58	49.48	0.65
Total				7651.13	100.00

[i] B. Tan, X. Zhang, P. J. Chua, G. Zhong, *Chem. Commun.* **2009**, 779-781.