Diastereoselective Synthesis of 2-Amino-spiro[4.5]decane-6-ones Through Synergistic Photocatalysis and Organocatalysis for [3 + 2] Cycloaddition of Cyclopropylamines with Olefins

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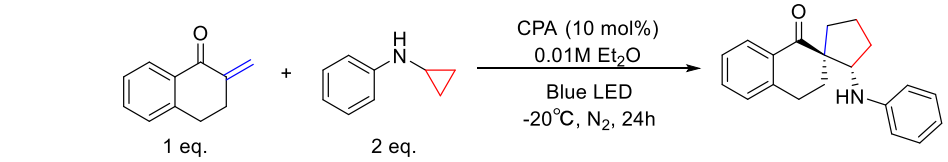
*Corresponding author's Email: lxfok@zju.edu.cn

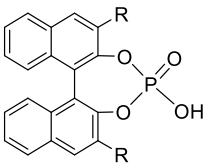
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1. Optimization of chiral phosphoric acids (CPAs)

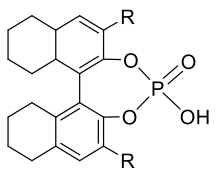
Table S1 Optimization of chiral phosphoric acids.[a]





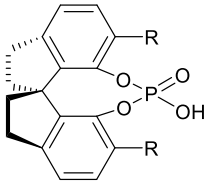
(R)-**4a**: R = 9-phenanthrenyl
(R)-**4b**: R = H
(R)-**4c**: R = Ph
(R)-**4d**: R = 1-naphthyl
(R)-**4e**: R = 2,4,6-(i-Pr)3Ph
(R)-**4f**: R = 3,5-(CF3)2Ph
(R)-**4g**: R = 3,5-(t-Bu)2-4-MeO-Ph
(R)-**4h**: R = 3,5-Ph2-Ph
(R)-**4i**: R = Triphenyl silicon
(R)-**4j**: R = 4-Ph-Ph
(R)-**4k**: R = 4-(2-naphthyl)-Ph
(R)-**4l**: R = 1-pyrenyl
(R)-**4m**: R = 9-anthrly
(R)-**4n**: R = 2-naphthyl
(R)-**4o**: R = 4-NO2-Ph
(R)-**4p**: R = 4-Cl-Ph
(R)-**4q**: R = 2,4,6-Cy3Ph

BINOL-PA **4**



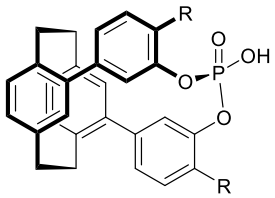
H8-BINOL-PA **5**

(R)-**5a**: R = Ph
(R)-**5b**: R = 2,4,6-(i-Pr)3Ph



SPA **6**

(S)-**6a**: R = Ph
(S)-**6b**: R = 2,4,6-(i-Pr)3Ph
(R)-**6c**: R = 3,5-(CF3)2Ph



Planar-PA **7**

(R)-**7a**: R = 9-phenanthrenyl

Entry	CPA	Yield(%)[b]	d.r.[c]	e.e.(%)[d]
1	(R)-**4a**	31	97:3	22
2	(R)-**4b**	45	93:7	5
3	(R)-**4c**	70	99:1	8
4	(R)-**4d**	22	79:21	3
5	(R)-**4e**	43	91:9	11
6	(R)-**4f**	23	81:19	10
7	(R)-**4g**	N.R.	-	-
8	(R)-**4h**	25	79:21	17
9	(R)-**4i**	16	80:20	19
10	(R)-**4j**	N.R.	-	-
11	(R)-**4k**	35	92:8	3
12	(R)-**4l**	N.R.	-	-
13	(R)-**4m**	21	85:15	28
14	(R)-**4n**	39	97:3	0
15	(R)-**4o**	N.R.	-	-
16	(R)-**4p**	N.R.	-	-
17	(R)-**4q**	N.R.	-	-
18	(R)-**5a**	19	80:20	4

19	(R)-**5b**	N.R.	-	-
20	(R)-**6a**	11	75:25	0
21	(R)-**6b**	N.R.	-	-
22	(R)-**6c**	5	79:21	8
23	(R)-**7a**	N.R.	-	-

[a] Reaction conditions: **1a** (0.025mmol, 1.0 equiv.), **2a** (0.05mmol, 2.0 equiv.), CPA (10 mol%). solvent (0.01M DCM), and blue LEDs (450 - 455 nm) under N_2 at -20 ℃ in 24h. [b] Isolated yields are shown. [c] The d.r. values were determined by HPLC. [d] The e.e. values were determined by HPLC.

2. NMR spectra and HPLC chromatograms of products

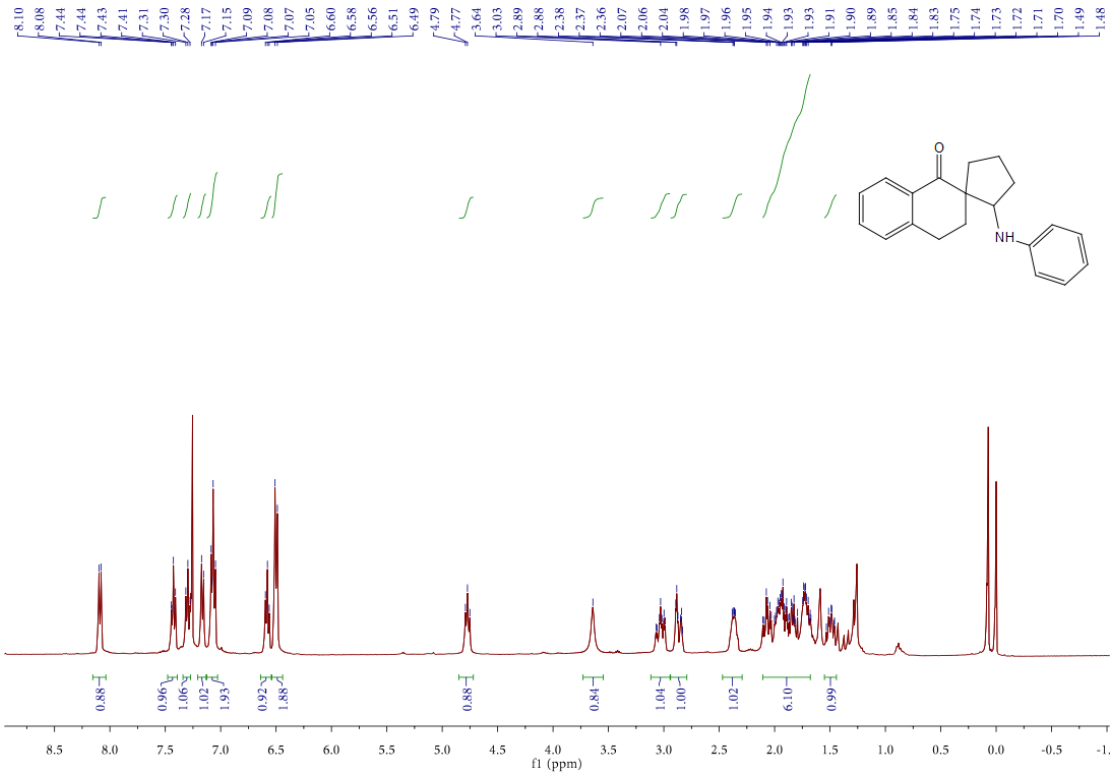


Figure S1. ^{1}H NMR spectra of

(1R',2S')-2-(phenylamino)-3',4'-dihydro-1'H-spiro[cyclopentane-1,2'-naphthalen]-1'-one (**3a**)

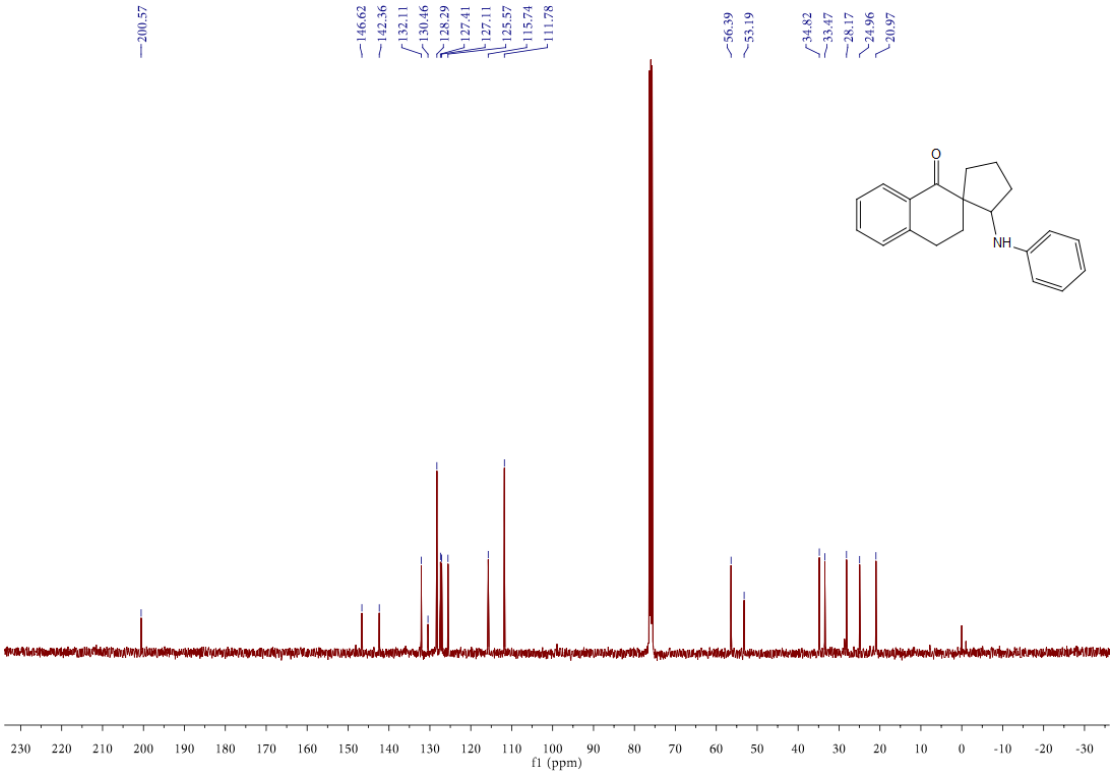
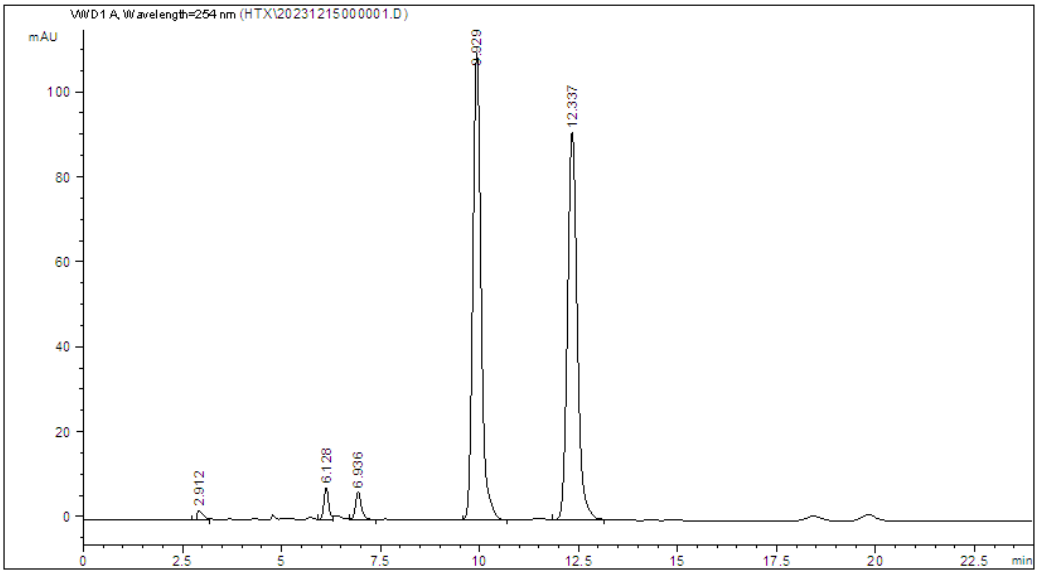


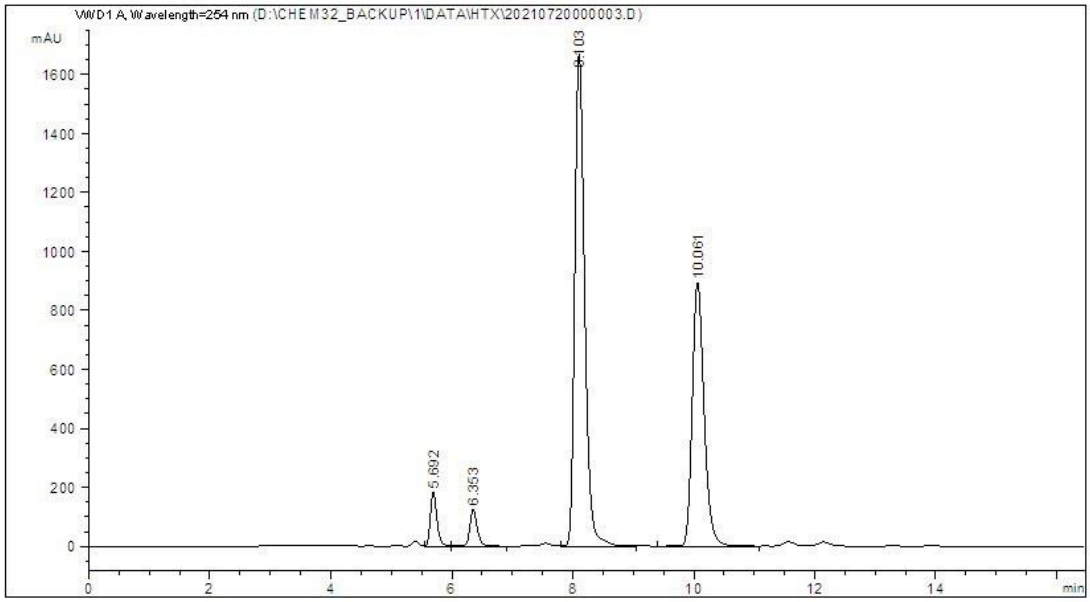
Figure S2. ^{13}C NMR spectra of

(1R',2S')-2-(phenylamino)-3',4'-dihydro-1'H-spiro[cyclopentane-1,2'-naphthalen]-1'-one (**3a**)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	2.912	BB	0.1417	22.25397	2.24837	0.6755
2	6.128	VV	0.1282	63.44696	7.58475	1.9258
3	6.936	VB	0.1576	69.33192	6.59638	2.1044
4	9.929	BB	0.2206	1585.41943	109.98901	48.1217
5	12.337	VB	0.2614	1554.15198	91.22398	47.1726
Totals :				3294.60426	217.64248	

Figure S3. HPLC spectra of (1R',2S')-2-(phenylamino)-3',4'-dihydro-1'H-spiro[cyclopentane-1,2'-naphthalen]-1'-one (**3a**)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.692	VV	0.1147	1393.00854	183.58784	4.1294
2	6.353	VB	0.1328	1099.55786	125.51884	3.2595
3	8.103	VV	0.1769	1.90575e4	1668.50073	56.4934
4	10.061	VB	0.2100	1.21840e4	893.97150	36.1178
Totals :				3.37341e4	2871.57891	

Figure S4. HPLC spectra of chirality (1R',2S')-2-(phenylamino)-3',4'-dihydro-1'H-spiro[cyclopentane-1,2'-naphthalen]-1'-one (**3a**)
(HPLC conditions: Chiral Separation Columns: AD-H; Flow rate: 1.0ml/min; Mobile phase: n-hexane : isopropanol = 90:10; Detection wavelength: 254nm.)

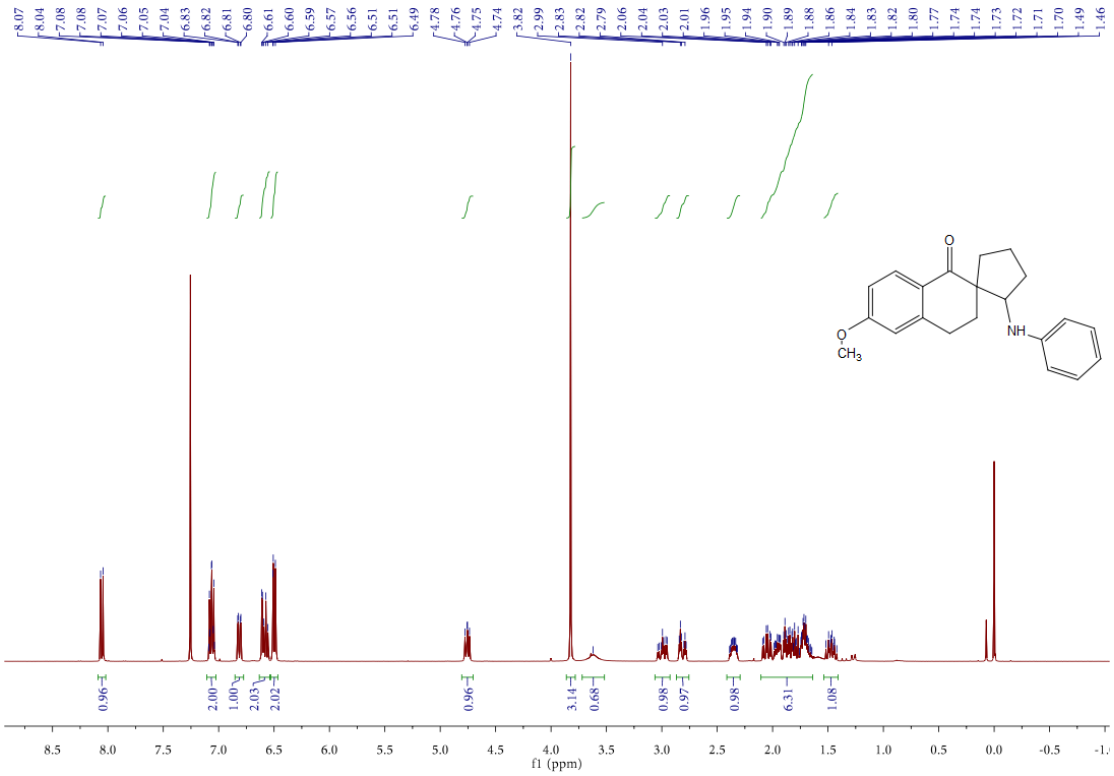


Figure S5. ^{1}H NMR spectra of
(1R',2S')-6'-methoxy-2-(phenylamino)-3',4'-dihydro-1'H-spiro[cyclopentane-1,2'-naphthalen]-1'-one (**3b**)

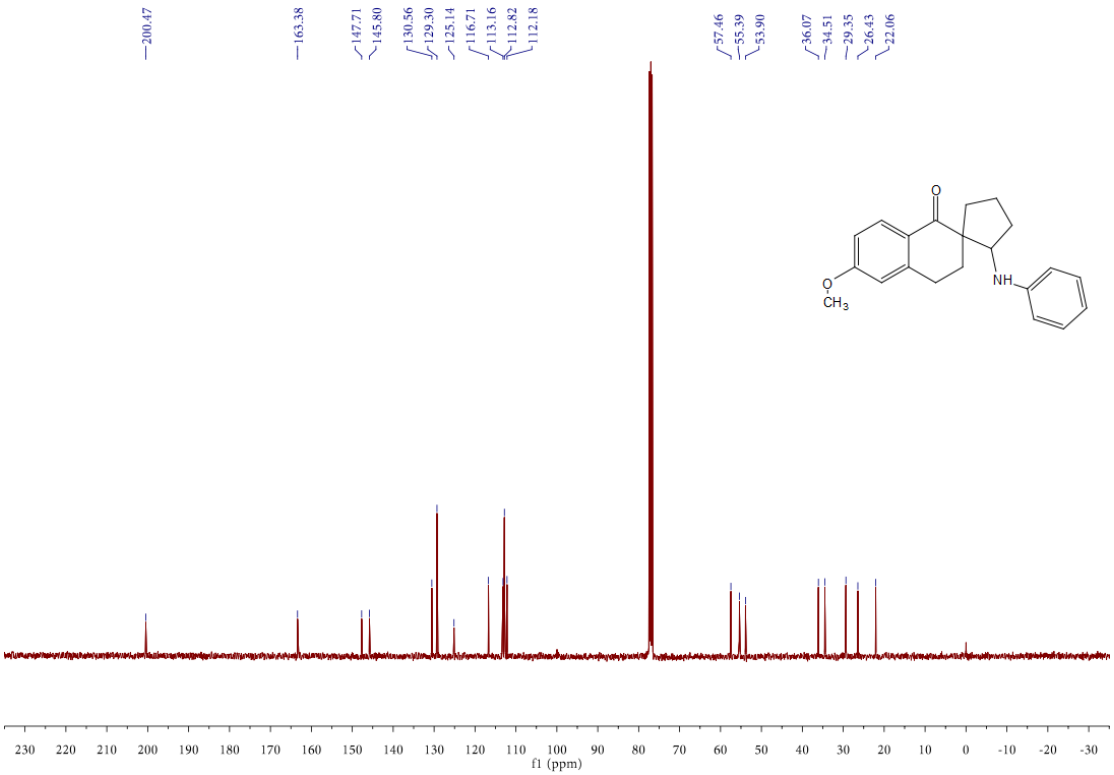
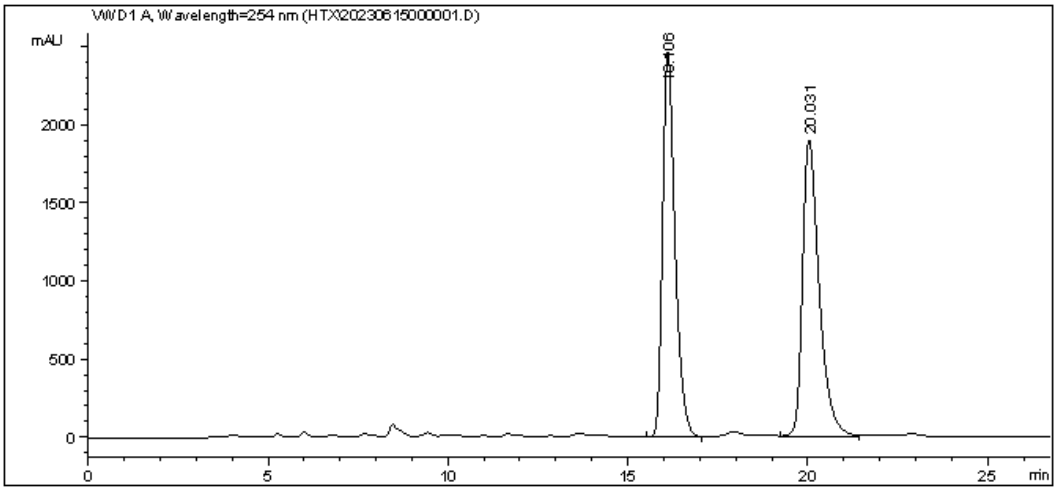


Figure S6. ^{13}C NMR spectra of
(1R',2S')-6'-methoxy-2-(phenylamino)-3',4'-dihydro-1'H-spiro[cyclopentane-1,2'-naphthalen]-1'-one (**3b**)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.106	VV	0.3660	5.95233e4	2466.44824	48.9255
2	20.031	VV	0.4911	6.21378e4	1905.62708	51.0745
Totals :				1.21661e5	4372.07532	

Figure S7. HPLC spectra of
(1R',2S')-6'-methoxy-2-(phenylamino)-3',4'-dihydro-1'H-spiro[cyclopentane-1,2'-naphthalen]-1'-one (**3b**)

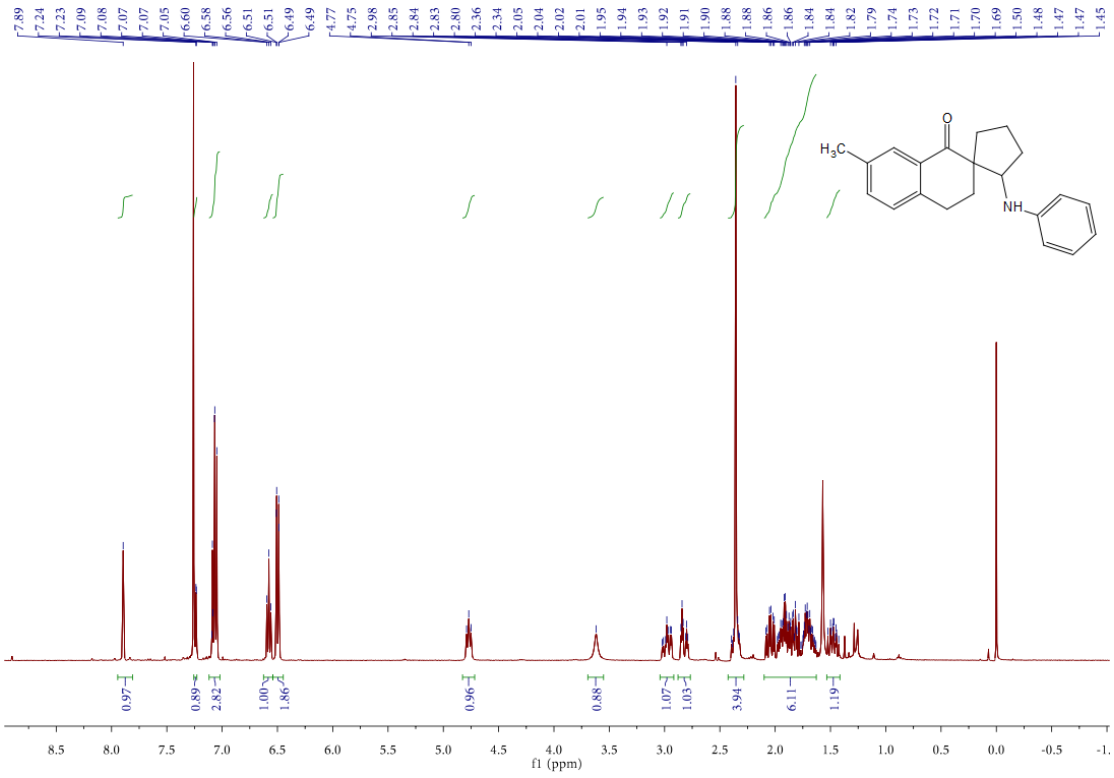


Figure S8. ^{1}H NMR spectra of
(1R',2S')-7'-methyl-2-(phenylamino)-3',4'-dihydro-1'H-spiro[cyclopentane-1,2'-naphthalen]-1'-one (**3c**)

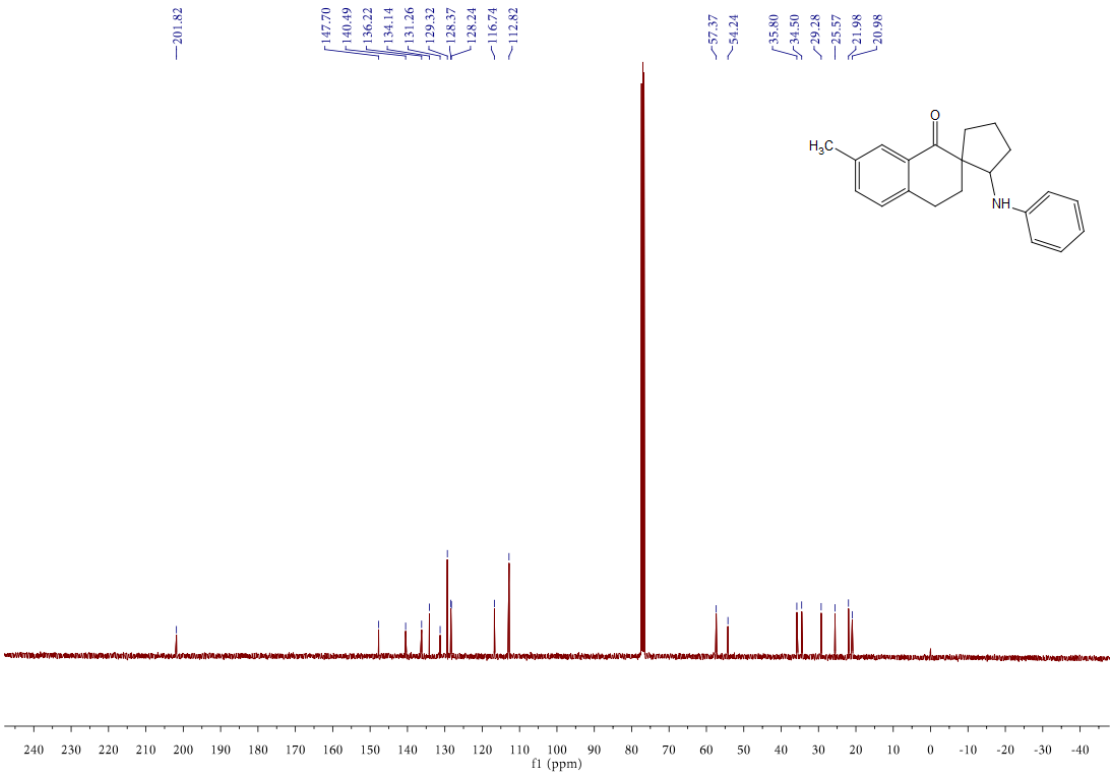
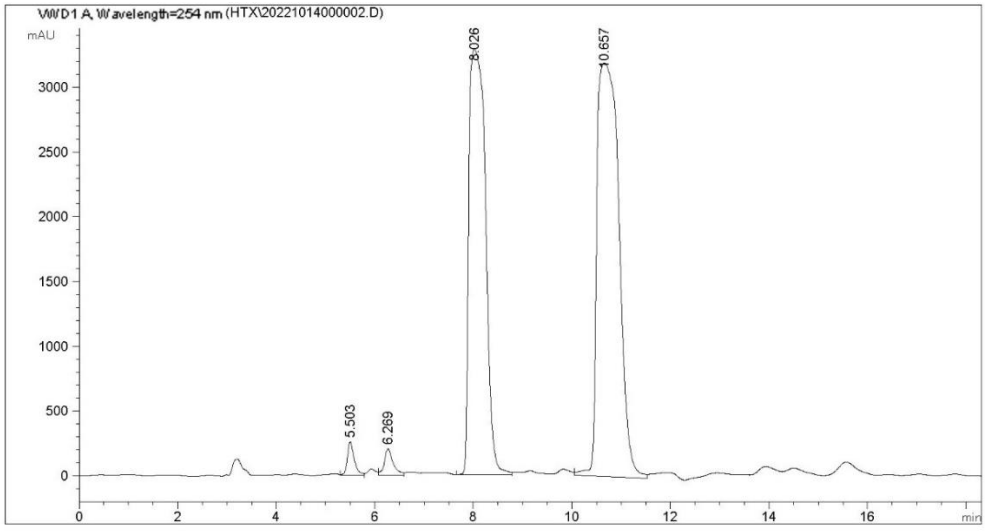


Figure S9. ^{13}C NMR spectra of
(1R',2S')-7'-methyl-2-(phenylamino)-3',4'-dihydro-1'H-spiro[cyclopentane-1,2'-naphthalen]-1'-one (**3c**)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.503	VV	0.1497	2541.79932	258.34521	1.4125
2	6.269	VV	0.1788	2513.51660	203.82912	1.3968
3	8.026	BV	0.3789	7.63239e4	3283.81641	42.4140
4	10.657	VV	0.5029	9.85706e4	3192.36597	54.7767
Totals :				1.79950e5	6938.35670	

Figure S10. HPLC spectra of
(1R',2S')-7'-methyl-2-(phenylamino)-3',4'-dihydro-1'H-spiro[cyclopentane-1,2'-naphthalen]-1'-one (**3c**)

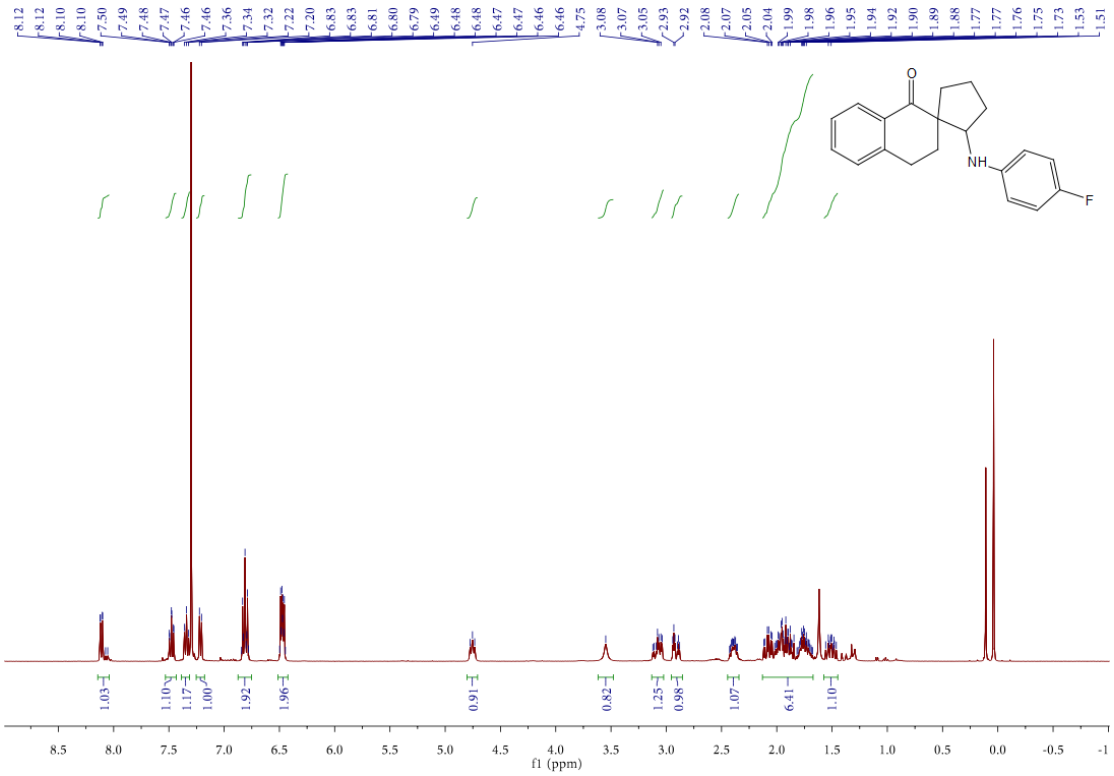


Figure S11. ^{1}H NMR spectra of
(1R',2S')-2-((4-fluorophenyl)amino)-3',4'-dihydro-1'H-spiro[cyclopentane-1,2'-naphthalen]-1'-one (**3d**)

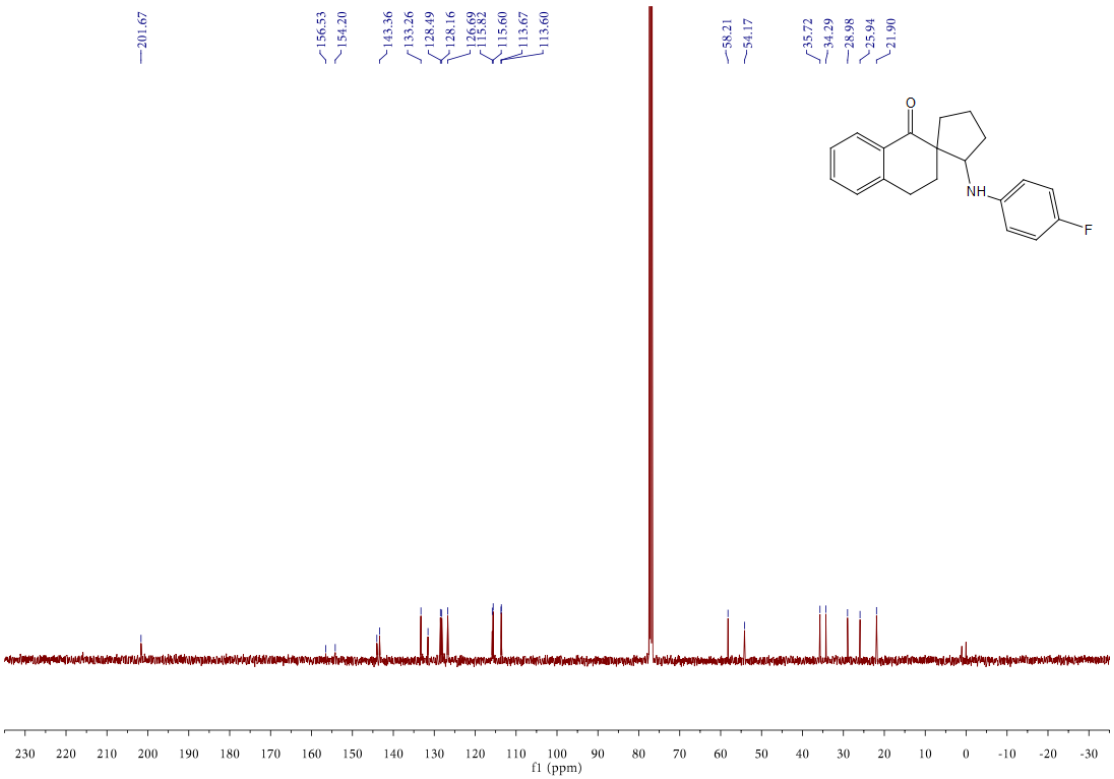
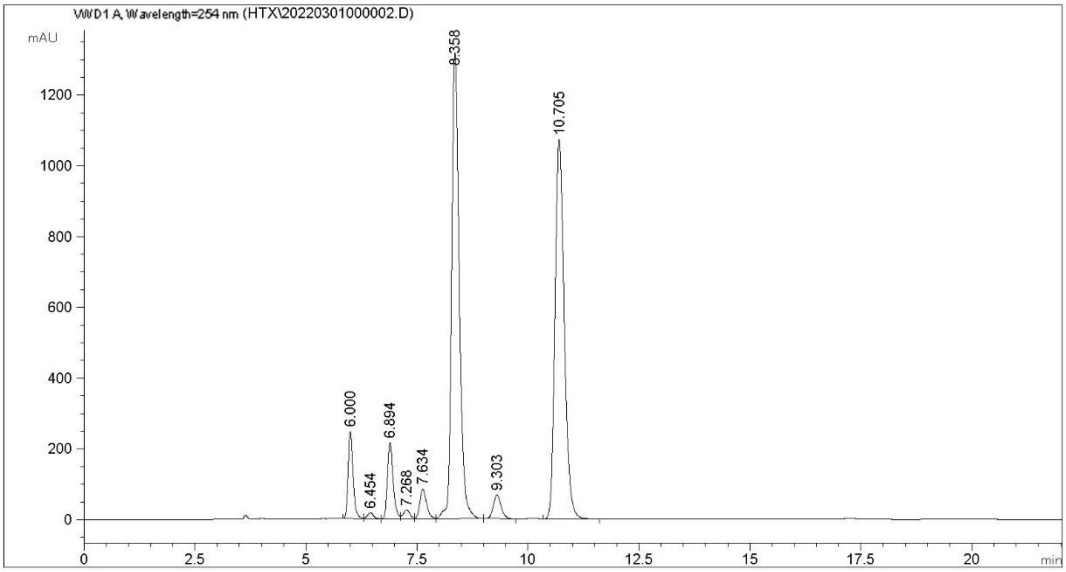


Figure S12. ^{13}C NMR spectra of
(1R',2S')-2-((4-fluorophenyl)amino)-3',4'-dihydro-1'H-spiro[cyclopentane-1,2'-naphthalen]-1'-one (**3d**)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.000	BV	0.1193	1913.08911	247.45752	5.1438
2	6.454	VB	0.1484	160.83778	16.53923	0.4325
3	6.894	BV	0.1363	1921.92236	215.01596	5.1676
4	7.268	VV	0.1601	256.60760	24.48452	0.6900
5	7.634	VV	0.1613	886.40588	83.78007	2.3833
6	8.358	VB	0.1828	1.56875e4	1315.19580	42.1798
7	9.303	BB	0.1861	826.16437	67.69513	2.2213
8	10.705	BV	0.2243	1.55395e4	1072.65894	41.7818
Totals :				3.71920e4	3042.82716	

Figure S13. HPLC spectra of
(1R',2S')-2-((4-fluorophenyl)amino)-3',4'-dihydro-1'H-spiro[cyclopentane-1,2'-naphthalen]-1'-one (**3d**)

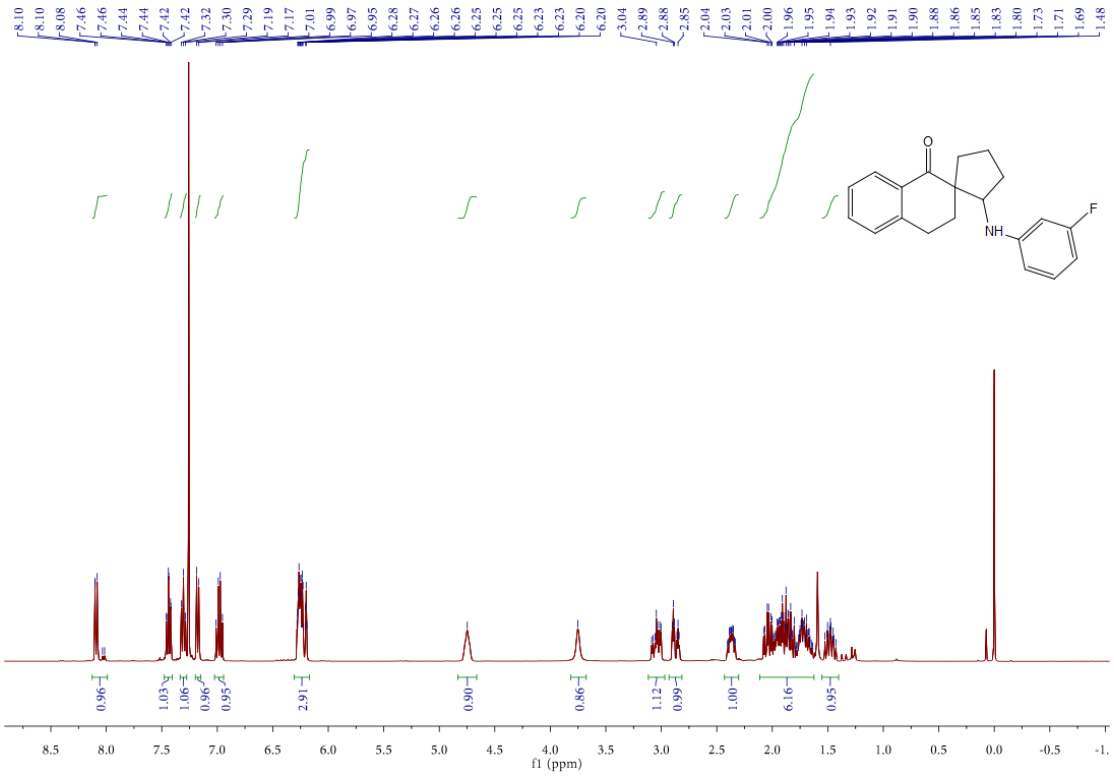


Figure S14. ^{1}H NMR spectra of
(1R',2S')-2-((3-fluorophenyl)amino)-3',4'-dihydro-1'H-spiro[cyclopentane-1,2'-naphthalen]-1'-one (**3e**)

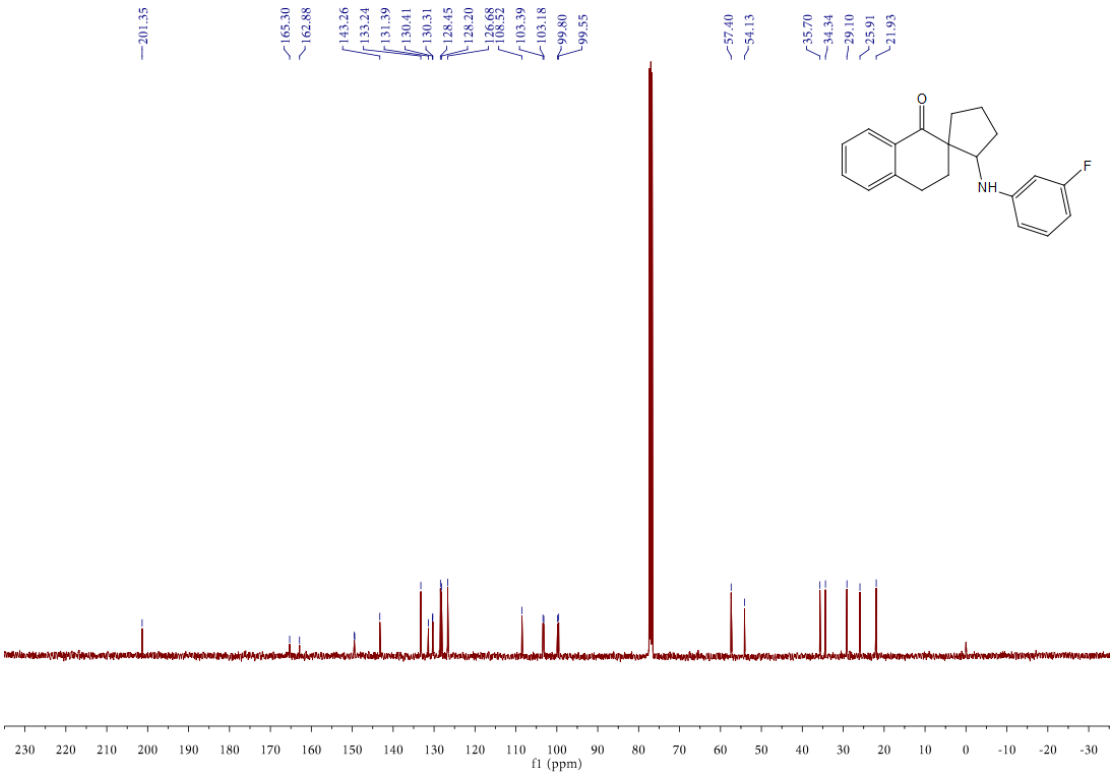
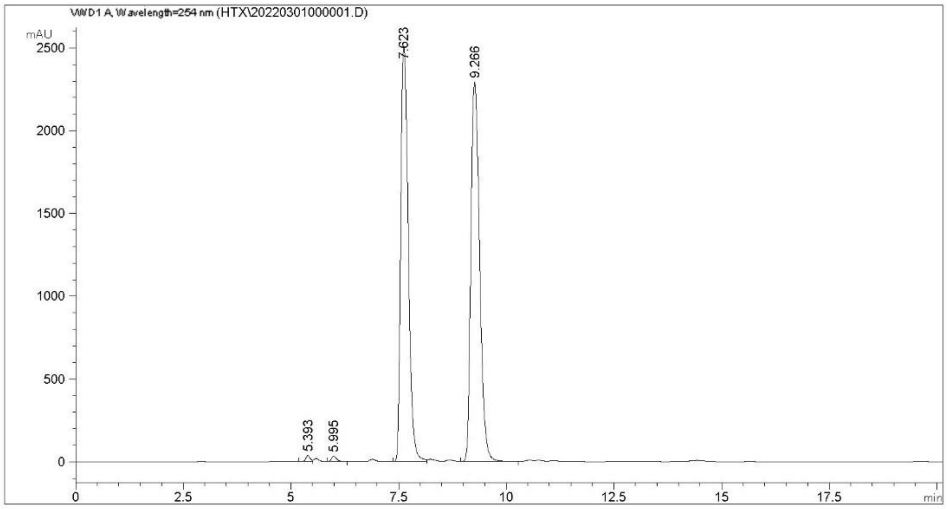


Figure S15. ^{13}C NMR spectra of
(1R',2S')-2-((3-fluorophenyl)amino)-3',4'-dihydro-1'H-spiro[cyclopentane-1,2'-naphthalen]-1'-one (**3e**)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.393	BV	0.1063	256.45306	37.37474	0.4033
2	5.995	BV	0.1231	272.67950	33.83696	0.4288
3	7.623	BV	0.1955	3.06651e4	2499.72998	48.2253
4	9.266	BB	0.2231	3.23929e4	2293.02222	50.9426
Totals :				6.35871e4	4863.96390	

Figure S16. HPLC spectra of
(1R',2S')-2-((3-fluorophenyl)amino)-3',4'-dihydro-1'H-spiro[cyclopentane-1,2'-naphthalen]-1'-one (**3e**)

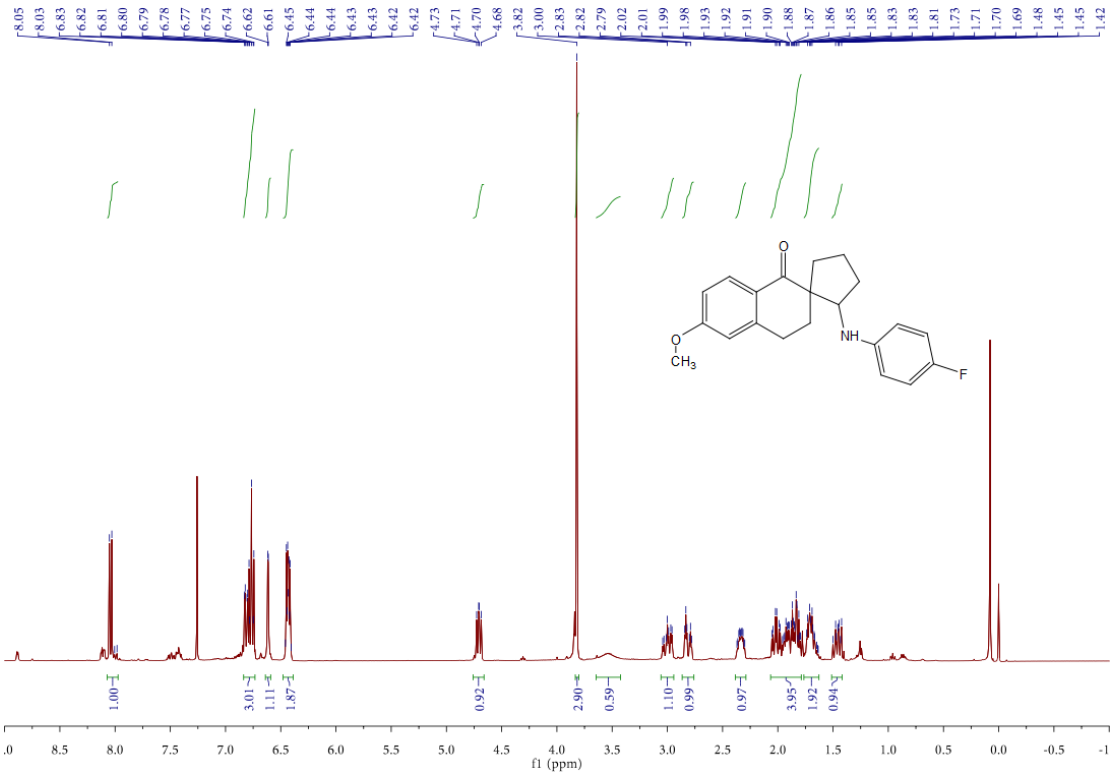


Figure S17. ^{1}H NMR spectra of
(1R',2S')-2-((4-fluorophenyl)amino)-6'-methoxy-3',4'-dihydro-1'H-spiro[cyclopentane-1,2'-naphthalen]-1'-one (**3f**)

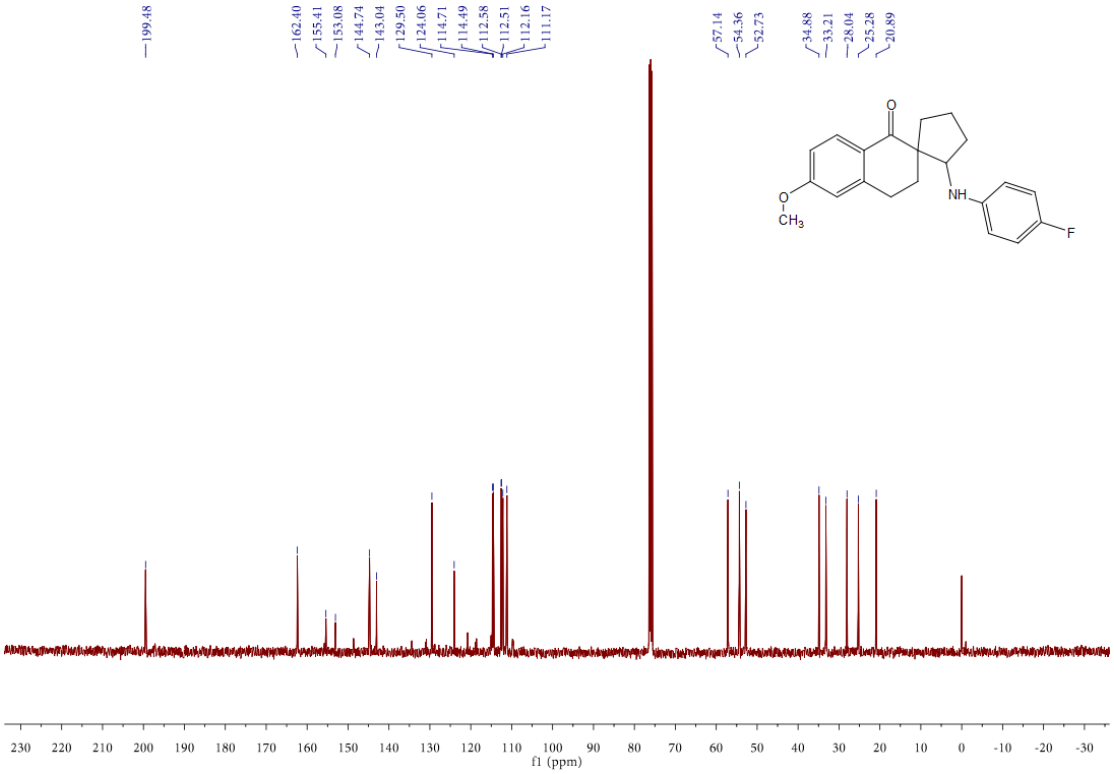
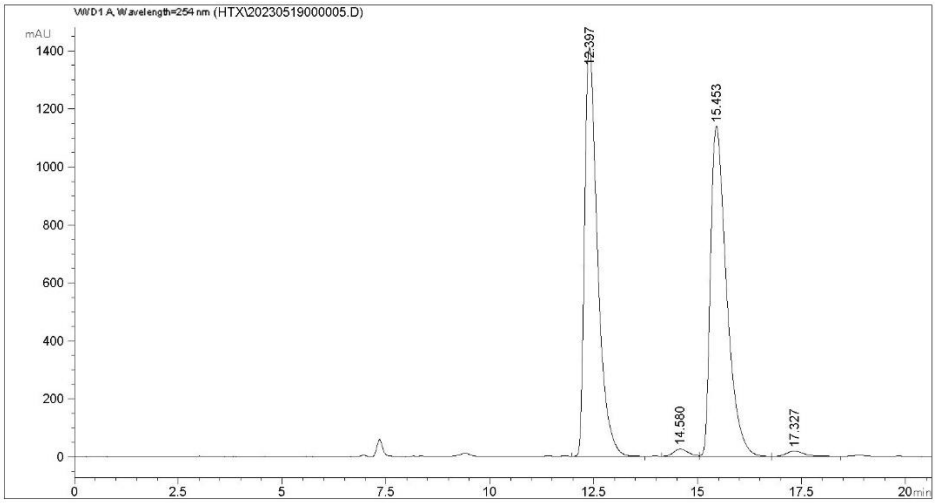


Figure S18. ^{13}C NMR spectra of
(1R',2S')-2-((4-fluorophenyl)amino)-6'-methoxy-3',4'-dihydro-1'H-spiro[cyclopentane-1,2'-naphthalen]-1'-one (**3f**)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.397	VB	0.3286	3.05520e4	1409.28943	49.0648
2	14.580	VV	0.3656	599.79279	25.15349	0.9632
3	15.453	VB	0.4126	3.05505e4	1136.46362	49.0624
4	17.327	BV	0.4623	566.35742	18.48345	0.9095
Totals :				6.22687e4	2589.39000	

Figure S19. HPLC spectra of
(1R',2S')-2-((4-fluorophenyl)amino)-6'-methoxy-3',4'-dihydro-1'H-spiro[cyclopentane-1,2'-naphthalen]-1'-one (**3f**)

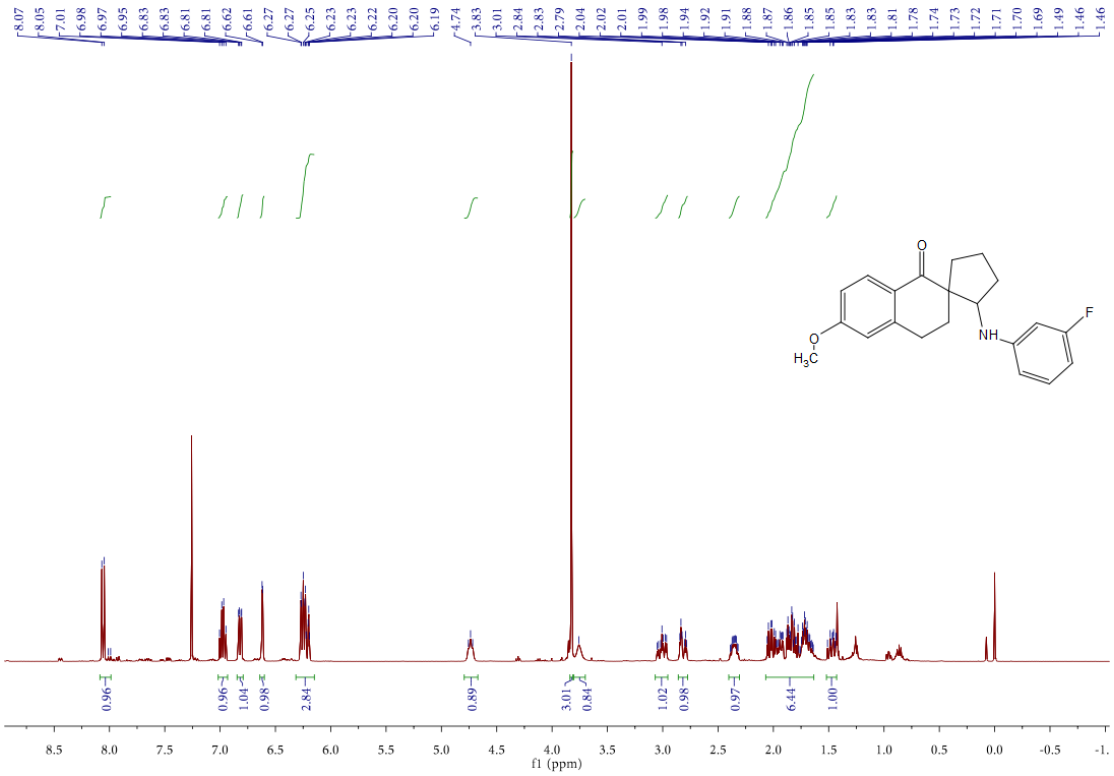


Figure S20. ^{1}H NMR spectra of (1R',2S')-2-((3-fluorophenyl)amino)-6'-methoxy-3',4'-dihydro-1'H-spiro[cyclopentane-1,2'-naphthalen]-1'-one (**3g**)

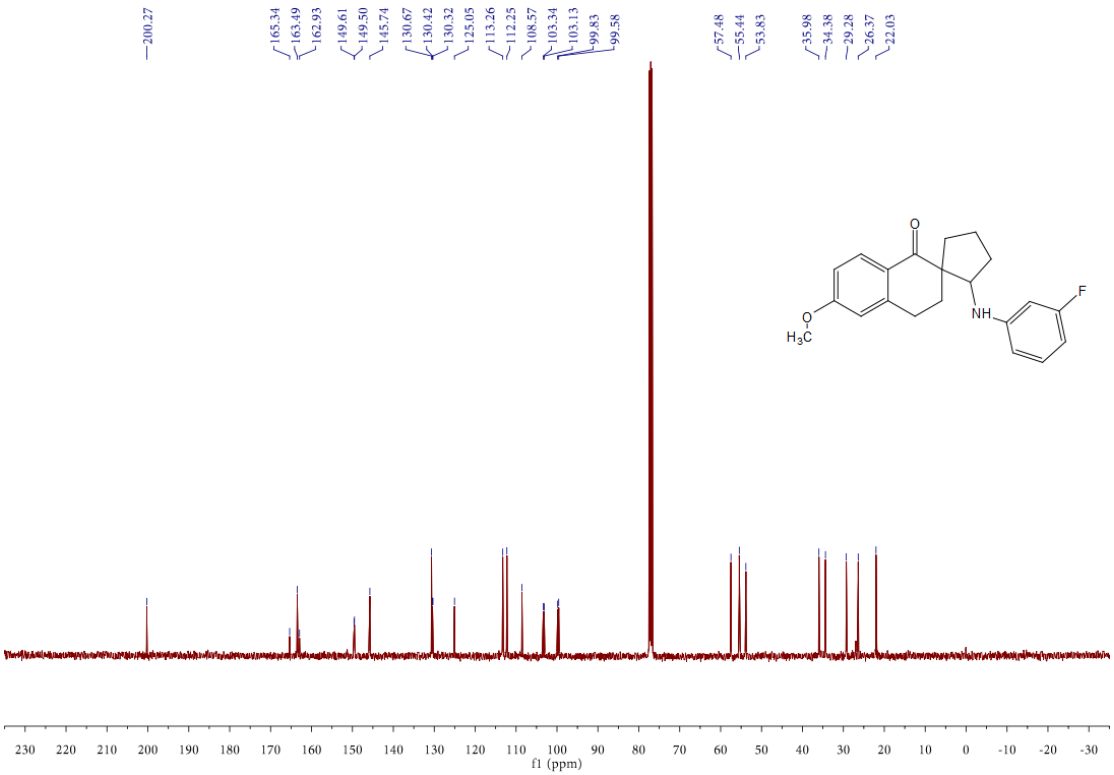
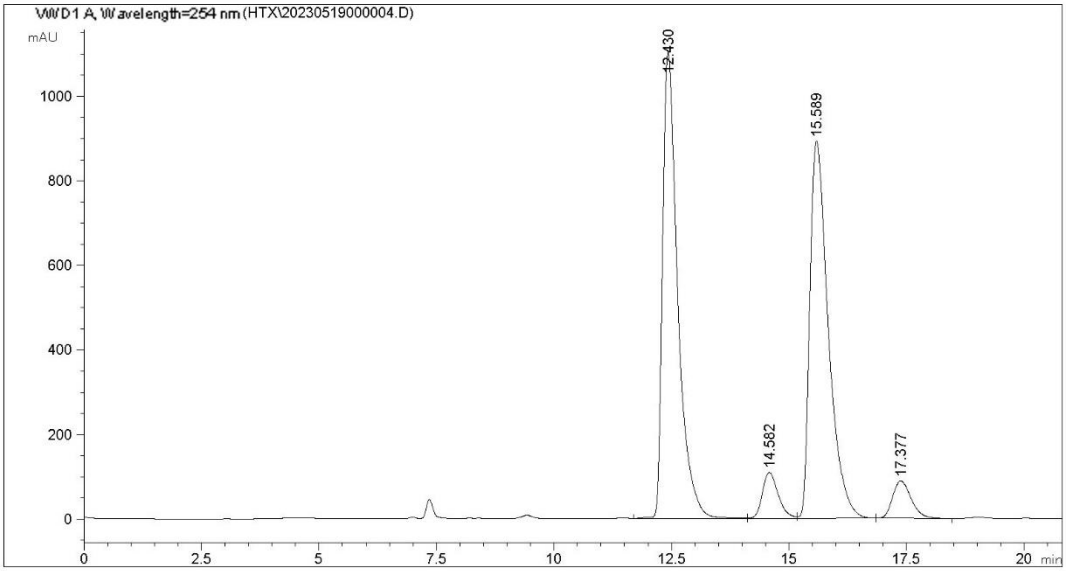


Figure S21. ^{13}C NMR spectra of
(1R',2S')-2-((3-fluorophenyl)amino)-6'-methoxy-3',4'-dihydro-1'H-spiro[cyclopentane-1,2'-naphthalen]-1'-one (**3g**)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.430	VV	0.3400	2.47078e4	1102.76270	45.6950
2	14.582	VV	0.3628	2532.32300	108.41159	4.6833
3	15.589	VB	0.4181	2.44008e4	892.05707	45.1273
4	17.377	BB	0.4242	2430.11816	88.77545	4.4943
Totals :				5.40710e4	2192.00681	

Figure S22. HPLC spectra of
(1R',2S')-2-((3-fluorophenyl)amino)-6'-methoxy-3',4'-dihydro-1'H-spiro[cyclopentane-1,2'-naphthalen]-1'-one (**3g**)

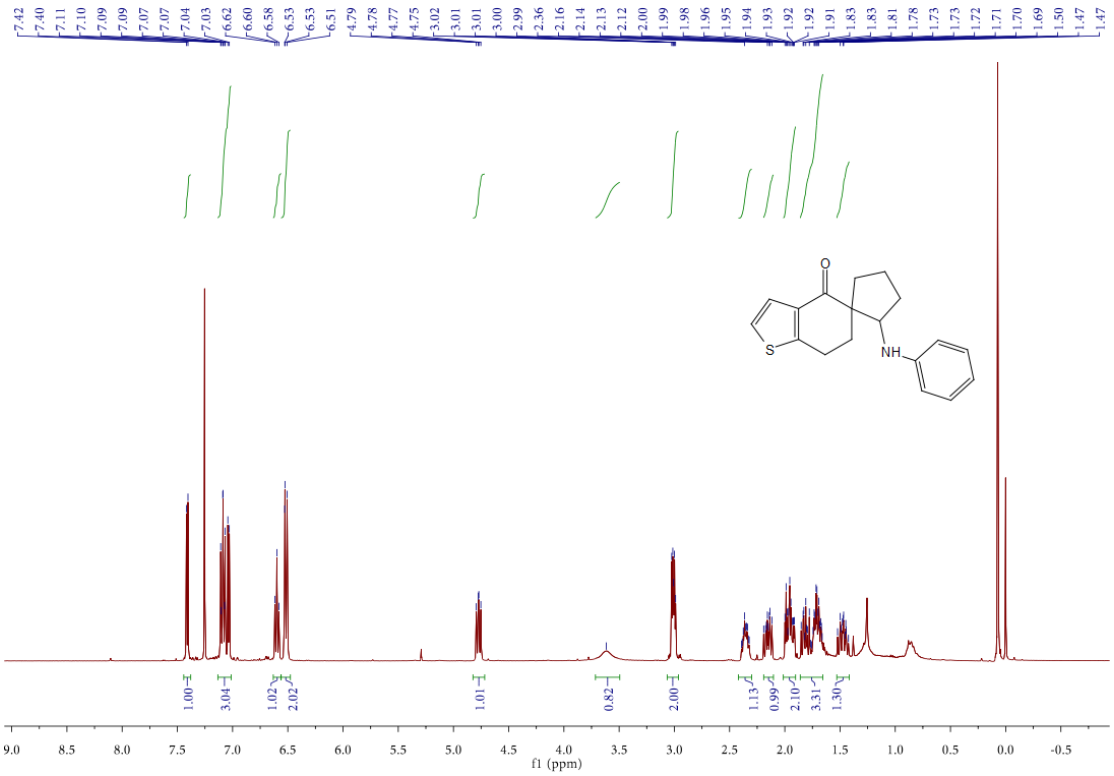


Figure S23. [1]H NMR spectra of
(2'S',5R')-2'-(phenylamino)-6,7-dihydro-4H-spiro[benzo[b]thiophene-5,1'-cyclopentan]-4-one (**3h**)

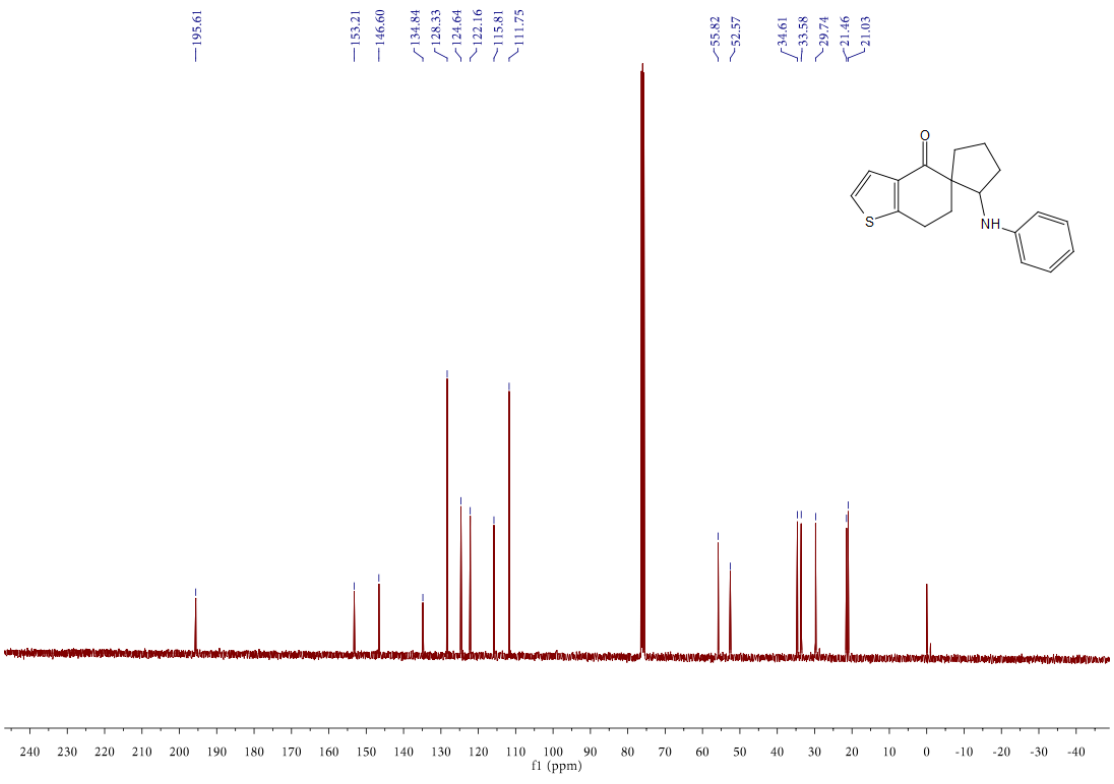
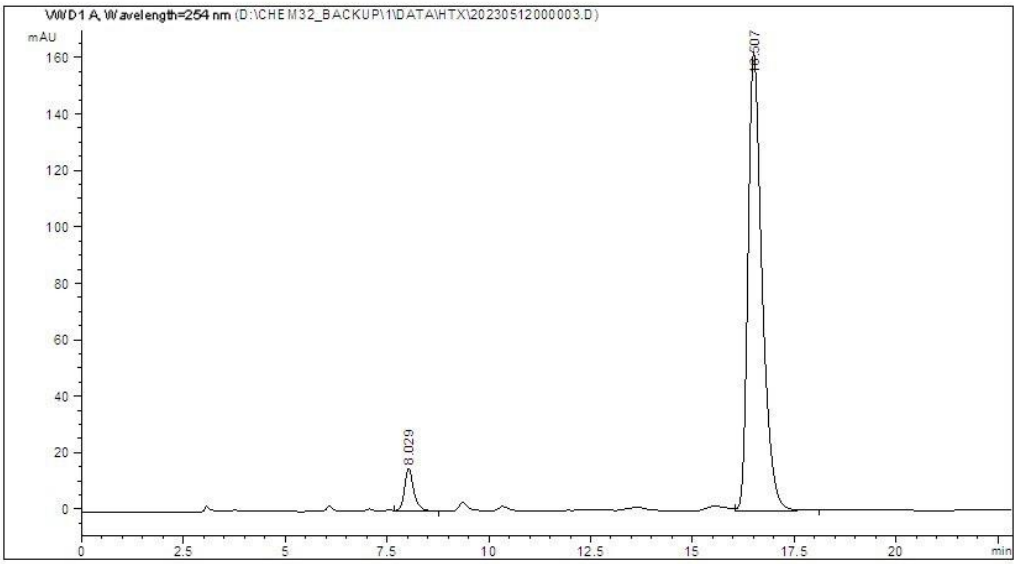


Figure S24. [13]C NMR spectra of
(2'S',5R')-2'-(phenylamino)-6,7-dihydro-4H-spiro[benzo[b]thiophene-5,1'-cyclopentan]-4-one (**3h**)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.029	VB	0.2440	244.40628	15.11399	5.9106
2	16.507	VB	0.3614	3890.64233	162.16293	94.0894
Totals :				4135.04861	177.27692	

Figure S25. HPLC spectra of
(2'S',5R')-2'-(phenylamino)-6,7-dihydro-4H-spiro[benzo[b]thiophene-5,1'-cyclopentan]-4-one (**3h**)

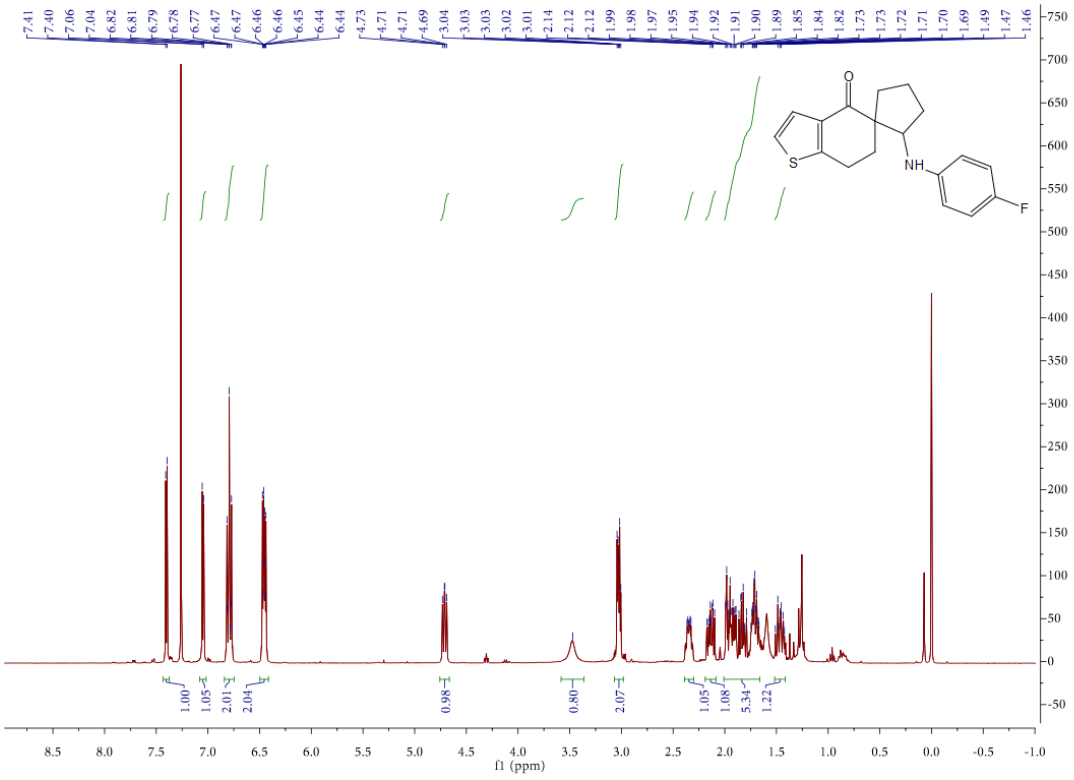


Figure S26. ^{1}H NMR spectra of
(2'S',5R')-2'-((4-fluorophenyl)amino)-6,7-dihydro-4H-spiro[benzo[b]thiophene-5,1'-cyclopentan]-4-one (**3i**)

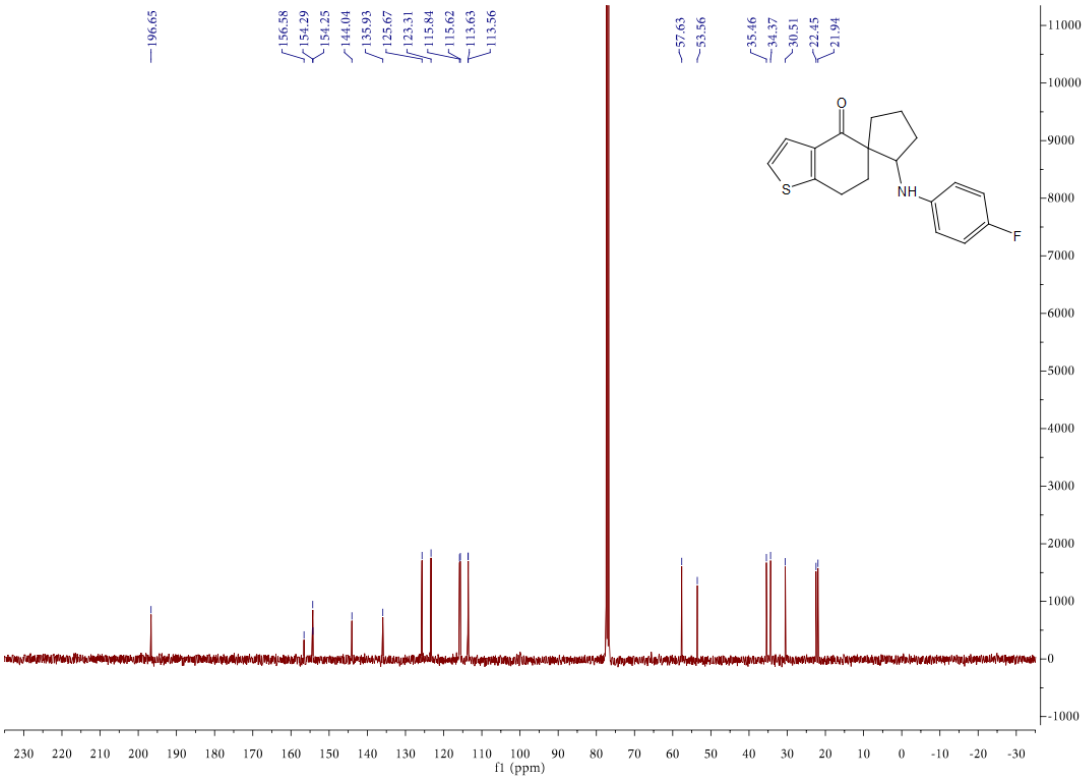
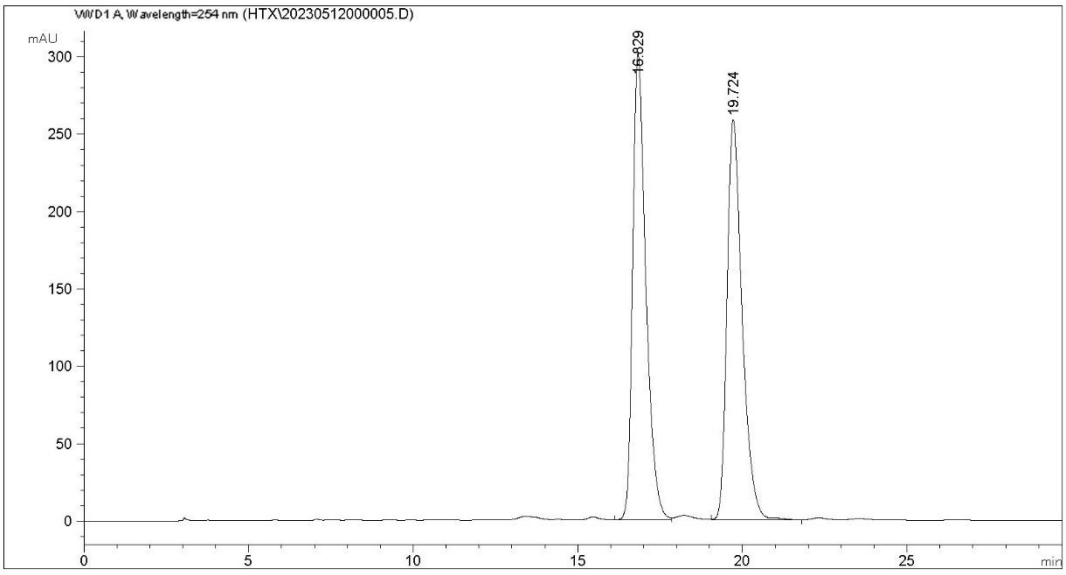


Figure S27. ^{13}C NMR spectra of

(2'S',5R')-2'-((4-fluorophenyl)amino)-6,7-dihydro-4H-spiro[benzo[b]thiophene-5,1'-cyclopentan]-4-one (**3i**)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.829	BV	0.4189	8412.17871	301.31732	50.3562
2	19.724	VB	0.4849	8293.18066	258.51340	49.6438
Totals :				1.67054e4	559.83072	

Figure S28. HPLC spectra of

(2'S',5R')-2'-((4-fluorophenyl)amino)-6,7-dihydro-4H-spiro[benzo[b]thiophene-5,1'-cyclopentan]-4-one (**3i**)

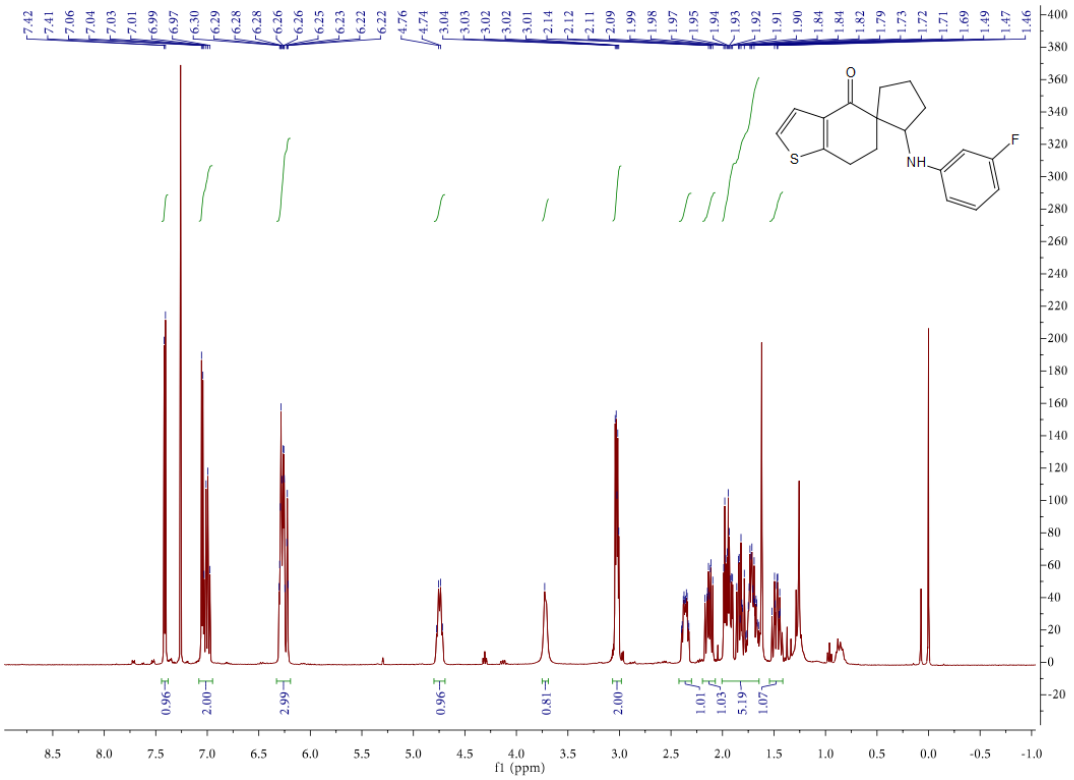


Figure S29. [1]H NMR spectra of
(2'S',5R')-2'-((3-fluorophenyl)amino)-6,7-dihydro-4H-spiro[benzo[b]thiophene-5,1'-cyclopentan]-4-one (**3j**)

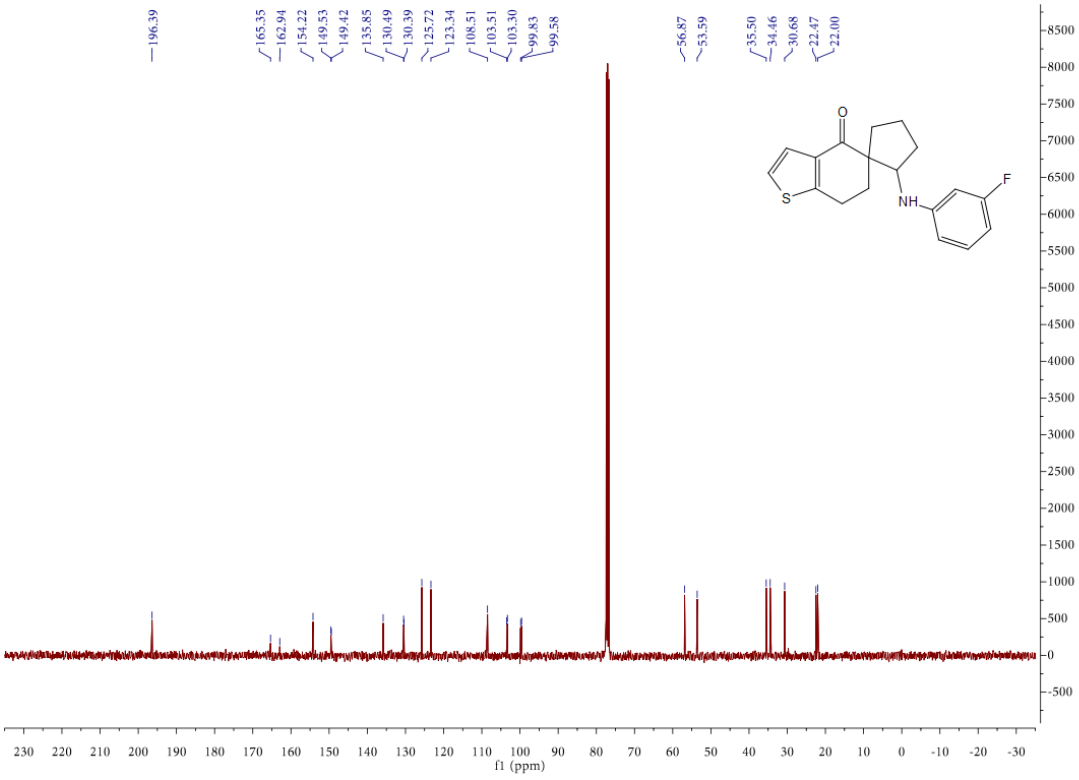
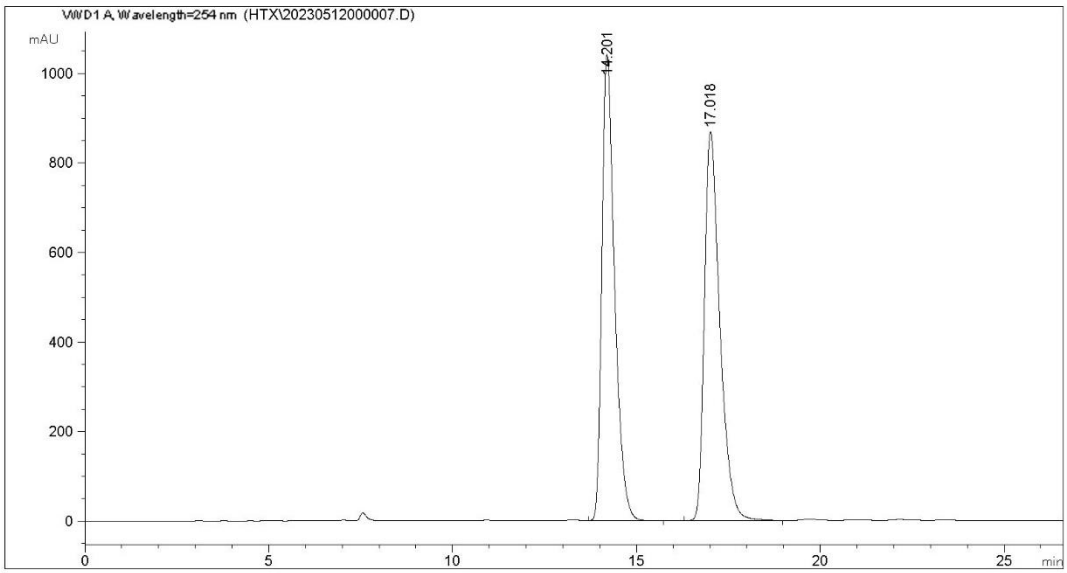


Figure S30. [13]C NMR spectra of
(2'S',5R')-2'-((3-fluorophenyl)amino)-6,7-dihydro-4H-spiro[benzo[b]thiophene-5,1'-cyclopentan]-4-one (**3j**)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.201	VV	0.3615	2.49899e4	1041.51733	49.5528
2	17.018	BV	0.4435	2.54410e4	868.83289	50.4472
Totals :				5.04310e4	1910.35022	

Figure S31. HPLC spectra of (2'S',5R')-2'-((3-fluorophenyl)amino)-6,7-dihydro-4H-spiro[benzo[b]thiophene-5,1'-cyclopentan]-4-one (**3j**)

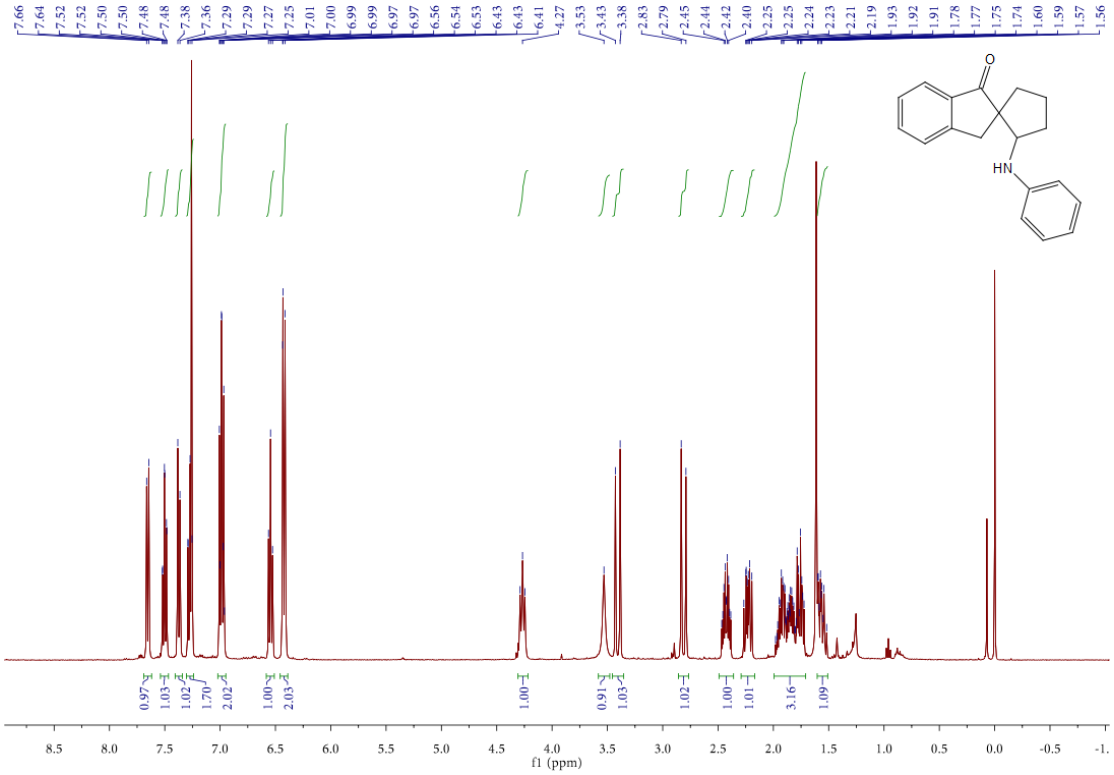


Figure S32. ^{1}H NMR spectra of (1R',2S')-2-(phenylamino)spiro[cyclopentane-1,2'-inden]-1'(3'H)-one (**3k**)

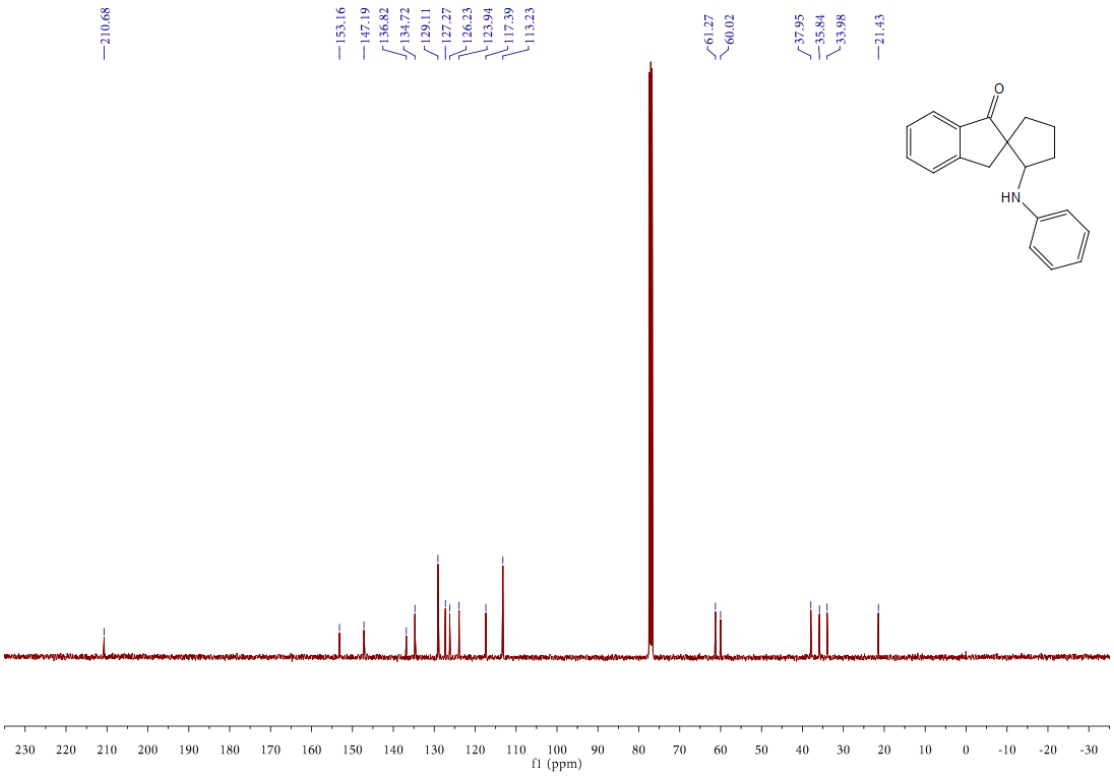
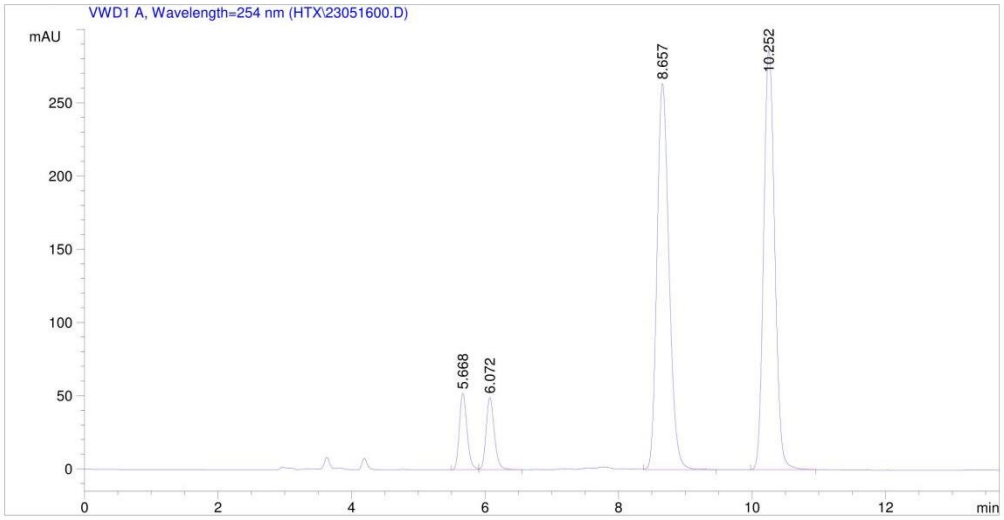


Figure S33. ^{13}C NMR spectra of (1R',2S')-2-(phenylamino)spiro[cyclopentane-1,2'-inden]-1'(3'H)-one (**3k**)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.668	BV	0.1236	416.70038	52.25051	5.6006
2	6.072	VB	0.1306	423.31079	49.36854	5.6894
3	8.657	VB	0.1942	3303.32471	263.71024	44.3975
4	10.252	BB	0.1792	3297.00317	286.90533	44.3125
Totals :				7440.33905	652.23462	

Figure S34. HPLC spectra of (1R',2S')-2-(phenylamino)spiro[cyclopentane-1,2'-inden]-1'(3'H)-one (**3k**)

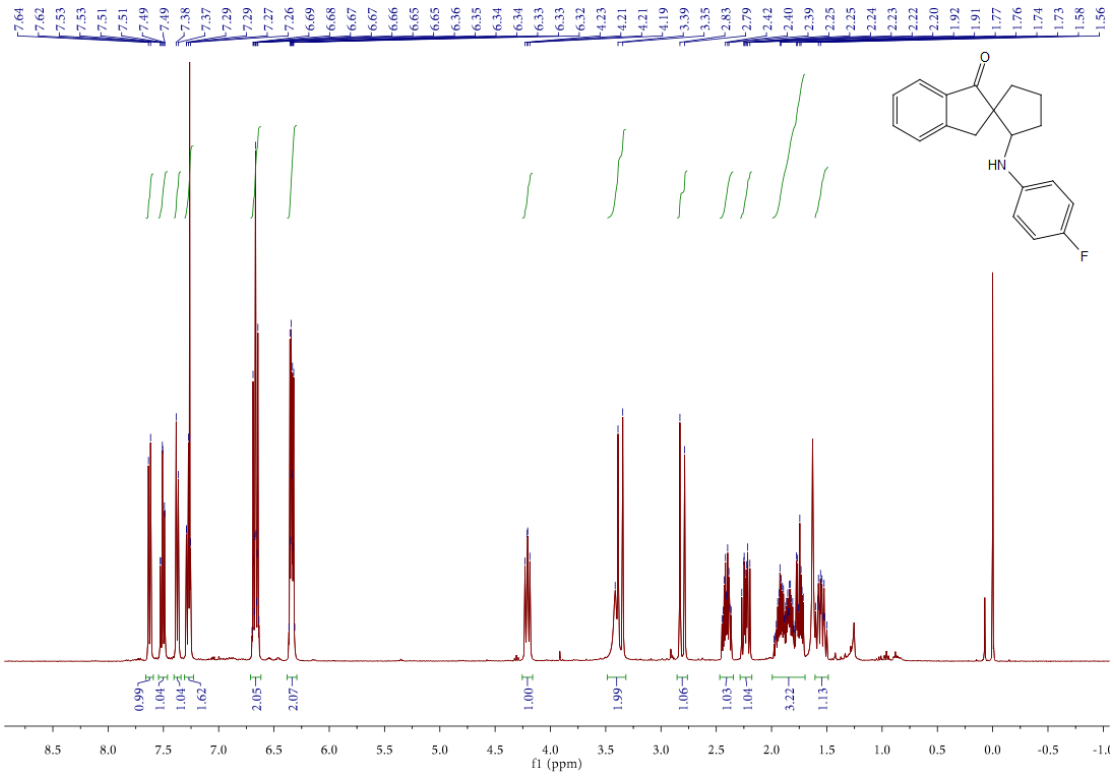


Figure S35. [1]H NMR spectra of (1R',2S')-2-((4-fluorophenyl)amino)spiro[cyclopentane-1,2'-inden]-1'(3'H)-one (**3l**)

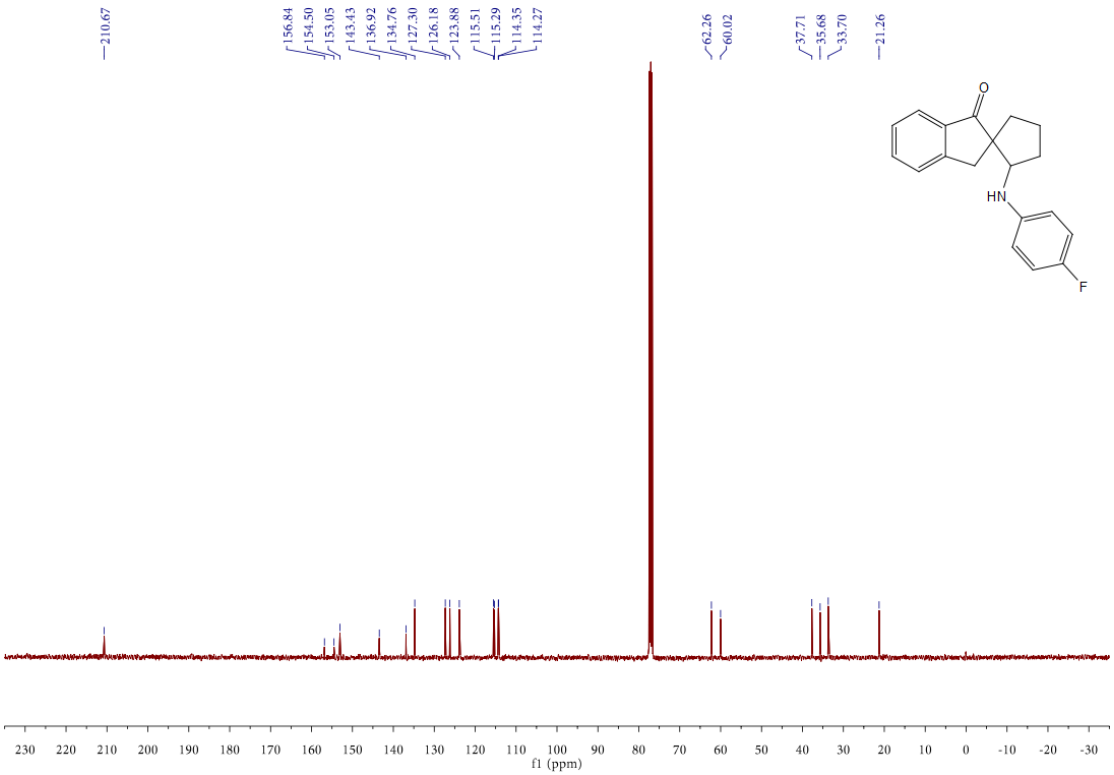
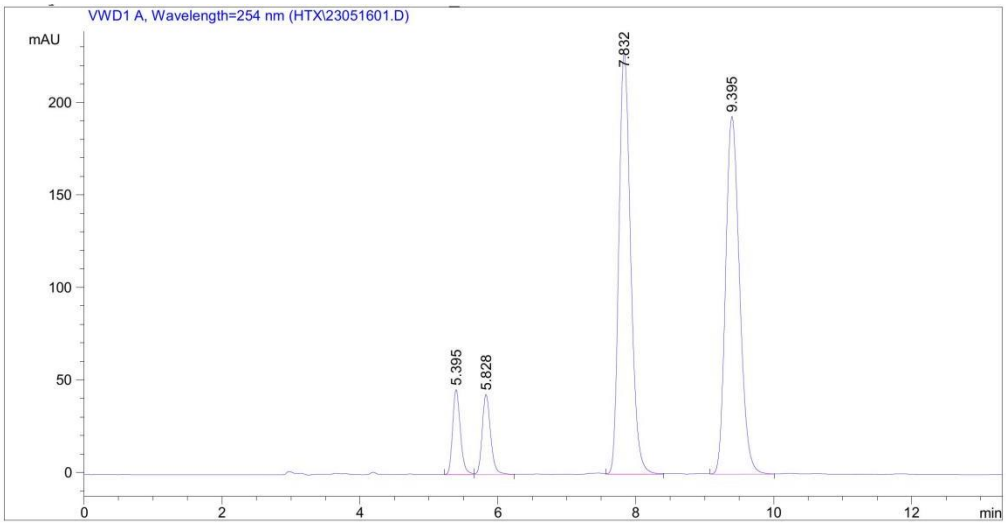


Figure S36. [13]C NMR spectra of (1R',2S')-2-((4-fluorophenyl)amino)spiro[cyclopentane-1,2'-inden]-1'(3'H)-one (**3l**)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.395	BV	0.1203	359.09619	45.94836	5.8298
2	5.828	VB	0.1293	366.10730	43.25925	5.9436
3	7.832	VB	0.1838	2710.00464	227.93382	43.9959
4	9.395	VB	0.2182	2724.47217	193.40393	44.2307
Totals :				6159.68030	510.54537	

Figure S37. HPLC spectra of (1R',2S')-2-((4-fluorophenyl)amino)spiro[cyclopentane-1,2'-inden]-1'(3'H)-one (**3l**)

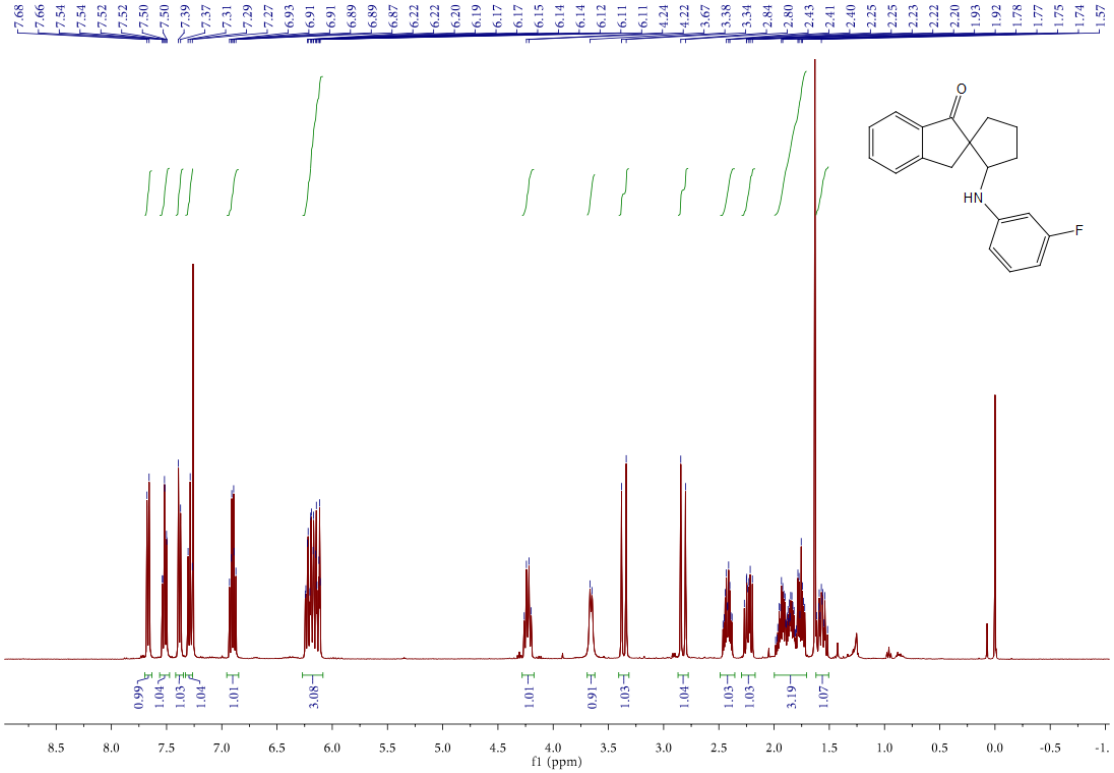


Figure S38. ^{1}H NMR spectra of (1R',2S')-2-((3-fluorophenyl)amino)spiro[cyclopentane-1,2'-inden]-1'(3'H)-one (**3m**)

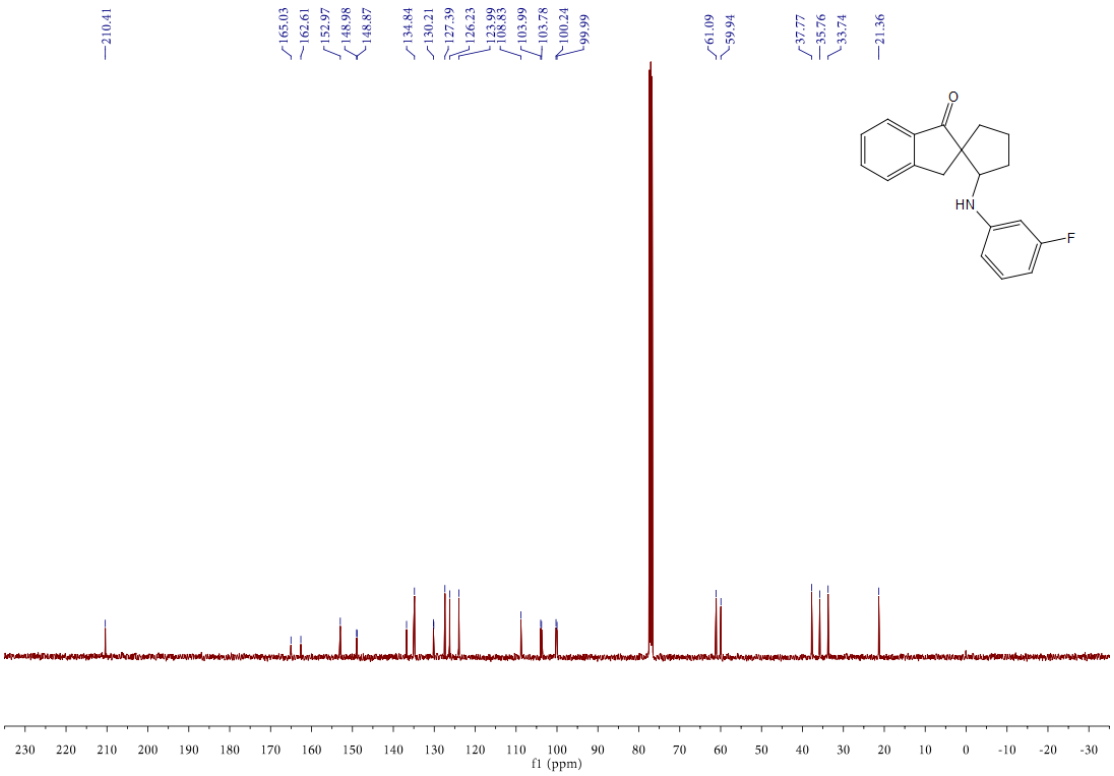
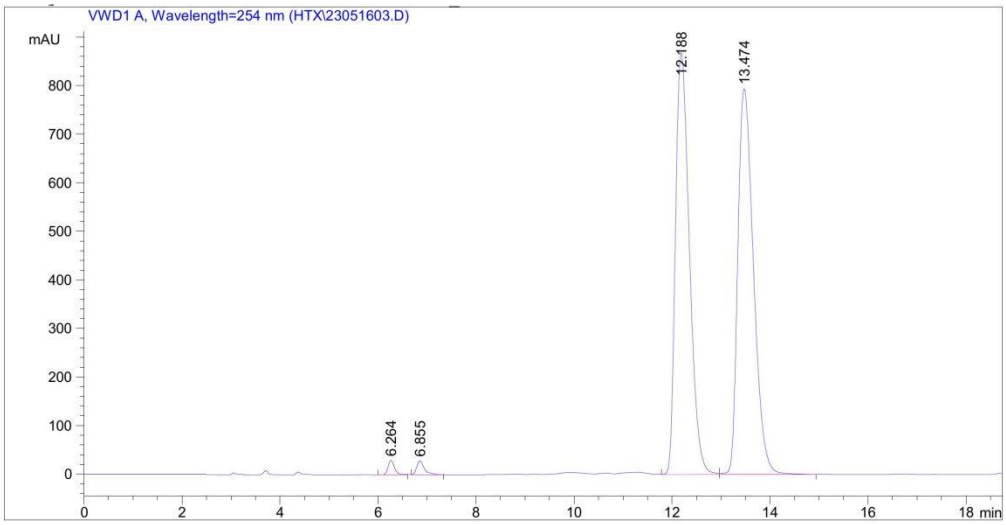


Figure S39. ^{13}C NMR spectra of (1R',2S')-2-((3-fluorophenyl)amino)spiro[cyclopentane-1,2'-inden]-1'(3'H)-one (**3m**)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.264	VB	0.1410	276.66153	30.01492	0.7813
2	6.855	BB	0.1658	315.52875	28.77416	0.8911
3	12.188	VV	0.3107	1.71737e4	868.92273	48.5007
4	13.474	VB	0.3464	1.76433e4	794.51428	49.8269
Totals :				3.54092e4	1722.22610	

Figure S40. HPLC spectra of (1R',2S')-2-((3-fluorophenyl)amino)spiro[cyclopentane-1,2'-inden]-1'(3'H)-one (**3m**)

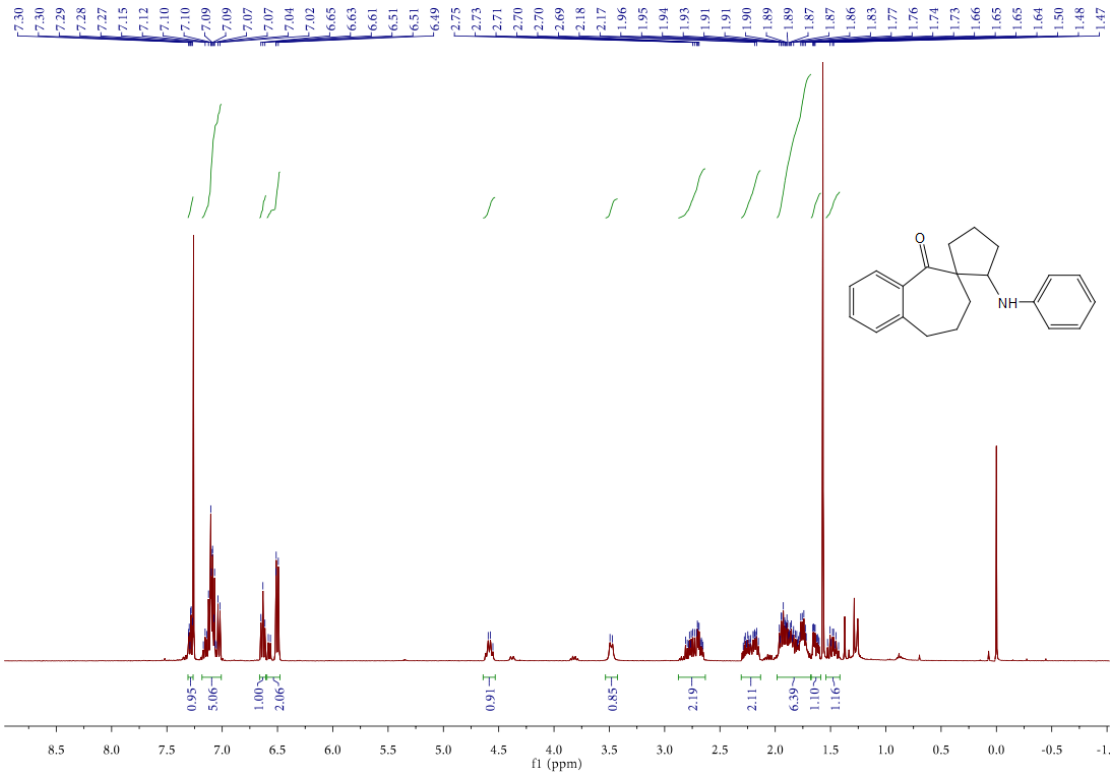


Figure S41. ^{1}H NMR spectra of
(2'S',6S')-2'-(phenylamino)-8,9-dihydrospiro[benzo[7]annulene-6,1'-cyclopentan]-5(7H)-one (**3n**)

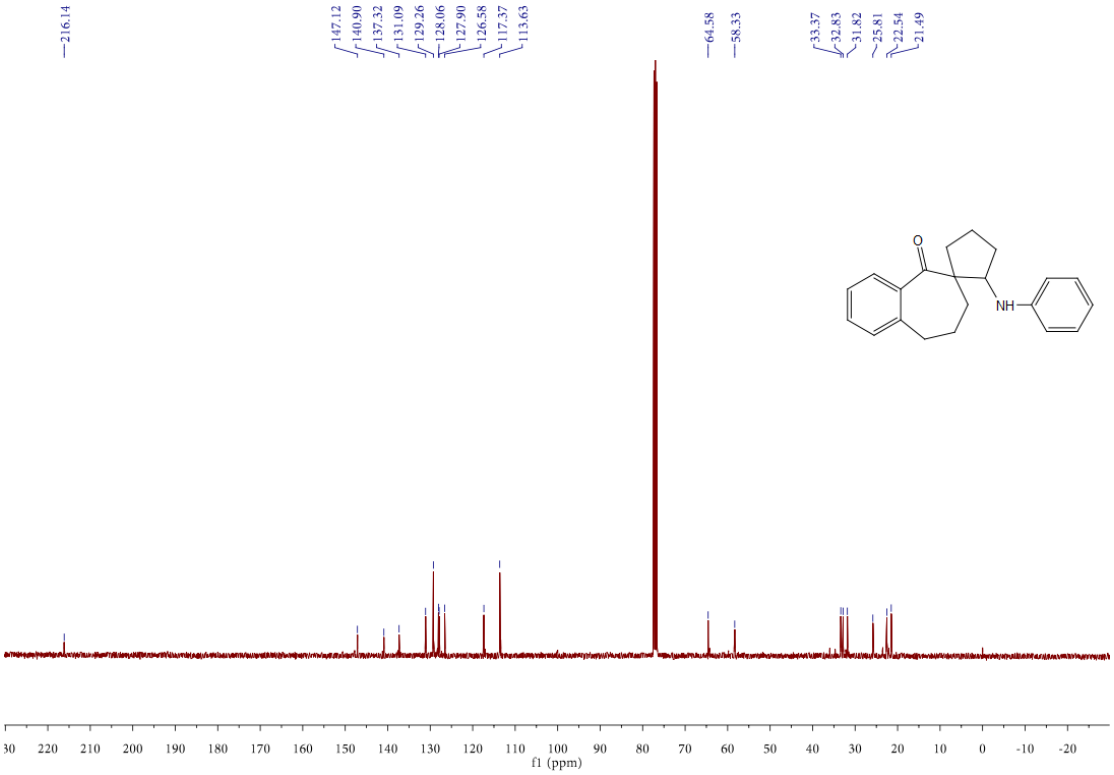
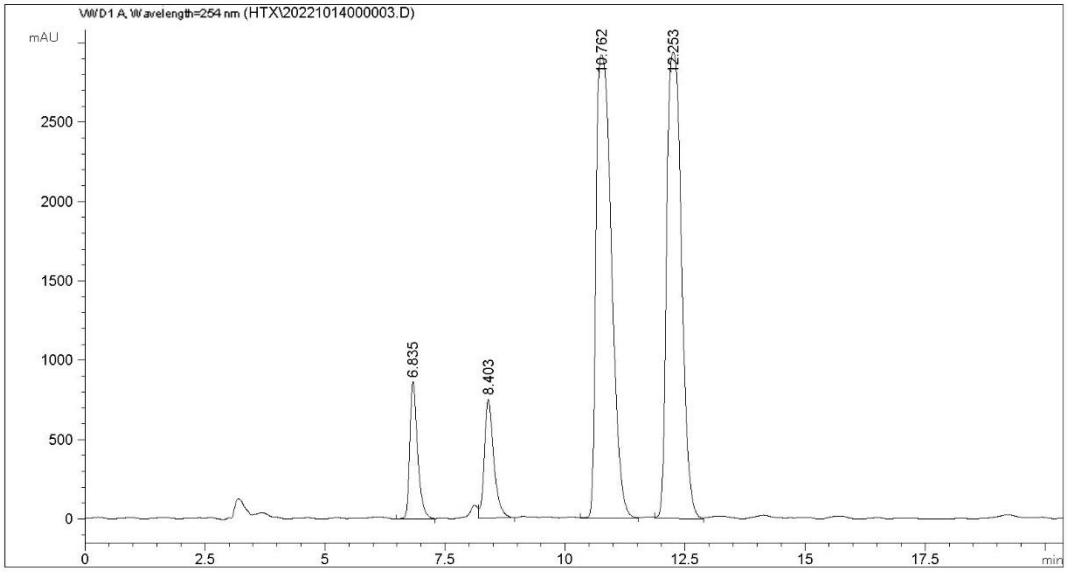


Figure S42. ^{13}C NMR spectra of
(2'S',6S')-2'-(phenylamino)-8,9-dihydrospiro[benzo[7]annulene-6,1'-cyclopentan]-5(7H)-one (**3n**)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.835	BV	0.1724	9740.60840	863.14856	6.5916
2	8.403	VB	0.2056	1.02086e4	748.92487	6.9083
3	10.762	VV	0.3533	6.50752e4	2919.14038	44.0374
4	12.253	VV	0.3395	6.27481e4	2937.05762	42.4626
Totals :				1.47772e5	7468.27142	

Figure S43. HPLC spectra of
(2'S',6S')-2'-(phenylamino)-8,9-dihydrospiro[benzo[7]annulene-6,1'-cyclopentan]-5(7H)-one (**3n**)

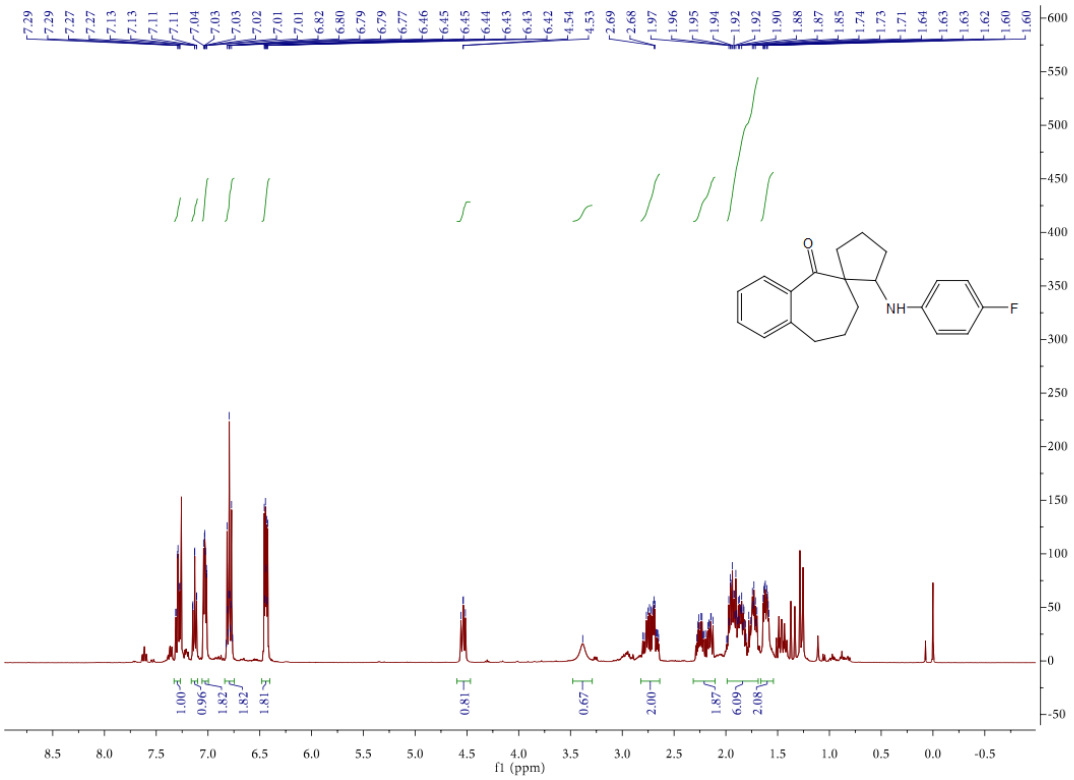


Figure S44. ^{1}H NMR spectra of
(2'S',6S')-2'-((4-fluorophenyl)amino)-8,9-dihydrospiro[benzo[7]annulene-6,1'-cyclopentan]-5(7H)-one (**3oo**)

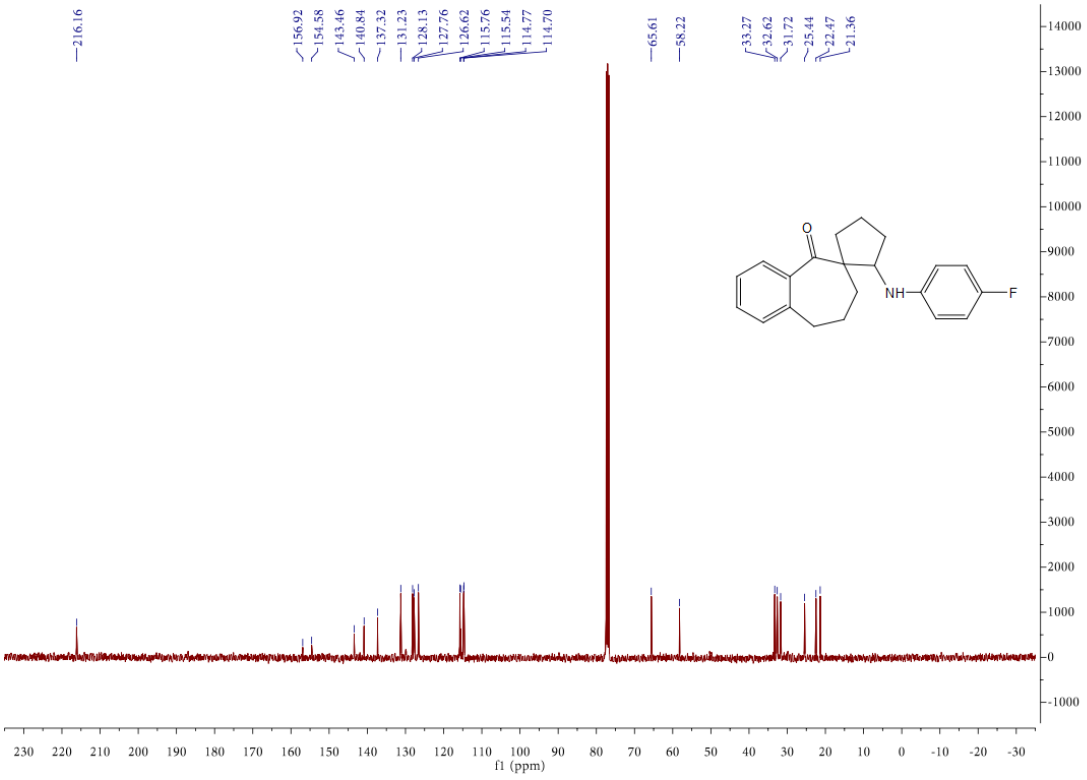
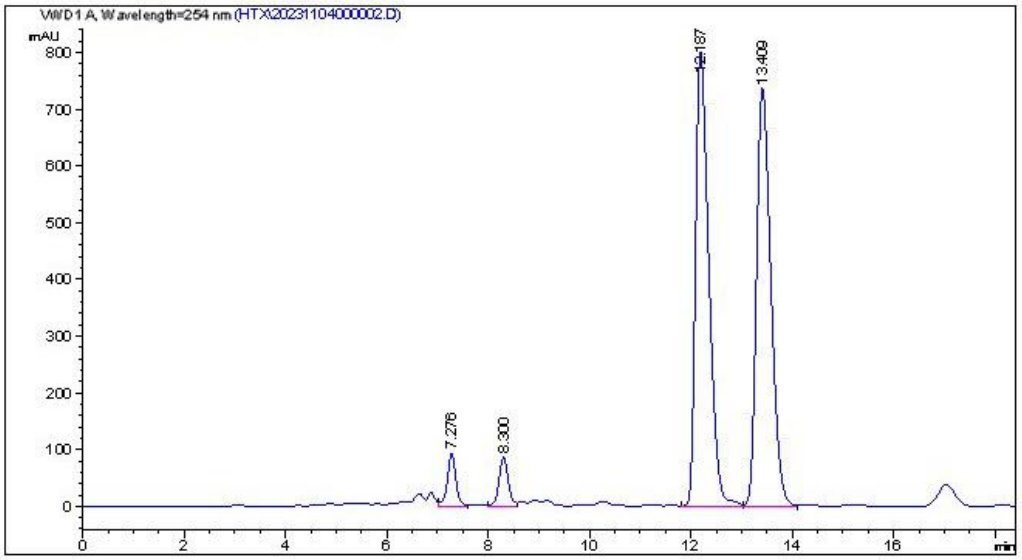


Figure S45. ^{13}C NMR spectra of
(2'S',6S')-2'-((4-fluorophenyl)amino)-8,9-dihydrospiro[benzo[7]annulene-6,1'-cyclopentan]-5(7H)-one (**3o**)



Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	7.276	VV	0.1799	1133.32214		95.03539	3.6086
2	8.300	VV	0.2010	1139.74768		86.95541	3.6291
3	12.187	VV	0.2793	1.45888e4		801.61487	46.4523
4	13.409	VV	0.3028	1.45441e4		737.75928	46.3100
Totals :				3.14059e4		1721.36494	

Figure S46. HPLC spectra of
(2'S',6S')-2'-((4-fluorophenyl)amino)-8,9-dihydrospiro[benzo[7]annulene-6,1'-cyclopentan]-5(7H)-one (**3o**)

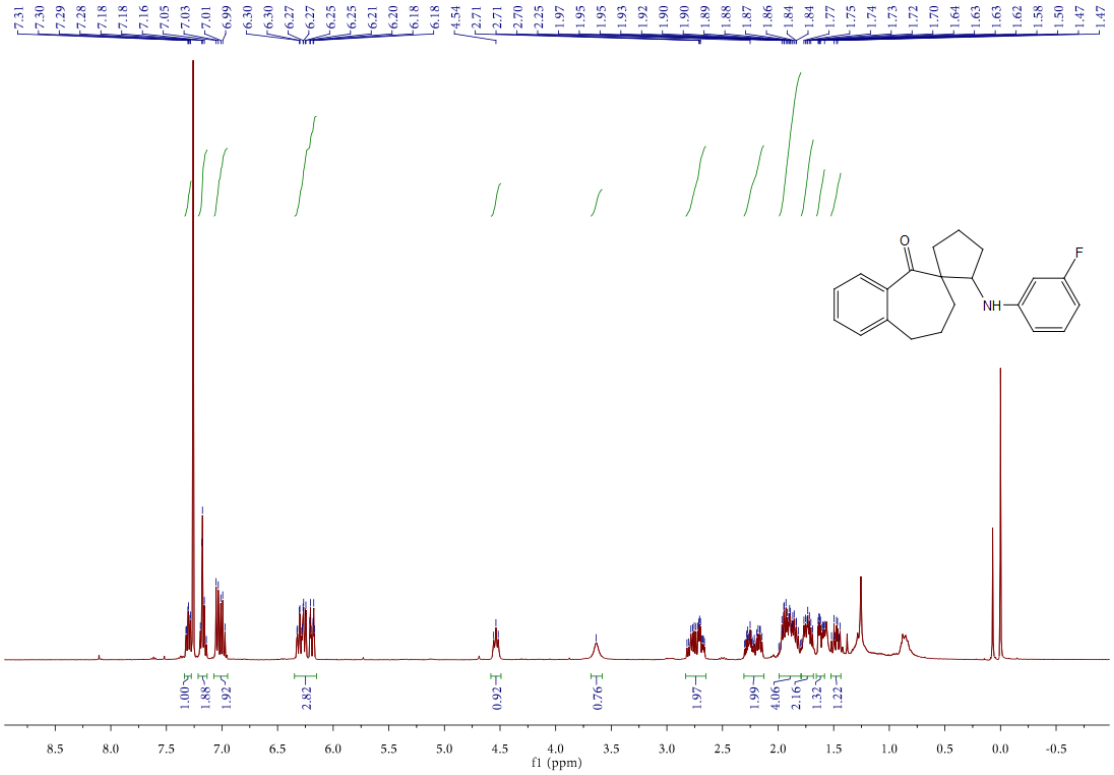


Figure S47. ^{1}H NMR spectra of
(2'S',6S')-2'-((3-fluorophenyl)amino)-8,9-dihydrospiro[benzo[7]annulene-6,1'-cyclopentan]-5(7H)-one (**3p**)

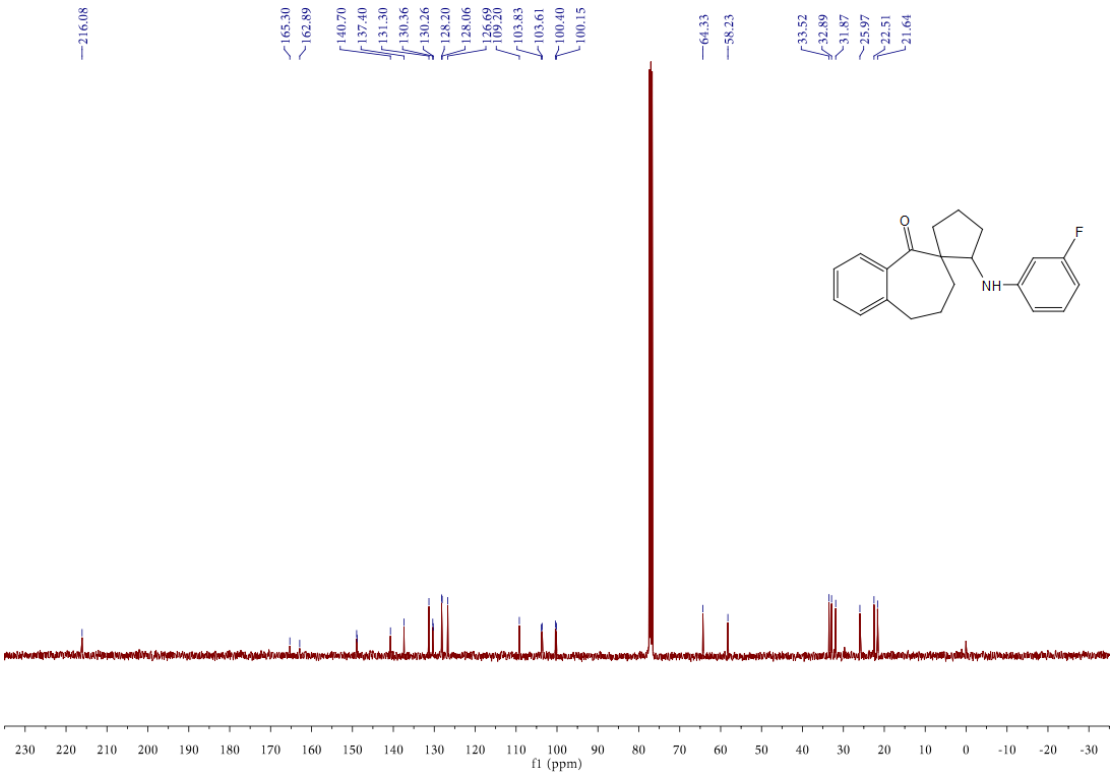
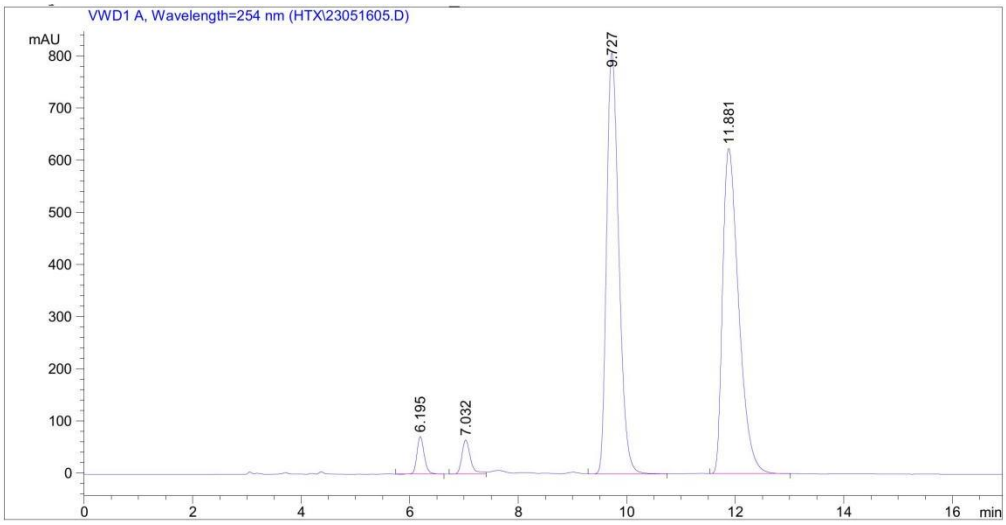


Figure S48. ^{13}C NMR spectra of
(2'S',6S')-2'-((3-fluorophenyl)amino)-8,9-dihydrospiro[benzo[7]annulene-6,1'-cyclopentan]-5(7H)-one (**3p**)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.195	VB	0.1454	685.63977	72.39680	2.5480
2	7.032	BV	0.1696	730.50610	65.43410	2.7148
3	9.727	VB	0.2439	1.26511e4	807.58887	47.0153
4	11.881	VB	0.3159	1.28413e4	623.80548	47.7219
Totals :				2.69086e4	1569.22525	

Figure S49. HPLC spectra of
(2'S',6S')-2'-((3-fluorophenyl)amino)-8,9-dihydrospiro[benzo[7]annulene-6,1'-cyclopentan]-5(7H)-one (**3p**)

3. X-Ray structure and crystal data of 3a

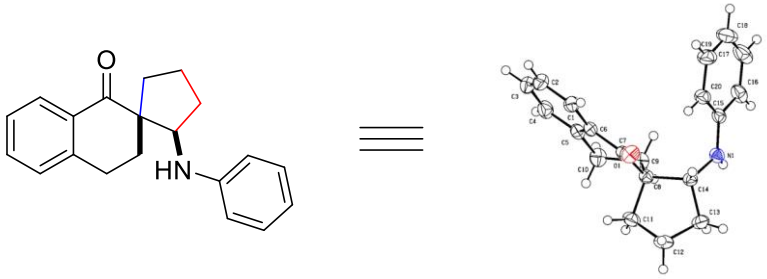


Table S2 Crystal data and structure refinement.	
Empirical formula	$C_{20}H_{21}NO$
Formula weight	291.38
Temperature/K	170.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.1695(2)
b/Å	19.2509(5)
c/Å	10.5517(2)
α/°	90
β/°	103.1850(10)
γ/°	90
Volume/Å^3	1615.72(7)
Z	4
ρ_{calc}g/cm^3	1.198
μ/mm^{-1}	0.073
F(000)	624.0
Crystal size/mm^3	0.32 × 0.1 × 0.07
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.494 to 54.256
Index ranges	-10 ≤ h ≤ 10, -24 ≤ k ≤ 24, -13 ≤ l ≤ 13
Reflections collected	24952
Independent reflections	3577 [R_{int} = 0.0361, R_{sigma} = 0.0206]
Data/restraints/parameters	3577/2/202
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0396, wR_2 = 0.0981
Final R indexes [all data]	R_1 = 0.0485, wR_2 = 0.1052
Largest diff. peak/hole / e Å^{-3}	0.28/-0.23