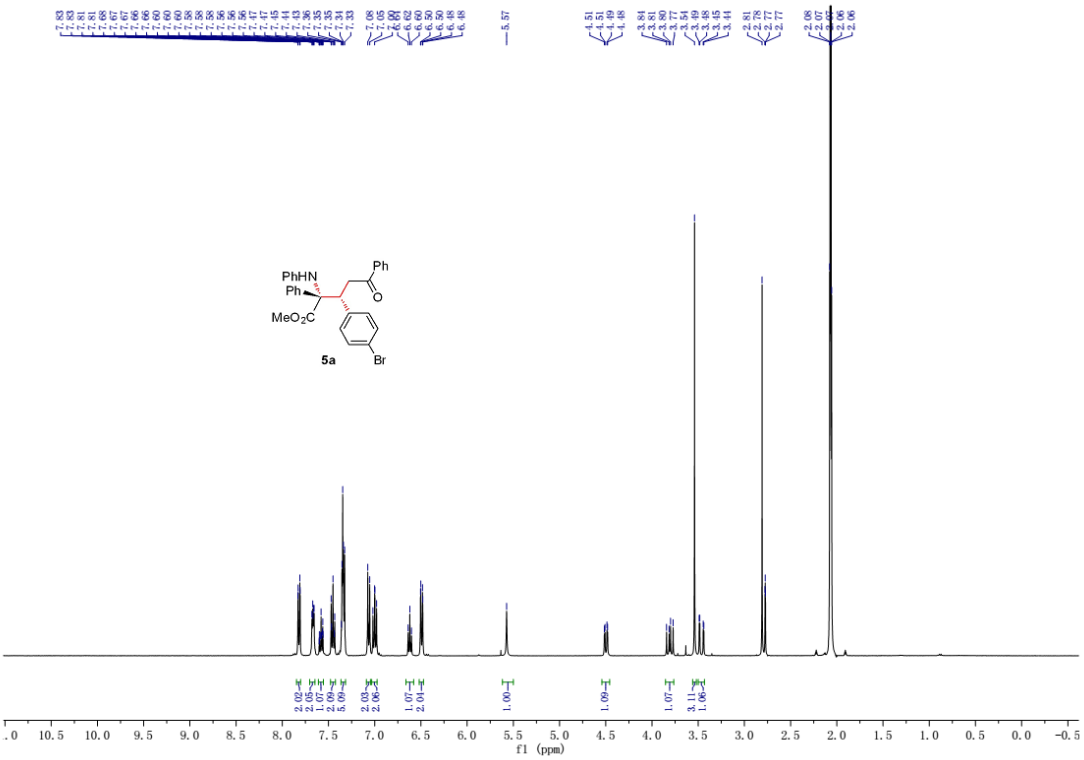
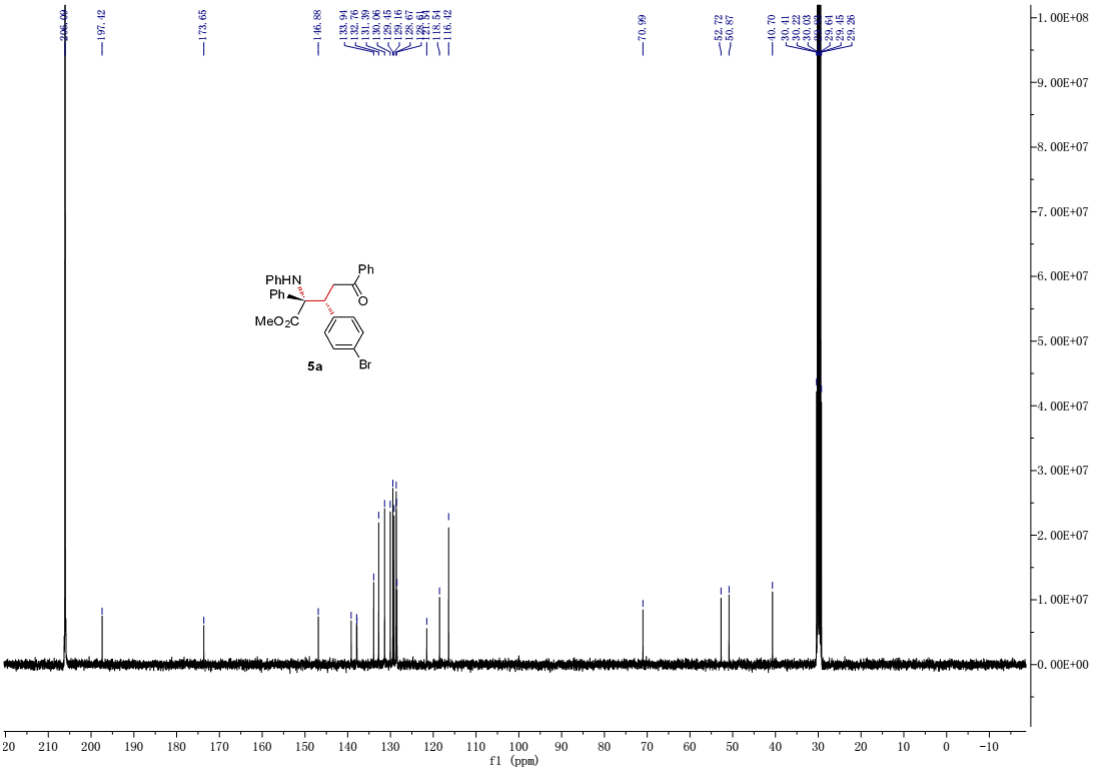
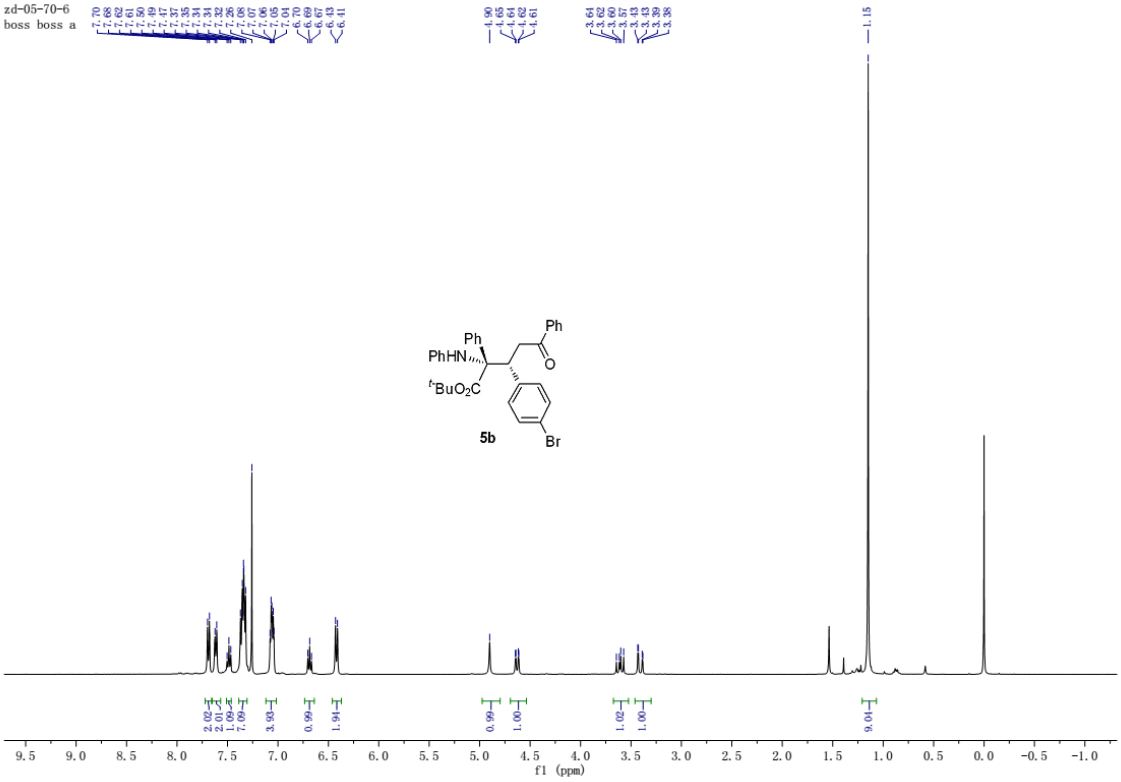


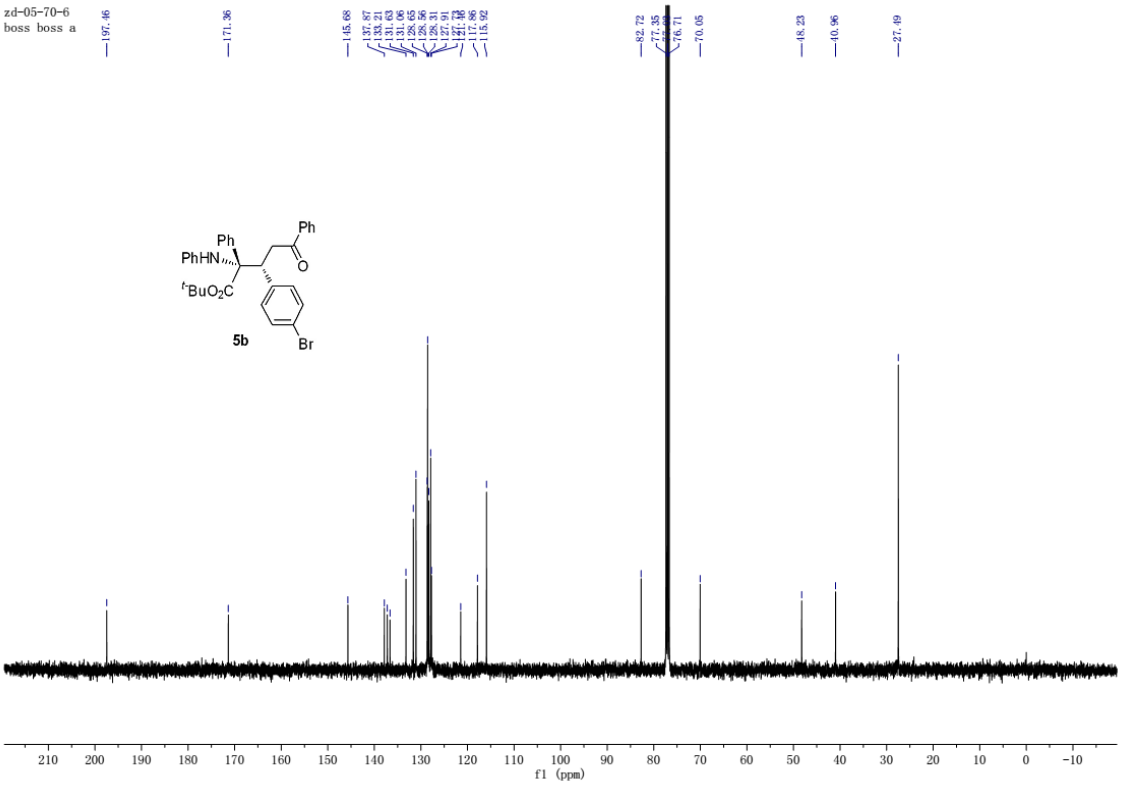
Supplementary Figure 1. ^{1}H NMR (400MHz, Acetone-d_6) spectrum for 5a



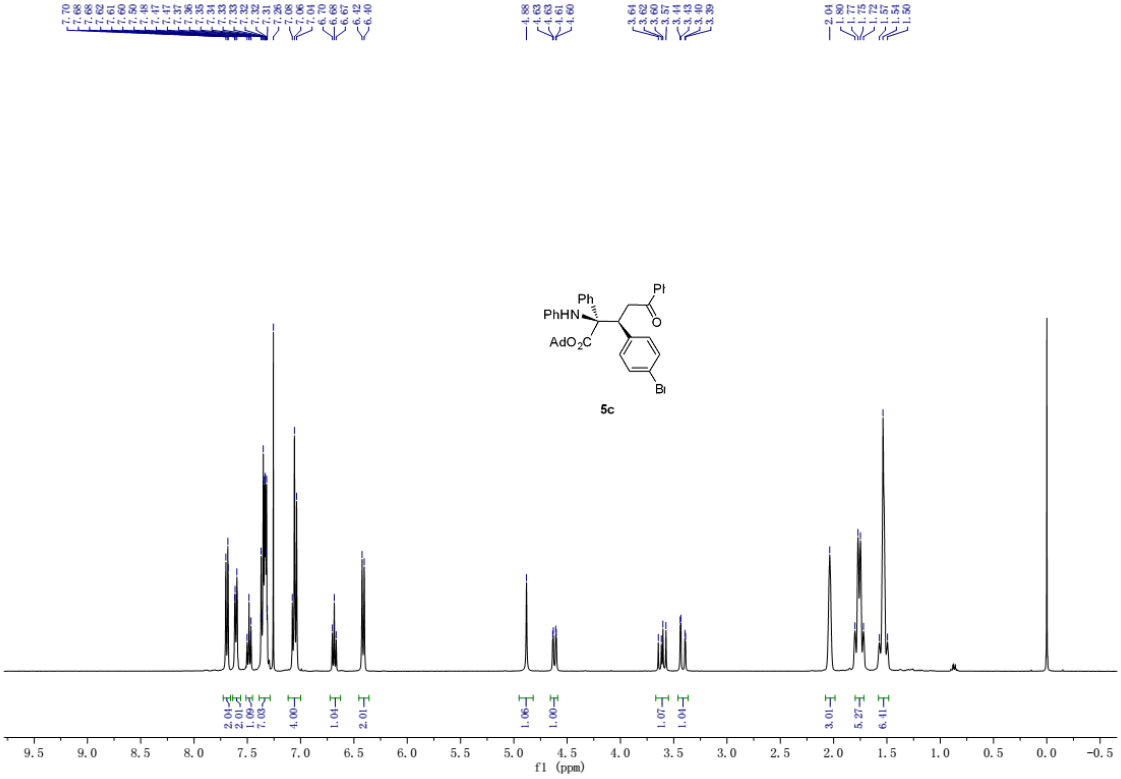
Supplementary Figure 2. ^{13}C NMR (100MHz, Acetone-d_6) spectrum for 5a



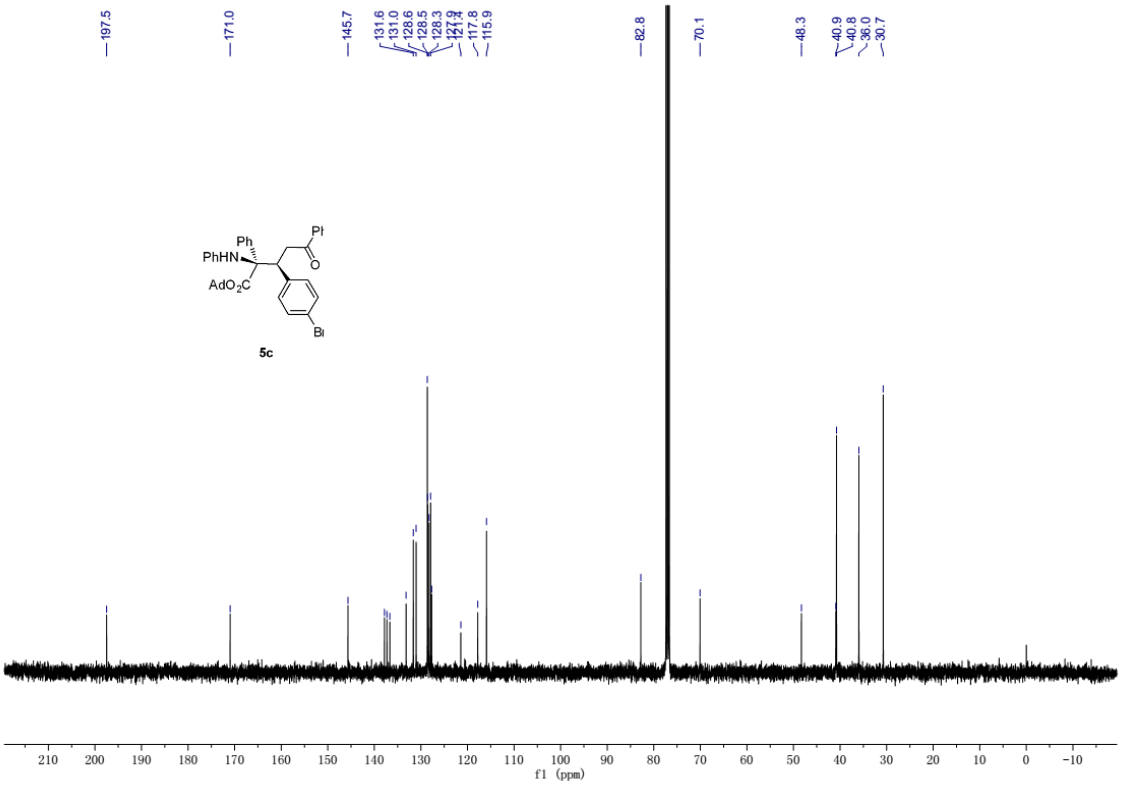
Supplementary Figure 3. ^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5b



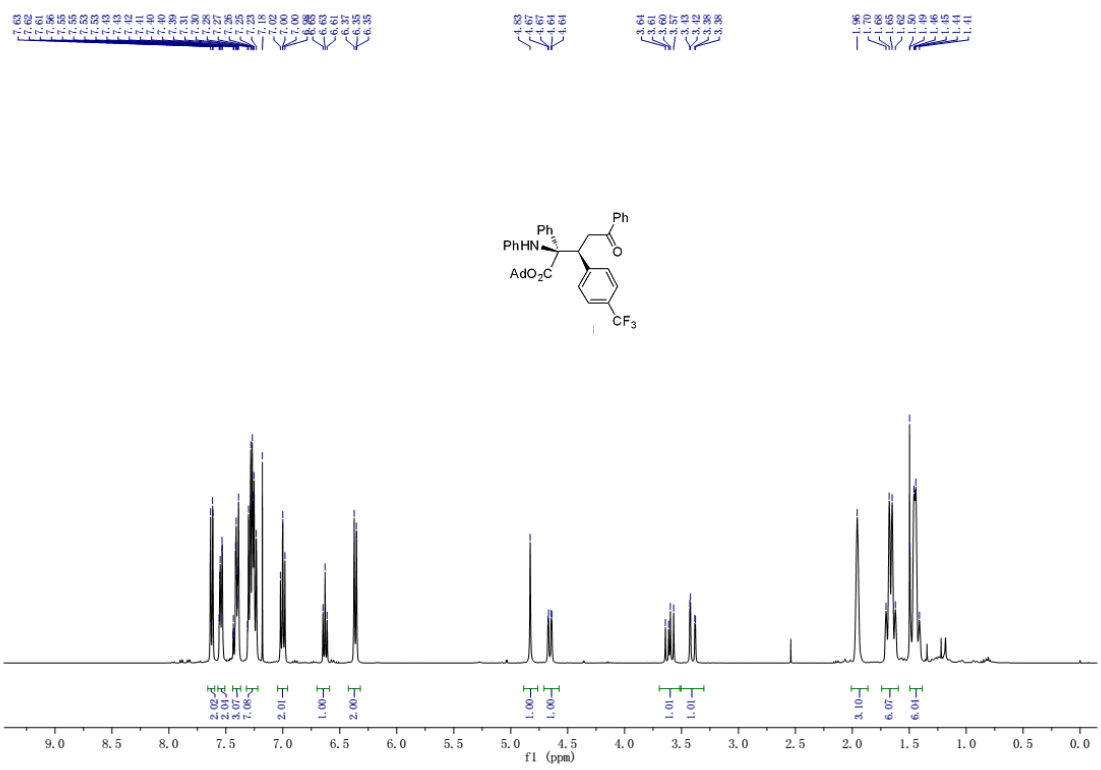
Supplementary Figure 4. ^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5b



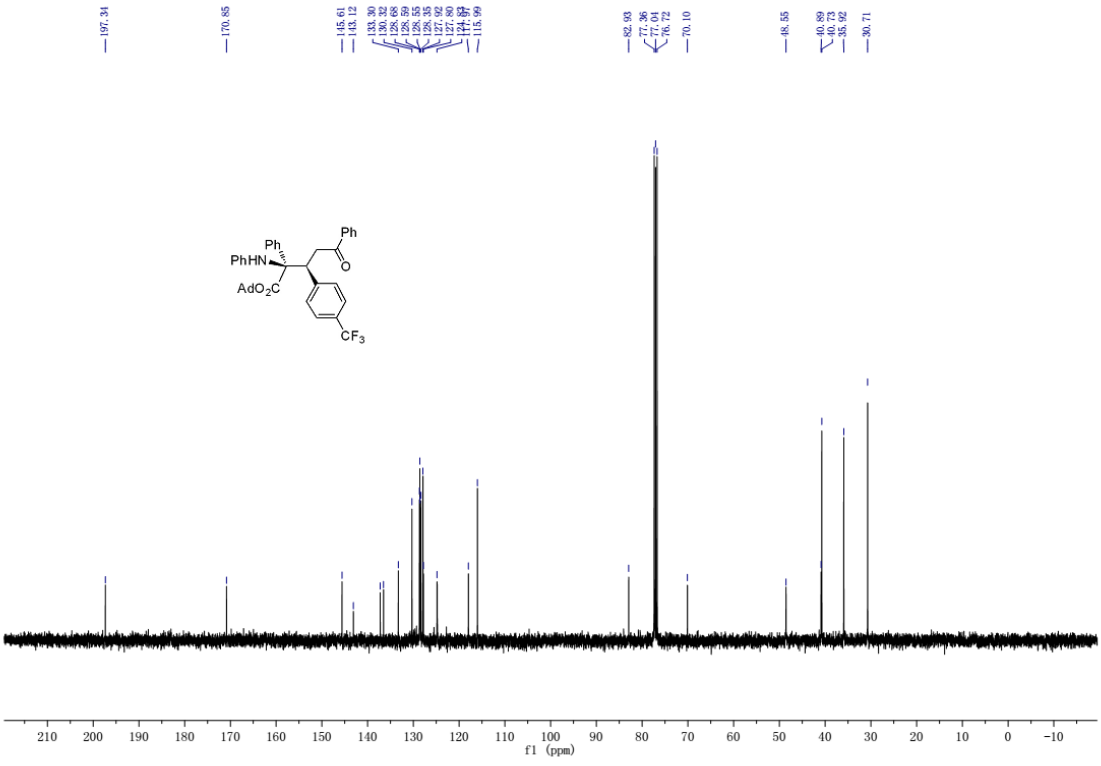
Supplementary Figure 5. ^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5c



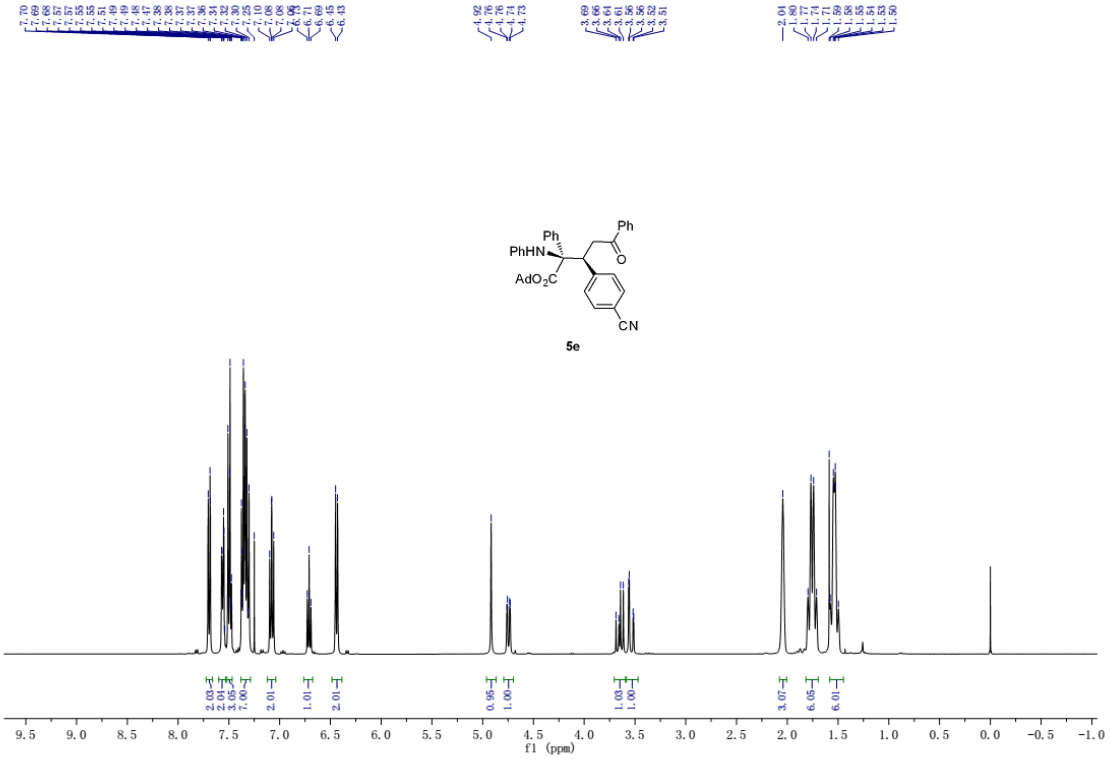
Supplementary Figure 6. ^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5c



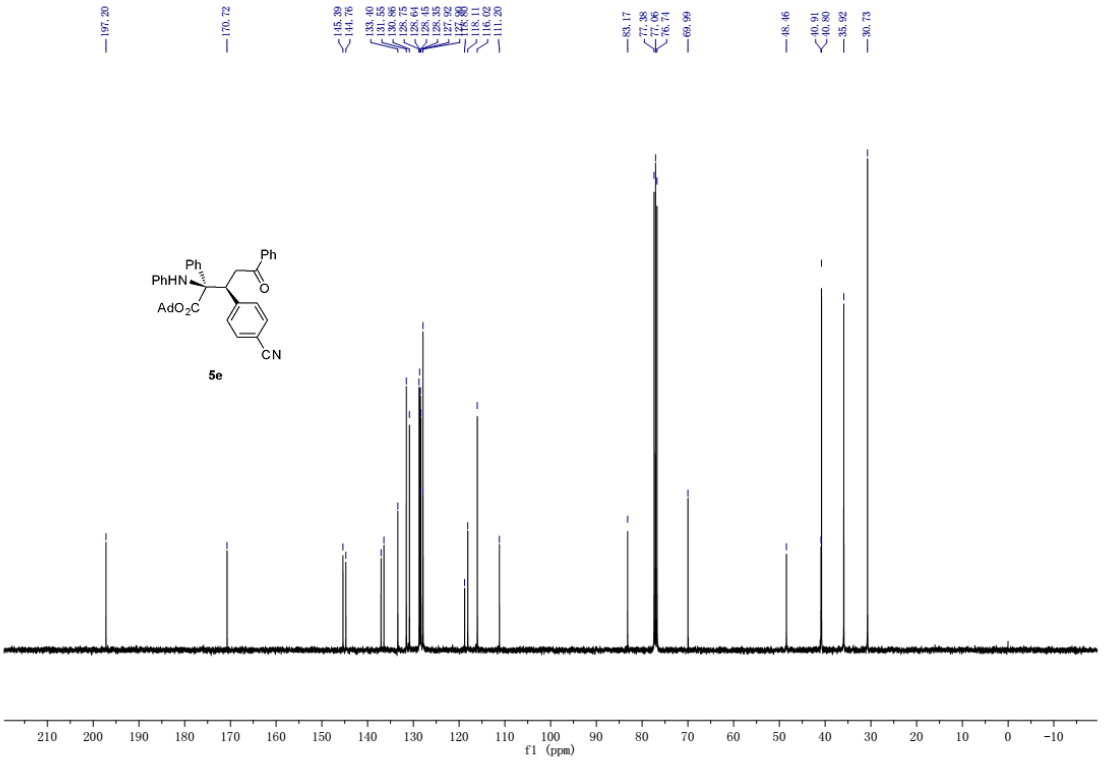
Supplementary Figure 7. ^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5d



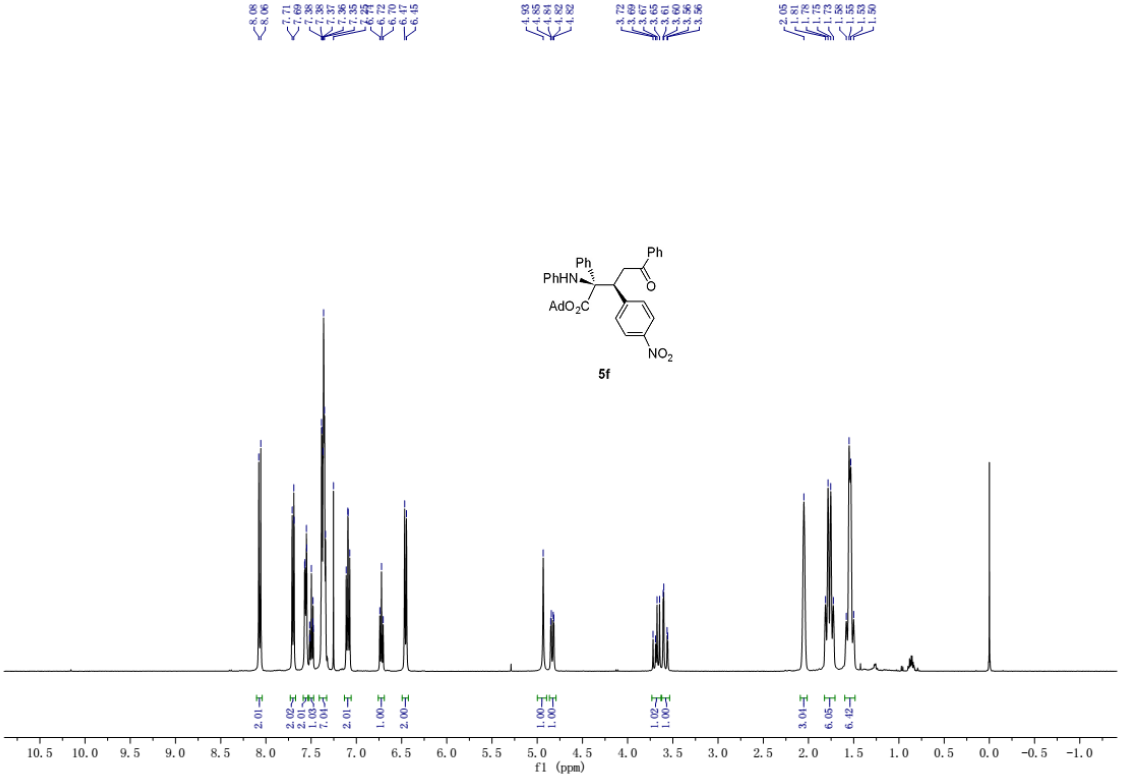
Supplementary Figure 8. ^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5d



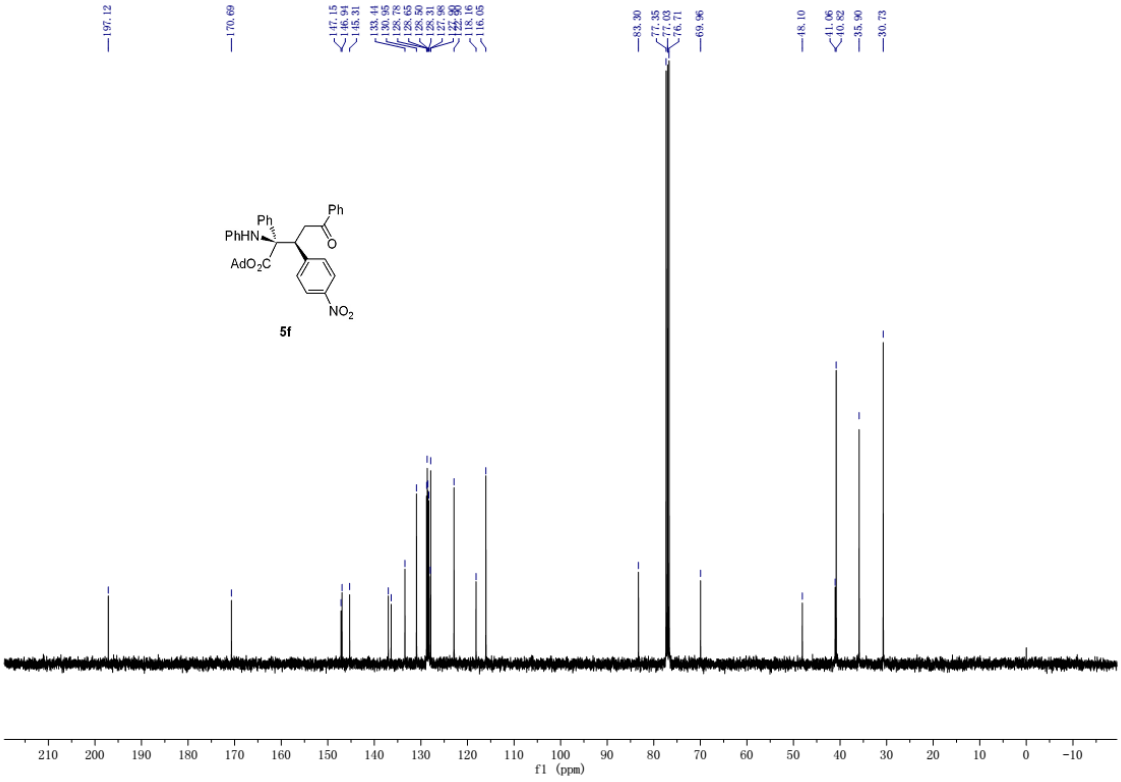
Supplementary Figure 9. ^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5e



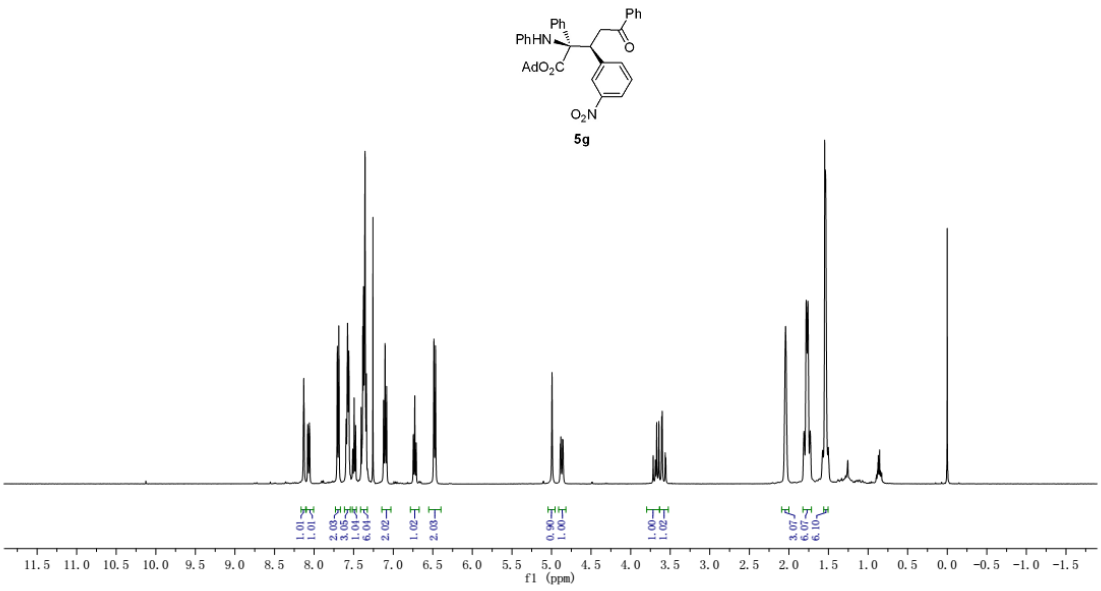
Supplementary Figure 10. ^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5e



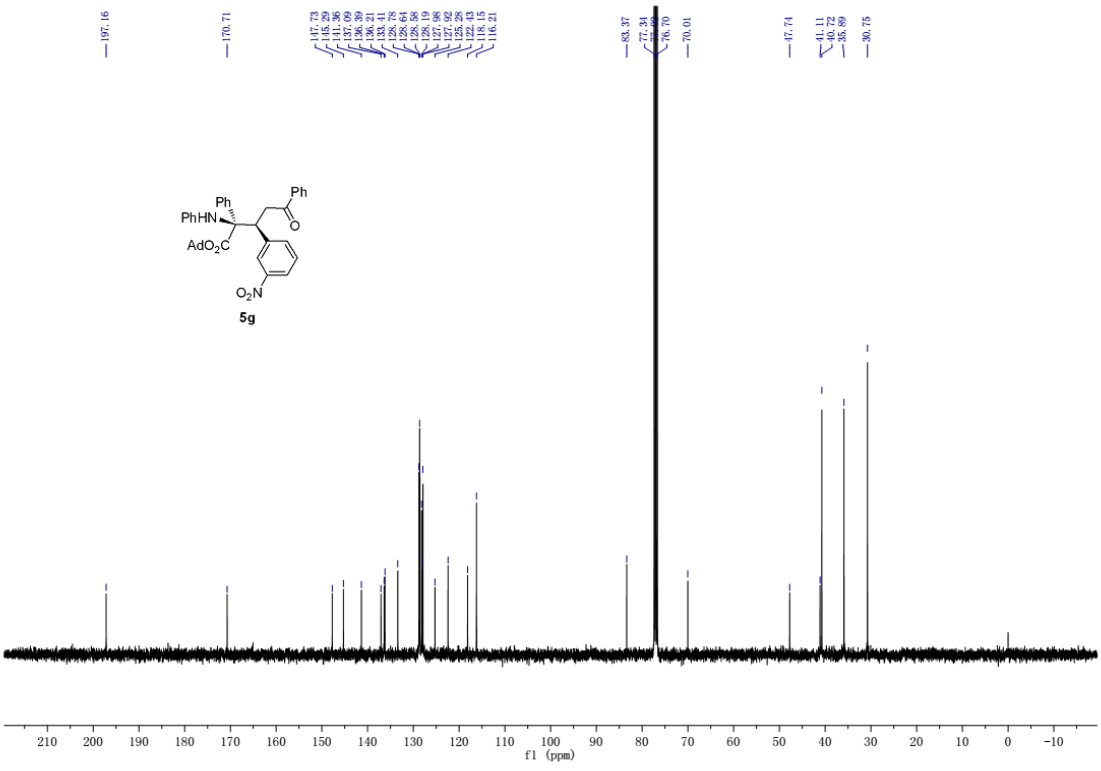
Supplementary Figure 11. ^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5f



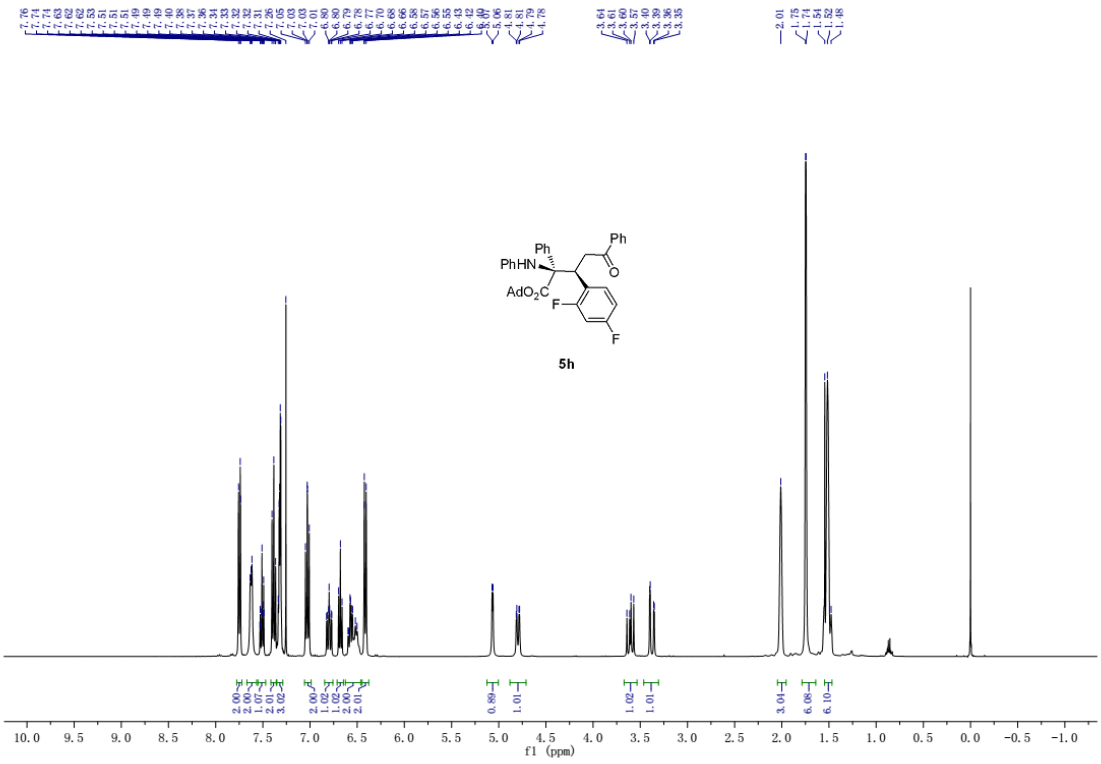
Supplementary Figure 12. ^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5f



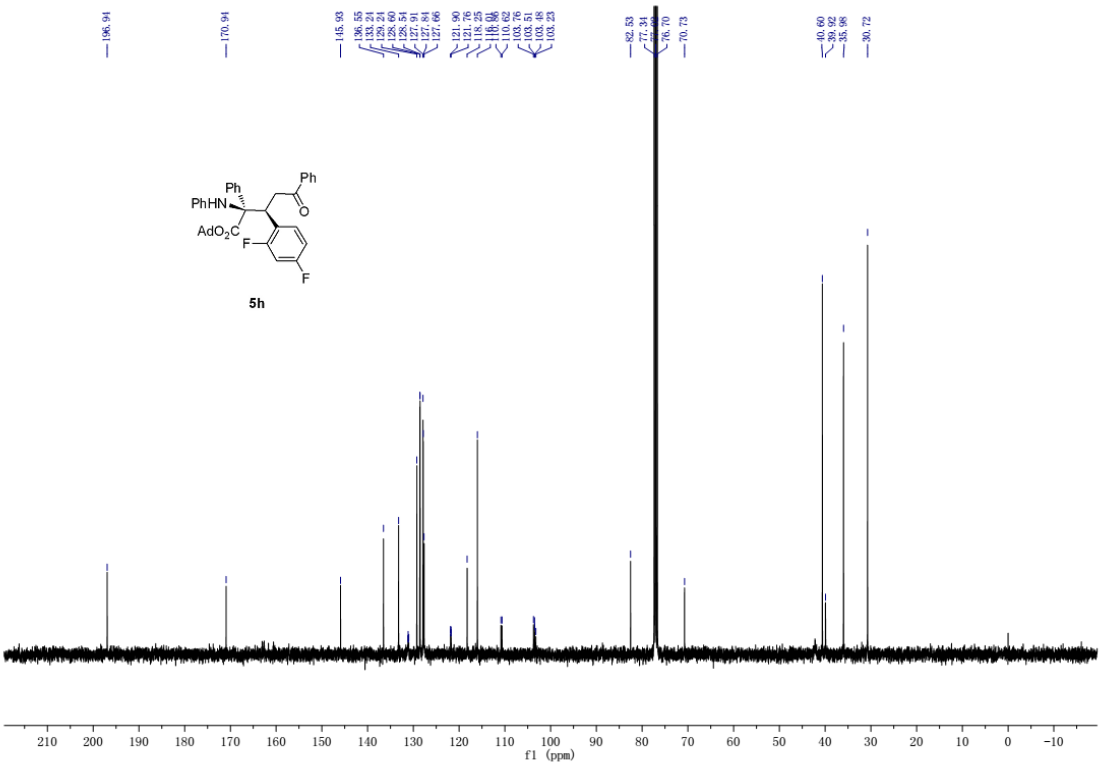
Supplementary Figure 13. ^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5g



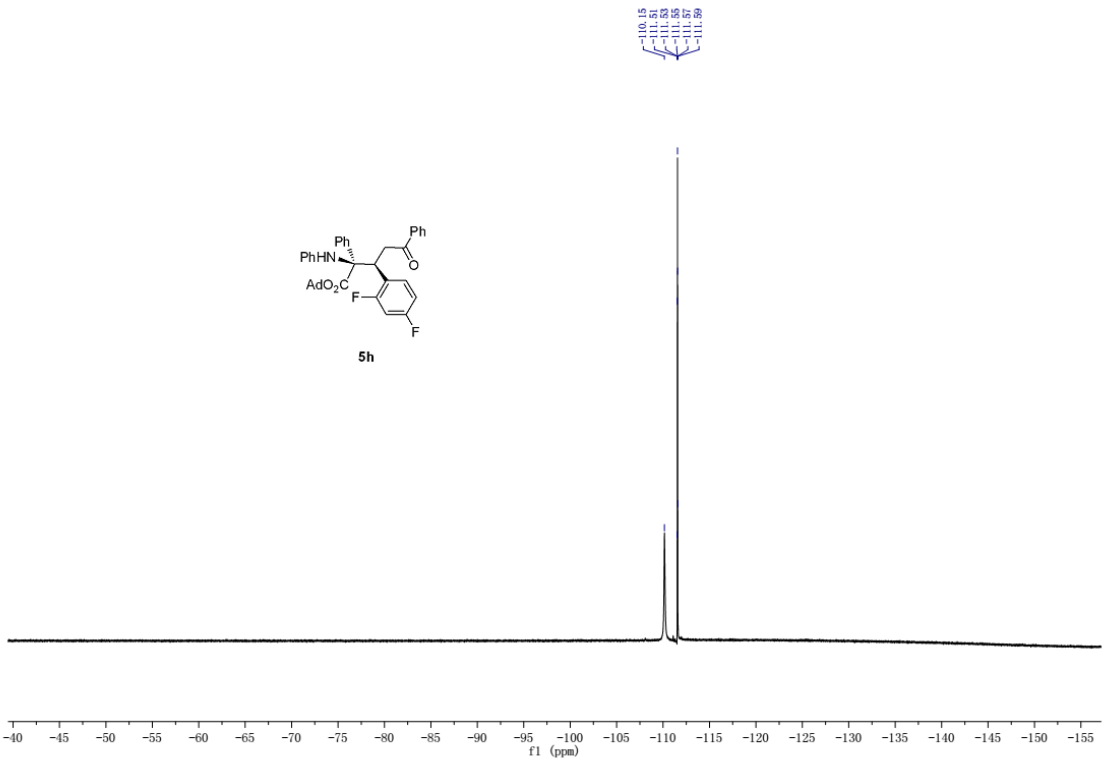
Supplementary Figure 14. ^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5g



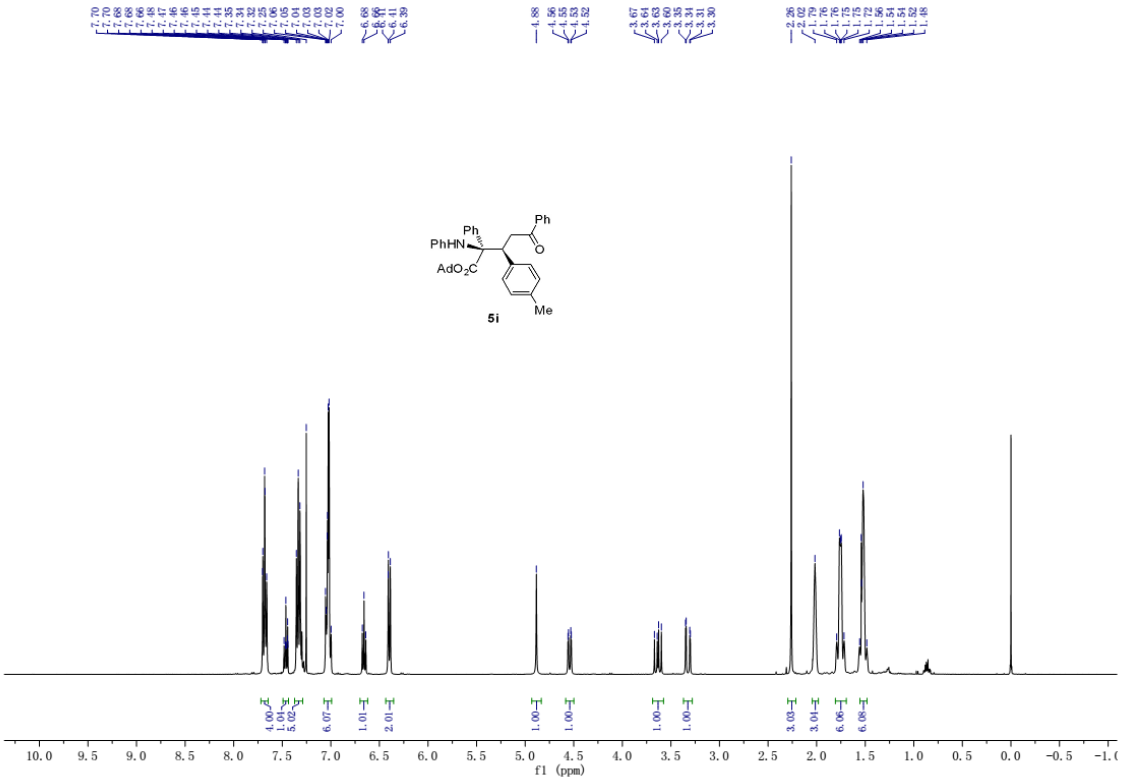
Supplementary Figure 15. ^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5h



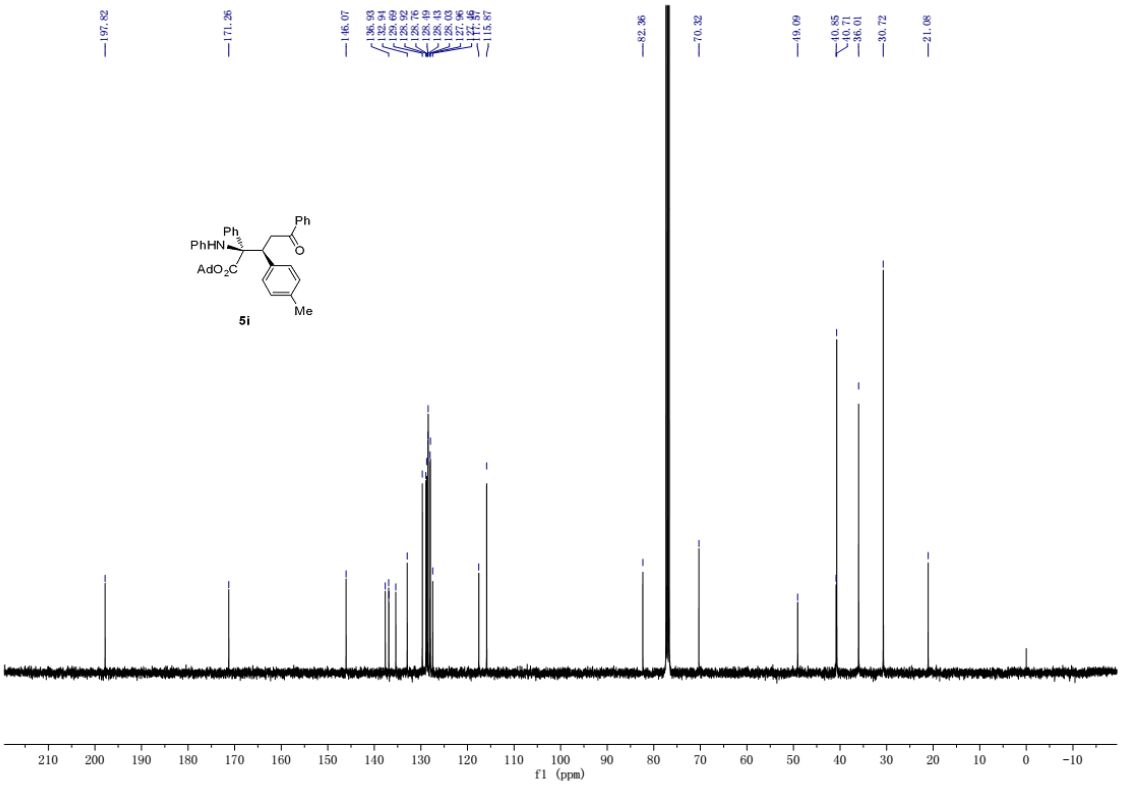
Supplementary Figure 16. ^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5h



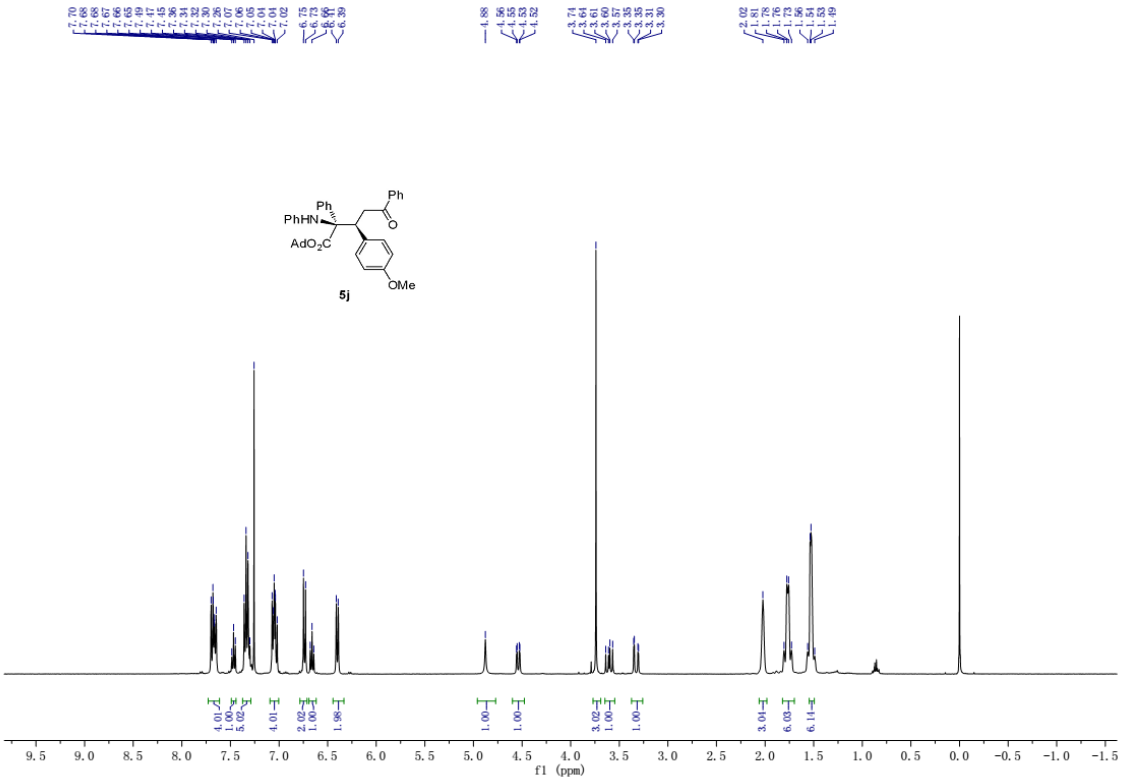
Supplementary Figure 17. ^{19}F NMR (376 MHz, $CDCl_3$) for 5h



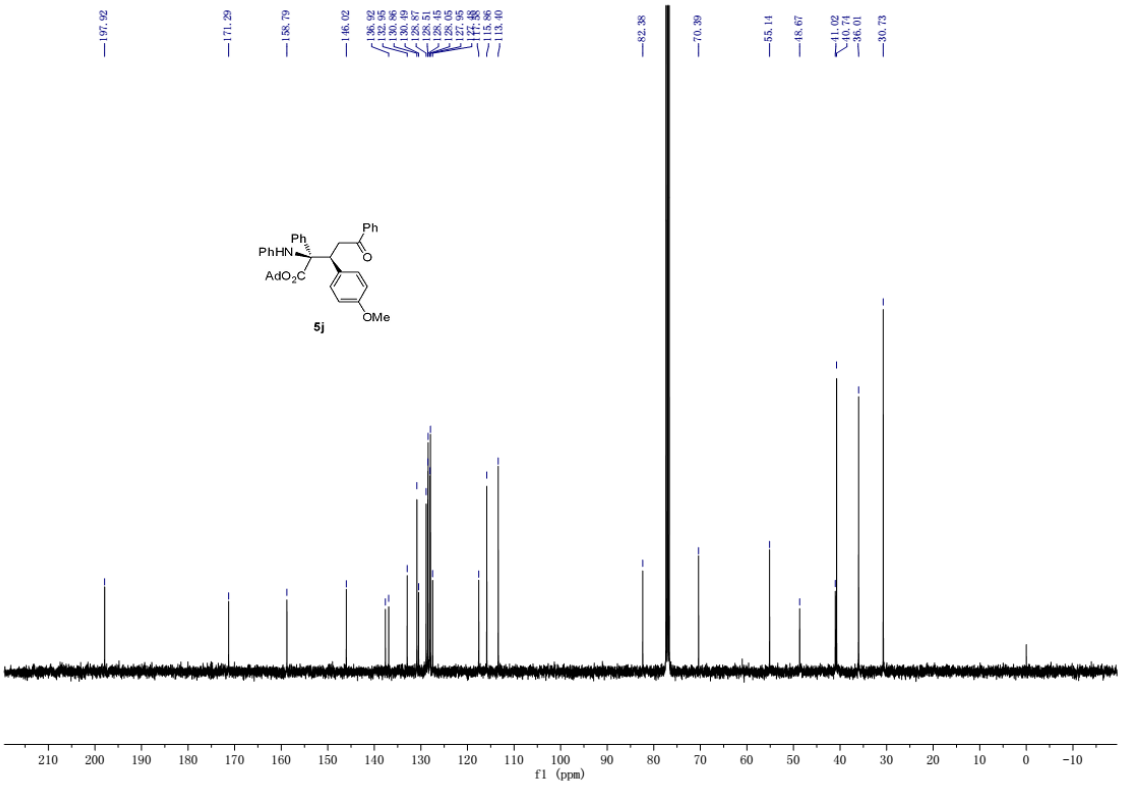
Supplementary Figure 18. ^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5i



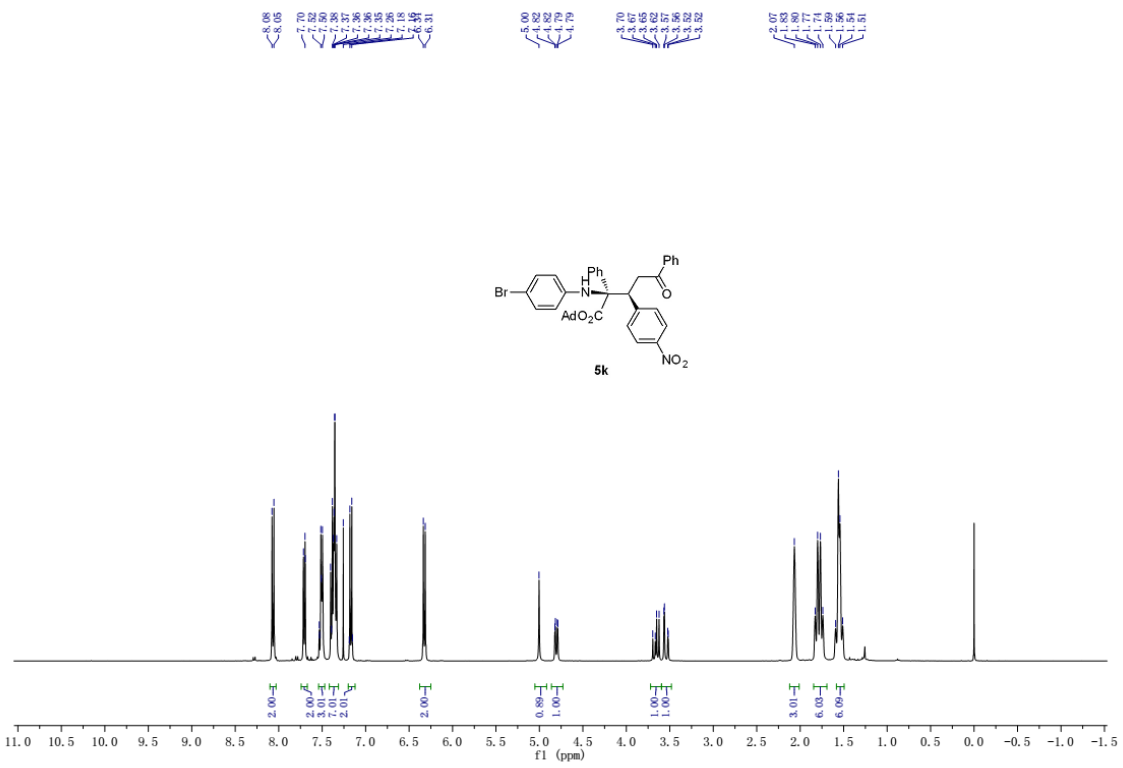
Supplementary Figure 19. ^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5i



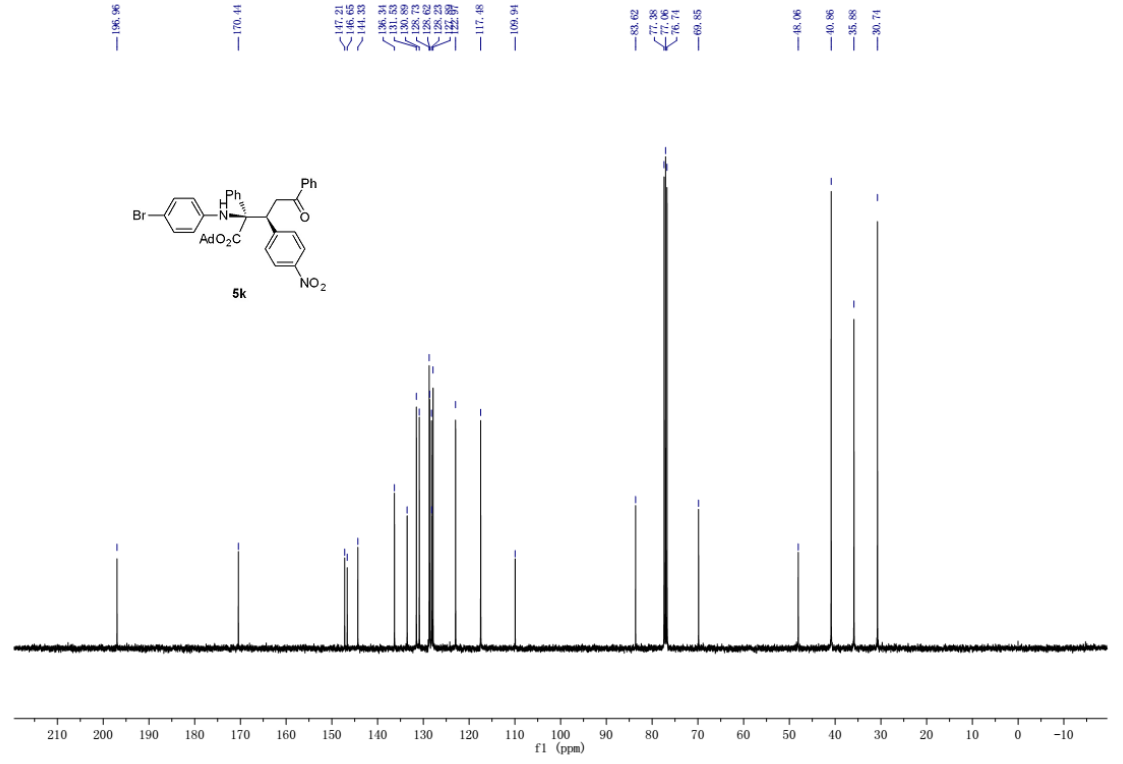
Supplementary Figure 20. ^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5j



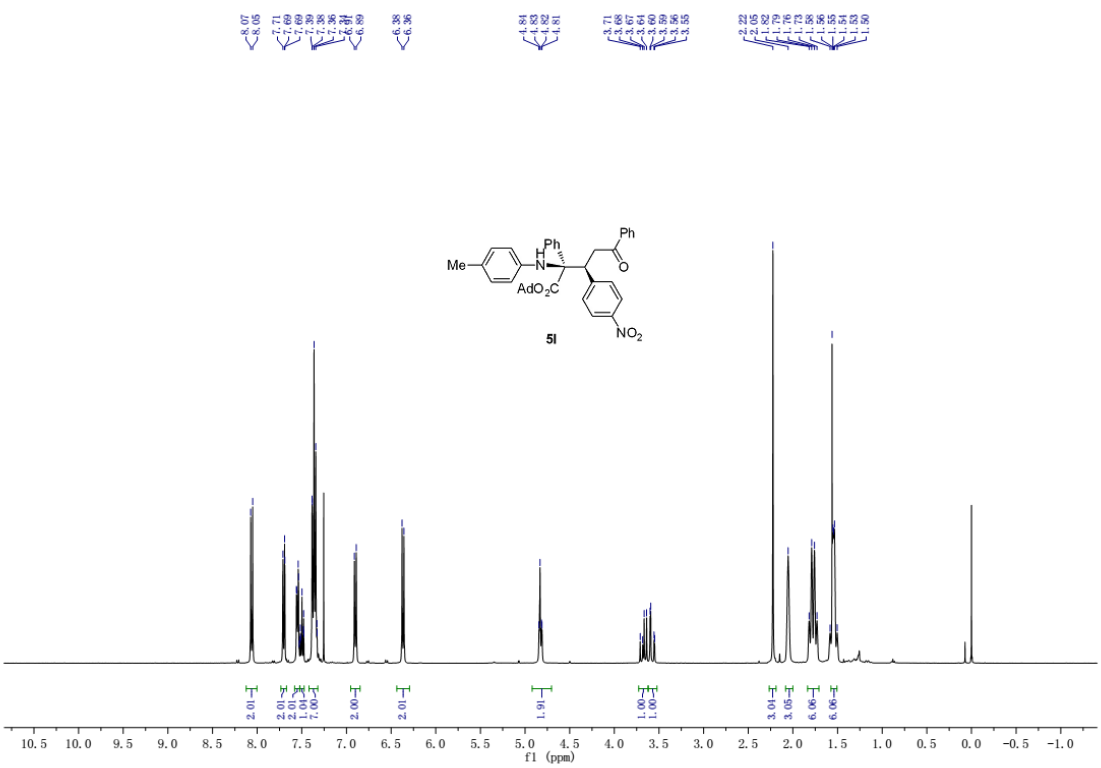
Supplementary Figure 21. ^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5j



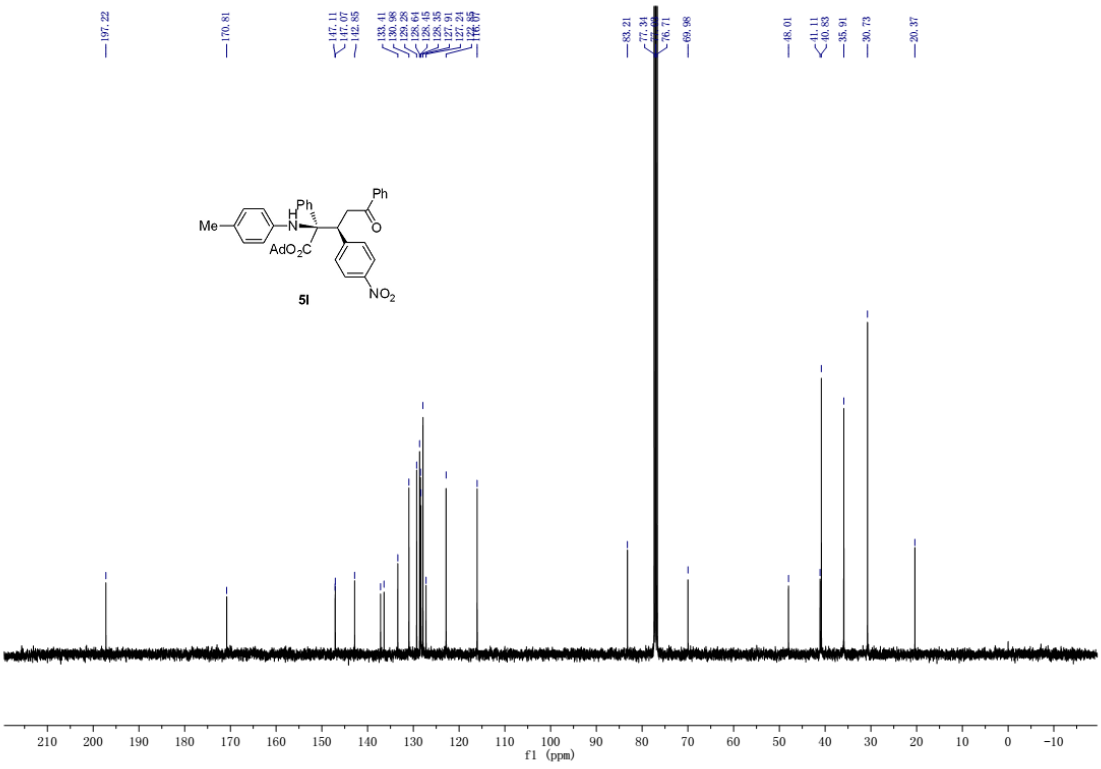
Supplementary Figure 22. ^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5k



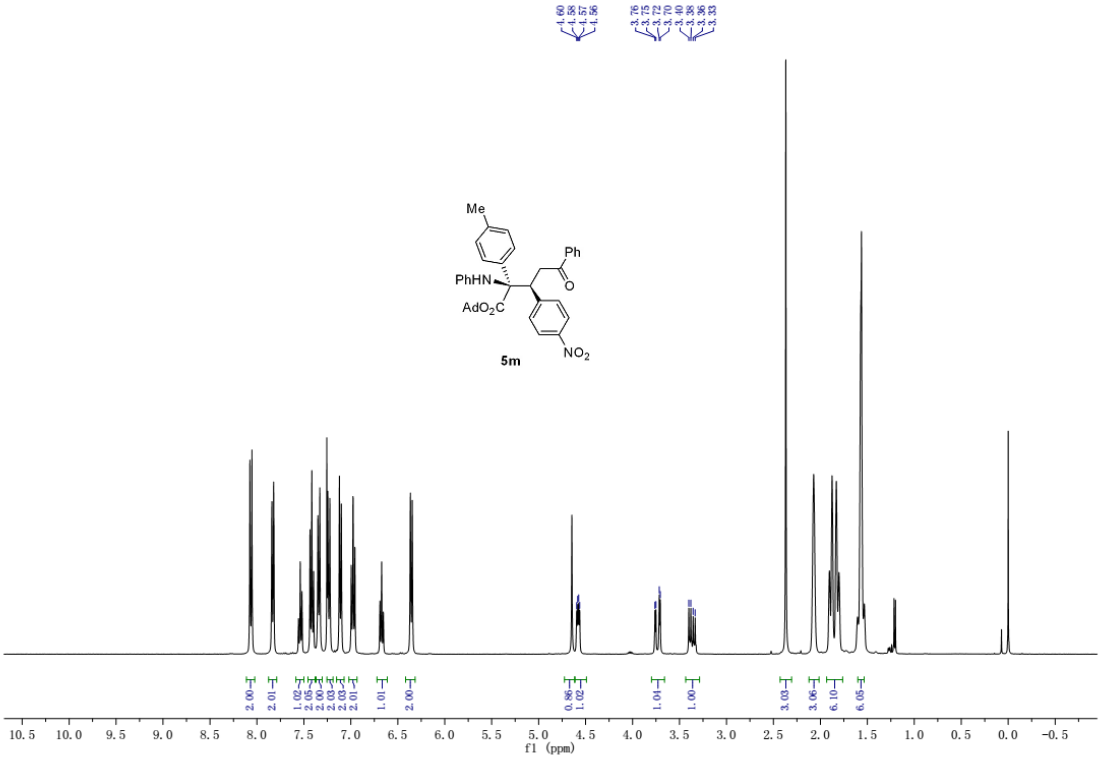
Supplementary Figure 23. ^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5k



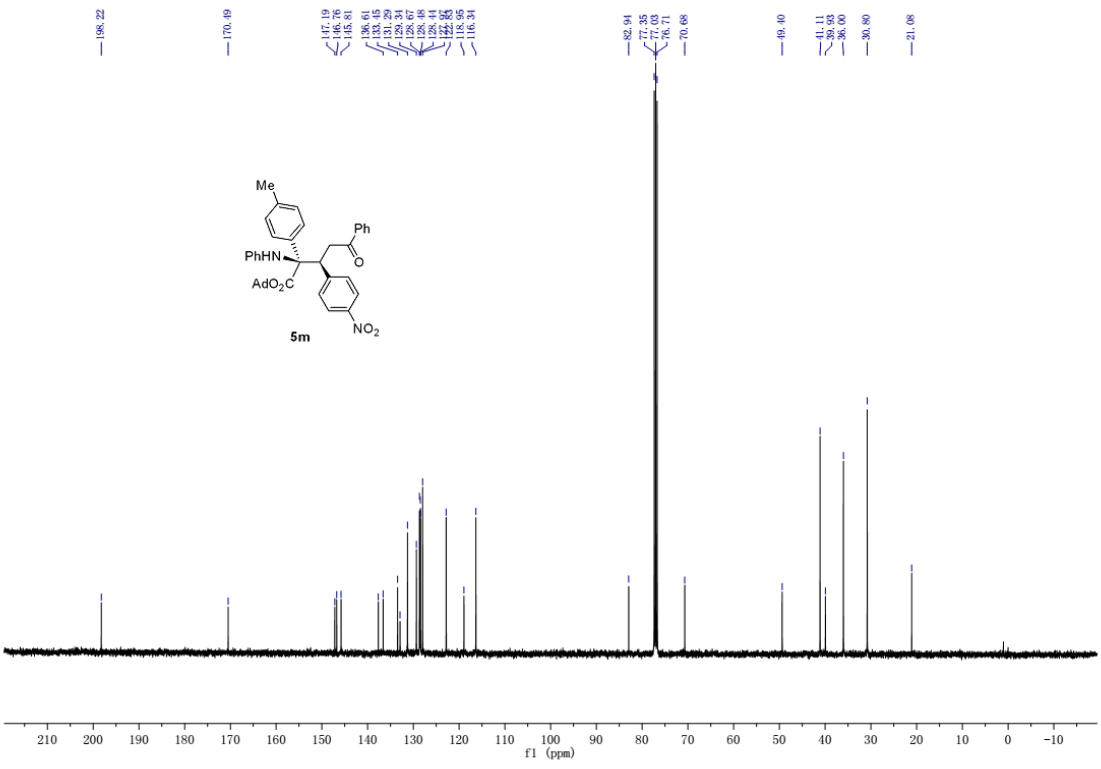
Supplementary Figure 24. ^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5l



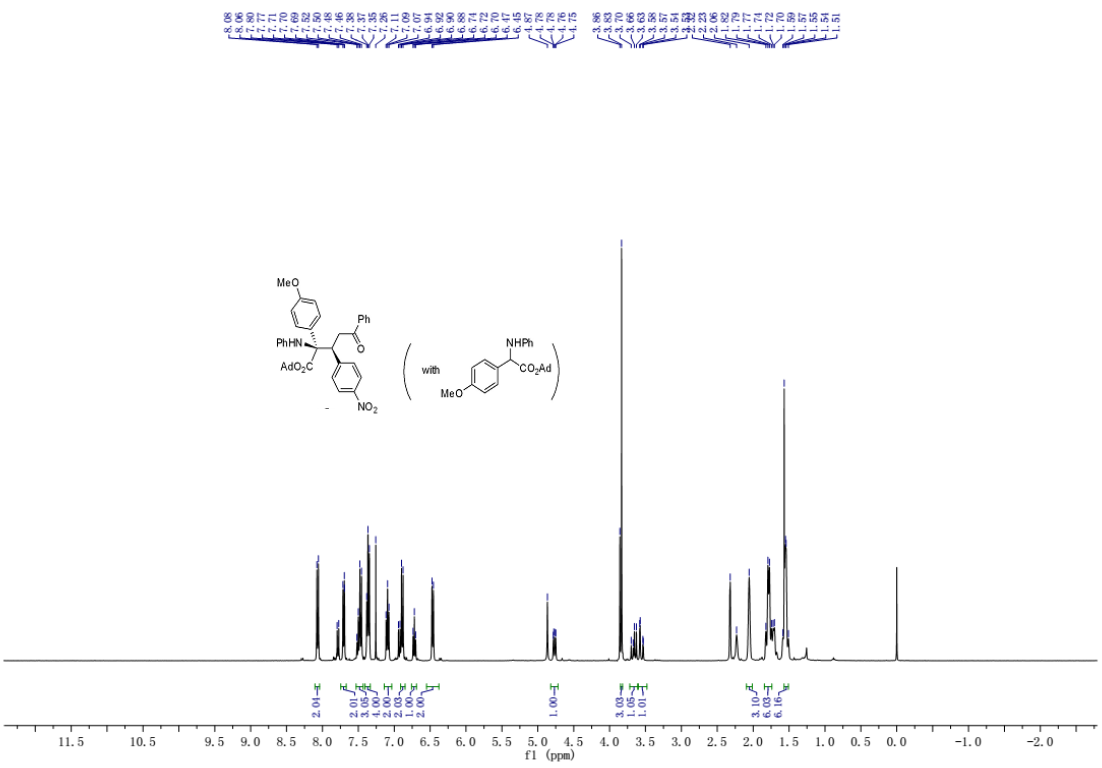
Supplementary Figure 25. ^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5l



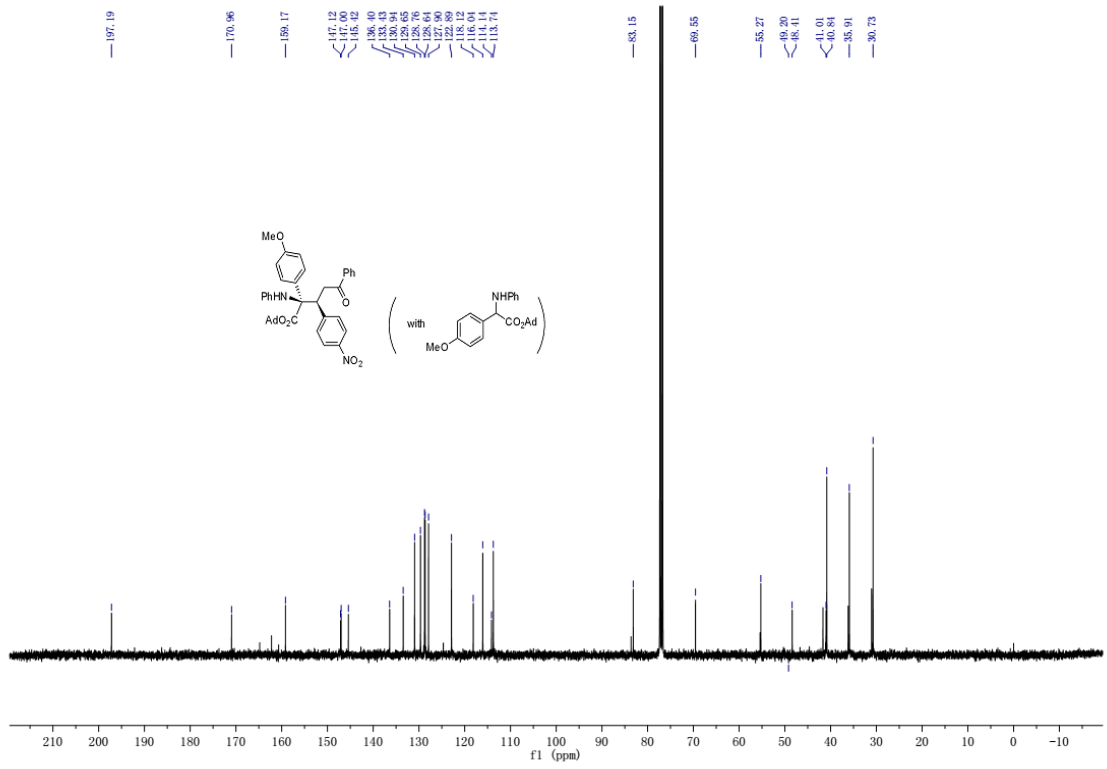
Supplementary Figure 26. ^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5m



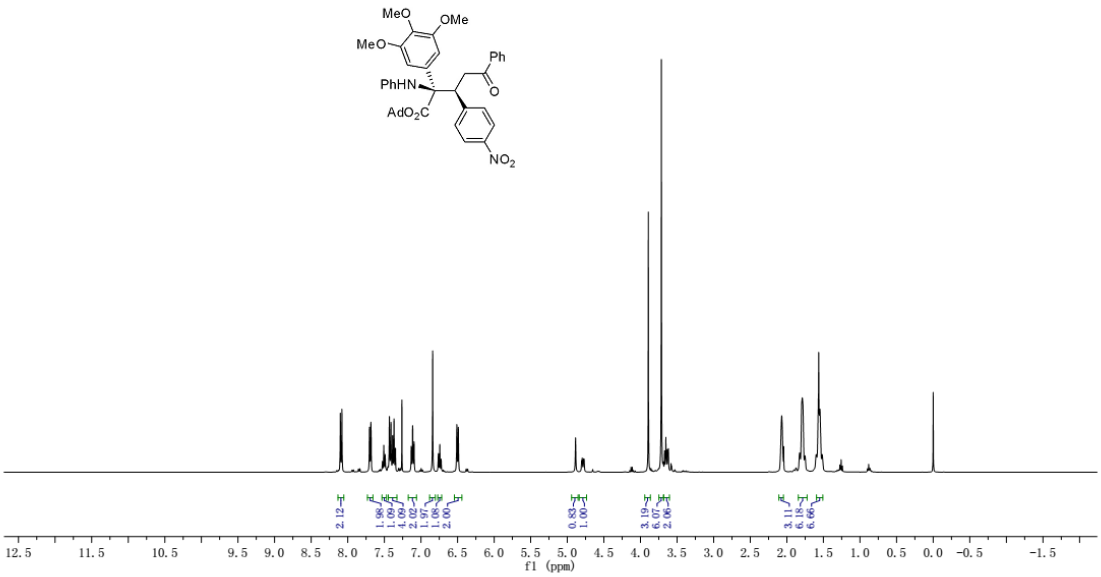
Supplementary Figure 27. ^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5m



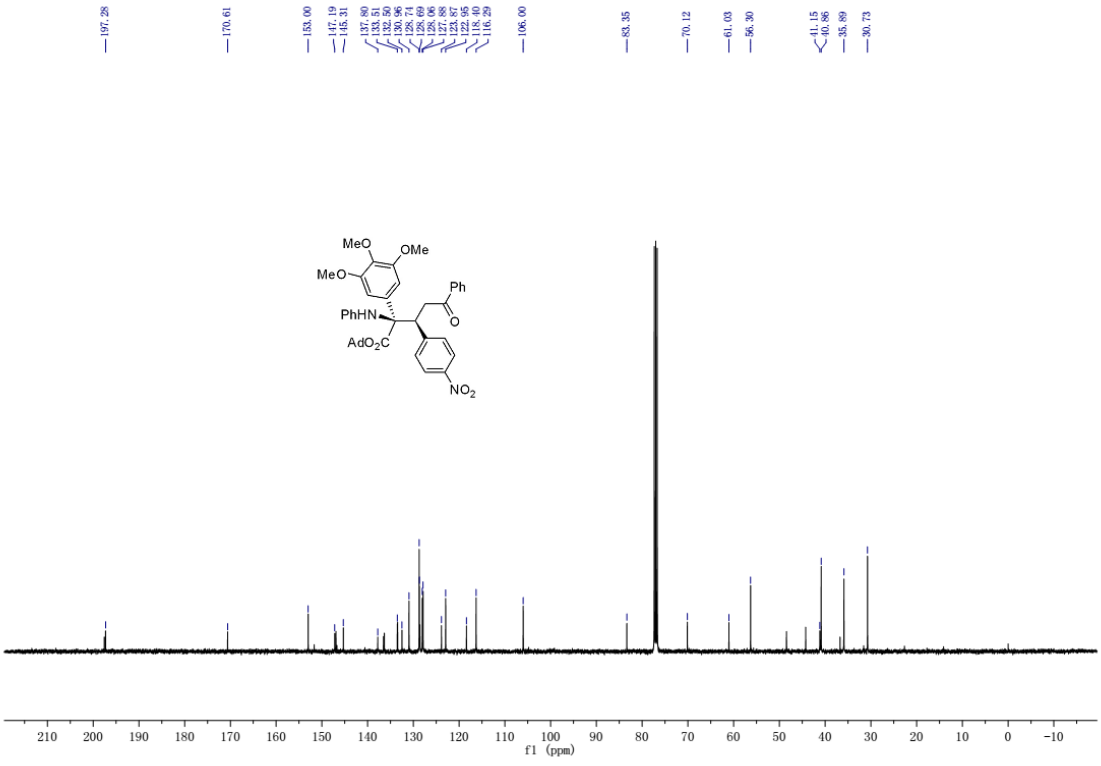
Supplementary Figure 28. ^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5n



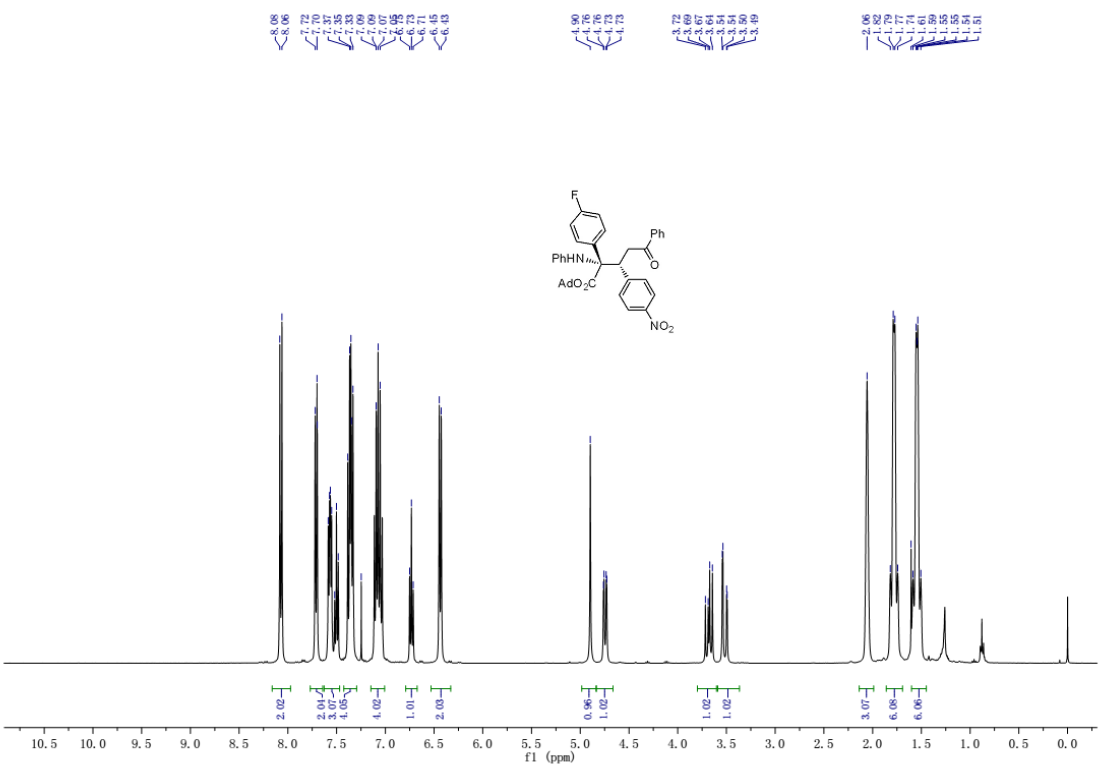
Supplementary Figure 29. ^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5n



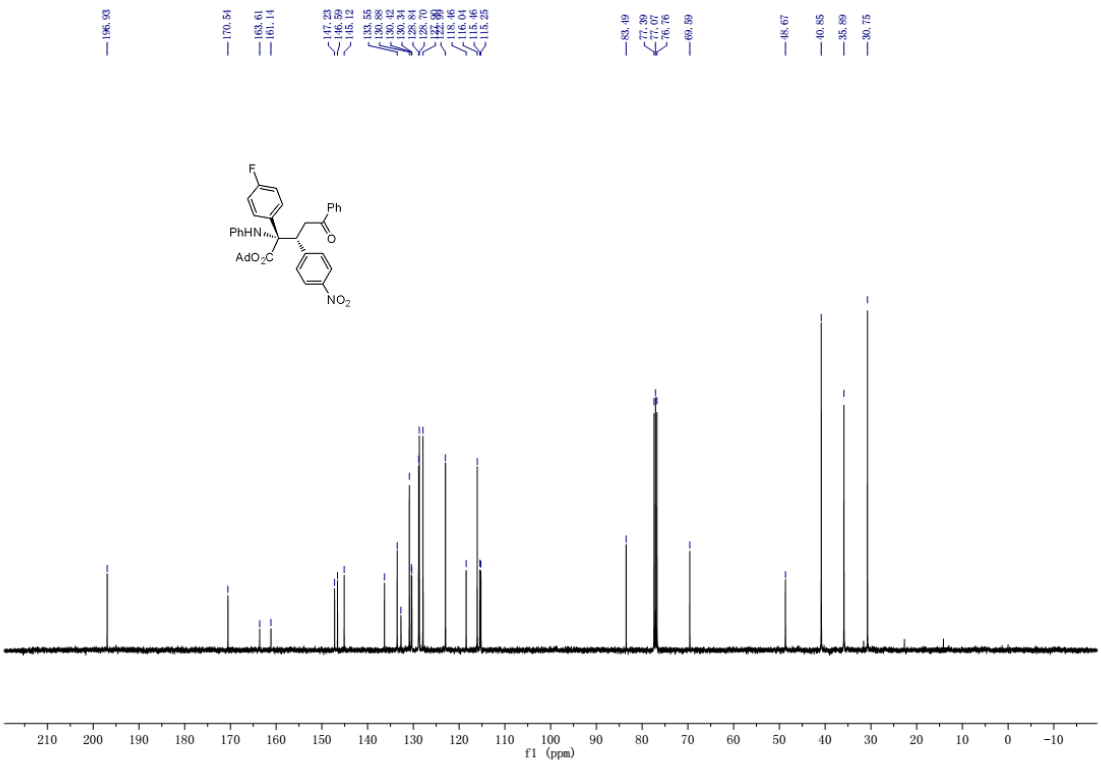
Supplementary Figure 30. ^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5o



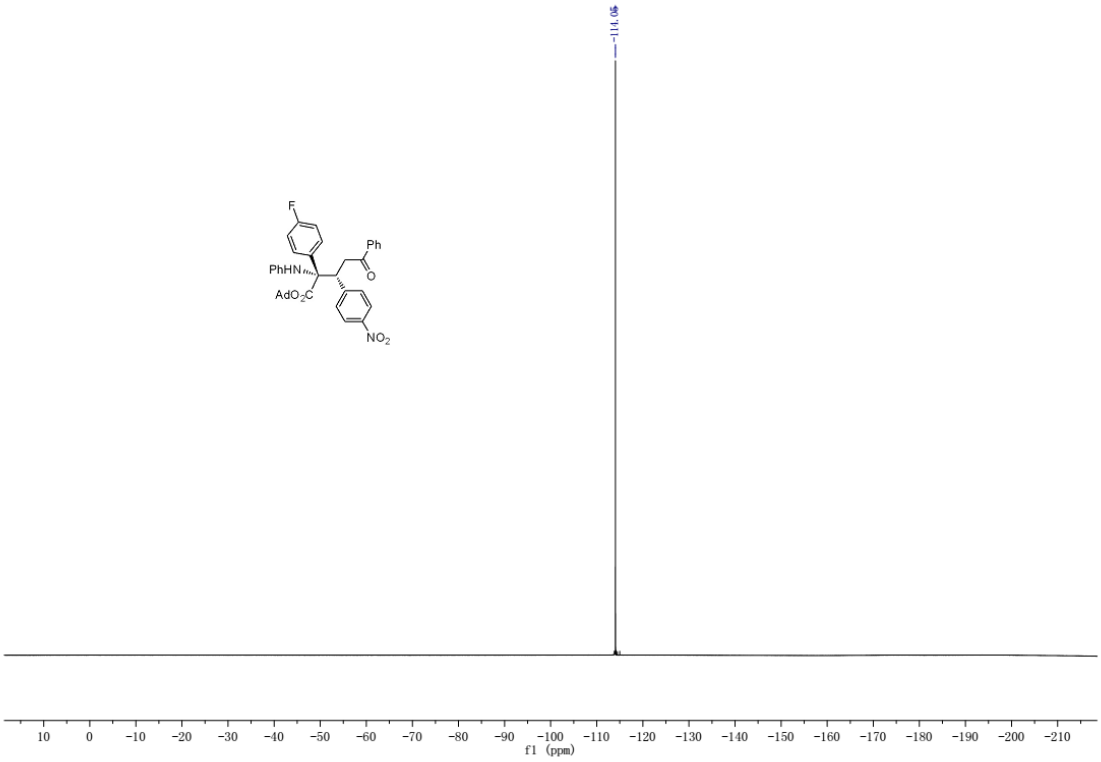
Supplementary Figure 31. ^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5o



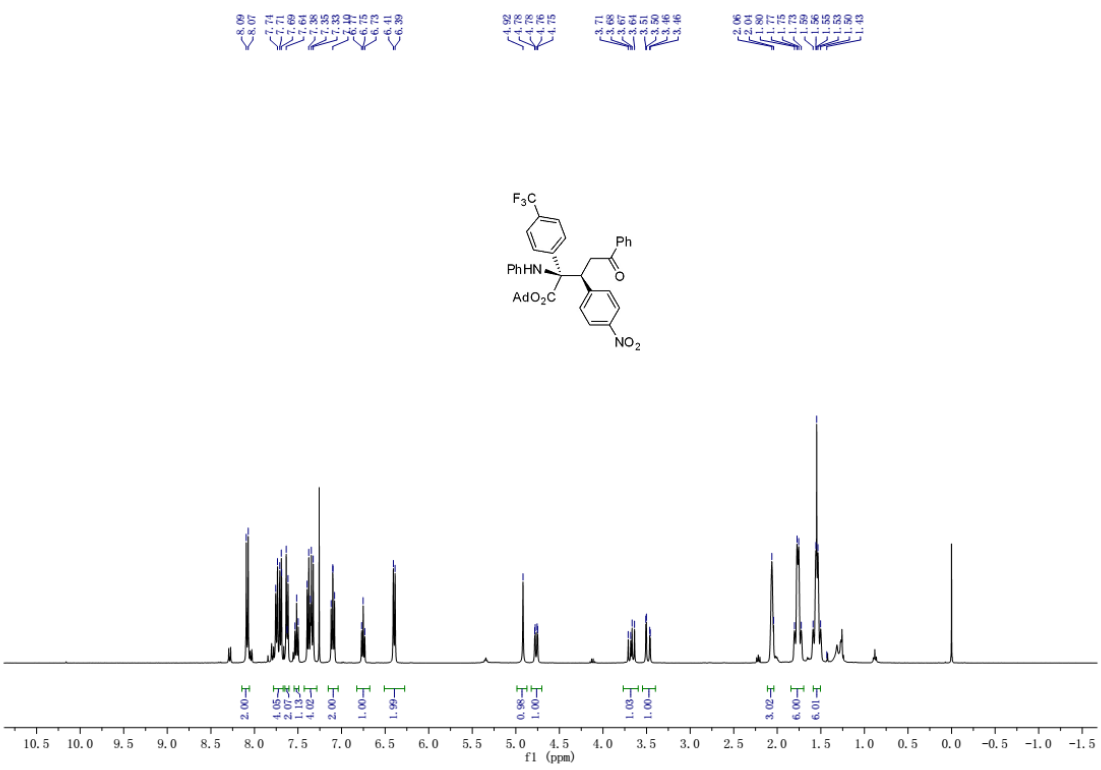
Supplementary Figure 32. ^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5p



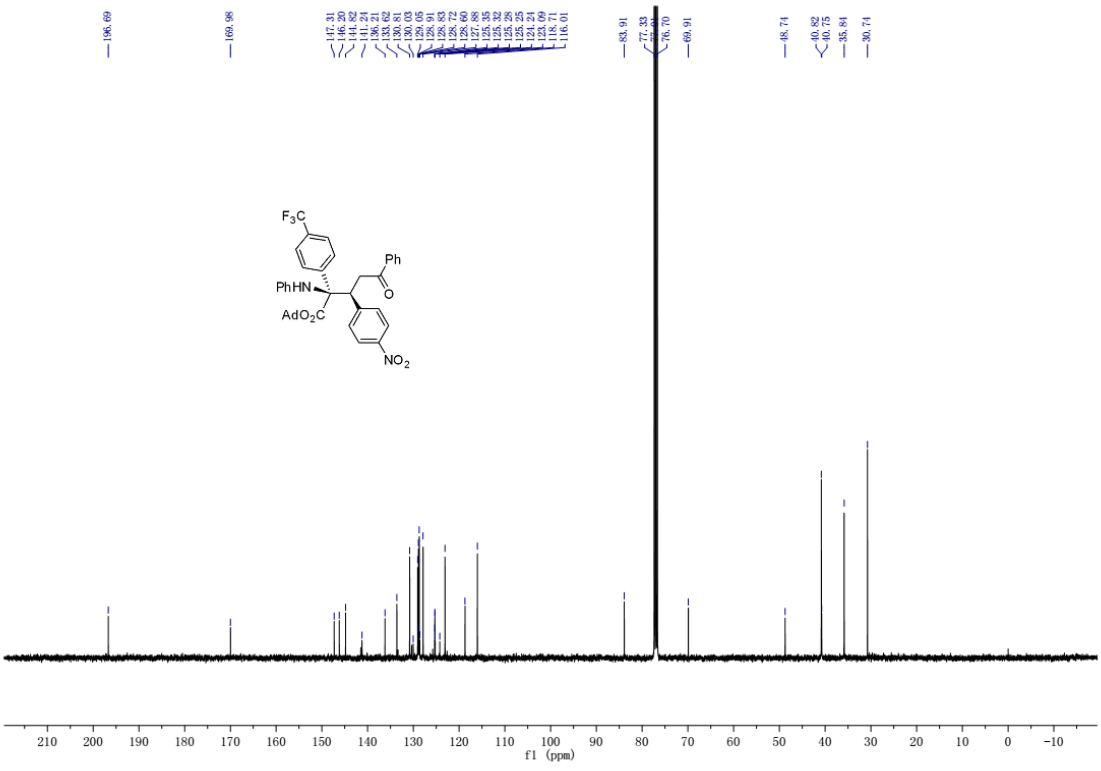
Supplementary Figure 33. ^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5p



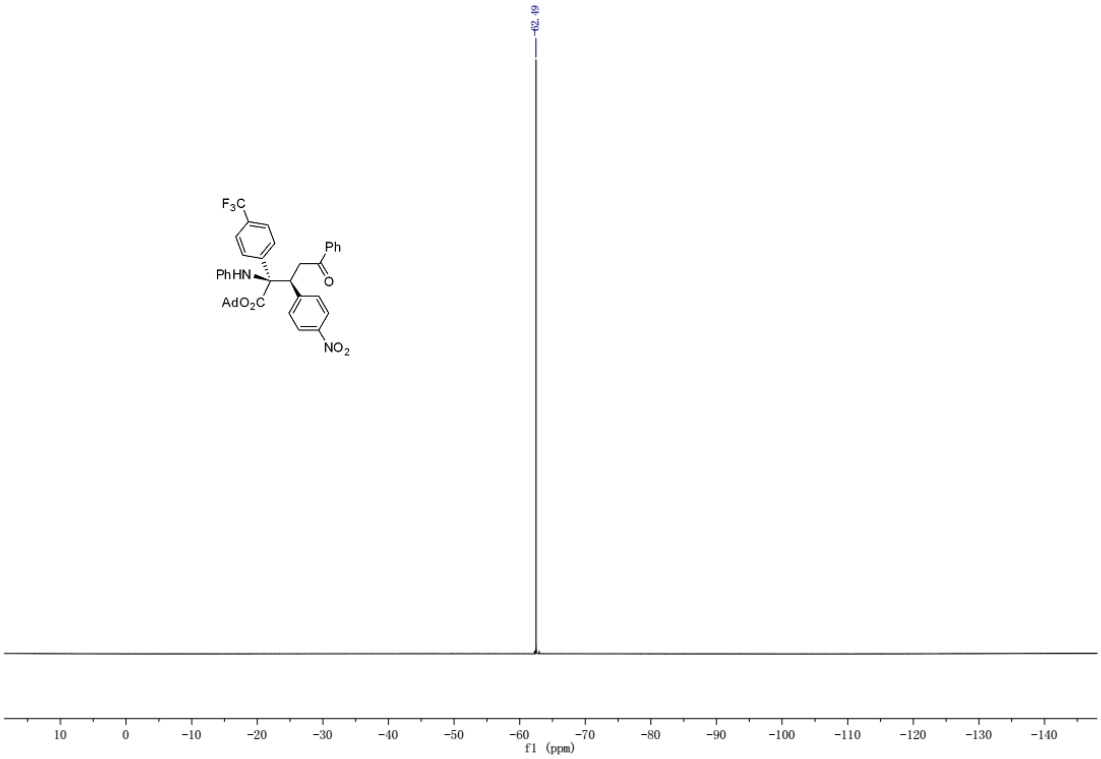
Supplementary Figure 34. ^{19}F NMR (376MHz, $CDCl_3$) spectrum for 5b



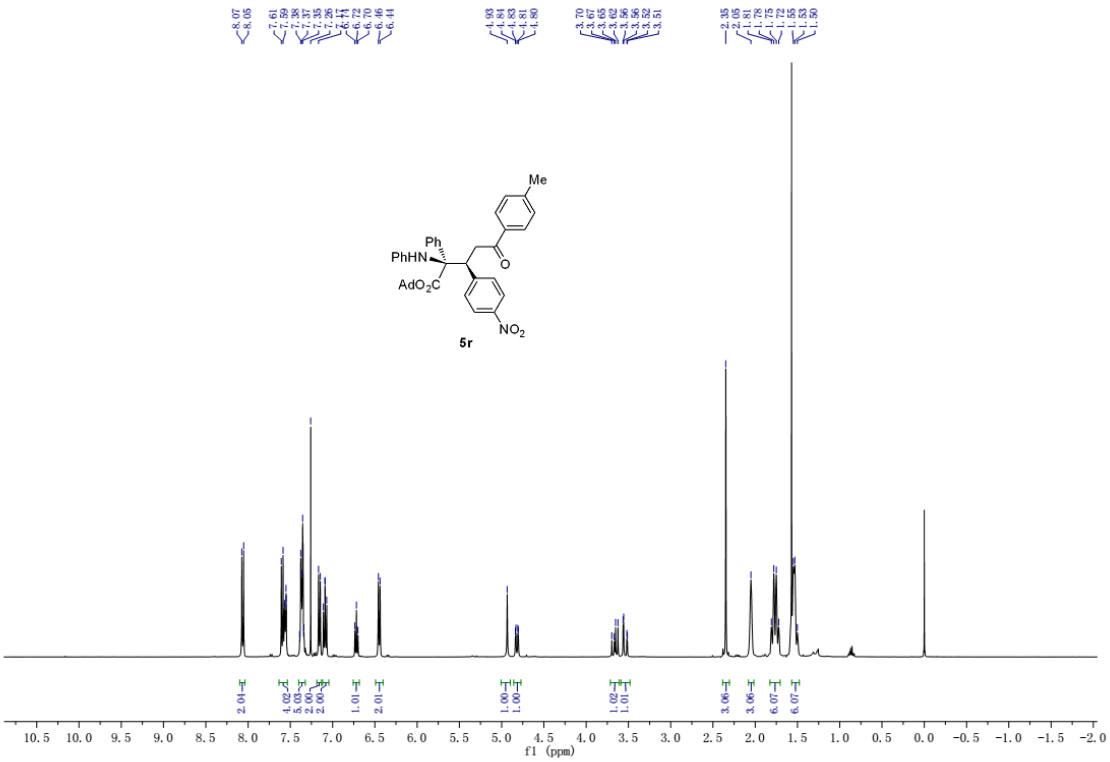
Supplementary Figure 35. ^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5q



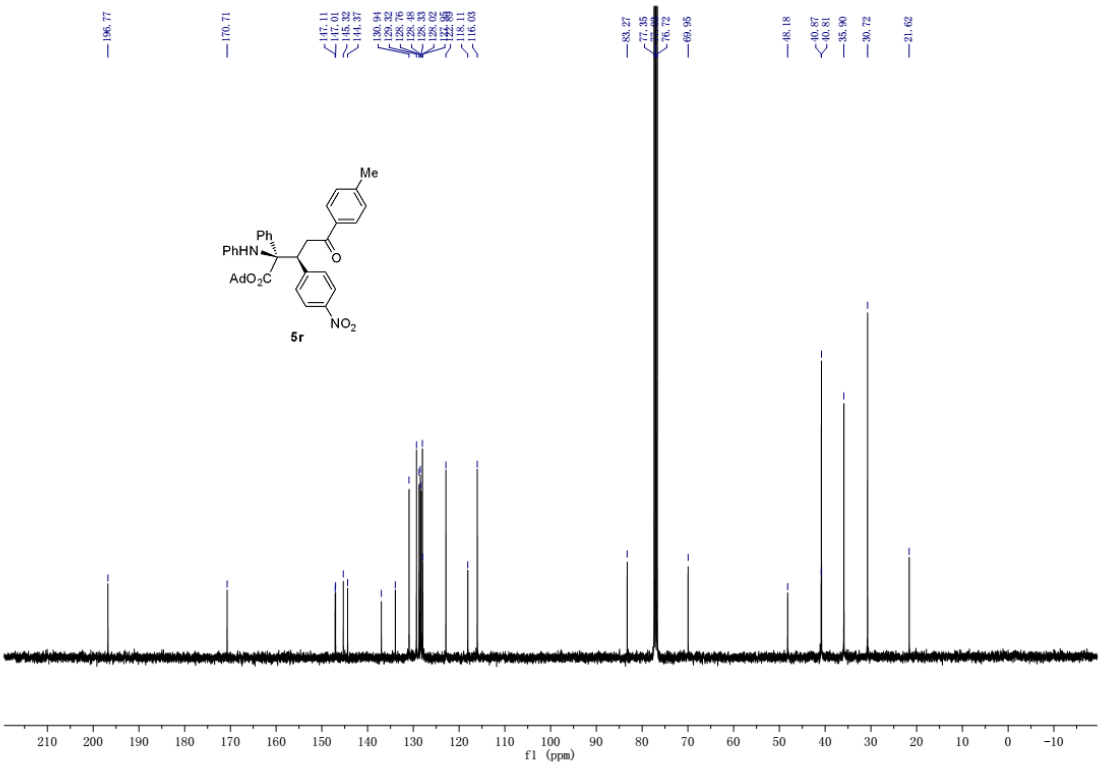
Supplementary Figure 36. ^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5q



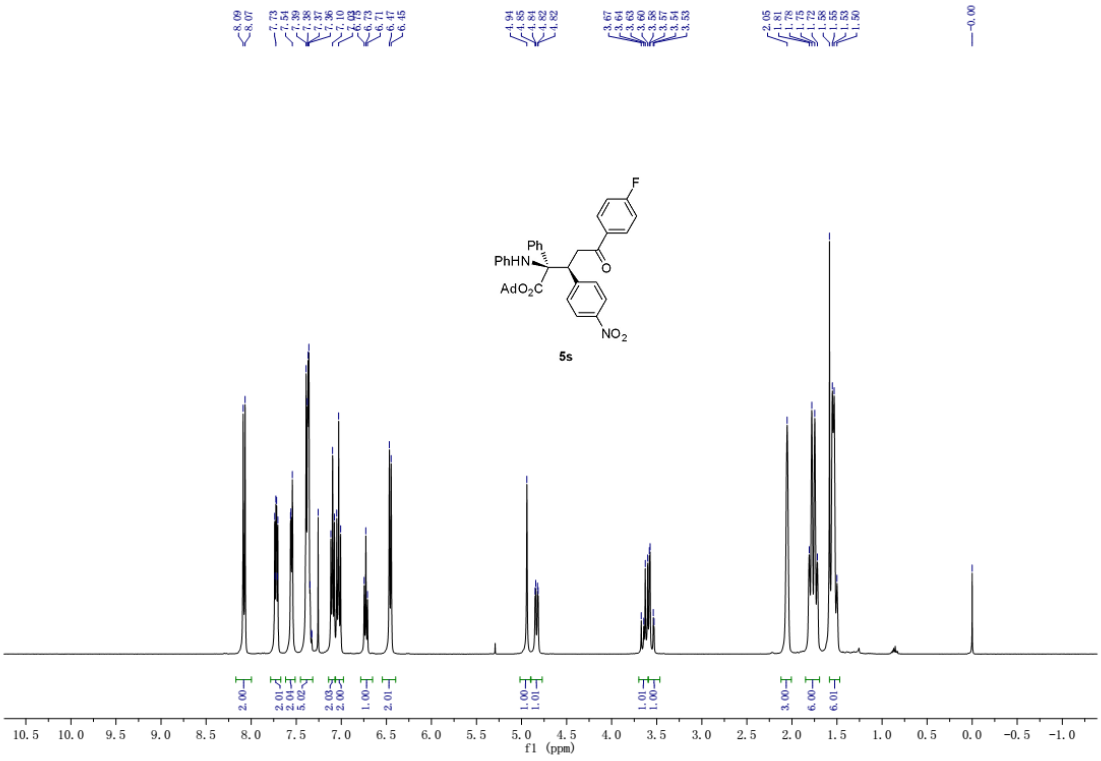
Supplementary Figure 37. ^{19}F NMR (376MHz, $CDCl_3$) spectrum for 5q



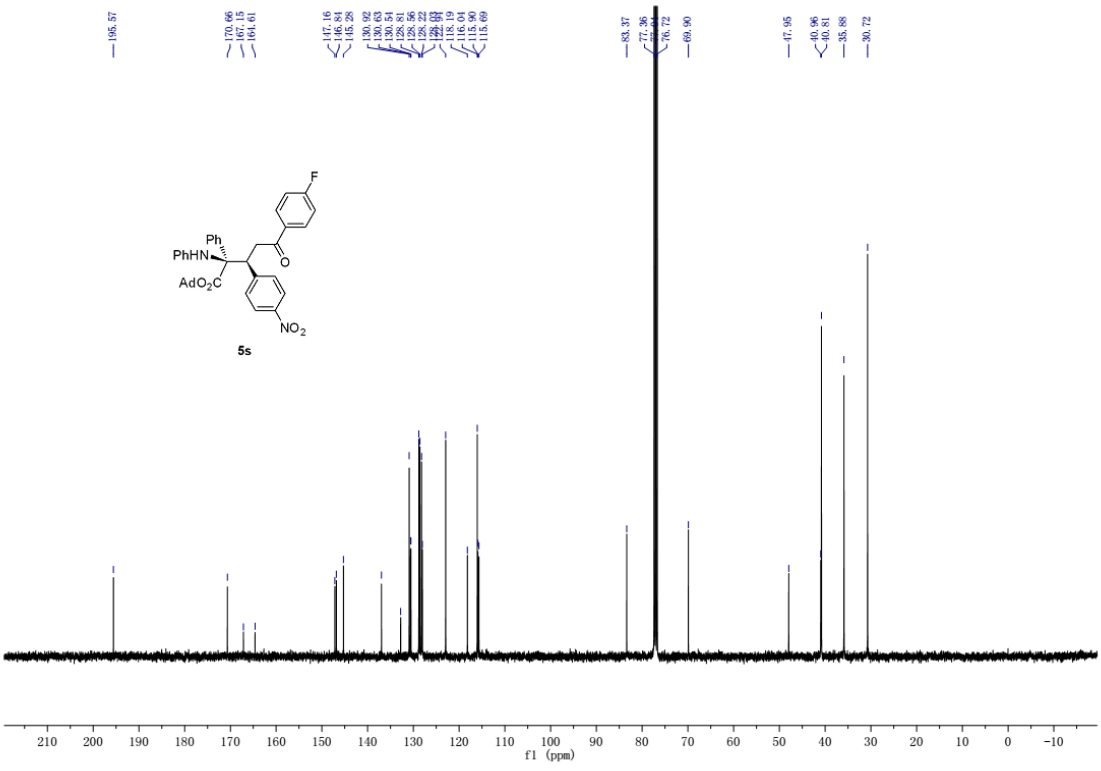
Supplementary Figure 38. ^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5r



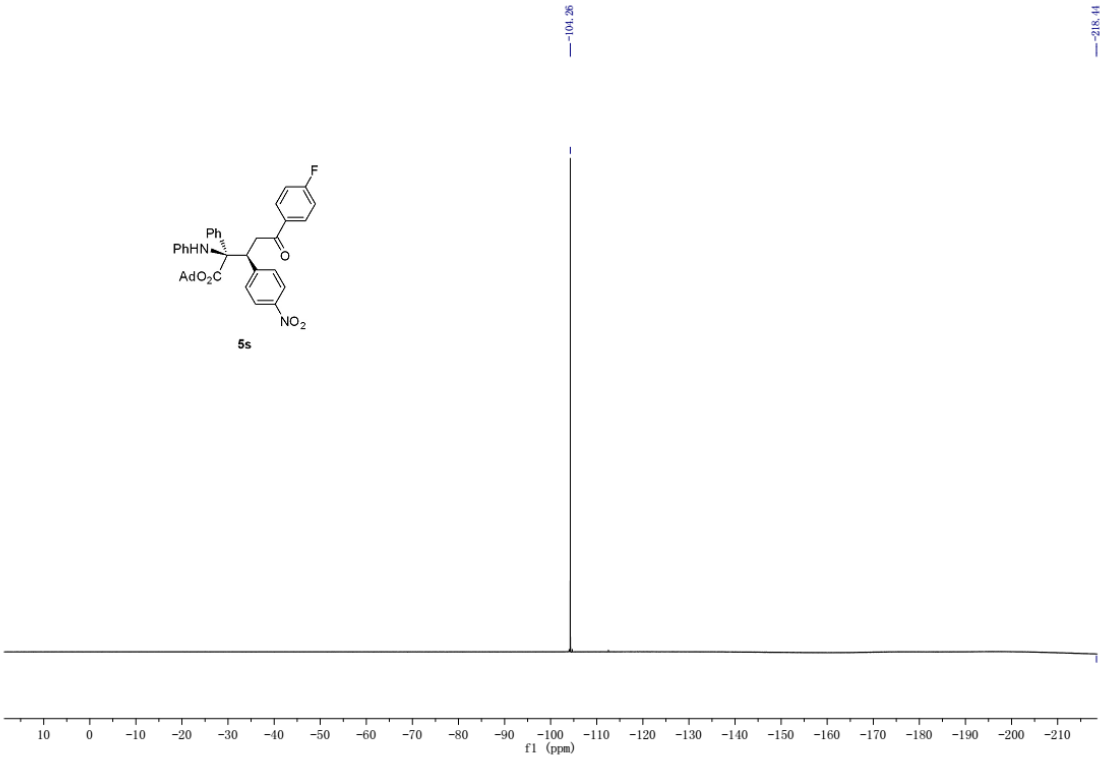
Supplementary Figure 39. ^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5r



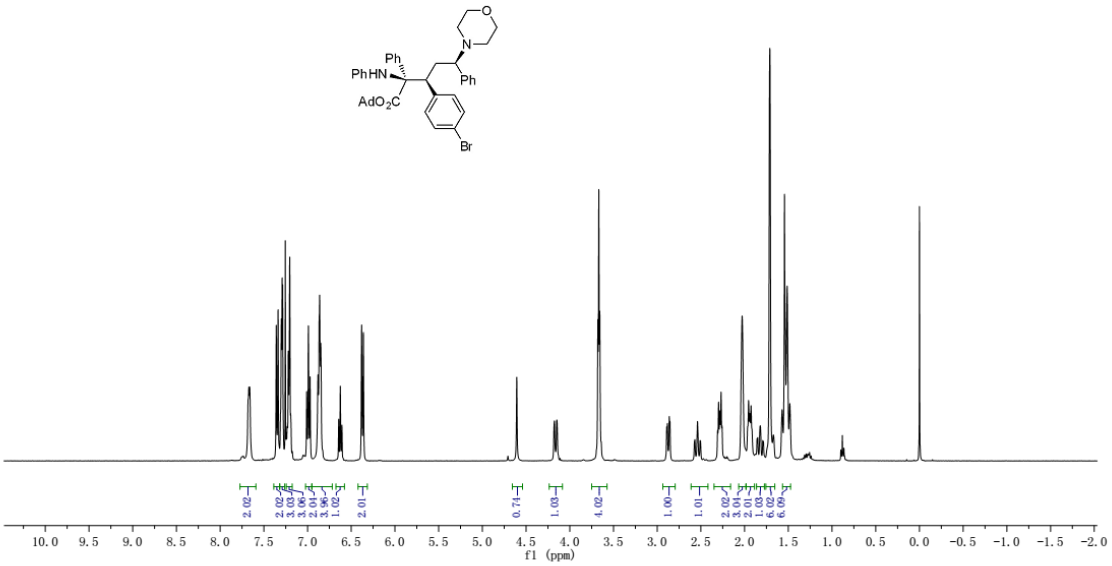
Supplementary Figure 40. ^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5s



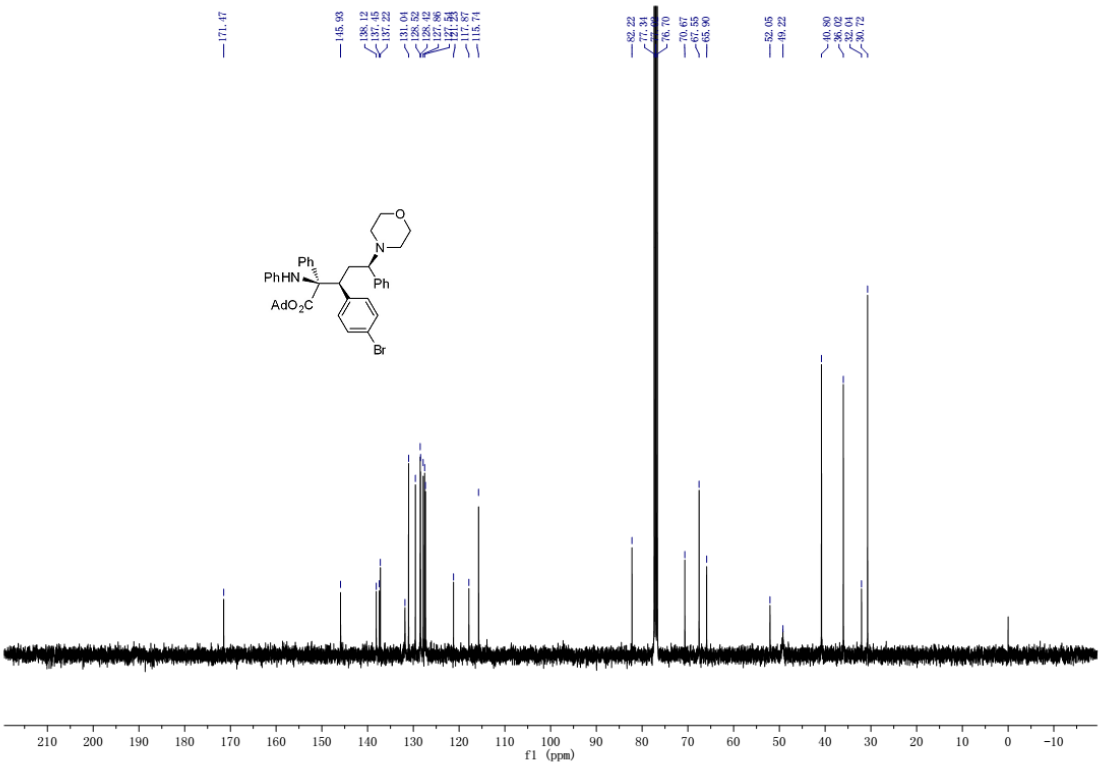
Supplementary Figure 41. ^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5s



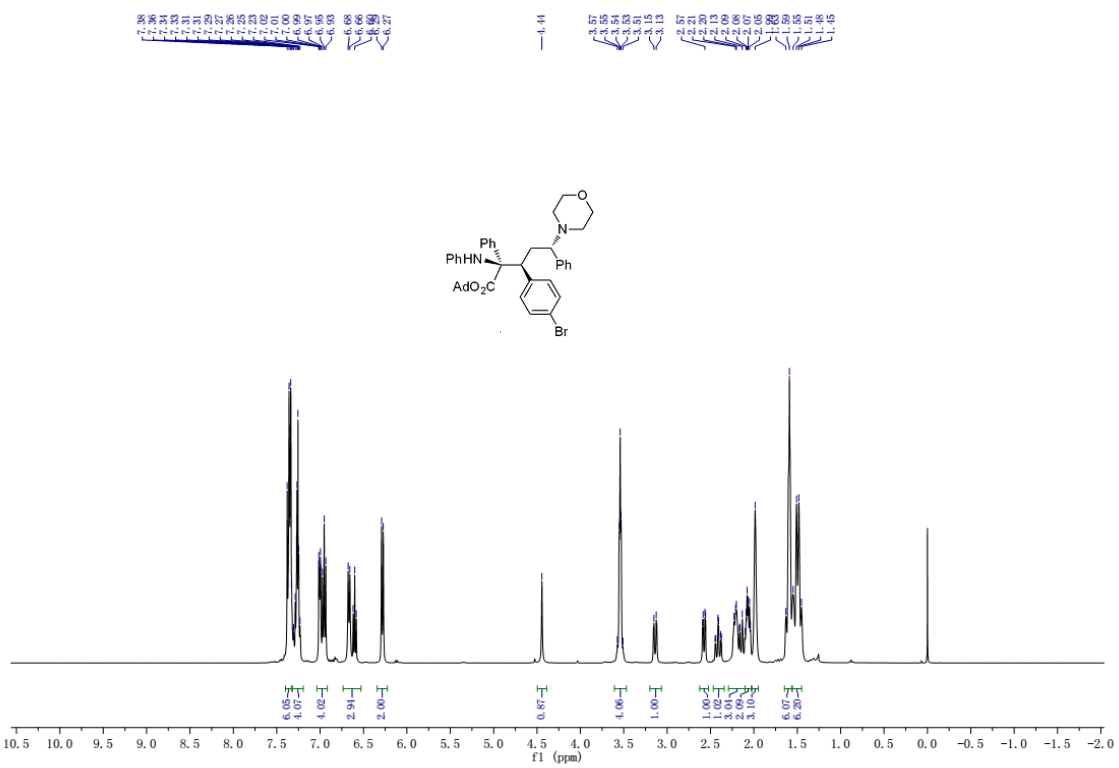
Supplementary Figure 42. ^{19}F NMR (376MHz, $CDCl_3$) spectrum for 5s



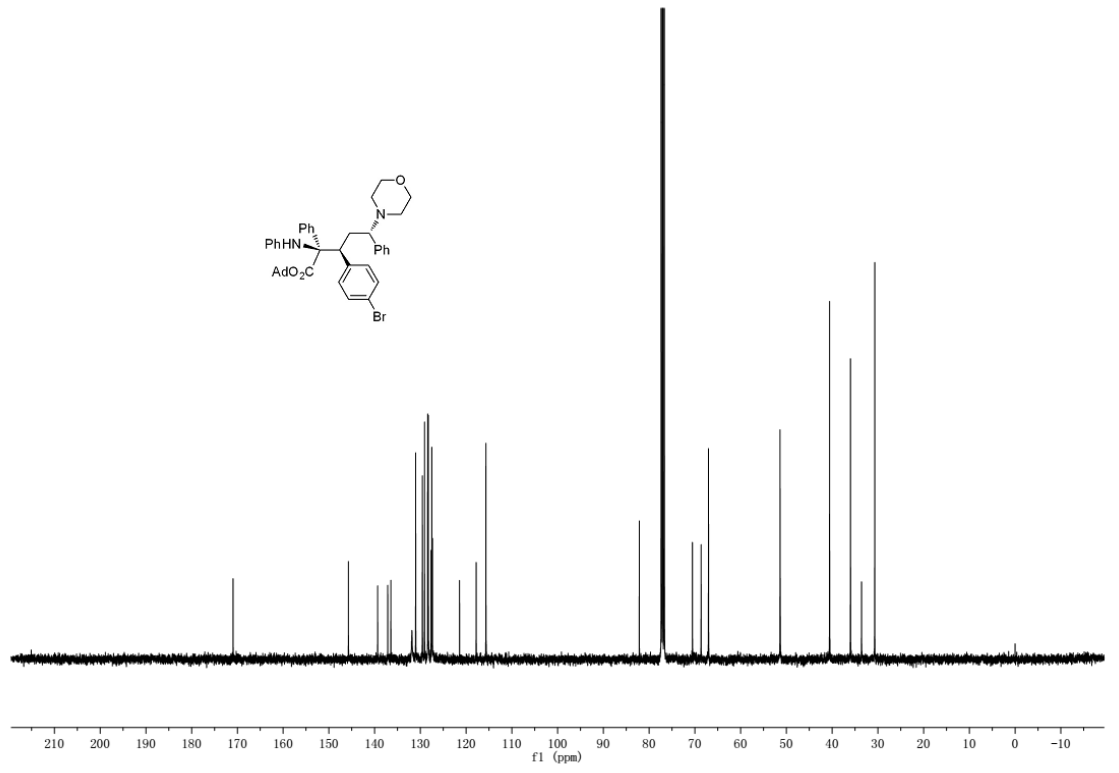
Supplementary Figure 43. ^{1}H NMR (400MHz, $CDCl_3$) spectrum for 11a



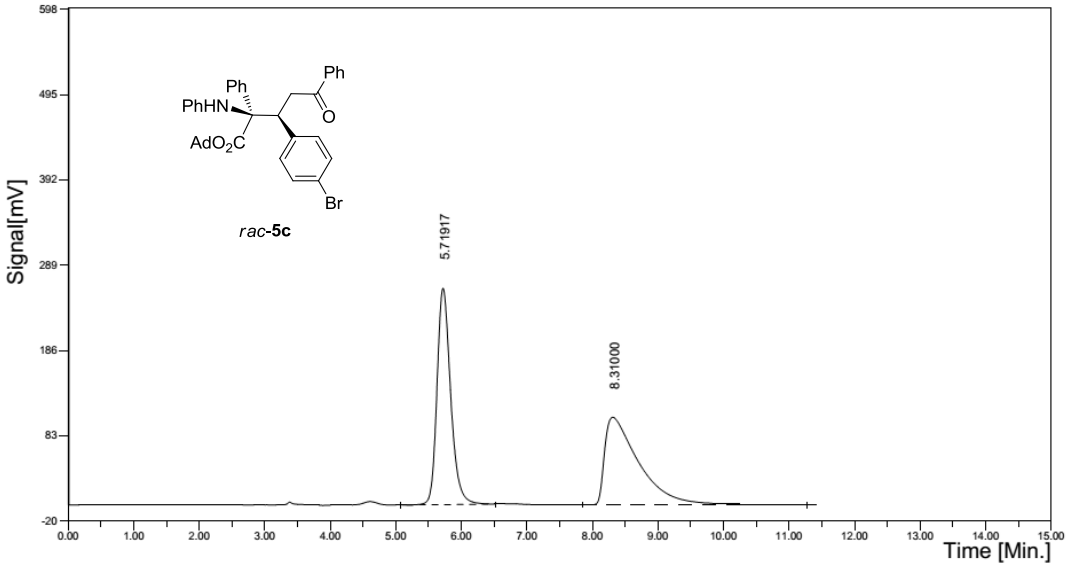
Supplementary Figure 44. ^{13}C NMR (100MHz, $CDCl_3$) spectrum for 11a



Supplementary Figure 45. ^{1}H NMR (400MHz, $CDCl_3$) spectrum for 11b

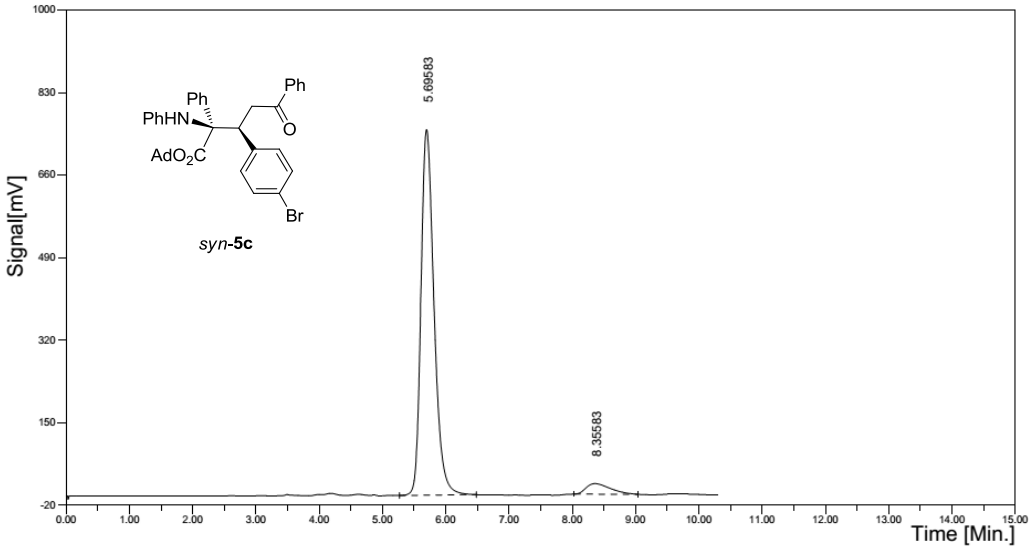


Supplementary Figure 46. ^{13}C NMR (100MHz, $CDCl_3$) spectrum for 11b



组分表

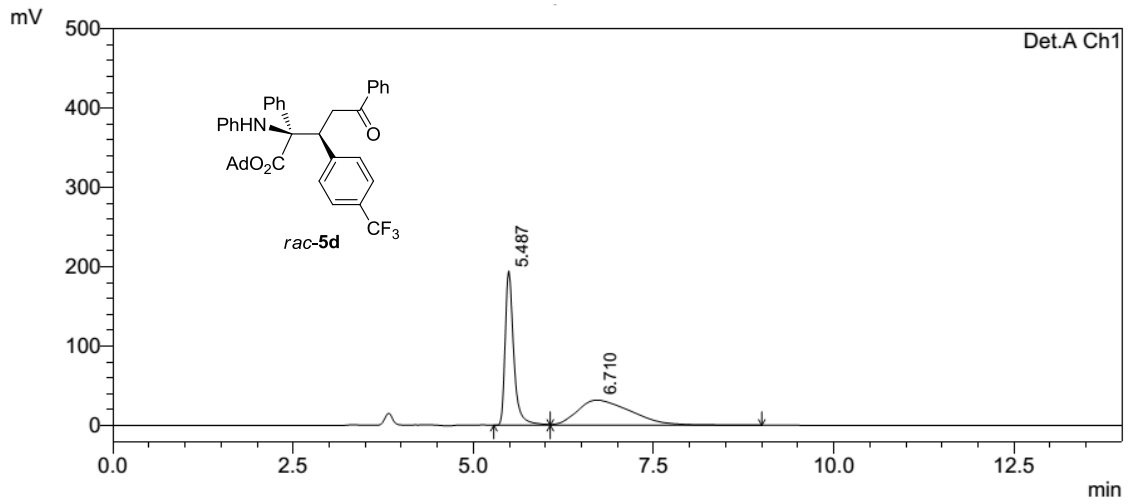
#	组分名	保留时间(min)	峰高(mV)	峰面积(mV.sec)	面积百分比(%)
1	Unknown	5.71917	261.15	3780.60	49.5839
2	Unknown	8.31000	105.76	3844.06	50.4161
合计			366.91	7624.66	100



组分表

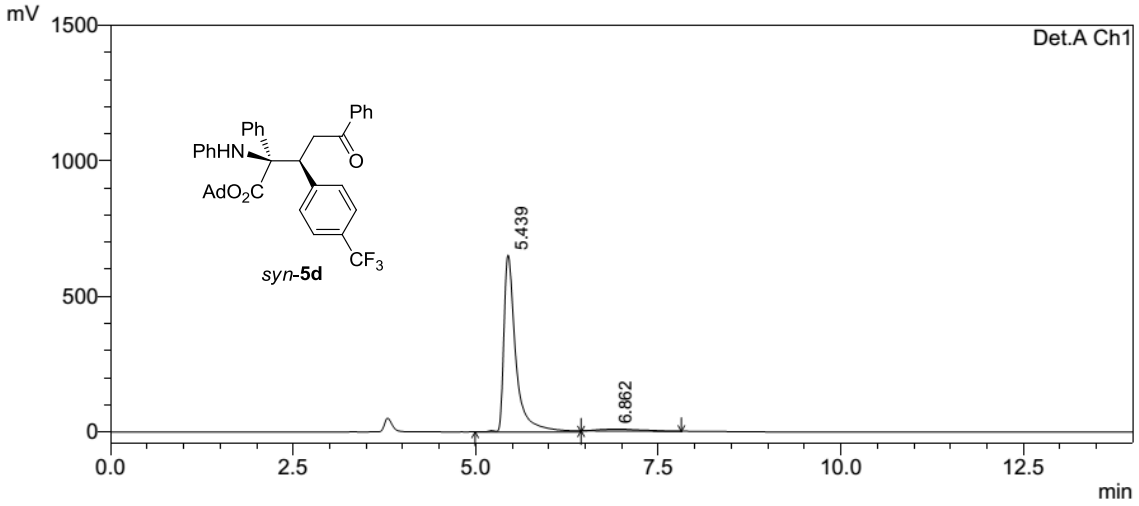
#	组分名	保留时间(min)	峰高(mV)	峰面积(mV.sec)	面积百分比(%)
1	Unknown	5.69583	752.74	10791.15	94.9074
2	Unknown	8.35583	21.74	579.04	5.0926
合计			774.48	11370.19	100

Supplementary Figure 47. Racemic (upper) and Enantioenriched (under) HPLC Traces for 5c.



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.487	1613497	194610	49.687	85.947
2	6.710	1633840	31820	50.313	14.053
Total		3247337	226431	100.000	100.000

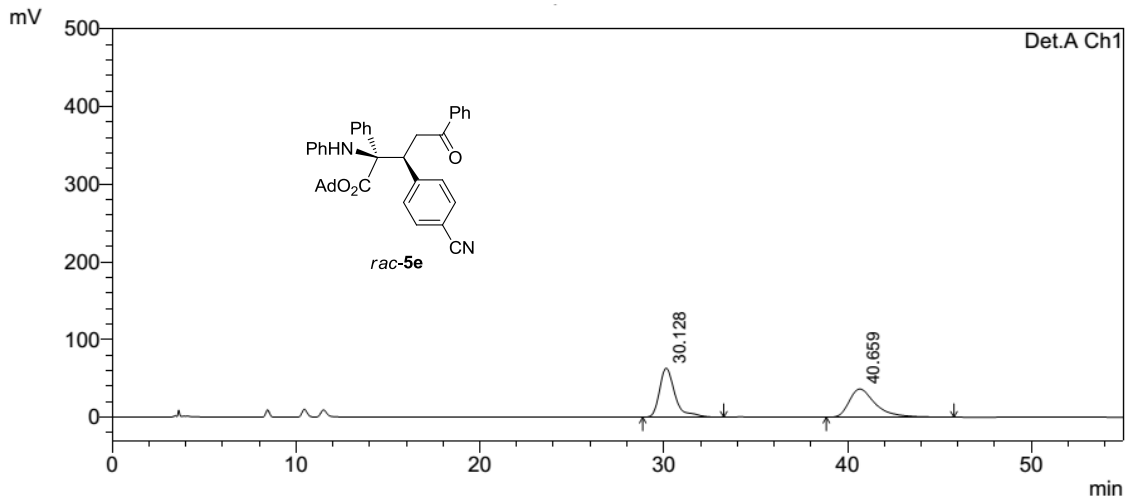


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.439	7454002	653259	96.126	98.959
2	6.862	300440	6875	3.874	1.041
Total		7754442	660134	100.000	100.000

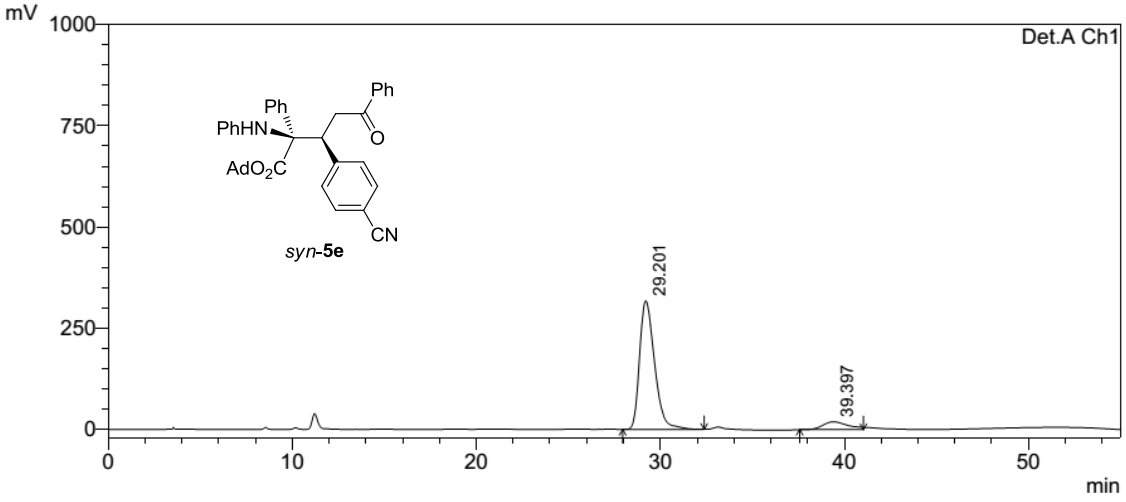
Supplementary Figure 48. Racemic (upper) and Enantioenriched (under) HPLC Traces for 5d.



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.707	6079522	118545	50.389	59.060
2	32.552	5985689	82173	49.611	40.940
Total		12065211	200718	100.000	100.000

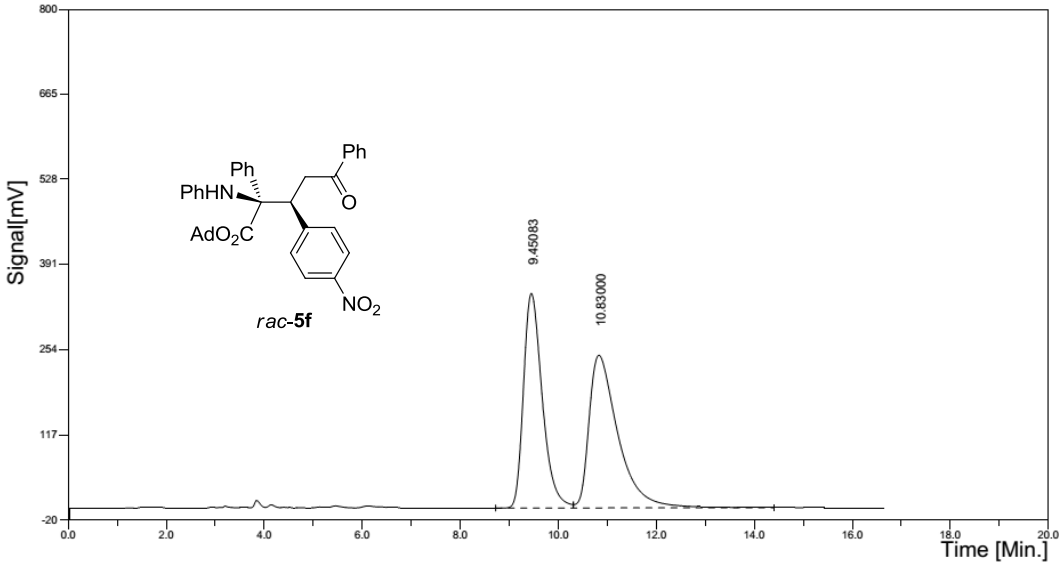


PeakTable

Detector A Ch1 254nm

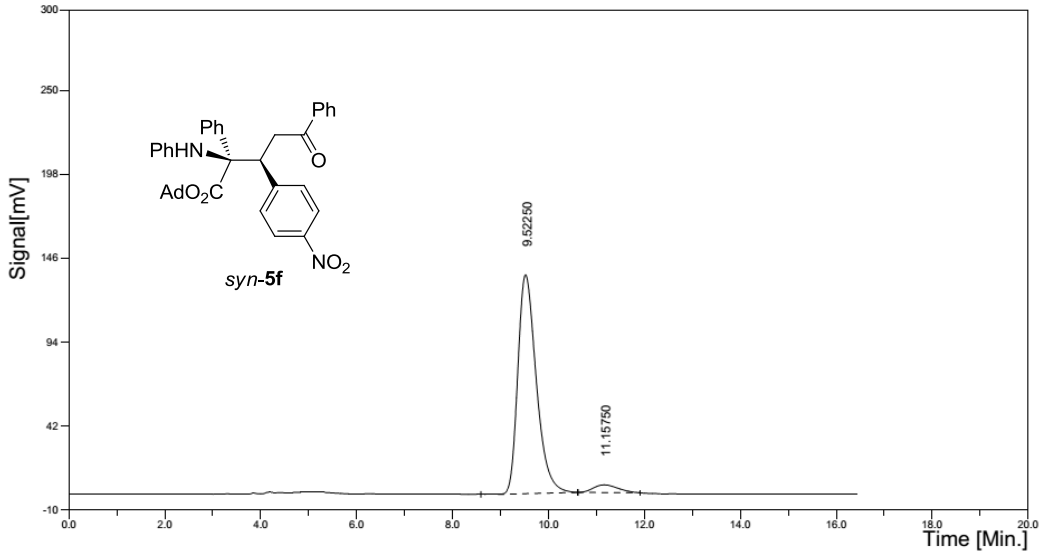
Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.201	17978593	317736	90.761	94.328
2	39.397	1830076	19105	9.239	5.672
Total		19808670	336841	100.000	100.000

Supplementary Figure 49. Racemic (upper) and Enantioenriched (under) HPLC Traces for 5e.



组分表

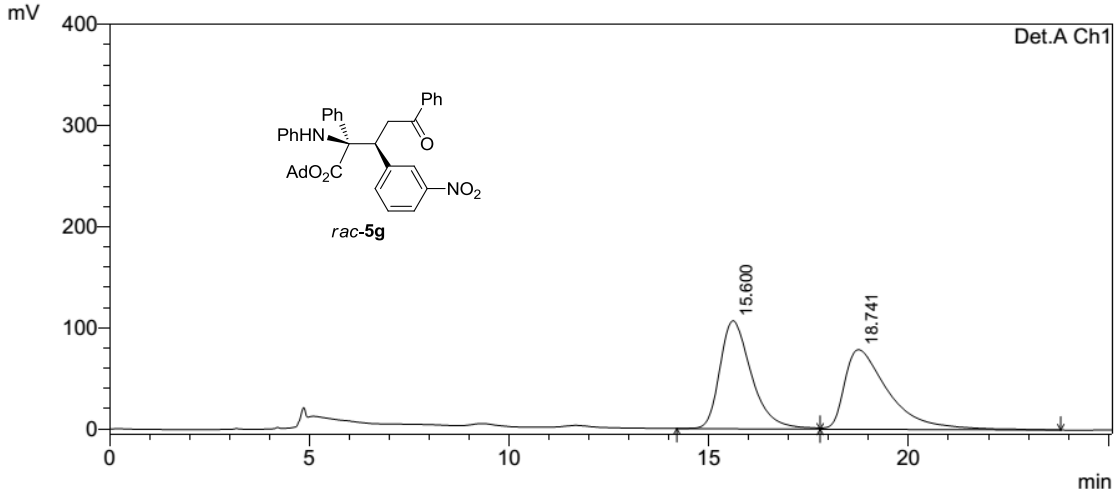
#	组分名	保留时间(min)	峰高(mV)	峰面积(mV.sec)	面积百分比(%)
1	Unknown	9.45083	344.45	9165.17	47.6229
2	Unknown	10.83000	245.12	10080.14	52.3771
合计			589.57	19245.31	100



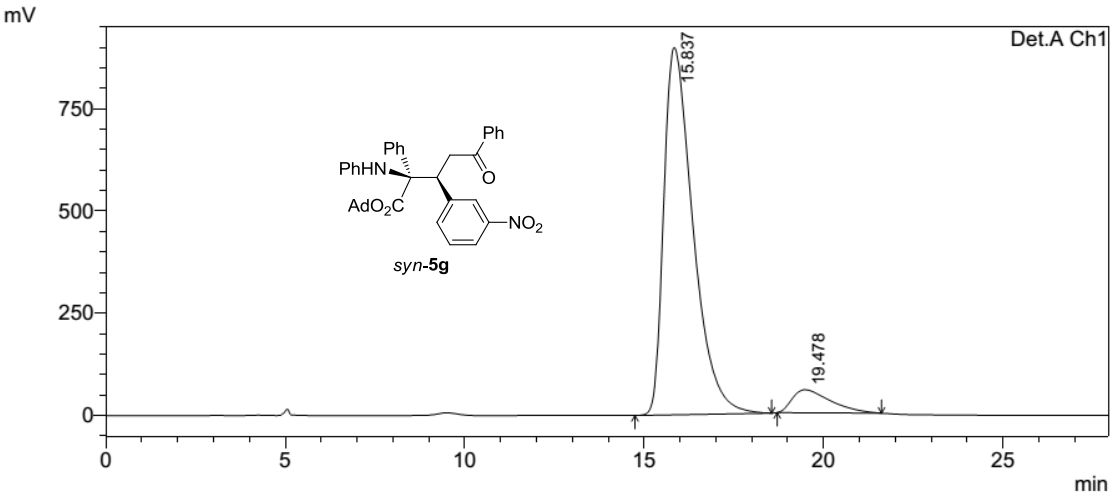
组分表

#	组分名	保留时间(min)	峰高(mV)	峰面积(mV.sec)	面积百分比(%)
1	Unknown	9.52250	135.59	3618.31	95.5065
2	Unknown	11.15750	4.76	170.24	4.4935
合计			140.35	3788.54	100

Supplementary Figure 50. Racemic (upper) and Enantioenriched (under) HPLC Traces for 5f.

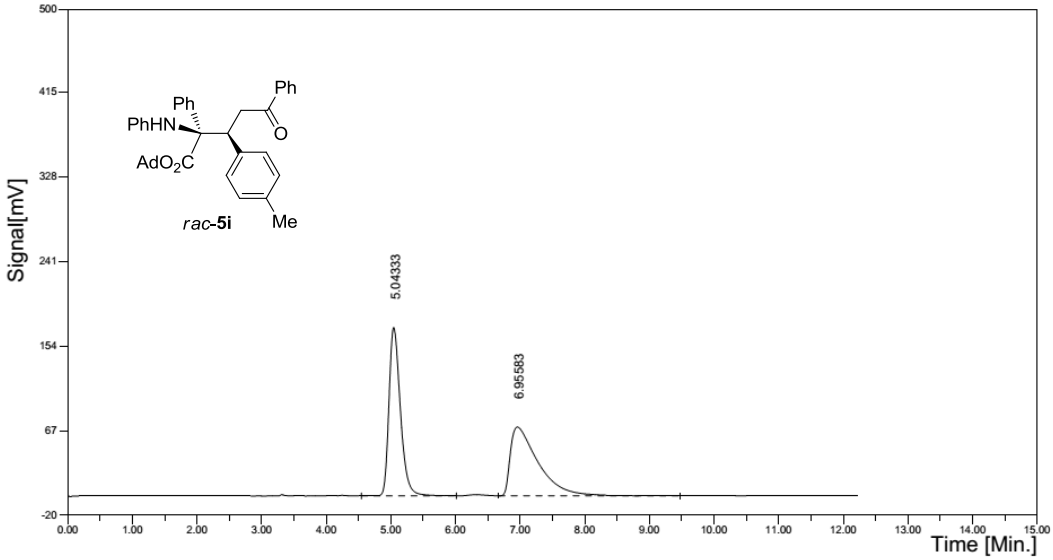


Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.600	5882471	106951	49.366	57.565
2	18.741	6033553	78840	50.634	42.435
Total		11916024	185791	100.000	100.000



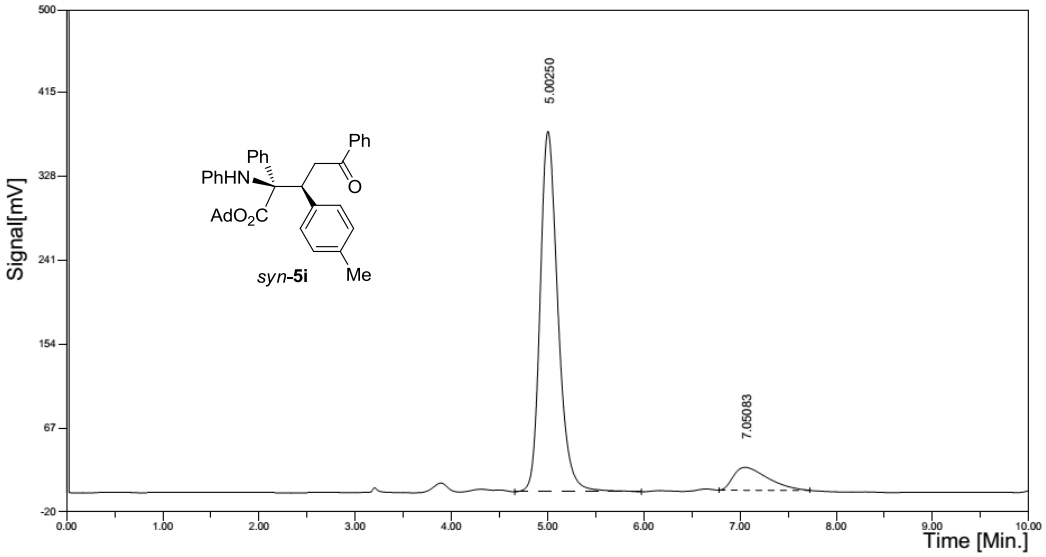
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.837	50850455	898497	92.364	94.102
2	19.478	4203863	56319	7.636	5.898
Total		55054317	954816	100.000	100.000

Supplementary Figure 51. Racemic (upper) and Enantioenriched (under) HPLC Traces for 5g.



组分表

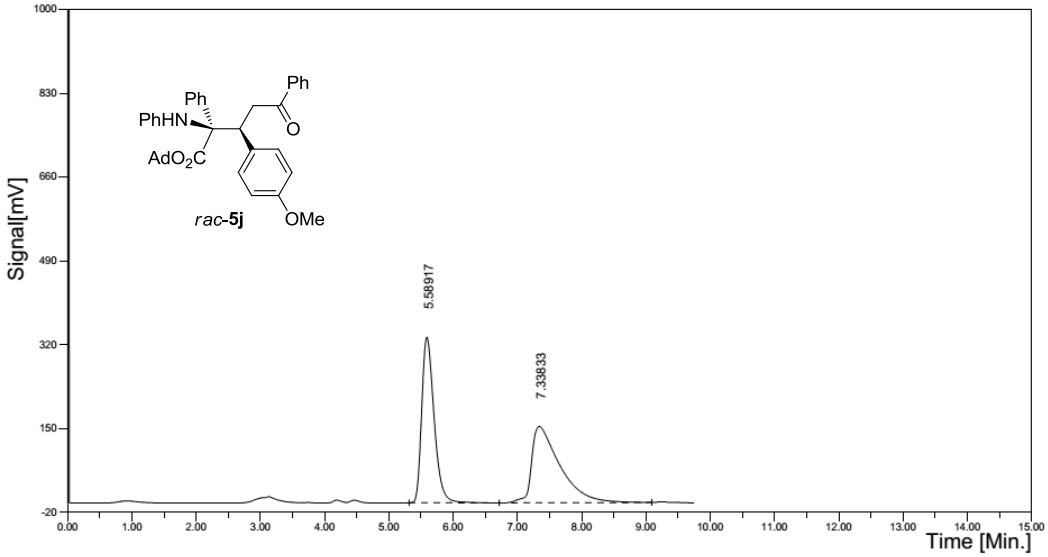
#	组分名	保留时间(min)	峰面积(mV.sec)	面积百分比(%)
1	Unknown	5.04333	2130.15	50.2019
2	Unknown	6.95583	2113.01	49.7981
合计			4243.16	100



组分表

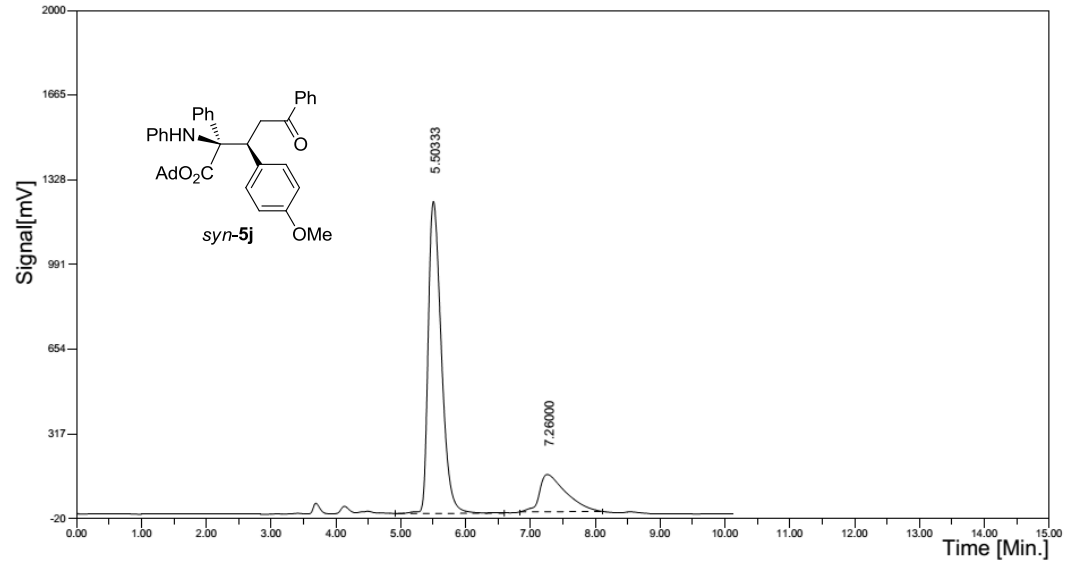
#	组分名	保留时间(min)	峰高(mV)	峰面积(mV.sec)	面积百分比(%)
1	Unknown	5.00250	373.56	4806.11	89.0627
2	Unknown	7.05083	23.72	590.21	10.9373
合计			397.28	5396.32	100

Supplementary Figure 52. Racemic (upper) and Enantioenriched (under) HPLC Traces for 5i.



组分表

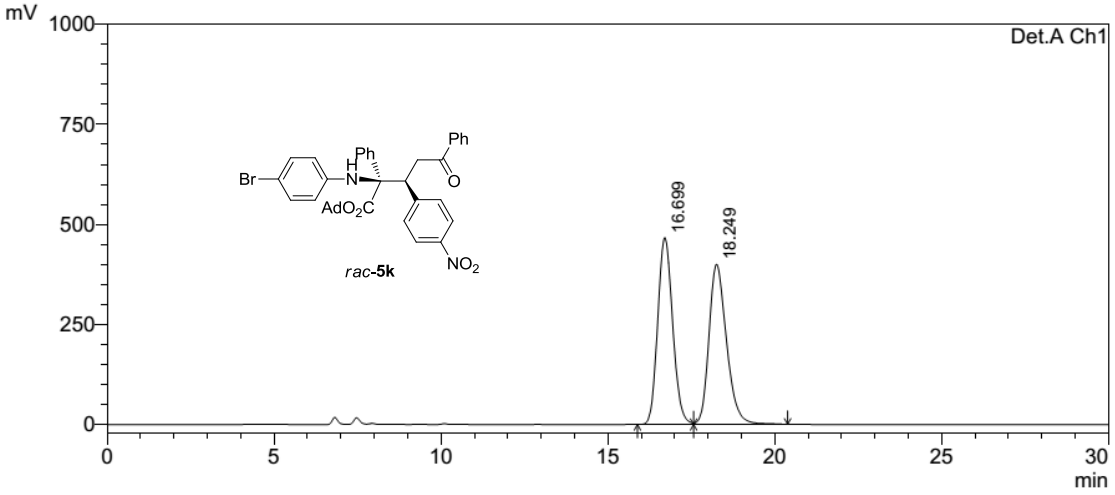
#	组分名	保留时间(min)	峰面积(mV.sec)	面积百分比(%)
1	Unknown	5.58917	4469.52	48.8083
2	Unknown	7.33833	4687.78	51.1917
合计			9157.30	100



组分表

#	组分名	保留时间(min)	峰面积(mV.sec)	面积百分比(%)
1	Unknown	5.50333	17408.27	80.5485
2	Unknown	7.26000	4203.88	19.4515
合计			21612.15	100

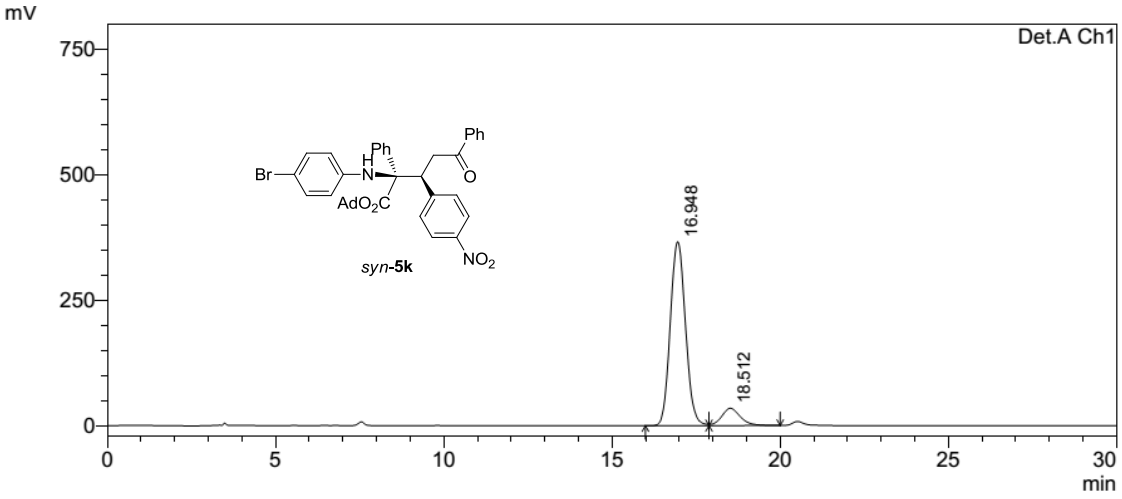
Supplementary Figure 53. Racemic (upper) and Enantioenriched (under) HPLC Traces for 5j.



PeakTable

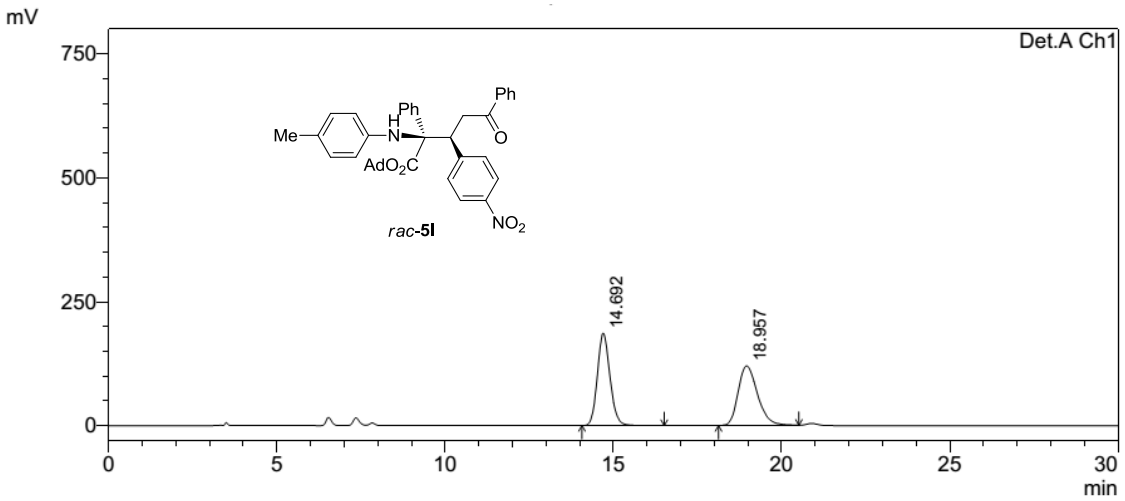
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.699	14519789	467081	49.881	53.857
2	18.249	14589280	400180	50.119	46.143
Total		29109069	867262	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.948	11511287	366736	89.764	91.406
2	18.512	1312621	34480	10.236	8.594
Total		12823908	401216	100.000	100.000

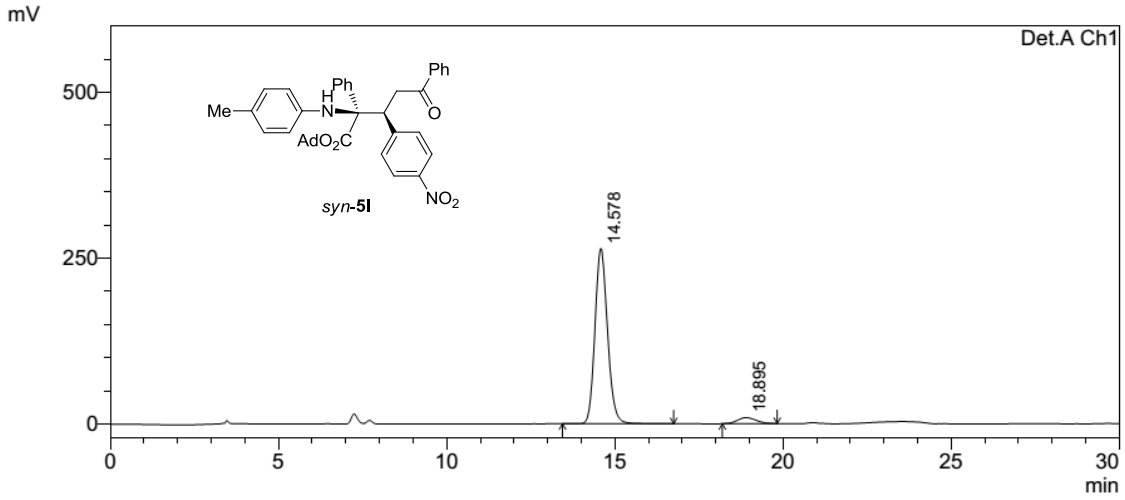
Supplementary Figure 54. Racemic (upper) and Enantioenriched (under) HPLC Traces for 5k.



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.692	4832852	186465	50.202	60.741
2	18.957	4793880	120520	49.798	39.259
Total		9626732	306985	100.000	100.000

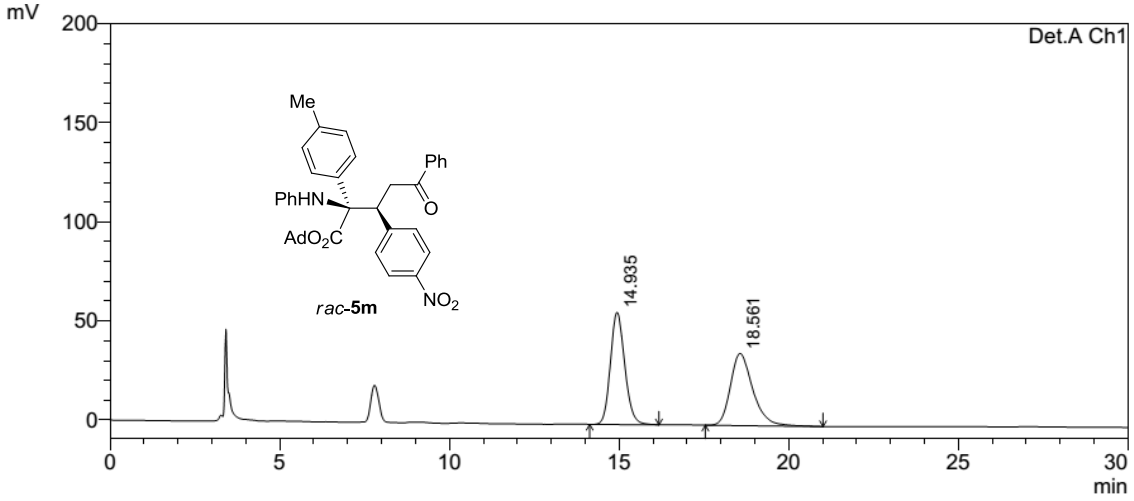


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.578	6841717	264277	95.100	96.659
2	18.895	352490	9134	4.900	3.341
Total		7194208	273411	100.000	100.000

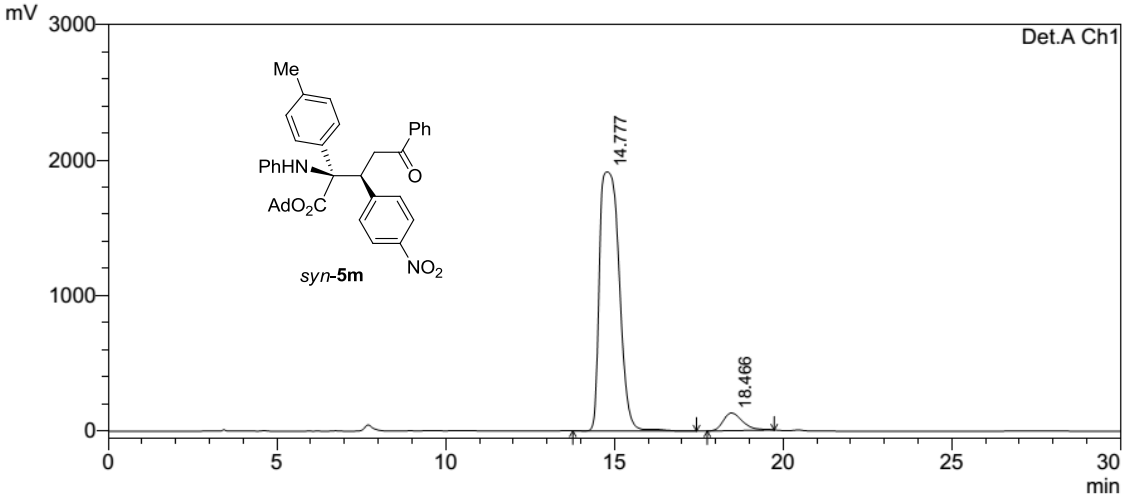
Supplementary Figure 55. Racemic (upper) and Enantioenriched (under) HPLC Traces for 5l.



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.935	1669171	56607	49.866	60.854
2	18.561	1678134	36413	50.134	39.146
Total		3347305	93020	100.000	100.000

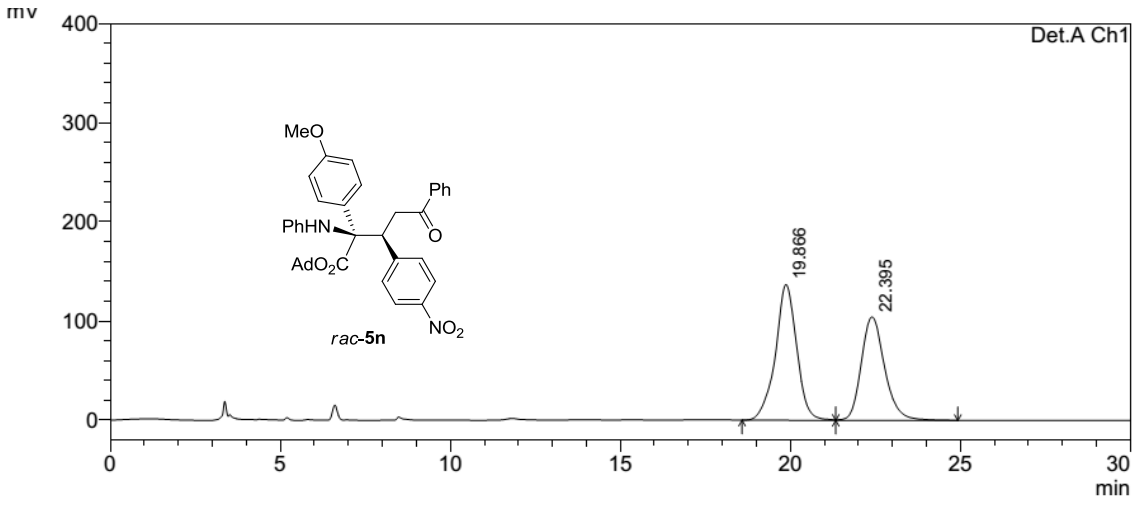


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.777	77619768	1912432	93.692	93.632
2	18.466	5225603	130062	6.308	6.368
Total		82845371	2042494	100.000	100.000

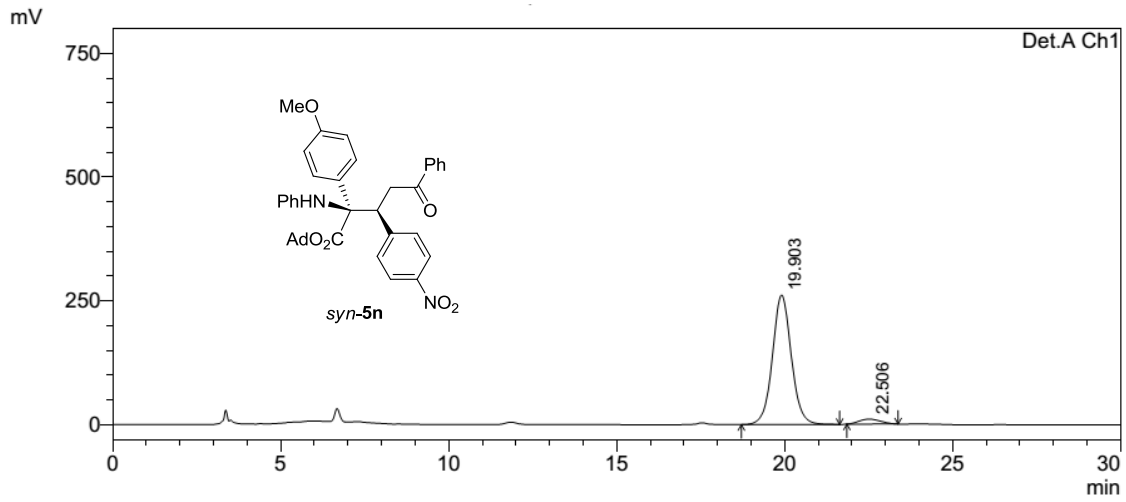
Supplementary Figure 56. Racemic (upper) and Enantioenriched (under) HPLC Traces for 5m.



PeakTable

Detector A Ch1 254nm

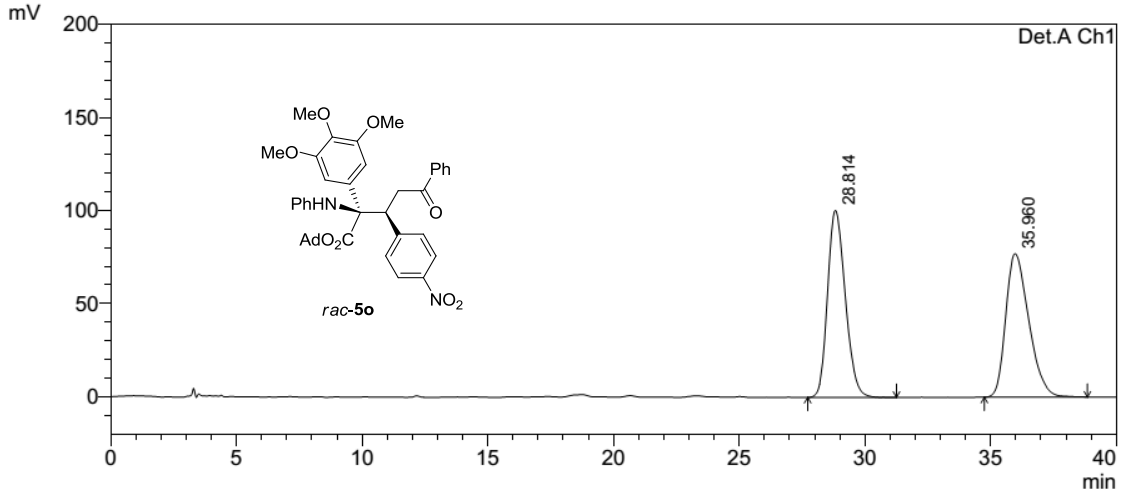
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.866	5957897	136857	54.407	56.752
2	22.395	4992767	104292	45.593	43.248
Total		10950664	241149	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.903	10242486	261749	95.812	96.301
2	22.506	447690	10055	4.188	3.699
Total		10690176	271804	100.000	100.000

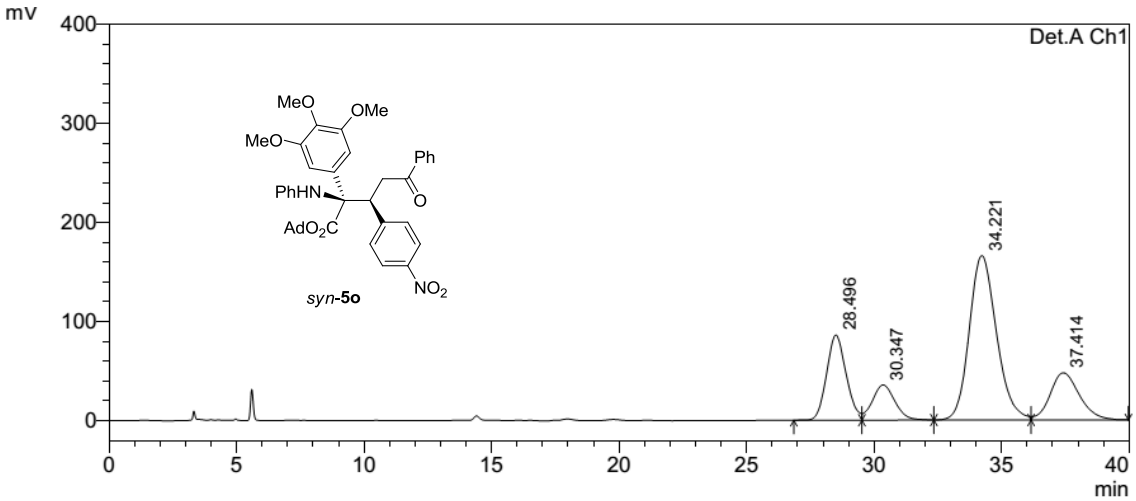
Supplementary Figure 57. Racemic (upper) and Enantioenriched (under) HPLC Traces for 5n.



PeakTable

Detector A Ch1 254nm

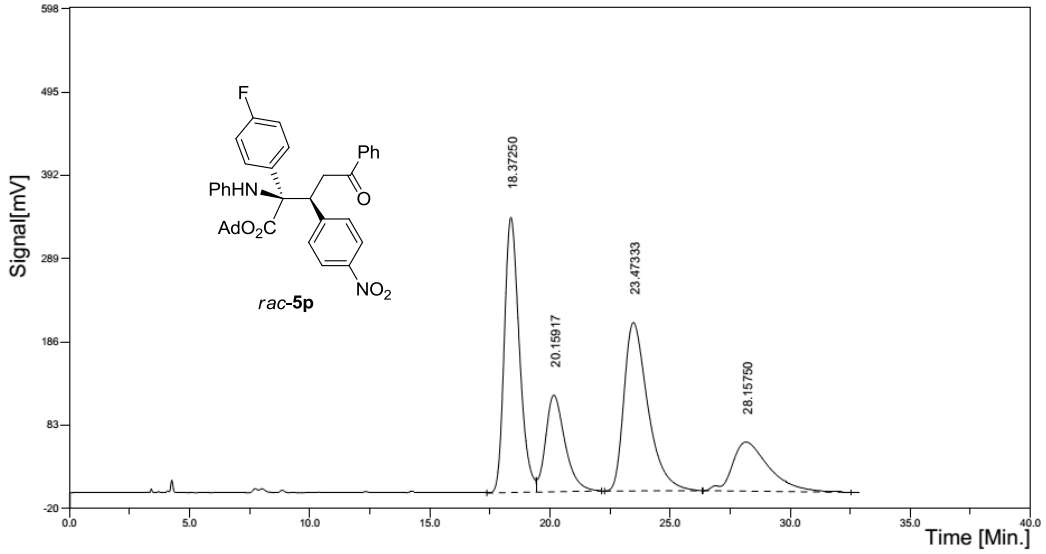
Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.814	4915782	100478	49.974	56.563
2	35.960	4920988	77162	50.026	43.437
Total		9836770	177639	100.000	100.000



Detector A Ch1 254nm

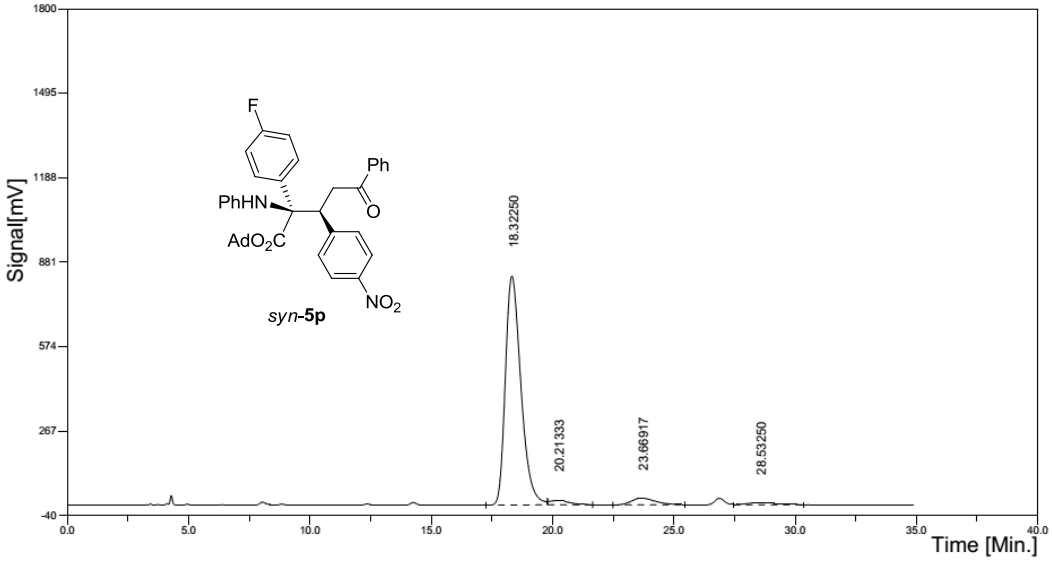
Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.496	4573494	86024	19.987	25.670
2	30.347	2181909	35512	9.535	10.597
3	34.221	12325109	165991	53.862	49.533
4	37.414	3802067	47588	16.616	14.200
Total		22882579	335115	100.000	100.000

Supplementary Figure 58. Racemic (upper) and Enantioenriched (under) HPLC Traces for 5o.



组分表

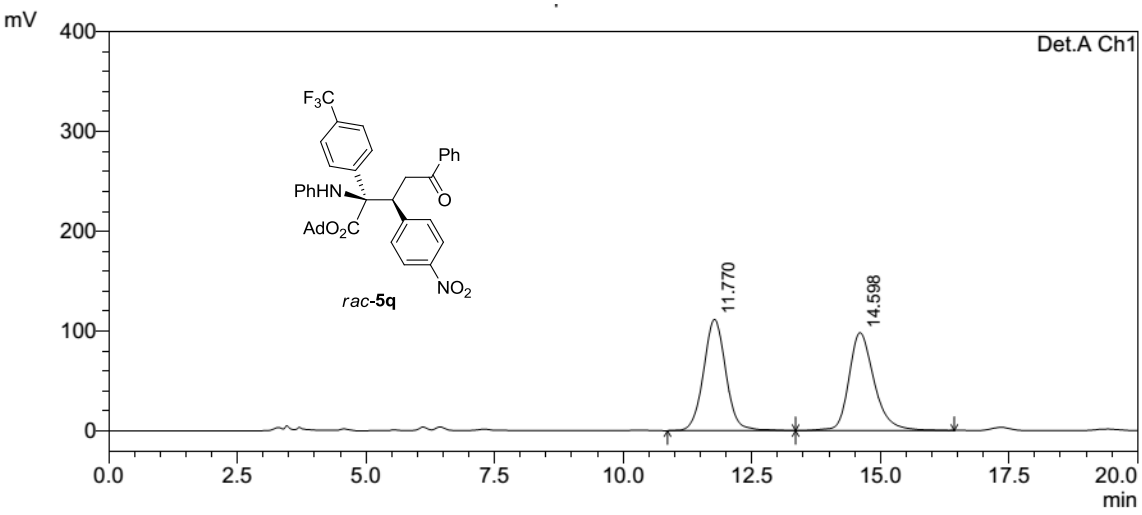
#	组分名	保留时间(min)	峰高(mV)	峰面积(mV. sec)	面积百分比(%)	样品含量(%)
1	Unknown	18. 37250	340. 09	14796. 35	34. 9050	0. 0000
2	Unknown	20. 15917	119. 37	6721. 79	15. 8569	0. 0000
3	Unknown	23. 47333	208. 24	14441. 80	34. 0686	0. 0000
4	Unknown	28. 15750	60. 71	6430. 40	15. 1695	100. 0000
合计			728. 41	42390. 34	100	



组分表

#	组分名	保留时间(min)	峰高(mV)	峰面积(mV. sec)	面积百分比(%)
1	Unknown	18. 32250	831. 28	37080. 48	92. 1988
2	Unknown	20. 21333	16. 25	900. 04	2. 2379
3	Unknown	23. 66917	24. 25	1653. 98	4. 1125
4	Unknown	28. 53250	6. 87	583. 48	1. 4508
合计			878. 65	40217. 98	100

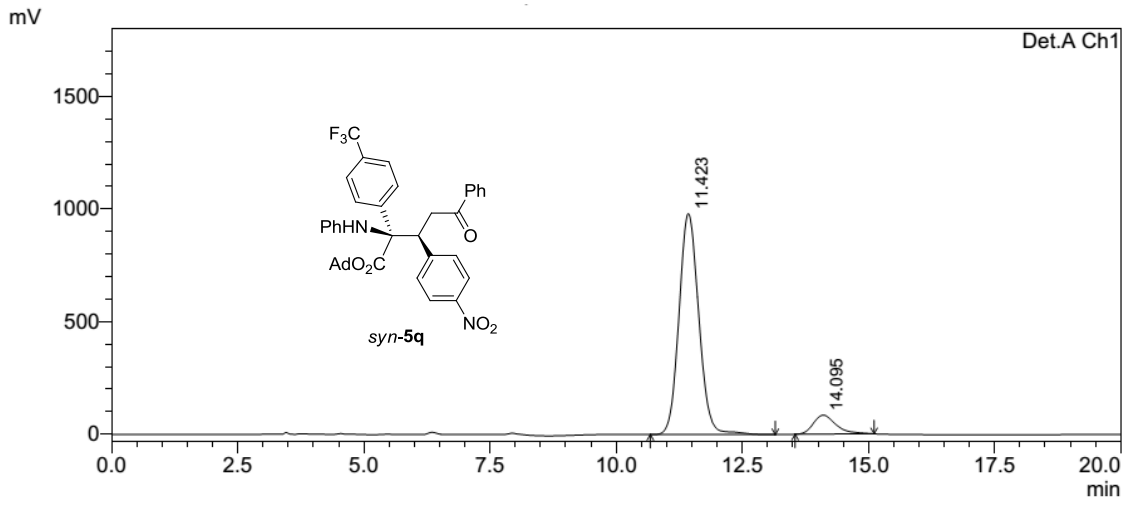
Supplementary Figure 59. Racemic (upper) and Enantioenriched (under) HPLC Traces for 5p.



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.770	3360887	111672	50.123	53.226
2	14.598	3344350	98134	49.877	46.774
Total		6705237	209806	100.000	100.000

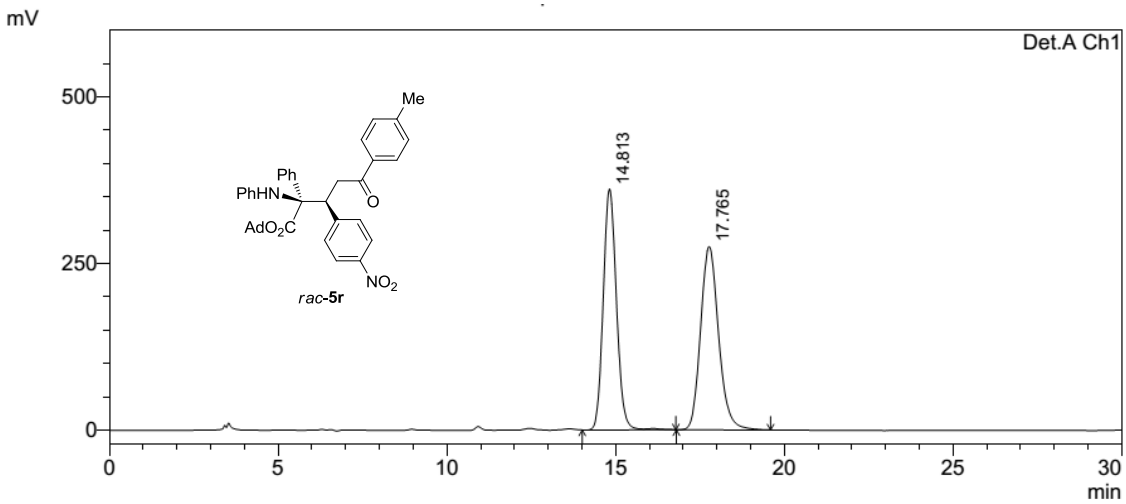


PeakTable

Detector A Ch1 254nm

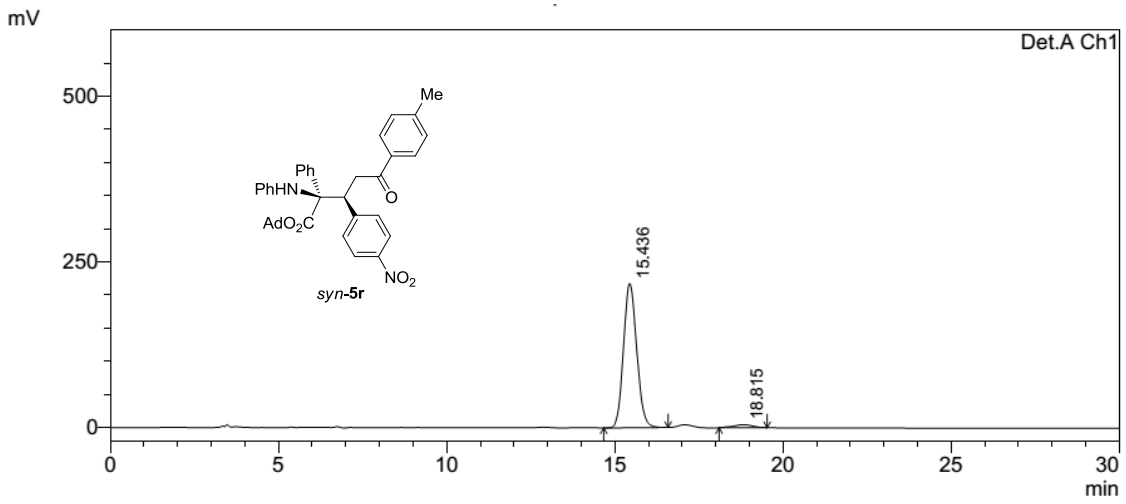
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.423	26800719	981177	91.036	92.096
2	14.095	2638948	84213	8.964	7.904
Total		29439667	1065390	100.000	100.000

Supplementary Figure 60. Racemic (upper) and Enantioenriched (under) HPLC Traces for 5q.



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.813	9847174	361677	49.116	56.818
2	17.765	10201746	274882	50.884	43.182
Total		20048921	636559	100.000	100.000

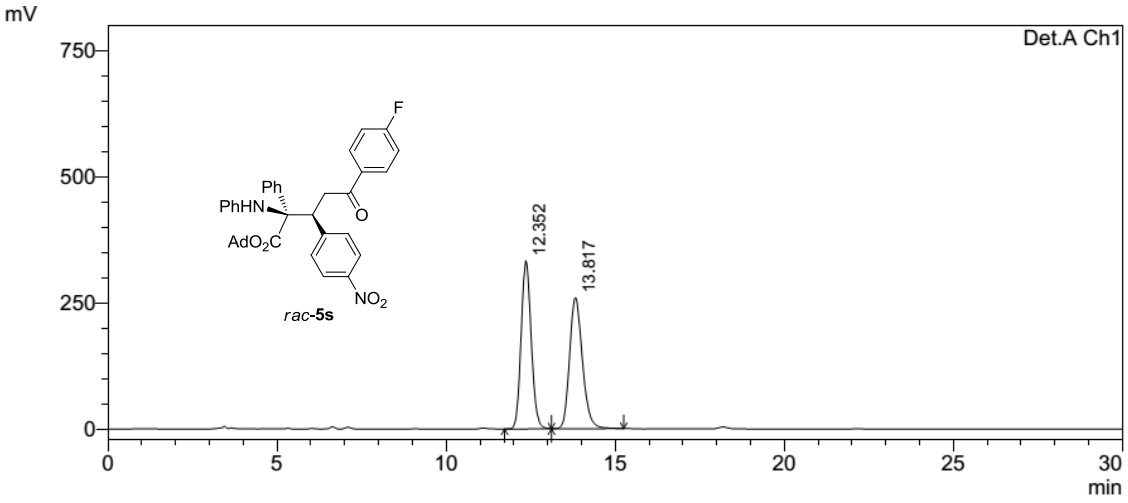


PeakTable

Detector A Ch1 254nm

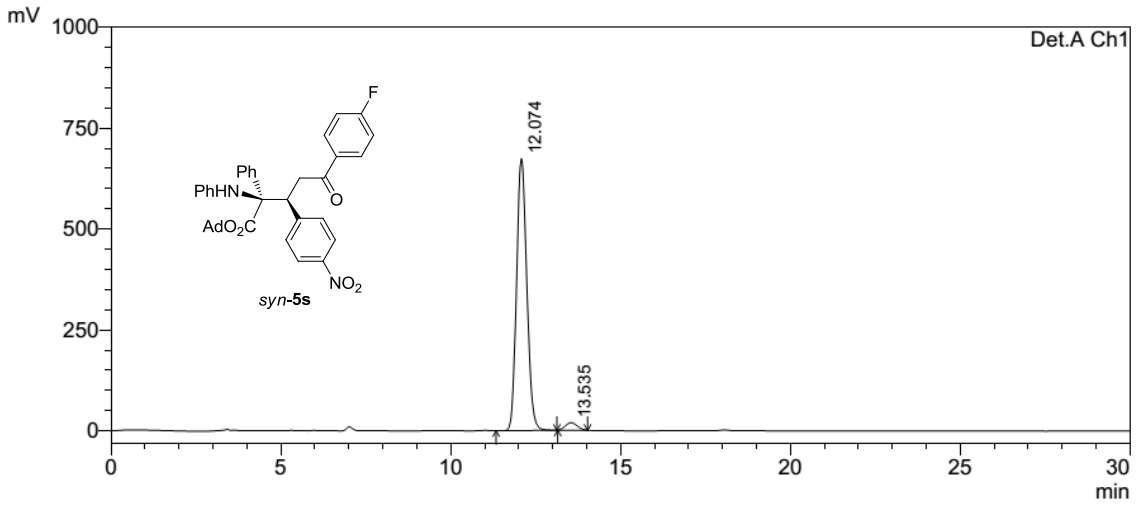
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.436	5949027	217885	96.972	97.922
2	18.815	185741	4624	3.028	2.078
Total		6134767	222509	100.000	100.000

Supplementary Figure 61. Racemic (upper) and Enantioenriched (under) HPLC Traces for 5r.



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.352	6933843	333912	50.124	56.207
2	13.817	6899638	260167	49.876	43.793
Total		13833481	594079	100.000	100.000

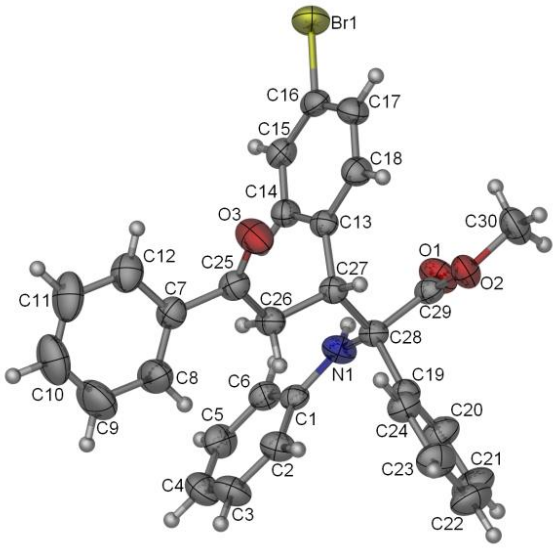


PeakTable

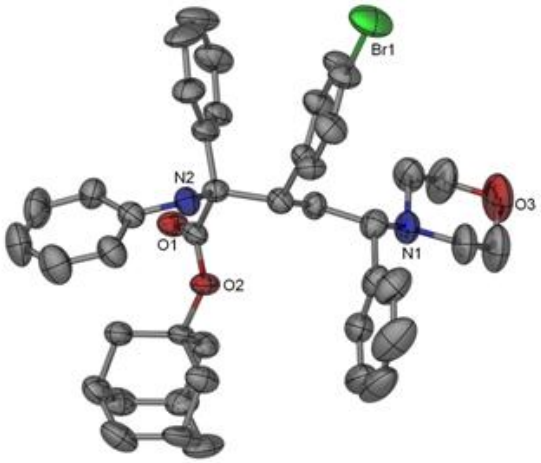
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.074	14067276	674269	96.907	97.318
2	13.535	448954	18585	3.093	2.682
Total		14516230	692854	100.000	100.000

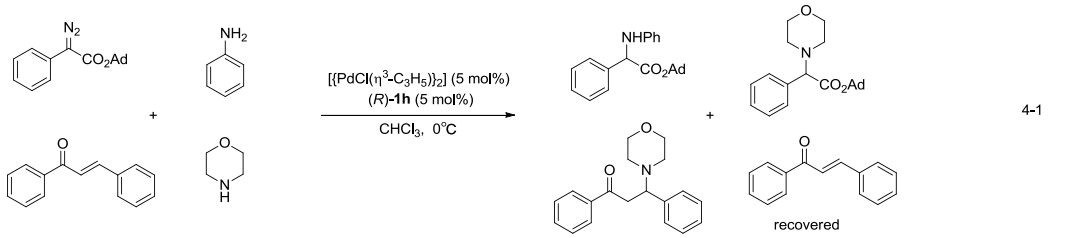
Supplementary Figure 62. Racemic (upper) and Enantioenriched (under) HPLC Traces for 5s.

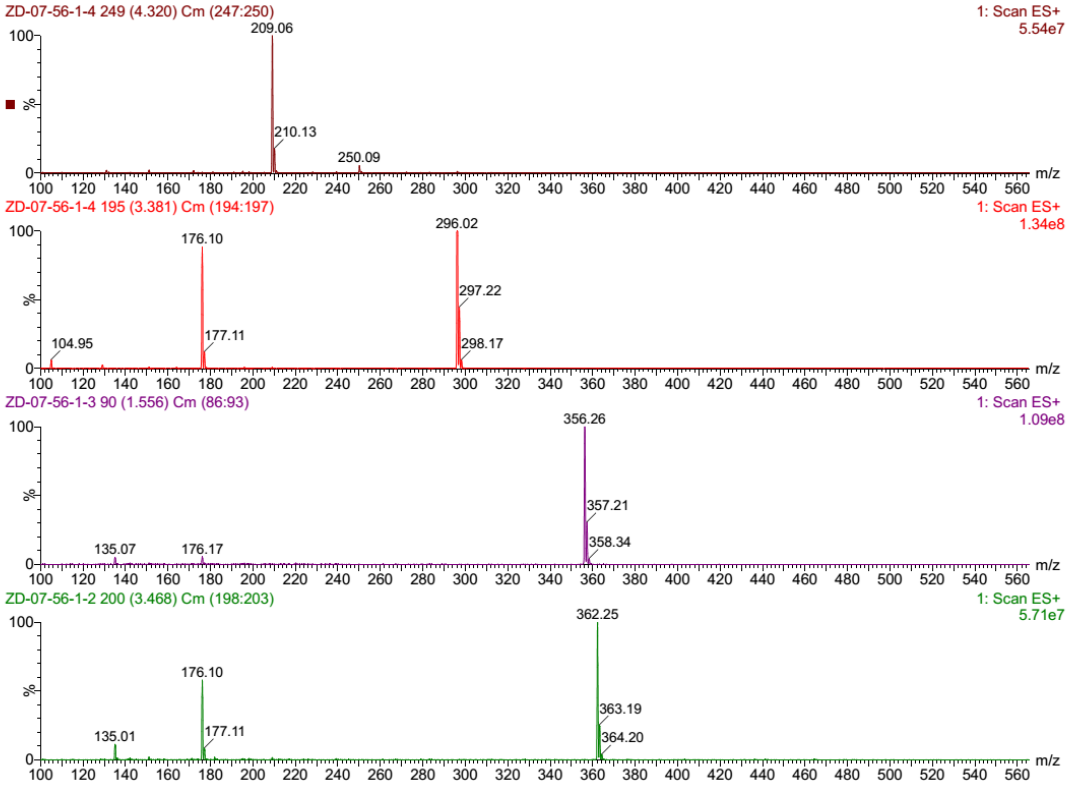


Supplementary Figure 63. Molecular structure and atom numbering scheme for 5a. (CCDC 981292)

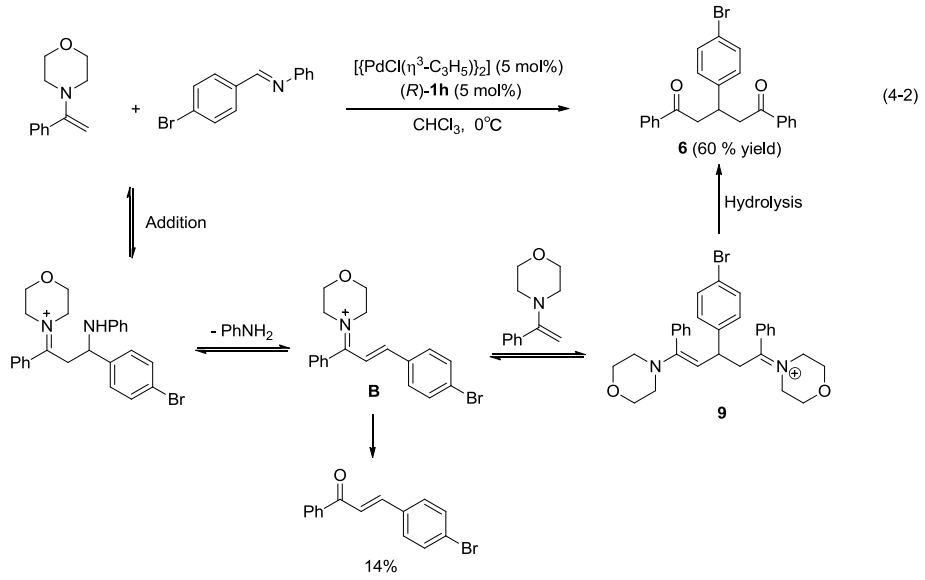


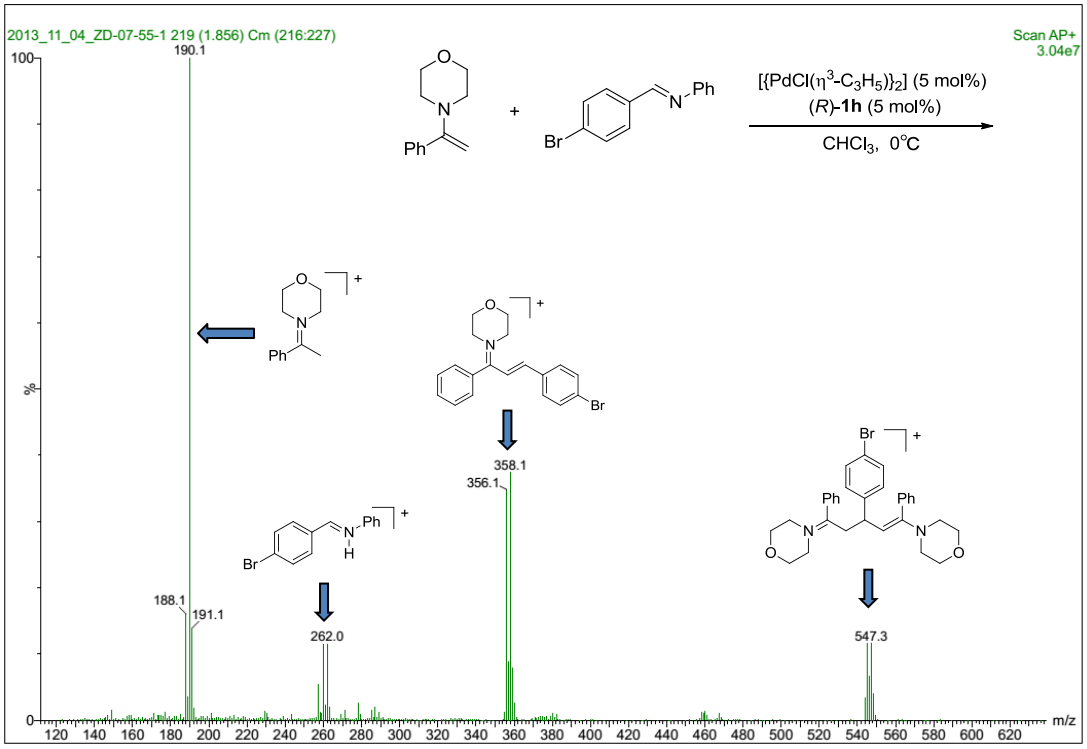
Supplementary Figure 64. Molecular structure and atom numbering scheme for 11b. (CCDC 999727)



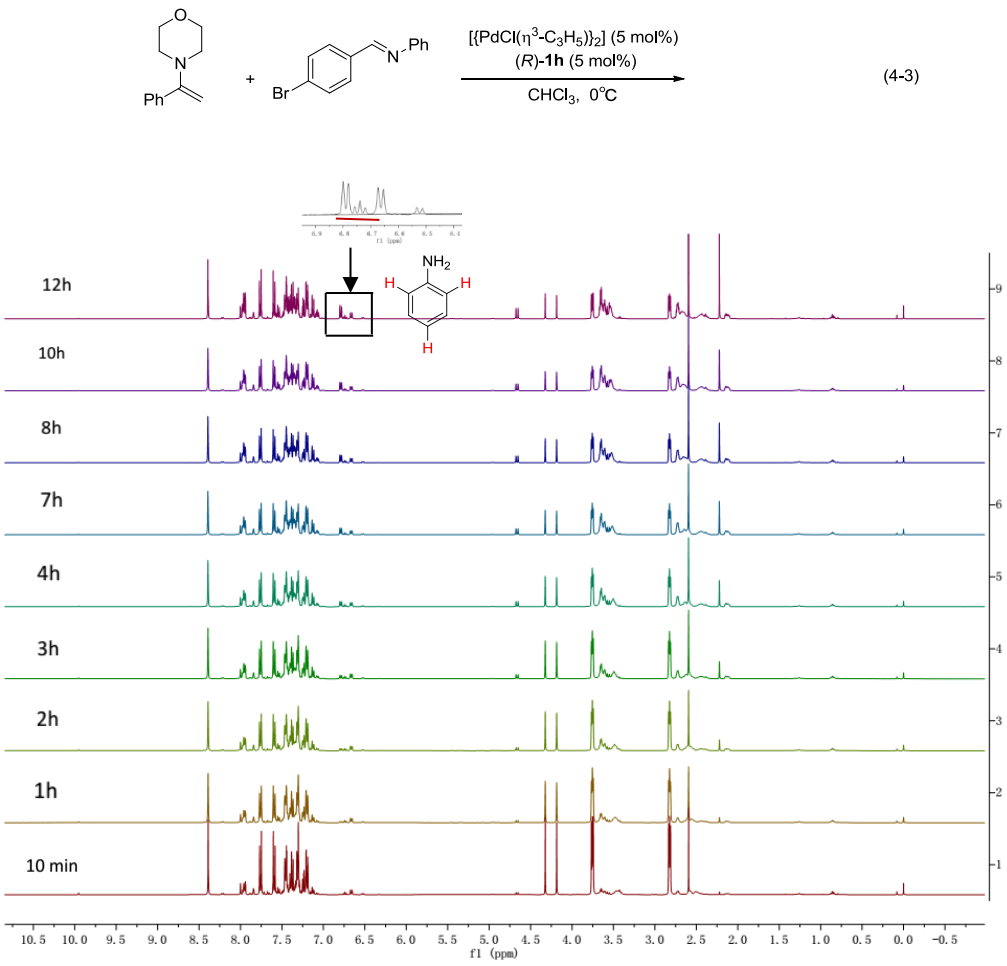


Supplementary Figure 65. Species detection of eq. (4-1) by LC-MS. In the equation 4-2, morpholine was used to activate the chalcone under the standard condition. No desired product 5 was detected as well. N-H insertion product from diazo compound and aniline, 1,4-addition product of morpholine to chalcone were detected by LC-MS. In this reaction, palladium catalyst was poisoned by morpholine leading to slow decomposition of diazo compound and the reaction became more complicated.

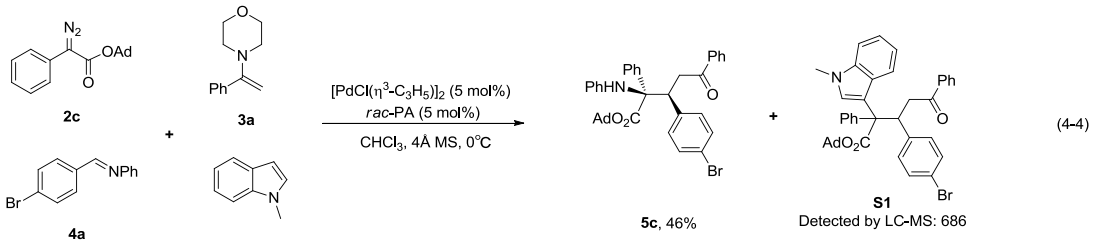


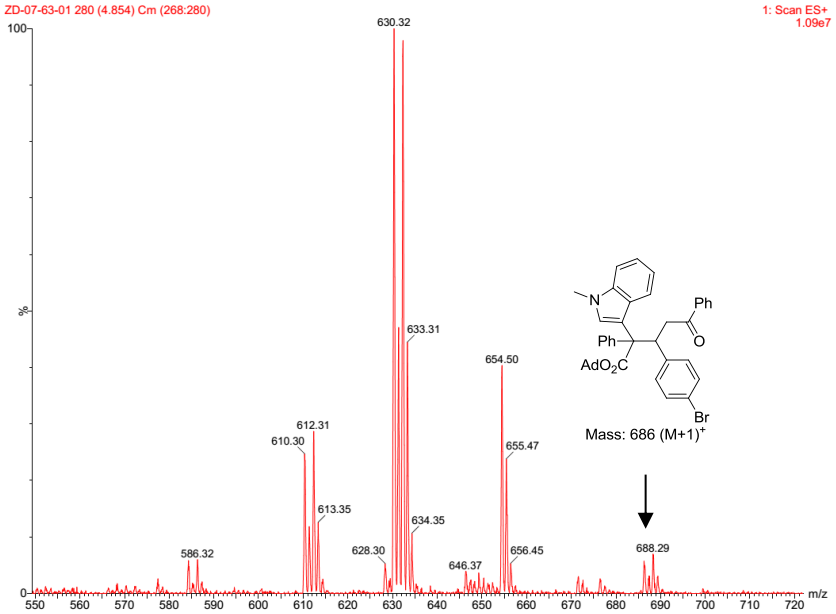


Supplementary Figure 66. ASAP-MS of the reaction in eq.(4-2). In the ASAP-MS spectrum (Supplementary Figure 66), iminium **B** and the precursor (**9**) of **6** were detected by employing the reaction mixture for the mass spectrum without any work-up procedure. These provided direct and strong evidence for the existence of iminium intermediate **B**.

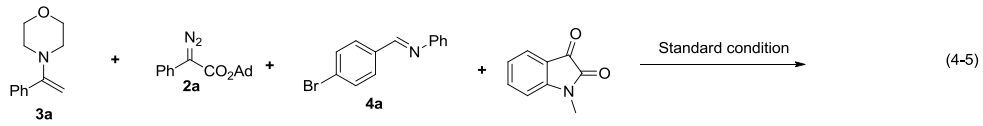


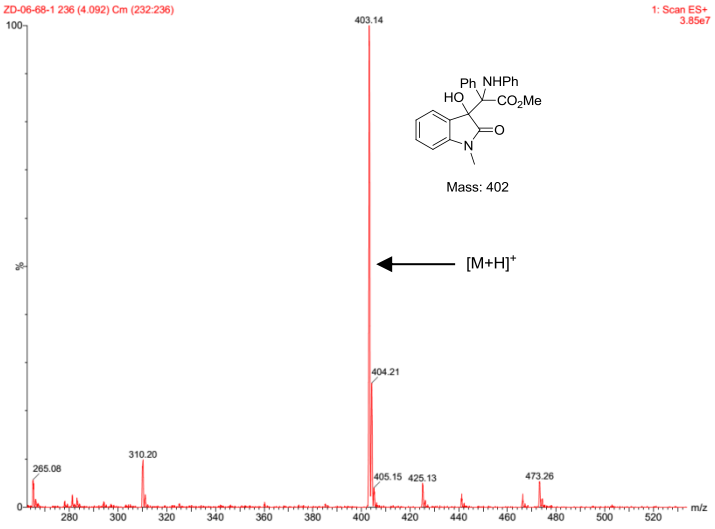
Supplementary Figure 67. ^{1}H NMR of the reaction mixture in eq.(4-3). In the ^{1}H NMR of the reaction mixture (reaction performed in an NMR tube), the reation was tracked. Aniline was detected and found to increase as reaction in process.



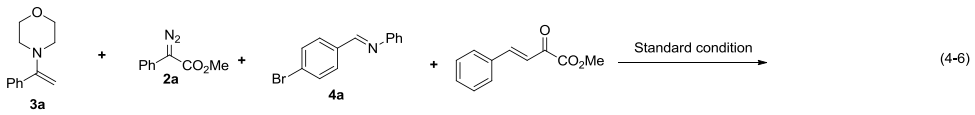


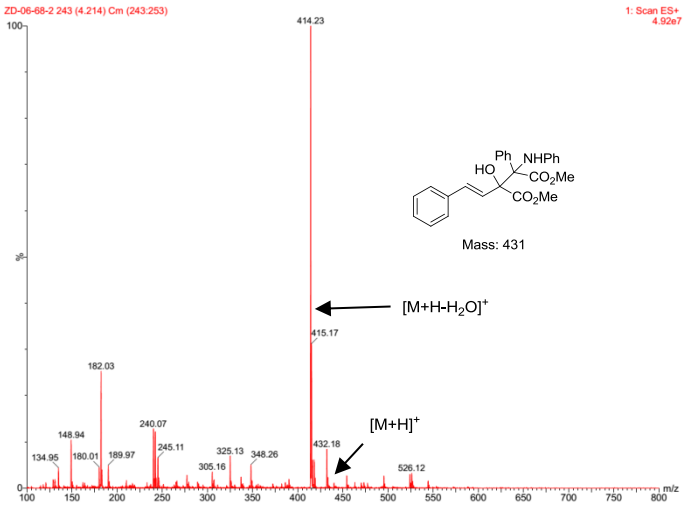
Supplementary Figure 68. Mass spectrum of S1. In eq.(4-4), N-methyl indole was added and the cross-coupling product **S1** was detected by LC-MS. This result undoubtedly supported the cleavage of C-N bond.



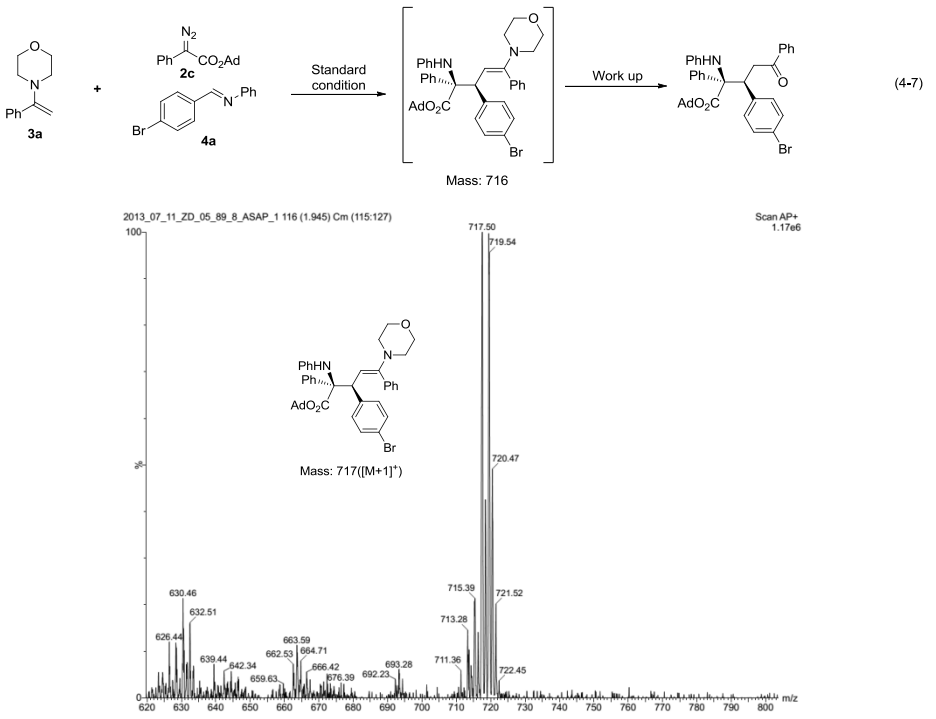


Supplementary Figure 69. Mass spectrum of eq.(4-5)(partial). To detect the cleavage of aniline, other acceptors such as isatin was added to the reaction. The aldol reaction products by trapping the ammonium ylides were detected by LR-MS.



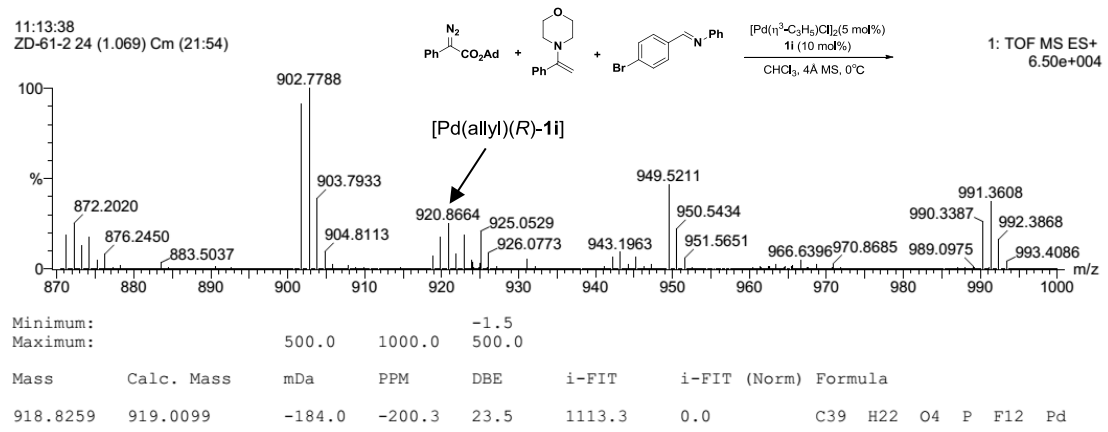


Supplementary Figure 70. Mass spectrum of eq.(4-6)(partial). To detect the cleavage of aniline, other acceptors such as α,β-unsaturated keto ester were added to the reaction. The aldol reaction products by trapping the ammonium ylides were detected by LR-MS.



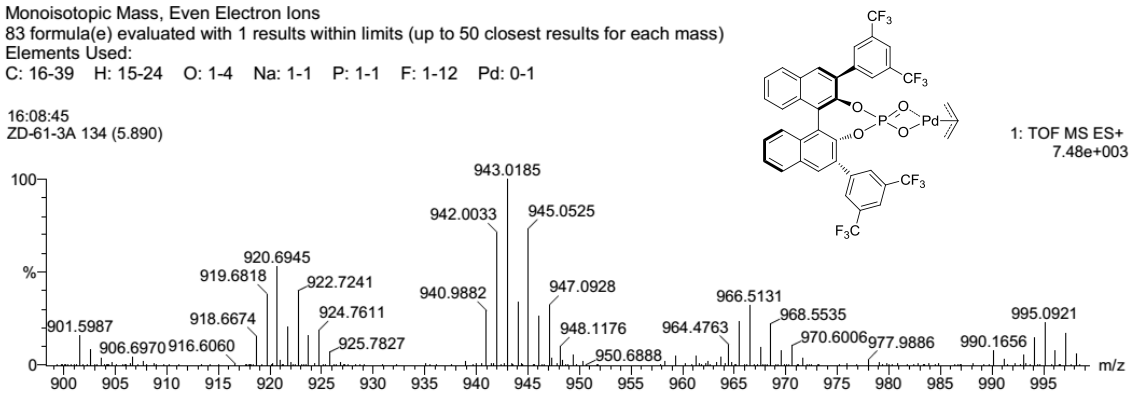
(4-7)

Supplementary Figure 71. ASAP-Mass spectrum of enamine intermediate G. To determined the product of aza-Michael addition before hydrolysis, the crude reaction mixture was subjected to the ASAP-MS spectrum without any work-up procedure. The enamine intermediate **G** was detected. The enamine intermediate can be transformed to the **11a** and **11b** by reduction as shown in the text.



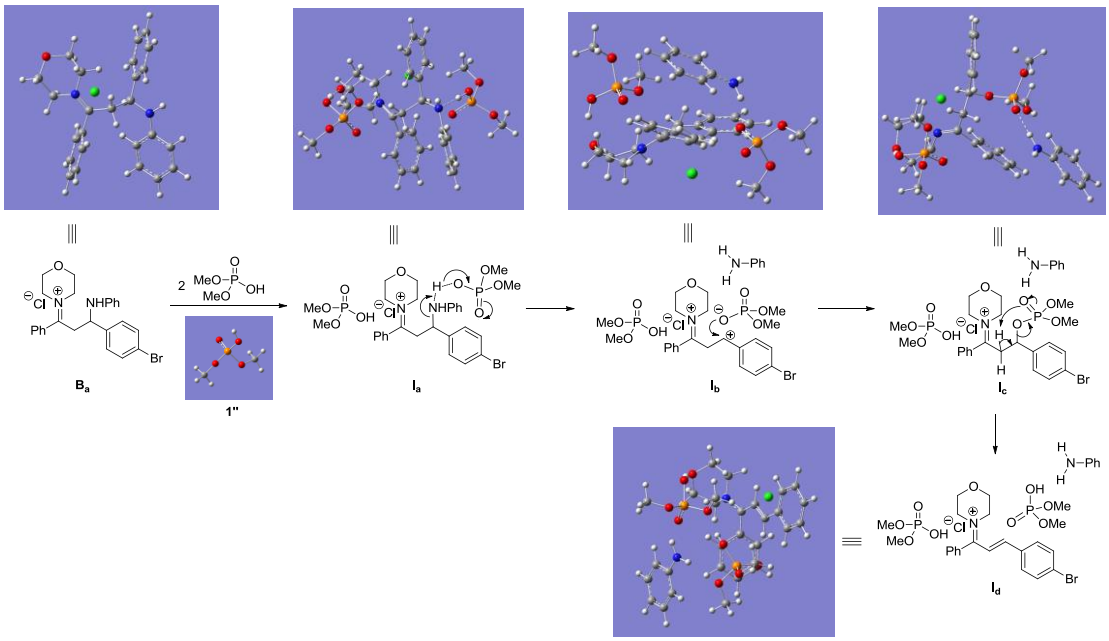
Minimum:				-1.5			
Maximum:		500.0	1000.0	500.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
918.8259	919.0099	-184.0	-200.3	23.5	1113.3	0.0	C39 H22 O4 P F12 Pd

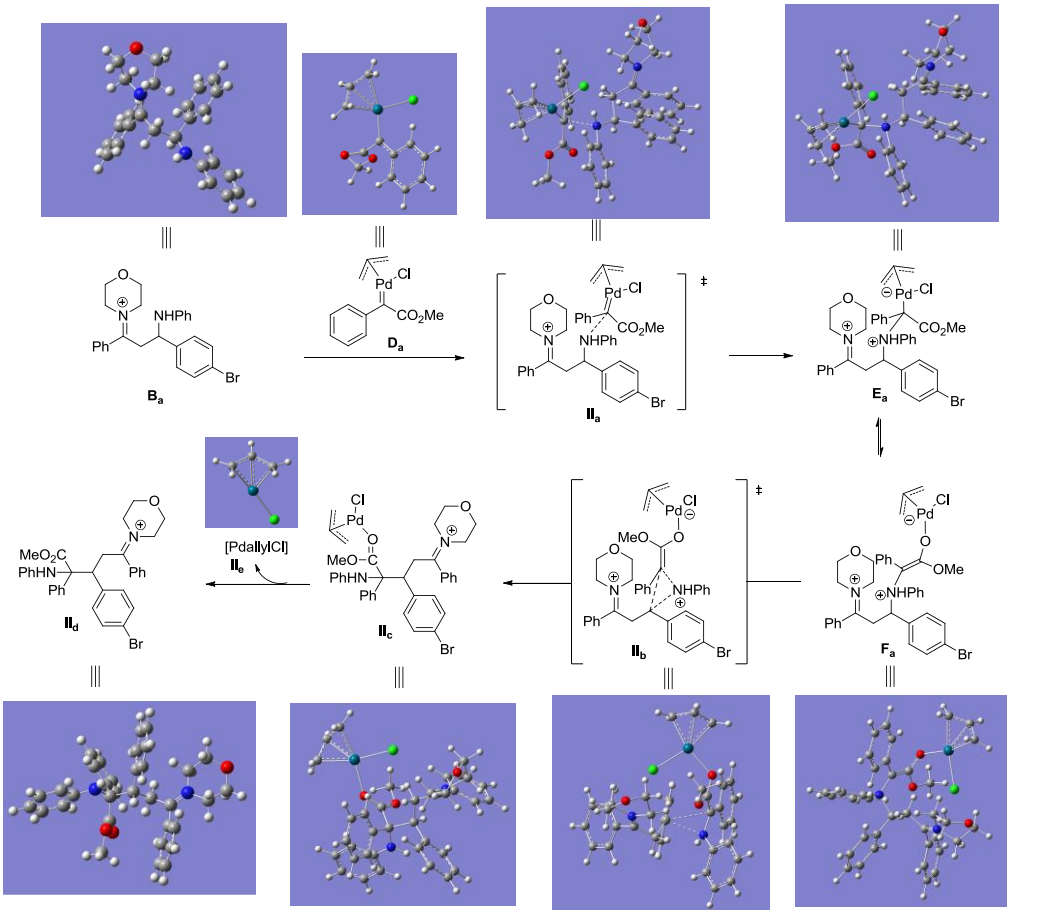
Supplementary Figure 72. HRMS spectrum for crude mixture. To investigate the active catalytic species, the reaction mixture was subjected to the HRMS. The palladium phosphate complex was detected.



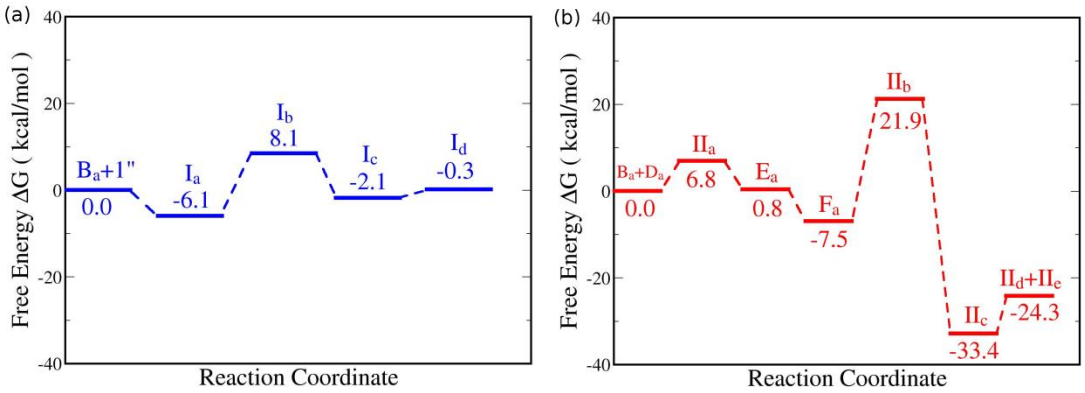
Minimum:				-1.5			
Maximum:		500.0	1000.0	500.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
940.9882	940.9918	-3.6	-3.8	23.5	229.0	0.0	C39 H21 O4 Na P F12 Pd

Supplementary Figure 73. HRMS of prepared [Pd(allyl)(*R*)-1i]

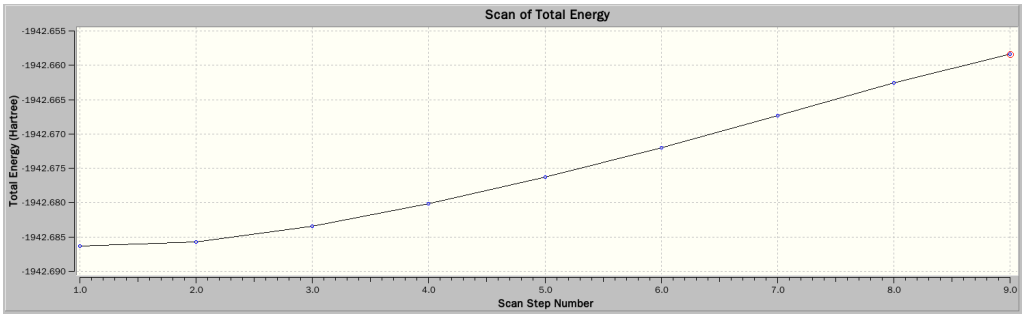




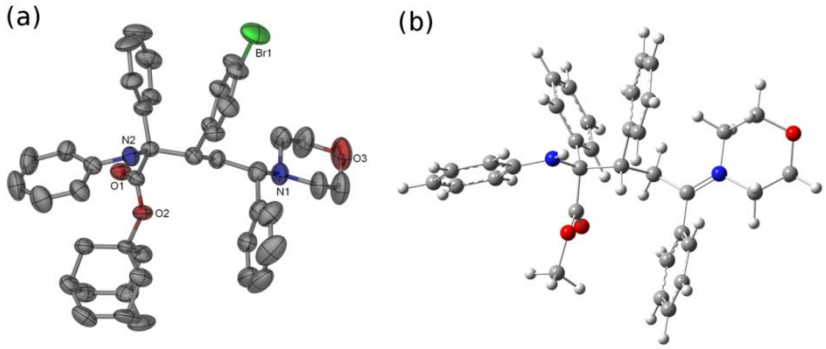
Supplementary Figure 74. (a). The pathway for the formation of iminium. **(b).** The pathway for the carbene-assisted rearrangement.



Supplementary Figure 75. (a) The blue curve denotes the calculated free energy profile for the elimination process of protonated reactant $\mathbf{B_a}$. (b) The red curve denotes the calculated free energy profile of the pathway that $\mathbf{B_a}$ reacts with carbenoid $\mathbf{D_a}$ to produce the final products via a C-N cleavage and C-C bond formation.



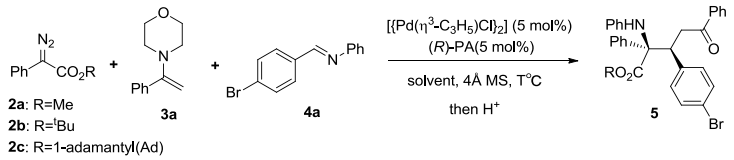
Supplementary Figure 76. The potential energy scan of the increased C-N bond distance in $\mathbf{I_a}$.

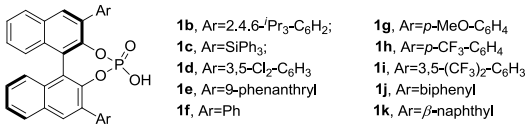


Supplementary Figure 77. (a) The X-ray crystal structure of **11b**. (b) The calculated structure $\mathbf{II_d}$ with DFT.

Supplementary Tables

Supplementary Table 1. Enantioselective investigation of three-component reaction of **2**, enamine **3a** and imine **4a***





entry	**2**	solvent	PA	T/℃	yield/%†	dr(*syn*:*anti*) ‡	ee/%§
1	**2b**	CH_2Cl_2	**1b**	0	----	----	----
2	**2b**	CH_2Cl_2	**1c**	0	----	----	----
3	**2b**	CH_2Cl_2	**1d**	0	48	>95:5	50
4	**2b**	CH_2Cl_2	**1f**	0	55	>95:5	27
5	**2b**	CH_2Cl_2	**1g**	0	60	>95:5	-35
6	**2b**	CH_2Cl_2	**1h**	0	55	>95:5	-35
7	**2b**	CH_2Cl_2	**1j**	0	49	>95:5	-33
8	**2b**	CH_2Cl_2	**1k**	0	41	>95:5	<5
9	**2b**	$(CH_2Cl)_2$	**1i**	0	35	>95:5	65
10	**2b**	Toluene	**1i**	0	--	--	--
11	**2b**	THF	**1i**	0	--	--	--
12	***2b***	***$CHCl_3$***	***1i***	***-15***	***56***	***>95:5***	***83***
13‖	**2b**	$CHCl_3$	**1i**	-35	48	>95:5	85
14	**2c**	$CHCl_3$	**1b**	0	52	>95:5	36
15	**2c**	$CHCl_3$	**1c**	0	48	>95:5	<3
16	**2c**	$CHCl_3$	**1d**	0	55	>95:5	77
17	**2c**	$CHCl_3$	**1e**	0	53	>95:5	10
18	**2c**	$CHCl_3$	**1f**	0	58	>95:5	39
19	**2c**	$CHCl_3$	**1g**	0	49	>95:5	38
20	**2c**	$CHCl_3$	**1h**	0	--	--	--
21	**2c**	$CHCl_3$	**1j**	0	60	>95:5	34
22	**2c**	$CHCl_3$	**1k**	0	59	>95:5	10
23	**2c**	CH_2Cl_2	**1i**	0	45	>95:5	64

24	**2c**	Toluene	**1i**	0	38	>95:5	86
25	**2c**	xylene	**1i**	0	41	>95:5	86
26	**2c**	THF	**1i**	0	--	--	--
27	**2c**	Et_2O	**1i**	0	43	>95:5	77
28	**2c**	$CHCl_3$	**1i**	-30	39	>95:5	88
29	**2c**	Toluene	**1i**	-10	35	>95:5	90

* According to General procedure 1, 0.2 mmol scale.

† Isolated yileds.

‡ Determined by 1H NMR analysis of crude mixture.

§ determined by chiral HPLC analysis.

‖ Running over 48 hrs.

Supplementary Discussion

DFT calculations

All the calculations of geometry optimizations were performed in the G09 software package[3] with the M06[4] method combined with the Lanl2dz basis set[5]. The frequency analysis was also performed to validate the energy minima and transition states. The solvent effects of chloroform were evaluated using the PCM model[6] at the M06/Lanl2dz level based on the gas-phase optimized structures. In this section, all discussed energies are Gibbs free energies calculated from frequency analysis at the temperature 298 K, including the corrections of solvation free energies estimated from the PCM model.

Except for the mechanism we proposed in the text, another pathways for the access to the final compound are possible. In order to get more information about the mechanism, DFT calculations were carried out. For the bond cleavage, modification and reassembly, we simplified the process and considered the first step, Mannich reaction. The formation of iminium is proposed in Supplementary Figure 74 (a), and the calculated energy profiles are presented in Supplementary Figure 11. The phosphoric acid is simplified as **1″** shown in Supplementary Figure 74 (a). In the Supplementary Figure 74(b), another possible mechanism, that the adduct $\mathbf{B_a}$ reacts with carbenoid and then undergoes C-N bond cleavage and C-C bond formation, is also considered. Allylpalladium chloride and methyl phenyldiazoacetate was used in the reaction to simplify the calculations.

The calculated free energy profiles for the two pathways are presented in Supplementary Figure 75.

Supplementary Figure 75(a) shows the calculated free energy profile for the process of bond cleavage of $\mathbf{B_a}$ to form aniline and iminium, which initiates from the interactions of $\mathbf{B_a}$ and phosphoric acid. In experiments, it was observed that the phosphoric acid as a catalyst effectively facilitates the reaction to move to products as it is mixed with reactants in solution. Thus, it is reasonable to take the phosphoric acid as a possible proton source for the protonation of $\mathbf{B_a}$. The complex $\mathbf{I_a}$ is stabilized by the formation of hydrogen bonding interactions between $\mathbf{B_a}$ and phosphoric acid, with releasing an energy of 6.1 kcal/mol. The C-N bond in $\mathbf{I_a}$ subsequently cleaves to yield the intermediate $\mathbf{I_b}$, concomitant with the hydrogen transfer from the phosphoric acid to the nitrogen atom. The potential energy scan of the C-N distance indicates that no transition state exists for the cleavage of C-N bond, as shown in Supplementary Figure 76. The resulted complex $\mathbf{I_b}$ is slightly endothermic by 8.1 kcal/mol and the calculated barrier for the C-N bond cleavage is 14.2 kcal/mol. The intermediate $\mathbf{I_b}$ is further stabilized by transforming to complex $\mathbf{I_c}$ with a exothermic energy of 2.1 kcal/mol. Then, the carbonic hydrogen is abstracted by the phosphate group to yield the $\mathbf{I_d}$, which dissociates and then underdoes subsequent transformations.

Supplementary Figure 75(b) shows the calculated free energy profile for the direct addition of the reactant $\mathbf{B_a}$ to the carbenoid $\mathbf{D_a}$. In solution, the direct coupling between the sp^2-hybrid carbon in $\mathbf{E_a}$ and the amino nitrogen via the transition state $\mathbf{II_a}$ has a modest energy barrier of 6.8 kcal/mol. The ylide product $\mathbf{E_a}$ appears to be not quite favorable in thermodynamics, with a slight endothermic 0.8 kcal/mol. Then, the ylide $\mathbf{E_a}$ rearranges to the enolate $\mathbf{F_a}$. In the next step, the C-N bond in $\mathbf{F_a}$ breaks and a new C-C bond forms through the transition state $\mathbf{II_b}$ to form a more stable intermediate $\mathbf{II_c}$ with a release of energy 25.9 kcal/mol. Nevertheless, the calculated energy of transition state $\mathbf{II_b}$ is higher than the reactants by 21.9 kcal/mol and the barrier for $\mathbf{F_a}$ to surmount the transition state $\mathbf{II_b}$ is highly up to 29.4 kcal/mol. Such a high energy barrier implies this reaction step is extremely slow and could be regarded as the rate-determining step of this pathway. The elimination of Pd complex from $\mathbf{II_c}$ only needs an energy of 9.1 kcal/mol to yield the products $\mathbf{II_d}$ and allylpalladium chloride $\mathbf{II_e}$. Supplementary Figure 775 shows that the calculated structure of product $\mathbf{II_d}$ is in a good agreement with the crystal structure measured by X-ray.

The comparison of free energy profiles of these two pathways by DFT calculations indicates that the bond cleavage pathway in the Supplementary Figure 75(a) is more favorable than the pathway in Figure 75(b). The rate-determining step for the C-N bond cleavage is from $\mathbf{I_a}$ to $\mathbf{I_b}$ and the calculated barrier is merely 14.2 kcal/mol. According to the transition state theory, the calculated reaction time corresponding to this barrier is 4.1×10^{-3} s, which accords with the experimental observation of rapid reactions. Nevertheless, the pathway of direct addition of $\mathbf{B_a}$ to $\mathbf{D_a}$ in the Supplementary Figure 75(b) needs to surmount a high energy barrier of 29.4 kcal/mol and the theoretical reaction time of this elementary step is 5.78×10^{8} s. Thus, the reaction along the pathway in the Supplementary Figure 75(b) is extremely slow and difficult to compete with the direct bond cleavage of $\mathbf{B_a}$.

In addition, it shoud be noted that the nitrogen atom of imine in $\mathbf{I_a}$ forms a hydrogen-bonding

interaction with the phosphoric acid. Such a stable complex prevents the direct addition of $\mathbf{D_a}$ to the nitrogen atom of $\mathbf{B_a}$ from yielding the ylide $\mathbf{E_a}$. Therefore, the DFT calculations support the priority of the intramolecular elimination of $\mathbf{B_a}$ and exclude the direct addition of $\mathbf{B_a}$ and $\mathbf{D_a}$ as an alternative reaction pathway. The modest barrier of C-N cleavage of $\mathbf{I_a}$ makes it easier to occur and follow the mechanism of the three-component reaction, which facilitates the subsequent processes involving the formation of ylide and the coupling of two active intermediate. These indicate the pathway we proposed in the three-component reaction is favorable and reasonable.

Coordinates of the Optimized Structures

Coordinates of the optimized structure $\mathbf{B_a}$:

Elements	X	Y	Z
C	7.88089500	9.94426100	-0.04873900
C	7.18978600	8.59061500	-0.17507800
C	5.80692400	9.95856200	-1.72922400
C	5.66566800	10.82165000	-0.48218800
H	8.44575500	10.14011300	-0.97222200
H	7.94790000	7.81433400	-0.29111600
H	6.55733900	10.36162700	-2.42903400
H	4.92672600	10.37717400	0.20329400
O	6.92111100	11.00223900	0.21654900
H	5.31020300	11.81483200	-0.76973300
H	4.84758600	9.87402000	-2.24754200
H	6.58290700	8.38349900	0.71697000
H	8.56645900	9.92850100	0.80142200
N	6.29373400	8.60201900	-1.36414000
C	6.15297500	7.56504600	-2.16601300
C	5.23292700	7.62736400	-3.33778400
C	4.08253600	6.81302300	-3.28149500
C	5.47067400	8.41976400	-4.47621100
C	3.16709600	6.80863800	-4.33869200
H	3.89512900	6.19123700	-2.40809800
C	4.55908500	8.39283500	-5.53878200
H	6.39666500	8.99412800	-4.52762200
C	3.40675900	7.59636400	-5.47388500
H	2.28140700	6.18387000	-4.28295900
H	4.75876200	8.99095200	-6.42245100
H	2.70652900	7.58089800	-6.30364600
C	6.70474000	6.21234400	-1.81175200
H	6.06682400	5.47133800	-2.30295600
H	6.65465300	6.04250000	-0.72854100
C	8.18887900	5.89253000	-2.31543400
C	9.20600900	6.02853100	-1.19860800

C	10.23654400	6.97859800	-1.29034700
C	9.12575600	5.20326200	-0.05977700
C	11.17047200	7.10301200	-0.25105200
H	10.26667900	7.63501200	-2.15953300
C	10.06211600	5.32564200	0.97501600
H	8.32598300	4.46632700	0.02419300
C	11.08651900	6.28075400	0.88225100
H	11.96155900	7.84303300	-0.32805400
H	9.99456300	4.68405700	1.84900600
H	11.81211700	6.38078800	1.68428300
C	7.17917400	5.12204100	-4.96565200
C	6.64312400	4.70971900	-6.19156800
C	6.60418600	3.35428600	-6.54618900
C	7.12204300	2.40380400	-5.65090600
C	7.65700200	2.79920900	-4.42311100
C	7.69244100	4.16555500	-4.06280200
H	7.23277800	6.18414800	-4.73798800
H	6.26643500	5.46195500	-6.87956600
H	6.18961500	3.04400400	-7.50017400
H	7.10800300	1.34879300	-5.91113500
H	8.05340500	2.05618500	-3.73261000
N	8.23079300	4.53620800	-2.83164800
H	8.74750800	3.84377900	-2.30377100
H	8.43647400	6.62712800	-3.09560100
Cl	8.57387800	9.06206500	-3.49923100

Coordinates of the optimized structure **I_a**:

Elements	X	Y	Z
C	7.13579000	9.68269300	0.69944200
C	7.37398400	8.48334000	-0.20968600
C	5.83964100	9.87958000	-1.58453000
C	5.00772700	10.24225100	-0.35458400
H	7.58651400	10.59296200	0.28924600
H	8.39712300	8.52911400	-0.60862600
H	6.67799600	10.56098500	-1.79642900
H	4.06557700	9.68261700	-0.34664400
O	5.70090100	9.87678700	0.88445700
H	4.80413700	11.31779200	-0.34272400
H	5.19503900	9.85936400	-2.46371300
H	7.20943300	7.54153800	0.32750200
H	7.55147200	9.49811300	1.69155900
N	6.45062800	8.54528100	-1.37840400
C	6.25585800	7.53568700	-2.18840700
C	5.50733200	7.72300800	-3.44967000

C	4.29015200	7.04439000	-3.64300000
C	6.07298600	8.51249700	-4.46827200
C	3.61869000	7.18111700	-4.86144700
H	3.87514300	6.45019600	-2.83219900
C	5.40566700	8.60898200	-5.69604000
H	7.03675600	9.00236000	-4.31315800
C	4.17929700	7.95768900	-5.89025700
H	2.66769900	6.67976400	-5.01325900
H	5.85866800	9.18554400	-6.49572600
H	3.66318100	8.04692300	-6.84216600
C	6.83138900	6.17144000	-1.94571000
H	6.17090700	5.46383200	-2.46044100
H	6.83523500	5.91126900	-0.88224700
C	8.27023600	6.06061600	-2.55663300
C	9.35148400	6.23000300	-1.50373700
C	10.36841100	7.17847800	-1.67196500
C	9.35175200	5.41090900	-0.35789700
C	11.36734100	7.31936800	-0.69830300
H	10.33392600	7.84930300	-2.52651700
C	10.35421600	5.54376300	0.61027000
H	8.56047000	4.67246800	-0.21194300
C	11.36488400	6.50456500	0.44163400
H	12.13883100	8.07137500	-0.83217100
H	10.35223000	4.90508300	1.48975500
H	12.14173400	6.61467600	1.19296300
C	6.84402500	4.87974500	-5.02454100
C	5.94737100	4.23127600	-5.88294900
C	5.75662500	2.84413800	-5.81569700
C	6.47667500	2.09632100	-4.87223500
C	7.36576500	2.73364400	-4.00016900
C	7.55218600	4.12575500	-4.07262000
H	7.01138400	5.95143200	-5.12043300
H	5.40386600	4.82278900	-6.61478200
H	5.06320800	2.35161700	-6.49042900
H	6.34400000	1.02002000	-4.81192700
H	7.92212400	2.15318300	-3.26549500
N	8.51801900	4.73474700	-3.20644000
H	8.90626500	4.06597500	-2.53876500
H	8.38976900	6.83772400	-3.32980000
H	9.77704700	5.22088900	-4.17014800
P	9.96258000	6.80244900	-5.87401700
O	10.09721500	5.96236200	-7.31996300
O	10.47011600	5.70220000	-4.75183300
O	8.54864300	7.45481300	-5.58572700

O	11.21972900	7.89675200	-6.03762500
C	11.42562700	8.91358400	-5.00205900
H	12.04542000	8.48506900	-4.20684000
H	11.95700600	9.72960100	-5.49108800
H	10.47286400	9.27630500	-4.58582900
C	9.84205300	6.66406600	-8.56730200
H	10.60741000	7.42913900	-8.73361300
H	9.89469200	5.90291100	-9.34524500
H	8.84622600	7.12317900	-8.55675500
P	4.42902000	6.60791800	1.06810800
O	4.09635200	6.92224400	-0.43626900
O	5.86110300	5.74384300	1.23616500
O	4.56520000	7.92342700	2.07691600
O	3.36917100	5.63072600	1.91914400
H	4.98561400	8.77835400	1.70422900
C	1.99265000	6.06473700	2.12448000
H	1.50400800	6.24534300	1.16065300
H	1.50184600	5.24244100	2.64282100
H	1.97212900	6.96955000	2.74015000
C	6.27880400	5.27390400	2.55550900
H	6.29872400	6.10636600	3.26745800
H	5.59259800	4.49818600	2.90423100
H	7.28224500	4.87040900	2.41735700
Cl	8.93208800	10.06808500	-2.64572000

Coordinates of the optimized structure **I_b**:

Elements	X	Y	Z
C	5.45008400	9.78026400	0.97928900
C	6.39478300	8.99162500	0.06836500
C	4.88470300	10.04850500	-1.57407500
C	3.66492000	9.82791600	-0.67219800
H	5.58615600	10.86581700	0.90198600
H	7.40783600	9.41481200	0.08120500
H	5.36976700	11.00859700	-1.35925900
H	3.04846000	9.00731100	-1.04875900
O	4.07480500	9.43036800	0.67583200
H	3.07398100	10.74842600	-0.60740900
H	4.58525300	10.05727800	-2.62173800
H	6.44202000	7.95458100	0.41910200
H	5.61938500	9.49079100	2.01865900
N	5.88755000	8.99204400	-1.33492600
C	6.33001500	8.15077000	-2.25905000
C	5.76904000	8.11637600	-3.61748900
C	4.37406100	8.01757500	-3.83469700

C	6.64668100	8.09284600	-4.72031600
C	3.87973400	7.93277900	-5.13668000
H	3.70808800	7.90748600	-2.98314100
C	6.14355300	8.03454800	-6.02614000
H	7.72680700	8.11760300	-4.60085700
C	4.76041800	7.95413400	-6.23320800
H	2.81090600	7.82646200	-5.29768600
H	6.87211000	8.03067500	-6.83634900
H	4.36822400	7.88796400	-7.24391900
C	7.41817900	7.17606000	-1.91208000
H	7.23720100	6.26574200	-2.50322300
H	7.32791700	6.87184700	-0.86655200
C	8.85681000	7.60270100	-2.24386900
C	9.91418700	6.90683200	-1.44809900
C	11.08099300	6.50211500	-2.12187300
C	9.79342400	6.67380000	-0.06635200
C	12.10776600	5.85896200	-1.41912800
H	11.15126800	6.67384600	-3.19674400
C	10.81918500	6.02940100	0.63410200
H	8.90539400	7.00895500	0.47124800
C	11.97825200	5.61824700	-0.04282000
H	13.00489300	5.54654600	-1.94472900
H	10.72525500	5.85528700	1.70263800
H	12.77605100	5.11908100	0.49975000
C	6.87454200	4.58957800	-4.07396900
C	5.52403700	4.51412700	-3.72644100
C	5.11537900	3.88522000	-2.53620100
C	6.09148800	3.31434600	-1.70376400
C	7.45114100	3.38820400	-2.03098200
C	7.86804800	4.04185900	-3.21840300
H	7.19423900	5.08867100	-4.98716400
H	4.78372600	4.95649800	-4.39031700
H	4.06161900	3.82626700	-2.27715400
H	5.78454400	2.80689300	-0.79018400
H	8.20436500	2.95584400	-1.37297300
N	9.19674100	4.18524600	-3.54284400
H	9.90423000	3.83885400	-2.91014200
H	9.07293800	7.49527300	-3.31489100
H	9.46552300	4.90760800	-4.22682700
P	9.98174800	7.18506700	-6.32140300
O	10.74624400	5.94893000	-7.19461100
O	9.53577800	6.55770300	-4.91737900
O	8.91862800	7.99202500	-7.18858100
O	11.36590200	8.17551500	-6.04316300

C	11.11776900	9.51208200	-5.55207600
H	10.61923000	9.48676100	-4.56925400
H	12.09352100	9.98934400	-5.44490700
H	10.49529500	10.07708100	-6.25678600
C	11.20741000	6.25259500	-8.53311200
H	11.99751800	7.01236700	-8.50197600
H	11.60320100	5.31845600	-8.93452500
H	10.37980900	6.61128900	-9.15683100
P	4.27774000	6.03567900	0.24977700
O	4.02918600	6.71533600	-1.14362600
O	5.89521200	5.81710400	0.61162900
O	3.65442900	6.94059700	1.51893300
O	3.65063500	4.52090400	0.55615200
H	3.63168100	7.92853200	1.33933700
C	2.22710100	4.27085300	0.36297400
H	1.93440400	4.51614100	-0.66424800
H	2.09180000	3.20614100	0.54564600
H	1.64359600	4.85800300	1.07928100
C	6.36151000	4.87666000	1.62747300
H	6.15014100	5.27709100	2.62455600
H	5.87362400	3.90774000	1.49739100
H	7.43572300	4.78526900	1.45926100
Cl	9.06239100	9.51821100	-1.96526200

Coordinates of the optimized structure **I_c**:

Elements	X	Y	Z
C	6.71640700	10.33341500	-0.85165700
C	7.19011600	8.89809000	-1.02417100
C	5.47094400	9.09815700	-2.82237500
C	4.56172400	9.90875400	-1.89599500
H	7.00029400	10.95732600	-1.70654300
H	8.21461000	8.90061700	-1.43339600
H	6.15070100	9.71169300	-3.43143200
H	3.71942500	9.29893800	-1.55408900
O	5.26640400	10.33570500	-0.68517900
H	4.18949700	10.79502700	-2.42023200
H	4.85058400	8.50456100	-3.49571200
H	7.13203500	8.36144100	-0.06950800
H	7.13223200	10.76838700	0.05846300
N	6.33585900	8.20136500	-2.02908700
C	6.46006100	6.91835000	-2.27234200
C	5.79955100	6.27145500	-3.41846400
C	4.96285500	5.15949400	-3.20791100

C	6.10289900	6.70916700	-4.72477900
C	4.39996700	4.50373900	-4.30683200
H	4.73962500	4.82732700	-2.19706000
C	5.55117000	6.02849000	-5.81460600
H	6.82146100	7.52363500	-4.85645400
C	4.70002100	4.93152800	-5.60881900
H	3.75401700	3.64612800	-4.14938200
H	5.79779900	6.34630500	-6.82379200
H	4.28170400	4.39458100	-6.45548500
C	7.37248800	6.06868700	-1.44142400
H	6.96643100	5.04970000	-1.40683700
H	7.45764500	6.43178900	-0.41249900
C	8.77313800	6.04937400	-2.08971100
C	9.85504200	5.44448900	-1.22957300
C	11.18704100	5.71643800	-1.59467400
C	9.59640800	4.63507200	-0.11085100
C	12.24776900	5.19217000	-0.84872300
H	11.37210100	6.34142700	-2.46576500
C	10.65970200	4.11116800	0.63913800
H	8.57370700	4.40599100	0.17914300
C	11.98467000	4.38984700	0.27440800
H	13.27232400	5.41249500	-1.13230500
H	10.45411500	3.48692800	1.50372800
H	12.80601700	3.98792700	0.86045700
C	5.40535200	1.40139700	-5.19439000
C	4.95292100	0.96795300	-6.44391300
C	3.80773700	0.16230300	-6.56518000
C	3.11630000	-0.20533600	-5.40038700
C	3.55525000	0.21932700	-4.14128000
C	4.70839700	1.02977600	-4.01877400
H	6.28681800	2.03758100	-5.12010300
H	5.50435400	1.26148700	-7.33448000
H	3.46549100	-0.17193600	-7.53998200
H	2.22849300	-0.82920100	-5.47135400
H	3.01182700	-0.07247800	-3.24350500
N	5.14136300	1.47388000	-2.78073800
H	4.68201900	1.14751200	-1.94419700
H	9.05686400	7.06660600	-2.41744200
P	8.51871200	3.71952700	-3.59753000
O	7.96316200	3.67601000	-5.16254400
O	7.62150200	2.95452400	-2.55797400
O	8.69614500	5.37427400	-3.39601300
O	10.08322200	3.11955600	-3.74132100
C	10.66363100	2.21516700	-2.75767700

H	9.87805000	1.69417200	-2.19869200
H	11.26575500	1.50068700	-3.31994200
H	11.29446800	2.79065500	-2.07247200
C	8.63083600	4.43561100	-6.22065300
H	9.64119600	4.04437600	-6.37559200
H	8.01644700	4.27853700	-7.10721300
H	8.66507000	5.49804200	-5.95650000
P	4.61705100	7.30451700	1.06547500
O	4.28503800	6.83509800	-0.39683000
O	6.15937400	6.84564200	1.54925300
O	4.52059300	8.94333600	1.34835100
O	3.69662200	6.69054700	2.32196900
H	4.76984100	9.59109500	0.60119700
C	2.27000700	6.98468000	2.38195200
H	1.76772000	6.61192000	1.48268400
H	1.90097500	6.45857100	3.26099400
H	2.11429800	8.06290500	2.48963200
C	6.59072500	7.04218600	2.93196000
H	6.48730400	8.09483200	3.21781300
H	5.99463900	6.41321400	3.59767700
H	7.63844400	6.74243300	2.95431300
H	6.01691700	1.99078000	-2.68713600
Cl	8.73350000	9.03176200	-3.81838800

Coordinates of the optimized structure $\mathbf{I_d}$:

Elements	X	Y	Z
C	5.15871400	9.75950400	0.16346700
C	6.40474600	9.01389800	-0.30207900
C	5.02718900	8.95818000	-2.35802200
C	3.72563200	8.83604100	-1.55425500
H	5.04317200	10.72708600	-0.33882900
H	7.23654500	9.72685300	-0.42438900
H	5.30262800	10.00186800	-2.57863600
H	3.26568300	7.85416300	-1.69905900
O	3.99042500	8.93497900	-0.10837400
H	3.02854300	9.63451400	-1.82990100
H	4.90873500	8.44830000	-3.31509600
H	6.66958800	8.23846400	0.42686300
H	5.18457900	9.92586200	1.24191300
N	6.15983200	8.36972400	-1.61531600
C	7.22903800	7.87252900	-2.28720000
C	7.03043100	7.24551500	-3.62660000
C	6.10727900	6.18795500	-3.76251900

C	7.81172200	7.63594900	-4.72647600
C	5.96349000	5.53405400	-4.99242200
H	5.46593400	5.89724100	-2.93273400
C	7.65306300	6.98741800	-5.95678700
H	8.49924600	8.46901000	-4.59977500
C	6.73223700	5.93767900	-6.09369800
H	5.24369800	4.72138800	-5.07693400
H	8.24843700	7.30343000	-6.80789700
H	6.60610900	5.44622000	-7.05545600
C	8.45223200	7.56535100	-1.56295000
H	7.00179300	4.27557700	-1.70266000
H	8.62733300	8.09739500	-0.63336400
C	9.37419200	6.66934400	-2.00610500
C	10.60704700	6.31248700	-1.30486100
C	11.44240200	5.33422800	-1.88912300
C	11.00136200	6.89053500	-0.07622900
C	12.63016200	4.94220100	-1.26197300
H	11.13937100	4.89984600	-2.84120300
C	12.18654000	6.49656300	0.54848400
H	10.39080600	7.66261300	0.38548400
C	13.00616100	5.51825800	-0.04006100
H	13.26688300	4.19512200	-1.72816000
H	12.48131000	6.95380800	1.48850800
H	13.92945700	5.21743500	0.44625000
C	4.08821200	1.70431900	-4.40350700
C	3.22852100	1.71439100	-5.50696900
C	2.08849100	2.53431800	-5.52347300
C	1.82444900	3.34643500	-4.40880000
C	2.68000400	3.35441200	-3.30212200
C	3.82927700	2.53206100	-3.28652700
H	4.95469700	1.04696500	-4.37618000
H	3.44059300	1.06534900	-6.35404400
H	1.42198200	2.53743600	-6.38051400
H	0.94979900	3.99223700	-4.40713700
H	2.50212700	4.02933000	-2.46770800
N	4.69149600	2.52490800	-2.19881300
H	4.43236500	2.93043400	-1.30920200
H	9.20913100	6.14518200	-2.94973400
P	8.33605800	3.16965700	-3.33597400
O	7.06667600	2.58686300	-4.25530400
O	7.63540500	3.52882900	-1.87953600
O	9.26570500	4.25167500	-3.99978200
O	9.11601000	1.72934100	-2.94971700
C	10.36765400	1.77386000	-2.21160700

H	10.23689400	2.30154800	-1.25905100
H	10.63700400	0.73432500	-2.02791800
H	11.14658100	2.26620000	-2.80546600
C	7.27637500	2.36639200	-5.68372500
H	7.90429900	1.48181000	-5.83262700
H	6.27954800	2.20840600	-6.09874500
H	7.74023300	3.24887400	-6.13923100
P	4.62789700	5.50348400	-0.21029400
O	3.79880900	5.75277000	-1.51641300
O	6.27144600	5.27191000	-0.48223400
O	4.48753700	6.67112100	0.95606900
O	4.29144800	4.07740600	0.61148400
H	4.18467300	7.59694200	0.62186900
C	2.96975400	3.88606800	1.20482700
H	2.19432400	3.95674600	0.43262100
H	2.98328900	2.88371700	1.62918400
H	2.80065000	4.63188000	1.98732600
C	7.18283100	5.05176300	0.65293500
H	7.00525200	5.80872900	1.42296200
H	7.02253500	4.04676400	1.05050100
H	8.18664200	5.14749700	0.23459800
H	5.60463900	2.09944300	-2.28362700
Cl	8.10993500	10.30031900	-2.82147600

Coordinates of the optimized structure **D_a**:

Elements	X	Y	Z
C	-1.13041400	5.91079500	2.52467300
C	-1.78181100	5.13431400	1.57157500
C	-2.06857700	3.76275800	1.83269400
C	-1.70101500	3.20840600	3.08982500
C	-1.06079500	3.99678800	4.04529100
C	-0.77049400	5.34135300	3.76112700
H	-0.90201100	6.95178100	2.32122500
H	-2.06164800	5.56882900	0.61442000
H	-1.96839500	2.17361100	3.29518100
H	-0.79447500	3.57486600	5.00825500
H	-0.26796100	5.95193800	4.50576400
C	-2.72889700	2.93280300	0.86676300
C	-3.24550000	3.56427500	-0.37018500
O	-2.66008000	3.55286200	-1.46549800
O	-4.46561800	4.13395000	-0.16159900
C	-5.16796500	4.65242600	-1.33304100
H	-6.12298300	5.01147500	-0.95443700

H	-4.59515400	5.46400500	-1.79063100
H	-5.31168200	3.85423900	-2.06662300
C	-2.54008100	-0.68749100	-0.50415400
Pd	-2.94096100	0.96820500	0.95698600
C	-2.66555900	-1.31069700	0.74583700
C	-1.60257700	0.38739800	-0.66176200
H	-1.62565200	1.00347600	-1.55560000
H	-0.64583800	0.34259700	-0.14058500
H	-3.32657800	-0.81559600	-1.24439000
H	-3.51193600	-1.94899500	0.97195900
H	-1.82862000	-1.34825300	1.44215800
Cl	-4.30868100	0.75454800	2.95089900

Coordinates of the optimized structure **II_a**:

Elements	X	Y	Z
C	7.88236300	7.84296500	1.64202200
C	7.22443200	6.80719700	0.74149000
C	5.49478800	8.61733200	0.72109300
C	5.60693800	8.41939800	2.23127600
H	8.27138100	8.67850900	1.04062700
H	7.95602400	6.43712700	0.01567300
H	6.06680400	9.50038700	0.41509800
H	5.06168900	7.51212500	2.53155600
O	6.98332800	8.33618900	2.66283400
H	5.16031300	9.27350600	2.74581600
H	4.45182800	8.75674500	0.42804000
H	6.87779700	5.94632900	1.32859700
H	8.72349900	7.37935500	2.16027100
N	6.04363800	7.40966600	0.03026600
C	5.48787300	6.84990500	-1.03079400
C	4.39788000	7.50158600	-1.77425800
C	3.31096600	6.72890000	-2.23486000
C	4.47974000	8.86482900	-2.13211900
C	2.30444800	7.32178100	-3.00235200
H	3.23569100	5.67482900	-1.97594500
C	3.48304800	9.44695100	-2.91695800
H	5.35438800	9.45112200	-1.85963500
C	2.38822000	8.67999000	-3.34516800
H	1.45955700	6.72860400	-3.33502400
H	3.56425600	10.48942700	-3.20522300
H	1.60999800	9.13536400	-3.94880900
C	5.92378000	5.48873400	-1.47498500
H	5.07480100	4.81456000	-1.28872200
H	6.74347000	5.10732600	-0.85935800

C	6.33235200	5.38656700	-2.97480100
C	6.95806000	6.68796000	-3.45664800
C	6.32716900	7.46568700	-4.43647200
C	8.17480100	7.12639600	-2.90162700
C	6.88690300	8.68403900	-4.84377600
H	5.39438000	7.11772200	-4.88038200
C	8.73371800	8.34522800	-3.30419200
H	8.71022100	6.49723700	-2.18652200
C	8.08688000	9.13087800	-4.27193400
H	6.39491800	9.27678700	-5.60890800
H	9.68049000	8.67159600	-2.88491800
H	8.52662200	10.06981900	-4.59329100
C	4.79466700	2.63316300	0.87661500
C	5.82845300	2.48953200	-0.05147500
C	5.56958500	2.43286000	-1.44578200
C	4.21512200	2.50404900	-1.86982000
C	3.18051200	2.64564200	-0.93823200
C	3.46340100	2.71646800	0.43584000
H	5.02107100	2.65956900	1.93779900
H	6.86025700	2.42244600	0.28843100
H	3.98492300	2.45246400	-2.92855000
H	2.15041800	2.67789400	-1.28051800
H	2.65515100	2.81178300	1.15476800
C	6.72643700	2.26083700	-2.35638100
C	6.37161200	1.88390100	-3.77886000
O	5.44350900	2.36209400	-4.45710600
O	7.21991100	0.95518200	-4.28668600
C	7.00218600	0.55306400	-5.67729600
H	7.75358600	-0.20998500	-5.87285900
H	5.99163700	0.15523500	-5.80312500
H	7.13916500	1.41852000	-6.33266600
C	9.45531900	-0.15945300	-0.82054500
Pd	8.54733000	1.78384100	-1.46432300
C	10.48771400	0.78881900	-0.76749600
C	8.70307100	-0.28724200	-2.03454800
H	7.79556100	-0.88270900	-2.05225000
H	9.19723000	-0.16471400	-2.99793000
H	9.05791100	-0.57403500	0.10271300
H	10.92564100	1.08694600	0.17898000
H	11.03906600	1.06333100	-1.66683600
Cl	9.11291900	4.06707100	-0.46915300
C	7.36761100	4.32756300	-5.56880500
C	8.08550100	4.14890600	-6.75676000
C	9.42624200	3.73793800	-6.72344000

C	10.05298700	3.51600100	-5.48759400
C	9.34796500	3.70629300	-4.29478400
C	8.00076900	4.10743000	-4.33464500
H	6.32250500	4.61717700	-5.60991700
H	7.59590900	4.33008200	-7.70856400
H	9.97833600	3.60180500	-7.64779100
H	11.09367400	3.20999400	-5.45205100
H	9.83991900	3.56123900	-3.33353000
N	7.29996600	4.25435100	-3.08607400
H	7.97172200	4.27791900	-2.29888100
H	5.44855100	5.14693500	-3.58233100

Coordinates of the optimized structure $\mathbf{E_a}$:

Elements	X	Y	Z
C	8.01904300	8.15804400	1.33690000
C	7.28787700	6.99697800	0.67692700
C	5.53212100	8.77634300	0.53878800
C	5.79582000	8.79914500	2.04183400
H	8.34833700	8.87664200	0.57004000
H	7.96090400	6.50311600	-0.02886600
H	6.03756900	9.62355300	0.06114000
H	5.32363000	7.92951300	2.52250400
O	7.21047700	8.82691800	2.33290800
H	5.36536500	9.70483800	2.47474700
H	4.46186600	8.84459100	0.32939200
H	6.97938500	6.25170900	1.42051000
H	8.90448200	7.77870100	1.85009400
N	6.06355200	7.50065600	-0.03650300
C	5.47130700	6.83305100	-1.01122800
C	4.32552700	7.38253000	-1.75444000
C	3.23961600	6.53867200	-2.07120600
C	4.33707800	8.70837200	-2.24039700
C	2.16733500	7.02738000	-2.82323100
H	3.21326800	5.51205800	-1.71082300
C	3.27471000	9.18368500	-3.01091100
H	5.20389300	9.34408600	-2.07379600
C	2.18277000	8.34831400	-3.29523800
H	1.32456500	6.38151900	-3.04425500
H	3.30033400	10.19701000	-3.39691500
H	1.35361100	8.72197500	-3.88697000
C	5.91401800	5.44389000	-1.35381900
H	5.06789700	4.77910900	-1.13302600
H	6.72605000	5.10446900	-0.70200100
C	6.33490300	5.27011500	-2.84934400

C	6.95639400	6.55193400	-3.36631900
C	6.32143200	7.27638300	-4.38425400
C	8.15482600	7.04180900	-2.81447800
C	6.86632600	8.48250500	-4.84415900
H	5.39974700	6.89226800	-4.82065900
C	8.70213200	8.24554200	-3.27244400
H	8.69742600	6.45751900	-2.06778400
C	8.05671800	8.97135400	-4.28694900
H	6.37180100	9.03061100	-5.64000800
H	9.63998600	8.60475500	-2.86023300
H	8.48818900	9.89820000	-4.65139400
C	4.79879800	2.22640500	0.61909700
C	5.87520000	2.29296700	-0.27521100
C	5.66897300	2.52722100	-1.64854600
C	4.33268300	2.64917500	-2.10029000
C	3.25311800	2.57585800	-1.21063400
C	3.48221400	2.37474800	0.15887700
H	4.98927200	2.03815200	1.67117300
H	6.88894700	2.16440500	0.09548200
H	4.12698500	2.79756200	-3.16019300
H	2.23675600	2.65067400	-1.58753100
H	2.64814200	2.30577600	0.85034700
C	6.83493800	2.60523700	-2.64220900
C	6.30621900	2.06089100	-3.93210000
O	5.87126900	2.73128500	-4.88961100
O	6.19369500	0.70272300	-3.91043600
C	5.43294400	0.09655900	-4.99962400
H	5.43828700	-0.97221700	-4.79177400
H	4.40984400	0.48655200	-5.00489000
H	5.90457600	0.31389500	-5.96107800
C	9.49106000	-0.27963500	-1.45557000
Pd	8.61914500	1.74036600	-1.69465800
C	10.49379500	0.62836600	-1.07048900
C	8.87723900	-0.11565500	-2.74029000
H	7.96649100	-0.65137100	-2.98254700
H	9.47881600	0.20933400	-3.59114000
H	9.00645700	-0.89896400	-0.70498400
H	10.82293600	0.68953300	-0.03861700
H	11.14355700	1.08804500	-1.81533100
Cl	8.98529200	3.90910200	-0.28151900
C	7.90455000	4.51533700	-5.34857500
C	8.86494600	4.64882700	-6.35688000
C	10.22369400	4.44156300	-6.08165000
C	10.62283700	4.10632400	-4.78179300

C	9.67126400	3.98655000	-3.76070200
C	8.31456200	4.18141600	-4.05400800
H	6.85651800	4.64530600	-5.58323600
H	8.54561900	4.90848200	-7.36090600
H	10.96239400	4.54432200	-6.87002200
H	11.67236100	3.95308200	-4.55226200
H	9.99329700	3.76349000	-2.74537000
N	7.34379500	4.09940200	-2.90785400
H	7.94177700	4.22753600	-2.05413600
H	5.47692700	4.98236700	-3.46792000

Coordinates of the optimized structure **F_a**:

Elements	X	Y	Z
C	3.57591500	5.79228700	-6.78163300
C	4.89499300	5.55811700	-6.05279600
C	4.56344400	7.99641300	-5.56707500
C	4.47050800	8.02464900	-7.09089100
H	2.75113800	5.84750400	-6.05416600
H	4.83139800	4.63207700	-5.47341700
H	3.57042000	8.07484000	-5.10914100
H	5.47793200	7.92307100	-7.51980200
O	3.59690700	6.98260800	-7.59582000
H	4.03996000	8.97490800	-7.41312700
H	5.18614200	8.82103200	-5.21284500
H	5.73957600	5.48079100	-6.75298700
H	3.37942200	4.95189100	-7.45128100
N	5.19335700	6.70486200	-5.14511000
C	6.10874700	6.63808100	-4.20327000
C	6.36182300	7.81031400	-3.33607000
C	7.57278600	8.51798000	-3.43277100
C	5.38664400	8.18275500	-2.39245100
C	7.79914500	9.60544400	-2.58019500
H	8.29590500	8.23394900	-4.19502000
C	5.63092500	9.25924800	-1.53314200
H	4.45943000	7.61774400	-2.31349700
C	6.83579600	9.97242000	-1.62746500
H	8.72152800	10.17094700	-2.66556100
H	4.88568800	9.54194400	-0.79730200
H	7.01916400	10.81405000	-0.96744500
C	6.85748000	5.35919800	-3.99838200
H	7.46199000	5.19455000	-4.90929600
H	6.14334800	4.52357700	-3.94647500
C	7.78171000	5.33198200	-2.78018700
C	7.06940000	5.15372800	-1.46271800

C	7.37774700	5.99422700	-0.38217500
C	6.12071000	4.12900300	-1.28418800
C	6.74997500	5.81863300	0.85679000
H	8.11277400	6.78702400	-0.51218500
C	5.49757300	3.94507400	-0.04432900
H	5.85671000	3.45930000	-2.10501100
C	5.81152600	4.79125500	1.02941700
H	6.99605400	6.47366100	1.68621400
H	4.77269600	3.14802900	0.08745900
H	5.33059500	4.64892500	1.99179600
C	7.72807800	0.81678600	-5.50340700
C	7.98966200	1.99474300	-4.79277100
C	9.10168000	2.82318000	-5.09985200
C	9.93322500	2.40619100	-6.17086000
C	9.66232900	1.23430000	-6.88085200
C	8.56131300	0.42672400	-6.55738200
H	6.86963600	0.20793700	-5.23452500
H	7.27321600	2.25002100	-4.00413300
H	10.79698100	3.01140800	-6.42304800
H	10.32897100	0.93763800	-7.68603600
H	8.36266800	-0.48644200	-7.10852500
C	9.38950300	4.05677800	-4.35959700
C	10.14033100	5.12531600	-4.85235700
O	10.72798600	5.16339800	-5.99315100
O	10.22768200	6.25294900	-4.03428300
C	10.99555100	7.37415600	-4.56905000
H	11.06239100	8.09187200	-3.74811100
H	11.98999000	7.04378300	-4.87751900
H	10.47163700	7.80767400	-5.42868000
C	10.49196100	5.77193600	-9.90427700
Pd	9.76105700	5.75576100	-7.84927100
C	9.08656200	6.01732900	-9.87738200
C	10.94961600	4.58381200	-9.27804300
H	12.00341700	4.45069100	-9.05424000
H	10.33965400	3.68061700	-9.30383700
H	11.18597600	6.57540000	-10.13430900
H	8.70015500	6.99977200	-10.12943200
H	8.38421100	5.18893300	-9.96982900
Cl	8.01376600	7.11254200	-6.70255000
C	10.58853200	4.92094400	-1.43442600
C	11.42481600	4.64652300	-0.34546500
C	11.36737700	3.40666900	0.30811300
C	10.46670400	2.42606000	-0.12884300
C	9.62372300	2.68815800	-1.21532900

C	9.69829000	3.93018000	-1.85348900
H	10.63990600	5.86799400	-1.95985900
H	12.12629100	5.40298800	-0.00889500
H	12.02080800	3.20536300	1.15043900
H	10.41856100	1.46448000	0.37061600
H	8.92480800	1.92626700	-1.56049600
N	8.76027600	4.14202400	-3.00184700
H	8.15555500	3.30775800	-2.96348600
H	8.42866300	6.21094600	-2.77037200

Coordinates of the optimized structure **II_b**:

Elements	X	Y	Z
C	6.24970300	7.50846100	-6.87287500
C	7.07263900	7.30342600	-5.60701300
C	4.99811400	8.38473000	-4.70383300
C	5.31322600	9.44591700	-5.75528000
H	5.41365900	6.79379500	-6.88901500
H	7.42060800	6.26570100	-5.54545000
H	4.24689700	7.67347700	-5.06814000
H	6.06965000	10.14469300	-5.36936400
O	5.78426300	8.87153200	-6.99709500
H	4.40532100	10.01370200	-5.97633700
H	4.62846800	8.84839100	-3.78655100
H	7.93308300	7.98599000	-5.59708800
H	6.88004700	7.32378600	-7.74534300
N	6.23439600	7.60511500	-4.39973500
C	6.55976500	7.20613100	-3.19478900
C	5.67828000	7.40675200	-2.02834900
C	6.18462200	8.03193400	-0.87245500
C	4.37105400	6.87660500	-2.03396700
C	5.37369300	8.16407700	0.25875500
H	7.19178100	8.44361900	-0.86480700
C	3.57886900	6.98658900	-0.88670200
H	4.00733800	6.33594600	-2.90754500
C	4.07340200	7.63566800	0.25498600
H	5.75252100	8.67052400	1.14001400
H	2.58036300	6.56287900	-0.88237400
H	3.45061400	7.72616100	1.13888900
C	7.81751500	6.39274000	-2.95173200
H	8.29502400	6.74272000	-2.03059900
H	8.54041900	6.46057200	-3.77049200
C	7.29721300	4.98479800	-2.83622600
H	6.76678900	4.63204700	-3.72034800
C	7.04481400	4.29323700	-1.62415300

C	7.63571700	4.65142300	-0.37722400
C	6.18582700	3.15698300	-1.68111700
C	7.36177300	3.90655800	0.76420400
H	8.30848300	5.50528600	-0.31269700
C	5.90302900	2.42863000	-0.52824200
H	5.73442100	2.89187400	-2.63640000
C	6.49358500	2.79722800	0.69151500
H	7.81554500	4.17310100	1.71272800
H	5.25048700	1.56398300	-0.57907400
H	6.28445100	2.22082300	1.58718200
C	9.25868800	0.40904800	-1.02406600
C	9.39050500	1.51749400	-1.86342100
C	8.59539700	1.66142800	-3.03658600
C	7.67725100	0.60916300	-3.32921800
C	7.54912900	-0.48976100	-2.47871500
C	8.32681100	-0.59938400	-1.31405700
H	9.89558000	0.32333000	-0.14843900
H	10.16205000	2.24773700	-1.62855300
H	7.09864200	0.66587100	-4.24510300
H	6.84582800	-1.27832600	-2.73201900
H	8.22914300	-1.46279500	-0.66358500
C	8.69221600	2.86323700	-3.84747100
C	8.02912500	3.05961500	-5.06168200
O	7.28114300	2.20996000	-5.68489800
O	8.27311300	4.29221400	-5.69265200
C	7.94033400	4.33428400	-7.10963200
H	8.40070900	5.24981000	-7.48933900
H	8.35438500	3.46558900	-7.62913900
H	6.85171600	4.34835500	-7.25046800
C	3.80502800	1.13974800	-7.15088200
Pd	5.12741100	2.38230800	-5.93359600
C	3.03649700	1.91838400	-6.23783800
C	4.82570700	0.31856200	-6.60208200
H	5.59607300	-0.10336400	-7.23955700
H	4.68575500	-0.16109200	-5.63287900
H	3.80217800	1.37623900	-8.21122400
H	2.41077200	2.72735100	-6.60097200
H	2.78122700	1.52097900	-5.25561600
Cl	4.78851200	4.71480900	-5.06364300
C	11.16317900	4.12776100	-5.07585900
C	12.36698200	4.68308500	-5.52090300
C	13.07868500	5.59790600	-4.72911500
C	12.57940000	5.95044400	-3.46405300
C	11.38309300	5.39753800	-3.00407600

C	10.66515200	4.47616400	-3.80380100
H	10.62252300	3.41589900	-5.69054400
H	12.75574900	4.39682800	-6.49334900
H	14.01097500	6.02195400	-5.08682100
H	13.12988200	6.64482600	-2.83672900
H	11.00544300	5.65079300	-2.01154400
N	9.46452300	3.96525900	-3.28488800
H	9.43394900	3.99006000	-2.26675000

Coordinates of the optimized structure **II_c**:

Elements	X	Y	Z
C	9.59955000	11.52517000	-9.93942700
Pd	11.63650200	12.32004100	-10.00932300
C	9.95261400	11.95266400	-11.25933200
C	9.71303700	12.47869000	-8.90190000
H	9.68694100	12.16796800	-7.86246000
H	9.52719200	13.53487400	-9.09490300
H	9.51996500	10.46661100	-9.70881000
H	10.11006400	11.22084700	-12.04523800
H	9.71057600	12.96178700	-11.59292700
Cl	13.39030100	12.23024500	-11.73344600
C	17.37128900	17.17357200	-13.42017100
C	16.58975600	16.24088300	-12.50141100
C	18.06426100	14.60055100	-13.69047900
C	17.41972700	15.26112000	-14.90598900
H	18.39519400	17.30569600	-13.03926700
H	16.58797100	16.64990100	-11.48747400
H	19.07376700	14.99543700	-13.53230100
H	16.39815200	14.87870500	-15.04457100
O	17.39593900	16.70355800	-14.78544800
H	17.99839400	15.02573600	-15.80189000
H	18.13140900	13.51952000	-13.82983200
H	15.55526400	16.13192700	-12.84876700
H	16.88883400	18.15287500	-13.43649100
N	17.22793400	14.88415000	-12.48143200
C	16.97412100	13.98656900	-11.54636000
C	17.68963800	12.69765800	-11.52163300
C	16.95690100	11.49520500	-11.45056900
C	19.10062900	12.66909900	-11.49965100
C	17.64006100	10.27527400	-11.39429100
H	15.86661300	11.50939100	-11.47852300
C	19.77143600	11.44713400	-11.40979900
H	19.66841100	13.59749800	-11.51001300
C	19.04209000	10.24818200	-11.36667000

H	17.07740700	9.34800500	-11.37159800
H	20.85545700	11.42727600	-11.37498100
H	19.56463300	9.29873300	-11.30990500
C	15.93085800	14.22123000	-10.50305300
H	15.12549500	13.49055500	-10.72594000
C	16.48263800	14.00996600	-9.07840600
H	16.88076600	12.98614600	-9.02132000
C	17.62002900	14.97452500	-8.79534200
C	17.47983100	16.36833200	-8.95247000
C	18.87212900	14.46488000	-8.40403300
C	18.56110700	17.22427400	-8.71185800
H	16.51400700	16.79678900	-9.22095100
C	19.95647100	15.32014100	-8.16286400
H	19.00093700	13.38712900	-8.29849500
C	19.80310000	16.70447300	-8.31638900
H	18.43189600	18.29717400	-8.81775100
H	20.91252600	14.90880100	-7.85444200
H	20.63779600	17.37103800	-8.12428200
C	13.14144100	17.07650400	-8.92475700
C	13.68913700	15.78741800	-8.93694900
C	14.61786200	15.39723600	-7.95130100
C	14.96049000	16.31424900	-6.94491000
C	14.40788200	17.60070300	-6.92824600
C	13.50208300	17.99102100	-7.92390900
H	12.42181400	17.36096000	-9.68684900
H	13.36230200	15.08566200	-9.70125600
H	15.66726400	16.00968500	-6.17853800
H	14.68185300	18.29281700	-6.13822400
H	13.07049400	18.98709400	-7.91152900
C	15.33381800	14.04272800	-7.98817300
C	14.36028200	12.88257200	-8.34668200
O	13.13792400	13.00567000	-8.54210300
O	14.99849800	11.70105900	-8.38352800
C	14.21445200	10.47519800	-8.56366800
H	14.93139200	9.66488000	-8.44523500
H	13.43899800	10.42502100	-7.79329600
H	13.76544000	10.46963700	-9.56441700
C	16.04903500	12.75486400	-4.51249800
C	15.42624000	12.36061000	-3.32681800
C	14.04119600	12.52309900	-3.16050800
C	13.29591800	13.09475000	-4.19862100
C	13.90776500	13.49871600	-5.39320800
C	15.29754200	13.32765400	-5.55988100
H	17.12256200	12.62094800	-4.63579000

H	16.02103300	11.92307800	-2.53060200
H	13.55859700	12.21685900	-2.23843200
H	12.22612100	13.24100500	-4.07953200
H	13.30779000	13.97330400	-6.16449600
N	15.97390000	13.70949100	-6.72995200
H	16.96766800	13.51460300	-6.75858000
H	15.47175500	15.20708300	-10.59119700

Coordinates of the optimized structure **II_d**:

Elements	X	Y	Z
C	11.86937900	10.71895000	1.03335500
C	10.92566200	10.75151500	-0.16294200
C	12.35745600	8.78335000	-0.76225900
C	13.44482100	9.83879500	-0.58169700
H	11.59244900	9.89428700	1.70754000
H	9.89779200	10.87937800	0.18617500
H	12.31769600	8.13519000	0.12025900
H	13.46857400	10.51087800	-1.45213100
O	13.25364600	10.60065500	0.63262300
H	14.41898400	9.35199600	-0.50003600
H	12.55333800	8.16415400	-1.64095800
H	11.18799900	11.57761100	-0.83589500
H	11.78107800	11.65372200	1.59055700
N	11.03416900	9.46528900	-0.93021700
C	10.08971000	9.03384400	-1.74440900
C	10.18493400	7.72072700	-2.40899600
C	9.91313300	7.61627700	-3.78928000
C	10.45549600	6.55303200	-1.66151700
C	9.96952200	6.36919500	-4.41926000
H	9.68850900	8.49923800	-4.38247700
C	10.46624900	5.30554100	-2.28975400
H	10.61362900	6.61431700	-0.58678700
C	10.23874700	5.21322400	-3.67215600
H	9.79780900	6.30071900	-5.48823500
H	10.65334900	4.40950300	-1.70798000
H	10.26752000	4.24539500	-4.16168000
C	8.84897600	9.82865200	-2.01746200
H	8.66855400	9.77799000	-3.09874200
C	7.64294800	9.18180500	-1.27113600
H	7.77173100	8.08739600	-1.29477200
C	7.64822600	9.59415400	0.18903500
C	7.49146600	10.93315100	0.59971900
C	7.89020800	8.60867800	1.16347000
C	7.57664000	11.26972200	1.95628300

H	7.29624700	11.71332700	-0.13368800
C	7.98109700	8.94579900	2.52275100
H	7.99682400	7.56774300	0.85675000
C	7.82751300	10.28022300	2.92119100
H	7.44126900	12.30224600	2.26281600
H	8.15987600	8.17339400	3.26414600
H	7.88847500	10.54692700	3.97134800
C	6.36621800	13.00656400	-3.49805500
C	6.63173700	11.63949600	-3.33780200
C	5.99666600	10.89942000	-2.31997300
C	5.07597500	11.56392400	-1.48832100
C	4.80772200	12.92700900	-1.65166200
C	5.45754000	13.65905600	-2.65514900
H	6.85733900	13.55477700	-4.29639600
H	7.29302600	11.15168100	-4.04462200
H	4.56939200	10.99819500	-0.71270300
H	4.08431000	13.41195500	-1.00369800
H	5.24563200	14.71516300	-2.78948900
C	6.28217200	9.41265100	-2.04274600
C	6.47633500	8.57328000	-3.34606700
O	6.80995600	8.99431800	-4.46085100
O	6.30906200	7.25035100	-3.08617300
C	6.22544700	6.34638600	-4.23036000
H	6.09660900	5.35374100	-3.80281100
H	5.35899900	6.62250200	-4.83874500
H	7.13438400	6.40449000	-4.83660000
C	3.11796000	7.70379000	-0.92416100
C	1.83588700	7.37009600	-1.36681900
C	1.36885100	7.82709300	-2.60935000
C	2.20482800	8.62936200	-3.39551700
C	3.49188000	8.97456700	-2.96202200
C	3.96201000	8.50660800	-1.71755500
H	3.47461700	7.34169500	0.03884100
H	1.19946900	6.75079200	-0.74173000
H	0.37276500	7.56748000	-2.95184700
H	1.85384300	9.00133500	-4.35373600
H	4.09797400	9.63054200	-3.58294200
N	5.24567200	8.80923200	-1.23344300
H	5.53834300	8.30946800	-0.40194300
H	8.94476900	10.88541600	-1.75595100

Coordinates of the optimized structure **II_e**:

Elements	X	Y	Z
C	-2.53031600	-0.67678600	-0.55102500

Pd	-3.07998600	0.71468300	1.02990400
C	-2.63693900	-1.32874600	0.72903100
C	-1.60954800	0.38190400	-0.65730900
H	-1.63673800	1.05109200	-1.51143800
H	-0.70595500	0.40382200	-0.04998000
H	-3.29436900	-0.82692300	-1.30784500
H	-3.47357600	-1.98994400	0.93311700
H	-1.75052000	-1.48344400	1.34338100
Cl	-4.27853700	1.09953400	3.00351200

Supplementary Methods

1. General Information

All ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{19}F NMR (376 MHz) spectra were recorded on Brucker Asend400 spectrometers in Acetone-d_6 or $CDCl_3$. Tetramethylsilane (TMS) served as an internal standard (δ = 0) for ^{1}H NMR, and $CDCl_3$ was used as internal standard (δ = 77.0) for ^{13}C NMR. Chemical shifts are reported in parts per million as follows: chemical shift, multiplicity (s =singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad). Infrared (IR) spectra were recorded on a NICOLET NEXUS 670 FT-IR spectrometer, ν_{max} in cm^{-1}. Melting points were uncorrected. Specific rotation was performed on Rudolph Research Analytical Autopol VI Polarimeter (λ= 589 nm, T = 20 ^{o}C). The racemic standards used in HPLC studies were prepared according to the general procedure using racemic BINOL-derived phosphoric acid catalyst *rac*-**1a**. Yields for all compounds were combined yields for all isomers unless otherwise indicated.

2. General procedure

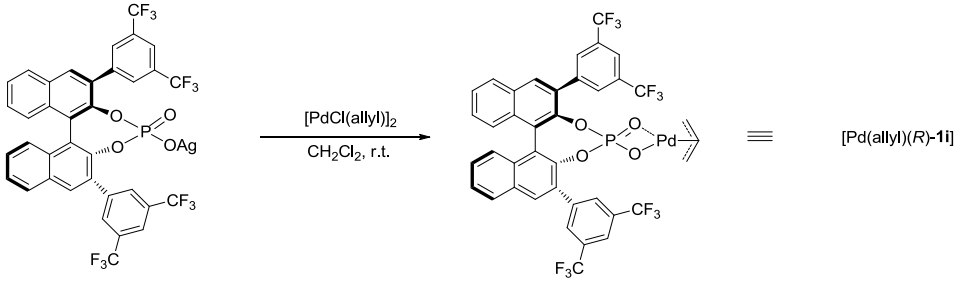
2.1 ***General Procedure 1*** **for preliminary optimization of the three-component reactions (Table 1 and Table SI 1):** To a 10-mL test tube with a plug $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (5.0 mol%), racemic phosphoric acid *rac*-**1a** (10 mol%), enamine **3a** (0.22mmol, 1.1 eq), imine **4a** (0.2 mmol, 1.0 eq) and 4Å molecular sieve (0.1 g) and 1.5 mL of CH_2Cl_2 were added and stirred in at ambient temperature or 0℃. The diazo compound **2a** (0.3 mmol, 1.5 eq) in 1.0 mL CH_2Cl_2 was introduced to the suspension over 1 h *via* a syringe pump. After completion of the addition, the mixture was stirred for another 5 min and then was hydrolysized by eluted through short column chromatography on silica gel (eluent: EtOAc/petroleum ether = 1/10~5) to give a crude product

which was subjected to ^{1}H NMR spectroscopy analysis for the determination of diastereoselectivity and to chiral HPLC for the ee values. Purification of the crude products by flash chromatography on silica gel (eluent: EtOAc/ petroleum ether = 1/80~50/1) afforded pure products.

2.2 *General Procedure 2* for optimization of the three-component reactions (Table 2 and Table S2): A suspension of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (5.0 mol%), chiral phosphoric acid **1**(5 mol%), imine **4** (0.2 mmol, 1.0 eq) and 4Å molecular sieve (0.1 g) was stirred in 1.5 mL of solvent at corresponding temperature and then the mixture of diazo compound **2** (0.3 mmol, 1.5 eq) and enamine **3a** (0.22 mmol, 1.1 eq) in 1.0 mL solvent was introduced to the suspension over 1 h *via* a syringe pump. Subsequent operations were similar to those in *general procedure 1*.

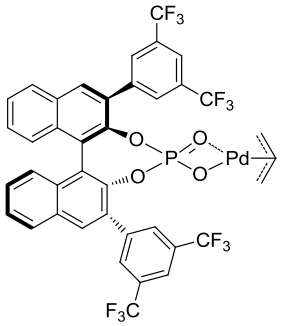
3. Preparation of chiral palladium phosphate

The chiral palladium-phosphate complex was prepared to verify it structure. The silver salt of phosphate was synthezed [1-2] and converted into the palladium phosphate complex.



To a flask (25 mL) with a stir bar was added silver phosphate (200.1 mg, 1.0 eq.) and 5 mL CH_2Cl_2 in dark. Subsequently allylpalladium chloride dimmer (41.5 mg, 1.0 eq.) was added to the flask in one portion under vigorous stirring and the stirring remained overnight. The mixture was filtered and the filtrate was concentrated to give a fluffy yellowish powder (quant.).

Allyl((2,6-bis(3,5-bis(trifluoromethyl)phenyl)-4-oxidodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yl)oxy)palladium [Pd(allyl)(*R*)-1i].



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 – 7.73 (m, 9H), 7.59 – 7.47 (m, 2H), 7.45 – 7.28 (m, 5H), 4.90 (s, 1H), 3.13 – 2.48 (m, 2H), 1.93 (br, 2H)..

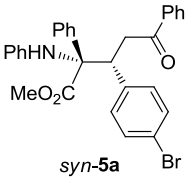
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 140.2, 132.7, 131.5, 131.3, 131.0, 130.9, 130.1, 128.4, 127.1, 127.0, 126.0, 124.8, 124.2, 123.1, 122.0, 120.9, 22.6.

^{31}P NMR (162 MHz, $CDCl_3$) δ 10.43-9.49 (br).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.46.

HRMS(ESI) Calcd. for $C_{39}H_{21}O_4NaPF_{12}Pd$ $(M+Na)^+$ 940.9918, Found: 940.9882.

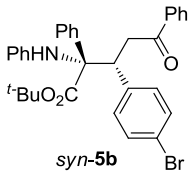
Analytical data of the products



syn-**5a**

(2S,3R)-methyl 3-(4-bromophenyl)-5-oxo-2,5-diphenyl-2-(phenylamino)pentanoate (**5a).**

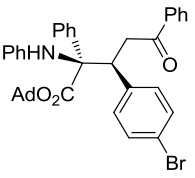
^{1}H NMR (400 MHz, Acetone) δ 7.82 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.70 – 7.63 (m, 2H), 7.61 – 7.55 (m, 1H), 7.49 – 7.42 (m, 2H), 7.37 – 7.31 (m, 5H), 7.06 (d, *J* = 8.5 Hz, 2H), 7.00 (dd, *J* = 8.6, 7.4 Hz, 2H), 6.62 (M, 1H), 6.49 (dd, *J* = 8.6, 0.9 Hz, 2H), 5.57 (s, 1H), 4.50 (dd, *J* = 11.2, 2.7 Hz, 1H), 3.81 (dd, *J* = 17.4, 11.2 Hz, 1H), 3.54 (s, 3H), 3.46 (dd, *J* = 17.4, 2.7 Hz, 1H); ^{13}C NMR (100 MHz, Acetone) δ 197.42, 173.65, 146.88, 139.19, 137.92, 137.84, 133.94, 132.76, 131.39, 130.06, 129.45, 129.16, 128.67, 128.61, 128.50, 121.54, 118.54, 116.42, 70.99, 52.72, 50.87, 40.70; FT-IR(KBr) $\tilde{\nu}$ 3399, 3358, 3054, 2949, 1727, 1691, 1678, 1599, 1500, 1446, 1430, 1325, 1266, 1180, 1073, 1007, 814, 748, 691, 657, 582 cm^{-1}; HRMS(ESI) *m/z*: calcd. for $C_{39}H_{38}NO_3NaBr$ $(M+Na)^+$ 550.0994, found 550.1005.



syn-**5b**

(2S,3R)-tert-butyl 3-(4-bromophenyl)-5-oxo-2,5-diphenyl-2-(phenylamino)pentanoate (**5b)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 - 6.67 (m, 2H), 7.64 - 7.60 (m, 2H), 7.51 - 7.46 (m, 1H), 7.40 – 7.25 (m, 7H), 7.15 – 6.87 (m, 6H), 6.71 - 6.66 (m, 1H), 6.42 (d, *J* = 7.8 Hz, 1H), 4.90 (s, 1H), 4.63 (dd, *J* = 11.3, 1.9 Hz, 1H), 3.61 (dd, *J* = 17.4, 11.5 Hz, 1H), 3.41 (dd, *J* = 17.4, 2.3 Hz, 1H), 1.15 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 171.46, 145.78, 137.9, 137.2, 136.6, 133.2, 131.6, 131.1, 128.7, 128.6, 128.3, 127.9, 127.7, 121.5, 117.9, 115.9, 82.7, 77.4, 77.0, 76.7, 70.1, 48.2, 41.06, 27.59; FT-IR(KBr) $\tilde{\nu}$ 3402, 3051, 2975, 2926, 1727, 1687, 1600, 1502, 1447, 1367, 1325, 1262, 1247, 1151, 1073, 1007, 815, 744, 684, 663, 546 cm^{-1}; HRMS(ESI) *m/z*: calcd. for $C_{33}H_{33}NO_3Br$ $(M+H)^+$ 570.1644, found 570.1644; HPLC (CHIRALCEL OD-H, λ= 254 nm, hexane/2-propanol = 150/1, Flow rate = 1.0 mL/min), 84% ee, t_{major} = 14.57 min, t_{minor} = 13.05 min.

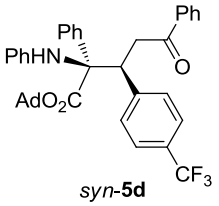


syn-**5c**

(2S,3R)-adamantan-1-yl 3-(4-bromophenyl)-5-oxo-2,5-diphenyl-2-(phenylamino)pentanoate (**5c)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.66 (m, 2H), 7.64 – 7.56 (m, 2H), 7.48 (dd, *J* = 10.5, 4.3 Hz, 1H), 7.39 – 7.29 (m, 7H), 7.09 - 7.02 (m, 1H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.41 (d, *J* = 7.8 Hz, 1H), 4.88 (s, 1H), 4.62 (dd, *J* = 11.4, 2.2 Hz, 1H), 3.61 (dd, *J* = 17.4, 11.5 Hz, 1H), 3.41 (dd, *J* = 17.4, 2.4 Hz, 1H), 2.04 (s, 3H), 1.76 (q, *J* = 11.4 Hz, 6H), 1.62 – 1.41 (m, 6H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 171.0, 145.7, 137.8, 137.3, 136.7, 133.2, 131.6, 131.0, 128.6, 128.5, 128.3, 127.9, 127.7, 121.4, 117.8,

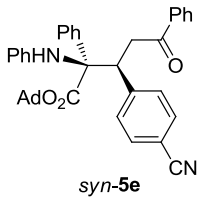
115.9, 82.8, 70.1, 48.3, 40.9, 40.8, 36.0, 30.7; FT-IR(KBr) $\tilde{\nu}$ 3404, 3052, 2912, 2852, 1728, 1687, 1600, 1502, 1447, 1354, 1322, 1259, 1235, 1176, 1073, 1053, 965, 747, 696, 684 cm^{-1}; HRMS(ESI) *m/z*: calcd. for $C_{39}H_{38}NO_3NaBr$ $(M+Na)^+$ 670.1933, found 670.1929; HPLC (CHIRALCEL OD-H, λ= 254 nm, hexane/2-propanol = 99/1, Flow rate = 1.0 mL/min), 88-90% ee, t_{major} = 5.74 min, t_{minor} = 8.47 min.



syn-**5d**

(2S,3R)-adamantan-1-yl 5-oxo-2,5-diphenyl-2-(phenylamino)-3-(4-(trifluoromethyl)phenyl)pentanoate (**5d).**

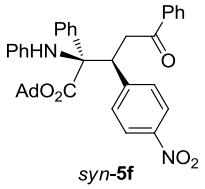
^1H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.72 (m, 2H), 7.67 – 7.58 (m, 2H), 7.55 – 7.47 (m, 1H), 7.42 – 7.35 (m, 2H), 7.35 – 7.29 (m, 3H), 7.03 (dd, *J* = 8.5, 7.4 Hz, 2H), 6.71 – 6.64 (m, 1H), 6.56 (ddd, *J* = 21.7, 14.0, 4.8 Hz, 2H), 6.44 – 6.38 (m, 2H), 5.07 (d, *J* = 3.9 Hz, 1H), 4.80 (dd, *J* = 11.5, 2.4 Hz, 1H), 3.61 (dd, *J* = 17.3, 11.6 Hz, 1H), 3.38 (dd, *J* = 17.3, 2.7 Hz, 1H), 2.01 (Br, 3H), 1.75 (M, 6H), 1.51 (M, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.34, 170.85, 145.61, 143.11, 137.26, 136.53, 133.29, 130.32, 128.68, 128.59, 128.55, 128.34, 127.92, 127.80, 124.92 – 124.68 (m), 117.97, 115.99, 82.93, 70.10, 48.55, 40.89, 40.73, 35.92, 30.71; FT-IR(KBr) $\tilde{\nu}$ 3400, 3056, 2913, 2854, 1725, 1691, 1600, 1501, 1447, 1424, 1325, 1236, 1166, 1126, 1068, 1050, 1017, 965, 832, 751, 691, 620 cm^{-1}; HRMS(ESI) *m/z*: calcd. for $C_{40}H_{38}NO_3F_3Na$ $(M+Na)^+$ 660.2701, found 660.2717; HPLC (CHIRALPAK IC, λ= 254 nm, hexane/2-propanol = 99.4/0.6, Flow rate = 1.0 mL/min), 92% ee, t_{major} = 5.44 min, t_{minor} = 6.86 min.



syn-**5e**

(2S,3R)-adamantan-1-yl 3-(4-cyanophenyl)-5-oxo-2,5-diphenyl-2-(phenylamino)pentanoate (**5e**).

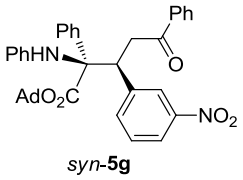
$[\alpha]_D^{20}$ = -59.3 (c = 0.135, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.67 (m, 2H), 7.59 – 7.52 (m, 2H), 7.52 – 7.46 (m, 3H), 7.39 – 7.28 (m, 7H), 7.08 (dd, *J* = 8.5, 7.4 Hz, 2H), 6.77 – 6.65 (m, 1H), 6.44 (d, *J* = 7.7 Hz, 2H), 4.92 (s, 1H), 4.75 (dd, *J* = 11.2, 2.5 Hz, 1H), 3.65 (dd, *J* = 17.6, 11.3 Hz, 1H), 3.54 (dd, *J* = 17.6, 2.7 Hz, 1H), 2.04 (Br, 3H), 1.75 (M, 6H), 1.64 – 1.44 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.20, 170.72, 145.39, 144.76, 137.07, 136.45, 133.40, 131.55, 130.86, 128.75, 128.64, 128.45, 128.35, 127.92, 127.90, 118.80, 118.11, 116.02, 111.20, 83.17, 77.38, 77.06, 76.74, 69.99, 48.46, 40.91, 40.80, 35.92, 30.73; FT-IR(KBr) $\tilde{\nu}$ 3401, 3349, 3056, 2910, 2853, 2227, 1726, 1677, 1601, 1501, 1449, 1354, 1252, 1231, 1184, 1052, 1019, 964, 877, 829, 750, 705, 688, 562 cm^{-1}; HRMS(ESI) *m/z*: calcd. for $C_{40}H_{38}N_2O_3Na$ $(M+Na)^+$ 617.2780, found 617.2778; HPLC (CHIRALPAK IC, λ= 254 nm, hexane/2-propanol = 98.5/1.5, Flow rate = 1.0 mL/min), 86% ee, t_{major} = 29.20 min, t_{minor} = 39.40 min.



syn-**5f**

(2S,3R)-adamantan-1-yl 3-(4-nitrophenyl)-5-oxo-2,5-diphenyl-2-(phenylamino)pentanoate (**5f)** .

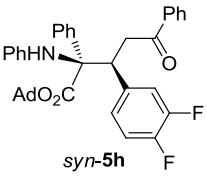
$[\alpha]_D^{20}$ = -10.4 (c = 0.08, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.8 Hz, 1H), 7.77 – 7.64 (m, 1H), 7.60 - 7.55 (m, 1H), 7.52 – 7.46 (m, 1H), 7.42 – 7.33 (m, 1H), 7.09 (dd, *J* = 8.4, 7.4 Hz, 1H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.46 (d, *J* = 7.8 Hz, 1H), 4.93 (s, 1H), 4.83 (dd, *J* = 11.2, 2.6 Hz, 1H), 3.68 (dd, *J* = 17.7, 11.2 Hz, 1H), 3.58 (dd, *J* = 17.7, 2.7 Hz, 1H), 2.05 (s, 1H), 1.77 (q, *J* = 11.4 Hz, 1H), 1.54 (q, *J* = 12.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.12, 170.69, 147.15, 146.94, 145.31, 137.02, 136.39, 133.44, 130.95, 128.78, 128.65, 128.50, 128.31, 127.98, 127.90, 122.90, 118.16, 116.05, 83.30, 69.96, 48.10, 41.06, 40.82, 35.90, 30.73; FT-IR(KBr) $\tilde{\nu}$ 3372, 3056, 2912, 2852, 1722, 1677, 1599, 1513, 1501, 1446, 1344, 1229, 1179, 1110, 1049, 857, 753, 711, 690 cm^{-1}; HRMS(ESI) *m/z*: calcd. for $C_{39}H_{38}N_2O_5Na$ $(M+Na)^+$ 637.2678, found 637.2698; HPLC (CHIRALCEL OD-H, λ= 254 nm, hexane/2-propanol = 97/3, Flow rate = 1.0 mL/min), 90% ee, t_{major} = 9.52 min, t_{minor} = 11.16 min.



syn-**5g**

(2S,3R)-adamantan-1-yl 3-(3-nitrophenyl)-5-oxo-2,5-diphenyl-2-(phenylamino)pentanoate (**5g)**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 8.07 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.74 – 7.66 (m, 2H), 7.62 – 7.54 (m, 3H), 7.52 – 7.46 (m, 1H), 7.43 – 7.31 (m, 6H), 7.10 (dd, *J* = 8.3, 7.5 Hz, 2H), 6.78 – 6.68 (m, 1H), 6.48 (d, *J* = 7.8 Hz, 2H), 4.99 (s, 1H), 4.87 (dd, *J* = 11.1, 2.5 Hz, 1H), 3.68 (dd, *J* = 17.8, 11.2 Hz, 1H), 3.58 (dd, *J* = 17.8, 2.7 Hz, 1H), 2.04 (br, 3H), 1.84 – 1.70 (m, 6H), 1.60 – 1.46 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.16, 170.71, 147.73, 145.29, 141.36, 137.09, 136.39, 136.21, 133.41, 128.78, 128.64, 128.58, 128.19, 127.98, 127.92, 125.28, 122.43, 118.15, 116.21, 83.37, 47.74, 41.11, 40.72, 35.89, 30.75; FT-IR(KBr) $\tilde{\nu}$ 3393, 3057, 2912, 2853, 1725, 1688, 1600, 1530, 1498, 1447, 1347, 1253, 1180, 1102, 1050, 753, 691 cm^{-1}; HRMS(ESI) *m/z*: calcd. for $C_{39}H_{38}N_2O_5Na$ $(M+Na)^+$ 637.2678, found 637.2663; HPLC (CHIRALPAK IC, λ= 254 nm, hexane/2-propanol = 99.5/0.5, Flow rate = 1.0 mL/min), 86% ee, t_{major} = 15.84 min, t_{minor} = 19.48 min.

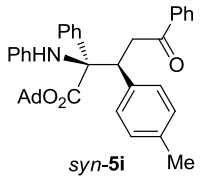


syn-**5h**

(2S,3R)-adamantan-1-yl 3-(3,4-difluorophenyl)-5-oxo-2,5-diphenyl-2-(phenylamino)pentanoate (**5h).**

$[\alpha]_D^{20}$ = -36.4 (c = 0.4483, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.72 (m, 2H), 7.67 – 7.58 (m, 2H), 7.55 – 7.47 (m, 1H), 7.42 – 7.35 (m, 2H), 7.35 – 7.29 (m, 3H), 7.03 (dd, *J* = 8.5, 7.4 Hz, 2H), 6.71 – 6.64 (m, 1H), 6.56 (ddd, *J* = 21.7, 14.0, 4.8 Hz, 2H), 6.44 – 6.38 (m, 2H), 5.07 (d, *J* = 3.9 Hz, 1H),

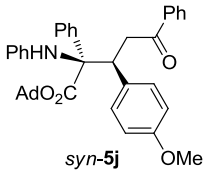
4.80 (dd, *J* = 11.5, 2.4 Hz, 1H), 3.61 (dd, *J* = 17.3, 11.6 Hz, 1H), 3.38 (dd, *J* = 17.3, 2.7 Hz, 1H), 2.01 (Br, 3H), 1.75 (M, 6H), 1.51 (M, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.94, 170.94, 145.93, 136.55, 133.24, 131.61 – 130.58 (m), 129.24, 128.60, 128.54, 127.91, 127.84, 127.66, 121.81 (dd, *J* = 13.8, 3.9 Hz), 118.25, 116.01, 110.74 (dd, *J* = 20.8, 3.1 Hz), 103.49 (dd, *J* = 28.2, 25.2 Hz), 82.53, 70.73, 40.60, 39.92, 35.98, 30.72; ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.15 (s), -111.30 – -112.30 (m); FT-IR(KBr) $\tilde{\nu}$ 3359, 3057, 2910, 2853, 1725, 1687, 1600, 1501, 1447, 1354, 1255, 1216, 1180, 1139, 1094, 1051, 966, 851, 749, 691 cm^{-1}; HRMS(ESI) *m/z*: calcd. for $C_{39}H_{37}NO_3F_2Na$ $(M+Na)^+$ 628.2639, found 628.2657.



syn-**5i**

(2S,3R)-adamantan-1-yl 5-oxo-2,5-diphenyl-2-(phenylamino)-3-(p-tolyl)pentanoate (5i).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 6.66 (m, 4H), 7.50 – 7.44 (m, 1H), 7.37 – 7.29 (m, 6H), 7.08 – 6.98 (m, 6H), 6.68 – 6.64 (m, *J* = 7.3 Hz, 1H), 6.42 – 6.38 (m, 2H), 4.88 (s, 1H), 4.54 (dd, *J* = 11.4, 2.4 Hz, 1H), 3.63 (dd, *J* = 17.2, 11.4 Hz, 1H), 3.32 (dd, *J* = 17.2, 2.5 Hz, 1H), 2.26 (s, 1H), 2.02 (s, 1H), 1.80 – 1.70 (m, 6H), 1.57 – 1.47 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 171.3, 146.1, 137.7, 136.9, 136.9, 135.4, 132.9, 129.7, 128.9, 128.8, 128.5, 128.4, 128.0, 128.0, 127.5, 117.6, 115.9, 82.4, 70.3, 49.1, 40.9, 40.7, 36.0, 30.7, 21.1; FT-IR(KBr) $\tilde{\nu}$ 3402, 3053, 2912, 2851, 1727, 1688, 1600, 1511, 1502, 1446, 1355, 1315, 1250, 1177, 1954, 966, 750, 733, 698 cm^{-1}; HRMS(ESI) *m/z*: calcd. for $C_{39}H_{38}NO_3NaBr$ $(M+Na)^+$ 670.1933, found 670.1929; HPLC (CHIRALCEL OD-H, λ= 254 nm, hexane/2-propanol = 99/1, Flow rate = 1.0 mL/min), 78% ee, t_{major} = 5.00 min, t_{minor} = 7.05 min.

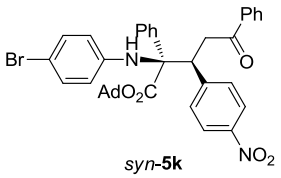


syn-**5j**

(2S,3R)-adamantan-1-yl 3-(4-methoxyphenyl)-5-oxo-2,5-diphenyl-2-(phenylamino)pentanoate (5j).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.61 (m, 4H), 7.49 – 7.44 (m, 1H), 7.37 – 7.30 (m, 5H), 7.09 – 7.00 (m, 4H), 6.77 – 6.72 (m, 2H), 6.69 – 6.63 (m, 1H), 6.40 (d, *J* = 7.8 Hz, 2H), 4.88 (s, 1H), 4.54 (dd, *J* = 11.4, 2.3 Hz, 1H), 3.74 (s, 3H), 3.60 (dd, *J* = 17.1, 11.5 Hz, 1H), 3.33 (dd, *J* = 17.1, 2.5 Hz, 1H), 2.02 (s, 3H), 1.77 (q, *J* = 11.6 Hz, 6H), 1.57 – 1.48 (d, *J* = 3.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 171.3, 158.8, 146.0, 137.6, 136.9, 133.0, 130.9, 130.5, 128.9, 128.5, 128.5, 128.1, 128.0, 127.5, 117.6, 115.9, 113.4, 82.4, 70.4, 55.1, 48.7, 41.0, 40.7, 36.0, 30.7; FT-IR(KBr) $\tilde{\nu}$ 3372, 3056, 2912, 2852, 1722, 1677, 1599, 1513, 1501, 1446, 1344, 1229, 1179, 1110, 1049, 857, 753, 711, 690 cm^{-1}.

HRMS(ESI) *m/z*: calcd. for $C_{40}H_{41}NO_4Na$ $(M+Na)^+$ 622.2933, found 622.2912; HPLC (CHIRALCEL OD-H, λ= 254 nm, hexane/2-propanol = 150/6, Flow rate = 1.0 mL/min), 62% ee, t_{major} = 5.50 min, t_{minor} = 7.26 min.

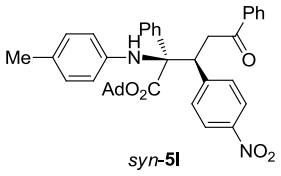


syn-**5k**

(2S,3R)-adamantan-1-yl

2-((4-bromophenyl)amino)-3-(4-nitrophenyl)-5-oxo-2,5-diphenylpentanoate (**5k).**

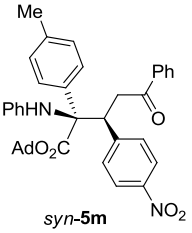
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.8 Hz, 2H), 7.74 – 7.66 (m, 1H), 7.54 – 7.46 (m, 3H), 7.42 – 7.30 (m, 7H), 7.19 – 7.12 (m, 2H), 6.32 (d, *J* = 8.9 Hz, 2H), 5.00 (s, 1H), 4.82 (dd, *J* = 2.4 Hz, 1H), 3.66 (dd, *J* = 17.6, 11.2 Hz, 1H), 3.54 (dd, *J* = 17.6, 2.6 Hz, 1H), 2.07 (s, 3H), 1.86 – 1.70 (m, 6H), 1.64 – 1.46 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 170.4, 147.2, 146.7, 144.3, 136.3, 133.6, 131.5, 130.9, 128.7, 128.6, 128.2, 128.2, 127.9, 123.0, 117.5, 109.9, 83.6, 77.4, 77.1, 76.7, 69.9, 48.1, 40.9, 35.9, 30.7; FT-IR(KBr) $\tilde{\nu}$ 3399, 2912, 2853, 1725, 1690, 1597, 1514, 1448, 1346, 1234, 1183, 1107, 1050, 857, 812, 734, 691 cm^{-1}; HRMS(ESI) *m/z*: calcd. for $C_{39}H_{37}N_2O_5NaBr$ $(M+Na)^+$ 715.1784, found 715.1768; HPLC (CHIRALPAK IC, λ= 254 nm, hexane/2-propanol = 98/2, Flow rate = 1.0 mL/min), 84% ee, t_{major} = 16.95 min, t_{minor} = 18.51 min.



syn-**5l**

(2S,3R)-adamantan-1-yl 3-(4-nitrophenyl)-5-oxo-2,5-diphenyl-2-(p-tolylamino)pentanoate (**5l).**

$[\alpha]_D^{20}$ = -74.2 (c = 0.3283, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.8 Hz, 2H), 7.75 – 7.66 (m, 2H), 7.57 – 7.53 (m, 2H), 7.53 – 7.46 (m, 1H), 7.40 – 7.32 (m, 7H), 6.90 (d, *J* = 8.2 Hz, 2H), 6.37 (d, *J* = 8.5 Hz, 2H), 4.87 – 4.78 (m, 2H), 3.67 (dd, *J* = 17.7, 11.2 Hz, 1H), 3.57 (dd, *J* = 17.7, 2.7 Hz, 1H), 2.22 (s, 3H), 2.05 (s, 3H), 1.85 – 1.69 (m, 6H), 1.60 – 1.48 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 170.8, 147.1, 147.1, 142.9, 137.2, 136.4, 133.4, 131.0, 129.3, 128.6, 128.5, 128.4, 127.9, 127.2, 122.9, 116.1, 83.2, 77.3, 77.0, 76.7, 70.0, 48.0, 41.1, 40.8, 35.9, 30.7, 20.4; FT-IR(KBr) $\tilde{\nu}$ 3389, 3060, 2911, 2853, 1725, 1690, 1594, 1524, 1493, 1447, 1346, 1319, 1295, 1253, 1234, 1180, 1105, 1049, 908, 857, 816, 734, 690 cm^{-1}; HRMS(ESI) *m/z*: calcd. for $C_{40}H_{40}N_2O_5Na$ $(M+Na)^+$ 651.2835, found 651.2805; HPLC (CHIRALPAK IC, λ= 254 nm, hexane/2-propanol = 98/2, Flow rate = 1.0 mL/min), 90% ee, t_{major} = 14.58 min, t_{minor} = 18.90 min.

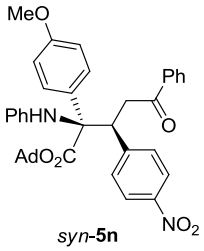


syn-**5m**

(2S,3R)-adamantan-1-yl 3-(4-nitrophenyl)-5-oxo-5-phenyl-2-(phenylamino)-2-(p-tolyl)pentanoate (**5m).**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.8 Hz, 2H), 7.88 – 7.78 (m, 2H), 7.59 – 7.50 (m, 1H), 7.46 – 7.38 (m, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.28 – 7.20 (m, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.02 – 6.93 (m,

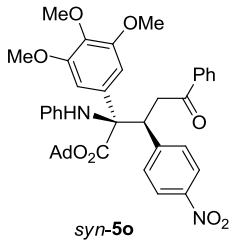
2H), 6.73 – 6.62 (m, 1H), 6.36 (d, *J* = 7.9 Hz, 1H), 4.65 (s, 1H), 4.58 (dd, *J* = 8.6, 4.3 Hz, 1H), 3.73 (dd, *J* = 18.4, 4.3 Hz, 1H), 3.37 (dd, *J* = 18.4, 8.7 Hz, 1H), 2.37 (s, 3H), 2.07 (br, 3H), 1.93 – 1.76 (m, 6H), 1.63 – 1.48 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 170.5, 147.2, 146.8, 145.8, 137.7, 136.6, 133.5, 132.9, 131.3, 129.3, 128.7, 128.5, 128.4, 128.0, 122.8, 119.0, 116.3, 82.9, 70.7, 49.4, 41.1, 39.9, 36.0, 30.8, 21.1; HRMS(ESI) *m/z*: calcd. for $C_{40}H_{40}N_2O_5Na$ $(M+Na)^+$ 651.2835, found 651.2825; HPLC (CHIRALPAK IC, λ= 254 nm, hexane/2-propanol = 98/2, Flow rate = 1.0 mL/min), 88% ee, t_{major} = 14.78 min, t_{minor} = 18.47 min.



syn-**5n**

(2S,3R)-adamantan-1-yl
-(4-methoxyphenyl)-3-(4-nitrophenyl)-5-oxo-5-phenyl-2-(phenylamino)pen- tanoate (5n).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.7 Hz, 2H), 7.74 – 7.67 (m, 2H), 7.55 – 7.43 (m, 3H), 7.40 – 7.32 (m, 4H), 7.14 – 7.04 (m, 2H), 6.89 (d, *J* = 9.0 Hz, 2H), 6.76 – 6.68 (m, 1H), 6.46 (d, *J* = 7.9 Hz, 2H), 4.77 (dd, *J* = 11.1, 2.3 Hz, 1H), 3.83 (s, 3H), 3.66 (dd, *J* = 17.7, 11.2 Hz, 1H), 3.56 (dd, *J* = 17.7, 2.6 Hz, 1H), 2.06 (s, 3H), 1.86 – 1.73 (m, 6H), 1.61 – 1.49 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 171.0, 159.2, 147.1, 147.0, 145.4, 136.40, 133.4, 130.9, 129.7, 128.8, 128.6, 127.9, 122.9, 118.1, 116.0, 114.1, 113.7, 83.2, 69.6, 55.3, 49.2, 48.4, 41.0, 40.8, 35.9, 30.7; FT-IR(KBr) $\tilde{\nu}$ 3400, 3055, 2912, 2856, 1727, 1598, 1512, 1500, 1446, 1349, 1250, 1177, 954, 965, 754, 733, 699 cm^{-1}; HRMS(ESI) *m/z*: calcd. for $C_{40}H_{40}N_2O_6Na$ $(M+Na)^+$ 667.2784, found 667.2788; HPLC (CHIRALPAK IC, λ= 254 nm, hexane/2-propanol = 97/3, Flow rate = 1.0 mL/min), 92% ee, t_{major} = 20.00 min, t_{minor} = 22.61 min.

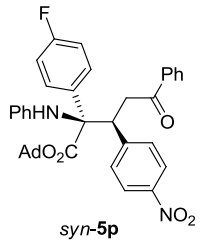


syn-**5o**

(2S,3R)-adamantan-1-yl 3-(4-nitrophenyl)-5-oxo-5-phenyl-2-(phenylamino)-2-(3,4,5-trimethoxy-phenyl)pentanoate (5o).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 10.5 Hz, 2H), 7.69 (d, *J* = 7.4 Hz, 2H), 7.52 (dd, *J* = 16.8, 9.4 Hz, 1H), 7.46 – 7.32 (m, 4H), 7.19 – 7.06 (m, 2H), 6.84 (s, 2H), 6.79 – 6.71 (m, 1H), 6.52 (d, *J* = 11.8 Hz, 2H), 4.89 (s, 1H), 4.79 (dd, *J* = 10.3, 2.8 Hz, 1H), 3.89 (s, 3H), 3.70 (s, 6H), 3.69 – 3.55 (m, 2H), 2.14 – 2.02 (m, 3H), 1.86 – 1.71 (m, 6H), 1.65 – 1.48 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 170.6, 153.0, 147.2, 145.3, 137.8, 133.5, 132.5, 131.0, 128.7, 128.7, 128.1, 127.9, 123.9, 123.0, 118.4, 116.3, 106.0, 83.4, 70.1, 61.0, 56.3, 41.2, 40.9, 35.9, 30.7; FT-IR(KBr) $\tilde{\nu}$ 3399, 2912, 2853, 1725, 1690, 1600, 1513, 1501, 1449, 1412, 1346, 1322, 1235, 1185, 1128, 1051, 1006, 857, 751, 693 cm^{-1}; HRMS(ESI) *m/z*: calcd. for $C_{42}H_{44}N_2O_8Na$ $(M+Na)^+$ 727.2995, found 727.3010; HPLC (CHIRALPAK IC, λ= 254 nm, hexane/2-propanol = 150/1, Flow rate = 1.0 mL/min), 40% ee, t_{major} =

14.57 min, t_{minor} = 13.05 min.

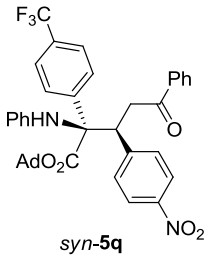


syn-**5p**

(2S,3R)-adamantan-1-yl

2-(4-fluorophenyl)-3-(4-nitrophenyl)-5-oxo-5-phenyl-2-(phenylamino)pen-tanoate (5p).

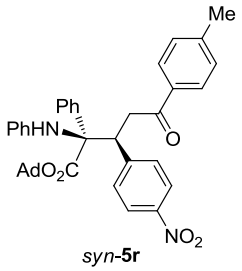
$[\alpha]_D^{20}$ = -80.1 (c = 0.6133, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.8 Hz, 2H), 7.75 – 7.67 (m, 2H), 7.61 – 7.46 (m, 3H), 7.42 – 7.28 (m, 4H), 7.15 – 7.00 (m, 4H), 6.80 – 6.62 (m, 1H), 6.44 (d, *J* = 7.8 Hz, 2H), 4.90 (s, 1H), 4.75 (dd, *J* = 11.2, 2.1 Hz, 1H), 3.68 (dd, *J* = 17.6, 11.4 Hz, 1H), 3.52 (dd, *J* = 17.6, 2.4 Hz, 1H), 2.06 (br, 3H), 1.86 – 1.68 (m, 6H), 1.64 – 1.46 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 170.5, 163.6, 161.1, 147.2, 146.6, 145.1, 136.3, 133.6, 132.7, 130.9, 130.4, 130.3, 128.8, 128.7, 127.9, 123.0, 118.5, 116.0, 115.5, 115.3, 83.5, 69.6, 48.7, 40.9, 35.9, 30.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.05; FT-IR(KBr) $\tilde{\nu}$ 3395, 3057, 2913, 2853, 1725, 1690, 1600, 1558, 1513, 1502, 1448, 1346, 1318, 1230, 1161, 1103, 1050, 857, 751, 691 cm^{-1}; HRMS(ESI) *m/z*: calcd. for $C_{39}H_{37}N_2O_5FNa$ $(M+Na)^+$ 655.2584, found 655.2582; HPLC (CHIRALPAK IC, λ= 254 nm, hexane/2-propanol = 98/2, Flow rate = 1.0 mL/min), 92% ee, t_{major} = 18.32 min, t_{minor} = 23.67 min.



syn-**5q**

(2S,3R)-adamantan-1-yl 3-(4-nitrophenyl)-5-oxo-5-phenyl-2-(phenylamino)-2-(4-(trifluoromethyl) phenyl)pentanoate (5q).

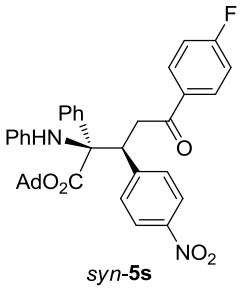
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.8 Hz, 2H), 7.78 – 7.67 (m, 4H), 7.66 – 7.60 (m, 2H), 7.55 – 7.47 (m, 1H), 7.41 – 7.29 (m, 4H), 7.10 (dd, *J* = 8.3, 7.5 Hz, 2H), 6.81 – 6.69 (m, 1H), 6.40 (d, *J* = 7.8 Hz, 2H), 4.92 (s, 1H), 4.77 (dd, *J* = 11.2, 2.3 Hz, 1H), 3.67 (dd, *J* = 17.6, 11.3 Hz, 1H), 3.48 (dd, *J* = 17.6, 2.5 Hz, 1H), 2.11 – 2.01 (m, 3H), 1.88 – 1.68 (m, 6H), 1.65 – 1.42 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 170.0, 147.3, 146.2, 144.8, 141.2, 136.2, 133.6, 130.8, 130.0, 129.1, 128.9, 128.8, 128.7, 128.6, 127.9, 125.3 (q, *J* = 6.8 Hz)., 124.2, 123.1, 118.7, 116.0, 83.91, 77.33, 77.0, 76.7, 69.9, 48.7, 40.8, 40.85, 35.8, 30.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.49; HRMS(ESI) *m/z*: calcd. for $C_{40}H_{37}N_2O_5Na$ $(M+Na)^+$ 705.2552, found 705.2533; HPLC (CHIRALPAK IC, λ= 254 nm, hexane/2-propanol = 98/2, Flow rate = 1.0 mL/min), 82% ee, t_{major} = 11.42 min, t_{minor} = 14.10 min.



syn-**5r**

(2S,3R)-adamantan-1-yl 3-(4-nitrophenyl)-5-oxo-2-phenyl-2-(phenylamino)-5-(p-tolyl)pentanoate (5r).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.8 Hz, 2H), 7.63 – 7.51 (m, 4H), 7.41 – 7.32 (m, 5H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.09 (dd, *J* = 8.4, 7.4 Hz, 2H), 6.77 – 6.67 (m, 1H), 6.45 (d, *J* = 7.8 Hz, 2H), 4.93 (s, 1H), 4.82 (dd, *J* = 11.4, 2.4 Hz, 1H), 3.66 (dd, *J* = 17.6, 11.4 Hz, 1H), 3.54 (dd, *J* = 17.6, 2.6 Hz, 1H), 2.35 (s, 3H), 2.09 –2.05 (br, 3H), 1.77 (q, *J* = 11.4 Hz, 6H), 1.60 – 1.47 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 170.7, 147.1, 147.0, 145.3, 144.4, 137.0, 134.0, 131.0, 129.3, 128.8, 128.5, 128.3, 128.0, 128.0, 122.9, 118.1, 116.0, 83.3, 70.0, 48.9, 40.9, 40.8, 35.9, 30.7, 21.6; FT-IR(KBr) $\tilde{\nu}$ 3394, 3056, 2919, 2853, 1725, 1711, 1679, 1603, 1524, 1501, 1447, 1346, 1318, 1235, 1180, 1107, 1050, 964, 857, 815, 750, 697 cm^{-1}; HRMS(ESI) *m/z*: calcd. for $C_{40}H_{40}N_2O_5Na$ $(M+Na)^+$ 651.2835, found 651.2815; HPLC (CHIRALPAK IC, λ= 254 nm, hexane/2-propanol = 97/3, Flow rate = 1.0 mL/min), 94% ee, t_{major} = 15.44 min, t_{minor} = 18.82 min.

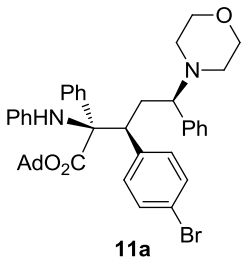


syn-**5s**

(2R,3S)-adamantan-1-yl

5-(4-fluorophenyl)-3-(4-nitrophenyl)-5-oxo-2-phenyl-2-(phenylamino)pen-tanoate (5s)

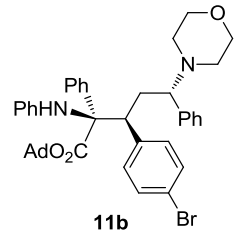
$[\alpha]_D^{20}$ = -79.1 (c = 0.2033, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.7 Hz, 1H), 7.79 – 7.67 (m, 1H), 7.61 – 7.51 (m, 1H), 7.44 – 7.31 (m, 1H), 7.15 – 7.06 (m, 1H), 7.06 – 6.97 (m, 1H), 6.79 – 6.68 (m, 1H), 6.46 (d, *J* = 7.9 Hz, 1H), 4.94 (s, 1H), 4.83 (dd, *J* = 10.8, 2.9 Hz, 1H), 3.64 (dd, *J* = 17.7, 10.9 Hz, 1H), 3.56 (dd, *J* = 17.6, 3.0 Hz, 1H), 2.05 (s, 1H), 1.86 – 1.63 (m, 1H), 1.58 – 1.46 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 170.7, 165.9 (d, *J* = 255.7 Hz), 147.2, 146.8, 145.3, 137.0, 132.8, 130.9, 130.6, 130.5, 128.8, 128.6, 128.2, 128.0, 122.9, 118.2, 116.0, 115.9, 115.7, 83.4, 77.4, 77.0, 76.7, 69.9, 48.0, 41.0, 40.801, 35.9, 30.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.26, -218.44; FT-IR(KBr) $\tilde{\nu}$ 3386, 3057, 2913, 2855, 1709, 1687, 1599, 1558, 1526, 1446, 1410, 1346, 1215, 1156, 1103, 1048, 993, 840, 748, 710 cm^{-1}; HRMS(ESI) *m/z*: calcd. for $C_{39}H_{37}N_2O_5FNa$ $(M+Na)^+$ 655.2584, found 655.2598; HPLC (CHIRALPAK IC, λ= 254 nm, hexane/2-propanol = 97/3, Flow rate = 1.0 mL/min), 94% ee, t_{major} = 12.04 min, t_{minor} = 13.54 min.



11a

(2R,3S,5R)-adamantan-1-yl 3-(4-bromophenyl)-5-morpholino-2,5-diphenyl-2-(phenylamino)pentanoate (11a).

$[\alpha]_D^{20}$ = -43.0 (c = 0.348, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 3.9 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.32 – 7.26 (m, 3H), 7.22 (dt, *J* = 10.7, 4.0 Hz, 3H), 7.03 – 6.95 (m, 2H), 6.92 – 6.78 (m, 4H), 6.68 – 6.57 (m, 1H), 6.37 (d, *J* = 8.0 Hz, 2H), 4.61 (s, 1H), 4.16 (d, *J* = 11.0 Hz, 1H), 3.67 (t, *J* = 4.4 Hz, 4H), 2.87 (dd, *J* = 11.7, 3.1 Hz, 1H), 2.54 (t, *J* = 12.0 Hz, 1H), 2.35 – 2.20 (m, 2H), 2.03 (s, 3H), 1.98 – 1.89 (m, 2H), 1.83 (dd, *J* = 19.0, 7.1 Hz, 1H), 1.76 – 1.65 (m, 6H), 1.58 – 1.38 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 145.9, 138.1, 137.5, 137.2, 131.9, 131.0, 129.6, 128.5, 128.4, 127.9, 127.5, 127.4, 121.2, 117.9, 115.7, 82.2, 77.3, 77.0, 76.7, 70.7, 67.6, 65.9, 52.1, 49.22, 40.80, 36.02, 32.0, 30.7; FT-IR(KBr) $\tilde{\nu}$ 3416, 3056, 3026, 1725, 1703, 1604, 1501, 1452, 1355, 1317, 1254, 1230, 1182, 1118, 1051, 1108, 967, 822, 751, 703, 553 cm^{-1}; HRMS(ESI) *m/z*: calcd. for $C_{43}H_{48}N_2O_3Br$ $(M+Na)^+$ 719.2848, found 719.2876.



11b

(2R,3S,5S)-adamantan-1-yl 3-(4-bromophenyl)-5-morpholino-2,5-diphenyl-2-(phenylamino)pentanoate (11b).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 6H), 7.31 – 7.19 (m, 4H), 7.03 – 6.91 (m, 4H), 6.74 – 6.53 (m, 3H), 6.28 (d, *J* = 7.8 Hz, 2H), 4.44 (s, 1H), 3.61 – 3.44 (m, 1H), 3.14 (d, *J* = 10.5 Hz, 1H), 2.58 (dd, *J* = 11.2, 3.2 Hz, 1H), 2.41 (td, *J* = 12.9, 3.3 Hz, 1H), 2.26 – 2.12 (m, 3H), 2.11 – 2.02 (m, 2H), 1.99 (s, 3H), 1.66 – 1.56 (m, 6H), 1.56 – 1.43 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$)δ 171.0, 145.7, 139.4, 137.1, 136.5, 131.9, 131.0, 129.6, 129.1, 128.4, 128.3, 127.67, 127.5, 127.4, 121.5, 117.8, 115.7, 82.2, 77.3, 77.0, 76.7, 70.5, 68.6, 67.0, 51.4, 40.6, 36.0, 33.6, 30.7; FT-IR(KBr) $\tilde{\nu}$ 3390, 3059, 3026, 2955, 2911, 2852, 2812, 1713, 1604, 1500, 1450, 1258, 1233, 1181, 1119, 1054, 1010, 876, 821, 759, 703, 547 cm^{-1}; HRMS(ESI) *m/z*: calcd. for $C_{43}H_{48}N_2O_3Br$ $(M+Na)^+$ 719.2848, found 719.2833.

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