Electronic Supplementary Information

Ruthenium hydride catalyzed α-alkylation of ketones with primary alcohols for access to bioactive molecules using the borrowing hydrogen approach

Ovender Singh,*[a, c] Youngsuk Kim,[c] Rahul Chauhan,[e] Junseong Lee,[a] Nidhi Tyagi*[b]

a. Department of Chemistry, Chonnam National University, Gwangju 61186, Republic of Korea ovendersingh@pusan.ac.kr; ovendersingh93@gmail.com

b. School of Chemical Sciences, Amity University Punjab, Sector 82A, IT City, International Airport Road, Mohali-140306, Punjab, India. Email: nnaithani@pb.anity.edu; nidhityagi999@gmail.com

c. Pusan National University, Geumjeong-gu, Busan, Republic of Korea.

d. Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247667, Uttarakhand, India.

.

.

Table of Content		
S. No.	**Experimental Details**	**Page No.**
1	Materials and Methods	4
2.	Single crystal X-ray crystallography details	4
3	Details of theoretical studies	4
Figure S1	^{1}H NMR spectrum of **a)** ligand (L^1) **b)** complex **1** in $CDCl_3$.	5
Figure S2.	a) Infrared spectrum of complex [$L^1RuH(CO)(PPh_3)_2$]; b) Theoretically predicted IR spectra of complex **1**	6
Figure S3	HRMS spectrum of ligand (L^1)	6
Figure S4	HRMS spectrum of complex [$L^1RuH(CO)(PPh_3)_2$]	7
Figure S5.	Cyclic voltammogram of **1** (1.0 mM) in THF vs Ag/AgCl. Electrolyte: Bu_4NPF_6 (0.1 M), scan rate = 0.1 V/s.	7
Figure S6	(a) Optimized geometry of complex [$L^1RuH(CO)(PPh_3)_2$] (b) Experimental and theoretical UV-Vis spectral analysis of complex **1**	8
Table S1	Co-ordinate parameters of complex [$L^1RuH(CO)(PPh_3)_2$]	9-11
Table S2	Crystal data and structure refinement for [$L^1RuH(CO)(PPh_3)_2$]	12
Table S3	Bond Lengths for [$L^1RuH(CO)(PPh_3)_2$]	13
Table S4	Bond Angles for [$L^1RuH(CO)(PPh_3)_2$]	14-15
Table S5	Optimization of reaction conditions for α-alkylation in different solvents and bases	16
Figure S7	Time dependent C-C coupled product formation during the reaction. **Reaction condition:** Acetophenone (1 mmol), benzyl alcohol (1 mmol), Cat. (0.1 mol%), base (0.15 equiv.), Solvent 2 mL at 120 °C for 24 h.	17
Table S6	Effect of catalyst loading on the α-alkylation of ketones using primary alcohols catalytic reaction	17
Table S7	Catalytic performance metrics including reactants, % yields, TON, TOF, and reaction conditions	18-19
Figure S8	^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P1**	20
Figure S9	$^{13}C\{^1H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P1**	20
Figure S10	^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P2**	21
Figure S11	$^{13}C\{^1H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P2**	21
Figure S12	^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P3**	22
Figure S13	$^{13}C\{^1H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P3**	22
Figure S14	^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P4**	23
Figure S15	$^{13}C\{^1H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P4**	23
Figure S16	^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P5**	24
Figure S17	$^{13}C\{^1H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P5**	24
Figure S18	^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P6**	25
Figure S19	$^{13}C\{^1H\}$ NMR Spectrum (100 MHz, $CDCl_3$) of **P6**	25
Figure S20	^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P7**	26
Figure S21	$^{13}C\{^1H\}$ NMR Spectrum (100 MHz, $CDCl_3$) of **P7**	26
Figure S22	^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P8**	27
Figure S23	$^{13}C\{^1H\}$ NMR Spectrum (100 MHz, $CDCl_3$) of **P8**	27
Figure S24	^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P9**	28
Figure S25	$^{13}C\{^1H\}$ NMR Spectrum (100 MHz, $CDCl_3$) of **P9**	28
Figure S26	^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P10**	29
Figure S27	$^{13}C\{^1H\}$ NMR Spectrum (100 MHz, $CDCl_3$) of **P10**	29
Figure S28	^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P11**	30
Figure S29	$^{13}C\{^1H\}$ NMR Spectrum (100 MHz, $CDCl_3$) of **P11**	30
Figure S30	^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P12**	31
Figure S31	$^{13}C\{^1H\}$ NMR Spectrum (100 MHz, $CDCl_3$) of **P12**	31
Figure S32	^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P13**	32
Figure S33	^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of **P13**	32
Figure S34	^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P14**	33
Figure S35	$^{13}C\{^1H\}$ NMR Spectrum (100 MHz, $CDCl_3$) of **P14**	33
Figure S36	^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P15**	34
Figure S37	$^{13}C\{^1H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P15**	34

Figure S38	^{1}H NMR Spectrum (500 MHz, $CDCl_3$) **P16**	35
Figure S39	$^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **16**	35
Figure S40	^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P17**	36
Figure S41	$^{13}C\{^{1}H\}$ NMR Spectrum (100 MHz, $CDCl_3$) of **P17**	36
Figure S42	^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P18**	37
Figure S43	$^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P18**	37
Figure S44	^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P19**	38
Figure S45	$^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P19**	38
Figure S46	^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P20**	39
Figure S47	$^{13}C\{^{1}H\}$ NMR Spectrum (100 MHz, $CDCl_3$) of **P20**	39
Figure S48	^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P21**	40
Figure S49	$^{13}C\{^{1}H\}$ NMR Spectrum (100 MHz, $CDCl_3$) of **P21**	40
Figure S50	^{1}H NMR Spectrum (500 MHz, DMSO-D_6) of **P22**	41
Figure S51	$^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, DMSO-D_6) of **P22**	41
Figure S52	^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P23**	42
Figure S53	^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of **P23**	42
Figure S54	^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P24**	43
Figure S55	$^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P24**	43
Figure S56	^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P25**	44
Figure S57	$^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P25**	44
Figure S58	^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P26**	45
Figure S59	$^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P26**	45
Figure S60	^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P27**	46
Figure S61	$^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P27**	46
Figure S62	^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P28**	47
Figure S63	$^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P28**	47
Figure S64	^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P29**	48
Figure S65	$^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P29**	48
Figure S66	^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P30**	49
Figure S67	$^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P30**	49
Figure S68	^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P31**	50
Figure S69	$^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P31**	50
Figure S70	^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P32**	51
Figure S71	$^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P32**	51
Figure S72	^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P33**	52
Figure S73	$^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P33**	52
Figure S74	^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P34**	53
Figure S75	$^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P34**	53
Figure S76	^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P35**	54
Figure S77	$^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P35**	54
Figure S78	^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P36**	55
Figure S79	$^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P36**	55
Figure S80	^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P37**	56
Figure S81	$^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P37**	56
Figure S82	^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P38**	57
Figure S83	$^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P38**	57
Figure S84	^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P39**	58
Figure S85	$^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P39**	58
Figure S86	^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P40**	59
Figure S87	$^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P40**	59
Figure S88	Determination of initial slopes for the product formation in the presence of excess PPh_3.	60
Figure S89	HRMS spectrum of Intermediate **C**	61
Figure S90	^{1}H NMR Spectrum (500 MHz, $CDCl_3$).	61
Figure S91	$^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$)	62
Figure S92	GC-PDD Chromatograms	62
Figure S93	GC-MS spectra of styrene reduction	63
Scheme S1	Control experiments	63
4.	References	64

1. Methods and Materials Synthesis

Reagents were purchased from commercial suppliers (Sigma-Aldrich and Alfa Aesar stored under N_2 conditions, and used as it is. All reactions were performed under anaerobic and dry conditions by using N_2-filled glove boxes. Ligand L1 (2-(2H-Benzotriazol-2-yl)-4,6-di-tert-pentylphenol), Trimethylamine and tris(triphenylphosphine)ruthenium(II) dichloride were purchased Sigma Aldrich. The formation and purity of synthesized compounds were confirmed by 1H-NMR spectra collected on a Bruker 400 MHz, NMR spectrometer. IR spectra were obtained with a Bruker EQIUINOX-55 spectrophotometer. The UV/Vis absorption spectra were recorded on a Shimadzu UV 3100 UV–Vis–NIR spectrophotometer. High resolution mass spectra (HRMS) were obtained on Agilent Q-TOF-Mass Spectrometer 6540-UHD LC/HRMS operating at 70 eV using direct inlet. Cyclic voltammetry experiments were conducted using an EmStat3-4WE potentiostat (PalmSens). A conventional three-electrode arrangement was using consisting a platinum wire as auxiliary electrode, glassy carbon as working electrode and the Ag(s)/AgCl as reference electrode. The measurement was performed in the presence of 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte, using complex concentration 10^{-3} M in THF in glove box under N_2.

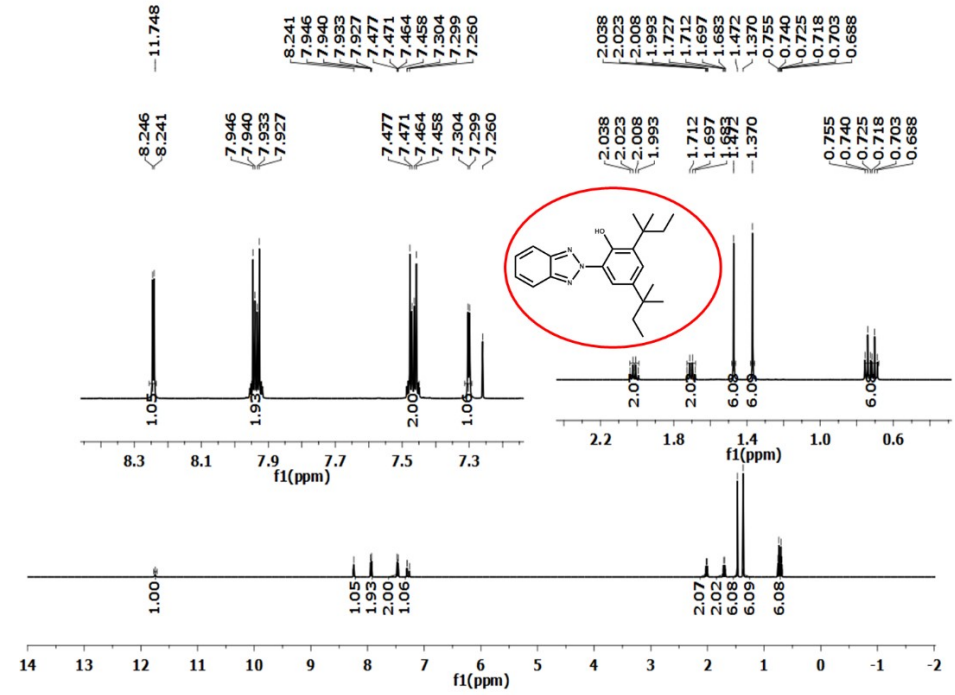
2. Single crystal X-ray crystallography study

The single crystal X-ray reflection data for complex [$L^1RuH(CO)(PPh_3)_2$] was recorded on a Bruker APEX-II CCD-based diffractometer with graphite-monochromate d MoKα radiation (0.7107 Å). The hemisphere of reflection data was collected as ω scan frames with 0.5% frame and an exposure time of 10 s/frame. The cell parameters were determined and refined using Bruker APEX2.[1, 2] The data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied using the SADABS program.[3] The complex structure was solved by direct methods and refined by full matrix least-squares using the SHELXTL program package[4] and Olex26 with anisotropic thermal parameters for all non-hydrogen atoms. [5] Images were created with DIAMOND.[6] The relevant data are summarized in Table S1.

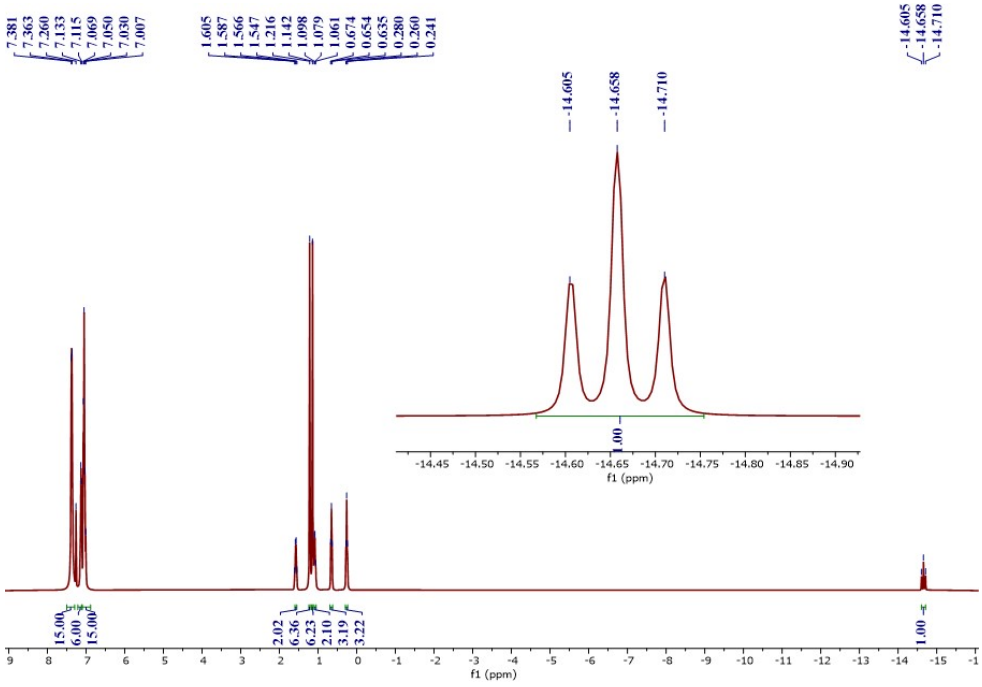
3. Details of theoretical studies: Geometry optimization calculations were performed using Gaussian 09 program package14 for complex **1**[7]. The complex was optimized using the B3LYP function and LANL2DZ basis set. The free energy change (ΔG) was calculated using the HOMO and LUMO gap between the two molecular orbitals. The Gauss View-5 graphical tool has been used for pictorial illustration of HOMO and LUMO frontier molecular orbitals[8].

4. Investigation: Homogeneity and Radical Participation: General catalytic reaction is described as follows. (i) Acetophenone (0.1 mmol), benzyl alcohol (0.1 mmol) and base (0.15 eq) in toluene (2 mL) along with catalyst (0.1 mol%) and one drop of mercury was charged into a Schlenk tube under inert nitrogen atmosphere. (ii) Acetophenone (0.1 mmol), benzyl alcohol (0.1 mmol) and base (0.15 eq) in toluene (2 mL) along with catalyst (0.1 mol%) and TEMPO (0.1 mmol) was charged into a Schlenk tube under inert nitrogen atmosphere.

The reaction mixture was stirred at 120 ^oC, completion of reaction was monitored by thin layer chromatography (TLC). After 6 h, the reaction mixture was purified via column chromatography in hexane. The eluted solvent was evaporated and isolated products were analysed by $^1H/^{13}C$ NMR techniques.



(a)



(b)

Figure S1. ^{1}H NMR spectrum of **a)** ligand (L^{1}) **b)** complex **1** in $CDCl_3$.

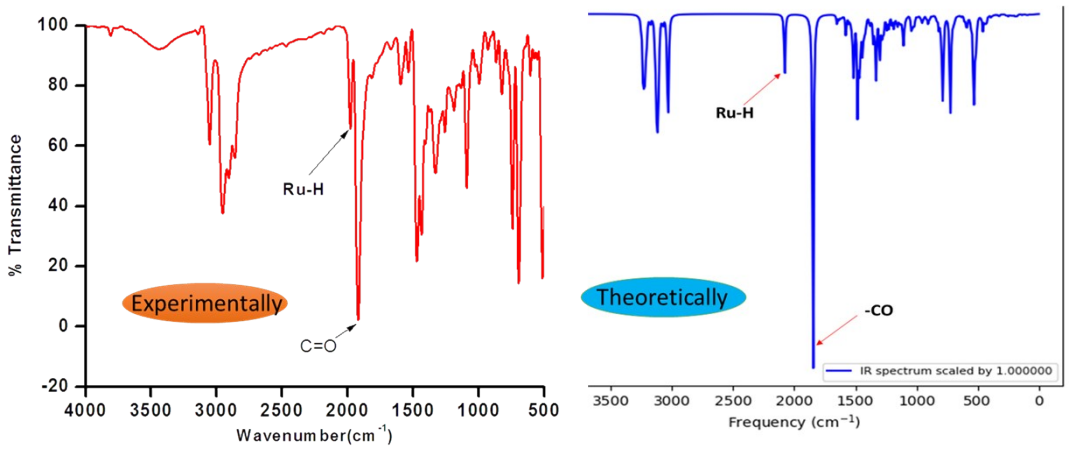


Figure S2. a) Infrared spectrum of complex [L^1RuH(CO)(PPh_3)$_2$]; b) Theoretically predicted IR spectra of complex **1**

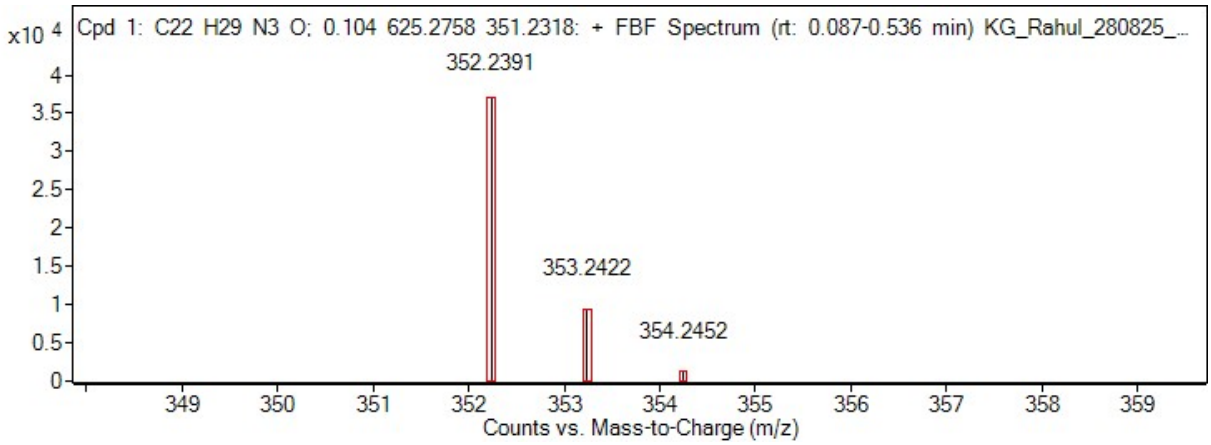


Figure S3 HRMS spectrum of ligand (L^1)

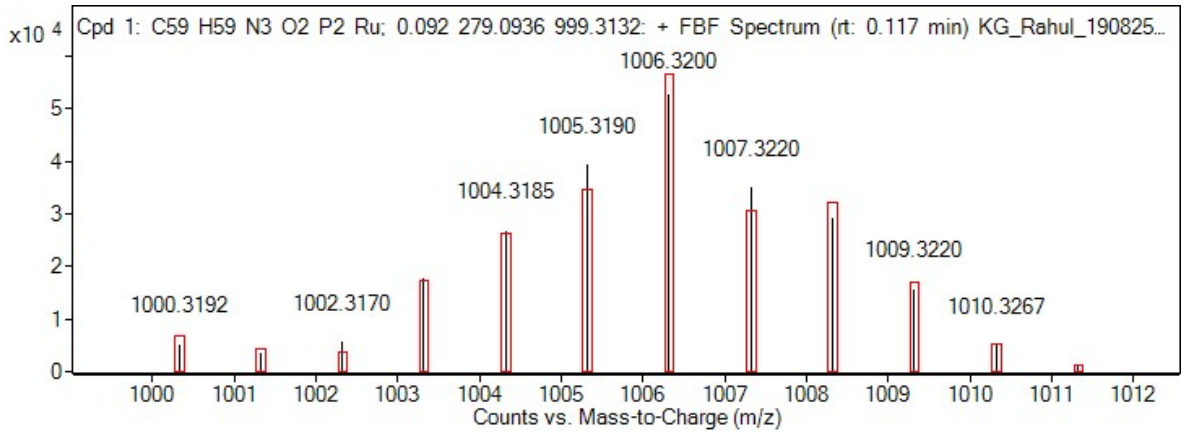


Figure S4 HRMS spectrum of complex $[L^1RuH(CO)(PPh_3)_2]$

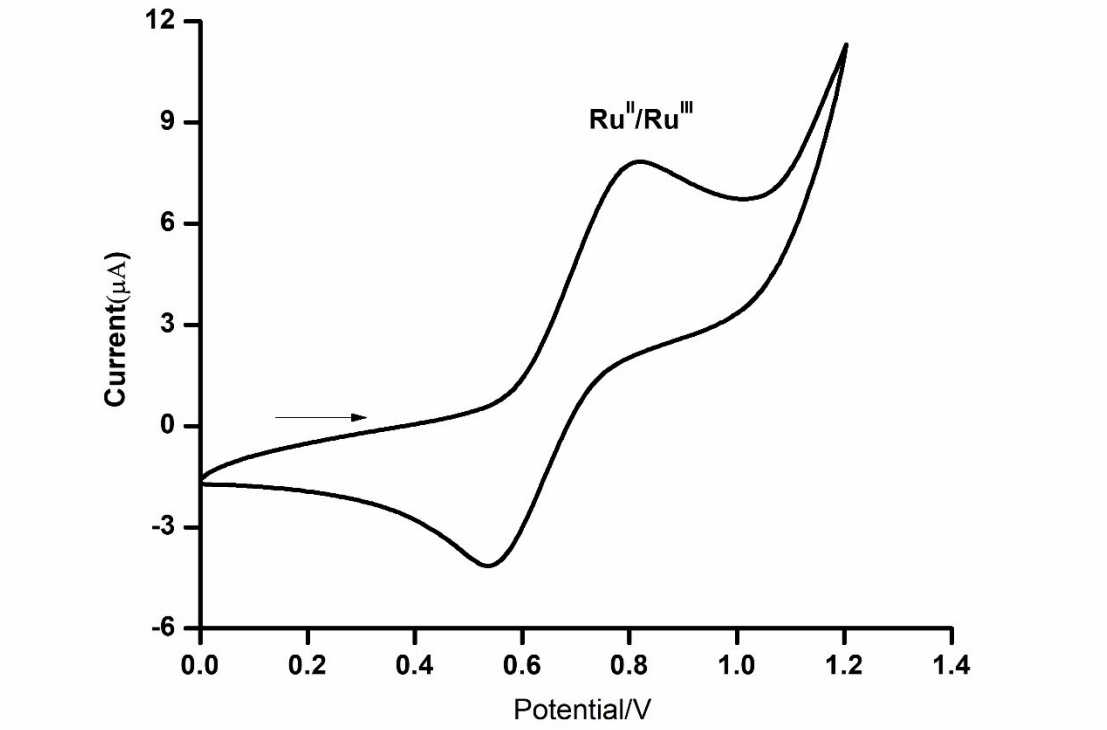
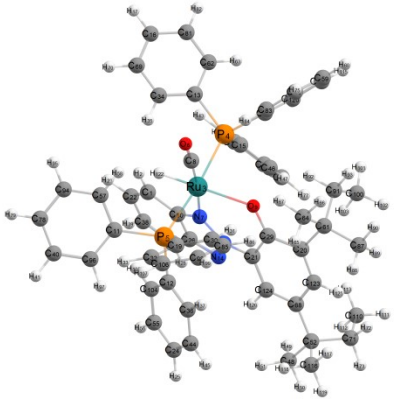
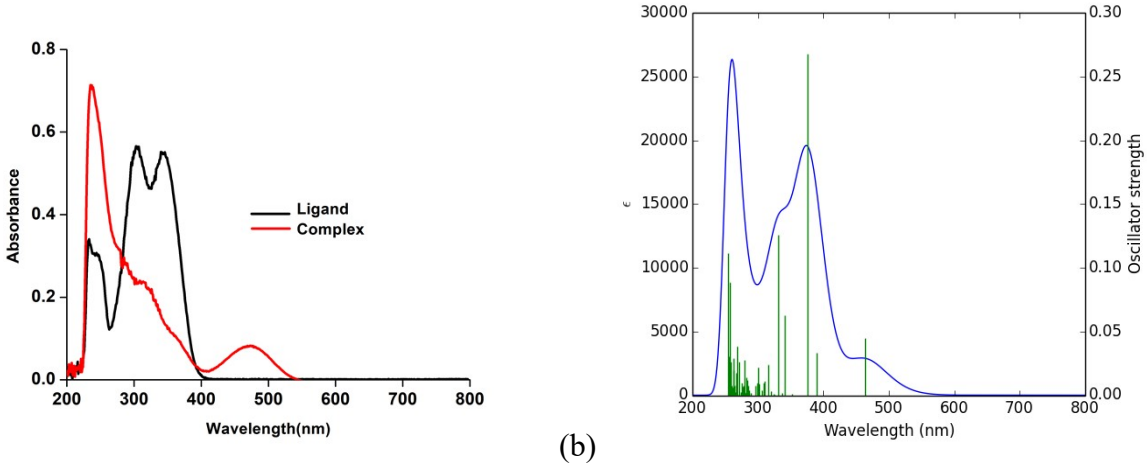


Figure S5. Cyclic voltammogram of **1** (1.0 mM) in THF vs Ag/AgCl. Electrolyte: Bu_4NPF_6 (0.1 M), scan rate = 0.1 V/s.



(a)



(b)

Figure S6. (a) Optimized geometry of complex [L^1RuH(CO)(PPh_3)$_2$], **1**. (b) Experimental and theoretical UV-vis spectral analysis of ruthenium complex.

Table S1. Co-ordinate parameters of complex [L^1RuH(CO)(PPh_3)$_2$]

C	-1.964876000000	1.931974000000	2.656590000000
H	-2.561719000000	2.247721000000	1.809303000000
Ru	-0.916764000000	0.766919000000	-0.687114000000
P	-2.735890000000	-0.889671000000	-0.271529000000
P	0.731698000000	2.613998000000	-1.001453000000
O	-1.961085000000	1.355584000000	-3.482748000000
N	-0.253022000000	0.571401000000	1.345567000000
C	-1.538755000000	1.086222000000	-2.394409000000
O	0.385934000000	-1.020245000000	-0.967100000000
N	0.839729000000	-0.136455000000	1.805792000000
C	-0.001736000000	4.355604000000	-0.897626000000
C	2.190954000000	2.710034000000	0.191396000000
C	-4.508393000000	-0.226945000000	-0.303033000000
N	0.994042000000	-0.090322000000	3.161335000000
C	-2.599005000000	-1.727608000000	1.410330000000
C	-7.157328000000	0.771012000000	-0.388081000000
H	-8.174568000000	1.153249000000	-0.422469000000
C	-2.881073000000	-2.355999000000	-1.462237000000
C	1.564073000000	2.619398000000	-2.693792000000
C	2.407196000000	-2.357022000000	-0.840150000000
C	1.787630000000	-0.879697000000	1.022119000000
C	-2.276478000000	2.319746000000	3.959263000000
H	-3.141423000000	2.954873000000	4.131933000000
C	4.343664000000	2.832160000000	2.024707000000
H	5.171531000000	2.883676000000	2.727534000000
C	-0.039604000000	0.696919000000	3.601711000000
C	-0.369846000000	1.089746000000	4.924451000000
H	0.232189000000	0.766593000000	5.767972000000
C	1.472473000000	-1.381898000000	-0.286936000000
C	1.818445000000	1.374104000000	-3.305113000000
H	1.514966000000	0.460086000000	-2.805088000000
C	1.944179000000	3.808218000000	-3.352235000000
H	1.745601000000	4.776390000000	-2.903098000000
C	-4.746884000000	1.152713000000	-0.464061000000
H	-3.905974000000	1.832804000000	-0.558141000000
C	3.494897000000	2.361511000000	-0.216437000000
H	3.685223000000	2.045377000000	-1.237567000000
C	-1.490099000000	1.902280000000	5.084408000000
H	-1.781268000000	2.230601000000	6.078702000000
C	0.223769000000	6.756332000000	-0.466538000000
H	0.833351000000	7.594970000000	-0.139623000000
C	-3.490580000000	-1.440589000000	2.463498000000
H	-4.313865000000	-0.748522000000	2.314367000000
C	4.566100000000	2.425300000000	0.695708000000

H	5.566954000000	2.158679000000	0.365588000000
C	-1.526730000000	-2.620817000000	1.636841000000
H	-0.823178000000	-2.842628000000	0.839863000000
C	5.553504000000	-1.529850000000	3.042981000000
H	4.800301000000	-1.800006000000	3.792306000000
H	6.540135000000	-1.778727000000	3.455687000000
H	5.513312000000	-0.441833000000	2.901944000000
C	5.348509000000	-2.277459000000	1.701084000000
C	-2.262127000000	-2.947678000000	3.941652000000
H	-2.133756000000	-3.417625000000	4.913598000000
C	3.040323000000	3.173280000000	2.438672000000
H	2.856209000000	3.487188000000	3.462969000000
C	-1.335239000000	4.572342000000	-1.306398000000
H	-1.949143000000	3.735073000000	-1.619710000000
C	-3.233439000000	-4.478450000000	-3.307367000000
H	-3.367617000000	-5.292502000000	-4.015430000000
C	2.049795000000	-3.168452000000	-2.113903000000
C	-5.609601000000	-1.106755000000	-0.188704000000
H	-5.451816000000	-2.175353000000	-0.073405000000
C	1.807798000000	-2.235663000000	-3.335151000000
H	2.694275000000	-1.617307000000	-3.531116000000
H	1.611682000000	-2.841089000000	-4.231599000000
H	0.949425000000	-1.585584000000	-3.155038000000
C	3.968488000000	-1.984781000000	1.072805000000
C	-6.065069000000	1.650283000000	-0.505972000000
H	-6.233488000000	2.716767000000	-0.633038000000
C	5.536653000000	-3.816883000000	1.931780000000
H	5.502060000000	-4.328697000000	0.959067000000
H	6.553242000000	-3.974708000000	2.324476000000
C	-2.847806000000	-3.201287000000	-3.758877000000
H	-2.681074000000	-3.023347000000	-4.818259000000
C	-1.362704000000	-3.229863000000	2.893287000000
H	-0.534910000000	-3.915953000000	3.053016000000
C	-1.107172000000	6.965438000000	-0.876767000000
H	-1.532261000000	7.966013000000	-0.866197000000
C	-0.825085000000	1.108532000000	2.480356000000
C	-6.924976000000	-0.610937000000	-0.229225000000
H	-7.762242000000	-1.298546000000	-0.140003000000
C	-2.669258000000	-2.148569000000	-2.842172000000
H	-2.366865000000	-1.176644000000	-3.214700000000
C	2.453430000000	1.316589000000	-4.560637000000
H	2.643382000000	0.352289000000	-5.024397000000
C	3.178779000000	-4.153045000000	-2.524910000000
H	4.100941000000	-3.621302000000	-2.796038000000
H	3.422407000000	-4.878794000000	-1.740510000000
H	2.850652000000	-4.718543000000	-3.407140000000

C	0.734907000000	-3.987318000000	-1.866201000000
H	-0.069853000000	-3.275796000000	-1.657648000000
H	0.477133000000	-4.492307000000	-2.810614000000
C	-1.883783000000	5.868888000000	-1.299453000000
H	-2.912022000000	6.018552000000	-1.619008000000
C	0.774886000000	5.460434000000	-0.482354000000
H	1.803618000000	5.319888000000	-0.164795000000
C	2.831674000000	2.503756000000	-5.216903000000
H	3.315482000000	2.460233000000	-6.189632000000
C	0.795059000000	-5.038027000000	-0.736670000000
H	-0.192793000000	-5.497736000000	-0.594889000000
H	1.505419000000	-5.845299000000	-0.957811000000
H	1.093726000000	-4.583124000000	0.217144000000
C	1.970050000000	3.109678000000	1.528920000000
H	0.973919000000	3.390029000000	1.861519000000
C	2.573939000000	3.749415000000	-4.610273000000
H	2.857788000000	4.670656000000	-5.112979000000
C	-3.323650000000	-2.049880000000	3.723016000000
H	-4.019149000000	-1.819468000000	4.526164000000
C	4.516463000000	-4.483466000000	2.878689000000
H	4.700287000000	-5.564740000000	2.939766000000
H	4.579865000000	-4.079443000000	3.896807000000
H	3.489642000000	-4.335613000000	2.520930000000
C	-3.441179000000	-4.693221000000	-1.931479000000
H	-3.738717000000	-5.674388000000	-1.569725000000
C	6.464538000000	-1.801833000000	0.721702000000
H	6.394478000000	-2.309454000000	-0.248565000000
H	6.389450000000	-0.721024000000	0.543225000000
H	7.458247000000	-2.013016000000	1.141192000000
C	-3.269750000000	-3.637905000000	-1.015300000000
H	-3.433369000000	-3.825987000000	0.041535000000
H	-1.888340000000	1.947163000000	-0.222249000000
C	3.606759000000	-2.594510000000	-0.163069000000
C	3.021390000000	-1.156152000000	1.663918000000
H	4.308899000000	-3.294290000000	-0.600888000000
H	3.197266000000	-0.700428000000	2.628104000000

Table S2 Crystal data and structure refinement for [L^1RuH(CO)(PPh_3)$_2$].	
Identification code	ovender81-1
Empirical formula	$C_{59}H_{59}N_4OP_2Ru$
Formula weight	1005.10
Temperature/K	296.15
Crystal system	monoclinic
Space group	C2/c
a/Å	24.3079(9)
b/Å	11.5688(3)
c/Å	36.6542(11)
α/°	90
β/°	101.743(2)
γ/°	90
Volume/Å^3	10091.9(6)
Z	8
ρ_{calc}g/cm^3	1.320
μ/mm^{-1}	0.419
F(000)	4177.8
Crystal size/mm^3	0.24 × 0.24 × 0.24
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.42 to 52.92
Index ranges	$-30 \leq h \leq 30$, $-14 \leq k \leq 14$, $-45 \leq l \leq 44$
Reflections collected	71832
Independent reflections	10317 [R_{int} = 0.0553, R_{sigma} = 0.0352]
Data/restraints/parameters	10317/0/614
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0445, wR_2 = 0.0966
Final R indexes [all data]	R_1 = 0.0556, wR_2 = 0.1017
Largest diff. peak/hole / e Å^{-3}	1.20/-1.13

Table S3 Bond Lengths for [L^1RuH(CO)(PPh_3)$_2$].

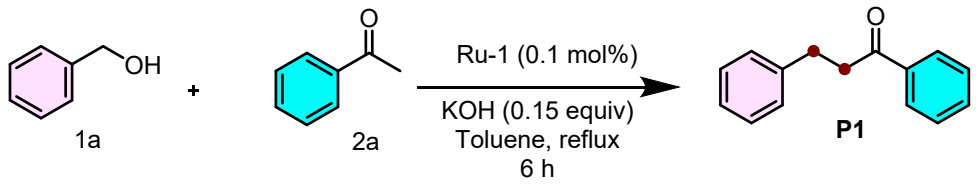
Atom	Atom	Length/Å		Atom	Atom	Length/Å
Ru1	P2	2.3751(7)		C26	C37	1.398(4)
Ru1	P1	2.3590(7)		C26	C41	1.383(4)
Ru1	O2	2.1802(19)		C26	C65	1.542(4)
Ru1	C53	1.864(3)		C27	C71	1.544(5)
Ru1	N3	2.149(2)		C28	C33	1.373(5)
P2	C4	1.829(3)		C29	C43	1.375(5)
P2	C36	1.824(3)		C29	C77	1.384(5)
P2	C38	1.843(3)		C31	C34	1.512(6)
P1	C9	1.835(3)		C32	C41	1.398(4)
P1	C11	1.843(3)		C33	C42	1.396(6)
P1	C25	1.826(3)		C34	C71	1.537(5)
C4	C14	1.387(4)		C36	C76	1.404(5)
C4	C46	1.401(4)		C36	C3	1.379(5)
O1	C53	1.131(4)		C38	C75	1.391(4)
N2	N1	1.328(3)		C38	C7	1.384(5)
N2	C32	1.433(3)		C40	C49	1.369(5)
N2	N3	1.347(3)		C40	C56	1.376(5)
N1	C15	1.358(4)		C42	C1	1.366(5)
C8	C9	1.384(4)		C44	C61	1.368(6)
C8	C43	1.396(4)		C44	C66	1.380(5)
C9	C48	1.389(4)		C47	C80	1.364(6)
O2	C12	1.303(3)		C47	C10	1.365(6)
C11	C57	1.389(4)		C48	C77	1.381(4)
C11	C85	1.385(4)		C49	C85	1.388(4)
C12	C24	1.447(4)		C50	C81	1.381(5)
C12	C32	1.410(4)		C51	C55	1.368(7)
C14	C5	1.391(4)		C51	C2	1.374(7)
C15	C21	1.391(4)		C55	C76	1.375(5)
C15	C28	1.420(4)		C56	C57	1.385(4)
C18	C71	1.520(5)		C58	C5	1.384(5)
C20	C46	1.374(5)		C59	C65	1.517(5)
C20	C58	1.379(5)		C61	C81	1.380(6)
C21	N3	1.357(3)		C65	C86	1.556(5)
C21	C1	1.408(4)		C65	C6	1.534(5)
C24	C37	1.376(4)		C69	C6	1.498(6)
C24	C71	1.533(4)		C75	C10	1.396(5)
C25	C50	1.398(4)		C80	C7	1.390(5)
C25	C66	1.391(4)		C3	C2	1.398(5)

Table S4 Bond Angles for [L^1RuH(CO)(PPh_3)$_2$].

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
P1	Ru1	P2	174.12(3)		O1	C53	Ru1	177.5(3)
O2	Ru1	P2	81.47(5)		C12	C32	N2	119.7(2)
O2	Ru1	P1	103.86(5)		C41	C32	N2	116.9(2)
C53	Ru1	P2	90.71(8)		C41	C32	C12	123.4(2)
C53	Ru1	P1	85.92(8)		C42	C33	C28	123.2(3)
C53	Ru1	O2	100.43(10)		C71	C34	C31	115.7(3)
N3	Ru1	P2	92.79(6)		C76	C36	P2	117.5(3)
N3	Ru1	P1	90.64(6)		C3	C36	P2	122.7(3)
N3	Ru1	O2	79.61(8)		C3	C36	C76	119.4(3)
N3	Ru1	C53	176.46(10)		C26	C37	C24	125.5(3)
C4	P2	Ru1	118.65(9)		C75	C38	P2	122.4(3)
C36	P2	Ru1	112.52(9)		C7	C38	P2	119.1(2)
C36	P2	C4	104.24(14)		C7	C38	C75	118.5(3)
C38	P2	Ru1	115.25(10)		C56	C40	C49	119.6(3)
C38	P2	C4	100.96(13)		C32	C41	C26	120.6(3)
C38	P2	C36	103.37(14)		C1	C42	C33	121.7(3)
C9	P1	Ru1	116.57(9)		C29	C43	C8	120.0(3)
C11	P1	Ru1	117.59(9)		C66	C44	C61	120.8(4)
C11	P1	C9	99.37(12)		C20	C46	C4	121.1(3)
C25	P1	Ru1	114.48(9)		C10	C47	C80	120.0(4)
C25	P1	C9	105.95(13)		C77	C48	C9	120.8(3)
C25	P1	C11	100.58(13)		C85	C49	C40	120.6(3)
C14	C4	P2	121.0(2)		C81	C50	C25	120.2(3)
C46	C4	P2	121.0(2)		C2	C51	C55	120.2(4)
C46	C4	C14	117.9(3)		C76	C55	C51	120.9(4)
C32	N2	N1	119.8(2)		C57	C56	C40	120.3(3)
N3	N2	N1	115.1(2)		C56	C57	C11	120.7(3)
N3	N2	C32	125.2(2)		C5	C58	C20	119.7(3)
C15	N1	N2	103.4(2)		C81	C61	C44	119.9(3)
C43	C8	C9	120.3(3)		N2	N3	Ru1	124.14(16)
C8	C9	P1	125.1(2)		C21	N3	Ru1	131.53(19)
C48	C9	P1	115.8(2)		C21	N3	N2	104.3(2)
C48	C9	C8	119.0(3)		C59	C65	C26	112.8(3)
C12	O2	Ru1	122.11(16)		C86	C65	C26	107.5(3)
C57	C11	P1	118.9(2)		C86	C65	C59	108.4(3)
C85	C11	P1	122.5(2)		C6	C65	C26	111.5(3)
C85	C11	C57	118.4(3)		C6	C65	C59	109.2(3)
C24	C12	O2	122.2(3)		C6	C65	C86	107.1(3)
C32	C12	O2	122.8(2)		C44	C66	C25	120.1(4)
C32	C12	C24	115.0(3)		C24	C71	C18	110.6(3)
C5	C14	C4	121.0(3)		C27	C71	C18	107.8(3)
C21	C15	N1	109.7(3)		C27	C71	C24	110.7(3)

C28	C15	N1	129.3(3)		C34	C71	C18	109.0(3)
C28	C15	C21	121.0(3)		C34	C71	C24	110.0(3)
C58	C20	C46	120.4(3)		C34	C71	C27	108.7(3)
N3	C21	C15	107.5(3)		C10	C75	C38	120.0(4)
C1	C21	C15	121.9(3)		C55	C76	C36	119.7(4)
C1	C21	N3	130.6(3)		C48	C77	C29	119.8(3)
C37	C24	C12	118.3(3)		C7	C80	C47	120.2(4)
C71	C24	C12	119.2(3)		C61	C81	C50	120.2(4)
C71	C24	C37	122.5(3)		C49	C85	C11	120.5(3)
C50	C25	P1	120.2(2)		C42	C1	C21	116.6(3)
C66	C25	P1	121.0(2)		C58	C5	C14	119.9(3)
C66	C25	C50	118.7(3)		C2	C3	C36	119.8(4)
C41	C26	C37	115.8(3)		C3	C2	C51	120.1(4)
C65	C26	C37	120.9(3)		C69	C6	C65	113.5(3)
C65	C26	C41	123.1(3)		C80	C7	C38	120.8(3)
C33	C28	C15	115.7(3)		C75	C10	C47	120.5(4)
C77	C29	C43	120.1(3)					

Table S5. Optimization of reaction conditions for α-alkylation in different solvents and bases.



Entry	Catalyst (0.1 mol%)	Base	Solvent	Yield (%)
1	-	KOH	Toluene	Trace
2	L[1]	KOH	Toluene	Trace
3	$RuCl_3$	KOH	Toluene	15%
4	$Ru(PPh_3)Cl_2$	KOH	Toluene	42%
5	**Ru-1**	KOH	Toluene	92%
6	**Ru-1**	^tBuOK	Toluene	56%
7	**Ru-1**	NaOH	Toluene	52%
8	**Ru-1**	K_2CO_3	Toluene	36%
9	**Ru-1**	KOH	DMF	21%
10	**Ru-1**	KOH	DMSO	25%
11	**Ru-1**	KOH	O-xylene	82%
12	**Ru-1**	KOH	dioxane	76%
13[a]	**Ru-1**	KOH	Toluene	70%
14[b]	**Ru-1 (0.005)**	KOH	Toluene	60%

Reaction condition: 1a (0.1 mmol), 2a (0.1 mmol), Cat. (0.1 mol%), base (0.15 equiv.), Solvent 2 mL at 120 °C for 6 h. Isolated Yield. [a]at 80 °C, [b]**Ru-1** (0.005 mol%).

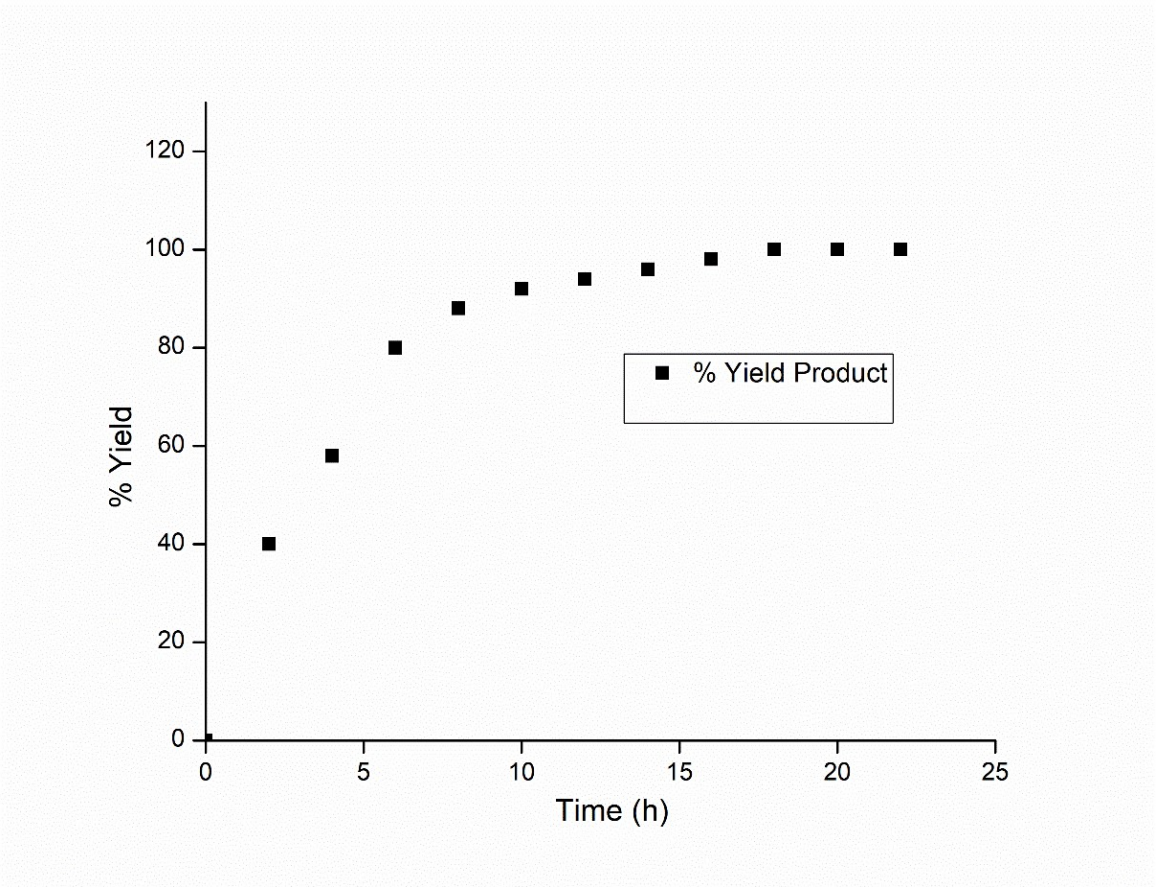


Figure S7. Time dependent C-C coupled product formation during the reaction. Reaction condition: Acetophenone (1 mmol), benzyl alcohol (1 mmol), Cat. (0.1 mol%), base (0.15 equiv.), Solvent 2 mL at 120 °C for 24 h.

Table S6. Effect of catalyst loading on the α-alkylation of ketones using primary alcohols catalytic reaction

Entry	Catalyst loading (mol%)	%Yield
1	0.5	94
2	0.1	92
3	0.01	84
4	0.001	76

Table S7. Catalytic performance metrics, including reactants, % yields, TON, TOF, and reaction conditions

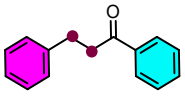
S. No	Reactant(s)-1	Reactant(s) -2	Compounds	% *Yield	TON/ TOF
1	Phenylmethanol	Acetophenone	1,3-diphenylpropan1-one	88	114/19
2	Phenylmethanol	4′-Methylacetophenone	3-phenyl-1-(p-tolyl)propan-1-one	80	116/19 .33
3	Phenylmethanol	4′-Methoxyacetophenone	1-(4-methoxyphenyl)-3-phenylpropan-1-one	92	126/21
4	Phenylmethanol	4′-Chloroacetophenone	1-(4-chlorophenyl)-3-phenylpropan-1-one	72	102/17
5	Phenylmethanol	4′-Bromoacetophenone	1-(4-bromophenyl)-3-phenylpropan-1-one	74	104/17 .33
6	Phenylmethanol	3-Acetylpyridine	3-phenyl-1-(pyridin-3-yl)propan-1-one	86	98/16. 33
7	Phenylmethanol	4′-(Trifluoromethyl)acetophenone	3-phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-one	78	93/15. 50
8	Phenylmethanol	1-(3-Methoxyphenyl)ethan-1-one	1-(3-methoxyphenyl)-3-phenylpropan-1-one	89	120/20
9	Phenylmethanol	1-(3-chlorophenyl)ethan-1-one	1-(3-chlorophenyl)-3-phenylpropan-1-one	73	106/17 .66
10	Phenylmethanol	1-(2-methoxyphenyl)ethan-1-one	1-(2-methoxyphenyl)-3-phenylpropan-1-one	82	118/19 .66
11	Phenylmethanol	1-(2-chlorophenyl)ethan-1-one	1-(2-chlorophenyl)-3-phenylpropan-1-one	76	104/1. 33
12	Phenylmethanol	1-mesitylethan-1-one	1-mesityl-3-phenylpropan-1-one	82	122/20 .33
13	Phenylmethanol	1-(naphthalen-2-yl)ethan-1-one	1-(naphthalen-2-yl)-3-phenylpropan-1-one	78	121/20 .16
14	Phenylmethanol	1-(benzo[d][1,3]dioxol-5-yl)ethan-1-one	1-(benzo[d][1,3]dioxol-5-yl)-3-phenylpropan-1-one	76	115/19 .16
15	Phenylmethanol	1-cyclopropylethan-1-one	1-cyclopropyl-3-phenylpropan-1-one	72	113/18 .83
16	Phenylmethanol	1-(thiophen-2-yl)ethan-1-one	3-phenyl-1-(thiophen-2-yl)propan-1-one	73	108/18 .64
17	Phenylmethanol	1-(1,2,3,4-tetrahydronaphthalen-2-yl)ethan-1-one	3-phenyl-1-(1,2,3,4-tetrahydronaphthalen-2-yl)propan-1-one	78	122/20 .14
18	1,3-phenylenedimethanol	1-(p-tolyl)ethan-1-one	3,3'-(1,3-phenylene)bis(1-(p-tolyl)propan-1-one)	80	114/18 .32
19	4-Methylbenzyl alcohol	Acetophenone	1-phenyl-3-(p-tolyl)propan-1-one	82	116/19 .33
20	4-Methoxybenzyl alcohol	Acetophenone	3-(4-methoxyphenyl)-1-phenylpropan-1-one	80	124/20 .66
21	4-Chlorobenzyl alcohol	Acetophenone	3-(4-chlorophenyl)-1-phenylpropan-1-one	78	103/17 .16

22	(4-(trifluoromethyl)phenyl)methanol	Acetophenone	1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one	72	96/16
23	methyl 4-(hydroxymethyl)benzoate	Acetophenone	methyl 4-(3-oxo-3-phenylpropyl)benzoate	78	119/19.83
24	(4-isocyanophenyl)methanol	Acetophenone	3-(4-isocyanophenyl)-1-phenylpropan-1-one	70	108/18
25	4-(hydroxymethyl)benzoic acid	Acetophenone	4-(3-oxo-3-phenylpropyl)benzoic acid	71	106/17.66
26	(4-nitrophenyl)methanol	Acetophenone	3-(4-nitrophenyl)-1-phenylpropan-1-one	62	92/14.24
27	(4-bromophenyl)methanol	Acetophenone	3-(4-bromophenyl)-1-phenylpropan-1-one	68	94/16.22
28	naphthalen-1-ylmethanol	Acetophenone	3-(naphthalen-1-yl)-1-phenylpropan-1-one	79	120/14
29	(4-(tert-butyl)phenyl)methanol	Acetophenone	3-(4-(tert-butyl)phenyl)-1-phenylpropan-1-one	80	104/16.24
30	(3-methoxyphenyl)methanol	Acetophenone	3-(3-methoxyphenyl)-1-phenylpropan-1-one	80	106/18.23
31	(2,4-dimethoxyphenyl)methanol	Acetophenone	3-(2,4-dimethoxyphenyl)-1-phenylpropan-1-one	82	112/18.14
32	Ferrocenemethanol	Acetophenone	3-phenyl-1-(ferrocynyl)propan-1-one	80	115/16.02
33	Acetophenone	pentan-1-ol	1-phenyloctan-1-one	75	106/18.60
34	Acetophenone	decan-1-ol	1-phenyltridecan-1-one	73	104/12.22
35	Acetophenone	2,6-dimethylhept-5-en-1-ol	5,9-dimethyl-1-phenyldec-8-en-1-one	75	108/11.24
36	Acetophenone	(Z)-hexadec-7-en-1-ol	(Z)-1-phenylnonadec-10-en-1-one	76	106/12.24
37	(4-methoxyphenyl)methanol	1-(2,4-dimethoxyphenyl)ethan-1-one	1-(2,4-Dimethoxyphenyl)-3-(4-methoxyphenyl)-1-propanone	70	118/17.24
38	(2,4-dimethoxyphenyl)methanol	1-(4-hydroxyphenyl)ethan-1-one	Loureirin A	73	122/13.54
39	phenylmethanol	1-(2-hydroxy-6-methoxyphenyl)ethan-1-one	Uvangoletin	79	112/14.26
40	(2,4,6-trimethoxyphenyl)methanol	1-(4-hydroxyphenyl)ethan-1-one	Loureirin B	79	106/16.02

Reaction conditions: Alcohol (2.2 mmol) and Ketone (2 mmol), catalyst (0.1 mol %), KOH (0.15eq), Toluene (4 mL), Temperature 120 °C, and reaction time 6 h. TON = mmol of substrate/mmol of catalyst; TOF = TON/Time (h). TON = turn over number and TOF = turn over frequency.

*** Yields are reported as isolated yields or reaction after column chromatography.**

^{1}H and ^{13} C NMR of C-C products:

Synthesis of P1: 

1,3-diphenylpropan-1-one (P1). 44.4 mg; 88% isolated yield; white solid: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.96 (d, 2H), 7.55 (t, 1H), 7.45 (t, 2H), 7.32 - 7.19 (m, 5H), 3.31 (t, 2H), 3.08 (t, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 199.3, 141.4, 137.0, 133.2, 128.7, 128.6, 128.5, 128.2, 126.3, 40.6, 30.3.

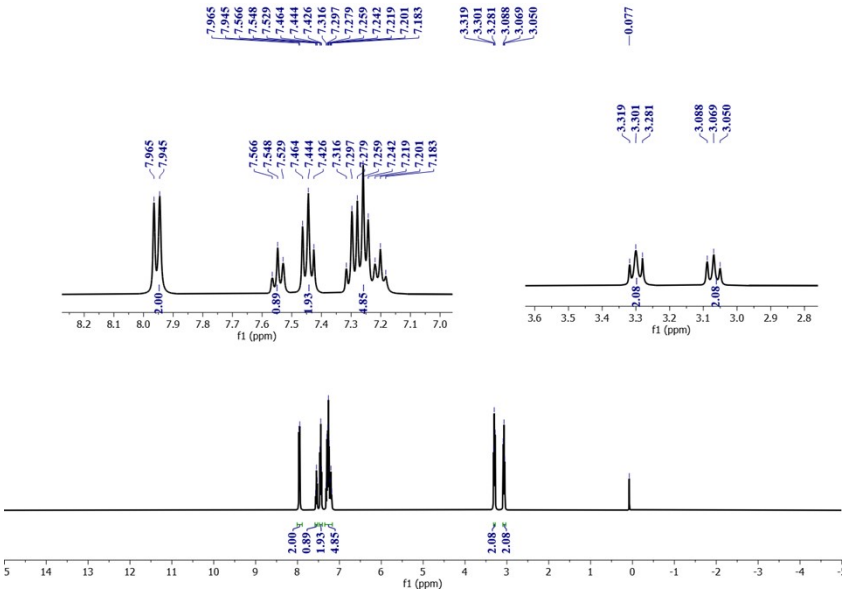


Figure S8. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P1**.

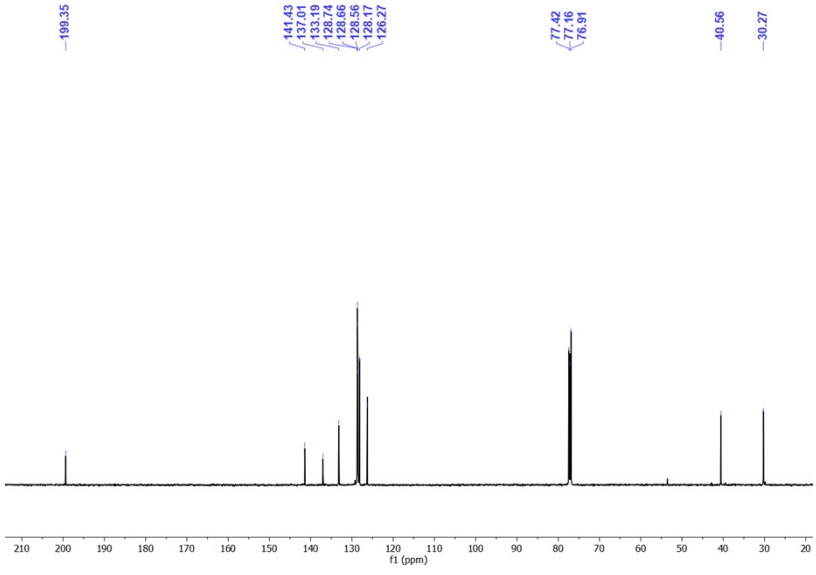
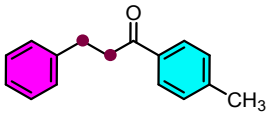


Figure S9. (a) ^{13}C{^{1}H} NMR Spectrum (125 MHz, $CDCl_3$) of **P1**.

Synthesis of P2:



3-phenyl-1-(p-tolyl)propan-1-one (P2). 40.2 mg; 80% isolated yield; brown solid: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.86 (d, 2H), 7.31 – 7.18 (m, 7H), 3.27 (t, 2H), 3.05 (t, 2H), 2.40 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 199.0, 144.0, 141.5, 134.5, 129.4, 128.6, 128.5, 128.3, 126.2, 40.5, 30.4, 21.8.

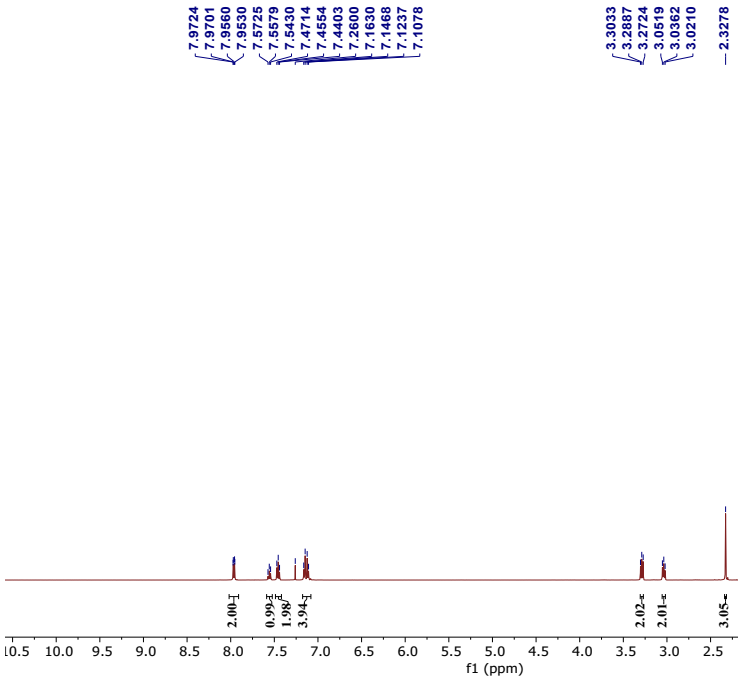


Figure S10. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P2**.

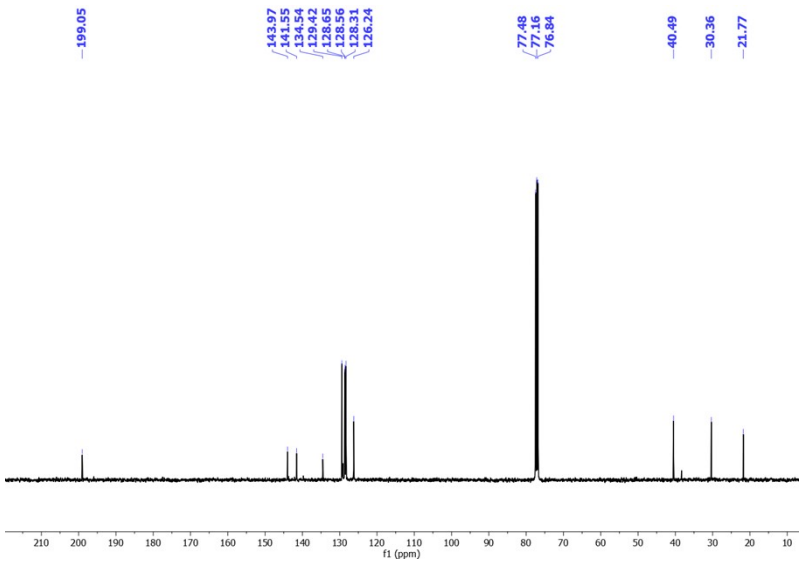
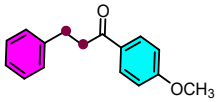


Figure S11. ^{13}C{^{1}H} NMR Spectrum (125 MHz, $CDCl_3$) of **P2**

Synthesis of P3:



1-(4-methoxyphenyl)-3-phenylpropan-1-one (P3). 40.6 mg; 92% isolated yield; white solid: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.53 – 7.48 (m, 2H), 7.36 – 7.21 (m, 6H), 7.10 – 7.07 (m, 1H), 3.83 (s, 3H), 3.28 (t, J_{H-H} = 7.2 Hz, 2H), 3.05 (t, J_{H-H} = 7.8 Hz, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 198.0, 163.6, 141.6, 130.5, 130.2, 128.6, 128.5, 126.2, 113.9, 55.6, 40.3, 30.5.

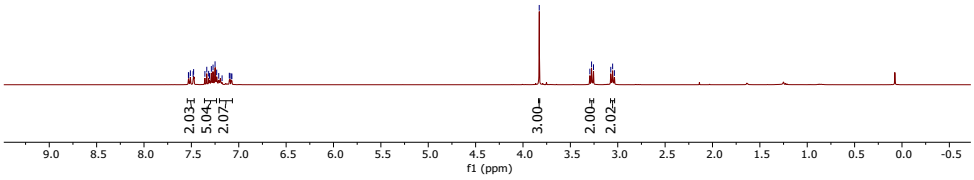


Figure S12. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P3**.

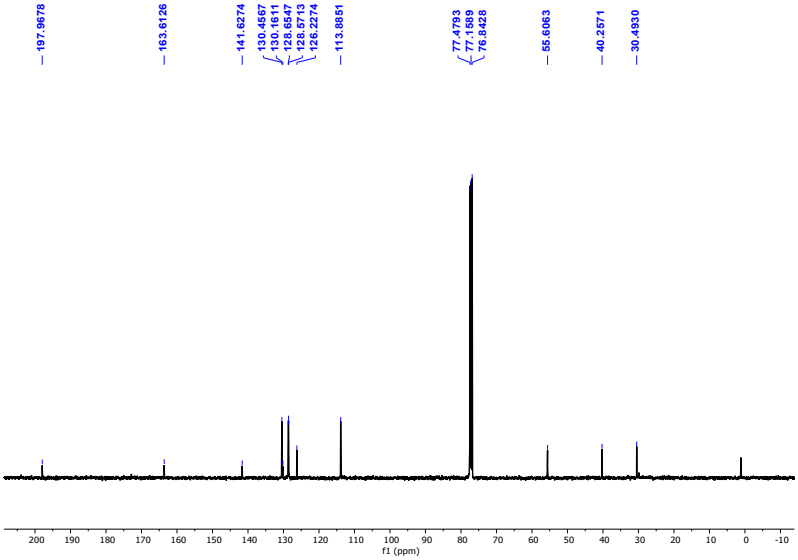
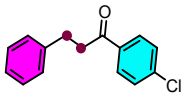


Figure S13. ^{13}C{^{1}H} NMR Spectrum (125 MHz, $CDCl_3$) of **P3**

Synthesis of P4:



1-(4-chlorophenyl)-3-phenylpropan-1-one (P4). 45.2 mg; 72% isolated yield; white solid: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.88 (d, 2H), 7.41 (d, 2H), 7.31 – 7.20 (m, 5H), 3.26 (t, 2H), 3.06 (t, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 198.1, 141.2, 139.6, 135.3, 129.6, 129.1, 128.7, 128.5, 126.4, 40.6, 30.2.

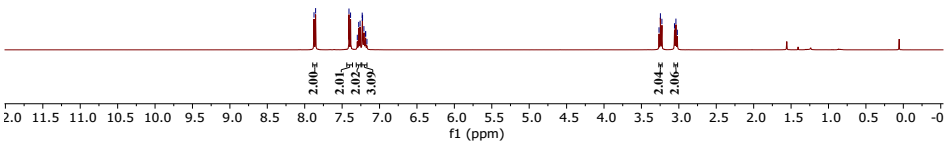


Figure S14. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P4**.

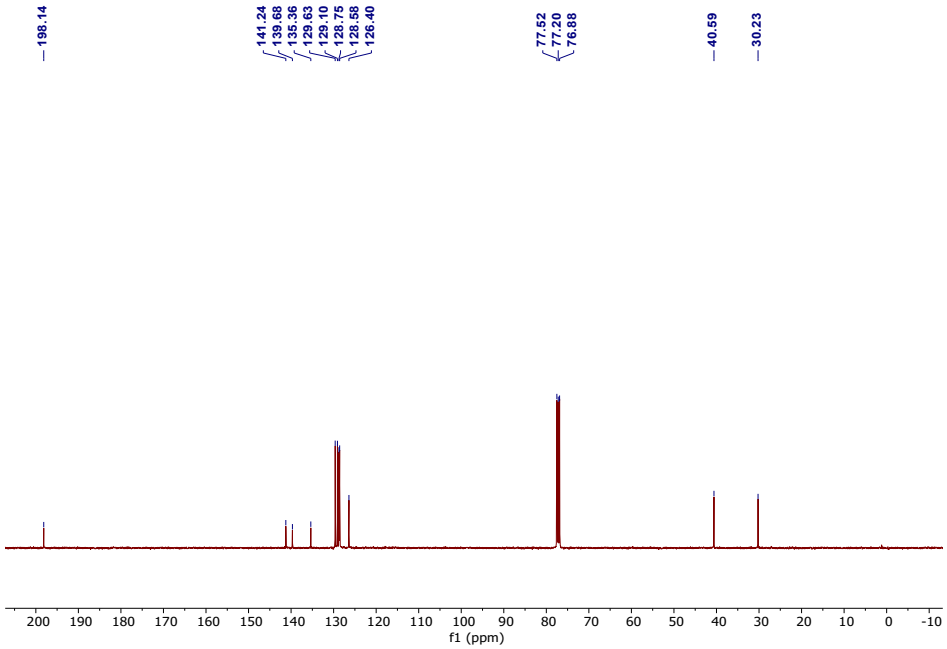
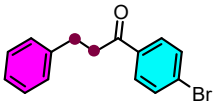


Figure S15. ^{13}C{^{1}H} NMR Spectrum (125 MHz, $CDCl_3$) of **P4**

Synthesis of P5: 

1-(4-bromophenyl)-3-phenylpropan-1-one (P5). 68.6 mg; 74% isolated yield; white solid: **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.80 (d, 2H), 7.58 (d, 2H), 7.29 (t, 2H), 7.24 - 7.19 (m, 3H), 3.25 (t, 2H), 3.05 (t, Hz, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 198.3, 141.2, 135.7, 132.0, 129.7, 129.6, 128.7, 128.5, 126.4, 40.5, 30.2.

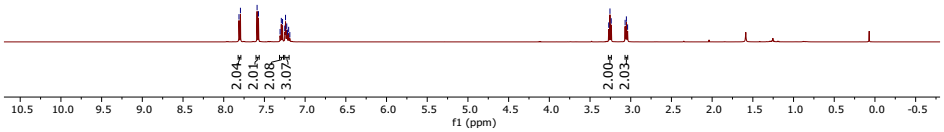


Figure S16. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P5**.

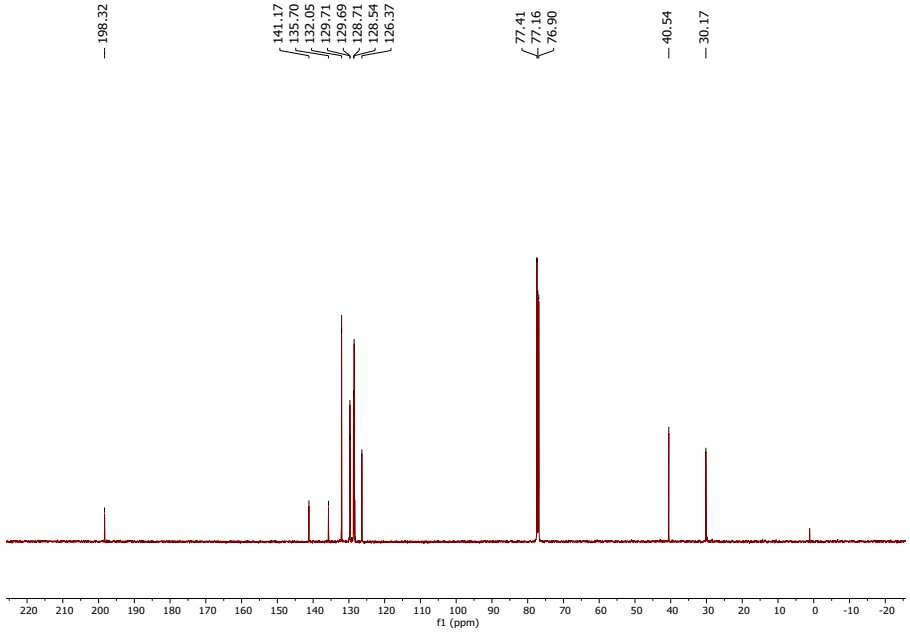
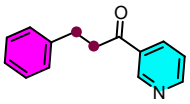


Figure S17. ^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of **P5**

Synthesis of P6:



3-phenyl-1-(pyridin-3-yl)propan-1-one (P6). 50.4 mg; 86% isolated yield; yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 9.12(s, 1H), 8.73 -8.72 (m, 1H), 8.19 – 8.17 (m, 1H), 7.38 -7.35 (m, 1H), 7.29 – 7.16 (m, 5H), 3.28 (t, 2H), 3.05 (t, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 198.1, 153.5, 149.6, 140.8, 135.4, 132.1, 128.7, 128.5, 126.4, 123.7, 40.7, 29.8.

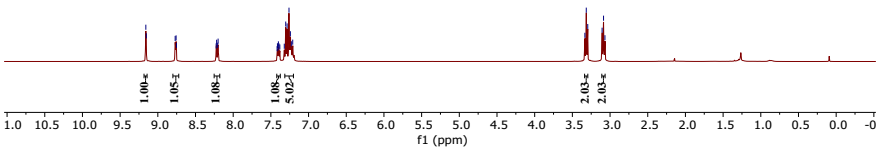


Figure S18. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P6**.

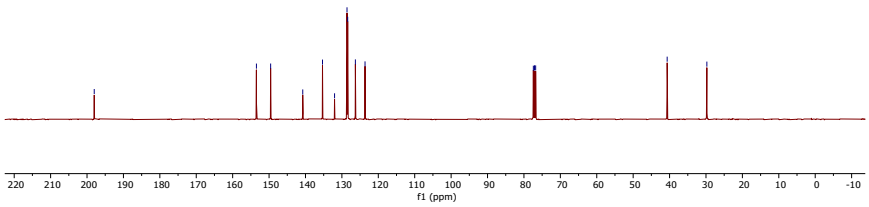
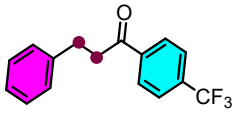


Figure S19. ^{13}C{^{1}H} NMR Spectrum (100 MHz, $CDCl_3$) of **P6**.

Synthesis of P7:



3-phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-one (P7). 68.4 mg; 78% isolated yield; yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.05 (d, H), 7.72 (d 2H), 7.33 – 7.22 (m, 5H), 3.33 (t, 2H), 3.09 (t, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 198.3, 141.0, 139.6, 134.4 (q, $J_{C\text{-}F}$ = 33 Hz), 128.7, 128.5, 128.4, 126.4, 125.8 (d, $J_{C\text{-}F}$ = 4.0Hz), 123.7 (d, $J_{C\text{-}F}$ = 272 Hz), 40.8, 30.0.

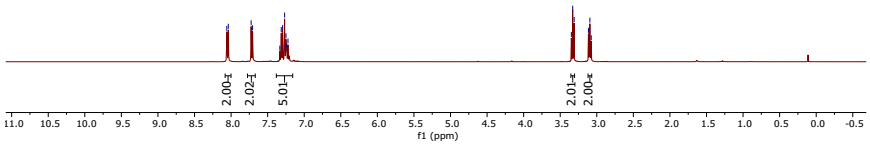


Figure S20. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P7**.

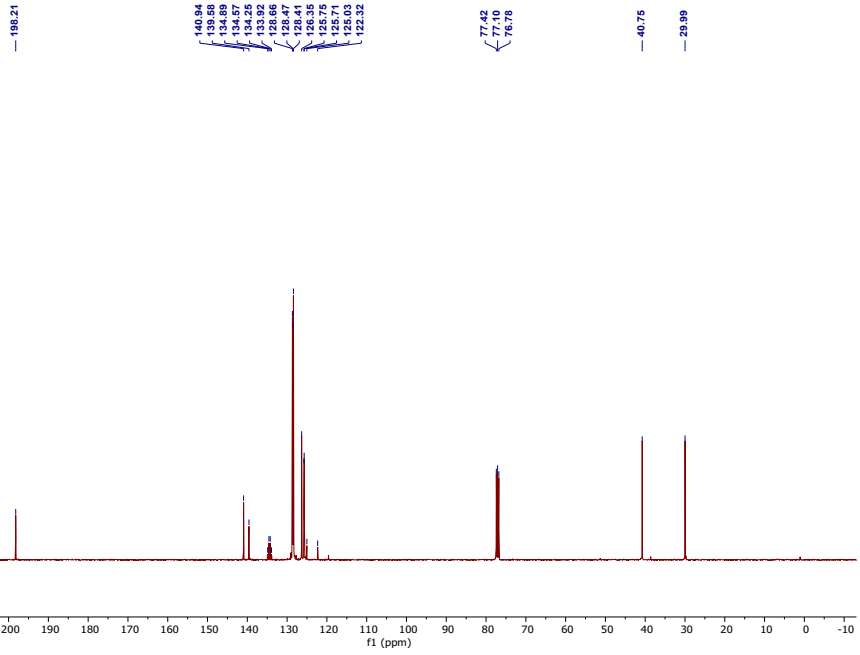
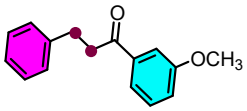


Figure S21. ^{13}C{^{1}H} NMR Spectrum (100 MHz, $CDCl_3$) of **P7**.



Synthesis of P8:

1-(3-methoxyphenyl)-3-phenylpropan-1-one (P8). 40.4 mg; 89% isolated yield; yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.55 – 7.49 (m, 2H), 7.37 – 7.19 (m, 6H), 7.11 -7.09 (m, 1H), 3.84 (s, 3H), 3.29 (t, 2H), 3.07 (t, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ =199.1, 159.9, 141.3, 138.3, 129.6, 128.6, 128.5, 126.2, 120.7, 119.6, 112.3, 55.5, 40.6, 30.2.

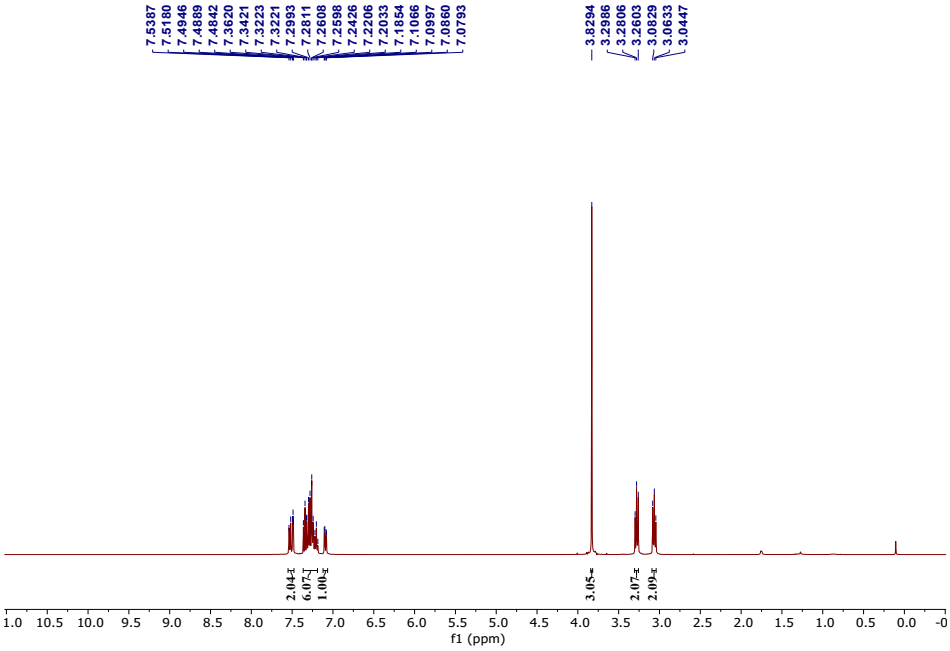


Figure S22. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P8**.

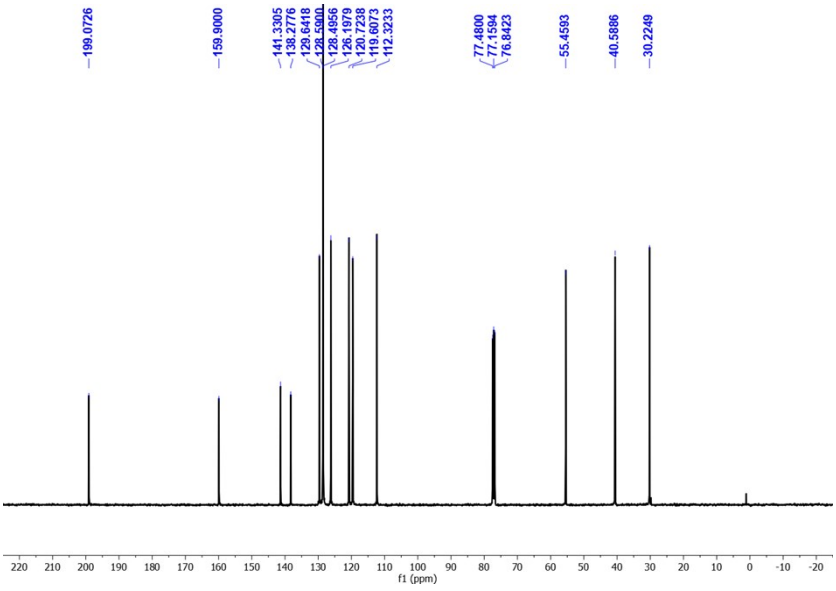
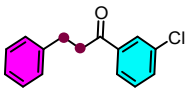


Figure S23. ^{13}C{^{1}H} NMR Spectrum (100 MHz, $CDCl_3$) of **P8**.

Synthesis of P9: 

1-(3-chlorophenyl)-3-phenylpropan-1-one (P9). 60.8 mg; 73% isolated yield; pale yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.91 (s, 1H), 7.81 (d, 1H), 7.52 – 7.50 (m, 1H), 7.40 – 7.35 (m, 1H), 7.32 – 7.19 (m, 5H), 3.27 (t, 2H), 3.03 (t, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 198.0, 141.1, 138.5, 135.1, 133.1, 130.1, 128.7, 128.5, 128.3, 126.3, 126.2, 40.6, 30.0.

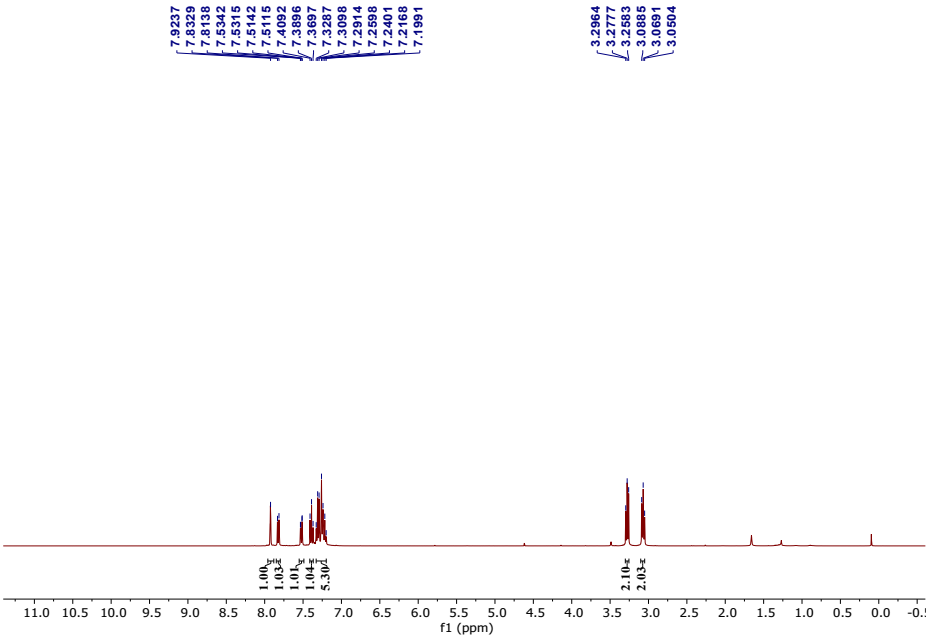


Figure S24. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P9**.

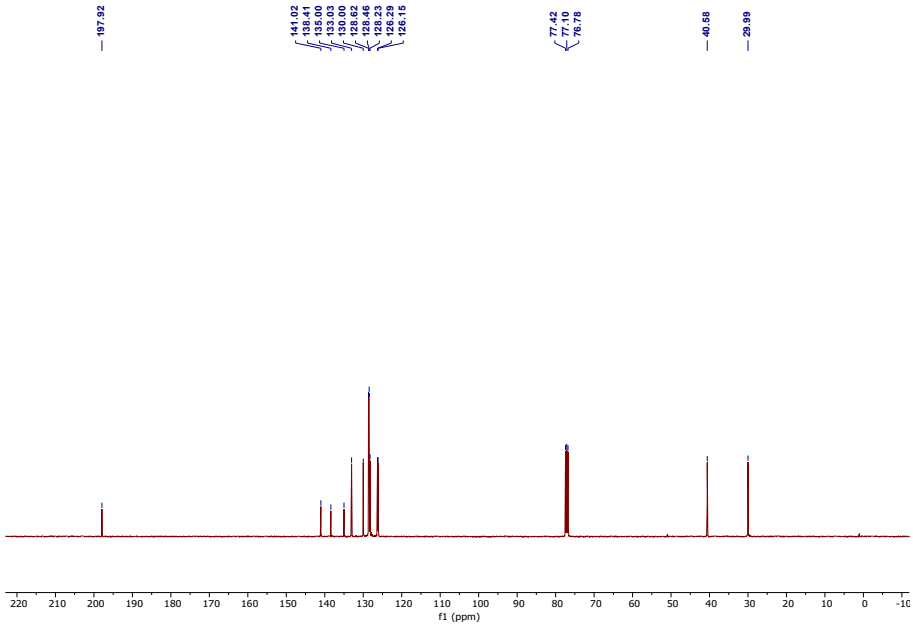
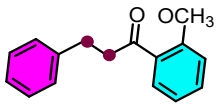


Figure S25. ^{13}C{^{1}H} NMR Spectrum (100 MHz, $CDCl_3$) of **P9**.

Synthesis of P10:



1-(2-methoxyphenyl)-3-phenylpropan-1-one (P10). 36.8 mg; 82% isolated yield; yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.71 – 7.68 (m, 1H), 7.48 – 7.43 (m, 1H), 7.31 – 7.18 (m, 5H), 7.02 – 6.95 (m, 2H), 3.88 (s, 3H), 3.31 (t, $J_{H\text{-}H}$ = 7.4 Hz, 2H), 3.02 (t, $J_{H\text{-}H}$ = 8.5 Hz, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 201.8, 158.6, 141.8, 133.5, 130.5, 128.6, 128.5, 128.3, 126.0, 120.8, 111.6, 55.6, 45.5, 30.6.

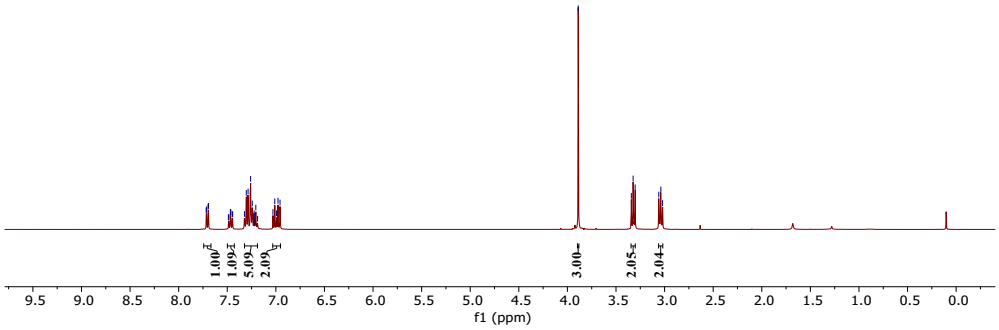


Figure S26. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P10**.

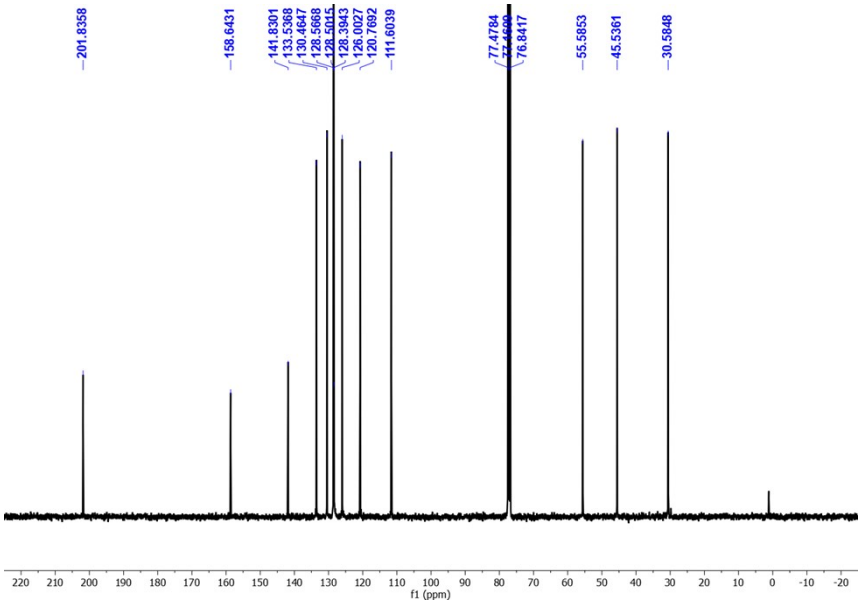
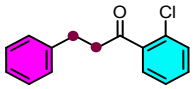


Figure S27. ^{13}C{^{1}H} NMR Spectrum (100 MHz, $CDCl_3$) of **P10**.

Synthesis of P11:



1-(2-chlorophenyl)-3-phenylpropan-1-one (P11). 62.4 mg; 76% isolated yield; white solid: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.39 – 7.33 (m, 3H), 7.30 – 7.24 (m, 3H), 7.22 – 7.18 (m, 3H), 3.26 (t, 2H), 3.04 (t, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 202.7, 140.9, 139.5, 131.8, 131.0, 130.6, 129.0, 128.6, 128.5, 127.0, 126.3, 44.7, 30.3.

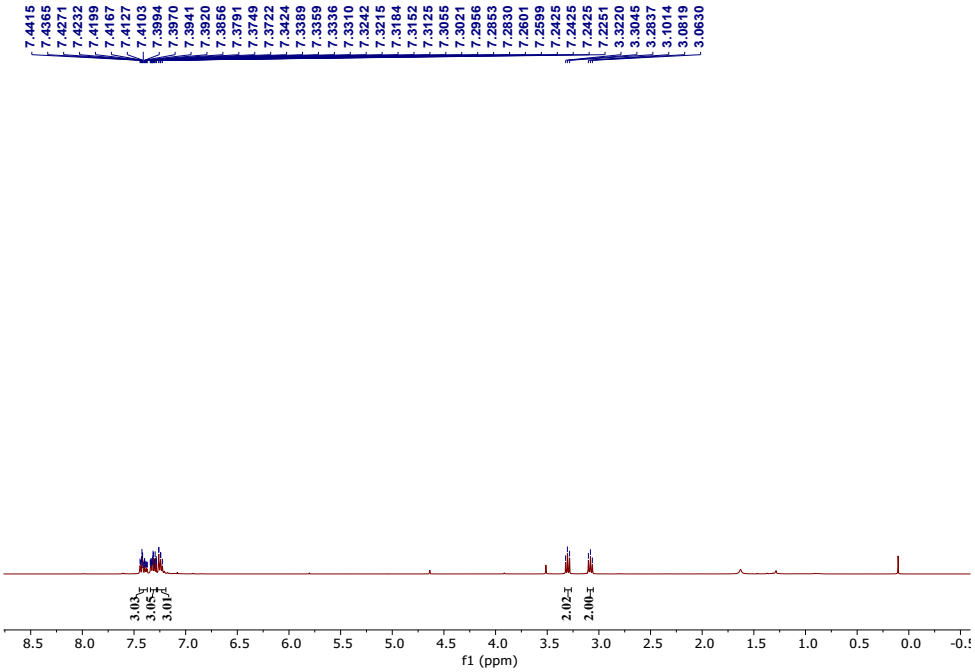


Figure S28. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P11**.

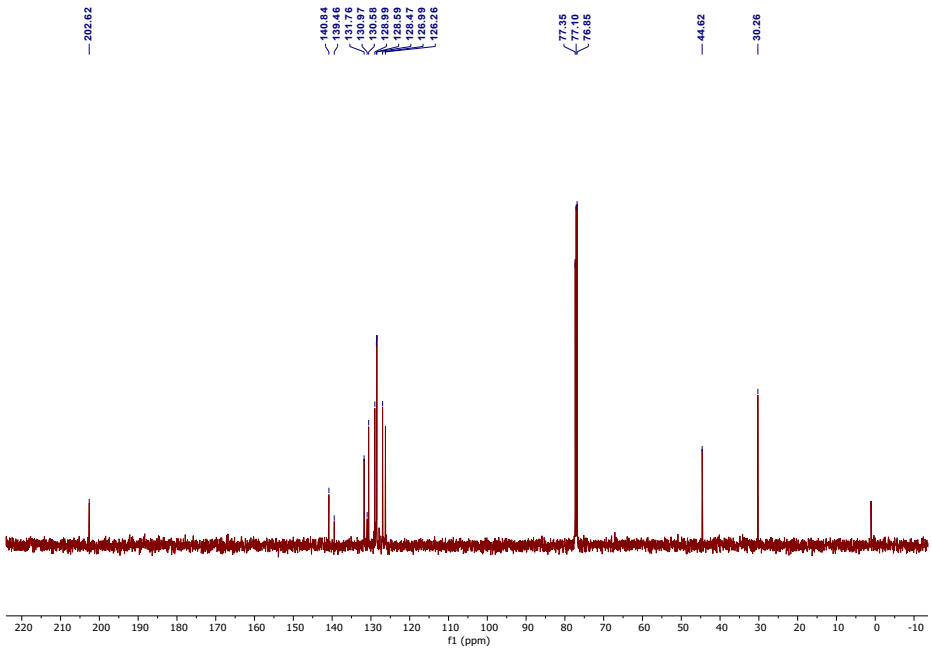
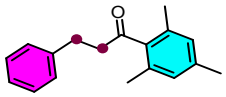


Figure S29. ^{13}C{^{1}H} NMR Spectrum (100 MHz, $CDCl_3$) of **P11**.

Synthesis of P12:



1-mesityl-3-phenylpropan-1-one (P12). 54.3 mg; 82% isolated yield; yellow solid: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.31 – 7.20 (m, 5H), 6.82 (s, 2H), 3.07 – 3.00 (m, 4H), 2.27 (s, 3H), 2.13 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 209.8, 141.1, 139.6, 138.5, 132.7, 128.6, 126.3, 46.5, 29.6, 21.1, 19.1.

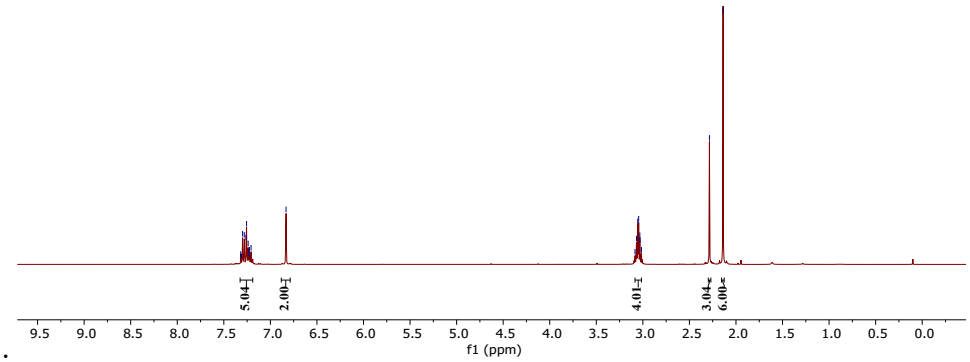


Figure S30. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P12**

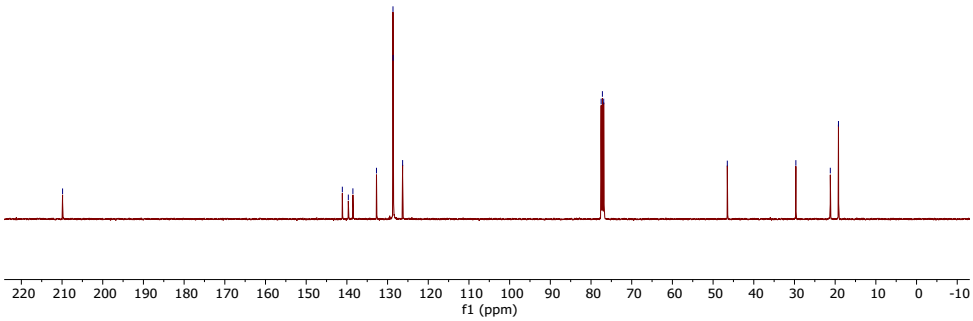
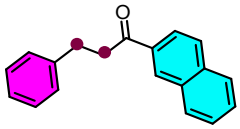


Figure S31. ^{13}C{^{1}H} NMR Spectrum (100 MHz, $CDCl_3$) of **P12**.



Synthesis of P13:

1-(naphthalen-2-yl)-3-phenylpropan-1-one (P13). 62.7 mg; 78% isolated yield; brown solid: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.46 (s, 1H), 8.04 (d, 1H), 7.94 – 7.86 (m, 3H), 7.61 -7.52 (m, 2H), 7.34 – 7.18 (m, 5H), 3.44 (t, 2H), 3.13 (t, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 199.3, 141.5, 135.7, 134.3, 132.7, 129.8, 129.7, 129.2, 128.7, 128.6, 128.5, 127.9, 126.9, 126.3, 124.0, 40.7, 30.4.

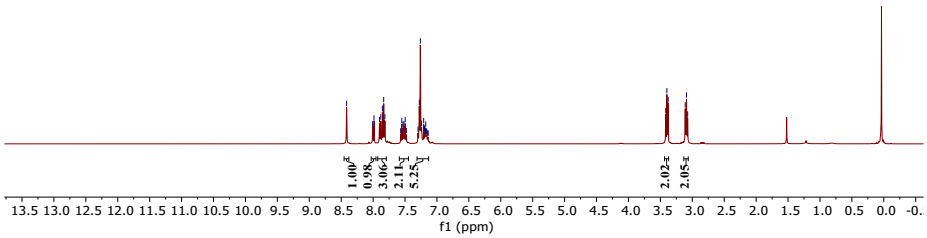


Figure S32. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P13**

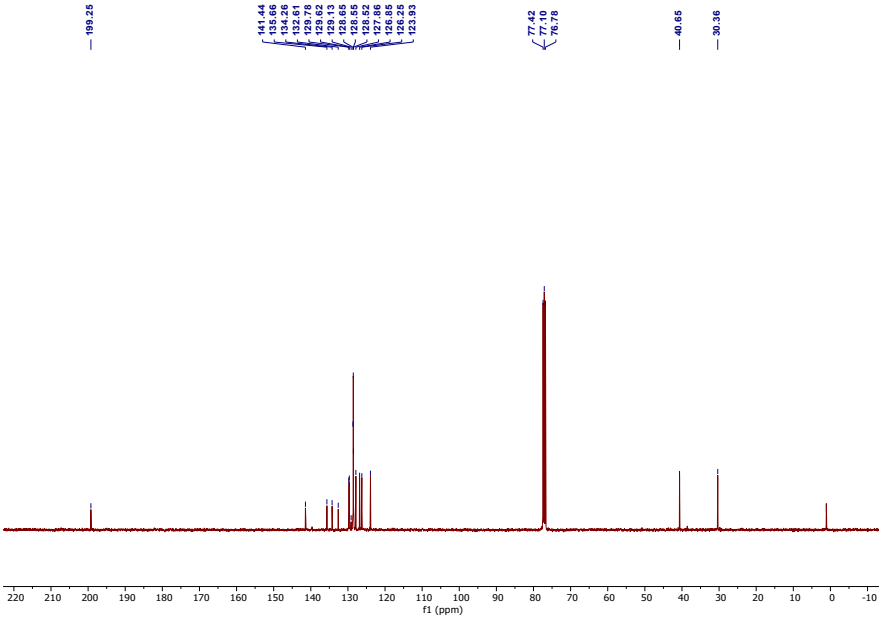
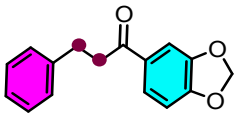


Figure S33. ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of **P13**.

Synthesis of P14:



1-(benzo[d][1,3]dioxol-5-yl)-3-phenylpropan-1-one (P14). 44.8 mg; 76% isolated yield; white solid: **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.56 – 7.54 (m, 1H), 7.44 (s, 1H), 7.31 – 7.20 (m, 5H), 6.83 (d, 1H), 6.03 (s, 2H), 3.22 (t, 2H), 3.05 (d, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 197.4, 151.8, 148.3, 141.5, 131.9, 128.6, 128.5, 126.2, 124.3, 108.0, 107.9, 101.9, 40.3, 30.5.

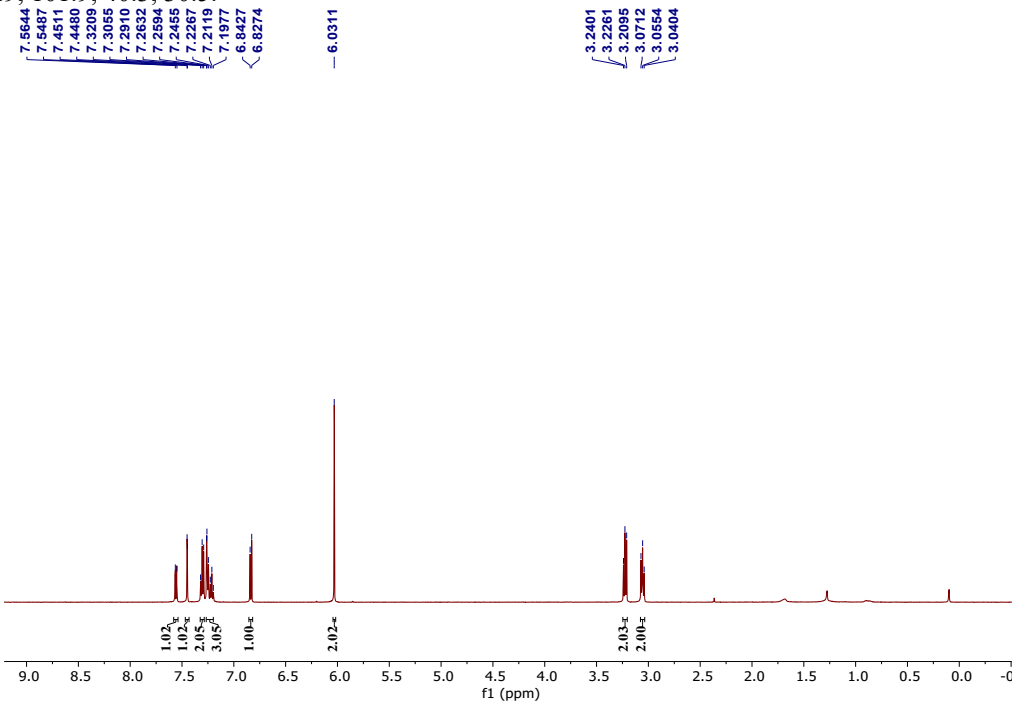


Figure S34. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P14**

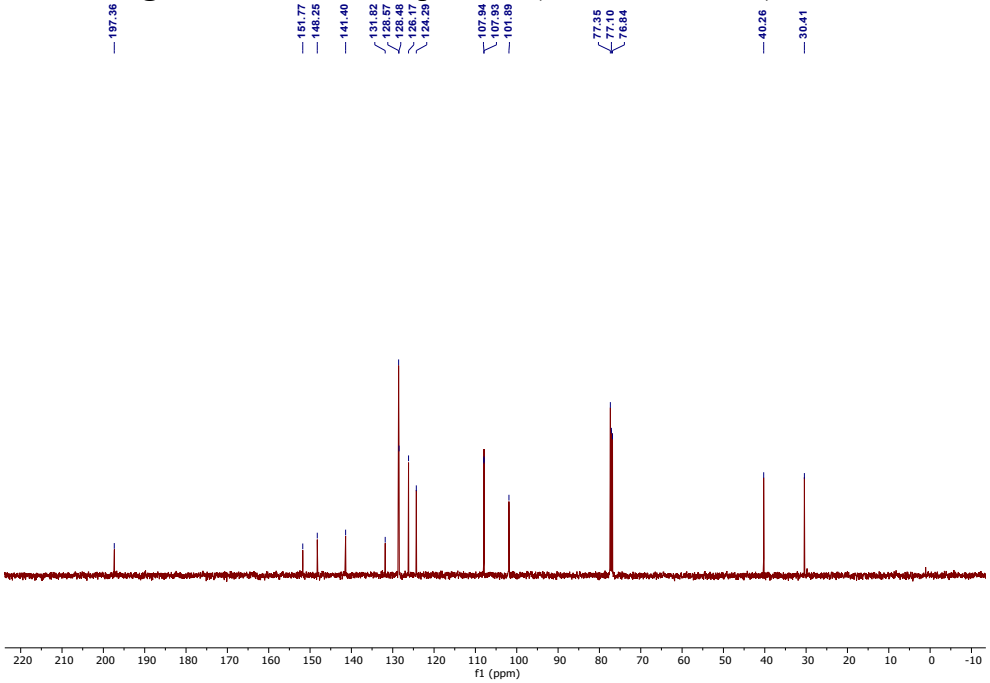
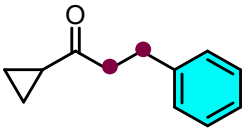


Figure S35. ^{13}C{^{1}H} NMR Spectrum (100 MHz, $CDCl_3$) of **P14**.



Synthesis of P15:

1-cyclopropyl-3-phenylpropan-1-one (P15). 38.0 mg; 72% isolated yield; pale yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.29 – 7.24 (m, 2H), 7.19 – 7.16 (m, 3H), 2.94 – 2.85 (m, 4H), 1.93 – 1.86 (m, 1H), 1.03 – 0.98 (m, 2H), 0.87 – 0.82 (m, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 210.1, 141.4, 128.6, 128.5, 126.2, 45.1, 30.1, 20.7, 10.8.

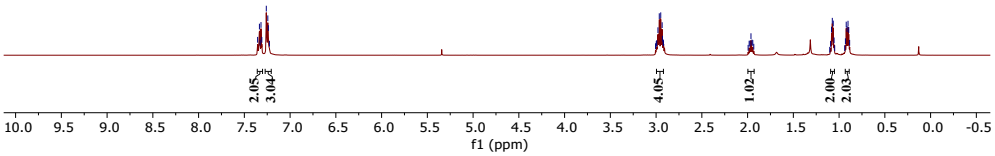


Figure S36 ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P15**.

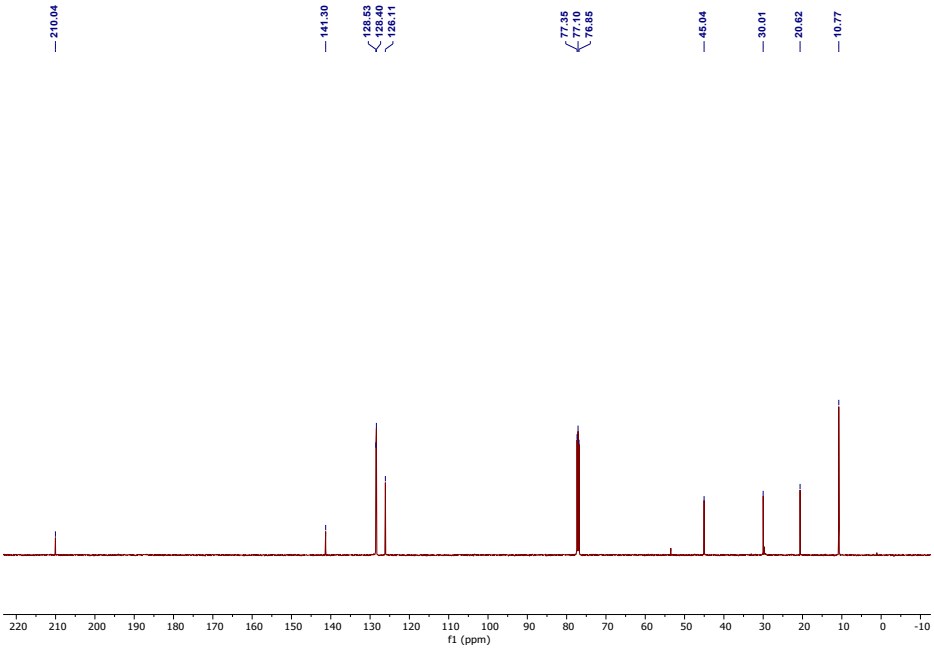
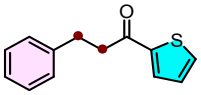


Figure S37. ^{13}C{^{1}H} NMR Spectrum (125 MHz, $CDCl_3$) of **P15**.

Synthesis of P16



3-phenyl-1-(thiophen-2-yl)propan-1-one (16) 42 mg, 73% isolated yield; white solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.96 (d, $J_{H,H}$ = 7.7 Hz, 2H), 7.55 (t, $J_{H,H}$ = 7.6 Hz, 1H), 7.45 (t, $J_{H,H}$ = 7.6 Hz, 2H), 7.11 (d, $J_{H,H}$ = 5.1 Hz, 1H), 6.91 (t, $J_{H,H}$ = 4.3 Hz, 1H), 6.86 (d, $J_{H,H}$ = 3.4 Hz, 1H), 3.34 (t, $J_{H,H}$ = 6.9 Hz, 2H), 3.29 (t, $J_{H,H}$ = 8.1 Hz, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 198.6, 143.9, 136.8, 133.2, 128.7, 128.1, 128.1, 126.9, 124.7, 123.4, 40.6, 24.2.

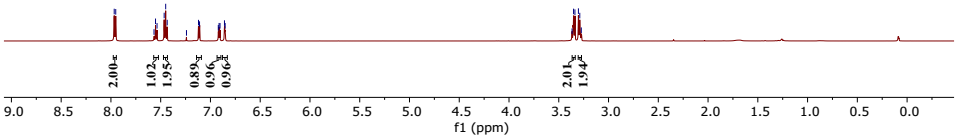


Figure S38 ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P16**.

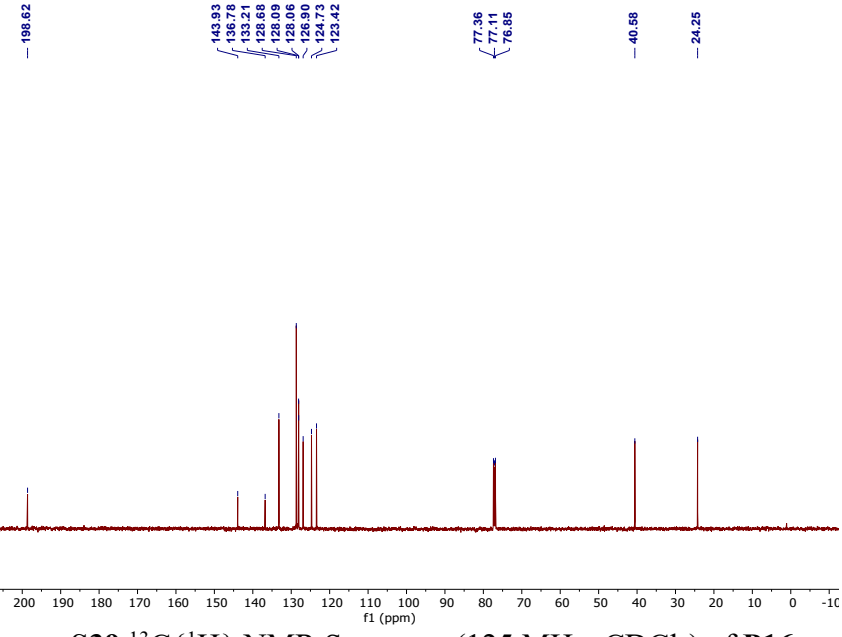
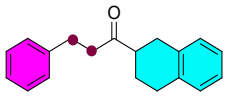


Figure S39 ^{13}C{^{1}H} NMR Spectrum (125 MHz, $CDCl_3$) of **P16**.

Synthesis of P17



3-phenyl-1-(1,2,3,4-tetrahydronaphthalen-2-yl)propan-1-one (P16) 108.4 mg, 78% isolated yield; white solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.08 (d, $J_{H,H}$ = 7.9 Hz, 1H), 7.47 – 7.43 (m, 1H), 7.31 (t, $J_{H,H}$ = 7.5 Hz, 3H), 7.25 – 7.20 (m, 4H), 3.50 (dd, $J_{H,H}$ = 13.7, 3.9 Hz, 1H), 2.92 (dt, $J_{H,H}$ = 8.9, 4.4 Hz, 2H), 2.77 – 2.70 (m, 1H), 2.65 (dd, $J_{H,H}$ = 13.6, 9.5 Hz, 1H), 2.13 – 2.08 (m, 1H), 1.81 – 1.73 (m, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 199.4, 144.0, 140.1, 133.3, 132.5, 129.3, 128.7, 128.4, 127.5, 126.6, 126.1, 49.4, 35.7, 28.6, 27.7.

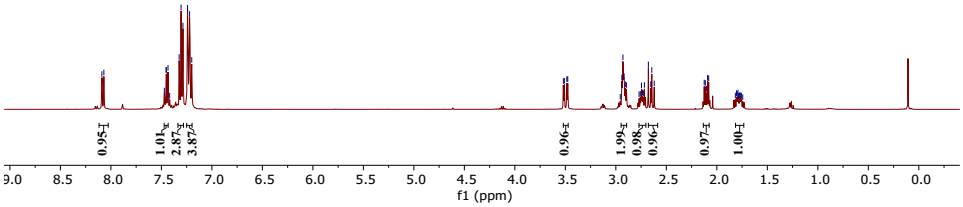


Figure S40 ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P17**.

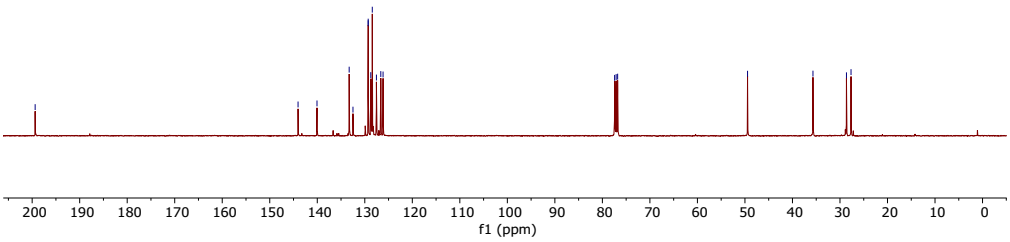
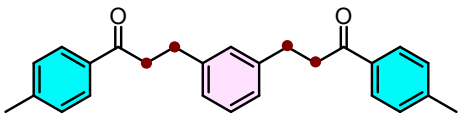
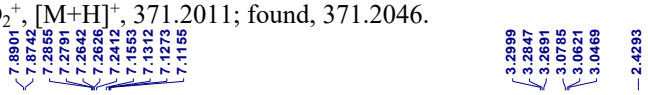


Figure S41 ^{13}C{^{1}H} NMR Spectrum (125 MHz, $CDCl_3$) of **P17**.



Synthesis of P18:

148.2 mg, 80% isolated yield; white solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.88 (d, $J_{H,H}$ = 7.9 Hz, 4H), 7.29 – 7.26 (m, 5H), 7.16 – 7.11 (m, 3H), 3.28 (t, $J_{H,H}$ = 7.8 Hz, 4H), 3.06 (t, $J_{H,H}$ = 7.9 Hz, 4H), 2.43 (s, 6H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 199.0, 143.9, 141.7, 134.5, 129.3, 128.8, 128.7, 128.3, 126.3, 40.4, 30.3, 21.7. **ESI-MS:** Calcd for $C_{26}H_{27}O_2^+$, $[M+H]^+$, 371.2011; found, 371.2046.



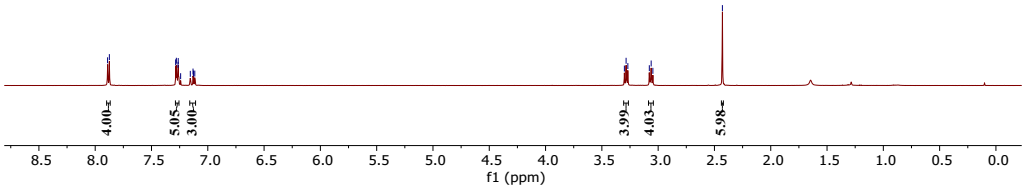


Figure S42 ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P18**.

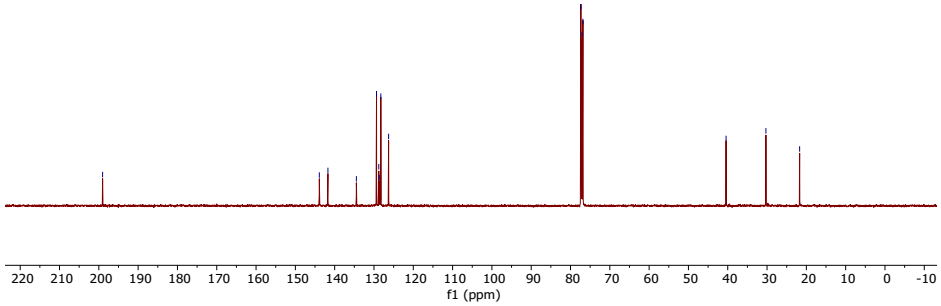
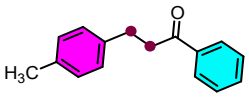


Figure S43 ^{13}C{^{1}H} NMR Spectrum (125 MHz, $CDCl_3$) of **P18**.

Synthesis of P19: 

1-phenyl-3-(p-tolyl)propan-1-one (P19). 54.9 mg; 82% isolated yield; yellow oil: **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.96 – 7.94 (m, 2H), 7.55 (t, J_{H-H} = 7.3 Hz, 1H), 7.44 (t, J_{H-H} = 7.7 Hz, 2H), 7.15 – 7.10 (m, 4H), 3.28 (t, J_{H-H} = 7.3 Hz, 2H), 3.02 (t, J_{H-H} = 8.1 Hz, 2H), 2.32 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 199.5, 138.3, 137.0, 135.8, 133.2, 129.3, 128.7, 128.4, 128.2, 40.8, 29.9, 21.1.

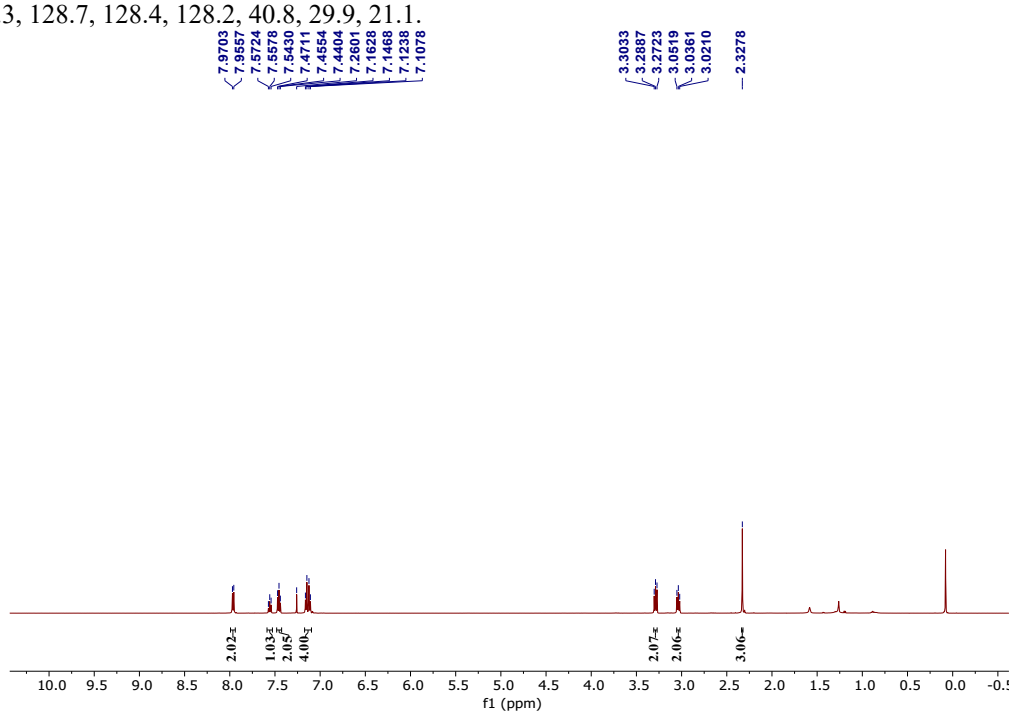


Figure S44. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) **P19**.

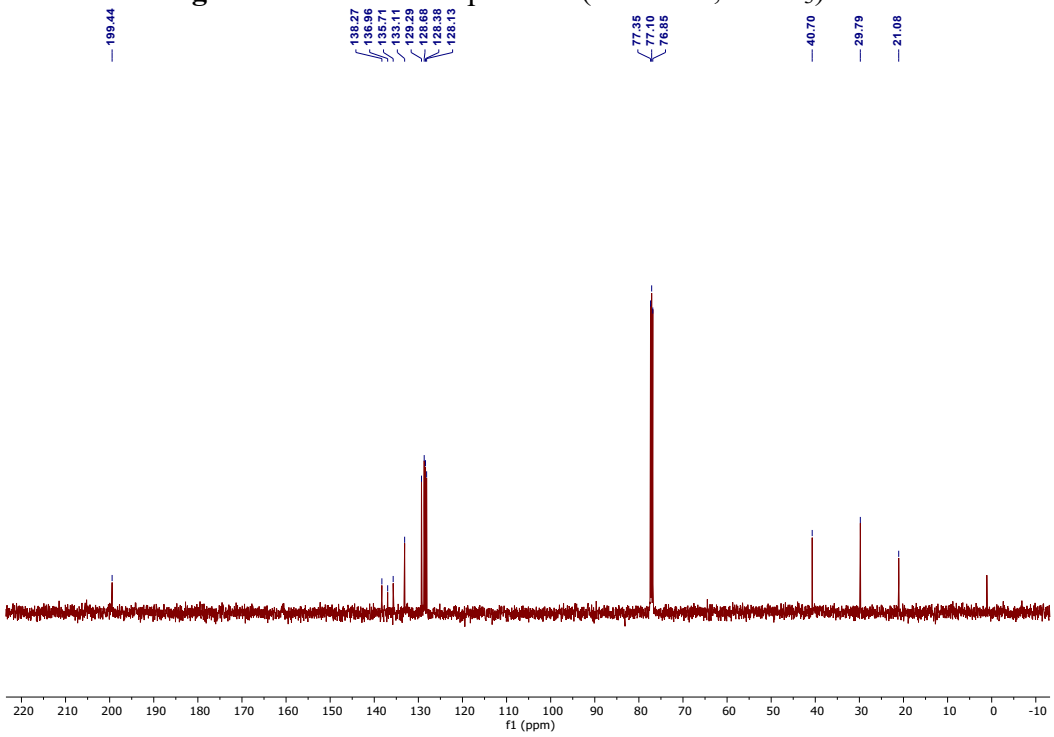
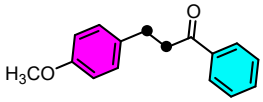


Figure S45. ^{13}C{^{1}H} NMR Spectrum (125 MHz, $CDCl_3$) of **19**.

Synthesis of P20:



3-(4-methoxyphenyl)-1-phenylpropan-1-one (P20). 44.0 mg; 80% isolated yield; yellow solid: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.94 (d, 2H), 7.56 (t, 1H), 7.44 (t, 2H), 7.17 (d, 2H), 6.84 (d, 2H), 3.78 (s, 3H), 3.27 (t, 2H), 3.02 (t, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 199.5, 158.1, 137.0, 133.4, 133.1, 129.4, 128.7, 128.1, 114.0, 55.3, 40.8, 29.4.

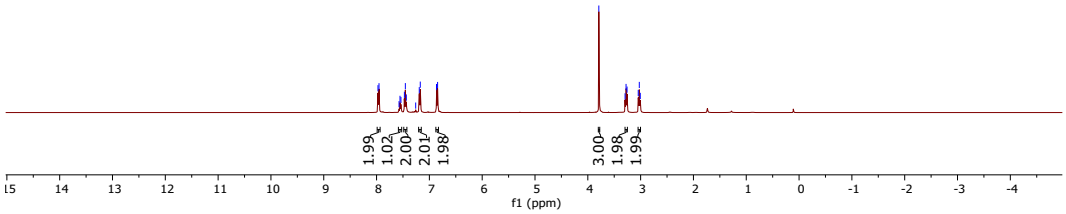
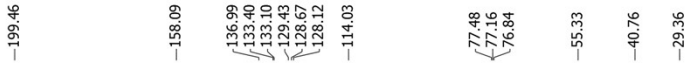


Figure S46. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P20**.



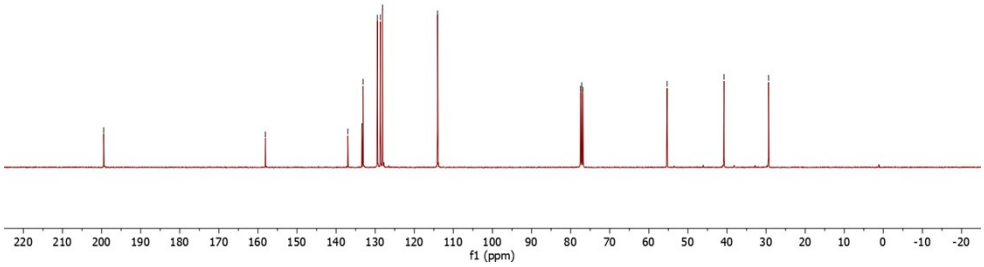
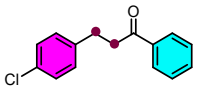
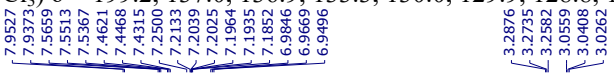


Figure S47. ^{13}C{^{1}H} NMR Spectrum (100 MHz, $CDCl_3$) of **P20**.

Synthesis of P21: 

3-(4-chlorophenyl)-1-phenylpropan-1-one (P21). 60.2 mg; 78% isolated yield; yellow solid: **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.94 (d, 2H), 7.55 (t, 1H), 7.45 (t, 2H), 7.21 – 7.18 (m, 2H), 6.97 (t, 2H), 3.27 (t, 2H), 3.04 (t, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 199.2, 137.0, 136.9, 133.3, 130.0, 129.9, 128.8, 128.1, 115.3, 40.5, 29.3.



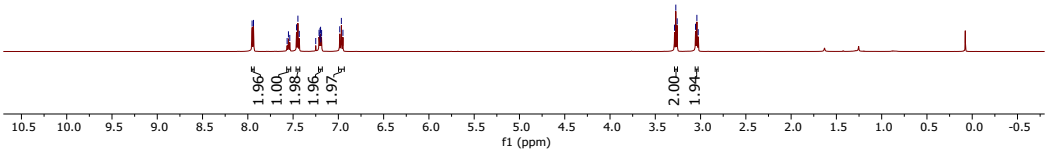


Figure S48. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P21**.

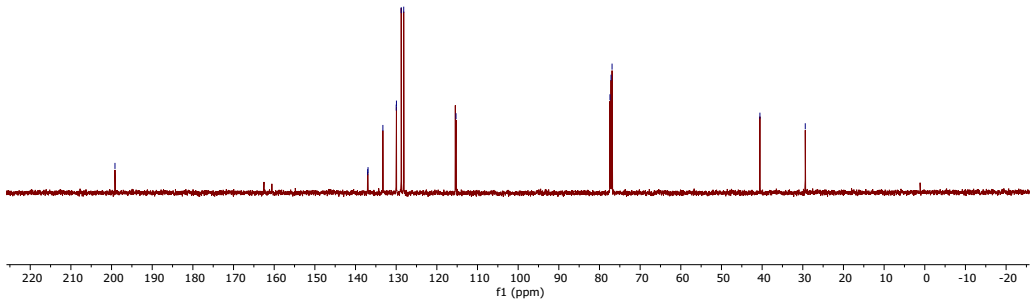
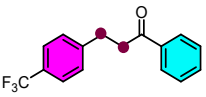


Figure S49. ^{13}C{^{1}H} NMR Spectrum (125 MHz, $CDCl_3$) of **P21**.

Synthesis of P22: 

1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (P22). 66.4 mg; 72% isolated yield; white solid: **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.95 (d, 2H), 7.57 – 7.53 (m, 3H), 7.45 (t, 2H), 7.36 (d, 2H), 3.32 (t, 2H), 3.13 (t, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 198.7, 145.6, 136.8, 133.4, 128.9, 128.8, 128.1, 125.6, 123.3, 39.9, 29.9.

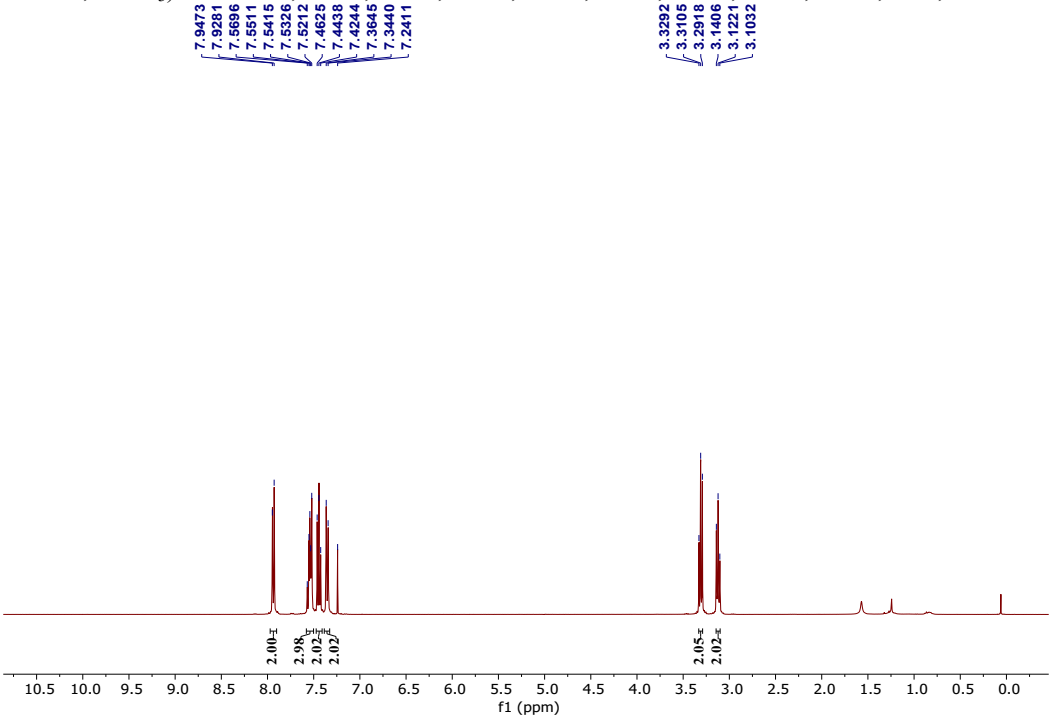


Figure S50. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P22**.

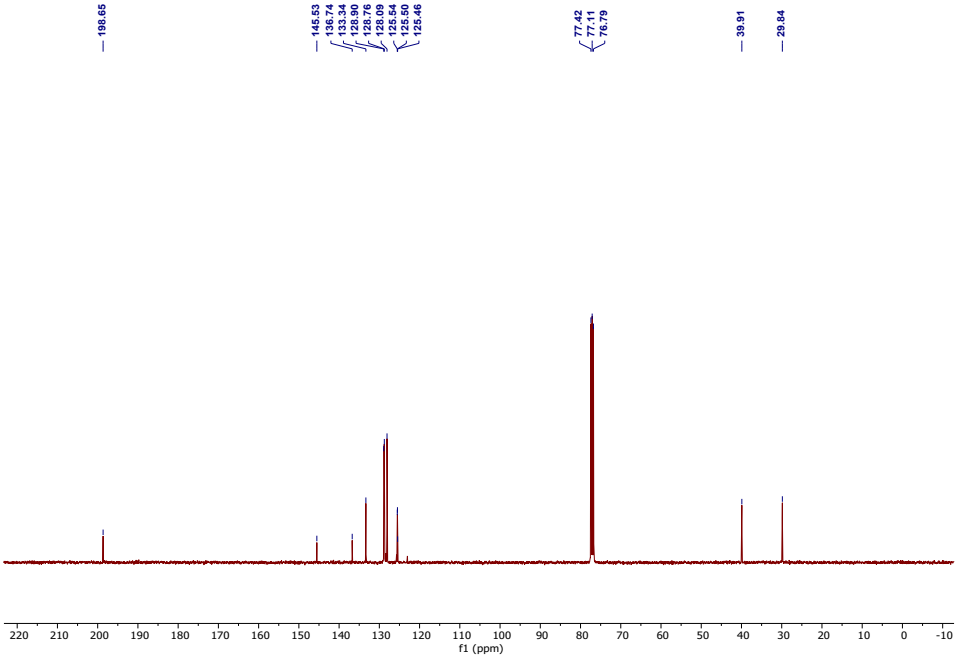
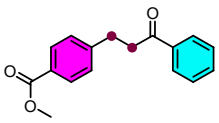


Figure S51. ^{13}C{^{1}H} NMR Spectrum (125 MHz, $CDCl_3$) of **P22**.



Synthesis of P23

methyl 4-(3-phenylpropanoyl)benzoate (P23). 60.6 mg; 78% isolated yield; white solid: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.97 – 7.93 (m, 4H), 7.57 – 7.53 (m, 1H), 7.44 (t, 2H), 7.31 (d 2H), 3.89 (s, 3H), 3.31 (t, 2H), 3.11 (t, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 198.8, 167.2, 146.9, 136.8, 133.3, 130.0, 128.8, 128.6, 128.3, 128.1, 52.1, 39.9, 30.1.

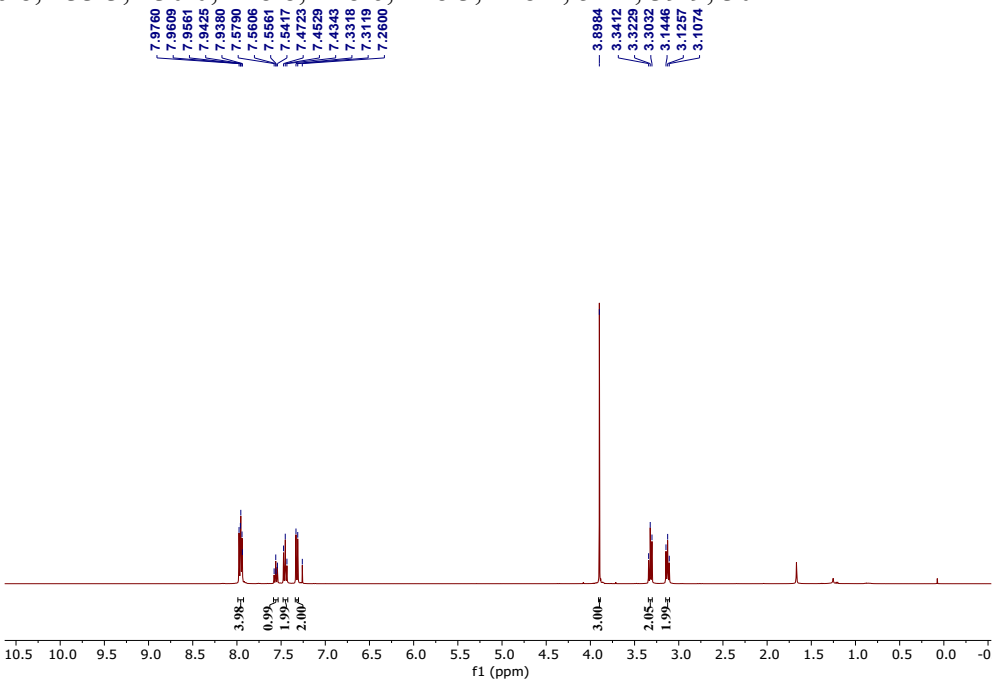


Figure S52. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P23**.

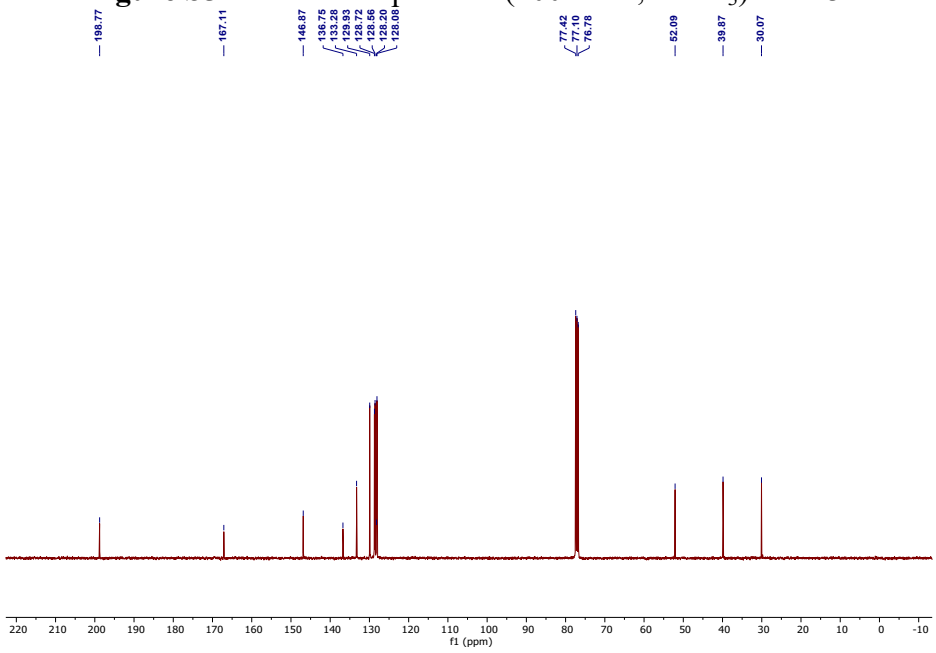
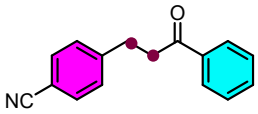


Figure S53. ^{13}C{^{1}H} NMR Spectrum (100 MHz, $CDCl_3$) of **P23**.

Synthesis of P24: 

4-(3-phenylpropanoyl)benzonitrile (P24). 50.2 mg; 70% isolated yield; white solid: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.01 (d, J_{H-H} = 8.5 Hz, 2H), 7.74 (d, J_{H-H} = 8.6 Hz, 2H), 7.31 – 7.21 (m, 5H), 3.30 (t, J_{H-H} = 7.1 Hz, 2H), 3.07 (t, J_{H-H} = 7.8 Hz, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 198.0, 140.8, 139.9, 132.7, 128.8, 128.6, 128.5, 126.5, 118.0, 116.5, 40.9, 30.0.

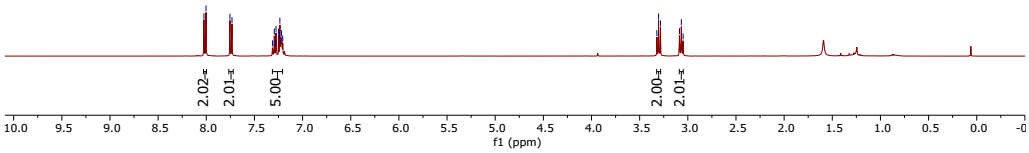
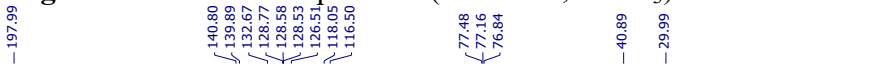


Figure S54. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **P24**.



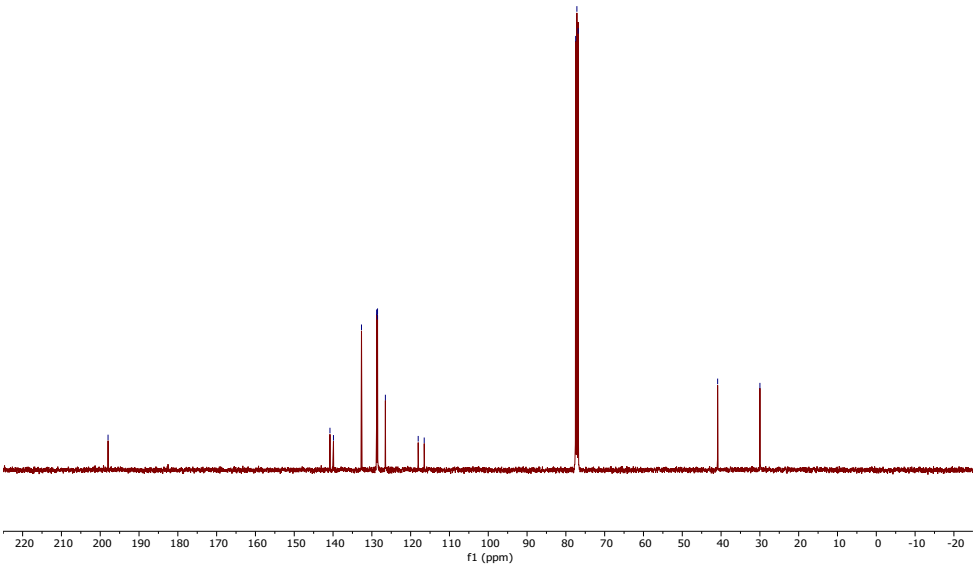
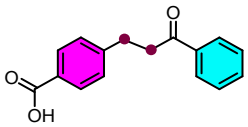
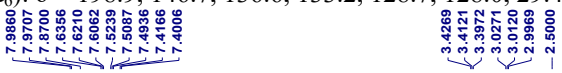


Figure S55. ^{13}C{^{1}H} NMR Spectrum (100 MHz, $CDCl_3$) of **P24.**



Synthesis P25:

4-(3-oxo-3-phenylpropyl)benzoic acid (P25). 50.1 mg; 71% isolated yield; yellow solid: **^{1}H NMR** (500 MHz, DMSO-D_6): δ =7.98 (d, 2H), 7.87 (s, 2H), 7.62 (t, 1H), 7.51 (t, 2H), 7.41 (d, 2H), 3.41 (t, 2H), 3.01 (t, 2H). **^{13}C{^{1}H} NMR** (125 MHz, DMSO-d_6): δ = 198.9, 146.7, 136.6, 133.2, 128.7, 128.0, 29.42.



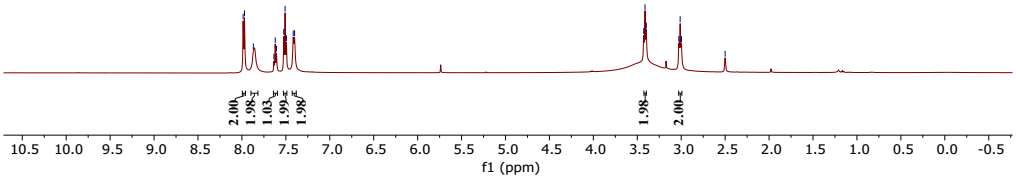
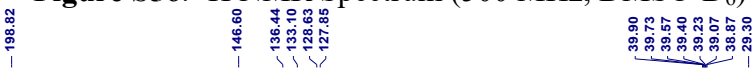


Figure S56. ^{1}H NMR Spectrum (500 MHz, DMSO-D_6) of **P25**.



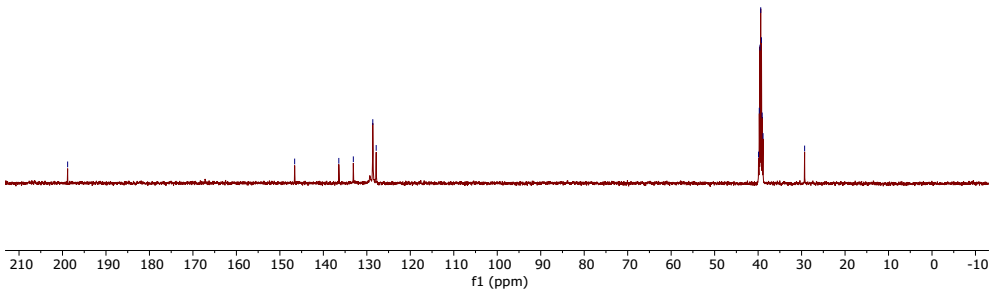
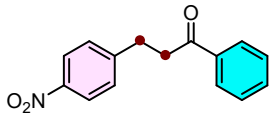


Figure S57. ^{13}C{^{1}H} NMR Spectrum (125 MHz, DMSO-D_6) of **P25**.

Synthesis P26: 

3-(4-nitrophenyl)-1-phenylpropan-1-one (26) 108.4 mg, 62% isolated yield; white solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.13 (d, $J_{H,H}$ = 8.2 Hz, 2H), 7.93 (d, $J_{H,H}$ = 7.9 Hz, 2H), 7.55 (d, $J_{H,H}$ = 7.2 Hz, 1H), 7.44 (t, $J_{H,H}$ = 7.6 Hz, 2H), 7.40 (d, $J_{H,H}$ = 8.4 Hz, 2H), 3.34 (t, $J_{H,H}$ = 7.5 Hz, 2H), 3.17 (t, $J_{H,H}$ = 7.3 Hz, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 198.2, 149.3, 146.6, 136.6, 133.4, 129.4, 128.8, 128.1, 123.8, 39.5, 29.8.

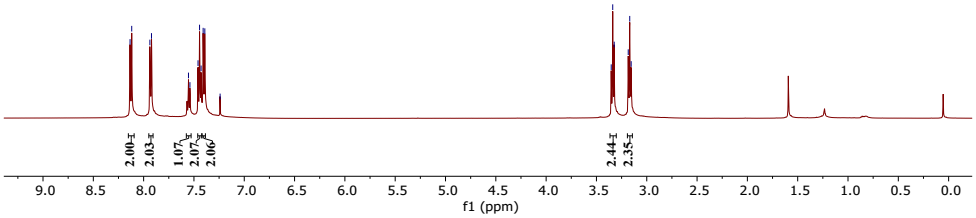


Figure S58. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P26**.

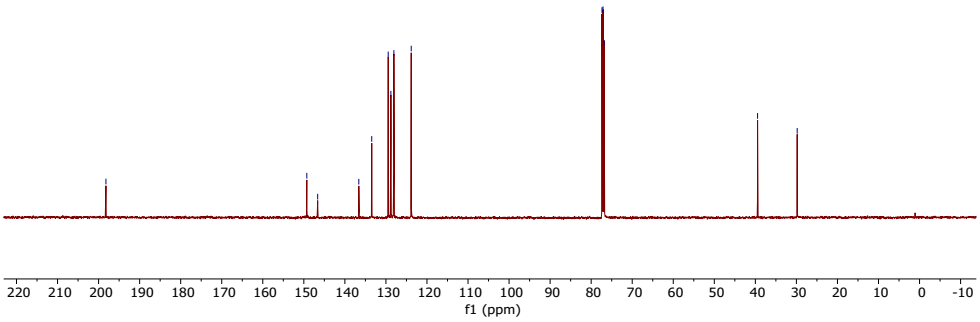
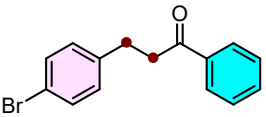
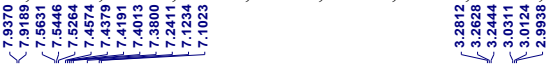


Figure S59. ^{13}C{^{1}H} NMR Spectrum (125 MHz, $CDCl_3$) of **P26**.

Synthesis P27



3-(4-bromophenyl)-1-phenylpropan-1-one (27): 122.9 mg, 85% isolated yield; white solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.93 (d, $J_{H,H}$ = 7.3 Hz, 2H), 7.54 (t, $J_{H,H}$ = 7.3 Hz, 1H), 7.44 (t, $J_{H,H}$ = 7.7 Hz, 2H), 7.39 (d, $J_{H,H}$ = 8.5 Hz, 2H), 7.11 (d, $J_{H,H}$ = 8.5 Hz, 2H), 3.26 (t, $J_{H,H}$ = 7.4 Hz, 2H), 3.01 (t, $J_{H,H}$ = 7.4 Hz, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 198.9, 140.3, 136.8, 133.3, 131.6, 130.3, 128.7, 128.1, 120.0, 40.2, 29.5.



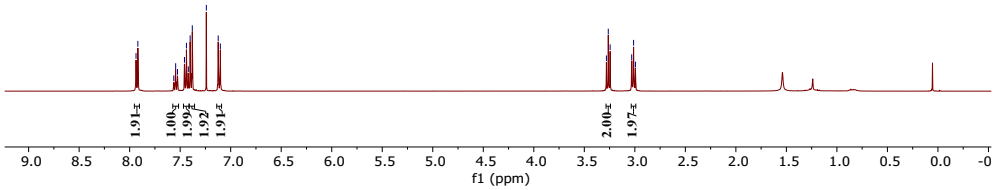


Figure S60. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P27**.

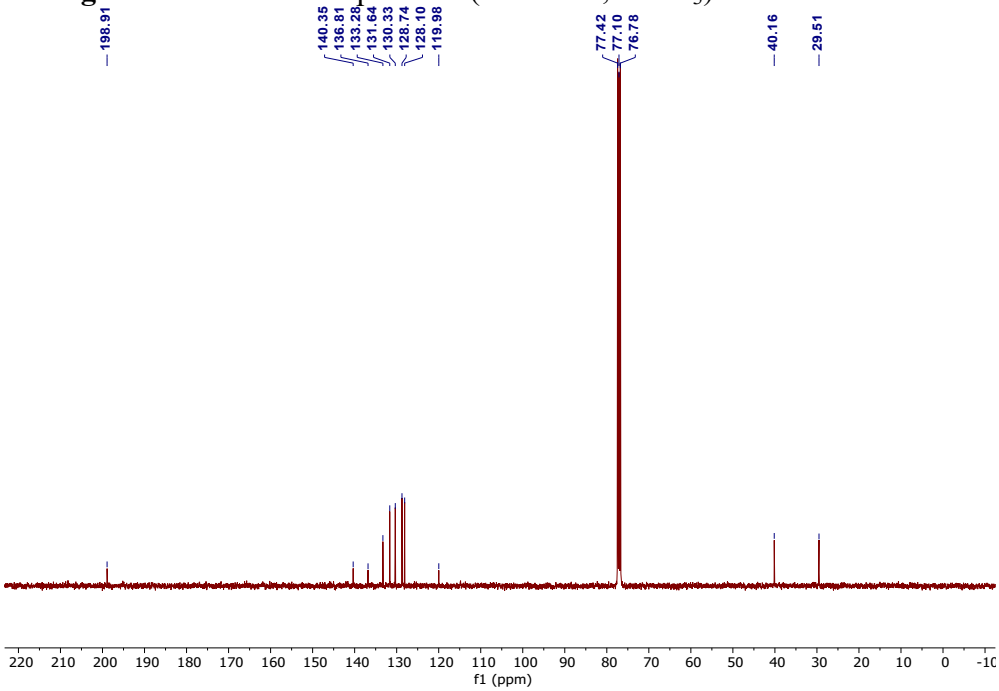
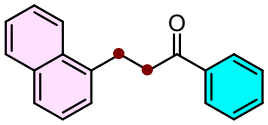


Figure S61. ^{13}C{^{1}H} NMR Spectrum (125 MHz, $CDCl_3$) of **P27**.



Synthesis P28

3-(naphthalen-1-yl)-1-phenylpropan-1-one (28): 114.5 mg, 79% isolated yield; white solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.04 (d, $J_{H,H}$ = 7.9 Hz, 1H), 7.96 – 7.93 (m, 2H), 7.86 (d, $J_{H,H}$ = 8.3 Hz, 1H), 7.75 – 7.70 (m, 1H), 7.54 – 7.38 (m, 7H), 3.53 (t, $J_{H,H}$ = 7.9 Hz, 2H), 3.42 (t, $J_{H,H}$ = 7.5 Hz, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 199.4, 137.4, 136.9, 133.2, 129.0, 128.7, 128.1, 127.1, 126.2, 126.2, 125.7, 125.7, 123.6, 39.8, 27.3.

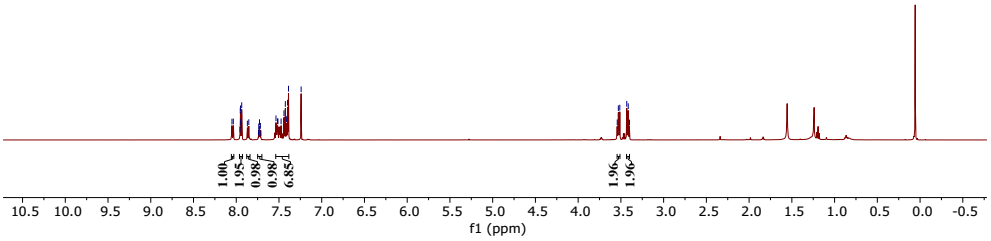


Figure S62. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P28**.

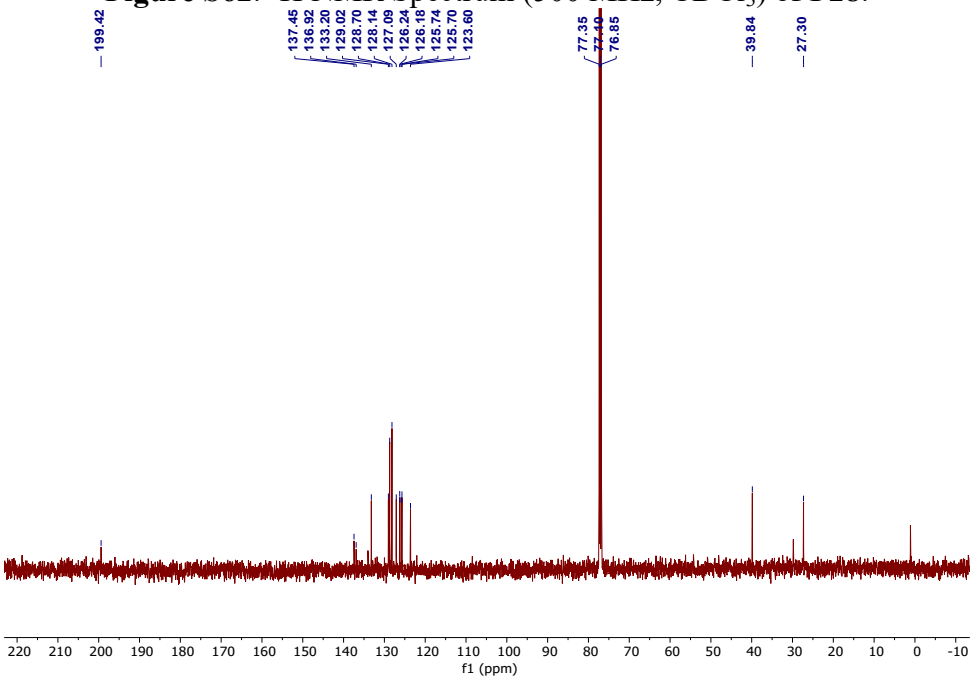
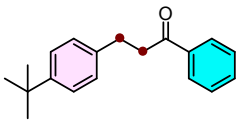
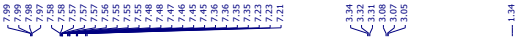


Figure S63. ^{13}C{^{1}H} NMR Spectrum (125 MHz, $CDCl_3$) of **P28**.



Synthesis P29:

Synthesis of 3-(4-(tert-butyl)phenyl)-1-phenylpropan-1-one(29) 54.6 mg, 80% isolated yield; oily liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ= 7.99-7.97 (dd, 2H), 7.58-7.55 (m, 1H), 7.48-7.45 (m, 2H), 7.36-7.35 (dd, 2H), 3.34-3.31(t, 2H), 3.08-3.05(t, 2H), 1.34 (s, 9H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): (125 MHz, $CDCl_3$): 199.45, 149.06, 138.30, 136.98, 133.14, 128.70, 128.19, 128.15, 125.52, 40.59, 34.48, 31.50, 29.67.



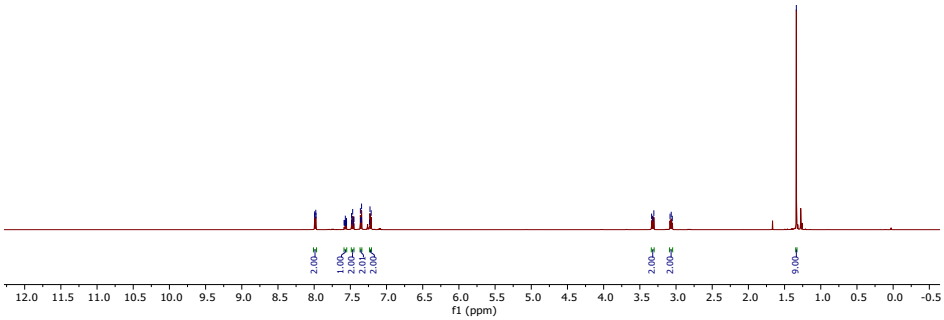


Figure S64. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P29**.

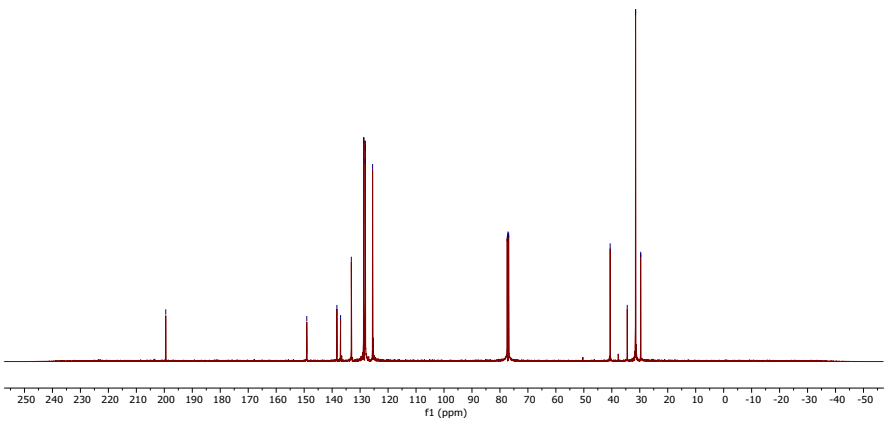
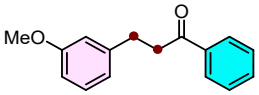


Figure S65. ^{13}C{^{1}H} NMR Spectrum (125 MHz, $CDCl_3$) of **P29**.



Synthesis of P30

Synthesis of 3-(3-methoxyphenyl)-1-phenylpropan-1-one(P30) 64 mg, 79% isolated yield; oily liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.98-7.96(dd, 2H), 7.58-7.55(m, 1H), 7.48-7.44(m, 2H), 7.26-7.21(m, 1H), 6.86-6.85(d, 1H), 6.81(s, 1H), 6.78-6.75(dd, 1H), 3.80(s, 3H), 3.32-3.29(t, 2H), 3.07-3.04(t, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): 199.29, 159.82, 143.02, 136.92, 133.17, 129.61, 128.70, 128.13, 120.86, 114.32, 111.50, 55.25, 40.45, 30.26.

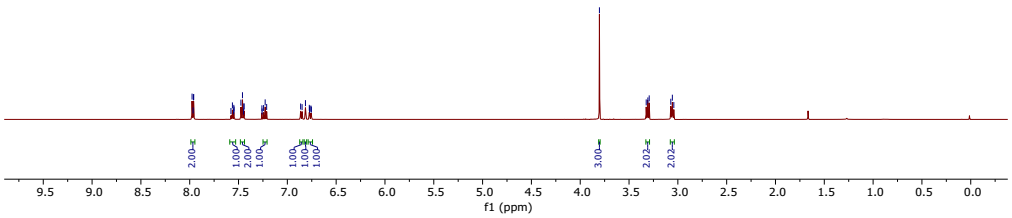


Figure S66. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P30**.

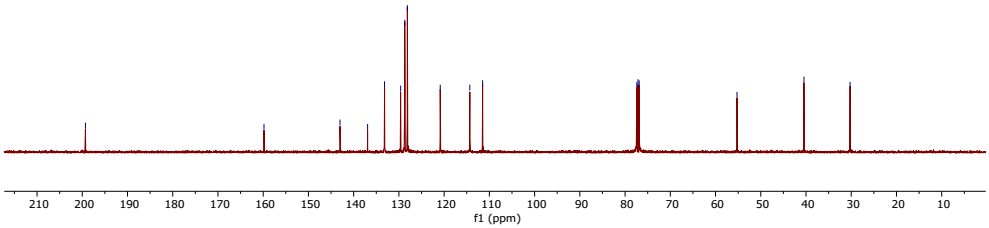
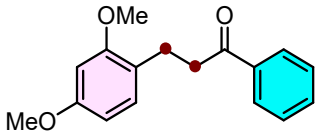
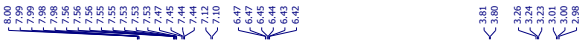


Figure S67. ^{13}C{^{1}H} NMR Spectrum (125 MHz, $CDCl_3$) of **P30**.



Synthesis P31

Synthesis of 3-(2,4-dimethoxyphenyl)-1-phenylpropan-1-one(P31) 46.6 mg, 82% isolated yield; oily liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ=8.00-7.98(dd, 2H), 7.56-7.53(m, 1H), 7.47-7.44(m, 2H), 7.12-7.10(d, 1H), 6.47-6.42(m, 2H), 3.81-3.80(d, 6H), 3.26-3.23(t, 2H), 3.01-2.98(t, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): 200.18, 159.52, 158.40, 137.02, 132.90, 130.37, 128.55, 128.14, 121.87, 103.88, 98.56, 55.38, 55.23, 39.23, 25.16.



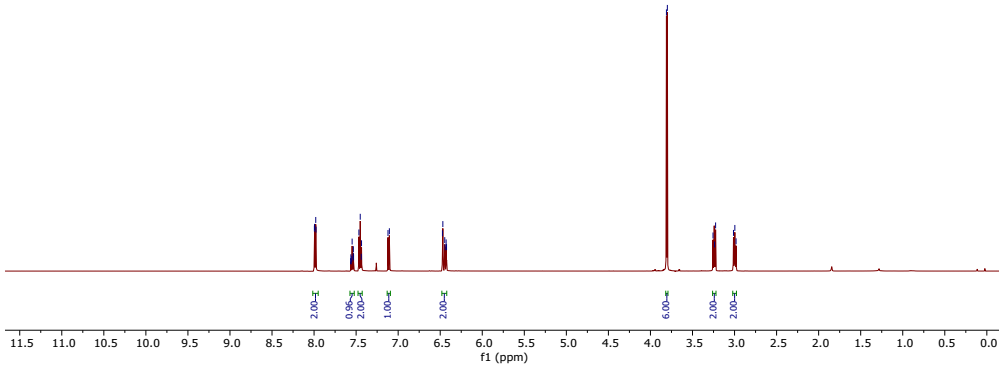


Figure S68. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P31**.

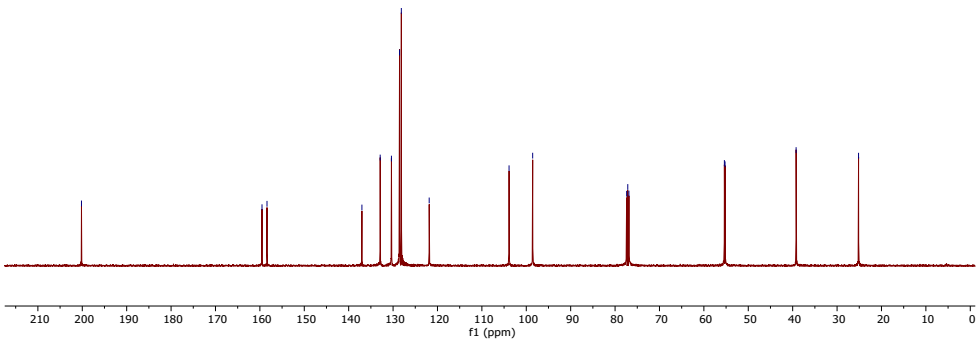
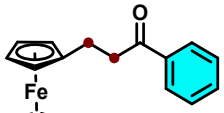


Figure S69. $^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P31**.



P32

Synthesis of 3-phenyl-1-(ferrocynyl)propan-1-one (P32) 138 mg 80% isolated yield; white solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.98 – 7.91 (m, 2H), 7.57 – 7.51 (m, 1H), 7.45 (t, $J_{H,H}$ = 7.7 Hz, 2H), 4.11 (s, 4H), 4.10 – 4.08 (m, 2H), 4.05 (q, $J_{H,H}$ = 2.3, 1.8 Hz, 2H), 3.18 (t, $J_{H,H}$ = 8.1 Hz, 2H), 2.77 (t, $J_{H,H}$ = 7.5 Hz, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 199.6, 137.0, 133.1, 128.7, 128.1, 88.1, 68.6, 68.2, 67.4, 40.4, 24.2.

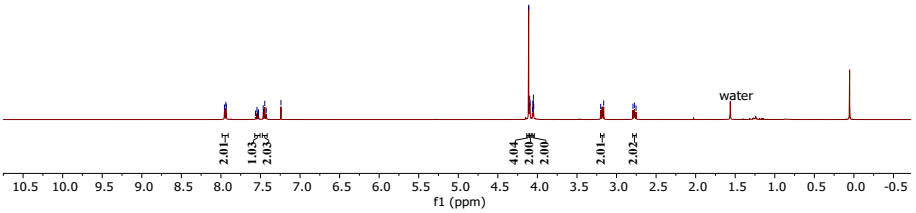


Figure S70. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P32**.

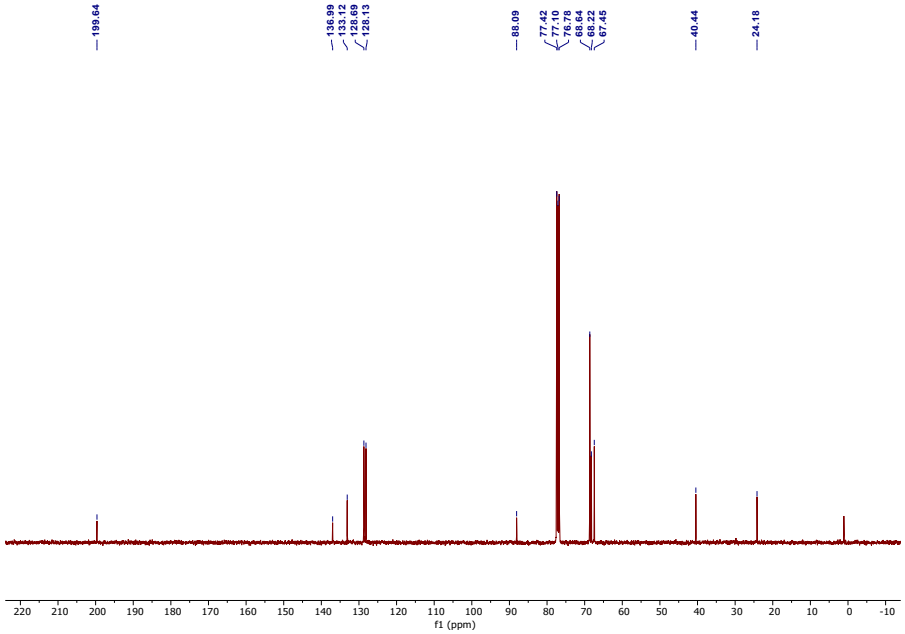
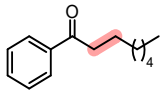


Figure S71. $^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P32**.

1-phenyloctan-1-one (32): 

Purified by column chromatography using silica gel and ethyl acetate-hexane as eluent 75%, isolated yield; white solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.94 (d, $J_{H,H}$ = 7.6 Hz, 2H), 7.53 (t, $J_{H,H}$ = 7.3 Hz, 1H), 7.43 (t, $J_{H,H}$ = 7.6 Hz, 2H), 2.94 (t, $J_{H,H}$ = 7.6 Hz, 2H), 1.71 (q, $J_{H,H}$ = 7.4 Hz, 2H), 1.34 – 1.24 (m, 8H), 0.88 – 0.84 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 200.7, 137.2, 132.9, 128.6, 128.1, 38.7, 31.8, 29.4, 29.2, 24.5, 22.7, 14.1.

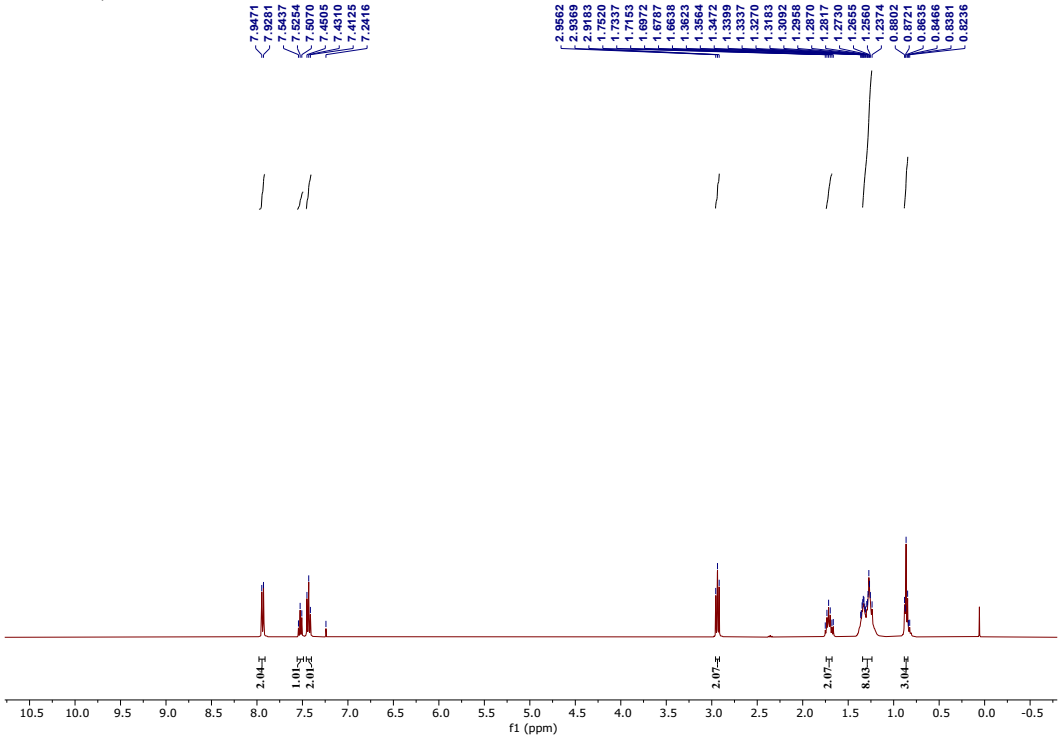


Figure S72. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P33**.

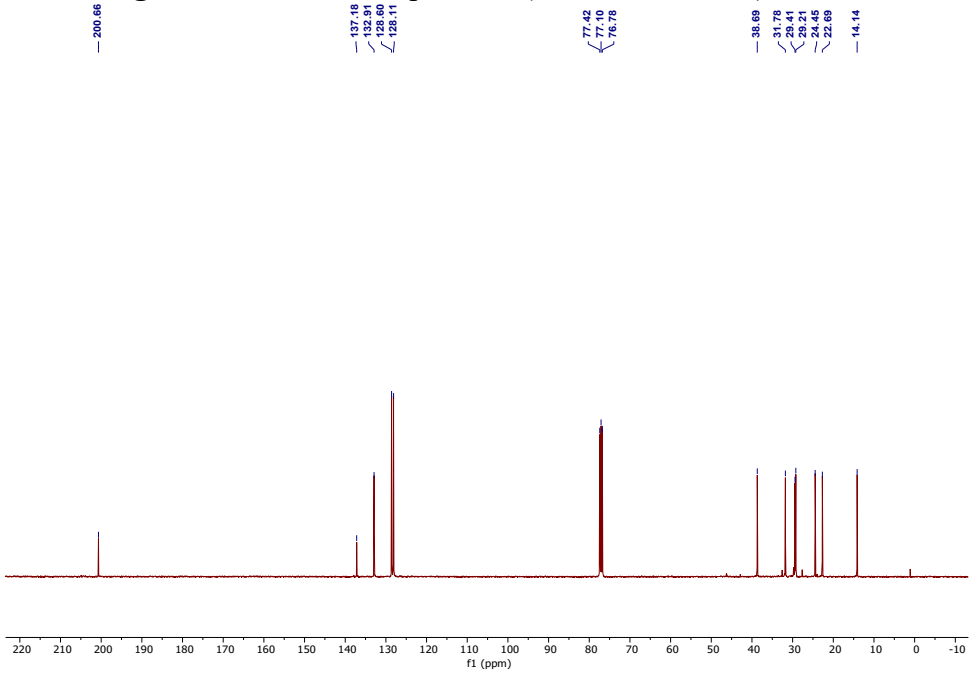
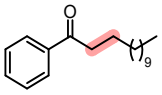


Figure S73. $^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P33**.



1-phenyltridecan-1-one (34):

Purified by column chromatography using silica gel and ethyl acetate-hexane as eluent 73% (100.2 mg) isolated yield; white solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.95 – 7.93 (m, 2H), 7.56 – 7.50 (m, 1H), 7.44 (dd, $J_{H,H}$ = 8.4, 7.0 Hz, 2H), 2.93 (d, $J_{H,H}$ = 7.5 Hz, 2H), 1.73 – 1.69 (m, 2H), 1.24 (s, 18H), 0.85 (d, $J_{H,H}$ = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 200.7, 137.2, 132.9, 128.6, 128.1, 38.7, 32.0, 29.7, 29.7, 29.6, 29.5, 29.4, 24.5, 22.8, 14.2.

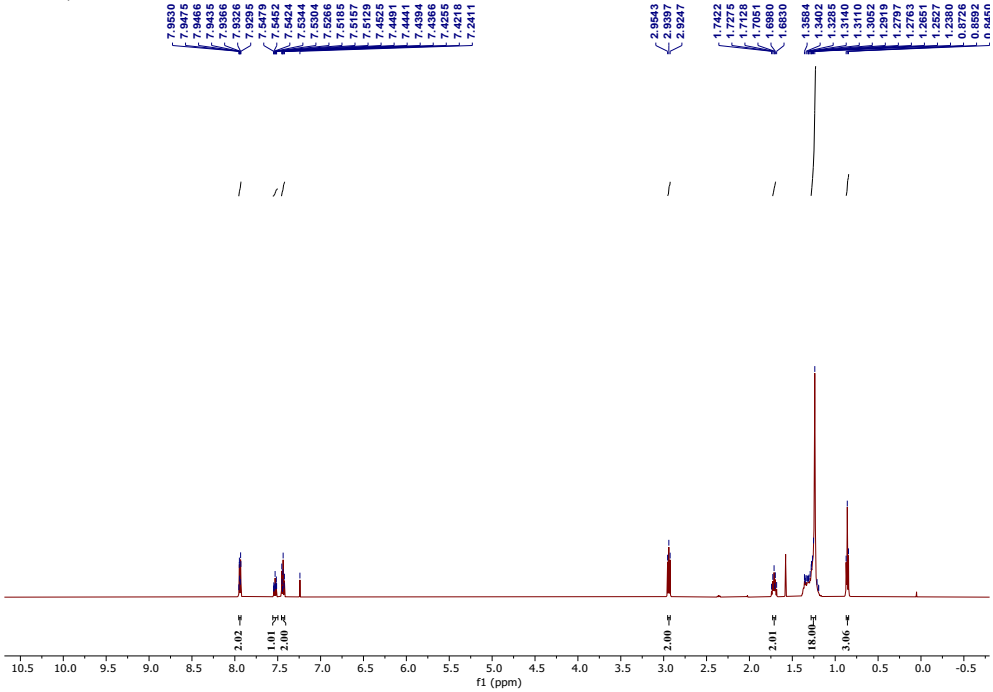


Figure S74. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P34**.

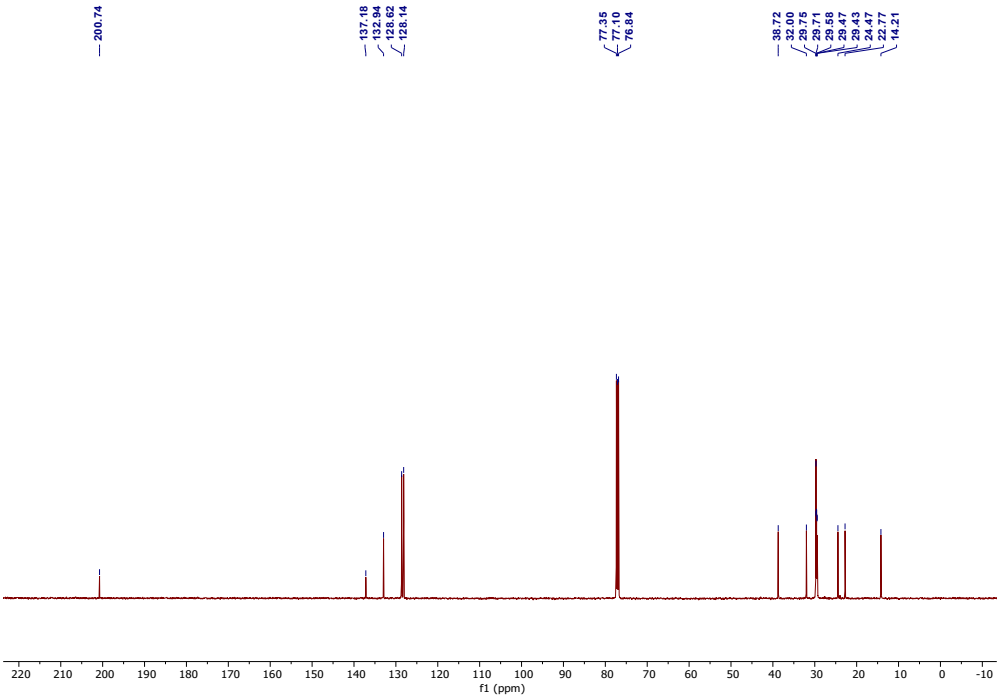
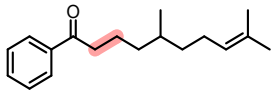


Figure S75. $^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P34**.



5,9-dimethyl-1-phenyldec-8-en-1-one (35):

Purified by column chromatography using silica gel and ethyl acetate-hexane as eluent 75% (96.9 mg) isolated yield; white solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.94 (d, $J_{H,H}$ = 7.6 Hz, 2H), 7.53 (t, $J_{H,H}$ = 7.4 Hz, 1H), 7.44 (t, $J_{H,H}$ = 7.6 Hz, 2H), 5.08 (t, $J_{H,H}$ = 7.4 Hz, 1H), 2.93 (t, $J_{H,H}$ = 7.4 Hz, 2H), 1.94 (dt, $J_{H,H}$ = 14.7, 6.8 Hz, 2H), 1.76 – 1.68 (m, 2H), 1.66 (s, 3H), 1.58 (s, 3H), 1.44 – 1.32 (m, 3H), 1.18 (m, 2H), 0.88 (d, $J_{H,H}$ = 6.2 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 200.7, 137.2, 132.9, 131.2, 128.6, 128.1, 125.0, 39.0, 37.0, 36.7, 32.4, 25.8, 25.6, 21.9, 19.5, 17.7.

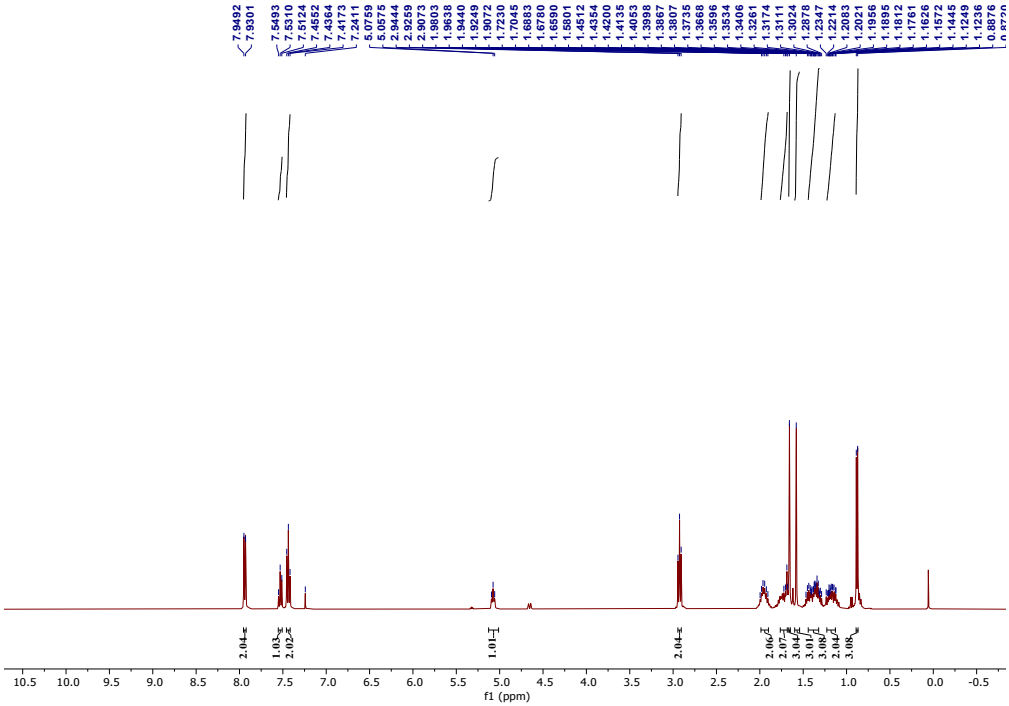


Figure S76. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P35**.

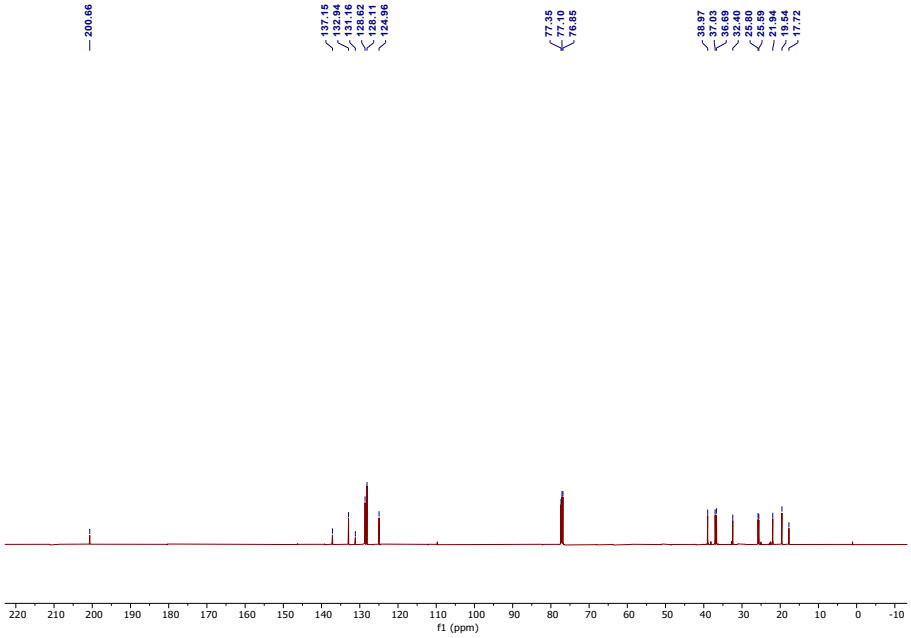
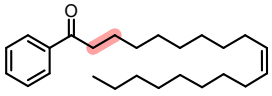


Figure S77. $^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P35**.

1-phenylnonadec-10-en-1-one (36): 

Purified by column chromatography using silica gel and ethyl acetate-hexane as eluent 76% (135.5 mg) isolated yield; white solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.93 (s, 2H), 7.53 (s, 1H), 7.43 (s, 2H), 5.34 (dt, $J_{H,H}$ = 14.6, 4.3 Hz, 2H), 2.94 (s, 2H), 1.95 (m, 4H), 1.72 (q, $J_{H,H}$ = 7.3 Hz, 4H), 1.24 (s, 23H), 0.86 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 200.7, 137.2, 132.9, 130.5, 130.4, 128.6, 128.1, 38.7, 32.7, 32.0, 29.8, 29.7, 29.6, 29.5, 29.3, 29.2, 27.3, 24.5, 22.8, 14.2.

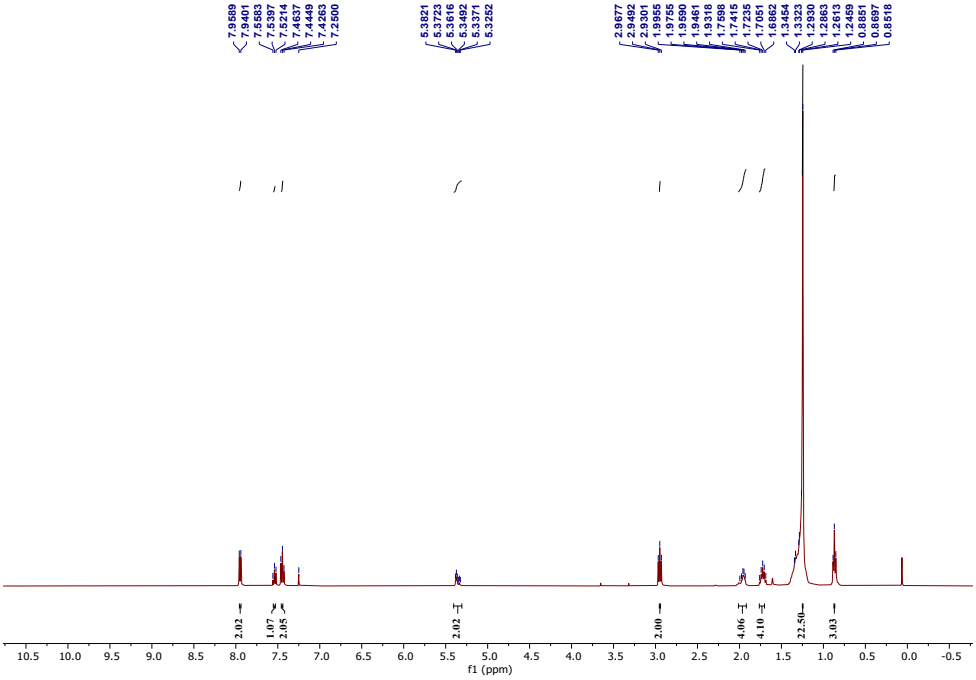


Figure S78. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P36**.

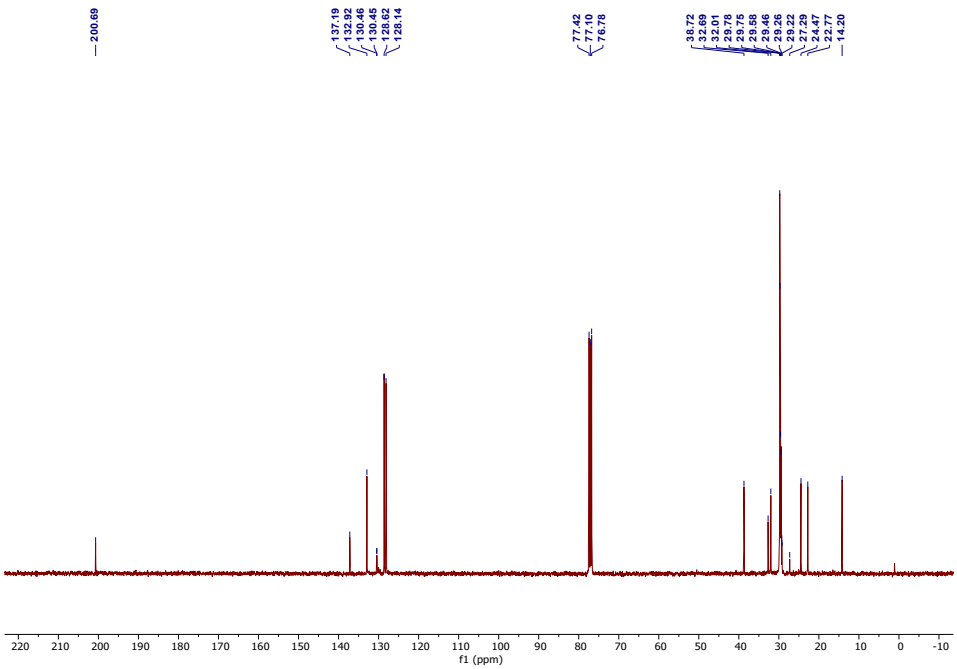
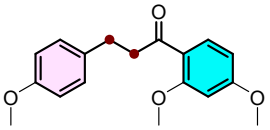


Figure S79. $^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P36**.



Synthesis P37

1-(2,4-dimethoxyphenyl)-3-(4-methoxyphenyl)propan-1-one (P37). 48.4 mg; 70% isolated yield; yellow solid: **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.80 (d, 1H), 7.15 (d, 2H), 6.82 (d, 2H), 6.53 – 6.50 (m, 1H), 6.44 (d, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.77 (s, 3H), 3.22 (t, 2H), 2.93 (t, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ =199.7, 164.5, 160.9, 157.9, 134.2, 132.9, 129.5, 121.2, 113.9, 105.2, 98.5, 55.6, 55.6, 55.5, 45.7, 29.9.

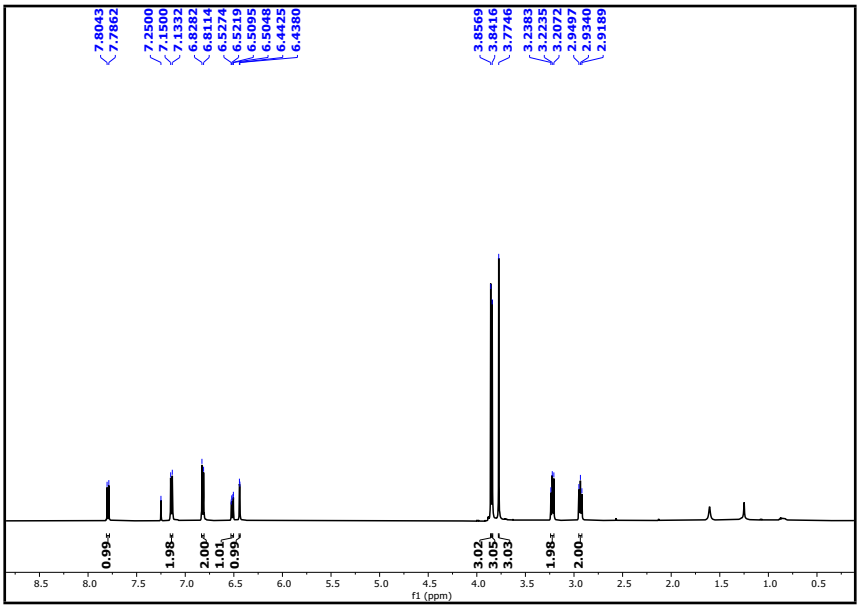


Figure S80. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P37**.

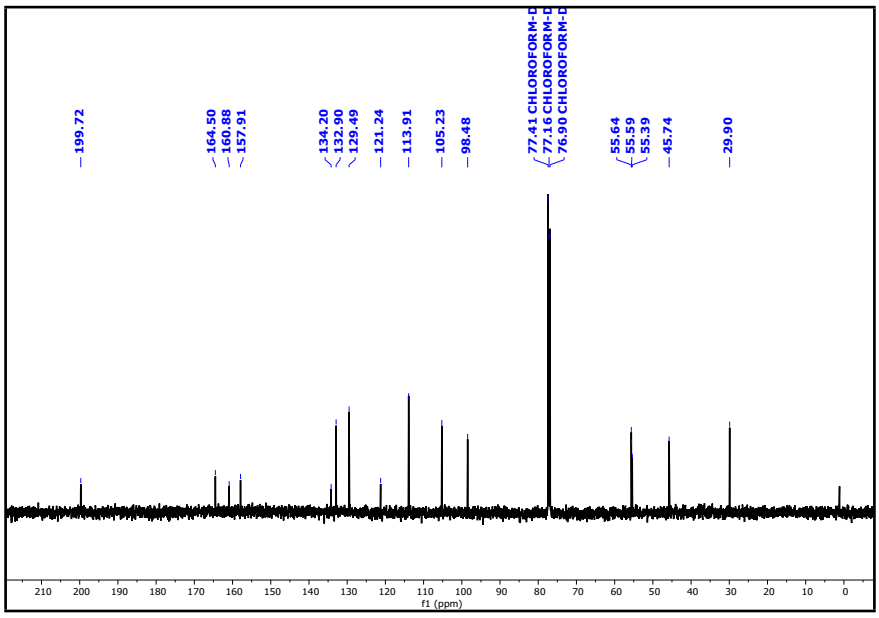
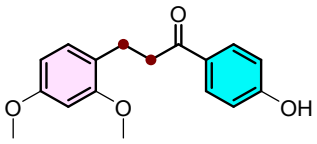


Figure S81. ^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of **P37**.



Synthesis P38

3-(2,4-dimethoxyphenyl)-1-(4-hydroxyphenyl)propan-1-one (P38). 48 mg; 73% isolated yield; yellow solid: **^{1}H NMR** (500 MHz, $CDCl_3$) : δ = 7.90 (d, 2H), 7.06 (d, 1H), 6.88 (d, 2H), 6.44 – 6.39 (m, 2H), 3.77 (s, 6H), 3.17 (t, 2H), 2.95 (t, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 200.1, 160.9, 159.5, 158.5, 131.0, 130.4, 122.0, 115.5, 104.0, 98.7, 55.5, 55.3, 39.0, 25.7.

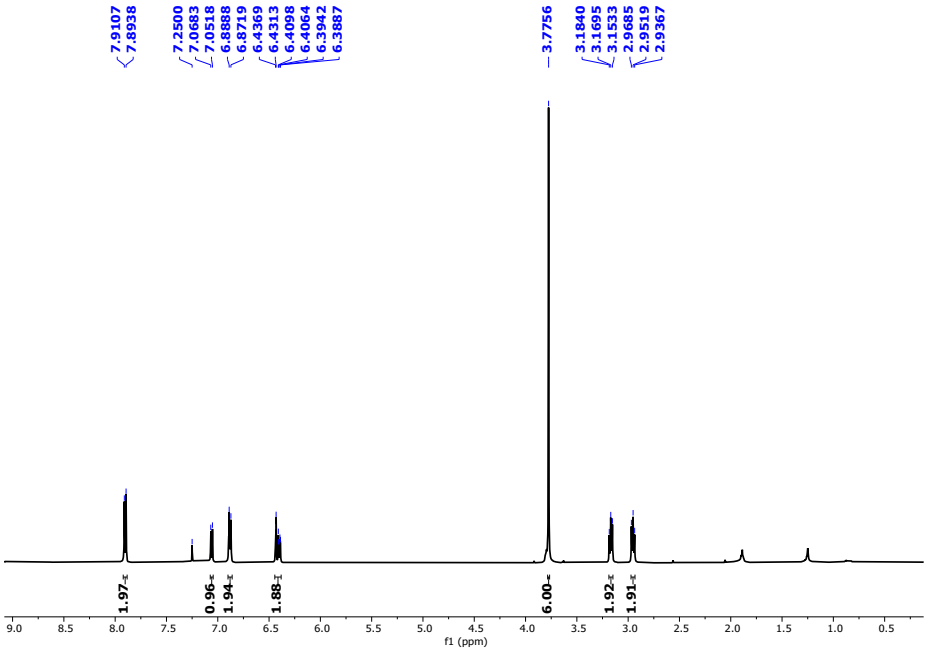


Figure S82. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P38**.

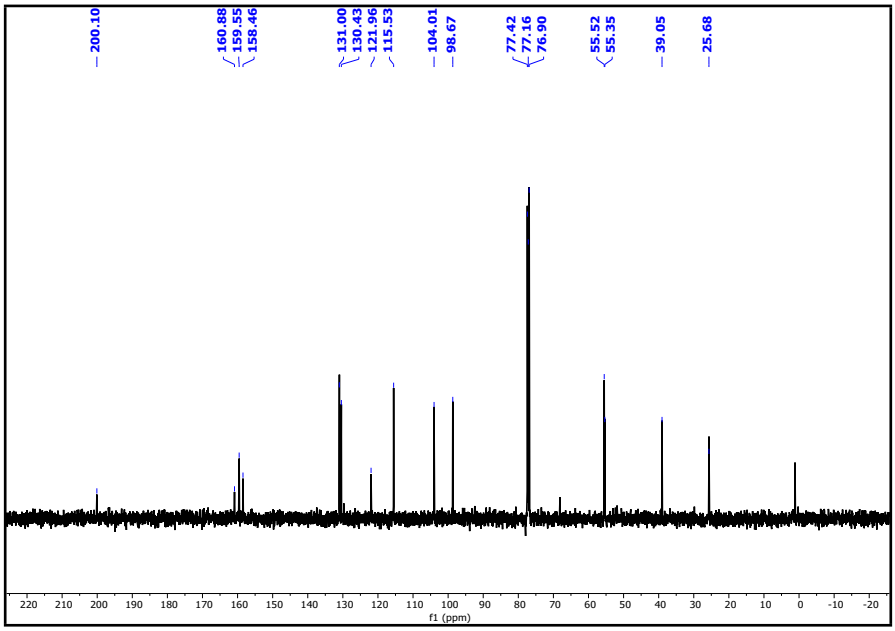
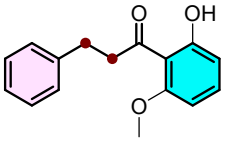


Figure S83. $^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P38**.



Synthesis P39

1-(2-hydroxy-6-methoxyphenyl)-3-phenylpropan-1-one (P39). 53.4 mg; 79% isolated yield; yellow oil: **^{1}H NMR** (500 MHz, $CDCl_3$)**:** δ = 13.20 (s, 1H), 7.35 – 7.23 (m, 6H), 6.58 (d, 1H), 6.38 (d, 1H), 3.87 (s, 3H), 3.38 (t, 2H), 3.01 (t, 2H).**$^{13}C\{^{1}H\}$ NMR** (125 MHz, $CDCl_3$): δ = 206.6, 164.8, 161.4, 141.7, 136.1, 128.6, 126.1, 111.3, 111.0, 101.3, 55.8, 46.6, 30.6.

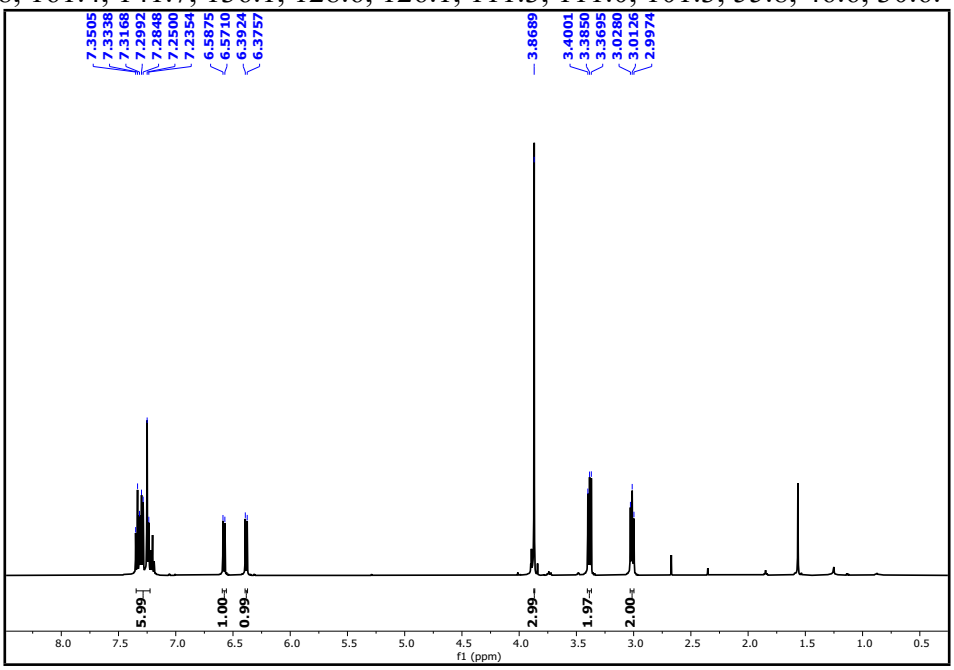


Figure S84. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P39**.

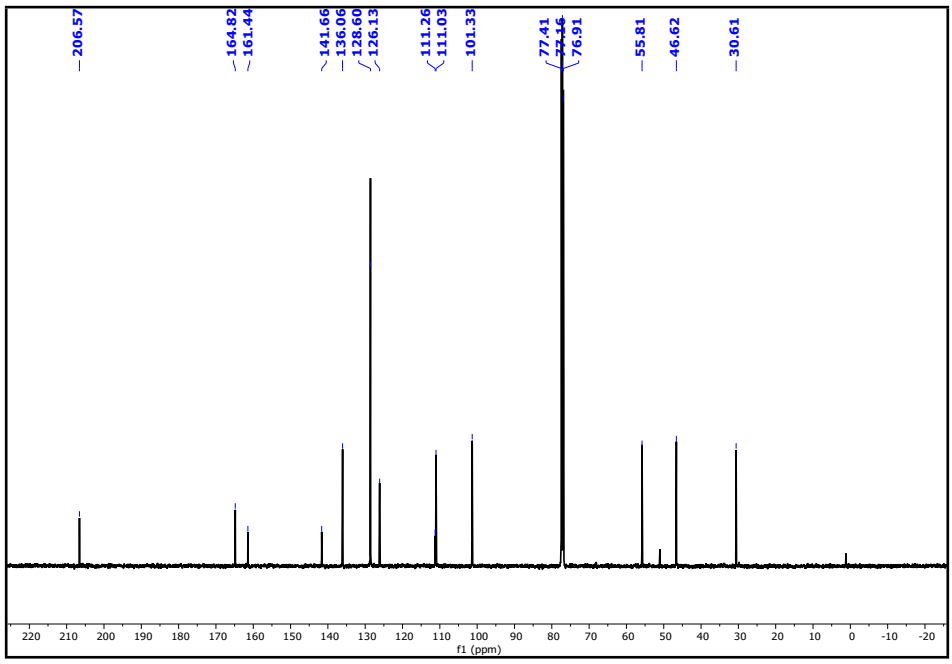
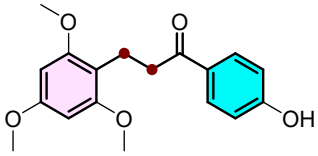


Figure S85. $^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P39**.



Synthesis P40

1-(4-hydroxyphenyl)-3-(2,4,6-trimethoxyphenyl)propan-1-one, 40. 55.0 mg; 79% isolated yield; yellow solid: **^{1}H NMR** (500 MHz, $CDCl_3$) : δ = 7.89 (d, 2H), 6.87 (d, 2H), 6.74 (s, 1H), 6.50 (s, 1H), 3.85 (s, 3H), 3.79 (s, 3H), 3.79 (s, 3H), 3.17 (t, 2H), 2.95 (t, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 199.6, 160.8, 151.7, 148.1, 142.9, 130.9, 129.8, 121.2, 115.5, 114.7, 97.9, 56.8, 56.4, 39.1, 25.8.

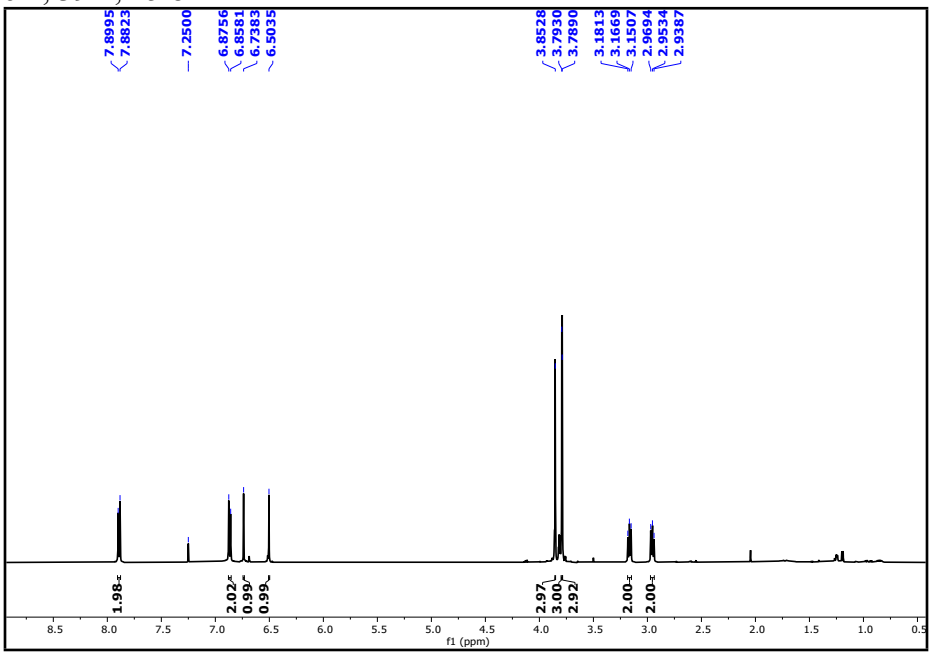


Figure S86. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **P40**.

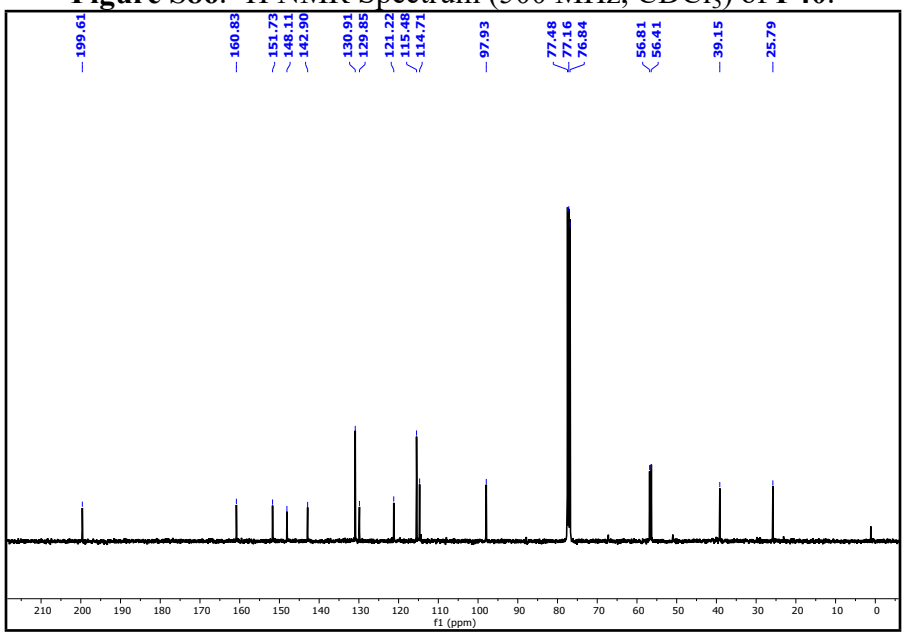


Figure S87. $^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **P40**.

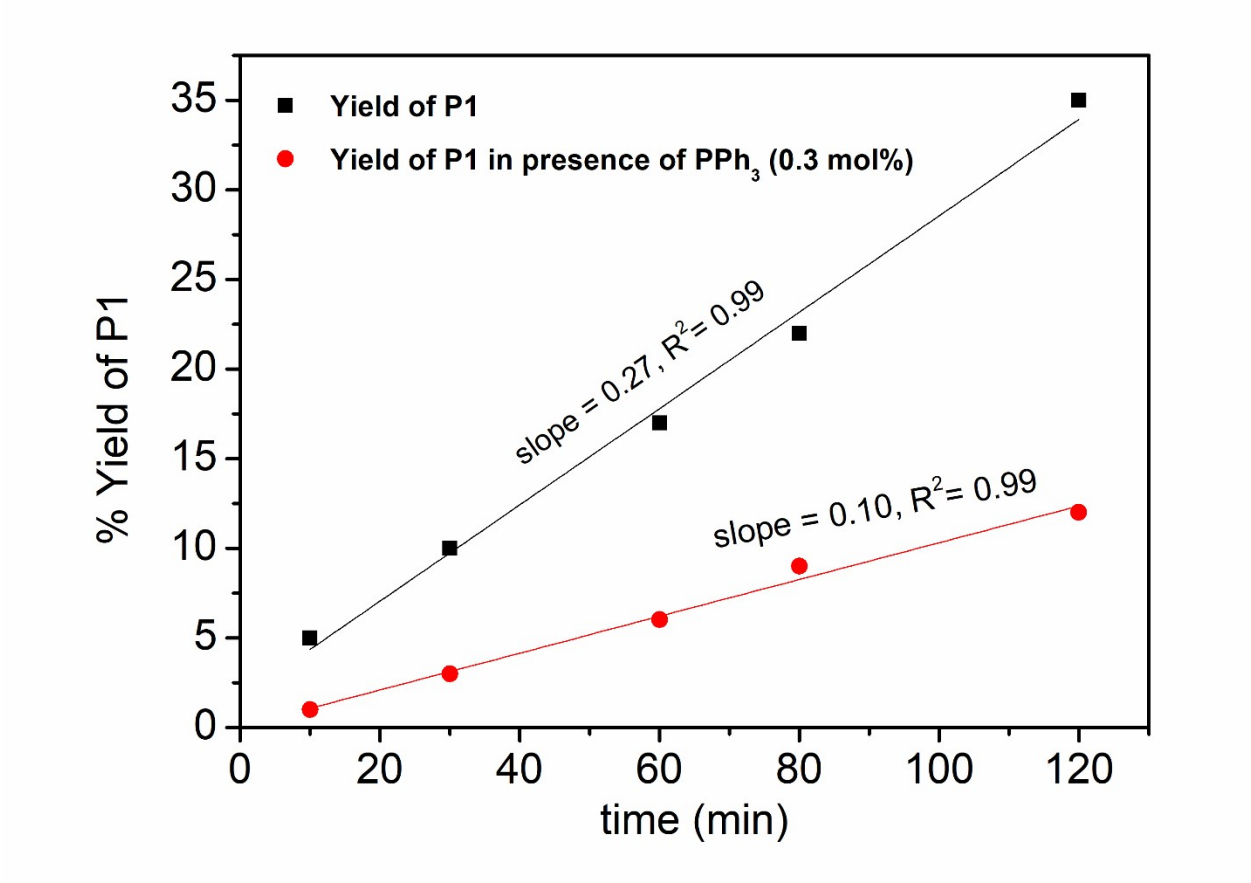


Figure S88. Determination of initial slopes for the product formation in the presence of excess PPh_3.

Experimental condition: Kinetic experiments were performed using a model α-alkylation reaction under catalytic conditions. In a typical experiment, complex **1** (0.1mol %) was dissolved in dry, degassed toluene under an inert atmosphere. The 4′-methoxyacetophenone 2 mmol) and phenylmethanol (2.2 mmol) were added, and the reaction mixture was heated at 120 °C. Apparent rate constants were determined by monitoring product formation as a function of time using ^{1}H NMR. To evaluate the effect of phosphine coordination, parallel experiments were conducted in the presence of added triphenylphosphine (PPh_3, 10 equiv. relative to Complex **1**). Initial rates were determined from the linear region of the product concentration versus time plots. In the absence of added PPh_3, a significantly higher apparent rate constant was observed. In contrast, the addition of excess PPh_3 resulted in a pronounced decrease in the apparent rate of product formation, indicating inhibition of the catalytic process. Experiments were repeated twice to ensure reproducibility.

---

e.

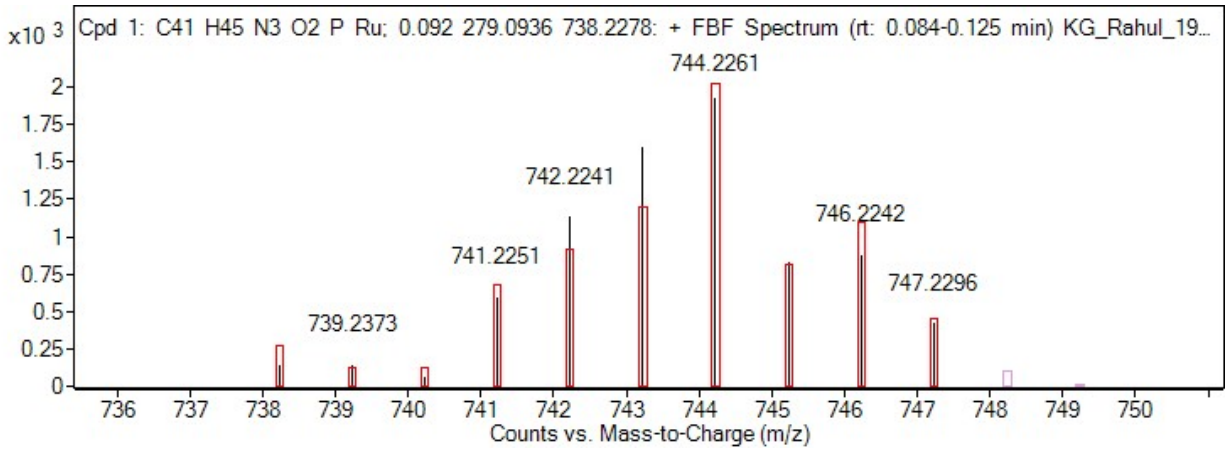


Figure S89.HRMS spectrum of Intermediate **C**

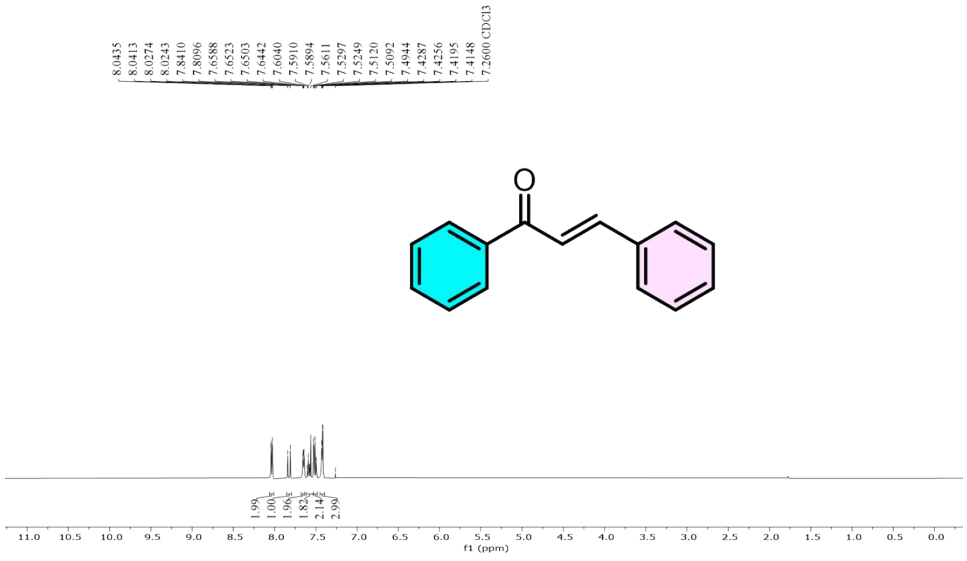


Figure S90. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$).

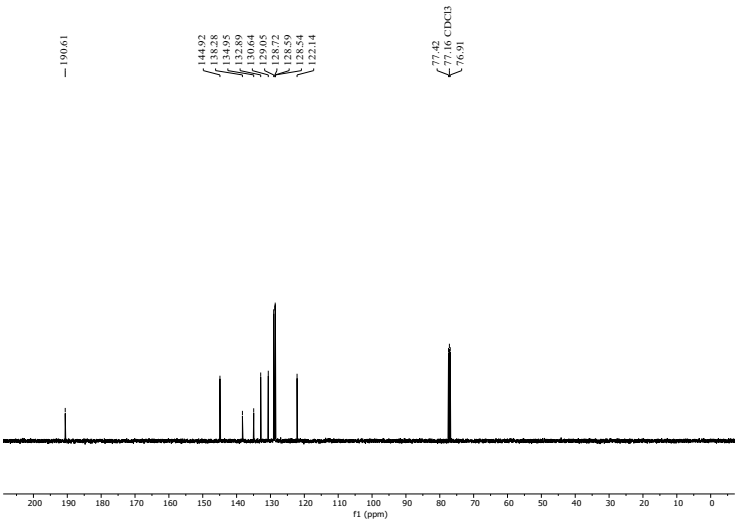
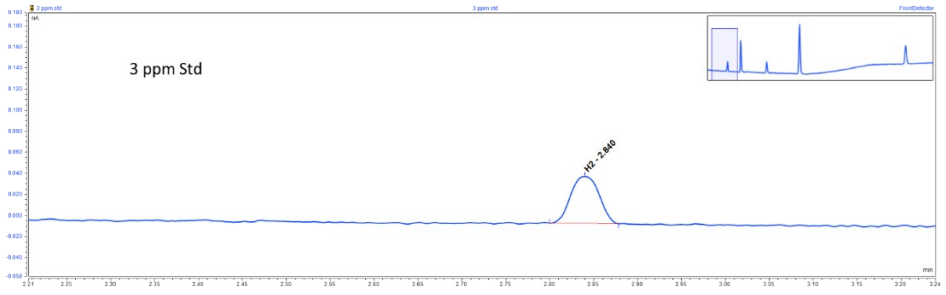
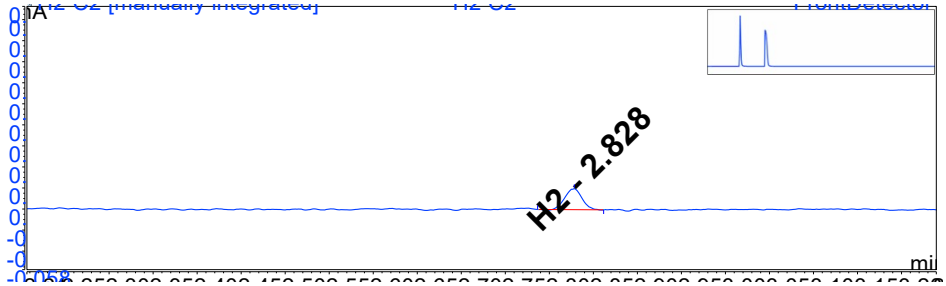


Figure S91. $^{13}C\{^{1}H\}$ NMR Spectrum (125 MHz, $CDCl_3$)



(a)

(b)



	A	B	C	D	E	F	G	H	I	J	K	L
1	Peak No.	Peak Name	Ret.Time min	Amount ppm	Rel.Area %	Area nA*min	Height nA	Type	Width (50%) min	Asym. EP	Resol. EP	Plates EP
2												
4	1	H2	2.828	0.8005	100.00	0.0004	0.02	BMB*	0.021	0.98	n.a.	99071
6	Maximum			0.8005	100.00	0.0004	0.02		0.021	0.98	0.00	99071
7	Minimum			0.8005	100.00	0.0004	0.02		0.021	0.98	0.00	99071
8	Sum			0.8005	100.00	0.0004	0.02					

(c)

Figure S92. GC–PDD chromatogram a) hydrogen standard (3 ppm) and; b) catalytic mixture from H tube (Scheme S1D); catalytic mixture from H tube (Scheme S1E).

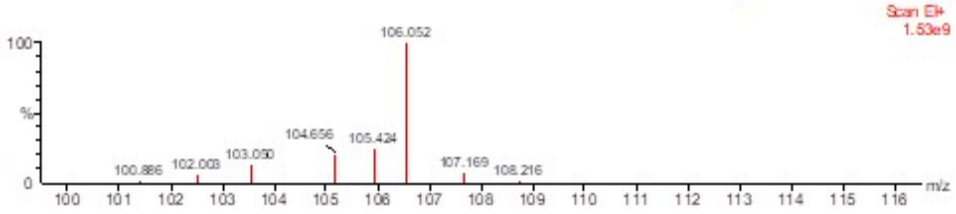
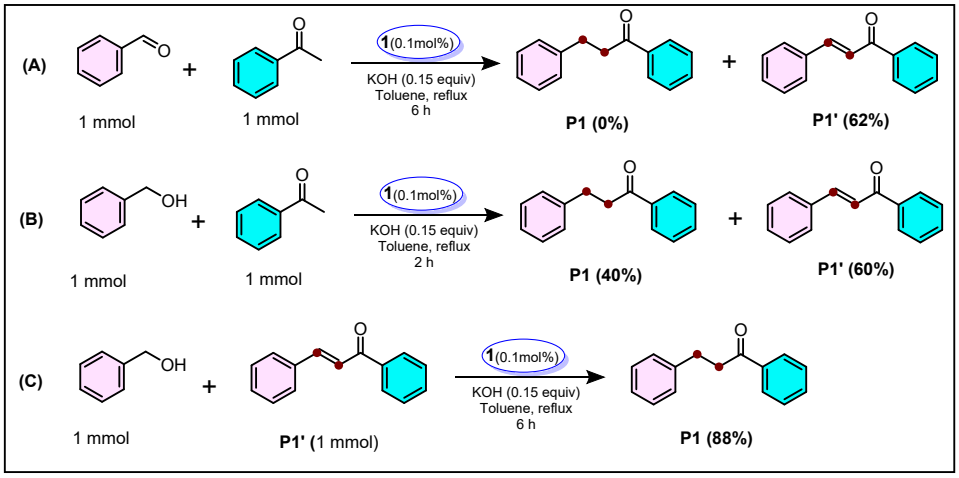
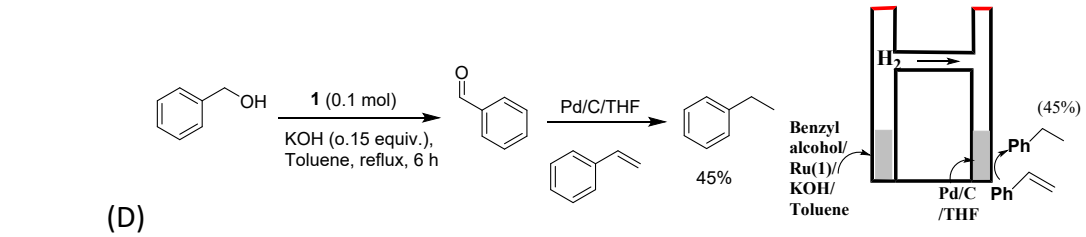
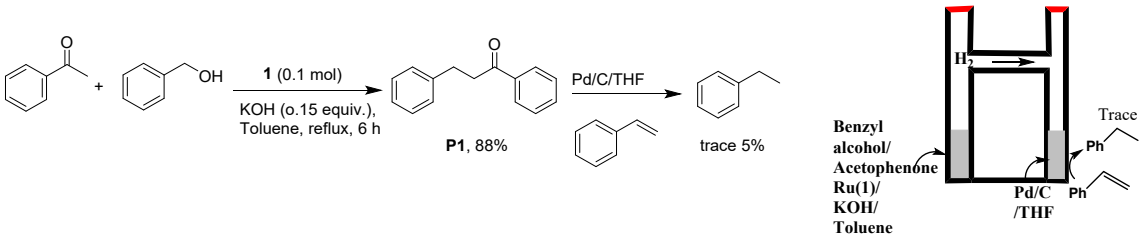


Figure S93. GC-MS spectra of styrene reduction.

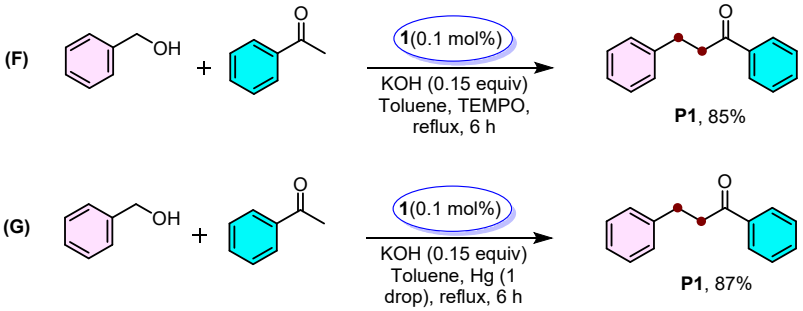




(D)



(E)



Scheme S1. Control experiments.

4. References

1. R. Freitag, T. J. Muller, J. Conradie, *J. Chem. Crystallogr.* 2014, **44** , 352.
2. N. Miyaura, A. Suzuki, *Chem. Rev.* 1995, **95**, 2457.
3. L. Krause, R. Herbst-Irmer, G.M. Sheldrick, D. J. Stalke, *Appl. Crystallogr*. 2015, **48**, 3.
4. G. Sheldrick, *Acta Cryst. C*, 2015, **71**, 3.
5. O. V. Dolomanov, L. J. Bourhis, R. 0J. Gildea, J.A.K. Howard, H. Puschmann, H., *J. Appl. Crystallogr*. 2009, **42**, 339.
6. S. Singh, R. Prasad, S. Upreti, N. Jha, A. Ramanan, *Acta. Crystallogr. Sect. E Struct.* 2006, **62**, 1014.

7. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision D.01*, Gaussian, Inc., Wallingford CT, 2009
8. R.D. Dennington, T.A. Keith, J. M. Millam, 2008 GaussView 5.0.8, Gaussian.