Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

The C_{sp}-C_{sp} Bond Cleavage and Fragments Coupling: Transition Metal-Free "Extrusion and Recombination" Approach towards Synthesis of 1,2-Diketones

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1. General Information

All starting materials were purchased from commercial suppliers (Sigma-Aldrich, Alfa-Aesar, SD fine chemicals, Merck, HI Media, Thermo Fisher Scientific) and were used without further purification unless otherwise indicated. All reactions were performed in a 10 mL reaction vial with magnetic stirring. Solvents used in extraction and purification were purchased from Merck, Thermo Fisher Scientific and used without further purification. Thin-layer chromatography (TLC) was performed on TLC plates purchased from Merck. Compounds were visualized with UV light (λ = 254 nm) and/or by immersion in $KMnO_4$ staining solution followed by heating. Products were purified by column chromatography on silica gel, 100 - 200 mesh. Melting points were determined in open capillary tubes on EZ-Melt automated melting point apparatus and are uncorrected. All the compounds were fully characterized by ^{1}H and ^{13}C NMR and further confirmed by EI-HRMS analysis. All HRMS are recorded in EI-QTOF method in acetonitrile solvent and GC-MS are recorded in the EI method in ethyl acetate solvent. ^{1}H (^{13}C) NMR spectra were recorded at 400 (100), 500 (125) and 600 (150) MHz on a Brucker spectrometer using $CDCl_3$ and DMSO-d_6 as a solvent. The ^{1}H and ^{13}C chemical shifts were referenced to residual solvent signals at $\delta_{H/C}$ 7.26/77.28 ($CDCl_3$) and $\delta_{H/C}$ 3.28/39.99 (DMSO-d_6) relative to TMS as internal standards. Coupling constants J [Hz] were directly taken from the spectra and are not averaged. Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), overlapped and br (broad).

2. Computational Methods

All theoretical calculations have been carried out using the Gaussian09 quantum chemical package.[1] Geometries of all structures and transition states involved in this study were optimized and characterized using hybrid exchange correlation functional, B3LYP[2] together with Pople's 6-31G(d,p)[3] basis set for all atoms in the solvent phase. Further single point energies were computed using the long-range dispersion corrected ωB97X-D[4] and M06-2X[5] with 6-31G(d,p) basis set for comparative studies. The solvent effect was characterized using a Conductor-like Polarizable Continuum Model (CPCM) using DMSO as solvent (ε=47.24).[6]

3. DFT calculations

Table S1. Solvent-phase Gibbs free energy of the reactants, corresponding transition state and product from DFT calculations at B3LYP/6-31G**

State	Gibbs free energy (in a.u)
Reactant (**1**)	-615.4687
A	-661.0493
B	-789.9308
C	-789.9565
D	-918.8135
TS-1	-1151.72

D_a	-917.6223
TS-2	-1150.521
E	-916.3817
F	-1533.826
3a	-534.0574
G	-344.8595
CO_2	-188.5891
4a	-689.8032
Product (**2a**)	-420.7434
I_2	-22.79689
OH^-	-75.86527
OH•	-75.73999
H_2O	-76.42141
^{t}BuO•	-232.925
^{t}BuOH	-233.5826
^{t}BuOOH	-308.7094

XYZ coordinates

1							
C	1.902668000	-0.000005000	-0.000006000	H	-5.974353000	1.522006000	1.521758000
C	-0.680462000	-0.000025000	-0.000004000	H	-7.219470000	0.000020000	-0.000005000
C	0.680462000	-0.000011000	-0.000007000	C	3.326327000	0.000000000	-0.000002000
C	-1.902668000	-0.000018000	-0.000004000	C	4.041468000	-0.860407000	0.860290000
C	-3.326327000	-0.000004000	-0.000002000	C	4.041470000	0.860410000	-0.860281000
C	-4.041475000	-0.860413000	-0.860284000	C	5.433904000	-0.856030000	0.855923000
C	-4.041463000	0.860413000	0.860278000	C	5.433912000	0.856040000	-0.855903000
C	-5.433913000	-0.856031000	-0.855913000	C	6.133758000	0.000008000	0.000011000
C	-5.433903000	0.856048000	0.855904000	H	3.495309000	-1.523560000	1.523346000
C	-6.133758000	0.000014000	-0.000004000	H	3.495321000	1.523564000	-1.523344000
H	-3.495323000	-1.523574000	-1.523339000	H	5.974363000	-1.521977000	1.521780000
H	-3.495307000	1.523567000	1.523335000	H	5.974362000	1.521994000	-1.521758000
H	-5.974372000	-1.521981000	-1.521766000	H	7.219470000	0.000005000	0.000021000
A							
C	0.289099000	-0.613478000	0.000135000	C	-0.687702000	1.779412000	0.000009000

C	0.687705000	-1.779403000	0.000055000	I	-3.357106000	0.063242000	0.000005000
I	3.357106000	-0.063243000	-0.000004000	C	-1.059269000	3.146270000	0.000047000
C	1.059268000	-3.146262000	0.000016000	C	-1.237697000	3.832207000	-1.221908000
C	1.237695000	-3.832200000	1.221970000	C	-1.237585000	3.832238000	1.221983000
C	1.237581000	-3.832231000	-1.221921000	H	-1.100857000	3.301032000	-2.157640000
H	1.100858000	-3.301025000	2.157702000	H	-1.100663000	3.301102000	2.157726000
H	1.100659000	-3.301094000	-2.157663000	C	-1.586288000	5.178375000	-1.213598000
C	1.586281000	-5.178370000	1.213660000	C	-1.586175000	5.178410000	1.213651000
C	1.586165000	-5.178404000	-1.213589000	H	-1.722666000	5.704279000	-2.153044000
H	1.722659000	-5.704275000	2.153106000	H	-1.722466000	5.704343000	2.153093000
H	1.722454000	-5.704337000	-2.153032000	C	-1.761642000	5.852088000	0.000026000
C	1.761631000	-5.852083000	0.000035000	H	-2.035416000	6.902590000	0.000027000
H	2.035401000	-6.902586000	0.000034000	I	6.133258000	0.916632000	-0.000038000
C	-0.289092000	0.613488000	-0.000071000	I	-6.133254000	-0.916638000	-0.000026000
B							
C	0.035715000	-0.431576000	-0.652572000	C	-0.040751000	-0.066920000	0.722461000
C	0.970843000	-0.046312000	-1.561003000	C	-0.991748000	0.648593000	1.387342000
I	-1.336292000	-2.046187000	-1.302008000	I	1.485736000	-1.085015000	2.026654000
C	2.020011000	0.971636000	-1.300800000	C	-2.139774000	1.347320000	0.749288000
C	1.756869000	2.176647000	-0.628293000	C	-3.282767000	1.594610000	1.535846000
C	3.323384000	0.725961000	-1.773966000	C	-2.138617000	1.786554000	-0.586284000
H	0.757198000	2.390152000	-0.271135000	H	-3.299358000	1.266538000	2.567830000
H	3.550973000	-0.209844000	-2.275739000	H	-1.273828000	1.619327000	-1.213634000
C	2.773414000	3.110227000	-0.434935000	C	-4.389602000	2.247002000	0.997431000
C	4.337878000	1.660366000	-1.570923000	C	-3.245800000	2.446993000	-1.117082000
H	2.553129000	4.042174000	0.076543000	H	-5.263071000	2.419788000	1.619006000
H	5.340070000	1.451018000	-1.931862000	H	-3.220072000	2.784142000	-2.148857000
C	4.065552000	2.855899000	-0.902731000	C	-4.376666000	2.677641000	-0.331319000
H	4.854348000	3.585791000	-0.748328000	H	-5.238235000	3.189471000	-0.749469000
O	1.024477000	-0.659067000	-2.767216000	O	-1.024630000	0.793859000	2.729331000
H	1.583259000	-0.141591000	-3.366256000	H	-0.331398000	0.250578000	3.143961000
C							
C	-0.195809000	-0.101365000	0.743348000	C	1.723753000	-0.044616000	-0.960961000
C	-1.723848000	-0.044371000	0.961019000	I	-0.698184000	-1.757781000	-1.900979000
I	0.697834000	-1.757961000	1.901036000	C	2.408128000	1.247475000	-0.647041000
C	-2.407910000	1.247851000	0.646925000	C	3.778084000	1.186076000	-0.332020000
C	-1.770422000	2.499707000	0.690370000	C	1.770731000	2.499413000	-0.689432000

C	-3.777617000	1.186682000	0.330840000	H	4.265268000	0.217541000	-0.309010000
H	-0.725502000	2.586781000	0.966826000	H	0.725611000	2.586745000	-0.965042000
H	-4.264869000	0.218196000	0.307062000	C	4.488412000	2.347367000	-0.046170000
C	-2.489351000	3.663678000	0.417082000	C	2.489955000	3.663203000	-0.416132000
C	-4.487630000	2.348164000	0.044942000	H	5.542198000	2.287936000	0.207535000
H	-1.990958000	4.626510000	0.466126000	H	1.991576000	4.626085000	-0.464318000
H	-5.541222000	2.288939000	-0.209613000	C	3.845152000	3.588999000	-0.087832000
C	-3.844302000	3.589722000	0.087696000	H	4.400403000	4.495923000	0.131361000
H	-4.399311000	4.496796000	-0.131485000	O	2.355679000	-1.018869000	-1.325078000
O	-2.356019000	-1.018431000	1.325197000	H	-0.276025000	0.770788000	-1.199110000
C	0.195698000	-0.101350000	-0.743238000	H	0.275981000	0.770696000	1.199302000

D

C	-4.857449000	0.985514000	0.334867000	C	2.814514000	1.449930000	0.866018000
C	-4.388222000	-0.292076000	0.647690000	C	4.388056000	-0.291792000	-0.648120000
C	-4.067016000	1.858406000	-0.422293000	H	2.769838000	-1.691169000	-0.472696000
H	-5.837615000	1.302255000	0.678922000	C	4.066978000	1.858237000	0.422813000
C	-3.131027000	-0.705564000	0.207000000	H	2.190597000	2.110964000	1.457378000
H	-5.002021000	-0.968993000	1.233623000	C	4.857306000	0.985678000	-0.334838000
C	-2.814472000	1.450309000	-0.865467000	H	5.001774000	-0.968450000	-1.234438000
H	-4.431389000	2.851947000	-0.664493000	H	4.431370000	2.851685000	0.665368000
C	-2.330078000	0.165289000	-0.553007000	H	5.837411000	1.302583000	-0.678920000
H	-2.769947000	-1.691348000	0.471941000	O	0.669962000	-1.821539000	-1.691294000
H	-2.190473000	2.111602000	-1.456451000	O	-0.669937000	-1.822210000	1.690791000
C	-1.001195000	-0.218435000	-1.083618000	C	-0.314722000	-1.551340000	-0.725107000
O	-0.375877000	0.520145000	-1.846376000	C	0.314755000	-1.551660000	0.724708000
C	1.001307000	-0.218943000	1.083763000	H	0.825018000	-0.966322000	-2.136882000
C	2.330097000	0.165030000	0.553101000	H	-0.824922000	-0.967173000	2.136747000
O	0.376069000	0.519336000	1.846877000	H	-1.041013000	-2.370823000	-0.716831000
C	3.130940000	-0.705488000	-0.207402000	H	1.040997000	-2.371182000	0.716085000

TS-1

C	5.394283000	-1.177643000	-0.651016000	H	-0.886141000	5.104843000	-1.499209000
C	4.368585000	-2.069768000	-0.330581000	H	-2.588822000	5.250765000	0.307213000
C	5.239614000	0.190664000	-0.399439000	O	-0.289018000	0.157593000	2.277653000
H	6.314288000	-1.546545000	-1.094716000	O	0.300730000	-1.728095000	-0.744781000
C	3.183465000	-1.602260000	0.236609000	C	0.504105000	-0.482775000	1.318088000
H	4.491178000	-3.131302000	-0.521059000	C	-0.245396000	-0.667974000	-0.045358000
C	4.063618000	0.660491000	0.173620000	H	0.076406000	1.060941000	2.344083000

H	6.036576000	0.884227000	-0.648922000	H	0.433043000	-1.391717000	-1.657978000
C	3.019264000	-0.229422000	0.492281000	H	0.731766000	-1.498798000	1.657225000
H	2.393632000	-2.304042000	0.470468000	H	-1.376002000	-0.961129000	0.315554000
H	3.929616000	1.716322000	0.381708000	O	-2.621235000	-1.325135000	0.741900000
C	1.808767000	0.333165000	1.133418000	C	-3.220238000	-2.297152000	-0.092108000
O	1.776249000	1.492145000	1.545418000	C	-3.273785000	-1.813880000	-1.552359000
C	-0.363923000	0.544516000	-0.979259000	H	-3.762242000	-0.836600000	-1.610638000
C	-0.983108000	1.824327000	-0.569487000	H	-2.264712000	-1.724085000	-1.966203000
O	0.093269000	0.386727000	-2.114677000	H	-3.830487000	-2.519591000	-2.177030000
C	-1.949186000	1.909884000	0.448728000	C	-4.656418000	-2.411557000	0.478029000
C	-0.617064000	2.983650000	-1.280026000	H	-5.178979000	-1.454329000	0.400752000
C	-2.526424000	3.143140000	0.752874000	H	-4.629069000	-2.715505000	1.527970000
H	-2.265982000	1.017219000	0.972477000	H	-5.211108000	-3.164339000	-0.091231000
C	-1.184017000	4.211816000	-0.958601000	H	-2.476855000	-3.972758000	1.075275000
H	0.119507000	2.902932000	-2.072180000	C	-2.489627000	-3.645383000	0.030887000
C	-2.141282000	4.292735000	0.059554000	H	-2.984583000	-4.417178000	-0.567886000
H	-3.281406000	3.205116000	1.530552000	H	-1.456985000	-3.549751000	-0.315446000
D_a							
C	4.935643000	-1.358475000	-0.853893000	C	-3.308080000	-0.861598000	0.661646000
C	3.970547000	-1.910953000	-0.008417000	C	-3.541058000	0.472516000	-1.359031000
C	4.853808000	-0.013010000	-1.230873000	C	-4.680456000	-1.105107000	0.651433000
H	5.752245000	-1.974374000	-1.218649000	H	-2.692332000	-1.287471000	1.445559000
C	2.920022000	-1.125123000	0.463612000	C	-4.908828000	0.224254000	-1.365844000
H	4.036415000	-2.953704000	0.285354000	H	-3.079289000	1.084054000	-2.126943000
C	3.810188000	0.776206000	-0.760964000	C	-5.479512000	-0.565269000	-0.359882000
H	5.604039000	0.414997000	-1.888346000	H	-5.126179000	-1.715713000	1.430156000
C	2.830971000	0.226992000	0.088186000	H	-5.533308000	0.642839000	-2.148861000
H	2.174709000	-1.569909000	1.112586000	H	-6.548175000	-0.757958000	-0.365129000
H	3.731977000	1.820940000	-1.041207000	O	-0.232486000	1.657638000	1.816392000
C	1.753777000	1.117536000	0.569602000	O	-0.248285000	-1.618958000	0.750067000
O	1.754846000	2.327834000	0.365688000	C	0.567641000	0.578696000	1.412143000
C	-1.286892000	0.239847000	-0.364503000	C	-0.322646000	-0.411420000	0.643414000
C	-2.729490000	-0.070425000	-0.346096000	H	0.161330000	2.433671000	1.366010000
O	-0.744371000	0.950382000	-1.203962000	H	0.967123000	0.039442000	2.280793000
TS-2							
C	-1.893649000	3.359291000	-1.401515000	H	-4.766818000	-1.320421000	1.944604000
C	-0.932084000	2.458933000	-1.865155000	H	-4.820613000	-1.775353000	-2.336448000

C	-2.056997000	3.568389000	-0.027119000	H	-6.030999000	-1.608538000	-0.172504000
H	-2.513704000	3.901658000	-2.108981000	O	1.960035000	-0.444231000	2.277799000
C	-0.139544000	1.748561000	-0.963325000	O	0.089531000	-2.209497000	1.728649000
H	-0.795258000	2.310757000	-2.931658000	C	1.155479000	-0.125693000	1.209719000
C	-1.258291000	2.879144000	0.878304000	C	0.151436000	-1.266185000	0.964077000
H	-2.803154000	4.269641000	0.332981000	H	1.926719000	0.341418000	2.864994000
C	-0.303735000	1.951524000	0.418251000	H	1.838597000	-0.014204000	0.194807000
H	0.616757000	1.067315000	-1.334460000	O	2.724317000	0.290290000	-0.790625000
H	-1.366472000	3.037228000	1.945909000	C	3.877695000	-0.523642000	-0.773774000
C	0.533455000	1.272960000	1.430618000	C	3.503901000	-2.010664000	-0.641512000
O	0.780817000	1.786947000	2.519428000	H	3.103945000	-2.217885000	0.356222000
C	-0.681713000	-1.334849000	-0.325174000	H	2.744692000	-2.276940000	-1.381454000
C	-2.155215000	-1.421584000	-0.240936000	H	4.383430000	-2.644857000	-0.789185000
O	-0.051198000	-1.419658000	-1.372694000	C	4.841199000	-0.077857000	0.339048000
C	-2.844609000	-1.325767000	0.980681000	H	4.363848000	-0.189180000	1.316239000
C	-2.877481000	-1.582189000	-1.437417000	H	5.116417000	0.972728000	0.203849000
C	-4.236537000	-1.393273000	1.000482000	H	5.755648000	-0.679907000	0.329972000
H	-2.301005000	-1.207063000	1.911238000	H	4.723317000	0.802559000	-2.297877000
C	-4.265796000	-1.650334000	-1.411892000	C	4.505576000	-0.260908000	-2.168999000
H	-2.331075000	-1.650608000	-2.371980000	H	5.440759000	-0.824243000	-2.247279000
C	-4.946560000	-1.556040000	-0.192056000	H	3.827767000	-0.583815000	-2.963263000

E							
C	0.000000000	6.083616000	-0.108570000	C	0.000000000	-0.815568000	0.830100000
C	0.000000000	5.343907000	1.074953000	C	0.000000000	-1.782541000	-0.394999000
C	0.000000000	5.420912000	-1.340464000	O	0.000000000	-1.258586000	1.954109000
H	0.000000000	7.169074000	-0.073267000	C	0.000000000	-3.269475000	-0.192277000
C	0.000000000	3.949045000	1.041631000	O	0.000000000	-1.313156000	-1.518640000
H	0.000000000	5.852709000	2.034072000	C	0.000000000	-3.949045000	1.041631000
C	0.000000000	4.031936000	-1.379887000	C	0.000000000	-4.031936000	-1.379887000
H	0.000000000	5.988050000	-2.266256000	C	0.000000000	-5.343907000	1.074953000
C	0.000000000	3.269475000	-0.192277000	H	0.000000000	-3.396696000	1.968482000
H	0.000000000	3.396696000	1.968482000	C	0.000000000	-5.420912000	-1.340464000
H	0.000000000	3.509783000	-2.329701000	H	0.000000000	-3.509783000	-2.329701000
C	0.000000000	1.782541000	-0.394999000	C	0.000000000	-6.083616000	-0.108570000
C	0.000000000	0.815568000	0.830100000	H	0.000000000	-5.852709000	2.034072000
O	0.000000000	1.313156000	-1.518640000	H	0.000000000	-5.988050000	-2.266256000
O	0.000000000	1.258586000	1.954109000	H	0.000000000	-7.169074000	-0.073267000

F

C	5.701146000	-1.650456000	-1.056214000	O	-0.384915000	-2.268759000	-0.679908000
C	5.110970000	-1.389858000	0.182814000	O	-1.595315000	-0.877265000	0.744108000
C	4.974692000	-1.446393000	-2.234352000	O	1.090507000	-1.241794000	1.248531000
H	6.725128000	-2.009106000	-1.105206000	C	-4.805555000	-2.612789000	0.572365000
C	3.792354000	-0.941394000	0.256220000	H	-5.409602000	-1.720763000	0.383762000
H	5.678815000	-1.536781000	1.096509000	H	-4.630129000	-3.127473000	-0.376588000
C	3.665203000	-0.982262000	-2.168637000	H	-5.370899000	-3.280548000	1.228308000
H	5.431209000	-1.646721000	-3.198815000	C	-3.713028000	-1.473187000	2.550566000
C	3.054681000	-0.734928000	-0.923669000	H	-2.765194000	-1.160148000	2.995382000
H	3.338696000	-0.735261000	1.215309000	H	-4.323566000	-0.584192000	2.365749000
H	3.092905000	-0.810590000	-3.073987000	H	-4.235584000	-2.107604000	3.272977000
C	1.661932000	-0.213036000	-0.956695000	O	-2.897430000	-1.353373000	0.250631000
O	1.220959000	0.348079000	-1.951203000	H	1.049042000	-2.140276000	0.881793000
C	-1.306232000	-0.278101000	-1.625271000	C	1.581110000	2.199150000	2.371168000
C	-1.867291000	1.094790000	-1.649417000	C	0.539785000	3.317257000	2.261327000
O	-1.355980000	-1.003080000	-2.616231000	H	0.772133000	3.975183000	1.418783000
C	-2.191228000	1.831035000	-0.496926000	H	-0.462566000	2.906827000	2.118077000
C	-2.123061000	1.654136000	-2.915921000	H	0.534570000	3.915817000	3.177274000
C	-2.753179000	3.102003000	-0.616452000	C	2.997989000	2.773545000	2.505550000
H	-2.019425000	1.405583000	0.481449000	H	3.742119000	1.973097000	2.541717000
C	-2.671695000	2.927191000	-3.029292000	H	3.232126000	3.435143000	1.666775000
H	-1.877236000	1.077253000	-3.800626000	H	3.066197000	3.351646000	3.431253000
C	-2.989538000	3.654528000	-1.877168000	C	1.261708000	1.226997000	3.508746000
H	-3.008897000	3.660642000	0.278697000	H	0.281300000	0.768772000	3.363683000
H	-2.854064000	3.352897000	-4.011263000	H	2.010702000	0.432392000	3.559271000
H	-3.422118000	4.647015000	-1.963228000	H	1.256076000	1.762404000	4.463137000
O	0.380416000	0.879477000	0.788296000	O	1.686951000	1.495510000	1.101844000

3a

C	2.115583000	-0.383835000	0.090997000	C	-3.126284000	-0.439721000	-0.095388000
C	0.999786000	0.680759000	0.043690000	H	-0.048530000	-1.874241000	-0.249853000
O	2.063885000	-1.395293000	0.759933000	H	-1.092982000	2.268928000	0.256294000
O	1.341144000	1.854276000	0.079677000	H	-2.444403000	-2.468871000	-0.356002000
C	-0.414643000	0.242865000	0.013738000	H	-3.509319000	1.668660000	0.172268000
C	-0.799095000	-1.098631000	-0.162153000	H	-4.178385000	-0.705700000	-0.136206000
C	-1.404021000	1.237828000	0.127728000	O	3.170064000	-0.011541000	-0.642046000
C	-2.151408000	-1.432869000	-0.218073000	H	3.858076000	-0.693648000	-0.539916000
C	-2.750786000	0.897827000	0.078280000				

G

C	2.012230000	-0.517366000	0.000010000
O	2.930421000	0.253564000	0.000006000
C	0.564895000	-0.232885000	-0.000041000
C	-0.338278000	-1.305509000	0.000021000
C	0.092555000	1.093331000	-0.000005000
C	-1.709620000	-1.056739000	-0.000012000
C	-1.277089000	1.334662000	0.000015000
C	-2.175961000	0.260596000	-0.000013000
H	0.044871000	-2.321098000	0.000023000
H	0.805917000	1.911193000	-0.000008000
H	-2.412617000	-1.883417000	0.000004000
H	-1.649516000	2.354344000	0.000014000
H	-3.244415000	0.453930000	0.000064000

4a

C	-1.727003000	-0.118506000	-0.029027000
O	-2.330294000	-1.142527000	-0.285192000
C	-0.235824000	-0.023570000	-0.009820000
C	0.449686000	1.194505000	-0.136851000
C	0.492313000	-1.216897000	0.110464000
C	1.844330000	1.217339000	-0.126204000
C	1.884471000	-1.190322000	0.130962000
C	2.562272000	0.027332000	0.014024000
H	-0.087668000	2.128199000	-0.279834000
H	-0.048867000	-2.153024000	0.194339000
H	2.368033000	2.161997000	-0.233077000
H	2.441744000	-2.116008000	0.236297000
H	3.647837000	0.047962000	0.026687000
O	-2.431094000	1.002798000	0.255006000
H	-1.851447000	1.709422000	0.575788000

2a

C	0.565738000	-0.522459000	0.782653000
C	-0.565734000	0.522516000	0.782622000
O	0.339189000	-1.592088000	1.339430000
O	-0.339229000	1.592125000	1.339455000
C	1.886674000	-0.171663000	0.207823000
C	2.111789000	1.032191000	-0.482213000
C	2.930306000	-1.106645000	0.330201000
C	3.363755000	1.293243000	-1.037217000
C	4.178606000	-0.840520000	-0.221609000
C	4.396249000	0.360743000	-0.906874000
C	-1.886668000	0.171683000	0.207810000
C	-2.111761000	-1.032182000	-0.482213000
C	-2.930321000	1.106640000	0.330193000

C	-3.363726000	-1.293267000	-1.037206000
C	-4.178620000	0.840482000	-0.221605000
C	-4.396241000	-0.360790000	-0.906860000
H	1.317466000	1.763034000	-0.580039000
H	2.738943000	-2.033577000	0.860365000
H	3.534542000	2.223475000	-1.569874000
H	4.982031000	-1.563931000	-0.122867000
H	5.370462000	0.568074000	-1.339662000
H	-1.317422000	-1.763008000	-0.580039000
H	-2.738975000	2.033581000	0.860349000
H	-3.534496000	-2.223507000	-1.569855000
H	-4.982061000	1.563875000	-0.122860000
H	-5.370452000	-0.568147000	-1.339638000

I_2

I	0.000000000	0.000000000	1.433073000
I	0.000000000	0.000000000	-1.433073000

OH^-

O	0.000000000	0.000000000	0.108510000
H	0.000000000	0.000000000	-0.868077000

OH radical

O	0.000000000	0.000000000	0.108882000

H_2O

O	0.000000000	0.000000000	0.119856000

H	0.000000000	0.000000000	-0.871059000

H	0.000000000	0.757281000	-0.479425000
H	0.000000000	-0.757281000	-0.479425000

^{t}BuO radical

C	-0.067555000	0.055418000	0.000000000
C	-0.515232000	-0.680356000	1.277926000
H	-0.182368000	-0.135862000	2.166132000
H	-1.606928000	-0.754534000	1.306065000
H	-0.103639000	-1.693926000	1.311334000
C	1.488389000	0.224767000	0.000000000
H	1.815187000	0.764682000	-0.891331000
H	1.815187000	0.764682000	0.891331000
H	1.935132000	-0.773906000	0.000000000
C	-0.515232000	-0.680356000	-1.277926000
H	-1.606928000	-0.754534000	-1.306065000
H	-0.182368000	-0.135862000	-2.166132000
H	-0.103639000	-1.693926000	-1.311334000
O	-0.515232000	1.362043000	0.000000000

^{t}BuOH

C	0.000905000	0.015128000	0.000000000
C	-0.487556000	-0.705750000	1.265181000
H	-0.160897000	-0.167015000	2.160248000
H	-1.582368000	-0.762604000	1.280118000
H	-0.099253000	-1.728313000	1.315911000
C	1.526475000	0.143335000	0.000000000
H	1.863724000	0.688514000	-0.887336000
H	1.863724000	0.688514000	0.887336000
H	1.998691000	-0.843307000	0.000000000
C	-0.487556000	-0.705750000	-1.265181000
H	-1.582368000	-0.762604000	-1.280118000
H	-0.160897000	-0.167015000	-2.160248000
H	-0.099253000	-1.728313000	-1.315911000
O	-0.487556000	1.371451000	0.000000000
H	-1.454265000	1.328760000	0.000000000

^{t}BuOOH

C	0.387742000	0.000001000	0.029811000
C	0.383934000	1.269987000	0.889601000
H	0.370774000	2.160348000	0.253299000
H	-0.492858000	1.295853000	1.540613000
H	1.279979000	1.306364000	1.516547000
C	1.568920000	-0.000063000	-0.949430000
H	1.546004000	-0.888960000	-1.586778000
H	1.546008000	0.888753000	-1.586891000

H	2.508459000	-0.000030000	-0.390055000
C	0.383925000	-1.269878000	0.889758000
H	-0.492866000	-1.295657000	1.540774000
H	0.370759000	-2.160317000	0.253566000
H	1.279970000	-1.306184000	1.516707000
O	-0.739991000	-0.000050000	-0.872300000
O	-1.966474000	0.000006000	-0.057011000
H	-2.611636000	-0.000097000	-0.781739000

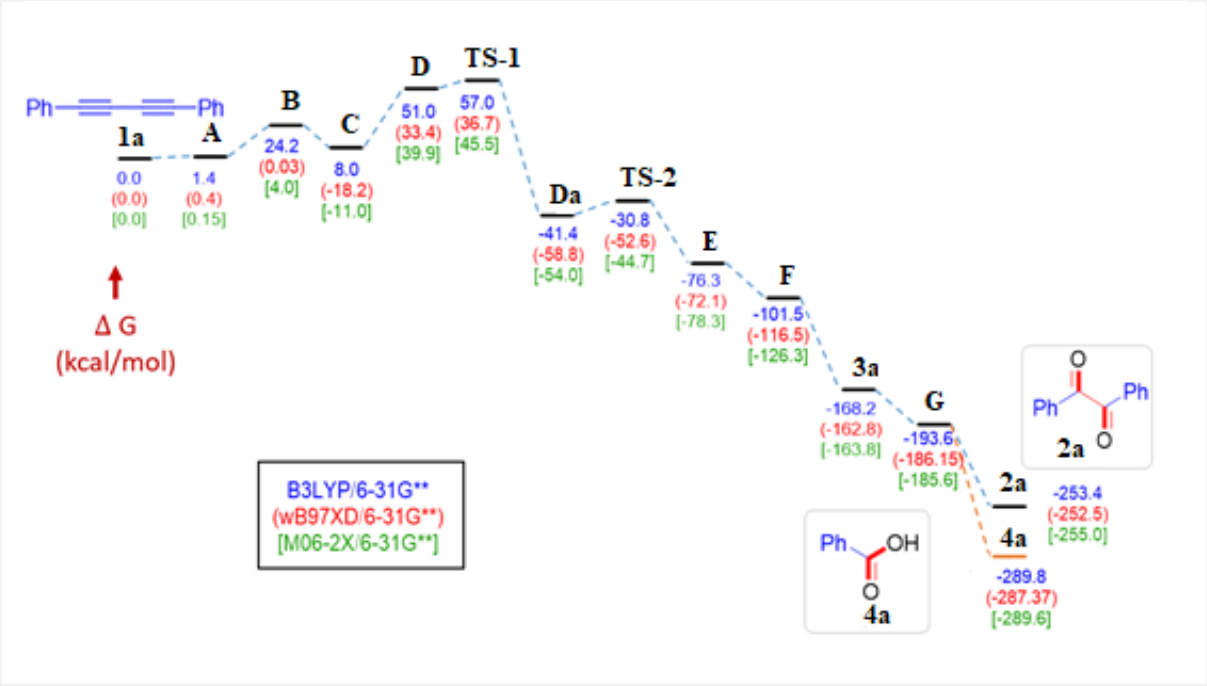


Figure S1. Free energy profile for favored reaction pathway at B3LYP/6-31G(d,p) in solvent phase (DMSO). Solvent phase single point energies at wB97XD/6-31G(d,p) and M06-2X/6-31G(d,p) are given in parentheses and brackets respectively.[1-6]

4. Detection of CO_2:

The formation of CO_2 in the reaction mixture was detected in a typical reaction with lime water.

Principle

The liberated carbon dioxide is used to produce a precipitate of calcium carbonate with the lime water.

The following reagents were prepared for the analysis.

Lime water solution: In a 50 mL volumetric flask, 1.0 g of $Ca(OH)_2$ was dissolved in 10 mL Milli-Q water, stoppered and stored in a cool place.

Procedure:

Reaction set up A: A 25 mL reaction vial fitted with a cork having an inlet was charged with a mixture of 1,4-diphenylbuta-1,3-diyne (**1a**) (0.5 mmol, 101 mg), tetra-*n*-butylammonium iodide (0.15 mmol, 55.4 mg), *tert*-butyl hydroperoxide (1.5 mmol, 135 mg, 0.145 mL) and DMSO (2 mL) and then heated at 140 °C.

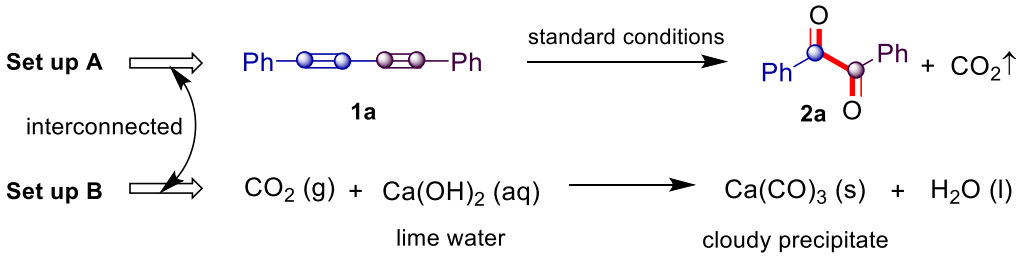
Reaction set up B: In another, a 25 mL test tube fitted with a cork having an inlet is loaded with 5 mL of lime water solution.

The reaction set up **A** and **B** are interconnected through a needle which is being immersed in lime water at one end and the other end being inserted from the top. Upon progression of

reaction, the lime water solution slowly turns cloudy which is indicating the liberation of carbon dioxide (Figure S2).

Figure S2. Detection of CO_2 though lime water experiment.

Observations:



Results:

The above experimental results showed the liberation of carbon dioxide during the reaction of **1a** under the standard reaction conditions.

5. Investigation of the reaction mechanism *via* Mass Spectrometry

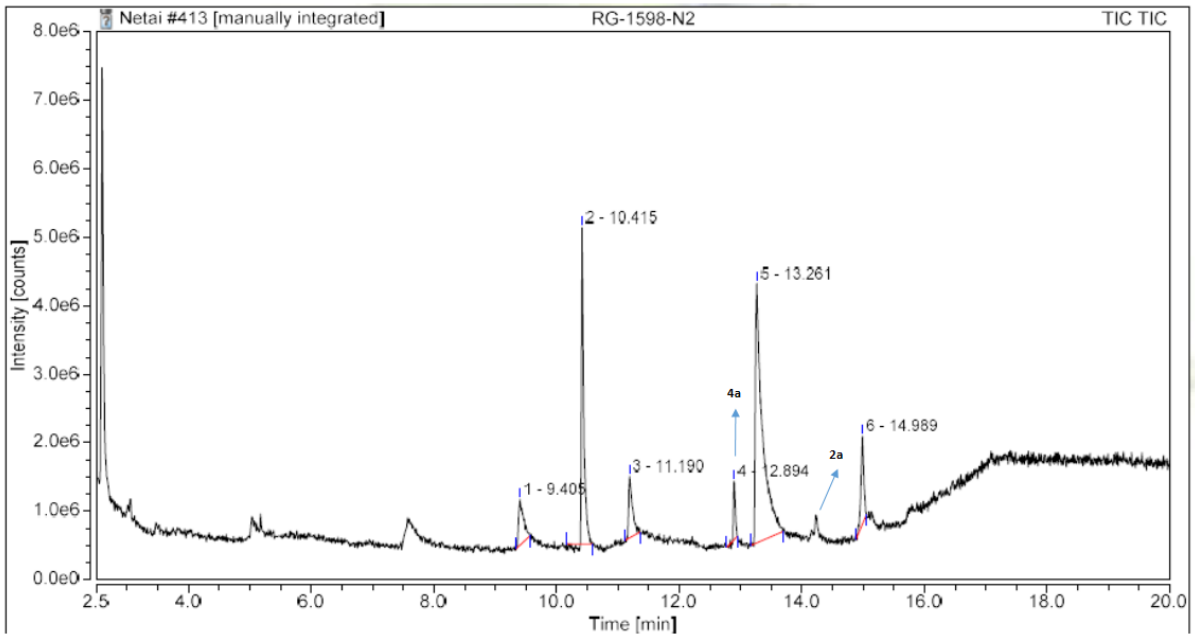


Figure 1a. After 5 h

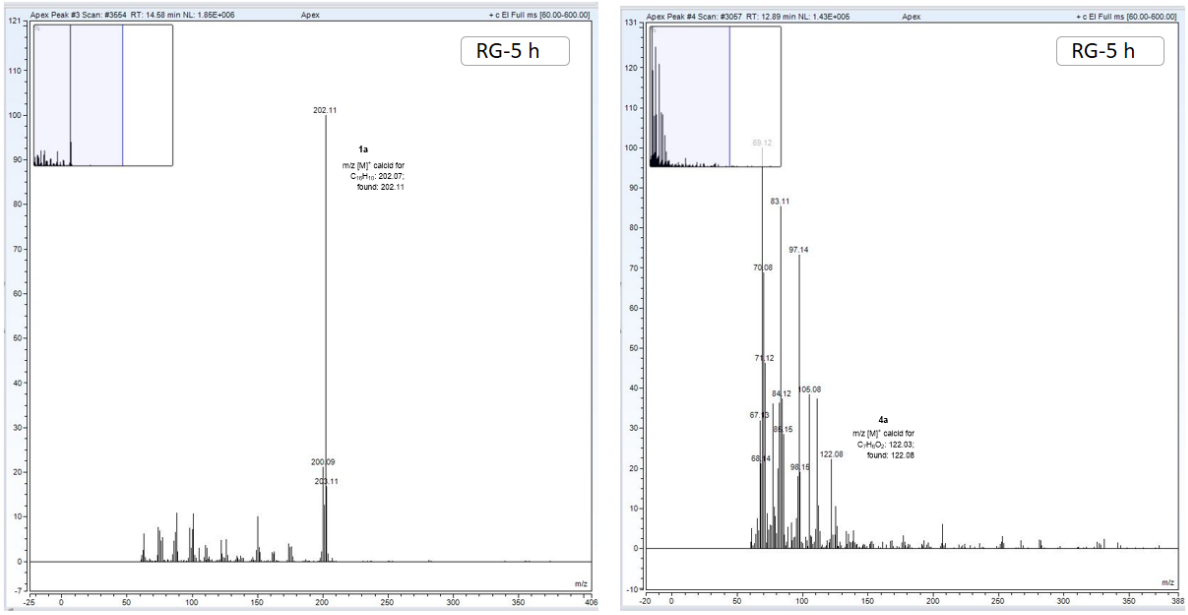


Figure 1a. After 5 h

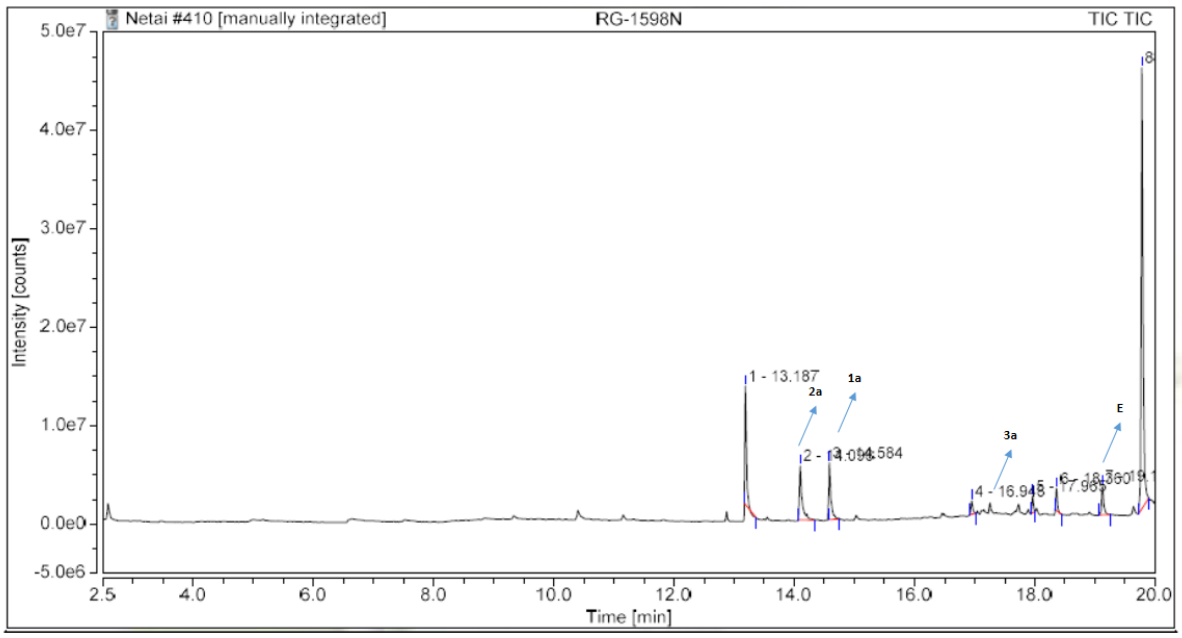


Figure 1b. After 10 h

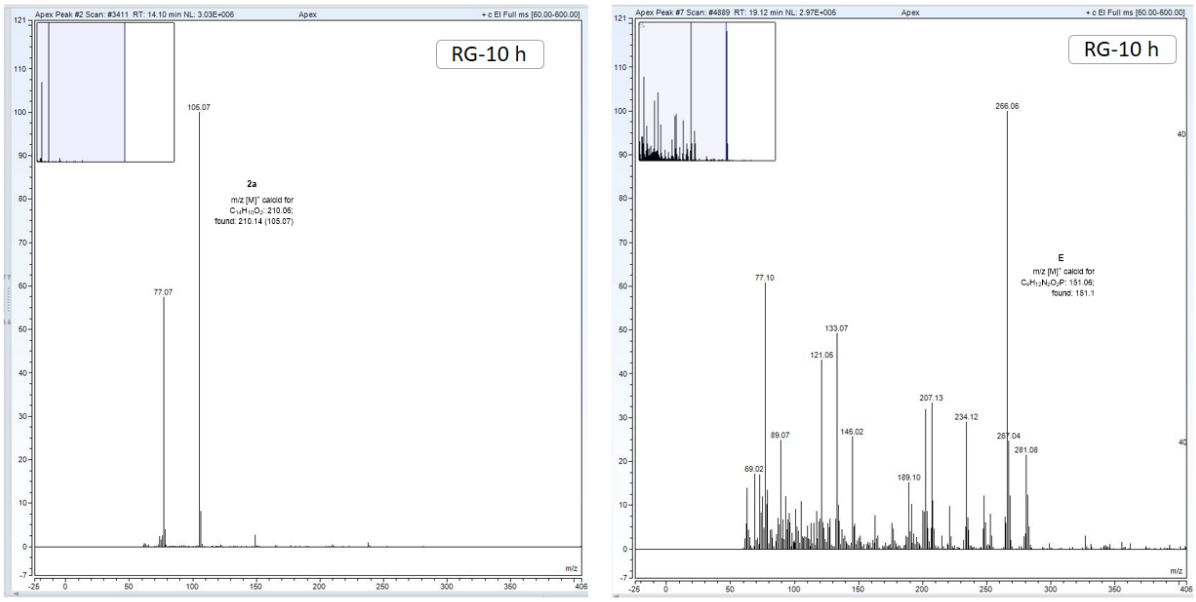


Figure 1b. After 10 h

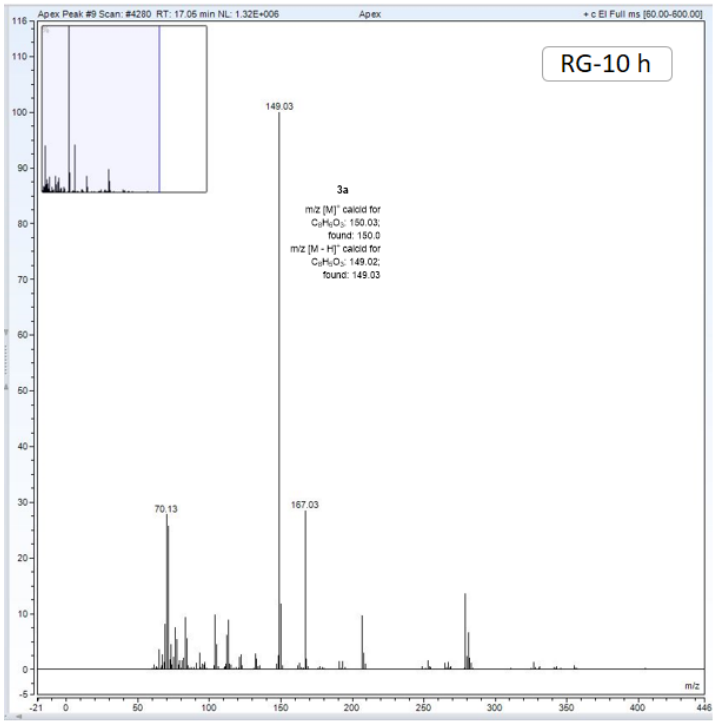


Figure 1b. After 10 h

Figure S3. Investigation of the reaction mechanism *via* Mass Spectrometry.

6. Kinetic monitoring of the reaction *via* gas chromatography

A 10 mL reaction vial was charged with a mixture of 1,4-diphenylbuta-1,3-diyne (**1a**) (0.5 mmol, 101 mg), tetra-*n*-butylammonium iodide (0.15 mmol, 55.4 mg), *tert*-butyl hydroperoxide (1.5 mmol, 135 mg, 0.145 mL), mesitylene (0.5 mmol, 60 mg) and DMSO (2 mL) and then the reaction vial was then closed and heated at 140 °C. The reaction was monitored by taking an aliquot of the reaction mixture and analysing the distribution of the products *via* gas chromatography at specified time interval (Table S2).

Table S2. Product distribution for thremetal-free C-C bond activation of **1a**.

Time (**h**)	[**1a**] %	[**2a**] %
0	100	0
2	85	5
4	70	13
6	52	19
8	41	27
10	30	34
12	21	42
14	11	51
16	6	59
18	0	68
20	0	76

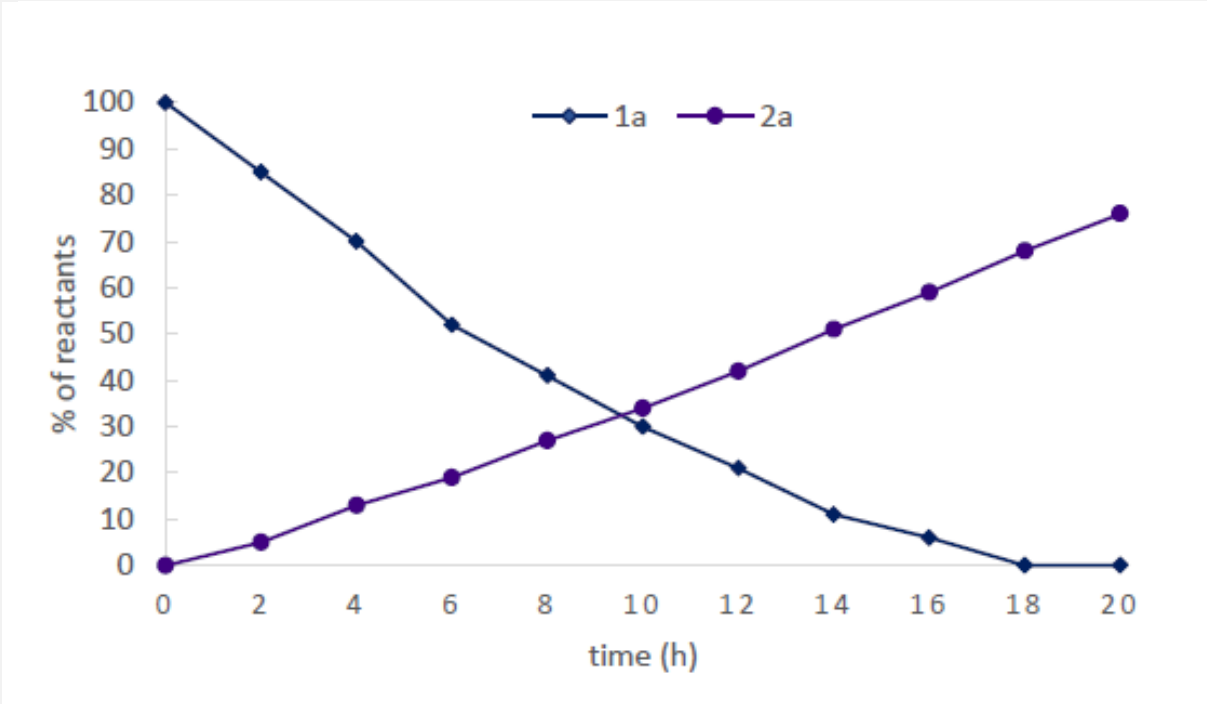
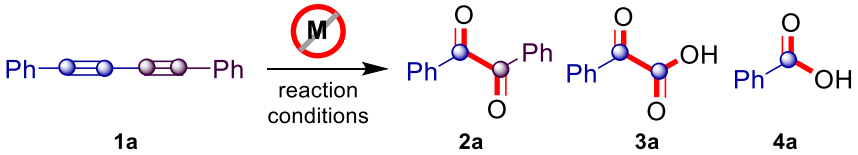


Figure S4. Kinetic analysis of the reaction of **1a** to produce **2a**.

7. Additional Optimization of the Reaction Conditions

Table S3. Optimization of conditions for the reaction of **1a**.[a]



1a 2a 3a 4a

S.N.	Catalyst (mol %)	Reagents (equiv.)	Conditions	yields[b], of **2a**/**3a**/**4a**
1	-	TBHP (3.0)	DMSO, 140 °C, 20 h	NR/0/0[c]
2	TBAI (30)	-	DMSO, 140 °C, 20 h	<10/0/0[c]
3	TBAI (30)	TBHP (3.0)	140 °C, 20 h	<10/0/0[c]
4	TBAI (30)	TBHP (3.0)	DMA, 140 °C, 20 h	44/0/0
5	TBAI (30)	TBHP (3.0)	dioxane, 140 °C, 20 h	21/<10/13
6	TBAI (30)	TBHP (3.0)	Toluene, 140 °C, 20 h	15/0/<10
7	TBAI (30)	$K_2S_2O_8$ (3.0)	DMSO, 140 °C, 20 h	27/0/10
8	TBAI (30)	Ph-Se-Se-Ph (3.0)	DMSO, 140 °C, 20 h	13/0/<10
9	TBAI (30)	*m*CPBA (3.0)	DMSO, 140 °C, 20 h	39/<10/16
10	TBAI (30)	pyridine *N*-oxide (3.0)	DMSO, 140 °C, 20 h	16/<10/<10

[a]All reactions were performed using 0.5 mmol **1a** in 2 mL solvent. [b]Isolated yields. [c]Complex reaction mixture.

8. General Experimental Procedure for the Synthesis of Symmetrical/Unsymmetrical 1,2-Diketones2a-y from 1,3-diynes 1a-x

A 10 mL reaction vial was charged with a mixture of symmetrical/unsymmetrical 1,3-diynes **1a-x** (0.5 mmol), tetra-*n*-butylammonium iodide (0.15 mmol, 55.4 mg), *tert*-butyl hydroperoxide (1.5 mmol, 135 mg, 0.145 mL) and DMSO (2 mL). The reaction vial was then closed and heated at 140 °C for 20 h. After completion of the reaction (progress was monitored by TLC; SiO_2, Hexane/EtOAc = 9:1), the mixture was diluted with ethyl acetate (15 mL) and water (20 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine (3 × 10 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude products were purified by column chromatography using silica gel (100-200 mesh) with hexane/EtOAc (9:1) as the eluent to obtain the desired products **2a-y**.

9. Analytical Data of Synthesized Symmetrical/Unsymmetrical 1,2-Diketones 2a-y

Benzil (**2a**)[7]; **Yellow solid**, **Yield**: 80 mg (76%); R_f= 0.60 (SiO_2, Hexane/EtOAc = 9:1); **Purification system**: Column chromatography (SiO_2, 100-200) (Hexane/EtOAc = 97:3); **m.p** = 100-101 °C (Lit[7] 101-102 °C); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.98 (d, ^3J = 8.0 Hz, 4H; 2-H), 7.67 (t, ^3J = 8.2 Hz, 2H; 4-H), 7.52 (t, ^3J = 7.9 Hz, 4H; 3-H) ppm; **^{13}CNMR** (100 MHz, $CDCl_3$) δ = 194.5 (C-5), 134.9 (C-4), 133.0 (C-1), 129.9 (C-3), 129.0 (C-2) ppm; **HRMS** (EI-QTOF, $[M + H]^+$): calculated for $C_{14}H_{11}O_2$: 211.0754; found: 211.0754.

1,2-Di-*o*-tolylethane-1,2-dione (**2b**)[7]; **Yellow solid**, **Yield**: 88 mg (74%); R_f= 0.60 (SiO_2, Hexane/EtOAc = 9:1); **Purification system**: Column chromatography (SiO_2, 100-200) (Hexane/EtOAc = 96:4); **m.p** = 80-81 °C (Lit[7] 81-82 °C); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.67 (dd, ^3J = 8.0 Hz, 2H; 6-H), 7.49 (td, ^3J = 7.6 Hz, 2H; 4-H), 7.34 (d, ^3J = 6.8 Hz, 2H; 3-H), 7.28 (t, ^3J = 7.6 Hz, 2H; 5-H), 2.71 (s, 6H; 8-H) ppm; **^{13}CNMR** (100 MHz, $CDCl_3$) δ = 197.0 (C-7), 141.6 (C-2), 133.7 (C-4), 133.1 (C-6), 132.7 (C-3), 131.9 (C-1), 126.1 (C-5), 22.0 (C-8) ppm; **HRMS** (EI-QTOF, $[M + H]^+$): calculated for $C_{16}H_{15}O_2$: 239.1067; found: 239.1067.

1,2-Di-*m*-tolylethane-1,2-dione (**2c**)[7]; **Yellow solid**, **Yield**: 84 mg (71%); R_f= 0.60 (SiO_2, Hexane/EtOAc = 9:1); **Purification system**: Column chromatography (SiO_2, 100-200) (Hexane/EtOAc = 97:3); **m.p** = 91-93 °C (Lit[7] 92-94 °C); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.78-7.76 (m, 4H; 2-H and 6-H), 7.47 (d, ^3J = 3.6 Hz, 2H; 4-H), 7.40 (t, ^3J = 7.2 Hz, 2H; 5-H), 2.41 (s, 6H; 8-H) ppm; **^{13}CNMR** (100 MHz, $CDCl_3$) δ = 195.0 (C-7), 139.1 (C-3), 135.8 (C-2), 133.2 (C-1), 130.3 (C-5), 129.0 (C-4), 127.3 (C-6), 21.4 (C-8) ppm; **HRMS** (EI-QTOF, $[M + H]^+$): calculated for $C_{16}H_{15}O_2$: 239.1067; found: 239.1064.

1,2-Bis(2-methoxyphenyl)ethane-1,2-dione (**2d**)[8]; **Pale white solid**, **Yield**: 92 mg (68%); R_f= 0.30 (SiO_2, Hexane/EtOAc = 9:1); **Purification system**: Column chromatography (SiO_2, 100-200) (Hexane/EtOAc = 92:8); **m.p** = 128-130°C (Lit[8] 130-131 °C); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.09 (dd, ^3J = 8.0 Hz, 2H; 6-H), 7.57 (td, ^3J = 8.0Hz, 2H; 4-H), 7.12 (td, ^3J = 7.8 Hz, 2H; 5-H), 6.96 (d, ^3J = 8.0 Hz, 2H; 3-H), 3.59 (s, 6H; 8-H) ppm; **^{13}CNMR** (100 MHz, $CDCl_3$) δ = 192.5 (C-7), 160.4 (C-2), 135.6 (C-4), 130.5 (C-6), 123.5 (C-1), 121.4 (C-5), 112.5 (C-3), 55.9 (C-8) ppm; **HRMS** (EI-QTOF, $[M + H]^+$): calculated for $C_{16}H_{15}O_4$: 271.0965; found: 271.0962.

1,2-Bis(4-methoxyphenyl)ethane-1,2-dione (**2e**)[8]; **Yellow solid**, **Yield**: 101 mg (75%); R_f= 0.20 (SiO_2, Hexane/EtOAc = 9:1); **Purification system**: Column chromatography (SiO_2, 100-200) (Hexane/EtOAc = 88:12); **m.p** = 133-134°C (Lit[8] 134-135 °C); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.94 (d, ^3J = 8.0 Hz, 4H; 2-H), 6.96 (d, ^3J = 8.0 Hz, 4H; 3-H), 3.88 (s, 6H; 6-H) ppm; **^{13}CNMR** (125 MHz, $CDCl_3$) δ = 193.4 (C-5), 164.8 (C-4), 132.3 (C-2), 126.3 (C-1), 114.3 (C-3), 55.6 (C-6) ppm; **HRMS** (EI-QTOF, $[M + H]^+$): calculated for $C_{16}H_{15}O_4$: 271.0965; found: 271.0965.

1,2-Bis(4-chlorophenyl)ethane-1,2-dione (**2f**)[7]; **Yellow solid**, **Yield**: 97 mg (70%); R_f= 0.65 (SiO_2, Hexane/EtOAc = 9:1); **Purification system**: Column chromatography (SiO_2, 100-200) (Hexane/EtOAc = 95:5); **m.p** = 195-196 °C (Lit[7] 194-195 °C); **^{1}H NMR** (400 MHz, $CDCl_3$): δ

= 7.92 (d, ^3J = 8.0 Hz, 4H; 2-H), 7.51 (d, ^3J = 8.0 Hz, 4H; 3-H) ppm; **^{13}CNMR** (100 MHz, $CDCl_3$) δ = 192.3 (C-5), 141.8 (C-4), 131.2 (C-1), 131.1 (C-2), 129.5 (C-3) ppm; **HRMS** (EI-QTOF, $[M + H]^+$): calculated for $C_{14}H_9Cl_2O_2$: 278.9974; found: 278.9976.

1,2-Bis(4-bromophenyl)ethane-1,2-dione (**2g**)[8]; **White solid**, **Yield**: 126 mg (69%); R_f= 0.55 (SiO_2, Hexane/EtOAc = 9:1); **Purification system**: Column chromatography (SiO_2, 100-200) (Hexane/EtOAc = 94:6); **m.p** = 227-228 °C (Lit[8] 229-230 °C); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.95 (dd, ^3J = 8.0 Hz, 4H; 2-H), 7.62 (dd, ^3J = 8.0 Hz, 4H; 3-H) ppm; **^{13}CNMR** (100 MHz, $CDCl_3$) δ = 192.53 (C-5), 132.51 (C-3), 131.53 (C-1), 131.28 (C-2), 130.75 (C-4) ppm; **HRMS** (EI-QTOF, $[M + H]^+$): calculated for $C_{14}H_9Br_2O_2$: 366.8964; found: 366.8964.

1,2-Di(naphthalen-1-yl)ethane-1,2-dione (**2h**)[9]; **Pale yellow solid**, **Yield**: 105 mg (68%); R_f= 0.45 (SiO_2, Hexane/EtOAc = 9:1); **Purification system**: Column chromatography (SiO_2, 100-200) (Hexane/EtOAc = 96:4); **m.p** = 191-192°C (Lit[9] 190-190.5 °C); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 9.35 (d, ^3J = 9.2 Hz, 2H; 9-H), 8.13 (d, ^3J = 8.0 Hz, 2H; 4-H), 8.03 (dd, ^3J = 8.0 Hz, 2H; 2-H), 7.96 (d, ^3J = 8.0 Hz, 2H; 6-H), 7.76 (td, ^3J = 8.0 Hz, 2H; 8-H), 7.64 (td, ^3J = 8.0 Hz, 2H; 3-H),7.49 (t, ^3J = 8.0 Hz, 2H; 7-H) ppm; **HRMS** (EI-QTOF, $[M + H]^+$): calculated for $C_{22}H_{15}O_2$: 311.1067; found: 311.1063.

1-Phenyl-2-(*p*-tolyl)ethane-1,2-dione (**2i**)[7]; **Yellow solid**, **Yield**: 83 mg (74%); R_f= 0.45 (SiO_2, Hexane/EtOAc = 9:1); **Purification system**: Column chromatography (SiO_2, 100-200) (Hexane/EtOAc = 96:4); **m.p** = 31-32 °C (Lit[7] 30-32 °C); **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 7.97 (d, ^3J = 8.0 Hz, 2H; 2-H), 7.87 (d, ^3J = 8.0 Hz, 2H; 6-H), 7.64 (tt, ^3J = 8.2 Hz, 1H; 8-H), 7.50 (td, ^3J = 8.6 Hz, 2H; 7-H), 7.30 (d, ^3J = 6.8 Hz, 2H; 3-H), 2.43 (s, 3H; 11-H) ppm; **^{13}CNMR** (150 MHz, $CDCl_3$) δ = 194.8 (C-10), 194.4 (C-9), 146.3 (C-4), 134.9 (C-8), 133.2 (C-5), 130.7 (C-1), 130.1 (C-2), 130.0 (C-3), 129.8 (C-9), 129.1 (C-6), 22.0 (C-11) ppm; **HRMS** (EI-QTOF, $[M + H]^+$): calculated for $C_{15}H_{13}O_2$: 225.0910; found: 225.0912.

1-(4-Chlorophenyl)-2-phenylethane-1,2-dione (**2j**)[7]; **Yellow solid**, **Yield**: 85 mg (70%); R_f= 0.50 (SiO_2, Hexane/EtOAc = 9:1); **Purification system**: Column chromatography (SiO_2, 100-200) (Hexane/EtOAc = 97:3); **m.p** = 70-71 °C (Lit[7] 69-71 °C); **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 7.97 (d, ^3J = 8.0 Hz, 2H; 6-H), 7.93 (d, ^3J = 8.0 Hz, 2H; 2-H), 7.67 (t, ^3J = 8.0 Hz, 1H; 8-H), 7.54-7.48 (m,4H; 3-H and 7-H) ppm; **^{13}CNMR** (150 MHz, $CDCl_3$) δ = 194.0 (C-9), 193.2 (C-10), 141.7 (C-4), 135.2 (C-8), 132.9 (C-5), 131.5 (C-1), 131.3 (C-2), 130.1 (C-3), 129.6 (C-7), 129.2 (C-6) ppm; **HRMS** (EI-QTOF, $[M + H]^+$): calculated for $C_{14}H_{10}ClO_2$: 245.0364; found: 245.0363.

1-(3-Bromophenyl)-2-phenylethane-1,2-dione (**2k**)[7]; **Yellow solid**, **Yield**: 92 mg (64%); R_f= 0.56 (SiO_2, Hexane/EtOAc = 9:1); **Purification system**: Column chromatography (SiO_2, 100-200) (Hexane/EtOAc = 97:3); **m.p** = 79-80 °C (Lit[10] 80-81 °C); **^{1}H NMR** (500 MHz, $CDCl_3$:DMSO-d_6 (8:2)): δ = 8.13 (t, ^4J = 1.8 Hz, 1H; 3-H), 7.96 (d, ^3J = 8.0 Hz, 2H; 10-H), 7.88 (dt, ^3J = 8.0 Hz, 1H; 5-H), 7.78 (ddd, ^3J = 6.9 Hz, 1H; 7-H), 7.67 (td, ^3J = 6.8 Hz, 1H; 4-H), 7.52 (d, ^3J = 8.0 Hz, 2H; 11-H), 7.39 (t, ^3J = 7.0 Hz, 1H; 6-H) ppm; **^{13}CNMR** (125 MHz, $CDCl_3$) δ = 193.55 (C-11), 192.85 (C-12), 137.69 (C-4), 137.17 (C-10), 134.71 (C-1), 132.67

(C-7), 132.46 (C-2), 130.61 (C-5), 129.97 (C-9), 129.13 (C-8), 128.59 (C-6), 123.54 (C-3) ppm; **HRMS** (EI-QTOF, $[M + H]^+$): calculated for $C_{14}H_{10}BrO_2$: 288.9859; found: 288.9859.

1-(4-Nitrophenyl)-2-phenylethane-1,2-dione (**2l**)[7]; **Yellow solid**, **Yield**: 78 mg (61%); R_f= 0.60 (SiO_2, Hexane/EtOAc = 9:1); **Purification system**: Column chromatography (SiO_2, 100-200) (Hexane/EtOAc = 97:3); **m.p** = 141-142°C (Lit[7] 140-141 °C); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.35 (d, ^3J = 8.0 Hz, 2H; 3-H), 8.17 (d, ^3J = 8.0 Hz, 2H; 2-H), 7.99 (dd, ^3J = 8.0 Hz, 2H; 6-H), 7.71 (tt, ^3J = 8.0 Hz, 1H; 8-H), 7.55 (tt, ^3J = 8.0 Hz, 2H; 7-H) ppm; **^{13}CNMR** (100 MHz, $CDCl_3$) δ = 192.9 (C-9), 192.1 (C-10), 151.2 (C-4), 137.4 (C-1), 135.5 (C-8), 132.5 (C-5), 131.0 (C-2), 130.1 (C-7), 129.3 (C-6), 124.2 (C-3) ppm; **HRMS** (EI-QTOF, $[M + H]^+$): calculated for $C_{14}H_{10}NO_4$: 256.0604; found: 256.0603.

1-Phenyl-2-(3-(trifluoromethyl)phenyl)ethane-1,2-dione (**2m**)[7]; **Pale yellow solid**, **Yield**: 85 mg (64%); R_f= 0.60 (SiO_2, Hexane/EtOAc = 9:1); **Purification system**: Column chromatography (SiO_2, 100-200) (Hexane/EtOAc = 98:2); **m.p** = 69-70°C (Lit[7] 68-69 °C); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.29-8.27 (m, 1H; 2-H), 8.17-8.14 (m, 1H; 4-H), 8.01-7.98 (m, 2H; 8-H), 7.93-7.9 (m, 1H; 6-H), 7.73-7.65 (m, 2H; 5-H and 10-H), 7.57-7.52 (t, ^3J = 8.0 Hz, 2H; 9-H) ppm; **^{13}CNMR** (100 MHz, $CDCl_3$) δ = 193.3 (C-11), 192.6 (C-12), 135.2 (C-10), 133.6 (C-1), 133.17 (C-6), 132.64 (C-7), 131.83 (q, J = 34.0 Hz, C-3), 131.11 (q, J = 4.0 Hz, C-4), 130.0 (C-9), 129.7 (C-5), 129.16 (C-8), 126.48 (q, J = 4.0 Hz, C-2), 124.76 (C-13) ppm; **HRMS** (EI-QTOF, $[M + H]^+$): calculated for $C_{14}H_{10}F_3O_2$: 267.0627; found: 267.0633.

4-(2-Oxo-2-phenylacetyl)benzonitrile (**2n**)[7]; **Yellow solid**, **Yield**: 69 mg (59%); R_f= 0.50 (SiO_2, Hexane/EtOAc = 9:1); **Purification system**: Column chromatography (SiO_2, 100-200) (Hexane/EtOAc = 98:2); **m.p** = 108-110 °C (Lit[7] 109-110 °C); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.09 (d, ^3J = 8.0 Hz, 2H; 3-H), 7.98 (d, ^3J = 8.0 Hz, 2H; 2-H), 7.82 (d, ^3J = 8.0 Hz, 2H; 6-H), 7.70 (t, ^3J = 8.0 Hz, 1H; 8-H), 7.54 (t, ^3J = 8.0 Hz, 2H; 7-H) ppm; **^{13}CNMR** (100 MHz, $CDCl_3$) δ = 193.1 (C-9), 192.49 (C-10), 135.96 (C-1), 135.51 (C-8), 132.88 (C-3), 132.5 (C-5), 130.3 (C-2), 130.1 (C-7), 129.3 (C-6), 117.98 (C-11), 117.66 (C-4) ppm; **HRMS** (EI-QTOF, $[M + H]^+$): calculated for $C_{15}H_{10}NO_2$: 236.0706; found: 236.0708.

Ethyl 4-(2-oxo-2-phenylacetyl)benzoate (**2o**)[11]; **Yellow solid**, **Yield**: 51 mg (36%); R_f= 0.20 (SiO_2, Hexane/EtOAc = 9:1); **Purification system**: Column chromatography (SiO_2, 100-200) (Hexane/EtOAc = 90:10); **m.p** = 73-75 °C (Lit[11] 75-76 °C); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.17 (d, ^3J = 8.0 Hz, 2H; 2-H), 8.04 (d, ^3J = 8.0 Hz, 2H; 3-H), 7.98 (d, ^3J = 8.0 Hz, 2H; 6-H), 7.68 (t, ^3J = 8.0 Hz, 1H; 8-H), 7.53 (t, ^3J = 8.0 Hz, 2H; 7-H) ppm; **^{13}CNMR** (100 MHz, $CDCl_3$) δ = 193.9 (C-9), 193.8 (C-10), 165.48 (C-11), 136.07 (C-1), 135.8 (C-4), 135.19 (C-8), 132.84 (C-5), 130.13 (C-3), 130.05 (C-2), 129.82 (C-7), 129.19 (C-6), 61.75 (C-12), 14.33 (C-13) ppm; **HRMS** (EI-QTOF, $[M + H]^+$): calculated for $C_{17}H_{15}O_4$: 283.0965; found: 283.0965.

4-(2-Oxo-2-phenylacetyl)benzoic acid (**2p**)[12]; **Pale yellow solid**, **Yield**: 37 mg (29%); R_f= 0.10 (SiO_2, Hexane/EtOAc = 5:5); **Purification system**: Column chromatography (SiO_2, 100-200) (Hexane/EtOAc = 70:30); **m.p** = 218-220°C (Lit[12] 219-221 °C); **^{1}H NMR** (400 MHz, $CDCl_3$:DMSO-d_6=8:2): δ = 8.11 (d, ^3J = 8.0 Hz, 2H; 3-H), 7.96 (d, ^3J = 8.0 Hz, 2H; 2-H), 7.90 (d, ^3J = 8.0 Hz, 2H; 6-H), 7.62 (t, ^3J = 8.0 Hz, 1H; 8-H), 7.47 (t, ^3J = 8.0 Hz, 2H; 7-H) ppm;

^{13}CNMR (100 MHz, $CDCl_3$:DMSO-d_6=8:2) δ = 194.1 (C-9), 194.0 (C-10), 167.3 (C-11), 136.5 (C-1), 135.8 (C-4), 135.2 (C-8), 132.7 (C-5), 130.3 (C-3), 130.0 (C-2), 129.7 (C-7), 129.17 (C-6) ppm; **HRMS** (EI-QTOF, $[M + H]^+$): calculated for $C_{15}H_{11}O_4$: 255.0652; found: 255.0651.

1-(*m*-Tolyl)-2-(*p*-tolyl)ethane-1,2-dione (**2q**)[7]; **Yellow solid**, **Yield**: 76 mg (64%); R_f= 0.40 (SiO_2, Hexane/EtOAc = 9:1); **Purification system**: Column chromatography (SiO_2, 100-200) (Hexane/EtOAc = 90:10); **m.p** = 60-61°C (Lit[7]61-62 °C); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.86 (d, ^3J = 8.0 Hz, 2H; 10-H), 7.78-7.74 (m, 2H; 3-H and 7-H), 7.45 (d, ^3J = 8.0 Hz, 1H; 5-H), 7.38 (t, ^3J = 8.0 Hz, 1H; 6-H), 7.30 (d, ^4J = 3.6 Hz, 2H; 11-H), 2.43 (s, 3H; 13-H), 2.40 (s, 3H; 14-H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 195.02 (C-1), 194.42 (C-8), 146.12 (C-12), 138.95 (C-4), 135.62 (C-5), 133.18 (C-3), 130.71 (C-9), 130.2 (C-2), 130.0 (C-10), 129.73 (C-11), 128.88 (C-6), 127.21 (C-7), 21.91 (C-13), 21.25 (C-14) ppm; **HRMS** (EI-QTOF, $[M + H]^+$): calculated for $C_{16}H_{15}O_2$: 239.1067; found: 239.1067.

1-(4-Methoxyphenyl)-2-*p*-tolylethane-1,2-dione (**2r**)[14]; **Yellow solid**, **Yield**: 94 mg (74%); R_f= 0.10 (SiO_2, Hexane/EtOAc = 9:1); **Purification system**: Column chromatography (SiO_2, 100-200) (Hexane/EtOAc = 94:6); **m.p** = 105-106 °C (Lit[14] 106-108 °C); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.93 (d, ^3J = 8.0 Hz, 2H; 2-H), 7.86 (d, ^3J = 8.0 Hz, 2H; 6-H), 7.29 (d, ^3J = 8.0 Hz, 2H; 7-H), 6.96 (d, ^3J = 8.0 Hz, 2H; 3-H), 3.88 (s, 3H; 11-H), 2.43 (s, 3H; 12-H) ppm; **^{13}CNMR** (100 MHz, $CDCl_3$) δ = 194.7 (C-10), 193.5 (C-9), 165.0 (C-4), 146.1 (C-8), 132.4 (C-2), 130.9 (C-5), 130.1 (C-6), 129.7 (C-7), 126.3 (C-1), 114.4 (C-3), 55.7 (C-11), 22.0 (C-12) ppm; **HRMS** (EI-QTOF, $[M + H]^+$): calculated for $C_{16}H_{15}O_3$: 255.1016; found: 255.1018.

1-(4-Bromophenyl)-2-(*p*-tolyl)ethane-1,2-dione (**2s**)[7]; **Yellow solid**, **Yield**: 100 mg (74%); R_f= 0.45 (SiO_2, Hexane/EtOAc = 9:1); **Purification system**: Column chromatography (SiO_2, 100-200) (Hexane/EtOAc = 95:5); **m.p** = 92-93 °C (Lit[7] 93-95 °C); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.87-7.82 (m, 4H; 2-H and 6-H), 7.66 (d, ^3J = 8.6 Hz, 2H; 3-H), 7.31 (d, ^3J = 7.6 Hz, 2H; 7-H), 2.44 (s, 3H; 11-H) ppm; **^{13}CNMR** (100 MHz, $CDCl_3$) δ = 193.6 (C-9), 193.5 (C-10), 146.4 (C-8), 132.4 (C-3), 131.9 (C-1), 131.2 (C-2), 130.5 (C-5), 130.4 (C-4), 130.1 (C-6), 129.8 (C-7), 22.0 (C-11) ppm; **HRMS** (EI-QTOF, $[M + H]^+$): calculated for $C_{15}H_{12}BrO_2$: 303.0015; found: 303.0023.

1-(2-Methoxyphenyl)-2-(*m*-tolyl)ethane-1,2-dione (**2t**)[7]; **Pale yellow solid**, **Yield**: 77 mg (74%); R_f= 0.30 (SiO_2, Hexane/EtOAc = 9:1); **Purification system**: Column chromatography (SiO_2, 100-200) (Hexane/EtOAc = 90:10); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.03 (d, ^3J = 8.0 Hz, 1H; 6-H), 7.74-7.71 (m, 2H; 8-H and 12-H), 7.60 (td, ^3J = 8.0 Hz, 1H; 4-H), 7.42 (d, ^3J = 8.0 Hz, 1H; 10-H), 7.37 (t, ^3J = 8.0 Hz, 1H; 11-H), 7.13 (t, ^3J = 8.4 Hz, 1H; 5-H), 6.94 (d, ^3J = 8.0 Hz, 1H; 3-H), 3.58 (s, 3H; 15-H), 2.41 (s, 3H; 16-H) ppm; **^{13}CNMR** (100 MHz, $CDCl_3$) δ = 194.8 (C-13), 193.8 (C-14), 160.6 (C-2), 138.7 (C-9), 136.5 (C-4), 134.7 (C-10), 133.0 (C-7), 130.7 (C-8), 129.9 (C-11), 128.7 (C-6), 126.8 (C-12), 124.1 (C-1), 121.7 (C-5), 112.6 (C-3), 55.9 (C-15), 21.4 (C-16) ppm; **HRMS** (EI-QTOF, $[M + H]^+$): calculated for $C_{16}H_{15}O_3$: 255.1016; found: 255.1016.

1-(3-Bromophenyl)-2-(4-chlorophenyl)ethane-1,2-dione (**2u**)[7]; **Yellow solid**, **Yield**: 111 mg (74%); R_f= 0.60 (SiO_2, Hexane/EtOAc = 9:1); **Purification system**: Column chromatography

(SiO_2, 100-200) (Hexane/EtOAc = 94:6); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.12 (td, ^3J = 3.2 Hz, 1H; 2-H), 7.92 (d, ^3J = 8.0 Hz, 2H; 8-H), 7.87 (dt, ^3J = 8.0 Hz, 1H; 4-H), 7.79 (ddd, ^3J = 6.9 Hz, 1H; 6-H), 7.51 (d, ^3J = 8.0 Hz, 2H; 9-H), 7.40 (td, ^3J = 8.0 Hz, 1H; 5-H) ppm; **^{13}CNMR** (100 MHz, $CDCl_3$) δ = 192.26 (C-11), 192.14 (C-12), 142.01 (C-10), 137.94 (C-4), 134.57 (C-11), 132.66 (C-2), 131.38 (C-8), 131.11 (C-7), 130.7 (C-9), 129.62 (C-5), 128.68 (C-6), 123.67 (C-3) ppm; **HRMS** (EI-QTOF, $[M + H]^+$): calculated for $C_{14}H_9BrClO_2$: 322.9469; found: 322.9469.

1-(Naphthalen-1-yl)-2-phenylethane-1,2-dione (**2v**)[7]; **Yellow solid**, **Yield**: 93 mg (72%); R_f= 0.50 (SiO_2, Hexane/EtOAc = 9:1); **Purification system**: Column chromatography (SiO_2, 100-200) (Hexane/EtOAc = 96:4); **m.p** = 83-84°C (Lit[7] 84-86 °C); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 9.30 (d, ^3J = 8.0 Hz, 1H; 9-H), 8.12 (d, ^3J = 8.0 Hz, 1H; 4-H), 8.03 (d, ^3J = 8.0 Hz, 2H; 14-H), 7.94-7.90 (m, 2H; 2-H and 6-H), 7.75 (t, 1H; 8-H),7.66-7.64 (m, 2H; 3-H and 16-H), 7.51-7.48 (m, 3H; 7-H and 15-H) ppm; **^{13}CNMR** (100 MHz, $CDCl_3$) δ = 197.1 (C-11), 194.5 (C-12), 135.9 (C-1), 135.0 (C-16), 134.7 (C-8), 134.1 (C-4), 133.7 (C-13), 131.0 (C-5), 130.0 (C-15), 129.4 (C-6), 129.0 (C-14), 128.8 (C-10), 128.5, 127.1, 126.0 (C-7), 124.4 (C-9) ppm; **HRMS** (EI-QTOF, $[M + H]^+$): calculated for $C_{18}H_{13}O_2$: 261.0910; found: 261.0913.

1-(4-Methylphenyl)-2-(1-naphthyl)ethane-1,2-dione (**2w**)[13]; **Yellow solid**, **Yield**: 89 mg (65%); R_f= 0.50 (SiO_2, Hexane/EtOAc = 9:1); **Purification system**: Column chromatography (SiO_2, 100-200) (Hexane/EtOAc = 95:5); **m.p** = 92-93 °C (Lit[13] 93-94 °C); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 9.30 (d, ^3J = 8.0 Hz, 1H; 9-H), 8.12 (d, ^3J = 8.0 Hz, 1H; 4-H), 7.95-7.90 (m, 4H; 2-H, 6-H and 14-H), 7.74 (t, 1H; 8-H),7.63 (t, ^3J = 8.0 Hz, 1H; 3-H), 7.48 (d, ^3J = 8.0 Hz, 1H; 7-H), 7.32 (d, ^3J = 8.0 Hz, 2H; 15-H),2.4 (s, 3H; 17-H) ppm; **^{13}CNMR** (100 MHz, $CDCl_3$) δ = 197.4 (C-11), 194.4 (C-12), 146.1 (C-16), 135.9 (C-1), 135.0 (C-8), 134.1 (C-4), 131.0, 130.27, 130.24,130.2, 129.88, 129.85, 129.81, 128.8, 127.1, 126.0, 124.5, 22.0 (C-17) ppm; **HRMS** (EI-QTOF, $[M + H]^+$): calculated for $C_{19}H_{15}O_2$: 275.1067; found: 275.1074.

Ethyl 4-(2-(naphthalen-1-yl)-2-oxoacetyl)benzoate (**2x**); **Pale yellow solid**, **Yield**: 81 mg (49%); R_f= 0.35 (SiO_2, Hexane/EtOAc = 9:1); **Purification system**: Column chromatography (SiO_2, 100-200) (Hexane/EtOAc = 97:3); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 9.29 (d, ^3J = 8.0 Hz, 1H; 9-H), 8.19-8.14 (m, 3H; 2-H, and 14-H), 8.09 (d, ^3J = 8.0 Hz, 2H; 15-H), 7.96 (d, ^3J = 8.0 Hz, 1H; 4-H), 7.89 (d, ^3J = 8.0 Hz, 1H; 6-H), 7.76 (t, ^3J = 8.0 Hz, 1H; 8-H), 7.65 (t, ^3J = 8.0 Hz, 1H; 3-H), 7.51 (d, ^3J = 8.0 Hz, 1H; 7-H),7.51 (d, ^3J = 8.0 Hz, 1H; 7-H), 4.4 (q, ^3J = 9.0 Hz, 2H; 18-H), 1.4 (t, ^3J = 8.0 Hz, 3H; 19-H) ppm; **^{13}CNMR** (100 MHz, $CDCl_3$) δ = 196.48 (C-12), 193.87 (C-11), 165.53 (C-17), 136.47 (C-13), 136.34 (C-1), 135.67 (C-16), 135.23 (C-8), 134.2 (C-4), 131.04 (C-10), 130.18 (C-15), 129.93 (C-14), 129.7, 128.95, 128.44, 127.33, 125.97 (C-7), 124.5 (C-9), 61.75 (C-18), 14.34 (C-19) ppm; **HRMS** (EI-QTOF, $[M + H]^+$): calculated for $C_{21}H_{17}O_4$: 333.1121; found: 333.1122.

1-Phenyl-2-(thiophen-2-yl)ethane-1,2-dione (**2y**); **Pale brown solid**, **Yield**: 63 mg (58%); R_f= 0.45 (SiO_2, Hexane/EtOAc = 9:1); **Purification system**: Column chromatography (SiO_2, 100-200) (Hexane/EtOAc = 96:4); **m.p** = 62-63 °C (Lit[15] 61.5-62.5 °C); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.04 (dd, ^3J = 8.0 Hz, 2H; 6-H), 7.84 (dd, ^3J = 8.0 Hz, 2H; 4-H), 7.80 (d, ^3J = 8.0

Hz, 1H; 2-H), 7.65 (t, ^{3}J = 8.0 Hz, 1H; 8-H), 7.50 (t, ^{3}J = 8.0 Hz, 2H; 7-H), 7.18 (t, ^{3}J = 8.0 Hz, 1H; 3-H) ppm; **^{13}CNMR** (100 MHz, $CDCl_3$) δ = 192.19 (C-10), 185.71 (C-9), 139.95 (C-1), 137.0 (C-2), 136.86 (C-8), 134.98 (C-5), 132.7 (C-2), 130.33 (C-7), 129.03 (C-6), 128.93 (C-3) ppm; **HRMS** (EI-QTOF, $[M + H]^+$): calculated for $C_{12}H_9O_2S$: 217.0318; found: 217.0320.

Benzoic acid (**4a**)[16]; **White solid**, **Yield**: 13 mg (21%); $\boldsymbol{R_f}$= 0.1 (SiO_2, Hexane/EtOAc = 9:1); **Purification system**: Column chromatography (SiO_2, 100-200) (Hexane/EtOAc = 85:15); **m.p** = 123-124°C (Lit[16] 124-126 °C); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.13 (d, ^{3}J = 8.0 Hz, 2H; 2-H), 7.64 (t, ^{3}J = 8.0 Hz, 1H; 4-H), 7.49 (t, ^{3}J = 8.0 Hz, 2H; 3-H) ppm; **^{13}CNMR** (100 MHz, $CDCl_3$) δ = 172.2 (C-5), 133.8 (C-4), 130.2 (C-2), 129.3 (C-1), 128.5 (C-3) ppm; **HRMS** (EI-QTOF, $[M + H]^+$): calculated for $C_7H_7O_2$: 123.0441; found: 123.0440.

10. NMR Spectral Data

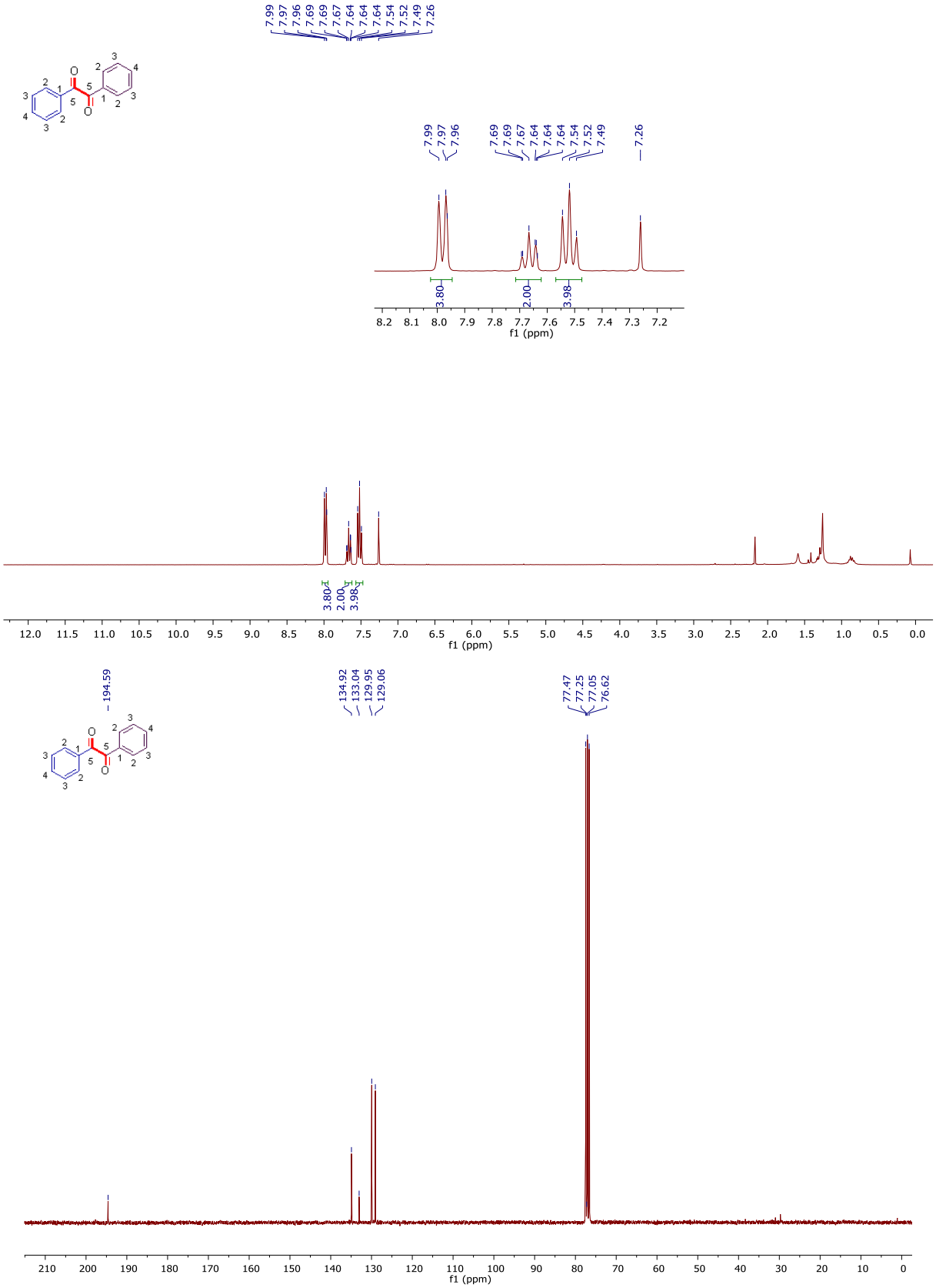


Figure S5. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **2a** in $CDCl_3$.

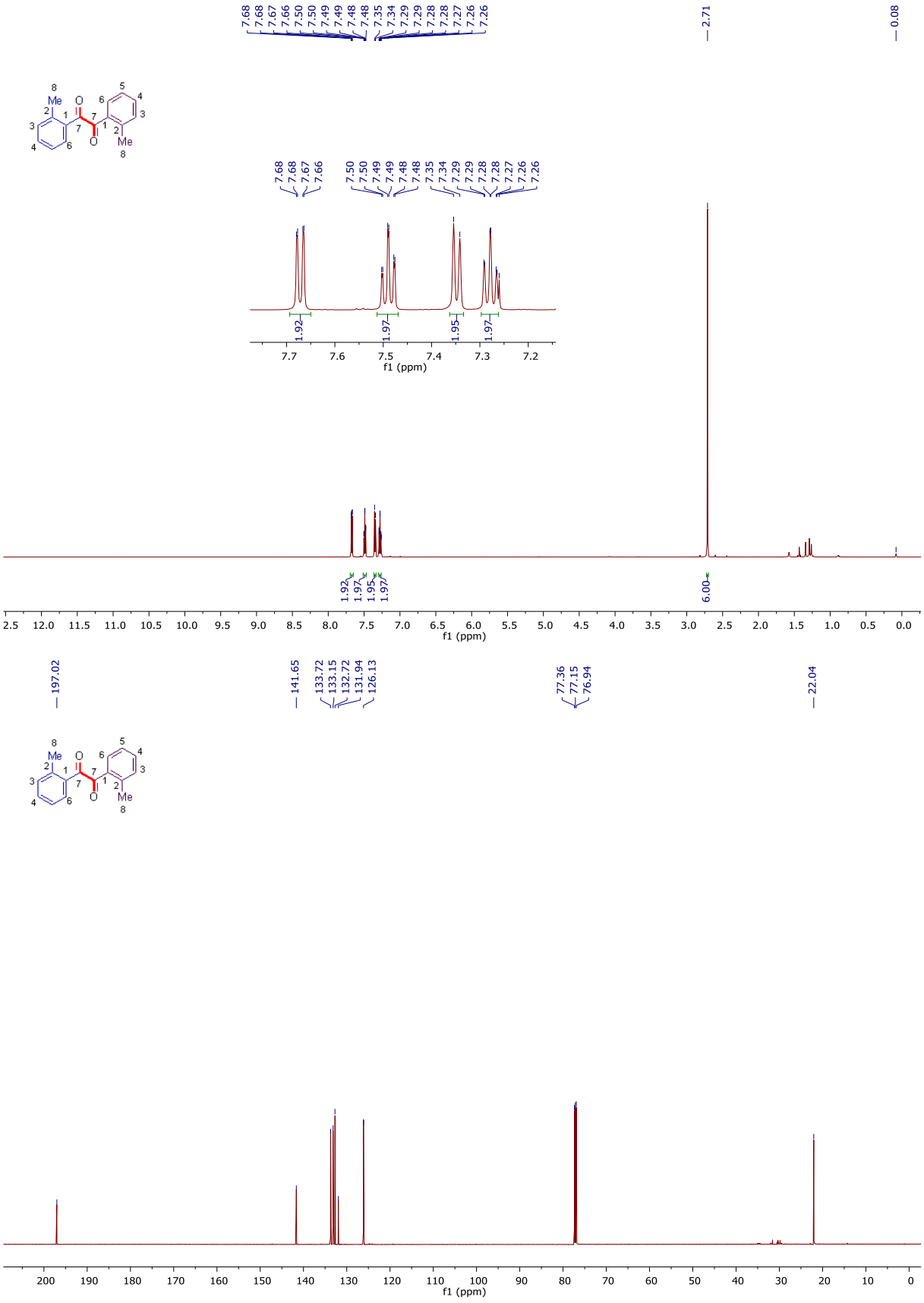


Figure S6. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **2b** in $CDCl_3$.

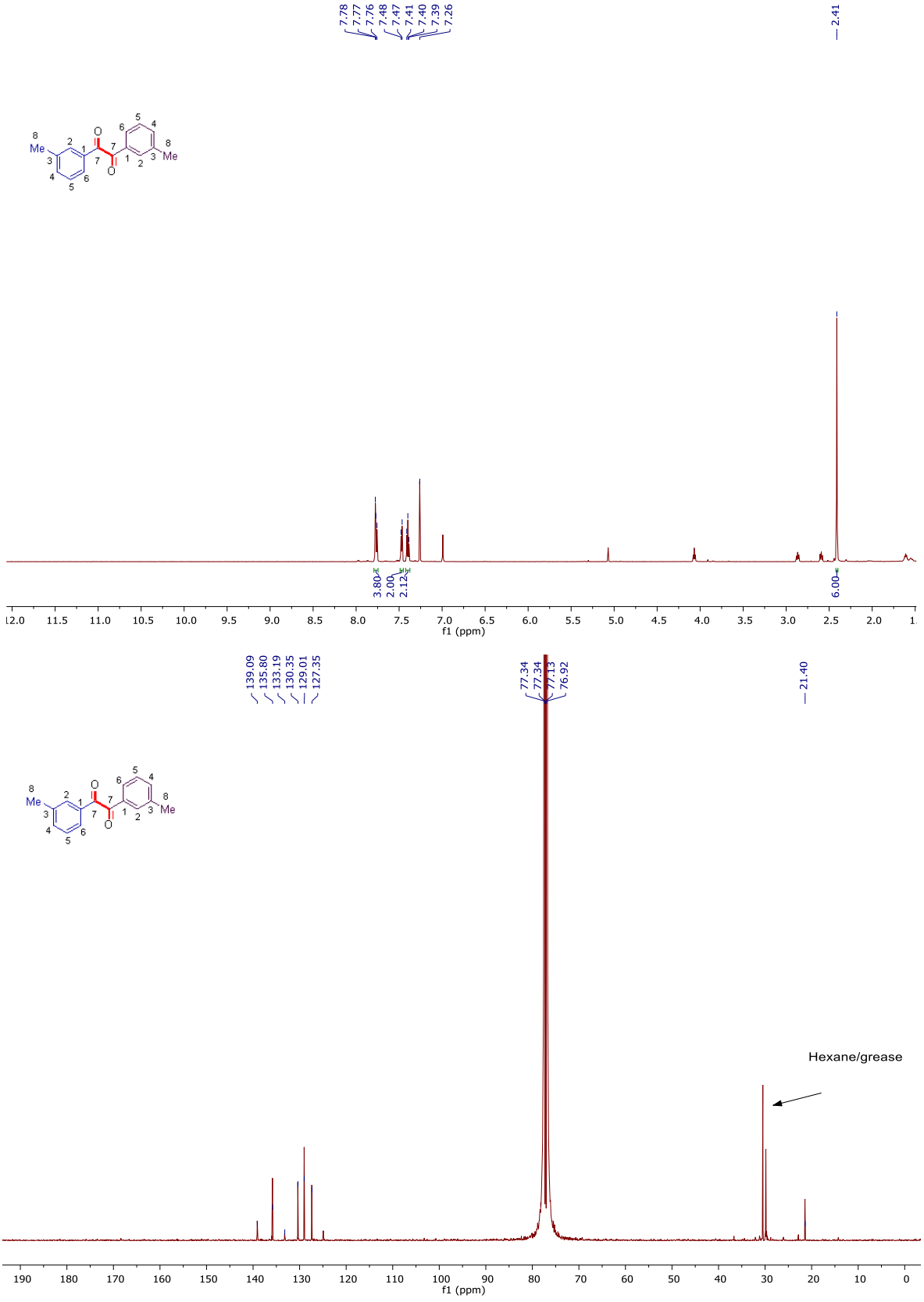


Figure S7. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **2c** in $CDCl_3$.

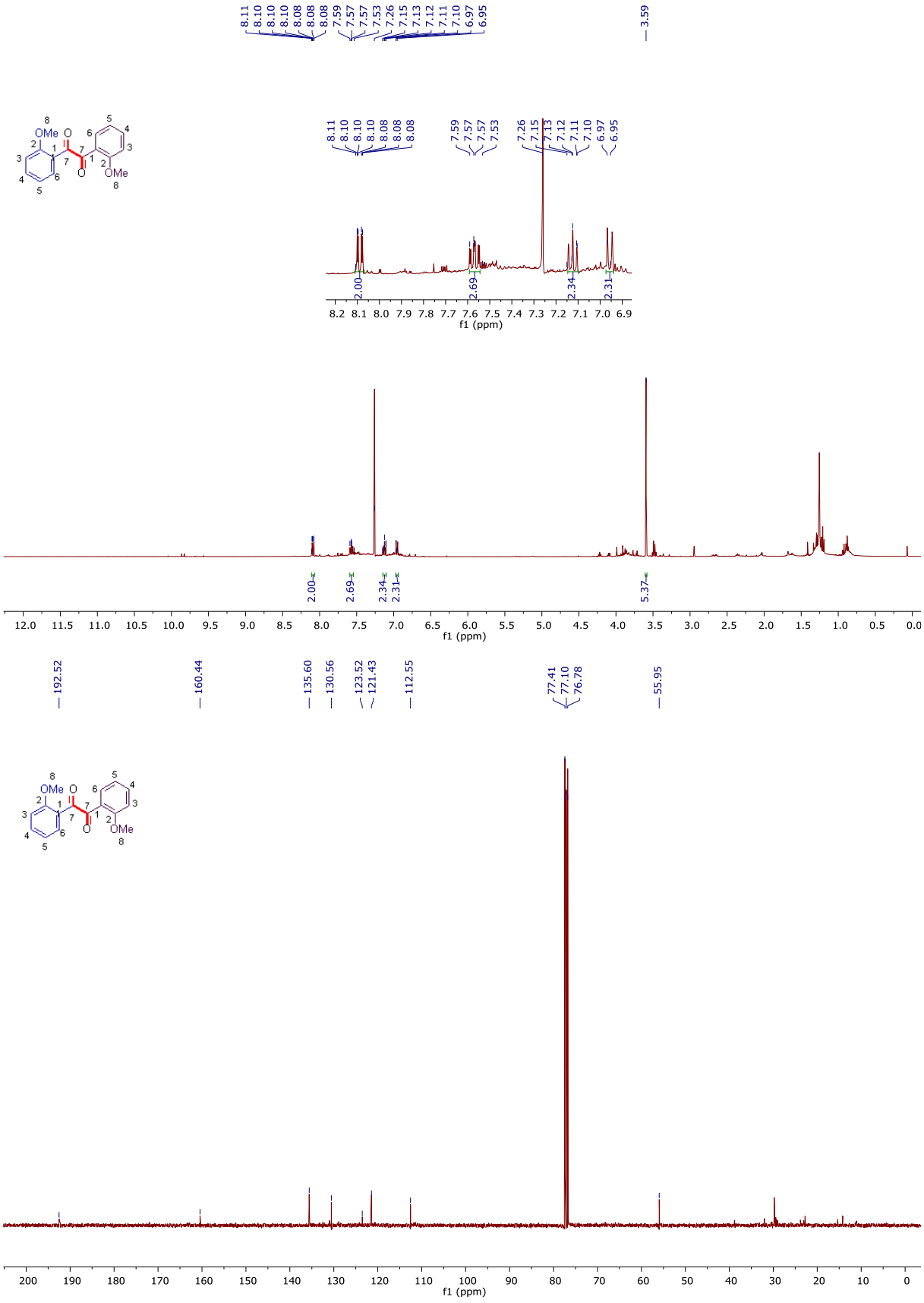


Figure S8. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **2d** in $CDCl_3$.

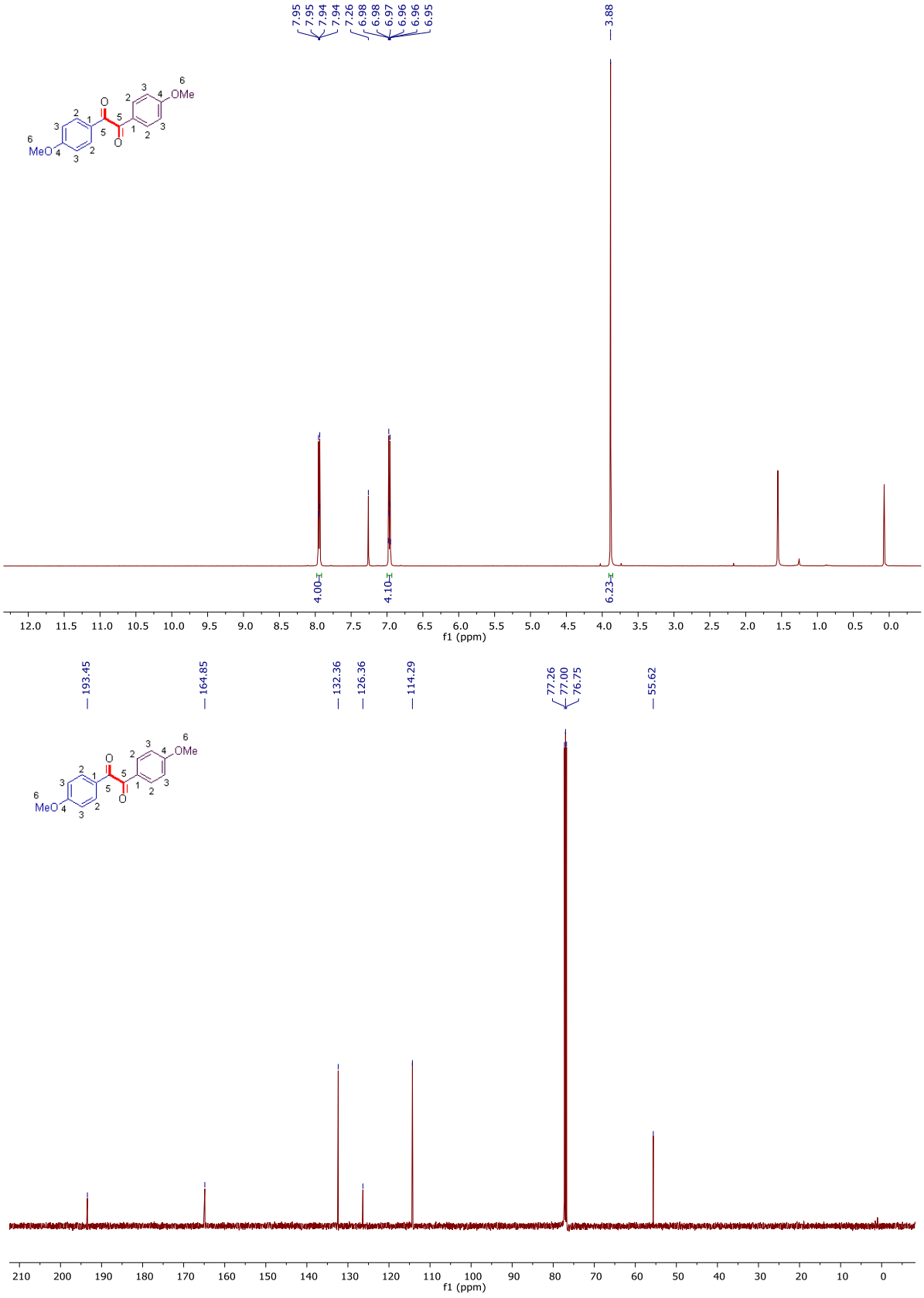


Figure S9. ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectra of **2e** in $CDCl_3$.

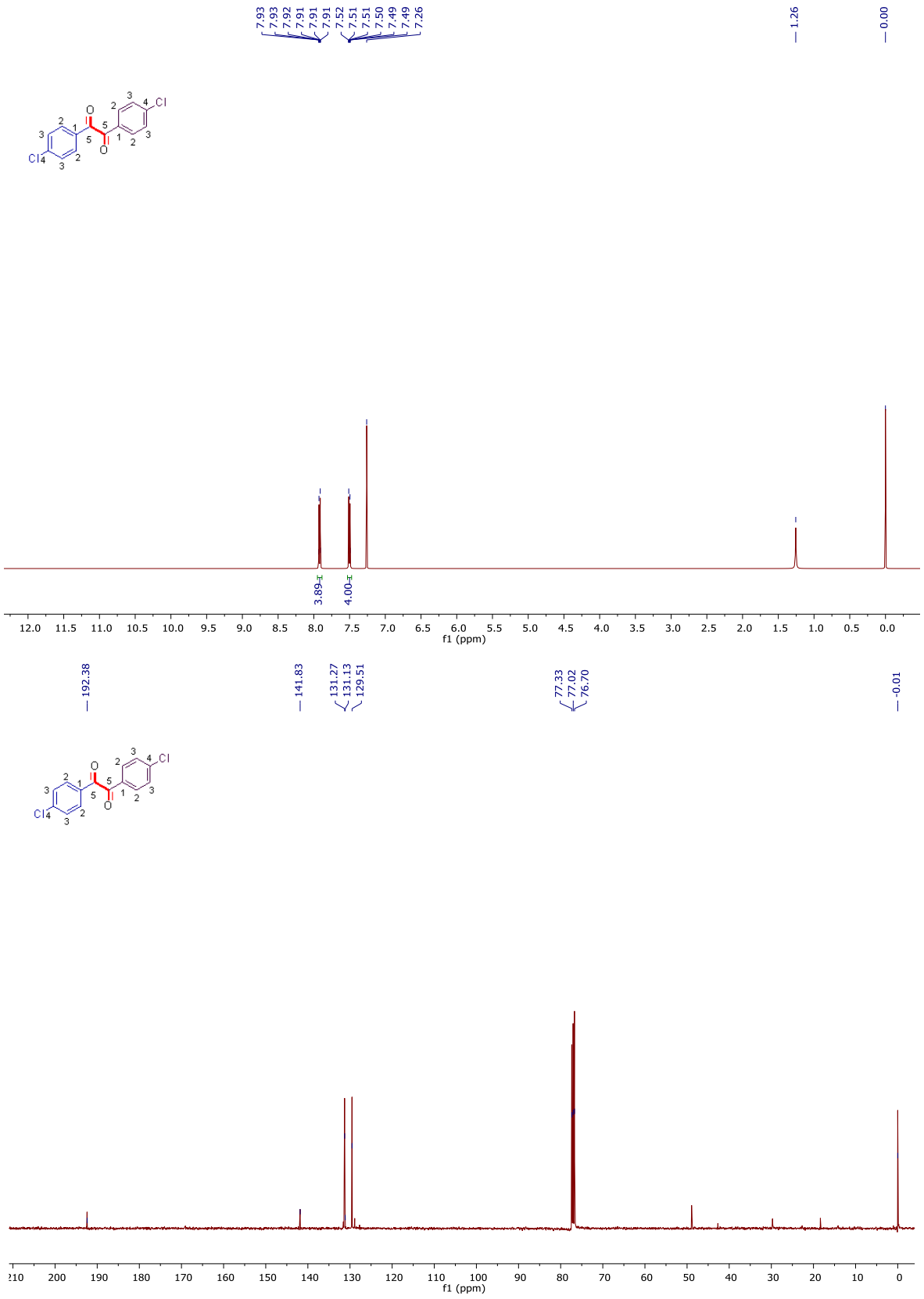


Figure S10. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **2f** in $CDCl_3$.

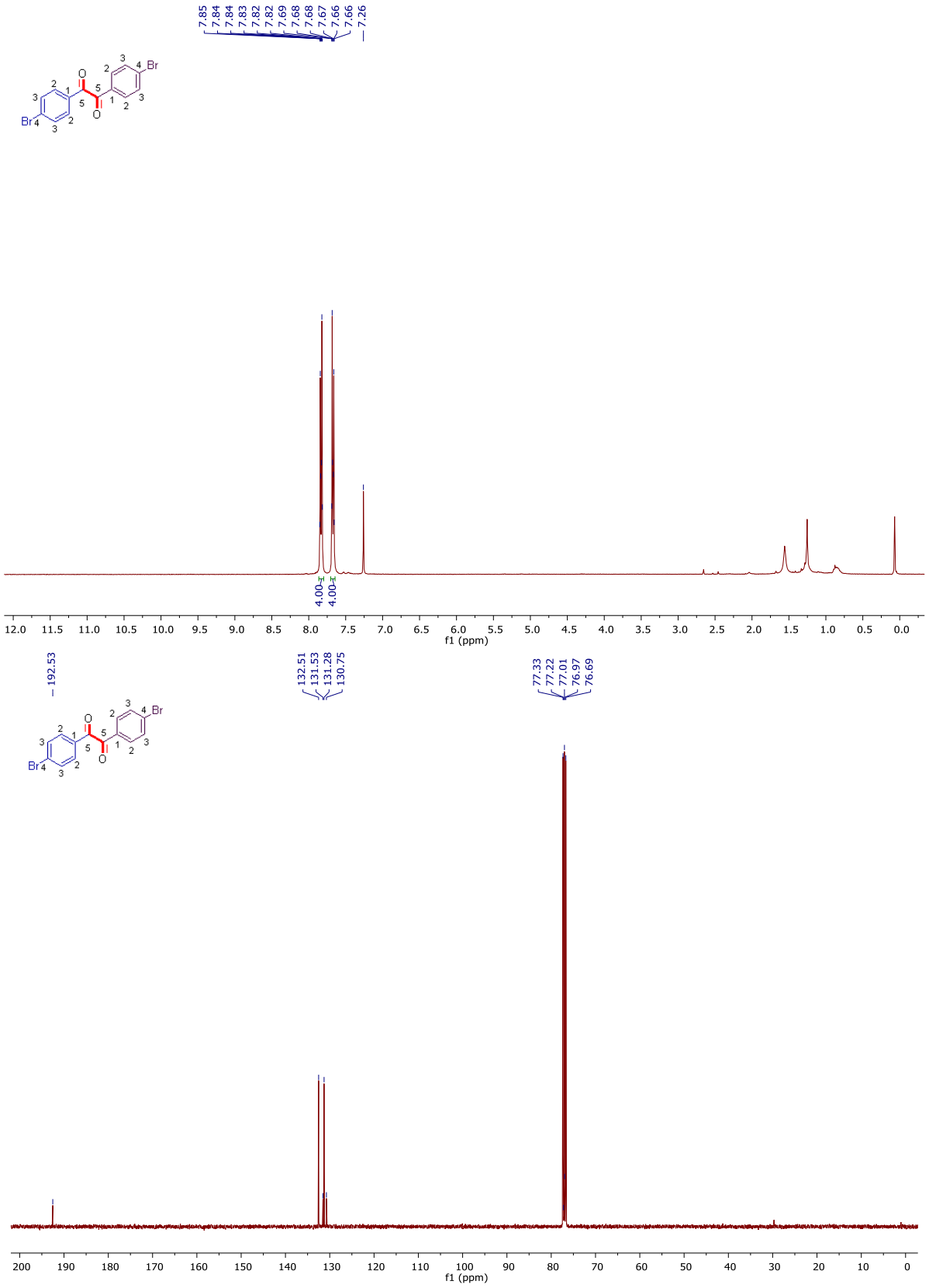


Figure S11. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **2g** in $CDCl_3$.

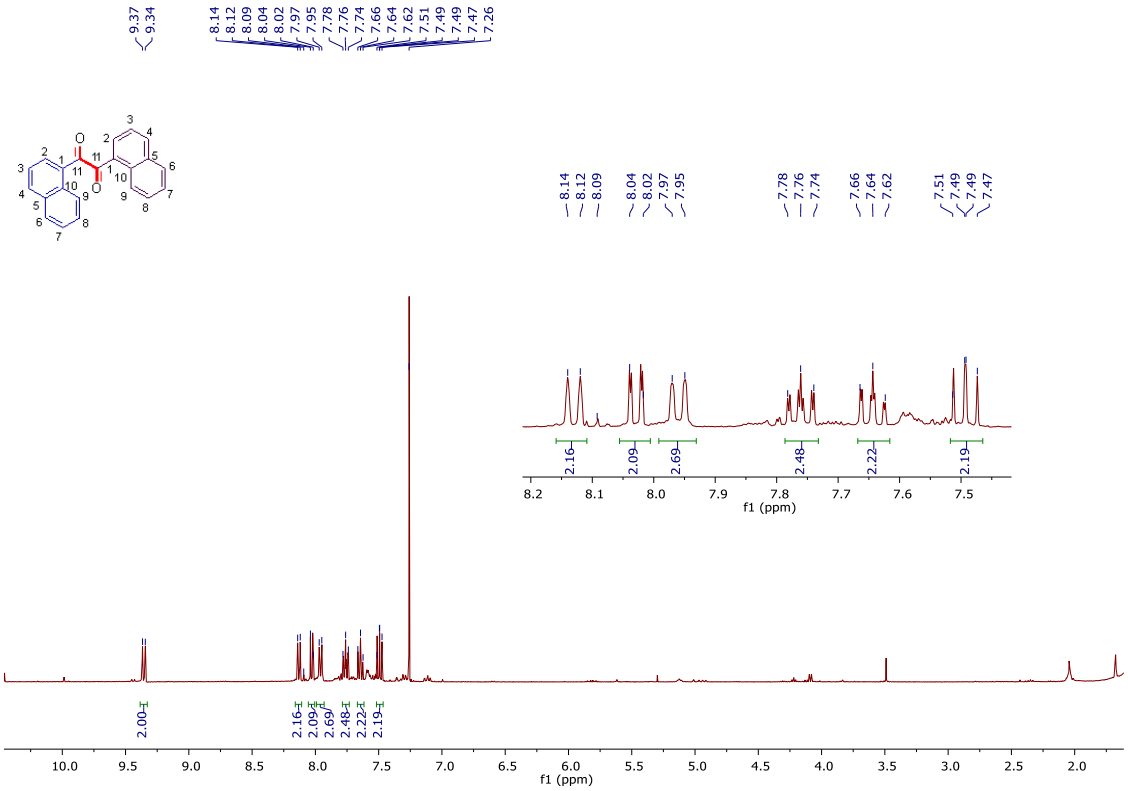


Figure S12. ^{1}H (400 MHz) NMR spectra of **2h** in $CDCl_3$.

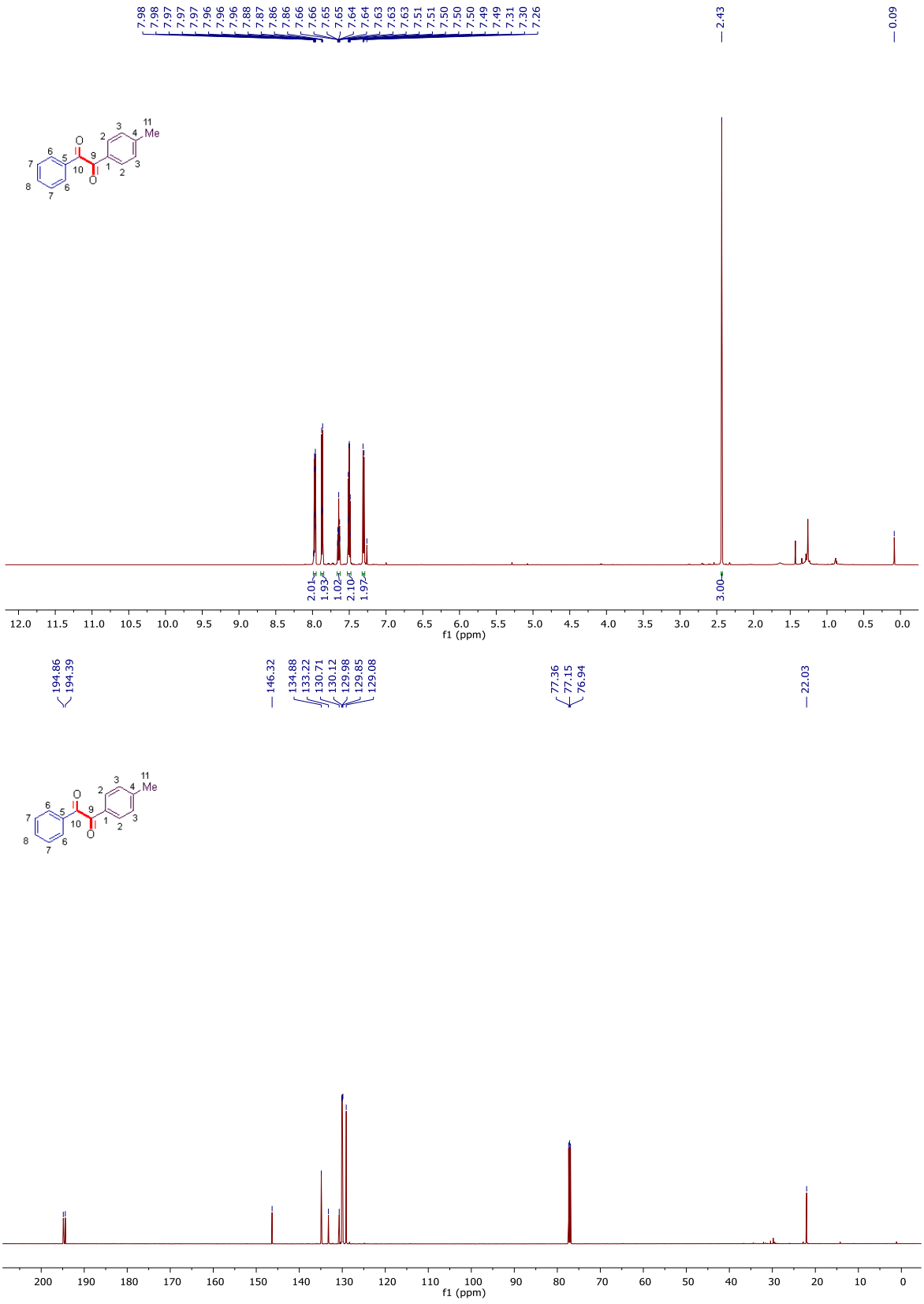


Figure S13. ^{1}H (600 MHz), ^{13}C (150 MHz) NMR spectra of **2i** in $CDCl_3$.

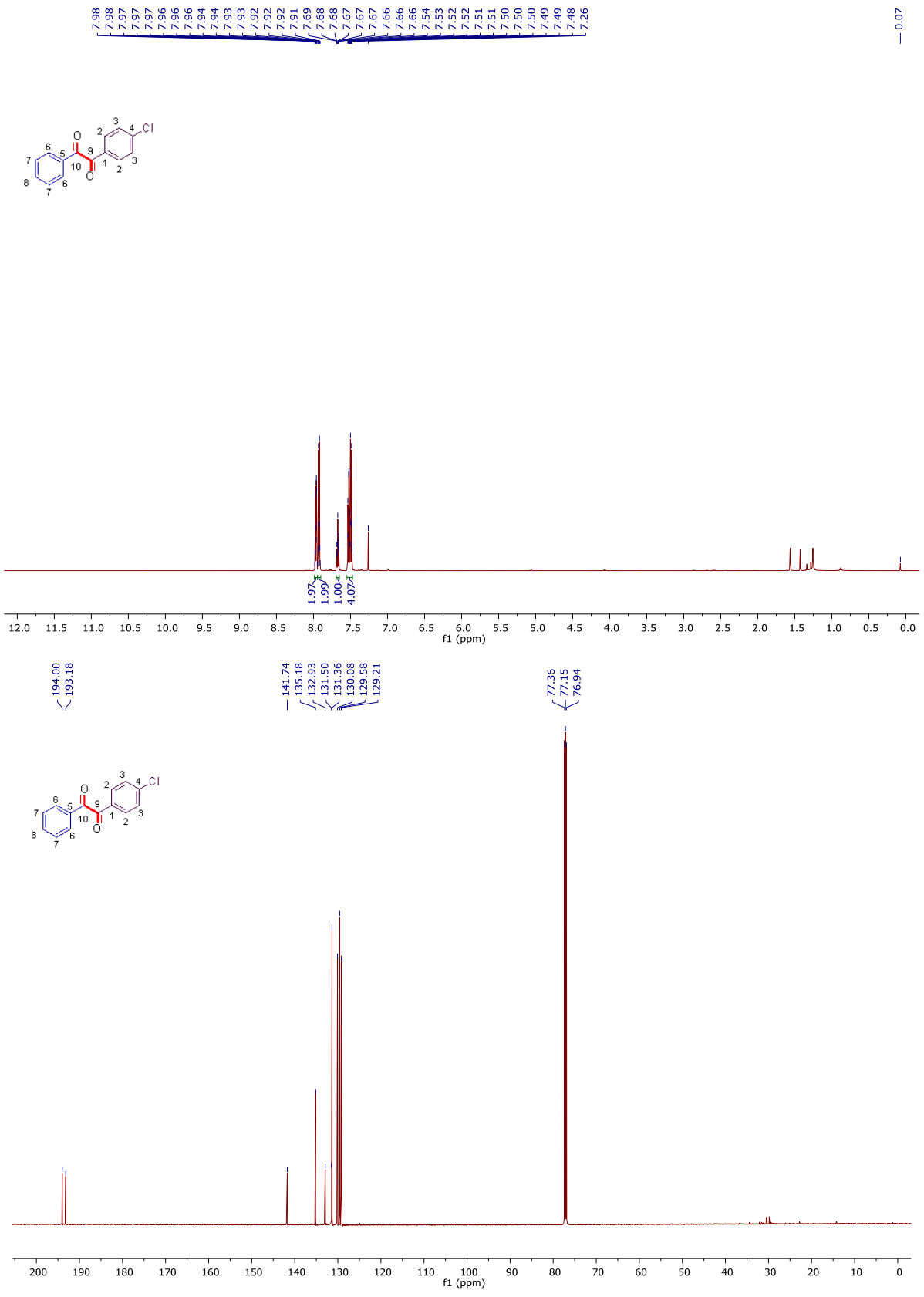


Figure S14. ^{1}H (600 MHz), ^{13}C (150 MHz) NMR spectra of **2j** in $CDCl_3$.

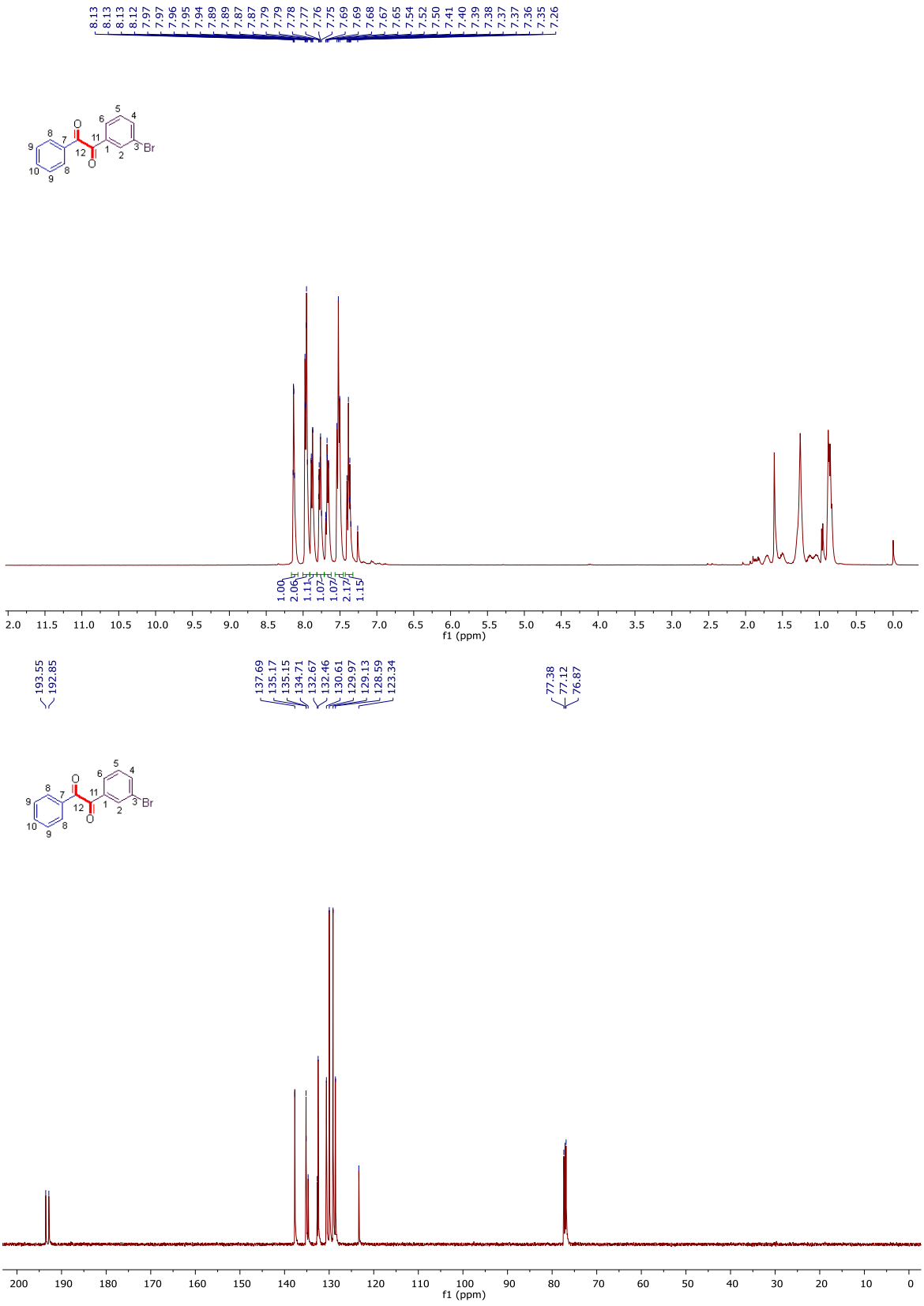


Figure S15. ^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectra of **2k** in $CDCl_3$.

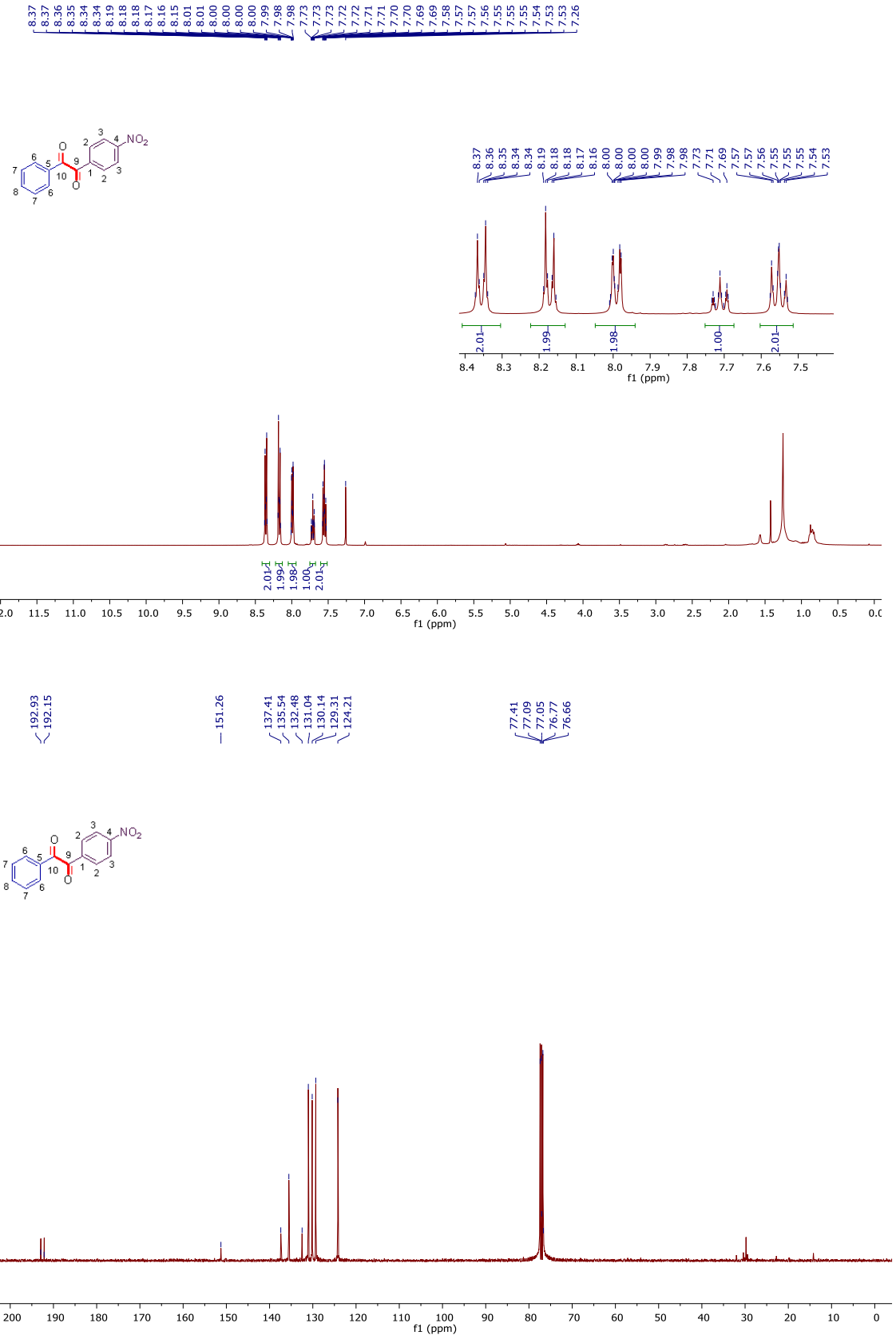


Figure S16. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **2l** in $CDCl_3$.

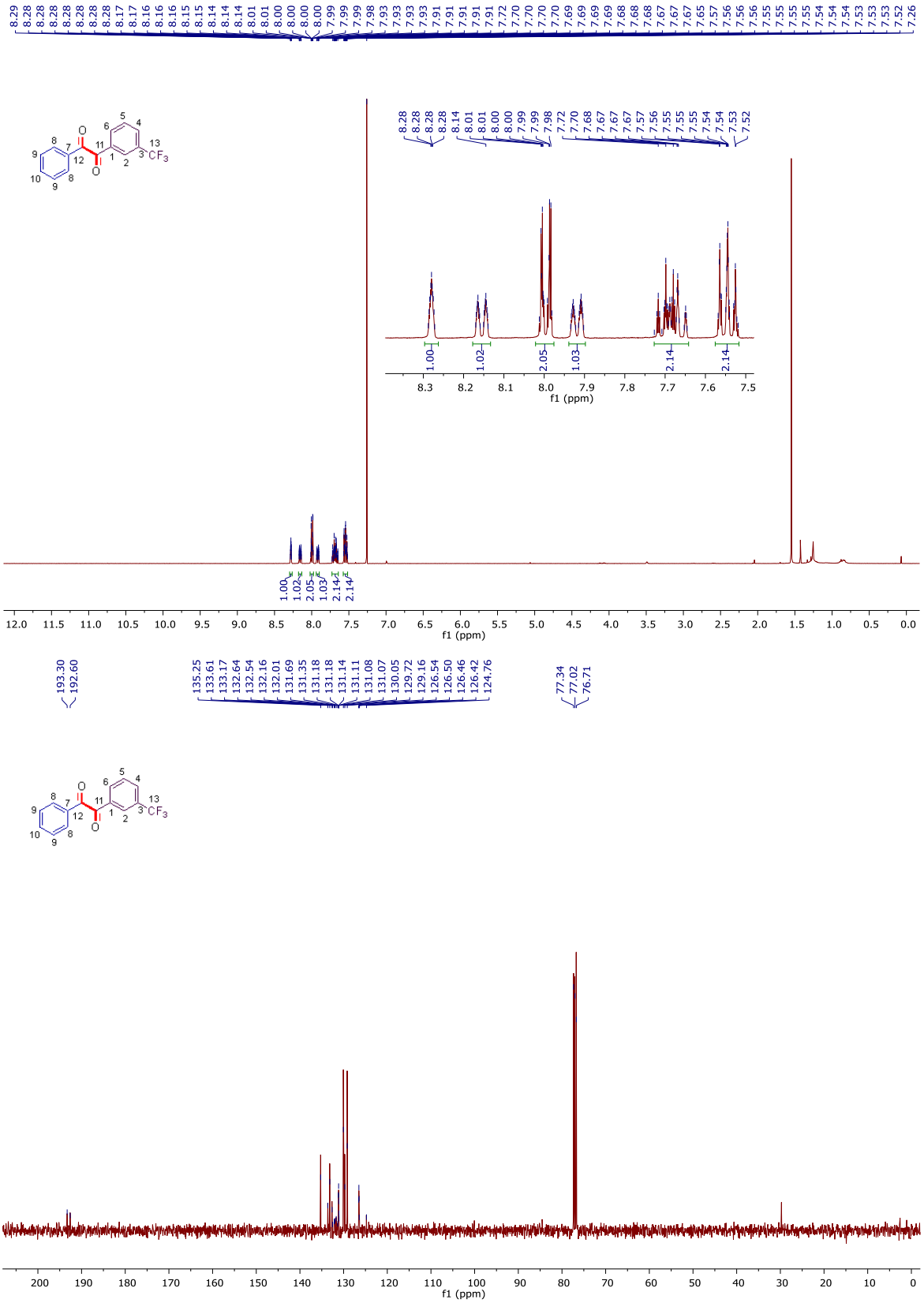


Figure S17. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **2m** in $CDCl_3$.

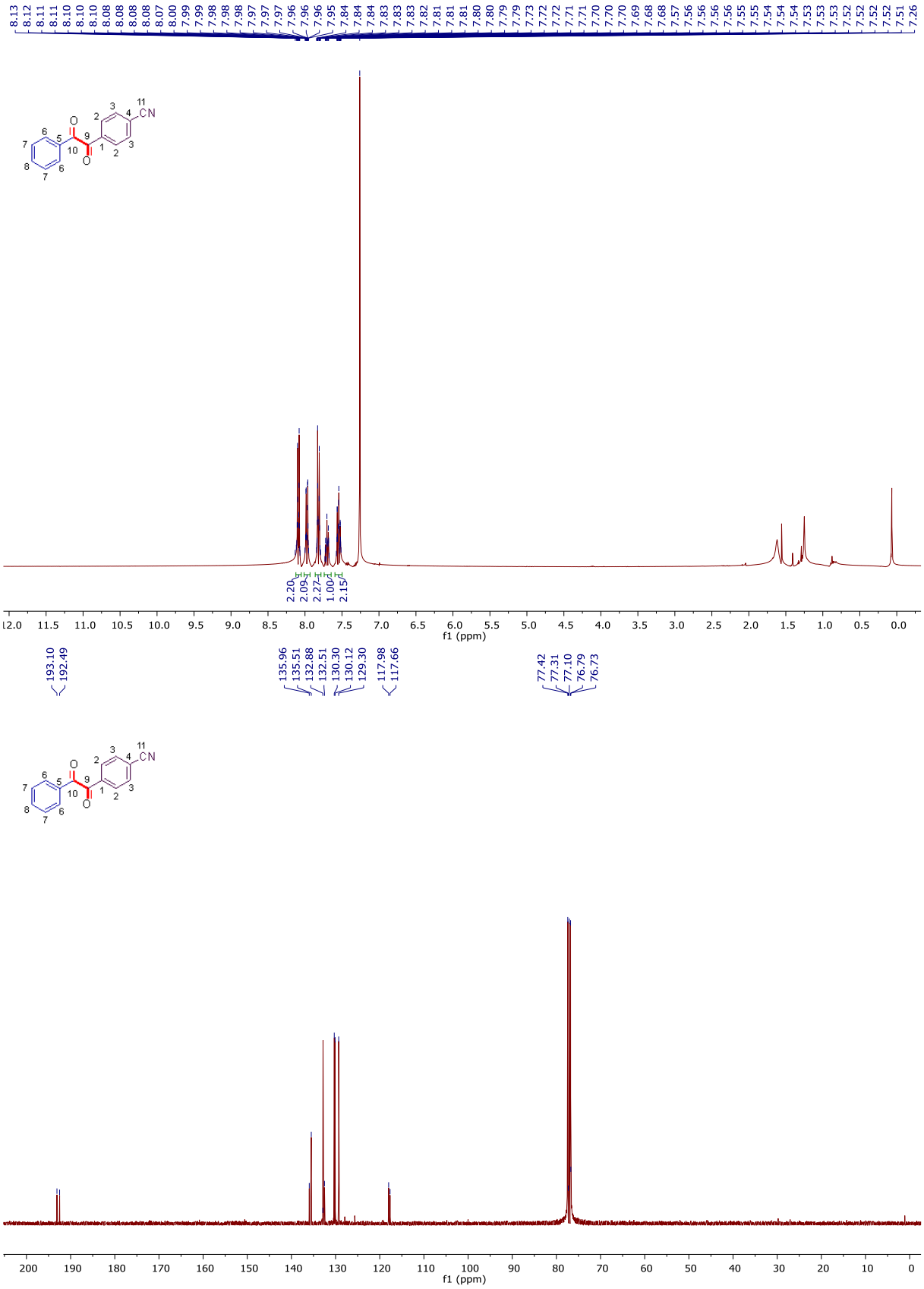


Figure S18. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **2n** in $CDCl_3$.

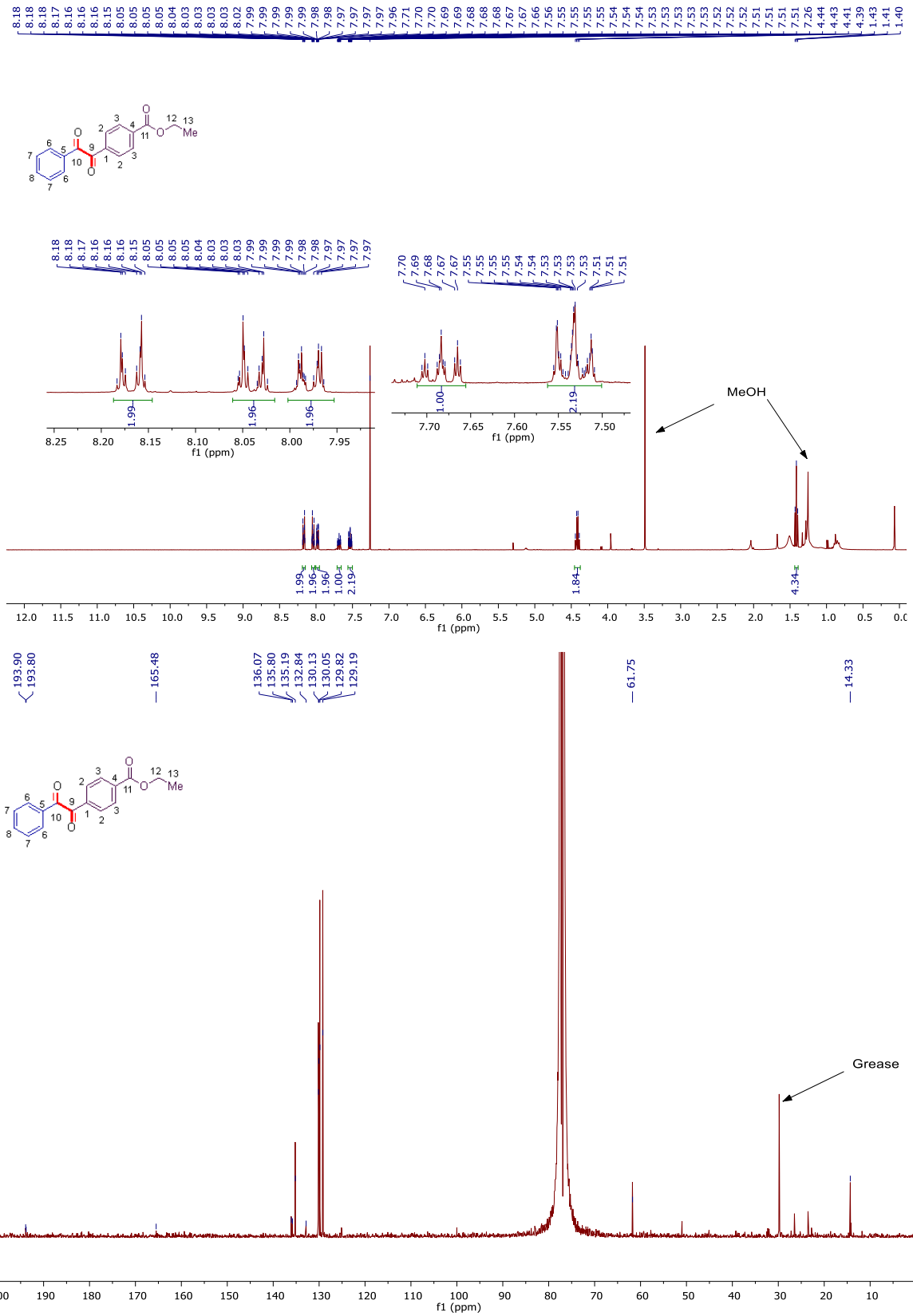


Figure S19. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **2o** in $CDCl_3$.

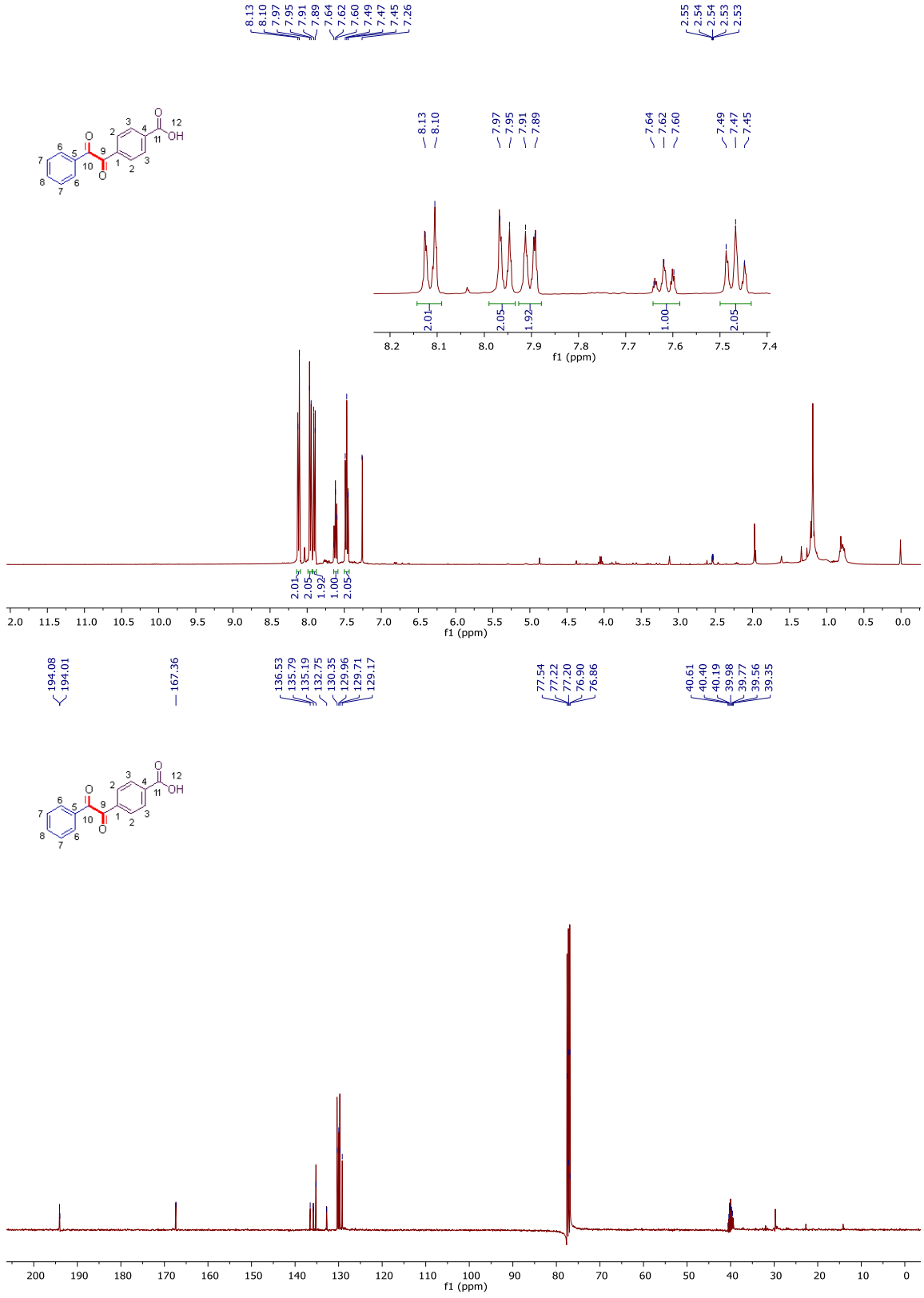


Figure S20. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **2p** in $CDCl_3$:DMSO-d_6 (8:2).

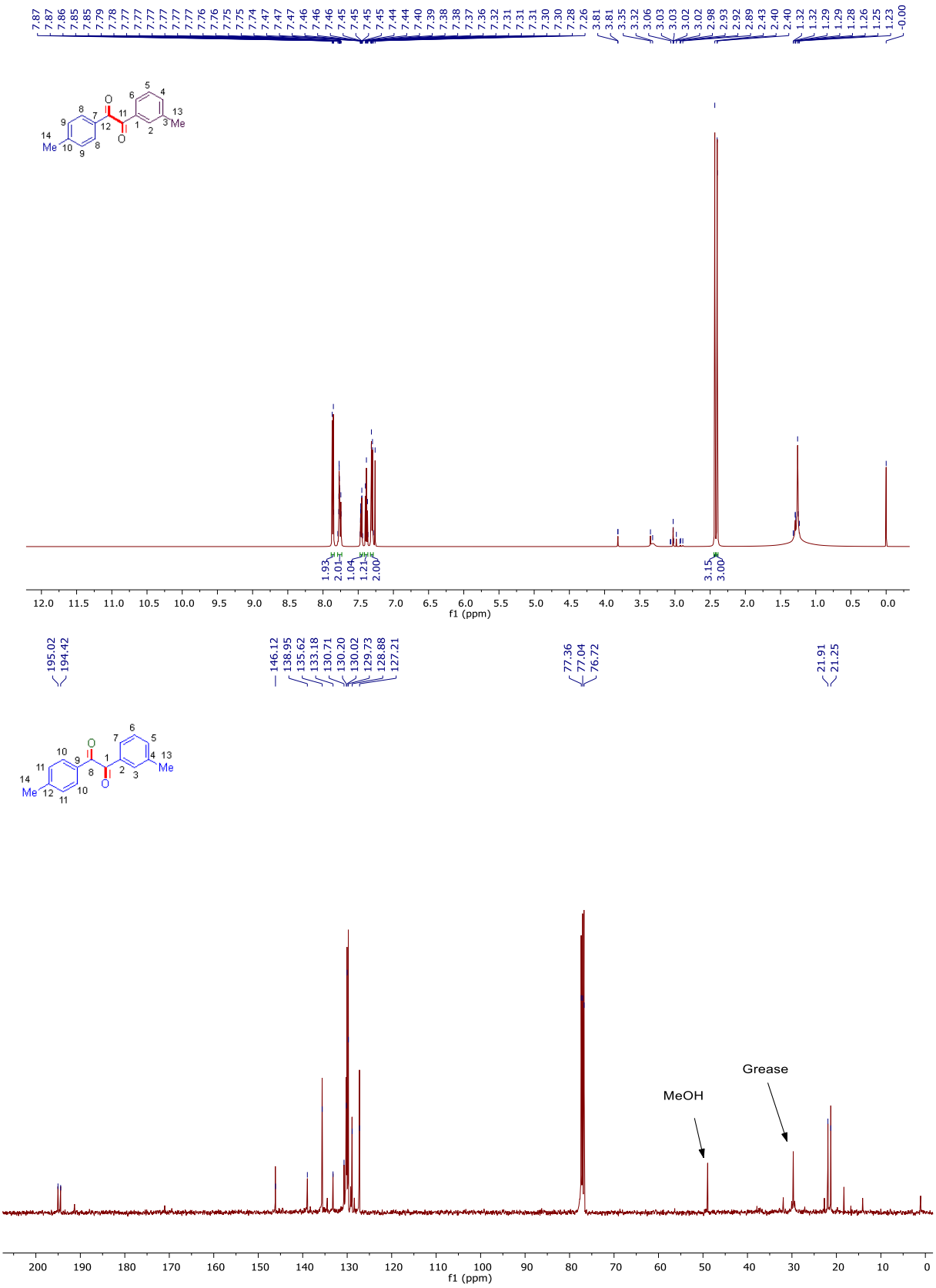


Figure S21. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **2q** in $CDCl_3$.

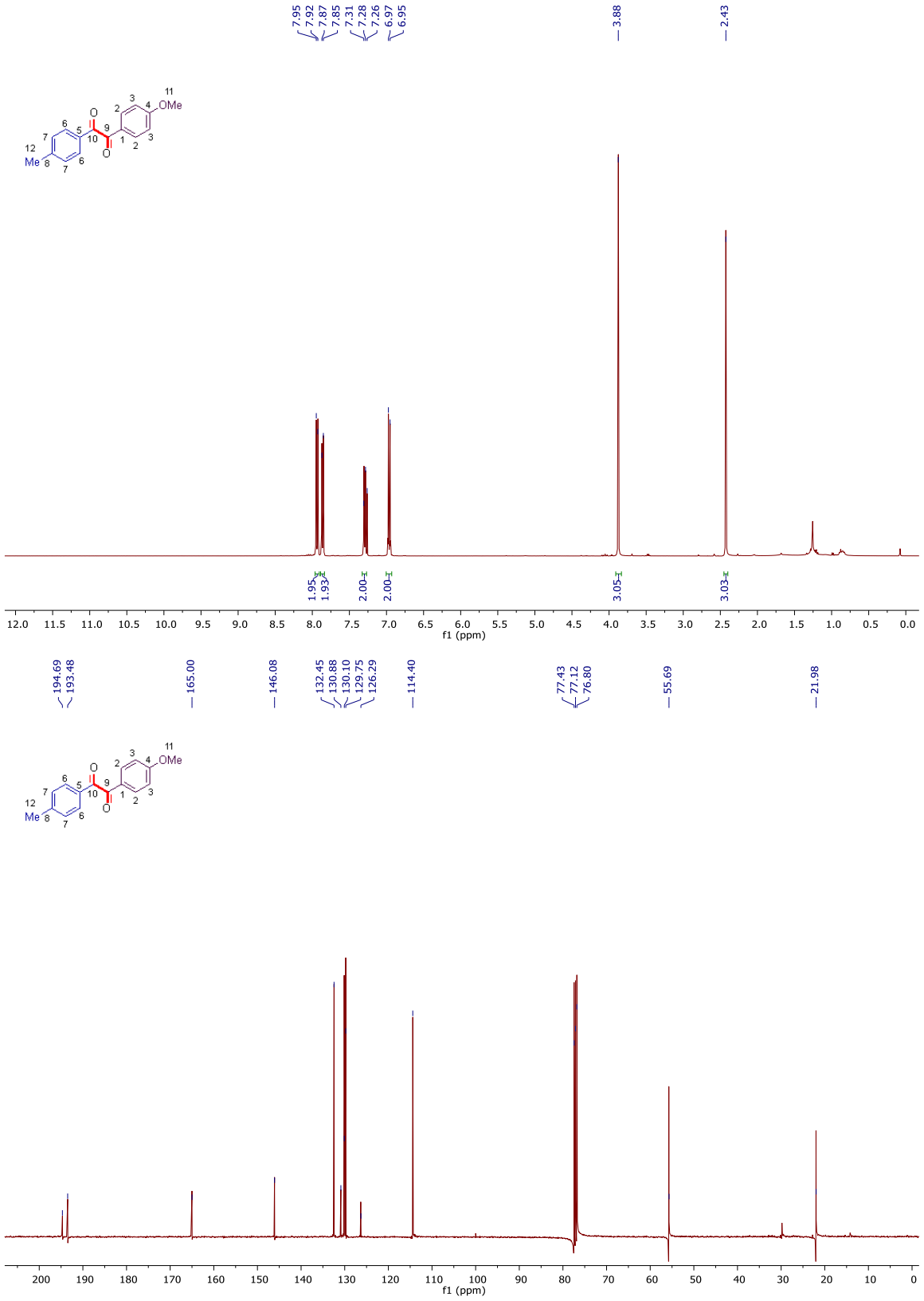


Figure S22. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **2r** in $CDCl_3$.

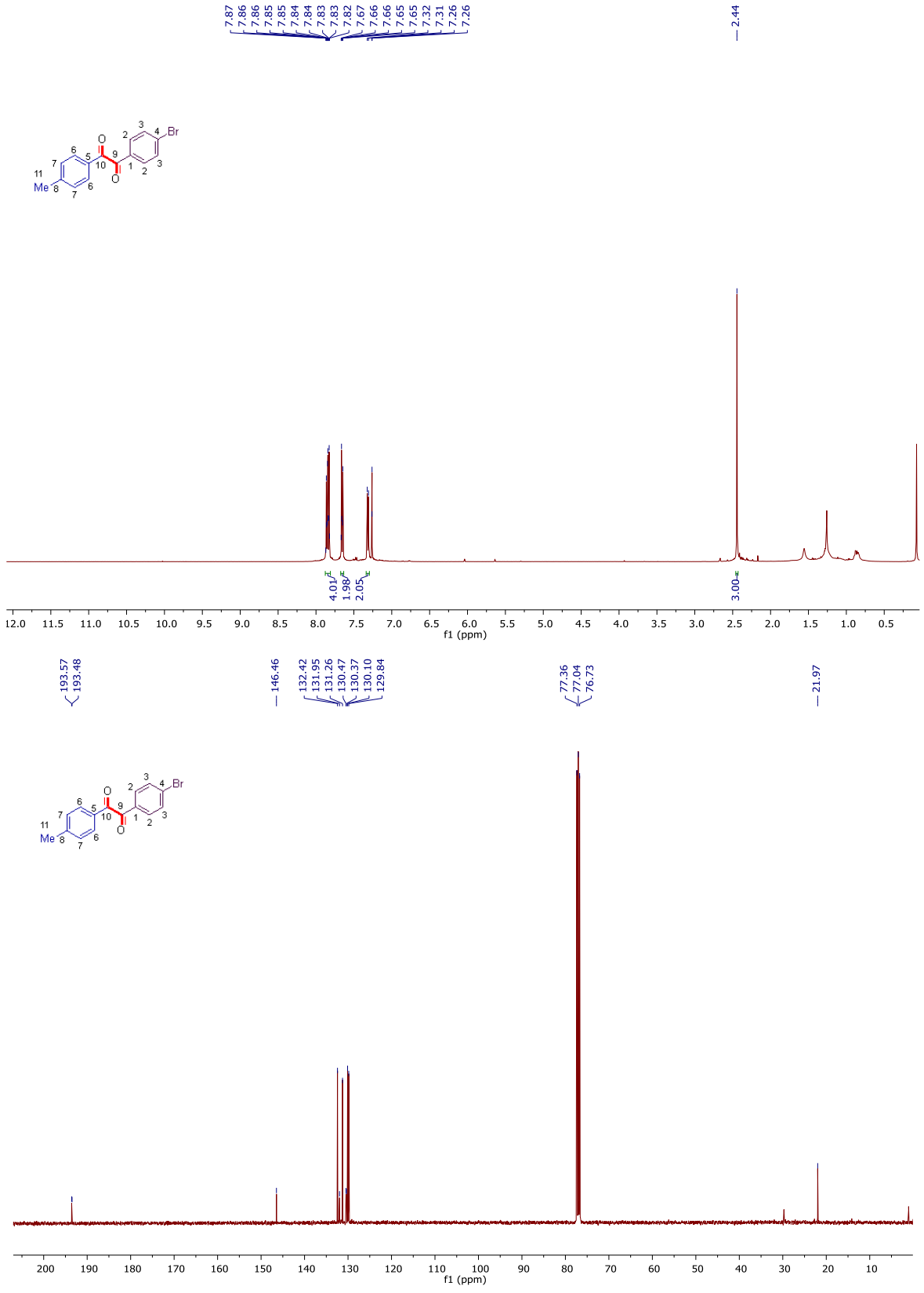


Figure S23. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **2s** in $CDCl_3$.

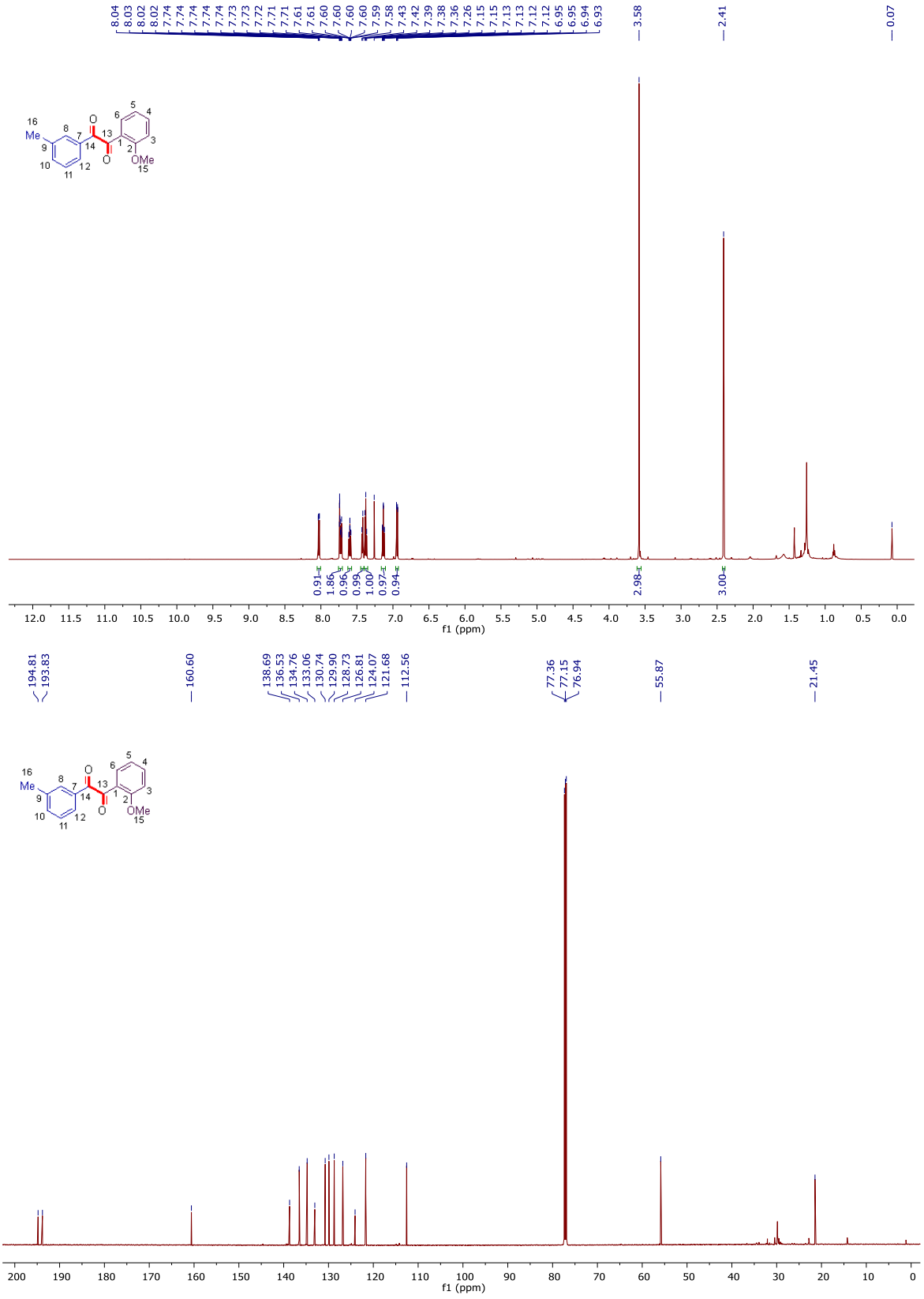


Figure S24. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **2t** in $CDCl_3$.

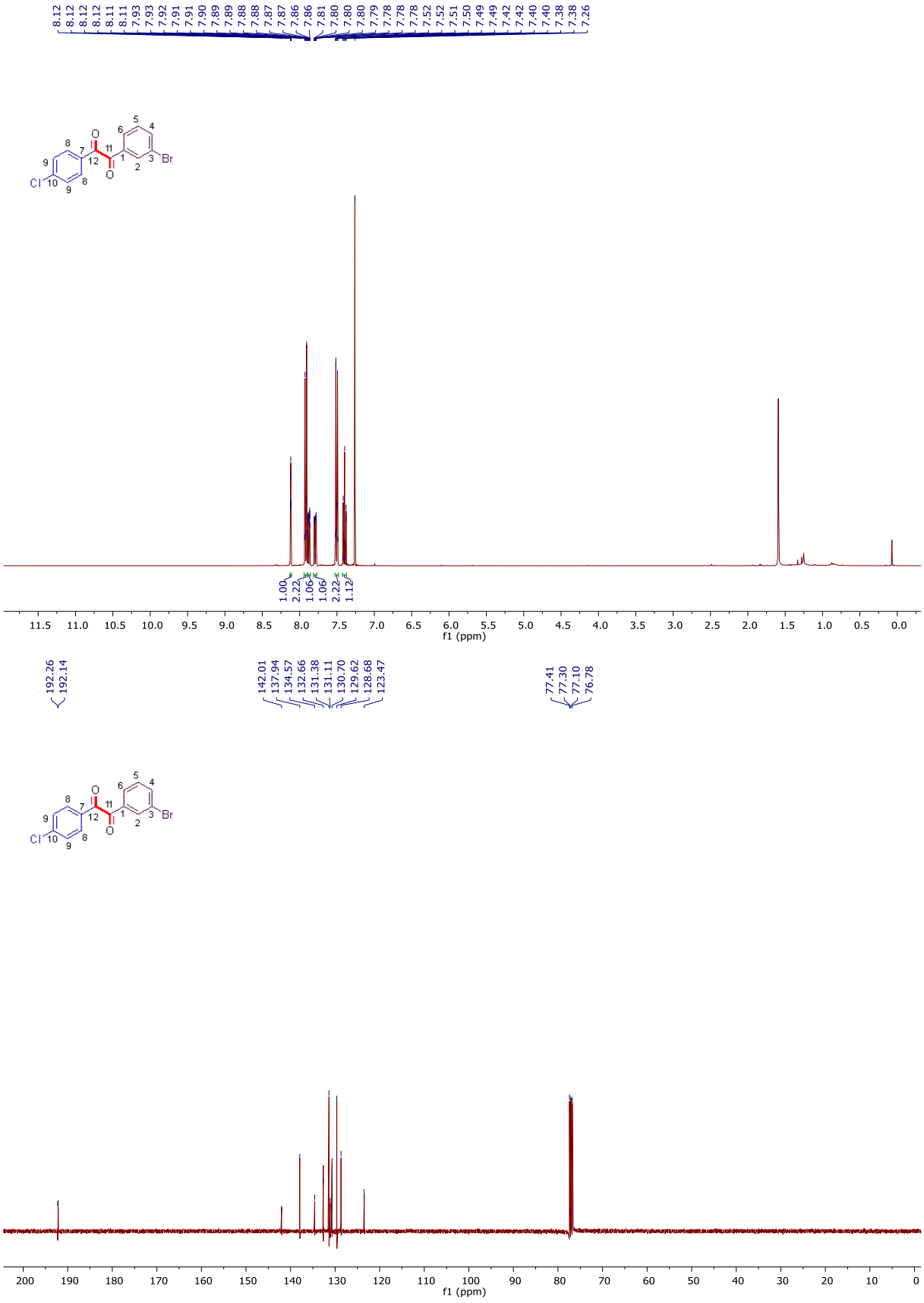


Figure S25. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **2u** in $CDCl_3$.

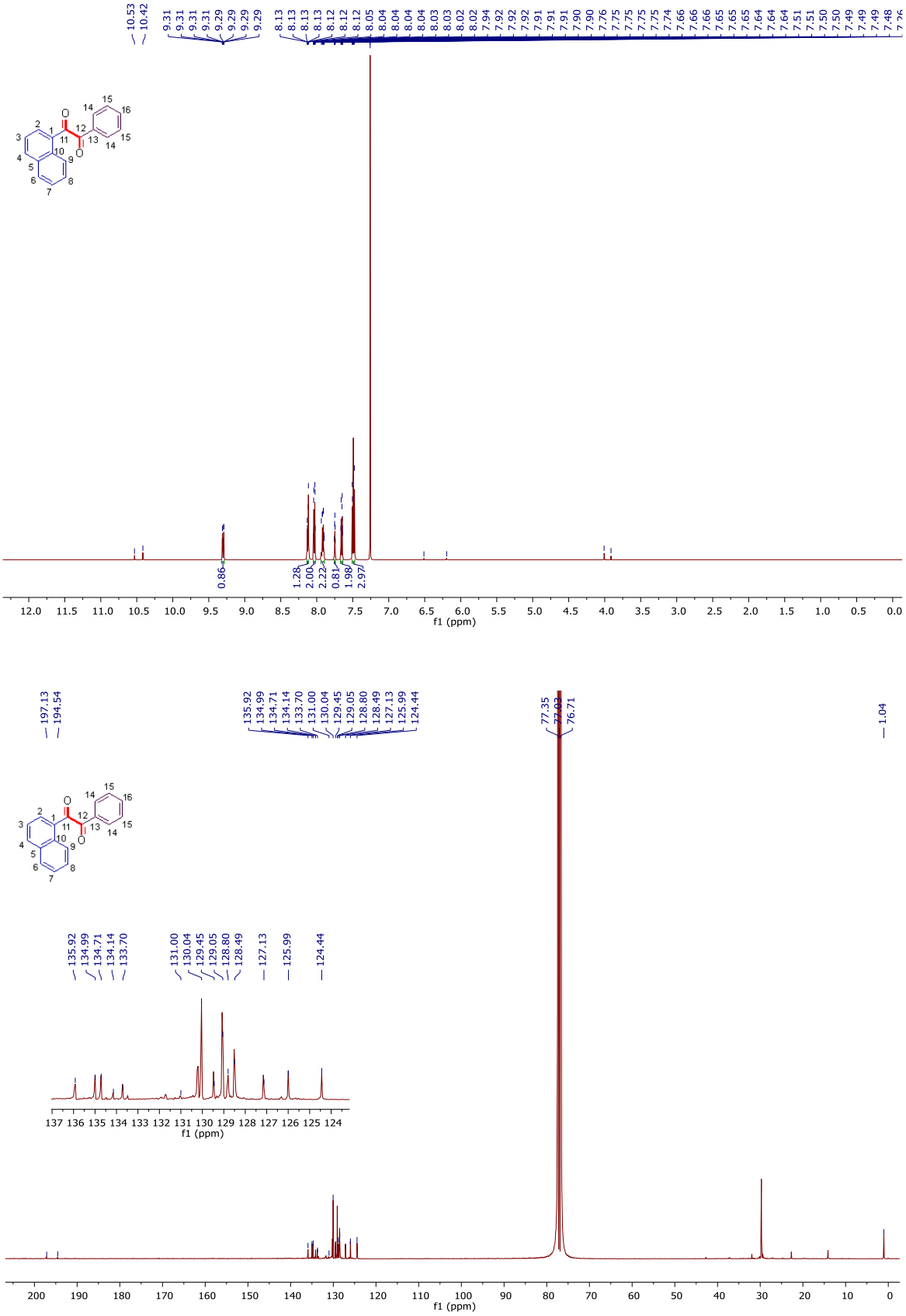


Figure S26. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **2v** in $CDCl_3$.

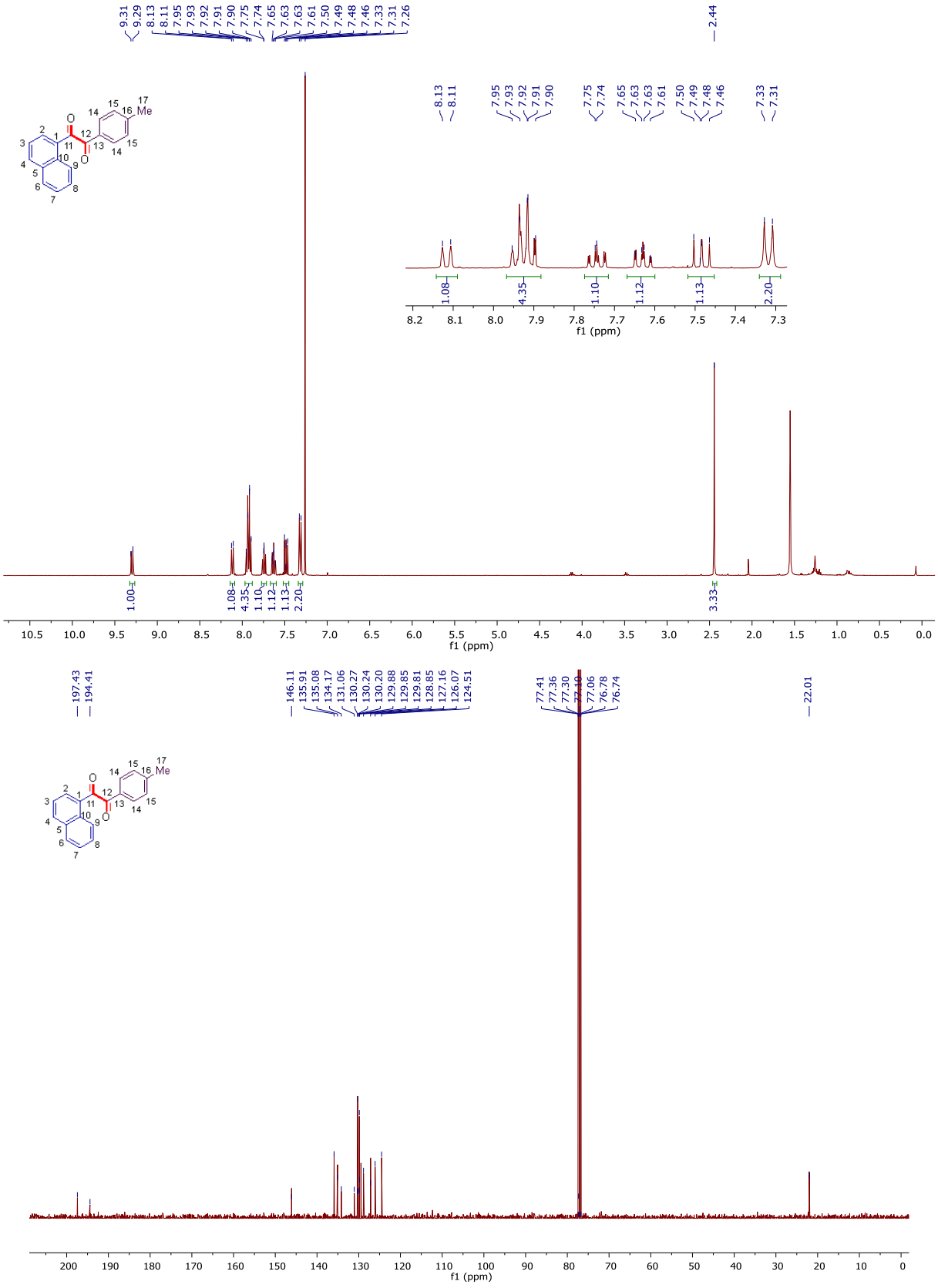


Figure S27. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **2w** in $CDCl_3$.

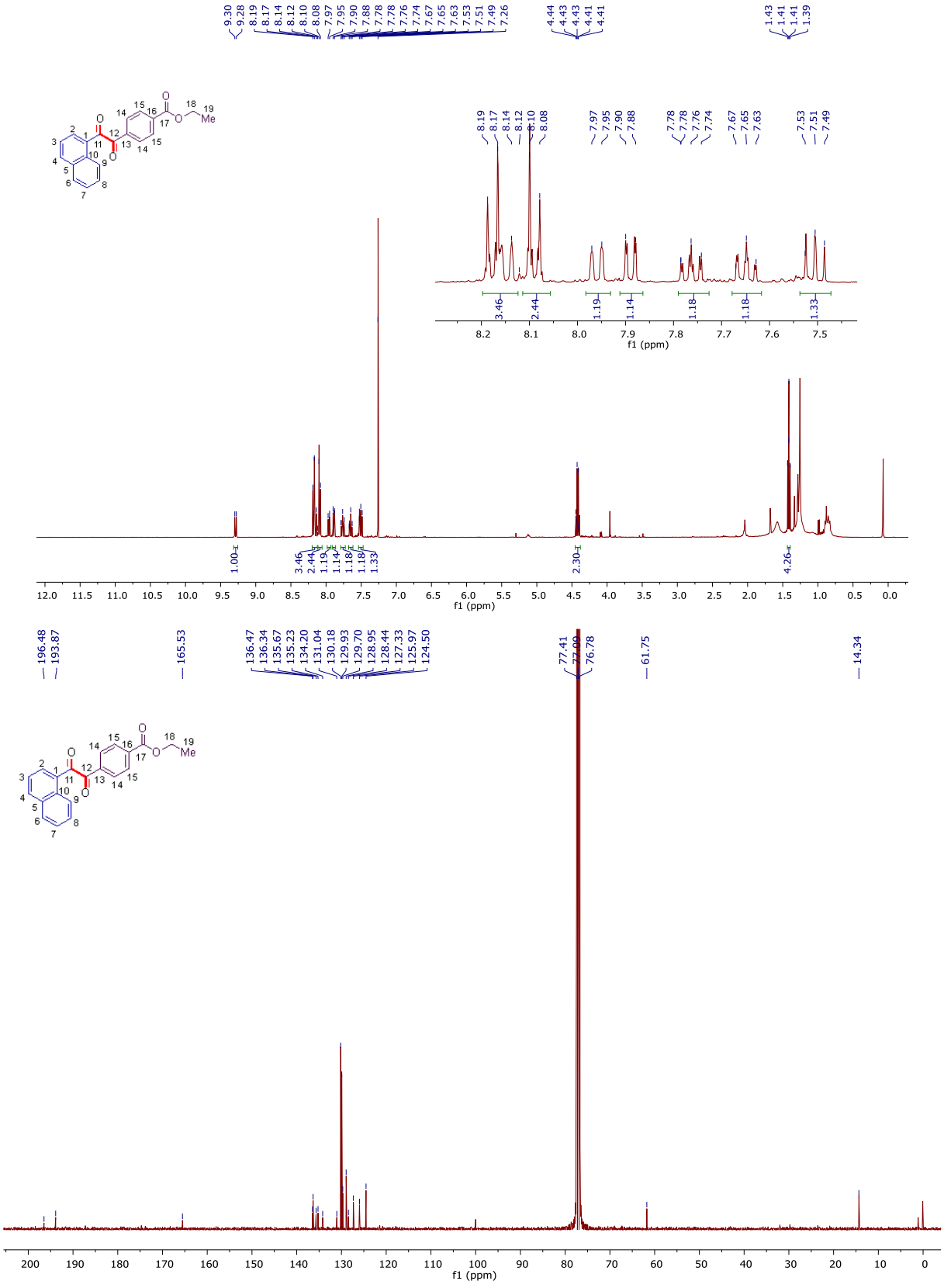


Figure S28. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **2x** in $CDCl_3$.

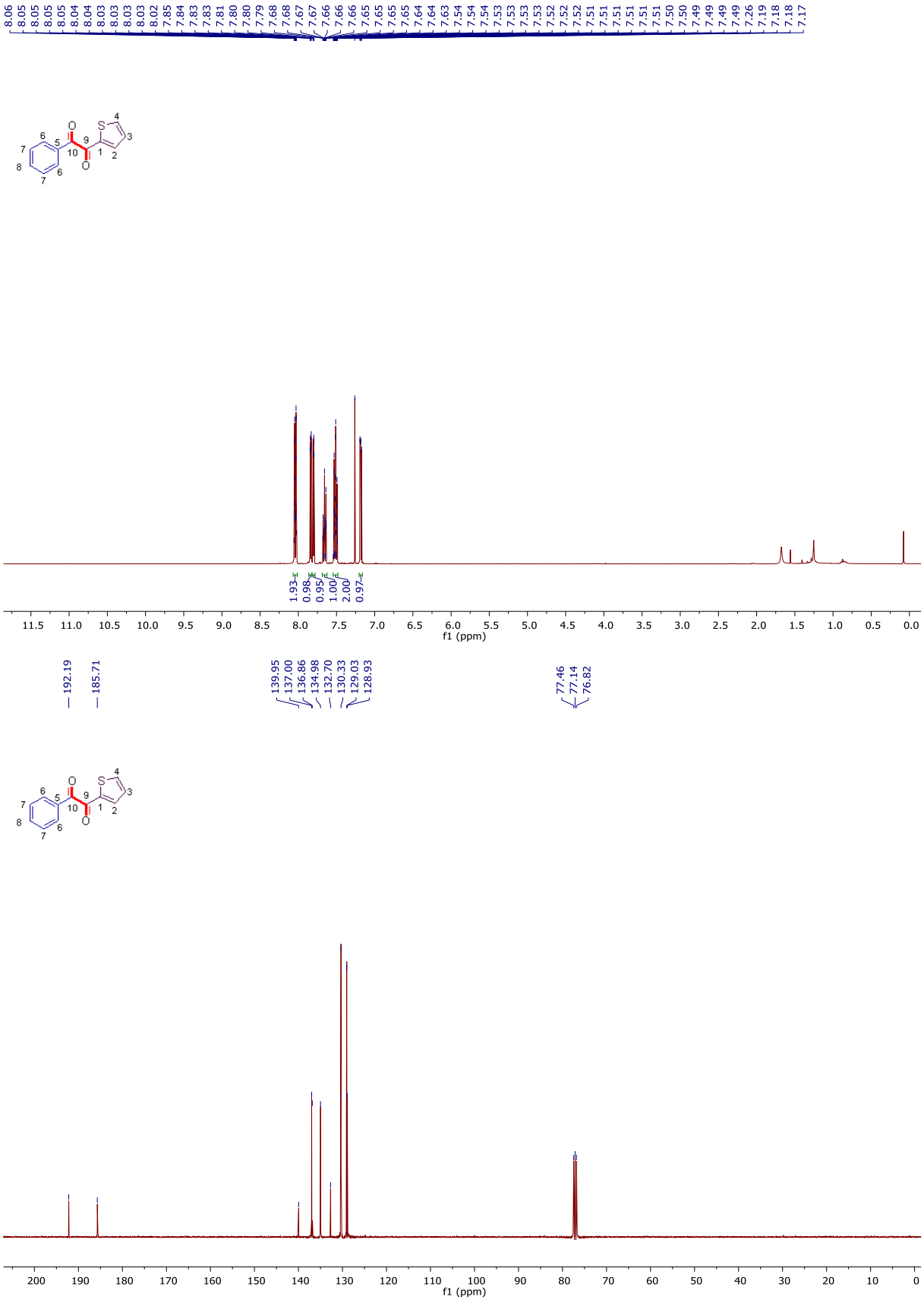


Figure S29. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **2y** in $CDCl_3$.

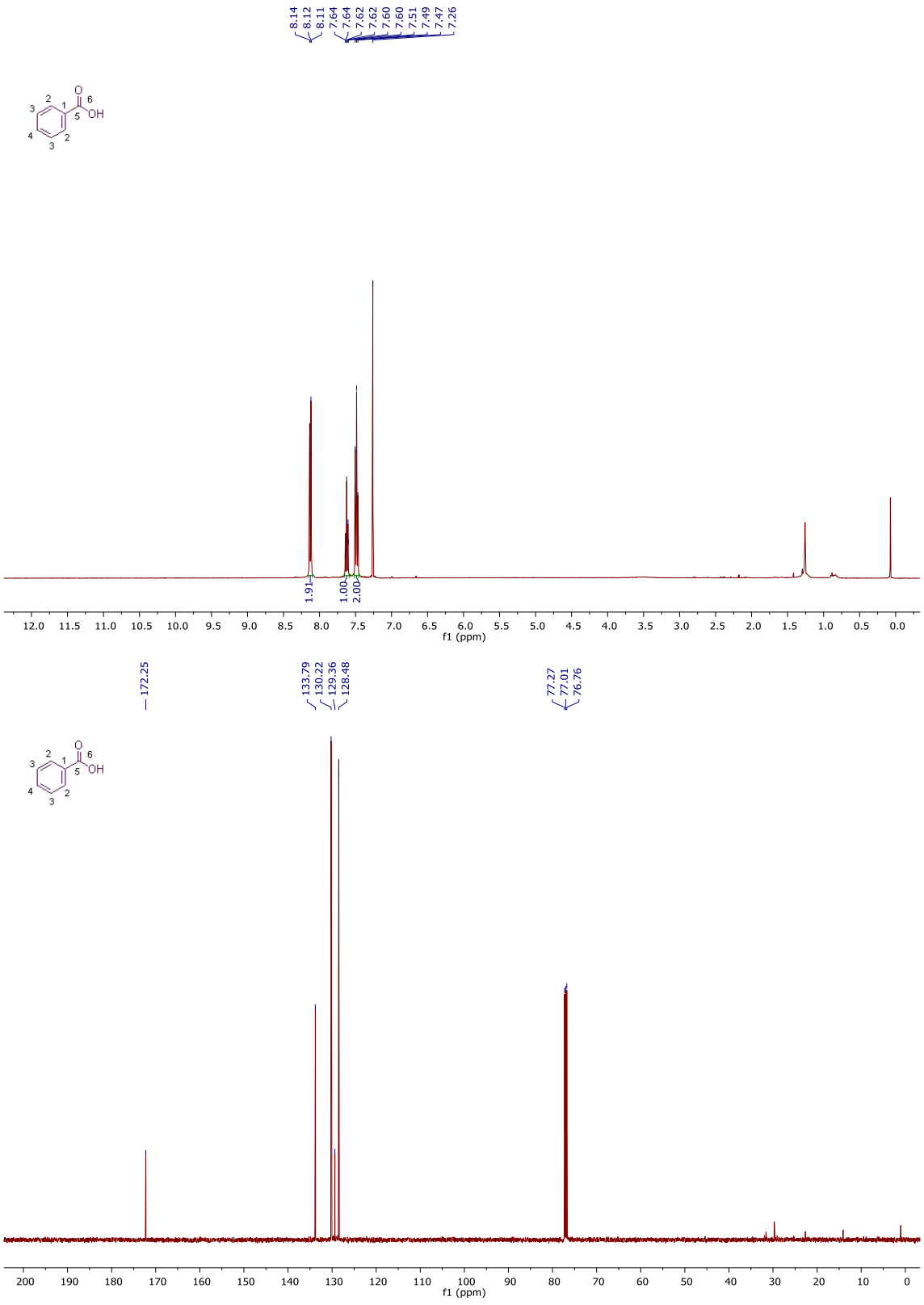


Figure 30. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **4a** in $CDCl_3$.

11. References

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