Regioselective Synthesis of 5-Metalated 2-Pyrones by Intramolecular Oxymetalation of Carbonyl-Ene-Yne Compounds Using Indium Trihalide

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Supporting Information

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1. Observation of Zwitterion Intermediate by ^{1}H NMR Spectroscopy and X-ray Crystallographic Analysis

Oxyindation of methyl (*Z*)-3,5-diphenylpent-2-en-4-ynoate **1b** (0.501 mmol, 0.131 g) with InI_3 (0.505 mmol, 0.250 g) was carried out in toluene (1 mL) at room temperature for 2 h to give a white solid, and then the toluene was evaporated and the residual solid was dissolved in $CDCl_3$. ^{1}H NMR spectroscopy measurements showed that the solid was mixture of two compounds, which were neither the metalated pyrone **3b** nor the starting material **1b** (Fig. S1). Recrystallization of the mixture from $CHCl_3$ and heptane provided a crystal and X-ray crystallographic analysis revealed that the one of the two components was the zwitterion intermediate **4b** (CCDC 1910563). Another could be the coordination complex **S1** because the signal of OMe was moved to lower magnetic field than that of **1b**. The tentative assignment was shown in Fig. S1 based on ^{1}H NMR spectrum of a zwitterion reported in our previous work[1], and we calculated the NMR yield of **4b** and **S1** by addition of 1,1,1,2-tetrachloroethane as an internal standard (**4b**: 0.095 mmol, 19%, **S1**: 0.396 mmol, 79%).

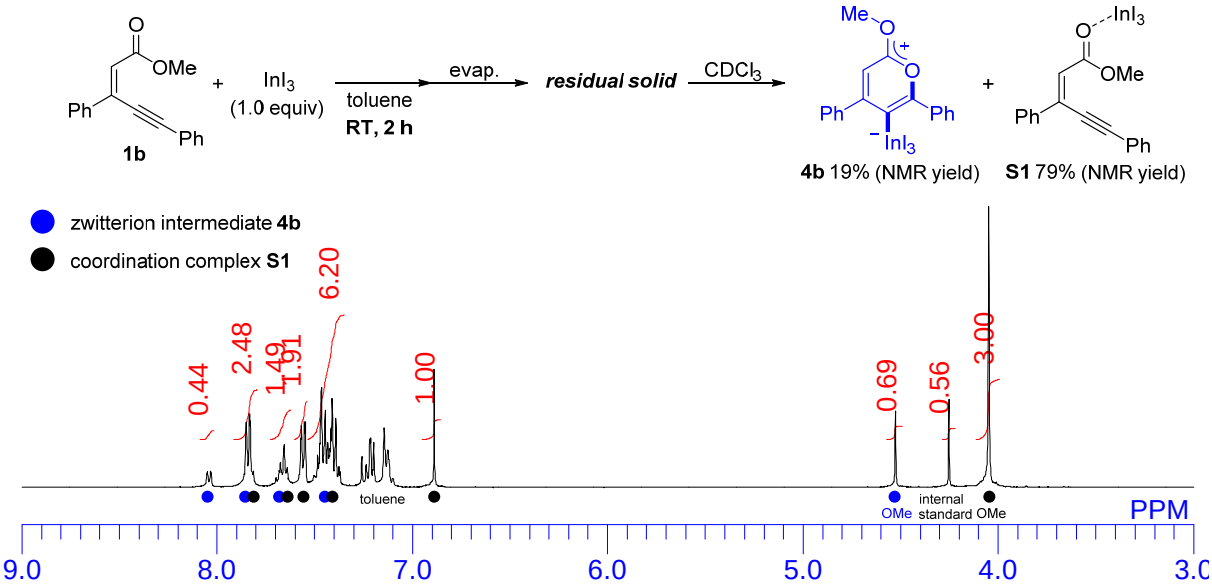
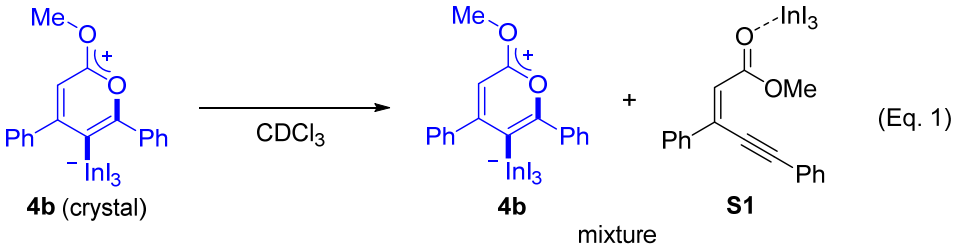
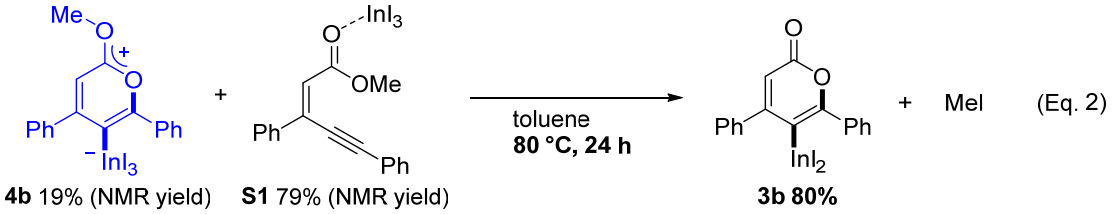


Fig. S1 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the solid obtained from oxyindation of **1b** with InI_3 at room temperature.

We tried to determine which of the signals was assigned to the zwitterion **4b** by measurement of ^{1}H NMR spectroscopy of the crystal **4b**, but the same mixture was observed in ^{1}H NMR spectrum. This result suggested that the retro-cyclization of the zwitterion **4b** might proceed to afford **S1** in the solution phase (Eq. 1).



The mixture of **4b** (0.095 mmol) and **S1** (0.396 mmol) was dissolved in toluene (1 mL) and the solution was heated at 80 °C in 24 h. The reaction mixture was washed by $CHCl_3$ to afford the metalated 2-pyrone **3b** (0.244 g, 80%) (CCDC 1910738) (Eq. 2).



2. Computational Analysis

We applied the HF/DFT hybrid method originally proposed by Becke, referenced as B3LYP three parameter hybrid functional. All calculations were performed with Gaussian09 rev.C.01, 6-31+G(d,p) for H, C, O, DGDZVP for Al, Ga, In, Br were used for basis sets. All molecular geometries were fully optimized and energies were calculated including thermal free energies correction by the normal mode analysis for each structure.

Comparison of various parameters for activation of carbonyl-ene-yne 1a by metal salts[a] (Table S1)

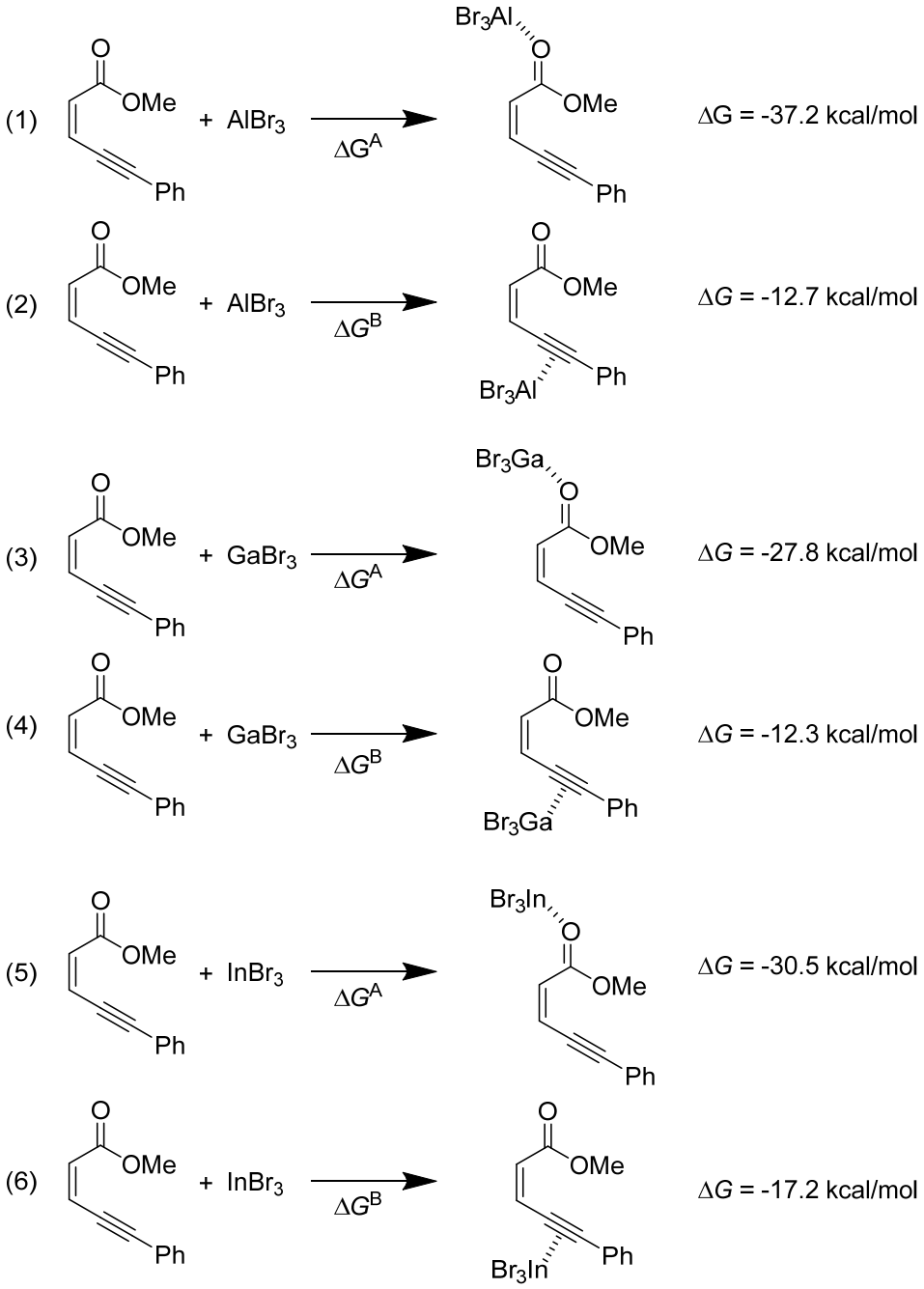
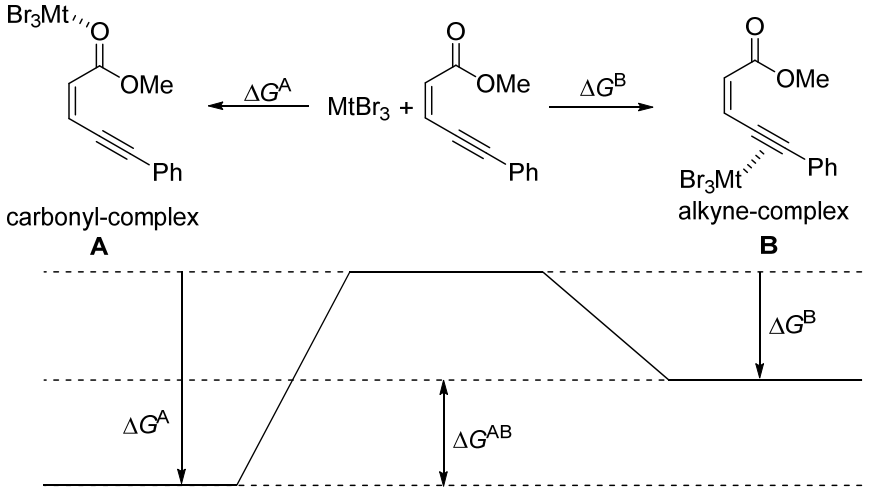


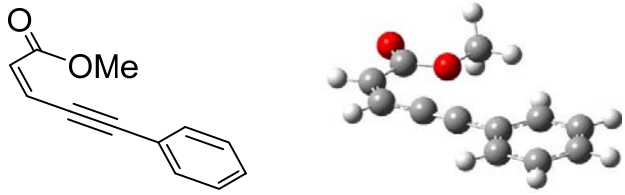
Table S1. Computed Gibbs Free Energy for Complexation of Metal Salts with Alkyne Moiety or Carbonyl Oxygen[a]



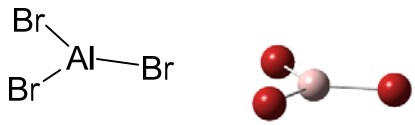
Entry	$MtBr_3$	ΔG^A	ΔG^B	ΔG^{AB}
1	$InBr_3$	-30.5	-17.2	13.3
2	$GaBr_3$	-27.8	-12.3	15.5
3	$AlBr_3$	-37.2	-12.7	24.5

Optimized structure of 1a, $AlBr_3$, $GaBr_3$, $InBr_3$, $AlBr_3$・1a(alkyne), $GaBr_3$・1a(alkyne), $InBr_3$・1a(alkyne), $AlBr_3$・1a (carbonyl), $GaBr_3$・1a (carbonyl), $InBr_3$・1a (carbonyl)

1a



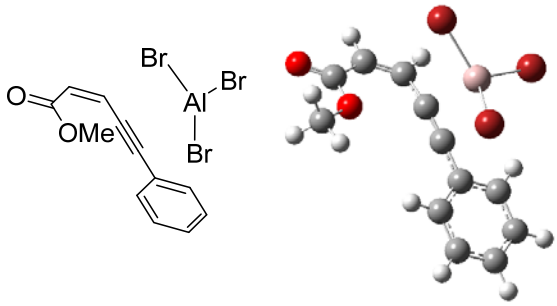
$AlBr_3$



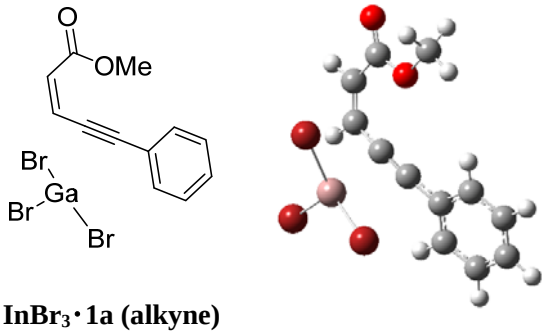
$GaBr_3$

$InBr_3$

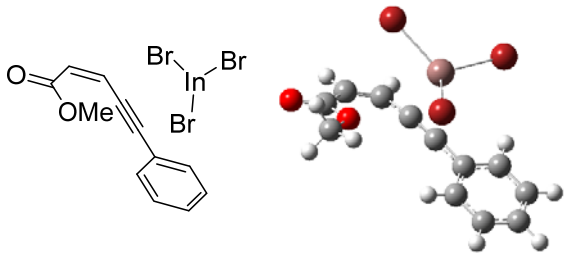
$AlBr_3$・1a (alkyne)



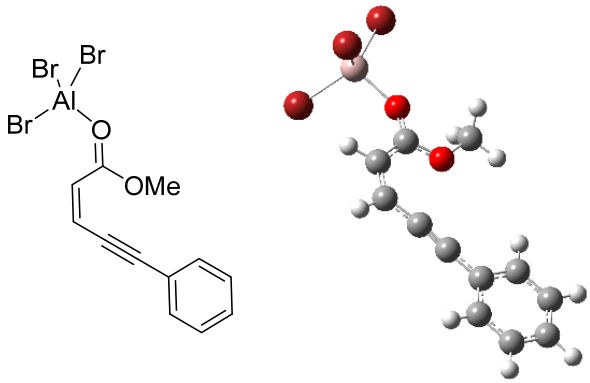
$GaBr_3$・1a (alkyne)



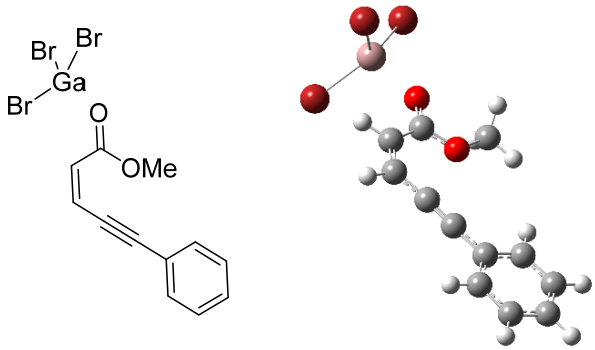
$InBr_3$・1a (alkyne)



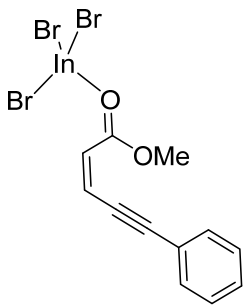
$AlBr_3$・1a (carbonyl)

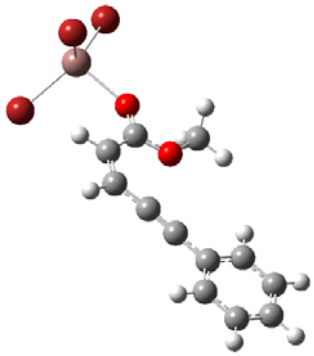


$GaBr_3$・1a (carbonyl)



$InBr_3$·1a (carbonyl)





$AlBr_3$

HETATM	1	Br	0	-0.000	2.253	0.000	Br
HETATM	2	Br	0	-1.951	-1.127	-0.000	Br
HETATM	3	Br	0	1.951	-1.127	-0.000	Br
HETATM	4	Al	0	0.000	0.000	0.000	Al

$GaBr_3$

HETATM	1	Ga	0	0.000	0.000	0.000	Ga
HETATM	2	Br	0	-0.000	2.295	0.000	Br
HETATM	3	Br	0	-1.988	-1.148	-0.000	Br
HETATM	4	Br	0	1.988	-1.148	-0.000	Br

$InBr_3$

HETATM	1	In	0	0.000	0.000	0.000	In
HETATM	2	Br	0	-0.000	2.492	0.000	Br
HETATM	3	Br	0	-2.159	-1.246	-0.000	Br
HETATM	4	Br	0	2.159	-1.246	-0.000	Br

1a

HETATM	1	C	0	4.345	-0.661	-0.001	C
HETATM	2	C	0	4.519	0.727	0.000	C
HETATM	3	C	0	3.402	1.570	0.001	C
HETATM	4	C	0	2.117	1.032	0.001	C
HETATM	5	C	0	1.930	-0.367	0.000	C
HETATM	6	C	0	3.063	-1.208	-0.001	C
HETATM	7	H	0	5.210	-1.318	-0.001	H
HETATM	8	H	0	5.520	1.150	0.000	H
HETATM	9	H	0	3.534	2.648	0.001	H
HETATM	10	H	0	1.246	1.679	0.001	H
HETATM	11	H	0	2.924	-2.285	-0.001	H

HETATM	12	C	0	0.617	-0.919	0.000	C
HETATM	13	C	0	-0.523	-1.350	0.000	C
HETATM	14	C	0	-1.786	-1.982	0.000	C
HETATM	15	C	0	-3.025	-1.433	0.000	C
HETATM	16	H	0	-1.743	-3.072	0.000	H
HETATM	17	H	0	-3.883	-2.097	0.000	H
HETATM	18	C	0	-3.412	-0.009	0.000	C
HETATM	19	O	0	-4.578	0.354	0.001	O
HETATM	20	O	0	-2.372	0.852	-0.001	O
HETATM	21	C	0	-2.720	2.247	-0.001	C
HETATM	22	H	0	-3.306	2.495	-0.889	H
HETATM	23	H	0	-3.301	2.496	0.891	H
HETATM	24	H	0	-1.771	2.783	-0.004	H

$AlBr_3$·1a (alkyne)

HETATM	1	C	0	0.416	0.716	-1.266	C
HETATM	2	C	0	-0.744	1.024	-0.990	C
HETATM	3	C	0	2.769	1.337	-1.841	C
HETATM	4	C	0	1.637	0.626	-2.013	C
HETATM	5	H	0	3.591	1.170	-2.528	H
HETATM	6	H	0	1.612	-0.107	-2.817	H
HETATM	7	C	0	-2.079	1.391	-0.684	C
HETATM	8	C	0	-2.332	2.460	0.204	C
HETATM	9	C	0	-3.643	2.842	0.469	C
HETATM	10	C	0	-4.707	2.165	-0.140	C
HETATM	11	C	0	-4.463	1.104	-1.019	C
HETATM	12	C	0	-3.156	0.714	-1.297	C
HETATM	13	H	0	-1.498	2.967	0.676	H
HETATM	14	H	0	-3.839	3.662	1.152	H
HETATM	15	H	0	-5.729	2.464	0.074	H
HETATM	16	H	0	-5.292	0.580	-1.484	H
HETATM	17	H	0	-2.952	-0.113	-1.969	H
HETATM	18	C	0	3.087	2.340	-0.797	C
HETATM	19	O	0	4.149	2.937	-0.772	O
HETATM	20	O	0	2.110	2.513	0.115	O
HETATM	21	C	0	2.411	3.429	1.187	C
HETATM	22	H	0	3.296	3.094	1.732	H
HETATM	23	H	0	2.587	4.432	0.790	H
HETATM	24	H	0	1.534	3.415	1.834	H
HETATM	25	Al	0	0.174	-1.186	0.238	Al
HETATM	26	Br	0	2.389	-1.563	0.678	Br

HETATM	27	Br	0	-0.791	-2.662	-1.241	Br
HETATM	28	Br	0	-1.050	-0.650	2.101	Br

$GaBr_3$·1a (alkyne)

HETATM	1	C	0	0.497	0.883	1.261	C
HETATM	2	C	0	-0.649	1.228	0.986	C
HETATM	3	C	0	2.937	1.260	1.636	C
HETATM	4	C	0	1.761	0.642	1.874	C
HETATM	5	H	0	3.803	0.955	2.213	H
HETATM	6	H	0	1.749	-0.147	2.624	H
HETATM	7	C	0	-1.957	1.702	0.697	C
HETATM	8	C	0	-3.068	1.195	1.405	C
HETATM	9	C	0	-4.343	1.687	1.138	C
HETATM	10	C	0	-4.524	2.681	0.169	C
HETATM	11	C	0	-3.426	3.188	-0.536	C
HETATM	12	C	0	-2.147	2.704	-0.278	C
HETATM	13	H	0	-2.918	0.420	2.149	H
HETATM	14	H	0	-5.196	1.293	1.681	H
HETATM	15	H	0	-5.521	3.059	-0.037	H
HETATM	16	H	0	-3.571	3.957	-1.288	H
HETATM	17	H	0	-1.289	3.085	-0.821	H
HETATM	18	C	0	3.253	2.324	0.655	C
HETATM	19	O	0	4.380	2.772	0.527	O
HETATM	20	O	0	2.198	2.741	-0.071	O
HETATM	21	C	0	2.485	3.749	-1.061	C
HETATM	22	H	0	2.877	4.650	-0.582	H
HETATM	23	H	0	3.217	3.375	-1.780	H
HETATM	24	H	0	1.534	3.953	-1.551	H
HETATM	25	Ga	0	0.059	-1.225	-0.231	Ga
HETATM	26	Br	0	0.017	-2.663	1.609	Br
HETATM	27	Br	0	2.037	-1.066	-1.443	Br
HETATM	28	Br	0	-1.885	-1.133	-1.503	Br

$InBr_3$·1a (alkyne)

HETATM	1	C	0	0.120	0.983	-1.704	C
HETATM	2	C	0	-1.044	1.114	-1.326	C
HETATM	3	C	0	2.479	1.622	-2.220	C
HETATM	4	C	0	1.308	1.011	-2.495	C
HETATM	5	H	0	3.274	1.576	-2.956	H
HETATM	6	H	0	1.226	0.473	-3.439	H
HETATM	7	C	0	-2.387	1.305	-0.905	C

HETATM	8	C	0	-2.696	2.280	0.068	C
HETATM	9	C	0	-4.020	2.490	0.441	C
HETATM	10	C	0	-5.042	1.733	-0.143	C
HETATM	11	C	0	-4.743	0.762	-1.106	C
HETATM	12	C	0	-3.423	0.543	-1.490	C
HETATM	13	H	0	-1.894	2.853	0.521	H
HETATM	14	H	0	-4.256	3.238	1.191	H
HETATM	15	H	0	-6.074	1.898	0.154	H
HETATM	16	H	0	-5.538	0.173	-1.553	H
HETATM	17	H	0	-3.177	-0.214	-2.226	H
HETATM	18	In	0	0.272	-0.881	0.263	In
HETATM	19	C	0	2.855	2.385	-1.007	C
HETATM	20	O	0	3.910	2.987	-0.918	O
HETATM	21	O	0	1.931	2.339	-0.028	O
HETATM	22	C	0	2.276	3.027	1.195	C
HETATM	23	H	0	3.200	2.615	1.607	H
HETATM	24	H	0	2.407	4.094	1.000	H
HETATM	25	H	0	1.441	2.847	1.871	H
HETATM	26	Br	0	2.730	-1.410	0.084	Br
HETATM	27	Br	0	-1.254	-2.649	-0.711	Br
HETATM	28	Br	0	-0.469	0.215	2.418	Br

$AlBr_3$·1a (carbonyl)

HETATM	1	C	0	-8.018	-0.631	-0.000	C
HETATM	2	C	0	-8.233	0.752	-0.000	C
HETATM	3	C	0	-7.144	1.631	0.000	C
HETATM	4	C	0	-5.843	1.134	0.000	C
HETATM	5	C	0	-5.616	-0.260	0.000	C
HETATM	6	C	0	-6.721	-1.139	-0.000	C
HETATM	7	H	0	-8.863	-1.313	-0.000	H
HETATM	8	H	0	-9.246	1.143	-0.000	H
HETATM	9	H	0	-7.311	2.704	0.000	H
HETATM	10	H	0	-4.994	1.808	0.000	H
HETATM	11	H	0	-6.548	-2.210	-0.000	H
HETATM	12	C	0	-4.292	-0.773	0.000	C
HETATM	13	C	0	-3.143	-1.189	0.000	C
HETATM	14	C	0	-1.879	-1.797	0.000	C
HETATM	15	C	0	-0.639	-1.231	0.000	C
HETATM	16	H	0	-1.899	-2.887	0.000	H
HETATM	17	H	0	0.228	-1.881	0.000	H
HETATM	18	C	0	-0.332	0.183	-0.000	C

HETATM	19	O	0	0.842	0.639	-0.000	O
HETATM	20	O	0	-1.342	1.027	-0.000	O
HETATM	21	C	0	-1.036	2.447	-0.000	C
HETATM	22	H	0	-0.464	2.703	0.893	H
HETATM	23	H	0	-0.465	2.703	-0.894	H
HETATM	24	H	0	-2.007	2.938	0.000	H
HETATM	25	Br	0	2.791	-1.211	-1.935	Br
HETATM	26	Br	0	2.791	-1.210	1.935	Br
HETATM	27	Br	0	3.812	2.011	-0.000	Br
HETATM	28	Al	0	2.629	0.043	-0.000	Al

$GaBr_3$·1a (carbonyl)

HETATM	1	C	0	8.232	-0.652	0.000	C
HETATM	2	C	0	8.457	0.730	-0.000	C
HETATM	3	C	0	7.374	1.617	-0.000	C
HETATM	4	C	0	6.070	1.128	-0.000	C
HETATM	5	C	0	5.832	-0.264	0.000	C
HETATM	6	C	0	6.931	-1.150	0.000	C
HETATM	7	H	0	9.072	-1.340	0.000	H
HETATM	8	H	0	9.473	1.114	-0.000	H
HETATM	9	H	0	7.549	2.688	-0.001	H
HETATM	10	H	0	5.225	1.809	-0.001	H
HETATM	11	H	0	6.750	-2.220	0.001	H
HETATM	12	C	0	4.502	-0.766	0.000	C
HETATM	13	C	0	3.348	-1.164	0.000	C
HETATM	14	C	0	2.073	-1.751	0.000	C
HETATM	15	C	0	0.844	-1.164	-0.000	C
HETATM	16	H	0	2.074	-2.842	-0.000	H
HETATM	17	H	0	-0.032	-1.800	-0.000	H
HETATM	18	C	0	0.559	0.260	-0.000	C
HETATM	19	O	0	-0.597	0.746	-0.000	O
HETATM	20	O	0	1.599	1.075	0.000	O
HETATM	21	C	0	1.331	2.500	0.000	C
HETATM	22	H	0	0.765	2.774	-0.892	H
HETATM	23	H	0	0.766	2.774	0.893	H
HETATM	24	H	0	2.314	2.968	-0.000	H
HETATM	25	Br	0	-2.554	-1.247	1.976	Br
HETATM	26	Br	0	-2.554	-1.248	-1.976	Br
HETATM	27	Br	0	-3.693	2.011	-0.000	Br
HETATM	28	Ga	0	-2.492	0.015	-0.000	Ga

$InBr_3$·1a (carbonyl)

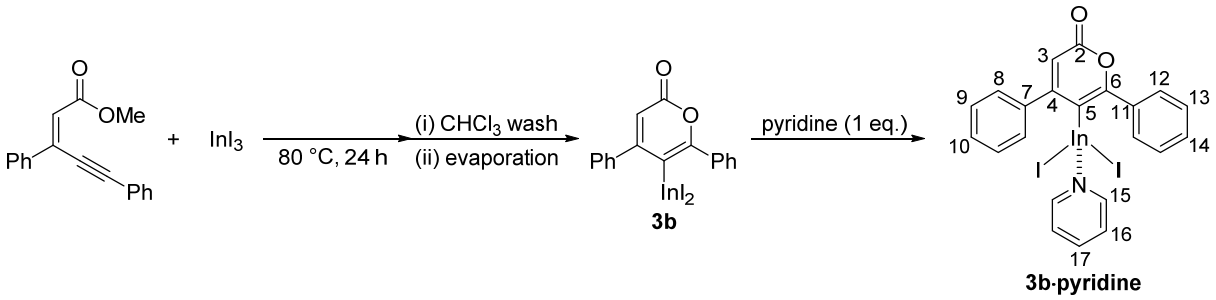
HETATM	1	C	0	-8.533	0.667	-0.038	C
HETATM	2	C	0	-8.780	-0.710	-0.032	C
HETATM	3	C	0	-7.712	-1.614	0.000	C
HETATM	4	C	0	-6.400	-1.147	0.029	C
HETATM	5	C	0	-6.140	0.241	0.023	C
HETATM	6	C	0	-7.225	1.145	-0.010	C
HETATM	7	H	0	-9.361	1.369	-0.063	H
HETATM	8	H	0	-9.801	-1.078	-0.054	H
HETATM	9	H	0	-7.904	-2.683	0.004	H
HETATM	10	H	0	-5.566	-1.841	0.054	H
HETATM	11	H	0	-7.026	2.212	-0.015	H
HETATM	12	C	0	-4.804	0.725	0.053	C
HETATM	13	C	0	-3.648	1.116	0.079	C
HETATM	14	C	0	-2.375	1.710	0.107	C
HETATM	15	C	0	-1.143	1.132	0.158	C
HETATM	16	H	0	-2.383	2.800	0.083	H
HETATM	17	H	0	-0.274	1.779	0.180	H
HETATM	18	C	0	-0.838	-0.289	0.200	C
HETATM	19	O	0	0.326	-0.748	0.204	O
HETATM	20	O	0	-1.870	-1.116	0.239	O
HETATM	21	C	0	-1.584	-2.536	0.274	C
HETATM	22	H	0	-1.038	-2.829	-0.625	H
HETATM	23	H	0	-0.995	-2.778	1.160	H
HETATM	24	H	0	-2.561	-3.016	0.311	H
HETATM	25	In	0	2.415	0.005	-0.025	In
HETATM	26	Br	0	3.663	-2.088	0.610	Br
HETATM	27	Br	0	2.448	1.937	1.615	Br
HETATM	28	Br	0	2.347	0.669	-2.465	Br

Table S2. Various parameters at 298.150K of all optimized structures (in hartree).

Compound	Zero-point correction (Hartree)	Thermal correction to Energy (Hartree)	Thermal correction to Enthalpy (Hartree)	Thermal correction to Gibbs Free Energy (Hartree)	Sum of electronic and zero-point Energies (Hartree)	Sum of electronic and thermal Energies (Hartree)	Sum of electronic and thermal Enthalpies (Hartree)	Sum of electronic and thermal Free Energies (Hartree)	imaginary frequency
1a	0.186851	0.199957	0.200902	0.144145	-613.520956	-613.507850	-613.506906	-613.563662	0
$AlBr_3$	0.003591	0.009506	0.010451	-0.029145	-7963.689214	-7963.683298	-7963.682354	-7963.721950	0
$GaBr_3$	0.002650	0.009029	0.009973	-0.031083	-9645.709776	-9645.703398	-9645.702454	-9645.743509	0
$InBr_3$	0.002184	0.008871	0.009816	-0.032874	-13463.207943	-13463.201256	-13463.200312	-13463.243002	0
$AlBr_3$• 1a(alkyne)	0.190885	0.212102	0.213047	0.131985	-8577.217762	-8577.196545	-8577.195600	-8577.276662	0
$GaBr_3$• 1a(alkyne)	0.189922	0.211727	0.212672	0.129788	-10259.235556	-10259.213750	-10259.212806	-10259.295689	0
$InBr_3$• 1a(alkyne)	0.189629	0.211582	0.212526	0.130453	-14076.742098	-14076.720145	-14076.719201	-14076.801274	0
$AlBr_3$• 1a(carbonyl)	0.192405	0.213029	0.213973	0.133971	-8577.257342	-8577.236718	-8577.235774	-8577.315776	0
$GaBr_3$• 1a(carbonyl)	0.191203	0.212400	0.213344	0.132290	-10259.261547	-10259.240349	-10259.239405	-10259.320460	0
$InBr_3$• 1a(carbonyl)	0.190646	0.212276	0.213220	0.129494	-14076.763988	-14076.742358	-14076.741414	-14076.825140	0

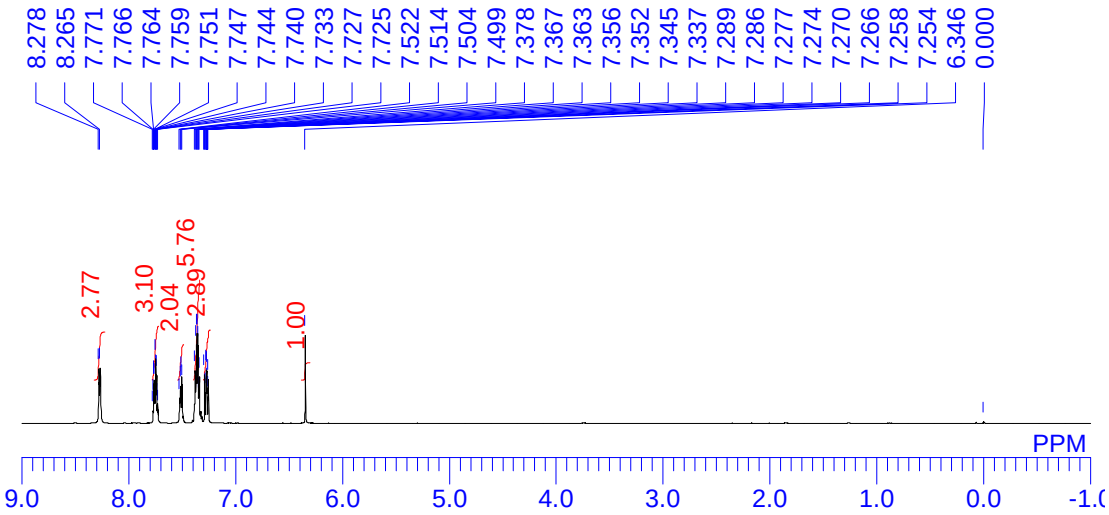
3 Isolation of Organoindium Compound

(2-oxo-4,6-diphenyl-2*H*-pyran-5-yl)indium diiodide pyridine complex (**3b·pyridine**)

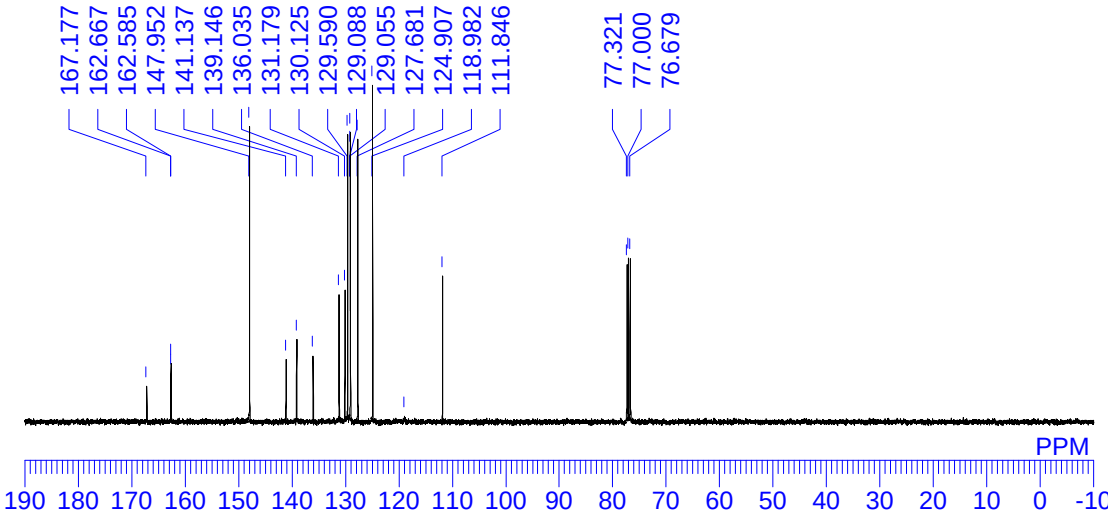


All operations were carried out in a nitrogen-filled glove box. To a 10 mL vial filled with InI_3 (0.502 mmol, 0.249 g) in toluene (1 mL) was added methyl (*Z*)-3,5-diphenylpent-2-en-4-ynoate (0.493 mmol, 0.129 g). The vial was sealed, and the mixture was stirred at 80 °C for 24 h. Then, the solvent was removed by decantation to obtain a white solid and the solid was washed by $CHCl_3$ (3 mL x 6). The residue was dried under vacuum to give the product **3b** as a white solid (0.297 g, 81%). **3b** was added to pyridine (0.399 mmol, 0.0316 g) and recrystallized from $CHCl_3$ and heptane to give a single crystal of **3b·pyridine**. The structure was determined by X-ray crystallographic analysis (CCDC 1910738). Characterization by NMR study was also carried out, and the spectra is shown below. ^{1}H NMR: (400 MHz, $CDCl_3$) 8.27 (d, J = 4.8 Hz, 2H, 15-H x 2), 7.77-7.72 (m, 3H), 7.54-7.48 (m, 2H, 8-H x 2), 7.36-7.34 (m, 6H), 7.28-7.26 (m, 2H, 16-H x 2), 6.35 (s, 1H, 3-H), ^{13}C NMR: (100 MHz, $CDCl_3$) 167.2 (s, C-6), 162.7 (s), 162.6 (s), 148.0 (d, C-15), 141.1 (s, C-7), 139.1 (d, C-17), 136.0 (s, C-11), 131.2 (d), 130.1 (d), 129.6 (d), 129.09 (d), 129.06 (d), 127.7 (d, C-8), 124.9 (d, C-16), 118.9 (s, C-5), 111.8 (d, C-3).

^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



4 References

[1] Y. Kita, T. Yata, Y. Nishimoto, K. Chiba, M. Yasuda, *Chem. Sci*. **2018**, *9*, 6041-6052.

5 X-ray crystallographic date

3,4,5,6-tetraphenyl-*2H*-pyran-2-one (**6m**) (CCDC 1910558).

6m was recrystallized in dichloromethane solvent.

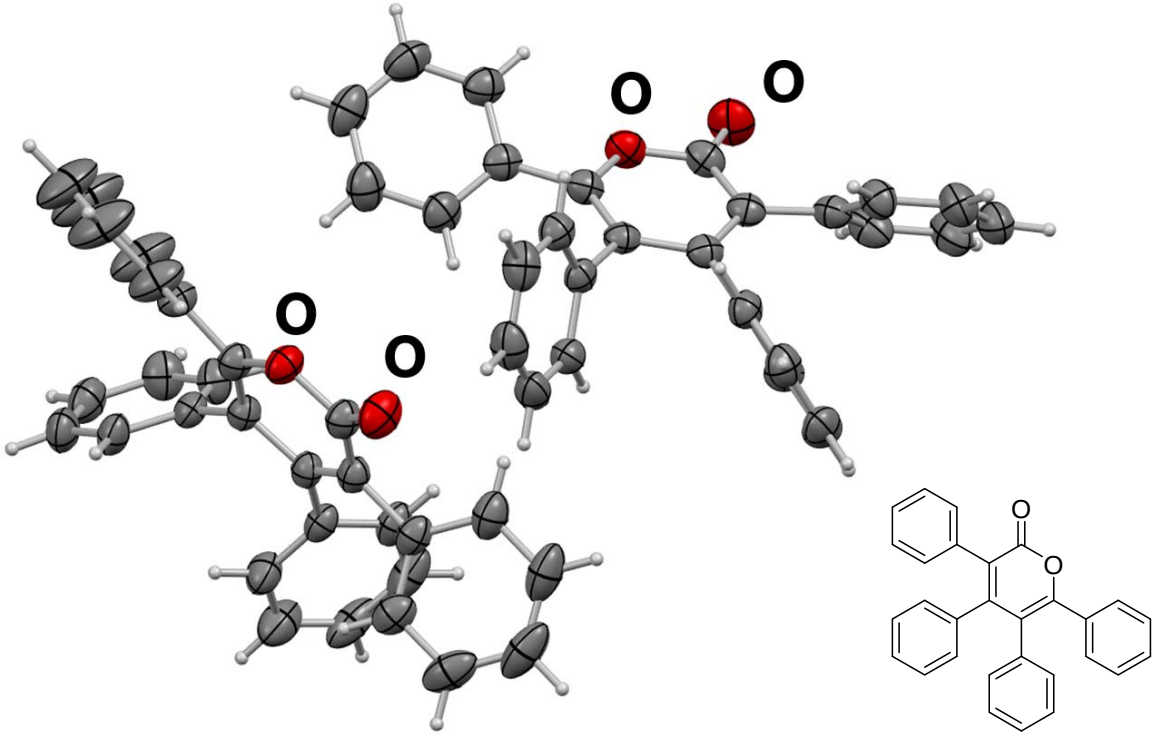


Figure S2. ORTEP drawing of 6m at the 50% probability level

Table S3. Crystal date and structure solution paramaters of 6m

Empirical Formula	$C_{29}H_{20}O_2$	Function Minimized	$\Sigma w (\|Fo\| - \|Fc\|)^2$
Formula Weight	400.48	Least Squares Weights	$1/\sigma^2(Fo)$
Crystal Color, Habit	None	No. Observations ($I > 2.00\sigma(I)$)	6515
Crystal Dimensions	None	No. Variables	599
Crystal System	triclinic	Reflection/Parameter Ratio	10.88
Lattice Type	Primitive	Residuals: R (I>2.00$\sigma(I)$)	0.0502
	a = 10.2861(4) Å	Residuals: wR (I>2.00$\sigma(I)$)	0.0453
	b = 12.2992(4) Å	Goodness of Fit Indicator	1.744
	c = 18.0217(7) Å	Max Shift/Error in Final Cycle	0.000
	V = 2123.76(14) Å^3	Maximum peak in Final Diff. Map	1.01 e$^-$/Å^3
	α = 85.011(3)°	Minimum peak in Final Diff. Map	-0.62 e$^-$/Å^3
	β = 79.264(3)°		
	γ = 71.536(3)°		
Space Group	P-1 (#2)		
Z value	4		
D_{calc}	1.252g/cm^3		
F_{000}	840.00		
μ(MoK$_\alpha$)	0.773 cm^{-1}		
Temperature	-150.0°C		

5-(4-methylbenzoyl)-3,4,6-triphenyl-*2H*-pyran-2-one (**7m**) (CCDC 1910562).
7m was recrystallized in dichloromethane solvent.

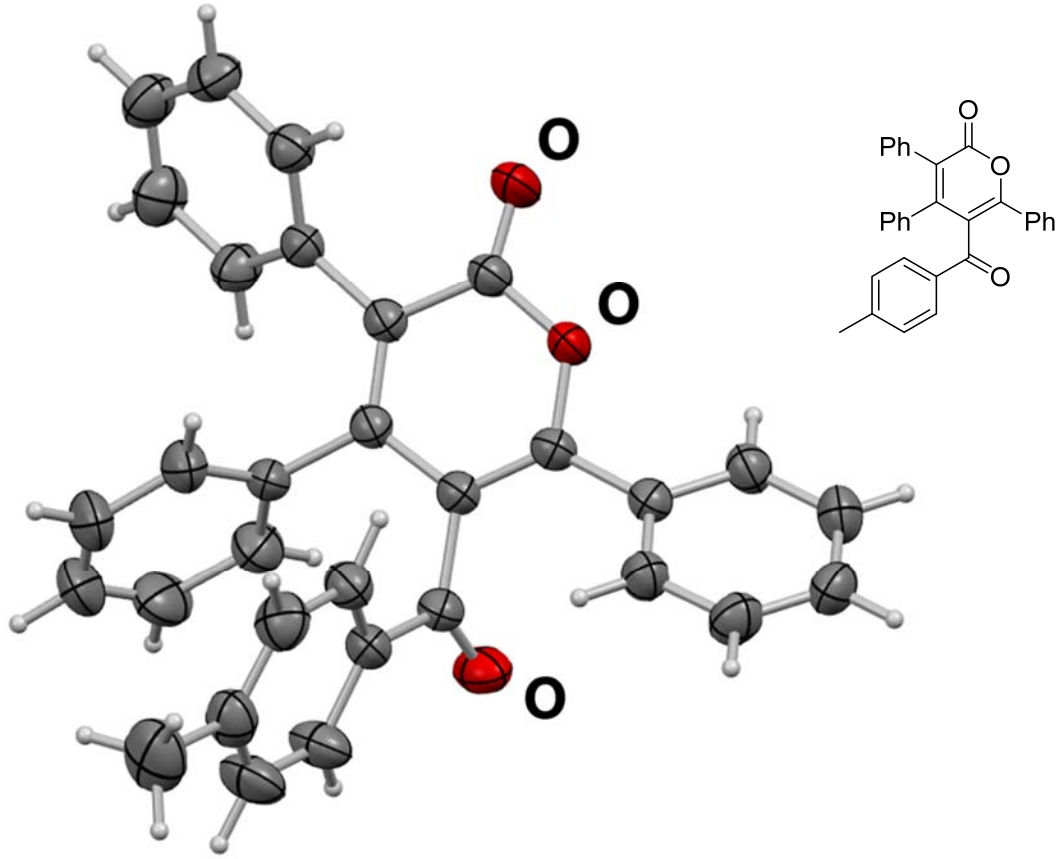


Figure S3. ORTEP drawing of 7m at the 50% probability level

Table S4. Crystal date and structure solution paramaters of 7m

Empirical Formula	$C_{31}H_{22}O_3$	Function Minimized	Σw (|Fo| - |Fc|)^2
Formula Weight	442.51	Least Squares Weights	1/[0.0018Fo2+1.0000□(Fo2)]
Crystal Color, Habit	None	No. Observations ($I > 2.00\sigma(I)$)	4216
Crystal Dimensions	None	No. Variables	330
Crystal System	monoclinic	Reflection/Parameter Ratio	12.78
Lattice Type	Primitive	Residuals: R (I>2.00$\sigma(I)$)	0.0433
	a = 10.4592(8) Å	Residuals: wR (I>2.00$\sigma(I)$)	0.0581
	b = 8.1844(6) Å	Goodness of Fit Indicator	0.963
	c = 13.6348(9) Å	Max Shift/Error in Final Cycle	0.000
	V = 1147.48(15) Å^3	Maximum peak in Final Diff. Map	1.16 e$^-$/Å^3
	β = 100.540(7)°	Minimum peak in Final Diff. Map	-1.06 e$^-$/Å^3
Space Group	$P2_1$ (#4)		
Z value	2		
D_{calc}	1.281g/cm^3		
F_{000}	464.00		
μ(MoK$_\alpha$)	0.814 cm^{-1}		
Temperature	-150.0°C		

6-cyclopropyl-3-ethyl-5-(4-methylbenzoyl)-4-phenyl-*2H*-pyran-2-one (**7l**) (CCDC 1910561). **7l** was recrystallized in dichloromethane solvent.

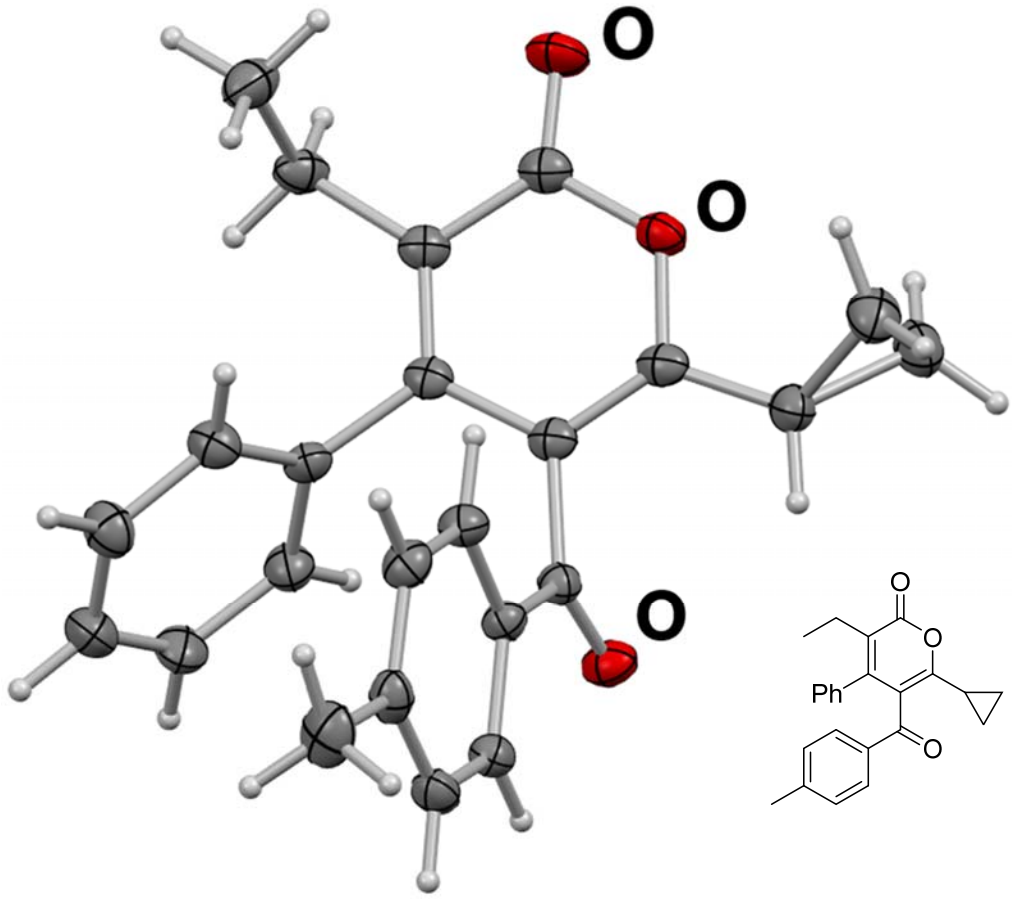


Figure S4. ORTEP drawing of 7l at the 50% probability level

Table S5. Crystal date and structure solution paramaters of 7l

Empirical Formula	$C_{24}H_{22}O_3$	Function Minimized	Σw (|Fo| - |Fc|)^2
Formula Weight	358.44	Least Squares Weights	1/[0.0070Fo2+1.0000□(Fo2)]
Crystal Color, Habit	None	No. Observations ($I > 2.00\sigma(I)$)	3974
Crystal Dimensions	None	No. Variables	266
Crystal System	monoclinic	Reflection/Parameter Ratio	14.94
Lattice Type	Primitive	Residuals: R (I>2.00$\sigma(I)$)	0.0537
	a = 8.4349(5) Å	Residuals: wR (I>1.00$\sigma(I)$)	0.1004
	b = 10.8431(5) Å	Goodness of Fit Indicator	0.981
	c = 20.7594(11) Å	Max Shift/Error in Final Cycle	0.018
	V = 1887.95(17) Å^3	Maximum peak in Final Diff. Map	0.59 e$^-$/Å^3
	β = 96.089(5)$^\circ$	Minimum peak in Final Diff. Map	-0.76 e$^-$/Å^3
Space Group	$P2_1/c$ (#14)		
Z value	4		
D_{calc}	1.261 g/cm^3		
F_{000}	760.00		
μ(MoK$_\alpha$)	0.819 cm^{-1}		
Temperature	-150.0°C		

3,4,6-triphenyl-5-(phenylethynyl)-2*H*-pyran-2-one (**8**) (CCDC 1915263).
8 was recrystallized in dichloromethane solvent.

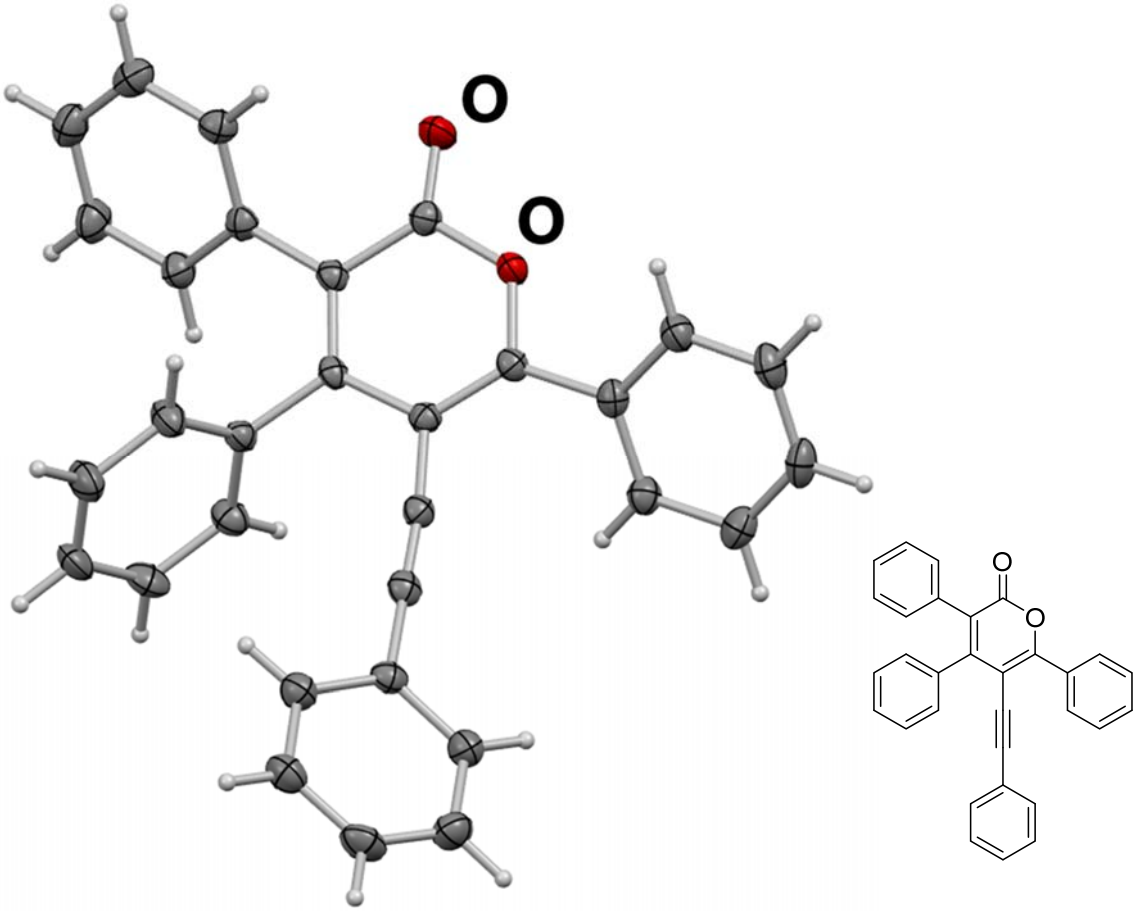


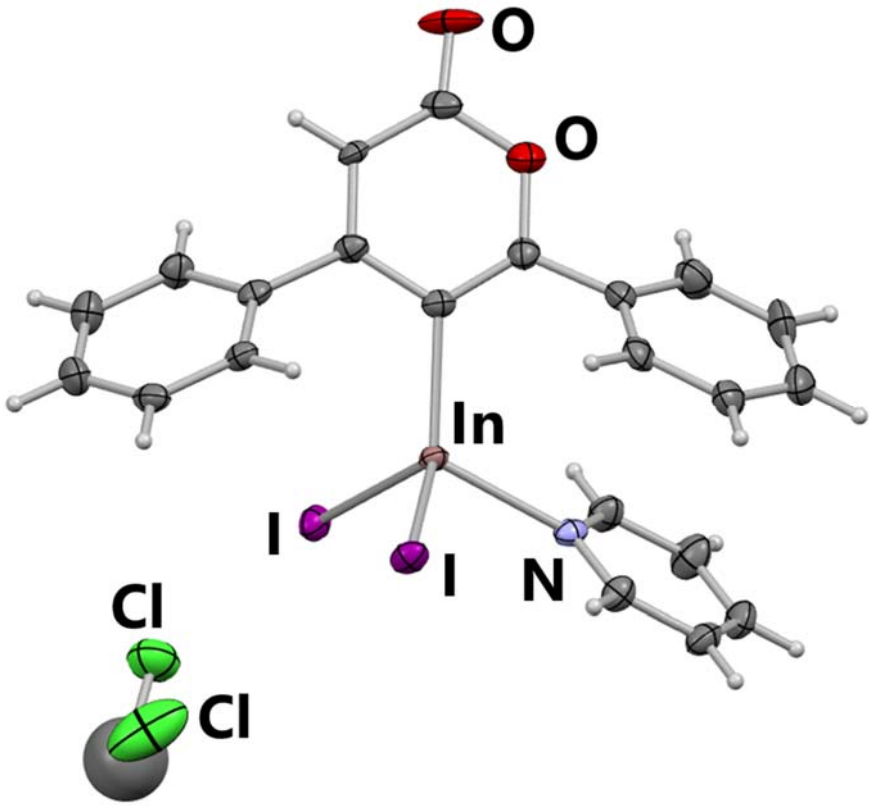
Figure S5. ORTEP drawing of 8 at the 50% probability level

Table S6. Crystal date and structure solution paramaters of 8

Empirical Formula	$C_{31}H_{20}O_2$	Reflections collected	9535
Formula Weight	424.47	Date/restraints/parameters	4347/2/298
Crystal Color, Habit	None	Residuals: R (I>2.00σ(I))	0.0462
Crystal Dimensions	None	Residuals: wR (I>2.00σ(I))	0.0894
Crystal System	monoclinic	Goodness of Fit Indicator	1.056
Lattice Type	Primitive	Flack parameter	-0.4(9)
	a = 10.0337(5) Å	Maximum peak in Final Diff. Map	0.19 e^-/Å^3
	b = 5.7858(3) Å	Minimum peak in Final Diff. Map	-0.19 e^-/Å^3
	c = 19.3039(10) Å		
	V = 1102.10(10) Å^3		
	β = 100.440(5)°		
Space Group	Pc (#7)		
Z value	2		
D_{calc}	1.279 g/cm^3		
F_{000}	444.00		
μ(MoK$_\alpha$)	0.079 cm^{-1}		
Temperature	-150.0°C		

(2-oxo-4,6-diphenyl-2H-pyran-5-yl)indium diiodide pyridine complex (**3b**·pyridine) (CCDC 1910738)

3b·pyridine was crystallized in chloroform and heptane solvent.



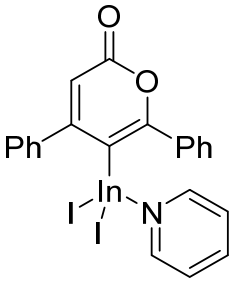


Figure S6. ORTEP drawing of 3b·pyridine at the 50% probability level

Table S7. Crystal date and structure solution paramaters of 3b·pyridine

Empirical Formula	$C_{23}H_{16}Cl_3I_2InNO_2$	Reflections collected	33110
Formula Weight	813.34	Date/restraints/parameters	6454/0/271
Crystal Color, Habit	None	Residuals: *R* (*I*>2.00σ(*I*))	0.0331
Crystal Dimensions	None	Residuals: *wR* (*I*>2.00σ(*I*))	0.1150
Crystal System	Orthorhombic	Goodness of Fit Indicator	0.892
Lattice Type	Primitive	Maximum peak in Final Diff. Map	1.04 $e^-/Å^3$
	a = 29.4767(8) Å	Minimum peak in Final Diff. Map	-1.06 $e^-/Å^3$
	b = 7.5456(2) Å		
	c = 21.7020(6) Å		
	V = 4826.9(2) $Å^3$		
Space Group	*Pbcn* (#60)		
Z value	8		
D_{calc}	2.238g/cm^3		
F_{000}	3064.00		
μ(MoK$_\alpha$)	3.892 cm^{-1}		
Temperature	-150.0°C		

zwitterion intermediate **4b** (CCDC 1910563)
4b was recrystallized in chloroform solvent.

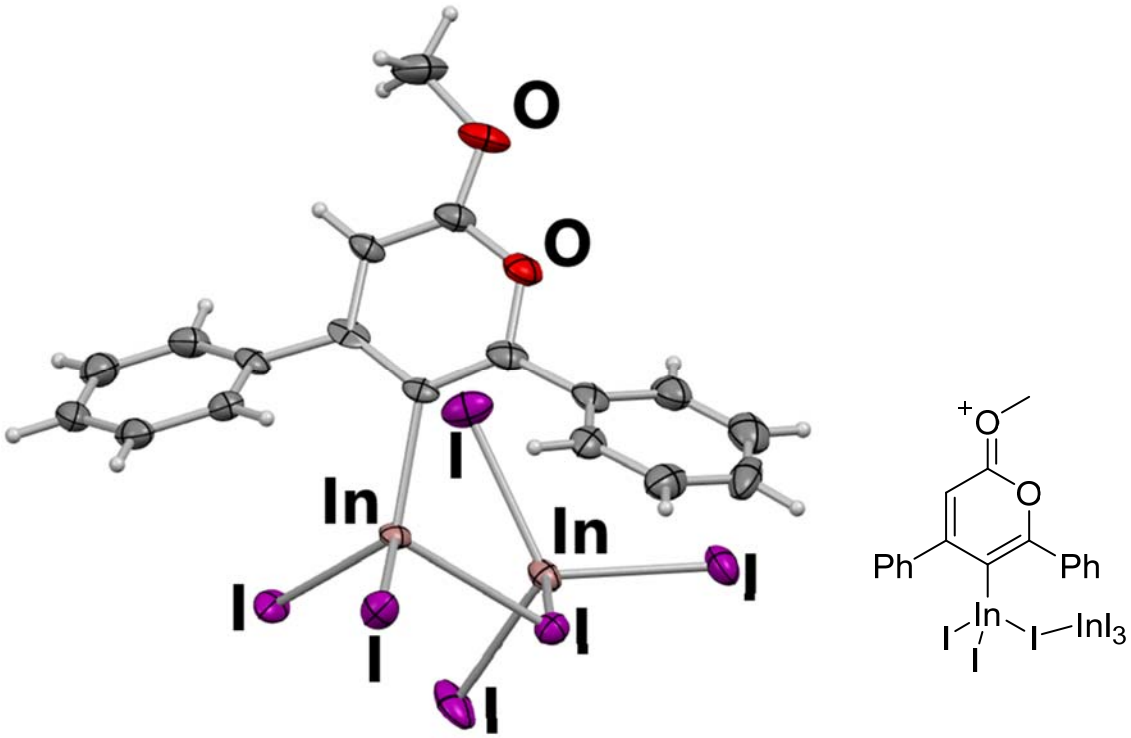


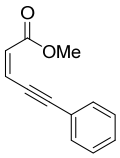
Figure S7. ORTEP drawing of 4b at the 50% probability level

Table S8. Crystal date and structure solution paramaters of 4b

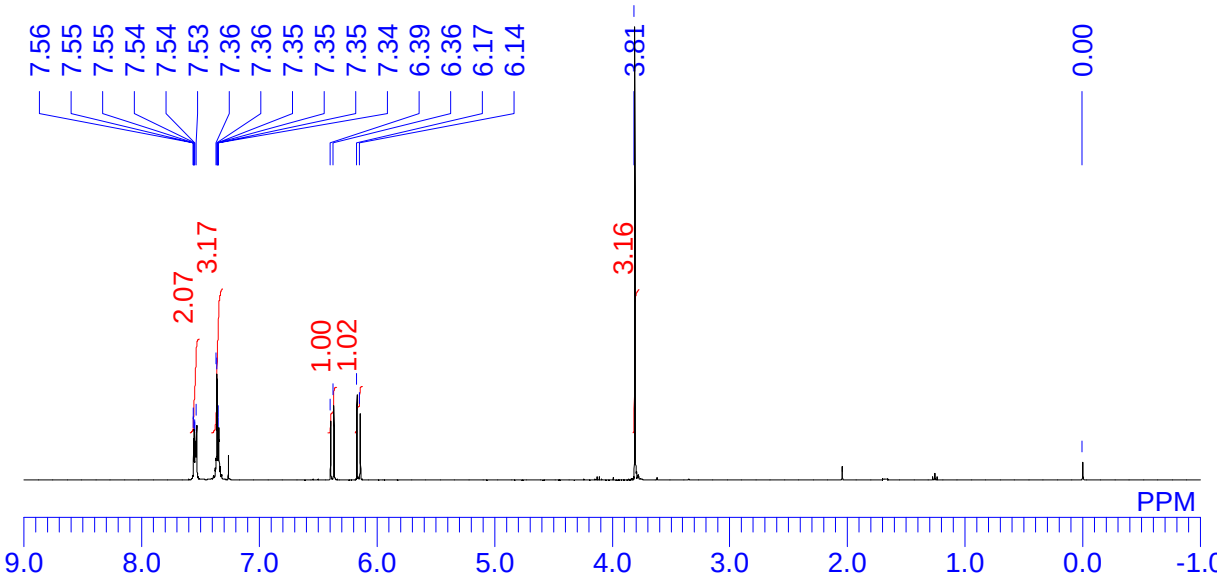
Empirical Formula	$C_{18}H_{14}I_6In_2O_2$	Function Minimized	Σw (|Fo| - |Fc|)^2
Formula Weight	1253.37	Least Squares Weights	1/□2(Fo)
Crystal Color, Habit	None	No. Observations ($I > 2.00\sigma(I)$)	5338
Crystal Dimensions	None	No. Variables	267
Crystal System	Orthorhombic	Reflection/Parameter Ratio	19.99
Lattice Type	Primitive	Residuals: R (I>2.00$\sigma(I)$)	0.0504
	a = 14.25000 Å	Residuals: wR (I>2.00$\sigma(I)$)	0.0546
	b = 14.31400 Å	Goodness of Fit Indicator	2.027
	c = 28.24020 Å	Max Shift/Error in Final Cycle	0.000
	V = 5760.28067 Å^3	Maximum peak in Final Diff. Map	1.85 e$^-$/Å^3
Space Group	*Pbca* (#61)	Minimum peak in Final Diff. Map	-1.79 e$^-$/Å^3
Z value	8		
D_{calc}	2.890g/cm^3		
F_{000}	4432.00		
μ(MoK$_\alpha$)	633.773 cm^{-1}		
Temperature	-150.0°C		

6 NMR spectra

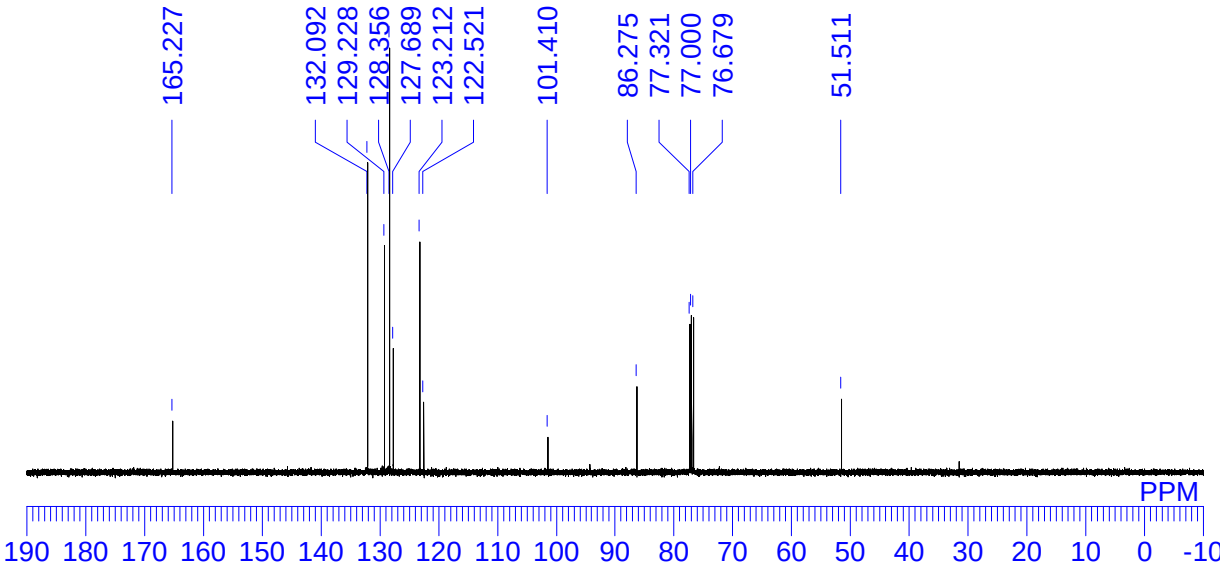
methyl (*Z*)-5-phenylpent-2-en-4-ynoate (**1a**)



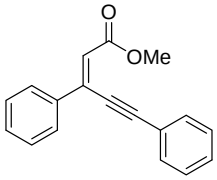
^{1}H NMR (400 MHz, $CDCl_3$)



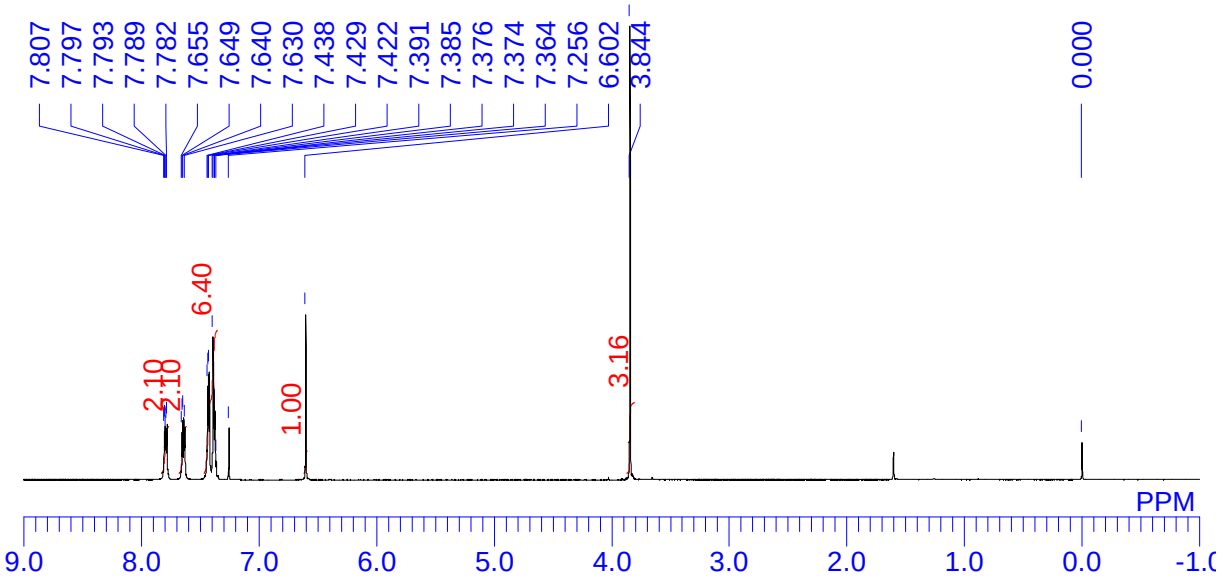
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



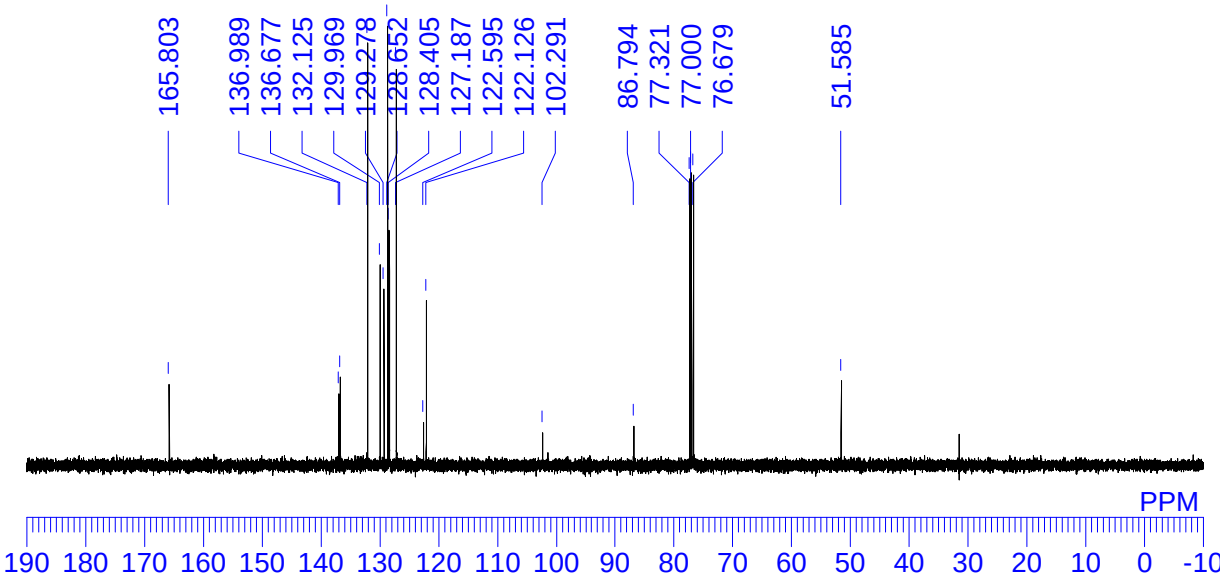
methyl (*Z*)-3,5-diphenylpent-2-en-4-ynoate (**1b**)



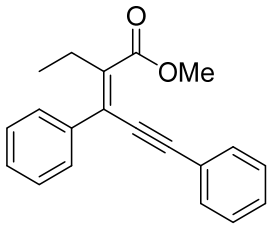
^{1}H NMR (400 MHz, $CDCl_3$)



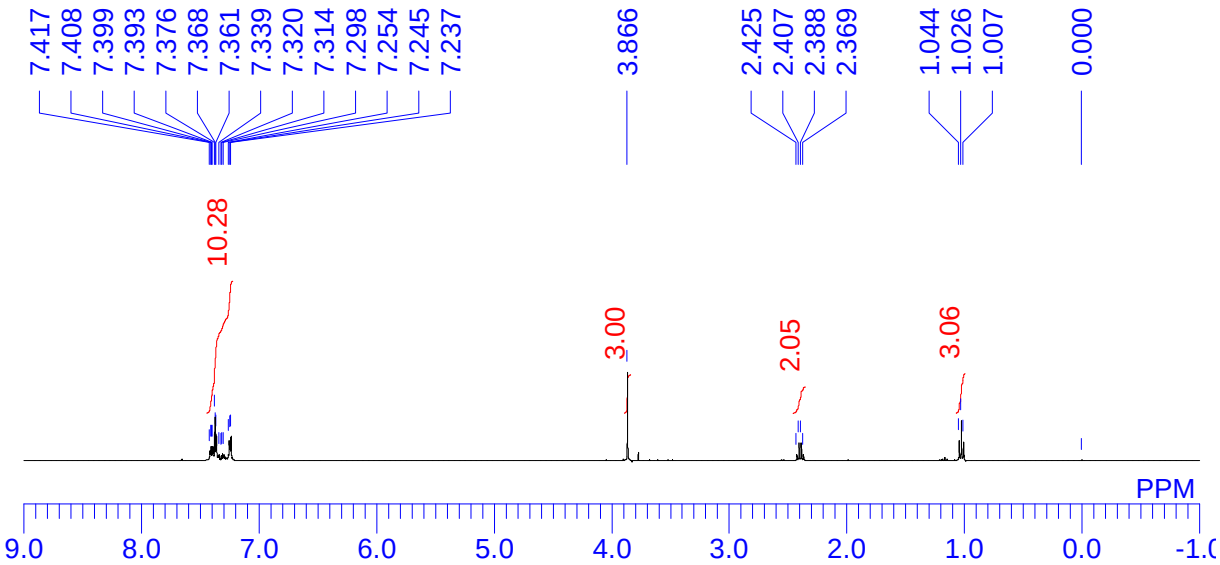
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



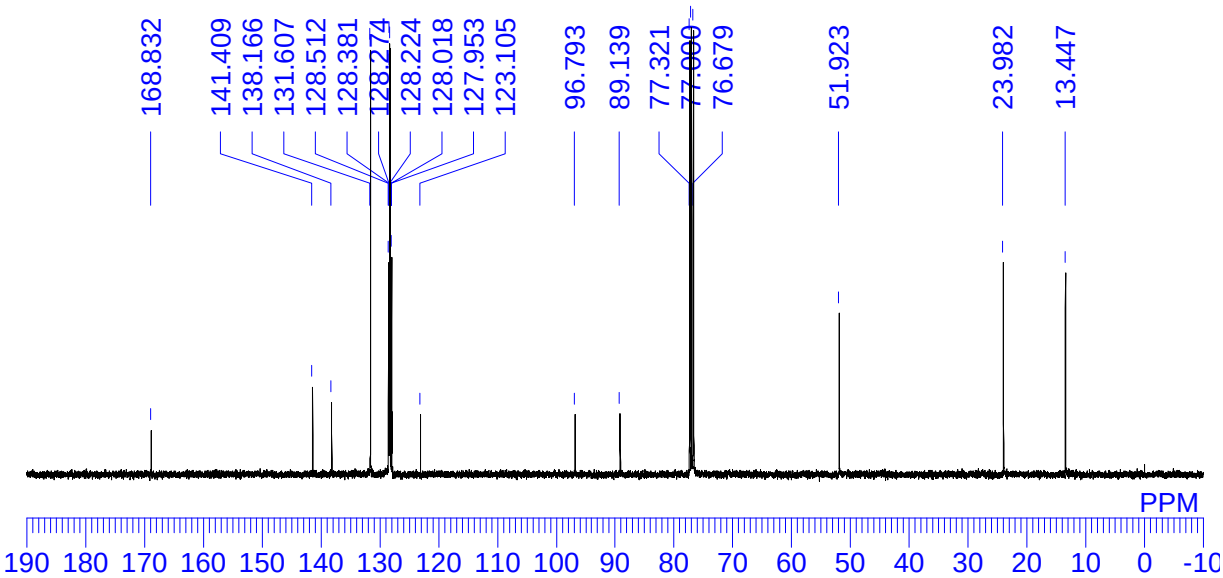
methyl (*Z*)-2-ethyl-3,5-diphenylpent-2-en-4-ynoate (**1c**)



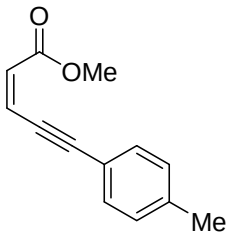
^{1}H NMR (400 MHz, $CDCl_3$)



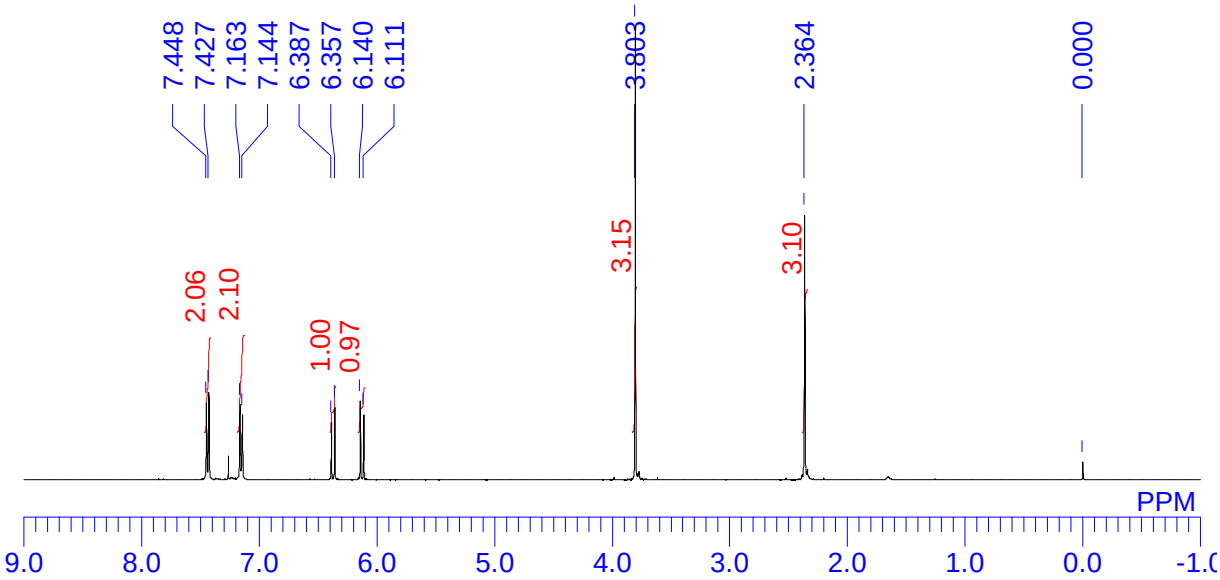
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



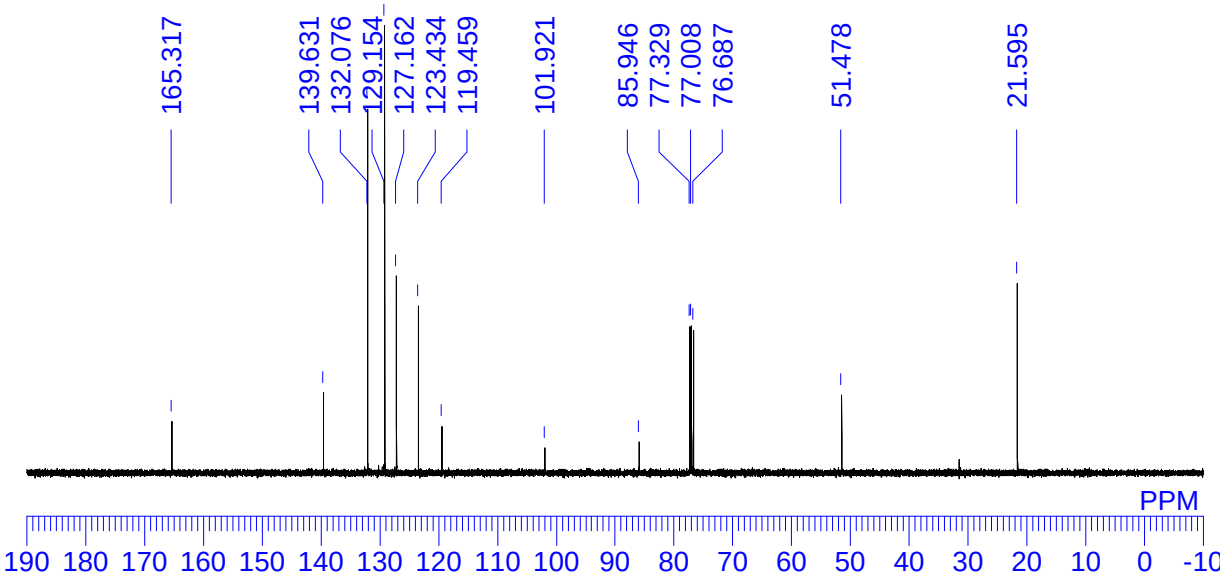
methyl (*Z*)-5-(p-tolyl)pent-2-en-4-ynoate (**1d**)



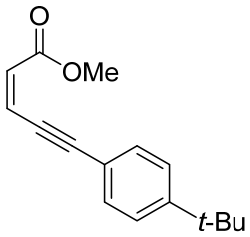
^{1}H NMR (400 MHz, $CDCl_3$)



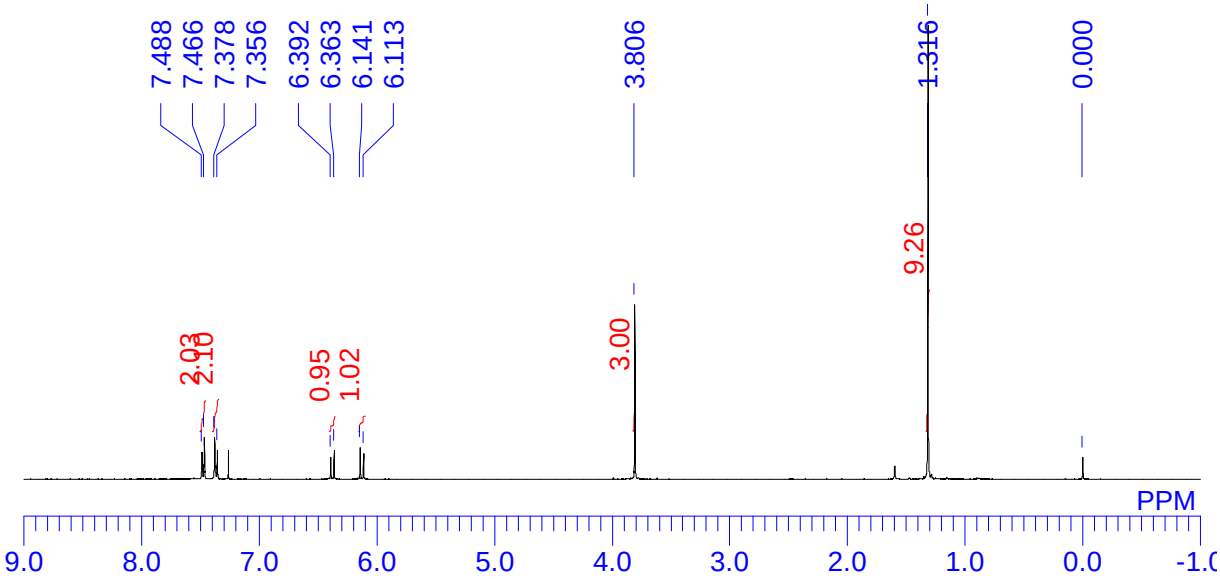
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



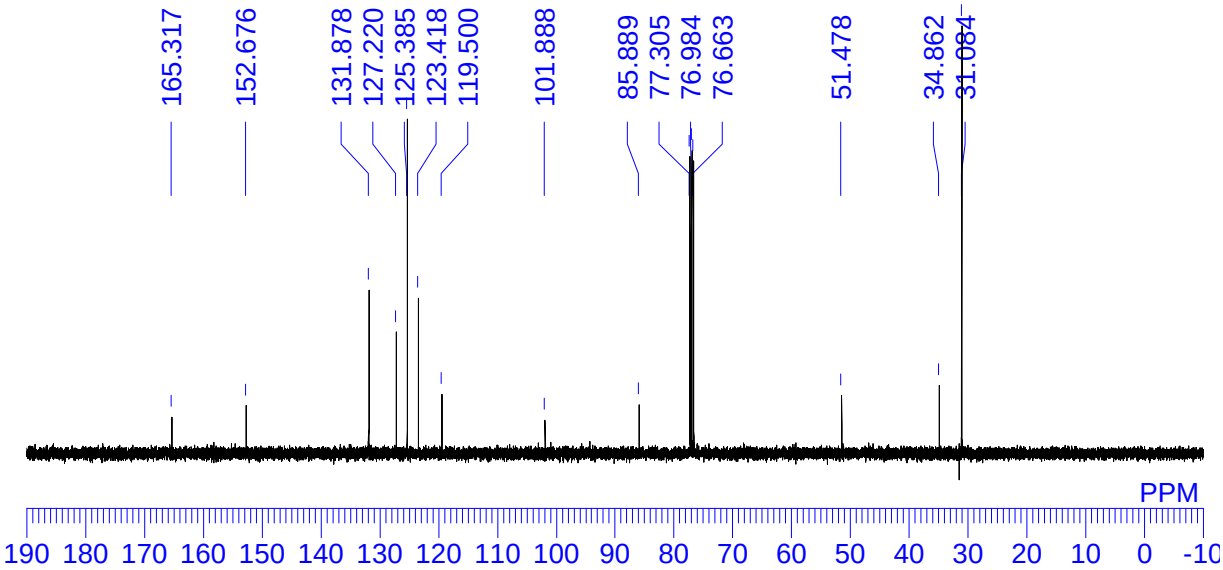
methyl (*Z*)-5-(4-(tert-butyl)phenyl)pent-2-en-4-ynoate (**1e**)



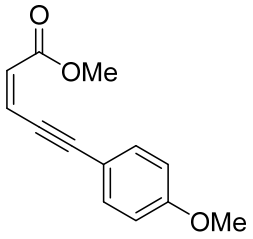
^{1}H NMR (400 MHz, $CDCl_3$)



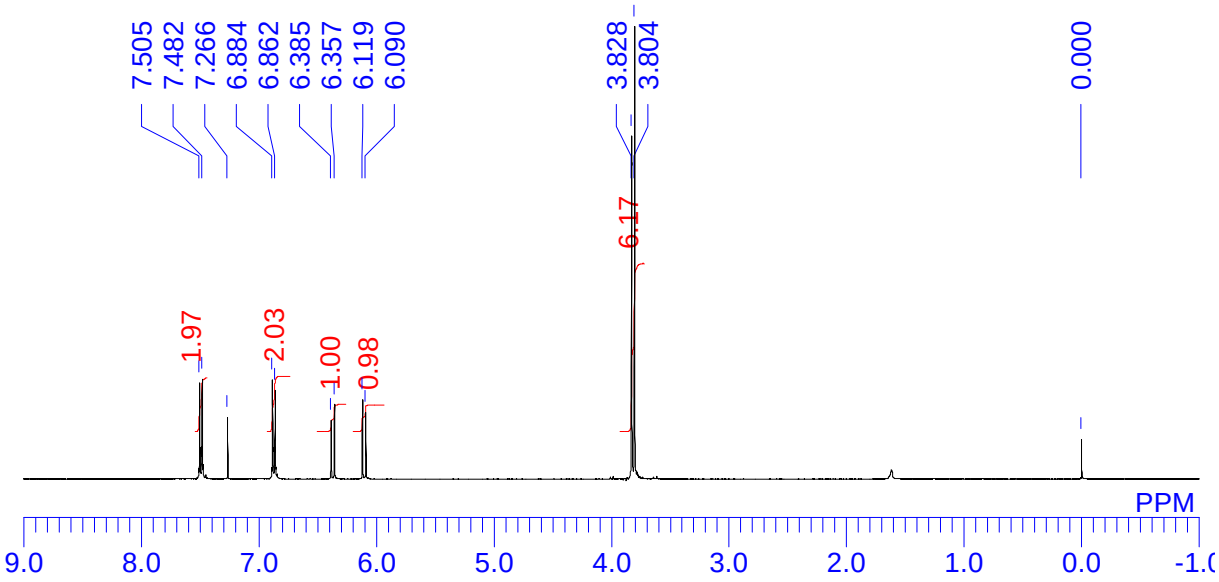
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



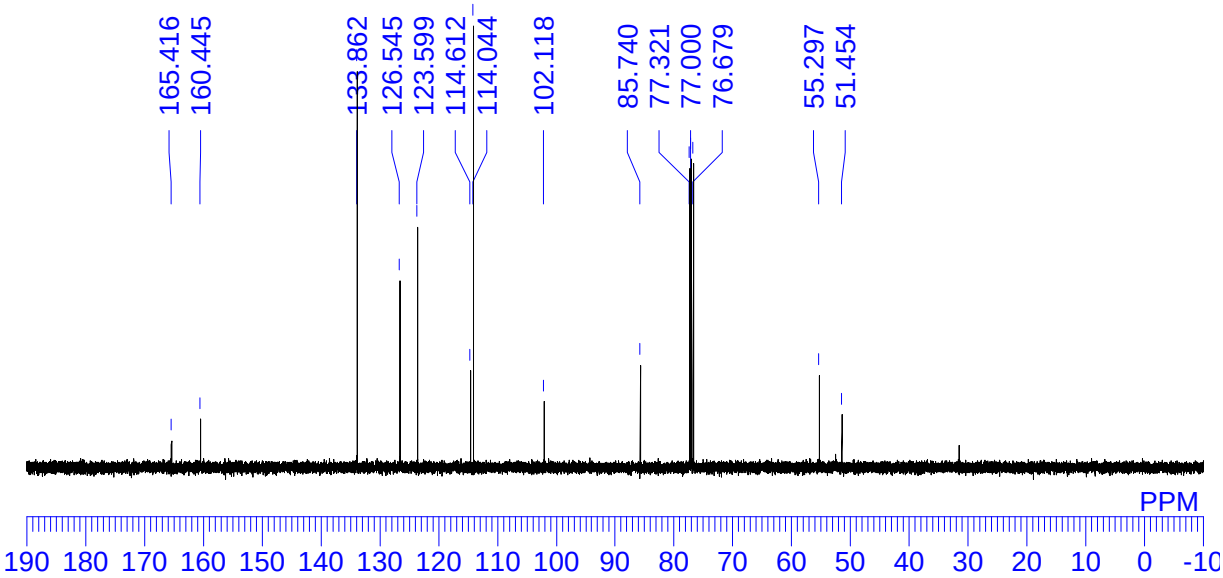
methyl (*Z*)-5-(4-methoxyphenyl)pent-2-en-4-ynoate (**1f**)



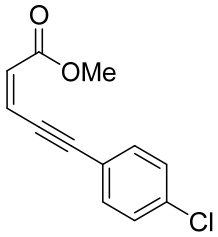
^{1}H NMR (400 MHz, $CDCl_3$)



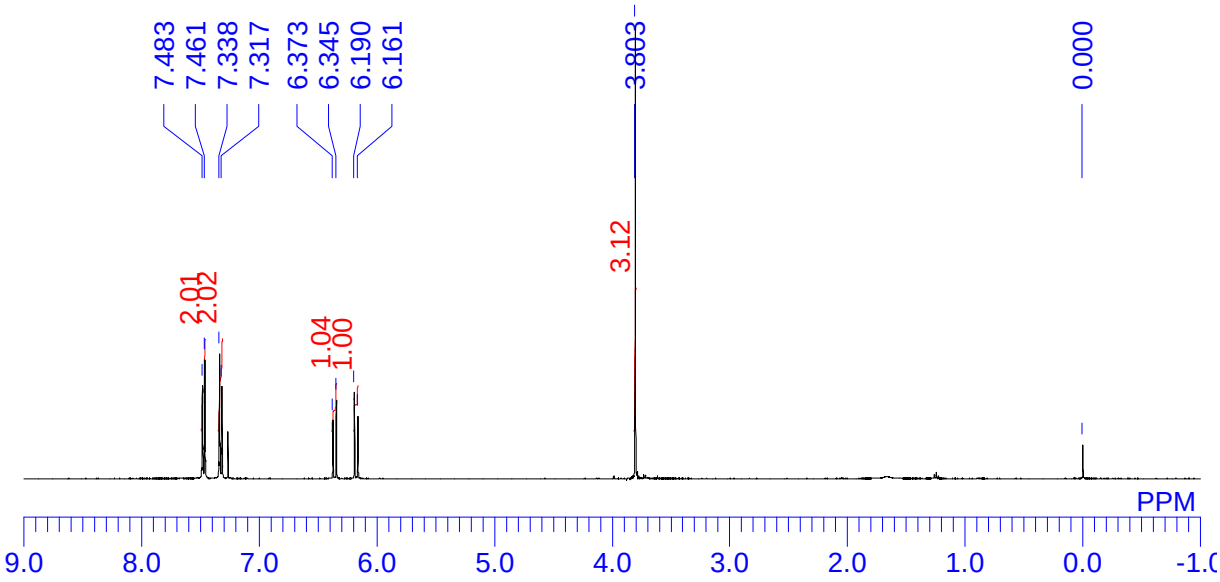
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



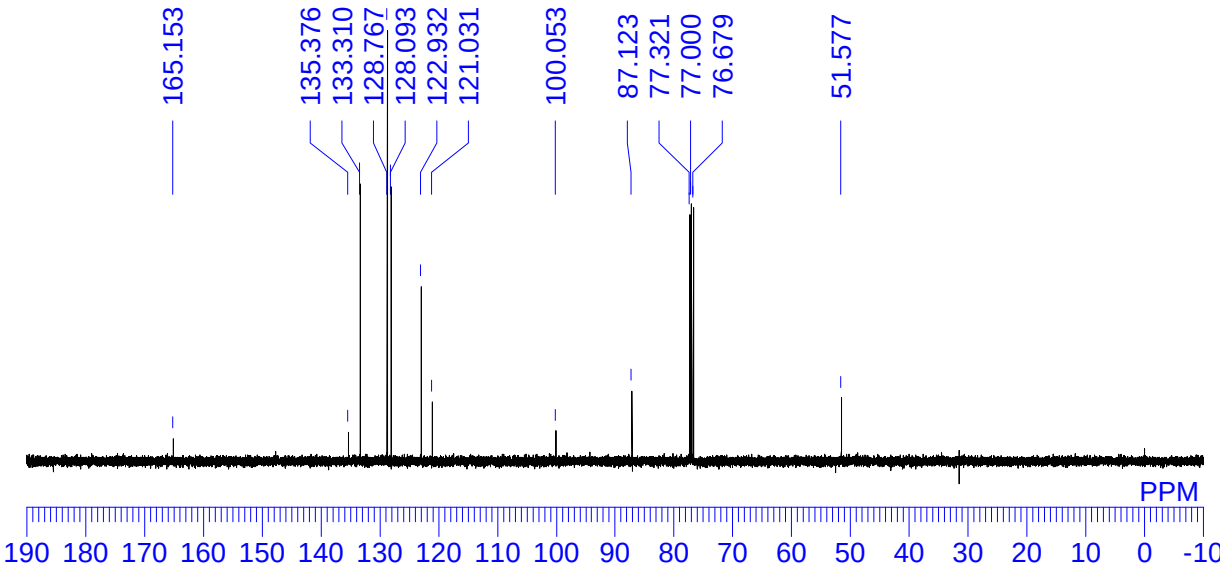
methyl (*Z*)-5-(4-chlorophenyl)pent-2-en-4-ynoate (**1g**)



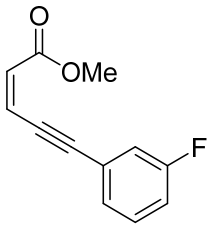
^{1}H NMR (400 MHz, $CDCl_3$)



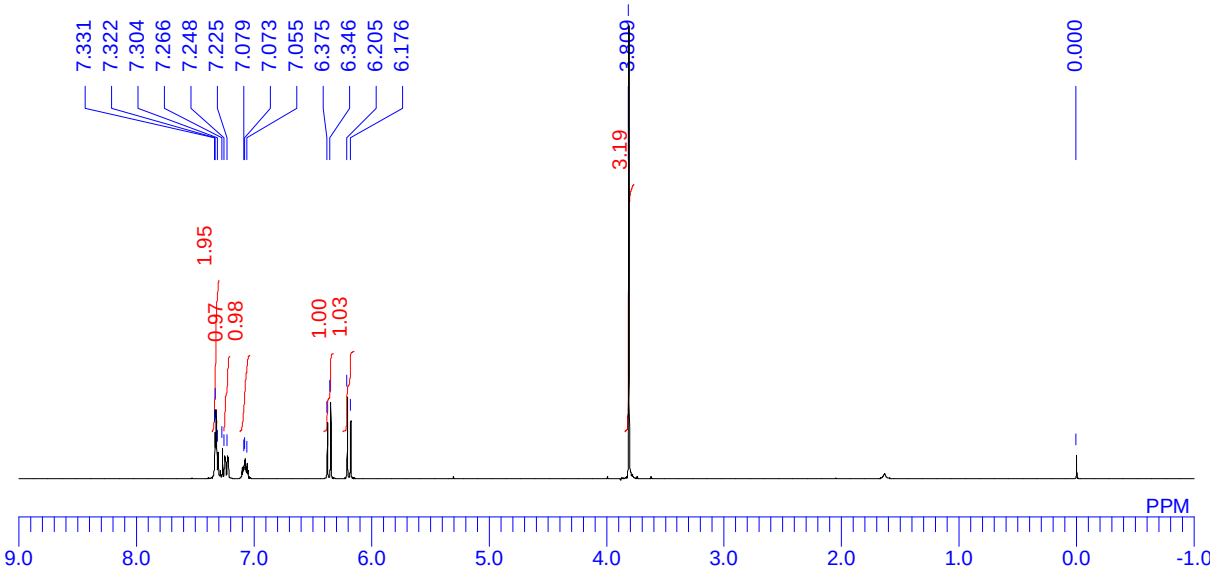
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



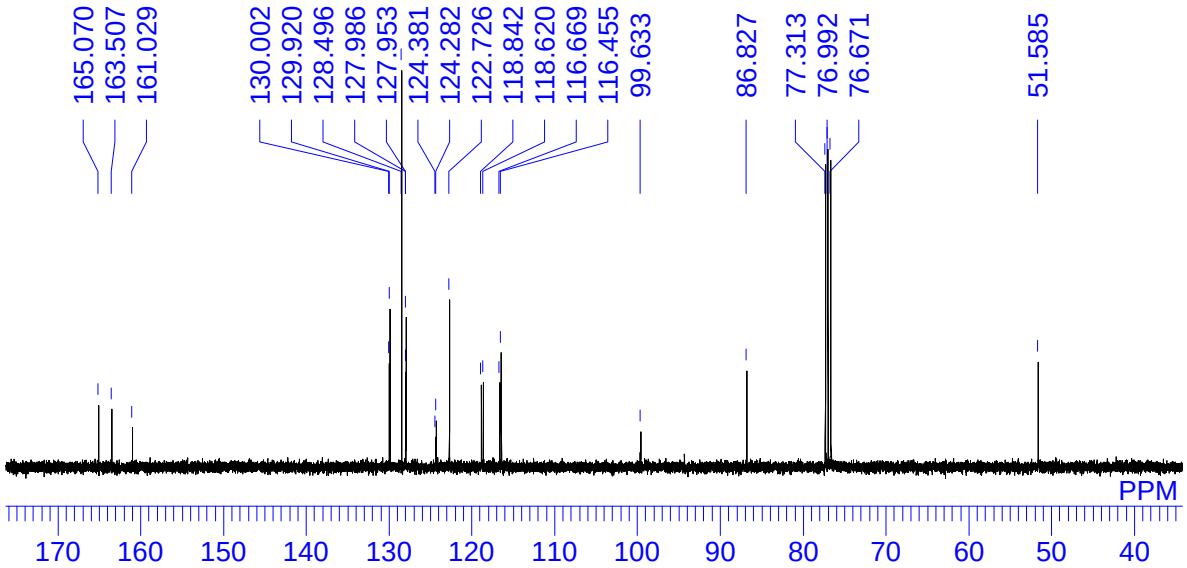
methyl (*Z*)-5-(3-fluorophenyl)pent-2-en-4-ynoate (**1h**)



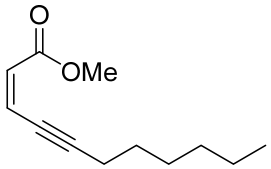
^{1}H NMR (400 MHz, $CDCl_3$)



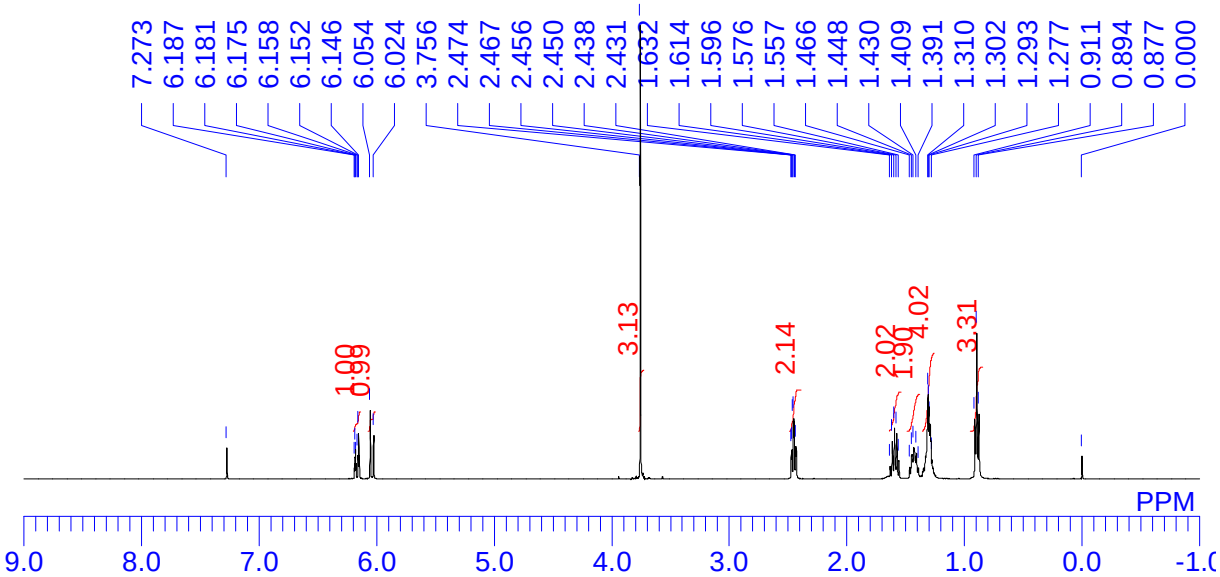
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



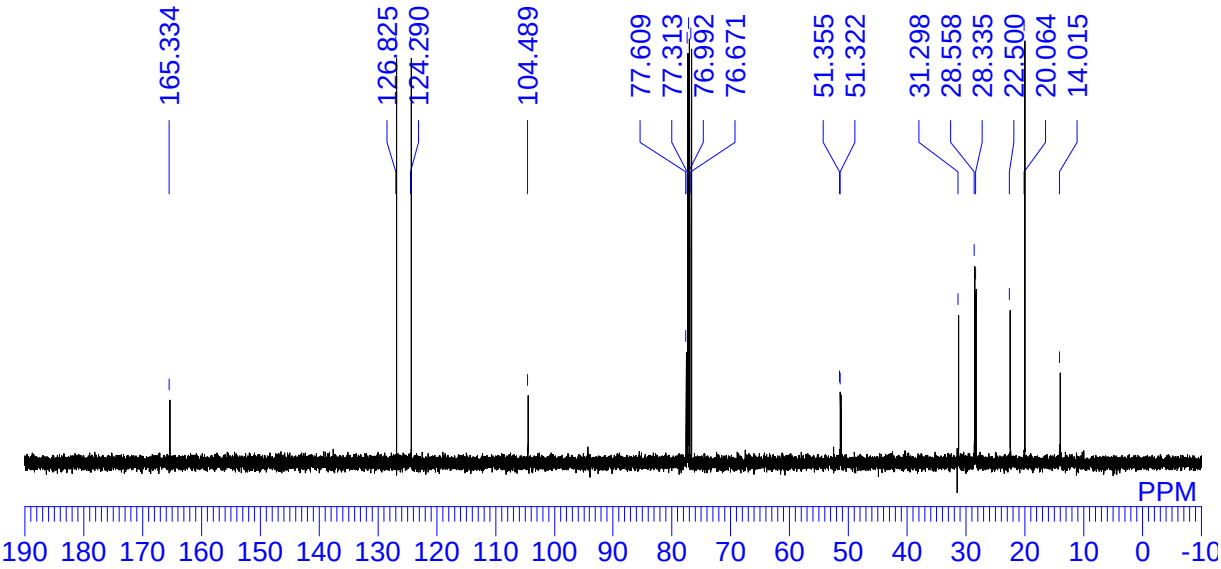
methyl (*Z*)-undec-2-en-4-ynoate (**1i**)



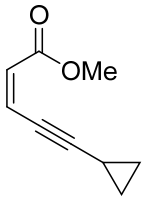
^{1}H NMR (400 MHz, $CDCl_3$)



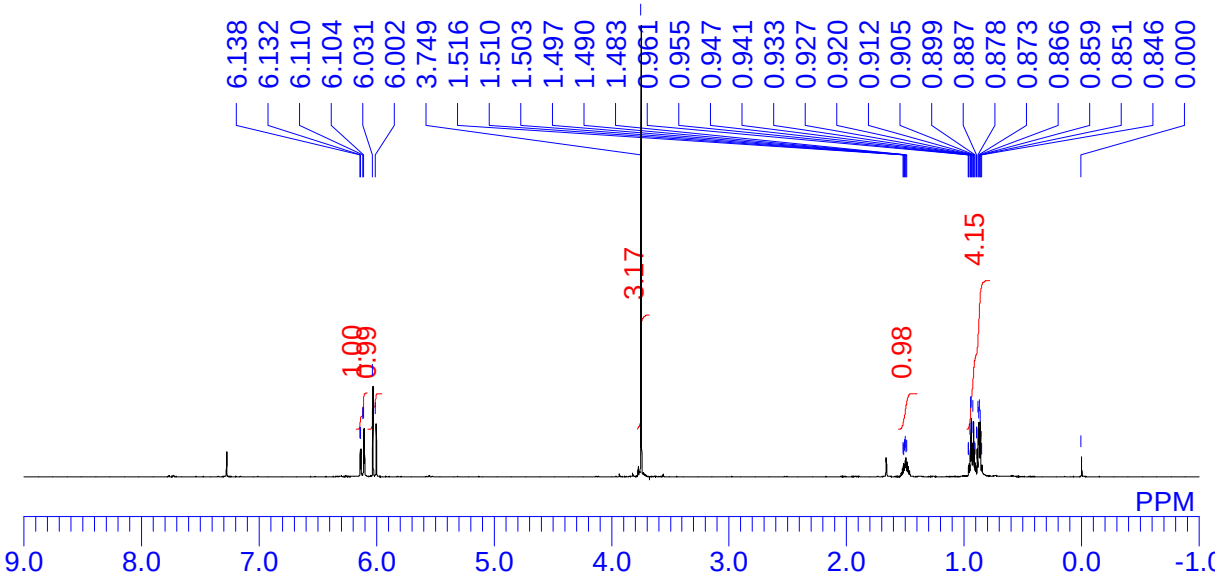
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



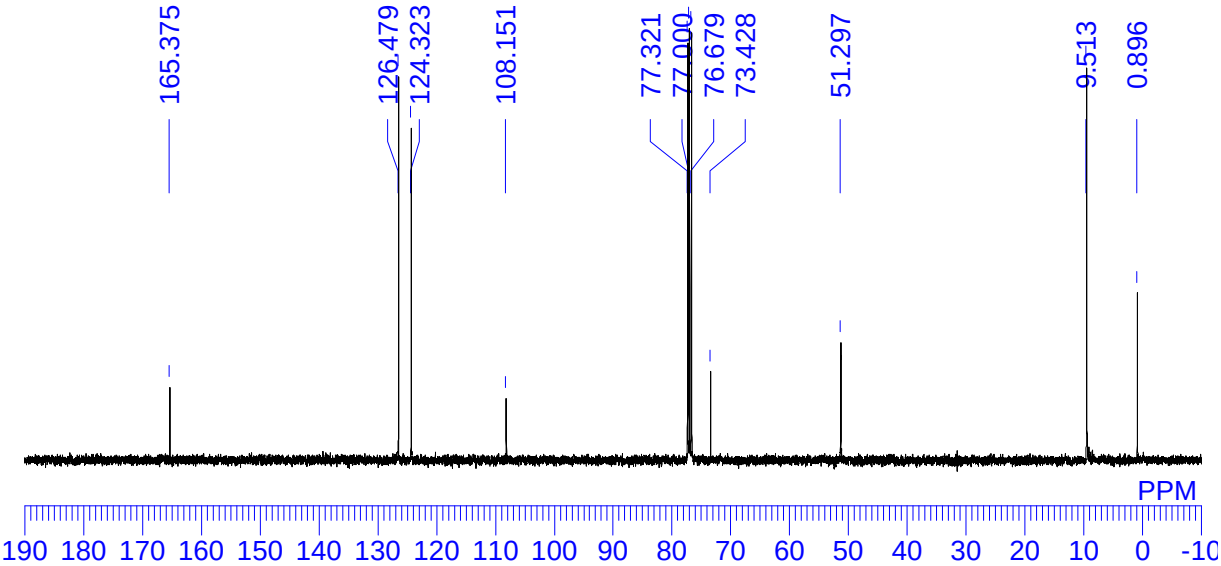
methyl (*Z*)-5-cyclopropylpent-2-en-4-ynoate (**1j**)



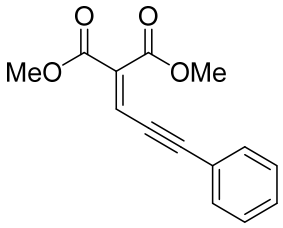
^{1}H NMR (400 MHz, $CDCl_3$)



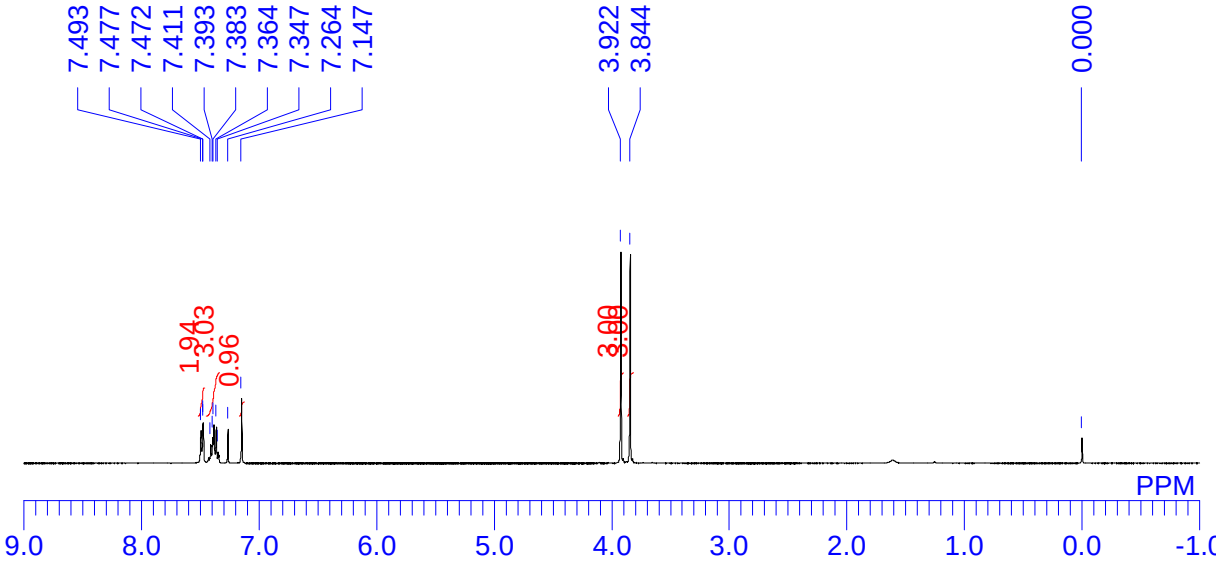
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



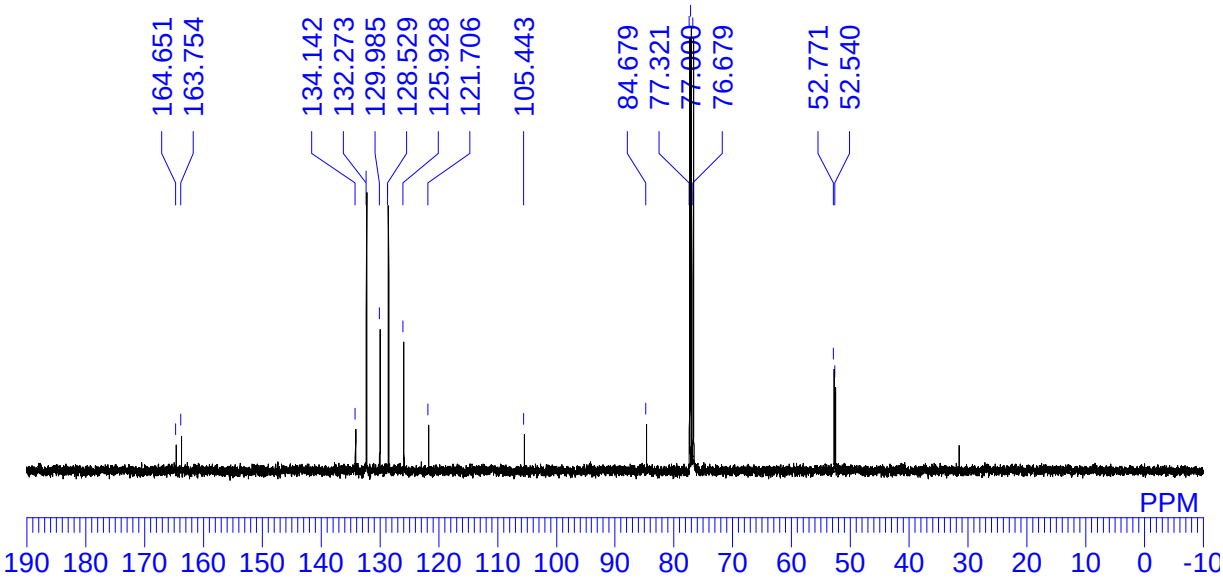
dimethyl 2-(3-phenylprop-2-yn-1-ylidene)malonate (**1k**)



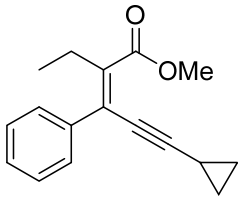
^{1}H NMR (400 MHz, $CDCl_3$)



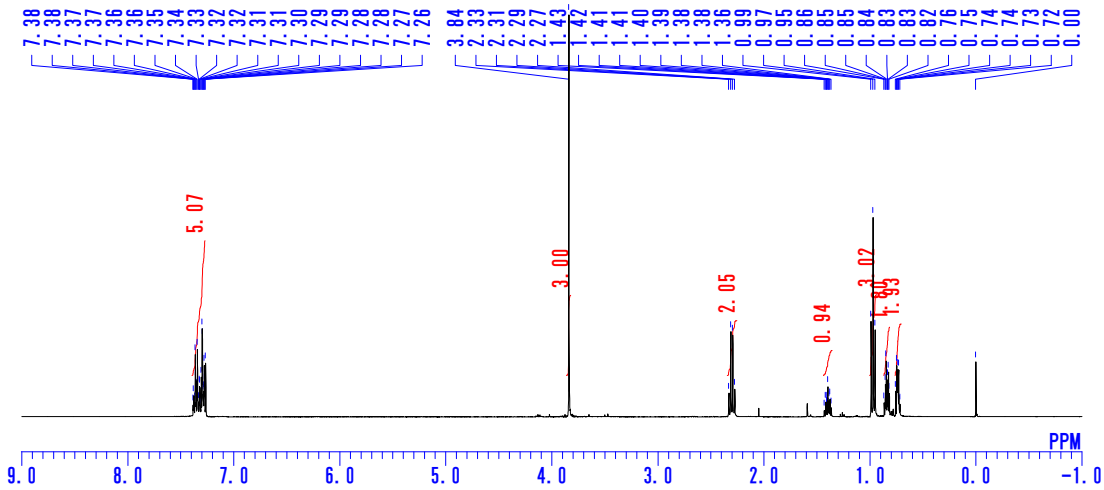
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



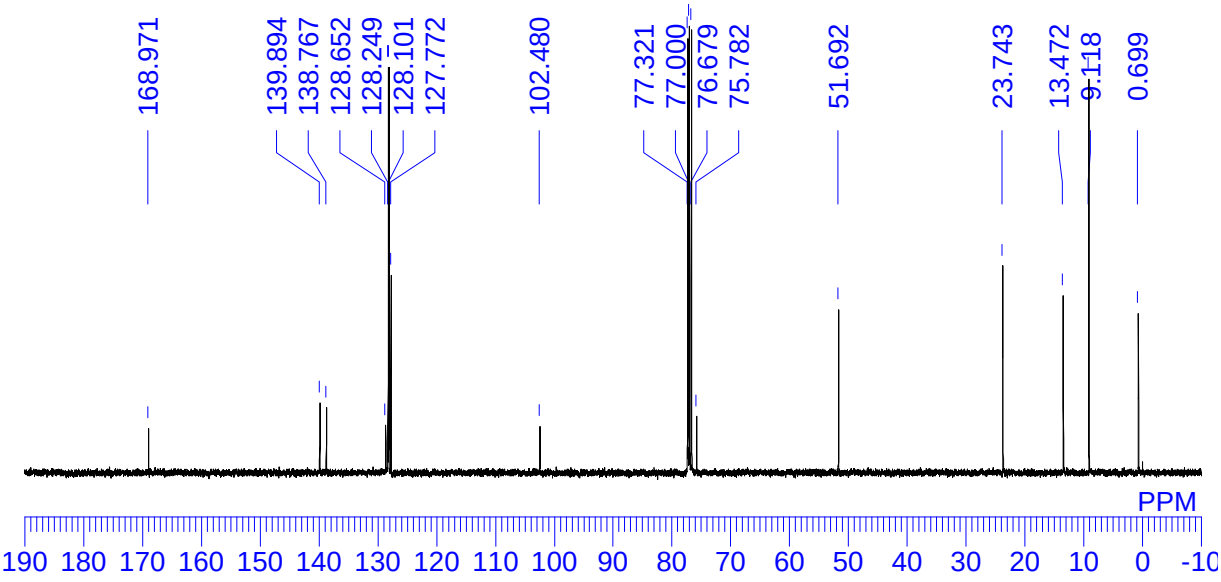
methyl (*Z*)-5-cyclopropyl-2-ethyl-3-phenylpent-2-en-4-ynoate (**1l**)



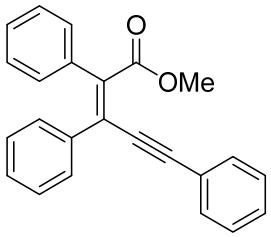
^{1}H NMR (400 MHz, $CDCl_3$)



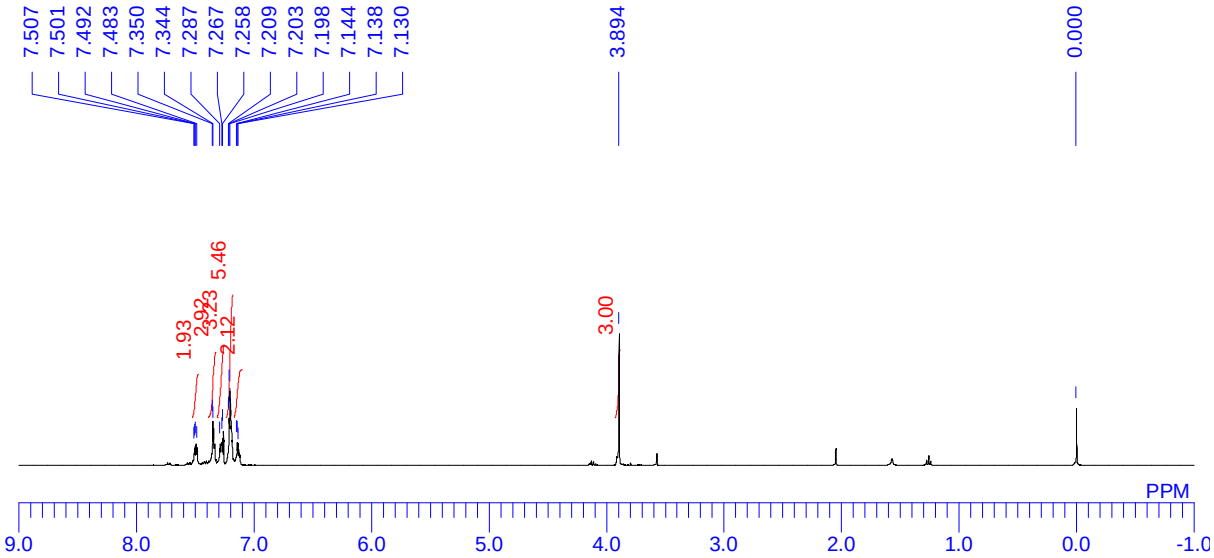
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



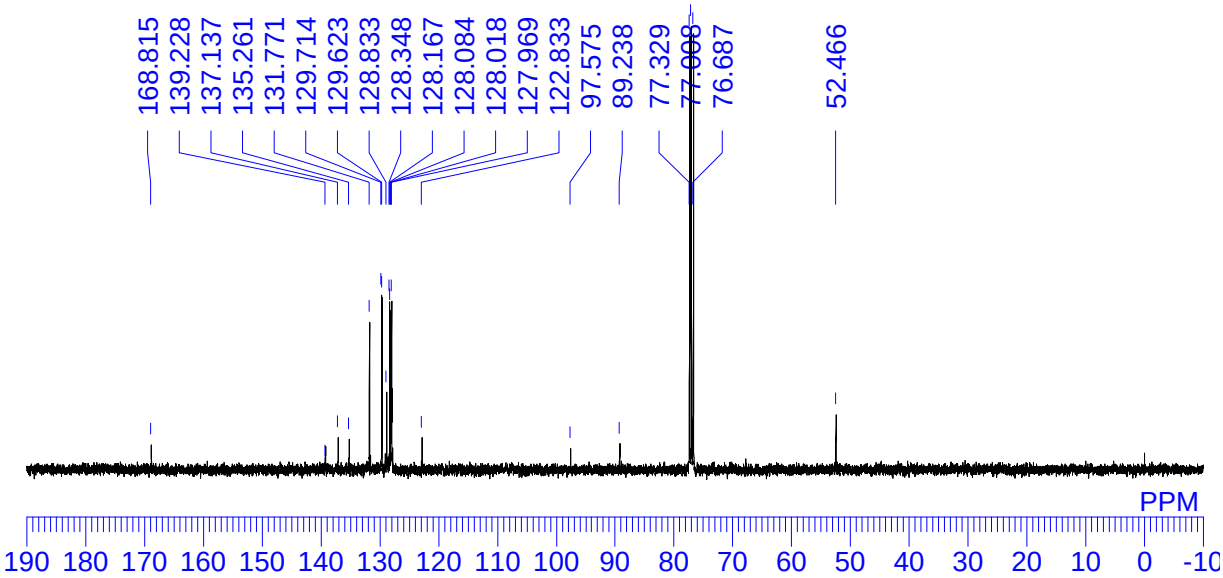
methyl (*Z*)-2,3,5-triphenylpent-2-en-4-ynoate (**1m**)



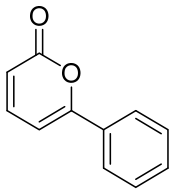
^{1}H NMR (400 MHz, $CDCl_3$)



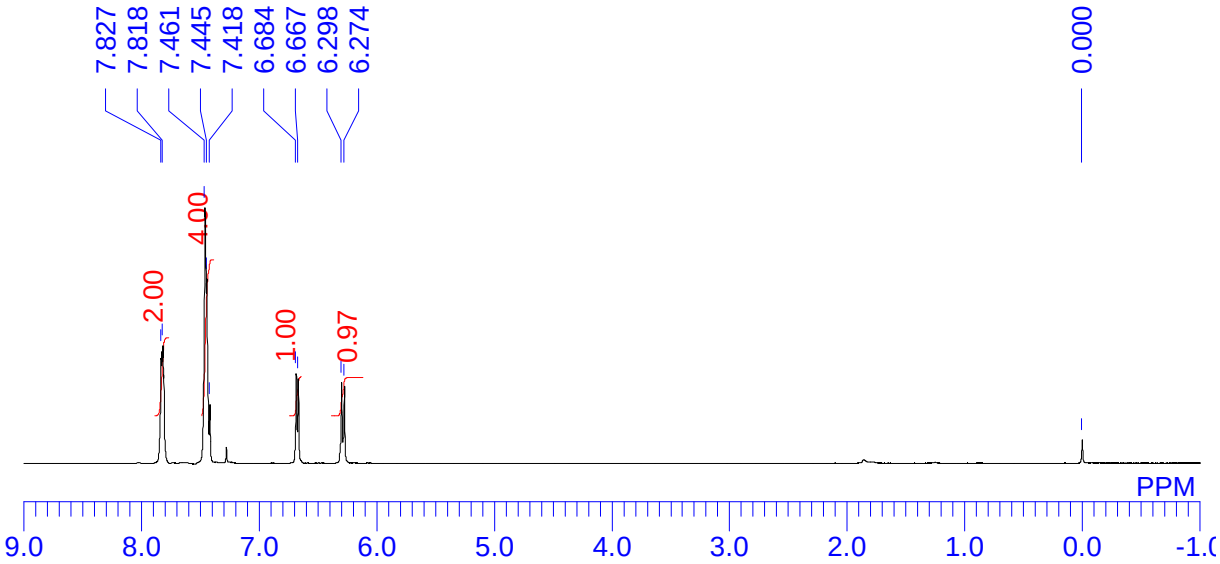
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



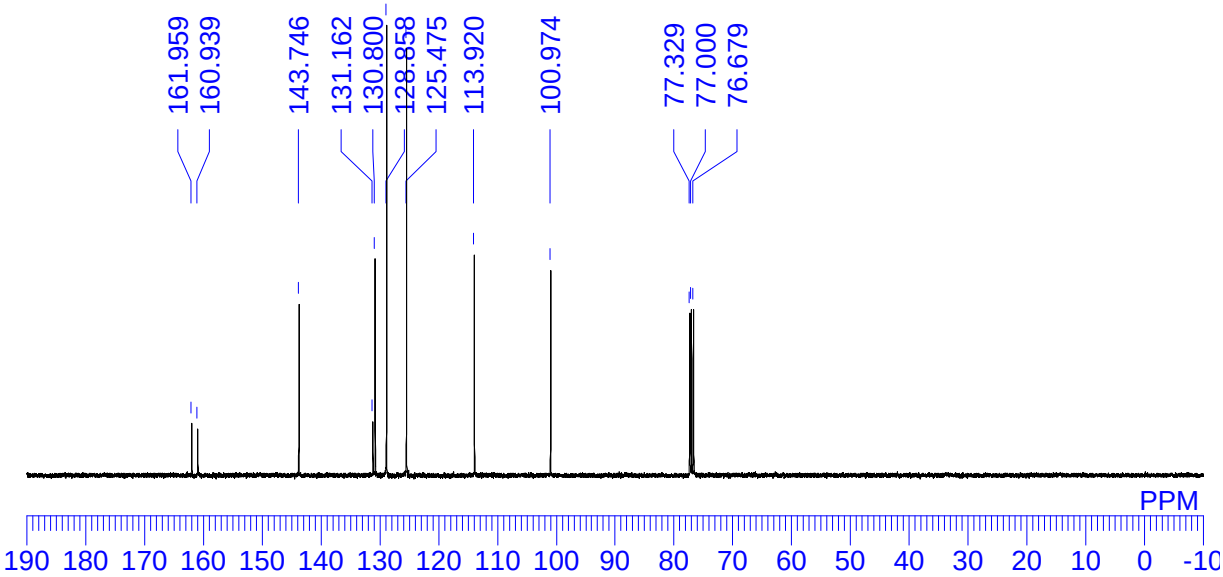
6-phenyl-*2H*-pyran-2-one (**2a**)



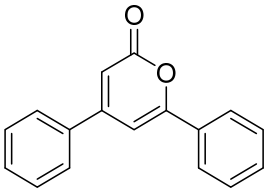
^{1}H NMR (400 MHz, $CDCl_3$)



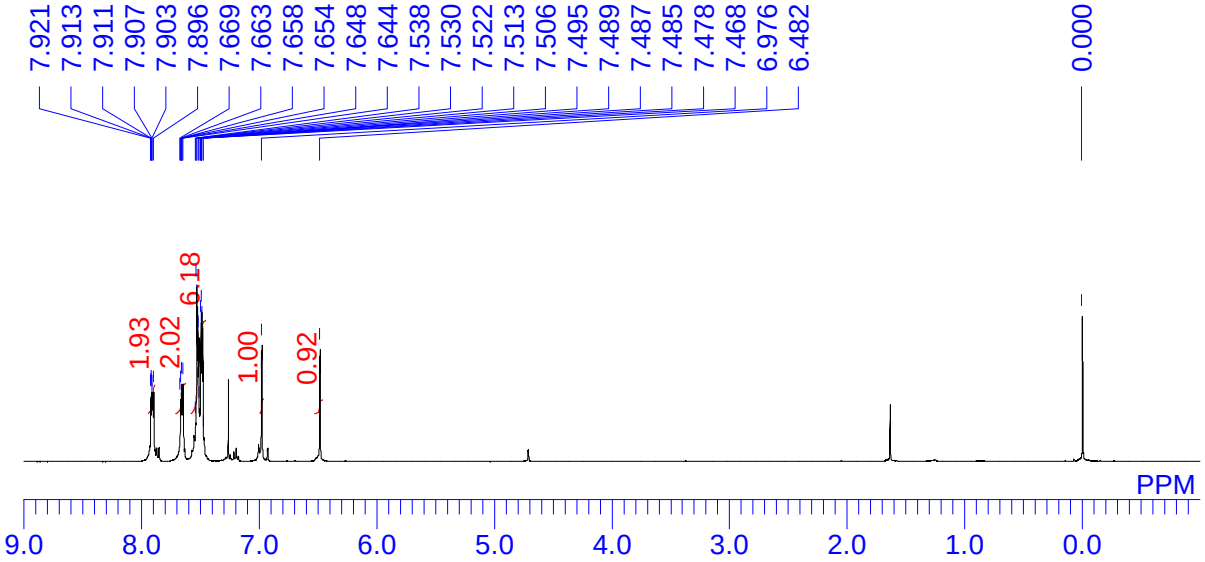
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



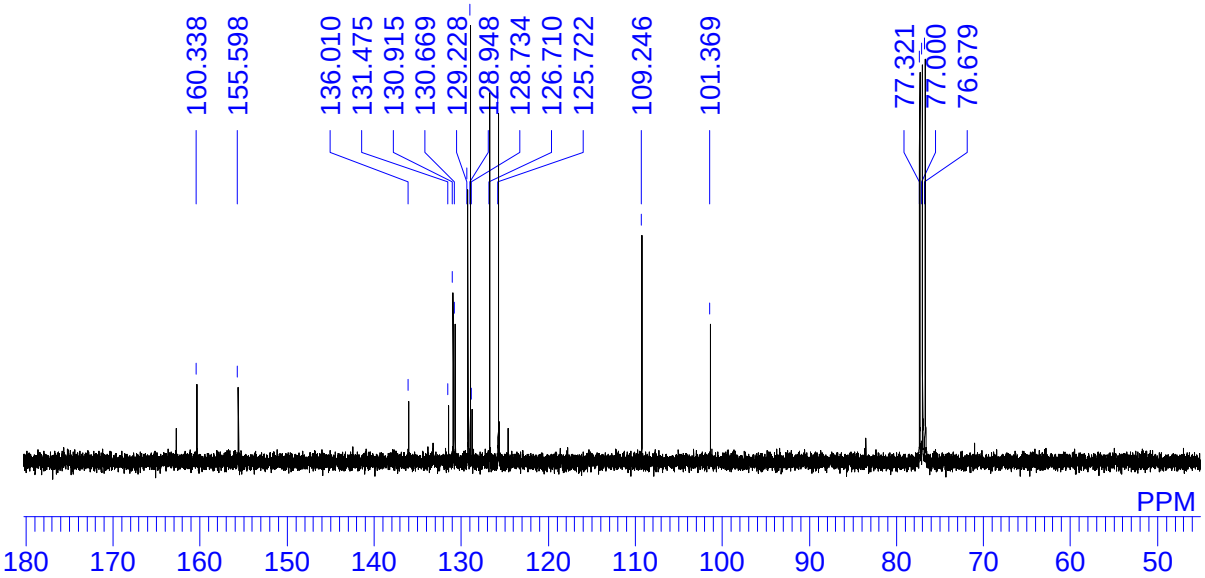
4,6-diphenyl-*2H*-pyran-2-one (**2b**)



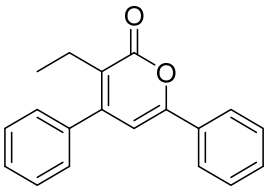
^{1}H NMR (400 MHz, $CDCl_3$)



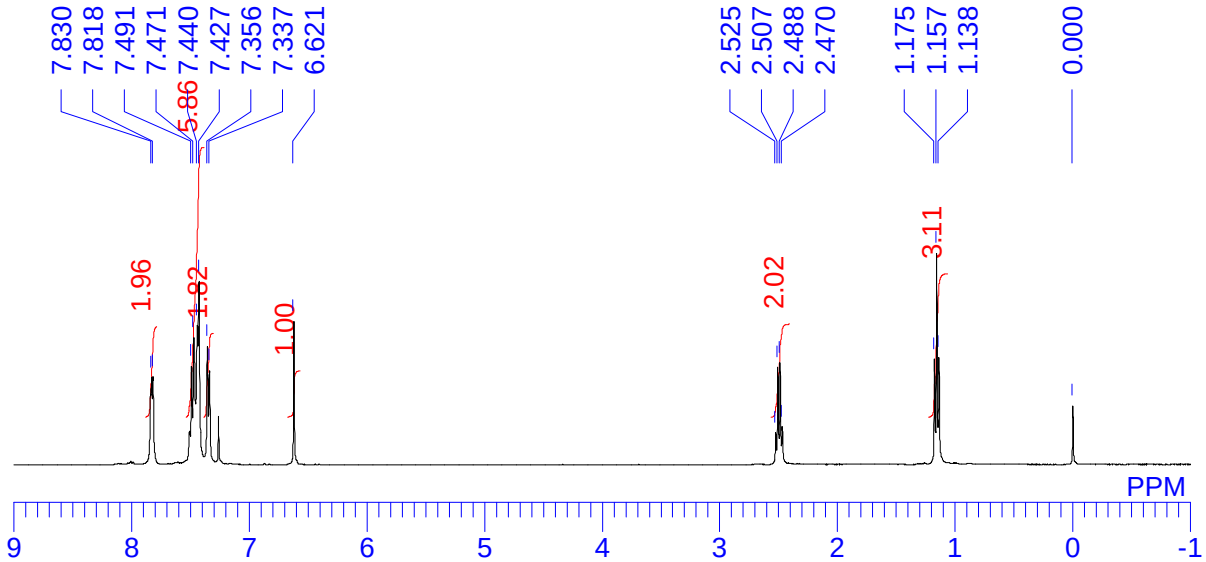
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



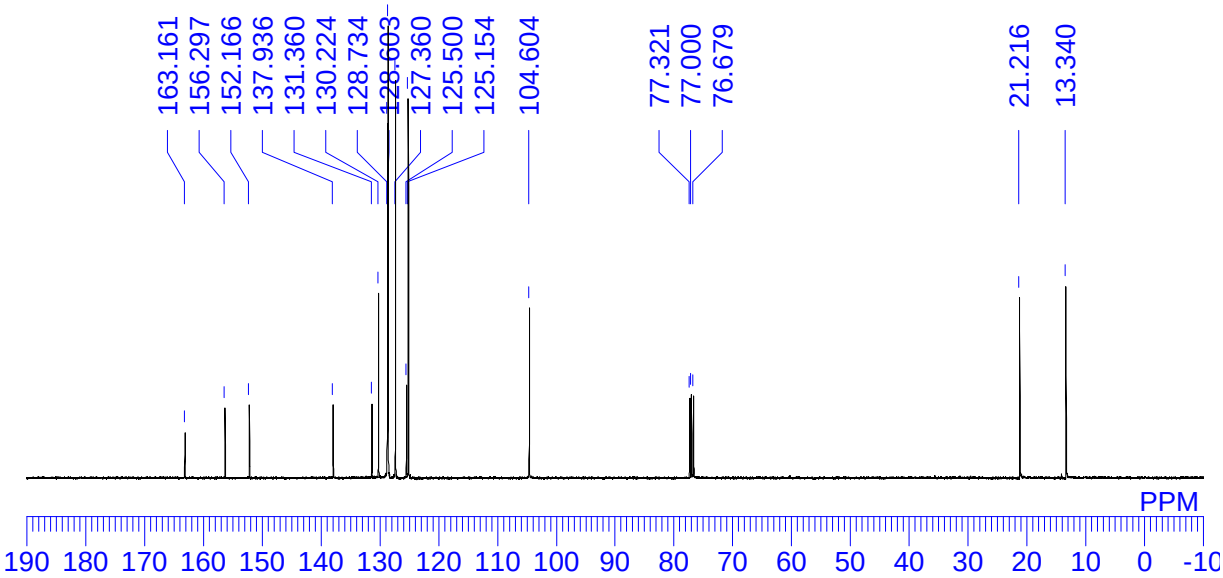
3-ethyl-4,6-diphenyl-*2H*-pyran-2-one (**2c**)



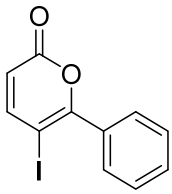
^{1}H NMR (400 MHz, $CDCl_3$)



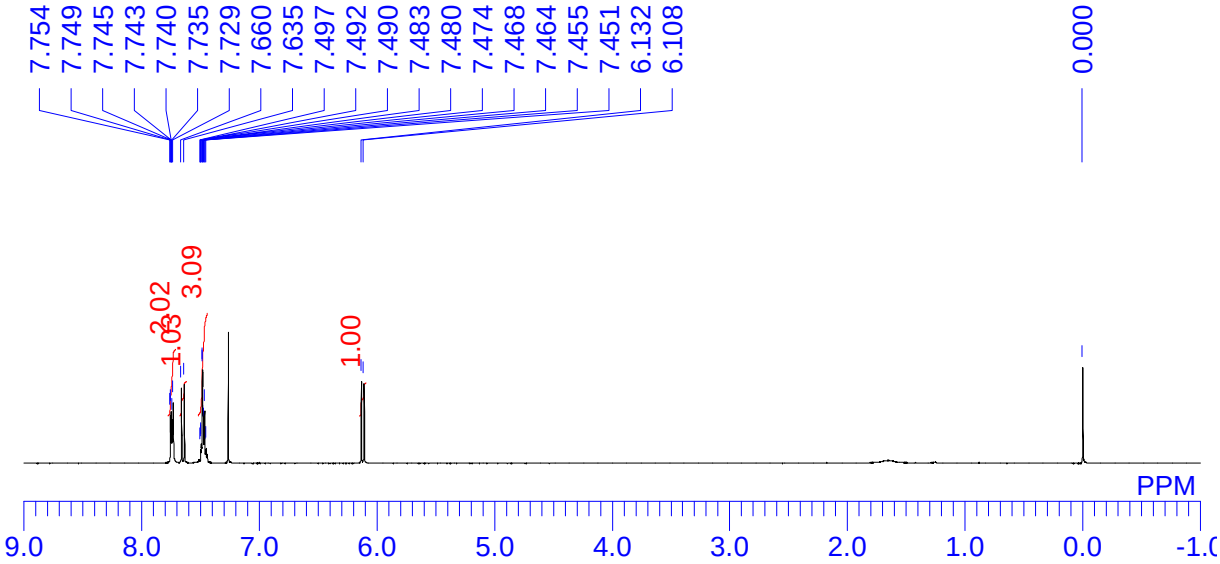
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



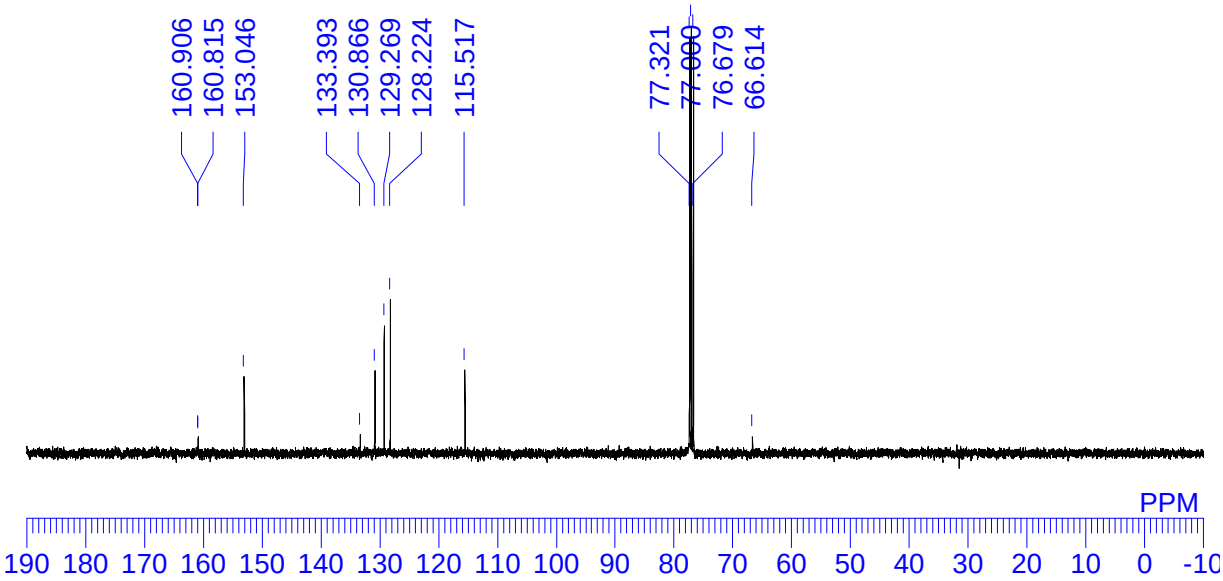
5-iodo-6-phenyl-*2H*-pyran-2-one (**5a**)



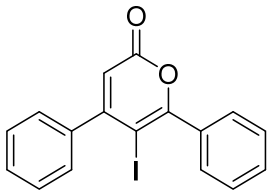
^{1}H NMR (400 MHz, $CDCl_3$)



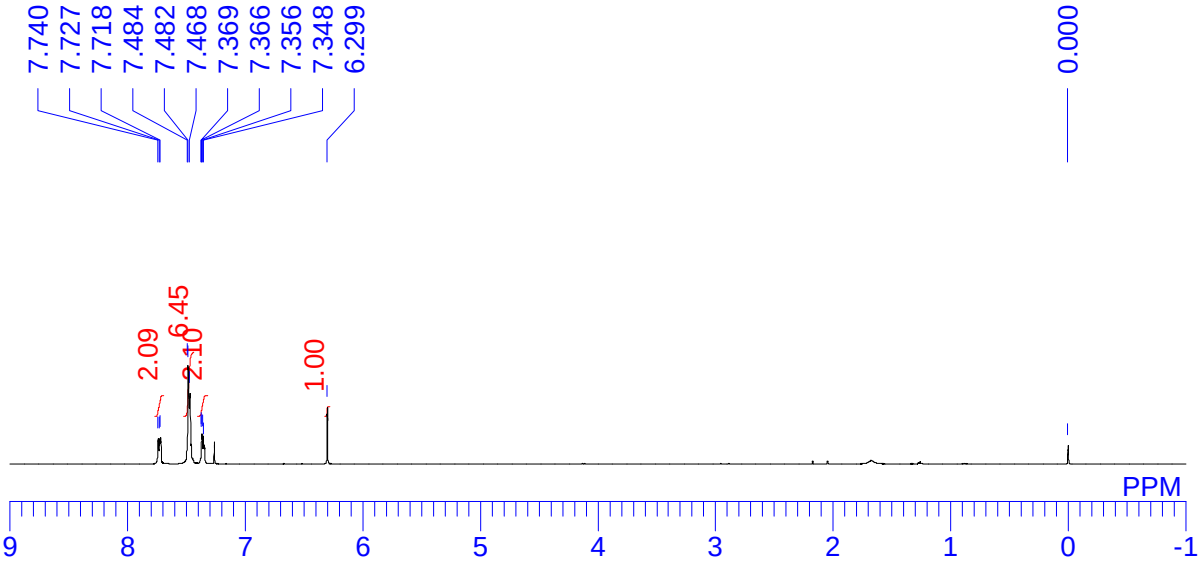
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



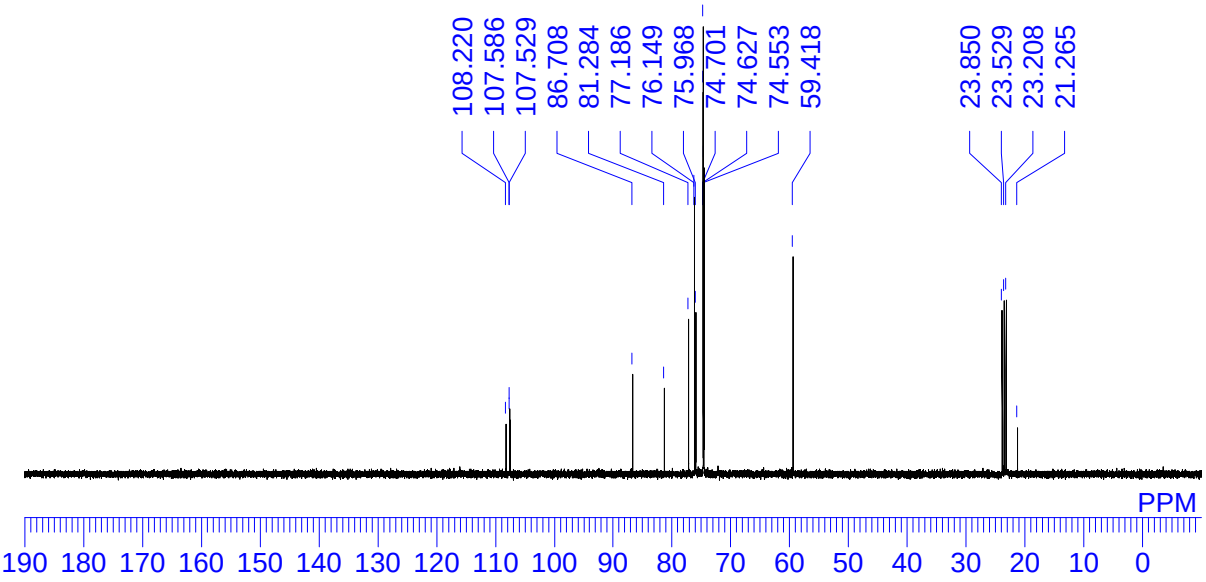
5-iodo-4,6-diphenyl-*2H*-pyran-2-one (**5b**)



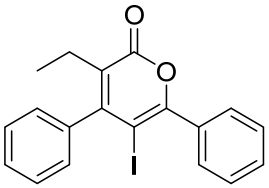
^{1}H NMR (400 MHz, $CDCl_3$)



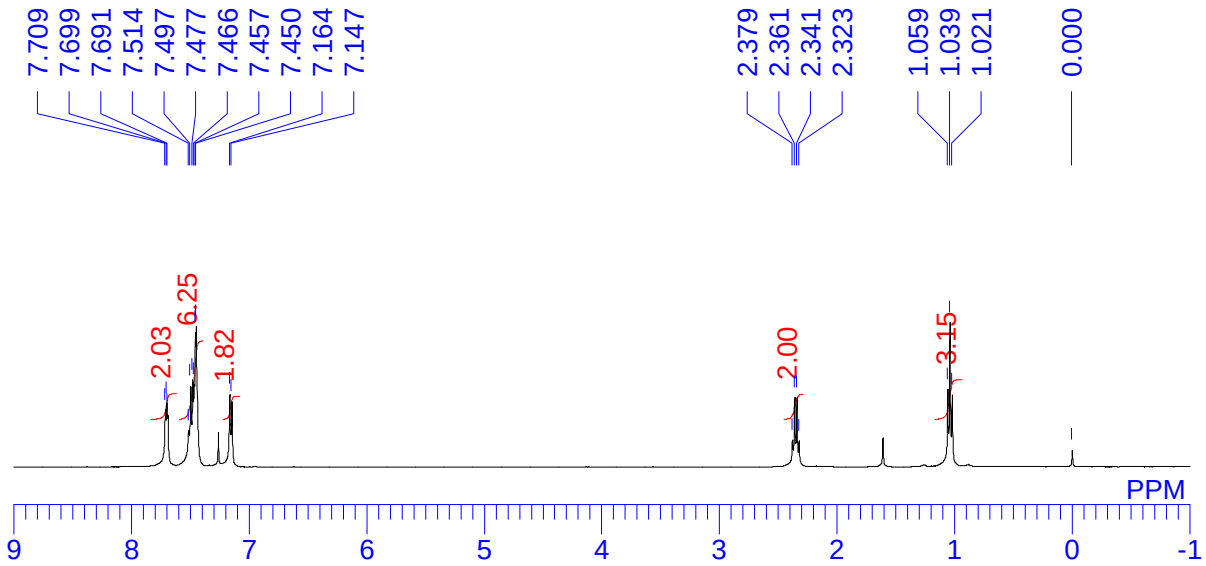
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



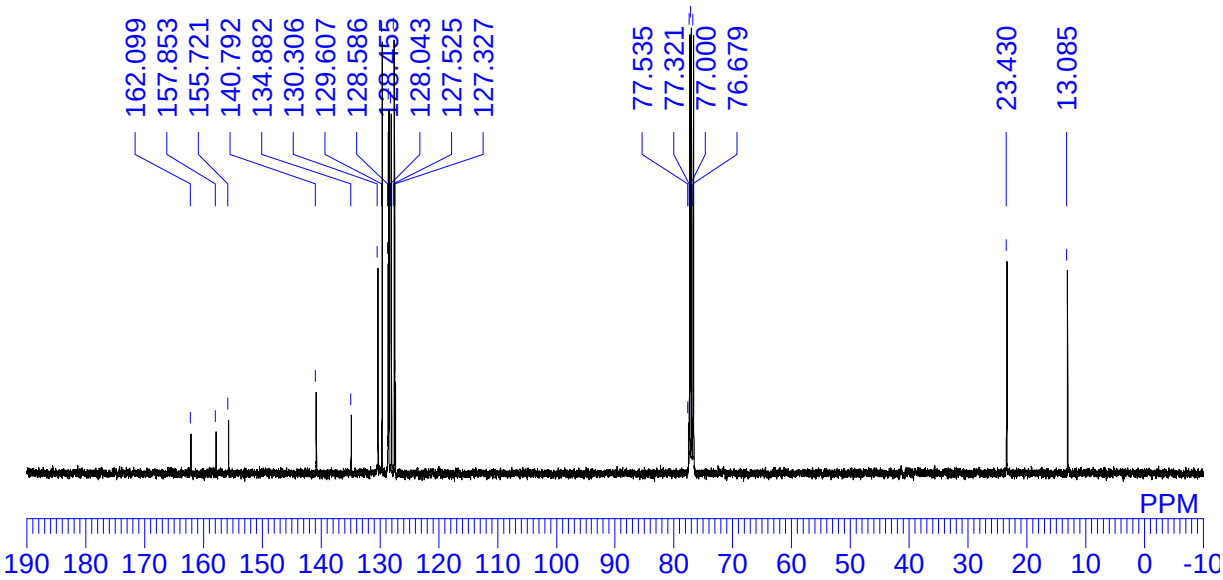
3-ethyl-5-iodo-4,6-diphenyl-*2H*-pyran-2-one (**5c**)



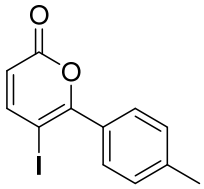
^{1}H NMR (400 MHz, $CDCl_3$)



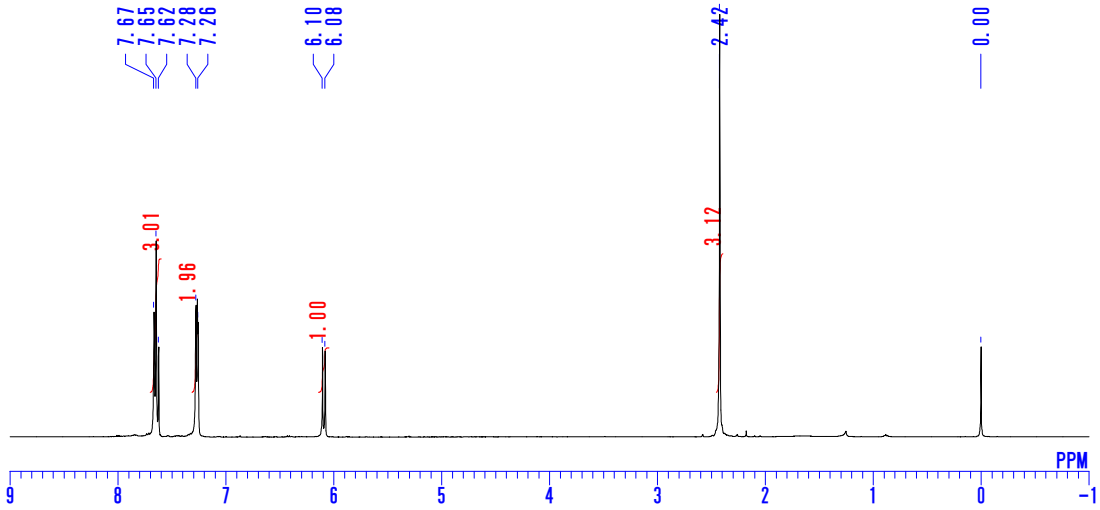
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



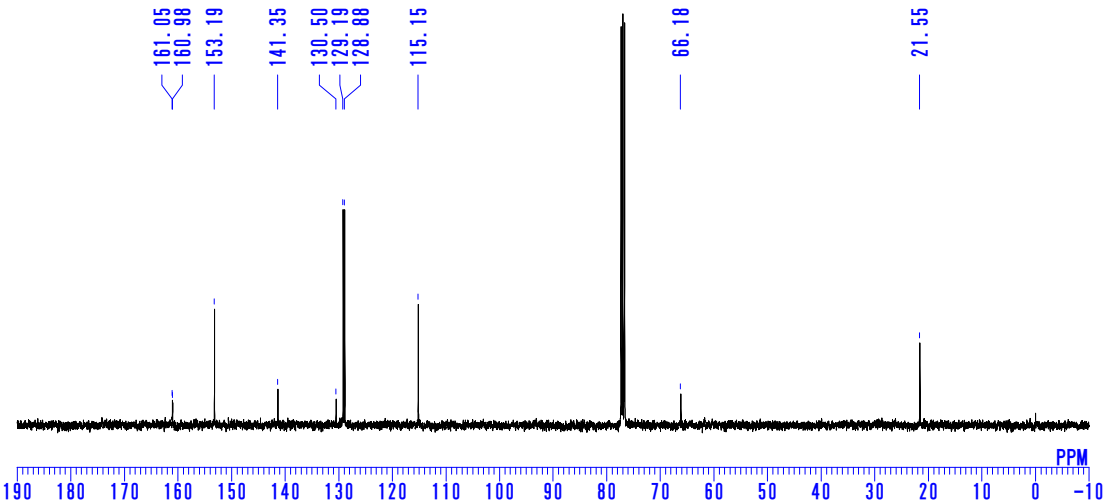
5-iodo-6-(p-tolyl)-*2H*-pyran-2-one (**5d**)



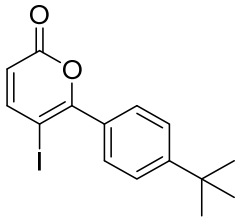
^{1}H NMR (400 MHz, $CDCl_3$)



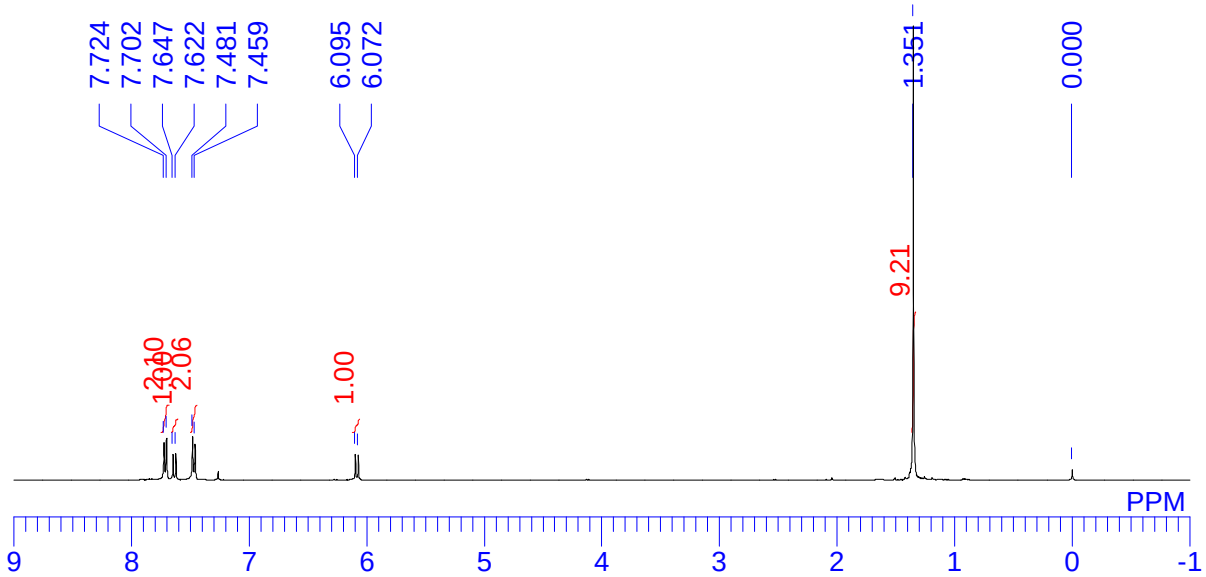
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



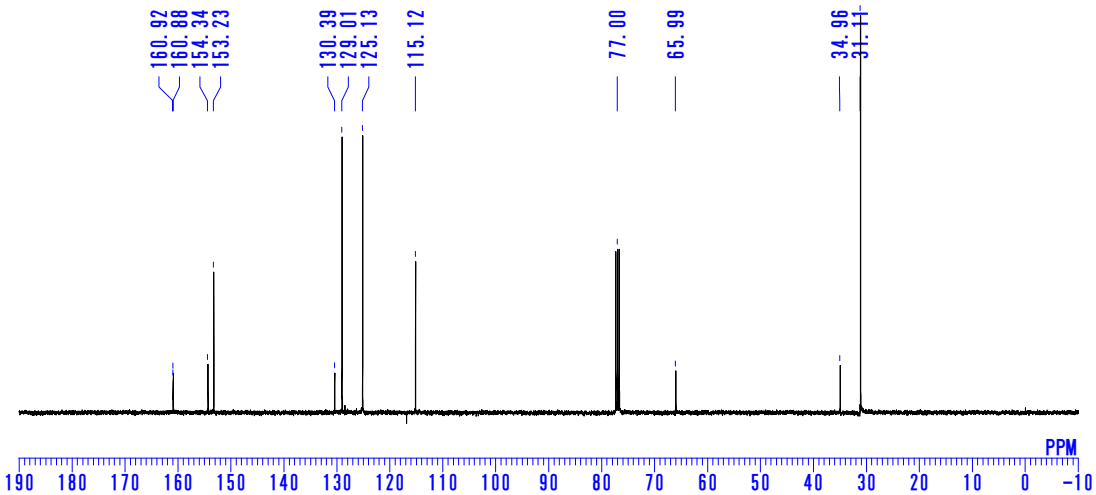
6-{4-(*tert*-butyl)phenyl}-5-iodo-2*H*-pyran-2-one (**5e**)



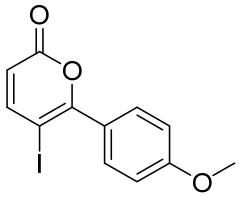
^{1}H NMR (400 MHz, $CDCl_3$)



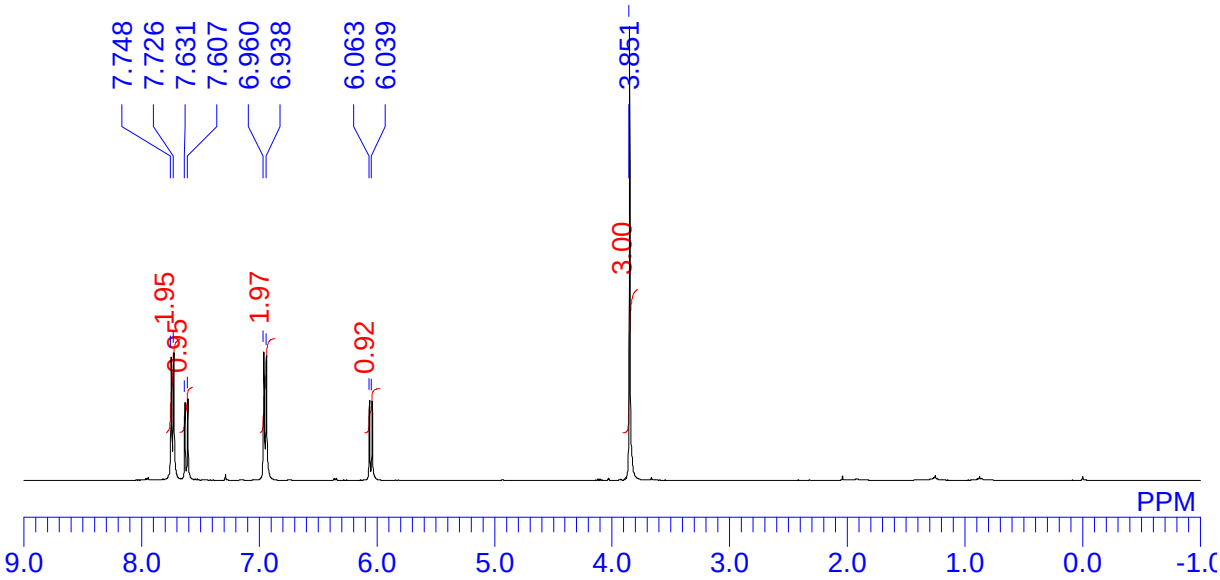
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



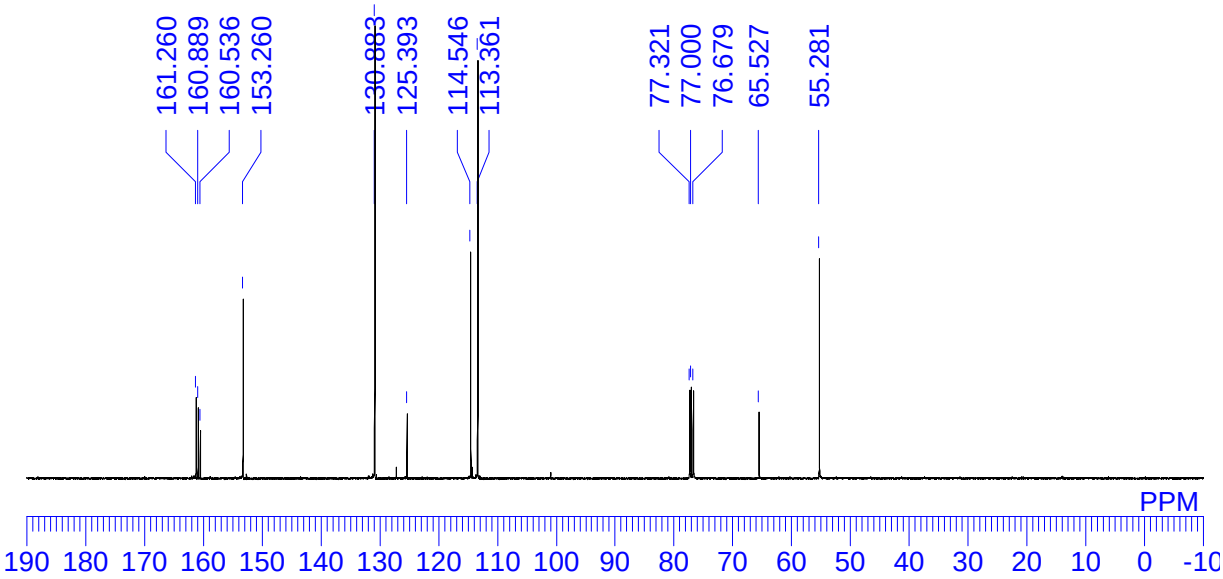
5-iodo-6-(4-methoxyphenyl)-*2H*-pyran-2-one (**5f**)



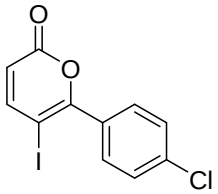
^{1}H NMR (400 MHz, $CDCl_3$)



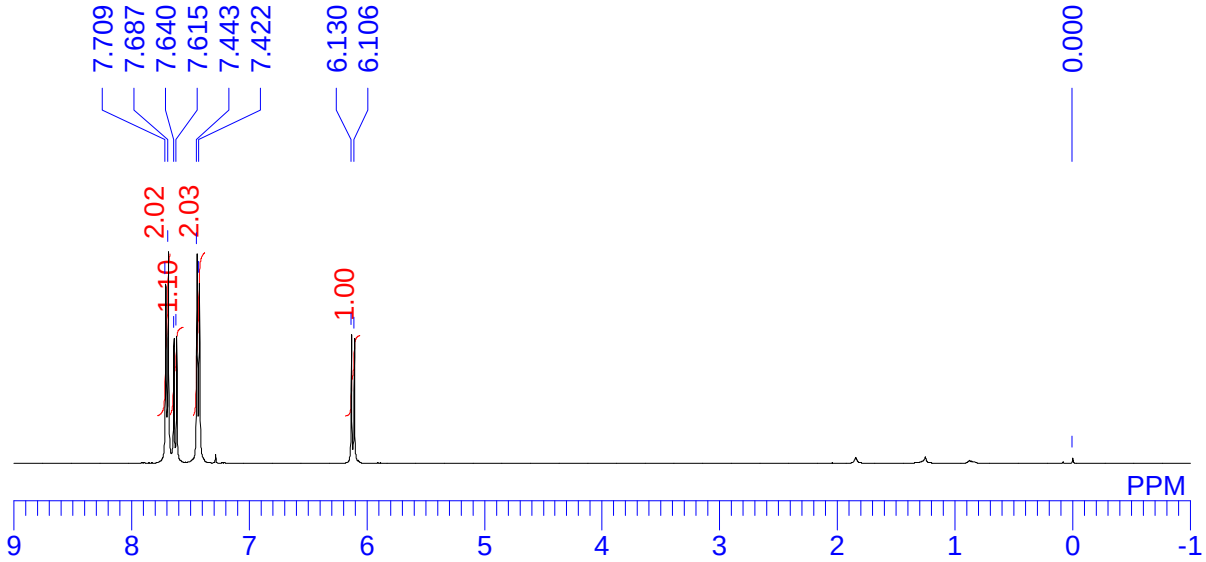
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



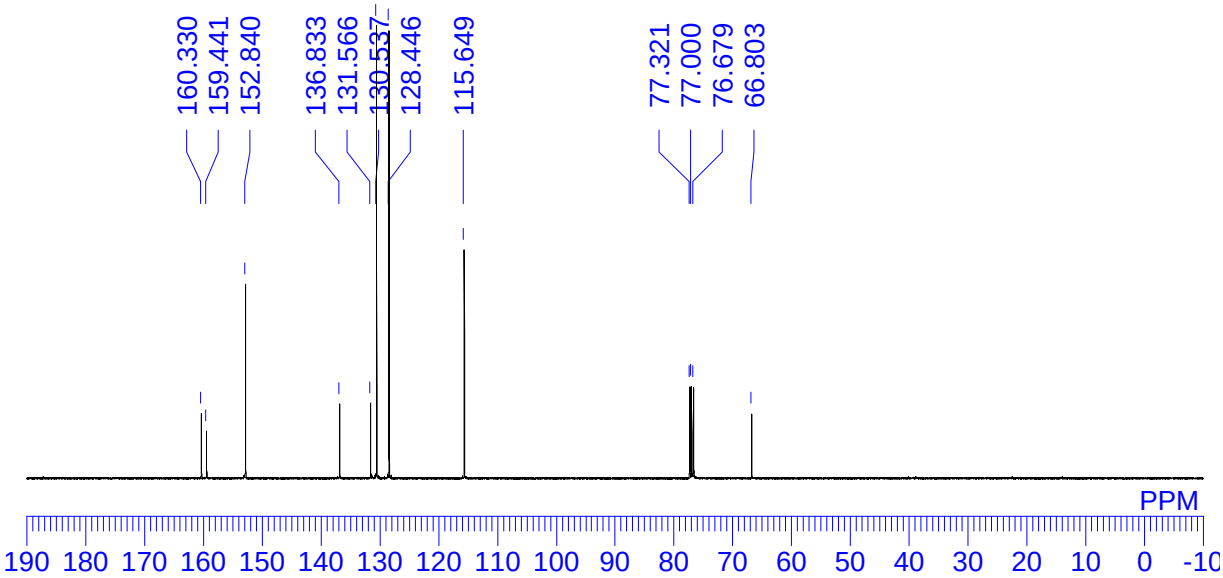
6-(4-chlorophenyl)-5-iodo-*2H*-pyran-2-one (**5g**)



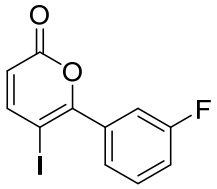
^{1}H NMR (400 MHz, $CDCl_3$)



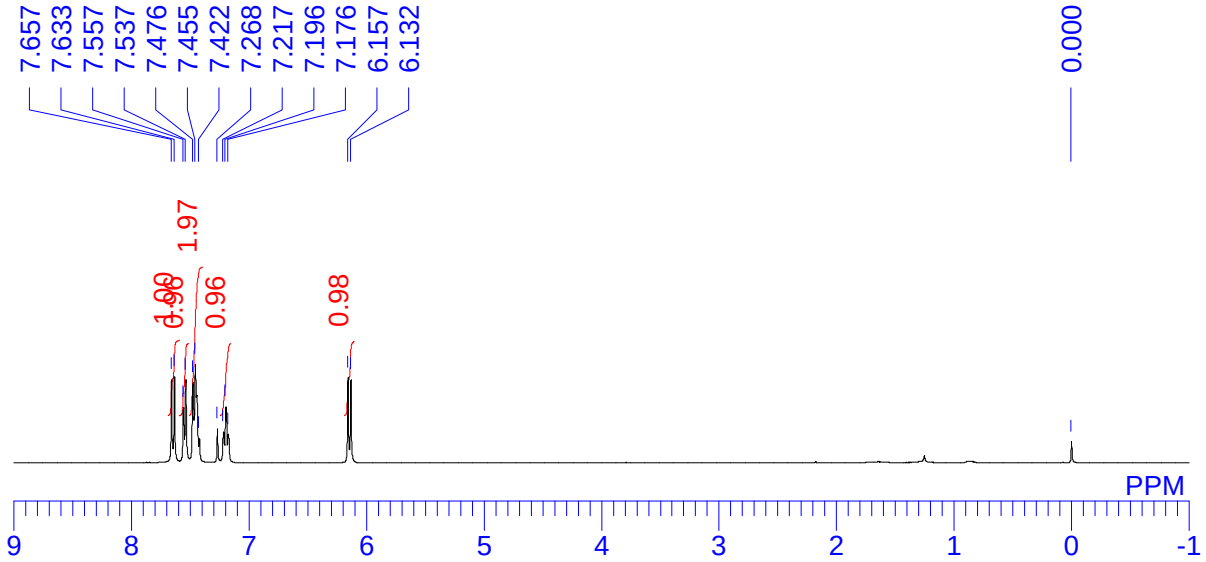
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



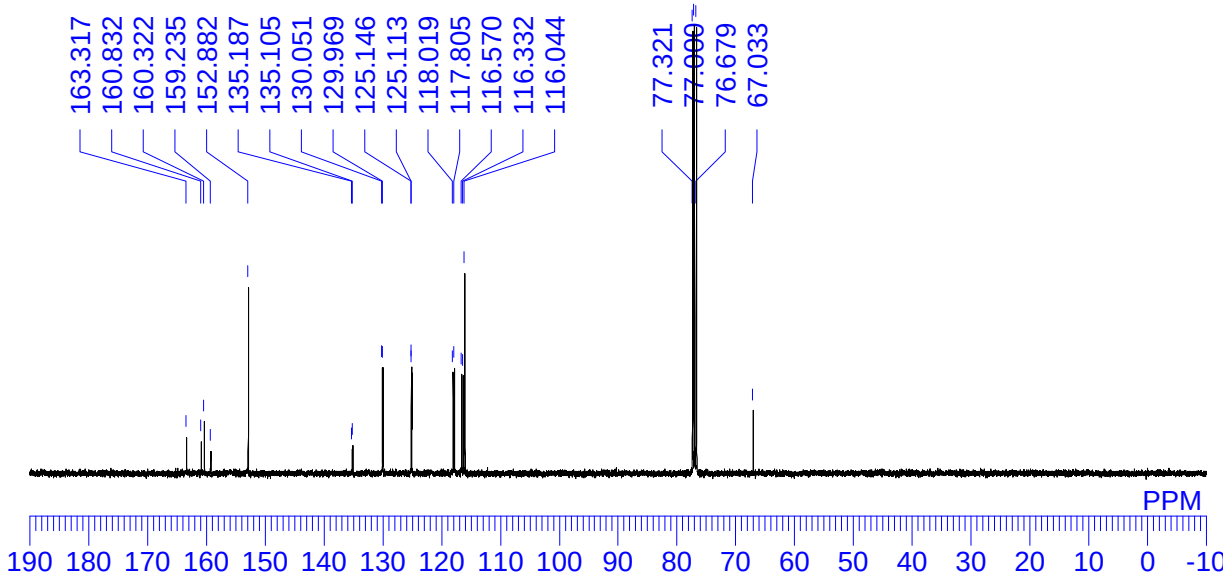
6-(3-fluorophenyl)-5-iodo-*2H*-pyran-2-one (**5h**)



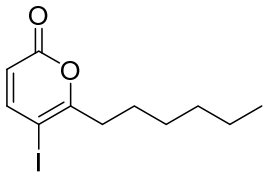
^{1}H NMR (400 MHz, $CDCl_3$)



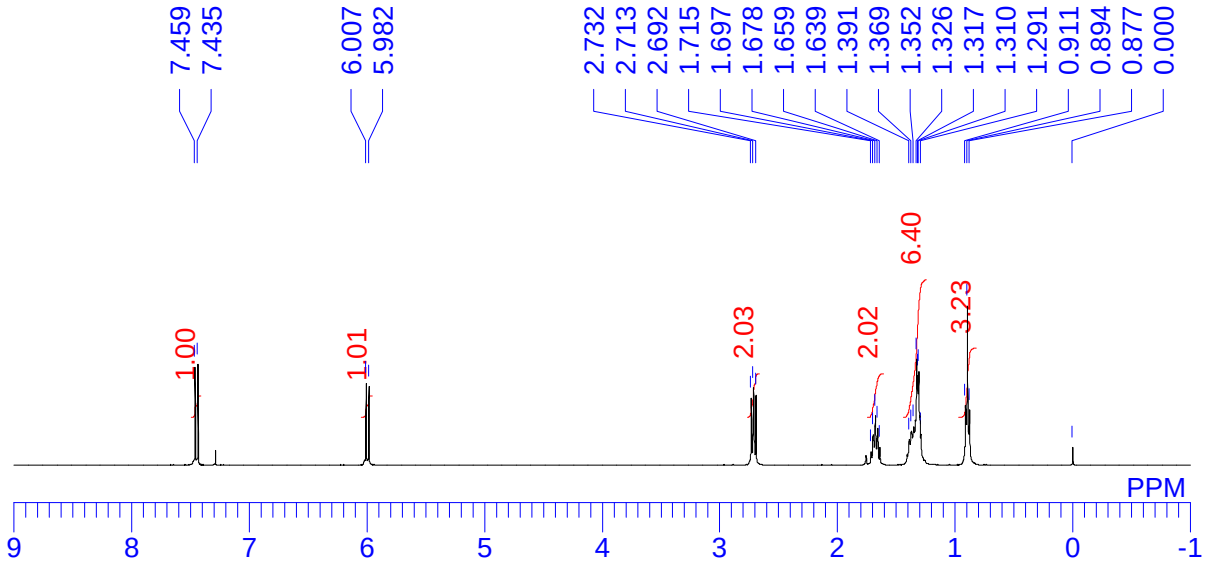
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



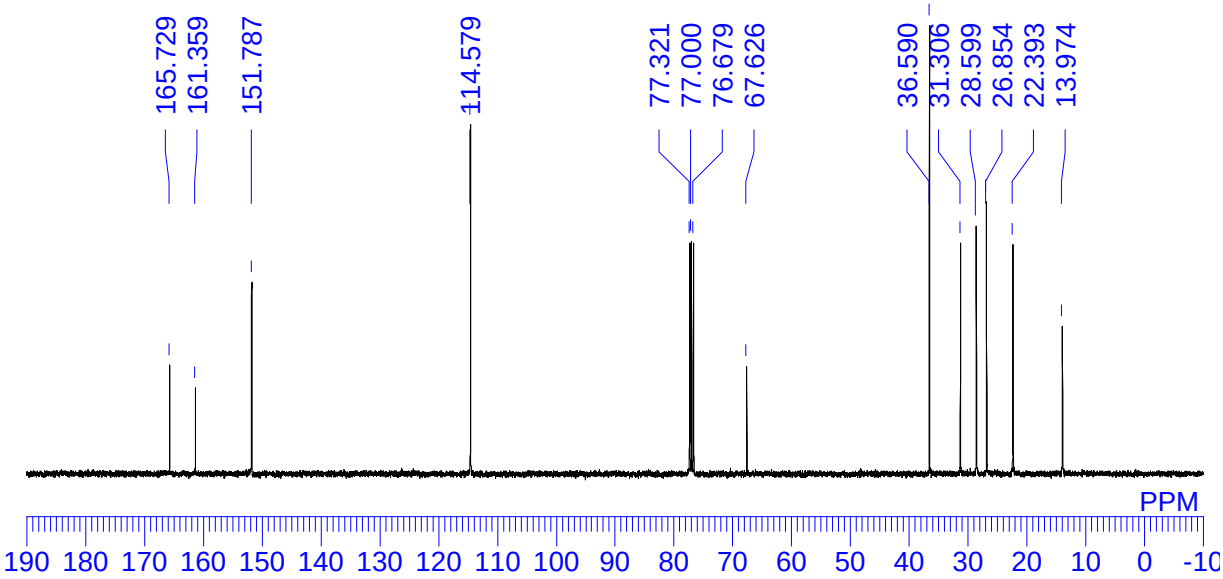
6-hexyl-5-iodo-*2H*-pyran-2-one (**5i**)



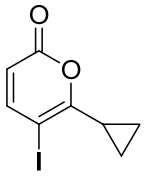
^{1}H NMR (400 MHz, $CDCl_3$)



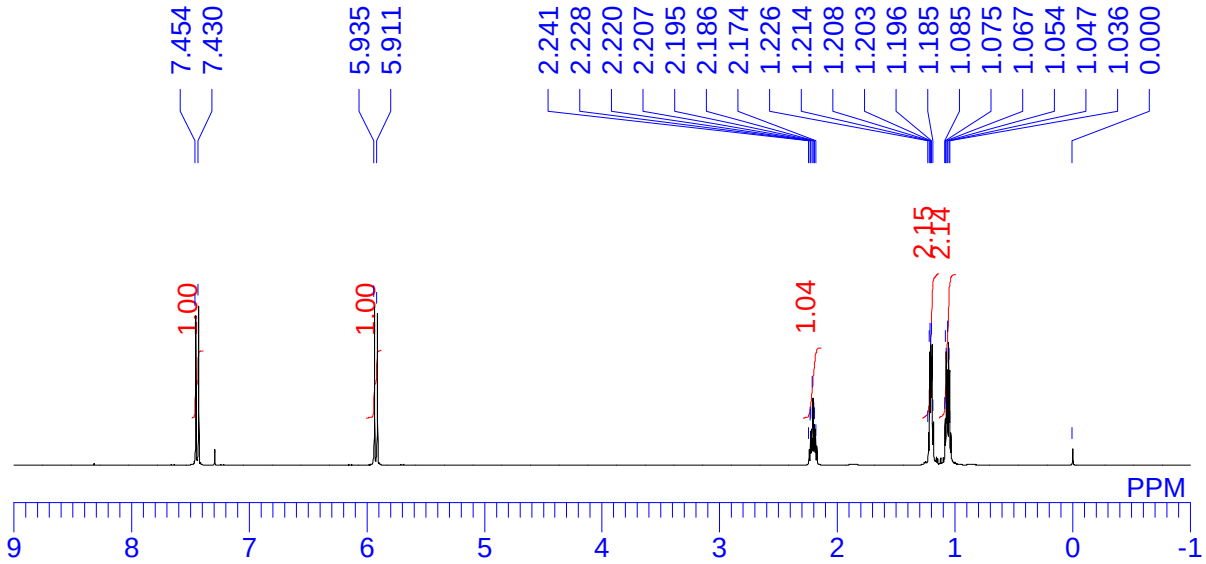
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



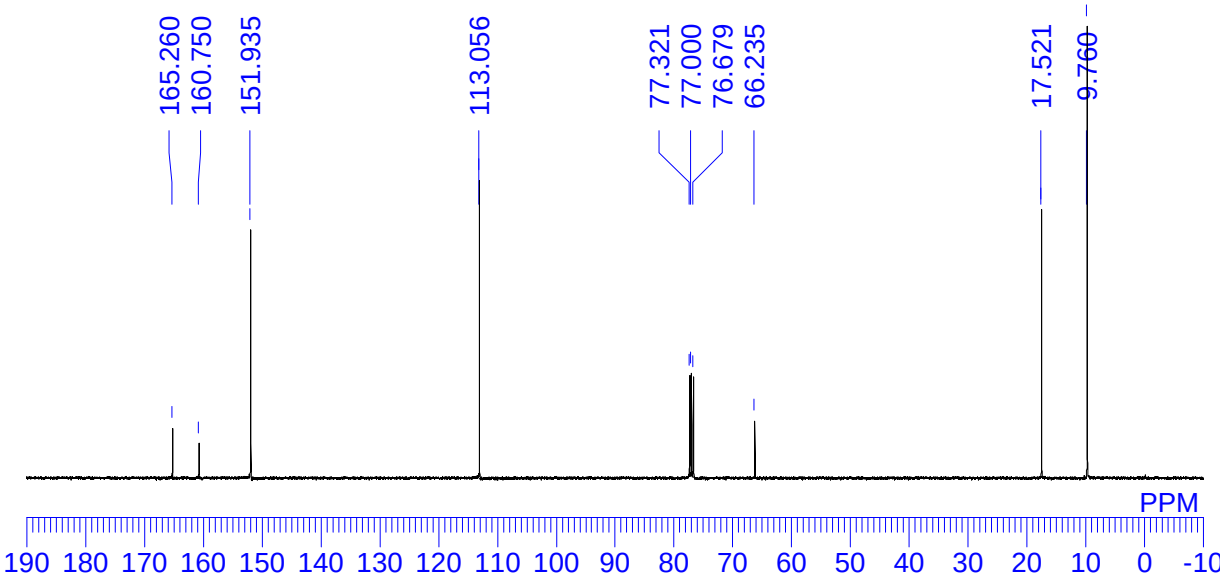
6-cyclopropyl-5-iodo-*2H*-pyran-2-one (**5j**)



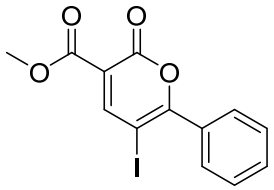
^{1}H NMR (400 MHz, $CDCl_3$)



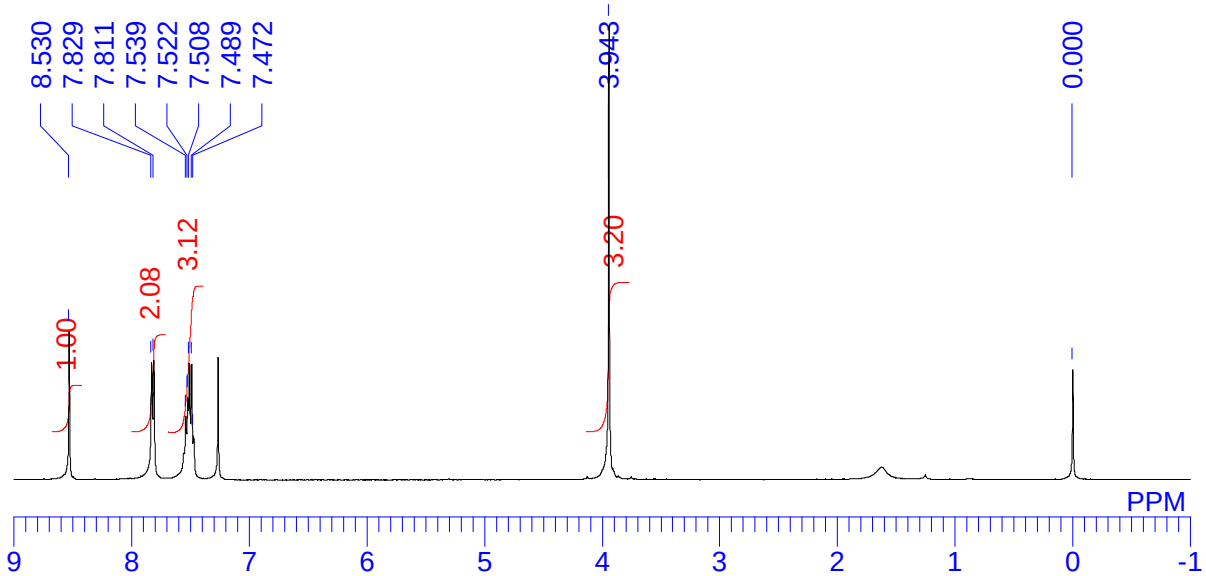
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



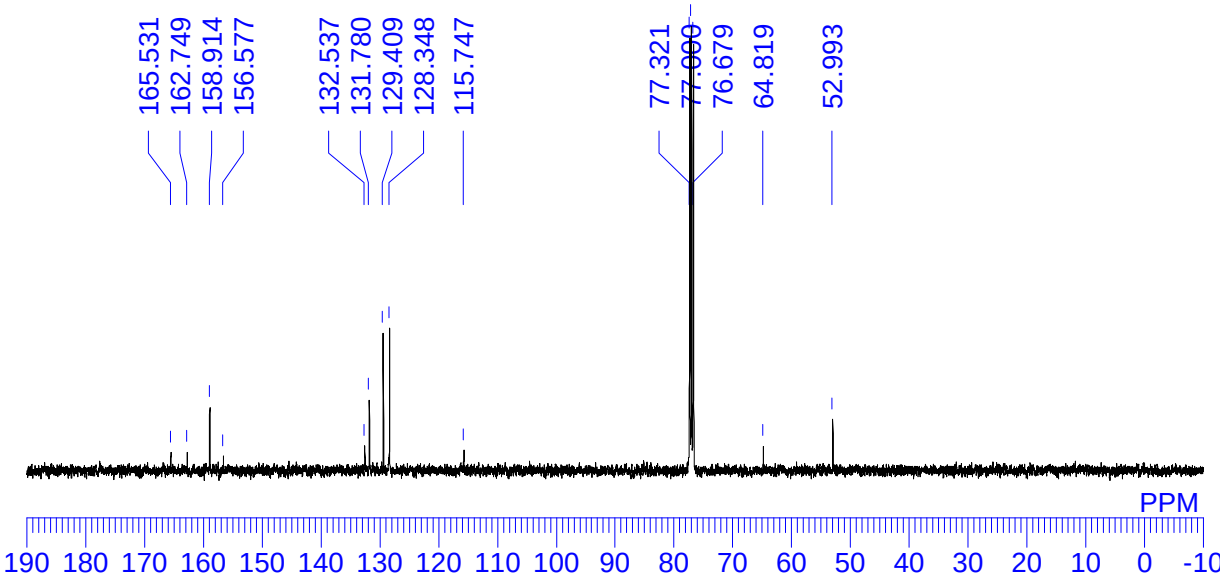
methyl 5-iodo-2-oxo-6-phenyl-*2H*-pyran-3-carboxylate (**5k**)



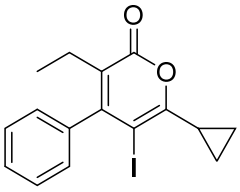
^{1}H NMR (400 MHz, $CDCl_3$)



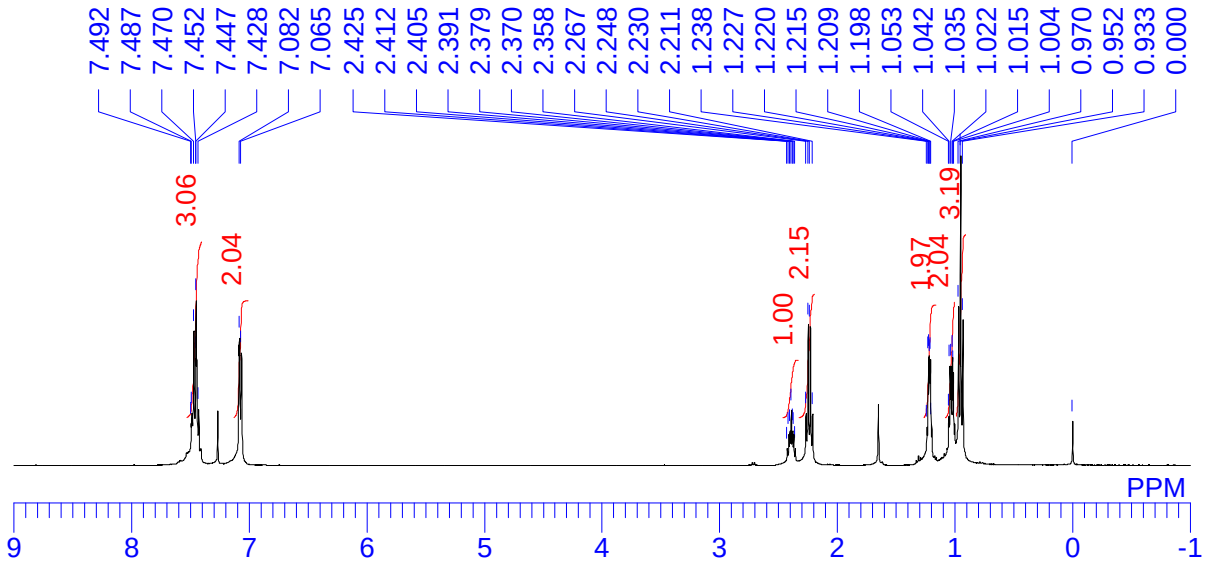
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



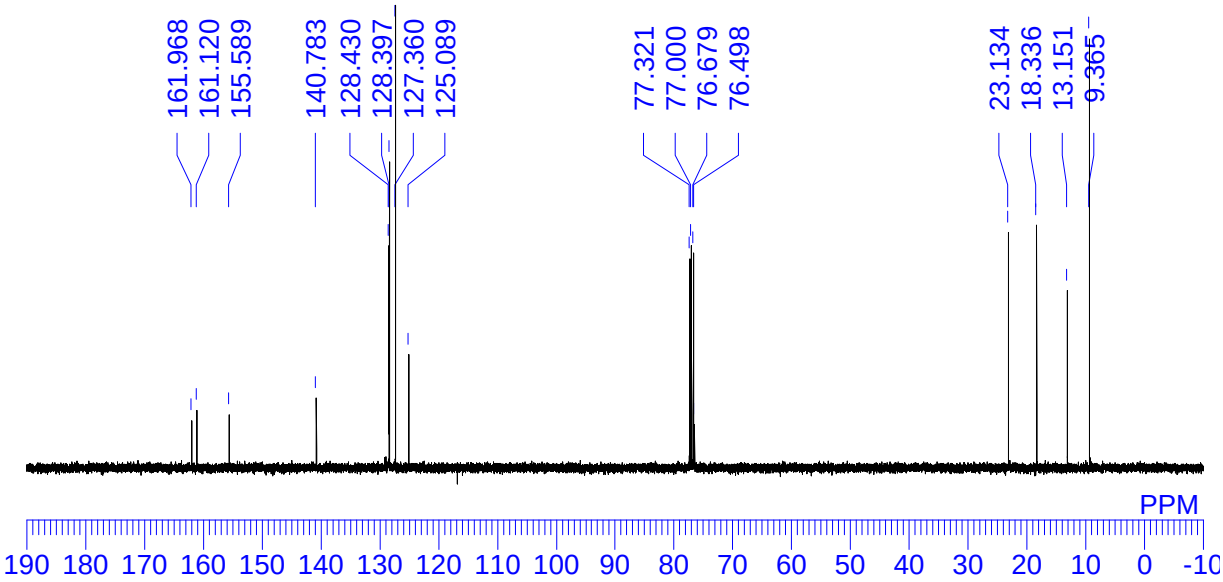
6-cyclopropyl-3-ethyl-5-iodo-4-phenyl-*2H*-pyran-2-one (**5l**)



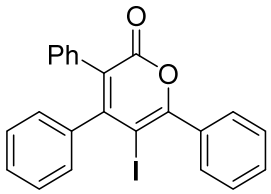
^{1}H NMR (400 MHz, $CDCl_3$)



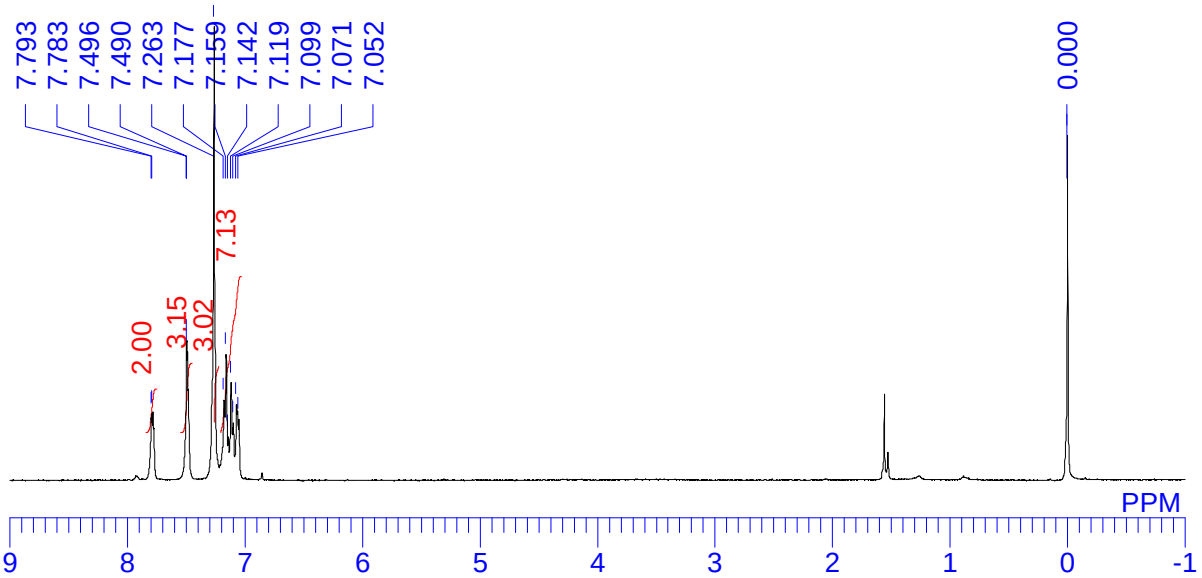
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



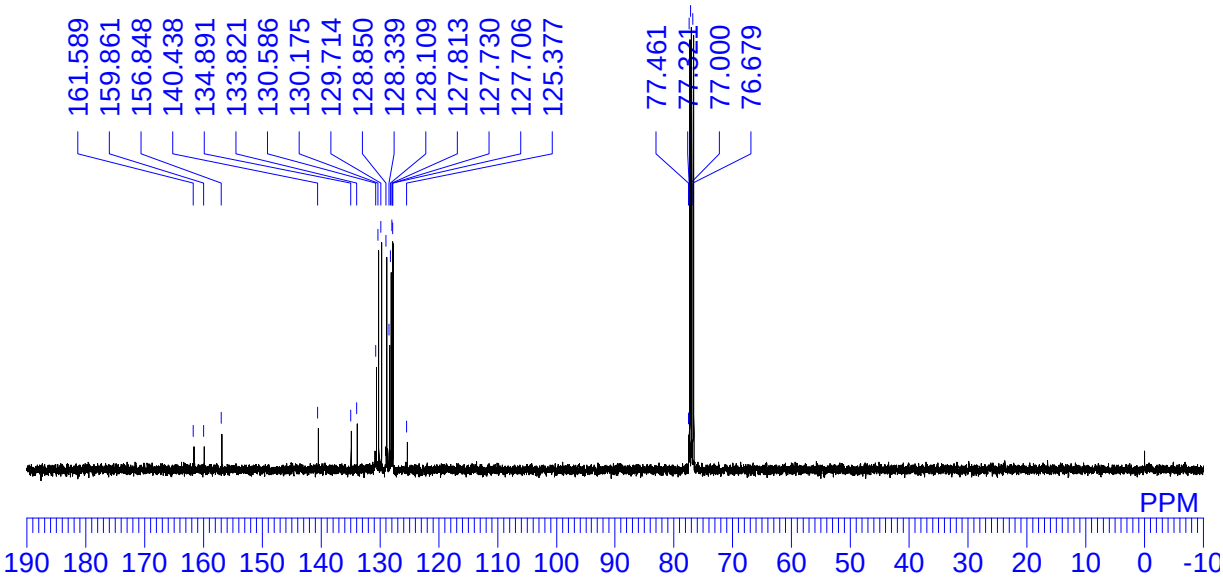
5-iodo-3,4,6-triphenyl-*2H*-pyran-2-one (**5m**)



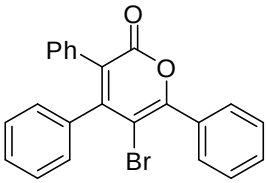
^{1}H NMR (400 MHz, $CDCl_3$)



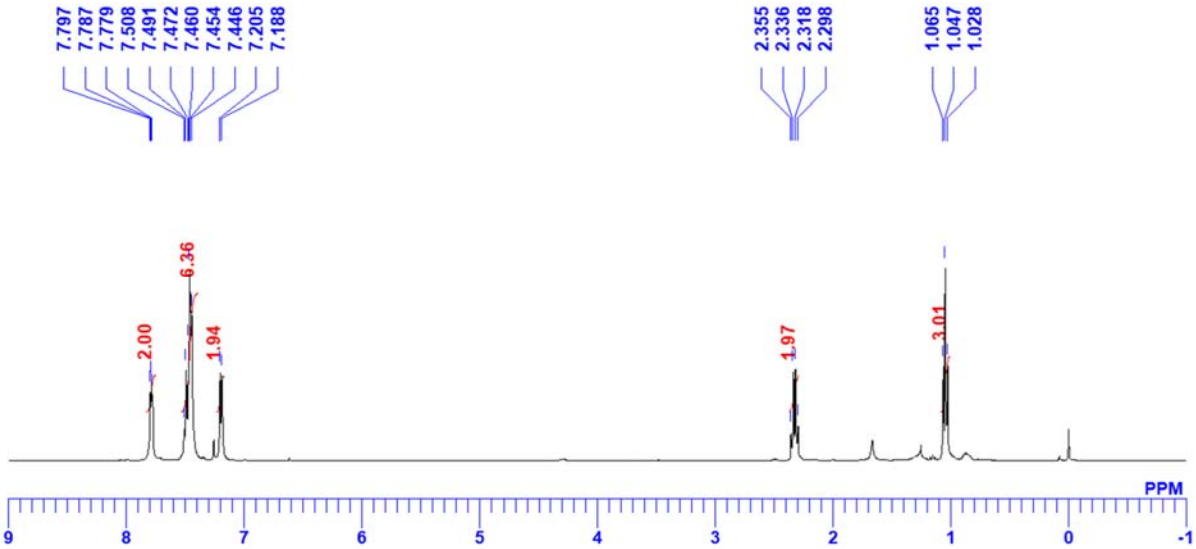
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



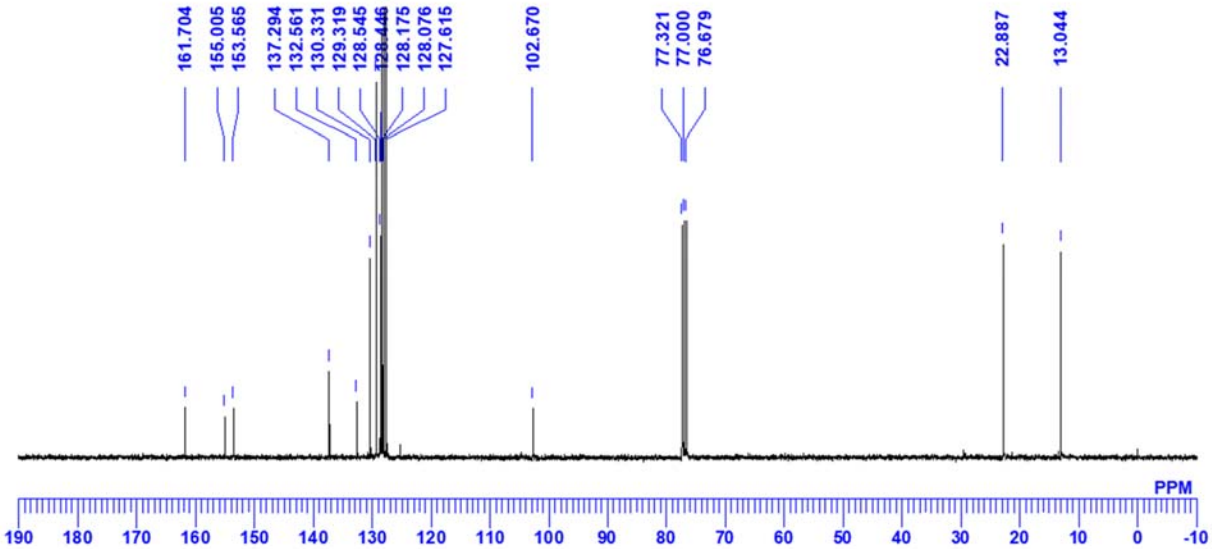
5-bromo-3-ethyl-4,6-diphenyl-2*H*-pyran-2-one (**5n**)



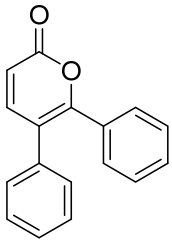
^{1}H NMR (400 MHz, $CDCl_3$)



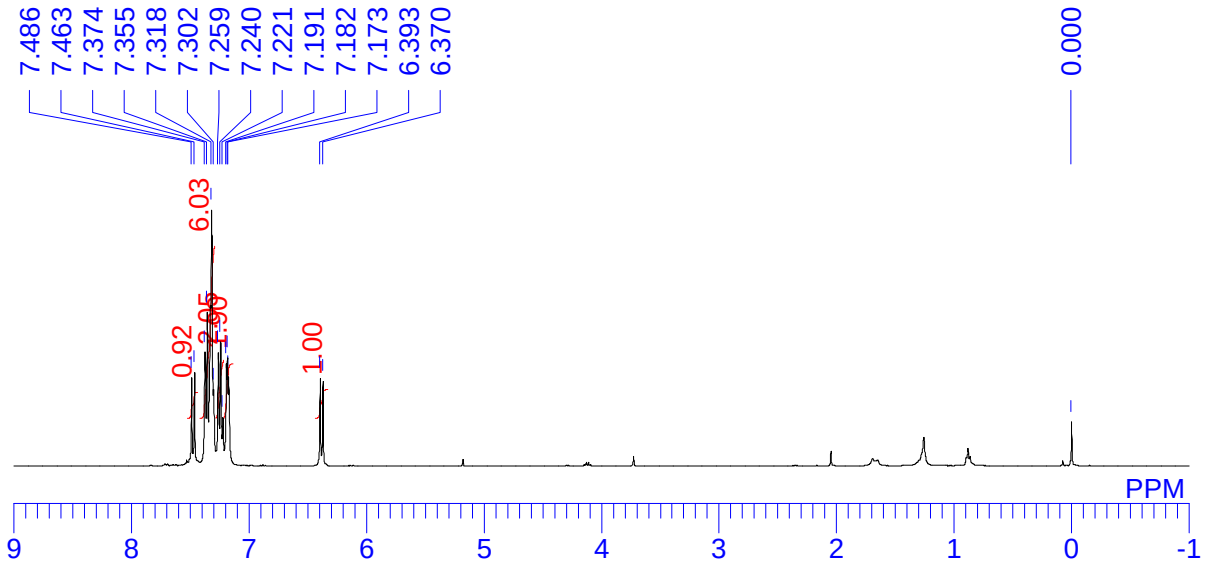
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



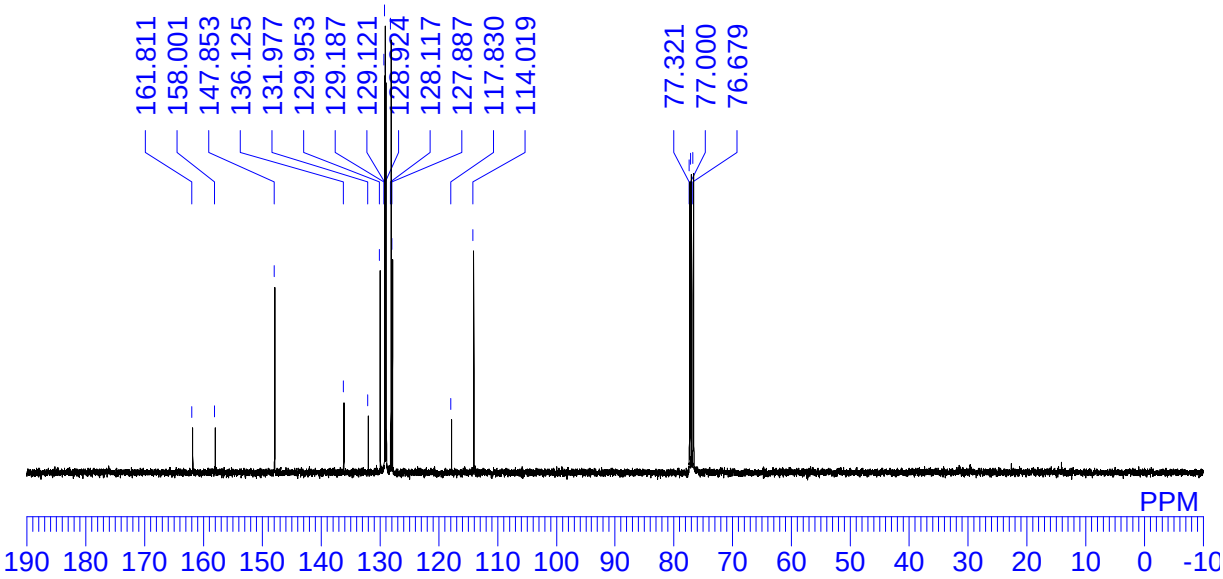
5,6-diphenyl-*2H*-pyran-2-one (**6a**)



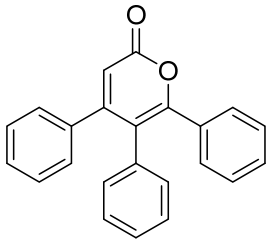
^{1}H NMR (400 MHz, $CDCl_3$)



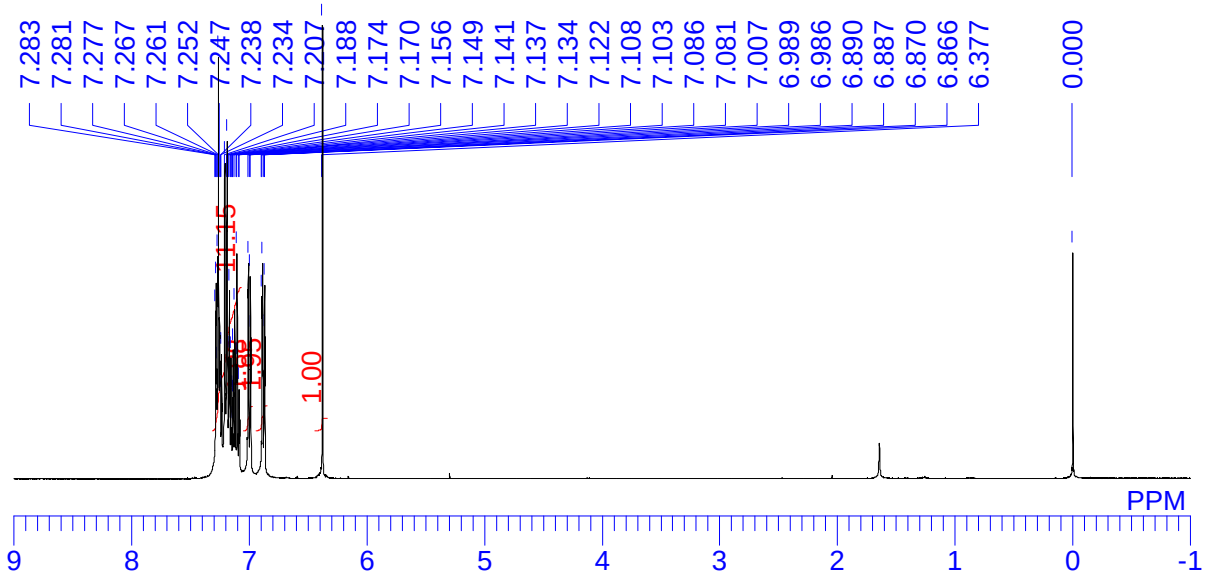
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



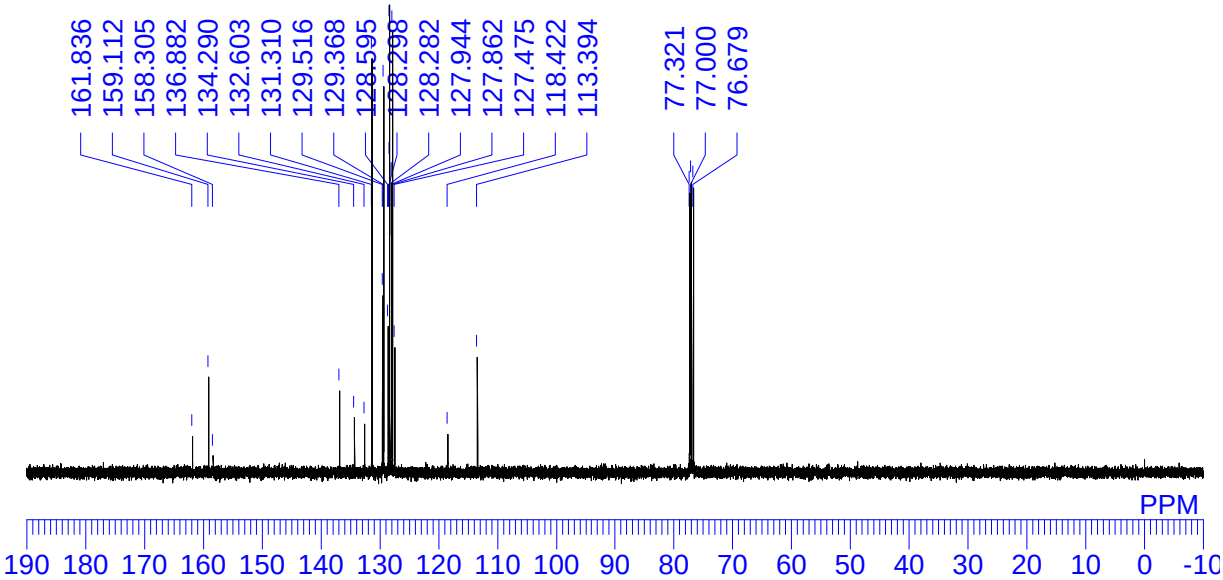
4,5,6-triphenyl-*2H*-pyran-2-one (**6b**)



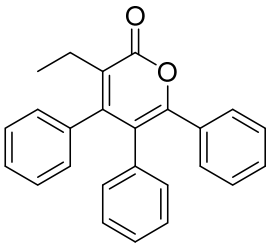
^{1}H NMR (400 MHz, $CDCl_3$)



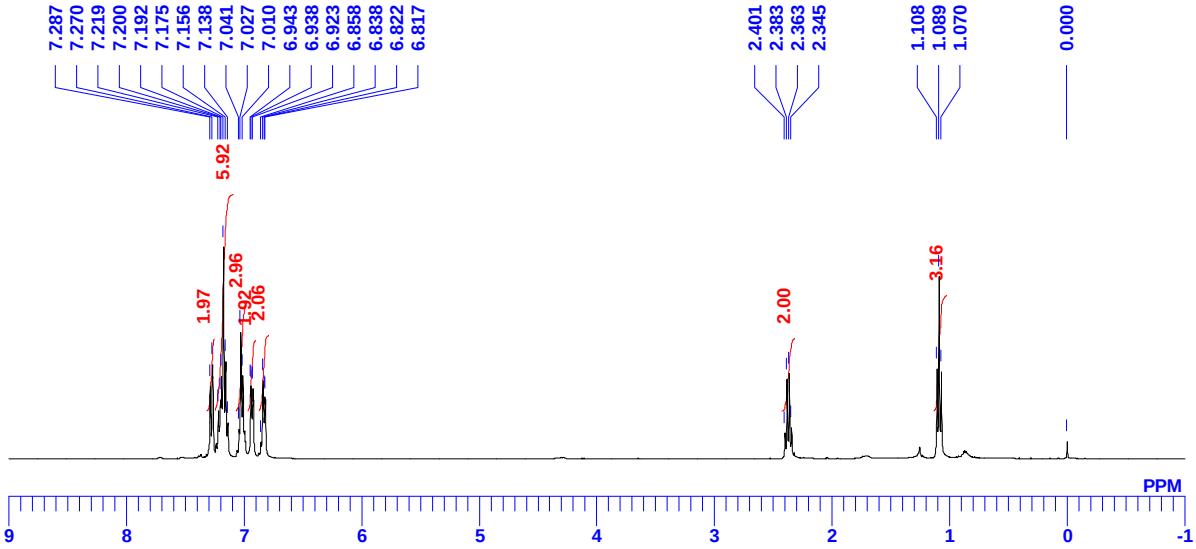
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



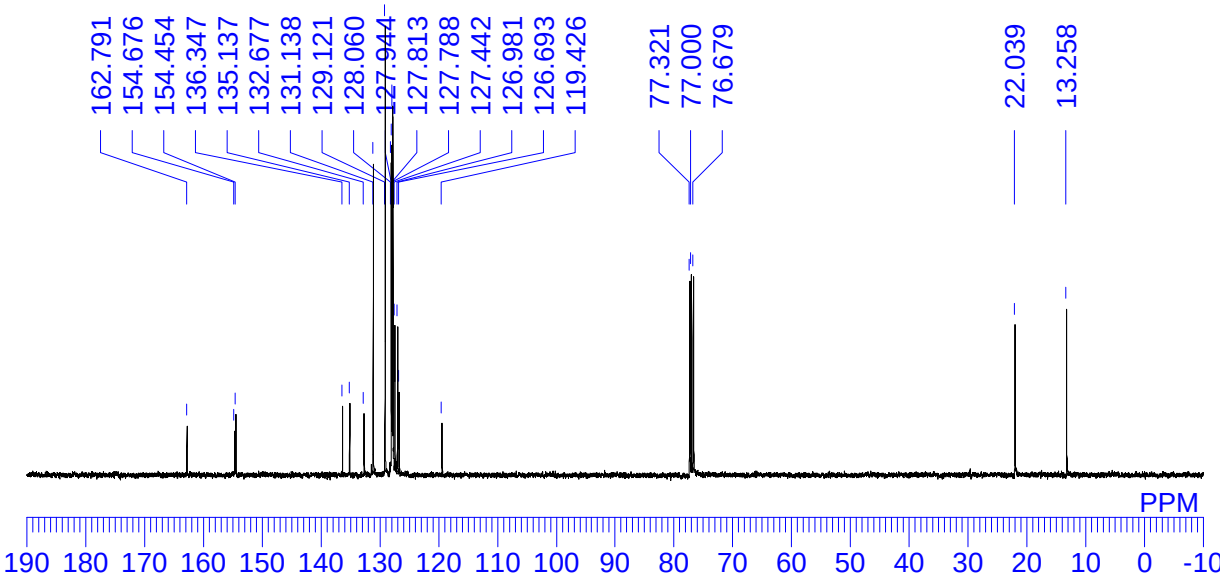
3-ethyl-4,5,6-triphenyl-*2H*-pyran-2-one (**6c**)



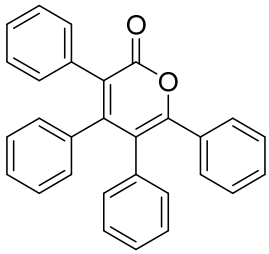
^{1}H NMR (400 MHz, $CDCl_3$)



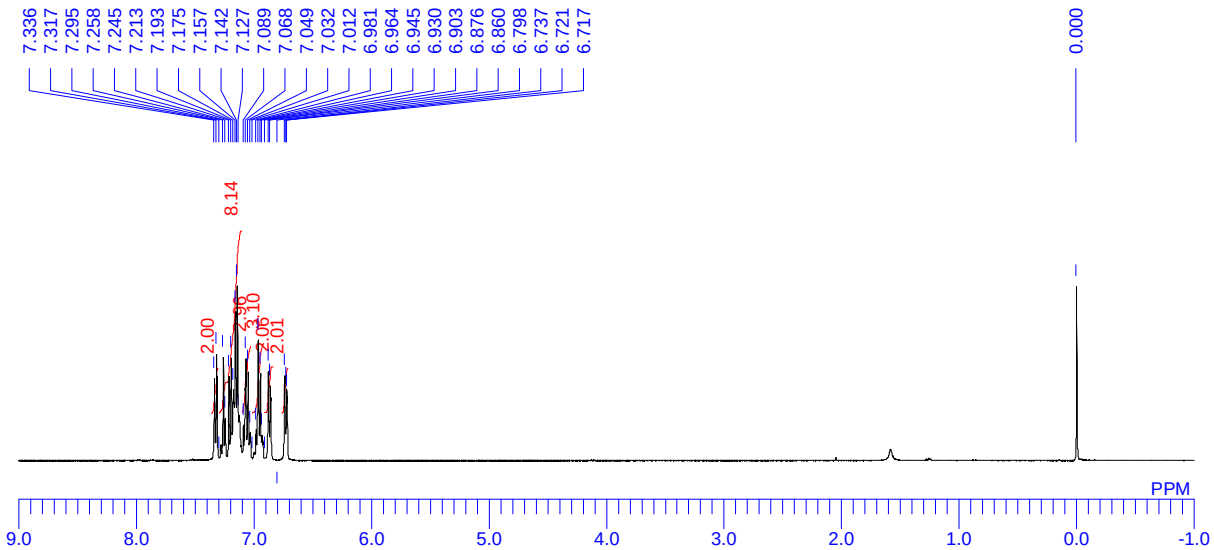
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



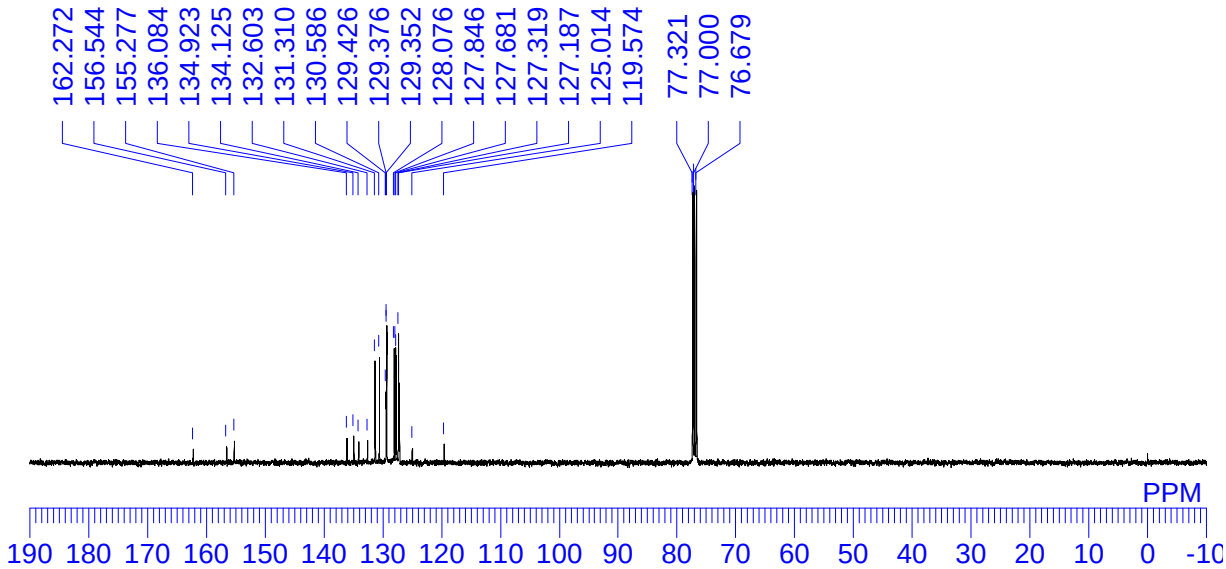
3,4,5,6-tetraphenyl-*2H*-pyran-2-one (**6m**)



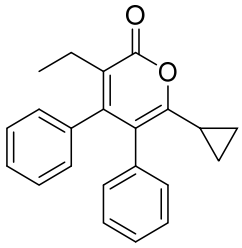
^{1}H NMR (400 MHz, $CDCl_3$)



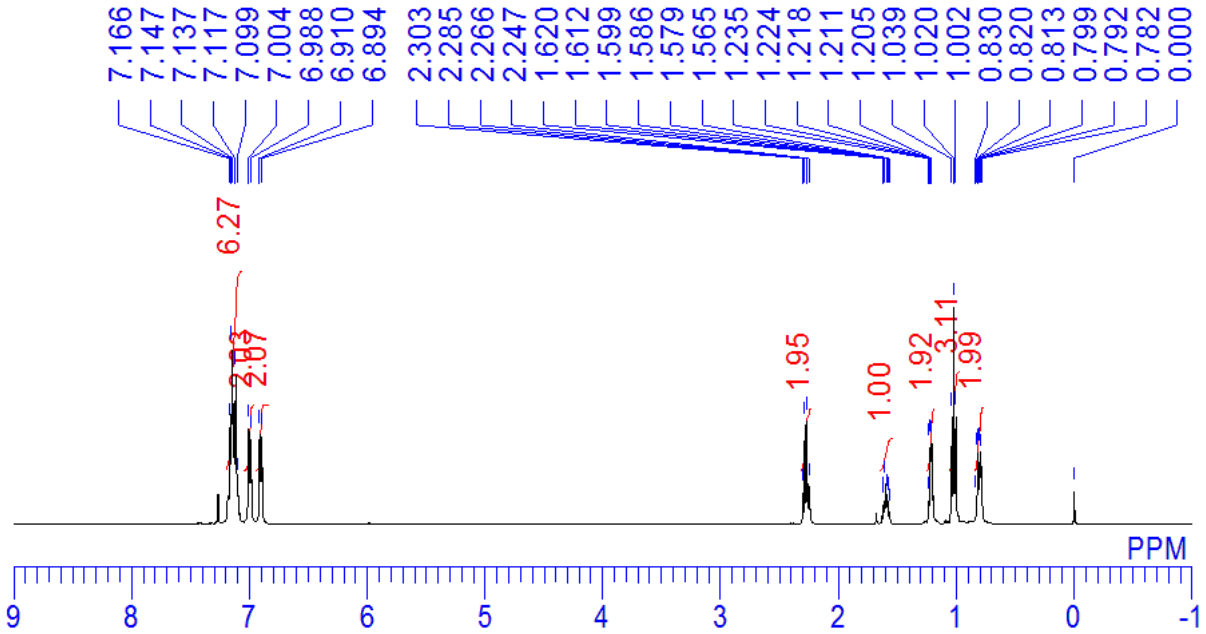
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



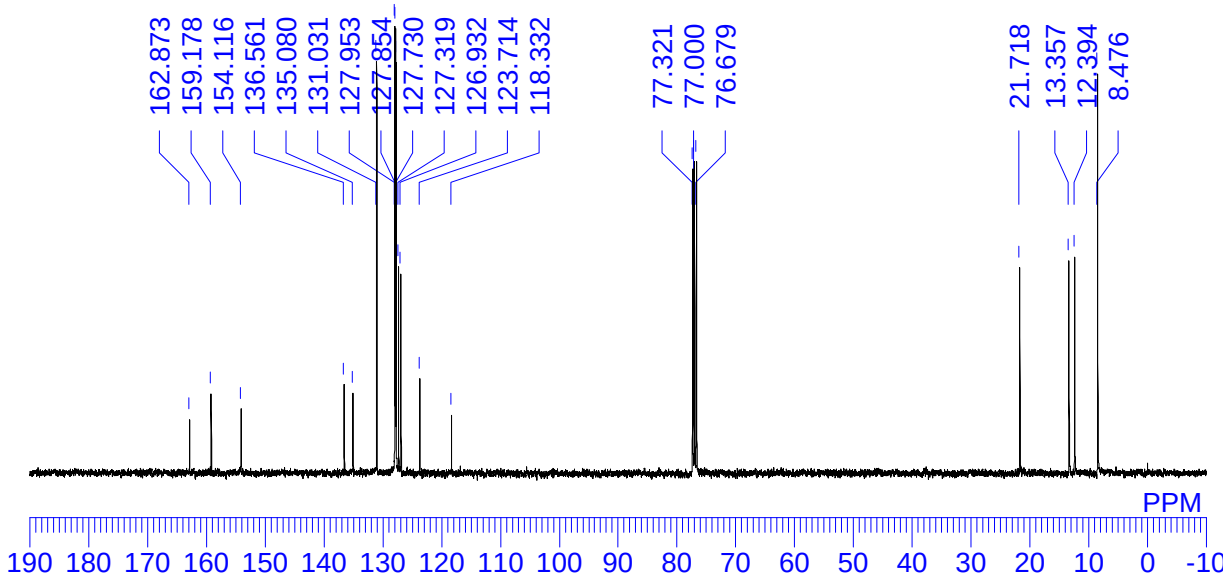
6-cyclopropyl-3-ethyl-4,5-diphenyl-*2H*-pyran-2-one (**6l**)



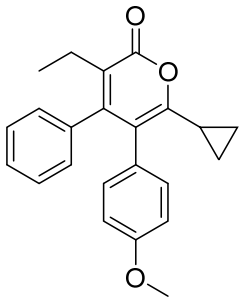
^{1}H NMR (400 MHz, $CDCl_3$)



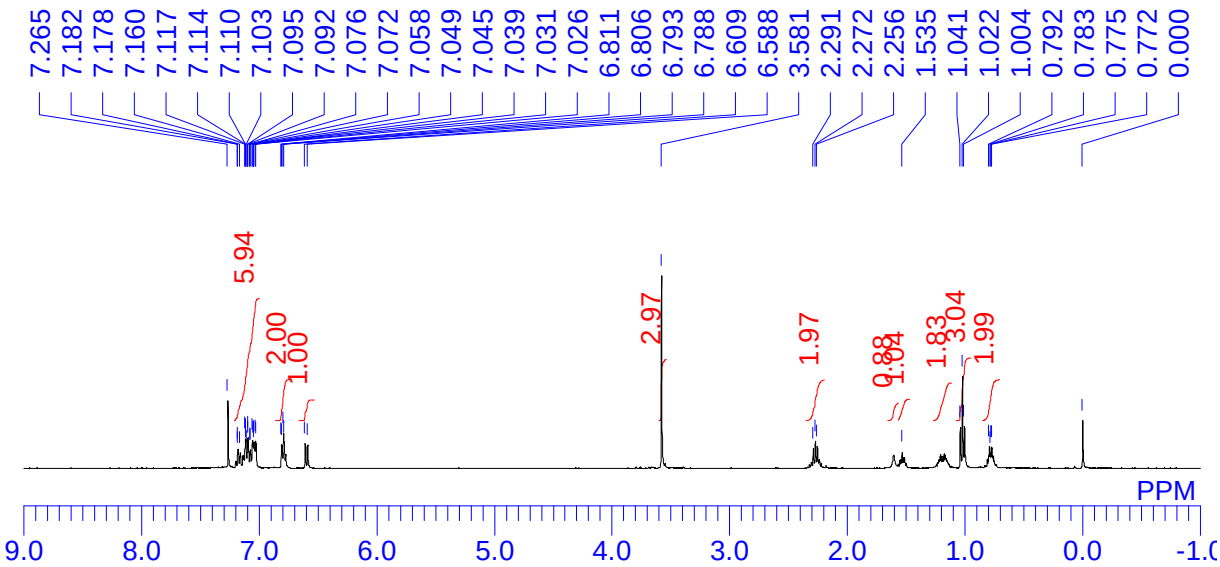
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



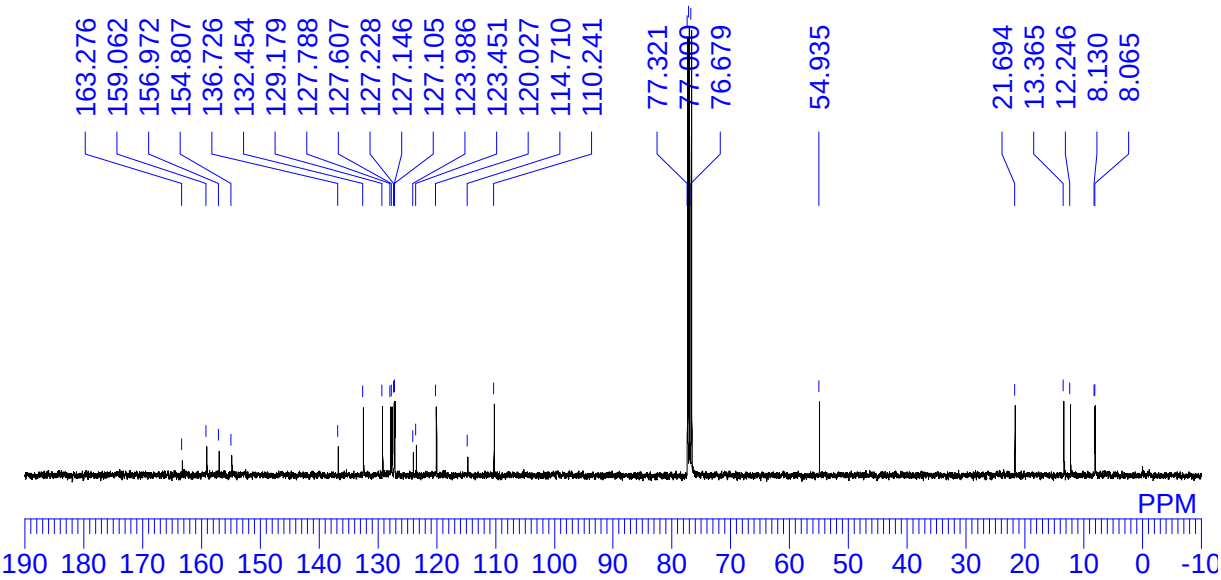
6-cyclopropyl-3-ethyl-5-(4-methoxyphenyl)-4-phenyl-*2H*-pyran-2-one (**6n**)



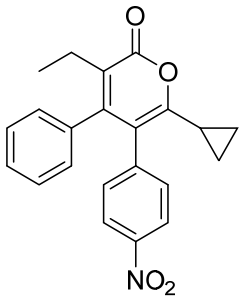
^{1}H NMR (400 MHz, $CDCl_3$)



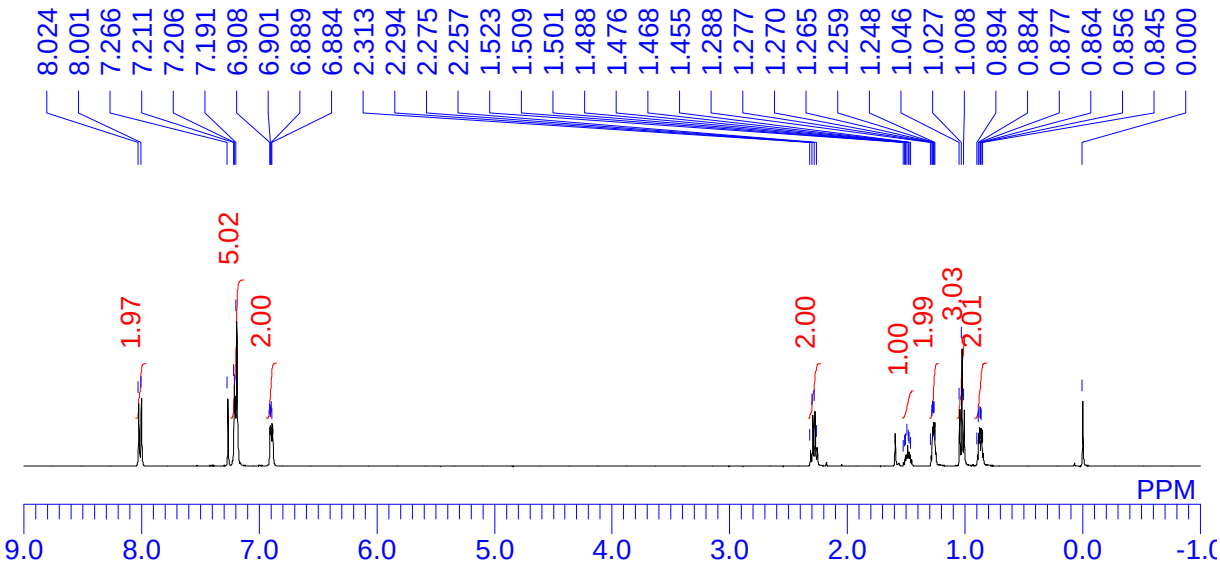
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



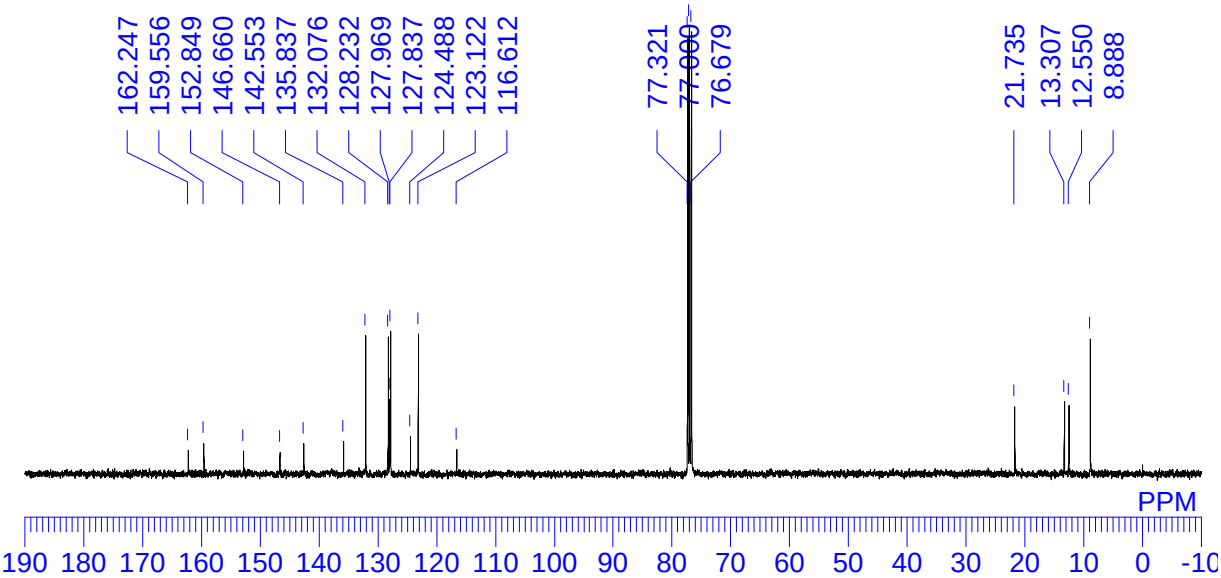
6-cyclopropyl-3-ethyl-5-(4-nitrophenyl)-4-phenyl-*2H*-pyran-2-one (**6o**)



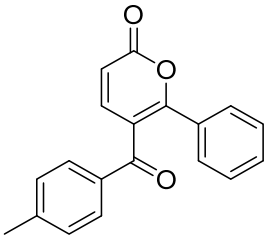
^{1}H NMR (400 MHz, $CDCl_3$)



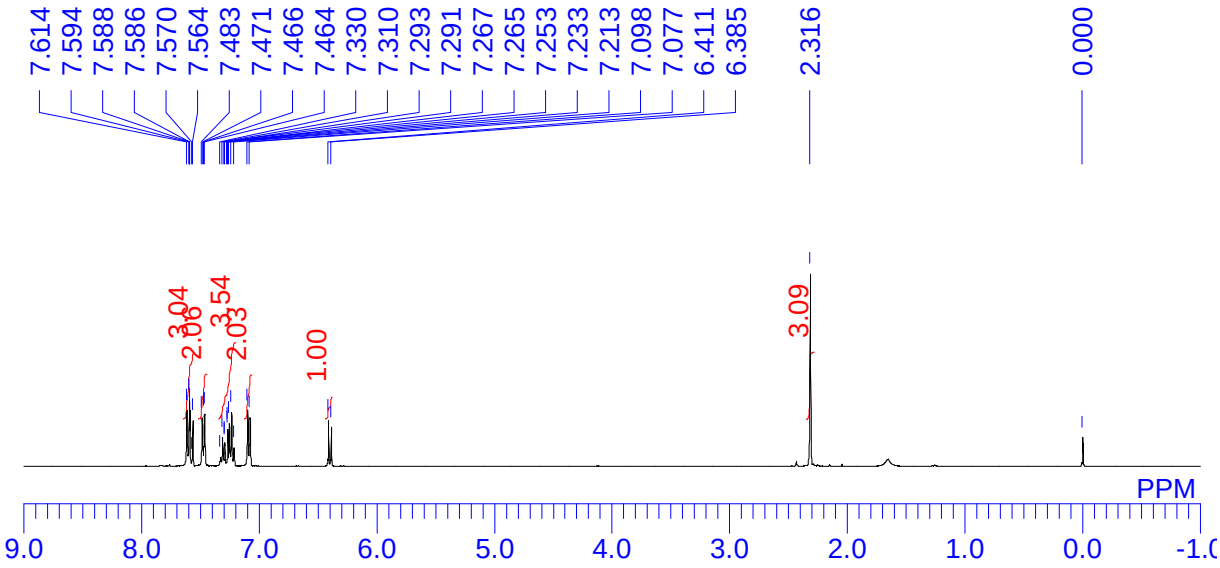
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



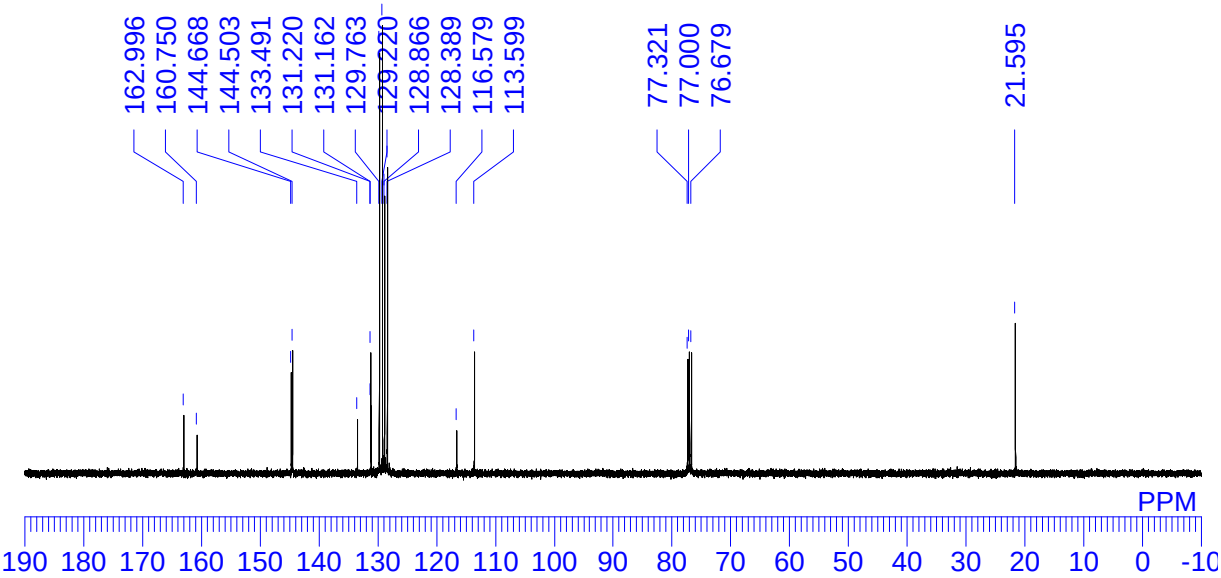
5-(4-methylbenzoyl)-6-phenyl-*2H*-pyran-2-one (**7a**)



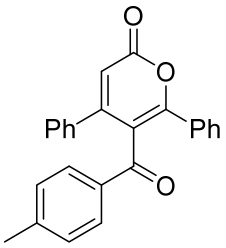
^{1}H NMR (400 MHz, $CDCl_3$)



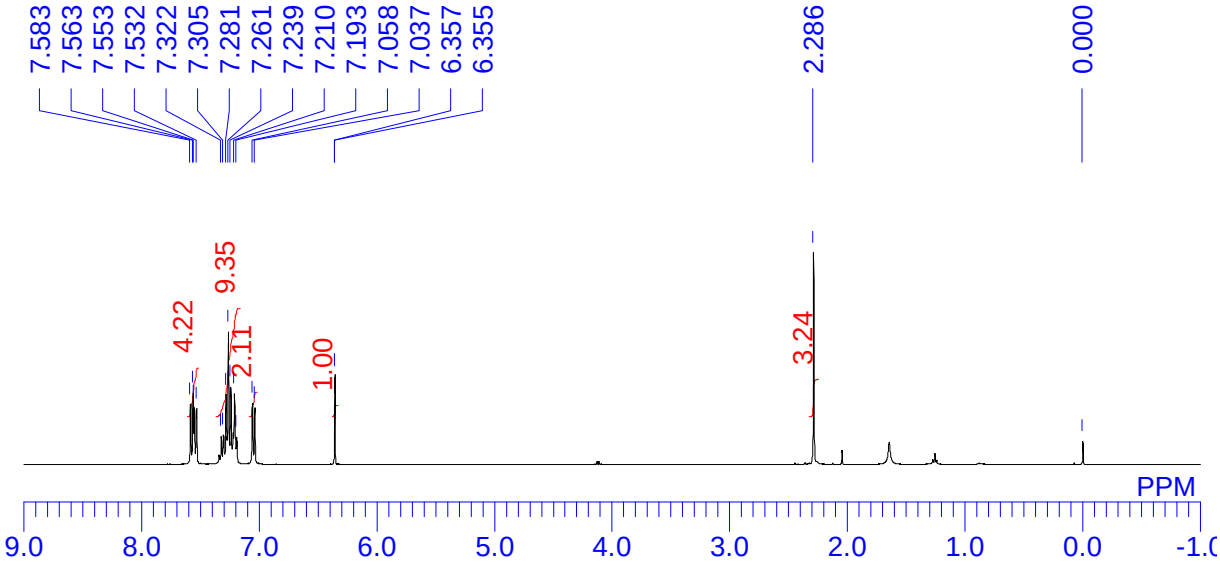
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



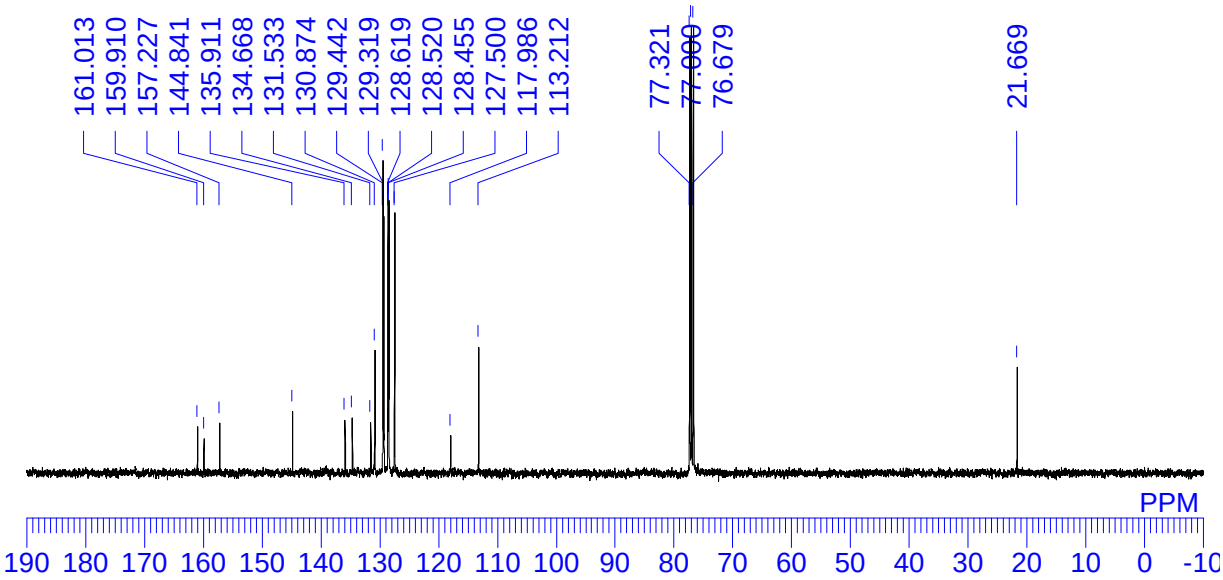
5-(4-methylbenzoyl)-4,6-diphenyl-*2H*-pyran-2-one (**7b**)



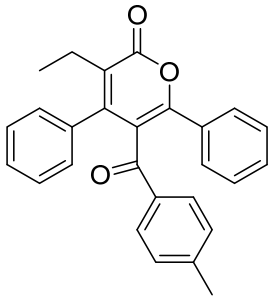
^{1}H NMR (400 MHz, $CDCl_3$)



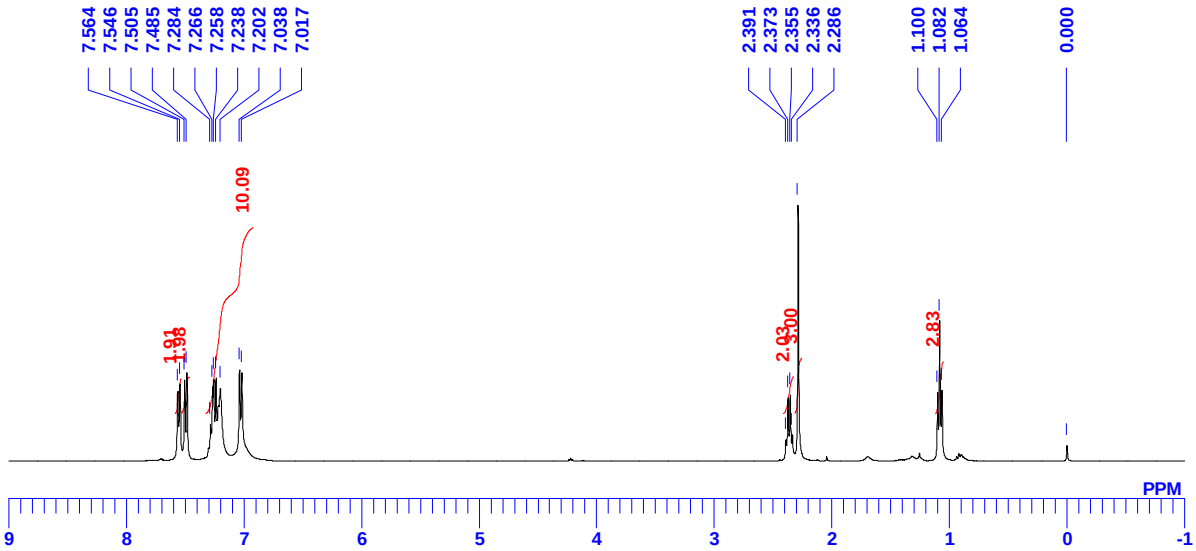
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



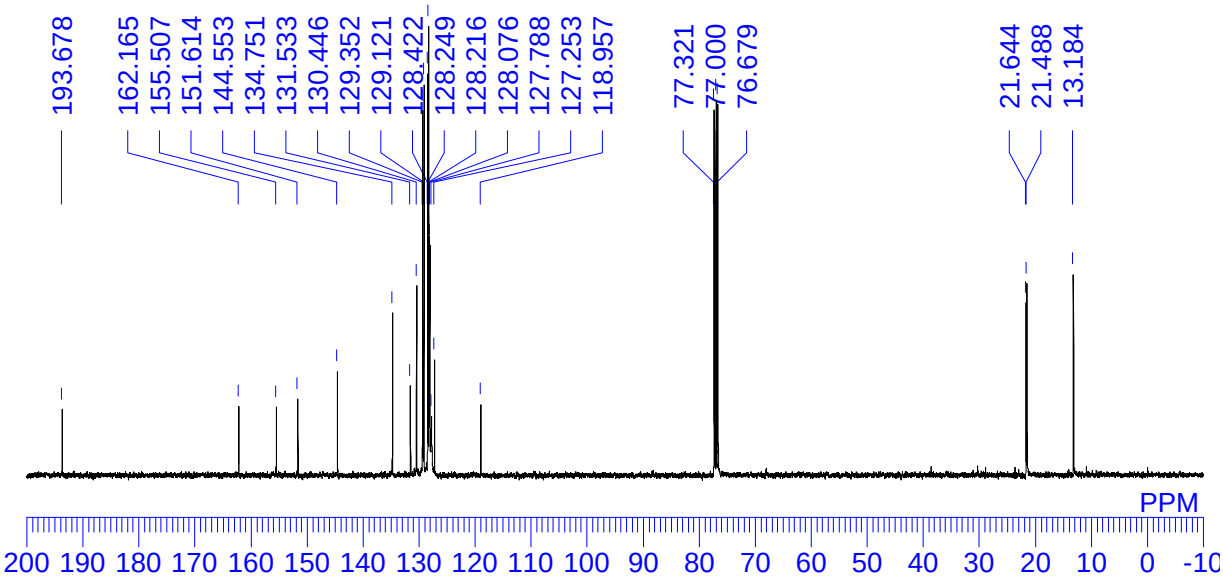
3-ethyl-5-(4-methylbenzoyl)-4,6-diphenyl-*2H*-pyran-2-one (**7c**)



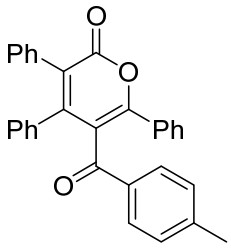
^{1}H NMR (400 MHz, $CDCl_3$)



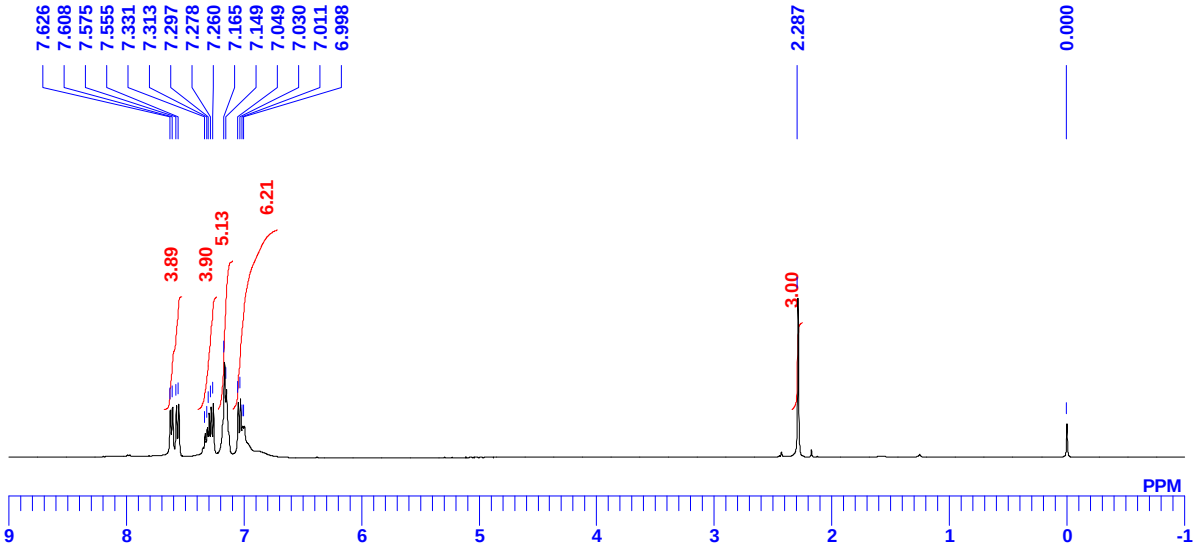
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



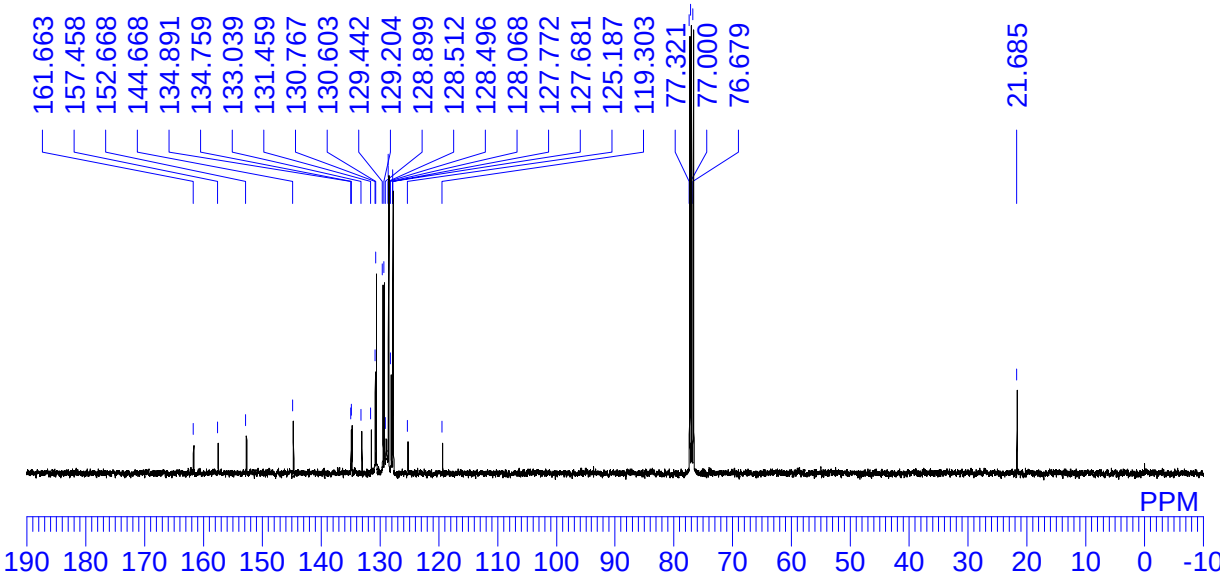
5-(4-methylbenzoyl)-3,4,6-triphenyl-*2H*-pyran-2-one (**7m**)



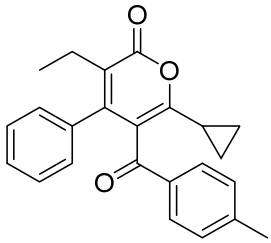
^{1}H NMR (400 MHz, $CDCl_3$)



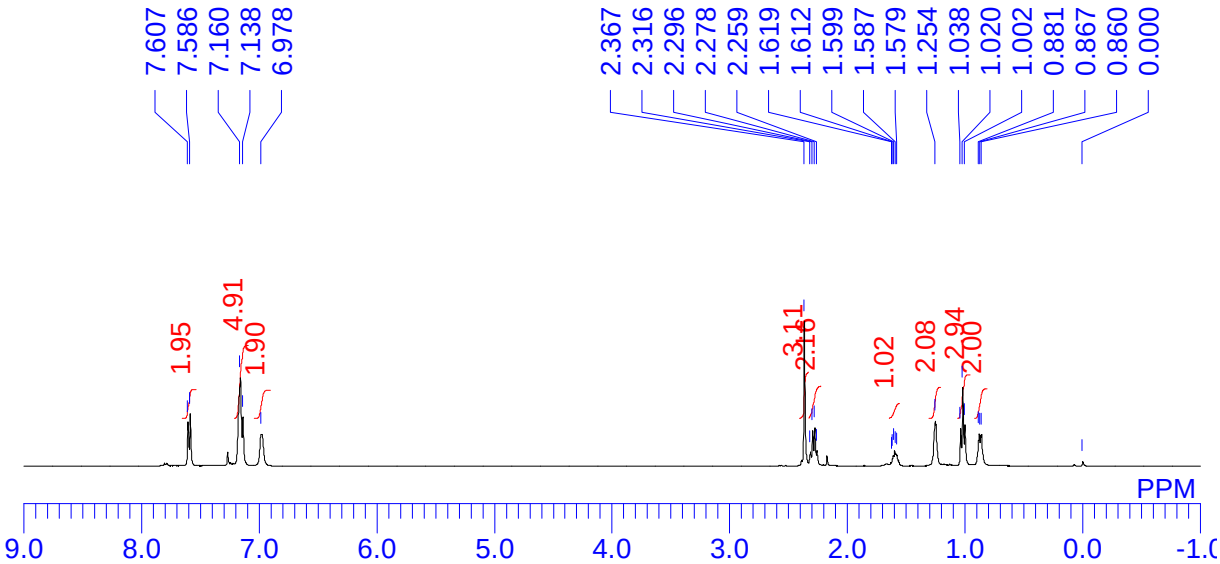
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



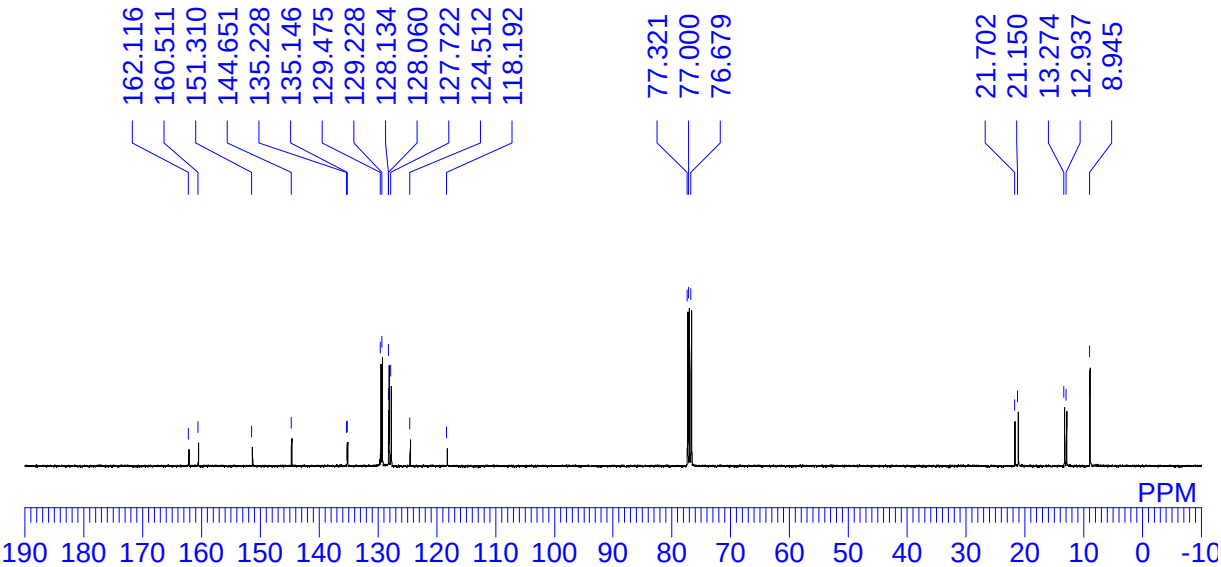
6-cyclopropyl-3-ethyl-5-(4-methylbenzoyl)-4-phenyl-*2H*-pyran-2-one (**7l**)



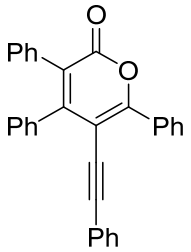
^{1}H NMR (400 MHz, $CDCl_3$)



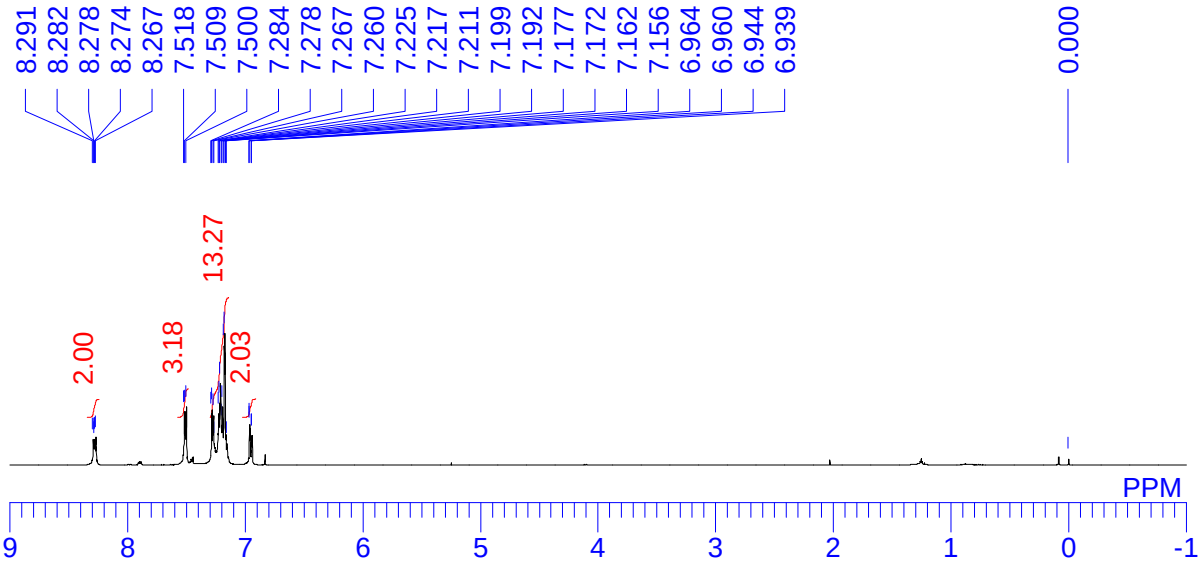
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



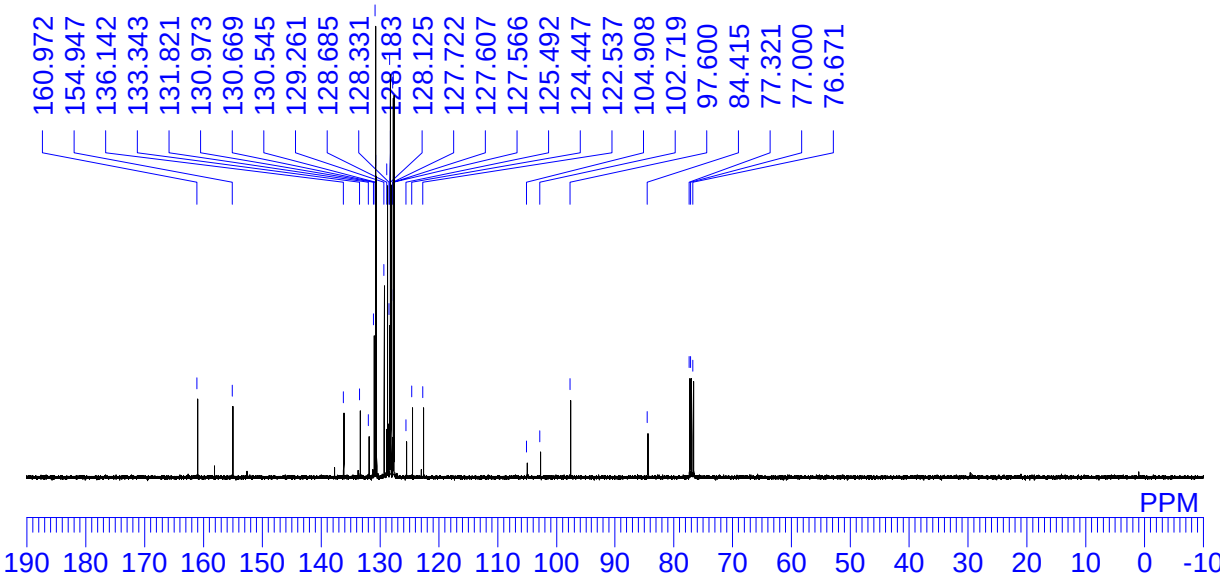
3,4,6-triphenyl-5-(phenylethynyl)-2*H*-pyran-2-one (**8**)



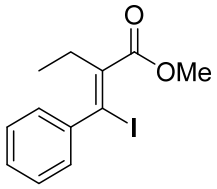
^{1}H NMR (400 MHz, $CDCl_3$)



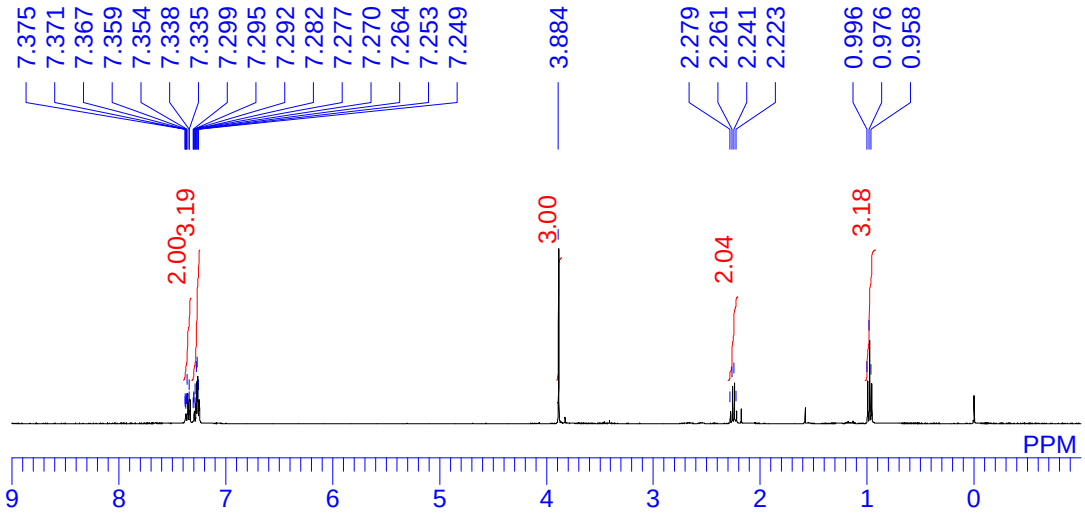
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



methyl (*Z*)-2-{iodo(phenyl)methylene}butanoate (**9**)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)